Bridging the gap between phenomenology and microscopic theory: Asymptotes in nematic colloids

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The Ornstein-Zernike equation is applied to nematic colloids with up-down symmetry to determine how the electrostatic analogy and other phenomenological results appear in molecular theory. In contrast to phenomenological approaches, the molecular theory does not assume particular boundary conditions (anchoring) at colloidal surfaces. For our molecular parameters the resulting anchoring appears to be realistic, neither rigid nor infinitely weak. For this case, the effective force between a colloidal pair at large separation remains essentially constant over the entire region of nematic stability. We show that a simple van der Waals approximation gives a potential of mean force that in some important aspects is similar to the phenomenological results obtained in the limit of weak anchoring; at large separations the potential varies as Σ^8, where Σ is the colloidal diameter. In contrast, the more sophisticated mean spherical approximation yields a Σ^6 dependence consistent with phenomenological calculations employing rigid boundary conditions. We show that taking proper account of the correlation (or magnetic coherence) length ξ inherent in the nematic sample is essential in an analysis of the Σ dependence. At infinite ξ the leading Σ dependence is Σ^6, but this shifts to Σ^8 when ξ is finite. The correlation length also influences the orientational behavior of the effective interaction. The so-called quadrupole interaction that determines the long-range behavior at infinite ξ transforms into a superposition of screened "multipoles" when ξ is finite. The basic approach employed in this paper can be readily applied to a broad range of physically interesting systems. These include patterned and nonspherical colloids, colloids trapped at interfaces, and nematic fluids in confined geometries such as droplets.

I. INTRODUCTION

Colloidal particles immersed in nematic fluids experience effective long-range interactions which can result in a variety of interesting spatial ordering of the colloidal particles [1]. These interactions result from colloid-induced distortions of the nematic order, and have been mainly described in the framework of phenomenological elastic theories, which address the director distribution around a single colloidal particle. This approach is expected to be relevant at distances that are long compared to the size of the colloidal particles. Note that by "effective" interaction we mean the change in free energy when the center-center distance of a pair of colloidal particles is moved from infinity to R. This effective interaction is also called the potential of mean force.

Most theoretical treatments are consistent in that the particular symmetry of the director field configuration about a single colloidal particle defines the effective intercolloidal interaction. So-called dipole configurations, where up-down symmetry with respect to the director is broken, result in the formation of colloidal chains along the bulk director. In contrast, quadrupole configurations lead to repulsive forces both along and perpendicular to the bulk director, with the maximum attraction occurring when the intercolloidal vector is at an angle of 49° with respect to the director. Phenomenological theories predict the asymptotic distance dependence of the effective potentials. These are $1/R^5$ in the quadrupole configuration [2–4], and $1/R^3$ in the dipole case [4]. Direct measurements of intercolloidal forces confirm these predictions at sufficiently large R [5–7]. However, the predicted dependence of the effective interactions on temperature and

on the colloidal diameter Σ can strongly depend on theoretical assumptions. Theories that impose weak boundary conditions at colloidal surfaces [3] predict the interaction of colloidal pairs with up-down symmetry to be proportional to $V^2\Sigma^8/K$, where K is the nematic elastic constant and V is the phenomenological anchoring energy. Given that experiments [8] indicate that V does not change with the temperature in the stable nematic regime, this result implies that the effective interactions will decrease as the temperature decreases (K increases). Another approach due to Ramaswamy *et al.* [2] and Lubensky *et al.* [4] is based on rigid boundary conditions and predicts interactions behaving as $\Sigma^6 K$. This not only implies a different Σ dependence, but also suggests that the effective colloidal interactions will become stronger as the temperature is decreased, in contrast to the result noted above. At present the dependence on temperature and/or colloidal diameter has not been determined experimentally.

In this paper we investigate asymptotic interactions in nematics colloids from a molecular perspective. We focus on how different asymptotes can be obtained employing correlation function theory. We note that correlation functions do not frequently appear in the phenomenological theory of liquid crystals, and that long-range phenomena are not commonly isolated in molecular approaches. It is clear that, if one wishes to bridge the gap between phenomenological and molecular pictures, it should be done at the level of asymptotic behavior where both approaches are directly comparable. Bridging this gap is one of the objectives of this paper.

We have suggested [9,10], that nematic colloids can be usefully investigated by employing integral equation methods that have been widely used in the theory of isotropic fluids, but only recently applied to anisotropic systems [11–14]. This approach begins at the level of molecular interactions modeled in physically relevant way. It is statistical mechanical in nature and rests on the Ornstein-Zernike (OZ) and Lovett equations for the pair and singlet distribution functions. The present work follows the same general approach, but focuses on analytical extraction of the long-range behavior of colloid-nematic and, particularly, colloid-colloid correlation functions. These in turn are used to obtain effective long-range interactions, which are directly comparable with phenomenological expressions.

The remainder of this paper is divided into five parts. The general approach is described in Sec. II, long-range correlations in the bulk nematic are discussed in Sec. III, nematic-colloid and colloid-colloid asymptotes at zero field are obtained in Sec. IV, and finite-field effects are considered in Sec. V. Finally our conclusions are summarized in Sec. VI.

II. GENERAL APPROACH

The equilibrium pair correlation functions for nematic colloids can be found by solving the OZ relationship

$$h_{\alpha\beta}(1,2) = c_{\alpha\beta}(1,2) + \sum_{\gamma=C,N} \int c_{\alpha\gamma}(1,3)\rho_{\gamma}(3)h_{\gamma\beta}(3,2)d(3), \tag{1}$$

where $c_{\alpha\beta}$ and $h_{\alpha\beta}$ are the direct and total pair correlation functions, $\rho_N(3)$ and $\rho_C(3)$ are the density distributions of the nematic (N) and colloidal (C) components, and α,β represent C or N. For a nematogen, the label 1 denotes $(\boldsymbol{R}_1, \hat{\boldsymbol{\omega}}_1)$, and for a spherical colloid $1 \equiv (\boldsymbol{R}_1)$. Equation (1) is combined with the exact Lovett equation that relates the direct pair correlation functions to the singlet densities [15]. The exact OZ equation must be solved in conjunction with another, approximate expression relating the total and direct correlation functions, such as the hypernetted chain (HNC) or mean spherical approximation (MSA) closures. The properties of different closures have been investigated in the theory of simple fluids. The model employed, the quantities of particular interest, as well as the difficulty of solution, influence the choice of closure for specific calculations. Properties such as order parameters, elastic constants [16], etc. can be calculated using the correlation functions.

For a system infinitely dilute in colloidal particles ($\rho_C \rightarrow 0$), the OZ equation becomes

$$h_{\alpha\beta}(1,2) = c_{\alpha\beta}(1,2) + \int c_{\alpha N}(1,3)\rho_N(3)h_{N\beta}(3,2)d(3). \tag{2}$$

Here, $\rho_N(\hat{\boldsymbol{\omega}})$ gives the orientational distribution in a pure nematic, and $\rho_N(1)[1+h_{NC}(1,2)]$ describes the distribution of nematic fluid about a colloidal particle. The latter function takes into account changes at a given point $\boldsymbol{R}_1$ induced by the colloidal particle at $\boldsymbol{R}_2$, including changes in local density

and in the orientational distribution of the nematic fluid. Here we are interested in the colloid-colloid potential of mean force, which at the HNC level [17] is given by

$$\phi_{CC}(1,2) = \beta^{-1}[c_{CC}(1,2) - h_{CC}(1,2)] + v_{CC}(1,2), \tag{3}$$

where $v_{CC}(1,2)$ is the direct pair interaction between the colloidal particles, and $\beta = 1/k_B T$, k_B being the Boltzmann constant and T the absolute temperature.

As in earlier work [13,14,18], we consider a model consisting of uniaxial nematogens interacting through a pair potential taken to be the sum of a hard-sphere interaction (sphere diameter σ) and an anisotropic part defined by

$$v(1,2) = v_2(R_{12})P_2(\hat{\boldsymbol{\omega}}_1 \cdot \hat{\boldsymbol{\omega}}_2), \tag{4}$$

$$v_2(R_{12}) = -A_N(z_N\sigma)^2 \frac{\exp(-z_N R_{12})}{R_{12}/\sigma}, \tag{5}$$

where $P_2(\hat{\boldsymbol{\omega}}_1 \cdot \hat{\boldsymbol{\omega}}_2)$ is the second-order Legendre polynomial, R_{12} is the center-center distance, the unit vector $\hat{\boldsymbol{\omega}}_i$ denotes the orientation of particle i, and A_N and z_N are the energy and the length parameters characterizing the interaction. The nematogen interaction with an external field is given by

$$v_N(1) = -W\sqrt{5}P_2(\hat{\boldsymbol{\omega}}_1 \cdot \hat{\boldsymbol{n}}), \quad W > 0, \tag{6}$$

where W is the field strength. This interaction orders the bulk director $\hat{\boldsymbol{n}}$ parallel to the field.

The OZ-Lovett equations for this model have been solved analytically in the MSA [13,14]. The model considered is relatively simple to allow analytical solutions to be obtained. However, it captures the main terms in the molecular interactions present in all nematogens, and we would expect the results to be quite general. As with many real substances, this model does not give smectic or columnar phases. Also, all three elastic constants of the model are equal, whereas experimentally elastic constants differ typically by a factor of 1–2, with the twist constant being the largest for diskotic and the smallest for calamitic (rodlike) molecules. Nevertheless, the single-constant assumption is usual in experimental analysis, unless smectic or columnar phases are being studied. Also, in phenomenology the single-constant formalism is considered to be a valuable tool, yielding insight into distortions in nematics (see Ref. [19], p. 104). Moreover, the interesting properties of effective colloidal interactions in nematics appear to be obtainable within the single-constant assumption.

The model colloidal particles are taken to be hard spheres of diameter Σ. Other direct colloid-colloid interactions could easily be included through the $v_{CC}(1,2)$ term in Eq. (3). The interaction of nematogens with the surface of a colloidal particle is modeled as

$$v_{CN}(1,2) = \begin{cases} \infty & \text{if } s_{12} < \sigma/2, \\ -A_C \exp[-z_C(s_{12}-\sigma/2)]P_2(\hat{\boldsymbol{\omega}}_1 \cdot \hat{\boldsymbol{s}}_{12}) & \text{if } s_{12} > \sigma/2, \end{cases} \tag{7}$$

where s_{12} is a vector connecting the nearest point of the surface of colloid 1 with the center of nematogen 2, and $\hat{\boldsymbol{s}}_{12} = \boldsymbol{s}_{12}/s_{12}$. Note that positive and negative values of A_C favor, respectively, perpendicular and parallel orientations of nematogen molecules with respect to the surface. For $z_C\sigma = 1$ the colloid-nematogen interaction range is of the order of the nematogen "length." The strength of the colloid-nematogen interaction is determined by A_C and z_C, and will vary for different surfactants. The magnitude of A_C depends on the surfactant concentration on the colloidal surfaces.

For micrometer and submicrometer colloidal particles, we have suggested an ansatz [20], namely, that the direct correlation function $c_{CN}(1,2)$ can be taken from the wall-nematic solution. This avoids having to solve Eq. (2) numerically for particular colloidal particles. We have found this to be a good approximation because the wall-nematic direct correlation function is short ranged outside the surface and rapidly tends to a constant on the inside, and thus is not very sensitive to surface curvature. This ansatz is convenient because within the MSA the wall-nematic direct correlation function can be obtained in explicit form [20]. This permits calculation of the density and orientational profiles [9] and effective colloid-colloid interactions [10]. Our earlier analytical solution [20,21] for a nematic in contact with tilted walls was obtained in the presence of an external field, which establishes a well-defined boundary condition at infinity. Infinitely far from the wall the director is constrained to be parallel to the field for all wall orientations. This boundary condition also holds for spherical colloids.

If we choose a coordinate system such that the z axis is parallel to the director $\hat{\boldsymbol{n}}$, the direct correlation functions obtained in the MSA can be expressed as spherical harmonic expansions

$$c_{NN}(R_{12},\hat{\boldsymbol{\omega}}_1,\hat{\boldsymbol{\omega}}_2) = \sum_{ll'=0,2} \sum_m c_{ll'm}^{NN}(R_{12})Y_{lm}(\hat{\boldsymbol{\omega}}_1)Y_{l'm}^*(\hat{\boldsymbol{\omega}}_2), \tag{8}$$

$$c_{CN}(\boldsymbol{R}_{12},\hat{\boldsymbol{\omega}}_2) = \sum_{ll'=0,2} \sum_m c_{ll'm}^{CN}(R_{12})Y_{lm}(\hat{\boldsymbol{R}}_{12})Y_{l'm}^*(\hat{\boldsymbol{\omega}}_2), \tag{9}$$

$$c_{NC}(\hat{\boldsymbol{\omega}}_1,\boldsymbol{R}_{12}) = \sum_{ll'=0,2} \sum_m c_{ll'm}^{NC}(R_{12})Y_{lm}(\hat{\boldsymbol{\omega}}_1)Y_{l'm}^*(\hat{\boldsymbol{R}}_{12}), \tag{10}$$

where $|m| \le l,l'$. Since all functions are real and invariant under the formal simultaneous interchange of both coordinates and species, $f_{CN}(1,2)=f_{NC}(2,1)$, $c_{ll'm}^{CN}(R_{12}) = (-1)^l c_{l'lm}^{NC}(R_{12})$ under the convention that $Y_{lm}^* = Y_{l-m}$. At the HNC level, the potential of mean force for a pair of colloidal particles has the form

$$-\beta\phi_{CC}(1,2) = h_{CC}(1,2) - c_{CC}(1,2) = \sum_{l=0,2,4} f_l^{CC}(R_{12})Y_{l0}(\hat{\boldsymbol{R}}_{12}). \tag{11}$$

The total correlation functions h_{NN} and h_{CN} have the same structure as Eqs. (8) and (9), respectively.

Any function of $\boldsymbol{R}$,

$$f(\ldots,\boldsymbol{R}) = \sum_{l=0,m}^{\infty} f_{lm}(R)Y_{lm}(\hat{\boldsymbol{R}}), \tag{12}$$

can be presented in k space as

$$f(\ldots,\boldsymbol{k}) = \sum_{l=0,m}^{\infty} f_{lm}(k)Y_{lm}(\hat{\boldsymbol{k}}), \tag{13}$$

in terms of Hankel transforms

$$f_{lm}(k) = 4\pi i^l \int_0^\infty dR\, R^2 j_l(kR)f_{lm}(R), \tag{14}$$

$$f_{lm}(R) = \frac{4\pi}{(2\pi)^3}(-i)^l \int_0^\infty dk\, k^2 j_l(kR)f_{lm}(k). \tag{15}$$

Fourier transforms of the correlation functions can be written as [22]

$$c_{NN}(\boldsymbol{k},\hat{\boldsymbol{\omega}}_1,\hat{\boldsymbol{\omega}}_2) = \sum_{ll'=0,2} \sum_m c_{ll'm}^{NN}(k)Y_{lm}(\hat{\boldsymbol{\omega}}_1)Y_{l'm}^*(\hat{\boldsymbol{\omega}}_2), \tag{16}$$

$$c_{CN}(\boldsymbol{k},\hat{\boldsymbol{\omega}}_2) = \sum_{ll'=0,2} \sum_m c_{ll'm}^{CN}(k)Y_{lm}(\hat{\boldsymbol{k}})Y_{l'm}^*(\hat{\boldsymbol{\omega}}_2), \tag{17}$$

$$-\beta\phi_{CC}(\boldsymbol{k}) = \sum_{l=0,2,4} f_l^{CC}(k)Y_{l0}(\hat{\boldsymbol{k}}). \tag{18}$$

Taking account of Eq. (2) in k space and expansions (8) and (9), $\beta\phi_{CC}(\boldsymbol{k})$ becomes

$$-\beta\phi_{CC}(\boldsymbol{k}) = \sum_{ll'=0,2} \sum_{LL'=0,2} \sum_m c_{lLm}^{CN}(k)$$
$$\times \langle Y_{Lm}(\hat{\boldsymbol{\omega}})Y_{L'm}^*(\hat{\boldsymbol{\omega}})\rangle_\omega h_{L'l'm}^{NC}(k)Y_{lm}(\hat{\boldsymbol{k}})Y_{l'm}^*(\hat{\boldsymbol{k}})$$
$$= \sum_{ll'} \sum_m [h_{ll'm}^{CC}(k) - c_{ll'm}^{CC}(k)]Y_{lm}(\hat{\boldsymbol{k}})Y_{l'm}^*(\hat{\boldsymbol{k}}), \tag{19}$$

where $\langle \cdots \rangle_\omega = \int f_N(\hat{\boldsymbol{\omega}})(\cdots)d\hat{\boldsymbol{\omega}}$, and $f_N(\hat{\boldsymbol{\omega}}_1) = \rho_N(1)/\rho_N$. Note that $Y_{lm}(\hat{\boldsymbol{k}})Y_{l'm}^*(\hat{\boldsymbol{k}})$ can always be expressed as a sum of $Y_{l0}(\hat{\boldsymbol{k}})$ in order to rewrite Eq. (19) in terms of $f_l^{CC}(k)$. Due to

the axial symmetry, Eqs. (2) are factored for different m, and the asymptotes connected with elastic behavior are determined by the OZ relations among harmonics with $m = \pm 1$.

In k space these are

$$h_{221}^{NN}(k) = c_{221}^{NN}(k) + c_{221}^{NN}(k)\rho_N \langle |Y_{21}|^2 \rangle_\omega h_{221}^{NN}(k), \quad (20)$$

$$h_{221}^{CN}(k) = c_{221}^{CN}(k) + c_{221}^{CN}(k)\rho_N \langle |Y_{21}|^2 \rangle_\omega h_{221}^{NN}(k)$$
$$= c_{221}^{CN}(k) + h_{221}^{CN}(k)\rho_N \langle |Y_{21}|^2 \rangle_\omega c_{221}^{NN}(k), \quad (21)$$

$$h_{221}^{CC}(k) - c_{221}^{CC}(k) = c_{221}^{CN}(k)\rho_N \langle |Y_{21}|^2 \rangle_\omega h_{221}^{NC}(k). \quad (22)$$

Note that $h_{221}^{\alpha\beta}(k) = h_{22-1}^{\alpha\beta}(k)$, since the correlation functions are real.

In the following sections we analyze Eqs. (20)–(22) in order to obtain asymptotes of different correlation functions in nematic colloids, and discuss their connection with phenomenological results.

III. LONG-RANGE CORRELATIONS IN THE BULK NEMATIC

The solution of the MSA combined with the Lovett equation for the bulk nematic is given in Ref. [14]. Here we focus on the long-range behavior of the bulk pair correlation function. It is the behavior of this bulk function that underlies the long-range, electrostaticlike behavior of the colloid-nematic and colloid-colloid correlation functions.

From Ref. [14] [see Eqs. (2.9)], the single-particle bulk distribution is given by

$$f_N(\hat{\boldsymbol{\omega}}) = \text{const} \times \exp[AY_{20}(w)] \quad \text{where} \quad A = \langle Y_{20} \rangle_\omega / \langle |Y_{21}|^2 \rangle_\omega, \quad (23)$$

and one also has the relationship

$$1 - \rho_N \langle |Y_{21}|^2 \rangle_\omega c_{221}^{NN}(k=0) = \beta W/A. \quad (24)$$

It follows from Eq. (20) that

$$h_{221}^{NN}(k) = c_{221}^{NN}(k)/[1 - \rho_N \langle |Y_{21}|^2 \rangle_\omega c_{221}^{NN}(k)]. \quad (25)$$

Taking Eq. (24) into account and expanding the denominator of Eq. (25) about $k=0$, we obtain

$$1 - \rho_N \langle |Y_{21}|^2 \rangle_\omega c_{221}^{NN}(k) \xrightarrow{k \to 0} \beta W/A$$
$$+ k^2 \rho_N \langle |Y_{21}|^2 \rangle_\omega \frac{4\pi}{6} \int c_{221}^{NN}(R)R^4 dR$$
$$+ O(k^4). \quad (26)$$

This can be rewritten as

$$1 - \rho_N \langle |Y_{21}|^2 \rangle_\omega c_{221}^{NN}(k) \xrightarrow{k \to 0} \beta W/A + k^2 B^2 + O(k^4), \quad (27)$$

where

$$B^2 = \frac{\langle |Y_{21}|^2 \rangle_\omega \beta K}{15 \rho_N S_2^2}, \quad (28)$$

the elastic constant K is given by the exact expression [16]

$$\beta K = 10\pi \rho_N^2 S_2^2 \int c_{221}^{NN}(R)R^4 dR, \quad (29)$$

and $S_2 = \langle Y_{20} \rangle_\omega / \sqrt{5}$ is the order parameter.

Noting that the inverse zeroth-order Hankel transform of $1/(k^2+x^2)$ is $\exp(-xR)/4\pi R$, Eqs. (25) and (27) yield

$$h_{221}^{NN}(R) \xrightarrow{R \to \infty} C \frac{\exp(-R/\xi)}{R}, \quad (30)$$

where the decay length

$$\xi = \sqrt{\frac{K}{W\rho_N S_2 3\sqrt{5}}}, \quad (31)$$

and the prefactor

$$C = (4\pi\rho_N B^2 \langle |Y_{21}|^2 \rangle_\omega)^{-1} = 3A^2(4\pi\beta K)^{-1}. \quad (32)$$

The expressions given above depend on the fact that we have assumed a separable potential with expansions truncated as in Eqs. (8) and (9). Apart from these assumptions, there is no model dependence.

Explicit expressions for the model defined by Eqs. (4)–(6) can be found in Ref. [13], and here we simply mention some results in terms of the molecular parameters that are useful for the present discussion. For our model at zero field, $\beta A_N \eta \langle |Y_{21}|^2 \rangle_\omega$ is a function of $z_N \sigma$ only [see Eq. (3.15) of [13]], and $B = [\sqrt{(z_N \sigma)^2 + 1} + 1]/(2z_N)$ [23]. Then, Eq. (32) implies that $h_{221}^{NN}(R \to \infty)$ varies as β at zero external field, and the model elastic constant is proportional to $(\rho_N S_2)^2$. The generalization for the case of finite external fields can be done following Ref. [14]. For instance, the model-dependent relationships given above hold for sufficiently small fields ($\beta W/A \ll 1$), which is the case of interest here. Thus, for small fields the correlation length takes the form

$$\xi = B\sqrt{\frac{A}{\beta W}} = \frac{1}{2z_N}\sqrt{\frac{A}{\beta W}}[\sqrt{(z_N \sigma)^2 + 1} + 1]. \quad (33)$$

Noting that A lies in the range 1–10 for a stable nematic, for $\beta W = 10^{-3} - 10^{-4}$ and $z_N \sigma = 1$, we estimate ξ to vary from tens to hundreds of nanometers for a typical nematogen (length in the nanometer range).

At sufficiently small fields, the asymptote of the complete total correlation is defined by harmonics with $|m|=1$. Thus, one has

$$h_{NN}(1,2) \xrightarrow{R \to \infty} C[Y_{21}(\hat{\boldsymbol{\omega}}_1)Y_{21}^*(\hat{\boldsymbol{\omega}}_2) + \text{c.c.}]\frac{\exp(-R/\xi)}{R}, \quad (34)$$

where c.c. denotes the complex conjugate of the first term within the square brackets.

It is possible to connect the relationships given above to more familiar phenomenological expressions [19]. It can be shown that ξ is analogous to the magnetic (electric) coherence length in phenomenological theories. For a nonpolar nematogen, W and the local electric field intensity E are related by $\Delta\alpha E^2 = 3\sqrt{5}W$, where $\Delta\alpha$ is the anisotropy of the

molecular polarizability. Employing the simple approximation for the dielectric anisotropy, $\Delta\epsilon = \rho_N S_2 \Delta\alpha$, yields the familiar expression

$$\xi = \sqrt{\frac{K}{\Delta\epsilon}} \frac{1}{E}, \tag{35}$$

for the electric (magnetic) coherence length [19].

Next consider correlations of the director fluctuations

$$\langle n_x(1) n_x(2) \rangle_{k_B T} = \int \frac{w_{1x} w_{1z} w_{2x} w_{2z}}{S_2^2} F_2^{NN}(1,2) d\hat{\boldsymbol{\omega}}_1 d\hat{\boldsymbol{\omega}}_2, \tag{36}$$

where $\langle n_x(1) n_x(2) \rangle$ is an element of the susceptibility matrix as defined in [24], $\hat{\boldsymbol{\omega}}_i$ is a unit vector along the molecular orientation, and $F_2^{NN}(1,2)$ is the two-particle distribution function

$$F_2^{NN}(1,2) = f_N(\hat{\boldsymbol{\omega}}_1)[1 + h_{NN}(1,2)] f_N(\hat{\boldsymbol{\omega}}_2). \tag{37}$$

Taking account of the uniaxial symmetry of $f_N(\hat{\boldsymbol{\omega}})$ and using Eq. (34), we obtain the well-known phenomenological expression

$$\langle n_x(1) n_x(2) \rangle_{k_B T} \xrightarrow{R \to \infty} \frac{1}{4\pi} \frac{k_B T}{K} \frac{\exp(-R/\xi)}{R}. \tag{38}$$

IV. ZERO-FIELD ASYMPTOTES FOR NEMATIC COLLOIDS

A. Colloid-nematic correlation functions

We consider the behavior of $h_{CN}(1,2)$ [or $h_{NC}(1,2)$] at large separations and zero field. As mentioned above, the total colloid-nematic correlation function describes changes in the local density and orientational distribution of the nematic fluid (including changes in the local director and local ordering) induced by a colloidal particle. For example, if a colloidal particle is located at position 1, the local director at position 2 can be defined as the direction $\hat{\boldsymbol{d}}_m(\boldsymbol{R}_{12})$ that maximizes the expression [9]

$$S(\boldsymbol{R}_{12}, \hat{\boldsymbol{d}}) = \int P_2(\hat{\boldsymbol{\omega}}_2 \cdot \hat{\boldsymbol{d}})[1 + h_{CN}(1,2)] \rho_N(\hat{\boldsymbol{\omega}}_2) d\hat{\boldsymbol{\omega}}_2. \tag{39}$$

The asymptote of $h_{CN}(1,2)$ can be found from Eq. (21) because only the harmonics $h_{221}^{CN}(R) = h_{22-1}^{CN}(R)$ are coupled with the elastic correlations discussed in the preceding section, and hence are responsible for long-range distortions. For our model potential (7) an approximate colloid-nematogen direct correlation function can be constructed from the analytically known wall-nematogen result [20]. For a spherical colloidal particle sufficiently large that curvature effects are unimportant, we have suggested the ansatz

$$c_{CN}(\boldsymbol{R}_{12}, \hat{\boldsymbol{\omega}}_2) \approx c_{WN}(s = \boldsymbol{R}_{12} - \hat{\boldsymbol{R}}_{12}\Sigma/2, \quad \hat{\boldsymbol{\omega}} = \hat{\boldsymbol{\omega}}_2), \tag{40}$$

where c_{WN} is the wall-nematogen direct correlation function found in Ref. [20] for any orientation $\hat{s}$ of the wall with respect to the field.

Using the explicit expression for $c_{221}^{CN}(\boldsymbol{R}_{12}, \hat{\boldsymbol{\omega}}_2) \approx c_{221}^{WN}(s = \boldsymbol{R}_{12} - \hat{\boldsymbol{R}}_{12}\Sigma/2, \ \hat{\boldsymbol{\omega}} = \hat{\boldsymbol{\omega}}_2)$ [see Eq. (20) of [20]] in Eq. (15) and noting that $j_2(x) = \frac{x^2}{15}(1 - \frac{x^2}{14} + \frac{x^4}{504} - \cdots)$, at zero field $c_{221}^{CN}(k)$ can be expanded at large Σ and small k to obtain

$$c_{221}^{CN}(k) \xrightarrow{k \to 0} -4\pi \frac{h_{221}^{WN}(s = \sigma/2)}{30 z_C} B[\Sigma^3 + O(\Sigma^2)] k^2 + O(k^4). \tag{41}$$

Here $h_{221}^{WN}(s = \sigma/2)$ is the contact value of the 221 harmonic of the wall-nematic correlation function with the same interaction parameters (A_C, z_C) as in the colloid-nematogen potential. At zero field the contact value, apart from a functional dependence on $z_C \sigma$ and $z_N \sigma$ (see Ref. [20]), is simply proportional to βA_C. The limit given by Eq. (41) is valid for very large colloids and sufficiently short-ranged anisotropic potentials ($\Sigma \gg \sigma$, $1/z_C$, $1/z_N$). For this case the leading term is proportional to Σ^3 and one can neglect lower powers of Σ.

The asymptote of the colloid-nematogen total correlation function is defined by $h_{221}^{CN}(R_{12})[Y_{21}(\hat{\boldsymbol{R}}_{12}) Y_{21}^*(\hat{\boldsymbol{\omega}}_2) + \text{c.c.}]$. It follows from Eq. (21) that

$$h_{221}^{CN}(k) = c_{221}^{CN}(k)[1 - \rho_N \langle |Y_{21}|^2 \rangle_\omega c_{221}^{NN}(k)]^{-1}. \tag{42}$$

The expansion about $k = 0$ can be found using Eqs. (41) and (27) to obtain

$$h_{221}^{CN}(k) \xrightarrow{k \to 0} -\frac{4\pi}{30} \frac{h_{221}^{WN}(s = \sigma/2)}{B z_C} \Sigma^3 + O(k^2). \tag{43}$$

Inverting the Hankel transform [note that $4\pi \frac{(-i)^2}{(2\pi)^3} \int_0^\infty dk \ k^2 j_2(kR) = -\frac{3}{4\pi} \frac{1}{R^3}$], one finds

$$h_{CN}(1,2) \xrightarrow{R \to \infty} \frac{1}{10} \frac{h_{221}^{WN}(s = \sigma/2)}{B z_C} \frac{\Sigma^3}{R_{12}^3} [Y_{21}(\hat{\boldsymbol{R}}_{12}) Y_{21}^*(\hat{\boldsymbol{\omega}}_2) + \text{c.c.}]. \tag{44}$$

For our model potential $h_{CN}(1,2)$ varies as β at zero external field [see above discussions of B and $h_{221}^{WN}(s = \sigma/2)$].

At this point a comment on the reliability of our analysis is in order. The ansatz taken from the wall-nematic problem is quantitatively accurate if $\xi < \Sigma$, but requires a small correction for the zero-field case. The reason is that the "elastic" correlation length in the nematic phase is infinite at zero field. In Ref. [25] we show that a simple scaling of the ansatz gives results numerically very close to the MSA solution of the OZ equation for nematic colloids in the presence of arbitrarily weak fields, including the zero-field case. For spherical colloids the scaling corrects the asymptote of the nematic distribution about a colloidal particle by a factor 5/4, but it *does not* change the dependence of the asymptotes on the colloidal diameter, or on the interparticle vector. The factor of 5/4 is not accidental and can be obtained analytically in the limit of $\Sigma \to \infty$ (for details see Ref. [25]).

B. The colloid-colloid potential of mean force

Consider a pair of colloidal particles (not necessarily identical) labeled by the superscripts (or subscripts) C and C'. From Eqs. (21) and (22) we obtain

$$h_{221}^{CC'}(k) - c_{221}^{CC'}(k) = \frac{c_{221}^{CN}(k)\rho_N\langle|Y_{21}|^2\rangle_\omega c_{221}^{NC'}(k)}{1 - \rho_N\langle|Y_{21}|^2\rangle_\omega c_{221}^{NN}(k)}. \quad (45)$$

At zero field and small k, Eq. (45) takes the form

$$h_{221}^{CC'}(k) - c_{221}^{CC'}(k) \xrightarrow{k\to 0} \rho_N\langle|Y_{21}|^2\rangle_\omega(4\pi)^2$$
$$\times \frac{h_{221}^{WN}(s=\sigma/2)}{z_C}\frac{h_{221}^{W'N}(s=\sigma/2)}{z_{C'}}\frac{\Sigma^3\Sigma'^3}{(30)^2}k^2$$
$$+ \cdots, \quad (46)$$

where we have used Eqs. (27) and (41). The contribution of the $m=\pm 1$ terms to the Fourier transform of the colloid-colloid potential of mean force, $-\beta\phi_{CC'}(\boldsymbol{R})$, is

$$[h_{221}^{CC'}(k) - c_{221}^{CC'}(k)][Y_{21}(\hat{\boldsymbol{k}})Y_{21}^*(\hat{\boldsymbol{k}}) + \text{c.c.}]$$
$$= [h_{221}^{CC'}(k) - c_{221}^{CC'}(k)]2\left[1 + \frac{\sqrt{5}}{7}Y_{20}(\hat{\boldsymbol{k}}) - \frac{4}{7}Y_{40}(\hat{\boldsymbol{k}})\right]$$
$$= \sum_{l=0,2,4} f_l^{CC'}(k)Y_{l0}(\hat{\boldsymbol{k}}). \quad (47)$$

Although in $\boldsymbol{k}$ space three terms occur on the right-hand side of Eq. (47), at zero field the $Y_{40}(\hat{\boldsymbol{k}})$ term *alone* determines the asymptotic behavior of the potential of mean force in $\boldsymbol{R}$ space. This can be seen explicitly from the finite-field analysis given below (Sec. V), and is evident from numerical calculations [10]. Thus, using the inverse Hankel transformation $f_l^{CC'}(R)=4\pi\frac{(-i)^l}{(2\pi)^3}\int_0^\infty dk\, k^2 j_l(kR)f_l^{CC'}(k)$ for $l=4$ and noting that $k^2Y_{40}(\hat{\boldsymbol{k}})$ becomes $105Y_{40}(\hat{\boldsymbol{R}})/4\pi R^5$ in $\boldsymbol{R}$ space, we obtain

$$\beta\phi_{CC'}(\boldsymbol{R}) \xrightarrow{R\to\infty} \frac{8\pi}{15}\frac{h_{221}^{WN}(s=\sigma/2)}{z_C}\frac{h_{221}^{W'N}(s=\sigma/2)}{z_{C'}}$$
$$\times \rho_N\langle|Y_{21}|^2\rangle_\omega\frac{\Sigma^3\Sigma'^3}{R^5}Y_{40}(\hat{\boldsymbol{R}}). \quad (48)$$

Note that the spherical harmonics are normalized in such a way that $Y_{00}(\hat{\boldsymbol{\omega}})\equiv 1$, in other words $Y_{l0}(\hat{\boldsymbol{R}})=\sqrt{2l+1}P_l(\hat{\boldsymbol{R}})$. In view of the zero-field scaling correction discussed in Ref. [25] and mentioned above, we note that any correction of asymptote (44) with a given factor results in a correction of asymptote (48) with the same factor squared. Thus, the asymptote of the potential of mean force should be scaled with the factor $(5/4)^2$. Again the dependence on R, Σ, and thermodynamic state parameters remains unchanged.

We mentioned above that, at the MSA level, $\beta A_N\rho_N\sigma^3\langle|Y_{21}|^2\rangle_\omega$ is a function of $z_N\sigma$ at $W=0$, and $h_{221}^{WN}(s=\sigma/2)\sim\beta$. Given this, it can be seen from Eq. (48) that in our model $\phi_{CC'}(\boldsymbol{R})$ does not depend on K or S_2, but only on particle interaction parameters $A_{C,N}$, $z_{C,N}$, Σ, and σ. Given these observations, for large colloids we would not expect much change in the intercolloidal forces at large separations throughout the whole region of stable nematic phase. It also implies that experimental measurements of these forces could provide information about particle interaction parameters, essentially at the molecular level. It is interesting to
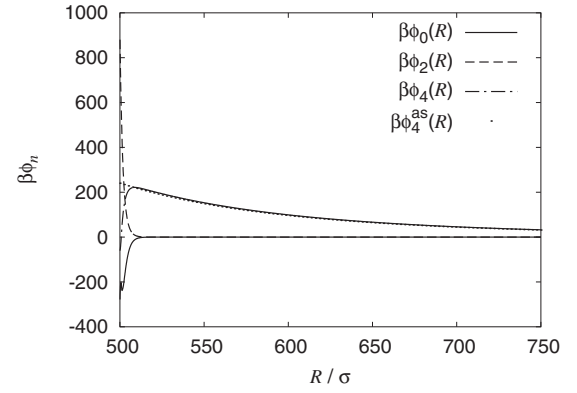

FIG. 1. Components of the colloid-colloid potential of mean force obtained using all harmonics in Eq. (19) and the asymptote $\beta\phi_4^{as}$ given by Eq. (48) for $z_C\sigma=1$, $\beta W=0$, and $\Sigma=500\sigma$. See [26] for other parameters of the model.

note that the result (48) can be linked with the picture based on the electrostatic analogy [4]. One can see from Eq. (48) that colloids with "friendly" parameters (A_C and $A_{C'}$ have the same sign), or with the same symmetry of surface interactions, repel at 0° and 90° with respect to the director, whereas colloids with "antagonistic" parameters (A_C and $A_{C'}$ have opposite signs) attract each other in these directions.

It is interesting to ask how well Eq. (48) can be mapped onto real physical situations. If we consider a pair of identical colloids with $\hat{\boldsymbol{R}}$ parallel or perpendicular to the director, the radial repulsive force has the form

$$F^{CC}(R) \xrightarrow{R\to\infty} \frac{75k_BT}{\sigma}\frac{h_{221}^{WN}(s=\sigma/2)^2}{(z_C\sigma)^2}\eta\langle|Y_{21}|^2\rangle_\omega\frac{\Sigma^6}{R^6}P_4(\hat{\boldsymbol{R}}\cdot\hat{\boldsymbol{n}}),$$

where $\eta=\pi\rho_N\sigma^3/6$ is the packing fraction. This expression includes the $(5/4)^2$ correction. We calculate the force for the parameters $z_C\sigma=z_N\sigma=1$, $\beta A_N=1$, and $\beta A_C=2-4$. These correspond to interactions that decay on length scales on the order of the nematogen dimensions, nematogen-nematogen interactions of order k_BT, and colloid-nematogen interactions of order $(2-4)k_BT$. We would expect these values to roughly describe a "typical" nematic colloid. For these parameters, $\beta A_N\eta\langle|Y_{21}|^2\rangle_\omega=0.312$ [Eq. (3.15) of Ref. [13] or Table I of Ref. [20]] and $h_{221}^{WN}(s=\sigma/2)=0.69-1.38$ (Fig. 3 of Ref. [21]). Then at 300 K and $R=2\Sigma$, we find that, parallel to the director, the colloids repel with a force $\approx 0.72-2.88$ pN. This is the same order of magnitude as the experimental value, $\approx 1.2-1.4$ pN, for a pair of colloidal particles in a quadrupole configuration at $R=2\Sigma$, and $\hat{\boldsymbol{R}}$ parallel to $\hat{\boldsymbol{n}}$ [see Fig. 4(a) of Ref. [7]].

Equation (48) is obtained taking account only of the "elastic harmonics" ($|m|=1$) in expansion (19). It is assumed that elastic deformations of the director field are dominant at long distances. This assumption becomes unsatisfactory near phase boundaries, where fluctuations in local ordering are large. In Figs. 1 and 2 we show the case of a stable nematic. Here we plot the components of the potential of mean force
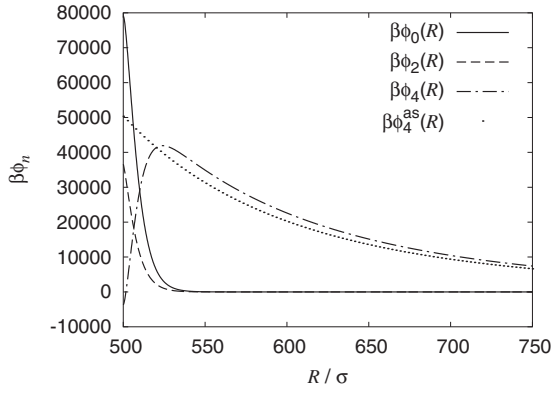
FIG. 2. As in Fig. 1, except that $z_C\sigma=0.2$.

$$\beta\phi_{CC}(\boldsymbol{R}_{12}) = \sum_{l=0,2,4} \beta\phi_l(R_{12})Y_{l0}(\hat{\boldsymbol{R}}_{12}), \qquad (49)$$

calculated numerically using all harmonics in Eq. (19), and compare with the asymptote (48). One observes that the asymptotic behavior sets in fast for $z_C\sigma=1$ (Fig. 1). It sets in more slowly for $z_C\sigma=0.2$ (Fig. 2). In addition, the condition $z_C\Sigma\gg 1$ does not hold as well as for $z_C\sigma=1$, and the contribution of lower powers of Σ in Eq. (41) is noticeable.

Comparing again with experiment, we note that the present theory does not explain the angular dependence of the colloid-colloid force shown in Fig. 4 of Ref. [7]. These experiments show significant deviation from quadrupolar behavior at values of R as large as 2Σ. From Figs. 1 and 2, we see that for the present model and theory the asymptotic quadrupolar limit sets in rapidly and additional harmonics are unimportant at separations for which significant deviations from quadrupolar behavior are reported. We do not know the origin of the discrepancy between our theory and the experiments reported in Ref. [7]. It could possibly stem from approximations in the theory, or perhaps our underlying model is lacking some physical property that is important in the experimental system. We plan to investigate both possibilities.

C. Interactions at the van der Waals level

It is interesting to compare the zero-field expressions obtained above with a simple van der Waals treatment. For the present model [Eq. (7)], the van der Waals approximation consists of setting the direct correlation function $c_{CN}(\boldsymbol{R}_{12},\hat{\boldsymbol{\omega}}_2)$ to $-\beta v_{CN}(1,2)$ outside the surface of the colloidal particle, and to -1 inside the hard core [27]. For harmonics of the direct correlation function this implies

$$c_{22m}^{CN}(R) = \begin{cases} \dfrac{\beta A_C}{5}\exp[-z_C(s_{12}-\sigma/2)] & \text{if } R > \dfrac{\Sigma+\sigma}{2}, \\ 0 & \text{if } R < \dfrac{\Sigma+\sigma}{2}, \end{cases}$$

$$(50)$$

$c_{000}^{CN}(s_{12}<\sigma/2)=-1$, and all other harmonics are zero. The Hankel transform of Eq. (50) can be expanded at small k to obtain

$$c_{221}^{CN}(k) \xrightarrow{k\to 0} -\frac{4\pi\beta A_C}{5}\frac{\Sigma^4 z_C^4 + 4\Sigma^3 z_C^3(2+z_C\sigma)+\cdots}{240 z_C^5}k^2 + O(k^4).$$

$$(51)$$

If one neglects lower powers of Σ and uses the condition $\Sigma\gg z_C^{-1}$, it follows from Eqs. (45) and (27) that

$$h_{221}^{CC'}(k) - c_{221}^{CC'}(k) \xrightarrow{k\to 0} \frac{\rho_N^2 S_2^2}{\beta K}15\left(\frac{4\pi\beta A_C}{5}\frac{\Sigma^4}{240 z_C}\right)$$

$$\times\left(\frac{4\pi\beta A_{C'}}{5}\frac{\Sigma'^4}{240 z_{C'}}\right)k^2 + \cdots + O(k^4).$$

$$(52)$$

Next consider the equilibrium colloid-nematogen interaction which determines the director orientation with respect to the surface normal $\hat{s}$. For example, if $A_C>0$ the director is parallel to $\hat{s}$. If we make the mean field assumption that the equilibrium nematic distribution near the wall is just the bulk distribution, then the average interaction energy expressed per unit area is

$$U = -\int_{\Sigma+\sigma/2}^{\infty} A_C \exp\left[-z_C\left(s-\frac{\Sigma+\sigma}{2}\right)\right]$$

$$\times\rho_N(\hat{\boldsymbol{\omega}}\cdot\hat{s})P_2(\hat{\boldsymbol{\omega}}\cdot\hat{s})d\hat{\boldsymbol{\omega}}\,d\hat{s} = -A_C\rho_N S_2/z_C. \quad (53)$$

Then, following the method of the previous section, one obtains a van der Waals expression for the asymptote of the effective colloidal interaction

$$\beta\phi_{CC'}(\boldsymbol{R}) \xrightarrow{R\to\infty} \frac{UU'}{K}\frac{\Sigma^4}{2}\frac{\Sigma'^4}{2}3.84\pi\frac{P_4(\hat{\boldsymbol{R}}\cdot\hat{n})}{R^5}. \quad (54)$$

We see that the van der Waals result gives the same angular and R dependence as the MSA ansatz [Eq. (48)], but differs in its Σ dependence, giving Σ^8 rather than Σ^6 for a pair of identical colloid particles. The van der Waals approximation is known to be valid if the interactions are weak, and if all correlation lengths are finite. The second condition is clearly not satisfied for bulk nematics at zero field, where ξ tends to infinity, and we believe that this explains the different Σ dependences. Indeed, in Sec. V, below, we show that the leading Σ dependence changes from Σ^6 at zero field to Σ^8 at finite field (ξ is finite).

It is interesting to note that, for identical colloidal particles, Eq. (54) clearly resembles the leading term in Eq. (6) of Ref. [3]. If one arbitrarily identifies the anchoring energy V with the average colloid-nematic interaction energy U, Eq. (54) differs from the result obtained for the weak anchoring limit by a factor of 1.8. We stress that the two approaches are essentially different. For example, in the elastic approach, which is employed in Ref. [3], the nematic is considered as locally uniaxial with the local order parameter equal to that of the bulk. In general, the van der Waals approach does not need these assumptions. However, the similarity of the two expressions does suggest that the weak anchoring limit is roughly equivalent to microscopic theory applied at the van der Waals level.

V. ASYMPTOTES AT WEAK BUT NONZERO FIELD

Here we consider asymptotic behavior at weak but nonzero field. At small k, the Hankel transform of $c_{221}^{CN}(R)$ can be expanded in the general form

$$c_{221}^{CN}(k) = -4\pi/15k^2(c_4 - k^2c_6/14 + k^4c_8/504 - \cdots),$$

$$(55)$$

where

$$c_{2n} = \int_0^\infty dR \ R^{2n}c_{221}^{CN}(R).$$

$$(56)$$

It follows from Eq. (27) that at small fields

$$h_{221}^{CN}(k) = \frac{c_{221}^{CN}(k)}{(k^2 + \xi^{-2})B^2}.$$

$$(57)$$

The inverse Hankel transform of Eq. (57) combined with the infinite expansion (55) is

$$h_{221}^{CN}(R) = -\frac{1}{4\pi B^2}\frac{e^{-R/\xi}[3 + R/\xi(3 + R/\xi)]}{R^3}\xi^2 c_{221}^{CN}(k = \xi^{-1}),$$

$$(58)$$

where we have used the relationship

$$\int_0^\infty dk \ j_2(kR)\frac{k^{2n}}{k^2 + \xi^{-2}} = \frac{e^{-R/\xi}\pi[3 + R/\xi(3 + R/\xi)]}{2R^3\xi^{2n-4}}. \quad (59)$$

Asymptotically, the total correlation function takes the form

$$h_{CN}(1,2) \overset{R\to\infty}{\to} h_{221}^{CN}(R)[Y_{21}(\hat{\boldsymbol{R}}_{12})Y_{21}^*(\hat{\boldsymbol{\omega}}_2) + \text{c.c.}], \quad (60)$$

where $h_{221}^{CN}(R)$ is defined by Eq. (58).

We note that the formal expansion (58) is correct for colloids of any size. It is interesting that the $\boldsymbol{R}$ dependence defined by Eq. (60) is exactly that obtained [3] for the director distribution around a large spherical colloidal particle in the limit of weak anchoring [see Eq. (10) of Ref. [3]]. In our theory the director distribution $\hat{\boldsymbol{d}}_m(\boldsymbol{R}_{12})$ is obtained [9] by finding the extremum of Eq. (39). It can be shown [28] that $\hat{\boldsymbol{d}}_m(\boldsymbol{R}_{12})$ has the same $\boldsymbol{R}$ dependence at large R if $h_{221}^{CN}(R) \ll A$, where A is the coefficient of the single-particle distribution function defined in Sec. III. In this case local deviations from the bulk director tend to zero, consistent with the analysis of Ref. [3], where the director distribution is obtained under the condition of infinitely small deviations of the local director from the bulk.

For large colloids we can again use the wall-nematogen result as discussed above. For nonzero external field, the correlation length is finite and the expansion (41) takes the form

$$c_{221}^{CN}(k) = -4\pi BC(\Sigma, z_C)k^2 + O(k^4), \quad (61)$$

$$C(\Sigma, z_C) \approx \frac{h_{221}^{WN}(s = \sigma/2)}{30z_C}[\Sigma^4/(8\xi) + \Sigma^3 + O(\Sigma^2)]. \quad (62)$$

Insertion of $-4\pi C(\Sigma, z_C)B$ instead of $\xi^2 c_{221}^{CN}(k = \xi^{-1})$ into Eq. (58) yields the asymptote of the colloid-nematic correlation function at weak, but nonzero, external fields. It is interesting

to observe that the Σ dependence of $h^{CN}(1,2)$ depends critically on the presence or absence of an external field. If there is no external field, $\xi = \infty$ and the Σ^4 term vanishes, leaving Σ^3 as the dominant term for large colloidal particles.

Following the method discussed above (Sec. IV B), we obtain the colloid-colloid potential of mean force at nonzero external field in the form

$$\beta\phi_{CC'}(\boldsymbol{R}) \overset{R\to\infty}{\to} \frac{4\pi}{\xi^5}C(\Sigma, z_C)C(\Sigma', z_{C'})\rho_N\langle|Y_{21}|^2\rangle_\omega\bigg(-2k_0(R/\xi)$$

$$-\frac{10}{7}k_2(R/\xi)P_2(\hat{\boldsymbol{R}}) + \frac{24}{7}k_4(R/\xi)P_4(\hat{\boldsymbol{R}})\bigg), \quad (63)$$

where

$$k_0(x) = e^{-x}/x, \quad k_2(x) = \frac{3 + 3x + x^2}{x^3}e^{-x},$$

$$k_4(x) = \frac{105 + 105x + 45x^2 + 10x^3 + x^4}{x^5}e^{-x}. \quad (64)$$

The expression (63) has a limited range of validity. First, it is assumed that changes in local ordering are not important at long distances, allowing us to neglect the harmonics with $|m| \neq 1$. Further, the expression is obtained for large Σ, but Σ must also be sufficiently smaller than the correlation length ξ that the k expansions can be truncated at k^2.

Despite these restrictions, Eq. (63) leads to several important observations. We see immediately that only the quadrupole term survives as $\xi \to \infty$, consistent with the statement made above (Sec. IV B). Also, as discussed earlier, in this limit the potential of mean force behaves as Σ^6. Significantly, we see that in the large Σ limit the Σ dependence shifts from Σ^6, when ξ is infinite, to Σ^8 if ξ is finite. We note that the correlation length can be finite in experimental nematic samples even without application of electric (or magnetic) fields, for example through interaction with walls or surfaces. Finally, Eq. (63) shows that at nonzero field the symmetry of effective interactions cannot be described as quadrupolelike even asymptotically. One can see that the quadrupole interaction transforms into a superposition of screened multipoles when the correlation length is finite.

Components of the effective colloid-colloid potential (49) at finite field are plotted in Fig. 3. Compared with Fig. 2, we note that $\phi_4(R_{12})$ becomes shorter ranged at finite field, as expected, but that the range of $\phi_0(R_{12})$ and $\phi_2(R_{12})$ is much increased. Note that, for the case shown, $\xi \approx 51\sigma$ and is almost ten times smaller than $\Sigma = 500\sigma$.

VI. CONCLUSIONS

In this paper, we have analyzed asymptotes of correlation functions in nematic colloids in an effort to bridge the gap between phenomenological results and microscopic theory. We have shown that asymptotes of the bulk nematogen-nematogen correlations are exact analogs of the correlations of director fluctuations first predicted by de Gennes [19]. Our approach, based on a general solution of the Ornstein-Zernike equation, allows explicit microscopic calculations of the density and orientational profiles, as well as of potentials
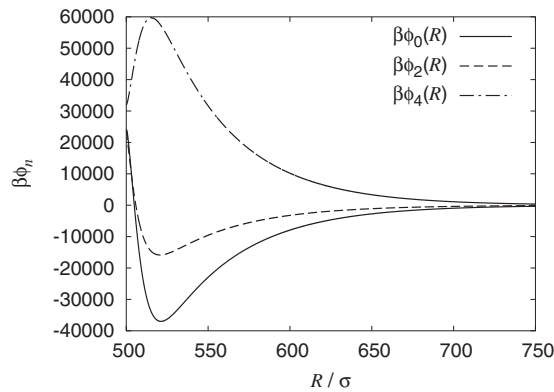
FIG. 3. Components of the colloid-colloid potential of mean force obtained using all harmonics for $z_C\sigma = 0.2$, $\beta W = 10^{-3}$, and $\Sigma = 500\sigma$. See [26] for other parameters of the model.

of mean force for large colloidal particles in nematic media at different length scales. Here we have concentrated on their asymptotic properties. We show that the electrostatic analogy postulated in Refs. [2,4] results from the fact that the correlation length ξ, the so-called magnetic coherence length, is infinite at zero field. In this limit the nematogen-nematogen pair correlation decays as $1/R$, in analogy with the Coulombic interaction.

In contrast to phenomenological approaches, the molecular theory does not assume specific boundary conditions (anchoring) at the surface of colloid particles. Instead, anchoring appears naturally through the colloid-nematic correlations. For the model and molecular parameters we employ, the resulting anchoring appears to be realistic; it is neither rigid nor particularly weak [9]. We find that the effective long-range colloid-colloid interaction does not change (or changes only little) throughout the region where the nematic phase is stable.

We show that a simple van der Waals treatment of the nematogen-colloid direct correlation function yields a colloid-colloid potential of mean force that resembles the phenomenological result obtained in the limit of weak anchoring [3]. In particular, at large distances it varies as Σ^8, where Σ is the colloidal diameter. The more sophisticated MSA ansatz approach predicts a Σ^6 dependence consistent with the result obtained by imposing rigid boundary conditions at colloidal surfaces [2,4]. We believe that the reason for this discrepancy lies in the fact that the van der Waals approximation does not take account of the fact that the correlation length ξ is infinite at zero field.

We have also considered the weak- but nonzero-field limit. We show that the quadrupole interaction found at zero field transforms into a superposition of screened multipoles when the correlation length is finite. Another interesting feature that emerges from our analysis is that, in the large-Σ limit, the Σ dependence of the potential of mean force shifts from Σ^6, when ξ is infinite (zero field), to Σ^8 if ξ is finite.

Finally, we note that the present technique, based on our ansatz and the MSA wall-nematic solution obtained for an arbitrary orientation of the wall with respect to the nematic director, has some additional advantages. The same analytical solution (with small adjustments) can be used for physically different systems, such as nonspherical colloids, colloids with a nonuniform distribution of surface surfactant (patterned colloids), colloids trapped at interfaces, and nematic droplets.

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where $\tilde{C}$ depends only on $z_N\sigma$. After some additional algebra one can get B expressed through $z_N\sigma$ explicitly.

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