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Density profile and order parameter of a hard ellipsoidal fluid confined to a slit

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Abstract

The density profile and order parameter of a fluid of hard axially symmetric ellipsoids confined in between two parallel hard walls is obtained by using the density functional theory. The required input direct correlation function of the homogeneous fluid is calculated by the variational method introduced by Marko (1989 *Phys. Rev.* **39** 2050) and the modified closest approach method proposed by Rickayzen (1998 *Mol. Phys.* **95** 393). Here the restricted orientation model, ROM, is extended to study a fluid comprising molecules which can be aligned in more than six directions, making it more representative of a normal fluid. The density profiles, the average number density and order parameter are obtained for different values of density and elongations. The results are in agreement with the previous theory and available Monte Carlo simulation results.

1. Introduction

The structure of inhomogeneous simple fluids [1–3] as well as inhomogeneous molecular fluids [4–6] has been studied by using the density functional theory. Both perturbative [7–10] and non-perturbative [11, 12] approaches have been used. Rickayzen and co-workers used a perturbative density functional based on a series expansion in the number density to find the density of a molecular fluid and applied this method to hard spheres [2], Lennard-Jones particles [13], charged hard spheres [14], binary hard spheres [15] and a dipolar fluid [16] confined in between planar walls. They also used a similar density functional based on an expansion, up to second order in density, together with the analogue of the Percus–Yevick (PY) and hyper-netted chain (HNC) equations, to find the density profile of a fluid with non-spherical molecules [17, 18]. They introduced a simple model in which the molecules are free to move, but their orientations are restricted to a few discrete directions [19, 20]. They called this a restricted orientation model (ROM). This model has been used, together with an ansatz for the direct correlation function (DCF) of the homogeneous fluid, to obtain the density profile

of a fluid of hard cylinders [17] and hard axially symmetric ellipsoids [21]. The approximate density functional developed in [17] and [21] is adequate for describing the thermodynamic properties of the homogeneous as well as inhomogeneous isotropic state, but it needs some improvements for studying the properties of the nematic state. In this work we improved the density functional theory and extend the ROM model by increasing the number of allowed directions. Then we use this extended model to obtain the density profile and order parameter of a hard ellipsoidal fluid (HE) confined by parallel hard walls. The DCF of the HE fluid is obtained, for arbitrary directions of the molecules, using a variational method proposed by Marko [22] rather than using the ansatz introduced by Rickayzen and co-workers [18, 21]. In section 2 we discuss the required density functional theory and how to find the coupled density integral equations. In section 3 the DCF of a HE fluid is introduced and finally in section 4 we obtain and discuss the results.

2. Theory

We consider a system of hard axially symmetric ellipsoids confined between two parallel hard walls, separated by a distance h . We choose the z -axis normal to the wall. The excess, $\Omega[\rho]$, of the grand potential with respect to its bulk value can be expressed as a functional of number density, $\rho(z, w)$, where z is 0 midway between the walls and $w \equiv (\theta, \varphi)$ denotes the molecular orientation. In the HNC approximation the grand potential per unit area is given by [18]

$$\begin{aligned} \frac{\Omega[\rho]}{(k_B T)A} = & \int dz dw \rho(z, w) \left[\ln \left(\frac{w_T \rho(z, w)}{\rho_B} \right) - 1 \right] + \frac{1}{k_B T} \int dz dw \rho(z, w) v_e(z, w) \\ & - \frac{1}{2} \int dz_1 dw_1 dz_2 dw_2 c(z_1, w_1, z_2, w_2, \rho_B) \\ & \times \left(\rho(z_1, w_1) - \frac{\rho_B}{w_T} \right) \left(\rho(z_2, w_2) - \frac{\rho_B}{w_T} \right), \end{aligned} \quad (1)$$

where A is the area perpendicular to the z -axis, ρ_B is the bulk density of the fluid, $v_e(z, w)$ is the external potential and $c(z_1, w_1, z_2, w_2; \rho_B)$ is defined as

$$c(z_1, w_1, z_2, w_2; \rho_B) = \frac{1}{A} \int dx_1 dy_1 dx_2 dy_2 C(\mathbf{r}_1, w_1, \mathbf{r}_2, w_2; \rho_B) \quad (2)$$

where $C(\mathbf{r}_1, w_1, \mathbf{r}_2, w_2; \rho_B)$ is the DCF of the homogeneous fluid. In equation (1), w_T is the total angle available to each molecule:

$$w_T = \int dw. \quad (3)$$

We assume that each molecule can be aligned in $N = 2m^2$ different directions, $w_{\alpha\beta} \equiv (\theta_\alpha, \varphi_\beta)$, and choose

$$\cos \theta_\alpha = -1 + \frac{2\alpha + 1}{m} \quad \alpha = 0, 1, \dots, m - 1 \quad (4)$$

and

$$\varphi_\beta = \frac{\beta\pi}{m} \quad \beta = 0, \dots, 2m - 1. \quad (5)$$

Equations (4) and (5) help us to choose all molecules' directions with equal weighting and we could easily use equations (1) and (3) approximated by

$$w_T = \int dw \left[\sum_{\alpha=0}^{m-1} \sum_{\beta=0}^{2m-1} \delta(w - w_{\alpha\beta}) \right] \quad (6)$$

and the density component within a particular direction, $w_{\alpha\beta} = (\theta_\alpha, \varphi_\beta)$, is defined as

$$\rho_{\alpha\beta}(z) = \int dw \delta(w - w_{\alpha\beta}) \rho(z, w) \quad (7)$$

and

$$\int dw \rho(z, w) = \sum_{\alpha\beta} \rho_{\alpha\beta}(z). \quad (8)$$

In a homogeneous fluid we can write

$$\sum_{\alpha,\beta} \rho_{\alpha\beta}(z) = N \rho_{\alpha\beta}(z) = \rho_B. \quad (9)$$

By using the above equations, the grand potential per unit area can be written as

$$\begin{aligned} \frac{\Omega[\rho_{\alpha\beta}]}{(k_B T) A} &= \sum_{\alpha,\beta} \int_{-h_\alpha/2}^{h_\alpha/2} dz \rho_{\alpha\beta} \left[\ln \left(\frac{N \rho_{\alpha\beta}(z)}{\rho_B} \right) - 1 \right] \\ &+ \frac{1}{k_B T} \sum_{\alpha,\beta} \int_{-h_\alpha/2}^{h_\alpha/2} dz \rho_{\alpha\beta}(z) v_c(z, w_{\alpha\beta}) \\ &- \frac{1}{2} \sum_{\alpha,\beta} \sum_{\gamma\delta} \int_{-h_\alpha/2}^{h_\alpha/2} dz_1 \int_{-h_\gamma/2}^{h_\gamma/2} dz_2 c_{\alpha\beta\gamma\delta}(z_1 - z_2) \\ &\times \left(\rho_{\alpha\beta}(z_1) - \frac{\rho_B}{N} \right) \left(\rho_{\gamma\delta}(z_2) - \frac{\rho_B}{N} \right), \end{aligned} \quad (10)$$

where we have defined

$$c_{\alpha\beta\gamma\delta}(z_1 - z_2) \equiv c(z_1, w_{\alpha\beta}, z_2, w_{\gamma\delta}; \rho_B). \quad (11)$$

The function $c_{\alpha\beta\gamma\delta}(z_1 - z_2)$ depends on the z component of the distance between two molecules, and $\rho_{\alpha\beta}(z) = 0$ for $|z| > h_\alpha/2$, where

$$h_\alpha = h - b - (a - b) \text{abs}[\cos \theta_\alpha], \quad (12)$$

and where $2a$ and $2b$ denote lengths of major and minor axes of the ellipsoids. If we minimize equation (10) with respect to the density we get a coupled integral equation:

$$\rho_{\alpha\beta}(z) = \frac{\rho_B}{N} \exp \left(\sum_{\gamma=0}^{m-1} \sum_{\delta=0}^{2m-1} \int dz_1 c_{\alpha\beta\gamma\delta}(z_1 - z) \left(\rho_{\gamma\delta}(z_1) - \frac{\rho_B}{N} \right) \right). \quad (13)$$

Symmetry about the z axis implies that for any value of the angle φ_β the density profiles are equal. Thus φ_β can be taken to be zero, and equation (13) can be written as

$$\rho_{\alpha 0}(z) = \frac{\rho_B}{N} \exp \left[\sum_{\gamma=0}^{m-1} \int dz_1 \left(\rho_{\gamma 0}(z_1) - \frac{\rho_B}{N} \right) \sum_{\delta=0}^{2m-1} c_{\alpha 0 \gamma \delta}(z_1 - z) \right]. \quad (14)$$

These coupled equations give the density of a non-uniform fluid in terms of the DCF of the homogeneous fluid. The choice of the DCF for hard ellipsoids is discussed in section 3, and the solution to the equations is presented in section 4.

3. The direct correlation function of hard ellipsoids

The DCF of hard ellipsoids required in equation (11) is calculated by means of the modified hard Gaussian overlap potential, given as [23–25]

$$U_{12}(\mathbf{r}_{12}, w_1, w_2) = \begin{cases} 0 & \text{if } r_{12} \geq R(\hat{r}_{12}, w_1, w_2) \\ \infty & \text{if } r_{12} < R(\hat{r}_{12}, w_1, w_2) \end{cases} \quad (15)$$

where $w_i = (\theta_i, \varphi_i)$ are polar and azimuthal angles describing the orientation of the major axis of particle i and $\hat{r}_{12} = \mathbf{r}_{12}/r_{12}$ is a unit vector along the line connecting the centres of the two particles. The modified closest approach parameter, $R(\hat{r}_{12}, w_1, w_2)$, introduced by Rickayzen [24], is given by

$$\frac{4b^2}{R^2} = \frac{1 - \chi[(\hat{r}_{12} \cdot \hat{w}_1)^2 + (\hat{r}_{12} \cdot \hat{w}_2)^2] - 2\chi^2(\hat{r}_{12} \cdot \hat{w}_1)(\hat{r}_{12} \cdot \hat{w}_2)(\hat{w}_1 \cdot \hat{w}_2)}{1 - \chi^2(\hat{w}_1 \cdot \hat{w}_2)} + \frac{\lambda[(\hat{r}_{12} \cdot \hat{w}_1)^2 - (\hat{r}_{12} \cdot \hat{w}_2)^2]}{1 - \chi^2(\hat{w}_1 \cdot \hat{w}_2)} \quad (16)$$

where

$$\chi = \frac{(k^2 - 1)}{(k^2 + 1)}. \quad (17)$$

In these equations, the elongation k is equal to a/b , and

$$\hat{w}_i = (\cos \varphi_i \sin \theta_i, \sin \varphi_i \sin \theta_i, \cos \theta_i) \quad (18)$$

with

$$\lambda = 1 - \chi - \frac{4b^2}{(a+b)^2}. \quad (19)$$

For closest approach, equation (16) gives the surface of the Mayer volume closer to an ellipsoid than the one introduced by Berne and Pechukas [23]. This point has been discussed by Rickayzen [24].

The DCF of a fluid of hard ellipsoids has been calculated by Allen *et al* [26] using the Monte Carlo simulation method. They compared their results with those obtained using various theories, and found the DCF given by Marko was closer to their simulation results than the others. Here we use the improved Pynn–Wulf [27, 28] expression for the DCF of hard ellipsoids proposed by Marko:

$$C(r_{12}, w_1, w_2) = C_{\text{PY}} \left(\left[\frac{|\mathbf{r}_2 - \mathbf{r}_1|}{R(\hat{r}_{12}, w_1, w_2)} \right] \right) [1 + \alpha p_2(\hat{w}_1 \cdot \hat{w}_2)] \quad (20)$$

where $p_2(t) = (3t^2 - 1)/2$, $C_{\text{PY}}(r)$ is the Percus–Yevick DCF [7] for hard spheres and $R(\hat{r}_{12}, w_1, w_2)$ is the closest approach of hard ellipsoids defined in equation (16). The parameter α is obtained by the same procedure as proposed by Marko. We also calculated the DCF of hard ellipsoids using the method of Letz and Latz [29]. The results are in agreement with those obtained by the Marko theory.

4. Results and discussion

As previously mentioned, in order to perform the calculation, we assume an isotropic state, $\eta(\text{packing fraction}) = \frac{4}{3}\pi ab^2\rho < 0.3$. We expect this to be true in the middle of the walls for $h > 40b$. This assumption is verified by our calculation since the angle-averaged number density, $\rho_{\text{ave}}(z) = [1/4\pi] \int \rho(z, w) dw$, is obtained to be ρ_{B} , and the order parameter, $Q_{zz}(z) = [1/4\pi] \int \rho(z, w) p_2(w) dw / \rho_{\text{ave}}(z)$, to be zero. As described in sections 2 and 3, the DCF of a homogeneous HE fluid is obtained using equation (20) and the variational method proposed by Marko [22]. Then the coupled integral equations, equation (14), are solved numerically to find the density profiles of an HE fluid confined between parallel hard walls. In our calculations, the number of allowed molecular directions is taken to be 6, 128 and 512 in space. We first consider $N = 6$ directions. In this case we do not need to use equations (4)–(6) and the major axes of the molecules are assumed to be parallel or perpendicular to the

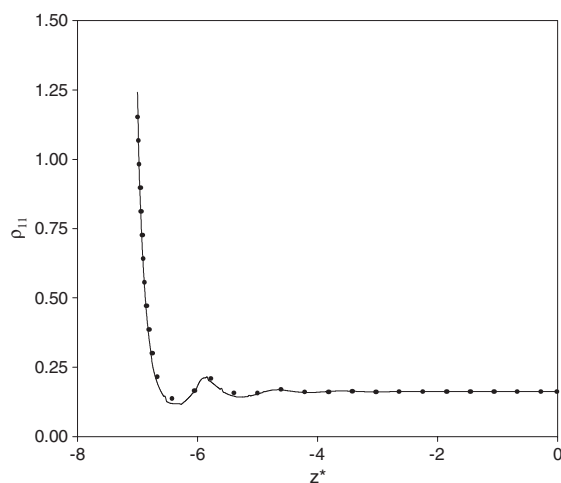


Figure 1. Number density profiles of the molecules parallel to the walls as a function of reduced distance from the wall, z^* for $k = 2.2$, $\rho_b = 0.24$ and $N = 6$. The solid curve is our calculation and the points are from Calleja and Rickayzen [16].

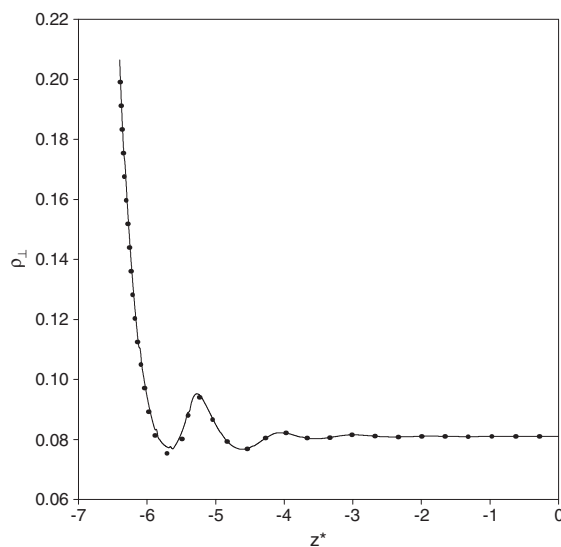


Figure 2. As figure 1 but for the number density of the molecules perpendicular to the walls.

walls. We obtain the number densities of the molecules parallel, $\rho_{\parallel} = 4\rho_1$, and perpendicular, $\rho_{\perp} = 2\rho_3$, to the walls. In figures 1 and 2 for elongation $k = 2.2$, $\rho_b = 0.24$ and the separation of the walls $h^* = h/2b = 15$, these densities are compared with the results obtained by Calleja and Rickayzen [21] from their ROM model. The results are in agreement. Now we extend the Rickayzen ROM model to the case where the number of restricted orientations is more than six. We first consider $m = 8$, giving $N = 128$. The density profiles are calculated for elongation $k = 2.2$, and the separation of the walls is $h^* = h/2b = 20$. In figure 3 the density profiles of the molecules are plotted as a function of the reduced coordinate $z^* = z/(2b)$, for a bulk density, $\rho_B = 0.24$. The density profiles of the molecules are shown in the directions given by

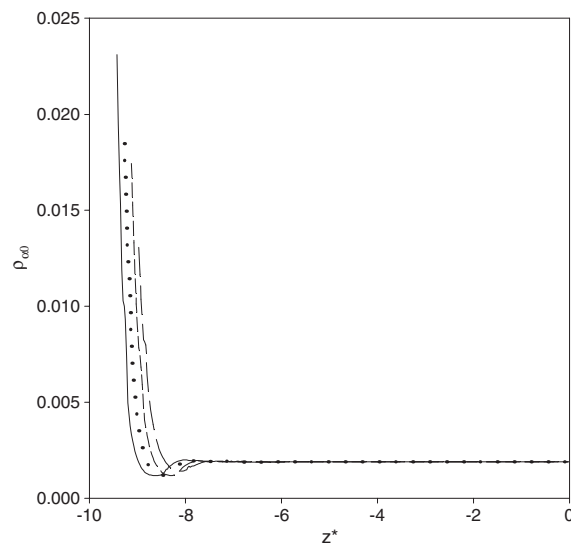


Figure 3. The number density profiles of the molecules as a function of z^* for $k = 2.2$, $\rho_b = 0.24$ and $N = 128$. The solid, dotted, short dashed and long dashed curves are due to $\cos \theta = 1/8, 3/8, 5/8$ and $7/8$, respectively, where $\phi = 0.0$.

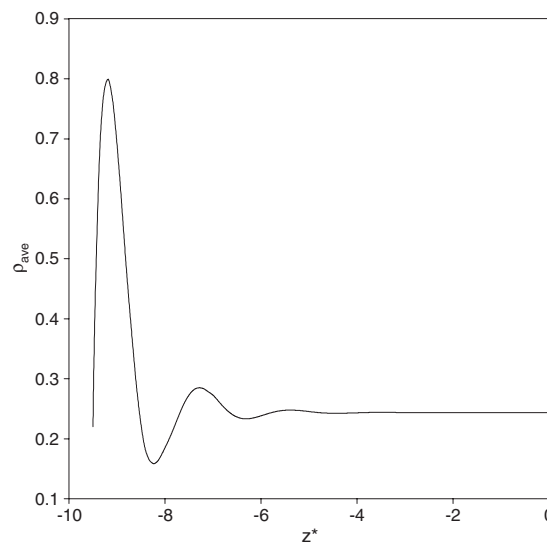


Figure 4. The average number density profile of the molecules as a function of z^* for $k = 2.2$, $\rho_b = 0.24$ and $N = 512$.

$\cos \theta_\alpha = 1/8, 3/8, 5/8$ and $7/8$, and $\phi = 0.0$. As shown in this figure, when $\cos \theta$ approaches zero, where the major axes of the molecules are nearly parallel to the walls, the number density of molecules close to the walls is bigger than the number density of the molecules in other directions. Next the results for $m = 16$, corresponding to $N = 512$, are shown, for which the fluid is more representative of the normal one. In figure 4 the angle-averaged number density is plotted as a function of z^* for $k = 2.2$, $\rho_B = 0.24$ and $h^* = h/2b = 20$. The order parameter

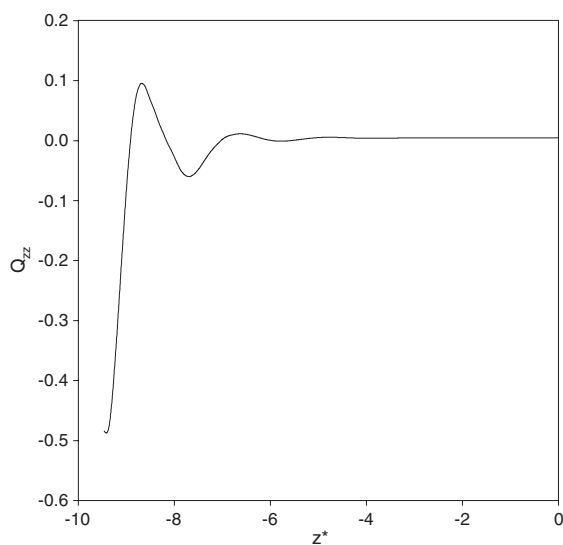


Figure 5. Order parameter $Q_{zz}(z)$ as a function of z^* for $k = 2.2$, $\rho_b = 0.24$ and $N = 512$.

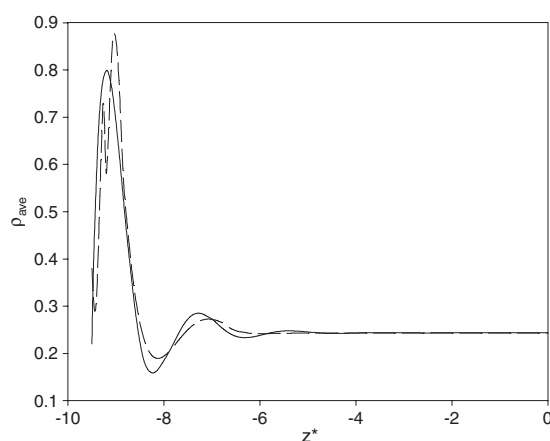


Figure 6. The average number density profile of the molecules as a function of z^* for $k = 2.2$, $\rho_b = 0.24$. The solid and dashed curves are for $N = 512$ and 128 respectively.

is also calculated for the same parameters and is plotted in figure 5. Now we obtain some more results for comparison. In figure 6, for the same parameters as used in figure 4, we have compared the angle-averaged density profiles of $N = 128$ and 512 . Due to the small number of allowed molecular orientations, the curve with $N = 128$ has some sharp peaks close to the wall, whereas the $N = 512$ curve has a smooth extremum. For the same parameters as used in figure 4, we have also compared the density profiles for $\rho_B = 0.16$ and $\rho_B = 0.24$ in figure 7. In this figure, for higher bulk densities, more particles are arranged in more layers and the amplitudes of the density oscillations are greater.

There are no published computer simulation results for confined hard ellipsoids introduced in section 2, equation (12), that can be directly compared with ours. Therefore we compare

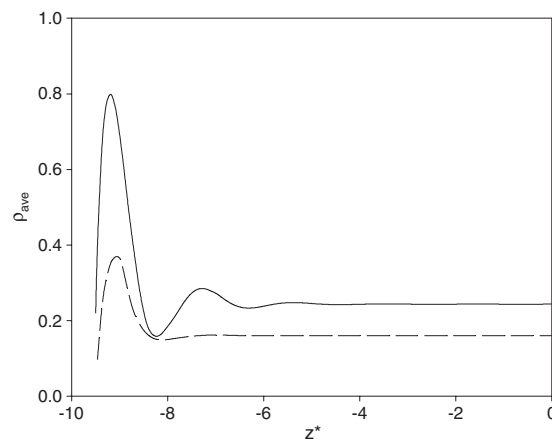


Figure 7. The average number density profile of the molecules as a function of z^* for $k = 2.2$, and $N = 512$. The solid and dashed curves are due to $\rho_b = 0.24$ and $\rho_b = 0.16$ respectively.

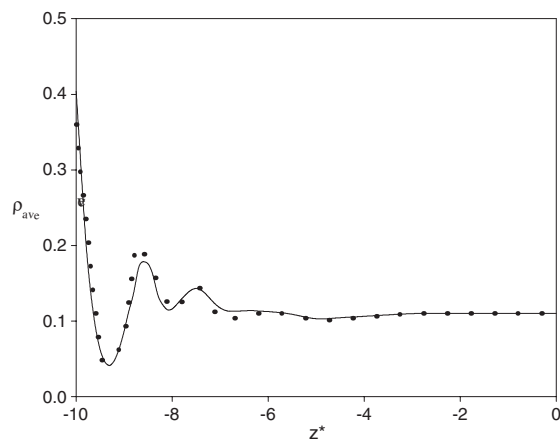


Figure 8. As figure 4 but for $k = 5$, $\rho_b = 0.11$. The solid curve is our calculation and the dots are from the Monte Carlo simulation of Cleaver and Teixeira [5].

with results obtained using a hard needle-wall potential [5, 30].

$$U_i(\theta_i, z_i) = \begin{cases} 0 & \text{if } z_i - z_0 \geq L/2 \cos \theta_i \\ \infty & \text{if } z_i - z_0 < L/2 \cos \theta_i \end{cases} \quad (21)$$

where z_0 represents the location of the wall, z_i represent the locations of the molecules' centres and in the case of a hard wall we use $L = 2a$. For this particle-wall potential, we calculate the angle-averaged number density, ρ_{ave} , and the order parameter, Q_{zz} , for $k = 5$, $\rho_B = 0.11$ and $h^* = 20$. In figures 8 and 9, we compare the results with those obtained by Cleaver and Teixeira [5]. They are in good agreement.

The main conclusions of this article are as follows. First a new density functional theory is introduced for molecular fluids, as an extension of the ROM model, to get a set of coupled integral equations for the densities of the molecules in some certain directions in a confined molecular fluid. Second, these calculations can be extended to larger sets of restricted orientations and to other molecular interactions such as hard rods, Gay-Berne particles or

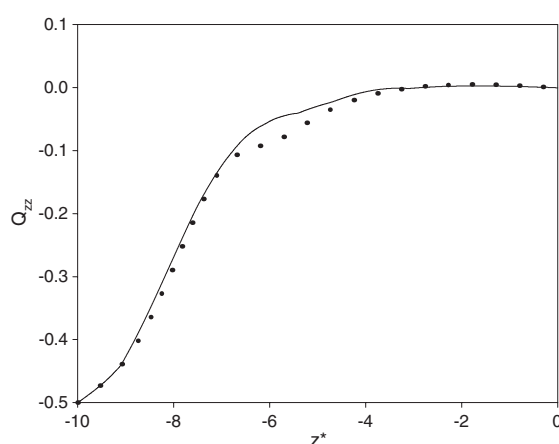


Figure 9. As figure 5 but for $k = 5$, $\rho_b = 0.11$. The solid curve is our calculation and the dots are from the Monte Carlo simulation of Cleaver and Teixeira [5].

molecular fluids with the dipole–dipole or other long-range interactions and also to different particle–wall interactions. Finally, we showed the planar alignment of rod-shaped molecules near hard walls, compared to the isotropic phase observed far from the walls.

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References

- [1] Evans R 1992 *Inhomogeneous Fluids* ed D Henderson (Amsterdam: Dekker)
- [2] Rickayzen G and Augousti A 1984 *Mol. Phys.* **52** 1355
- [3] Moradi M and Kavosh Tehrani M 2001 *Phys. Rev. E* **36** 21202
- [4] Chrzanowska A, Teixeira P I C, Ehrentraut H and Cleaver D J 2001 *J. Phys.: Condens. Matter* **13** 4715
- [5] Cleaver D J and Teixeira P I C 2001 *Chem. Phys. Lett.* **338** 1
- [6] van Roij R, Dijkstra M and Evans R 2000 *J. Chem. Phys.* **113** 7689
- [7] Hansen J P and McDonald I R 1976 *Theory of Simple Liquids* (London: Academic)
- [8] Choudhury N and Ghosh S K 1996 *J. Chem. Phys.* **104** 9563
- [8] Choudhury N and Ghosh S K 1996 *Phys. Rev. E* **53** 3847
- [9] Allen M P 1999 *Mol. Phys.* **96** 1391
- [10] Cheung D L and Schmid F 2004 *J. Chem. Phys.* **120** 9185
- [11] Yi J-Ho and Kim S-C 1997 *J. Chem. Phys.* **107** 8147
- [12] Tarazona P 1985 *Phys. Rev. A* **31** 2672
- [12] Tarazona P, Bettolo Marconi U M and Evans R 1987 *Mol. Phys.* **60** 573
- [13] Moradi M 1991 *J. Sci. I. R. Iran* **2** 74
- [14] Grimson M J and Rickayzen G 1981 *Mol. Phys.* **42** 767
- [15] Moradi M and Rickayzen G 1988 *Mol. Phys.* **66** 143
- [16] Moradi M and Kavosh Tehrani M 2001 *Iran. J. Sci. Technol., Trans. A* **25** 377
- [17] Rickayzen G 1993 *Mol. Phys.* **80** 1093
- [18] Kalpaxis P and Rickayzen G 1993 *Mol. Phys.* **80** 391
- [19] van Roij R, Dijkstra M and Evans R 2000 *Europhys. Lett.* **49** 350
- [20] Dijkstra M, van Roij R and Evans R 2001 *Phys. Rev. E* **63** 051703
- [21] Calleja M and Rickayzen G 1995 *J. Phys.: Condens. Matter* **7** 8839

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- [22] Marko J F 1989 *Phys. Rev. A* **39** 2050
 - [23] Berne B J and Pechukas P 1972 *J. Chem. Phys.* **64** 4213
 - [24] Rickayzen G 1998 *Mol. Phys.* **95** 393
 - [25] de Miguel E and Martin del Rio E 2003 *J. Chem. Phys.* **118** 1852
 - [26] Allen M P, Mason C P, de Miguel E and Stelzer J 1995 *Phys. Rev. E* **52** R25
 - [27] Pynn R 1974 *Solid State Commun.* **14** 29
 - [28] Wulf A 1977 *J. Chem. Phys.* **67** 2254
 - [29] Letz M and Latz A 1999 *Phys. Rev. E* **60** 5865
 - [30] Barmes F and Cleaver D J 2004 *Phys. Rev. E* **69** 61705