A generalized mean-spherical-approximation model for a hard-sphere fluid containing an arbitrary-size hard sphere: the density profiles near curved walls

1994 J. Phys.: Condens. Matter 6 8383

(http://iopscience.iop.org/0953-8984/6/41/004)

J. Phys.: Condens. Matter 6 (1994) 8383–8389. Printed in the UK

A generalized mean-spherical-approximation model for a hard-sphere fluid containing an arbitrary-size hard sphere: the density profiles near curved walls

M Ginoza, T Kinjo and M Yasutomi

Department of Physics, College of Science, University of the Ryukyus, Nishihara-Cho, Okinawa 903-01, Japan

Received 23 May 1994

Abstract. *On the basis of the analytical solution of the Ornstein–Zernike equation in our* previous paper, a model is presented for the calculation of the fluid density profiles near curved walls. The result of the model is compared with the computer-simulation data, and the agreement is reasonably good. An effect of wall curvature and the cavity free energy are discussed.

1. Introduction

In order to understand surface phenomena, the structure of a hard-sphere fluid near a hard wall has been studied intensively by means of computer simulations (Liu and Kalos 1974, Snook and Henderson 1978, Henderson and van Swol 1984, Lupkowski and van Swol 1990) and with a number of theoretical methods. The latter include theories starting from the Ornstein–Zernike (OZ) equation (Henderson *et al* 1976, Waisman *et al* 1976, Thompson *et al* 1980, Henderson *et al* 1980, Plischke and Henderson 1986). Much progress has been made in the understanding of the fluid structure: for example, the density profile near a flat wall.

In the theoretical works above, the total system of a fluid and a wall has been treated as a limiting mixture in which one of the species is dilute enough and infinitely large, namely, a solution consisting of solvent hard spheres and an infinitely large, solute hard sphere. Since a real wall generally may consist of many local curved surfaces with various finite curvatures, the size effect of the solute hard sphere on the structure would be interesting. Recently, Degreve and Henderson (1994) presented the simulation data of the fluid density profiles near a solute hard sphere of varying radius.

In our previous paper (Ginoza 1994), we presented the simple mean-spherical-approximation (MSA) solution of the OZ equation in a hard-sphere Yukawa fluid containing an arbitrary-size solute hard sphere. This solution prompts us to calculate the density profiles in the case of varying radius. The aim of the present paper is to use the solution and investigate the fluid density profiles near curved walls.

This paper is organized as follows: in section 2 and the appendix, we describe our model (the MSA solution) briefly. It is then applied to the calculation of density profiles near curved walls in section 3. The paper concludes with a summary and discussion in section 4.

0953-8984/94/418383+07$19.50

2. The model

Let us consider a fluid in a volume V with temperature T. The fluid consists of N_1 solvent hard spheres with diameter σ_1 and a solute hard sphere with diameter σ_2. We regard the fluid as a two-component mixture in the dilute limit

$$\rho_2\sigma_2^3 \to 0 \tag{1}$$

where ρ_2 is the number density of the solute spheres.

The static structure of the mixture is described by the total correlation function $h_{ij}(r)$ and the direct correlation function $c_{ij}(r)$, which are related to each other via the OZ equation. For the OZ equation, we shall apply the following closure relations:

$$g_{ij}(r) = h_{ij}(r) + 1 = 0 \qquad r < \sigma_{ij} = (\sigma_i + \sigma_j)/2 \tag{2a}$$

$$c_{ij}(r) = (K_{ij}/r)e^{-z(r-\sigma_{ij})} \qquad r > \sigma_{ij} \tag{2b}$$

where K_{ij} and z are parameters either given by the MSA condition or determined from other physical criteria in the case of the generalized MSA (Waisman 1973). In this paper, we will apply the latter case. In the limit of equation (1), the resultant structure of the mixture does not depend on K_{22}. Therefore, without any loss of physical meaning, we may choose K_{ij} to be (Ginoza 1994)

$$K_{ij} = KZ_iZ_j \qquad (i, j = 1, 2). \tag{3}$$

The OZ equation in the Baxter formalism (Baxter 1970) with the closure relations (2*a*) and (2*b*) has been solved (Blum and Høye 1978, Blum 1980). The solution is given in terms of the Baxter function, $Q_{ij}(r)$, as follows:

$$Q_{ij}(r) = Q_{ij}^0(r) + D_{ij}\,e^{-zr} \tag{4a}$$

where

$$Q_{ij}^0(r) = \begin{cases} \frac{1}{2}(r-\sigma_{ij})(r-\lambda_{ji})A_j + (r-\sigma_{ij})\beta_j + C_{ij}(e^{-zr} - e^{-z\sigma_{ij}}) & \text{for } \lambda_{ji} < r < \sigma_{ij} \\ 0 & \text{otherwise} \end{cases} \tag{4b}$$

where $\lambda_{ji} = (\sigma_j - \sigma_i)/2$. In the factorizable case like equation (3), the expressions for the coefficients in equations (4*a*) and (4*b*) can be extremely simple, given in terms of functions of a set of five parameters: two system parameters ($\eta(=\pi\rho\sigma_1^3/6)$, σ_1/σ_2) and three model parameters, ρ being the number density ($\rho = N_1/V$) (see the appendix).

On the basis of the model defined by the Baxter function above, thermodynamical properties and static structures of the fluid in consideration can be discussed: $h_{ij}(r)$ is obtained from the following integral equation (Baxter 1970);

$$2\pi r h_{ij}(r) = -\frac{d}{dr}Q_{ij}(r) + 2\pi\rho\int_{\lambda_{j1}}^{\infty} dt\, h_{i1}(|t-r|)(r-t)Q_{1j}(t) \tag{5}$$

where we used equation (1).

3. The density profiles near the curved walls

There are several ways of calculating $g_{ij}(r)$ from the Baxter function (see, for example, Chang and Sandler (1994) and references therein). In this paper, we perform the direct numerical integration of the following equation, which is obtained from equation (5) in the usual way:

$$2\pi r g_{ij}(r) = A_j(r - \sigma_j/2) + \beta_j - zC_{ij}e^{-zr} + 2\pi\rho\sigma_1 \int_0^x ds\,(\sigma_{i1} + \sigma_1 s)g_{i1}(\sigma_{i1} + \sigma_1 s)Q_{1j}(\lambda_{j1} + \sigma_1(x - s)) \qquad (6)$$

where x is defined by $r = \sigma_{ij} + \sigma_1 x$. From equation (6), we obtain immediately (Ginoza 1994)

$$g_{i1}(\sigma_{i1}) = (1/2\pi\sigma_{i1})[\sigma_i A_1/2 + \beta_1 - zC_{i1}e^{-z\sigma_{i1}}] = g_{i1}^{\mathrm{HS}} + c_{i1}(\sigma_{i1})(X_1/Z_1)X_i/Z_i \qquad (7)$$

where $g_{i1}^{\mathrm{HS}} = [1 + f(\eta)/(1 + \sigma_1/\sigma_i)]/\Delta$.

Now, our model is characterized by equation (2*b*), which is specified by three parameters: z, $c_{11}(\sigma_1)$ and $c_{12}(\sigma_{12})$. In order to investigate the density profiles, we shall determine these model parameters as functions of η and σ_1/σ_2 in the spirit of the generalized MSA (Waisman 1973). We adjust model parameters according to the procedure below. This procedure relies on an accurate approximation to the pressure, p, of the hard-sphere fluid (Carnahan and Starling 1969):

$$p/\rho k_{\mathrm{B}}T = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3. \qquad (8)$$

Let us first discuss how to determine z and $c_{11}(\sigma_1)$. For this purpose, we first note the following, well known thermodynamic relations for the hard-sphere fluid:

$$p/\rho k_{\mathrm{B}}T = 1 + 4\eta g_{11}(\sigma_1) \qquad (9)$$

$$\rho k_{\mathrm{B}}TK_T = S(0) \qquad (10)$$

where k_{B} is the Boltzmann constant. K_T is the isothermal compressibility, and with the use of equation (8) we can obtain

$$\rho k_{\mathrm{B}}TK_T = (1 - \eta)^4/(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4). \qquad (11)$$

$S(0)$ is the value of the static structure factor in the small-wave-vector limit, and in the Baxter formalism of the OZ equation it is well known that $S(0)$ is related to the coefficient, A_1, of $Q_{ij}(r)$ as

$$S(0) = (2\pi/A_1)^2. \qquad (12)$$

Now, once η is given, we can obtain the values of the left-hand sides of equations (9) and (10) from equations (8) and (11), respectively. On the other hand, the right-hand sides of equations (9) and (10) are given on the basis of our model: as a matter of fact, they are implicit functions of z and $c_{11}(\sigma_1)$. Therefore, equations (9) and (10) work as the criteria to determine z and $c_{11}(\sigma_1)$. Actually, we can obtain explicit functions for z and $c_{11}(\sigma_1)$ with the use of equations (7), (12), (A1), (A2), (A3), and (A4):

$$z\sigma_1 = [f_1(f_2 - f_0) - f_0\sqrt{f_1(f_1 + 2f_0 f_2 - f_2^2)}]/(f_2^2/2 - f_0 f_2) \tag{13}$$

with $f_0 = (1+2\eta)/\Delta$, $f_1 = 3(\eta/\Delta)^3$, and $f_2 = f_0 - \sqrt{1+4\eta+4\eta^2-4\eta^3+\eta^4}/\Delta$

$$\Gamma\sigma_1 = (f_1 - z\sigma_1 f_2/2)/f_0 \tag{14}$$

$$c_{11}(\sigma_1) = (f_1/6\eta)(Z_1/X_1)^2 \tag{15}$$

with the definition (A2*e*).

Let us next discuss the matter of $c_{12}(\sigma_{12})$. This means the determination of the η and σ_{12} dependences of $c_{12}(\sigma_{12})$. We first note the following exact relation:

$$p/\rho k_B T = g_{12}(\sigma_{12}) \qquad (\sigma_1/\sigma_{12} \to 0). \tag{16}$$

Equations (9) and (16) with equation (8) give a $g_{12}(\sigma_{12})$ η dependence at $\sigma_1/\sigma_{12} = 1$ and 0, respectively, but not otherwise. Following Degreve and Henderson (1994), let us assume that $g_{12}(\sigma_{12})$ is linear with respect to σ_1/σ_{12}. Since $g_{12}(\sigma_{12})$ is equal to $g_{11}(\sigma_1)$ at $\sigma_1/\sigma_{12} = 1$ and to $g_{12}(\infty)$ at $\sigma_1/\sigma_{12} = 0$, we obtain

$$g_{12}(\sigma_{12}) = g_{11}(\sigma_1)\sigma_1/\sigma_{12} + g_{12}(\infty)(1 - \sigma_1/\sigma_{12}). \tag{17}$$

Substitution of equation (A2*f*) into equation (7) and the use of equation (17) with equations (9) and (16) yield η and σ_{12} dependences of $c_{12}(\sigma_{12})$ as follows:

$$c_{12}(\sigma_{12}) = [\Phi_0(z\sigma_1, \eta, 1) + \Gamma\sigma_1\Phi_1(z\sigma_1, \eta, 1)][1 + \Gamma\sigma_1\phi_0(z\sigma_1, x)] \times \left[g_{\rm DH} - g_{12}^{\rm HS} - \frac{f_1}{6\eta}\left\{\frac{\sigma_1}{\sigma_{12}} - \frac{\sigma_2}{\sigma_{12}}\frac{\Phi_0(z\sigma_1, \eta, x) + \Gamma\sigma_1\Phi_1(z\sigma_1, \eta, x)}{1 + \Gamma\sigma_1\phi_0(z\sigma_1, x)}\right\}\right] \tag{18}$$

where $x = \sigma_1/\sigma_2$ and

$$g_{\rm DH} = (1/\Delta^3)[(1 - \eta/2)\sigma_1/\sigma_{12} + (1 + \eta + \eta^2 - \eta^3)(1 - \sigma_1/\sigma_{12})]. \tag{19}$$

Degreve and Henderson (1994) found that equation (17) with equations (9) and (16) gives a result in a quite good agreement with their computer-simulation result. Since equation (18) is equivalent to equation (17) in the logic of our model, the model inherits the same result.

Now, let us investigate the density profiles near the curved walls with the use of model parameters easily calculated from equations (13), (14), (15) and (18) with equation (19). In figure 1, the behaviour of the radial distribution function, $g_{12}(r)$, is shown as a function of x in the case of $\eta = 0.30$ and $\sigma_1/\sigma_2 = 0.0850$, where $r = \sigma_{12} + \sigma_1 x$. The full curve is the present result and the dotted curve is that of the simulation by Degreve and Henderson (1994). The agreement is reasonably good.

In figure 2, we show the σ_1/σ_2 dependence of $g_{12}(r)$ in the cases of $\eta = 0.40$, $\sigma_1/\sigma_2 = 1.0$ (the full curve), 0.1 (the dotted curve) and 0.01 (the dashed curve). From the figure, it is obvious that a decrease of σ_1/σ_2 results in an amplification of the oscillatory behaviour of $g_{12}(r)$. We also investigated the cases of $\sigma_1/\sigma_2 = 10^{-4}$ and 10^{-8}, but the value of $g_{12}(r)$ has no significant change from that of $\sigma_1/\sigma_2 = 0.01$. No change of the conclusion is introduced by other values of η, but the first minimum of g_{12} for $\sigma_1/\sigma_2 = 0.01$ becomes negative for $\eta > 0.45$. This is the usual breakdown of the theory.

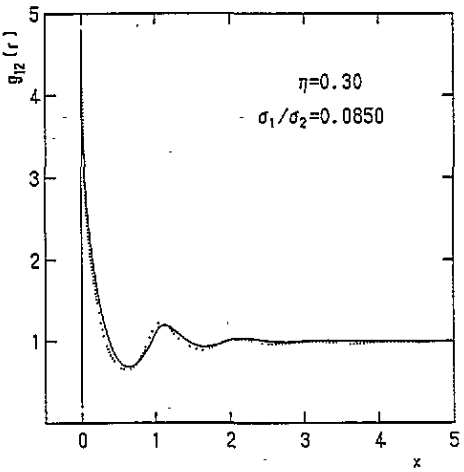

Figure 1. The radial distribution function, $g_{12}(r)$, as a function of x in the case of $\eta = 0.30$ and $\sigma_1/\sigma_2 = 0.0850$, where $r = \sigma_{12} + \sigma_1 x$. The full curve is the present result and the dotted one is that of the simulation by Degreve and Henderson (1994).

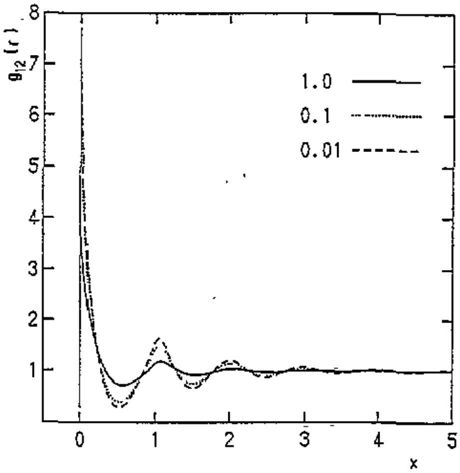

Figure 2. The σ_1/σ_2 dependence of $g_{12}(r)$ with $r = \sigma_{12} + \sigma_1 x$, where $\eta = 0.40$ and $\sigma_1/\sigma_2 = 1.0$ (the full curve), 0.1 (the dotted curve) and 0.01 (the dashed curve).

4. Summary and discussion

We have presented the generalized MSA model on the basis of the analytical solution in our previous paper (Ginoza 1994). With the use of model parameters determined by three criteria given by equations (9), (10) and (16) and the assumption given by equation (17), we have applied the model to the calculation of the radial distribution function between solvent and solute spheres, $g_{12}(r)$.

Regarding the contact value of $g_{12}(r)$, the model parameters are chosen so as to reproduce the approximate expression (equation (19)) by Degreve and Henderson (1994) which is in quite good agreement with their simulation data. We have compared the calculated behaviour of $g_{12}(r)$ with that of the simulation in the case of $\eta = 0.30$ and $\sigma_1/\sigma_2 = 0.0850$ (Degreve and Henderson 1994), and the agreement is reasonably good. The size effect of the solute sphere on $g_{12}(r)$ has been investigated, and it has been concluded that a decrease of σ_1/σ_2 results in an amplification of the oscillatory behaviour of $g_{12}(r)$, but no significant change in the region of $\sigma_1/\sigma_2 < 0.01$.

The cavity free energy, $W(r)$, is the reversible work required to produce a spherical cavity of radius r in the fluid. This is calculated by using the fact that the cavity affects the remainder of the fluid in the same way as the solute hard sphere in the fluid. Since it can be calculated from the contact value of $g_{12}(r)$ (Reiss *et al* 1959), it is interesting to compare the result of our model with the Monte Carlo result of Attard (1993). As described above, our model gives equation (17) for the expression of the contact value of $g_{12}(r)$. Using equation (17), we obtain

$$w(\lambda) = \beta W(r) = -\log(1-\eta) + 24\eta[\tfrac{1}{2}\{g_{11}(\sigma_1) - g_{12}(\infty)\}(\lambda^2 - \tfrac{1}{4}) + \tfrac{1}{3}g_{12}(\infty)(\lambda^3 - \tfrac{1}{8})] \tag{20}$$

where $\lambda = r/\sigma_1 + \frac{1}{2}$ and $g_{11}(\sigma_1)$ and $g_{12}(\infty)$ are given by equations (9) and (16) with equation (8), respectively. In table 1, we show the present result of equation (20), the

Monte Carlo result (Attard 1993) and the result of scaled-particle theory (Reiss *et al* 1959, Reiss 1965, Lebowitz *et al* 1965). The agreement is quite good in the region where the cavity is larger than the fluid hard spheres, $\lambda > 1$.

Table 1. The cavity free energy, $\beta W(r)$, in hard-sphere fluids at various densities, $\rho\sigma_1^3$: MC, Monte Carlo result (Attard 1993); P, present result by equation (20); SPT, scaled particle theory.

	$\rho\sigma_1^3 = 0.4$			$\rho\sigma_1^3 = 0.6$		
λ	MC	SPT	P	MC	SPT	P
0.55	0.4	0.33	0.32	0.5	0.54	0.49
0.65	0.7	0.59	0.56	1.0	1.04	0.90
0.75	1.0	0.98	0.93	1.8	1.82	1.61
0.85	1.6	1.52	1.46	2.9	2.95	2.67
0.95	2.2	2.24	2.17	4.4	4.49	4.15
1.05	3.1	3.16	3.08	6.4	6.53	6.12
1.15	4.3	4.31	4.22	8.9	9.10	8.65
1.25	5.7	5.72	5.62	11.9	12.30	11.79

Our model is characterized by equation (2*b*), where $c_{11}(r)$ and $c_{12}(r)$ have the same 'damping factor', $\exp(-zr)$. Henderson *et al* (1980) characterized $c_{11}(r)$ and $c_{12}(r)$ by different 'damping factors', but they treated the case of $\sigma_1/\sigma_2 = 0$.

Appendix. The coefficients of the Baxter functions

The expressions of the coefficients in equations (4*a*) and (4*b*) are as follows† (Ginoza 1994):

$$A_j = (2\pi/\Delta)[1 + f(\eta)\sigma_j/\sigma_1] + (\pi/\Delta)P_N a_j \tag{A1a}$$

$$\beta_j = (\pi/\Delta)\sigma_j + \Delta_N a_j \tag{A1b}$$

$$D_{ij} = -Z_i a_j \, e^{z\sigma_{ij}} \tag{A1c}$$

$$C_{ij} = (Z_i - (1/z)\, e^{-z\sigma_i} B_i e^{z\sigma_i/2}) a_j \, e^{z\sigma_{ij}} \tag{A1d}$$

where $\Delta = 1 - \eta$, $f(\eta) = 3\eta/\Delta$

$$\sigma_1^2 P_N = (12\eta/\pi z\sigma_1)[1 + z\sigma_1 + \Gamma\sigma_1 + f(\eta)]X_1 \tag{A2a}$$

$$\sigma_1 \Delta_N = -[4f(\eta)/(z\sigma_1)^2][1 + z\sigma_1/2 + \Gamma\sigma_1 + f(\eta)]X_1 \tag{A2b}$$

$$a_j/\sigma_1^2 = \pi\Gamma\sigma_1 X_j/3\eta X_1^2 \tag{A2c}$$

$$B_i e^{z\sigma_i/2} = -\Gamma X_i - (1 + z\sigma_i/2)\Delta_N - f(\eta)(\sigma_i/\sigma_1^2)X_1 \tag{A2d}$$

with

$$X_1/Z_1 = 1/[\Phi_0(z\sigma_1, \eta, 1) + \Gamma\sigma_1\Phi_1(z\sigma_1, \eta, 1)] \tag{A2e}$$

$$\frac{X_2}{Z_2} = \frac{1}{1 + \Gamma\sigma_1\phi_0(z\sigma_1, \sigma_1/\sigma_2)} + \frac{X_1\sigma_2}{Z_2\sigma_1}\left[\frac{\sigma_1}{\sigma_2} - \frac{\Phi_0(z\sigma_1, \eta, \sigma_1/\sigma_2) + \Gamma\sigma_1\Phi_1(z\sigma_1, \eta, \sigma_1/\sigma_2)}{1 + \Gamma\sigma_1\phi_0(z\sigma_1, \sigma_1/\sigma_2)}\right]. \tag{A2f}$$

† In equations (6*a*), (6*b*), (6*c*), (6*d*) and (6*g*) in our previous paper (Ginoza 1994), a_j is replaced erroneously by σ_j. For these equations read equations (A1*a*), (A1*b*), (A1*c*), (A1*d*) and (A2*c*), respectively.

Functions used above are defined as follows:

$$\phi_0(z,x) = (1 - e^{-z/x})/z \tag{A3a}$$

$$\psi_1(z,x) = [x - z/2 - (x + z/2)\,e^{-z/x}]/z^3 \tag{A3b}$$

$$\Phi_0(z,y,x) = x + f(y)\phi_0(z,x) - 4f(y)\psi_1(z,x)[1 + z/2 + f(y)] \tag{A3c}$$

and

$$\Phi_1(z,y,x) = x\phi_0(z,x) - 4f(y)\psi_1(z,x) \tag{A3d}$$

while the parameter Γ in equations (A2*a*–*f*) is the physical solution of the following equation (Ginoza 1994):

$$\Gamma^2 + z\Gamma + K\pi\rho X_1^2 = 0. \tag{A4}$$

References

Attard P 1993 *J. Chem. Phys.* **98** 2225
Baxter R J 1970 *J. Chem. Phys.* **52** 4559
Blum L 1980 *J. Stat. Phys.* **22** 661
Blum L and Høye J S 1978 *J. Stat. Phys.* **19** 317
Carnahan N F and Starling K E 1969 *J. Chem. Phys.* **51** 635
Chang J and Sandler S I 1994 *Mol. Phys.* **81** 735
Degreve L and Henderson D 1994 *J. Chem. Phys.* **100** 1606
Ginoza M 1994 *J. Phys.: Condens. Matter* **6** 1439
Henderson D, Abraham F F and Barker J A 1976 *Mol. Phys.* **31** 1291
Henderson D, Lebowitz J L, Blum L and Waisman E 1980 *Mol. Phys.* **39** 47
Henderson J R and van Swol F 1984 *Mol. Phys.* **51** 991
Lebowitz J L, Helfand E and Praestgaad E 1965 *J. Chem. Phys.* **43** 774
Liu K S and Kalos M H 1974 *Phys. Rev.* A **10** 303
Lupkowski M and van Swol F 1990 *J. Chem. Phys.* **93** 737
Plischke M and Henderson D 1986 *Proc. R. Soc.* A **404** 323
Reiss H 1965 *Adv. Chem. Phys.* **9** 1
Reiss H, Frisch H and Lebowitz J L 1959 *J. Chem. Phys.* **31** 369
Snook I K and Henderson D 1978 *J. Chem. Phys.* **68** 2134
Thompson N E, Isbister D J, Bearman R J and Freasier B C 1980 *Mol. Phys.* **39** 27
Waisman E 1973 *Mol. Phys.* **25** 45
Waisman E, Henderson D and Lebowitz J L 1976 *Mol. Phys.* **32** 1373