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# Density-functional theory of curvature elasticity in nematic liquids. II. Effect of long-range dispersion interactions

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The theory of curvature elasticity in nematics described in earlier papers is reformulated and simplified. The extent to which the "splay," twist, and "bend" constants $(K_1,K_2,K_3)$ of nematic liquid crystals differ from one another and the way they depend upon the degree of alignment (as characterized by the nematic order parameters $\overline{P}_n$) are determined by the structure of the medium which in turn is characterized by the correlation functions. The direct correlation functions of the isotropic liquid in terms of which the elastic constants are expressed have broad functional similarities for systems with rather different intermolecular potentials. An approximate scheme is proposed to estimate the values of the direct pair correlation function. Numerical results for the elastic constants are presented for a range of hard-core sizes and shapes and dispersional strengths and anisotropies. It is found that the effect of the long-range dispersion interactions on the elastic constants is determined not only by the angle-dependent part of the forces, but, and more significantly, by the coupling between the isotropic part and anisotropic hard-core repulsions through the pair correlation function. The attractive interactions are found to make significant contributions to $K_i$ in ordinary nematics (nematics of rod-shaped molecules) when $x_0$ (length-to-width ratio) is small ($\lesssim 3.0$) and in discotic nematics when $1/x_0$ is large (i.e., $\gtrsim 3.0$). Qualitative features exhibited by our calculation for both the ordinary and the discotic nematics are in agreement with the experiment.

## I. INTRODUCTION

The Frank elastic constants are a measure of the 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 director $\hat{n}(\mathbf{r})$, the free energy associated with the distortion is written as[1]

$$\Delta F_d=\tfrac{1}{2}\int d\mathbf{r}[K_1(\nabla\cdot\hat{n})^2+K_2(\hat{n}\cdot\nabla\times\hat{n})^2+K_3(\hat{n}\times\nabla\times\hat{n})^2]\;, \tag{1.1}$$

where $K_1$, $K_2$, and $K_3$ are elastic constants. The first term in this equation gives energy associated with splay, the second that associated with twist or torsion, and the third that associated with flexion or bend. Thus the Frank elastic constants $K_i$ characterize the free-energy increase associated with the three normal modes of deformation of the oriented nematic state.

The phenomenological theory of Landau and de Gennes,[2] in which the Helmholtz free energy is expressed in powers of the *order parameters* and its gradient, gives

$$K_1=K_3=(2L_1+L_2)\overline{P}_2^{\,2} \text{ and } K_2=2L_1\overline{P}_2^{\,2}\;, \tag{1.2}$$

where $\overline{P}_2=\frac{1}{2}(3\,\overline{\cos^2\theta}-1)$ ($\theta$ being the angle between the director and molecular symmetry axis) and $L_1$ and $L_2$ are phenomenological constants appearing in the Landau free-energy density. The overbar indicates the ensemble average. The above result is obtained by restricting oneself to axially symmetric molecules and expanding the free-energy density up to second order in the order parameter $\overline{P}_2$. Thus, to order $\overline{P}_2^{\,2}$, $K_1=K_3$ and all three elastic constants vary with temperature as $\overline{P}_2^{\,2}$. Experimentally, however, one finds that $0.5<K_3/K_1<3.0$ and $0.5<K_2/K_1<0.8$ for long elongated molecules.[3]

In another approach[4-10] one begins with a model, be it in the form of the molecular shape or of the intermolecular potentials, and proceeds to calculate excess free-energy density due to distortion. These calculations are invariably based on assumptions as to the relative importance of the repulsive and attractive parts of the intermolecular interactions. For a special case of anisotropic dispersion interaction between spherical molecules (Maier-Saupe model), Nehring and Saupe[4] found, up to order $\overline{P}_2^{\,2}$,

$$K_1{:}K_2{:}K_3=5{:}11{:}5\;. \tag{1.3}$$

This is not in agreement with the experimental finding that for long-elongated molecules (i.e., for ordinary nematic phase) $K_2$ is the smallest of the three elastic constants. For discotic nematic, however, $K_2$ is largest. The following general results, first reported by Priest,[5] are found to be in good qualitative agreement with experiment:

$$\begin{aligned}\frac{K_1}{\overline{K}}&=1+\Delta-3\Delta'(\overline{P}_4/\overline{P}_2)\;,\\ \frac{K_2}{\overline{K}}&=1-2\Delta-\Delta'(\overline{P}_4/\overline{P}_2)\;,\\ \frac{K_3}{\overline{K}}&=1+\Delta+\Delta\Delta'(\overline{P}_4/\overline{P}_2)\;,\end{aligned} \tag{1.4}$$

where

$$\bar{K}=\tfrac{1}{3}(K_1+K_2+K_3)$$

and

$$\bar{P}_4=\tfrac{1}{8}(35\,\overline{\cos^4\theta}-30\,\overline{\cos^2\theta}+3)\,.$$

The quantities $\Delta$ and $\Delta'$ are constants depending on molecular properties: In order to calculate them, further approximations have to be made.

The combined effect of repulsive and attractive forces has been considered by Poniewierski and Stecki[11] and Gelbart and Ben-Shaul.[8] In many of the earlier works[4-10] the potential-energy function plays an explicit role, whereas the structure of the liquid crystals (which enters via a variety of considerations concerning excluded volume of correlations, packing geometry, etc.) plays only an implicit one.

The theory described by Singh[12] and others[13] is based on a density-functional approach, which allows one to write a formally exact expression for the free energy in terms of the *direct pair correlation functions.* The direct correlation functions which appear in this expression are functionals of the single-particle density distribution $\rho(\mathbf{x})$, where $\mathbf{x}$ indicates both the position coordinate $\mathbf{r}$ of a molecule and its orientation $\mathbf{\Omega}$, described by Euler angles $\alpha$, $\phi$, and $\psi$. Using the functional Taylor expansion, the direct correlation function of a nonuniform system is expressed in terms of the direct correlation functions of the isotropic liquid[14] at the same number density $\rho$. This procedure is briefly reviewed in Sec. II.

In the previous paper in this series,[15] hereafter referred to as I, we assumed that any change in the *direct pair correlation function* (DPCF) $c_2$ due to distortion is of order $q^2$ (where $q$ is the wave number associated with the distortion) and therefore makes no contribution of order $q^2$ in the free energy. In Sec. II, however, we show that this approximation is not needed.

The purpose of this paper is to present and discuss the contributions of the long-range dispersion interaction to the Frank elastic constants. In I we reported the numerical values of the three elastic constants for systems composed of hard ellipsoids of revolution. In this paper we recalculate them using the formulation described in Sec. II. The model system which we investigate here is described in Sec. III. We also discuss in this section the approximations used for numerical enumerations. The results are presented and discussed in Sec. IV. The paper is concluded in Sec. V with a brief summary and concluding remarks.

## II. BASIC THEORY

The Helmholtz free energy $F$ of a system of nonspherical molecules of arbitrary symmetry contained in a volume $V$ at temperature $T$ is

$$\beta F=\beta F_{\rm id}+H\,, \tag{2.1}$$

where $\beta^{-1}$ is Boltzmann's constant times temperature and $\beta F_{\rm id}$ is the reduced Helmholtz free energy for the ideal gas:

$$\beta F_{\rm id}=\int \rho(\mathbf{x})\{\ln[\rho(\mathbf{x})\Lambda]+\beta u^{e}(\mathbf{x})-1\}d\mathbf{x}\,. \tag{2.2}$$

Here $\Lambda$ is the cube of the thermal wavelength associated with a molecule and $u^{e}(\mathbf{x})$ is the potential at $\mathbf{x}$ due to external field. $H$ 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 $u(\mathbf{x}_i,\mathbf{x}_j)$.

The functional $H$ acts as a generating functional for the correlation functions[16,17]

$$\frac{\delta^n H}{\prod_{i=1}^{n}\delta\rho(\mathbf{x}_i)}=-c_n(\mathbf{x}_1,\ldots,\mathbf{x}_n;\{\rho\})\equiv -c_n\{\rho\}\,, \tag{2.3}$$

where $c_n$ are direct $n$-body correlation functions. The functional dependence of $c_n$ on $\rho(\mathbf{x})$ is indicated by curly brackets { }; $-kTc_1(\mathbf{x}_1;\{\rho\})$ is the solvent-mediated effective potential field acting at $\mathbf{x}_i$. The function $c_2(\mathbf{x}_1,\mathbf{x}_2;\{\rho\})$ is the Ornstein-Zernike direct pair correlation function.

The functional integration of (2.3) for $n=1$ leads to

$$H\{\rho\}=-\int d\mathbf{x}_1\rho(\mathbf{x}_1)\int_0^1 d\alpha\, c_1(\mathbf{x}_1,\alpha\rho(\mathbf{x}_1))\,. \tag{2.4}$$

The parameter $\alpha$ characterizes a path in the space of the density. The existence of the functional $H$ [Eq. (2.3)] guarantees that the above result is independent of the path of integration.[18] In a nonuniform system, $\rho(\mathbf{x})$ is a function of $\mathbf{x}$ (i.e., position and orientation) and $c_n$ a functional of $\rho(\mathbf{x})$.

Since a uniform nematic phase is translationally invariant,

$$\rho(\mathbf{x}_1)=\rho_0 f(\mathbf{\Omega}_1)\,, \tag{2.5}$$

where $\rho_0$ is the mean number density and $f(\mathbf{\Omega}_1)$ is the singlet orientational distribution function normalized to unity,

$$\int f(\mathbf{\Omega}_1)d\mathbf{\Omega}_1=1\,. \tag{2.6}$$

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

Any deformation in the liquid crystal will cause the orientational distribution to be distorted in space from whatever form it had in the perfectly 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, $f$ has the same uniaxial form with only the axis varying, we write

$$f(\mathbf{r},\mathbf{\Omega})=f_0(\mathbf{r},\mathbf{\Omega})[1+t(\mathbf{r}_1,\mathbf{\Omega})]\,, \tag{2.7}$$

where

$$f_0(\mathbf{r},\mathbf{\Omega})\equiv f(\hat{\mathbf{e}}\cdot\hat{n}(\mathbf{r}))\,. \tag{2.8}$$

The term in $t$ in (2.7) represents the stress-induced changes in the form of the distribution function. In the case of long-wavelength distortion this term makes no contribution to the Frank elastic constants. In (2.8), $\hat{\mathbf{e}}$ is a unit vector along a molecular symmetry axis and $\hat{n}(\mathbf{r})$ is the local director.

Functional Taylor expansion is used to express the direct one-particle correlation function of a distorted nematic phase in terms of the direct correlation functions of the isotropic liquid at the same number density $\rho_0$. Thus

$$
\begin{aligned}
c_1(\mathbf{x}_1,\{\rho\}) = {} & c_1(\mathbf{x}_1,\rho_0) + \sum_{n=2}^{\infty} \frac{1}{(n-1)!} \int \sum_{i=2}^{n} [d\mathbf{x}_i \delta\rho_0(\mathbf{x}_i)] c_n(\rho_0) + \int d\mathbf{x}_2 [\delta\rho(\mathbf{x}_2) - \delta\rho_0(\mathbf{x}_2)] c_2(\rho_0) \\
& + 2 \int d\mathbf{x}_2 \int d\mathbf{x}_3 \rho_0(\mathbf{x}_3) [\delta\rho(\mathbf{x}_2) - \delta\rho_0(\mathbf{x}_2)] c_3(\rho_0) \\
& + \int d\mathbf{x}_2 \int d\mathbf{x}_3 [\delta\rho(\mathbf{x}_2) - \delta\rho_0(\mathbf{x}_2)][\delta\rho(\mathbf{x}_3) - \delta\rho_0(\mathbf{x}_3)] c_3(\rho_0) + \cdots \;, \qquad (2.9)
\end{aligned}
$$

where

$$
\begin{aligned}
& \delta\rho(x_i) \equiv \rho(\mathbf{x}_i) - \rho_0 = \rho_0(f_0(\mathbf{r}_i,\mathbf{\Omega}_i) - 1) \;, \\
& \delta\rho_0(x_i) \equiv \rho_0(f(\mathbf{r}_1,\mathbf{\Omega}_i) - 1) \;, \qquad (2.10)
\end{aligned}
$$

and

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

Substitution of Eq. (2.9) in (2.4) and (2.1) leads to

$$
\beta F = \beta F_u + \beta \Delta F_d \;, \qquad (2.11)
$$

where

$$
\beta F_u = \beta F_{\mathrm{id}} + H(\rho_0) - \sum_{n=2} \frac{1}{n!} \int \prod_{i=1}^{n} [d\mathbf{x}_i \delta\rho_0(\mathbf{x}_i)] c_n(\rho_0) \qquad (2.12)
$$

and

$$
\begin{aligned}
\beta \Delta F_d = {} & -\tfrac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \delta\rho_0(\mathbf{x}_1) [\delta\rho(\mathbf{x}_2) - \delta\rho_0(\mathbf{x}_2)] c_2(\rho_0) - \tfrac{1}{3} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \int d\mathbf{x}_3 \delta\rho_0(\mathbf{x}_1) \delta\rho_0(\mathbf{x}_2) [\delta\rho(\mathbf{x}_2) - \delta\rho_0(\mathbf{x}_2)] c_3(\rho_0) \\
& - \tfrac{1}{6} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \int d\mathbf{x}_3 \delta\rho_0(\mathbf{x}_1) [\delta\rho(\mathbf{x}_2) - \delta\rho_0(\mathbf{x}_2)][\delta\rho(\mathbf{x}_3) - \delta\rho_0(\mathbf{x}_3)] c_3(\rho_0) + \cdots \;, \qquad (2.13)
\end{aligned}
$$

with

$$
H(\rho_0) = -\rho_0^2 \int d\mathbf{x}_1 \int d\mathbf{x}_2 \int_0^{\alpha} d\alpha' c_2(\alpha' \rho_0) \;.
$$

Here the quantity $\beta F_u$ is the reduced Helmholtz free energy of the undistorted nematic phase with preferred axis corresponding to that at $\mathbf{r}_i$ and which remains constant throughout the sample. $\beta \Delta F_d$ is the free energy associated with the distortion. It may be noted that $\beta \Delta F_d$ is expressed here in terms of $c_n(\rho_0)$, whereas in I it is expressed in terms of

$$
\bar{c}_n(\rho_0) = \int_0^1 d\alpha \int_0^{\alpha} d\alpha' c_n(\alpha' \rho_0) \;. \qquad (2.14)
$$

As mentioned above, in I we replaced $c_2\{\rho\}$ of a distorted nematic by $c_2(\rho_0 f(\mathbf{\Omega}))$ of a uniform nematic on the grounds that the change in $c_2$ due to distortion makes no contribution to $\beta \Delta F_d$. The derivation given here is free from this assumption and is therefore more rigorous.

We followed a method described in I to derive expressions for the Frank elastic constants from the expression of $\beta \Delta F_d$. The result is

$$
K_i = K_i^{(0)} + K_i^{(1)} + \cdots \;, \qquad (2.15)
$$

where

$$
K_i^{(0)} = -\rho_0^2 kT \int d\mathbf{r}_{12} \int d\mathbf{\Omega}_1 \int d\mathbf{\Omega}_2 r_{12}^2 \delta f(\mathbf{\Omega}_1,0) F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2) c_2(\rho_0) \;, \qquad (2.16)
$$

$$
K_i^{(1)} = -\tfrac{2}{3} \rho_0^3 kT \int d\mathbf{r}_{12} \int d\mathbf{r}_3 \int d\mathbf{\Omega}_1 \int d\mathbf{\Omega}_2 \int d\mathbf{\Omega}_3 r_{12}^2 \delta f(\mathbf{\Omega}_1,0) \delta f(\mathbf{\Omega}_3,0) F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2) c_3(\rho_0) \;. \qquad (2.17)
$$

Here

$$
F_i(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2) = f'(\mathbf{\Omega}_2,0) \left\{ \begin{array}{cc} -(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{x}}) & (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{z}}) \\ \multicolumn{2}{c}{0} \\ (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{x}}) & (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{z}}) \end{array} \right\} + \tfrac{1}{2} f''(\mathbf{\Omega}_2,0) \left\{ \begin{array}{c} (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{x}})^2 \\ (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{y}})^2 \\ (\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{z}})^2 \end{array} \right\} \qquad (2.18)
$$

and $\delta f(\boldsymbol{\Omega}_i,0)=f(\boldsymbol{\Omega}_i,0)-1$. $i$ stands for 1,2,3 and $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ stand for unit vectors along the specified $X$, $Y$, and $Z$ axes:

$$f'(\boldsymbol{\Omega}_2,0)=\sum_L \bar{P}_L[Y_{L,1}(\boldsymbol{\Omega}_2)-Y_{L,-1}(\boldsymbol{\Omega}_2)]P'_{L,1}(1)\ , \tag{2.19}$$

$$f''(\boldsymbol{\Omega}_2,0)=\sum_L \bar{P}_L\{Y_{L,0}(\boldsymbol{\Omega}_2)P''_{L,0}(1) + [Y_{L,2}(\boldsymbol{\Omega}_2)+Y_{L,-2}(\boldsymbol{\Omega}_2)]\}P''_{L,2}(1)\ , \tag{2.20}$$

where

$$\begin{aligned} P''_{L,0}(1)&=-\tfrac{1}{2}L(L+1)\left[\frac{2L+1}{4\pi}\right]^{1/2}, \\ P'_{L,1}(1)&=-P'_{L,-1}(1) \\ &=-\tfrac{1}{2}L(L+1)\left[\frac{(L-1)!}{(L+1)!}\frac{2L+1}{4\pi}\right]^{1/2}, \\ P''_{L,2}(1)&=P''_{L,-1}(1) \\ &=\tfrac{1}{4}(L-1)L(L+1)(L+2)\left[\frac{(L-2)!}{(L+2)!}\frac{2L+1}{4\pi}\right]^{1/2}. \end{aligned} \tag{2.21}$$

Since isotropic liquid is translationally invariant, the direct correlation functions $c_2$ and $c_3$ appearing in (2.16) and (2.17) depend only on the relative separation of molecules and not on their individual positions. Thus

$$\begin{aligned} c_2(\rho_0)&=c_2(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2;\rho_0)\ , \\ c_3(\rho_0)&=c_3(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2,\boldsymbol{\Omega}_3;\rho_0)\ . \end{aligned} \tag{2.22}$$

Since our knowledge of the direct three-body correlation functions is meager even for atomic fluids, we use the following relation to simplify the terms involving them:

$$\frac{\partial c_2(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)}{\partial\rho_0} =\int\int c_3(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2,\boldsymbol{\Omega}_3)d\mathbf{r}_3 d\boldsymbol{\Omega}_3\ . \tag{2.23}$$

## III. APPROXIMATIONS AND DERIVATION OF WORKING EQUATIONS

### A. Pair potential model

Let the model system under investigation be fully described by a potential function which depends on orientations and relative centers-of-mass coordinates of molecules but is independent of rotational momenta and internal vibrational states. Since the flexibility of liquid-crystal-forming molecules (particularly in their alkyl end chains) is believed to be important in many instances, the assumption that the molecules are rigid may not be realistic. It may also be remembered that the symmetry of the nematogenic molecules is never as high as $D_{\infty,h}$; real molecules are more lathlike than cylindrical. However, for many real systems, the terms in the pair potential energy which result from deviations from cylindrical symmetry are small and can be treated by perturbation. Moreover, as shown in Sec. II, the potential function does not appear explicitly in our formulation. It appears only through the direct correlation functions. The direct correlation functions are found to have broad functional similarities for systems with rather different intermolecular potentials and it is relatively easy to guess a form for them which mimics the essential feature of the system.

The pair potential function is assumed to have the form

$$u(\mathbf{x}_1,\mathbf{x}_2)=u_0(\mathbf{x}_1,\mathbf{x}_2)+u_a(\mathbf{x}_1,\mathbf{x}_2)\ . \tag{3.1}$$

Here $u_0(\mathbf{x}_1,\mathbf{x}_2)$ represents the repulsion between hard ellipsoids of revolution parametrized by the length-to-width ratio $x_0=a/b$, where $2a$ and $2b$ denote, respectively, the lengths of the major (axis of revolution) and minor axes of the ellipsoids. $u_a(\mathbf{x}_1,\mathbf{x}_2)$ represents the long-range attraction.

For $u_0$ we choose

$$u_0(\mathbf{x}_1,\mathbf{x}_2)\equiv u_0(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2) =\begin{cases}\infty & \text{for } r_{12}\lesssim D(\boldsymbol{\Omega}_{12})\\ 0 & \text{for } r_{12}>D(\boldsymbol{\Omega}_{12}),\end{cases} \tag{3.2}$$

where $D(\boldsymbol{\Omega}_{12})$ $[\equiv D(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_{12})]$ is the distance of closest approach of two molecules with relative orientation given by $\boldsymbol{\Omega}_{12}$. For $D(\boldsymbol{\Omega}_{12})$ we use the expression given by Berne and Pechukas,[19]

$$D(\boldsymbol{\Omega}_{12})=2b\left[1-\chi\frac{(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)^2+(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)^2-2\chi(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)}{1-\chi^2(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)^2}\right]^{-1/2}, \tag{3.3}$$

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

The $u_a$ is assumed to have the following form:

$$u_a(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)=-\frac{c_i}{r_{12}^6}-\frac{c_a}{r_{12}^6}P_2(\cos\theta_{12})\ , \tag{3.4}$$

where $c_i$ and $c_a$ are constants related to the isotropic and anisotropic dispersion interactions and $\theta_{12}$ is the angle between the symmetry axes of the two molecules. The effect of the slowly varying attractive potential on the structure of the liquid is small and can be approximated by the first-order perturbation.

A system interacting via a pair potential $u_0$ will henceforth be referred to as a reference system and the potential $u_a$ a perturbation potential.

### B. The direct correlation functions and decoupling approximations

The correlation functions appearing in (2.15)—(2.18) are not known even for a system of hard ellipsoids of revolution. The solutions of the integral equations of a liquid-state theory such as the hypernetted chain equation, the Percus-Yevick (PY) equation, the mean spherical approximation, or the optimized random-phase approximation are difficult and time consuming to obtain.[20]

In I we used an approximation for the DPCF of a system interacting via a pair potential $u_0$, in which we took the Wertheim-Thiele[21] analytic solution of the PY equation for a system of hard spheres of diameter $d_0$ and replaced the diameter $d_0$ by the distance of closest approach $D(\Omega_{12})$, i.e.,

$$c_2^{(0)}(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)=c_2^{(0)}(r_{12}/D(\Omega_{12}))$$

$$=\begin{cases} a_1+b_1r_{12}^*+\frac{1}{2}\eta a_1(r_{12}^*)^3 & \text{for } r_{12}^*\lesssim 1\\ 0 \quad \text{for } r_{12}^*>1, \end{cases} \tag{3.5}$$

where

$$r_{12}^*=r_{12}/D(\Omega_{12})\ .$$

$$a_1=-(1+2\eta)^2/(1-\eta)^4\ ,$$

$$b_1=6\eta(1+\tfrac{1}{2}\eta)^2/(1-\eta)^4\ ,$$

and $\eta=\rho_0 v$, $v=(\pi/6)x_0(2b)^3$, the molecular volume. As explained elsewhere,[15,22] this approximation decouples the translational and orientational degrees of freedom and is therefore called the decoupling approximation. This form of the DPCF for hard ellipsoids of revolution gives reasonable results for the Frank elastic constants[15] and the isotropic-nematic as well as isotropic-plastic transitions.[22]

In order to obtain the DPCF for a system interacting via a pair potential $u$, we adopt the following perturbation scheme. We noted earlier that $H$ is functional of pair potential $u$ and satisfies the following relation:[16,17]

$$\frac{\delta H}{\delta u(\mathbf{x}_1,\mathbf{x}_2)}=\tfrac{1}{2}\beta\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)g(\mathbf{x}_1,\mathbf{x}_2)\ . \tag{3.6}$$

The functional integration of (3.6) leads to

$$H\{\rho,u\}=H\{\rho,u_0\}+\tfrac{1}{2}\beta\int_0^1 d\lambda\int d\mathbf{x}_1\int d\mathbf{x}_2\,\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)u_a(\mathbf{x}_1,\mathbf{x}_2)g(\mathbf{x}_1,\mathbf{x}_2;\lambda)\ , \tag{3.7}$$

where $H\{\rho,u_0\}$ represents the reduced excess free energy of the reference system as a functional of $\rho(\mathbf{x})$ which is held fixed during the process of increasing $u_a$. $\lambda$ is a perturbation parameter defined by the relation

$$u(\mathbf{x}_1,\mathbf{x}_2,\lambda)=u_0(\mathbf{x}_1,\mathbf{x}_2)+\lambda u_a(\mathbf{x}_1,\mathbf{x}_2)\ . \tag{3.8}$$

Clearly, $\lambda=0$ describes the reference system of hard ellipsoids of revolution and $\lambda=1$ the physical system of interest. The single-particle density distribution function $\rho(\mathbf{x})$ is held fixed in (3.7) as the perturbation potential is switched on.

Equation (3.7) is exact. Its evaluation, however, requires knowledge of the pair distribution function $g(\mathbf{x}_1,\mathbf{x}_2;\lambda)$ for a system interacting via a pair potential (3.8) at fixed density $\rho(\mathbf{x})$. Simple perturbation theory for the pair correlation function leads to

$$g(\mathbf{x}_1,\mathbf{x}_2;\lambda)=g^{(0)}(\mathbf{x}_1,\mathbf{x}_2)+\lambda[\delta g(\mathbf{x}_1,\mathbf{x}_2)]_0+\cdots\ , \tag{3.9}$$

where $g^{(0)}(x_1,x_2)$ is the pair correlation function of the reference system and $\delta g(\mathbf{x}_1,\mathbf{x}_2)$ the first-order perturbation correction. When this is substituted in (3.7) we obtain the reduced excess free energy correct to first order in perturbation

$$H\{\rho,u\}=H\{\rho,u_0\}+\tfrac{1}{2}\beta\int d\mathbf{x}_1\int d\mathbf{x}_2\,\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)\times u_a(\mathbf{x}_1,\mathbf{x}_2)g^{(0)}(\mathbf{x}_1,\mathbf{x}_2)\ . \tag{3.10}$$

From relation (2.3) for $n=2$ and (3.10) we get

$$c_2(\mathbf{x}_1,\mathbf{x}_2)=c_2^{(0)}(\mathbf{x}_1,\mathbf{x}_2)-\beta u_a(\mathbf{x}_1,\mathbf{x}_2)g^{(0)}(\mathbf{x}_1,\mathbf{x}_2)+\cdots\ , \tag{3.11}$$

where $c_2^{(0)}$ is the DPCF for the reference system. If $g^0(\mathbf{x}_1,\mathbf{x}_2)$ is taken equal to unity, (3.11) reduces to

$$c_2(\mathbf{x}_1,\mathbf{x}_2)=c_2^{(0)}(\mathbf{x}_1,\mathbf{x}_2)-\beta u_a(\mathbf{x}_1,\mathbf{x}_2)\ , \tag{3.12}$$

which is equivalent to the random-phase approximation (RPA) for the structure factor.[23] We can therefore call (3.11) the extended random-phase approximation (ERPA). It may, however, be noted that the RPA or ERPA has a drawback in that it predicts a distribution function $g(\mathbf{x}_1,\mathbf{x}_2)$ which can be nonzero inside the hard core. This unphysical feature of the RPA is remedied by means of a self-consistency requirement[24] or by an optimization procedure.[25] Such a procedure is not attempted here because the ERPA gives good accounts of the thermodynamic properties.

In the decoupling approximation,

$$\begin{aligned} g^{(0)}(\mathbf{x}_1,\mathbf{x}_2) &\equiv g^{(0)}(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2) \\ &= g^{(0)}(r_{12}/D(\Omega_{12})) \\ &= g^{(0)}_{\rm hs}(r^*_{12}) \, , \end{aligned} \tag{3.13}$$

where $g^{(0)}_{\rm hs}(r^*_{12})$ is the radial distribution function of a fluid of hard spheres at packing fraction $\eta=\rho_0 v$. The decoupling approximation, as has been discussed in I and elsewhere,[22] is good for calculating the thermodynamic properties of the isotropic liquid but appears to overemphasize the anisotropy in the pair correlation function for a parallel configuration of molecules and underestimates it for a perpendicular configuration. This defect of the decoupling approximation does not appear to be of serious consequence in the calculation of the elastic constants.

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

$$\begin{aligned} & c_3(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23};\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2,\boldsymbol{\Omega}_3) \\ &\quad = c_3\left[\frac{r_{12}}{D(\Omega_{12})},\frac{r_{13}}{D(\Omega_{13})},\frac{r_{23}}{D(\Omega_{23})}\right] \\ &\quad = c_3(r^*_{12},r^*_{13},r^*_{23}) \, . \end{aligned}$$

### C. The Frank elastic constants in the decoupling approximation

The Frank elastic constant can be written as

$$K_i=\sum_n (K^{(n)}_{i,r}+K^{(n)}_{i,a}) \, , \tag{3.14}$$

where subscripts $r$ and $a$ indicate, respectively, the contributions arising from the repulsive and attractive parts of the interaction. In the decoupling approximation, their expression reduces to

$$K^{(0)}_{i,r}=-\rho_0^2 kT\hat{c}_2(\rho_0)\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2\int d\hat{\mathbf{r}}_{12}\delta f(\boldsymbol{\Omega}_1,0)F_i(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)D^5(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_{12}) \, , \tag{3.15}$$

$$\begin{aligned} K^{(1)}_{i,r}=-\tfrac{2}{3}\rho_0^3 kT\hat{c}\,'_2(\rho_0)\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2\int d\boldsymbol{\Omega}_3\delta f(\boldsymbol{\Omega}_1,0)\delta f(\boldsymbol{\Omega}_3,0)\int d\hat{\mathbf{r}}_{12}D^4(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_{12})F_i(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2) & \\ \times\int d\hat{\mathbf{r}}_{13}D^2(\hat{\mathbf{r}}_{13},\boldsymbol{\Omega}_{13})\int d\hat{\mathbf{r}}_{23}D^2(\hat{\mathbf{r}}_{23},\boldsymbol{\Omega}_{23}) \, , & \end{aligned} \tag{3.16}$$

$$K^{(0)}_{i,a}=-\rho_0^2 I_4(\rho^*)\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2\int d\hat{\mathbf{r}}_{12}\delta f(\boldsymbol{\Omega}_1,0)F_i(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)[c_i+c_a P_2(\cos\theta_{12})]D^{-1}(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_{12}) \, , \tag{3.17}$$

and

$$\begin{aligned} K^{(1)}_{i,a}=-\tfrac{2}{3}\rho_0^3 I'_4(\rho^*)\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2\int d\boldsymbol{\Omega}_3\delta f(\boldsymbol{\Omega}_1,0)\delta f(\boldsymbol{\Omega}_3,0)\int d\hat{\mathbf{r}}_{12}\int d\hat{\mathbf{r}}_{13}\int d\hat{\mathbf{r}}_{23}F_i(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)D^2(\hat{\mathbf{r}}_{13},\boldsymbol{\Omega}_{13})D^2(\hat{\mathbf{r}}_{23},\boldsymbol{\Omega}_{13}) & \\ \times D^{-2}(\hat{\mathbf{r}}_{12},\boldsymbol{\Omega}_{12})[c_i+c_a P_2(\cos\theta_{12})] \, . & \end{aligned} \tag{3.18}$$

Here

$$\begin{aligned} \hat{c}_2(\rho_0) &= \int_0^1 dr^*_{12}(r^*_{12})^4 c_2(r^*_{12},\rho_0) \\ &= -\frac{4\eta^2-11\eta+16}{80(1-\eta)^4} \, , \\ \hat{c}\,'_2(\rho_0) &= \frac{\delta c_2(\rho_0)}{\delta\rho_0} \, , \end{aligned} \tag{3.19}$$

and

$$I_4(\rho^*)=\int_0^\infty (r^*_{12})^{-2} g^{(0)}_{\rm hs}(r^*_{12})dr^*_{12} \, . \tag{3.20}$$

$I_4(\rho^*)$ is obtained from the exact radial distribution function for hard spheres generated from computer simulations. Combining the known density expansion for $g^{(0)}_{\rm hs}(r^*_{12})$ and the Monte Carlo values, Larsen *et al.*[26] have found the following series for $I_4(\rho^*)$:

$$\begin{aligned} I_4(\rho^*)=\frac{1}{4\pi}[12.5664+3.8894\rho^*-0.0817(\rho^*)^2 & \\ -0.0845(\rho^*)^3+0.7512(\rho^*)^4-0.6802(\rho^*)^5] \, , & \end{aligned} \tag{3.21}$$

where

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

$$I'_4(\rho^*)=\frac{\delta I_4(\eta)}{\delta\eta} \, .$$

## IV. RESULTS AND DISCUSSIONS

Our theory involves expansion to increasingly higher order in the direct correlation functions. Thus

$$K_i=\sum_{n=0}^{\infty} K^{(n)}_i \, , \tag{4.1}$$

where $K^{(0)}_i$ contains the pair correlation function, $K^{(1)}_i$ the three-body correlation function, and so on. The contribution to each elastic constant arising from $K^{(0)}_i$ is written as a double sum over contributions which are quadratic in the order parameters $\overline{P}_L$, i.e.,

$$K^{(0)}_i=\sum_L{}'\sum_{L'}{}' K^{(0)}_i(L,L') \, . \tag{4.2}$$

The prime on the summation in (4.2) indicates the restriction that only even $L$ has to be considered. The odd terms vanish because molecules do not distinguish "up" from "down." $K^{(1)}_i$ is expressed as a triplet sum over contributions which are cubic in the order parameter $\overline{P}_L$:

$$K^{(1)}_i=\sum_L{}'\sum_{L'}{}'\sum_{L''}{}' K^{(1)}_i(L,L',L'') \, . \tag{4.3}$$

From symmetry considerations one finds

$$K^{(0)}_i(L,L')=K^{(0)}_i(L',L) \, ,$$

$$K^{(1)}_i(L,L',L'')=K^{(1)}_i(L',L,L'')=K^{(1)}_i(L'',L',L) \, ,$$

etc., for all $i,n$ and $L,L',L''$. Thus each term of the series (4.2) and (4.3) can be written, respectively, as

$$K_i^{(0)}=K_i^{(0)}(2,2)+2K_i^{(0)}(2,4)+\cdots\ , \tag{4.4a}$$

$$K_i^{(1)}=K_i^{(1)}(2,2,2)+\cdots\ , \tag{4.4b}$$

where $K_i^{(0)}(L,L')\propto\overline{P}_L\overline{P}_{L'}$ and $K_i^{(1)}\propto\overline{P}_L\overline{P}_{L'}\overline{P}_{L''}$. Since $\overline{P}_2>\overline{P}_4>\overline{P}_6\cdots$ and $\overline{P}_4/\overline{P}_2\simeq0.25$ for a typical nematic, we evaluate only those terms which are written explicitly in the series (4.4). The computational method adopted here is described in detail in I.

In Tables I and II we list the contribution of individual terms of the series (4.1) and (4.4) for $x_0=3.0$ and $x_0=1/3.0$, respectively, for systems of prolate and oblate molecules. All the results tabulated and graphed here are for $\overline{P}_2=0.5$, $\overline{P}_4=0.15$, $\eta=0.45$, $c_i=1.0\times10^{-56}$ erg cm$^6$, and $c_a/c_i=0.05$. For prolate molecules we take $T=400$ K and $2b=5.0$ Å. These parameters with $x_0=3.0$ crudely simulate an ordinary nematic phase (nematic phase of elongated molecules) of PAA (para-azoxyanisole). The temperature 400 K lies in the middle of the thermal range (390—408 K) of the nematic phase of PAA at atmospheric pressure. A PAA molecule can roughly be taken to be 15 Å long and 5 Å wide. Though the geometry of the molecule is not strictly ellipsoidal, it can roughly be approximated to be a prolate ellipsoid of revolution of $x_0=3.0$.

A system having flat disclike molecules exhibits a discotic nematic phase.[27] This phase is distinguished from ordinary nematics by indications of the anisotropy of the dielectric permittivity and other tensor characteristics. With $T=600$ K, $2b=15$ Å, and $x_0=1/3.0$, we may crudely simulate a discotic nematic phase of hexa-$n$-hexyloxy benzoate ($n=4$) of triphenylene.[27,28]

A number of observations can be made from Tables I and II. The series (4.4a) is found to converge rapidly for both systems of prolate and oblate molecules and for both repulsive and attractive interactions. The terms written explictly in (4.4a), however, are insufficient for systems of large $x_0$ (prolate) and $1/x_0$ (oblate). For a reference system of prolate molecules with $x_0=3.0$, $|\,2K_{i,r}^{(0)}(2,4)/K_{i,r}^{(0)}(2,2)\,|$ is found to be 0.24, 0.17, and 0.32, respectively, for $K_{1,r}^{(0)}$, $K_{2,r}^{(0)}$, and $K_{3,r}^{(0)}$. These numbers for oblate molecules with $x_0=1/3.0$ are 0.19, 0.045, and 0.26, respectively. From these numbers we conclude that the higher-order terms of the series (4.4a) are not negligible, at least for those systems for which the value of $x_0$ deviates considerably from unity. The situation appears better in the case of attractive interactions. For a system of prolate molecules (with $x_0=3.0$), $|\,2K_{i,a}^{(0)}(2,4)/K_{i,a}^{(0)}(2,2)\,|$ is of the order of 0.095, 0.078, and 0.128, respectively, for $i=1$, 2, and 3, whereas for a system of oblate molecules ($x_0=1/3.0$), these numbers are 0.078, 0.037, and 0.102. From these numbers we conclude that the series (4.4a) converges faster for the long-range attractive interactions than the hard-core repulsion.

The contribution of higher-order terms in the series (4.4a) can be approximated with the help of a simple [1,0] Padé approximant. Thus

$$K_i^{(0)P}=K_i^{(0)}(2,2)\left[1-\frac{2K_i^{(0)}(2,4)}{K_i^{(0)}(2,2)}\right]^{-1}. \tag{4.5}$$

These values are also given in Tables I and II and compared with $K_i^{(0)}=K_i^{(0)}(2,2)+2K_i^{(0)}(2,4)$. We find, as argued above, that while the contribution of higher-order terms in the series (4.4a) is almost negligible for the long-range dispersion interactions, for all $x_0$, it is small but not negligible for the hard-core replusion in a system of large anisotropy in the hard-core interaction. This is also obvious from Figs. 1 and 2 in which we plot the contribution of individual terms of the series (4.4a) as a function of $x_0$ and $1/x_0$ for the reference system and the perturbation potential, respectively. We find that as $x_0$ deviates from unity, the contribution of higher-order terms increases; for the perturbation potential, however, $K_i^{(0)P}$ and $K_i^{(0)}$ are almost identical on the graph (Fig. 2) even for $x_0$ (or $1/x_0$)$\simeq5.0$.

One may note from Fig. 2 that while the contribution of the long-range dispersion interactions to the Frank elastic constants decreases with $x_0$ in the system of prolate molecules, it increases with $1/x_0$ in the case of oblate molecules. This trend is reversed from the one found in the case of hard-core repulsion (see Fig. 1). This can be understood from the fact that the major contribution to the $K_{i,a}^{(0)}$ comes from the angle-independent part of the

TABLE I. Contributions of individual terms in the series (4.1) and (4.4) to each elastic constant for both hard-core repulsions and attractive interactions for a system of prolate ($x_0=3.0$) ellipsoids of revolution. For the results shown here, $\overline{P}_2=0.5$, $\overline{P}_4=0.15$, $\eta=0.45$, $T=400$ K, $2b=5$ Å, $c_i=1.0\times10^{-56}$ erg cm$^6$, and $c_a/c_i=0.05$. The values for $K_i$ are given in units of $10^{-7}$ dyn ($K_i=K_{i,r}^{PP}+K_{i,a}^{PP}$; $K_1=12.72$, $K_2=5.77$, $K_3=20.11\times10^{-7}$ dyn).

| | $K_{i,r}$ | | | $K_{i,a}$ | | |
|---|---|---|---|---|---|---|
| | $K_1$ | $K_2$ | $K_3$ | $K_1$ | $K_2$ | $K_3$ |
| $K_i^{(0)}(2,2)$ | 12.97 | 6.28 | 12.97 | 3.26 | 1.28 | 3.26 |
| $2K_i^{(0)}(2,4)$ | −3.15 | −1.05 | 4.20 | 0.31 | 0.10 | −0.42 |
| $K_i^{(0)}$ | 9.82 | 5.23 | 17.17 | 3.57 | 1.38 | 2.84 |
| $K_i^{(0)}P$ | 10.45 | 5.39 | 19.18 | 3.61 | 1.39 | 2.89 |
| $K_i^{(1)}(2,2,2)$ | −1.48 | −1.18 | −2.08 | −0.05 | −0.04 | −0.08 |
| $K_i$ | 8.34 | 4.05 | 15.09 | 3.52 | 1.34 | 2.76 |
| $K_i^P$ | 8.97 | 4.21 | 17.10 | 3.56 | 1.35 | 2.81 |
| $K_i^{PP}$ | 9.16 | 4.42 | 17.30 | 3.56 | 1.35 | 2.81 |

TABLE II. Contributions of individual terms in the series (4.1) and (4.4) to each elastic constant for both hard-core repulsion and attractive interactions for a system of oblate ($1/x_0=3.0$) ellipsoids. For the results shown here, $\bar{P}_2=0.5$, $\bar{P}_4=0.15$, $\eta=0.45$, $T=600$ K, $2b=15.0$ Å, $c_i=1.0\times10^{-56}$ erg cm$^6$, and $c_a/c_i=0.05$. The values for $K_i$ are given in units of $10^{-7}$ dyn. ($K_i=K_{i,r}^{PP}+K_{i,a}^{PP}$; $K_1=8.87$, $K_2=10.63$, $K_3=5.53\times10^{-7}$ dyn).

| | $K_{i,r}$ | | | $K_{i,a}$ | | |
|---|---|---|---|---|---|---|
| | $K_1$ | $K_2$ | $K_3$ | $K_1$ | $K_2$ | $K_3$ |
| $K_i^{(0)}(2,2)$ | 8.12 | 11.45 | 8.12 | 0.343 | 0.241 | 0.343 |
| $2K_i^{(0)}(2,4)$ | 1.57 | 0.52 | −2.09 | −0.027 | −0.009 | 0.035 |
| $K_i^{(0)}$ | 9.69 | 11.97 | 6.03 | 0.316 | 0.232 | 0.378 |
| $K_i^{(0)P}$ | 10.06 | 12.00 | 6.46 | 0.317 | 0.232 | 0.382 |
| $K_i^{(1)}(2,2,2)$ | −1.76 | −1.83 | −1.62 | −0.009 | −0.008 | −0.011 |
| $K_i$ | 7.93 | 10.14 | 4.41 | 0.307 | 0.224 | 0.367 |
| $K_i^P$ | 8.30 | 10.17 | 4.84 | 0.308 | 0.224 | 0.371 |
| $K_i^{PP}$ | 8.56 | 10.41 | 5.16 | 0.308 | 0.224 | 0.371 |

dispersion interactions (see Figs. 5 and 6). Thus, the $K_{i,a}^{(0)}$ emphasize the region where the intermolecular separation is small. The availability of this region decreases with increasing $x_0$ in the case of prolate molecules in which we have fixed $2b$. Contrary to this, the availability of the region of small intermolecular separation increases with increasing $1/x_0$ and keeping $2b$ fixed in a system of oblate molecules.

The magnitude of $K_i^{(1)}(2,2,2)$ is found to be small for both the reference and perturbation potentials and for both the prolate and oblate molecules. This led us to neglect the contribution of higher-order terms in the series

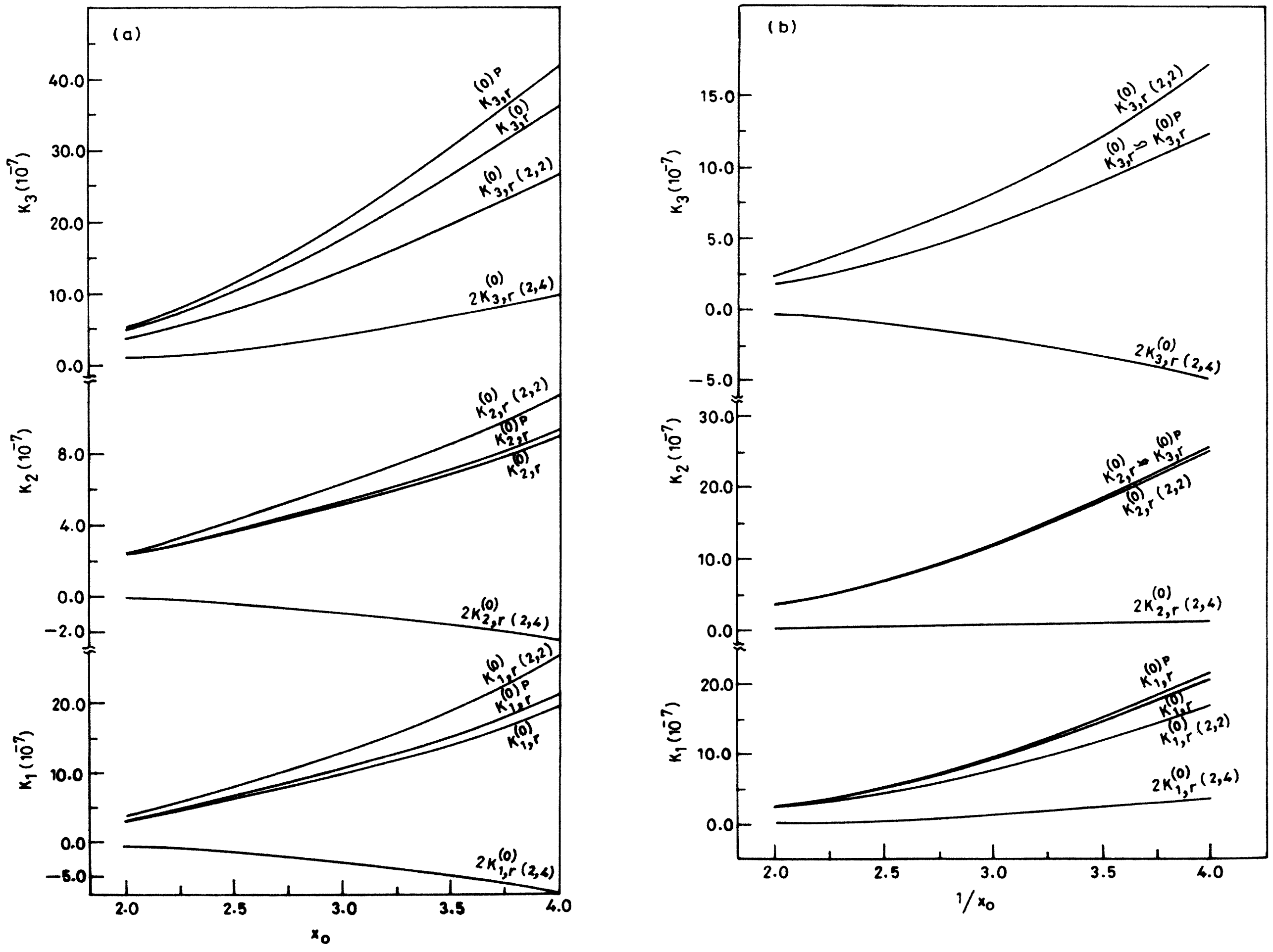

FIG. 1. (a) Contribution of the hard-core repulsion to individual terms of the series (4.4) for each elastic constant, as a function of $x_0$ for prolate ellipsoids. (b) Same as in (a) but as a function of $1/x_0$ for oblate ellipsoids.

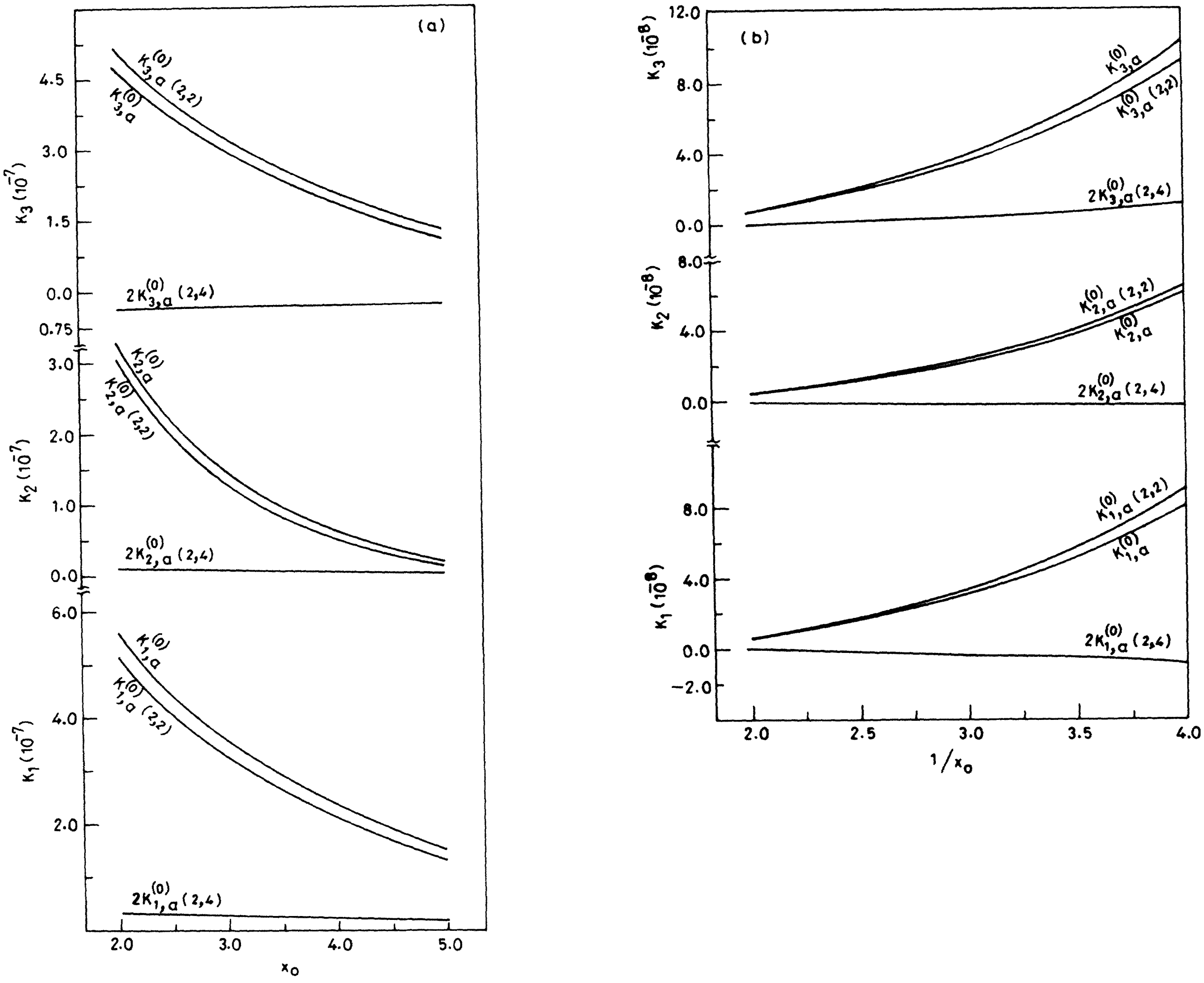

FIG. 2. Contribution of the long-range interactions to individual terms of the series (4.4) for each elastic constant, as a function of $x_0$ for prolate ellipsoids. (b) Same as in (a) but as a function of $1/x_0$ for oblate ellipsoids.

(4.4b).. We believe that the error caused due to this is negligible.

Next we examine the convergence of the series (4.1). $K_i^{(1)}$ is found to be very small compared to $K_i^{(0)}$ for all $i$. For example, the magnitude of $|K_{i,r}^{(1)}/K_{i,r}^{(0)}|$ is found to be of the order of 0.15, 0.22, and 0.12 for a hard ellipsoid of revolution of $x_0=3.0$. For long-range dispersion interactions one finds, for $x_0=3.0$, $|K_{i,a}^{(1)}/K_{i,a}^{(0)}|$ to be of the order of 0.01, 0.03, and 0.03, respectively, for $i=1$, 2, and 3. For oblate molecules with $x_0=1/3.0$ one finds that $|K_{i,r}^{(1)}/K_{i,r}^{(0)}|$ is 0.18, 0.15, and 0.26 and $|K_{i,a}^{(1)}/K_{i,a}^{(0)}|$ is 0.028, 0.034, and 0.029, respectively, for $i=1$, 2, and 3. These numbers indicate that the series (4.1) converges fairly rapidly in both systems. For long-range dispersion interactions, it appears sufficient to truncate the series with its first term. For the hard-core interactions we can apply the [1,0] Padé approximant to assess the contribution of higher-order terms in (4.1). Thus

$$K_{i,r}^{PP}=K_{i,r}^{(0)P}\left[1-\frac{K_{i,r}^{(1)}}{K_{i,r}^{(0)P}}\right]^{-1} \tag{4.6}$$

The last row of Tables I and II lists the values of $K_i^{PP}$. They are compared with $K_i=K_i^{(0)}+K_i^{(1)}$ and $K_i^P=K_i^{(0)P}+K_i^{(1)}$. From these tables and Figs. 3(a) and 3(b), in which we plot the contribution of the individual terms of the series (4.1) as a function of $x_0$ and $1/x_0$, respectively, it is obvious that the contribution of higher-order terms of the series (4.1) is small even for hard-core repulsion.

In Figs. 4(a) and 4(b) we compare the contributions arising from the long-range dispersion interactions and the hard-core repulsion to the Frank elastic constants. The contributions are plotted as a function of $x_0$ and $1/x_0$, respectively. We find that in a system of prolate molecules with small $x_0\lesssim 4.0$, the attractive interactions make a substantial contribution to the elastic constants. As $x_0$ increases, the repulsive interaction dominates. For $x_0\gtrsim 5.0$, the contribution of the attractive interactions appears to be negligible. In the case of oblate molecules, the relative contribution of the dispersion interactions increases with $1/x_0$. It becomes measurable only after $1/x_0\gtrsim 3.0$. At small values of $1/x_0$ the contribution is negligible. From Figs. 4(a) and 4(b) it appears that while for prolate molecules the contribution of the attractive interactions must be included (especially if $x_0\lesssim 4.0$) in the

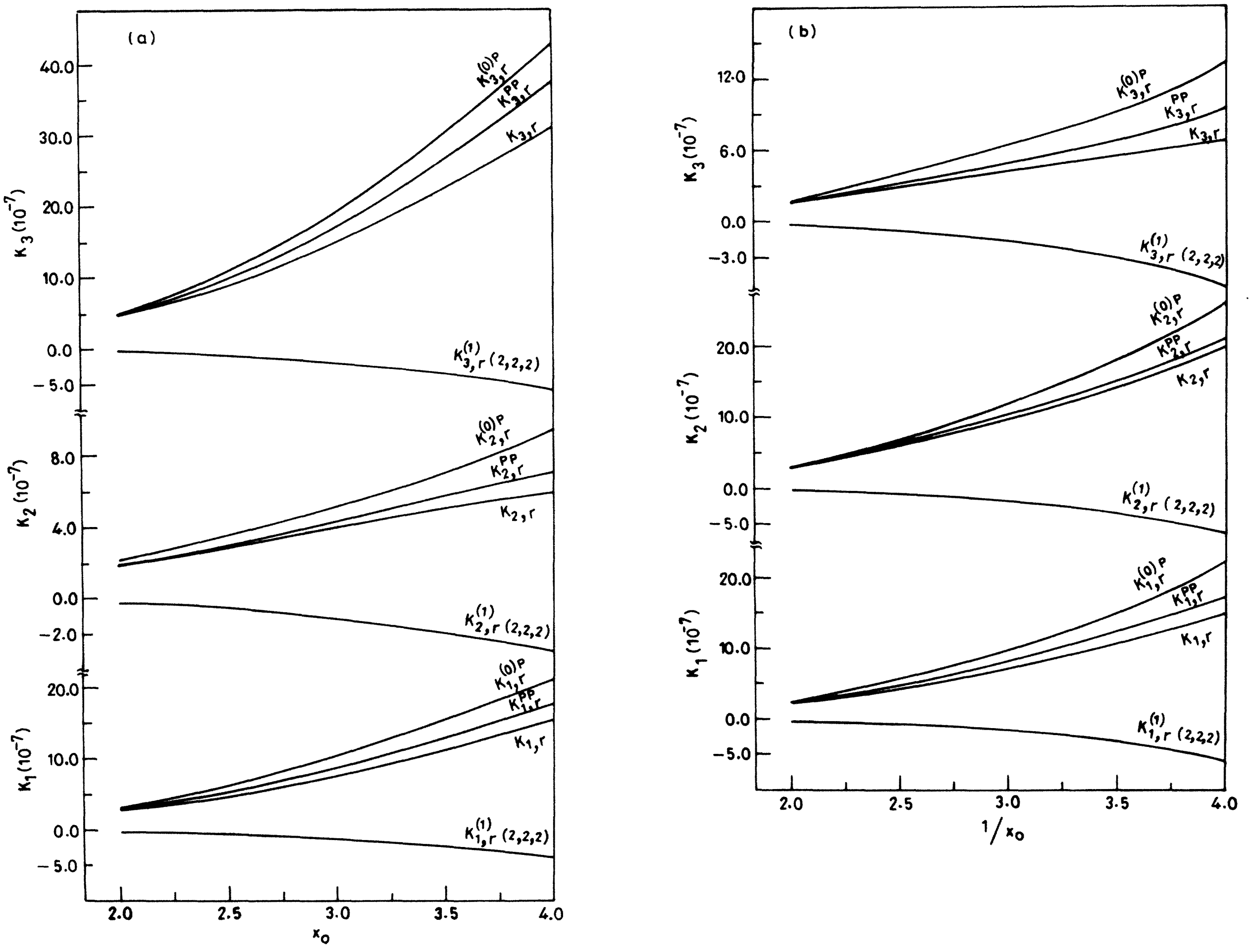

FIG. 3. (a) Contribution of the hard-core repulsion to individual terms of the series (4.1) for each elastic constant, as a function of $x_0$ for prolate ellipsoids. (b) Same as in (a) but as a function of $1/x_0$ for oblate ellipsoids.

calculation of the elastic constants, it may be neglected for a system of oblate molecules if $x_0 \gtrsim 0.34$.

Figures 5(a) and 5(b) give the values of $K_i$ as a function of $c_a/c_i$. It is seen from these figures that for both systems, the $K_i$ are insensitive to the magnitude of the anisotropic dispersion interaction. But the $K_i$ are sensitive to the magnitude of the isotropic dispersion interaction. This is shown in Figs. 6(a) and 6(b) in which we plot $K_i$ as a function of $c_i$ for a given $c_a/c_i$ $(=0.05)$ for the system of prolate and oblate molecules. The coupling between the isotropic attraction and anisotropic hard-core repulsion through the pair correlation function is responsible for this contribution. This coupling was neglected in theories based on the Maier-Sanpe model, but it was featured, for example, in the generalized van der Waal's treatment of Gelbart and Ben-Shaul.[8]

In agreement with the results reported in I and elsewhere,[5] we find that for a system of prolate ellipsoids, $K_i^{(0)}(2,2)=K_3^{(0)}(2,2)>K_2^{(0)}(2,2)$ for all $x_0$. The fact that $K_1 \neq K_3$ is primarily due to the contribution of $2K_i^{(0)}(2,4)$. In particular, we find that $2K_{i,r}^{(0)}(2,4)$ is positive for $K_3$ and negative for $K_1$ and $K_2$. But $2K_{i,a}(2,4)$ is negative for $K_3$ and positive for $K_1$ and $K_2$. However, $2K_{i,a}^{(0)}(2,4)$ is very small compared to $2K_{i,r}^{(0)}(2,4)$ for all values of $i$. This suggests that $K_3 > K_1$ for long-elongated molecules in agreement with the experiment. It may also be noted that the presence of strong long-range dispersion interaction decreases the value of the ratio $K_3/K_1$ which is found to be increasing with $x_0$. $K_i^{(1)}$ is found to be negative and larger in magnitude for $i=3$ than for $i=1$ and 2. Therefore, the $K_{i,a}^{(1)}$ contribution will also decrease the value of the ratio $K_3/K_1$.

For oblate ellipsoids we find $K_2^{(0)}(2,2)>K_1^{(0)}(2,2)=K_3^{(0)}(2,2)$. $2K_{i,r}^{(0)}(2,4)$ is found to be negative for $i=3$ and positive for $i=1$ and 2 for hard-core repulsion. On the other hand, $2K_{i,a}^{(0)}(2,4)$ is positive for $i=3$ and negative for $i=1$ and 2 for attractive interactions. Since the magnitude of $2K_i^{(0)}(2,4)$ is small, we find the general relation $K_2 > K_1 > K_3$ which is intuitively correct.[29] The fact that the twist deformation is most difficult to apply in a discotic nematic phase is thus borne out by our calculation.

Our calculation confirms the following findings,[5,8,15]

$$\tfrac{1}{3}K_1^{(0)}(2,4)=K_2^{(0)}(2,4)=-\tfrac{1}{4}K_3^{(0)}(2,4)$$

and

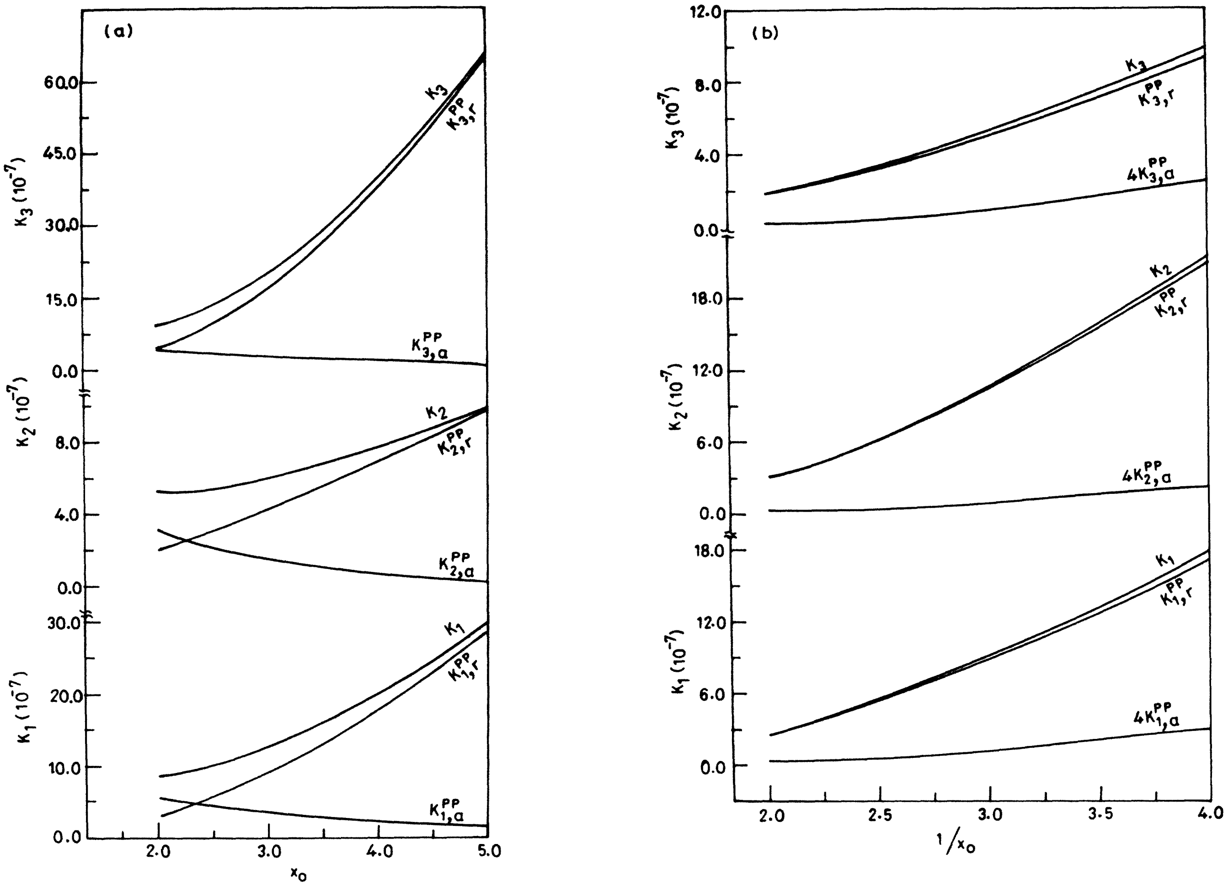

FIG. 4. (a) Comparison of the contributions of the repulsive and attractive interactions to the elastic constants of a system of prolate molecules as a function of $x_0$. The values $K^{PP}_{i,r}$ and $K^{PP}_{i,a}$ are those obtained in Eq. (4.6). (b) Same as in (a) but as a function of $1/x_0$ for oblate ellipsoids. Since the values of $K^{PP}_{i,a}$ are very small they have been magnified by a factor of 4 on the graph.

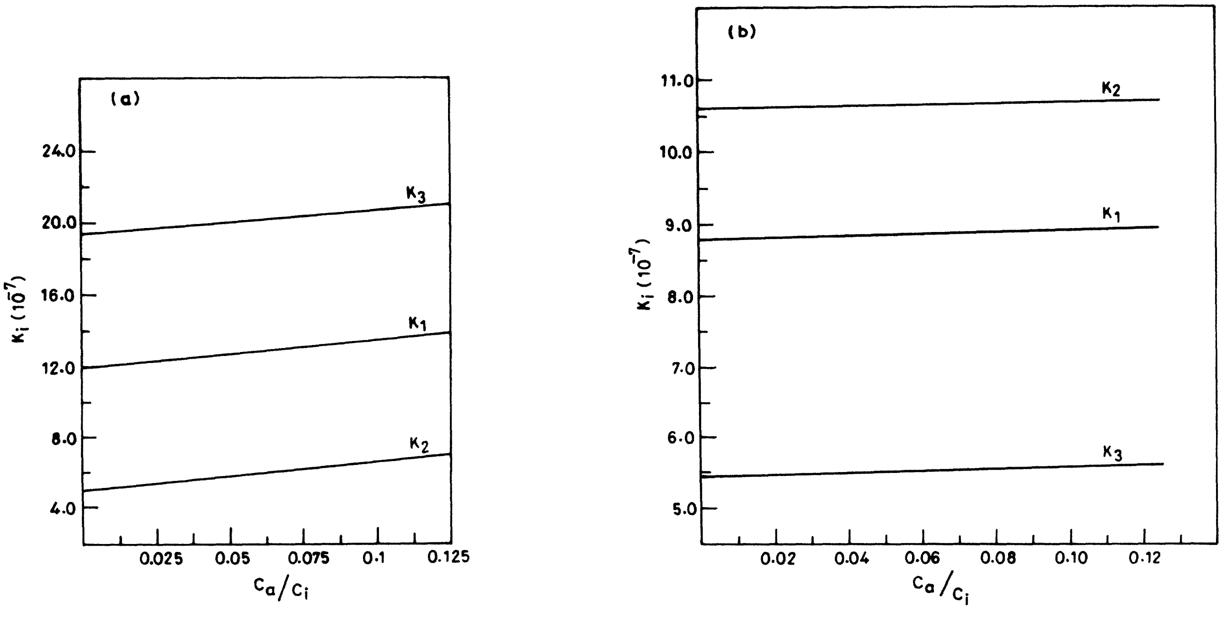

FIG. 5. (a) Elastic constants plotted as a function of $c_a/c_i$ for $x_0=3.0$ (prolate ellipsoids) with $c_i=1.0\times10^{-56}$ erg cm$^6$. (b) Same as in (a) for $1/x_0=3.0$ (oblate ellipsoids).

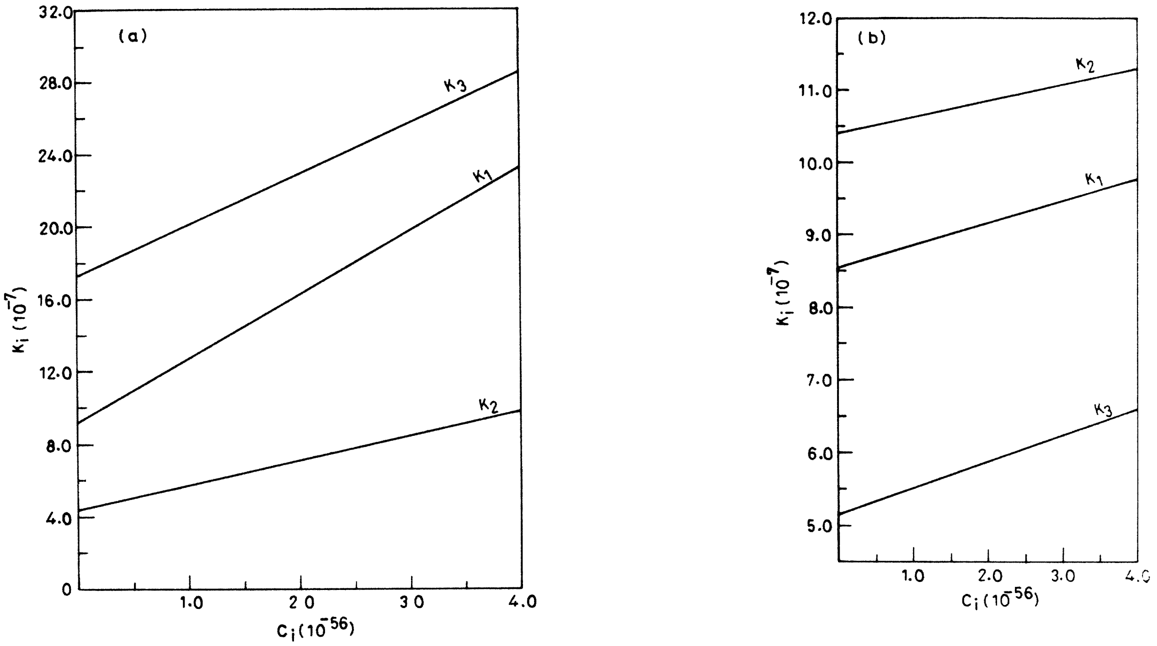

FIG. 6. (a) Elastic constants plotted as a function of $c_i$ (isotropic interaction strength parameter) for $x_0=3.0$ (prolate ellipsoids) with $c_a/c_i=0.05$. (b) Same as in (a) for $1/x_0=3.0$ (oblate ellipsoids).

$$K_1^{(0)}(2,2)=K_3^{(0)}(2,2) ,$$

which hold good for all $x_0$ (prolate as well as oblate) and are independent of potential models.

From Table I we find, for PAA at 400 K, $K_1$:$K_2$:$K_3$=2.2:1:3.5 compared to the observed ratios of 2.0:1:3.2.[30] The absolute magnitude (12.7, 5.8, and $20.1\times10^{-7}$ dyn) of our calculated elastic constants are, however, somewhat higher than the experiment (7.0, 3.5, and $11.2\times10^{-7}$ dyn). The values of the $K_i$'s are very sensitive to the values of the parameters used in the calculation. No attempt has been made here to fit the experimental data by adjusting the parameters. Further, we may note that it is difficult to measure the absolute values of the elastic constants.[3,30,31] It is the ratios $K_3/K_1$ and $K_2/K_1$ which are measured more accurately. From experimental data one finds the following: (i) The ratio $K_2/K_1$ lies within 0.5—0.7 and is more or less independent of the temperature and only slightly depends on $x_0$, (ii) $K_3/K_1$ increases with increasing $x_0$ for rigid molecules, and (iii) for molecules with flexible alkylene chains, the ratio $K_3/K_1$ decreases with increasing chain length. In Fig. 7 we plot calculated values of the ratios $K_2/K_1$ and $K_3/K_1$ as a function of $x_0$ for both prolate and oblate ellipsoids. For this calculation, $\overline{P}_4/\overline{P}_2$ is taken to be equal to 0.3 and independent of $x_0$ (this may not be true in real systems). Our calculation agrees qualitatively with the experiment. In order to understand (iii) we note that the $\overline{P}_2\overline{P}_4$ attractive interaction contributions tend to make $K_1$ larger than $K_3$, whereas the opposite is true for $\overline{P}_2\overline{P}_4$ hard-core repulsion terms. If molecular polarizability increases sufficiently through a homologous series of compounds, $2K_{i,a}(2,4)$ grow faster than $2K_{i,r}(2,4)$ and account in this way for a decreasing value of $K_3/K_1$.

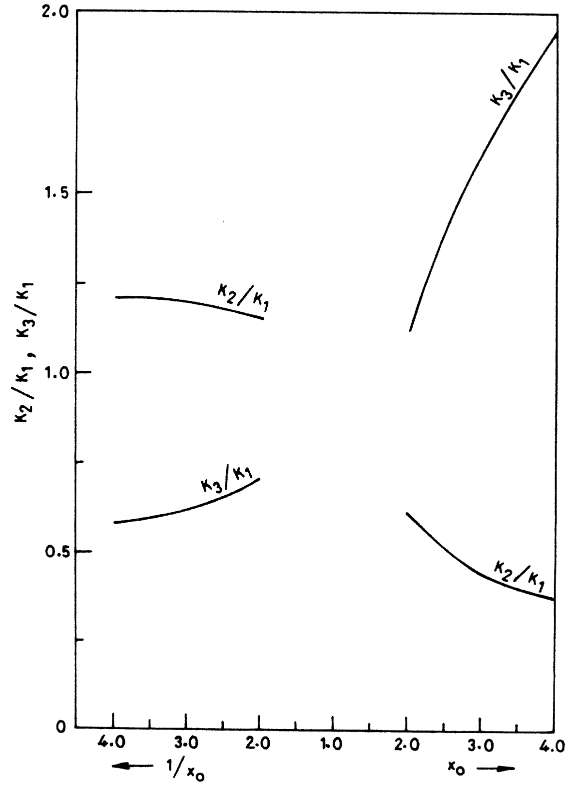

FIG. 7. Ratios $K_2/K_1$ and $K_3/K_1$ plotted as a function of $x_0$ for prolate and $1/x_0$ for oblate ellipsoids.

## V. SUMMARY AND CONCLUSIONS

A modified version of the density-functional theory developed in earlier papers has been used to calculate the elastic constants of ordinary as well as discotic nematic phase. The theory involves expansion in successively higher-order direct correlation functions $c_n$ of the isotropic liquid at the same number density $\rho$. In I, this series was written in terms of $\bar{c}_n$ defined by (2.14). A series written in terms of $c_n$ converges faster than the one written in terms of $\bar{c}_n$. This can be understood from the fact that

$$c_n = \frac{\delta^2}{\delta\rho^2}\int_0^1 d\alpha \int_0^\alpha d\alpha' \left[\bar{c}_n + 2\rho\frac{\delta\bar{c}_n}{\delta\rho} + \frac{1}{2}\rho^2\frac{\delta^2\bar{c}_n}{\delta\rho^2}\right]$$

and

$$\frac{\delta c_n}{\delta\rho} = \int c_{n+1}d\mathbf{x}_{n+1} ,$$

$$\frac{\delta^2 c_n}{\delta\rho^2} = \int\int c_{n+2}d\mathbf{x}_{n+1}d\mathbf{x}_{n+2} .$$

This means that a term involving $c_2$ in series (4.1) is equivalent in some approximate sense to terms involving $\bar{c}_n$, $\bar{c}_{n+1}$, and $\bar{c}_{n+2}$ of series (4.7) of I. In I, it was assumed that the change in $c_2$ due to distortion of the uniform nematic makes no contribution to the elastic constants. The derivation given in this paper is free from this assumption.

Our theory of curvature elasticity in the nematics requires as input the direct correlation function of an isotropic system as a function of number density and temperature. Although the integral equations of liquid-state theory can always be solved numerically to give information about $c_2$ as a function of intermolecular separation and orientations, such solutions in practice are often quite difficult or time consuming to obtain. For this reason, we employ the simple analytic model of Eq. (3.5) for hard linear molecules which, while in no sense exact, may quite effectively play much the same role for molecular fluids that the Wertheim-Thiele[21] solution of the PY equation played for atomic fluids. One deficiency of Eq. (3.5) is, however, immediately apparent in the limit of vanishing intermolecular separation $\mathbf{r}_{12}$: It yields a constant $a_1$ with no orientation dependence at all, contrary to known behavior of $c_2(\mathbf{x}_1,\mathbf{x}_2)$ for a simple molecular system.[32] Equation (3.5) may thus be expected to be qualitatively incorrect for small values of $\mathbf{r}_{12}$. This need not be a serious flaw, however, for we want $c_2(\mathbf{x}_1,\mathbf{x}_2)$ as an integrand where it will first be multiplied by a power of $\mathbf{r}_{12}$, a step which would in any case wash out most of the short-range structure of a more correct $c_2(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)$.

The decoupling approximation introduces anisotropy in the pair correlation function. In case of prolate molecules, for example, when two molecules are parallel, $c_2$ is most anisotropic and the surfaces of constant $c_2$ are prolate spheriods of axial ratio $x_0$, with the long axes of the spheriods pointing along $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$. When $\hat{\mathbf{e}}_1\perp\hat{\mathbf{e}}_2$, $c_2$ is most isotropic, the surfaces of constant $c_2$ are then oblate spheriods with the symmetry axis along $\hat{\mathbf{e}}_1\times\hat{\mathbf{e}}_2$, and the axial ratio of this spheriod is $\frac{1}{2}(1+x_0^2)^{1/2}<x_0$. It therefore seems that the decoupling approximation overestimates the anisotropy in the DPCF for the parallel configuration and underestimates that for perpendicular configurations. In spite of this defect, the decoupling approximation has been found to yield the values of the compressibility factor in very good agreement with the machine simulation results.[33]

Though Poniewierski and Stecki[11] gave expressions for the Frank elastic constants which are equivalent to that of $K_i^{(0)}$ of this work, they took the zero-density limit for the DPCF, i.e.,

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

The result of Gelbart and Ben-Shaul[8] can be found from the expression of $K_i^{(0)}$ by using the following relation:

$$c(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)=\frac{1}{1-\eta}(e^{-\beta u_0(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)}-1) \\ -\beta u_a(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2) . \tag{5.2}$$

The factor $1/(1-\eta)$ is believed to take care of the higher-body packing entropy effects. As shown by Barboy and Gelbart,[34] however, though (5.2) is a significant improvement over (5.1) (as far as contribution of repulsive interactions is concerned), 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. The attractive interaction part of (5.1) and (5.2) corresponds to the RPA as given by (3.12). While Ref. 11 employs precisely the same potential as the present paper, Ref. 8 considers a more elaborate form of the intermolecular dispersional interactions.

For a system of prolate ellipsoids which model ordinary nematic phases of rigid elongated molecules, we find $K_3>K_1>K_2$. This relation changes to $K_2>K_1>K_3$ for a system of oblate ellipsoids which models the discotic nematic phase. These results are in agreement with experiment[3,31,35] and with the theoretical results reported earlier.[15] Further, we find that for prolate ellipsoids, the ratio $K_3/K_1$ increases with $x_0$ which is in agreement with experiment.[31,35] In view of the fact that the potential model and the parameters used in the calculation only crudely simulate a real system, the agreement is heartening.

The assumption that the long-range dispersion interaction acts between the molecular centers may not be true. An alternative approach would be to assume the attractive as well as repulsive interaction distributed along the molecules, i.e., embedded interaction site model.[36] Further, the softness in the repulsive core and the dependence of the pair interaction on $\mathbf{r}\cdot\boldsymbol{\Omega}$ should be taken into account. As pointed out in the preceding section, the flexibility of the alkyl chain of molecules plays an important role in determining the relative values of the three principal elastic constants. The geometry of the molecule, however, does not appear to have a significant effect on $K_3/K_1$.[35]

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