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Theoretical models for the nematic twist-bend phase and the Landau de Gennes theory of Longa and Tomczyk

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ABSTRACT
We present a critical analysis of the existing phenomenological theories of the nematic twist-bend phase including the models proposed by Dozov and Selinger and the more general Landau de Gennes theory of L. Longa and W. Tomczyk. The role of the flexoelectric polarisation is considered in detail as well as the stabilisation of the nanoscale helical structure of the twist-bend phase. In particular we focus into the mechanism of the reduction of the bend elastic constant determined by negative flexoelectric corrections and discuss why the splay elastic constant is not reduced at all. A molecular theory of elasticity of bent-core nematics, which also enables one to describe the reduction of the bend elastic constant, is considered in detail as well. Finally we consider two different tensor orientational order parameters of the twist-bend phase which describe all kinds of uniaxial and local biaxial ordering of bent-core molecules in the twist-bend phase.

Reduction of the bend elastic constant
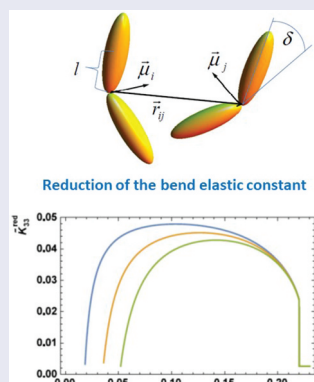
1. Introduction

The discovery of the nematic twist-bend phase has been one of the most fascinating discoveries in the field of liquid crystals during the past few decades because this phase is a rare example of the spontaneous chiral symmetry breaking in a three-dimensional fluid without positional order. The twist-bend phase possesses a helical structure with a nanoscale pitch which indicates that it appears as a result of a strong instability in the homogeneous nematic ground state. The twist-bend phase (NTB) was independently predicted by Meyer [1] and Dozov [2] and later discovered experimentally in the system of mesogenic dimers, in which rigid cores are connected by a flexible aliphatic chain [3–5], in bent-core liquid crystals (LC) [6,7] and in other systems with strongly bend molecules. It has also been established experimentally that in the NTB phase

the nematic director describes the oblique helicoid with the extremely short pitch of approximately few molecular lengths [3–9].

Dozov [2] has assumed that in the system of bent-core molecules the bend elastic constant can vanish at a certain temperature leading to an elastic instability and the growth of bend deformations. The bend deformation is accompanied by the twist one because the bend alone cannot fill the space while the oblique helicoidal structure can be homogeneous in the bulk without any defects. The twist-bend phase has also been studied by computer simulations [7,10–12]. In particular, recent large-scale simulations by M. Wilson [11] have confirmed the predominant role of the bent molecular shape compared with the role of chiral molecular conformations. It should be noted that the assumption about the dramatic decrease of the bend elastic constant

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on approach to the twist bend phase has been confirmed experimentally by several authors [5,13–15].

An interesting phenomenological model of the NTB phase has been proposed by Selinger [16] who has assumed that the Frank elastic constants may be reduced significantly by the negative flexoelectric corrections proportional to the squares of the flexoelectric coefficients. These corrections are negligibly small in conventional nematics due to the relatively small values of the flexoelectric coefficients. However, Selinger has taken into account that the flexoelectric coefficients may strongly increase with the decreasing temperature if the material is close to the transition into the virtual ferroelectric phase. One notes that this ferroelectric phase may not be observed as it may be globally unstable with respect to other low-temperature phases. If the nematic is relatively close to the virtual ferroelectric phase, the corresponding component of nematic dielectric susceptibility can be very large and hence the flexoelectric corrections may be comparable to the bare elasticity coefficients.

A detailed Landau de Gennes theory of the NTB phase has recently been developed by Lech Longa et al. [17–20] taking into account biaxiality and considering an interaction between several helicity modes. In this way it has been possible to consider a number of possible structures including the NTB phase and to study their relative stability. In particular, the theory has been used to quantitatively fit the experimental data on the temperature variation of the main parameters of the NTB phase including the anomalously low bend elastic constant of the nematic above the transition into the NTB phase. The effect of the external electric field on the helical structure of NTB phase has also been considered [18].

The first molecular theory of the NTB phase has been developed by Greco and Ferrarini [12,21,22] taking into consideration the Maier-Saupe type interaction between different arms of the model bent-core molecules. In this theory the biaxiality is also taken into account and it has been emphasised that there is no unique definition of the director in the oblique helical structure [22] similar to the smectic C phase [23,24]. As a result a number of uniaxial and biaxial order parameters as well as the pitch of the helical structure have been calculated. The molecular model of the NTB phase, proposed by Greco and Ferrarini, has been generalised by Longa and Tomchuck [25,26] taking into consideration the biaxiality of the arms of the bent core molecules.

In this paper we briefly review and critically analyse the existing phenomenological theory of the NTB phase with a special emphasis on the contribution of Lech Longa and his group.

2. Elementary model of Dozov

Dozov has predicted the NTB phase [2] long before it has been discovered experimentally. The theoretical model of Dozov is based on the assumption that the bend elastic constant K_{33} vanishes at some temperature which results in the spontaneous bend deformation. It has been recognised in [2] that the pure spontaneous bend solution in the bulk is impossible without defects and is generally energetically unstable, and hence two other one-dimensional solutions have been proposed. The first solution corresponds to the one-dimensional splay bend phase which we do not consider here while the second solution is the continuous tilted helical structure of the director which corresponds to the NTB phase. It has also been assumed that the spontaneous bend is stabilised by the higher order elastic terms which are proportional to the fourth power of the director gradients. In particular, the director distribution in the NTB phase is assumed to be described by the following expression:

$$\mathbf{n}(x) = (\cos\theta, \sin\theta\sin\phi, \sin\theta\cos\phi,), \qquad (1)$$

where θ is the director tilt angle and $\phi = qx$.

Taking this into account the free energy density of the NTB phase is expressed as:

$$F_{NTB} = \frac{1}{2}\left(K_{22}\theta^4 k^2 + K_{33}\theta^2 k^2 + C\theta^2 k^4\right), \qquad (2)$$

where the last term which is proportional to k^4 describes the combined effect of the higher order elastic terms.

Minimization of this free energy yields simple expressions for the tilt angle θ and the wave number k of the heliconical structure:

$$\theta = -\frac{K_{33}}{3K_{11}}, \quad k^2 = -\frac{K_{33}}{3C}. \qquad (3)$$

where $K_{33} < 0$. Both θ and k^2 vanish at the second-order transition which occurs at the critical temperature when $K_{33} = 0$.

It should be noted that no mechanism of the softening of the bend elastic constant is proposed in [2]. This is the main drawback of the Dozov model which is directly addressed in the more detailed theory developed by Shamid et al. [16] considered in the following section.

3. Phenomenological theory of Shamid, Dukkal and Selinger

In contrast to the Dozov model which takes into consideration only elastic terms, the so-called Selinger model is based on the flexoelectric effect and hence the free energy of the NTB phase depends both on the

director deformations and on the polarisation induced by the bend deformation:

$$F = \frac{1}{2}K_{11}\mathbf{S}^2 + \frac{1}{2}K_{22}T^2 + \frac{1}{2}K_{33}\mathbf{B}^2 + \frac{1}{2}\mu P^2 - e_{10}(\mathbf{P} \cdot \mathbf{S})$$
$$- e_{30}(\mathbf{P} \cdot \mathbf{B}) + \frac{1}{4}vP^4 + \frac{1}{2}\kappa(\nabla \mathbf{P})^2,$$

(4)

where $\mathbf{S} = \mathbf{n}(\nabla \cdot \mathbf{n})$ is the splay deformation vector, $\mathbf{B} = (\mathbf{n} \times (\nabla \times \mathbf{n}))$ is the bend deformation vector and $T = (\mathbf{n} \cdot (\nabla \times \mathbf{n}))$ is the twist deformation pseudoscalar. Here the first three terms represent the standard Frank elastic energy where K_{11}, K_{22}, K_{33} are the 'bare' elastic constants. The next two terms describe the flexoelectric effect which describes a coupling between the polarisation $\mathbf{P}$ and the bend and splay deformation vectors. Here e_{10} and e_{30} are the splay and bend bare flexoelectric coefficients, respectively. The fifth term is the dielectric energy of the polar nematic $\frac{1}{4}vP^4$ which is included to stabilise the value of the polarisation. Finally, the last term stabilises the spontaneous bend deformation.

The main advantage of the Selinger model is the clear mechanism of the reduction of bend and splay elastic constants determined by negative flexoelectric corrections. Such a reduction can readily be described neglecting for simplicity the last two terms in the free energy (4). Indeed minimisation of the reduced free energy (4) (without the last two terms) with respect to polarisation $\mathbf{P}$ yields

$$\mathbf{P} = \mu^{-1}e_{10}\mathbf{S} + \mu^{-1}e_{30}\mathbf{B}, \qquad (5)$$

Substituting the polarisation (5) back into reduced free energy (4) one obtains the effective elastic energy

$$F = \frac{1}{2}\tilde{K}_{11}\mathbf{S}^2 + \frac{1}{2}K_{22}T^2 + \frac{1}{2}\tilde{K}_{33}\mathbf{B}^2, \qquad (6)$$

where $\tilde{K}_{11}$ and $\tilde{K}_{33}$ are the effective splay and bend elastic constants with negative flexoelectric corrections:

$$\tilde{K}_{11} = K_{11} - \frac{1}{2}\mu^{-1}e_{10}^2; \tilde{K}_{33} = K_{33} - \frac{1}{2}\mu^{-1}e_{30}^2 \quad (7)$$

One notes that the flexoelectric corrections are negative and thus they diminish the values of the bend and splay elastic constants. One notes, however, that in conventional nematics the values of the flexoelectric coefficients are sufficiently small and hence the flexoelectric corrections can be neglected. On the other hand, flexoelectric corrections may increase significantly if the coefficient μ is sufficiently small, i.e. if the system is close to the transition into the virtual ferroelectric phase. This phase may actually not be observed as it may be globally unstable. It is well

known that above the transition into the ferroelectric phase the temperature variation of the dielectric susceptibility is described by the Curie-Weiss law. Hence the coefficient μ, which has the meaning of the inverse dielectric susceptibility, can approximately be expressed as $\mu = \mu'(T - T_0)$ where T_0 is the transition temperature into the virtual ferroelectric phase. Substituting the expression $\mu = \mu'(T - T_0)$ into (5) one concludes that the bend elastic constant vanishes when $T = T_c = T_0 - (2\mu'K_{33})^{-1}e_{30}^2$.

The parameters of the NTB phase can now be determined by substitution of the director profile (1) and the polarisation profile $\mathbf{P}(x) = (0, -p\cos(qx), p\sin(qx))$ into the free energy (4). One obtains

$$F = \frac{1}{2}K_{22}\sin^4\theta q^2 + \frac{1}{4}K_{33}sin^2(2\theta)q^2 - \frac{1}{2}e_{30}\sin(2\theta)pq$$
$$+ \frac{1}{4}vp^4 + \frac{1}{2}\mu'(T - T_0)p^2 + \frac{1}{2}\kappa p^2 q^2.$$

(8)

Minimisation of the free energy with respect to p, θ and q yields the following results:

$$\sin\theta \approx \frac{K_{33}}{2e_{30}}\left(\frac{\mu'}{K_{22}}\right)^{1/2}(T_c - T)^{1/2}, \qquad (9)$$

$$p \approx \frac{K_{33}^2\mu'}{4e_{30}^2}\left(\frac{\mu'}{K_{22}}\right)^{1/2}(T_c - T), \qquad (10)$$

$$q \approx \frac{1}{2}\left(\frac{3\mu'}{2\kappa}\right)^{1/2}(T_c - T)^{1/2}. \qquad (11)$$

Thus the Selinger model describes the second-order transition into the NTB phase. Directly below the transition the period of the helical structure $2\pi/q$ is infinite and then it decreases as $(T_c - T)^{-1/2}$. The tilt angle in the NTB phase increases from zero as $(T_c - T)^{1/2}$ and the polarisation increases linearly as $(T_c - T)$. One can also clarify the origin of the elastic instability which induces the transition into the NTB phase directly from the free energy (8) by expanding the polarisation in terms of q. Indeed, assuming that the polarisation is small, minimisation of the free energy (4) yields at small q:

$$p = \frac{e_{30}\sin(2\theta)q}{\mu'(T - T_0) + \kappa q^2}$$
$$\approx \frac{e_{30}\sin(2\theta)q}{\mu'(T - T_0)}\left(1 - \frac{\kappa}{\mu'(T - T_0)}\right). \qquad (12)$$

Substituting the polarisation (12) back into Equation (8). and keeping only the quadratic terms in q and θ one obtains:

$$
\begin{aligned}
F &\approx \frac{1}{2}\theta^2 \frac{K_{33}}{(T-T_0)}\left(T-T_0-\frac{e_{30}^2}{K_{33}\mu'}\right)q^2+\ldots \\
&= \frac{1}{2}\theta^2 \frac{K_{33}}{(T-T_0)}(T-T_c)q^2+\ldots
\end{aligned}
\quad (13)
$$

The elastic instability occurs when the coefficient in the q^2 term vanishes i.e. when $T=T_c$.

Thus the Selinger model provides a clear mechanism of the transition into NTB phase related to the reduction of the bend elastic constant by negative flexoelectric corrections. There is also no need to take into consideration higher order elastic terms to stabilise the heliconical structure. At the same time the model is slightly oversimplified and as a result it does not describe quantitatively some properties including, in particular, the splay elastic constant K_{11}. Indeed, the effective splay elastic constant (see Equation (7)) is given by $\tilde{K}_{11}=K_{11}-\frac{1}{2}(\mu'(T-T_0))^{-1}e_{10}^2$. One notes that the flexoelectric correction to the splay constant also diverges when $T\to T_0$ and hence K_{11} should also decrease with the decreasing temperature even when the splay flexoelectric coefficient e_{10} is smaller then the bend coefficient e_{30}. Experimentally, however, the temperature variation of K_{11} in bent-core nematics, which exhibit the NTB phase, is similar to the one in conventional calamitic nematics [13–15]. Thus one needs a more detailed theory to describe the behaviour of all elastic constants above the NTB phase. In the next section we summarise the molecular theory of elasticity of bent-core nematics and in Section 5 we discuss the Q-tensor theory developed by Lech Longa and his group.

4. Molecular theory of elasticity of bent-core nematics

A molecular theory of elasticity of nematic LCs can be developed [27–29] using the density functional approach (see, for example [30–32]). In this approach, the free energy of a liquid crystal, F, is a function of the orientational distribution function for biaxial molecules $f(\mathbf{x})$ where $\mathbf{x}=(\mathbf{a},\mathbf{b})$ and where ρ is the number density of molecules, the unit vectors a and b are in the direction of the long and short molecular axis respectively. The free energy can then be expanded around its value in the isotropic phase in terms of $\Delta f = f - f_0$ where $f_0 = \frac{1}{8\pi^2}$ is the one particle distribution function in the isotropic phase (see [28] for more details):

$$
\begin{aligned}
F &= \rho k_B T \int f(\mathbf{x})\ln[f(\mathbf{x})\Lambda]\,d\mathbf{x}d\mathbf{r} \\
&\quad -\frac{1}{2}k_B T\rho^2\int C_{2I}(\mathbf{x}_1,\mathbf{r}_{12},\mathbf{x}_2)\Delta f(\mathbf{x}_1)\Delta f(\mathbf{x}_2)d\mathbf{r}_{12}d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{r}_1,
\end{aligned}
\quad (14)
$$

where $\mathbf{r}_{12}$ is the intermolecular vector and $C_{2I}(\mathbf{x}_1,\mathbf{r}_{12},\mathbf{x}_2)$ is the direct pair correlation function of the isotropic phase.

The direct pair correlation function can be approximated in several different ways including the so called Parsons-Lee approximation [33,34]. In this approximation one assumes that the direct correlation function can be written in the scaled form, i.e. $C_{2I}(\mathbf{x}_1,\mathbf{r}_{12},\mathbf{x}_2)=C_2(r_{12}/\sigma_{12})$ where $\sigma_{12}=\sigma_{12}(\mathbf{x}_1,\mathbf{u}_{12},\mathbf{x}_2)$ is the minimum distance of approach for two rigid molecules '1' and '2' which depends on their relative orientation, and where the unit vector $\mathbf{u}_{12}=\mathbf{r}_{12}/r_{12}$.

Simple interpolation (between three orientations) of σ_{12} for two uniaxial hard spherocylinders, of diameter d and with L being the length of the cylindrical part, is the following

$$
\sigma_{12}=d+\frac{L-d}{2}\left((\mathbf{a}_1\cdot\mathbf{u}_{12})^2+(\mathbf{a}_2\cdot\mathbf{u}_{12})^2\right). \quad (15)
$$

In the nematic phase composed of bent-core molecules one can employ the following modification of the Parsons-Lee approximation [27]. In this case the pair correlation function for bent-core molecules i and j composed of the two uniaxial arms rigidly joined together at a bend angle α can be written as a sum of the correlation functions between different arms using the Parsons-Lee approximation:

$$
C_{2I}(\mathbf{x_i},\mathbf{r}_{ij},\mathbf{x_j})\approx\sum_{\nu,\mu}C_2\left(\frac{r_{\nu\mu}}{\sigma_{\nu\mu}}\right) \quad (16)
$$

where $\sigma_{\nu\mu}=\sigma_{\nu\mu}(\mathbf{a}_{i,\nu},\mathbf{u}_{\nu\mu},\mathbf{a}_{j,\mu})$. Here $\mathbf{a}_{i,\nu}$ is the unit vector along the primary axis of the arm ν of the molecule i, $\mathbf{a}_{j,\mu}$ is the primary axis of the arm μ of the molecule j, $\mathbf{r}_{\nu\mu}$ is the vector between the centre of the arm ν of the molecule i and the centre of the arm μ of the molecule j and $\mathbf{u}_{\nu\mu}=\mathbf{r}_{\nu\mu}/r_{\nu,\mu}$.

Introducing the new variables $\mathbf{r}'_{\nu\mu}=\mathbf{r}_{\nu\mu}/\sigma_{\nu\mu}$ the second term in Equation (14) can be written in the form:

$$
\begin{aligned}
H &= -\frac{1}{2}k_B T\rho^2\int d\mathbf{r}_1\sum_{\nu,\mu}\int_1^\infty C_2(r'_{\nu\mu})(r'_{\nu\mu})^2 \\
&\quad \left(\int\Delta f(\mathbf{x}_1)\Delta f(\mathbf{x}_2)\sigma_{\nu\mu}^3 d\mathbf{x}_1 d\mathbf{x}_2\right)dr'_{\nu\mu}d\mathbf{u}_{\nu\mu},
\end{aligned}
\quad (17)
$$

where only the product $\Delta f(\mathbf{x}_1)\Delta f(\mathbf{x}_2)\sigma_{\nu\mu}^3$ depends on the orientation of the two molecules $\mathbf{x}_1,\mathbf{x}_2$. One notes that Equation (17) describes the free energy of an inhomogeneous nematic phase which is the sum of

the free energy of the homogeneous state and the distortion energy. The distortion free energy can be separated by expanding the orientational distribution function $f(\mathbf{x}, \mathbf{n}(\mathbf{r}_2))$ at the position $\mathbf{r}_2$ around the point $\mathbf{r}_1$:

$$f(\mathbf{x}, \mathbf{n}(\mathbf{r}_2)) = f(\mathbf{x}, \mathbf{n}(\mathbf{r}_1)) + (\mathbf{r}_{12} \cdot \quad)f((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2)$$
$$+ \frac{1}{2}(\mathbf{r}_{12} \cdot \quad)^2 f((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2) + \dots$$

(18)

taking into account that only quadratic terms contribute to the free energy of nonchiral nematics Equation (18) can be expressed as

$$f(\mathbf{x}, \mathbf{n}(\mathbf{r}_2)) - f(\mathbf{x}, \mathbf{n}(\mathbf{r}_1)) \approx \frac{1}{2}\frac{\partial f}{\partial \mathbf{n}} \cdot (\mathbf{r}_{12} \cdot \quad)^2 \mathbf{n} + \frac{1}{2}\frac{\partial^2 f}{\partial \mathbf{n}^2}$$
$$: ((\mathbf{r}_{12} \cdot \quad)\mathbf{n})^2.$$

(19)

Substituting $\mathbf{r}_{12} = \mathbf{r}_{\nu\mu}\sigma_{\nu\mu}$ and $\mathbf{u}_{12} = \mathbf{u}_{\nu\mu}$ into Equations (19) and (17), one obtains the following expression for the free energy of the inhomogeneous nematic:

$$F = F_0 + \int F_d(\mathbf{r})d\mathbf{r},$$

(20)

where F_0 is the free energy of the homogeneous phase and the distortion free energy F_d is given by

$$F_d(\mathbf{r}) = -\frac{1}{2}k_B T \rho^2 \lambda \sum_{\nu,\mu} \int \sigma_{\nu\mu}^5 f(\mathbf{x}_1) \left(\frac{\partial f}{\partial \mathbf{n}} \cdot (\mathbf{u}_{\nu\mu} \cdot \quad)^2 \mathbf{n}\right)$$
$$+ \frac{\partial^2 f}{\partial \mathbf{n}^2} : ((\mathbf{u}_{\nu\mu} \cdot \quad)\mathbf{n})^2)d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{u}_{\nu\mu},$$

(21)

where

$$\lambda = -\int_1^\infty C_2(r)r^5 dr.$$

In Equation (21) the function $\sigma_{\nu\mu}$ depends only on $(\mathbf{a}_\nu \cdot \mathbf{u}_{\nu\mu})$ and $(\mathbf{a}_\mu \cdot \mathbf{u}_{\nu\mu})$ and thus it can be expanded in Legendre polynomials $P_n(\mathbf{a}_\nu \cdot \mathbf{u}_{\nu\mu})$ and $P_n(\mathbf{a}_\mu \cdot \mathbf{u}_{\nu\mu})$. The lowest order term in the expansion of $\sigma_{\nu\mu}^5$ which contributes to the elastic constants can be expressed as [27] $\frac{20}{9}d^3(L-d)^2 P_2(\mathbf{a}_\nu \cdot \mathbf{u}_{\nu\mu})P_2(\mathbf{a}_\mu \cdot \mathbf{u}_{\nu\mu})$. Substituting this expression into Equation (21), averaging over the orientations of the two molecules and integrating over the intermolecular vector $\mathbf{r}_{12}$ one obtains relatively simple expressions for the elastic constants of bent core nematics [27]:

$$K_{11} = -k_B T \frac{\pi}{5}\rho^2 \lambda \kappa \tilde{S}^2,$$

(22)

and

$$K_{22} = K_{33} = -k_B T \frac{\pi}{15}\rho^2 \lambda \kappa \tilde{S}^2,$$

(23)

where $\kappa = 20d^3(L-d)^2/9$. Here $\tilde{S}$ is the orientational order parameter of the single arm i of the bent-core molecule which depends on the bend angle α:

$$\tilde{S} = \langle P_2(\mathbf{a}_i \cdot \mathbf{n})\rangle$$
$$= \frac{3}{2}\langle(\mathbf{a} \cdot \mathbf{n})^2\rangle \cos 2\alpha + \frac{3}{2}\langle(\mathbf{b} \cdot \mathbf{n})^2\rangle \sin 2\alpha - \frac{1}{2}$$
$$= S\cos 2\alpha + \frac{1}{2}(1 - S + D)\sin 2\alpha,$$

(24)

where $\mathbf{a}_i = \mathbf{a}\cos\alpha + \mathbf{b}\sin\alpha$ is the unit vector in the direction of the long axis of an arm i and where $S = \langle P_2(\mathbf{a} \cdot \mathbf{n})\rangle$ is the nematic order parameter of the whole molecule while $D = \langle(\mathbf{b} \cdot \mathbf{n})^2\rangle - \langle(\mathbf{c} \cdot \mathbf{n})^2\rangle$ are the biaxiality order parameter of the biaxial bent-core molecule in the uniaxial nematic phase, and $\mathbf{c}$ is the second short molecular axis.

One notes that Equations (22,23) describe the so-called bare elastic constants, i.e. the ones without flexo-electric corrections. The temperature variation of the reduced bare elastic constants $K_{ii}^{red} = \frac{d}{-\lambda t J(\rho^*)^2}K_{ii}$ is presented in Figure 1, where the nondimensional density $\rho^* = \rho d^2 L$, the nondimensional temperature $t = \frac{k_B T}{J}$ and where J is the Maier-Saupe interaction constant. One can readily see that the bare elastic constants are decreasing with the increasing bend angle α although their temperature variation is qualitatively very similar to the one for rod-like molecules. This means that the polar molecular shape itself does not lead to any decrease of the elastic constants with the decreasing temperature if polar effects are not taken into account.

Finally it should be noted that in this approximation $K_{22} = K_{33}$ which is related to the fact that we
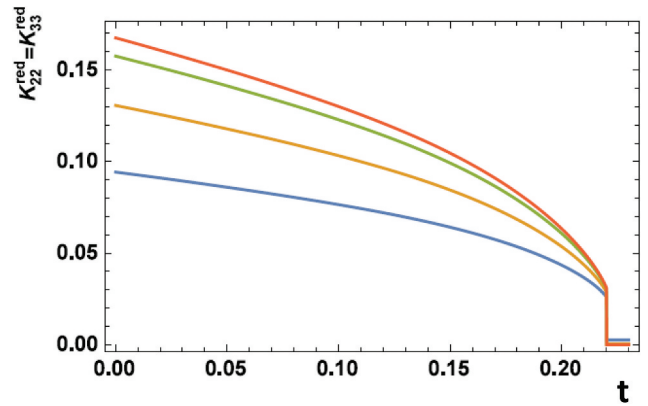

Figure 1. (Colour online) Temperature variation of the bare bend nondimensional elastic constant K_{33} (i.e. Without flexoelectric correction) for different values of the bend angle α: 0 (red), $\pi/18$ (green), $\pi/9$ (orange), $\pi/6$ (blue). The nondimensional temperature $t = \frac{k_B T}{J}$ where J is the Maier-Saupe interaction constant.

have only taken into account the quadratic contributions in a. It is well known that the difference between K_{22} and K_{33} is determined by the higher orientational order parameters including, in particular, $\langle P_4(\mathbf{a} \cdot \mathbf{n}) \rangle$. The corresponding contribution has been evaluated in [29].

5. Reduction of elastic constants by flexoelectric corrections in bent-core nematics

In the distorted liquid crystal the orientational distribution function is modified, and in the case of small orientational deformation it contains a small correction $h(\mathbf{a}, \mathbf{b}, \mathbf{n})$ which is generally polar:

$$f(\mathbf{a}, \mathbf{b}, \mathbf{n}) = f_0(\mathbf{a}, \mathbf{b}, \mathbf{n})(1 + h(\mathbf{a}, \mathbf{b}, \mathbf{n})), \qquad (25)$$

where $f_0(\mathbf{a}, \mathbf{b}, \mathbf{n})$ is the orientational distribution function of the undistorted nematic phase and the small correction $h = h_f + h_p$ is a sum of two terms. The function $h_f \sim {}_\alpha n_\beta$ is proportional to the gradients of the director while the function $h_p \sim \langle \mathbf{b} \rangle$ is proportional to the polar order parameter $\langle \mathbf{b} \rangle$ which determines the polarisation due to the polar ordering of short molecular axes. One notes that another polar order parameter $\langle \mathbf{a} \rangle = 0$ because $\mathbf{a}$ is always Equationuationuivalent to $-\mathbf{a}$ due to the C_{2v} symmetry of a bent-core molecule. Then the average molecular dipole in the distorted nematic phase can be expressed as:

$$< \mathbf{d} > = \int \mathbf{d} f_0(\mathbf{a}, \mathbf{b}, \mathbf{n}) h(\mathbf{a}, \mathbf{b}, \mathbf{n}) d\mathbf{b} d\mathbf{a}, \qquad (26)$$

where the molecular dipole

$$\mathbf{d} = \mu_\perp \mathbf{b}. \qquad (27)$$

Here the polar correction to the orientational distribution function $h(\mathbf{a}, \mathbf{b}, \mathbf{n})$ should be determined using a corresponding molecular-statistical theory.

The one-particle distribution function of the distorted liquid crystal can be determined by minimisation of the free energy with respect to $f(\omega)$ taking into account the normalisation condition. One obtains

$$\delta\left(F + \lambda \int \rho(\omega) d\omega\right) \delta\rho(\omega) = -k_B T C_1(\omega) + k_B T \ln f(\omega) + \Lambda + \lambda = 0, \qquad (28)$$

where the lagrange multiplier λ is determined from the normalization condition, $f(\omega)$ is the one-particle distribution of the distorted nematic, given by Equation (25) and $C_1(\omega)$ is the one-particle correlation function. Let us now perform the functional Taylor expansion of the function $C_1(\rho(\omega))$ in the right hand side of Equation (28) about the local distribution $f_0(\omega)$:

$$C_1(\rho) = C_1(\rho_0(\omega)) + \rho \int C_2(\rho_0(\omega_1), \rho_0(\omega_2))(f(\omega_2)$$
$$-f_0(\omega_2))d\omega_2 + \dots, \qquad (29)$$

where $C_2(\rho_0(\omega_1), \rho_0(\omega_2))$ is the pair direct correlation function. One notes that he higher order terms in the expansion (which are determined by higher order direct correlation functions) do not contribute to the flexoelectric effect because they are proportional to the higher powers of $(f(\omega_2) - f_0(\omega_2))$ and hence to the higher powers of the orientational deformation.

The difference $(f(\omega_2) - f_0(\omega_2))$ in the second term in the right hand side of Equation (29) can be expressed as $(f(\omega) - f_0(\omega)) = f_0((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2)h(\omega)$ by using Equation (25). Performing the gradient expansion of the function $f_0((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2)$ to the first order one finally obtains:

$$(f(\omega) - f_0(\omega)) = (\mathbf{r}_{12} \cdot \quad) f_0((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2)$$
$$+ f_0((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2)h(\omega). \qquad (30)$$

Substituting Equation (30) into Equation (29) and then into the general Equation (28) and expanding $\ln f$ in Equation (28) to the first order of the small function h one obtains the following integral Equationuationuation for the correction $h(\omega)$:

$$h(\mathbf{x}_1) = -\rho \, C_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{r}_{12})(\mathbf{r}_{12} \cdot \quad) f_0((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2) d\mathbf{x}_2 d\mathbf{r}_{12} -$$
$$- \rho \, C_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{r}_{12}) f_0((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2) h(\mathbf{x}_2) d\mathbf{x}_2 d\mathbf{r}_{12}, \qquad (31)$$

where $\mathbf{x} = (\mathbf{a}, \mathbf{b})$.

In the general case the correction $h(\mathbf{a}, \mathbf{b})$ is a sum of the 'symmetric' and the 'antisymmetric' parts:

$$h(\mathbf{a}, \mathbf{b}) = h_s(\mathbf{a}, \mathbf{b}) + h_a(\mathbf{a}, \mathbf{b}), \qquad (32)$$

In this section we assume that the direct correlation function can be expressed as

$$C_{2I}(\mathbf{x}_1, \mathbf{r}_{12}, \mathbf{x}_2) \approx \sum_{v,\mu} C_2\left(\frac{r_{v\mu}}{\sigma_{v\mu}}\right)$$
$$- \frac{1}{k_B T} \Theta(r_{12} - d) U_{dd}(\mathbf{b}_1, \mathbf{b}_2, \mathbf{r}_{12}), \qquad (33)$$

where the first term is a sum of the correlation functions between different arms of the two molecules expressed in the Parsons-Lee approximation (see Equation (16)), $\Theta(r_{12} - d)$ is the step function which describes the steric cut-off and the second term is the dipole-dipole interaction potential for bent-core molecules.

Combining Equations (31–33) the polar correction to the orientational distribution function of the polar bent-core nematic can be expressed as:

$$h_a(\mathbf{b}_1, \mathbf{a}_1) = -\frac{4\pi}{3k_B T}\mu_\perp (\mathbf{b}_1 \cdot \mathbf{P}) - \frac{1}{k_B T}\mu_\perp (\mathbf{b}_1 \cdot \mathbf{E})$$

$$-\frac{\rho}{12}L^2(L-d)\lambda_3 \int \left[(\mathbf{a}_1 \cdot \mathbf{u})^2 + (\mathbf{a}_2 \cdot \mathbf{u})^2\right]$$

$$\sin^2\alpha (\mathbf{b}_1 \cdot \mathbf{b}_2) f_0((\mathbf{a}_2 \cdot \mathbf{n})^2, (\mathbf{b}_2 \cdot \mathbf{n})^2) h(\mathbf{b}_2, \mathbf{a}_2)$$

$$d\mathbf{a}_2 d\mathbf{b}_2 d\mathbf{u} - \frac{1}{2}\rho L d(L-d)^2 \lambda_2 \int P_2(\mathbf{a}_2 \cdot \mathbf{u})$$

$$P_2(\mathbf{a}_1 \cdot \mathbf{u})((\mathbf{a}_1 \cdot \mathbf{u}) - (\mathbf{a}_2 \cdot \mathbf{u}))(\mathbf{u} \cdot \ \ )$$

$$f_0((\mathbf{a}_2 \cdot \mathbf{n})^2, (\mathbf{b}_2 \cdot \mathbf{n})^2) d\mathbf{a}_2 d\mathbf{b}_2 d\mathbf{u}.$$

$$(34)$$

Now the polarisation $\mathbf{P}$ can be expressed as:

$$\mathbf{P} = -\rho \int \mu_\perp \mathbf{b} f_0((\mathbf{a} \cdot \mathbf{n})^2, (\mathbf{b} \cdot \mathbf{n})^2) h(\mathbf{b}, \mathbf{a}) d\mathbf{a} d\mathbf{b}$$

$$= -\frac{\pi}{3}\frac{\rho \mu_\perp^2}{2k_B T}\mathbf{P} - \frac{\rho \mu_\perp^2}{2k_B T}\mathbf{E} - \frac{1}{2}\rho^2 \mu_\perp \lambda_2 \sin\alpha L d(L-d)\tilde{S}^2$$

$$\int \frac{1}{2}\left[\frac{1}{3}(2+S)\mathbf{u} - S\mathbf{n}(\mathbf{n} \cdot \mathbf{u})\right]$$

$$P_2(\mathbf{n} \cdot \mathbf{u})(\mathbf{u} \cdot \ \ )P_2(\mathbf{n} \cdot \mathbf{u}) d\mathbf{u}$$

$$+ \frac{1}{24}\rho \lambda_3 \sin^2\alpha L^2(L-d)\tilde{S} \int \left[\frac{1}{3}(2+S)\mathbf{P} - S\mathbf{n}(\mathbf{n} \cdot \mathbf{P})\right](\mathbf{n} \cdot \mathbf{u})^2 d\mathbf{u},$$

$$(35)$$

where $(\mathbf{u} \cdot \ )P_2(\mathbf{n} \cdot \mathbf{u}) = 3(\mathbf{n} \cdot \mathbf{u})(\mathbf{u} \cdot \ )(\mathbf{n} \cdot \mathbf{u})$. Here we have decoupled the averages over short and long molecular axes (thus neglecting the corresponding third rank polar order parameters). In this case $\langle b_\alpha b_\beta \rangle = (\delta_{\alpha\beta} - \langle a_\alpha a_\beta \rangle)/2 = \left[(1/3)(2+S)\delta_{\alpha\beta} - Sn_\alpha n_\beta\right]$ if the order parameter $D = 0$.

Let us assume for simplicity that the director varies slowly in the (x, z) plane and that the local director $\mathbf{n} \parallel \mathbf{z}$. Then in the case of pure splay the flexoelectric polarization $\mathbf{P} \parallel \mathbf{n} \parallel \mathbf{z}$ and the only non-zero component of splay is $\ _x n_x$. In this case $P = P_z = \tilde{e}_{11}\ _x n_x$, where $\tilde{e}_{11}$ is the effective splay flexo coefficient. Substituting these components into Equation (35) and integrating over $\mathbf{u}$ one obtains the following expression for $\tilde{e}_{11}$:

$$\tilde{e}_{11} = e_{11}\left(1 - \frac{1}{3}(4\pi\chi_0 - 2(1+2S)A_0 \sin^2(\alpha))\right)^{-1},$$

$$(36)$$

where

$$A_0 = \frac{\rho \lambda_3}{108}L^2(L-d) = \frac{\rho^* \lambda_3}{108}\frac{L(L-d)}{d^2} \equiv \frac{\varepsilon}{108}\frac{L(L-d)}{d^2},$$

$$(37)$$

and

$$\chi_0 = \frac{\rho \mu_\perp^2}{k_B T} = \frac{\rho \mu_\perp^2}{tJ} \equiv \frac{\psi_0}{t}.$$

$$(38)$$

Here e_{11} is the so-called bare flexoelectric coefficient which is obtained by neglecting polar intermolecular interactions (that is the last two terms in the denominator in Equation (41):

$$e_{11} = -\frac{8\pi}{315}\nu \sin(\alpha)\tilde{S}^2(1-S).$$

$$(39)$$

where

$$\nu = \frac{2}{3}\rho^2 \lambda_2 \mu_\perp d L(L-d)^2.$$

$$(40)$$

In the case of pure bend $\mathbf{P} \parallel \mathbf{x} \perp \mathbf{n}$ and the only nonzero component of bend is $\ _z n_x$. Here $P = P_x = \tilde{e}_{33}\ _z n_x$, where $\tilde{e}_{33}$ is the effective bend flexo coefficient. Substituting these components into Equation (35) one obtains the following expression for $\tilde{e}_{33}$:

$$\tilde{e}_{33} = e_{33}\left(1 - \frac{1}{3}(4\pi\chi_0 - (2+S)A_0 \sin^2(\alpha))\right)^{-1}, \quad (41)$$

where e_{33} is the undressed bend flexo coefficient:

$$e_{33} = -\frac{8\pi}{315}\nu \sin(\alpha)\tilde{S}^2(2+S).$$

$$(42)$$

Finally the effective elastic constants with negative flexoelectric corrections are given by the following Equationuationuations:

$$\tilde{K}_{11} = K_{11} - \frac{1}{2}\left(1 - \frac{1}{3}(4\pi\chi_0 - 2(1+2S)A_0 \sin^2(\alpha))\right)^{-1}, e_{11}^2; \quad (43)$$

$$\tilde{K}_{33} = K_{33} - \frac{1}{2}\left(1 - \frac{1}{3}(4\pi\chi_0 - (2+S)A_0 \sin^2(\alpha))\right)^{-1}, e_{33}^2, \quad (44)$$

where the bare elastic constants are given by Equations (39 and 42), and χ_0 is expressed by Equation (38).

As discussed in the previous section, the bare elastic constants are not renormalised by the flexoelectric polarisation and possess a standard temperature dependence, *i.e.* grow monotonically with the decreasing temperature. This growth is mainly determined by the increase of the nematic order parameter S. In contrast, the effective bend elastic constant with the flexoelectric correction is rather small everywhere in the nematic phase, decreases with the decreasing temperature and reduces to zero as shown in Figure 2. The behavior of the bend constant is strongly effected by the nondimensional dipole-dipole interaction parameter $\psi_0 = \rho \mu_\perp^2 / J$ which is proportional to the square of the molecular transverse dipole. At the same time the temperature variation of the effective splay elastic constant, presented in Figure 3, is qualitatively similar to the typical variation of the splay constant for conventional nematics. This behavior is very similar to the one observed experimentally [13].
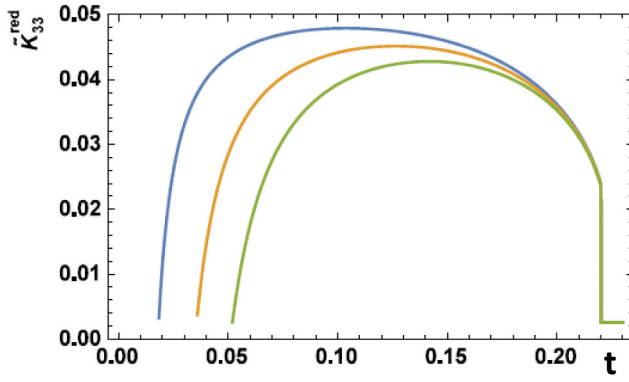
Figure 2. (Colour online) Temperature variation of the effective bend nondimensional elastic constant K_{33} (i.e. With flexoelectric correction) for different values of the nondimensional dipole-dipole interaction parameter ψ_0 from the top : 0.003 (blue), 0.006 (orange), 0.009 (green) and for $a = \pi/6$. The nondimensional temperature $t = \frac{k_B T}{J}$ where J is the Maier-Saupe interaction constant.
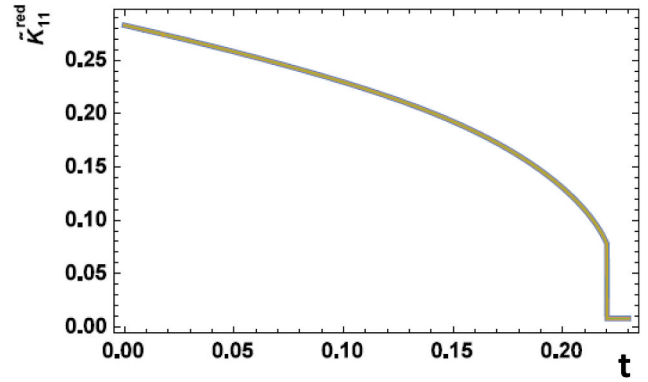

Figure 3. (Colour online) Temperature variation of the effective splay nondimensional elastic constant K_{11} (i.e. With flexoelectric correction) for different values of the nondimensional dipole-dipole interaction parameter ψ_0 from the top : 0.003 (blue), 0.006 (orange), 0.009 (green) and for $a = \pi/6$. Note that all three curves coincide. The nondimensional temperature $t = \frac{k_B T}{J}$ where J is the Maier-Saupe interaction constant.

6. Landau – de Gennes theory of the NTB phase proposed by Lech Longa

The most general Landau – de Gennes theory of the NTB phase has been proposed by Longa and Tomchuk [20] based on the biaxial Q-tensor approach. Longa and Tomczuk have also considered a competition between different modulated polar nematic phases and constructed the corresponding phase diagrams. In this theory the authors do not use the ansats which describe the helical distribution of the director but consider a general form of the biaxial tensor order parameter $Q_{ij}(z)$ which is consistent with the symmetry of the one-dimensional polar distorted nematic phase.

One notes that in any one-dimensional periodic nematic phase with tilted director the local symmetry is characterised by the C_{2h} point symmetry group if the phase is nonchiral and by the C_2 group if the phase is chiral. In both cases there exists only one local symmetry axis $\mathbf{h}$ which is normal to the wave vector $\mathbf{k}$ of the periodic structure and to the tilt plane. Thus the unit vector $\mathbf{h}$ must be the primary axis of any macroscopic second rank tensor including the tensor order parameter Q_{ij}. Taking this into account the tensor order parameter Q_{ij} can be expressed as a sum of three mutually orthogonal tensors (which is a slightly simplified form of Equation (6) in [20] suitable for the NTB phase):

$$Q_{ij} = S_k(k_i k_j - \delta_{ij}/3) + \frac{1}{2}P_k(c_i c_j - h_i h_j)$$
$$+ \frac{1}{2}C(k_i c_j + c_i k_j), \qquad (45)$$

where the unit vector $\mathbf{c}$ is perpendicular to $\mathbf{k}$ and $\mathbf{h}$, and where S_k, P_k and C are the three independent orientational order parameters of the periodic nematic phase. Here S_k is the uniaxial orientational order parameter with respect to the wave vector $\mathbf{k}$, P_k is the biaxial order parameter in the plane perpendicular to $\mathbf{k}$ and C is the tilt order parameter which specifies the tilt of the director. These order parameters are discussed in detail in [23] in the case of the Smectic C phase and considered also in the following section.

In the NTB phase the unit vectors $\mathbf{h}$ and $\mathbf{c}$ rotate about the z axis which is parallel to $\mathbf{k}$:

$$\mathbf{h} = (\cos(kz + \phi), \sin(kz + \phi), 0);$$
$$\mathbf{c} = (\sin(kz + \phi), -\cos(kz + \phi), 0), \qquad (46)$$

where ϕ is the phase.

Now the Landau de Gennes free energy of the NTB phase can be expressed in terms of the order parameter $\mathbf{Q}$ and its gradients and the polarisation $\mathbf{P}$ induced by the gradients of $\mathbf{Q}$:

$$F = \int (f_{Qb} + f_{Qel} + f_P + f_{QP}), \qquad (47)$$

where f_{Qb} is the bulk free energy density, f_{Qel} is the elastic energy and the last two terms f_P and f_{QP} depend on the polarisation.

The bulk free energy contains the scalar invariants composed of the tensor order parameter $Q_{\mu,\nu}$. There exists only two independent invariants $I_2 = tr(\mathbf{Q}^2)$ and $I_3 = tr(\mathbf{Q}^3)$, and hence f_{Qb} can be written in the following form where terms up to the sixth order in $\mathbf{Q}$ are taken into account [20]:

$$f_{Qb} = a_0 \frac{(T - T*)}{T_{NI}} I_2 - bI_3 + cI_2^2 + dI_2I_3 + e(I_2^3 - 6I_3^2) + fI_3^2, \quad (48)$$

where T_{NI} is the nematic-isotropic transition temperature.

The elastic energy f_{Qel} contains a large amount of higher order terms composed of the derivatives $Q_{\mu,\nu,\alpha}$ and the tensor $Q_{\mu,\nu}$ itself. One notes that the simplest approximation for the elastic energy contains only two second-order terms $L_1^{(2)} Q_{\alpha\beta,\gamma} Q_{\alpha\beta,\gamma}$ and $L_2^{(2)} Q_{\alpha\beta,\beta} Q_{\alpha\gamma,\gamma}$. This approximation is sufficient for many purposes but the main disadvantage is that it yields the same values for splay and bend elastic constants. In the Longa's theory [20] three additional third order terms of the type $Q\partial Q\partial Q$ are taken into consideration in order to lift the degeneracy between bend and splay deformations. In addition three fourth order terms $QQ\partial Q\partial Q$ are also taken into account to stabilise the inhomogeneous structure of the phase. As a result the elastic energy is expressed as [20]:

$$f_{Qel} = L_1^{(2)} Q_{\alpha\beta,\gamma} Q_{\alpha\beta,\gamma} + L_2^{(2)} Q_{\alpha\beta,\beta} Q_{\alpha\gamma,\gamma} \quad (49)$$

$$+ L_{14}^{(4)} \left(\lambda_2 Q_{\mu\nu,\nu} + Q_{\alpha\beta} Q_{\alpha\mu,\beta} \right)^2 \quad (50)$$

$$+ L_6^{(4)} \left(\lambda_3 Q_{\beta\nu,\nu} + Q_{\alpha\beta} Q_{\alpha\mu,\mu} \right)^2 \quad (51)$$

$$+ L_7^{(4)} \left(\lambda_4 Q_{\beta\mu,\nu} + Q_{\alpha\beta} Q_{\alpha\mu,\nu} \right)^2. \quad (52)$$

where $\lambda_2 = L_2^{(3)}/2L_{14}^{(4)}, \lambda_3 = L_3^{(3)}/2L_6^{(4)}, \lambda_4 = L_4^{(3)}/2L_7^{(4)}$.

Finally the polarisation dependent terms f_P and f_{PQ} are given by

$$f_P = a_{p0} \frac{(T - T_P)}{T_{NI}} P^2 + \Lambda_4 P^4 + b_P (\ \mathbf{P})^2, \quad (53)$$

$$f_{PQ} = -\varepsilon_P \mathbf{P} \cdot (\ \cdot \mathbf{Q}) - \Lambda_{QP} P_\alpha Q_{\alpha\beta} P_\beta. \quad (54)$$

One notes that the last term in Equation (55) is not included into the free energy employed in the Selinger model. This term, however, is very important as it enables one to understand why the splay elastic constant is not reduced in contrast to the bend one. Indeed, let us neglect for simplicity the last two terms in Equation (54), assume that the tensor $\mathbf{Q}$ is uniaxial and then minimise the sum $f_P + f_{PQ}$ with respect to polarization. One obtains

$$\mathbf{P} = \mathbf{P}_s + \mathbf{P}_b, \quad (55)$$

$$\mathbf{P}_b = \frac{\varepsilon_P S(\mathbf{n} \cdot \ )\mathbf{n}}{2a_{p0}(T - T_P - \Delta T_P)/T_{NI}}, \quad (56)$$

$$\mathbf{P}_s = \frac{\varepsilon_P S\mathbf{n}(\ \cdot \mathbf{n})}{2a_{p0}(T - T_P + 2\Delta T_P)/T_{NI}}, \quad (57)$$

where $\Delta T_P = \Lambda_{QP} S T_{NI}/6a_{p0}$. Substituting Equations (57 and 58) back into the reduced free energy $f_{PQ} + a_{p0} \frac{(T - T_P)}{T_{NI}} P^2$ one obtains the following flexoelectric corrections to the bend and splay elastic constants:

$$\Delta K_{33} = -\frac{\varepsilon_P^2 S^2}{2a_{p0}(T - T_P - \Delta T_P)/T_{NI}}, \quad (58)$$

$$\Delta K_{11} = -\frac{\varepsilon_P^2 S^2}{2a_{p0}(T - T_P + 2\Delta T_P)/T_{NI}}, \quad (59)$$

One can readily see that the corrections to splay and bend elastic constants diverge at different temperatures $T_{Pb} = T_P + \Delta T_P$ and $T_{Pb} = T_P - 2\Delta T_P$, respectively, where $T_{Pb} = T_{PS} + 3\Delta T_P$. If ΔT_P is sufficiently large the bend flexoelectric correction ΔK_{33} may reduce the total bend elastic constant to zero at some temperature while splay correction remains negligibly small. In this case the temperature variation of the splay elastic constant is qualitatively similar to that in conventional calamitic nematics which corresponds to the experimental data.

In the frame work of the general Landau-de Gennes theory developed by Longa et al. the elastic constants are also renormalised by the flexoelectric effect although in a more complicated way. In particular, different elasticity coefficients in Equation (49) are renormalised in a different way:

$$L_{2,eff}^{(2)} = L_2^{(2)} - \frac{\varepsilon_P^2}{a_P}; \quad (60)$$

$$L_{3,eff}^{(3)} = L_3^{(3)} - \frac{\Lambda_{QP}\varepsilon_P^2}{4a_P^2}; \quad (61)$$

$$L_{6,eff}^{(4)} = L_6^{(4)} - \frac{\Lambda_{QP}^2\varepsilon_P^2}{4a_P^3}; \quad (62)$$

where $a_P = a_{p0} \frac{(T - T_P)}{T_{NI}}$.

Finally the results of the Landau de Gennes theory have been used to fit the experimentally observed temperature variation of several material parameters of nematic LCs which exhibit the NTB phase. It has been showm that the variation of all three elastic constants in the nematic phase above the NTB phase can be described by the general Landau theory in the quantitative way. One notes that the theory simultaneously describes the reduction of the bend elastic constant and the 'classical' behaviour of the splay and twist constants.

7. Uniaxial and biaxial order parameters of the NTB phase

The NTB is intrinsically locally biaxial because of the deviation of the director **n** from the wave vector **k** of the helical structure. Thus any macroscopic second rank tensor after diagonalisation in the NTB phase can be expressed as a sum of the uniaxial and the biaxial parts. In particular the averaged molecular tensor $\langle a_i a_j - (1/3)\delta_{ij}\rangle$ can be written in the form:

$$Q_{ij} = \langle (a_i a_j - (1/3)\delta_{ij})\rangle = S(n_i n_j - \delta_{ij}/3) + \frac{1}{2}P(m_i m_j - h_i h_j), \quad (63)$$

where P is the biaxial order parameter. One notes that only one eigenvector **h** of the tensor Q_{ij} is fixed by the symmetry of the NTB phase as it is parallel to the C_2 symmetry axis which is perpendicular to the tilt plane. The other two eigenvectors **n** and **m** are parallel to the tilt plane but their orientation is not specified by any symmetry. As a result the primary axes of different macroscopic tensors are not necessarily parallel in the NTB phase due to its low symmetry. In particular the orientation of the primary axis (i.e. the director **n**) is not uniquely defined and is generally different for different tensors. As a result the NTB phase may be characterised by a number of 'directors' and hence by different tilt angles depending of how many macroscopic tensors are taken into consideration.

Taking this uncertainty into account it may be more consistent to express all macroscopic tensors in the same universal frame based on the wave vector **q** and the unit vector **h**⊥**q** in the direction of the C_{2h} symmetry axis. In this frame, the tensor order parameter Q_{ij} is not diagonal, and can be expressed as:

$$Q_{ij} = S_k(k_i k_j - \delta_{ij}/3) + \frac{1}{2}P_k(c_i c_j - h_i h_j) + \frac{1}{2}C(k_i c_j + c_i k_j), \quad (64)$$

where S_k, P_k and C are the three independent orientational order parameters of the NTB phase.

Here the order parameter S_k characterises the ordering of long molecular axes along the wave vector **k** and the order parameter P_k describes the biaxiality of distribution of long molecular axes in the plane perpendicular to **k**. Finally, C is the tilt order parameter which describes the tilt of the axes of the tensor Q with respect to **k**. One notes that both order parameters C and P_k vanish in the uniaxial smectic A phase where the tensor Q_{ij} is uniaxial and orthogonal in the **k** frame. It can be

shown that at small tilt angles $P_k \propto \Theta^2$ and hence P_k is the secondary order parameter of the Smectic A – Smectic C transition which describes the biaxiality of the phase.

Finally the vector tilt order parameter **C** can be defined as

$$C_i = \varepsilon_{ijk}Q_{kj} = C(\mathbf{c} \times \mathbf{k})_i, \quad (65)$$

i.e. $\mathbf{C} = C(\mathbf{c} \times \mathbf{k})$ which describes both the direction and the magnitude of the tilt.

One notes that the three terms in Equation (66)) are mutually orthogonal. Hence the order parameters S_k, P_k and C can be expressed as:

$$S_k = \frac{3}{2}Q_{ij}(k_i k_j - \frac{1}{3}\delta_{ij}) = \frac{3}{2}S(\cos 2\Theta - \frac{1}{3}) + \frac{3}{4}P\sin 2\Theta, \quad (66)$$

$$P_k = Q_{ij}(c_i c_j - h_i h_j) = S\sin 2\Theta + \frac{1}{2}P(\cos 2\Theta + 1), \quad (67)$$

$$C = Q_{ij}(c_i k_j + k_i c_j) = S\sin 2\Theta - \frac{1}{2}P\sin 2\Theta, \quad (68)$$

where we have used Equation (65) and have taken into account that $\mathbf{n} = \mathbf{k}\cos\Theta + \mathbf{c}\sin\Theta$ and $\mathbf{m} = -\mathbf{k}\sin\Theta + \mathbf{c}\cos\Theta$.

Solving the system of Equationuationnuations Equation (68) with respect to S, P and Θ one obtains the following expressions for the tilt angle Θ and the order parameters S and P in terms of the order parameters S_k, P_k and C:

$$\tan 2\Theta = \frac{C}{S_k - 0.5P_k}, \quad (69)$$

$$S = \frac{1}{4}S_k + \frac{3}{8}P_k + \frac{3\,C}{4\sin 2\Theta}, \quad (70)$$

$$P = \frac{1}{2}S_k + \frac{3}{4}P_k - \frac{C}{2\sin 2\Theta}. \quad (71)$$

At small tilt angles $\tan 2\Theta \approx 2\Theta$ and $P_k \propto \Theta^2$. It follows then from the first Equationuationnuation above that in this limit the scalar tilt order parameter $C \approx 2S\Theta$ is indeed proportional to the tilt angle Θ while the biaxial order parameter is very small.

One notes that this description is very similar to the one used in the theory of Smectic C* LCs [23,35] because the point symmetry is the same. It should be noted also that from the molecular theory point of view it is more convenient to use the tilt order parameter C because it is explicitly expressed as a well defined ensemble average of the corresponding molecular

expression while the tilt angle Θ cannot be expressed in this way.

One notes also that in this section the tensor order parameter **Q** is defined as a statistical average of the molecular invariant tensor $a_i a_j - \delta_{ij}/3$. At the same time the NTB phase is composed of strongly biaxial molecules and hence it is also possible to consider the independent molecular invariant tensor $b_i b_j - c_i c_j$ and the corresponding independent tensor order parameter $B_{ij} = \langle (b_i b_j - c_i c_j) \rangle$ which can be expressed in the same general form as Equation (66):

$$B_{ij} = D_k(k_i k_j - \delta_{ij}/3) + \frac{1}{2} B_k(c_i c_j - h_i h_j)$$
$$+ \frac{1}{2} C_B(k_i c_j + c_i k_j). \tag{72}$$

Here the order parameter D_k describes the uniaxial ordering of short axes of bent core molecules along the wave vector **k**, the order parameter B_k specifies the biaxial ordering of short molecular axes in the plane perpendicular to **k**, and the order parameter C_B describes the tilt of the tensor B_{ij} with respect to **k**.

It is reasonable to assume (and this is confirmed by existing experimental data) that the nematic order parameter S in the NTB phase is rather high. In this case the biaxial ordering of primary molecular axes should be week and hence $P_k \ll S_k$. At the same time the uniaxial ordering of short axes of bent-core molecules should also be week and therefore $D_k \ll S_k$ as well. Thus in the first approximation it is possible to neglect the order parameters P_k and D_k and express the tensors Q_{ij} and B_{ij} in the simplified form:

$$Q_{ij} \approx S_k(k_i k_j - \delta_{ij}/3) + \frac{1}{2} C(k_i c_j + c_i k_j), \tag{73}$$

$$B_{ij} \approx \frac{1}{2} B_k(c_i c_j - h_i h_j) + \frac{1}{2} C_B(k_i c_j + c_i k_j). \tag{74}$$

In this approximation the tensor order parameter Q_{ij} mainly describes the uniaxial ordering of long molecular axes while the tensor B_{ij} describes the biaxial ordering of short axes. Simultaneously the parameter C specifies the tilt of the primary director (the primary axis of the tensor Q_{ij}) according to the Equationuationnuation $\tan 2\Theta \approx C/S_k$ while the parameter C_B determines the second tilt angle Θ_B, i.e. the tilt of the axes of B_{ij}.

Taking this analyses of the order parameters into account one concludes that it may be more convenient to develop the general Landau – de Gennes theory of the NTB phase in terms of the two independent tensor order parameters $Q_{ij} = \langle (a_i a_j - \delta_{ij}/3) \rangle$ and $B_{ij} = \langle (b_i b_j - c_i c_j) \rangle$ rather then in terms of the single tensor Q_{ij} which formally includes all types of orientational order. The advantage of such an approach is that one can readily separate the effects of unixial and biaxial ordering of bent-core molecules on the structure and properties of the NTB phase and similar inhomogeneous phases. This kind of theory, however, is still to be developed.

8. Discussion

All existing phenomenological theories of the NTB phase are based on the assumption (confirmed by experimental data) that the bend elastic constant vanishes at some temperature triggering an instability of the homogeneous nematic phase. The generally accepted mechanism of such an instability is related to the flexoelectric polarisation, proportional to the bend and splay deformations which generally results in the negative flexoelectric corrections to the bend and splay elastic constants of the nematic phase. This mechanism has been first considered in detail by Selinger et al. [16], and a more general Landau- de Gennes theory has been developed later ny Longa et al. [20]. In particular, the theory of Longa et al. enables one to explicitly explain why in the nematic composed of bent-core molecules only the bend elastic constant is reduced while the variation of the splay elastic constant is qualitatively similar to the one observed in conventional calamitic nematics. Similar ideas have also been employed in the molecular-statistical theory of elasticity of bent-core nematics [27,29] which also enables one to understand why only the bend elastic constant is reduced. The theory of Longa et al. also takes into consideration the local biaxiality of the NTB phase and has been used to predict and describe the whole family of one-dimensional inhomogeneous nematic phases [20]. Finally, the experimentally determined temperature variations of the elastic constants,tilt angle in the NTB phase and the pitch of the nanoscale helical structure have been fitted qualitatively using the results of this theory.

From our point of view the important uncertainty of the existing phenomenological theory of the NTB phase is related to the stabilisation of the helical structure. When the bend elastic constant vanishes, the corresponding director deformations begin to grow and they should be stabilised by some higher order terms resulting in the heliconical structure. In the first model of the NTB phase proposed by Dozov [2] it was assumed that the structure is stabilised by the higher order elastic terms proportional to the fourth power of the deformations. Unfortunately there are too many of such terms to be included in the theory, and later Selinger et al. have shown [16]

that the heliconical structure can be stabilised by a single term in the free energy expansion which is quadratic in the gradients of the polarisation. One notes that in the perfect NTB phase only $(\nabla \cdot \mathbf{P})$ is nonzero and hence the corresponding term takes the form $\kappa(\nabla \times \mathbf{P})^2$. At the same time $(\nabla \cdot \mathbf{P}) = 0$ and therefore there are no displacement charges in the NTB phase. In contrast, $(\nabla \cdot \mathbf{P})$ is different from zero in the splay-bend nematic phase as well as in some other periodic phases considered in [20]. In these cases the electrostatic interaction between displacement charges should be taken into account in the total free energy. This is not straightforward, however, as the charge-charge interaction is long range and is not analytic in $\mathbf{k}$ which does not allow an expansion in powers of $\mathbf{k}$.

Another unsolved problem in the general theory of the NTB phase is a relationship between simple molecular models proposed by Ferrarini et al. [12,21,22] and Longa et al. [25,26]. Firstly it is not clear if the reduction of the bend elastic constant described in [21] is directly related to the flexoelectric effect. Secondly the mechanism of the stabilisation of the heliconical structure in the framework of these simple models is also unclear. In particular, the gradients of the polarisation are not taken explicitly into account in these models and hence the mechanism of stabilisation proposed by Selinger et al. [16]. does not seem to be relevant here. The clarification of these points may shed more light onto the mechanisms of the transition into the NTB phase.

Acknowledgments

Disclosure statement

No potential conflict of interest was reported by the author(s).

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