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# Elastic constants of nematic liquid crystals of uniaxial symmetry

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## Abstract

We study, in detail, the influence of molecular interactions on the Frank elastic constants of uniaxial nematic liquid crystals composed of molecules of cylindrical symmetry. This work is based on a weighted density functional formalism developed by us in a previous paper (Singh *et al* 1992 *Phys. Rev. A* **30** 583). A brief summary of the status of theoretical development for the elastic constants of nematics is presented. Considering a pair potential having both repulsive and attractive parts, numerical calculations are reported for three nematics: MBBA, PAA and 8OCB. For these systems the length-to-width ratio  $x_0$  is estimated from the experimentally determined structure of the molecules. The repulsive interaction is represented by a repulsion between hard ellipsoids of revolution (HER) and the attractive potential is represented by the quadrupole and dispersion interactions. From the numerical results we observe that in the density range of nematics the contributions of the quadrupole and dispersion interactions are small as compared to the repulsive HER interaction. The inclusion of attractive interactions reduces the values of elastic constant ratios. The absolute values of elastic constants are sensitive to the values of potential parameters. The elastic constants and their ratios are in agreement with the experimental and computer simulation values. The temperature variation of elastic constants and their ratios are reported and compared with the experimental values. It is found that the calculated values are in agreement with the experimental data. The twist elastic constant has a weak temperature dependence but a pronounced influence is found on the bend elastic constants.

## 1. Introduction

In a previous paper [1] (hereafter referred to as I), we developed a theory based on the density functional formalism [2] for the deformation free-energy of any systems with continuous broken symmetry, and applied the theory to derive expressions for the elastic constants of

nematic and smectic-A phases of uniaxial ( $D_{\infty h}$ ) symmetry. In the second paper [3] the theory was applied to derive expressions for all the 12 bulk elastic constants of the biaxial nematic phase of orthorhombic symmetry. These expressions of elastic constants are written in terms of order parameters that characterize the nature and amount of ordering in the phase and the structural parameters involving the generalized spherical harmonic coefficients of the direct pair correlation function of an effective isotropic liquid, the density of which is determined using a criterion of the weighted density functional formalism [4]. In the present paper the numerical evaluation of elastic constants for the uniaxial nematic phase is reported and the theoretical values are compared with the available experimental and computer simulation data.

According to continuum theory [5], the bulk elastic properties of nematics can be described by three invariants  $K_1$ ,  $K_2$  and  $K_3$  which are known as Frank elastic constants and are associated with the restoring forces opposing splay, twist and bend distortions, respectively. The distortion free-energy density is written as

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

where  $\hat{\mathbf{n}}$ , the director, indicates the preferred direction of the long-axes of the molecules. These elastic constants control almost exclusively the structure and properties of nematic liquid crystals at mesoscopic length scale. Expressions which connect to the microscopic properties of the mesophase are thus obviously of interest. It is difficult to measure experimentally the absolute values of these elastic constants [6–9]. Their ratios  $K_2/K_1$  and  $K_3/K_1$  can be measured more accurately [9–11]. For high duty liquid crystal displays [12], the ratio  $K_3/K_1$  is desired to be as small as possible. The elastic moduli are temperature and density dependent. The dependence on the density is pronounced. A number of measurements are reported which show that  $K_1$  and  $K_2$  have weak temperature dependences, whereas  $K_3$  rapidly increases with temperature, and that when the nematic–smectic-A transition temperature is approached from above,  $K_1$  does not show any sharp change but  $K_2$  and  $K_3$  increase anomalously.

The present paper is organized as follows: in section 2, we describe, in brief, the status of the theoretical development for the elastic constants of the uniaxial nematics and summarize the working equations used in the calculation. The numerical evaluation and results are presented in section 3. The paper ends with a summary and conclusions in the last section.

## 2. Theoretical development and working equations

First we shall comment, in brief, on the status of the theoretical development of elastic constants of uniaxial nematics. Detail of these works are well documented elsewhere [11, 13].

In the Landau–de-Gennes theory the free-energy density is assumed to be an analytic function of the order parameter tensor. To the extent that the order parameter is small, the free-energy density is expressed as an expansion in its various orders and gradient terms. The elastic free-energy density up to second order in the order parameter is written in terms of two elastic constants  $L_1$  and  $L_2$  which are related to the Frank elastic constants as

$$K_1 = \frac{9}{2} (L_1 + \frac{1}{2} L_2) \overline{P}_2^2 \quad (2)$$

$$K_2 = \frac{9}{2} L_1 \overline{P}_2^2 \quad (3)$$

and

$$K_1 = K_3. \quad (4)$$

Thus the elastic constant moduli  $K_i$  vary with temperature like  $\overline{P}_2^2$ . The prediction  $K_1 = K_3$  is not consistent with the experimental observation. However, this is an artifact of the derivation

in which only the gradient terms of  $\overline{P}_2$  order parameter have been considered. If the  $\overline{P}_4$  term is also included in the free-energy expansion, all the three elastic constants will be different.  $\overline{P}_l$  represent the Legendre polynomial order parameters. Using an expansion of the intermolecular potential in spherical harmonics Priest [14] also arrived at the same conclusion. For the special case of dispersion forces, Nehring and Saupe [15] calculated (up to the order  $\overline{P}_2^2$ ) the ratio of the elastic constants and got the result  $K_i \propto \overline{P}_2^2$ , and

$$K_1:K_2:K_3 = 5:11:5.$$

This is not in agreement with the experimental finding. Apart from the temperature dependence of the elastic constants, via  $\overline{P}_2$  order parameter, there is also a dependence on the density. Priest [14] showed that the deviation from the equality  $K_1 = K_3$  is related in a simple way to the ratio  $\overline{P}_4/\overline{P}_2$  and

$$K_1/\overline{K} = 1 + \Delta - \Delta'(\overline{P}_4/\overline{P}_2) + \dots \quad (5)$$

$$K_2/\overline{K} = 1 - 2\Delta - \Delta'(\overline{P}_4/\overline{P}_2) + \dots \quad (6)$$

$$K_3/\overline{K} = 1 + \Delta + 4\Delta'(\overline{P}_4/\overline{P}_2) + \dots \quad (7)$$

where  $\overline{K} = \frac{1}{3}(K_1 + K_2 + K_3)$ . The quantity  $\Delta$  and  $\Delta'$  are positive constants which depend on the molecular properties. For the case of hard spherocylinders, the constants  $\Delta$  and  $\Delta'$  were found to depend on the length–width ratio,  $x_0$ , of the molecules. Most of the hard rod models [11] are strictly valid only for the very long and thin rods and they usually predict too large a value for  $K_3$  and cannot reproduce the temperature dependences of the elastic constants.

Several workers [11, 13] have evaluated the elastic constants for the van der Waals type potential described by hard spherocylinders with superimposed attractive interactions. While the Stecki and Poniewierski [16] treatment is based on the direct correlation function approach, a mean field (MF) approximation has been adopted by Kimura *et al* [17]. These authors found that  $K_3 > K_1 > K_2$  and that the temperature dependences of their ratios are in accordance with the experiment. Using generalized van der Waals (GVDW) theory [18], which couples the contributions of the short- and long-range pair potentials, the elastic moduli were evaluated in a model based on the distributed harmonic forces [19] between the molecules. In this work both the repulsive and attractive forces have been considered as being distributed along the molecules. This approach disregards the temperature dependence of elastic constants and assumes perfect orientational order, i.e.  $\overline{P}_2 = \overline{P}_4 = 1$ . It is a variant on the ideas of Gelbart and co-workers [18] who studied the combined effect of repulsive and attractive forces. Zakhrov [20] evaluated the elastic constants and order parameters by using a theory that is based on the method of conditional distribution (MCD) [21]. This method introduces a concept of reduced distribution functions which obey infinite chains of integro-differential equations. For arbitrary equations of the chains based on the concept of the mean-force potential (MFP) [22, 23] a truncated procedure was adopted. The numerical solution exhibits certain qualitative features. The order parameters decrease with increasing volume and temperature. While the observed values of  $K_1/\overline{K}$  and  $K_2/\overline{K}$  increase with increasing volume, the values of  $K_3/\overline{K}$  decreases with it.  $K_1/\overline{K}$  increases strongly with the length–width ratio and  $K_2/\overline{K}$  decreases with it, and  $0.5 < K_3/K_1 < 3.0$  and  $0.5 < K_2/K_1 < 0.8$ .

Several workers have considered the application of the density functional theory to study the elastic properties of nematics. A detailed account of these works are summarized elsewhere by one of us [11, 13]. In this theory an exact expression for the elastic free-energy is obtained in terms of order parameters and direct correlation functions. The correlation functions of the ordered phases are, in general, not known and hence need to be approximated. The functional Taylor expansion is performed to obtain the  $n$ -particle direct correlation function of an inhomogeneous system from the  $n$ - and higher-order direct correlation functions of a

uniform system. The elastic constants of nematics were calculated for a number of model systems using approximate forms of the pair correlation function of the medium. However, none of these approximate forms of the pair correlation function gives the structure of the medium correctly, and so the results reported are not expected to be accurate. An alternative method has been proposed [24] to evaluate the direct correlation functions in nematic fluids of soft ellipsoids from the computer simulations and then using these correlation functions elastic constants are determined from the Poniewierski–Stecki theory [16]. Osipov and Hess [25] have used the model of perfect local orientational order to write explicit expressions for the elastic constants of calamitic and discotic nematics. This work [25] is based on the Poniewierski and Stecki [16] density functional approach and assumes ellipsoidal shape for the equipotential surfaces to relate the direct correlation function to that of the sphere fluid by means of the affine transformation. They have discussed the dependence of the ratio  $K_3/K_1$  on  $x_0$ .

### 2.1. Weighted density functional approach: expression for the elastic constants

The density functional theory (DFT) has developed as a cost-effective procedure for studying the physical properties of non-uniform systems. An excellent account of the DFT and its application has been given by Singh [2]. A brief but self-contained account of the DFT in a form appropriate to the development of the properties of the liquid crystalline phase is summarized by one of us [11, 13].

The main idea of the theory is stated here. The single particle density distribution  $\rho(\mathbf{x})$  provides us with a convenient variational quantity to specify an arbitrary state of a system. One may consider a variational thermodynamic potential  $W(T, P, [\rho(\mathbf{x})])$  as a function of  $\rho(\mathbf{x})$ . The vector  $\mathbf{x}$  indicates both the location  $\mathbf{r}$  of the centre of a molecule and its relative orientations  $\Omega$  described by Euler angles  $\Phi, \theta$  and  $\Psi$ . For an isotropic uniform system,  $\rho(\mathbf{x})$  is independent of positions and orientations. The equilibrium state of the system at a given  $T$  and  $P$  is described by the density  $\rho(T, P, \mathbf{x})$  corresponding to the minimum of  $W$  with respect to  $\rho(\mathbf{x})$ . This forms the basis of the density functional theory.

The basic thermodynamic potential used to determine the isothermal elastic properties of a system, consisting of  $N$  particles in volume  $V$  at temperature  $T$ , is the Helmholtz free-energy  $A[\rho]$ . Elasticity is associated with the behaviour of  $A[\rho]$  with respect to small deformation of the system away from the equilibrium(ground) state [1]. In the density functional formalism,  $\Delta A[\rho]$ , which represents the excess reduced free-energy arising due to intermolecular interactions, can be used as a generating function for the correlation functions. Adopting this procedure and using the symmetry of the system, the free-energy can be expressed as

$$\beta A = \beta A_u + \beta \Delta A_e \quad (8)$$

where  $\beta A_u$  is the reduced Helmholtz free-energy of a system of undistorted phase and  $\Delta A_e$  is the free-energy associated with the distortion.  $\beta = 1/k_B T$ , where  $k_B$  is the Boltzmann constant.

In the weighted density functional approach the contribution to the free-energy due to the deformation is written as [1]

$$\beta \Delta A_e[\rho] = \frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 [\rho_e(\mathbf{x}_1)\rho_e(\mathbf{x}_2) - \rho(\mathbf{x}_1)\rho(\mathbf{x}_2)] C^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \bar{\rho}) \quad (9)$$

where  $\rho_e(\mathbf{x}_i)$  and  $\rho(\mathbf{x}_i)$  represent, respectively, the singlet distribution functions corresponding to the deformed and undeformed phases, respectively. Here the  $C^{(2)}$  represents the direct pair correlation function (DPCF) of an effective isotropic liquid. The effective density  $\bar{\rho}$  is found

using the relation [4],

$$\bar{\rho} = \frac{1}{\rho_0 V} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \rho(\mathbf{x}_1) \rho(\mathbf{x}_2) \omega(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}) \quad (10)$$

where  $\rho_0$  is the averaged density of the ordered phase and  $\omega$  is a weight factor.  $\bar{\rho}[\rho]$  is viewed here as a functional of  $\rho(\mathbf{x})$ . To ensure that the approximation becomes exact in the limit of a uniform system, the weight factor  $\omega$  must satisfy the normalization condition

$$\int d\mathbf{x}_2 \omega(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}) = \mathbf{1}. \quad (11)$$

In writing equation (9) it is assumed that the direct pair correlation function does not change due to the deformation.

The elastic constants are defined by the second-order term of expansion of the free-energy of the deformed state around the free-energy of the equilibrium (ground) state in the ascending powers of a parameter, which measures the deformation. The first term of this expansion is balanced by the equilibrium stresses of the ground state. One defines the elastic free-energy per volume as

$$\frac{E_e}{V} = \frac{1}{V} [\Delta A_e[\rho] + P(V_d - V)]$$

where  $V_d$  is the volume of the deformed sample and  $P$  the isotropic pressure.

For  $\rho(\mathbf{x})$  and  $\rho_e(\mathbf{x})$  we write the usual expansion [1] in terms of Fourier series and Wigner rotation matrices, in which order parameters appear as expansion coefficients. Since the isotropic fluid DPCF is an invariant pairwise function, we write its spherical harmonic expansion [26]. Assuming that molecule 1 at the origin with a principal director  $\hat{\mathbf{n}}(\mathbf{r}_1)$  pointing in the direction of the space-fixed (SF) Z-axis and molecule 2 is at a distance  $\mathbf{r}_{12}$  from the origin where  $\hat{\mathbf{n}}(\mathbf{r}_2)$  represents the direction of the local principal director (see figure 1 in [1]), using the rotational properties of generalized spherical harmonics, exploiting the molecular and phase symmetries of the system and carrying out angular integrations, we obtain the elastic free-energy density for a uniaxial nematic phase of axially symmetric molecules

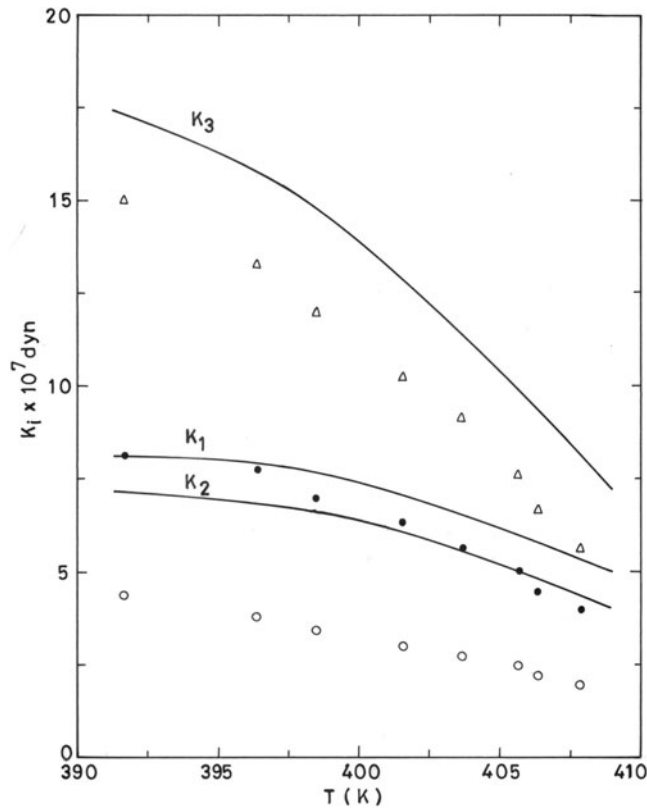
$$\begin{aligned} \frac{1}{V} \beta \Delta A_e[\rho] = & -\frac{1}{2} \rho_n^2 \sum'_{l_1 l_2 l} \sum_m \left[ \frac{(2l_1 + 1)(2l_2 + 1)}{(4\pi)^2} \right]^{1/2} \bar{P}_{l_1} \bar{P}_{l_2} C_g(l_1 l_2 l, omm) \\ & \times \int d\mathbf{r}_{12} C_{l_1 l_2 l}(\mathbf{r}_{12}) \left[ \left( \frac{4\pi}{2l_2 + 1} \right)^{1/2} Y_{l_2 m}(\Delta\chi(\mathbf{r}_{12})) - 1 \right] Y_{lm}^*(\hat{\mathbf{r}}_{12}) \end{aligned} \quad (12)$$

where  $\rho_n$  is the nematic number density. The prime on the summation indicates that  $l_1$  and  $l_2$  are even.  $\hat{\mathbf{r}}_{12} = \mathbf{r}_{12}/|\mathbf{r}_{12}|$  is unit vector along the intermolecular axis,  $C_g$  are the Clebsch–Gordon coefficients,  $C_{l_1 l_2 l}$  are the spherical harmonic expansion coefficients of the direct pair correlation function of an isotropic liquid, and  $\Delta\chi(\mathbf{r}_{12})$  represents the angle between the principal director at  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . Confining the variation of the director at  $\mathbf{r}_2$  in a plane, the  $Y_{l_2 m}(\Delta\chi(\mathbf{r}_{12}))$  is expressed [1] in terms of the distortion angle which is assumed to be small. Performing the angular integration over  $\hat{\mathbf{r}}_{12}$  and comparing equation (12) with equation (1), the following expressions for the elastic constants of uniaxial nematic phase composed of cylindrically symmetric molecules are obtained,

$$\beta K_i = \sum'_{l_1, l_2} \beta K_i(l_1, l_2). \quad (13)$$

The terms of this series were evaluated for  $2 \leq l_1, l_2 \leq 8$  and are given in I. The explicit expressions for the first few terms of the series can be written as

$$\beta K_1(2, 2) = \left( \frac{5}{4\pi} \right)^{1/2} \rho_n^2 \bar{P}_2^2 \left[ \frac{1}{2} J_{220} - \frac{1}{\sqrt{14}} J_{222} \right] \quad (14)$$



**Figure 1.** Comparison between the calculated (full curves) and experimental [6] values of elastic constants for PAA ( $x_0 = 2.87$ ) as a function of temperature. ●, ○ and △ represent, respectively, the experimental values of  $K_1$ ,  $K_2$  and  $K_3$ .

$$\beta K_1(2, 4) = -\frac{3}{4} \left( \frac{5}{\sqrt{14\pi}} \right) \rho_n^2 \bar{P}_2 \bar{P}_4 J_{242} \quad (15)$$

$$\beta K_1(4, 4) = \left( \frac{5}{4\pi} \right)^{1/2} \rho_n^2 \bar{P}_4^2 \left[ \sqrt{5} J_{440} - \frac{13}{2\sqrt{77}} J_{442} \right] \quad (16)$$

$$\beta K_2(2, 2) = \left( \frac{5}{4\pi} \right)^{1/2} \rho_n^2 \bar{P}_2^2 \left[ \frac{1}{2} J_{220} + \sqrt{\frac{2}{7}} J_{222} \right] \quad (17)$$

$$\beta K_2(2, 4) = \left( \frac{1}{3} \right) \beta K_1(2, 4) \quad (18)$$

$$\beta K_2(4, 4) = \left( \frac{5}{4\pi} \right)^{1/2} \rho_n^2 \bar{P}_4^2 \left[ \sqrt{5} J_{440} + \frac{47}{2\sqrt{77}} J_{442} \right] \quad (19)$$

$$\beta K_3(2, 2) = \beta K_1(2, 2) \quad (20)$$

$$\beta K_3(2, 4) = -\frac{4}{3} \beta K_1(2, 4) \quad (21)$$

and

$$\beta K_3(4, 4) = \left( \frac{5}{4\pi} \right)^{1/2} \rho_n^2 \bar{P}_4^2 \left[ \sqrt{5} J_{440} + \frac{17}{\sqrt{77}} J_{442} \right]. \quad (22)$$

The structural parameters appearing in these expressions are defined as

$$J_{l_1 l_2 l} = \int r_{12}^4 dr_{12} C_{l_1 l_2 l}(r_{12}). \quad (23)$$

### 3. Calculation and results

For evaluating the values of elastic constants (equation (13)) we need the values of order parameters (as a function of temperature), generalized spherical harmonic coefficients of the direct pair correlation function (DPCF) of an effective fluid (as a function of density and length–width ratio  $x_0$ ), and information about the constituent molecules, namely, electric multipole moments, geometry of the repulsive core, length–width ratio, etc, as input parameters.

Since in the limit of long-wavelength distortions the magnitude of the order parameters are assumed to remain unchanged, the values of the order parameters at a given temperature and density may be either determined experimentally or calculated from a theory. While reasonably accurate values of the order parameter  $\overline{P}_2$  from the experimental data are available for a number of systems over a range of temperatures, our knowledge about  $\overline{P}_4$  is scant. In the calculation here we use the values of  $\overline{P}_2$  as determined by the experiments and estimate  $\overline{P}_4$  as  $\overline{P}_4/\overline{P}_2 = \overline{P}_2^2$ . We have found that the values of  $\overline{P}_4$  as a function of temperature for PAA estimated in this way are in good agreement with the experimental data [27] of deuteriated *p*-azoxyanisole obtained from coherent neutron scattering experiments. Using available experimental data of  $\overline{P}_2$  for PAA [28] and MBBA [29] we draw smooth curves and the values of  $\overline{P}_2$  used in the calculation correspond to these curves. For 8OCB we use the experimental values of  $\overline{P}_2$  as measured by Madhusudana and Pratibha [10].

The *C*-harmonic coefficients  $C_{l_1 l_2 l}$  for a given system can, in principle, be found either by solving the Ornstein–Zernike equation with suitable closure relation [26, 30], or by adopting a perturbative scheme which is based on the fact that the fluid structure at high densities is primarily controlled by the repulsive part of the interaction. However, such calculations for non-axial molecules are very complicated and may need enormous computational efforts to generate reliable data for *C*-harmonic coefficients [31].

In the rigid molecular approximation it is assumed that the intermolecular potential energy depends upon only the position of the centre of mass and on its orientations. This kind of approach neglects the flexibility of the molecular structure which plays an important role in the stability of many liquid crystalline phases. In view of various complexities in the intermolecular interactions, one is often forced to construct models to map the molecules. We consider here a model potential described by hard ellipsoids of revolution with superimposed attractive (electrostatic) interactions. As discussed below, due to symmetry reasons the contributions of dipole–dipole and dipole–quadrupole interactions to the free-energy, and hence to the elastic constants, vanish.

We adopt the following form for the interaction potential between two molecules having prolate ellipsoidal symmetry

$$u(\mathbf{r}_{12}, \Omega_1, \Omega_2) = (u_{\text{HER}} + u_{\text{qq}} + u_{\text{dis}})(\mathbf{r}_{12}, \Omega_1, \Omega_2) \quad (24)$$

where  $u_{\text{HER}}$  represents the repulsion between hard ellipsoids of revolution (HER) and the subscripts qq and dis indicate, respectively, the interactions arising due to the quadrupole–quadrupole and dispersion forces. The explicit form of these interactions are given in I [1].

In this paper we study the influence of HER, quadrupole and dispersion interactions on the elastic properties of three nematics: *p*-azoxyanisole (PAA), *N*-*p*-methoxybenzylidene-*p*-butylaniline (MBBA) and 4'-*n*-octyloxy-4-cyanobiphenyl (8OCB). We compare the calculated values of elastic constants with the experimental and simulation data.



The molecular structures of PAA and MBBA were determined by  $^{14}\text{N}$  nuclear quadrupole resonance [32] and line shape [33] studies. We have used this structure of a molecule to estimate the value of  $x_0$  from the bond lengths and bond angles of the constituent units. For 8OCB the usual chemical structure has been used to estimate  $x_0$ . The estimated values of  $x_0$  are 2.68, 2.87 and 4.88 for MBBA, PAA and 8OCB, respectively.

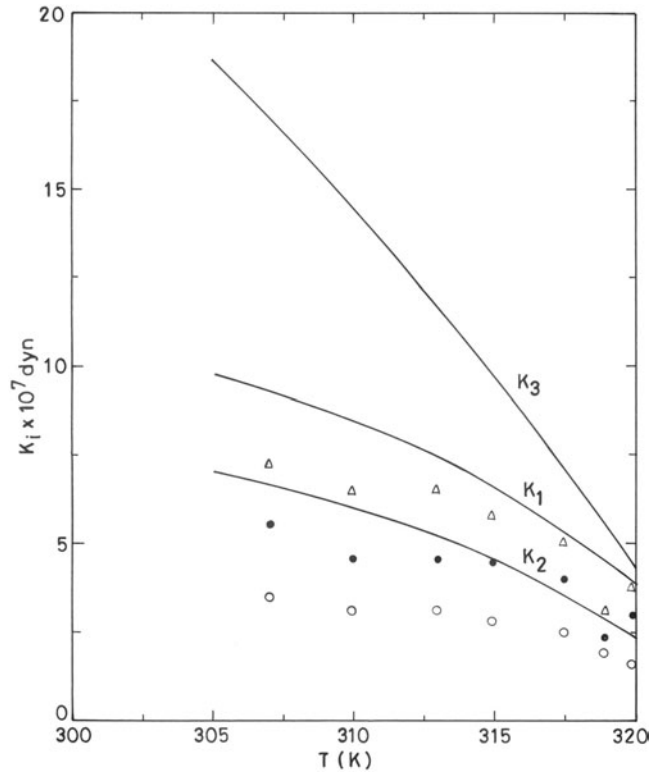
For evaluating structural parameters,  $J_{l_1 l_2 l}$ , as a function of density and  $x_0$ , the values of  $C$ -harmonic coefficients  $C_{l_1 l_2 l}$  for the potential model (24) are needed. As the evaluation of  $C_{l_1 l_2 l}$  is difficult, in a calculation only a finite number of  $C_{l_1 l_2 l}$  for any orientation dependent function can be handled. It has been shown [1, 30] that for the potential model (24) the inclusion of all the harmonic coefficients up to indices  $l_1, l_2 = 4$  makes the series fully convergent. The  $C$ -harmonic coefficients in the body-fixed (BF) frame are written as an expansion series involving u-potential harmonics and correlation function g-harmonics. The space-fixed (SF) frame harmonic coefficients are found by the usual linear transformation [26]. From the fact that  $C$ -harmonic coefficients which contribute to the free-energy of uniaxial mesophase of cylindrically symmetric molecules have even  $l_1$  and  $l_2$  indices and that the  $C_{\text{HER}}$ -harmonics survive only for the even values of  $l_1$  and  $l_2$  indices, we note that only those interactions will contribute to the  $C$ -harmonics which have non-vanishing u-harmonics for the even values of  $l_1$  and  $l_2$  indices. For the electrostatic (dipole–dipole, dipole–quadrupole and quadrupole–quadrupole) interactions the non-vanishing potential harmonic coefficients in the BF frame are  $u_{110}^{\text{dd}}, u_{111}^{\text{dd}}, u_{120}^{\text{dq}}, u_{121}^{\text{dq}}, u_{220}^{\text{qq}}, u_{221}^{\text{qq}}$  and  $u_{222}^{\text{qq}}$ . Therefore, we concluded in I that the dip–dip and dip–quad interactions do not contribute to the free energy and hence to the elastic constants.

The PY closure relation has been solved by Singh and co-workers [30] for the  $g_{\text{HER}}, h_{\text{HER}}$  and  $C_{\text{HER}}$  harmonics for  $x_0 = 3.00, 3.25, 3.50$  and  $4.00$ . Taking their results we estimated in I the values of  $C_{l_1 l_2 l}$  for the quadrupolar and dispersion interactions. Adopting the same procedure we have evaluated here these harmonics for  $x_0 = 2.68, 2.87$  and  $4.88$ . With known  $C$ -harmonic coefficients we evaluated the values of structural parameters as a function of reduced density  $\rho^* (= \rho_n d_0^3)$  where  $d_0$  is the molecular diameter.

We evaluate the contribution of the individual terms of the series

$$K_i = K_i(2, 2) + 2K_i(2, 4) + K_i(4, 4) \quad (25)$$

for the repulsive (HER), dispersion and quadrupole interactions for three values of  $x_0 = 2.68(\text{MBBA}), 2.87(\text{PAA})$  and  $4.88(8\text{OCB})$ . In the calculation we observe that the absolute values of the elastic constants are sensitive to the values of potential parameters, namely quadrupole moment  $\Theta^{*2} (= \Theta^2 / \epsilon_0 d_0^3)$ ,  $\epsilon_0 / k_B$  and  $d_0$ . However, we have made no attempt here to fit the experimental data by adjusting these parameters. We preferred to perform calculations for several sets of parameters and thus investigate the effect of these parameters on the elastic constants. Taking the values of  $\epsilon_0 / k_B = 525 \text{ K}$  and  $d_0 = 5.36 \text{ \AA}$  Tsykalo and Bagmet [34] found in their MD study good quantitative agreement for the temperature dependence of the order parameter between the theoretical and experimental data of PAA ( $x_0 = 3.0$ ). The values of  $\epsilon_0 / k_B$  for PAA ( $x_0 = 3$ ) were estimated by Singh and Singh [35] on the assumption that the liquid–solid transition temperatures at the triple point obey a simple scaling law,  $T_t^* (= k_B T_t / \epsilon_0) = C'$  where  $C'$  is a constant independent of  $x_0$ . Taking  $C' = 0.68$  (the reduced triple point temperature for the Lennard-Jones (12-6) system) they found that  $\epsilon_0 / k_B = 575 \text{ K}$ . The values of  $\epsilon_0 / k_B$  and  $d_0$  selected by us for PAA ( $x_0 = 2.87$ ) are consistent with these values and for the other two systems MBBA and 8OCB the values of potential parameters have been chosen corresponding to their length–width ratios. As the value of quadrupole moment increases, for a given set of  $\epsilon_0 / k_B$  and  $d_0$ , the absolute values of elastic constants  $K_i$  increase but the values of their ratios decrease. With increasing value of molecular diameter, for the given values of  $\Theta^{*2}$  and  $\epsilon_0 / k_B$ , the absolute values of  $K_i$  decrease whereas



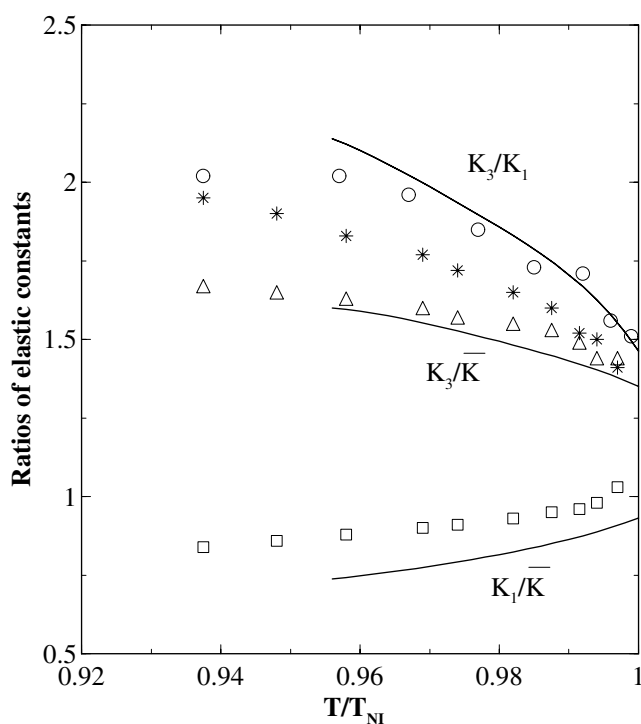
**Figure 2.** Comparison between the calculated (full curves) and experimental [7] values of elastic constants for MBBA ( $x_0 = 2.68$ ) as a function of temperature. ●, ○ and △ represent, respectively, the experimental values of  $K_1$ ,  $K_2$  and  $K_3$ .

the values of their ratios increase. For given values of  $\Theta^{*2}$  and  $d_0$  a small increase in  $K_i$  but a slight decrease in their ratios is found with increasing values of  $\epsilon_0/k_B$ .

A number of observations regarding relative contributions of HER, dispersion and quadrupole interactions have been made from this calculation. The series (25) is found to converge rapidly for the molecules interacting via the interaction potential (24). In the density range of nematics the contributions of quadrupole and dispersion interactions are small as compared to the repulsive HER interaction. For a given  $x_0$ ,  $K_3^{\text{HER}}(2, 4)$  is positive whereas  $K_2^{\text{HER}}(2, 4)$  and  $K_1^{\text{HER}}(2, 4)$  are negative. Consequently, we find that  $K_3^{\text{HER}} > K_1^{\text{HER}} > K_2^{\text{HER}}$  and the ratio  $(K_3^{\text{HER}}/K_1^{\text{HER}}) > (K_2^{\text{HER}}/K_1^{\text{HER}})$ . From a MD simulation for a HER system of  $x_0 = 3.0$  at  $\rho_n^* = 0.354$ , Allen and Frankel [36] found that  $(K_2^{\text{HER}}/K_1^{\text{HER}}) = 0.929$  and  $(K_3^{\text{HER}}/K_1^{\text{HER}}) = 3.414$ . Here in this work we have found that:

- (i) for  $x_0 = 2.87$  (PAA),  $\rho_n^* = 0.315$ ,  $(K_2^{\text{HER}}/K_1^{\text{HER}}) = 0.772$  and  $(K_3^{\text{HER}}/K_1^{\text{HER}}) = 2.008$  and
- (ii) for  $x_0 = 2.68$  (MBBA),  $\rho_n^* = 0.35$ ,  $(K_2^{\text{HER}}/K_1^{\text{HER}}) = 0.691$  and  $(K_3^{\text{HER}}/K_1^{\text{HER}}) = 1.272$ .

The corresponding experimental values of these ratios  $K_2^{\text{HER}}/K_1^{\text{HER}}$  and  $K_3^{\text{HER}}/K_1^{\text{HER}}$  as quoted by Allen and Frenkel [36] for a comparison with simulation results are, respectively, for PAA 0.63 and 2.50 and for MBBA 0.618 and 1.455. Our results for the HER system is in accordance with that of Allen and Frankel [36] and Osipov and Hess [25] results. We find that for all the three systems the ratios  $K_2^{\text{HER}}/K_1^{\text{HER}}$  and  $K_3^{\text{HER}}/K_1^{\text{HER}}$  are higher than the experimental values



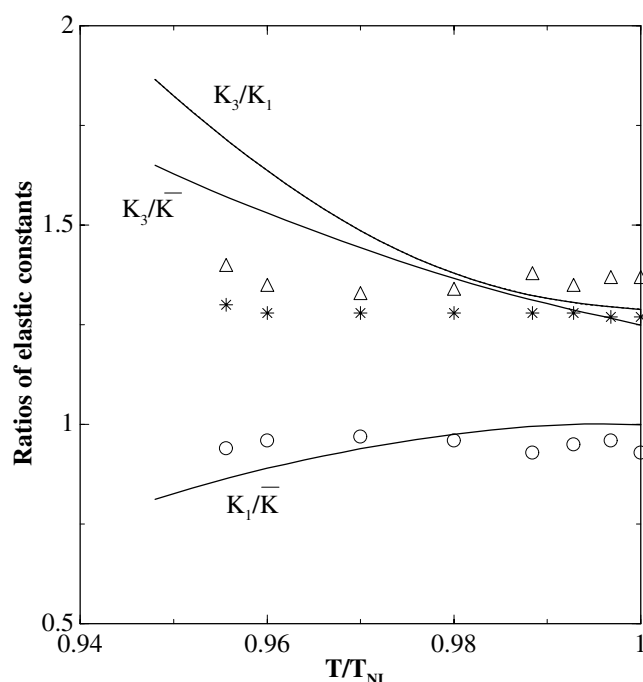
**Figure 3.** Comparison between the calculated (full curves) and experimental values of the elastic constants ratios for PAA as a function of temperature. The experimental ratios [6] are shown as  $K_3/K_1$ :  $\circ$  and  $*$ ;  $K_3/\bar{K}$ :  $\triangle$  and  $K_1/\bar{K}$ :  $\square$ .

and that the inclusion of dispersion and quadrupole interactions reduces the values of elastic constant ratios  $K_2/K_1$  and  $K_3/K_1$ .

For a given  $x_0$  and quadrupole moment the contribution of  $K_i^{qq}(4, 4)$  is much smaller as compared to  $K_i^{qq}(2, 2)$ . As the value of the quadrupole moment increases the contribution of each individual term of the series (25) and  $K_i^{qq}$  increase significantly. The numerical values of  $K_1^{qq}$  and  $K_3^{qq}$  are positive whereas  $K_2^{qq}$  is negative. The influence of the dispersion interaction on the elastic constants is small as compared to the quadrupole interaction.

The temperature dependence of the elastic constants are mainly due to the variation of order parameters with temperature. Experimentally it is difficult to determine the absolute values of the elastic constants. It is the ratios  $K_2/K_1$  and  $K_3/K_1$  which are usually measured and are more accurate. In addition to these ratios the other ratios which are found more accurately from the experiments are  $K_i/\bar{K}$ . In accordance with the experiments we observe, for all the systems, that the ratio  $K_3/K_1$  decreases significantly with the increasing temperature whereas the ratio  $K_2/K_1$  is more or less independent of the temperature. So here in the following figures we show a comparison between the calculated and experimental values of  $K_i$  for the PAA, MBBA and elastic constant ratios  $K_3/K_1$ ,  $K_1/\bar{K}$  and  $K_3/\bar{K}$  for the PAA, MBBA and 8OCB.

Figure 1 compares the value of  $K_i$  as a function of temperature for PAA. It can be seen that the theoretical values are consistent with the experimental data. However, the theory gives higher values for  $K_3$  and  $K_2$  whereas the values of  $K_1$  are in reasonable agreement with the experiment. In the case of MBBA (figure 2) a rapid increase in  $K_3$  with the temperature has



**Figure 4.** Comparison between the calculated (full curves) and experimental values [7] of the elastic constant ratios for MBBA as a function of temperature. The experimental ratios are shown as  $K_3/K_1$ :  $\Delta$ ;  $K_3/\bar{K}$ : \* and  $K_1/\bar{K}$ :  $\circ$ .

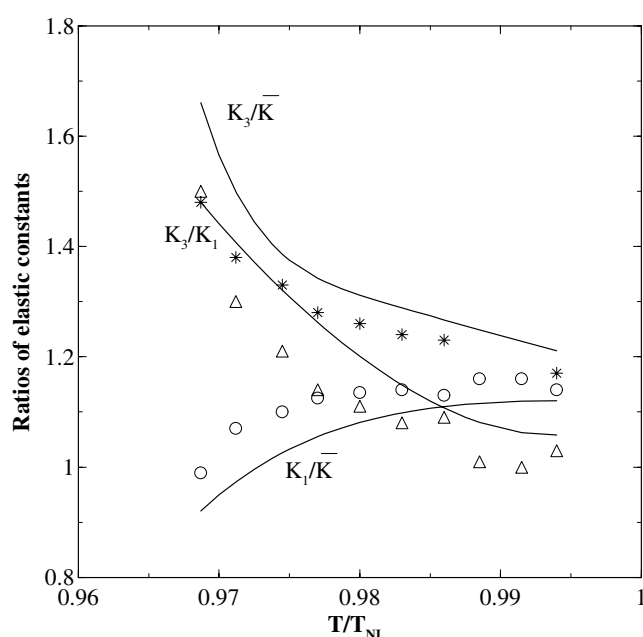
been found as compared to its experimental values.  $K_1$  and  $K_2$  show a reasonable agreement between theory and experiment.

Figures 3–5 show a comparison between the temperature dependences of calculated and experimental values of  $K_3/K_1$ ,  $K_1/\bar{K}$  and  $K_3/\bar{K}$  for PAA, MBBA and 8OCB, respectively. It can be seen that for all of these systems theoretical values are consistent with the experimental data. In the case of PAA (figure 3) the ratio  $K_3/K_1$  decreases significantly with temperature. A weak temperature dependence is found for the ratios  $K_3/\bar{K}$  and  $K_1/\bar{K}$ . As temperature increases the values of  $K_3/\bar{K}$  decrease whereas  $K_1/\bar{K}$  increase. A similar trend is found for the MBBA (figure 4). In the case of 8OCB (figure 5) a similar but more pronounced variation of these ratios with temperature is observed. As physically expected near the nematic–smectic-A transition a pronounced increase in the ratio  $K_3/K_1$  and  $K_3/\bar{K}$  is found but the ratio  $K_1/\bar{K}$  shows a sudden decrease. Further, we have found that in the vicinity of the  $S_A$  phase the divergence in  $K_3$  is more dominant than that of  $K_2$ .

Table 1 shows the variation of elastic constant ratios with length–width ratio near the nematic–isotropic transition temperature. It can be seen that with  $x_0$  the ratios  $K_3/K_1$  and  $K_3/\bar{K}$  increase whereas  $K_1/\bar{K}$  and  $K_2/\bar{K}$  decrease.

#### 4. Summary and conclusions

Using a molecular theory as developed by us [1] for the elastic free-energy of molecular ordered phases, we have calculated the elastic constants of uniaxial nematic liquid crystal composed of molecules of cylindrical symmetry. This theory is based on the weighted density functional formalism [4] and writes exact relations for the elastic constants in terms of the order parameters



**Figure 5.** Comparison between the calculated (full curves) and experimental [10] values of elastic constants ratios for 8OCB as a function of temperature. The experimental ratios are shown as  $K_3/K_1$ :  $\Delta$ ;  $K_3/\bar{K}$ : \* and  $K_1/\bar{K}$ :  $\circ$ .

**Table 1.** Ratio of elastic constants of nematic liquid crystals near the nematic–isotropic transition temperature  $T_{NI}$ .

$x_0$	$K_3/K_1$	$K_3/\bar{K}$	$K_1/\bar{K}$	$K_2/\bar{K}$
2.68	1.211	1.276	1.053	0.747
2.87	1.458	1.34	0.919	0.739
4.88	1.542	1.409	0.917	0.682

characterizing the nature and amount of ordering, and the structural parameters involving the harmonic coefficients of direct pair correlation function. No accurate information about the correlation functions for an inhomogeneous system is available. However, it can be found for an isotropic fluid either by solving the integral equation theories of the liquid state or by computer simulation. So the theory writes relations for the elastic constants in terms of the direct pair correlation functions of an effective isotropic liquid having density determined by the scheme of Denton and Ashcroft [4].

For evaluating the elastic constants we need in the theory, as input parameters, the values of order parameters,  $\bar{P}_2$  and  $\bar{P}_4$ , as a function of temperature,  $C$ -harmonic coefficients,  $C_{l_1 l_2 l}$ , as a function of density and length–width ratio and the molecular parameters. In the calculation we use the value of  $\bar{P}_2$  as obtained from experiments and estimate  $\bar{P}_4$  as  $\bar{P}_4/\bar{P}_2 = \bar{P}_2^2$ . The length–width ratio of a molecule has been estimated from its structure as determined by experiments. The  $C$ -harmonic coefficients have been determined by solving the PY closure relation.

The influence of repulsive interaction described by hard ellipsoids of revolution (HER) and attractive (dispersion and quadrupole) interactions on the elastic constants of three nematics,

PAA, MBBA and 8OCB has been investigated. The calculated values have been compared with experimental and simulation data and a reasonable agreement has been found.

The values of elastic constants ratios for the HER system are higher than the experimental values but are consistent with the MD simulation of Allen and Frenkel [36]. Further, we have found that inclusion of dispersion and quadrupole interactions in the pair potential reduces the values of elastic constant ratios. The temperature dependences of the elastic constants and its ratios have been investigated. It is observed that the calculated values are in reasonable agreement with the experimental data. We have seen that these values are sensitive to the values of the input parameters. So, as more accurate values of these parameters become available, more accurate values for the elastic constants will result from the theory.

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