

Orientational structure of dipolar hard-spherical colloids

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We have studied the orientational structure of a dipolar hard-spherical colloid on a homogeneous isotropic phase. The results are expressed as a function of the dipolar strength μ and volume fraction ϕ of dipolar colloids, and the refractive index of the scattering medium, n_s . The study is based on the self-correlation of the orientation density of the dipolar colloids, which is the static orientational structure factor $[F(q)]$, where q is the wave vector. The importance of this quantity is that for very low ϕ values, it can be probed in a depolarized light scattering experiment. We have found that the structure of the suspension is better observed for high n_s . $F(q)$ presents a different behavior for dilute and dense concentrations, it is also observed that the position of its minimum depends on ϕ . The response of a dipolar colloid due to its collective orientational behavior is also studied, using as an “ordering parameter” the static orientational structure factor at $q=0$ [$F(q=0)$]. The study is performed for isochores as a function of μ . We have divided the analysis into five regimes, from very low to very high ϕ values, i.e., $\phi=0.00524, 0.1, 0.2, 0.35, \text{ and } 0.45$. Our analysis suggests that the dipolar colloid evolves to an orientationally ordered phase when the dipolar strength is increased, for all concentrations except for the lowest value case, $\phi=0.00524$. When $\phi=0.1$ the dipolar colloid reaches the transition suddenly, whereas for the very low regime, the slope of $F(q=0)$ first increases as if the dipolar colloid would evolve to an orientationally ordered phase; but near the transition the slope is inverted, resulting in a no global orientational order. Thus, our results suggest that in the very low regime a dipolar colloid may have a reentrant transition.

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I. INTRODUCTION

The structural properties of colloidal dispersions of spherical macroparticles are well understood on the basis of the interactions among those particles [1,2]. The basis for the understanding of these properties is the radial distribution function $g(r)$, which can be obtained accurately using integral equation theories or molecular simulations [3]. The Fourier transform of $g(r)$ is the self-correlation function of density fluctuations $F(q)$, which, for example, can be measured using a static light scattering experiments and provides an important link between the microstructure and experiments. It is well known that the $q \rightarrow 0$ limit of $F(q)$ is an observable related to the isothermal compressibility [3].

In contrast, structural properties of thermotropic non-spherical colloids [4] (those experiencing a phase transition over temperature) are not as well known as those of spherical colloids. Whereas hard-spherical colloids can only form an isotropic liquid phase and a crystalline solid phase, there are many nonspherical colloids in nature that can form liquid crystalline phases, which exhibit a degree of ordering intermediate between the isotropic fluid and the crystalline solid when the temperature is decreased. It is well known that this rich variety of phase transitions in thermotropic colloids is due to the collective positional orientational behavior of the colloidal particles. An example of a thermotropic colloid is a dipolar colloidal suspension [5], i.e., hard-spherical macro-

particles with an axially symmetric dipolar interaction. The importance of these systems is not only because dipolar interactions are omnipresent in nature, but also because they play a prominent role in many artificial systems, such as ferrofluids and electrorheological fluids, etc. Recent work [6–8] has shown that the behavior of dipolar model fluids is much more complex than previously expected. It has been found that at high dipolar strength and low volume fraction, the system tends to associate into chains and ring aggregates occasionally, while at higher volume fraction the dipolar colloid can spontaneously form a ferroelectric fluid phase. In the low density phase, the dipolar hard spheres form dimers and chainlike clusters instead of the isotropic clusters observed in liquids formed by molecules interacting via dispersion forces only. A usual condensation is seen if an additional attractive force is included, as in the Stockmayer fluid. From Monte Carlo simulations results, no liquid-gas coexistence has been observed at the dipolar strengths and densities expected [9]. It is important to mention that Stevens and Grest found that dipolar soft spheres, at low reduced density $\rho^* \sim 10^{-2}$ ($\sim \phi=0.0052$), associate into chains that are entangled and thus exhibit no global orientational order [10].

Structural properties are obtained by ensemble averages of different projections of the correlation function $g(\mathbf{r}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$, where \mathbf{r} is the relative position between two dipoles given by $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, where \mathbf{r}_1 and \mathbf{r}_2 are the positions of the centers of mass of macroparticles 1 and 2, $\hat{\mathbf{u}}_1$ and

$\hat{\mathbf{u}}_2$ are the unit vectors along the orientations of the dipoles in macroparticles 1 and 2.

In this paper we focus our attention on colloidal suspensions of hard spheres with an axially symmetric dipolar interaction potential on an homogeneous isotropic phase. Our goal is to develop an approach considering the experimental conditions of the depolarized light scattering (DLS) experiments [1]. This approach is based on the fluctuational effects of the traceless symmetric tensor of the orientation density on the structural properties of thermotropic colloids, which bridge the gap between the microscopic interactions and the macroscopic properties of dipolar colloids. In order to describe the collective positional orientational behavior of dipolar colloids, in Sec. II we provide the experimental conditions of DLS. The collective positional orientational variable is defined, which can be probed in DLS. The equilibrium positional orientational fluctuations of the collective variable is also provided. In Sec. III details for obtaining the projections using reference hypernetted chain (RHNC) equation theory are given. In Sec. IV we present the results for the static orientational structure factor of dipolar colloids, as a function of the wave vector, for different values of the dipolar strength and volume fraction of the colloidal particles. We also analyze the response of the static orientational structure factor due to the refractive index of the scattering medium. In Sec. V the limit $q \rightarrow 0$ for the static orientational structure factor is analyzed, as a function of the volume fraction and the dipolar strength. The projections $g(000;r)$ and $g(220,r)$ versus neighboring layers of dipolar colloids as a function of volume fractions are also presented. Concluding remarks are given in Sec. V.

II. CORRELATION OF THE ORIENTATION DENSITY

In order to develop an approach for describing the collective positional and orientational behavior of dipolar colloids, we assume that the macroparticles are characterized by a polarizability tensor, which is optically uniaxial, and described by a dielectric tensor of the form

$$\tilde{\epsilon} = \bar{\epsilon} \mathbf{I} + \Delta \epsilon [\hat{\mathbf{u}} \hat{\mathbf{u}} - \frac{1}{3} \mathbf{I}], \quad (1)$$

where $\bar{\epsilon} = (2\epsilon_{\perp} + \epsilon_{\parallel})/3$ is the average of the dielectric constants, ϵ_{\perp} and ϵ_{\parallel} are the dielectric constants perpendicular and parallel to the symmetry axis of the dipolar macroparticle, respectively, $\Delta \epsilon$ is the difference between the two dielectric constants (the anisotropic polarizability), and $\hat{\mathbf{u}}$ is the unit vector in the direction of the symmetry axis of the macroparticle. In Eq. (1), \mathbf{I} is the unit tensor and $\hat{\mathbf{u}} \hat{\mathbf{u}}$ represents the dyadic product.

From Eq. (1), we observe that the main fluctuations of the dielectric tensor will be given by the fluctuations of $\hat{\mathbf{u}}$. In consequence, we define the traceless symmetric tensor of the orientation density [4] for N macroparticles in Fourier space,

$$\mathbf{Q}(q,t) = \frac{1}{\sqrt{N}} \sum_l \frac{3}{2} [\hat{\mathbf{u}}_l(t) \hat{\mathbf{u}}_l(t) - \frac{1}{3} \mathbf{I}] e^{i\mathbf{q} \cdot \mathbf{r}(t)}, \quad (2)$$

which is the dynamical variable appropriate for describing the collective positional orientational behavior of the dipolar colloid. Here the behavior is due to the fluctuations of the orientation of the dipole and the position of the center of mass of the macroparticle l , $\hat{\mathbf{u}}_l$, and \mathbf{r}_l , respectively [4], and \mathbf{q} is the wave vector. In a depolarized light scattering experiment in the VH geometry the self-correlation of the traceless symmetric tensor of the orientation density can be measured. The VH geometry is the situation in which the incident field is linearly polarized in the vertical direction and the scattered field is observed in the horizontal plane. The static orientational structure factor is written as

$$F(q,0) = \langle [\hat{\mathbf{n}}_s \cdot \mathbf{Q}(q,0) \cdot \hat{\mathbf{n}}_0] [\hat{\mathbf{n}}_s \cdot \mathbf{Q}^*(q,0) \cdot \hat{\mathbf{n}}_0] \rangle, \quad (3)$$

where $\hat{\mathbf{n}}_s$ and $\hat{\mathbf{n}}_0$ are the unit vectors in the polarization direction of the incident light and the detected one, respectively, $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_0$ being the scattering vector, where \mathbf{k}_s and \mathbf{k}_0 are the wave vectors in the directions of propagation of the incident and the detected. The magnitude of \mathbf{q} , assuming elastic light scattering, is given by

$$|\mathbf{q}| = 2k \sin \frac{\theta_s}{2}, \quad (4)$$

where $k = 2\pi n_s / \lambda$ is the magnitude of the wave vector, n_s is the refractive index of the scattering medium, λ is the wavelength in vacuum and θ_s is the angle between \mathbf{k}_s and \mathbf{k}_0 , which is called the scattering angle.

From Eq. (3), it can be seen that we are just computing equilibrium fluctuations of the component $[\mathbf{Q}(q,t)]_{s_0}$ of the traceless symmetric tensor of the orientation density, which are determined by the polarization vectors. Other components are not taken into account due to the symmetry properties of the orientation density and the potential interaction.

In order to proceed with the calculation of the fluctuational effects of the traceless symmetric tensor of the orientation density, we first rewrite Eq. (3) in a more convenient form. The unit vectors $\hat{\mathbf{n}}_0$ and $\hat{\mathbf{n}}_s$ are taken in the VH geometry [11],

$$\hat{\mathbf{n}}_0 = \hat{\mathbf{k}},$$

$$\hat{\mathbf{n}}_s = \sin \theta_s \hat{\mathbf{i}} + \cos \theta_s \hat{\mathbf{j}}, \quad (5)$$

where $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$, and $\hat{\mathbf{k}}$ are the unit vectors in the direction of the laboratory's axis and $\hat{\mathbf{u}}_l$ is written in spherical coordinates,

$$\hat{\mathbf{u}}_l = \sin \theta_l \cos \psi_l \hat{\mathbf{i}} + \sin \theta_l \sin \psi_l \hat{\mathbf{j}} + \cos \theta_l \hat{\mathbf{k}}. \quad (6)$$

Now from Eqs. (3), (5), and (6), together with the definition of spherical harmonics [12]

$$Y_{2,\pm 1}(\theta, \psi) = \sqrt{5/8\pi} \sin \theta \cos \theta e^{\pm i\psi}, \quad (7)$$

we obtain

$$\begin{aligned}
F(q,0) = & \frac{2\pi}{N} \sum_{l,m=1}^N \{ \langle Y_{2\bar{1}}^*(\Omega_l^0) e^{-i\mathbf{q}\cdot\mathbf{r}_l^0} Y_{2\bar{1}}(\Omega_m^0) e^{i\mathbf{q}\cdot\mathbf{r}_m^0} \\
& + Y_{2\bar{1}}^*(\Omega_l^0) e^{-i\mathbf{q}\cdot\mathbf{r}_l^0} Y_{2\bar{1}}(\Omega_m^0) e^{i\mathbf{q}\cdot\mathbf{r}_m^0} \rangle \\
& + \langle Y_{2\bar{1}}^*(\Omega_l^0) e^{-i\mathbf{q}\cdot\mathbf{r}_l^0} Y_{2\bar{1}}(\Omega_m^0) e^{i\mathbf{q}\cdot\mathbf{r}_m^0} \\
& + Y_{2\bar{1}}^*(\Omega_l^0) e^{-i\mathbf{q}\cdot\mathbf{r}_l^0} Y_{2\bar{1}}(\Omega_m^0) e^{i\mathbf{q}\cdot\mathbf{r}_m^0} \rangle \times (\cos^2 \theta_s \\
& - \sin^2 \theta_s) + \langle Y_{2\bar{1}}^*(\Omega_l^0) e^{-i\mathbf{q}\cdot\mathbf{r}_l^0} Y_{2\bar{1}}(\Omega_m^0) e^{i\mathbf{q}\cdot\mathbf{r}_m^0} \\
& - Y_{2\bar{1}}^*(\Omega_l^0) e^{-i\mathbf{q}\cdot\mathbf{r}_l^0} Y_{2\bar{1}}(\Omega_m^0) e^{i\mathbf{q}\cdot\mathbf{r}_m^0} \rangle \\
& \times 2i \cos \theta_s \sin \theta_s \}, \tag{8}
\end{aligned}$$

where $\Omega_l^0 \equiv (\theta_l(0), \psi_l(0))$ denotes the polar angles, which specify the direction of the dipole of the macroparticle l at $t=0$, \mathbf{r}_l^0 is the position of the center of mass of macroparticle l at $t=0$, Y_{ab}^* means complex conjugation, and $\bar{1} \equiv -1$. From Eq. (8) we note that $F(q,0)$ depends on the magnitude of \mathbf{q} , i.e., k and the scattering angle θ_s . For convenience we simplify its expression by taking k as a parameter, that is, the refractive index n_s ,

$$\frac{q\sigma}{(2k\sigma)} = \sin \frac{\theta_s}{2}, \tag{9}$$

where σ is the diameter of the macroparticle. In this way, the results are parametrized in terms of the refractive index of the solvent.

In Eq. (8) the equilibrium ensemble is taken in a canonical ensemble. The equilibrium distribution is given by

$$P_{\text{eq}}(\mathbf{r}^N, \Omega^N) = \frac{1}{Z} \exp \left[- \frac{\Phi(\mathbf{r}^N, \Omega^N)}{k_B T} \right], \tag{10}$$

where $k_B T$ is the thermal energy and

$$Z = \int d\mathbf{r}^N d\Omega^N \exp \left[- \frac{\Phi(\mathbf{r}^N, \Omega^N)}{k_B T} \right] \tag{11}$$

is the configurational integral. In Eqs. (10) and (11) $\mathbf{r}^N = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ and $\Omega^N = (\Omega_1, \dots, \Omega_N)$. Thus, the brackets in Eq. (8) mean [12] the following:

$$\langle \dots \rangle = \int d\mathbf{r} d\Omega_1 d\Omega_2 g(\mathbf{r}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \dots, \tag{12}$$

where $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $g(\mathbf{r}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$ is the angle-dependent pair correlation function, which gives the probability of finding a macroparticle with center of mass at \mathbf{r} and dipole pointing along $\hat{\mathbf{u}}_2$, if there is a macroparticle with the center at the origin having its dipole along $\hat{\mathbf{u}}_1$. The angle-dependent pair correlation function is given by

$$\begin{aligned}
g(\mathbf{r}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = & \left(\frac{N(N-1)(4\pi)^2}{\rho^2} \right) \\
& \times \int d\mathbf{r}^{N-2} d\Omega^{N-2} P_{\text{eq}}(\mathbf{r}^N, \Omega^N), \tag{13}
\end{aligned}$$

where ρ is the bulk concentration of dipolar colloidal particles. The angle-dependent pair correlation function can be computed using integral equation theories, which are based on the Ornstein-Zernike equation with the appropriate closure relation [13], Monte Carlo [4,14] and molecular dynamic [4] simulations, and perturbation theories [15]. In our approach, this quantity is assumed as input. In the following section we discuss the RHNC approach used for computing $g(\mathbf{r}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$.

III. DIPOLAR MODEL AND RHNC STRUCTURE

Let us assume a colloidal suspension of hard-spherical macroparticles with a point dipole embedded at the center of the macroparticle in a carrier solution. Standard scaled variables are used $\mu^{*2} = 1/T^*$, $T^* = k_B T \sigma^3 / \mu^2$, where $k_B T$ is the thermal energy. The pair angular-dependent interaction potential is given by

$$u(\mathbf{r}, \Omega_1, \Omega_2) = \begin{cases} - \frac{\mu^{*2} D(\Omega_r, \Omega_1, \Omega_2)}{r^3} & \text{for } r > \sigma \\ \infty & \text{for } r < \sigma \end{cases} \tag{14}$$

where r is the magnitude of the vector \mathbf{r} with orientation $\Omega_r = (\theta_r, \psi_r)$. The dipolar orientation for the macroparticle is denoted by Ω_l and $D(\Omega_r, \Omega_1, \Omega_2)$ is the angular dependence of the pair potential,

$$D(\Omega_r, \Omega_1, \Omega_2) = 3(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_1)(\hat{\mathbf{r}} \cdot \hat{\mathbf{u}}_2) - (\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2). \tag{15}$$

All the structural information on the dipolar colloid is contained in the total and direct correlation functions $h(1,2)$ and $c(1,2)$, where $(1, 2)$ is a short notation representing $(\mathbf{r}, \Omega_1, \Omega_2)$. These correlation functions were calculated by iterative solution of the Ornstein-Zernike equation

$$h(1,2) = c(1,2) + \frac{\rho}{4\pi} \int d3 h(1,3)c(3,2), \tag{16}$$

combined with the exact relation between $u(1,2)$, $h(1,2)$, $c(1,2)$, and the bridge function $B(1,2)$,

$$1 + h(1,2) = \exp[-\beta u(1,2) + h(1,2) - c(1,2) + B(1,2)]. \tag{17}$$

In this work we use RHNC [5,13], which approximates $B(1,2)$ with the hard-sphere bridge function. We use the Verlet-Weiss $B(1,2)$ expression. The solution of Eq. (16) is given in terms of projections of the angular-dependent pair correlation function $g(1,2) = h(1,2) + 1$, which are the coefficients of an expansion on a spherical invariant basis. Two different expansions are widely used depending of the choice of the reference frame [12]; we just focus on the so-called laboratory one, which is given by

$$\begin{aligned}
g(1,2) = & \sum_{l_1 l_2 l} \sum_{m_1 m_2 m} g(l_1 l_2 l; r) C(l_1 l_2 l, m_1 m_2 m) \\
& \times Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2) Y_{lm}^*(\Omega_r), \tag{18}
\end{aligned}$$

where $C(l_1 l_2 l; m_1 m_2 m)$ are the Clebsch-Gordan coefficients and $g(l_1 l_2 l; r)$ are the projections in spherical invariants of $g(1,2)$.

Some of the coefficients of the expansion in Eq. (18) have a direct physical interpretation, i.e., the isotropic quantity $g(000;r)$ is the center-center distribution function [7], regardless of the orientations of the macroparticles. Another important projection is the anisotropic quantity $g(220;r)$. For rods, this function is a measure of the average angular correlations at separation r [15], which vanishes for all r in the isotropic phase, whereas for a fully aligned phase it is equal to 1 and negative if the rods have the tendency to be perpendicular to each other [16]. For dipolar colloids, the larger $g(220;r)$, the higher the probability that two dipoles, separated by a distance r , align (either parallel or antiparallel), regardless of their relative positional arrangement [5].

IV. STATIC ORIENTATIONAL STRUCTURE FACTOR

In this section, we present the results obtained for the static orientational structure factor [$F(q)$], as a function of $q \neq 0$, which describes the positional and orientational correlations between the macroparticles. To obtain $F(q\sigma)$, parametrized with k [see Eq. (9)], we substitute Eq. (18) into Eq. (8), and after a lengthy algebraic calculation, and integrating in the angular coordinates, we have

$$\begin{aligned}
 F(q\sigma) = & 1 + \frac{3}{4} \frac{\phi}{\sqrt{\pi^3}} \left\{ \frac{2}{\sqrt{5}} \int_1^\infty dx x^2 g(220;x) F_{00}(q\sigma x) \right. \\
 & + \int_1^\infty dx x^2 g(222;x) \left[-\frac{2}{\sqrt{14}} F_{20}(q\sigma x) \right. \\
 & + \sqrt{3/7} FF_{22}(q\sigma x) S_1(q\sigma) \\
 & + 2\sqrt{3/7} FF_{22}(q\sigma x) S_2(q\sigma) \left. \right] - \int_1^\infty dx x^2 g(224;x) \\
 & \times \left[2\sqrt{8/35} F_{40}(q\sigma x) + \frac{2}{\sqrt{7}} FF_{42}(q\sigma x) S_1(q\sigma) \right. \\
 & \left. \left. + \frac{4}{\sqrt{7}} FF_{42}(q\sigma x) S_2(q\sigma) \right] \right\}, \quad (19)
 \end{aligned}$$

where $\phi = \pi \rho \sigma^3 / 6$ is the volume fraction of the macroparticles. The functions $F_{a0}(q\sigma x)$, $FF_{ab}(q\sigma x)$, and $S_a(q\sigma)$ in Eq. (19) are given in the Appendix.

It is important to stress here that Eq. (19) is, in general, valid for hard-spherical colloids interacting via an arbitrary symmetric potential, and depends on temperature and density through the projections $g(22l;x)$, and on the refractive index of the solvent through the parameter k , as given by Eq. (9). From Eq. (19), we see that a linear integral equation approach is unable to calculate the static orientational structure factor.

First, it is normalized to $F(q) \rightarrow 1$ for $q \rightarrow \infty$. Concerning the parameter $k\sigma$, we have calculated $F(q\sigma)$ for several values of the refractive index of the scattering medium (k

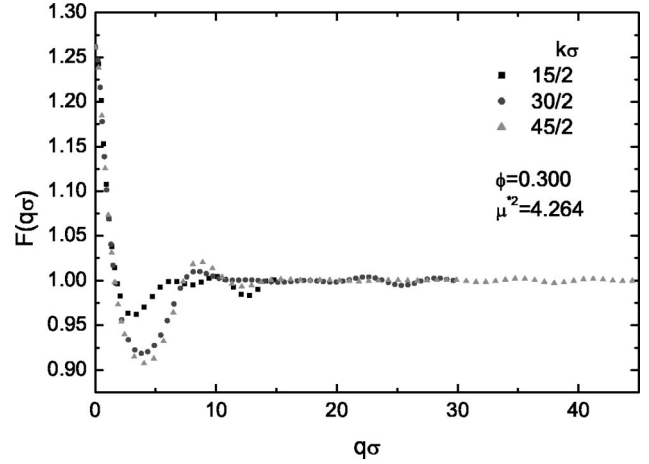


FIG. 1. Static orientational structure factor versus $q\sigma$ for $\phi = 0.3$ and $\mu^{*2} = 4.264$ and three different values of $k\sigma$, as indicated in the figure.

$\sim n_s$). The results, given in Fig. 1, show us that this approach is very sensitive to the refractive index of the scattering medium and the details of the structure are better seen for higher values of n_s . Therefore, the structure of the suspension is better observed for high values of n_s . From Fig. 1 we see that the position and the depth of the minimum are scaled by n_s . An important difference between the static structure factor and the orientational one is that the main peak is a maximum for the former [3], while being a minimum for the latter. From Eq. (19) we see that the static orientational structure factor depends just on the projections $g(22l;x)$ with $l = 0, 2$, and 4 , then the minimum is related to the probability of finding a dipolar particle parallel or antiparallel to the first one at the scattering angle θ_s . Consequently, the static orientational structure factor is related to the information on the positions and the orientations between two dipolar macroparticles.

In Figs. 2 and 3 we have plotted $F(q\sigma)$ versus $q\sigma$ with the parameter $k\sigma = \frac{30}{2}$ for convenience, for $\phi = 0.35$ and two values of the dipolar strength, $\mu^{*2} = 3$ and 3.5 , and for

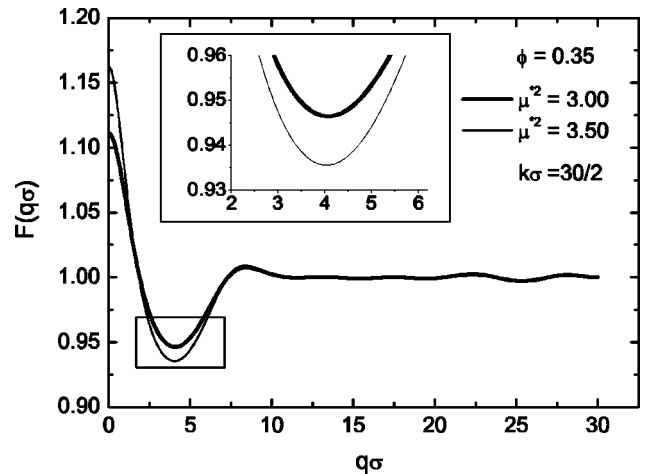


FIG. 2. Static orientational structure factor versus $q\sigma$ for $\phi = 0.35$ and $\mu^{*2} = 3.0$ and 3.5 , both with $k\sigma = 30/2$.

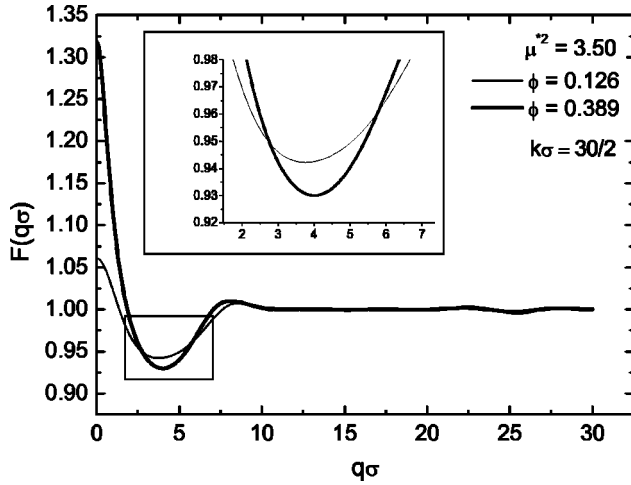


FIG. 3. Static orientational structure factor versus $q\sigma$ for $\mu^{*2} = 3.50$, and $\phi = 0.126$ and 0.389 , both with $k\sigma = 30/2$.

$\mu^{*2} = 3.5$ and two values of the volume fraction, $\phi = 0.126$ and 0.389 , respectively. From these figures we can conclude that the minimum position does not depend on μ^{*2} but depends on ϕ of dipolar colloids, as in the usual static structure factor. The depth of the minimum depends on μ^{*2} and ϕ . It is important to note that the results are parametrized with $k\sigma = \frac{30}{2}$ because the depth and the position of the minimum are scaled with the parameter $k\sigma$, and we can see that with this parametrization these properties are better analyzed. By simplicity, hereafter we parametrize our results with $k\sigma = \frac{45}{2}$ only.

An important feature of the dipolar colloid is that it presents a disordered-ordered phase transition when the temperature (dipolar strength) is decreased (increased). The ordered phases depend on the volume fraction of the dipolar colloids. In order to get a complete picture we have investigated several regimes of ϕ at decreasing temperature (increasing dipolar strength). We have defined five regimes and we have chosen one representative value of ϕ for each. The following increasing-dipole-strength phases are considered: (1) very low, $\phi = 0.00524$; (2) low, $\phi = 0.1$ (chainlike phase); (3) intermediate, $\phi = 0.2$ (mixed chainlike and ferroelectric phase); (4) high, $\phi = 0.35$ (ferroelectric phase); and (5) very high, $\phi = 0.45$ (ferroelectric phase). We give special attention to the very low regime since the depolarized light scattering experiments can be performed therein.

In Fig. 4 we have plotted $F(q\sigma)$ versus $q\sigma$ for each volume fraction and a value of the dipolar strength. The μ^{*2} used in each ϕ corresponds to the closest value of the dipolar strength, where the RHNC fails to give a solution. These values have already been obtained by Klapp and Forstmann [5], except for the very low regime. They found that by increasing μ^{*2} , from the very high to low regimes, the dipolar colloid has a strong tendency to reach the instability line, which can be considered as the stability limit of the homogeneous isotropic phase [5]. However, it is important to stress here that the RHNC predictions overestimate the temperatures when compared with the computer simulation values.

From Fig. 4, we see that by starting with the very low

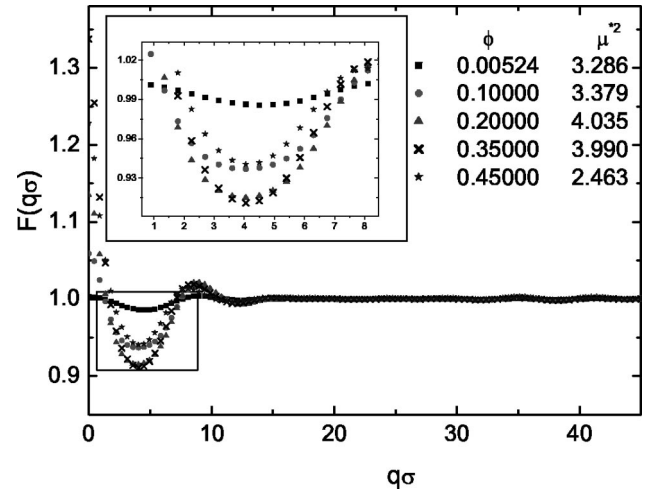


FIG. 4. Static orientational structure factor versus $q\sigma$ for the representatives values of ϕ and their corresponding highest values of μ^{*2} , as indicated in the plot.

value of the volume fraction, the depth increases with ϕ till 0.35 and then it decreases by increasing ϕ , showing a different behavior at very high volume fraction. We have analyzed this feature for other values of the volume fraction, and we have essentially observed the same behavior. A more precise value of ϕ in which the dipolar colloid changes its behavior occurs for $\phi \sim 0.288$. After this value there is no increase, but it decreases with the volume fraction. It is well known that for low ϕ the ordered phase corresponds to a chainlike phase, whereas for higher values of ϕ a ferroelectric phase occurs. This is consistent with our results, which predict different translational orientational behavior for dilute and concentrated dipolar colloids near to the phase transition.

In this paper, we are interested in the very low volume fraction regime, because this is the regime attainable with depolarized light scattering experiments. In Fig. 5 the static orientational structure factor is presented as a function of $q\sigma$ for different values of ϕ in the very low regime, from

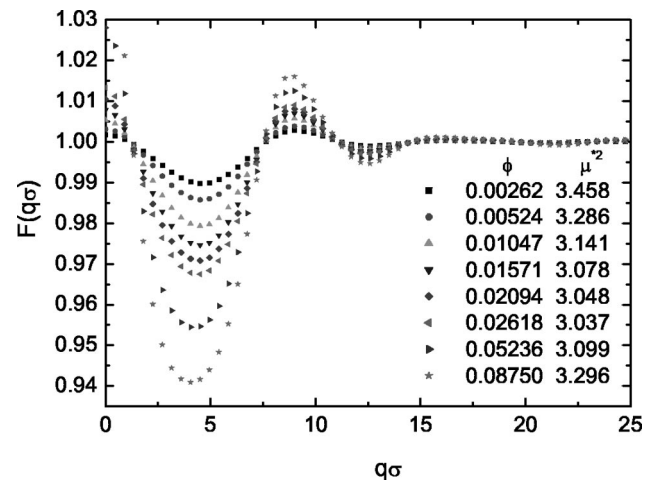


FIG. 5. Static orientational structure factor as function of $q\sigma$ for very low values of ϕ and their corresponding highest values of μ^{*2} , as indicated in the plot.

0.002 62 up to 0.0875, and for their corresponding highest value of dipolar strength. From this figure we see that if we increase the volume fraction, the high of the first maximum also increases, which indicates that at higher volume fractions the probability to find a dipole parallel or antiparallel is bigger than for lower volume fractions. We can conclude that we do not observe any other interesting behavior in the static orientational structure factor in this very low regime.

Finally from Fig. 3 we observe that the static orientational structure factor is very sensible at very short q . We study this feature in the following section.

V. ORDERING PARAMETER

From Eq. (2) we observe that in the $q \rightarrow 0$ limit we obtain

$$\mathbf{Q}(0) = \frac{1}{\sqrt{N}} \sum_j \frac{3}{2} [\hat{\mathbf{u}}_j^0 \hat{\mathbf{u}}_j^0 - \frac{1}{3} \mathbf{I}], \quad (20)$$

which is the collective symmetric ordering tensor [4]. Consequently, $F(q\sigma=0)$ is an observable that is related to the orientational behavior of the colloidal particles in the suspension, given by

$$F(q\sigma=0) = 1 + \frac{3\phi}{\sqrt{5}\pi^3} \int_1^\infty dx x^2 g(220;x), \quad (21)$$

which we call the ‘‘ordering parameter.’’ We can understand $F(q\sigma=0)$ by analyzing $g(220;r)$. In an homogeneous isotropic phase, this quantity is a projection of the angular-dependent pair correlation function, which is related to the probability that two macroparticles separated by a distance r align (parallel or antiparallel). On the other hand, in an ordered phase, the same quantity is related to the nematic order parameter s . The macroscopic state of a nematic phase is characterized by the traceless symmetric ordering tensor [4]

$$\mathbf{S} = \frac{3}{2} [\hat{\mathbf{s}}\hat{\mathbf{s}} - \frac{1}{3} \mathbf{I}], \quad (22)$$

where $\hat{\mathbf{s}}$ is the nematic director. The parameter s is the average value of the largest eigenvalue of the traceless symmetric ordering tensor. For example, s vanishes in an homogeneous isotropic phase, while s has a finite value for a nematic phase [4]. Then, in an homogeneous isotropic phase $F(q\sigma=0)$ is related to the fluctuations in the number of macroparticles that are breaking the orientational symmetry. In consequence, the ordering parameter can be derived only in the grand canonical ensemble. The observable $F(q\sigma=0)$ tells us if a dipolar colloid can evolve from an isotropic to an orientationally ordered phase.

It is important to mention here that Eq. (21) defines an observable, which can be probed in a depolarized light scattering experiment in the VH geometry. In order to analyze the ordering parameter $F(q\sigma=0)$, we first analyze the behavior through an isotherm. In Fig. 6 we have plotted $F(q\sigma=0)$ versus ϕ for $T^* = (\mu^{*2} = 3.5)^{-1}$. We know that for this isotherm, the dipolar colloid has two points on the instability line, for low and high values of ϕ [5]. Each value of ϕ , the highest and the lowest, corresponds to the closest

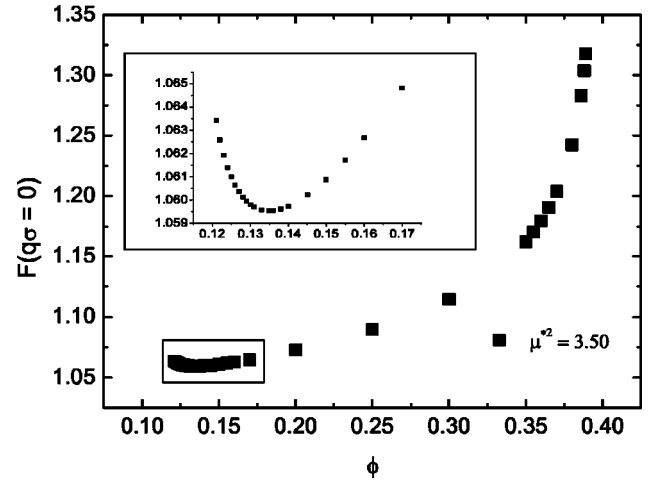


FIG. 6. Ordering parameter versus ϕ for the isotherm $T^* = (\mu^{*2} = 3.5)^{-1}$.

point in which the RHNC fails to give a solution. We observe in Fig. 6 that the ordering parameter increases too fast near of the instability line, that is, for low and high values of ϕ , as can be seen in the inset in Fig. 6. Thus, as a result of the presence of an orientationally ordered phase, the ordering parameter increases.

In order to proceed with the analysis we have divided the study into five regimes of volume fractions, defined in the preceding section, from very low to very high values. Figure 7 shows the results for the ordering parameter for each ϕ as a function of μ^{*2} . The highest μ^{*2} in each curve corresponds to the closest point where the RHNC fails to give a solution. From very high to low volume fractions at decreasing temperature (increasing dipolar strength), we observe that the ordering parameter enlarges, which means that the dipolar colloid evolves to an ordered phase. Another important feature that can be observed from this figure is that for the representative value of the low regime ($\phi=0.1$), the ordering parameter increases monotonically with μ^{*2} , but near the phase transition the increasing rate suddenly is much

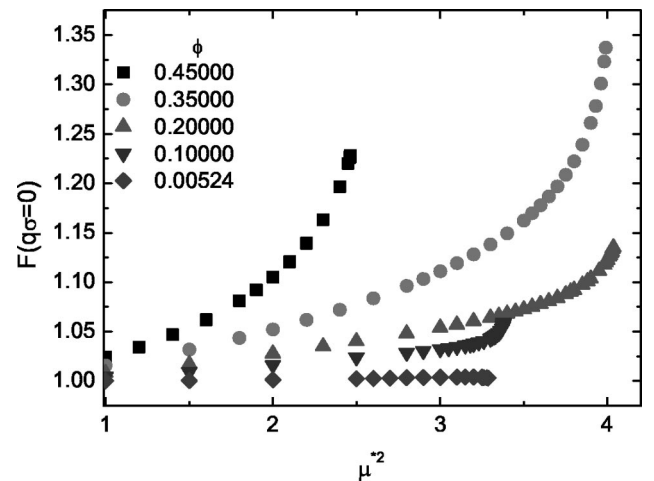


FIG. 7. Ordering parameter versus μ^{*2} for the representative values of ϕ , as indicated in the figure.

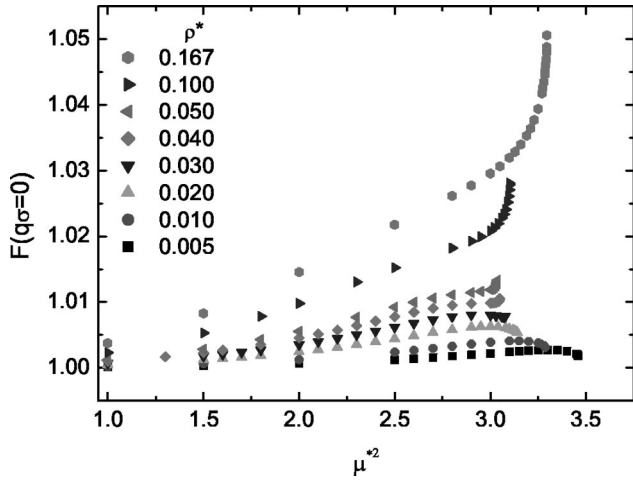


FIG. 8. Ordering parameter as function of μ^{*2} for different values of ϕ in the very low regime, as indicated in the figure.

bigger. At the low regime, the transition from the isotropic to the ordered phase is obtainable in a progressive and continuous way, but near the transition a very rapid increment in the order is observed. It is important to note that this behavior at low concentration has already been observed by Levesque and Weis [6]. For the other regimes, this behavior is not observed. For the very low regime ($\phi=0.005$) a different behavior is observed. The ordering parameter goes down at increasing dipolar strength, which indicates that the system would not reach an ordered phase, but would remain in a disorder phase, that is, at least in a phase characterized by a no global orientational order.

We focus our attention on the very low regime mainly for two reasons: first there is no indication of an ordered transition, and second it is important because this is where the depolarized light scattering experiments are attainable. In Fig. 8 the ordering parameter is presented as a function of the dipolar strength for $\rho^*=0.005$ ($\phi=0.00262$) up to 0.167 (0.0875). From this figure, we observe that the dipolar colloid reaches the instability line for a density $\rho^*\sim 0.04$ ($\phi\sim 0.021$). For lower concentrations, the ordering parameter starts increasing with the dipolar strength, but near the transition it suddenly goes down, indicating that the dipolar colloid does not reach the instability line. Stevens and Grest have found that a dipolar soft fluid, at very low densities ($\rho^*\sim 0.01$), associates into chains that are entangled and thus exhibit no global orientation order [10]. Consequently, in the very low regime our results suggest that a dipolar colloid may have a reentrant phase.

We have observed the behavior of the ordering parameter versus dipolar strength for other values of ϕ , but no important difference was observed that we have not already discussed up now.

We now analyze the concentration and the orientation of dipolar colloids near the instability line in the five regimes studied here. In order to realize this study, we analyze the projections $g(000;r)$ and $h(220;r)$ versus the neighboring layers. In Figs. 9 and 10, g_{av} and $h_{220_{av}}$ represent the concentration and the number of macroparticles aligned in each layer, respectively. In each figure four plots are shown: first

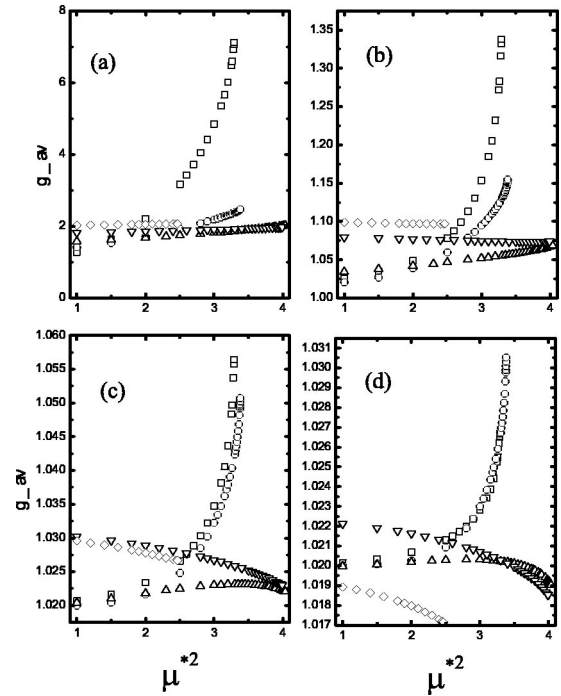


FIG. 9. g_{av} as function of μ^{*2} for each layer first (a), second (b), third (c), and fourth (d). The symbol curves represent each regime: squares the very low, circles the low, up triangles the intermediate, down triangles the high, and diamonds the very high.

(a), second (b), third (c), and fourth (d) neighbor layers (where we have defined the layers as intervals determined by multiples of σ). Each plot has five symbol curves, which correspond to the different regimes defined as follows: squares for the very low, circles for the low, up triangles for

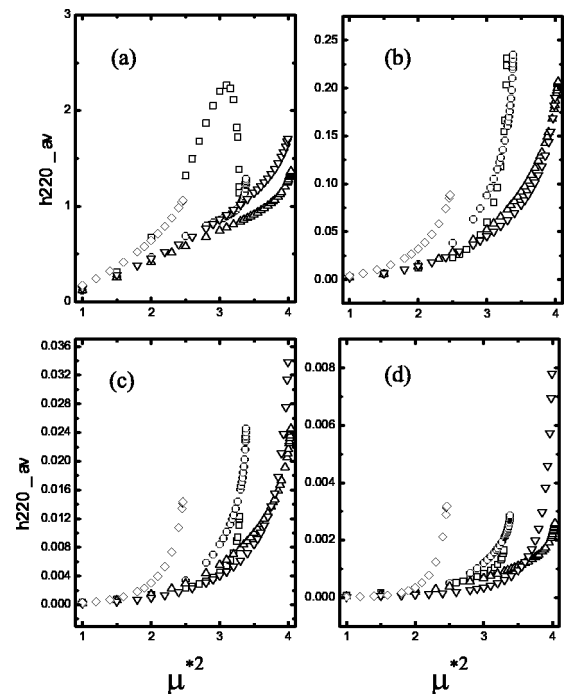


FIG. 10. The same as Fig. 9 for $h_{220_{av}}$.

the intermediate, down triangles for the high, and diamonds for the very high regime. The graphs for each layer were obtained by integrating each projection considering the different intervals in the following way:

$$g^i = \frac{1}{\sigma} \int_{(i-1)\sigma}^{i\sigma} g(x) dx, \quad (23)$$

where $g(x)$ represents $g(000;r)$ and $h(220;r)$, g^i is g_{av} and $h_{220,av}$, and i is the neighboring layer.

Figure 9 and 10 show different positional and orientational behavior for the different regimes. The very low regime is characterized by a high occupation in the four layers, while the alignment in the first layer starts increasing, but near the instability line it decreases. For the following layers, in the very low regime, the alignment decreases. The low regime presents a small occupation for the first two layers, while in the third and fourth layers its occupation increases. Concerning its alignment, the low regime presents, in the second and third layers, a high alignment, while for the first and fourth layers, a small alignment is observed. The intermediate regime presents a poor occupation in the four layers, nevertheless, in the third and fourth layers its occupation decreases near of the transition. For its alignment, the intermediate regime, for all the regimes except the fourth, presents a high alignment. The high regime presents a poor occupation for all the layers and its occupation decreases for the third and fourth layers. Concerning its alignment, the high regime presents a high alignment in the four layers. Finally, the very high regime presents also a poor occupation in the four layers, and for the third and fourth layers, its occupation decreases. The alignment of the very high regime is characterized by a poor number in the four layers. We can conclude that near the instability line with respect to its concentration, the very low and the low regimes present more occupation, while the very high regime is more empty. While with respect to its alignment, the high regime is the one with the largest number, and the very high regime is one with a poor alignment.

Our results predict different ordered phases for the five regimes, in accordance with previous results [5]. The more important prediction is that for the very low concentration, the dipolar hard-spherical colloid may have a reentrant phase.

VI. CONCLUDING REMARKS

The orientational structure of dipolar hard-spherical colloids is studied on an homogeneous isotropic phase. The study is based on the fluctuational effects of the orientation density on the orientational structural properties. We have reported results for the static orientational structure factor $F(q\sigma)$ and the ordering parameter, $F(q\sigma=0)$. These properties depend on the volume fraction and the dipolar strength of the colloids. The static orientational structure factor is also a function of the refractive index of the scattering medium. An advantage of this approach is that these structural properties can be measured in a depolarized light scattering experiment in the VH geometry [1] at very low concentrations.

The results show that the static orientational structure factor is better observed for large values of the refractive index of the scattering medium. Contrary to the static structure factor, the orientational one presents a minimum as the main peak. The position of this minimum depends only on the volume fraction. This minimum is related to the probability to find a dipolar macroparticle parallel or antiparallel to another dipolar macroparticle localized in the origin of the laboratory frame. To analyze the positional orientational behavior we have defined five regimes of the volume fraction, from very low up to very high concentrations. We have observed that near the instability line, but still in the homogeneous isotropic phase, the depth of the minimum increases with the volume fraction up to $\phi \sim 0.288$ (i.e., $\rho^* \sim 0.549$) and then decreases. Consequently, a dipolar colloid presents different behavior for dilute and dense concentrations. The latter is characterized by a reduction of the depth of the minimum at increasing values of the volume fraction. From the results presented here, we can see that if the depth of the minimum of the static orientational structure factor is higher than ~ 7.5 , the dipolar colloid does not evolve to an ordered phase.

In order to analyze the response of a dipolar colloid to its collective orientational behavior, we have studied the ordering parameter $F(q\sigma=0)$. The results show that the parameter is able to predict whether a dipolar colloid would evolve to an orientationally ordered phase (instability line). We have studied the ordering parameter for each isochore regime already defined. The results predict the presence of an orientationally ordered phase by increasing the dipolar strength from low to very high concentrations. For a low volume fraction ($\phi=0.1$), the alignment increases smoothly as the dipolar strength increases too, but near the instability line the alignment suddenly increases very fast. For the very low regime a different behavior is observed. The ordering parameter starts with a positive slope, but near the transition the slope becomes negative, resulting in a reduction of the ordering parameter. According to our results, for concentrations lower than $\phi=0.021$, the dipolar colloid does not evolve to an orientationally ordered phase. This result seems to indicate that a reentrant transition could be happening.

Our final analysis is focused on the concentration and collective orientation of a dipolar colloid for each one of the considered regimes. In each case, the study considered four neighboring layers. To analyze the concentration, we plotted $g(000;r)$ as function of the dipolar strength for each regime and layer, while for the number of macroparticles with a preferred orientation we plotted $g(220;r)$. The results show that, if it exists, the reentrant increasing-dipolar-strength phase has layers with a higher occupation of particles near the transition, while the ferroelectric increasing-dipolar-strength phase has a higher number of macroparticles with a preferred orientation.

In summary, we have applied a theoretical approach, which is able to describe the positional and orientational behavior of dipolar colloids near of the instability line. The results predict the well-known existence of orientationally ordered phases from low to high concentrations, but predicts a possible reentrant increasing-dipolar-strength phase at very

low values of the volume fraction.

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APPENDIX

We give the explicit expressions for $F_{l0}(x)$, $FF_{lm}(x)$, and $S_l(x)$ that appear in Eq. (19)

$$F_{00}(x) = 2 \frac{\sin x}{x}, \quad (\text{A1})$$

$$F_{20}(x) = \sqrt{5} \left[-\frac{\sin x}{x} + 3 \frac{\sin x}{x^3} - 3 \frac{\cos x}{x^2} \right], \quad (\text{A2})$$

$$F_{40}(x) = \frac{9}{4} \left[\frac{\sin x}{x} - 45 \frac{\sin x}{x^3} + 105 \frac{\sin x}{x^5} \right] \quad (\text{A3})$$

$$+ 10 \frac{\cos x}{x^2} - 105 \frac{\cos x}{x^4}, \quad (\text{A4})$$

$$FF_{22}(x) = 2 \sqrt{\frac{3}{2}} S_3(q\sigma) F_{20}(x), \quad (\text{A5})$$

$$FF_{22}(x) = -\sqrt{\frac{3}{2}} S_4(q\sigma) F_{20}(x), \quad (\text{A6})$$

$$FF_{42}(x) = \frac{20}{3\sqrt{10}} S_3(q\sigma) F_{40}(x), \quad (\text{A7})$$

$$FF_{42}(x) = -\frac{40}{3\sqrt{10}} S_4(q\sigma) F_{40}(x), \quad (\text{A8})$$

$$S_1(x) = 1 - 8 \left(\frac{x}{2k\sigma} \right)^2 + \frac{1}{2} \left(\frac{x}{2k\sigma} \right)^4, \quad (\text{A9})$$

$$S_2(x) = x \left[1 - \frac{1}{2} \left(\frac{x}{2k\sigma} \right)^2 \right] \left[1 - \frac{1}{4} \left(\frac{x}{2k\sigma} \right)^2 \right]^{1/2}, \quad (\text{A10})$$

$$S_3(x) = 1 - \frac{1}{2} \left(\frac{x}{k\sigma} \right)^2, \quad (\text{A11})$$

$$s_4(x) = \frac{x}{2k\sigma} \left[1 - \left(\frac{x}{2k\sigma} \right)^2 \right]^{1/2}. \quad (\text{A12})$$

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