

RESEARCH ARTICLE

Polar interactions between bent–core molecules as a stabilizing factor for inhomogeneous nematic phases with spontaneous bend deformationsM. A. Osipov^a and G. Pająk^b^a*Department of Mathematics and Statistics, University of Strathclyde, Livingstone Tower, Richmond Street, Glasgow, Scotland, UK;*^b*M. Smoluchowski Institute of Physics, Department of Statistical Physics, Jagiellonian University, Lojasiewicza 11, 30-348 Kraków, Poland.**(October 2, 2016)*

It is generally accepted that the transition into the twist–bend nematic phase (N_{TB}) is driven by an elastic instability related to the reduction of the bend elastic constant. Here we use a molecular–statistical theory to show that sufficiently strong polar interactions between bent–shaped molecules may lead to experimentally observed reduction of the bend elastic constant in the nematic phase even if electrostatic dipole–dipole interactions are not taken into account. We propose a simple model of bent–core particles and derive explicit analytical expressions which enable one to understand how polar molecular shape affects the elastic constants, and, in particular, the important role of the bend angle. Numerical graphs showing temperature variations of all elastic constants are also presented including the variation of the bend and splay elastic constants before and after the renormalization determined by local polar order of molecular steric dipoles and the corresponding polar correction to the one–particle distribution function.

Keywords: Elasticity, liquid crystals, thermodynamics, analytical and numerical techniques, twist–bend, nematics

1. Introduction

In recent years the new inhomogeneous nematic phases have been observed [1–13], and the study of the detailed structure of these phases is currently the most topical issue in liquid crystals research. The experiments for oligomers and bent–core systems indicate that there are at least two types of modulated nematic structures with one-dimensional periodicity. One of them is the so called twist–bend nematic phase (N_{TB}) in which the director is assumed to precess on the cone [14] at the molecular length–scale, while the other is the splay–bend nematic phase (N_{SB}) where the main director performs modulations in a plane. The transition into these phases is generally explained by an elastic instability related to a strong decrease and even vanishing of the effective bend elastic constant. This, in turn, can be explained by assuming that the system is close to the virtual ferroelectric phase. Then the reduction may be determined by the negative flexoelectric [15, 16] correction which is anomalously large due to pretransitional effects [17, 18]. In our recent paper [18] we have calculated the flexoelectric coefficients and the effective elastic constants of bent–core nematics with transverse electric dipoles using the same molecular model and have shown how the bend elastic constant can vanish at a certain temperature. On the other hand, it has been shown that the N_{TB} phase with very low values of the elastic constants may be exhibited by the system of bent particles without electric dipoles [19].

The transition to the N_{TB} phase can also be driven entropically [20] without taking flexoelectricity into account. In this paper we present a molecular theory which enables one to understand why anomalously low values of the effective bend elastic constant can be obtained taking into

consideration only the polar molecular shape. We employ our previous simple molecular models [21, 22] together with some approximations to explain the origin of the elastic instability which drives a transition into a modulated phase with spontaneous bend deformations. Here it is worth noting that in principle such periodic director distributions may differ from the conventional ones [14]. For example, the periodic structures may contain various polarization waves [23], and one nonconventional has indeed been confirmed by simple molecular modeling [24]. Further extension of the phenomenological model [17] takes into account also the biaxial ordering in bent-core systems [25]. More general phenomenological approach is built upon an extension of the Landau-de Gennes theory [26] with a possibility of the direct transition from the isotropic to the N_{TB} phase [27] which has recently been observed experimentally [28, 29]. One notes that there exists also an alternative description based on the analogy between one period of the N_{TB} phase and one smectic layer [30–32]. In addition, phenomenological models of the N_{TB} phase have been proposed [33, 34] where the vanishing bend elastic constant is not necessary for stabilization of the corresponding modulated structure.

2. Microscopic theory of nematic elasticity

When the pair interaction potential between two particles $V_{eff}(1, 2) = V_{eff}(\mathbf{r}_{12}, \mathbf{a}_1, \mathbf{a}_2, \mathbf{b}_1, \mathbf{b}_2)$ is given explicitly as a function of orientational and positional variables, the free energy density of the nematic phase in the molecular field approximation can be expressed as:

$$\frac{F}{V} = \rho k_B T \int f_1(i) \ln f_1(i) d(i) + \frac{1}{2} \rho^2 \int V_{eff}(1, 2) f_1(1) f_1(2) d(1) d(2) d\mathbf{r}_{12}, \quad (1)$$

where (i) means the set of orientational and translational coordinates of the molecule 'i', *i.e.* $(i) = (\mathbf{r}_i, \mathbf{a}_i, \mathbf{b}_i)$ where \mathbf{a}_i and \mathbf{b}_i are the unit vectors along the long and the short molecular axis, respectively. Note that eq.(1) is also valid in the distorted state, that is when the director $\mathbf{n} = \mathbf{n}(\mathbf{r})$ is positionally dependent.

2.1 Distortion free energy of nematic phases

In the homogenous uniaxial nematic state the orientational one-particle distribution function $f_1 = f_0(\mathbf{n}, \mathbf{a}, \mathbf{b}) = f_0((\mathbf{n} \cdot \mathbf{a})^2, (\mathbf{n} \cdot \mathbf{b})^2)$ because the phase is nonpolar hence there is only a quadratic dependence on all orientational variables. In contrast, in the distorted nematic state the distribution function generally possesses a small polar correction (h) which is linear in both the polar vectors of bend ($\mathbf{B} = \mathbf{n} \times (\nabla \times \mathbf{n})$) and splay ($\mathbf{S} = \mathbf{n}(\nabla \cdot \mathbf{n})$) deformations. In the first approximation the orientational distribution function of the distorted nematic can be expressed as:

$$f_1(\mathbf{n}(\mathbf{r}), \mathbf{a}, \mathbf{b}) = f_0((\mathbf{n} \cdot \mathbf{a})^2, (\mathbf{n} \cdot \mathbf{b})^2)[1 + h(\mathbf{n}(\mathbf{r}), \mathbf{a}, \mathbf{b})]. \quad (2)$$

In the general case eq.(1) presents the free energy of the inhomogeneous state and it can be expressed as a sum of the free energy of the homogenous phase F_0 and the distortion free energy:

$$F_d = \int F_d(\mathbf{r}) d\mathbf{r}, \quad (3)$$

where $F_d(\mathbf{r})$ is the distortion free energy density which is expressed in terms of the gradient of the director and the corresponding elastic constants. The distortion free energy can be separated from F_0 by using the gradient expansion of the distribution function $f_1(2) = f_1(\mathbf{n}(\mathbf{r}_2), \mathbf{a}_2, \mathbf{b}_2)$ in eq.(1):

$$f_1(2) = f_1(1) + (\mathbf{r}_{12} \cdot \nabla) f_1(1) + \frac{1}{2} (\mathbf{r}_{12} \cdot \nabla)^2 f_1(1) + \dots, \quad (4)$$

where \mathbf{r}_{12} is the intermolecular vector. Now equations (2) and (4) can be substituted into eq.(1) keeping the terms which are quadratic in the gradients of the director and in h . One notes that the linear terms vanish due to symmetry reasons, and as a result the distortion free energy density can be expressed as:

$$\begin{aligned} F_d = & \frac{1}{2}k_B T \rho \int f_0(\omega_1, \mathbf{n}(\mathbf{r}_1)) h^2(\omega_1) d\omega_1 \\ & + \frac{1}{2}\rho^2 \int f_0(\omega_1, \mathbf{n}(\mathbf{r}_1)) V_{eff}(\mathbf{r}_{12}, \omega_1, \omega_2) h(\omega_1) h(\omega_2) f_0(\omega_2, \mathbf{n}(\mathbf{r}_1)) d\omega_1 d\omega_2 d\mathbf{r}_{12} \\ & + \frac{1}{2}\rho^2 \int f_0(\omega_1, \mathbf{n}(\mathbf{r}_1)) V_{eff}(\mathbf{r}_{12}, \omega_1, \omega_2) h(\omega_1) (\mathbf{r}_{12} \cdot \nabla) f_0(\omega_2, \mathbf{n}(\mathbf{r}_1)) d\omega_1 d\omega_2 d\mathbf{r}_{12} \\ & + \frac{1}{4}\rho^2 \int f_0(\omega_1, \mathbf{n}(\mathbf{r}_1)) V_{eff}(\mathbf{r}_{12}, \omega_1, \omega_2) (\mathbf{r}_{12} \cdot \nabla)^2 f_0(\omega_2, \mathbf{n}(\mathbf{r}_1)) d\omega_1 d\omega_2 d\mathbf{r}_{12}, \end{aligned} \quad (5)$$

where $\omega_i = (\mathbf{a}_i, \mathbf{b}_i)$ are all orientational degrees of freedom of the molecule i . This general formulae can in principle be applied to any effective pair potential with polar contributions. One notes that the last term in eq.(5) yields the expressions for the so-called undressed elastic constants which are calculated without taking into account any polar intermolecular interactions. A detailed molecular theory of undressed elastic constants of nematics is presented in our previous paper [18] (see also earlier works [35–39]). At the same time the corrections to the elastic constants, determined by various polar intermolecular interactions are determined by all other terms in the distortion free energy density (5).

2.2 Corrections to the elastic constants

The general equation (5) can be employed to calculate the elastic constants only if explicit expressions for the effective pair interaction potential are known. On the other hand some results can be obtained in a generic form. In the general case the effective potential $V_{eff}(\mathbf{r}_{12}, \omega_1, \omega_2)$ can be decomposed into a sum of polar and nonpolar parts

$$V_{eff}(\mathbf{r}_{12}, \omega_1, \omega_2) = V_0(\mathbf{r}_{12}, \omega_1, \omega_2) + V_p(\mathbf{r}_{12}, \omega_1, \omega_2), \quad (6)$$

where $V_0(\mathbf{r}_{12}, \omega_1, \omega_2)$ is invariant under sign inversion of both \mathbf{a} s and \mathbf{b} s while $V_p(\mathbf{r}_{12}, \omega_1, \omega_2)$ changes sign under sign inversion of the vector \mathbf{b} for molecules having C_{2v} symmetry.

One notes that nonpolar potential $V_0(\mathbf{r}_{12}, \omega_1, \omega_2)$ does not contribute to the integrals in the second and in the third terms in the r.h.s of eq.(5) if the molecules are nonchiral. Indeed, under the integrals in these terms in eq.(5) the functions h are polar in \mathbf{b} s while the potential $V_0(\mathbf{r}_{12}, \omega_1, \omega_2)$ is nonpolar in these vectors, and as a result the integrals vanish after integration over \mathbf{b}_1 and \mathbf{b}_2 .

The polar vectors of splay \mathbf{S} and bend \mathbf{B} deformations induce the polar order of the short molecular axis \mathbf{b}_i in the nematic phase characterized by polar order parameter $\mathbf{P} = \langle \mathbf{b}_i \rangle$. This order parameter is expected to be very small as it is proportional to weak director gradients. Then the polar interaction potential $V_p(\mathbf{r}_{12}, \omega_1, \omega_2)$ can be expanded in powers of \mathbf{b}_1 and \mathbf{b}_2 up to first order:

$$\begin{aligned} V_p(\mathbf{r}_{12}, \omega_1, \omega_2) \approx & b_{1\alpha} T_{\alpha\beta} b_{2\beta} + b_{1\alpha} N_{\alpha\beta\gamma} q_{\beta\gamma}^{(2)} + b_{2\alpha} N_{\alpha\beta\gamma} q_{\beta\gamma}^{(1)} \\ & + b_{1\alpha} N_{\alpha\beta\gamma} q_{\beta\mu}^{(2)} q_{\mu\gamma}^{(1)} + b_{2\alpha} N_{\alpha\beta\gamma} q_{\beta\mu}^{(1)} q_{\mu\gamma}^{(2)}, \end{aligned} \quad (7)$$

where $q_{\beta\gamma}^{(i)} = a_{1\alpha} a_{2\alpha} - \frac{1}{3} \delta_{\alpha\beta}$. In eq.(7) the tensors $\hat{\mathbf{T}}$ and $\hat{\mathbf{N}}$ depend on the intermolecular vector \mathbf{r}_{12} . Taking into account only linear and quadratic terms in the unit vector $\mathbf{u}_{12} = \mathbf{r}_{12}/r_{12}$ one obtains

$$T_{\alpha\beta} = I_0(\mathbf{r}_{12}) \delta_{\alpha\beta} + I_1(\mathbf{r}_{12}) u_\alpha u_\beta + I_2(\mathbf{r}_{12}) \left(q_{\alpha\beta}^{(1)} + q_{\alpha\beta}^{(2)} \right), \quad (8)$$

$$N_{\alpha\beta\gamma} = J_1(\mathbf{r}_{12})\delta_{\alpha\beta}u_\gamma + J_2(\mathbf{r}_{12})\delta_{\alpha\gamma}u_\beta + J_3(\mathbf{r}_{12})\delta_{\gamma\beta}u_\alpha. \quad (9)$$

Such a polar interaction can now be used in eq.(5). The term $\mathbf{b}_1 \cdot \hat{\mathbf{T}} \cdot \mathbf{b}_2$ is polar in both \mathbf{b}_1 and \mathbf{b}_2 , and therefore it contributes only to the second term in eq.(5). At the same time the terms with \hat{N} tensor contribute only to the third term in eq.(5) as they are odd in \mathbf{u}_{12} . Finally, the first term in eq.(5) is evaluated by expanding the polar correction h in powers of the unit vector \mathbf{b} along the short molecular axis. Keeping the first order terms one obtains

$$h(i) \approx \mathbf{b}_i \cdot \mathbf{m}, \quad (10)$$

where \mathbf{m} is a constant vector which can be expressed in terms of the polar order parameter \mathbf{P} as

$$\mathbf{P} = \int f_0(\omega)h(\omega)\mathbf{b}d\omega \approx \hat{\mu} \cdot \mathbf{m}, \quad (11)$$

where

$$\mu_{\alpha\beta} = \langle b_\alpha b_\beta \rangle \approx \frac{1}{6} ((2+S)\delta_{\alpha\beta} - 3Sn_\alpha n_\beta). \quad (12)$$

Here we neglect the small biaxial order parameter $D = \langle (\mathbf{b} \cdot \mathbf{n})^2 \rangle - \langle (\mathbf{c} \cdot \mathbf{n})^2 \rangle$ where $\mathbf{c} = \mathbf{b} \times \mathbf{a}$ is the unit vector in the direction of the second short axis. Inverting eq.(11) one obtains

$$\mathbf{m} = \frac{6}{(2+S)}\mathbf{P}_\perp + \frac{3}{1-S}\mathbf{P}_\parallel, \quad (13)$$

where $S = \langle P_2(\mathbf{a} \cdot \mathbf{n}) \rangle$ and $\mathbf{P} = \mathbf{p}_\perp + \mathbf{p}_\parallel$ and where \mathbf{p}_\parallel is parallel to \mathbf{n} while \mathbf{p}_\perp is normal to the director \mathbf{n} . Substituting eqs.(10-13) into the first term of eq.(5) one obtains

$$F_{d1} = \frac{1}{2}\rho k_B T \langle h^2(\omega_1) \rangle_0 \approx \frac{1}{2}\rho k_B T p_\alpha \mu_{\alpha\beta}^{-1} p_\beta = \frac{3}{1-S}p_\parallel^2 + \frac{6}{2+S}p_\perp^2. \quad (14)$$

After substitution of eqs.(7-9) the third term in eq.(5) for $J_0 \equiv J_1 = J_2 = J_3$ (*i.e.* for the case when the tensor $N_{\alpha\beta\gamma}$ weights equally all intermolecular directions) can be expressed as:

$$F_{d3} = \frac{1}{3}\rho^2 S J_{03} [(\mathbf{p}_\perp \cdot \mathbf{B}) + (\mathbf{p}_\parallel \cdot \mathbf{S})], \quad (15)$$

while the second term can be written in the following form

$$F_{d2} = \frac{1}{2}\rho^2 (I - \frac{1}{3}S I_{22}) p_\perp^2 + \frac{1}{2}\rho^2 (I + \frac{2}{3}S I_{22}) p_\parallel^2, \quad (16)$$

where $I = I_{02} + I_{12}/3$ and $J_{03} = \int J_0(r)r^3 dr$, $I_{02} = \int I_0(r)r^2 dr$, $I_{12} = \int I_1(r)r^2 dr$, $I_{22} = \int I_2(r)r^2 dr$. Here we have decoupled the averages of short and long molecular axes assuming that $\langle b_\alpha q_{\alpha\beta} \rangle \approx \langle b_\alpha \rangle \langle q_{\alpha\beta} \rangle$.

The sum of these three terms $F_d(\mathbf{P}) = F_{d1} + F_{d2} + F_{d3}$ describes the part of the distortion free energy which depends on the polar order parameter \mathbf{P} . Minimization of $F_d(\mathbf{P})$ with respect to \mathbf{P} yields

$$\mathbf{P} = \frac{1}{3} \frac{8S J_{03}}{\rho I - \frac{1}{3}\rho S I_{22} + \frac{6k_B T}{2+S}} \mathbf{B} + \frac{\rho S(1-S)J_{03}}{\rho(1-S)(3I + 2S I_{22}) + 9k_B T} \mathbf{S}. \quad (17)$$

The expression for \mathbf{P} can now be substituted into the distortion free energy $F_d(\mathbf{p})$. After doing this the contribution F_d to the total distortion free energy is reduced to the standard form $-\Delta K_{11}\mathbf{S}^2 - \Delta K_{33}\mathbf{B}^2$ where $-\Delta K_{11}$ and $-\Delta K_{33}$ are the corresponding negative corrections to the splay and bend elastic constants respectively, determined by polar interactions. As a result one obtains the following expressions for the effective splay and bend elastic constants:

$$K_{11} = K_{11}^0 - \frac{1}{6} \frac{\rho^3 S^2 (1-S) J_{03}^2}{\rho(1-S)(3I + 2SI_{22}) + 9k_B T}, \quad (18)$$

$$K_{33} = K_{33}^0 - \frac{1}{6} \frac{\rho^3 S^2 (2+S) J_{03}^2}{\rho(2+S)(3I - SI_{22}) + 18k_B T}, \quad (19)$$

where K_{11}^0 and K_{33}^0 are the bare splay and bend elastic constants, respectively which are not related to polar intermolecular interactions and are determined by the fourth term in eq.(5). Explicit expressions for these constants will be presented in the following section.

One notes that according to eqs.(18)-(19) there indeed exist negative corrections to both bend and splay elastic constants which are determined by polar intermolecular interactions of the proper mathematical form. In particular, the corrections are proportional to the coupling constant J_{03} which enters the eq.(9) for the tensor \hat{N} , that is the coupling constant between the short axis of one bent-core molecule and the molecular quadrupole tensor of the neighboring molecule.

3. Molecular model for the bent-core nematic

In this paper we incorporate the simple model for the intermolecular interaction, which we have studied earlier [21]. In this model the arms of bent-core molecules interact with the arms of the neighbouring molecules via the second Legendre polynomial term (Maier-Saupe type interaction):

$$V_{eff}(\mathbf{r}_{12}, \omega_1, \omega_2) = -J \sum_{i,j} \frac{P_2(\mathbf{e}_{1,i} \cdot \mathbf{e}_{2,j})}{r_{ij}^6}, \quad (20)$$

where the distance between interacting centers are given by: $\mathbf{r}_{ij} = \mathbf{r}_{12} + L(\mathbf{e}_{2,j} - \mathbf{e}_{1,i})/2$. Summation in eq.(20) runs over all arms (\uparrow and \downarrow) of the two interacting bent-shaped molecules (see Fig.1), so consequently there are four terms in this sum. Each part is then expanded in powers of ϵ equal to arm-length over intermolecular distance which is assumed to be less than one. The effective pair potential reads:

$$V_{eff}(\mathbf{r}_{12}, \omega_1, \omega_2) \approx -\frac{J}{r_{12}^6} \sum_{i,j} P_2(\mathbf{e}_{1,i} \cdot \mathbf{e}_{2,j}) \times \left(1 - 3\epsilon \mathbf{u}_{12} \cdot (\mathbf{e}_{2,j} - \mathbf{e}_{1,i}) + 3\epsilon^2 (2(\mathbf{u}_{12} \cdot (\mathbf{e}_{2,j} - \mathbf{e}_{1,i}))^2 - \frac{1}{2}(1 - \mathbf{e}_{2,j} \cdot \mathbf{e}_{1,i})) \right). \quad (21)$$

Undressed elastic constants are determined by those parts of potential (21) which are even in \mathbf{u}_{12} , \mathbf{a}_1 and \mathbf{a}_2 . We assume here that the biaxiality order parameter D can be neglected for undressed elastic constants. These elastic constants can be expressed by substituting the potential (21) into the last term in eq.(5) and using the method described in detail in our previous paper [18]. Finally, after all integrations and averaging the potential (21) makes the following contribution to the bare

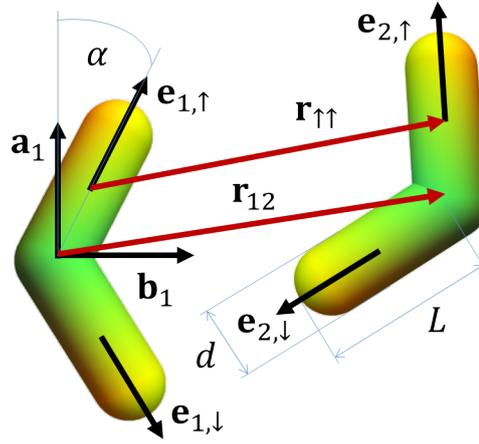


Figure 1. (Colour online) The model two bent-shaped molecules where each of them is composed of two uniaxial arms which interact between different molecules via second Legendre polynomial. Opening angle of the molecule is given by $\pi - 2\alpha$ and the distance between the two molecules is equal to: $\mathbf{r}_{12} = \mathbf{r}_{ij} + L(\mathbf{e}_{1,i} - \mathbf{e}_{2,j})/2$ for i and j being either \uparrow or \downarrow , and where \mathbf{r}_{ij} corresponds to distance between vectors located at the half-length ($\frac{L}{2}$) along of the attracting arms.

elastic constants

$$K_{11}^0 = K_0 + \kappa \left[-\frac{4}{105} S \langle P_4 \rangle + \frac{8}{315} S^2 \right], \quad (22)$$

$$K_{22}^0 = K_0 - \kappa \left[\frac{4}{105} S \langle P_4 \rangle + \frac{16}{315} S^2 \right], \quad (23)$$

$$K_{33}^0 = K_0 + \kappa \left[\frac{16}{105} S \langle P_4 \rangle + \frac{8}{315} S^2 \right], \quad (24)$$

where

$$K_0 = \left(3J \cos^4(\alpha) \rho^2 [2\sigma^{-1} - 3L^2 \sigma^{-3}] + \frac{4}{9} \kappa \right) S^2, \quad (25)$$

$$\kappa = 54L^2 J \rho^2 \sigma^{-3} \cos^6(\alpha) \quad (26)$$

and where σ is the average steric cut-off distance. In the majority of intermolecular configurations one arm of a bent-core molecule touches one arm of the neighbouring molecule and thus the distance σ varies between L and D . Taking into account that the results are not very sensitive to the particular values of σ , one may use the following estimate $\sigma \approx (L + d)/2$ for simplicity. One notes also that for the Maier-Saupe type distribution function the order parameter $\langle P_4 \rangle$ is not independent [40] and can be expressed explicitly in terms of the interaction constant and the order parameter S :

$$\langle P_4 \rangle = \frac{7}{12} + \frac{5}{12} S - \frac{35}{12} \frac{k_B T}{J}. \quad (27)$$

Behaviour of bare elastic constants in reduced units ($K_{ii}^{red} = \frac{d}{J\rho^2} K_{ii}^0$) are presented in Figs.2-3, where temperature is also given in dimensionless units: $t = \frac{k_B T}{J}$. The largest values of elastic constants are for rod-like particles, and it is diminished when the molecular polarity is increased. All elastic constants are positive and exhibit monotonic behaviour as a function of temperature. Modification of temperature variations of the elastic constants by polar terms in the one-particle distribution function can introduce the divergent contributions and exact formulas for this model are given in the following paragraph.

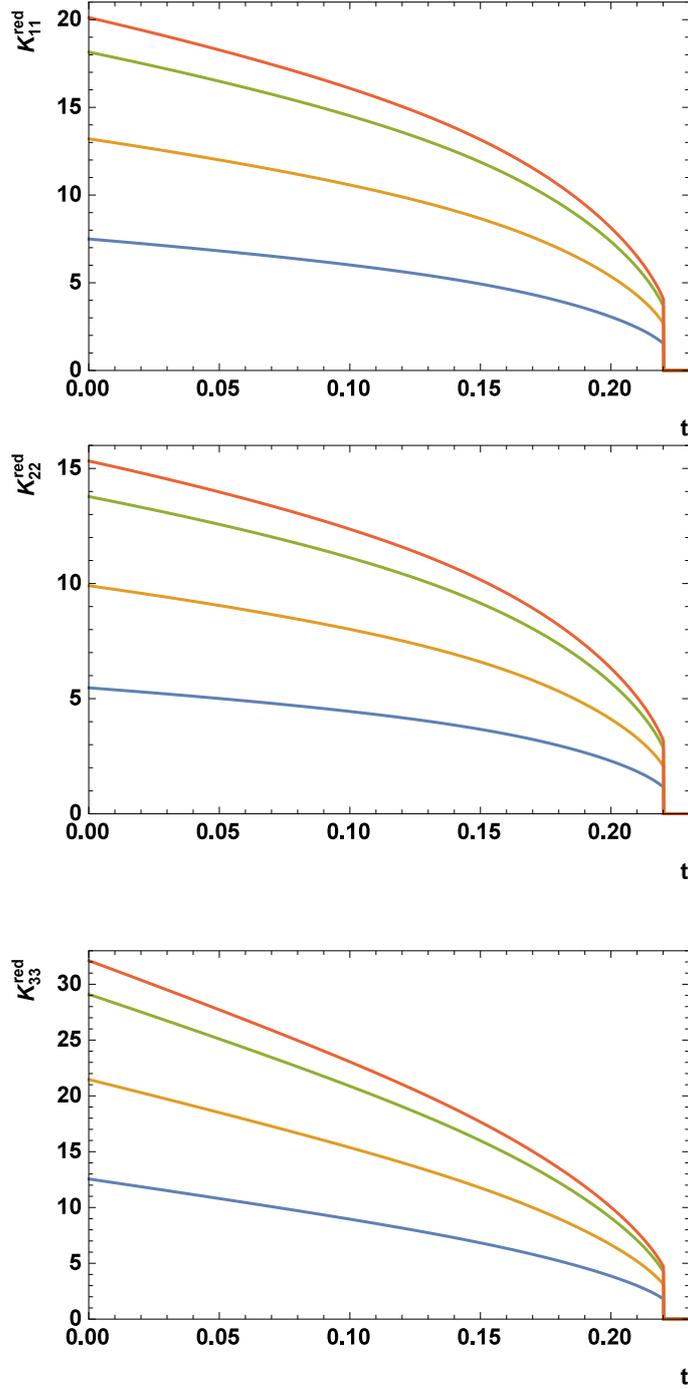


Figure 2. (Colour online) Undressed elastic constants in reduced units $K_{ii}^{red} = \frac{d}{J\rho^2} K_{ii}^0$ where K_{ii}^0 are given by eqs.(22)-(24) for $\sigma = 0.7L$ and for four opening angles from the very top: 180° (red), 160° (green), 140° (orange) and 120° (blue), which correspond to the parameter α equal to: 0 , $\frac{\pi}{18}$, $\frac{\pi}{9}$ and $\frac{\pi}{6}$, respectively.

The corrections to the elastic constants in the total distortion free energy (5) stem from the linear terms in \mathbf{b}_1 and \mathbf{b}_2 in the potential (21). Substituting the potential (21) into the first three terms of the general eq.(5) one obtains the following contribution to the distortion free energy

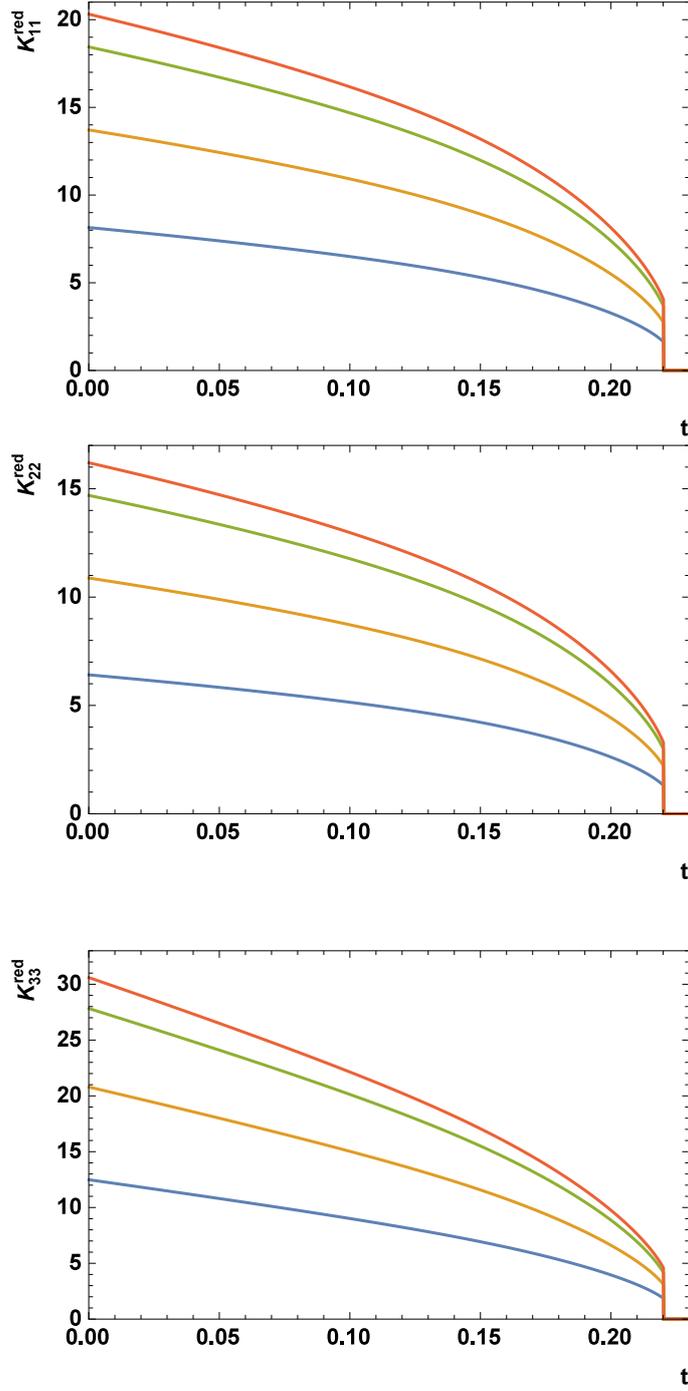


Figure 3. (Colour online) Undressed elastic constants in reduced units $K_{ii}^{red} = \frac{d}{J\rho^2} K_{ii}^0$ where K_{ii}^0 are given by eqs.(22)-(24) for $\sigma = L$ and for four opening angles from the very top: 180° (red), 160° (green), 140° (orange) and 120° (blue), which correspond to the parameter α equal to: 0 , $\frac{\pi}{18}$, $\frac{\pi}{9}$ and $\frac{\pi}{6}$, respectively.

which depends on the polar order parameter $\mathbf{P} = \langle \mathbf{b} \rangle$:

$$F_d(\mathbf{P}) = \frac{1}{2} \left(A + B + \rho k_B T \frac{3}{1-S} \right) P_{\parallel}^2 + \frac{1}{2} \left(A + \rho k_B T \frac{6}{2+S} \right) P_{\perp}^2 \quad (28)$$

$$- C \left[(2S+1)(\mathbf{P}_{\perp} \cdot \mathbf{B}) + (1-S)(\mathbf{P}_{\parallel} \cdot \mathbf{S}) \right],$$

where

$$C = \pi\rho^2 S J L \sigma^{-3} \sin \alpha \cos^4 \alpha, \quad (29)$$

$$B = -\frac{192\pi}{5} \rho^2 J L^2 \sigma^{-5} \sin^2 \alpha (5S^2 - 2S), \quad (30)$$

$$A = \frac{4\pi}{5} \rho^2 J L^2 \sigma^{-5} \sin^2 \alpha \left[5 - 9 \cos^4 \alpha \left(\frac{5}{3} (2S^2 + 1) + \frac{16}{9} \right) \right]. \quad (31)$$

Minimization of the distortion free energy $F_d(\mathbf{P})$ given by eq.(28) with respect to \mathbf{P} yields:

$$P_{\parallel} = \frac{C(1-S)^2}{3\rho k_B T + (A+B)(1-S)} \mathbf{S}, \quad (32)$$

$$P_{\perp} = \frac{C(2S+1)(2+S)}{6\rho k_B T + A(2+S)} \mathbf{B}. \quad (33)$$

Substituting these expressions back into the equation for $F_d(\mathbf{p})$ one obtains the following expressions for the effective splay and bend elastic constants which contain the negative corrections:

$$K_{11} = K_{11}^0 - \frac{1}{2} \frac{C^2(1-S)^3}{3\rho k_B T + (A+B)(1-S)}, \quad (34)$$

$$K_{33} = K_{33}^0 - \frac{1}{2} \frac{C^2(2S+1)^2(2+S)}{6\rho k_B T + A(2+S)}, \quad (35)$$

where the bare elastic constants are given by eqs.(22)-(24). Here one notes that the quantity C given by (29) vanishes when $\alpha = 0$, and hence the polar order parameter $\mathbf{P} = \mathbf{P}_{\parallel} + \mathbf{P}_{\perp}$ vanishes. As a result there are no corrections to the elastic constants when $\alpha = 0$ as it should be for rod-like molecules. One notes that the denominators of corrections in eqs.(34)-(35) may produce divergence

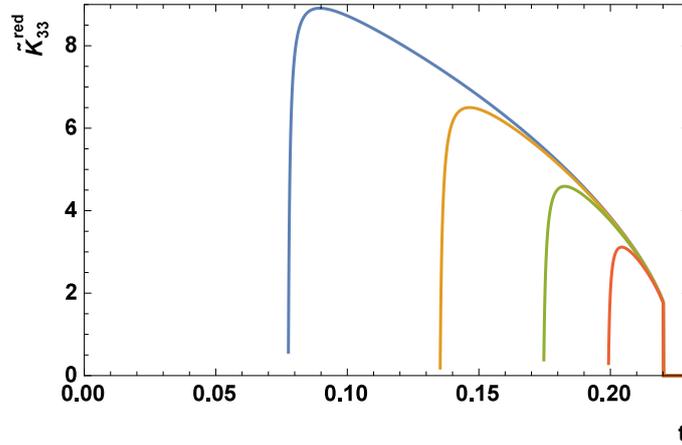


Figure 4. (Colour online) Effective bend elastic constant in reduced units $\tilde{K}_{33}^{red} = \frac{d}{J\rho^2} K_{33}$ where K_{33} is given by eq.(35) for $\sigma = 0.7L$, $\alpha = \frac{\pi}{6}$ and for four values of $\rho^* = \frac{\rho}{d^2L}$ from the very top: 0.01 (blue), 0.02 (orange), 0.03 (green), and 0.04 (red).

at some non-zero temperature and thus strongly renormalize the corresponding elastic constants. However, it is reasonable to assume that the corresponding temperatures are well below the nematic range. Temperature variation of the effective bend elastic constants is presented in Fig.4 in reduced units ($\tilde{K}_{33}^{red} = \frac{d}{J\rho^2} K_{33}$) for $\sigma = 0.7L$ and $\alpha = \frac{\pi}{6}$. Here we have introduced the scaled number density

$\rho^* = \rho d^{-2} L^{-1}$. The effective bend elastic constant given by eq.(35), is always smaller than the bare constant presented in Fig.2, and vanishes at some temperature which increases with the increasing parameter ρ^* which is proportional to the number density and inversely proportional to the product of d^2 and L *i.e.* the average molecular volume. The variation of the effective bend elastic constants for another value of $\sigma = L$ is presented in Fig.5, where one can see that all curves are not so steep as in the case of $\sigma = 0.7L$. It is also possible to calculate numerically the effective splay elastic

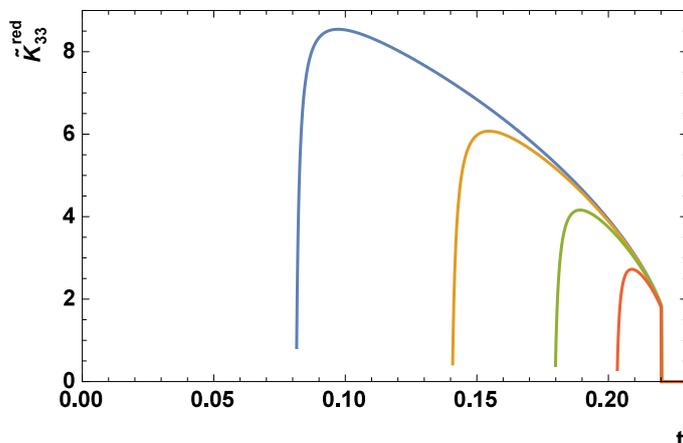


Figure 5. (Colour online) Effective bend elastic constant in reduced units $\tilde{K}_{33}^{red} = \frac{d}{J\rho^2} K_{33}$ where K_{33} is given by eq.(35) for $\sigma = L$, $\alpha = \frac{\pi}{6}$ and for four values of $\rho^* = \frac{\rho}{d^2 L}$ from the very top: 0.01 (blue), 0.02 (orange), 0.03 (green), and 0.04 (red).

constant, but for values of the parameters used in this paper the effective splay elastic constant does not differ from the undressed splay elastic constant and thus we do not present the corresponding curves. Here we obtained the reduction only for bend elastic constants originating from the steric polarity of molecules which may be considered as a source of instability towards the stabilization of modulated phases with bend deformations.

4. Summary

In this paper we have presented a general molecular-statistical theory of the effective elastic constants for bent-core nematics taking into account the polar contribution to the one-particle orientational distribution function. Explicit expressions for the effective elastic constants have been obtained which contain negative corrections determined by polar intermolecular interactions. The correction to the bend elastic constant can be sufficiently large and as a result the bend constant may vanish at some temperature within the nematic range. Moreover, the correction may even diverge at some non-zero temperature but it is reasonable to assume that the corresponding temperature is below the range of stability of the nematic phase. In contrast, the correction to the splay elastic constant appears to be negligibly small which is mainly related to the fact that molecules having C_{2v} symmetry possess only transverse steric dipoles. The analytical expressions (and the profiles of the bend elastic constant presented in the figures) have been obtained using a simple model interaction potential between bent-core molecules based on the Maier-Saupe type of interaction between uniaxial arms of such molecules [21]. This model contains only one coupling constant, and consequently it is possible to study directly the effect of the molecular bend angle and the armlength (or equivalently the average intermolecular distance) on the effective elastic constants.

The expressions for the so-called bare elastic constants, which do not contain corrections determined by polar interactions, have also been obtained. The bare elastic constants reach their largest values for rod-like molecules which corresponds to the zero value of the bend angle α . The bare constants decrease monotonically with the increasing bend angle but the corresponding re-

duction is not very large for all reasonable values of the bend angle α . At the same time sufficiently strong polar interactions contribute to the large negative correction to the effective bend elastic constant which may vanish at some temperature. At this temperature the homogeneous nematic phase loses its stability and the system may undergo a transition into a modulated nematic phase with a spontaneous bend deformation. Moreover, the results of the present paper indicate that a dramatic decrease of the bend elastic constant above the transition into the twist–bend phase may be described qualitatively taking into account only polar interactions determined by the polar shape of the bent–shaped molecules. In this case the agreement between the theoretical and the experimental temperature variations of the bend elastic constant is not very good but it can be improved by taking transverse electric dipoles into consideration [18]. Finally, we note that in the analyzed model with the inclusion of steric polar corrections the effective splay elastic constants remain unaffected.

Acknowledgement(s)

The authors are grateful to G. R. Luckhurst and A. Ferrarini for interesting discussions.

Funding

Grant No. DEC-2013/11/B/ST3/04247 of the National Science Centre in Poland.

References

- [1] Šepelj M, Lesac A, Baumeister U, Diele S, Nguyen HL, Bruce DW. Intercalated liquid–crystalline phases formed by symmetric dimers with an α,ω -diiminoalkylene spacer. *J. Mat. Chem.* 2007;**17**:1154–1165.
- [2] Görtz V, Southern C, Roberts NW, Gleeson HF, Goodby JW. Unusual properties of a bent–core liquid–crystalline fluid. *Soft Matter* 2009;**5**:463–471.
- [3] Panov VP, Nagaraj M, Vij JK, Panarin YuP, Kohlmeier A, Tamba MG, Lewis RA, Mehl GH. Spontaneous Periodic Deformations in Nonchiral Planar–Aligned Bimesogens with a Nematic–Nematic Transition and a Negative Elastic Constant. *Phys. Rev. Lett.* 2010;**105**:167801.
- [4] Cestari M, Diez-Berart S, Dunmur DA, Ferrarini A, de la Fuente MR, Jackson DJB, López DO, Luckhurst GR, Perez-Jubindo MA, Richardson RM, Salud J, Timimi BA, Zimmermann H. Phase behavior and properties of the liquid–crystal dimer 1''',7'''-bis(4–cyanobiphenyl–4'-yl) heptane: A twist–bend nematic liquid crystal. *Phys. Rev. E* 2011;**84**:031704.
- [5] Borshch V, Kim YK, Xiang J, Gao M, Jáklí A, Panov VP, Vij JK, Imrie CT, Tamba MG, Mehl GH, Lavrentovich OD. Nematic twist–bend phase with nanoscale modulation of molecular orientation. *Nat. Commun.* 2013;**4**:2635.
- [6] Chen D, Porada JH, Hooper JB, Klitnick A, Shen Y, Tuchband MR, Korblova E, Bedrov D, Walba DM, Glaser MA, MacLennan JE, Clark NA. Chiral heliconical ground state of nanoscale pitch in a nematic liquid crystal of achiral molecular dimers. *PNAS* 2014;**110**:15931–15936.
- [7] Adlem K, Čopič M, Luckhurst GR, Mertelj A, Parri O, Richardson RM, Snow BD, Timimi BA, Tuffin RP, Wilkes D. Chemically induced twist–bend nematic liquid crystals, liquid crystal dimers, and negative elastic constants. *Phys. Rev. E* 2013;**88**:022503.
- [8] Chen D, Nakata M, Shao R, Tuchband MR, Shuai M, Baumeister U, Weissflog W, Walba DM, Glaser MA, MacLennan JE, Clark NA. Twist–bend heliconical chiral nematic liquid crystal phase of an achiral rigid bent–core mesogen. *Phys. Rev. E* **89**, 022506 (2014).
- [9] Mandle RJ, Davis EJ, Lobato SA, Vol CCA, Cowling SJ, Goodby JW. Synthesis and characterisation of an unsymmetrical, ether–linked, fluorinated bimesogen exhibiting a new polymorphism containing the NTB or 'twist–bend' phase. *Phys. Chem. Chem. Phys.* 2014;**16**:6907–6915.
- [10] Robles-Hernández B, Sebastián N, de la Fuente MR, López DO, Diez-Berart S, Salud J, Blanca Ros M, Dunmur DA, Luckhurst GR, Timimi BA. Twist, tilt, and orientational order at the nematic to twist–

- bend nematic phase transition of 1'',9''-bis(4-cyanobiphenyl-4'-yl) nonane: A dielectric, ^2H NMR, and calorimetric study. *Phys. Rev. E* 2015;**92**:062505.
- [11] Wang Y, Singh G, Agra-Kooijman DM, Gao M, Bisoyi HK, Xue C, Fisch MR, Kumar S, Li Q. Room temperature heliconical twist-bend nematic liquid crystal. *CrystEngComm* 2015;**17**:2778–2782.
 - [12] Yoshizawa A, Kato Y, Sasaki H, Takanishi Y, Yamamoto J. Chiral conglomerates observed for a binary mixture of a nematic liquid crystal trimer and 6OCB. *Soft Matter* 2015;**11**:8827–8833.
 - [13] Mandle RJ, Goodby JW. A Liquid Crystalline Oligomer Exhibiting Nematic and Twist-Bend Nematic Mesophases. *ChemPhysChem* 2016;**17**:967–970.
 - [14] Dozov I. On the spontaneous symmetry breaking in the mesophases of achiral banana-shaped molecules. *Europhys. Lett.* 2001;**56**:247–253.
 - [15] Meyer RB. Piezoelectric Effects in Liquid Crystals. *Phys. Rev. Lett.* 1969;**22**:918.
 - [16] Osipov MA. Molecular theory of flexoelectricity in nematic liquid crystals. In: Buka A, Éber N, editors. *Flexoelectricity in liquid crystals. Theory, Experiment and Applications*. Imperial College Press; 2013. p. 9–32.
 - [17] Shamid SM, Dhakal S, Selinger JV. Statistical mechanics of bend flexoelectricity and the twist-bend phase in bent-core liquid crystals. *Phys. Rev. E* 2013;**87**:052503.
 - [18] Osipov MA, Pajžak G. Effect of polar intermolecular interactions on the elastic constants of bent-core nematics and the origin of the twist-bend phase. *Eur. Phys. J. E* 2016;**39**:45.
 - [19] Greco C, Luckhurst GR, Ferrarini A. Molecular geometry, twist-bend nematic phase and unconventional elasticity: a generalised Maier-Saupe theory. *Soft Matter* 2014;**10**:9318–9323.
 - [20] Greco C, Ferrarini A. Entropy-Driven Chiral Order in a System of Achiral Bent Particles. *Phys. Rev. Lett.* 2015;**115**, 147801.
 - [21] Osipov MA, Pajžak G. Influence of dipole-dipole correlations on the stability of the biaxial nematic phase in the model bent-core liquid crystal. *J. Phys.: Condens. Matter* 2012;**24**:142201.
 - [22] Osipov MA, Pajžak G. Molecular theory of proper ferroelectricity in bent-core liquid crystals. *Eur. Phys. J. E* 2014;**37**:79.
 - [23] Lorman VL, Mettout B. Unconventional Mesophases Formed by Condensed Vector Waves in a Medium of Achiral Molecules. *Phys. Rev. Lett.* 1999;**82**:940.
 - [24] Vanakaras AG, Photinos DJ. A molecular theory of nematic-nematic phase transitions in mesogenic dimers. *Soft Matter* 2016;**12**:2208–2220.
 - [25] Vaupotič N, Čepič M, Osipov MA, Gorecka E. Flexoelectricity in chiral nematic liquid crystals as a driving mechanism for the twist-bend and splay-bend modulated phases. *Phys. Rev. E* 2014;**89**:030501(R).
 - [26] Longa L, Trebin HR. Spontaneous polarization in chiral biaxial liquid crystals. *Phys. Rev. A* 1990;**42**:3453.
 - [27] Longa L, Pajžak G. Modulated nematic structures induced by chirality and steric polarization. *Phys. Rev. E* 2016;**93**:040701(R).
 - [28] Archbold CT, Davis EJ, Mandle RJ, Cowling SJ, Goodby JW. Chiral dopants and the twist-bend nematic phase induction of novel mesomorphic behaviour in an apolar bimesogen. *Soft Matter* 2015;**11**:7547–7557.
 - [29] Dawood AA, Grossel MC, Luckhurst GR, Richardson RM, Timimi BA, Wells NJ, Yousif YZ. On the twist-bend nematic phase formed directly from the isotropic phase. *Liq. Cryst.* 2016;**43**:2–12.
 - [30] Kats EI, Lebedev VV. Landau theory for helical nematic phases. *JETP Letters* 2014;**100**:110–113.
 - [31] Meyer C, Dozov I. Local distortion energy and coarse-grained elasticity of the twist-bend nematic phase. *Soft Matter* 2016;**12**:574–580.
 - [32] Pardaev SA, Shamid SM, Tamba MG, Welch C, Mehl GH, Gleeson JT, Allender DW, Selinger JV, Ellman B, Jákli A, Sprunt S. Second harmonic light scattering induced by defects in the twist-bend nematic phase of liquid crystal dimers. *Soft Matter* 2016;**12**:4472–4482.
 - [33] Virga EG. Double-well elastic theory for twist-bend nematic phases. *Phys. Rev. E* 2014;**89**:052502.
 - [34] Barbero G, Evangelista LR, Rosseto MP, Zola RS, Lelidis I. Elastic continuum theory: Towards understanding of the twist-bend nematic phases. *Phys. Rev. E* 2015;**92**:030501(R).
 - [35] Gelbart WM, Ben-Shaul A. Molecular theory of curvature elasticity in nematic liquids. *J. Chem. Phys.* 1982;**77**:916.
 - [36] Somosa AM, Tarazona P. Density functional theory of the elastic constants of a nematic liquid crystal. *Mol. Phys.* 1991;**72**:911–926.
 - [37] Poniewierski A, Stecki J. Statistical theory of the elastic constants of nematic liquid crystals. *Mol. Phys.* 1979;**38**:1931–1940.

- [38] Osipov MA, Hess S. The elastic constants of nematic and nematic discotic liquid crystals with perfect local orientational order. *Mol. Phys.* 1993;**78**:1191–1201.
- [39] Kapanowski A. Statistical theory of elastic constants of biaxial nematic liquid crystals. *Phys. Rev. E* 1997;**55**:7090.
- [40] Gorkunov MV, Osipov MA, Kapernaum N, Nonnenmacher D, Giesselmann F. Molecular theory of smectic ordering in liquid crystals with nanoscale segregation of different molecular fragments. *Phys. Rev. E* 2011;**84**:051704.