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Orientational relaxation for small wavevectors of rod-like Brownian particles

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We present a theorical study of the kinetic orientational relaxation of a colloidal monodispersed system of stiff and long rods, for small wavevectors. This process is described by the dynamic structure factor. The relationship between this factor with the fluctuations of the second order parameter is provided in the limit of wavevectors going to zero. The second order parameter is computed with the Smoluchowski formalism, neglecting hydrodynamic interactions, and using the Maier-Saupe potential for the rods interaction. Considering suitable properties, the isothermal orientation susceptibility proposed is able to localize the isotropic and nematic concentrations in qualitative agreement with well known computer simulations results. At relaxation our model predicts a single value for the maximum of the orientation property proposed, which it is reached at different times, according to the concentration.

Keywords: Orientational relaxation; phase transition; second order parameter; smoluchowski equation.

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1. Introduction

Many classes of soft matter microstructures exhibit a tailored response and transport properties because of the interactions of rods [1–5]. Some soft matter materials are the well known Tobacco Mosaic Virus and the fd virus, the richness of these materials is due to their various ordered phases, where the most commonly are the isotropic and nematic [6–8]. In this work we focus on the description of the nematic isotropic phase transition in stiff and long colloidal rods from a kinetic point of view. One of the challenges of the description of the phase transition is its relation with mechanical response functions, that are the most accessible properties in an experiment. For instance the mechanical susceptibility provides us with a mechanical stability condition [9]. In particular it is well known that the structure factor in the limit of very small wave vectors is the isothermal compressibility, which can be probed in a light scattering experiment.

The aim of this work is to describe the orientational relaxation by monitoring the dynamic structure factor at small wavevectors in a colloid of hard, long and stiff rods initially aligned.

The idea behind it is to demonstrate what we can learn by applying the machinery of statistical thermodynamics to a simple model: hard, long and stiff rods in suspension, which exhibit the nematic isotropic phase transition. There are two motives in this approach. The former is simply that the study of a simple model provides insight, while the latter is the close relation to experiments (or computer "experiments") showing the complex features of relevance in our model.

The nematics phase in liquid crystals has been studied using different approaches; experimentally, via dispersion of depolarized light [10], by simulation [7] or theoretically [11–13]. The pioneering Onsager's work concerns itself with a density functional approach to compute free energy in order to describe the isotropic nematic phase transition [12]. Another approach is the kinetic approach of the Smoluchowski equation [13], which is able to describe the nematic isotropic phase transitions. In this work we focus on the calculation of the second order parameter by using the Smoluchowski formalism in order to describe the nematic isotropic phase transition and its connection with a mechanical response function.

Because the dynamic structure factor can be monitored by means of a time resolved small angle depolarized dynamic light scattering experiment [14], we follow the orientational relaxation of rods by observing the time evolution of the dynamic structure factor [15]. Initially the rods are perfectly aligned by using an external field, therefore they themselves return to the equilibrium state when the external field is removed. As will be seen the dynamic structure factor can be written in terms of the parameters of order two and four. The second order parameter is calculated from the equation of evolution of the orientational order parameter tensor $S(\tau)$, which is obtained from the Smoluchowski equation and the closure relation provided by Dhont [16], valid at equilibrium. Like this author, we extend the validity of this closure for nonequilibrium. The fourth order parameter is obtained directly from the closure relation cited above. At the limit of the wavevector going to zero, we will show the connection of the fluctuations of the second order parameter with the self structure factor, the main quantity in the description of the nematic isotropic phase transition.

The work is organized as follows. Because the second order plays an important role we start with its definition and evaluation; therefore in Sec. 2 the Smoluchowski formalism is given, using the Maier-Saupe potential together with an appropriate closure relation, the time evolution and its equilibrium values of the second order parameter are computed. In

Sec. 3 the dynamic structure factor for small wavevectors is provided; using results from the previous section, this quantity is expressed in terms of the second order parameter only. In Sec. 4 fluctuations of the second order parameter are defined. Here also is shown the relationship between them with the dynamic structure factor. Using the statistical mechanics tools the interpretation of the self structure factor as a mechanical response is also given. In Sec. 5 results are provided. We begin with general results using only experimental conditions and the closure relation over the description of the nematic isotropic phase transition, that is, as this process can be monitored by the dynamic structure factor measured in a depolarized light scattering experiment in VH geometry which considers the polarization direction of the incident light n_0 perpendicular to that of the detected scattered ligh n_i [15], in this work the dynamic structure factor is calculated using these conditions. Connections with the mechanical response on the predictions of the isotropic nematic concentration values are given with the inclusion of the Maier-Saupe potential. The orientational relaxation is also provided for small wavevectors as function of the concentration. At the end of the section, results for the isothermal orientation susceptibility with respect to the nematic isotropic phase transition are provided. Finally in the last Section, concluding remarks are given.

2. Second order parameter

Consider a colloidal suspension formed by N hard, long and stiff rods embedded in a solvent. Very long and thin rods are considered, with L and D their length and thickness respectively, whose volume fraction scales as $\sim D/L$, the position and orientation of the rod are $\mathbf{r}$ and $\widehat{\mathbf{u}}$, respectively. The orientation is the unit vector along the long axis of the rod. To find the temporal evolution of the orientational one body probability density function (PDF) in the overdamped limit one starts from the N-particle Smoluchowski equation. Integration of this equation for hard, very long and thin rigid rods, neglecting hydrodynamic interactions, leads to the following equation of motion for $P(\widehat{u},t)$, the orientational one body PDF of one rod [13],

$$\frac{\partial P(\widehat{u},t)}{\partial t}=D_r\widetilde{R}\left[\widetilde{R}P(\widehat{u},t)-\beta P(\widehat{u},t)\widetilde{R}V^{\text{eff}}(\widehat{u},t)\right]. \quad (1)$$

Here, D_r is the rotational diffusion coefficient of a single non-interacting rod, $\beta = 1/k_BT$ is the inverse of the thermal energy, $\widetilde{R}(...) = \widehat{u}\times\nabla_{\widehat{u}}(...)$ is the rotation operator and $V^{\text{eff}}(\widehat{u},t)$ is the Maier-Saupe effective interaction potential for rods, equal to [17]

$$V^{\text{eff}}(\widehat{u},t) = DL^2\rho\frac{\pi}{4}\left(\frac{21}{8}-\frac{15}{8}\widehat{u}\widehat{u}:\mathbf{S}(t)\right), \quad (2)$$

where ρ is the density of rods and $\mathbf{S}(t)$ is the orientation order parameter tensor, given by

$$\mathbf{S}(t) = \langle\widehat{u}\widehat{u}\rangle = \oint d\widehat{u}\,[\widehat{u}\widehat{u}]\,P(\widehat{u},t). \quad (3)$$

In equilibrium the largest eigenvalue of the orientation order parameter tensor is the well known nematic parameter. In general the order parameters are defined as the average of Legendre polynomials, $\langle p_l\rangle$, the importance of these quantities is that they quantify the degree of order in each particular ordered phase as in the case of multiaxial nematics [18]. The nematic parameter is related with the second order parameter, which is the average of the second Legendre polynomial and it quantifies the axial nematic phase. In this work we will propose another important feature of the second order parameter. Going back to the calculation of the orientation order parameter tensor, operating on both sides of Eq. (1) with $\oint d\widehat{u}\,[\widehat{u}\widehat{u}]$ and using Eq. (2), the effective potential, leads to the time-dependent equation for the orientational order parameter tensor

$$\begin{aligned}\frac{1}{3}\mathbf{I} = {} & \frac{\partial\mathbf{S}(\tau)}{\partial\tau}+\mathbf{S}(\tau)\\ & -\frac{5}{4}\phi\left[\mathbf{S}(\tau)\cdot\mathbf{S}(\tau)-\mathbf{S}^4(\tau):\mathbf{S}(\tau)\right],\end{aligned} \quad (4)$$

with the reduced time defined as $\tau = 6D_rt$, and $\phi = L/D\varphi$ is a dimensionless "concentration" and the volume fraction of the cylindrical rods reads as $\varphi = (\pi/4)D^2L\rho$ and $\mathbf{S}^4 = \langle\widehat{u}\widehat{u}\widehat{u}\widehat{u}\rangle$ is the fourth orientational order tensor. In order to obtain an equation of motion for $S(\tau)$, we used the closure relation provided by Dhont [16], where the symmetric matrix involved for our case is $S(\tau)$. Under this consideration the closure is expressed as,

$$\begin{aligned}\mathbf{S}^4(\tau):\mathbf{S}(\tau) = {} & \frac{2}{5}\,\mathbf{S}(\tau)\cdot\mathbf{S}(\tau)\\ & +\frac{3}{5}\mathbf{S}(\tau)\mathbf{S}(\tau):\mathbf{S}(\tau),\end{aligned} \quad (5)$$

then, the Eq. (4) becomes

$$\begin{aligned}\frac{1}{3}\mathbf{I} = {} & \frac{\partial\mathbf{S}(\tau)}{\partial\tau}+\mathbf{S}(\tau)\\ & -\frac{3}{4}\phi\left[\mathbf{S}(\tau)\cdot\mathbf{S}(\tau)-\mathbf{S}(\tau)\mathbf{S}(\tau):\mathbf{S}(\tau)\right].\end{aligned} \quad (6)$$

For homogeneous phases, $\mathbf{S}(\tau)$ is expressed as a diagonal tensor, in case of an isotropic phase all the components are equal to $1/3$, whereas for nematics the two small coefficients are equal and the highest is known as the nematic order parameter, $\lambda(=\langle\cos^2\theta\rangle)$. As a result the time-dependent equation for λ is written as

$$\frac{\partial\lambda}{\partial\tau}+\left(1+\frac{3}{8}\phi\right)\lambda-\frac{3}{2}\phi\lambda^2+\frac{9}{8}\phi\lambda^3=\frac{1}{3}. \quad (7)$$

In equilibrium, the variation of λ with respect to time is equal to zero, and solving Eq. (7), one obtains,

$$\lambda = \frac{3\phi\pm\sqrt{-32\phi+9\phi^2}}{6\phi}, \quad (8)$$

These two solutions are positive by varying the value of ϕ. However, only the solution that has the square root with the positive sign is that which has physical meaning, because it satisfies the condition that the second order parameter, $\langle p_2\rangle = (1/2)(3\lambda - 1)$, is positive.

Finally in nonequilibrium Eq. (7) is solved numerically obtaining the time dependent evolution of the nematic parameter. In equilibrium, the nematic order parameter is the quantity of central importance in describing the isotropic nematic phase transition as we will see below. For nonequilibrium we will express all the properties in terms of the second order parameter, which can be written in terms of the nematic parameter, as

$$\langle p_2(\tau)\rangle = \frac{1}{2}\left(3\lambda(\tau) - 1\right). \tag{9}$$

As in the equilibrium state, our proposal is to show the relevance of the second order parameter also in nonequilibrium states. Because of the use of the Maier-Saupe potential, Eq. (2), in order to close our model in terms only of the second order parameter it is needed a closure relation between fourth and second order parameters. The four order parameter is given by:

$$\langle p_4(\tau)\rangle = \frac{1}{8}\big(35\langle\cos^4\theta\rangle - 30\langle\cos^2\theta\rangle + 3\big). \tag{10}$$

Where $\langle p_2(\tau)\rangle$ satisfies that

$$\langle\cos^2\theta\rangle = \frac{1}{3}\big(2\langle p_2(\tau)\rangle + 1\big). \tag{11}$$

It is necessary to express $\langle\cos^4\theta\rangle$ in terms of $\langle\cos^2\theta\rangle$. This is achieved, using the Dhont closure relation [16], where the symmetrical matrix involved in this case is such that all its elements are equal to zero, except $(M)_{33} = 1$, so

$$\langle\cos^4\theta\rangle = \big(\mathbf{S}^4(\tau) : M\big)_{33} = \frac{2}{5}\langle\cos^2\theta\rangle + \frac{3}{5}\langle\cos^2\theta\rangle^2 \tag{12}$$

Replacing Eq. (11) and Eq. (12) in Eq. (10), we obtain that the fourth order parameter can be expressed in terms of the second order parameter as

$$\langle p_4(\tau)\rangle = -\frac{1}{6}\langle p_2(\tau)\rangle + \frac{7}{6}\langle p_2(\tau)\rangle^2. \tag{13}$$

Thus we have the input necessary for the description of our colloid in equilibrium and during the relaxation process, that is the second order parameter.

3. Dynamic structure factor at small wavevectors

Because our main aim is describing the orientational relaxation of the colloid by monitoring the dynamic structure factor measured in a depolarized light scattering experiment in VH geometry. Initially consider rods perfectly aligned and in $\tau = 0$ the constriction is removed and the colloid evolves to an equilibrium, isotropic or nematic state depending on the value of its concentration. The advantage for the orientational description in this analysis is the separation of the time scales for orientational (τ_o) and positional relaxation (τ_p), thus during reorientation of the rods their position coordinates adapt relatively fast to the new orientation configuration; this is because, the ration between these time scales is given by [15].

$$\frac{\tau_p}{\tau_o} \approx \left(\frac{l_p}{L}\right)^2$$

Now, since, for there to be hard rod interaction, l_p(a typical relative displacement necessary so that the centers of mass of the rods to reach their isotropic equilibrium state) has to be much smaller than L (the size of a rod), it is concluded that $(\tau_p/\tau_o) \ll 1$. With this aim in mind, in this section the dynamic structure factor is defined as well as its relationship with the second order parameter fluctuations. The importance of these quantities is that they can be measured by means of an appropriate experiment as well as with computer simulations.

In order to observe the orientational properties in homogeneous phases, the dynamic structure factor is monitored, as we mention it can be probed in a depolarized light scattering experiment in VH geometry. In the case of rods, the dynamic structure factor is expressed as

$$\begin{aligned} F(\mathbf{k},\tau) = {} & \frac{1}{N}\frac{1}{\langle j_0^2(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}})\rangle} \\ & \times \sum_{l,n}^{N}\langle(\widehat{\mathbf{n}}_s\cdot\widehat{\mathbf{u}}_l)(\widehat{\mathbf{n}}_s\cdot\widehat{\mathbf{u}}_n)(\widehat{\mathbf{n}}_o\cdot\widehat{\mathbf{u}}_l) \\ & \times\ (\widehat{\mathbf{n}}_o\cdot\widehat{\mathbf{u}}_n) j_0\left(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}}_l\right) j_0\left(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}}_n\right) \\ & \times\ e^{i\mathbf{k}\cdot(\mathbf{r}_l - \mathbf{r}_n)}\rangle. \end{aligned} \tag{14}$$

where the average involves a time-dependent PDF. $j_0((1/2)L\mathbf{k}\cdot\widehat{\mathbf{u}})$ is the spherical Bessel function of zero order, $\widehat{\mathbf{n}}_s$ and $\widehat{\mathbf{n}}_o$ are the unit vectors for the detected and the incident polarization directions, respectively and $\big\langle j_0^2((1/2)L\mathbf{k}\cdot\widehat{\mathbf{u}})\big\rangle$ is the form factor.

For simplicity the spherical Bessel function of zero order will be denoted as j_0 without its argument. By convenience, the dynamic structure factor is divided into its self and distinct part

$$F(k,\tau) = F^{\text{self}}(k,\tau) + F^{dist}(k,\tau). \tag{15}$$

where self dynamic structure factor is given by

$$\begin{aligned} F^{\text{self}}(k,\tau) = {} & \frac{1}{N}\sum_{i=1}^{N}\big\langle(\hat{n}_s\cdot\hat{u}_i)^2(\hat{n}_o\cdot\hat{u}_i)^2 \\ & \times \frac{j_0^2(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}}_i)}{\langle j_0^2(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}})\rangle}\big\rangle, \end{aligned} \tag{16}$$

and the distinct part is written as

$$
\begin{aligned}
F^{\text{dist}}(k,\tau)=\frac{1}{N}\sum_{i\neq j}^{N}&\langle(\hat{n}_s\cdot\hat{u}_i)(\hat{n}_o\cdot\hat{u}_i)(\hat{n}_s\cdot\hat{u}_j)(\hat{n}_o\cdot\hat{u}_j)\\
&\times\frac{j_0(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}}_i)j_0(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}}_j)}{\langle j_0^2(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}})\rangle}\\
&\times\exp\{-i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)\}\rangle.
\end{aligned}
\tag{17}
$$

From Eq. (14), to compute the self and distinct part of the dynamic structure factor is necessary to know the one body PDF $P(\widehat{\mathbf{u}},\tau)$ and the two body PDF $P(\mathbf{r}-\mathbf{r}',\widehat{\mathbf{u}},\widehat{\mathbf{u}}',\tau)$ only, the latter is approached as, in homogeneous phases,

$$
\begin{aligned}
P(\mathbf{r}-\mathbf{r}',\widehat{\mathbf{u}},\widehat{\mathbf{u}}',\tau)=\frac{1}{V^2}&P(\widehat{\mathbf{u}},\tau)P(\widehat{\mathbf{u}}',\tau)\\
&\times g(\mathbf{r}-\mathbf{r}',\widehat{\mathbf{u}},\widehat{\mathbf{u}}'),
\end{aligned}
\tag{18}
$$

where $g(\mathbf{r}-\mathbf{r}',\widehat{\mathbf{u}},\widehat{\mathbf{u}}')$ is the pair correlation function assumed in equilibrium, for which the Boltzmann approach is used and V is the volume of the colloid. The validity of the approximation for the pair correlation function is in the isotropic and nematic states, which are homogeneous phases. In Eq. (18) we neglect the temporal dependence for the pair correlation function, because no attempt has been made to incorporate it in the analysis of the Smoluchowski equation.

By choosing the directions for the polarization vectors in a convenient way [20], the self structure factor is rewritten as

$$
F^{\text{self}}(k,\tau)=1+\frac{5}{7}\frac{\langle j_0^2p_2\rangle}{\langle j_0^2\rangle}-\frac{12}{7}\frac{\langle j_0^2p_4\rangle}{\langle j_0^2\rangle},
\tag{19}
$$

On the other hand, to compute the distinct part of the dynamic structure factor, we require the Fourier transform of the total correlation function $h(\vec{r}-\vec{r}',\hat{u},\hat{u}')=g(\vec{r}-\vec{r}',\hat{u},\hat{u}')-1$, which is given by [15],

$$
\begin{aligned}
h(\mathbf{k},\widehat{\mathbf{u}},\widehat{\mathbf{u}}')=-2DL^2\,|\widehat{\mathbf{u}}\times\widehat{\mathbf{u}}'|\,&j_0\Big(\frac{1}{2}D\mathbf{k}\cdot(\widehat{\mathbf{u}}\times\widehat{\mathbf{u}}')\Big)\\
&\times j_0\Big(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}}\Big)j_0\Big(\frac{1}{2}L\mathbf{k}\cdot\widehat{\mathbf{u}}'\Big).
\end{aligned}
\tag{20}
$$

In last equations the time dependency it is also considered in the one body PDF.

The natural dimensionless units of the above expression are considering $L\mathbf{k}\equiv\mathbf{q}$ then $D\mathbf{k}=(D/L)\mathbf{q}$ because L/D is large, then a good approximation is taking $j_0((1/2)(D/L)\mathbf{q}\cdot(\widehat{\mathbf{u}}\times\widehat{\mathbf{u}}'))\simeq 1$, then the total correlation function becomes

$$
\begin{aligned}
h(\mathbf{q},\widehat{\mathbf{u}},\widehat{\mathbf{u}}')=-2DL^2\,|\widehat{\mathbf{u}}\times\widehat{\mathbf{u}}'|\,&j_0\Big(\frac{1}{2}\mathbf{q}\cdot\widehat{\mathbf{u}}\Big)\\
&\times j_0\Big(\frac{1}{2}\mathbf{q}\cdot\widehat{\mathbf{u}}'\Big).
\end{aligned}
\tag{21}
$$

The consequence of this aproximation is that the distinct part can be expressed in terms of the self one

$$
F^{\text{dist}}(q,\tau)=\frac{1}{4}\phi\left\langle j_0^2\right\rangle\left(F^{\text{self}}(q,\tau)\right)^2.
\tag{22}
$$

Therefore, the *Dynamic Structure Factor for small wavevectors* of a colloidal system of stiff and long rods is given by

$$
F(q,\tau)=F^{\text{self}}(q,\tau)+\frac{1}{4}\phi\left\langle j_0^2\right\rangle\left(F^{\text{self}}(q,\tau)\right)^2.
\tag{23}
$$

We note that $F(q,\tau)$ is only a function of F^{self}. To obtain the quantities involved in this factor, we need to do a Taylor series development of j_0

$$
j_0(x)=1-\frac{1}{3!}x^2+\frac{1}{5!}x^4+O(x^6).
\tag{24}
$$

Considering terms up to fourth power in the dimensionless wavevector in j_0 and up to the fourth order parameter contributions in the self structure factor, the averages involved in Eq. (19) are expressed

$$
\begin{aligned}
\left\langle j_0^2\right\rangle=1&-\frac{1}{36}q^2-\frac{17}{11520(5)}q^4\\
&-\left(\frac{1}{18}q^2+\frac{17(4)}{11520(7)}q^4\right)\langle p_2\rangle\\
&-\frac{17(8)}{11520(35)}q^4\langle p_4\rangle.
\end{aligned}
\tag{25}
$$

$$
\begin{aligned}
\left\langle j_0^2p_2\right\rangle=\langle p_2\rangle&-\frac{29}{504}q^2+\frac{17}{115200}q^4\\
&+\left(\frac{1}{36}q^2+\frac{17}{40320}q^4\right)\langle p_2\rangle\\
&+\left(-\frac{1}{35}q^2+\frac{17}{100800}q^4\right)\langle p_4\rangle.
\end{aligned}
\tag{26}
$$

and

$$
\begin{aligned}
\left\langle j_0^2p_4\right\rangle=\langle p_4\rangle&-\frac{28}{495}q^2-\frac{17}{153605}q^4\\
&+\left(\frac{41}{5544}q^2-\frac{68}{215047}q^4\right)\langle p_2\rangle\\
&-\left(\frac{109}{1540}q^2+\frac{136}{1075235}q^4\right)\langle p_4\rangle.
\end{aligned}
\tag{27}
$$

Therefore by the way of the dynamic structure factor and the equilibrium, the relaxation process can be studied for small wavevectors using this simple approximation.

Nevertheless in the next section the relevance of the limit for wavevector going to zero is analyzed with its physical interpretation, that is the relationship between the dynamic structure factor and the dynamic fluctuations of the second order parameter.

4. Relationship between dynamic structure factor and the second order parameter dynamic fluctuations

In this section the limit of wavevector going to zero is studied, the advantage of this limit is the connection between the self dynamic structure factor and the nonequilibrium susceptibility, which is the self correlation of the second order parameter, therefore is more convenient to refer to the self part as isothermal orientation susceptibility as can be see below. One reason for the identification with only the self part is due to the fact that the susceptibility concept is related with the fluctuations of a one body microscopic property with its corresponding measurable macroscopic quantity. Here we will see that the microscopic property is the second order parameter and the macroscopic the self structure factor.

By considering the limit of the dimensionless wavevectors as going to zero, the spherical Bessel function of zero order is equal to one, therefore the dynamic structure factor can be written as

$$F(q=0,\tau)=F^{\text{self}}(q=0,\tau)+\frac{\phi}{4}\left(F^{\text{self}}(q=0,\tau)\right)^2. \quad (28)$$

where

$$F^{\text{self}}(q=0,\tau)=1+\frac{5}{7}\langle p_2(\tau)\rangle-\frac{12}{7}\langle p_4(\tau)\rangle. \quad (29)$$

Now, by using the closure relation in Eq. (5), the self dynamic structure factor can be written in terms of the second order parameter only, that is

$$F^{\text{self}}(q=0,\tau)=1+\langle p_2(\tau)\rangle-2\langle p_2(\tau)\rangle^2. \quad (30)$$

It is important to mention that this quantity is hold for colloids in a homogeneous phases, as the isotropic and nematic, independent of any model used for the description of the colloid. In the former only the experimental condition was used whereas the second has in addition the closure relation between second and fourth order parameter.

Now in order to go into the concept of fluctuations, we start defining the nonequilibrium fluctuations of the second order parameter as

$$\alpha_l \equiv p_2^l-\left\langle p_2^l\right\rangle$$

where $\langle\cdots\rangle$ indicates a nonequilibrium average. Therefore the nonequilibrium fluctuations correlations are given by

$$C(\tau)=\frac{1}{N}\sum_{l,m}^{N}\left\langle \alpha_l\alpha_m\right\rangle. \quad (31)$$

In Eq. (31) the temporal dependency is again assumed through the N-body probability density function as in the dynamic structure factor. In this last equation it is clear that the correlation between the nonequilibrium fluctuations is a two body property, such as the dynamic structure factor.

In the same way as was previously done for the dynamic structure factor, the nonequilibrium fluctuations correlations can be expressed in terms of the second order parameter only, taking into account homogeneous phases and the Maier-Saupe potential. When the closure relation Eq. (5) is used, the expression for the self nonequilibrium fluctuations of the second order parameter is exactly the same as that for the dynamic self structure factor the limit of wavevector going to zero, Eq. (30). Therefore the quantity probed in the depolarized light scattering experiment is the nonequilibrium correlations of the second order parameter in this limit and as consequence the same expressions for the self part of these properties. It is important to observe that this equivalence in the expressions is also valid when the average is in equilibrium. The relevance of this correlation is that it can be probed in a well defined experiment, in the results section the predictions of this relationship will be provided for nonequilibrium and equilibrium orientational fluctuations. We will see below the importance of the self correlation of the second order parameter in the description of the orientational relaxation and the values of the concentration at which the isotropic nematic phase transition occurs.

Now we focus on its physical interpretation. From its role played the self structure factor, with the limit of dimensionless wavevector going to zero, could be identified as an isothermal orientation susceptibility in the sense that this quantity is the second order parameter fluctuation. To observe this identification we are able to make a gedanken experiment in which an external force E is applied, which will be an orientational force, the Hamiltonian of the colloid is

$$\widetilde{H}=K+\sum_{j\neq l}V(\mathbf{r}_{jl},\widehat{\mathbf{u}}_j,\widehat{\mathbf{u}}_l)+\widetilde{M}E$$

where K is the kinetic energy, the second term is the potential energy and in the last $\widetilde{M}$ is the conjugated mechanical response to the external force E. Because the susceptibility concept is at the limit of zero external force it is not necessary to provide information about it, playing only a role in the limiting process. The average of the mechanical response is computed, using an appropriate equilibrium ensemble, as

$$\langle M\rangle^{eq}=\frac{Tr\left[\widetilde{M}e^{-\beta\widetilde{H}}\right]}{Tr\left[e^{-\beta\widetilde{H}}\right]},$$

after some usual algebraic steps [9], one arrives at

$$\begin{aligned}\chi_\beta&=\left(\frac{\partial\langle M\rangle^{eq}}{\partial E}\right)_{T,E=0}\\&=\beta\left[\left\langle\widetilde{M}^2\right\rangle^{eq}-\left(\left\langle\widetilde{M}\right\rangle^{eq}\right)^2\right].\end{aligned} \quad (32)$$

where χ_β is a mechanical response function due to orientation. Thus, identifying $\langle M^*\rangle^{eq}=\langle p_2\rangle^{eq}$, we can associate, the self structure factor in the limit of wavevector going to zero with this mechanical response function, hereafter referred to as *isothermal orientation susceptibility*, is derived, where $\langle M^{*}\rangle^{eq}$ means dimensionless. Nevertheles the asociation is in equilibrium; in our model this interpretation is done also during the relaxation process.

5. Results

This section starts with nonequilibrium and equilibrium general results from the properties measured in a depolarized light scattering experiment together with those derived by the use of the colloidal model proposed in this work. Also numerical results will be analyzed, in all of them we separate our analysis according to the concentration values of the colloid in equilibrium, that is for isotropic and nematic phases. Thus for simplicity we only use and denote *isotropic* when we refer to the former and *nematic* for the latter. We continue describing the behaviour of the second order parameter together with its relaxation time and in the same manner the temporal evolution of the dynamic structure factor. The second subsection will describe the relaxation of the colloid by means of the dynamic structure factor for small wavevectors. Finally in the last subsection results for the limit of the wavevector going to zero will be described, focusing on the isothermal orientation susceptibility.

5.1. General properties

The nematic isotropic phase transition in a colloid suspension of stiff and long rods is well known. From our colloidal model, equation Eq. (8) predicts the value of the concentration at which this transition occurs, that is, ϕ_I=32/9=3.56. Comparing our result for $\phi_I = 3.56$ with those obtained by computer simulations $\phi_I^S = 3.29$ [7], and the one obtained by Frenkel using the Onsager's model $\phi_I^{OM} = 3.45$ [19], our model is in qualitative agreement.

On the other hand, the isotropic to nematic spinodal concentration ϕ_N is obtained following the Dhont's proposal [13], which consists of making a small perturbation $\delta S(\tau)$ around the isotropic equilibrium state. The nematic tensor $S(\tau) = 1/3\ I + \delta S(\tau)$ is substituted for Eq. (7) and is considered up to linear order in $\delta S(\tau)$, identifying in this way an effective orientational coefficient D_r^{eff}, given by the expression $D_r^{\text{eff}} = (1 - 1/4\ \phi)$. The isotropic nematic spinodal point is obtained when $D_r^{\text{eff}} = 0$, that is $\phi_N = 4$ which coincides with the exact value given by Onsager [12]. Let us comment that our result differs from that obtained by Dhont, $\phi_N^{Dhont} = 5$, due to the Maier-Saupe effective potential used by this author [13].

As was already mention in this section the results are separated in two regions depending on whether the concentration of the colloid is in isotropic or nematic phase when it is in equilibrium. From our kinetic model, Eq. (8), it is only possible to move from nematic isotropic phase transition, thus with this restriction the separation will be for lower than isotropic concentration and larger than it, which we call *isotropic* and *nematic* for simplicity, as was already mentioned, that which is lower than $\phi_I = 32/9$ is *isotropic* and if larger is *nematic*.

The analysis starts considering the most general expression for the self structure factor dependent on time, $F^{\text{self}}(q{=}0,\tau)$, Eq. (29). This property takes the value 1 when the colloid suspension is in an isotropic phase, where $\langle p_2(\tau)\rangle = \langle p_4(\tau)\rangle = 0$, or when the following relationship is satisfied

$$\langle p_4(\tau)\rangle = \frac{5}{12}\langle p_2(\tau)\rangle. \tag{33}$$

Now, by replacing Eq. (13) in Eq. (33) we find that

$$\langle p_2(\tau)\rangle = \frac{1}{2}. \tag{34}$$

which is satisfied in the isotropic or in the nematic phase, depending to the concentration. We must mention that the expression given in Eq. (33) has already been reported for the equilibrium case [20].

Another important situation is when the $F^{\text{self}}(q = 0, \tau)$ reaches its maximum, that is where the slope of this property is equal to zero. From Eq. (30) we find,

$$\frac{dF^{\text{self}}(q = 0, \tau)}{d\tau} = (1 - 4\langle p_2\rangle)\,\frac{d\langle p_2\rangle}{d\tau} \tag{35}$$

So $F^{\text{self}}(q = 0, \tau)$ is maximum when

$$\langle p_2(\tau)\rangle = \frac{1}{4}. \tag{36}$$

It is easy to see that the second derivative with respect to the dimensionless time is negative, so the value one quarter for the second order parameter corresponds to a maximum, as we will corroborate with the numerical results below. It is important to mention that Eqs. (34) and (36) are independent of any colloidal model, the only important assumptions are with respect to the homogeneity of the phase, the experiment proposed and the closure relation between the second and fourth order parameters. We must mention that these features are only held for *isotropic*, that is for concentrations lower than $\phi_I = 32/9$, as will see below in our numerical analysis.

We use our colloidal model in order to find predictions for the nematic isotropic phase transition. Thus, in equilibrium using our model Eq. (8) in the general predictions, the second order parameter equal to one half corresponds to a concentration $\phi = 4$, whereas its value is equal to one quarter at a concentration $\phi = 32/9$. Therefore the two important values from our general results together with our model predict that the maximum of the self structure factor corresponds to nematic concentration, whereas its value is equal one to isotropic concentration. According to our identification of the self structure factor as a mechanical susceptibility, our model predicts that this property is able to localize the isotropic and nematic concentrations.

Focusing on the nonequilibrium behaviour, during the relaxation the self structure factor has a maximum only for ϕ smaller that ϕ_I, that is in *isotropic*. For *nematic* it does not have a maximum but it goes to a plateau which corresponds to its nematic concentration value in equilibrium. For each concentration the time spends of the second order parameter for taking the value equal one quarter is different, nevertheless in all of them the isothermal orientation susceptibility will have the maximum value $F^{\rm self}_{\rm max} = 1.125$. On the other hand this value corresponds to an angle $\theta = \pi/2$. In this time the rods have an orientation about $\pi/2$ relative to the polarization directions as was observed previously [15]. For the another value of the second order parameter, it looks like that of an isotropic phase due to the value of the self structure factor equal one. Below using numerical results we have opportunity to say more about the consequences of the self structure factor. For the moment these are the meanings of the values for the second order parameter in the relaxation process, one corresponds to a maximum value and the other to the similitude with the isotropic phase. In the next subsections the relaxation times are computed for the important features predicted by this model.

5.2. Second order parameter

The second order parameter, Eq. (9), is plotted in Fig. 1 as function of time for different concentrations. Here the behaviour is observed the behaviour depending of whether the colloid is *isotropic* or *nematic*. For the former at long times it goes to zero whereas for the latter goes to values different from zero. The relaxation process predicts a second order parameter equal to one half for the nematic concentration as it was corroborated from our model in the previous subsection.

Another observation in Fig. 1 is that the second order parameter takes the value of one quarter only for concentrations in *isotropic*. Taking only the equilibrium values for the second order parameter as function of the concentration the results are reported in Fig. 2. We can appreciate that for cocentrations greater than or equal to 3.6 the system is in the nematic phase, since $\langle p_2(\tau)\rangle$ is different from zero for any time.

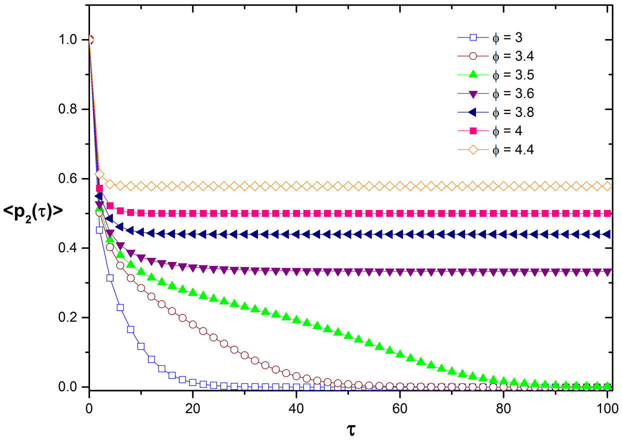

FIGURE 1. Second order parameter as function time for different concentrations ϕ as indicated in the figure. For $\phi < 3.5$ we have an isotropic phase, whereas for $\phi \geq 3.6$ the system presents a nematic phase since the order parameter takes an asymptotic value as shown in the figure. So between 3.5 and 3.6 we have the isotropic to nematic phase transition.

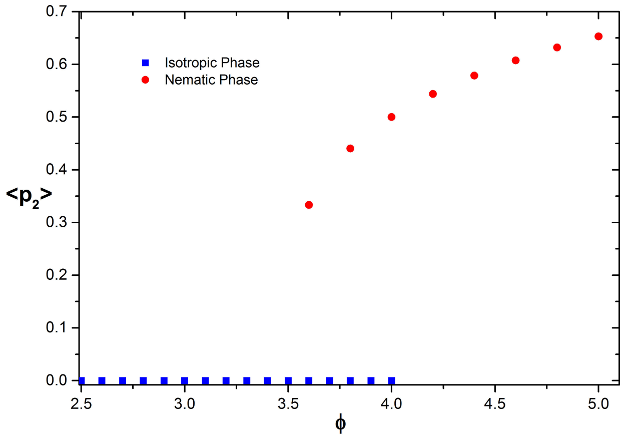

FIGURE 2. Second order parameter at equilibrium as function of the concentrations. We find that $\phi_I = 3.56$ and $\phi_N = 4$ that are consistent with the literature data.

Here we clearly see, nematics is derived from Eq. (8) whereas the isotropic region with the help of a perturbation analysis is derived, as was already mention in the previous subsection. From Fig. 2 we observe three different regions: when the concentration is lower than ϕ_I any isochoric process has only one stable point, for concentrations between ϕ_I and ϕ_N will have two stable points, finally for concentrations larger than ϕ_N has only one point stable again. In the middle region any isochoric line will have two points, one in isotropic phase and the second in nematics. In this manner this model predicts different behaviour depending of the value of the concentration.

Defining the relaxation time $\tau_{\rm rel}$ as the value at which the order parameter reaches its equilibrium value, the dynamic structure factor increase in *isotropic* and decrease in *nematic* as function of the concentration. The different values of the relaxation times in *isotropic* and *nematic* obey the different concentrations and the equilibrium value for the second order parameter in the nematic phase. For *isotropic* the increment of the relaxation time obeys the effect of the direct interactions between rods, whereas the reduction of the relaxation time is due to the closing value of the initial alignment with respect to its *nematic* value, that for higher concentrations smaller relaxation times, because it is closer to its asymtotic value as the concentration is increased. Similar behaviour is found when it is used the self structure factor.

5.3. Orientational relaxation for small wavevectors

The dynamic structure factor for small dimensionless wavevectors is analyzed in this section. An experiment is assumed in which a colloid of stiff and long rods are perfectly aligned by means of an external field; at $\tau = 0$ the field is removed and the rods evolve to an isotropic or nematic phase, depending on the concentration. The relaxation is monitored by means of the dynamic structure factor, the quantity measured in a depolarized light scattering experiment in the VH geometry, given by Eq. (14). The time dependent behaviour for the order parameter is provided by the Smoluchowski

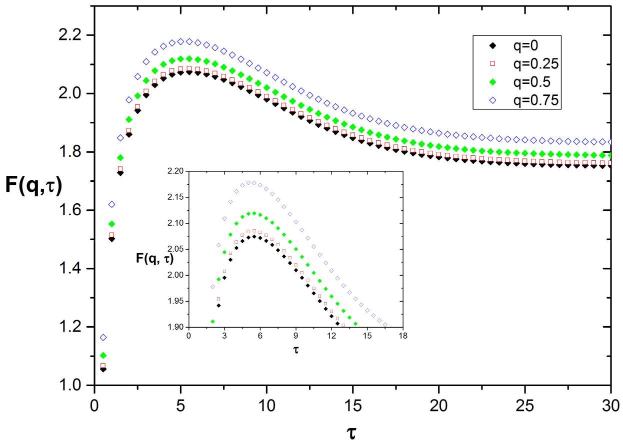

FIGURE 3. Dynamic structure factor as function of the reduced time for different dimensionless wavevectors, as indicated in the figure.For any value of q, $F(q,\tau = 0) = 0$. In the inset is observed the maximum and the differences with respect to different dimensionless wavevectors. All curves follow the same qualitative behavior.

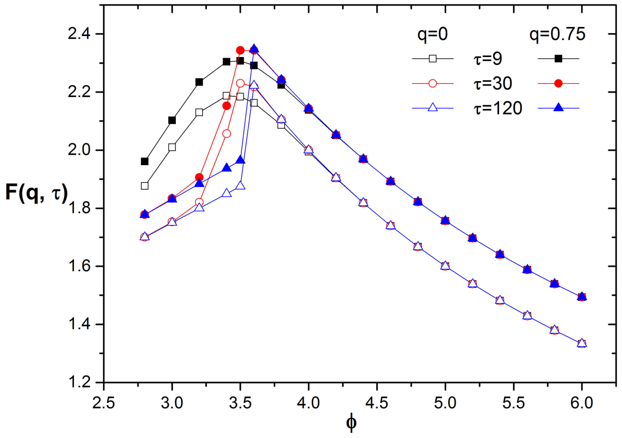

FIGURE 4. Dynamic structure factor as function of the concentration for two dimensionless wavevetors for different reduced times as indicated in the figure. When the system are in the equilibrium state there is discontinuity, we have a jump in $\phi = 3.56$.

equation, Eq. (7), solved with the initial condition of a full alignment of the rods and using Eqs. (15), (19) and (22).

In Fig. 3 is reported results for different values for q and $\phi = 3$ as function of the reduced time for the dynamic structure factor. The results do not show difference for $q = 0$ and 0.25, whereas for higher values of the dimensionless wavevectors a small quantitative difference is predicted. In the case of the self structure factor the relaxation observed has the same features as the dynamic structure factor, they are not reported explicitly.

The important feature is that for small dimensionless wavevectors all the plots have similar qualitative behaviour. Results for a concentration in *nematic* is not reported because these present similar characteristics, the only important difference is that they do not have a maximum but they go into a plateau according to their concentration, but the equivalent behaviour for small dimensionless wavevectors is similar, which is the important detail.

In Fig. 4 the dynamic structure factor is reported as a function of the concentration, the plot shows the evolution of the dynamic structure function for different times and two values of the dimensionless wavevector $q = 0$ and $q = 0.75$, whose equilibrium value at long times corresponds to the static structure factor.

In this Figure each symbol corresponds to a different time, for $\tau = 9, 30$ and 120. The Figure clearly describes how the phase transition occurs, that is, at the beginning a continuous curve is predicted and around $\tau \approx 90$, point no reported, the breaking of the continuous curve is observed and the discontinuity appears, indicating the first order character of the phase transition. As in the Fig. 3 here also the qualitative behaviour is independent of the value of the dimensionless wavevectors considered.

In a previous subsection was predict that the self structure factor in the limit of dimensionless wavevector going to zero has a maximum when the second order parameter takes the value equal to one quarter, independent of the concentration, within *isotropic* only. Therefore from Eq. (29), this maximum corresponds to $F^{\rm self}_{\rm max} \simeq 1.125$ and $\theta \simeq 45^\circ$. This angle is valid for the dynamic structure factor also, that is, it presents a maximum at the same value of the second order paramenter, the difference is that this maximum value depends on the concentration, that it does not have a single value as in the case of the self structure factor. This means that the maximum value of the dynamic structure factor, in *isotropic*, is taken when in average the rods are aligned to 45° respect to the initial alignment, as was already previously predicted [15]. In Fig. 5 is reported the self structure factor for $q = 0$ as function of the concentration for different times indicated in the Figure. In equilibrium it clearly shows the values for the isotropic and nematic concentrations as reported in a previous subsection, the maximum value and when it takes the value equal to one.

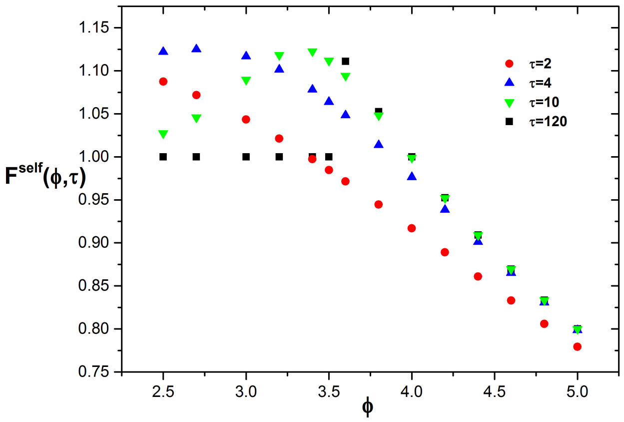

FIGURE 5. Self structure factor as function of the concentration for different reduced times, indicated in the figure for $q = 0$. When the system are in the equilibrium state, the Self Structure Factor present the first order transition.

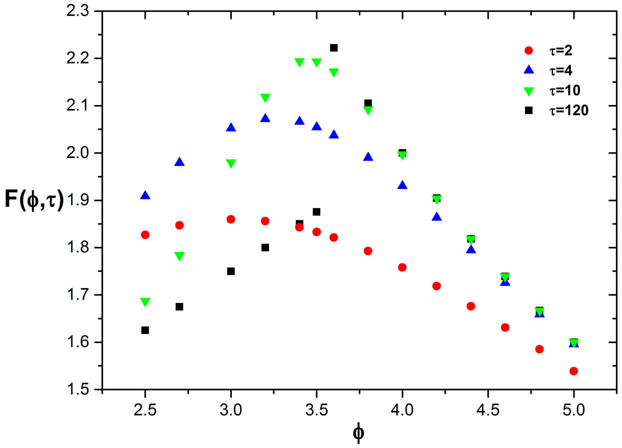

FIGURE 6. Dynamic structure factor as function of the concentration, for different reduced times indicated in the figure for $q = 0$. The discontinuity in the structure factor shows that the phase transition occurs by varying the concentration.

TABLE I. Behavior of F^{self} in the phase transition using Eq. (32) in equilibrium for different values of the concentration at $q = 0$.

Concentration	Self Structure Factor
$\phi < 3.56$	$F^{\text{self}} = 1$
$3.56 < \phi < 4$	$F^{\text{self}} > 1$
$\phi = 4$	$F^{\text{self}} = 1$
$\phi > 4$	$F^{\text{self}} < 1$

Now, in Fig. 6 is reported results for the dynamic structure factor for the same values as Fig. 5. Curves for intermediate times looks like a continuos phase transition as in a dipolar colloid [20]. This behaviour is a remanent of the external field used for the initial alignment. The main information of the phase transition comes from the self dynamic structure factor at the limit of dimensionless wavevector going to zero, showing the relevance of this limit.

5.4. Isothermal orientation susceptibility

As was shown in a previous section, it is reasonable to identify the self structure factor of the dimensionless wavevector equal to zero as a mechanical susceptibility, which we called isothermal orientation susceptibility.

From Fig. 5 is observed that during the relaxation process for times larger than 0 the isothermal orientation susceptibility takes values lower, higher or equal to one, only at $\tau = 0$ it is equal to zero. At equilibrium in Table I is reported results for the different situations found for this response function.

In the *isotropic* and for $\phi = 4$, nematic concentration, $F^{\text{self}} = 1$, when it takes values higher than one the colloid has a concentration between the isotropic and nematic concentrations, that is $\phi_I \prec \phi \prec \phi_N$. Finally when $F^{\text{self}} \prec 1$ the colloid is in *nematic*. This says that for values higher than one of the isothermal orientation susceptibility the colloid has two stable points, one in the isotropic phase and the second in the nematic phase, whereas for lower than one the colloid has only one stable point. From Eqs. (29) and (33) we can express these conditions in terms of the second and fourth order parameters, that is $F^{\text{self}} \succ 1$ corresponds to $\langle p_4\rangle \prec (5/12)\langle p_2\rangle$ and $F^{\text{self}} \prec 1$ with $\langle p_4\rangle \succ (5/12)\langle p_2\rangle$. It is important to note that these last conditions are independent of the model used and is only a consequence of the experimental conditions for rods at $q = 0$. Also in figure 6 is predicted the isotropic concentration, $\phi = 32/9$, at the maximum of the isothermal orientation susceptibility. The relevance of this novel property is mainly the ability to predict the isotropic and nematic values of the concentration.

With respect of the relaxation process the isothermal orientation susceptibility is able to predict when the rods have an alignment to $45°$ with respect to the direction of the polarization direction, in this situation the isothermal orientation susceptibility has a maximum, in *isotropic*, depending of the value of the concentration of the colloid, time is necesary to get this maximum, in *nematic* the maximum of F^{self} is substituted by a plateau reached in equilibrium whose value depends on the concentration. We must mention that this maximum is reached in *isotropic* during the relaxation process whereas for *nematic* it is reached in equilibrium. Finally because in the relaxation the isothermal orientation susceptibility starts the value of zero it then reachs its value one at initial times, at this time the colloid presents a similar condition as that of the isotropic phase in equilibrium.

6. Conclusions

In this work we propose a simple theoretical model that allows us to observe the relaxation process of a colloidal system formed by stiff and long rods, via the dynamic structure factor, which has as input the order parameter two. The study is based on the Smoluchowski formalism neglecting the hydrodynamic interactions together with the Maier-Saupe potential for the interaction between them.

The advantage of having an explicit expression for the dynamic structure factor lies in its possible comparison with simulation and experimental data that allow us to test our theoretical results.

At wavevector equal to zero was shown that the dynamic structure factor is the collective correlations to the fluctuations of the second order parameter. Its self part was also identified with an isothermal orientation susceptibility. The relevance of this quantity is that is able to predict the isotropic and nematic concentrations in which the colloid has the nematic isotropic phase transition through the second order parameter in equilibrium, we find that $\phi_I = 3.56$ and $\phi_N = 4$, that is, we improve the results of Frenkel using of Onsager's model [19] and it is closer to that reported in simulation given in [7].

The results were supported with the assumption of the Maier-Saupe potential for a colloid with a nematic isotropic phase transition, thus one would expect that these predictions could be valid for different colloids which hold the same conditions.

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