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Solution of the Ornstein–Zernike Equation for a Mixture of Hard Ions and Yukawa Closure

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The solution of the Ornstein–Zernike equation with Yukawa closure discussed in an earlier paper is simplified and extended to the more general case of several exponentials with real or complex exponents. The interesting case of an ionic mixture with Yukawa closure is solved explicitly. This case corresponds to ionic melts (molten salts).

KEY WORDS: Mean spherical model; mixtures; Yukawa closure; Ornstein–Zernike equation; generalized mean spherical model; molten salts.

1. INTRODUCTION

In recent papers[1,2] we found solutions of the Ornstein–Zernike (OZ) equation for systems of hard spheres with Yukawa closure for various cases of pure fluids and mixtures. This work extended the work of Waisman *et al.*[3,4] of the solution of the Yukawa closure for a single-component fluid.

In our previous work the Fourier transform[5,6] method was used, which led to relatively simple sets of algebraic equations, and also gave explicit formulas for most of the relevant quantities.

One of the more interesting applications of this solution is the generalized mean spherical approximation[8] of ionic melts. In this case, the system is a mixture of charged, hard spheres of different size. The direct correlation function for distances larger than contact is

$$c_{ij}(r) = -\beta e_i e_j/\epsilon_0 r + K_{ij} e^{-z(r-\sigma_{ij})}/r, \qquad r > \sigma_{ij}$$

where $\beta = 1/kT$ is the Boltzmann factor, e_i is the electric charge of ion i, σ_{ij} is the distance at contact of the pair (i, j), and ϵ_0 is the dielectric constant.

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Here K_{ij} and z are constants to be adjusted by physical arguments (self-consistency). While this problem has been extensively discussed by Stell and collaborators[4,8,9] for the restricted case of equal size ions, a discussion for the more realistic case of different sizes is still missing. Our solution is a step in this direction.

The solution of this case is also of interest for the problem of spin-glasses, or configurationally disordered spin systems.[10]

Furthermore, the general case with an arbitrary number of exponentials can be solved explicitly (although it is very complicated), so that in principle, the parameters can be adjusted to satisfy some other closure, such as the HNC or LHNC.

In Section 2 we give a brief summary of our previous work and also the formal solution of the general case with an arbitrary number of Yukawas.

In Section 3 we elaborate further on the single-Yukawa case[2] and give a more explicit solution in terms of a single set of parameters. When the exponent $z \to 0$ and an "electroneutrality" condition is imposed, then this solution becomes identical to the MSA for the ionic melt.[11,12,14]

Finally, in Section 4 we give the results for the case of an ionic melt with a Yukawa closure for the general case of unequal diameters. (The case of equal-size ions was solved also by Mou and Mazo.[12]) This result is obtained from the general solution of the two-Yukawa case.

2. FORMAL SOLUTION

Consider first the OZ equation for a mixture of spherical molecules:

$$h_{ij}(r) = c_{ij}(r) + \sum_{l} \rho_l \int d\mathbf{r}_1\, c_{il}(r_1) h_{lj}(|\mathbf{r} - \mathbf{r}_1|) \tag{1}$$

where $h_{ij}(r)$ is the (indirect) pair correlation function between species i and j, $c_{ij}(r)$ is the direct correlation function of the same pair, and ρ_l is the number density of species l. The molecules in our system have a repulsive spherical hard core of diameter σ_l. Since the hard molecules cannot overlap,

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

where $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ is the distance of closest approach. As in our previous work,[2] the general closure of the problem is to require that

$$c_{ij}(r) = \sum_{m} K_{ij}^{m} e^{-z_m(r - \sigma_{ij})}/r, \qquad r > \sigma_{ij} \tag{3}$$

The parameters K_{ij}^{m} and z_m are either given by the problem, which is the case of the mean spherical approximation (MSA), or are determined from some other physical criteria (GMSA,[8] OZVA,[9] etc.).

The procedure is a generalization of our previous work,[2] but there are some differences in the details. The OZ equation in Fourier space is

$$\sum_{l} [\delta_{il} + \rho_l \tilde{h}_{il}(k)][\delta_{lj} - \rho_j \tilde{c}_{lj}(k)] = \delta_{ij} \tag{4}$$

where $\tilde{h}_{il}(k)$ and $\tilde{c}_{il}(k)$ are the three-dimensional Fourier transforms of $h_{il}(r)$ and $c_{il}(r)$. For disordered systems $\tilde{h}_{il}(k) < \infty$ on the real k axis, and, following Baxter,[5] we write

$$\delta_{lj} - \rho_j \tilde{c}_{lj}(k) = \sum_{t} [\delta_{lt} - \rho_t \tilde{Q}_{lt}(k)][\delta_{tj} - \rho_j \tilde{Q}_{jt}(-k)] \tag{5}$$

It can be shown by detailed analysis that

$$\tilde{Q}_{ij}(k) = \int_{\lambda_{ji}}^{\infty} dr\, e^{ikr} Q_{ij}(r) \tag{6}$$

where

$$\lambda_{ji} = \tfrac{1}{2}(\sigma_j - \sigma_i) \tag{7}$$

The function $Q_{ij}(r)$ can be shown[2,5] to be of the form

$$Q_{ij}(r) = Q_{ij}^0(r) + \sum_{n} D_{ij}^n e^{-z_n r} \tag{8}$$

where

$$\begin{aligned} Q_{ij}^0(r) &= \tfrac{1}{2}(r - \sigma_{ij})^2 q_{ij}'' + (r - \sigma_{ij}) q_{ij}' \\ &\quad + \sum_{n} C_{ij}^n (e^{-z_n r} - e^{-z_n \sigma_{ij}}) \qquad \text{for} \quad \lambda_{ji} < r \leqslant \sigma_{ij} \\ &= 0 \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{otherwise} \end{aligned} \tag{9}$$

The problem of solving the OZ equation is thus reduced to the problem of finding the coefficients of $Q_{ij}(r)$. Let us first write (9) in a slightly different form:

$$Q_{ij}^0(r) = \frac{1}{2}(r - \sigma_{ij})(r - \lambda_{ji}) A_{ij} + (r - \sigma_{ij})\beta_{ij} + \sum_{n} C_{ij}^n (e^{-z_n r} - e^{-z_n \sigma_{ij}}) \tag{10}$$

where

$$A_{ij} = q_{ij}'' \tag{11}$$

$$\beta_{ij} = q_{ij}' - (\sigma_i/2) q_{ij}'' \tag{12}$$

We get conditions for these coefficients by taking the inverse Fourier transform of the defining equation (5):

$$2\pi r c_{ij}(r) = -Q_{ij}'(r) + \sum_{l} \rho_l \int dr_1\, Q_{jl}(r_1) Q_{il}'(r_1 + r) \tag{13}$$

For large $r > \sigma_{ij}$ we need

$$e^{z_n \sigma_{ij}} 2\pi K_{ij}^n = z_n \sum_l D_{il}^n [\delta_{lj} - \rho_l \tilde{Q}_{jl}(iz_n)] \tag{14}$$

which is one of the sought equations.

Furthermore, from (4) and (5), we get

$$\sum_l [\delta_{il} + \rho_l \tilde{h}_{il}(k)][\delta_{lt} - \rho_t \tilde{Q}_{lt}(k)] = \{\mathbf{I} - \boldsymbol{\rho}\tilde{\mathbf{Q}}(-k)\}_{it}^{-1} \tag{15}$$

and since the right-hand side is analytical and has no poles on the lower half of the complex k plane, we may get the Fourier inverse by closing a contour around it. The result is

$$2\pi r h_{ij}(r) = -Q_{ij}'(r) + 2\pi \sum_l \rho_l \int dr_1\, (r - r_1) h_{il}(|r - r_1|) Q_{lj}(r_1) \tag{16}$$

From here and (2) we get, using (10), that

$$A_{ij} \equiv A_j = 2\pi\left(1 - \sum_l \rho_l T_{lj}^{(0)}\right) \tag{17}$$

$$\beta_{ij} \equiv \beta_j = 2\pi\left[\frac{\sigma_j}{2} + \sum_i \rho_l \left(T_{lj}^{(0)} - \frac{\sigma_j}{2} T_{lj}^{(0)}\right)\right] \tag{18}$$

where we have defined the moments

$$T_{ij}^{(n)} = \int_{\lambda_{ji}}^{\infty} dr\, r^n Q_{ij}(r) \tag{19}$$

From (8) and (9) we find, after a short calculation,

$$T_{lj}^{(0)} = -\frac{\sigma_l^2 \beta_j}{2} - \frac{\sigma_l^3 A_j}{12} - \sum_n e^{-z_n \sigma_{lj}} \left[(C_{lj}^n + D_{lj}^n) z_n \varphi_1(-z_n, \sigma_l) - D_{lj}^n \frac{1}{z_n}(1 + z_n \sigma_l)\right] \tag{20}$$

$$T_{lj}^{(1)} - \frac{\sigma_j T_{lj}^{(0)}}{2} = \frac{\sigma_l^3 \beta_j}{12} + \sum_n e^{-z_n \lambda_{jl}} \left[(C_{lj}^n + D_{lj}^n) z_n \psi_1(z_n, \sigma_l) + D_{lj}^n \frac{e^{-z\sigma_l}}{z_n^2}\left(1 + \frac{z_n \sigma_l}{2}\right)\right] \tag{21}$$

where

$$\varphi_1(z, \sigma) = (1/z^2)(1 - z\sigma - e^{-z\sigma}) \tag{22}$$

$$\psi_1(z, \sigma) = (1/z^3)[1 - \tfrac{1}{2}z\sigma - e^{-z\sigma}(1 + \tfrac{1}{2}z\sigma)] = \frac{\sigma^2}{2z} e^{-z\sigma/2} i_1(\tfrac{1}{2}z\sigma) \tag{23}$$

$$i_1(x) = (1/x^2)(\sinh x - x \cosh x) \tag{24}$$

We now solve (17) and (18) for A_j and β_j: This yields

$$\beta_j = \frac{\pi\sigma_j}{\Delta} + \frac{2\pi}{\Delta}\sum_n \mu_j{}^n \tag{25}$$

$$A_j = \frac{2\pi}{\Delta}\left(1 + \frac{1}{2}\zeta_2\beta_j + \sum_n m_j{}^n\right) \tag{26}$$

with

$$\zeta_m = \sum \rho_l(\sigma_l)^m \tag{27}$$

$$\Delta = 1 - \tfrac{1}{6}\pi\zeta_3 \tag{28}$$

and

$$\mu_j{}^n = \sum_l \rho_l e^{-z_n\lambda_{jl}}\left[(C_{lj}^n + D_{lj}^n)z_n\psi_1(z_n, \sigma_l) + D_{lj}^n \frac{e^{-z_n\sigma_l}}{z_n{}^2}\left(1 + \frac{z_n\sigma_l}{2}\right)\right] \tag{29}$$

$$m_j{}^n = \sum_l \rho_l e^{-z_n\sigma_{jl}}\left[(C_{lj}^n + D_{lj}^n)z_n\varphi_1(-z_n, \sigma_l) - D_{lj}^n \frac{1}{z_n}(1 + z_n\sigma_l)\right] \tag{30}$$

From the third and higher derivatives of (16) we get the set of conditions

$$C_{ij}^n + D_{ij}^n = \sum_l \gamma_{il}(z_n)D_{lj}^n \tag{31}$$

with

$$\gamma_{il}(z_n) = 2\pi\rho_l\tilde{g}_{il}(z_n)/z_n \tag{32}$$

and

$$\tilde{g}_{il}(z_n) = \int_0^\infty dr\, e^{-z_n r} r g_{il}(r), \qquad g_{il}(r) = 1 + h_{il}(r) \tag{33}$$

Using (31), we eliminate C_{lj}^n from (29) and (30):

$$\mu_j{}^n = \sum_t \rho_t C_t{}^\mu(z_n)D_{tj}^n e^{-z_n\sigma_{jt}} \tag{34}$$

$$m_j{}^n = \sum_t \rho_t C_t{}^m(z_n)D_{tj}^n e^{-z_n\sigma_{jt}} \tag{35}$$

with

$$C_t{}^\mu(z_n) = \sum_l \gamma_{tl}(z_n)e^{z_n\sigma_{tl}}z_n\psi_1(z_n, \sigma_l) + \frac{1}{z_n^2}\left(1 + \frac{z_n\sigma_t}{2}\right) \tag{36}$$

$$C_t{}^m(z_n) = \sum_l \gamma_{tl}(z_n)e^{-z_n\lambda_{tl}}z_n\varphi_1(-z_n, \sigma_l) - \frac{1}{z_n}\left(1 + z_n\sigma_t\right) \tag{37}$$

So far, we have reduced the algebraic problem to two sets of parameters, $\tilde{g}_{ij}(z_n)$ and D_{ij}^n, and we have one set of equations (14). The other set is obtained from Eq. (16) by Laplace transformation. Following a procedure described in Ref. 2, Eqs. (30)–(33), we get (in the notation of Ref. 2)

$$\sum_l 2\pi\tilde{g}_{il}(s)[\delta_{lj} - \rho_l\tilde{Q}_{lj}(is)] = \frac{e^{-s\sigma_{ij}}}{s^2}(q''_{ij} + sq'_{ij}) - \sum_n \frac{e^{-(s+z_n)\sigma_{ij}}}{s+z_n} z_n C^n_{ij} \quad (38)$$

The required set of equations is obtained from (38) by making $s = z_n$. Using (11), (12), (25), (26), and (6), we get, after some lengthy but straightforward algebra,

$$\begin{aligned}&2\pi\tilde{g}_{ij}(z_n)e^{z_n\sigma_{ij}} - A_j C_i^{\mu}(z_n) - \beta_j C_i^{1}(z_n)\\ &+ \sum_m \left\{\frac{1}{z_n + z_m}\left[z_m C^m_{ij} e^{-z_m\sigma_{ij}} - z_n \sum_l \gamma_{il}(z_n) D^m_{lj} e^{-z_m\lambda_{jl}} e^{z_n\sigma_{il}}\right]\right.\\ &\left. - z_n \sum_l \gamma_{il}(z_n) e^{z_n\sigma_{il}} C^m_{lj} e^{-z_m\lambda_{jl}}[\varphi_0(z_n + z_m, \sigma_l) + e^{-(z_n+z_m)\sigma_l}\varphi_0(-z_n, \sigma_l)]\right\} = 0\end{aligned} \quad (39)$$

with

$$\varphi_0(s, \sigma) = (1/s)(1 - e^{-s\sigma}) \quad (40)$$

and

$$C_i^1(s) = \frac{1}{s} + \sum_l \gamma_{il} e^{s\sigma_{il}} s\varphi_1(s, \sigma_l) \quad (41)$$

with $\varphi_1(s, \sigma_l)$ given by (22).

This is a set of linear equations for D^n_{ij} in terms of $\tilde{g}_{ij}(z_n)$ only. This set of equations can be solved, and substituted into (14), to get a set of nonlinear equations for $\tilde{g}_{ij}(z_n)$. A physical branch of the solution has to be chosen from the manifold of solutions.

Using (38), we can write (14) in a slightly more convenient form

$$\begin{aligned}&2\pi \sum_l z_n K^n_{il}\gamma_{lj}(z_n)\, e^{z_n\sigma_{il}}\\ &= \sum_k \rho_k \frac{e^{-z_n\sigma_{jk}}}{z_n} D^n_{ik}\left[A_k\left(1 + \frac{z_n\sigma_j}{2}\right) + z_n\beta_k - z_n^2 \sum_m \frac{z_m}{z_n + z_m} e^{-z_m\sigma_{jk}} C^m_{jk}\right]\end{aligned} \quad (42)$$

where A_k is given by (26), B_k by (25), and C^m_{jk} by (31).

These sets of equations, (39) and (42), constitute the formal solution of the given problem, since we can calculate all the coefficients in the functions $Q_{ij}(r)$, (8), from $\tilde{g}_{ij}(z_n)$, and therefore, the pair correlation functions and the thermodynamic properties. In the next section we will show that for the case of one Yukawa some remarkable simplifications occur.

3. THE ONE-YUKAWA CASE AND THE LIMIT OF IONIC MELTS

When the Yukawa closure has only one set of exponentials, that is,

$$c_{ij}(r) = K_{ij}e^{-z(r-\sigma_{ij})}/r \tag{43}$$

then the equations of the preceding section simplify considerably.

First notice that (39) becomes, with (25) and (26),

$$2\pi\tilde{g}_{ij}(z)e^{z\sigma_{ij}} - \frac{2\pi}{\Delta}\left(1 + \frac{1}{2}\zeta_2\frac{\pi}{\Delta}\sigma_j\right)C_i^{\mu}(z) - \frac{\pi}{\Delta}\sigma_j C_i^{1}(z)$$
$$= \frac{2\pi}{\Delta}\left(m_j + \frac{\pi}{\Delta}\zeta_2\mu_j\right)C_i^{\mu}(z) + \frac{2\pi}{\Delta}\mu_j C_i^{1}(z)$$
$$+ \frac{1}{2}\sum_l \{\gamma_{il}(z)e^{z\sigma_{il}}[C_{lj}(z\varphi_0(z,\sigma_l))^2 + D_{lj}]e^{-z\lambda_{jl}}\} - \frac{1}{2}C_{ij}e^{-z\sigma_{ij}} \tag{44}$$

Furthermore, using (31), (34), (35), and the fact that

$$\sigma_t + \frac{2}{z}\left[1 + \sum_l \gamma_{il}(z)e^{z\sigma_{il}}z\varphi_0(z\sigma_l)\right] - \sum_l \sigma_l(1 + e^{-z\sigma_l})e^{z\sigma_{tl}}\gamma_{tl} = 2zC_t^{\mu}(z) \tag{45}$$

we get

$$\tfrac{1}{2}\sum_{k,t}\Omega_{ik}\Omega_{kt}^{*}D_{tj}e^{-z\sigma_{jt}} = \Upsilon_{ij}(z) \tag{46}$$

with

$$\Omega_{ik} = (2\pi/\Delta)C_i^{\mu}(z)\rho_k\sigma_k - \gamma_{ik}e^{z\sigma_{ik}}z\varphi_0(z,\sigma_k) - \delta_{ik} \tag{47}$$

$$\Omega_{kt}^{*} = (2\pi/\Delta)C_t^{\mu}(z)\rho_t\sigma_k - \gamma_{kt}e^{z\sigma_{kt}}z\varphi_0(z,\sigma_k) - \delta_{kt} \tag{48}$$

$$\Upsilon_{ij}(z) = 2\pi\tilde{g}_{ij}(z)e^{z\sigma_{ij}} - (2\pi/\Delta)[1 + \tfrac{1}{2}\zeta_2(\pi/\Delta)\sigma_j]C_i^{\mu}(z) - (\pi/\Delta)\sigma_j C_i^{1}(z) \tag{49}$$

In matrix form, we write

$$\tfrac{1}{2}\,\mathbf{\Omega\Omega^{*}e}^{-z\sigma/2}\mathbf{De}^{-z\sigma/2} = \mathbf{\Upsilon} \tag{50}$$

which can be solved to yield

$$\mathbf{D} = 2\mathbf{e}^{z\sigma/2}[(\mathbf{\Omega}^{*})^{-1}\mathbf{\Omega}^{-1}\mathbf{\Upsilon}]\mathbf{e}^{z\sigma/2} \tag{51}$$

Using (25), (26), (34), and (35), we get from (42)

$$2\pi\sum_l e^{z\sigma_{il}}K_{il}\gamma_{lj}(z) = \sum_k \rho_k e^{-z\sigma_{jk}}D_{ik}\left(\frac{1}{z}\frac{\pi}{\Delta}\sigma_k + \frac{2\pi}{\Delta}\left(1 + \frac{1}{2}\zeta_2\sigma_k\frac{\pi}{\Delta}\right)\right.$$
$$\times\frac{1}{z^2}\left(1 + \frac{z\sigma_j}{2}\right) + \sum_t D_{tk}e^{-z\sigma_{tk}}\left\{\frac{1}{2}\delta_{tj} - \gamma_{jt}e^{-z\lambda_{jt}} + \frac{2\pi}{\Delta}\left[C_t^{m}(z) + \zeta_2\frac{\pi}{\Delta}C_t^{\mu}(z)\right]\right.$$
$$\left.\left.\times\frac{1}{z^2}\left(1 + \frac{z\sigma_j}{2}\right) + \frac{1}{z}\frac{2\pi}{\Delta}C_t^{\mu}(z)\right\}\right) \tag{52}$$

Equations (51) and (52) must be solved numerically for the set $\gamma_{ij}(z)$.

Let us also show that if

$$K_{ij} \to \beta e_i e_j/\epsilon_0, \qquad z \to 0 \tag{53}$$

where $\beta = 1/kT$ is the Boltzmann factor and e_i is the ionic charge, then we get the limit of the MSA for the ionic mixture.[11-13] This will be not only an instructive example, but also will serve as an introduction to our next section, where we will discuss the GMSA for the case of different diameters.

First, notice that for $z \to 0$

$$\varphi_1(z, \sigma_l) \to -\sigma_l^2/2, \qquad \psi_1(z, \sigma_l) \to -\sigma_l^3/12 \tag{54}$$

Furthermore, from (14) and (53) we must have

$$D_{ij} = -z_i a_j^0 \tag{55}$$

$$(4\pi\beta/\epsilon_0) \sum_i \rho_i e_i^2 = \sum_i \rho_i (a_i^0)^2 \tag{56}$$

Using these relations and the electroneutrality

$$\sum_i \rho_i e_i = 0 \tag{57}$$

we get from (25) and (26) the results for the ionic MSA[11,13,14]

$$\beta_j = \pi\sigma_j/\Delta + a_j^0 \Delta_N \tag{58}$$

$$A_j = \frac{2\pi}{\Delta}\left(1 + \frac{1}{2}\zeta_2 \frac{\pi}{\Delta}\sigma_j\right) + \frac{\pi}{\Delta} a_j^0 P_n \tag{59}$$

with

$$\Delta_N = \frac{\pi}{\Delta}\left(\frac{1}{4}\sum_i \rho_i e_i \sigma_i^2 + \frac{1}{6}\sum_l \rho_l \sigma_l^3 B_l\right) \tag{60}$$

$$B_l = \sum_i \rho_i e_i \left[2\pi \int_0^\infty dr\, r h_{il}(r)\right] \tag{61}$$

$$P_n = \sum_k \rho_k \sigma_k (e_k + \sigma_k B_k + \sigma_k \Delta_N) \tag{62}$$

Furthermore, from (31), we get the set of constants C_{ij} (which are divergent now!)

$$C_{ij} = \lim_{z\to 0} a_j^0 (e_i - B_i/z) \tag{63}$$

Using (8), we get the quantity $Q_{ij}(\lambda_{ji})$

$$Q_{ij}(\lambda_{ji}) = \lim_{z\to 0} [-\sigma_i\beta_j + C_{ij}(e^{-z\lambda_{ji}} - e^{-z\sigma_{ji}}) + D_{ij} e^{-z\lambda_{ji}}] \tag{64}$$

which, by virtue of (63) and (58), yields

$$Q_{ij}(\lambda_{ji}) = -\sigma_i\sigma_j\pi/\Delta - a_j^0(e_i + \sigma_i N_i) \tag{65}$$

with

$$N_i = B_i + \Delta_N \tag{66}$$

which is our previous expression [Eq. (2.33) of Ref. 13]. The symmetry of $Q_{ij}(\lambda_{ji})$ is a crucial condition in the solution of the general mixture of hard ions.

Finally, we get an expression for a_j as a function of N_i (or, equivalently B_i, which is the excess internal energy parameter[13]) from the limit for $z \to 0$ of (51):

$$a_j{}^0 = -(2/D_a)[N_j + (\pi/2\Delta)\sigma_j P_n], \qquad D_a = \sum_k \rho_k(e_k + N_k\sigma_k)^2 \tag{67}$$

which is also our previous expression.

As was discussed in Refs. 12 and 14, Eqs. (56), (64), and (67) constitute the formal solution to the MSA of the primitive model of electrolytes of different sizes.

4. THE CASE OF THE IONIC MIXTURE WITH YUKAWA CLOSURE

We consider now the somewhat more complicated case of a mixture of different size ions.[1] From our general results of Section 2, and using a limiting procedure similar to that described in the last section, we get, from (25) and (26),

$$\beta_j = (\pi/\Delta)\sigma_j + a_j\Delta_N + (2\pi/\Delta)\mu_j \tag{68}$$

and

$$A_j = (2\pi/\Delta)[1 + (\pi/2\Delta)\zeta_2\sigma_j + \tfrac{1}{2}a_jP_n + m_j + (\pi/\Delta)\mu_j] \tag{69}$$

where we have used the definitions of the last section.

Furthermore, from (38) and (39) we get one set of equations by setting $z_n = 0$,

$$a_j = a_j{}^0 - \frac{2}{D_a}\left\{\frac{\pi}{\Delta}\mu_jP_n + \frac{\pi}{\Delta}m_j\Delta_N + \sum_l \rho_l\left[-e_l + \sum_t e_t\gamma_{lt}(z)ze^{-z\lambda_{tl}} - B_le^{z\sigma_l}\right]D_{lj}e^{-z\sigma_{lj}}\right\} \tag{70}$$

where

$$a_j^0 = -(2/D_a)[N_j + \tfrac{1}{2}(\pi/\Delta)\sigma_jP_n] \tag{71}$$

$$D_a = \sum_k \rho_k(e_k + N_k\sigma_k)^2 \tag{72}$$

Using (34) and (35), we get

$$a_j = a_j{}^0 - \frac{2}{D_a}\sum_l \rho_l\Lambda_l(z)D_{lj}e^{-z\sigma_{lj}} \tag{73}$$

with

$$\Lambda_l(z) = \frac{\pi}{\Delta} P_n C_l^{\mu}(z) + \frac{\pi}{\Delta} \Delta_N C_l^M(z) - e_l - B_l e^{z\sigma_l} + \sum_t e_t \gamma_{lt}(z) z e^{-z\lambda_{tl}} \quad (74)$$

Next, consider Eqs. (38) and (39) for $z_n = z$: After much algebra, we get

$$2\pi \tilde{g}_{ij}(z) - \frac{2\pi}{\Delta}\left(1 + \frac{1}{2}\zeta_2 \frac{\pi}{\Delta}\sigma_j\right) C_i^{\mu}(z) - \frac{\pi}{\Delta}\sigma_j C_i^m(z)$$

$$= a_j \Lambda_i^*(z) - \frac{1}{2}\sum_{k,t} \Omega_{ik}\Omega_{kt}^* D_{tj} e^{-z(\sigma_{tj}+\sigma_{ij})} \quad (75)$$

where

$$\Lambda_i^*(z) = \frac{\pi}{\Delta} P_n C_i^{\mu}(z) + \frac{1}{z} N_i + \sum_l \gamma_{il}(z) e^{z\sigma_{il}}[z\varphi_1(z, \sigma_l) - e_l] \quad (76)$$

Combining (73) and (76) will give us a set of equations for D_{ij}:

$$e^{z\sigma_{ij}}\left\{2\pi \tilde{g}_{ij}(z) - \frac{2\pi}{\Delta}\left(1 + \frac{1}{2}\zeta_2 \sigma_j \frac{\pi}{\Delta}\right) C_i^{\mu}(z) - \frac{\pi}{\Delta}\sigma_j C_i^m(z) - a_j^0 \Lambda_i^*(z)\right\}$$

$$= \sum_t \left[\rho_t \Lambda_i^*(z) \Lambda_t(z) e^{z\sigma_{ij}} - \frac{1}{2}\sum_k \Omega_{ik}(z)\Omega_{kt}^*(z)\right] D_{tj} e^{-z\sigma_{tj}} \quad (77)$$

which gives D_{tj} as a function of the excess energy parameters N_j, a_j^0, and $\tilde{g}_{ij}(z)$.

These parameters are calculated from the symmetry condition (64), which now reads

$$Q_{ij}(\lambda_{ji}) = Q_{ji}(\lambda_{ij}) \quad (78)$$

with

$$Q_{ij}(\lambda_{ji}) = -\sigma_i\sigma_j(\pi/\Delta) - a_j^0(e_i + N_i\sigma_i) + (C_{ij} + D_{ij})(e^{-z\lambda_{ji}} - e^{-z\sigma_{ij}}) + D_{ij}e^{z\sigma_{ij}} \quad (79)$$

Another set of equations is obtained from the limit of (14) for $z_0 \to 0$, which yields (63)

$$\frac{4\pi\beta}{\epsilon_0}\sum_i \rho_i(e_i)^2 = \sum_k \rho_k(a_k)^2 \quad (80)$$

Finally, if we take Eq. (14) for $z_n = z$, we will get an equation for the parameters $\tilde{g}_{ij}(z)$:

$$2\pi \sum_l K_{il}\gamma_{ij}(z)\, e^{z\sigma_{il}}$$

$$= \frac{1}{z}\sum_{k,t} \rho_k e^{-z\sigma_{jk}} D_{ik} \Xi_{jt} D_{tk} e^{-z\sigma_{tk}}$$

$$+ \frac{1}{z}\sum_k \rho_k e^{-z\sigma_{jk}} D_{ik}\left[\frac{\pi}{\Delta}\sigma_k + \frac{2\pi}{\Delta}\left(1 + \frac{1}{2}\zeta_2\sigma_k\frac{\pi}{\Delta}\right)\left(1 + \frac{z\sigma_j}{2}\right)\right] \quad (81)$$

with

$$\Xi_{jt} = \rho_t \left\{ \frac{2\pi}{\Delta} C_t^m(z) + \frac{2\pi}{\Delta} C_t^\mu(z) \left[1 + \frac{1}{2z}\left(1 + \frac{z\sigma_j}{2}\right) \frac{\pi}{\Delta} \zeta_2 \right] - \frac{1}{2} z\gamma_{jt} e^{-z\lambda_{jt}} + \frac{z}{2} \delta_{jt} \right\} \tag{82}$$

For the specific case of a binary mixture, Eq. (79) can be solved in a simple way, yielding [together with (80)] two equations for two unknowns N_1, N_2 (or B_1, B_2) as functions of $\gamma_{ij}(z)$ [or $\tilde{g}_{ij}(z)$]. These equations can be solved by computer.

5. DISCUSSION OF PROPERTIES

The results of the preceding sections can be used to compute the properties of the system under study. Our results here are a mere extension of those of our previous work,[2] so that we will only quote them.

From Eqs. (10) and (16), we see that the contact pair distribution function is

$$g_{ij}(\sigma_{ij}^+) = \frac{1}{2\pi\sigma_{ij}} [Q'_{ij}(\sigma_{ij})] = \frac{1}{2\pi\sigma_{ij}} \left[\beta_j + \frac{\sigma_i A_j}{2} - \sum_n z_n C_{ij}^n e^{-z_n \sigma_{ij}} \right] \tag{83}$$

where A_j, β_j, C_{ij}^n are given by (25), (26), and (31) in the most general case, or by similar expressions in the particular cases discussed in Sections 3 and 4. From (83) we can compute the virial pressure for the ionic mixture case using the formula[15]

$$\Delta p = \frac{1}{3} \left[\frac{1}{\epsilon_0} \sum_i \rho_i e_i B_i + \frac{2\pi}{\beta} \sum_{i,j} \rho_i \rho_j \sigma_{ij}^3 g_{ij}(\sigma_{ij}^+) \right] \tag{84}$$

where Δp is the excess pressure, and B_i is given by Eq. (61).

The internal energy is obtained directly by integrating the standard expression, with the result (for the ionic case of Section 4)

$$-\beta\, \Delta E = \frac{1}{\epsilon_0} \sum_i \rho_i e_i B_i \tag{85}$$

Unfortunately, the very elegant results of Høye and Stell for the MSA[16] do not apply directly to the present case, and we have no explicit formula for the excess properties calculated from the internal energy.

Let us finally remark that the Laplace transform of the pair correlation function can be obtained for the general case from Eq. (38):

$$\sum_l 2\pi \tilde{g}_{il}(s)[\delta_{lj} - \rho_l \tilde{Q}_{lj}(s)] = \frac{e^{-s\sigma_{ij}}}{s^2} \left[\beta_j \left(1 + \frac{s\sigma_i}{2}\right) + A_j \right] - \sum_n \frac{e^{-(s+z_n)\sigma_{ij}}}{s + z_n} z_n C_{ij}^n \tag{86}$$

with

$$\tilde{Q}_{lj}(s) = \left\{\left[\beta_j \varphi_1(s, \sigma_l) + A_j \psi_1(s, \sigma_l) + \sum_n C_{lj}^n \left[\frac{e^{-(s+z_n)\lambda_{jl}} - e^{-(s+z_n)\sigma_{jl}}}{s + z_n} - \frac{e^{-z_n \sigma_{lj}}}{s}(e^{-s\lambda_{jl}} - e^{-s\sigma_{jl}})\right] + \sum_n D_{lj}^n \frac{e^{-(s+z_n)\lambda_{jl}}}{s + z_n}\right\}\right. \tag{87}$$

where β_j and A_j are given as functions of D_{ij}^n and $\tilde{g}_{ij}(z_n)$ by (25) and (26); D_{ij}^n and C_{ij}^n are related by (31); and the functions $\psi_1(z, \sigma)$ and $\varphi_1(z, \sigma)$ are defined by (22) and (24).

We hope to come back to this problem in the near future and discuss the results numerically.

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