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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 work¹ (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

$$\begin{aligned} v_{ij}(r) &= \infty, & r < R_{ij}, \\ &= e_i e_j / \epsilon r, & r > R_{ij}, \end{aligned} \quad (1a)$$

in three dimensions, and

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

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

$$\sum_{j=1}^m \rho_j e_j = 0, \quad (2)$$

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

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

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

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

It was shown in I that for the two-component case the direct correlation functions $C_{ij}(r)$ for $r < R_{ij}$ (knowledge of which solves the problem) are polynomials in r . For the 3D case the polynomials are of order three, while in the 1D case they are of order one.

The coefficients of these polynomials, which depend on ρ_i, e_i, R_i , and β/ϵ , were shown in I to be the solution of certain algebraic equations. The solution of these equations in certain cases, and the consequent derivation from them of the MSM predictions for the structure and thermodynamic properties of these electrolytes is the aim of the present paper. We shall also compare some of the MSM results with those obtained from machine computations on these systems, as well as with the predictions of other theories.

The outline of this paper is as follows. In Sec. II we present the explicit form of the $C_{ij}(r)$, as well as the thermodynamic functions for the two-component one-dimensional system for all values of the quantities $R_1, R_2, e_1, e_2, \rho_1, \rho_2$; consistent with the overall neutrality requirement. We also present in an explicit form the Laplace transform of the "charge cloud" density about an ion for the case $R_1=R_2, e_1=-e_2$.

In Sec. III we give the explicit solution for the direct correlation matrix $C_{ij}(r)$ and the relevant thermodynamics for the symmetrical three-dimensional case, i.e., $R_1=R_2=\dots=R_m$. These results generalize the results we have reported on briefly earlier² in which we considered the two component case $R_1=R_2$. We also give explicitly the Laplace transform of the charge cloud density when $m=2$, and $e_1=-e_2$.

In Sec. IV we deal with a 3D system of the following particular characteristics: one of the components has zero distance of closest approach, $R_1=0$, and its ionic charge $e_1 \rightarrow 0$ while $\rho_1 \rightarrow \infty$ in such a way as to preserve the overall electrical neutrality; that is $\rho_1 e_1 + \rho_2 e_2 = 0$; ρ_2 and R_2 being finite and positive. We remark that this limit is not the same as what is usually called the uniform background case,³ even though the distance of closest approach between two ions of type one is zero, the presence of an ion of type one at a position \mathbf{r} excludes the possibility of the center of an ion of type two being within a distance $\frac{1}{2}R_2$ from \mathbf{r} . We shall call this case the "dense point limit." Finally in Sec. V we discuss our results.

II. CHARGED HARD SHEETS IN ONE DIMENSION

We deal here with the properties of a two-component electrically neutral mixture of parallel charged hard sheets in thermal equilibrium.

A. Direct Correlation Functions

As mentioned in the Introduction, the components of the direct correlation matrix, $C_{ij}(r)$, are in the MSM approximation found to be linear functions of r for $r < R_{ij} \equiv (R_i + R_j)/2$, where the coefficients of these linear functions satisfy the algebraic equations

obtained in Sec. IV of I. Solving those equations yields the following expression for the direct correlation functions,

$$C_{11}(r) = \tilde{C}_{11}(r) + (\kappa/2\rho) (\rho_2/\rho_1) (1 + \kappa R_1/2) + \beta e_1^2 r / 4\epsilon, \quad r < R_1$$

$$= \tilde{C}_{11}(r) + \beta e_1^2 r / 2\epsilon, \quad r > R_1 \tag{4'}$$

$$C_{12}(r) = \tilde{C}_{12}(r) + -(\kappa/2\rho) (1 + \kappa R_2/2), \quad r \leq \lambda \equiv (R_2 - R_1)/2 \geq 0,$$

$$= \tilde{C}_{21}(r) + \beta e_1 e_2 (r - \lambda) / 4\epsilon - (\kappa/2\rho) (1 + \kappa R_2/2),$$

$$\lambda \leq r < R_{21} \equiv (R_1 + R_2)/2$$

$$= \tilde{C}_{21}(r) + \beta e_1 e_2 r / 2\epsilon, \quad r > R_{21}. \tag{4''}$$

Here κ is the inverse Debye⁴ length for this one-dimensional problem, given by $\kappa^2 = (\beta/\epsilon) (\rho_1 e_1^2 + \rho_2 e_2^2)$, ρ is the total number density, $\rho = \rho_1 + \rho_2$. The $\tilde{C}_{ij}(r)$ are the direct correlation functions for the uncharged hard rods "reference" system obtained when $e_1 = e_2 = 0$, in the MSM approximation which coincides with the PY approximation when only hard core potentials are present and happens to be exact in the 1D hard rods case.⁵ $\tilde{C}_{11}(r)$ is given by (again from Ref. 5)

$$-\tilde{C}_{11}(r) = (1 - 2\rho_2\lambda - \rho r) (1 - \xi)^{-2}, \quad r < R_1$$

$$= 0, \quad r > R_1 \tag{5a}$$

$$-\tilde{C}_{21}(r) = (1 - 2\rho_2\lambda) (1 - \xi)^{-2}, \quad r < \lambda$$

$$= (1 - 2\rho_2\lambda - \rho(r - \lambda)) (1 - \xi)^{-2}, \quad \lambda < r < R_{21}$$

$$= 0, \quad r > R_{21} \tag{5b}$$

where $\xi = \rho_1 R_1 + \rho_2 R_2$. The element $C_{22}(r)$ is obtained from the expressions (4') and (5a) that gives $C_{11}(r)$ by interchanging ρ_1, e_1, R_1 with ρ_2, e_2, R_2 and vice versa. The expressions for $C_{ij}(r)$, for $r > R_{ij}$ in (42) and (5a) follow directly from the assumptions of the MSM approximation, Eq. (3).

B. Thermodynamic Properties

To obtain the thermodynamic quantities of our system once the $C_{ij}(r)$ and hence the $g_{ij}(r)$ are known, we could, as is well known, use several different methods; for example the relation between the compressibility and the integrals of $C_{ij}(r)$, the virial theorem, or we can obtain the excess energy per unit volume from $g_{ij}(r)$ using the following relationship,

$$\beta E^{ex}(\rho, \beta) \equiv \beta \sum_{i,j=1}^2 \rho_i \rho_j \int_{R_{ij}}^{\infty} g_{ij}(r) v_{ij}(r) dr, \tag{6}$$

and then integrate the excess energy with respect to β to find the Helmholtz free energy, $a(\rho, \beta)$. The pressure can then be obtained from $a(\rho, \beta)$ by differentiation with respect to the density. All these methods must yield precisely the same result for a given thermodynamic quantity if the *exact* radial distribution func-

tions are used. However, when the $g_{ij}(r)$ are obtained from an approximate theory, like the MSM, the result for a given thermodynamic quantity depends on the procedure by which it was obtained. A useful criteria for a "good approximation" is that the different answers are "close".

It turns out that for the MSM we can obtain the excess energy per unit volume $E^{ex}(\rho, \beta)$, without explicitly obtaining $g_{ij}(r)$, because $E^{ex}(\rho, \beta)$ is related to the coefficients of the linear functions which give the direct correlation matrix $C_{ij}(r)$, $r < R_{ij}$, in the fashion we have described in I. Using those relationships we find for the 1D case

$$\beta E^{ex}(\rho, \beta) = \kappa/4 + (\kappa^2/8) (|e_1| R_1 + |e_2| R_2) / (|e_1| + |e_2|). \quad (6')$$

Using the expression for $E^{ex}(\rho, \beta)$ we obtain the Helmholtz free energy per unit volume $a(\rho, \beta)$, as

$$\beta a(\rho, \beta) = \beta \tilde{a}(\rho, \beta) + \int_0^\beta E^{ex}(\rho, \beta') d\beta' = \beta \tilde{a}(\rho, \beta) + \kappa/2 + (\kappa^2/8) (|e_2| R_2 + |e_1| R_1) / (|e_1| + |e_2|). \quad (7)$$

Here $\tilde{a}(\rho, \beta)$ is the exact Helmholtz free energy for the uncharged hard rods "reference system." From the expression for $a(\rho, \beta)$ we can obtain the osmotic coefficient, $\phi_a(\rho, \beta) \equiv \beta p_a/\rho$, i.e.,

$$\phi_a(\rho, \beta) - 1 = \beta \rho \partial / \partial \rho [a(\rho, \beta) \rho^{-1}] - 1 = [\tilde{\phi}(\rho, \beta) - 1] - \kappa/4\rho. \quad (8)$$

Here $\tilde{\phi}(\rho, \beta) = (1-\xi)^{-1}$, is the osmotic coefficient of the reference system and by p_a and ϕ_a we indicate the pressure and osmotic coefficient of the MSM obtained via the expression for the Helmholtz free energy per unit volume, $a(\rho, \beta)$ given in Eq. (7).

Equation (8) gives the deviation of the osmotic coefficient $\phi_a(\rho, \beta)$ from the ideal gas value which is 1, as a sum of two contributions: (i) the deviation of the osmotic coefficient of the uncharged hard rods reference system from the ideal gas one, plus (ii) the deviation from 1 of the osmotic coefficient obtained from the linearized Debye-Hückel (DH) theory for a system of charges with sheets of zero thickness.

A different aspect of the MSM solution is obtained by looking at the radial distribution functions at contact, $g_{ij}(R_{ij}^+)$. It follows from I and from the expression (4) and (5) for $C_{ij}(r)$ that

$$g_{ij}(R_{ij}^+) = -C_{ij}(R_{ij}^-) + \beta e_i e_j R_{ij} / 2\epsilon = (1-\xi)^{-1} - \beta e_i e_j / 2\epsilon \kappa. \quad (9)$$

It is immediately seen from (9) that the contact value of the radial distribution function is again, as in the case of $\phi_a(\rho, \beta)$, the sum of 2 terms; the first, $(1-\xi)^{-1}$, being just the values of the exact contact

radial distribution functions for the uncharged reference system and the second one is just equal to $g_{ij}^{DH}(0^+) - 1$, where $g_{ij}^{DH}(0^+)$ is the value for the radial distribution functions at contact (i.e. at $r=0^+$) of the DH theory.

We can also easily derive the osmotic coefficient using the 1D virial theorem, obtaining,

$$\begin{aligned} \phi_v(\rho, \beta) &= 1 - \beta E^{ex}(\rho, \beta) \rho^{-1} + \rho^{-1} \sum_{i,j=1}^2 \rho_i \rho_j R_{ij} g_{ij}(R_{ij}^+) \\ &= 1 - \beta E^{ex}(\rho, \beta) \rho^{-1} + \xi(1-\xi)^{-1} - \rho^{-1} \frac{\beta}{2\epsilon} \sum_{i,j=1}^2 \rho_i \rho_j e_i e_j R_{ij} \\ &= (1-\xi)^{-1} - \frac{\kappa}{4\rho} - \frac{\kappa^2}{8\rho} \frac{(|e_2| R_2 + |e_1| R_1)}{|e_2| + |e_1|}. \quad (10) \end{aligned}$$

To obtain (10) we have used the expressions of $g_{ij}(R_{ij}^+)$ given by Eq. (9) and the fact that

$$\sum_{i,j=1}^2 \rho_i \rho_j e_i e_j R_{ij} = \rho_1^2 e_1^2 R_1 + \rho_2^2 e_2^2 R_2 + 2\rho_1 \rho_2 e_1 e_2 R_{21} = 0,$$

because of the over-all electrical-neutrality condition, $\rho_1 e_1 + \rho_2 e_2 = 0$, and the additivity of the diameters of the hard rods, $2R_{21} = R_1 + R_2$.

Comparing $\phi_v(\rho, \beta)$ with $\phi_a(\rho, \beta)$ shows that they differ by a density independent term, namely,

$$\begin{aligned} \phi_v - \phi_a &= \frac{\kappa^2}{8\rho} \frac{(|e_2| R_2 + |e_1| R_1)}{|e_1| + |e_2|} \\ &= \frac{\beta}{8\epsilon} \frac{|e_1 e_2| (|e_2| R_2 + |e_1| R_1)}{|e_1| + |e_2|}. \quad (11) \end{aligned}$$

As in the DH theory we find that for small values of the densities the MSM becomes unphysical because both p_v and p_a get negative (the term $\kappa/4\rho \sim \rho^{-1/2}$, makes the pressure negative as $\rho \rightarrow 0$). On the other hand as $\xi \rightarrow 1$ (close packing), the hard rods term predominates as one would expect, the part involving the electrical interactions becoming negligible compared to the $(1-\xi)^{-1}$ term. The self-consistency of the MSM approximation gets better when the electrostatic energy at contact becomes small compared to kT in which case $\phi_v - \phi_a$ becomes small as compared with either ϕ_v or ϕ_a . This is indeed what we would expect *a priori* to be the region in which the MSM approximation is "good."

C. Structure Functions of the Primitive Model Electrolyte

For the special case, $R_1 = R_2 = R$, $e_1 = -e_2 = e$, and hence $\rho_1 = \rho_2 = \rho/2$, (usually called the "primitive model electrolyte") the Laplace transforms of the radial distribution functions assume a very simple form. To obtain them explicitly we make use of the fact that for this case the expressions for the direct correlation functions given by (4'), (4''), (5a), and (5b) are rather simple, and use the equations that give the

Laplace transforms of the radial distribution functions in terms of the Laplace transforms of the direct correlation functions we obtained for the 1D MSM in Sec. IV of I. For this case the direct correlation functions are given by

$$C_{ij}(r) = \tilde{C}(r) + f(r)(2\delta_{ij} - 1), \quad (11')$$

where $\tilde{C}(r)$ is the MSM-PY solution for the one-component fluid of uncharged hard rods of thickness R , at density ρ [obtained by setting $\lambda=0$ in Eq. (5a)] and

$$f(r) = (\kappa/2\rho)[1 + (\kappa R/2)] + \beta e^2 r/4\epsilon, \quad r < R \\ = \beta e^2 r/2\epsilon, \quad r > R. \quad (11'')$$

We can now obtain expressions for the two independent functions; $g(r) \equiv g_{11}(r) + g_{12}(r)$, and $G(r) \equiv g_{11}(r) - g_{12}(r)$ (clearly $g_{11} = g_{22}$ and $g_{12} = g_{21}$). We find that

$$g(r) = 2\tilde{g}(r), \quad (11''')$$

where $\tilde{g}(r)$ is radial distribution function of an uncharged one-dimensional system of hard rods with diameter R and density ρ , and

$$\tilde{G}(s) \equiv \int_0^\infty e^{-sr} G(r) dr = -(2\kappa/\rho)[(2s + \kappa)e^{sR} + \kappa]^{-1}. \quad (11''')$$

It is seen from (11') that for the primitive model electrolyte the MSM approximation gives a $g(r)$ which is entirely independent of the charges on the hard sheets. Equation (11'''), on the other hand, shows that the density of the "charge cloud" surrounding a fixed ion sitting at $r=0$, $\frac{1}{2}\rho eG(r)$ will have "oscillations" as a function of r . This is in accordance with the Stillinger-Lovett moment relations, discussed in part one,¹ which predicts such oscillations (at sufficiently high densities) when $R \neq 0$. When $R \rightarrow 0$, $\tilde{G}(s) \rightarrow -(\kappa/\rho)[s + \kappa]^{-1}$, the DH result, which does not give oscillations in the charge cloud density.

Finally we note that it may be readily verified from (11''') that $G(r) = 0$ for $r < R$ as required by (3).

III. THE SYMMETRIC 3D CASE

The system we are going to describe in this chapter is characterized by m species of ions, with charges e_1, e_2, \dots, e_m , such that

$$\sum_{i=1}^m \rho_i e_i = 0,$$

where ρ_i is the number density of species i . The hard sphere diameters of all m species are the same, $R_{ii} \equiv R_{jj}$. No restriction is made on the charges e_i . In particular the inclusion of a neutral species is allowed.

A. Direct Correlation Functions

The direct correlation matrix $C_{ij}(r)$ is found to be [solving the algebraic equations for the coefficients of the polynomials that give $C_{ij}(r)$ for $r < R_{ij}$ discussed

in Sec. III.E of I]

$$C_{ij}(r) = \tilde{C}(r; \xi, \beta) - (\beta/\epsilon R) e_i e_j (2B - B^2 r/R), \quad r < R \\ = -\beta e_i e_j / \epsilon r, \quad r > R. \quad (12)$$

Here $\tilde{C}(r; \xi, \beta)$ is the direct correlation function obtained by Wertheim⁶ and Thiele⁷ as the solution of the PY approximate integral equation for a fluid of neutral hard spheres of diameter R , reduced density $\xi \equiv (\pi \rho R^3/6) \equiv (\pi/6)(\rho_1 + \dots + \rho_m) R^3$, B is given by

$$B = x^{-2}[x^2 + x - x(1 + 2x)^{1/2}], \quad (13)$$

where

$$x^2 = \kappa^2 R^2 = [(4\pi\beta/\epsilon) \sum_{i=1}^m \rho_i e_i^2] R^2,$$

κ being the inverse Debye length for this case.

B. Thermodynamic Properties

As in the 1D case of Sec. II we get the excess energy per unit volume directly from our solution (as explained in I),

$$E^{ex}(x, \beta) = \frac{1}{2} \sum_{i,j=1}^m \int_R^\infty g_{ij}(r) \frac{e_i e_j}{\epsilon r} 4\pi r^2 dr \\ = - \frac{x^2 + x - x(1 + 2x)^{1/2}}{4\pi\beta R^3}. \quad (14)$$

It is clear that E^{ex} is only a function of ρ through x , i.e., there is no explicit dependence on the reduced density ξ . It is further seen that $E^{ex}(x, \beta) \leq 0$ for all $x \geq 0$.

Following the method used in the 1D case we obtain the Helmholtz free energy density from the excess energy per unit volume, finding

$$\beta a(x, \beta, \xi) = \beta \tilde{a}(\xi, \beta) \\ - (12\pi R^3)^{-1} [3x^2 + 6x + 2 - 2(1 + 2x)^{3/2}]. \quad (15)$$

Here $\tilde{a}(\xi, \beta)$ is the PY-MSM Helmholtz free energy density for the uncharged hard sphere reference system which depends, as discussed in Sec. II, by which way it is obtained from the approximate \tilde{C}_{ij} . From the expression for $a(x, \beta, \xi)$ we derive the osmotic coefficient obtaining,

$$\phi_a(x, \xi, \beta) = \tilde{\phi}(\beta, \xi) \\ + [3x + 3x(1 + 2x)^{1/2} - 2(1 + 2x)^{3/2} + 2]/(72\xi). \quad (16)$$

Again, $\tilde{\phi}(\beta, \xi)$ refers to the reference system in the MSM-PY approximation.

To obtain the osmotic coefficient via the virial theorem the contact value of the radial distribution functions, $g_{ij}(R^+)$, are needed. The MSM gives the following expressions for these contact values:

$$g_{ij}(R^+) = \tilde{g}(R^+) - (\beta/\epsilon R) e_i e_j (1 - B)^2, \quad (17)$$

where B has already been given in (13), and $\tilde{g}(R^+)$ is the contact value for the radial distribution of the reference system in the PY approximation. Equation

TABLE I. Comparison of MC results for the osmotic coefficient with the HNC, PYA, MSM, and MEX theoretical treatments. All $R=4.25 \text{ \AA}$, $\epsilon=78.5$, $T=298^\circ\text{K}$.

C_2^a Moles per liter	$\phi = \beta p / \rho$							
	MC ^b	HNC _V ^c	HNC _C	PYA _V ^d	PYA _C	MSM _V ^e	MSM _B	MEX ^f
0.00911	0.9701±0.0008	0.9703	0.9705	0.9703	0.9705	0.9687	0.9709	0.9707
0.10376	0.9445±0.0012	0.9453	0.9458	0.9452	0.9461	0.9312	0.9454	0.9452
0.42502	0.9774±0.0046	0.9796	0.9800	0.9765	0.9844	0.9446	0.9806	0.9787
1.0001	1.094±0.005	1.0926	1.0906	1.0789	1.1076	1.039	1.097	1.091
1.9676	1.346±0.009	1.3514	1.3404	1.3114	1.386	1.2757	1.3595	1.342

^a This is the stoichiometric molarity of the electrolyte.
^b MC are the Monte Carlo calculations performed by D. N. Card and J. P. Valleau reported in Ref. (8) and also previously [P. N. Card and J. P. Valleau, J. Chem. Phys. **52**, 6232 (1970)].
^c HNC means the value of the corresponding quantities obtained by solving numerically the hypernetted chain approximation. See Ref. 8 and J. C. Rasiiah and H. Friedman, J. Chem. Phys. **50**, 3965 (1969); **48**, 2742 (1968). Subindices V and C refer to the virial and compressibility "roots" of the osmotic pressure.

^d PYA values are from the works, cited in c and are the numerical solution of the Percus-Yevick approximation as modified by Allnatt, Mol. Phys. **8**, 533 (1964).
^e MSM refers to the mean spherical model and the subindices V and E correspond to the Virial theorem and the excess energy "roots" of the osmotic coefficients as explained in the present paper.
^f MEX refers to the mode expansion of H. C. Andresen and P. Chandler, J. Chem. Phys. **54**, 26 (1971); **53**, 547 (1970) and *ibid.* (to be published).

(17) shows that the contact value of the radial distribution function is greater than the one of the reference system for oppositely charged ions and lesser than it for similarly charged ions, which is certainly in accord with our expectations. On the other hand (17) appears "too linear" in the charges and temperature, as can be seen from the fact that the contact term in the virial theorem, i.e.,

$$R^3 \sum_{i,j=1}^m \rho_i \rho_j g_{ij}(R^+)$$

gives the uncharged spheres result. Also the compressibility, related to the integral of the direct correlation matrix, gives just the PY uncharged hard spheres compressibility.

The fact that the contact term gives just the uncharged hard sphere result make it reasonable to believe that the osmotic coefficient ϕ_a , derived from the Helmholtz free energy gives a better result than the virial one ϕ_v which is given by

$$\phi = \tilde{\phi}_v + (\beta/3\rho) E^{ex} = \tilde{\phi}_v - [x^2 + x - x(1+2x)^{1/2}]/(72\xi), \tag{18}$$

where $\tilde{\phi}_v$ is the osmotic coefficient for the uncharged hard spheres system obtained from the virial theorem. Expanding ϕ_a and ϕ_v in powers of x one sees that they agree up to order x^3 (the DH order term). Their difference is small for small values of x as compared with either ϕ_v or ϕ_a .⁸ Tables I and II display the agreement obtained with machine computations and other theories for water-like solutions ($\epsilon=78.5$) of two-components 1-1 electrolytes of equal diameters, $R=4.25 \text{ \AA}$, at $T=298^\circ\text{K}$. These figures are from Ref. 8, where there are also other interesting comparisons.

C. Structure Functions of the Primitive Model Electrolyte

Restricting ourselves as in Sec. II to a two component system with $e_1 = -e_2$ and hence $\rho_1 = \rho_2 = \frac{1}{2}\rho$ (and $R_1 = R_2 = R$) we find that $C_{ij}(r)$ has the same structure as in the 1D case given in (11'). $\tilde{C}(r)$ is now the direct correlation function of an uncharged system of hard spheres of diameter R and density ρ obtained from the PY-MSM integral equations⁶⁻⁷ (which is not the same as the exact one) and $f(r)$ is a new function [given

TABLE II. Comparison of MC results of $\beta l^2 r / \rho$ and CONTACT with results from the HNC, PYA, and MSM theories. With $R=4.25 \text{ \AA}$, $\epsilon=78.5$, $T=298.0^\circ\text{K}$.

C_2^a Moles per liter	$\beta l^2 r / \rho$				Contact $\equiv 2[g_{11}(R^+) + g_{12}(R^+)]$			
	MC ^b	HNC	PYA	MSM	MC	HNC	PYA	MSM
0.00911	0.1029±0.0013	0.1014	0.1014	0.0992	0.0044±0.0007	0.0041	0.0041	0.0017
0.10376	0.2739±0.0014	0.2714	0.2712	0.2675	0.0359±0.0011	0.0357	0.0351	0.0203
0.42502	0.4341±0.0017	0.4295	0.4285	0.4264	0.1217±0.0045	0.1228	0.1194	0.0867
1.0001	0.5516±0.0016	0.5447	0.5418	0.5405	0.2777±0.0045	0.2741	0.2595	0.2191
1.9676	0.6511±0.0020	0.6460	0.6376	0.6362	0.5625±0.0088	0.5668	0.5240	0.4878

^a This is the stoichiometric molarity of the electrolyte.

^b See footnotes to Table I.

in (12)]. We then find, in analogy with Eqs. (11''') and (11''''), that

$$g(r) \equiv g_{11}(r) + g_{12}(r) = 2\tilde{g}(r) \tag{19a}$$

and

$$\begin{aligned} \tilde{G}(s) &\equiv \int_0^\infty e^{-sr} [g_{11}(r) - g_{12}(r)] dr \\ &= -s(2p^2/\pi\rho) [s^2 + 2ps - 2p^2] e^{sR} - 2p^2]^{-1}, \end{aligned} \tag{19b}$$

where $p = [(1 + 2\kappa R)^{1/2} - 1]/(2R)$. When $R \rightarrow 0$, $\tilde{G}(s) \rightarrow -\kappa^2 [2\pi\rho(s + \kappa)]^{-1}$ the Debye-Hückel result.

Equation (19b) has an extremely simple form and it would be very interesting to compare its predictions for the oscillations in the charge cloud density about a fixed ion,⁹ $2\pi r^2 \rho e [g_{11}(r) - g_{12}(r)]$ with the results of machine computations.

IV. THE 3D "DENSE POINT LIMIT" CASE

This case is obtained by the following limiting process. First we take the limit $R_1 = 0$, then the limit $\rho_1 \rightarrow \infty$, $e_1 \rightarrow 0$ preserving the over-all electrical neutrality condition $\rho_1 e_1 + \rho_2 e_2 = 0$.

To give the explicit MSM solution for this case, it is convenient to define the Fourier transform of a function $f(r)$ by,

$$F(f(r)) \equiv \hat{f}(k) = 4\pi \int_0^\infty (\sin kr / kr) r^2 f(r) dr, \tag{20}$$

then the Fourier transform of the 2-particle distribution function $h_{ij}(r) \equiv [g_{ij}(r) - 1]$, are given by¹⁰

$$\hat{h}_{11}(k) = \rho_2 \hat{\alpha}_{21}^2(k) / D(k), \tag{21a}$$

$$\hat{h}_{12}(k) = \hat{h}_{21}(k) = \hat{\alpha}_{21}(k) / D(k), \tag{21b}$$

$$\hat{h}_{22}(k) = [1 - D(k)] / [\rho_2 D(k)]. \tag{21c}$$

The function $\hat{\alpha}_{21}(k)$ is the Fourier transform of $\alpha_{21}(r)$ which is given by

$$\begin{aligned} \alpha_{21}(r) &= -(1 - \xi)^{-1}, \quad r < \frac{1}{2}R_2 \\ &= 0, \quad r > \frac{1}{2}R_2 \end{aligned} \tag{22}$$

and $D(k)$ is given by the following expression,

$$\begin{aligned} D(k) &= 1 - \rho_2 \tilde{C}(k; \rho_2, R_2) - \rho_2 [\hat{\beta}_{22}(k) + \hat{\gamma}_{22}(k)] \\ &+ \rho_2^2 [\hat{\beta}_{22}(k) \hat{\alpha}_{22}(k) + 2\hat{\beta}_{22}(k) \hat{\alpha}_{21}(k) - 2\hat{\alpha}_{21}(k) \hat{\gamma}_{21}(k)]. \end{aligned} \tag{23}$$

The function $\tilde{C}(k; \rho_2, R)$ is the Fourier transform of the direct correlation function obtained by Wertheim⁶ as the solution of the PY equation for a one-component fluid of hard spheres of diameter R_2 and density ρ_2 , $\hat{\beta}_{22}(k)$ is the Fourier transform of $-\beta e_2^2 / \epsilon r$, i.e.,

$$\hat{\beta}_{22}(k) = -4\pi e_2^2 / \epsilon k^2, \tag{24}$$

and $\hat{\alpha}_{22}(k)$, $\hat{\gamma}_{21}(k)$, and $\hat{\gamma}_{22}(k)$ are Fourier transforms

of the functions $\alpha_{22}(r)$, $\gamma_{21}(r)$, and $\gamma_{22}(r)$ given by the expressions

$$\begin{aligned} -\alpha_{22}(r) &= [\xi / (1 - \xi)^2] (1 - \frac{3}{2}r/R_2 + 6r^2/R_2^3), \quad r \leq R_2 \\ &= 0, \quad r > R_2 \end{aligned} \tag{25a}$$

$$\begin{aligned} -\gamma_{21}(r) &= -B/\xi + \beta e_2^2 / \epsilon r, \quad r \leq \frac{1}{2}R_2 \\ &= 0, \quad r > \frac{1}{2}R_2 \end{aligned} \tag{25b}$$

and

$$\begin{aligned} -\gamma_{22}(r) &= -(\beta e_2^2 / \epsilon r) + (P + B/\xi) + (\delta r / R_2) + 6\xi P r^3 / R_2^3, \\ & \quad r \leq R_2 \\ &= 0, \quad r > R_2. \end{aligned} \tag{25c}$$

Here $\xi = \pi \rho_2 R_2^3 / 6$, and B , P , and δ are given by

$$\begin{aligned} 12B &= x^2 + x(1 + 2\xi)(1 - \xi)^{-1} \\ &\times \{1 - [1 + 2x(1 - \xi)^2(1 + 2\xi)^{-2}]^{1/2}\}, \end{aligned} \tag{26a}$$

$$\begin{aligned} 4P &= -(1 + 2\xi)^2(1 - \xi)^{-4} \\ &\times \{1 - [1 + 2x(1 - \xi)^2(1 + 2\xi)^{-2}]^{1/2}\}^2, \end{aligned} \tag{26b}$$

$$6\delta = P(1 - 8\xi - 2\xi^2)\xi^{-1} - 6B\xi^{-1} + x^2\xi^{-1}/4, \tag{26c}$$

where x is defined by, $x^2 \equiv \kappa^2 R_2^2 \equiv (4\pi\beta/\epsilon)\rho_2 e_2^2 R_2^2$, and κ is the inverse Debye length for this case.

We obtain, in the manner described in Sec. II, the excess energy per unit volume as

$$\begin{aligned} E^{ex}(\beta, \xi, x) &= -12B/4\pi\beta R^3 \\ &= -\{x^2 + x(1 + 2\xi)(1 - \xi)^{-1} \\ &\times [1 - (1 + 2x(1 - \xi)^2(1 + 2\xi)^{-2})^{1/2}]\} / 4\pi\beta R^3. \end{aligned} \tag{27}$$

Comparing the expressions of Eq. (27) and Eq. (14), which give the excess energy per unit volume for the dense point case and the symmetric case respectively, we notice that they have very similar forms, the most important difference is the dependence of E^{ex} on ξ in the dense point limit case.

The contact values of $g_{ij}(r)$, $g_{ij}(R_{ij}^+)$, are given in the following way

$$g_{22}(R_2^+) = \tilde{g}_{22}(R_2^+) - \gamma_{22}(R_2^-), \tag{28a}$$

$$g_{12}(R_2^+/2) = g_{21}(R_2^+/2) = \tilde{g}_{21}(R_2^+), \tag{28b}$$

$$g_{11}(0^+) = \tilde{g}_{11}(0^+), \tag{28c}$$

where $\tilde{g}_{ij}(R_{ij}^+)$ are the contact values of the radial distribution functions obtained by Lebowitz⁵ in his solution of the PY equation for a mixture of neutral hard-spheres when $R_1 = 0$.

Equations (28b) and (28c) show that the contact values of g_{21} and g_{11} are the same as in the uncharged hard spheres case.

V. DISCUSSION

The mean spherical model appears to be a useful first order approximation for electrolytes. It yields, as

we have seen, simple analytic expressions for both the thermodynamic properties and structure functions of primitive electrolytes. Comparison with machine computations indicate that these expressions are close to the exact values at molar concentrations far higher than those at which the classical Debye-Hückel theory is useful (the DH theory is so poor at these concentrations that it is not even included in the tables).

The mode expansion method of Anderson and Chandler¹¹ can be thought of as the next approximation to the properties of electrolytes going one step beyond the MSM. The corrections to the results of the MSM which they obtain further improve the agreement with the machine computations. This is true even for 2-2 primitive model electrolytes when the ratio of the potential energy at contact to the kinetic energy, $\beta e^2/\epsilon R$, is quite large. Further systematic approximations may be obtained through the use of graphical expansions along the lines of Stell and Lebowitz¹² to which the mode expansion is closely related.¹³

The main feature of these models is their "separation" of the effects of the long range Coulomb interactions from the effects of the short range (hard core) interactions. The system in which the particles interact only via the short range interactions is used as a reference system whose properties are assumed known or can be well approximated by the Percus-Yevick equation. In contrast, the Debye-Hückel theory uses the ideal gas as a reference system. The other approximate theories, referred to in the tables, treat the short and long range parts of the potential on a more or less equal footing. This makes it hard to use them as the starting points for systematic expansions especially tailored to take advantage of the long range nature of the Coulomb potential, even though they predict the properties of primitive electrolytes rather accurately.

We would like to emphasize here that the particularly nice feature of the MSM, in our eyes, is its amenability to an analytic solution: a feature shared,

at the present time, only by the DH theory. (While we have not yet succeeded in obtaining explicit results for 3D systems of unequal diameters, $R_1 \neq R_2$, we have not given up hope either.) This will facilitate, we expect, its application to systems and problems not discussed here. Indeed, Wertheim¹⁴ has recently succeeded in obtaining an exact solution of the MSM for a system of hard spheres with dipoles at their centers. We also hope that the availability of an analytic solution will yield a better understanding of the physical nature of the approximations made and thus of the true structure of electrolytes.

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