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Model for calculation of density profiles of a hard-sphere fluid near curved walls

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Abstract. The generalized mean spherical approximation model presented in the previous paper is extended to the case of the analytical solution of the Ornstein–Zernike equation with the closure relations which are given by Yukawa functions with different damping factors. The calculated result of the density profiles is compared with the recent computer simulation data.

1. Introduction

In the previous paper (Ginoza *et al* 1994), we presented a model for calculation of the fluid density profiles of a hard-sphere fluid near curved walls and compared the calculated density profiles with the recent computer simulation data of Degreve and Henderson (1994). The model is based on the analytical solution of the Ornstein–Zernike (OZ) equation with the closure relations consisting of Yukawa functions with the *same* damping factors (Ginoza 1994). The aim of this paper is to extend the model to the case of *different* damping factors. This attempt corresponds to an application of the two-Yukawa case of the mean spherical approximation (MSA) solution by Blum (1980).

2. The extended model

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

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

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 $c_{ij}(r)$: in the limit of equation (1), $h_{22}(r)$ and $c_{22}(r)$ are not needed. To the OZ equation, we shall apply the following closure relations with *different* damping factors:

$$g_{i1}(r) = h_{i1}(r) + 1 = 0 \qquad r < \sigma_{i1} = \frac{\sigma_i + \sigma_1}{2} \tag{2a}$$

$$c_{i1}(r) = \frac{K_{i1}}{r} \mathrm{e}^{-z_i(r-\sigma_{i1})} \qquad r > \sigma_{i1} \tag{2b}$$

where $i = 1,\ 2$. Therefore, the model is characterized by K_{11}, K_{21} $(= K_{12})$, z_1 and z_2, which are determined from other physical criteria according to the spirit of the generalized MSA (Waisman 1973a).

Let us write equation (2b) as follows:

$$c_{i1}(r) = \sum_{n=1}^{2} \frac{K_{i1}^{(n)}}{r} \mathrm{e}^{-z_n r} \qquad r > \sigma_{i1} \tag{3a}$$

where

$$\begin{aligned} &K_{11}^{(1)} = K_{11}\mathrm{e}^{z_1\sigma_1} \qquad K_{11}^{(2)} = 0 \\ &K_{21}^{(1)} = K_{12}^{(1)} = 0 \qquad K_{21}^{(2)} = K_{12}^{(2)} = K_{21}\mathrm{e}^{z_2\sigma_{21}}. \end{aligned} \tag{3b}$$

The OZ equation in the Baxter formalism with the closure relations (2a) and (3a) has been solved formally (Blum and Høye 1978, Blum 1980). The solution is given in terms of the Baxter function, $Q_{i1}(r)$, as follows:

$$Q_{i1}(r) = Q_{i1}^{0}(r) + \sum_{n=1}^{2} D_{i1}^{(n)} \mathrm{e}^{-z_n r} \tag{4a}$$

where

$$Q_{i1}^{0}(r) = \begin{cases} \frac{1}{2}(r-\sigma_{i1})(r-\lambda_{1i})A_1 + (r-\sigma_{i1})\beta_1 + \sum_{n=1}^{2} C_{i1}^{(n)}(\mathrm{e}^{-z_n r} - \mathrm{e}^{-z_n\sigma_{i1}}) \\ \qquad \text{for } \lambda_{1i} < r < \sigma_{i1}) \\ 0 \qquad \text{otherwise} \end{cases} \tag{4b}$$

where $\lambda_{1i} = (\sigma_1 - \sigma_i)/2$ and $i = 1,\ 2$. Note that there is no need to consider $Q_{22}(r)$ in the limit of equation (1).

Now, regarding the coefficients in equations (4a) and (4b), we first note that in the limit of equation (1), the OZ equation determining the static structure of the solvent does not couple to the solute: $h_{11}(r)$ (or $Q_{11}(r)$) is given by the MSA solution in the case of the pure fluid (Waisman 1973b, Blum and Høye 1978). The coefficients of the solution are determined by η $(=\pi\rho\sigma_1^3/6)$, K_{11} and z_1, ρ being the number density of solvent spheres. The most simple expressions for A_1, β_1, $D_{11}^{(1)}$ $(=D_{11})$ and $C_{11}^{(1)}$ $(=C_{11})$ are available in the previous paper (Ginoza 1994) with the replacement of z, Z_1 and K in that paper by z_1, unity and K_{11}, respectively, while $D_{11}^{(2)} = C_{11}^{(2)} = 0$ as shown below (see equation (6a)).

As for $D_{21}^{(n)}$ and $C_{21}^{(n)}$, they are determined by the following algebraic equations (Blum 1980, see also Ginoza 1986): in the limit of equation (1),

$$\frac{2\pi K_{i1}^{(n)}}{z_n} = D_{i1}^{(n)}[1 - \rho\widetilde{Q}_{11}(\mathrm{i}z_n)] \tag{5a}$$

$$C_{i1}^{(n)} = -D_{i1}^{(n)} + 2\pi\rho\widetilde{g}_{i1}(z_n)\frac{D_{11}^{(n)}}{z_n} \tag{5b}$$

$$\begin{aligned} &2\pi\widetilde{g}_{i1}(z_n)[1 - \rho\widetilde{Q}_{11}(\mathrm{i}z_n)] \\ &\quad = \left[\left(1 + \frac{z_n\sigma_i}{2}\right)A_1 + z_n\beta_1\right]\frac{\mathrm{e}^{-z_n\sigma_{i1}}}{z_n{}^2} - \sum_{m=1}^{2} C_{i1}^{(m)}\mathrm{e}^{-(z_n+z_m)\sigma_{i1}}\frac{z_m}{z_n+z_m} \end{aligned} \tag{5c}$$

where

$$\widetilde{Q}_{11}(\mathrm{i}s) = \int_0^\infty \mathrm{d}r\ Q_{11}(r)\mathrm{e}^{-sr} \qquad \widetilde{g}_{i1}(s) = \int_0^\infty \mathrm{d}r\ r g_{i1}(r)\mathrm{e}^{-sr}.$$

From equations (3*b*), (5*a*) and (5*b*), we get immediately the following:

$$C_{11}^{(2)} = D_{11}^{(2)} = D_{21}^{(1)} = 0 \tag{6a}$$

$$C_{21}^{(1)} = 2\pi\rho\widetilde{g}_{21}(z_1)\frac{D_{11}}{z_1} \tag{6b}$$

$$C_{21}^{(2)} = -D_{21}^{(2)} = -\frac{2\pi K_{21}^{(2)}}{z_2}\frac{1}{1-\rho\widetilde{Q}_{11}(\mathrm{i}z_2)}. \tag{6c}$$

Substitution of equations (6*b*) and (6*c*) into equation (5*c*) yields an equation for $\widetilde{g}_{21}(z_1)$ in terms of known coefficients. Thus, all coefficients in equations (4*a*) and (4*b*) can be obtained as explicit functions of η, σ_1/σ_2, K_{11} (or $c_{11}(\sigma_1)$), K_{12} (or $c_{12}(\sigma_{12})$), z_1 and z_2. Henderson *et al* (1980) characterized $c_{11}(r)$ and $c_{12}(r)$ outside spheres by *different* damping factors in the same way as here, but they treated the case of $\sigma_1/\sigma_2 = 0$.

Once we know the Baxter function, there are several ways to calculate the density profiles near curved walls. In this paper, we employ the method to perform the direct numerical integration of the following equation which is obtained from the OZ equation in the usual way:

$$\begin{aligned}2\pi r g_{i1}(r) = {} & A_1\left(r - \frac{\sigma_1}{2}\right) + \beta_1 - \sum_{n=1}^{2} z_n C_{i1}^{(n)}\mathrm{e}^{-z_n r} \\ & + 2\pi\rho\sigma_1\int_0^x \mathrm{d}s\ (\sigma_{i1}+\sigma_1 s)\ g_{i1}(\sigma_{i1}+\sigma_1 s)\ Q_{11}(\sigma_1(x-s))\end{aligned} \tag{7}$$

where x is defined by $r = \sigma_{i1} + \sigma_1 x$. From equation (7), we get immediately

$$g_{i1}(\sigma_{i1}) = \frac{1}{2\pi\sigma_{i1}}\left[\frac{\sigma_i A_1}{2} + \beta_1 - \sum_{n=1}^{2} z_n C_{i1}^{(n)}\mathrm{e}^{-z_n\sigma_{i1}}\right]. \tag{8}$$

3. Choice of the model parameters

Now, our model is characterized by equation (2*b*), which is specified by four parameters: z_1, z_2, $c_{11}(\sigma_1)$ and $c_{12}(\sigma_{12})$. As in the previous paper (Ginoza *et al* 1994), we shall determine these model parameters in the spirit of the generalized MSA (Waisman 1973a). We adjust these 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):

$$\frac{p}{\rho k_\mathrm{B} T} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}. \tag{9}$$

As in the previous paper, we first determine z_1 and $c_{11}(\sigma_1)$ by the criteria that the model is consistent with the following, well known thermodynamic relations for the hard-sphere fluid:

$$\frac{p}{\rho k_B T} = 1 + 4\eta g_{11}(\sigma_1) \tag{10}$$

$$\rho k_B T K_T = S(0) \tag{11}$$

where k_B is the Boltzmann constant, K_T is the isothermal compressibility and $S(0)$ is the value of the static structure factor in the small-wave-vector limit. In the previous paper (Ginoza *et al* 1994), we obtained explicitly z_1 and $c_{11}(\sigma_1)$ which satisfy equations (8), (9), (10) and (11): these are functions of η and the explicit expressions are given by equations (13) and (15) in that paper, respectively.

Let us next determine $c_{12}(\sigma_{12})$. This means to determine η and σ_{12} dependences of $c_{12}(\sigma_{12})$. As in the previous paper (Ginoza *et al* 1994), we note the exact relation as

$$\frac{p}{\rho k_B T} = g_{12}(\sigma_{12}) \qquad \left(\frac{\sigma_1}{\sigma_{12}} \to 0\right) \tag{12}$$

and we assume that $g_{12}(\sigma_{12})$ is linear with respect to σ_1/σ_{12} (Degreve and Henderson 1994). 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 get

$$g_{12}(\sigma_{12}) \equiv g_{DH} = \frac{1}{(1-\eta)^3}\left[\left(1 - \frac{\eta}{2}\right)\frac{\sigma_1}{\sigma_{12}} + (1 + \eta + \eta^2 - \eta^3)\left(1 - \frac{\sigma_1}{\sigma_{12}}\right)\right] \tag{13}$$

where we used $g_{11}(\sigma_1)$ and $g_{12}(\infty)$ obtained from equations (10) and (12) with the use of equation (9). Then we employ the criterion that both equations (8) and (13) are consistent. With the use of equations (6*b*), (6*c*) and the equation for $\widetilde{g}_{21}(z_1)$, the criterion yields η and σ_{12} dependences of $c_{12}(\sigma_{12})$ as follows:

$$c_{12}(\sigma_{12}) = \frac{g_{DH} - g_0}{g_1} \tag{14}$$

where

$$g_0 = \frac{A_1}{2\pi}\left(1 - \frac{\sigma_1}{2\sigma_{12}}\right) + \frac{\beta_1}{2\pi\sigma_{12}} - \frac{2\Psi}{z_1\sigma_{12}}\left[\frac{A_1}{2\pi}\left(1 + \frac{z_1\sigma_2}{2}\right) + \frac{\beta_1}{2\pi}z_1\right] \tag{15a}$$

$$g_1 = \left(1 - \frac{2\Psi z_1}{z_1 + z_2}\right)\frac{1}{1 - \rho\widetilde{Q}_{11}(\mathrm{i}z_2)} \tag{15b}$$

with

$$\Psi = \frac{\rho}{2z_1}D_{11}\,\mathrm{e}^{-2z_1\sigma_{12}} \Big/ \left[1 - \rho\widetilde{Q}_{11}(\mathrm{i}z_1) + \frac{\rho}{2z_1}D_{11}\,\mathrm{e}^{-2z_1\sigma_{12}}\right] \tag{16}$$

Straightforwardly, it is shown that at $z_1 = z_2$, equation (14) with equations (15*a*) and (15*b*) is equivalent to equation (18) in the previous paper (Ginoza *et al* 1994).

Finally, let us discuss how to adjust the parameter, z_2. For this purpose, following Waisman *et al* (1976), we shall use a relation as follows:

$$\rho \int \mathrm{d}\boldsymbol{r}\ h_{12}(\boldsymbol{r}) = \{[1 - \beta\partial p/\partial\rho_2]/[\beta\partial p/\partial\rho_1]\}_{\rho_2=0} \tag{17}$$

where p is the pressure of a binary mixture with densities ρ_1 and ρ_2. This relation is a generalization of equation (11), and it is derived by using some general relations (Lebowitz 1964). If we get an expression of the right-hand side of this relation as a function of system parameters, η and σ_1/σ_{12}, we may use this as a determination equation of z_2 since the left-hand side may be given model dependently. For the system in consideration, we rewrite equation (17) as

$$J = f(\eta, R_0) \tag{18}$$

where $R_0 = \sigma_1/\sigma_{12}$,

$$J = \frac{1}{\sigma_1\sigma_{12}^2}\int_{\sigma_{12}}^{\infty} \mathrm{d}r\ r^2\ h_{12}(r) \tag{19a}$$

$$f(\eta, R_0) = 1/(3R_0) + (R_0^2/24\eta)\{[1 - \beta\partial p/\partial\rho_2]/\beta\partial p/\partial\rho_1\}_{\rho_2=0}. \tag{19b}$$

Now, available approximate expressions of p (Lebowitz 1964, Mansoori *et al* 1971) give the right-hand side of equation (19b) as a power polynomial with respect to R_0 like $c_{-1}/R_0 + c_0 + c_1R_0 + c_2R_0{}^2$. On the assumption of this functional form, we shall determine four coefficients by following conditions: $f(\eta, R_0) = f_{\mathrm{WHL}}(\eta)$ in the limit of $R_0 \to 0$, $= f_{\mathrm{CS}}(\eta)$ at $R_0 = 1$ and $= 0$ in the limit of $\eta \to 0$, where

$$f_{\mathrm{WHL}}(\eta) = [9\eta(1+2\eta) + \eta^2(4-\eta)(1-4\eta)]/6[(1+2\eta)^2 - \eta^3(4-\eta)] \tag{20a}$$

$$f_{\mathrm{CS}}(\eta) = \tfrac{1}{3} + (\eta - 4)/12(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4). \tag{20b}$$

Equation (20a) is the equation (54) in the work by Waisman *et al* (1976) and equation (20b) is $f(\eta, 1)$ which is calculated with the use of equation (9). In this way, we get

$$f(\eta, R_0) = R_0 f_{\mathrm{CS}}(\eta) + (1 - R_0) f_{\mathrm{WHL}}(\eta). \tag{21}$$

On the other hand, equation (19a) is calculated on the basis of our model: expanding equation (5c) in powers of z_n and equating coefficients of like powers of z_n (Waisman *et al* 1976), we get

$$\begin{aligned} J = \sigma_1^{-1}\sigma_{12}^{-2}A_1^{-2}\Bigg[(\sigma_2A_1/2+\beta_1)\Bigg\{-\sum_{m=1}^{2}C_{21}^{(m)}\mathrm{e}^{-z_m\sigma_{12}} + \pi\rho T_{11}^{(2)} + \sigma_{12}(\sigma_1A_1/2-\beta_1)\Bigg\} \\ -A_1\Bigg(\sum_{m=1}^{2}C_{21}^{(m)}\mathrm{e}^{-z_m\sigma_{12}}/z_m - \pi\rho T_{11}^{(3)}/3 + \pi\sigma_{12}\rho T_{11}^{(2)}\Bigg)\Bigg] \end{aligned} \tag{22}$$

where

$$T_{11}^{(n)} = \int_0^{\infty} \mathrm{d}r\ r^n Q_{11}(r). \tag{23a}$$

Equation (8) and equation (5c) with equation (6b) are regarded as a system of linear equations with respect to $C_{21}^{(1)}$ and $C_{21}^{(2)}$. This system gives

$$\sum_{m=1}^{2} C_{21}^{(m)} e^{-z_m\sigma_{12}} = \frac{\chi_1 - \chi_2}{z_1} + \frac{\chi_2}{z_2} \tag{23b}$$

$$\sum_{m=1}^{2} C_{21}^{(m)} e^{-z_m\sigma_{12}}/z_m = \frac{\chi_1 - \chi_2}{z_1^2} + \frac{\chi_2}{z_2^2} \tag{23c}$$

where

$$\begin{aligned} \chi_1 &= \sigma_2 A_1/2 + \beta_1 - 2\pi\sigma_{12} g_{12}(\sigma_{12}) \\ \chi_2 &= [1 - 2z_1\Psi/(z_1+z_2)]^{-1}\{\chi_1 - (2\Psi/z_1)[(1+z_1\sigma_2/2)A_1 + z_1\beta_1]\}. \end{aligned} \tag{23d}$$

Below, we shall use equation (13) for $g_{12}(\sigma_{12})$ in equation (23d). It should be noted that though equation (22) with equations (23a–d) and (13) is rather complex, it is an explicit function of η, R_0, z_1 and z_2. Therefore, equation (18) with equations (21) and (22) is regarded as a determination equation of z_2.

Now, Ψ has a factor like $\exp(-2z_1\sigma_{12})$ according to equation (16), and as will be seen below, $2z_1\sigma_{12} > 10$ for interesting values of system parameters: Ψ is sufficiently small and negligible. In this case, the determination equation of z_2 is simply a quadratic equation, and its physical solution is as follows:

$$(z_2\sigma_1)^{-1} = [\sqrt{1 - 4w_1(w_2 + w_3 - w_4)} - 1]\chi_3/(2A_1R_0) \tag{24}$$

where

$$\begin{aligned} w_1 &= A_1R_0/(2\pi\sigma_1 g_{\mathrm{DH}} - \chi_3) \\ w_2 &= (6\eta T_{11}^{(2)} R_0 - \sigma_1^4 B_1)/(\sigma_1^3\chi_3) \\ w_3 &= 2\eta A_1 R_0 (T_{11}^{(3)} R_0 - 3\sigma_1 T_{11}^{(2)})/(\sigma_1^3\chi_3^2) \\ w_4 &= \sigma_1^3 A_1^2 f(\eta, R_0)/\chi_3^2 \end{aligned}$$

with $\chi_3 = \sigma_1 A_1 + (\beta_1 - \sigma_1 A_1/2)R_0$.

4. Summary and discussion

When the system parameters, η and R_0, are given, we get values of z_1 and $c_{11}(\sigma_1)$ from equations (13) and (15) in the previous paper (Ginoza *et al* 1994) and those of $c_{12}(\sigma_{12})$ and z_2 from equations (14) and (24) above, respectively. In figures 1 and 2, behaviours of $c_{12}(\sigma_{12})$ and z_2 are shown as functions of η in cases of $R_0 = 1.0$, 0.5, 0.1 and 0.0, respectively. The respective curves in the case of $R_0 = 1.0$ are the same curves as those of $c_{11}(\sigma_1)$ and z_1. For $R_0 < 0.01$, there are no significant changes of the values from those in $R_0 = 0.01$ in either figure. The physical solution of the determination equation of z_2 disappears in the region of very small values of η.

In figures 3 and 4, behaviours of $g_{12}(r)$ are shown as functions of x in cases of ($\eta = 0.324$, $\sigma_1/\sigma_2 = 0.0850$) and ($\eta = 0.219$, $\sigma_1/\sigma_2 = 0.0850$), respectively, where

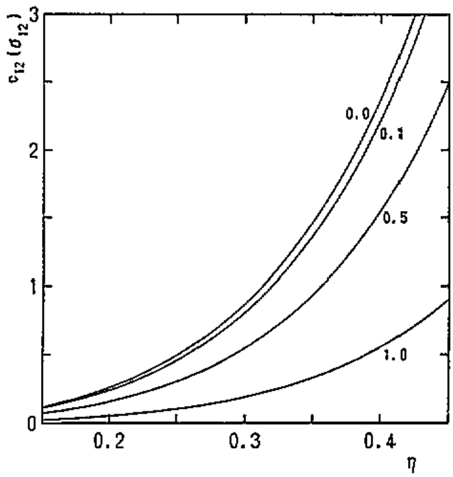

Figure 1. The behaviours of $c_{12}(\sigma_{12})$, obtained from equation (14), as functions of η in cases of $R_0 = 1.0$, 0.5, 0.1 and 0.0. The curve in the case of $R_0 = 1.0$ is the same curve as that of $c_{11}(\sigma_1)$.

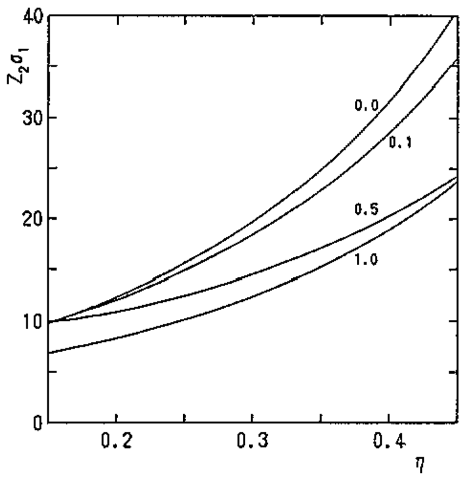

Figure 2. The behaviours of z_2, obtained from equation (24), as functions of η in cases of $R_0 = 1.0$, 0.5, 0.1 and 0.0. The curve in the case of $R_0 = 1.0$ is the same curve as that of z_1.

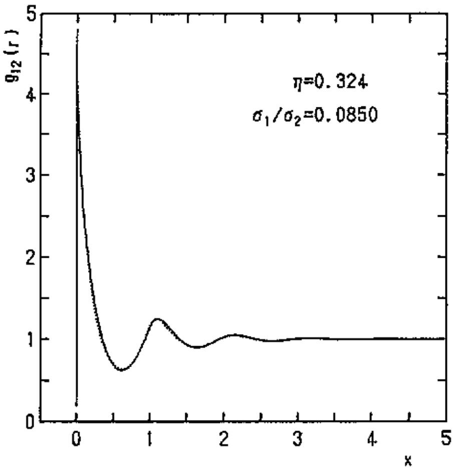

Figure 3. The behaviour of $g_{12}(r)$ as a function of x in the case of $\eta = 0.324$ and $\sigma_1/\sigma_2 = 0.0850$, where $r = \sigma_{12} + \sigma_1 x$. The full curve is the present result, while the dotted curve is that of the simulation by Degreve and Henderson (1994).

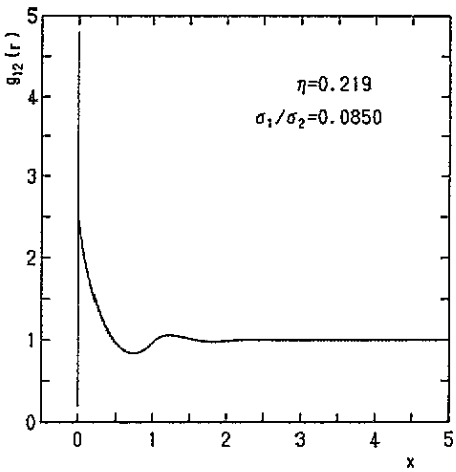

Figure 4. The same as in figure 3, but in the case of $\eta = 0.219$.

$r = \sigma_{12} + \sigma_1 x$. In the respective figures, full curves are the present results and dotted curves are those of the simulation by Degreve and Henderson (1994). The agreements are reasonably good. We investigated the σ_1/σ_2 dependence of $g_{12}(r)$ for various values of η. Regarding this, the conclusion described in the previous paper (Ginoza *et al* 1994) is also satisfied in the extended model here.

In this paper, the MSA model in the previous paper (Ginoza *et al* 1994) has been extended to the case of the Yukawa closures with different damping factors characterized by equation

(2*b*). As is seen from equation (3*a*), our attempt corresponds to an application of the two-Yukawa case of the MSA solution by Blum (1980). The extended model is characterized by four parameters: z_1, $c_{11}(\sigma_1)$, $c_{12}(\sigma_{12})$ and z_2. These model parameters are adjusted in such ways that the model is consistent with some exact relations like equations (10), (11), (12) and (17) as well as the Carnahan–Starling pressure, where we employed two reasonable assumptions expressed by equations (13) and (17). The superiority of the extended model to the model in the previous paper is (a) the consistency with more exact relations and (b) a closer agreement with computer simulation data (Degreve and Henderson 1994).

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