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Elastic constants of uniaxial nematic liquid crystals: A comparison between theory and experiment

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Elastic constants of uniaxial nematic liquid crystals: a comparison between theory and experiment

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Using the unified molecular theory developed in our earlier paper (1992, *Phys. Rev.* A, **45**, 974) we study in detail the influence of molecular interactions on the fundamental elastic properties of uniaxial nematic liquid crystals composed of molecules of cylindrical symmetry. The expressions for the elastic moduli associated with 'splay', 'twist' and 'bend' modes of deformations are written in terms of order parameters characterizing the nature and amount of ordering in the phase and the structural parameters which involve the generalized spherical harmonic coefficients of the direct pair correlation function of an effective isotropic liquid. Numerical calculations are done for a model system, the molecules of which have prolate ellipsoid of revolution symmetry and interact via a pair potential having both repulsive and attractive parts. The repulsive interaction is represented by a repulsion between hard ellipsoids of revolution. The attractive potential is represented by the dispersion and electrostatic interactions. Results for the elastic constants are reported for a range of molecular length–width ratio, temperature, density and molecular parameters and are compared with the experimental values of *p*-azoxyanisole (PAA) and 4′-*n*-octyloxy-4-cyanobiphenyl (8OCB). It is found that the inclusion of electrostatic interactions reduces the values of the ratios K_2/K_1 and K_3/K_1. The absolute values of the elastic constants and their ratios are in good agreement with the experimental and computer simulation values. The temperature dependence of the elastic constants and their ratios is studied. It is observed that the twist elastic constant has a weak temperature dependence but a pronounced influence is observed on the bend moduli. We also observed a pronounced increase in the values of the twist and bend elastic constants on approaching the nematic–smectic A transition temperature.

1. Introduction

Using weighted density functional formalism [1], in a previous paper [2] (hereafter referred to as I and SSR theory), we developed a unified molecular theory to derive an expression for the distortion free-energy of ordered phases in molecular systems in terms of the order parameters characterizing the phase structure and the molecular correlation functions of an effective isotropic liquid. This theory can be used to study the elastic constants of molecular ordered phases (liquid crystals, plastic crystals and crystalline solids). The theory was applied [2, 3] to derive expressions for the elastic constants of uniaxial phases (uniaxial nematic, N_u, and smectic A, S_A) and the nematic biaxial phase (orthorhombic nematic, N_b) of liquid crystals. The purpose of the present paper is twofold: we study in detail the influence of the molecular interactions, temperature, density, etc., on the elastic constants of uniaxial nematic liquid crystals composed of molecules of cylindrical symmetry and compare the numerical results with the experimental data of *p*-azoxyanisole (PAA) and 4′-*n*-octyloxy-4-cyanobiphenyl (8OCB).

On the basis of symmetry arguments the elastic continuum theory [4, 5] (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 distortion modes. The distortion free-energy can be written as

$$\Delta A_e = \frac{1}{2}\int d\mathbf{r}\,[K_1(\nabla\cdot\hat{\mathbf{n}})^2 + K_2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2] \qquad (1)$$

where $\hat{\mathbf{n}}(\mathbf{r})$ is the director at the point $\mathbf{r}$ and the subscript e stands for the distortion. It is difficult to measure experimentally the absolute values of these elastic constants [6–9]. It is the ratios K_2/K_1 and K_3/K_1 which can be measured more accurately. These moduli are temperature and density dependent. The dependence on the density is pronounced. A number of measurements are reported [9–11] 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.

This paper is organized as follows. Assuming that the readers are familiar with the density functional formalism [1] and the details of the SSR theory [2] we summarize in the following section a brief account of the theory and the working equations. Section 3 is devoted to the numerical calculations and gives a detailed description (variation with temperature, density and molecular parameters) of the elastic constants. The paper ends with §4, the summary and conclusions.

2. Brief outline of SSR theory and working equations

Elasticity is concerned with the behaviour of the Helmholtz free-energy $A[\rho(\mathbf{x})]$ with respect to a small deformation of the system away from its equilibrium state. The square bracket indicates that A is a function of the single-particle density distribution $\rho(\mathbf{x})$ where $\mathbf{x}(\equiv \mathbf{r}, \mathbf{\Omega})$ specify both the position and orientation of a molecule. Adopting the procedure as outlined in the I and elsewhere [1] we express the elastic free-energy as [2]

$$\beta \Delta A_{\mathrm{e}}[\rho] = -\frac{1}{2} \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2 \, [\rho_{\mathrm{e}}(\mathbf{x}_1)\rho_{\mathrm{e}}(\mathbf{x}_2) - \rho_{\mathrm{o}}(\mathbf{x}_1)\rho_{\mathrm{o}}(\mathbf{x}_2)] \, C^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \rho_f) \tag{2}$$

where $\rho_{\mathrm{e}}(\mathbf{x}_i)$ and $\rho_{\mathrm{o}}(\mathbf{x}_i)$ represent, respectively, the singlet distribution functions corresponding to the deformed and undeformed phases. In an approach [12] as followed by us [2], ρ_f is replaced by a weighted density, $\bar{\rho}[\rho]$, of the reference fluid. Here $\bar{\rho}[\rho]$ is viewed as a function of $\rho(x)$.

Assuming that molecule 1 is at the origin with a principal director $\hat{\mathbf{n}}(r_1)$ pointing in the direction of the space-fixed (SF) Z axis and molecule 2 is at a distance r_{12} from the origin where $\hat{\mathbf{n}}(r_2)$ represents the direction of the local principal director (see figure 1 in [2]) and using the rotational properties of generalized spherical harmonics [13], the SSR theory gives [2]

$$\begin{aligned} \frac{\beta \Delta A_{\mathrm{e}}[\rho]}{V} = -\frac{1}{2}\rho_0^2 \sum_{l_1, l_2, l} \; \sum_{m_1, m_2, m, m'} \; \sum_{n_1, n_2} \sum_{\mathbf{G}} & \times [(2l_1+1)(2l_2+1)]^{-1} C_{\mathrm{g}}(l_1 l_2 l, m_1 m m') \\ & \times Q_{l_1 m_1 n_1}(\mathbf{G}) Q_{l_2 m_2 n_2}(-\mathbf{G}) \int \mathrm{d}\mathbf{r}_{12} \\ & \times [\exp(\mathrm{i}\mathbf{G}_{\mathrm{e}} \cdot \mathbf{r}_{12}) D^{l_2}_{m m_2}(\Delta\chi(\mathbf{r}_{12})) \\ & - \exp(\mathrm{i}\mathbf{G} \cdot \mathbf{r}_{12})] Y^*_{lm'}(\hat{\mathbf{r}}_{12}) \\ & \times C(l_1 l_2 l; n_1 n_2; r_{12}). \end{aligned} \tag{3}$$

This equation is the basic equation for the distortion free-energy density of molecular ordered phases (liquid crystals, plastic crystals and crystalline solids). 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. $D^l_{mn}(\mathbf{\Omega})$ are the generalized spherical harmonics, $\mathbf{G}$ is the reciprocal lattice vector of the crystalline structure that might be present in the ordered phase and $C_{\mathrm{g}}(l_1 l_2 l, m_1 m m')$ are 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 $C(l_1 l_2 l; \mathrm{n}_1 \mathrm{n}_2; \mathrm{r}_{12})$ are the harmonic expansion coefficients of the direct pair correlation function (DPCF) of an isotropic liquid in terms of generalized spherical harmonics. The order parameters, $Q_{lmn}(\mathbf{G})$, which measure the nature and amount of ordering, are defined as

$$Q_{lmn}(\mathbf{G}) = \frac{2l+1}{N} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{\Omega} \, \rho(\mathbf{r}, \mathbf{\Omega}) \exp[\mathrm{i}\mathbf{G} \cdot \mathbf{r}] D^{l*}_{mn})(\mathbf{\Omega}). \tag{4}$$

Since no positional correlation exists in a nematic liquid crystal, equation (4) reduces to

$$Q_{lmn}(0) = (2l+1) \int \mathrm{d}\mathbf{\Omega} \, \mathrm{f}(\mathbf{\Omega}) D^{l*}_{mn}(\mathbf{\Omega}) \tag{5}$$

where $\mathrm{f}(\mathbf{\Omega})$ is the orientational singlet distribution function normalized to unity

$$\int \mathrm{d}\mathbf{\Omega} \, \mathrm{f}(\mathbf{\Omega}) = 1. \tag{6}$$

Exploiting the molecular and phase symmetries we obtain for a uniaxial nematic phase of axially symmetric molecules,

$$\begin{aligned} \frac{1}{V}\beta \Delta A_{\mathrm{e}}[\rho] = -\frac{1}{2}\rho_{\mathrm{n}}^2 \sum_{l_1, l_2, l}' \sum_m \left[\frac{(2l_1+1)(2l_2+1)}{(4\pi)^2}\right]^{1/2} \bar{P}_{l_1} \bar{P}_{l_2} & \\ \times C_{\mathrm{g}}(l_1 l_2 l, 0mm \int \mathrm{d}\mathbf{r} \, C_{l_1 l_2 l}(r) & \\ \times \left\{\left(\frac{4\pi}{2l_2+1}\right)^{1/2} Y_{l_2 m}(\Delta\chi(\mathbf{r})) - 1\right\} Y^*_{lm'}(\hat{\mathbf{r}}) & \end{aligned} \tag{7}$$

where ρ_{n} is the nematic number density and $\bar{P}_l$ are the Legendre polynomial order parameters. The subscript 12 has been dropped. The prime on the summation indicates that l_1 and l_2 are even.

Confining the variation of $\hat{\mathbf{n}}(\mathbf{r}_2)$ in a plane $Y_{l_2 m}(\Delta\chi(\mathbf{r}))$ is expressed [2] in terms of the distortion angle which is assumed to be small. Performing the integration over $\hat{\mathbf{r}}$ and comparing equation (7) with equation (1), we get the expression for the Frank elastic constants. The result can be written as an expansion series

$$\beta K_i = \sum_{l_1, l_2}' \beta K_i(l_1, l_2) \tag{8}$$

where $i = 1$, 2 and 3 stand for the splay, twist and bend elastic constants, respectively. The terms of series (8) were evaluated in the I [2] for $2 \leqslant l_1, l_2 \leqslant 8$. We write the explicit expressions for the first few terms of the series as

$$\beta K_1(2,2) = \left(\frac{5}{4\pi}\right)^{1/2} \rho_n^2 \bar{P}_2^2 \left[\frac{1}{2} J_{220} - \frac{1}{(14)^{1/2}} J_{222}\right], \quad (9\,a)$$

$$\beta K_1(2,4) = -\frac{3}{4}\left(\frac{5}{(14\pi)^{1/2}}\right) \rho_n^2 \bar{P}_2 \bar{P}_4 J_{242}, \quad (9\,b)$$

$$\beta K_1(4,4) = \left(\frac{5}{4\pi}\right)^{1/2} \rho_n^2 \bar{P}_4^2 \left[(5)^{1/2} J_{440} - \frac{13}{2(77)^{1/2}} J_{442}\right], \quad (9\,c)$$

$$\beta K_2(2,2) = \left(\frac{5}{4\pi}\right)^{1/2} \rho_n^2 \bar{P}_2^2 \left[\frac{1}{2} J_{220} + \left(\frac{2}{7}\right)^{1/2} J_{222}\right], \quad (10\,a)$$

$$\beta K_2(2,4) = \frac{1}{3} \beta K_1(2,4), \quad (10\,b)$$

$$\beta K_2(4,4) = \left(\frac{5}{4\pi}\right)^{1/2} \rho_n^2 \bar{P}_4^2 \left[(5)^{1/2} J_{440} + \frac{47}{2(77)^{1/2}} J_{443}\right], \quad (10\,c)$$

$$\beta K_3(2,2) = \beta K_1(2,2), \quad (11\,a)$$

$$\beta K_3(2,4) = -\frac{4}{3} \beta K_1(2,4), \quad (11\,b)$$

and

$$\beta K_3(4,4) = \left(\frac{5}{4\pi}\right)^{1/2} \rho_n^2 \bar{P}_4^2 \left[(5)^{1/2} J_{440} + \frac{17}{(77)^{1/2}} J_{442}\right]. \quad (11\,c)$$

In these expressions $J_{l_1 l_2 l}$ is defined as

$$J_{l_1 l_2 l} = \int r^4 \, \mathrm{d}r \, C_{l_1 l_2 l}(r) \quad (12)$$

and are called the structural parameters.

3. Calculations and results

We consider a model system of molecules having prolate ellipsoidal symmetry and interacting via a pair potential

$$u(\mathbf{r}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) = (u^{\mathrm{HER}} + u^{\mathrm{dd}} + u^{\mathrm{dq}} + u^{\mathrm{qq}} + u^{\mathrm{dis}})(\mathbf{r}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \quad (13)$$

where u^{HER} represents the repulsion between hard ellipsoids of revolution (HER) parametrized by the length-to-width ratio $x = a/b$ ($2a$ and $2b$ denote, respectively, the length of the major and minor axes of the ellipsoids). The terms with superscripts dd, dq, qq and dis indicate, respectively, the interactions arising due to the dipole–dipole, dipole–quadrupole, quadrupole–quadrupole and dispersion forces. The explicit forms of these interactions are given in I [2].

It is obvious from equations (8)–(12) that the structural parameters $J_{l_1 l_2 l}$ (equation (12)), the density and the order parameters $\bar{P}_2, \bar{P}_4, \ldots$, are the input parameters in the calculation of the elastic constants. As shown in I since the structure of the isotropic liquid is primarily controlled by a harsh repulsive interaction, a first order perturbation theory can be used [2, 14, 15] to evaluate the direct pair correlation function (DPCF) of the system. The spherical harmonic coefficients of the DPCF can be obtained [16] by solving the Ornstein–Zernike (OZ) equation using the Percus–Yevick (PY) closure relation. As this evaluation is a difficult calculation, only a finite number of the spherical harmonic coefficients for any orientation dependent function can be handled. It has been found [2, 17] that for the interaction potential described by equation (13) the inclusion of all the harmonics up to indices $l_1, l_2 = 4$ makes the series fully convergent. As C-harmonic coefficients contribute to the free-energy of uniaxial liquid crystals composed of molecules of axial symmetry having even l_1, l_2 indices, all the numerical results obtained are for the 14 harmonics (values of $l_1 l_2 l$: 000, 200, 220, 221, 222, 400, 420, 440, 421, 422, 441, 442, 443 and 444).

The PY closure relation has been solved by Ram and Singh [17] for the g^{HER}, h^{HER} and C^{HER} harmonics for $x = 3{\cdot}0$, $3{\cdot}25$, $3{\cdot}5$ and $4{\cdot}0$. Taking their results we have evaluated in I [2] C-harmonics for quadrupolar and dispersion interactions for $x = 3{\cdot}0$. We evaluate here these harmonics for $x = 3{\cdot}25$, $3{\cdot}5$ and $4{\cdot}0$. With known C-harmonics the values of the structural parameters are calculated as a function of reduced density ρ_n^* $(= \rho_n d_0^3)$ where d_0 is the molecular diameter. For the electrostatic (dd, dq, qq) interactions the nonvanishing potential harmonic coefficients in the Body-fixed (BF) frame are; u_{110}^{dd}, u_{111}^{dd}, u_{120}^{dq}, u_{121}^{dq}, u_{220}^{qq}, u_{221}^{qq} and u_{222}^{qq}. In the case of the repulsive and dispersion interactions all the 14 u-harmonic coefficients are nonvanishing. From the fact that the BF C-harmonic coefficients with only even l_1 and l_2 indices contribute to the free-energy of a uniaxial mesophase of axial molecules and that the BF C^{HER}-harmonic coefficients only survive for the even values of l_1 and l_2, it is concluded that only those of l_1 and l_2 will contribute to the free-energy which have nonvanishing u-harmonics for the even values of l_1 and l_2. For these reasons it was concluded [2] that the dd and dq interactions do not contribute to the free-energy and hence to the elastic constants.

For the numerical calculation of the elastic constants we need to know the values of the order parameters $\bar{P}_2, \bar{P}_4, \ldots$, as a function of temperature and density, the

Table 1. Contributions of individual interaction terms in the series (14) to each elastic constant. The results shown correspond to $x = 3{\cdot}0$, $\eta = 0{\cdot}495$, $\bar{P}_2 = 0{\cdot}5541$, $\bar{P}_4 = 0{\cdot}2294$ and $x = 4{\cdot}0$, $\eta = 0{\cdot}436$, $\bar{P}_2 = 0{\cdot}60755$, $\bar{P}_4 = 0{\cdot}2834$. $T^*(=KT/\varepsilon_0) = 1{\cdot}0$ and $\Theta^{*2}(=\Theta^2/\varepsilon_0 d_0^5) = 10.0$. $K_i^* = d_0 \varepsilon_0^{-1} K_i$.

x	(l_1, l_2)	$K_1^{*\mathrm{HER}}$	$K_2^{*\mathrm{HER}}$	$K_3^{*\mathrm{HER}}$	$K_1^{*\mathrm{dis}}$	$K_2^{*\mathrm{dis}}$	$K_3^{*\mathrm{dis}}$	$K_1^{*\mathrm{qq}}$	$K_2^{*\mathrm{qq}}$	$K_3^{*\mathrm{qq}}$	$\frac{K_3^{\mathrm{HER}}}{K_1^{\mathrm{HER}}}$	$\frac{K_2^{\mathrm{HER}}}{K_1^{\mathrm{HER}}}$	$\frac{K_3}{K_1}$	$\frac{K_2}{K_1}$
3·0	(2, 2)	0·962440	0·589532	0·962440	0·124643	0·186754	0·124643	0·126645	0·090742	0·126645				
	(2, 4)	−0·248124	−0·082708	0·330832	−0·016975	−0·005658	0·022634	0·037734	0·012578	−0·050312				
	(4, 4)	0·062446	0·014284	0·079338	0·021610	0·030323	0·018560	−0·091215	−0·143797	−0·072810				
	K_i^*	0·528638	0·438400	1·703442	0·112303	0·205761	0·188474	0·110898	−0·027900	−0·046788	3·222	0·829	2·453	0·819
4·0	(2, 2)	0·957396	0·581090	0·957396	0·133543	0·131875	0·133543	0·397650	0·020197	0·397650				
	(2, 4)	−0·270873	−0·090291	0·361164	−0·005728	−0·001909	0·007638	−0·006352	−0·002117	0·008470				
	(4, 4)	0·120689	0·031527	0·151895	0·046220	0·045180	0·046580	−0·338175	−0·362253	−0·329775				
	K_i^*	0·536339	0·432035	1·831619	0·168307	0·173237	0·195399	0·046770	−0·346282	0·084810	3·415	0·805	2·810	0·344

structural parameters as a function of x and density, and the values of the potential parameters ε_0/k, d_0 and quadrupole moment Θ. Here ε_0 is a constant with unit of energy. While reasonably accurate values of $\bar{P}_2$ from experimental data are available for a number of systems over a range of temperatures, our knowledge of $\bar{P}_4$ is scant. No reliable values are available for the other parameters.

We evaluate the contributions of the individual terms of the series

$$K_i = K_i(2,2) + 2K_i(2,4) + K_i(4,4) \qquad (14)$$

for the repulsive (HER), dispersion and quadrupole interactions for the different values of x ($=3{\cdot}0$, $3{\cdot}25$, $3{\cdot}5$ and $4{\cdot}0$). In table 1 these contributions are given for $x = 3{\cdot}0$ and $4{\cdot}0$. A number of observations can be made from this table. The series (14) is found to converge rapidly for prolate molecules interacting via the interaction potential (13). For a given x, as already known, we find $K_1^{\rm HER}(2,2) = K_3^{\rm HER}(2,2) > K_2^{\rm HER}(2,2)$. $K_1^{\rm HER} \neq K_3^{\rm HER}$ is primarily due to the contribution of $2K_i^{\rm HER}(2,4)$. In particular, $K_3^{\rm HER}(2,4)$ is positive whereas both $K_1^{\rm HER}(2,4)$ and $K_2^{\rm HER}(2,4)$ are negative. As a result we find that $K_3^{\rm HER} > K_1^{\rm HER} > K_2^{\rm HER}$, which is in good agreement with other studies [18, 19]. Further, the ratio $(K_3^{\rm HER}/K_1^{\rm HER}) > (K_2^{\rm HER}/K_1^{\rm HER})$, which is in accordance with the simulation work [19]. As the values of x increases, the contributions of $K_1^{\rm HER}$ and $K_3^{\rm HER}$ increase but $K_2^{\rm HER}$ decreases. The ratio $K_3^{\rm HER}/K_1^{\rm HER}$ increases whereas the ratio $K_2^{\rm HER}/K_1^{\rm HER}$ decreases. Although the absolute values of $K_i^{\rm HER}$ increase linearly with temperature, the values of their ratios do not change with temperature.

For the dispersion interaction we find that $K_2^{*\rm dis} > K_3^{*\rm dis} > K_1^{*\rm dis}$ for $x = 3{\cdot}0$ but the difference in the values of these constants decreases as x increases, and for $x = 4{\cdot}0$ their values become almost equal. Here $K_i^*(=d_0\varepsilon_0^{-1}K_i)$ is the reduced elastic constant. Both $K_1^{*\rm dis}$ and $K_3^{*\rm dis}$ increase with x whereas $K_2^{*\rm dis}$ decreases as x increases. In the case of the quadrupole interaction, we observe that for a given x and quadrupole moment the contribution of $K_i^{*\rm qq}(4,4)$ is much smaller as compared to $K_i^{*\rm qq}(2,2)$. As the value of the quadrupole moment increases the contributions of each individual term of the series (14) increases significantly, and also in the case of $K_i^{*\rm qq}$. The numerical values of both the elastic constants $K_1^{*\rm qq}$ and $K_3^{*\rm qq}$ are positive whereas the value of $K_2^{*\rm qq}$ is negative. For $x = 3{\cdot}0$ the value of $K_3^{*\rm qq}$ is slightly smaller than $K_1^{*\rm qq}$, but the trend is reversed in case of $x = 4{\cdot}0$. With the increase of x it is observed that the contributions of each term of the series to the elastic constant decrease.

In table 2 we list the relative contributions of the HER, dispersion and quadrupole interactions to the elastic constants for $x = 3$ at 400 K and $x = 4{\cdot}0$ at 350 K. We also give the values of the ratios K_3/K_1 and K_2/K_1 and compare the results with the experimental data of *p*-azoxyanisole (PAA) and 4′-*n*-octyloxy-4-cyanobiphenyl (8OCB). For the calculations we have used the following values of the parameters:

(i) for $x = 3{\cdot}0$, $\rho_n^* = 0{\cdot}3151$, $\bar{P}_2 = 0{\cdot}5541$, $\bar{P}_4 = 0{\cdot}2294$, $\varepsilon_0/k = 575$ K, $d_0 = 5$ Å, $\Theta = -20 \times 10^{-26}$ esu, and
(ii) for $x = 4{\cdot}0$, $\rho_n^* = 0{\cdot}2082$, $\bar{P}_2 = 0{\cdot}6075$, $\bar{P}_4 = 0{\cdot}2834$, $\varepsilon_0/k = 600$ K, $d_0 = 5{\cdot}5$ Å and $\Theta = -25 \times 10^{-26}$ esu.

These values of ρ_n^*, $\bar{P}_2$ and $\bar{P}_4$ correspond to the isotropic–nematic transition in a hard core system [17]. Other parameters for $x = 3$ and 4 crudely simulate, respectively, the nematic phases of PAA and 8OCB. Taking the values of $\varepsilon_0/k = 525$ K and $d_0 = 5{\cdot}36$ Å Tsykalo and Bagmet [21] found in their molecular dynamics (MD) study good quantitative agreement for the temperature dependence of the order parameter between the calculated and experimental data of PAA. The value of ε_0/k for PAA was estimated by Singh and Singh [14, 22] on the assumption that the liquid (crystal)–solid transition temperature at the triple point obeys a simple scaling law, $T_t^*(=kT_t/\varepsilon_0) = c'$, where c' is a constant independent of x. Taking $c' = 0{\cdot}68$ (reduced triple point temperature for the Lennard–Jones (12-6) system) they found that $\varepsilon_0/k = 575$ K. This is a fairly reasonable value because it gives the energy of interaction in the minimum energy configuration of two PAA molecules equal to $8{\cdot}37$ kJ mol^{-1} which is in good agreement with the values obtained from an approximate quantum mechanical calculation [23].

In the calculation we observe that the absolute values of the elastic constants are sensitive to the values of the molecular parameters. However, we have made no attempt here (see table 2) to fit the experimental data by adjusting these parameters. We prefer to show the relative contributions of the different branches of interaction. Further, we note that it is difficult to measure the absolute values of the elastic constants [6–9]. It is the ratios K_3/K_1 and K_2/K_1 which are measured with the greatest accuracy. From the MD simulation for a HER system of $x = 3$ at $\rho_n^* = 0{\cdot}354$, Allen and Frankel [19] found that $K_2^{\rm (HER)}/K_1^{\rm (HER)} = 0{\cdot}929$ and $K_3^{\rm (HER)}/K_1^{\rm (HER)} = 3{\cdot}414$, whereas the values obtained by us here for $\rho_n^* = 0{\cdot}315$ are $0{\cdot}829$ and $3{\cdot}222$, respectively. Our results for the HER system are in good agreement with that of the Allen and Frankel [19] results. We find that at each x the ratios $K_2^{\rm (HER)}/K_1^{\rm (HER)}$ and $K_3^{\rm (HER)}/K_1^{\rm (HER)}$ are higher than the experimental values. Further, it can be seen from table 2 that the inclusion of dispersion and quadrupole interactions reduces the values of K_2/K_1 and K_3/K_1. This trend is in accordance with experimental results. In both the cases for $x = 3$

Table 2. Contributions of the different interaction terms to each elastic constant and a comparison with the experimental values. The values of K_i are given in units of 10^{-7} dyne.

		Calculated values				Experimental values	
						PAA	
x	i	K_i^{HER}	K_i^{dis}	K_i^{qq}	K_i	(Ref. [20])	(Ref. [6])
3·0	1	5·8361	1·7822	2·3538	9·9721	7·00	6·66
	2	4·8399	3·2653	−0·0708	8·0344	4·30	3·37
	3	18·8058	2·9909	1·5810	23·3777	17·00	11·25
	K_2/K_1	0·829			0·805	0·614	0·506
	K_3/K_1	3·222			2·344	2·428	1·689
						8OCB (Ref. [10])	
4·0	1	4·7100	2·5338	0·8034	8·0472	3·10	
	2	3·7940	2·6078	−0·0066	6·3952	2·13	
	3	16·0849	2·9416	0·8893	19·9158	3·60	
	K_2/K_1	0·805			0·794	0·687	
	K_3/K_1	3·415			2·475	1·161	

and 4, the theoretical values of these ratios are in good agreement with the experimental values.

3.1. *Variation of elastic constants with temperature*

The temperature dependences of the elastic constants are mainly due to the variation of the order parameters $\bar{P}_2$ and $\bar{P}_4$ with temperature. While accurate values of $\bar{P}_2$ are available for a number of systems over a range of temperature and density from experiment, our knowledge of $\bar{P}_4$ is scant. However, with a little reflection one finds that the values of the ratio $\bar{P}_4/\bar{P}_2$ should decrease with temperature and increase with density and the length-to-width ratio. Here we calculate the values of K_i using the experimental values of $\bar{P}_2$ for PAA and 8OCB. For PAA two sets of calculations are performed corresponding to $\bar{P}_4$ values as estimated from $\bar{P}_4=\bar{P}_2^2$ and $\bar{P}_4=\bar{P}_2^3$. Figure 1 shows the variation of $\bar{P}_2$ and $\bar{P}_4/\bar{P}_2$ $(=\bar{P}_2^2)$ with temperature for PAA. It can be seen that the approximated values of $\bar{P}_4/\bar{P}_2 \simeq \bar{P}_2^2$ are in good agreement with the experimental data [24] of deuteriated PAA, as obtained from coherent neutron scattering experiments. In the case of $\bar{P}_2$ we first put all the experimental data [25] of $\bar{P}_2$ on the curves and then draw a smooth curve. The values of $\bar{P}_2$ used in the calculation correspond to this smooth curve.

Figure 2 shows the contributions of the individual terms $K_i^*(l_1,l_2)$ and K_i^* for $x=3{\cdot}0$ as a function of temperature. We see that $K_1^* \neq K_3^*$ because of the contributions of the term involving $\bar{P}_4/\bar{P}_2$. The contribution of this term to K_i^* is positive for $i=3$ and negative for $i=1$ and 2. The contribution of the term involving $(\bar{P}_4/\bar{P}_2)$ is positive for $i=1$ and 3 and negative for $i=2$ and $|K_3^*(4,4)|>|K_1^*(4,4)|>|K_2^*(4,4)|$. The K_2^* term has a weak temperature dependence but a pronounced temperature influence is observed for K_3^*.

A comparison between the experimentally measured [6, 7] (for PAA) and theoretically calculated $(x=3)$ values of elastic constants are made in figure 3. Two sets of theoretical values, as obtained by estimating $\bar{P}_4/\bar{P}_2=\bar{P}_2$ and $\bar{P}_4/\bar{P}_2=\bar{P}_2^2$, are plotted. The contributions of HER interactions are also plotted in the figure. It can be observed that the calculated elastic constants are consistent with the experimental data [6–9]. These results show the important role of repulsive as well as attractive interactions. The theoretical values of K_i^* as obtained by using $\bar{P}_4/\bar{P}_2=\bar{P}_2^2$ are closer to the experimental data as compared to those obtained from $\bar{P}_4/\bar{P}_2 \simeq \bar{P}_2$.

The calculated values of the ratios $K_2^{(\mathrm{HER})}/K_1^{(\mathrm{HER})}$,

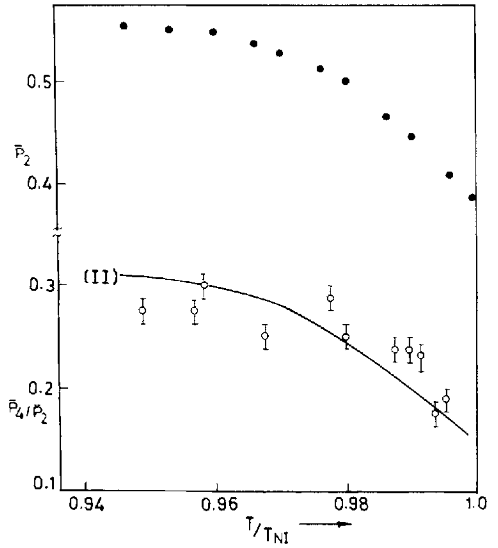

Figure 1. Values of order parameters $\bar{P}_2$ and $\bar{P}_4/\bar{P}_2$ as a function of temperature. (●) experimental $\bar{P}_2$ [25] (see text); (ɸ) experimental $\bar{P}_4/\bar{P}_2$ of deuteriated PAA [24]; full-line curve is estimated as $\bar{P}_4/\bar{P}_2 \simeq \bar{P}_2^2$.

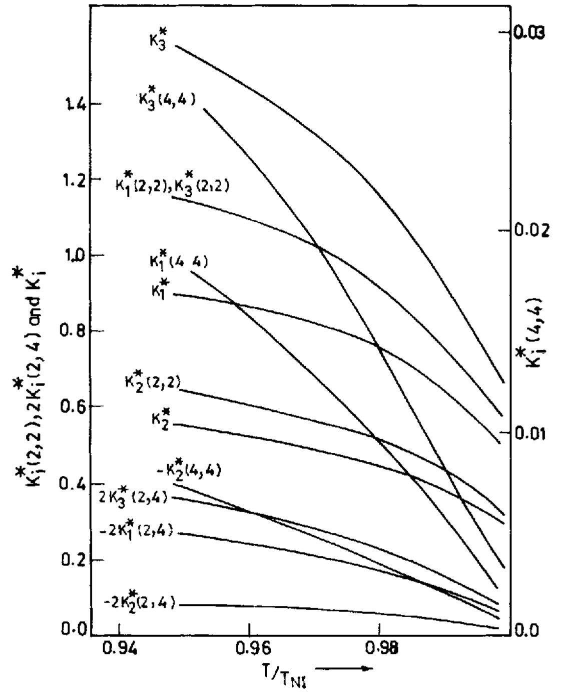

Figure 2. Contribution of individual terms of the $K_i^*(l_1, l_2)$ of the series (14) and K_i^* for $x = 3{\cdot}0$ as a function of temperature. The values plotted correspond to $\bar{P}_4/\bar{P}_2 \simeq \bar{P}_2^2$ and $K_i^* = d_0\varepsilon_0^{-1}K_i$.

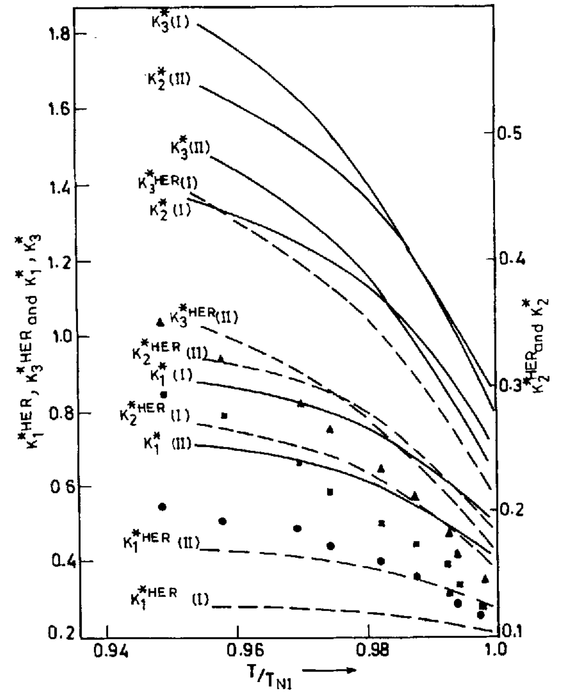

Figure 3. Comparison between the calculated and experimental [6, 7] values of the reduced elastic constants K_i^* for $x = 3{\cdot}0$. The calculated values shown as I and II correspond to $\bar{P}_4/\bar{P}_2 \simeq \bar{P}_2$ and $\bar{P}_4/\bar{P}_2 \simeq \bar{P}_2^2$, respectively.

$K_3^{(\mathrm{HER})}/K_1^{(\mathrm{HER})}$, K_2/K_1 and K_3/K_1 for $x = 3{\cdot}0$ are compared with the experimental data [6, 7] of PAA in figure 4. It can be seen that at all temperatures the inclusion of the attractive interactions decreases the ratios K_2/K_1 and K_3/K_1. The ratios K_2/K_1 and K_3/K_1 both decrease with increasing temperature. The ratio K_2/K_1 lies within 0·624–0·614 (for the first set) and 0·608–0·584 (for the second set) and is more or less independent of temperature. On the other hand, a significant decrease in the ratio K_3/K_1 with temperature is observed. A similar trend in the variation of ratios K_2/K_1 and K_3/K_1 with temperature has also been observed in other substances [7, 8, 26, 27].

In addition to the above ratios the other quantity which one can find fairly accurately from the experiments is $K_i/\bar{K}$ where $\bar{K} = (K_1 + K_2 + K_3)/3$. In figure 5, we plot this quantity for $x = 3$ as a function of temperature. We find that the values of the ratio $K_i/\bar{K}$ have a weak temperature dependence. The value of $K_3/\bar{K}$ decreases with temperature whereas the values of $K_1/\bar{K}$ and $K_2/\bar{K}$ increase with temperature. The calculated values of $K_i/\bar{K}$ (second set $\bar{P}_4 = \bar{P}_2^3$) are in good agreement with the experimental values [6–9]. We also find in the calculation that the values of $K_i/\bar{K}$ are only slightly affected by the values of x. While $K_3/\bar{K}$ increases with x, other ratios $K_2/\bar{K}$ and $K_1/\bar{K}$ decrease with x.

In order to compare the calculated values of the elastic

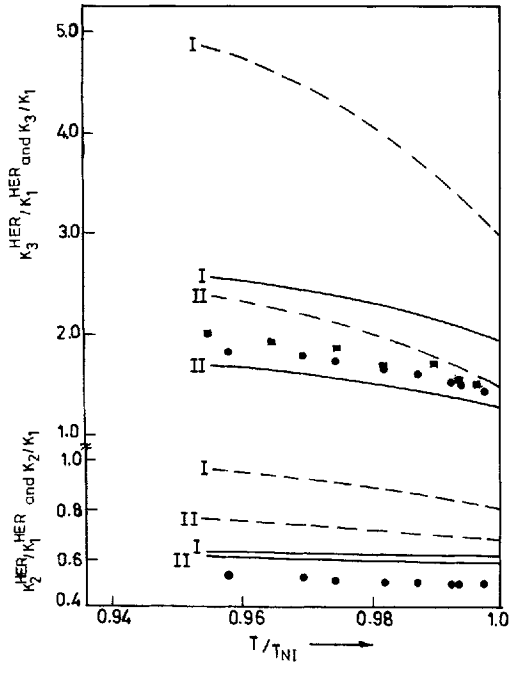

Figure 4. Comparison between the calculated and experimental values (●) [6] and (■) [7] of the ratio of elastic constants for PAA as a function of temperature. The symbols I and II have the same meanings as in figure 3. The HER contributions are shown by dashed lines.

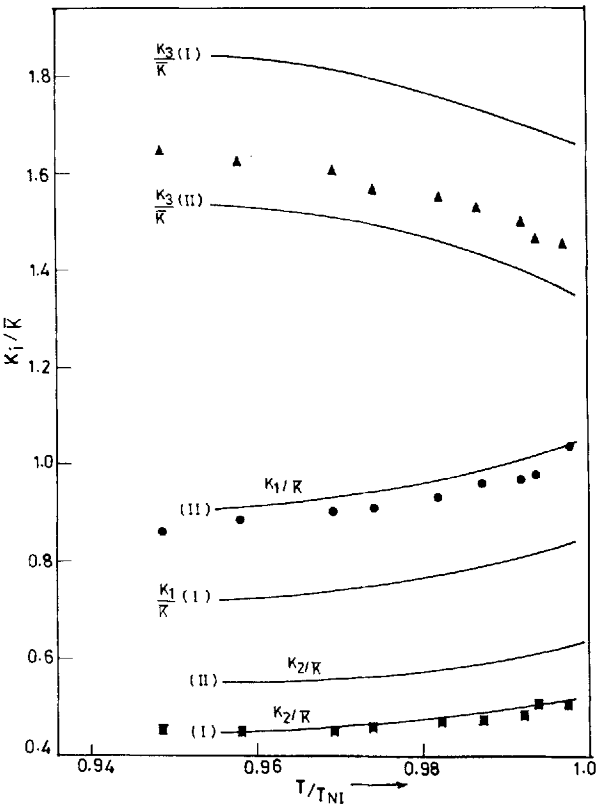

Figure 5. Comparison between the calculated and experimental [7] values of the ratio $K_i/\bar{K}$ for PAA as a function of temperature. The symbols I and II have the same meanings as in figure 3. (●), (■) and (△) represent, respectively, the experimental values of $K_1/\bar{K}$, $K_2/\bar{K}$ and $K_3/\bar{K}$. Here $\bar{K}=(K_1+K_2+K_3)/3$.

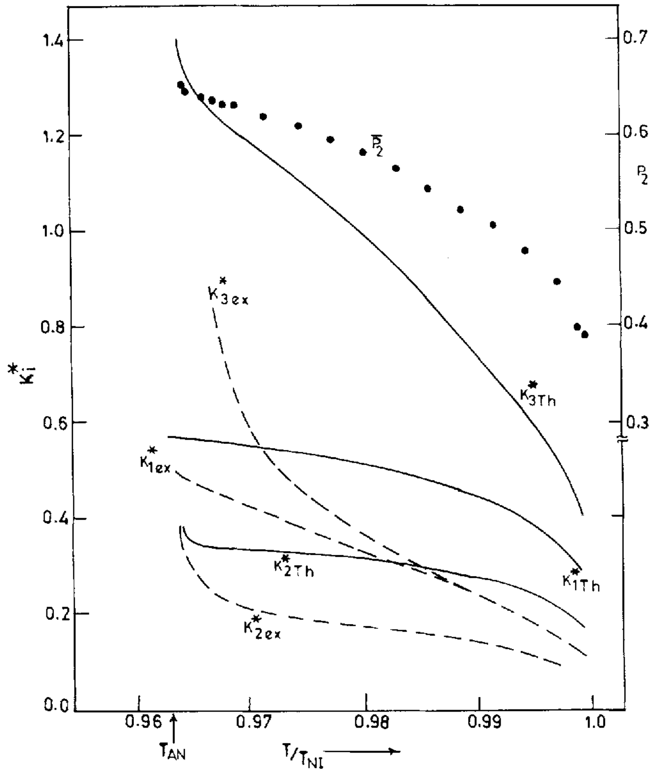

Figure 6. Comparison between the calculated and experimental [10] values of the reduced elastic constants for 8OCB as a function of temperature. (●) Represents the values [10] of $\bar{P}_2$ used in the calculation. The broken and full line represent, respectively, the experimental and calculated values of K_i^*.

constants for $x=4{\cdot}0$ with the experimental data [10] we perform a model calculation. Madhusudana and Pratibha [10] 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. For the calculation we estimate the fourth-Legendre order parameter as $\bar{P}_4=\bar{P}_2^3$. The calculated values of K_i are compared with the experimental values in figure 6. A comparison between the theoretical and experimental values of the ratios K_i/K_1 are made in figure 7. In view of the uncertainties in the experimental data it can be concluded that the theoretical results agree well with the experimental ones. The calculated values of K_3 and K_3/K_1 are large as compared to the experimental values. It can further be observed from these figures that as expected physically when we approach the nematic–smectic A transition a signature of pronounced increase in the values of K_2 and K_3 are clearly observed.

4. Summary and conclusions

A unified molecular theory as developed by us [2] for the elastic constants of ordered phases of molecular systems (liquid crystals, plastic crystals and crystalline solids) has been used to calculate the elastic constants of the uniaxial nematic phase composed of molecules of axial symmetry. This theory is based on the density functional formalism [1] and forms exact relations for the elastic constants in terms of the order parameters characterizing the nature and amount of ordering, and in terms of the correlation functions of an effective liquid. The density of the effective liquid is obtained by adopting the scheme of Denton and Ashcroft [12].

In our theory the values of the order parameters $(\bar{P}_2, \bar{P}_4, \ldots)$, the structural parameters $(J_{l_1 l_2 l})$ involving spherical harmonic coefficients $(C_{l_1 l_2 l}(r))$ of the DPCF of an effective fluid as a function of temperature and density, and the information about the constituent molecules, namely, electric multiple moments, length-to-width ratio, diameter, etc., are inputs for the evaluation of the elastic constants. The values of $\bar{P}_2$ obtained from the experimental observations have been used in the calculation. No reliable values are available for $\bar{P}_4$; the values estimated by us from $\bar{P}_4/\bar{P}_2 \simeq \bar{P}_2^2$ are close to the experimental values [24] for deuteriated PAA. While one can,

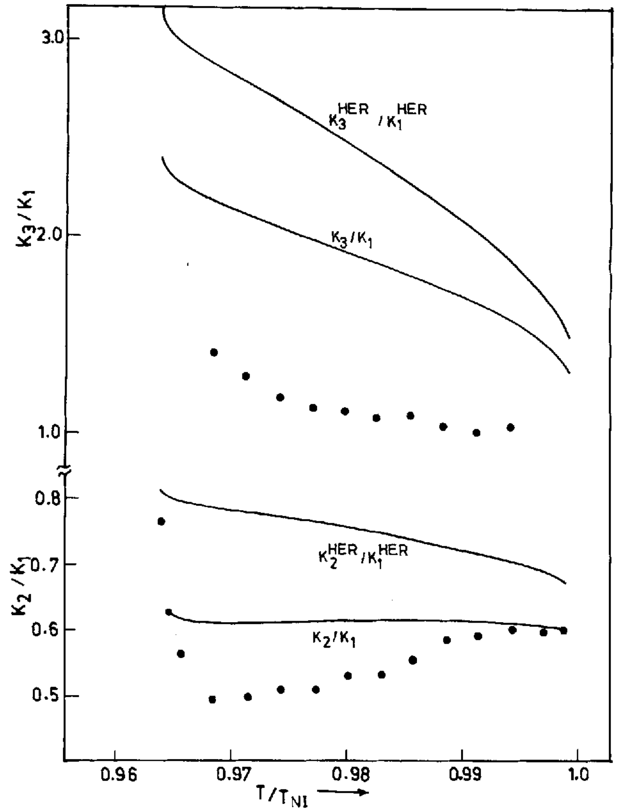

Figure 7. Comparison between the calculated and experimental [10] values of the ratio of the elastic constants for 8OCB as a function of temperature.

in principle, obtain from the quantum mechanical calculations the values of the potential parameters, at present, our knowledge of them is scant. In principle, the $C_{l_1 l_2 l}(r)$ harmonics for a given system can be obtained either by solving the Ornstein–Zernike (OZ) equation with suitable closure relations [13, 16] or by adopting a perturbation expansion method [14, 15]. These harmonic coefficients have been obtained by solving the OZ equation using the Percus–Yevick closure relation for a HER system [17] and using a perturbation method for a model system interacting via quadrupole and dispersion interactions in addition to hard-core repulsion.

In the calculation it has been found that the absolute values of the elastic constants are sensitive to the values of the molecular parameters. The values of the elastic constant ratios for the HER system are in good agreement with the simulation values [19]. The inclusion of dispersion and quadrupole interactions in the calculation reduces the values of the ratios K_3/K_1 and K_2/K_1. The variations of the elastic constants and of their ratios K_3/K_1 and K_2/K_1 with temperature have been studied. It is observed that the calculated values of the elastic constants and their ratios K_3/K_1, K_2/K_1, $K_3/\bar{K}$, $K_2/\bar{K}$ and $K_1/\bar{K}$ for $x = 3{\cdot}0$ are in good agreement with the experimental values of PAA. For $x = 4{\cdot}0$ the calculated values agree well with the experimental values for 8OCB. As discussed above, these values are sensitive to the values of the input parameters. As our knowledge of these input parameters improves, more accurate values for the elastic constants will be obtained.

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