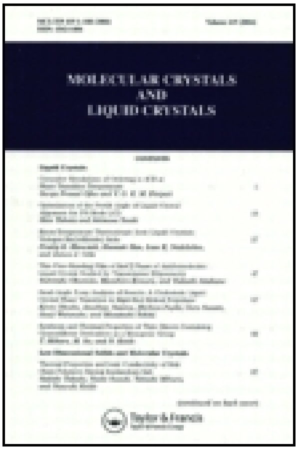

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

The Influence of Induction Interaction on the Curvature Elasticity of Nematic Liquid Crystals

S. Singh [a] & K. Rajesh [a]
[a] Department of Physics, Banaras Hindu University, Varanasi, 221005, India

Version of record first published: 04 Oct 2006.

To cite this article: S. Singh & K. Rajesh (1991): The Influence of Induction Interaction on the Curvature Elasticity of Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 200:1, 133-144

To link to this article: http://dx.doi.org/10.1080/00268949108044236

Mol. Cryst. Liq. Cryst., 1991, Vol. 200, pp. 133–144
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

The Influence of Induction Interaction on the Curvature Elasticity of Nematic Liquid Crystals

S. SINGH and K. RAJESH
Department of Physics, Banaras Hindu University Varanasi-221005, India

(Received July 27, 1990; in final form October 19, 1990)

We study the influence of induction interaction on the fundamental elastic properties of nematic liquid crystals using a theory based on density functional formalism. Numerical calculations for the elastic moduli associated with 'splay,' 'twist' and 'bend' modes of deformation are reported for a model system described by an interaction potential having a reference part and a perturbation part. The reference interaction is represented qualitatively by the Berne-Pechukas model. The perturbation potential is represented by the attractive interaction which is described by induction interaction. Results for elastic constants are reported for a range of molecular length-width ratio, polarizability, dipole moment, temperature and density. We find that the contribution of induction interaction is small but non-negligible. The contribution is sensitive to the values of molecular parameters and density.

Keywords: curvature elasticity, nematics, density functional

1. INTRODUCTION

The extent to which the anisotropy of molecular interactions contribute to the properties of liquid crystals have been a subject of active investigation in recent years. The complexity of intermolecular interactions for species forming liquid crystals makes such studies difficult and subject to uncertainty. Of particular importance is the study of curvature elasticity which is connected with spatial changes of the orientation of the director field $\hat{n}(\mathbf{r})$. In the limit of long-wavelength deformation the curvature elasticity of a uniaxial nematic can be described in terms of continuum theory by five elastic constants but only three of them can describe the bulk properties.[1] The deformation free-energy may be defined as

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

The coefficients K_1, K_2 and K_3 are the Frank elastic constants corresponding to the distortions known as splay, twist (or torsion) and bend (or flexion), respectively.

The study of these moduli is of crucial significance from both practical and fundamental points of view. They reflect several qualitative features about the range and anisotropy of the spatial and orientational correlation functions. Their study, even at the macroscopic level, always generates indirect clues about the nature and various anisotropies of molecular interactions.

A theory based on the density functional approach has been developed by Singh[2] for nonuniform nematic liquid crystals. This theory allows to write formally exact expressions for the Helmholtz free-energy of a system in terms of direct correlation functions which is functional of single particle density distribution. The theory has been applied (i) to the calculation of the elastic constants for model systems; hard ellipsoids of revolution,[3] and Berne-Pechukas Gaussian overlap model,[4] and (ii) to study the effects of dispersion interaction[5] (referred to as I). In the present paper, we investigate the influence of induction interaction on the elastic constants of nematic liquid crystals adopting a similar procedure as outlined in I. The numerical results are given for ordinary nematic (rod-shape) as well as for discotic nematic (disk-shape). A brief account of the theory and working equations are given in section 2. Section 3 presents the results and discussions.

2. THEORY AND WORKING EQUATIONS

We consider a system of N-axially symmetric nonspherical nematogenic molecules contained in a volume V at temperature T. The total potential energy of interaction is approximated as the sum of the interaction energies of pairs

$$u(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \sum_{i=1}^{N} u^e(\mathbf{x}_i) + \sum_{i>j=1}^{N} u(\mathbf{x}_i, \mathbf{x}_j) \tag{2}$$

where $\mathbf{x}_i(\equiv \mathbf{r}_i, \Omega_i)$ indicates both the location $\mathbf{r}_i$ of the centre of the ith molecule and its relative orientation Ω_i described by Euler angles θ_i, ϕ_i. The volume element $d\mathbf{x}_i$ is equivalent to $d^3\mathbf{r}_i \, d\Omega_i$ where $d^3\mathbf{r}_i = dx_i \, dy_i \, dz_i$ and $d\Omega_i = 1/4\pi \sin\theta_i \, d\theta_i \, d\phi_i$. $u_e(\mathbf{x}_i)$ is the potential energy of a molecule at position $\mathbf{r}_i$ with relative orientation Ω_i due to external forces, and $u(\mathbf{x}_i, \mathbf{x}_j)$ is the intermolecular pair potential for molecules i and j.

Adopting the procedure as outlined in I, we write the total Helmholtz free-energy of the system as

$$\beta F = \beta F_u + \beta F_d \tag{3}$$

where βF_u is the reduced Helmholtz free-energy of a system of undistorted nematic phase in which the preferred axis remains constant throughout the sample,

$$\beta F_u = \beta F_{id}\{\rho_o(\mathbf{x})\} + \beta\Delta F(\rho_o) - \sum_{n=2} \frac{1}{n!} \int \prod_{i=1}^{n} d\mathbf{x}_i \, \delta\rho_o(\mathbf{x}_i) C_n(\rho_o) \tag{4}$$

and βF_d is the free-energy associated with the distortion,

$$\beta F_d = -\frac{1}{2}\int d\mathbf{x}_1 \int d\mathbf{x}_2\, [\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \rho_o(\mathbf{x}_1)\rho_o(\mathbf{x}_2)]C_2(\rho_o)$$

$$-\frac{1}{3}\int d\mathbf{x}_1 \int d\mathbf{x}_2 \int d\mathbf{x}_3\, \Delta\rho(\mathbf{x}_1)\Delta\rho(\mathbf{x}_2)\Delta\rho(\mathbf{x}_3)C_3(\rho_o) \qquad (5)$$

here $\rho(\mathbf{x}_i)$ and $\rho_o(\mathbf{x}_i)$ represent, respectively, the single particle density distribution functions corresponding to deformed and undeformed nematic phases. In a distorted system $\rho(\mathbf{x})$ is a functional of x and C_n, the direct n-body correlation functions, is a functional of $\rho(\mathbf{x})$. $\beta\Delta F(\rho_o)$ is the reduced Helmholtz free-energy of a system of undistorted nematic phase of density ρ_o. The last term in Equation (4) represents a correction to excess free-energy due to orientational ordering in the system. βF_{id} is the reduced Helmholtz free-energy for the ideal gas, and

$$\delta\rho_o(\mathbf{x}_i) = \rho_o(\mathbf{x}_i) - \rho_o$$

$$\Delta\rho(\mathbf{x}_i) = \rho(\mathbf{x}_i) - \rho_o(x_i)$$

The single-particle density distribution function can be written as

$$\rho(\mathbf{x}) = \rho_o f(\mathbf{r}, \Omega) \qquad (6)$$

where ρ_o is the mean number density. For a uniform nematic phase the single particle orientational distribution function is independent of position and is normalized to unity

$$\int d\Omega\, f_o(\Omega) = 1 \qquad (7)$$

Any distortion in the liquid crystal will cause the orientational distribution to be distorted in space from whatever form it had in the ordered nematic. Since the principal effect of an orientational stress is to cause the director to vary spatially in such a way that at each point in space singlet orientational distribution has the same uniaxial form with only the axis varying, we write[6]

$$f(\mathbf{r}, \Omega) = f_o(\mathbf{r}, \Omega)[1 + t(\mathbf{r}, \Omega)] \qquad (8)$$

where

$$f_o(\mathbf{r}, \Omega) = f(\hat{e} \cdot \hat{n}(\mathbf{r}))$$

Here $\hat{e}$ is a unit vector along a molecular symmetry axis and $\hat{n}(\mathbf{r})$ is the local director. The term t represents the stress-induced changes in the form of the distribution function. In the limit of long-wavelength distortion this term makes no contribution to the Frank elastic constants.

Functional Taylor expansion is used to write the direct correlation functions of a distorted nematic phase in terms of the direct correlation functions of the isotropic liquid at the same number density ρ_o and from the expression of βF_d the Frank elastic constants are derived in terms of successive higher order correlation functions of the isotropic liquid,[3]

$$K_i = K_i^{(o)} + K_i^{(1)} + \dots \tag{9}$$

where

$$K_i^{(o)} = -\rho_o^2\, kT \int d\mathbf{r}_{12}\mathbf{r}_{12}^2 \int d\Omega_1 \int d\Omega_2\, \delta f(\Omega_1, o)[\Delta\theta f'(\Omega_2, o) + \frac{1}{2}(\Delta\theta)^2 f''(\Omega_2, o)]C_2(\rho_o) \tag{10}$$

and

$$K_i^{(1)} = -\frac{2}{3}\rho_o^2\, kT \int d\mathbf{r}_{12}\mathbf{r}_{12}^2 \int d\mathbf{r}_3 \int d\Omega_1 \int d\Omega_2 \int d\Omega_3\, \delta f(\Omega_1, o) \cdot \delta f(\Omega_3, o)[\Delta\theta f'(\Omega_2, o) + \frac{1}{2}(\Delta\theta)^2 f''(\Omega_2, o)]C_3(\rho_o) \tag{11}$$

with

$$\Delta\theta = \begin{pmatrix} -(\hat{r}_{12}\cdot\hat{x})(\hat{r}_{12}\cdot\hat{z}) \\ 0 \\ (\hat{r}_{12}\cdot\hat{x})(\hat{r}_{12}\cdot\hat{z}) \end{pmatrix}; \quad (\Delta\theta)^2 = \begin{pmatrix} (\hat{r}_{12}\cdot\hat{x})^2 \\ (\hat{r}_{12}\cdot\hat{y})^2 \\ (\hat{r}_{12}\cdot\hat{z})^2 \end{pmatrix} \tag{12}$$

Here i stands for 1, 2 and 3 corresponding to splay, twist and bend elastic constants, respectively, and $\hat{x}$, $\hat{y}$, $\hat{z}$ are unit vectors along the specified X, Y, Z axes.

For a uniaxial phase composed of cylindrically symmetric molecules

$$\delta f(\Omega_i, o) = f(\Omega_i, o) - 1 \tag{13}$$

$$f'(\Omega_2, o) = 4\pi \sum_{\ell} \bar{P}_\ell b_{\ell 1}(Y_{\ell 1}(\Omega_2) - Y_{\ell \underline{1}}(\Omega_2)) \tag{14}$$

$$f''(\Omega_2, o) = 4\pi \sum_{\ell} \bar{P}_\ell [b_{\ell o} Y_{\ell o}(\Omega_2) + b_{\ell 2}(Y_{\ell 2}(\Omega_2) + Y_{\ell 1}(\Omega_2))] \tag{15}$$

$Y_{\ell m}(\Omega)$ are spherical harmonics of order ℓ and

$$b_{\ell o} = -\frac{1}{2}\ell(\ell+1)\left(\frac{2\ell+1}{4\pi}\right)^{1/2} \tag{16}$$

$$b_{\ell 1} = -b_{\ell \underline{1}} = -\frac{1}{2}\left(\frac{\ell(\ell+1)(2\ell+1)}{4\pi}\right)^{1/2} \tag{17}$$

$$b_{\ell 2} = b_{\ell \underline{2}} = \frac{1}{4}\left(\frac{(\ell-1)\ell(\ell+1)(\ell+2)(2\ell+1)}{4\pi}\right)^{1/2} \tag{18}$$

$\bar{P}_\ell$ is the ℓth Legendre polynomial order parameters defined as

$$\bar{P}_\ell = \frac{1}{2}\int_o^\pi \sin\theta_2 d\theta_2 f(\Omega_2, o) P_\ell(\cos\theta_2) \tag{19}$$

Since three-body direct pair correlation functions are not known exactly, the terms involving them are approximated by the relation

$$\frac{\partial C_2(\mathbf{r}_{12}, \Omega_1, \Omega_2)}{\partial\rho_o} = \iint C_3(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{23}, \Omega_1, \Omega_2, \Omega_3)\, d\mathbf{r}_3\, d\Omega_3 \tag{20}$$

We write the pair potential energy of the interaction $u(\mathbf{x}_1, \mathbf{x}_2)$ as a sum of two parts,

$$u(\mathbf{x}_1, \mathbf{x}_2) = u_o(\mathbf{x}_1, \mathbf{x}_2) + u_p(\mathbf{x}_1, \mathbf{x}_2) \tag{21}$$

where $u_o(\mathbf{x}_1, \mathbf{x}_2)$ represents the reference potential and is described by Bern-Pechukas potential model[7]

$$\begin{aligned} u_o(\mathbf{x}_1, \mathbf{x}_2) &\equiv u_o(\mathbf{r}_{12}, \Omega_1, \Omega_2) \\ &= 4\varepsilon(\hat{r}_{12}, \Omega_1, \Omega_2)\left[\left(\frac{\sigma(\hat{r}_{12}, \Omega_1\, \Omega_2)}{r_{12}}\right)^{12} - \left(\frac{\sigma(\hat{r}_{12}, \Omega_1, \Omega_2)}{r_{12}}\right)^{6}\right] \end{aligned} \tag{22}$$

The perturbation potential $u_p(x_1, \mathbf{x}_2)$ is represented by attractive interaction which is described by induction interaction[8]

$$u_p(\mathbf{x}_1, \mathbf{x}_2) \equiv u_a(\mathbf{r}_{12}, \Omega_1, \Omega_2) = -\frac{1}{2}\left(\frac{\alpha\mu^2}{r_{12}^6}\right)[3(\hat{r}_{12}\cdot\hat{e}_1)^2 + 3(\hat{r}_{12}\cdot\hat{e}_2)^2 + 2] \tag{23}$$

where α and μ are, respectively, the molecular polarizability and dipole moment.

Equation (22) represents correctly, at least qualitatively, the shape of the molecular rigid core and the attractive dispersion interaction. It is valid for oblate as well as prolate shapes of arbitrary anisotropy. The angle dependent strength and range parameters are given, respectively, by

$$\varepsilon(\hat{r}_{12}, \Omega_1, \Omega_2) = \varepsilon_o[1 - \chi^2(\hat{e}_1 \cdot \hat{e}_2)^2]^{-1/2} \tag{24a}$$

and

$$\sigma(\hat{r}_{12}, \Omega_1, \Omega_2) = \sigma_o D(\hat{r}_{12}, \Omega_1, \Omega_2) \tag{24b}$$

where

$$D(\hat{r}_{12}, \Omega_1, \Omega_2) = \left[1 - \chi \frac{(\hat{r}_{12} \cdot \hat{e}_1)^2 + (\hat{r}_{12} \cdot \hat{e}_2)^2 - 2\chi(\hat{r}_{12} \cdot \hat{e}_1)(\hat{r}_{12} \cdot \hat{e}_2)}{1 - \chi^2(\hat{e}_1 \cdot \hat{e}_2)^2}\right]^{-1/2} \tag{24c}$$

is the distance of closest approach of two molecules with relative orientation, $\Omega_{12} \cdot \hat{e}_1$ and $\hat{e}_2$ are the unit vectors along the symmetry axes of two interacting molecules, ε_o and σ_o are the constants with units of energy and length, respectively, and

$$\chi = \frac{x^2 - 1}{x^2 + 1}$$

is an anisotropy parameter. x is the length-width ratio of a molecule. For rod-shape (prolate) molecules $x > 1$ whereas for disk shape (oblate) molecules $x < 1$.

We adopt a similar method as described in I for the evaluation of elastic constants. The direct pair correlation function is approximated as

$$C_2(\mathbf{x}_1, \mathbf{x}_2) = C_2^{(o)}(\mathbf{x}_1, \mathbf{x}_2) - \beta u_a(\mathbf{x}_1, \mathbf{x}_2) g^{(o)}(\mathbf{x}_1, \mathbf{x}_2)$$

where $C_2^{(o)}$ is the direct pair correlation function for the reference system and $g^{(o)}$ the pair distribution function.

Using the decoupling approximation,[9] we write the Frank elastic constants as

$$K_i = \sum_n (K_{i,o}^{(n)} + K_{i,a}^{(n)}) \tag{27}$$

where the subscript o and a indicate, respectively, the contributions arising from the reference and attractive (perturbation) parts of the pair interaction. The contribution of the reference part of the interaction have been evaluated by Singh and

Singh[4] as a function of x, T and density and have been found to increase with increasing x for prolate and with $1/x$ for oblate molecules. A weak temperature and strong density dependences have been observed. The softness of the repulsive core of the interaction has large effect on K_i and depends on the values of x, T and density. For the induction interaction contributions, we write

$$K_{i,a}^{(n)} = K_{i,a}^{(o)} + K_{i,a}^{(1)} \tag{28}$$

where

$$K_{i,a}^{(o)} = -\alpha\mu^2\rho_o^2 I_4(\rho^*) \int d\Omega_1\, \delta f(\Omega_1, o) \int d\Omega_2 \int d\hat{r}_{12}\, D^{-1}(\hat{r}_{12}, \Omega_{12}) \cdot \left[\Delta\theta f'(\Omega_2, o) + \frac{1}{2}(\Delta\theta)^2 f''(\Omega_2, o)\right][2 + P_2(\cos\theta_1) + P_2(\cos\theta_2)] \tag{29}$$

and

$$K_{i,a}^{(1)} = -\frac{2}{3}\alpha\mu^2\rho_o^3 I_4'(\rho^*) \int d\Omega_1\, \delta f(\Omega_1, o) \int d\Omega_2 \int d\Omega_3\, \delta f(\Omega_3, o) \cdot \int d\hat{r}_{12} \int d\hat{r}_{13} \int d\hat{r}_{23} \left[\Delta\theta f'(\Omega_2, o) + \frac{1}{2}(\Delta\theta)^2 f''(\Omega_2, o)\right] D^{-2}(\hat{r}_{12}, \Omega_{12}) \cdot D^2(\hat{r}_{13}, \Omega_{13}) D^2(\hat{r}_{23}, \Omega_{23})[2 + P_2(\cos\theta_1) + P_2(\cos\theta_2)] \tag{30}$$

$I_4(\rho^*)$ defined as

$$I_4(\rho^*) = \int_o^\infty r_{12}^{*-2} g_{hs}^{(o)}(r_{12}^*)\, dr_{12}^*$$

is obtained from the following series[10]

$$I_4(\rho^*) = \frac{1}{4\pi}[12.5664 + 3.8894\,\rho^* - 0.0817\,\rho^{*2} - 0.0845\,\rho^{*3} + 0.7512\,\rho^{*4} - 0.6802\,\rho^{*5}]$$

where

$$\rho^* = \frac{6}{\pi}\eta$$

$$I_4'(\rho^*) = \frac{\delta I_4(\rho^*)}{\delta\rho^*}$$

with

$$\eta = \rho_o v$$

$$v = \frac{\pi}{6} x(2\mathrm{b})^3, \text{ is the molecular volume.}$$

3. RESULTS AND DISCUSSIONS

The theory used here involves expansion to increasing higher order in the direct correlation functions. Thus

$$K_i = \sum_{n=0}^{\infty} K_i^{(n)} \tag{31}$$

where

$$K_i^{(n)} = K_{i,o}^{(n)} + K_{i,a}^{(n)} \tag{32}$$

$K_i^{(o)}$ contains the pair correlation function, $K_i^{(1)}$ the three-body correlation function, and so on. We evaluate the contribution to each elastic constants arising from $K_i^{(o)}$ as a double sum over contributions which are quadratic in the order parameters $\bar{P}_\ell$, i.e.,

$$K_i^{(o)} = \sum_{\ell}{}' \sum_{\ell'}{}' K_i^{(o)}(\ell, \ell') \tag{33}$$

The prime on the summation sign indicates that only even ℓ has to be considered. Similarly $K_i^{(1)}$ is expressed as a triplet sum over contributions which are cubic in the order parameters $\bar{P}_\ell$,

$$K_i^{(1)} = \sum_{\ell}{}' \sum_{\ell'}{}' \sum_{\ell''}{}' K_i^{(1)}(\ell, \ell', \ell'') \tag{34}$$

The symmetry considerations show that for all i, n, ℓ, ℓ' and ℓ'',

$$K_i^{(o)}(o, \ell) = K_i^{(o)}(\ell, o) = 0$$

$$K_i^{(o)}(\ell, \ell') = K_i^{(o)}(\ell', \ell)$$

$$K_i^{(1)}(\ell, \ell', \ell'') = K_i^{(1)}(\ell', \ell, \ell'') = K_i^{(1)}(\ell'', \ell', \ell)$$

Thus each term of the series (33) and (34) can be written, respectively, as

$$K_i^{(o)} = K_i^{(o)}(2, 2) + 2K_i^{(o)}(2, 4) + \dots \tag{35a}$$

$$K_i^{(1)} = K_i^{(1)}(2, 2, 2) + \dots \tag{35b}$$

where

$$K_i^{(o)}(\ell, \ell') \propto \bar{P}_\ell \bar{P}_{\ell'}$$

and

$$K_i^{(1)}(\ell, \ell', \ell'') \propto \bar{P}_\ell \bar{P}_{\ell'} \bar{P}_{\ell''}$$

Since $\bar{P}_2 > \bar{P}_4 > \bar{P}_6 > \dots$ and for a typical nematic $\bar{P}_4/\bar{P}_2 = 0.25$, we evaluate only those terms which are written explicitly in the series Equation (35). The computational method adopted for evaluating these terms are described in detail in I. From the numerical enumerations we find that the series Equation (31) converges rapidly for both systems of prolate and oblate molecules and for both the reference and perturbation parts of the pair potential Equation (21). For the perturbation contributions the terms written in series Equation (35) are sufficient. Therefore, the higher order terms are ignored. However, for the reference potential it was shown[4] that the higher order terms are to be included in Equation (35a) and has been evaluated[4] using a [1, 0] Pade′ approximant.

We discuss first the effects of length-to-width ratio x, the polarizability α and dipole moment μ on the contributions of long-range induction interaction to the elastic constants. The numerical results obtained are given, respectively, in Figures 1 and 2 for systems of prolate ($x > 1$) and oblate ($x < 1$) molecules. The results plotted corresponds to $\bar{P}_2 = 0.5$, $\bar{P}_4 = 0.15$ and $\eta = 0.45$. For prolate molecules we take $T = 400$ K and 2b = 5.0 A. For $x = 3.0$ these parameters crudely corresponds to an ordinary nematic phase of PAA. At the atmospheric pressure the temperature $T = 400$ K lies in the middle of thermal range (390–408 K) for the nematic phase of PAA. Though the actual geometry of the molecule is not strictly ellipsoidal, we can roughly assume the system to be a prolate ellipsoid of revolution with $x = 3.0$. The discotic nematic phase is distinguished from ordinary nematics by indications of the anisotropy of the dielectric permittivity and other tensorial properties. We assume that the value $T = 600$ K, 2b = 15 A with $x = 1/3.0$ roughly simulate a discotic nematic phase of hexa-n-hexyloxy benzoate of triphenylene.[11]

A number of observations can be made from the Figures 1 and 2. In case of prolate ellipsoids the contribution to K_i of the induction interaction $K_{i,a}$ is positive for $i = 1$ and negative for $i = 2$ and 3. For oblate molecules it is positive in case of $i = 1$ and 3 and negative for $i = 2$. The magnitude of the contribution in case of prolate molecules decreases with increasing x when $i = 1$ and 2 and increases for $i = 3$. For oblate molecules the contribution increases for all i with increasing $1/x$. This can be understood from the fact that the major contribution to $K_{i,a}^{(o)}$ comes from the angle-independent part of the induction interaction. Thus, the $K_{i,a}^{(o)}$ emphasize the region where the intermolecular separation is small. The decrease in the magnitude of $K_{i,a}^{(o)}$ with increasing x for prolate molecules of fixed 2b shows that the availability of this region has decreased. Contrary to this, the increase in the availability of the region of small intermolecular separation with increasing x (prolate) or $1/x$ (oblate) and keeping 2b fixed leads to an increase in the magnitude of $K_{i,a}^{(o)}$. In I Singh and Singh[5] evaluated the contribution of $K_{i,a}$ of dispersion interaction described by $u_{\text{dis}}(r_{12}, \Omega_1, \Omega_2) = -r_{12}^{-6}(c_i + c_a P_2(\cos\theta_{12}))$ where c_i and c_a are potential parameters and θ_{12} is the angle between the symmetry axes of the two molecules and found that the contribution was always positive and decreased with x in the system of prolate molecules and increased with $1/x$ in the case of oblate molecules.

From the Figures 1 and 2 it can be seen that for both the systems the contribution of induction interaction to K_i for all i increases by increasing the value of the polarizability at a given value of dipole moment. Similar trend is observed with

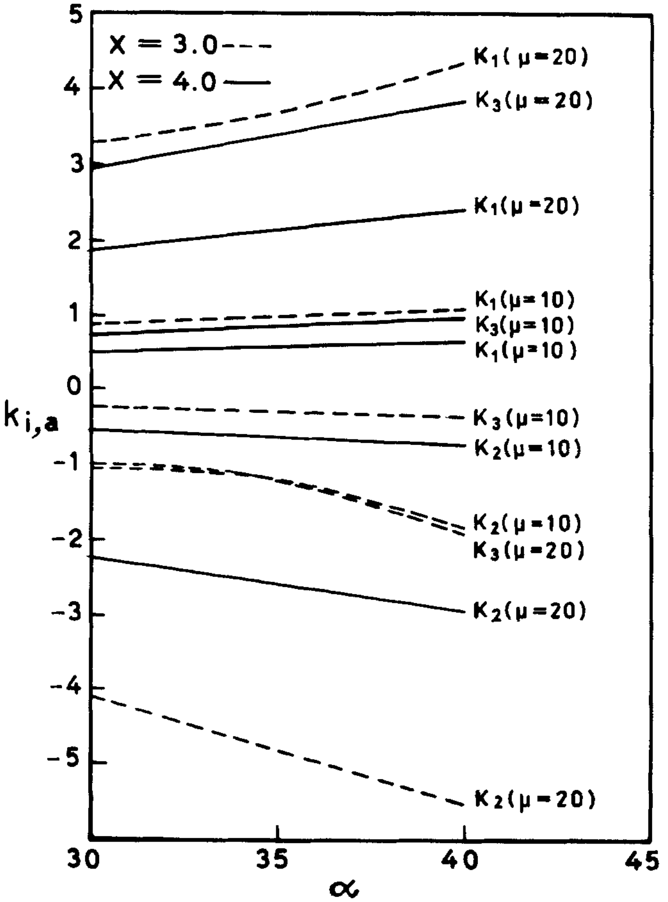

FIGURE 1 Contribution of induction interaction $K_{i,a}$ as a function of polarizability α at a given value of dipole moment μ for prolate ellipsoids. The subscripts 1, 2 and 3 on K indicate the value of i, μ, α and $K_{i,a}$ are in units of 10^{-30} cm, $10^{-40}\ J^{-1}\ c^2\ m^2$ and 10^{-7} dyne, respectively.

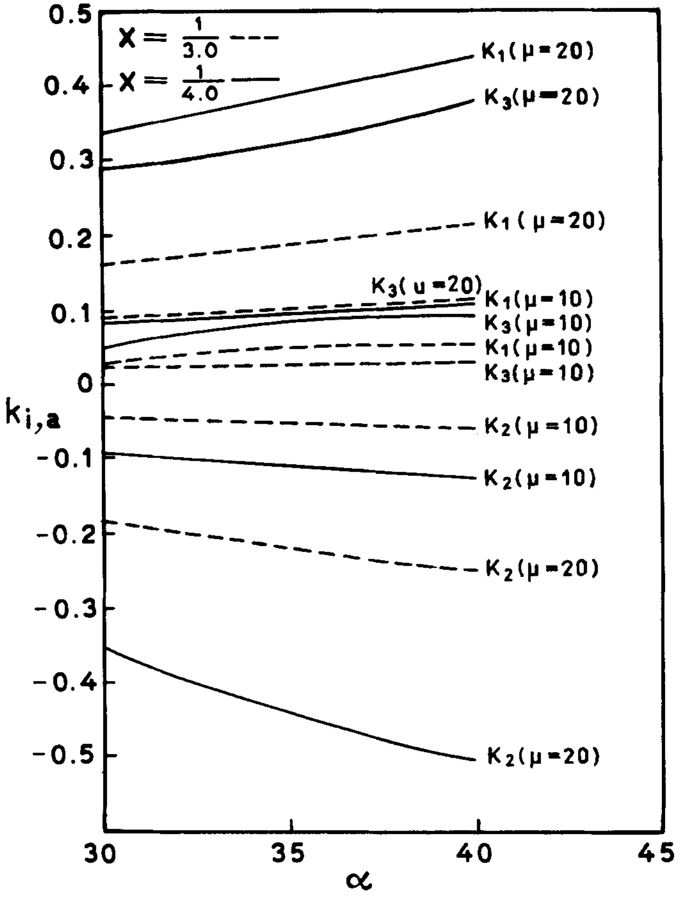

FIGURE 2 Contribution of induction interaction $K_{i,a}$ as a function of polarizability α at a given value of dipole moment μ for oblate ellipsoids. Other details are same as in Figure 1.

increasing value of dipole moment at a fixed value of polarizability. However, an increase in the value of dipole moment has more pronounced influence on the induction interaction contribution as compared to the increase in the polarizability value.

We close this section by comparing the contributions to K_i arising from the reference interaction (BP model) and the perturbation (induction) interaction and with a discussion on the temperature and density dependence of K_i. In case of the reference interaction contribution $K_{i,o}$ it was found[4] that for the parameters as taken in Figures 1 and 2 the absolute magnitude when $i = 1, 2$ and 3 are, respectively, (4.90, 2.39 and 9.26) × 10^{-7} dyne for prolate molecules of $x = 3.0$ and (4.58, 5.58 and 2.76) × 10^{-7} dyne for oblate molecules for $x = 1/3.0$. The induction interaction contribution is sensitive to the values of polarizability and dipole moment. For $\alpha = 30 \times 10^{-40} J^{-1} C^2 m^2$ and $\mu = 10 \times 10^{-30}$ Cm we find that in case of prolate system the induction interaction contribution $K_{i,a}$ for $i = 1, 2$ and 3 are, respectively, 15%, 47% and 2.8% as compared to reference part contribution.

The corresponding contribution for oblate molecules are 1.16%, 1.19% and 1.01% which are almost negligible. However, this contribution becomes non-negligible when $1/x > 4.0$. The induction interaction contribution increases linearly with T and density. This trend is similar as found[4] in case of reference potential. In calculating these contributions it has been assumed that $\bar{P}_4/\bar{P}_2 = 0.3$ and is temperature and density independent. With a little reflection one finds that the value of $\bar{P}_4/\bar{P}_2$ should increase with density and x and decrease with temperature. Due to this dependence of $\bar{P}_4/\bar{P}_2$ on T and density a weak temperature but strong density dependence of K_i are observed. It is seen that $K_1 \neq K_3$ is because of the contribution of term involving $\bar{P}_4/\bar{P}_2$. Our calculation shows, that for prolate molecules the induction interaction increases the value of K_1 but decreases K_2 and K_3. In case of oblate molecule very small increase in the values of K_1 and K_3 and decrease in K_2 are observed. Since the contribution of induction interaction is small as compared to that of reference potential we find that $K_3 > K_1 > K_2$ for a system of prolate molecules and $K_2 > K_1 > K_3$ in case of oblate molecules. This trend is in accordance with the experimental observations.[12]

Acknowledgment

We are grateful to Professor Y. Singh for many useful suggestions during the progress of this work. K. Rajesh is grateful to the UGC, Special Assistance Programme for the financial support.

References

1. J. Nehring and A. Saupe, *J. Chem. Phys.*, **54**, 337 (1971).
2. Y. Singh, *Phys. Rev.*, **A30**, 583 (1984).
3. Y. Singh and K. Singh, *Phys. Rev.*, **A33**, 3481 (1986).
4. K. Singh and Y. Singh, *Phys. Rev.*, **A35**, 3535 (1987).
5. K. Singh and Y. Singh, *Phys. Rev.*, **A34**, 548 (1986).
6. J. P. Straley, *Phys. Rev.*, **A14**, 1835 (1976).
7. B. J. Berne and P. Pechukas, *J. Chem. Phys.*, **56**, 4213 (1972).
8. H. Margenau and N. R. Kestner, "Theory of intermolecular forces" (Pergamon Press, 1971).
9. J. D. Parson, *Phys. Rev.*, **A19**, 1225 (1979).
10. B. Larsen, J. C. Rasaiah and G. Stell, *Mol. Phys.*, **33**, 987 (1977).
11. H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **63**, 231 (1981).
12. W. H. de Jeu, "Physical properties of liquid crystalline materials" (Gordon and Breach, New York, 1980). F. Leenhouts, A. J. Dekker and W. H. de Jeu, *Phys. Lett.*, **72A**, 155 (1979).