The Computation of the Thermodynamic Properties of Aqueous Electrolyte Solutions by Means of the Perturbation Theory of Fluids

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A useful method to investigate the thermodynamic properties of aqueous electrolyte solutions was presented on the basis of the perturbation theory of fluids, where a *primitive model* was used as a reference system. A perturbation potential of a square type was applied. An analytical solution of the mean spherical model (MSM) equation obtained by Waisman and Lebowitz was used as the thermodynamic functions of the reference system, and an ionic distribution function in electrolyte solutions was derived. The values of the energy parameters which represent the depth of the well were determined by a comparison of the observed values of the thermodynamic quantities with the calculated ones.

Some remarkable progress in the field of electrolyte solution theory has been made recently,[1–7] the most important example coming from the application of the methods developed in the theory of liquids.[8–10] In many of these studies a simple model ("primitive model"[5]) has been used, where each ion behaves as a charged hard sphere imbedded in a continuum with a macroscopic value of the dielectric constant.

An analytical solution of the drirect correlation function for the model was obtained from the mean spherical model (MSM)[9] equation by Waisman and Lebowitz.[5] It may be said to be the only analytical solution which has been obtained through the statistical thermodynamic treatment of electrolyte solutions since the proposition of the Debye-Hückel theory.

A way to improve the primitive model is to take into account the effect of ions upon the liquid structure of solvents. It is well-known that water molecules around ions are not always bound strictly about the ions in aqueous solutions.[11–13] At room temperature, water molecules around very small (Li^+) or polyvalent (Mg^{2+}, Ca^{2+}) ions are considered to be less mobile than those in bulk water due to ion-water interactions (*positive hydration*), while in the case of comparatively large ions, such as Cs^+ and I^-, water molecules around ions become more mobile than those in bulk water (*negative hydration*).[11–13] Such ion-water interaction produces very complicated effects upon ion-ion interactions. Gurney represented the additional interactions by a term of the overlapping of cospheres in which solvent molecules are in a different state from those in bulk water.[11] Rasaiah[6] and Ramanathan and Friedman[7] solved numerically the hypernetted chain (HNC) equation,[8] where the interaction potential of an ion pair cotains a contribution from the overlapping of the cospheres.

On the basis of a model similar to that mentioned above, an alternative method for the improvement of the "primitive model" will be presented in this paper using the perturbation method in the theory of liquids;[10,14] the primitive model is used as a reference system, and the contribution from the overlapping of cospheres is regarded as a perturbation.

Perturbation Method

The basic idea of the perturbation theory is to represent the potential energy of a system as a sum of two terms:

$$U = U^{(0)} + U^{(1)}, \tag{1}$$

where $U^{(0)}$ is the potential energy of the unperturbed system ("reference system"), and $U^{(1)}$, the perturbation energy. It is assumed that $U^{(0)}$ and $U^{(1)}$ are a sum of pair potentials. The equation for the Helmholtz free energy of a multicomponent system is expressed straightforwardly by the perturbation theory as follows:

$$\beta A/N = \beta A^{(0)}/N + (2\pi\beta/\rho)\sum_{i,j=1}^{\sigma}\rho_i\rho_j\int_0^{\infty}g_{ij}^{(0)}(r)u_{ij}^{(1)}(r)r^2\mathrm{d}r. \tag{2}$$

Here, the subscripts i and j are used to distinguish the species in the system; $A^{(0)}$ and $g_{ij}^{(0)}(r)$, the Helmholtz free energy and the radial distibution function of the reference system, respectively; $u_{ij}^{(1)}(r)$, the perturbation potential of a pair of molecules; ρ_i, the number density of i-th component; N, the total number of molecules; ρ, the total number density $(=\sum_i^{\sigma}\rho_i)$ and $\beta=(kT)^{-1}$.

In the present case, the pair potential, $u_{ij}^{(0)}(r)$, of the reference system is givn by:

$$\begin{aligned} u_{ij}^{(0)}(r) &= \infty, \qquad r \leq R_{ij}, \\ &= e_ie_j/\varepsilon r, \quad r > R_{ij}, \end{aligned} \tag{3}$$

where e_i is the charge of the i-th type of ions; R_{ij}, the distance of the closest approach between ions of the i and j types, $R_{ij}=(R_{ii}+R_{ij})/2$, and ε, the macroscopic dielectric constant of the solvent. The interaction attributed to the effect of the overlap of cospheres, which is regarded as a perturbation, must have a very complicated form. Here, we will represent the potential by a simple form,[6,15] that is, a square well or a square mound potential, as follows:

$$\begin{aligned} u_{ij}^{(1)}(r) &= 0, \qquad r \leq R_{ij}, \\ &= d_{ij}, \quad R_{ij} < r < R_{ij} + b_{ij}, \\ &= 0, \qquad R_{ij} + b_{ij} \leq r. \end{aligned} \tag{4}$$

Here, d_{ij} is the depth (the height) of the well (mound), and b_{ij}, the width of the well (mound). Since the $u_{ij}^{(1)}(r)$ used here is the potential of the mean force averaged over the coordinate of the solvent molecules, which means the free energy of pair interaction between ions, the thermodynamic quantities derived are "osmotic quantities." For instance, the derivative of the free energy by the volume of solution is not the pressure but the osmotic pressure.[16] From Eq. (2), we obtained this equation for the energy per unit volume:[2,6]

$$E = E^{(0)} + \frac{1}{2}\sum_{i,j=1}^{\sigma} \rho_i \rho_j \int_0^{\infty} \frac{\partial[\beta u_{ij}^{(1)}(r)]}{\partial \beta} g_{ij}^{(0)}(r) 4\pi r^2 \mathrm{d}r, \tag{5}$$

where $E^{(0)}$ is the energy per unit volume of the reference system given by:

$$E^{(0)} = \frac{1}{2}\sum_{i,j=1}^{\sigma} \rho_i \rho_j \int_0^{\infty} \frac{\partial[\beta u_{ij}^{(0)}(r)]}{\partial \beta} g_{ij}^{(0)}(r) 4\pi r^2 \mathrm{d}r. \tag{6}$$

By substituting Eq. (3) into Eq. (6), we obtained the following expression:

$$E^{(0)} = \left(1 + \frac{\partial \ln \varepsilon}{\partial \ln T}\right) E^{\rm el}. \tag{7}$$

$E^{\rm el}$ is given by:

$$E^{\rm el} = (1/2) \sum_{i,j=1}^{\sigma} \rho_i \rho_j \int_0^{\infty} \frac{e_i e_j}{\varepsilon r} g_{ij}^{(0)}(r) 4\pi r^2 \mathrm{d}r. \tag{8}$$

Description of the Reference System

Analytical Solution of MSM Equation. We use the analytical solution of the MSM equation for the primitive model, which was derived by Waisman and Lebowitz,[5] as the reference system in the perturbation method.[6] According to MSM,

$$\begin{aligned} g_{ij}^{(0)}(r) &= 0, & r &\leq R_{ij} \\ C_{ij}^{(0)}(r) &= -\beta e_i e_j/\varepsilon r, & r &> R_{ij} \end{aligned} \tag{9}$$

where $C_{ij}^{(0)}(r)$ is the direct correlation function of the reference system. Using the conditions in Eq. (9), Waisman and Lebowitz solved the Ornstein-Zernike equation by a method which was identical with Wertheim's[17] way of solving the Percus-Yevick (PY) equation[8] for a single-component fluid of hard spheres. The final solution was obtained only for the case in which the hard-sphere diameter of all the species were the same. The direct correlation function, $C_{ij}^{(0)}(r)$, derived was:

$$\begin{aligned} C_{ij}^{(0)}(r) &= \tilde{C}(r;\xi;\beta) - (\beta/\varepsilon R) e_i e_j (2B - B^2 r/R), \quad r \leq R \\ &= -\beta e_i e_j/\varepsilon r, \quad r > R \end{aligned} \tag{10}$$

where $\tilde{C}\ (r;\ \xi,\ \beta)$ is the Wertheim solution, and R, the distance of the closest approach of the ion pair which is common to all the pairs. ξ and B are the parameters given by:

$$\xi = \pi R^3 \rho/6, \tag{11}$$

$$B = x^{-2}[x^2 + x - x(1+2x)^{1/2}], \tag{12}$$

where x is the product of the Debye-Hückel parameter, κ, and the hard-sphere diameter, R,

$$x^2 = \kappa^2 R^2 = [(4\pi\beta/\varepsilon)\sum_i^{\sigma} \rho_i e_i^2] R^2. \tag{13}$$

Thermodynamic Functions. The free energy and energy per unit volume were given by:

$$\begin{aligned} \beta a(x,\beta;\xi) = \beta\tilde{a}(\xi,\beta) &- (12\pi R^3)^{-1}[3x^2 + 6x + 2 \\ &-2(1+2x)^{3/2}], \end{aligned} \tag{14}$$

$$\begin{aligned} E^{\rm el}(x,\beta) &= (1/2)\sum_{i,j}^{\sigma} \rho_i \rho_j \int \frac{e_i e_j}{\varepsilon r} g_{ij}^{(0)}(r) 4\pi r^2 \mathrm{d}r \\ &= -\frac{x^2 + x - x(1+2x)^{1/2}}{4\pi\beta R^3}. \end{aligned} \tag{15}$$

Here, $\tilde{a}\ (\xi,\ \beta)$ is the free energy per unit volume of a hard-sphere fluid, which is derived by integrating the Wertheim's formula for the equation of state over the density.[17]

Radial Distribution Function. We have derived the radial distribution function, $g_{ij}^{(0)}(r)$, by an inverse Laplace transform from the function given by Waisman and Lebowitz.[5] The mathematical details are described in the Appendix. The resulting equation consists of the following two terms:

$$g_{ij}(y) = \tilde{g}_{ij}(y) + g_{ij}^{\rm el}(y), \tag{16}$$

where y is the separation between an ion pair reduced by the distance of the closest approach, R. The first term of Eq. (16) is the radial distribution function obtained as the solution of the PY equation for the hard-sphere fluid, which was calculated by Bearman and his coworkers in the range of $1 \leq y \leq 6$.[18,19] The second term is the part related to the charge distribution, which is given by (see Appendix):

$$\begin{aligned} g^{\rm el}(y) &= g_1^{\rm el}(y), & &\text{for } 1 \leq y \leq 2, \\ &= g_1^{\rm el}(y) + g_2^{\rm el}(y), & &\text{for } 2 \leq y \leq 3, \\ &= g_1^{\rm el}(y) + g_2^{\rm el}(y) + g_3^{\rm el}(y), & &\text{for } 3 \leq y \leq 4, \end{aligned} \tag{17}$$

where $g_1^{\rm el}\ (y)$, $g_2^{\rm el}\ (y)$, and $g_3^{\rm el}\ (y)$ are:

$$\begin{aligned} g_1^{\rm el}(y) = (\pm 2q^2/12\xi y)\{&\sin[q(y-1)] \\ &- \cos[q(y-1)]\} \exp[-q(y-1)], \end{aligned} \tag{18a}$$

$$\begin{aligned} g_2^{\rm el}(y) = (\pm 1/12\xi y)[&2(y-2)q^3\{\cos[q(y-2)] \\ &+ \sin[q(y-2)]\} - 2q^2 \sin[q(y-2)]] \\ &\times \exp[-q(y-2)], \end{aligned} \tag{18b}$$

$$\begin{aligned} g_3^{\rm el}(y) = (\pm 1/12\xi y)[&2q^4(y-3)^2\{\cos[q(y-3)] \\ &- \sin[q(y-3)]\} - 2q^3(y-3) \\ &\times \{3\cos[q(y-3)] + \sin[q(y-3)]\} \\ &+ 6q^2 \sin[q(y-3)]] \exp[-q(y-3)]. \end{aligned} \tag{18c}$$

Here, q is a parameter given by:

$$q = \{(1+2\kappa R)^{1/2} - 1\}/2. \tag{19}$$

The form of $g_{ij}\ (y)$ calculated in the range of $1 \leq y \leq 4$ is shown in Figs. 1(a)—(c). Eq. (16) shows that the distribution law of ions in electrolyte solutions is influenced by two different factors: the distribution law characteristic of hard-sphere fluids, which originates from the short-range repulsion between molecules, and a distribution law similar to the Debye-Hückel type which is caused by the long-range Coulombic interaction. While the Debye-Hückel-like distribution is dominant at low concentrations, the total distribution approaches that of a hard-sphere fluid at high concentrations. The change in the shape of the distribution curves with the concentration (Fig. 1) appears to represent such a feature in the distribution of ions.

The curve of $g_{ij}(y)$ has an oscillation that becomes outstanding with an increase in the concentration. This property of $g_{ij}(y)$ in electrolyte solutions was first predicted by Kirkwood and Poirier;[20] it was later formulated by Stillinger and Lovett[21] as a "second moment condition." Recently, Card and his coworkers confirmed the property through a Monte Carlo calculation.[22]

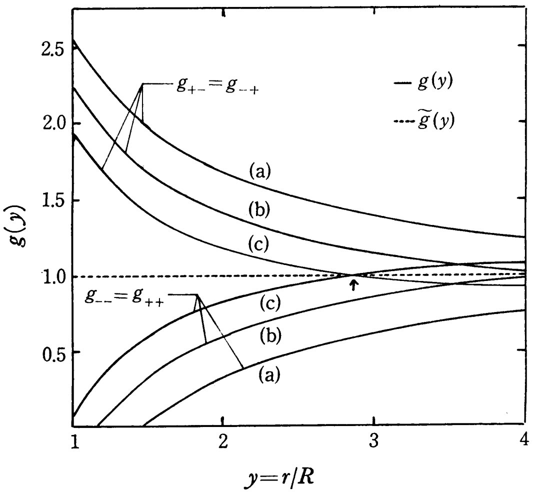

Fig. 1(a). The radial distribution functions computed from MSM equation for the primitive model at $\rho R^3=$ 0.001, 0.01, and 0.05 at 25 °C assuming that $R=4.0$ Å and $\tilde{g}(y)\simeq 1.0$ for $y>1$. (a) $\rho R^3=0.001$, (b) $\rho R^3=0.01$, (c) $\rho R^3=0.05$. In the curve (c), the inversion (oscillation) occurs at the point which is indicated by an arrow.

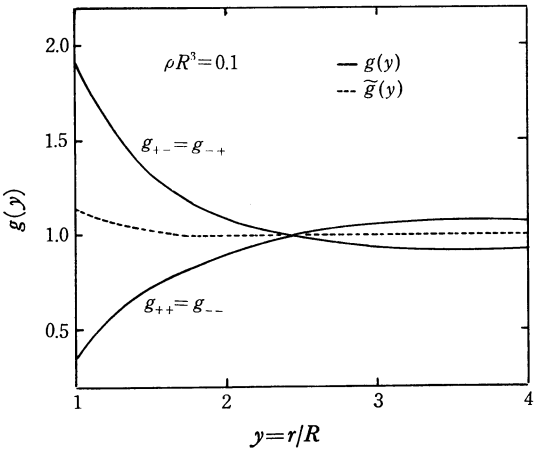

Fig. 1(b). The radical distribution function at $\rho R^3=0.1$. Values calculated by Throop and Bearman is used for $g(y)$ in this figure and the following.

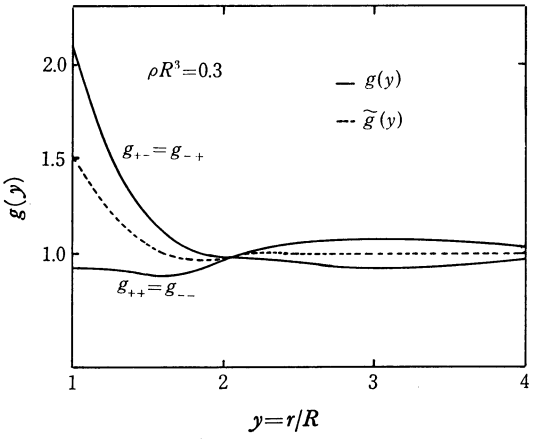

Fig. 1(c). The radial distribution functions at $\rho R^3=0.3$.

Computation of Thermodynamic Functions

Free Energy. After substituting Eq. (4) and changing the variable, r, to a reduced variable, y, we obtain from Eq. (2):

$$\beta(A-A^{(0)})/N = 3\xi J\beta d_{ij}, \tag{20}$$

$$J = \int_1^{1+a} g_{ij}(y)y^2\mathrm{d}y, \tag{21}$$

where a is b_{ij}/R. The contribution from like-like terms in Eq. (2) is ignored. Since the values of $\xi(=\pi R^3\rho/6)$ are smaller than 0.05 in this concentration range (smaller than 1.0 M in molarity),[23] we can safely suppose that $\tilde{g}_{ij}(y)=1$. Thus, Eq. (16) is written as:

$$g_{ij}(y) = 1 + g_{ij}^{\mathrm{el}}(y). \tag{16$'$}$$

After substituting Eqs. (16′), (17), and (18) into Eq. (21), we get:

$$\begin{aligned} J &= (1/3)\{(1+a)^3-1\}+(1/12\xi)\{[(2q+2aq+1)\sin(aq) \\ &\quad +\cos(aq)]\exp(-aq)-1\}, \quad \text{for } R\geq b_{ij}, \\ &= (1/3)\{(1+a)^3-1\}+(1/12\xi)\{[(2q+2aq+1)\sin(aq) \\ &\quad +\cos(aq)]\exp(-aq)+[2(a^2-1)q^2+(3a+1)q-1] \\ &\quad \times\cos[q(a-1)]\exp[-q(a-1)]-[5(1+a)q-2q \\ &\quad +3]\sin[q(a-1)]\exp[-q(a-1)]-4q\}, \\ &\qquad\qquad \text{for } R\leq b_{ij}\leq 2R. \end{aligned} \tag{24}$$

As the hard-sphere radii of ions, Pauling's crystal radii are used.[24] The width of the well, b_{ij}, is equal to the diameter of the water molecule, 2.76 A.[6] The parameter, d_{ij}, is dtermined by fitting the calculated values of A with the one observed at 0.5 M. In this paper, the experimental values of the thermodynamic quantities are transformed into the McMillan-Mayer system according to Friedman's procedure, and the comparison between the calculated and observed values is made in the McMillan-Mayer system.[25] The values of

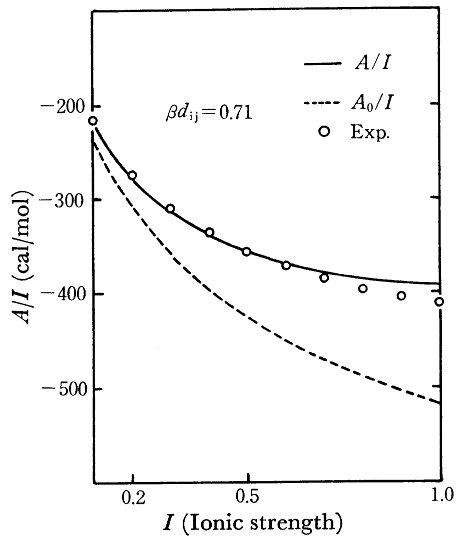

Fig. 2. Calculated and experimental Helmholtz free energy for aqueous solutions of NaCl at 25 °C. The broken line and the solid one are calculated values for the reference system and the system with a square well (or mound) potential as a perturbation, respectively and circles the experimental ones. It is assumed that $\beta d_{+-}=0.71$ and $\beta d_{++}=\beta d_{--}=0$.

TABLE 1. THE VALUES OF βd_{ij} WHICH GIVE THE BEST FIT BETWEEN OBSERVED AND CALCULATED VALUES OF FREE ENERGY

	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-		0.72	0.65		
Cl^-	1.84	0.71	0.09	−0.16	−0.53
Br^-	1.74	0.72	0.07	−0.26	−0.61
I^-	2.02	0.73	0.08	−0.41	−0.76

d_{ij} are tabulated for some 1-1 electrolytes in Table 1. In Fig. 2, the agreement between the observed and calculated values of free energy in the concentration range up to 1.0 M is shown for NaCl as an example.

Energy. The second term of Eq. (5) becomes:

$$\frac{1}{2}\sum_{i,j=1}\rho_i\rho_j E_{ij}\int_R^{R+b_{ij}} g_{ij}^{(0)}(r)4\pi r^2 \mathrm{d}r, \tag{25}$$

where E_{ij} is defined by:

$$E_{ij} = d_{ij} - T\frac{\partial d_{ij}}{\partial T}. \tag{26}$$

Eq. (5) is given by:

$$\frac{\beta(E-E^{(0)})}{\rho/2} = 6\xi J\beta E_{ij}. \tag{27}$$

The observed value with which the calculated value of E is compared is the relative apparent molal heat content.[6,7] The values of E_{ij} determined by a comparison of the observed values of E with the calculated ones are tabulated in Table 2, together with the values of $(-\partial d_{ij}/\partial T)$. The agreement between the observed and calculated values of E in the concentration range up to 1.0 M is very good, as is shown for NaCl in Fig. 3.

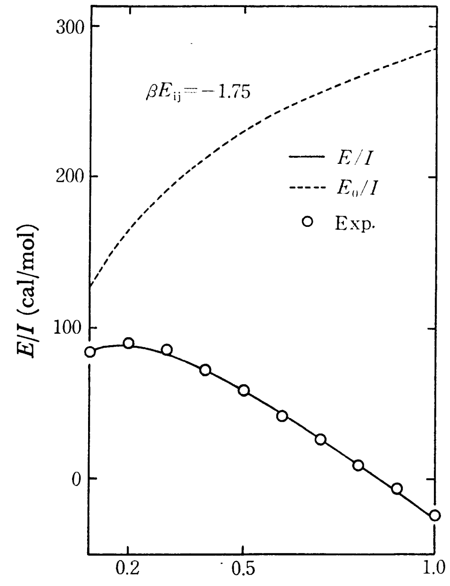

Fig. 3. Calculated and experimental excess energy for aqueous solution of NaCl at 25 °C. The broken line and the solid one are calculated values for the reference system and the system with a square well (or mound) potential as a perturbation, respectively. It is assumed that $\beta E_{+-} = -1.75$, $\beta E_{++} = \beta E_{--} = 0$.

TABLE 2. THE VALUES OF βE_{ij} (UPPER RIGHT HALF OF TABLE) AND k^{-1} $(-\partial d_{ij}/\partial T)$ (LOWER LEFT HALF)

	Li^+	Na^+	K^+	F^-	Cl^-	Br^-
Li^+					0.03	−0.03
Na^+					−1.75	−1.80
K^+				−0.66	−1.55	−1.80
F^-			−1.31			
Cl^-	−1.81	−2.46	−1.84			
Br^-	−1.77	−2.52	−1.81			

Discussion

Interpretation of the Parameter, d_{ij}. In the present computation, an energy parameter, d_{ij}, is used as an adjustable one. We will here discuss the physical meaning of the parameter. When two ions come close enough together so that their cospheres overlap each other, as is shown in Fig. (4), some of the water molecules in the cospheres are displaced. Thus, if the water molecules in the cospheres are in a state of lower free energy than those in bulk water, the overlap of the cospheres gives rise to an increase in the free energy of the water molecules which were in the cosphere before the overlap occurres, and the resulting contribution to the interaction between two ions is repulsive. When the water molecules in the cospheres are in a state of higher free energy than those in bulk water, the converse effect appears by the overlap of the cospheres, which is attractive. Thus, the plus and minus which appear in the sign of d_{ij} in Table 1 can be reasonably interpreted. This interpretation of the parameter, d_{ij}, coincides with that of Rasaiah.[6]

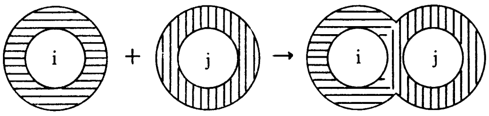

Fig. 4. Schematic representations of the process in which cospheres overlap.

Temperature Dependence of d_{ij}. As may be seen in Table 2, the signs of all the values of $(-\partial d_{ij}/\partial T)$ are minus. In the case of K^+, this sign is consistent with an intuitive picture, since the cospheres around the ions are considered to constitute a structure-breaking region, where water molecules are in a state of higher "entropy" than those in bulk water; the overlap of cospheres would thus lead to a net decrease in the "entropy." In the case of Li^+, it is difficult to interpret the sign of $(-\partial d_{ij}/\partial T)$, because the cospheres around the ions are expected to be in a state of lower "entropy." One possible explanation, which was given by Rasaiah,[6] is that $(-\partial d_{ij}/\partial T)$ is determined by the outer region far away from the nearest neighbor cosphere. This is plausible, since the structure-breaking region is considered to extend outside the cosphere in the case of very small ions, such as Li^+ and polyvalent ions (Mg^{2+}, Ca^{2+}, *etc.*).

Appendix

The Derivation of the Radial Distribution Function, $g_{ij}(y)$, from the Function Given by Waisman and Lebowitz. It is convinient to start from Eq. (23) in Ref. (5a), which defines a function $\boldsymbol{L}(s)$.[5] That is:

$$\boldsymbol{L}(s) = \boldsymbol{G}(s)\boldsymbol{H}^T(-s). \tag{A,1}$$

Here, $\boldsymbol{G}(s)$ is a matrix whose (i,j)-element is a Laplace transform of the radial distribution function, $g_{ij}(y)$, of ions of the j type around an ion of i type:

$$G_{ij}(s) = 12(\eta_i\eta_j)^{1/2}\int_{R_{ij}}^{\infty} rg_{ij}(r)e^{-sr}\mathrm{d}r, \tag{A,2}$$

where η_i is $\pi\rho_i/6$. $\boldsymbol{H}^T(-s)$ is a transpose of a matrix, $\boldsymbol{H}(-s)$, in which the sign of variables is changed to give this equation:

$$\boldsymbol{H}(s) = \boldsymbol{A} - s^2\boldsymbol{F}(s) - (\gamma^2/4)(s\boldsymbol{D}+2\boldsymbol{V}), \tag{A,3}$$

where γ and D_{ij}, the (i,j)-element of $\boldsymbol{D}$, are:

$$\gamma^2 = 8\pi\beta/\varepsilon \text{ and } D_{ij} = (\rho_i\rho_j)^{1/2}e_ie_j,$$

respectively. In Eq. (A, 3), $\boldsymbol{F}(s)$ is a matrix whose (i,j)-element is a Laplace transform of the direct correlation function.

$$F_{ij}(s) = -12(\eta_i\eta_j)^{1/2}\int_0^{R_{ij}} r\left(C_{ij}(r)+\frac{\beta e_ie_j}{\varepsilon r}\right)e^{-sr}\mathrm{d}r. \tag{A,4}$$

The (i,j)-element of $\boldsymbol{L}(s)$ in Eq. (A,1) has been shown, on the basis of a consideration of the analyticity in the complex s-plane, to have this form:[5]

$$L_{ij}(s) - s^{-2}A'_{ij} = 2M_{ij}. \tag{A,5}$$

When the hard-sphere diameters of all species are equal, we get the following equalities:

$$A_{ij} = A_{ji} = A_{ii} = A_{jj} = A, \tag{A,6a}$$

$$A'_{ij} = A'_{ji} = A'_{ii} = A'_{jj} = A', \tag{A,6b}$$

$$V_{ij} = V_{ji} = -V_{ii} = -V_{jj} = -V, \tag{A,6c}$$

$$M_{ii} = M_{jj}, \quad M_{ij} = M_{ji} \tag{A,6d}$$

and $A'=12\,\eta A$, where $\eta=\sum_i\eta_i$. By virtue of these equalities, the quadratic equations (28a)—(28e) in Ref. (5a) are reduced to a readily solvable form, and the solutions are:

$$A = 6\eta\frac{(2\xi+1)^2}{(1-\xi)^4}, \quad A' = 72\eta^2\frac{(2\xi+1)^2}{(1-\xi)^4},$$

$$M_{ij} = -\frac{6\eta}{R^2}\left\{\frac{6R\xi(1+\xi/2)^2}{(1-\xi)^4}+\frac{\beta e_ie_jB^2}{\varepsilon}\right\},$$

$$V_{ij} = -\frac{12\eta\beta e_ie_jB}{R(\gamma^2/2)\varepsilon},$$

$$M \equiv M_{ii} + M_{ij} = -\frac{72\eta R\xi(1+\xi/2)^2}{R^2(1-\xi)^4},$$

$$M' \equiv M_{ii} - M_{ij} = -\frac{12\eta\beta e^2B^2}{\varepsilon R^2}. \tag{A,7}$$

Now, multiplying the two sides of Eq. (A, 1) by an inverse of the matrix, $\boldsymbol{H}^T(-s)$, we get:

$$\boldsymbol{G}(s) = \boldsymbol{L}(s)\boldsymbol{H}^T(-s)^{-1} \tag{A,8}$$

Therefore, the (i,j)-element, $G_{ij}(s)$, of the matrix, $\boldsymbol{G}(s)$, is given by:

$$G_{ij}(s) = \{L_{ij}(s)H_{ii}(-s)-L_{ii}(s)H_{ji}(-s)\}D(s)^{-1}. \tag{A,9}$$

Here, $D(s)$ is a determinant of the matrix, $\boldsymbol{H}^T(-s)$; it is given by:

$$\begin{aligned}D(s) &= \{A_{ii}-s^2F_{ii}(-s)-(\gamma^2/4)(-sD_{ii}+2V_{ii})\}^2\\ &\quad -\{A_{ij}-s^2F_{ji}(-s)-(\gamma^2/4)(-sD_{ji}+2V_{ji})\}^2.\end{aligned} \tag{A,10}$$

Condisering the equalities in Eqs. (A, 7), the right-hand side of Eq. (A, 10) can be factores to give:

$$\begin{aligned}D(s) &= \{-s^2[F_{ii}(-s)-F_{ji}(-s)]-2(\gamma^2/4)(-sD+2V)\}\\ &\quad \times \{2A-s^2[F_{ii}(-s)+F_{ji}(-s)]\}.\end{aligned} \tag{A,11}$$

By reference to Eqs. (A, 6) and (A, 7), the numerator of the right-hand side of Eq. (A, 9) is found to be given by:

$$\begin{aligned}&L_{ij}(s)H_{ii}(-s) - L_{ii}(s)H_{ji}(-s)\\ &\quad = -(s^{-2}A'+2M_{ii})\{A-s^2F_{ji}(-s)-(\gamma^2/4)(sD-2V)\}\\ &\qquad +(s^{-2}A'+2M_{ij})\{A-s^2F_{ii}(-s)-(\gamma^2/4)(-sD+2V)\}\\ &\quad = (s^{-2}A'+M)\{-s^2[F_{ii}(-s)-F_{ji}(-s)]\\ &\qquad -2(\gamma^2/4)(-sD+2V)\}-M'\{2A-s^2[F_{ii}(-s)\\ &\qquad +F_{ji}(-s)]\}.\end{aligned} \tag{A,12}$$

Thus,

$$\begin{aligned}G_{ij}(s) &= \frac{s^{-2}A'+M}{2A-s^2[F_{ii}(-s)+F_{ji}(-s)}\\ &\quad -\frac{M'}{-s^2[F_{ii}(-s)-F_{ji}(-s)]-2(\gamma^2/4)(-sD+2V)}.\end{aligned} \tag{A,13}$$

By the substitution of the expression for $F_{ij}(-s)$, which is obtained by combining Eq. (10) with Eq. (A, 4), Eq. (A,13) becomes:

$$G_{ij}(s) = \frac{1}{2}\frac{sL_1(s)}{L_1(s)+S_1(s)\mathrm{e}^{Rs}} - \frac{1}{2}\frac{sL_2}{L_2+S_2(s)\mathrm{e}^{Rs}}. \tag{A,14}$$

Here, $L_1(s)$, L_2, $S_1(s)$, and $S_2(s)$ are given by:

$$L_1(s) = 12\xi[(1+\xi/2)Rs+(2\xi+1)], \tag{A,15a}$$

$$\begin{aligned}S_1(s) &= (1-\xi)^2(sR)^3 + 6\xi(1-\xi)(sR)^2\\ &\quad + 18\xi^2(sR) - 12\xi(1+2\xi),\end{aligned} \tag{A,15b}$$

$$L_2 = -2p^2, \tag{A,15c}$$

$$S_2(s) = (s^2+2ps+2p^2)e^{sR} - 2p^2, \tag{A,15d}$$

where p is a parameter defined by:

$$p = \{(1+2\kappa R)^{1/2}-1\}/2R. \tag{A,16}$$

The expression for the radial distribution function is obtained by taking an inverse Laplace transform of Eq. (A, 14). Changing r and s to y and t respectively through the $r=Ry$ and $s=t/R$ relations, we get the final equation:

$$g_{ij}(y) = \tilde{g}_{ij}(y) + g_{ij}^{\mathrm{el}}(y). \tag{A,17}$$

Here, $\tilde{g}_{ij}(y)$, $g_{ij}(y)$, and $g_{ji}^{\mathrm{el}}(y)$ are given by:

$$g_{ij}(y) = \frac{1}{2\pi iy}\int_{\delta-i\infty}^{\delta+i\infty}\frac{1}{12\xi}G_{ij}(y)\mathrm{e}^{ty}\mathrm{d}t, \tag{A,18a}$$

$$g_{ij}(y) = \frac{1}{2\pi iy}\int_{\delta-i\infty}^{\delta+i\infty}\frac{tL_1(t)\mathrm{e}^{yt}\mathrm{d}t}{12\xi[L_1(t)+S_1(t)\mathrm{e}^t]}, \tag{A,18b}$$

$$g_{ij}^{\mathrm{el}}(y) = \frac{1}{2\pi iy}\int_{\delta-i\infty}^{\delta+i\infty}\frac{tL_2\mathrm{e}^{yt}\mathrm{d}t}{12\xi[L_2+S_2(t)\mathrm{e}^t]}, \tag{A,18c}$$

where $L_1(t)$, $S_1(t)$, L_2, and $S_2(t)$ are:

$$L_1(t) = 12\xi[(1+\xi/2)t+(2\xi+1)], \tag{A,19a}$$

$$\begin{aligned}S_1(t) &= (1-\xi)^2t^3 + 6\xi(1-\xi)t^2 + 18\xi^2t\\ &\quad - 12\xi(1-2\xi),\end{aligned} \tag{A,19b}$$

$$L_2(t) = -2q^2, \tag{A,19c}$$

$$S_2(t) = t^2 + 2qt + 2q^2, \tag{A,19d}$$

and

$$q = \{(1+2\kappa R)^{1/2}-1\}/2. \tag{A,20}$$

In Eq. (A, 17), the first term is Wertheim's solution of the PY equation for a hard-sphere fluid; the integral in Eq. (A, 18b) was evaluated by Bearman and his co-workers using the residue theorem in the range of $1<y<6$.[18,19] The second term, which is characteristic of electrolyte solutions, can also be evaluated in a similar way. After the denominator of the integrand is expanded to the power series in $L_2/S_2(t)$, Eq. (A, 18c) is written by:

$$g_{ij}^{\mathrm{el}}(y) = \frac{1}{12\xi y}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty}\exp\left[t(y-n)\right]\left[\frac{L_2}{S_2(t)}\right]^n t\mathrm{d}t. \tag{A,21}$$

The path of integration is to be taken to the right of all the poles of $1/S_2(t)$. Thus, the integral for $y<n$ is zero and that for $y>n$ is evaluated by means of the residue theorem. The resulting equations in the range of $1\leq y\leq 4$ are:

$$\begin{aligned} g^{\mathrm{el}}(y) &= g_1^{\mathrm{el}}(y), \quad \text{for } 1\leq y\leq 2, \\ &= g_1^{\mathrm{el}}(y) + g_2^{\mathrm{el}}(y), \quad \text{for } 2\leq y\leq 3, \\ &= g_1^{\mathrm{el}}(y) + g_2^{\mathrm{el}}(y) + g_3^{\mathrm{el}}(y), \quad \text{for } 3\leq y\leq 4, \end{aligned} \tag{A,22}$$

where $g_1^{\mathrm{el}}(y)$, $g_2^{\mathrm{el}}(y)$, and $g_3^{\mathrm{el}}(y)$ are

$$\begin{aligned} g_1^{\mathrm{el}}(y) = {} & (\pm 2q^2/12\xi y)\{\sin[q(y-1)] \\ & - \cos[q(y-1)]\}\exp[-(y-1)], \end{aligned} \tag{A,23a}$$

$$\begin{aligned} g_2^{\mathrm{el}}(y) = {} & (\pm 1/12\xi y)[2(y-2)q^3\{\cos[q(y-2)] \\ & - \sin[q(y-2)]\} - 2q^2\sin[q(y-2)]] \\ & \times \exp[-q(y-2)], \end{aligned} \tag{A,23b}$$

$$\begin{aligned} g_3^{\mathrm{el}}(y) = {} & (\pm 1/12\xi y)[2q^4(y-3)^2\{\cos[q(y-3)] \\ & + \sin[q(y-3)]\} - 2q^3(y-3) \\ & \times \{3\cos[q(y-3)]+\sin[q(y-3)]\} \\ & + 6q^2\sin[q(y-3)]]\exp[-q(y-3)]. \end{aligned} \tag{A,23c}$$

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