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An Extension of the Analytical Solution of the Ornstein–Zernike Equation with the Yukawa Closure

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The analytical solution of the Ornstein–Zernike equation with one Yukawa closure of the factorizable-coefficient case is extended from the scalar-factorization case to the vector-factorization case. As a result, the scaling parameter is extended from a scalar quantity to a matrix quantity, and the scaling matrix $\hat{\Gamma}$ is given by the physical solution of the matrix equation: $\hat{\Gamma}^2 + z\hat{\Gamma} + \pi\hat{D}\hat{K} = 0$.

KEY WORDS: Yukawa closure; analytical models; Ornstein–Zernike equation; liquids.

1. INTRODUCTION

The analytical solution of the Ornstein–Zernike (OZ) equation has been studied by many workers in the case of the hard sphere Yukawa closure: for the one Yukawa case, the closure is

$$
\begin{aligned}
g_{ij}(r) &= 0, \qquad && r < \sigma_{ij} = (\sigma_i + \sigma_j)/2 \\
c_{ij}(r) &= \frac{K_{ij}}{r} e^{-zr}, \qquad && r > \sigma_{ij}
\end{aligned}
\tag{1}
$$

where $g_{ij}(r)$ and $c_{ij}(r)$ are the radial distribution function and the direct correlation function, respectively, and σ_i is the diameter of hard-spherical particle of ith component of a fluid mixture. In the Baxter formalism, the formal solution of the OZ equation with this closure is given by[1,2]

$$
Q_{ij}(r) = Q^0_{ij}(r) + D_{ij} e^{-zr} \tag{2a}
$$

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where

$$Q_{ij}^0(r) = 0, \qquad r > \sigma_{ij} \quad \text{or} \quad r < \lambda_{ji} = (\sigma_j - \sigma_i)/2$$
$$= \tfrac{1}{2}(r - \sigma_{ij})(r - \lambda_{ji}) A_j + (r - \sigma_{ij}) \beta_j + C_{ij}(e^{-zr} - e^{-z\sigma_{ij}}), \qquad \lambda_{ji} < r < \sigma_{ij} \tag{2b}$$

The coefficients of the solution, A_j, β_j, C_{ij}, and D_{ij}, are defined to be the physical solution of the system of nonlinear algebraic equations.[1,2] Since the system of equations is too difficult to solve generally, one of the present authors considered the following factorizable-coefficient case:[3,4]

$$K_{ij} = K d_i d_j \tag{3}$$

In fact, this case gives considerable simplifications for solving the system of equations and reduces the problem to solving the following nonlinear equation for the single scaling parameter Γ:[3,5]

$$\Gamma^2 + z\Gamma + \pi D K = 0 \tag{4}$$

where D is the function of Γ (see below). All the coefficients above are given in terms of the rational functions of Γ.

Now, the factorizable case defined by Eq. (3) has been actually useful in applications. An extension of the solution to the following *matrix-factorization* case, however, would be more useful and interesting:

$$K_{ij} = \mathbf{d}_i^{\mathrm{T}} \hat{K} \mathbf{d}_j = \sum_{n=1}^{M} d_i^{(n)} K^{(n)} d_j^{(n)} \tag{5}$$

where $\mathbf{d}_j$ is the column vector corresponding to its transposed vector defined by

$$\mathbf{d}_j^{\mathrm{T}} = (d_j^{(1)}, d_j^{(2)}, \ldots, d_j^{(M)}) \tag{6a}$$

and $\hat{K}$ is a $M \times M$ matrix whose (nm)-element is defined by

$$(\hat{K})_{nm} = K^{(n)} \delta_{nm} \tag{6b}$$

The extension is obvious in comparison of Eqs. (3) and (5); this would make the application wider. Below, we shall denote a vector and a $M \times M$ matrix by a bold-faced letter like $\mathbf{d}_j$ and a hatted letter like $\hat{M}$, respectively.

The aim of the present paper is to discuss the extension of the case of Eq. (3) to that of Eq. (5). The main result is that all the coefficients above are given by the single scaling matrix $\hat{\Gamma}$ which is the physical solution of the following matrix equation:

$$\hat{\Gamma}^2 + z\hat{\Gamma} + \pi\hat{D}\hat{K} = 0 \tag{7}$$

2. COEFFICIENTS IN THE MATRIX FACTORIZATION CASE

In the previous paper,[4] we discussed the Blum–Høye solution[1,2] in the following M-Yukawa case:

$$c_{ij}(r) = \sum_{n=1}^{M} K^{(n)} d_i^{(n)} d_j^{(n)} \frac{1}{r} \mathrm{e}^{-z_n r}, \qquad r > \sigma_{ij} \tag{8}$$

As was discussed there, this case actually gives the remarkable simplification. The reduction of the problem to solving Eq. (4) for Γ, however, was discussed only in the one Yukawa term case ($M = 1$). As far as the authors are aware, in a more general case no one has discussed this kind of reduction except for Blum *et al.* (see also Section 4).[6]

Now, let us consider the following special case for Eq. (8):

$$z_n = z \qquad \text{for} \quad n = 1, 2, ..., M \tag{9}$$

It is obvious that the extension described in Section 1 is equivalent to the special case of Eq. (8) with Eq. (9). Therefore, we shall follow our previous work.[4,5] The special form of Eq. (5) and the basic assumption of the Baxter formalism permit us to write the following expression for D_{ij}:

$$D_{ij} = -\mathbf{d}_i^{\mathrm{T}} \mathbf{a}_j \mathrm{e}^{z\sigma_j/2} \tag{10}$$

where the vector $\mathbf{a}_j$ is determined later. This is the key expression to make the problem remarkably simple. As in the previous paper, we get the following:

$$C_{ij} = (\mathbf{d}_i^{\mathrm{T}} - \mathbf{B}_i^{\mathrm{T}}/z)\, \mathbf{a}_j \mathrm{e}^{z\sigma_j/2} \tag{11}$$

$$\beta_j = \frac{\pi}{\Delta} \sigma_j + \mathbf{\Delta}_{\mathrm{N}}^{\mathrm{T}} \mathbf{a}_j \tag{12}$$

$$A_j = \frac{2\pi}{\Delta} \left(1 + \frac{\pi\zeta_2}{2\Delta} \sigma_j\right) + \frac{\pi}{\Delta} \mathbf{P}_{\mathrm{N}}^{\mathrm{T}} \mathbf{a}_j \tag{13}$$

where $\zeta_n = \sum_l \rho_l \sigma_l^n$ with ρ_l (the particle number density of lth component), $\eta = \frac{1}{6}\pi\zeta_3 = 1 - \Delta$,

$$\mathbf{B}_l = 2\pi \sum_l \rho_l \mathbf{d}_l \int_0^\infty dr\, r\, \mathrm{e}^{-zr} g_{il}(r) \tag{14}$$

$$\mathbf{\Delta}_\mathrm{N} = -\frac{2\pi}{\Delta} \sum_l \rho_l \sigma_l^2 \left[\psi_1(z\sigma_l)\, \sigma_l \mathbf{B}_l \mathrm{e}^{z\sigma_l/2} + \frac{1 + z\sigma_l/2}{(z\sigma_l)^2} \mathbf{d}_l \mathrm{e}^{-z\sigma_l/2} \right] \tag{15}$$

$$\mathbf{P}_\mathrm{N} = \sum_l \rho_l \sigma_l \mathbf{X}_l - \frac{\Delta}{\pi} z \mathbf{\Delta}_\mathrm{N} \tag{16}$$

As seen from Eqs. (10–16), our problem is reduced to determining the set of vectors: $\{\mathbf{a}_j, \mathbf{B}_j\}$. This set is determined by the following equations[4]:

$$\hat{M} \mathbf{a}_j = -\mathbf{\Pi}_j \tag{17}$$

$$\frac{2\pi}{z} \hat{K} \mathbf{d}_j \mathrm{e}^{-z\sigma_j/2} + \frac{1}{2z} \sum_l \rho_l \mathbf{a}_l \mathbf{a}_l^\mathrm{T} \mathbf{d}_j \mathrm{e}^{-z\sigma_j/2} + \sum_l \mathbf{a}_l \mathscr{I}_{jl}$$
$$+ \frac{1}{2} \sum_l \rho_l \mathbf{a}_l \mathbf{a}_l^\mathrm{T} \left[\varphi_0(z\sigma_j)\, \sigma_j \mathbf{X}_j - \frac{2\pi}{\Delta} \psi_1(z\sigma_j)\, \sigma_j^3 \sum_k \rho_k \sigma_k \mathbf{X}_k \right] = 0 \tag{18}$$

where

$$\mathscr{I}_{jl} = \delta_{lj} - \frac{2\pi}{\Delta} \psi_1(z\sigma_j)\, \rho_l \sigma_j^3 \left(1 + \frac{\pi\zeta_2}{2\Delta} \sigma_l \right) - \frac{\pi}{\Delta} \varphi_1(z\sigma_j)\, \rho_l \sigma_l \sigma_j^2 \tag{19}$$

$$\mathbf{X}_j = \mathbf{d}_j \mathrm{e}^{-z\sigma_j/2} + \sigma_j \mathbf{B}_j \mathrm{e}^{z\sigma_j/2} \varphi_0(z\sigma_j) + \sigma_j \mathbf{\Delta}_\mathrm{N} \tag{20}$$

$$\mathbf{\Pi}_j = \mathbf{B}_j \mathrm{e}^{z\sigma_j/2} + \left(1 + \frac{z\sigma_j}{2} \right) \mathbf{\Delta}_\mathrm{N} + \frac{\pi}{2\Delta} \sigma_j \sum_l \rho_l \sigma_l \mathbf{X}_l \tag{21}$$

$$\hat{M} = \frac{1}{2} (\hat{D} + \hat{t} - \hat{t}^\mathrm{T}) \tag{22}$$

with

$$\hat{D} = \sum_l \rho_l \mathbf{X}_l \mathbf{X}_l^\mathrm{T} \tag{23}$$

$$\hat{t} = \frac{1}{z} \sum_l \rho_l \mathbf{B}_l e^{z\sigma_l/2} (\sigma_l \mathbf{B}_l^\mathrm{T} \mathrm{e}^{z\sigma_l/2} \varphi_0(z\sigma_l) + \mathbf{d}_l \mathrm{e}^{-z\sigma_l/2}) \tag{24}$$

The functions in the equations above are defined as follows:

$$\psi_1(x) \equiv [1 - x/2 - (1 + x/2)\, \mathrm{e}^{-x}]/x^3$$
$$\varphi_1(x) \equiv (1 - x - \mathrm{e}^{-x})/x^2$$
$$\varphi_0(x) \equiv (1 - \mathrm{e}^{-x})/x$$

Since $\hat{M}$ and $\mathbf{\Pi}_j$ are functions of $\{\mathbf{B}_j\}$ as seen from Eq. (15) and Eqs. (20)–(24), we can solve Eq. (17) and get $\mathbf{a}_j$ in terms of functions of $\{\mathbf{B}_j\}$. The substitution of this result into Eq. (18) gives us equations for $\{\mathbf{B}_j\}$. However, the equations would be too complicated to solve. As a matter of fact, in the case of Eq. (1) with Eq. (3) the simple method-of-solution of the equations has been given by Blum[7] and by Ginoza.[3–5] In the next section, we will discuss that the same kind of simple method-of-solution remains successful in the case of Eq. (1) with Eq. (5), as well.

3. THE SIMPLE METHOD-OF-SOLUTION

From the symmetry relation of $Q_{ij}(\lambda_{ji}) = Q_{ji}(\lambda_{ij})$, we get

$$\mathbf{a}_j = \hat{A}\mathbf{X}_j, \qquad (\hat{A}^{\mathrm{T}} = \hat{A}) \tag{25}$$

Using Eqs. (17) and (25), we can successively transform the sum of the third- and the forth-terms of Eq. (18) as follows:

$$\begin{aligned} \hat{A}\left[\sum_l \mathbf{X}_l \mathscr{I}_{jl} - \frac{1}{2}\hat{D}\hat{M}^{-1}\left(\varphi_0(z\sigma_j)\,\sigma_j \mathbf{\Pi}_j - \frac{2\pi}{\Delta}\psi_1(z\sigma_j)\,\sigma_j^3 \sum_k \rho_k \sigma_k \mathbf{\Pi}_k\right)\right] \\ = \hat{A}\left[\sum_l \mathbf{X}_l \mathscr{I}_{jl} - \frac{1}{2}\hat{D}\hat{M}^{-1}\left(\sum_l \mathbf{X}_l \mathscr{I}_{jl} - \mathbf{d}_j e^{-z\sigma_j/2}\right)\right] \\ = \hat{A}\mathbf{d}_j e^{-z\sigma_j/2} \end{aligned} \tag{26}$$

where we used the definitions of (19), (20), and (21) in the second step and also we used in the last step

$$\hat{M} = \tfrac{1}{2}\hat{D} \tag{27}$$

this being obtained from Eq. (22) and the symmetry relation of $g_{ij}(\sigma_{ji}) = g_{ji}(\sigma_{ij})$. With the use of Eq. (26), Eq. (18) is written as

$$\left[\frac{2\pi}{z}\hat{K} + \frac{1}{2z}\sum_l \rho_l \mathbf{a}_l \mathbf{a}_l^{\mathrm{T}} + \hat{A}\right]\mathbf{d}_j e^{-z\sigma_j/2} = 0$$

Thus, using Eqs. (23) and (25) we get

$$\frac{2\pi}{z}\hat{K} + \frac{1}{2z}\hat{A}\hat{D}\hat{A} + \hat{A} = 0 \tag{28}$$

On the other hand, if we define $\hat{\Gamma}$ by

$$\mathbf{\Pi}_j = -\hat{\Gamma}\mathbf{X}_j \tag{29}$$

from Eqs. (17), (25), (27), and (29) we get

$$\hat{\Gamma} = \hat{M}\hat{\Lambda} = \tfrac{1}{2}\hat{D}\hat{\Lambda} \tag{30}$$

Equations (28) and (30) gives Eq. (7).

4. DISCUSSION

As pointed out in Section 2, obtaining all the coefficients in Eqs. (2a) and (2b) is reduced to determining the set of vectors: $\{\mathbf{a}_j, \mathbf{B}_j\}$. In order to determine the set, we first regard Eqs. (15), (20), and (29) with Eq. (21) as the system of coupled linear equations for $\{\mathbf{X}_j\}$, $\{\mathbf{B}_j\}$ and $\mathbf{\Delta}_{\mathrm{N}}$. Then, we solve the system and obtain expressions of $\mathbf{X}_j$, $\mathbf{B}_j$ and $\mathbf{\Delta}_{\mathrm{N}}$ in terms of functions of $\hat{\Gamma}$. Finally, we get $\hat{\Gamma}$ as the physical solution of Eq. (7). Since the system can be solved because of the linearity of the equations in respect of $\{\mathbf{X}_j\}$, $\{\mathbf{B}_j\}$ and $\mathbf{\Delta}_{\mathrm{N}}$, after all, our problem is reduced to solving Eq. (7). The case of $M = 1$ produces the result in our previous work.[4, 5]

As a matter of fact, the case of Eq. (8) without Eq. (9) was discussed by Blum *et al.*[6] The many useful equations are obtained in their work. As far as the present authors are aware, however, in this general case no one has succeeded yet in giving such a simple method-of-solution for the equations as in the preceding section.

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