Integral Equation theory of a system of nematic quadrupoles

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Abstract—We have studied a system of nematic quadrupoles interacting via inverse power potential of the form $U \approx (\sigma/r)^5$ (σ is the diameter of the particles and r is the separation between them), both in 3-dimension and 2-dimension . Pair correlation function has been calculated by solving Rogers–Young (RY) integral equation theory. Thermodynamic consistency has been obtained ensuring the equality of pressure calculated by virial and compressibility routes.

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Introduction

Over last 30 years Integral Equation Theories are most sophisticated tool to investigate the topology of complex fluids[1,2].The whole integral equation theory stand on the Ornstein-Zernike (OZ) equation which is a relation between total correlation function h(r) and the direct correlation function c(r). In order to solve OZ, another equation connecting c(r) and h(r) is needed. Whereas OZ is an exact relation, the second one is an approximation and known as closure relation. Many closure relations are available in literature[3,4], among them Percus-Yevick (PY) and hyper-netted Chain (HNC) closures are the most frequently used relations. However Monte Carlo (MC) and Molecular Dynamics (MD) computer simulations studies have revealed various shortcomings of these equations and hence efforts have been made to develop more accurate closure relations [5].

The main problem in PY and HNC is that both are effected by thermodynamic inconsistency that means getting different results of the same quantity from different thermodynamic path. In order to overcome this problem of inconsistency, Rogers and Young proposed a new closure relation between c(r) and h(r) with an adjustable parameter to help in interpolating the PY and HNC values and to insure the consistency of the pressure calculated by various routs[7]. The results obtained by using Rogers and Young (RY) approximations are far accurate than the above mentioned approximations and also compares well with the results of MC and MD simulations.

In this paper we have studied a worked on a simple one component system which is interacting a potential which varies as the 5^{th} power of the inverse interparticle separation. We have employed Roger-Young closure and have calculated pair structures of the fluid phase as a function of various strength parameters of the potential. The paper is arranged as follows: In section II, we discuss the potential model. This will be followed by a brief discussion of the details of the integral equation theory and its solution procedure in section III. In section IV we will present and discuss our results. Finally, we conclude in section V.


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II. Model Potential

We consider a system consisting of *N* spherical colloidal particle suspended in a nematic solvent. The interaction of the liquid crystal molecules do the surface of colloids gives rise to a distortion in nematic director field. The colloidal particles are considered to interact with each other via the director distortion mediated elastic interaction which varies as $U(r) = \epsilon\ (\sigma/r)^n$. In the condition of weak homeotropic surface anchoring the value of n can be taken to be equal to 5. It corresponds to the case of interaction between two elastic quadrapoles in analogy with the interaction between the electric quadrupoles.

We define dimensionless interparticle separation by r*= r/a where $a= (3/4\pi\rho)^{(\frac{1}{3})}$ is the ion-sphere radius. Putting the value of $\rho_0 = \frac{\sqrt{2}}{\sigma_0^3}$ (number density) and ρ =N/V and r= r/a the potential can be expressed in the form

$$\beta\, u(r)=\Gamma / r^5 \tag{1}$$

Where $\Gamma= (4\pi\sqrt{2}z/3)^{5/3}$ with $z= (N\sigma^3/\sqrt{2}v)(\varepsilon/K_BT)^{\frac{3}{5}}$, is the coupling parameter determining the strength of interaction.

III. Integral equation theory

Integral equation theory involves in writing an exact relation between the total pair-correlation function h(r) and direct pair-correlation function c(r). Such a relation is called OZ, which is written as [6]

$$h(r)-c(r) = \rho \int h(r')c(r-r')dr \tag{2}$$

Where h(r) is related to the radial distribution function g(r) as h(r) =g(r)-1. In practice OZ equation is solved by writing it into k-space by using the Hankel transforms of the pair-correlation functions. The general form of Hankel transform of a function f(r) written as,

$$f(k)= 4\pi(-p)^m \int_0^\infty dr\, r^2\, f(r) J_m(kr) \tag{3}$$

$$f(r)= \frac{4\pi}{(2\pi)^3}(-p)^m \int_0^\infty dk\, k^2\, f(k) J_m(kr) \tag{4}$$

where $J_m(kr)$ is the spherical Bessel function of order m.

We have solved OZ, by using Roger- Young closure written as,

$$h(k)=c(k)+\rho\, h(k)\, c(k) \tag{5}$$

We have solved OZ, by using Roger- Young closure written as,

$$g(r)= e^{-\beta r}[1+\frac{e^{f(r)\gamma(r)}-1}{f(r)}] \tag{6}$$

Where $\gamma(r)$ = h(r)-c(r) and f(r) is the mixing function has a limit $0 \le f(r) \le 1$.

It is written as, $f(r) = 1-\exp^{-\alpha r}$, where α is the mixing parameter.

In order to determine the value of mixing parameter, we start by choosing its value arbitrarily and solve the integral equation theory. The resulting pair-correlation function are used to calculate the pressure from virial route using the relation

$$p= \rho KT [1- \frac{\rho}{2dKT} \int \frac{du}{dr} r g(r) dr] \tag{7}$$

where d is the dimension of the space and the excess pressure from compressibility route can be written as,

$$\beta\frac{dP}{d\rho} = 1-4\pi\rho\int c(r)r^2dr \qquad \text{for 3D} \tag{8}$$

$$\beta\frac{dp}{d\rho} = 1-2\pi\rho\int c(r)r^2dr \qquad \text{for 2D} \tag{9}$$

In order to obtain the thermodynamic consistency, pressure calculated from these two routes must be equal.

Algorithm

The numerical solution of OZ and RY-closure is performed following the iteration cycle,

$c(r)^{j} \rightarrow c(r)^{j} \rightarrow$ (o-z)$\gamma(k)^{j} \rightarrow \gamma(r)^{j} \rightarrow$ (closure) $c(r)^{new}$

where superscript j denote the j^{th} iterate. Iterative procedure involves the following steps:

a. First we make an initial guess for $c(r)^{j}$.

b. This is transformed to k space by $c(k)^{j}$ Hankel transform [Eq.3].

c. This $c(k)^{j}$ is then substituted in the OZ equation[Eq.2] to get the value of $\gamma(k)^{j}$ $(=h(k)^{j} - c(k)^{j})$

d. By using inverse Hankel transform [Eq.4] step $\gamma(k)^{j}$ converted to $\gamma(r)^{j}$.

e. This $\gamma(r)^{j}$ is substitute in the RY closure [Eq.6] we get the new $c(r)^{new}$.

f. The above steps (b) to (e) are repeated until a fixed point is reached satisfying the criterion for the convergence,

$$\left|c(r)^{new} - c(r)^{j}\right|_{\max} \le 10^{-5} \tag{10}$$

g. If $c(r)^{new}$ satisfies the criterion then it is the expected solution. However, if it does not satisfy then a new input for the $(j+1)^{th}$ iteration has to be generated before going to step (b).

The speed of convergence of the iterative procedure is very sensitive to the new input for the successive iteration. One method to generate the $(j+1)^{th}$ input is by mixing the j^{th} and the 'new' values as

$$c(r)^{j+1} = xc(r)^{j} + (1-x)c(r)^{n} \tag{11}$$

Where x is a number having a value between 0 and 1. The function of x is to avoid large differences between successive iterates and therefore to prevent divergence.

In order to check the accuracy of our method of calculation, we have compared in Figure 1 the radial distribution function obtained by solving the RY-integral equation theory to the Brownian dynamic simulation[8] for a system of colloids interacting via a potential varying as $1/r^3$. We see here that for this system the results obtained by RY-theory is in excellent agreement with the simulation. It provides us the confidence regarding the accuracy of the procedure of the solution.

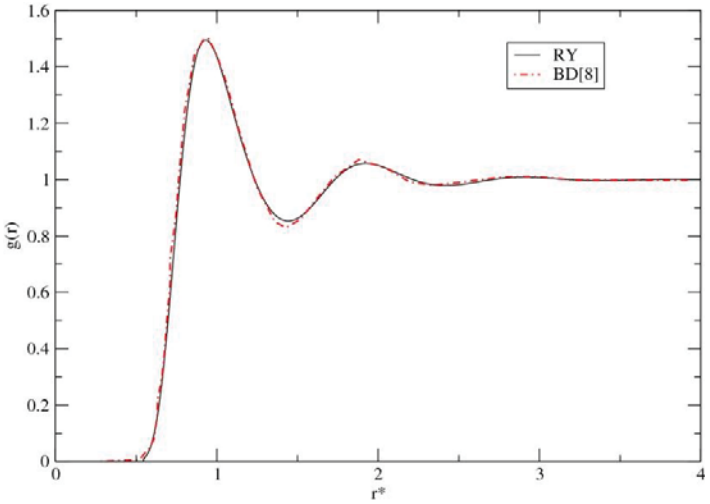


Figure 1. Plot representing comparison of g(r) calculated by Roger-Young's closure and Brownian dynamic simulation[8] at Γ = 1.44 in 2D system for the potential $\frac{\Gamma}{r^3}$.

IV. Results and Discussion

2D Case

Γ	$\frac{\beta P^v}{\rho}$	$\frac{\beta P^c}{\rho}$	$\frac{P^c}{P^v}$
10	66.21	69.84	1.054
15	96.68	98.77	1.021
20	129.01	128.67	0.997

Table 1. Comparison of pressure from virial and compressibility route for 2-dimension.

In Table 1, we have tabulated the values of pressure of a system in two-dimensional plane, calculated by using virial and compressibility roots for various values of strength parameter. We found that for one particular value of alpha the values of pressure calculated through both the routes are almost same. Hence we conclude that for this value of alpha, the requirement of self-consistency is satisfied.

In Figure 2 , we have plotted the radial distribution curve for the case of 2D. We observe again that the peak height increases with the increase in strength of repulsive interaction. One interesting feature to be mentioned here is the relative heights if peaks and the structures in 3D and 2D radial distribution

functions. We found here that for the same strength of repulsive interaction, the radial distribution function for 2D case is more intense and of longer range than that of 3D case

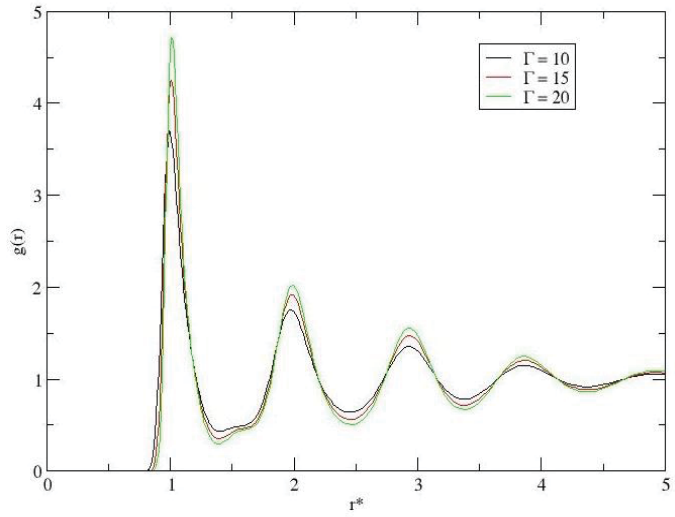


Figure 2. Plot of radial distribution function g(r) at Γ =10, 15 and 20 for the case of 2D

A. 3D case

Γ	$\frac{\beta P^v}{\rho}$	$\frac{\beta P^c}{\rho}$	$\frac{P^c}{P^v}$
10	102.082	103.57	1.014
15	152.99	151.13	0.987
20	200.28	198.04	0.988

Table2 . Comparison of pressure from virial and compressibility route for 3-dimensio

In Table 1, we have listed the virial and compressibility pressures for the system in bulk. We observe here that the values of pressure in 3D are higher than that for 2D case. Again for a particular value of mixing parameter the virial and compressibility pressures are very close to each other and hence this value of mixing parameter may be considered for the solution of OZ.

Using above value of alpha in Roger-Young closure we solved the OZ equation. In Figure 1 we have plotted the radial distribution function corresponding to Gamma=10, 15, and 20. We observe that the peak height of g(r) increases with the increase in Gamma. This indicates enhanced local ordering with the increase in the strength of repulsive interaction.

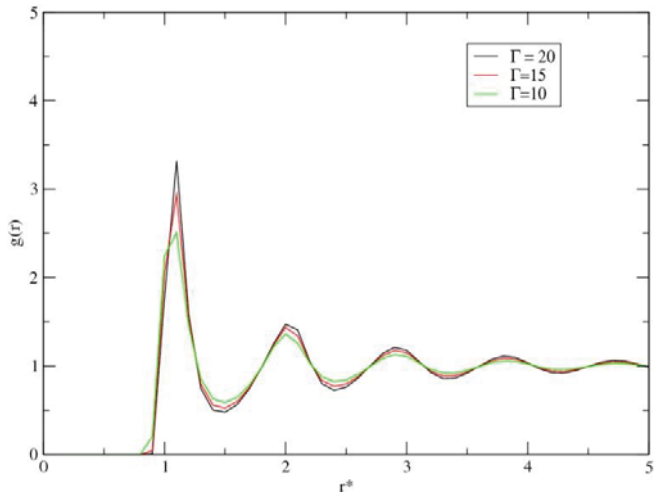


Figure 3. Plot of radial distribution function g(r) at Γ =10, 15 and 20 for the case of 3D

V. Conclusions

In this work we have determined , the pair structures of a system of particles interacting confined in 3D/2D space and interacting via a potential varying as 5^{th} power of the interparticle separation. We have solved Roger-Young integral equation theory by determining the mixing parameter which satisfy the consistency of virial and compressibility pressure. We have presented the radial distribution curves of 2D and 3D case and have shown that the radial distribution curves of 2D case is not only nor intense but exhibit longer range. In future we intend to use the pair structure in density functional theory to determine the topology of the phases exhibited by quadrupole system.

Acknowledgment

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References

[1] Hansen J.P and McDonald I.R. 1986 *Theory of simple liquids*, Academic Press.London.2nd edition.

[2] Caccamo .C 1996 Phys. Rep. 274,1 .

[3]Born M and Green H S, Proc R Soc.London,Ser. A 1946 188,10.

[4] Percus J K and Yevick G J 1958 Phys.Rev.110, 1

[5]Rosenfeld Y and Ashcroft N Y, 1979 *Theory of simple classical fluids: Universality in the short-range structure* 20, Phys.Rev.A, 3.

[6]Hus M, Zalar M , Urbic T 2013 ,138 J. Chem. Phys. 224508,

[7]Singh R C, Ram J and Singh Y 1996 *Thermodynamically self-consistent Integral-equation theory for pair-correlation functions of a molecular Fluid* 54 Phys. Rev. E 1.

[8]Hoffmann N, Likos C N and Lowen H 2006*Microphase structuring in two –dimensional magnetic colloid mixtures* 18 J.Phys.:Condense. Matter