Mean Spherical Model Integral Equation for Charged Hard Spheres* I. Method of Solution

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The thermodynamic properties and radial distribution function of a "primitive model electrolyte" are calculated in the Mean Spherical Model (MSM) approximation. The system considered is formally described as a classical fluid of charged hard spheres (hard sheets in one dimension). The interaction potential between an ion of species i and an ion of species j, $v_{ij}(r)$ is the sum of a Coulomb part and a hard core part $q_{ij}(r)=\infty$ for $r<R_{ij}$ or 0 otherwise. The MSM approximation consists of supplementing the fact that the radial distribution function $g_{ij}(r)$ is zero for $r<R_{ij}$ by equating the Ornstein–Zernike direct correlation function $C_{ij}(r)$ to $-\beta v_{ij}(r)$ for $r>R_{ij}$, β being the inverse temperature. In this paper, which is the first of two in this topic, we give the method of solution for this approximation and obtain $C_{ij}(r)$ for $r<R_{ij}$ as polynomials in r, which have a structure similar to that found in the PY approximation for a mixture of uncharged hard spheres. We give the solution up to a set of algebraic equations in the polynomial coefficients. In the second paper we discuss the explicit solution and derived thermodynamic quantities.

I. THE PRIMITIVE MODEL FOR STRONG ELECTROLYTES

The simplest model system which retains the main features of strong electrolytic solutions is the primitive model of electrolytes.[1] It consists of approximating the solvent by a continuum in which the ions are imbedded—this continuum having a dielectric constant ϵ different from the vacuum dielectric constant—the ions themselves interact with two-body additive forces with the interaction potential between an ion of type i and one of type j a distance r apart given by

$$\begin{aligned} v_{ij}(r) &= \infty, \qquad r<R_{ij} \\ &= e_ie_j/\epsilon r, \qquad r>R_{ij}. \end{aligned} \tag{1}$$

Here e_i is the charge of the ith type of ion and R_{ij} is the distance of closest approach between an ion of type i and one of type j, $R_{ij}=\frac{1}{2}(R_{ii}+R_{jj})$, i.e., we are treating the ions as charged hard spheres with diameters $R_i\equiv R_{ii}$. We assume over-all electrical neutrality, that is

$$\sum_{j=1}^{m} \rho_j e_j = 0, \tag{2}$$

where ρ_j is the number density (assumed spatially uniform) of species j and m is the number of species. We will also consider a one-dimensional analog of the primitive model, given by a system of infinite parallel hard planes with charge e_j uniformly distributed over the surface, thickness R_j, and number density ρ_j interacting via the pair potential $v_{ij}(|x|)$ ($|x|$ being the distance between the positions of the center of the charged sheets on the real line):

$$\begin{aligned} v_{ij}(x) &= \infty, \qquad |x|<R_{ij} \\ &= -e_ie_j|x|/2\epsilon, \qquad |x|>R_{ij}, \end{aligned} \tag{3}$$

where we impose the same condition of hard core additivity, $R_{ij}=\frac{1}{2}(R_{ii}+R_{jj})$, and electrical neutrality as in the 3-dimensional case.[2] Throughout this work, unless otherwise stated, we will consider a two-component system characterized by (ρ_1, e_1, R_1) and (ρ_2, e_2, R_2). Therefore the electrical neutrality condition is given by $\rho_1e_1+\rho_2e_2=0$ and we choose for definiteness $R_2\geq R_1$.

As indicated already by our assumption of spatial uniformity of the densities ρ_i we imagine our system to be very large: *formally* (as a limit) of infinite size. We shall assume that the radial distribution functions $g_{ij}(r)$ of these systems exist in this limit,[4] and consider a method for finding them in an approximate way. We restrict ourselves to classical systems.

The Ornstein–Zernike[6] direct correlation matrix $C_{ij}(r)$ is defined by the relationship

$$h_{ij}(r)=C_{ij}(r)+\int_{\text{all space}} d\mathbf{r}' \times \sum_{l=1}^{2} \rho_l h_{il}(|\mathbf{r}'|)C_{lj}(|\mathbf{r}-\mathbf{r}'|), \tag{4}$$

where $h_{ij}(r)\equiv g_{ij}(r)-1$ and $C_{12}(r)=C_{21}(r)$ because $g_{12}(r)\equiv g_{21}(r)$ by the definition of the $g_{ij}(r)$.

An important contribution to the understanding of electrolyte solution properties was made by Debye and Hückel[7] in 1923. They considered the case of point charges in the limit of infinite ionic dilution. In the language of the pair correlation functions the Debye–Hückel theory corresponds to setting the direct correlation functions $C_{ij}(r)$ equal to $C_{ij}^{\mathrm{DH}}(r)=-\beta e_ie_j/\epsilon r$, $0<r<\infty$. When this direct correlation function is used, the solution of Eq. (4) for the radial distribution function is given by

$$g_{ij}^{\mathrm{DH}}(r)=1-(\beta/\epsilon)e_ie_j\exp(-\chi r)/r, \tag{5}$$

where $\chi^2=4\pi(\beta/\epsilon)\sum_l \rho_l e_l^2$. The deficiencies of this approximation have been discussed over the years;

the most obvious one is

$$g_{ii}^{\mathrm{DH}}(r) \underset{r\to 0}{\longrightarrow} -\infty .$$

However the thermodynamic quantities derived from these distribution functions have been found correct in the low concentration limit. Physically the main feature of the D–H theory is the asymptotic behavior of $h_{ij}(r)$,

$$|h_{ij}(r)| \underset{r\to\infty}{\longrightarrow} \text{constant} \exp(-\chi r)/r,$$

which gives a quantitative form to the very important idea of "screening" of the Coulomb potential between two ions by the formation of charge "clouds" around each ion.

Recently Stillinger and Lovett[8] obtained new moment relations which the exact radial distribution functions of an electrolyte must satisfy,[9] these are

$$4\pi \int_0^\infty dr \sum_{l=1}^{2} \rho_l e_l g_{il}(r) r^2 = -e_i, \qquad \text{for each } i, \tag{6a}$$

$$4\pi \int_0^\infty dr \sum_{l,m=1}^{2} \rho_l \rho_m e_l e_m g_{lm}(r)^2 r^4 = -6 \sum_{l=1}^{2} \rho_l e_l^2/\chi^2. \tag{6b}$$

The relation (6a), which we shall call the zeroth moment relation corresponds to the well known local electroneutrality conditions. We shall call the relation (6*b*) the second moment relation. We note that the approximate $g_{ij}^{\mathrm{DH}}(r)$ fulfill (6a) and (6b).

Stillinger and Lovett also prove that (6a) and (6b) imply the presence of oscillations in the charge cloud density around a given ion, for high enough concentration of the solute when hard spheres interactions are present between ions. For instance in the case of $e_1=-e_2=|e|$, $\rho_1=\rho_2$, $R_1=R_2$, (6a) and (6b) imply that the charge cloud density around a positive ion—given by

$$Q_+(r) = 4\pi r^2[\rho_1 e_1 g_{11}(r) + \rho_2 e_2 g_{12}(r)]$$
$$= 4\pi r^2 \rho_1 |e| [g_{11}(r) - g_{12}(r)]$$

—cannot be negative for all r's if $\chi R \geq 6^{1/2}$. In the language of the Ornstein–Zernike direct correlation function the zeroth and second moments relations can be obtained using Fourier transforms.[10] Defining the Fourier transform of $C_{ij}(r)$:

$$\hat{C}_{ij}(k) = \int C_{ij}(r) \exp(i\mathbf{k}\cdot\mathbf{r}) d\mathbf{r},$$

the moment relations are satisfied if

$$\hat{\xi}_{ij}(k) = \hat{C}_{ij}(k) + 4\pi\beta e_i e_j/\epsilon k^2 \tag{7}$$

has the properties:

(i) $\lim_{k\to\infty} k^2 \hat{\xi}_{ij}(k) = 0,$

and (ii) $\xi_{ij}(k)$ is twice differentiable in the neighborhood of $k=0$. In physical space this means that to have the moment relations it is sufficient that the functions $\xi_{ij}(r) \equiv C_{ij}(r) + \beta e_i e_j/\epsilon r$ go to 0 as $r\to\infty$ faster than r^{-1} [in the sense defined by (7)], and behave "reasonably" at $r=0$.

Other recent developments in the field of electrolytes include the work of Rasaiah and Friedman,[11] Rasaiah[12] and Anderson and Chandler.[13] They have improved greatly the accuracy to which the properties of the primitive model of strong electrolytes are known. Of particular importance is the availability of accurate computer experiments which constitute the "experimental results" for comparison with theoretical computations. Such computations have been carried out recently by Card and Valleau,[14] as well as by Vorontsov-Veliaminov and Eliasheich.[15]

We shall compare our results with those of these authors in Paper II of this work.

II. THE MEAN SPHERICAL APPROXIMATION FOR STRONG ELECTROLYTES

The mean spherical model (MSM) approximate integral equation was constructed by Lebowitz and Percus[16] as a generalization to continuum fluids with hard spheres interactions of the spherical model for Ising spin systems which are isomorphic to lattice gases. The exact statement that $g_{ij}(r)$ vanishes for $r<R_{ij}$ is supplemented in the MSM by setting $C_{ij}(r)$ equal to $-\beta v_{ij}(r)$ for $r>R_{ij}$; therefore in our case we have

$$g_{ij}(r) = 0 \quad \text{for} \quad r<R_{ij},$$
$$C_{ij}(r) = -\beta e_i e_j/\epsilon r \quad \text{for} \quad r>R_{ij}. \tag{8}$$

From (8) it is clear that when e_1, $e_2=0$ the MSM coincides with the Percus–Yevick approximate equation for a mixture of uncharged hard spheres, while for R_1, $R_2=0$ the MSM reduces to the Debye–Hückel approximation. Furthermore since

$$C_{ij}(r) + \beta e_i e_j/\epsilon r \equiv C_{ij}^{(0)}(r) \tag{9}$$

vanishes in the MSM for $r>R_{ij}$ the radial distribution functions obtained from this model will satisfy the Stillinger–Lovett moment relations. We shall indeed make use of the relations in obtaining the exact solution of the MSM equations.[17]

In terms of $C_{ij}^{(0)}(r)$ the Ornstein–Zernike relation [Eq. (4)] becomes

$$h_{ij}(r) - C_{ij}^{(0)}(r) - \sum_l \rho_l \int h_{il}(|\mathbf{r}'|) C_{lj}^{(0)}(|\mathbf{r}-\mathbf{r}'|) d\mathbf{r}'$$
$$= -\beta e_i e_j/\epsilon r - (\beta/\epsilon) \sum_l \rho_l e_l e_j \int [h_{il}(r') d\mathbf{r}'/|\mathbf{r}-\mathbf{r}'|]$$
$$\equiv u_{ij}(r). \tag{10}$$

We work now with the right-hand side of Eq. (10). Performing the integrations over angles in the second term we obtain

$$u_{ij}(r)=-\frac{\beta e_ie_j}{\epsilon r}-\frac{4\pi\beta}{\epsilon}\sum_l \rho_l e_l e_j\left(r^{-1}\int_0^r h_{il}(x)x^2dx+\int_r^\infty h_{il}(x)xdx\right)$$

$$=-\frac{\beta e_ie_j}{\epsilon r}-\frac{4\pi\beta}{\epsilon r}\sum_l \rho_l e_l e_j\int_0^\infty h_{il}(x)x^2dx-\frac{4\pi\beta}{\epsilon}\sum_l \rho_l e_l e_j\left(-r^{-1}\int_r^\infty h_{il}(x)x^2dx+\int_r^\infty h_{il}(x)xdx\right), \qquad (10')$$

but

$$\frac{\beta e_ie_j}{\epsilon r}+\frac{4\pi\beta}{\epsilon r}\sum_l \rho_l e_l e_j\int_0^\infty h_{il}(x)x^2dx=0,$$

because of condition (6a). Therefore (10) becomes

$$h_{ij}(r)-C_{ij}^{(0)}(r)-\sum_l \rho_l\int h_{il}(r')C_{ij}^{(0)}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'=\tfrac{1}{2}\gamma^2\sum_l \rho_l e_l e_j\left(r^{-1}\int_r^\infty h_{il}(x)x^2dx-\int_r^\infty h_{il}(x)xdx\right), \qquad (11)$$

where we have defined $\gamma^2=8\pi\beta/\epsilon$.

The task then is to solve the nonlinear integral equation (11) with the "boundary conditions" $h_{ij}(r)=-1$ for $r<R_{ij}$ and $C_{ij}^{(0)}=0$ for $r>R_{ij}$ when the condition $\sum_l \rho_l e_l=0$ is satisfied.

III. SOLUTION FOR THE THREE-DIMENSIONAL MSM

A. The Integral Equation

The techniques we use here, follow closely those used by Lebowitz[18] in solving the PY equation for a mixture of uncharged hard spheres, which are a generalization to the mixtures of Wertheim's[19] way of solving the PY equation for a single component fluid of hard spheres. It is easy to see why one would utilize the techniques of Ref. 18, by noting that if the left hand side of Eq. (11) is equated to 0, Eq. (11) would be exactly the PY equation for uncharged hard spheres with $C_{ij}^{(0)}(r)$ the full direct correlation function for that problem.

We define the matrix $\sigma_{ij}(r)$ by

$$[12(\eta_i\eta_j)^{1/2}r]^{-1}\sigma_{ij}(r)=-C_{ij}^{(0)}(r)\quad\text{for}\quad r<R_{ij},$$
$$=g_{ij}(r)\quad\text{for}\quad r>R_{ij}, \qquad (12)$$

where $\eta_i=(\pi/6)\rho_i$.

Using bipolar coordinates for the convolution term in the left-hand side of (11) and recalling the over-all electrical neutrality condition $\sum_l \rho_l e_l=0$, (11) becomes in terms of $\sigma_{ij}(r)$

$$\sigma_{ij}(r)-A_{ij}r+\sum_l\int_{y\geq R_{il}}^\infty dy\sigma_{il}(y)\times\int_{u=|r-y|<R_{lj}}^{\min(r+y,R_{lj})}\sigma_{lj}(u)du=-\tfrac{1}{2}\gamma^2 r\sum_l D_{lj}\times\int_{\max(r,R_{il})}^\infty\sigma_{il}(x)dx+\tfrac{1}{2}\gamma^2\sum_l D_{lj}\times\int_{\max(r,R_{il})}^\infty\sigma_{il}(x)xdx. \qquad (13)$$

The condition $|r-y|<R_{lj}$ means that the integral vanishes if $|r-y|\geq R_{lj}$. Here we have introduced the matrix $D_{ij}(\mathsf{D})_{ij}=(\rho_i\rho_j)^{1/2}e_ie_j$, "the charge matrix" which is known, and $A_{ij}=(\mathsf{A})_{ij}=2\pi(\rho_i\rho_j)^{1/2}a_j$ where

$$a_j=1-4\pi\sum_l \rho_l\int_0^{R_{lj}}C_{lj}^{(0)}(x)x^2dx$$
$$=1+2\sum_l(\rho l/\rho_j)^{1/2}\int_0^{R_{lj}}\sigma_{lj}(x)xdx. \qquad (14)$$

Next we differentiate (13) with respect to r, obtaining

$$\sigma_{ij}^{(1)}(r)-A_{ij}-\sum_l\int_{R_{il}}^\infty dy\sigma_{il}(y)\sigma_{lj}(|\mathbf{r}-\mathbf{y}|)\times\theta(R_{lj}-|r-y|)+P_{ij}(r)=-\tfrac{1}{2}\gamma^2\sum_l D_{lj}\int_{\max(r,R_{il})}^\infty\sigma_{il}(x)dx. \qquad (15)$$

Here $\sigma_{ij}^{(n)}$ stands for the nth derivative of σ_{ij} with respect to r, and $\theta(x)$ is the Heaviside function $\theta(x)=0$ for $x<0$, $\theta(x)=1$ for $x>0$. The term $P_{ij}(r)$ is zero for $(i,j)\neq(1,2)$ since for these elements the upper bound on the u integration in (13) is independent of r. Hence $P_{ij}(r)=\delta_{i1}\delta_{j2}P(r)$, where

$$P(r)=\sum_l\int_{R_{il}+r}^{R_{l2}}\sigma_{il}(y-r)\sigma_{l2}(y)dy\quad\text{for}\quad r\leq\lambda\equiv\tfrac{1}{2}(R_2-R_1),$$
$$P(r)=0\quad\text{for}\quad r>\lambda. \qquad (15')$$

From (13) and (15) it follows immediately that

$$\sigma_{ij}(0)=-(\gamma^2/4)D_{ij}$$
$$\sigma_{ij}^{(1)}(0)=A_{ij}-(\gamma^2/2)V_{ij}\quad\text{for}\quad(i,j)\neq(1,2) \qquad (16)$$

where

$$V_{ij}=\sum_l B_{il}D_{lj},$$

$$B_{il}=\int_{R_{il}}^{\infty}\sigma_{il}(x)dx=12(\eta_i\eta_l)^{1/2}\int_{R_{il}}^{\infty}xg_{il}(x)dx. \quad (16')$$

It is seen from (16′) that V_{ij} is related to the average potential energy per unit volume, which is given by

$$E^{ex}=\epsilon^{-1}\sum_i V_{ii} \quad (16'')$$

From (13) we also can deduce directly that

$$\sigma_{12}(r)=\sigma_{21}(r)=-(\gamma^2/4)D_{21}+(A_{21}-(\gamma^2/2)V_{21})r, \quad \text{for } r<\lambda \quad (17)$$

B. Continuity Properties of $\sigma_{ij}(r)$

By inspecting Eq. (13) we see that $\sigma_{ij}(r)$ is continuous everywhere ($r\geq 0$). From (15), one can prove that $\sigma_{ij}^{(1)}$ is also continuous everywhere. By differentiating (15) once more one shows that $\sigma_{ij}^{(2)}(r)$ is continuous at $r=R_{ij}$, and that $\sigma_{21}^{(2)}(r)$ is *discontinuous* at $r=\lambda$. By induction one can also prove that $\sigma_{ii}^{(n)}(r)$ is continuous for $0<r<R_{ij}$, $\forall n$, and that $\sigma_{21}^{(n)}(r)$ is continuous for $\lambda<r<R_{21}$, $\forall n$. Also we know explicitly from (17) that $\sigma_{21}^{(n)}(r)$ is continuous for $0<r<\lambda$, $\forall n$.

We can also see that $\sigma_{ij}^{(2)}(r)$ is discontinuous for $r=R_{il}+R_{lj}$, $l=1, 2$. Therefore it should be noticed that when the case $R_1\rightarrow 0$ is considered the fact that the discontinuities "move in" must be taken into account. Namely $\sigma_{21}^{(2)}$ becomes discontinuous at $r=\lambda=R_{21}=R_2/2$. Also $\sigma_{22}^{(2)}$ becomes discontinuous at $r=R_2$ and $\sigma_{11}^{(2)}$ at $r=0$.

C. The Laplace Space Equation

Taking the Laplace transform of both sides of (15) we obtain the following matrix equation in the s-Laplace space:

$$s[\mathbf{G}(s)+\mathbf{F}(s)]-\mathbf{A}/s-\mathbf{G}(s)[\mathbf{F}(s)-\mathbf{F}(-s)]-\mathbf{\Gamma}(s)$$
$$=(\gamma^2/4)\mathbf{D}-(\gamma^2/2s)\mathbf{V}+(\gamma^2/2s)\mathbf{G}(s)\mathbf{D}, \quad (18)$$

where

$$G_{ij}(s)=\int_{R_{ij}}^{\infty}\exp(-sr)\sigma_{ij}(r)dr, \quad (18')$$

$$F_{ij}(s)=\int_0^{R_{ij}}\exp(-sr)\sigma_{ij}(r)dr, \quad (18'')$$

$$\Gamma_{ij}(s)=\delta_{i1}\delta_{j2}\Gamma_{12}(s)=\delta_{i1}\delta_{j2}[P(-s)-P(s)], \quad (18''')$$

where

$$P(s)=\int_0^{\lambda}\exp(-sr)P(r)dr.$$

$\Gamma_{12}(s)$ is not an independent function, it is determined by the conditions $G_{ij}(s)=G_{ji}(s)$ and $F_{ij}(s)=F_{ji}(s)$ which are implied by the symmetry of $g_{ij}(r)$ and $C_{ij}(r)$.

Multiplying (18) by s and regrouping terms we get

$$\mathbf{G}(s)[\mathbf{I}s^2-s\mathbf{F}^{\pm}(s)-(\gamma^2/2)\mathbf{D}]$$
$$=\mathbf{A}-s^2\mathbf{F}(s)+s\mathbf{\Gamma}(s)-(\gamma^2/4)(s\mathbf{D}+2\mathbf{V}), \quad (19)$$

where $\mathbf{F}^{\pm}(s)=\mathbf{F}(s)-\mathbf{F}(-s)$ and $\mathbf{I}$ is the identity matrix.

We can write (19) in a more compact form, namely

$$\mathbf{G}(s)=\mathbf{H}(s)\mathbf{K}(s) \quad (20)$$

$$\mathbf{H}(s)=\mathbf{A}-s^2\mathbf{F}(s)+s\mathbf{\Gamma}(s)-(\gamma^2/4)(s\mathbf{D}+2\mathbf{V})$$

$$\mathbf{K}(s)=[\mathbf{I}s^2-s\mathbf{F}^{\pm}(s)-(\gamma^2/2)\mathbf{D}]^{-1}.$$

From its definition we have that $\mathbf{K}(s)=\mathbf{K}(-s)=\mathbf{K}^T(s)$, where T indicates the transpose of the matrix.

D. Analyticity in the Complex s Plane

We think of (19) and (20) as functional (matrix) equations extending the definition of the functions under consideration to the whole complex s plane.

Since we are considering a disordered liquid away from the phase transition region, $g_{ij}(r)$ should go to 1 as $r\rightarrow\infty$ sufficiently rapidly. In fact a possible condition for having a disordered fluid[20] is given by

$$\int_0^{\infty}|g_{ij}(r)-1|dr<\infty. \quad (21)$$

Requiring Eq. (21) implies that $G_{ij}(s)-12(\eta_i\eta_j)^{1/2}s^{-2}$ is analytic for Re$s>0$ and bounded on the imaginary axis. We shall actually assume that $G_{ij}(s)-12(\eta_i\eta_j)^{1/2}s^{-2}$ is analytic in the closed right-hand side of the complex s-plane,[21] i.e., Re$s\geq 0$. Also if $rC_{ij}^{(0)}(r)$ is uniformly bounded $F_{ij}(s)$ is an entire function of s. We shall look for the solution of the MSM which satisfied these conditions. From the same arguments it follows that $\Gamma_{12}(s)$ is an entire function of s.

Furthermore, using these analyticity properties of $\mathbf{G}(s)$, $\mathbf{F}(s)$, and $\mathbf{\Gamma}(s)$ and the conclusions we have obtained in Sec. III.B about the smoothness of $\sigma_{ij}(r)$

the following asymptotic expressions are apparent:

$$\lim_{\mathrm{Re}s\to\infty} F_{ii}(s)=s^{-1}[\sigma_{ii}(0)-\sigma_{ii}(R_i)\exp(-sR_i)]+s^{-2}[\sigma_{ii}^{(1)}(0)-\sigma_{ii}^{(1)}(R_i)\exp(-sR_i)]+\cdots,$$

$$\lim_{\mathrm{Re}s\to\infty} F_{21}(s)=s^{-1}[\sigma_{21}(0)-\sigma_{21}(R_{21})\exp(-sR_{21})]+s^{-2}[\sigma_{21}^{(1)}(0)-\sigma_{21}^{(1)}(R_{21})\exp(-sR_{21})]$$
$$+s^{-3}\{\sigma_{21}^{(2)}(0)-[\sigma_{21}^{(2)}(\lambda^+)-\sigma_{21}^{(2)}(\lambda^-)]\exp(-s\lambda)-\sigma_{21}^{(2)}(R_{21})\exp(-sR_{21})\}+\cdots,$$

$$\lim_{\mathrm{Re}s\to\infty} F_{ij}(-s)=\exp(sR_{ij})[s^{-1}\sigma_{ij}(R_{ij})-s^{-2}\sigma_{ij}^{(1)}(R_{ij})+s^{-3}\sigma_{ij}^{(2)}(R_{ij})+\cdots],$$

$$\lim_{\mathrm{Re}s\to\infty} G_{ij}(s)=\exp(-sR_{ij})[s^{-1}\sigma_{ij}(R_{ij})+s^{-2}\sigma_{ij}^{(1)}(R_{ij})+s^{-3}\sigma_{ij}^{(2)}(R_{ij})\cdots],$$

$$\lim_{\mathrm{Re}s\to\infty} \Gamma(s)=O(s^{-2}\exp(s\lambda)]. \tag{22}$$

Several things should be noticed. First we denote by $f(a^+)$ and $f(a^-)$ the values of a function $f(r)$ when r approaches a from the right and from the left, respectively. Second in the expressions for $F_{ij}(s)$ when $n\geq 3$ one must write in the asymptotic expression $\sigma_{ij}^{(n)}(R_{ij}^-)$ to differentiate from the expression for $G_{ij}(s)$ in which the corresponding form is $\sigma_{ij}^{(n)}(R_{ij}^+)$. Up to $n\leq 2$ we have written $\sigma_{ij}^{(n)}(R_{ij})$ because for $n=0$, 1, 2, $\sigma_{ij}^{(n)}(R_{ij}^-)=\sigma_{ij}^{(n)}(R_{ij}^+)$. Finally the symbol $O(\ )$ indicates the same order, that is

$$\lim_{\mathrm{Re}s\to\infty} \Gamma_{12}(s)=O[s^{-2}\exp(\lambda s)]$$

iff

$$\lim_{\mathrm{Re}s\to\infty} [\Gamma_{12}(s)/s^{-2}\exp(\lambda s)]=\text{constant}.$$

E. Solution for the Three-Dimensional Case

We now define the matrix $\mathbf{L}(s)$

$$\mathbf{L}(s)\equiv\mathbf{G}(s)\mathbf{H}^T(-s)=\mathbf{H}(s)\mathbf{K}(s)\mathbf{H}^T(-s), \tag{23}$$

then

$$\mathbf{L}^T(-s)=\mathbf{H}(s)\mathbf{G}^T(-s)=\mathbf{H}(s)\mathbf{K}^T(-s)\mathbf{H}^T(-s)$$
$$=\mathbf{H}(s)\mathbf{K}(s)\mathbf{H}^T(-s)=\mathbf{L}(s), \tag{23'}$$

where we have used the property $\mathbf{K}^T(-s)=\mathbf{K}(s)$. Rewriting (22) in component form we have:

$$L_{ij}(s)=\sum_l G_{il}(s)H_{jl}(-s). \tag{23''}$$

It follows from the definition of $\mathbf{H}(s)$ and the fact that $\mathbf{F}(s)$ and $\mathbf{\Gamma}(s)$ are entire, that $\mathbf{H}(s)$ is also entire. Combining this with the required analyticity of $G_{ij}(s)-12(\eta_i\eta_j)^{1/2}s^{-2}$ in the right half-plane, $\mathrm{Re}s\geq 0$, we obtain that $L_{ij}(s)-12s^{-2}\sum_l(\eta_i\eta_l)^{1/2}H_{jl}(0)$ is also analytic in the closed right-hand plane. It follows therefore from the symmetry of $\mathbf{L}(s)$, given in (23), that $L_{ij}(s)-s^{-2}A_{ij}'$ is entire; the definition of A_{ij}' being

$$A_{ij}'=12\sum_l(\eta_i\eta_l)^{1/2}H_{jl}(0)=12\sum_l(\eta_i\eta_l)^{1/2}A_{jl}.$$

The last equality obtains because

$$\sum_l(\eta_i\eta_l)^{1/2}V_{jl}=0$$

from the definition of V_{jl} and the over-all electrical neutrality condition.

We can now prove, using in a straightforward way the asymptotic expressions (22), that

$$L_{ii}(s)-s^{-2}A_{ii}'=L_{ii}(-s)-s^{-2}A_{ii}'$$

is bounded along every ray in the s plane, and that

$$L_{21}(s)\exp(\lambda s)-A_{21}'[\lambda s^{-1}+s^{-2}]$$
$$=L_{12}(-s)\exp(\lambda s)-A_{21}'[\lambda s^{-1}+s^{-2}]$$

is also bounded along every ray. Therefore, from the theory of functions of a complex variable,[22] $L_{ii}(s)-s^{-2}A_{ii}'$ is a constant, we shall call $2M_{ii}$. Similarly $L_{21}(s)\exp(\lambda s)-A_{21}'[\lambda s^{-1}+s^{-2}]$ is also a constant; we shall call it $2M_{21}$.

The above result is the crucial part of our solution. Using this result we can now take the inverse Laplace transforms of the right side of (23''), taking also into account the asymptotic form for F_{ij}, G_{ij}, $\Gamma_{ij}(s)$, and the continuity properties of $\sigma_{ij}(r)$ to obtain that

$$\sigma_{ii}(r)=-(\gamma^2/4)D_{ii}+[A_{ii}-(\gamma^2/2)V_{ii}]r+M_{ii}r^2$$
$$+A_{ii}'r^4/2,\quad \text{for}\quad r<R_i, \tag{24}$$

and

$$\sigma_{21}(r)=\sigma_{12}(r)=-(\gamma^2/4)D_{21}+[A_{21}-(\gamma^2/2)V_{21}]r,$$
$$\text{for}\quad r\leq\lambda,$$

$$\sigma_{21}(r)=\sigma_{12}(r)=-(\gamma^2/4)D_{21}+[A_{21}-(\gamma^2/2)V_{21}]r$$
$$+M_{21}(r-\lambda)^2+A_{21}'(R_2-R_1)(r-\lambda)^3+(A_{21}'/2)(r-\lambda)^4,$$
$$\text{for}\quad \lambda<r<R_{21}. \tag{25}$$

Knowing $\sigma_{ij}(r)$, for $r<R_{ij}$, gives us $C_{ij}(r)$ for $r<R_{ij}$ and hence the full formal solution of the MSM. Therefore what it is left now to obtain the explicit solution to our problem is to solve for the unknown coefficients in Eqs. (24) and (25). D_{ij} is known A_{ij} and A_{ij}' are known in terms of a_1 and a_2. On the other hand V_{21} is known in terms of V_{22} from the over-all electrical neutrality condition. The $(i,j)=(1,2)$ element is irrelevant because $\sigma_{21}(r)=\sigma_{12}(r)$. Therefore we have

seven unknowns, namely

$$(a_1, a_2, V_{11}, V_{22}, M_{11}, M_{22}, M_{21}).$$

We should remark that the form of $\sigma_{ij}(r)$ for $r<R_{ij}$ is quite similar to the form of $\sigma_{ij}^{\text{HS}}(r)$, the uncharged hard spheres PY solution. We obtain polynomials of the same order as in that case, the main difference being the presence of a constant term $-(\gamma^2/4)D_{ij}$ which is absent in the uncharged case.

Now, the defining equation, Eq. (14), for a_1 and a_2 are *two linear equations* in the seven unknowns. The extra equations we need, come from the continuity of $\sigma_{ij}^{(n)}(R_{ij})$ for $n=0$, 1, 2 in the following way: We have proven that $L_{ii}(s)-s^{-2}A_{ii}'=\text{constant}=2M_{ii}$, on the other hand by definition of

$$L_{ii}(s), L_{ii}(s)=\sum_l G_{il}(s)H_{il}(-s).$$

It then follows that

$$\sum_l G_{il}(s)H_{il}(-s)=L_{ii}(s)=2M_{ii}+s^{-2}A_{ii}', \tag{26}$$

similarly

$$\exp(\lambda s)\sum_l G_{2l}H_{1l}(-s)=L_{21}(s)\exp(\lambda s)$$
$$=2M_{21}+\lambda A_{21}'s^{-1}+A_{21}'s^{-2}. \tag{27}$$

We can now use in (26) and (27) the asymptotic expressions we obtained in (22) [which as we already indicated contained the continuity of $\sigma_{ij}^{(n)}(r)$ for $n=0$, 1, 2 at R_{ij}]. Equating the coefficients of s^0, s^{-1}, and s^{-2} we derive the following equations

$$2M_{ii}=-X_{i1}^2-X_{i2}^2, \tag{28a}$$

$$A_{ii}'=-2[X_{i1}Z_{i1}+X_{i2}Z_{i2}]+Y_{i1}^2+Y_{i2}^2, \tag{28b}$$

$$2M_{21}=-X_{21}(X_{11}+X_{22}), \tag{28c}$$

$$\lambda A_{21}'=X_{21}(Y_{11}-Y_{22})+Y_{21}(X_{22}-X_{11}), \tag{28d}$$

$$A_{21}'=-Z_{21}(X_{11}+X_{22})+Y_{21}(Y_{11}+Y_{22})-X_{21}(Z_{11}+Z_{22}), \tag{28e}$$

where

$$X_{ij}=\sigma_{ij}(R_{ij}),$$
$$Y_{ij}=\sigma_{ij}^{(1)}(R_{ij}),$$
$$Z_{ij}=\sigma_{ij}^{(2)}(R_{ij}). \tag{28f}$$

Since X_{ij}, Y_{ij}, Z_{ij} are evaluated in terms of the unknowns using (24) and (25), (28a) through (28e) constitute seven quadratic equations in our seven unknowns. We should, however, realize that not all of them are independent because of the following property implied by the symmetry of our problem, i.e.,

$$\sigma_{22}(r)\leftrightarrow\sigma_{11}(r)$$

when $R_2\leftrightarrow R_1$, $\rho_2\leftrightarrow\rho_1$, $e_2\leftrightarrow e_1$. That is, $\sigma_{11}(r)$ obtains from $\sigma_{22}(r)$ by interchanging R_1, ρ_1, e_1 with R_2, ρ_2, e_2 and vice versa.

In general there are several solutions for (14) and (28), but it is always possible to choose the physical one unambiguously, as we will show in several special cases in Paper II.

Finally we remark that it follows from (24) and (25) and the definition of $\sigma_{ij}(r)$ that $C_{ij}(r)$ is finite at $r=0$, because the term $-\gamma^2/4D_{ij}$ appearing in $\sigma_{ij}(r)$ for $r<R_{ij}$ exactly cancels out the "continuation" of the Coulomb potential inside the core, introduced in (9).

IV. SOLUTION TO THE ONE-DIMENSIONAL MSM FOR CHARGED HARD SHEETS

The MSM for this case is given by the relations

$$g_{ij}(r)=0, \quad \text{for} \quad r<R_{ij},$$
$$C_{ij}(r)=\beta e_ie_jr/2\epsilon, \qquad r>R_{ij}, \tag{29}$$

where r is the distance between the centers of two charged sheets. The sheets of type i have a thickness $R_i\equiv R_{ii}$.

The moment conditions equivalent to (6a) and (6b) are in this case

$$2\sum_l \rho_le_l\int_{R_{il}}^\infty g_{il}(r)dr=-e_i \tag{30a}$$

and

$$2\sum_{l,m}\rho_le_l\rho_me_m\int_{R_{lm}}^\infty g_{lm}(r)r^2dr=-\frac{2}{\chi^2}\sum_l\rho_le_l^2, \tag{30b}$$

where $\chi^2=(\beta/\epsilon)\sum_l\rho_le_l^2$; χ^{-1} being the Debye length for this *id* problem. We define

$$C_{ij}(r)\equiv C_{ij}^{(0)}(r)+\beta e_ie_jr/2\epsilon. \tag{31}$$

Therefore $C_{ij}^{(0)}(r)=0$ for $r>R_{ij}$. Next we introduce the function $\sigma_{ij}(r)$ by

$$(\rho_i\rho_j)^{-1/2}\sigma_{ij}(r)=g_{ij}(r), \qquad r>R_{ij},$$
$$=-C_{ij}^{(0)}(r), \qquad r<R_{ij}. \tag{32}$$

In terms of $\sigma_{ij}(r)$ the one-dimensional Ornstein–Zernike equation becomes

$$\sigma_{ij}(r)-A_{ij}+\sum_l\int_{|y|>R_{il},|r-y|<R_{lj}}\sigma_{il}(|y|)\sigma_{lj}(|r-y|)dy$$
$$=-\tfrac{1}{2}\gamma^2\sum_l D_{lj}\int_{\max(r,R_{il})}^\infty[r\sigma_{il}(y)-y\sigma_{il}(y)]dy, \tag{33}$$

where $\gamma^2=2\beta/\epsilon$, $D_{ij}=(\rho_i\rho_j)^{1/2}e_ie_j$, and

$$A_{ij}=(\rho_i\rho_j)^{1/2}a_j$$
$$=(\rho_i\rho_j)^{1/2}\left[1+2\sum_l\left(\frac{\rho_l}{\rho_j}\right)^{1/2}\int_0^{R_{lj}}\sigma_{lj}(y)dy\right]. \tag{34}$$

Following the reasoning we used in the 3D case we can prove that

(i) $\sigma_{ij}(r)$ is continuous everywhere,
(ii) $\sigma_{ij}^{(1)}(r)$ is continuous across $r=R_{ij}$,

(iii) $\sigma_{21}^{(1)}(r)$ is discontinuous for $r=\lambda\equiv(R_2-R_1)/2$,
(iv) $\sigma_{ii}^{(n)}(r)$ is continuous for all n's for $0<r<R_{ij}$ and that
(v) $\sigma_{21}^{(n)}(r)$ is continuous for $0<r<\lambda$ and for $\lambda<r<R_{21}$, $\forall n$.

We also have from (33) that

$$\sigma_{ii}(0)=A_{ii}+(\gamma^2/2)V_{ii},$$

$$\sigma_{21}(r)=A_{21}+(\gamma^2/2)V_{21}+(\gamma^2/4)D_{21}r, \qquad r<\lambda, \quad (35)$$

where

$$V_{ij}=\sum_l D_{lj}B_{il}=\sum_l D_{lj}\int_{R_{il}}^{\infty} y\sigma_{il}(y)\,dy.$$

Taking the Laplace transform of (33) we obtain

$$\mathsf{G}(s)=\mathsf{H}(s)\mathsf{K}(s). \quad (36)$$

Here

$$\mathsf{H}(s)=\mathsf{A}s-s^2\mathsf{F}(s)-s^2\mathbf{\Gamma}(s)+(\gamma^2/4)(\mathsf{D}+2s\mathsf{V}), \quad (36')$$

$$\mathsf{K}(s)=\{s^2\mathsf{I}+s^2[\mathsf{F}(s)+\mathsf{F}(-s)]-(\gamma^2/2)\mathsf{D}\}^{-1}, \quad (36'')$$

where

$$F_{ij}(s)=\int_0^{R_{ij}}\sigma_{ij}(r)\exp(-sr)\,dr, \quad (36''')$$

$$G_{ij}(s)=\int_{R_{ij}}^{\infty}\sigma_{ij}(r)\exp(-sr)\,dr. \quad (36'''')$$

I is the identity matrix, and $\Gamma_{ij}(s)=\delta_{i1}\delta_{j2}[U_{12}(s)+U_{12}(-s)]$, where

$$U_{12}(s)=\int_0^{\lambda}\exp(-sr)\,U_{12}(r)\,dr,$$

$U_{12}(r)$ being given by

$$U_{12}(r)=\sum_l\int_{R_{1l}+r}^{R_{l2}}\sigma_{1l}(y)\sigma_{l2}(|r-y|)\,dy, \qquad r<\lambda$$

$$U_{12}(r)=0, \qquad r>\lambda. \quad (36''''')$$

It is clear that $\mathsf{K}(s)=\mathsf{K}(-s)=K^T(-s)$. Also we have that $\mathsf{H}(s)$ is entire because by the same arguments as in the 3D case $\mathsf{F}(s)$ and $\mathbf{\Gamma}(s)$ are entire. On the other hand we require that $G_{ij}(s)-(\rho_i\rho_j)^{1/2}/s$ be analytic for $\mathrm{Re}\,s\geq 0$. Therefore if we define $\mathsf{L}(s)=\mathsf{G}(s)\mathsf{H}^T(-s)$ we know that $\mathsf{L}(s)=\mathsf{L}^T(s)$; and this implies $L_{ij}(s)-s^{-1}\sum_l(\rho_i\rho_l)^{1/2}H_{jl}(0)$ is an entire function of s. But we can see that $\sum_l(\rho_i\rho_l)^{1/2}H_{jl}(0)$ vanishes, namely

$$\sum_l(\rho_i\rho_l)^{1/2}H_{jl}(0)=(\gamma^2/4)\sum_l(\rho_i\rho_l)^{1/2}D_{jl}=0$$

because of over-all electrical neutrality. Therefore $\mathsf{L}(s)$ is an entire function of s.

Furthermore we can prove that $L_{ii}(s)$ and $L_{21}(s)\exp(\lambda s)$ are bounded along every ray in the complex s plane. Hence in analogy with the 3D case,

$$L_{ii}=M_{ii}=\text{constant},$$

$$L_{21}\exp(\lambda s)=M_{21}=\text{constant}. \quad (37)$$

We can obtain the value of M_{ij} by calculating

$$L_{ij}(0)=\lim_{s\to 0}\sum_l G_{il}(s)H_{jl}(-s)=M_{ij}.$$

Writing $G_{il}(s)=P_{il}(s)+(\rho_i\rho_l)^{1/2}s^{-1}$, $P_{il}(s)$ will be finite when $s\to 0$. Thus

$$L_{ij}(0)=\lim_{s\to 0}\sum_l[P_{il}(s)+(\rho_i\rho_l)^{1/2}s^{-1}]\times[-A_{jl}s+(\gamma^2/4)D_{jl}]$$

$$=\sum_l(\rho_i\rho_l)^{1/2}A_{jl}+(\gamma^2/4)\lim_{s\to 0}\sum_l G_{il}(s)D_{jl}. \quad (38)$$

Recalling the definition of $G_{il}(s)$ and D_{jl} we obtain for the second term in the right hand side of (38)

$$\tfrac{1}{4}\gamma^2\lim_{s\to 0}\sum_l G_{il}(s)D_{jl}=\tfrac{1}{4}\gamma^2(\rho_i\rho_j)^{1/2}e_j\sum_l\rho_l e_l\times\int_{R_{il}}^{\infty}g_{il}(x)\,dx=-\tfrac{1}{8}\gamma^2D_{ij}. \quad (39)$$

Here we have used explicitly the first moment relation (30a). Therefore we have

$$L_{ij}(0)=-A_{ij}'-(\gamma^2/8)D_{ij}, \quad (40)$$

where

$$A_{ij}'=\sum_l(\rho_i\rho_l)^{1/2}A_{jl}.$$

Now, using the definition of $L_{ij}(s)$ one can take the inverse Laplace transform of $L_{ij}(s)$ and obtain for $(i,j)\neq(1,2)$ that

$$\sigma_{ii}(r)=A_{ii}+(\gamma^2/2)V_{ii}+(\gamma^2/8)D_{ii}r-A_{ii}'r, \qquad r<R_i,$$

$$\sigma_{21}(r)=A_{21}+(\gamma^2/2)V_{21}+(\gamma^2/4)D_{21}r, \qquad r<\lambda,$$

$$\sigma_{21}(r)=A_{21}+(\gamma^2/2)V_{21}+(\gamma^2/4)D_{21}r-[(\gamma^2/8)D_{21}+A_{ii}'](r-\lambda) \quad \text{for} \quad \lambda<r<R_{21}. \quad (41)$$

To solve the problem completely we have to find the quantities a_1, a_2, V_{11}, and V_{22}. Equation (34) gives us two linear equations in these quantities. To get the needed extra equations we use the continuity of $\sigma_{ij}(r)$ at $r=R_{ij}$ in the same manner as in the 3D case obtaining

$$A_{ij}'+(\gamma^2/8)D_{ij}=\sum_l\sigma_{il}(R_{il})\sigma_{lj}(R_{lj}),$$

$$\text{for} \quad (i,j)\neq(1,2) \quad (42)$$

which constitute three equations, but again, not all of them independent because of the symmetry between σ_{11} and σ_{22}. We will show in Paper II that for this case it is possible to solve explicitly for any combination of (R_1, e_1, ρ_1) and (R_2, e_2, ρ_2), subject of course to $\rho_1e_1+\rho_2e_2=0$.

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Mean Spherical Model Integral Equation for Charged Hard Spheres.* II. Results

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We continue our investigation of the solution of the mean spherical model integral equation for systems of charged hard spheres and charged hard sheets (in one dimension). The general method of solution was presented in Paper I of this series. This paper contains explicit expressions for the structure functions and thermodynamic properties of a variety of such systems in one and three dimensions. The results all have a very simple form and are in good agreement with various machine computations. When the charges on the particles vanish our results coincide with those obtained from the Percus–Yevick equation for hard spheres while in the limit of zero hard core diameters the results go over into those obtained from the linearized Debye–Hückel theory.

I. INTRODUCTION

In the first part of this work[1] (to which we shall refer to as I) we have obtained the formal solution of the mean spherical model (MSM) integral equation for a mixture of charged hard spheres in three dimensions and charged hard parallel sheets in one dimension. The systems under consideration are required to be over-all electrically neutral.

We recall here briefly the statement of the problem as well as the results we have obtained in I.

The interaction potential between an ion of species i and another ion of species j is given by

$$\begin{aligned} v_{ij}(r) &= \infty, \qquad r<R_{ij}, \\ &= e_ie_j/\epsilon r, \qquad r>R_{ij}, \end{aligned} \tag{1a}$$

in three dimensions, and

$$\begin{aligned} v_{ij}(r) &= \infty, \qquad r<R_{ij}, \\ &= -e_ie_jr/2\epsilon, \qquad r>R_{ij}, \end{aligned} \tag{1b}$$

in one dimension.

Here r is the distance between the centers of two hard spheres (3D) or two hard sheets (1D), R_{ij} is the distance of closest approach between an ion of type i and an other of type j and satisfies the additivity condition $R_{ij}=(R_i+R_j)/2\equiv(R_{ii}+R_{jj})/2$, e_i is the charge of an ion of type i. The over-all electrical-neutrality condition is given by

$$\sum_{j=1}^{m}=\rho_je_j=0, \tag{2}$$

where ρ_j is the number density of species j, considered spacially uniform, and m is the number of different species in the mixture. β is the reciprocal temperature and ϵ the phenomenological dielectric constant of the solvent in which the ions are imbedded.

The MSM integral equation for these systems is given by

$$\begin{aligned} g_{ij}(r) &= 0, \qquad r<R_{ij} \\ C_{ij}(r) &= -\beta v_{ij}(r), \qquad r>R_{ij} \end{aligned} \tag{3}$$

where $g_{ij}(r)$ are the radial distribution functions, and $C_{ij}(r)$ are the Ornstein–Zernike direct correlation functions defined by the relationship

$$g_{ij}(r)-1=C_{ij}(r)+\int_{\text{all space}}\sum_l \rho_l[g_{il}(|\mathbf{r}'|)-1]C_{lj}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'. \tag{4}$$