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Elastic constants of uniaxial nematic liquid crystals of non-cylindrically symmetric molecules

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We study in detail the influence of deviations from the molecular cylindrical symmetry on the fundamental elastic properties of uniaxial nematic liquid crystals. Results for the elastic constants are obtained for a range of molecular length–width ratio, temperature, density and molecular parameters. We compare calculated values with the experimental data of 8 OCB. It is observed that the effect of non-cylindrical molecular symmetry on the values of elastic constants of uniaxial of a nematic phase is small.

The present investigation concerns the analysis of the influence of deviations from the molecular cylindrical symmetry on the elastostatics of uniaxial nematic liquid crystals. The elastic constants are written as a sum of two parts: the first part represents the contribution to elastic constants due to molecular axial symmetry, whereas the second is the contribution arising from non-cylindrical molecular symmetry. We observe that the contribution due to the breaking of axial molecular symmetry is small.

Using density functional formalism [1], and in a previous paper [2; hereafter referred to as I and SSR theory] of this series we developed a unified molecular theory to derive an expression for the distortion free-energy of ordered phases of molecular systems in terms of the order parameter characterizing the structure of the phase and the molecular correlation functions of an effective isotropic liquid. The application of SSR theory was considered [2, 3] with respect to the elastostatics of uniaxial nematic, smectic A and biaxial orthorhombic nematic mesophases. The influence of molecular interactions on the elastic constants of uniaxial mesophases were studied. Recently, we have evaluated [4] the relative contributions of HER (hard ellipsoids of revolution), electrostatics and dispersion interactions on the splay, twist and bend elastic constants of the uniaxial nematic phase of molecules of cylindrical symmetry for a range of molecular length–width ratio, temperature, density and molecular parameters, and the results have been found to be in good agreement with the experimental and computer simulation values. A summarising over-

view to date of the developments in the area of elasto-statics of liquid crystals has been presented previously by one of us [5].

The introduction of biaxiality in the molecular shape and/or the intermolecular interaction has been found [6, 7] to have a pronounced effect on the uniaxial nematic–isotropic transition; both the order parameters and the first order character of the uniaxial nematic–isotropic transition are greatly reduced from that of the comparable uniaxial bodies. We analyse here the contribution to the elastic constants of uniaxial nematics arising due to non-cylindrical molecular symmetry.

The elasticity is concerned with the behaviour of the Helmholtz free-energy with respect to a small deformation of the system away from its equilibrium state. On the basis of symmetry arguments, the elastic continuum theory [8, 9] (long-wavelength deformation) shows that the distortion free-energy density of a uniaxial nematic phase is composed of three invariants K_1, K_2 and K_3 which are known as the Frank elastic constants and are associated, respectively, with the splay, twist and bend modes of distortion. The distortion free-energy can be written as

$$\Delta A_e = \frac{1}{2} \int dr [K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2] \tag{1}$$

where $\mathbf{n}(r)$ is the director at the point r and the subscript e stands for the distortion.

The expression obtained in SSR theory [2] for the distortion free-energy density of molecular ordered phases in the limit of long-wavelength distortion is

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written as

$$\frac{1}{V}\beta\Delta A_{\mathrm{e}}[\rho]$$

$$= -\frac{1}{2}\rho_{\mathrm{o}}^2 \sum_{l_1,l_2l} \sum_{m_1,m_2,m,m'} \sum_{n_1,n_2} \sum_{\mathbf{G}}$$

$$\times [(2l_1+1)(2l_2+1)]^{-1} C_g(l_1 l_2 l, m_1 m m') Q_{l_1 m_1 n_1}(\mathbf{G})$$

$$\times Q_{l_2 m_2 n_2}(-\mathbf{G}) \int d\mathbf{r}_{12} [\exp(i\mathbf{G}\cdot\mathbf{r}_{12}) D_{mm_2}^{l_2}(\Delta\chi(\mathbf{r}_{12}))$$

$$- \exp(i\mathbf{G}\cdot\mathbf{r}_{12})] Y_{lm'}^*(\hat{\mathbf{r}}_{12}) C(l_1 l_2 l; n_1 n_2; r_{12}), \qquad (2)$$

where ρ_{o} is the mean number density of the system and $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/|\mathbf{r}_{12}|$ is a unit vector along the intermolecular axis. $D_{mn}^l(\Delta\chi)$ are the generalized spherical harmonics, $\mathbf{G}$ the reciprocal lattice vectors of the crystalline structure that might be present in the ordered phase, $Q_{lmn}(\mathbf{G})$ are the order parameters and C_g the Clebsch–Gordon coefficients. $\Delta\chi(\mathbf{r}_{12})$ represents the angle between the principal directors at $\mathbf{r}_1$ and $\mathbf{r}_2$ and $C(l_1 l_2 l; n_1 n_2; r_{12})$ are the harmonic expansion coefficients of the direct pair correlation function of an isotropic liquid in terms of generalized spherical harmonics.

Assuming uniaxial symmetry for the nematic phase ($m_1 = m_2 = 0$) and that the symmetry plane is perpendicular to the director (l_1 and l_2 even) we write the Frank elastic constants as an expansion series:

$$\beta K_i = \sum_{l_1,l_2} \beta K_i^{(n_1 n_2)}(l_1, l_2), \qquad (3)$$

where for the uniaxial nematic phase composed of molecules having non-cylindrical symmetry we obtain

$$\beta K_1^{(n_1 n_2)}(l_1, l_2) = -\frac{4\pi}{3(5)^{1/2}}\rho_{\mathrm{n}}^2 \sum_{n_1,n_2} (2l_2+1)^{-1/2} \overline{D_{0n_1}^{l_1^*} D_{0n_2}^{l_2^*}}$$

$$\times \left\{ \frac{1}{2}(5)^{1/2} b_{l_2,0} C_g(l_1 l_2 0, 000) J_{l_1 l_2 0}^{n_1 n_2} \right.$$

$$- \frac{1}{2} b_{l_2,0} C_g(l_1 l_2 2, 000) J_{l_1 l_2 2}^{n_1 n_2}$$

$$+ (6)^{1/2} b_{l_2,1} C_g(l_1 l_2 2, 011) J_{l_1 l_2 2}^{n_1 n_2}$$

$$\left. + \left(\frac{3}{2}\right)^{1/2} b_{l_2,2} C_g(l_1 l_2 2, 022) J_{l_1 l_2 2}^{n_1 n_2} \right\}, \quad (4)$$

$$\beta K_2^{(n_1 n_2)}(l_1, l_2) = -\frac{4\pi}{6(5)^{1/2}}\rho_{\mathrm{n}}^2 \sum_{n_1,n_2} (2l_2+1)^{-1/2} \overline{D_{0n_1}^{l_1^*} D_{0n_2}^{l_2^*}}$$

$$\times \{ (5)^{1/2} b_{l_2,0} C_g(l_1 l_2 0, 000) J_{l_1 l_2 0}^{n_1 n_2}$$

$$- b_{l_2,0} C_g(l_1 l_2 2, 000) J_{l_1 l_2 2}^{n_1 n_2}$$

$$+ (6)^{1/2} b_{l_2,2} C_g(l_1 l_2 2, 022) J_{l_1 l_2 2}^{n_1 n_2} \}, \qquad (5)$$

$$\beta K_3^{(n_1 n_2)}(l_1, l_2) = -\frac{4\pi}{3(5)^{1/2}}\rho_{\mathrm{n}}^2 \sum_{n_1,n_2} (2l_2+1)^{-1/2} \overline{D_{0n_1}^{l_1^*} D_{0n_2}^{l_2^*}}$$

$$\times \left\{ \frac{1}{2}(5)^{1/2} b_{l_2,0} C_g(l_1 l_2 0, 000) J_{l_1 l_2 0}^{n_1 n_2} \right.$$

$$+ b_{l_2,0} C_g(l_1 l_2 2, 000) J_{l_1 l_2 2}^{n_1 n_2}$$

$$\left. - (6)^{1/2} b_{l_2,1} C_g(l_1 l_2 2, 011) J_{l_1 l_2 2}^{n_1 n_2} \right\}. \qquad (6)$$

Here the structural parameter $J_{l_1 l_2 l}^{n_1 n_2}$ is defined as

$$J_{l_1 l_2 l}^{n_1 n_2} = \int r_{12}^4 \, dr_{12} \, C(l_1 l_2 l, n_1 n_2, r_{12}), \qquad (7)$$

ρ_{n} is the nematic density and $\overline{D_{0n}^{l^*}}$ are the orientational order parameters and

$$b_{l_2,0} = -\frac{1}{2}l_2(l_2+1)\left[\frac{2l_2+1}{4\pi}\right]^{1/2},$$

$$b_{l_2,1} = -b_{l_2,1} = -\frac{1}{2}l_2(l_2+1)\left[\frac{(2l_2+1)(l_2-1)!}{4\pi(l_2+1)!}\right]^{1/2}$$

and

$$b_{l_2,2} = b_{l_2,2}$$

$$= \frac{1}{4}(l_2-1)l_2(l_2+1)(l_2+2)\left[\frac{(2l_2+1)(l_2-2)!}{4\pi(l_2+2)!}\right]^{1/2}.$$

In the limit $n_1 = n_2 = 0$ (i.e. the molecules with cylindrical symmetry) the above relations reduce to the expressions given elsewhere [2, 4] and correspond to the case of a uniaxial nematic of axial molecules. Using the symmetry properties of spherical harmonics [10, 11] and the values of the C_g coefficients we obtain the explicit results for $\beta K_i^{(n_1 n_2)}(l_1, l_2)$ for $2 \leqslant l_1, l_2 \leqslant 8$ and $0 \leqslant n_1, n_2 \leqslant 2$. In the calculation we take the first two terms of the series (3).

For the calculation of the values of the order parameters $\bar{P}_2$, $\bar{P}_4$, $D_{02}^{2^*}$, $D_{02}^{4^*}$, the structural parameters $J_{l_1 l_1 l}^{00}$ and J_{220}^{02}, J_{222}^{02}, J_{220}^{22}, J_{222}^{22}, J_{242}^{20}, J_{242}^{02}, J_{242}^{22}, etc. of an effective fluid and the information about the constituent molecules, (for example, the quadrupole moment, geometry of the repulsive core, length–width ratio, etc.) are required as input parameters. While reasonably accurate values of $\bar{P}_2$ are available for a number of systems over a range of temperature from experiments, very little information is available about the order parameters $\bar{P}_4$, $D_{02}^{2^*}$ and $D_{02}^{4^*}$. The order parameters $\bar{P}_2$ and $\bar{P}_4$ measure the alignment of molecular e_z axis along the space-fixed Z axis (or the director). The order parameters $D_{02}^{2^*}$ and $D_{02}^{4^*}$ measure the difference in the alignment of the molecular e_x and e_y axes along the director. In the case of axially symmetric molecules the molecular axes e_x and e_y are indistinguishable and both $D_{02}^{2^*}$ and $D_{02}^{4^*}$

vanish. For obtaining values of structural parameters (equation (7)) one requires the values of the C-harmonics which can be found by solving the OZ equation using the P Y closure equation. We evaluated [4, 12] these harmonics for a system of axial molecules interacting via HER, quadrupolar and dispersion interactions. Such calculations for a system composed of non-axial molecules are very complicated and may need enormous computational efforts to generate reliable data for C-harmonics. Therefore, instead of evaluating $J_{l_1 l_2 l}^{n_1 n_2}$ by solving the OZ equation we prefer to estimate their values via an indirect method.

We performed a model calculation based on the experimental data of 8OCB (4'-n-octyloxy-4-cyano-biphenyl). Madhusudana and Pratibha [13] have measured the elastic constants K_1, K_2 and K_3 and the order parameter $\bar{P}_2$ of 8OCB in the nematic phase as a function of temperature. We estimated the other order parameters such as $\bar{P}_4 \simeq \bar{P}_2^3$ and $D_{02}^{4*} = D_{02}^{2*2}$. For the molecular parameters of 8OCB we use the following data in the calculation: $x = 4\cdot0$, $\rho_n = 1\cdot1\,\mathrm{g\,cm}^{-3}$, $d_o = 5\cdot5\,\text{Å}$, $\varepsilon_o/k = 650\,\mathrm{K}$ and $\theta = -40 \times 10^{-26}\,\mathrm{esu\,cm}^2$. Here x (=a/b, $2a$ and $2b$ denote, respectively, the length of the major and minor axes of the ellipsoids) is the length-to-width ratio of the ellipsoid, θ the quadrupole moment, ε_o a constant with unit of energy and d_o the molecular diameter.

Adopting a similar method as described in SSR theory and [4] we calculate the structural parameters $J_{l_1 l_2 l}^{00}$ for the HER, dispersion and quadrupole interactions for $x = 4$ and $\rho_n = 1\cdot1\,\mathrm{g\,cm}^{-3}$. Using these values of $J_{l_1 l_2 l}^{00}$ we evaluate the elastic constants K_i^{00} ($i = 1, 2, 3$) corresponding to the axial symmetry of molecules as a function of temperature ranging from 340·4 K to 352 K. For evaluating the contribution to K_i due to the non-axial symmetry of the molecules, the values of the structural parameters J_{220}^{02}, J_{222}^{02}, J_{220}^{22}, J_{222}^{22}, J_{242}^{02}, J_{242}^{20}, J_{242}^{22}, etc., are required. We adopt the indirect method to estimate these parameters. The experimental values of the splay elastic constants K_1 as a function of temperature are used to approximate $J_{l_1 l_2 l}^{n_1 n_2}$. The contribution K_1^{00} corresponding to axial molecules is calculated at eight temperatures between 352 K and 340·4 K. The structural parameters, as listed above, are estimated by solving a set of equations, one corresponding to each temperature, so that the calculated values of K_1 (= $K_1^{00} + K_1^{n_1 n_2}$) are in agreement with the experimental values. Using the values of $J_{l_1 l_2 l}^{n_1 n_2}$ as estimated from this indirect procedure we calculate the contributions due to non-axial molecular symmetry, to the twist and bend elastic constants. It is observed that the contributions of the non-axial term are small, of the order of 10 to 15 per cent, as compared to the contributions of the axial term.
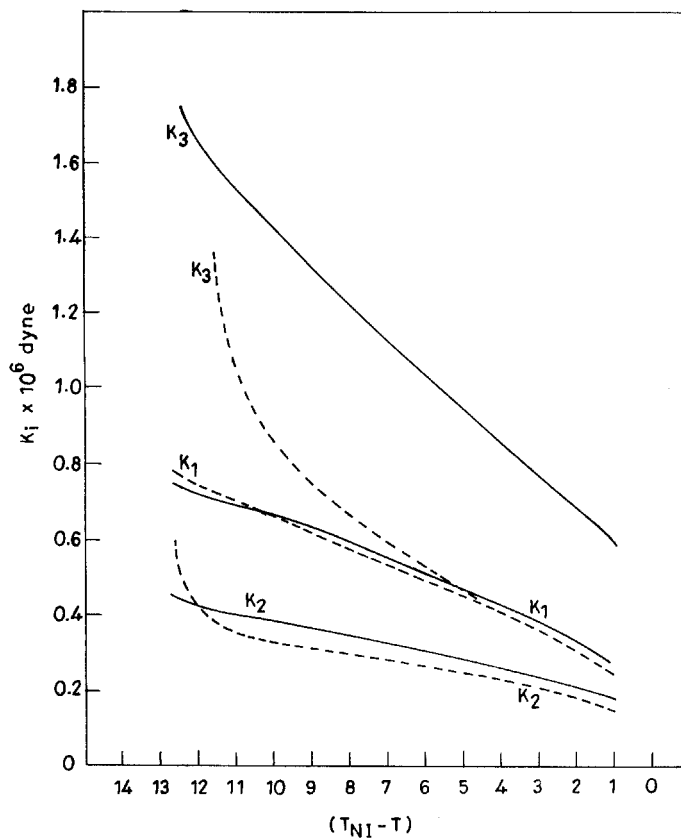

Figure 1. Variation of splay, twist and bend elastic constants of 8OCB. The broken and full lines represent, respectively, the experimental and calculated values.

In figure 1 we compare the calculated values of K_i ($=K_i^{00} + K_i^{n_1 n_2}$; $i = 1, 2, 3$) with the experimental values [13]. In view of experimental uncertainties it can be concluded that the theoretical result agrees well with the experimental one. Our calculated values of K_3 are large compared to the experimental values. It is important to note that as physically expected when we approach the nematic–smectic A transition, a signature of a pronounced increase in the values of K_2 and K_3 is clearly observed.

It is thus found that the effect of departure from the axial molecular symmetry on the values of elastic constants of a uniaxial nematic phase is small.

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