Journal of Statistical Physics, Vol. 19, No. 4, 1978

Solution of the Ornstein–Zernike Equation with Yukawa Closure for a Mixture

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Received January 3, 1978

The Ornstein–Zernike equation with Yukawa closure $[c_{ij}(r) = K_{ij}e^{-z(r-\sigma_{ij})}/r$ for $r > \sigma_{ij}]$ for a mixture is solved. We utilize the Fourier transform or factorization technique introduced by Baxter. The general solution is obtained in the form of algebraic equations.

KEY WORDS: Ornstein–Zernike equation; Baxter method; mixture.

1. INTRODUCTION

In a recent paper,[1] the factorization method of Baxter[2] was used to generalize the solution of the Ornstein–Zernike (OZ) equation with Yukawa closure, first obtained by Waisman[3] and later extended by Waisman, Høye, and Stell[4] to the case of an arbitrary number of exponentials.

As was shown in this work,[1] the factorization method leads to an easier and more explicit set of equations, which can be solved more systematically than the equations resulting from the analysis of the Laplace transform. One of the interesting cases to which the Yukawa closure of the OZ equation (GMSA)[5] has not been applied is the mixture of hard spheres of different diameters. Another one which is closely related is a "spin-glass," or configurationally disordered spin system.[6] For both systems we have to consider the OZ equation for the general mixture of spherical molecules

$$h_{ij}(r) = c_{ij}(r) + \sum_{l} \rho_l \int d\mathbf{r}'\, c_{il}(r')h_{lj}(|\mathbf{r} - \mathbf{r}'|) \tag{1}$$

where $h_{ij}(r)$ is the pair correlation function between species i and j, $c_{ij}(r)$ is the direct correlation function for the same pair, and ρ_l is the number density of

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0022-4715/78/1000-0317$05.00/0

species i. Furthermore, the molecules of our system are spherical with an additive hard core σ_i. In other words, we require that

$$h_{ij}(r) = -1 \qquad \text{for} \quad r < \sigma_{ij} \tag{2}$$

with

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j)$$

This condition prevents the overlap of the molecules. The closure of the problem is of the general form

$$c_{ij}(r) = \sum_n K_{ij}^n e^{-z_n(r-\sigma_{ij})}/r \qquad \text{for} \quad r > \sigma_{ij} \tag{3}$$

where K_{ij}^n and z_n are parameters either given by the problem, which is the case of the mean spherical approximation (MSA),[7] in which $c_{ij}(r) = -\beta\varphi_{ij}(r)$ (for $r > \sigma_{ij}$), where $\varphi_{ij}(r)$ is the interaction potential, or in the case of the GMSA,[5] where these parameters are determined by either requiring thermodynamic consistency between the different ways of calculating the thermodynamic properties or use some other input which is considered known. The simplest closure of the OZ equation is the Percus–Yevick closure for hard spheres, for which $c(r) = 0$ for $r > \sigma_{ij}$. The solution of this case was first found by Lebowitz,[8] who used the Wertheim Laplace transform method.[9] Baxter[10] rederived and generalized the results of the mixture by using his Fourier transform factorization technique. The interesting point here is that the factorization technique yields rather general scaling relations for all the properties of the mixture.

The case of the general ionic mixture[11] also admits a quite general solution with an interesting scaling property that depends on the ionic shielding of the mean field that the individual ions see[12] in the fluid. Finally, a similar but more complex scaling is possible for the solution of the case of a mixture of arbitrary size ions and dipoles.[13]

In the next section we will outline the method of solution, while some simple applications will be discussed in Section 3.

2. METHOD OF SOLUTION

The procedure used here is essentially a generalization of our previous work for the one-component case.[1] The OZ equation in Fourier space is

$$\tilde{h}_{ij}(k) = \tilde{c}_{ij}(k) + \sum_l \rho_l \tilde{c}_{il}(k)\tilde{h}_{lj}(k) \tag{4}$$

where $\tilde{h}_{ij}(k)$ and $\tilde{c}_{ij}(k)$ are the three-dimensional Fourier transforms $h_{ij}(r)$

and $c_{ij}(r)$, respectively, and the sum goes over all the components of the mixture. If there are no long-range correlations, then $\tilde{h}_{ij}(k) < \infty$ for all real k, and we can write, following Baxter,[2,10]

$$\delta_{ij} - (\rho_i \rho_j)^{1/2} \tilde{c}_{ij}(k) = \sum_l \tilde{Q}_{il}(k) \tilde{Q}_{jl}(-k) \tag{5}$$

with δ_{ij} as the Kronecker delta. It can then be shown that the components of the factor correlation function matrix must be of the form

$$\tilde{Q}_{ij}(k) = \delta_{ij} - (\rho_i \rho_j)^{1/2} \int_{S_{ji}}^{R_{ij}} dr\, e^{ikr} Q_{ij}(r) \tag{6}$$

where

$$R_{ij} = \tfrac{1}{2}(R_i + R_j), \qquad S_{ij} = \tfrac{1}{2}(R_i - R_j) \tag{7}$$

and R_i is the range parameter of the direct correlation function, such that

$$c_{ij}(r) = 0 \qquad \text{for} \quad r > R_{ij}$$

Equation (6), which is the result of Liouville theorem type arguments and the asymptotic behavior of the Fourier transform,[2,10] tells us that

$$Q_{ij}(r) = 0 \qquad \text{for} \quad r > R_{ji}, \quad r < S_{ji}$$

Substitution of (6) into (5) and (4), followed by Fourier inversions, leads to the set of coupled equations

$$2\pi r c_{ij}(r) = Q'_{ij}(r) + \sum_l \rho_l \int Q_{jl}(t) Q'_{il}(r+t)\, dt \tag{8}$$

for $S_{ji} < r < R_{ji}$, and

$$2\pi r h_{ij}(r) = -Q'_{ij}(r) + 2\pi \sum_l \rho_l \int dt\, (r-t) h_{il}(|r-t|) Q_{lj}(t) \tag{9}$$

for $r > S_{ji}$, where the range of the integrals is determined by the range of $Q_{ij}(r)$, and its derivative $Q'_{ij}(r)$.

The solution of the given problem consists in finding the explicit form of the factor correlation functions $Q_{ij}(r)$. For our problem as given by (2) and (3) this can be done, in spite of the fact that the range $R_i \to \infty$, because either from the asymptotic behavior or by contour integration,[14] we deduce from (5) or (8) that [for $r > S_{ji} = \frac{1}{2}(\sigma_j - \sigma_i)$]

$$Q_{ij}(r) = Q^0_{ij}(r) + \sum_n D^n_{ij} e^{-z_n r} \tag{10}$$

where again D^n_{ij} is a constant, and $Q^0_{ij}(r) = 0$ for $r > \sigma_{ij}$.

However, for notational simplicity we will from here on drop the index n, i.e., we keep only one Yukawa term in (3) or one exponential in (10), since the generalization to a sum of such terms is obvious.[1] The form of $Q_{ij}^0(r)$ is found from Eq. (9) and condition (2). Notice that the crucial part of the solution is the short-range property of $Q_{ij}^0(r)$, which closes Eq. (9). An inspection of this equation will then show that

$$Q_{ij}^0(r) = \tfrac{1}{2}(r - \sigma_{ij})^2 q_{ij}'' + (r - \sigma_{ij})q_{ij}' + C_{ij}(e^{-zr} - e^{-z\sigma_{ij}}) \tag{11}$$

for

$$\lambda_{ji} < r < \sigma_{ji} \qquad \text{with} \quad \lambda_{ji} = \tfrac{1}{2}(\sigma_j - \sigma_i) \tag{12}$$

The form of (11) is chosen so as to satisfy the continuity of $Q_{ij}^0(r)$ at $r = \sigma_{ij}$, a condition which follows from Eq. (8).

The problem is now to find algebraic equations that determine the coefficients q_{ij}'', q_{ij}', C_{ij}, and D_{ij}. By considering (9) for $r < \sigma_{ij}$ we obtain directly three sets of equations when the core condition (2) and Eqs. (10) and (11) are utilized. The constant term and the coefficient of the r term then give the following two sets of equations:

$$A_j = q_{ij}'' = 2\pi\Big[1 - \sum_l \rho_l T_0^{lj}\Big] \tag{13}$$

$$B_j = -\sigma_{ij}q_{ij}'' + q_{ij}' = 2\pi \sum_l \rho_l T_1^{lj} \tag{14}$$

where we have defined the moments

$$T_n^{ij} = \int_{\lambda_{ji}}^{\infty} dt\, t^n Q_{ij}(t) = \left(-\frac{\partial}{\partial s}\right)^n \hat{Q}_{ij}(s)\bigg|_{s=0} \tag{15}$$

with

$$\hat{Q}_{ij}(s) = \int_{\lambda_{ji}}^{\infty} dt\, e^{-st} Q_{ij}(t) \tag{16}$$

Using the explicit form (10) and (11) of $Q_{ij}(r)$, some calculation will show that

$$(1 - \xi_3 - 3\sigma_j\xi_2)A_j - 6\xi_2 B_j = 2\pi(1 + M_j) \tag{17}$$

$$\tfrac{3}{2}\sigma_j^2\xi_2 A_j + (1 - \xi_3 + 3\sigma_j\xi_2)B_j = 2\pi N_j \tag{18}$$

with

$$\xi_n = \tfrac{1}{6}\pi \sum_l \rho_l \sigma_l^n \tag{19}$$

$$M_j = \sum_l \rho_l e^{-\lambda_{jl}z}\Big[z\sigma_l^2 e^{-z\sigma_l}\varphi_1(-z\sigma_l)C_{lj} - \frac{1}{z} D_{lj}\Big] \tag{20}$$

$$N_j = \sum_l \rho_l e^{-\lambda_{jl}z}\Big\{ze^{-z\sigma_l}\sigma_l^2[\sigma_l\varphi_2(-z\sigma_l) - \lambda_{jl}\varphi_1(-z\sigma_l)]C_{lj} + \frac{1 + z\lambda_{jl}}{z^2} D_{lj}\Big\} \tag{21}$$

where we have used the incomplete gamma functions

$$\varphi_1(x) = (1/x^2)(1 - x - e^{-x}), \qquad \varphi_2(x) = (1/x^3)(1 - x + \tfrac{1}{2}x^2 - e^{-x}) \tag{22}$$

Solutions of Eqs. (17) and (18) with respect to A_j and B_j leads to

$$\begin{aligned} A_j &= A_j{}^0(1 + M_j) - 4(1/\sigma_j{}^2)B_j{}^0N_j \\ B_j &= B_j{}^0(1 + M_j) + [A_j{}^0 + 4(1/\sigma_j)B_j{}^0]N_j \end{aligned} \tag{23}$$

or from (13) and (14)

$$q'_{ij} = q^{0\prime}_{ij}(1 + M_j) + A_i{}^0N_j \tag{24}$$

where the superscript zero denotes the Percus–Yevick hard-core system. We recall that

$$\begin{aligned} q^{0\prime}_{ij} &= [2\pi/(1 - \xi_3)^2][\tfrac{3}{2}\sigma_i\sigma_j\xi_2 + \sigma_{ij}(1 - \xi_3)] \\ A_j{}^0 &= [2\pi/(1 - \xi_3)^2](1 - \xi_3 + 3\sigma_j\xi_2) \\ B_j{}^0 &= [2\pi/(1 - \xi_3)^2](-\tfrac{3}{2}\sigma_j{}^2\xi_2) \end{aligned} \tag{25}$$

As we will see in the next section, both q'_{ij} and A_j are simply related to physical properties of the system.

The coefficient of the e^{-zr} term of Eq. (9) gives a third set of equations. We then find it convenient due to the core condition (2) to replace $h_{ij}(r)$ by

$$g_{ij}(r) = h_{ij}(r) + 1 \tag{26}$$

and we obtain

$$-C_{ij} = \sum_l [\delta_{il} - 2\pi\rho_l\hat{g}_{il}(z)/z]D_{lj} \tag{27}$$

where the Laplace transform of $g_{ij}(r)$ is given by

$$\hat{g}_{ij}(s) = \int_0^\infty dr\, e^{-sr}rg_{ij}(r) \tag{28}$$

Now we have reduced the set of unknowns by eliminating q''_{ij}, q'_{ij}, and C_{ij}, but we still have to find two additional sets of equations for D_{ij} and $\hat{g}_{ij}(z)$. One set of equations is obtained from Eq. (8). In particular, if $r > \sigma_{ij}$,

$$2\pi K_{ij}/z = \sum_l D_{il}[\delta_{lj} - \rho_l\hat{Q}_{jl}(z)] \tag{29}$$

The other set of equations is obtained from Eq. (9) by considering its Laplace transform. For $r < \sigma_{ij}$ Eq. (9) reduces to

$$\begin{aligned} 0 = 2\pi r - Q'_{ij}(r) &- 2\pi \sum_l \rho_l \int_{\lambda_{jl}}^\infty dt\,(r - t)Q_{lj}(t) \\ &+ 2\pi \sum_l \rho_l \int_r^\infty dt\,(r - t)g_{il}(|r - t|)Q_{lj}(t) \end{aligned} \tag{30}$$

which leads to Eqs. (13), (14), and (27), while for $r > \sigma_{ij}$ we should have

$$2\pi r g_{ij}(r) = 2\pi r + zD_{ij}e^{-zr} - 2\pi \sum_l \rho_l \int_{\lambda_{jl}}^{\infty} dt\,(r - t)Q_{lj}(t)$$

$$+ 2\pi \sum_l \rho_l \int_{\lambda_{jl}}^{\infty} dt\,(r - t)g_{il}(|r - t|)Q_{lj}(t) \tag{31}$$

We then find it advantageous to take the analytic continuation of (30) for $r > \sigma_{ij}$ and subtract it from (31) to obtain

$$2\pi r g_{ij}(r) = (r - \sigma_{ij})q''_{ij} + q'_{ij} - zC_{ij}e^{-zr}$$

$$+ 2\pi \sum_l \rho_l \int_{\lambda_{jl}}^{r} dt\,(r - t)g_{il}(|r - t|)Q_{lj}(t) \tag{32}$$

But this is nothing but a simple convolution integral equation, which by Laplace transformation yields

$$\sum_l 2\pi \hat{g}_{il}(s)[\delta_{lj} - \rho_l \hat{Q}_{lj}(s)] = \frac{e^{-s\sigma_{ij}}}{s^2}\left[q''_{ij} + sq'_{ij} - \frac{s^2 z}{s + z} e^{-z\sigma_{ij}}C_{ij}\right] \tag{33}$$

with $\hat{Q}_{lj}(s)$ defined by (16). When $s = z$ we get expressions for $\hat{g}_{ij}(z)$, which give the remaining set of equations.

Summarizing, we have a set of two coupled matrix equations. One of them is Eq. (29), while the other one is Eq. (33) when q''_{ij}, q'_{ij}, and C_{ij} are substituted by (13), (24), (25), and (27) to give

$$\sum_l 2\pi \hat{g}_{il}(z)[\delta_{lj} - \rho_l \hat{Q}_{lj}(z)]$$

$$= e^{-z\sigma_{ij}}\left\{(A_j^0 + zq_{ij}^{0\prime})(1 + M_j) + \left(-4\frac{1}{\sigma_j^2}B_j^0 + zA_i^0\right)N_j\right.$$

$$\left. + \frac{z^2}{2} e^{-z\sigma_{ij}} \sum_l \gamma_{il} D_{lj}\right\} \tag{34}$$

where

$$\gamma_{ij} = \delta_{ij} - 2\pi \rho_j \hat{g}_{ij}(z)z \tag{35}$$

From (20), (21), and (27) we then get

$$M_j = -\sum_{l,k} \rho_l e^{-z\lambda_{jl}}\left\{z\sigma_l^2 e^{-z\sigma_l}\varphi_1(-z\sigma_l)\gamma_{lk} + \frac{1}{z}\delta_{lk}\right\}D_{kj}$$

$$N_j = \sum_{l,k} \rho_l e^{-z\lambda_{jl}}\left\{-ze_l^{-z\sigma_l}\sigma_l^2[\sigma_l\varphi_2(-z\sigma_l) - \lambda_{jl}\varphi_1(-z\sigma_l)]\gamma_{lk}\right.$$

$$\left. + \frac{1 + z\lambda_{jl}}{z}\delta_{lk}\right\}D_{kj} \tag{36}$$

and from (11)

$$\hat{Q}_{ij}^0(z) = e^{-z\lambda_{ij}}\left\{(1 + M_j)\sigma_i^2[\varphi_1(z\sigma_i)q_{ij}^{0\prime} + \sigma_i\varphi_2(z\sigma_i)A_j^0] + N_j\sigma_i^2\left[\varphi_1(z\sigma_i)A_i^0 - 4B^0\frac{\sigma_i}{\sigma_j^2}\varphi_2(z\sigma_i)\right] - \frac{1}{2z}e^{-z\lambda_{ji}}(1 - e^{-z\sigma_i})^2\sum_l \gamma_{il}D_{lj}\right\} \tag{37}$$

Although the equations appear to be algebraically complex, there are only two sets of unknowns, e.g., the γ_{ij} [or $\hat{g}_{ij}(z)$] and the D_{ij} if the K_{ij} (besides z, ρ_i, and σ_i) are considered known. It may be noted that the set of equations (34) is linear in D_{ij} and thus has a unique solution with respect to D_{ij} when the γ_{ij} are considered known, and (29) will then give K_{ij} explicitly. However, with K_{ij} instead of γ_{ij} as known one must expect multiple solutions to occur, of which only one is acceptable.[4]

3. DISCUSSION

The results of the preceding section can be used to compute properties of physical interest of the system under consideration. There are often different ways of calculating these properties, and what we want to do in this section is to survey some of the simpler relations to the factor correlation functions $Q_{ij}(r)$. First, we conclude from Eq. (9) that the contact value of $g_{ij}(r)$ is determined by the jump of $Q_{ij}'(r)$ at $r = \sigma_{ij}$. We have

$$g_{ij}(\sigma_{ij}+) = \frac{1}{2\pi\sigma_{ij}}[q_{ij}' - zC_{ij}e^{-z\sigma_{ij}}] \tag{38}$$

It is also clear that, from (5), (6), and (13), the inverse compressibility via the fluctuation theorem is

$$\chi^{-1} = \frac{\partial\beta p}{\partial\rho} = 1 - \frac{1}{\rho}\sum_{ij}\rho_i\rho_j\tilde{c}_{ij}(0) = \frac{1}{\rho}\sum_j \rho_j\left(\frac{A_j}{2\pi}\right)^2 \tag{39}$$

where p is pressure and $\rho = \sum_i \rho_i$.

In passing, we also notice that a physical requirement on $g_{ij}(r)$ is the exchange symmetry

$$g_{ij}(r) = g_{ji}(r) \tag{40}$$

From (24) and (38) this implies that any acceptable solution of the equations of the last paragraph must satisfy

$$q_{ij}^{0\prime}M_j + A_i^0N_j - zC_{ij}e^{-z\sigma_{ij}} = q_{ij}^{0\prime}M_i + A_j^0N_i - zC_{ji}e^{-z\sigma_{ji}} \tag{41}$$

In the MSA we find a simple expression for the excess internal energy ΔE per unit volume, which is given by

$$-\beta\,\Delta E = 2\pi \sum_{i,j} \rho_i\rho_j K_{ij} e^{\sigma_{ij}z}\hat{g}_{ij}(z) \tag{42}$$

The recent work of Høye and Stell[15] can be used to compute the excess thermodynamic properties in the MSA via the internal energy. We quote the "energy" excess osmotic coefficient

$$\phi^E = \frac{\beta p^E}{\rho} = \frac{1}{12\pi\rho} \sum_{ij} \rho_i\rho_j\sigma_{ij}[(q'_{ij})^2 - (q^{0\prime}_{ij})^2] + J \tag{43}$$

where in the present case with Yukawa interaction the virial integral becomes

$$J = \frac{2\pi}{3} \sum_{ij} \rho_i\rho_j K_{ij} e^{\sigma_{ij}z}\left[z\,\frac{\partial \hat{g}_{ij}(s)}{\partial s}\bigg|_{s=z} - \hat{g}_{ij}(z)\right] \tag{44}$$

The excess free energy is then given by

$$-\beta\,\Delta A = \rho\,\Delta\phi^E - \beta\,\Delta E - \tfrac{1}{2}\rho[\chi^{-1} - \chi_0^{-1}] \tag{45}$$

where χ_0^{-1} as defined by (39) is the inverse compressibility of the hard-core reference problem. Finally, the excess chemical potential $\mu_i{}^E$ of particle i in the MSA is

$$-\beta\rho_i\mu_i{}^E = \tfrac{1}{2} \sum_j \rho_i\rho_j[\tilde{c}_{ij}(0) - \tilde{c}^0_{ij}(0)] + 2\pi \sum_j \rho_i\rho_j K_{ij} e^{z\sigma_{ij}}\hat{g}_{ij}(z) \tag{46}$$

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