Density and Polarization Profiles of Dipolar Hard Ellipsoids Confined between Hard Walls: A Density Functional Theory Approach

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The density and polarization profiles of the dipolar hard ellipsoids confined between hard walls are studied using the density functional theory (DFT). The Hyper-Netted Chain (HNC) approximation is used to write excess grand potential of the system with respect to the bulk value. The number density is expanded up to zero and first order in polarization to find the results. For the zero order in polarization, the coupled integral equations for the directional densities are obtained. Then, for the first order in polarization the coupled integral equations for the directional densities and polarization profiles are obtained. To simplify the calculations we use restricted orientation model (ROM) for the orientation of ellipsoids to find the density and polarization profiles. We also apply an electric field and write an expression for the excess grand potential of the system and obtain the coupled integral equations for the density and polarization profiles again. Finally, we calculate the density and polarization profiles for different cases and compare the obtained results.

Keywords: Dipolar hard ellipsoids, Density functional theory, Density profile, Polarization profile, Confined fluids

INTRODUCTION

Due to the equilibrium properties of homogeneous and inhomogeneous dipolar fluids especially with dipole-dipole interactions, these fluids have recently attracted much attention [1-9]. A dipolar hard sphere model is a system of hard sphere with embedded point dipoles at the center and it has been found to be a simple but still useful model to study the equilibrium properties of this kind of fluids either theoretically or by computer simulation techniques. These fluids with polar molecules mainly represent two important physical features, *viz.* the short-ranged repulsions and the long-ranged orientation dependent electrostatic interactions. Recent studies have shown that these interactions often show unexpected behavior [10]. The simplest example of an inhomogeneous dipolar fluid is the interface between a dipolar hard sphere fluid and a neutral hard wall [11].

Density functional theory (DFT) has been proven to be a

powerful tool in the study of thermodynamic and structural properties of bulk and non-uniform phase of molecular fluid and liquid crystals particularly in two and three dimensions [6,7,12]. DFTs have also been used to study the thermodynamics of homogeneous molecular fluids and structural properties of inhomogeneous molecular fluids, such as hard ellipses [12], hard circular cylinders, and hard Gaussian overlap fluid [2,13] confined between planar walls. Moradi and Rickayzen [14] used a density functional formalism, based on the hyper-netted chain (HNC) approximation, to obtain number density and polarization of dipolar hard spheres between hard walls in the presence of a weak electric field.

Osipov *et al.* [15] found that the behavior of dipole-dipole interaction could be treated by separating the direct correlation function (DCF) for the fluid into short and long range parts. They investigated the formal problems of constructing a density functional theory of dipolar fluids and proposed an explanation for the failure of all existing density-functional theories to describe the behavior of

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strongly dipolar fluids as observed in computer simulations.

Cheung and Schmid [16] studied a system of soft ellipsoidal molecules confined between two planner walls using classical density functional theory. Both the isotropic and nematic phases were considered. They evaluated the excess free energy using two different *Ansa ̈tze* and the intermolecular interaction which was incorporated using two different DCFs for the fluids and the calculated density, and finally they compared the order parameters to the simulation results for the same system. Varga *et al.* [17] used a density functional approach to describe the orientational ordering of nonpolar and dipolar Gay-Berne fluids. Moradi *et al.* [18] obtained the interaction forces between nano-circular particles suspended in a hard-ellipse fluid. Moradi and Avazpour [2] have studied the density profiles of a hard Gaussian overlap (HGO) fluid confined in between hard walls using the density functional theory. Here, we extend this system to a hard ellipsoidal fluid with dipole-dipole interaction. This kind of systems has not been studied very much; so because of its importance, we use the same density functional theory, HNC approximation, to find the density and polarization profiles of a dipolar hard ellipsoidal fluid confined between two parallel hard walls. Then, we examine the effect of external electric field on the density and polarization profiles.

This article is organized as follows: In Sec. 2 we describe excess grand potential using the density functional theory of molecular fluids confined between planar walls, and obtain the direct correlation function (DCF) for dipolar hard ellipsoidal molecules. In Sec. 3 we calculate the density and polarization profiles of these molecules. In Sec. 4 we obtain and discuss the results. Finally, in Sec 5 we present the conclusion.

THEORY

Grand Potential and Density Number

For a model fluid containing hard ellipsoidal molecules carrying electric dipole moment at the center and in the presence of an external potential $V(\mathrm{r},\omega)$, the excess grand potential with respect to its bulk is a unique functional of number density. Up to second order in density and using HNC approximation the excess grand potential is given as

[2,14] :

$$\beta\Delta\Omega[\rho] = \int d\vec{r}\, d\omega \rho(\vec{r},\omega)\left[\ln\frac{\omega_T\rho(\vec{r},\omega)}{\rho_b}-1\right]+\int d\vec{r}\, d\omega\rho(\vec{r},\omega)V_{ext}(\vec{r},\omega)$$
$$-\frac{1}{2}\int d\vec{r}_1 d\omega_1 d\vec{r}_2 d\omega_2 C\left(\vec{r}_{12},\omega_1,\omega_2\right)\left[\rho(\vec{r}_1,\omega_1)-\frac{\rho_b}{\omega_T}\right]\left[\rho(\vec{r}_2,\omega_2)-\frac{\rho_b}{\omega_T}\right]$$
$$(1)$$

where $C\left(\vec{r}_{12},\omega_1,\omega_2\right)$ is the DCF for homogeneous molecular fluid, ρ_b is the bulk density, $\beta = \dfrac{1}{k_B T}$, $\omega_i \equiv \theta_i,\varphi_i$ denotes the orientation of ith molecule and $\rho(\vec{r},\omega)$ is the number density at point $\vec{r}$ with generally molecular orientation $\omega \equiv \theta,\varphi$ and ω_T is the total solid angle available to the molecules. We approximate the number density as

$$\rho(\vec{r},\omega) = \rho_0(\vec{r},\omega) + \delta\rho(\vec{r},\omega), \qquad (2)$$

where $\rho_0(\vec{r},\omega)$ is the number density in the absence of dipole-dipole interaction. Due to the symmetry of spherical molecules, the electric dipole moment located in the center of these molecules can lie freely in any directions and there are no preferred directions for them. However, we assume the dipole moments in ellipsoids are aligned in direction of major axis and because of the dominance of short range interaction, they cannot rotate freely. For the first order approximation, we assume there is a linear relationship between density and local polarization profiles. At first, we continue calculation without considering the second term in above Eq. (2).

In a dipolar hard ellipsoidal fluid, the pair interaction potential is given by the dipole-dipole interaction $u_{dd}\left(\vec{r}_{12},\omega_1,\omega_2\right)$ plus the hard ellipsoidal pair potential $u_{HE}\left(\vec{r}_{12},\omega_1,\omega_2\right)$.

$$u\left(\vec{r}_{12},\omega_1,\omega_2\right) = u_{dd}\left(\vec{r}_{12},\omega_1,\omega_2\right) + u_{HE}\left(\vec{r}_{12},\omega_1,\omega_2\right) \qquad (3)$$

Where $u_{dd}\left(\vec{r}_{12},\omega_1,\omega_2\right)$ and $u_{HE}\left(\vec{r}_{12},\omega_1,\omega_2\right)$ is given by [1]:

$$u_{dd}\left(\vec{r}_{12},\omega_1,\omega_2\right) = \frac{-m^2}{r_{12}^3}\left(3\left(\hat{m}_1.\hat{n}\right)(\hat{m}_2.\hat{n}) - \hat{m}_1.\hat{m}_2\right) \qquad (4)$$

$$u_{HE}\left(\vec{r}_{12},\omega_1,\omega_2\right) = \begin{cases} 0 & r_{12} > \sigma\left(\hat{n},\omega_1,\omega_2\right) \\ \infty & r_{12} < \sigma\left(\hat{n},\omega_1,\omega_2\right) \end{cases} \qquad (5)$$

where $\hat{n} = \vec{r}_{12}\big/\left|\vec{r}_{12}\right|$ is a unit vector in the direction of the vector joining the center of two particles, $\sigma\left(\hat{n},\omega_1,\omega_2\right)$ is the closest approach distance of ellipsoids, m is the magnitude of dipole moment and $\hat{m}_i$ is a unit vector along the dipole moment of ellipsoids and is given by:

$$\hat{m}_i = \sin\theta_i\cos\varphi_i\,\hat{i} + \sin\theta_i\sin\varphi_i\,\hat{j} + \cos\theta_i\,\hat{k} \qquad (6)$$

and

$$r_{12} = \sqrt{(x_2-x_1)^2 + (y_2-y_1)^2 + (z_2-z_1)^2} \qquad (7)$$

According to mean spherical approximation (MSA), we can define DCF for dipole-dipole interaction as [19,20]:

$$C_{dd}\left(\vec{r}_{12},\omega_1,\omega_2\right) = -\beta\,u_{dd}\left(\vec{r}_{12},\omega_1,\omega_2\right) \qquad (8)$$

Therefore, we have

$$C\left(\vec{r}_{12},\omega_1,\omega_2\right) = C_{HE}\left(\vec{r}_{12},\omega_1,\omega_2\right) - \beta\,u_{dd}\left(\vec{r}_{12},\omega_1,\omega_2\right) \qquad (9)$$

Since each molecule can be aligned in all directions, to simplify the problem we apply the restricted orientation model (ROM) and choose N available directions for each molecule; in this case the total solid angle ω can be written as [2]:

$$\omega_T = \int d\omega = \sum_{\alpha=1}^{N}\Delta\omega_\alpha \square N\Delta\omega \qquad (10)$$

For the density component within a particular direction and corresponding sector, $\rho_\alpha(\vec{r})$ we can write:

$$\int\limits_{\omega\ in\ \alpha} d\omega\rho\left(\vec{r},\omega\right) = \rho_\alpha(\vec{r}) \qquad (11)$$

In the homogeneous case for any position $\vec{r}$ we have:

$$\int d\omega\rho\left(\vec{r},\omega\right) = \rho_b = N\rho_\alpha(\vec{r}) \qquad (12)$$

By inserting Eq. (9) into Eq. (1), the dipolar contribution to the excess grand potential can be obtained as:

$$\beta\Delta\Omega_{dip}\left[\rho(\vec{r},\omega)\right] = \frac{\beta m^2}{2}\int d\vec{r}_1 d\vec{r}_2 d\omega_1 d\omega_2\left(\rho(\vec{r}_1,\omega_1) - \frac{\rho_b}{N}\right)\left(\rho(\vec{r}_2,\omega_2) - \frac{\rho_b}{N}\right)$$
$$\times\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}\{[3\left(\frac{x_2-x_1}{r_{12}}\sin\theta_1\cos\varphi_1\right) + \left(\frac{y_2-y_1}{r_{12}}\sin\theta_1\sin\varphi_1\right)$$
$$+\left(\frac{z_2-z_1}{r_{12}}\cos\theta_1\right)][(\frac{x_2-x_1}{r_{12}}\sin\theta_2\cos\varphi_2) + \left(\frac{y_2-y_1}{r_{12}}\sin\theta_2\sin\varphi_2\right)$$
$$+\left(\frac{z_2-z_1}{r_{12}}\cos\theta_2\right)] - [\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)]\} \qquad (13)$$

Now we consider a system of dipolar hard ellipsoids confined between two parallel hard walls and choose the z-axis normal to the walls. The excess grand potential per unit area with respect to its bulk value in the presence of dipole-dipole interaction can be written as:

$$\beta\Delta\Omega_A = \sum_\alpha\int dz_1\rho_\alpha(z_1)(\ln\frac{N\rho_\alpha(z_1)}{\rho_b} - 1) + \beta\sum_\alpha\int dz_1\rho_\alpha(z_1)V(z_1,\omega_\alpha) - \frac{1}{2}\sum_{\alpha,\beta}\int dz_1 dz_2 C_{\alpha\beta}(z_1-z_2)$$
$$\times[\rho_\alpha(z_1) - \frac{\rho_b}{N}][\rho_\beta(z_2) - \frac{\rho_b}{N}] + \frac{\beta m^2}{2}\sum_{\alpha,\beta}\int dz_1 dx_2 dy_2 dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}[\rho_\alpha(z_1) - \frac{\rho_b}{N}]$$
$$\times[\rho_\beta(z_2) - \frac{\rho_b}{N}]\{[3(\frac{x_2-x_1}{r_{12}}\sin\theta_{1\alpha}\cos\varphi_{1\alpha}) + (\frac{y_2-y_1}{r_{12}}\sin\theta_{1\alpha}\sin\varphi_{1\alpha}) + (\frac{z_2-z_1}{r_{12}}\cos\theta_{1\alpha})]$$
$$\times[(\frac{x_2-x_1}{r_{12}}\sin\theta_{2\beta}\cos\varphi_{2\beta}) + (\frac{y_2-y_1}{r_{12}}\sin\theta_{2\beta}\sin\varphi_{2\beta}) + (\frac{z_2-z_1}{r_{12}}\cos\theta_{2\beta})]$$
$$-[\cos\theta_{1\alpha}\cos\theta_{2\beta} + \sin\theta_{1\alpha}\sin\theta_{2\beta}\cos(\varphi_{1\alpha}-\varphi_{2\beta})]\} \qquad (14)$$

where

$$C_{\alpha\beta}(z_1-z_2) = \iint dx_2 dy_2 C_{\alpha,\beta}\left(\vec{r}_{12},\omega_{1\alpha},\omega_{2\beta}\right)$$

And indices α,β show directions of dipolar hard ellipsoids. If we minimize Eq. (14) with respect to the density $\rho_\alpha(z_1)$, the coupled integral equations of directional density profiles can be obtained as:

$$\rho_\alpha(z_1)=\frac{\rho_b}{N}\exp\{-\beta V(z_1,\omega_\alpha)+\sum_\beta\int dz_2 C_{\alpha\beta}(z_1-z_2)\left[\rho_\beta(z_2)-\frac{\rho_b}{N}\right]-\beta m^2\sum_\beta\int dx_2dy_2dz_2\Theta(r_{12}-\sigma)$$

$$\times\frac{1}{r_{12}^3}\left(\rho_\beta(z_2)-\frac{\rho_b}{N}\right)\{[3\left(\frac{x_2-x_1}{r_{12}}\sin\theta_{1\alpha}\cos\varphi_\alpha\right)+\left(\frac{y_2-y_1}{r_{12}}\sin\theta_{1\alpha}\sin\varphi_\alpha\right)+\left(\frac{z_2-z_1}{r_{12}}\cos\theta_{1\alpha}\right)]$$

$$\times[\left(\frac{x_2-x_1}{r_{12}}\sin\theta_{2\beta}\cos\varphi_{2\beta}\right)+\left(\frac{y_2-y_1}{r_{12}}\sin\theta_{2\beta}\sin\varphi_{2\beta}\right)+\left(\frac{z_2-z_1}{r_{12}}\cos\theta_{2\beta}\right)]$$

$$-[\cos\theta_{1\alpha}\cos\theta_{2\beta}+\sin\theta_{1\alpha}\sin\theta_{2\beta}\cos(\varphi_\alpha-\varphi_{2\beta})]\}$$

(15)

In the second step, we use the density profile, Eq. (2), considering the second term, $\delta\rho(\vec{r},\omega)$. Because each molecule has a dipole moment which may be aligned in any direction, therefore there is a local polarization $\vec{P}(\vec{r})$ which can be defined as:

$$\vec{P}(\vec{r})=\int d\omega\vec{m}\rho(\vec{r},\omega)=\sum_{\alpha=1}^{N}\vec{m}_\alpha\rho_\alpha(\vec{r})$$

(16)

The expression $\delta\rho(\vec{r},\omega)$ can be expanded in terms of the Legendre polynomials, $P_l(\theta)$, as [2]:

$$\delta\rho(\vec{r},\omega)=\sum_{l=0}^{\infty}a_l(\vec{r})P_l(\theta)$$

(17)

Since the confined dipolar hard ellipsoidal fluid is cylindrically symmetric about the *z*-axis and the DCF which has been used here is assumed to be a function of the first-order Legendre polynomial, only the term containing a_1 contributes in Eq. (17). So, we can write [14]:

$$\rho(\vec{r},\omega)=\rho_0(\vec{r},\omega)+\frac{\vec{m}.\vec{P}(\vec{r},\omega)}{m^2}$$

(18)

where $\rho_0(\vec{r},\omega)$ is the number density in the absence of dipole-dipole interaction and the second term is the contribution of the first order in polarization. Here, if we define $\rho_0(\vec{r},\omega)\equiv\rho(\vec{r},\omega)$ and substitute Eq. (18) in Eq. (1) after some mathematical manipulation, the excess grand potential is given by:

$$\beta\Delta\Omega=\int\int d\omega d\vec{r}\left[\rho(\vec{r},\omega)+\frac{\vec{m}.\vec{P}(\vec{r},\omega)}{m^2}\right](\ln\frac{N}{\rho_b}\left[\rho(\vec{r},\omega)+\frac{\vec{m}.\vec{P}(\vec{r},\omega)}{m^2}\right]-1)+\beta\int\int d\omega d\vec{r}[\rho(\vec{r},\omega)+\frac{\vec{m}.\vec{P}(\vec{r},\omega)}{m^2}]V(\vec{r},\omega)$$

$$-\frac{1}{2}\int\int d\omega_1 d\omega_2 d\vec{r}_1 d\vec{r}_2 C_{HE}(\vec{r}_{12},\omega_1,\omega_2)\left[\rho(\vec{r}_1,\omega_1)+\frac{\vec{m}.\vec{P}(\vec{r}_1,\omega_1)}{m^2}-\frac{\rho_b}{N}\right]\left[\rho(\vec{r}_2,\omega_2)+\frac{\vec{m}.\vec{P}(\vec{r}_2,\omega_2)}{m^2}-\frac{\rho_b}{N}\right]$$

$$+\frac{\beta m^2}{2}\int\int d\omega_1 d\omega_2 d\vec{r}_1 d\vec{r}_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}\left(\rho(\vec{r}_1,\omega_1)+\frac{\vec{m}.\vec{P}(\vec{r}_1,\omega_1)}{m^2}-\frac{\rho_b}{N}\right)\left(\rho(\vec{r}_2,\omega_2)+\frac{\vec{m}.\vec{P}(\vec{r}_2,\omega_2)}{m^2}-\frac{\rho_b}{N}\right)$$

$$\times\{\left(\frac{x_2-x_1}{r_{12}}\sin\theta_1\cos\varphi_1\right)+\left(\frac{y_2-y_1}{r_{12}}\sin\theta_1\sin\varphi_1\right)+\left(\frac{z_2-z_1}{r_{12}}\cos\theta_1\right)][\left(\frac{x_2-x_1}{r_{12}}\sin\theta_2\cos\varphi_2\right)$$

$$+\left(\frac{y_2-y_1}{r_{12}}\sin\theta_2\sin\varphi_2\right)+\left(\frac{z_2-z_1}{r_{12}}\cos\theta_2\right)]-[\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)]\}$$

(19)

In the following, by using some approximations similar to those suggested in reference [14], the entropy term, the first term in above expression, can be written as:

$$\int\int d\vec{r}d\omega\left[\rho(\vec{r},\omega)+\frac{\vec{m}.\vec{P}(\vec{r},\omega)}{m^2}\right](\ln\frac{N}{\rho_b}\left[\rho(\vec{r},\omega)+\frac{\vec{m}.\vec{P}(\vec{r},\omega)}{m^2}\right]-1)=\int\int d\vec{r}d\omega\rho(\vec{r},\omega)(\ln\frac{N}{\rho_b}\left[\rho(\vec{r},\omega)\right]-1)$$

$$+\frac{1}{2}\int\int d\vec{r}d\omega\frac{P^2(\vec{r},\omega)}{m^2\rho(\vec{r},\omega)}$$

Again, we consider a system of dipolar hard ellipsoids confined between two parallel hard walls and using above equation, the excess grand potential per unit area is written as:

$$\beta\frac{\Delta\Omega}{A}=\sum_\alpha\int dz_1\rho_\alpha(z_1)\left(\ln\frac{N\rho_\alpha(z_1)}{\rho_b}-1\right)+\frac{1}{2}\sum_\alpha\int dz_1\frac{P_\alpha^2(z_1)}{m^2\rho_\alpha(z_1)}+\beta\sum_\alpha\int dz_1[\rho_\alpha(z_1)+\frac{P_\alpha(z_1)A_\alpha}{m}]V(z_1,\omega_\alpha)$$

$$-\frac{1}{2}\sum_{\alpha\beta}\int\int dz_1dz_2 C_{\alpha\beta}(z_1-z_2)\left[\rho_\alpha(z_1)-\frac{\rho_b}{N}+\frac{P_\alpha(z_1)A_\alpha}{m}\right]\left[\rho_\beta(z_2)-\frac{\rho_b}{N}+\frac{P_\beta(z_2)A_\beta}{m}\right]$$

$$+\frac{\beta m^2}{2}\sum_{\alpha\beta}\int\int dx_2dy_2dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}\left(\rho_\alpha(z_1)-\frac{\rho_b}{N}+\frac{P_\alpha(z_1)A_\alpha}{m}\right)\left(\rho_\beta(z_2)-\frac{\rho_b}{N}+\frac{P_\beta(z_2)A_\beta}{m}\right)B_{\alpha\beta}$$

(20)

where A_α and $B_{\alpha,\beta}$ are given by:

$$A_\alpha=\sin\theta_\alpha\cos\varphi_\alpha+\sin\theta_\alpha\sin\varphi_\alpha+\cos\theta_\alpha$$

(21)

$$B_{\alpha\beta}=\{3[\left(\frac{x_2-x_1}{r_{12}}\sin\theta_{1\alpha}\cos\varphi_\alpha\right)+\left(\frac{y_2-y_1}{r_{12}}\sin\theta_{1\alpha}\sin\varphi_\alpha\right)+\left(\frac{z_2-z_1}{r_{12}}\cos\theta_{1\alpha}\right)][\left(\frac{x_2-x_1}{r_{12}}\sin\theta_{2\beta}\cos\varphi_{2\beta}\right)$$

$$+\left(\frac{y_2-y_1}{r_{12}}\sin\theta_{2\beta}\sin\varphi_{2\beta}\right)+\left(\frac{z_2-z_1}{r_{12}}\cos\theta_{2\beta}\right)]-[\cos\theta_{1\alpha}\cos\theta_{2\beta}+\sin\theta_{1\alpha}\sin\theta_{2\beta}\cos(\varphi_\alpha-\varphi_{2\beta})]\}$$

(22)

If we minimize the excess grand potential per unit area with respect to directional density $\rho_\alpha(z_1)$ and polarization, the equilibrium density and polarization satisfy the coupled integral equations below:

$$\rho_\alpha(z_1)=\frac{\rho_b}{N}\exp\{\frac{P^2_\alpha(z_1)}{2m^2\rho^2_\alpha(z_1)}-\beta V(z_1,\omega_\alpha)+\sum_\beta dz_2 C_{\alpha\beta}(z_1-z_2)\left[\rho_\beta(z_2)-\frac{\rho_b}{N}+\frac{P_\beta(z_2)A_\beta}{m}\right]$$

$$-\beta m^2\sum_\beta\int dx_2 dy_2 dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}\left[\rho_\beta(z_2)-\frac{\rho_b}{N}+\frac{P_\beta(z_2)A_\beta}{m}\right]B_{\alpha,\beta}\} \tag{23}$$

$$P_\alpha(z_1)=mA_\alpha\rho_\alpha(z_1)\{-\beta V(z_1,\omega_\alpha)+\sum_\beta dz_2 C_{\alpha\beta}(z_1-z_2)\left[\rho_\beta(z_2)-\frac{\rho_b}{N}+\frac{A_\beta P_\beta(z_2)}{m}\right]$$

$$-\beta m^2\sum_\beta\int dx_2 dy_2 dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}B_{\alpha,\beta}\left(\rho_\beta(z_2)-\frac{\rho_b}{N}+\frac{A_\beta P_\beta(z_2)}{m}\right)\} \tag{24}$$

Direct Correlation Function of Hard Ellipsoids

The DCF for hard ellipsoids, required for the above equations, has been calculated by Allen *et al.* [21]. They used Monte Carlo simulation to find the DCF of hard ellipsoids and compared the results with Marko's [22], which were in a reasonable agreement. Here, we use the improved Pynn-Wulf [23,24] expression for the DCF of hard ellipsoids proposed by Marko:

$$C\left(\vec{r}_{12},\omega_1,\omega_2\right)=C_{PY}\left(\frac{|\vec{r}_1-\vec{r}_2|}{\sigma\left(\hat{n},\omega_1,\omega_2\right)}\right)\left[1+\alpha P_2\left(\hat{\omega}_1.\hat{\omega}_2\right)\right] \tag{25}$$

where $P_2(\mu)=(3\mu^2-1)/2$ and α is obtained by the same procedure as proposed by Marko, C_{PY} is Percus-Yevick's DCF for hard spheres [25], $\sigma(\hat{n},\omega_1,\omega_2)$ is the closest approach of hard ellipsoids. The modified closest approach introduced by Rickayzen [26] is given by:

$$\sigma(\hat{n},\omega_1,\omega_2)=2b[1-\chi\frac{(\hat{r}_{12}.\hat{\omega}_1)^2+(\hat{r}_{12}.\hat{\omega}_2)^2-2\chi(\hat{r}_{12}.\hat{\omega}_1)(\hat{r}_{12}.\hat{\omega}_2)(\hat{\omega}_1.\hat{\omega}_2)}{1-\chi^2(\hat{\omega}_1.\hat{\omega}_2)^2}$$

$$+\frac{\lambda\left[(\hat{r}_{12}.\hat{\omega}_1)^2-(\hat{r}_{12}.\hat{\omega}_2)^2\right]^2}{1-\chi^2(\hat{\omega}_1.\hat{\omega}_2)^2}]^{-1/2} \tag{26}$$

where:

$$\chi=\frac{a^2-b^2}{a^2+b^2}\qquad,\qquad\lambda=1-\chi\frac{4b^2}{(a+b)^2} \tag{27}$$

Parameters *2a* and *2b* denote the lengths of major and minor axis of the ellipsoids. In the following, we assume *2b* is a

unit length. The mentioned DCF depends on the orientation of the molecules and in our calculation this function is used to solve the coupled integral equations and find the density and polarization profiles.

CALCULATION OF THE DENSITY AND POLARIZATION PROFILES

Now, we use Eq. (15) to find the density profile and Eqs. (23) and (24) to find density and polarization profiles. In these cases, the density and polarization profiles are only functions of *z* variable; the number density and polarization have nonzero value in between the walls and zero everywhere. Also, here it is assumed that the dipole moments are aligned in direction of major axis of ellipsoids. We consider the restricted orientation model (ROM) and assume the center of molecules can move between the walls and these molecules are aligned only in six particular directions $\pm x$, $\pm y$ and $\pm z$, where the notations ± 1, ± 2, ± 3 are used here, respectively. By applying the required symmetries, it can be written:

$$\rho_1(z)=\rho_2(z),\qquad\rho_{-1}(z)=\rho_{-2}(z),\qquad\rho_3(z)\neq\rho_{-3}(z)$$
$$P_{-1}(z)=P_{-2}(z),\qquad P_1(z)=P_2(z) \tag{28}$$

$$C_{\pm\alpha,\pm\beta}(z)=C_{\alpha,\beta}(z)$$
$$C_{13}(z)=C_{31}(z)=C_{32}(z)=C_{23}(z),\quad C_{11}(z)=C_{22}(z) \tag{29}$$

In Fig. 1, the geometry of dipolar hard ellipsoids to show their dipole moments and the closest approach and the confined ellipsoids in ROM model are presented.

At first, we obtain the integral equations of density profiles $\rho_1(z),\rho_{-1}(z),\rho_3(z),\rho_{-3}(z)$ from Eq. (15) as:

$$\rho_1(z_1)=\frac{\rho_b}{6}\exp\{2\{\int_{-(h/2-b)}^{h/2-b}dz_2\{C_{11}(z_1-z_2)+C_{12}(z_1-z_2)\}[\rho_1(z_2)+\rho_{-1}(z_2)-\frac{\rho_b}{3}]$$
$$+\int_{-(h/2-a)}^{h/2+a}dz_2 C_{13}(z_1-z_2)[\rho_3(z_2)+\rho_{-3}(z_2)-\frac{\rho_b}{3}]\}-\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b}dz_2$$
$$\times\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}[(3\frac{(x_1-x_2)^2}{r_{12}^2}+3\frac{(x_1-x_2)(y_1-y_2)}{r_{12}^2}-1)(\rho_1(z_2)-\rho_{-1}(z_2))$$
$$-\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a}dz_2\Theta(r_{12}-\sigma)3\frac{(x_1-x_2)(z_1-z_2)}{r_{12}^5}(\rho_3(z_2)-\rho_{-3}(z_2))]\} \tag{30}$$
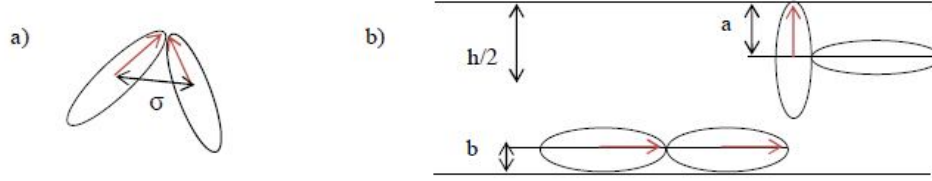
Fig. 1. a) Geometry of dipolar hard ellipsoids and their closest approach. b) Schematic representation of the dipolar hard ellipsoids confined between two hard walls, ROM model.

$$\rho_3(z_1) = \frac{\rho_b}{6}\exp\Big\{\frac{P_3^2(z_1)}{m^2\rho_3^2(z_1)} + 2\Big\{\int_{-(h/2-a)}^{h/2-a} dz_2 C_{33}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\frac{\rho_b}{3}) + \tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)]$$
$$+2\int_{-(h/2-b)}^{h/2-b} dz_2 C_{13}(z_1-z_2)[\rho_1(z_2)+\rho_{-1}(z_2)-\frac{\rho_b}{3}) + \tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)]\Big\} + \beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2$$
$$\times\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}[(3\frac{(x_1-x_2)(z_1-z_2)}{r_{12}^2}+3\frac{(z_1-z_2)(y_1-y_2)}{r_{12}^2})(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2))$$
$$+\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}(3\frac{(z_1-z_2)^2}{r_{12}^2}-1)\Big(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2))\Big]\Big\}$$
(31)

$$P_3(z_1)=m\rho_3(z_1)\Big\{2\Big\{\int_{-(h/2-b)}^{h/2-b} dz_2\{C_{11}(z_1-z_2)+C_{12}(z_1-z_2)\}[(\rho_1(z_2)+\rho_{-1}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)]$$
$$+\int_{-(h/2-a)}^{h/2-a} dz_2 C_{13}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)]\Big\}-\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2$$
$$\times\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}[(3\frac{(x_1-x_2)^2}{r_{12}^2}+3\frac{(x_1-x_2)(y_1-y_2)}{r_{12}^2}-1)(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2))$$
$$-\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2 3\frac{(x_1-x_2)(z_1-z_2)}{r_{12}^5}\Big(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)+P_{-3}(z_2))\Big]\Big\}$$
(32)

$$P_{-3}(z_1)=-m\rho_{-3}(z_1)\Big\{2\Big\{\int_{-(h/2-b)}^{h/2-b} dz_2\{C_{11}(z_1-z_2)+C_{12}(z_1-z_2)\}[(\rho_1(z_2)+\rho_{-1}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)]$$
$$+\int_{-(h/2-a)}^{h/2-a} dz_2 C_{13}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)]\Big\}+\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2$$
$$\times\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}[(3\frac{(x_1-x_2)^2}{r_{12}^2}+3\frac{(x_1-x_2)(y_1-y_2)}{r_{12}^2}-1)(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2))$$
$$+\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2 3\frac{(x_1-x_2)(z_1-z_2)}{r_{12}^5}\Big(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)+P_{-3}(z_2))\Big]\Big\}$$
(33)

where $\rho_1(z)$, $\rho_{-1}(z)$, $\rho_3(z)$, and $\rho_{-3}(z)$ represent density profiles of molecules along +x, -x, +z, and -z directions, respectively.

In the next step, we use Eq. (23) for our confined fluid to find the integral equations for the density profiles as follow:

$$\rho_1(z_1)=\frac{\rho_b}{6}\exp\Big\{\frac{P_1^2(z_1)}{m^2\rho_1^2(z_1)}+2\Big\{\int_{-(h/2-b)}^{h/2-b} dz_2\{C_{11}(z_1-z_2)+C_{12}(z_1-z_2)\}[(\rho_1(z_2)+\rho_{-1}(z_2)-\frac{\rho_b}{3})$$
$$+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)]+\int_{-(h/2-a)}^{h/2-a} dz_2 C_{13}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)]\Big\}$$
$$-\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}(3\frac{(x_1-x_2)^2}{r_{12}^2}+3\frac{(x_1-x_2)(y_1-y_2)}{r_{12}^2}-1)(\rho_1(z_2)-\rho_{-1}(z_2)$$
$$+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2))+-\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)3\frac{(x_1-x_2)(z_1-z_2)}{r_{12}^5}$$
$$\times\Big(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)+P_{-3}(z_2)]\Big\}$$
(34)

$$\rho_{-1}(z_1)=\frac{\rho_b}{6}\exp\Big\{\frac{P_{-1}^2(z_1)}{m^2\rho_{-1}^2(z_1)}+2\Big\{\int_{-(h/2-b)}^{h/2-b} dz_2\{C_{11}(z_1-z_2)+C_{12}(z_1-z_2)\}[(\rho_1(z_2)+\rho_{-1}(z_2)-\frac{\rho_b}{3})$$
$$+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)]+\int_{-(h/2-a)}^{h/2-a} dz_2 C_{13}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)]\Big\}$$
$$+\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}(3\frac{(x_1-x_2)^2}{r_{12}^2}+3\frac{(x_1-x_2)(y_1-y_2)}{r_{12}^2}-1)(\rho_1(z_2)-\rho_{-1}(z_2)$$
$$+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2))+\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)3\frac{(x_1-x_2)(z_1-z_2)}{r_{12}^5}$$
$$\times\Big(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)+P_{-3}(z_2)]\Big\}$$
(35)

$$\rho_3(z_1)=\frac{\rho_b}{6}\exp\Big\{\frac{P_3^2(z_1)}{m^2\rho_3^2(z_1)}+2\Big\{\int_{-(h/2-a)}^{h/2-a} dz_2 C_{33}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)]$$
$$+2\int_{-(h/2-b)}^{h/2-b} dz_2 C_{13}(z_1-z_2)[\rho_1(z_2)+\rho_{-1}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)]\Big\}-\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2$$
$$\times\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}[(3\frac{(x_1-x_2)(z_1-z_2)}{r_{12}^2}+3\frac{(z_1-z_2)(y_1-y_2)}{r_{12}^2})(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2))$$
$$-\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}(3\frac{(z_1-z_2)^2}{r_{12}^2}-1)\Big(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2))\Big]\Big\}$$
(36)

$$\rho_{-3}(z_1)=\frac{\rho_b}{6}\exp\Big\{\frac{P_{-3}^2(z_1)}{m^2\rho_{-3}^2(z_1)}+2\Big\{\int_{-(h/2-a)}^{h/2-a} dz_2 C_{33}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)]$$
$$+2\int_{-(h/2-b)}^{h/2-b} dz_2 C_{13}(z_1-z_2)[\rho_1(z_2)+\rho_{-1}(z_2)-\frac{\rho_b}{3})+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)]\Big\}+\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2$$
$$\times\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}[(3\frac{(x_1-x_2)(z_1-z_2)}{r_{12}^2}+3\frac{(z_1-z_2)(y_1-y_2)}{r_{12}^2})(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2))$$
$$+\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)\frac{1}{r_{12}^3}(3\frac{(z_1-z_2)^2}{r_{12}^2}-1)\Big(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2))\Big]\Big\}$$
(37)

and we obtain the polarization profiles from Eq. (24) as:

$$
\begin{aligned}
P_1(z_1) = m\rho_1(z_1)\{2\{\int_{-(h/2-b)}^{h/2-b} dz_2 \{C_{11}(z_1-z_2)+C_{12}(z_1-z_2)\}[(\rho_1(z_2)+\rho_{-1}(z_2)-\tfrac{\rho_b}{3})+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)] \\
+\int_{-(h/2-a)}^{h/2-a} dz_2 C_{13}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\tfrac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2))]\}-\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2 \\
\times\Theta(r_{12}-\sigma)\tfrac{1}{r_{12}{}^3}(3\tfrac{(x_1-x_2)^2}{r_{12}{}^2}+3\tfrac{(x_1-x_2)(y_1-y_2)}{r_{12}{}^2}-1)(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2)) \\
-\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)3\tfrac{(x_1-x_2)(z_1-z_2)}{r_{12}{}^5}\left(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)+P_{-3}(z_2))\right)\}\}
\end{aligned}
$$

$$(38)$$

$$
\begin{aligned}
P_{-1}(z_1) = -m\rho_{-1}(z_1)\{2\{\int_{-(h/2-b)}^{h/2-b} dz_2 \{C_{11}(z_1-z_2)+C_{12}(z_1-z_2)\}[(\rho_1(z_2)+\rho_{-1}(z_2)-\tfrac{\rho_b}{3})+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2)] \\
+\int_{-(h/2-a)}^{h/2-a} dz_2 C_{13}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\tfrac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2))]\}+\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2 \\
\times\Theta(r_{12}-\sigma)\tfrac{1}{r_{12}{}^3}(3\tfrac{(x_1-x_2)^2}{r_{12}{}^2}+3\tfrac{(x_1-x_2)(y_1-y_2)}{r_{12}{}^2}-1)(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2)) \\
+\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)3\tfrac{(x_1-x_2)(z_1-z_2)}{r_{12}{}^5}\left(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)+P_{-3}(z_2))\right)]\}\}
\end{aligned}
$$

$$(39)$$

$$
\begin{aligned}
P_3(z_1) = m\rho_3(z_1)\{2\{\int_{-(h/2-a)}^{h/2-a} dz_2 C_{33}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\tfrac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)] \\
+2\int_{-(h/2-b)}^{h/2-b} dz_2 C_{13}(z_1-z_2)[\rho_1(z_2)+\rho_{-1}(z_2)-\tfrac{\rho_b}{3})+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2))]\}-\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2 \\
\times\Theta(r_{12}-\sigma)\tfrac{1}{r_{12}{}^3}(3\tfrac{(x_1-x_2)(z_1-z_2)}{r_{12}{}^2}+3\tfrac{(z_1-z_2)(y_1-y_2)}{r_{12}{}^2})(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2)) \\
-\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)\tfrac{1}{r_{12}{}^3}(3\tfrac{(z_1-z_2)^2}{r_{12}{}^2}-1)\left(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2))\right)]\}\}
\end{aligned}
$$

$$(40)$$

$$
\begin{aligned}
P_{-3}(z_1) = -m\rho_{-3}(z_1)\{2\{\int_{-(h/2-a)}^{h/2-a} dz_2 C_{33}(z_1-z_2)[(\rho_3(z_2)+\rho_{-3}(z_2)-\tfrac{\rho_b}{3})+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2)] \\
+2\int_{-(h/2-b)}^{h/2-b} dz_2 C_{13}(z_1-z_2)[\rho_1(z_2)+\rho_{-1}(z_2)-\tfrac{\rho_b}{3})+\tfrac{1}{m}(P_1(z_2)-P_{-1}(z_2))]\}+\beta m^2\int dx_2\int dy_2\int_{-(h/2-b)}^{h/2-b} dz_2 \\
\times\Theta(r_{12}-\sigma)\tfrac{1}{r_{12}{}^3}(3\tfrac{(x_1-x_2)(z_1-z_2)}{r_{12}{}^2}+3\tfrac{(z_1-z_2)(y_1-y_2)}{r_{12}{}^2})(\rho_1(z_2)-\rho_{-1}(z_2)+\tfrac{1}{m}(P_1(z_2)+P_{-1}(z_2)) \\
+\beta m^2\int dx_2\int dy_2\int_{-(h/2-a)}^{h/2-a} dz_2\Theta(r_{12}-\sigma)\tfrac{1}{r_{12}{}^3}(3\tfrac{(z_1-z_2)^2}{r_{12}{}^2}-1)\left(\rho_3(z_2)-\rho_{-3}(z_2)+\tfrac{1}{m}(P_3(z_2)-P_{-3}(z_2))\right)]\}\}
\end{aligned}
$$

$$(41)$$

By solving the above equations and applying the boundary condition, we can obtain density and polarization profiles of confined dipolar hard ellipsoids. These boundary conditions depend on the orientation of the molecules, so we can write the number density of molecules parallel to the walls, $\rho_{\parallel}$, and the molecules perpendicular to the walls, $\rho_{\perp}$, as:

$$
\begin{cases}
\rho_{\parallel}=0 & for \quad |z|>\left(\dfrac{h}{2}-b\right) \\[2mm]
\rho_{\perp}=0 & for \quad |z|>\left(\dfrac{h}{2}-a\right)
\end{cases}
$$

$$(42)$$

Since these molecules are confined between two parallel hard walls, the density profiles are zero outside the walls and the total density is the sum of directional densities, so we have only parallel and perpendicular densities and we can write [2]:

$$
\rho_{total}(z)=\sum_{\alpha=1}^{6}\rho_{\alpha}(z)=\rho_{\parallel}(z)+\rho_{\perp}(z)
$$

$$(43)$$

where

$$
\rho_{\perp}(z)=\rho_3(z)+\rho_{-3}(z) \quad , \quad \rho_{\parallel}(z)=2\rho_1(z)+2\rho_{-1}(z)
$$

$$(44)$$

As explained, we can obtain the number density and polarization profiles by using boundary conditions, Eq. (42), and the DCF for the fluid that was introduced in previous section.

The Effect of External Electric Field

If the molecules are inserted in an electric field, $\vec{E}(\vec{r})$, the following term is added to the excess grand potential:

$$
-\beta\int d\vec{r} E(\vec{r})P(\vec{r})
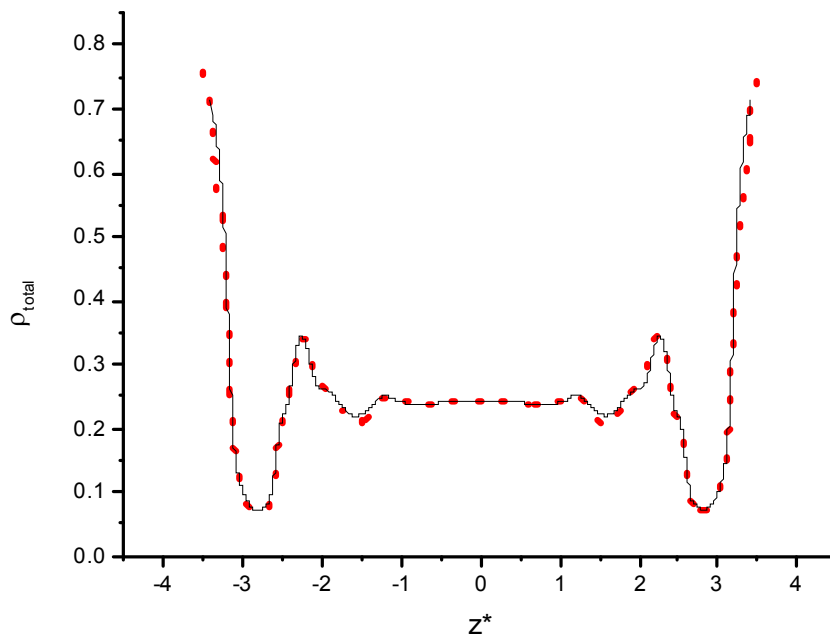$$

$$(45)$$

Using Eq. (16) we can write Eq. (45) as below:
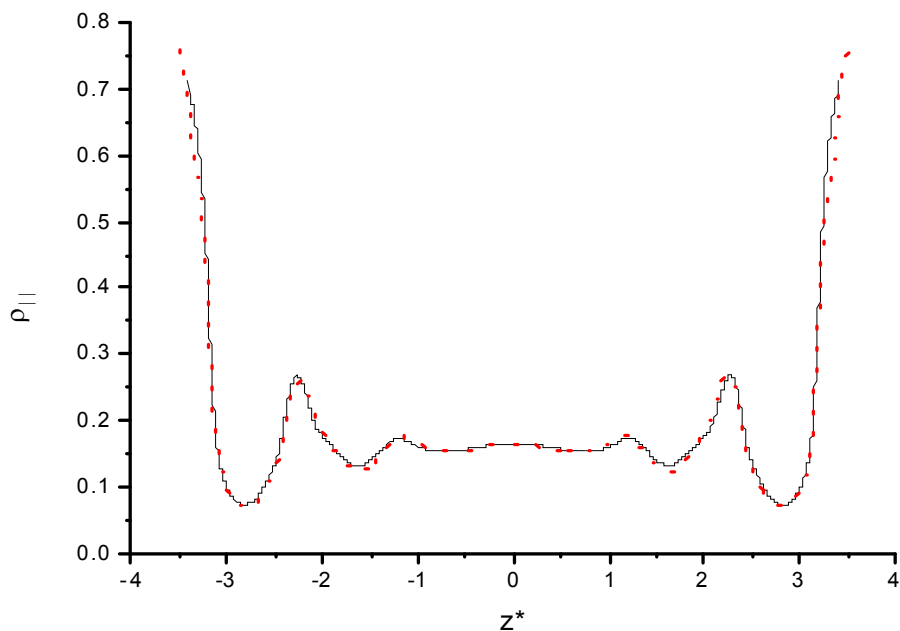
Fig. 2. The density profiles of molecules parallel to the walls for k = 2.2, $\rho_b^* = 0.239$ and h* = 8. The solid curve is calculated for dipolar hard ellipsoids for zero order and dots are calculated for the first order in polarization.
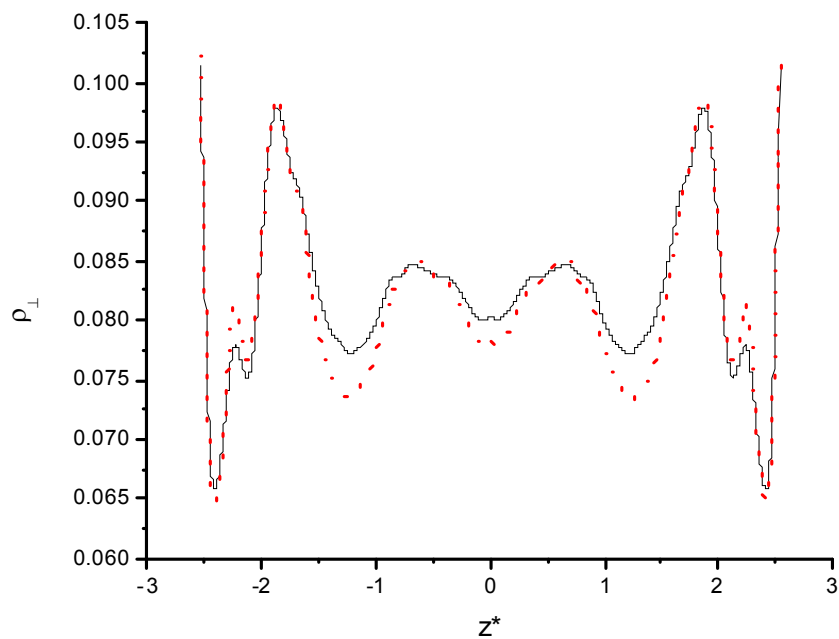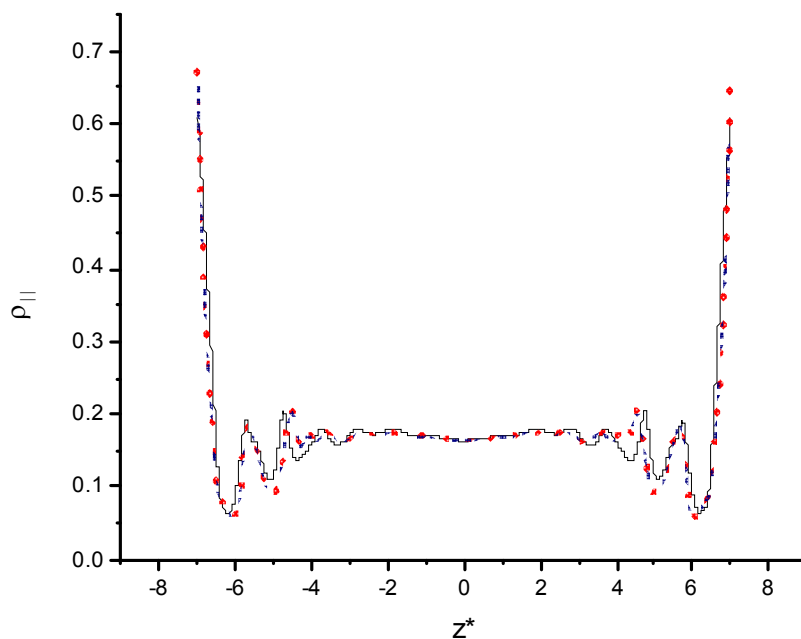

Fig. 3. As Fig. 2 but for the density profiles of molecules perpendicular to the walls.

Fig. 4. As Fig. 2 but for total number density of molecules.

Fig. 5. The density profiles of molecules parallel to the walls for k = 2.2, $\rho_b^* = 0.239$ and h* = 15. The solid curve is calculated for dipolar hard ellipsoid for zero order, and dots are calculated for the first order in polarization and dashed are in the presence of electric field.
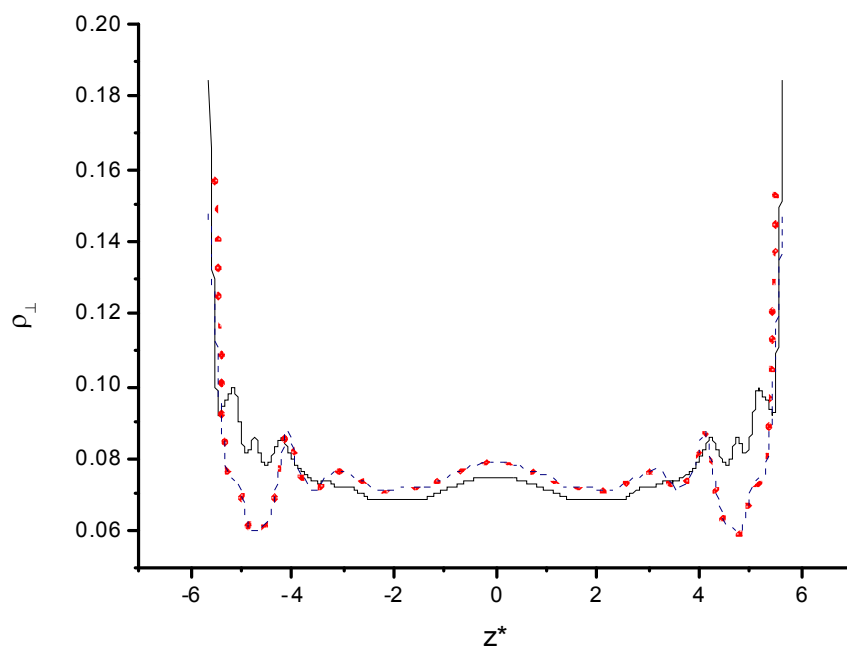
Fig. 6. As Fig. 5 but for the density profiles of molecules perpendicular to the walls.

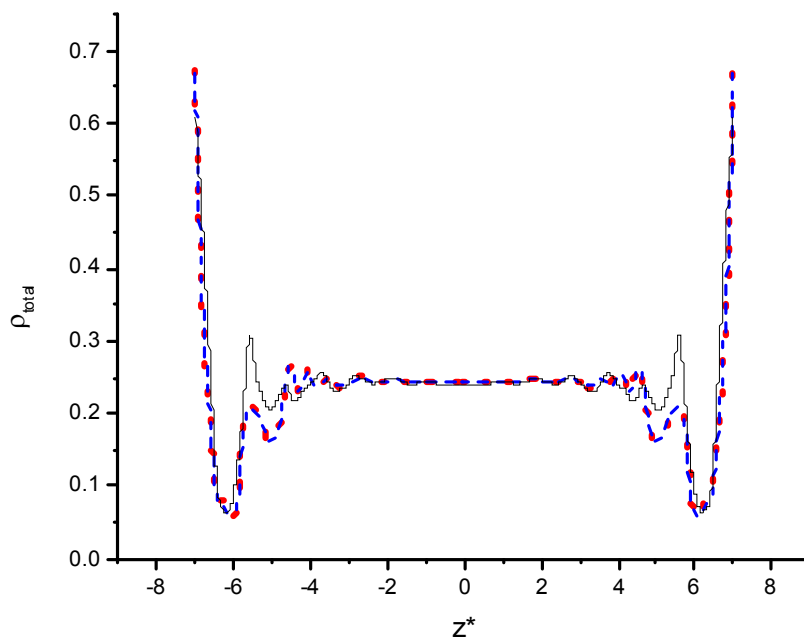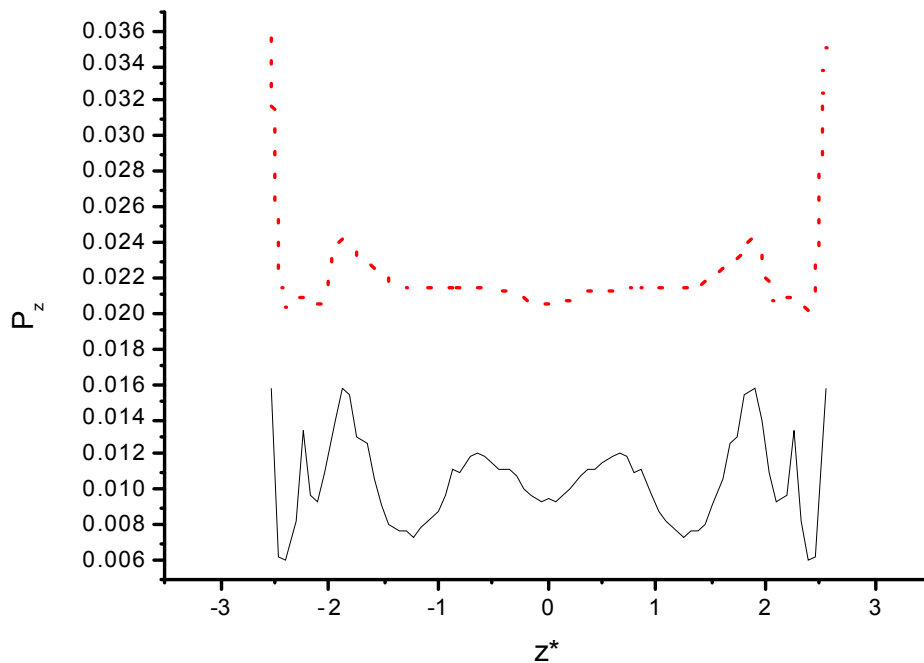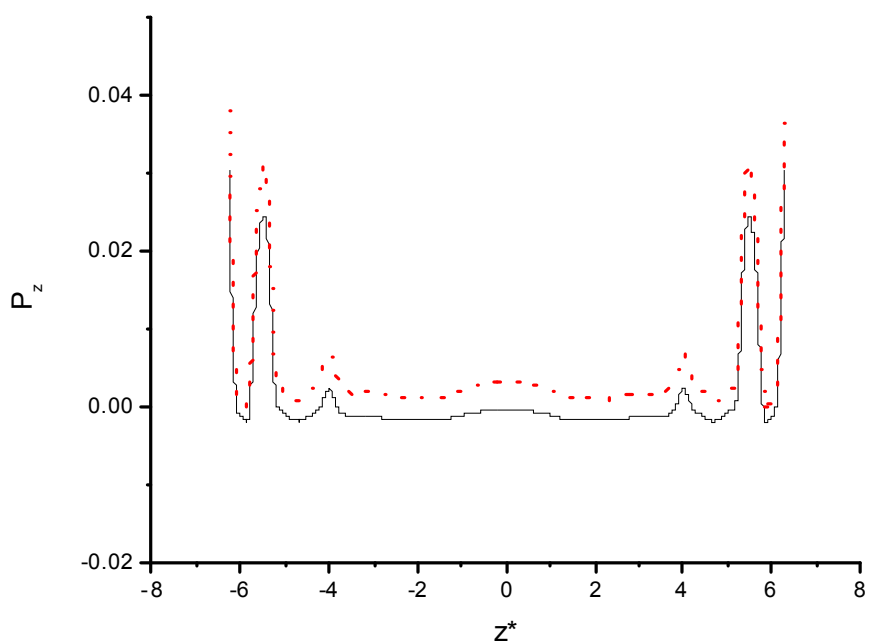**Fig. 7.** As Fig. 5 but for the total number density profiles of molecules.

Fig. 8. The perpendicular polarization of molecules for k = 2.2., $\rho_b^* = 0.239$ and h* = 8. Solid curve is calculated for dipolar hard ellipsoidal fluid in the absence of electric field and dots are calculated in the presence of electric field.

Fig. 9. As Fig. 8 but for h* = 15.

$$-\beta m \sum_\alpha \int d\vec{r} E_\alpha(\vec{r}) \rho_\alpha(\vec{r}) \cos\theta_\alpha \qquad (46)$$

If we assume that the electric field is along the z axis, perpendicular to the walls, the integral equations (36) and (37) are changed and the terms $-\beta m E_0$ +and $\beta m E_0$ are added to their right hand side, respectively. E_0 is the magnitude of electric field.

RESULTS AND DISCUSSION

The obtained integral equations could be solved numerically using the ROM model with N = 6 to obtain the density and polarization profiles of a dipolar hard ellipsoidal fluid confined between two parallel hard walls. As described in section 2.2, the DCF of a homogeneous hard ellipsoidal fluid is obtained using Eq. (25). In our calculations, these molecules can only be aligned in 6 directions. It is assumed that the major axes of the molecules are parallel or perpendicular to the walls. We obtained the density and polarization profiles for two different values of the reduced wall separation. At first, we solved the coupled integral Eq. (30) to (33) numerically to obtain the density profiles. The obtained reduced number densities of the molecules parallel and perpendicular to the walls are plotted in Figs. (2) and (3), the total density profile of the molecules is shown in Fig. (4). These densities are calculated for elongation k = 2.2, reduced bulk density ρ_b* = 0.239 and reduced separation of the walls h* = h/2b = 8. In these figures, the density profiles are also compared with the density profiles obtained by the first order approximation in polarization, Eqs. (34)-(37). When the major axes of the molecules are perpendicular to the walls, there are relatively large discrepancies at maximum and minimum of the density profiles while for the molecules parallel to the walls the differences are small. As clearly seen in these figures, the existence of higher peaks in the density oscillation is due to considering first order approximation in polarization. Then, by using Eqs. (34)-(41), we obtained the number density and polarization profiles of this system. Similar to Figs. (2)-(4), in Figs. (5), (6) and (7) the number density profiles are plotted as a function of z* = z/2b for k = 2.2, ρ_b* = 0.239 and h* = 15. As seen in these figures, for the density profiles calculated

from the first order in polarization, there are some shifts in the density curves compared to the case of zero order. When the major axes of the molecules are perpendicular to the walls, there is also a shift in the density in vertical direction while for the molecules parallel to the walls these differences are small. In these figures, the density profiles of dipolar hard ellipsoidal fluid in the presence of electric field are also shown. The values chosen for the reduced dipole moment and the reduced electric field are given by:

$$m^{*2} = \frac{\beta m^2}{4\pi\varepsilon_0\sigma^3} = 0.5, \qquad E_0^* = \frac{4\pi\varepsilon_0\sigma^3 E_0}{m} = 0.4 \qquad (47)$$

In this case, the calculated density profiles are plotted in Figs. (5)-(7) and the polarization profiles are shown in Figs. (8) and (9) for two reduce separations of the walls. In these figures the polarization profiles of dipolar hard ellipsoidal fluid in the presence and absence of electric field are compared.

According to the equation $\beta P = -\partial(\beta\Omega)/\partial V$ [27] for our system, we can write

$$\beta P_\alpha = -\frac{\partial(\beta\Omega)}{\partial h_\alpha} \qquad (48)$$

where h_α is the distance between the hard walls and P_α is the partial pressure of the ellipsoids which make angle θ_α with respect to z-axis. Inserting Eq. (14) into Eq. (48) and after some mathematics, the pressure at the wall can be obtained as:

$$\beta P(h) = \beta \sum_\alpha P_\alpha(h) = <\rho_w> \qquad (49)$$

In this equation $<\rho_w>$ is the average number density of the hard ellipsoids in all directions at the hard wall. Eq. (49) is satisfied by any fluid at contact with a hard surface [28]. As our calculation shows, we can obtain the partial reduced pressure from the directional densities of molecules at the wall ρ_α^ω as:

$$\beta P_\alpha(h) = \rho_\alpha^\omega(h) \qquad (50)$$

Table 1. The Densities and Pressures of Dipolar Hard Ellipsoidal Fluid at the Hard Wall

$h^* = h/2b$	$\rho_\parallel$	$\rho_\perp$	$<\rho_w>$	βP
8	0.75886	0.10232	0.43059	0.43059
15	0.67267	0.14739	0.41003	0.41003

In Table 1, the calculated pressures and densities of dipolar hard ellipsoidal fluid at hard wall for two different separations of the walls are shown.

The density and polarization profiles of hard dipolar fluid confined between hard walls have been reported in reference [14]. In that article, it was shown that the spheres are located near the hard wall as a layer and the maximum of the profiles are located in the distance bigger than the diameter of sphere from the wall. About the dipolar hard ellipsoids, in ROM model, for the ellipsoids parallel to the wall, the maximum of the density profiles is located at the *3b* distance from the actual wall and for the ellipsoids perpendicular to the wall, the maximum of the density profile is located at *3a* distance from the wall. These locations are definitely affected by each other, because the parallel and perpendicular ellipsoids are existed together. .

CONCLUSIONS

The HNC density functional theory is used to consider dipolar hard ellipsoids confined between two parallel hard walls. At the first step, the excess grand potential with respect to its bulk as a unique functional of density was introduced. The DCF of homogeneous dipolar hard ellipsoidal fluid is the main required input. Then, we used two approximations for the density, zero and first order in polarization, to find the excess grand potential. The minimization of the excess grand potential with respect to the density and polarization gave us some coupled integral equations to obtain the number density and polarization profiles. We also used ROM model to find the density and polarization profiles between two parallel hard walls. We obtained density and polarization profiles for two different wall separations. The results showed that for the zero and

first order in polarization, the location of maximums and minimums of the density profiles are not changed but their amounts become bigger in the case of first order of polarization. Finally, when we applied the electric field, the location and the amount of the peaks of extremums, with respect to the absence of electric field, are not changed very much but the polarization profiles perpendicular to the walls are changed and become larger in the presence of electric field.

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