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Calculating elastic constants of bent-core molecules from Onsager-theory-based tensor model

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ABSTRACT

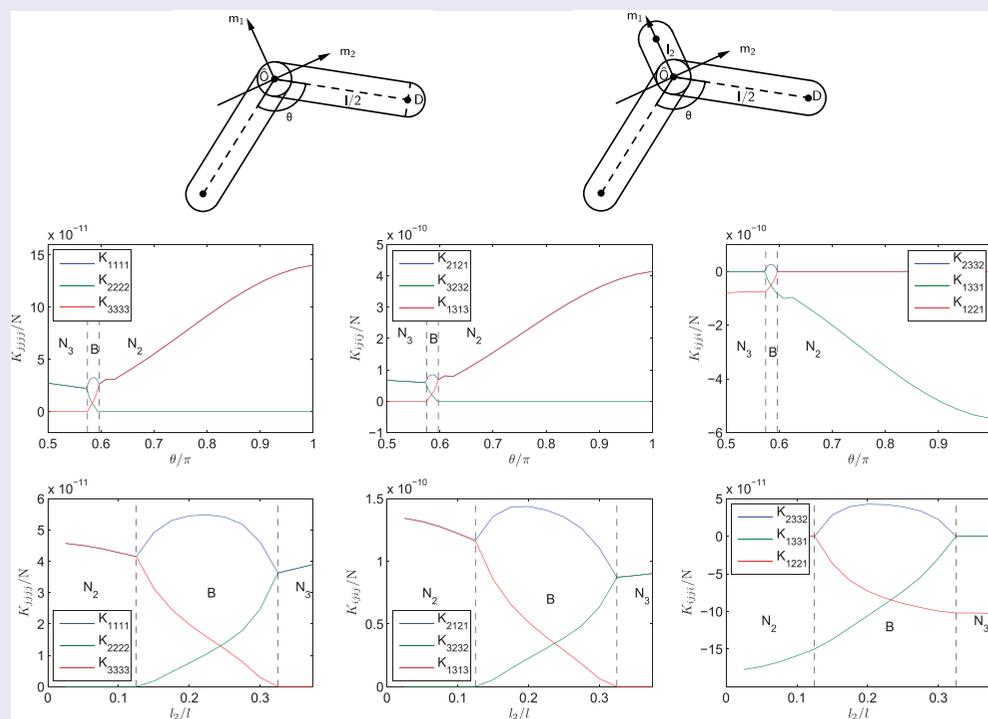
The orientational elasticity of the uniaxial and the biaxial nematic phases is deduced earlier. For bent-core molecules with hardcore interaction, we examine how the molecular shape affects the elastic constants of these phases. The calculation is built on a tensor model based on the Onsager theory. The elastic constants are expressed by the coefficients in the tensor model, and these coefficients are derived from molecular parameters. We calculate the elastic constants of bent-core molecules as functions of the bending angle, concentration and thickness. We also examine the elastic constants of star molecules, where we focus on the effect of the extra arm.

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1. Introduction

Elasticity is a significant property of homogeneous nematic phases. In equilibrium, these phases show anisotropy only orientationally. Their elasticity is exhibited by deformation in answer to boundary effects and external forces. For the commonly observed uniaxial nematic phase, the orientational distribution is axisymmetric about a vector n . When the deformation is slight, the local orientational distribution can be

regarded as identical to equilibrium, with the axis n varying in space. In this view, the elastic energy is a functional of $n(x)$. Up to second-order derivatives, it is known as the Oseen–Frank energy [1],

$$F_{\text{OF}} = \int dx \frac{1}{2} [K_1 (\nabla \cdot n)^2 + K_2 (n \cdot \nabla \times n)^2 + K_3 |n \times (\nabla \times n)|^2], \quad (1)$$

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where three terms represent the energy of splay, bend and twist, respectively. The above elastic energy is also incorporated in the Ericksen–Leslie hydrodynamic model [2].

The Oseen–Frank energy is significant for the measurability of the elastic constants K_i . By exerting an external force, it is able to induce particular deformations. Then, by comparing the work done by the external force and the elastic energy (1), we are able to calculate K_i . Measurements have been done for rod-like molecules at an early stage [3–6]. In recent works, the elastic constants have been measured for the uniaxial phase formed by bent-core molecules [7–14], and their analogues, including L-shaped molecules [15,16] and T-shaped molecules [17].

Molecules of complex architectures may show other nematic phases. The prediction of these phases is initiated quite early [18], of which the biaxial nematic phase has been verified for bent-core molecules [19,20]. The phase transitions involving the biaxial nematic phase have been studied extensively (see Ref. [21] and the references therein). Since the orientational distribution is not axisymmetric, a local orthonormal frame is needed when considering the deformation. The form of elastic energy depends on the phase symmetry. For the biaxial nematic phase, the form of second-order orientational elasticity has been discussed in previous works and also built into dynamic models [22–26].

Since the elasticity originates from molecular interaction, it is significant to find out how the elastic constants are affected by the molecular architecture. A clear understanding of this would be helpful to design materials of desired elastic properties. For rod-like molecules, K_i are calculated from the concentration and the thickness in a recent work [27]. The calculation is built on a tensor model based on the Onsager theory. By assuming that the eigenvalues of the tensor are identical to the equilibrium values, the elastic energy can be reduced to the Oseen–Frank energy, with the elastic constants expressed by coefficients in the tensor model. Since these coefficients are derived from molecular parameters, it finally establishes the relationship of molecular parameters and the elastic constants.

In contrast to the uniaxial phase, no measurement of the elastic constants for the biaxial nematic phase is reported to our knowledge. Thus, it is more desirable to build the relationship between the molecular parameters and the elastic constants. A few theoretical calculations have been done from a molecular perspective [28–30], which focus on some general formulations. Only in Ref. [29] is an ellipsoidal molecule examined, where the elastic constants are calculated as functions of the temperature while the effect of molecular shape is not studied.

Analogous to the tensor model for rod-like molecules, we have derived a tensor model for bent-core molecules from molecular theory [31]. In particular, by assuming that a molecule has two joint cylindrical arms, the coefficients in the tensor model are computed from the Onsager theory. We have obtained a phase diagram about molecular parameters in [31], which includes different types of uniaxial nematic phases, as well as the biaxial nematic phase. Hence, similar to rod-like molecules, we can obtain the elastic constants of the uniaxial and biaxial nematic phases. We examine how the elastic constants depend on the bending angle, concentration and thickness. Moreover, the tensor model is appropriate for rigid molecules with the same molecular symmetry. Thus, we are able to apply the same procedure to star molecules that possess an extra arm compared with bent-core molecules. For the elastic constants of star molecules, we will focus on how they are affected by the length of the third arm.

The rest of the paper is organised as follows. In Section 2, we briefly describe the tensor model and the homogeneous phases. In Section 3, we describe the derivation of the orientational elasticity and the calculation of the elastic constants. The results are shown in Section 4. A concluding remark is given in Section 5.

2. The tensor model

Here, we summarise the main points about the tensor model and the nematic phase diagram and refer to Ref. [31] for details.

In the tensor model, we adopt the molecular geometry shown in Figure 1. A bent-core molecule has two identical arms, of the length $l/2$ and thickness D , joint with an angle θ . A star molecule has a third arm of the length l_2 towards the arrowhead. The two molecules are fully rigid. Thus, we can put an orthonormal frame $(\hat{O}; m_1, m_2, m_3)$ on the molecule to represent its position and orientation. The frame m_i can be represented by Euler angles (ψ, ϕ, ψ') , and the differential of the orthonormal frame is denoted by $dv = \sin \phi d\phi d\psi d\psi' / 8\pi^2$.

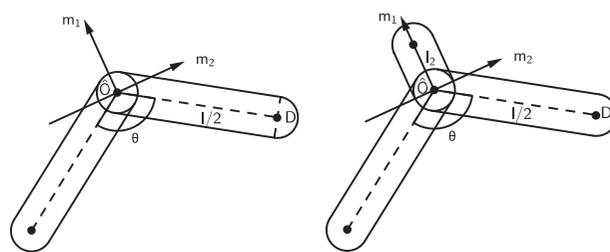


Figure 1. A bent-core molecule and a star molecule with their body-fixed orthonormal frames.

We use two symmetric second-order tensors and a vector,

$$\mathbf{Q}_1 = \langle m_1 m_1 \rangle, \quad \mathbf{Q}_2 = \langle m_2 m_2 \rangle, \quad p = \langle m_1 \rangle,$$

to express the orientation. The components of p and \mathbf{Q}_v are denoted as p_i and Q_{vij} . Here, $\langle \cdot \rangle = \int dv \langle \cdot \rangle f$ denotes the average about the Boltzmann distribution

$$f = \frac{1}{Z} \exp(b \cdot m_1 + \mathbf{B}_1 : m_1 m_1 + \mathbf{B}_2 : m_2 m_2), \quad (2)$$

over all the orientations, where Z is the normalisation factor,

$$Z = \int dv \exp(b \cdot m_1 + \mathbf{B}_1 : m_1 m_1 + \mathbf{B}_2 : m_2 m_2).$$

The vector b and the matrices \mathbf{B}_1 and \mathbf{B}_2 are uniquely determined by p , \mathbf{Q}_1 and \mathbf{Q}_2 (see Ref. [31]).

The free energy is written as follows:

$$\frac{F[\mathbf{Q}_1, \mathbf{Q}_2, p]}{k_B T} = \int dx \left\{ \begin{array}{l} cf \log f + \frac{c^2}{2} (c_{01} |p|^2 + c_{02} |\mathbf{Q}_1|^2 + c_{03} |\mathbf{Q}_2|^2 + 2c_{04} \mathbf{Q}_1 : \mathbf{Q}_2) \\ + c^2 (c_{11} p_j \partial_i Q_{1ij} + c_{12} p_j \partial_i Q_{2ij}) \\ + \frac{c^2}{4} \left[c_{22} |\nabla \mathbf{Q}_1|^2 + c_{23} |\nabla \mathbf{Q}_2|^2 + 2c_{24} \partial_i Q_{1jk} \partial_i Q_{2jk} \right. \\ \left. + 2c_{27} \partial_i p_j \partial_j p_i + 2c_{28} \partial_i Q_{1ik} \partial_j Q_{1jk} \right. \\ \left. + 2c_{29} \partial_i Q_{2ik} \partial_j Q_{2jk} + 4c_{2,10} \partial_i Q_{1ik} \partial_j Q_{2jk} \right] \end{array} \right\}, \quad (3)$$

where c is the concentration, k_B is the Boltzmann constant and T is the absolute temperature. The sum over repeated indices is assumed, and $|\mathbf{Q}_1|^2 = \mathbf{Q}_1 : \mathbf{Q}_1 = \mathbf{Q}_{1ij} \mathbf{Q}_{1ij}$. The first index k of a coefficient c_{kj} represents the total order of derivatives in that term.

The coefficients are derived as functions of molecular parameters. They satisfy the scaling property $c_{kj} \propto l^{k+3}$ and depend on dimensionless parameters: the bending angle θ , the ratio $\eta = D/l$, and for star molecules also l_2/l . For bent-core molecules, we use the dimensionless parameter $\alpha = c l^2 D$ to express the concentration, representing the number of molecules in a cuboid with edges of the lengths l , l and D . For star molecules, we use $\alpha = cl(l + l_2)D$. The calculation of c_{kj} is based on the hardcore molecular interaction.

Each homogeneous phase corresponds to a minimizer of the bulk energy,

$$\begin{aligned} \frac{F_{\text{bulk}}[\mathbf{Q}_1, \mathbf{Q}_2, p]}{cV k_B T} &= b \cdot p + \mathbf{B}_1 : \mathbf{Q}_1 + \mathbf{B}_2 : \mathbf{Q}_2 - \log Z \\ &+ \frac{c}{2} (c_{01} |p|^2 + c_{02} |\mathbf{Q}_1|^2 + c_{03} |\mathbf{Q}_2|^2 + 2c_{04} \mathbf{Q}_1 : \mathbf{Q}_2). \end{aligned} \quad (4)$$

Bent-core molecules and star molecules can exhibit the uniaxial and biaxial nematic phases, where $p = 0$. They are characterised by the eigenvalues of \mathbf{Q}_i . For convenience, we also consider the tensor $\mathbf{Q}_3 = \langle m_3 m_3 \rangle = \mathbf{I} - \mathbf{Q}_1 - \mathbf{Q}_2$. In the uniaxial nematic phase (N_i), each \mathbf{Q}_i is uniaxial with the same axis, that is,

$$\mathbf{Q}_i = s_i \left(nn - \frac{\mathbf{I}}{3} \right) + \frac{\mathbf{I}}{3}, \quad i = 1, 2, 3, \quad (5)$$

where $s_1 + s_2 + s_3 = 0$. It always holds that only one of s_i is positive. If s_i is positive, the phase is denoted as N_i , in which m_i gathers near the axis n , while the other two m_j accumulate near the plane perpendicular to n . In the biaxial nematic phase (B), the tensors can be written as

$$\mathbf{Q}_i = q_{i1} n_1 n_1 + q_{i2} n_2 n_2 + q_{i3} n_3 n_3. \quad (6)$$

Here, (n_1, n_2, n_3) is the shared eigenframe of three \mathbf{Q}_i . The principal eigenvector of each \mathbf{Q}_i is different. Thus, we can permute n_i to let $q_{ii} > q_{ij}$ ($j \neq i$), that is, let n_i be the principal eigenvector of \mathbf{Q}_i . Note that the \mathbf{Q}_i in the uniaxial phase can also be expressed by (6). For the N_i phase, we let $n = n_i$, then

$$q_{ki} = \frac{(2s_k + 1)}{3}, \quad q_{kj} = \frac{(1 - s_k)}{3}; \quad (7)$$

$$k = 1, 2, 3, \quad j \neq i.$$

In homogeneous systems, the frame (n_1, n_2, n_3) represents the macroscopic axes and does not affect the free energy. When deformation exists, it can be described by the spatial variation of (n_i) .

The phase diagrams of bent-core molecules and star molecules about the molecular parameters are given in Ref. [31]. With an intermediate α , bent-core molecules show N_2 , B , N_3 successively as θ decreases from π . It is also the case for star molecules as l_2/l increases from zero. The twist-bend phase also occurs in the phase diagrams, but we are not going to discuss it in this work.

3. The elastic constants

3.1. The form of orientational elasticity

For the uniaxial phase, the Oseen–Frank elastic energy is appropriate. But for the biaxial phase, an alternative elastic energy is needed. In the following few paragraphs, we briefly review the derivation of the orientational elasticity in Ref. [22]. The derivation is based on the symmetry of the orientational distribution, and the elasticity includes both bulk and surface terms. In what follows, we only retain the bulk terms and will discard surface terms.

First, we discuss the derivatives of the frame (n_1, n_2, n_3) . Consider the directional derivatives of n_μ . The derivative of n_μ along the direction n_λ is written as $(n_\lambda \cdot \nabla)n_\mu$. We write down its components in the frame (n_1, n_2, n_3) . Its ν component is expressed as $n_{\nu j} n_{\lambda i} \partial_i n_{\mu j}$. Using the equality $n_{\nu j} n_{\mu j} = \delta_{\mu\nu}$, we have

$$n_{\nu j} n_{\lambda i} \partial_i n_{\mu j} = -n_{\mu j} n_{\lambda i} \partial_i n_{\nu j}.$$

From this equation, we know that ∇n_μ has nine degrees of freedom, denoted as

$$\begin{aligned} D_{11} &= n_{1i} n_{2j} \partial_i n_{3j}, & D_{12} &= n_{1i} n_{3j} \partial_i n_{1j}, & D_{13} &= n_{1i} n_{1j} \partial_i n_{2j}, \\ D_{21} &= n_{2i} n_{2j} \partial_i n_{3j}, & D_{22} &= n_{2i} n_{3j} \partial_i n_{1j}, & D_{23} &= n_{2i} n_{1j} \partial_i n_{2j}, \\ D_{31} &= n_{3i} n_{2j} \partial_i n_{3j}, & D_{32} &= n_{3i} n_{3j} \partial_i n_{1j}, & D_{33} &= n_{3i} n_{1j} \partial_i n_{2j}. \end{aligned} \quad (8)$$

The orientational elasticity is given by polynomials of D_{ij} . The biaxial nematic phase requires the $n_i \rightarrow -n_i$ symmetry. Therefore, each n_i must appear even times, making the first-order terms vanish. Generally, a quadratic form of D_{ij} has 45 terms. The symmetry reduces it to 15 terms, including D_{ij}^2 and six coupling terms $D_{11}D_{22}$, $D_{12}D_{21}$, $D_{22}D_{33}$, $D_{23}D_{32}$, $D_{33}D_{11}$, $D_{31}D_{13}$. The linear combinations of the coupling terms include three surface terms, such as

$$\partial_i n_{2i} \partial_j n_{2j} - \partial_i n_{2j} \partial_j n_{2i} = 2(D_{33}D_{11} - D_{31}D_{13}). \quad (9)$$

Thus, the elastic energy is reduced to 12 bulk terms,

$$F_{Bi} = \int dx \frac{1}{2} \left[\begin{aligned} &K_{1111}D_{11}^2 + K_{2222}D_{22}^2 + K_{3333}D_{33}^2 \\ &+ K_{1212}D_{12}^2 + K_{2121}D_{21}^2 + K_{2323}D_{23}^2 + K_{3232}D_{32}^2 + K_{3131}D_{31}^2 + K_{1313}D_{13}^2 \\ &+ K_{1221}D_{12}D_{21} + K_{2332}D_{23}D_{32} + K_{1331}D_{13}D_{31} \end{aligned} \right]. \quad (10)$$

There are 12 elastic constants in total.

The Oseen–Frank energy can also be expressed by (10). Let us choose $n = n_2$ as an example. For the derivative of n_2 , we have

$$\begin{aligned} \nabla \cdot n_2 &= -D_{31} + D_{13}, & n_2 \cdot \nabla \times n_2 &= D_{33} + D_{11}, \\ n_3 \cdot \nabla \times n_2 &= -D_{23}, & n_1 \cdot \nabla \times n_2 &= -D_{21}. \end{aligned}$$

Note that $|n_2 \times \nabla \times n_2|^2 = (n_1 \cdot \nabla \times n_2)^2 + (n_3 \cdot \nabla \times n_2)^2$. Along with (9), it is easy to see that (10) is reduced to the Oseen–Frank energy if the following equalities hold,

$$\begin{aligned} K_{3131} &= K_{1313} = K_1, & K_{1111} &= K_{3333} = K_2, & K_{2121} &= K_{2323} = K_3, \\ K_{1331} &= 2(K_2 - K_1), & K_{2222} &= K_{3232} = K_{1212} = K_{2332} = K_{1221} = 0. \end{aligned} \quad (11)$$

These equalities have been derived in Ref. [22] and will also be illustrated in our derivation of elastic constants.

We can give deformation patterns of n_i that leave only one of D_{ij} nonzero, drawn in Figure 2. They are classified into two cases: $D_{ii} \neq 0$ and $D_{ij} \neq 0$. For each case, we give one example, and the other patterns can be obtained by permuting the axes n_i . Below, n_i are functions of the location (x, y, z) , and (\mathbf{e}_i) is the space-fixed orthonormal basis.

- $D_{11} \neq 0$. Let

$$n_1 = e_3, n_2 = e_1 \cos z + e_2 \sin z, n_3 = e_1 \sin z - e_2 \cos z.$$

Here, n_2 and n_3 show twist while n_1 is constant. For the case $D_{ii} \neq 0$, n_i is constant. Thus, we name it as the twist pattern, denoted by \mathbb{T}_i .

- $D_{13} \neq 0$. We use cylindrical coordinates. Denote $(x, y, z) = (r \cos \theta, r \sin \theta, z)$, and let

$$\begin{aligned} n_3 &= e_3, n_2 = e_r = e_1 \cos \theta + e_2 \sin \theta, n_1 \\ &= e_\theta = e_1 \sin \theta - e_2 \cos \theta. \end{aligned}$$

We name it as the splay bend pattern and use the notation $\mathbb{S}_i \mathbb{B}_j$ to denote the one in which n_i shows splay and n_j shows bend, while n_k is constant. Here, (ijk) is a permutation of (123) . The pattern $\mathbb{S}_i \mathbb{B}_j$ corresponds to $D_{jk} \neq 0$.

The constants K_{iiii} and K_{ijij} could be measured by generating the above patterns.

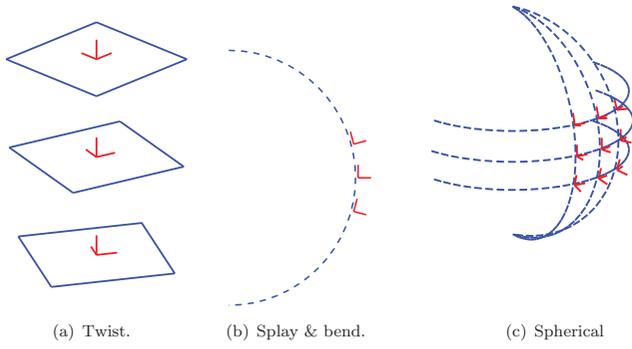


Figure 2. (Colour online) Deformation patterns.

orthonormal frame on the sphere: write $(x, y, z) = (r \sin \theta \cos \varphi, r \sin \theta \sin \varphi, r \cos \theta)$, then

$$\begin{aligned} n_1 &= e_r = e_1 \sin \theta \cos \varphi + e_2 \sin \theta \sin \varphi + e_3 \cos \theta, \\ n_2 &= e_{1a} = e_1 \sin \varphi - e_2 \cos \varphi, \\ n_3 &= e_{1o} = e_1 \cos \theta \cos \varphi + e_2 \cos \theta \sin \varphi - e_3 \sin \theta, \end{aligned}$$

where n_1, n_2, n_3 point towards radial, latitudinal and longitudinal direction, respectively. In this case, we have $D_{21}, D_{23}, D_{32} \neq 0$, leading to four nonvanishing terms in the elastic energy:

$$K_{2121}D_{21}^2 + K_{2323}D_{23}^2 + K_{3232}D_{32}^2 + K_{2332}D_{23}D_{32}.$$

If all the patterns in **Figure 2** can be generated, we could measure K_{ijji} as we already know K_{ijij} .

3.2. The derivation of elastic constants

When discussing the elastic constants, we assume that the eigenvalues are equal to those in the homogeneous case and only the eigenframe varies. In this case, we assume that $p = 0$, which can be expected to be a good approximation if the deformation is not drastic. Then, the elastic energy can be written as

We point out that the coefficients in the tensor model satisfy

$$c_{22}, c_{23}, c_{28}, c_{29} > 0, \quad c_{22}c_{23} > c_{24}^2, \quad c_{28}c_{29} > c_{2,10}^2. \quad (13)$$

The inequalities about c_{28}, c_{29} and $c_{2,10}$ are actually stronger than those given in Ref. [31] that guarantee the positive definiteness of the elastic energy (12),

$$\begin{aligned} &2c_{28} + c_{22}, \quad 2c_{29} \\ &+ c_{23} > 0, \quad (2c_{28} + c_{22})(2c_{29} + c_{23}) > (2c_{28} + c_{22})^2, \end{aligned} \quad (14)$$

because (14) do not require c_{28}, c_{29} to be positive. As we will show later, (13) imply some relations between elastic constants.

Next, we express the elastic constants as functions of c_{2j} and the eigenvalues q_{ik} . Since the eigenvalues are determined by minimising the bulk energy (4), they are functions of the bulk coefficients c_{0j} , which are also derived from molecular parameters. Thus, the elastic constants are eventually expressed as functions of molecular parameters c, l, η and θ ,

$$K_{ijij} = c^2 k_B T K_{ijij} (c_{2j}(l, \eta, \theta), q_{ik}(c_{0j}(l, \eta, \theta))).$$

Write the tensors in the form of (6). Note that the following equalities hold,

$$\begin{aligned} \partial_i(n_{1j}n_{1k})\partial_i(n_{2j}n_{2k}) &= -2(D_{13}^2 + D_{23}^2 + D_{33}^2) \stackrel{\Delta}{=} -2A_3, \\ \partial_i(n_{2j}n_{2k})\partial_i(n_{3j}n_{3k}) &= -2(D_{11}^2 + D_{21}^2 + D_{31}^2) \stackrel{\Delta}{=} -2A_1, \\ \partial_i(n_{3j}n_{3k})\partial_i(n_{1j}n_{1k}) &= -2(D_{12}^2 + D_{22}^2 + D_{32}^2) \stackrel{\Delta}{=} -2A_2, \\ \partial_i(n_{1i}n_{1k})\partial_j(n_{2j}n_{2k}) &= -D_{13}^2 - D_{23}^2 - D_{12}D_{21} + D_{23}D_{32} \\ &\quad + D_{31}D_{13} \stackrel{\Delta}{=} -B_3, \\ \partial_i(n_{2i}n_{2k})\partial_j(n_{3j}n_{3k}) &= -D_{21}^2 - D_{31}^2 + D_{12}D_{21} - D_{23}D_{32} \\ &\quad + D_{31}D_{13} \stackrel{\Delta}{=} -B_1, \\ \partial_i(n_{3i}n_{3k})\partial_j(n_{1j}n_{1k}) &= -D_{12}^2 - D_{32}^2 + D_{12}D_{21} + D_{23}D_{32} \\ &\quad - D_{31}D_{13} \stackrel{\Delta}{=} -B_2, \end{aligned}$$

together with $I = n_1n_1 + n_2n_2 + n_3n_3$, we have

$$\frac{F_e}{k_B T} = \frac{F - F_{\text{bulk}}}{k_B T} = \int dx \frac{c^2}{4} \left[c_{22} |\nabla \mathbf{Q}_1|^2 + c_{23} |\nabla \mathbf{Q}_2|^2 + 2c_{24} \partial_i Q_{1jk} \partial_i Q_{2jk} \right. \\ \left. + 2c_{28} \partial_i Q_{1ik} \partial_j Q_{1jk} + 2c_{29} \partial_i Q_{2ik} \partial_j Q_{2jk} + 4c_{2,10} \partial_i Q_{1ik} \partial_j Q_{2jk} \right]. \quad (12)$$

$$\begin{aligned}\partial_i(n_{1j}n_{1k})\partial_i(n_{1j}n_{1k}) &= 2(A_2 + A_3), & \partial_i(n_{1i}n_{1k})\partial_j(n_{1j}n_{1k}) &= B_2 + B_3, \\ \partial_i(n_{2j}n_{2k})\partial_i(n_{2j}n_{2k}) &= 2(A_3 + A_1), & \partial_i(n_{2i}n_{2k})\partial_j(n_{2j}n_{2k}) &= B_3 + B_1, \\ \partial_i(n_{3j}n_{3k})\partial_i(n_{3j}n_{3k}) &= 2(A_1 + A_2), & \partial_i(n_{3i}n_{3k})\partial_j(n_{3j}n_{3k}) &= B_1 + B_2.\end{aligned}$$

Denote

$$\begin{aligned}d_1 &= c_{22}(q_{12} - q_{13})^2 + c_{23}(q_{22} - q_{23})^2 + 2c_{24}(q_{12} - q_{13})(q_{22} - q_{23}), \\ d_2 &= c_{22}(q_{13} - q_{11})^2 + c_{23}(q_{23} - q_{21})^2 + 2c_{24}(q_{13} - q_{11})(q_{23} - q_{21}), \\ d_3 &= c_{22}(q_{11} - q_{12})^2 + c_{23}(q_{21} - q_{22})^2 + 2c_{24}(q_{11} - q_{12})(q_{21} - q_{22}), \\ e_1 &= c_{28}(q_{12} - q_{13})^2 + c_{29}(q_{22} - q_{23})^2 + 2c_{2,10}(q_{12} - q_{13})(q_{22} - q_{23}), \\ e_2 &= c_{28}(q_{13} - q_{11})^2 + c_{29}(q_{23} - q_{21})^2 + 2c_{2,10}(q_{13} - q_{11})(q_{23} - q_{21}), \\ e_3 &= c_{28}(q_{11} - q_{12})^2 + c_{29}(q_{21} - q_{22})^2 + 2c_{2,10}(q_{11} - q_{12})(q_{21} - q_{22}).\end{aligned}\tag{15}$$

Then, the elastic energy becomes

$$\begin{aligned}F_e &= \int dx \frac{c^2 k_B T}{2} (d_1 A_1 + d_2 A_2 + d_3 A_3 + e_1 B_1 + e_2 B_2 + e_3 B_3) \\ &= \int dx \frac{c^2 k_B T}{2} \left[\begin{aligned} &d_1 D_{11}^2 + d_2 D_{22}^2 + d_3 D_{33}^2 \\ &+ (d_1 + e_1)(D_{21}^2 + D_{31}^2) + (d_2 + e_2)(D_{12}^2 + D_{32}^2) + (d_3 + e_3)(D_{13}^2 + D_{23}^2) \\ &- (e_1 + e_2 - e_3)D_{12}D_{21} - (e_2 + e_3 - e_1)D_{23}D_{32} - (e_3 + e_1 - e_2)D_{31}D_{13} \end{aligned} \right].\end{aligned}$$

Thus, we obtain

$$\begin{aligned}K_{jjjj} &= c^2 k_B T d_j, \quad K_{ijij} = c^2 k_B T (d_j + e_j), \quad K_{ijji} \\ &= c^2 k_B T (e_1 + e_2 + e_3 - 2e_i - 2e_j), \quad (i \neq j).\end{aligned}\tag{16}$$

For the uniaxial phase, the eigenvalues are given by (7). Thus, for the N_2 phase, we have $d_1 = d_3$, $e_1 = e_3$ and $d_2 = e_2 = 0$. Therefore, by (11), we deduce that

$$\begin{aligned}K_1 &= K_3 = K_{2121} = K_{3131} = K_{1313} \\ &= K_{2323}, \quad K_2 = K_{1111} = K_{3333}.\end{aligned}\tag{17}$$

Similarly, for the N_3 phase, we obtain

$$\begin{aligned}K_1 &= K_3 = K_{3232} = K_{1212} = K_{2121} \\ &= K_{3131}, \quad K_2 = K_{1111} = K_{2222}.\end{aligned}\tag{18}$$

Note that some elastic constants we deduce above are equal. In particular, for the uniaxial phase, $K_1 = K_3$ always holds. This is because our tensor model includes tensors

up to the second order only. In the calculation of the elastic constants of rod-like molecules in Ref. [27], the fourth-order tensor $\mathbf{M} = \langle mmmm \rangle$ is included in the tensor model so that K_1 and K_3 can be separated. For bent-core molecules, however, to include fourth-order tensors will make the free energy have over 50 terms. For this reason, we choose not to include them to keep the free energy concise.

4. Results and discussion

As we mentioned in Section 2, we pose the frame (n_1, n_2, n_3) such that $q_{ii} \geq q_{ij}$, that is, $\pm n_i$ is the preferred direction of m_i . Thus, we are able to discuss the elastic constants for both uniaxial and biaxial phases in terms of $K_{ij'j'}$ and then recognise them as K_1, K_2, K_3 by (17) for N_2 , and by (18) for N_3 . By $c_{2j} \propto l^5$, we have

$$K_{ij'j'} \propto k_B T c^2 l^5 = \frac{k_B T}{D} \cdot \frac{a^2}{\eta}.$$

We are not expecting to compare our results directly with the values obtained from experiments, since we have adopted a simple molecular architecture, and have only included the hardcore interaction. Moreover, because we have not included the higher order tensors, it always holds $K_{ijij} = K_{kjkj}$ for $i, k \neq j$, ($K_1 = K_3$ for the uniaxial phase). Thus, we will not distinguish them in the following. However, we can figure out some connections between the molecular shape and the elastic constants. In particular, the elastic constants of square terms D_{jj}^2 and D_{ij}^2 describe the resistance of the corresponding deformation patterns in Figure 2. By comparing the elastic constants, we can compare the resistance of these patterns.

Without calculating the values of the elastic constants, we can capture some features from (16). The elastic energy is always positive definite. This actually comes from the positive definiteness of the tensor model. We can also verify from (16), (15) and (13) that $K_{ijij}^2 < 4K_{ijij}K_{jjji}$ by noting that $q_{i1} + q_{i2} + q_{i3} = 1$. Moreover, for the N_3 and the N_2 phases, it always holds $K_3 > K_2$, which has been observed for the N_2 phase in the experiments we mentioned in Section 1. It originates from $K_3 - K_2 = c^2 k_B T e_1 > 0$, guaranteed by (13). In general cases, it is possible that $e_i < 0$ when only (14) holds and $c_{28}, c_{29} < 0$. That $e_i > 0$ also implies $K_{ijij} > K_{jjji}$ for the biaxial phase.

We choose $T = 400$ K and $D = 5 \times 10^{-10}$ m, the same as in Ref. [27]. First, we examine the K_i of the uniaxial phase as functions of α when $\theta = 3\pi/4$ and $D/l = 1/20$ near the $I - N_2$ transition value, plotted in Figure 3. We can see that the order of magnitude of K_i lies within 10^{-12} N and 10^{-11} N, which is consistent with the experimental results mentioned in Section 1. When α is small, K_i do not differ too much, and they

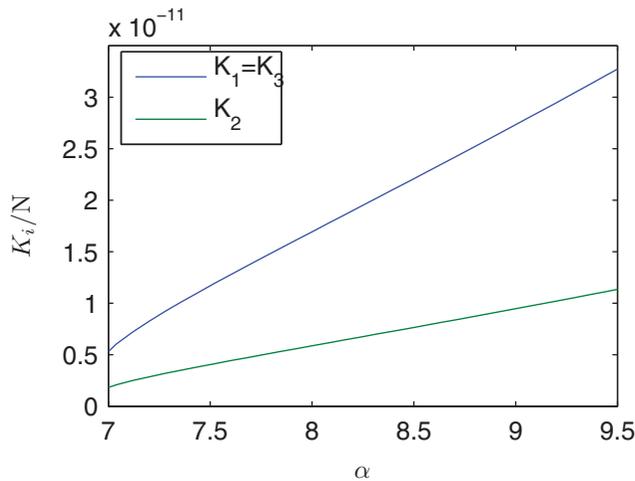


Figure 3. (Colour online) Elastic constants of bent-core molecules about α , with $\theta = 3\pi/4$, $\eta = 1/20$.

increase as α grows. These features are similar to rod-like molecules [27].

Next, we examine the effect of the bending angle θ . We fix $\alpha = 20$ for $\eta = 1/20, 1/40$. The elastic constants are plotted in Figure 4, and their values are close for the two η . In the N_2 region, K_i decrease as the angle decreases, suggesting that the N_2 phase formed by longer molecules is more resistant. In the N_3 region, K_i decrease as the angle increases, suggesting that the N_3 phase formed by molecules more like a disc is more resistant.

Then, we focus on the biaxial region. In this region, K_{2222} and K_{3333} vary monotonely from zero to K_{1111} , while K_{1111} itself shows a bulge, making it the largest among K_{iiii} . The same feature is observed for K_{2121} , K_{3232} and K_{1313} . The elastic constants for coupling terms satisfy $K_{2332} > 0$ while $K_{1331}, K_{1221} < 0$. The relation between K_{2222} and K_{3333} , as well as K_{1313} and K_{3232} , depends on θ . To see it more clearly, we plot the elastic constants at $\theta = 19\pi/32$ and $37\pi/64$, showing $N_2 \rightarrow B$ and $N_3 \rightarrow B$ transitions, respectively (Figure 5). When $\theta = 19\pi/32$, we have $K_{2121} > K_{1313} > K_{3232}$, $K_{1111} > K_{3333} > K_{2222}$ and $K_{2332} > 0 > K_{1221} > K_{1331}$; when $\theta = 37\pi/64$, we have $K_{2121} > K_{3232} > K_{1313}$, $K_{1111} > K_{2222} > K_{3333}$ and $K_{2332} > 0 > K_{1331} > K_{1221}$.

Finally, we study how the elastic constants of star molecules depend on the length of the third arm l_2 (Figure 6). Fix $\theta = 2\pi/3$, $\eta = 1/40$, $\alpha = cl(l + l_2)D = 20$. The elastic constants show similar features as Figure 4. To be specific, in the two uniaxial regions, K_i decrease when l_2/l approaches the biaxial region. In the biaxial region, K_{1111} and K_{2121} are the largest among K_{jjij} and K_{ijij} , respectively, and $K_{2332} > 0 > K_{1331}, K_{1221}$. The relation between K_{2222} and K_{3333} is relevant to l_2/l so do K_{1313} , K_{3232} and K_{1221}, K_{1331} .

We compare our approach (for which some relevant details are presented in Ref. [31]) with that given in Ref. [29]. Both approaches start from molecular theory and derive macroscopic expressions by expansion of the kernel function that describes the microscopic interaction. However, the expansion formulas are different, especially when dealing with orientational variables. This is where the two approaches diverge at an early stage of calculation. We point out that neither of the two approaches relies on the specific form of microscopic interaction, although the choices are distinct when examining specific molecules. For the ellipsoidal molecule studied in Ref. [29], the microscopic interaction adopted is the modified Lennard–Jones potential with orientational dependent coefficients, which is different from the hardcore potential we choose.

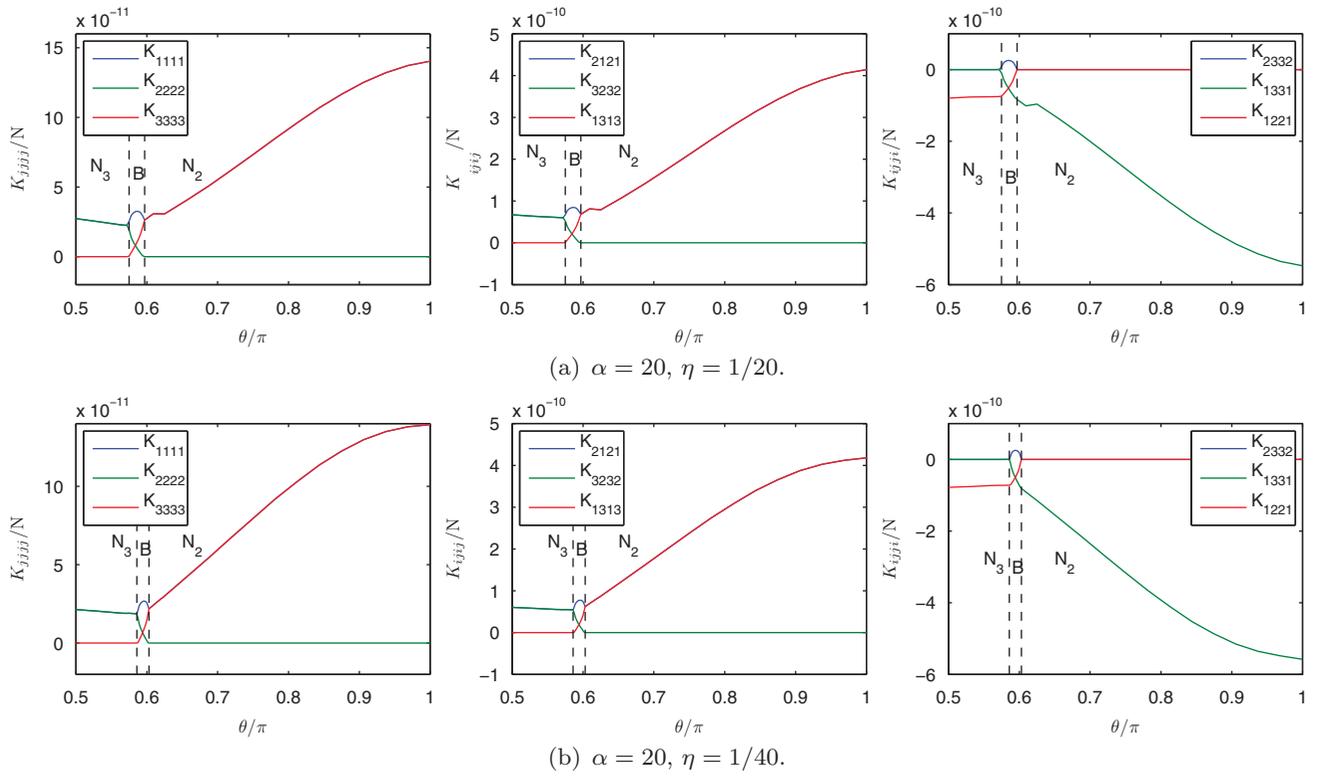


Figure 4. Elastic constants of bent-core molecules about θ .

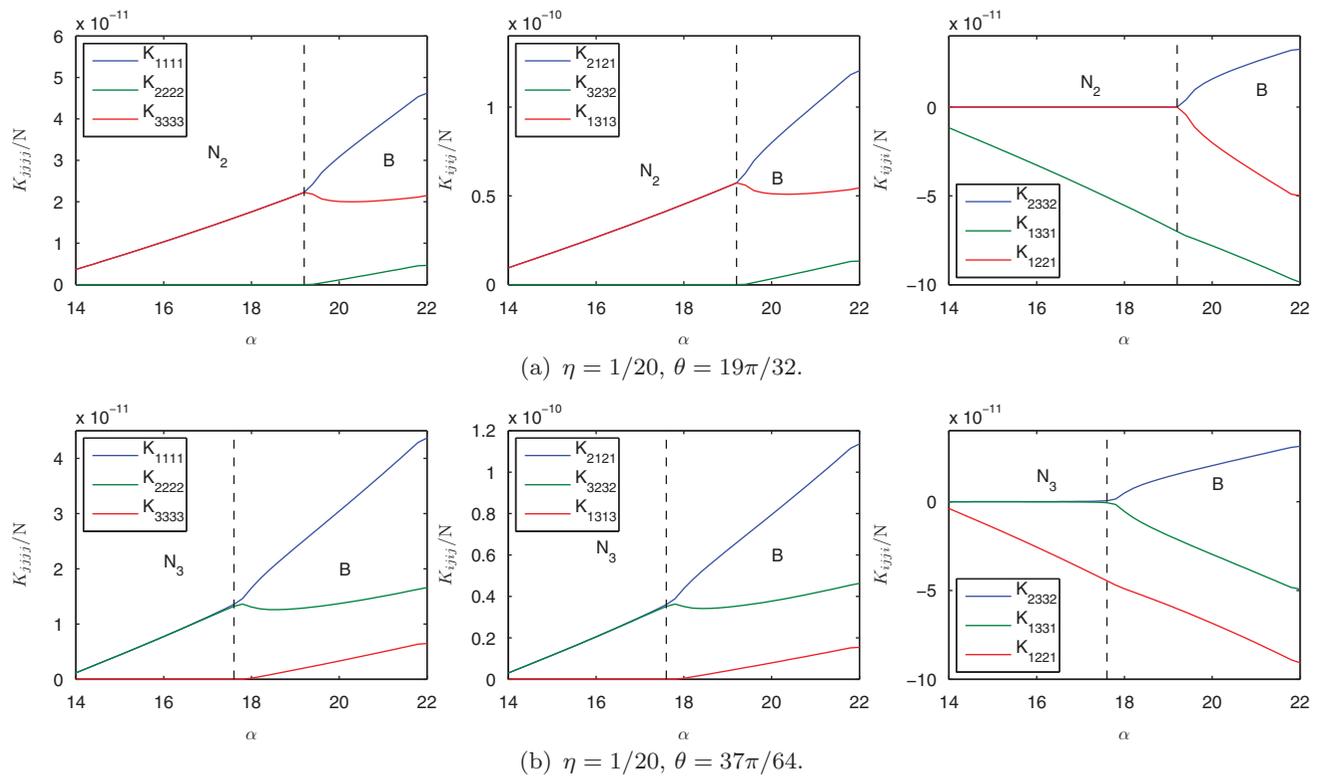


Figure 5. Elastic constants of bent-core molecules about α .

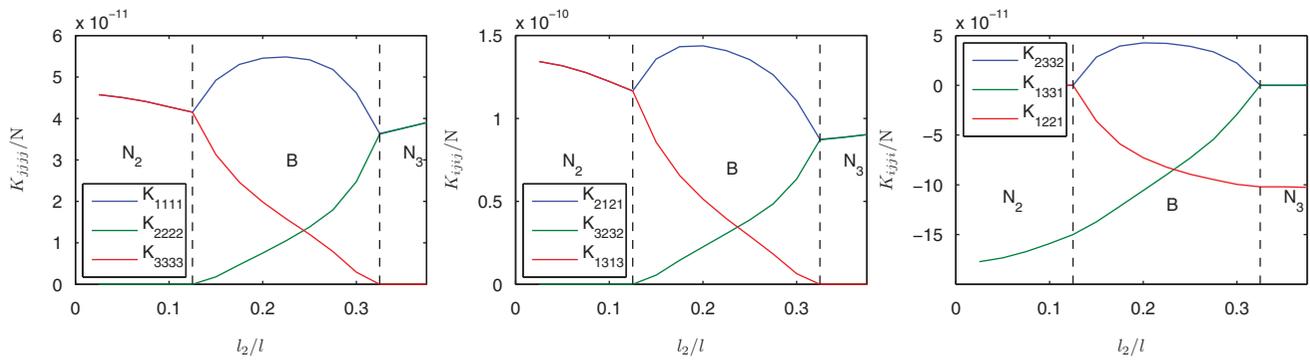


Figure 6. (Colour online) Elastic constants of star molecules about l_2/l , with $\theta = 2\pi/3$, $\eta = 1/40$, $\alpha = 20$.

5. Conclusion

Armed with an Onsager-theory-based tensor model, we calculate the elastic constants of the uniaxial and the biaxial nematic phases of bent-core molecules and star molecules with hardcore interaction. The elastic constants are expressed by the coefficients in the tensor model, and these coefficients are derived from molecular parameters. We study how the elastic constants are affected by the molecular shape. In particular, they are examined as functions of the concentration, the bending angle, the thickness for both molecules and also the length of the third arm for star molecules.

The current approach does not distinguish some of the elastic constants. To accomplish this, terms involving higher order tensors need to be included in the tensor model. Meanwhile, if we are able to incorporate other interactions into the tensor model, we can examine the elastic constants of molecules with these interactions.

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