ABSTRACT: The Mean Spherical Approximation for the Primitive Model of Electrolytes by Eduardo M. Waisman

The mean spherical model approximate integral equation applied to the primitive model for electrolytes is investigated. The primitive model for electrolytes considers the solvent only insofar as using the dieletric constant ε of the medium in the Coulomb interaction between ions, which have additive hard core diameters. The solution is electrically neutral.

The mean spherical model consists of approximating the direct correlation function for $r > R_{ij}$ (R_{ij} hard core diameter) by $-\beta$ times the Coulomb potential, β is the reciprocal temperature $\frac{1}{K_B T}$ with K_B the Boltzman constant and realizing that the radial correlation function must vanish for $r < R_{ij}$.

$$c_{ij} = -\beta e_i e_j / \varepsilon r \ , \ r > R_{ij} \ , \ g_{ij}(r) = 0 \quad r < R_{ij}$$

where e_i, e_j are the charges of the ions of species i and j. The exact solution for the direct correlation function for a binary electrolyte is obtained in the case $R_1 = R_2$ and the thermodynamis following from the solution analyzed. The general structure for the general case of different sizes of hard spheres is also obtained and its implications analyzed. The techniques employed in this work follow closely those used by Lebowitz in solving the Percus Yevick equation for fluids of hard spheres[1] with unequal hard core diameters.

This Committee of this Doctoral Dissertation

Consisted of

Joel L. Lebowitz, Chairman
George Stell, PH.D.
Gerald Horowitz, PH.D.
Johannes Groeneveld, PH.D.

TABLE OF CONTENTS

Probably the acknowledgement section is not meant to philosophize, but I can not resist the temptation of expressing a few ideas about the act of getting the Ph.D. degree in Physics.

Everybody knows it takes a long time to reach the stage at which one is ready to write his dissertation, and it is just fair to emphasize that those years are an important part of one's life. On that light it is not without serious doubts that looking backwards I ask myself if it was worth the effort put in obtaining a "pass" to enter to the "Ph.D. Physicists Club," for the number of rituals I, with all the graduate students of my generation not only at Belfer but at all American Universities, was involved in was certainly not small, not always rational and clear. And looking forward at least the shadows of two big problems confront us: the financial and employment crisis in the Physics world and the problem of relevancy; that is: in the subworld of "publish or perish" in what direction is physics advancing in the context of the difficult and confused world of today? What, if any at all, is our contribution to better human knowledge and better the quality of human life suppose to be? I wish I could know the answers.

One of the rewarding aspects of the process of doing research on statistical mechanics leading to this dissertation has been to meet Dr. Joel L. Lebowitz, to whom, I want to express my deep appreciation for three main reasons: First, for his dedication in helping me through all aspects of this research, and by dedication I mean time Dr. Lebowitz has spent teaching me physics and guiding me in the task of learning, dedication I consider a very important manifestation of responsibility towards a student from his thesis advisor; Second, for the fact that Dr. Lebowitz is largely responsible for many of the ideas herein contained, and in third place because he helped me in difficult moments of my personal life to overcome obstacles in my academic career.

I am grateful to the Air Force Office of Scientific Research (Grant 68-1416) for its financial support during my dissertation research.

I want to express my appreciation to Jennie Ramirez for her patience and dedication in typing the text of this work.

I want to thank Jerry Bank for his help in the calculations of Table I and Peter Linhart for his encouragement during the time I have worked for him in AT&TCo., while also doing research in the subject of this work.

I want also to thank Dr. Jose Litvak because without his help I never could have gotten to graduate school.

I really wish my father were alive to enjoy with me the satisfactions of fulfilling a dream. I express my infinite gratitude to him, even if he is not alive, and to my mother for their love.

Finally, the person who most participated, and helped me, in moments of frustration and happiness along these years, in every possible way, who shared my doubts, problems and enthusiasm is my wife Martha to whom I dedicate this work.

Eduardo Waisman

Abstract

The mean spherical model approximate integral equation applied to the primitive model for electrolytes is investigated. The primitive model for electrolytes considers the solvent only insofar as using the dieletric constant $\mathcal{E}$ of the medium in the Coulomb interaction between ions, which have additive hard core diameters. The solution is electrically neutral.

The mean spherical model consists of approximating the direct correlation function for $r > R_{ij}$ (R_{ij} hard core diameter) by $-\beta$ times the Coulomb potential, β is the reciprocal temperature $\frac{1}{K_B T}$ with K_B the Boltzman constant and realizing that the radial correlation function must vanish for $r < R_{ij}$.

$$c_{ij} = -\beta e_i e_j / \mathcal{E} r \;, \; r > R_{ij} \;, \; g_{ij}(r) = 0 \quad r < R_{ij}$$

where e_i, e_j are the charges of the ions of species i and j. The exact solution for the direct correlation function for a binary electrolyte is obtained in the case $R_1 = R_2$ and the thermodynamis following from the solution analyzed. The general structure for the general case of different sizes of hard spheres is also obtained and its implications analyzed. The techniques employed in this work follow closely those used by Lebowitz in solving the Percus Yevick equation for fluids of hard spheres[1] with unequal hard core diameters.

CHAPTER I: The Primitive Model for Electrolytes

The simplest description of electrolytes is given by the so called primitive model. In this picture the solvent is only considered through the dielectric constant of the medium and the ions are thought to be charged hard spheres with additive diameters. (In this work we concern ourselves with the equilibrium properties of such a system for temperatures and densities for which the method of the Classical Statistical Mechanics theory are valid and meaningful. For aqueous solutions these temperatures are mostly room temperatures with densities of the order of 1 mol/liter). Therefore the primitive model consists of assuming that the potential energy of a system with m different kinds of ions is given by

(1.1) $$V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_{i<j} v_{ij}(|\vec{r}_i - \vec{r}_j|)$$

where $$v_{ij}(r) = q_{ij}(r) + e_i e_j / \varepsilon r$$

here N is the total number of ions of which we have N_1 of them with charge e_1, diameter R_1, N_i of charge e_i and diameter R_i, etc, such that as to make the overall system electrically neutral, that is

(1.2) $$\sum_{i=1}^{m} N_i e_i = \sum_{i=1}^{m} \rho_i e_i = 0$$

ρ_i is the average number density of ions of species i.

$q_{ij}(r)$ represents the hard spheres interaction between ions

$$q_{ij}(r) = \begin{cases} \infty & \text{if } r < R_{ij} \\ 0 & \text{if } r > R_{ij} \end{cases}$$

(1.3) $$R_{ii} = R_i \quad \text{and} \quad R_{ij} = (R_i + R_j)/2 \; ; \text{for } i \neq j$$

For simplicity we shall consider from here on a two-component system characterized by (e_1, R_1, ρ_1) and (e_2, R_2, ρ_2) with $R_2 \geqslant R_1$; $R_{21} = \frac{R_1 + R_2}{2}$ and $\rho_1 e_1 + \rho_2 e_2 = 0$

for definiteness $R_2 \geqslant R_1$. Therefore all sums ($\sum_{\ell}$) are meant to be $\sum_{\ell=1}^{2}$.*

Before going on with the theory of electrolytes it is convenient to introduce the Statistical Mechanics functions we are going to use.

We will refer to the radial distribution function:

(1.4) $$\rho_i g_{ij} \left(\vec{r}_i , \vec{r}_j ; \{n(\vec{r}_i)\}, \{n(\vec{r}_j)\}; \rho_{k \neq i,j} , \beta ; V \right)$$

which is the probability density of finding an ion of species i at $\vec{r}_i$ if an ion of species j is at $\vec{r}_j$ independently of the positions of the N-2 other ions; $g_{ij} = g_{ji}$

Purposely we have indicated in (1.4) the full dependence of g_{ij}, here β is the reciprocal temperature V is the volume, $n(\vec{r}_i)$ is the local number

---

* Many of the considerations, however, we make throughout this work are valid for the case $m > 2$ kind of ions.

density of ions of species i. The question whether the limiting function g_{ij} exists as $V \to \infty$ and the number density going to ρ_i is an open question. We will assume its existence and notice that in this limit and in the absence of external fields (homogeneity limit)*

$$g_{ij} = g_{ij}\left(|\vec{r}_i - \vec{r}_j|, \rho_1, \ldots \rho_i, \ldots \rho_m, \beta\right) \tag{1.5}$$

We will not write explicitly unless needed the dependence of g_{ij} on ρ_i and β .

We know some of the properties of the exact $g_{ij}(r)$ before solving.

Namely,

$$g_{ij}(r) = 0 \quad \text{for} \quad r < R_{ij} \tag{1.5a}$$

which is just the statement of hard spheres impenetrability.

$g_{ij}(r) \underset{r \to \infty}{\longrightarrow} 1$ (at least for a single phase system) in such a way as to make the following integral convergent:

$$\int_0^\infty |g_{ij}(r) - 1|\, r\, dr < \infty \tag{1.5b}$$

We will also use the direct correlation $C_{ij}(r)$ functions of Ornstein and Zernike[6] defined in the infinite volume limit for homogenous system by $(h_{ij} \equiv g_{ij} - 1)$

$$h_{ij}(r) \equiv C_{ij}(r) + \int_{V \to \infty} \sum_{\ell} \rho_\ell\, h_{i\ell}(|\vec{r}\,'|)\, C_{\ell j}(|\vec{r} - \vec{r}\,'|)\, d^3\vec{r}\,' \tag{1.6}$$

---

* The thermodynamic limit has been shown to exist only recently by Lebowitz and Lieb in reference (13) for systems of particles interacting via Coulomb interaction if the particles have hard cores, or the Pauli exclusion principle is valid for the quantum domain. A further requirement of the proof is the overall electroneutrality of the fluid, and it is only valid for the free energy density, existence has not been proven rigorously so far, for the correlation functions.

And we know $C_{ij}(r) = C_{ji}(r)$

From the point of view of the rigorous Statistical Mechanics theory it is in principle possible to solve for g_{ij} from its definition. In practice the problem is so complicated that in 50 years of existence of the model the approximations used are only valid for very low ion concentrations.*

It is the scope of this dissertation to investigate the properties of a particular approximation to the primitive model, we shall define it in Chapter 2 called the mean spherical model (m.s.m.).

It is well known that for the rigorous theory all the different methods of obtaining the thermodynamics of the system in question are equivalent, for instance from the knowledge of $g_{ij}(r)$ it is possible to calculate the pressure calculating the free energy with $g_{ij}(r)$, get it from the Virial theorem or the compressibility relation, etc. When dealing with approximations, however, the different methods will yield different results for the thermodynamics of the given system. Keeping this in mind we will make explicit whenever working out thermodynamic properties via which way we have done it.

The most important approximation was made 47 years ago by Debye and Hückel[2] and it is valid for the limit of

---

* The extreme long range of the Coulomb potential adds a big part to the complications. Among other things the expansions techniques of the f-bond Mayer Theory[12],[14] can not be applied without special modifications, because the Virial coefficients diverge (even though the functions are assumed to exist), so resummations using parameters other than the density are needed.

infinitely diluted electrolytes with zero diameters of hard cores.* It was derived with completely different techniques than the ones we use here, but it is equivalent to the assumption that the direct correlation function is given by

$$C_{ij}(r) = -\beta\, e_i e_j / \varepsilon r \qquad 0 < r < \infty \tag{1.7}$$

Yielding

$$g_{ij}(r) = 1 - \frac{\beta}{\varepsilon} e_i e_j \, e^{-\kappa r}/r \tag{1.8}$$

$\kappa^2 = 4\pi \frac{\beta}{\varepsilon} \sum_{\ell} \rho_\ell e_\ell^2$; κ is called the inverse Debye length. From (1.8) all the thermodynamics can be calculated for the system. All the deficiencies of this approximation have been discussed over the years (the most obvious one $|g_{ij}| \xrightarrow[r \to 0]{} \infty$), yet it has been proven correct in the very low concentration limit and its main feature is that assymptotically as $r \to \infty$; $-1 + g_{ij} \to \text{Constant}\ \frac{e^{-\kappa r}}{r}$ which is a property of the screening of the Coulomb potential due to the electrical neutrality of the electrolyte.

---

* We refer to the original D-H theory, later attempts took account of the hard sphere part of the ion-ion interaction.

A recent new development for the theory of electrolytes is the work by Stillinger and Lovett[15] in which through rigorous and phenomenological considerations, they prove the existence of moment relations. We shall call these the Stillinger-Lovett moment relations for the exact radial correlation function.

They are:

(1.9a) $$4\pi \sum_{l} \rho_l e_l \int_0^\infty g_{il}(r)\, r^2\, dr = -e_i$$

which are the well-known local electroneutrality conditions and

(1.9b) $$4\pi \sum_{l,m} \rho_l \rho_m e_l e_m \int_0^\infty g_{lm}(r)\, r^4\, dr = -6 \sum_l \rho_l e_l^2 / \chi^2$$

In particular the Debye Hückel approximated g_{ij} fulfill these two moment conditions.

Besides giving a new element to judge a given approximation, Stillinger-Lovett prove in reference (16) that (1.9a) and (1.9b) prove the existence of oscillations in the charge cloud density for high enough ion concentrations if hard spheres interactions are present between ions.*

---

* We define the charge cloud density by

$$Q_j(r) = \sum_l \rho_l e_l g_{jl}(r) = \sum_l \rho_l e_l g_{lj}(r)$$

For simplicity we will just reproduce the argument for the case $e_1 = -e_2 = e$; $\rho_1 = \rho_2 = \rho$; $R_1 = R_2 = R$. For this case we have (we can integrate from r=R because of (1.5a)).

(1.10a) $$4\pi\rho \int_R^\infty \left[g_{11}(r) - g_{12}(r) \right] r^2 \, dr = -1$$

and

(1.10b) $$4\pi\rho \int_R^\infty \left[g_{11}(r) - g_{12}(r) \right] r^4 \, dr = -6/x^2.$$

If we assume $g(r) \equiv g_{11}(r) - g_{12}(r) < 0$ (as in the Debye Huckel approximation) we have noticing that $r^4 \geq r^2 R^2$ for $r \geq R$ from (1.10b) $4\pi\rho R^2 \int_R^\infty g(r) \, r^2 \, dr \geq -6/x^2$ using (1.10a) this implies $-R^2 \geq -6/x^2$ or $x^2 R^2 \leq 6$ which shows that for $x^2 R^2 \geq 6$ g(r) can not be always negative. We shall call $x_{crit} \equiv (xR)_{crit}$ the value of x such that if $x > x_{crit}$ roots of g(r) = o equation exist.

Finally other recent contribution to the understanding of the primitive model comes from the work of Rasaiah and Friedman.[7] They have done extensive calculations for the primitive model using different approximations leading to various integral equations. They have come to the conclusion that the hypernetted-chain approxmation is the best among the ones they considered for the primitive model. In a later paper they compare their results with machine calculations done by P. N. Voronstov-Veliamirov and A.M. Eliashevich. We shall compare some of our results with this work for $R_1 = R_2 = R$ and $e_1 = -e_2 = e$ for various densities in Chapter 3.

CHAPTER II

Motivations for the Mean Spherical Model

The mean spherical model approximate integral equation was constructed by Lebowitz and Percus[8] as a generalization to continuum systems of the well known spherical model for Ising spin systems. It consists of approximating the direct correlation function of the fluid by $-\beta v_{ij}(r)$ for $r > R_{ij}$ and recognizing the fact that the radial distribution function $g_{ij}(r)$ must be zero for $r < R_{ij}$ where R_{ij} is the distance of closest approach between molecules of class i and j. Therefore we have

$$
\begin{aligned}
g_{ij}(r) &= 0 \quad \text{for } r < R_{ij} \\
C_{ij}(r) &= -\beta v_{ij}(r) \quad \text{for } r > R_{ij}
\end{aligned}
\tag{2.1}
$$

For the primitive model of electrolytes we therefore obtain

$$
\begin{aligned}
g_{ij}(r) &= 0 \quad \text{for } r < R_{ij} \\
C_{ij}(r) &= -\beta e_i e_j / \varepsilon r \quad \text{for } r > R_{ij}
\end{aligned}
\tag{2.2}
$$

The several arguments that make this approximation plausible are:

(a) The original Debye-Hückel[2] theory for infinitely diluted electrolytes is included in the m.s.m. when $R_{ij} \to 0$

(b) When expanding graphically.

$$C_{ij}(r) = -\beta v_{ij}(r) \quad \forall r ;\ 0 < r < \infty$$

is the first order approximation in the high temperature limit[9].

(c) When $e_i \to 0$ we recover the P.Y. approximation for the uncharged hard spheres system that works extremely well when compared with the rigorous Statistical Mechanics Theory and experiments.

(d) As a kind of a posteriori argument we have found meaningful cases for which we have obtained the exact solution for the m.s.m. (namely $R_1 = R_2 = R$ equal size of hard cores); and we are confident that the m.s.m. can be solved exactly in other cases.

(e) Imposing the valid condition that $rC_{ij}(r)$ remains bounded for $r < R_{ij}$ (of course by construction it is already bounded for $r > R_{ij}$), the m.s.m. satisfies the Stillinger-Lovett relations for the primitive model of electrolytes as we have discussed it in Chapter I.

The proof we are going to give was constructed by Groeneveld[11] and works not only for the m.s.m. but any theory of electrolytes (like the m.s.m.) for which it is true that

$$\hat{C}_{ij}(k)^{*} = -4\pi e_i e_j \beta/\varepsilon k^2 + \xi_{ij}(k)$$

(2.3)

Where $\lim_{k\to 0} k^2 \xi_{ij}(k) = 0$; $\hat{C}_{ij}(k)$

is the 3-dimensional Fourier transform of $C_{ij}(r)$ and (2.3) is the statement that $C_{ij}(r) = -\beta e_i e_j/\varepsilon r + o\left(\frac{1}{r}\right)$ as $r \to \infty$ and that $\lim_{r\to 0} C_{ij}(r)r$ exists and it is finite.

It is straightforward to see that Stillinger-Lovett moment relations are in Fourier space given by

(2.4a) $$\lim_{k\to 0} \sum_{l} \rho_l e_l \hat{g}_{il}(k) = \lim_{k\to 0} \sum_{l} \rho_l e_l \hat{h}_{il}(k) = -e_i$$

and $\lim_{k\to 0} \sum_{l,m} \rho_l \rho_m e_l e_m \, d^2 \hat{g}_{lm}(k)/dk^2 =$

(2.4b) $$= \lim_{k\to 0} \sum_{l,m} \rho_l \rho_m e_l e_m \, d^2 \hat{h}_{lm}(k)/dk^2 = \varepsilon/2\pi\beta$$

$\hat{g}_{ij}(k)$ and $\hat{h}_{ij}(k)$ are the 3-dimensional Fourier transforms of $g_{ij}(r)$ and $h_{ij}(r)$ respectively. Using the convolution theorem for 3-dimensional Fourier transform the defining relation between $C_{ij}(r)$ and $g_{ij}(r)$ (eq.1.6) becomes in Fourier space:

---

* The 3-dimensional Fourier transform of a function $\gamma(\vec{r})$ is defined by

$$\hat{\gamma}(\vec{k}) = \int_V \gamma(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}\, d^3\vec{r}$$

then if $\gamma(\vec{r}) = \gamma(|\vec{r}|)$ it implies $\hat{\gamma}(\vec{k}) = \hat{\gamma}(|\vec{k}|)$

(II.5) $\hat{h}_{ij}(k) = \hat{c}_{ij}(k) + \sum_{\ell} \rho_\ell \hat{h}_{i\ell}(k)\hat{c}_{\ell j}(k)$

or in matrix notation: $\underline{\underline{\hat{h}}}(k) = \underline{\underline{\hat{c}}}(k)\left[\underline{\underline{I}} - \underline{\underline{\rho}}\,\underline{\underline{\hat{c}}}(k)\right]^{-1}$

$\underline{\underline{\rho}} \equiv \begin{pmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{pmatrix} \qquad \underline{\underline{I}} \equiv \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$

Going to the k=o limit we can write from (2.5).

$$\lim_{k\to 0} \sum_{\ell} \left(\hat{h}_{i\ell}(k)\right)\left(\delta_{\ell j} - \rho_\ell \hat{c}_{\ell j}(k)\right) = \lim_{k\to 0} \hat{c}_{ij}(k)$$

Multiplying through by k^2 and imposing (2.3) we have

$$-\lim_{k\to 0} \sum_{\ell} \hat{h}_{i\ell}(k)\rho_\ell k^2 \hat{c}_{\ell j}(k) = \lim_{k\to 0} \hat{c}_{ij}(k)\,k^2$$

or

$$\lim_{k\to 0} \sum_{\ell} \hat{h}_{i\ell}(k)\rho_\ell e_\ell e_j = -e_i e_j$$

which takes us to the desired relation: $\lim_{k\to 0} \sum_{\ell} \rho_\ell e_\ell \hat{h}_{i\ell}(k) = -e_i$

For the second moment relation we have from (2.5)

$$\underline{\underline{\hat{h}}}(k) = \frac{\underline{\underline{\hat{c}}}(k) - \Delta(k)\begin{pmatrix} \rho_2 & 0 \\ 0 & \rho_1 \end{pmatrix}}{1 - \rho_1\hat{c}_{11} - \rho_2\hat{c}_{22} + \rho_1\rho_2\Delta(k)}$$

where

$$\Delta(k) \equiv \det \underline{\underline{\hat{c}}}(k) = \hat{c}_{11}(k)\hat{c}_{22}(k) - \left(\hat{c}_{12}(k)\right)^2 = \det \underline{\underline{\xi}}(k),$$

the last equality follows from (2.3) so we will have

(using (2.3) again)

$$\sum_{l,m} \rho_l \rho_m e_l e_m \hat{h}_{lm}(k) =$$

$$= \frac{-4\pi \frac{\beta}{\varepsilon k^2}\left(\rho_1 e_1^2 + \rho_2 e_2^2\right)^2 + \sum_{l,m} \rho_l \rho_m e_l e_m \xi_{lm} - \det \underline{\underline{\xi}}\, \rho_1 \rho_2 \left(\rho_1 e_1^2 + \rho_2 e_2^2\right)}{1 + 4\pi \frac{\beta}{\varepsilon k^2}\left(\rho_1 e_1^2 + \rho_2 e_2^2\right) - \rho_1 \xi_{11} - \rho_2 \xi_{22} + \rho_1 \rho_2 \det \underline{\underline{\xi}}}$$

differentiating twice and going to $k \to o$ limit we get

$$\lim_{k \to 0} \sum_{l,m} \rho_l \rho_m e_l e_m\, d^2 \hat{h}_{lm}(k)/dk^2 = \lim_{k \to 0} \frac{d^2}{dk^2} \frac{\left(\rho_1 e_1^2 + \rho_2 e_2^2\right)^2}{\rho_1 e_1^2 + \rho_2 e_2^2 - \varepsilon k^2/4\pi\beta} =$$

$$= \varepsilon/2\pi\beta$$

which is the wanted result. Here we have assumed that

$\xi_{ij}(k)$ is twice differentiable near $k=o$.

CHAPTER III: The mean spherical model (m.s.m.)

As we already said the m.s.m. for the primitive model of an electrolyte consists of the following equations:

(3.1a) $$g_{ij}(r) = 0 \qquad \text{for} \quad r < R_{ij}$$

(3.1b) $$C_{ij}(r) = -\beta v_{ij}(r) = -\beta \frac{e_i e_j}{\varepsilon r} \qquad \text{for} \quad r > R_{ij}$$

Equation (3.1a) is a true statement that the exact radial distribution function must satisfy and comes about from the impenetrability of hard spheres. Therefore (3.1b) constitutes the approximation to the exact theory given by the m.s.m.

Since we already have the equation relating $C_{ij}(r)$ with $g_{ij}(r)$ eq. 1.6 , solving the m.s.m. consists of obtaining $C_{ij}(r)$ for $r < R_{ij}$ such that $g_{ij}(r)=0$ for $r < R_{ij}$, and conjunctly with (3.1b) C_{ij} determined $\forall r$, then $g_{ij}(r)$ is determined by inverting the relationship between g_{ij} and C_{ij}.

Rewriting the defining equation between g_{ij} and C_{ij} (Eq. 1.6).

(3.2) $$h_{ij}(r) = C_{ij}(r) + \sum_{\ell} \rho_\ell \int_{V\to\infty} h_{i\ell}(|\vec{r}'|)\, C_{\ell j}(|\vec{r}-\vec{r}'|)\, d^3\vec{r}'$$

where we have introduced $h_{ij}(r)=g_{ij}(r)-1$. We now define a matrix C°_{ij} such that

(3.3) $$C_{ij}(r) \equiv C^{\circ}_{ij}(r) - \beta e_i e_j / \varepsilon r$$

It is immediately seen that $C^{\circ}_{ij}(r) = o$ for $r > R_{ij}$ to satisfy (3.1b).

Using the electrical neutrality of the electrolyte solution $\sum_{\ell} \rho_\ell e_\ell = 0$, we notice

(3.4)
$$\sum_{\ell} \rho_\ell \int_V C_{\ell j}(|\vec{r}-\vec{r}'|)\, d^3\vec{r}' = {}^{*}$$
$$= \sum_{\ell} \rho_\ell \int_V C^{(o)}_{\ell j}(|\vec{r}-\vec{r}'|)\, d^3\vec{r}' - \frac{\beta}{\varepsilon} e_j \overbrace{\sum_{\ell} \rho_\ell e_\ell}^{o} \int_V \frac{d^3\vec{r}'}{|\vec{r}-\vec{r}'|} =$$
$$= \sum_{\ell} \rho_\ell \int_V C^{(o)}_{\ell j}(|\vec{r}-\vec{r}'|)\, d^3\vec{r}'$$

With exactly the same arguments we have

(3.5) $$\sum_{\ell} \rho_\ell e_\ell e_j \int_V \frac{h_{i\ell}(|\vec{r}'|)}{|\vec{r}-\vec{r}'|}\, d^3\vec{r}' = \sum_{\ell} \rho_\ell e_\ell e_j \int_V \frac{g_{i\ell}(|\vec{r}'|)\, d^3\vec{r}'}{|\vec{r}-\vec{r}'|}$$

---

* Here V is the volume of the system that is then made to go to the $V \to \infty$; $\rho_i \to$ const, $\rho_j \to$ constant thermodynamic limit that as we stated in Chapter I was proven to exist for the partition function by Lebowitz and Lieb (13) and it is assumed to exist for the pair correlation function we are here working with. Besides we work throughout with the mean densities ρ_ℓ which implies, of course, the limit $V \to \infty$.

Now substituting (3.3) and (3.5) in (3.2) we get: (When no dependence on distances is indicated we understand the function to be dependent on r).

(3.6)
$$h_{ij} = C^{o}_{ij} - \frac{\beta}{\varepsilon r} e_i e_j + \sum_{l} \rho_l \int_V h_{il}(|\vec{r}\,'|)\, C^{o}_{lj}(|\vec{r}-\vec{r}\,'|)\, d^3\vec{r}\,' - \frac{\beta}{\varepsilon} \sum_{l} \rho_l e_l e_j \int_V h_{il}(|\vec{r}\,'|) \frac{d^3\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}$$

We now work in spherical coordinates with the second integral in the right hand-side of equation (3.6), namely $I = \int_0^\infty x^2 g_{il}(x) \int \frac{d\Omega}{|\vec{r}-\vec{r}\,'|}$; performing the angular integration ; I becomes

$$I = \frac{4\pi}{r} \int_0^r g_{il}(x)\, x^2 dx + 4\pi \int_r^\infty g_{il}(x)\, x\, dx$$

Further I can be written

(3.7)
$$I = \frac{4\pi}{r} \int_0^\infty g_{il}(x)\, x^2 dx - \frac{4\pi}{r} \int_r^\infty g_{il}(x)\, x^2 dx + 4\pi \int_r^\infty g_{il}(x)\, x\, dx$$

On the other hand the (Equation 1.9a) implies

(3.8)
$$4\pi \sum_{l} \rho_l e_l \int_0^\infty g_{il}(x)\, x^2 dx = - e_i$$

Therefore equation (3.6) with the help of (3.7) and (3.8) reads :

(3.9)
$$h_{ij} - C^{o}_{ij} - \sum_{l} \rho_l \int_V h_{il}(|\vec{r}\,'|)\, C^{o}_{lj}(|\vec{r}-\vec{r}\,'|)\, d^3\vec{r}\,' =$$
$$= - \frac{4\pi\beta}{\varepsilon} \sum_{l} \rho_l e_l e_j \left[\int_r^\infty g_{il}(x)\, x\, dx - \frac{1}{r} \int_r^\infty g_{il}(x)\, x^2 dx \right]$$

The left-hand side of this equation equated to zero would be precisely the P.Y. equation for pure hard spheres potential if instead of $\overset{\circ}{C}_{ij}$ we had the full (hard spheres) C_{ij}. Recalling the techniques Lebowitz[1] employs we see that we can use the same manipulations for the left-hand side of equation (3.9) because as in the case of pure hard spheres we also have here,

(a) $\overset{\circ}{C}_{ij}(r) = 0 \quad \text{for } r > R_{ij}$

(b) We only will admit solutions such that $\overset{\circ}{C}_{ij}(r)\, r$ is bounded for $0 \leq r \leq R_{ij}$

(c) $h_{ij}(r) = -1 \quad$ for $\quad r < R_{ij}$

We therefore define

(3.10)
$$\sigma_{ij}(r) = 2\pi\sqrt{\rho_i \rho_j}\; r \begin{cases} g_{ij} & \text{for } r > R_{ij} \\ -\overset{\circ}{C}_{ij} & \text{for } r < R_{ij} \end{cases}$$

Multiplying both sides of equation (3.9) by $2\pi\sqrt{\rho_i\rho_j}\, r$ and using bipolar coordinates for the left hand-side, we obtain

(3.11)
$$\sigma_{ij} - A_{ij} r + \sum_{\ell} \int_{R_{i\ell} \leq y}^{\infty} dy\, \sigma_{i\ell}(y) \int_{|r-y|<R_{\ell j}}^{\text{Min}[r+y;\, R_{\ell j}]^{*}} \sigma_{\ell j}(u)\, du =$$
$$= -4\pi \frac{\beta}{\varepsilon} r \sum_{\ell} \sqrt{\rho_\ell \rho_j}\, e_\ell e_j \int_{\text{Max}[r, R_{i\ell}]} \sigma_{i\ell}(x)\, dx + \frac{4\pi\beta}{\varepsilon} \sum_{\ell} \sqrt{\rho_\ell \rho_j}\, e_\ell e_j \int_{\text{Max}[r, R_{i\ell}]} \sigma_{i\ell}(x)\, x\, dx$$

* When $|r-y|<R_{\ell j}$ and $y > R_{i\ell}$ we understand that the double integral vanishes for r's such that the two inequalities are not simultaneously satisfied.

Where $A_{ij} = 2\pi\sqrt{\rho_i\rho_j}\; a_j =$

$$= 2\pi\sqrt{\rho_i\rho_j}\left[1 - \sum_\ell \rho_\ell \int_V c_{\ell j}(|\vec{r}'|)\, d^3\vec{r}'\right] =$$

$$= 2\pi\sqrt{\rho_i\rho_j}\left[1 - 4\pi\sum_\ell \rho_\ell \int_0^{R_{\ell j}} c^{(0)}_{\ell j}(x)\, x^2\, dx\right]; \text{ with}$$

$$x = |\vec{r}'|$$

Differentiating $\frac{d}{dr}$ both sides we get, (since we have assumed $R_2 \geq R_1$, it follows that

$$\mathrm{Min}\,[r+y;\, R_{\ell j}] = R_{\ell j} \quad \text{unless } (i,j) = (1,2))$$

$$\sigma_{ij}^{(1)*} - A_{ij} - \sum_\ell \int_{\substack{|r-y| < R_{\ell j} \\ y > R_{i\ell}}} dy\, \sigma_{i\ell}(y)\, \sigma_{\ell j}(|\vec{r}-y|)\, \mathrm{sign}\,(r-y) +$$

$$+ P_{ij}(r) = -4\pi \frac{\beta}{\mathcal{E}} \sum_\ell \sqrt{\rho_\ell\rho_j}\; e_\ell e_j \int_{\mathrm{Max}\,[r,\, R_{i\ell}]}^{\infty} \sigma_{i\ell}(x)\, dx$$

$$\text{where} \quad P_{ij}(r) = \delta_{i1}\delta_{j2} \begin{cases} 0 & \text{if } r \geq \frac{R_2 - R_1}{2} \equiv \lambda \\ \displaystyle\sum_\ell \int_{R_{1\ell}+r}^{R_{\ell 2}} \sigma_{1\ell}(z-r)\, \sigma_{\ell 2}(z)\, dz; & r \leq \lambda \end{cases}$$

---

* We use the notation $\sigma_{ij}^{(1)}$, $\sigma_{ij}^{(2)}$ to mean first and second derivatives with respect to r respectively.

From equation (3.11) we have for $(i,j) \neq (1,2)$

(but that's enough because we know $\sigma_{12}(r) = \sigma_{21}(r)\ \forall r$)

$$\sigma_{ij}(0) = \frac{4\pi\beta}{\varepsilon} \sum_{l} \sqrt{\rho_l \rho_j}\, e_l e_j \int_{R_{il}}^{\infty} \sigma_{il}(x)\, x\, dx$$

(the double integral term vanishes because $|r-y| = y$ for

r=o and $y > R_{il} \geq R_{ej}$ for $(i,j) \neq (1,2)$

therefore the U integral is null).

Rewriting $\sigma_{il}(x)$ in terms of its definition (3.10) and remembering $g_{il}(r) = 0$ for $r < R_{il}$ we have

$$\sigma_{ij}(0) = \frac{4\pi\beta}{\varepsilon} \sum_{l} \sqrt{\rho_j \rho_i}\; 2\pi \rho_l e_l e_j \int_{0}^{\infty} g_{il}(x)\, x^2 dx =$$

(3.13)

$$= -\frac{2\pi\beta}{\varepsilon} \sqrt{\rho_i \rho_j}\, e_i e_j \equiv -\frac{K^2}{4} D_{ij} \equiv -\frac{K^2}{4} (\underline{\underline{D}})_{ij}^{*}$$

Where we used again Equation (1.9a).

---

* We have defined $K^2 \equiv 8\pi\beta/\varepsilon$ and $D_{ij} \equiv \sqrt{\rho_i \rho_j}\, e_i e_j$.

Here $\sigma_{ij}(0) \neq 0$ and this is an important difference between our case and the pure hard spheres one.

From equation (3.12) we have (again $(i,j) \neq (1,2)$ and the integral on the left hand-side vanishes for $r = 0$)

(3.14) $$\sigma_{ij}^{(1)}(0) = A_{ij} - 4\pi \frac{\beta}{\varepsilon} \sum_{\ell} \sqrt{\rho_\ell \rho_j}\, e_\ell e_j \int_{R_{i\ell}}^{\infty} \sigma_{i\ell}(x)\,dx =$$

$$= A_{ij} - \frac{K^2}{2} V_{ij} \; ; \quad \text{with } (\underline{\underline{V}})_{ij} = V_{ij} \equiv \sum_{\ell} B_{i\ell} D_{\ell j}$$

where $$B_{i\ell} = \int_{R_{i\ell}}^{\infty} \sigma_{i\ell}(x)\,dx$$

It also follows from (3.12) that

(3.15) $$\sigma_{21}(r) = \sigma_{12}(r) = \left(A_{21} - \frac{K^2}{2} V_{21}\right) r$$

for $r \leq \lambda$.

III.1 Smoothness of σ_{ij}

By inspecting equation (2.11) we see that σ_{ij} (r) can not have any δ-like singularities in its entire range of definition and furthermore we also can prove from equation (3.11) and its derivatives that:

(a) $\sigma_{ii}(r)$; $\sigma_{ii}^{(1)}(r)$; $\sigma_{ii}^{(2)}(r)$; $\sigma_{21}^{(1)}(r)$

are continuous for $0 < r < \infty$ and

(b) $\sigma_{21}^{(2)}(r)$ is discontinuous only across $r = \lambda$, for $0 < r \leq R_{21}$

It is easily seen that the only points at which one might expect discontinuities in σ_{ij} and its 2 first derivatives are $r = R_{i\ell}$; $r = R_{i\ell} + R_{\ell j}$; $\ell = 1,2$; and $r = \lambda$. For $(i,j) \neq (1,2)$ we have from equation (3.11) and (3.12) that σ_{ij} and $\sigma_{ij}^{(1)}$ are continuous everywhere, particularly across R_{ij} and λ, because if we write from equations (3.11) and (3.12) $\sigma_{ij}(r+\varepsilon) - \sigma_{ij}(r)$; and $\sigma_{ij}^{(1)}(r+\varepsilon) - \sigma_{ij}^{(1)}(r)$; $\varepsilon > 0$ we see that all the other terms in the equations are continuous. Next we can prove that

. $\sigma_{ij}^{(2)}$ is continuous across R_{ij}

.. $\sigma_{21}^{(2)} = \sigma_{12}^{(2)}$ is discontinuous across λ

... $\sigma_{ij}^{(2)}$ is discontinuous across $R_{i\ell}+R_{ij}$

To see this we rewrite equation (3.12) replacing the condition in the integral of the left hand-side that if $|r-y| < R_{\ell j}$ it vanishes, by a Heaviside function

$$\mathcal{H}(R_{\ell j} - |r-y|) \; ; \quad \mathcal{H}(u) \begin{array}{ll} \nearrow 0 & u<0 \\ \searrow 1 & u>0 \end{array}$$

Eq. (3.12) becomes then for

$$(i,j) \neq (1,2)$$

$$\sigma_{ij}^{(1)} - A_{ij} - \sum_{\ell} \int_{R_{i\ell}}^{\infty} dy\, \sigma_{i\ell}(y)\, \sigma_{\ell j}(|r-y|)\, \mathrm{sign}\,(r-y)\, \mathcal{H}(R_{\ell j} - |r-y|) =$$

$$= -\frac{4\beta}{\varepsilon} \sum_{\ell} \sqrt{\rho_\ell \rho_j}\, e_\ell e_j \int_{\mathrm{Max}[r, R_{i\ell}]}^{\infty} \sigma_{i\ell}(x)\, dx$$

Differentiating we obtain

$$\sigma_{ij}^{(2)} - \sum_{\ell} \frac{d}{dr} Q_{ij\ell} = 4\pi \frac{\beta}{\varepsilon} \sum_{\ell} \sqrt{\rho_\ell \rho_j}\, e_\ell e_j\, \sigma_{i\ell}(r)\, \mathcal{H}(r - R_{i\ell}) = \tag{3.17}$$

$$= -2 \sum_{\ell} \sigma_{\ell j}(0)\, \sigma_{i\ell}(r)\, \mathcal{H}(r - R_{i\ell})$$

where

$$Q_{ij\ell}(r) = \int_{R_{i\ell}}^{\infty} dy\, \sigma_{i\ell}(y)\, \sigma_{\ell j}(|r-y|)\, \mathrm{sign}(r-y)\, \mathcal{H}(R_{\ell j} - |r-y|)$$

and the last equality in Eq. (3.16) follows from (3.13). Now

$$\frac{d}{dr} Q_{ij\ell}(r) = \int_{R_{i\ell}}^{\infty} dy\, \sigma_{i\ell}(y)\, \sigma_{\ell j}^{(1)}(|r-y|)\, \mathrm{sign}\,(r-y)\, \mathcal{H}(R_{\ell j} - |r-y|) +$$

$$+ 2 \int_{R_{i\ell}}^{\infty} dy\, \sigma_{i\ell}(y)\, \sigma_{\ell j}(|r-y|)\, \delta(r-y)\, \mathcal{H}(R_{\ell j} - |r-y|) + \int_{R_{i\ell}}^{\infty} dy\, \sigma_{i\ell}(y)\, \sigma_{\ell j}(|r-y|)\, \delta((y-(r+R_{\ell j})) +$$

$$+ \int_{R_{i\ell}}^{\infty} dy\, \sigma_{i\ell}(y)\, \sigma_{\ell j}(|r-y|)\, \delta(r - R_{\ell j} - y)$$

Calling the four terms of the derivative of $Q_{ij\ell}$

Q_o, Q_1, Q_2, Q_3 we have

Q_o continuous everywhere

$$Q_1 = \begin{cases} 0 & \text{if } r < R_{i\ell} \\ 2\, \sigma_{i\ell}(r)\, \sigma_{\ell j}(0) & r > R_{i\ell} \end{cases}$$

$$Q_2 = \begin{cases} (i,j) = (2,1) & \begin{cases} 0 & \text{if } r < \lambda \\ \sigma_{i\ell}(r+R_{\ell j})\, \sigma_{\ell j}(R_{\ell j}) & ;\ r > \lambda \end{cases} \\ i = j & \sigma_{i\ell}(r+R_{\ell j})\, \sigma_{\ell j}(R_{\ell j}) \quad \forall r \end{cases}$$

(3.18)

$$Q_3 = \begin{cases} \to 0 & \text{if} \quad r < R_{i\ell} + R_{\ell j} \\ \to -\sigma_{i\ell}(r - R_{\ell j})\,\sigma_{\ell j}(R_{\ell j}), & \text{for } r > R_{i\ell} + R_{\ell j} \end{cases}$$

Putting (3.18) back in (3.17) we see that the discontinuity in $\frac{d}{dr}\sum_{\ell} Q_{ij}$ is just cancelled with the discontinuity for the right hand-side at $R_{i\ell}$. Clearly this shows that the statements (a) and (b) of page 23 are true.

III.2 The Laplace Space Equation for the m.s.m.

To seek the solution for the m.s.m. we take the Laplace transform of equation (3.12), that is, given $f(r)$ its Laplace transform is defined by

$$\mathcal{L}\left(f(r)\right) = \int_0^\infty f(r)\, e^{-sr}$$

The Laplace transform of the left hand-side of equation (3.12) yields the same expression that the P.Y. equation for uncharged hard spheres did with the exception of the fact that $\sigma_{ij}(0) \neq 0$ for the charged system (Eq. 3.13), so recalling that

$$\mathcal{L}\left(\sigma_{ij}^{(1)}(r)\right) = s\mathcal{L}\left(\sigma_{ij}(r)\right) - \sigma_{ij}(0)$$

we get for the left hand-side: (using (3.13).

$$s\left[\underline{\underline{G}}(s)+\underline{\underline{F}}(s)\right]+\frac{K^2}{4}\underline{\underline{D}}-\underline{\underline{A}}/s+\underline{\underline{G}}(s)\left[\underline{\underline{F}}(s)-\underline{\underline{F}}(-s)\right]-\underline{\underline{\Gamma}}(s)=$$

$$=\mathcal{L}\left[-\frac{K^2}{2}\sum_{l}\sqrt{\rho_l\rho_j}\,e_l e_j\int_{Max[r,R_{il}]}^{\infty}\sigma_{il}(x)\,dx\right.=$$

$$=-\frac{K^2}{2s}\underline{\underline{V}}+\frac{K^2}{2}\underline{\underline{G}}(s)\underline{\underline{D}}$$

where $\left(\underline{\underline{G}}\right)_{ij}=G_{ij}(s)=\int_{R_{ij}}^{\infty}\sigma_{ij}(r)\,e^{-sr}\,dr$

(3.B) $$\left(\underline{\underline{F}}\right)_{ij}=F_{ij}(s)=\int_0^{R_{ij}}\sigma_{ij}(r)\,e^{-sr}\,dr$$

$$\left(\underline{\underline{\Gamma}}\right)_{ij}=\Gamma_{ij}(s)=\delta_{i1}\delta_{j2}\Gamma_{12}(s)=\delta_{i1}\delta_{j2}\left[P(-s)-P(s)\right]$$ where

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

The matrices $\underline{\underline{V}}$, $\underline{\underline{D}}$ have already been defined and so have P(r) and K.

Grouping :

(3.19) $$\underline{\underline{G}}(s)\left[\underline{\underline{I}}\,s^2-s\underline{\underline{F}}^{\pm}(s)-\frac{K^2}{2}\underline{\underline{D}}\right]=$$

$$=\left[\underline{\underline{A}}-s^2\underline{\underline{F}}(s)+s\underline{\underline{\Gamma}}(s)-\frac{K^2}{4}\left(s\underline{\underline{D}}+2\underline{\underline{V}}\right)\right]$$

where $\underline{\underline{F}}^{\pm}(s)$ is a short-hand symbol for $\underline{\underline{F}}(s)-\underline{\underline{F}}(-s)$

Solving for $\underline{\underline{G}}$:

$$\underline{\underline{G}}(s) = \left[\underline{\underline{A}} + s\underline{\underline{\Gamma}} - s^2\underline{\underline{F}} - \frac{K^2}{4}(s\underline{\underline{D}} + 2\underline{\underline{V}})\right] \cdot$$

$$\cdot \left[s^2\underline{\underline{I}} - s\underline{\underline{F}}^{\pm}(s) - \frac{K^2}{2}\underline{\underline{D}}\right]^{-1} = \underline{\underline{H}}(s)\,\underline{\underline{K}}(s)$$

(3.20)

where

$$\underline{\underline{H}}(s) = \underline{\underline{A}} + s\underline{\underline{\Gamma}} - s^2\underline{\underline{F}} - \frac{K^2}{4}(s\underline{\underline{D}} + 2\underline{\underline{V}})$$

$$\underline{\underline{K}}(s) = \left[\underline{\underline{I}}\,s^2 - s\underline{\underline{F}}^{\pm}(s) - \frac{K^2}{2}\underline{\underline{D}}\right]^{-1}$$

We can verify that equation (3.19) goes to the correct P.Y. uncharged hard spheres equation when e_i, $e_j \to 0$ because then $\underline{\underline{D}} \to 0$ and $\underline{\underline{V}} \to 0$ and we recover the equation we had for that case (eq. (21) ref. (1)).

The other limit $R_{ij} \to o$ should give the Debye-Hückel result[(2)], when $R_{ij} \to o$. In this case

$$F_{ij}(s);\ \Gamma_{ij}(s) \to 0 \qquad A_{ij} \to 2\pi\sqrt{\rho_i\rho_j}$$

and

(3.20) becomes in this limit:

$$\underline{\underline{G}}(s) = \frac{\left(\underline{\underline{A}} - \frac{K^2}{4}s\underline{\underline{D}} - \frac{K^2}{2}\underline{\underline{V}}\right)\left(s^2\underline{\underline{I}} - \frac{K^2}{2}\underline{\underline{D}}^*\right)}{s^2\left(s^2 - \frac{K^2}{2}(D_{11} + D_{22})\right)}$$

where $D^* = \begin{pmatrix} D_{22} & -D_{21} \\ -D_{21} & D_{11} \end{pmatrix}$; and we used that: $D_{12} = D_{21}$

but $\underline{\underline{D}} \; \underline{\underline{D}}^* = \underline{\underline{V}} \; \underline{\underline{D}}^* = 0$

and $\varkappa^2 = \frac{K^2}{2} (D_{11} + D_{22})$

($\varkappa$ is the Debye inverse length) giving

$$(3.20a) \qquad \underline{\underline{G}}(s) = \frac{s^2\left(\underline{\underline{A}} - \frac{K^2}{4} s \underline{\underline{D}} - \frac{K^2}{2} \underline{\underline{V}}\right) - \frac{K^2}{2} \underline{\underline{A}}\,\underline{\underline{D}}^*}{s^2 (s+\varkappa)(s-\varkappa)}$$

We know we must have $\underline{\underline{G}}(s) = \underline{\underline{A}}\, s^{-2} +$ other terms ......

(see (3.22)

for $g_{ij}(r) \to 1$, when $r \to \infty$

Then we obtain from (3.20a) after some algebra

$$(3.20b) \qquad \underline{\underline{G}}(s) = \frac{\underline{\underline{A}}}{s^2} - \frac{K^2}{4} \frac{s\underline{\underline{D}} + 2\underline{\underline{V}}}{(s+\varkappa)(s-\varkappa)} \quad \text{besides.}$$

The factor $s-\varkappa$ in the denominator must be cancelled out by the numerator, otherwise the existence of such a factor means that $g_{ij}(r)$ would have a $e^{\varkappa r}$ mode which is not physically possible. This requires

$$s\,\underline{\underline{D}} + 2\,\underline{\underline{V}} = (s-\varkappa)\,\underline{\underline{D}} \Rightarrow$$

$$\underline{\underline{V}} = -\frac{\varkappa}{2}\,\underline{\underline{D}}$$

which recalling the definition of $\underline{\underline{B}}$ is indeed the Debye-[2] Hückel result and from (3.20b)

$$\underline{\underline{G}}(s) = \underline{\underline{A}}/s^2 - \frac{K^2}{4}\frac{\underline{\underline{D}}}{s+x}$$

, and going back to physical space :

$$\sigma_{ij}(r) = A_{ij} - \frac{K^2}{4}\sqrt{\rho_i\rho_j}\, e_i e_j\, e^{-xr}$$

or

(3.20d)
$$g_{ij}(r) = 1 - \frac{K^2}{8\pi} e_i e_j \frac{e^{-xr}}{r}$$

which is exactly what we wanted.

III.3 The s-complex plane

We consider (3.20) in the s-complex plane. Following closely Lebowitz's techniques[1]. First of all $F_{ij}(s)$ is an entire function because we have assumed $rC_{ij}^{(o)}$ bounded and it is a Laplace transform over the finite interval (o, R_{ij}). Furthermore from the continuity properties of σ_{ij} and its derivatives.

(3.21)
$$\lim_{s\to\infty} F_{ii}(s) = \frac{1}{s}\left(\sigma_{ii}(0) - \sigma_{ii}(R_i)e^{-sR_i}\right) + \frac{1}{s^2}\left(\sigma_{ii}^{(1)}(0) - \sigma_{ii}^{(1)}(R_i)e^{-sR_i}\right) + \frac{1}{s^3}\left(\sigma_{ii}^{(2)}(0) - \sigma_{ii}^{(2)}(R_i)e^{-sR_i}\right) + \ldots\ldots$$

$$\lim_{s\to\infty} F_{21}(s) = \frac{1}{s}\left(\sigma_{21}(0) - \sigma_{21}(R_{21})e^{-sR_{21}}\right) + \frac{1}{s^2}\left(\sigma_{21}^{(1)}(0) - \sigma_{21}^{(1)}(R_{21})e^{-sR_{21}}\right) + \frac{1}{s^3}\left[\sigma_{21}^{(2)}(0) + \left(\sigma_{21}^{(2)}(\lambda^+) - \sigma_{21}^{(2)}(\lambda^-)\right)e^{-s\lambda} - \sigma_{21}^{(2)}(R_{21})e^{-sR_{21}}\right] + \ldots\ldots$$

It follows that $\underline{\underline{H}}(s)$ is an entire function of s. On the other hand the solutions of the m.s.m. that are physically meaningful are those for which $g_{ij}(r) \xrightarrow[r\to\infty]{} 1$ in such a way as to have $\int_0^\infty r\,|g_{ij}(r)-1|\,dr < \infty$ * ; This requires that: $G_{ij}(s) - 2\pi\sqrt{\rho_i\rho_j}/s^2$ is an analytic function of s in the closed right-hand plane of the complex s-plane.

And we can see that for $s \to \infty$

$$G_{ij}(s)_{s\to\infty} = \frac{1}{s}\,\sigma_{ij}(R_{ij})\,e^{-sR_{ij}} + \frac{1}{s^2}\,\sigma_{ij}^{(1)}(R_{ij})\,e^{-sR_{ij}} + \frac{1}{s^3}\,\sigma_{ij}^{(2)}(R_{ij})\,e^{-sR_{ij}} + \ldots\ldots \tag{3.23}$$

From its definition $\Gamma_{12}(s) \xrightarrow[s\to\infty]{} O\left(e^{\lambda s}/s^2\right)$ and it is an even function $\Gamma_{12}(s) = \Gamma_{12}(-s)$.**

Now we write K(s) explicitly;

$$K(s) = \underline{\underline{I}}(s)/d(s)$$

---

* As a matter of fact this condition must be satisfied for any disordered fluid, see reference (10).

** $\Gamma_{12}(s)$ is not independent of the other quantities, it gets determined by the condition

$$G_{21}(s) = G_{12}(s).$$

$$(3.24)\qquad \underline{\underline{T}}(s) = \begin{bmatrix} s^2 - s\,F_{22}^{\pm}(s) - \frac{K^2}{2} D_{22} & s\,F_{12}^{\pm}(s) + \frac{K^2}{2} D_{21} \\ & \\ T_{21} = T_{12} & s^2 - s\,F_{11}^{\pm}(s) - \frac{K^2}{2} D_{11} \end{bmatrix}$$

and $$d(s) = s^4 + s^2\left[F_{11}^{\pm}F_{22}^{\pm} - (F_{21}^{\pm})^2\right] - s^3\left[F_{11}^{\pm} + F_{22}^{\pm}\right] - s^2\frac{K^2}{2}(D_{11} + D_{22}) +$$
$$+ \; s\frac{K^2}{2}\left(D_{11}F_{22}^{\pm} + D_{22}F_{11}^{\pm} - 2D_{21}F_{21}^{\pm}\right)$$

We have used here the fact that $F_{21}(s) = F_{12}(s)$ and $D_{21} = D_{12}$. It becomes transparent that $\underline{K}(s) = \underline{K}(-s) = \underline{K}^T(s)$ where the superscript T indicates the transpose of the corresponding matrix.

Next we define the matrix

$$(3.25)\quad L(s) = G(s)\, H^T(-s) \quad \text{or in components}$$

$$L_{ij}(s) = \sum_{\ell} G_{i\ell}(s)\, H_{j\ell}(-s)$$

As already stated $G_{i\ell}(s) - 2\pi\sqrt{\rho_i\rho_\ell}/s^2$ is analytical in the closed right hand s plane and $\underline{\underline{H}}(s)$ is entire. Therefore

$$L_{ij}(s) - \frac{2\pi}{s^2}\sum_{\ell}\sqrt{\rho_i\rho_\ell}\, H_{j\ell}(0) = \sum_{\ell} G_{i\ell}(s)\, H_{j\ell}(-s) - \frac{2\pi}{s^2}\sum_{\ell}\sqrt{\rho_i\rho_\ell}\, H_{j\ell}(0)$$

will be analytical in the closed right hand plane

And we also have

$$\sum_{\ell} \sqrt{\rho_i \rho_\ell}\; H_{j\ell}(0) = \sum_{\ell} \sqrt{\rho_i \rho_\ell}\; (A_{j\ell} - \frac{K^2}{2} V_{j\ell}) =$$

$$= \sum_{\ell} \sqrt{\rho_i \rho_\ell}\; A_{j\ell}$$

because

$$\sum_{\ell} \sqrt{\rho_i \rho_\ell}\; V_{j\ell} = \sum_{\ell, m} \sqrt{\rho_i \rho_\ell}\; B_{jm} D_{m\ell} =$$

$$= \sqrt{\rho_i} \sum_{m} B_{jm} \sum_{\ell} \sqrt{\rho_\ell}\, D_{\ell m} = \sqrt{\rho_i} \sum_{m} B_{jm} \sqrt{\rho_m}\, e_m \sum_{\ell} \rho_\ell e_\ell =$$

$$= 0 \;, \quad \text{because} \quad \sum_{\ell} \rho_\ell e_\ell = 0$$

Therefore, calling $(\underline{\underline{A}}')_{ij} = A'_{ij} = 2\pi \sum_{\ell} \sqrt{\rho_i \rho_\ell}\, A_{j\ell}$ the matrix $\underline{\underline{L}}(s) - \underline{\underline{A}}'(s)^{-2}$ is analytic in the closed right hand s plane; besides

$$\underline{\underline{L}}(s) = \underline{\underline{G}}(s)\; \underline{\underline{H}}^T(-s) =$$

$$= \underline{\underline{H}}(s)\; \underline{\underline{K}}(s)\; \underline{\underline{H}}^T(-s)$$

and $$\underline{\underline{L}}^T(-s) = \left[\underline{\underline{G}}(-s)\; \underline{\underline{H}}^T(s)\right]^T = \underline{\underline{H}}(s)\; \underline{\underline{G}}^T(-s) =$$

$$= \underline{\underline{H}}(s)\; \underline{\underline{K}}^T(-s)\; \underline{\underline{H}}^T(-s) = \underline{\underline{H}}(s)\, \underline{\underline{K}}(s)\, \underline{\underline{H}}^T(-s)$$

(3.26) which proves $\underline{\underline{L}}(s) = \underline{\underline{L}}^T(-s)$

Since $\underline{\underline{A}}' = (\underline{\underline{A}}')^T$ it follows that

(3.26a) $\underline{\underline{L}}(s) - \underline{\underline{A}}' s^{-2}$ is entire (all its (i,j) elements are entire functions of s).

III.4 Behavior of $\underline{\underline{L}}(s)$

We rewrite

$$\underline{\underline{L}}(s) = \underline{\underline{H}}(s)\,\underline{\underline{H}}(-s)\,\underline{\underline{T}}(s)/d(s)$$

and notice that as $|\mathrm{Re}\, s| \to \infty$

$$\underset{|\mathrm{Re}\, s| \to \infty}{d(s) \longrightarrow} s^2\left[F_{11}^{\pm} F_{22}^{\pm} - (F_{21}^{\pm})^2\right] \longrightarrow O\left(e^{s(R_1+R_2)}\right)$$

On the other hand as $\mathrm{Re}\, s \to +\infty$ we see (using 3.21 for) $(i,j) \neq (1,2)$

$$\underset{\mathrm{Re}\, s \to \infty}{H_{ij}(s) \longrightarrow} A_{ij} - s\,\sigma_{ij}(0) - \sigma_{ij}^{(1)}(0) - \frac{1}{s}\,\sigma_{ij}^{(2)}(0) -$$

$$- \frac{K^2}{4} s D_{ij} - \frac{K^2}{2} V_{ij} = -\frac{1}{s}\,\sigma_{ij}^{(2)}(0)$$

because $\sigma_{ij}(0) = -\frac{K^2}{4} D_{ij}$ (see Eq. (3.13)

$\sigma_{ij}^{(1)}(0) = -\frac{K^2}{2} V_{ij}$ (see Eq. (3.14)

and from (3.15) $\sigma_{21}^{(2)}(0) = 0$. It immediately follows

(3.27a) $$\lim_{\mathrm{Re}\, s \to \infty} H_{ii}(s) = -\frac{1}{s}\,\sigma_{ii}^{(2)}(0)$$

(3.27b) $$\lim_{\mathrm{Re}\, s \to \infty} H_{21}(s) = O\left(e^{-s\lambda}/s\right)$$

For $H_{12}(s)$ the dominant term as $\mathcal{R}e\, s \to +\infty$ comes from $s\, \Gamma_{12}(s)$

Yielding

(3.27c) $$\lim_{\mathcal{R}e\, s \to \infty} H_{12}(s) = O\left(e^{s\lambda}/s\right)$$

With this in mind we can prove that $L_{22}(s) = L_{22}(-s)$ and $L_{11}(s) = L_{11}(-s)$ are bounded along every ray in the s complex plane.

We will give here the proof for $L_{22}(s)$, but exactly the same reasoning applies for $L_{11}(s)$. We have

$$d(s)\, L_{22}(s) = H_{21}(s)\left[H_{11}(-s)\, T_{12}(s) + H_{12}(-s)\, T_{22}(s)\right] + H_{22}(s)\left[H_{21}(-s)\, T_{12}(s) + H_{12}(-s)\, T_{22}(s)\right]$$

but $$\lim_{\mathcal{R}e\, s \to \infty} H_{11}(-s)\, T_{12}(s) + H_{12}(-s)\, T_{22}(s) =$$

$$= \lim_{\mathcal{R}e\, s \to \infty} s^2 F_{11}(-s)\, \Gamma_{12}(-s) = O\left(e^{s(R_1+\lambda)}/s\right)$$

which implies

$$\lim_{\mathcal{R}e\, s \to \infty} H_{21}(s)\left[H_{11}(-s)\, T_{12}(s) + H_{12}(-s)\, T_{22}(s)\right] =$$

$$= O\left(e^{sR_1}/s^2\right)$$

For the second term we have

$$\lim_{Re\,s\to\infty} \left[H_{21}(-s)\, T_{12}(s) + H_{22}(-s)\, T_{22}(s)\right] =$$

$$\lim_{Re\,s\to\infty} \left[s^3 \left(F_{21}(-s)\right)^2 - s^3 F_{22}(-s)\, F_{11}(-s)\right]$$

$$= O\left[s\, e^{s(R_1+R_2)}\right]$$

which hence shows

$$\lim_{Re\,s\to\infty} H_{22}(s)\left[H_{21}(-s)\, T_{12}(s) + H_{22}(-s)\, T_{22}(s)\right] =$$

$$= O\left(e^{s(R_1+R_2)}\right)$$

which definitely means

(3.28) $$\lim_{Re\,s\to\infty} L_{22}(s) = \lim_{Re\,s\to\infty} L_{22}(-s) = \text{constant of } s.$$

But we know that an entire function bounded along every ray must be a constant.(3)

So we have, defining these constants as $2\delta_{22}$ and $2\,\delta_{11}$,

$$L_{22} - \frac{A'_{22}}{s^2} \equiv 2\delta_{22}$$

(3.29a) $$L_{11} - \frac{A'_{11}}{s^2} \equiv 2\delta_{11}$$

Turning now to $L_{21}(s)$ we have

$$L_{21}(s)\, d(s) = H_{21}(s)\left\{H_{11}(-s)\, T_{11}(s) + H_{12}(-s)\, T_{12}(s)\right\} +$$

$$+ H_{22}(s)\left\{H_{22}(-s)\, T_{21}(s) + H_{12}(-s)\, T_{22}(s)\right\}$$

Analyzing the 1st term

$$\lim_{Re\, s\to\infty} H_{21}(s)\left[H_{11}(-s)\,T_{11}(s)+H_{12}(-s)\,T_{12}(s)\right]=$$

$$=\lim_{Re\, s\to\infty} s^3\left[F_{11}(-s)\,F_{22}(-s)-\left(F_{12}(-s)\right)^2\right]\cdot O\left(e^{s\lambda}/s\right)$$

$$=\quad O\left(e^{s(R_1+R_2-\lambda)}\right).$$

For the second term we obtain

$$\lim_{Re\, s\to\infty} H_{22}(s)\left[H_{22}(-s)\,T_{21}(s)+H_{12}(-s)\,T_{22}(s)\right]=$$

$$=\quad O\left(\tfrac{1}{s}\right)\lim_{s\to\infty} s^2\,\Gamma_{12}(-s)\,F_{11}(-s)=$$

$$=\quad O\left(e^{s(R_1+\lambda)}/s^2\right)$$

In conclusion :

(3.30a) $$\lim_{Re\, s\to\infty} L_{21}(s)\,e^{\lambda s}=\text{constant of } s$$

Finally

$$L_{21}(-s)\,d(s)=H_{11}(s)\left[T_{11}(s)H_{21}(-s)+T_{21}(s)H_{22}(-s)\right]+$$

$$+\;H_{12}(s)\left[T_{12}(s)\,H_{21}(-s)+T_{22}(s)\,H_{22}(-s)\right]$$

and $$\lim_{Re\, s\to\infty} L_{21}(-s)\,d(s)=O\left(\frac{e^{s\lambda}}{s^3}\right)\lim_{Re\, s\to\infty} s^5\left[\left(F_{12}(-s)\right)^2-F_{11}(-s)F_{22}(-s)\right]=$$

$$=\quad O\left(e^{s\lambda}\cdot e^{s(R_1+R_2)}\right)\qquad \text{or :}$$

(3.30b) $$\lim_{Re\, s\to\infty} L_{21}(-s)\,e^{-s\lambda}=\text{constant of } s$$

which shows that the function $L_{21}(s)e^{\lambda s} - A'_{21}\left[\frac{1}{s^2} + \frac{\lambda}{s}\right]$ is entire and bounded along every ray, hence a constant we are going to call $2\delta_{21}$:

(3.29b) $$L_{21}(s)e^{\lambda s} - A'_{21}\left[\frac{1}{s^2} + \frac{\lambda}{s}\right] \equiv 2\delta_{21}$$

The term $\frac{\lambda}{s}$ comes about because:

being $L_{21}(s) - A'_{21}/s^2$ entire implies

$$\underset{s \to 0}{L_{21}(s)} \to \frac{A'_{21}}{s^2} + \text{constant} + o(s)$$

Therefore

$$\underset{s \to 0}{L_{21}(s)\, e^{\lambda s}} \to \frac{A'_{21}}{s^2} + \frac{A'_{21}\lambda}{s} + \text{constant} + o(s)$$

Therefore

$$L_{21}\, e^{\lambda s} - A'_{21}\left[\frac{1}{s^2} + \frac{\lambda}{s}\right]$$

is

analytical everywhere including s=o, i.e. entire.

Now one can take the inverse Laplace transform of (3.29a) and (3.29b) and exactly following reference (1) we find

(3.31) $$\delta_{ii}(r) = -\frac{K^2}{4}D_{ii} + \left(A_{ii} - \frac{K^2}{2}V_{ii}\right) + \delta_{ii}r^2 + \frac{A'_{ii}}{2}r^4$$

$$\text{for } r < R_i$$

$$\sigma_{21}(r) = \sigma_{12}(r) = -\frac{K^2}{4} D_{21} + \left(A_{21} - \frac{K^2}{2} V_{21}\right) r \quad \text{for } r < \lambda \tag{3.31.}$$

$$\sigma_{21}(r) = \sigma_{12}(r) = -\frac{K^2}{4} D_{21} + \left(A_{21} - \frac{K^2}{2} V_{21}\right) r + \delta_{21} x^2 +$$

$$+ 2\lambda \left(\frac{\rho_1}{\rho_2}\right)^{1/2} A_{22}' x^3 + \left(\frac{\rho_1}{\rho_2}\right)^{1/2} \frac{A_{22}'}{2} x^4 ; \quad \text{for } \lambda < r < R_{21}, \text{ where } x = r - \lambda$$

The main difference between the structure of Eq. (3.31) and the one obtained by Lebowitz for the P.Y. for uncharged hand spheres is the presence of a constant term in the polynomial forms, that comes about from the fact

$$\sigma_{ij}(0) = -\frac{K^2}{4} D_{ij}$$

What is now left to solve completely the m.s.m. is finding the unknown coefficients of the polynominals of (3.31). Namely, the unknowns are:

$$a_1,\ a_2,\ \delta_{11},\ \delta_{22},\ \delta_{21},\ V_{11},\ V_{22},\ ^{*}$$

7 unknowns, and to find them we shall use the continuity of

$$\sigma_{ij}^{(n)} \ ; \quad n = 0, 1, 2$$

at $r = R_{ij}$.

To determine the unknown coefficients of the polynomial σ_{ij} is for $r < R_{ij}$.

---

* We have $A_{22} = 2\pi \rho_2 a_2$; $A_{21} = 2\pi \sqrt{\rho_1 \rho_2}\, a_1$, $A_{11} = 2\pi \rho_1 a_1$ and $\rho_1 V_{21} + \rho_2 V_{22} = 0$. The coefficients for $(i,j) = (1,2)$ are not needed because we know

$$\sigma_{12}(r) = \sigma_{21}(r) \quad \forall r \quad 0 \leq r < \infty$$

we use

(3.33) $$L_{ii} = 2\delta_{ii} + A'_{ii}/s^2 = G_{i1}(s) H_{1i}(-s) + G_{i2}(s) H_{2i}(-s)$$

calling
$$x_{ij} \equiv \sigma_{ij}(R_{ij})$$
$$y_{ij} \equiv \sigma_{ij}^{(1)}(R_{ij})$$
$$z_{ij} \equiv \sigma_{ij}^{(2)}(R_{ij})$$

We know (using the continuity of $\sigma_{ij}^{(n)}(r)$; $n = 0, 1, 2$ across R_{ij} and (3.21, to 3.23)

$$\lim_{Re\, s \to \infty} G_{i\ell}(s) H_{\ell i}(-s) = \lim_{Re\, s \to \infty} -s^2 G_{i\ell}(s) F_{\ell i}(-s) =$$

$$= -s^2 \left(\frac{x_{i\ell}}{s} + \frac{y_{i\ell}}{s^2} + \frac{z_{i\ell}}{s^3} + \ldots \right)\left(\frac{1}{s} x_{\ell i} - \frac{y_{\ell i}}{s^2} + \frac{z_{\ell i}}{s^3} + \ldots \right)$$

Equating terms of the same order in s in (3.33) it follows

(3.34a) $$2\delta_{ii} = -\sum_\ell x_{i\ell}^2 \; ; \quad (3.34a, \delta)$$

$$A'_{ii} = -2 \sum_\ell x_{i\ell} z_{\ell i} + \sum_\ell y_{i\ell}^2 \; ; (3.34a, A')$$

And also

$$\lim_{Re\, s \to \infty} L_{21}(s) e^{\lambda s} = 2\delta_{21} + \frac{\lambda A'_{21}}{s} + \frac{A'_{21}}{s^2} =$$

$$= \lim_{Re\, s \to \infty} \left[G_{21}(s) H_{11}(-s) + G_{22}(s) H_{12}(-s) \right] e^{\lambda s} =$$

$$= -\lim_{Re\, s \to \infty} s^2 \left\{ \left[\frac{x_{21}}{s} + \frac{y_{21}}{s^2} + \frac{z_{21}}{s^3} + \ldots \right]\left[\frac{x_{11}}{s} + \frac{z_{11}}{s^3} - \frac{y_{11}}{s^2} \right] + \right.$$
$$\left. + \left[\frac{x_{22}}{s} + \frac{y_{22}}{s^2} + \frac{z_{22}}{s^3} + \ldots \right]\left[\frac{x_{21}}{s} - \frac{y_{21}}{s^2} + \frac{z_{21}}{s^3} + \ldots \right] \right\}$$

Equating terms of same order in s

$$
(3.34b)\quad \begin{cases} 2\,\delta_{21} = -x_{21}\,(x_{11}+x_{22}) & ;\ (3.34b,\delta) \\ A'_{21} = -z_{21}\,(x_{11}+x_{22}) - x_{21}\,(z_{11}+z_{22}) + y_{21}\,(y_{11}+y_{22}) & ;\ (3.34b,A') \\ \lambda A'_{21} = x_{21}\,(y_{11}-y_{22}) + y_{21}\,(x_{22}-x_{11}) & ;\ (3.34b,\lambda A') \end{cases}
$$

The other equations we have to our disposal are the 2 linear equations coming from the definition of a_j

$$
(3.34c)\quad a_j = 1 - 2\sum_{\ell}\sqrt{\frac{\rho_\ell}{\rho_j}}\int_0^{R_{ej}} \sigma_{\ell j}(r)\, r\, dr
$$

Some of the equations of set (3.34) are not independent of the others because we know we should automatically have the solution for $\sigma_{22}(r)$ when we get $\sigma_{11}(r)$ or vice versa, that is

$$
\sigma_{22}(r) \xleftrightarrow[\substack{R_2 \leftrightarrow R_1 \\ \rho_2 \leftrightarrow \rho_1 \\ e_2 \leftrightarrow e_1}]{(2,2) \leftrightarrow (1,1)} \sigma_{11}(r)
$$

and σ_{21} remaining invariant under the transformation $(2,2) \longleftrightarrow (1,1)$.

That means we have a total of 5 independent quadratic equations (general conics) and 2 linear equations for the seven unknowns (namely the polynomial coefficients). The structure of equations (3.34) is identical with the one obtained for the pure hard sphere case in Reference 1, in terms of X_{ij}; Y_{ij}, Z_{ij}. Of course the coefficients will be different because the polynominals differ by a constant term and the fact that in the r term we now have $A_{ij} - \frac{K^2}{2} V_{ij}$ rather than just A_{ij}.

The solution for equal size charged hard spheres

We have been able to solve the system of algebraic equations (3.34) for the case $R_1 = R_2$, that is for equal size charged hard spheres. To find the answer we define

(3.35) $$\delta_{ij}(r) \equiv \delta_{ij}^{(0)}(r) + \eta_{ij}(r) \quad \text{for } r < R_{ij}$$

where $$\delta_{ij}^{(0)}(r) = -2\pi \sqrt{\rho_i \rho_j}\, r\, C^{(0)}(r) \quad \text{for } r < R_{ij}{}^{*}$$

$C^{(0)}(r)$ is the polynomial found by Wertheim[4] and Thiele[5] that solves the P.Y. for equal size uncharged hard spheres.

---

* We should emphasize $C^{(0)}(r)$ for inverse temperature β and density $\rho = \rho_1 + \rho_2$

We then write (calling $R_1 = R_2 = R$)

$$x_{ij} \equiv \sqrt{\rho_i \rho_j}\, X^o + X^*_{ij} \quad ; \quad X^o = 2\pi \left(r\, g^o(r) \right)_{r=R}$$

$$y_{ij} \equiv \sqrt{\rho_i \rho_j}\, y^o + y^*_{ij} \quad ; \quad y^o = 2\pi \frac{d}{dr} \left(r\, g^o(r) \right)_{r=R}$$

$$z_{ij} \equiv \sqrt{\rho_i \rho_j}\, z^o + z^*_{ij} \quad ; \quad z^o = 2\pi \frac{d^2}{dr^2} \left(r\, g^o(r) \right)_{r=R}$$

$$A_{ij} \equiv A^o_{ij} + A^*_{ij} \quad ; \quad a_j \equiv a^o_j + a^*_j$$

$$\delta_{ij} \equiv \delta^o_{ij} + \delta^*_{ij} \quad ; \quad A'_{ij} = A'^o_{ij} + A'^*_{ij}$$

The subscript o here means the reference system, i.e., the uncharged hard sphere system; $g^o(r)$ being the radial distribution function for the reference system.

The solution to the algebraic equations (3.34) is in this case given by

$$\eta_{ij}(r) = -\frac{K^2}{4} D_{ij} \left(1 + 2br + 4cr^2 \right) \tag{3.36}$$

and we show it as following: Replacing the η_{ij} of equation (3.36) in the linear equations (3.34C) for a_j we have

$$a_j = 1 - 2 \sum_l \sqrt{\frac{\rho_l}{\rho_j}} \int_0^{R_{lj}} \sigma^{(0)}_{lj}(r)\, r\, dr + \frac{K^2}{2} \int_0^{R_{lj}} (1 + 2br + 4cr^2)\, r\, dr \cdot \sum_l \sqrt{\frac{\rho_l}{\rho_j}} D_{lj},$$

but $$\sum_l \sqrt{\frac{\rho_l}{\rho_j}} D_{lj} = e_j \sum_l \rho_l e_l = 0,$$

which implies : $a_j = a^o$ or $a^*_1 = a^*_2 = 0$

From their definitions it is obvious then that

$A^{*}_{ij} = 0$ which is consistent with the form (3.36).

For the equations (3.34a,δ) and (3.34b,δ) we have realizing that we can rewrite for instance (3.34a,δ) as

$$2\,\delta^{0}_{ii} + 2\,\delta^{*}_{ii} = -(x^{0}_{21})^2 - (x^{0}_{ii})^2 - (x^{*}_{21})^2 - (x^{*}_{ii})^2 -$$
$$- 2\,x^{0}_{21}\,x^{*}_{21} - 2\,x^{0}_{ii}\,x^{*}_{ii}$$

By definition and the mentioned fact that the algebraic structure is the same for the reference system as for the m.s.m. we have

$$2\,\delta^{0}_{ii} = -(x^{0}_{21})^2 - (x^{0}_{ii})^2,$$

on the other hand,

$$-2\,(x^{*}_{21}\,x^{0}_{21} + x^{*}_{ii}\,x^{0}_{ii}) = \frac{K^2}{2}\,x^{0}\,(1+2bR+4cR^2)(\sqrt{\rho_1\rho_2}\,D_{21} + \rho_i\,D_{ii}) =$$
$$= \frac{K^2}{2}\,x^{0}\,(1+2bR+4cR^2)\,(\rho_1\rho_2\,e_1 e_2 + \rho_i^2 e_i^2) = 0$$

that is, the "cross" terms vanishes and we obtain

$$-2\,K^2 c\,D_{11} = -\frac{K^4}{16}\,(1+2bR+4cR^2)^2\,(D_{21}^2 + D_{11}^2)$$
$$-2\,K^2 c\,D_{22} = -K^4/16\,(1+2bR+4cR^2)^2\,(D_{21}^2 + D_{22}^2)$$
$$-2\,K^2 c\,D_{21} = -K^4/16\,(1+2bR+4cR^2)^2\,D_{21}\,(D_{11} + D_{22}),$$

but since $\dfrac{D_{11}^2 + D_{21}^2}{D_{11}} = \dfrac{D_{22}^2 + D_{21}^2}{D_{22}} = D_{11} + D_{22}$

the 3 equations yield the same equation:

$$c = \frac{K^2}{32}\,(D_{11} + D_{22})\,(1+2bR+4cR^2)^2 \tag{3.37a}$$
$$= \frac{\varkappa c^2}{16}\,(1+2bR+4cR^2)^2$$

Turning to equation (3.34b, λA'), since $\lambda = \frac{R_2 - R_1}{2} = 0$ we should have :

$$x^*_{21}\,(y^*_{11} - y^*_{22}) + y^*_{21}\,(x^*_{22} - x^*_{11}) \equiv 0$$

$$x^*_{21}\,(y^*_{11} - y^*_{22}) + y^*_{21}\,(x^*_{22} - x^*_{11}) = \left[D_{21}\,(D_{11} - D_{22}) + D_{21}\,(D_{22} - D_{11})\right] \cdot$$

$$\cdot\ \frac{K^4}{8}\,(1 + 2bR + 4cR^2)(2b + 8cR) \equiv 0$$

Finally we get from (3.34a,A') and (3.34b,A') a single equation (again remembering the relations for the reference system and the fact that in these 2 equations it is also straightforward to verify that the cross terms vanish.).

Cross terms being products of the form $X^* Z^\circ$, etc.)

Namely $\frac{K^4}{16}\,(2b + 8cR)^2 - K^4 c\,(1 + 2bR + 4cR^2) = 0.$

Solving for c yields

(3.37b) $\qquad c = b^2/4$

Substituting (3.37b) in (3.37a) we obtain

(3.38) $$B \equiv bR = \left(-x^2 - x + x\sqrt{1+2x}\right)x^{-2} \; ; \; x \equiv \varkappa R$$

$$Q \equiv cR^2 = B^2/4$$

where in solving (3.37a) and (3.37b) we have selected the roots that give the correct Debye-Hückel limit when $R \to 0$

That is $$\lim_{R \to 0} b(\rho, R, \beta) = -\frac{\varkappa}{2}$$

So for the case $R_1 = R_2 = R$ the solution to the m.s.m. is given by following direct correlation function

(3.39) $$C_{ij}(r) = C^0(r) + \frac{\beta}{\varepsilon} e_i e_j \left(2\frac{B}{R} + 4Q\frac{r}{R^2}\right) \text{ for } r < R$$

with B and Q given by equations (3.38).

To get $g_{ij}(r)$ for $r > R$ it is necessary to perform an inverse Fourier or Laplace transform numerically. There are a couple of things worth mentioning even without doing this computations.

. From the relationship between $\hat{h}_{ij}(k)$ and $\hat{C}_{ij}(k)$ in Fourier space (see Eq. (2.4)) one has (using the result of (3.39)

$$\hat{h}_{ij}(k) = \hat{C}^{o}(k) + \frac{\beta}{\varepsilon} e_i e_j f(k) + \hat{C}^{o}(k) \sum_{\ell} \rho_\ell \hat{h}_{i\ell}(k) + $$
$$+ f(k) \frac{\beta}{\varepsilon} \sum_{\ell} \rho_\ell e_\ell e_j \hat{h}_{i\ell}(k)$$

$f(k)$ is the Fourier transform of $\left(2\frac{B}{R} + 4Q\frac{r}{R^2}\right)$; $r < R$

So one gets $\hat{h}_{i1} - \hat{h}_{i2} = \frac{\beta}{\varepsilon} e_i (e_1 - e_2) f(k) +$

$$+ \frac{\beta}{\varepsilon} f(k) \rho_i e_i (e_1 - e_2) [\hat{h}_{i1} - \hat{h}_{i2}]$$

so calling $\hat{h}_{i1} - \hat{h}_{i2} = \hat{h}_i(k)$ and $\frac{\beta}{\varepsilon} e_i(e_1 - e_2) f(k) = \hat{C}_i(k)$

it follows

$$\hat{h}_i(k) = \hat{C}_i(k) + \rho_i \hat{C}_i(k) \hat{h}_i(k) \tag{3.40}$$

Thus we have eliminated explicitly the pure uncharged hard spheres part, so when integrating numerically the inversion consists of taking the inverse of the pure hard spheres and the functions $\hat{h}_i$ (only one of them) explicitly.

.. One should also be able numerically to detect the charge cloud density oscillations given by $Q_i(r) = \sum_l \rho_l e_l g_{il}(r)$ and determine the critical x for which the first zeros of the function $g_{ii}(r) - g_{ij}\ ;\ j \neq i$ occur; that is for $x < x_{crit},\ g_{ii}(r) - g_{ij}(r) \neq 0 \ \forall r$, $j \neq i$ and for $x = x_{crit},\ g_{ii} - g_{ij} = 0$, $i \neq j$; that is the equation has roots for some $0 < r < \infty$.

... Another necessary test our radial distribution should pass is $g_{ij}(r = R) \geq 0$ for some physical region in the (x, y) ; $(X \equiv xR;\ y = (\rho_1 + \rho_2)R^3)$ plane.

To test this we have $g_{ij}(R) = g^o(R) - \frac{\beta}{\varepsilon R} e_i e_j (1 + 2B + 4Q)$

(3.41)
$$g_{ij}(R) = g^o(R) - \frac{\beta}{\varepsilon R} e_i e_j \ (1 + B)^2$$

So the physical region is determined by

(3.42)
$$g^o(R) \geq \mathrm{Max}\left[\frac{\beta}{\varepsilon R} e_i^2 \ (1 + B)^2\right].$$

and of course $g^o(R) \geq 0$ (we know that even for the pure uncharged hard spheres P.Y. $g^o(R)$ gets negative above a certain density).

Another fact which is physically desirable is

$g_{ij}(R) \overset{i \neq j}{>} g_{ii}(R)$ and it is obvious that this is satisfied in our case. (The probability of having 2 particles of opposite charge at the distance of closest approach should be bigger than the probability of having particles of the same charge in the same situation.)

Thermodynamics for the equal size charged hard spheres

It is well known(14) that the thermodynamic properties of a system can be computed in many different ways like virial or compressibility pressure, from the energy form, etc. All of these are the same for the exact Statistical Mechanics formulation. But when approximation to the exact theory are introduced, as in the m.s.m., one expects discrepancies among the different methods of computing the thermodynamics of a given system.

We get the thermodynamics calculating the excess energy of the system (energy over the ideal gas for the same density $\rho_1 + \rho_2 = \rho$). We know

$$E^{\mu} = \frac{1}{2} \sum_i \sum_j \rho_i \rho_j \int_R^{\infty} \frac{e_i e_j}{\varepsilon r} g_{ij}(r)\, 4\pi r^2 dr =$$

$$= \frac{1}{\varepsilon} \sum_i \sum_j \rho_i \rho_j\, e_i e_j\, 2\pi \int_R^{\infty} r\, g_{ij}(r)\, dr$$

So we have

$$E^{ex} = \frac{1}{\varepsilon} \sum_i \sum_j D_{ij} \int_R^\infty \sigma_{ij}(r)\, dr = \frac{1}{\varepsilon} \sum_i \sum_j B_{ij}\, D_{ji} =$$

$$= \frac{1}{\varepsilon} \sum_i V_{ii} = \frac{1}{\varepsilon}\, b \sum_i D_{ii} = \frac{b}{\varepsilon} \left(\rho_1 e_1^2 + \rho_2 e_2^2\right) =$$

$$= \frac{B x^2}{4\pi R^3 \beta}$$

From E^{ex} we can get the Helmholtz free energy density $a(\rho, \beta)$

(3.43) $$\beta a - \beta a^\circ = \int_0^\beta E^{ex}(\rho, \beta')\, d\beta' =$$

$$= - \frac{1}{12\pi R^3} \left(6x + 3x^2 + 2 - 2(1+2x)^{3/2} \right)$$

which goes $\xrightarrow[R \to 0]{} - \varkappa^3/12\pi$ the Debye-Hückel limiting law; next we get the osmotic pressure.

(3.44) $$p^{osm}/\rho = \rho \left.\frac{\partial \rho a}{\partial \rho}\right)_\beta = p^\circ/\rho + \frac{1}{4\pi\rho R^3} \left[x + x(1+2x)^{1/2} - \frac{2}{3}(1+2x)^{3/2} + \frac{2}{3} \right]$$

a^o, P^o being the Helmholtz free energy density and pressure for the uncharged hard spheres system.

We compare our results for a particular case with Rasaiah and Friedman's[(7)], that they have obtained as we explained in Chapter (I), in Table I coming from reference[(17)].

TABLE I. Comparison of results of M.S.M. with HNC[1] aqueous solution for 1–1 electrolyte; $T=25°C$; $R=4.6$ Å; $Z=1$; $\epsilon=78.358$ and assumed temperature independent.

C (moles)[a]	ρR^3	$x=KR$	$-E^{ex}$ (cal/mole·liter) M.S.M.	$-E^{ex}$ (cal/mole·liter) HNC	$(\beta P/\rho)$ M.S.M.	$(\beta P/\rho)$ HNC
0.002	0.0002	0.0677	58.514	58.983	0.9848	0.98444
0.020	0.0024	0.2141	163.743	165.778	0.9630	0.96272
0.200	0.0234	0.6770	388.449	390.052	0.9644	0.96406
0.900	0.1056	1.4362	600.862	605.028	1.1412	1.1356
1.000	0.1172	1.5138	617.003	621.663	1.1728	1.1666

[a] C: moles of electrolyte per liter.

CHAPTER IV

Open Questions

We want to summarize in this last chapter some of the questions that, in our opinion, deserve further thought and investigation in the future.

A) To have the solution for the general case of the binary primitive electrolyte ($R_1 \neq R_2$) the algebraic equations (3-34) must be solved. This would give a much greater degree of flexibility in comparing with experiments and other theories. The question whether it is possible to solve (3-34) in closed (analytical) form, and therefore the m.s.m., is a very relevant one in asserting its usefulness for the general case.

B) Solution of the m.s.m. for systems with more than two components would be a powerful achievement. In particular the simplest possible description of the solvent-solvent; solvent-solute interaction which could be a system with three species of ions $e_1 = 0$, $e_2 = -e_3$; $R_1 = R_2 = R_3$, seems to be a very interesting case for research and appears as soluble with the techniques of this present work.

C) A number of calculations are needed for the case $R_1 = R_2$, namely

- . Numerical Fourier transform to obtain $g_{ij}(r)$ explicitly and the already discussed oscillations of the charge cloud density for $x \geqslant x_{crit}$ (x_{crit} to be found by this calculation).

- .. More examples for different parameter R, e, ρ, as constructed in Table 1.

- ... Comparison between the already obtained free energy pressure (3-44) with pressure obtained through the virial theorem and compressibility relations (see ref. 7).

D) A most interesting point is whether the m.s.m. could be applied to molten salts systems.

1. J.L. LEBOWITZ, PHYS. REV., 133, 895 (1964)

2. P. DEBYE AND E. HÜCKEL, PHYSIK Z 24, 195, 305 (1923)

3. See, e.g., E.C. TITCHMARSH, The Theory of Functions (OXFORD UNIVERSITY PRESS, LONDON, 1939)

4. M. WERTHEIM, PHYS. REV. LETTERS 8, 321 (1963)

5. E. THIELE, J. CHEM. PHYS. 38, 1959 (1963)

6. L.S. ORNSTEIN, F. ZERNIKE, PROC. ACAD. SCI. AMSTERDAM 17, 793 (1914)

7. J.C. RASAIAH AND H.L. FRIEDMAN, J. CHEM. PHYS., 48, 2742 (1968)
   " " " , 50, 2965 (1969)

8. J.L. LEBOWITZ AND J. PERCUS, PHYS. REV., 144, 251 (1966)

9. G. STELL, "CLUSTER EXPANSIONS FOR CLASSICAL SYSTEMS IN EQUILIBRIUM", II - 171 of "THE EQUILIBRIUM THEORY OF CLASSICAL FLUIDS, W.A. BENJAMIN, INC., NEW YORK, 1964, BY H.L. FRISCH AND J.L. LEBOWITZ

10. R.J. BAXTER, PHYS. REV. 154, 170 (1967)

11. J. GROENEVELD (PRIVATE COMMUNICATION)

12. J.E. MAYER, J. CHEM. PHYS., 18, 1426 (1950)

13. J.L. LEBOWITZ AND E. LIEB, PHYS. REV. LETTERS 22, 631 (1969)

14. H.L. FRIEDMAN, IONIC SOLUTION THEORY (INTERSCIENCE PUBLISHERS, INC., NEW YORK, 1962)

15. F.H. STILLINGER, JR. AND R. LOVETT, J. CHEM. PHYS. 49, 1991 (1968)

16. F.H. STILLINGER, JR. AND R. LOVETT, J. CHEM. PHYS. 48, 3858 (1968)

17. E. WAISMAN AND J.L. LEBOWITZ, J. CHEM. PHYS. 52, 4307 (1970)