Correlation function II: Electrolytes

L. BLUM

Department of Physics, University of Puerto Rico
P.O. Box 23343, Río Piedras, PR 00931-3343

J.N. HERRERA

Facultad de Ciencias Físico-Matemáticas
Benemérita Universidad Autónoma de Puebla
Apartado postal 1152, 72001 Puebla, Pue., México

AND

J.F. ROJAS-RODRÍGUEZ

Instituto de Física
Benemérita Universidad Autónoma de Puebla
Apartado postal J-48, 72570 Puebla, Pue., México

ABSTRACT. In this work we discuss the Debye-Hückel (DH) for a classical electrolyte and the Primitive Model (PM) for ionic solutions. Using the formalism of distribution function theory we derive the Mean Spherical Approximation (MSA). The factor correlation functions and the thermodynamic properties are calculated explicitly.

RESUMEN. En este trabajo discutimos la teoría clásica de electrólitos de Debye-Hückel y estudiamos el Modelo Primitivo (PM) para soluciones iónicas con el formalismo de la teoría de funciones de distribución en la Aproximación Esférica Media (MSA). Se calculan explícitamente las funciones factor de las funciones de correlación y las propiedades termodinámicas.

1. INTRODUCTION

In a previous paper [1] (hereafter called I), we disscused the distribution function and the factor correlation function theories. We now study charged systems, such as models for an electrolytic solution. Ionic liquids have certain properties that are absent in fluids composed of neutral particles (see Ref. [1]), and many of their distinguishing characteristics are associated in some way with the slow, r^{-1}, decay of the Coulomb potential. In the electrolyte model the ions are represented by charged hard spheres and the solvent (water in most cases) by a continuum or by neutral hard spheres with a charge distribution. We will discuss models that admit analytic solutions:

1. The primitive model, in which the ions are charged spheres, and the solvent is a dielectric continuum;
2. the elementary model, in which the solvent is a point dipole in a hard sphere;

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3. the basic model, in which we add a potential of tetraehedral octupolar symmetry to mimic the hydrogen bonds.

While model (1) is pretty well understood, model (2) is being developed and model (3) is just barely being started.

We will center our discusssion around the MSA (mean spherical approximation) of Lebowitz and Percus [2], wich is an analytically solvable theory. In principle, solutions for all three models of ionic solutions are obtained in the MSA, because the MSA is solvable for non central forces also.

Ionic solutions are liquids consisting of a solvent formed from neutral, polar molecules, and a solute that dissociates into positive and negative ions. They vary widely in complexity: in the classic electrolyte solutions, the cations and anions are of comparable size and absolute charge, whereas macromolecular ionic solutions contain both macroions (charged polymer chains or coils, micelles, charged colloidal particles, etc.) and microscopic counterions [3]. We will discuss only the classic ionic solutions.

2. THE PRIMITIVE MODEL AND DEBYE-HÜCKEL(DH) THEORY

Consider a neutral mixture of charged hard spheres of diameter σ_i, charge $z_i e$ (where e is the charge of the electron), number density $\rho_i = \frac{N_i}{V}$ (where N_i is the number of ions of species i enclosed in a volume V). The number of species is s. The equivalence of this system of units, to the normal or molar concentration c_+ is given by [4]

$$\rho_i = c_+ \, \nu_i \, 6.02252 \times 10^{-4} \text{ Å}^{-3}, \tag{1}$$

where ρ_i is expressed in number of particles per cubic Angstrom and ν_i is the stoichiometric coefficient. The temperature of the system is 25 °C or $T = 298.13$ K, and the relative dielectric constant of water is 78.4. We will use Boltzmann's constant $k_\mathrm{B} = 1.38 \times 10^{-16}$ erg/K, and also $\beta = \frac{1}{k_\mathrm{B}T}$. The electrolyte solution is represented by a random, neutral array of charges. We would like to know the thermodynamic properties of our system, quantities such as the internal energy E, the free energy A, the pressure P, and so on.

We start by computing the energy per particle (E/N). Neglecting boundary effects, the charge distribution around a given ion i is

$$q_i(r) = e \sum_{j=1}^{s} z_j \rho_j^{(i)}(r), \tag{2}$$

where $\rho_j^{(i)}(r)$ is the conditional density of ions j in the neighborhood of i. In statistical mechanics this function is usually expresed in terms of the pair correlation function

$$g_{ij}(r) = \frac{\rho_j^{(i)}(r)}{\rho_j} = g_{ji}(r) = \frac{\rho_i^{(j)}(r)}{\rho_i}, \tag{3}$$

which is a symmetric function in the exchange of particles i and j (see paper I). From a simple analogy to the atmospheric pressure equation, the density $\rho(r)$ of the atmosphere is given by

$$\rho(r) = \rho_0 e^{-\beta m g r}, \tag{4}$$

where the term mgr represents the potential energy of a particle of mass m at a height r, g is the acceleration of gravity. More generally $\rho(r)$ becomes $\rho_j^i(r)$, particle i is the earth.

We can define a potential of the mean force $w_{ij}(r)$ such that

$$g_{ij}(r) = e^{-\beta w_{ij}(r)}. \tag{5}$$

Our central problem will be to determine this potential of mean force [1]. There are a number of requirements on it, however.

We write

$$w_{ij}(r) = e z_j \varphi_i(r) + \zeta_{ij}(r), \tag{6}$$

where the first term is purely electrostatic and $\zeta_{ij}(r)$ contains all the remaining contributions, such as excluded volume. In other words

$$\begin{aligned} g_{ij}(r) &= e^{-\beta e z_j \varphi_i(r)} \\ &\simeq 1 - \beta e z_j \varphi_i(r). \end{aligned} \tag{7}$$

If we assume $\zeta_{ij}(r) \cong 0$, then the electrostatic potential must satisfy the Poisson equation in the form (the Poisson equation is valid also when $\zeta_{ij} \neq 0$)

$$\nabla^2 \varphi_i(r) = -\frac{4\pi}{\epsilon_0} q_i(r), \tag{8}$$

and using (2) and (5)

$$\nabla^2 \varphi_i(r) = -\frac{4\pi}{\epsilon_0} e \sum_{j=1}^{s} \rho_j z_j e^{-\beta e z_j \varphi_i(r)}, \tag{9}$$

which is the Poisson-Boltzmann or Milner equation [5]. Even for the simplest possible case, the equal size and equal charge electrolyte ($\sigma_+ = \sigma_- = \sigma$, $z_+ = -z_-$), this equation cannot be solved in closed form. But there are asymptotic regimes in which we can solve it. If σ is very small the conditional probability density must be of the form

$$\lim_{\sigma \to 0} \rho(\sigma) = e^{-\beta e z_j \varphi_i^0(r)}, \tag{10}$$

where $\varphi_i^0(r) = \frac{e z_i}{\epsilon_0 r}$ is the bare Coulomb interaction, or, in other words, when two charges come very close, their own interaction will dominate over the interactions of the other surrounding charges.

Another limiting case is when the central ion is very large. Then $\varphi_i(r)$ must be small, and we know that, for $\lim r \to \infty$,

$$g_{ij}(r) = 1,$$
$$w_{ij} \to 0,$$
$$\varphi_{ij}(r) \to 0, \tag{11}$$

and, following Debye and Hückel (DH), we can expand the exponential in Eq. (9), to obtain [6]

$$\nabla^2 \varphi_i(r) = \kappa^2 \varphi_i(r), \tag{12}$$

where

$$\kappa^2 = \frac{4\pi\beta e^2}{\epsilon_0} \sum \rho_j z_j^2 \tag{13}$$

defines the Debye screening length. There are several ways of solving the Eq. (12). Consider, for simplicity, only the restricted case in which all ions are of equal size. Then the distance of closest approach is σ. We have to transform the gradient to spherical coordinates [7] but since φ does not depend on the angles, we simply get

$$\frac{1}{r}\frac{\partial^2}{\partial r^2} r\varphi_i(r) = \kappa^2 \varphi_i(r). \tag{14}$$

The general solution of this equation is

$$r\varphi_i(r) = A_i e^{-\kappa(r-\sigma)} + B_i e^{\kappa(r-\sigma)}. \tag{15}$$

The only way to satisfy boundary condition (11) is to require that $B_i = 0$. The value of A_i is obtained form Gauss's theorem, or more simply, from boundary condition (10), since for $r \to 0$

$$r\varphi_i(r) = \frac{z_i e}{\epsilon_0}\left(\frac{1}{1+\kappa\sigma}\right). \tag{16}$$

The full solution for the potential is

$$\varphi_i(r) = \frac{z_i e}{\epsilon_0} \frac{e^{-\kappa(r-\sigma)}}{r(1+\kappa\sigma)}, \tag{17}$$

and according to (8) and (16) the charge density is

$$q_i(r) = -\frac{\epsilon}{4\pi}\nabla^2\varphi_i(r) = -\frac{z_i e}{4\pi}\frac{1}{r}\frac{\partial^2}{\partial r^2}e^{-\kappa(r-\sigma)}$$
$$= -\frac{z_i e}{4\pi}\frac{\kappa^2}{r}e^{-\kappa(r-\sigma)}. \tag{18}$$

This charge distribution satisfies the electroneutrality condition

$$- z_i e = \int d\mathbf{r} \, q_i(\mathbf{r}), \tag{19}$$

which can be verified by integration: substitution of 18) into (19) leads to

$$\sum_j z_j 4\pi \int_0^\infty dr \, r^2 \, h_{ij}(r) \, \rho_j = -z_i. \tag{20}$$

This is a completely general and rigorous sum rule that must be obeyed by the distribution functions of any good theory of electrolytic solutions. It means that an ionic cloud surrounding a given ion just has enough charge to neutralize that ion. The charge distribution, in our theory, is exponentially decaying with a mean distance of decay equal to $1/\kappa$.

The excess energy of charging up the system is, from (18) and Coulomb's formula (10 ff),

$$\Delta E^{\text{ch}} = \tfrac{1}{2} \left[\frac{4\pi e^2}{\epsilon_0} \right] \sum_{i,j} \rho_i \, \rho_j \, z_i \, z_j \int dr \, r^2 \, g_{ij}(r) \frac{1}{r}$$

$$= -\sum_i \frac{\rho_i (e z_i)^2}{2\epsilon_0} \frac{1}{\sigma + \frac{1}{\kappa}}. \tag{21}$$

This is the energy of a system of spherical capacitors of radius $(\sigma + \frac{1}{\kappa})$. The internal energy has a lower bound [8]. Imagine that we increase κ [Eq. (13)], either by charging up the ions $(z_i \to \infty)$ or by letting the temperature drop $(\beta \to \infty)$ and letting the density $(\rho_i \to \infty)$. Physically, this is equivalent to immersing all our ions in liquid metal. Then the screening length $\frac{1}{\kappa}$ is zero: the system is a perfect screening system, and the energy

$$\Delta E^{\text{ch}} = -\sum_i \frac{\rho_i (e z_i)^2}{2\epsilon_0 \sigma} \tag{22}$$

is a rigorous lower bound for the energy of any system of hard charged ions.

From

$$\Delta A = \Delta E - T \Delta S, \tag{23}$$

$$\frac{\partial \Delta A}{\partial T} = -\Delta S, \tag{24}$$

$$\frac{\partial \Delta A / T}{\partial (1/T)} = \Delta E, \tag{25}$$

we get

$$\Delta A = \frac{1}{\beta} \int_0^\beta d\beta' \Delta E(\beta') \tag{26}$$

From Eq. (22) in the infinite dilution limit we get the Debye-Hükel excess charging energy

$$\Delta E = -\frac{\kappa^3}{8\pi\beta}.$$

Substituting this into (26) leads to

$$\Delta A = -\frac{\kappa^3}{12\pi\beta} = -\frac{\kappa^3}{8\pi\beta} + \frac{\kappa^3}{24\pi\beta} = \Delta E + \frac{\kappa^3}{24\pi\beta}. \tag{27}$$

And from (24)

$$\Delta S = -\frac{\kappa^3}{24\pi T}.$$

The excess osmotic coefficient, defined by

$$\phi = 1 + \frac{\beta\Delta P}{\rho}, \tag{28}$$

with ρ = salt concentration = ρ_i for the restricted case, can be obtained from the free energy, using the relation

$$\left(\frac{\partial \Delta A}{\partial V}\right)_T = -\Delta P. \tag{29}$$

After some algebra we get

$$\phi - 1 = -\frac{\kappa^3}{24\pi \sum_i \rho_i}. \tag{30}$$

The excess Gibbs free energy is

$$\frac{\Delta G}{\sum_i N_i} = \frac{\Delta A}{\sum_i N_i} = \frac{\Delta P}{\sum_i \rho_i}, \tag{31}$$

and using (29) and (30) we get for the mean electrostatic activity coefficient $\gamma_\pm$ the following relation:

$$\ln \gamma_\pm = \frac{\Delta G}{\sum_i \rho_i} = \frac{\beta\Delta E}{\sum_i \rho_i} = -\frac{\kappa^3}{8\pi \sum_i \rho_i}. \tag{32}$$

3. The MSA for the equal size primitive model

In the previous section we discussed the simplest possible theory, in which the potential of mean force $w_{ij}(r)$, [see Eq. (6)], was set equal to the electrostatic potential. This means that we ignore all the other contributions to the ionic interactions, notably those of the hard-core, which accounts for two very important effects:

a) They prevent the collapse of the system: classical electroneutral Coulomb (ionic) systems are unstable, because the (+) and the (−), form pairs of unbounded negative energy. This is a rigorous result in statistical mechanics [1].

b) The excluded volume effect: only one ion can be placed in a given position in space. In the DH theory, the ions of the screening cloud are points, and do not exclude each other. Clearly, the size of the screening cloud of finite size ions must be larger than the DH cloud.

What we want to do now is to include the hard core effects into the calculation of the structure of the ionic cloud. Or, what is equivalent, to charge up a system of hard spheres. This is the basic idea of the mean spherical approximation. A convenient treatment of mixtures of neutral hard spheres is provided by the Percus-Yevick (PY) theory [2].

Consider now the following approximation: take the OZ equation [1]

$$h_{ij}(r) - c_{ij}(r) = \sum_k \rho_k \int dr_1 h_{ik}(r_1) c_{kj}(|\mathbf{r} - \mathbf{r_1}|), \tag{33}$$

and use:

i) The hard core condition for separations $r < \sigma$

$$h_{ij}(r) = -1. \tag{34}$$

ii) The "Debye-Hückel" (really, MSA) boundary condition for $r \geq \sigma$

$$c_{ij}(r) = -\beta u_{ij}(r) = -\beta \frac{e^2}{\epsilon_0} \frac{z_i z_j}{r}. \tag{35}$$

In the Debye-Hückel limit of zero ionic size the Eq. (33) can be written

$$h_{ij}(r) = -\frac{\beta e^2}{\epsilon_o} \frac{z_i z_j}{r} - \sum_l \rho_l \int d\mathbf{r_1} h_{ik}(r_1) \left[\frac{\beta e^2}{\epsilon_0} \frac{z_l z_j}{|\mathbf{r} - \mathbf{r_1}|} \right], \tag{36}$$

using Eq. (7) for $h_{ij}(r)$ we get the integral form of the Poisson Boltzmann equation (9) (see also appendix A)

$$-\beta z_j e \varphi_i(r) = -\frac{\beta z_i z_j e^2}{\epsilon_o r} - \sum_k \rho_k \int d\mathbf{r_1} \frac{\beta e^2 z_j z_k}{\epsilon_o |\mathbf{r} - \mathbf{r_1}|} \varphi_i(\mathbf{r_1}). \tag{37}$$

The mathematical solution follows the steps outlined for the case of neutral hard spheres. There is, however, one problem in using the Wiener-Hopf factorization described for the hard sphere case in paper I: if we take the Fourier transform of Eq. (35), we get

$$\int d\mathbf{r} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{r} \cong \frac{1}{k^2}, \tag{38}$$

which has a double pole at the origin, that is, on the real axis. This violates one of the conditions for the factorization [1]. We may, however get around this difficulty by shifting the poles away from the origin. This is done using

$$c_{ij}(r) = -\beta \frac{e^2}{\epsilon_o} z_i z_j \lim_{\mu \to 0} \frac{e^{-\mu|\mathbf{r}|}}{|\mathbf{r}|}. \tag{39}$$

We can check, that, just as in Eqs. (A.30) and (A.31), (see appendix), the Fourier transform of (39) is

$$\tilde{c}_{ij}(k) = -\beta \frac{e^2 z_i z_j}{\epsilon_0} 4\pi \frac{1}{k^2 + \mu^2}\bigg|_{\mu \to 0}, \tag{40}$$

which has two poles located at $k = \pm i\mu$. The Fourier transform of the Orstein-Zernike equation

$$\lim_{\mu \to 0} \sum_k [\delta_{ik} + \rho_i h_{ik}(k)] \left[\delta_{kj} - \rho_k c_{kj}^\circ + \frac{4\pi\beta e^2}{\epsilon_0} \rho_k \frac{z_k z_j}{k^2 + \mu^2}\right] = \delta_{ij} \tag{41}$$

This is a matrix equation and, therefore, complicated. If we restrict our analysis to the symmetric 1-1 electrolyte of equal size ions then, we have the symmetries

$$h_{11} = h_{22}, \qquad h_{12} = h_{21}, \qquad \rho_1 = \rho_2 = \rho. \tag{42}$$

In that case the OZ equation can be written as

$$\begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix} - \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} = \rho \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix} * \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix}, \tag{43}$$

where $(*)$ denotes the convolution integral:

$$* \to \int dr_3\, h(r_{13})\, c(r_{32}). \tag{44}$$

Because of the symmetries (42) the OZ equation can be diagonalized by a similarity transformation using

$$\mathbf{S} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}; \qquad \mathbf{S}^{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}. \tag{45}$$

It is easy to verify that, for example,

$$S \begin{pmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{pmatrix} S^{-1} = \begin{pmatrix} h_{11} + h_{12} & 0 \\ 0 & h_{11} - h_{12} \end{pmatrix}. \tag{46}$$

Therefore, the OZ equation (43) becomes a system of two uncoupled, OZ equations. If we define

$$h^\circ(r) = \tfrac{1}{2}[h_{11}(r) + h_{12}(r)], \tag{47}$$

$$h(r) = \tfrac{1}{2}[h_{11}(r) - h_{12}(r)], \tag{48}$$

then we get one "normal" equation

$$h^\circ(r) - c^\circ(r) = 2\rho \int d\mathbf{r}_1 c^\circ(|\mathbf{r} - \mathbf{r}_1|) h^\circ(\mathbf{r}_1), \tag{49}$$

which has the normal boundary conditions for hard spheres and another "special" equation for the charge interactions:

$$h(\mathbf{r}) - c(\mathbf{r}) = \rho \int d\mathbf{r}_1 c(|\mathbf{r} - \mathbf{r}_1|) h(\mathbf{r}_1), \tag{50}$$

in which the boundary conditions now have changed. In fact, it is easy to verify that

$$h(r) = 0, \qquad r < \sigma, \tag{51}$$

$$c(r) = -\frac{\kappa^2}{\rho r}, \qquad r \geq \sigma, \tag{52}$$

where

$$\kappa^2 = \frac{8\pi \beta e^2}{\epsilon_0} \rho = \frac{4\pi \beta e^2}{\epsilon} \sum_i \rho_i z_i^2 \tag{53}$$

is the Debye screening parameter. Instead of (41) we now have

$$\lim_{\mu \to 0} [1 + \rho h(k)] \left[1 - \rho c(k) + \frac{\kappa^2}{k^2 + \mu^2} \right] = 1. \tag{54}$$

We follow now, step by step, the procedure used in solving the hard sphere case [1]. We write

$$\left[1 - \rho c(k) + \frac{\kappa^2}{k^2 + \mu^2} \right] = \left[1 + \rho Q(k) + \frac{\rho A}{\mu - ik} \right] \cdot \left[1 - \rho Q(-k) + \frac{\rho A}{\mu - ik} \right]. \tag{55}$$

The inverse Fourier transform of this expression yields

$$-S(r) + \frac{\kappa^2}{\rho} \frac{e^{-\mu r}}{2\mu} = -Q(r) + A + \rho \int_r^\sigma dr_1 \, Q(r_1) \, Q(r_1 - r)$$

$$-\rho \int_r^\sigma dr_1 \, Q(r_1) \, A - \rho \int_r^{\sigma+r} dr_1 \, A \, Q(r_1 - r)$$

$$+\rho \, A^2 \frac{e^{-\mu r}}{2\mu}. \tag{56}$$

If we take the limit $\mu \to 0$, then (56) requires that

$$\kappa^2 = \rho^2 A^2 \tag{57}$$

and, furthermore, $S(r) = 2\pi \int_r^\sigma ds \, s \, c(s)$ is zero at $r = \sigma$, from where we deduce that, due to continuity,

$$Q(\sigma) = 0. \tag{58}$$

Consider now the equation for the pair distribution function (see paper I)

$$[1 + \rho h(k)] \left[1 - \rho Q(k) + \frac{\rho A}{\mu + ik} \right] = \frac{1}{1 - \rho Q(-k) + \frac{\rho A}{\mu - ik}}. \tag{59}$$

The Fourier inversion is exactly that of the hard sphere case. We get

$$J(r) = Q(r) - A + \rho \int_0^\infty dr_1 \, J(r - r_1) \, Q(r_1) - \rho \int_r^\infty dr_1 \, J(r - r_1) \, A, \tag{60}$$

since now $q(r)$ has become $Q(r) - A$, where A is a constant over the range of r_1 from 0 to ∞. The last term is apparently divergent. Let us write it in the form

$$\int_r^\infty dr_1 \, J(r - r_1) = -\int_0^r dr_1 \, J(r - r_1) + \int_0^\infty dr_1 \, J(r - r_1), \tag{61}$$

but remember that

$$J(r) = 2\pi \int_r^\infty ds \, s \, h(s); \tag{62}$$

so that the last term becomes

$$\rho \int_r^\infty dr_1 \, J(r_1) = \rho \int_0^\infty dr_1 \, J(r - r_1) = 2\pi\rho \int_0^\infty dr_1 \int_{r_1}^\infty ds \, s \, h(s)$$

$$= 2\pi\rho \int_0^\infty ds \, s \, h(s) \int_0^s dr_1 = 2\pi\rho \int_0^\infty ds \, s^2 \, h(s) = -\frac{1}{2}, \tag{63}$$

where the last identity is a consequence of the electroneutrality sum rule for the correlation function $h(r)$, (20). Putting it all together yields

$$J(r) = Q(r) - \frac{A}{2} + \rho \int_r^\sigma dr_1\, J(r - r_1)\, Q(r_1) - \rho A \int_0^r dr_1\, J(r - r_1). \qquad (64)$$

Using the condition (51), we find the surprisingly simple result

$$J(r) = 2\pi \int_r^\infty ds\, s\, h(s) = b_0, \quad \text{for} \quad r < \sigma, \qquad (65)$$

(we should later see that b_0 is in itself an interesting quantity, namely the excess internal energy E).

Now (64) is

$$b_0 = Q(r) - \frac{A}{2} + \rho b_0 \int_0^\sigma dr_1\, Q(r_1) - \rho A\, b_0 r, \qquad (66)$$

so that

$$0 = Q'(r) - \rho A b_0, \qquad (67)$$

and because of the requirement (58)

$$Q(r) = \rho A b_0 (r - \sigma), \qquad (68)$$

so that, taking (66) at $r = 0$,

$$b_0 = -\rho A b_0 \sigma - \frac{A}{2} - \rho b_0 \frac{\rho A b_0 \sigma^2}{2}, \qquad (69)$$

$$\rho A \sigma = -\frac{2 b_0 \rho \sigma}{(1 + \rho b_0 \sigma)^2} = \kappa \sigma. \qquad (70)$$

To make connection with the Debye- Hückel theory, we define

$$\rho b_0 = -\frac{1}{\sigma + \frac{1}{\Gamma}}, \qquad (71)$$

so that we get, from (71),

$$\kappa \sigma = 2\Gamma \sigma (1 + \Gamma \sigma) \qquad (72)$$

or

$$(1 + 2\Gamma \sigma)^2 = (1 + 2\kappa \sigma),$$

and the physical root for Γ is (a comparison between Γ and κ is given in Ref. [9])

$$2\Gamma\sigma = \sqrt{1 + 2\kappa\sigma} - 1. \tag{73}$$

Let us compute the direct correlation function too. Removing the $\frac{1}{\mu}$ singularity, and taking derivatives of (56), we get

$$
\begin{aligned}
2\pi\, rc(r) &= -Q'(r) + \rho \int_r^\sigma dr_1 Q'(r_1) Q(r - r_1) + \rho A Q(r) - \frac{\rho A^2}{2} \\
&= -\rho A b_0 + \rho^2 A b_0 \rho A b_0 \int_r^\sigma dr_1 (r_1 - r - \sigma) - \frac{\rho A^2}{2} + (\rho A)^2 b_0 (r - \sigma) \\
&= \rho A^2 \left[\frac{\rho b_0 \sigma r}{\sigma} + \frac{\rho^2 b_0^2 \sigma^2 r}{2\sigma^2} \right] = \frac{(\rho A \sigma)^2}{\sigma^2} b_o r \left(1 + \frac{\rho b_o r}{2} \right);
\end{aligned} \tag{74}
$$

this later expression leads to

$$2\pi c(\sigma) = -\frac{\kappa^2}{\rho_o} \frac{1}{\sigma + \frac{1}{\Gamma}} \left(1 + \frac{\sigma}{2 \left(\sigma + \frac{1}{\Gamma} \right)} \right).$$

We can compute the excess pair correlation function by taking the derivative of (64)

$$-2\pi\, rh(r) = Q'(r) - 2\pi\rho \int_0^\sigma dr_1\, Q(r_1)\,(r - r_1)\,h(r - r_1) - \rho A\, J(0), \tag{75}$$

but now $h(r - r_1)$ is zero for $r - r_1 < \sigma$, since $Q'(r)$ and $Q(r)$ are zero for $r > \sigma$

$$2\pi\, rh(r) = \rho A b_0 + 2\pi\rho \int_0^{r-\sigma} dr_1\, Q(r_1)\,(r - r_1)\,h(r - r_1). \tag{76}$$

This equation can be solved by Laplace transformation (which, in the complex plane, is equal to the half-plane Fourier transform (FT)):

$$h(s) = \int dr\, e^{-sr}\, r\, h(r). \tag{77}$$

We get

$$h(s) = -\frac{2\Gamma^2 s}{\rho} \frac{e^{-s\sigma}}{s^2 + 2s\Gamma + 2\Gamma^2[1 - exp(-s\sigma)]}, \tag{78}$$

which should be contrasted to the DH expression $\frac{1}{k^2+\kappa^2}$ for the FT of the corresponding function. For small concentrations we get, for the more general case, the symmetric expression

$$h_{ij}(r) \cong -\frac{\beta e^2}{\epsilon_0 r} \frac{z_i z_j}{(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)} e^{-2\Gamma(r - \sigma_{ij})}, \tag{79}$$

which is exponentially decaying, but with a different screening length [9, 10]. In general, however, the function $h(r)$ will be oscillating, modulated by the hard core diameter σ.

4. Thermodynamic properties

The excess energy can be computed with the help of the pair distribution function [1,10,11] from Eq. (21):

$$\Delta E = 2\pi \int_0^\infty dr \, r^2 \sum_{i,j} \rho_i \, \rho_j \, g_{ij}(r) \, \frac{z_i z_j e^2}{r \epsilon_0}. \tag{80}$$

Using (45)–(46) and (34) manipulations becomes

$$\Delta E = \frac{4\pi e^2}{\epsilon_0} \rho^2 \int_0^\infty dr \, r \, h(r) = \frac{2e^2 \rho^2}{\epsilon_0} b_0, \tag{81}$$

and, using the definition of b_0 in (3.33),

$$\Delta E = \frac{2e^2}{\epsilon_0} \rho^2 b_0 = -\frac{e^2 \rho}{\epsilon_0} \frac{1}{\frac{\sigma}{2} + \frac{1}{2\Gamma}}, \tag{82}$$

where we have also used the relation for b_0. The new screening length 2Γ is clearly that of the MSA. The same picture emerges as in the DH theory: The energy of charging up the system is that of a collection of spherical capacitor of radius $\frac{\sigma}{2} + \frac{1}{2\Gamma}$. This, in spite of the complicated form of the pair correlation functions. The same simple result is true for the general mixture of arbitrary size ions.

Using formula (26) we can compute the free energy excess of the ionic system:

$$\Delta A = \frac{1}{\beta} \int_0^\beta d\beta_1 \, \Delta E(\beta_1) = \frac{1}{\beta} \int_0^\Gamma d\Gamma' \, \frac{\partial \beta}{\partial \Gamma'} \Delta E(\Gamma'). \tag{83}$$

Now we know that, from Eq. (72),

$$\kappa^2 = \frac{8\pi e^2 \rho \beta}{\epsilon_0} = 4\Gamma^2 (1 + \Gamma \sigma)^2$$

or

$$\frac{\pi e^2 \rho}{\epsilon_0} \frac{\partial \beta}{\partial \Gamma} = \Gamma(1 + \Gamma \sigma)(1 + 2\Gamma \sigma). \tag{84}$$

Substituting (82) and (84) into (83) yields

$$\Delta A = -\frac{2}{\pi \beta} \int_0^\Gamma d\Gamma' \, \Gamma'^2 \, (1 + 2\Gamma' \sigma) = -\frac{1}{\pi \beta} \left[\tfrac{2}{3} \Gamma^3 + \sigma \Gamma^4 \right] \tag{85}$$

or

$$\Delta A = \Delta E + \frac{\Gamma^3}{3\pi \beta}, \tag{86}$$

which should be compared to (27). Indeed they are the same if we substitute 2Γ for κ using (28), (29) and

$$\frac{\partial \Gamma}{\partial \rho} = \frac{\pi \beta e^2}{2\epsilon_0} \frac{1}{\Gamma(1 + \Gamma \sigma)(1 + 2\Gamma \sigma)}, \tag{87}$$

we get the very simple result

$$\phi - 1 = -\frac{\Gamma^3}{3\pi \rho}. \tag{88}$$

Finally, the Gibbs free energy per molecule, *i.e.*, the chemical potential $\mu = \frac{\partial G}{\partial n}$, can be calculated:

$$\ln \gamma_\pm = \tfrac{1}{2}\beta A + \phi - 1 = \tfrac{1}{2}\beta \Delta E \tag{89}$$

This completes the derivation of these properties of ionic solutions in the MSA. Comparison of the thermodynamic properties to computer simulations shows that for low valence and high concentrations, the MSA is comparable to the HNC (hypernetted chain equation) for the activity and osmotic coefficients. For low concentrations and high valence it is not very good [11]. There are a large number of papers in which different ways of correcting this are proposed. A recent approximation, which gives very good results (comparable to the HNC) for 2–2 salts over a range of concentrations varying from 0.00625 M to 2M [11], consists in writing

$$g(r) = A \exp(h^{\text{MSA}}(r))S(x) + g^{\text{MSA}}(r)(1 - S(x)), \tag{90}$$

where $S(x)$ is a switching function (generally linear) which also ensures that the electroneutrality condition (20) is satisfied. The nice feature of the MSA is that the simplicity of the results for the equal size case persists for arbitrary mixtures. So, we get to a good approximation:

$$4\Gamma^2 = \frac{4\pi \beta e^2}{\epsilon_0} \sum_i \rho_i \left\{ \frac{z_i}{1 + \Gamma \sigma_i} \right\}^2, \tag{91}$$

which is now a higher degree algebraic equation. Often, one can use the equal size equation (32) with the mean diameter

$$\bar{\sigma} = \frac{\sum_i \rho_i \sigma_i z_i^2}{\sum_i \rho_i z_i^2} \tag{92}$$

as our initial guess for the solution. The excess internal energy is [11]

$$\Delta E = -\frac{e^2}{\epsilon_0} \Gamma \sum_i \frac{\rho_i z_i^2}{1 + \sigma_i \Gamma}, \tag{93}$$

which again is the sum of the charging energies of a collection of spherical capacitors. The Helmholtz free energy yields, as before,

$$\Delta A = \Delta E + \frac{\Gamma^3}{3\pi\beta}, \tag{94}$$

and, just as before,

$$\phi - 1 = -\frac{\Gamma^3}{3\pi \sum_i \rho_i} \tag{95}$$

and

$$\ln \gamma_\pm = \frac{\beta \Delta E}{\sum_i \rho_i} = -\frac{e^2 \Gamma}{\epsilon_o \sum_i \rho_i} \sum_k \frac{\rho_k z_k^2}{1 + \Gamma \sigma_k}. \tag{96}$$

The general solution of the MSA is very useful in many cases to represent the properties of a large variety of eletrolytes and its mixtures, form concentrations ranging from very dilute to almost molten salts [11].

The remarkable fact is that these simple expressions remain true for the case of associating ions [12].

APPENDIX A: INTEGRAL AND FOURIER REPRESENTATION

The solution procedure of the linearized Poisson-Boltzmann equation used above is not suited to include hard core effects of the ions. The most we can do is to give a size to the central ion, but that makes the pair distribution function asymmetric. To include the hard core effects in a symmetric way, we have to change the formalism. We notice, first, that Poisson's equation (8) relates the potential $\varphi_i(r)$ to the charge distribution $q_i(r)$. We can formally integrate this equation to yield

$$\varphi_i(r) = \frac{1}{\epsilon_0} \int d\mathbf{r}_1 \frac{q_i(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r_1}|}, \tag{A.1}$$

which is equivalent to adding up the Coulomb potential at $\mathbf{r}$ produced by all the charges in the system. Clearly, (A.1) must be the same as (8), therefore

$$\nabla_r^2 \varphi_i(r) = \frac{1}{\epsilon} \int d\mathbf{r}_1 \, q_i(\mathbf{r}_1) \, \nabla_r^2 \left[\frac{1}{|\mathbf{r} - \mathbf{r_1}|} \right]. \tag{A.2}$$

For this to be true we must have

$$\int d\mathbf{r}_1 \, q_i(\mathbf{r}_1) \, \nabla_r^2 \left[\frac{1}{|\mathbf{r} - \mathbf{r_1}|} \right] = -4\pi q_i(\mathbf{r}). \tag{A.3}$$

We introduce the Dirac δ function:

$$\delta(x) = \begin{cases} 1, & \text{if } x \neq 0, \\ 0, & \text{if } x = 0, \end{cases} \tag{A.4}$$

so that

$$\int_{-\infty}^{\infty} dx \, \delta(x) = 1. \tag{A.5}$$

And in three dimensions

$$\delta(\mathbf{r}) = \delta(x)\delta(y)\delta(z), \tag{A.6}$$

which means that if

$$\nabla_r^2 \left\{ \frac{1}{|\mathbf{r} - \mathbf{r_1}|} \right\} = -4\pi\delta(\mathbf{r} - \mathbf{r_1}), \tag{A.7}$$

then (A.3) reads

$$\int d\mathbf{r}_1 \, q_i(\mathbf{r}_1) \left[-4\pi\delta(\mathbf{r} - \mathbf{r_1}) \right] = -4\pi q_i(\mathbf{r}_1), \tag{A.8}$$

which is what we wanted.

We notice that if we multiply (A.7) by $\frac{ez_i}{\epsilon_0}$ we get Poisson's equation for a point charge, the charge density being $q_i(\mathbf{r}) = z_i e \delta(\mathbf{r})$.

We would like to separate the contribution to the potential due to the central particle. In this case (A.1) reads

$$\varphi_i(r) = \frac{z_i e}{\epsilon_0 r} + \int d\mathbf{r}_1 \, \frac{1}{\epsilon_0 |\mathbf{r} - \mathbf{r_1}|} \sum_j \rho_j \, z_j e \, g_{ij}(\mathbf{r}_1). \tag{A.9}$$

In the DH approximation $g_{ij}(r)$, or also the new quantity

$$h_{ij}(r) = g_{ij}(r) - 1, \tag{A.10}$$

is written

$$h_{ij}(r) = -\beta e z_i \, \varphi_j(r). \tag{A.11}$$

Now substituting (A.11) into (A.9) and using the electroneutrality condition

$$\sum_i \rho_i z_i = 0, \tag{A.12}$$

we get

$$- \beta z_j e\, \varphi_i(r) = -\frac{\beta z_i z_j e}{\epsilon_0 r} - \sum_k \rho_k \int d\mathbf{r}_1 \frac{\beta e^2 z_j z_k}{\epsilon_0 |\mathbf{r} - \mathbf{r}_1|}\, \varphi_i(\mathbf{r}_1) \qquad (A.13)$$

or

$$h_{ij}(r) = c_{ij}(r) - \sum_k \rho_k \int d\mathbf{r}_1\, c_{kj}(|\mathbf{r} - \mathbf{r}_1|) h_{ik}(r), \qquad (A.14)$$

where we have made the identification

$$c_{ij}(r) = -\frac{\beta e^2}{\epsilon_0} \frac{z_i z_j}{r} = -\beta u_{ij}(r). \qquad (A.15)$$

Equation (A.14) can be derived for a much more general class of distributions and is know under the name of Ornstein-Zernike (OZ) equation [1].

In the discussion of the solution of the OZ equation it will be necessary to unify both descriptions of the Poisson equation: this can be achieved by using the FT technique. Our discussion of the FT will also serve as an introduction to the mathematical techniques used in solving the MSA.

The FT of a function is defined by

$$\tilde{f}(k) = \int_{-\infty}^{\infty} dx\, e^{ikx}\, f(x). \qquad (A.16)$$

The inverse FT is given by

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{-ikx}\, \tilde{f}(k). \qquad (A.17)$$

Substituting (A.16) into (A.17):

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{-ikx} \int_{-\infty}^{\infty} dx_1\, e^{ikx_1}\, f(x_1), \qquad (A.18)$$

which is true, since

$$\delta(x - x_1) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{ik(x - x_1)} \qquad (A.19)$$

is a representation of Dirac's delta function. In three dimensions:

$$\tilde{F}(k) = \int_{-\infty}^{\infty} d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, F(\mathbf{r}), \qquad (A.20)$$

$$F(\mathbf{r}) = \frac{1}{8\pi^3} \int d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, \tilde{F}(k). \qquad (A.21)$$

Now take the Laplacian of $F(r)$:

$$\nabla^2 F(\mathbf{r}) = \frac{1}{8\pi^3} \int d\mathbf{k} \, (-k^2) \, e^{-i\mathbf{k}\cdot\mathbf{r}} \, \tilde{F}(\mathbf{k}). \tag{A.22}$$

Consider now the Poisson equation

$$\nabla^2 \varphi_i(r) = -\frac{4\pi}{\epsilon_0} \left[q_i(r) - z_i e \delta(r) \right], \tag{A.23}$$

where we have now included the point charge corresponding to the central ion. In the linearized Bolzmann approximation

$$\nabla^2 \varphi_i(r) = \kappa^2 \varphi_i(r) + \frac{4\pi}{\epsilon_0} z_i e \, \delta(r). \tag{A.24}$$

We now take the 3–dimensional FT:

$$\tilde{\varphi}_i(k) = \int d\mathbf{r} \, e^{i\mathbf{k}\cdot\mathbf{r}} \, \varphi_i(r) \tag{A.25}$$

$$= \frac{4\pi}{k} \int_0^\infty dr \, r \, \sin(kr) \, \varphi_i(r), \tag{A.26}$$

$$= 4\pi \int_0^\infty dr \, cos(kr) \int_r^\infty ds \, s \, \varphi_i(s). \tag{A.27}$$

Also

$$\int d\mathbf{r} \, e^{i\mathbf{k}\cdot\mathbf{r}} \, \delta(r) = 1 \tag{A.28}$$

and from the Fourier inverse of (A.22) is

$$\int d\mathbf{r} \, e^{i\mathbf{k}\cdot\mathbf{r}} \left[\nabla^2 \varphi_i(r) \right] = -\kappa^2 \tilde{\varphi}_i(k) - k^2 \, \tilde{\varphi}(k). \tag{A.29}$$

Putting it all together, the transform of (A.23) is

$$- k^2 \tilde{\varphi}_i(k) = \kappa^2 \, \tilde{\varphi}_i(k) + \frac{4\pi z_i e}{\epsilon_0} \tag{A.30}$$

or

$$\tilde{\varphi}_i(k) = -\frac{4\pi z_i e}{\epsilon_0} \frac{1}{k^2 + \kappa^2}. \tag{A.31}$$

To compute $\varphi_i(r)$ we need to perform the inverse FT

$$\varphi_i(r) = \frac{1}{8\pi^3} \int d\mathbf{k} \, e^{-i\mathbf{k}\cdot\mathbf{r}} \frac{4\pi z_i e}{\epsilon_0} \frac{1}{k^2 + \kappa^2}. \tag{A.32}$$

There are two ways of doing this:

1. Compare to the FT of $\frac{e^{-\kappa r}}{r}$.
2. Use contour integration: to do that we must close a contour around the lower half complex k-plane, where we get a contribution only from the pole located at $k = -i\kappa$.

On the other hand, the Fourier Tronsform of Eq. (A.13) yields

$$\tilde{\varphi}_i = -\frac{z_i e}{\epsilon_0 k^2} - \frac{\kappa^2}{k^2}\tilde{\varphi}_i(k), \tag{A.33}$$

where we have used the property of the Fourier Transform of the convolution of two functions. We remember that the fourier convolution $f * g$ of two functions $f(x)$ and $g(x)$ is defined by the integral [13]

$$f * g(x) = \int_{-\infty}^{\infty} f(x - \zeta)g(\zeta)\,d\zeta. \tag{A.34}$$

In terms of FT we have

$$\text{FT}(f * g(x)) = \text{FT}(f)\,\text{FT}(g), \tag{A.35}$$

and

$$\text{FT}\left(\frac{1}{r}\right) = \frac{1}{k^2}, \tag{A.36}$$

therefore

$$\tilde{\varphi}_i(k) = -\frac{z_i e}{\epsilon_0}\frac{1}{k^2 + \kappa^2}, \tag{A.37}$$

which is the same results that obtained from the differential equation (A.31).

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