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Density-functional theory of curvature elasticity in nematic liquids. I

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A density-functional theory for the Frank elastic constants described in an earlier paper is reformulated and simplified. The excess free energy of aligned nematic liquids subjected to curvature (i.e., "splay," "twist," and "bend") deformations is written in terms of the direct correlation functions of the isotropic liquids. This leads to expansion of the elastic constants in successively higher-order direct correlation functions. The truncation of this series at an early stage is found to introduce large error. The number of terms explicitly considered and the use of a [1,0] Padé approximant make our calculation reliable. The other expansion which our theory involves is one in powers (products) of order parameters. These order parameters are the coefficients of a spherical harmonic expansion of an orientational singlet distribution. The convergence of this series is also tested for a simple model of hard ellipsoids of revolution. Qualitative features exhibited by our calculation for both ordinary and discotic nematics are in agreement with the results of previous workers and experiments. While this paper focuses on the role of packing forces the theory can be generalized to include dispersion and other long-range interactions, noncylindrical geometry, and nonrigidity of molecules.

I. INTRODUCTION

In a previous paper[1] (hereafter referred to as I) one of us developed a formal theory for the statistical mechanics of nonuniform liquid crystals and used it to derive expressions for the Frank elastic constants of nematic phases. The purpose of this paper is to present and discuss the numerical results obtained for systems composed of hard ellipsoids of revolution conveniently parametrized by the length-to-width ratio $x_0=2a/2b$, where $2a$ and $2b$ denote the lengths of the major and minor axes of the ellipsoids. The model includes as limiting cases both hard-platelet and hard-needle systems. All these systems are of physical interest because they represent primitive models for the real liquid crystals.

The Frank elastic constants are a measure of the free energy associated with long-wavelength distortions of the nematic state in which the local preferred direction of molecular orientation varies in space. If the local preferred direction at the point $\mathbf{r}$ is parallel to the director $\hat{\mathbf{n}}(\mathbf{r})$, the free energy associated with the distortion may be written as[2,3]

$$F=\frac{1}{2}\int d\mathbf{r}[K_1(\nabla\cdot\hat{\mathbf{n}})^2+K_2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2+K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2] . \tag{1.1}$$

The distortions corresponding to K_1, K_2, and K_3 are called splay, twist, and bend, respectively. The Frank elastic constants K_i characterize the free-energy increase associated with the three normal modes of deformation of the ordered nematic state.

Understanding 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 (in display devices). Secondly, they provide unusually sensitive probes of the microscopic structure of the orientationally ordered state. Valuable information can be obtained from their study regarding the nature and importance of various anisotropies of intermolecular potentials, and of spatial and orientational correlation functions.

There are several calculations[4-10] of the elastic constants of the nematic phase based on assumptions as to the relative importance of the repulsive and attractive parts of the intermolecular interactions. In these works the potential energy function plays an explicit role whereas the structure of the liquid crystal (which enters via a variety of considerations concerning excluded volume correlations, packing geometry, etc.) plays only an implicit one. The complexity of the intermolecular potential for species that form liquid crystals is such as to make such calculations both difficult and subject to uncertainty. The theory outlined in I, in contrast, makes the role of the structure of the medium explicit while leaving the role of the intermolecular potential implicit. The direct correlation functions in terms of which the elastic constants are expressed have broad functional similarities for systems with rather different intermolecular potentials.

Prior to I, Poniewierski and Stecki[9] derived expressions for the Frank elastic constants in terms of the direct pair correlation functions using a very laborious star-integral approach. The same expressions were recently rederived by Lipkin *et al.*[11] following a method similar to that described in I.

In Sec. II we summarize and reformulate some results of I which are relevant to our present study. The theory developed here is based on a density-functional formalism which is conceptually simple, contains as few independent approximations as appears presently feasible, and is solved without resorting to such simplification as the low-density approximation. It requires as input the direct correlation function of a uniform system as a function of number density and temperature, as well as the local free energy. The latter, of course, may be obtained from the former in various ways, e.g., by means of a compressibility sum rule. The formalism correctly reproduces linear-response theory.

The density-functional formalism has already been used to give a formal description of the isotropic-nematic[1,12] and the nematic—smectic-A (Ref. 13) transitions. In a separate paper[14] (hereafter referred to as II), we applied the theory to study the properties and characteristics of isotropic-nematic and isotropic-plastic transitions in a system of hard ellipsoids of revolution. Prolate as well as oblate ellipsoids were considered. We have found, in agreement with computer simulation results,[15] a remarkable symmetry between systems with inverse length-to-breadth ratios. Such symmetry is not found in the case of the elastic constants (Sec. IV).

The model system which we investigate in this paper is described in Sec. III. We also discuss in this section the approximations used for numerical enumerations. The results are presented in Sec. IV. The molecular theory of the curvature elasticity as presented in Sec. II involves expansion in successively higher-order direct correlation functions and in products of the order parameters. The convergence of these expansions is tested in Sec. IV. The numerical values of all three elastic constants are given as functions of the length-to-breadth ratio of the molecules. The paper is concluded in Sec. V with a discussion of extensions and implications of the present work.

II. STATISTICAL MECHANICS OF A NONUNIFORM SYSTEM AND THE FRANK ELASTIC CONSTANTS OF A NEMATIC PHASE

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

$$U(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N)=\sum_{i=1}^{N}u^{e}(\mathbf{x}_i)+\sum_{i>j=1}^{N}u(\mathbf{x}_i,\mathbf{x}_j)\ , \tag{2.1}$$

where, for economy of notation, we use vector $\mathbf{x}_i$ to indicate both the location $\mathbf{r}_i$ of the center of the ith molecule and its relative orientation $\mathbf{\Omega}_i$ described by Euler's angles ψ, ϕ, and ξ. The volume element $d\mathbf{x}_i$ is equal to $d^3\mathbf{r}_i d\Omega_i$, where $d^3\mathbf{r}=dx\,dy\,dz$ and

$$d\mathbf{\Omega}_i=\frac{1}{8\pi^2}\sin\psi\,d\psi\,d\phi\,d\xi\ ,$$

$u^{e}(\mathbf{x}_i)$ 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.

The Helmholtz free energy F of the system is

$$\beta F=\beta F_{\mathrm{id}}+H\ , \tag{2.2}$$

where β^{-1} is Boltzmann's constant times temperature and βF_{id} the reduced Helmholtz free energy for the ideal gas

$$\beta F_{\mathrm{id}}=\int\rho(\mathbf{x})[\ln\rho(\mathbf{x})\Lambda+\beta u^{e}(\mathbf{x})-1]d\mathbf{x}\ , \tag{2.3}$$

where

$$\Lambda=\int\exp(-\beta E_k)dp_1\cdots dp_s/h^s\ ,$$

s being the number of degrees of freedom of a molecule, E_k is its kinetic energy, and h Planck's constant. H is the excess reduced Helmholtz free energy arising from the intermolecular interactions and is a functional of the single-particle density distribution $\rho(\mathbf{x})$ and pair potential u.

The function H can be used as a generating functional for the correlation functions,[16,17]

$$\frac{\delta^n H}{\prod_{i=1}^{n}\delta\rho(\mathbf{x}_i)}=-c_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n,\{\rho\})=-c_n\{\rho\}\ , \tag{2.4}$$

where c_n are direct n-body correlation functions. The functional dependence of c_n on $\rho(\mathbf{x})$ is indicated by curly brackets. $-kTc_1(\mathbf{x}_j;\{\rho\})$ is considered to be a *solvent-mediated effective potential field* acting at $\mathbf{x}_1$. The function $c_2(\mathbf{x}_1,\mathbf{x}_2;\{\rho\})$ is the Ornstein-Zernike direct pair correlation function (DPCF) and is related to the pair correlation function $h(\mathbf{x}_1,\mathbf{x}_2)=g(\mathbf{x}_1,\mathbf{x}_2)-1$ as follows:

$$h(\mathbf{x}_1,\mathbf{x}_2)=c_2(\mathbf{x}_1,\mathbf{x}_2)+\int\rho(\mathbf{x}_3)h(\mathbf{x}_2,\mathbf{x}_3)c_2(\mathbf{x}_1,\mathbf{x}_3)d\mathbf{x}_3\ . \tag{2.5}$$

If we start from zero density and want to build up a system in which density at $\mathbf{x}_1$ is $\rho(\mathbf{x}_1)$ and at $\mathbf{x}_2$ is $\rho(\mathbf{x}_2)$, etc., then H of the resulting system is most conveniently obtained by functional integration of (2.4) for $n=2$, which leads to

$$H\{\rho\}=-\int d\mathbf{x}_1\int d\mathbf{x}_2\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)\bar{c}_2\{\rho\}\ , \tag{2.6}$$

$$\bar{c}_2\{\rho\}=\int_0^1 ds\int_0^s ds'c_2(s'\rho)\ . \tag{2.7}$$

The existence of the functional βF guarantees that the above results are independent of path of integration. This fact helps enormously in simplifying the statistical-mechanical theory for a nonuniform system.[18,19] In a nonuniform system $\rho(\mathbf{x})$ is a function of position and orientation and c_2 is a functional of $\rho(\mathbf{x})$.

A homogeneous nematic phase is translationally invariant. Thus

$$\rho(\mathbf{x})\equiv\rho(\mathbf{r},\mathbf{\Omega})=\rho_0 f(\mathbf{\Omega})\ , \tag{2.8}$$

where ρ_0 is the mean number density and $f(\mathbf{\Omega})$ the singlet orientational distribution function normalized to unity,

$$\int f(\mathbf{\Omega})d\mathbf{\Omega}=1\ . \tag{2.9}$$

For a uniform nematic, $f(\mathbf{\Omega})$ is independent of position.

In a distorted nematic the orientational distribution varies spatially in a very complicated way. However, for our purpose it is sufficient to allow it to vary only to the extent that the director $\hat{\mathbf{n}}(\mathbf{r})$ does, i.e., the distribution of angles that the molecular long axis makes with the locally preferred direction remains the same throughout the sample; only the director changes. To be more specific, let $f(\theta)=f(\cos\theta=\hat{\mathbf{e}}\cdot\hat{\mathbf{z}})$ describe the probability in the homogeneous nematic of finding a molecule whose long axis $\hat{\mathbf{e}}$ makes an angle θ with respect to the space-fixed z axis. Then in the case of distortion, the orientational distribution at $\mathbf{r}$ is given by $f(\theta)=f(\hat{\mathbf{e}}\cdot\hat{\mathbf{n}}(\mathbf{r}))$, i.e., it looks the same as in the undistorted nematic except for the locally preferred direction changing according to $\hat{\mathbf{n}}(\mathbf{r})$. 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. But the difference between $f(\hat{\mathbf{e}}\cdot\hat{\mathbf{n}}(\mathbf{r}))$ and the actual f in the case of long-wavelength distortions makes no contribution to the Frank elastic constants.

With any distortion we may associate a wave number q. The increase in the free energy due to a long-wavelength distortion will be proportional to q^2 because the symmetry of the system ensures that distortions corresponding to q and $-q$ are equivalent. Any change in $f(\theta)$, apart from a rotation of the preferred direction due to a distortion, will also be of order q^2. Since the thermodynamically stable state $[\hat{\mathbf{n}}(\mathbf{r})=\hat{\mathbf{z}}]$ is stationary with respect to variation of the form of $f(\theta)$, changes in the form of $f(\theta)$ due to distortions will make no contributions of order q^2 to the increase in the free energy.[5]

Since $c_2\{\rho\}$ is a functional of $f(\theta)$, any change in c_2 due to distortion will be of the order q^2. Therefore the change in $c_2\{\rho\}$ due to distortion will make no contribution of order q^2 to the increase in the free energy. Thus we take for c_2 the value corresponding to the undistorted nematic, i.e., $c_2\{\rho\}$ in (2.6) should be replaced by $c_2(\rho_0 f(\mathbf{\Omega}))$. The free energy of a distorted nematic phase correct to the order of q^2 is

$$\beta F=\beta F_{\text{id}}-\rho_0^2\int d\mathbf{x}_1\int d\mathbf{x}_2 f(\mathbf{\Omega}_1,\mathbf{r}_1)f(\mathbf{\Omega}_2,\mathbf{r}_1)\bar{c}_2(\rho_0 f(\mathbf{\Omega}))$$
$$-\rho_0^2\int d\mathbf{x}_1\int d\mathbf{x}_2 f(\mathbf{\Omega}_1,\mathbf{r}_1)[f(\mathbf{\Omega}_2,\mathbf{r}_2)-f(\mathbf{\Omega}_2,\mathbf{r}_1)]$$
$$\times\bar{c}_2(\rho_0 f(\mathbf{\Omega}))\ . \tag{2.10}$$

In the notations adopted here and below

$$c_n(\rho_0 f(\mathbf{\Omega}))\equiv c_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n;\rho_0 f(\mathbf{\Omega}))\ . \tag{2.11}$$

Functional Taylor expansion can now be used to express the direct correlation function of a uniform nematic phase in terms of the direct correlation functions of the isotropic liquid at the same number density ρ_0. Thus

$$\bar{c}_2(\rho_0 f(\mathbf{\Omega}))$$
$$=\bar{c}_2(\rho_0)+\rho_0\int\bar{c}_3(\rho_0)[f(\mathbf{\Omega}_3)-1]d\mathbf{x}_3$$
$$+\tfrac{1}{2}\rho_0^2\int\int\bar{c}_4(\rho_0)[f(\mathbf{\Omega}_3)-1][f(\mathbf{\Omega}_4)-1]d\mathbf{x}_3 d\mathbf{x}_4\ . \tag{2.12}$$

Substituting this in (2.10) we get

$$\beta F=\beta F^u+\beta\Delta F \tag{2.13a}$$

with

$$\beta\Delta F=\sum_{n=0}\beta\Delta F^{(n)}\ , \tag{2.13b}$$

where

$$\beta F^u(\rho_0 f(\mathbf{\Omega}))=\beta F_{\text{id}}-\rho_0^2\int d\mathbf{x}_1\int d\mathbf{x}_2 f(\mathbf{\Omega}_1,\mathbf{r}_1)f(\mathbf{\Omega}_2,\mathbf{r}_1)\bar{c}_2(\rho_0 f(\mathbf{\Omega}))\ , \tag{2.13c}$$

$$\beta\Delta F^{(0)}=-\rho_0^2\int d\mathbf{x}_1\int d\mathbf{x}_2 f(\mathbf{\Omega}_1,\mathbf{r}_1)[f(\mathbf{\Omega}_2,\mathbf{r}_2)-f(\mathbf{\Omega}_2,\mathbf{r}_1)]\bar{c}_2(\rho_0)\ , \tag{2.14}$$

$$\beta\Delta F^{(1)}=-\rho_0^3\int d\mathbf{x}_1\int d\mathbf{x}_2\int d\mathbf{x}_3 f(\mathbf{\Omega}_1,\mathbf{r}_1)[f(\mathbf{\Omega}_3,\mathbf{r}_1)-1][f(\mathbf{\Omega}_2,\mathbf{r}_2)-f(\mathbf{\Omega}_2,\mathbf{r}_1)]\bar{c}_3(\rho_0)\ , \tag{2.15}$$

$$\beta\Delta F^{(2)}=-\tfrac{1}{2}\rho_0^4\int d\mathbf{x}_1\int d\mathbf{x}_2\int d\mathbf{x}_3\int d\mathbf{x}_4 f(\mathbf{\Omega}_1,\mathbf{r}_1)[f(\mathbf{\Omega}_3,\mathbf{r}_1)-1][f(\mathbf{\Omega}_4,\mathbf{r}_1)-1][f(\mathbf{\Omega}_2,\mathbf{r}_2)-f(\mathbf{\Omega}_2,\mathbf{r}_1)]\bar{c}_4(\rho_0)\ . \tag{2.16}$$

The quantity $\beta F^u(\rho_0 f(\mathbf{\Omega}))$ is the reduced Helmholtz free energy of a system of undistorted nematic phase with preferred axis corresponding to that at $\mathbf{r}_1$ and which remains constant throughout the sample. $\beta\Delta F$ is the free energy associated with the distortion. In (2.14)—(2.16) the $\beta\Delta F^{(n)}$ are expressed in terms of the direct correlation functions of the isotropic liquid of the same number density ρ_0. The subscript n in $\beta\Delta F^{(n)}$ indicates the order of contribution to the excess free energy arising from the correction in the direct correlation function of the isotropic liquid owing to orientational ordering in a uniform nematic phase. Thus $\beta\Delta F^{(0)}$ represents the contribution which is found when the isotropic liquid DPCF is used; $\beta\Delta F^{(1)}$ and $\beta\Delta F^{(2)}$ are due to first- and second-order corrections to the DPCF. The series (2.13b) is found to converge fast (see Sec. IV).

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

$$\hat{\mathbf{n}}(\mathbf{R})=\hat{\mathbf{x}}\sin\chi_n(\mathbf{R})+\hat{\mathbf{z}}\cos\chi_n(\mathbf{R})\ . \tag{2.17}$$

$\chi_n(\mathbf{R})$ is the angle between the director at $\mathbf{R}$ and the director at the origin, i.e., $\cos\chi_n(\mathbf{R})=\hat{\mathbf{z}}\cdot\hat{\mathbf{n}}(\mathbf{R})$. The long-wavelength distortions correspond to the change in the director over some characteristic length of the system being small, i.e., $\chi_n\sim qd\ll 1$; d may be taken to be the range of the direct correlation function. In this limit[8]

$$\chi_n(\mathbf{R})=\begin{cases} qx-q^2xz+O(q^3) & \text{for splay}\\ qy & \text{for twist}\\ qz+q^2xz+O(q^3) & \text{for bend}\ .\end{cases} \tag{2.18}$$

From (1.1) we get for the distortion free-energy density around the origin

$$\Delta a(0)=\begin{cases}\frac{1}{2}K_1q^2+O(q^4) & \text{for splay}\\ \frac{1}{2}K_2q^2+O(q^4) & \text{for twist}\\ \frac{1}{2}K_3q^2+O(q^4) & \text{for bend ,}\end{cases} \qquad (2.19)$$

where

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

Since in pure splay, twist, and bend the deformed nematic has the same local structure everywhere, the above results do not depend upon the choice of the origin.

From (2.13)–(2.16) we get the following expression for the free-energy density around $\mathbf{R}=0$;

$$\begin{aligned}\beta F&=\int d^3\mathbf{R}\,\beta a(\mathbf{R})\\ &=\int d^3\mathbf{R}[\beta a^u(\mathbf{R})+\beta\Delta a(\mathbf{R})]\ ,\end{aligned} \qquad (2.20)$$

where

$$\begin{aligned}\beta a^u(0)=\rho_0\int d\boldsymbol{\Omega}\,f(\boldsymbol{\Omega},0)[\ln f(\boldsymbol{\Omega},0)+\ln\rho_0+\ln\Lambda-1]&\\ -\rho_0^2\int d\mathbf{r}\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2 f(\boldsymbol{\Omega}_1,0)f(\boldsymbol{\Omega}_2,0)&\\ \times\bar{c}_2(\rho_0 f(\boldsymbol{\Omega}))&\end{aligned} \qquad (2.21)$$

and

$$\beta\Delta a(0)=\beta\Delta a^{(0)}(0)+\beta\Delta a^{(1)}(0)+\beta\Delta a^{(2)}(0) \qquad (2.22a)$$

with

$$\beta\Delta a^{(0)}(0)=-\rho_0^2\int d\mathbf{r}\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2 f(\boldsymbol{\Omega}_1,0)G(\chi_n(\mathbf{r}))\bar{c}_2(\rho_0)\ , \qquad (2.22b)$$

$$\beta\Delta a^{(1)}(0)=-\rho_0^3\int d\mathbf{r}\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2[f(\boldsymbol{\Omega}_1,0)-1]G(\chi_n(\mathbf{r}))\left[\frac{\delta\bar{c}_2(\rho_0)}{\delta\rho_0}+\int d\mathbf{r}_3\int d\boldsymbol{\Omega}_3[f(\boldsymbol{\Omega}_3,0)-1]\bar{c}_3(\rho_0)\right]\ , \qquad (2.22c)$$

$$\beta\Delta a^{(2)}(0)=-\tfrac{1}{2}\rho_0^4\int d\mathbf{r}\int d\mathbf{r}_3\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2\int d\boldsymbol{\Omega}_3[f(\boldsymbol{\Omega}_1,0)-1][f(\boldsymbol{\Omega}_3,0)-1]G(\chi_n(\mathbf{r}))\frac{\delta\bar{c}_3(\rho_0)}{\delta\rho_0}\ . \qquad (2.22d)$$

Here

$$G(\chi_n(\mathbf{r}))\equiv[f(\boldsymbol{\Omega}_2,\chi_n(\mathbf{r}))-f(\boldsymbol{\Omega}_2,0)]\ .$$

$\beta a^u(\mathbf{R})$ is the free-energy density at point R of an undeformed nematic liquid crystal and $\beta\Delta a(\mathbf{R})$ is the free-energy density of deformation expressed in terms of the direct correlation function $c_n(\rho_0)$ of the isotropic liquid. Since $\chi_n(\mathbf{r})$ is the angle between the director at $\mathbf{r}$ (where molecule 2 is located) and the director at the origin, we write in (2.22) $f(\boldsymbol{\Omega},\mathbf{R}+\mathbf{r})=f(\boldsymbol{\Omega},\chi_n(\mathbf{r}))$. For an undeformed system $\chi_n(\mathbf{r})=0$.

In writing (2.22) we have made use of the following exact relations.[14,15]

$$\frac{\delta\bar{c}_2(\rho_0)}{\delta\rho_0}=\int c_3(\rho_0)d\mathbf{x}_3$$

and (2.23)

$$\frac{\delta\bar{c}_3(\rho_0)}{\delta\rho_0}=\int c_4(\rho_0)d\mathbf{x}_4\ .$$

If the distortion angle is small, i.e., $\chi_n(\mathbf{r})\ll 1$, we can expand $f(\boldsymbol{\Omega},\chi_n(\mathbf{r}))$ as a power series in χ_n. Keeping terms to order q^2, one gets

$$\begin{aligned}G(\chi_n(\mathbf{r}))&\equiv f(\boldsymbol{\Omega}_2,\chi_n(\mathbf{r}))-f(\boldsymbol{\Omega}_2,0)\\ &=f'(\boldsymbol{\Omega}_2,0)\begin{Bmatrix}qz-q^2xz\\ qy\\ qz+q^2xz\end{Bmatrix}\\ &\quad+\frac{1}{2}f''(\boldsymbol{\Omega}_2,0)\begin{Bmatrix}q^2x^2\\ q^2y^2\\ q^2z^2\end{Bmatrix}+\cdots\ ,\end{aligned} \qquad (2.24)$$

where x, y, and z are the Cartesian components of $\mathbf{r}$ in the space-fixed coordinate system and

$$\begin{aligned}f'(\boldsymbol{\Omega}_2,0)&=[\partial f(\boldsymbol{\Omega}_2,\chi_n(\mathbf{r}))/\partial\chi_n]_{\chi_n=0}\ ,\\ f''(\boldsymbol{\Omega}_2,0)&=[\partial^2 f(\boldsymbol{\Omega}_2,\chi_n(\mathbf{r}))/\partial\chi_n^2]_{\chi_n=0}\ .\end{aligned} \qquad (2.25)$$

For a uniaxial nematic phase with a symmetry plane perpendicular to a director and composed of cylindrically symmetric molecules, the singlet orientational distribution $f(\boldsymbol{\Omega})$ has to depend only on the angle θ between the director and the molecular symmetry axis, where the director is parallel to the space-fixed z axis, and we have[1]

$$f(\boldsymbol{\Omega}_1,0)\equiv f(\cos\theta_1)=1+\sum_{L'\geq 2}{}'\,(2L'+1)\bar{P}_{L'}P_{L'}(\cos\theta_1)\ , \qquad (2.26)$$

where

$$\bar{P}_{L'}=\tfrac{1}{2}\int_0^\pi f(\boldsymbol{\Omega}_1,0)P_{L'}(\cos\theta_1)\sin\theta_1 d\theta_1$$

is the orientational order parameter of the nematic phase. The prime on the summation in (2.26) indicates the restriction that only even L' have to be considered. The odd terms vanish because molecules do not distinguish "up" from "down." Molecule 2 has the same distribution function, but its orientation is defined with respect to the local director at vector $\mathbf{r}$, i.e.,

$$\begin{aligned}f(\boldsymbol{\Omega}_2,\chi_n(\mathbf{r}))&\equiv f(\cos\tilde{\theta}_2)\\ &=1+\sum_{L\geq 2}{}'(2L+1)\bar{P}_L P_L((\cos\tilde{\theta}_2))\ .\end{aligned} \qquad (2.27a)$$

Here $\tilde{\theta}_2$ is the angle between the long axis of molecule 2 and the local director, $\cos\tilde{\theta}_2=\hat{\mathbf{e}}_2\cdot\hat{\mathbf{n}}(\mathbf{r})$.

Using the addition theorem for spherical harmonics we can rewrite (2.27a) in terms of the space-fixed angles $\mathbf{\Omega}_2$ and the distortion angle $\chi_n(\mathbf{r})$:

$$f(\mathbf{\Omega}_2,\chi_n(\mathbf{r}))=1+\sum_{L>2}{}' \bar{P}_L \sum_{M} Y_{LM}(\mathbf{\Omega}_2)Y^*_{LM}(\chi_n(\mathbf{r}),0) \ , \tag{2.27b}$$

where

$$Y_{LM}(\mathbf{\Omega}_2)=Y_{LM}(\theta_2,\varphi_2)$$

and

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

is the associated Legendre function of degree L and order M.

Equation (2.24) involves the first and second derivative of $f(\mathbf{\Omega}_2,0)$. Using the explicit forms of the Legendre functions it can be shown that $P'_{LM}(1)=0$ for all $M\neq\pm1$ and $P''_{LM}(1)=0$ for all $M\neq0$, ±2 and that[5]

$$\begin{aligned}
P''_{L,0}(1)&=-\tfrac{1}{2}L(L+1)\left[\frac{2L+1}{4\pi}\right]^{1/2} ,\\
P'_{L,1}(1)&=-P'_{L,-1}(1)\\
&=-\tfrac{1}{2}L(L+1)\left[\frac{(L-1)!}{(L+1)!}\,\frac{2L+1}{4\pi}\right]^{1/2} ,\\
P''_{L,2}(1)&=P''_{L,-2}(1)=\tfrac{1}{4}(L-1)L(L+1)(L+2)\\
&\quad\times\left[\frac{(L-2)!}{(L+2)!}\,\frac{2L+1}{4\pi}\right]^{1/2}
\end{aligned} \tag{2.27c}$$

Using (2.27c) we get

$$f'(\mathbf{\Omega}_2,0)=\bar{P}_L[Y_{L,1}(\mathbf{\Omega}_2)-Y_{L,-1}(\mathbf{\Omega}_2)]P'_{L,1}(1) \ , \tag{2.28}$$

$$\begin{aligned}
f''(\mathbf{\Omega}_2,0)=\bar{P}_L\{&Y_{L,0}(\mathbf{\Omega}_2)P''_{L,0}(1)\\
&+[Y_{L,2}(\mathbf{\Omega}_2)+Y_{L,-2}(\mathbf{\Omega}_2)]P''_{L,2}(1)\} \ .
\end{aligned} \tag{2.29}$$

From (2.20), (2.23), (2.24), and (2.19) we get for the elastic constants

$$K_i=\sum_n K_i^{(n)} \tag{2.30}$$

with

$$K_i^{(0)}=-2\rho_0^2kT\int d\mathbf{r}_{12}r_{12}^2\int d\mathbf{\Omega}_1\int d\mathbf{\Omega}_2 f(\mathbf{\Omega}_1,0)F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)\bar{c}_2(\rho_0) \ , \tag{2.31a}$$

$$K_i^{(1)}=-2\rho_0^3kT\int r_{12}^2d\mathbf{r}_{12}\int d\mathbf{\Omega}_1\int d\mathbf{\Omega}_2[f(\mathbf{\Omega}_1,0)-1]F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)\left[\frac{\delta c_2(\rho_0)}{\delta\rho_0}+\int d\mathbf{r}_3\int d\mathbf{\Omega}_3[f(\mathbf{\Omega}_3,0)-1]c_3(\rho_0)\right] , \tag{2.31b}$$

$$K_i^{(2)}=-\rho_0^4kT\int d\mathbf{r}_{12}r_{12}^2\int d\mathbf{r}_3\int d\mathbf{\Omega}_1\int d\mathbf{\Omega}_2\int d\mathbf{\Omega}_3[f(\mathbf{\Omega}_1,0)-1][f(\mathbf{\Omega}_3,0)-1]F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)\frac{\delta\bar{c}_3(\rho_0)}{\delta\rho_0} \ , \tag{2.31c}$$

where

$$\begin{aligned}
F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=&f'(\mathbf{\Omega}_2,0)\begin{Bmatrix}-(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{z}})\\ (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{x}})(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{z}})\end{Bmatrix}\\
&+\frac{1}{2}f''(\mathbf{\Omega}_2,0)\begin{Bmatrix}(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{x}})^2\\ (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{y}})^2\\ (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{z}})^2\end{Bmatrix}
\end{aligned} \tag{2.32}$$

and i stands for 1, 2, and 3 and $\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}$ are unit vectors along the space-fixed x, y, and z axes. Since the isotropic liquid is translationally invariant the direct correlation functions c_2 and c_3 appearing in (2.31) depend only on the relative separation of molecules and not on their individual positions. Thus

$$\begin{aligned}
\bar{c}_2(\rho_0)&=\bar{c}_2(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2) \ ,\\
\bar{c}_3(\rho_0)&=c_3(\mathbf{r}_{12},\mathbf{r}_{23},\mathbf{r}_{13},\mathbf{\Omega}_1,\mathbf{\Omega}_2,\mathbf{\Omega}_3) \ .
\end{aligned} \tag{2.33}$$

The three-body direct correlation functions c_3 which appear in (2.31b) and (2.31c) are not known even for a system of hard spheres. The *decoupling approximation* which is described in the following section, however, allows us to reduce the integrals involving c_3 in terms of the derivative of c_2. More will be said on this point in Sec. III.

III. APPROXIMATIONS AND DERIVATION OF WORKING EQUATIONS

The potential energy of interaction of a pair of hard ellipsoids of revolution is represented as

$$u(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=\begin{cases}\infty, & \mathbf{r}_{12}<D(\mathbf{\Omega}_{12})\\ 0, & \mathbf{r}_{12}>D(\mathbf{\Omega}_{12})\end{cases} \tag{3.1}$$

where $D(\mathbf{\Omega}_{12})$ $[\equiv D(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12})]$ is the distance of closest approach of two molecules with relative orientation $\mathbf{\Omega}_{12}$. For $D(\mathbf{\Omega}_{12})$ we use the expression given by the Gaussian model of Berne and Pechukas,[20]

$$D(\mathbf{\Omega}_{12})=D(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12})$$
$$=D_0\left[1-\chi\frac{(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)^2+(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)^2-2\chi(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)}{1-\chi^2(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)^2}\right]^{-1/2}, \tag{3.2}$$

where $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are unit vectors along the symmetry axes of two interacting hard ellipsoids, $D_0=2b$, and

$$\chi=\frac{x_0^2-1}{x_0^2+1} . \tag{3.3}$$

$\hat{\mathbf{r}}_{12}$ is a unit vector along the intermolecular axis.

The correlation functions appearing in (2.31) are not known for this system. The solution of the integral equations of the liquid state theory, such as the hypernetted-chain (HNC) equation, the Percus-Yevick (PY) equation, the mean spherical approximations (MSA), etc., are difficult to obtain.[21]

In II we used an approximation in which we took the analytic solution of Wertheim[22] and Thiele[23] for the DPCF in the PY approximation[24] for a system of hard spheres of diameter d_0 and replaced the diameter d_0 by the distance of closest approach $D(\mathbf{\Omega}_{12})$ (Refs. 25 and 26), i.e.,

$$c_2(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=c_2(r_{12}/D(\mathbf{\Omega}_{12}))$$
$$=a_1+b_1r_{12}^*+\tfrac{1}{2}a_1\eta(r_{12}^*)^3 \quad \text{for } r_{12}^*<1$$
$$=0 \quad \text{for } r_{12}^*>1 , \tag{3.4}$$

where

$$r_{12}^*=r_{12}/D(\mathbf{\Omega}_{12}) ,$$
$$a_1=-(1+2\eta)^2/(1-\eta)^4 ,$$
$$b_1=6\eta(1+\tfrac{1}{2}\eta)^2/(1-\eta)^4 ,$$

and $\eta=\rho_0 v$, $v=(\pi/6)x_0(2b)^3$, the molecular volume. This approximation decouples the translational and orientational degrees of freedom and is therefore called the *decoupling approximation.* We have already seen in II that this form of the DPCF gives reasonable results for the properties of the isotropic-plastic and isotropic-nematic transitions.

For the direct three-body correlation function we use the following relations:

$$c_3(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23},\mathbf{\Omega}_1,\mathbf{\Omega}_2,\mathbf{\Omega}_3)$$
$$=c_3\left[\frac{r_{12}}{D(\mathbf{\Omega}_{12})},\frac{r_{13}}{D(\mathbf{\Omega}_{13})},\frac{r_{23}}{D(\mathbf{\Omega}_{23})}\right]$$
$$=c_3(r_{12}^*,r_{13}^*,r_{23}^*) . \tag{3.5}$$

In the decoupling approximation, the expressions for the elastic constants reduces to

$$K_i^{(0)}=-2\rho_0^2kT\hat{\bar{c}}_2(\rho_0)\int d\mathbf{\Omega}_1\int d\mathbf{\Omega}_2\,d\hat{\mathbf{r}}_{12}\,f(\mathbf{\Omega}_1,0)F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)D^5(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12}) , \tag{3.6a}$$

$$K_i^{(1)}=-2\rho_0^3kT\hat{\bar{c}}_2'(\rho_0)\int d\mathbf{\Omega}_1[f(\mathbf{\Omega}_1,0)-1]$$
$$\times\int d\mathbf{\Omega}_2\int d\hat{\mathbf{r}}_{12}F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)$$
$$\times\left[D^5(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12})+\int d\mathbf{\Omega}_3[f(\mathbf{\Omega}_3,0)-1]\right.$$
$$\left.\times\int d\hat{\mathbf{r}}_{13}\int d\hat{\mathbf{r}}_{23}D^4(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12})D^2(\hat{\mathbf{r}}_{23},\mathbf{\Omega}_{23})D^2(\hat{\mathbf{r}}_{13},\mathbf{\Omega}_{13})\right] , \tag{3.6b}$$

$$K_i^{(2)}=-\rho_0^4kT\hat{\bar{c}}_2''(\rho_0)\int d\mathbf{\Omega}_1[f(\mathbf{\Omega}_1,0)-1]\int d\mathbf{\Omega}_3[f(\mathbf{\Omega}_3,0)-1]\int d\mathbf{\Omega}_2\int d\hat{\mathbf{r}}_{12}\int d\hat{\mathbf{r}}_{23}\int d\hat{\mathbf{r}}_{13}D^4(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12})D^2(\hat{\mathbf{r}}_{13},\mathbf{\Omega}_{13})$$
$$\times D^2(\hat{\mathbf{r}}_{23},\mathbf{\Omega}_{23})F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2) , \tag{3.6c}$$

Here

$$\hat{\bar{c}}_2(\rho_0)=\int_0^1 dr^*(r^*)^4\bar{c}_2(r^*,\rho_0)$$
$$=(8-28\eta+17\eta^2)/160\eta(1-\eta)^2$$
$$+\ln(1-\eta)/20\eta^2 \tag{3.7}$$

and

$$\hat{\bar{c}}_2'(\rho_0)=\frac{\delta\hat{\bar{c}}_2(\rho_0)}{\delta\rho_0},\quad \hat{\bar{c}}_2''(\rho_0)=\frac{\delta^2\hat{\bar{c}}_2(\rho_0)}{\delta\rho_0^2} . \tag{3.8}$$

In the decoupling approximation, as mentioned above, the translational and rotational degrees of freedom are decoupled. As a result we get integrals of the type $\int c_3(\rho_0)dr_3^*$ and $\int \delta c_3(\rho_0)/\delta\rho_0 dr_3^*$ which are reduced to $\delta c_2(\rho_0)/\delta\rho_0$ and $\delta^2c_2(\rho_0)/\delta\rho_0^2$, respectively.

In Fig. 1 we plot the quantities $-\hat{\bar{c}}_2(\rho_0)$, $-\eta\hat{\bar{c}}_2'(\rho_0)$, and $-\eta^2\hat{\bar{c}}_2''(\rho_0)/2$ as a function of the packing fraction η. As density increases the derivative terms became more important. Thus the convergence of the series of the Frank elastic constants in the ascending order of the direct correlation functions may be slower as density increases.

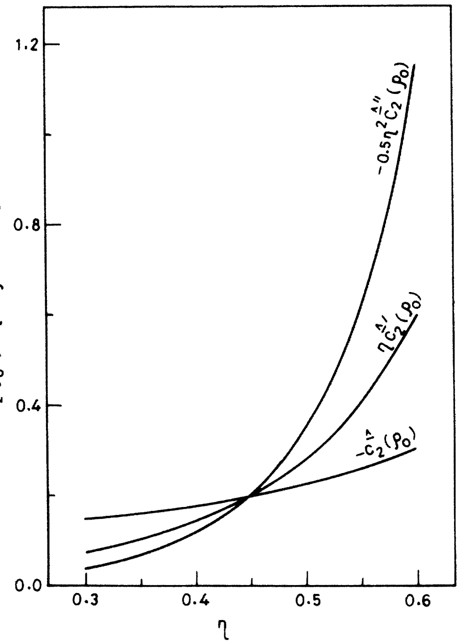

FIG. 1. Variation of $-\hat{c}(\rho_0)$, $-\eta\hat{c}'(\rho_0)$, and $-0.5\eta^2\hat{c}''(\rho_0)$ with packing fraction η.

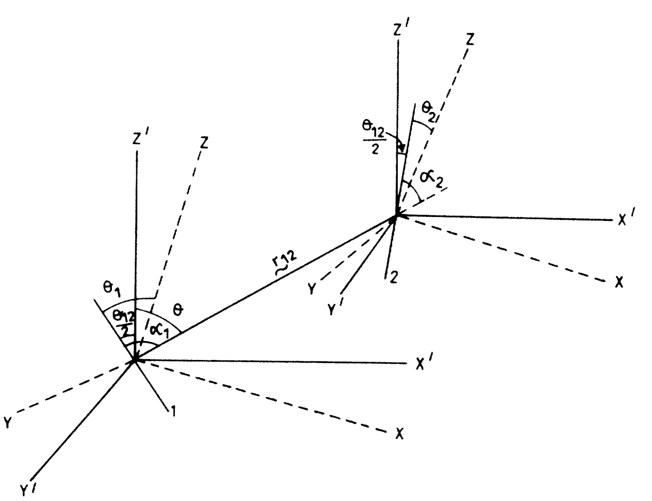

FIG. 2. Definition of angular variables for two linear molecules in space- and body-fixed frames of reference. Body-fixed frame is labeled by a prime.

IV. CALCULATIONS AND RESULTS

We begin this rather long section with general remarks on the calculational procedure. Then the details of results for the hard ellipsoids of revolution are described and compared with the results of other workers whenever possible.

A. Calculational procedure

We may recall that molecule 1 is at the origin with orientation $\mathbf{\Omega}_1$ and molecule 2 is at $\mathbf{r}$ with orientation $\mathbf{\Omega}_2$ with respect to the space-fixed frame of reference. The integrations over $\mathbf{\Omega}_1$ and $\mathbf{\Omega}_2$ in (3.6) are carried out only after integrating over $\hat{\mathbf{r}}_{12}$. For this we find it useful to transform to a "body-fixed" frame of reference.

Let the body-fixed yz plane (hereafter denoted by a prime) be the plane which contains the first molecule axis and which is parallel to the axis of molecule 2. Furthermore, let the body-fixed z' axis be obtained by rotating $\hat{\mathbf{e}}_1$ clockwise in the $y'z'$ plane by the angle $\theta_{12}/2$. θ_{12} is, of course, the angle between the two molecular axes. Thus $\hat{\mathbf{e}}_2$, which lies in a plane parallel to $y'z'$ and a distance x' from it, makes an angle $\theta_{12}/2$ with respect to the z' axis. $x'y'z'$ form a right-handed coordinate system as shown in Fig. 2.

With the help of geometry in the body-fixed frame of reference, we can write

$$\cos\alpha_1=\cos\theta\cos(\theta_{12}/2)+\sin(\theta_{12}/2)\sin\theta\sin\varphi\ ,$$
$$\cos\alpha_2=\cos\theta\cos(\theta_{12}/2)-\sin(\theta_{12}/2)\sin\theta\sin\varphi\ , \tag{4.1}$$

where (θ,φ) represent orientation of intermolecular axis $\mathbf{r}_{12}$ and α_1 and α_2 are angles between $\mathbf{r}_{12}$ and axes of molecule 1 and 2, respectively. The relationship between the primed and unprimed coordinate system is given by the transformation matrix[5]

$$\begin{bmatrix} x\\ y\\ z\end{bmatrix}=\begin{bmatrix}\dfrac{y_1z_2-y_2z_1}{\sin(\theta_{12})} & \dfrac{x_1-x_2}{2\sin(\theta_{12}/2)} & \dfrac{x_1+x_2}{2\cos(\theta_{12}/2)}\\ \dfrac{z_1x_2-z_2x_1}{\sin(\theta_{12})} & \dfrac{y_1-y_2}{2\sin(\theta_{12}/2)} & \dfrac{y_1+y_2}{2\cos(\theta_{12}/2)}\\ \dfrac{x_1y_2-y_2x_1}{\sin(\theta_{12})} & \dfrac{z_1-z_2}{2\sin(\theta_{12}/2)} & \dfrac{z_1+z_2}{2\cos(\theta_{12}/2)}\end{bmatrix}\begin{bmatrix} x'\\ y'\\ z'\end{bmatrix}, \tag{4.2}$$

where x_1,y_1,z_1 are the coordinates of the unit vector parallel to $\mathbf{\Omega}_1$ and x_2,y_2,z_2 are those of that parallel to $\mathbf{\Omega}_2$. In terms of these quantities we now have

$$x^2=\frac{(y_1z_2-y_2z_1)^2}{\sin^2(\theta_{12})}(x')^2+\frac{(x_1-x_2)^2}{4\sin^2(\theta_{12}/2)}(y')^2+\frac{(x_1+x_2)^2}{4\cos^2(\theta_{12}/2)}(z')^2+\text{cross terms}\ . \tag{4.3}$$

There are corresponding terms for y^2, z^2, xz, etc. Due to reflection symmetry in three coordinate planes, cross terms do not contribute to the integral. Hence the integrals which need to be evaluated are of the type

$$R_{xx}^{(t)}(\theta_{12})=\int d\hat{\mathbf{r}}'(\hat{\mathbf{r}}'\cdot\hat{\mathbf{x}}')^2D^t(\mathbf{\Omega}_{12})\ , \tag{4.4a}$$

$$R_{yy}^{(t)}(\theta_{12})=\int d\hat{\mathbf{r}}'(\hat{\mathbf{r}}'\cdot\hat{\mathbf{y}}')^2D^t(\mathbf{\Omega}_{12})\ , \tag{4.4b}$$

$$R_{zz}^{(t)}(\theta_{12})=\int d\hat{\mathbf{r}}'(\hat{\mathbf{r}}'\cdot\hat{\mathbf{z}}')^2D^t(\mathbf{\Omega}_{12}) \tag{4.4c}$$

with $t=4$ and 5. They are first evaluated in the body-fixed geometry and are then transformed to the space-fixed geometry using (4.2).

In (3.6) the $\int d\hat{\mathbf{r}}$ integrals sit under

$$\int d\mathbf{\Omega}_1 \int d\mathbf{\Omega}_2 = \frac{1}{16\pi^2}\int_0^{\pi}\sin\theta_1 d\theta_1 \int_0^{2\pi} d\varphi_1 \int_0^{\pi}\sin\theta_2 d\theta_2 \int_0^{2\pi} d\varphi_2 \tag{4.5}$$

integrals. For each value of θ_1, θ_2, φ_1, and φ_2 in the outer fourfold integrals, one can compute

$$\theta_{12}=\cos^{-1}[\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\varphi_2-\varphi_1)] \tag{4.6}$$

and evaluate $R_{jj}(\theta_{12})$ for this value of θ_{12}. However, in actual calculation we first compute $R_{jj}(\theta_{12})$ at equally spaced values of θ_{12} between 0 and π and then used a linear interpolation scheme to evaluate them at the θ_{12} values arising from the outer $\mathbf{\Omega}_1$ and $\mathbf{\Omega}_2$ integrations. We found that 120 values of θ_{12} were sufficient for the linear interpolation.

All that remains now is evaluation of complicated integrals over $\mathbf{\Omega}_1$ and $\mathbf{\Omega}_2$. These fourfold integrals are reduced to onefold by following a method suggested by Priest.[5] The details of this reduction and the values for the expansion coefficients can be obtained from the authors on request. Thus the problem of evaluating the elastic constants of the nematic phase is reduced to one which can be done on a hand calculator.

B. Contributions of the individual terms and convergence of the series

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

$$K_i=\sum_{n=0}^{\infty} K_i^{(n)} . \tag{4.7}$$

As mentioned above, $K_i^{(0)}$ contains the pair correlation function, $K_i^{(1)}$ the three-body correlation function, and so on. $K_i^{(1)}$ consists of two terms:

$$K_i^{(1)}=K_i^{(1,1)}+K_i^{(1,2)} , \tag{4.8a}$$

where

$$K_i^{(1,1)}=-2\rho_0^3kT\hat{\mathbf{c}}_2'(\rho_0)\int d\mathbf{\Omega}_1[f(\mathbf{\Omega}_1,0)-1]\int d\mathbf{\Omega}_2\int d\hat{\mathbf{r}}_{12}F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)D^5(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12}) , \tag{4.8b}$$

$$K_i^{(1,2)}=-2\rho_0^3kT\hat{\mathbf{c}}_2'(\rho_0)\int d\mathbf{\Omega}_1\int d\mathbf{\Omega}_2\int d\mathbf{\Omega}_3[f(\mathbf{\Omega}_1,0)-1]\int d\hat{\mathbf{r}}_{12}\int d\hat{\mathbf{r}}_{23}\int d\hat{\mathbf{r}}_{13}[f(\mathbf{\Omega}_3,0)-1]F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2) \times D^4(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12})D^2(\hat{\mathbf{r}}_{23},\mathbf{\Omega}_{23})D^2(\hat{\mathbf{r}}_{13},\mathbf{\Omega}_{13}) . \tag{4.8c}$$

The contribution to 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 $\bar{P}_L$. Thus

$$K_i^{(l)}=\sum_L{}'\sum_{L'}{}' K_i^{(l)}(L,L') . \tag{4.9}$$

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

$$K_i^{(m)}=\sum_L{}'\sum_{L'}{}'\sum_{L''}{}' K_i^{(m)}(L,L',L'') . \tag{4.10}$$

Here and below the superscript (l) stands for (0) or (1,1) and (m) for (1,2) or (2).

From symmetry considerations it is straightforward to show that $K_i(L,L')=K_i(L',L)$, $K_i(L,L',L'')=K_i(L',L,L'')=K_i(L'',L',L)$, etc. for all i, n, and L, L', L''. We also find that $K_i^{(0)}(0,L')=0$ for all i and L'. Thus each term of the series (4.9) and (4.10) can be written, respectively, as

$$K_i^{(l)}=K_i^{(l)}(2,2)+2K_i^{(l)}(2,4)+\cdots , \tag{4.11a}$$

$$K_i^{(m)}=K_i^{(m)}(2,2,2)+\cdots , \tag{4.11b}$$

where

$$K_i^{(l)}(L,L')\propto\bar{P}_L\bar{P}_{L'}$$

and

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

Since $\bar{P}_2>\bar{P}_4>\bar{P}_6>\cdots$ and $\bar{P}_4/\bar{P}_2\simeq 0.25$ for a typical nematic, we evaluate only those terms which are written explicitly in the series (4.11).

The convergence of the series (4.7) and (4.11) is expected to be good for $x_0\simeq 1$ but poor for a system of molecules with large anisotropy in intermolecular interactions. To test this we list in Table I the contributions of individual terms of the series (4.7) and (4.11) for $x_0=4.0$ and 0.25. All the results tabulated and graphed here and below are for $\bar{P}_2=0.5$, $\bar{P}_4=0.15$, $\eta=0.45$, $2b=5.0$ Å, and $T=400$ K.

A number of observations can be made from Table I. Though series (4.11a) is found to converge rapidly the number of terms written explicitly are not enough for large x_0 (prolate) and $1/x_0$ (oblate). For prolate ellipsoids $|2K_i^{(l)}(2,4)/K_i^{(l)}(2,2)|$ is of the order of 0.27, 0.21, and 0.37, respectively, for $K_1^{(l)}$, $K_2^{(l)}$, and $K_3^{(l)}$, indicating the non-negligibility of higher-order terms for $x_0=4.0$. The situation appears little better in the case of oblate ellipsoids; $|2K_i^{(l)}(2,4)/K_i^{(l)}(2,2)|$ is of the order of 0.21, 0.05, and 0.028, respectively, for $K_1^{(l)}$, $K_2^{(l)}$, and $K_3^{(l)}$, values showing better convergence than the one found in the case of prolate ellipsoids. The contribution of higher-order terms in the series (4.11a) can be approximated with the help of a simple [1,0] Padé approximant. Thus

$$K_i^{(l)P}=K_i^{(l)}(2,2)\left[1-\frac{2K_i^{(l)}(2,4)}{K_i^{(l)}(2,2)}\right]^{-1} . \tag{4.12}$$

TABLE I. Contributions of individual terms of the series (4.7) and (4.11) to each elastic constant for both systems of prolate ($x_0=4.0$) and oblate ($x_0=0.25$) ellipsoids of revolution. For the results shown here $\bar{P}_2=0.5$, $\bar{P}_4=0.15$, $\eta=0.45$, $T=400$ K, $2b=5.0$ Å. The values for K_i are given in units of 10^{-7} dyne.

		$x_0=4.0$			$x_0=0.25$	
	K_1	K_2	K_3	K_1	K_2	K_3
$K_i^{(0)}(2,2)$	6.675	2.824	6.675	8.599	12.450	8.599
$2K_i^{(0)}(2,4)$	-1.844	-0.615	2.458	1.843	0.614	-2.458
$K_i^{(0)}$	4.831	2.209	9.133	10.442	13.064	6.141
$K_i^{(0)P}$	5.240	2.320	10.570	10.940	13.100	6.690
$K_i^{(1,1)}(2,2)$	6.750	2.855	6.750	8.696	12.589	8.696
$2K_i^{(1,1)}(2,4)$	-1.864	-0.621	2.486	1.864	0.621	-2.485
$K_i^{(1,1)}$	4.866	2.234	9.236	10.566	13.210	6.211
$K_i^{(1,1)P}$	5.290	2.340	10.685	10.980	13.240	6.760
$K_i^{(1,2)}(2,2,2)$	-0.509	-0.391	-0.746	-1.522	-1.596	-1.374
$K_i^{(1)}$	4.376	1.843	8.490	9.038	11.614	4.841
$K_i^{(1)P}$	4.781	1.949	9.939	9.640	11.820	5.620
$K_i^{(2)}(2,2,2)$	-0.510	-0.392	-0.746	-1.524	-1.598	-1.376
K_i	8.700	3.660	16.880	17.960	23.080	9.060
K_i^P	9.510	3.880	19.763	18.870	23.150	10.700
K_i^{PP}	9.560	3.940	19.820	19.260	23.510	11.200

These values are also given in Table I for each $K_i^{(l)}$ and are compared with $K_i^{(l)}=K_i^{(l)}(2,2)+2k_i^{(l)}(2,4)$. We find, as argued above, that the contribution of higher-order terms in the series (4.11a) are small but not negligible, at least for large x_0 (prolate) and $1/x_0$ (oblate). This is obvious from Figs. 3 and 4 in which we plot the contribution of individual terms of the series (4.11a), respectively, as a function of x_0 for prolate molecules and $1/x_0$ for oblate molecules. We find that as x_0 deviates from unity, the contribution of higher-order terms increases.

The magnitude of $K_i^{(m)}(2,2,2)$ is found to be small for both prolate as well as oblate ellipsoids. This led us to neglect the contribution of higher-order terms in the series (4.11b). We believe that the error caused due to this would be negligible.

Next we examine the convergence of the series (4.7). We find that for both prolate as well as oblate molecules $K_i^{(0)}(L,L')\simeq K_i^{(1,1)}(L,L')$ and $K_i^{(1,2)}(2,2,2)\simeq K_i^{(2)}(2,2,2)$. However, $K_i^{(m)}(2,2,2)\ll K_i^{(l)}(2,2)$. Thus, while $K_i^{(1)}$ are almost as important as $K_i^{(0)}$, $K_i^{(2)}$ are very small in magnitude compared to $K_i^{(0)}$ or $K_i^{(1)}$. The magnitude of $K_i^{(2)}/K_i^{(1)}$ is found for the prolate ellipsoids of $x_0=4.0$ to be of the order of 0.11, 0.20, and 0.08, and for the oblate ellipsoids of $1/x_0=4.0$ to be 0.16, 0.14, and 0.25, respectively, for $i=1$, 2, and 3. These numbers indicate that the series (4.7) converges fairly rapidly. However, we can apply the [1,0] Padé approximant to assess the contribution of higher-order terms in (4.7). Thus

$$K_i^{PP}=K_i^{(0)P}+K_i^{(1)P}\left[1-\frac{K_i^{(2)}}{K_i^{(1)P}}\right]^{-1} . \tag{4.13}$$

It may be recalled that in case of molecular liquids the [1,0] Padé approximant has been found to yield excellent results for thermodynamic properties even for a diverging series.[27,28] We therefore believe that the Padé approximant given by (4.12) and (4.13) to sum the series (4.11a) and (4.7), respectively, would yield accurate results for all values of x_0.

The last row of Table I lists the values of K_i^{PP}. They are compared with $K_i=K_i^{(0)}+K_i^{(1,1)}+K_i^{(1,2)}+K_i^{(2)}$ and $K_i^P=K_i^{(0)P}+K_i^{(1)P}+K_i^{(2)}$. From this table and Figs. 5 and 6, in which we plot the contribution of the individual terms of the series (4.7), as a function of x_0 and $1/x_0$, respectively, it is obvious that the contributions of higher-order terms of the series (4.7) are small and in some cases negligible.

C. Results

For prolate ellipsoids we find that $K_1^{(l)}(2,2)=K_3^{(l)}(2,2)>K_2^{(l)}(2,2)$ for all x_0. The fact that $K_1\neq K_3$ is primarily due to the contribution of $2K_i^{(l)}(2,4)$. In particular, we find that $2K_i^{(l)}(2,4)$ is positive for K_3 and negative for K_1 and K_2. This suggests $K_3>K_1$ in agreement with experiment.[29] On the other hand, for oblate ellipsoids $K_2^{(l)}(2,2)>K_1^{(l)}(2,2)=K_3^{(l)}(2,2)$ and $2K_2^{(l)}(2,4)$ is negative for K_3 and positive for K_1 and K_2. Since the magnitude of $2K_i^{(l)}(2,4)$ is small, we find the general relation $K_2>K_1>K_3$ for oblate ellipsoids which is intuitively correct.[10,30] The fact that the twist deformation is most difficult to apply in a discotic phase is thus borne out by our calculation.

In agreement with the results of previous workers, our calculation suggests the following general relations:

$$\tfrac{1}{3}K_1^{(l)}(2,4)=K_2^{(l)}(2,4)=-\tfrac{1}{4}K_3^{(l)}(2,4)\ ,$$

and

$$K_1^{(l)}(2,2)=K_3^{(l)}(2,2)\ ,$$

which hold good for all x_0 (prolate as well as oblate) and are independent of potential models. For a system of prolate ellipsoids which model ordinary nematic phase, we find $K_3>K_1>K_2$. This relation changes to $K_2>K_1>K_3$ (see Fig. 7) for a system of oblate ellipsoids which models the discotic nematic phase. These results are in agreement with experiment[29] and with the results of previous workers. Further, we find that for prolate ellipsoids the ratio K_3/K_1 increases with x_0 and is in quantitative agreement with experiment.[29]

The perfect symmetry between the system with inverse length-to-breadth ratios found in the case of a phase diagram[14,15] does not exist in case of deformations (see Fig. 7).

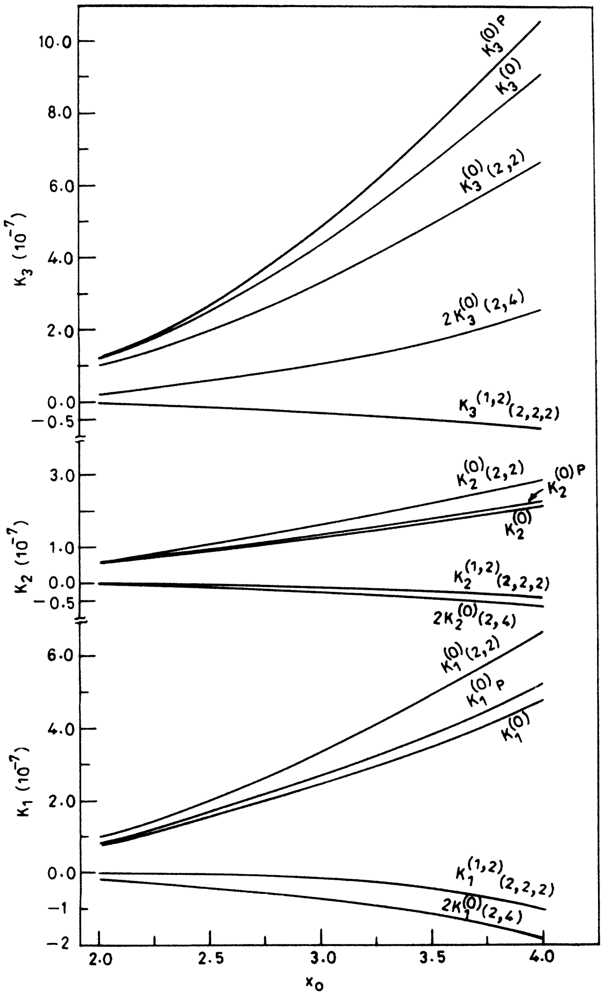

FIG. 3. Contribution of individual terms of the series (4.11) to each elastic constant as a function of x_0 for prolate ellipsoids. The results obtained from the [1,0] Padé approximant (4.12) are compared with those found from the relation $K_i^{(l)}=K_i^{(l)}(2,2)+2K_i^{(l)}(2,4)$. For the packing fraction $\eta=0.45$ we find $K_i^{(0)}(L,L')\simeq K_i^{(1,1)}(L,L')$ and $K_i^{(1,2)}(2,2,2)\simeq K_i^{(2)}(2,2,2)$. On the scale of the graph these quantities are indistinguishable from each other and are therefore shown by one graph only.

V. DISCUSSION

The calculation presented in the above section clearly indicates the importance of the term $K_i^{(1,1)}$ for all the three elastic constants. $K_i^{(1,1)}$ are found to be almost equal to $K_i^{(0)}$ in magnitude and sign for all values of i. This is in accordance with the result of Singh and Abraham[18] for a nonuniform hard-sphere fluid. The excess-free-energy correction $\beta\delta f^{(1)}$ (which involves first derivative of the DPCF of uniform system) was found[18] to be almost equal in magnitude and sign to $\beta\Delta f^{(0)}$ (which contains the DPCF of the uniform system) at every point in the interface region. From Fig. 1 it is also clear that the importance of $K_i^{(1,1)}$ and the other higher terms ($K_i^{(1,2)}, K_i^{(2)}$, etc.) of the series (4.7) will increase with the density. These terms were not considered by the previous workers.

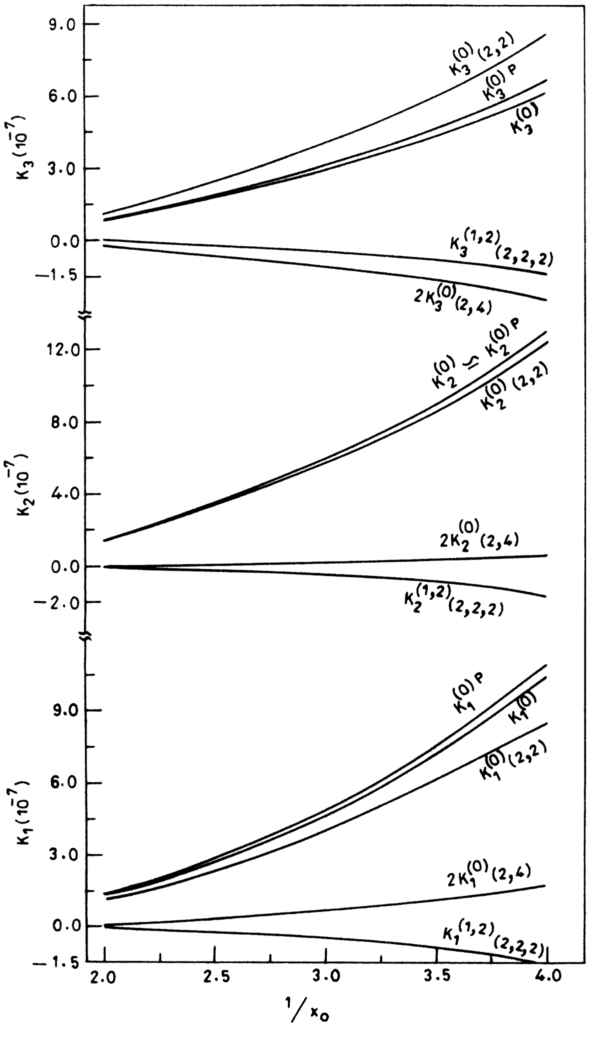

FIG. 4. Same as Fig. 3, but as a function of $1/x_0$ for oblate ellipsoids.

If we neglect all terms except $K_i^{(0)}$ in (4.7) and take the zero-density limit for DPCF, i.e.,

$$c(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_{12})\to e^{-\beta u(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)}-1\ , \tag{5.1}$$

the expression for the elastic constants given in Sec. II will reduce to those of Priest[5] and Straley.[6] Their theory is in fact a direct extension of the Onsager theory of orientational ordering in hard-rod gases; only the second virial coefficient is retained in the density expansion of the free energy.

Though Poniewierski and Stecki[9] gave expressions for the Frank elastic constants which are equivalent to that of $K_i^{(0)}$ of this work, they used (5.1) in evaluating the numerical values of K_i. Thus their calculation fails to consider higher than two-body-packing entropy effects. The result of Gelbart and Ben-Shaul[8] for the repulsive interaction can be found from the expression of $K_i^{(0)}$ by using the following relation:

$$\bar{c}(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=\frac{1}{2}\frac{1}{1-\eta}(e^{-\beta u(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)}-1)\ . \tag{5.2}$$

The factor $1/(1-\eta)$ is believed to take care of the effect of the higher-body-packing entropy effects. As shown by Barboy and Gelbart,[31] however, though (5.2) is a significant improvement over (5.1), it is not good enough to yield the correct compressibility factor for hard spherocylinders. The contributions of order $1/(1-\eta)^2$ and higher must be included to provide accurate $\beta P/\rho$ data.

Before our theory can be used to interpret real experiments, the calculational part of our work must be extended in several ways. First, it is important to account for the long-range dispersion interactions.[8,9] In particular, the coupling between isotropic attraction and anisotropic hard core repulsion through pair correlation function is important[32] in determining the relative values of the three principal elastic constants. The effects due to softness in the repulsive core and the dependence of the pair interaction $\mathbf{r}\cdot\mathbf{\Omega}$ should be taken into account. It may also be remembered that the symmetry of the nematogenic mole-

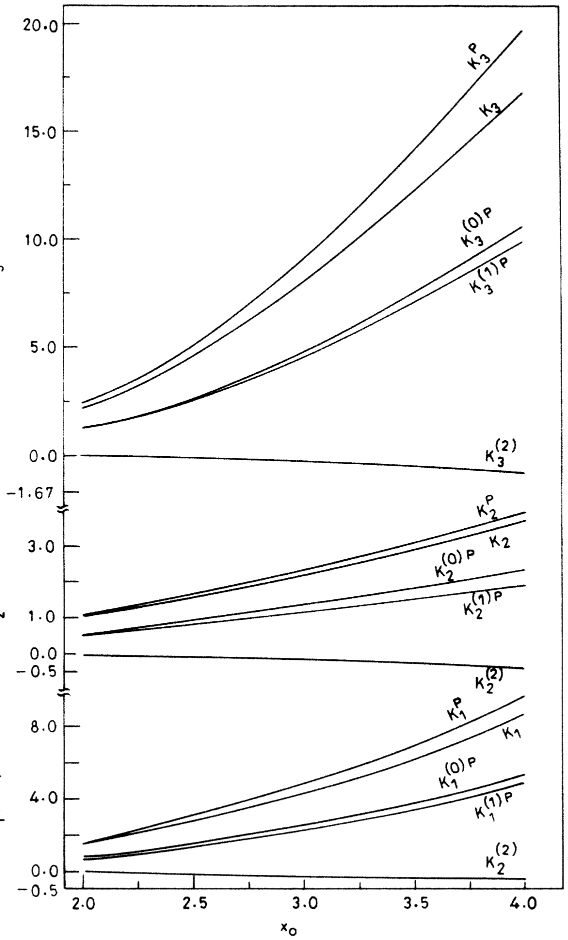

FIG. 5. Contribution of individual terms of the series (4.7) to each elastic constant as a function of x_0 for prolate ellipsoids. The results obtained from [1,0] Padé approximant (4.13) are compared with those found from the relations $K_i=K_L^{(0)}+K_i^{(1)}+K_i^{(2)}$ and $K_i^P=K_L^{(0)P}+K_i^{(1)P}+K_i^{(2)}$. For $\eta=0.45$ we find $K_i^{PP}\simeq K_i^P$. These two quantities are indistinguishable on the scale of the graph and are shown by one graph only. This indicates the convergence of the series (4.7).

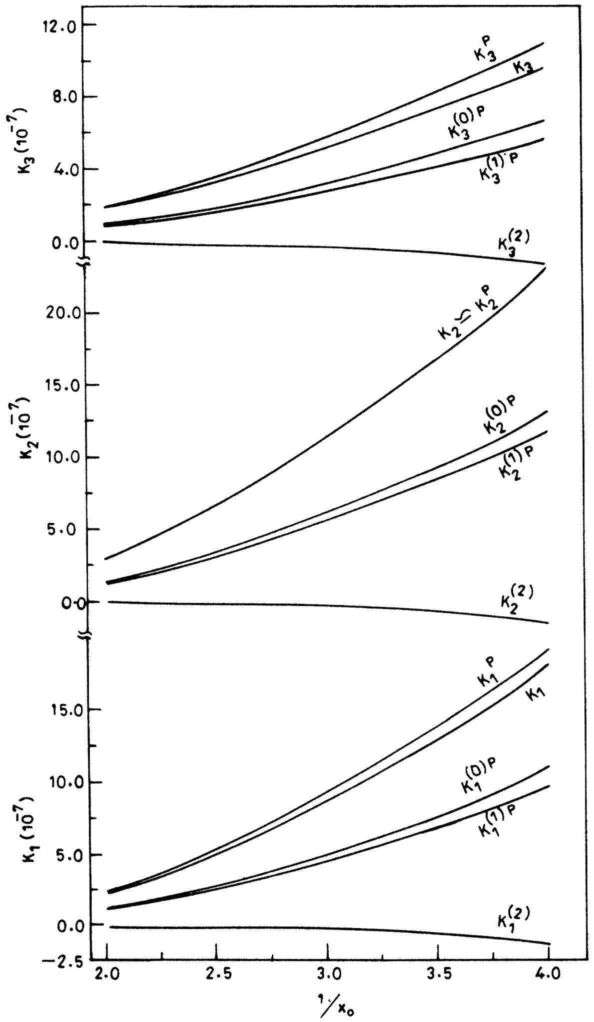

FIG. 6. Same as Fig. 5, but a function of $1/x_0$ for oblate ellipsoids.

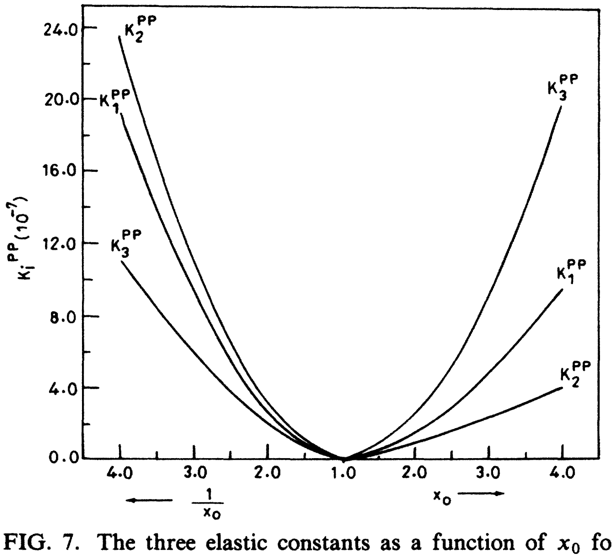

FIG. 7. The three elastic constants as a function of x_0 for prolate and $1/x_0$ for oblate ellipsoids.

cules is never as high as $D_{\infty h}$, the real molecules are more lathlike than cylindrical.[33] Further, the flexibility in the alkyl chain of molecules is believed to be important in many instances.

These topics are all worthy of future quantitative investigation. It would seem most appropriate at present, however, to first develop some information concerning the accuracy of the approach we have presented. The approach is based upon (1) the density-functional formalism and the functional Taylor expansion to express the free energy of a deformed nematic phase in terms of the direct correlation functions of the uniform isotropic liquid of the same number density ρ_0 and (2) the decoupling approximation which expresses the DPCF of a system of ellipsoids of revolution in terms of DPCF of a system of hard spheres.

The truncation of the series (2.12) or (4.7) at an early stage is bound to introduce large error. This fact, as pointed out above, has been ignored in most of the published work.[4–11] The number of terms explicitly considered here and the use of the [1,0] Padé approximant make our calculation reliable.

Though the decoupling approximation introduces anisotropy in the pair correlation function and is exact at very low density, it cannot be exact at liquid density. It is easy to see that when two molecules are parallel, c is most anisotropic and the surfaces of constant c are prolate spheroids of axial ratio x_0, with the long axes of spheroids pointing along $\hat{e}_1$ and $\hat{e}_2$. When $\hat{e}_1 \perp \hat{e}_2$, c is most isotropic, the surfaces of constant c are then oblate spheroids with the symmetry axis along $\hat{e}_1 \times \hat{e}_2$, the axial ratio of this spheroid being $\frac{1}{2}(1+x_0^2)^{1/2}<x_0$. It therefore seems that the decoupling approximation overemphasizes the anisotropy in DPCF for the parallel configuration and underestimates that for perpendicular configurations.

The decoupling approximation has, however, been found to yield the values of the compressibility factor in very good agreement with the computer simulation results.[14,15] This justifies the use of it for the DPCF for a system of hard ellipsoids.

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