Direct Correlation Function of Hard Molecular Fluid

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ABSTRACT

We study the direct correlation function (DCF) of a classical fluid of non-spherical molecules. The components of the fluid are hard spherocylinder (SC) molecules. The required homogeneous (DCF) is obtained by solving Orenstein-Zernike (OZ) integral equation numerically, using the Percus-Yevich (PY) approximation and the procedure proposed by Ram and co-workers. We also obtained the closest approach between two spherocylinders by using two different methods, first extending the algorithm proposed by Vega and Lago by introducing a new geometry and second use the finite element procedure. Results are in agreement in two methods. The calculation is performed for various values of packing fractions of the fluid and for the aspect ratio, L/D=5.0,10.0. The coefficient expansions of DCF are obtained. The results are in agreement with the other recent works.

Keywords: Molecular fluid, direct correlation function, hard spherocylinder.

1. INTRODUCTION

The problem is the prediction of the physical properties of simple and multi-component molecular fluids based on the information about molecular shapes and intermolecular interactions. Considerable progress, however, has been made over the last two decades in understanding the behavior of these fluids at the molecular level by considering simplified models.

For these fluids we can consider models in which molecules are treated as hard particles with a given shape (Allen et al., 1993). The main reasons to study systems of hard convex bodies is that they provide us with simple references systems which are used for the investigation of more realistic systems such as liquid crystals (Colot et al., 1988).

Among simple geometric forms, the spherocylinder would seem to approximate best the shape of the most nematgenic molecules. For this reason, a fluid of rigid SC is useful model for investigating the fundamental nature of the nematic-isotropic phase transition in liquid crystals.

In the recent years, there have been many investigations of the structural properties of interface and confined molecular fluids using the liquid state such as integral equation (Ward and Lado, 1988; Hansen and McDonald, 1986) density functional theory (Rickayzen, 1995; Calleja and Rickayzen, 1995; Chrzanowska et al., 2001; Velasco et al., 2002) and computer simulations (Allen and Frenkel, 1987; Savenko and Marjolein Dijkstra, 2005).Since the integral equation theory has been found to be quite successful in describing molecular fluids, this theory is used inorder to study the fluid.

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The direct correlation function (DCF) plays an important role in describing thermodynamical properties and the structure of simple (Henderson et al., 1994; Stelzer et al., 1995; Moradi and Shahri, 2003), molecular (Ram et al., 1994; Letz and Latz, 1999; Singh et al., 1996) and multicomponent fluids (Patra and Ghosh, 2003; Moradi and Khordad, 2006; DuBois and Perera, 2002; Biben and Hansen, 1991). The DCF can be used to calculate the equation of state (Barrio and Solana, 2001), free energy (Tang and Wu, 2004), phase transition (Marko, 1989; Singh and Singh, 1986), elastic constants (Ponievierski and Stecki, 1979; Phuong et al., 2001; Avazpour et al., 2010), etc.

In our work, we consider a system composed of hard SC particles and obtain the DCF of this system. We use the Ornstein-Zernike (OZ) integral equation (Ornestin, and Zernike, 1914) by the Percus-Yevick (PY) approximation (Percus, and Yevick, 1958) to study this system.

This article organized as follows: In Sec.2, we introduce the SC model and explain how to find the DCF of this model by OZ equation, in Sec.3 the methods of calculating the closest approach between SC molecules are described. In Sec.4, we report and discuss the results and finally in Sec.5 our conclusions are summarized.

2. DCF OF SC

In the SC model, system formed by cylinders of length L and diameter D terminating in hemispheres at the two bases. These spherocylinders interact according to the potential:

$$u(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2)=\begin{cases}\infty & \sigma\left(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2\right)<D \\ 0 & \sigma\left(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2\right)>D\end{cases} \tag{1}$$

where $\Omega_i=(\theta_i,\varphi_i)$ is describes the orientation of particle i and $\vec{r}$ is a vector along the line connecting the centers of the two particles and $\sigma(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2)$ is the closest approach between the segments constituting the axis of the cylinder.

The DCF of fluid with non-spherical molecules can be defined through the OZ equation (Ornestin, and Zernike, 1914)

$$h(r_1,\Omega_1,r_2,\Omega_2)=c(r_1,\Omega_1,r_2,\Omega_2)+\frac{\rho}{4\pi}\int d\Omega_3\int dr_3 c(r_1,\Omega_1,r_3,\Omega_3)h(r_3,\Omega_3,r_2,\Omega_2) \tag{2}$$

where r_i is the position of the center of mass and ρ shows the number density of the molecules. The symbols h and c are the well-known total and direct correlation functions.

To solve OZ equation, we first introduce the expansion of DCF. There are two common choices for this expansion. In one expansion, the molecular orientations are referred to an intermolecular reference frame in which the polar axis is along the intermolecular vector $\vec{r}_{12}$, body frame (BF). In the other one, the molecular orientations are defined in a space-fixed or laboratory frame (LF) of reference. We expand the angular dependence of the correlation functions, h or c, using orthogonal basis set of harmonics.

Expansions in BF is

$$c(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2)=\sum_{l_1,l_2,m}c(l_1,l_2,m;r)Y_{l_1}^{m}(\hat{\Omega}_1)Y_{l_2}^{-m}(\hat{\Omega}_2) \tag{3}$$

and in LF can be defined by

$$c(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2)=\sum_{l_1,l_2,l}c(l_1,l_2,l;r)\phi_{l_1,l_2,l}(\hat{\Omega}_1,\hat{\Omega}_2,\hat{\Omega}_r). \tag{4}$$

Where $\hat{\Omega}_r$ is the unit vector along $\vec{r}$, $c(l_1,l_2,m;r)$ and $c(l_1,l_2,l;r)$ are the expansion coefficients in body and laboratory frames. $\phi_{l_1,l_2,l}(\hat{\Omega}_1,\hat{\Omega}_2,\hat{\Omega}_r)$ is rotational invariant given by

$$\phi_{l_1,l_2,l}(\hat{\Omega}_1,\hat{\Omega}_2,\hat{\Omega}_r)=\sum_{m_1,m_2,m} C(l_1,l_2,l;m_1,m_2,m)Y_{l_1}^{m_1}(\hat{\Omega}_1)Y_{l_2}^{m_2}(\hat{\Omega}_2)Y_l^{m^*}(\hat{\Omega}_r) \tag{5}$$

Where $C(l_1,l_2,l;m_1m_2m)$ is a Clebsch-Gordan coefficient and Y_l^m is the spherical harmonics, and * indicates the complex conjugate. In BF expansion, the z-axis of the coordinate system was chosen along the axis connecting the two molecules that are correlated. Therefore, we only need to deal with one index m. To find the direct correlation function the following procedure is required:

(1) Guess an initial value for $c(l_1,l_2,m;r)$.

(2) Calculate the expansion coefficient in LF by using the first step

$$c(l_1,l_2,l;r)=\sum_m \sqrt{\frac{4\pi}{2l+1}}\,c(l_1,l_2,m;r)C(l_1,l_2,l;m,-m,0) \tag{6}$$

(3) Use Fourier-Hankel transformation to obtain the coefficients in the Fourier space

$$c(l_1,l_2,l;k)=4\pi(-i)^l\int_0^\infty drr^2 j_l(kr)c(l_1,l_2,l;r) \tag{7}$$

(4) The coefficients $c(l_1,l_2,l;k)$ are used to obtain

$$c(l_1,l_2,m;k)=\sum_l \sqrt{\frac{2l+1}{4\pi}}\,c(l_1,l_2,l;k)C(l_1,l_2,l;m,-m,0) \tag{8}$$

These three equations transform a two particle correlation function from r frame in real space into a function in k space; within the complete set of the spherical harmonics we can transform the OZ equation as

$$h(l_1,l_2,m;k)=c(l_1,l_2,m;k)+\frac{\rho}{4\pi}\sum_l c(l_1,l,m;k)h(l,l_2,m;k) \tag{9}$$

This can be written in matrix form for each m and k value

$$\underline{\underline{h}}(m;k)=\underline{\underline{c}}(m;k)+\frac{\rho}{4\pi}\underline{\underline{c}}(m;k)\underline{\underline{h}}(m;k) \tag{10}$$

where $\underline{\underline{c}}$ and $\underline{\underline{h}}$ are symmetry matrices with indices l_1 and l_2.

Here we introduce an auxiliary function $\underline{\underline{y}}(m;k)$

$$\underline{\underline{y}}(m;k)=\underline{\underline{h}}(m;k)-\underline{\underline{c}}(m;k) \tag{11}$$

(5) The OZ equation is written as

$$\underline{\underline{y}}(m;k)=\frac{\rho}{4\pi}\left[1-\frac{\rho}{4\pi}\underline{\underline{c}}(m;k)\right]^{-1}\left[\underline{\underline{c}}(m;k)\right]^2 \tag{12}$$

and it is solved for $y(l_1,l_2,m;k)$.

(6) Converting $y(l_1,l_2,m;k)$ to $y(l_1,l_2,l;k)$ yields

$$y(l_1,l_2,l;k)=\sum_m \sqrt{\frac{4\pi}{2l+1}}\, y(l_1,l_2,m;k)C(l_1,l_2,l;m,-m,0) \qquad (13)$$

(7) By using the inverse Fourier-Hankel transform we can get $y(l_1,l_2,l;r)$

$$y(l_1,l_2,l;r)=\frac{i^l}{2\pi^2}\int_0^\infty dk k^2 j_l(kr) y(l_1,l_2,l;k) \qquad (14)$$

(8) These expansions are used to obtain $y(l_1,l_2,m;r)$

$$y(l_1,l_2,m;r)=\sum_l \sqrt{\frac{2l+1}{4\pi}}\, y(l_1,l_2,l;r)C(l_1,l_2,l;m,-m,0) \qquad (15)$$

(9) To solve the OZ equation, we require an appropriate closure relation. Here we apply the PY closure relation (Percus, and Yevick, 1958)

$$c(1,2)=f(1,2)[y(1,2)+1] \qquad (16)$$

where $f(1,2)$ is the Mayer function and is defined by

$$f(1,2)=\exp(-\beta u(1,2))-1 \qquad (17)$$

and for the pair potential energy of interaction between particles, which defined in Eq.(1) is

$$f(1,2)=f(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2)=\begin{cases} -1 & \sigma(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2)<D \\ 0 & \sigma(\vec{r},\hat{\Omega}_1,\hat{\Omega}_2)>D \end{cases} \qquad (18)$$

(10) We can determine $c(l_1,l_2,m;r)$ with the help of the PY equation

$$\begin{aligned} c(l_1,l_2,m;r) &= \frac{1}{4\pi}\sum_{\substack{l_1'l_2'\\ l_1''l_2''}} \sqrt{\frac{(2l_1'+1)(2l_2'+1)(2l_1''+1)(2l_2''+1)}{(2l_1+1)(2l_2+1)}} \\ &\times C(l_1',l_1'',l_1;0,0,0)C(l_2',l_2'',l_2;0,0,0)\sum_{m'm''} C(l_1',l_1'',l_1;m',m'',m) \qquad (19) \\ &\times C(l_2',l_2'',l_2;-m',-m'',-m) f(l_1',l_2',m';r)\left[y(l_1'',l_2'',m'';r)+4\pi\delta_{000}^{l_1''l_2''m''}\right] \end{aligned}$$

Where $f(l_1,l_2,m;r)$ is the Mayer expansion coefficient and given by

$$f(l_1,l_2,m;r)=\int d\hat{\Omega}_1 \int d\hat{\Omega}_2\, f(r,\hat{\Omega}_1,\hat{\Omega}_2) Y_{l_1}^m(\hat{\Omega}_1) Y_{l_2}^{m^*}(\hat{\Omega}_2) \qquad (20)$$

With these new values of $c(l_1,l_2,m;r)$, we return to step (2) and repeat the next steps again. This iteration is continued until a required convergency is achieved. By using these coefficients, we can obtain the DCF of SC fluid.

3. CLOSEST APPROACH BETWEEN HARD SC MOLECULES

In molecular liquid theory calculating the closest approach between two molecules is very important. In order to calculate the DCF of the fluid it is necessary to calculate the closet approach between the molecules, therefore, we calculate the closest approach of two SCs by using two different methods.

In the first method we use a fast algorithm proposed by Vega and Lago(Vega and Lago, 1994). They actually applied their method for calculating the closest approach between two rods and we extend this to find the closest approach between two SCs.

In the second method we use the finite element procedure to find the closest approach. In this method, the main axis of the SCs (cylinders axis) are divided into equal parts.

With having direction $(\hat{\Omega}_1)$, diameter, length of SC and $\vec{r}_{12}$ the vector that connects the centers of SCs, the coordinate of the begin and end of the main axis of the cylinder can be determined and given by

$$\vec{A}=\vec{r}_{12}+\frac{L_1}{2}\hat{\Omega}_1 \ ;\vec{B}=\vec{r}_{12}-\frac{L_1}{2}\hat{\Omega}_1 \tag{21}$$

To divide this segment (axis of cylinder) into n equal parts from the following equation is used

$$F_i=\frac{(i-1)B+(n-i+1)A}{n} \tag{22}$$

where F_i is the coordinate of the ith node.

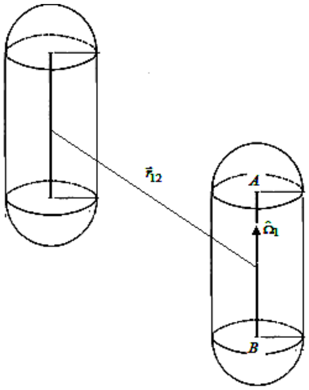

Fig. 1. Coordinates and orientation of two SCs

The main axis of the other cylinder is divided into m equal parts similarly. Now, the distances between the pairs of points listed from each cylinder which is the combination of 2 from m+n are calculated. The minimum value from the calculated distances is chosen. Finally, we subtract this value from the half diameter of the each SC that value is the closest approach between SCs. These methods are more general and can also be used for the mixtures.

3. RESULTS AND DISCUSSION

We solve the OZ integral equation numerically to find the DCF of hard SC fluid. For calculating the DCF of the fluid, it is required to calculate the closet approach between the molecules, therefore, we calculate the closest approach of two SCs by using two different methods which described. According to the results shown in the Table 1, for the aspect ratio, L/D=5.0, these methods are in good agreement. Here L and D are the length and diameter of SC, respectively. In order To make the calculation more accurate, we use the average of these two methods. All values are randomly selected.

Table 1. Calculated closest approach of SCs with L/D=5.0, the angles are in radian.

r	θ	φ	θ_1	φ_1	θ_2	φ_2	**Vega & Lago Method**	**Finite Element Method**
2.8591	1.2419	5.1896	2.7181	2.6025	2.4872	5.1296	0	0
4.2640	1.3555	1.8970	1.3601	1.5154	1.9937	2.3071	0.2196	0.2177
11.7971	2.5181	1.2959	0.6010	4.5526	3.0588	4.4264	6.5927	6.5851
1.4388	2.3084	3.1228	2.7033	1.6170	0.8722	1.8106	0.1033	0.1016
5.5697	3.0763	2.9350	0.6200	3.2049	0.6594	3.6442	2.9350	2.5141
3.7358	1.3938	5.2771	3.0850	2.5906	1.0920	4.1983	2.2485	2.5141
6	0	0	0	0	0	0	0	0
2.8719	1.5483	6.0874	2.5982	0.8067	2.6460	4.9604	1.2461	1.2437
3.7071	0	0	0.785	1.57	0.785	1.57	0	0

In Table1 r, $\Omega_i = (\theta_i, \varphi_i)$ and $\Omega = (\theta, \varphi)$ are the distance between the centers of SCs, orientation of ith molecule and orientation of the vector which connects the center of SCs respectively.

Now, we can calculate the Mayer function with Eq. (18). The packing fraction of SC can be given by

$$\eta = \rho\left[\frac{4}{3}\pi(\frac{D}{2})^3\right] + \left[\pi(\frac{D}{2})^2 L\right] \qquad (23)$$

In Figure 2, the selected DCF expansion coefficients for packing fraction $\eta = 0.5$ with aspect ratio L/D=5.0 are plotted.

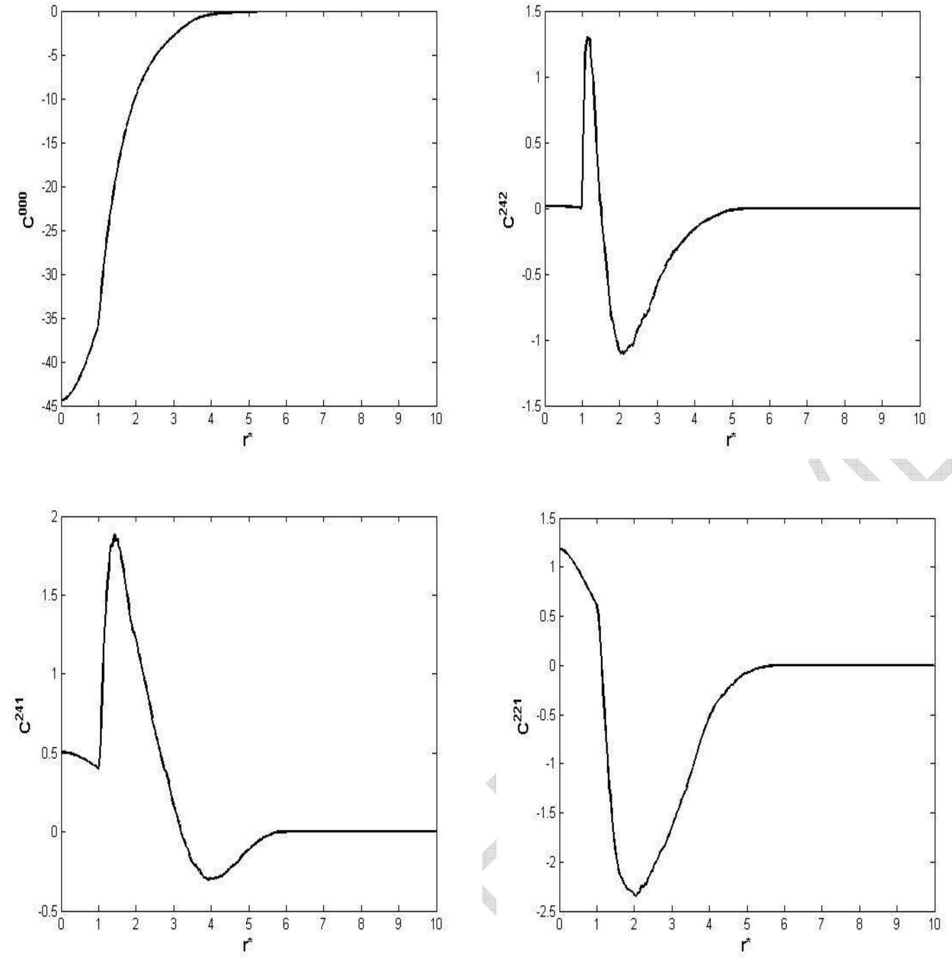

Fig. 2. Selected expansion coefficients of the DCF of hard SCs as a function of the reduced distance, $r^* = \frac{r}{D}$, for $\eta = 0.5$.

In Figure 3 the selected DCF expansion coefficients of DCF for packing fraction $\eta = 0.441$ with aspect ratio L/D=5.0 are plotted.

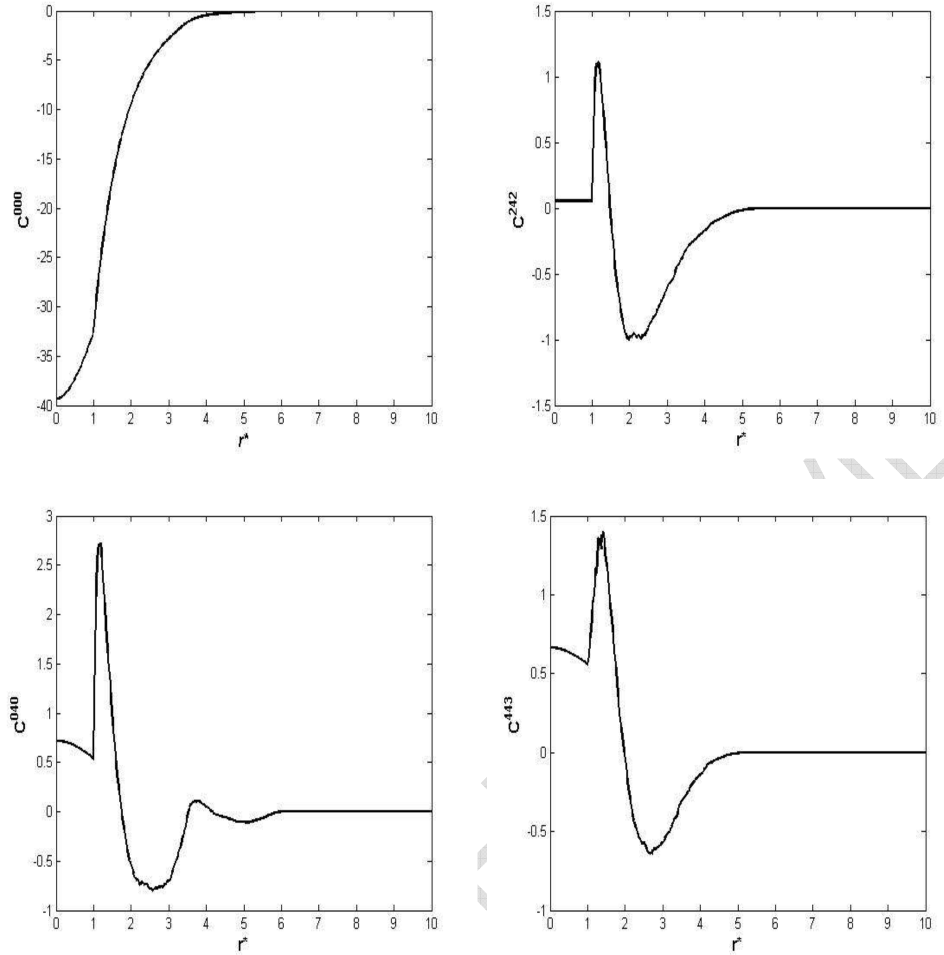

Fig. 3. Selected expansion coefficients of the DCF of hard SCs as a function of the reduced distance, $r^* = \dfrac{r}{D}$, for $\eta = 0.441$.

In the following, the expansion coefficients are compared with computer simulation (Savenko and Marjolein Dijkstra, 2005) in Figure 4. These coefficients are calculated in LF for aspect ratio L/D=10 and $\eta = 0.1592$ .The obtained expansion coefficients of the DCF using the PY integral equation are in good agreement with the coefficients provided by computer simulation.

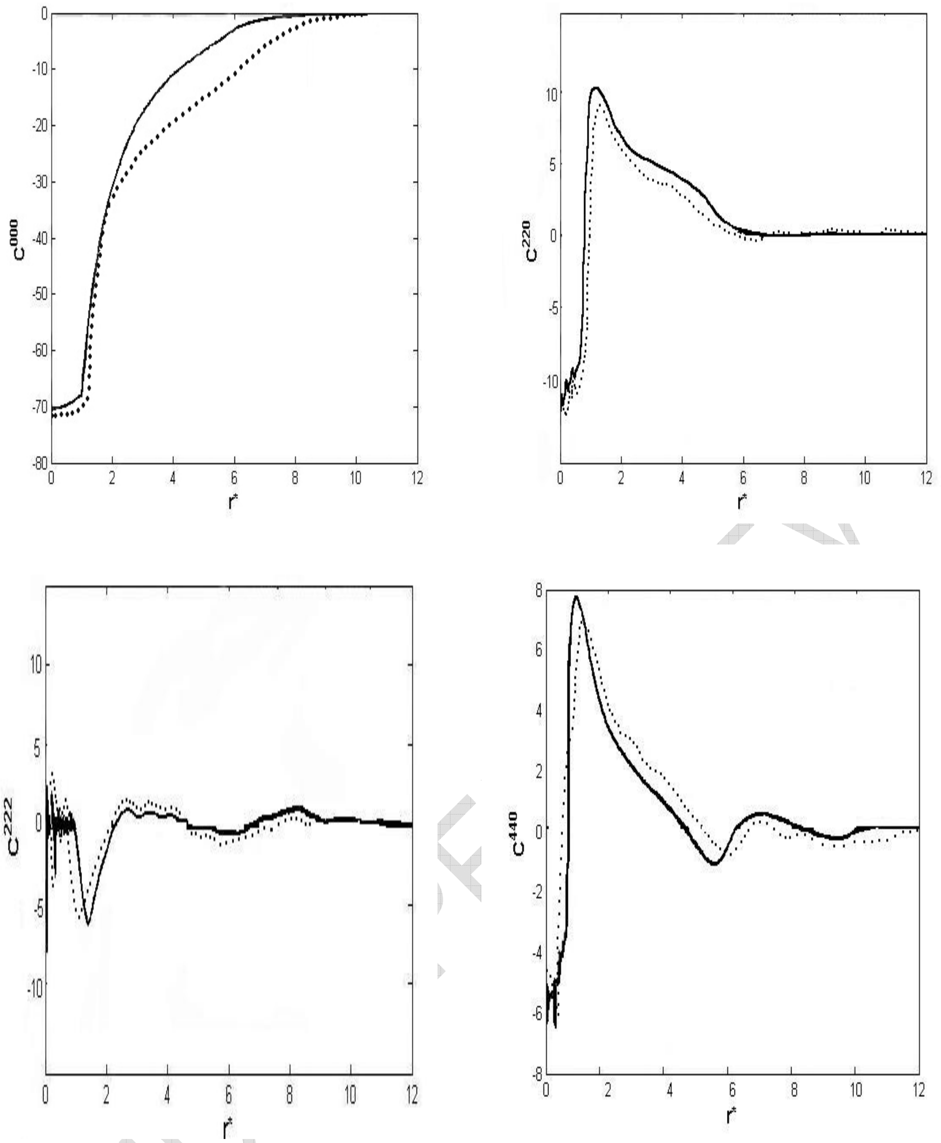

Fig. 4. Selected expansion coefficients of the DCF as a function of reduced distance $r^* = \frac{r}{D}$**, for** $\eta = 0.1592$ **and L/D=10.0 in LF. The solid and dotted curves are due to our results and simulation (Savenko and Marjolein Dijkstra, 2005), respectively.**

4. CONCLUSION

For studying a system containing spherical and non-spherical members knowing the DCF is required. We consider a system composed of hard SC particles and obtain the DCF of this package. We use the integral equation by the PY closure. First, we should define how to calculate closest approach between two molecules and, then, compare these methods. As shown in Table 1 these methods are in fairly agreement. With calculating closest approach, the expansion coefficients of DCF are obtained. These coefficients are plotted for different packing fraction and aspect ratio. Finally, we compared the expansion coefficients with computer simulation, which are in good agreement.

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