## Elastic constants of discotic (nematic) liquid crystals: effect of packing

Kalyan Singh; N. S. Pandey

## PLEASE SCROLL DOWN FOR ARTICLE

# Elastic constants of discotic (nematic) liquid crystals: effect of packing

by KALYAN SINGH and N. S. PANDEY*†

Department of Physics and Electronics, Ram Manohar Lohia Avadh University,
Faizabad 224001, Uttar Pradesh, India

Using a previously developed theory of nematic liquid crystals (Singh, Y., and Singh, K., 1986, *Phys. Rev. A*, **33,** 3481) we present the calculation of elastic constants of discotic-nematic liquid crystals and study the variation of elastic constants with packing fraction. The expressions for 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 structural parameters. Numerical calculations are done for a model system, the molecules of which are hard oblate ellipsoids of revolution. It is observed that elastic constants are very sensitive to packing density and become larger with increase of shape anisotropy.

## 1. Introduction

The study of elastic constants of liquid crystals is important for a number of reasons. In the first place, they appear in the description of virtually all phenomena where the orientation of the director is manipulated by external fields (e.g. in display devices). Secondly they provide unusually sensitive probes of the microscopic structure of the orientationally ordered state. Since the discovery of liquid crystals consisting of disc-like molecules [1, 2] these substances have attracted considerable attention due to their potential importance in applications on the one hand, and the very interesting physics of the mesophases themselves on the other hand. Gasproux [3] gave a classification of all observed mesophases, including a number of columnar and nematic phases. In the present paper we restrict ourselves to the nematic phases of discotic liquid crystals.

The Frank elastic constants are a measure of free energy associated with long-wavelength distortion of the nematic state in which the local preferred direction of molecular orientation varies in space. If the local preferred direction at the point **r** is parallel to the direction $\hat{\mathbf{n}}(\mathbf{r})$ the free energy associated with distortion is written as [4]

$$F = \frac{1}{2} \int d\mathbf{r} [K_1 (\mathrm{V} \ \hat{\mathbf{n}})^2 + K_2 (\hat{\mathbf{n}} \ \mathrm{V} \times \hat{\mathbf{n}})^2 + K_3 (\hat{\mathbf{n}} \times \mathrm{V} \times \hat{\mathbf{n}})^2]$$

(1)

* Author for correspondence.
† Central Forensic Science Laboratory, Sector 36A, Chandigarh 160036, India.

where $K_1$, $K_2$ and $K_3$ are elastic constants known as splay, twist and bend, respectively. Thus they characterize the free energy increase associated with three normal modes of deformation of the oriented discotic-nematic phase. A representation of splay, twist and bend deformations of disc-like molecules is given in figure 1. Singh and Singh [5] have developed a density functional theory for nematic liquid crystals and reported their results at fixed packing fraction. The purpose of this paper is to present numerical results for a system composed of hard oblate ellipsoids of revolution (which crudely simulates a discotic-nematic phase) at various packing fractions. Oblate ellipsoids are parametrized by the length to width ratio $x_0 = 2a/2b$, where $2a$ and $2b$ are respectively lengths of the major and minor axes of the ellipsoids. A brief theory and working equations are given in §2 and results and discussion in §3.

## 2. Theory and working equations

We consider a system of nonspherical molecules of arbitrary symmetry in a volume $V$ at temperature $T$. When there are $N$ particles in the system, the configuration energy $U$ is approximated as

$$U(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \sum_{i=1}^{N} U^{\mathrm{e}}(\mathbf{x}_i) + \sum_{i>j=1}^{N} U(\mathbf{x}_i, \mathbf{x}_j) \quad (2)$$

where for economy of notation we use vector $\mathbf{x}_i$ to indicate both the location $\mathbf{r}_i$ of the centre of mass of the $i^{\mathrm{th}}$ molecule and its relative orientation $\Omega_i$ described by Euler's angles $(\psi, \phi, \xi)$. $U^{\mathrm{e}}(\mathbf{x}_i)$ is the potential energy of a molecule at position $\mathbf{r}_i$ due to external forces,

Splay (K1) for rod-like and disk-like molecules



Twist (K2) for rod-like and disc-like molecules



Bend (K3) for rod-like and disc-like molecules

Figure 1. Representation of splay, twist and bend in rod-like and disc-like molecules.

and $U(\mathbf{x}_i, \mathbf{x}_j)$ is the intermolecular pair potential for molecules $i$ and $j$.
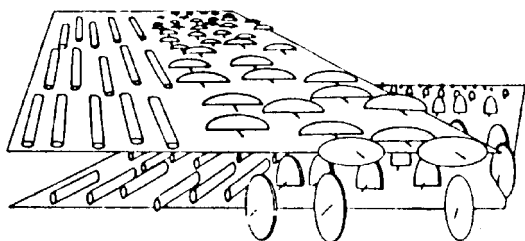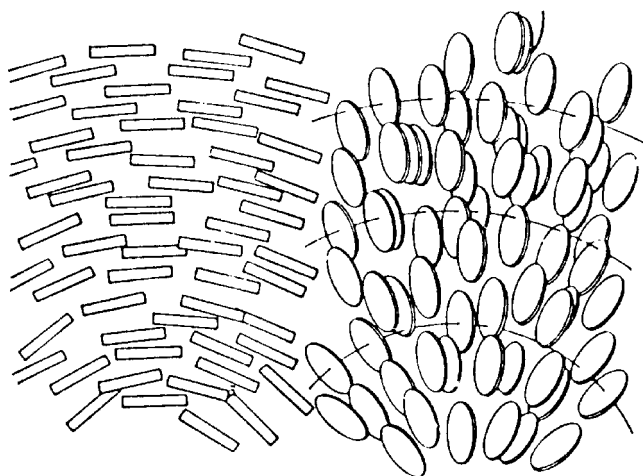
The Helmholtz free energy, $F$, of the system is

$$\beta F = \beta F_{id} + H \tag{3}$$

where $\beta F_{id}$ is the reduced Helmholtz free energy for the ideal gas, and function $H$ is used as a generating functional for the correlation functions and arises from intermolecular interactions. $H$ is also a functional of single particle density distribution $\rho(\mathbf{x})$ and pair potential $U$. A homogeneous discotic (nematic) phase is translationally invariant. Thus

$$\rho(\mathbf{x}) = \rho_0 f(\Omega) \tag{4}$$

where $\rho_0$ is the mean number density and $f(\Omega)$ the singlet orientational distribution function normalized to unity

$$\int f(\Omega)\, \mathrm{d}\Omega = 1, \tag{5}$$

$f(\Omega)$ is independent of position for a uniform nematic phase.

In a distorted discotic (nematic) the orientational distribution varies spatially in a complicated way. For our purpose it is sufficient to allow it to vary only to the extent that the director $\hat{\mathbf{n}}(\mathbf{r})$ does. In general, however, any deformation will cause the orientational distribution to be distorted in space from whatever form it had in the perfectly ordered nematic state. But the difference between $f(\hat{\mathbf{e}}\ \hat{\mathbf{n}}(\mathbf{r}))$ and the actual $f$ in the case of long wavelength distortions makes no contribution to the Frank elastic constants [6].

In order to derive molecular expressions for the $K_i$ values, we first choose an arbitrary point at $\mathbf{R} = 0$ in the deformed discotic state as the origin of a space fixed coordinate system. The $z$-axis of this system is taken as parallel to the director at origin, i.e. $\hat{\mathbf{z}} = \hat{\mathbf{n}}(R = 0)$. For pure splay, twist and bend deformations, the variation in $\hat{\mathbf{n}}(R)$ are always confined to a plane. If the $x$-axis is chosen such that $(x, z)$ is the plane containing $\hat{\mathbf{n}}(\mathbf{R})$,

$$\hat{\mathbf{n}}(R) = \hat{\mathbf{x}} \sin \chi_n(\mathbf{R}) + \hat{\mathbf{z}} \cos \chi_n(\mathbf{R}) \tag{6}$$

$\chi_n(R)$ is the angle between the director at $\mathbf{R}$ and the director at the origin and is given by [6]

$$\chi_n(R) = \begin{cases} qx - q^2xz + 0(q^3) & \text{for splay} \\ qy & \text{for twist} \\ qz + q^2xz + 0(q^3) & \text{for bend} \end{cases} \tag{7}$$

where $q$ is the wave number associated with any distortion. From equations (1) and (6) we get distortion free energy density around the origin (in terms of $K_1$, $K_2$, $K_3$) as

$$\Delta a(0) = \begin{cases} \dfrac{1}{2}K_1 q^2 + (0)q^4 & \text{splay} \\ \dfrac{1}{2}K_2 q^2 + (0)q^4 & \text{twist} \\ \dfrac{1}{2}K_3 q^2 + (0)q^4 & \text{bend} \end{cases} \tag{8}$$

and distortion free energy as

$$\Delta F = \int_V \Delta a(\mathbf{R}) \, d^3\mathbf{R}. \qquad (9)$$

Following Singh and Singh [5] $K_1$, $K_2$ and $K_3$ are given by

$$K_i = \sum K_i^{(n)} \qquad (10)$$

with

$$K_i^{(0)} = -2\rho_0^2 kT \int d\mathbf{r}_{12} r_{12}^2 \int d\Omega_1 \int d\Omega_2 f(\Omega_1, 0)$$

$$\times F_i(\hat{\mathbf{r}}_{12}, \Omega_1, \Omega_2) \mathbf{C}_2(\rho_0) \qquad (11\,a)$$

$$K_i^{(1)} = -2\rho_0^3 kT \int r_{12}^2 \, d\mathbf{r}_{12} \int d\Omega_1 \int d\Omega_2$$

$$\times [f(\Omega_1, 0) - 1] F_i(\hat{\mathbf{r}}_{12}, \Omega_1, \Omega_2)$$

$$\times \left[ \frac{\delta \mathbf{C}_2(\rho_0)}{\delta \rho_0} + \int d\mathbf{r}_3 \int d\Omega_3 [f(\Omega_3, 0) - 1] \mathbf{C}_3(\rho_0) \right] \qquad (11\,b)$$

$$K_i^{(2)} = -\rho_0^4 kT \int r_{12}^2 \, d\mathbf{r}_{12} \int d\mathbf{r}_3 \int d\Omega_1 \int d\Omega_2 \int d\Omega_3$$

$$\times [f(\Omega_1, 0) - 1][f(\Omega_3, 0) - 1)] \, F_i(\hat{\mathbf{r}}_{12}, \Omega_1, \Omega_2)$$

$$\times \frac{\delta \mathbf{C}_3(\rho_0)}{\delta \rho_0}. \qquad (11\,c)$$

Here

$$F_i(\hat{\mathbf{r}}_{12}, \Omega_1, \Omega_2) = f'(\Omega_2, 0) \begin{Bmatrix} -(\hat{\mathbf{r}}_{12} \ \hat{\mathbf{x}}) & (\hat{\mathbf{r}}_{12} \ \hat{\mathbf{z}}) \\ 0 & \\ (\hat{\mathbf{r}}_{12} \ \hat{\mathbf{x}}) & (\hat{\mathbf{r}}_{12} \ \hat{\mathbf{z}}) \end{Bmatrix}$$

$$+ \frac{1}{2} f''(\Omega_2, 0) \begin{Bmatrix} (\hat{\mathbf{r}}_{12} \ \hat{\mathbf{x}})^2 \\ (\hat{\mathbf{r}}_{12} \ \hat{\mathbf{y}})^2 \\ (\hat{\mathbf{r}}_{12} \ \hat{\mathbf{z}})^2 \end{Bmatrix} \qquad (12)$$

and $i$ stands for 1, 2 and 3. $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ are unit vectors along the space fixed coordinate axes $x$, $y$ and $z$ which are Cartesian components of $\mathbf{r}$. $f'(\Omega_2, 0)$ and $f''(\Omega_2, 0)$ are first and second order derivatives of $f(\Omega_2, \chi_n(r_{12}))$ with $\chi_n(r_{12}) = 0$ where $r_{12}$ is the intermolecular distance.

For a uniaxial nematic phase with a symmetry plane perpendicular to a director and composed of cylindrically symmetric molecules, the singlet orientational distribution $f(\Omega)$ depends only on the angle $\theta$ between the director and the molecular symmetry axis, where the director is

parallel to the space fixed $z$-axis, and we have

$$f(\Omega_1, 0) \equiv f(\cos \theta_1) = 1 + \sum_{L' \geqslant 2}{}' (2L' + 1)\mathbf{P}_{L'} P_{L'}(\cos \theta_1) \qquad (13)$$

where $\mathbf{P}_L = 1/2 \int_0^\pi f(\Omega_1, 0) \ P_L(\cos \theta_1) \sin \theta_1 \, d\theta_1$ is the orientational order parameter of the nematic phase. The prime on the summation in equation (13) indicates the restriction that only even $L'$ have to be considered. The odd terms vanish because molecules do not distinguish 'up' and 'down'.

Molecule 2 has the same distribution function but its orientation is defined with respect to the local director at vector $\mathbf{r}_{12}$, i.e.

$$f(\Omega_2, \chi_n(r_{12})) \equiv f(\cos \tilde{\theta}_2)$$

$$= 1 + \sum_{L \geqslant 2}{}' (2L + 1)\mathbf{P}_L P_L(\cos \tilde{\theta}_2) \qquad (14)$$

where $\tilde{\theta}_2$ is the angle between the long axis of molecule 2 and the local director, $(\cos \tilde{\theta}_2) = \hat{\mathbf{e}}_2 \ \hat{\mathbf{x}}(\mathbf{r}_{12})$. Using the addition theorem for spherical harmonics we can write equation (14) in terms of space-fixed angles $\Omega_2$ axial to the distortion angle $\chi_n(\mathbf{r}_{12})$:

$$f(\Omega_2, \chi_n(\mathbf{r}_{12})) = 1 + 4\pi \sum_{L \geqslant 1}{}' \mathbf{P}_L \sum_M Y_{LM}(\Omega_2) \sum Y_{LM}^*(\chi_\eta, 0) \qquad (15)$$

where

$$Y_{LM} = Y_{LM}(\theta_2, \phi_2)$$

and

$$Y_{LM}(\chi_\eta, 0) = P_{LM}(\cos \chi_\eta) \ P_{LM}(\cos \chi_\eta)$$

is the associated Legendre function of degree $L$ and order $M$. Using the explicit forms of Legendre functions and following Singh and Singh [5], we get

$$f'(\Omega_2, 0) = 4\pi \sum_L \mathbf{P}_L [Y_{L1}(\Omega_2) - Y_{L-1}(\Omega_2)] P_{L1}'(1) \qquad (16)$$

$$f''(\Omega_2, 0) = 4\pi \sum_L \mathbf{P}_L \{Y_{L0}(\Omega_2) P_{L0}''(1)$$

$$+ [Y_{L2}(\Omega_2) + Y_{L-2}(\Omega_2)] P_{L2}''(1)\}. \qquad (17)$$

The potential energy of interaction of a pair of molecules is represented as

$$U(\mathbf{r}_{12}, \Omega_1, \Omega_2) = \begin{cases} \infty, & r_{12} < D(\Omega_{12}) \\ 0, & r_{12} > D(\Omega_{12}) \end{cases} \qquad (18)$$

where $D(\Omega_{12})[\equiv D(\mathbf{r}_{12}, \Omega_{12})]$ is the distance of closest approach of two molecules with relative orientation $\Omega_{12}$ and is given by the Gaussian model of Berne and

Pechukas [7] as

$$D(\Omega_{12}) = D_0 \left[ 1 - \frac{\chi}{\begin{array}{c} (\hat{\mathbf{r}}_{12} \ \hat{\mathbf{e}}_1)^2 + (\hat{\mathbf{r}}_{12} \ \hat{\mathbf{e}}_2)^2 \\ - 2\chi(\hat{\mathbf{r}}_{12} \ \hat{\mathbf{e}}_1)(\hat{\mathbf{r}}_{12} \ \hat{\mathbf{e}}_2)(\hat{\mathbf{e}}_1 \ \hat{\mathbf{e}}_2) \\ \hline 1 - \chi^2(\hat{\mathbf{e}}_1 \ \hat{\mathbf{e}}_2)^2 \end{array}} \right]^{-1/2}$$

(19)

where $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are unit vectors along symmetry axes of two interacting hard oblate ellipsoids, $D_0 = 2b$ and $\chi = (x_0^2 - 1)/(x_0^2 + 1)$; $\hat{\mathbf{r}}_{12}$ is a unit vector along the intermolecular axes.

For correlation functions appearing in equation (11) we use the decoupling approximation of Parson [8] and take analytical solutions of Werthein [9] and Thiele [10], giving

$$C_2(r_{12}, \Omega_1, \Omega_2) = C_2(r_{12}/D(\Omega_{12})) = C_2(n_2^*)$$
$$= a_1 + b_1 n_2^* + (1/2)a_1 \eta (n_2^*)^3 \quad \text{for } n_2^* < 1$$
$$= 0 \qquad\qquad\qquad \text{for } n_2^* > 1$$

(20)

where

$$n_2^* = r_{12}/D(\Omega_{12})$$
$$a_1 = -(1 + 2\eta)^2/(1 - \eta)^4$$
$$b_1 = 6\eta[1 + (1/2)\eta]^2/(1 - \eta)^4$$

(21)

and $\eta(=\rho_0 v)$ is the packing fraction; $v = (\pi/6)x_0(2b)^3$ is the molecular volume.

A decoupling approximation decouples the translational and orientational degrees of freedom. In the decoupling approximation, the expression for the elastic constants reduces to

$$K_i^{(0)} = -2\rho_0^2 kT\, \mathbf{\check{C}}_2'(\rho_0) \int d\Omega_1 \int d\Omega_2\, d\hat{\mathbf{r}}_{12}\, f(\Omega_1, 0)$$
$$\times F_i(\hat{\mathbf{r}}_{12}, \Omega_1, \Omega_2) D^5(\hat{\mathbf{r}}_{12}, \Omega_{12})$$

(22 a)

$$K_i^{(1)} = -2\rho_0^3 kT\, \mathbf{\check{C}}_2'(\rho_0) \int d\Omega_1 [f(\Omega_1, 0) - 1]$$

$$\times \int d\Omega_2 \int d\hat{\mathbf{r}}_{12} F_i(\hat{\mathbf{r}}_{12}, \Omega_1, \Omega_2)$$

$$\times \left[ D^5(\hat{\mathbf{r}}_{12}, \Omega_{12}) + \int d\Omega_3 [f(\Omega_3, 0) - 1] \int d\hat{\mathbf{r}}_{13} \right.$$

$$\left. \times \int d\hat{\mathbf{r}}_{23} D^4(\hat{\mathbf{r}}_{12}, \Omega_{12}) D^2(\hat{\mathbf{r}}_{23}, \Omega_{23}) D^2(\hat{\mathbf{r}}_{13}, \Omega_{13}) \right]$$

(22 b)

$$K_i^{(2)} = -\rho_0^4 kT\, \mathbf{\check{C}}_2''(\rho_0) \int d\Omega_1 [f(\Omega_1, 0) - 1]$$

$$\times \int d\Omega_3 [f(\Omega_3, 0) - 1] \int d\Omega_2 \int d\hat{\mathbf{r}}_{12}$$

$$\times \int d\hat{\mathbf{r}}_{23} \int d\hat{\mathbf{r}}_{13} D^4(\hat{\mathbf{r}}_{12}, \Omega_{12}) D^2(\hat{\mathbf{r}}_{13}, \Omega_{13})$$

$$\times D^2(\hat{\mathbf{r}}_{23}, \Omega_{23}) F_i(\hat{\mathbf{r}}_{12}, \Omega_1, \Omega_2)$$

(22 c)

where

$$\mathbf{\check{C}}_2(\rho_0) = \int dn_2^*(n_2^*) C_2(n_2^*, \rho_0)$$
$$= (8 - 28\eta + 17\eta^2)/160\,\eta(1 - \eta)^2 + \ln(1 - \eta)/20\eta^2$$

(23)

and

$$\mathbf{\check{C}}_2'(\rho_0) = \delta \mathbf{\check{C}}_2(\rho_0)/\delta\rho_0, \quad C_2''(\rho_0) = \delta^2 \mathbf{\check{C}}_2(\rho_0)/\delta\rho_0^2.$$

(24)

Integrals involving $D^5$, $D^4$, $D^2$, various powers of $D(\Omega_{12})$, are evaluated using expansion in terms of Legendre polynomials. We have adopted the same calculation procedures as Singh and Singh [5], which are discussed in detail by them.

### 3. Results and discussion

The model system under consideration is composed of hard oblate ellipsoids of revolution parametrized by length to width ratio $x_0(<1 \cdot 0)$. The quantities $-C_2(\rho_0)$, $-\eta C_2'(\rho_0)$ and $-\eta^2 C_2''(\rho_0)$ as functions of packing fraction $\eta$ have been plotted in figure 2. As the density increases the derivative terms become more important. Thus the convergence of the series of Frank elastic constants in the ascending order of the direct correlation functions may become slower as density increases.

The theory developed above involves expansions in (i) the increasing order of direct correlation functions, and (ii) the degree of the order parameter products $\mathbf{P}_L \mathbf{P}_{L'}$ and $\mathbf{P}_L \mathbf{P}_{L'} \mathbf{P}_L$. Thus

$$K_i = \sum_{n=0}^{\infty} K_i^{(n)}$$

(25)

where $K_i^{(0)}$ contains the pair correlation functions, $K_i^{(1)}$ the three body correlation function and so on. $K_i^{(1)}$ consists of two terms

$$K_i^{(1)} = K_i^{(1,1)} + K_i^{(1,2)}.$$

(26)

The contribution of each elastic constant arising from $K^{(0)}$ and $K^{(1,1)}$ can be written as a double sum over contributions which are quadratic in the order parameters $\mathbf{P}_L$. Thus

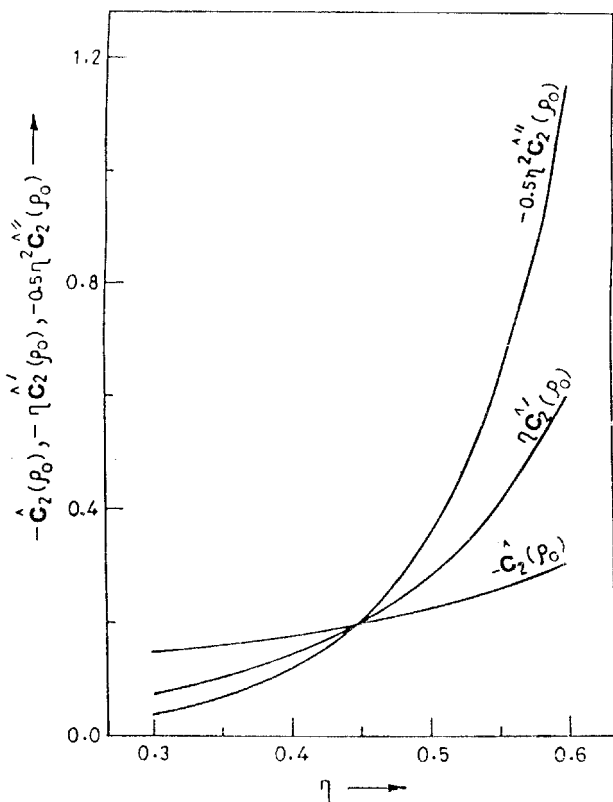$$K_i^{(1)} = \sum_L {}'\sum_{L'} {}' K_i^{(1)}(L, L').$$

(27)

Figure 2. The variation of $-\hat{\mathbf{C}}_2(\rho_0)$, $-\eta\hat{\mathbf{C}}_2'(\rho_0)$ and $\eta^2\hat{\mathbf{C}}_2''(\rho_0)/2$ as functions of packing fraction $\eta$.

$K_i^{(1,2)}$ and $K_i^{(2)}$ can be expressed as a triplet sum over contributions which are cubic in order parameters $\mathbf{P}_L$

$$K_i^{(m)} = \sum_L {}'\sum_{L'} {}'\sum_L {}' K_i^{(m)}(L, L', L''). \qquad (28)$$

The prime on summation in equations (27) and (28) indicates the restriction that only even $L$ have to be considered because molecules do not distinguished 'up' from 'down' and odd terms vanish. Here and below, superscript $(1)$ stands for $(0)$ or $(1, 1)$ and $(m)$ for $(1, 2)$ or $(2)$. Each term of series (27) and (28) can be written as

$$K_i^{(1)} = K_i^{(1)}(2, 2) + 2K_i^{(1)}(2, 4) + \qquad (29\,a)$$

$$K_i^{(m)} = K_i^{(m)}(2, 2, 2) + \qquad (29\,b)$$

where

$$K_i^{(1)}(L, L') \propto \mathbf{P}_L\mathbf{P}_{L'}$$

and

$$K_i^{(m)}(L, L', L'') \propto \mathbf{P}_L\mathbf{P}_{L'}\mathbf{P}_L. \qquad (30)$$

The convergence of equations (25) and (28) is expected to be good for $x \approx 1$ but poor for a system of molecules with large anisotropy in intermolecular interactions. To test this we list in the table the contribution of individual terms of the series (25) for $x_0 = 0.333$ for $\mathbf{P}_2 = 0.50$, $\mathbf{P}_4 = 0.15$, $\eta = 0.5$ and $0.4$, $2b = 15.0\,\text{Å}$ and $T = 600\,\text{K}$. These parameters crudely simulate a discotic nematic phase of triphenylene hexa-$n$-hexyloxybenzoate.

A number of observations can be made from the table. Even though series (29) is found to converge rapidly, the number of terms written explicitly are not enough for oblate ellipsoids of revolution. $[2K_i^{(1)}(2, 4)/K_i^{(1)}(2, 2)]$ is of order of $0.21$, $0.05$ and $0.028$ respectively for $K_i^{(1)}$, $K_2^{(1)}$ and $K_3^{(1)}$, indicating that higher order terms should not be neglected for $x_0 > 0.333$. The contribution of

Table. Contribution of individual terms of the series (25) and (29) to the elastic constants for hard-core repulsion for oblate ($x = 0.33$) ellipsoids of revolution. Here for $\mathbf{P}_2 = 0.5$, $\mathbf{P}_4 = 0.15$, $T \approx 600$ K, $2b = 5.0$ A and $\eta = 0.5$ and $0.4$. The values for $K_i$ are given in units of $10^{-7}$ dyne.

| Elastic constant | $\eta = 0.5$ | | | $\eta = 0.4$ | | |
|---|---|---|---|---|---|---|
| | $K_1$ | $K_2$ | $K_3$ | $K_1$ | $K_2$ | $K_3$ |
| $K_i^{(0)}$ (2, 2) | 5·645 | 7·962 | 5·645 | 2·883 | 4·066 | 2·883 |
| $2K_i^{(0)}$ (2, 4) | 1·090 | 0·363 | − 1·453 | 0·557 | 0·186 | − 0·742 |
| $K_i^{(0)}$ | 6·735 | 8·325 | 4·192 | 3·440 | 4·252 | 2·140 |
| $K_i^{(0)\mathrm{p}}$ | 6·995 | 8·342 | 4·489 | 3·570 | 4·260 | 2·292 |
| $K_i^{(1,1)}$ (2, 2) | 7·121 | 10·043 | 7·121 | 2·333 | 3·290 | 2·333 |
| $2K_i^{(1,1)}$ (2, 4) | 1·275 | 0·485 | − 1·833 | 0·450 | 0·150 | − 0·600 |
| $K_i^{(1,1)\mathrm{p}}$ | 8·496 | 10·501 | 5·288 | 2·783 | 3·440 | 1·733 |
| $K_i^{(1,1)}$ | 8·825 | 10·522 | 5·663 | 2·890 | 3·447 | 1·855 |
| $K_i^{(1,2)}$ (1, 2, 2) | −0·768 | −0·797 | −0·708 | −0·251 | −0·261 | −0·252 |
| $K_i^{(1)\mathrm{p}}$ | 7·728 | 9·704 | 4·580 | 2·533 | 3·179 | 1·481 |
| $K_i^{(2)}$ (2, 2, 2) | −0·951 | −0·988 | −0·877 | −0·203 | −0·211 | −0·187 |
| $K_i$ | 13·512 | 17·041 | 7·895 | 5·769 | 7·220 | 3·434 |
| $K_i^{\mathrm{p}}$ | 14·101 | 17·079 | 8·567 | 6·006 | 7·235 | 3·708 |
| $K_i^{\mathrm{p,p}}$ | 14·201 | 17·170 | 8·698 | 6·020 | 7·248 | 3·727 |

higher order terms in the series (29) can be approximated with the help of a simple [1, 0] Pade approximant. Thus,

$$K_i^{(1)p} = K_i^{(1)}(2, 2)\{1 - [2K_i^{(1)}(2, 4)/K_i^{(1)}(2, 2)]\}^{-1}.$$

$$(31)$$

These values are given in the table for each $K_i^{(1)}$ and are compared with values without the Pade approximant. We observe that the contribution of higher-order terms in series (29) is small but not negligible. $K_i^{(m)}(2, 2, 2)$ is also found to be small for oblate ellipsoids. The convergence of series (25) is also fairly good. However, we can approximate it to assess the contribution of higher-order terms in (25) applying [1, 0] Pade approximant. Thus

$$K_i^{pp} = K_i^{(0)p} + K_i^{(1)p}\{1 - [K_i^{(2)}/K_i^{(1)p}]^{-1}\}.$$   $(32)$

It may be recalled that in the case of molecular liquids the [1, 0] Pade approximation has been found to yield excellent results for thermodynamic properties even for a diverging series [11, 12]. We therefore believe that the Pade approximant would yield accurate results for all values of $x_0$.

For oblate molecules, $K_i^{(1)}(2, 2) > K_i^{(1)}(2, 2) = K_3^{(1)}(2, 2)$, and $2K_2^{(1)}(2, 4)$ is negative for $K_3$ and positive for $K_1$ and $K_2$. Since the magnitude of $2K_i^{(1)}(2, 4)$ is small we find the general relation $K_2 > K_1 > K_3$ for oblate ellipsoids, which is intuitively correct [13]. For disc-like molecules these deformations shown in figure (1) should convince us that it is more difficult to twist a plane of disc-like molecules than it is to twist a plane of rodlike molecules, and it is a very difficult deformation to apply. Hence, we expect $K_2$ to be the largest elastic constant for disc-like molecules, whereas for rodlike molecule it is the smallest among three. Hence the relation among $K_i$s for discotic nematics is $K_2 > K_1 > K_3$.

Our calculation suggests the following general solution:

$$(1/3)K_i^{(1)}(2, 4) = K_2^{(1)}(2, 4) = -(1/4)K_3^{(1)}(2, 4)$$

and

$$K_1^{(1)}(2, 2) = K_3^{(1)}(2, 2)$$

which holds for all $x_0$ and at all packing fractions and is independent of potential model. In figures 3–5 we have plotted, respectively, $K_1$, $K_2$ and $K_3$ as a function of packing fraction ($\eta$) for three values of $x_0$ (=0·25, 0·33 and 0·55). The elastic constants for all modes of deformation are very sensitive to packing fraction. We also observe that as anisotropy increases (i.e. $x_0$ moves from 0·55 to 0·25), the variation of elastic moduli becomes more sensitive to $\eta$ values. A similar study has been reported by Somoza and Tarazona [14] for rod-shaped molecules.
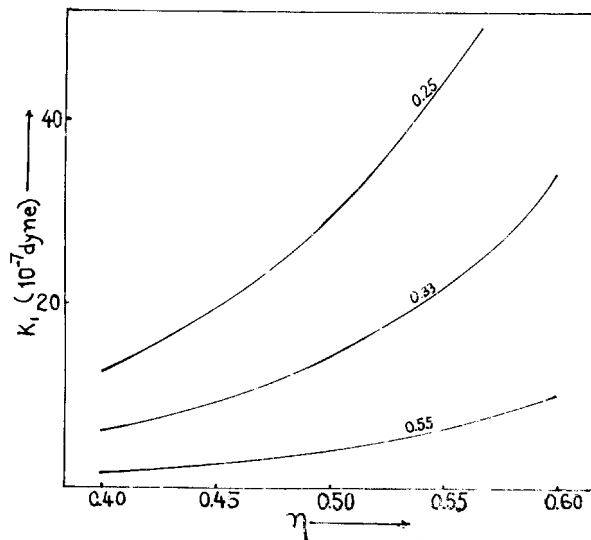


Figure 3. The variation of splay elastic constant $K_1$ with packing fraction $\eta$ for oblate system.
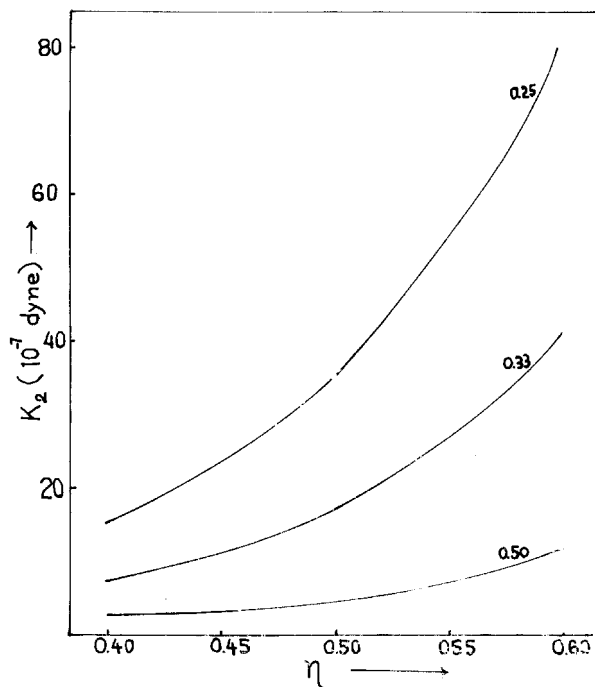


Figure 4. The variation of twist elastic constant $K_2$ with packing fraction $\eta$ for oblate system.

In the table $K_1$, $K_2$ and $K_3$ are given for two values of $\eta$ (0·5 and 0·4) which are, respectively, 14·20, 17·17 and 8·698 and 6·02, 7·25 and 3·73 in units of $10^{-7}$ dyne. We have not compared these results with experimental values because of the non-availability of data for any real system, but we anticipate that our results will be helpful in the further study of discotics.
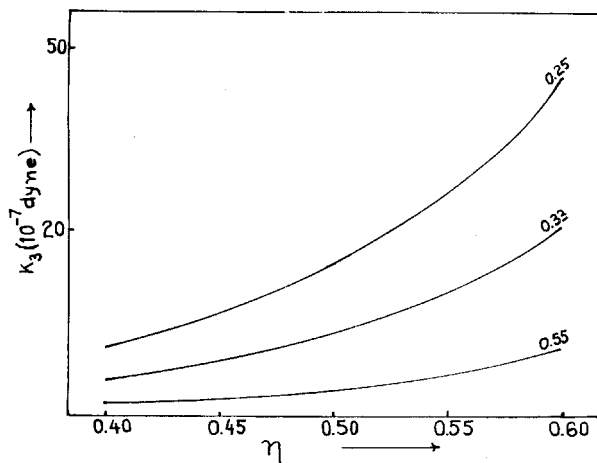
Figure 5. The variation of bend elastic constant $K_3$ with packing fraction $\eta$ for oblate system.

are then oblate spheroids with the symmetry axis along $\hat{e}_1 \times \hat{e}_2$, the axial ratio of this spheroid being $(1/2)(1 + x_0^2)^{1/2} < x_0$.

Although the decoupling approximation introduces anisotropy in the pair correlation function and is exact at very low density, it cannot be exact at liquid density. However, it has been found to yield values for the compressibility factor in very good agreement with machine simulated results. When $\hat{e}_1$ is perpendicular to $\hat{e}_2$, $C$ is most isotropic, the surfaces of constant $C$

## References

[1] BROOKS, J. D., and TAYLOR, G. H., 1965, *Carbon*, **3**, 185.
[2] CHANDRASEKHAR, S., SADASHIVA, B. K., and SURESH, K. A., 1977, *Pramana*, **9**, 471.
[3] GASPORRONX, H., 1981, *Mol. Cryst. liq. Cryst.*, **63**, 231.
[4] DE GENNES, P. G., 1974, *The Physics of Liquid Crystals* (Oxford: Claredon Press).
[5] SINGH, Y., and SINGH, K., 1986, *Phys. Rev. A*, **33**, 3481.
[6] GELBART, W. M., and BENSHAUL, A., 1982, *J. chem. Phys.*, **77**, 916.
[7] BERNE, B. J., and PECHUKAS, P., 1972, *J. chem. Phys.*, **56**, 4213.
[8] PARSON, J. D., 1979, *Phys. Rev. A*, **19**, 1225.
[9] WERTHEIM, M. S., 1963, *Phys. Rev. Lett.*, **10**, 321.
[10] THIELE, E., 1963, *J. chem. Phys.*, **38**, 1958.
[11] VERLET, L., and WEIS, J. J., 1974, *Mol. Phys.*, **28**, 665.
[12] STELL, G., RASSAIH, J. C., and NARANG, H., 1972, *Mol. Phys.*, **23**, 393.
[13] SOKALSKI, K., and RUIJGROK, TH. W., 1982, *Physica*, **113A**, 126.
[14] SOMOZA, A. M., and TARAZONA, P., 1989, *Phys. Rev. A*, **40**, 6069.