Journal of Statistical Physics, Vol. 66, Nos. 1/2, 1992

On the Analytical Solution of the Ornstein–Zernike Equation with Yukawa Closure

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Received April 16, 1991

We discuss the solution of the Ornstein–Zernike equation for most general closure consisting of a sum of M Yukawa-type exponentials. A formal solution for the factored case is bound for an arbitrary mixture of hard spheres introducing a general scaling matrix Γ of dimensions $M \times M$. A sufficient number of equations for this matrix is obtained from symmetry considerations and the boundary condition. We discuss also restricted and semirestricted case, for which explicit solutions in terms of the scaling parameters and input parameters are found.

KEY WORDS: Liquids; dense fluids; analytical models; Yukawa potentials.

1. INTRODUCTION

Analytical solutions of equations for fluid mixtures are necessary to study phase transitions. Since the early work of Lebowitz,(1) much progress has been achieved. In particular, the solution of the Yukawa closure of the Ornstein–Zernike (OZ) equation by Waisman(2) has made possible a number of extensions and generalizations to rather general closures of arbitrary mixtures of spherical objects.(3–11) There has been a number of very interesting calculations using these solutions.(13–16)

The solution of the general closure of the hard-core OZ equation

$$c_{ij}(r) = \sum_{n=1}^{M} K_{ij}^{(n)} e^{-z_n r}/r \tag{1}$$

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0022-4715/92/0100-0249$06.50/0

was discussed in earlier publications.[7-9] Considerable simplifications were achieved by Ginoza, who also discussed an interesting solvable case for the arbitrary polydisperse mixture of hard spheres.[10,11] If

$$K_{ij}^{(n)} = K^{(n)} d_i^{(n)} d_j^{(n)} \tag{2}$$

then a full solution of the Yukawa closure can be found for the case $M=1$, in terms of a scaling parameter Γ. Much more manageable equations are obtained for the more general case.

In our work we give the general solution of the polydisperse case with M arbitrary. The solution in much more complex than the single Yukawa case because now it is necessary to introduce a scaling matrix $\mathbf{\Gamma}$, and the normal boundary conditions have to be supplemented by symmetry relations to achieve a full solution. In the last section we discuss the semirestricted case in which subsets of components satisfy electroneutrality relations of the type

$$\sum_i d_i^{(n)} \rho_i \sigma_i^t = 0, \qquad t = 0, 1, 2,... \tag{3}$$

where ρ_i is the number density and σ_i is the diameter of species i. The sum is over arbitrary subsets of component of the mixture. For this semirestricted case we obtain a full and explicit solution.

2. BASIC FORMALISM

We study the Ornstein–Zernike (OZ) equation

$$h_{ij}(12) = c_{ij}(12) + \sum_k \int d3\, h_{ik}(13)\, \rho_k c_{kj}(32) \tag{4}$$

where $h_{ij}(12)$ is the molecular total correlation function and $c_{ij}(12)$ is the molecular direct correlation function, ρ_i is the number density of the molecules i, and $i = 1, 2$ is the position $\mathbf{r}_i$, $\mathbf{r}_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and σ_{ij} is the distance of closest approach of two particles i, j. The direct correlation function is

$$c_{ij}(r) = \sum_{n=1}^{M} K_{ij}^{(n)} e^{-z_n r}/r, \qquad r > \sigma_{ij} \tag{5}$$

and the pair correlation function is

$$h_{ij}(r) = g_{ij}(r) - 1 = -1, \qquad r \leqslant \sigma_{ij} \tag{6}$$

We use the Baxter–Wertheim[18,19] (BW) factorization of the OZ equation

$$[\mathbf{I}-\rho\tilde{\mathbf{H}}(\mathbf{k})][\mathbf{I}-\rho\tilde{\mathbf{C}}(k)]=\mathbf{I} \tag{7}$$

where $\mathbf{I}$ is the identity matrix, and we have used the notation

$$\tilde{\mathbf{H}}(\mathbf{k})=2\int_0^\infty dr\cos(kr)\,\mathbf{J}(r) \tag{8}$$

$$\tilde{\mathbf{C}}(k)=2\int_0^\infty dr\cos(kr)\,\mathbf{S}(r) \tag{9}$$

The matrices $\mathbf{J}$ and $\mathbf{S}$ have matrix elements

$$J_{ij}(r)=2\pi\int_r^\infty ds\,sh_{ij}(s) \tag{10}$$

$$S_{ij}(r)=2\pi\int_r^\infty ds\,sc_{ij}(s) \tag{11}$$

$$[\mathbf{I}-\rho\tilde{\mathbf{C}}(k)]=[\mathbf{I}-\rho\tilde{\mathbf{Q}}(k)][\mathbf{I}-\rho\tilde{\mathbf{Q}}^T(k)] \tag{12}$$

where $\tilde{\mathbf{Q}}^T(-k)$ is the complex conjugate and transpose of $\tilde{\mathbf{Q}}(k)$. The first matrix is nonsingular in the upper half complex k plane, while the second is nonsingular in the lower half complex k plane.

It can be shown that the factored correlation functions must be of the form

$$\tilde{\mathbf{Q}}(k)=\mathbf{I}-\rho\int_{\lambda_{ji}}^\infty dr\,e^{ikr}\,\tilde{\mathbf{Q}}(r) \tag{13}$$

where we used the following definition:

$$\lambda_{ji}=\tfrac{1}{2}(\sigma_j-\sigma_i) \tag{14}$$

$$\mathbf{S}(r)=\mathbf{Q}(r)-\int dr_1\,\mathbf{Q}(r_1)\,\rho\,\mathbf{Q}^T(r_1-r) \tag{15}$$

Similarly, from Eqs. (12) and (7) we get, using the analytical properties of $\mathbf{Q}$ and Cauchy's theorem,

$$\mathbf{J}(r)=\mathbf{Q}(r)+\int dr_1\,\mathbf{J}(r-r_1)\,\rho\,\mathbf{Q}(r_1) \tag{16}$$

The general solution is discussed in refs. 8 and 10, and yields

$$q_{ij}(r) = q_{ij}^0(r) + \sum_{n=1}^{M} D_{ij}^{(n)} e^{-z_n r}, \qquad \lambda_{ji} < r \tag{17}$$

$$q_{ij}^0(r) = (1/2)\, A_j[(r-\sigma_j/2)^2 - (\sigma_i/2)^2] + \beta_j[(r-\sigma_j/2) - (\sigma_i/2)] + \sum_{n=1}^{M} C_{ij}^{(n)} e^{-z_n\sigma_j/2}[e^{-z_n(r-\sigma_j/2)} - e^{-z_n\sigma_i/2}], \qquad \lambda_{ji} < r < \sigma_{ij} \tag{18}$$

The solution of this system of equations leads to

$$\beta_j = \frac{\pi}{\Delta}\sigma_j + \frac{2\pi}{\Delta}\sum_n \mu_j^{(n)} \tag{19}$$

and

$$A_j = \frac{2\pi}{\Delta}\left[1 + \frac{1}{2}\zeta_2\beta_j + \sum_n M_j^{(n)}\right] \tag{20}$$

Furthermore, the coefficients of all the exponentials must satisfy Eq. (16),

$$C_{ij}^{(n)} + D_{ij}^{(n)} = \sum_k \gamma_{ik}^{(n)} D_{kj}^{(n)} \tag{21}$$

We have used

$$\zeta_n = \sum_k \rho_k \sigma_k^n \tag{22}$$

$$\Delta = 1 - \pi\zeta_3/6 \tag{23}$$

$$\gamma_{ij}^{(n)} = 2\pi\tilde{g}_{ij}(z_n)\rho_j/z_n \tag{24}$$

$$\mu_j^{(n)} = \sum_k \rho_k C_k^{\mu}(z_n) D_{kj}^{(n)} e^{-z_n\sigma_{kj}} \tag{25}$$

$$M_j^{(n)} = \sum_k \rho_k C_k^{M}(z_n)\, D_{kj}^{(n)} e^{-z_n\sigma_{kj}} \tag{26}$$

$$\tilde{g}_{ij}(s) = \int_0^\infty dr\, r g_{ij}(r) e^{-sr} \tag{27}$$

$$C_k^{\mu}(z_n) = \sum_l \sigma_l^2 e^{z_n\sigma_{kl}} \gamma_{kl}^{(n)} z_n \sigma_l \psi_1(z_n\sigma_l) + \frac{1 + z_n\sigma_k/2}{z_n^2} \tag{28}$$

$$C_k^{\ddot{M}}(z_n) = \sum_l \sigma_l e^{z_n\lambda_{kl}} \gamma_{kl}^{(n)} z_n \sigma_l \phi_1(-z_n\sigma_l) - \frac{1 + z_n\sigma_k}{z_n} \tag{29}$$

with

$$\psi_1(x) = [1 - x/2 - (1 + x/2)e^{-x}]/x^3 \tag{30}$$

$$\phi_1(x) = (1 - x - e^{-x})/x^2 \tag{31}$$

$$\phi_0(x) = (1 - e^{-x})/x \tag{32}$$

The following relation is useful:

$$x^2\psi_1(x) = -1 + (1 + x/2)\,\phi_0(x) \tag{33}$$

Some quantities will be of interest:

$$q_{ij}(\lambda_{ji}) = -\sigma_i\beta_j + \sum_m \left[(C_{ij}^{(m)} + D_{ij}^{(m)})e^{-z_m\lambda_{ji}} - C_{ij}^{(m)}e^{-z_m\sigma_{ji}}\right] \tag{34}$$

which can be expressed as

$$q_{ij}(\lambda_{ji}) = -\sigma_i\sigma_j\frac{\pi}{\Delta} - \sum_m F_{ij}^{(m)} \tag{35}$$

where we have defined the convenient quantity

$$F_{ij}^{(m)} = \frac{2\pi}{\Delta}\sigma_i\mu_j^{(m)} - (C_{ij}^{(m)} + D_{ij}^{(m)})e^{-z_m\lambda_{ji}} + C_{ij}^{(m)}e^{-z_m\sigma_{ji}} \tag{36}$$

or

$$F_{ij}^{(m)} = \frac{2\pi}{\Delta}\sigma_i\mu_j^{(m)} - \left[(C_{ij}^{(m)} + D_{ij}^{(m)})(1 - e^{-z_m\sigma_i}) + D_{ij}^{(m)}e^{-z_m\sigma_i}\right]e^{-z_m\lambda_{ji}} \tag{37}$$

Because of the symmetry of the direct correlation function, we require from Eq. (15)

$$q_{ij}(\lambda_{ji}) = q_{ji}(\lambda_{ij}) \tag{38}$$

which implies that $F_{ij}^{(m)}$ must satisfy the symmetry relation

$$F_{ij}^{(m)} = F_{ji}^{(m)} \tag{39}$$

Using the relations (25) and (26), we verify

$$M_j^{(m)} + \mu_j^{(m)}\left(z_m + \frac{\pi}{\Delta}\zeta_2\right) = \frac{1}{2}\mathscr{S}_j^{(m)} \tag{40}$$

with

$$\mathscr{S}_j^{(m)} = \sum_l \rho_l \sigma_l F_{lj}^{(m)} \tag{41}$$

We change Eq. (20) to

$$A_j = A_j^0 + \frac{\pi}{\Delta} \sum_m \left[\mathscr{S}_j^{(m)} - 2z_m \mu_j^{(m)}\right] \tag{42}$$

where

$$A_j^0 = \frac{2\pi}{\Delta}\left[1 + \frac{1}{2}\zeta_2 \frac{\pi}{\Delta}\sigma_j\right] \tag{43}$$

We obtain the contact pair correlation function from the discontinuity of the first derivative of the factor function $q_{ij}(r)$, Eq. (17):

$$y_{ij}^{(0)} \equiv 2\pi\sigma_{ij}\, g_{ij}(\sigma_{ij}) = q'_{ij}(\sigma_{ji}^-) - q'_{ij}(\sigma_{ji}^+) = A_j(\sigma_i/2) + \beta_j - \sum_{m=1}^{M} z_m C_{ij}^{(m)} e^{-z_m \sigma_{ij}} \tag{44}$$

Using the continuity relation[6,24]

$$q'_{ij}(\lambda_{ji}) + q'_{ji}(\lambda_{ij}) = -\sum_k \rho_k q_{ij}(\lambda_{ki})\, q_{ij}(\lambda_{kj}) \tag{45}$$

and

$$q'_{ij}(\lambda_{ji}) = -A_j(\sigma_i/2) + \beta_j - \sum_{m=1}^{M} z_m (C_{ij}^{(m)} + D_{ij}^{(m)}) e^{-z_m \lambda_{ji}} \tag{46}$$

we get the following relation for the contact pair distribution function:

$$2\pi\sigma_{ij}\, g_{ij}(\sigma_{ij}) - 2\pi\sigma_{ij}\, g_{ij}^0(\sigma_{ij}) = \frac{1}{2}\sum_m \left[z_m(F_{ij}^{(m)} + F_{ji}^{(m)}) - \sum_{k,n} \rho_k F_{kj}^{(m)} F_{ki}^{(n)}\right] \tag{47}$$

where $g_{ij}^0(\sigma_{ij})$ is the contact pair distribution of the hard-sphere reference system.

From Eq. (16) we can show that the Laplace transform of the pair correlation function must satisfy the consistency relation

$$2\pi \sum_l \tilde{g}_{il}(z_n)[\delta_{lj} - \rho_l \tilde{q}_{jl}(iz_n)] = \tilde{q}_{ij}^{0'}(iz_n) \tag{48}$$

where

$$\tilde{q}_{ij}^{0\prime}(iz_n) = \int_{\sigma_{ij}}^{\infty} dr\, e^{-r_n r}[q_{ij}^0(r)]'$$

$$= \left[\left(1 + \frac{z_n \sigma_i}{2}\right) A_j + z_n \beta_j\right] \frac{e^{-z_n \sigma_{ij}}}{z_n^2} - \sum_m \frac{z_m}{z_n + z_m} e^{-(z_n + z_m)\sigma_{ij}} C_{ij}^{(m)} \qquad (49)$$

The Laplace transform of Eqs. (17) and (18) yields

$$e^{z_n \lambda_{ji}} \tilde{q}_{ij}(iz_n) = \sigma_i^3 \psi_1(z_n \sigma_i) A_j + \sigma_i^2 \phi_1(z_n \sigma_i) \beta_j$$
$$+ \sum_m \frac{1}{z_n + z_m} [(C_{ij}^{(m)} + D_{ij}^{(m)}) e^{-z_m \lambda_{ji}} - C_{ij}^{(m)} e^{-z_m \sigma_{ji}}$$
$$- z_m z_n \sigma_i \phi_0(z_n \sigma_i)\, C_{ij}^{(m)} e^{-z_m \sigma_{ji}}] \qquad (50)$$

Using Eq. (44), we get

$$\tilde{q}_{ij}^{0\prime}(iz_n) = e^{-z_n \sigma_{ij}}/z_n^2 \left[A_j + z_n\, y_{ij}^{(0)} + z_n \sum_m \frac{z_m^2}{z_n + z_m} e^{-z_m \sigma_{ij}} C_{ij}^{(m)} \right] \qquad (51)$$

After some lengthy but straightforward algebra we find the following simplification of the result of Ginoza[10]:

$$\Pi_{ij}^{(n)} = \sum_m \sum_t \frac{e^{-z_m \sigma_{ij}}}{z_n + z_m} D_{tj}^{(m)} \sum_l \rho_l [z_m \Omega_{il}^{(n)} \Omega_{tl}^{(m)} - \Omega_{tl}^{(m)} \Pi_{il}^{(n)} + \Omega_{il}^{(n)} \Pi_{tl}^{(m)}] \qquad (52)$$

where

$$\Omega_{ij}^{(m)} = C_i^{\mu}(z_m) \frac{2\pi}{\Delta} \rho_i \sigma_j - \gamma_{ji}^{(m)} z_m \sigma_j \phi_0(z_m \sigma_j) e^{z_m \delta \sigma_{ij}} - \delta_{ij} \qquad (53)$$

and

$$\Pi_{ij}^{(m)} = -C_i^{\mu}(z_m) \frac{2\pi}{\Delta} \rho_i \left(1 + \frac{z_m \sigma_j}{2}\right) + \gamma_{ji}^{(m)} z_m e^{z_m \sigma_{ji}} - \frac{\pi}{2\Delta} \sigma_j \sum_l \rho_l \sigma_l \Omega_{il}^{(m)} \qquad (54)$$

Notice that

$$F_{ij}^{(m)} = \sum_l \Omega_{li}^{(m)} D_{lj}^{(m)} e^{-z_m \sigma_{ji}} \qquad (55)$$

and also that $\Pi_{ij}^{(m)}$ and $\Omega_{ij}^{(m)}$ are functions of the same set of parameters, and therefore

$$\delta_{ij} + \Omega_{ij}^{(m)} + \sigma_j \phi_0(z_m \sigma_j) \Pi_{ij}^{(m)}$$
$$= -\frac{2\pi}{\Delta}\left[C_i^{\mu}(z_m)\, \rho_i z_m^2 \sigma_j^3 \psi_1(z_m \sigma_j) + \sigma_j^2 \phi_0(z_m \sigma_j) \sum_l \rho_l \sigma_l \Omega_{il}^{(m)} \right] \qquad (56)$$

The MSA closure condition (5) yields

$$2\pi K_{ij}^{(n)}/z_n = \sum_l D_{il}^{(n)}[\delta_{lj} - \rho_l \tilde{q}_{jl}(iz_n)] \tag{57}$$

This expression can be combined with (48) to obtain an expression for the excess MSA energy due to the interaction n

$$\sum_l \gamma_{jl}^{(n)} K_{il}^{(n)} = \frac{1}{2\pi} \sum_l \rho_l D_{il}^{(n)} \tilde{q}_{jl}^{0'}(iz_n) \tag{58}$$

Equations (52) and (58) are the full solution of the general problem, since we have a set of algebraic equations for $\gamma_{ji}^{(m)}$ as a function of $K_{ij}^{(m)}$: We must, however, first solve Eq. (52) for the unknown $D_{ij}^{(m)}$.

3. FACTORED INTERACTION: GENERAL CASE

As was observed by Ginoza,[10,11] when the interaction is of the form

$$K_{ij}^{(n)} = K^{(n)} d_i^{(n)} d_j^{(n)} \tag{59}$$

then the solution simplifies considerably. Let us first define the energy parameter[9]

$$B_j^{(n)} = \sum_i z_n d_i^{(n)} \gamma_{ji}^{(n)} \tag{60}$$

Then, from Cauchy's theorem and Eq. (15), we get

$$D_{ij}^{(n)} = -d_i^{(n)} a_j^{(n)} e^{z_n \sigma_j/2} \tag{61}$$

Furthmore, from Eq. (21) we get

$$C_{ij}^{(n)} = (d_i^{(n)} - B_i^{(n)}/z_n) a_j^{(n)} e^{z_n \sigma_j/2} \tag{62}$$

After much algebra we find[10,11]

$$\frac{2\pi}{\Delta} \mu_j^{(n)} = a_j^{(n)} \Delta^{(n)} \tag{63}$$

where

$$\Delta^{(n)} = -\frac{2\pi}{\Delta} \sum_t C_t^{\mu}(z_n)\, d_t^{(n)} e^{-z_n \sigma_t/2} \tag{64}$$

From Eq. (35) we obtain

$$F_{ij}^{(n)} = X_i^{(n)} a_j^{(n)} \tag{65}$$

where we have defined

$$X_i^{(n)} = -\sum_t \Omega_{ti}^{(n)} d_t^{(n)} e^{-z_n\sigma_t/2}$$
$$= d_i^{(n)} e^{-z_n\sigma_i/2} + \sigma_i B_i^{(n)} e^{z_n\sigma_i/2}\phi_0(z_n\sigma_i) + \sigma_i \Delta^{(n)} \tag{66}$$

The contact pair correlation function (44) becomes

$$2\pi\sigma_{ij}\, g_{ij}(\sigma_{ij}) = 2\pi\sigma_{ij}\, g_{ij}^0(\sigma_{ij}) + \sum_n (\Pi_i^{(n)} - z_n X_i^{(n)}) a_j^{(n)} \tag{67}$$

where we have defined [see Eq. (54)]

$$\Pi_j^{(n)} = \sum_t \Pi_{tj}^{(n)} d_t^{(n)} e^{-z_n\sigma_t/2}$$
$$= B_j^{(n)} e^{z_n\sigma_j/2} + \left(1 + \frac{z_n\sigma_j}{2}\right)\Delta^{(n)} + \frac{\pi}{2\Delta}\sigma_j \sum_l \rho_l\sigma_l X_l^{(n)} \tag{68}$$

Equation (54) now becomes

$$-\Pi_j^{(n)} = \sum_m \frac{1}{z_n + z_m} a_j^{(m)} \sum_l \rho_l [z_m X_l^{(n)} X_l^{(m)} + X_l^{(m)} \Pi_l^{(n)} - X_l^{(n)} \Pi_l^{(m)}] \tag{69}$$

For any given value of n the parameter $\Pi_j^{(n)}$, $X_j^{(n)}$ are related to each other, since they are only functions of the external parameters and $B_j^{(n)}$. From Eqs. (66) and (68) we have

$$\sum_l \Pi_l^{(n)} \mathscr{I}_{jl}^{(n)} = \sum_l X_l^{(n)} \mathscr{J}_{jl}^{(n)} - d_i^{(n)} e^{-z_n\sigma_i/2} \tag{70}$$

where

$$\mathscr{I}_{jl}^{(n)} = \delta_{jl}\sigma_j\phi_0(z_n\sigma_j) - \frac{2\pi}{\Delta}\rho_l\sigma_l\sigma_j^3\psi_1(z_n\sigma_j) \tag{71}$$

and

$$\mathscr{J}_{jl}^{(n)} = \delta_{jl} + \sigma_j^2\phi_0(z_n\sigma_j)\frac{\pi}{2\Delta}\rho_l\sigma_l - \frac{2\pi}{\Delta}\rho_l\sigma_j^3\psi_1(z_n\sigma_j)\left[1 + \left(\zeta_2\frac{\pi}{2\Delta}\right)\sigma_l + \frac{\sigma_l z_n}{2}\right] \tag{72}$$

This equation can be written in the form

$$\sigma_j\phi_0(z_n\sigma_j)\Pi_j^{(n)} - X_j^{(n)} + d_i^{(n)} e^{-z_n\sigma_i/2}$$
$$= z_n^2\sigma_j^3\psi_1(z_n\sigma_j)\Delta^{(n)} + \frac{\pi}{2\Delta}\sigma_j^2\phi_0(z_n\sigma_j)\sum_l \sigma_l\rho_l X_l^{(n)} \tag{73}$$

The closure condition (57) is

$$2\pi K^{(n)} d_j^{(n)} \frac{e^{-z_n\sigma_j/2}}{z_n} + \sum_l a_l^{(n)} \mathscr{I}_{jl}^{(n)}$$

$$-\sum_m \frac{1}{z_n+z_m}\left(\sum_k \rho_k a_k^{(n)} a_k^{(m)}\right)\left[\sum_l \mathscr{I}_{jl}^{(n)}(\Pi_l^{(m)} - z_m X_l^{(m)}) - \mathscr{I}_{jl}^{(n)} X_l^{(m)}\right] = 0 \tag{74}$$

A different closure is obtained from Eq. (58),

$$2\pi K^{(n)} B_j^{(n)} \frac{e^{z_n\sigma_j/2}}{z_n}$$

$$= -\frac{2\pi}{\Delta z_n^2}\sum_l \rho_l a_l^{(n)}\left\{1 + \frac{z_n\sigma_l}{2} + \sigma_l\left[\left(1+\zeta_2\frac{\pi}{2\Delta}\sigma_j\right)z_n + \zeta_2\frac{\pi}{2\Delta}\right]\right\}$$

$$-\sum_m \frac{1}{z_n+z_m}\left(\sum_k \rho_k a_k^{(n)} a_k^{(m)}\right)$$

$$\times\left[\Pi_j^{(m)} - z_m X_j^{(m)} + \frac{z_m}{z_n}\Delta^{(m)} + \frac{\pi}{\Delta z_n}P^{(m)}\left(z_n + z_m + \frac{1}{2}\sigma_j z_n z_m\right)\right] \tag{75}$$

where $P^{(m)}$ is defined by

$$P^{(m)} = -\frac{2}{z_m}\sum_l \rho_l\left[\sigma_l \Pi_l^{(m)} + X_l^{(m)}\left(1+\zeta_2\frac{\pi}{2\Delta}\sigma_l\right)\right]$$

$$= \sum_l \rho_l \sigma_l X_l^{(m)} - \frac{\Delta}{\pi} z_m \Delta^{(m)} \tag{76}$$

A full solution of the multi-Yukawa, multicomponent mixture requires the introduction of a scaling parameter. The most convenient scaling relation is obtained from Eq. (69),

$$\Pi_i^{(n)} = -\sum_m \Gamma_{mn} X_i^{(m)} \tag{77}$$

where Γ_{mn} is an $M \times M$ matrix of scaling parameters. From the symmetry of the direct correlation function at the origin, Eqs. (35) and (65), we have

$$q_{ij}(\lambda_{ji}) = q_{ji}(\lambda_{ij})$$

$$\sum_n X_i^{(n)} a_j^{(n)} = \sum_n X_j^{(n)} a_i^{(n)} \tag{78}$$

which implies that

$$a_i^{(n)} = \sum_m \Lambda_{mn} X_i^{(m)} \tag{79}$$

and also that there are $M(M-1)/2$ symmetry relations

$$\Lambda_{mn} = \Lambda_{nm} \tag{80}$$

From the symmetry of the contact pair correlation function (44) we get

$$g_{ij}(\sigma_{ij}) = g_{ji}(\sigma_{ij})$$

$$\sum_n (\Pi_i^{(n)} - z_n X_i^{(n)}) a_j^{(n)} = \sum_n (\Pi_j^{(n)} - z_n X_j^{(n)}) a_i^{(n)} \tag{81}$$

from which we get the scaling relation

$$\Pi_i^{(n)} - z_n X_i^{(n)} = \sum_m \Upsilon_{mn} a_i^{(m)} \tag{82}$$

and a new set of $M(M-1)/2$ symmetry relations

$$\Upsilon_{mn} = \Upsilon_{nm} \tag{83}$$

The three scaling matrices $\mathbf{\Gamma}$, $\mathbf{\Lambda}$, and $\mathbf{\Upsilon}$ are related to each other. From Eqs. (77), (80), and (82) we get by substitution

$$-(\mathbf{\Gamma} + \mathbf{z} \cdot \mathbf{I}) = \mathbf{\Upsilon} \cdot \mathbf{\Lambda} \tag{84}$$

where $\mathbf{z}$ is a diagonal matrix of elements z_n, and $\mathbf{I}$ is the unit matrix.

Furthermore, using the scaling relations and Eq. (69) we get

$$\tilde{\mathbf{M}} \cdot \mathbf{\Lambda} = \mathbf{\Gamma} \tag{85}$$

where the matrix $\tilde{\mathbf{M}}$ has elements

$$[\tilde{\mathbf{M}}]_{mn} = \frac{1}{z_n + z_m} \sum_l \rho_l [z_m X_l^{(n)} X_l^{(m)} + X_l^{(m)} \Pi_l^{(n)} - X_l^{(n)} \Pi_l^{(m)}] \tag{86}$$

Solving these equations yields

$$\tilde{\mathbf{M}}^{-1} \cdot \mathbf{\Gamma} = \mathbf{\Lambda} \tag{87}$$

and

$$-(\mathbf{I} + \mathbf{z} \cdot \mathbf{\Gamma}^{-1}) \cdot \tilde{\mathbf{M}} = \mathbf{\Upsilon} \tag{88}$$

The symmetry requirements are then

$$\tilde{\mathbf{M}}^{-1}\cdot\mathbf{\Gamma}=\mathbf{\Gamma}^{T}\cdot[\tilde{\mathbf{M}}^{-1}]^{T} \tag{89}$$

and

$$(\mathbf{I}+\mathbf{z}\cdot\mathbf{\Gamma}^{-1})\cdot\tilde{\mathbf{M}}=\tilde{\mathbf{M}}^{T}\cdot(\mathbf{I}+[\mathbf{\Gamma}^{-1}]^{T}\cdot\mathbf{z}) \tag{90}$$

where the superscript T indicates that the transpose of the matrix is taken. We have therefore a total of $M(M-1)$ symmetry relations, which together with the M closure equations (74) or (75) gives the required equations for the M^2 elements of the matrix $\mathbf{\Gamma}$.

4. THE SEMIRESTRICTED CASE

In spite of simplifications of the last section, the solution of the numerical equations for the factored interaction case is still complicated. As is the case for ionic systems,[20–29] a much simpler set of equations is obtained when an electroneutrality relation is satisfied. If we also assume that all the moments of the diameters are zero

$$\sum_i d_i^{(n)}\rho_i\sigma_i^t=0, \qquad t=0,1,2,\ldots$$

then one can show that $P^{(m)}$ and $\Delta^{(m)}$ are also zero. We remark that this does not imply necessarily that all the ions should be of the same size, but that subsets of ions of equal size are neutral.

From Eq. (73) we get now

$$\sigma_j\phi_0(z_n\sigma_j)\Pi_j^{(n)}-X_j^{(n)}+d_j^{(n)}e^{-z_n\sigma_j/2}=0 \tag{91}$$

From Eq. (68) we find

$$\Pi_j^{(n)}=B_j^{(n)}e^{z_n\sigma_j/2} \tag{92}$$

and from Eq. (66)

$$X_j^{(n)}=d_j^{(n)}e^{-z_n\sigma_j/2}+\sigma_jB_j^{(n)}e^{z_n\sigma_j/2}\phi_0(z_n\sigma_j) \tag{93}$$

Using the scaling relation (77), we obtain from Eq. (91)

$$\sum_m[\delta_{mn}+\sigma_j\phi_0(z_n\sigma_j)\Gamma_{mn}]X_j^{(m)}=d_j^{(n)}e^{-z_n\sigma_j/2} \tag{94}$$

which yields an explicit (actually as explicit as possible!) expression for $X_j^{(m)}$ in terms of the scaling parameter matrix $\mathbf{\Gamma}$. Similarly, we can write the matrix $\tilde{\mathbf{M}}$

$$[\tilde{\mathbf{M}}]_{mn}=\frac{1}{z_n+z_m}\sum_{p,q}(z_m\delta_{mq}\delta_{pn}-\Gamma_{pn}\delta_{mq}+\Gamma_{qm}\delta_{pn})\tilde{D}_{pq} \tag{95}$$

with

$$\tilde{D}_{pq} = \sum_l \rho_l X_l^{(p)} X_l^{(q)} \tag{96}$$

which, because of Eq. (94), is also an explicit function of $\boldsymbol{\Gamma}$.

In the semirestricted case the closure relations are, from Eq. (75),

$$\frac{2\pi}{z_n} K^{(n)} \Pi_j^{(n)} = -\sum_m \frac{1}{z_n + z_m} \left(\sum_k \rho_k a_k^{(n)} a_k^{(m)} \right) (\Pi_j^{(m)} - z_m X_j^{(m)}) \tag{97}$$

and from the scaling we get

$$\sum_p \left[\frac{2\pi}{z_n} K^{(n)} \Gamma_{np} + \sum_m \frac{1}{z_n + z_m} \left(\sum_k \rho_k a_k^{(n)} a_k^{(m)} \right) (\Gamma_{mp} + z_m \delta_{pm}) \right] X_j^{(p)} = 0 \tag{98}$$

which is a homogeneous system of equations for $X_j^{(p)}$. It has a nontrivial solution only when the determinant of the matrix enclosed by the square brackets is zero. Thus there are M closure conditions arising from this condition. This is the generalization to the multi-Yukawa formula.[11]

ACKNOWLEDGMENT

We acknowledge support from the National Science Foundation through grants NSF-CHE-89-01597 and Epscor RII-86-10677.

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