

UNIVERSITY OF PUERTO RICO – RIO PIEDRAS CAMPUS
FACULTY OF NATURAL SCIENCES
DEPARTMENT OF PHYSICS

**An analysis of the Fluctuation potential in the modified
Poisson-Boltzmann theory for primitive model electrolytes**

by

Ernesto Ulloa Dávila

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AN ANALYSIS OF THE FLUCTUATION POTENTIAL IN THE
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PRIMITIVE MODEL ELECTROLYTES

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Lutful Bari Bhuiyan
Department of Physics
Thesis Adviser

Date

Ronald G. Selsby
Department of Physics
Committee Member

Date

Edwin Quiñones,
Department of Chemistry
Committee Member

Date

José F. Nieves,
Department of Physics
Chairman of the Department

Date

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APPENDIX C

**An Analysis of the Fluctuation Potential in the Modified Poisson – Boltzman Theory
for Restricted Primitive Model Electrolytes**

E. Ulloa – Dávila, L. B. Bhuiyan,

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Dedication

To my wife Rosana and my daughter Natalia for their love and understanding.

List of Abbreviations

Abbreviation:	Description:
ADH	Asymmetric Debye-Hückel
DH	Debye-Hückel
FP	Fluctuation Potential
HNC	Hyper-Netted Chain
KBBGY	Kirkwood Bogoluvov Born Green Yvon
MEP	Mean Electrostatic Potential
MPB	Modified Poisson – Boltzmann
MSA	Mean Spherical Approximation
OZ	Ornstein – Zernicke
PB	Poisson – Boltzmann
PM	Primitive Model
PMF	Potential of Mean Force
RDF	Radial Distribution Function
RPM	Restricted Primitive Model
SPB	Symmetric Poisson Boltzmann

Abstract

The fluctuation potential problem in the modified Poisson-Boltzmann approach to charged fluids is analyzed to obtain an approximate analytic solution for a symmetric valency restricted primitive model electrolyte. The solution is valid for all ranges of inter-ionic distances, including contact values. The structure of the electrolyte is described using radial distribution functions determined through the implementation of the fluctuation potential solution in the theory. Aspects of thermodynamics of the solution, viz., configurational reduced energies and osmotic coefficients are also calculated. Results have been obtained for symmetric valency 1:1 electrolyte system with the following physical parameters: ionic diameter $d = 4.25 \times 10^{-10}$ m, relative permittivity $\epsilon_r = 78.5$, absolute temperature $T = 298$ K, and molar concentrations $c = 0.1038$ M, 0.425 M, 1.00 M, and 1.968 M. The ion-ion radial distribution functions are compared with the corresponding results from the symmetric Poisson-Boltzmann and the conventional modified Poisson-Boltzmann theories. Contact values of the radial distributions, reduced configurational energies, and osmotic coefficients have also been compared, as functions of electrolyte concentration, with these theories, and additionally with the Debye-Hückel theory and Monte Carlo simulation data from the literature. The results show very good agreement with the Monte Carlo data, and some improvement for radial distribution contact values and osmotic coefficients relative to these theories. The reduced energy curve shows excellent agreement with Monte Carlo data for molarities up to 1 mol/dm^3 . Radial distribution contact values for the charge asymmetric RPM 2:1 valency system at the same physical parameters of the 1:1, except for valence, case were also calculated and compared with the corresponding hypernetted chain theory from the literature. Good agreement was

found for all concentrations considered. An ion size asymmetric primitive model extension to the theory is also presented. Osmotic coefficients are calculated and compared to simulation data from the literature for a primitive model electrolyte at the physical parameters: diameter of the large negative ion is $4.25 \times 10^{-10} \text{m}$, the temperature $T=298\text{K}$, the dielectric constant of the electrolyte $\epsilon_r = 78.5$, electrolyte concentration 0.425mol/dm^3 , and the size asymmetry parameter $\alpha = 0.4, 0.6, \text{ and } 0.8$. Good agreement between the results and the MC simulation was found.

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Chapter 1

Introduction

The field of coulomb fluids have been a consistently active area of research in statistical mechanics over the years. The area includes among others, ionic liquids, electrolytes, molten salts, colloids and polyelectrolytes. For recent reviews on the subject The reader is referred to the following articles [1, 2, 3]. Theoretical progress in this area was limited until the development of statistical mechanics based liquid state theory [4, 5, 6, 7, 8].

A widely used model used in the development of formal statistical mechanical theories of ionic solutions treats the solvent as a structureless, continuous dielectric medium with a relative permittivity ϵ_r , and the solute particles as charged hard spheres of diameters d_i and charges $Z_s e_s$, with Z_s being the valence of species s , satisfying the global charge neutrality condition,

$$\sum_S Z_s e_s = Z_+ e_+ + Z_- e_- = 0 \quad (1)$$

This is the so called primitive model (PM) of ionic solutions. When the ions are of the same size, it is called the restricted primitive model (RPM). Computer simulations of the RPM and PM over the years (see for example, references [9, 10, 11, 12, 13, 14]) have shown the usefulness of these models in interpreting experimentally determined structures and thermodynamics of charged fluid systems. Furthermore, the simulation data has proved invaluable in theoretical development.

A subdivision in the PM is related to the magnitude of the charges of the anions and cations. If all the charges have the same magnitude it is referred as valence symmetric,

and valence asymmetric otherwise. The notation (q:q) or (q:p) refers to charge symmetric, and charge asymmetric, respectively. For example, RPM (1:2) refers to same size ions with charges 1+ and 2-.

In statistical mechanics, the PM in liquid state physics has been studied using two main approaches: The first is the Ursell-Mayer cluster expansion [1, 2, 5] or the distribution function method [2-4]. This method is based on separating the N-body partition function of the system into a kinetic component and a configurational integral given by,

$$Z_Q = \frac{1}{N!} \int \exp[-\beta\Phi_N(q_1, q_2, \dots, q_N)] d\Omega, \quad (2)$$

where Φ is the molecular potential energy function, and then expanding equation 2 in terms of topologically distinct set of graphs representing integrals of the so called Mayer-functions [3-5]. The cluster expansion method was developed as an extension of the MacMillan Mayer theory of non-electrolyte solutions [15]. The essential result of the Mc Millan Mayer theory is that establishes a rigorous one-to-one correspondence between the equations of imperfect gas theory and a dilute solution of non-electrolytes. The long range coulomb interaction of ions in the solutions causes the virial coefficients to diverge when the Mc Millan-Mayer theory is applied to electrolyte solutions [4]. This problem was solved by Mayer [16]. He showed that although individual cluster integrals diverged, it is possible to combine the infinite parts of all the virial coefficients B_n for $n \geq 2$, so that they mutually cancel giving a finite result. Ionic solution theory based on the cluster expansion is detailed in reference [1].

The distribution function approach to ionic solutions is based in distribution functions giving probabilities of configurational groupings of two, three, and more particles. Correlation functions for n fixed particles are given by

$$g^{(n)}(r_1, \dots, r_n) = \frac{\Omega^n N!}{N^n (N - m)!} \frac{\int \dots \int e^{-\beta U_w} dr_{n+1} \dots dr_N}{Z_N}, \quad (3)$$

where Z_n is the configurational integral. This function gives the probability of a particular configuration of n fixed particles [4]. Of particular importance is the $g^{(2)}(r_1, r_2) = g(1,2)$ pair correlation function since it can be determined experimentally, and thermodynamic functions can be calculated from it [2-4].

In order to obtain the pair correlation function $g(1,2)$ from the molecular pair potential $\Phi(1,2)$, two main routes are used, viz.,

1. The Kirkwood, Bogolubov, Born, Green, Yvon (KBBGY) hierarchies [3]
2. The Ornstein-Zernike (OZ) equation [2, 3, 5].

The KBBGY hierarchies is an infinite set of equations relating correlation functions for n and $n+1$ fixed particles, and also the molecular potential, and the so called charge parameter ξ [3, 4, 5]. To determine the pair correlation function, using the KBBGY hierarchy, a closure relation between the pair correlation function $g(1,2)$ and the triplet correlation $g(1,2,3)$ must be provided to break the hierarchy. One such relation is the superposition approximation [5] given by

$$g(1,2,3) = g(1,2)g(2,3)g(3,1), \quad (4)$$

which is tantamount to saying that the triplet distribution is equal to the product of the pair distributions. Physically, this implies that the correlation of particles one and two is independent of the presence of the third particle [5].

The OZ method for calculating the pair correlation function from the pair potential is based on the definition of a new correlation function, called the direct correlation function $c(1,2)$. In the OZ approach the total correlation between two ions may be considered to be comprised of two parts: the direct correlation between the two particles, and the indirect correlation due to the presence of a third particle. The total correlation function $h(1,2)$ is then written as the sum of the direct correlation $c(1,2)$ and the indirect correlation averaged over all positions of the third particle. This is clearly shown by the OZ equation [5] given by

$$h(1,2) = c(1,2) + \rho \int c(1,3)h(2,3)d3, \quad (5)$$

which may be regarded as a definition for the direct correlation function $c(1,2)$ [5]. The total correlation function is related to the pair correlation function by

$$h(1,2) = g(1,2) - 1, \quad (6)$$

and so the OZ equation can be regarded as an integral equation for the pair correlation function in terms of the unknown function $c(1,2)$. To solve the OZ equation a closure relation between the direct $c(1,2)$ and the total correlation $h(1,2)$ functions must be provided. Among well-known closures are: the Percus-Yevick (PY) [17], the Hypernetted chain (HNC) [18], and the mean spherical approximation (MSA) [19]. Some early studies by Rasiah and Friedman [20, 21, 22] have shown that the HNC gives rather good results in ionic solution theory.

The second broad approach, which is our interest in this thesis, rests on obtaining the same pair correlation function $g(1,2)$ through a potential approach based on the Poisson's equation. The first theory for ionic solutions along this line is the celebrated classical theory of Debye and Hückel (DH) [23]. The DH theory is obtained by the

linearization of the Poisson-Boltzmann (PB) equation which relates the mean electrostatic potential of the solution, with the ionic charge density given by the Boltzmann's statistical distribution of ions [23].

The DH equation's solution gives the mean electrostatic potential $\Psi(1,2)$ around a central ion. This potential is used to construct pair correlation functions given by

$$g(1,2) = ne^{-\beta Z_2 \Psi(1,2)}. \quad (7)$$

where n is the bulk density and $\Psi(1,2)$ is the mean electrostatic potential. The theory predicts that each ion in a solution will be surrounded by a neutralizing atmosphere of opposite charged counter-ions [4]. It is known that DH theory is a low concentration exact limiting law in ionic solution theory, meaning that the theory correctly describes the thermodynamic properties of all solutions as the concentration tends to zero [4]. Potential theories of ionic solutions are based on the PB equation or the DH theory. In this theories the pair correlation function is given by

$$g(1,2) = e^{-\beta W(1,2)} \quad (8)$$

where the function $W(1,2)$ is called the potential of mean force. It includes all the forces in the models, including electrostatic forces and volume exclusion effects [2, 3, 4]. DH theory is a mean field theory, incapable of describing interionic correlations, so is only valid for very low concentrations [4]. So in order to make progress in the potential theory of solutions, ion correlations must be included. Kirkwood showed through a rigorous statistical mechanical analysis [24], that the main approximations in the classical theories are the omission of (i) ionic exclusion volume effects, and (ii) the fluctuation potential term, which involves the inter-ionic correlations. There have been many attempts since

Kirkwood to improve upon the PB/DH theory notable among which has been the extensive work done by Outhwaite and co-workers (see for example, references [25, 26, 27, 28, 29, 30, 31, 32, 33, 34]), who within the framework of the PM, have analyzed Kirkwood's methods and obtained estimates for the fluctuation term. These efforts have resulted in what is known in the literature as the modified Poisson-Boltzmann (MPB) approach to the ionic solution theory.

In the modified Poisson-Boltzmann (MPB) theory, which is our interest in the present work, the classical mean electrostatic approach of the DH theory is extended to include inter-ionic correlations by expressing the KBBGY hierarchies in terms of electrostatic mean potentials. In this theory, the mean electrostatic potential is expressed in terms of the fluctuation potential $\phi(1, 2; 3)$ (see for example, reference [33]) 3 is the field point, while there are fixed ions at 1 and 2), which measures deviations from the superposition principle of Kirkwood [24], and therefore contains information on the interionic correlations in the theory. The superposition principle, in terms of the fluctuation potential, is then given by

$$\Psi(1,2;3) = \Psi(1;3) + \Psi(2;3) + \Phi(1,2;3) . \quad (9)$$

This equation states that the mean potential at field point 3 is the sum of the direct potentials of particles 1 and 2, and the correlated potential contribution at field point 3 from the simultaneous presences of particles 1 and 2 [14]. Expressed in terms of the mean potentials, the fluctuation potential is given by [30, 33]

$$\phi(1,2;3) = \frac{1}{4\pi\epsilon_r\epsilon_0} \sum_s e_s \rho \int \frac{[\rho^s(1,2;q) - \rho^s(1;q) - \rho^s(2;q)]dr_q}{r_q}, \quad (10)$$

where e_s is the charge and $\rho_s(\{n\}; q)$ is the number density of the s th species of ions at \mathbf{r}_q with n fixed particles at \mathbf{r}_i ($i = 1, \dots, n$) with the sum being over all species, ϵ_0 is the vacuum permittivity, and ϵ_r the relative permittivity (dielectric constant) of the solvent. In the simplest language the fluctuation potential is the inter-ionic correlations expressed in potential form. Essentially, the MPB improves upon the classical PB theory by incorporating (i) ionic exclusion volume effects, and (ii) inter-ionic correlation effects. This potential procedure solves for the mean electrostatic potential $\psi(r)$ as opposed to the integral equations that attempt to solve directly for the radial distribution function $g_{ij}(r_i, r_j)$. Outhwaite and co-workers [27, 28, 29, 30, 31, 32, 33] have further symmetrized the classical PB theory and the MPB theory so that the Onsager relation, $g_{ij}(r) = g_{ji}(r)$ is satisfied for a homogeneous fluid. They have also coupled an exclusion volume term to the symmetrized PB theory, and call it the symmetric Poisson-Boltzmann (SPB) theory [30, 31, 32].

The fluctuation potential in MPB theory obeys a system of linearized partial differential equations given by equations 19-22 of reference [26]. An approximate solution is also given, that is valid only for large interionic separations where approximate spherical symmetry is valid [26, 33]. As explained by Outhwaite, one of the main problems in present MPB theory is the restriction of the fluctuation potential solution to large interionic separations [33]. The problem has also been mentioned in reference [35], as a possible cause of a small discrepancy between MPB osmotic coefficients and the corresponding Monte Carlo values of Card and Valleau [9], and Rasiah, Card, and Valleau [10]. The fluctuation potential problem is also mentioned by Outhwaite, Molero, and Bhuiyan [32] in the context of the PM of ionic solutions.

A clear statement of the aforesaid problem can be found in the paper by Outhwaite [33]. This paper presents a clear pedagogical introduction to MPB theory for bulk ionic solutions. The paper introduces the symmetric and asymmetric formulations of MPB and, presents a clear exposition to the fluctuation potential problem for RPM electrolytes. A detailed account for the setting of the fluctuation potential linearized system of equations is presented, and is followed by the approximate solution for $\phi(1,2;3)$ that is valid for approximate spherical symmetry, and large interionic separations. The solution can also be found in an earlier paper [26]. The basic equation for RPM MPB are then given in terms of the reduced potential $u = r\psi(1,2)$ in reference [33]. This version of MPB was not used in this research, since it includes the approximate solution of the fluctuation potential. Instead we started our treatment of the fluctuation potential problem starting from equation 36 of reference [33]. Outhwaite pointed at the two main problems of MPB theory:

- (a) the linearization of equation 36 outside the exclusion volumes,
- (b) the restriction of the solution of the fluctuation potential to large separations of the ions.

After a detailed study of this paper [33] we realized that to properly address the problem of the fluctuation potential a different system of equations was needed. In this work, a formulation based on pair correlation functions, as sources of the fluctuation potential was preferred, Instead of reformulation based on mean electrostatic potential. This paper [33] was invaluable, as a main source for our project. The main purpose of this work is to find a solution to the fluctuation potential system of equations that is valid for all range of ionic separations, including small distances and contact. This solution has the advantage of simplicity that can provide insight into the eventual fully numerical methods

for solving this kind of problems. The approximate analytical solution for $\phi(1, 2; 3)$ can serve as a guide to solving the problem numerically without using the approximations of this research.

For calculating thermodynamic properties like reduced configurational energies $-U/NkT$, and osmotic coefficients ϕ , the theory presented in the excellent reference [35] was used. In that reference thermodynamic properties, and radial distribution function contact values were calculated, and compared with the Monte Carlo data from Card and Valleau [9], and Rasiah, Card, and Valleau [10]. The essential results in this paper [35] are summarized in tables 5-7 of this reference, where radial distribution function's (RDF) contact values for like $g_A(a)$, and unlike $g_B(a)$ ions, configurational energies $-U/NkT$, and osmotic coefficients are compared for theories DH, PB, MPB, with the corresponding Card Valleau (CV), and Rasiah, Card Valleau (RCV) values for RPM (1:1) electrolyte solution with parameters: $\sigma = 4.25\text{\AA}$, $\epsilon=78.5$, $T=298\text{K}$, and molar concentrations of 0.00911, 0.1038, 0.425, 1.00, and 1.968. The method presented in reference [35] was instrumental, in this work, for the calculation of configurational energy, and osmotic coefficients. An improvement in the agreement between the MPB values calculated with the fluctuation potential obtained in this research ($\text{MPB}_{\text{this-work}}$) and traditional MPB from this reference is the first step in the validation of the fluctuation potential solution presented here.

An important paper by Outhwaite, Molero, and Bhuiyan [32], addresses the application of MPB to the calculation of PM radial distribution functions (RDFs) and thermodynamic properties for size-asymmetric, and valence asymmetric electrolytes, and a comparison with the Monte Carlo simulations of Valleau and Cohen [11], Valleau, Cohen, and Card [12] for same size electrolytes, and Abramo et al. [14], and Rodge [13]

for unequal size electrolytes. The results agree well with the MC results but discrepancies began appearing at high concentrations for large variations of ion size or unsymmetrical valences. At the conclusion of the paper, the authors attributed this limitations to the inadequate treatment of the fluctuation potential problem. An expressed that they expected a full numerical solution of the fluctuation potential problem to overcome these restrictions [32].

The fluctuation potential approximate solution presented in this dissertation, expresses the sources of ionic charge in the fluctuations potential system of equations in terms of the radial distribution functions (RDFs) from the Debye-Hückel theory (Appendix B) which is valid only for ions of equal sizes (RPM) so a future extension of the solution to unequal ion sizes will require the extension of DH theory to ionic size asymmetry.

The model developed in this dissertation also incorporates the possibility of an iterative solution. The MPB pair correlations functions from this work are use as initial functions in an iterative algorithm where ionic volume effects, size and charge asymmetry are considered from the beginning. This approach incorporates the best features of this research but does not suffer from the limitations of the approximations made for the sake of analytical progress.

The organization of this thesis is as follows. Chapter 2 presents a brief introduction to MPB theory for the PM model. This chapter is based in the paper entitled “A modified Poisson-Boltzmann approach to homogeneous ionic solutions” which presents a clear pedagogical introduction to MPB theory for bulk ionic solutions [33]. We start by giving details of the interaction potentials of the model, a brief introduction to the PB equation and the MPB theory approach. The dimensionless formulation of MPB as well as the

definition of the dimensionless parameters in this work is presented in Appendix A and B. We then proceed to the main theoretical development of this work based on the restrictive primitive models. In this part the set of differential equations for the fluctuation potential in dimensionless form is developed and an approximate solution is found using ordinary electrostatics.

In chapter 3 of this thesis a model for asymmetric size DH based on reference [36] is presented. In reference 36 Zuckerman, Fisher and Bekiranov presents an extension of the DH theory primarily on the 1:1 additive hard-sphere electrolyte with, say, negative ion diameters, σ_{-} , larger than positive ion diameters σ_{++} . The treatment highlights the crucial importance of the charge-unbalance “border zones” around each ion into which other ions of only one species may penetrate. The symmetrical formulation of MPB required to treat unequal ion sizes requires the calculation of discharge potentials Ψ^0 [33]. This potentials represents the mean potential of a discharged central ion at a field point in the solution. It’s mentioned by Outhwaite in reference [33] that this discharge potential is zero for ions of equal sizes, so in order to account for discharge potentials within the framework of DH theory, size exclusion effects must be implemented. Although the main subject of this work is the fluctuation potential for RPM, the calculation of the fluctuation potential including size and/or charge asymmetry represents a very important project for the future. The approximate solution to the fluctuation potential for the PM use the definition of these “border zones” to set DH equations that takes into account charge and/or size asymmetry.

In chapter 4 we utilize solution of the fluctuation potential to present structural and thermodynamic results for a 1:1 valence RPM electrolyte. We start by showing three-dimensional plots of the fluctuation potential solution. The plots show the fluctuation

potential at a planar slice passing through the center of the ions for two ionic separations and for the like and unlike ion cases. A physical interpretation of the results in terms ionic correlation energy is presented. To further test the solution's validity, configurational energies, and osmotic coefficients are calculated and compared to the Monte Carlo (MC) simulation data of Card and Valleau [21], and Rasiah, Card, and Valleau [22].

The following publication has come out of this thesis,

"An analysis of the fluctuation potential in the modified Poisson-Boltzmann theory for restricted primitive model electrolytes", E. O. Ulloa-Dávila and L. B. Bhuiyan, *Condens. Matter Phys.*, **20**, 43801 (2017) ; DOI: 10.5488/CMP.20.43801

Chapter 2

Model and Theory

In this Chapter we will be describing the physical model of the electrolyte that we used in this research and the modified Poisson-Boltzmann theory employed to solve the model.

2.1 Molecular Model

As indicated in the Introduction, the model electrolyte system used in this study consists of a binary, symmetric valence RPM electrolyte at room temperature. The total potential energy in the Hamiltonian is thus

$$U = \sum_{i < j}^N u_{ij} \quad (11)$$

$$u_{ij} = \begin{cases} \infty, \dots, \dots, r < \sigma_{ij} \\ \frac{e^2 Z_i Z_j}{4\pi\epsilon_0 \epsilon_r r}, \dots, r > \sigma_{ij} \end{cases} \quad (12)$$

where u_{ij} is the ion-ion interaction potential, Z_s is the valence of ion species s , e is the magnitude of the fundamental charge, r is the distance between the centers of two ions of types i and j , and $\sigma_{ij} = a_i + a_j = (\sigma_i + \sigma_j)/2$ is obtained by adding the ionic radii $a_i = \sigma_i/2$ and $a_j = \sigma_j/2$, where σ_i and σ_j are the diameters of ions i and j respectively. The relative permittivity ϵ_r is assumed to be uniform throughout the entire system.

2.2 Theory

The formulation of the SPB and the (traditional) MPB have appeared in the literature (see for example, references [27, 30, 31, 32]). Here we will restrict ourselves to outlining the principal ideas of the MPB theory, the main steps leading to the equations governing the fluctuation potential, and their solution.

In the canonical ensemble, the mean electrostatic potential $\psi(\{n\};q)$ at the field point \mathbf{r}_q for fixed ions at $\mathbf{r}_1 \dots \mathbf{r}_n$ is given by

$$\begin{aligned} \psi(\{n\};q) &= \left\langle \sum_{k=1}^N e_k v(k;q) \right\rangle = \\ &= \sum_{k=1}^n e_k v(k,q) + e_+ \int v(n+1,q) \rho^+(\{n\};n+1) d(n+1) \\ &+ e_- \int v(n+1,q) \rho^-(\{n\};n+1) d(n+1), \end{aligned} \quad (13)$$

where $n \ll N$,

$$v(k,l) = \frac{1}{4\pi\epsilon_0\epsilon_r r_{kl}}, \quad (14)$$

and

$$\rho^\alpha(\{n\};n+1) = (N_\alpha - n_\alpha) \frac{\int e^{-\beta U} d(n+2) \dots dN}{e^{-\beta U} d(n+1) \dots dN} \quad (15)$$

is the number density of ions of charged state α at \mathbf{r}_{n+1} for n fixed ions, and q_k is the charge of the k -th species ion. We note that in terms of valence Z_k of the species, $e_k = eZ_k$.

Equation (14) for the mean electrostatic potential $\psi(\{n\};q)$ at the field point q can be represented diagrammatically by representing potentials to the field point using solid lines and ionic correlation by dotted lines. For example for the case of $n=1$,

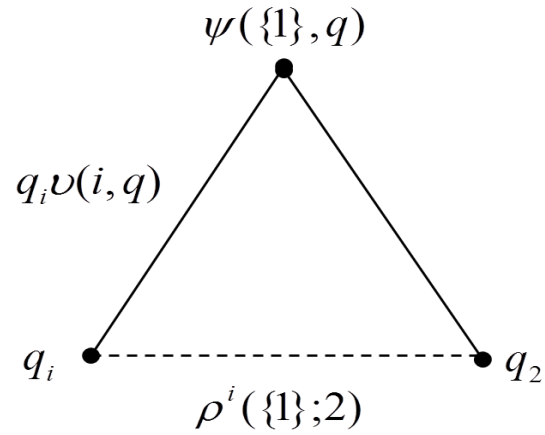


Figure 1 Mean electrostatic potential diagram for one fixed ion

or for the case of two fixed ions,

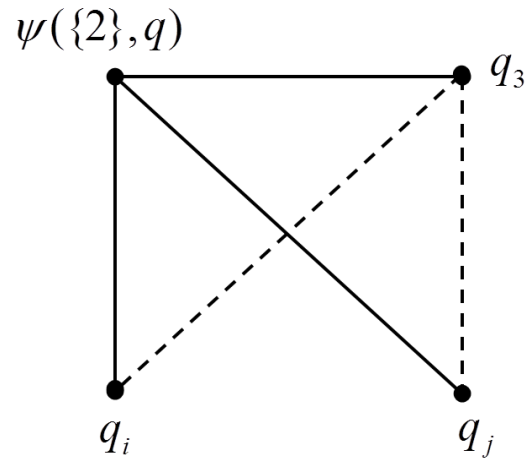


Figure 2 Mean electrostatic potential diagram for two fixed ions.

Applying the Laplacian operator to equation (13) gives the generalized Poisson equation

$$\nabla_q^2 \psi(\{n\}, q) = -\frac{1}{\varepsilon_0 \varepsilon_r} \sum_{k=1}^n e_k \delta(\vec{r}_k - \vec{r}_q) - \frac{1}{\varepsilon_0 \varepsilon_r} \sum_{\alpha} e_{\alpha} \rho^{\alpha}(\{n\}, q), \quad (16)$$

where $\delta(\vec{r})$ is the 3-D Dirac delta function. The first term on the right gives the direct potential contribution from the n fixed ions, while the second term gives the mean potential from the correlated ion density in the liquid.

For $n=1$ we have

$$\psi(1;2) = \frac{e_1}{4\pi\epsilon_0\epsilon_r r_{12}} + \frac{1}{4\pi\epsilon_0\epsilon_r} \sum_{\alpha} e_{\alpha} \int \frac{\rho_{\alpha}(1,q) dq}{r_{2q}}, \quad (17)$$

$$\nabla_q^2 \psi(1;2) = -\frac{e_1}{\epsilon_0\epsilon_r} \delta(\vec{r}_1 - \vec{r}_2) - \frac{1}{\epsilon_0\epsilon_r} \sum_{\alpha} e_{\alpha} \rho_{\alpha}(1,2), \quad (18)$$

For $n=2$, we have

$$\psi(1,2;3) = \frac{e_1}{4\pi\epsilon_0\epsilon_r r_{13}} + \frac{e_2}{4\pi\epsilon_0\epsilon_r r_{23}} + \frac{1}{4\pi\epsilon_0\epsilon_r} \sum_{\alpha} e_{\alpha} \int \frac{\rho_{\alpha}(1,2;q) dq}{r_{3q}}, \quad (19)$$

$$\nabla_3^2 \psi(1,2;3) = -\frac{1}{\epsilon_0\epsilon_r} e_1 \delta(\vec{r}_1 - \vec{r}_3) - \frac{1}{\epsilon_0\epsilon_r} e_2 \delta(\vec{r}_2 - \vec{r}_3) - \frac{1}{\epsilon_0\epsilon_r} \sum_{\alpha} e_{\alpha} \rho_{\alpha}(1,2;3) \quad (20)$$

The application of equations (17-20) relies upon the implementation of a closure relationship between conditional densities and mean electrostatic potentials. The Kirkwood charging process provides such a relationship [13]. In the Kirkwood charging process an ion i at \mathbf{r}_1 has a charge $\lambda_i q_i$, where the charge coupling parameter λ_i satisfies $0 \leq \lambda_i \leq 1$, so that

$$U = \sum_{i<j}^N u_{ij}^s + \sum_{j \neq i}^N u_{ij}^e(\lambda_i) + \sum_{j<k}^N u_{jk}^e, \quad (21)$$

where u_{ij}^s represents the short range interaction and u_{ij}^e is the electric interaction between ions. Taking the natural logarithm of the number densities $\{n\}$ and $\{n+1\}$, differentiating each with respect to the charge coupling parameter, and subtracting gives

$$\rho^s(\{n\}; n+1) = \rho^s(\{n\}; n+1 \mid \lambda_1 = 0) \times \exp \left\{ -\beta e_i \int_0^1 \lim_{q \rightarrow 1} [\psi(\{m+1\}; q) - \psi(\{m\}; q)] d\lambda_1 \right\} \quad (22)$$

For $n=1$, we have

$$\rho^s(1;2) = \rho^s(1;2 \mid \lambda_1 = 0) \exp \left\{ -\beta e_i \int_0^1 \lim_{q \rightarrow 1} [\psi(1,2; q) - \psi(1; q)] d\lambda_1 \right\}. \quad (23)$$

Writing

$$\psi(1,2; q) = \psi(1; q) + \psi(2; q) + \phi(1,2; q), \quad (24)$$

where $\phi(1,2; q)$ is the fluctuation potential that describes the departure from linear superposition of the mean electrostatic potential at the field point q from that of the two individual ions. This equation is generally taken as the definition of fluctuation potential.

Thus equation (23) gives,

$$g_{ij} = g_{ij}(\lambda_1 = 0) \exp \left\{ -\beta e_i [\psi(2;1) + \int_0^1 \phi(1,2;1) d\lambda_1] \right\} \quad (25)$$

where we have used $\rho_s(1,2) = \rho_s g_{ij}$. Alternatively,

$$g_{ij} = g_{ij}(\lambda_2 = 0) \exp \left\{ -\beta e_j [\psi(1;2) + \int_0^1 \phi(1,2;2) d\lambda_2] \right\}, \quad (26)$$

when charging ion 2 instead of ion 1.

The MPB Poisson's equation for the (q;q) same size problem is given by

$$\nabla^2 \psi(1;2) = -\frac{1}{\epsilon_0 \epsilon_r} e_i \delta(\vec{r}_1 - \vec{r}_2) - \frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s \zeta_{i,s} \exp \left\{ -\beta e_s \left[\psi(1;2) + \int_0^1 \phi(1,2;2) d\lambda_2 \right] \right\}, \quad (27)$$

where $\zeta_{i,s}$ are the excluded volume term, and ϕ the fluctuation potential.

The Poisson – Boltzmann theories can be derived from equation (27) by setting $\phi = 0$, and

$$\zeta_{i,s} = \begin{cases} 0, & r \leq \sigma_{ij} \\ 1, & r > \sigma_{ij} \end{cases}. \quad (28)$$

As shown before the radial distribution functions g_{ij} can be expressed in an unsymmetrical way either by Kirkwood charging ion 1 or ion 2 respectively

$$g_{ij} = \zeta_{ij}(\lambda_1 = 0) \exp\{-\beta e_i [\psi(2;1) + \int_0^1 \phi(1,2;1) d\lambda_1]\}, \quad (29)$$

or

$$g_{ij} = \zeta_{ij}(\lambda_2 = 0) \exp\{-\beta e_j [\psi(1;2) + \int_0^1 \phi(1,2;2) d\lambda_2]\}. \quad (30)$$

This unsymmetrical formulation restricts the theory to equal size and valence case. The unsymmetrical formulation of equations (29) and (30) can be overcome by deriving a symmetrical MPB equation. A symmetrical formulation of the MPB equation is derived by putting $q_i = 0$ in equation (29) and $q_j = 0$ in equation (30), substituting for $\zeta_{j,i}$, $\zeta_{i,j}$ in equations (29) and (30), respectively, and then combining the results we get

$$g_{ij} = g_{ij}^0 \exp\left\{-\frac{\beta e_j}{2} [\psi_i + \psi_i^0 + \int_0^1 (\phi(1,2;2) + \phi(1,2;2|e_i = 0)) d\lambda_2] - \frac{\beta e_i}{2} [\psi_j + \psi_j^0 + \int_0^1 (\phi(1,2;1) + \phi(1,2;1|e_j = 0)) d\lambda_1]\right\}, \quad (31)$$

where $g_{ij}^0 = g_{ij}(q_i=0, q_j=0)$, $\psi_i^0 = \psi(1;2|q_i=0)$, and $\psi_j^0 = \psi(2;1|q_j=0)$.

The superscript zero in equation (31) represents the corresponding quantity for a particular uncharged ion. The discharged mean potentials ψ^0 and discharged fluctuation potential ϕ^0 are due to ionic charge imbalances created by size asymmetric effects and therefore are zero for the RPM which is the main focus of this research.

Equation (31) with the fluctuation potential neglected gives the pair correlation function in the SPB theory, valid for symmetric or asymmetric ion sizes and valences, expressed in terms of the excluded volume term $g_{ij}^0 = \zeta_{ij}$ and the mean potentials ψ, ψ^0 .

To calculate pair correlation functions using the MPB theory we need a procedure to calculate the fluctuation potential $\phi(1,2;3)$. We begin by formulating the fluctuation potential problem in the RPM for a symmetric valence electrolyte, viz., $|Z_+| = |Z_-|$, consisting of N ions and satisfying global electro neutrality $\sum_s Z_s \rho_s = 0$. We will follow closely the notations used in reference [28].

The equations (17-20) can be expressed in terms of the radial distribution (or pair correlation) functions. For example, $g_{1\alpha}(1,q) = \rho_\alpha(1,q)/\rho_\alpha$ is related to the probability of finding an ion of species α of mean number density ρ_α , given an ion at 1, and so on and so forth. The Poisson equations follow (cf. equations 18, 20)

$$\nabla^2 \psi(1;3) = -\frac{e_i}{\epsilon_0 \epsilon_r} \delta(\vec{r}_1 - \vec{r}_3) - \frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s g_{is}(1,3), \quad (35)$$

$$\nabla^2 \psi(2;3) = -\frac{e_j}{\epsilon_0 \epsilon_r} \delta(\vec{r}_2 - \vec{r}_3) - \frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s g_{js}(2,3), \quad (36)$$

$$\nabla^2 \psi(1,2;3) = -\frac{e_i}{\epsilon_0 \epsilon_r} \delta(\vec{r}_1 - \vec{r}_3) - \frac{e_j}{\epsilon_0 \epsilon_r} \delta(\vec{r}_2 - \vec{r}_3) - \frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s g_{ijs}(1,2;3) \quad (37)$$

The distributions can, in turn, can be defined in terms of the potentials of mean force W viz., the doublet

$$g_{ij}(1,2) = \exp(-\beta W_{ij}(1,2)) \quad (38)$$

or the triplet

$$g_{ij}(1,2,3) = \exp(-\beta W_{ijk}(1,2,3)) \quad (39)$$

where W_{ij} , W_{ijk} , are the pair and triplet potentials of mean force, respectively. Here, $\beta=1/(k_B T)$ with k_B the Boltzmann constant and T the temperature. Hence the conditional relation obtains as

$$g_{ijk}(1,2;3) = e^{-\beta[W_{ik}(1,3)+W_{jk}(2,3)+w_{ijk}(1,2;3)]} \quad (40)$$

The term w_{ijk} is the potential of mean force associated with the departure from linear superposition of the pair potentials. A hierarchy of such equations can be constructed for higher order correlations. At the lowest order the classical PB theory follows upon neglecting $w_{ijk}(1,2;3)$, and to improve upon the PB, we need a procedure to estimate this term.

In the MPB formulation the hierarchy is broken at the triplet level by a closure condition that relates the w_{ijk} with the fluctuation potential ϕ_{ij} [33].

$$w_{ijk}(1,2;3) = e_k \phi_{ij}(1,2;3). \quad (41)$$

It is of interest to contrast this MPB closure with the Debye-Hückel closure

$$W_{ij}(1,2) = e_j \psi(1,2) \quad (42)$$

For the RPM system with finite ion diameter $2\sigma_{ii} = 2\sigma_{jj} = \sigma$, the Poisson equations 35-37 can be expressed in terms of the potentials of mean force as

$$\nabla^2 \psi(1;3) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s e^{-\beta W(1,3)}, \quad (43)$$

$$\nabla^2 \psi(2;3) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s e^{-\beta W(2,3)}, \quad (44)$$

$$\nabla^2 \psi(1,2;3) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s e^{-\beta[W(1,3)+W(2,3)+e_s \phi(1,2;3)]} \quad (45)$$

where the MPB closure (equation 41) has been use in equation 45. Equations 43 and 44 are exact, for one fixed ion in position 1 and 2, but equation 45 incorporates the deviation of the superposition principle in the form of the fluctuation potential term. To obtain an equation for the fluctuation potential, we subtract equations 43 and 44 from 45,

$$\begin{aligned} \nabla^2[\psi(1,2;3) - \psi(1,3) - \psi(2,3)] &= \nabla^2\phi(1,2;3) \\ &= -\frac{1}{\varepsilon} \sum_s e_s \rho_s \left\{ e^{-\beta[W(1,3)+W(2,3)=e_s\phi(1,2;3)]} - e^{-\beta W(1,3)} - e^{-\beta W(2,3)} \right\}, \end{aligned} \quad (46)$$

or more compactly

$$\nabla^2\phi(1,2;3) = -\frac{1}{\varepsilon_0 \varepsilon_r} \sum_s e_s \rho_s \left[g(1,3)g(2,3)e^{-\beta e_s \phi(1,2;3)} - g(1,3) - g(2,3) \right]. \quad (47)$$

Equation 47 is the basic nonlinear equation in the fluctuation potential problem. The corresponding equation for the fluctuation potential in terms of pair and triplet correlation function illustrates an important concept concerning the nature of the fluctuation potential. Subtracting equations 35 and 36 from 37 we have,

$$\begin{aligned} \nabla^2[\psi(1,2;3) - \psi(1,3) - \psi(2,3)] &= \\ &= \nabla^2\phi(1,2;3) \\ &= -\frac{e_i}{\varepsilon_0 \varepsilon_r} \delta(\vec{r}_1 - \vec{r}_3) - \frac{e_j}{\varepsilon_0 \varepsilon_r} \delta(\vec{r}_2 - \vec{r}_3) - \frac{1}{\varepsilon_0 \varepsilon_r} \sum_s e_s \rho_s g_{ijs}(1,2;3) \\ &\quad + \frac{e_i}{\varepsilon_0 \varepsilon_r} \delta(\vec{r}_1 - \vec{r}_3) + \frac{1}{\varepsilon_0 \varepsilon_r} \sum_s e_s \rho_s g_{is}(1,3) \\ &\quad + \frac{e_j}{\varepsilon_0 \varepsilon_r} \delta(\vec{r}_2 - \vec{r}_3) + \frac{1}{\varepsilon_0 \varepsilon_r} \sum_s e_s \rho_s g_{js}(2,3) \\ &= -\frac{1}{\varepsilon_0 \varepsilon_r} \sum_s e_s \rho_s \left[g_{ijs}(1,2;3) - g_{is}(1,3) - g_{js}(2,3) \right] \end{aligned}$$

$$\nabla^2 \phi(1,2;3) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s [g_{ijs}(1,2;3) - g_{is}(1,3) - g_{js}(2,3)]. \quad (48)$$

It is clear from equation 48 that the charge density source for fluctuation potential is associated with the charge atmospheres of the triplet and doublet densities.

Defining,

$$\begin{aligned} g(1,3^+) &= \exp[-\beta q_+ \psi(1,3)] \\ g(2,3^+) &= \exp[-\beta q_+ \psi(2,3)] \\ g(1,3^-) &= \exp[-\beta q_- \psi(1,3)] \\ g(2,3^-) &= \exp[-\beta q_- \psi(2,3)] \end{aligned} \quad (49)$$

we can expand the summation over species as

$$\begin{aligned} \nabla^2 \phi(1,2;3) &= -\frac{1}{\epsilon_0 \epsilon_r} e_+ \rho_+ [g(1,3^+)g(2,3^+)e^{-\beta e_+ \phi(1,2;3)} - g(1,3^+) - g(2,3^+)] \\ &+ e_- \rho_- [g(1,3^-)g(2,3^-)e^{-\beta e_- \phi(1,2;3)} - g(1,3^-) - g(2,3^-)] \end{aligned} \quad (50)$$

where a number with the superscript notation with a positive or negative sign represents the presence of the corresponding ion at the referred position in space.

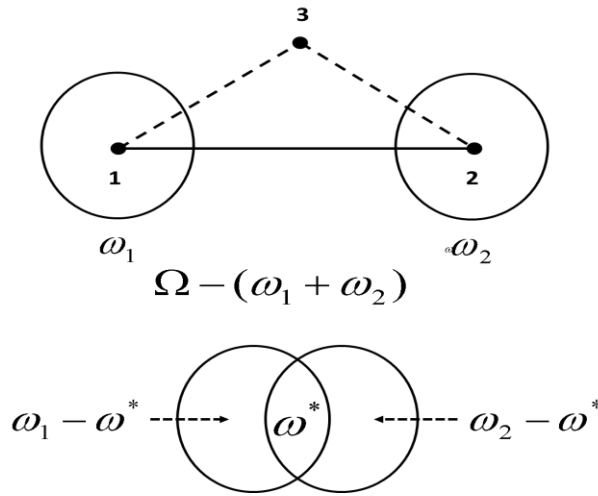


Figure 3 Fluctuation potential geometry for the restricted primitive model

Figure 3 shows the geometry of the fluctuation potential set of equations. Ω represents the total volume of the ionic solution, ω_1 and ω_2 represent the exclusion volumes of ion 1 and 2 respectively. 1 and 2 are the centers of the ions, 3 is the field point in space, and ω^* is the overlap volume. Region I ($\Omega - \omega_1 - \omega_2$) is the bulk volume defined as the total volume minus the exclusion volumes of ions 1 and 2. Region II and III are the interior of the exclusion volume of ion 1 and 2 minus the overlap volume. These regions are represented as $\omega_1 - \omega^*$, and $\omega_2 - \omega^*$ respectively. No ions of species 1 can penetrate region I so $g(1,3^+) = g(1,3^-) = 0$ in region I, and no ions of species 2 can penetrate region II so $g(2,3^+) = g(2,3^-) = 0$ in region II. Region IV is the overlap volume. The nonlinear system of equations governing the fluctuation potential are then given by the following expressions

$$\begin{aligned}
 I : \Omega - (\omega_1 - \omega_2) \\
 \nabla^2 \phi(1,2;3) = -\frac{1}{\epsilon_0 \epsilon_r} [e_+ \rho_+ [g(1,3^+)g(2,3^+)e^{-\beta e_+ \phi(1,2;3)} - g(1,3^+) - g(2,3^+)] \\
 + e_- \rho_- [g(1,3^-)g(2,3^-)e^{-\beta e_- \phi(1,2;3)} - g(1,3^-) - g(2,3^-)]] \quad (51)
 \end{aligned}$$

$$\begin{aligned}
 II : \omega_1 - \omega^* \\
 \nabla^2 \phi(1,2;3) = -\frac{1}{\epsilon_0 \epsilon_r} [e_+ \rho_+ g(2,3^+) + e_- \rho_- g(2,3^-)] \quad (52)
 \end{aligned}$$

$$\begin{aligned}
 III : \omega_2 - \omega^* \\
 \nabla^2 \phi(1,2;3) = -\frac{1}{\epsilon_0 \epsilon_r} [e_+ \rho_+ g(1,3^+) + e_- \rho_- g(1,3^-)] \quad (53)
 \end{aligned}$$

$$\begin{aligned}
 IV : \omega^* \\
 \nabla^2 \phi(1,2;3) = 0, \quad (54)
 \end{aligned}$$

After expressing the Laplacian in ionic diameter scale, and imposing the global electro-neutrality condition equations (Appendix A) we have the set of dimensionless fluctuation potential equations for the size symmetric case

$$\begin{aligned} -\left(\frac{\epsilon_0 \epsilon_r}{e^2 \beta \rho \sigma^2}\right) \nabla_d^2 [e\beta\phi(1,2;3)] &= \left(\frac{Z_+ Z_-}{Z_- - Z_+}\right) [g(1,3^+) g(2,3^+) e^{-Z_+ e\beta\phi(1,2;3)} \\ &- g(1,3^-) g(2,3^-) e^{-Z_- e\beta\phi(1,2;3)} - g(1,3^+) - g(2,3^+) + g(1,3^-) + g(2,3^-)] \end{aligned} \quad (55)$$

Defining the dimensionless fluctuation potential as follows

$$\Phi(1,2;3) = e\beta\phi(1,2;3) \quad , \quad (56)$$

we have

$$\begin{aligned} -\left(\frac{\epsilon_0 \epsilon}{e^2 \beta \rho \sigma^2}\right) \nabla^2 [\Phi(1,2;3)] &= \left(\frac{Z_+ Z_-}{Z_- - Z_+}\right) [g(1,3^+) g(2,3^+) e^{-Z_+ \Phi(1,2;3)} \\ &- g(1,3^-) g(2,3^-) e^{-Z_- \Phi(1,2;3)} - g(1,3^+) - g(2,3^+) + g(1,3^-) + g(2,3^-)] \end{aligned} \quad (57)$$

Finally we express the parameters of the model in the dimensionless packing fraction η , the plasma coupling Γ , and $y_0 = \sqrt{24\eta\Gamma}$ (appendix A), to get the set of dimensionless

fluctuation potential equations for the size symmetric case

$$\begin{aligned} I : \Omega - (\omega_1 + \omega_2) \\ -\frac{1}{y_0^2} \nabla^2 \Phi(1,2;3) &= \left(\frac{Z_+ Z_-}{Z_- - Z_+}\right) [g(1,3^+) g(2,3^+) e^{-Z_+ \Phi(1,2;3)} \\ &- g(1,3^-) g(2,3^-) e^{-Z_- \Phi(1,2;3)} - g(1,3^+) - g(2,3^+) + g(1,3^-) + g(2,3^-)] \end{aligned} \quad , \quad (58)$$

$$\begin{aligned} II : \omega_1 \\ -\frac{1}{y_0^2} \nabla^2 \Phi(1,2;3) &= \left(\frac{Z_+ Z_-}{Z_- - Z_+}\right) [-g(2,3^+) + g(2,3^-)] \end{aligned} \quad (59)$$

$$\begin{aligned} III : \omega_2 \\ -\frac{1}{y_0^2} \nabla^2 \Phi(1,2;3) &= \left(\frac{Z_+ Z_-}{Z_- - Z_+}\right) [-g(1,3^+) + g(1,3^-)] \end{aligned} \quad (60)$$

$$IV : \omega^* \quad (61)$$

$$\nabla^2 \Phi(1,2;3) = 0$$

The boundary conditions are that the fluctuation potential and its normal derivative are continuous across boundaries.

To find an approximate solution to the system of equations we define the quantity P from equations (58-61) as follows

$$\nabla^2 \Phi(1,2;3) = -y_0^2 P[\Phi, g(1,3), g(2,3)] \quad , \quad (62)$$

with formal solution given by [37, 38]

$$\Phi(1,2;3) = \int_{\Omega} \frac{y_0^2}{r} P[\Phi, g(1,3), g(2,3)] dr \quad , \quad (63)$$

we can now write equations 58-61 in terms of P as follows,

$$I : \Omega - (\omega_1 + \omega_2)$$

$$-\frac{1}{y_0^2} \nabla^2 \Phi(1,2;3) =$$

$$P_I[\Phi, g(1,3), g(2,3)] = \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) [g(1,3^+) g(2,3^+) e^{-Z_+ \Phi(1,2;3)} - g(1,3^-) g(2,3^-) e^{-Z_- \Phi(1,2;3)} - g(1,3^+) - g(2,3^+) + g(1,3^-) + g(2,3^-)] \quad , \quad (64)$$

$$II : \omega_1$$

$$-\frac{1}{y_0^2} \nabla^2 \Phi(1,2;3) = P_{II} [g(1,3), g(2,3)], \quad (65)$$

$$= \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) [-g(2,3^+) + g(2,3^-)]$$

$$III : \omega_2$$

$$-\frac{1}{y_0^2} \nabla^2 \Phi(1,2;3) = P_{III} [g(1,3), g(2,3)], \quad (66)$$

$$= \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) [-g(1,3^+) + g(1,3^-)]$$

$$\begin{aligned}
IV : \omega^* \\
\nabla^2 \Phi(1,2;3) = P_{IV} . \\
P_{IV} = 0
\end{aligned} \tag{67}$$

It's important to note that the P in regions II and III are not explicit functions of the fluctuation potential. The radial distribution functions $g(1,3)$ and $g(2,3)$ are implicit functions of the fluctuation potential.

In order to make progress in the solution to the fluctuation potential problem our first step is to approximate the radial distribution functions $g(1,3)$ and $g(2,3)$, in the source functions, with exponentials of the linearized dimensionless Boltzmann equation's solutions. For the RPM, and later for the PM, this linearized solutions of the Boltzmann takes the form of linear combinations of screened Yukawa potentials of the form

$$\Psi(r_d) = \sum_i c_i(\eta, \Gamma, \alpha) \frac{e^{-\mu_i(\eta, \Gamma, \alpha)r}}{r} , \tag{68}$$

where the c coefficients and the screening scales μ are functions of the parameters of the dimensionless model. This choice is consistent with the boundary conditions for the fluctuation potential, which requires the decay of the fluctuation potential as we move away from ion's centers 1 and 2. For simplicity, we use the Debye-Hückel potentials (Appendix B) instead of the summation of Yukawa potentials

$$\begin{aligned}
\Psi_{\pm}(r) = \Gamma Z_{\pm} \frac{e^{-yr}}{(1+y)r} , \\
y = \kappa_D \sigma = \sqrt{-y_0^2 Z_+ Z_-} = \sqrt{-24\eta \Gamma Z_+ Z_-}
\end{aligned} \tag{69}$$

where κ_D is the usual Debye-Hückel parameter (Appendix B). Exponentiation of these potentials defines our approximation for the radial distribution functions, we get

$$\begin{aligned}
g(1,3^+) (= g_{DH}(1,3^+)) &= \exp[-Z_+ \Psi_1(1,3)] \\
g(2,3^+) (= g_{DH}(2,3^+)) &= \exp[-Z_+ \Psi_2(2,3)] \\
g(1,3^-) (= g_{DH}(1,3^-)) &= \exp[-Z_- \Psi_1(1,3)] \\
g(2,3^-) (= g_{DH}(2,3^-)) &= \exp[-Z_- \Psi_2(2,3)]
\end{aligned} \tag{70}$$

where the subscripts in the Yukawa potentials refers to the charged state of the central ion, and the signs in the Z represents the charged state of the ion at field point 3. Inserting the radial distribution functions (equation 70) in the integral of equation 63 will render the contribution to the fluctuation potential from charge in regions I and II as an ordinary integral in space.

The next step is to obtain an approximation for the P in the bulk region, outside ions 1 and 2. In this region the function P is non-linear in the fluctuation potential. Inserting the radial distribution functions 70 with DH functions (equation 69), and linearizing, gives for the P in region I

$$\begin{aligned}
P_I[\Phi, g(1,3), g(2,3)] &= \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) [g(1,3^+)g(2,3^+)(1 - Z_+ \Phi) \\
&\quad - g(1,3^-)g(2,3^-)(1 - Z_- \Phi) - g(1,3^+) - g(2,3^+) + g(1,3^-) + g(2,3^-)] \\
&= \left(\frac{Z_+ Z_-}{Z_+ - Z_-} \right) [Z_+ g(1,3^+)g(2,3^+) - Z_- g(1,3^-)g(2,3^-)] \Phi(1,2;3) + \\
&\quad \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) [g(1,3^+)g(2,3^+) - g(1,3^-)g(2,3^-) \\
&\quad - g(1,3^+) - g(2,3^+) + g(1,3^-) + g(2,3^-)]
\end{aligned} \tag{71}$$

For small fluctuation potential, we neglect the right hand side of equation 71. For example for a symmetric valency 1:1 RPM electrolyte, the theme of this work, we have noted that the DH radial distributions in equation 71 are of order of unity for the physical parameters and the range of concentrations used. If the fluctuation potential is of order of 10^{-2} or less then the right hand of equation 71 will be of similar order and

can be neglected as a first approximation for such a system. Under this approximation the Fluctuation potential is given by,

$$\Phi(1,2;3) = \frac{y_0^2}{4\pi} \left[\int_{\omega_1} \frac{F_1[g(2, q^+), g(2, q^-)] dV_q}{|\vec{r}_{\alpha q} - \vec{r}_3|} + \int_{\omega_2} \frac{F_2[g(1, q^+), g(1, q^-)] dV_q}{|\vec{r}_q - \vec{r}_3|} \right. \\ \left. \int_{\Omega - (\omega_1 + \omega_2)} \frac{F_3[g(1, q^+), g(1, q^-), g(2, q^+), g(2, q^-)] dV_q}{|\vec{r}_q - \vec{r}_3|} \right] \quad (72)$$

, where the F are defined by,

$$F_1[g(2, q^+), g(2, q^-)] = \frac{Z_+ Z_-}{Z_- - Z_+} [-g(2, q^+) + g(2, q^-)] , \quad (73)$$

$$F_2[g(1, q^+), g(1, q^-)] = \frac{Z_+ Z_-}{Z_- - Z_+} [-g(1, q^+) + g(1, q^-)] , \quad (74)$$

and

$$F_3[g(1, q^+), g(1, q^-), g(2, q^+), g(2, q^-)] = \\ \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) [g(1, q^+)g(2, q^+) - g(1, q^-)g(2, q^-) - g(1, q^+) - g(2, q^+) \\ + g(1, q^-) + g(2, q^-)] \quad (75)$$

In this work the integral of equation 72 is calculated by discretization of space, which is discussed in the next Chapter in connection with the numerical solution.

The calculation of the MPB pair correlation functions utilizes the symmetric formulation (31) in reduced variables, with zero discharge mean potentials $\Psi^0 = 0$ and zero discharge fluctuation potentials $\Phi^0 = 0$ (size symmetric), given by,

$$g(1,2) = \zeta_{12} \exp \left\{ -\frac{Z_2}{2} [\Psi(1;2) + \int_0^1 \Phi(1,2;2|e_2 = \lambda_2 Z_2) d\lambda_2] - \frac{Z_1}{2} [\Psi(2;1) + \int_0^1 \Phi(1,2;1|e_1 = \lambda_1 Z_1) d\lambda_1] \right\} \quad (76)$$

We note that equation (76) reduces to the simpler expression,

$$g(1,2) = \zeta_{12} \exp \left\{ -Z_2 [\Psi(1;2) + \int_0^1 \Phi(1,2;2|e_2 = \lambda_2 Z_2) d\lambda_2] \right\} \quad (77)$$

for the 1:1 RPM electrolyte.

DH functions are used for $\Psi(1;2)$ and an analytic expression for the Percus-Yevick (PY) radial distribution functions for of hard spheres [4] have been used for the excluded volume term, which can be used up to $\sim 2M$ concentration, given by

$$\begin{aligned} \zeta_{ij} = g_{12}^{HS} &= 0 & r < \sigma \\ \zeta_{ij} = g_{12}^{HS} &= 1 + 8\eta \left[1 - \frac{3}{4} \left(\frac{r}{\sigma} \right) - \frac{1}{16} \left(\frac{r}{\sigma} \right)^3 \right] & \sigma < r < 2\sigma \\ \zeta_{ij} = g_{12}^{HS} &= 1 & r > 2\sigma \end{aligned} \quad (78)$$

A useful way of testing the fluctuation potential solution is through subsequent evaluation of structure and thermodynamics of the electrolyte solution. For the calculation of osmotic coefficients ϕ and reduced configurational energy U we used equation 12 from reference [15], written in dimensionless reduced variables as,

$$\phi - 1 = U / 3NkT + 2\eta [g_A(1) + g_B(1)] \quad (79)$$

And

$$U / Nk_B T = \frac{y_0^2}{4} \int_1^\infty [g_A(y) + g_B(y)](y) d(y) \quad , \quad (80)$$

where $y = r/\sigma$ (reduced radial distance), g_A and g_B are radial distribution functions for like and unlike ions respectively, and the argument of 1 in g_A and g_B in equation (79) refers to contact value.

Chapter 3

Size/Charge Asymmetric Fluctuation Potential

The effects of size asymmetry enters the symmetric MPB equation through the potentials ψ and the discharge potentials ψ^0 . In this thesis we confine ourselves with the two-species size-asymmetric primitive model (SAPM), which consists of equal numbers, $N_+ = N_-$, of positive and negative ions with hard-core diameters $\sigma_- > \sigma_+$, and charges of equal magnitudes $q_+ = -q_- = Z_{\pm}e$. The complementary case $\sigma_+ > \sigma_-$ follows trivially by symmetry. We assume additivity of the diameters

$$\sigma_{+-} = \frac{\sigma_+ + \sigma_-}{2} \quad (81)$$

The degree of size asymmetry will be described by the fractional deviation from σ_{+-} , namely

$$\delta_+ = \frac{\sigma_{++} - \sigma}{\sigma} \quad (82)$$

$$\delta_- = \frac{\sigma_{--} - \sigma}{\sigma} \quad (83)$$

The diameter ratio is given in terms of the asymmetry as,

$$\alpha = \frac{\sigma_+}{\sigma_-} = \frac{1 - \delta_-}{1 + \delta_-}. \quad (84)$$

The asymmetric size model, is naturally more complicated than the symmetrical size case. To set the PB or linearized PB equation for a system of different size ions in a solution, three distinct concentric spherical shells or zones must be accounted for. Hard sphere ion volume exclusion effects will result in the existence of regions around the central ion where only the smaller ionic species will be able to penetrate. Let suppose, for example, that we

have the situation of a central positive ion with diameter ordering in size according to $\sigma_+ < \sigma_{+-} < \sigma_-$. Following reference [36], we term this case the “inner” case since like-like diameter of the central ion is less than σ_{+-} . No ion center can enter the interior zone $0 < r < \sigma_+$. The sub-border zone is defined by $\sigma_+ < r < \sigma_{+-}$. This zone can only be populated with the center of the smaller positive ions. Finally the exterior zone $r > \sigma_{+-}$ can be populated by the charged centers of both ionic species. When a larger negative ion is chosen to be the central ion there is also a “super-border” zone, $\sigma_{+-} < r < \sigma_-$, into which only positive charges may enter.

The starting point in this asymmetric size DH model is the Poisson equation that relates the electrostatic averaged potential with the corresponding averaged charge density. Here we consider a two species model with hard sphere charges $q_{\pm} = Z_{\pm}e$ located at the spheres center. With the collisional diameter restricted as $\sigma_{++} \leq \sigma \equiv \sigma_{+-} \leq \sigma_{--}$.

Following [36] we define ψ_{α} to be the average electrostatic potential at a fixed central ion due to all other ions. The superscripts $<$ and $>$ will serve as reminders of the relative ions sizes. The subscript α will refer to ionic $+$ or $-$ charge (ionic species).

Calculation of the potential $\psi_{\alpha}(T, \rho)$ begins by fixing ion of species α at the origin. The induced electrostatic potential, $\phi(\vec{r})$ and corresponding charge density, $\rho(\vec{r})$ are then related by the averaged Poisson equation, namely,

$$\nabla^2 \langle \phi(\vec{r}) \rangle_{\alpha} = -\frac{1}{\epsilon_0 \epsilon_r} \langle \rho(\vec{r}) \rangle_{\alpha} \quad (85)$$

, where the subscript α indicates that the average is taken with a charge of species α at the origin. The ion potential follows from the limit

$$\psi_\alpha(T, \rho) = \lim_{r \rightarrow 0} \left[\langle \phi(\vec{r}) \rangle_\alpha - \frac{q_\alpha}{4\pi\epsilon} \right], \quad (86)$$

, which eliminates the self-interaction of the fixed charge at the origin.

We now approximate the average charge density, $\langle \rho(\vec{r}) \rangle_\alpha$ by the linearization of the exponential in the Boltzmann factor, yielding

$$\langle \rho(\vec{r}) \rangle_\alpha \cong \sum_{s=+,-} q_s \rho_s \exp[-\beta q_s \langle \phi(\vec{r}) \rangle_\alpha], \quad (87)$$

$$\cong \sum_{s=+,-} q_s \rho_s [1 - \beta q_s \langle \phi(\vec{r}) \rangle_\alpha], \quad (88)$$

, where $\beta = 1/k_B T$. In the size asymmetric model, the approximate charge density must be allowed to take a different form in each of the three distinct zones around the central ion. Thus, for example, for a fixed positive smaller ion at the center one has

$$\langle \rho_q(r) \rangle_+ = q_+ \delta(r) \quad r < \sigma_{++} \quad (89)$$

$$\cong q_+ \rho_+ [1 - \beta q_+ \langle \phi(r) \rangle_+] \quad \sigma_{++} < r < \sigma \quad (90)$$

$$\cong -(\kappa_D^2) \langle \phi(r) \rangle_+ \quad r > \sigma \quad (91)$$

Here the inverse Debye length is defined the usual way via

$$\kappa_D^2 = \frac{\beta e^2}{\epsilon_0 \epsilon_r} \sum_\alpha \rho_\alpha Z_\alpha^2. \quad (92)$$

It can be seen in this expression that the sub-border zone ($\sigma_{++} < r < \sigma = \sigma_{+-}$) can be populated only by the smaller positive ions, so only q_+ appears at the right-hand side of the equation. The exterior zone ($r > \sigma$) can be populated by both species so the the equation follows the standard Debye-Hückel form. Equations (89-91) represent the complete reduction of the linearized Poisson equation to the asymmetric Debye-Hückel theory

(ADH). For the case of the larger central negative ion a complementary “super-border zone” ($\sigma_{+-} < r < \sigma_{--}$) into which + charges may penetrate must be included.

The symmetric MPB formulation for ions of asymmetric sizes (equation 76) requires the calculation of the electrostatic potential terms ψ_i and ψ_j for central positive and negative ions respectively. Also “discharge potentials” ψ_i^0 and ψ_j^0 , that represents the mean electrostatic potentials for the central ions considered as neutral hard spheres with the rest of the ions in the solution with the usual charges, need to be included in the symmetric MPB equation 76. In this chapter the ADH model system of equations is set in unit less form and solved exactly, for standard electrostatic boundary conditions of continuity of the potential ψ and the radial derivative of the potential $\frac{\partial \psi}{\partial r}$, at the boundaries of the different charged zones.

We start by casting the ADH equation in unit-less variables. We take the negative ion as the larger diameter σ_- . The opposite case follows by symmetry. The spatial dimension is scaled with respect to the larger ion, in the present case, the negative one. The parameters of the model are the packing fraction η the plasma coupling Γ , and the size parameter α . The ADH equation is

$$\nabla^2 \Psi = \frac{y^2}{Z_- - Z_+} \left[e^{-Z_+ \Psi} - e^{-Z_- \Psi} \right] \quad (93)$$

, where

$$y^2 = -24\eta\Gamma \left(\frac{Z_- - Z_+}{Z_- \alpha^3 - Z_+} \right) Z_+ Z_- \quad , \quad (94)$$

(Appendix A). For central positive smaller ion the ADH equations are

$$\nabla^2 \psi(r) = -\frac{\rho}{\varepsilon_0 \varepsilon_r} = -\frac{q_+}{\varepsilon_0 \varepsilon_r} \delta(r), \quad r < \sigma_{++} \quad (95)$$

$$\nabla^2 \psi(r) = -\frac{\rho}{\varepsilon_0 \varepsilon_r} = -\frac{q_+ \rho_+}{\varepsilon_0 \varepsilon_r} [1 - \beta q_+ \psi(r)], \quad \sigma_{++} < r < \sigma \quad (96)$$

$$\nabla^2 \psi(r) \cong \kappa_D^2 \psi(r). \quad r > \sigma \quad (97)$$

This equations are written in dimensionless units. Starting with the innermost region we have

$$\frac{1}{\sigma^2} \nabla^2 \left(\frac{\Psi}{e\beta} \right) = -\frac{1}{\varepsilon_0 \varepsilon_r} Z_+ e \delta(r)$$

, where we have defined the dimensionless potential as

$$\Psi = e\beta\psi(r)$$

Then after some manipulation we get

$$\nabla^2 \Psi = -4\pi Z_+ \delta(r), \quad 0 < r < \alpha \quad (98)$$

, with standard solution

$$\begin{aligned} \Psi_1(r) &= \Gamma Z_+ \int \frac{\delta(r)}{r} d^3\vec{r} \\ &= \Gamma \frac{Z_+}{r} + C_1, \end{aligned} \quad (99)$$

, where C_1 is the first constant of integration to be evaluated later from the boundary conditions.

The second sub-border zone can only be populated by the smaller species, in this case the positive ions. We start by writing equation (96) in unit-less dimensions

$$\nabla^2 \Psi = \frac{1}{r} \frac{d}{dr} \left(r^2 \frac{d}{dr} \Psi \right) = \frac{y^2}{Z_- - Z_+} [1 - Z_+ \Psi], \quad \alpha < r < \frac{\alpha+1}{2} \quad (100)$$

The solution to equation (100) was obtained to be

$$\Psi_2(r) = \frac{1}{Z_+} + C_2 \frac{e^{-\xi r}}{r} + C_3 \frac{e^{+\xi r}}{r}. \quad (101)$$

Where ξ is given by

$$\xi = y \sqrt{\frac{Z_+}{Z_+ - Z_-}}. \quad (102)$$

The equation for the outer zone is the standard DH equation with solution given by

$$\Psi_3(r) = C_4 \frac{e^{-y_0 r}}{r}, \quad r > \frac{\alpha + 1}{2} \quad (103)$$

To evaluate the constants $C_1, C_2, C_3,$ and $C_4,$ standard electrostatic boundary conditions of continuity of potential function $\Psi,$ and its normal derivative $\frac{\partial \Psi}{\partial r},$ are implemented at the

borders of each zone. The result is the following linear system of equations

At boundary $r = \alpha,$ we have

$$\Psi_1(\alpha) = \Psi_2(\alpha),$$

$$\Gamma \frac{Z_+}{\alpha} + C_1 = C_2 \frac{e^{-\xi \alpha}}{\alpha} + C_3 \frac{e^{+\xi \alpha}}{\alpha} + \frac{1}{Z_+} \quad (104)$$

, and

$$\partial_n \Psi_1(\alpha) = \partial_n \Psi_2(\alpha),$$

$$-\Gamma \frac{Z_+}{\alpha^2} = -C_2 \frac{e^{-\xi \alpha}}{\alpha} \left(\frac{1}{\alpha} + \xi \right) + C_3 \frac{e^{+\xi \alpha}}{\alpha} \left(-\frac{1}{\alpha} + \xi \right), \quad (105)$$

, at $r = \frac{\alpha + 1}{2}$

$$\Psi_2\left(\frac{\alpha + 1}{2}\right) = \Psi_3\left(\frac{\alpha + 1}{2}\right), \quad (106)$$

$$\frac{1}{Z_+} + 2C_2 \frac{e^{-\xi \left(\frac{\alpha+1}{2}\right)}}{\alpha+1} + 2C_3 \frac{e^{+\xi \left(\frac{\alpha+1}{2}\right)}}{\alpha+1} = 2C_4 \frac{e^{-y \left(\frac{\alpha+1}{2}\right)}}{\alpha+1}, \quad (107)$$

, and

$$\partial_n \Psi_2 \left(\frac{\alpha+1}{2} \right) = \partial_n \Psi_3 \left(\frac{\alpha+1}{2} \right), \quad (108)$$

$$\begin{aligned} & -2C_2 \frac{e^{-\xi \left(\frac{\alpha+1}{2}\right)}}{\alpha+1} \left(\frac{2}{\alpha+1} + \xi \right) + 2C_3 \frac{e^{+\xi \left(\frac{\alpha+1}{2}\right)}}{\alpha+1} \left(-\frac{2}{\alpha+1} + \xi \right) \\ & = -2C_4 \frac{e^{-y \left(\frac{\alpha+1}{2}\right)}}{\alpha+1} \left(\frac{2}{\alpha+1} + y \right) \end{aligned} \quad (109)$$

To solve for the constants C_1 , C_2 , C_3 and C_4 , we express equations (104-109) in matrix form

$$A \cdot C = B, \quad (110)$$

, where

$$C = \begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{bmatrix},$$

$$A = \begin{bmatrix} -\alpha & e^{-\xi \cdot \alpha} & e^{+\xi \alpha} & 0 \\ 0 & e^{-\xi \left(\frac{\alpha+1}{2}\right)} & e^{+\xi \left(\frac{\alpha+1}{2}\right)} & -e^{-y \left(\frac{\alpha+1}{2}\right)} \\ 0 & e^{-\xi \cdot \alpha} \left(\frac{1}{\alpha} + \xi \right) & -e^{+\xi \cdot \alpha} \left(-\frac{1}{\alpha} + \xi \right) & 0 \\ 0 & -e^{-\xi \cdot \left(\frac{\alpha+1}{2}\right)} \left(\frac{2}{\alpha+1} + \xi \right) & e^{+\xi \cdot \left(\frac{\alpha+1}{2}\right)} \left(-\frac{2}{\alpha+1} + \xi \right) & e^{-y \left(\frac{\alpha+1}{2}\right)} \left(\frac{2}{\alpha+1} + y \right) \end{bmatrix},$$

$$B = \begin{bmatrix} -\frac{\alpha}{Z_+} + \Gamma Z_+ \\ -\frac{\alpha+1}{2Z_+} \\ \Gamma \frac{Z_+}{\alpha} \\ \alpha \\ 0 \end{bmatrix}.$$

The explicit expressions for the matrix of the coefficients was obtained by solving the linear system of equations. The results, for central smaller positive ion, are as follows

$$C_1 = -\frac{F_1}{G_1}$$

$$F_1 = -e^{2\alpha \cdot \xi} y_0 + e^{(1+\alpha)\xi} y + e^{2\alpha \cdot \xi} \xi + e^{(1+\alpha)\xi} \xi - 2e^{\alpha \cdot \xi + \frac{1}{2}(1+\alpha)\xi} \xi - e^{\alpha \cdot \xi + \frac{1}{2}(1+\alpha)\xi} y$$

$$+ e^{2\alpha \cdot \xi} y \alpha \xi + e^{(1+\alpha)\xi} y \alpha \xi - e^{\alpha \cdot \xi + \frac{1}{2}(1+\alpha)\xi} y \alpha \xi - e^{2\alpha \cdot \xi} y Z_+^2 \Gamma \xi - e^{(1+\alpha)\xi} y Z_+^2 \Gamma \xi$$

$$- e^{2\alpha \cdot \xi} \alpha \xi^2 + e^{(1+\alpha)\xi} \alpha \xi^2 + e^{2\alpha \cdot \xi} Z_+^2 \Gamma \xi^2 - e^{(1+\alpha)\xi} Z_+^2 \Gamma \xi^2$$

$$G_1 = Z_+ \left[e^{2\alpha \cdot \xi} y - e^{(1+\alpha)\xi} y - e^{2\alpha \cdot \xi} \xi - e^{(1+\alpha)\xi} \xi - e^{2\alpha \cdot \xi} y \alpha \xi - e^{(1+\alpha)\xi} y \alpha \xi + e^{2\alpha \cdot \xi} \alpha \xi^2 - e^{(1+\alpha)\xi} \alpha \xi^2 \right]$$
(111)

$$C_2 = \frac{F_2}{G_2}$$

$$F_2 = e^{\alpha \cdot \xi + \frac{1}{2}(1+\alpha)\xi} \times$$

$$\left[2e^{\alpha \cdot \xi} + e^{\alpha \cdot \xi} y + e^{\alpha \cdot \xi} y \alpha + 2e^{\frac{1}{2}(1+\alpha)\xi} y Z_+^2 \Gamma - 2e^{\alpha \cdot \xi} \alpha \xi - e^{\alpha \cdot \xi} y \alpha \xi - e^{\alpha \cdot \xi} y \alpha^2 \xi + 2e^{\frac{1}{2}(1+\alpha)\xi} Z_+^2 \Gamma \xi \right]$$

$$G_2 = 2Z_+ \times$$

$$\left[-e^{2\alpha \cdot \xi} y + e^{(1+\alpha)\xi} y + e^{2\alpha \cdot \xi} \xi + e^{(1+\alpha)\xi} \xi + e^{2\alpha \cdot \xi} y \alpha \xi + e^{(1+\alpha)\xi} y \alpha \xi - e^{2\alpha \cdot \xi} \alpha \xi^2 + e^{(1+\alpha)\xi} \alpha \xi^2 \right]$$
(112)

$$\begin{aligned}
C_3 &= -\frac{F_3}{G_3} \\
F_3 &= -2e^{\frac{1}{2}(1+\alpha)\xi} - e^{\frac{1}{2}(1+\alpha)\xi} y - e^{\frac{1}{2}(1+\alpha)\xi} y\alpha - 2e^{\alpha\cdot\xi} yZ_+^2\Gamma - 2e^{\frac{1}{2}(1+\alpha)\xi} \alpha\xi - e^{\frac{1}{2}(1+\alpha)\xi} y\alpha\xi \\
&\quad - e^{\frac{1}{2}(1+\alpha)\xi} y\alpha^2\xi + 2e^{\alpha\cdot\xi} Z_+^2\Gamma\xi \\
G_3 &= 2Z_+[e^{2\alpha\cdot\xi} y - e^{(1+\alpha)\xi} y - e^{2\alpha\cdot\xi} \xi - e^{(1+\alpha)\xi} \xi - e^{2\alpha\cdot\xi} y\alpha\xi - e^{(1+\alpha)\xi} y\alpha\xi + e^{2\alpha\cdot\xi} \alpha\xi^2 - e^{(1+\alpha)\xi} \alpha\xi^2]
\end{aligned} \tag{113}$$

$$\begin{aligned}
C_4 &= \frac{F_4}{G_4} \\
F_4 &= e^{y\left(-1+\frac{1+\alpha}{2}\right)} [2e^{2\alpha\cdot\xi} - 2e^{(1+\alpha)\xi} + e^{2\alpha\cdot\xi} \xi + e^{(1+\alpha)\xi} \xi - e^{2\alpha\cdot\xi} \alpha\xi - e^{(1+\alpha)\xi} \alpha\xi \\
&\quad + 4e^{\alpha\cdot\xi + \frac{1}{2}(1+\alpha)\xi} Z_+^2\Gamma\xi - e^{2\alpha\cdot\xi} \alpha\xi^2 + e^{(1+\alpha)\xi} \alpha\xi^2 - e^{2\alpha\cdot\xi} \alpha^2\xi^2 + e^{(1+\alpha)\xi} \alpha^2\xi^2] \\
G_4 &= 2Z_+(-e^{2\alpha\xi} y + e^{(1+\alpha)\xi} y + e^{2\alpha\xi} \xi + e^{(1+\alpha)\xi} \xi + e^{2\alpha\xi} y\alpha\xi - e^{2\alpha\xi} \alpha\xi^2 + e^{(1+\alpha)\xi} \alpha\xi^2)
\end{aligned} \tag{114}$$

For central negative (larger ion) there are three boundary zones

Zone I:

$$r < \frac{1+\alpha}{2},$$

This region is populated by the central ion only. We will call this region the “interior zone”.

Zone II:

$$\frac{1+\alpha}{2} < r < 1$$

This region can only be populated by the center of the smaller positive ions due to volume exclusion effects. We will call this region the “super border zone”. This a charge imbalance zone.

Zone III:

$$r > 1$$

This region can be populated by both ionic species. We will call this region the exterior zone. It follows standard DH theory.

The ADH equations for central negative larger ion are

$$\nabla^2 \psi(r) = -\frac{q_-}{\epsilon_0 \epsilon_r} \delta(r) \quad r < \sigma_{+-} \quad (115)$$

$$\nabla^2 \psi(r) = -\frac{q_+ \rho_+}{\epsilon_0 \epsilon_r} [1 - \beta q_+ \psi(r)] \quad \sigma_{+-} < r_\sigma < \sigma_- \quad (116)$$

$$\nabla^2 \psi(r) = \kappa_D^2 \psi(r) \quad r > \sigma_- \quad (117)$$

, or in unit-less dimensions

$$\nabla^2 \Psi = -4\pi \Gamma Z_- \delta(r) \quad r < \frac{1+\alpha}{2} \quad (118)$$

$$\nabla^2 \Psi = \frac{1}{r} \frac{d}{dr} \left(r^2 \frac{d}{dr_{\sigma_-}} \Psi \right) = \frac{y^2}{Z_- - Z_+} [1 - Z_+ \Psi], \quad \frac{1+\alpha}{2} < r < 1 \quad (119)$$

$$\nabla^2 \Psi = \frac{y^2}{Z_- - Z_+} [e^{-Z_+ \Psi} - e^{-Z_- \Psi}] \quad r > 1 \quad (120)$$

The solutions for this system of equations was found to be

$$\Psi_I(r) = \Gamma \frac{Z_-}{r} + D_1, \quad r < \frac{1+\alpha}{2} \quad (121)$$

$$\Psi_{II}(r) = \frac{1}{Z_+} + D_2 \frac{e^{+\xi r}}{r} + D_3 \frac{e^{-\xi r}}{r}, \quad \frac{1+\alpha}{2} < r < 1 \quad (122)$$

$$\Psi_{III}(r) = D_4 \frac{e^{-\gamma r}}{r}, \quad r > 1 \quad (123)$$

As before, to obtain the D coefficients, standard electrostatic boundary conditions of continuity of the potentials and their normal derivatives are implemented. The column matrix of the coefficients satisfies the matrix equation

$$A_2 \cdot D = B_2,$$

, where

$$D = \begin{bmatrix} D_1 \\ D_2 \\ D_3 \\ D_4 \end{bmatrix}$$

, and

$$A_2 = \begin{bmatrix} -\frac{\alpha+1}{2} & e^{\frac{\xi^{\alpha+1}}{2}} & e^{-\frac{\xi^{\alpha+1}}{2}} & 0 \\ 0 & e^{\xi} & e^{-\xi} & -e^{-y} \\ 0 & \frac{2}{\alpha+1} \left(-\xi + \frac{2e^{\frac{\xi^{\alpha+1}}{2}}}{\alpha+1} \right) & \frac{2}{\alpha+1} \left(\xi + \frac{2e^{-\frac{\xi^{\alpha+1}}{2}}}{\alpha+1} \right) & 0 \\ 0 & e^{\xi}(\xi-1) & e^{-\xi}(\xi+1) & e^{-y}(y_0+1) \end{bmatrix},$$

$$B_2 = \begin{bmatrix} -\frac{\alpha+1}{2Z_+} + \Gamma Z_- \\ -\frac{1}{Z_+} \\ 4\Gamma \frac{Z_+}{(1+\alpha)^2} \\ 0 \end{bmatrix}.$$

The solution of the above system gives for the D coefficients

$$\begin{aligned}
D_1 &= 2 \frac{(2Z_+^2\Gamma - 1 - \alpha)}{-1 - \alpha} - \frac{H_1}{I_1} - \frac{J}{K} \\
H_1 &= 2e^\xi (2e^{\frac{1}{2}(1+\alpha)\xi} + 2e^{\frac{1}{2}(1+\alpha)\xi} y + 2e^\xi y Z_+ Z_- \Gamma - e^{\frac{1}{2}(1+\alpha)\xi} \xi - e^{\frac{1}{2}(1+\alpha)\xi} y \xi \\
&\quad - e^{\frac{1}{2}(1+\alpha)\xi} \alpha \xi - e^{\frac{1}{2}(1+\alpha)\xi} y \alpha \xi + 2e^\xi Z_+ Z_- \Gamma \xi) \\
I_1 &= Z_+ (-1 - \alpha) (2e^{2\xi} y - 2e^{(1+\alpha)\xi} y + 2e^\xi \xi + e^{(1+\alpha)\xi} \xi + e^{2\xi} y \xi + e^{(1+\alpha)\xi} y \xi \\
&\quad + e^{2\xi} y \alpha \xi + e^{(1+\alpha)\xi} y \alpha \xi + e^{2\xi} \xi^2 - e^{(1+\alpha)\xi} \xi^2 + e^{2\xi} \alpha \xi^2 - e^{(1+\alpha)\xi} \alpha \xi^2) \\
J &= 2e^{\frac{1}{2}(1+\alpha)\xi} (-2e^\xi - 2e^\xi y - 2e^{\frac{1}{2}(1+\alpha)\xi} y Z_+ Z_- \Gamma - e^\xi \xi - e^\xi y \xi - e^\xi y \alpha \xi + 2e^{\frac{1}{2}(1+\alpha)\xi} Z_+ Z_- \Gamma \xi) \\
K &= Z_+ (-1 - \alpha) (2e^{2\xi} y - 2e^{(1+\alpha)\xi} y + 2e^{2\xi} \xi + 2e^{(1+\alpha)\xi} \xi + e^{2\xi} y \xi + e^{(1+\alpha)\xi} y \xi + e^{2\xi} y \alpha \xi \\
&\quad + e^{(1+\alpha)\xi} y \alpha \xi + e^{2\xi} \xi^2 - e^{(1+\alpha)\xi} \xi^2 + e^{2\xi} \alpha \xi^2 - e^{(1+\alpha)\xi} \alpha \xi^2)
\end{aligned} \tag{124}$$

$$\begin{aligned}
D_2 &= \frac{H_2}{I_2} \\
H_2 &= -2e^\xi - 2e^\xi y - 2e^{\frac{1}{2}(1+\alpha)\xi} y Z_+ Z_- \Gamma - e^\xi \xi - e^\xi y \xi - e^\xi \alpha \xi - e^\xi y \alpha \xi + 2e^{\frac{1}{2}(1+\alpha)\xi} Z_+ Z_- \Gamma \xi \\
I_2 &= Z_+ (2e^{2\xi} y - 2e^{(1+\alpha)\xi} y + 2e^{2\xi} \xi + 2e^{(1+\alpha)\xi} \xi + e^{2\xi} y \xi + e^{(1+\alpha)\xi} y \xi + e^{2\xi} y \alpha \xi + e^{(1+\alpha)\xi} y \alpha \xi \\
&\quad + e^{2\xi} \xi^2 - e^{(1+\alpha)\xi} \xi^2 + e^{2\xi} \alpha \xi^2 - e^{(1+\alpha)\xi} \alpha \xi^2)
\end{aligned} \tag{125}$$

$$\begin{aligned}
D_3 &= \frac{H_3}{I_3} \\
H_3 &= e^{\xi + \frac{1}{2}(1+\alpha)\xi} (2e^{\frac{1}{2}(1+\alpha)\xi} + 2e^{\frac{1}{2}(1+\alpha)\xi} y + 2e^\xi y Z_+ Z_- \Gamma - e^{\frac{1}{2}(1+\alpha)\xi} y \xi - e^{\frac{1}{2}(1+\alpha)\xi} \xi - e^{\frac{1}{2}(1+\alpha)\xi} y \xi \\
&\quad - e^{\frac{1}{2}(1+\alpha)\xi} \alpha \xi - e^{\frac{1}{2}(1+\alpha)\xi} y \alpha \xi + 2e^\xi Z_+ Z_- \Gamma \xi) \\
I_3 &= Z_+ (2e^{2\xi} y - 2e^{(1+\alpha)\xi} y + 2e^{2\xi} \xi + 2e^{(1+\alpha)\xi} \xi + e^{2\xi} y \xi + e^{(1+\alpha)\xi} y \xi + e^{2\xi} y \alpha \xi + e^{(1+\alpha)\xi} y \alpha \xi \\
&\quad + e^{2\xi} \xi^2 - e^{(1+\alpha)\xi} \xi^2 + e^{2\xi} \alpha \xi^2 - e^{(1+\alpha)\xi} \alpha \xi^2)
\end{aligned} \tag{126}$$

$$D_4 = -\frac{H_4}{I_4}$$

$$H_4 = e^y (2e^{2\xi} - 2e^{(1+\alpha)\xi} - e^{2\xi}\xi - e^{(1+\alpha)\xi}\xi + e^{2\xi}\alpha\xi + e^{(1+\alpha)\xi}\alpha\xi - 4e^{\xi + \frac{1}{2}(1+\alpha)\xi} Z_+ Z_- \Gamma \xi - e^{2\xi}\xi^2 + e^{(1+\alpha)\xi}\xi^2 - e^{2\xi}\alpha\xi^2 + e^{(1+\alpha)\xi}\alpha\xi^2)$$

$$I_4 = Z_+ (2e^{2\xi} y - 2e^{(1+\alpha)\xi} y + 2e^{2\xi}\xi + 2e^{(1+\alpha)\xi}\xi + e^{2\xi} y_0 \xi + e^{(1+\alpha)\xi} y \xi + e^{2\xi} y \alpha \xi + e^{(1+\alpha)\xi} y \alpha \xi + e^{2\xi}\xi^2 - e^{(1+\alpha)\xi}\xi^2 + e^{2\xi}\alpha\xi^2 - e^{(1+\alpha)\xi}\alpha\xi^2)$$

(127)

Discharge potentials ψ_i^0 and ψ_j^0 represents the mean potential function of a charged solution where the central ions i and j respectively are uncharged. This is

$$\begin{aligned} \psi_i^0 &= \psi_i(1; |e_i = 0) \\ \psi_j^0 &= \psi_j(2; |e_j = 0) \end{aligned} \quad (128)$$

If all the ions have the same size then the discharge potentials are zero. The reason for this is that discharge potentials are the result of charge imbalance zones due to ionic exclusion volume effects. Setting the central smaller ion charge to zero, we have

$$\langle \rho_q(r) \rangle_+ = 0 \quad r < \sigma_{++} \quad (129)$$

$$\cong q_+ \rho_+ [1 - \beta q_+ \langle \phi(r) \rangle_+] \quad \sigma_{++} < r < \sigma \quad (130)$$

$$\cong -(\kappa_D^2) \langle \phi(r) \rangle_+ \quad r > \sigma \quad (131)$$

, or in ionic scale dimensionless units

$$\nabla^2 \psi(r) = -\frac{\rho}{\epsilon_0 \epsilon_r} = 0, \quad r < \sigma_{++} \quad (132)$$

$$\nabla^2 \psi(r) = -\frac{\rho}{\epsilon_0 \epsilon_r} = -\frac{q_+ \rho_+}{\epsilon_0 \epsilon_r} [1 - \beta q_+ \psi(r)], \quad \sigma_{++} < r < \sigma \quad (133)$$

$$\nabla^2 \psi(r) \cong \kappa_D^2 \psi(r) \quad r > \sigma \quad (134)$$

For central larger negative ion we have

$$\nabla^2 \psi(r) = 0, \quad r < \sigma_{+-} \quad (135)$$

$$\nabla^2 \psi(r) = -\frac{q_+ \rho_+}{\varepsilon} [1 - \beta q_+ \psi(r)], \quad \sigma_{+-} < r < \sigma_- \quad (136)$$

$$\nabla^2 \psi(r) = -\kappa_D^2 \psi(r), \quad r > \sigma_- \quad (137)$$

or in unit-less dimensions

$$\nabla^2 \Psi = 0 \quad r < \frac{1+\alpha}{2} \quad (138)$$

$$\nabla^2 \Psi = \frac{1}{r} \frac{d}{dr} \left(r^2 \frac{d}{dr} \Psi \right) = \frac{y^2}{Z_- - Z_+} [1 - Z_+ \Psi], \quad \frac{1+\alpha}{2} < r < 1 \quad (139)$$

$$\nabla^2 \Psi = \frac{y^2}{Z_- - Z_+} [e^{-Z_+ \Psi} - e^{-Z_- \Psi}] \quad r > 1 \quad (140)$$

Analytical exact solutions for the above systems of equations are given by

$$\Psi_{1D}(r) = J_1, \quad r < \alpha \quad (141)$$

$$\Psi_{2D}(r) = \frac{1}{Z_+} + J_2 \frac{e^{-\xi r}}{r} + J_3 \frac{e^{+\xi r}}{r}, \quad \alpha < r < \frac{\alpha+1}{2} \quad (142)$$

$$\Psi_{3D}(r) = J_4 \frac{e^{-y r}}{r}, \quad r > \frac{\alpha+1}{2} \quad (143)$$

for smaller central discharged ion, and

$$\Psi_{1D}(r) = K_1, \quad r < \frac{1+\alpha}{2} \quad (144)$$

$$\Psi_{1D}(r) = \frac{1}{Z_+} + K_2 \frac{e^{+\xi r}}{r} + K_3 \frac{e^{-\xi r}}{r}, \quad \frac{1+\alpha}{2} < r < 1 \quad (145)$$

$$\Psi_{1D}(r) = K_4 \frac{e^{-y r}}{r_\sigma}, \quad r > 1 \quad (146)$$

for larger central discharged ion.

To obtain the J and K coefficients, standard electrostatic boundary conditions of continuity of the discharged potentials and their normal derivatives are implemented. The column matrix of the coefficients satisfies the matrix equations

$$A_3 \cdot J = B_3, \quad (147)$$

$$A_4 \cdot K = B_4,$$

, where

$$J = \begin{bmatrix} J_1 \\ J_2 \\ J_3 \\ J_4 \end{bmatrix},$$

$$A_3 = \begin{bmatrix} -\alpha & e^{-\xi \cdot \alpha} & e^{+\xi \alpha} & 0 \\ 0 & e^{-\xi \left(\frac{\alpha+1}{2}\right)} & e^{+\xi \left(\frac{\alpha+1}{2}\right)} & -e^{-y_0 \left(\frac{\alpha+1}{2}\right)} \\ 0 & e^{-\xi \cdot \alpha} \left(\frac{1}{\alpha} + \xi\right) & -e^{+\xi \cdot \alpha} \left(-\frac{1}{\alpha} + \xi\right) & 0 \\ 0 & -e^{-\xi \left(\frac{\alpha+1}{2}\right)} \left(\frac{2}{\alpha+1} + \xi\right) & e^{+\xi \left(\frac{\alpha+1}{2}\right)} \left(-\frac{2}{\alpha+1} + \xi\right) & e^{-y_0 \left(\frac{\alpha+1}{2}\right)} \left(\frac{2}{\alpha+1} + y_0\right) \end{bmatrix},$$

$$B_3 = \begin{bmatrix} -\frac{\alpha}{Z_+} \\ \alpha+1 \\ 0 \\ 0 \end{bmatrix},$$

, for central smaller positive ion, and

$$K = \begin{bmatrix} K_1 \\ K_2 \\ K_3 \\ K_4 \end{bmatrix},$$

$$A_4 = \begin{bmatrix} -\frac{\alpha+1}{2} & e^{\frac{\xi^{\alpha+1}}{2}} & e^{-\frac{\xi^{\alpha+1}}{2}} & 0 \\ 0 & e^{\xi} & e^{-\xi} & -e^{-y} \\ 0 & \frac{2}{\alpha+1} \left(-\xi + \frac{2e^{\frac{\xi^{\alpha+1}}{2}}}{\alpha+1} \right) & \frac{2}{\alpha+1} \left(\xi + \frac{2e^{-\frac{\xi^{\alpha+1}}{2}}}{\alpha+1} \right) & 0 \\ 0 & e^{\xi}(\xi-1) & e^{-\xi}(\xi+1) & e^{-y}(y+1) \end{bmatrix}.$$

$$B_4 = \begin{bmatrix} -\frac{\alpha+1}{2Z_+} \\ \frac{1}{Z_+} \\ 0 \\ 0 \end{bmatrix}.$$

The solution of the above systems gives for the J and K coefficients

$$J_1 = \frac{V_1}{\theta_1}$$

$$\begin{aligned} v_1 &= -e^{2\alpha\xi} y + e^{(1+\alpha)\xi} y + e^{2\alpha\xi} \xi + e^{(1+\alpha)\xi} \xi - 2e^{\alpha\xi + \frac{1}{2}(1+\alpha)\xi} \xi - e^{\alpha\xi + \frac{1}{2}(1+\alpha)\xi} y\xi \\ &+ e^{2\alpha\xi} y\alpha\xi + e^{(1+\alpha)\xi} y\alpha\xi - e^{2\alpha + \frac{1}{2}(1+\alpha)\xi} y\alpha\xi - e^{2\alpha\xi} \alpha\xi^2 + e^{(1+\alpha)\xi} \alpha\xi^2 \\ \theta_1 &= Z_+ (-e^{2\alpha\xi} y + e^{(1+\alpha)\xi} y + e^{2\alpha\xi} \xi + e^{(1+\alpha)\xi} \xi + e^{2\alpha\xi} y\alpha\xi + e^{(1+\alpha)\xi} y\alpha\xi \\ &- e^{2\alpha\xi} \alpha\xi^2 + e^{(1+\alpha)\xi} \alpha\xi^2) \end{aligned} \quad (148)$$

$$J_2 = -\frac{V_2}{\theta_2}$$

$$\begin{aligned} v_2 &= e^{2\alpha\xi + \frac{1}{2}(1+\alpha)\xi} (2 + y + y_0\alpha)(\alpha\xi - 1) \\ \theta_2 &= 2Z_+ (-e^{2\alpha\xi} y + e^{(1+\alpha)\xi} y + e^{2\alpha\xi} \xi + e^{(1+\alpha)\xi} \xi + e^{2\alpha\xi} y\alpha\xi + e^{(1+\alpha)\xi} y\alpha\xi \\ &- e^{2\alpha\xi} \alpha\xi^2 + e^{(1+\alpha)\xi} \alpha\xi^2) \end{aligned} \quad (149)$$

$$J_3 = \frac{V_3}{\theta_3}$$

$$\begin{aligned} v_3 &= e^{\frac{1}{2}(1+\alpha)\xi} (2 + y + y\alpha)(\alpha\xi + 1) \\ \theta_3 &= 2Z_+ (e^{2\alpha\xi} y - e^{(1+\alpha)\xi} y - e^{2\alpha\xi} \xi - e^{(1+\alpha)\xi} \xi - e^{2\alpha\xi} y\alpha\xi - e^{(1+\alpha)\xi} y\alpha\xi + e^{2\alpha\xi} \alpha\xi^2 \\ &- e^{(1+\alpha)\xi} \alpha\xi^2) \end{aligned} \quad (150)$$

$$\begin{aligned}
J_4 &= \frac{V_4}{\theta_4} \\
v_4 &= e^{y(-1+\frac{1+\alpha}{2})} (-2e^{2\alpha\xi} + 2e^{(1+\alpha)\xi} - e^{2\alpha\xi} - e^{(1+\alpha)\xi}\xi + e^{2\alpha\xi}\alpha\xi + e^{(1+\alpha)\xi}\alpha\xi + e^{2\alpha\xi}\alpha\xi^2 \\
&\quad - e^{(1+\alpha)\xi}\alpha\xi^2 + e^{2\alpha\xi}\alpha^2\xi^2 - e^{(1+\alpha)\xi}\alpha^2\xi^2) \\
\theta_4 &= 2Z_+(e^{2\alpha\xi}y - e^{(1+\alpha)\xi}y - e^{2\alpha\xi}\xi - e^{(1+\alpha)\xi}\xi - e^{2\alpha\xi}y\alpha\xi - e^{(1+\alpha)\xi}y\alpha\xi + e^{2\alpha\xi}\alpha\xi^2 \\
&\quad - e^{(1+\alpha)\xi}\alpha\xi^2)
\end{aligned} \tag{151}$$

$$\begin{aligned}
K_1 &= \frac{U_1}{\zeta_1} \\
u_1 &= -2e^{2\xi}y + 2e^{(1+\alpha)\xi}y - 2e^{2\xi}\xi - 2e^{(1+\alpha)\xi}\xi + 4e^{\xi+\frac{1}{2}(1+\alpha)\xi} - e^{2\xi}y\xi - e^{(1+\alpha)\xi}y\xi \\
&\quad + 4e^{\xi+\frac{1}{2}(1+\alpha)\xi}y\xi - e^{2\xi}y\alpha\xi - e^{(1+\alpha)\xi}y\alpha\xi - e^{2\xi}\xi^2 + e^{(1+\alpha)\xi}\xi^2 - e^{2\xi}\alpha\xi^2 + e^{(1+\alpha)\xi}\alpha\xi^2 \\
\zeta_1 &= Z_+(-2e^{2\xi}y + 2e^{(1+\alpha)\xi}y - 2e^{2\xi}\xi - 2e^{(1+\alpha)\xi}\xi - e^{2\xi}y\xi - e^{(1+\alpha)\xi}y\xi - e^{2\xi}y\alpha\xi \\
&\quad - e^{(1+\alpha)\xi}y\alpha\xi - e^{2\xi}\xi^2 + e^{(1+\alpha)\xi}\xi^2 - e^{2\xi}\alpha\xi^2 + e^{(1+\alpha)\xi}\alpha\xi^2)
\end{aligned} \tag{152}$$

$$\begin{aligned}
K_2 &= -\frac{V_2}{\zeta_2} \\
v_2 &= e^\xi(1+y)(2+\xi+\alpha\xi) \\
\zeta_2 &= Z_+(2e^{2\xi}y - 2e^{(1+\alpha)\xi}y + 2e^{2\xi}\xi + 2e^{(1+\alpha)\xi}\xi + e^{2\xi}y\xi + e^{(1+\alpha)\xi}y\xi + e^{2\xi}y\alpha\xi \\
&\quad + e^{2\xi}y\alpha\xi + e^{(1+\alpha)\xi}y\alpha\xi + e^{2\xi}\xi^2 - e^{(1+\alpha)\xi}\xi^2 - e^{(1+\alpha)\xi}\xi^2 + e^{2\xi}\alpha\xi^2 - e^{(1+\alpha)\xi}\alpha\xi^2)
\end{aligned} \tag{153}$$

$$\begin{aligned}
K_3 &= -\frac{V_3}{\zeta_2} \\
v_3 &= e^{\xi+(1+\alpha)\xi}(1+y)(\xi-2+\alpha\xi)
\end{aligned} \tag{154}$$

$$\begin{aligned}
K_4 &= \frac{V_4}{\zeta_4} \\
v_4 &= e^y(2e^{2\xi} - 2e^{(1+\alpha)\xi} - e^{2\xi}\xi - e^{(1+\alpha)\xi}\xi + e^{2\xi}\alpha\xi + e^{(1+\alpha)\xi}\alpha\xi - e^{2\xi}\xi^2 \\
&\quad + e^{(1+\alpha)\xi}\xi^2 - e^{2\xi} - e^{2\xi}\alpha\xi^2 + e^{(1+\alpha)\xi}\alpha\xi^2) \\
\zeta_4 &= Z_+(-2e^{2\xi}y + 2e^{(1+\alpha)\xi}y - 2e^{2\xi}\xi - 2e^{(1+\alpha)\xi}\xi - e^{2\xi}y\xi - e^{(1+\alpha)\xi}y\xi - e^{2\xi}y\alpha\xi \\
&\quad - e^{(1+\alpha)\xi}y\alpha\xi - e^{2\xi}\xi^2 + e^{(1+\alpha)\xi}\xi^2 - e^{2\xi}\alpha\xi^2 + e^{(1+\alpha)\xi}\alpha\xi^2)
\end{aligned} \tag{155}$$

Having obtained electrostatic potentials for charged $\Psi(1;2)$, and discharged $\Psi^0(1,2)$ central charges, we use equations 80 for the pair correlation functions. The source functions

F_1 , F_2 , and F_3 are calculated with equations 73, 74, and 75 with the asymmetric Debye-Hückel radial distribution functions calculated here. From equation 71 we define function G as follows

$$\begin{aligned}
& P_I[\Phi, g(1, q), g(2, q)] \\
&= \left(\frac{Z_+ Z_-}{Z_+ - Z_-} \right) [Z_+ g(1, q^+) g(2, q^+) - Z_- g(1, q^-) g(2, q^-)] \Phi(1, 2; q) + \\
& \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) [g(1, q^+) g(2, q^+) - g(1, q^-) g(2, q^-) \\
& - g(1, q^+) - g(2, q^+) + g(1, q^-) + g(2, q^-)] \\
&= G[g(1, q^+), g(1, q^-), g(2, q^+), g(2, q^-)] \Phi(1, 2; q) \\
&+ F_3[g(1, q^+), g(1, q^-), g(2, q^+), g(2, q^-)]
\end{aligned} \tag{156}$$

, with G given by

$$\begin{aligned}
& G[g(1, q^+), g(1, q^-), g(2, q^+), g(2, q^-)] \\
&= \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) [-Z_+ g(1, q^+) g(2, q^+) + Z_- g(1, q^-) g(2, q^-)]
\end{aligned} \tag{157}$$

Including the term linear in $\Phi(1, 2; q)$ in the integral of equation 72 we get,

$$\begin{aligned}
\Phi(1, 2; 3) &= \frac{y_0^2}{4\pi} \left[\int_{\omega_1} \frac{F_1[g(2, q^+), g(2, q^-)] dV_q}{|\vec{r}_q - \vec{r}_3|} + \int_{\omega_2} \frac{F_2[g(1, q^+), g(1, q^-)] dV_q}{|\vec{r}_q - \vec{r}_3|} \right. \\
& \left. \int_{\Omega - (\omega_1 + \omega_2)} \frac{F_3[g(1, q^+), g(1, q^-), g(2, q^+), g(2, q^-)] dV_q}{|\vec{r}_q - \vec{r}_3|} \right] \\
&+ \int_{\Omega - (\omega_1 + \omega_2)} G[g(1, p^+), g(1, p^-), g(2, p^+), g(2, p^-)] \\
&\times \left\{ \int_{\omega_1} \frac{F_1[g(2, q^\pm)]}{|\vec{r}_q - \vec{r}_p|} dV_q + \int_{\omega_2} \frac{F_2[g(1, q^\pm)]}{|\vec{r}_q - \vec{r}_p|} dV_q + \int_{\Omega - (\omega_1 + \omega_2)} \frac{F_3[g(1, q^\pm), g(2, q^\pm)]}{|\vec{r}_q - \vec{r}_p|} dV_q \right\} \frac{dV_p}{|\vec{r}_p - \vec{r}_3|}
\end{aligned} \tag{158}$$

This represents the fluctuation potential for symmetric asymmetric valences and sizes in this model. For the pair correlation functions, we use the symmetric formulation MPB, (equation 76) given, in dimensionless reduced variables by,

$$g_{ij} = g_{ij}^0 \exp \left\{ -\frac{Z_j}{2} [\Psi_i + \Psi_i^0 + \int_0^1 (\Phi(1,2;2) + \Phi(1,2;2|Z_i = 0)) d\lambda_2] \right. \\ \left. - \frac{Z_i}{2} [\Psi_j + \Psi_j^0 + \int_0^1 (\Phi(1,2;1) + \phi(1,2;1|Z_j = 0)) d\lambda_1] \right\} \quad (159)$$

, where the excluded volume term can be approximated by

$$g_{ij}^0 = g_{ij}(Z_i = Z_j = 0) = H(r_\sigma - \sigma_{ij}) \quad (160)$$

, where σ_{ij} is the contact separation, and $H(r_\sigma - \sigma_{ij})$ is the Heaviside unit step function. This completes the MPB_{this-work} solution for the primitive model.

Osmotic coefficients for the primitive model electrolyte can be calculated using equation 5 from reference [32],

$$\phi = 1 + (2\pi/3\rho) \sum_s \sum_t n_s n_t g_{st}(a_{st}) a_{st}^3 + \beta E / 3\rho \quad (161)$$

expressed in dimensionless form using the parameters defined in this work as

$$\phi = 1 + \beta E / 3N + \eta_{\sigma-} [g_{++}(\alpha)\alpha^3 + \frac{(\alpha+1)^3}{4} g_{+-}(\frac{\alpha+1}{2}) + g_{--}(1)] \quad (162)$$

with energy given by

$$\beta E / N = (U_{++} + U_{--} + U_{+-}) \quad (163)$$

where

$$U_{++} = \frac{\gamma_{\sigma-}^2}{8} \int_\alpha^\infty g_{++}(r) r dr \quad (164)$$

$$U_{--} = \frac{\gamma_{\sigma-}^2}{8} \int_1^\infty g_{--}(r) r dr \quad (165)$$

$$U_{+-} = -\frac{\gamma_{\sigma^-}^2}{4} \int_{(\alpha+1)/2}^{\infty} g_{+-}(r) r dr \quad (166)$$

with

$$\eta_{\sigma^-} = \frac{\pi}{6} \rho \sigma_-^3 \quad (167)$$

$$\Gamma_{\sigma^-} = \frac{\beta e^2}{4\pi \epsilon_r \epsilon_0 \sigma_-} \quad (168)$$

$$\gamma_{\sigma^-} = \sqrt{24 \eta_{\sigma^-} \Gamma_{\sigma^-}} \quad (169)$$

Where σ_- is the larger negative ion diameter and r represents the scaled distance r/σ_- .

Chapter 4

Numerical solution

The calculation of the fluctuation potential $\Phi(1,2;3)$ was achieved by creating a Cartesian grid in space with scaled distance of 10% of the ionic diameter, which in our dimensionless units is 1, so in this calculations the grid spacing is 0.1. This grid was created to represent the physical regions in the fluctuation potential problem as shown in figure 3. Those regions consist in the spherical regions ω_1 and ω_2 that correspond to the boundaries of the physical ions 1 and 2, and the rest of the solution which is denoted by $\Omega - (\omega_1 + \omega_2)$ and represents the ionic excluded volume. The functions F_1 and F_2 , (equations 73 and 74 respectively), represent the charge density associated with regions ω_1 and ω_2 in the integral of equation 63. The boundary of the rectangular Cartesian grid representing figure 3 was defined by a parameter Λ , which represents the distance scale between the ionic boundaries ω_1, ω_2 to the boundary of the volume Ω . This parameter was chosen in such a way that the fluctuation potential solutions tend to zero at the exterior boundary of the grid. We call this parameter the fluctuation potential spatial decay parameter. It should be large enough to allow the fluctuation potential to decay to zero, in order to fulfill the electrostatics boundary conditions. Usually this parameter was between three and five ionic diameters for the highest concentration but was found to be considerably larger than for small concentrations. The ionic solution's volume Ω is represented by a grid space with the dimensionless spatial scale h , expressed in ionic diameters. Grid vectors are represented by

$$\vec{R} = \langle i, j, k \rangle \quad (170)$$

, where i, j, k are integers. Coordinates in ionic diameter space are then given by

$$\begin{aligned}
x_\sigma &= h(i-1) \\
y_\sigma &= h(j-1) \\
z_\sigma &= h(k-1)
\end{aligned}
\tag{171}$$

The integral in equation 72 is then represented by a summation in grid space as,

$$\Phi(1,2;\bar{R}_3) = \frac{y_0^2}{4\pi} \sum \frac{P[g(1,q^\pm), g(2,q^\pm)]\Delta}{\|\bar{R}_q - \bar{R}_3\|}
\tag{172}$$

, where P is the source function, and Δ is the cell unit volume in ionic diameter grid space. That is

$$\Delta = h^3
\tag{173}$$

The fluctuation potential solution was an integral over regions ω_1 and ω_2 . The summation used to numerically calculate the integral included approximately eight thousand terms, one for each point inside regions ω_1 and ω_2 . To produce figures 4-6 the fluctuation potential was calculated at each point in a planar slice passing through the centers of ω_1 and ω_2 . For contact distance between the regions ω_1 and ω_2 , and $\Lambda = 5$, this planar slice contains approximately ten thousand points. The simplicity of equation 72, and the approximation of the g_{ij} in equation 70 with DH functions, are what make the calculations fairly tenable.

The calculations of the pair correlation functions were performed in a similar grid as the one used for the three-dimensional figures but the fluctuation potential was only calculated at the center of region ω_2 (figure 3), and used in equation 81, where the Kirkwood charge integral of the fluctuation potential is calculated. The calculation of reduced configurational energies and osmotic coefficients was achieved from formulas 79 and 80 for the RPM (1:1). For the PM (1:1) case the osmotic coefficient was calculated

from equation (162). Radial distribution contact values for the charge asymmetric RPM (1:2) case were calculated using equation (76).

Chapter 5

Results and Discussion

In this work the fluctuation potential was obtained numerically by solving the integral of equation 72 for the restricted primitive model case (1:1), neglecting ionic charge in region $\Omega - (\omega_1 + \omega_2)$. The physical parameters for the RPM used were ---- common ionic diameter of 4.25\AA , dielectric constant (relative permittivity) $\epsilon_r = 78.5$, which is tantamount to having a water-like solvent, and absolute temperature $T = 298\text{K}$. The concentrations used were, in moles per liter, of 0.1038, 0.425, 1.00, and 1.968. One reason for using these physical parameters is that these have been used earlier in the literature and for which MC simulation data exist [9, 10]. Radial distribution functions were calculated with equation (77). Osmotic coefficients ϕ and reduced configurational energies $-U/Nk_B T$ have been calculated with equations 79 and 80. The numerical procedure involved is described briefly in chapter 4. In what follows we discuss the results for RPM (1:1), RPM (2:1) and PM (1:1) cases studied in this research. Sections 5.1 and 5.2 refers to RPM (1:1) case which was the main focus of this work.

5.1 Fluctuation potential

Three-dimensional representations of the fluctuation potential $\Phi(1,2;3)$ for various configurations of the monovalent ions are shown in figures (4-6), which are calculated on a planar slice passing through the centers of ions 1 and 2 (figure 3). To our best knowledge such representation of the fluctuation potential does not exist in the literature. The plots shows the fluctuation potential $\phi(1,2;3)$ obtained from equation 72 as mentioned before,

following the linearization of the fluctuation potential in the bulk region I and the smallness of $\Phi(1,2;3)$, the P function in bulk region I is taken as zero, neglecting charge density for that region.

The behavior of the fluctuation potential in figures (4-6) can be understood in terms of the charge density associated with the functions F1 and F2, inside regions ω_1 and ω_2 . Figure 4 shows the fluctuation potential for a planar slice passing through the centers of two positive ions of charge +1 each. The charge density contributed by the spherical region 1 associated to the positive ion in region ω_1 is calculated using function F1 (equation 73) which is a function of $g(2,3)$, where the point 3 is bounded to be inside region ω_1 . The positive sign in the fluctuation potential in region 1 is given by the sign of $-g(2,3^+)+g(2,3^-)$. Since the charge in position 2 is positive the second term associated with unlike charges is greater in magnitude than the first term in F1 causing an overall positive fluctuation potential in region 1. The positive sign in region 2 can be understood in similar terms.

Figure 5 shows the fluctuation potential for a positive ion +1 in region ω_1 and a negative ion -1 in region ω_2 . For this case the functions $g(1,3)$ and $g(2,3)$ in F1 and F2 conspire to cause the sign of the fluctuation potential around region 1 to be opposite in sign to the charge of ion 1 and vice versa for ion 2. To see this first we look at $-g(2,3^+)+g(2,3^-)$ for F1. If the ion in region 2 is negative then the first term associated with unlike charge is giving a negative sign in region 1 where the positive physical ion is located. On the other hand the fluctuation potential in region 2 is calculated using F2 where the charge density is given by $-g(1,3^+)+g(1,3^-)$. It can clearly be seen that the second positive term in this expression is the larger one because it is linked to unlike charges. So it can generally be stated that the fluctuation potential for like ions near the vicinity of the ions is of the same

polarity of that of the physical ions and is of opposite polarity for unlike ions. This peculiar behavior is a consequence of the fluctuation potential in region ω_1 (equations 65) being related to the $g(2,3)$ centered at region ω_2 , and that the fluctuation potential in region ω_2 (equations 66) being related to the $g(1,3)$ centered at the opposite region ω_1 . This combined with the relative magnitudes of like and unlike ions g 's in functions F1 and F2 explain the behavior of the polarities of $\Phi(1,2;3)$.

The smallness of $\Phi(1,2;3)$, specially for large inter-ionic separations, can be understood in terms of the dominant charge density in equations 65 and 66. The charge density in ω_1 is a function of the $g(2,3)$ where the point 3 is in region ω_1 and the point 2 is in the center of region ω_2 , and the charge density of region ω_2 is a function of $g(1,3)$ where point 3 is inside region ω_2 and point 1 is at the center of region ω_1 . As interionic separation is increased, the dominant functions in F1 and F2 associated with unlike ions decrease, while the g 's associated with like charges tend to one. It is apparent from Eqns. 73 and 74 that F1 and F2 both tend to zero for large distances, and increase for contact distances, as in figure (6), where the fluctuation potential for similar charges is seen to become quite large compared with that in figure (4). This means that for small separation of the ions the fluctuation potential term becomes important for the calculation of the g_{ij} . Figures (4-6) show that the fluctuation potential is largest near the regions of ions 1 and 2.

In figure (4) we have ions of the same sign, and it is clear that the fluctuation potential is manifested as an increase in electrostatic energy of the ions since the fluctuation potential is of the same sign as the ions. For ions of opposite sign, we can see from figure (5) that the sign of the fluctuation potential is opposite to that of the ion in the vicinity. This leads to a decrease in potential electrostatic energy giving rise to attractive

inter-ionic correlation interaction in this case. This implies, and from what has been known in the literature, that the sign of the fluctuation potential in the vicinity of ion 1 is mostly due to the cloud of counter ion (from ion 2) and vice versa. The results further show that the fluctuation potential increases with electrolyte concentration. It can be seen from figure 4 and 5, that the fluctuation potential increases as the separation of the ions is decreased, establishing the importance of having a solution that is valid at short distances. Figure 6 is the fluctuation potential calculated at contact distance $r/\sigma = 1$. The results show that fluctuation potential increases with molarity, meaning that as molarity increases the short distance behavior of the theory is affected by not only by the excluded volume effects, but also by the fluctuation potential.

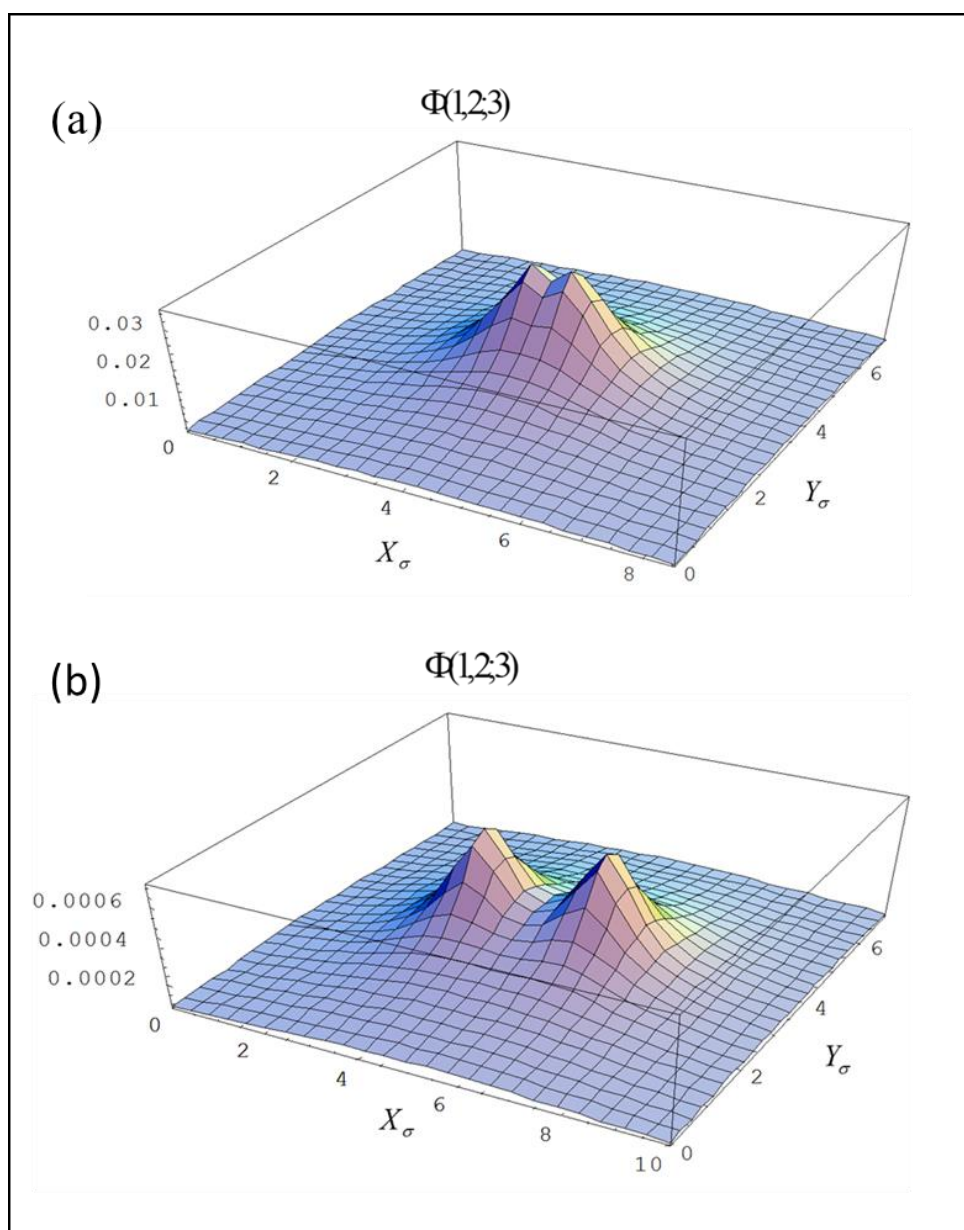


Figure 4 Fluctuation potential $\phi(1,2;3)$ for $Z_1=Z_2=+1$, $\sigma=4.25\text{\AA}$, $\epsilon=78.5$, $T=298\text{K}$, $c=1.968\text{M}$. Reduce interionic distance r/σ : (a) 1.5, (b) 3.

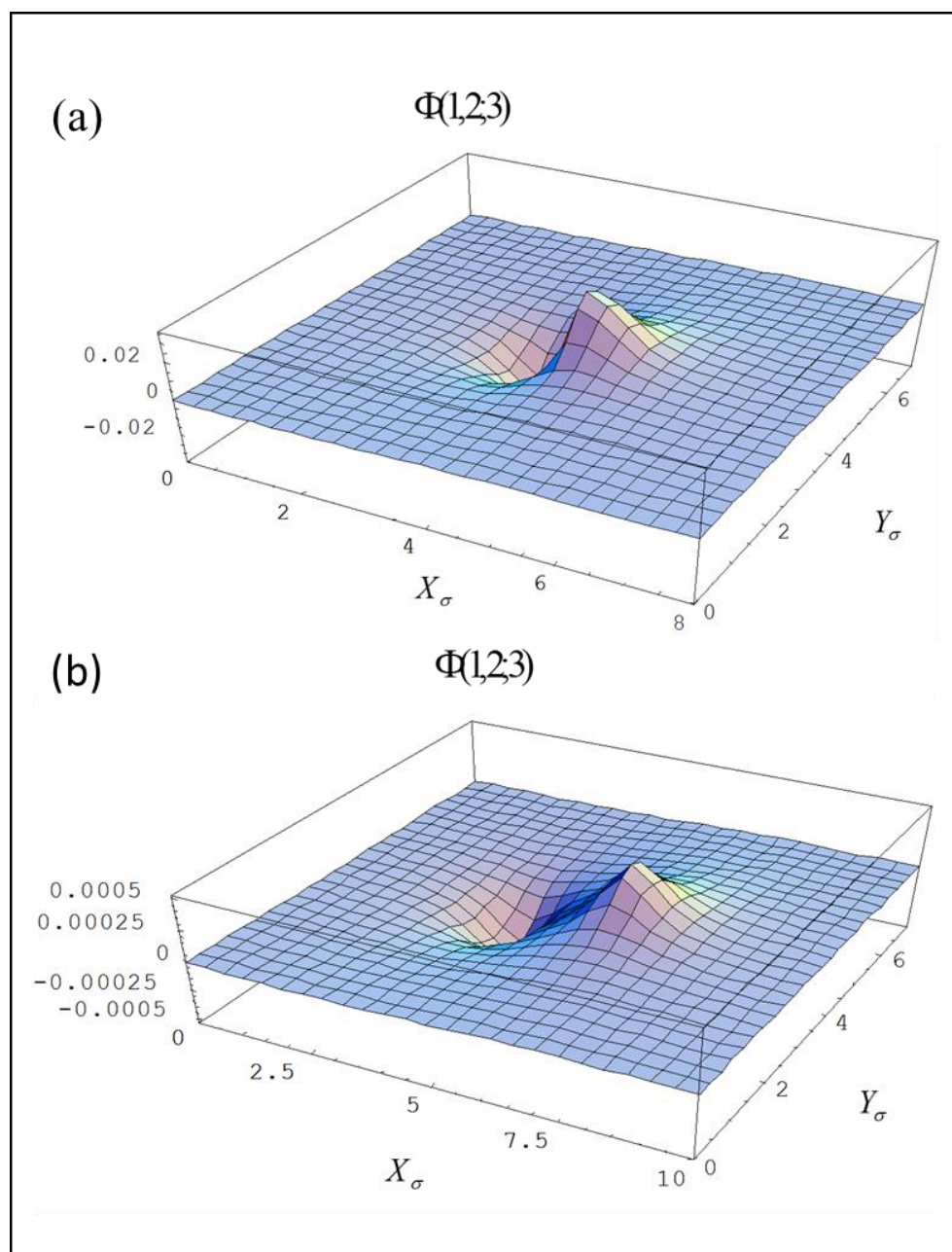


Figure 5 Fluctuation potential $\phi(1,2,3)$ for $Z_1=+1$, $Z_2=-1$, $\sigma=4.25\text{\AA}$, $\epsilon=78.5$, $T=298\text{K}$, $c=1.968\text{M}$. Reduce interionic distance r/σ : (a) 1 (contact), (b) 3.

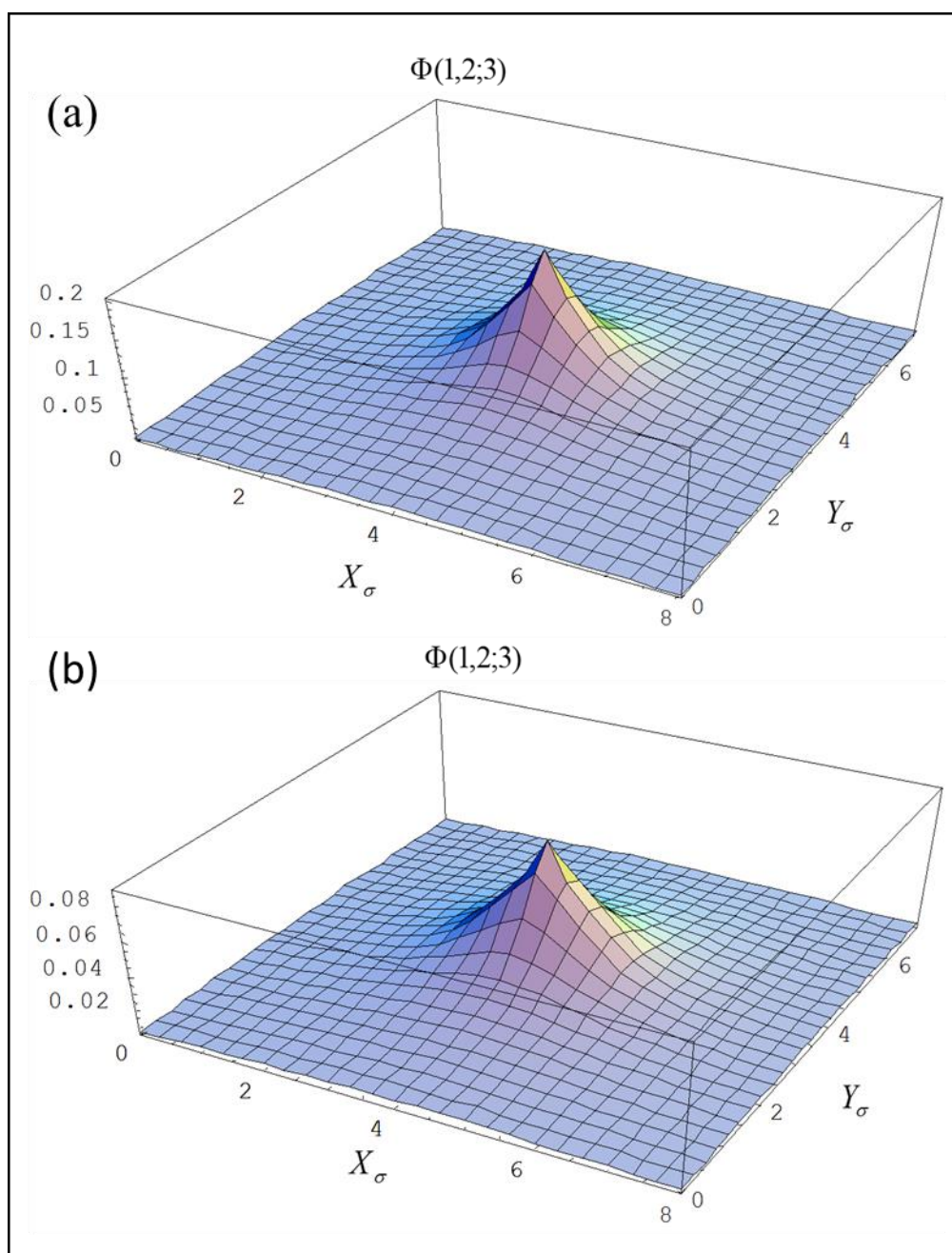


Figure 6 Fluctuation potential $\phi(1,2;3)$ for $Z_1=Z_2=+1$, $\sigma=4.25\text{\AA}$, $\epsilon=78.5$, $T=298\text{K}$, $c=1.968\text{M}$. Reduce interionic distance $r/\sigma=1$ (contact) for concentrations: (a) $c=1.968\text{M}$, (b) $c=0.1038\text{M}$.

5.2 Structure and Thermodynamics

In Tables 1-3 we show the contact values, the reduced configurational energies, and the osmotic coefficients for the Debye-Hückel (DH), the symmetric-Poisson-Boltzmann (SPB), the traditional modified Poisson-Boltzmann (MPB), the Card and Valleau Monte Carlo (MC)[9], the Rasiyah, Card, and Valleau Monte Carlo (MC) [10], and the modified Poisson-Boltzmann from this work (MPB_{this-work}).

$C(\text{mol}/\text{dm}^3)$	$g_{++}(1) = g_{--}(1)$					$g_{+-}(1)$				
	DH	SPB	MPB	MPB (this-work)	MC	DH	SPB	MPB	MPB (this-work)	MC
0.1038	-0.158	0.321	0.311	0.302	0.319	2.16	3.19	3.30	3.33	3.25
0.425	0.121	0.443	0.417	0.399	0.418	1.88	2.50	2.66	2.62	2.62
1.000	0.299	0.573	0.530	0.500	0.505	1.70	2.14	2.42	2.23	2.23
1.968	0.433	0.752	0.686	0.633	0.706	1.57	2.20	2.40	2.38	2.38

Table 1 Contact values of the radial distribution functions $g_{ij}(d)$ from different theories. The common diameter of the ions is $4.25 \times 10^{-10} \text{ m}$, the temperature $T = 298 \text{ K}$, and the dielectric constant of the electrolyte $\epsilon_r = 78.5$. The MC values are from reference [9].

$C(\text{mol}/\text{dm}^3)$	DH	SPB	MPB	MPB (this-work)	MC
0.1038	0.261	0.267	0.274	0.274	0.274
0.425	0.400	0.407	0.436	0.439	0.434
1.000	0.490	0.500	0.555	0.550	0.552
1.968	0.556	0.572	0.663	0.699	0.651

Table 2 Reduced configurational energy $-U/(Nk_B T)$ from different theories. The common diameter of the ions is $4.25 \times 10^{-10} \text{ m}$, the temperature $T = 298 \text{ K}$, and the dielectric constant of the electrolyte $\epsilon_r = 78.5$. The MC values are from reference [10].

$C(\text{mol}/\text{dm}^3)$	SPB	MPB	MPB <i>(this-work)</i>	MC
0.1038	0.946	0.945	0.944	0.945
0.425	0.985	0.981	0.98	0.977
1.000	1.11	1.10	1.10	1.094
1.968	1.37	1.37	1.33	1.364

Table 3 Osmotic coefficient ϕ from different theories. The common diameter of the ions is $4.25 \times 10^{-10} \text{ m}$, the temperature $T = 298 \text{ K}$, and the dielectric constant of the electrolyte $\epsilon_r = 78.5$. The MC values are from reference [9]

Table 1 shows contact values for the three models, and the Card -Valleau MC for concentration 1 M [9]. For the radial distribution at contact distance, the values from this work and the corresponding ones from traditional MPB are very close to the generally Rasiah-Card-Valleau MC [10], but the SPB shows a tendency to be smaller than the MC for unlike ions, and larger than the MC values for like ions. Results from Table 1 show that MPB_{this-work} and MPB are closest to the MC results than the corresponding SPB values for both like and unlike ions. The contact values for the radial distribution functions for like ions, from the present theory, are slightly closer to the MC result [9] than that from the SPB and MPB. This is probably due to a better treatment of the fluctuation potential in this work. Overall, the contact values from the present theory are consistent with the other theories and show very good agreement with the MC simulation data.

Figure 7 shows the radial distribution functions obtained in this research along with the corresponding SPB and the traditional MPB theories at 1 M electrolyte concentration. The results are very similar for distances bigger than 2 ionic diameters. But importantly,

the present results and that from the conventional MPB theory are almost identical. This testifies to the viability of the present treatment.

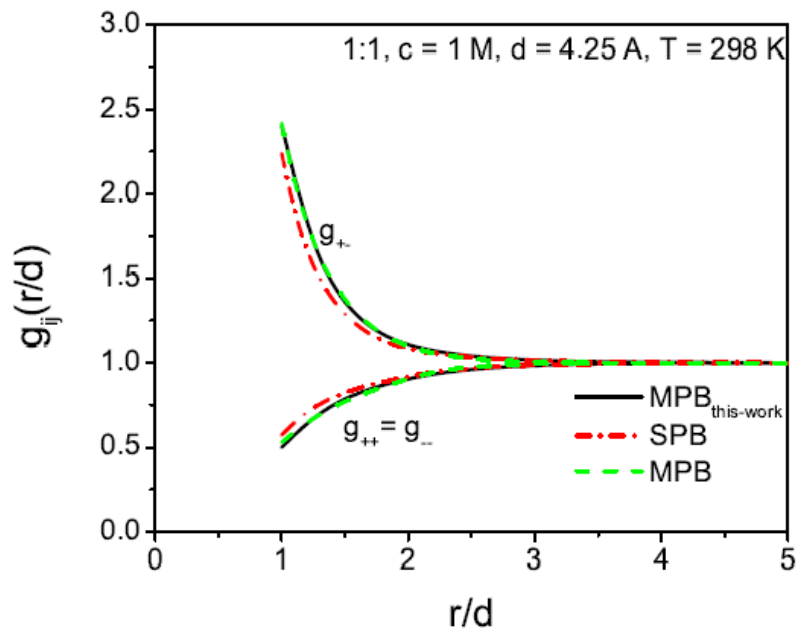


Figure 7 Cation-cation and cation-anion radial distribution functions for Symmetric-Boltzmann (SPB), modified Poisson Boltzmann (MPB), and the theory presented in this work ($MPB_{this-work}$)

Tables 2 and 3 show the reduced configurational energies, and the osmotic coefficients from the DH, SPB, MPB, MC [9, 10], and this work. These values are also presented in graphic form as in figures 8 and 9, respectively. The reduced configurational energy curves (figure 8) show excellent agreement between the MPB and this work, and with the MC curve up to 1 M concentration. At the highest 1.968 M concentration the MPB is a little closer to the MC. Figure (9) shows osmotic coefficients for the theories and the relevant MC data [9, 10]. These curves show a generally very good agreement between the MC results and the theories.

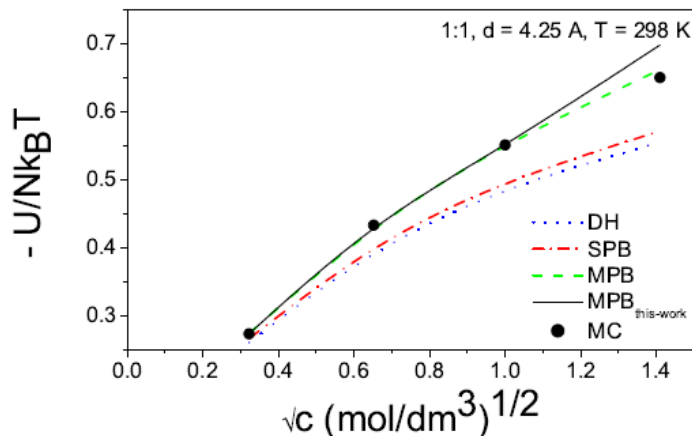


Figure 8 The reduced configurational energy for a 1:1 restricted primitive model electrolyte at ionic diameter $d = 4.25 \times 10^{-10} \text{ m}$, dielectric constant $\epsilon_r = 78.5$, and temperature $T = 298 \text{ K}$, versus the square root of the electrolyte concentration c , for the Debye-Hückel, theory, the symmetric Poisson-Boltzmann theory, the modified Poisson-Boltzmann theory, and the theory presented in this work. Legend as given in the figure. The Monte Carlo results are from references [9] and [10].

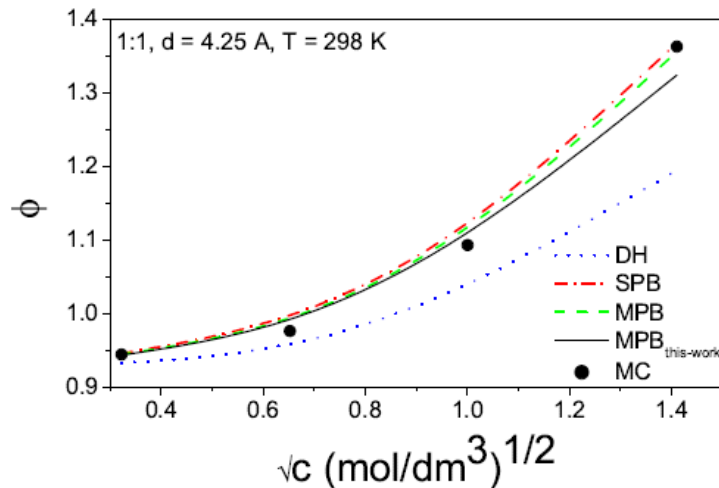


Figure 9 The osmotic coefficient for a 1:1 restricted primitive model electrolyte at ionic diameter $d = 4.25 \times 10^{-10} \text{ m}$, dielectric constant $\epsilon_r = 78.5$, and temperature $T = 298 \text{ K}$, versus the square root of the electrolyte concentration c , for the Debye-Hückel, theory, the symmetric Poisson-Boltzmann theory, the modified Poisson-Boltzmann theory, and the theory presented in this work. Legend as given in the figure. The Monte Carlo results are from references [9] and [10].

5.3 Charge Asymmetric Case Radial Distribution Contact values

c(mol/dm ³)	$g_{+-}(1)$		$g_{++}(1)$		$g_{--}(1)$	
	HNC	MPB _{this-work}	HNC	MPB _{this-work}	HNC	MPB _{this-work}
0.00067	24.65	24.049	0.0017	0.0023	0.2318	0.2271
0.005	18.29	18.4	0.0033	0.0035	0.2712	0.2666
0.05	9.31	9.28	0.0106	0.0097	0.3894	0.4002
0.1	7.287	7.37	0.0157	0.015	0.4311	0.4722
0.2	5.623	5.73	0.0258	0.0241	0.479	0.5618
0.26667	5.06	5.14	0.0286	0.0297	0.5025	0.6381
0.4	4.389	4.416	0.0376	0.0406	0.5419	0.66689
0.6	3.855	3.801	0.0505	0.056	0.5932	0.6921
0.8	3.562	3.431	0.0636	0.072	0.6413	0.7251
1	3.383	3.576	0.0772	0.0886	0.6888	0.7483
1.3333	3.229	3.26708	0.1019	0.1174	0.7706	0.77453

Table 4 Comparison of the radial distribution functions contact values $g_{ij}(d)$ from HNC and this work for RPM 2-1 case. The common diameter of the ions is $4.25 \times 10^{-10} m$, the temperature $T = 298 K$, and the dielectric constant of the electrolyte $\epsilon_r = 78.5$. The HCN values are from reference [20].

Table 4 shows radial distribution functions contact values calculated for the charge asymmetric case RPM (2:1), using equation (76). The corresponding HCN values were obtained from the results of Rasiah and Friedman [20], which are considered to give the best results for ionic solution theory [20, 21, 22]. The results shows good agreement for all concentrations considered.

5.4 Size asymmetric Case Osmotic Coefficients

α	$g_{++}(\alpha)$	$g_{+-}(\frac{\alpha+1}{2})$	$g_{--}(1)$
0.2	0.000521989	7.3112	0.398237
0.4	0.0320528	5.14152	0.39079
0.6	0.123494	3.974470	0.381779
0.8	0.240527	3.26284	0.371116

Table 5 Radial distribution contact values for primitive model 1:1 electrolyte. The diameter of the large negative ion is 4.25×10^{-10} m, the temperature $T=298$ K, the dielectric constant of the electrolyte ϵ_r , and the size asymmetry parameter $\alpha = 0.2, 0.4, 0.6,$ and 0.8 .

α	$\Phi_{this-work}$	Φ_{MC}
0.2	0.9437	
0.4	0.9143	0.904±0.003
0.6	0.9276	0.925±0.002
0.8	0.9419	0.948±0.003

Table 6. Comparison of osmotic coefficient ϕ for primitive model 1:1 electrolyte and MC simulations. The diameter of the large negative ion is 4.25×10^{-10} m, the temperature $T=298$ K, the dielectric constant of the electrolyte ϵ_r , and the size asymmetry parameter $\alpha = 0.2, 0.4, 0.6,$ and 0.8 . MC simulation data from Abrano *et al* [14].

Table 5 and 6 shows calculation results of radial distribution contact values and osmotic coefficients for the size asymmetric primitive model electrolytes with physical parameters: molar concentration $c=0.425$ mol/dm³, absolute temperature $T=298$ K, relative dielectric permittivity $\epsilon_r=78.5$, and ionic size ratio $\alpha (= \sigma_+/\sigma_-)$ with $\sigma_- = 4.25 \times 10^{-10}$ m of $\alpha=0.4, 0.6,$ and 0.8 .

Table 5 Shows contact values for the radial distribution functions where calculated using equation (159) using the potentials ψ and discharge potentials ψ^0 given by equations (99-103), (121-123), and (141-143). For the volume exclusion term a step function (equation 160) was used.

Table 6 shows osmotic coefficients calculated using equation (161). A comparison with the MC osmotic coefficients from reference [14] shows good agreement for the concentration studied.

Chapter 6

Conclusion

In this thesis we have made an approximate analysis of the fluctuation potential in the modified Poisson-Boltzmann theory of bulk electrolyte solutions. An analytical solution of the fluctuation potential equation, albeit approximate, was obtained for symmetric valency 1:1 electrolytes in the RPM. This solution was later employed to obtain the structure and thermodynamics of the electrolyte in terms of ion-ion radial distribution functions, reduced excess energy, and the osmotic coefficients, respectively.

One of the main problems in the present MPB theory is the use of an approximate solution to the fluctuation potential problem that is restricted to large inter-ionic separations, where approximate spherical symmetry is valid [33]. This work is an attempt to overcome the separation restriction through an approximate analytical solution for the fluctuation potential. The solution is represented as an integral over ionic charge density in space. The integral was numerically implemented for the simplest case, a RPM (1:1) electrolyte. The resultant radial distribution functions, configurational energies, and osmotic coefficients were compared and contrasted with the corresponding results from the PB, SPB, traditional MPB and MC simulation data.

The fluctuation potential is a central ingredient in a potential approach to the theory (of charged fluids) such as the modified Poisson-Boltzmann theory. The fluctuation potential solution developed in this work, with approximations to make analytical progress and for symmetric systems, is a preliminary attempt to assess the implications of such a solution. In such cases due to the linearization of the fluctuation potential in the bulk region I (equation (72)) and the small magnitude of $\Phi(1, 2; 3)$, the P function in bulk region I can

be taken to be zero, thus neglecting charge density for that region. A less approximate and nearly full treatment could be achieved by solving for the fluctuation potential in region I using equation (64) with P_I being given by equation (72) in conjunction with equation (71). An intermediate procedure (between the above two situations) to obtain a better, viable, and still feasible approximation for $\Phi(1, 2; 3)$ in region I would be to solve equation (64) (with P_I given by equation (72)) by writing it in the form

$$\nabla^2\Phi(1,2;3) = C\Phi(1,2;3) \quad (174)$$

where the quantity C contains the valencies Z_+ , Z_- , and has spatial dependence through $g(1, 3)$ and $g(2, 3)$. Thus although C is not a constant per se, it can be assumed to be approximately constant for the purposes of solution to equation (174). An approximate analytic form of $\Phi(1, 2; 3)$ in region I, whose value is not necessarily zero, would then be available. Equation (174) has some parallels to a similar equation for the fluctuation potential in the MPB formalism in the planar electric double layer [39]. Such procedure will be useful for higher and multivalent electrolytes when the magnitude of the fluctuation potential in region I is likely to be significant and hence P_I can no longer be neglected. This will be a focus of our future work.

The three-dimensional plots of the fluctuation potential give valuable insight into the correlations between ions. Furthermore, the present structural and thermodynamic results point in the right direction and are indicative of the potential usefulness of a full solution of the fluctuation potential. The radial distribution functions, especially at contact distance separation between the ions, the reduced excess energy, and osmotic coefficients show an improvement over that from the PB (or SPB), and an overall very good agreement with the predictions from the traditional MPB theory and Monte Carlo results.

Future work, will also include, the numerical evaluation of the third term in equation 72, and the calculation of the full fluctuation potential solution from equation (158) and the implementation of some form of hard spheres RDF for binary solutions, instead of the use of a Heaviside function in equation (160), to calculate accurate radial distribution functions, and thermodynamic properties, for size asymmetric cases.

The MPB description of the electric double layer phenomenon is an area where the present techniques might have some significance since the fluctuation potential plays an equally important role in the theoretical framework for the inhomogeneous fluid at the interface. In the MPB approach to the double layer theory in planar [39, 40], cylindrical [41, 42, 43], and spherical [44, 45] symmetries, the form of the corresponding fluctuation potential used is rather approximate and generally suffers from similar defects as those vis-a-vis the traditional MPB theory for the bulk. The statistical mechanical methods used in this paper are quite general and can be extended and adapted to interfacial double layer geometry where an analogous fluctuation potential analysis might prove useful.

Another area of possible relevance for this study is in the theoretical analysis of charged fluid systems with variable dielectric constant (relative permittivity). The topic has attracted a lot of recent research attention (see for example, references [46, 47, 48]) and has been shown to be relevant for important technological systems, viz., super-capacitors [49, 50]. In the electric double layer the MPB has been found to be capable of dealing with systems having an inhomogeneous dielectric constant [39, 40]. Very recently, the MPB was applied to a double layer system with three different dielectric constants [51], although the associated fluctuation potential problem could only be solved for point ions. Thus again

a fluctuation analysis in such situations along the lines of the present work could be valuable.

The complete solution of the fluctuation potential equation, valid for a general case and for asymmetry in ionic size and/or valency will involve a numerical solution comprising an iterative algorithm. Our solution here might prove useful in such a procedure. Such a project is contemplated in the future.

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Appendix A

The Dimensionless Poisson-Boltzmann Equation

The Poisson equation for the spherically symmetrical field of an ion is given by

$$\nabla^2 \phi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) = \frac{-\rho}{\varepsilon} \quad (\text{A.1})$$

Where ϕ is the electrostatic potential, r the radial distance from the ion's center, ε is the liquid's dielectric constant, and ρ the density of charge.

In the Poisson-Boltzmann theory it is assumed that ions are distributed in space following the Boltzmann's distribution. The charge density is then given by:

$$\rho = \sum_s q_s \rho_s e^{-q_s \phi} = q_+ \rho_+ e^{-q_+ \beta \phi} + q_- \rho_- e^{-q_- \beta \phi} \quad (\text{A.2})$$

Where q_+ , q_- , ρ_+ and ρ_- are the ions respective charges and particle concentrations.

Inserting equation A.2 in equation A.1 we get:

$$\nabla^2 \phi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) = \sum_s q_s \rho_s e^{-q_s \beta \phi} \quad (\text{A.3})$$

The condition of global charge neutrality is given by,

$$\sum_s q_s \rho_s = q_+ \rho_+ + q_- \rho_- = 0 \quad (\text{A.4})$$

The global particle concentration is given by,

$$\rho = \frac{N_+ + N_-}{\Omega} = \frac{N_+}{\Omega} + \frac{N_-}{\Omega} = \rho_+ + \rho_- \quad (\text{A.5})$$

Using the global charge neutrality conditions (A.4), the ions concentrations can be expressed in terms of the global ionic concentration as follows,

$$\rho_+ = \frac{q_-}{q_- - q_+} \rho \quad (\text{A.6})$$

$$\rho_- = \frac{q_+}{q_+ - q_-} \rho \quad (\text{A.7})$$

, or in terms of the ion valences,

$$q_+ = Z_+ e \quad (\text{A.8})$$

$$q_- = Z_- e \quad (\text{A.9})$$

$$\rho_+ = \frac{Z_-}{Z_- - Z_+} \rho \quad (\text{A.10})$$

$$\rho_- = \frac{Z_+}{Z_+ - Z_-} \rho \quad (\text{A.11})$$

To cast the Poisson Boltzmann equation in dimensionless form we define the dimensionless electrostatic potential,

$$\Psi \equiv e\beta\phi(r), \quad (\text{A.12})$$

The packing fraction,

$$\eta \equiv \frac{\pi}{6} (\rho_+ \sigma_+^3 + \rho_- \sigma_-^3) = \frac{\pi}{6} \rho \sigma^3 \quad (\text{A.13})$$

, and the plasma parameter

$$\Gamma \equiv \frac{e^2 \beta}{4\pi \epsilon_r \epsilon_0 \sigma} \quad (\text{A.14})$$

Where we have used equal ionic diameters,

$$\sigma = \sigma_+ = \sigma_-,$$

Defining,

$$y_0 \equiv \sqrt{24\eta\Gamma}, \quad (\text{A.15})$$

we have,

$$y_0^2 = 24\eta\Gamma = \frac{\sigma^2 \rho e^2 \beta}{\varepsilon_r \varepsilon_0} \quad (\text{A.16})$$

, finally obtain,

$$\nabla^2 \Psi(r) = -y_0^2 \left(\frac{Z_+ Z_-}{Z_- - Z_+} \right) (e^{-Z_+ \Psi(r)} - e^{-Z_- \Psi(r)}). \quad (\text{A.17})$$

The PB equation for the asymmetrical size case is the same form as equation 14 but the distance scale is set to the larger ion diameter and the packing fraction and plasma coupling parameters are then given by

$$\eta = \frac{\pi}{6} \sigma_-^2 \rho \frac{Z_- \alpha^3 - Z_+}{Z_- - Z_+} \quad (\text{A.18})$$

$$\Gamma = \frac{\beta e^2}{4\pi \varepsilon_0 \varepsilon_r \sigma_-} \quad (\text{A.19})$$

The PB equation for asymmetric size ions is given by

$$\nabla^2 \Psi(r) = \frac{y^2}{Z_- - Z_+} (e^{-Z_+ \Psi(r)} - e^{-Z_- \Psi(r)}) \quad (\text{A.20})$$

Where y is given by

$$y = \sqrt{-24\eta\Gamma \frac{Z_- - Z_+}{Z_- \alpha^3 - Z_+} Z_+ Z_-}. \quad (\text{A.21})$$

Appendix B

Dimensionless Debye-Hückel Potentials

The Poisson-Boltzmann equation is a nonlinear elliptical partial differential equation. Being nonlinear, this equation is generally difficult to solve. The Debye-Hückel theory approximation consists of the linearization of the PB equation by expanding the exponential in the Boltzmann term. Thus, keeping only terms linear in Ψ , we write

$$\begin{aligned}\nabla^2\Psi(r) &= -y_0^2\left(\frac{Z_+Z_-}{Z_- - Z_+}\right)\left(e^{-Z_+\Psi(r)} - e^{-Z_-\Psi(r)}\right) \\ &\cong -y_0^2Z_+Z_-\Psi(r)\end{aligned}$$

So the dimensionless linearized PB equation becomes the dimensionless Debye-Hückel equation

$$\nabla^2\Psi(r) = -y_0^2Z_+Z_-\Psi(r). \quad (\text{B.1})$$

, defining

$$y \equiv \sqrt{-y_0^2Z_+Z_-} = \sqrt{-24\Gamma\eta Z_+Z_-}. \quad (\text{B.2})$$

Debye-Hückel equation in reduced dimensionless variables is then given by,

$$\nabla^2\Psi(r) = y^2\Psi(r) \quad (\text{B.3})$$

, with solution,

$$\Psi(r) = \Gamma\frac{Z_{\pm}}{r} - \Gamma\frac{Z_{\pm}y}{y+1} \quad 0 < r < 1 \quad (\text{B.4})$$

, and

$$\Psi(r) = \Gamma\frac{Z_{\pm}e^{-y(r-1)}}{(1+y)r} \quad r > 1 \quad (\text{B.5})$$

Appendix C

An analysis of the fluctuation potential in the modified Poisson-Boltzmann theory for restricted primitive model electrolytes

E.O. Ulloa-Dávila, L.B. Bhuiyan

Laboratory of Theoretical Physics, Department of Physics, Box 70377, University of Puerto Rico, San Juan, Puerto Rico 00936-8377, USA

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An approximate analytical solution to the fluctuation potential problem in the modified Poisson-Boltzmann theory of electrolyte solutions in the restricted primitive model is presented. The solution is valid for all inter-ionic distances, including contact values. The fluctuation potential solution is implemented in the theory to describe the structure of the electrolyte in terms of the radial distribution functions, and to calculate some aspects of thermodynamics, viz., configurational reduced energies, and osmotic coefficients. The calculations have been made for symmetric valence 1:1 systems at the physical parameters of ionic diameter 4.25×10^{-10} m, relative permittivity 78.5, absolute temperature 298 K, and molar concentrations 0.1038, 0.425, 1.00, and 1.968. Radial distribution functions are compared with the corresponding results from the symmetric Poisson-Boltzmann, and the conventional and modified Poisson-Boltzmann theories. Comparisons have also been done for the contact values of the radial distributions, reduced configurational energies, and osmotic coefficients as functions of electrolyte concentration. Some Monte Carlo simulation data from the literature are also included in the assessment of the thermodynamic predictions. Results show a very good agreement with the Monte Carlo results and some improvement for osmotic coefficients and radial distribution functions contact values relative to these theories. The reduced energy curve shows excellent agreement with Monte Carlo data for molarities up to 1 mol/dm³.

Key words: *electrolytes, restricted primitive model, fluctuation potential, modified Poisson-Boltzmann theory*

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1. Introduction

One of the more consistently active areas of research in the statistical mechanics of fluids over the years has been in the field of Coulomb fluids. These encompass among others, electrolytes, ionic liquids, molten salts, colloids, and polyelectrolytes, the practical relevance of which extend from biological systems to industrial chemical processes. The literature on this is vast and theoretical progress was limited until the application of liquid state theory [1–5] based on classical statistical mechanics. We would like to cite here a few of the recent reviews on the subject [6–8].

A widely used model used in the development of formal statistical mechanical theories of ionic solutions treats the solvent as a structureless, continuous dielectric medium with a relative permittivity ϵ_r , and the solute particles as charged hard spheres of arbitrary diameters d_i and charges $Z_s e$ with Z_s being the valence of species s . This is the so-called primitive model (PM) of ionic solutions. When the ions are of the same size, it is called the restricted primitive model (RPM). Computer simulations of the RPM and PM over the years (see for example, references [9–14]) have shown the usefulness of these models in interpreting experimentally determined structures and thermodynamics of charged fluid systems. Furthermore, the simulation data have proved to be invaluable in theoretical development.

The statistical mechanics of primitive models in liquid state physics has followed two broad paths: In the first, the focus is on computing the pair correlation function or the radial distribution function $g_{ij}(r_i, r_j)$ from the inter-molecular pair potential $u_{ij}(r_i, r_j)$ starting from the Ursell-Mayer cluster expansion [1–3], or the distribution function method [3, 5]. Two main routes are used, viz., the Kirkwood, Bogolubov, Born, Green, Yvon (KBBGY) hierarchies (see for example, reference [5]) and the Ornstein-Zernike (OZ) equation [2, 3, 5]. The KBBGY hierarchies relate correlation functions for n and $n + 1$ fixed particles, the molecular potential, and a charge parameter ξ . To evaluate the pair correlation function, for example, a closure relation between the pair correlation function $g_{ij}(r_i, r_j)$ and the next higher order correlation function, that is, the triplet correlation $g_{ijk}(r_i, r_j, r_k)$ must be provided to break the hierarchy. One such relation is the superposition approximation [3]. In the OZ approach, the total correlation between two ions is considered to consist of two parts: the direct correlation function $c_{ij}(r_i, r_j)$ between the two particles, and the indirect correlation $h_{ij}(r_i, r_j)$, which takes into account the presence of a third particle. This is clearly shown by the OZ equation (see for example, reference [3]), which is often regarded as a definition of the direct correlation function. To solve the OZ equation, a closure relation between the direct and the total correlation functions is required. Among the more well known closures are: the Percus-Yevick (PY) [15], the Hyper-netted chain (HNC) [16], and the mean spherical approximation (MSA) [17].

In the second method, which is our interest in the present work, the focus is on obtaining the same $g_{ij}(r_i, r_j)$, but through a potential approach to the theory based on the Poisson's equation. The classical theoretical analysis of electrolyte solutions in this regard is that of Debye and Hückel (DH) [18], which is a linearized version of the corresponding non-linear Poisson-Boltzmann (PB) equation. A key theoretical paper on an assessment of the inherent approximations in the Poisson-Boltzmann (PB) equation, and hence in the linearized DH equation is due to Kirkwood [19]. Kirkwood showed through a statistical mechanical analysis that the main approximations in the classical theories are the omission of (i) ionic exclusion volume effects, and (ii) the fluctuation potential term, which involves the inter-ionic correlations. There have been many attempts since Kirkwood to improve upon the PB/DH theory notable among which has been the extensive work done by Outhwaite and co-workers (see for example, references [20–29]), who within the framework of the PM, have analyzed Kirkwood's methods and obtained estimates for the fluctuation term. The resulting modified Poisson-Boltzmann (MPB) approach to ionic solutions is thus based on extending the classical mean electrostatic potential approach of DH theory by expressing the distribution functions in the Kirkwood, Bogolubov, Born, Green, Yvon (KBBGY) hierarchies in terms of mean electrostatic potentials. Essentially, the MPB improves upon the classical PB theory by incorporating (i) ionic exclusion volume effects, and (ii) inter-ionic correlation effects. This potential procedure solves for the mean electrostatic potential $\psi(r)$ as opposed to the integral equations that attempt to solve directly for the radial distribution function $g_{ij}(r_i, r_j)$. Outhwaite and co-workers [22–28] have further symmetrized the classical PB theory and the MPB theory so that the Onsager relation, $g_{ij}(r) = g_{ji}(r)$ is satisfied for a homogeneous fluid. They have also coupled an exclusion volume term to the symmetrized PB theory, and call it the symmetric Poisson-Boltzmann (SPB) theory [25–27].

In the MPB theory, the mean electrostatic potential is expressed in terms of the fluctuation potential $\phi(1, 2; 3)$ (see for example, reference [28]) (3 is the field point, while there are fixed ions at 1 and 2), which measures deviations from the superposition principle of Kirkwood [19], and, therefore, contains information on the interionic correlations in the theory. Expressed in terms of the mean potentials, the fluctuation potential is given by [25, 28]

$$\psi(1, 2; 3) = \psi(1, 3) + \psi(2, 3) + \phi(1, 2; 3). \quad (1)$$

This equation is a statement that the mean potential at field point 3 is the sum of the direct potentials of particles fixed at 1 and 2, and the correlated potential contribution at the field point from the simultaneous presence of particles at 1 and 2. As we will see in the next section, the fluctuation potential can be written in terms of distributions functions as

$$\phi(1, 2; 3) = \frac{1}{4\pi\epsilon_0\epsilon_r} \sum_s e_s \int \left[\frac{\rho_s(1, 2; q) - \rho_s(1; q) - \rho_s(2; q)}{\mathbf{r}_q} \right] d\mathbf{r}_q, \quad (2)$$

where e_s is the charge and $\rho_s(\{n\}; q)$ is the number density of the s -th species of ions at \mathbf{r}_q with n fixed particles at \mathbf{r}_i ($i = 1, \dots, n$) with the sum being over all species, ϵ_0 is the vacuum permittivity, and ϵ_r the relative permittivity (dielectric constant) of the solvent.

In the simplest language, the fluctuation potential is the inter-ionic correlations expressed in potential form. The fluctuation potential $\phi(1, 2; 3)$ obeys a system of partial, non-linear, differential equations, and for the RPM case, the linearized version of the equations is given in reference (see for example, reference [28, 29]). An approximate solution, valid for large inter-ionic separation, under the assumption of spherical symmetry, was found by Outhwaite [21]. One of the main problems in present MPB theory is the restriction of the fluctuation potential for large inter-ionic separations, where approximate spherical symmetry is valid. In the present work, an approximate analytical solution to the fluctuation potential problem is found, that is valid for the whole range of interionic distances. This solution has an advantage of simplicity that can provide insight into the eventual fully numerical methods for solving this kind of problems. The approximate analytical solution for $\phi(1, 2; 3)$ can serve as a guide to solving the problem numerically without using the approximations of this research.

The organization of this paper is as follows. In the following section (section 2) we start by giving details of the interaction potentials of the model, a brief introduction to the PB equation and the MPB theory approach. We then proceed to the main theoretical development of this work based on the primitive models. In this part, the set of differential equations for the fluctuation potential in dimensionless form is developed and an approximate solution is found using ordinary electrostatics.

In section 3 we utilize solution of the fluctuation potential to present structural and thermodynamic results for a 1:1 valence RPM electrolyte. We start by showing three-dimensional plots of the fluctuation potential solution. The plots show the fluctuation potential at a planar slice passing through the center of the ions for two ionic separations and for the like and unlike ion cases. A physical interpretation of the results in terms of ionic correlation energy is presented. To further test the solution's validity, configurational energies, and osmotic coefficients are calculated and compared to the Monte Carlo (MC) simulation data of Card and Valleau [9], and Rasiah, Card, and Valleau [10].

In section 4 we present some conclusions out of this work and stress the importance of the approach for future work that may involve a full iterative process using the solution presented here but without the approximations made.

2. Model and theory

2.1. Molecular model

As indicated in the introduction, the model electrolyte system used in this study consists of a binary, symmetric valence RPM at room temperature.

The ion-ion interaction potential in the Hamiltonian is thus

$$u_{ij}(r) = \begin{cases} \infty, & r < d, \\ \frac{e^2 Z_i Z_j}{4\pi\epsilon_0\epsilon_r r}, & r > d, \end{cases} \quad (3)$$

where Z_s is the valence of ion species s , e is the magnitude of the fundamental charge, r is the distance between the centres of two ions of types i and j , respectively, and d is the common ionic diameter. The relative permittivity ϵ_r is assumed to be uniform throughout the entire system.

2.2. Theory

The formulation of the SPB and the (traditional) MPB have already appeared elsewhere in the literature (see for example, references [22, 25–27]), and will not be repeated here. We will restrict ourselves to outlining the main steps leading to the equations governing the fluctuation potential and their solution.

We begin by formulating the fluctuation potential problem in the restricted primitive model for a symmetric valence electrolyte, viz., $|Z_+| = |Z_-|$, consisting of N ions and satisfying global electroneutrality $\sum_s Z_s \rho_s = 0$. We will closely follow the notations used in reference [28]. In the defining relation for the fluctuation potential in equation (1), the mean electrostatic potentials $\psi(1; 3)$, $\psi(2; 3)$, and $\psi(1, 2; 3)$ can

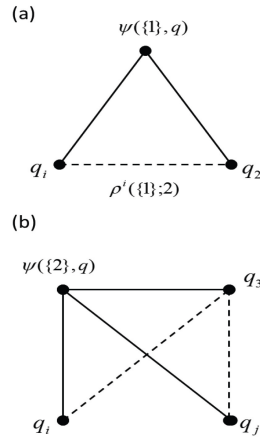


Figure 1. Diagrammatic representation of the mean electrostatic potential at field point q due to n fixed charges. Solid lines represents direct potential, and dotted lines represent potential due to ionic correlation. (a) $n = 1$, (b) $n = 2$.

be formally written as

$$\psi(1; 3) = \frac{e_1}{4\pi\epsilon_0\epsilon_r r_{13}} + \frac{1}{4\pi\epsilon_0\epsilon_r} \sum_{\alpha} \int e_{\alpha} \frac{\rho_{\alpha}(1, q)}{r_{3q}} dq, \quad (4)$$

$$\psi(2; 3) = \frac{e_2}{4\pi\epsilon_0\epsilon_r r_{23}} + \frac{1}{4\pi\epsilon_0\epsilon_r} \sum_{\alpha} \int e_{\alpha} \frac{\rho_{\alpha}(2, q)}{r_{3q}} dq, \quad (5)$$

and,

$$\psi(1, 2; 3) = \frac{e_1}{4\pi\epsilon_0\epsilon_r r_{13}} + \frac{e_2}{4\pi\epsilon_0\epsilon_r r_{23}} + \frac{1}{4\pi\epsilon_0\epsilon_r} \sum_{\alpha} \int e_{\alpha} \frac{\rho_{\alpha}(1, 2; q)}{r_{3q}} dq, \quad (6)$$

where e_1, e_2 are the charges of the fixed ions at 1 and 2, respectively, and the sum runs over all the ionic species. Figure 1 shows the mean electrostatic potential at a field point q due to 1 and 2 fixed ions, respectively. Subtracting the equations (4) and (5) from equation (6) leads to the earlier equation (2). The Poisson equations follow

$$\nabla^2 \psi(1; 3) = -\frac{e_1}{\epsilon_0\epsilon_r} \delta(\mathbf{r}_1 - \mathbf{r}_3) - \frac{1}{\epsilon_0\epsilon_r} \sum_{\alpha} e_{\alpha} \rho_{\alpha}(1, 3), \quad (7)$$

$$\nabla^2 \psi(2; 3) = -\frac{e_2}{\epsilon_0\epsilon_r} \delta(\mathbf{r}_2 - \mathbf{r}_3) - \frac{1}{\epsilon_0\epsilon_r} \sum_{\alpha} e_{\alpha} \rho_{\alpha}(2, 3), \quad (8)$$

and,

$$\nabla^2 \psi(1, 2; 3) = -\frac{1}{\epsilon_0\epsilon_r} e_1 \delta(\mathbf{r}_1 - \mathbf{r}_3) - \frac{1}{\epsilon_0\epsilon_r} e_2 \delta(\mathbf{r}_2 - \mathbf{r}_3) - \frac{1}{\epsilon_0\epsilon_r} \sum_{\alpha} e_{\alpha} \rho_{\alpha}(1, 2; 3). \quad (9)$$

Here, the operator ∇ is understood to operate on the coordinates of the field point. These equations can also be expressed in terms of the distribution functions using for example, $g_{1\alpha}(1, q) = \rho_{\alpha}(1, q)/\rho_{\alpha}$, and so on and so forth, with ρ_{α} being the mean number density of ion species α . The distributions can, in turn, be defined in terms of the potentials of mean force W , viz., the doublet

$$g_{ij}(1, 2) = \exp[-\beta W_{ij}(1, 2)] \quad (10)$$

or the triplet

$$g_{ijk}(1, 2, 3) = \exp[-\beta W_{ijk}(1, 2, 3)], \quad (11)$$

where W_{ij} , W_{ijk} are the pair and triplet potentials of mean force, respectively. Also, $\beta = 1/(k_B T)$ with k_B the Boltzmann constant and T the absolute temperature. Hence, the conditional distribution,

$$g_{ijk}(1, 2; 3) = \exp\{-\beta[W_{ik}(1, 3) + W_{jk}(2, 3) + w_{ijk}(1, 2; 3)]\}. \quad (12)$$

The term w_{ijk} is the potential of mean force associated with the departure from linear superposition of the pair potentials. A hierarchy of such equations can be constructed for higher order correlations. At the lowest order, the classical PB theory follows upon neglecting $w_{ijk}(1, 2; 3)$, and to improve upon the PB, we need a procedure to estimate this term.

In the MPB formulation, the hierarchy is broken at the triplet level by a closure condition that relates the w_{ijk} with the fluctuation potential ϕ_{ij} [28]

$$w_{ijk}(1, 2; 3) = e_k \phi_{ij}(1, 2; 3). \quad (13)$$

It is of interest to contrast this MPB closure with the Debye-Hückel closure

$$W_{ij}(1, 2) = e_j \psi(1; 2). \quad (14)$$

For the RPM system with a finite ion diameter d , the Poisson equations (7)–(9) can be expressed in terms of the potentials of mean force as

$$\nabla^2 \psi(1; 3) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s e^{-\beta W_{is}(1,3)}, \quad (15)$$

$$\nabla^2 \psi(2; 3) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s e^{-\beta W_{js}(2,3)}, \quad (16)$$

$$\nabla^2 \psi(1, 2; 3) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s \exp\{-\beta [W_{is}(1, 3) + W_{js}(2, 3) + e_s \phi(1, 2; 3)]\}, \quad (17)$$

where the MPB closure (13) has been used in equation (17). The equations (15) and (16) are exact, for one fixed ion in position 1 and 2, but equation (17) incorporates the deviation from the superposition principle in the form of the fluctuation potential term. To obtain an equation for the fluctuation potential [equation (1)], we subtract equations (7) and (8) from (9),

$$\nabla^2 \phi(1, 2; 3) = -\frac{1}{\epsilon_0 \epsilon_r} \sum_s e_s \rho_s [g(1, 3)g(2, 3)e^{-\beta e_s \phi(1,2;3)} - g(1, 3) - g(2, 3)]. \quad (18)$$

Equation (18) is the base nonlinear equation in the fluctuation potential problem. The equation also suggests that the charge density source for fluctuation potential is associated with the charged atmospheres of the triplet and doublet densities.

To illustrate the geometry of the fluctuation potential problem, one can expand the summation over species as

$$\begin{aligned} \nabla^2 \phi(1, 2; 3) = & -\frac{1}{\epsilon_0 \epsilon_r} e_+ \rho_+ [g(1, 3^+)g(2, 3^+)e^{-\beta e_+ \phi(1,2;3)} - g(1, 3^+) - g(2, 3^+)] \\ & + e_- \rho_- [g(1, 3^-)g(2, 3^-)e^{-\beta e_- \phi(1,2;3)} - g(1, 3^-) - g(2, 3^-)], \end{aligned} \quad (19)$$

where a number with a superscript notation with a positive or negative sign represents the presence of the corresponding ion at the referred position in space.

Figure 2, represents the geometry of the fluctuation potential system of equations with Ω being the total volume of the ionic solution, ω_1 and ω_2 represent the exclusion volumes of ion 1 and 2, respectively, ω^* is the overlap volume, and 3 is the field point. Region I [$\Omega - (\omega_1 + \omega_2)$] is the bulk volume defined as the total volume minus the exclusion volumes of ions 1 and 2. Region II ($\omega_1 - \omega^*$) and III ($\omega_2 - \omega^*$) are the interior of the exclusion volumes of ion1 and 2 minus the overlap volume. Region IV is the overlap

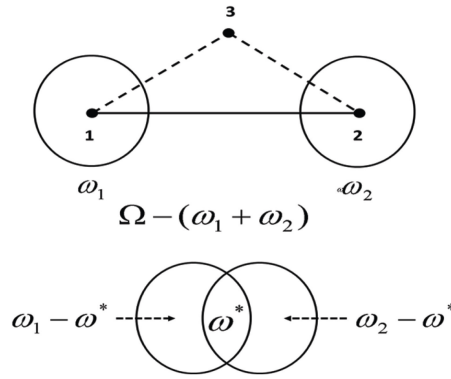


Figure 2. Geometry of the ionic exclusion volumes within the restricted primitive model showing the various regions of validity of the fluctuation potential equation (see text).

volume. The nonlinear system of equations governing the fluctuation potential are then given by the following expressions

$$\text{I : } \quad \Omega - (\omega_1 + \omega_2) \quad \nabla^2 \phi(1, 2; 3) = -\frac{1}{\varepsilon_0 \varepsilon_r} e_+ \rho_+ [g(1, 3^+) g(2, 3^+) e^{-\beta e_+ \phi(1, 2; 3)} - g(1, 3^+) - g(2, 3^+)] \\ + e_- \rho_- [g(1, 3^-) g(2, 3^-) e^{-\beta e_- \phi(1, 2; 3)} - g(1, 3^-) - g(2, 3^-)], \quad (20)$$

$$\text{II : } \quad \omega_1 - \omega^* \quad \nabla^2 \phi(1, 2; 3) = -\frac{1}{\varepsilon_0 \varepsilon_r} [e_+ \rho_+ g(2, 3^+) + e_- \rho_- g(2, 3^-)], \quad (21)$$

$$\text{III : } \quad \omega_2 - \omega^* \quad \nabla^2 \phi(1, 2; 3) = -\frac{1}{\varepsilon_0 \varepsilon_r} [e_+ \rho_+ g(1, 3^+) + e_- \rho_- g(1, 3^-)], \quad (22)$$

$$\text{IV : } \quad \omega^* \quad \nabla^2 \phi(1, 2; 3) = 0. \quad (23)$$

At this point it is convenient to work in terms of reduced (dimensionless) quantities. Here, the relevant ones are the reduced mean electrostatic potential $\Psi = e\beta\psi$, the reduced fluctuation potential $\Phi = e\beta\phi$, and $y_0 = \sqrt{24Z_+Z_- \eta \Gamma}$. Also, $\eta = (\pi/6) \sum_s \rho_s d^3$ is the volume or packing fraction and $\Gamma = Z_+ Z_- e^2 / (4\pi \varepsilon_0 \varepsilon_r k_B T d)$ is the plasma coupling parameter. After expressing the Laplacian in ionic diameter scale, and imposing global electro-neutrality, we have a set of dimensionless fluctuation potential equations for the size symmetric case

$$\text{I : } \quad \Omega - (\omega_1 + \omega_2) \quad -\frac{1}{y_0^2} \nabla_d^2 \Phi(1, 2; 3) = \frac{Z_+ Z_-}{Z_- - Z_+} [g(1, 3^+) g(2, 3^+) e^{-Z_+ \Phi(1, 2; 3)} \\ - g(1, 3^-) g(2, 3^-) e^{-Z_- \Phi(1, 2; 3)} - g(1, 3^+) - g(2, 3^+) + g(1, 3^-) + g(2, 3^-)], \quad (24)$$

$$\text{II : } \quad \omega_1 - \omega^* \quad -\frac{1}{y_0^2} \nabla_d^2 \Phi(1, 2; 3) = \frac{Z_+ Z_-}{Z_- - Z_+} [-g(2, 3^+) + g(2, 3^-)], \quad (25)$$

$$\text{III : } \quad \omega_2 - \omega^* \quad -\frac{1}{y_0^2} \nabla_d^2 \Phi(1, 2; 3) = \frac{Z_+ Z_-}{Z_- - Z_+} [-g(1, 3^+) + g(1, 3^-)], \quad (26)$$

$$\text{IV : } \quad \omega^* \quad \nabla_d^2 \Phi(1, 2; 3) = 0. \quad (27)$$

The boundary conditions are that the fluctuation potential and its normal derivative are continuous across the boundaries. Denoting the right-hand sides of these equations by P, we can write them in a general form

$$\nabla^2 \Phi(1, 2; 3) = -y_0^2 \text{P}[\Phi, g(1, 3), g(2, 3)], \quad (28)$$

with a formal solution [30, 31]

$$\Phi(1, 2; 3) = \int_{\Omega} \frac{y_0^2}{r_d} \text{P}[\Phi, g(1, 3), g(2, 3)] d\mathbf{r}_d. \quad (29)$$

Specifically, we have in the various regions

$$\text{I : } \quad \Omega - (\omega_1 + \omega_2) \quad -\frac{1}{y_0^2} \nabla_d^2 \Phi(1, 2; 3) = P_{\text{I}}[\Phi, g(1, 3), g(2, 3)] = \frac{Z_+ Z_-}{Z_- - Z_+} [g(1, 3^+)g(2, 3^+)e^{-Z_+ \Phi(1, 2; 3)} - g(1, 3^-)g(2, 3^-)e^{-Z_- \Phi(1, 2; 3)} - g(1, 3^+) - g(2, 3^+) + g(1, 3^-) + g(2, 3^-)], \quad (30)$$

$$\text{II : } \quad \omega_1 - \omega^* \quad -\frac{1}{y_0^2} \nabla_d^2 \Phi(1, 2; 3) = P_{\text{II}}[g(1, 3), g(2, 3)] = \frac{Z_+ Z_-}{Z_- - Z_+} [-g(2, 3^+) + g(2, 3^-)], \quad (31)$$

$$\text{III : } \quad \omega_2 - \omega^* \quad -\frac{1}{y_0^2} \nabla_d^2 \Phi(1, 2; 3) = P_{\text{III}}[g(1, 3), g(2, 3)] = \frac{Z_+ Z_-}{Z_- - Z_+} [-g(1, 3^+) + g(1, 3^-)], \quad (32)$$

$$\text{IV : } \quad \omega^* \quad \nabla_d^2 \Phi(1, 2; 3) = P_{\text{IV}}, \quad P_{\text{IV}} = 0. \quad (33)$$

In order to make analytical progress, we approximate the radial distribution functions $g(1, 3)$ and $g(2, 3)$, in the various P's appearing in the above equations by their DH values

$$\begin{aligned} g(1, 3^+) (= g_{\text{DH}}(1, 3^+)) &= \exp[-Z_+ \Psi_1^{\text{DH}}(1, 3)], \\ g(2, 3^+) (= g_{\text{DH}}(2, 3^+)) &= \exp[-Z_+ \Psi_2^{\text{DH}}(2, 3)], \\ g(1, 3^-) (= g_{\text{DH}}(1, 3^-)) &= \exp[-Z_- \Psi_1^{\text{DH}}(1, 3)], \\ g(2, 3^-) (= g_{\text{DH}}(2, 3^-)) &= \exp[-Z_- \Psi_2^{\text{DH}}(2, 3)], \end{aligned} \quad (34)$$

where the subscript in Z represents the sign of the charge state of the ion at the field point 3. Inserting the radial distribution functions (34) in the integrals in equation (29) will render the contribution to the fluctuation potential in regions II and III as ordinary integrals in space.

To obtain an approximation for P in the bulk region I, outside ions 1 and 2, we use the properties of the radial distribution functions in the various regions, and expand the exponents up to linear terms, leading to

$$\begin{aligned} P_{\text{I}}[\Phi, g(1, 3), g(2, 3)] &= \frac{Z_+ Z_-}{Z_- - Z_+} [g(1, 3^+)g(2, 3^+)(1 - Z_+ \Phi) - g(1, 3^-)g(2, 3^-)(1 - Z_- \Phi) \\ &\quad - g(1, 3^+) - g(2, 3^+) + g(1, 3^-) + g(2, 3^-)] \\ &= \frac{Z_+ Z_-}{Z_+ - Z_-} [Z_+ g(1, 3^+)g(2, 3^+) - Z_- g(1, 3^-)g(2, 3^-)] \Phi(1, 2; 3). \end{aligned} \quad (35)$$

For a small fluctuation potential, we neglect the right-hand side of equation (35). For example, for a symmetric valence 1:1 RPM electrolyte, the theme of this work, we have noted that the DH radial distributions in equation (34) are of the order unity for the physical parameters and the range of concentrations used. If the fluctuation potential is of the order 10^{-2} or less, then the right-hand side of equation (35) will be of a similar order and can be neglected as a first approximation for such a system. Under these approximations, the fluctuation potential is given by,

$$\Phi(1, 2; 3) = \frac{y_0^2}{4\pi} \left\{ \int_{\omega_1} \frac{F_1[g(2, q^+), g(2, q^-)]}{|\mathbf{r}_{qd} - \mathbf{r}_{3d}|} dV_q + \int_{\omega_2} \frac{F_2[g(1, q^+), g(1, q^-)]}{|\mathbf{r}_{qd} - \mathbf{r}_{3d}|} dV_q \right\}, \quad (36)$$

where

$$F_1[g(2, q^+), g(2, q^-)] = \frac{Z_+ Z_-}{Z_- - Z_+} [-g(2, q^+) + g(2, q^-)], \quad (37)$$

and

$$F_2[g(1, q^+), g(1, q^-)] = \frac{Z_+ Z_-}{Z_- - Z_+} [-g(1, q^+) + g(1, q^-)]. \quad (38)$$

The integral in equation (36) needs to be calculated numerically. This was done by discretization of space, and will be discussed in the next section.

A useful way of testing the fluctuation potential solution is through subsequent evaluation of the structure and thermodynamics of the electrolyte solution. We have utilized the MPB formulation in reference [28] to calculate the pair correlation functions,

$$g(1, 2) = \zeta_{12} \exp \left\{ -Z_2 [\Psi(1; 2) + \int_0^1 \Phi(1, 2; 2) d\lambda_2] \right\}, \quad (39)$$

where the DH functions (34) are used for $\Psi(1; 2)$ and an analytic expression for the Percus-Yevick (PY) radial distribution functions for hard spheres [4] have been used for the excluded volume term, ζ_{12} . The integral implies charging up of the ion at \mathbf{r}_2 .

For the calculation of osmotic coefficients ϕ and the reduced configurational energy $U/(Nk_B T)$, we use equation (12) from reference [32], written in dimensionless reduced variables as,

$$\phi - 1 = U/3Nk_B T + 2\eta[g_A(1) + g_B(1)], \quad (40)$$

and

$$U/Nk_B T = \frac{y_0^2}{4} \int_1^\infty [g_A(r') + g_B(r')] r' dr', \quad (41)$$

where $r' = r/d$ with g_A and g_B corresponding to like and unlike ions, respectively, and the argument 1 of g_A and g_B in (40) refers to the contact value.

3. Results

All calculations in this work pertain to (1:1) symmetric valence RPM electrolyte for ions of common diameter $d = 4.25 \times 10^{-10}$ m, in a continuum dielectric medium of relative permittivity $\epsilon_r = 78.5$, and at temperature $T = 298$ K, which is akin to a water-like solvent at room temperature. We have utilized electrolyte concentrations of 0.1038, 0.425, 1.00, and 1.968 mol/dm³. One reason for using these physical parameters is that these have been used earlier in the literature (see for example, reference [29] and for which MC simulation data exist [9, 10]). The SPB and the conventional MPB equations were solved numerically using a quasi-linearization iteration scheme [33]. The procedure has been used with much success in earlier works [24–27] and we refer the reader to these references for further details.

The fluctuation potential was obtained numerically by solving the integral in equation (36). The radial distribution functions $g_{ij}(r)$ were then calculated using the fluctuation potential solution in equation (39), while the osmotic coefficient ϕ , and the reduced configurational energy $-U/(Nk_B T)$ have been determined through equations (40) and (41), respectively. In what follows we will briefly describe the numerical procedure involved before taking up the discussion of the results.

3.1. Numerical solution

The calculation of the fluctuation potential $\Phi(1, 2; 3)$ was achieved by creating a Cartesian grid in space with scaled distance of 10% of the ionic diameter, which in our dimensionless units is 1, so that in the present context, the grid spacing is 0.1. This grid was created to represent the physical regions involved in the fluctuation potential problem as shown in figure 2. Those regions consist of the spherical regions ω_1 and ω_2 , which correspond to the boundaries of the ions 1 and 2, and the rest of the solution region, which is denoted by $\Omega - (\omega_1 + \omega_2)$. The region $(\omega_1 + \omega_2)$ is denoted as the ionic excluded volume. The quantities F_1 and F_2 [equations (37) and (38), respectively] represent the charge densities associated with the regions ω_1 and ω_2 in the integral of equation (36). The boundary of the rectangular Cartesian grid representing figure 2 was defined by a parameter Λ , which represents the distance from the boundary of the ions to the edge of the grid. This parameter was chosen in such a way that the fluctuation potential solutions tend to zero at the exterior boundary of the grid. Usually this parameter was between 3 and 5 ionic diameters for the highest concentration but was found to a lot larger than at

the lower concentrations. The fluctuation potential solution is an integral over the regions ω_1 and ω_2 . The summation used to numerically calculate the integral included approximately eight thousand terms for a point inside regions ω_1 and ω_2 . To produce the figures 3–5, the fluctuation potential was calculated at each point in a planar slice passing through the centers of ω_1 and ω_2 . For contact distance between the regions ω_1 and ω_2 , and $\Lambda = 5$, this planar slice contains approximately ten thousand points. The simplicity of equation (36) and the approximation of the g_{ij} in equation (34) in terms of the corresponding DH functions are what makes the calculations fairly tenable.

The evaluation of the pair correlation functions was performed in a similar grid as the one used for the three-dimensional figures but now the fluctuation potential was only required to be calculated at the center of region ω_2 (figure 2), and the solution used in equation (39), where the Kirkwood charge integral over the fluctuation potential is calculated. The calculation of osmotic coefficient and the reduced configurational energy was achieved using the formulae (40) and (41), respectively.

3.2. Fluctuation potential

We begin this discussion with the analysis of the three-dimensional representations of the fluctuation potential $\Phi(1, 2; 3)$ shown in figures 3–5. To our best knowledge, such representation of the fluctuation potential does not presently exist in the literature. The plots show the fluctuation potential $\Phi(1, 2; 3)$ obtained from equation (36) with the various g 's approximated through equations (34). The behaviour pattern of the fluctuation potential in these figures can be understood in terms of the charge density associated with the quantities F_1 and F_2 , inside the regions ω_1 and ω_2 . Figure 3 shows the fluctuation potential for a planar slice passing through the centers of two positive ions of valence +1 each. The charge density contributed by the spherical region ω_1 due to the positive ion in this region is calculated using F_1 [equation (37)], which is a function of $g(2, 3)$, where the point 3 is inside region ω_1 . The positive sign in the fluctuation potential in region ω_1 is given by the sign of $-g(2, 3^+) + g(2, 3^-)$. Since the charge at position 2 is positive, the second term associated with unlike charges is greater in magnitude than the

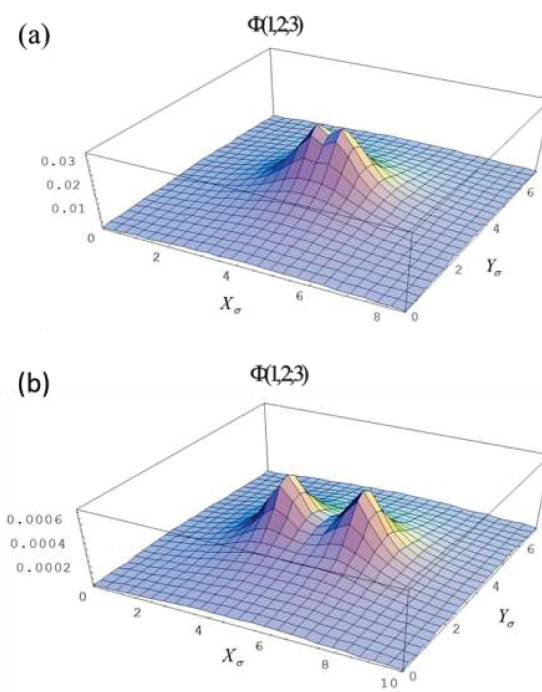


Figure 3. (Color online) Fluctuation potential $\phi(1, 2; 3)$ for $Z_1 = Z_2 = +1$ at ionic diameter $d = 4.25 \times 10^{-10}$ m, dielectric constant $\epsilon_r = 78.5$, temperature $T = 298$ K, and electrolyte concentration $c = 1.968$ mol/dm³. Reduced interionic distance r/d : (a) 1.5, (b) 3.

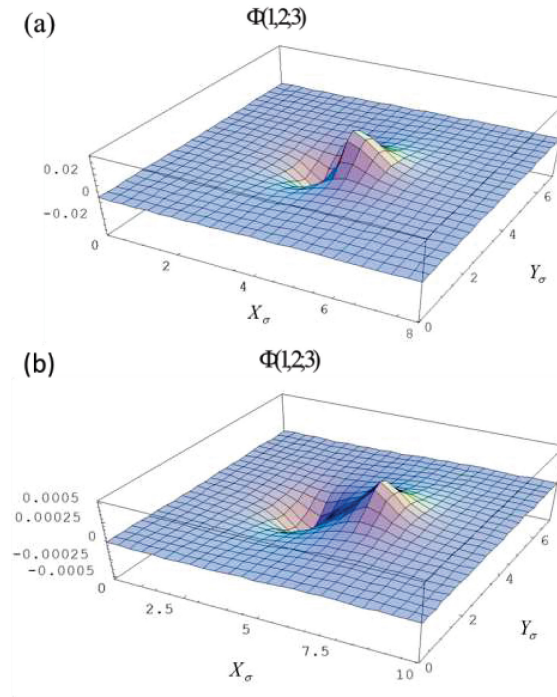


Figure 4. (Color online) Fluctuation $\phi(1, 2; 3)$ for $Z_1 = 1$, $Z_2 = -1$ at ionic diameter $d = 4.25 \times 10^{-10}$ m, dielectric constant $\epsilon_r = 78.5$, temperature $T = 298$ K, and electrolyte concentration $c = 1.968$ mol/dm³. Reduced interionic distance r/d : (a) 1 (contact), (b) 3. Note that $r/d = 1$ corresponds to the contact distance.

first term in F_1 causing an overall positive fluctuation potential in region ω_1 . The positive sign in region ω_2 has similar origins and thus analogous interpretations.

Figure 4 shows the fluctuation potential for a positive ion (valence +1) in region ω_1 and a negative ion (valence -1) in region ω_2 . In contrast to the situation in figure 3, in this case the functions $g(1, 3)$ and $g(2, 3)$ in F_1 and F_2 lead to the sign of the fluctuation potential in regions ω_1 and ω_2 to be opposite to the signs of the ions 1 and 2, respectively. To see this, we first look at the fluctuation potential in region ω_1 calculated through F_1 with the charge density given by $-g(2, 3^+) + g(2, 3^-)$. As the ion in region ω_2 is negative, the first term associated with this unlike charge dominates giving an overall negative sign to the fluctuation potential in region ω_1 where the positive ion is located. On the other hand, the fluctuation potential in region ω_2 is calculated using F_2 where the charge density is given by $-g(1, 3^+) + g(1, 3^-)$. The second (positive) term here is the larger one in magnitude again being linked to the unlike charge, and hence the positive sign of the fluctuation potential in region ω_2 . So, it can generally be stated that the fluctuation potential for like ions near the vicinity of these ions is of the same sign as that of the physical ions and is of the opposite sign for unlike ions. This peculiar behavior is a consequence of the fluctuation potential in ω_1 being related to the $g(2, 3)$ centred at 2, and that the fluctuation potential in region ω_2 being related to the $g(1, 3)$ centred at the opposite region ω_1 . This combined with the relative magnitudes of the g 's in functions F_1 and F_2 explain the behavior of the polarities in $\Phi(1, 2; 3)$.

The magnitude of the $\Phi(1, 2; 3)$ that we have noted in the course of the present calculations, is generally small, especially for large inter-ionic separations. The reasons for this can again be traced to the dominant charge density appearing in equation (36). For instance, the charge density in region ω_1 is a function of $g(2, 3)$ where the field point 3 is in region ω_1 and the point 2 is at the center of region ω_2 , and similarly the charge density in region ω_2 is a function of $g(1, 3)$ where the field point 3 is in region ω_2 and point 1 is at the center of region ω_1 . As the inter-ionic separation is increased, the dominant functions in F_1 and F_2 associated with the unlike ions decrease, while the g 's associated with the like charges tend to 1. It is clear from equations (37) and (38) that both F_1 and F_2 tend to zero at large distances but increase at contact distances, as evident in figure 5. Significantly, the fluctuation potential for similar charges is

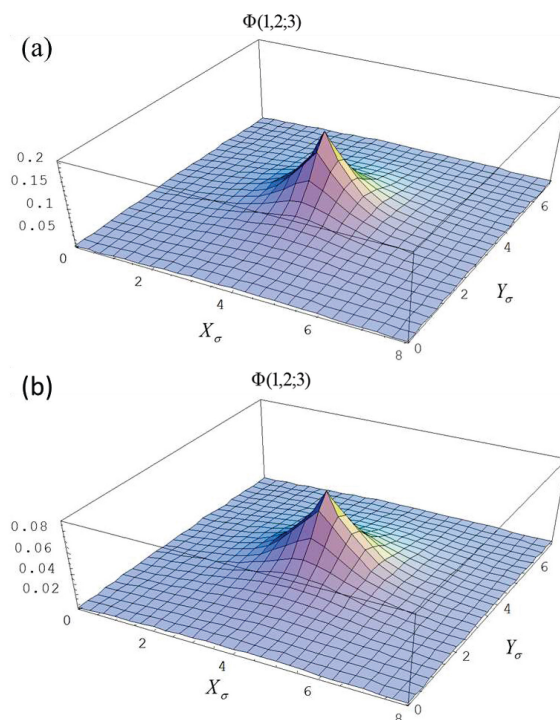


Figure 5. (Color online) Fluctuation $\phi(1, 2; 3)$ for $Z_1 = Z_2 = +1$ at ionic diameter $d = 4.25 \times 10^{-10}$ m, dielectric constant $\epsilon_r = 78.5$, temperature $T = 298$ K, and reduced interionic distance $r/d = 1$, and electrolyte concentration: (a) $c = 1.968$ mol/dm³, (b) $c = 0.1038$ mol/dm³. Note that $r/d = 1$ corresponds to the contact distance.

seen to become quite large compared with that in figure 3. This suggests that for small separation of the ions, the fluctuation potential term becomes important in evaluating g_{ij} . Figures 3–5 indeed show that the fluctuation potential is the largest in the immediate vicinity of ions 1 and 2.

Another point regarding the fluctuation potential worthy of note is the relationship between the fluctuation potential and the electrostatic energy of the ions. In figure 3 we have ions of the same sign, and clearly the fluctuation potential manifests as an increase in electrostatic energy of the ions since the fluctuation potential is of the same sign as the ions. For ions of opposite sign as in figure 4, the sign of the fluctuation potential is opposite to that of the ion in the vicinity. This leads to a decrease in electrostatic potential energy leading to attractive inter-ionic correlation in this case. This implies, consistent with what has been known in the literature, that the sign of the fluctuation potential in the vicinity of ion 1 is mostly due to the cloud of counter ion (from ion 2) and vice versa. It can be seen further from figures 3 and 4, that the fluctuation potential increases as the separation of the ions decreases, establishing the importance of having a solution that is valid at short distances. Our results also show that the fluctuation potential increases with electrolyte concentration.

3.3. Structure and thermodynamics

In figure 6, we present the radial distribution functions obtained in this work along with the corresponding curves for the SPB and MPB theories at 1 mol/dm³ concentration. It is clear that the curves are very similar for distances larger than 2 ionic diameters. Importantly, the present results and the MPB results are almost identical. The contact values for the radial distribution functions for like ions, from the present theory, are slightly closer to the MC result [9] than that from the SPB and MPB. This is probably due to a better treatment of the fluctuation potential in this work. Table 1 shows contact values $g_{ij}(1)$ and for comparison purposes, the corresponding results from the SPB, the MPB, and the MC [9, 10] data are also included. The contact values from the present theory are consistent with the other

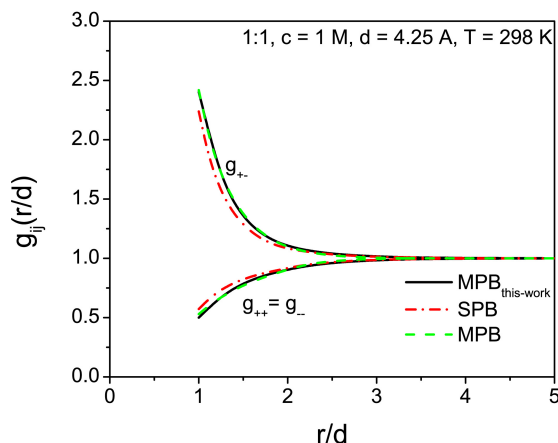


Figure 6. (Color online) The radial distribution functions $g_{ij}(r)$ for a 1:1 restricted primitive model electrolyte at ionic diameter $d = 4.25 \times 10^{-10}$ m, dielectric constant $\epsilon_r = 78.5$, temperature $T = 298$ K in the symmetric-Boltzmann theory, the modified Poisson Boltzmann theory, and the theory presented in this work. The legend as given in the figure.

Table 1. Contact values of the radial distribution functions $g_{ij}(1)$ from different theories. The common diameter of the ions is $d = 4.25 \times 10^{-10}$ m, the temperature $T = 298$ K, and the dielectric constant of the electrolyte $\epsilon_r = 78.5$. The MC values are from reference [9].

c (mol/dm ³)	$g_{++}(1) = g_{--}(1)$					$g_{+-}(1)$				
	DH	SPB	MPB	MPB _{this-work}	MC	DH	SPB	MPB	MPB _{this-work}	MC
0.1038	-0.158	0.321	0.311	0.302	0.319	2.16	3.19	3.30	3.33	3.25
0.425	0.121	0.443	0.417	0.399	0.418	1.88	2.50	2.66	2.68	2.62
1.000	0.299	0.573	0.530	0.500	0.505	1.70	2.14	2.42	2.40	2.23
1.968	0.433	0.752	0.686	0.633	0.706	1.57	2.20	2.40	2.31	2.38

theories and show a very good agreement with the MC simulation data. Tables 2 and 3 show reduced configurational energies, and osmotic coefficients from the Debye-Hückel, SPB, MPB, and MC [9, 10], and this work. These values are also presented in a graphic form as in figures 7 and 8, respectively. The reduced configurational energy curves (figure 7) show an excellent agreement between the MPB and this work with the MC curve up to 1 mol/dm³ concentration. At the highest 1.968 mol/dm³ concentration, the MPB is a little closer to the MC. Figure 8 shows osmotic coefficients for the theories and the relevant MC data [9, 10]. These curves show a generally very good agreement between the MC results and the theories.

Table 2. Reduced configurational energy $-U/(Nk_B T)$ from different theories. The common diameter of the ions is $d = 4.25 \times 10^{-10}$ m, the temperature $T = 298$ K, and the dielectric constant of the electrolyte $\epsilon_r = 78.5$. The MC values are from reference [10].

c (mol/dm ³)	DH	SPB	MPB	MPB _{this-work}	MC
0.1038	0.261	0.267	0.274	0.274	0.274
0.425	0.400	0.407	0.436	0.439	0.434
1.000	0.490	0.500	0.555	0.550	0.552
1.968	0.556	0.572	0.663	0.699	0.651

Table 3. Osmotic coefficient ϕ from different theories. The common diameter of the ions is $d = 4.25 \times 10^{-10}$ m, the temperature $T = 298$ K, and the dielectric constant of the electrolyte $\epsilon_r = 78.5$. The MC values are from reference [9].

c (mol/dm ³)	SPB	MPB	MPB _{this-work}	MC
0.1038	0.946	0.945	0.944	0.945
0.425	0.985	0.981	0.980	0.977
1.000	1.11	1.10	1.10	1.094
1.968	1.37	1.37	1.33	1.364

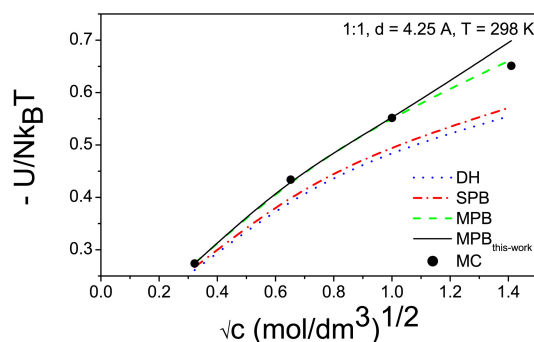


Figure 7. (Color online) The reduced configurational energy for a 1:1 restricted primitive model electrolyte at ionic diameter $d = 4.25 \times 10^{-10}$ m, dielectric constant $\epsilon_r = 78.5$, and temperature $T = 298$ K, versus the square root of the electrolyte concentration c , for the Debye-Hückel theory, the symmetric Poisson-Boltzmann theory, the modified Poisson-Boltzmann theory, and the theory presented in this work. Legend as given in the figure. The Monte Carlo results are from references [9] and [10].

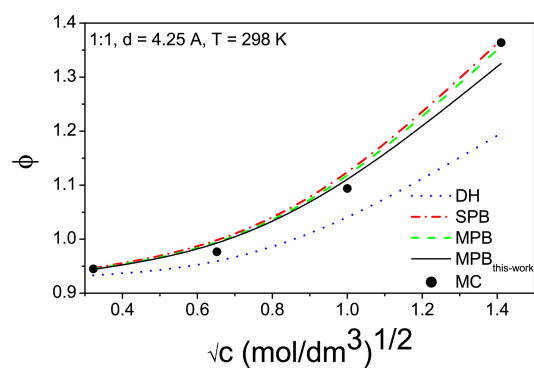


Figure 8. (Color online) The osmotic coefficient for a 1:1 restricted primitive model electrolyte at ionic diameter $d = 4.25 \times 10^{-10}$ m, dielectric constant $\epsilon_r = 78.5$, and temperature $T = 298$ K, versus the square root of the electrolyte concentration c , for the Debye-Hückel theory, the symmetric Poisson-Boltzmann theory, the modified Poisson-Boltzmann theory, and the theory presented in this work. Legend as given in the figure. The Monte Carlo results are from references [9] and [10].

4. Conclusions

In this study we have made an analysis of the fluctuation potential in the modified Poisson-Boltzmann theory of bulk electrolyte solutions. An approximate analytical solution of the fluctuation potential equation was obtained for symmetric valence 1:1 electrolytes in the RPM. This solution was later utilized to obtain structural and thermodynamic descriptions of the electrolyte in terms of ion-ion radial distribution functions, reduced excess energy, and the osmotic coefficients, respectively.

The fluctuation potential is a central ingredient in a potential approach to the theory (of charged fluids) such as the modified Poisson-Boltzmann theory. The fluctuation potential solution developed in this work, albeit with approximations to make analytical progress and for symmetric 1:1 valence systems, is a preliminary attempt to assess the implications of such a solution. In such cases, due to the linearization of the fluctuation potential in the bulk region I [equation (35)] and the small magnitude of $\Phi(1, 2; 3)$, the P function in bulk region I can be taken to be zero, thus neglecting charge density for that region. A less approximate and nearly full treatment could be achieved by solving for the fluctuation potential in region I using equation (29) with P_1 being given by equation (35) in conjunction with equation (34). An intermediate procedure (between the above two situations) to obtain a better, viable, and still feasible approximation for $\Phi(1, 2; 3)$ in region I would be to solve equation (30) [with P_1 given by equation (35)] by writing it in the form

$$\nabla^2\Phi(1, 2; 3) = C\Phi(1, 2; 3), \quad (42)$$

where the quantity C contains the valencies Z_+ , Z_- , and has spatial dependence through $g(1, 3)$ and $g(2, 3)$. Thus, although C is not a constant per se, it can be assumed to be approximately constant for the purposes of solution to equation (42). An approximate analytic form of $\Phi(1, 2; 3)$ in region I, whose value is not necessarily zero, would then be available. Equation (42) has some parallels to a similar equation for the fluctuation potential in the MPB formalism in the planar electric double layer [34]. Such a procedure will be useful for higher and multivalent electrolytes when the magnitude of the fluctuation potential in region I is likely to be significant and hence P_1 can no longer be neglected. This will be a focus of our future work.

The MPB description of the electric double layer phenomenon is an area where the present techniques might have some significance since the fluctuation potential plays an equally important role in the theoretical framework for the inhomogeneous fluid at the interface. In the MPB approach to the double layer theory in planar [34, 35], cylindrical [36–38], and spherical [39, 40] symmetries, the form of the corresponding fluctuation potential used is rather approximate and generally suffers from similar defects as those vis-a-vis the traditional MPB theory for the bulk. The statistical mechanical methods used in this paper are quite general and can be extended and adapted to interfacial double layer geometry where an analogous fluctuation potential analysis might prove useful.

Another area of possible relevance for this study is in the theoretical analysis of charged fluid systems with a variable dielectric constant (relative permittivity). The topic has attracted a lot of recent research attention (see for example, references [41–43]) and has been shown to be relevant for important technological systems, viz., super-capacitors [44, 45]. In the electric double layer, the MPB has been found to be capable of dealing with systems having an inhomogeneous dielectric constant [34, 35]. Very recently, the MPB was applied to a double layer system with three different dielectric constants [46], although the associated fluctuation potential problem could only be solved for point ions. Thus, again a fluctuation analysis in such situations along the lines of the present work could be valuable.

The three-dimensional plots of the fluctuation potential give a valuable insight into the correlations between ions. Furthermore, the present structural and thermodynamic results point in the right direction and are indicative of the potential usefulness of a full solution of the fluctuation potential. The radial distribution functions, especially at contact distances between the ions, the reduced excess energy, and osmotic coefficients show an expected improvement over that from the PB (or SPB), and overall, tend to be in a very good agreement with the predictions from the traditional MPB theory and Monte Carlo simulations.

The fluctuation potential problem is a challenging one. A complete solution of the fluctuation potential equation, valid for a general case and for asymmetry in ionic size and/or valence will involve a numerical solution comprising an iterative algorithm. Our solution here might prove useful in such an involved procedure. Such a project is contemplated in the near future.

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Аналіз флуктуаційного потенціалу в модифікованій теорії Пуасона-Больцмана обмеженої примітивної моделі електролітів

Е.О. Уллоа-Давіля, Л.Б. Буян

Лабораторія теоретичної фізики, відділ фізики, А/с 70377, Університет Пуерто-Ріко, Сан Хуан, Пуерто-Ріко, США

Представлено наближений аналітичний розв'язок проблеми флуктуаційного потенціалу в модифікованій теорії Пуасона-Больцмана для обмеженої примітивної моделі електролітів. Цей розв'язок є дійсним для всіх міжіонних відстаней, включаючи контактні значення. Розв'язок для флуктуаційного потенціалу імплементовано у дану теорію з метою опису структури електроліта в термінах радіальних функцій розподілу, а також з метою обчислення деяких аспектів термодинаміки, а саме, конфігураційної редукованої енергії та осмотичних коефіцієнтів. Обчислення проведено для систем із симетричною валентністю 1:1 при фізичних параметрах іонного діаметру 4.25×10^{-10} м, при відносній проникності 78.5, при абсолютній температурі 298 К, і при молярних концентраціях 0.1038, 0.425, 1.00 і 1.968. Радіальні функції розподілу порівнюються з відповідними результатами симетричної теорії Пуасона-Больцмана та стандартної і модифікованої теорій Пуасона-Больцмана. Проведено порівняння контактних значень радіальних розподілів, редукованих конфігураційних енергій і осмотичних коефіцієнтів як функцій концентрації електроліта. Деякі дані Монте Карло симуляцій з літератури включено в оцінювання термодинамічних передбачень. Результати показують дуже добре узгодження з результатами Монте Карло та деяке покращення для осмотичних коефіцієнтів та контактних значень радіальних функцій розподілу стосовно вищезгаданих теорій. Крива редукованої енергії показує чудове узгодження з даними Монте Карло для молярностей аж до 1 моль/дм³.

Ключові слова: електроліти, обмежена примітивна модель, флуктуаційний потенціал, модифікована теорія Пуасона-Больцмана