Morphology of Colloidal Particles Dispersed in Nematic Solvent

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Abstract. We have studied a system of spherical colloidal particles suspended in nematic liquid crystal confined to a two-dimensional plane. The dispersed colloidal particles pervert the uniform orientation of nematic resulting in topological defects. This small change in director field induces elastic interaction in the system. Considering the system exhibiting octopolar symmetry, the interaction of the particles can be described by octopole-octopole interaction potential which on some suitable scaling has the form, $\beta u(r) \approx \Gamma/r^7$, where Γ is dimensionless interaction strength parameter. We have calculated the pair correlation function and radial distribution function of the system by employing Roger-Young's integral equation theory, where the mixing parameter α, is obtained by demanding the consistency in pressure via virial and compressibility routs. With the increase in interaction strength, the system is found to become more ordered.

1. Introduction

Liquid crystals were discovered in 1888 by an Austrian botanist Friedrich Reinitzer [6] while studying the melting behaviour of cholesteryl benzoate. He noticed that the turbid fluid formed at 145.5 ^{0}C transformed to a conventional clear liquid at 178 ^{0}C. He concluded that a new state of matter had been discovered that was intermediate between the crystalline solid and isotropic liquid phases. This phase was later termed liquid crystal by Otto Lehmann [1] who performed the first polarized optical microscopic measurements on liquid crystals. The materials which exhibit this phase are called mesogens [2, 3]. The dispersion of colloidal particles in nematic liquid crystal, also known as nematic colloids has evoked potential interest among the researchers over last few decades because of its wide applications mainly as a biological sensors [4-7], photonic Crystal devices [8], topological memory devices [9,10] etc. This inclusion of particles perverts the long range orientational order of nematic liquid crystal which is marked by the presence of director deformation mediated elastic interaction in the system. Such contortion in director field can be described by Laplace equation leading to the multipole expansion of the director field which is quite similar to electrostatic multipole expansion [11]. These interactions are found to depend upon the nematic director profile and accordingly system can be characterized by dipole-dipole and quadrupole-quadrupole interaction potential [12-14].

However, Chernyshuk et al. has shown that octopole-octopole interaction potential comes into picture when the system carry hedgehog director configuration [15]. Apparently, it has been experimentally [16] observed that the intermolecular interaction in a system of charged colloidal particles attached to water-nonpolar fluid (such as oil) interface in the presence of an external electric field E_o directed normal to the interface, is governed by the octopolar moments leading to a weak short range repulsion. The pair correlation function contains the structural information of fluid. In this paper, our main aim is to calculate the pair correlation function of the system by considering the octopole term as a leading contributor to the interaction potential. We have used Roger-Young's integral equation theory to calculate the pair correlation functions at various grid points of coupling strength parameter. We found notable changes in pair correlation peak with the variation of the characterizing parameters of the system. The paper is organized as follows : in Section 2, we have describe the interaction potential and model of the system followed by the details of the liquid integral equation theory along with the solution procedure in Section 3 and the result in section 4. We finally conclude in Section 5.

2. Model Potential

Let us consider a system of N axially symmetrical colloidal particle dispersed in a nematic liquid crystal confined to a two-dimensional plane of area A. The particle are assumed to induce deformations of the director in the perpendicular directions (homeotropic anchoring) and makes the director field from the undeformed n = (0, 0, 1) (n||z) to deformed n = (n_x, n_y, 1) one. The symmetry of the director deformation mediated elastic interaction is assumed to be such that the particles interact via octopole-octopole interaction potential given by the expression [15-17]

$$\beta U = \beta K \frac{\Omega^2}{r^7} \tag{1}$$

Where $\beta = 1/k_B T$, with k_B being the Boltzmann constant and T is the absolute temperature. Ω is the strength of the elastic octopole moment of the particle, K is Frank elastic constant of the nematic and r is the separation between the colloidal particles. By introducing the average interparticle separation $a = 1/\sqrt{\rho}$, where ρ is number density, as characteristic length scale of the system, we can define the dimensionless interaction strength parameters

$$\Gamma = \beta K \Omega^2 \rho^{7/2} \tag{2}$$

using Eq. (2), we can write Eq. (1) as

$$\beta U = \frac{\Gamma}{x^7} ; \qquad \text{With } x = r/a \ (= \text{r*}) \tag{3}$$

interaction strength Γ can be expressed in terms of the dimensionless scaled density ρ^* and temperature t^* as

$$\Gamma = \frac{(\rho^*)^{7/2}}{t^*} \tag{4}$$

where $\rho^* = l^2\rho$ and $t^* = k_B T/\varepsilon$. Here, l $(=\Omega^2/a)$ is the natural length scale and ε $(=Ka)$ is the natural energy scale**.**

3. Integral equation theory

The determination of the pair structure of a uniform fluid amounts to the calculation of the radial distribution function (RDF) g(r) and the direct correlation function (DCF) c(r). By introducing the total correlation function h(r) = g(r) – 1, the former two quantities are connected via the Ornstein Zernike (OZ) relation

$$h(r) = c(r) + \rho \int d^D r' c(|r - r'|)h(r') \tag{5}$$

where D is the dimensionality of the space which is 2 in the present case. The OZ equation is exact and couples two unknown functions, h(r) and c(r). In order to determine them, another equation connecting these two unknowns, is needed. The total correlation function can be expressed in terms of the direct correlation function as

$$h(r) = exp[\beta u(r) + h(r) - c(r) + B(r)] - 1 \qquad (6)$$

where u(r) denotes the pair potential and B(r) is the so-called bridge function.[18] By introducing certain approximations for the bridge function, an approximate equation is obtained which is known as a closure. It is the closure through which interparticle interaction enters into the formulation. Both the RDF as well as the DCF can be obtained by solving Eqs. (5) and (6) self-consistently. By setting the bridge function equal to zero, we obtain the hypernetted chain (HNC) closure, which has proved to yield good results for long-ranged pair potentials in three dimensions. The Percus-Yevick (PY) closure is obtained by choosing the following expression for the bridge function:

$$B_{PY}(r) = -[h(r) + 1 - c(r)] + 1 + ln[h(r) + 1 - c(r)] \qquad (7)$$

The PY closure furnishes accurate results for short-range interactions (such as the hard-sphere potential) in three dimensions. A particularly reliable closure relation is provided by the Rogers Young [19] that 'interpolates' between the two and has the form

$$h(r) = exp[-\beta u(r)]\left[1 + \frac{exp[f(r)\{h(r)-c(r)\}]-1}{f(r)}\right] - 1 \qquad (8)$$

where f(r) [= 1– exp(-αr)] is called mixing functions which include a tunable parameter α that is chosen in order to enforce thermodynamic consistency by guaranteeing the equality between the virial and fluctuational compressibility. In this work we have employed the Rogers-Young closure to solve the OZ equation. To solve OZ equation, we first transform it into its Fourier form by using Fourier-Bessel transform of a function p(r) in 2D [20] defined as

$$p(k) = 2\pi \int_0^\infty p(r)J_n(kr)rdr \qquad (9)$$

$$p(r) = \frac{2\pi}{(2\pi)^2}\int_0^\infty p(k)J_n(kr)kdk \qquad (10)$$

where J_n(kr) are the Bessel functions of first kind. Putting Fourier transforms of h and c in Eq. (5) we get

$$h^{'}(k) = c^{'}(k) + \rho \, c^{'}(k) \, h^{'}(k) \qquad (11)$$

we then solve Eq. (11) and Eq. (8) iteratively at several grid points of interaction strength Γ. The following steps are required to solve these equations numerically:

1. Firstly we take initial guess for $c(r)^i$.
2. Then by using Eq. (9), we transform it into k-space $c^{'}(k)^i$.
3. On substituting the value of $c^{'}(k)^i$ in Eq. (11), we obtain $y^{'}(k)^i$ $(= h^{'}(k)^i – c^{'}(k)^i)$.
4. Putting the value of y(r) (after transforming $y^{'}(k)$ to y(r) by using Eq. (10)) in Eq. (8), we get $c(r)^{new}$.
5. We repeat steps (2-4) until convergence is obtained i.e.,
$$\left|c(r)^{new} - c(r)^i\right|_{max} \leq 10^{-3} \qquad (12)$$
6. If we obtain the convergence then we take it as a final solution otherwise we take a new input $(i +1)^{th}$ by mixing the ith and the 'new' values such as
$$c(r)^{i+1} = \alpha c(r)^i + (1- \alpha) \, c(r)^{new} \qquad (13)$$

and steps (2-5) are repeated.

Here, the value of α varies between 0 and 1. Now if we obtain the value of h(r) then we can get the structure factor S(k) which can be obtained by scattering experiment [21], by using the relation given below

$$S(k) = 1 + \rho h^{'}(k) \tag{14}$$

4. Results and Discussion

In this section we present some representative plots of pair correlation functions directly related to the structural arrangement of particles in the fluid. In Fig. 1, we have plotted the radial distribution function (RDF) at different value of the interaction strength i.e. Γ = 5, 10, 15, 20. We observe that the radial distribution function (RDF) exhibit structures which become more prominent with the increase in interaction strength. The principle peak represents the location of most populated cell. In other words it indicates the most probable position of the colloidal particles. The probability of occupying the successive cells is seen to decrease with the increase in distance which signals the absence of long range order. We also observe a solder in RDF located at a distance approximately square root times of the distance of first peak. The solder if found to become more prominent with the increase in interaction strength.

Increase in Γ means decrease in temperature which leads to a decrease in particles kinetic energy which in turn results in an enhanced attraction between the particles causing enhanced ordering at shorter distances. For increasing interaction strength, the height of the main peak increases steadily, whereas the peak position does not change. The result is physically reasonable: we can assume that Γ is increased by making some external changes, such as reducing the temperature field or enhancing the strength of some external electric or magnetic field, without changing the total number of particle in the system. Then, the typical interparticle distances within the first coordination shell remain almost unchanged and only the degree of local ordering is affected, due to the increasingly strong repulsions.
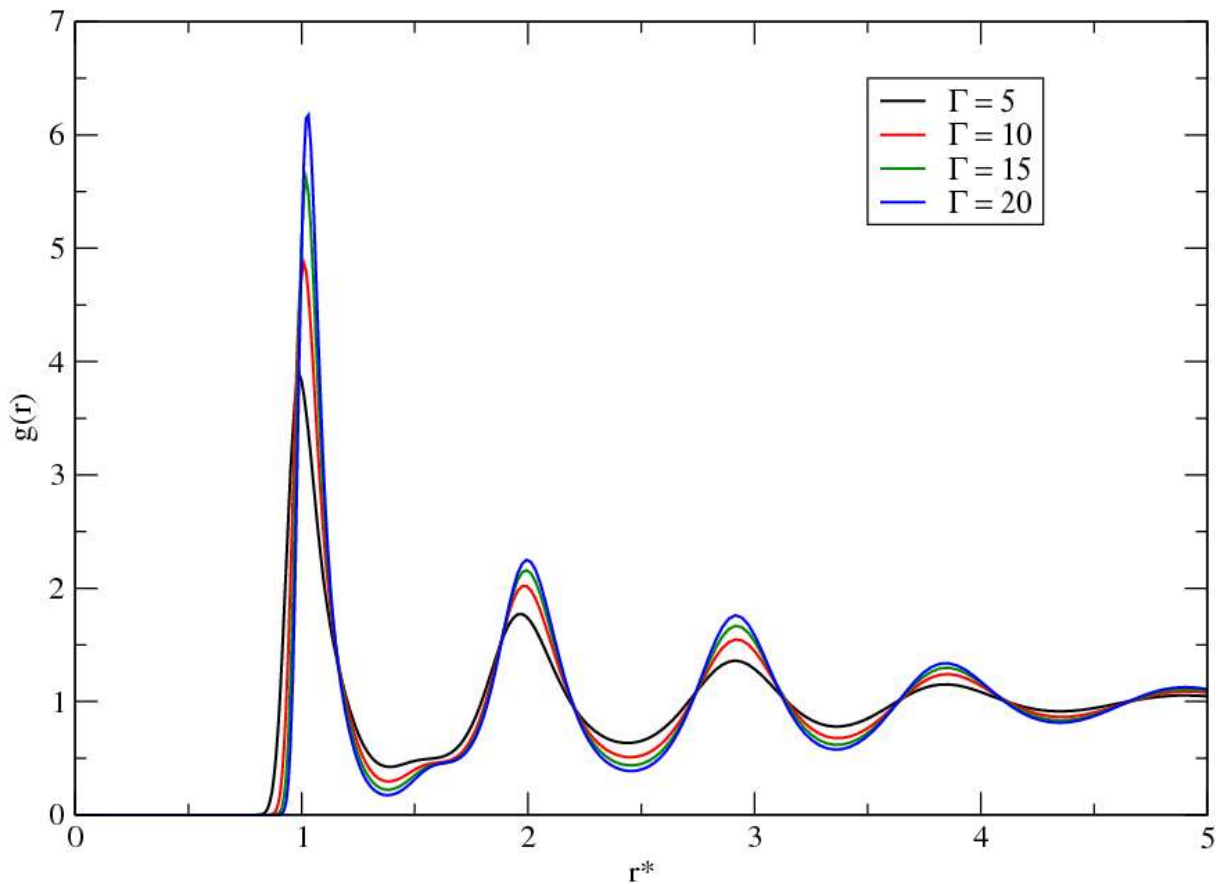
Figure 1. Graph showing variation of g(r) with Γ (interaction strength).

These features of the structure of the system can also be seen in the curves of structure factor shown in Fig.2. Structure factor is an important experimentally measurable physical quantity which is directly related to the RDF through its Fourier transform. The peaks of the structure factor S(k) can be seen to shift slightly to the lower k-side, which confirms the above conclusion that the interparticle interaction becomes more repulsive with the increase in Γ. The peak height of the structure factor curve is also found to increase with the increasing interaction strength. These results are similar to the experimental and computer simulation results of Hoffmann et al [22,23] on a system of superparamagnetic colloidal particles confined to a two dimensional air-water interface.
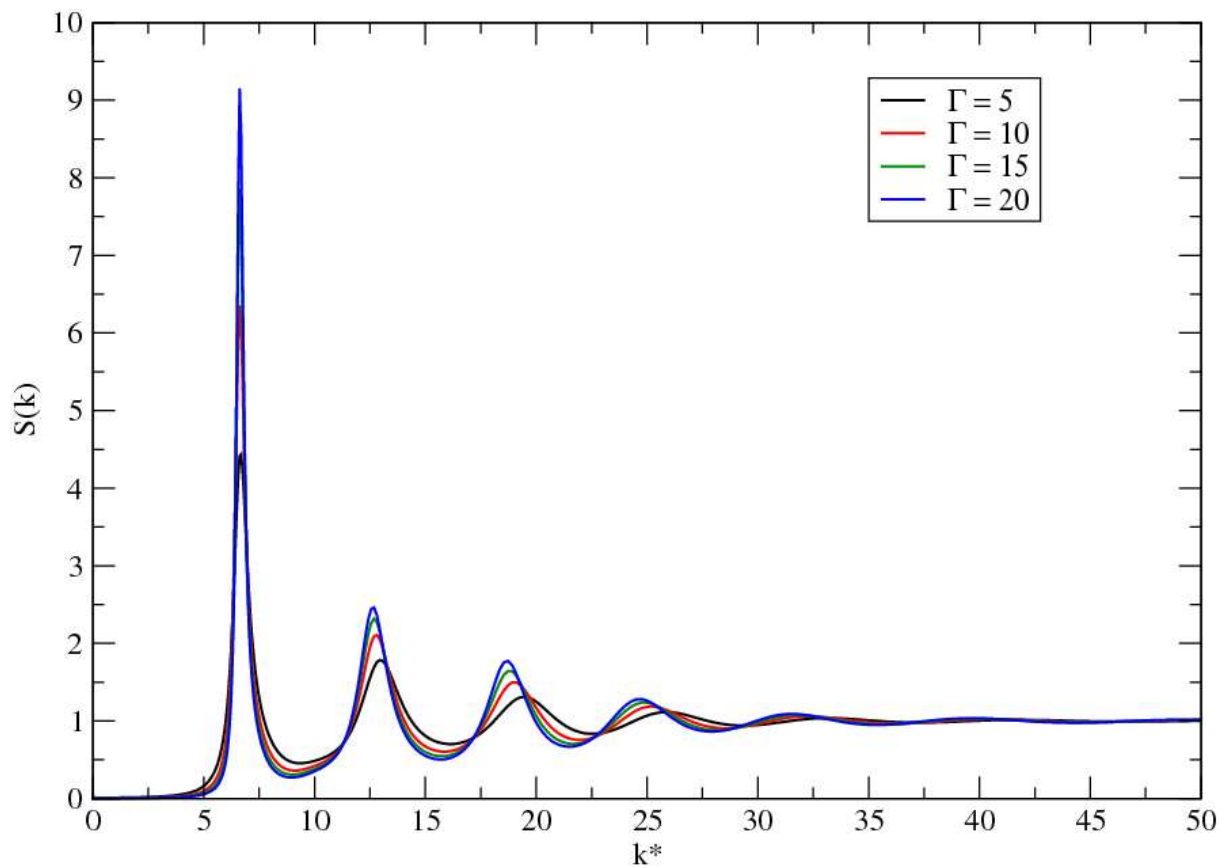
Figure 2. Graph showing variation of S(k) with Γ (interaction strength).

5. Conclusions

We have studied a one component system of nematic colloids confined in a two dimensional plane in which interaction between the particles is governed by repulsive octopole-octopole interaction potential. We have introduced a dimensionless interaction strength parameter to calculate the pair correlation function of the system by using Roger-Young integral equation theory. We observe a significant change in the local ordering of the particle in the system with the increase in the interaction strength parameter. The radial distribution and structure factor curves are found to have a strong short range structure which is seen to enhance both in size and range with the increase in Γ. The pair correlation function calculated in this study will be used in density functional theory of freezing to study the phase diagram of octopoler nematic colloids in two dimensions.

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