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Molecular theory for freezing of a system of hard ellipsoids: Properties of isotropic-plastic and isotropic-nematic transitions

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The theory for isotropic-nematic transition at constant pressure described in an earlier paper is extended to include isotropic-plastic transition. The transition is located from the structural information about the liquid using the first-principles order-parameter theory of freezing. This theory makes the role of the structure of the medium explicit and the role of the intermolecular interaction implicit. For the plastic phase, order parameters are the coefficients of a Fourier expansion of the spatially varying single-particle density $\rho(\mathbf{r},\mathbf{\Omega})$ in terms of the reciprocal lattice of the plastic. For the nematic phase, order parameters are the coefficients of a spherical harmonic expansion of an orientational singlet distribution. The theory predicts that the equilibrium positional freezing (plastic) on fcc lattice takes place for the value of $\hat{c}^{1}_{0,0}$ $[=1-1/S(|\mathbf{G}_m|)$, where $S(|\mathbf{G}_m|)$ is the first peak in the structure factor of the center of mass] $\simeq 0.67$ [or $S(|\mathbf{G}_m|)\simeq 3.07$]. The equilibrium orientational freezing (nematic) takes place when the orientational correlation $\hat{c}^{0}_{2,2}\simeq 4.45$. For a simple model of hard ellipsoids of revolution parametrized by length-to-width ratio X_0, we find that the plastic phase stabilizes first for $0.57 \lesssim X_0 \lesssim 1.75$ and the nematic phase for $X_0 < 0.57$ and $X_0 > 1.75$. These values are in reasonable agreement with the computer-simulation results. We also find, in agreement with computer simulation, a remarkable symmetry between the systems with inverse length-to-width ratios.

I. INTRODUCTION

In a previous paper[1] hereafter referred to as I, one of us developed a density functional description of liquid crystals and obtained formally exact expansions for thermodynamic functions and single-particle density distributions in terms of *direct correlation functions*. The properties of the uniform nematic phase including the isotropic-nematic phase transition at constant pressure were discussed. In this approach, the properties of the ordered phase (liquid crystals, plastics, and crystalline solids) on its transition (melting) line are related to the direct correlation function of the coexisting isotropic liquid. The ordered phase is regarded as a calculable perturbation on the liquid at the transition.[2,3] 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 $X_0=a/b$, where $2a$ and $2b$ denote lengths of major and minor axes of the ellipsoids. This model includes as limiting cases the hard-spheres, hard-platelets, and hard-needles systems. All these systems are of physical interest because they represent primitive models for real liquids, solids, plastics, and liquid crystals. Constant-pressure Monte Carlo simulation has recently been used by Frenkel *et al.*[4] to study some of these systems.

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

$$U(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=\begin{cases}\infty, & \mathbf{r}_{12}<D(\mathbf{\Omega}_{12})\\ 0, & \mathbf{r}_{12}\geq D(\mathbf{\Omega}_{12})\ ,\end{cases} \tag{1.1}$$

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 overlap model of Berne and Pechukas,[5]

$$D(\mathbf{\Omega}_{12})=D(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12}) =D_0\left[1-\chi\frac{(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)^2+(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)^2-2\chi(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)}{1-\chi^2(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)^2}\right]^{-1/2}, \tag{1.2}$$

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

$$\chi=\frac{X_0^2-1}{X_0^2+1}\ , \tag{1.3}$$

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

We focus attention in this paper on the jump in order parameters, density, and change in density at the isotropic-nematic and isotropic-plastic transitions. The nematic and plastic phases are characterized, respectively, by order parameters $\overline{P}_L$ and μ_q which appear in the single-particle density distribution $\rho(\mathbf{x})$ in the following way:

$$\rho(\mathbf{x})=\rho(\mathbf{r},\boldsymbol{\Omega})=\rho_0\sum_{L,m,n}Q_{Lmn}(q)\exp(i\mathbf{G}_q\cdot\mathbf{r})D^L_{m,n}(\boldsymbol{\Omega}) \tag{1.4a}$$

with

$$Q_{Lmn}(q)=\frac{2L+1}{N}\int d\mathbf{r}\int d\boldsymbol{\Omega}\,\rho(\mathbf{r},\boldsymbol{\Omega})e^{-i\mathbf{G}_q\cdot\mathbf{r}}D^{L*}_{m,n}(\boldsymbol{\Omega})\ , \tag{1.4b}$$

where ρ_0 is average number density and $\mathbf{G}_q$ are reciprocal lattice vectors of the crystalline phase. The Q_{Lmn} are the order parameters and the $D^L_{m,n}(\boldsymbol{\Omega})$ are the Wigner rotation matrices. For economy of notation, we use vector $\mathbf{x}$ to indicate both the location $\mathbf{r}$ of the center of a molecule and its relative orientation $\boldsymbol{\Omega}$ described by Euler angles ψ, φ, and ξ:

$$d\boldsymbol{\Omega}=\frac{1}{8\pi^2}\sin\psi\,d\psi\,d\varphi\,d\xi\ .$$

Integration in (1.4b) is extended to the sample volume V for position and to the usual domain of $0\leq\psi\leq\pi$, $0\leq\phi<2\pi$, and $0\leq\xi\leq2\pi$ for angles. The orthogonality condition for the Wigner rotation matrices is

$$\int d\boldsymbol{\Omega}D^{L*}_{m,n}(\boldsymbol{\Omega})D^{L'}_{m',n'}(\boldsymbol{\Omega})=\frac{1}{2L+1}\delta_{L,L'}\delta_{m,m'}\delta_{n,n'}\ .$$

For a uniaxial ordered phase with a symmetry plane perpendicular to a director ($D_{\infty h}$ symmetry) and composed of cylindrically symmetric molecules, the singlet orientational distribution must depend only on the angle θ between the director and the molecular symmetry axis. Accordingly, we have

$$\rho(\mathbf{r},\boldsymbol{\Omega})=\rho_0\sum_L{}'\sum_q Q_{L00}(q)e^{(i\mathbf{G}_q\cdot\mathbf{r})}P_L(\cos\theta)\ , \tag{1.5}$$

where the prime on the summation indicates the restriction that only even L has to be considered. The odd terms vanish because molecules do not distinguish "up" from "down." $P_L(\cos\theta)$ is the Legendre polynomial of even order L. From (1.4b) we get

$$Q_{000}(0)=1\ , \tag{1.6a}$$

$$Q_{000}(q)=\mu_q=\frac{1}{N}\int\int\rho(\mathbf{r},\boldsymbol{\Omega})e^{-i\mathbf{G}_q\cdot\mathbf{r}}d\mathbf{r}\,d\boldsymbol{\Omega}\ , \tag{1.6b}$$

$$Q_{L00}(0)=Q_{L,0}=(2L+1)\bar{P}_L=\frac{2L+1}{N}\int d\mathbf{r}\int d\boldsymbol{\Omega}\,\rho(\mathbf{r},\boldsymbol{\Omega})P_L(\cos\theta)\ , \tag{1.6c}$$

and

$$Q_{L00}(q)=Q_{L,q}=(2L+1)\tau_{L,q}=\frac{2L+1}{N}\int d\mathbf{r}\int d\boldsymbol{\Omega}\,\rho(\mathbf{r},\boldsymbol{\Omega})\times e^{-i\mathbf{G}_q\cdot\mathbf{r}}P_L(\cos\theta)\ . \tag{1.6d}$$

Here μ_q, $\bar{P}_L$, and $\tau_{L,q}$ are, respectively, positional, orientational, and mixed positional-orientational order parameters.[6] At constant pressure the transitions are accompanied by change in density. We will, therefore, use the following expression for singlet distribution:

$$\rho(\mathbf{r},\boldsymbol{\Omega})=\rho_l\left[1+\Delta\rho^*+\sum_L{}'\sum_q{}'Q_{L,q}e^{i\mathbf{G}_q\cdot\mathbf{r}}P_L(\cos\theta)\right]\ . \tag{1.7}$$

The primes on the summations indicate the condition that L is even and that L and q both cannot be zero simultaneously.

For a plastic which has a crystalline lattice for the center of mass of molecules but orientational distribution-like liquid, $L=m=n=0$. Thus

$$\rho(\mathbf{r},\boldsymbol{\Omega})\equiv\rho(\mathbf{r})=\left[1+\Delta\rho^*+\sum_q\mu_q e^{i\mathbf{G}_q\cdot\mathbf{r}}\right]\ , \tag{1.8}$$

where $\Delta\rho^*=(\rho_0-\rho_l)/\rho_l$ is the fractional change in density due to transition (at constant pressure), ρ_0 is the mean number density of the plastic phase, and ρ_l is the density of the coexisting isotropic liquid. The Fourier coefficients μ_q are the order parameters of the isotropic-plastic transition and measure the amplitude of the spontaneous density waves set up in the system at the transition. Both $\Delta\rho^*$ and μ_q depend upon the type of crystal lattice $\{\mathbf{G}_q\}$.

For a uniaxial nematic phase with cylindrically symmetric molecules,

$$\rho(\mathbf{r},\boldsymbol{\Omega})=\rho_l[\Delta\rho^*+f(\boldsymbol{\Omega})]\ , \tag{1.9}$$

where

$$f(\boldsymbol{\Omega})=1+\sum_{L>2}{}'(2L+1)\bar{P}_LP_L(\cos\theta) \tag{1.10}$$

is an orientational singlet distribution normalized to unity

$$\int f(\boldsymbol{\Omega})d\boldsymbol{\Omega}=1\ .$$

Here $d\boldsymbol{\Omega}=\frac{1}{2}\sin\theta\,d\theta$ and

$$\bar{P}_L=\frac{1}{2\rho_l}\int\rho(\mathbf{r},\boldsymbol{\Omega})P_L(\cos\theta)\sin\theta\,d\theta$$

is the orientational order parameter of the nematic phase.

The isotropic-plastic transition is strongly first order in three dimensions, marked by large discontinuities in the entropy, density, and order parameters. On the other hand, the isotropic-nematic transition is weakly first order, characterized by small entropy and density change and latent heat.

We believe that the isotropic-plastic transition, like the isotropic-solid transition, occurs when liquid (translational) correlations attain a particular size. This is to say that the Hansen-Verlet rule,[7] which states that any (atomic) fluid system will crystallize when the first peak of its static (translational) structure factor reaches a height of 2.85 (to within 15%) independent of the nature of the interaction potential, also holds good for the plastic transition. The fact that the transition is structural in nature is used to make quasiuniversal predictions. For this, the approach we adopt here is a generalization of the method of Ramakrishnan and Yussouff[2] for molecular systems.

The theory of isotropic-nematic transition has been developing in three major directions. One uses the phenomenological theory of Landau and de Gennes,[8] in which the Helmholtz free energy is expressed in powers of the order parameters and its gradient, requiring in the process five or more adjustable parameters to be determined by experiments. While this theory is physically appealing and mathematically convenient, it has many drawbacks, including a lack of quantitative predictive power about the phase diagram. In another approach, mainly developed by Faber,[9] the nematic phase is treated as a continuum, in which a set of modes involving periodic distortion of an initially uniform director field is thermally excited. All orientational disorder is assumed to be due to mode excitations. For a system of N molecules, $2N$ modes are counted corresponding to all rotational degrees of freedom. This theory works well near the solid-nematic transition but fails close to the nematic-isotropic transition.

In the molecular field theories[10,11] one begins with a model in the form of molecules or intermolecular potentials and proceeds to calculate the solvent mediated anisotropic potential (effective one-body potential or pseudopotential) acting on each individual molecule. Such calculations need full knowledge of the pair-correlation functions.[12]

The mean-field method adopted in this paper is based on a density functional approach, which allows writing formally exact expressions for thermodynamic functions and one-particle distribution functions in terms of the direct correlation functions. Through a perturbative approach, the free energy and the one-particle density distribution of the nematic phase are related to the correlation functions of the coexisting isotropic liquid. Thus the same approach is adopted here to study both the isotropic-plastic and isotropic-nematic transitions, differing only in computational details. The following conditions lead to the following phases: $\mu_q \neq 0$, $\overline{P}_L = 0$, $\tau_{L,q} = 0$, plastic phase; $\mu_q = 0$, $\overline{P}_L \neq 0$, $\tau_{L,q} = 0$, nematic phase; and $\mu_q \neq 0$, $\overline{P}_L \neq 0$, $\tau_{L,q} \neq 0$, crystalline-solid phase. The smectic phase, which is obtained when density waves set up in one direction, is not considered here.

This paper is organized as follows. In Sec. II we discuss the basic formalism of the density functional theory applied to study phase transition in a molecular system of arbitrary symmetry. Final expressions for the order parameters and the difference in the grand thermodynamic potentials of the isotropic and ordered phases are given in terms of the direct correlation functions of the coexisting isotropic liquid at the transition. The approximations involved for numerical enumerations are elaborated in Sec. III. The results are presented and discussed for the isotropic-plastic and isotropic-nematic transitions in Sec. IV.

II. GENERAL THEORY

We begin by summarizing and reformulating some of the results of I which are relevant to our present study.

In the absence of external field one formally writes for the single-particle density distribution

$$\rho(\mathbf{x}) = \frac{e^{\beta\mu + c(\mathbf{x})}}{\Lambda}\,, \tag{2.1}$$

where β is the inverse temperature, μ the chemical potential, and Λ the cube of thermal wavelength associated with a molecule. $-kTc(\mathbf{x})$ is the solvent mediated potential field acting at $\mathbf{x}$. The one-particle direct correlation function $c(\mathbf{x})$, which is a functional of the single-particle density distribution $\rho(\mathbf{x})$, is related to the direct pair-correlation function by the following relation:[13]

$$\frac{\delta c(\mathbf{x}_1)}{\delta\rho(\mathbf{x}_2)} = c(\mathbf{x}_1,\mathbf{x}_2)\,. \tag{2.2}$$

The Ornstein-Zernike (OZ) equation relates the direct pair-correlation function (DPCF) $c(\mathbf{x}_1,\mathbf{x}_2)$ to the total pair-correlation function $h(\mathbf{x}_1,\mathbf{x}_2) = g(\mathbf{x}_1,\mathbf{x}_2) - 1$:

$$h(\mathbf{x}_1,\mathbf{x}_2) = c(\mathbf{x}_1,\mathbf{x}_2) + \int \rho(\mathbf{x}_3) h(\mathbf{x}_1,\mathbf{x}_3) c(\mathbf{x}_2,\mathbf{x}_3) d\mathbf{x}_3\,. \tag{2.3}$$

The functional integration of (2.2) from some initial density ρ_l (of isotropic liquid) to final density $\rho(\mathbf{x})$ (of the ordered phase) gives

$$c(\mathbf{x}_1;\{\rho(\mathbf{x})\}) = c(\mathbf{x}_1;\rho_l) + \int \tilde{c}(\mathbf{x}_1,\mathbf{x}_2;\rho(\mathbf{x}))\delta\rho(\mathbf{x}_2) d\mathbf{x}_2\,, \tag{2.4}$$

where

$$\tilde{c}(\mathbf{x}_1,\mathbf{x}_2;\rho(\mathbf{x})) = \int_0^1 d\alpha\, c(\mathbf{x}_1,\mathbf{x}_2;[\rho_l + \alpha\{\delta\rho(\mathbf{x})\}])$$

and

$$\delta\rho(\mathbf{x}_i) = \rho(\mathbf{x}_i) - \rho_l\,. \tag{2.5}$$

In writing the above equations we have indicated by curly brackets the functional dependence of the quantities on the single-particle distribution.

By a functional Taylor expansion we find that

$$c(\mathbf{x}_1,\mathbf{x}_2;[\rho_l + \alpha\{\delta\rho(\mathbf{x})\}]) = c(\mathbf{x}_1,\mathbf{x}_2;\rho_l) + \alpha \int c(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3;\rho_l)\delta\rho(\mathbf{x}_2) d\mathbf{x}_3 + \cdots\,. \tag{2.6}$$

Combining (2.4)–(2.6) and (2.1) we get

$$\ln[\rho(\mathbf{x}_1)/\rho_l] = \int c(\mathbf{x}_1,\mathbf{x}_2;\rho_l)\delta\rho(\mathbf{x}_2) d\mathbf{x}_2 + \tfrac{1}{2}\int\int c(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3;\rho_l) \times \delta\rho(\mathbf{x}_2)\delta\rho(\mathbf{x}_3) d\mathbf{x}_2 d\mathbf{x}_3\,. \tag{2.7}$$

This is a nonlinear equation and relates the single-particle density distribution of the ordered phase to the direct correlation functions, assumed known, of the coexisting liquid.

The Helmholtz free energy A of a system of N molecules contained in a volume V with temperature T is written as[13]

$$\beta A = \int \rho(\mathbf{x})[\ln\rho(\mathbf{x})\Lambda - 1] d\mathbf{x} + H\,, \tag{2.8}$$

where H, the excess reduced Helmholtz free energy arising from the interparticle interactions, is related to the direct one-particle correlation function $c(\mathbf{x})$ by the relation

$$\frac{\delta H}{\delta\rho(\mathbf{x})}=-c(\mathbf{x};\{\rho(\mathbf{x})\})\ . \tag{2.9}$$

The functional integration of (2.9) from ρ_l to $\rho(\mathbf{x})$ and use of the relations given by (2.4)–(2.6) lead to

$$\begin{aligned}H=&-\int d\mathbf{x}\,c(\mathbf{x},\rho_l)\delta\rho(\mathbf{x})\\&-\tfrac{1}{2}\int\int d\mathbf{x}_1d\mathbf{x}_2c(\mathbf{x}_1,\mathbf{x}_2;\rho_l)\delta\rho(\mathbf{x}_1)\delta\rho(\mathbf{x}_2)\\&-\tfrac{1}{6}\int d\mathbf{x}_1\int d\mathbf{x}_2\int d\mathbf{x}_3c(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3;\rho_l)\\&\qquad\times\delta\rho(\mathbf{x}_1)\delta\rho(\mathbf{x}_2)\delta\rho(\mathbf{x}_3)+\cdots\ .\end{aligned}\tag{2.10}$$

The grand-canonical thermodynamic potential

$$-W=\beta A-\beta\int\rho(\mathbf{x})\mu\,d\mathbf{x}$$

is given as

$$\begin{aligned}-W=&-W_l-\int\delta\rho(\mathbf{x})d\mathbf{x}\\&+\tfrac{1}{2}\int d\mathbf{x}_1\int d\mathbf{x}_2[\rho(\mathbf{x}_1)+\rho_l]\delta\rho(\mathbf{x}_2)c(\mathbf{x}_1,\mathbf{x}_2;\rho_l)\\&+\tfrac{1}{6}\int d\mathbf{x}_1\int d\mathbf{x}_2\int d\mathbf{x}_3[2\rho(\mathbf{x}_1)+\rho_l]\delta\rho(\mathbf{x}_2)\\&\qquad\times\delta\rho(\mathbf{x}_3)c(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3;\rho_l)+\cdots\ ,\end{aligned}\tag{2.11}$$

where $-W_l$ is the grand-canonical thermodynamic potential of the isotropic liquid.

Equations (2.7) and (2.11) are the basic equations of the theory of freezing[2] and of interfaces of ordered phase and its melt.[14] One attempts to find solutions of $\rho(\mathbf{x})$ of (2.7) which have symmetry of the ordered phase. These solutions, inserted in (2.11), give the grand potential difference between the ordered and liquid phases. The phase with the lowest grand potential is taken as the stable phase. Phase coexistence occurs at the value of ρ_l which makes $-\Delta W=0$ for the ordered and liquid phases.

Because of translational invariance in the isotropic phase, the correlation functions depend only on the relative distances and not on individual position vectors. Thus

$$c(\mathbf{x}_1,\mathbf{x}_2;\rho_l)=c(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2;\rho_l)\ ,$$

$$c(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3;\rho_l)=c(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23};\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2,\boldsymbol{\Omega}_3;\rho_l)\ ,$$

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

$$\frac{\partial c(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2;\rho_l)}{\partial\rho_l}=\int c(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23};\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2,\boldsymbol{\Omega}_3;\rho_l)d\mathbf{r}_3d\boldsymbol{\Omega}_3\ . \tag{2.12}$$

Substituting (1.7) into (2.7) and (2.11) and integrating and using (2.12) results in, respectively,

$$\begin{aligned}\ln\left[1+\Delta\rho^*+{\sum_L}'{\sum_q}'Q_{L,q}e^{i\mathbf{G}_q\cdot\mathbf{r}_1}P_L(\cos\theta_1)\right]&=\Delta\rho^*[\hat{\hat{C}}{}^{0}_{0,0}(\theta_1)+\tfrac{1}{2}\eta\Delta\rho^*\hat{\hat{C}}{}^{0'}_{0,0}(\theta_1)]+\sum_{q\neq0}\mu_qe^{i\mathbf{G}_q\cdot\mathbf{r}_1}[\hat{\hat{C}}{}^{q}_{0,0}(\theta_1)+\eta\Delta\rho^*\hat{\hat{C}}{}^{q'}_{0,0}(\theta_1)]\\&\quad+{\sum_{L\geq2}}'\bar{P}_L[\hat{\hat{C}}{}^{0}_{L,0}(\theta_1)+\eta\Delta\rho^*\hat{\hat{C}}{}^{0'}_{L,0}(\theta_1)]+{\sum_{L\geq2}}'\sum_{q\neq0}\tau_{L,q}e^{i\mathbf{G}_q\cdot\mathbf{r}_1}[\hat{\hat{C}}{}^{q}_{L,0}(\theta_1)+\eta\Delta\rho^*\hat{\hat{C}}{}^{q'}_{L,0}(\theta_1)]+A\ ,\end{aligned}\tag{2.13}$$

$$\begin{aligned}-\frac{\Delta w}{N}=&-\Delta\rho^*+\tfrac{1}{2}\Delta\rho^*[(2+\Delta\rho^*)\hat{c}{}^{0}_{0,0}+\tfrac{1}{3}\eta\Delta\rho^*(3+2\Delta\rho^*)\hat{c}{}^{0'}_{0,0}]+{\sum_{L\neq0}}'\bar{P}_L(1+\Delta\rho^*)(\hat{c}{}^{0}_{L,0}+\eta\Delta\rho^*\hat{c}{}^{0'}_{L,0})\\&+\tfrac{1}{2}\sum_{q\neq0}|\mu_q|^2[\hat{c}{}^{q}_{0,0}+\eta(1+2\Delta\rho^*)\hat{c}{}^{q'}_{0,0}]+{\sum_{L\geq2}}'\sum_{q\neq0}\mu_q\tau_{L,q}[\hat{c}{}^{q}_{L,0}+\eta(1+2\Delta\rho^*)\hat{c}{}^{q'}_{L,0}]\\&+\tfrac{1}{2}{\sum_{L\geq2}}'{\sum_{L'\geq2}}'\bar{P}_L\bar{P}_{L'}[\hat{c}{}^{0}_{L,L'}+\eta(1+2\Delta\rho^*)\hat{c}{}^{0'}_{L,L'}]+\tfrac{1}{2}{\sum_{L\geq2}}'{\sum_{L'\geq2}}'\sum_{q\neq0}\tau_{L,q}\tau_{L',q}[\hat{c}{}^{q}_{L,L'}+\eta(1+2\Delta\rho^*)\hat{c}{}^{q'}_{L,L'}]+B\ ,\end{aligned}\tag{2.14}$$

where

$$\hat{\hat{C}}{}^{q}_{L,0}(\theta_1)=(2L+1)\rho_l\int c(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)e^{i\mathbf{G}_q\cdot\mathbf{r}_{12}}P_L(\cos\theta_2)d\mathbf{r}_{12}d\boldsymbol{\Omega}_2\ , \tag{2.15}$$

$$\hat{c}{}^{q}_{L,L'}=(2L+1)(2L'+1)\rho_l\int c(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)e^{i\mathbf{G}_q\cdot\mathbf{r}_{12}}P_L(\cos\theta_1)P_{L'}(\cos\theta_2)d\mathbf{r}_{12}d\boldsymbol{\Omega}_1d\boldsymbol{\Omega}_2 \tag{2.16}$$

are structural parameters related to the Fourier transformed direct correlation functions of the fluid phase:

$$\begin{gathered}G_0=0\ ,\\ \hat{\hat{C}}{}^{q'}_{L,0}(\theta_1)=\eta\frac{\partial}{\partial\eta}(\hat{\hat{C}}{}^{q}_{L,0}(\theta_1)/\eta),\quad\hat{c}{}^{q'}_{L,L'}=\eta\frac{\partial}{\partial\eta}(\hat{c}{}^{q}_{L,L'}/\eta)\ ,\end{gathered}\tag{2.17}$$

etc. Here

$$A=\tfrac{1}{2}\rho_l^2\sum_{q,q'}{}'\sum_{L,L'}{}'Q_{L,q}Q_{L',q'}\int d\mathbf{r}_2\int d\mathbf{r}_3\int d\mathbf{\Omega}_2\int d\Omega_3 P_L(\cos\theta_2)P_{L'}(\cos\theta_3)e^{i(\mathbf{G}_q\cdot\mathbf{r}_2+\mathbf{G}_q\cdot\mathbf{r}_3)}c(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23},\mathbf{\Omega}_1,\mathbf{\Omega}_2,\mathbf{\Omega}_3)+\cdots \tag{2.18}$$

and

$$\begin{aligned}B=\tfrac{1}{6}\rho_l^2\sum_{L,L',L''}{}'\sum_{q,q'q''}{}'Q_{L,q}Q_{L',q'}Q_{L'',q''}&\\ \times\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3\int d\mathbf{\Omega}_1\int d\mathbf{\Omega}_2\int d\mathbf{\Omega}_3 P_L(\cos\theta_1)P_{L'}(\cos\theta_2)P_{L''}(\cos\theta_3)&\\ \times e^{i(\mathbf{G}_q\cdot\mathbf{r}_1+\mathbf{G}_{q'}\cdot\mathbf{r}_2+\mathbf{G}_{q''}\cdot\mathbf{r}_3)}c(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23},\mathbf{\Omega}_1,\mathbf{\Omega}_2,\mathbf{\Omega}_3)+\cdots\ .&\end{aligned} \tag{2.19}$$

Equations (2.13) and (2.14) are expansions in increasing nonlinearities, with respect to the order parameters, as well as in increasing order of the direct correlation functions.

III. APPROXIMATIONS AND DERIVATION OF WORKING EQUATIONS

The correlation functions appearing in (2.13)–(2.19) are in general not known. The solutions of integral equations such as the hypernetted-chain equation, the Percus-Yevick (PY) equation, the mean spherical approximation, or the optimized random-phase approximation are difficult to obtain. This is because the solutions of these equations involve, even for axially symmetric rigid molecules, repetitive sixfold numerical integration and require the calculation of the full anisotropic pair-correlation function—a procedure that is numerically very complicated but can be accomplished by spherical harmonic expansion.[15]

For hard spheres, the OZ equation (2.3) has been solved analytically by Wertheim[16] and Thiele[17] in the PY approximation. The solution

$$\begin{aligned}c(r/d_0)&=a+b(r/d_0)+\tfrac{1}{2}a\eta(r/d_0)^3 \quad \text{for } r/d_0<1\\ &=0 \quad \text{for } r/d_0>1\ ,\end{aligned} \tag{3.1}$$

where d_0 is the diameter of a hard sphere,

$$\begin{aligned}a&=-(1+2\eta)^2/(1-\eta)^4\ ,\\ b&=6\eta(1+\tfrac{1}{2}\eta)^2/(1-\eta)^4\ ,\end{aligned} \tag{3.2}$$

and $\eta=\rho v$, v $(=\frac{1}{6}\pi\rho d_0^3)$ being the molecular volume, is found to yield quantitatively good results for the properties of fluids for $\eta\leq 0.40$ and qualitatively good results for densities $\eta>0.40$. The PY $c(r)$ is found to be too negative for all values of r.[18] Further, the PY radial distribution function $g(r)$ is found to present two major defects.[19] First, the value at contact is too low, i.e., the PY approximation underestimates the height of the first peak and $g(r)$ oscillates slightly out of phase with the computer results. These defects of the PY theory are removed by using the Waisman[20]-Henderson-Blum (WHB)[21] expression for $c(r)$:

$$\begin{aligned}c(r/d_0)&=c_{\mathrm{PY}}(r/d_0)-K\left[a_1+b_1(r/d_0)+\tfrac{1}{2}\eta a_1(r/d_0)^3+v_1\frac{1-\exp(-Zr/d_0)}{Z(r/d_0)}\right] \quad \text{for } r/d_0\leq 1\\ &=K\frac{\exp[-Z(r/d_0-1)]}{r/d_0} \quad \text{for } r/d_0>1\ ,\end{aligned} \tag{3.3}$$

where

$$a_1=Z^{-1}f_1(\eta),\quad b_1=Z^{-1}f_2(\eta)\ ,$$

$$f_1(\eta)=\frac{-24\eta(1+6\eta+12\eta^2+8\eta^3)}{(1-\eta)(1+2\eta-3\eta^2-4\eta^3+4\eta^4)}\ ,$$

$$f_2(\eta)=4\left[1-\frac{(1-8\eta-2\eta^2)(1+6\eta+12\eta^2+8\eta^3)}{(1-\eta)(1+2\eta-3\eta^2-4\eta^3+4\eta^4)}\right]\ ,$$

$$\frac{K}{Z}=-\eta^3\frac{4-\eta}{(1-\eta)^4}[f_1(\eta)]^{-1}\ ,$$

and

$$K=\frac{\eta^2}{2(1-\eta)^3}-\frac{K}{Z}[(1+\tfrac{1}{2}\eta)f_1(\eta)+f_2(\eta)]\ .$$

There is no such analytic or semianalytic solution for the system of hard ellipsoids. We therefore approximate the DPCF for this system by using the PY or WHB results for hard spheres with the hard-spheres diameter d_0 replaced by the distance of the closest approach $D(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12})$. Thus

$$c(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=c(\mathbf{r}_{12}/D(\mathbf{\Omega}_{12}))=c(r^*)\ , \tag{3.4}$$

where $r^*=\mathbf{r}_{12}/D(\mathbf{\Omega}_{12})$ and $c(r^*)=c_{\mathrm{PY}}(r^*)$ or $c_{\mathrm{WHB}}(r^*)$. Such an approximation has already been used by Pynn[22] and Wulf.[23] As will be clear below, this approximation completely decouples the orientational and positional degrees of freedom and is referred to as the decoupling approximation.[24]

Though the decoupling approximation introduces anisotropy in the pair correlation and is exact at very low density, since $c(\mathbf{r}_{12}/D(\mathbf{\Omega}_{12}))\sim\exp[-\beta u(\mathbf{r}_{12},D(\mathbf{\Omega}_{12}))]-1$, 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 the spheroids pointing along $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ [Eq. (1.2)]. When $\hat{\mathbf{e}}_1 \perp \hat{\mathbf{e}}_2$, c is most isotropic, the surfaces of constant c are then oblate spheroids with the symmetry axis along $\hat{\mathbf{e}}_1 \times \hat{\mathbf{e}}_2$, and the axial ratio of this spheroid is $[\frac{1}{2}(1+X_0^2)]^{1/2} < X_0$.

In order to check the accuracy of the relation (3.4), we calculate compressibility factor $\beta P/\rho$ of the isotropic liquid using the compressibility equation

$$\frac{\partial(\beta P)}{\partial \rho} = 1-\rho \int c(\mathbf{r}_{12},\mathbf{\Omega}_1,\mathbf{\Omega}_2)d\mathbf{r}_{12}d\mathbf{\Omega}_1 d\mathbf{\Omega}_2 \tag{3.5}$$

and the PY $c(r)$. When (3.4) and (3.1) are used and integration is performed, one gets

$$\frac{\beta P}{\rho} = 1+\frac{4\eta-2\eta^2+\eta^3}{(1-\eta)^3}F_1(\mathcal{X}) , \tag{3.6}$$

where

$$F_1(\mathcal{X})=(1-\mathcal{X}^2)^{-1/2}(1-\tfrac{1}{6}\mathcal{X}^2-\tfrac{1}{40}\mathcal{X}^4-\tfrac{1}{112}\mathcal{X}^6-\cdots) .$$

In writing (3.6), use has been made of the excluded volume[24]

$$\begin{aligned} V_{\text{exc}} &= \tfrac{1}{3}\int D^3(\hat{\mathbf{r}}_{12},\mathbf{\Omega}_{12})d\hat{\mathbf{r}}_{12} \\ &= 8v(1-\mathcal{X}^2)^{-1/2}(1-\mathcal{X}^2\cos^2\theta_{12})^{1/2} . \end{aligned} \tag{3.7}$$

The results obtained from (3.6) for $X_0=1.0$, 2.0, and 3.0 are compared with the values obtained by machine simulations as a function of ρ_l^* in Fig. 1. The agreement is very good and justifies the use of the decoupling approximation for the DPCF for a system of hard ellipsoids.

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

$$c(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23};\mathbf{\Omega}_1,\mathbf{\Omega}_2,\mathbf{\Omega}_3) = c\left[\frac{\mathbf{r}_{12}}{D(\mathbf{\Omega}_{12})},\frac{\mathbf{r}_{13}}{D(\mathbf{\Omega}_{13})},\frac{\mathbf{r}_{23}}{D(\mathbf{\Omega}_{23})}\right] . \tag{3.8}$$

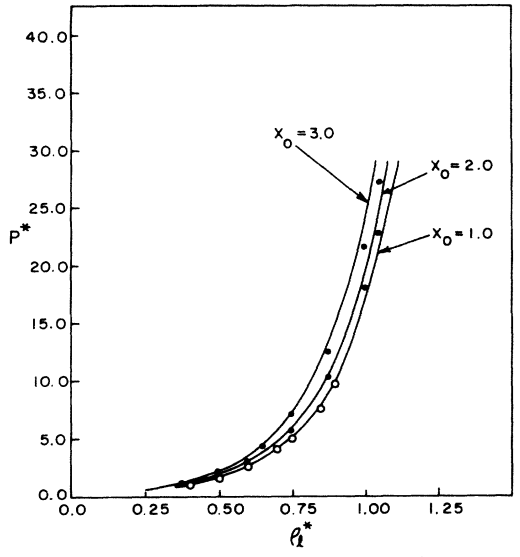

FIG. 1. Liquid phase reduced pressure (P^*) is shown as a function of the reduced density (ρ_l^*) for three values of $X_0=1.0$, 2.0, and 3.0. Here $\rho_l^*=\rho_l V_u$ and $P^*=\beta P V_u$, where $V_u=8ab^2=8X_0b^3$. ——, results from Eq. (3.6); ●, Monte Carlo values of Frenkel *et al.* (Ref. 4); ○, computer-simulation values for hard-spheres ($X_0=1.0$) system [J. A. Barker and D. Henderson, Mol. Phys. **21**, 187 (1971)].

When (3.4) is substituted in (2.15)–(2.17) we get

$$\hat{\hat{C}}{}^{q}_{0,0}(\theta_1)=\hat{\hat{c}}{}^{q}_{0,0} , \tag{3.9}$$

$$\hat{\hat{C}}{}^{q}_{L,0}(\theta_1)=P_L(\cos\theta_1)\hat{\hat{c}}{}^{q}_{L,L} , \tag{3.10}$$

$$\hat{\hat{C}}{}^{q\prime}_{0,0}(\theta_1)=\frac{\partial}{\partial\eta}(\hat{\hat{C}}{}^{q}_{0,0}(\theta_1)/\eta) ,$$

$$\hat{\hat{c}}{}^{q\prime}_{0,0}=\frac{\partial}{\partial\eta}(\hat{\hat{c}}{}^{q}_{0,0}/\eta) ,$$

etc., where

$$\hat{\hat{c}}{}^{q}_{0,0}=24\eta F_1(\mathcal{X})I(G_q) , \tag{3.11}$$

$$\hat{\hat{c}}{}^{q}_{L,L}=-24\eta F_L(\mathcal{X})I(G_q) , \tag{3.12}$$

$$I(G_q)=\int c(r^*)(r^*)^2\frac{\sin(G_q r^*)}{G_q r^*}dr^* , \tag{3.13}$$

with

$$F_2(\mathcal{X})=\tfrac{1}{3}\mathcal{X}^2(1-\mathcal{X}^2)^{-1/2}(1+\tfrac{3}{14}\mathcal{X}^2+\tfrac{5}{56}\mathcal{X}^4+\tfrac{25}{528}\mathcal{X}^6+\cdots) , \tag{3.14}$$

$$F_4(\mathcal{X})=\tfrac{1}{35}\mathcal{X}^4(1-\mathcal{X}^2)^{-1/2}(1+\tfrac{15}{22}\mathcal{X}^2+\tfrac{525}{1184}\mathcal{X}^4+\cdots) , \tag{3.15}$$

etc. It may be noted here that owing to the decoupling approximation (3.4), the contribution arising due to orientational degrees of freedom, $F_L(\mathcal{X})$, is separated from that of the positional degrees of freedom, $I(G_q)$.

There is little knowledge about the numerical values of A and B even for such simple systems as that of hard spheres. The preliminary molecular-dynamics calculations[25] near the triple point, however, indicate that even around the first peak of the structure factor, $S(G_q)$, which is a Fourier transform of the pair-correlation function, the numerical values of A and B are very close to zero. For the remainder of this paper, both A and B are, therefore, set equal to zero.

Fourier decompositions of (2.13) give the following important relations:

$$1+\Delta\rho^*=\int\int d\mathbf{r}_1 d\theta_1 \sin\theta_1 J(\mathbf{r}_1,\theta_1) , \tag{3.16}$$

$$\mu_p=\int\int d\mathbf{r}_1 d\theta_1 \sin\theta_1 e^{-i\mathbf{G}_p\cdot\mathbf{r}_1}J(r_1,\theta_1) , \tag{3.17}$$

$$\bar{P}_{L'}=\int\int d\mathbf{r}_1 d\theta_1 \sin\theta_1 P_{L'}(\cos\theta_1)J(\mathbf{r}_1,\theta_1) , \tag{3.18}$$

etc., where

$$\begin{aligned} J(\mathbf{r}_1,\theta_1)=\frac{1}{2V}\exp\Bigg[& \sum_q B(q)e^{i\mathbf{G}_q\cdot\mathbf{r}_1}+\sum_{L\geq 2}{}' B(L)P_L(\cos\theta_1) \\ & +\sum_{q\neq 0}\sum_{L>2}{}' B(L,q)e^{i\mathbf{G}_q\cdot\mathbf{r}_1} \\ & \times P_L(\cos\theta_1)+\Delta\rho^* B_0\Bigg] , \end{aligned} \tag{3.19}$$

$$B_0=\hat{c}^{\,0}_{0,0}+\tfrac{1}{2}\eta\Delta\rho^*\hat{c}^{\,0\prime}_{0,0}\ , \tag{3.20}$$

$$B(q)=\mu_q(\hat{c}^{\,q}_{0,0}+\eta\Delta\rho^*\hat{c}^{\,q\prime}_{0,0})\ , \tag{3.21}$$

$$B(L)=\overline{P}_L(\hat{c}^{\,0}_{L,L}+\eta\Delta\rho^*\hat{c}^{\,0\prime}_{L,L})\ , \tag{3.22}$$

$$B(L,q)=\tau_{L,q}(\hat{c}^{\,q}_{L,L}+\eta\Delta\rho^*\hat{c}^{\,q\prime}_{L,L})\ . \tag{3.23}$$

Equations (3.16)–(3.18) are highly nonlinear and complicated. They are solved numerically to find regions of temperature and density for which a periodic solution (in position and/or in orientation) has bifurcated from the uniform liquidlike solution. In principle, there are an infinite number of order parameters μ_q, $\overline{P}_L$, and $\tau_{L,q}$ so that solving these equations and (3.10) could be very difficult. The following simplifications are, however, possible.

The $\hat{c}^{\,q}_{0,0}$ has a sharp peak at $G_q=|\mathbf{G}_m|$ which can be identified as the smallest reciprocal lattice vector **G** of the crystalline lattice. This mode produces the largest response potential and most strongly affects the free energy balance.[2] Other order-parameter modes play significantly smaller roles and can be approximated by the perturbative method. Indeed, satisfactory results have been found by retaining only one order-parameter mode corresponding to the smallest reciprocal lattice vector set $\{\mathbf{G}_m\}$ in the study of the transition of isotropic atomic liquid to the body-centered-cubic (bcc) lattice or to the two-dimensional hexagonal-closed-packed structure. For the face-centered-cubic (fcc) lattice it is enough to retain two order-parameter modes, namely, $\{\mathbf{G}_q\}=(2\pi/a)(\pm1,\pm1,\pm1)$ and $\{\mathbf{G}_p\}=(2\pi/a)(\pm3,\pm1,\pm1)$ (here a is lattice parameter). The effect of other modes, which are small, on freezing parameters has been found by the perturbation method.

Though we cannot say very much about the rate of convergence of expansion (1.10) in general, close to the transition, where $\overline{P}_2\sim0.45$, the series converges rapidly and can be truncated after the term with $L=4$. The two—order-parameter theory should, therefore, be adequate to study the isotropic-nematic transition properties.

Another simplification arises from the possibility that at small values of X_0 (≤1.5) the plastic phase with $\overline{P}_L=0$, $\tau_{L,q}=0$ stabilizes first, whereas at large X_0 (≥2.5) the nematic phase with $\mu_q=0$, $\tau_{L,q}=0$ occurs first. We therefore take $\overline{P}_L=0$, $\tau_{L,q}=0$ in calculating the properties of the isotropic-plastic transition and $\mu_q=0$, $\tau_{L,q}=0$ for the isotropic-nematic transition. This simplification, however, excludes us from predicting the properties of the isotropic-solid transition for which $\mu_{q\neq0},\tau_{L,q}\neq0$ and from finding the upper and lower values of X_0 for plastic and nematic transitions, respectively. This will be one of the subjects of a future paper.

IV. RESULTS AND DISCUSSIONS

A. Isotropic-plastic transition

Calculation has been done by assuming the crystalline lattice of the plastic phase to be fcc with lattice parameter a determined self-consistently by the relation

$$a=(4/\rho_0)^{1/3},\quad \rho_0=\rho_l(1+\Delta\rho^*)\ . \tag{4.1}$$

In preferring the fcc lattice, we were guided by the fact that in computer-simulation studies,[26] the hard-spheres system is found to crystallize on the fcc lattice. Though such a choice *a priori* is not needed, it simplifies the computational work considerably. The possibility of getting other types of thermodynamically-more-stable lattices (i.e., the possibility of a plastic-plastic transition) as we change X_0 is not explored here. Because of the existence of only a small number of Bravis lattices, it will simplify the matter considerably if we first look for freezing of the fluid into a prescribed plastic lattice and defer the problem of the relative thermodynamic stability of the different plastic lattices to a later study.

TABLE I. Isotropic-plastic transition parameters in two—order-parameter theory. For each X_0, the first row indicates the values calculated from $c_{\rm PY}(r)$ and the second, from $c_{\rm WHB}(r)$.

X_0	$F_1(X)$	ρ_l^*	$\Delta\rho^*$	μ_1	μ_2	$\hat{c}^{\,0}_{0,0}$	$\hat{c}^{\,1}_{0,0}$	$\hat{c}^{\,2}_{0,0}$
1.0	1.000	0.943	0.064	0.966	0.770	−59.019	0.666	0.276
		0.951	0.068	0.971	0.775	−55.271	0.663	0.277
1.25	1.017	0.930	0.067	0.969	0.772	−56.157	0.667	0.275
		0.938	0.072	0.974	0.778	−52.596	0.663	0.276
1.50	1.056	0.904	0.074	0.975	0.777	−50.849	0.668	0.272
		0.911	0.079	0.981	0.784	−47.649	0.664	0.273
1.75	1.109	0.873	0.081	0.982	0.782	−45.766	0.671	0.268
		0.880	0.087	0.988	0.789	−42.930	0.667	0.269
2.00	1.170	0.844	0.089	0.988	0.786	−41.610	0.675	0.264
		0.849	0.095	0.995	0.793	−39.090	0.672	0.264
2.25	1.238	0.816	0.095	0.993	0.788	−38.395	0.682	0.258
		0.821	0.102	1.000	0.796	−36.134	0.678	0.259

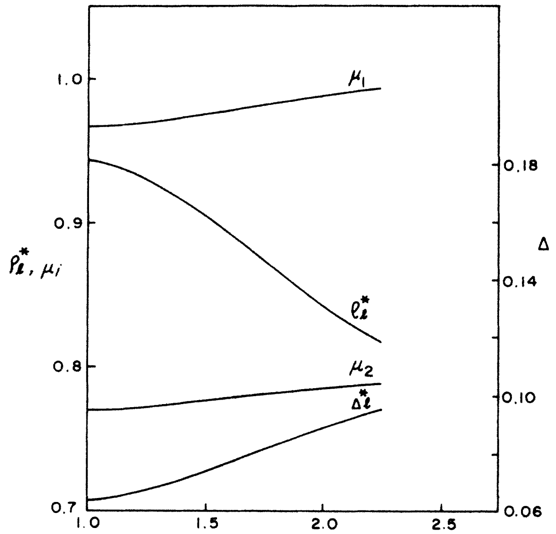

FIG. 2. Isotropic-plastic transition parameters obtained from two—order-parameter theory, using PY values of $c(r)$, are shown as a function of X_0.

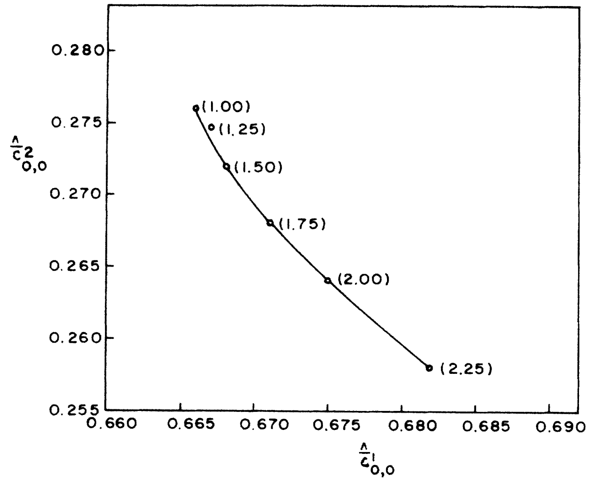

FIG. 3. Structural parameters $\hat{c}\,^2_{0,0}$ vs $\hat{c}\,^1_{0,0}$ for isotropic-plastic transitions. Values of X_0 for each point are indicated in parentheses on the curve.

We retain only two order-parameter modes corresponding to $\{\mathbf{G}_q\}$ mentioned in Sec. III. The first mode has 8 members and the second 24. Further, following Haymet[27] the value of the series $\sum_q \mu_q e^{i\mathbf{G}_q\cdot\mathbf{r}}(\hat{c}\,^{q'}_{0,0})$ is taken equal to zero. The computational method adopted[2,27,28] here is described in detail elsewhere. Results for several values of X_0 are listed in Table I. For each X_0, the first row lists the values of quantities obtained using the PY $c(r)$ and the second, the WHB $c(r)$. The difference in the values of the two sets is very small. The variation of order parameters and the density of transitions are plotted in Fig. 2 as a function of X_0.

We note that $\hat{c}\,^1_{0,0}=1-1/S(G_m)$ [$\simeq 0.674$ or $S(G_m)\simeq 3.07$] is very nearly constant to within ±5% at the transition as we vary X_0 from 1 to 2.25. This shows that the Hansen-Verlet criterion holds well for the isotropic-plastic transition. We also find that the second peak in the structure factor attains a value equal to 1.36 to within ±2% at the transition for $1 \le X_0 \le 2.25$. We, however, note that $\hat{c}\,^1_{0,0}$ tends to increase and $\hat{c}\,^2_{0,0}$ decrease as X_0 is increased. This is shown in Fig. 3 in which a $c^2_{0,0}$ versus $c^1_{0,0}$ graph is plotted. The values of X_0 for which points are plotted are indicated in parentheses on the curve. An interesting feature of this graph is that it has a negative slope showing that if $\hat{c}\,^1_{0,0}$ increases (with X_0), then freezing occurs for a smaller $\hat{c}\,^2_{0,0}$, and vice versa. This curve can be considered as a freezing line described in terms of the structural correlation. For a given X_0, above the line the plastic phase is more stable due to strong structural correlations in the centers of mass, while below the line the fluid phase is more stable. We further note that the importance of the second peak in the structure factor lessens as X_0 is increased, implying the possibility of transition on the bcc lattice for large X_0.

For $X_0=1$, i.e., for the hard-spheres system, the values of the density ρ_l^* change in density, $\Delta\rho^*$, and order parameters μ_1 and μ_2 are in excellent agreement with the values reported by other workers[2,27] and with the values obtained from computer simulations.[26]

B. Isotropic-nematic transition

The results obtained from two order-parameter approximations are listed in Table II. For each X_0, the first row lists the value of the quantities obtained from the PY $c(r)$ and the second, from the WHB $c(r)$. Again we find that these two sets of $c(r)$ give almost identical values for all the quantities characterizing the transition. The general trend is that the WHB $c(r)$ gives slightly higher values (almost negligible except for ρ_l^*) for all the quantities at the transition under investigation. This behavior is similar to that found in the case of the isotropic-plastic transition. This leads us to conclude that the PY $c(r)$ is good enough to study the properties at the transition.

In Fig. 4 we plot the variation of ρ_l^* and other order parameters with X_0. The general features of these quantities are in agreement with the experiment. The value of the ratio $\overline{P}_4/\overline{P}_2$ is found to depend weakly on X_0. It varies between 0.29 and 0.39 as the value of X_0 changes from 1.5 to 4.0. We also find that the one—order-parameter approximation gives values for ρ_l^*, $\overline{P}_2$, $\hat{c}\,^0_{0,0}$, $\hat{c}\,^0_{2,2}$, and $\Delta\rho^*$ which are very near to those found from the two—order-parameter approximation. This suggests, though indirectly, that the effects of higher order parameters on these quantities at the transition are negligible.

An interesting feature can be noted from Table II: the $\hat{c}\,^0_{2,2}$ ($\sim$4.45) remains almost constant at the transition as X_0 is varied from 1.5 to 4.0. This value is somewhat lower than that found from the Maier-Saupe theory. It should, however, be noted that the Maier-Saupe theory is the one—order-parameter theory and neglects the change in volume at the transition.

There is, however, a tendency of decreasing $\hat{c}\,^0_{2,2}$ as X_0 is increased. This is shown in Fig. 5 in which we plot $\hat{c}\,^0_{4,4}$

TABLE II. Isotropic-nematic transition parameters in two—order-parameter theory. For each X_0, the first row indicates the values calculated from $c_{\mathrm{PY}}(r)$ and the second, from $c_{\mathrm{WHB}}(r)$.

X_0	$F_1(\chi)$	$F_2(\chi)$	$F_4(\chi)$	ρ_l^*	$\Delta\rho^*$	$\bar{P}_2$	$\bar{P}_4$	$\hat{c}^{\,0}_{0,0}$	$\hat{c}^{\,0}_{2,2}$	$\hat{c}^{\,0}_{4,4}$
1.50	1.056	0.055	0.001	1.003	0.005	0.447	0.131	−86.531	4.525	0.062
				1.027	0.005	0.447	0.131	−86.532	4.526	0.062
1.75	1.109	0.106	0.003	0.880	0.010	0.462	0.140	−47.223	4.511	0.113
				0.899	0.010	0.462	0.140	−47.225	4.512	0.113
2.00	1.170	0.164	0.006	0.793	0.016	0.480	0.151	−32.151	4.495	0.166
				0.808	0.016	0.480	0.151	−32.151	4.496	0.166
2.25	1.238	0.226	0.011	0.725	0.022	0.498	0.163	−24.592	4.480	0.215
				0.738	0.022	0.498	0.163	−24.594	4.480	0.215
2.50	1.311	0.290	0.017	0.671	0.028	0.515	0.175	−20.189	4.464	0.260
				0.683	0.028	0.515	0.175	−20.191	4.465	0.259
2.75	1.387	0.356	0.024	0.628	0.034	0.532	0.186	−17.366	4.450	0.298
				0.638	0.034	0.532	0.186	−17.367	4.452	0.297
3.00	1.467	0.422	0.032	0.591	0.040	0.547	0.197	−15.430	4.437	0.332
				0.600	0.040	0.547	0.197	−15.432	4.439	0.331
3.25	1.548	0.488	0.040	0.560	0.046	0.562	0.208	−14.037	4.425	0.362
				0.568	0.046	0.562	0.208	−14.039	4.426	0.361
3.50	1.632	0.554	0.048	0.532	0.052	0.575	0.218	−12.997	4.414	0.385
				0.540	0.052	0.575	0.218	−12.998	4.415	0.384
3.75	1.718	0.620	0.057	0.508	0.057	0.587	0.226	−12.197	4.404	0.406
				0.515	0.057	0.588	0.226	−12.199	4.405	0.405
4.00	1.805	0.686	0.066	0.487	0.062	0.598	0.235	−11.567	4.394	0.424
				0.493	0.062	0.599	0.235	−11.569	4.396	0.423

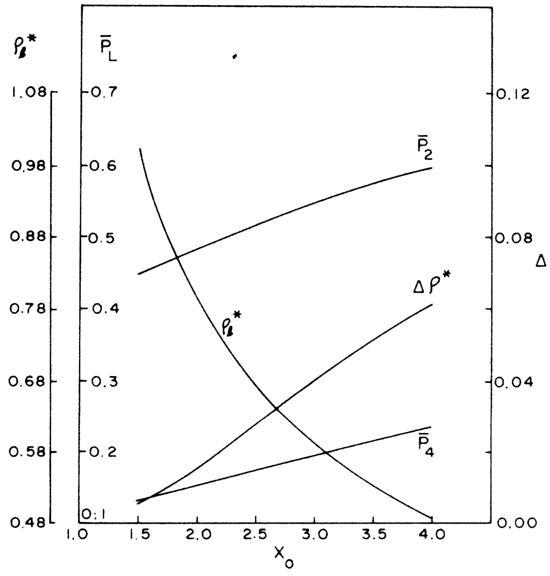

FIG. 4. Isotropic-nematic transition parameters obtained from two—order-parameter theory, using PY values of $c(r)$, are shown as a function of X_0.

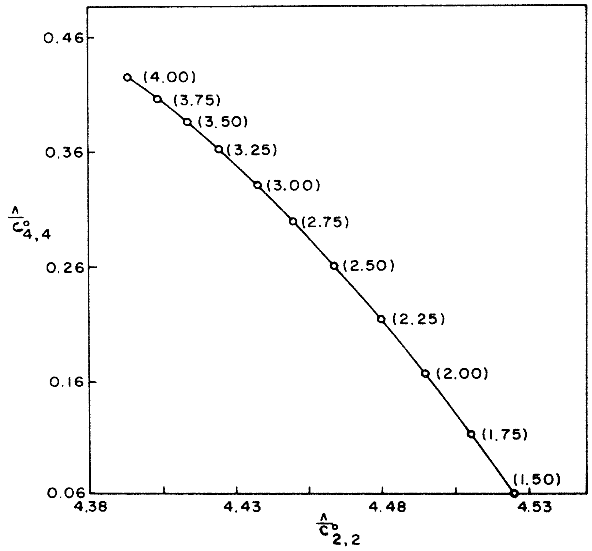

FIG. 5. Structural parameters $\hat{c}^{\,0}_{4,4}$ vs $\hat{c}^{\,0}_{2,2}$ for isotropic-nematic transitions. Values of X_0 for each point are indicated in parentheses on the curve.

versus $\hat{c}^{0}_{2,2}$. The value of X_0 for each point on the graph is given in parentheses. The graph is very nearly a straight line with a negative slope showing that if $\hat{c}^{0}_{4,4}$ increases (with X_0), orientational freezing occurs for smaller $\hat{c}^{0}_{2,2}$. This line can also be regarded as an orientational freezing line described in terms of the structural correlation. For a given X_0, above the line the nematic phase is more stable due to strong orientational correlation, while below the line the isotropic phase is more stable.

We wish to emphasize in conclusion that the values of the structural parameters $\hat{c}^{1}_{0,0}, \hat{c}^{2}_{0,0}$ and $\hat{c}^{0}_{2,2}, \hat{c}^{0}_{4,4}$ found by us for the isotropic-plastic and the isotropic-nematic transitions, respectively, are "universal" and do not depend in any appreciable way upon the approximations used for the $c(r)$. The decoupling approximation only affects the individual values of the contributions arising from orientational and positional parts of the DPCF. As argued in Sec. III, the decoupling approximation appears to overemphasize the anisotropy in the DPCF for the parallel configurations and underestimates it for the perpendicular orientations. This may lead to overestimation of the orientational contribution to $\hat{c}^{q}_{L,L}$, which is expressed as $F_L(X)$, and underestimation of the positional contribution $\eta I(G_q)$. This may explain why the values of ρ_l^* found by us at the transition are somewhat lower than those estimated by the computer simulations.[4]

For the range of X_0 considered here we find complete symmetry between the systems with inverse length-to-width ratios. This is in agreement with computer-simulation results.[4] We find that in the system of hard ellipsoids of revolution, the plastic phase stabilizes first for $0.56 \lesssim X_0 \lesssim 1.75$ and the nematic phase for $X_0 > 1.75$ and $X_0 < 0.56$. As mentioned earlier, we have not explored in this paper the range of X_0 for which a crystalline solid is found to stabilize first. Calculations for the phase diagram of a system of ellipsoids with a suitable approximation for the DPCF are in progress and will be reported in a future paper.

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