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Solution of the Mean Spherical Approximation for Hard Ions and Dipoles of Arbitrary Size

L. Blum[1]

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The general solution of the mean spherical approximation (MSA) for an arbitrary mixture of hard spherical ions and dipoles, in which the ions can be of different size, is found. This solution is given in terms of three parameters that are calculated by solving an algebraic equation. Two of these parameters are scaling parameters required to satisfy the general symmetry of the pair correlation functions, and are similar to the one introduced in the solution of the MSA for an ionic mixture in earlier work. For equal size and low ionic concentration, we get a rather explicit solution of the MSA, which is formally similar to the Waisman–Lebowitz solution of the restricted primitive model, but with a concentration-dependent dielectric constant.

KEY WORDS: Mean spherical approximation; electrolytes; nonprimitive electrolytes.

1. INTRODUCTION

One of the important aspects of the theory of electrolytic solutions is the proper understanding of the solvation effects. By this we understand the difference in the behavior and structure of a real ionic solution in which the ions and the solvent are real molecules and the so-called primitive model in which the solvent is considered as a continuum that pervades the entire system. Aqueous solutions are certainly the most interesting systems, but here, and in spite of the very impressive progress in our understanding of liquid water, our knowledge of the structure and interactions of the molecules and the fluid is far from complete. Moreover, even if we knew the detailed structure and interactions of water, it would be a real task to study

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[1] Physics Department, College of Natural Sciences, University of Puerto Rico, Rio Piedras, Puerto Rico.

the statistical mechanics of simple ions with it. Therefore a model that is more realistic than the primitive model, such as the mixture of hard ions and dipoles, could yield helpful information.

For the primitive model it has been shown that the mean spherical approximation (MSA) of Lebowitz, Percus, and Yevick(1,2) is not only a tractable approximation, but also leads to quite good agreement with computer experiments. The final analytical solution of the restricted (equal-size) case was obtained by Waisman and Lebowitz(3) and yielded excellent agreement with the more elaborate calculations using the hypernetted chain approximation (HNC) and the machine calculations using the Monte Carlo technique. In his rather beautiful work, Wertheim(4) showed that the MSA had also an analytical solution for a system of hard dipoles.

We do not expect the MSA to be numerically very accurate in this case, at least in the interesting case of high dielectric constant (dipole moment). It should be quite reasonable for the weak coupling limit, in which the dielectric constant is low (20).

At any rate, the results of the MSA can be improved systematically either using the graphical expansions of Andersen and Chandler(5) or the GMSA of Waisman(6) and Høye *et al.*(7) Final word on the accuracy of any of these approximation schemes can be obtained only by comparison with machine computations, which are presently unavailable.

The case of a mixture of equal-size ions and hard spheres was solved some time ago by the present author(8) and independently by Adelman and Deutch.(9) The results of these works do not seem to be in complete agreement for all concentrations of the electrolyte, but they are for low concentrations. In the present work we want to give the solution of the MSA for the case in which we have an arbitrary mixture of hard ions and one species of solvent, represented by hard ions. We recall that in the case of the primitive model, the solution of the MSA was given in terms of a single scaling parameter 2Γ.(10) This scaling length has the same physical interpretation as the Debye shielding length, and considering the asymptotic form of the pair correlation function for low ionic concentrations, we can also conclude that indeed 2Γ is the shielding length for the system. In the present work, the symmetrization condition requires two, rather than one, scaling parameters. A simplistic interpretation of this is provided by the idea that now we will need two different types of screening, one of ions by ions and another of ions by dipoles. The solution consists in showing that all the properties of the system can be expressed as functions of the two scaling parameters and the dipole–dipole excess energy parameter, and that these quantities can be found by solving a system of algebraic equations. For the case in which all the ions are of equal size (but the solvent can be of different size) we get a set of three equations that can be shown to be identical with those of Ref. 8. Furthermore, the solution given in that paper is pushed a little further and an explicit expression for the excess energy parameter of the ion–ion interaction is found. The result shows that the thermodynamic properties are given by the same formulas of the restricted primitive model, but with a concentration-dependent dielectric constant, for sufficiently low ionic concentration. A very brief discussion of the thermodynamic properties is given in the last section.

2. METHOD OF SOLUTION

The method of solution derives from our earlier work on the equal-size mixture of ions and dipoles and on the mixture of unequal size ions.(8,10) The notation will be similar to that employed in these works. Our system is composed of a mixture of $n - 1$ components of diameter σ_i, electrovalence z_i, and number density ρ_i ($1 \leqslant i \leqslant n - 1$). The role of the solvent is played by an assembly of hard spheres of diameter σ_n, number density ρ_n, and dipole moment μ^1. Since the ions are spherical, the pair correlation function $g_{ij}(r_{ij})$ depends only on the center-to-center distance

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \tag{1}$$

where $\mathbf{r}_i$ is the position of ion i. For the correlations involving the dipoles, we need to know also the relative orientations. A convenient way of describing these correlations is the invariant expansion formalism described in earlier work(11,12)

$$g_{ij}(\mathbf{X}_i, \mathbf{X}_j) = \sum_{m,n,l} \hat{g}_{ij}^{mnl}(r_{ij})\Phi^{mnl}(\mathbf{\Omega}_i, \mathbf{\Omega}_j, \hat{R}_{ij}) \tag{2}$$

where $\mathbf{X}_i \equiv \mathbf{\Omega}_i$, R_i and $\mathbf{\Omega}_i \equiv \alpha_i, \beta_i, \gamma_i$ are the three Euler angles that give the orientation of the molecule i. The orientation of the intermolecular, center-to-center vector $\mathbf{R}_{ij}$ is given by $\hat{R}_{ij} = \theta_i, \varphi_i$. The coefficients $\hat{g}$ depend only on the center-to-center distance r_{ij}, while the angular dependence of the correlations is given by the invariant products

$$\Phi^{mnl} = [(2m+1)(2n+1)]^{1/2} \sum_{\mu'\nu'\lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} D^m_{0\mu'}(\mathbf{\Omega}_i) D^n_{0\nu'}(\mathbf{\Omega}_j) D^l_{0\lambda'}(\hat{R}_{ij}) \tag{3}$$

where we have used the customary notation for the Wigner 3-j symbols, and generalized spherical harmonics $D^m_{\mu\mu'}(\mathbf{\Omega}_i)$(13) (we will use the notation and conventions of Edmonds(13) throughout).

The coefficients in the expansion (2) are not dependent on the choice of any particular reference frame. A rather convenient expansion, which we call the irreducible representation (IRREP), is obtained by taking a reference frame with the z axis along the $\mathbf{R}_{ij}$ vector. Then, after a slight rearrangement, we obtain

$$g_{ij}(\mathbf{X}_i, \mathbf{X}_j) = \sum_{m,n,\chi} g^{mn}_{ij,\chi}(\mathbf{R}_{ij})\Phi^{mn}_{\chi}(\mathbf{\Omega}_i, \mathbf{\Omega}_j) \tag{4}$$

with

$$g^{mn}_{ij,\chi} = \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \hat{g}^{mnl}_{ij} \tag{5}$$

and

$$\Phi^{mn}_{\chi} = [(2m+1)(2n+1)]^{1/2} D^{m}_{0\chi}(\mathbf{\Omega}_i) D^{n}_{0,-\chi}(\mathbf{\Omega}_j) \tag{6}$$

With this expansion, the Ornstein–Zernike equation becomes a set of matrix equations, each for a value of χ. If the order of the highest multipole in a particular expansion is n, there will be $2n+1$ matrix equations for $|\chi| \leqslant n$. We should remark that the IRREP expansion (4) is very similar to the helicity expansion used in high-energy nuclear physics. Let us put this in a more explicit form: Consider the IRREP expansion for the indirect correlation function $h_{ij} = g_{ij} - 1$, and also for the direct correlation function c_{ij}.(14) To avoid unnecessary repetitions, let us designate either h_{ij} or c_{ij} by the generic notation f_{ij}: The Fourier Bessel transform of the IRREP coefficient is related to the invariant coefficient of (2) by

$$F^{mn}_{ij,\chi}(k) = (-)^{\chi} 4\pi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} (i)^l \int_0^\infty dr\, r^2 j_l(kr) \hat{f}^{mnl}_{ij}(r) \tag{7}$$

where $j_l(kr)$ is the standard notation for the spherical Bessel function of order l. A convenient integral representation of this function is(15)

$$j_l(kr) = (1/2i^l) \int_0^1 dt\, P_l(t)[e^{ikrt} + (-)^l e^{-ikrt}] \tag{8}$$

where $P_l(t)$ is the Legendre polynomial of order l. Using now the symmetry

$$\hat{f}^{mnl}_{ij} = (-)^l \hat{f}^{nml}_{ji} \tag{9}$$

we can write (7) in compact matrix form

$$\mathbf{F}_{\chi}(k) = \int_0^\infty dr\, [e^{ikr}\mathscr{F}_{\chi}(r) + e^{-ikr}\mathscr{F}_{\chi}^{T}(r)], \qquad \mathbf{F}_{\chi}(k) = F_{\chi}^{T}(-k) \tag{10}$$

where $\mathscr{F}^T$ is the transpose of the matrix $\mathscr{F}$. By direct substitution we find that the matrix elements of (10) are given by

$$\mathscr{F}^{mn}_{ij,\chi}(r) = (-)^{\chi} 2\pi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \int_r^\infty dr_1\, r_1 P_l(r/r_1) \hat{f}^{mnl}_{ij}(r_1) \tag{11}$$

The inverse transformation from $\mathscr{F}_{ij,\chi}^{mn}$ to $f_{ij}^{mnl}(r)$ is given in Appendix A. We should also notice that there is a direct relation to the expansions given by Wertheim in his original work on dipoles.(4) Let us designate by $\mathbf{J}_\chi$ the transform of $\mathbf{h}^l$ and by $\mathbf{S}_\chi$ the transform of $\mathbf{c}^l$. In other words

$$J_{ij,\chi}^{mn}(r) = (-)^\chi 2\pi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \int_r^\infty dr_1\, r_1 P_l(r/r_1) \hat{h}_{ij}^{mnl}(r_1) \tag{12}$$

and

$$S_{ij,\chi}^{mn}(r) = (-)^\chi 2\pi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \int_r^\infty dr_1\, r_1 P_l(r/r_1) \hat{c}_{ij}^{mnl}(r_1) \tag{13}$$

Using now (10), (12), and (13), we get the matrix OZ equation in Fourier space and in the irreducible representation

$$[I + \boldsymbol{\rho}^{1/2} \mathscr{H}_\chi(k) \boldsymbol{\rho}^{1/2}][I - \boldsymbol{\rho}^{1/2} \mathbf{C}_\chi(k) \rho^{1/2}] = I \tag{14}$$

To define the mathematical problem, we need now to give the closure of the OZ equation, that is, a relation between $\mathbf{C}_\chi(r)$ and $\mathbf{H}_\chi(r)$ outside the hard core. The simplest closure is the MSA,(1–4) in which the direct correlation function outside the hard core is proportional to the interaction potential. In terms of the invariant coefficients (2) we have

$$\hat{c}_{ij}^{mnl}(r) = -\beta u_{ij}^{mnl}(r), \qquad r > \sigma_{ij} \tag{15}$$

with

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \tag{16}$$

$\beta = 1/kT$ is the usual Boltzmann thermal factor. For electrostatic multipolar interaction, the pair potential can be expanded as

$$u_{ij}(\mathbf{X}_i, \mathbf{X}_j) = \sum_{mnl} u^{mnl}(r_{ij}) \hat{\Phi}^{mnl}(\boldsymbol{\Omega}_i \boldsymbol{\Omega}_j \hat{\mathbf{R}}_{ij}) \tag{17}$$

with coefficients(16)

$$u^{mnl}(r) = \delta_{l,m+n}(-)^m \left[\frac{(2l+1)!}{(2m+1)!\,(2n+1)!}\right]^{1/2} \frac{\mu^m \mu^n}{r^{l+1}}$$

where μ^m is the (linear in our case) multipole moment of order m. The MSA is mathematically simple, because it decouples the IRREPS. But this means that the cluster graphs corresponding to this approximation will be missing part of the contributions of the dipole–dipole interaction to the center-to-center correlation function.

Combining (13) and (15) with the relation

$$\int_r^\infty dr_1\, r_1 P_l\left(\frac{r}{r_1}\right) \frac{1}{r_1^{l+1}} = \frac{1}{r^{l-1}} \int_0^1 dx\, P_l(x) x^{l-2} = 0 \qquad \text{for} \quad l \geqslant 2 \tag{18}$$

we have that for the dipole–dipole correlation function the boundary condition is(4)

$$S_{\chi}^{11} = 0, \qquad r \geqslant \sigma_h \tag{19}$$

where we recall that the index n corresponds to the solvent. For the ion–dipole interaction the integral for the boundary condition (13) yields

$$\int_0^1 dx\, P_1(x)/x = 1$$

Furthermore, we see from the 3-j symbols of (13) that only $\chi = 0$ will have ion–dipole matrix elements. Physically, this is due to the cylindrical symmetry of the ion–dipole interaction. Then

$$S_0^{01}(r) = z_i \alpha_1, \qquad r \geqslant \sigma_{ih} \tag{20}$$

where

$$\alpha_1 = (4\pi/\sqrt{3})\beta e \mu^1 \tag{21}$$

(The elementary charge is e throughout.)

Finally, it is clear that for the ion–ion interaction ($l = 0$) the integral (18) of Eq. (13) will diverge. For this reason, we will have to introduce a convergence factor $e^{-\mu r_1}$ that we cancel out at the end of the calculation.

Hence

$$\int_r^{\infty} dr_1\, r_1 e^{-\mu r_1}/r_1 = e^{-\mu r_1}/\mu \tag{22}$$

and

$$S^{00}(r) = {\alpha_0}^2 z_i z_j e^{-\mu r_1}/\mu, \qquad r \geqslant \sigma_{ij} \tag{23}$$

with

$${\alpha_0}^2 = 4\pi\beta e^2 \tag{24}$$

Let us now rewrite the OZ equation with a new direct correlation function(3) in which the long-range interactions have been subtracted: That is, if

$$\hat{c}_{ij}^{mnl}(r) = \hat{c}_{ij}^{mnl(0)}(r) - \beta u_{ij}^{mnl}(r) \tag{25}$$

where $\hat{c}_{ij}^{mnl(0)}$ is the short-ranged direct correlation function that is zero for $r \geqslant \sigma_{ij}$. Calling $\mathbf{C}_0{}^0(k)$ the Fourier transform of this function [defined according to (11)], we get the OZ equation for $\chi = 0$

$$[I + \boldsymbol{\rho}^{1/2}\mathscr{H}_0(k)\boldsymbol{\rho}^{1/2}]\{I - \boldsymbol{\rho}^{1/2}[\mathbf{C}_0{}^0(k) - D_0(k)]\boldsymbol{\rho}^{1/2}\} = I \tag{26}$$

The structure of the matrices $\mathbf{H}_0$ and $\mathbf{C}_0$ is similar: Explicitly, the $\mathbf{C}_0$ matrix for the $\chi = 0$ IRREP is

$$\begin{pmatrix} C_{ij}^{00} & C_{in}^{00} & C_{in}^{01} \\ C_{nj}^{00} & C_{nn}^{00} & C_{nn}^{01} \\ C_{nj}^{10} & C_{nn}^{10} & C_{nn}^{11} \end{pmatrix}$$

where C_{ij}^{00} is the coefficient for the ion–ion correlation, C_{in}^{00} is the spherically symmetric ion-core–dipole-core correlation, while C_{in}^{01} is the angle-dependent electrostatic contribution to this interaction. In the MSA, both of these correlations are decoupled, but in the general case, one would expect them to depend on each other. Similarly, for the dipoles, the element C_{nn}^{00} corresponds to the hard-core interaction of the solvent molecules, while C_{nn}^{11} corresponds to the purely electrostatic interaction. The matrix $D_0(k)$ is also an $n + 1$ square matrix, since we have to include the charge $z_n = 0$ for the solvent molecules. (Incidentally, the case of molecules with dipolar moments and charges is rather interesting for the theory of protein solutions.) We have

$$\mathbf{D}_0(k) = \begin{pmatrix} z_i z_j[\alpha_0^2/(k^2 + \mu^2)] & 0 & z_i[\alpha_1/(\mu - ik)] \\ 0 & 0 & 0 \\ z_j[\alpha_1/(\mu + ik)] & 0 & 0 \end{pmatrix} \tag{27}$$

The helicity $\pm\chi = 1$ OZ equation for the ion–dipole mixture turns out to be the same as for the case of the pure dipole case:

$$[1 + \rho_n \mathscr{H}_1(k)][1 - \rho_n C_1(k)] = 1 \tag{28}$$

which has only one component for the electrostatic solvent–solvent interactions.

The next step in the solution is the Wiener–Hopf factorization of the$^{(18,19)}$ direct correlations. For $\chi = 0$ we have

$$\{I - \boldsymbol{\rho}^{1/2}[\mathbf{C}_0{}^0(k) - \mathbf{D}_0(k)]\boldsymbol{\rho}^{1/2}\} = \mathbf{Q}(k)\mathbf{Q}^T(-k) \tag{29}$$

but from the parity and asymptotic behavior of the left-hand side of (29) in the complex plane, we know that the matrix elements of the Baxter factor correlation function $\mathbf{Q}(k)$ must be of the form

$$Q_{ij}^{mn}(k) = \delta_{ij}\delta_{mn} - (\rho_i\rho_j)^{1/2}\left[\int_{\lambda_{ji}}^{\sigma_{ji}} dr\, e^{ikr} Q_{ij}^{mn}(r) - A_{ij}^{mn} \int_{\lambda_{ji}}^{\infty} dr\, e^{r(ik-\mu)}\right] \tag{30}$$

where $m, n = 0, 1$; $1 \leqslant i, j \leqslant n$; and

$$\lambda_{ji} = \tfrac{1}{2}(\sigma_j - \sigma_i) \tag{31}$$

To get further constraints on $Q(k)$, let us examine the inverse Fourier transform of (29)

$$\begin{aligned} &S_{ij}^{mn}(r) + D_{ij}^{mn}(r)\varphi^{mn}(r) \\ &\quad = [-Q_{ij}^{mn}(r) + A_{ij}^{mn}]\theta(r - \lambda_{ji}) + [-Q_{ji}^{nm}(-r) + A_{ji}^{nm}]\theta(-r - \lambda_{ij}) \\ &\qquad + \sum_{kn_1} \rho_k \left\{ \varphi^{00}(r) A_{ik}^{mn_1} A_{jk}^{nn_1} + \int_{[\lambda_{ki},\lambda_{kj}+r]}^{[\sigma_{ki},\sigma_{kj}+r]} dr_1\, Q_{ik}^{mn_1}(r_1) Q_{jk}^{nn_1}(r_1 - r) \right. \\ &\qquad \left. - \int_{[\lambda_{ki},r+\lambda_{kj}]}^{\sigma_{ki}} dr_1\, A_{jk}^{nn_1} Q_{ik}^{mn_1}(r_1) - \int_{[\lambda_{kj},\lambda_{ki}-r]}^{\sigma_{kj}} dr_1\, A_{ik}^{mn_1} Q_{jk}^{nn_1}(r_1) \right\} \end{aligned} \tag{32}$$

where D_{ij}^{mn} are the coefficients, and $\varphi^{mn}(r)$ are the radial dependent parts of the matrix elements of the matrix $\mathbf{D}_0(r)$. In other words,

$$\begin{aligned} D_{ij}^{00} &= \alpha_0{}^2 z_i z_j; & \varphi^{00}(r) &= e^{-\mu|r|}/2\mu \\ D_{in}^{01} &= \alpha_1 z_i; & \varphi^{01}(r) &= e^{-r\mu}\theta(r) \\ D_{ni}^{10} &= \alpha_1 z_i; & \varphi^{10}(r) &= e^{+r\mu}\theta(-r) \end{aligned} \tag{33}$$

In (32) we have also used the notation $\theta(x)$ for the Heaviside function, and the square brackets $[x, y]$ in the limits of the integrals indicate either the least upper bound or the largest lower bound.

If we multiply (32) by μ and then take the $\mu \to 0$ limit, we get

$$D_{ij}^{00} = \sum_k \rho_k A_{ik}^{0n_1} A_{jk}^{0n_1} \tag{34}$$

But $\mathbf{D}_0$ is a very singular matrix, and it has only two nonzero eigenvalues. It can be shown therefore that the above relation also implies that $\mathbf{A}$ is also singular, and that

$$A_{ik}^{0n} = z_i a_k{}^n, \qquad A_{ik}^{1n} = 0, \qquad n = 0, 1 \tag{35}$$

(where $a_k{}^n$ is defined by this relation) so that, using (27), we get

$$\alpha_0{}^2 = \sum_k \rho_k (a_k{}^0)^2 + \rho_n (a_n{}^1)^2 \tag{36}$$

where $\alpha_0{}^2$ is defined by (24). This equation is the generalization of Eq. (14) of Ref. 8b.

From the continuity of $S_{ij}^{mn}(r)$ at the boundary $r = \sigma_{ij}$ we get from (32)

$$Q_{ij}^{mn}(\sigma_{ij}) = 0 \tag{37}$$

Also from (32), and for $r > \sigma_{ij}$, we need

$$D_{in}^{01} = A_{in}^{01} - \sum_{kn_1} \rho_k A_{ik}^{0n_1} K_{nk}^{1n_1} \tag{38}$$

where we have used the notation

$$K_{ij}^{mn} = \int_{\lambda_{ji}}^{\sigma_{ji}} dr\, Q_{ij}^{mn}(r) \tag{39}$$

Because of (35) and using (21) and (27), we see that the boundary condition (38) can be rewritten in the more compact form

$$\alpha_1 = a_n{}^1(1 - \rho_n K_{nn}^{11}) - \sum_{j \leqslant n-1} \rho_j a_j{}^0 K_{nj}^{10} \tag{40}$$

which again is the generalization for the mixture of the corresponding relation for the pure ionic case. Another relation that will be needed is the symmetry relation

$$Q_{ij}^{00}(\lambda_{ji}) - A_{ij}^{00} = Q_{ji}^{00}(\lambda_{ij}) - A_{ji}^{00} \tag{41}$$

which again is quite similar to the one of the ionic case. This condition ensures that $\mathbf{C}_0(k)$ has the correct symmetry under the transformation $k \to -k$.

The functional form of $\mathbf{Q}(r)$ is obtained from the Fourier inverse of

$$[\mathbf{I} + \boldsymbol{\rho}^{1/2}\mathscr{H}_0(k)\boldsymbol{\rho}^{1/2}]Q(k) = [\mathbf{Q}^T(-k)]^{-1} \tag{42}$$

which is

$$J_{ij}^{mn}(r) = Q_{ij}^{mn}(r) - A_{ij}^{mn} + \sum_{kn_1} \rho_k \int_{\lambda_{jk}}^{\infty} dr_1\, J_{ik}^{mn_1}(r - r_1)[Q_{kj}^{n_1 n}(r_1) - A_{kj}^{n_1 n}] \tag{43}$$

where we have included in $Q_{ij}^{mn}(r)$ the Heaviside function that makes this function zero for $r \geqslant \sigma_{ij}$.

Consider now the form of $J_{ij}(r)$ for $r < \sigma_{ij}$: From (12) and since

$$\hat{h}_{ij}^{mnl}(r) = 0, \qquad m, n, l \neq 0; \quad r < \sigma_{ij} \tag{44}$$

$$\hat{h}_{ij}^{000}(r) = -1, \qquad r < \sigma_{ij} \tag{45}$$

we get

$$\mathbf{J}(r) = \begin{bmatrix} \mathbf{J}^{00} & \mathbf{0} \\ \mathbf{0} & I^{11} \end{bmatrix} + \begin{bmatrix} \mathbf{0} & \mathbf{J}^{01} \\ \mathbf{J}^{10} & 0 \end{bmatrix} r + \begin{bmatrix} \boldsymbol{\pi} & \mathbf{0} \\ \mathbf{0} & J^{11} \end{bmatrix} r^2 \tag{46}$$

where the constants are explicitly given by

$$J_{ij}^{00} = 2\pi \int_0^{\infty} dr\, r\hat{h}_{ij}^{000}(r) \tag{47}$$

$$J_{in}^{01} = -J_{ni}^{10} = -(2\pi/\sqrt{3}) \int_0^{\infty} dr\, \hat{h}_{in}^{011}(r) \tag{48}$$

$$J_{nn}^{11} = \tfrac{3}{2}(2/15)^{1/2} 2\pi \int_0^{\infty} dr\, \hat{h}_{nn}^{112}(r)/r \tag{49}$$

$$I^{11} = -2\pi \left\{ (1/\sqrt{3}) \int_0^{\infty} dr\, r\hat{h}_{nn}^{110}(r) + (1/\sqrt{30}) \int_0^{\infty} dr\, \hat{h}_{nn}^{112}(r) \right\} \tag{50}$$

It is quite simple to see that (46) and (43) imply that **Q**(r) must be a polynomial of the second degree. Furthermore, because of (37), we see that it must be of the form

$$Q_{ij}^{mn}(r) = Q_{ij}^{mn\prime}(r - \sigma_{ij}) + \tfrac{1}{2}Q_{ij}^{mn\prime\prime}(r - \sigma_{ij})^2 \tag{51}$$

After some rather tedious algebra (see Appendix B) we find the following relations for the parameters a_j^n of (35):

$$a_j^0 = -(2/D_\Omega)[N_j + (\pi/2\Delta)\sigma_j P_n - (\rho_n\sigma_n^2/4D)\Omega^{10}\eta_j] \tag{52}$$

where we have used the following definitions (n is always the label for the solvent species, and all the summations are over the ionic species only, unless otherwise indicated):

$$N_j = \sum_l [\delta_{lj} + (\pi/6\Delta)\rho_l\sigma_l^3]\left[\sum_k \rho_k z_k(J_{kl}^{00} + \tfrac{1}{4}\pi\sigma_n^2)\right] \tag{53}$$

$$\Delta = 1 - \tfrac{1}{6}\pi \sum_{l=1}^{n-1} \rho_l\sigma_l^3 \tag{54}$$

$$P_n = \sum_{k=1}^{n-1} \rho_k\sigma_k(N_k\sigma_k + z_k) \tag{55}$$

$$\nu_i = (1/\Delta_n) \sum_{k=1}^{n-1} [\delta_{ik} + \rho_k\sigma_k^3(\pi/6\Delta)]J_{nk}^{10} \tag{56}$$

$$\Delta_n = 1 - b_2/6 \tag{57}$$

$$b_2 = \rho_n\sigma_n^3 J_{nn}^{11} \tag{58}$$

$$\eta_j = \sum_k^{n-1} \nu_k[\delta_{kj} + (\pi/2\Delta)\rho_k\sigma_k^2\sigma_j] \tag{59}$$

$$\Omega^{10} = \sum_{k=1}^{n-1} \rho_k\sigma_k\nu_k(N_k\sigma_k + z_k) + \sigma_n\beta_n^{10}/3 \tag{60}$$

with

$$\beta_n^{10} = \sum_{k=1}^{n-1} \rho_k z_k J_{nk}^{10} = \Delta_n \sum \rho_k z_k \nu_k \tag{61}$$

$$D = 1 + \tfrac{1}{4}\rho_n\sigma_n^2 \sum_{k=1}^{n-1} \rho_k(\sigma_k\nu_k)^2 \tag{62}$$

and finally

$$\begin{aligned} D_\Omega = (1/D)\Bigg\{&\sum_k^{n-1} \rho_k(N_k\sigma_k + z_k - \tfrac{1}{12}\rho_n\sigma_n^3\beta_n^{10}\nu_k\sigma_k)^2 \\ &+ \sum_{k,l}^{n-1} \rho_k\rho_l[(N_k\sigma_k + z_k)\nu_l\sigma_l - (N_l\sigma_l + z_l)\nu_k\sigma_k]^2\Bigg\} \end{aligned} \tag{63}$$

Also,

$$a_n{}^1 = [2/(D_\Omega)][\tfrac{1}{3}\sigma_n\beta_n^{10} + \tfrac{1}{2}\Omega^{10}y_0\Delta_n] \tag{64}$$

where

$$\eta_0 = \sum^{n-1} \rho_k z_k{}^2 \tag{65}$$

$$y_0 = (1 + \tfrac{1}{3}b_2)/(\Delta_n{}^2 D) \tag{66}$$

From here we get the coefficients of the factor correlation function $\mathbf{Q}(r)$ (51) for the ion–ion interactions (for clarity we drop the superscripts from Q_{ij}^{00})

$$Q'_{ij} = \frac{2\pi}{\Delta}\left(\sigma_{ij} + \frac{\pi}{4\Delta}\sigma_i\sigma_j\right) - \frac{1}{2}D_\Omega a_i{}^0 a_j{}^0 - \frac{\rho_n\sigma_n{}^2\eta_i\eta_j}{2D} \tag{67}$$

and

$$Q''_j = \frac{2\pi}{\Delta}\left(1 + \frac{\pi}{2\Delta}\zeta_2\sigma_j\right) + \frac{\pi}{2\Delta}a_j{}^0 P_n - \frac{\pi}{2\Delta}\frac{\rho_n\sigma_n{}^2}{D}\eta_j P_\nu \tag{68}$$

where we introduced

$$P_\nu = \sum_k^{n-1} \rho_k\sigma_k{}^2\nu_k \qquad \text{and} \qquad \zeta_i = \Sigma\rho_k(\sigma_k)^i \tag{69}$$

It will be interesting to note that Q'_{ij} is directly related to the value of the pair correlation function $g_{ij}(r)$ at contact, while Q''_j is directly related to the compressibility. As will be seen below, both P_n and P_ν are small quantities in dilute systems (and are also zero for equal ionic sizes), so that in this case the compressibility of the MSA is just that of the PY hard-sphere mixture (a well-known result for the MSA).

The value of $Q_{ij}^{00}(\lambda_{ji}) - A_{ij}^{00}$ required by the symmetry condition (41) is

$$-Q_{ij}^{00}(\lambda_{ji}) + A_{ij}^{00} = (\pi/\Delta)\sigma_i\sigma_j + a_j{}^0 M_i - \rho_n\sigma_n{}^2\nu_i\sigma_i\eta_j/2D \tag{70}$$

where we have used

$$M_i = N_i\sigma_i + z_i - (\rho_n\sigma_n{}^2/4D)\Omega^{10}\nu_i\sigma_i \tag{71}$$

As has been the case in our earlier work in the case of ionic mixtures,(10) we do not have enough equations to close the problem, since there is a set of $2n + 1$ unknown parameters for only three boundary conditions, (36), (40) and (79), given below. This has to do with the nonuniqueness of the Wiener–Hopf factorization (29) for matrices. For any arbitrary n, the exact number of additional equations required by the symmetry of the direct correlation function is satisfied only if the following scaling relations are true:

$$a_j{}^0 = 2\Gamma_0 M_j/D_\Omega - \Gamma_1\nu_j\sigma_j\rho_n\sigma_n{}^2/2D \tag{72}$$

$$\eta_j = \Gamma_1 M_j \tag{73}$$

The above relations are a conjecture at this point, and we have no rigorous proof of their validity, other than the fact that they lead to the correct results for the equal-size case, which was obtained without this assumption.(8) For the pure ionic case we know that this procedure leads to correct and consistent results, as we have shown very recently:

$$M_j = (1/\Delta_j^M)\{z_j - \sigma_j^2(\pi/2\Delta)[P_M + P_\nu\Gamma_1\sigma_j\rho_n\sigma_n^2 D_\Omega/4D]\} \tag{74}$$

$$\nu_j = (1/\Delta_j^M)\{\Gamma_1 z_j - \sigma_j(\pi/2\Delta)[P_M\Gamma_1\sigma_j + (1 + \Gamma_0\sigma_j)P_\nu]\} \tag{75}$$

with

$$\Delta_j^M = 1 + \Gamma_0\sigma_j - (\Gamma_1\sigma_j)^2\rho_n\sigma_n^2 D_\Omega/4D \tag{76}$$

$$P_M = \sum_k^{n-1} \rho_k\sigma_k M_k \tag{77}$$

These relations, together with (52)

$$a_j^0 = -(2/D_\Omega)[N_j + (\pi/2\Delta)\sigma_j P_n - \rho_n\sigma_n^2\Omega^{10}\eta_j/4D]$$

and (64)

$$a_n^1 = [2/(D_\Omega)](\tfrac{1}{3}\sigma_n\beta_n^{10} + \tfrac{1}{2}\Omega^{10}y_0\Delta_n)$$

are the closure of the mathematical problem of the solution of the MSA for the general mixture of ions and one kind of hard dipole: We have to find the interaction parameters a_j, N_j, and ν_j as functions of only three scaling-interaction parameters Γ_0, Γ_1, b_2. The situation becomes quite similar to that of the solution of the general ionic mixture, where we had to introduce a scaling parameter Γ_0.(21) In that case, too, the scaling parameter had a direct physical meaning: It was the inverse shielding length for the ionic correlations. In the present case, we do have two Debye-like shielding lengths, corresponding to the ion–ion correlation (Γ_0) and to the dipole–ion correlations (Γ_1). The parameter b_2 is just the excess energy parameter of the dipole–dipole interaction.

The complete solution of the mathematical problem is achieved by solving a set of three algebraic equations for the three parameters Γ_0, Γ_1, and b_2 to the three coupling parameters defined by (21), (24), and the coupling parameter for the dipole–dipole interaction(4)

$$\alpha_0^2 = 4\pi\beta e^2, \qquad \alpha_2^2 = (4\pi/3)\beta(\mu')^2, \qquad \alpha_1 = \alpha_0\alpha_2 \tag{78}$$

Two of these equations are already given by (36) and (40). The third of these equations is obtained from the analysis of (32) and the boundary condition (15). The analysis follows the lines of Wertheim's solution(4) for the pure dipole case, and the reader is referred to this work for a detailed discussion (see also Refs. 8 and 9). The result turns out to be the logical generalization of the corresponding condition (16) of Ref. 8 for the all-equal-size case:

$$y_1{}^2 + \rho_n \alpha_2{}^2 = (1 - \rho_n K_{nn}^0)^2 + \rho_n \sum \rho_k [K_{nk}^0]^2 \tag{79}$$

where

$$y_1 = (1 - \tfrac{1}{6} b_2)/(1 + \tfrac{1}{12} b_2)^2 \tag{80}$$

Substituting the values of K_0^{nn} and K_0^{nk} obtained in Appendix B [Eqs. (B30) and (B31)], we get, after some algebra,

$$\alpha_0{}^2 = \sum_k^{n-1} \rho_k (a_k{}^0)^2 + \rho_n (a_n{}^1)^2 \tag{81}$$

$$\alpha_0(\alpha_2 - \alpha_0 \Lambda^{10}) = \sum_k^{n-1} \rho_k a_k{}^0 \kappa_k + y_0 a_n{}^1 \tag{82}$$

$$y_1{}^2 + \rho_n(\alpha_2 - \alpha_0 \Lambda^{10})^2 = y_0{}^2 + \rho_n \sum_k^{n-1} \rho_k \kappa_k{}^2 \tag{83}$$

where we have used the notation

$$\Lambda^{10} = \sigma_n{}^2 \Omega^{10}/(4D\Delta_n) \tag{84}$$

and

$$\kappa_k = \sigma_n{}^2 \eta_k/(2D\Delta_n) \tag{85}$$

The resolution of the system of equations (81)–(83) has to be done numerically and the proper physically acceptable solution has to be selected from all the possible ones. Perhaps a way of accomplishing this is to start at low concentrations using the results of the next section, and then solve for increasing concentrations using the solution of the previous value as an initial guess.

3. THE EQUAL IONIC SIZE CASE

If the ions are all of the same diameter, but the solvent is still of different size, then the solution of the preceding paragraph can be pushed further, and as a matter of fact, it can be brought to a form that clearly suggests the primitive model for the electrolytic mixture. We remark that the results of this section represent an extension of the previous results(8,9) to the case of different diameter hard dipoles, and also a rather more complete solution, since we are able to show that for low concentrations the result reduces to the Waisman–Lebowitz solution for the primitive model.(3) Another bonus is that the number and electrovalence of the ions are arbitrary.

It can be appreciated that since all the ions are of equal size, then the quantities P_M, P_n, and P_ν defined by (55), (69), and (77) are zero. Furthermore, Δ_j^M, (76), does not depend on the index j any more, because all the ions are equally big, so that from (74) and (75) we see that M_j and ν_j are simply proportional to the ionic charge z_j, and we write

$$M_j = z_j M, \qquad N_j = z_j N \tag{86}$$

$$\nu_j = z_j \nu \tag{87}$$

Replacing now into (52) and (64), we get

$$a_j^0 = z_j a_0 \tag{88}$$

$$a_0 = -(2/DD_\Omega)[N - \tfrac{1}{4}\rho_n \sigma_n^2 \nu^2 \eta_0 (\sigma + \tfrac{1}{3}\sigma_n \Delta_n)] \tag{89}$$

and

$$a_n^1 \equiv a_1 = [2\eta_0 \Delta_n/(D_\Omega)]\{\tfrac{1}{3}\sigma_n + \tfrac{1}{2}y_0[\sigma(1 + N\sigma) + \tfrac{1}{3}\sigma_n \Delta_n]\} \tag{90}$$

where y_0 is given by (66) and we recall that

$$\eta_0 = \sum \rho_k z_k^2$$

For (62) and (63) we get the much simpler expressions

$$D_\Omega = (\eta_0/D)[1 + N\sigma - \tfrac{1}{12}\rho_n \sigma_n^3 \sigma \Delta_n \eta_0 \nu^2]^2 \tag{91}$$

$$D = 1 + \tfrac{1}{4}\rho_n \sigma_n^2 \sigma^2 \eta_0 \nu^2 \tag{92}$$

All of these results are in full agreement with our previous ones in Ref. 8. We turn now to Eqs. (81)–(83): From the above equation and (85) we can also write

$$\alpha_0^2 = \eta_0 a_0^2 + \rho_n a_1^2 \tag{93}$$

$$\sqrt{\rho_n}\, \alpha_0(\alpha_2 - \alpha_0 \Lambda^{10}) = \sqrt{\rho_n}\, \eta_0 a_0 \kappa + y_0 a_1 \sqrt{\rho_n} \tag{94}$$

$$y_1^2 + \rho_n(\alpha_2 - \alpha_0 \Lambda^{10})^2 = y_0^2 + \rho_n \eta_0 \kappa^2 \tag{95}$$

with

$$\Lambda^{10} = \sigma_n^2 \nu \eta_0[\sigma(1 + N\sigma) + \tfrac{1}{3}\sigma_n \Delta_n]/(4D\Delta_n); \qquad \kappa = \nu\sigma_n^2/(2D\Delta_n) \tag{96}$$

In matrix form the same set is

$$\begin{bmatrix} \sqrt{\eta_0}\, a_0 & \sqrt{\rho_n}\, a_1 \\ (\rho_n \eta_0)^{1/2}\kappa & y_0 \end{bmatrix} \begin{bmatrix} \sqrt{\eta_0}\, a_0 & (\rho_n \eta_0)^{1/2}\kappa \\ \sqrt{\rho_n}\, a_1 & y_0 \end{bmatrix} = \begin{bmatrix} \alpha_0^2 & \sqrt{\rho_n}\, \alpha_0(\alpha_2 - \alpha_0 \Lambda^{10}) \\ \alpha_0 \sqrt{\rho_n}\, (\alpha_2 - \alpha_0 \Lambda^{10}) & \rho_n(\alpha_2 - \alpha_0 \Lambda^{10})^2 + y_1^2 \end{bmatrix} \tag{97}$$

But the same relationship must hold for the determinants of these matrices, which then leads to the conclusion that

$$\sqrt{\eta_0}\, a_0 y_0 - \rho_n \sqrt{\eta_0}\, a_1 \kappa = \alpha_0 y_1 \tag{98}$$

We can further eliminate a_1 between (98) and (94), so that

$$a_0^2 \eta_0 [y_0^2 + \rho_n \eta_0 \kappa^2] - 2 a_0 \alpha_0 \sqrt{\eta_0}\, y_0 y_1 + \alpha_0^2 [y_1^2 - \rho_n \eta_0 \kappa^2] = 0 \tag{99}$$

and from this

$$a_0 = \alpha_0 / (\epsilon' \eta_0)^{1/2} \tag{100}$$

with the effective, ionic-concentration-dependent dielectric constant

$$(\epsilon')^{-1/2} = \frac{y_1 y_0 + (\rho_n \eta_0)^{1/2} \kappa (y_0^2 - y_1^2 + \rho_n \eta_0 \kappa^2)^{1/2}}{y_0^2 + \rho_n \eta_0 \kappa^2} \tag{101}$$

Here we choose the sign of the discriminant so as to have a decreasing dielectric constant with increasing ionic concentration. We see also that Eq. (101) has the proper limiting behavior for $\eta_0 \to 0$, since it becomes the Wertheim dielectric constant(4)

$$\epsilon^{-1/2} = y_1 / y_0 = \Delta_n^3 / [(1 + \tfrac{1}{3} b_2)(1 + \tfrac{1}{12} b_2)^2] \tag{102}$$

An explicit solution for the ionic interaction parameter N can be found using (89) and (91)

$$x = \frac{-2N\sigma + \frac{1}{2}\sigma_n b_1^2 (\sigma/\sigma_n + \frac{1}{3}\Delta_n)}{(1 + N\sigma - \frac{1}{12}\sigma^2 \Delta_n b_1^2)^2} \tag{103}$$

where we have introduced

$$b_1^2 = \rho_n \sigma_n^3 \eta_0 \nu^2 \tag{104}$$

$$x = \sigma^3 \alpha_0 (\eta_0 / \epsilon')^{1/2} \tag{105}$$

which is a second degree equation for $N\sigma$, which is easily solved to yield

$$\begin{aligned} N\sigma = {} & \tfrac{1}{4}\sigma b_1^2 (\sigma/\sigma_n + \tfrac{1}{3}\Delta_n) + x^{-1}\{-1 - x[1 + \sigma^2 b_1^2/(4\sigma_n)] \\ & + [1 + 2x(1 + \sigma^2 b_1^2 / 4\sigma_n)]^{1/2}\} \end{aligned} \tag{106}$$

The ion–dipole interaction parameter ν can be obtained by eliminating a_0 between (85) and (88)

$$a_1 = [\alpha_0 / (y_0^2 + \rho_n \eta_0 \kappa^2)][y_0(\alpha_2 - \alpha_0 \Lambda^{10}) - \sqrt{\eta_0}\, y_1 \kappa] \tag{107}$$

or, using (90) and (96a),

$$\begin{aligned} & \frac{2\Delta_n}{D_\Omega} \left(\frac{\nu \eta_0 \sigma_n}{3} + 2D\Delta_n \Lambda^{10} \frac{y_0}{\sigma_n^2} \right) \\ & = \frac{\alpha_0}{y_0^2 + \rho_n \eta_0 \kappa^2} [y_0(\alpha_2 - \alpha_0 \Lambda^{10}) - \sqrt{\eta_0}\, y_1 \kappa] \end{aligned} \tag{108}$$

where Λ^{10} is given by (96), D_Ω by (91), and κ by (96). This equation does not have a closed form solution and therefore has to be solved numerically.

In the dilute solution regime, in which $\eta_0 \ll 1$ but $\sqrt{\eta_0}$ is still finite, and we keep only the terms of the first order in $\sqrt{\eta_0}$, a very substantial simplification occurs, and we get from (106), (96), and (108) the following set of equations:

$$N\sigma = [-1 - x + (1 + 2x)^{1/2}]/x \tag{109}$$

$$x = \sigma^3 \alpha_0 \sqrt{\eta_0}\, [y_1/y_0 + \nu \rho_n \sqrt{\eta_0}\, \alpha_2 \sigma_n{}^2/(2 y_0{}^2 \Delta_n)] \tag{110}$$

$$\nu = \frac{\alpha_0 \alpha_2 [1 + (1 + N\sigma)^2]}{2 y_0 \Delta_n \{\frac{1}{3}\sigma_n + \frac{1}{2} y_0 [\sigma(1 + N\sigma) + \frac{1}{3}\sigma_n \Delta_n]\}} \tag{111}$$

and

$$1/\sqrt{\epsilon_W} = y_1/y_0$$

The equation for b_2, the dipolar interaction term, remains unchanged from the pure dipole case, so that Wertheim's result remains unchanged in this case, that is, the parameter b_2 is independent, in this regime of the ionic concentration.(4) We remark also that (109) is formally identical with the MSA primitive model result,(3) albeit with a density-dependent dielectric constant.

4. THERMODYNAMIC PROPERTIES

One of the features of the MSA is that it yields fairly simple expressions for the excess thermodynamic properties of the mixtures when calculated via the internal energy.(20) For the primitive model of simple salts the calculated properties are in good general agreement with computer simulations. It should be remembered also that the same quantities calculated from the pressure or compressibility relations are in rather poor agreement with each other and with the computer experiments, and this is a reflection of the inconsistency of the MSA. A similar inconsistency arises when we try to compute the energy directly from the quantities N_i, ν_i, and b_2 [see Eqs. (53), (56), and (58)]

$$\Delta E_0 = e^2 \sum_i \rho_i z_i N_i + (2/\sqrt{3}) e \mu' \rho_n \Delta_n \sum_i \rho_i z_i \nu_i - \tfrac{2}{3} \rho_n (\mu^1)^2 b_2 / \sigma_n{}^3 \tag{112}$$

Now the excess energy of the solution with respect to the solvent is

$$\Delta E = \Delta E_0 - \tfrac{2}{3}(\mu^1)^2 b_2(\rho_i = 0)/\sigma_n{}^3 \tag{112a}$$

In fact, replacing the low-density limit for the case discussed in Section 3 [Eqs. (109)–(110)], we do not get the properly screened, MSA primitive model result in the infinite-dilution limit

$$\Delta E = (e^2/\epsilon_W) \sum \rho_i z_i N_i \tag{113}$$

A more natural way of calculating the excess energy is provided by the use of an effective dielectric constant, such as discussed by Adelman in a recent work⁽²²⁾; this effective dielectric constant is concentration dependent, and is given in our case by

$$\epsilon = (1/y_1{}^2)\{(1 - \rho_n K^0_{nn})^2 + \rho_n \sum \rho_k [K^0_{nk}]^2\} \tag{113a}$$

Whether this dielectric constant is equal to the one given by (101) is an open question that is left for a future investigation.

The remaining thermodynamic properties are then computed from the energy relations: The free energy A is obtained from the integral

$$\Delta A = \int_0^\beta d\beta' \, \Delta E(\beta') \tag{114}$$

and the excess osmotic coefficient $\Delta\phi = \beta\, \Delta P/\rho$, where ΔP is the excess osmotic pressure and ρ is the concentration of the electrolyte

$$\Delta\phi = \rho\, \partial(\beta\, \Delta A)/\partial\rho \tag{115}$$

Finally, the excess activity coefficient can be calculated from the thermodynamic relation

$$\Delta \ln \gamma_\pm = \Delta\phi + \beta\, \Delta A/\rho$$

Rather simple formulas were recently derived by Høye and Stell⁽²⁰⁾ and Blum and Høye⁽²¹⁾ for the excess properties of the primitive model and also for the pair correlation function. However, these points will be left for future investigations.

APPENDIX A. THE TRANSFORMS OF THE CORRELATION FUNCTION

The inverse of the transformation (11) is given by (we drop the indices for clarity in the notation)

$$\mathscr{F}_\chi(r) = (-)^\chi 2\pi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \int_r^\infty dr_1\, P_l(r/r_1) \hat{f}^l(r_1)$$

and is obtained, first, by the orthogonality of the 3-j symbols⁽¹³⁾

$$F_l(r) = (2l + 1) \sum_{\chi=-l}^{l} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \mathscr{F}_\chi(r) \tag{A1}$$

where

$$F_l(r) = 2\pi \int_r^\infty dr_1\, P_l(r/r_1) \hat{f}^l(r_1) \tag{A2}$$

and $P_l(x)$ is the Legendre polynomial. Consider now the Fourier transform of $F_l(r)$, $\tilde{F}(k)$. Using the integral representation of the spherical Bessel functions$^{(15)}$

$$j_l(kr) = (1/2i^l)\int_{-1}^{1} dt\, P_l(t)e^{ikrt} \tag{A3}$$

we get

$$\tilde{F}_l(k) = 2\pi\int_{-\infty}^{\infty} dr\, e^{ikr}F_l(r) = 4\pi i^l\int_0^{\infty} dr\, r^2 j_l(kr)\hat{f}_l(r) \tag{A4}$$

Now the inverse of this transform can be obtained from the orthogonality relation of the spherical Bessel functions:

$$\int_0^{\infty} dk\, k^2 j_l(kr)j_l(kr') = (\pi/2rr')\,\delta(r - r') \tag{A5}$$

so that

$$\hat{f}_l(r) = (i^{-l}/2\pi^2)\int_0^{\infty} dk\, k^2 j_l(kr)\tilde{F}_l(k) \tag{A6}$$

Using (A4) in this relation, we see that

$$\hat{f}_l(r) = \int_0^{\infty} dr_1\, F_l(r_1)\left\{\frac{1}{2\pi^2 i^l}\int_0^{\infty} dk\, k^2 j_l(kr)[e^{ikr_1} + (-)^l e^{-ikr_1}]\right\} \tag{A7}$$

Using distribution theory, the second integration can be calculated explicitly:

$$\hat{f}_l(r) = \frac{(-)^{l+1}}{2\pi}\int_0^{\infty} dr_1\, F_l(r_1)\int_0^{1} dt\, P_l(t)\,\frac{\partial^2}{\partial t^2}\,[\delta(rt + r_1) + (-)^l\,\delta(rt - r_1)] \tag{A8}$$

where $\delta(x)$ is the Dirac delta function. Integration by parts and using (A1) and (A2) gives us the desired inverse transformation:

$$\begin{aligned}\hat{f}_l(r) = {} & -[(2l + 1)/2\pi]\sum_{\chi=-l}^{l}\begin{pmatrix} m & n & l \\ \chi & -\chi & 0\end{pmatrix} \\ & \times\int_0^{\infty} dr_1\,\mathscr{F}_\chi(r_1)\Big\{(1/r)[\delta'(r - r_1) + \delta'(r + r_1)] \\ & - (1/r^2)[P_l'(1)\,\delta(r - r_1) + (-)^l P_l'(1)\,\delta(r + r_1)] \\ & + (1/r^3)P_l''\left(\frac{r_1}{r}\right)[\theta(r - r_1) + (-)^l\theta(r + r_1)]\Big\}\end{aligned} \tag{A9}$$

APPENDIX B. THE ALGEBRAIC SOLUTION OF (43)

Let us first rewrite (43) in matrix form

$$\mathbf{J}(r) = \mathbf{Q}(r) - \mathbf{A} + \frac{1}{2}\begin{bmatrix} \mathbf{a}^0 & a^1 \\ \mathbf{0} & 0 \end{bmatrix}$$

$$+ \int_\lambda^\sigma dr_1\, \mathbf{J}(r - r_1)\rho\mathbf{Q}(r_1) + \int_0^{\lambda - r} dr_1\, \mathbf{J}^T(r_1)\rho\mathbf{A} \qquad \text{(B1)}$$

where we recall that $\mathbf{J}(r)$ is a matrix polynomial of the form (46)

$$\mathbf{J}(r) = \begin{bmatrix} \mathbf{J}^{00} & \mathbf{0} \\ \mathbf{0} & I^{11} \end{bmatrix} + r\begin{bmatrix} \mathbf{0} & \mathbf{J}^{01} \\ \mathbf{J}^{10} & 0 \end{bmatrix} + r^2\begin{bmatrix} \boldsymbol{\pi} & \mathbf{0} \\ \mathbf{0} & 0 \end{bmatrix} \qquad \text{(B2)}$$

and we have used the electroneutrality condition$^{(8,10)}$

$$\sum_k^{n-1} \rho_k \int_0^\infty dr_1\, J_{ik}^{00}(r_1) A_{kj}^{00} = -\tfrac{1}{2} A_{ij}^{00} \qquad \text{(B3)}$$

The algebraic problem is to substitute (51) into (B1) and solve the resulting equations for the coefficients $a_k{}^n$ of (35). While this is a well-defined algebraic problem, it can be very messy if the proper strategy is not used. For simplicity in the notation, let us drop the superscripts m, n and write (51) in the form

$$Q_{ij}(r) = Q'_{ij}(r - \sigma_{ij}) + \tfrac{1}{2} Q''_j (r - \sigma_{ij})^2 \qquad \text{(B4)}$$

Define also the moments

$$K_{ij}^m = \int_{\lambda_{ji}}^{\sigma_{ji}} dr\, r^m Q_{ij}(r) \qquad \text{(B5)}$$

It seems that the most convenient route is to use as independent variables $Q_{ij}(\lambda_{ji})$ and K_{ij}^0:

$$K_{ij}^0 = -(\sigma_i{}^2/2) Q'_{ij} + (\sigma_i{}^3/6) Q''_j \qquad \text{(B6)}$$

$$Q_{ij}(\lambda_{ji}) = -\sigma_i Q'_{ij} + (\sigma_i{}^2/2) Q''_j \qquad \text{(B7)}$$

From (B4) and (B5) we also get

$$Q'_{ij}(\sigma_j/2) = -(1/\sigma_i) Q_{ij}(\lambda_{ji}) \qquad \text{(B8)}$$

$$Q''_j = (12/\sigma_i{}^3)[(\sigma_i/2) Q_{ij}(\lambda_{ji}) + K_{ii}^0] \qquad \text{(B9)}$$

and also

$$(\sigma_j/2)K^0_{ij} - K'_{ij} = (\sigma_i^2/12)Q_{ij}(\lambda_{ji}) \tag{B10}$$

Using these relations, we find the first derivative of (B1) at $r = \sigma_j/2$:

$$\begin{bmatrix} \boldsymbol{\pi\sigma} & \mathbf{J}^{01} \\ \mathbf{J}^{10} & J^{11}\sigma_n \end{bmatrix} + \begin{bmatrix} \mathbf{J}^{00} + \frac{1}{4}\boldsymbol{\pi\sigma}^2 & \frac{1}{2}\mathbf{J}^{01}\boldsymbol{\sigma} \\ \frac{1}{2}\mathbf{J}^{10}\boldsymbol{\sigma} & I^{11} + \frac{1}{4}J^{11}\sigma_n{}^2 \end{bmatrix}\boldsymbol{\rho}\mathbf{A}$$

$$= -\left[\mathbf{I} - \begin{bmatrix} \boldsymbol{\pi} & \mathbf{0} \\ \mathbf{0} & J^{11} \end{bmatrix}\boldsymbol{\rho\sigma}^3/6\right](1/\boldsymbol{\sigma})\mathbf{Q}_\lambda + \begin{bmatrix} \mathbf{0} & \mathbf{J}^{01} \\ \mathbf{J}^{10} & 0 \end{bmatrix}\boldsymbol{\rho}\mathbf{K}^0 \tag{B11}$$

where $\mathbf{Q}_\lambda$ is the matrix with elements $Q_{ij}(\lambda_{ji})$. Another relation is obtained from the second derivative of (B1)

$$-\tfrac{1}{12}\boldsymbol{\rho\sigma}^3\begin{bmatrix} \boldsymbol{\pi\sigma} & \mathbf{J}^{01} \\ \mathbf{J}^{10} & J^{11}\sigma_n \end{bmatrix}\boldsymbol{\rho}\mathbf{A}$$

$$= \mathbf{I} - \tfrac{1}{2}\boldsymbol{\rho\sigma}\mathbf{Q}_\lambda - \left\{\mathbf{I} - \tfrac{1}{6}\boldsymbol{\rho\sigma}^3\begin{bmatrix} \boldsymbol{\pi} & \mathbf{0} \\ \mathbf{0} & J^{11} \end{bmatrix}\right\}\{\mathbf{I} - \boldsymbol{\rho}\mathbf{K}^0\} \tag{B12}$$

Since

$$\mathbf{W} = \mathbf{I} - \tfrac{1}{6}\boldsymbol{\rho\sigma}^3\begin{bmatrix} \boldsymbol{\pi} & \mathbf{0} \\ \mathbf{0} & J^{11} \end{bmatrix} = \begin{bmatrix} \delta_{ik} - \frac{1}{6}\pi\rho_k\sigma_k{}^3 & \mathbf{0} \\ \mathbf{0} & 1 - \frac{1}{6}b_2 \end{bmatrix} \tag{B13}$$

where $b_2 = \rho_n\sigma_n{}^3J^{11}$, is a Jacobi matrix, the general inverse is simple to obtain:

$$\mathbf{W}^{-1} = \begin{bmatrix} \delta_{ik} + (\pi/6\Delta)\rho_k\sigma_k{}^3 & \mathbf{0} \\ \mathbf{0} & 1/\Delta_n \end{bmatrix} \tag{B14}$$

with

$$\Delta_n = 1 - \tfrac{1}{6}b_2; \qquad \Delta = 1 - \tfrac{1}{6}\pi\sum_k^{n-1}\rho_k\sigma_k{}^3 \tag{B15}$$

Now we can solve (B12) for $\mathbf{I} - \boldsymbol{\rho}\mathbf{K}^0$:

$$\mathbf{I} - \boldsymbol{\rho}\mathbf{K}^0 = \begin{bmatrix} \mathbf{I} + \boldsymbol{\rho\sigma}^3\boldsymbol{\pi}/6\Delta & \mathbf{0} \\ \mathbf{0} & 1/\Delta_n \end{bmatrix}[\mathbf{I} - \tfrac{1}{2}\boldsymbol{\rho\sigma}\mathbf{Q}_\lambda] + \tfrac{1}{12}\boldsymbol{\rho\sigma}^3\begin{bmatrix} \boldsymbol{\pi}\chi_1/\Delta \\ \beta^{10}/\Delta_n \end{bmatrix}[\mathbf{a}^0, a_n{}^1] \tag{B16}$$

where

$$\chi_m = \sum \rho_k z_k \sigma_k{}^m \tag{B17}$$

$$\beta^{10} = \sum \rho_k z_k J^{10}_{nk} \tag{B18}$$

Replacing (B16) into (B11), and solving for $\mathbf{I} - \boldsymbol{\rho\sigma}\mathbf{Q}_\lambda/2$, we find

$$\mathbf{I} - \tfrac{1}{2}\boldsymbol{\rho\sigma}\mathbf{Q}_\lambda = \left\{\begin{bmatrix}\mathbf{I} & \mathbf{0}\\ \mathbf{0} & 0\end{bmatrix} + \frac{1}{D}\begin{bmatrix}\tfrac{1}{2}\boldsymbol{\rho\sigma}^2\boldsymbol{\nu}\\ 1\end{bmatrix}[\tfrac{1}{2}\rho_n\sigma_n{}^2\boldsymbol{\nu}^2,\ 1]\right\}\left\{I + \frac{\boldsymbol{\rho\sigma}^2}{2\Delta}\begin{bmatrix}\boldsymbol{\pi} & 0\\ 0 & J^{11}\end{bmatrix}\boldsymbol{\sigma}\right\}$$

$$+ \tfrac{1}{2}\boldsymbol{\rho\sigma}^2\begin{bmatrix}\mathbf{N} - (1/4D)\rho_n\sigma_n{}^2\Omega^{10}\boldsymbol{\nu}\\ \sigma_n\beta^{10}/6 + \Omega^{10}/2D\end{bmatrix}[\mathbf{a}^0,\ a_n{}^1] \tag{B19}$$

where we used the following notation

$$[\mathbf{N}]_i = N_i = \sum_k^{n-1}\left(\delta_{ik} + \frac{\pi}{6\Delta}\rho_k\sigma_k{}^3\right)\left(\frac{\pi}{4}\chi_2 + \sum_l \rho_l z_l J_{kl}^{00}\right) \tag{B20}$$

$$\nu_i = \frac{1}{\Delta_n}\sum_k^{n-1}\left(\delta_{ik} + \rho_k\sigma_k{}^3\frac{\pi}{6\Delta}\right)J_{nk}^{00} \tag{B21}$$

$$\beta^{10} = \sum_i \rho_l z_l J_{nl}^{10} = \Delta_n\sum_l \rho_l z_l \nu_l \tag{B22}$$

$$\Omega^{10} = \sum_k \rho_k\nu_k[N_k\sigma_k{}^2 + z_k(\sigma_k + \tfrac{1}{3}\sigma_n\Delta_n)] \tag{B23}$$

$$D = 1 + \tfrac{1}{4}\rho_n\sigma_n{}^2\sum_k \rho_k(\sigma_k\nu_k)^2 \tag{B24}$$

$$\eta_j = \sum_l \nu_l[\delta_{lj} + (\pi/2\Delta)\rho_l\sigma_l{}^2\sigma_j] \tag{B25}$$

From (B19) we get the matrix elements of $\mathbf{Q}_\lambda$: For ionic interactions ($m = 0, n = 0$) we have

$$-Q_{ij}(\lambda_{ji}) = -A_{ij}^{00} + \sigma_i\sigma_j\frac{\pi}{\Delta}$$

$$+ a_j{}^0\left(N_i\sigma_i + z_i - \frac{\rho_n\sigma_n{}^2\Omega^{10}}{4D}\sigma_i\nu_i\right) - \frac{\rho_n\sigma_n{}^2}{2D}\sigma_i\nu_i\eta_j \tag{B26}$$

while for the ion–dipole interactions we get

$$-Q_{in}^{01}(\lambda_{ni}) = -A_{in}^{01} - \sigma_i\eta_j/D + a_n{}^1[N_i\sigma_i + z_i - (\rho_n\sigma_n{}^2\Omega^{10}/4D)\sigma_i\nu_i] \tag{B27}$$

$$-Q_{nj}^{10}(\lambda_{jn}) = \sigma_n\eta_j/D + a_j{}^0(-\tfrac{1}{6}\sigma_n{}^2\beta^{10} + \sigma_n\Omega^{10}/2D) \tag{B28}$$

Replacing (B19) into (B16) yields $\mathbf{I} - \boldsymbol{\rho}\mathbf{K}^0$. The relevant matrix elements for our calculation are

$$-\rho_n K_{nn}^{11} = (1/\Delta_n{}^2)(1 + \tfrac{1}{3}b_2) + a_n{}^1\rho_n\sigma_n{}^2\Omega^{10}/(4D\Delta_n) \tag{B29}$$

$$-\rho_n K_{nj}^{10} = (\rho_n\sigma_n{}^2/2D\Delta_n)\eta_j + a_n{}^1\rho_n\sigma_n{}^2\Omega^{10}/(4D\Delta_n) \tag{B30}$$

To calculate the coefficients $[\mathbf{a}^0, a_n{}^1]$ of (35), we take (B1) at the point $r = \lambda_{ji}$, combine with (B11) and (B12), and multiply by the row vector $[\boldsymbol{\rho}\mathbf{z}, 0]$. We get

$$\left\{\left[\pi\chi_1\boldsymbol{\sigma}, \sum_k \rho_k z_k \sigma_k J_{kn}^{01}\right]\tfrac{1}{2}(\mathbf{I} - \boldsymbol{\rho}\mathbf{K}^0) + [\boldsymbol{\pi}\chi_1, 0]\boldsymbol{\rho}\mathbf{K}^1\right\}$$
$$= -\tfrac{1}{2}[\boldsymbol{\rho}\mathbf{z}, 0]\mathbf{Q}_\lambda - \tfrac{1}{2}\left\{\sum_k \rho_k z_k \sigma_k\left(\sum_l \rho_l z_l J_{lk}^{00} - \tfrac{1}{4}\pi\chi_2\right)\right\}[\mathbf{a}^0, a_n{}^1] \tag{B31}$$

Using the relations (B8)–(B10) and (B16) we arrive at

$$\tfrac{1}{2}[\mathbf{a}^0, \mathbf{a}_n{}^1]\left[\eta_0 + \sum_i \rho_i\sigma_i z_i\left(\sum_l \rho_l z_l J_{li}^{00} + \tfrac{1}{4}\pi\chi_2\right)\right]$$
$$= \tfrac{1}{2}\left[\sum_i \rho_i z_i Q_{ij}(\lambda_{ji}), 0\right] - [\mathrm{N}, 0]\left\{\mathbf{I} - \tfrac{1}{2}\boldsymbol{\rho\sigma}\mathbf{Q}_\lambda + \tfrac{1}{12}\boldsymbol{\rho\sigma}^3\right.$$
$$\left.\times \begin{bmatrix}\boldsymbol{\pi}\chi_1 \\ \beta^{10}\end{bmatrix}[\mathbf{a}^0, a_n{}^1]\right\} - [\mathbf{0}, \tfrac{1}{6}\beta^{01}\sigma_n] - \tfrac{1}{6}[\mathbf{0}, \beta^{01}\sigma_n][\mathbf{I} - \tfrac{1}{2}\boldsymbol{\rho\sigma}\mathbf{Q}_\lambda] \tag{B32}$$

where

$$\eta_0 = \sum_k^{n-1} \rho_k z_k{}^2 \tag{B33}$$

Substituting (B19) into this relation yields

$$\tfrac{1}{2}D_\Omega[\mathbf{a}^0, a_n{}^1]$$
$$= [-(\pi/2\Delta)\chi_1\boldsymbol{\sigma}, \tfrac{1}{3}\sigma_n\beta^{10}]$$
$$+ \{-[\mathrm{N}, 0] + (\Omega^{10}/2D)[\tfrac{1}{2}\rho_n\sigma_n{}^2\boldsymbol{\nu}, 1]\}\left\{\mathbf{I} + (\boldsymbol{\rho\sigma}^2/2\Delta)\begin{bmatrix}\boldsymbol{\pi} & \mathbf{0} \\ \mathbf{0} & J^{11}\end{bmatrix}\sigma\right\} \tag{B34}$$

where

$$D_\Omega = \sum_k \rho_k(N_k\sigma_k + z_k)^2 + \tfrac{1}{4}\rho_n\sigma_n{}^2[(\sigma_n\beta^{10}/3)^2 - (\Omega^{10})^2/D] \tag{B35}$$

which is in complete agreement with our previous result.(3) A swift calculation also yields

$$Q'_{ij} = (2\pi/\Delta)[\sigma_{ij} + (\pi/4\Delta)\sigma_i\sigma_j\zeta_2] - \tfrac{1}{2}D_\Omega a_i{}^0 a_j{}^0 - \rho_n\sigma_n{}^2\eta_i\eta_j/2D \tag{B36}$$

and

$$Q''_j = (2\pi/\Delta)[1 + (\pi/2\Delta)\zeta_2\sigma_j] + (\pi/2\Delta)a_j{}^0 \sum_k \rho_k\sigma_k(N_k\sigma_k + z_k)$$
$$- (\pi/2\Delta D)\rho_n\sigma_n{}^2\eta_j \sum_k \rho_k\sigma_k{}^2\nu_k \tag{B37}$$

with $\zeta_2 = \sum \rho_k\sigma_k{}^2$.

APPENDIX C. EXPLICIT SOLUTION FOR M_j AND ν_j

The explicit forms of M_j and ν_j are obtained from (72) and (73): The resulting system of equations is

$$\begin{pmatrix} z_j - \sigma_j^2(\pi/2\Delta)P_M \\ (\pi/2\Delta)\sigma_j^2 P_\nu \end{pmatrix} = \begin{pmatrix} 1 + \Gamma_0\sigma_j & \Gamma_1\sigma_j D_\Omega(\rho_n\sigma_n^2/4D) \\ \Gamma_1\sigma_j & 1 \end{pmatrix}\begin{pmatrix} M_j \\ -\nu_j\sigma_j \end{pmatrix} \tag{C1}$$

with

$$P_M = \sum \rho_i\sigma_i M_i \tag{C2}$$

$$P_\nu = \sum \rho_i\sigma_i^2\nu_i \tag{C3}$$

and the remaining quantities are defined in (52) and thereafter. Solution of (C1) yields

$$\begin{pmatrix} M_j \\ -\nu_j\sigma_j \end{pmatrix} = \frac{1}{\Delta_j^M}\begin{pmatrix} 1 & -\Gamma_1\sigma_j D_\Omega(\rho_n\sigma_n^2/4D) \\ -\Gamma_1\sigma_j & 1 + \Gamma_0\sigma_j \end{pmatrix}\begin{pmatrix} z_j - \sigma_j^2(\pi/2\Delta)P_M \\ (\pi/2\Delta)\sigma_j^2 P_\nu \end{pmatrix} \tag{C4}$$

with

$$\Delta_j^M = 1 + \Gamma_0\sigma_j - (\Gamma_1\sigma_j\sigma_n)^2\rho_n D_\Omega/4D \tag{C5}$$

Now the unknown parameters P_M and P_ν can be found by substitution of M_j and $\nu_j\sigma_j$ obtained from (C4) into the defining relations (C2) and (C3). The result is again a system of two coupled equations for P_M and P_ν

$$\begin{pmatrix} \displaystyle\sum_j \frac{\rho_j\sigma_j z_j}{\Delta_j^M} \\ \displaystyle\Gamma_1 \sum_j \frac{\rho_j\sigma_j^2 z_j}{\Delta_j^M} \end{pmatrix} = \begin{pmatrix} \displaystyle 1 + \frac{\pi}{2\Delta}\sum_j \frac{\rho_j\sigma_j^3}{\Delta_j^M} & \displaystyle\Gamma_1 \frac{\pi\rho_n\sigma_n^2 D_\Omega}{8D\Delta}\sum_j \frac{\rho_j\sigma_j^4}{\Delta_j^M} \\ \displaystyle\Gamma_1 \frac{\pi}{2\Delta}\sum_j \frac{\rho_j\sigma_j^4}{\Delta_j^M} & \displaystyle 1 + \frac{\pi}{2\Delta}\sum_j \rho_j\sigma_j^3 \frac{1 + \Gamma_0\sigma_j}{\Delta_j^M} \end{pmatrix}\begin{pmatrix} P_M \\ P_\nu \end{pmatrix} \tag{C6}$$

We then would solve (C6) and replace the result into (C4). This gives explicit formulas for M_j and ν_j. Replacing these results into the equations of Section 2 and Appendix B will give us explicit expressions for all the quantities as functions of Γ_0, Γ_1, and b_2. The resulting expressions are rather lengthy and will not be given here.

For not too concentrated solutions, however, the quantities P_M and P_ν are expected to be small and therefore can be neglected

$$P_M \approx P_\nu \approx 0 \tag{C7}$$

so that

$$M_j = z_j/\Delta_j^M \tag{C8}$$

$$\nu_j = -\Gamma_1 z_j/\Delta_j^M \tag{C9}$$

from which the relevant parameters (52), etc., are

$$\Omega^{10} = \Gamma_1 D \sum_k (\rho_k z_k^2/\Delta_k^M)(\tfrac{1}{3}\Delta_n \sigma_n - \sigma_k/\Delta_k^M) \tag{C10}$$

$$\beta^{10} = -\Gamma_1 \Delta_n \sum_k \rho_k z_k^2/\Delta_k^M \tag{C11}$$

$$D = 1 + \tfrac{1}{4}\rho_n \sigma_n^2 \sum_k \rho_k \sigma_k^2 z_k^2/(\Delta_k^M)^2 \tag{C12}$$

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