

Orientational order in simple dipolar fluids: Density-functional theory and absolute-stability conditions

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The formation of ferroelectric liquid crystals by simple dipolar models is investigated using density-functional theory and absolute-stability analysis. It is emphasized that for such systems well defined results can only be found by specifying exactly how the long-range dipolar interactions are treated. Explicit formal expressions are derived for mean-reaction-field boundary conditions and these are combined with integral-equation approximations in order to obtain numerical results for fluids of dipolar hard and soft spheres. The calculations predict isotropic-to-ferroelectric-nematic transitions in qualitative agreement with computer simulations. The quantitative agreement, however, is rather poor.

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I. INTRODUCTION

In recent computer-simulation studies [1, 2] we have shown that fluids of strongly interacting dipolar soft spheres can form ferroelectric liquid crystals and similar results have since been found for dipolar hard spheres [3]. The precise nature of the liquid-crystal phase depends upon the state parameters. At higher temperatures, one obtains nematic liquid crystals in the sense that there is orientational order but no long-range spatial structure. At lower temperatures, phases with columnar correlations are also found. As shown by de Leeuw, Perram, and Smith[4], for dipolar systems the application of periodic boundary conditions with Ewald summation techniques is not straightforward since the necessary sums over dipolar interactions are only conditionally convergent. Therefore, in order to assure convergence it is necessary to surround the "infinitely" periodic sample with a continuum characterized by some dielectric constant ϵ' . The extremes, $\epsilon' = 1$ and $\epsilon' = \infty$, occur when the sample is surrounded by vacuum or a conductor, respectively. In simulations with $\epsilon' = \infty$ perfect or "single-domain" ferroelectric liquid crystals are obtained. With $\epsilon' = 1$ the system breaks down into two antiparallel ferroelectric domains such that the net polarization of the sample is zero. These observations are consistent with the behavior of ferroelectric solids [5].

The purpose of the present paper is to investigate the isotropic-to-ferroelectric-liquid-crystal transition from another perspective. We examine density-functional theory [6-10] and absolute-orientational-stability conditions [11] for fluids of dipolar particles. It is shown that for infinite systems these formalisms lead to indeterminate expressions and that in order to obtain well-defined results it is necessary to precisely specify how

the long-range dipolar interactions are handled. We derive explicit expressions by applying mean-reaction-field methods [12, 13]. This approach is analogous to the boundary conditions used in the computer simulations in that the sample is surrounded with a continuum of dielectric constant ϵ' , and the resulting density-functional theory and stability relationships depend upon this parameter. We note that in our earlier work with dipolar hard ellipsoids [10], the importance of specifying boundary conditions when applying density-functional theory and stability conditions to dipolar fluids was not properly recognized and in fact the expressions employed in [10] are consistent with choosing $\epsilon' = 1$. However, we have shown that for the models and state parameters considered in [10] the results obtained do not depend upon the value of ϵ' .

Here we report a density-functional and stability analysis for fluids of dipolar soft and hard spheres. The direct correlation functions required as input are obtained by solving the hypernetted-chain (HNC) or reference hypernetted-chain (RHNC) approximations [14]. The phase behavior obtained is qualitatively consistent with the computer simulations, but the quantitative agreement is poor.

The remainder of this article is divided into three parts. The density-functional theory for dipolar particles is discussed in Sec. II, the conditions for absolute stability are given in Sec. III, numerical results are presented in Sec. IV, and our conclusions are briefly summarized in Sec. V.

II. DENSITY-FUNCTIONAL THEORY

In density-functional theory [6-8], the grand potential $\Omega = -PV$ (P is the pressure and V is the volume of the sample) is considered to be a functional of the singlet

density $\rho(1)$. To second order, it is not difficult to show [9, 10] that the difference in grand potential $\Delta\Omega$ between nematic and isotropic phases can be expressed in the form

$$\beta\Delta\Omega = \int d(1) \left\{ \rho_N(1) \ln \left(\frac{\rho_N(1)}{\bar{n}_I} \right) - [\rho_N(1) - \bar{n}_I] \right\} - \frac{1}{2} \int d(1)d(2)c(12; \bar{n}_I)[\rho_N(1) - \bar{n}_I] \times [\rho_N(2) - \bar{n}_I], \quad (2.1)$$

where the subscripts I and N indicate the isotropic and nematic phases, $c(12; \bar{n}_I)$ is the direct correlation function of the isotropic phase, n_I is the number density of the isotropic phase, $\bar{n}_I = n_I/4\pi$ and $\beta = 1/kT$. Also in Eq. (2.1), $(1) \equiv (\mathbf{r}_1, \Omega_1)$ and $d(1) = d\mathbf{r}_1 d\Omega_1$, where \mathbf{r}_1 and Ω_1 specify the position and orientation of particle 1. In order to find coexisting isotropic and nematic phases, Eq. (2.1) is minimized with respect to $\rho_N(1)$ and coexistence occurs when the condition $\beta\Delta\Omega = 0$ is satisfied.

For axially symmetric molecules, the singlet density of the nematic phase can be expanded in the form [9, 10]

$$\rho_N(1) = \rho_N(\Omega) = \bar{n}_I \left[1 + \sum_{m \geq 0} b_m P_m(\cos \theta) \right] = \bar{n}_I F(\cos \theta), \quad (2.2a)$$

where θ describes the orientation of the symmetry axis

with respect to the director and $P_m(\cos \theta)$ represents the usual Legendre polynomials. Also, here

$$b_0 = \frac{n_N - n_I}{n_I} \quad (2.2b)$$

is the fractional change in density associated with the isotropic-nematic transition and

$$b_m = \left(\frac{n_N}{n_I} \right) (2m + 1) \langle P_m \rangle, \quad (2.2c)$$

where $\langle P_m \rangle$ is the m th rank order parameter.

Equation (2.1) can be immediately reduced to the form

$$\frac{\beta\Delta\Omega}{V} = \frac{n_I}{2} \int_{-1}^{+1} dx F(x) \ln F(x) - n_I b_0 - \frac{1}{2} I, \quad (2.3a)$$

where

$$I = \frac{1}{V} \int d(1)d(2)c(12; \bar{n}_I)[\rho_N(1) - \bar{n}_I][\rho_N(2) - \bar{n}_I], \quad (2.3b)$$

and $x = \cos \theta$. It is the evaluation of the integral I which must be considered with care for dipolar fluids.

In order to evaluate I , we expand $c(12)$ in rotational invariants, $\Phi_{\mu\nu}^{mnl}(12)$, to obtain [14, 15]

$$c(12) = \sum_{\substack{m, n, l \\ \mu, \nu}} c_{\mu\nu}^{mnl}(r) \Phi_{\mu\nu}^{mnl}(12), \quad (2.4a)$$

where

$$\Phi_{\mu\nu}^{mnl}(\Omega_1, \Omega_2, \Omega_r) = f^{mnl} \sum_{\mu', \nu', \lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} R_{\mu'\mu}^m(\Omega_1) R_{\nu'\nu}^n(\Omega_2) R_{\lambda'0}^l(\Omega_r), \quad (2.4b)$$

f^{mnl} is a nonzero constant, the 3- j symbol has its usual notation, $R_{\mu'\mu}^m(\Omega)$ is a Wigner generalized spherical harmonic [16], and Ω_r describes the orientation of $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. For axially symmetric particles, symmetry requires that $\mu = \nu = 0$ and for notational simplicity these indices shall be dropped henceforth.

Choosing the director to be along the laboratory fixed z axis, and using the relationships

$$P_m(\Omega) = R_{00}^m(\Omega), \quad (2.5a)$$

$$\int d\Omega R_{00}^{m_1}(\Omega) R_{00}^{m_2}(\Omega) = \frac{4\pi}{2m_1 + 1} \delta_{m_1 m_2} \delta_{m_1 0}, \quad (2.5b)$$

together with properties of the 3- j symbols, Eq. (2.3b) can be partially integrated and reduced to the form

$$I = n_I^2 \sum_{m, n, l} \frac{b_m b_n}{(2m+1)(2n+1)} f^{mnl} \begin{pmatrix} m & n & l \\ 0 & 0 & 0 \end{pmatrix} \times \int d\mathbf{r} c^{mnl}(r) R_{00}^l(\Omega_r). \quad (2.6)$$

Further, the remaining integral can be written as

$$\int d\mathbf{r} c^{mnl}(r) R_{00}^l(\Omega_r) = \int d\Omega_r R_{00}^l(\Omega_r) \int_0^\infty dr r^2 c^{mnl}(r) = \delta_{l0} 4\pi \int_0^\infty dr r^2 c^{mnl}(r), \quad (2.7)$$

where we have used the orthogonality property of the generalized spherical harmonics. If all of the $c^{mnl}(r)$ coefficients are short ranged such that $\int_0^\infty dr r^2 c^{mnl}(r)$ exists, then we immediately have

$$I = n_I^2 \sum_m \frac{b_m^2}{(2m+1)^2} f^{m00} \begin{pmatrix} m & m & 0 \\ 0 & 0 & 0 \end{pmatrix} \bar{c}^{m00}(0), \quad (2.8)$$

where $\bar{c}^{m00}(0)$ is the Fourier transform of $c^{m00}(r)$ evaluated at $k = 0$ [see Eq. (2.14b)]. For the choice

$$f^{mnl} = l! / \begin{pmatrix} m & n & l \\ 0 & 0 & 0 \end{pmatrix}, \quad (2.9)$$

Eqs (2.3a) and (2.8) yield

$$\frac{\beta\Delta\Omega}{V} = \frac{n_I}{2} \int_{-1}^{+1} dx F(x) \ln F(x) - n_I b_0 - \frac{n_I^2}{2} \sum_{m \geq 0} \frac{\tilde{c}^{mm0}(0)}{(2m+1)^2} b_m^2, \quad (2.10)$$

which is the density-functional expression employed in [9, 10].

However, the pair potential for point dipoles, $u_{\text{DD}}(12)$, can be expressed in the form

$$u_{\text{DD}}(12) = -\frac{\sqrt{30}}{f^{112}} \frac{\mu^2}{r^3} \Phi^{112}(12), \quad (2.11)$$

where μ is the dipole moment, and hence

$$c^{112}(r) \sim -\beta u_{\text{DD}}(12) = \frac{\sqrt{30}}{f^{112}} \frac{\beta\mu^2}{r^3}, \quad (2.12)$$

as $r \rightarrow \infty$. Thus for the dipolar case the final expression in Eq. (2.7) is undefined for an infinite system and cannot be evaluated without specifying boundary conditions. This means that in general Eq. (2.10) cannot be applied to systems of dipolar particles, or, more precisely, its application implies a particular boundary condition. We will return to this point below.

Another way to expose this problem is to define the Fourier transform

$$\tilde{I}(\mathbf{k}) = \frac{1}{V} \int d(1)d(2) e^{i\mathbf{k}\cdot\mathbf{r}} c(12; \bar{n}_I) [\rho_N(1) - \bar{n}_I] \times [\rho_N(2) - \bar{n}_I], \quad (2.13)$$

which, if $c(12; \bar{n}_I)$ is short ranged, will yield the required integral I in the limit $k \rightarrow 0$. In order to evaluate $\tilde{I}(\mathbf{k})$, we Fourier transform $c(\mathbf{r}, \Omega_1, \Omega_2)$ and expand the transform $\tilde{c}(\mathbf{k}, \Omega_1, \Omega_2)$ in rotational invariants to obtain [14, 15]

$$\tilde{c}(\mathbf{k}, \Omega_1, \Omega_2) = \sum_{m,n,l} \tilde{c}^{mnl}(k) \Phi^{mnl}(\Omega_1, \Omega_2, \Omega_k), \quad (2.14a)$$

where the $\tilde{c}^{mnl}(k)$ are Hankel transforms defined by

$$\tilde{c}^{mnl}(k) = 4\pi i^l \int dr r^2 j_l(kr) c^{mnl}(r), \quad (2.14b)$$

with $j_l(kr)$ denoting a spherical Bessel function of order l . Performing the angular integrals yields

$$\tilde{I}(\mathbf{k}) = n_I^2 \sum_{m,n,l} \frac{b_m b_n}{(2m+1)(2n+1)} f^{mnl} \begin{pmatrix} m & n & l \\ 0 & 0 & 0 \end{pmatrix} \times \tilde{c}^{mnl}(k) R_{00}^l(\Omega_k). \quad (2.15)$$

If $c^{mnl}(r)$ is short ranged (i.e., decays more rapidly than $1/r^3$), then

$$\lim_{k \rightarrow 0} \tilde{c}^{mnl}(k) = \delta_{mn} \delta_{l0} \tilde{c}^{mnl}(0), \quad (2.16)$$

and taking the $k \rightarrow 0$ limit of $\tilde{I}(\mathbf{k})$ we immediately recover the result for I given by Eq. (2.8).

However, as noted above, for dipolar fluids $c^{112}(r)$ de-

cays as $1/r^3$ and [17]

$$\lim_{k \rightarrow 0} \tilde{c}^{112}(k) = -\frac{4\pi\sqrt{30}}{3f^{112}} \beta\mu^2, \quad (2.17)$$

which obviously does not vanish at $k = 0$. Therefore, for dipolar systems Eq. (2.15) gives

$$\lim_{k \rightarrow 0} \tilde{I}(\mathbf{k}) = n_I^2 \frac{b_1^2}{9} f^{112} \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} \lim_{k \rightarrow 0} \tilde{c}^{112}(k) R_{00}^2(\Omega_k) + n_I^2 \sum_{m \geq 0} \frac{b_m^2}{(2m+1)^2} f^{mm0} \begin{pmatrix} m & m & 0 \\ 0 & 0 & 0 \end{pmatrix} \tilde{c}^{mm0}(0). \quad (2.18)$$

We see that the first term on the right-hand side of Eq. (2.18) depends upon the orientation of the vector \mathbf{k} . Thus for an infinite dipolar sample the $k \rightarrow 0$ limit is not uniquely defined.

One way to obtain well-defined results for dipolar systems is to employ mean-reaction-field boundary conditions [12, 13, 4]. In this picture, each particle is viewed as sitting at the center of a truncation sphere of radius R_C which is surrounded by a continuum characterized by the dielectric constant ϵ' . The total configurational energy U is then written as the sum of two parts

$$U = \sum_{i < j} \sum_{(r_{ij} < R_C)} u(ij) - \frac{1}{2} \sum_i \mathbf{R}_i \cdot \boldsymbol{\mu}_i, \quad (2.19)$$

where $u(ij)$ is the pair potential including the dipolar term, $\boldsymbol{\mu}_i$ is the dipole associated with particle i , and \mathbf{R}_i is the reaction field at particle i resulting from polarization of the continuum. It is obvious that the first term arises from the interaction of all particles at separations less than R_C and that the second term is the interaction with the surrounding continuum. The factor of $\frac{1}{2}$ takes into account the work required to polarize the continuum. Using explicit expressions for the reaction field [18], it is not difficult to show [12, 13] that U can be expressed in the form

$$U = \sum_{i < j} u_e(ij) + \text{const}, \quad (2.20a)$$

where

$$u_e(12) = \begin{cases} u(12) + u_{\text{RF}}(12), & r < R_C \\ 0, & r > R_C \end{cases} \quad (2.20b)$$

$$u_{\text{RF}}(12) = -f(\epsilon') \mu^2 \Phi^{110}(12) / R_C^3, \quad (2.20c)$$

$$f(\epsilon') = 2(\epsilon' - 1) / (2\epsilon' + 1), \quad (2.20d)$$

and here and henceforth we use the definition of f^{mnl} given by Eq. (2.9). Therefore, if we consider ϵ' to be simply a constant independent of state parameters and of conditions "inside" the sample, the dipolar system with reaction-field boundary conditions can be thought of as an infinite sample with particles interacting through the effective pair potential $u_e(12)$ defined above.

Since the dipolar interactions are truncated, the effec-

tive potential is short ranged and it is not difficult to show [12] that

$$\lim_{R_C \rightarrow \infty} \lim_{k \rightarrow 0} \tilde{c}_e^{112}(k; R_C) = 0, \quad (2.21a)$$

$$\lim_{R_C \rightarrow \infty} \lim_{k \rightarrow 0} \tilde{c}_e^{110}(k; R_C) = \tilde{c}^{110}(0) + 4\pi\beta f(\epsilon')\mu^2/3, \quad (2.21b)$$

$$\lim_{R_C \rightarrow \infty} \lim_{k \rightarrow 0} \tilde{c}_e^{mm0}(k; R_C) = \tilde{c}^{mm0}(0), \quad m \neq 1 \quad (2.21c)$$

where the subscript e identifies the direct correlation function associated with the effective system and the $\tilde{c}^{mm0}(0)$ are those for an infinite dipolar fluid.

We can now employ these relationships together with Eqs. (2.8) or (2.18) to obtain the reaction-field result

$$I = n_I^2 \frac{b_1^2}{9} \frac{4\pi\beta f(\epsilon')\mu^2}{3} + n_I^2 \sum_{m \geq 0} \frac{b_m^2}{(2m+1)^2} \tilde{c}^{mm0}(0), \quad (2.22)$$

and the grand potential difference can be expressed in the form

$$\begin{aligned} \frac{\beta\Delta\Omega}{V} &= \frac{n_I}{2} \int_{-1}^{+1} dx F(x) \ln F(x) - n_I b_0 \\ &\quad - \frac{n_I}{2} \frac{b_1^2}{9} [n_I \tilde{c}^{110}(0) + 3f(\epsilon')y] \\ &\quad - \frac{n_I^2}{2} \sum_{m \neq 1} \frac{\tilde{c}^{mm0}(0)}{(2m+1)^2} b_m^2, \end{aligned} \quad (2.23)$$

where $y = 4\pi\beta n_I \mu^2/9$. It is clear that the density-functional results will depend upon the dielectric constant of the surrounding continuum. If the surrounding continuum is taken to be a vacuum then, $\epsilon' = 1$, $f(\epsilon') = 0$ and Eq. (2.23) reduces to Eq. (2.10). This choice of ϵ' amounts to a simple spherical truncation of the dipolar potential and this is the only boundary condition for which Eq. (2.10) is valid.

III. ABSOLUTE-STABILITY THEORY

General conditions for the absolute stability of an isotropic fluid have been derived by Stecki and Kloczkowski [11]. If one considers stability with respect to fluctuations of nematic (or ferroelectric) symmetry their general expression reduces to the form

$$\sum_{m \geq 0} \bar{n}_I^2 b_m^2 \left(\frac{4\pi}{2m+1} \right) - \bar{n}_I I > 0, \quad (3.1)$$

where I is just the integral defined by Eq. (2.3b) and discussed above. For short-range potentials, Eqs (3.1), (2.8), and (2.9) immediately yield the condition

$$1 - \frac{n_I}{2m+1} \tilde{c}^{mm0}(0) > 0, \quad (3.2)$$

which must be satisfied for all $m \geq 0$ if the isotropic phase is to be stable. The $m = 0$ case is just the usual condition for mechanical stability and is not of much interest here. If Eq. (3.2) is satisfied for $m = 0$ but not for some higher values of m then the system is orientationally unstable and will spontaneously form an orientationally ordered phase. For nonferroelectric nematics the stability condition will be violated only for even values of m . If violations also occur for odd values of m then the liquid-crystal phase will be ferroelectric.

For dipolar fluids with reaction-field boundary conditions we have

$$1 - \frac{n_I}{2m+1} \tilde{c}_e^{mm0}(0) > 0, \quad (3.3)$$

which in the limit $R_C \rightarrow \infty$ gives

$$1 - \frac{n_I}{3} \tilde{c}^{110}(0) - f(\epsilon')y > 0, \quad (3.4a)$$

$$1 - \frac{n_I}{2m+1} \tilde{c}^{mm0}(0) > 0, \quad m \neq 1 \quad (3.4b)$$

where we have employed Eqs. (2.21). It is interesting to note that for an infinite isotropic dipolar fluid the dielectric constant ϵ can be expressed in the form [17, 19, 20]

$$\epsilon - 1 = \frac{3y}{1 - n_I \tilde{c}^{110}(0)/3 - y}. \quad (3.5)$$

Thus for conducting boundary conditions [i.e., $\epsilon' = \infty$, $f(\epsilon') = 1$], Eq. (3.4a) is the necessary condition for $\epsilon - 1$ to be positive and finite. In other words, with conducting boundary conditions the system becomes unstable with respect to ferroelectric fluctuations at the point where the dielectric constant diverges.

We would also like to point out that an interesting earlier discussion of the instability of the isotropic phase with respect to dipolar ordering has been given by Høye and Stell [21]. Their theory also predicts the possible existence of a ferroelectric phase.

IV. RESULTS

We have carried out calculations for dipolar soft and hard spheres defined by the pair potentials

$$u(12) = u_{ss}(r) \text{ or } u_{hs}(r) + u_{DD}(12), \quad (4.1a)$$

where $u_{DD}(12)$ is as in Eq. (2.11) and the soft- and hard-sphere interactions are given by

$$u_{ss}(r) = 4\epsilon_{ss}(\sigma/r)^{12}, \quad (4.1b)$$

$$u_{hs}(r) = \begin{cases} \infty, & r < d \\ 0, & r > d. \end{cases} \quad (4.1c)$$

Here, ϵ_{ss} and σ are parameters characterizing the soft-sphere potential and d is the hard-sphere diameter.

It is convenient to describe dipolar soft-sphere fluids with the reduced density $n^* = n\sigma^3$, the reduced temperature $T^* = kT/\epsilon_{ss}$, and the reduced dipole moment $\mu^* = (\mu^2/\epsilon_{ss}\sigma^3)^{1/2}$. Similarly, dipolar hard-sphere

TABLE I. The results given by the density-functional theory for dipolar soft spheres (DSS) and dipolar hard spheres (DHS). For the dipolar soft spheres, $T^* = 1.35$ and $\mu^* = (\mu^2/\epsilon_{ss}\sigma^3)^{1/2} = 2.0914$ and for the dipolar hard spheres $\mu^* = (\mu^2/kTd^3)^{1/2} = 1.8$. n_I^* is the density of the isotropic phase at the transition, b_0 is the fractional density change, and the $\langle P_m \rangle$ are order parameters.

Model	n_I^*	b_0	$\langle P_1 \rangle$	$\langle P_2 \rangle$	$\langle P_3 \rangle$	$\langle P_4 \rangle$	$\langle P_5 \rangle$	$\langle P_6 \rangle$
DSS	0.8010	0.033	0.679	0.428	0.233	0.114	0.047	0.015
DHS	0.7550	0.073	0.727	0.485	0.282	0.146	0.064	0.020

systems can be described by specifying $n^* = nd^3$ and $\mu^* = (\mu^2/kTd^3)^{1/2}$. For dipolar hard spheres we report results at different densities for $\mu^* = 1.8$. For dipolar soft spheres we consider the isotherm $T^* = 1.35$ with $\mu^* = 2.0914$. This particular value of μ^* was chosen such that $\mu^*/\sqrt{T^*} = 1.8$ making the dipolar interactions of comparable importance in both the hard- and soft-sphere systems. All calculations for dipolar hard spheres were carried out using the RHNC theory with Verlet-Weis hard-sphere correlation functions [22]. For dipolar soft spheres exact reference correlation functions are not available in convenient form and the HNC approximation was used throughout.

The results obtained from the density-functional calculations are given in Table I. We see that first-order ferroelectric transitions occur for both systems in qualitative agreement with the computer simulations [1–3]. However, quantitatively, the theory is poor and predicts transitions at values of the dipole moment which are significantly too small. For example, for dipolar soft spheres at $T^* = 1.35$, $n_I^* = 0.8$ the true isotropic-to-ferroelectric-nematic transition occurs at $\mu^* \approx 2.5$. We will see below that a serious problem with the present calculations originates with the integral-equation approximations used in order to obtain the direct correlation functions. These approximations tend to overemphasize the long-range dipolar correlations [23] and, consequently, predict absolute-stability limits at densities and/or dipole moments which are too low. Thus, if exact direct correlation functions were available, the density-functional theory might be more accurate than

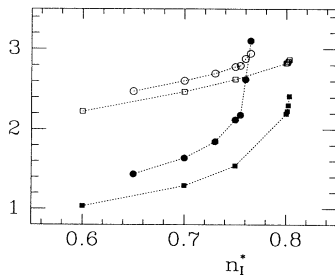


FIG. 1. Coefficients occurring in the expansion (2.23). The open and solid circles are $n_I\tilde{c}^{110}(0) + 3y$ (i.e., $\epsilon' = \infty$) and $n_I\tilde{c}^{220}(0)$ for dipolar hard spheres with $\mu^* = (\mu^2/kTd^3)^{1/2} = 1.8$. The open and solid squares are $n_I\tilde{c}^{110}(0) + 3y$ and $n_I\tilde{c}^{220}(0)$ for dipolar soft spheres at $T^* = 1.35$ and $\mu^* = (\mu^2/\epsilon_{ss}\sigma^3)^{1/2} = 2.0914$. The dotted lines are to guide the eye.

the present calculations suggest [24].

It is instructive to note that the sign of the coefficient $n_I\tilde{c}^{110}(0) + 3f(\epsilon')y$ occurring in Eq. (2.23) depends upon the value of ϵ' . For $\epsilon' = \infty$, $f(\epsilon') = 1$, and (see Fig. 1) $n_I\tilde{c}^{110}(0) + 3f(\epsilon')y$ is similar to $n_I\tilde{c}^{220}(0)$ in that it is a positive increasing function of n_I^* . Thus Eq. (2.23) can be minimized by nonzero values of b_1 yielding an isotropic-to-ferroelectric-nematic transition [25]. At the other extreme, for $\epsilon' = 1$, $f(\epsilon') = 0$, and $n_I\tilde{c}^{110}(0) + 3f(\epsilon')y$ is negative at all densities and clearly we would not expect Eq. (2.23) to be minimized by nonzero values of b_1 . Our numerical calculations are consistent with this deduction and no transition is predicted for $\epsilon' = 1$. We know from computer simulations [2, 3] (and from other considerations [5]) that with $\epsilon' = 1$ the ferroelectric liquid crystals break down into antiparallel ferroelectric domains with no net polarization. The singlet density defined by Eq. (2.2a) assumes a perfect or “single-domain” liquid crystal and cannot account for domain structure. Thus, insofar as the present calculations do not predict a perfect ferroelectric liquid crystal when $\epsilon' = 1$, they are consistent with the computer simulations. For relatively large finite values of ϵ' , $n_I\tilde{c}^{110}(0) + 3f(\epsilon')y$ can also be positive and allow ferroelectric transitions. In practice we found liquid-crystal crystal phases for values of $\epsilon' > 75$ for dipolar soft spheres and $\epsilon' > 18$ for dipolar hard spheres. Of course for these systems we have no way of knowing whether or not the perfect ferroelectric nematic liquid crystals are thermodynamically more stable than those consisting of antiparallel ferroelectric domains. The present theory simply tells us that they are more stable than the isotropic phase.

The static dielectric constants obtained for infinite sys-

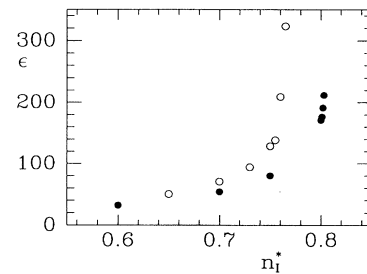


FIG. 2. The dielectric constants for dipolar hard (open circles) and soft (solid circles) spheres. The results for dipolar hard and soft spheres were obtained with the RHNC and HNC theories, respectively. The temperature and dipole moments are as in Fig. 1.

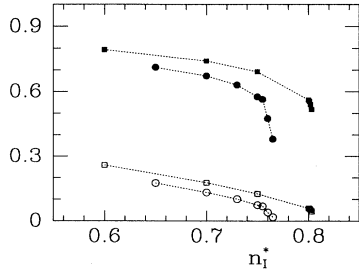


FIG. 3. The stability conditions obtained for dipolar hard and soft spheres with $\epsilon' = \infty$. The results for dipolar hard spheres are represented by circles and those for dipolar soft spheres with squares. The open and solid symbols are $1 - n_I \bar{c}^{110}(0)/3 - y$ and $1 - n_I \bar{c}^{220}(0)/5$. The temperature and dipole moments are as in Fig. 1. The dotted lines are to guide the eye.

tems of dipolar hard and soft spheres are shown in Fig. 2, and the stability conditions for $\epsilon' = \infty$ are plotted in Fig. 3. We see that, as discussed in Sec. III, for $\epsilon' = \infty$ the system becomes unstable with respect to the ferroelectric nematic phase at densities which coincide with the divergence of the dielectric constants. Furthermore, the absolute-stability limits occur at densities which are only slightly higher than the transition densities predicted by the density-functional theory. Therefore, as mentioned above, we conclude that much of the quantitative inaccuracy in the present density-functional calculations must come from the integral-equation input [26]. We note [see Eq. (3.4a)] that for values of $\epsilon' < \infty$ isotropic dipolar fluids do not become absolutely unstable with respect to the perfect ferroelectric at the point where the infinite system dielectric constant diverges. Possibly these systems become unstable with respect to structures with antiparallel ferroelectric domains, but again the present analysis does not take account of this possibility.

One further observation is of interest. For dipolar fluids the pair distribution function $g(12)$ can be expanded in rotational invariants as in Eq. (2.4a). Also, for an infinite isotropic system, the static dielectric constant is given by the well-known relationship [17]

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = y[1 + \frac{1}{3}n_I \bar{g}^{110}(0)], \quad (4.2)$$

where $\bar{g}^{110}(0)$ is the Fourier transform of $g^{110}(r)$ evaluated at $k = 0$. The growth of the long-range dipolar correlations which lead to the divergence of ϵ is illustrated in Fig. 4 where we have plotted $r^2 g^{110}(r)$. We note that $g^{110}(r) \equiv 3\langle \mu_1 \cdot \mu_2 \rangle_r / \mu^2$, where $\langle \rangle_r$ indicates an ensemble average at r , and hence $g^{110}(r)$ becomes more positive as the dipoles align. From Fig. 4 it is obvious that $g^{110}(r)$ becomes positive everywhere and grows rapidly in both range and magnitude as the density is increased. The resulting divergence of $\bar{g}^{110}(0)$ leads to the divergence of ϵ .

V. SUMMARY AND CONCLUSIONS

In this paper we have employed density-functional theory and absolute-stability conditions in order to investi-

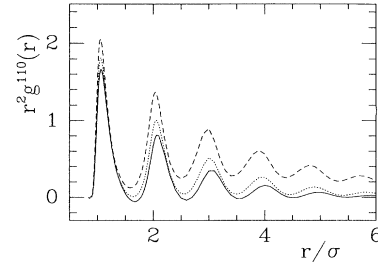


FIG. 4. The function $r^2 g^{110}(r)$ for dipolar soft spheres. The temperature and dipole moment are as in Fig. 1. The solid, dotted, and dashed curves are for $n_I^* = 0.7, 0.75,$ and 0.80 , respectively.

gate the isotropic-to-ferroelectric nematic transition in simple dipolar fluids. It is shown that a proper application of these theories to dipolar systems requires that one specify exactly how the long-range dipolar forces are treated. We obtain explicit determinate expressions by surrounding the sample with a continuum of dielectric constant ϵ' and applying mean-reaction-field boundary conditions. This is analogous to the boundary conditions used in computer simulations.

Numerical calculations were carried out for dipolar hard and soft spheres using direct correlation functions given by the RHNC and HNC approximations, respectively. For $\epsilon' = \infty$, the density-functional theory predicts isotropic-to-ferroelectric-nematic transitions in qualitative agreement with the computer simulations. However, qualitatively, the theory is poor and the predicted transitions occur at dipole moments which are too low compared with the simulations. Also, for a given temperature and dipole moment, the absolute-stability limits occur at densities which are only slightly higher than those at the thermodynamic transitions. This indicates that for a strongly interacting system, the integral-equation theories tend to overestimate the long-range dipolar correlations. Thus inaccurate direct correlation functions clearly make a major contribution to the quantitative inaccuracy of the present density-functional theory.

For the systems we have considered, the density-functional theory also predicts ferroelectric nematics for values of ϵ' greater than ~ 75 for dipolar soft spheres and greater than ~ 18 for dipolar hard spheres. For lower values of ϵ' no transitions are predicted. This is also in qualitative accord with computer simulations which indicate that for low values of ϵ' the ferroelectric nematic phase breaks down into antiparallel ferroelectric domains. The present density-functional theory and stability analysis considers only perfect ferroelectric liquid crystals and does not take account of possible domain formation.

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- [25] For the dipolar ellipsoids considered in [10] $n_I \bar{c}^{110}(0) + 3f(\infty)y$ does not become sufficiently positive to produce a ferroelectric phase and hence the results obtained with $\epsilon' = \infty$ are identical to those found for $\epsilon' = 1$. Thus the conclusions reached in [10] are unaltered.
- [26] We note that this is also true for fluids of nondipolar particles. For example, for hard ellipsoids the absolute stability limit given by the HNC theory comes before the isotropic-nematic transition density determined by computer simulations [9].