Orientational distribution for dipolar and quadrupolar colloids driven by an external field

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We study the ordering in dipolar and quadrupolar colloids driven by an appropiate external field, which is low structured at zero field strength. This study consists of analyzing the predictions involved by the one body probability density function, as function of the strength of the field, which is the solution of the equilibrium Smoluchowski equation, without hydrodynamic interactions. Because of the symmetry of the dipole and quadrupole, for the former an axial nematic-like phase is predicted, wheras for the latter a biaxial nematic-like phase is predicted. In the study we consider different fields, for the dipole only the orientation of the field is changed, whereas for the quadrupole the gradient of the field is also changed. The alignment of the multipolar colloids for high values in field is independent of the different fields studied in both moments, but their alignment for low values depends on the field features. The change in curvature of the one body probability density functions for the moments analyzed is predicted in field strength values with a different meaning. For the quadrupole moment an anomalous perpendicular alignment of the particles is predicted, which does not ocurr for the dipole moment. Our results are described as a generalized point of view in the Landau-de Gennes theory for the nematic isotropic phase transition driven by an external field.

Keywords: Multipolar colloid; nematics; orientational distribution.

Estudiamos el ordenamiento en coloides dipolares y cuadrupolares por inducción de un campo externo apropiado, los cuales sin campo son poco estructurados. El estudio consiste en analizar las predicciones de la densidad de probabilidad de un cuerpo como función de la intensidad del campo, la cual es solución de equilibrio de la ecuación de Smoluchowski, sin interacciones hidrodinámicas. Debido a la simétria de el dipolo y el cuadrupolo, para el primero una fase tipo nemática axial es predicha, mientras que para el cuadrupolo una tipo nemática biaxial es predicha. En el estudio se consideran diferentes campos, para el dipolo solo la orientación es variada, mientras que para el cuadrupolo también se cambia el gradiente del campo. A valores grandes del campo el proceso de alineamiento es independiente de los diferentes campos usados, en ambos momentos, aunque el alineamiento a campos pequeños depende de la orientación del campo. El cambio en curvatura de la densidad de probabilidad de un cuerpo de los diferentes momentos estudiados aparecen en puntos con diferente interpretación. Para el coloide cuadrupolar un alineamiento anomalo perpendicular es observado, lo cual no ocurre para el coloide dipolar. Desde un punto de vista generalizado, nuestros resultados son interpretados en el esquema de la teoría de Landau-de Gennes para la transición de fase nematico isotropica en presencia de un campo externo.

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

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1. Introduction

One of the challenges in colloidal crystals is to describe and to locate phase transitions. The most common way is by finding discontinuities in the order parameters, one of them is the so called nematic order parameter, in which its discontinuity predicts the localization of the isotropic nematic transition [1, 2].The first prediction of the existence of nematics is due to Onsager in long hard rods [3]. The isotropic nematic transition for rods can be described by using computer simulations [4]or from an appropriate experiment [5].

The experimental observations using various techniques show that the order parameters decrease monotonically as the temperature is raised in the mesophase range and drop abruptly to zero at the transition. Depending on the mesogenic material the nematic-isotropic transition occurs at values between 0.25 - 0.5 in the second order parameter. Thus the nematic-isotropic transition is first order in nature, though it is relatively weak thermodynamically because only an orientational order is lost at this transition and the heat of transition is only 1 kJ/mol [2]. In the case of multipolar colloids, mainly dipole and quadrupole moment, in both of them an axially symmetric ordered phase already exists, in absence of an external field. For the dipole it is called ferroelectric whereas for the quadrupole "v" structures, the former resembles an axial nematic order and the latter a biaxial nematic order. We must emphasize that the ferroelectric as well as "v" phases are not taken into account in this study [6, 7, 15]. Both phases are reached at high densities, out of scope of this work.

In 1970 de Gennes and Pincus predicted the formation of linear chains of particles in ferrofluids at zero magnetic field [8]. Several years after Butter et al were able to show in situ linear chain structures in ferrofluids at zero field and very low densities [9]. In response to an external magnetic field, they also observed an induced alignment in the chains. Another important characteristic in colloids driven by an external field is the inexistence of a discontinuous transition but rather a continuous one. In the case of a second order transition, the order parameters are not discontinuous, but continuous, therefore we need to find an alternative mechanism in order to localize and to describe the second order transitions. It is also possible to find second order transitions without an external field. The transition between uniaxial nematic and biaxial nematic is an instance of second order transition, which was predicted from a theoretical basis by Freiser [11]. He showed that the simplest generation of interaction employed in the Maier-Saupe theory leads to a first order isotropic nematic transition followed, at lower temperature, by a second order transition to a biaxial state. In example, this exotic behavior can be expected when the molecules do not present an effectively uniaxial symmetry or with axial symmetry together with the application of an appropriate external field [2, 10].

On the other hand, when the second order parameter versus temperature for different values of the external field is plotted, it is possible to find a coexistence curve like the well known liquid vapor one. It is observed for small values of the field that there exists a first order transition between paranematic and the nematic phase. The order parameter jump decreases with increasing field until its critical value is reached at which point there is no jump any more. At this point the transition becomes continuous [2, 10]. Because in this work the aim is to study the response of the colloid driven by an external field only, this feature is out of the scope. From a theoretical point of view, the role of external fields on the physical properties of the nematic isotropic phase transition can be examined within the framework of the Landau-de Gennes theory. The application of fields leads to an extra term in the free energy, in which appears the anisotropic part of the magnetic susceptibility. This last important physical property involves conditions of the alignment with respect to the orientation of the field. For positive values they align parallel to the field, whereas for negative values the alignment is not parallel but perpendicular with respect to the orientation of the field [2, 10]. In this work these implications will be studied over the alignment of the particles.

Nowadays several methods for colloidal synthesis of nanoparticles of different shapes are available [12, 13], for example hard perfect tetragonal parallelepipeds, in which is predicted the existence of a biaxial nematic phase onto a perpendicular projection of the nematic director [14]. Another example is in a colloid of spherical shape, but with a quadrupolar interaction. In this colloid, by means of computer simulations, the existence of a biaxial nematic phase is observed [15]. In the case of induced biaxial nematic, we can mention hard rods driven by an external flow. For an uniaxial nematics, the projection of the rods onto the plane perpendicular to the director are isotropically distributed, while for a biaxial nematic the orientation of the rods in this projection have a second preferred direction [16].

Another important feature in induced alignment with an external field is observed for low fields the particles align with the field, however for high values in a field the alignment is not parallel but in an anomalous perpendicular orientation with the field. A feature observed for instance in boarlike goethite particles driven by a magnetic field, they first align parallel to the magnetic field at low field strength, but they turn perpendicular to the field at high strength [17]. Also this behavior is observed in charged rods driven by an external field. For high concentrations the alignment is found to change from parallel to the electric field to an anomalous perpendicular orientation, whose dependency is on the field amplitude and frequency [18].

In recent papers one of us predicted the existence of a biaxial nematic-like phase, an anomalous change of the orientation of the particles from one direction to another perpendicular to the first one is already predicted. This prediction is carried out on quadrupolar colloids, *i.e.*, on a colloid of hard spherical particles with a point quadrupole moment at the center of mass [19, 20] (hereafter referred as paper I and II, respectively). In fact in these two papers we also studied the behavior of a dipolar colloid. Here a similar feature is predicted. In a generalized point of view, in this paper we describe the response of the multipolar colloid driven by an external field. For low fields the particles align in the field orientation and for high values the orientation would not be in the field direction but in a generalized “perpendicular” orientation.

The aim of this paper is to do a systematic and extensive study of this anomalous behavior in dipolar and quadrupolar colloids. We use the same ideas as in the previous work [19]. In this case, we take additional orientations of the external fields for the dipole and for the quadrupole different gradients are considered together with additional orientations of the field. The formalism used in this paper is based on the assumption that the equilibrium of the colloid is provided by the equilibrium solutions of the Smoluchowski equation [22, 23]. The paper is written in the following way: In Sec. 2 we start with the ideas of the Landau-de Gennes theory for the nematic isotropic phase transition driven by an external field in subsection A. Definitions of the multipolar colloid and the additional fields used are provided in subsection B. We write the ideas of the formalism to compute the one body probability density function (pdf), the main quantity to realize in this study, also in subsection B. In Sec. 3 our results are given for dipole and quadrupole moment for the fields considered in both moments and gradients in the quadrupolar case. The section is divided in two subsections, the first one considering the influence of the external field on a single particle, whereas in subsection B interaction between colloidal particles is also taken into account. In Sec. 4 concluding remarks are provided.

2. Multipolar colloids and orientational distribution

The main ingredients to study in ordered phases are the order parameters together with the one body probability density function (pdf) at equilibrium. In this paper we focus on the latter only, the former will be reported in another work. In Subsec 1, we provide the ideas and physical consequences of the Landau-de Gennes theory for the nematic isotropic phase transition in presence of an external field. In the second part of this section, we define the colloid in study and the Smoluchowski formalism for computing the one body equilibrium pdf.

2.1. Landau-de Gennes theory for nematic isotropic phase transitions in an external field

In this work the aim is to analyze the physical consequences of the nematic isotropic phase transition driven by an external field, then we focus on the ideas of Landau-de Gennes theory for the case in which the system is driven by an external field [2,10]. The idea is to propose a generalization of the Landau-de Gennes theory for multipolar colloids. We start with the definition of the generalized order parameter tensor, according to the multipolar moment,

$$\mathbf{Q}^{\ell}=\frac{\Delta\overleftrightarrow{\chi}^{\ell}}{\chi^{\ell}_{\max}}, \tag{1}$$

where $\Delta\overleftrightarrow{\chi}^{\ell}$ is the anisotropic part of the generalized susceptibility tensor and $\chi^{\ell}_{\max}$ is the maximal anisotropy that would be observed for a perfectly ordered nematic phase. The choice of $\mathbf{Q}^{\ell}$ reflects that the orientational order is the only general aspect in which the nematic an isotropic phase differ, in which, the absence of ferroelecticity is incorporated for the case $\ell=1$ for example. Therefore, in the Landau-de Gennes theory the presence of the field leads to an extra term in the free energy, which in our case would read as

$$U^{\ell}=-\chi^{\ell}_{\max}\mathbf{Q}^{\ell}\odot\mathbf{F}^{\ell}. \tag{2}$$

where $\mathbf{F}^{\ell}$ is the tensor field according to the order of the ℓth multipolar moment and $\odot$ represents a generalized inner product.

In our microscopic description, the general definition of the external field potential is [21]

$$\phi^{\ell}_{\text{ext}}=-\frac{1}{(2\ell-1)!!}M_{\ell}\mathbf{P}^{\ell}\odot\nabla^{\ell-1}\mathbf{E}_0, \tag{3}$$

where $\mathbf{P}^{\ell}$ is the tensor Legendre polynomial of order ℓ, M_{ℓ} is the multipole moment of order ℓ, with 1 and 2 corresponding to dipole and quadrupole moments, respectively, and $\mathbf{E}_0$ is the external field. From Eqs. (2) and (3), we could associate $\chi^{\ell}_{\max}$ with $1/((2\ell-1)!!M_{\ell})$ and $\mathbf{Q}^{\ell}$ with $\mathbf{P}^{\ell}$. This is based on the definitions of the order parameters, they are the average on an equilibrium ensemble of the Legendre polynomials. An important physical consequence of the Landau-de Gennes theory is that for $\chi^{\ell}_{\max}$ positive the alignment of the colloidal particles is parallel to the orientation of the field, however when $\chi^{\ell}_{\max}$ is negative the orientation is not parallel but perpendicular to the orientation of the field. These important physical features predict that there exists a biaxial nematic phase. In the next section we discuss the implications of these physical consequences of the Landau-de Gennes theory over our study in the induced isotropic nematic phase transition in dipolar and quadrupolar colloids.

2.2. One body equilibrium probability density function

We consider a colloid of hard spherical particles with a linear dipole or quadrupole moment in their center of mass. The potential energy consists of two terms, the multipolar interaction and the external field. Thus it reads, from paper I,

$$\Phi(\mathbf{r}^N,\widehat{\mathbf{u}}^N)=\sum_{i\neq j}\phi_M(\mathbf{r}_{ij},\widehat{\mathbf{u}}_i,\widehat{\mathbf{u}}_j)+\sum_{l}\phi_{\text{ext}}(\widehat{\mathbf{u}}_l), \tag{4}$$

where $\phi_M(\mathbf{r}_{ij},\widehat{\mathbf{u}}_i,\widehat{\mathbf{u}}_j)$ is the multipolar pair interaction potential and $\phi_{\text{ext}}(\widehat{\mathbf{u}}_l)$ the external field, which drives the colloid. In Eq. (4) $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, with $\mathbf{r}_l$ the position of the center of mass of the lth particle and $\widehat{\mathbf{u}}_l$ the orientation of the multipolar moment. In general the multipolar expansion is written as [21],

$$\phi_M(\mathbf{r}_{ij},\widehat{\mathbf{u}}_i,\widehat{\mathbf{u}}_j)=\sum_{l_1l_2l}\sum_{m_1m_2m}u^{l_1l_2l}_M(r_{ij})C(l_1l_2l;m_1m_2m)\times Y^{i}_{l_1m_1}Y^{j}_{l_2m_2}Y^{*r_{ij}}_{lm}, \tag{5}$$

here $u^{l_1l_2l}_M(r_{ij})$ are the multipolar coefficients, $C(l_1l_2l;m_1m_2m)$ is the Clebsh-Gordan coefficient and $Y^{l}_{l_1m_1}$ is the spherical harmonic, the super index denotes colloidal particles or the angular dependences of $\mathbf{r}_{ij}$. The corresponding multipolar coefficient for the dipole moment is

$$u^{112}_D(r_{ij})=-4\pi\sqrt{\frac{8\pi}{15}}\frac{\mu^2}{r^3_{ij}}, \tag{6}$$

and for the quadrupole moment is

$$u^{224}_Q(r_{ij})=\frac{8\pi}{3}\sqrt{\frac{14\pi}{3}}\frac{\Theta^2}{r^5_{ij}}. \tag{7}$$

In Eqs. (6) and (7) μ and Θ are the dipole and quadrupole moment, respectively and $r_{ij}=|\mathbf{r}_{ij}|$. For the dipole, the orientation of the external field is analyzed in two situations, parallel and antiparallel of the Z-axis, these are, respectively, [21]

$$\phi^{D}_{\text{ext}}(\cos\theta_l)=\pm\mu E_0\cos\theta_l, \tag{8}$$

where E_0 is the strength of the external field and θ_l is the angle between the direction of the field and the orientation of the dipole moment of the lth particle. The case considered in paper I corresponds to the negative in Eq. (8). The quadrupole is richer. First, now the field is chosen with constant gradient, positive or negative. For the orientation of the field we propose one case in the Z-axis and the other in the plane perpendicular to Z, that is in the XY plane, thus we define the external field as, for parallel to Z,

$$\mathbf{E} = \pm z E_0 \widehat{\mathbf{k}}, \tag{9}$$

and for perpendicular to Z as

$$\mathbf{E} = \pm E_0 (x\widehat{\mathbf{i}} + y\widehat{\mathbf{j}}). \tag{10}$$

From the definition of the external field in multipoles [21], we already have two different situations. First as we will see, the alignment of the particles is the same for the negative sign in Eq. (9) and positive sign in Eq. (10), then we assemble the field as

$$\phi^{Q}_{\text{ext}}(\cos\theta_l) = -\frac{1}{2}\Theta E_0 \cos^2\theta_l = \frac{1}{2}\Theta E_0 \sin^2\theta_l, \tag{11}$$

and another situation is when we take the positive sign in Eq. (9) and the negative sign in Eq. (10), thus

$$\phi^{QM}_{\text{ext}}(\cos\theta_l) = \frac{1}{2}\Theta E_0 \cos^2\theta_l = -\frac{1}{2}\Theta E_0 \sin^2\theta, \tag{12}$$

in these last two equations θ_l is the angle of the symmetry axis of the quadrupole moment with Z-axis. In Eq. (11) the first equality corresponds to the case with negative gradient in the Z-axis, and the second one with a positive gradient in the plane perpendicular to the Z-axis. Whereas in Eq. (12) we are in the inverse situation, the first equality corresponds to the positive gradient in the Z-axis, and another with negative gradient in the perpendicular plane to the Z-axis. In order to simplify the study Eq. (11) will be referred to as case I and Eq. (12) as case II. The first equality in Eq. (11) was already studied in paper I.

The one body pdf, P_1^M, is assumed as an equilibrium solution of the Smoluchowski equation, from paper I, neglecting hydrodynamic interactions,

$$\left\{\widehat{R}_1^2 + \beta\widehat{R}_1\cdot[\widehat{R}_1\phi^M_{ext}]\right\} P_1^M(\widehat{\mathbf{u}}_1)$$
$$-\rho\beta\widehat{R}_1\cdot P_1^0(\widehat{\mathbf{u}}_1)\int d\widehat{\mathbf{u}}_2 \overrightarrow{\tau}(\widehat{\mathbf{u}}_1,\widehat{\mathbf{u}}_2)P_1^0(\widehat{\mathbf{u}}_1) = 0, \tag{13}$$

where $\widehat{R}$ is the orientational operator, ρ is the density, $P_1^0(\widehat{\mathbf{u}}_1)$ is the solution of Eq. (13) with $\rho = 0$, which is for a single particle driven by the external field only, β is the thermal energy, M is the multipolar moment and the torque $\overrightarrow{\tau}(\widehat{\mathbf{u}}_1,\widehat{\mathbf{u}}_2)$

$$\overrightarrow{\tau}(\widehat{\mathbf{u}}_1,\widehat{\mathbf{u}}_2) = -\int d\mathbf{r}_{ij}$$
$$\times\left[\widehat{R}_1\phi_M(\mathbf{r}_{ij},\widehat{\mathbf{u}}_1,\widehat{\mathbf{u}}_2)\right] g(\mathbf{r}_{ij},\widehat{\mathbf{u}}_1,\widehat{\mathbf{u}}_2), \tag{14}$$

where $g(\mathbf{r}_{ij},\widehat{\mathbf{u}}_1,\widehat{\mathbf{u}}_2)$ is the pair correlation function. This quantity is computed by assuming the Boltzmann approximation and it is taken into account up to second order in its Taylor expansion, that is up to fourth degree in the moment. Due to the linear approach in density and the second order contribution in the Taylor expansion in the pair correlation function, $P_1^M(\widehat{\mathbf{u}}_1)$ is restricted to low values in density and multipolar moments, this implies that our colloid is in an isotropic phase in absence of the external field. With this approach it is not possible to get a self alignment.

The solution of Eq. (13) is obtained as an expansion of Legendre polynomials, $p_l(\cos\theta)$,

$$P_1^M(\widehat{\mathbf{u}}_1) = \sum_l \alpha_l p_l(\cos\theta), \tag{15}$$

with $\alpha_l \equiv \langle p_l\rangle$ being the order parameters. The problem is reduced to calculate the coefficients in Eq. (15). Therefore, substitution of Eq. (15) into Eq. (13) and equating resulting coefficients in Legendre Polynomials, the order parameters can be computed [19].

3. Results

Following paper I, we assume a low structured colloid in absence of the external field, that is, in this condition the colloid would be in an isotropic phase. It is composed of hard spherical particles with point dipole or quadrupole in their center of mass. The dimensionless density is $\rho^* = \rho\sigma^3 = 0.005$ for both moments. Here σ is the diameter of the spherical particle and ρ is the density. The dimensionless dipole and quadrupole moments are defined as $\mu^{*2} = \beta\mu^2/\sigma^3$, $\Theta^{*2} = \beta\Theta^2/\sigma^5$, respectively and $E_0^*M=\beta ME_0$. Both dimensionless moments are taken equal to 0.40. For these values in density and multipolar moments the colloid is in the isotropic phase [15, 24].

In an experimental point of view, a dipolar colloid is a dispersion of magnetic nanoparticles with a single magnetic domain. For high density and magnetic moment the dispersion goes into a ferroelectric nematic phase [7], on the contrary, at

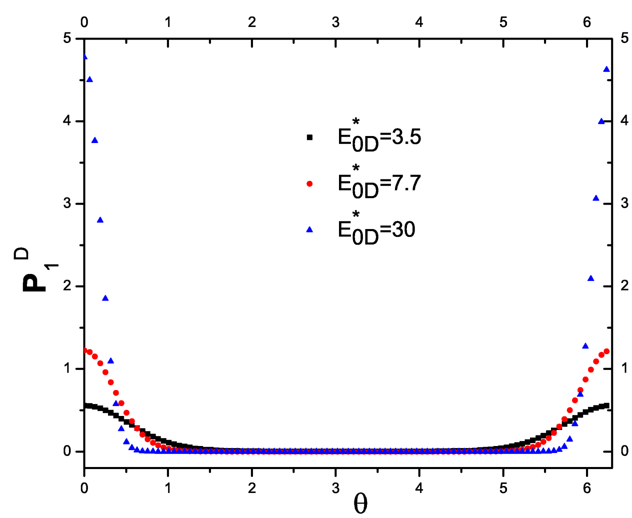

FIGURE 1. One body probability density function versus θ for a dipolar colloid for differents field strength, as indicated in the figure. The field is parralel to the Z-axis.

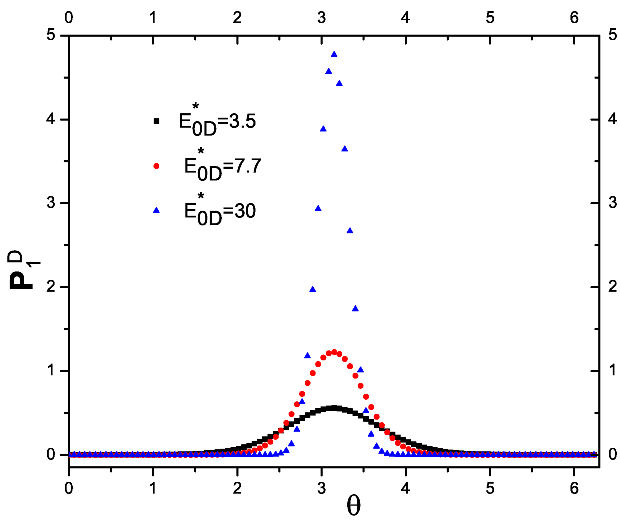

FIGURE 2. One body probability density function versus θ for a dipolar colloid for differents field strength, as indicated in the figure. The field is antiparralel to the Z-axis.

low density and high magnetic moment it aggregates, forming dipolar chains [24]. Experimental results suggest a maximal attraction more than two times the thermal energy, getting an aggregation in this value [25], for values of $\mu^{*2} < 2$ the colloid does not aggregate. Therefore in our case the colloid does not aggregate, that is for $\mu^{*2} = 0.4$ and $\rho^* < 0.3$ the dispersion is already in an isotropic phase [24]. The interaction energy of a dipole of magnetic moment μ aligned with a magnetic field H is equal to μH. The average degree of alignment of the magnetic dipoles depends on the ratio of $\mu H/k_B T$ because thermal motion tends to destroy the alignment. Considering experimental data, with $\mu^{*2} = 1.3$, which is close to the water molecule dimensionless moment ($\mu^{*2} = 1.8$), and $H = 1.2x10^{-6}$ A/m gives $E^*_{0D} = 4.479$, for these experimental data the colloid would start its alignment. For lower values, as is our case, one would expect a higher strength of the dimensionless field, and a similar conclusion for the quadrupole moment as well.

3.1. A single particle driven by an external field

The study starts with a single particle driven by the external field. As was mentioned above, this study is based on the analysis of the one body pdf, function of the polar angle. In this case the one body pdf, Eq. (15) resembles the behavior expected for the dipole. Therefore we observe that the particles align in the field orientation, that is in the positive or negative orientation of the Z-axis, depending on the field direction, as can be seen for different values in the dimensionless field as the function of the polar angle in Figs. 1 and 2, respectively. The former corresponds to the positive sign in Eq. (8) and the latter to the negative sign in Eq. (8). Nevertheless, if we increase the field strength the alignment does not change. It is always parallel to the field orientation.

Following the ideas of Landau-de Gennes we could interpret these results from a different point of view in both cases Figs. 1 and 2. We assume a field in the positive Z-direction only, then the sign is considered in the maximal anisotropy $\chi_{\max} = \pm\beta\mu E_0$. Therefore, when $\chi_{\max}$ is positive the alignment is parallel to the orientation of the field, contrary to the negative value where the alignment is not parallel but antiparallel. This different interpretation is in agreement with the Landau-de Gennes theory as a generalized point of view, the particles align in the only contrary orientation possible.

The quadrupolar behavior is more interesting, as was above mentioned. Here, we observe the same alignment in each of the options fields written in Eqs. (11) and (12). Therefore our results are reported in terms of these two cases. For the former the quadrupole moments align perpendicular to the Z-direction, that is with $\theta = \pi/2$ and $3\pi/2$, as we see in the plot as function of the polar angle for different values in the strength of the field in Fig. 3, while for the latter they align parallel and antiparallel to the Z-axis, observed in Fig. 4, for the one body pdf. According to the definitions of the fields in Eqs. (11) and (12), if the gradient of the field is positive then the particles align in the field orientation also, whereas if the gradient is negative then the alignment is not in the field orientation but in an anomalous perpendicular way.

We must emphasize, the perpendicular alignment with respect to the orientation of the field is due to the negative gradient of the field only. On the other hand, as in the case of dipole we could also interpret these results by way of the Landau-de Gennes theory. In this case $\chi_{\max} = \beta\Theta E_o$ is always taken positive, the sign is associated with the gradient of the field, one sees immediately that our results are in agreement with this theory. That is for negative gradient the anomalous perpendicular alignment is predicted.

From the results predicted for the alignment of single particle driven by an external field, we observe that the ordering reached depends on the multipolar moment. For the dipole in the field orientation, that is parallel or antiparallel to it. For the quadrupole we have two possible orientations one parallel

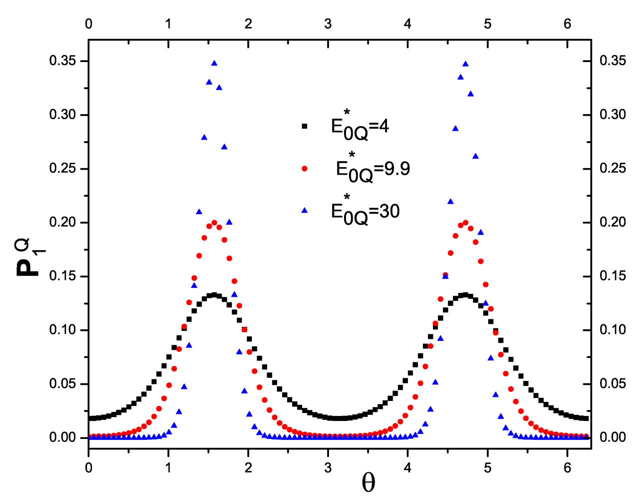

FIGURE 3. One body probability density function versus θ for a cuadrupolar colloid for differents field strength, as indicated in the figure. The orientation field is for case I.

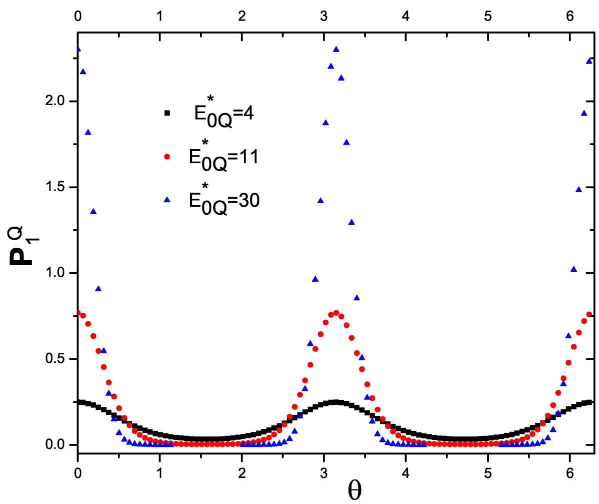

FIGURE 4. One body probability density function versus θ for a cuadrupolar colloid for differents field strength, as indicated in the figure. The orientation field is for case II.

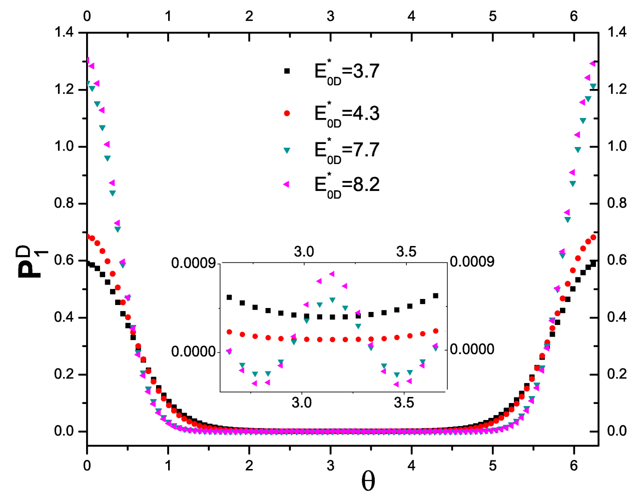

FIGURE 5. One body probability density function versus θ for the four interesting values of the fields strength.

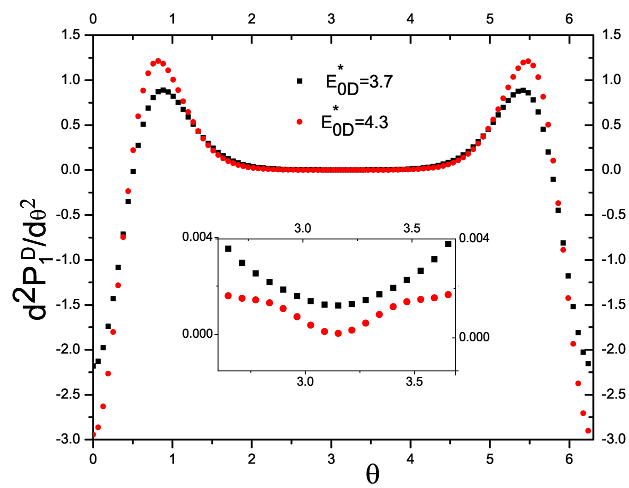

FIGURE 6. Second derivative of the one body probability density function versus θ, for a dipolar colloid. These values are in which the curvature changes its monotonous behavior and when takes the value equal to zero.

and antiparallel to the Z-axis and the another perpendicular to the Z-axis, that is in the X Y plane. The former corresponds to positive gradients and the latter to negative ones. In a general point of view these results could be visualized into the Landau-de Gennes theory, where the response for negative values implies an opposing orientation to the first one, where the word "opposing" depends on the multipole moment, as it is already observed for dipole and quadrupole moments.

It is important to mention, there does not exist a biaxial nematic phase in a single particle driven by an external field. What is responsible for the biaxial nematic phase is the pair interaction between quadrupolar colloids, driven by the external field in our model.

In this way, our results are compatible with the prediction of the Landau-de Gennes Theory. One important question in a continuous phase transition is to localize it. In paper I we have proposed an alternative manner to get this challenge. Following these ideas, in this work we give ourselves the homework of carrying out an extensive study in multipolar colloids, focusing on dipole and quadrupole moments only. With this in mind, we compute the one body pdf as the solution of the Smoluchowski equation restricting ourselves to low structured colloids.

3.2. Nematic-like phase in multipolar colloids driven by an external field

In colloids the situation is richer than for a single particle driven by an external field. Here the interaction between particles plays an important role, in our model this is introduced in the pair approximation. We first study the case of the dipolar interaction. We have two orientations in the field, both on the same axis (Z), but in positive and negative direction. The results show us that the particles first align in the field orientation and after that to some critical field strength where they reach a second alignment. The behavior is already the same at the end in both situations, parallel and antiparallel, the difference is only the initial orientation. Therefore we focus on one of the two cases only, the positive. The negative was already discussed in paper I. An extensive study of the one body pdf and its first and second derivative as function of the polar angle, provides us with the existence of four important values of the field strength. In Fig. 5 we plot the one body pdf, as function of θ, for these four values $E_{0D}^{*} = 3.7, 4.3, 7.7$ and 8.2. In the inset the second alignment is clearly observed for the higher field strength. In order to analyze the behavior of the colloid we focus on the curvature around of $\theta = \pi$, in which the second alignment would appear at higher values in the field. For the values of the field strength 3.7 and 4.3, an interesting behavior was predicted. In Fig 6 the second derivative of this quantity for these two values is plotted, as the function of the polar angle, the former gives us the value in which the curvature starts to change

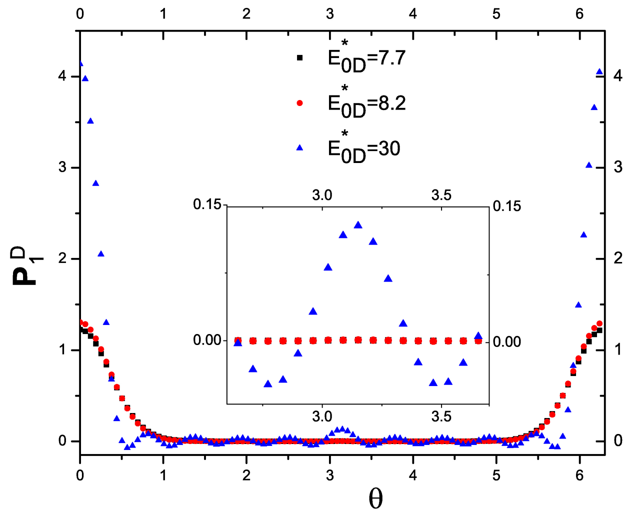

FIGURE 7. One body probability density function versus θ for a dipolar colloid around the transition.

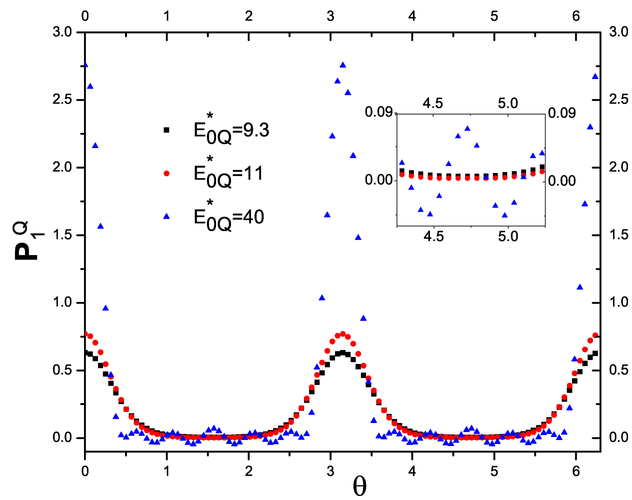

FIGURE 8. One body probability density function versus θ for a quadrupolar colloid around the transition.

its monotonous behavior and the latter when the curvature takes its value equal to zero, as it is easily observed in the inset in Fig. 6. On the other hand, the last two values plotted in Fig. 5 of field strength, 7.7 and 8.2, correspond to the values in which the alignment antiparallel to the field orientation starts, as it can be observed in Fig. 7. In this plot we also report $E^*_{0D} = 30$, in order to see the existence of the second alignment clearly. Therefore the prediction is an axial nematic-like phase, as was previously predicted [19]. The parallel and antiparallel orientation is due to the combination of both effects, the external field and the direct dipolar interactions. This behavior in a single particle driven by the field is not predicted. Contrary to the low values in the field strength, the localization of the second alignment is not easy. In paper II we also proposed an additional physical property which is able to localize this value. This analysis is out of the focus of this work, it will be published in the future.

For the quadrupolar interaction, the predictions are similar in a generalized point of view with those corresponding to the dipole interaction. We begin with case II, Eq. (12), here only two important field strength values are predicted, these are again found by visualizing changes in curvature, as in the dipolar case. The difference is that now these values together also predict the second alignment. In Fig. 8 we plot the one body pdf for these two values, $E^*_{0Q} = 9.3$ and 11, as function of the polar angle. In this figure it is also reported for $E^*_{0Q} = 40$, because in this value is easy to see that there exists a biaxial nematic-like phase. In Fig. 9 we plot their corresponding curvature for the lower two values in Fig. 8 and in the inset for the region in θ in which the biaxial phase appears. The value $E^*_{0Q} = 9.3$ is when the curvature begins to change its monotonous behavior and for 11 when it takes the value equal to zero, as can be seen in the inset in Fig. 9. On the other hand, the difference with case I is only the difference in values, $E^*_{0Q} = 8.9$ and 9.9, which have the same meaning, the former the point where the monotonous behavior of the curvature changes and the latter when it takes

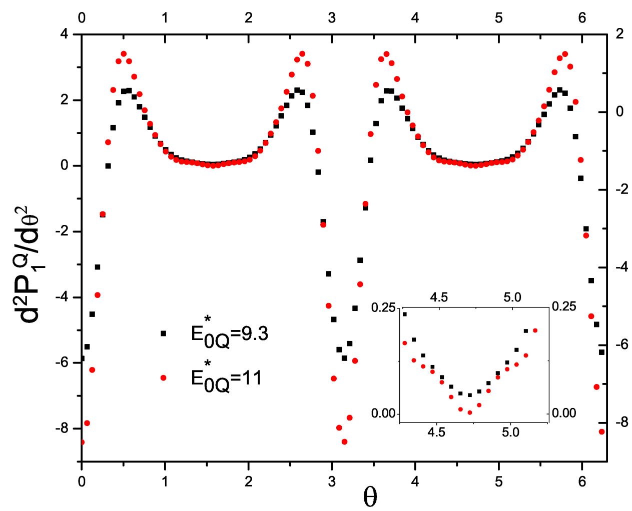

FIGURE 9. Second derivative of the one body probability density function for a quadrupolar colloid versus θ. These values are in which the curvature changes its monotonous behavior and when takes thet value equal to zero.

the value equal to zero. In both cases these values start the biaxiality as was already predicted in paper I and II. As in the dipole moment, here the final biaxial phase is observed in all the situations considered. The difference is only in the first alignment, it depends on the sign of the gradient. As was observed in a single particle driven by an external field, here the particles align first in the field direction for positive gradient of the field and perpendicular when the gradient is negative. We must emphasize that the existence of the biaxial phase is due to the effect of both interactions presents, the external field and the pair interactions.

From the results for both moments studied, the prediction of the second alignment does not correspond to the same characteristics in the one body pdf for both moments. In the quadrupolar the change in curvature coincides with this second alignment, whereas for the dipole it is not the situation observed. One could say that the explanation for this difference is in the different nematic-like phase reached, biaxial for quadrupolar and axial for the dipolar. In paper II we discussed these points, they are on the critical values of the self orientational structure factor, the quantity related to the isothermal compressibility. The dipole corresponds to the point in which the first derivative of the self orientational structure factor is equal to zero, whereas for the quadrupole the second derivative of this quantity is equal to zero. As a consequence we could associate the change in curvature in the one body pdf with those points in which some derivative of the self orientational structure factor is equal to zero. These observations will be analyzed in another work, they require an extensive study of the self orientational structure factor, which is out of the scope of this paper.

4. Concluding remarks

We present a systematic and extensive study of the ordering in dipolar and quadrupolar low structured colloids driven by an external field. The study is realized as to the predictions of the one body pdf, which are provided by the equilibrium solutions of the Smoluchowski equation. In each case different fields are analyzed, where their form is imposed by the symmetry of the multipole. As a consequence of these symmetries, for the dipole an axial nematic-like phase is predicted, and for the quadrupole an axial is not predicted but rather a biaxial nematic-like phase.

In all the cases analyzed, at the end the final phase is the same for each multipole, the difference is the first alignment, which depends on the orientation of the field for the dipolar colloid and also the field gradient for the quadrupolar colloid. Due to the biaxial symmetry in the quadrupolar moment an anomalous alignment is predicted, that is for negative gradient the particles align perpendicular to the field orientation, which is not predicted for dipolar colloids. From a generalized point of view, we could see that our results are in complete agreement with the Landau-de Gennes theory for the nematic-isotropic phase transition driven by an external field. The implication is that the source of the negative sign, maximal anisotropy, external field or even the order parameter do not matter, if that is the case, the prediction is then a generalized contrary alignment with respect to the field, where the word "contrary" depends on the order of the multipole moment.

An important difference of the multipole moments studied is when the monotonous behavior of the curvature changes, they appear at fields strength values with different interpretation. For the quadrupole corresponds to that when the biaxiality starts, whereas for the dipole it does not correspond to the equivalent point but to a lower value of the field strength.

From our results we find an interesting mechanism in the formation of ordered phases in particles driven by an external field. Depending on the symmetry of the molecules, different phases may be predicted, which are richer for particles with more symmetry axis. In this paper it is predicted for one symmetry a nematic-like phase, whereas for biaxial symmetry a biaxial nematic-like phase. As a consequence, we could open the possibility to find exotic nematic-like phases of higher symmetry.

These results show one mechanism to manipulate ordering in colloids, which is responsible for the construction of different alignments, and provides us with a simple method to study higher multipolar order. This method could be used for the prediction of more anomalous ordering as was the case for the prediction of the quadrupolar moment.

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