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Induced nematic-like phase in dipolar and quadrupolar colloids

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We compute the one-body probability density function of a dipolar and a quadrupolar colloid driven by an external ordering field. Colloids with low structure in the absence of the external field, and with axially symmetric coupling potential are assumed. To compute the one-body probability density function, it is assumed that the dynamics of the colloid are given by the Smoluchowski equation without hydrodynamic interactions. We use an appropiate homogeneous external field for each moment. The results for the one-body probability density function predict an axial nematic-like phase for the dipole moment, whereas a biaxial nematic-like phase is predicted for the quadrupole moment.

Keywords: Colloid; nematics; multipole; one-body density function.

Calculamos la densidad de probabilidad de un cuerpo de un coloide dipolar y uno cuadrupolar controlados por un campo externo ordenador. Consideramos un coloide con poca estructura en ausencia del campo externo y con potencial de interacción axialmente simétrico. Para calcular la función de densidad de probabilidad suponemos que la dinámica del coloide esta dada por la ecuación de Smoluchowski sin interacciones hidrodinámicas. Usamos un campo homogeneo externo apropiado para cada momento. Los resultados, para la función de densidad de probabilidad de un cuerpo, predicen una fase axial tipo nemática para el dipolo, mientras que una fase biaxial tipo nemática se obtiene para el momento cuadrupolar.

Descriptores: Coloide; nematico; multipolo; función de densidad de un cuerpo.

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1. Introduction

Certain materials do not show a single transition from solid to liquid, but rather a cascade of transitions involving new phases. The symmetry properties of these phases are intermediate between those of a liquid and those of a crystal. These materials are called liquid crystals. These are systems in which a liquid-order exists in at least one direction of space and in which some degree of anisotropy is present [1–3].

The simplest and best known liquid-crystalline phase is nematics, which has no long-range positional order, but does exhibit orientational order. In nematic liquid crystals the molecules are, on average, aligned with their symmetry axes parallel to each other. A preferred direction $\widehat{\mathbf{n}}$ is thus defined, called the nematic director.

In recent years, colloidal dispersions in nematic liquid crystals have emerged as a novel type of soft matter [4]. An important example of soft material which has this behavior is the multipolar colloids, that is, their structure and properties are easily changed by temperature, composition, or external fields or flows. Interacting dipolar hard spheres self-assemble in a ferroelectric state, at high density and coupling strengths, which is an axial nematic ferroelectric phase [5,6]. Klapp and Patey have also shown the possibility of obtaining an induced ferroelectric state which is driven by an external field [6], for high density and low coupling strength. Recent experimental results have shown in situ that a ferrofluid self-assembles in chains at low densities and high coupling strength [7], which was predicted many years ago by de Gennes and Pincus [8]. When vitrified in a permanent magnetic field, these chains align and form thick elongated structures, also forming an axial phase [7]. However, this vitrified phase is not a nematic phase because the colloid also exhibits a positional order.

In addition to the uniaxial nematic phase, there also exist biaxial nematics. One might be surprised to find a biaxial phase in a system with an axially symmetric shape, since no molecular interaction in such a system can produce a macroscopic ordering that is less symmetric than the molecules themselves. The second macroscopic axis must then have an external cause for axially symmetric systems. On the other hand, a self-assembly in a biaxial nematic phase may be expected for molecules that are not (not even effectively) axially symmetric. Most of the known biaxial nematics are mixtures of rod-like and plate-like molecules [2, 9]. This biaxial phase has been questioned, and evidence has been found that the mixture undergoes a transition to two coexisting uniaxial phases rather than a single biaxial phase [10, 11]. Using computer simulations, Ibarra-Avalos et al have found a biaxial phase for a quadrupolar colloid, at high density and low temperature, in the absence of an external field [12]. Another important example in which biaxiality does play an important role is in tumbling nematics in a shear flow of ellipsoidal molecules, for intermediate and large shear rates [13]

There are, in principle, three possibilities that may lead to the spontaneous formation of a one-component biaxial nematic phase:

a) a molecular symmetry that is not (effectively) uniaxial,

b) strong correlations of molecules leading to aggregates of molecules that have no uniaxial symmetry and,

c) the application of an external field.

Because many of the applications of liquid crystals are related to their ability to respond strongly to the presence of an external field, in this work the discussion is restricted to the third possibility.

Since the multipolar colloidal suspensions present a rich variety of phases as liquid crystals, in this work we study the response of dilute colloids of hard-sphere particles with asymmetric coupling interactions driven by an external field. The idea is to analyze phases which exhibit a certain degree of orientational order, between liquid and crystal, in analogy with liquid crystals. We analyze the case in which the ordered states reached are nematic-like, that is, they show alignment with the nematic director, which in this case corresponds to the direction of the external field.

The multipolar colloids are studied by combining ideas about liquid crystals with colloidal theory. Some of the most important quantities used to describe the ordering in dilute colloids are the one- and two-body probability density functions [14]. For computing these density functions, it is assumed that the dynamics of the colloid are given by the Smoluchowski equation [15–17]. Because we have in mind dilute colloids, the hydrodynamic interactions are neglected. Thus, the probability density functions will be equilibrium solutions of the Smoluchowski equation.

To describe the nematic-like phase in a dipolar and quadrupolar colloid driven by an external field, we consider the simplest homogeneous tensor field in each multipole [18]. We show that these tensor fields lead us to an axial nematic-like phase for the dipolar colloid, whereas a biaxial nematic-like phase is obtainde for the quadrupolar colloid.

In Sec. 2 the colloid, dipolar and quadrupolar, as well as the appropriate external homogeneous tensor fields for each multipole moment, are defined. In Sec. 3 the one- and two-body probability density functions solving the equilibrium Smoluchowski equation are computed. We also provide the approximations used in this work in order to obtain a description up to linear order in density and fourth order in coupling strength. In Sec. 4 using the one-body probability density function, results for dipole and quadrupole moments are presented. Different phases for each moment are predicted. An axial phase is predicted for the dipolar colloid, whereas a biaxial phase for the quadrupolar colloid is predicted. Section 5 offers some concluding remarks.

2. Multipolar colloid driven by a field

In order to study the physical consequences of linear multipolar colloids driven by an external field, in this section we define the system as well as the corresponding tensor field for each moment. Let us consider a colloidal suspension of hard-spherical particles with a linear dipole or quadrupole moment embedded at the center of the particle in a carrier solution. The configuration of the suspension can be denoted by a $6N$ dimensional vector $(\mathbf{r}^N, \hat{\mathbf{u}}^N)$ with $3N$ dimensional vectors $\mathbf{r}^N = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$, $\hat{\mathbf{u}}^N = (\hat{\mathbf{u}}_1, \ldots, \hat{\mathbf{u}}_N)$, where $\mathbf{r}_i$ and $\hat{\mathbf{u}}_i$ give, the position of the center and the direction of the multipole moment of particle i respectively. The potential energy of the multipolar colloid has the form

$$\Phi(\mathbf{r}^N, \hat{\mathbf{u}}^N) = \Phi_{MP}(\mathbf{r}^N, \hat{\mathbf{u}}^N) + \Phi_{EXT}(\hat{\mathbf{u}}^N), \tag{1}$$

where $\Phi_{MP}(\mathbf{r}^N, \hat{\mathbf{u}}^N)$ and $\Phi_{EXT}(\hat{\mathbf{u}}^N)$ are the interparticle potential and the external ordering field potential, respectively. We assume that the former is given by the sum of the interparticle potentials for isolated pairs of particles (pairwise additivity approximation). For particles with no internal rotation, and which are in their ground electronic and vibrational states, the pair potential is assumed to depend only on the interparticle separation vector $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, and on particle orientations $\hat{\mathbf{u}}_1$ and $\hat{\mathbf{u}}_2$ [18]. For the linear dipole moment we have

$$\phi^D(\mathbf{r}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = \sum_{m_1 m_2 m} u^{112}(r) \times C(112, m_1 m_2 m) Y^1_{1m_1} Y^2_{1m_2} Y^{*r}_{2m}, \tag{2}$$

where $C(112, m_1 m_2 m)$ is the Clebsch-Gordan coefficient, $Y^1_{1m_1} = Y_{1m_1}(\hat{\mathbf{u}}_1)$ is the spherical harmonic and $u^{112}(r)$ is given by

$$u^{112}(r) = -4\pi \sqrt{\frac{8\pi}{15}} \frac{\mu^2}{r^3}, \tag{3}$$

where $r = |\mathbf{r}|$ and μ is the dipole moment. For the linear quadrupole moment we have

$$\phi^Q(\mathbf{r}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = \sum_{m_1 m_2 m} u^{224}(r) \times C(224, m_1 m_2 m) Y^1_{2m_1} Y^2_{2m_2} Y^{*r}_{4m}, \tag{4}$$

where $u^{224}(r)$ is given by

$$u^{224}(r) = \frac{8\pi}{3} \sqrt{\frac{14\pi}{3}} \frac{\Theta^2}{r^5}, \tag{5}$$

and Θ is the quadrupole moment. The information of the carrier solution is contained in each moment.

For the external ordering field potential $\Phi_{EXT}(\hat{\mathbf{u}}^N)$ is considered

$$\Phi_{EXT}(\hat{\mathbf{u}}^N) = \sum_{i=1}^{N} \phi^{MP}_{EXT}(\hat{\mathbf{u}}_i), \tag{6}$$

where $\phi^{MP}_{EXT}(\hat{\mathbf{u}}_i)$ is the potential interaction between the external ordering field and the i-th particle. For the dipole moment,

$$\phi^D_{EXT}(\hat{\mathbf{u}}_i) = -\mu \hat{\mathbf{u}}_i \cdot \mathbf{E}^D, \tag{7}$$

where $\mathbf{E}^D = E_0 \hat{\mathbf{k}}$ is the external homogeneous field, and E_0 is the field strength. For the quadrupole moment,

$$\phi^Q_{EXT}(\hat{\mathbf{u}}_i) = -\frac{1}{3} \mathbf{Q}_i \colon \nabla \mathbf{E}^Q, \tag{8}$$

where $\mathbf{Q}_i$ is the traceless quadrupole moment tensor defined by

$$\mathbf{Q}_i = \frac{\Theta}{2}(3\hat{\mathbf{u}}_i \hat{\mathbf{u}}_i - \mathbf{I}), \tag{9}$$

where $\widehat{\mathbf{u}}_i\widehat{\mathbf{u}}_i$ represents the dyadic product and $\mathbf{I}$ is the unit tensor. In Eq. (8), $\mathbf{E}^Q = E_0 z\widehat{\mathbf{k}}$ is the external field, so that $\nabla\mathbf{E}^Q = E_0\widehat{\mathbf{k}}\widehat{\mathbf{k}}$ is a constant gradient field. In both cases an electric field is used; for the dipole a constant field is used, whereas for the quadrupole the electric field is linear in the z-direction. The simplest external ordering tensor field is chosen at each moment, inasmuch as this is sufficient for obtaining nematic-like phases in each case.

3. One body density function

The reduced n-body probability density function (pdf) $P_n(\mathbf{r}^n, \widehat{\mathbf{u}}^n)$ can be obtained from the N-body pdf $P_N(\mathbf{r}^N, \widehat{\mathbf{u}}^N)$ by integrating out all but n of the N variables. Thus we find a hierarchy of equations of motion for the reduced pdf, which makes them impossible to solve without some approximation which terminates the hierarchy [16]. This work considers values up to $n = 2$, since the greatest quantities we measure experimentally can be expressed in terms of one-body or two-body pdf's. Due to the hierachy, the equation of motion for $P_n(\mathbf{r}^n, \widehat{\mathbf{u}}^n)$ depends on $P_{n+1}(\mathbf{r}^{n+1}, \widehat{\mathbf{u}}^{n+1})$; therefore this hierachy is truncated, considering until two-body, neglecting contributions of three-body. Consequence, the equation of motion for the one-body depends on the two-body pdf. Thus, we must solve the one-body pdf consistently with the two-body one. The physical reason for this is that, as we shall see, if we only consider the equation of motion for the one-body pdf, neglecting the two-body pdf, then we are not taking into account the presence of the other particles in the colloid.

The dynamics of the colloid are described by the N-body Smoluchowski equation valid in the overdamped limit, that is for times $t \gg t_B$, where t_B is Brownian time [15, 16]. This is the equation for the N-body pdf of the phase space coordinates for the multipolar colloid. Its integration, neglecting hydrodynamic interactions, leads to the following equation for the two-body pdf $P_2(\mathbf{r},\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2)$ in the equilibrium state:

$$\begin{aligned} 0 = \Big\{ & 2D_0^T\nabla_r^2 + D_0^R\left(\widehat{R}_1^2 + \widehat{R}_2^2\right) + 2\beta D_0^T\nabla_r\cdot\left[\nabla_r\phi_{MP}\right] \\ & + \left[\widehat{R}_1\cdot\left(\widehat{R}_1\phi_{MP}\right) + \widehat{R}_2\cdot\left(\widehat{R}_2\phi_{MP}\right)\right] \\ & \qquad + \left[\widehat{R}_1\cdot\left(\widehat{R}_1\phi_{EXT}\right) + \widehat{R}_2\cdot\left(\widehat{R}_2\phi_{EXT}\right)\right]\Big\} \\ & \qquad\qquad \times\beta D_0^R P_2\left(\mathbf{r}, \widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2\right). \end{aligned} \tag{10}$$

Here D_0^T and D_0^R are the translational and rotational diffusion coefficients, respectively, of a single non-interacting colloidal particle. β is the thermal energy and $\widehat{R}\ldots = \widehat{\mathbf{u}}\times\nabla_{\widehat{\mathbf{u}}}\cdots$ is the gradient operator in the orientation space. The solution for Eq. (10) is

$$P_2(\mathbf{r}, \widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2) = cP_1^0(\widehat{\mathbf{u}}_1)P_1^0(\widehat{\mathbf{u}}_2)g(\mathbf{r},\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2), \tag{11}$$

where $P_1^0(\widehat{\mathbf{u}}_1)$ is the one-body equilibrium pdf for a non-interacting colloid, dipolar and quadrupolar, driven by an external field, which can be written as

$$P_1^0(\widehat{\mathbf{u}}_1) = c_1 e^{-\beta\phi_{EXT}(\widehat{\mathbf{u}}_1)}. \tag{12}$$

This one-body equilibrium pdf is also a solution for the Smoluchowski equation considering non-interacting colloids in the presence of the external field. $g(\mathbf{r},\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2)$ is the pair correlation density function, which is approximated by

$$g(\mathbf{r},\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2) = 1 - \beta\phi_{MP}(\mathbf{r},\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2) + \cdots \tag{13}$$

In the thermodynamic limit, the normalization constant $c = V^2$, while c_1 depends on each multipole. For the dipole moment we get

$$c_1^D = \frac{1}{4\pi}\frac{E_{0D}^*}{\mathrm{Si}\,nhE_{0D}^*}, \tag{14}$$

where $E_{0D}^* = \beta\mu E_0$ is the reduced field strength and $\mathrm{Si}\,nhx$ is the hyperbolic sine. For the quadrupole moment we get

$$c_1^Q = \frac{1}{2\sqrt{\pi^3}}\frac{\sqrt{\frac{E_{0Q}^*}{2}}}{Erfi[\sqrt{\frac{E_{0Q}^*}{2}}]}, \tag{15}$$

where the reduced field strength is defined as $E_{0Q}^* = \beta\Theta E_0$ and $Erfi[x]$ is the imaginary error function.

In using Eq. (13), the effect of the external field on $g(\mathbf{r}, \widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2)$ is neglected, because this quantity is nothing more than the equilibrium conditional pdf for the position $\mathbf{r}_1$ and $\mathbf{r}_2$ of two particles with prescribed orientations $\widehat{\mathbf{u}}_1$ and $\widehat{\mathbf{u}}_2$ for linear order in density. The assumption here is that the effect of an external field on positional correlations is much less pronounced than its aligning effect on the one-body equilibrium pdf. From the results obtained by Patey and Klapp [6], it is observed that in the case of dipolar particles for low density, a high reduced field strength is necessary to induce orientational order, whereas for high density a low external field strength is necessary. Consequence we believe that for the values of density considered in this work, for both multipoles, a high external field is required so that the colloid will undergo certain ordering; this means that our approximation in Eq. (13) is reasonable for low values of the field. Comparing with the results of Patey and Klapp, we feel that the approximation given by Eq. (13) is reasonable for values up to $E_0^* \lesssim 14$. As we shall see below, the main predictions of this work are for values which lie in this range.

In order to compute the one-body equilibrium pdf, the N-body equilibrium Smoluchowski equation again is integrated. Integrating this we obtain the following equation for $P_1(\widehat{\mathbf{u}})$:

$$\begin{aligned} 0 = \Big\{ & \widehat{R}_1^2 - \rho\beta\widehat{R}_1\cdot P_1^0(\widehat{\mathbf{u}}_1)\int d\widehat{\mathbf{u}}_2\,\overrightarrow{\tau}(\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2)P_1^0(\widehat{\mathbf{u}}_2) \\ & + \beta\widehat{R}_1\cdot\left[\widehat{R}_1\phi_{Ext}\right]\Big\}P_1(\widehat{\mathbf{u}}), \end{aligned} \tag{16}$$

where ρ is the density of the colloid. To write Eq. (16), Eq. (11) is used in the second term [16]. The torque $\overrightarrow{\tau}(\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2)$ is given by

$$\overrightarrow{\tau}(\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2) = -\int d\mathbf{r}\left[\widehat{R}_1\phi_{MP}\right]g(\mathbf{r}, \widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2). \tag{17}$$

It is observed in Eq. (16) that if the two-body pdf is neglected [Eq. (11)], then this becomes the equation for a one-body pdf in presence of the external field, that is, without coupling between particles.

It is assumed that the solution of Eq. (16) is given by a spherical harmonic series

$$P_1(\widehat{\mathbf{u}}_1) = \sum_{l=0}^{\infty} \sum_{p=-l}^{l} \alpha_{lp} Y_{lp}^{1}, \tag{18}$$

where the coefficients are given by

$$\alpha_{lp} = \int d\widehat{\mathbf{u}}_1 P_1(\widehat{\mathbf{u}}_1) Y_{lp}^{*1}. \tag{19}$$

In evaluating the integral in Eq. (16), we expand the entire integral in a spherical harmonic series also. Hence

$$\sum_{l=0}^{\infty} \sum_{p=-l}^{l} \gamma_{lp} Y_{lp}^{1} = \rho\beta \widehat{R}_1 \cdot P_1^0(\widehat{\mathbf{u}}_1) \times \int d\widehat{\mathbf{u}}_2 \overrightarrow{\tau}(\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2) P_1^0(\widehat{\mathbf{u}}_2), \tag{20}$$

with

$$\gamma_{lp} = \beta \int d\widehat{\mathbf{u}}_1 Y_{lp}^{*1} \widehat{R}_1 \cdot \left[P_1^0(\widehat{\mathbf{u}}_1) \int d\widehat{\mathbf{u}}_2 \overrightarrow{\tau}(\widehat{\mathbf{u}}_1, \widehat{\mathbf{u}}_2) P_1^0(\widehat{\mathbf{u}}_2) \right]. \tag{21}$$

The integral in Eq. (17) is well defined only after the boundary conditions are specified. For the case of the dipole moment, we consider an (infinite) sample surrounded by a conductor. Such conditions are often applied (approximately) in computer simulations [19] and have been used in integral studies [20] and density functional theory treatments [21] of dipolar spheres as well. These boundary conditions are a reasonable choice because, for example, they eliminate depolarization fields which tend to favor domain structures rather than the homogeneous orientational order considered. The boundary conditions are implemented using the so-called mean reaction field [6]. Similar conditions are used for the quadrupole moment.

In induced nematics, the one-body equilibrium pdf must be invariant under rotation about the direction of the director (external field) [14]. Therefore, $P_1(\widehat{\mathbf{u}}_1)$ has to depend only on the angle θ between the moment direction and the external ordering homogeneous field direction. Hence, the expansion in spherical harmonics Eq. (18) reduces to a Legendre polynomial expansion, because this is the suitable basis set for the external field chosen [Eqs. (7) and (8)]. Therefore, Eq. (18) can be written as

$$P_1(\cos\theta) = \sum_{l=1}^{\infty} \alpha_l p_l(\cos\theta), \tag{22}$$

where $p_l(\cos\theta)$ is the Legendre polynomial of order l. In Eq. (22), the coefficients α_l are given by

$$\alpha_l = \int d\widehat{\mathbf{u}} p_l(\cos\theta) P_1(\cos\theta). \tag{23}$$

To compute the α_l coefficients for each moment considered, we substitute the expansions Eq. (22) and (20) into Eq. (16). By equating coefficients of the same Legendre polynomial order, we get $\alpha_l = \alpha_l(\gamma_{lp=0})$; and finally, γ_{lp} coefficients are computed using Eq. (21). General expressions for the first two coefficients α_l in the expansion and for $\gamma_{lp=0}$ are provided in the Appendix, for both moments. We do not report all the expressions because nothing is learned from them and they are lengthy. Terms up to 14 are considered for the dipole, and up to 12 for the quadrupole. Observing the behavior of the one-body equilibrium pdf, we believe that it must be sufficient to give the essential features correctly, because the peaks presented do not change their position with the different number of terms in the expansion. It is hard to say anything about the convergence of the expansion of Eq. (22) with increasing the reduced field strength. To have an idea about this convergence with increasing, the difference between two consecutive terms of the expansion is computed. Comparing these differences, we observe whether the difference decreases or increases when subsequent pairs are considered. The reduced field strength is increased until the consecutive differences no longer decrease, but increase. The maximum values of the reduced field strength are approximately 45 for the dipole and 50 for the quadrupole.

As an application of the approach developed here, the induced-assembly in dipolar and quadrupolar colloids is described in the next section, considering the system as a function of the external reduced field strength, for fixed density and multipole moment strength.

4. Nematic-like phase

This section presents results for colloids that have a low structure in the absence of the external ordering field, that is, for low density and low multipole moment strength as well. Standard scaled variables are used for the density, $\rho^* = \rho\sigma(= 0.005$ for both moments) where σ is the diameter of the colloidal particle, and the dipole and quadrupole moments are scaled as follows: $\mu^{*2} = \beta\mu^2/\sigma^3(= 0.40)$ and $\Theta^{*2} = \beta\Theta^2/\sigma^5(= 0.40)$, respectively.

We first discuss briefly the case of non-interacting dipolar and quadrupolar colloids driven by an external ordering field. To analyze this case, we consider the one-body equilibrium pdf, given by Eq. (12), which is the equilibrium solution of the Smoluchowski equation for one-body neglecting the two-body pdf contribution. In the non-interacting case the one-body equilibrium pdf is an exponential function of the external potential with its appropriate normalization constant. For the dipole moment, the external potential is given by Eq. (7) and the normalization constant by Eq. (14), whereas for the quadrupole moment they are given by Eqs. (8) and (15), respectively. In the case of the dipole, its one-body equilibrium pdf, as a function of the external reduced field strength, presents two peaks, at $\theta = 0$ and 2π. Therefore it predicts an axial phase, with all the dipole moments parallel to the external field. For the quadrupole moment, the one-body equilibrium pdf predicts an axial phase also. In this case, the equilibrium pdf, as a function of the external reduced field strength, presents three peaks, at $\theta = 0$, π and 2π. The difference here, compared with the dipole moment, is that we now have parallel and antiparallel quadrupole moments in the direction of the external field. Both moments present an axial nematic-like phase when a colloid is driven by an external ordering field without taking into account the interaction between particles. It is important to note that both ordered phases, for each moment, are independent of the value of the external reduced field strength, that is, the same phase is obtained for low and high values of the field; the difference is only in the height of the peaks.

The situation is clearly more complicated with interacting particles. By computing the one-body equilibrium pdf, we obtain a nematic-like phase for both reduced moments also, as in the non-interacting case. From the results obtained in the last section, two different nematic-like phases are observed in both moments, depending on the external reduced field strength. This difference is clearly observed in the quadrupolar colloid. Considering small values of the reduced field strength, the one-body equilibrium pdf for the dipole presents one peak in $\theta = \pi$, as can be seen in Fig. 1. This means that the dipole moment is antiparallel to the external field. In the case of the quadrupole moment $P_1(\cos\theta)$ presents two peaks, for $\theta = \pi/2$ and $3\pi/2$, which can be seen in Fig. 2. The directions of the quadrupole moments are perpendicular to the external field direction. In both cases, we observe that the influence of the external field together with the interactions between macroparticles leads to an axially symmetric orientational order. The difference is that one is aligned parallel to the direction of the field, whereas the other is aligned perpendicularly. Contrary to non-interacting dipolar colloids, the dipole moment now presents antiparallel alignment. In the same manner, the quadrupole moment presents an orientation change with respect to the non-interacting colloid, which is now in a perpendicular, instead of a parallel and antiparallel, alignment.

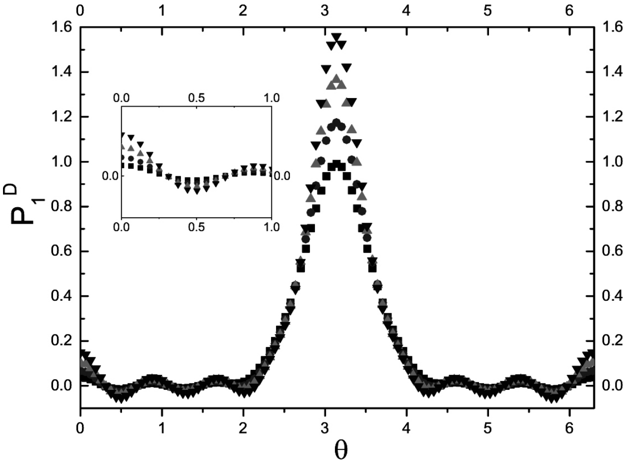

FIGURE 1. One-body probability density function versus θ for a dipolar colloid for different E^*_{0D}: ■ 6, ● 7, ▲ 8, and ▼ 9.

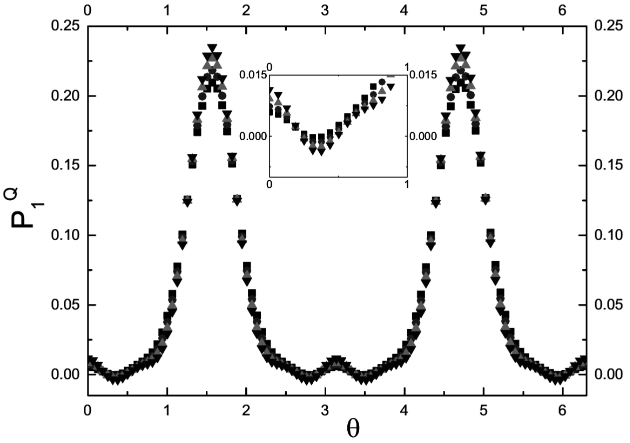

FIGURE 2. One-body probability density function versus θ for a quadrupolar colloid for differents E^*_{0Q}: ■ 11, ● 12, ▲ 13, and ▼ 14.

In Figs. 1 and 2 our main prediction is observed, namely, the values of reduced field strength for which each moment would have a phase transition. For the dipole moment, this value lies between 8.13 and 8.18, whereas for the quadrupole moment it occurs between 12.50 and 12.55. It is important to note that these transition phase values of reduced field strength do not present a quantitative change when different numbers of terms are considered in the expansion [Eq. (22)].

For high reduced field strength, the ordered phase reached is different, mainly for the quadrupole moment. For the dipole, three peaks are observed, in the one-body pdf: at $\theta = 0$, π and 2π, as is shown in Fig. 3. Thus, an axially symmetric phase with parallel and antiparallel dipole moments in the direction of the field is obtained. For the quadrupolar colloid, P_1 presents five peaks: at $\theta = 0$, $\pi/2$, π, $3\pi/2$ and 2π, as shown in Fig. 4, and corresponds to a biaxially symmetric phase, which has quadrupole moments parallel, antiparallel and perpendicular to the direction of the external field. Therefore, the results predict a different nematic-like phase for the dipolar and quadrupolar colloids: for the former an axial phase, whereas for the latter, a biaxial phase. From the results, Figs. 1–4, a cooperative effect in each moment for interacting colloids is observed. Therefore, both moments present first an ordered transitional phase, which could be a pretransitional phase, and finally they reach an ordered nematic-like phase. This pretransitional phase is dominated by the effective coupling strength, driven by the external field, whereas the final phase is a cooperative effect between the reduced field strength and the effective coupling strength. In fact, in Eq. (16) it is possible to define an effective coupling potential by using the second term in this equation.

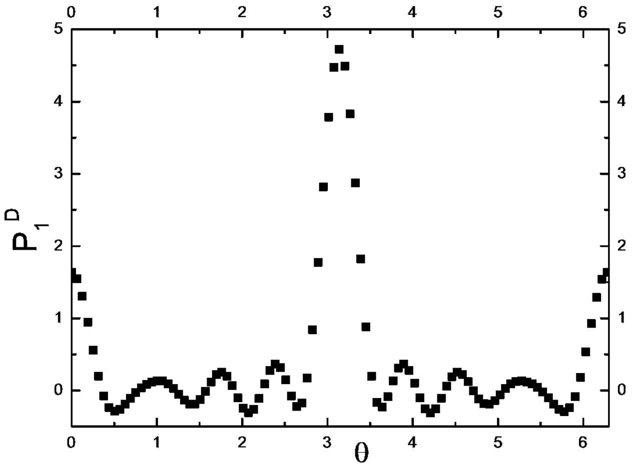

FIGURE 3. One-body probability density function versus θ for a dipolar colloid for $E^*_{0D} = 30$.

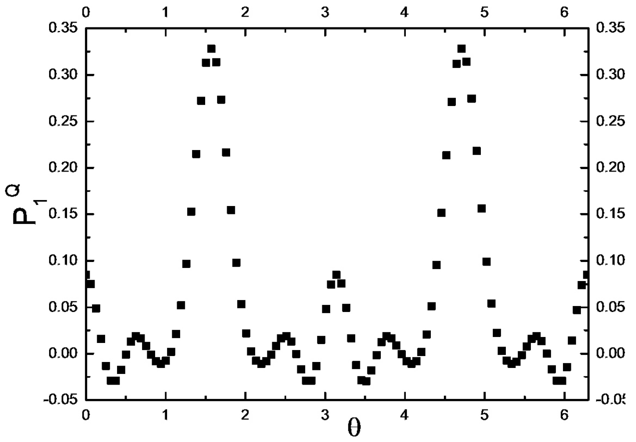

FIGURE 4. One-body probability density function versus θ for a quadrupolar colloid for $E^*_{0Q} = 30$.

From Figs. 1–4 one can see that the one-body equilibrium pdf takes negative values between the peaks, which is of course unphysical. This is a numerical error due to the approximation in terms of the Legendre polynomials, Eq. (22). The physical value is the average which can be seen in these figures going to zero between the peaks. On the other hand, it is observed from these Figs. (1–4) that the qualitative description of the alignment reached for the colloids is not affected by this numerical error.

Considering self-assembly at high density and coupling strength or at low density driven by an appropriate field, it is observed that it is possible to obtain a similar phase in dipolar and quadrupolar colloids: for the former, an axially symmetric phase, whereas for the latter a biaxially symmetric phase. Our physical scheme of the biaxial phase reached is that a quadrupolar colloid is not an effectively axially symmetric system, because of the linear order of the quadrupole considered.

5. Concluding remarks

We develop the easiest model for computing the induced-assembly of dipolar and quadrupolar colloids up to linear order in density, and fourth order for the multipole moment strength. We reported results for both multipoles as a function of the reduced field strength, at fixed density and coupling strength. Using the ideas of colloidal theories to describe the order reached by the multipolar colloids, we compute the one-body equilibrium pdf, which is assumed to be the equilibrium solution of the one-body Smoluchowski equation. In this approach, hydrodynamic interactions are neglected, a reasonable assumption for linear order in density. The two-body equilibrium pdf is a necessary ingredient in solving the one-body Smoluchowski equation. To solve this equation consistently, it is also assumed that the two-body function is also provided by the Smoluchowski equation, obtaining this input as its equilibrium solution also.

Considering a homogeneous electric field for the dipole moment and a constant gradient electric field for the quadrupole, an axial nematic-like phase is obtained for the former, whereas for the latter, we get a biaxial nematic-like phase. These ordered phases are also observed in dipolar and quadrupolar colloids at high densities and coupling strengths with a self-assembly process. We believe that this feature of the quadrupolar colloid is due to the fact that it is not effectively uniaxial. Induced assembly in non-interacting colloids is also observed; the results show aligned phases which are axially symmetric. We believe that the difference between a non-interacting and an interacting colloid is due to a co-operative effect between the reduced field and the coupling strength.

We note that this approach can be applied for multipole moments of higher order also. The results reported here can be used as a reference for other theories, computer simulations or experimental results. Thus, the idea is to take this model as a starting base and to improve it, considering, for instance, concentrated colloids, in which the pairwise additive approximation does not hold, a feature that represents a real challenge.

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A Appendix

In this appendix we provide the expressions for the first two α_l coefficients in the expansion Eq. (22) in terms of the $\gamma_{lp=0}$ coefficients.

For the dipole, the first two coefficients are α_1 and α_2; therefore we have, $\alpha_1^D = FD_{11} + \rho^* FD_{12}$, and $\alpha_2^D = FD_{21} + \rho^* FD_{22}$.

The coefficients FD_{ij} are given by

$$FD_{11}[E0^*_D] = -\frac{7}{2\sqrt{3\pi}}\frac{E0^*_D FD1[E0^*_D]}{FD2[E0^*_D]},$$

$$\begin{aligned}FD_{12}[E0^*_D] &= \frac{7}{2}\frac{FD1[E0^*_D]\gamma^D_{10}[E0^*_D]}{FD2[E0^*_D]} + \frac{\sqrt{15}}{2}\frac{E0^*_D FD3[E0^*_D]\gamma^D_{20}[E0^*_D]}{FD2[E0^*_D]} + \frac{1}{12}\sqrt{\frac{7}{3}}\frac{E0^{*2}_D FD4[E0^*_D]\gamma^D_{30}[E0^*_D]}{FD2[E0^*_D]}\\
&+ \frac{\sqrt{3}}{20}\frac{E0^{*3}_D FD5[E0^*_D]\gamma^D_{40}[E0^*_D]}{FD2[E0^*_D]} + \frac{7}{30}\sqrt{\frac{11}{3}}\frac{E0^{*4}_D FD6[E0^*_D]\gamma^D_{50}[E0^*_D]}{FD2[E0^*_D]} + \frac{1}{2}\sqrt{\frac{13}{3}}\frac{E0^{*5}_D FD7[E0^*_D]\gamma^D_{60}[E0^*_D]}{FD2[E0^*_D]}\\
&+ \frac{17\sqrt{5}}{8}\frac{E0^{*6}_D FD8[E0^*_D]\gamma^D_{70}[E0^*_D]}{FD2[E0^*_D]} + \frac{119}{1656}\sqrt{\frac{17}{3}}\frac{E0^{*7}_D FD9[E0^*_D]\gamma^D_{80}[E0^*_D]}{FD2[E0^*_D]}\\
&+ \frac{595}{138}\sqrt{\frac{19}{3}}\frac{E0^{*8}_D FD10[E0^*_D]\gamma^D_{90}[E0^*_D]}{FD2[E0^*_D]} + \frac{119\sqrt{7}}{2530}\frac{E0^{*9}_D FD11[E0^*_D]\gamma^D_{100}[E0^*_D]}{FD2[E0^*_D]}\\
&+ \frac{357}{44}\sqrt{\frac{3}{23}}\frac{E0^{*10}_D FD12[E0^*_D]\gamma^D_{110}[E0^*_D]}{FD2[E0^*_D]} + \frac{595}{3588\sqrt{3}}\frac{E0^{*11}_D FD13[E0^*_D]\gamma^D_{120}[E0^*_D]}{FD2[E0^*_D]}\\
&+ \frac{1479}{598}\frac{E0^{*12}_D \gamma^D_{130}[E0^*_D]}{FD2[E0^*_D]} + \frac{17}{690}\sqrt{\frac{29}{3}}\frac{E0^{*13}_D \gamma^D_{140}[E0^*_D]}{FD2[E0^*_D]},\end{aligned}$$

$$FD_{21}[E0^*_D] = \frac{3}{2}\sqrt{\frac{5}{\pi}}\frac{E0^{*2}_D FD3[E0^*_D]}{FD2[E0^*_D]},$$

$$\begin{aligned}FD_{22}[E0^*_D] &= \frac{3\sqrt{15}}{2}\frac{E0^*_D FD3[E0^*_D]\gamma^D_{10}[E0^*_D]}{FD2[E0^*_D]} - \frac{15}{2}\frac{FD3[E0^*_D]\gamma^D_{20}[E0^*_D]}{FD2[E0^*_D]} - \frac{5}{12\sqrt{35}}\frac{E0^*_D FD4[E0^*_D]\gamma^D_{30}[E0^*_D]}{FD2[E0^*_D]}\\
&- \frac{9}{12\sqrt{5}}\frac{E0^{*2}_D FD5[E0^*_D]\gamma^D_{40}[E0^*_D]}{FD2[E0^*_D]} - \frac{14}{12}\sqrt{\frac{11}{5}}\frac{E0^{*3}_D FD6[E0^*_D]\gamma^D_{50}[E0^*_D]}{FD2[E0^*_D]} - \frac{\sqrt{65}}{2}\frac{E0^{*4}_D FD7[E0^*_D]\gamma^D_{60}[E0^*_D]}{FD2[E0^*_D]}\\
&- \frac{17(56925)\sqrt{3}}{91080}\frac{E0^{*5}_D FD8[E0^*_D]\gamma^D_{70}[E0^*_D]}{FD2[E0^*_D]} - \frac{7(55)(17)\sqrt{5(17)}}{91080}\frac{E0^{*6}_D FD9[E0^*_D]\gamma^D_{80}[E0^*_D]}{FD2[E0^*_D]}\\
&- \frac{17(7)(12)(275)\sqrt{5(19)}}{91080}\frac{E0^{*7}_D FD10[E0^*_D]\gamma^D_{90}[E0^*_D]}{FD2[E0^*_D]} - \frac{17(7)(12)(3)\sqrt{5(21)}}{91080}\frac{E0^{*8}_D FD11[E0^*_D]\gamma^D_{100}[E0^*_D]}{FD2[E0^*_D]}\\
&- \frac{17(12285)\sqrt{23}}{39468\sqrt{5}}\frac{E0^{*9}_D FD12[E0^*_D]\gamma^D_{110}[E0^*_D]}{FD2[E0^*_D]} - \frac{17(11)(175)}{39468\sqrt{5}}\frac{E0^{*10}_D FD13[E0^*_D]\gamma^D_{120}[E0^*_D]}{FD2[E0^*_D]}\\
&- \frac{17(11)(2)(1305)\sqrt{3}}{39468\sqrt{5}}\frac{E0^{*11}_D \gamma^D_{130}[E0^*_D]}{FD2[E0^*_D]} - \frac{17(11)(13)\sqrt{29}}{39468\sqrt{5}}\frac{E0^{*12}_D \gamma^D_{140}[E0^*_D]}{FD2[E0^*_D]},\end{aligned}$$

where the $\gamma^D_{l0}[E0^*_D]$ coefficients are given by

$$\gamma^D_{l0}[E0^*_D] = \frac{8\pi}{135}\sqrt{\frac{1}{2}l(l+1)}\frac{\mu^{*4}E0^{*2}_D}{\mathrm{Si}\,nh[E0^*_D]^2}F^D_{l00}[E0^*_D]\left(F^D_{00}[E0^*_D] + F^D_{1\underline{1}}[E0^*_D]\right).$$

The functions $FDl[E0^*_D]$, $F^D_{l00}[E0^*_D]$ and $F^D_{ij}[E0^*_D]$ are lengthy expressions which we do not provide explicitly.

For the quadrupole, the first two coefficients are α_2 and α_4, because all the odd coefficients are zero. Therefore, we have

$$\alpha^Q_2 = FQ_{21} + \rho^* FQ_{22},$$

and

$$\alpha^Q_4 = FQ_{41} + \rho^* FQ_{42}$$

The coefficients FQ_{ij} are given by

$$FQ_{21}[E0^*_Q] = -\frac{17\sqrt{5}}{2}\frac{E0^*_Q FQ1[E0^*_Q]}{FQ2[E0^*_Q]},$$

$$\begin{aligned} FQ_{22}[E0^*_Q] = {} & \frac{85}{2}\frac{FQ1[E0^*_Q]\gamma^Q_{20}[E0^*_Q]}{FQ2[E0^*_Q]} + \frac{85(513513)}{255255\sqrt{5}}\frac{E0^*_Q FQ3[E0^*_Q]\gamma^Q_{40}[E0^*_Q]}{FQ2[E0^*_Q]} \\ & + \frac{85(4)(429)\sqrt{13}}{255255\sqrt{5}}\frac{E0^{*2}_Q FQ4[E0^*_Q]\gamma^Q_{60}[E0^*_Q]}{FQ2[E0^*_Q]} + \frac{85(4)(2)(3289)\sqrt{17}}{255255\sqrt{5}}\frac{E0^{*3}_Q FQ5[E0^*_Q]\gamma^Q_{80}[E0^*_Q]}{FQ2[E0^*_Q]} \\ & + \frac{85(4)(2)(600)(13)\sqrt{21}}{255255\sqrt{5}}\frac{E0^{*4}_Q FQ6[E0^*_Q]\gamma^Q_{100}[E0^*_Q]}{FQ2[E0^*_Q]} + \frac{85(4)(2)(600)(594)}{255255\sqrt{5}}\frac{E0^{*5}_Q \gamma^Q_{120}[E0^*_Q]}{FQ2[E0^*_Q]}, \end{aligned}$$

and

$$FQ_{41}[E0^*_Q] = \frac{171}{2\sqrt{\pi}}\frac{E0^{*2}_Q FQ3[E0^*_Q]}{FQ2[E0^*_Q]},$$

$$\begin{aligned} FQ_{42}[E0^*_Q] = {} & \frac{171}{2\sqrt{5}}\frac{E0^*_Q FQ3[E0^*_Q]\gamma^Q_{20}[E0^*_Q]}{FQ2[E0^*_Q]} - \frac{171}{4}\frac{FQ9[E0^*_Q]FQ3[E0^*_Q]\gamma^Q_{40}[E0^*_Q]}{FQ2[E0^*_Q]} \\ & - \frac{429\sqrt{13}}{3003}\frac{E0^*_Q FQ9[E0^*_Q]FQ4[E0^*_Q]\gamma^Q_{60}[E0^*_Q]}{FQ2[E0^*_Q]} - \frac{2(3289)\sqrt{17}}{3003}\frac{E0^{*2}_Q FQ9[E0^*_Q]FQ5[E0^*_Q]\gamma^Q_{80}[E0^*_Q]}{FQ2[E0^*_Q]} \\ & - \frac{2(600)(13)\sqrt{21}}{3003}\frac{E0^{*3}_Q FQ9[E0^*_Q]FQ6[E0^*_Q]\gamma^Q_{100}[E0^*_Q]}{FQ2[E0^*_Q]} - \frac{2(600)(594)}{3003}\frac{E0^{*4}_Q FQ9[E0^*_Q]\gamma^Q_{120}[E0^*_Q]}{FQ2[E0^*_Q]}, \end{aligned}$$

where the $\gamma^Q_{l0}[E0^*_Q]$ coefficients are given by

$$\begin{aligned} \gamma^Q_{l0}[E0^*_Q] = {} & \frac{32}{315}\sqrt{\frac{l(l+1)}{6}}\frac{\Theta^{*4}E0^*_Q}{Erfi[\sqrt{\frac{E0^*_Q}{2}}]}\left(3F^Q_{l00}[E0^*_Q]\left(-F^Q_{2\underline{2}}[E0^*_Q] - \frac{2}{5}F^Q_{1\underline{1}}[E0^*_Q] + \frac{3}{5}F^Q_{00}[E0^*_Q]\right)\right. \\ & \left. +\sqrt{6}F^Q_{l01}[E0^*_Q]\left(\frac{31}{10}F^Q_{2\underline{2}}[E0^*_Q] + \frac{8}{5}F^Q_{1\underline{1}}[E0^*_Q] - \frac{3}{2}F^Q_{00}[E0^*_Q]\right)\right). \end{aligned}$$

The functions $FQl[E0^*_D]$, $F^Q_{l00}[E0^*_D]$, $F^Q_{l01}[E0^*_D]$ and $F^D_{ij}[E0^*_D]$ are also lengthy expressions and are not provided explicitly.

We do not give the explicit expressions for the other coefficients, but they will be provided by the author upon request.

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