INTEGRAL EQUATION FORMULATIONS
OF THE ELECTRICAL DOUBLE LAYER

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PREFACE

This dissertation is an account of work carried out between March 1978 and December 1980 at the Department of Applied Mathematics, Research School of Physical Sciences, Australian National University, for the degree of Doctor of Philosophy.

All the work presented in Chapters 3-9 is the result of a close collaboration between myself and my supervisor, Dr. Derek Chan, but final responsibility for errors and confusions rests entirely with me. Professor Barry Ninham and Dr. John Mitchell were closely involved in the material described in Chapter 4, and Chapter 9 is the product of the joint efforts of myself, Dr. Derek Chan and Glen Walker.

The material described here in Sections 3.1 and 3.2 and in Chapters 4, 5 and 7 has been accepted for publication. In addition, the contents of Section 3.3 and Chapter 9 have been submitted for publication.

None of the work reported here has been submitted to any institute of learning for any degree.

Steven Carnie
1. S. Carnie, J.N. Israelachvili and B.A. Pailthorpe
"Lipid packing and transbilayer asymmetries of mixed lipid vesicles"

2. S.L. Carnie and D.Y.C. Chan
"The structure of electrolytes at charged surfaces: ion-dipole mixtures"

"The structure of electrolytes at charged surfaces: the primitive model"

4. S.L. Carnie and D.Y.C. Chan
"The statistical mechanics of the electrical double layer: Stress tensor and contact conditions"

5. S.L. Carnie and D.Y.C. Chan
"Ionic adsorption from a primitive model electrolyte — non-linear treatment"
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The Commonwealth Government of Australia has financially supported me during my stint as a graduate student through a Commonwealth Postgraduate Research Award, supplemented by the Australian National University.

The work reported in this thesis was carried out in a beautiful setting—a rambling series of rooms shrouded in wisteria; saved in a last-ditch battle from untimely demolition by a rogue bulldozer; perching peacefully overlooking the confluence of Sullivan's Creek and Lake Burley Griffin; surrounded by the incarnadine flashes of rosellas and the majestic flight of pelicans—the Applied Mathematics Department, Research School of Physical Sciences, Australian National University. Professor Barry Ninham has succeeded in bringing together a group of mathematicians, physicists, chemists and engineers who share a sense of excitement about science, and, more unusual, a willingness and eagerness to collaborate, co-operate and communicate with each other for the enlightenment of all. The democratic attitude in the department, where students are both seen and heard, is reflected in the existence of a valve in the students' office (the "dungeon") that controls the heating in Barry's office directly above. Anyone who has experienced such an atmosphere will bear witness to the concomitant productivity and satisfaction, and for these achievements I am sincerely grateful to Barry Ninham.

Many thanks go to my supervisor, Dr. Derek Chan, for his constant help and encouragement, his exasperation at my literary abilities and his selflessness in losing the vast majority of our tennis encounters, just for the sake of boosting my ego. Thanks also go to Derek and Florence for their indirect role as catalyst to my marriage, and to Felicity for keeping Derek off my back for the past year.
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The manuscript was typed by my (sister-in-law)², Miss Norma Chin, who only growled at me marginally more than usual.

My family has shown constant interest in my efforts and I owe them a debt of gratitude for their continual help and moral support.

Lastly, thanks for her support, encouragement (not to say insistence) and cooking to my wife and erstwhile landlady, 紗之喜.
ABSTRACT

In this thesis integral equation techniques, developed in liquid state physics over the last twenty years, are applied to a study of the electrical double layer.

The classical ideas of Gouy, Chapman and Stern, which have provided the foundation for subsequent work in double layer theory, are briefly presented in the first introductory chapter. In Chapter 2 the various choices for Hamiltonian models of electrolytes are introduced and the numerous approximate methods for calculating both bulk electrolyte and double layer properties are listed.

New conditions, which are exact for the Hamiltonian models considered, for non-uniform electrolytes are derived in Chapter 3. After the definition of the pressure tensor in inhomogeneous electrolytes is clarified, new contact conditions are derived which treat ions of different size, image forces and ion-dipole mixtures against a charged wall. A new condition on the fluctuation potential is also derived, which reduces to the Stillinger-Lovett condition for the case of uniform electrolyte.

Part 2 of the thesis is restricted to the consideration of Primitive Model electrolytes. The hypernetted chain closure is used for wall-ion interactions and the mean spherical approximation is employed for the description of bulk interactions. The resultant equations are applied to the case of electrolyte against a uniformly charged, non-polarizable, hard surface – both for indifferent electrolyte in Chapter 4 and for adsorbing electrolyte (where the adsorption potential is modelled by Baxter's sticky potential) in Chapter 5. An attempt is made in Chapter 6 to include image and local ionic activity effects in the abovementioned formalism, with largely disappointing results.
The effect of solvent structure is investigated in Part 3 of the thesis through the use of an ion-dipole mixture model of the electrolyte. In Chapter 7 the electrostatic properties of the solution near the surface are found in the mean spherical approximation for the case of an ion-dipole mixture against a uniformly charged, hard wall. Ionic and dipolar adsorption from an ion-dipole mixture is considered in the mean spherical approximation in Chapter 8, where the linearized hypernetted chain equations are also derived. Both Chapter 7 and 8 reveal Stern layer behaviour as a natural consequence of ion-dipole mixture models in double layer theory. In an effort to provide a more realistic model solvent, thermodynamic perturbation theory is used in Chapter 9 to estimate the effects of a water-like quadrupole moment on the thermodynamic properties of the hard sphere dipolar fluid, with the conclusion that dipole-quadrupole coupling is important.
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CHAPTER 1

CLASSICAL THEORY

1.1 GOUY-ChAPMAH THEORY

The distribution of ions in an electrolyte near a charged surface is termed the electrical double layer. Throughout this thesis we assume that the behaviour of such a system can be described by classical statistical mechanics.

The classical theory of electrokinetics is due to Gouy [1] and Chapman [2]. The ions are treated as point charges and the solvent is modelled by a continuum of dielectric constant $\varepsilon$. The local concentration of an ion of species $i$, $n_i(x)$, is assumed to differ from the bulk concentration $n_i$ by a Boltzmann factor, viz.

$$n_i(x) = n_i \exp(-\frac{z_i kT}{\varepsilon} \phi(x)),$$

where $k = k_B T$, $e$ is the protonic charge, $z_i$ is the valence of ion $i$, and $\phi(x)$ is the mean electrostatic potential in the electrolyte.

Combining Eq. (1.1.1) with Poisson's equation (for planar geometry)

$$\frac{\partial^2\phi}{\partial x^2} = -\frac{1}{\varepsilon} \sigma^D(x),$$

where $\sigma^D(x)$ is the charge density and

$$\sigma^D(x) = \sum z_i n_i(x),$$

we obtain the Poisson-Brilouin equation

$$\frac{\partial^2\phi}{\partial x^2} = -\frac{z_i kT}{\varepsilon} \phi(x) \exp(-\frac{z_i kT}{\varepsilon} \phi(x)).$$
CHAPTER 1

CLASSICAL THEORY

1.1 GOUY-CHAPMAN THEORY

The distribution of ions in an electrolyte near a charged surface is termed the electrical double layer. Throughout this thesis we assume that the behaviour of such a system can be described by classical statistical mechanics.

The classical theory of the double layer is due to Gouy [1] and Chapman [2]. The ions are treated as point charges and the solvent is modelled by a continuum of dielectric constant \( \epsilon \). The local concentration of an ion of species \( i \), \( \rho_i(x) \), is assumed to differ from the bulk concentration \( \rho_i \) by a Boltzmann factor, viz.

\[
\rho_i(x) = \rho_i \exp[-\beta z_i e \psi(x)],
\]

where \( \beta = 1/kT \), \( e \) is the protonic charge, \( z_i \) is the valence of ion \( i \) and \( \psi(x) \) is the mean electrostatic potential in the electrolyte.

Combining Eq. (1.1.1) with Poisson's equation (for planar geometry)

\[
\frac{d^2 \psi}{dx^2} = -\frac{4\pi}{\epsilon} \rho^{\text{CH}}(x),
\]

where \( \rho^{\text{CH}}(x) \) is the charge density and

\[
\rho^{\text{CH}}(x) = \sum_j z_j e \rho_j(x),
\]

we obtain the Poisson-Boltzmann equation

\[
\frac{d^2 \psi}{dx^2} = -\frac{4\pi}{\epsilon} \sum_j z_j e \exp[-\beta z_j e \psi(x)].
\]
In order to find the spatial distribution of ions away from a single wall, we need to solve Eq. (1.1.4) subject to the appropriate boundary conditions. Since we take the zero of potential to be that of the bulk electrolyte, we require

$$\psi(x) \to 0 \quad \text{as} \ x \to \infty.$$  \hspace{1cm} (1.1.5)

The remaining boundary condition depends somewhat on the nature of the surface. For a surface with specified surface potential, $\psi_0$, we would use

$$\psi(0) = \psi_0,$$  \hspace{1cm} (1.1.6)

whereas for a surface with specified surface charge density, $\sigma_0$, the appropriate boundary condition is

$$\frac{d\psi(x)}{dx} \bigg|_{x=0} = \frac{4\pi \sigma_0}{c}.$$  \hspace{1cm} (1.1.7)

The case of a surface containing dissociating groups introduces a more complicated boundary condition.

For example, a surface can contain acidic groups (AH) [3] which obey the reaction

$$AH \rightleftharpoons A^- + H^+.$$  \hspace{1cm} (1.1.8)

This reaction is governed by the equilibrium constant

$$K \equiv \frac{[H^+]_S [AH^-]}{[AH]}.$$  \hspace{1cm} (1.1.9)

The surface charge density is then given by

$$\sigma_0 = -\frac{N_S c}{(1 + [H^+]_S / K)},$$  \hspace{1cm} (1.1.10)

where $N_S$ is the surface density of dissociating groups and the surface concentration of hydrogen ions is
\[ [H^+]_S = [H^+] \exp[-\beta\psi(0)]. \] (1.1.11)

The appropriate boundary condition at the surface is then
\[ \frac{d\psi(x)}{dx} \bigg|_{x=0} = \frac{4\pi N_S e}{\varepsilon [1 + \exp[-\beta\psi(0)] [H^+]/K]} . \] (1.1.12)

These considerations can be easily generalized to a surface with both basic and acidic surface groups [4]. Throughout most of this thesis, we shall consider only the simple boundary condition, Eq. (1.1.7).

Eq. (1.1.4) can be simplified for small \( \psi(x) \) by linearization of the Boltzmann factor. Since the bulk electrolyte is electrically neutral,
\[ \sum_i \rho_i z_i = 0 \] (1.1.13)

Eq. (1.1.4) then becomes
\[ \frac{d^2\psi}{dx^2} = \kappa^2 \psi(x) , \] (1.1.14)

where
\[ \kappa^2 = 4\pi\beta e^2 \sum_i \rho_i z_i^2 / \varepsilon . \] (1.1.15)

\( \kappa \) is the Debye inverse screening length. It also arises in the Debye-Hückel theory of dilute electrolytes [5], in which the Poisson-Boltzmann equation is first linearized and then used to describe the potential about a central ion in bulk electrolyte. This linearized theory gives the exact limiting laws for the thermodynamic properties of electrolytes in the limit of infinite dilution [6].

Eq. (1.1.14) can be solved subject to Eqs. (1.1.5) and (1.1.7) for any electrolyte to give
\[ \psi(x) = \frac{4\pi \sigma_0}{\varepsilon K} \exp(-\kappa x) \] (1.1.16)

and so, from the linearized form of Eq. (1.1.1),
\[ \rho_i(x) = \rho_i - \frac{4n\beta e\sigma_0}{\varepsilon\kappa} \rho_{-i}z_i \exp(-\kappa x). \quad (1.1.17) \]

This last equation shows the expected result — ions of the same sign as the surface charge (co-ions) are depleted near the surface; ions of the opposite sign (counterions) are adsorbed. The exponential decay shows that the effect of the surface charge is screened by the intervening electrolyte, with the screening more complete as the electrolyte concentration increases.

For systems such as the mercury electrode, the surface potential, \( \psi_0 \), is a measurable quantity. From Eq. (1.1.16),

\[ \psi_0 = \frac{4\pi\sigma_0}{\varepsilon\kappa}. \quad \text{DH} \quad (1.1.18) \]

The linearization that leads to Eqs. (1.1.14)-(1.1.18), however, can only be justified for \( \beta e\psi < 1 \) (i.e. \( \psi < 25 \text{ mV at room temperature} \)). In many experimental systems, this criterion is not satisfied and Eq. (1.1.4) must be solved. This contrasts with the universal nature of Eq. (1.1.14) in the theory of dilute electrolytes. An interesting discussion of this point is given in Ref. 7.

For a general electrolyte, the analytic solution of Eq. (1.1.4) quickly involves lengthy manipulations with special functions [3] but for symmetric (\( z:z \)) electrolytes the solution is immediate. For a 1:1 electrolyte, Eq. (1.1.4) gives [1,2,8]

\[ \psi(x) = \frac{2}{\beta e} \ln \left[ \frac{1 + \gamma \exp(-\kappa x)}{1 - \gamma \exp(-\kappa x)} \right] = \frac{4}{\beta e} \tanh^{-1} [\gamma \exp(-\kappa x)], \quad (1.1.19) \]

where

\[ \gamma = \frac{\exp(\beta e\psi / 2) - 1}{\exp(\beta e\psi / 2) + 1}, \quad (1.1.20) \]

and

\[ \psi_0 = \frac{2}{\beta e} \sinh^{-1} \left( \frac{2n\beta e\sigma_0}{\varepsilon\kappa} \right). \quad \text{GC} \quad (1.1.21) \]

\( \rho_i(x) \) is then given by Eq. (1.1.1). For small \( \sigma_0 \) or large \( \kappa \) (i.e. high
concentrations), Eq. (1.1.21) reduces to Eq. (1.1.18). The main features of Gouy-Chapman theory (i.e. Eqs. (1.1.19)-(1.1.21)) are that (i) for fixed $\kappa$, $\psi_0$ increases sublinearly with $\sigma_0$ (cf. the linear relationship of Eq. (1.1.18)) (see Fig. 1); (ii) for fixed $\sigma_0$, $\psi_0$ increases with decreasing electrolyte concentration; and (iii) counterions are adsorbed more than co-ions are depleted (since the co-ion density cannot become negative, which is possible in the linearized case) (see Fig. 2). Notice also that the asymptotic behaviour as $x \to \infty$ of $\psi(x)$ is just the same as for the linearized case.

The Poisson-Boltzmann equation for a symmetric electrolyte can also be solved analytically to give the potential profile between two interacting double layers [8,9]. Throughout this thesis we focus our attention on the single double layer.

1.2 THE STERN LAYER AND THE STERN ADSORPTION ISONERM

An immediate objection to Gouy-Chapman theory is that nowhere is the finite size of the ions taken into account. This is especially serious near the surface where, for the surface potentials used in mercury electrode experiments, the calculated concentration of ions near the surface can be well above the physically possible limit. In order to avoid this unphysical result, Stern [10] introduced three new features to the model of the double layer.

The first modification was to allow the ions in the double layer to approach no closer than a certain distance, $d$, to the surface (see Fig. 3). In this first layer, the inner layer or Stern layer, there is no charge and so the potential is a linear function of distance. If we still take the solvent to be a continuum of dielectric constant $\epsilon$ up to the surface, we then have, from Eq. (1.1.7),
Fig. 1: The surface potential, \( \psi_0 \), as a function of surface charge for 0.1 M indifferent 1:1 electrolyte as given by the Gouy-Chapman (GC) and linearized Gouy-Chapman (DH) theories.
Fig. 2: Ionic densities as a function of distance from the surface for 0.1 M electrolyte, $\sigma_b = 3.2 \, \mu\text{C/cm}^2$ according to the Gouy-Chapman (-----) and linearized Gouy-Chapman (---) expressions. $h_i(x) \equiv [\rho_i(x) - \rho_i]/\rho_i$ so that regions for which $h_i(x) < -1$ represent unphysical behaviour.
Fig. 3: Classical model of the double layer incorporating Stern's modifications.
Beyond this plane, the $\beta$-plane, the ions are treated as point charges and Gouy-Chapman theory holds. Thus we have the modified Gouy-Chapman expression

\[ \psi_0 = G \psi_\beta + \frac{4\pi \sigma_0}{k_e} \left( \frac{d}{d - 1} \right) \] (1.2.1)

The differential capacitance of the double layer around a dropping mercury electrode can be measured directly [11]. The total differential capacitance is given by

\[ \frac{1}{C_0} = \frac{d\psi_0}{d\sigma_0} = \frac{4\pi d}{k_e} + \frac{4\pi}{k_e} \left( 1 + \frac{2\beta e \sigma_0}{k_e} \right) \] (1.2.4)

For concentrations less than $10^{-3}$ M, the second term in Eq. (1.2.4) (which gives the diffuse layer capacitance) dominates. At concentrations where $\kappa d \approx 1$ (about 1 M, since $d$ must be roughly an ionic diameter) the two terms in Eq. (1.2.4) are comparable. For $d = 4 \, \text{Å}$ and aqueous solutions where $k_e = 80$, we would then obtain $C_0 \approx 100 \, \mu F/cm^2$. Experimentally, however, the observed differential capacitance is much smaller than this, usually 10-30 $\mu F/cm^2$. This feature was incorporated into the model by proposing a smaller dielectric constant $\varepsilon_s$ in the Stern layer than in the diffuse layer.

We then write

\[ \psi_0 = \psi_\beta + \frac{4\pi \sigma_0}{\varepsilon_s} d \] (1.2.5)

so that

\[ \psi_0 = \frac{4\pi \sigma_0}{\varepsilon_s} d + \frac{2}{\beta e} \sinh^{-1} \left( \frac{2\beta e \sigma_0}{k_e} \right) \] (1.2.6)

\[ \approx \frac{4\pi \sigma_0}{\varepsilon_k} \left( 1 + \frac{\varepsilon}{\varepsilon_s} \kappa d \right) \beta e \psi_0 < 1. \] (1.2.7)
Neither $d$ nor $\varepsilon_s$ can be measured directly: only the ratio $d/\varepsilon_s$ is experimentally accessible. The measured capacitance values correspond to values of $\varepsilon_s$ between 3 and 15 (depending on the choice of $d$). This low value is usually attributed to dielectric saturation caused by the strong electric fields close to the surface, or by an "ordered" layer of water next to the surface. Similar low capacitances are also measured in other solvents, however [12].

The final modification due to Stern was the introduction of an adsorption isotherm to describe the adsorption of ions from the diffuse layer into the $\beta$-plane. There is a charge density $\sigma_\beta$ in the $\beta$-plane, beyond which Gouy-Chapman theory holds. Stern used a Langmuir isotherm [13]

$$\sigma_\beta = \frac{N_s z_\beta e}{1 + \frac{N_A}{M \varepsilon} \exp(+\beta [z_\beta e\psi_\beta + \phi_\beta])}, \quad (1.2.8)$$

where $N_s$ is the adsorption site density on the surface, $z_\beta$ is the valence of the adsorbing ion, $N_A$ is Avogadro's number, $M$ is the molecular weight of the solvent, $n$ the bulk concentration of adsorbing ion, and $\phi_\beta$ the specific adsorption potential. For dilute solutions and for $\beta(z_\beta e\psi_\beta + \phi_\beta)$ not too large and negative, Eq. (1.2.8) can be simplified to

$$\sigma_\beta = N_s z_\beta e \frac{nM}{N_A} \exp(-\beta z_\beta e\psi_\beta) \exp(-\beta\phi_\beta). \quad (1.2.9)$$

Eq. (1.2.8) contains the feature of adsorbed surface charge density saturation. As $\phi_\beta \rightarrow -\infty$ (i.e. strong adsorption), $\sigma_\beta$ tends to a limit

$$\sigma_\beta^{\text{max}} = N_s z_\beta e. \quad (1.2.10)$$

Eq. (1.2.9) does not contain this feature but is a good approximation to Eq. (1.2.8) for low surface coverage. The quantities $\sigma_\beta, \psi_\beta, \psi_o$
can then be found from Eqs. (1.2.6) and (1.2.8), together with the equation from Gouy-Chapman theory,

\[ \psi_{\beta} = -\frac{2}{\beta e} \sinh^{-1} \left( \frac{2\pi\beta e\sigma_d}{\varepsilon k} \right), \tag{1.2.11} \]

where

\[ \sigma_d = -\sigma_0 - \sigma_B. \tag{1.2.12} \]

Further modifications to the model have been provided [14], which replace the \( \beta \)-plane by two planes: the Inner Helmholtz plane (IHP), at which adsorbed charges lie, and the Outer Helmholtz plane (OHP) which is the plane of closest approach of the diffuse layer. The OHP is considered to be further out from the surface than the IHP by virtue of the hydration shell present around diffuse layer ions but absent from the adsorbed ions. Such models, with two inner layer capacitances, are used to explain experimental data for latex surfaces [15] and oxide surfaces [16,17]. Models in which the dielectric constant varies continuously with the distance from the surface have also been proposed [18]. We shall not discuss such models further since for our purposes the simple ideas of Stern are sufficient for comparison with our new theoretical results.

Theories which include effects such as electrostriction and dielectric saturation have also been proposed [19,20]. Such effects are also beyond the scope of this thesis and await further developments in the theory of polar fluids.

1.3 APPLICATIONS OF CLASSICAL DOUBLE LAYER THEORY

In this section, we give a brief list of the numerous applications of classical double layer theory. We also discuss the major theoretical limitations of Gouy-Chapman theory, which will...
motivate the more detailed statistical mechanical treatment in this thesis.

The original motivation for Gouy-Chapman theory and the modifications of Stern [10] and Grahame [14] came from experimental work on the electrocapillarity (i.e. surface tension) and differential capacitance of the mercury/aqueous solution interface. The theory can also be applied for non-aqueous solvents [12]. The mercury electrode still provides the most accurate measurements against which double layer theory can be tested. Classical theory is used as a basis for theoretical investigations of non-equilibrium electrode processes [21, 22].

In most other colloidal systems, the surface potential cannot be measured independently and electrophoresis measurements are performed instead. The theory of electrophoresis [23] (which uses Gouy-Chapman theory for the equilibrium ionic distributions about the colloidal particles) relates the measured mobility to the potential at the surface of hydrodynamic shear - the zeta potential. Measurements of titratable surface charge and zeta potential can be made for many systems, notably silver iodide sols [24], polymer latices [15], various oxide surfaces [16,17] and charged lipid vesicles [25]. Classical double layer theory (with certain modifications) is used in the interpretation of these experiments.

Another area of application of double layer theory is the determination of forces between colloidal particles. Two charged colloidal particles in electrolyte feel a repulsive force due to the overlapping of their double layers. The balance between this repulsive force and the van der Waals attraction forms the basis of the theory of colloidal stability [8,9]. It is possible that these
double layer forces play a role in intercellular interactions [26,27]. The effect of monovalent and divalent ions on the repulsive double layer forces has been used to explain the stability of grana thylakoid membranes of chloroplasts [28].

Several other fields with a biological flavour have used Gouy-Chapman-Stern theory, in particular the study of counterion binding of polyelectrolytes [29], studies of charged lipid monolayers [24,30-32] and studies of the adsorption of ions and charged molecules into lipid bilayers [33-35]. Other applications in biology are mentioned in Ref. 33.

In many of the systems mentioned above, Gouy-Chapman-Stern theory gives surprisingly good (qualitative) results considering the main assumptions of the theory:

(1) ion size is neglected except through the Stern layer and the adsorption isotherm;

(2) solvent structure is neglected except through the Stern layer dielectric constant, $\varepsilon_s$;

(3) image effects are ignored; and

(4) the surface charge is taken to be uniformly spread over the surface.

Improved agreement with experiment has been obtained by more careful consideration of finite ion size in the Stern layer, especially for charged monolayers, the mercury electrode and in the study of the coagulation of AgI sols [36]. Molecular models of the solvent in the Stern layer have also led to closer agreement with experimental values of the differential capacitance of the mercury electrode [37].

In this thesis, we aim to incorporate the effects of finite ion size and solvent structure into the theory of the double layer through
the application of modern statistical mechanical theories of electrolytes. Image effects are also discussed in Chapter 6. The choice of models for the double layer and of approximate methods to solve the statistical mechanics are discussed in the following chapter.

REFERENCES


CHAPTER 2

STATISTICAL MECHANICAL BACKGROUND

2.1 HAMILTONIAN MODELS FOR ELECTROLYTES

In this chapter we provide the background for an understanding of modern statistical mechanical theories of electrolytes. We shall use some of the models and approximations derived from the investigation of bulk electrolyte to elucidate the effects of finite ion size and solvent structure on the electrical double layer.

In the search for a model of electrolytes that takes into account the finite size of the ions, we must first decide on the level at which we wish to specify the Hamiltonian of the electrolyte. Throughout this thesis we consider all averaging over electronic and internal nuclear motions to have been performed.

All ions and molecules can then be specified by their shapes, permanent multipole moments, polarizabilities, etc. In Friedman's terminology [1] this is the Born-Oppenheimer (BO) level. Let us consider a fluid of molecules of species \((\alpha, \beta, \ldots)\) with activities \((\varepsilon_{\alpha}, \varepsilon_{\beta}, \ldots)\) and numbers \((N_{\alpha}, N_{\beta}, \ldots)\) in a volume \(V\) at temperature \(T\). The set of all species is denoted \(\{\alpha\}\), the set of all activities \(\{\varepsilon_{\alpha}\}\) and so on. The grand partition function for the fluid can then be written

\[
\Xi_{\text{BO}} (\{\varepsilon_{\alpha}\}) = \sum_{N_{\alpha} \geq 0} \sum_{N_{\beta} \geq 0} \ldots \{\Pi \varepsilon_{\alpha}^{N_{\alpha}} \} \int_{V} d\{N_{\alpha}, \ldots, N_{\beta}\} \exp(-\beta U_{\{N_{\alpha}\}}),
\]

(2.1.1)
where $\beta = 1/kT$ and $k$ is Boltzmann's constant, and $-z_{\alpha} , \ldots , -z_{\alpha}$ are the coordinates of the $N_{\alpha}$ particles of species $\alpha$ so that $\{ -z_{\alpha} , \ldots , -z_{\alpha}\}$ denotes the set of coordinates of all particles in the system.

$U_{\{N_{\alpha}\}}(\{ -z_{\alpha} , \ldots , -z_{\alpha}\})$ is the potential function of the Hamiltonian of the fluid. For a one-component fluid, there is no alternative to the BO-level formulation. The grand partition function can be approximately evaluated by diagrammatic expansion, integral equation methods or computer simulation. Thermodynamic properties can then be generated from the partition function.

For a multicomponent fluid generally and an electrolyte in particular, another level of description is possible. Many solution thermodynamic quantities are functions only of the free energy of the solution in excess of that of the pure solvent (for example, the osmotic pressure). McMillan and Mayer [2] showed that it was formally possible to write the grand partition function which generates these excess thermodynamic quantities in terms of just the ionic species.

For an electrolyte with ions of species $(i,j, \ldots )$, activities $(\hat{z}_{i}, \hat{z}_{j}, \ldots )$ and numbers $(N_{i}, N_{j}, \ldots )$, this grand partition function is

$$
\Xi_{MM}(\{\hat{z}_{i}\}) = \Sigma_{N_{i} \geq 0} \Sigma_{N_{j} \geq 0} \left( \Pi_{\{i\}} \frac{N_{i}}{N_{i}^{\dagger}} \right) \int_{V} \exp(-\beta U_{\{N_{i}\}}(\{\hat{z}_{i}\})) \, d(\{\hat{z}_{i}\}, \ldots , N_{1})
$$

(2.1.2)

where

$$
\hat{z}_{i} = \frac{z_{i}}{\beta} \lim_{\hat{z}_{i} \to 0} \frac{\rho_{i}}{\hat{z}_{i}}
$$

(2.1.3)

and $U_{\{N_{i}\}}(\{\hat{z}_{i} , \ldots , N_{1}\})$ is the potential of the forces among the $\{N_{i}\}$ solute molecules at fixed locations, averaged over all configurations of the solvent molecules, in the limit $\{\hat{z}_{i}\} \to 0$. A comparison of Eqs. (2.1.1) and (2.1.2) shows that $\Xi_{MM}$ is the same functional of $\{\hat{z}_{i}\}$ and $\hat{U}_{\{N_{i}\}}$ as $\Xi_{BO}$ is of $\{\hat{z}_{\alpha}\}$ and $U_{\{N_{\alpha}\}}$. This entails that the methods used to evaluate $\Xi_{BO}$ for one-component fluids can be used to calculate $\Xi_{MM}$.
for electrolytes.

A prerequisite for the use of such methods, however, is some knowledge of $\tilde{U}_{(N_i)}$. A common approximation is to take the potential to be pairwise additive so that

$$\tilde{U}_{(N_i)} = \sum_{i<j} \tilde{u}_{ij}(r) \quad (r = |r_i - r_j|). \quad (2.1.4)$$

The asymptotic form of the pair potential is given by Coulomb's law

$$\tilde{u}_{ij}(r) \to \frac{z_i z_j e^2}{\varepsilon r} \quad \text{as } r \to \infty, \quad (2.1.5)$$

where $z_i, z_j$ are the valencies of ions $i$ and $j$, $e$ is the protonic charge and $\varepsilon$ is the dielectric constant of the solvent. At low separations there is a strong repulsion between ions due to electron orbital overlap. A particularly simple form for the repulsive potential is the hard sphere potential

$$u_{ij}(r) = \begin{cases} \infty & r < R_{ij} \smallskip \\ 0 & r > R_{ij} \end{cases}, \quad (2.1.6)$$

where $R_{ij}$ is the distance of closest approach of ions $i$ and $j$. Model electrolytes, in which the ions are treated as hard spheres with embedded point charges and the solvent is regarded as a structureless continuum of dielectric constant $\varepsilon$, so that the asymptotic form Eq. (2.1.5) holds up to contact, are called Primitive Model (PM) electrolytes. The Primitive Model electrolyte is specified by the equation

$$\tilde{u}_{ij}^{PM}(r) = \begin{cases} \frac{z_i z_j e^2}{\varepsilon r} & r > R_{ij} \smallskip \\ \infty & r < R_{ij} \end{cases}, \quad (2.1.7)$$

where

$$R_{ij} = \frac{1}{2}(R_i + R_j) \quad (2.1.8)$$
and \( R_i \) and \( R_j \) are the diameters of ions of type \( i \) and \( j \), respectively.

If all ions are taken to be the same size, we obtain the Restricted Primitive Model (RPM) of electrolytes, specified by

\[
\tilde{u}_{ij}^{\text{RPM}}(r) = \begin{cases} \\
\frac{z_i z_j e^2}{\epsilon r} & r > R \\
\infty & r < R \\
\end{cases}
\]

where \( R \) is the diameter of all species. The RPM is the simplest MM-level model of electrolytes. More refined MM-level models have been developed [3], which have the form

\[
\tilde{u}_{ij}(r) = \frac{z_i z_j e^2}{\epsilon r} + \text{COR}_{ij}(r) + \text{CAV}_{ij}(r) + \text{GUR}_{ij}(r) \quad 0 < r < \infty,
\]

where \( \text{COR}_{ij}(r) \) represents the steep repulsive term due to electron orbital overlap, \( \text{CAV}_{ij}(r) \) represents effects due to the polarization of each charge by the other and \( \text{GUR}_{ij}(r) \) provides a parametrization of effects due to solvent structure and dielectric saturation. \( \text{COR}_{ij}(r) \) can be taken to be a hard-sphere potential but softer potentials (with either power law or exponential form) have also been used [3]. The term \( \text{GUR}_{ij}(r) \) is based on the work of Gurney [4].

In Part 2 of this thesis we deal exclusively with RPM electrolytes, whereas in Part 3 we use some simple BO-level models of electrolytes in the double layer problem. We term these latter models Civilized Models (CM) after Stokes [5]. For the remainder of this chapter and in Part 2 we suppress the overbar and superscript of \( \tilde{u}_{ij}^{\text{RPM}}(r) \), since we shall always be using the RPM solvent-averaged potential unless explicitly stated otherwise.

For the double layer problem we also need to decide on a model for the charged surface. A fundamental treatment would involve the
band structure of the surface states of the wall. We ignore such features and we usually take the wall to be hard, uniformly charged and non-polarizable. In Chapter 6 we relax the last restriction and consider the effect of images.

2.2 STATISTICAL MECHANICAL THEORIES OF ELECTROLYTES

Once our model for the electrolyte and the wall has been specified we need to solve the statistical mechanics for the system. For this purpose we shall require concepts and equations developed in the field of liquid state physics.

The central concept required from liquid state physics is that of the pair distribution function \( g_{ij}(r) \). This function gives the probability of finding two particles of species \( i \) and \( j \) at separation \( r \). Hence, \( \rho_i g_{ij}(r) \) gives the local density of species \( i \) about a particle of species \( j \). As \( r \to \infty \), the local density must tend to the bulk density and the total correlation function, given by

\[
\chi_{ij}(r) = g_{ij}(r) - 1
\]

vanishes for large separations. \( n \)-particle distribution functions \( g^{(n)}(r_1, \ldots, r_n) \) can also be defined which give the probability of finding \( n \) particles at positions \( r_1, \ldots, r_n \).

The thermodynamic properties of the fluid can be found from the pair distribution function in three ways. For a simple 1-component fluid, these routes are given by [6]:

the compressibility equation

\[
\rho_k T \chi_T = 1 + \rho \int dr \chi(r)
\]

where \( \chi_T \) is the isothermal compressibility.
\[ \chi_T \equiv \frac{1}{\rho} \left( \frac{\partial p}{\partial \rho} \right)_T, \]  

(2.2.3)

the virial equation

\[ \frac{\partial p}{\partial \rho} = 1 - \frac{1}{6} \beta \rho \int dr \ r \ \frac{\partial u}{\partial r} g(r), \]  

(2.2.4)

where \( p \) is the pressure of the fluid, and

the energy equation

\[ \frac{E}{N} = \frac{3}{2} kT + \frac{1}{2} \rho \int dr \ u(r) \ g(r), \]  

(2.2.5)

where \( E/N \) is the internal energy per particle. For example, the isothermal compressibility \( \chi_T \) could be found directly from Eq. (2.2.2), by the use of Eqs. (2.2.4) and (2.2.3) or by the use of Eq. (2.2.5) and the equations

\[ E = \frac{3}{2} \beta A \]  

(2.2.6)

\[ p = -\left( \frac{3A}{\partial V} \right)_T \]  

(2.2.7)

and Eq. (2.2.3). For an exact \( g(r) \), any method of calculation will give the same result. Since the methods of liquid state physics (apart from computer simulations) give only approximate pair distribution functions, however, the three routes will give inconsistent results. There are theories that use adjustable parameters to eliminate this inconsistency [7,8] but we shall not consider such theories in this thesis. We therefore need to specify both the approximation method and the thermodynamic route when reporting thermodynamic results of liquid state physics calculations.

For a MM-level electrolyte, the generalizations of Eqs. (2.2.2), (2.2.4) and (2.2.5) are [9,10]:

\[ \left( \frac{\partial \Theta_{i j}}{\partial \mu_{i j}} \right)_{T, V, \mu_K, \mu_S} = \beta [\rho_i \delta_{i j} + \rho_{-i} \rho_j \int dr h_{i j}(r)], \]  

(2.2.8)
where $\mu_j$ is the chemical potential of species j, $\mu_s$ is the chemical potential of the solvent and $\delta_{ij}$ is the Kronecker delta function;

$$\phi = 1 - \frac{1}{\beta \rho} \sum_{ij} \rho_i \rho_j \int dr \frac{\partial u_{ij}}{\partial \rho} g_{ij}(r),$$  \hspace{1cm} (2.2.9)

where $\rho = \sum \rho_i$ and $\phi$ is the osmotic coefficient, defined by

$$\phi = \frac{\rho \rho_{osm}}{\rho},$$  \hspace{1cm} (2.2.10)

and $\rho_{osm}$ is the osmotic pressure; and

$$\frac{E}{N} = \frac{3}{2} kT + \frac{1}{2\rho} \sum_{ij} \rho_i \rho_j \int dr \frac{\partial}{\partial \beta} \left( \beta u_{ij} \right) g_{ij}(r),$$  \hspace{1cm} (2.2.11)

where now $E/N$ is the internal energy per ion and $u_{ij}$ can be a function of temperature since it is a solvent-averaged potential.

We shall now discuss the numerous theoretical approaches for obtaining the pair distribution function and thermodynamic properties of PM electrolytes. We divide these approaches into four main classes:

A: the potential approach,

B: integral equation theories,

C: series expansions, and

D: computer simulation.

A. The Potential Approach

This approach stems from Kirkwood's [11] investigations into electrolyte theory. Kirkwood showed that the two major corrections to the Poisson-Boltzmann theory of electrolytes (i.e. Eq. (1.1.4)) were an excluded volume term due to finite ion size and the fluctuation potential — a finite ion size correction to the electrostatic interaction.
In order to obtain expressions for the excluded volume term and the fluctuation potential, Outhwaite derived hierarchies of equations for the potential \( \psi(\{n\}, q) \), the mean electrostatic potential at \( r_q \) given \( \{n\} \) ions fixed in the electrolyte. One set of equations for \( \psi(\{n\}, q) \) has been obtained [12-14] from the Kirkwood hierarchy [15, 16] of equations for n-particle distribution functions and another set has been derived [17] from the Bogoliubov-Born-Green-Yvon (BBGY) [18-20] hierarchy. The hierarchies for the potential are truncated by closures relating the n-body distribution function and \( \psi(\{n\}, q) \) in the same way as Eq. (1.1.1) relates the ionic density and the mean electrostatic potential [21]. The equations derived from the Kirkwood hierarchy form the Modified Poisson-Boltzmann (MPB) theory of electrolytes. This formalism generates the MPB1, MPB2, MPB3 and MPB4 theories, which are distinguished by the approximations used for the excluded volume term. The various theories derived from the BBGY hierarchy are similarly denoted BBGY1, BBGY2 and BBGY3. Numerical results for primitive model electrolytes have been given for both the MPB equations [22-24] and the BBGY equations [25].

B. Integral Equation Theories

The BBGY hierarchy can also be truncated by using the Kirkwood superposition approximation [15] which expresses the 3-body distribution function in terms of pair distribution functions

\[
g^{(3)}(r_1, r_2, r_3) = g(|r_1 - r_2|) \ g(|r_2 - r_3|) \ g(|r_3 - r_1|). \tag{2.2.12}
\]

This defines the BGY integral equation, which has been solved for RPM electrolytes by Croxton and McQuarrrie [26].

Other liquid state integral equations are most easily described
in terms of the direct correlation function, \( c_{ij}(r) \), which is defined by the Ornstein-Zernike equation [27]

\[
h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int \! dr' \ c_{ik}(|r - r'|) h_{kj}(r'). \tag{2.2.13}
\]

A further relation between \( c_{ij}(r) \) and \( h_{ij}(r) \) is required and various approximate closures have been proposed and tested against computer simulations. Amongst these closures are the Percus-Yevick (PY) closure [28]

\[
c_{ij}(r) = g_{ij}(r) [1 - \exp(\beta u_{ij}(r))] \quad \text{PY} \tag{2.2.14}
\]

and the hypernetted chain (HNC) closure [29-31]

\[
c_{ij}(r) = -\beta u_{ij}(r) + h_{ij}(r) - \ln(1 + h_{ij}(r)), \quad \text{HNC} \tag{2.2.15}
\]

where \( u_{ij}(r) \) is the potential between particles of species \( i \) and \( j \). These closures can be derived by truncating functional Taylor expansions of the pair distribution function [32] or by neglecting certain classes of diagrams in the cluster expansion of \( g(r) \) [33]. The HNC equation includes more diagrams than the PY equation but comparison with computer simulation is still the only criterion for preferring one closure over the other. The PY closure appears superior for rapidly-varying, short-ranged potentials (e.g. the hard sphere fluid) whereas the HNC is more accurate for softer, longer-ranged potentials.

For fluids with a hard sphere core of diameter \( R \), \( g_{ij}(r) \) can be found from the solution of Eq. (2.2.13) subject to

\[
h_{ij}(r) = -1 \quad r < R \tag{2.2.16}
\]

and one of Eqs. (2.2.14) or (2.2.15) for \( r > R \). Another closure can be found from linearization of Eqs. (2.2.14) or (2.2.15) to give

\[
c_{ij}(r) = -\beta u_{ij}(r) \quad r > R. \tag{2.2.17}
\]
Eqs. (2.2.16) and (2.2.17) then define the mean spherical approximation (MSA) [34], which has been solved analytically for RPM electrolytes [35]. The HNC and PY closures (with modifications due to Allnatt [36]) have been solved numerically for RPM electrolytes [10, 37-39].

C. Series Expansions

The first systematic statistical mechanical treatment of PM electrolytes is due to Mayer [40] who expanded the free energy in a cluster expansion [41] and resummed the most divergent terms. He obtained the Debye-Hückel limiting law and additional terms expressed as an expansion in ionic concentration. Details may be found in Ref. 42. This virial expansion, however, converges very slowly.

Other expansions have been proposed which treat the Coulombic potential as a perturbation about the reference system (e.g. for PM electrolytes, the reference system is the hard sphere fluid). Stell and Lebowitz [43], using the so-called γ- and Γ-ordering techniques [44,45], derived an expansion in κ about the reference system of the free energy of PM electrolytes. In optimized cluster theory [46-48], the cluster expansions for the free energy and g(r) are recast in terms of a renormalized potential that does not contain the long-range problems of the Coulomb potential. The convergence of the resultant expansions in ionic concentration about the reference system can be optimized by proper choice of the perturbation potential in the physically meaningless region r < R.

Various kinds of mixed perturbation theories have been proposed. An expansion of the free energy about the MSA value in terms of $\rho^* \ (= \rho_R^3)$ and $\beta^* \ (= \beta z^2 e^2 / \epsilon R)$ has been given [49]. Certain
truncations of the series turn out to be identical to the results of optimized mode expansions [50-52]. The series can also be combined with Mayer's virial series to give yet more approximate theories [45]. Some of these techniques can be applied to the pair distribution function (e.g. the QUAD theory) and the direct correlation function (e.g. the QUADc approximation), but most give expressions only for the free energy and so give thermodynamic rather than structural information about PM electrolytes.

D. Computer Simulation

Since all the theories mentioned above are based on an approximate Hamiltonian, direct comparison with experiment cannot distinguish defects of the model from defects of the approximation. Exact calculations for the specified Hamiltonian can be performed using Monte Carlo techniques [53,54] and these serve as tests for the various approximations of types A, B and C. Monte Carlo results have been reported for 1:1 [55] and 2:2 [56,57] RPM electrolytes.

Other tests involve the accuracy to which local electroneutrality and the Stillinger-Lovett second moment condition [58,59] are satisfied. These conditions require that

\[ \sum_j \rho_j z_j \int h_{ij}(r) \, dr + z_i = 0 \quad (2.2.18) \]

and

\[ \sum_{jk} \rho_j z_j \rho_k z_k \int h_{jk}(r) \, r^2 \, dr + \frac{6}{\kappa^2} \sum_j \rho_j z_j^2 = 0. \quad (2.2.19) \]

Further self-consistency tests are discussed in Ref. 1.

Most of the theories mentioned above give reasonably accurate thermodynamics for 1:1 RPM electrolytes. The HNC, MPB and optimized cluster theory give the most accurate thermodynamics for 2:2 RPM electrolytes. The MSA gives surprisingly good agreement for thermo-
dynamic properties (provided the energy equation is used) considering its analytic nature. The MSA distribution functions, however, are not as accurate and this reflects the unrealistic symmetry of $g_{++}(r)$ and $g_{+-}(r)$ about the hard sphere distribution function. Indeed, for low concentrations $g_{++}(R)$ is negative — an unphysical result. The most accurate structural theories for 2:2 RPM electrolytes are the BGY, MPB and HNC theories — all of which require extensive numerical computations.

The success of the HNC equation has prompted further investigations using the refined MM-level model of Eq. (2.1.10) and comparison of these results with experiment [3,60-63].

Only recently have theoretical efforts turned to BO-level electrolytes. For convenience, we discuss the theories in the same manner as for PM electrolytes.

A. The Potential Approach

Outhwaite [64,65] has tackled ion-dipole mixtures using the MPB formalism with fairly disappointing results. A recent paper on ion-dipole mixtures [66] also uses essentially the potential approach.

B. Integral Equation Theories

The MSA has been solved analytically for ion-dipole mixtures [67-71] and a modified form of the HNC theory — the LHNC theory — has been solved numerically for the same system [72].

C. Series Expansions

Cluster expansions were used by Adelman [73,74] in his
investigations of the ionic concentration-dependent dielectric constant. $\gamma$-ordering techniques have been used by Høye and Stell [75-77] to obtain asymptotic results for the pair distribution functions (also obtained by Chan et al. [78]) and mean field thermodynamic results.

D. Computer Simulation

The only Monte Carlo results to date have investigated the potential of mean force between two ions in a dipolar solvent at infinite dilution [79,80]. The prospects for Monte Carlo simulation of bulk BO-level electrolytes at finite ion concentration are not good.

2.3 THEORIES OF THE ELECTRICAL DOUBLE LAYER

We shall now describe the various theories for the electrical double layer proposed up to 1978 (when this thesis was commenced) using the classification of the previous section.

A. The Potential Approach

Just as the work of Gouy and Chapman [81,82] preceded that of Debye and Hückel [83] by several years, so did the application of Kirkwood's ideas [11] to the electrical double layer precede the MPB theory of bulk electrolytes. Using the Kirkwood hierarchy of equations and an approximation due to Loeb [84] (which has been tested by Williams [85]) a modified Poisson-Boltzmann equation for the double layer was constructed [86-89]. A theory for the double layer has also been derived from the BBGY hierarchy [90] but proves to be less useful than the MPB theory.
B. Integral Equation Theories

We can derive an integral equation formulation of the double layer by the following trick. Consider a system of charged hard spheres of valence $z_0$, $+1$, $-1$, densities $\rho_0$, $\rho_1$, $\rho_2$ and diameter $R_0$, $R_1$ and $R_2$, respectively, where species 0 are large colloidal particles and species 1 and 2 represent the bathing electrolyte. By taking the limit $\rho_0 \to 0$, $R_0 \to \infty$ and $z_0 \to \infty$ such that

$$\rho_0 R_0^3 \to 0$$  \hspace{1cm} (2.3.1)

and

$$z_0 \to \pi R_0^2 \sigma_0$$ \hspace{1cm} (2.3.2)

we can obtain the Ornstein-Zernike equation for the wall-ion correlation functions

$$h_{i0}(x) = c_{i0}(x) + \sum_j \rho_j \int dr' h_{i0}(r') c_{ij}(|r-r'|). \hspace{1cm} (2.3.3)$$

The use of various approximate closures between $h_{i0}(x)$ and $c_{i0}(x)$ for the case of simple fluids at a hard wall has been investigated by Sullivan and Stell [91]. $c_{ij}(r)$ is the bulk direct correlation function and can be given to a good approximation by the integral equation theories discussed above. The use of the MSA closure between $h_{i0}(x)$ and $c_{i0}(x)$ and $c_{ij}^{MSA}(r)$ leads to the MSA/MSA theory of the double layer [92]. This can be solved analytically and yields the expression

$$\psi_0 = \frac{4\pi \sigma_0}{\epsilon \kappa} \left( 1 + \frac{\sqrt{1 + 2\kappa R}}{2} \right) \hspace{1cm} (2.3.4)$$

which reduces to Eq. (1.2.3) with $d = \frac{1}{2} R$ as $\kappa R \to 0$.

A study of the double layer using the BGY approach has been given by Stillinger and Kirkwood [93].
C. Series Expansions

Only the beautiful paper of Buff and Stillinger [94] has used cluster expansions to investigate the double layer. To my knowledge, none of the other series techniques have been applied to the double layer.

D. Computer Simulation

No simulation work had been reported up to 1978.

An interesting feature of all the theories discussed above is the appearance of decaying oscillatory wall-ion distribution functions for $\kappa R$ larger than some critical value. As an example, in the MSA,

$$h_{10}(x) \sim z_1 \exp(-\kappa_{\text{MSA}} x), \quad (2.3.5)$$

where $\kappa_{\text{MSA}}/\kappa$ is the solution of the transcendental equation [95]

$$(e^{\kappa R} y = 1 + \kappa R \left(1 + \frac{1}{B}\right) y - \frac{\kappa R}{B} y^2, \quad (2.3.6)$$

and

$$B = (\sqrt{1+2\kappa R} - 1 - \kappa R)/\kappa R. \quad (2.3.7)$$

For $\kappa R \leq 1$, the two roots with smallest real parts (which determine the asymptotic behaviour) are purely real. As $\kappa R \to 0$, the smallest root tends to 1 and we recover Eq. (1.1.17). For finite $\kappa R$, the smallest root is greater than unity and so $h_{10}(x)$ decays faster than in the Gouy-Chapman case. At $\kappa R = 1$, the decay is about 25% faster. At the critical value $\kappa R_c = 1.229$ the two real roots coalesce and reappear as complex conjugates. The asymptotic behaviour then becomes oscillatory decay.

This behaviour has been observed for the BGY theory [93] for $\kappa R > 1.03$, for the MPB theory [89] for $\kappa R > 1.24$ and for the BBGY
theory [90] for $\kappa R > 1.72$. This behaviour is determined solely by the bulk interactions, i.e. $c_{ij}(r)$ in Eq. (2.3.3).

Up to 1978 the treatment of BO-level models of the double layer were limited to theories of the monolayer of solvent adjacent to the charged surface [96-109]. No ions were permitted in the monolayer and the solvent layers further out from the surface were treated as a dielectric continuum. The more complex theories contain many parameters in order to simulate solvent clustering, and can give qualitative agreement with differential capacitance measurements from the Hg electrode in various solvents [108,109].

An obvious deficiency of Eq. (2.3.4) is the linear relationship between surface potential and surface charge. This can be easily rectified if we use the HNC closure between $h_{10}(x)$ and $c_{10}(x)$. We obtain

$$
\ln[1+h_{10}(x)] = -\beta u_{10}(x) + \sum_j \rho_j \int \frac{d\mathbf{r'}}{4\pi} h_{10}(\mathbf{r'}) c_{ij}(|\mathbf{r} - \mathbf{r'}|)
$$

(2.3.8)

In Part 2 of this thesis we investigate Eq. (2.3.8) with the choice $c_{ij}^{\text{MSA}}(r)$ (which we term the HNC/MSA theory of the double layer).

Independently, Henderson, Blum and Smith [110] solved Eq. (2.3.8) with $c_{ij}^{\text{HNC}}(r)$. The BGY approach has also recently been applied to the double layer [111], new MPB results are available [112] and, most importantly, reliable Monte Carlo results have been reported [113,114].

In Part 1 of this thesis, we derive certain exact results for both MM and BO-level model electrolytes against a charged surface (indeed, for any inhomogeneous electrolyte).

In Part 2 we restrict our attention to RPM electrolytes. We solve the HNC/MSA equations for both indifferent electrolyte (Chapter 4) and adsorbing electrolyte (Chapter 5). In Chapter 6 we investigate
the possibility of treating image forces via an integral equation formulation, and compare with the potential approach and the BGY approach.

In Part 3 we present the first results for a BO-level double layer theory – an ion-dipole mixture in the MSA – both for an indifferent electrolyte (Chapter 7) and for an electrolyte with adsorbing ions and dipoles (Chapter 8). In Chapter 9 we present some results for a model which attempts to incorporate water-like quadrupolar effects into the description of the polar solvent.

REFERENCES


CHAPTER 2

EXACT RESULTS FOR INHOMOGENEOUS ELECTROLYTES

3.1 THE STRAIN TENSOR IN INHOMOGENEOUS ELECTROLYTES

One of the few exact results in the theory of the electrical double layer is the so-called contact condition. For a deionized primitive model electrolyte at a uniformly charged flat hard wall, the contact condition is [1]

\[ \mathbf{e} = \mathbf{e}_w \]

In this equation, \( \mathbf{e} \) is the electrolyte electric field and \( \mathbf{e}_w \) is the number density of ionic species at the plane of closest approach, i.e., a distance of \( \varepsilon_0 \) from the wall. This contact plane defines the origin of the coordinate \( z \), normal to the wall. The electric field at contact, \( E(0) \), is related to the electric surface charge density \( \sigma_w \) of the wall by

\[ E(0) = \frac{\sigma_w}{\varepsilon_0} \]

Eq. (3.1.1) has a simple interpretation: the pressure derived on the wall is equal to the total ion-molecule transfer to the wall plus 20% normal component of the solution electroviscous stress tensor.

In the proof of Eq. (3.1.1), Underwood and 21 [1] start with the equation

\[ \frac{\partial \mathbf{e}}{\partial t} = \mathbf{D}(\mathbf{e}) \]
CHAPTER 3

EXACT RESULTS FOR INHOMOGENEOUS ELECTROLYTES

3.1 THE STRESS TENSOR IN INHOMOGENEOUS ELECTROLYTES

One of the few exact results in the theory of the electrical double layer is the so-called contact condition. For a Restricted Primitive Model electrolyte at a uniformly charged flat hard wall, the contact condition is [1]

$$p = kT \sum_\alpha \rho_\alpha(0) - \varepsilon \frac{E(0)^2}{8\pi}.$$  \hspace{1cm} (3.1.1)

In this equation, $p$ is the bulk pressure of the electrolyte and $\rho_\alpha(0)$ is the number density of ionic species $\alpha$ at the plane of closest approach, i.e. a distance of $\frac{R}{4}$ from the wall. This contact plane defines the origin of the coordinate $x$, normal to the wall. The electric field at contact, $E(0)$, is related to the uniform surface charge density, $\sigma_0$, of the wall by

$$E(0) = \frac{4\pi \sigma_0}{\varepsilon}.$$  \hspace{1cm} (3.1.2)

Eq. (3.1.1) has a simple interpretation – the pressure exerted on the wall is equal to the total momentum transfer to the wall plus the normal component of the Maxwell electrostatic stress tensor.

In the proof of Eq. (3.1.1), Henderson et al. [1] start with the equation

$$\frac{dp}{dx} + \sum_\alpha \rho_\alpha(x) \frac{dv_\alpha}{dx} = 0,$$  \hspace{1cm} (3.1.3)
where $v_\alpha(x)$ is the direct Coulomb interaction between the wall and an ion of species $\alpha$. Olivares and McQuarrie [2] pointed out that this seems to contradict the equation

$$\frac{dp}{dx} + \sum_\alpha z_\alpha e \rho_\alpha(x) \frac{d\psi}{dx} = 0, \quad (3.1.4)$$

where $z_\alpha$ is the valence of species $\alpha$, and $\psi(x)$ is the mean electrostatic potential. Eq. (3.1.4) has been used by Langmuir, Derjaguin, Landau, Verwey and Overbeek [3] as a starting point in the theory of colloidal stability. In their analysis Olivares and McQuarrie [2] concluded that Eq. (3.1.3) is correct and that Eq. (3.1.4) involves two approximations.

In this section, we clarify the concept of the pressure tensor in a non-uniform electrolyte and hence show that Eq. (3.1.3) is not applicable to electrolytes and that Eq. (3.1.4) is exact for an electrolyte against a uniformly charged hard wall, contrary to earlier work [2]. In Sec. 3.2 we give a general proof of Eq. (3.1.1) for a Restricted Primitive Model electrolyte (neglecting images) and then apply the same method to derive new contact conditions for (a) an Unrestricted Primitive Model electrolyte, neglecting images; (b) a Restricted Primitive Model electrolyte, including images; and (c) a Civilized Model (e.g. ion-dipole mixture) electrolyte. These contact conditions are exact for the models considered and will serve as useful consistency checks on any approximate treatment of such models. In Sec. 3.3 we use the non-uniform Ornstein-Zernike equation to derive conditions for inhomogeneous electrolytes that reduce to the Stillinger-Lovett condition for bulk electrolytes (both MM- and BO-level electrolytes).

We consider an electrolyte consisting of $v$ ionic species each
having valence \( z_\alpha, \alpha = 1, \ldots, n \). For simplicity we will consider first a Primitive Model electrolyte. The charged wall may be regarded as an external field so that the Hamiltonian which describes the electrical double layer has the form

\[
H = \sum_{\alpha=1}^{n} \sum_{i} V_\alpha(r_{i\alpha}) + \frac{1}{2} \sum_{\alpha=1}^{n} \sum_{\beta=1}^{n} U_{\alpha\beta}(r_{i\alpha}, r_{j\beta}), \quad (3.1.5)
\]

where \( V_\alpha \) describes the interaction between an ion of species \( \alpha \) located at \( r_{i\alpha} \) with the charged wall (external field) and the interaction between ions belonging to species \( \alpha \) and \( \beta \) is given by \( U_{\alpha\beta} \).

The formal definition of the stress tensor in terms of the classical phase space probability distribution function which obeys the Liouville equation is given in Kirkwood's original papers [4, 5] and a readable summary of this work is given by Olivares and McQuarrie [2]. The reader is referred to these papers for details.

At equilibrium, the force on every volume element of the electrolyte must be zero. Therefore the divergence of the total stress tensor at any point \( \mathbf{r} \) must vanish, viz.

\[
\nabla \cdot \mathbf{\sigma} = \nabla \cdot \mathbf{\sigma}_K + \nabla \cdot \mathbf{\sigma}_U + \nabla \cdot \mathbf{\sigma}_V = 0. \quad (3.1.6)
\]

The three contributions to the total stress tensor have the following forms at equilibrium:

- the kinetic contribution

\[
\mathbf{\sigma}_K = -[kT \sum_{\alpha} \rho_\alpha(r)] \mathbf{I}, \quad (3.1.7)
\]

- the contribution from the intermolecular potentials

\[
\nabla \cdot \mathbf{\sigma}_U = - \sum_{\alpha\beta} \int \mathbf{d}r' \rho_\alpha^{(2)}(r, r') \, \nabla \cdot U_{\alpha\beta}(r, r') \quad (3.1.8)
\]
and the contribution from the external field

\[ \nabla \cdot g_{\alpha \beta} \equiv - \sum \rho_{\alpha}(r) \nabla \cdot \nabla \pm_{\alpha}(r). \quad (3.1.9) \]

Notice that \( u_{\alpha \beta}(r, r') \) does not have to be a function only of the separation \( |r - r'| \) for Eq. (3.1.8) to be valid. In Eq. (3.1.8) \( \rho_{\alpha \beta}(r, r') \) is the two-particle density distribution function which can be written as

\[ \rho_{\alpha \beta}^{(2)}(r, r') \equiv \rho_{\alpha}(r) g_{\alpha \beta}(r, r') \rho_{\beta}(r') \]

\[ \equiv \rho_{\alpha}(r) [1 + h_{\alpha \beta}(r, r')] \rho_{\beta}(r'), \quad (3.1.10) \]

where \( g_{\alpha \beta}(r, r') \) and \( h_{\alpha \beta}(r, r') \) reduce to the familiar pair distribution function and indirect (total) correlation function in the bulk electrolyte, away from the effects of the external field.

In order to write Eq. (3.1.6) in the usual macroscopic form we need to identify the mechanical (or hydrostatic) pressure tensor, \( \mathcal{P} \). For uncharged fluids with short range intermolecular potentials, we can use Kirkwood's definition \([4,5]\) :

\[ \mathcal{P}(r) = \mathcal{P}_{\nabla} g_{\alpha \beta}(r, r') \rho_{\alpha}(r) \rho_{\beta}(r') \nabla \cdot \nabla \pm_{\alpha}(r) \]

\[ \pm_{\alpha}(r) = \mathcal{P}_{\nabla} g_{\alpha \beta}(r, r') \rho_{\alpha}(r) \rho_{\beta}(r') \nabla \pm_{\alpha}(r) \quad (3.1.11) \]

In which \( \nabla \cdot \nabla \pm_{\alpha}(r) \) can be identified as the external force. In one dimension Eq. (3.1.12) reduces to Eq. (3.1.3).
bulk \((x \to \infty)\), but approaches a finite constant value. However this constant term is cancelled by a similar contribution from \(\nabla \cdot \mathbf{g}_V\). The reason for this behaviour is the presence of long range Coulomb interactions which give rise to an additional component of the stress tensor — the Maxwell electrostatic stress tensor. This term describes the body force exerted on a charged fluid by the electric field within the fluid. To identify the Maxwell stress tensor we need to separate the long range Coulombic terms in the Hamiltonian by writing

\[
\mathbf{V}_\alpha = z_\alpha e \mathbf{v}^C + \mathbf{v}_\alpha^S, \tag{3.1.13}
\]

\[
\mathbf{U}_{\alpha\beta} = z_\alpha z_\beta e^2 \mathbf{u}^C + u_{\alpha\beta}^S, \tag{3.1.14}
\]

where \(v^C\) and \(u^C\) are the Coulombic interactions and \(v^S\) and \(u^S\) are the remaining short range potentials. Eq. (3.1.6) can now be written as

\[

\nabla \cdot \mathbf{g}_T = - \nabla \cdot \mathbf{p}(\mathbf{r}) + \nabla \cdot \mathbf{g}_M(\mathbf{r}) - \sum_\alpha \rho_\alpha(\mathbf{r}) \nabla v^S_\alpha(\mathbf{r}) = 0, \tag{3.1.15}
\]

where the Maxwell stress tensor, \(\mathbf{g}_M\), is

\[
\nabla \cdot \mathbf{g}_M(\mathbf{r}) = - \sum_\alpha z_\alpha e \rho_\alpha(\mathbf{r}) \nabla \psi(\mathbf{r}), \tag{3.1.16}
\]

the mean electrostatic potential, \(\psi(\mathbf{r})\), has the usual definition

\[
\psi(\mathbf{r}) = \mathbf{v}^C(\mathbf{r}) + \int d\mathbf{r}' \left[ \sum_\beta z_\beta e \rho_\beta(\mathbf{r}) \mathbf{u}^C(|\mathbf{r} - \mathbf{r}'|) \right], \tag{3.1.17}
\]

and the appropriate definition of the pressure tensor in a non-uniform Coulombic system is

\[
\nabla \cdot \mathbf{p}(\mathbf{r}) = kT \sum_\alpha \nabla \rho_\alpha(\mathbf{r}) + \sum_\alpha \rho_\alpha(\mathbf{r}) \int d\mathbf{r}' \rho_\beta(\mathbf{r}') \times \left[ g_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \nabla \cdot \mathbf{u}^S(\mathbf{r}, \mathbf{r}') + z_\alpha z_\beta e^2 h_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \nabla \cdot \mathbf{v}^C(\mathbf{r} - \mathbf{r}') \right]. \tag{3.1.18}
\]

Thus for Coulombic systems, the exact result, Eq. (3.1.15), should be used instead of Eq. (3.1.12). In one dimension, Eq. (3.1.15) becomes
\[
\frac{dp(x)}{dx} + \sum_\alpha z_\alpha e \rho_\alpha(x) \frac{d\psi(x)}{dx} + \sum_\alpha \rho_\alpha(x) \frac{dv^S_\alpha(x)}{dx} = 0 \quad (3.1.19)
\]

which, in the absence of short range potentials from the wall, reduces to the exact result of Langmuir, Derjaguin, Landau, Verwey and Overbeek, Eq. (3.1.4).

3.2 CONTACT CONDITIONS

Although the contact condition given by Eq. (3.1.1) can be written down from simple force balance considerations, a derivation based on statistical mechanics is nonetheless valuable. We shall give a proof of Eq. (3.1.1) which is applicable to a Restricted Primitive Model electrolyte near a charged hard wall. With straightforward modifications we can derive analogous contact conditions for (a) an Unrestricted Primitive Model electrolyte, neglecting image effects, (b) a Restricted Primitive Model electrolyte with image effects at the wall, and (c) a Civilized Model electrolyte (e.g. ion-dipole mixture).

The starting point of our proof is the potential of average force on an ion of species \( \alpha \), \( \psi_\alpha(r) \) which is defined by

\[
\psi_\alpha(r) = -\frac{1}{\kappa T} \left( \sum_\alpha \rho_\alpha - \sum_\alpha \rho_\alpha \psi_\alpha \right) \quad (3.2.1)
\]

From Eqs. (3.1.6) and (3.1.7) we see that \( \psi_\alpha(r) \) indeed satisfies the familiar equation

\[
\nabla \cdot \sigma_{T \alpha} = -kT \sum_\alpha \nabla \rho_\alpha - \sum_\alpha \rho_\alpha \nabla \psi_\alpha = 0 \quad (3.2.2)
\]

and using Eqs. (3.1.15) - (3.1.18) we find

\[
\nabla \psi_\alpha(r) = \nabla u_\alpha^s(r) + z_\alpha e \nabla \psi(r) + \int dr' \sum_\beta \rho_\beta(r') \times \left[ g_{\alpha\beta}(r,r') \nabla u_{\alpha\beta}(r,r') + z_\alpha z_\beta e^2 h_{\alpha\beta}(r,r') \nabla u^c(|r-r'|) \right] \quad (3.2.3)
\]
For a Restricted Primitive Model electrolyte at a charged hard wall, the short range potential between the wall and an ion is

\[ v^S_{\alpha}(r) = \begin{cases} \infty & x < 0 \\ 0 & x > 0 \end{cases} \]

(3.2.4)

where \( x \) is the normal distance from the wall. The short range ion-ion interaction potential is given by a pair potential

\[ u^S_{\alpha\beta}(r,r') = u^S_{\alpha\beta}(|r-r'|) \]

(3.2.5)

In one dimension, Eq. (3.2.2) reduces to

\[ d\rho_{\alpha}(x) \quad d\psi(x) = \int_{\alpha} \rho_{\alpha}(x) \quad \frac{d\psi(x)}{dx} \]

(3.2.6)

Integrating Eq. (3.2.6) from \( x = 0^- \) to \( x = L \) and using Eq. (3.2.3) we get

\[ kT \sum_{\alpha} \frac{d\rho_{\alpha}(x)}{dx} = \int_{\alpha} \rho_{\alpha}(x) \quad \frac{d\psi(x)}{dx} + I(L) \]

(3.2.7)

where the mean electrostatic potential is

\[ \psi(x) = \frac{4\pi}{\varepsilon} \int_{x}^{\infty} dx' (x - x') \sum_{\alpha} z_{\alpha} e \rho_{\alpha}(x') \]

(3.2.8)

the integral \( I(L) \) is

\[ I(L) = \int_{0}^{L} dx \int_{x}^{\infty} dx' \sum_{\alpha\beta} \rho_{\alpha}(x) \rho_{\beta}(x') \int d^2 \hat{r}' \]

\[ \left[ g_{\alpha\beta}(r,r') \frac{d}{dx} u^S_{\alpha\beta}(|r-r'|) + z_{\alpha} z_{\beta} e^2 h_{\alpha\beta}(r,r') \frac{d}{dx} u^c(|r-r'|) \right] \]

(3.2.9)

and \( \hat{R}' = (y', z') \) denotes the transverse coordinates. The contact condition follows from the limit of Eq. (3.2.7) as \( L \to \infty \).

Consider the contribution to \( I(L) \) due to the integral from \( x' = 0 \) to \( L \), namely,
\[ \int_0^L dx \int_0^L dx' \sum_{\alpha \beta} \rho_\alpha(x) \rho_\beta(x') \int d^2 \vec{r} \]
\[ \times \left( g_{\alpha\beta}(\vec{r}, \vec{r}') \frac{d}{dx} u^s_{\alpha\beta}(|\vec{r} - \vec{r}'|) + z_{\alpha\beta} e^2 h_{\alpha\beta}(\vec{r}, \vec{r}') \frac{d}{dx} u^c(|\vec{r} - \vec{r}'|) \right). \]

This integral is the sum of the x-component of the internal forces between all ions confined in the slab \((0, L)\); by Newton's third law this sum is zero. Mathematically, this integral vanishes because of the symmetry properties with respect to \(x\) and \(x'\). Thus Eq. (3.2.9) becomes

\[ I(L) = \int_0^L dx \int_0^L dx' \sum_{\alpha \beta} \rho_\alpha(x) \rho_\beta(x') \int d^2 \vec{r} \]
\[ \times \left( g_{\alpha\beta}(\vec{r}, \vec{r}') \frac{d}{dx} u^s_{\alpha\beta}(|\vec{r} - \vec{r}'|) + z_{\alpha\beta} e^2 h_{\alpha\beta}(\vec{r}, \vec{r}') \frac{d}{dx} u^c(|\vec{r} - \vec{r}'|) \right). \]

In the limit \(L \to \infty\), only the large \(x'\) behaviour of the integrand is required. Also since \(\frac{d}{dx} u^s_{\alpha\beta}\) and \(h_{\alpha\beta}\) are essentially zero unless \(r \approx r'\) the major contribution to the dx integral will also come from large values of \(x \leq L\). Thus as \(L \to \infty\) we can replace the correlation functions \(g_{\alpha\beta}\) and \(h_{\alpha\beta}\) by their bulk values

\[ \lim_{x, x' \to \infty} g_{\alpha\beta}(r, r') = g^{\text{Bulk}}_{\alpha\beta}(|r - r'|) \]
\[ \lim_{x, x' \to \infty} h_{\alpha\beta}(r, r') = h^{\text{Bulk}}_{\alpha\beta}(|r - r'|) - 1 = h^{\text{Bulk}}_{\alpha\beta}(|r - r'|). \]

Using Eqs. (3.2.10) - (3.2.12) together with the definition

\[ g_{\alpha\beta}(|x - x'|) = 2\pi \int_0^\infty \frac{dR \mathcal{R}}{R} \left( g^{\text{Bulk}}_{\alpha\beta}(R) \frac{d}{dr} u^s_{\alpha\beta}(r) + z_{\alpha\beta} e^2 h^{\text{Bulk}}_{\alpha\beta}(r) \frac{d}{dr} u^c(r) \right) \]
\[ r = \left( R^2 + (x - x')^2 \right)^{\frac{1}{2}} \]

we obtain
Eq. (3.2.15b) follows from the symmetry properties of the integrand
with respect to \( x \) and \( x' \) plus the fact that \( \rho_{\alpha}(x) = 0, \, x < 0 \) for all \( \alpha \)
(cf. Eq. (3.2.4)). Eq. (3.2.15f) is just the usual virial equation of
state \((\rho_{\alpha} \equiv \rho_{\alpha}(\infty))\) for the configurational part of the bulk pressure.

The required contact condition, Eq. (3.1.1), follows from Eq.
(3.2.7) and (3.2.15g) \((L \to \infty)\)
\[
kT \sum_{\alpha} \rho_{\alpha}(0) = p + \int_{0}^{\infty} dx \sum_{\alpha} z_{\alpha} \rho_{\alpha}(x) \frac{d\psi(x)}{dx}
= p + \frac{eE^{2}(0)}{8\pi},
\]
where the last integral has been simplified using the Poisson equation
\[
\frac{d^{2}\psi}{dx^{2}} = -\frac{4\pi}{\varepsilon} \sum_{\alpha} z_{\alpha} \rho_{\alpha}(x), \quad x > 0
\]
and the definition
\[
E(0) = -\left(\frac{d\psi}{dx}\right)_{x=0}.
\]
The above derivation of the contact condition, with slight modifications, can include effects such as different ion sizes, imaging at the wall and the molecular nature of the solvent. As the proofs for these cases are similar to that for a Restricted Primitive Model, we shall only point out the necessary changes and omit the details.

A. Ion Size Effects

We consider a generalization of the short range part of the wall-ion interaction to the form (cf. Eq. (3.2.4))

\[
v^S_{\alpha}(r) = \begin{cases} 
\infty & x < d_{\alpha} \\
= v^S(x) , & x > d_{\alpha}
\end{cases}
\]

where \( v^S_{\alpha} \) is an arbitrary short range function and \( d_{\alpha} \) specifies the position of the contact plane of species \( \alpha \). To derive the contact condition we integrate Eq. (3.2.6) from \( x = x_{min} = \min(d_{\alpha}^+) \) to \( x = L \) and use the fact that \( \rho_{\alpha}(x) = 0, x < d_{\alpha} \) because of Eq. (3.2.20). The contact condition follows as before by taking the limit \( L \to \infty \); the result is

\[
kT \sum_{\alpha} \rho_{\alpha}(d_{\alpha}) = p + \int_{x_{min}}^{\infty} dx \sum_{\alpha} z_{\alpha} \rho_{\alpha}(x) \frac{dv^S_{\alpha}(x)}{dx} + \int_{x_{min}}^{\infty} dx \sum_{\alpha} \rho_{\alpha}(x) \frac{dv^S_{\alpha}(x)}{dx}.
\]

B. Image Effects

We examine the effects of imaging at the charged wall within the realm of the Primitive Model. As a consequence effects due to the molecular nature of the solvent are not considered. The inclusion of image effects will add extra terms to the Hamiltonian. These extra terms are obtained from continuum electrostatics. The electrostatic
potential on an ion $\alpha$ at $x$ due to the direct interaction with its image charge is

$$v_{I,es}^{I,es}(x) = \frac{z_\alpha e}{2\varepsilon(x+d)},$$  \hspace{1cm} (3.2.22)

where $\varepsilon_w$ is the dielectric constant of the wall and $d$ is the distance between the plane of closest approach at $x=0$ and the dielectric discontinuity. As ion $\alpha$ approaches the wall, the image charge also moves. The self-image force is thus equal to $-\frac{z_\alpha e}{2\varepsilon(x+d)}$, which gives

$$f_{I,es}^{I,es}(x) = \frac{z_\alpha e}{4\varepsilon(x+d)}.$$  \hspace{1cm} (3.2.23)

so that the potential appearing in the Hamiltonian is actually

$$v_{I,es}^{I,es}(x) = -\frac{z_\alpha e}{4\varepsilon(x+d)} = \frac{z_\alpha e}{4\varepsilon(x+d)}.$$  \hspace{1cm} (3.2.24)

Consequently, when we use the definition of the average force, $-\frac{z_\alpha e}{2\varepsilon(x+d)}$, with image effects included, we add on $f_{I,es}^{I,es}(x)$ to the term in $V_{I,es}^\alpha$ to give the force exerted on an ion of species $\alpha$. This notation avoids confusion between the potentials of Eqs. (3.2.22) and (3.2.24). The image interaction between different ions, via the wall, produces no such problems and will introduce into the Hamiltonian a three-body potential of the form

$$u_{I,es}^{I,es}(r,r') = \frac{z_\alpha z_\beta e^2}{\varepsilon[(x+x'+2d)^2 + (y-y')^2 + (z-z')^2]}.$$  \hspace{1cm} (3.2.25)

The derivation of the contact condition parallels that for the Restricted Primitive Model considered above. The new expression for the average force/volume in the $x$-direction at a distance $x$ from the
wall is
\[
\kappa T \sum_\alpha \frac{d\rho_\alpha(x)}{dx} = - \sum_\alpha \rho_\alpha(x) \frac{dW_\alpha(x)}{dx}
\]
\[
= \sum_\alpha \rho_\alpha(x) \psi_\alpha(x) \frac{d}{dx} - \sum_\alpha \rho_\alpha(x) \frac{dv^s_\alpha(x)}{dx}
\]
\[
- \sum_{\alpha\beta} z_\alpha z_\beta e^{2\rho_\alpha(x)} \int dx' \rho_\beta(x') h_{\alpha\beta}(r, r') \frac{d}{dx} u_I(r, r')
\]
\[
- \sum_\alpha \rho_\alpha(x) \int dx' \rho_\beta(x') \left\{ f_{\alpha\beta}(r, r') \frac{d}{dx} u^s_{\alpha\beta}(|r - r'|) \right\}
\]
\[
+ z_\alpha z_\beta e^{2h_{\alpha\beta}(r, r')} \frac{d}{dx} u^c(|r - r'|),
\] (3.2.26)

where the first and fourth terms on the right hand side are additional contributions due to image effects. If we integrate Eq. (3.2.26) from \(x = 0^+\) to \(\infty\) using Eq. (3.2.15) to evaluate the last integral we get the required contact condition
\[
\kappa T \sum_\alpha \rho_\alpha(0) = p + \frac{eE^2(0)}{8\pi} + \int_0^\infty dx \sum_\alpha \rho_\alpha(x) \frac{dv^s_\alpha(x)}{dx} + \int_0^\infty dx \sum_\alpha \rho_\alpha(x) f^I_\alpha(x)
\]
\[
+ \int_0^\infty dx \int dx' \sum_{\alpha\beta} z_\alpha z_\beta e^{2\rho_\alpha(x)} \rho_\beta(x') h_{\alpha\beta}(r, r') \frac{d}{dx} u_I(r, r').
\] (3.2.27)

The additional terms in the contact condition due to image effects are from the direct self image force \(f^I_\alpha\) and the three-body interaction between different ions. We note, however, a knowledge of \(h_{\alpha\beta}(r, r')\) is required to apply this result as a test of internal consistency of a calculation.

C. Ion-Dipole Mixtures

We derive the contact condition for an ion-dipole mixture at a planar charged wall. To avoid the complication of image terms in the Hamiltonian the wall is taken to have unit dielectric constant. The final answer, which is an exact result, will contain implicitly
imaging effects at the wall since the ions are in effect in a solvent (dipoles) whose dielectric constant is different to that of the wall. To avoid the problem of cancelling divergent terms, we consider initially the wall to be a sphere of radius \( R_a \), and we only take the limit \( R_a \to \infty \) to obtain results at a planar wall after all long range terms have been removed.

To alleviate the notation, we use \( \alpha \) to denote either ions or dipoles. All functions introduced in earlier discussions of the Primitive Model electrolyte will be generalized to include the full complement of angular variables \( \omega = (\theta, \phi) \) and where they are redundant, for example, for ionic quantities, the angular variables are to be treated as "dummy" variables. Specifically, the long range Coulomb potential \( \psi^C(\alpha, r) \) will become \( \psi^C(\alpha, r, \omega) \) which can denote the wall-ion or wall-dipole electrostatic interaction potential. Similarly, \( u^c_{\alpha\beta}(r, r'; \omega, \omega') \) can be the ion-ion, ion-dipole or dipole-dipole electrostatic interaction potential. The quantity \( z_\alpha e \) can be the charge (monopole moment) or the dipole moment. The derivation is a straightforward generalization of that given earlier.

The result for the contact density, where the plane of contact is assumed to be the same for all species is

\[
\begin{align*}
\kappa T \Sigma \rho_\alpha (0) &= p + \int_0^\infty dx \rho^c(x) \frac{d\psi(x)}{dx} + \int_0^\infty dx \int \frac{d\omega}{4\pi} \Sigma \rho_\alpha(x, \omega) \frac{d}{dx} \psi^S(x, \omega),
\end{align*}
\]

where

\[
\rho_\alpha(0) \equiv \int \frac{d\omega}{4\pi} \rho_\alpha(x=0, \omega)
\]

and

\[
p = -\frac{1}{2(4\pi)^2} \Sigma \rho_\alpha \rho_\beta \int \frac{x^2}{r} \left[ \int d\omega d\omega' \left( g_{\alpha\beta} \left( r; \omega, \omega' \right) \frac{d}{dr} u^s_{\alpha\beta}(r; \omega, \omega') \right) ight. \\
+ \left. z_\alpha z_\beta e^2 h_{\alpha\beta} \left( r; \omega, \omega' \right) \frac{d}{dr} u^c_{\alpha\beta}(r; \omega, \omega') \right]
\]
is the bulk pressure \cite{6}. The mean electrostatic potential has the
definition (cf. Eq. (3.2.8))
\begin{equation}
\psi(x) = 4\pi \int_x^\infty dx' (x - x') \rho^C(x') - 4\pi \int_x^\infty \rho(x') \, dx',
\end{equation}
\begin{equation}
(3.2.31)
\end{equation}
where the polarization density \( \rho(x) \) is given by
\begin{equation}
\rho(x) = \frac{1}{4\pi} \int d\omega \, \rho_{\text{dipole}}(x, \omega) (\hat{\omega}, \omega).
\end{equation}
\begin{equation}
(3.2.32)
\end{equation}
and the charge density \( \rho^C(x) \) is given by
\begin{equation}
\rho^C(x) = \sum_{\alpha} z_{\alpha} e^{\rho_{\alpha}(x)}.
\end{equation}
\begin{equation}
(3.2.33)
\end{equation}
Using the definitions of the displacement field \( D(x) \)
\begin{equation}
\frac{dD(x)}{dx} = 4\pi \rho^C(x)
\end{equation}
\begin{equation}
(3.2.34)
\end{equation}
and the electric field \( E(x) \)
\begin{equation}
E(x) = -\frac{d\psi(x)}{dx}
\end{equation}
\begin{equation}
(3.2.35)
\end{equation}
we can rewrite Eq. (3.2.28) as
\begin{equation}
kT \sum_{\alpha} \rho_{\alpha}(0) = \rho + \frac{1}{4\pi} \int_0^D(0) E \, dD + \frac{1}{4\pi} \int_0^D dx \int_0^{\infty} d\omega \sum_{\alpha} \rho_{\alpha}(x, \omega) \frac{d}{dx} \psi_{\alpha}(x, \omega),
\end{equation}
\begin{equation}
(3.2.36)
\end{equation}
where the second term on the right hand side is just the expression
for the stress tensor for a general, possibly non-linear, dielectric.
Thus, Eq. (3.2.36) contains implicitly all image effects (at a wall of
unit dielectric constant) and non-linear effects such as dielectric
saturation in an ion-dipole mixture. Although we have assumed the
solvent molecule to be a dipole, the proof remains valid even if the
solvent has higher multipole moments (e.g. dipole + quadrupole). Eq.
(3.2.36) will still be valid provided, where necessary, the angular
variable \( \omega \) is generalized to denote the three Euler angles, the angular
normalization factor $4\pi$ is replaced by $8\pi^2$, $u_{\alpha\beta}^{C}(r',r';\omega,\omega')$ is to denote any multipole electrostatic interaction and the mean electrostatic potential is to include contributions from the higher multipoles. For a linear dielectric, $D = \varepsilon E$, Eq. (3.2.36) reduces to the Primitive Model result.

3.3 STILLINGER-LOVETT CONDITIONS FOR INHOMOGENEOUS ELECTROLYTES

Two exact conditions on the distribution functions of bulk electrolytes are the equations

$$\sum_{j} \rho_{j} z_{j} \int h_{ij}(r) \, dr + z_{i} = 0 \quad (3.3.1)$$

which is just the requirement for electroneutrality, and

$$\sum_{jk} \rho_{j} z_{j} \rho_{k} z_{k} \int h_{jk}(r) \, dr + 6 \sum_{j} \rho_{j} z_{j}^{2}/\kappa^{2} = 0 \quad (3.3.2)$$

the second-moment condition of Stillinger and Lovett [7,8]. For bulk McMillan-Mayer level electrolytes, Eq. (3.3.2) has been derived [9] from the usual Ornstein-Zernike equation

$$h_{ij}(r) = c_{ij}(r) + \sum_{k} \rho_{k} \int dr' c_{ik}(|r - r'|) h_{kj}(r') \quad (3.3.3)$$

by using the condition that, if

$$c_{ij}(r) = -\frac{\beta z_{i} z_{j} e^{2}}{\varepsilon r} + c_{ij}^{0}(r) \quad (3.3.4)$$

then $c_{ij}^{0}(r)$ is short-ranged in the sense that

$$\int dr \, c_{ij}^{0}(r) \quad \text{is finite} \quad (3.3.5)$$

The condition Eq. (3.3.5) has been demonstrated by Stell [10] (based on work with J. Groeneveld).
In a similar way, Eq. (3.3.2) has been derived for bulk ion-dipole mixtures [11]. If we write (d stands for dipoles, i,j,... for ions)

\[ c_{ij}(r) = -\frac{\beta z_i z_j e^2}{r} + c_{ij}^0(r) \]  
(3.3.6)

and

\[ c_{di}(r,\omega) = \beta z_i e_{\omega} V\left(\frac{1}{r}\right) + c_{di}^0(r,\omega) \]  
(3.3.7)

then it is plausible to assume that

\[ \int dr c_{ij}^0(r) \quad \text{and} \quad \int dr c_{di}^0(r,\omega) \quad \text{are finite}. \]  
(3.3.8)

When Eq. (3.3.8) is used in the Ornstein-Zernike equations for ion-dipole mixtures and certain integrals of dipolar distribution functions are interpreted in terms of the dielectric constant, Eq. (3.3.2) results.

The methods of Ref. 9 show implicitly that the MSA and HNC theories for MM-level electrolytes obey both electroneutrality and the Stillinger-Lovett condition. In the same way, implicitly in Ref. 11 and explicitly elsewhere it has been shown that the MSA [12,13], LHNC [13] and QHNC [13] theories for ion-dipole mixtures obey electroneutrality and the Stillinger-Lovett condition.

The chief technical tool of Refs. 9 and 11, the Fourier transform, is applicable only because of the symmetry of bulk fluids and is not available for inhomogeneous systems. We therefore need to derive Eq. (3.3.2) by a different route that can be carried over to non-uniform electrolytes.

We consider for simplicity McMillan-Mayer level electrolytes with pair potentials. Using Eq. (3.3.4) in Eq. (3.3.3), we find
\[ h_{ij}(r) = -\frac{\beta z_i e^2}{r} \left\{ z_j + \int \frac{dr'}{\Sigma_k} \rho_k h_{kj}(r') \right\} \]

\[ -\frac{\beta z_i e}{\varepsilon} \frac{4\pi}{r} \int_0^\infty dr' \left( r' - \frac{r'^2}{r} \right) \Sigma_k z_k e \rho_k h_{kj}(r') \]

\[ + c_{ij}^0 (r) + \Sigma_k \rho_k \int dr' c_{ik}^0 (|r-r'|) h_{kj}(r') , \]  

(3.3.9)

where we have expanded \(|r-r'|^{-1}\) in Legendre polynomials and simplified. Since we know that \(h_{ij}(r)\) is a short-range (decaying) function, the term in braces must vanish, and electroneutrality – Eq. (3.3.1) – assures this. Eq. (3.3.9) can be written in the form

\[ h_{ij}(r) = -\beta z_i e \phi_j (r) + c_{ij}^0 (r) + \Sigma_k \rho_k \int dr' c_{ik}^0 (|r-r'|) h_{kj}(r') , \]

(3.3.10)

where

\[ \phi_j (r) = \frac{z_j e}{\varepsilon r} + \int \frac{dr'}{\Sigma_k} \frac{\rho_k z_k e h_{kj}(r')}{\varepsilon |r-r'|} \]

(3.3.11)

\[ = \frac{4\pi}{\varepsilon} \int_0^\infty dr' \left( r' - \frac{r'^2}{r} \right) \Sigma_k \rho_k z_k e h_{kj}(r') . \]

(3.3.12)

\(\phi_j (r)\) is the mean electrostatic potential given an ion of species \(j\) fixed at the origin. We can now take Eqs. (3.3.10) and (3.3.1) to find

\[-z_i = \Sigma_j \rho_j z_j \int dr h_{ij}(r)\]

\[ = -\beta z_i \int dr \Sigma_j \rho_j z_j \phi_j (r) + \int dr \Sigma_j \rho_j z_j c_{ij}^0 (r) \]

\[ + \int dr \int dr' \Sigma_{jk} \rho_k \rho_j z_j c_{ik}^0 (|r-r'|) h_{kj}(r') . \]

(3.3.13)

Since \(c_{ik}^0 (r)\) is short-ranged, we can write the last term as

\[ \int dr \Sigma_k \rho_k c_{ik}^0 (r) \int dr' \rho_j z_j h_{kj}(r') = \int dr \Sigma_k \rho_k c_{ik}^0 (r) (-z_k) \]

(3.3.14)

by Eq. (3.3.1). The last two terms on the right hand side of Eq.
(3.3.13) thus cancel and we are left with
\[ \beta \sum_j z_j \rho_j e \int dr \phi_j(r) = 1. \]  
(3.3.15)

We now use the expression Eq. (3.3.12) for \( \phi_j(r) \) since all the divergent terms in Eq. (3.3.11) have been explicitly cancelled. This enables us to substitute Eq. (3.3.12) into Eq. (3.3.15), reverse the orders of integration and perform the second integration to yield Eq. (3.3.2). The equivalence of Eqs. (3.3.2) and (3.3.15) was first shown by Outhwaite [14]. Our Stillinger-Lovett condition for inhomogeneous electrolytes is the generalization of Eq. (3.3.15).

We now consider non-uniform McMillan-Mayer level electrolytes. The non-uniform Ornstein-Zernike equation (see Ref. 15) is
\[ h_{ij}(r,r') = c_{ij}(r,r') + \sum_k d_{ik}(r,r'') \rho_k(r'') h_{kj}^{(r'',r')}. \]  
(3.3.16)

We write
\[ c_{ij}(r,r') = - \beta z_1 z_j e^2 G(r,r') + c_{ij}^0(r,r'), \]  
(3.3.17)
where \( G(r,r') \) is the potential at \( r \) due to a unit test charge at \( r' \) in a continuum of dielectric constant \( \varepsilon \). For the case of electrolyte against a charged wall, \( G(r,r') \) will have both a Coulombic term and a long-range term due to images. Considering Eq. (3.3.5), we here make the plausible assumption
\[ \int dr' c_{ij}^0(r,r') \text{ is finite.} \]  
(3.3.18)

Using Eq. (3.3.17), Eq. (3.3.16) becomes
\[ h_{ij}(r,r') = - \beta z_1 z_j e G(r,r') + \int dr'' G(r,r'') \sum_k d_{ik}(r,r'') \rho_k(r'') h_{kj}^{(r'',r')} \]
\[ + c_{ij}^0(r,r') + \sum_k d_{ik}(r,r'') \rho_k(r'') h_{kj}^{(r'',r')} \]  
(3.3.19)
where now \( \phi_j(r, r') \) is the change in mean electrostatic potential at \( r \) due to fixing an ion of species \( j \) at \( r' \).

For \( r' \) fixed and \( r \to \infty \), it is clear that in order to keep the term in braces in Eq. (3.3.19) short-ranged we require

\[
\begin{align*}
\int & dr'' \Sigma_k \rho_k(r') \, h_{k j}(r'', r') = 0, \\
\int & dr'' \Sigma_k \rho_k(r') \, h_{k j}(r'', r') = 0,
\end{align*}
\]

the condition of local electroneutrality in non-uniform electrolytes.

By analogy with the bulk electrolyte example, we can use Eqs. (3.3.20) and (3.3.21) to write

\[
\begin{align*}
- z_i & = \int dr' \Sigma_j \rho_j(r') \, z_j \, h_{i j}(r, r') \\
& = - \beta z \int dr' \Sigma_j \rho_j(r') \, \phi_j(r, r') + \int dr' \Sigma_j \rho_j(r') \, z_j \, c_{i j}^0(r, r') \\
& \quad + \int dr' \Sigma_k \rho_k(r') \, h_{k j}(r'', r') \\
& \quad \int dr'' \Sigma_k \rho_k(r'') \, c_{i k}^0(r, r'') \, h_{k j}(r'', r'). \quad (3.3.22)
\end{align*}
\]

Using the condition Eq. (3.3.18) and Eq. (3.3.21) we can rewrite the last term of Eq. (3.3.21) as

\[
\begin{align*}
\int & dr'' \Sigma_k \rho_k(r'') \, c_{i k}^0(r, r'') \int dr' \Sigma_j \rho_j(r') \, z_j \, h_{k j}(r'', r') \\
& = \int dr'' \Sigma_k \rho_k(r'') \, c_{i k}^0(r, r'') (-z_k) \quad (3.3.23)
\end{align*}
\]

and so cancel the last two terms on the right hand side of Eq. (3.2.21) to obtain

\[
\beta \int dr' \Sigma_j \rho_j(r') \, \phi_j(r, r') = 1. \quad (3.3.24)
\]

Eq. (3.3.24) is the generalization of Eq. (3.3.15) to inhomogeneous electrolytes. The proof of the equivalence of Eqs. (3.3.15) and
(3.3.2) requires the symmetry properties of bulk fluid distribution functions. Eq. (3.3.24) therefore cannot be explicitly reduced to a simple integral over the distribution functions and so a direct equivalent of Eq. (3.3.2) is not available. Nevertheless, Eq. (3.3.24) should serve as a check for theories of the double layer which calculate $\phi_j(r,r')$ or $h_{ij}(r,r')$.

Eq. (3.3.24) also holds for ion-dipole mixtures (neglecting electronic polarizability effects). The required Ornstein-Zernike equations are ($\omega$ and $\Omega$ are the angular coordinates of the dipoles)

$$h_{ij}(r,r') = c_{ij}(r,r') + \sum_k \int dr'' c_{ik}(r,r'') \rho_i(r'') h_{kj}(r'',r')$$

and

$$h_{id}(r,r',\Omega) = c_{id}(r,r',\Omega) + \sum_k \int dr'' c_{ik}(r,r'') \rho_i(r'') h_{kd}(r'',r',\Omega)$$

where $G_{\text{ion}}(r,r')$ is the potential at $r$ due to a unit test charge at $r'$ in vacuum and $G_{\text{dip}}(r,r')$ is the potential at $r$ due to a unit test dipole at $r'$ in vacuum. In bulk,

$$G_{\text{ion}}(r,r') = \frac{1}{|r-r'|}$$

and

$$G_{\text{dip}}(r,r',\Omega) = \frac{(r-r') \cdot \hat{n}(\Omega)}{|r-r'|^3}.$$
\[
\int \text{d}r' \, c_{ij}^0 (r, r') \quad \text{and} \quad \int \text{d}r' \, c_{id}^0 (r, r', \Omega) \quad \text{are finite.} \tag{3.3.31}
\]

Substituting Eqs. (3.3.27) and (3.3.28) into Eqs. (3.3.25) and (3.3.26), the long-range terms vanish because of Eq. (3.3.21) and the condition of electroneutrality about a dipole

\[
\int \text{d}r'' \sum_k z_k \rho_k (r'') \, h_{kd} (r'', r', \Omega) = 0. \tag{3.3.32}
\]

Eq. (3.3.28) can be written in the form

\[
h_{ij} (r, r') = -\beta z_i e \, \phi_j (r, r') + c_{ij}^0 (r, r') + \sum_k \int \text{d}r'' \, c_{ik}^0 (r, r'') \, \rho_k (r'') \, h_{kj} (r'', r')
\]

\[
+ \int \text{d}r'' \int \frac{\text{d}w}{4\pi} c_{id}^0 (r, r'', \omega) \, \rho_d (r'', \omega) \, h_{dj} (r'', r', \omega), \tag{3.3.33}
\]

where

\[
\phi_j (r, r') = z_j e \, g_{\text{ion}} (r, r') + \int \text{d}r'' \, g_{\text{ion}} (r, r'') \sum_k \rho_k (r'') \, z_k e \, h_{kj} (r'', r')
\]

\[
+ \int \text{d}r'' \int \frac{\text{d}w}{4\pi} g_{\text{dip}} (r, r'', \omega) \, \rho_d (r'', \omega) \, \mu h_{dj} (r'', r', \omega) \tag{3.3.34}
\]

is the change in mean electrostatic potential at \( r' \) upon fixing an ion of species \( j \) at \( r' \). We substitute Eq. (3.3.33) into Eq. (3.3.21) and the second and third terms cancel as before. Using Eq. (3.3.31), the fourth term can be written

\[
\int \frac{\text{d}w}{4\pi} \, c_{id}^0 (r, r'', \omega) \, \rho_d (r'', \omega) \, h_{dj} (r'', r', \omega) \tag{3.3.35}
\]

and so vanishes by Eq. (3.3.32). The final result is Eq. (3.3.24).

The usefulness of the exact conditions derived in this and the previous section is as follows. From the previous section we can see that unless a theory of the double layer obeys Eq. (3.2.11) it will
not give the correct form for the contact condition. Even in this case, if the $h_{ab}(r,r')$ reduce to bulk correlation functions that are inaccurate, then the appropriate pressure derived from the theory will differ from the actual pressure of the model system and the contact condition will still be violated. For some theories, a simple formula can be derived for the contact density (an example is given in Chapter 4). Comparison of this formula with the exact expression allows an estimate of the deficiencies of the theory. Comparison between the theory-dependent formula and numerical results provides a check on numerical calculations. For theories where no simple formula exists, however, these two effects cannot be separated, and the contact condition must give a somewhat cruder estimate of the accuracy of the theory.

From the results of this section, it is clear that in double-layer theories that obey Eqs. (3.3.16) - (3.3.18) (for MM-level electrolyte) the condition given in Eq. (3.3.24) will be obeyed. This Stillinger-Lovett condition can then be used as a check on computational accuracy. For other theories, the Stillinger-Lovett condition can be used to estimate the seriousness of the approximations made in the theory.

REFERENCES


PART 2

PRIMITIVE MODEL ELECTROLYTES

In this section we give a formal derivation of an equation for the one-particle density distribution function of non-uniform fluids. From this result we can see the exact status of the INC wall-ion closure and the possibility of going beyond this approximation. In Section 4.2 we examine the INC/NQA approach in detail and establish its relation to earlier work by analytically extracting results in the limit of low ionic concentration. Numerical results such as the ionic density profiles, the surface charge-surface potential relationship and the double layer capacitance are given in Section 4.3. The contact condition for ionic/bulk separation of the double layer is derived in the appendix.

Consider a system of particles \( p_1, p_2, \ldots, p_N \), where \( N \) is the number of particles of component \( i \). The Hamiltonian for this system...
CHAPTER 4
NON-LINEAR THEORY WITH FINITE ION SIZE - THE HNC/MSA APPROACH

4.1 DERIVATION OF THE HNC WALL-ION CLOSURE

In this chapter we study the structure of non-adsorbing RPM electrolyte at a uniformly charged, hard, non-polarizable surface. The solvent is taken to be an inert continuum that provides a uniform dielectric constant $\varepsilon$ up to the surface. Therefore effects such as inner layer properties, image forces, dielectric saturation and electrostriction have been neglected. Recent work suggests that such effects may be soon derived for BO-level electrolytes [1,2].

In this section we give a formal derivation of an equation for the one-particle density distribution function of non-uniform fluids. From this result we can see the exact status of the HNC wall-ion closure and the possibility of going beyond this approximation. In Section 4.2 we examine the HNC/MSA approach in detail and establish its relation to earlier work by analytically extracting results in the limit of low ionic concentration. Numerical results such as the ionic density profiles, the surface charge - surface potential relationship and the double layer capacitance are given in Section 4.3. The contact condition for HNC/bulk theories of the double layer is derived in the appendix.

Consider a system of particles $\{N_i\} = \{N_1, N_2, \ldots\}$, where $N_i$ is the number of particles of component $i$. The Hamiltonian for this system
in an external field is
\[
H(\{N_i\} \mid \lambda) = H_0(\{N_i\}) + \lambda \int \! dr \! \sum_j \phi_j(r) \hat{\rho}_j(r),
\]
(4.1.1)
where \(\phi_j(r)\) is the interaction between a particle of species \(j\) at \(r\) with the external field which vanishes in the limit \(r \to \infty\). The density operator for component \(j\) is
\[
\hat{\rho}_j(r) = \sum_{\alpha=1}^{N_j} \delta(r - \hat{r}_j) \delta(r - \hat{r}_\alpha).
\]
(4.1.2)

The coupling parameter \(\lambda\) is a formal device by which the external field can be varied continuously. The limit \(\lambda = 0\) corresponds to a uniform bulk fluid with Hamiltonian \(H_0(\{N_i\})\) and the external field is at full strength at \(\lambda = 1\). If the system is in equilibrium with a bulk fluid at uniform concentration \(\rho_i\) and chemical potential \(\mu_i\), the thermodynamic potential, \(\Omega(\lambda)\), for the system in an external field is given by (\(\beta = 1/kT\))
\[
e^{-\beta \Omega(\lambda)} = \sum_{\{N_i\}} \frac{\hbar}{N_i!} e^{-\beta \sum_i N_i \mu_i} \int \! dr \! dp e^{-\beta H(\{N_i\} \mid \lambda)}.
\]
(4.1.3)

By differentiating with respect to \(\lambda\) we can show that
\[
\frac{\partial \Omega(\lambda)}{\partial \lambda} = \int \! dr \sum_i \rho_i(r) \frac{\partial}{\partial \lambda} \phi_i(r)
\]
(4.1.4)
and
\[
\frac{\partial \rho_i(r\mid \lambda)}{\partial \lambda} = -\beta \int \! dr' \sum_j \phi_j(r') \left[ \{ \hat{\rho}_j(r') \} \hat{\rho}_i(r) \} - \langle \hat{\rho}_j(r') \rangle \langle \hat{\rho}_i(r) \rangle \right],
\]
(4.1.5)
where
\[
\rho_i(r\mid \lambda) = \langle \hat{\rho}_i(r) \rangle
\]
(4.1.6)
is the number density of component \(i\) and \(\langle \rangle\) denotes the ensemble average taken with respect to \(H(\{N_i\} \mid \lambda)\). Using the definition of the
pair distribution function $g_{ij}(r, r'| \lambda)$ between species $i$ and $j$:

$$\rho_i(r | \lambda) g_{ij}(r, r'| \lambda) \rho_j(r'| \lambda) = \langle \delta_i(r) \delta_j(r') \rangle - \rho_i(r | \lambda) \delta_{ij} \delta(r - r')$$

(4.1.7)

we can rewrite Eq. (4.1.5) as

$$\frac{\partial \ln \rho_i(r | \lambda)}{\partial \lambda} = -\beta \left\{ \phi_i(r) + \int dr' \Sigma j \rho_j(r'| \lambda) h_{ij}(r, r'| \lambda) \right\},$$

where

$$h_{ij}(r, r'| \lambda) = g_{ij}(r, r'| \lambda) - 1.$$  

(4.1.8)

Now we can use the non-uniform Ornstein-Zernike equation [3]

$$h_{ij}(r, r'| \lambda) = c_{ij}(r, r'| \lambda) + \sum_k \int dr'' c_{ik}(r, r''| \lambda) \rho_k(r''| \lambda) h_{kj}(r'', r'| \lambda)$$

(4.1.10)

to recast Eq. (4.1.8) in terms of a non-uniform direct correlation function $c_{ij}(r, r'| \lambda)$

$$\ln \left( \frac{\rho_i(r | \lambda)}{\rho_i(r | \lambda = 1)} \right) = -\beta \phi_i(r) + \int_0^1 d\lambda \int dr' \Sigma j c_{ij}(r, r'| \lambda) \frac{\partial \rho_j(r'| \lambda)}{\partial \lambda}$$

(4.1.11)

with

$$\rho_i(r | \lambda) \equiv \rho_i(r | \lambda = 1).$$  

(4.1.12)

Since we have not made any approximations Eq. (4.1.11) is therefore exact. A similar result has been derived using the density functional method [4,5].

To proceed further we need to have some knowledge of the non-uniform direct correlation function $c_{ij}(r, r'| \lambda)$. Provided the external field is not too strong a very plausible approximation is

$$c_{ij}(r, r'| \lambda) \approx c_{ij}(r, r'| \lambda = 0) = c_{ij}^{\text{bulk}}(|r - r'|).$$

(4.1.13)

Since $c_{ij}(r, r'| \lambda)$ reflects the direct interaction between ions $i$ and $j$ in the presence of the external field, the approximation to replace it
by the bulk direct correlation function $c_{ij}^{\text{bulk}}(|r - r'|)$ is expected to
be much less serious than a similar approximation on the indirect
correlation function $h_{ij}(r, r'|\lambda)$. We note that the use of Eq.
(4.1.13) for the electrical double layer problem automatically
neglects image interactions [6].

Combining Eqs. (4.1.11) and (4.1.13) we get

$$
\mathcal{U}_i \left( \frac{\rho_i(r)}{\rho_i} \right) = -\beta \phi_i(r) + \int \, d_{r'} \sum_j c_{ij}^{\text{bulk}} (|r - r'|) \left[ \rho_j(r') - \rho_j \right]. \tag{4.1.14}
$$

For the electrical double layer problem, the external field $\phi_i$ is due
to the presence of the charged surface — treated initially as a large
spherical particle of diameter $R_0$. Consequently we can immediately
recognise Eq. (4.1.14) as the Ornstein-Zernike equation for the
surface-ion indirect correlation function with an HNC closure for the
surface-ion direct correlation function. We note that the form of
$c_{ij}^{\text{bulk}}$ has been left unspecified. If the exact bulk direct correlation
function is known (e.g. from machine simulations) it can be used in
Eq. (4.1.14); otherwise any reasonable approximate representation of
$c_{ij}^{\text{bulk}}$ may be used and this will constitute a further approximation.

For an electrical double layer at a planar interface, we need to
reduce Eq. (4.1.14) to a one-dimensional form. The potential $\phi_i(r)$
contains a hard core part which ensures

$$
\rho_i(r) = 0, \quad r < R_{io} \equiv \frac{1}{2}(R + R_o). \tag{4.1.15}
$$

For $r > R_{io}$, $\phi_i(r)$ is the Coulomb potential, hence Eq. (4.1.14) becomes

$$
\mathcal{U}_i \left( \frac{\rho_i(r)}{\rho_i} \right) = \frac{\beta z_i z_o e^2}{\epsilon r} + \int \, d_{r'} \sum_j c_{ij} (|r - r'|) \left[ \rho_j(r') - \rho_j \right], \quad r > R_{io}. \tag{4.1.16}
$$

In the planar limit, $R_o \to \infty$, the divergence in the first term of Eq.
(4.1.16) is exactly cancelled by a similar divergence in the second
term. To demonstrate this we make the formal decomposition

\[ c_{ij}(|r - r'|) = -\frac{\beta z_i z_j e^2}{\varepsilon |r - r'|} + c^0_{ij}(|r - r'|), \quad 0 < |r - r'| < \infty, \]

(4.1.17)

where \( c^0_{ij} \) is now a short ranged function. Combining Eqs. (4.1.16) and
(4.1.17) together with the bulk electroneutrality condition

\[ \sum_i \rho_i z_i = 0 \]

(4.1.18)

we get, after doing the angular integrations,

\[
\ln \left( \frac{\rho_i(r)}{\rho_i} \right) = -\left( \frac{\beta z_i e^2}{\varepsilon r} \right) \left\{ z_0 + \int dr' \Sigma z_j \rho_j(r') \right\} \\
- \frac{4\pi \beta z_i e}{\varepsilon} \int dr' r' \left( 1 - \frac{r'}{r} \right) \Sigma z_j \rho_j(r') \\
+ \int dr' \Sigma z_j c^0_{ij}(|r - r'|) [\rho_j(r') - \rho_j]. \quad (4.1.19)
\]

The term in braces vanishes because the charge in the diffuse double
layer must balance the surface charge, that is,

\[ z_0 = -\int dr' \Sigma z_j \rho_j(r'). \]

(4.1.20)

We can now safely take the planar limit, \( R_0 \to \infty, z_0 \to \infty \) with constant
surface charge density \( \sigma_o = z_0 e/\pi R_o^2 \), by changing to one-dimensional
variables \( x = r - R_1, y = r' - R_1 \) and by defining the surface-ion
indirect correlation function

\[ h_i(x) = \left( \frac{\rho_i(x + R_1)}{\rho_i} \right) - 1 \]

(4.1.21)

so that Eqs. (4.1.15) and (4.1.19) become

\[ h_i(x) = -1, \quad x < 0 \]

(4.1.22)
\begin{align}
\log[1 + h_1(x)] &= -\beta z_i e\psi(x) + \sum_j \rho_j \int_{-\infty}^{\infty} dy C_{ij}^0(|x-y|) h_j(y), \quad x > 0, \\
\text{where} \\
C_{ij}^0(x) &= 2\pi \int_{x}^{\infty} ds s C_{ij}^0(s) \\
\text{and} \\
\psi(x) &= \frac{4\pi}{\varepsilon} \int_{x}^{\infty} dy(x-y) \sum_j \rho_j z_j e h_j(y) \\
is the mean electrostatic potential. It is easy to verify that \(\psi(x)\)
satisfies the one-dimensional Poisson equation subject to the
boundary conditions (cf. Eq. (4.1.20))
\begin{align}
\left. \frac{d\psi}{dx} \right|_{x=0} &= -\frac{4\pi \sigma_0}{\varepsilon} = \frac{4\pi}{\varepsilon} \int_{0}^{\infty} dy \sum_j \rho_j z_j e h_j(y) \\
\psi(x) &\to 0 \quad \text{as} \quad x \to \infty.
\end{align}
The Poisson-Boltzmann result is a special limit of Eq. (4.1.23) with
\(C_{ij}^0 = 0\), which is a good approximation at low ionic densities [7].

From Eq. (4.1.23) it is possible to derive the following result
for the contact values of \(h_1(x)\) (see Appendix)
\begin{align}
kT \sum_i \rho_i [1 + h_1(0)] = \frac{1}{2}(kT \sum_i \rho_i + \chi^{-1}) + \frac{\varepsilon E^2}{8\pi},
\end{align}
where \(E = 4\pi \sigma_0 / \varepsilon\) and \(\chi\) is the isothermal compressibility of the
Restricted Primitive Model electrolyte given by
\begin{align}
\chi = -\frac{1}{V} \left. \frac{\partial V}{\partial \rho} \right|_T = \beta \left( \sum_i \rho_i - \sum_{i,j} \rho_i \rho_j \int dr c_{ij}^0(r) \right)^{-1}.
\end{align}
Eq. (4.1.28) should be compared with the exact result which also
neglects image interactions (see Chapter 3 for a derivation)
\begin{align}
kT \sum_i \rho_i [1 + h_i(0)] = p + \frac{\varepsilon E^2}{8\pi}
\end{align}
and with the Poisson-Boltzmann result which approximates the pressure.
of the bulk electrolyte, \( p \), in Eq. (4.1.30) by the ideal gas limit, 
\[ kT \sum_{i} \rho_i \]
Contrary to the conjecture by Henderson et al. [8] who used the HNC - \( c_{ij}^{0} \), the contact value at zero field should be 
\[ \frac{1}{2} (kT \sum_{i} \rho_{i} + \chi_{HNC}^{-1}) \] and not \( (kT \sum_{i} \rho_{i} / \chi_{HNC})^{1/2} \). Furthermore, the HNC surface-ion closure alone, independent of the choice for \( c_{ij}^{0} \), is sufficient to guarantee the correct asymptotic quadratic dependence of the contact values on the surface charge density. This suggests that the failure of the HNC/HNC result [8] to obey the \( E^2 \) dependence is probably due to problems associated with having to cancel \textit{numerically} the divergence discussed under Eq. (4.1.16). Finally, we note that the \( E^2 \) dependence is only a consequence of the long ranged nature of the Coulomb potential and electroneutrality so that the exact result, Eq. (4.1.30), does not appear to be a very severe test of various approximate theories of the electrical double layer.

It is now clear that in order to go beyond the HNC surface-ion closure, we would need to return to Eq. (4.1.11) and find a closure for \( c_{ij}(r, r' | \lambda) \) that is better than the approximation given by Eq. (4.1.13) which is limited to low or moderate surface charge densities.

### 4.2 THE HNC/MSA EQUATIONS AND EARLIER THEORIES

In lieu of an exact form for the short ranged part of the bulk ionic direct correlation function \( c_{ij}^{0}(r) \) we shall need an approximate representation. We have already mentioned that the choice \( c_{ij}^{0}(r) = 0 \) reduces to the Gouy-Chapman theory, which neglects ion size. Restricting ourselves to 1:1 electrolytes, we know that both the MSA and HNC approximations give reasonably accurate descriptions of bulk electrolyte thermodynamics in the range of concentration \( 10^{-2} \text{ M} - 1 \text{ M} \) [9,10]. The HNC approximation gives superior distribution functions
but the MSA $c_{ij}^0(r)$ is known analytically, so it has the advantage from a pedagogical viewpoint since the physical content of the HNC/MSA approximation can be exhibited explicitly and the cancellation of divergent terms, discussed under Eq. (4.1.16) can also be carried out analytically. In principle, the divergent terms can be cancelled analytically for the HNC approximation provided $c_{ij}^{\text{HNC}}(r)$ rather than $c_{ij}^{\text{HNC}}(r)$ is calculated. This does not appear to have been done, however [8]. Bearing these remarks in mind we now consider in detail the effects of finite ion size on the structure of the electrical double layer based on the HNC/MSA.

Using the MSA form for $c_{ij}^0$, Eq. (4.1.23) becomes

$$\ln[1 + h_1(x)] = -\beta z_1 \psi(x) + \sum_i \rho_j \int_{x-R}^{x+R} dy c_{ij}^{\text{MSA}}(|x-y|) h_j(y), \quad x > 0,$$

(4.2.1)

where

$$c_{ij}^{\text{MSA}}(x) = c^{\text{PYHS}}(x) + z_1 z_j c^C(x).$$

(4.2.2)

$c^{\text{PYHS}}(x)$ is obtained from the solution of the Percus-Yevick hard sphere fluid [11]

$$c^{\text{PYHS}}(x) = \frac{\pi R^2}{(1 - \eta)^4} \left\{ - \frac{1}{5} \eta(1 + 2\eta)^2 \left[ 1 - \frac{x^5}{R^5} \right] + \eta(\eta + 2)^2 \left[ 1 - \frac{x^3}{R^3} \right] - (1 + 2\eta)^2 \left[ 1 - \frac{x^2}{R^2} \right] \right\}, \quad x < R$$

(4.2.3)

$$= 0, \quad x > R$$

with

$$\eta = \frac{\pi R^3}{6} \sum_i \rho_i.$$

(4.2.4)

$c^C(x)$ is given by [10]

$$c^C(x) = \frac{2\pi \beta z^2}{e} R \left\{ \frac{B^2}{3} \left[ 1 - \frac{x^3}{R^3} \right] + B \left[ 1 - \frac{x^2}{R^2} \right] + \left[ 1 - \frac{x}{R} \right] \right\}, \quad x < R$$

(4.2.5)

$$= 0, \quad x > R.$$
where
\[ B = \frac{[(1 + 2KR)^\frac{1}{2} - 1 - KRJ}{KR} \]  \hspace{1cm} (4.2.6)

and \( \kappa \) is the inverse Debye screening length
\[ \kappa^2 = \frac{4\pi^2 e^2}{\varepsilon} \sum \rho_i z_i^2. \]  \hspace{1cm} (4.2.7)

Equations (4.2.1) - (4.2.7) together with Eqs. (4.1.22), (4.1.25) and (4.1.26) constitute the HNC/MSA treatment of the electrical double layer. The solution of these equations will give the relation between the surface charge and surface potential at the planar interface.

The potential at the charged surface, \( \psi_o \), and the potential at the plane of closest approach of the ions, \( \psi_\beta = \psi(x=0) \) (see Fig. 1) are related by

\[ \psi_o = \psi_\beta + \frac{2\pi \sigma R}{\varepsilon} \]  \hspace{1cm} (4.2.8)

We shall compare our results with those of the Gouy-Chapman theory plus a Stern layer correction (MGC). In the MGC theory, finite ion size effects are accounted for by defining a region adjacent to the surface of one radius thick from which all (point) ions are excluded. In this case, \( \psi_\beta \) is given by

\[ \psi_\beta = \frac{2kT}{e} \arcsinh \left[ \frac{2\pi e\sigma}{e\kappa kT} \right]. \]  \hspace{1cm} (4.2.9)

In order to demonstrate explicitly the difference between the HNC/MSA and MGC theories, we observe that the LHS of Eq. (4.2.1) is by definition proportional to the potential of mean force, \( W_i(x) \) between an ion of type \( i \) and the charged surface. Using the known MSA expressions for \( C_{ij}^O \) we can obtain a density expansion for \( W_i(x) \) in terms of the bulk density of the electrolyte:

\[ W_i(x) = z_i \psi(x) + W_i^{(2a)}(x) + W_i^{(2b)}(x) + W_i^{(3)}(x) + \ldots, \]  \hspace{1cm} (4.2.10)
where
\[ W^{(2a)}_i(x) = \int_{x}^{\infty} dx' \left\{ \int_{A} dA \cdot \hat{\mathbf{x}} \rho_{\text{NUM}}(x') kT \right\} \quad (4.2.11) \]

\[ W^{(2b)}_i(x) = -\frac{z_i e}{\varepsilon} \int_{V} dr' \frac{\rho_{\text{CH}}(x')}{|x - x'|} \quad (4.2.12) \]

\[ W^{(3)}_i(x) = \frac{z_i e \kappa}{\varepsilon} \int_{V} dr' \rho_{\text{CH}}(x') \quad (4.2.13) \]

and
\[ \rho_{\text{NUM}}(x) = \sum_{i} \rho_{i} [1 + h_i(x)] \quad (4.2.14) \]

\[ \rho_{\text{CH}}(x) = \sum_{i} \rho_{i} \frac{z_i e}{\varepsilon} h_i(x) \quad (4.2.15) \]

are the number and charge densities in the double layer. There are two types of effects due to finite ion size. The first, and more obvious one is the hard sphere excluded volume effect. The other is a size effect on the electrostatic interaction. We shall consider their contribution to the potential of mean force between an ion and the surface, \( W_i(x) \), in detail.

The first term on the RHS of Eq. (4.2.10) is the mean electrostatic potential energy for a point ion at \( x \) and is the only term in the MGC expression for \( W_i(x) \). The next two terms \( W^{(2a)}_i \) and \( W^{(2b)}_i \) are of the same order in density. \( W^{(2a)}_i \) accounts for pure hard sphere interactions between the ions, and in the HNC/MSA the stress tensor due to such interactions is approximated by \( [\rho_{\text{NUM}}(x) kT] I \). Thus the integral in braces in Eq. (4.2.11), which is taken over the surface of a sphere of radius \( R \) around an ion centred at \( x \), is just the \( x \)-component of the force exerted on the ion, and \( W^{(2a)}_i \) is the work done against this force. Apart from a misprinted factor of \( \frac{1}{2} \) this is identical to the Buff and Stillinger excluded volume term [12]. Since the average ionic density in the region 0 to \( x \) is larger than that in
the region $x$ to $\infty$, $W_i^{(2a)}$ is a repulsive contribution to the potential of mean force. It will tend to thicken the double layer and increase the magnitude of the electrostatic potential relative to that predicted by the MGC theory.

We now consider the term $W_i^{(2b)}$, Eq. (4.2.12). Since the first term on the RHS of Eq. (4.2.10), $z_1e\psi(x)$ is the mean electrostatic energy of a point ion located at $x$, it has also included electrostatic interactions between ion $i$ and all other ions whose centres are within a distance less than $R$ from $x$. As the ion $i$ has a finite size, these extra interactions must be subtracted from $z_1e\psi(x)$. $W_i^{(2b)}$ represents this correction because the integral in Eq. (4.2.12), which is taken over the volume of a sphere of radius $R$ around an ion centred at $x$, is the negative of the electrostatic interaction between an ion at $x$ and all ions within a distance $R$ from $x$. Since the sign of the diffuse layer charge, $\rho_{CH}(x)$, is opposite to that of the potential, $\psi(x)$, the term $W_i^{(2b)}(x)$ is an attractive correction for counter-ions and repulsive for co-ions. The net result is a compression of the double layer in which the counter-ions are present in the majority. Therefore the correction term $W_i^{(2b)}(x)$ will decrease the magnitude of the electrostatic potential relative to that predicted by the MGC theory. The term $z_1e\psi(x) + W_i^{(2b)}(x)$ is identical to the cavity term, $z_1e\psi_{cav}(x)$, of Buff and Stillinger [12], that is

$$z_1e\psi_{cav}(x) = z_1e\psi(x) + W_i^{(2b)}(x)$$

$$= \frac{1}{2}z_1e[\psi(x + R) + \psi(x - R)]. \quad (4.2.16)$$

The term $W_i^{(3)}(x)$ represents a correction on $W_i^{(2b)}(x)$ due to rearrangements of the self atmosphere of ion $i$ [13]. It is clear that
its effect is opposite to that of $W_{i}^{(2b)}(x)$ but is a correction of lower order in density.

While we have only considered the leading terms in the density expansion of the potential of force, the HNC/MSA contains higher order corrections for finite ion size due to pure hard sphere effects (terms such as $W_{i}^{(2a)}$) as well as finite size corrections to the electrostatics (terms such as $W_{i}^{(2b)}, W_{i}^{(3)}$). The relative importance of these two effects will be assessed in a numerical solution of the HNC/MSA equations.

It is interesting to observe that the first few terms of the density expansion of the HNC/MSA potential of mean force, Eqs. (4.2.10) - (4.2.13), is identical to the exact density expansion based on the potential theory approach [6, 12, 13]. At first sight this may seem surprising because at low concentrations the MSA predicts unphysical behaviour for the bulk pair distribution functions between ions – that is, the bulk pair distribution function between co-ions becomes negative near contact. However, since the MSA exhibits the exact Debye-Hückel limiting law this unphysical behaviour near contact has negligible effects on the bulk thermodynamic properties which depend on integrals of the distribution functions. Thus it is suggestive that the HNC/MSA surface charge-surface potential relationship, which is also a thermodynamic result dependent on integrals of wall-ion distribution functions, will be quite reasonable at low concentrations in spite of the problems with bulk MSA distribution functions.
4.3 RESULTS AND CONCLUSIONS

The HNC/MSA equations [Eqs. (4.1.22), (4.1.25), (4.1.26) and (4.2.1) - (4.2.7)] have been solved by a direct iteration method for a 1:1 electrolyte at concentrations 0.01, 0.1 and 0.5 mole dm$^{-3}$ and surface charge density 0 - 80 μC/cm$^2$. Other solution parameters $\varepsilon = 78.5$, $T = 298$ K and $R = 4.25$ Å were chosen to correspond to earlier Monte Carlo calculations [9]. The numerical scheme has been tested against the Gouy-Chapman theory ($C_{ij}^0 = 0$) and the MSA/MSA (replacing $\ln[1 + h_i(x)]$ by $h_i(x)$ in Eq. (3.2.1)) with agreement to within 1% for all parameter ranges. The contact conditions, Eq. (4.1.28), is satisfied to within 2% for 0.5 M, and to within 1% for the lower concentrations.

The counter-ion and co-ion distribution functions in the HNC/MSA and the MGC theory are compared in Figs. 1 and 2 for a bulk electrolyte of concentration 0.1 M and a surface charge density of 16 μC/cm$^2$. In the vicinity of the charged surface where the local ionic concentration is high, the various correction terms outlined in Eq. (4.2.10) are expected to be important. For example, the excluded volume, $W_1^{(2a)}$, and electrostatic, $W_1^{(2b)}$, corrections tend to repel co-ions from the surface and this is reflected in co-ion correlation function being more negative near the surface in the HNC/MSA than in MGC theory. In the same region, the counter-ions are more strongly adsorbed in the HNC/MSA which indicates that the electrostatic correction is more important in this case. Further away from the surface, the HNC/MSA and MGC results intersect in order to preserve charge neutrality, cf. Eq. (4.1.26). Because of this crossover, the ionic adsorption excesses

$$\Gamma_i = \rho_i \int_0^\infty h_i(x) \, dx$$

(4.3.1)
Fig. 1: The wall-ion total correlation function for the co-ions of a RPM electrolyte of bulk concentration 0.1 M, ionic diameter $R = 4.25 \, \text{Å}$ near a surface with intrinsic charge density $\sigma_0 = 16 \, \mu\text{C/cm}^2$ ($T = 298 \, \text{K}, \varepsilon = 78.5$) for the HNC/MSA (—) and MGC (— — —) theories.
Fig. 2: The wall-ion total correlation function for the counterions of a RPM electrolyte near a charged surface according to the HNC/MSA (-----) and MGC (---) theories. All parameters are the same as for Fig. 1. An arcsinh vertical scale has been used.
for the HNC/MSA are practically identical to those of the MGC theory throughout the range of electrolyte concentrations and surface charge densities that we have studied. The overall picture is that the HNC/MSA density profiles which include finite ion size effects are of shorter range than those of MGC. This is in agreement with the observation that the effective decay length of the potential or density profile $\kappa_{\text{eff}}^{-1}$ due to using $c_{ij}^{\text{MSA}}$ is smaller than the familiar Debye length $\kappa^{-1}$ [14]. The deviations from MGC theory presented in Figs. 1 and 2 are confirmed in recent Monte Carlo calculations [15].

The implication of this on the surface charge-surface potential relationship is that for the same surface charge the HNC/MSA surface potentials $\psi_0$ and $\psi_\beta$ are lower than the MGC values (Figs. 3 - 5) because the surface potential is a measure of the degree of charge separation, see Eq. (4.1.25). We also note that for low to moderate surface charge densities, there is little difference between the HNC/MSA and MGC theory owing to the mutually cancelling effects due to excluded volume and electrostatic corrections. This serendipity has been reported before [16]. The comparison of HNC/MSA surface potentials and Monte Carlo calculations [15] is given in Fig. 6. For $\sigma_0 < 20 \ \mu\text{C/cm}^2$, it seems that HNC/MSA gives fairly good results, slightly overestimating the surface potential. Since we have shown that the HNC/MSA contains the correct low-order terms in the density expansion of $\mathcal{W}_1(x)$, it seems unlikely that such agreement is purely fortuitous. Surprisingly the HNC/HNC results are not as accurate for $10^{-2}$ and $10^{-1}$ M electrolytes (but shows close agreement with the MC results for 1 M electrolyte) (see Table 1). The large discrepancy between HNC/HNC and HNC/MSA results is a mystery since one would expect the HNC closure to be more accurate. Since Henderson et al.
Fig. 3: The potential at the charged surface $\psi_0$ (-----) and the potential at the plane $x = 0$ $\psi_0$ (----) as a function of surface charge density $\sigma_0$ for 0.01 M electrolyte. Other parameters as for Fig. 1.
Fig. 4: As for Fig. 3 but at 0.1 M electrolyte concentration.
Fig. 5: As for Fig. 3 but at 0.5 M electrolyte concentration.
Fig. 6: Surface potential at the plane of closest approach, \( \psi_B \), as a function of surface charge density for indifferent RPM electrolyte with the parameters as in Fig. 1. Curves are given for 0.01 M (A) and 0.1 M electrolyte (B) according to the IMC/MSA (—) and MGC (— — —) theories. I show the Monte Carlo results of Torrie and Valleau.
[8] report some problems in satisfying the contact condition and since
the divergences are cancelled numerically, it is possible that
numerical errors are responsible.

From curve B of Fig. 6 we can see that the curvature of the
HNC/MSA line is too large for \( \sigma_0 > 20 \mu\text{C/cm}^2 \). This suggests that the
maxima in \( \psi_B \) as a function of surface charge density shown in Figs.
3-5 may not actually occur in a PM double layer. This conjecture is
strengthened by the failure of the MC results to show a maximum in \( \psi_B \)
for 1 M electrolyte. Conclusive proof, however, awaits MC work for
higher surface charges than reported so far for 0.1 M and 0.01 M
electrolytes.

This failure of HNC-type theories at high surface charge is due
to the neglect in Eq. (4.1.13) of effects due to the enhanced local
ionic density near the wall. One possible remedy, suggested by
previous work in non-uniform fluid systems [4], is to use an
approximation

\[
c_{ij}^0 (r, r'; \lambda) \approx - \frac{\beta z_i z_j e^2}{4 \pi \varepsilon} \frac{\delta}{\varepsilon |r - r'|} + c_{ij}^{\text{obulk}} (|r - r'|; \bar{\rho}) , \tag{4.3.2}
\]

where \( \bar{\rho} \) is some average density over the range of \( c_{ij}^{\text{obulk}} \) (which is
short ranged). For example, \( \bar{\rho} = \frac{1}{2} \left[ \rho(r) + \rho(r') \right] \) and \( \bar{\rho} = \rho \left[ \frac{1}{2} (r + r') \right] \)
would be two possible choices. In any case, such effects appear only
to be important for \( \sigma_0 > 20 \mu\text{C/cm}^2 \) — a surface charge density achieved
usually only in Hg electrode measurements.

Finally in Fig. 7 we show the differential diffuse layer
capacitance given by

\[
C_B = \frac{\partial \sigma_0}{\partial \psi_B} \tag{4.3.3}
\]
as a function of surface potential for an electrolyte concentration of
Fig. 7: The capacitance of the diffuse double layer $C_\beta$ as a function of the potential at the plane $x = 0$, $\psi_\beta$. Electrolyte concentration is 0.5 M, other parameters as in Fig. 1.
Table 1

$e\psi_B/kT$ vs. $\sigma_0$ for MGC, HNC/MSA, HNC/HNC, Monte Carlo

<table>
<thead>
<tr>
<th>$\sigma_0$ (charges/Å²)</th>
<th>10^{-2} M</th>
<th>10^{-1} M</th>
<th>1 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGC</td>
<td>5.44</td>
<td>3.17</td>
<td>1.40</td>
</tr>
<tr>
<td>HNC/MSA</td>
<td>5.24</td>
<td>2.99</td>
<td>1.10</td>
</tr>
<tr>
<td>HNC/HNC ($\pm 0.05$)</td>
<td>4.75</td>
<td>2.90</td>
<td>1.09</td>
</tr>
<tr>
<td>MC</td>
<td>5.05 ± 0.05</td>
<td>2.88 ± 0.05</td>
<td>1.22</td>
</tr>
</tbody>
</table>

* indicates calculations were performed with $R = 2.76$ Å. Monte Carlo and HNC/HNC results have been taken from Ref. 15.
0.5 mole dm\(^{-3}\). The larger values of \(C_s\) in the HNC/MSA is again a reflection that for low to moderate surface charges the diffuse layer is more compact when ion size effects are included.

It should be emphasized that in mercury electrode measurements the large differential capacitances shown in Fig. 7 are totally obscured by the small inner layer capacitance. The diffuse layer contributes significantly only at low concentrations (<10\(^{-2}\) M) around the point of zero charge where the HNC/MSA is only marginally different from MGC results. The good fit of Grahame's data [17] in this regime with MGC results is thus not unexpected.

In conclusion, for electrolyte concentration (≤ 0.1 M) and surface charge densities (≤ 20 μC/cm\(^2\)) of interest to colloid chemistry, the modified Gouy-Chapman theory gives a good description of the PM electrolyte at a uniformly charged, non-polarizable surface. Deviations from the MGC curves are well described by the HNC/MSA treatment.

APPENDIX

CONTACT CONDITION FOR THE HNC/MSA EQUATIONS

We derive the expression for the contact values for the surface-fluid distribution function for (a) an electrolyte against a charged wall and (b) a non-electrolyte fluid mixture at a surface. The wall-fluid direct correlation function is assumed to be given by the HNC closure.
Consider first the electrolyte problem. From Eq. (4.1.23) the potential of mean force of ionic species \( i \) at a distance \( x \) from the wall is

\[
\Phi_i(x) = \beta z_i \psi(x) + \sum_j \frac{1}{2} \int_{-\infty}^{\infty} dy C_{ij}^0(|x-y|) h_j(y). 
\]  
(4.A.1)

The force acting on a slab of fluid confined between the planes \( x = 0 \) and \( x = L \) by the fluid in \( x > L \) is

\[
F(L) = -\sum_i \rho_i \int_0^L dx [1 + h_i(x)] \frac{d\Phi_i(x)}{dx}. 
\]  
(4.A.2)

Using the first equality in Eq. (4.A.1), the force acting on the fluid in \( x \geq 0 \) is

\[
F(\infty) = kT \sum_i \rho_i \int_0^\infty \frac{dh_i(x)}{dx} dx = -kT \sum_i \rho_i h_i(0). 
\]  
(4.A.3)

Another expression for \( F(\infty) \) can be derived using the second equality in Eq. (4.A.1) for \( \Phi_i(x) \). From the one-dimensional Poisson equation and Eq. (4.1.26) we have the identity

\[
\sum_i \rho_i z_i e \int_0^\infty [1 + h_i(x)] \frac{d\psi(x)}{dx} dx = \frac{2\pi \sigma_a^2}{\varepsilon} = \frac{\varepsilon E^2}{8\pi}. 
\]  
(4.A.4)

Thus combining Eqs. (4.A.1) - (4.A.4) we have

\[
F(\infty) = -kT \sum_i \rho_i h_i(0) = -\frac{\varepsilon E^2}{8\pi} + \lim_{L \to \infty} I(L), 
\]  
(4.A.5)

where

\[
I(L) = 2\pi kT \sum_{i,j} \rho_i \rho_j \int_{-\infty}^{\infty} dy \int_0^L dx [1 + h_i(x)](x-y) C_{ij}^0(|x-y|) h_j(y). 
\]  
(4.A.6)

Since \( I(L) \) only involves short ranged direct correlation functions, the evaluation of this term is the same for cases (a) and (b). To evaluate this we replace \( h_j(y) \) by \( g_j(y) = 1 + h_j(y) \) since the dy
integral is odd about $y = x$. Putting $t = x - y$ we get

$$I(L) = 2\pi kT \sum_{i,j} \rho_i \rho_j \int_0^\infty dt \int_0^L dx \, g_i(x) [g_j(x-t) - g_j(x+t)]$$

Putting $t = x - y$ we get

$$I(L) = 2\pi kT \sum_{i,j} \rho_i \rho_j \int_0^\infty dt \int_0^L dx \, [g_i(x) g_j(x+t)]$$

where the second member of Eq. (4.A.7) follows from $g_i(x) = 0$, $x < 0$ (see Eq. (4.1.22)). Now as $L \to \infty$ and since $c_{ij}$ is a short ranged function, the integrand in brackets may be replaced by unity because $h_i(x) \to 0$ as $x \to \infty$. Thus from Eq. (4.A.5) we have the result

$$kT \sum_{i,j} \rho_i h_i(0) = \frac{eE^2}{8\pi} - \frac{1}{2} kT \sum_{i,j} \rho_i \rho_j \tilde{c}_{ij}(0)$$

where $\tilde{c}_{ij}(k)$ is the three-dimensional Fourier transform of $c_{ij}(r)$. From the Kirkwood-Buff theory [18], the compressibility of a fluid mixture is

$$\chi = \frac{8}{\pi} \left( \sum_i \rho_i - \sum_{i,j} \rho_i \rho_j \tilde{c}_{ij}(0) \right)^{-1}$$

For an electrolyte

$$\sum_{i,j} \rho_i \rho_j \tilde{c}_{ij}(0) = \sum_{i,j} \rho_i \rho_j \tilde{c}_{ij}(0)$$

because of the bulk electroneutrality condition (see Eqs. (4.1.17) and (4.1.18)). Combining Eqs. (4.A.8) and (4.A.9) we have the desired result, Eq. (4.1.28),

$$kT \sum_{i} \rho_i [1 + h_i(0)] = \frac{eE^2}{8\pi} + \frac{1}{2} (kT \sum_{i} \rho_i + \chi^{-1})$$

For the case of a simple fluid (non-electrolyte) at a surface where the surface-fluid potential consists of a hard core part plus a tail $v_i(x)$, $\beta z_i c_{ij}(x)$ in Eq. (4.1.1) is replaced by $\beta v_i(x)$ in the HNC approximation, and the result for the contact value is
\[ \frac{kT \sum \rho_i \left[1 + h_i(0) \right]}{i} = \sum \rho_i \int_0^\infty \left[1 + h_i(x) \right] \frac{dv_i(x)}{dx} \, dx + \frac{1}{2} \left( kT \sum \rho_i + X^{-1} \right). \] 

(4.1.11)

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CHAPTER 5
FINITE ION SIZE AND IONIC ADSORPTION

5.1 DERIVATION OF HNC/MSA EQUATIONS

In this chapter we extend the results of the previous chapter to enable consideration of specific or non-Coulombic interactions between the ions and the surface. This extension to adsorbing electrolyte is achieved through modelling the short-ranged specific adsorption interactions by Baxter's sticky potential [1]. We can then derive the HNC/MSA equations for RPM adsorbing electrolyte. Just as the connection between modified Gouy-Chapman theory, cluster expansion results [2], the potential approach [3] and the HNC/MSA equations was demonstrated in Chapter 4, so in Section 5.2 we compare the HNC/MSA treatment of ionic adsorption from a RPM electrolyte with earlier theories [2,4-6]. Numerical results for both thermodynamic (surface potential) and structural (distribution functions) quantities are presented in Section 5.3, chiefly for the case representing anion adsorption onto a mercury electrode.

The electrolyte is taken to be an RPM electrolyte with ionic diameter R and the surface is assumed to be hard, uniformly charged and non-polarizable.

The surface or wall is taken initially as a large spherical particle of diameter $R_0$ and carries a charge $z_0e$. The planar result is obtained in the limit $R_0 \to \infty$, which is to be taken at constant
surface charge density of the wall: \( \sigma_0 = z_0 e/\pi R_0^2 \). We shall call \( \sigma_0 \) the intrinsic charge density on the wall. The interaction potential between an ion of species \( i \) and the wall is written as

\[
u_{i0}(r) = u_{i0}^S(r) + u_{i0}^c(r), \quad (5.1.1)
\]

where

\[
u_{i0}^c(r) = \frac{z_i z_0 e^2}{\varepsilon r}, \quad 0 < r < \infty \quad (5.1.2)
\]

is the Coulomb potential, and \( u_{i0}^S(r) \) is the non-Coulombic or specific interaction taken to be of the form

\[
u_{i0}^S(r) = \infty, \quad r < R_{i0} \equiv \frac{1}{2}(R + R_i)
\]

\[
u_{i0}^S(r) = \Phi_i(r), \quad r > R_{i0}. \quad (5.1.3)
\]

The structure of the electrolyte at the wall is obtained by solving the Ornstein-Zernike (OZ) equations for the ion-wall indirect correlation function \( h_{i0}(r) \)

\[
h_{i0}(r) = c_{i0}(r) + \sum_j \rho_j \int dr' c_{ij}(|r-r'|) h_{j0}(r'). \quad (5.1.4)
\]

For the moment, we take the bulk direct correlation functions \( c_{ij}(r) \) to be known functions. The wall-ion HNC closure, whose status has been considered elsewhere (see Ref. 7 and Section 4.1) may now be used to provide an additional relation between \( h_{i0} \) and \( c_{i0} \)

\[
1 + h_{i0}(r) = \exp[-\beta u_{i0}(r) + h_{i0}(r) - c_{i0}(r)]
\]

\[
= \exp\left[-\beta u_{i0}^S(r)\right] \exp\left[-\beta u_{i0}^c(r) + h_{i0}(r) - c_{i0}(r)\right]. \quad (5.1.5)
\]

We parametrize the Boltzmann factor associated with the short range specific potential by a Dirac \( \delta \)-function
\begin{equation}
\exp\left(-\beta u_i^{S}\left(r\right)\right) = a_i \delta(r - R_{i0}), \quad \text{for } r < R_{i0} \tag{5.1.6}
\end{equation}

\begin{equation}
= 1, \quad \text{for } r > R_{i0}
\end{equation}

where

\begin{equation}
4\pi R_{i0}^2 a_i = \int_{r > R_{i0}} e^{-\beta \phi_i(r)} (e^{\delta(r)} - 1) \, dr. \tag{5.1.7}
\end{equation}

Equations (5.1.4) - (5.1.6) require \( h_{i0} \) and \( c_{i0} \) to have the form

\begin{equation}
\begin{aligned}
h_{i0}(r) &= b_i \delta(r - R_{i0}) + h_{i0}^+(r) \tag{5.1.8} \\
c_{i0}(r) &= b_i \delta(r - R_{i0}) + c_{i0}^+(r)
\end{aligned}
\end{equation}

with

\begin{equation}
h_{i0}^+(r) = -1, \quad \text{for } r < R_{i0} \tag{5.1.9}
\end{equation}

\begin{equation}
1 + h_{i0}^+(r) = \exp\left(-\beta u_i^c(r) + h_{i0}^+(r) - c_{i0}^+(r)\right), \quad \text{for } r > R_{i0}. \tag{5.1.10}
\end{equation}

The "starred" functions contain no delta functions and \( b_i \) is a constant that is determined by matching coefficients of the delta functions in Eq. (5.1.5)

\begin{equation}
b_i = a_i \left( \exp\left(-\beta u_i^c + h_{i0}^+ - c_{i0}^+\right) \right)_{r = R_{i0}^+} \\
= a_i [1 + h_{i0}^+(R_{i0}^+)], \tag{5.1.11}
\end{equation}

where the second equality follows from Eq. (5.1.10).

We proceed to obtain a set of one-dimensional integral equations for ionic distribution functions at a plane surface. We begin by separating explicitly the long-ranged part of the bulk direct correlation function

\begin{equation}
c_{ij}(r) = \frac{\beta z_i z_j e^2}{\epsilon r} + c_{ij}^o(r), \quad 0 < r < \infty, \tag{5.1.12}
\end{equation}

where \( c_{ij}^o \) is a short-ranged function. Combining Eqs. (5.1.4), (5.1.8) and (5.1.10) it is straightforward to show that \( r > R_{i0} \)
\[ \ln[1 + h_{1o}^*(r)] = -\frac{\beta z_1 e}{e} \left\{ z_0 e + 4\pi \eta^2 \rho_\beta + 4\pi e \int_{R_{1o}^+}^{\infty} dr' r'^2 \Sigma \rho_j z_j h_{j0}(r') \right\} \]

\[ - \beta z_1 e \psi(r) + \Sigma \rho_j \int dr' c_{ij}^0 (|r' - r|) h_{j0}(r'), \quad (5.1.13) \]

where

\[ \sigma_\beta \equiv \Sigma \rho_j z_j e b_j \quad (5.1.14) \]

is the adsorbed surface charge density and

\[ \psi(r) = \frac{4\pi}{e} \lim_{r \to \infty} dr' r' \left( 1 - \frac{r'}{r} \right) \Sigma \rho_j z_j e h_{j0}(r') \quad (5.1.15) \]

is the mean electrostatic potential. The three terms in braces in Eq. (5.1.13) mutually cancel because of electroneutrality since they represent, respectively, the intrinsic charge on the wall, the adsorbed charge and the charge in the diffuse part of the double layer.

We can now take the planar limit \((R_0 \to \infty)\) using the substitutions

\[ x = r - R_{1o} \]
\[ y = r' - R_{1o} \]

\[ h_1(x) = h_{1o}^*(x + R_{1o}) = h_{1o}^*(r). \quad (5.1.16) \]

Equations (5.1.9) and (5.1.13) simplify to

\[ h_1(x) = -1, \quad x < 0 \quad (5.1.18) \]

\[ \ln[1 + h_1(x)] = -\frac{\beta z_1 e \psi(x)}{e} + \Sigma \rho_j \int_{-\infty}^{\infty} dy c_{ij}^0 (|x - y|) h_j(y) \]

\[ + \Sigma \rho_j b_j c_{ij}^0 (x), \quad x > 0, \quad (5.1.19) \]

where

\[ c_{ij}^0 (x) = 2\pi \int_x^{\infty} dr r c_{ij}^0 (r) \quad (5.1.20) \]

\[ \psi(x) = \frac{4\pi}{e} \int x dy (x - y) \Sigma \rho_j z_j e h_j(y). \quad (5.1.21) \]
Eqs. (5.1.18) - (5.1.21) have to be solved subject to the boundary conditions
\[ \sigma_0 + \sigma_\beta + \int_0^\infty dx \sum_i z_i e h_i(x) = 0 \quad (5.1.22) \]
\[ b_i = a_i [1 + h_i(0^+)] \quad (5.1.23) \]

The adsorption parameter \( a_i \) is related to the non-Coulombic adsorption potential \( \Phi_i(x) \) by (cf. Eq. (5.1.7))
\[ a_i = \int_0^\infty \left( e^{-\beta \Phi_i(x)} - 1 \right) dx \quad (5.1.24) \]
and the potential at the charged wall, \( \psi_0 \), is given by
\[ \psi_0 = \psi_\beta + \frac{2\pi R}{e} \sigma_0 \quad (5.1.25) \]
where
\[ \psi_\beta \equiv \psi(x=0) = -\frac{4\pi}{e} \int_0^\infty dy \sum_i z_i e h_i(y) \quad (5.1.26) \]
is the potential at the plane of adsorbed charges. Once the bulk direct correlation functions \( c^0_{ij}(r) \), the adsorption potentials \( \Phi_i(x) \) and the intrinsic surface charge density \( \sigma_0 \) are specified, the properties of the electrical double layer can be determined by solving Eqs. (5.1.8) - (5.1.26).

We observe that the inclusion of ionic adsorption gives rise to an additional term in the potential of mean force between an ion and the charged wall — the last term in Eq. (5.1.19). It is easy to see that this term represents hard sphere and short-range electrostatic interactions between ion \( i \) in the diffuse layer and all the adsorbed ions. The presence of this additional term alters the equation for the contact density of the ions. The new contact condition can be derived by using the identity.
\[ \sum \rho_i [1 + h_i(0)] = \sum \rho_i - \int_0^\infty dx \sum \rho_i [1 + h_i(x)] \frac{d}{dx} \ln[1 + h_i(x)] \] (5.1.27)

Substituting Eq. (5.1.19) into Eq. (5.1.27) and using the techniques of the Appendix of Chapter 4 we find

\[ \sum \rho_i [1 + h_i(0)] = \frac{2\pi \beta}{e} (\sigma_0 + \sigma_0^*)^2 + \beta \left( \sum \rho_i + \frac{\beta}{\chi} \right) + 2\pi \int_0^\infty dx x \sum \rho_i [1 + h_i(x)] \left( \sum \rho_i b_1 c_{ij}^0(x) \right), \] (5.1.28)

where, as before,

\[ \chi = \beta \left( \sum \rho_i - \sum \rho_i \rho_j \int dr c_{ij}^0(r) \right)^{-1} \] (5.1.29)

is the isothermal compressibility of the electrolyte. The result given by Eq. (5.1.28) serves as a useful check on the internal consistency of numerical calculations.

So far, we have made no assumptions about the bulk properties of the electrolyte. As in the previous chapter, we use the MSA for bulk electrolyte interactions. Hence Eqs. (5.1.18) - (5.1.26) and Eqs. (4.2.2) - (4.2.7) define the HNC/MSA treatment of ionic adsorption from an RPM electrolyte.

5.2 COMPARISON WITH EXISTING THEORIES OF IONIC ADSORPTION

In order to clarify the approximations inherent in the HNC/MSA equations, we first consider two simplifications: (i) the point ion limit \((R \to 0)\) and (ii) the limit of small potentials \(|\beta \psi_\beta| < 1\) but \(R \neq 0\). In the third part of this section, we examine the contributions to the potential of mean force in the HNC/MSA equations and compare with earlier "discrete-ion" theories of ionic adsorption.
A. The Point-Ion Limit

The neglect of ion size within the HNC/MSA is equivalent to setting

\[ \zeta_i^0(r) = 0 \]  

so that Eq. (5.1.19) gives

\[ \ln[1 + h_1(x)] = -\beta z_1 e \psi(x) \]  

which, together with Poisson's equation, gives the Gouy-Chapman theory.

For simplicity we consider a 1:1 electrolyte with one adsorbing species, which we take to be species 2. Therefore in the point-ion limit, the adsorbed surface charge density is

\[ \sigma\beta = \rho_2 z_2 e \exp(-\beta z_2 e \psi) \]  

We can compare this result with the Stern isotherm,

\[ \sigma\beta = \frac{z_2 e N_s}{1 + \frac{N_A}{\rho_2 M} \exp(\beta z_2 e \psi + \beta \phi_2)} \]  

where \( N_s \) is the surface density of adsorption sites, \( N_A \) is Avogadro's number, \( M \) is the molecular weight of the solvent and \( \phi_2 \) is the specific adsorption potential. As \( \phi_2 \) becomes more negative, the adsorption becomes stronger and eventually the adsorbed surface charge density saturates to the value

\[ \sigma_{\beta}^{\text{max}} = z_2 e N_s \]  

as \( \beta \phi_2 \to -\infty \). At low coverage, we can simplify Eq. (5.2.4) to

\[ \sigma\beta = \rho_2 z_2 e \left\{ \frac{N}{N_A} \right\} \exp(-\beta \phi_2) \exp(-\beta z_2 e \psi) \]  

which is of the same form as Eq. (5.2.3) with
\[ a_2 \equiv \left( \frac{N_M}{N_A} \right) \exp(-\beta \phi_2) \quad \text{(5.2.7)} \]

If we use the Gouy-Chapman result

\[ \beta \psi_\beta = 2 \sinh^{-1} \left( \frac{2 \pi \beta e}{eK} (\sigma_\beta + \sigma_0) \right) \equiv 2 \sinh^{-1}(\tilde{\sigma}_t) \quad \text{(5.2.8)} \]

in Eq. (5.2.3), we find

\[ \sigma_\beta = \rho_2 z_2 e a_2 [\tilde{\sigma}_t + (\tilde{\sigma}_t^2 + 1)^{\frac{1}{2}}]^{-2z_2} \quad \text{(5.2.9)} \]

from which it is easy to verify that \( \sigma_\beta \) does not saturate in the strong adsorption limit, \( a_2 \to \infty \). In our model, this lack of saturation in the point-ion limit is not unexpected since there is no extra parameter corresponding to \( N_s \), the adsorption site density. Therefore, in the point-ion limit, the HNC/MSA theory of ion adsorption is equivalent to the Gouy-Chapman-Stern model at low surface coverage.

In the absence of an intrinsic surface charge, \( \sigma_0 = 0 \), our model can be made to mimic a neutral surface that acquires a charge by a surface reaction of the kind

\[ A + H^+ \rightleftharpoons AH^+ \quad \text{(5.2.10)} \]

which can be regarded as the adsorption of, say, hydrogen ions. The reaction is governed by a dissociation constant \( K \)

\[ K = \frac{[A][H^+]_S}{[AH^+]} \quad \text{(5.2.11)} \]

where \([H^+]_S\) is the concentration of adsorbing ions at the surface. In the point-ion limit, we have

\[ [H^+]_S = \rho_2 [1 + h_2(0)] = \rho_2 \exp(-\beta z_2 e \psi_\beta) \quad \text{(5.2.12)} \]

In this mass-action model, the adsorbed surface charge density is [8]
\[ \sigma_\beta = \frac{z_2 eN_s}{1 + \frac{K}{\rho_2} \exp(\beta z_2 e\psi_\beta)} \]  
\hspace{1cm} (5.2.13)

which reduces to the weak adsorption result
\[ \sigma_\beta = z_2 e\rho_2 \frac{N_s}{K} \exp(-\beta z_2 e\psi_\beta) \]  
\hspace{1cm} (5.2.14)

provided \( K >> \rho_2 \), or equivalently
\[ \text{pH} > \text{pK} \]  
\hspace{1cm} (5.2.15)

where \( \text{pH} = -\log_{10} \rho_2 \), \( \text{pK} = -\log_{10} K \). Hence by comparing Eqs. (5.2.3) and (5.2.14) we can identify \( a_2 \) with \( N_s/K \) as long as Eq. (5.2.15) is satisfied. Thus ion adsorption in the point-ion limit of the HNC/MSA at \( \sigma_0 = 0 \) is equivalent to the weak adsorption regime of the mass-action model.

\section*{B. Linearized Equations (\( R \neq 0 \))}

For the case of small potentials \( (|\beta e\psi_\beta| < 1) \), the left hand side of Eq. (5.1.19) can be linearized and we recover the MSA for an interface with both intrinsic and adsorbed surface charges. An analytic solution is presented in the Appendix to this chapter. The result for the surface potential is
\[ \psi_\beta = \frac{4\pi}{\epsilon K} \left[ \sigma_\beta + \sigma_0 (1 + \frac{4\pi \rho_2 e a_2}{\epsilon K B}) \right] \]  
\hspace{1cm} (5.2.16)

which is just the sum of the potentials due to the intrinsic and adsorbed surface charges \([6,9]\). The adsorption isotherm is
\[ \sigma_\beta = \rho_2 z_2 e b_2 = \frac{\rho_2 z_2 e a_2 \frac{1 + 2\eta}{(1 - \eta)^2} - \frac{4\pi \beta z_2 e^2 \sigma_0}{\epsilon K}}{1 + \rho_2 a_2 \frac{\pi R^2}{1 - \eta} + \frac{4\pi \beta z_2^2 e^2}{\epsilon K} (1 + B)} \]  
\hspace{1cm} (5.2.17)

This expression is only valid if
\[
\frac{4\pi \beta z_2 \sigma_d}{\varepsilon \kappa} \leq \frac{1 + 2\eta}{(1 - \eta)^2}
\] (5.2.18)

otherwise the distribution function \([1 + h_2(x)]\) will be negative at contact.

The diffuse layer charge density is given by

\[
\rho_{CH}(x) = -\sigma_0 \kappa + \sum_i \rho_i z_i^2 \sigma_\beta Q_{11}(x) + \sum_i \rho_i z_i^2 \int_0^x Q_{11}(y) \rho_{CH}(x - y) \, dy,
\] (5.2.19)

where

\[
Q_{11}(x) = -\frac{4\pi \beta e^2}{\varepsilon \kappa}, \quad x > R
\] (5.2.20)

and

\[
Q_{11}^0(x) = \frac{4\pi \beta e^2}{\varepsilon \kappa} B \left(1 - \frac{x}{R} \right), \quad x < R
\] (5.2.21)

so that \(Q_{11}^0(x) = 0, \quad x > R\).

Eq. (5.2.19) can be rewritten as

\[
\rho_{CH}(x) = -(\sigma_0 + \sigma_\beta) \kappa + \sum_i \rho_i z_i^2 \sigma_\beta Q_{11}^0(x) - \kappa \int_0^x \rho_{CH}(y) \, dy
\]

\[
+ \sum_i \rho_i z_i^2 \int_0^R Q_{11}^0(y) \rho_{CH}(x - y) \, dy
\] (5.2.22)

so that Eqs. (5.2.16) - (5.2.22) are the generalizations of Eqs. (2.20), (2.32) and (2.39) of Ref. 6 to the case of an interface with both intrinsic and adsorbed surface charge.

We note that the linear result, Eq. (5.2.17), like Eq. (2.39) of Ref. 6 (which can be obtained from Eq. (5.2.17) by setting \(\sigma_0 = 0\)), implies that the adsorbed surface charge density, \(\sigma_\beta\), will saturate in the strong adsorption limit, \(a_2 \to \infty\).
This saturation is still present in the limit $R = 0$. Moreover, we observe that the linear result in the $R = 0$ limit can also be obtained by linearization of Eqs. (5.2.3) and (5.2.8) which in their non-linear form do not show any saturation in $\sigma_\beta$ as $a_2 \to \infty$. Thus the form of saturation of $\sigma_\beta$ implied by Eq. (5.2.23) and Eq. (3.29) of Ref. 6 is an artifact of linearization.

In the present model of ion adsorption there is no parameter corresponding to the adsorption site density, $N_S$. Nevertheless, excluded volume interactions in the adsorbed layer can result in saturation when the adsorption density approaches the two-dimensional close packed limit. However, lateral interactions are not handled properly in the HNC/MSA so we do not expect a natural upper bound in the adsorption density to emerge from our calculation. Even so, as we shall see in the next section, at low surface coverage where the HNC/MSA is expected to be applicable we can see interesting and significant differences between the point-ion Gouy-Chapman-Stern theory and the HNC/MSA.

C. HNC/MSA Equations

We now examine the contribution to the HNC/MSA potential of mean force due to the adsorption of finite ion size ions. As in the previous chapter we analytically extract correction terms to the Gouy-Chapman result in the limit of low ionic density. Using the density expansion of $C_{ij}^{\text{MSA}}$ in Eq. (5.1.19) we can write the potential of mean
The force of species $i$ in the form

$$W_i(x) = z_i e^\psi(x) + W_i(2a)(x) + W_i(2b)(x) + ... + W_i^{\text{ad}}(2a)(x) + W_i^{\text{ad}}(2b)(x) + ...$$

(5.2.24)

where only terms up to linear order in the ionic density are exhibited. The Gouy-Chapman theory only keeps the first term on the right hand side of Eq. (5.2.24). The terms $W_i^{(2a)}$ and $W_i^{(2b)}$ which are of the same order (linear) in ionic density have been considered in detail in Chapter 4. To recapitulate, they represent, respectively, finite ion size contributions to the excluded volume and electrostatic interactions in the diffuse double layer. The ion size corrections to the interaction between an ion of species $i$ located at $x$ with the adsorbed layer are given by the terms

$$W_i^{\text{ad}}(2a)(x) = R \left( \frac{a_2}{R} \rho_2 [1 + h_2(0)] kT \right) \pi (R^2 - x^2), \quad x < R$$

$$= 0, \quad x > R \quad (5.2.25)$$

$$W_i^{\text{ad}}(2b)(x) = - z_i R \left( \frac{a_2}{R} \rho_2 [1 + h_2(0)] \right) \frac{e^2}{E} 2\pi (R - x), \quad x < R$$

$$= 0 \quad x > R \quad (5.2.26)$$

These two terms are of the same order in the bulk density of adsorbing ions (species 2) and they originate from the last term of Eq. (5.1.19). A simple physical interpretation of $W_i^{\text{ad}}(2a)$ and $W_i^{\text{ad}}(2b)$ is as follows.

The first term $W_i^{\text{ad}}(2a)(x)$ can be interpreted as $R$ times the $x$-component of the force exerted on a sphere of radius $R$ centred at $x$ (that is, the co-sphere of an ion of diameter $R$) as it is inserted into a layer of thickness $R$ of ideal gas of density $\left( \frac{a_2}{R} \rho_2 [1 + h_2(0)] \right)$, located adjacent to the charged wall (see Fig. 1). Consequently this term will act to repel all ions from the surface and increase the extent of the diffuse layer.
The second term, \( W_1^{\text{ad}(2b)}(x) \) is \( R \) times the electrostatic force between a point-ion at \( x \) and a uniform volume charge of density \(- z_2 e a_2 R [1 + h_2(0)]\) contained in the conical section subtended by the interaction of the co-sphere and the plane \( x = R \) (see Fig. 1). A more appropriate physical picture of this contribution should only involve the spherical cap bounded by the plane \( x = R \). At contact, \( x = 0 \), both interpretations give the same result. \( W_1^{\text{ad}(2b)} \) is always attractive for the adsorbing species and repulsive for the indifferent ion. When the adsorbing species is also the counter-ion this term acts to decrease the extent of the diffuse layer.
Fig. 1: Schematic illustration of the overlap between the co-sphere of an ion in the diffuse layer and the layer of adsorbed ions.
The separation of the potential of mean force into separate contributions from the diffuse and adsorbed layers and the interpretation of the adsorbed layer contribution as $R$ times a force is a consequence of the delta-function nature of our adsorption potential. Even so, it is still valid to conclude that, as a result of ion adsorption, ion size corrections to the potential of mean force consist of two types: hard sphere excluded volume terms which tend to increase the extent of the diffuse layer and ion size corrections to the electrostatic interaction (self atmosphere terms) whose effect depends on the relative signs of the adsorbing species and the net surface charge. From Eqs. (5.2.25) and (5.2.26) it is easy to verify, at least to lowest order in density, that ion size corrections to the electrostatic interaction are more important. The same is true for the diffuse layer terms, $W_1^{(2a)}$ and $W_1^{(2b)}$, which have been considered in detail for the case with no ion adsorption in Chapter 4.

We now compare the HNC/MSA equations with earlier theories of ion adsorption \cite{2,5}. Using Eqs. (5.1.14), (5.1.19), (5.1.23) and (5.2.24) we can write our adsorption isotherm as

$$\sigma_\beta = \rho_2 a_2 e z_2 \exp\left\{-\beta \left( z_2 e \psi_\beta + W_2^{(2a)}(0) + W_2^{(2b)}(0) + \cdots \right) + W_2^{ad(2a)}(0) + W_2^{ad(2b)}(0) + \cdots \right\}.$$ \hspace{1cm} (5.2.27)

This can be compared with Levine et al.'s expression \cite{10}

$$\sigma_\beta = \frac{\alpha}{n_0} \left( \frac{N_s z_2 e - p \sigma_\beta \rho a}{\rho - 1} \right) \exp\{-\beta \left[ \phi_2 + z_2 e \psi_\beta + z_2 e \psi_\beta \right]\},$$ \hspace{1cm} (5.2.28)

where $\alpha$ is the activity of the species 2 in the bulk electrolyte, $N_s$ is the maximum adsorption site density, $n_0$ is the density of water molecules in the aqueous phase, $\phi_2$ is the real specific adsorption
potential and $\phi_2$ is the self-atmosphere potential of the adsorbed ion. The parameter $p_a$ specifies the number of sites that an adsorbed ion occupies [10].

Since our model has no fixed adsorption sites, we do not have the same pre-exponential term, except for $a_2$ which can be clearly identified with $\exp(-\beta \phi_2)$. The term due to the mean electrostatic potential is common to both Eqs. (5.2.27) and (5.2.28) but terms like $w_2^{(2a)}(0)$ and $w_2^{(2b)}(0)$ do not appear in Eq. (5.2.28) since the diffuse layer is treated in the point-ion limit by Levine et al. [3]. Adsorbed layer repulsive terms such as $w_2^{ad(2a)}(0)$ are also absent from Eq. (5.2.28). The self-atmosphere term which had been invoked to explain various experimental anomalies can be identified with $w_2^{ad(2b)}(0)$. However, a comparison of $w_2^{ad(2b)}(0)$ with the expression for the self-atmosphere term [10] will reveal that the latter is larger by a factor $\sim \varepsilon/\varepsilon_S$ where $\varepsilon_S$ is the dielectric constant of the inner layer (or Stern layer). The reason for the difference is that our model takes the dielectric constant of the solvent to be the bulk value, $\varepsilon$, up to the surface rather than making a further assumption about the presence of a Stern layer. A consequence of this is that, when using Eq. (5.2.28), much smaller values of $\phi_2$ (viz. $a_2$) are required in order to obtain dramatic deviations from Gouy-Chapman-Stern theory. Indeed, this larger value for the self-atmosphere term is crucial for an explanation of experimental results.

Buff and Stillinger [2] have used cluster expansions to derive an adsorption isotherm that expresses the contributions $w_2^{ad(2a)}(0)$ and $w_2^{ad(2b)}(0)$ in terms of the equation of state and pair distribution functions of the two-dimensional fluid of discharged adsorbed ions. This feature is lost in our treatment because use of the Ornstein-
Zernike equation Eq. (5.1.4) together with a simple closure between \( c_{1o}(r) \) and \( h_{1o}(r) \) entails loss of information about lateral interactions in the fluid. Such lateral interactions are crucial for a proper description of the contributions to the potential of mean force from the adsorbed layer.

5.3 RESULTS AND CONCLUSIONS

As in Chapter 4, the HNC/MSA equations, Eqs. (5.1.14), (5.1.18) - (5.1.26) and (4.2.2) - (4.2.27), were solved by direct iteration with parameters \( \varepsilon = 78.5 \), \( T = 298 \) K, \( R = 4.25 \) Å for a range of concentrations (0.01 M - 0.5 M). The contact condition Eq. (5.1.28) was satisfied to within 5% for 0.5 M electrolyte and to within 1% for the lower concentrations.

Most of our calculations have been performed with a view to represent a physical system such as anionic adsorption on mercury. In this case, the adsorbing species (species 2) are anions, the intrinsic surface charge, \( \sigma_0 \), has a range of values (-30 \( \mu \)C/cm\(^2\) - +40 \( \mu \)C/cm\(^2\)) and \( a_2/R \) is varied from 0.1 to 100. We also briefly discuss some calculations where the adsorbing species are cations, \( \sigma_0 = 0 \) and \( a_2 \) is fixed by the identification mentioned beneath Eq. (5.2.15). This is meant to represent an interface that acquires surface charge by a surface association reaction.

For the purpose of comparison we also present results in the point-ion limit, \( R = 0 \). This limit is tantamount to replacing Eq. (5.1.19) by Eqs. (5.2.1) and (5.2.2).

Numerical results for the surface potential-surface charge \( (\psi_0 - \sigma_0) \) relationship are presented in Figs 2-4 for 1:1 electrolytes.
of concentrations 0.01 M, 0.1 M and 0.5 M, respectively. Allowing for
the change in scale from Fig. 2 to Fig. 3, one can see that as the
electrolyte concentration is decreased, differences between the
HNC/MSA and the point-ion limit for $\sigma_0 < 10 \mu C/cm^2$ decrease; for
$\sigma_0 > 10 \mu C/cm^2$, these differences increase.

The potential at the point of zero charge ($\psi_{pzc}$) appears to
develop more rapidly with concentration for the HNC/MSA than for the
point-ion limit — the difference depending on the parameter $a_2$. This
is in accord with the usual invocation of discrete charge effects to
explain the Esin-Markov effect, namely that the experimentally
measured values of $d\psi_{pzc}/d LN_c$ are two or three times higher than that
theoretically attainable in the point-ion limit [11-13]. Our results
show only small deviations from the point-ion limit, and the reason is
that our adsorbed layer self-atmosphere term (Eq. (5.2.25)) is smaller
than the usual one [3] by a factor $e/e_s$ because we have not postulated
the a priori existence of the Stern layer.

The general form of the results in Figs. 2-4 can be explained
using the results of the previous section. For negative $\sigma_0$, where the
adsorbing anions are co-ions and are therefore repelled from the
surface as a result of electrostatic interactions, there is little
adsorption except for the largest value of $a_2$ so that the $\psi_B$ vs. $\sigma_0$
curves in this regime are almost the same as the case of no adsorption.
For positive values of $\sigma_0$ where the adsorbing anions are now the
counter-ions, there is appreciable adsorption as the effects of the
new terms, $W_i^{ad}$, in the potential of mean force become significant (see
Eqs. (5.2.24) - (5.2.26)). In fact these terms are responsible for the
increasing differences between the HNC/MSA and point-ion limit result
as $a_2$ is increased. The above comments can be applied to most of the
Fig. 2: Surface potential, $\psi_B$, as a function of intrinsic surface charge, $\sigma_0$, at 0.01 M for adsorption strengths $a_2/R$: (a) 0.1, (b) 1.0, (c) 5.0. (--- HNC/MSA), (-- -- point-ion limit.)
Fig. 3: Surface potential, $\psi_\beta$, as a function of intrinsic surface charge, $\sigma_0$, at 0.1 M for adsorption strengths $a_z/R$: (a) 0.1, (b) 1.0, (c) 5.0. (—— INC/MSA), (——— point-ion limit). The vertical bar marked A indicates the parameters appropriate to case A discussed in the text.
Fig. 4: Surface potential, $\psi_0$, as a function of intrinsic surface charge, $\sigma_0$, at 0.5 M for adsorption strengths $a_2/R$: (a) 0.1, (b) 1.0, (c) 5.0, (d) 100. (--- HNC/MSA), (--- point-ion limit). The vertical bars marked B and C indicate the parameters appropriate to cases B and C discussed in the text.
surface charge vs. surface potential curves shown in Figs. 2-4. The case $a_2/R = 100, 0.5 \text{ M}$ (Fig. 4, curves d) is interesting and deserves further comments. At $\sigma_0 = 0$, the HNC/MSA potential-at-zero-charge is larger in magnitude than the point-ion result. This is because adsorption is enhanced by the dominant finite ion size correction to the electrostatic interaction between an ion and the adsorbed surface charge $-w_1^{ad(2b)}$ in Eq. (5.2.26) — which always attracts the adsorbing ions towards the surface. As $\sigma_0$ becomes negative, the contribution from $w_1^{ad(2b)}$ to the adsorbing species is counter-acted by a similar term $w_1^{(2b)}$ in the potential of mean force (cf. Eq. (5.2.24)) which accounts for the ion size correction to the interaction between ions in the diffuse layer. The term $w_1^{(2b)}$ repels co-ions from the surface — for $\sigma_0 < 0$, the adsorbing anions are co-ions. Thus the mutual cancellation of $w_1^{(2b)}$ and $w_1^{ad(2b)}$ for the adsorbing anions is responsible for the crossover between the HNC/MSA and point-ion limit result where in the latter case both $w_1^{(2b)}$ and $w_1^{ad(2b)}$ are assumed to be zero.

An interesting and important common feature among the results given in Figs. 2-4 is the maximum in $\psi_B$ as a function of $\sigma_0$. In the absence of ion adsorption the maxima in $\psi_B$ occur at around $+40 \mu\text{C/cm}^2$ in the concentration range between 0.1 M and 0.5 M. As a result of ion adsorption the maxima move to lower values of $\sigma_0$ as the adsorption strength, $a_2$, increases. Indeed, for $a_2/R = 100, 0.5 \text{ M}$, the maximum occurs at a small negative value of $\sigma_0$ ($-10 \mu\text{C/cm}^2$) — a feature that appears in Grahame's experiments on the adsorption of $\text{I}^-$ on mercury [14]. However, the maximum in Fig. 4, curve d, is shallower than that given by existing theories [3] that have been constructed to explain the experimental observations — the reason for the difference is the
absence of an inner or Stern layer of low dielectric constant.

The adsorbed surface charge density, $\sigma_B$, as a function of $\sigma_0$ is shown in Fig. 5. The small differences between the HNC/MSA curves and the point-ion curves show that $\sigma_B$ is less sensitive than $\psi_B$ to finite ion size effects. These differences become smaller as the electrolyte concentration is lowered. In all cases where the adsorbing species is the counter-ion, the magnitude of $\sigma_B$ is increased when finite ion size effects are included. This is to be expected in view of the effects of $W_{1}(2b)(x)$ and $W_{i}^{ad}(2b)(x)$ which have been discussed above.

An advantage of integral equation formulations of the double layer is that structural as well as thermodynamic information can be obtained. We now examine the wall-ion distribution functions for three cases of interest. The relevant properties of these cases are summarized in Table 1 as well as being indicated in Figs. 3 and 4. We note that in all cases the surface potentials are low to moderate, $|e\psi_B/\kappa T| \leq 3$, and the surface charges, $\sigma_0$, are in the regime where we should have some confidence in the HNC/MSA, $\sigma_0 \leq 20 \mu C/cm^2$.

To illustrate the interplay between ion adsorption and ion size effects we compare the HNC/MSA results with those obtained in the point-ion limit where ion size effects are ignored.

The wall-ion distribution functions for case A are shown in Figs. 6 and 7. From Fig. 3 we can see that ion size effects reduce $\psi_B$ and therefore must increase the amount of ion adsorbed, i.e. $|q_B|$ must increase. Consequently the contact value of the total correlation function, $h_2(0)$, of the adsorbing anions (which are also the counterions in this example), must be higher in the HNC/MSA. This result is
Fig. 5: Adsorbed surface charge, $\sigma_\beta$, as a function of intrinsic surface charge, $\sigma_0$, at 0.5 M.

(----- HNC/MSA), (----- point-ion limit).
Table 1
Parameters for the distribution functions shown in Figs. 6 - 11.

<table>
<thead>
<tr>
<th>Case</th>
<th>Concentration (M)</th>
<th>$a_z/R$</th>
<th>$\sigma_0$ (µC/cm$^2$)</th>
<th>$\sigma_0/\varepsilon R^2$</th>
<th>HNC/MSA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\sigma_0$ (µC/cm$^2$)</td>
</tr>
<tr>
<td>A</td>
<td>0.1</td>
<td>5</td>
<td>16.0</td>
<td>0.181</td>
<td>-13.6</td>
</tr>
<tr>
<td>B</td>
<td>0.5</td>
<td>5</td>
<td>10.7</td>
<td>0.120</td>
<td>-8.8</td>
</tr>
<tr>
<td>C</td>
<td>0.5</td>
<td>100</td>
<td>3.2</td>
<td>0.036</td>
<td>-15.0</td>
</tr>
</tbody>
</table>
Fig. 6: Case A. Wall-ion total correlation function for the indifferent species at 0.1 M, $a_2/R = 5$. HNC/MSA (---), point-ion limit (---).
Fig. 7: Case A. As in Fig. 6 but for the adsorbing species.
consistent with the observation that for $\sigma_0 > 0$ both ion size electrostatic corrections to the potential of mean force, $W_1^{(2b)}$ and $W_1^{\text{ad}(2b)}$, which are the dominant correction terms, act to attract the counter-ion and adsorbing ions towards the surface. In the contact condition, Eq. (5.1.28), the third term on the right hand side is now of the same magnitude as the second term. Because of the lower net surface charge, the adsorption excess

$$\Gamma_i = \rho_i \int_0^\infty h_i(x) \, dx \quad (5.3.1)$$

of species 2 is decreased and $h_2(x)$ is a shorter ranged function than that in the point-ion limit. As for species 1, the non-adsorbing cation (co-ion), all ion size correction terms in Eq. (5.2.24) serve to repel these ions from the surface. The contact value of $h_1(x)$ therefore becomes more negative and the crossover between HNC/MSA and the point-ion result is due both to the smaller net surface charge and to the need to preserve electroneutrality. The cusps in $h_1(x)$ and $h_2(x)$ at $x = R$ are artifacts of the use of the MSA for the bulk direct correlation functions $c_1^{\text{OMSA}}$ is discontinuous at $x = R$ whereas $c_1^{\text{OHNC}}$, for example, does not have this discontinuity.

The distribution functions for case B are given in Figs. 8 and 9. In the point-ion limit the surface has a small positive net surface charge. However, ion size effects, as discussed in case A, are sufficient to increase $|\sigma_\beta|$ to make the surface become net negative. The increase in $|\sigma_\beta|$ implies that the contact value of adsorbing anions, $h_2(0)$, must also increase. Since the surface is net negative the adsorbing anions, species 2, are also the co-ions so $h_2(x)$ must eventually become negative. The repulsion of the non-adsorbing species (1) (counter-ions) from the surface by $W_1^{\text{ad}(2b)}$ and the constraint of electroneutrality leads to the form of $h_1(x)$ shown in
Fig. 8: Case B. Wall-ion total correlation function for the indifferent species at 0.5 M, $a_2/R = 5$. HNC/MSA (———), point-ion limit (---).
Fig. 9: Case B. As in Fig. 8 but for the adsorbing species.
Fig. 8. The cusps at \( x = R \) are again artifacts of using \( \text{CoMSA}_{ij} \). We note that in case B the adsorption excesses in the HNC/MSA are of the opposite sign to those in the point-ion limit.

In case C, Figs. 10 and 11, the adsorbing anions, species 2, are now the co-ions because the surface is net negative. However, adsorption still takes place against the electrostatic repulsion of co-ions because of the large adsorption parameter \( (a_2/R = 100) \). The indifferent cation (species 1) is repelled from the wall, predominantly because of the finite ion size electrostatic correction, \( \tilde{w}_{1}^{\text{ad}(2b)}(x) \). This is reflected in a lowering of \( h_1(0) \) relative to the point-ion value.

Although the cusps at \( x = R \) are artifacts of using \( \text{CoMSA}_{ij} \), it is tempting to interpret the maxima in \( h_1(x) \) at \( x = R \) in Figs. 8 and 10 as an ion pairing phenomenon between the adsorbed anion and the non-adsorbing cation in the diffuse part of the double layer.

We reiterate our earlier remarks that in the three cases discussed above, the range of surface potentials and surface charges are in the regime where one would have some confidence in the HNC/MSA. Therefore it seems worthwhile to test the predictions of the HNC/MSA, in particular the results for the distribution functions shown in Figs. 8-11, against Monte Carlo experiments. To build in an adsorbed layer of ions in the Monte Carlo calculation, it is necessary to specify the value of the intrinsic surface charge \( \sigma_0 \) and the value of the adsorbed charge \( \sigma_B \), thereafter ions in the adsorbed layer are only permitted to move in the plane \( x = 0 \) during the sampling procedure.

In Fig. 12 we show the surface potential versus pH for a surface where the model of ionic adsorption is given by Eqs. (5.2.11) -
Fig. 10: Case C. Wall-ion total correlation function for the indifferent species of 0.5 M, $a_2/R = 100$. HNC/MSA (---), point-ion limit (-- --).
Fig. 11: Case C. As in Fig. 10 but for the adsorbing species.
Fig. 12: Surface potential $\psi_B$ as a function of adsorbing ion concentration at zero intrinsic surface charge. HNC/MSA (-----), point-ion limit (-----).
We would of course require a three-component electrolyte, e.g. HCl/NaCl, in order to fix pH and \( \kappa R \) independently. The special properties of \( C_{ij}^{\text{MSA}}(x) \) for a symmetric RPM electrolyte allow us to keep all equations the same as for a two-component electrolyte, except that \( a_2 \) is replaced by \( \frac{10^{11} N_s}{N_A R} \), where \( N_s \) is in cm\(^{-2} \), \( N_A \) is Avogadro's number and \( R \) is in Å. The surface potential is larger for the HNC/MSA than for the point-ion limit, for the same reasons that \( \psi_{pzc} \) is more negative for the HNC/MSA in Fig. 4. The only difference is that the adsorbing species for Fig. 12 is cationic.

In this chapter we have presented the first calculations of \( h_i^1(x) \) for adsorbing electrolyte against a charged surface that take finite ion size into account. Comparison with simplifying limits has shown the limitations of the treatment. The adsorption isotherm derived from the HNC/MSA equations lacks any saturation of adsorbed surface charge. This is necessary to even qualitatively obtain surface charge vs. pH relationships of surfaces with fixed adsorption sites, e.g. latex or oxide surfaces.

The second limitation is our omission of an inner layer dielectric constant \( \varepsilon_s \) that is substantially smaller than that of bulk solvent. This \textit{a priori} postulation of an inner layer is necessary to obtain quantitative results for the differential capacitance and the magnitude of the "discreteness-of-charge" effect. In Part 3 of this thesis we examine whether an inner layer can be derived from a Civilized Model electrolyte against a charged surface.

Even with these limitations, the HNC/MSA theory of ionic adsorption from a PM electrolyte shows interesting thermodynamic and structural behaviour (see especially Figs. 8-11) in regimes where we should have some confidence in the results.
APPENDIX

MSA/MSA THEORY OF IONIC ADSORPTION

In this appendix we shall use Baxter's method of factorizing the Ornstein-Zernike equation [15] to analytically solve the MSA/MSA equations for adsorbing electrolyte against a charged surface. Since we use Baxter's method extensively in Part 3 of this thesis, we shall first use the simple case of the bulk RPM electrolyte in the MSA to illustrate the use of Baxter's method.

Because of the symmetry of the MSA, we can write the correlation functions in the form

\[ f_{ij}(r) = f^{HS}_{ij}(r) + z_iz_j f^{C}(r), \quad (f = h \text{ or } c) \]  

which, when substituted into the Ornstein-Zernike equation

\[ \tilde{h}_{ij}(k) = \tilde{c}_{ij}(k) + \sum_k \rho_k \tilde{c}_{ik}(k) \tilde{h}_{kj}(k) \]  

yields

\[ \tilde{h}^{HS}(k) = \tilde{c}^{HS}(k) + \rho_s \tilde{c}^{HS}(k) \tilde{h}^{HS}(k) \]  

and

\[ \tilde{h}^{C}(k) = \tilde{c}^{C}(k) + \rho_c \tilde{c}^{C}(k) \tilde{h}^{C}(k), \]  

where

\[ \sum_j \rho_{j,j} = \rho_s \]  

and

\[ \sum_j z_{j,j} = \rho_c. \]

Eqs. (5.A.3) and (5.A.4) need to be solved subject to the boundary conditions

\[ h^{HS}(r) = -1, \quad r < R \]  

and

\[ h^{HS}(r) = 0, \quad r > R \]
and
\[ h^c(r) = 0, \quad r < R \] (5.A.9)
\[ c^c(r) = -\frac{6e^2}{\varepsilon r}, \quad r > R, \] (5.A.10)

where we have used the MSA closure on \( c_{ij}(r) \). Eqs. (5.A.3), (5.A.7) and (5.A.8) are just the Percus-Yevick equations for hard spheres.

Baxter's method can be most easily explained for a single component fluid. In this case,
\[ \tilde{h}(k) = \tilde{c}(k) + \rho \tilde{c}(k) \tilde{h}(k) \] (5.A.11)
which can be written
\[ [1 + \rho \tilde{h}(k)][1 - \rho \tilde{c}(k)] = 1. \] (5.A.12)

For a disordered fluid \( \tilde{h}(k) \) must be finite and \( 1 - \rho \tilde{c}(k) \) has no zeros on the real \( k \) axis. Using the fact that \( \tilde{c}(k) \) is an even function of \( k \), it can then be proved by construction that
\[ 1 - \rho \tilde{c}(k) = [1 - \rho \tilde{q}(k)][1 - \rho \tilde{q}(-k)], \] (5.A.13)
where \( \tilde{q}(k) \) is analytic, has no zeros in the region \( \text{Im}(k) > -\varepsilon \) (\( \varepsilon \) is arbitrarily small) and \( \tilde{q}(-k) \) is the complex conjugate of \( \tilde{q}(k) \).

Substituting Eq. (5.A.13) into Eq. (5.A.12) we obtain
\[ [1 + \rho \tilde{h}(k)][1 - \rho \tilde{q}(k)] = [1 - \rho \tilde{q}(-k)]^{-1}. \] (5.A.14)

Eq. (5.A.13) can be written in the form
\[ \tilde{c}(k) = \tilde{q}(k) + \tilde{q}(-k) - \rho \tilde{q}(k) \tilde{q}(-k) . \] (5.A.15)

We can now define the one-dimensional Fourier transform
\[ F(r) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikr} \tilde{f}(k) \, dk \] (5.A.16)
so that
\[ F(r) = 2\pi \int_{|r|}^{\infty} s f(s) \, ds \] (5.A.17)
or
where the properties of \( q(k) \) ensure that \( Q(r) \) is a real function with the property

\[
Q(r) = 0, \quad r < 0 .
\]

(5.A.19)

If \( c(r) \) is a finite-ranged function, e.g. \( c^{HS}(r) \) since

\[
c^{HS}(r) = 0, \quad r > R ,
\]

(5.A.20)

it can also be shown that

\[
Q^{HS}(r) = 0, \quad r > R .
\]

(5.A.21)

Taking the one-dimensional Fourier transform of Eq. (5.A.14) and closing in the lower half-plane, we get

\[
H^{HS}(r) = Q^{HS}(r) + \rho \int_0^R Q^{HS}(s) H^{HS}(r - s) \, ds .
\]

(5.A.22)

Using Eq. (5.A.18) we then find

\[
-2\pi \rho h^{HS}(r) = Q^{HS}(r) - 2\pi \rho \int_0^r Q^{HS}(s)(r - s) h^{HS}(|r - s|) \, ds .
\]

(5.A.23)

By using Eq. (5.A.7) and the fact that \( Q^{HS}(r) \) is continuous at \( r = R \) so that

\[
Q^{HS}(R) = 0
\]

(5.A.24)

we can evaluate \( Q^{HS}(r) \) for \( r < R \) from Eq. (5.A.23). In particular, we find

\[
Q^{HS}(r) = \beta \alpha_1 (r^2 - R^2) + \alpha_2 (r - R), \quad 0 < r < R ,
\]

(5.A.25)

where

\[
\alpha_1 = 2\pi \left( 1 - \rho \int_0^R Q^{HS}(s) \, ds \right)
\]

(5.A.26)

\[
\alpha_2 = 2\pi \rho \int_0^R Q^{HS}(s) s \, ds .
\]

(5.A.27)

Eq. (5.A.25) can then be used to determine \( \alpha_1 \) and \( \alpha_2 \) with the result
\[ \alpha_1 = 2\pi \frac{(1 + 2\eta)}{(1 - \eta)^2} \]  
(5.A.28)

\[ \alpha_2 = -\frac{3\pi \eta}{(1 - \eta)^2} \]  
(5.A.29)

where

\[ \eta = \frac{\pi}{6} \rho_s R^3 \]  
(5.A.30)

From a knowledge of \( Q^{HS}(r) \), we can Fourier transform Eq. (5.A.15) to get

\[ c^{HS}(r) = Q^{HS}(r) - \rho_s \int_0^{R-r} Q^{HS}(s) Q^{HS}(r + s) \, ds \]  
(5.A.31)

to get the usual solution for the Percus-Yevick equation for hard spheres [16].

If \( c(r) \) is not a finite-ranged function, only certain special functional forms of \( c(r) \) lead to an analytical solution. Fortunately, one of these forms is the Coulomb potential. We first introduce a convergence factor into \( c_c(r) \) and split this into short-ranged and long-ranged parts

\[ c_c(r) = -\frac{\beta e^2}{\varepsilon r} e^{-\mu r} + c^o(r), \quad r > 0 \]  
(5.A.32)

where

\[ c^o(r) = 0, \quad r > R \]  
(5.A.33)

which has the Fourier transform

\[ \tilde{c}^c(k) = \tilde{c}^o(k) - \frac{4\pi \beta e^2}{\varepsilon(k^2 + \mu^2)} \]  
(5.A.34)

where \( \tilde{c}^o(0) \) is finite. The analytic properties of Eq. (5.A.34) ensure that \( 1 - \rho \tilde{c}^o(k) \) has no zeros in the strip \( |\text{Im}(k)| < \varepsilon < \mu \) so that the splitting given by Eq. (5.A.13) is again possible. As before, since \( \tilde{q}(k) \) is analytic in the upper half plane, we find

\[ Q^c(r) = 0, \quad r < 0 \]  
(5.A.35)

The easiest way to obtain the form of \( Q^c \) for large \( r \) is to use
Eq. (5.A.15). From Eq. (5.A.34) we see that it is necessary that

\[ \tilde{q}(k) = \tilde{q}^0(k) - \frac{iA_{11}}{k + i\mu}, \]  

(5.A.36)

where \( \tilde{q}^0(0) \) is finite. Substituting Eqs. (5.A.36) and (5.A.34) into Eq. (5.A.15) we find

\[ \frac{4\pi\sigma e^2}{\varepsilon} = \rho_c A_{11}^2 \]  

(5.A.37)

so that

\[ \rho_c A_{11} = \kappa \]  

(5.A.38)

and

\[ Q^c(r) = Q^0(r) - A_{11} \theta(r), \]  

(5.A.39)

where \( \theta(r) \) is the Heaviside step function, and

\[ Q^0(r) = 0, \quad r > R \]  

(5.A.40)

because of Eq. (5.A.33).

In order to find \( Q^c(r) \) explicitly we use

\[ H^c(r) = Q^c(r) + \rho_c \int_0^R Q^c(s) H_c(r - s) - \rho_c A_{11} \int_R^\infty H(r - s) \, ds. \]  

(5.A.41)

Now, from Eqs. (5.A.9) and (5.A.17), it is clear that

\[ H^c(r) = H^c(R) \equiv H_{11} \quad \text{for} \quad r < R. \]  

(5.A.42)

Differentiating Eq. (5.A.41) and using the continuity of \( Q^0(r) \) at \( R \), we find

\[ Q^0(r) = \rho_c A_{11} H_{11}(r - R). \]  

(5.A.43)

To find an expression for \( H_{11} \), we evaluate Eq. (5.A.41) at \( r = R \) and find

\[ H_{11} = -A_{11} + \rho_c H_{11}(-A_{11} R - 2\rho_c H_{11} A_{11} R^2) - \rho_c A_{11} \int_0^\infty H^c(t) \, dt. \]  

(5.A.44)

The last term in Eq. (5.A.44) can be evaluated by using the condition of local electroneutrality. From Eq. (5.A.17) we see that \( H(r) \) is an even function, so that
but local electroneutrality states that
\[ \sum_j \rho_j z_j \tilde{\gamma}_{ij}(0) = -z_i \]
which becomes
\[ \rho_c \tilde{h}^c(0) = -1. \]
Finally, we get
\[ H_{11} = -\beta A_{11} + \rho_c H_{11} (-A_{11} R - \beta \rho_c H_{11} A_{11} R^2) \]
with the solution
\[ \rho_c H_{11} R = \left( \frac{(1 + 2\kappa R)\beta - 1 - \kappa R}{\kappa R} \right) \]
which is just B of Waisman and Lebowitz [17] and given in Eq. (4.2.6).

For fluid mixtures, Baxter's factorization can be generalized provided the matrix \( \tilde{c}(k) \) satisfies
\[ \tilde{c}(k) = \tilde{c}^T(-k). \]
Then we can derive the equations
\[ \tilde{c}_{ij}(k) = \tilde{q}_{ij}(k) + \tilde{q}_{ij}(-k) - \sum_k \rho_k \tilde{q}_{ki}(k) \tilde{q}_{kj}(-k) \]
and
\[ H_{ij}(r) = Q_{ij}(r) + \sum_k \rho_k \int_0^{\infty} ds Q_{ik}(s) H_{kj}(r - s), \]
where
\[ Q_{ij}(r) = 0, \quad r < \frac{\beta}{2} (R_i - R_j) \equiv S_{ij} \]
and, for cases where
\[ c_{ij}(r) = 0, \quad r > \frac{\beta}{2} (R_i + R_j) \equiv R_{ij} \]
\[ Q_{ij}(r) = 0, \quad r > R_{ij}. \]

We can now solve the MSA equations for the case of a 1:1 RPM electrolyte adsorbing against a charged wall. We start from the Ornstein-Zernike equation for the wall-ion distribution functions
\[ h_{i0}(r) = c_{i0}(r) + \sum_j \rho_j \int dr' c_{ij}^{\text{MSA}}(|r - r'|) h_{j0}(r') \]  

(5.A.56)

and the fact that, for the RPM electrolyte, we have

\[ c_{ij}^{\text{MSA}}(r) = c_{i}^{\text{HS}}(r) + z_{ij} c_{i1}^{c}(r) \]  

(5.A.57)

to obtain

\[ h_{10}^{\text{HS}}(r) = \sum_i \frac{\rho_i h_{10}^{i}(r)}{\rho_{\text{S}}} = c_{10}^{\text{HS}}(r) + \rho_{\text{S}} \int dr' c_{i1}^{\text{HS}}(|r - r'|) h_{i0}^{\text{HS}}(r') \]  

(5.A.58)

and

\[ h_{10}^{c}(r) = \sum_i \frac{\rho_i z_i h_{10}^{i}(r)}{\rho_{\text{C}}} = c_{10}^{c}(r) + \rho_{\text{C}} \int dr' c_{i1}^{c}(|r - r'|) h_{i0}^{c}(r') \]  

(5.A.59)

In the HNC closure,

\[ 1 + h_{i0}(r) = e^{-\beta u_{i0}^{S}(r)} \exp[-\beta u_{i0}^{c}(r) + h_{i0}(r) - c_{i0}(r)] \]  

(5.A.60)

we parametrize the short-ranged potential by

\[ -\beta u_{i0}^{S}(r) = a_i \delta(r - R_{10}), \quad r < R_{10} \]  

\[ = 1, \quad r > R_{10} \]  

(5.A.61)

and linearize the Coulombic part to obtain

\[ 1 + h_{i0}(r) = e^{-\beta u_{i0}^{S}(r)} \exp[1 + h_{i0}(r) - \beta u_{i0}^{c}(r) - c_{i0}(r)] \]  

(5.A.62)

which implies

\[ c_{i0}(r) = -\frac{\beta z_i e^2}{\varepsilon r}, \quad r > R_{10} \]  

(5.A.63)

Eqs. (5.A.56), (5.A.61) and (5.A.62) imply

\[ h_{i0}(r) = b_i \delta(r - R_{19}) + h_{i0}^{*}(r) \]  

(5.A.64)

\[ c_{i0}(r) = b_i \delta(r - R_{10}) + c_{i0}^{*}(r) \]  

where

\[ b_i = a_i [1 + h_{i0}(R_{10}^+)] \]  

(5.A.65)

The boundary conditions for Eqs. (5.A.58) and (5.A.59) then become
\[ h_{10}^{\text{HS}}(r) = -1 + \sum_j \rho_j b_j \frac{\delta(r - R_{10})}{\rho_s}, \quad r < R_{10} \]  
\[ c_{10}^{\text{HS}}(r) = 0, \quad r > R_{10} \]  
\[ h_{10}^c(r) = \sum \rho_j b_j \frac{\delta(r - R_{10})}{\rho_c} \equiv \sigma_b \frac{\delta(r - R_{10})}{\epsilon \rho_c}, \quad r < R_{10} \]  
\[ c_{10}^c(r) = -\frac{\beta z_0 e^2}{\epsilon r}, \quad r > R_{10} \]

respectively.

Using Baxter's factorization for \( h_{10}^{\text{HS}}(r) \), we then find
\[ Q_{10}^{\text{HS}}(r) = 0, \quad r > R_{10} \]  
so that
\[ H_{10}^{\text{HS}}(r) = Q_{10}^{\text{HS}}(r) + \rho_s \int_0^R Q_{11}(s) H_{10}^{\text{HS}}(r - s) \, ds, \]  
where \( Q_{11}(s) \) is given by Eqs. (5.A.25) - (5.A.30). The presence of the delta function in Eq. (5.A.66) then shows that
\[ Q_{10}^{\text{HS}}(r) = Q_{11}(r) + B_{10}, \quad S_{10} < r < R_{10}, \]  
where
\[ B_{10} = 2\pi R_{10} \sum_j \rho_j b_j. \]

We can now take the planar limit. Setting
\[ h_{10}^{\text{HS}}(r) = h^{\text{HS}}(x), \]  
where
\[ x = r - R_{10} \]
and taking the limit \( R_0 \to \infty \), we find from Eq. (5.A.69) for \( r > R_{10} \)
\[ h^{\text{HS}}(x) = (\sum_j \rho_j b_j) Q_{11}(x) + \rho_s \int_0^R Q_{11}(y) h^{\text{HS}}(x - y) \, dy. \]  

By applying Baxter's factorization to \( h_{10}^c(r) \), we find
which gives
\[ \tilde{q}^c_{10}(k) = \tilde{q}^o_{10}(k) - \frac{i\Lambda_{10}}{k + \imath\mu} \]  
(5.A.74)

and so
\[ 4\pi e^2 z_0 \frac{\rho c}{\varepsilon} = \rho c A_{11} A_{10} \]  
(5.A.75)

and
\[ A_{10} = z_0 A_{11} , \]  
(5.A.76)

and
\[ Q^c_{10}(r) = -z_0 A_{11} + Q^o_{10}(r) , \quad r > S_{10} \]  
\[ = 0 , \quad r < S_{10} , \]  
(5.A.77)

where
\[ Q^o_{10}(r) = 0 , \quad r > R_{10} . \]  
(5.A.78)

From the equation
\[ H^c_{10}(r) = Q^c_{10}(r) + \rho c \int_0^R Q^c_{11}(s) H^c_{10}(r - s) \, ds - \rho c A_{11} \int_{R_{10}}^{\infty} H^c_{10}(r - s) \, ds \]  
(5.A.79)

we can show (by using Eq. (5.A.67)) that
\[ Q^o_{10}(r) = \rho c A_{11} H_{10}(r - R_{10}) + \frac{2\pi R_{10} \sigma}{\varepsilon \rho c} , \quad S_{10} < r < R_{10} , \]  
(5.A.80)

where
\[ H_{10} \equiv 2\pi \int_{-R_{10}}^{\infty} ds \, s h^c_{10}(s) . \]  
(5.A.81)

By evaluating Eq. (5.A.79) at \( R_{10} \) and using electroneutrality about the wall, we can find \( H_{10} \)
\[ H_{10} = -\frac{2\pi R_{10} \sigma}{\varepsilon \rho c} - \frac{\frac{1}{2} z_0 A_{11}}{1 - \rho c \int_0^R Q^c_{11}(s) \, ds - \rho c A_{11} S_{10}} \]  
(5.A.82)

By differentiating Eq. (5.A.79), setting
\[ h^c_{10}(r) = h^c(x) \]  
(5.A.83)

and using Eq. (5.A.82), we find, in the limit \( R_0 \to \infty, z_0 \to \pi R_0^2 \sigma_0/e \)
\[ h^c(x) = \frac{\sigma_0 Q^c_{11}(x)}{e} - \frac{\sigma_0 A_{11}}{e} + \rho c \int_0^x Q^c_{11}(y) h^c(x - y) \, dy \]  
(5.A.84)
since
\[ h_c(x) = 0, \quad x < 0. \]  
(5.A.85)

Thus we have derived Eqs. (5.2.19) - (5.2.22) and since
\[ h_{10}^*(0^+) = h_{10}^{HS}(0^+) + z_1 h_1^c(0^+) \]  
(5.A.86)

we can use Eqs. (5.A.65), (5.A.73) and (5.A.84) to derive the adsorption isotherm, Eq. (5.2.17).

The surface potential \( \psi \equiv \psi(2R_0) \) is given by
\[
\psi_0 = \frac{z_0 e}{\varepsilon} + \frac{4\pi}{\varepsilon} \int_{R_0}^{\infty} ds \sum_j \rho_j z_j h_j(s) 
= \frac{2e}{\varepsilon} \left[ \frac{z_0}{R_0} + \rho_h H_1 \right]. 
\]  
(5.A.87)
\[
\text{Using Eq. (5.A.82), we then find in the limit } R_0 \to \infty, z_0 \to \pi R_0^2 \sigma_0 / e 
\psi_0 = \frac{4\pi}{\varepsilon K} [\sigma_\beta + \sigma_0 (1 - \rho_c) \int_0^{R} Q_{11}^c(s) ds - \beta_k R] \]  
(5.A.88)

which, upon using Eq. (5.A.43) and remembering
\[ \psi_0 = \psi_\beta + \frac{4\pi \sigma_0}{\varepsilon} \beta R \]  
(5.A.89)
yields Eq. (5.2.16).

REFERENCES


CHAPTER 6
IMAGES AND LOCAL ION ACTIVITY EFFECTS

6.1 BBGY FORMULATION OF THE DOUBLE LAYER

In this chapter we discuss the possibility of extending the methods of Chapters 4 and 5 to include effects such as image forces due to a dielectric discontinuity at the surface and corrections due to the local ionic activities. To this end we reformulate the double layer problem in terms of the BBGY hierarchy (which arises from a simple force balance picture) and then transform via a non-uniform Ornstein-Zernike equation into an equation that involves the non-uniform short-ranged direct correlation function $c^0(r,r')$. Suitable approximations for $c^0(r,r')$ then recover the HNC/MSA equations of Chapters 4 and 5. We also compare extensively with the modified Poisson-Boltzmann equation approach [1] and with other theories based on the BBGY hierarchy [2-4].

Consider a RPM electrolyte against a charged dielectric interface.

The Hamiltonian for the electrolyte can be written as

$$H = \sum_\alpha \sum_i V_\alpha(r_i^\alpha) + \frac{1}{2} \sum_\alpha \sum_\beta \sum_i U_{\alpha\beta}(r_i^\alpha, r_j^\beta), \quad (6.1.1)$$

where $V_\alpha(r_i^\alpha)$ denotes the interaction between an ion of species $\alpha$ located at $r_i^\alpha$ and the surface and $U_{\alpha\beta}(r_i^\alpha, r_j^\beta)$ denotes the interaction between ions of species $\alpha$ and $\beta$. We split these.
potentials into components due to Coulombic interactions, image forces and the remaining short-range potentials. Thus we have

$$V_\alpha(r_{ij}) = z_\alpha e v^c(r_{ij}) + z_\alpha e v^I(r_{ij}) + v^S_\alpha(r_{ij}), \quad (6.1.2)$$

where $z_\alpha e$ is the charge on species $\alpha$. Similarly,

$$U_{\alpha\beta}(r_{ij}, r_{ik}) = z_\alpha z_\beta e^2 G(r_{ij}, r_{ik}) + u^S_{\alpha\beta}(|r_{ij} - r_{ik}|), \quad (6.1.3)$$

where $G(r_{ij}, r_{ik})$ is the Green's function for Laplace's equation for the geometry under consideration. For a planar surface,

$$G(r_{ij}, r_{ik}) = G^c(r_{ij}, r_{ik}) + G^I(r_{ij}, r_{ik}) \quad (6.1.4)$$

$$= \frac{1}{\epsilon|\mathbf{r}_{ij} - \mathbf{r}_{ik}|} - \frac{\Delta}{\epsilon|\mathbf{r}_{ij} - \mathbf{r}_{ik}|}, \quad (6.1.5)$$

where

$$\mathbf{r}_{ij} = \mathbf{r}_{ij} + 2\hat{x}_{ij} \quad (6.1.6)$$

and

$$\Delta = \frac{\epsilon_w - \epsilon}{\epsilon_w + \epsilon}, \quad (6.1.7)$$

where $\epsilon_w$ is the dielectric constant of the wall, and $\epsilon$ that of the solvent in the RPM electrolyte.

The force on particle $i_\alpha$ at $\mathbf{r}$ due to the other (fixed) ions and the surface is then given by

$$\mathbf{f}_{i_\alpha}(r) = -\nabla_r H(r, r_{ij}, \ldots) \quad (6.1.8)$$

$$= -\nabla_r v^S_\alpha(r) - z_\alpha e \nabla_r v^c(r) + f^I_{i_\alpha}(r)$$

$$- \sum_{\beta} \sum_{j_\beta} u^S_{\alpha\beta}(|r - r_{ij}|) - z_\alpha e \sum_{\beta} z_\beta e \nabla_r G(r, r_{ij}), \quad (6.1.9)$$

Some care must be taken with the term $f^I_{i_\alpha}(r)$, the direct image force on
particle \( i_\alpha \). For planar geometry, the ion \( i_\alpha \) at distance \( x \) from the wall interacts with an image charge of magnitude \(-z_\omega e\Delta \) located at a distance \( x \) behind the wall. The electrostatic image potential is thus

\[
G^I(r, r^im) = -\frac{\Delta z_\omega e}{2x}.
\]  

(6.1.10)

However, since the image charge moves as the ion approaches the wall, the direct image force is given by

\[
f^I_{-\alpha}(r) = -z_\omega e \frac{d}{d(2x)} G^I(2x) \hat{x} = -\frac{(z_\omega e)^2 \Delta \hat{x}}{4x^2}.
\]  

(6.1.11)

so that the potential appearing in the Hamiltonian is in fact

\[
v^I_\alpha(r) = -\frac{(z_\omega e)\Delta}{4x}.
\]  

(6.1.12)

For more general geometry,

\[
f^I_\alpha(r) = -z_\omega e \{ \nabla_r G^I(r, r') \}_{r \rightarrow r'}.
\]  

(6.1.13)

These difficulties do not arise with the cross-image terms due to \( G^I(r, r_j) \).

The electrostatic potential at an ion \( i_\alpha \) at \( r \) due to other (fixed) ions and the surface is given by

\[
\hat{\psi}_i(\alpha) = \sum_{\beta} \sum_{j \neq \beta} z_\omega e G(r, r_j) + G^I(r, r^im) + \psi^c(r)
\]  

(6.1.14)

from which it follows that

\[
\hat{F}_i(\alpha) = \hat{F}^S_i(\alpha) - z_\omega e \nabla_r \hat{\psi}_i(\alpha) - z_\omega e \nabla_r v^I_i(r) + (z_\omega e)^2 \frac{\Delta}{4x^2}.
\]  

(6.1.15)

(6.1.16)
for planar geometry, where $F_\alpha^S(r)$ is the force due to short-range potentials. From Eq. (6.1.16), we can see that in the absence of image forces, the usual relationship between the electrostatic component of the force and the electrostatic potential is obeyed.

Taking the particle of interest to be $l_\alpha^\prime$, we can write the force operator in the form

$$
\hat{F}_{l_\alpha^\prime} (r) = -\nabla_r V_\alpha (r) - \Sigma \Sigma \int \delta (r' - r_\beta^\prime) U_{\alpha\beta} (r, r') \, dr'. \quad (6.1.17)
$$

We can then average over all ions (except $l_\alpha$) and form the average force on particle $l_\alpha$

$$
F_\alpha (r) \equiv \langle \hat{F}_{l_\alpha} (r) \rangle \equiv \frac{\int dr_2 \ldots dr_N \hat{F}_{l_\alpha} (r) \, e^{-\beta H}}{\int dr_2 \ldots dr_N \, e^{-\beta H}} \quad (6.1.18)
$$

and use the expressions for the one-particle density function

$$
\rho_\alpha (r) = N_\alpha \int dr_2 \ldots dr_N \frac{e^{-\beta H}}{Z}, \quad (6.1.19)
$$

where

$$
Z \equiv \int dr_1 \ldots dr_N e^{-\beta H} \quad (6.1.20)
$$

is the canonical partition function and the two-particle density function

$$
\rho^{(2)}_{\alpha\beta} (r, r') = N_\alpha (N_\beta - \delta_{\alpha\beta}) \int dr_2 \ldots dr_N \frac{e^{-\beta H}}{Z} \quad (6.1.21)
$$

$$
\rho_{\alpha^\prime} (r) \rho_{\beta^\prime} (r') g_{\alpha\beta} (r, r') \quad (6.1.22)
$$

to obtain

$$
F_\alpha (r) = -\nabla_r v_\alpha^S (r) - z_\alpha e \nabla_r (v_\alpha^S (r) - v_\alpha^I (r)) - \Sigma \int dr' [\nabla_r U_{\alpha\beta} (r, r')] \rho_\beta (r') g_{\alpha\beta} (r, r') - z_\alpha e \int dr' [\nabla_r G (r, r')] \Sigma \beta \Sigma c \rho_\beta (r') g_{\alpha\beta} (r, r') \quad (6.1.23)
$$
By writing
\[ g_{\alpha \beta}(r, r') = 1 + h_{\alpha \beta}(r, r') \] (6.1.24)

Eq. (6.1.23) becomes
\[
\begin{align*}
F_{\alpha}(r) &= -\nabla_r v_{\alpha}^S(r) - z_{\alpha} e \nabla_r v_{\alpha}^I(r) - z_{\alpha} e \nabla_r \psi(r) \\
&\quad - \sum_{\beta} \int dr' \left[ \nabla_r u_{\alpha \beta}^S(|r - r'|) \right] \rho_{\beta}(r') g_{\alpha \beta}(r, r') \\
&\quad - z_{\alpha} e \int dr' \left[ \nabla_r G(r, r') \right] \sum_{\beta} \rho_{\beta}(r') h_{\alpha \beta}(r', r),
\end{align*}
\] (6.1.25)

where
\[
\psi(r) = v^C(r) + \int dr' G(r, r') \sum_{\beta} \rho_{\beta}(r')
\] (6.1.26)
is the mean electrostatic potential. It should be noted that when we consider electrolyte around a uniformly charged spherical colloidal particle, we have
\[
\int dr' G^I(r, r') \sum_{\beta} \rho_{\beta}(r') = 0
\] (6.1.27)
and there is no direct contribution from image forces. Eq. (6.1.27) can be proved from the Green's function (the z axis is the line joining the test charge and the centre of the particle)
\[
G^I(r, r') = \frac{1}{\varepsilon} \sum_{n=0}^{\infty} \frac{p_n(\cos \theta)}{n+1} \frac{\tilde{R}^{2n+1}}{r^{n+1}} \frac{n(\varepsilon - \varepsilon_w)}{n \varepsilon_w + (n+1)\varepsilon},
\] (6.1.28)

where \( \tilde{R} \) is the radius of the colloidal particle and \( \varepsilon_w \) is its dielectric constant. If the charge density is spherically symmetric, then the factor \( n(\varepsilon - \varepsilon_w) \) ensures that the angular integration results in Eq. (6.1.27). By extension, the same is true for a uniformly charged plane, in which case \( \psi(x) \) reduces to the previous expression
\[
\psi(x) = \frac{4\pi}{\varepsilon} \int_{-\infty}^{\infty} dy (x - y) \sum_{\beta} \rho_{\beta}(y)
\] (6.1.29)
and the image forces contribute to \( \psi(x) \) only through their effect on \( \rho_{\beta}(y) \). For non-uniform surface charge, however, the image forces
contribute directly to the mean electrostatic potential [5]. From now on, we deal only with uniform surface charge.

The last term in Eq. (6.1.25) is called the fluctuation term or self-atmosphere term, since it describes the force acting on ion α due to the double layer around that same ion. In bulk, such a term would vanish by symmetry but because the ionic atmosphere is distorted by the external field, an extra force exists on the ion.

Eq. (6.1.25) is the first equation in the Bogoliubov-Born-Green-Yvon hierarchy. $g_{αβ}(r,r')$ is related to higher order distribution functions through the remaining members of the hierarchy. A closure relation for $g_{αβ}(r,r')$ is therefore required in order to truncate the hierarchy and effect a solution. Croxton and McQuarrie [4] have recently solved Eq. (6.1.25) (neglecting short-range and image interactions) subject to the approximation

$$g_{αβ}(r,r') = g_{αβ}^\text{bulk}(|r-r'|)$$

which is equivalent to the Kirkwood superposition approximation in bulk fluids [6]. This approximation has the consequence that the local electroneutrality condition

$$-z_α = \int_\mathbb{R}^3 \Sigma_β z_β n_β(r') h_{αβ}(r,r')$$

is not satisfied. Using the same method as Pastor and Goodisman [7], Croxton and McQuarrie remedy this defect by writing

$$h_{αβ}(r,r') = f_α(x) h_{αβ}^\text{bulk}(|r-r'|) f_β(x')$$

and determine $f(x)$ from Eq. (6.1.31). The effect of this procedure on the surface potential-surface charge relationship is marked.
particular, the maximum in surface potential ($\psi$), that appears when Eq. (6.1.30) is used, is absent when local electroneutrality is enforced through Eq. (6.1.31). Croxton and McQuarrie have also suggested the approximation [3]

$$g_{\alpha\beta}(r,r') \approx g_{\alpha\beta}^{\text{bulk}}(|r-r'|) \exp \left( -\frac{\Delta z_{\alpha} z_{\beta} e^2}{\epsilon k T} \frac{e^{-\kappa |r-r'|}}{|r-r'|^{\text{im}}} \right)$$  \hspace{1cm} (6.1.33)

in order to try to incorporate image effects into the BGY theory of the double layer.

Because of the close relationship between the BBGY hierarchy and the derivation of the contact condition given in Chapter 3, and the fact that in all the theories mentioned above

$$h_{\alpha\beta}(r,r') \rightarrow h_{\alpha\beta}^{\text{bulk}}(|r-r'|) \quad \text{as} \quad r_r \rightarrow \infty,$$

it is clear that the BBGY theories of the double layer all give the exact contact condition with $p = p^\text{BGY}$. Only with the imposition of Eq. (6.1.31) do they obey local electroneutrality. Whether such theories obey the condition given by Eq. (3.3.24) is an open question.

6.2 THE KIRKWOOD CHARGING PROCESS

Another hierarchy of equations, which form the basis for the modified Poisson-Boltzmann approach to the double layer [1], can be derived by extending to inhomogeneous electrolytes the charging process used by Kirkwood in bulk electrolyte theory [8].

Consider the Hamiltonian for an electrolyte in an external field

$$H(\lambda) = H_0 + \lambda \left( \sum_{\alpha} \sum_{j_{\beta}} z_{\alpha} z_{\beta} e^2 G(r_{1_{\alpha}}, \mathbf{r}_{j_{\beta}}) + z_{\alpha} e \nu^c(r_{1_{\alpha}}) + z_{\alpha} e \nu^i(r_{1_{\alpha}}) \right),$$

\hspace{1cm} (6.2.1)
where the ion $l_\alpha$ at $r_{l_\alpha}$ has charge $\lambda z_{\alpha} e$ and as we vary $\lambda$ from 0 to 1 we progressively include the electrostatic interactions between ion $l_\alpha$ and the rest of the system. $H_0$ is the Hamiltonian of the electrolyte when ion $l_\alpha$ is discharged. Notice that $\lambda$ is a different coupling constant to that used in Chapter 4.

We can regard the ion $l_\alpha$ to be a separate species and so define the singlet distribution function of ion $l_\alpha$ at strength $\lambda$ as

$$\rho_\alpha(r_{l_\alpha} | \lambda) = \int \frac{dr_2 \ldots dr_{-N_\alpha} e^{-\beta H(\lambda)}}{Z(\lambda)}, \quad (6.2.2)$$

where

$$Z(\lambda) = \int dr_{l_\alpha} \ldots dr_{-N_\alpha} e^{-\beta H(\lambda)}. \quad (6.2.3)$$

Since there is only one ion of type $l_\alpha$, $\rho_\alpha(r_{l_\alpha} | \lambda)$ is related to the potential of mean force of ion $l_\alpha$ at strength $\lambda$ by

$$\rho_\alpha(r_{l_\alpha} | \lambda) = \frac{1}{V} \exp[-\beta W(r_{l_\alpha} | \lambda)], \quad (6.2.4)$$

where $V$ is the volume of the system. This contrasts with the usual relationship

$$\rho_\alpha(r) = N_\alpha \int \frac{dr_2 \ldots dr_{-N_\alpha} e^{-\beta H}}{Z}$$

$$= \frac{N_\alpha}{V} \exp[-\beta W_\alpha(r)]. \quad (6.2.5)$$

If we differentiate Eq. (6.2.4) with respect to $\lambda$, we find
\[
\frac{\partial}{\partial \lambda} \left[ \exp\left[ -\beta W_\alpha (r_1, \lambda) \right] \right] = \beta z_\alpha e^{v_\alpha (r_1)} \exp\left[ -\beta W_\alpha (r_1, \lambda) \right] - 2\beta z_\alpha e^{v_\alpha (r_1)} \exp\left[ -\beta W_\alpha (r_1, \lambda) \right] - \frac{\partial}{\partial \lambda} \ln Z(\lambda) \exp\left[ -\beta W_\alpha (r_1, \lambda) \right]
\]

\[
G(r_1, r_2) z_\beta e^{(N_\beta - \delta_{\alpha \beta})} \int dr_2 \cdots dr_N \exp \left[ -\beta W_\alpha (r_1, \lambda) \right] e^{-\beta H(\lambda)}
\]

\[
\frac{\partial}{\partial \lambda} \left[ \exp\left[ -\beta W_\alpha (r_1, \lambda) \right] \right] = \beta z_\alpha e^{v_\alpha (r_1)} \exp\left[ -\beta W_\alpha (r_1, \lambda) \right]
\]

\[
\rho_{\alpha \beta}^{(2)} (r_1, r_2 | \lambda) = (N_\beta - \delta_{\alpha \beta}) \int \frac{dr_2 \cdots dr_N \exp \left[ -\beta W_\alpha (r_1, \lambda) \right] e^{-\beta H(\lambda)}}{Z(\lambda)}
\]

\[
\frac{\partial}{\partial \lambda} \left[ \exp\left[ -\beta W_\alpha (r_1, \lambda) \right] \right] = \beta z_\alpha e^{v_\alpha (r_1)} \exp\left[ -\beta W_\alpha (r_1, \lambda) \right] - \frac{\partial}{\partial \lambda} \ln Z(\lambda)
\]

Eq. (6.2.9) can be integrated formally to yield (for an ion at \( r \))

\[
W_\alpha (r | 1) = W_\alpha (r | 0) + z_\alpha e^{v_\alpha (r)} + z_\alpha e^{v_\alpha (r)} + kT \ln \left[ \frac{Z(1)}{Z(0)} \right]
\]

\[
+ z_\alpha e^{\int_0^1 dr' G(r, r') \sum_{\beta} z_\beta e^{\rho_{\beta} (r' | \lambda)} g_{\alpha \beta} (r, r' | \lambda)}
\]
Since $\rho_\beta(r|\lambda)$ is the singlet distribution function of ions of species $\beta$ given there is one ion with charge $\lambda z_\alpha e$, $\rho_\beta(r|\lambda)$ is essentially independent of $\lambda$. Writing

$$g_{\alpha\beta}(r, r'|\lambda) = 1 + h_{\alpha\beta}(r, r'|\lambda)$$  \hspace{1cm} (6.2.11)

we can use Eq. (6.1.26) to write

$$W_\alpha(r|1) = W_\alpha(r|0) + z_\alpha e \psi(r) + z_\alpha e \nu_\alpha(r) + kT \ln \left( \frac{Z(1)}{Z(0)} \right) + z_\alpha e \int_0^1 dr' G(r, r') \sum_\beta z_\beta e \rho_\beta(r') h_{\alpha\beta}(r, r'|\lambda).$$  \hspace{1cm} (6.2.12)

Since the density function of species $\alpha$ is given by

$$\rho_\alpha(r) = \rho_\alpha(r|\lambda) = \rho_\alpha \exp[-\beta(W_\alpha(r|1) - W_\alpha(\infty|1))],$$  \hspace{1cm} (6.2.13)

we need to evaluate

$$W_\alpha(r|1) - W_\alpha(\infty|1) = W_\alpha(r|0) - W_\alpha(\infty|0) + z_\alpha e \psi(r) + z_\alpha e \nu_\alpha(r)$$

$$+ z_\alpha e \int_0^1 d\lambda \int dr' G(r, r') \sum_\beta z_\beta e \rho_\beta(r') h_{\alpha\beta}(r, r'|\lambda)$$

$$- G(\infty, r') \sum_\beta z_\beta e \rho_\beta(r') h_{\alpha\beta}(\infty, r'|\lambda).$$  \hspace{1cm} (6.2.14)

This equation can be compared with the BBGY equation, Eq. (6.1.25).

The short-range interactions explicitly shown in Eq. (6.1.25) have been subsumed into $W_\alpha(r|0) - W_\alpha(\infty|0)$, and the distance integration necessary to express Eq. (6.1.25) in terms of $W_\alpha(r)$ has been replaced by a coupling constant integration in the last term of Eq. (6.2.14).

Once again, a closure approximation on $h_{\alpha\beta}(r, r'|\lambda)$ is required.

Buff and Stillinger have solved a linearized form of Eq. (6.2.14) subject to Eq. (6.1.30) in a study of the surface tension of ionic solutions [9]. The modified Poisson-Boltzmann theory [1] uses a
different closure due to Loeb [10], which we discuss in the next section.

6.3 LOEB's CLOSURE FOR THE FLUCTUATION POTENTIAL

The equations for \( W_\alpha (r) \) derived both from the BBGY hierarchy (Eq. (6.1.25)) and from the Kirkwood hierarchy (Eq. (6.2.12)) can be simply expressed in terms of the fluctuation potential \( \phi_\alpha (r, r') \) introduced in Chapter 3. The mean electrostatic potential at \( r \) given an ion of species \( \alpha \) at \( r' \), \( \psi_\alpha (r, r') \) is just

\[
\psi_\alpha (r, r') = z_\alpha e G(r, r') + v^c (r) + \int dr'' G(r, r'') \sum_\beta z_\beta e \rho_\beta (r'') h_{\alpha \beta} (r', r'').
\]

(6.3.1)

The fluctuation potential \( \phi_\alpha (r, r') \), defined by

\[
\phi_\alpha (r, r') = \psi_\alpha (r, r') - \psi (r)
\]

(6.3.2)

is then

\[
\phi_\alpha (r, r') = z_\alpha e G(r, r') + \int dr'' G(r, r'') \sum_\beta z_\beta e \rho_\beta (r'') h_{\alpha \beta} (r', r'').
\]

(6.3.3)

Eq. (6.1.25) can then formally be integrated to yield

\[
\rho_\alpha (x_1) = \rho_\alpha \xi_\alpha (x_1) \exp \left\{ - \beta z_\alpha e \left[ z_\alpha e v^T_\alpha (x_1) + \psi (x_1) \right] \right\}
\]

(6.3.4)

\[
+ \int_{-\infty}^{x_1} \hat{x} \cdot \lim_{r' \to r} \nabla_r [\phi_\alpha (r, r') - z_\alpha e G(r, r')] \right\},
\]

where \( \xi_\alpha (x_1) \) incorporates all the short-ranged potential contributions and \( \hat{x} \) is the unit vector normal to the wall. Eq. (6.3.4) is the basis for the BBGY theory of the double layer due to Outhwaite [2].

In a similar way, Eq. (6.2.13) can be written

\[
\rho_\alpha (r) = \rho_\alpha \xi_\alpha (r) \exp \left\{ - \beta z_\alpha e [\psi (r) + \eta_\alpha (r)] \right\},
\]

(6.3.5)

where
\begin{equation}
\tau_\alpha(r) = \exp[-\beta(W_\alpha(r|0) - W_\alpha(\infty|0))] \tag{6.3.6}
\end{equation}

\begin{equation}
\frac{\int dr_2 \ldots dr_N \exp[-\beta H_\alpha(r,r_2 \ldots r_N)]]}{\int dr_2 \ldots dr_N \exp[-\beta H_\alpha(\infty, r_2 \ldots r_N)]]} \tag{6.3.7}
\end{equation}

and

\begin{equation}
\eta_\alpha(r) = v_\alpha^1(r) + \int_0^1 d\lambda \left\{ \lim_{r' \to r} \left[ \phi_\alpha(r,r'|\lambda) - \lambda z_\alpha e G(r,r') \right] \right\}_{\text{bulk}} \tag{6.3.8}
\end{equation}

\begin{equation}
= \int_0^1 d\lambda \left\{ \lim_{r' \to r} \left[ \phi_\alpha(r,r'|\lambda) - z_\alpha e G^c(r,r') \right] \right\} - \lim_{r' \to r} \left[ \phi_\alpha(r,r'|\lambda) - \lambda z_\alpha e G^c(r,r') \right]_{\text{bulk}} \tag{6.3.9}
\end{equation}

Eqs. (6.3.5) - (6.3.9) are the basis for the modified Poisson-Boltzmann equation approach to double layer theory [1,11,12].

In order to evaluate the fluctuation potential, we can use Eq. (6.3.3) to show

\begin{equation}
\nabla^2 \phi_\alpha(r,r') = -\frac{4\pi}{\varepsilon} \left[ z_\alpha e \delta(r-r') + \sum_{\beta} z_\beta e \rho_\beta(r) h_{\alpha\beta}(r',r) \right] \tag{6.3.10}
\end{equation}

We need some closure between \( h_{\alpha\beta} \) and \( \phi_\alpha \) in order to proceed. Both the BBGY and MPB theories employ a closure due to Loeb [10]

\begin{equation}
\eta_{\alpha\beta}(r',r) = \exp[-\beta z_\beta e \phi_\alpha(r,r')] \tag{6.3.11}
\end{equation}

that relates the fluctuation potential and the two-particle distribution function in much the same way as the mean potential and the one-particle density function are related by Gouy-Chapman theory. Higher-order closures have been discussed by Outhwaite [13].

Combining Eqs. (6.3.10) and (6.3.11) we get
\[
\n\frac{\nabla^2}{\mathbf{r}} \phi_{\alpha}(\mathbf{r}, \mathbf{r'}) = - \frac{4\pi}{\varepsilon} [z_{\alpha} \varepsilon \delta(\mathbf{r} - \mathbf{r'}) \\
+ \sum_{\beta} z_{\beta} \varepsilon \rho_{\beta}(\mathbf{r}) [\exp(-\beta z_{\beta} \varepsilon \phi_{\alpha}(\mathbf{r}, \mathbf{r'})) - 1)]
\] (6.3.12)

which, upon linearization, yields

\[
\frac{\nabla^2}{\mathbf{r}} \phi_{\alpha}(\mathbf{r}, \mathbf{r'}) = - \frac{4\pi}{\varepsilon} z_{\alpha} \varepsilon \delta(\mathbf{r} - \mathbf{r'}) + \kappa^2(\mathbf{r}) \phi_{\alpha}(\mathbf{r}, \mathbf{r'}),
\] (6.3.13)

where

\[
\kappa^2(\mathbf{r}) = \frac{4\pi \varepsilon^2 \sum_{\beta} \rho_{\beta}(\mathbf{r}) z_{\beta}^2}{\varepsilon}.
\] (6.3.14)

If we take

\[
\kappa^2(\mathbf{r}) = \kappa^2(\infty) = \frac{4\pi \varepsilon^2 \sum_{\beta} \rho_{\beta} z_{\beta}^2}{\varepsilon}
\] (6.3.15)

we can solve Eq. (6.3.13) subject to the appropriate boundary conditions at the surface to obtain

\[
\phi_{\alpha}(\mathbf{r}, \mathbf{r'}) = z_{\alpha} \varepsilon \int_0^{\infty} dk \, k J_0(k(\rho - \rho')) \\
\times \left\{ \frac{e^{-p|x-x'|}}{\varepsilon p} - \frac{k\varepsilon}{k\varepsilon+p}\frac{e^{-p(x+x')}}{\varepsilon p} \right\},
\] (6.3.16)

where \(p^2 = \kappa^2 + k^2\) and \(\mathbf{r} = (\rho, \mathbf{x})\) in cylindrical coordinates. For \(\varepsilon_w = 0\), \(\phi_{\alpha}(\mathbf{r}, \mathbf{r'})\) reduces to the Onsager-Samaras result [14]

\[
\phi_{\alpha}(\mathbf{r}, \mathbf{r'}) = z_{\alpha} \varepsilon \left\{ \frac{\exp(-\kappa|\mathbf{r} - \mathbf{r'}|)}{\varepsilon|\mathbf{r} - \mathbf{r'}|} + \frac{\exp(-\kappa|\mathbf{r} - \mathbf{r'}^\text{im}|)}{\varepsilon|\mathbf{r} - \mathbf{r'}^\text{im}|} \right\}.
\] (6.3.17)

For a metallic surface, the solution is given by Eq. (6.3.17) but with the sign of the second term reversed.

A less drastic approximation [10] is to take

\[
\kappa^2(x) = \kappa^2(x')
\] (6.3.18)

and solve approximately to obtain
\[
\phi_\alpha(r, r') = z_\alpha^e \left( \exp( - \kappa(x') |r - r'| ) \right) + f \exp( - \kappa(x') |r - r'|_{im} ) \left( \frac{e}{|r - r'|} \right),
\]

(6.3.19)

where \( f = +1 (-1) \) if \( \varepsilon = 0 (\infty) \). The solution given by Eq. (6.3.19) has been tested by Williams [15] against the solution of the equation

\[
\nabla^2 r, \phi_\alpha(r, r') = - \frac{4\pi}{\varepsilon} z_\alpha^e \delta(r - r') + \kappa^2 GC(x) \phi_\alpha(r, r'),
\]

(6.3.20)

where

\[
\kappa^2 GC(x) = \frac{4\pi \beta \varepsilon^2}{\varepsilon} \sum \beta \rho_B^{GC}(x)
\]

(6.3.21)

and \( \rho_B^{GC}(x) \) is given in Chapter 1. The discrepancy between the two methods for \( f = +1 (-1) \) was estimated to be 5% (20%) at \( \psi_0 = 25 \) mV and 10% (40%) for \( \psi_0 = 100 \) mV. Notice that Eq. (6.3.19) takes into account the effect on the fluctuation potential of the variation of ionic density in the double layer.

For an RPM electrolyte, we can use the hard sphere condition

\[
g_{\alpha\beta}(r, r') = 0, \quad |r - r'| < R
\]

(6.3.22)

to derive the exact equation

\[
\nabla^2 r, \phi_\alpha(r, r') = - \frac{4\pi}{\varepsilon} z_\alpha^e \delta(r - r') - \nabla^2 r, \psi(r), \quad |r - r'| < R.
\]

(6.3.23)

The most commonly adopted procedure for determining the fluctuation potential [2,11,12] has been to assume a functional form for \( \phi_\alpha \) similar to Eq. (6.3.19) for \( |r - r'| > R \) and then solve Eq. (6.3.23) approximately subject to electrostatic boundary conditions at \( |r - r'| = R \). The fluctuation potential is then determined everywhere.

It turns out that the BBGY approach [2] requires a more accurate determination of the fluctuation potential than MPB theories. In addition, it is difficult to estimate the factor \( \xi_\alpha(x) \) in Eq. (6.3.4).
We therefore present the results of just the MPB theory of the double layer. The approximate treatment of the fluctuation potential described in the preceding paragraph leads to \([1]\)

\[
\eta_\alpha(r) = \frac{z_\alpha e}{2\epsilon R} (F - F_{\text{bulk}}) + L[\psi(r)].
\]  \hspace{1cm} (6.3.24)

The first term represents contributions from images and the effect of \(\kappa^2(x)\) on the local ionic activities. The second term includes the cavity potential described in Chapter 4 and a term like \(w_\alpha^{(3)}(r)\) in Eq. (4.2.13). As \(R \to 0\), the second term in Eq. (6.3.24) vanishes but the first term becomes

\[
\frac{z_\alpha e}{2\epsilon R} (F - F_{\text{bulk}}) \to \frac{z_\alpha e}{2\epsilon} \left( -\kappa + \kappa_{\text{bulk}} + f \exp(-2\kappa x) \right). \hspace{1cm} (6.3.25)
\]

The last term in Eq. (6.3.25) is clearly due to imaging and the remainder describes the attraction that an ion feels due to the change in local ionic activity as the ion approaches the wall. The electrostatic part of the ionic activity of a Debye-Hückel electrolyte is just \(-\frac{(z_\alpha e)^2}{2\epsilon} \kappa\) so that the ion prefers to be near the wall where \(\kappa\) is locally higher than in bulk. The methods of Chapter 4 (in particular Eq. (4.1.13)) give rise to equations that omit the term \(F - F_{\text{bulk}}\) and also neglect any image or local \(\kappa\) effects in \(L[\psi(x)]\).

A disadvantage of the MPB approach, however, is the difficulty in estimating \(\zeta_\alpha(x)\). The most accurate expression used in the MPB calculations has been (in the MPB4 theory) \([16]\)

\[
\zeta_{\alpha}^{\text{MPB4}}(x) = 1 + \beta w_\alpha^{(2a)}(x), \hspace{1cm} (6.3.26)
\]

where \(w_\alpha^{(2a)}(x)\) is given in Chapter 4. This can be compared with the expression from Chapter 4.
We can recover Eq. (6.3.26) by linearizing the exponential and retaining only terms of lowest order in ionic density. From this comparison, it seems clear that the HNC/MSA equations treat excluded volume effects more accurately than does the MPB approach. This superiority, however, is counterbalanced by weaknesses in accounting for image forces and local ionic activity effects.

6.4 AN MSA-TYPE CLOSURE FOR THE BBGY EQUATION

In this section we outline a theory that links the methods of Chapter 4 with the theories based on evaluation of the fluctuation potential [1,2]. We start from Eq. (6.1.25) and use the non-uniform Ornstein-Zernike equation

$$h_{\alpha\beta}(r,r') = c_{\alpha\beta}(r,r') + \sum_{\gamma} \int dr'' c_{\alpha\gamma}(r,r'') \rho_{\gamma}(r'') h_{\gamma\beta}(r'',r')$$  \hspace{1cm}(6.4.1)

to define the direct correlation function $c_{\alpha\beta}(r,r')$. If we formally write

$$c_{\alpha\beta}(r,r') = c_{\alpha\beta}^0(r,r') - \beta z_{\alpha} z_{\beta} e^2 G(r,r')$$  \hspace{1cm}(6.4.2)

and use Eq. (6.4.1) we can write Eq. (6.1.25) in the form

$$F_{\alpha}(r) = -\nabla_r v_{\alpha}^S(r) - z_{\alpha} e \nabla_r v_{\alpha}^I(r) - z_{\alpha} e \nabla_r \psi(r)$$

$$- \int dr' \sum_{\beta} \left[ \nabla_r u_{\alpha\beta}^S(r,r') \right] \rho_{\beta}(r') + h_{\alpha\beta}(r,r')$$

$$+ kT \left[ \nabla_r \left[ h_{\alpha\alpha}(r,r') - c_{\alpha\alpha}^0(r,r') + \beta z_{\alpha} e^2 G(r,r') \right] \right]_{r' \to r}$$

$$- kT \int dr' \sum_{\beta} \left[ \nabla_r c_{\alpha\beta}^0(r,r') \right] \rho_{\beta}(r') h_{\alpha\beta}(r,r')$$  \hspace{1cm}(6.4.3)

which, from Eq. (6.1.13), becomes
and we have succeeded in explicitly canceling the long-ranged direct image term. Eq. (6.4.4) is exact so that both the contact condition and local electroneutrality are satisfied. We can now investigate the effect of various approximations.

The simplest choice for \( c_{ab}(r,r') \) is the approximation

\[
c_{ab}(r,r') = 0 \quad \text{all } r,r'
\]  

(6.4.5)

which is equivalent to a Debye-Hückel closure on \( c_{ab}(r,r') \). \( h_{ab}(r,r') \) then satisfies the equation

\[
\nabla^2 h_{ab}(r,r') = 4\pi [\beta z_\alpha z_\beta e^2 \delta(r,r') + \beta z_\alpha e \sum_\gamma z_\gamma e \rho_\gamma(r) h_{ab}(r,r')] 
\]

(6.4.6)

from which it follows that

\[
h_{ab}(r,r') = -z_\beta e \phi_\alpha(r,r'),
\]

(6.4.7)

where \( \phi_\alpha(r,r') \) satisfies Eq. (6.3.13). This shows that the closure (6.4.5), not unexpectedly, is equivalent to the linearization of Eq. (6.3.12). Thus we can use the various approximations discussed in Section 6.3 to recover the Onsager-Samaras expression [15], and the expressions for \( \phi_\alpha \) given by other workers [2,11,12].

For point ions, it is clear that \( \phi_\alpha(r,r') \) is proportional to \( \lambda \) and since

\[
\lim_{r \to r'} \nabla_r f(r,r') = \frac{1}{\lambda} \nabla_r \lim_{r \to r'} f(r,r') 
\]

(6.4.8)
provided \( f(r, r') = f(r', r) \), the BBGY and Kirkwood charging processes yield the same result. The two approximations differ, however, for the RPM electrolyte.

An alternative approximation for \( c_{\alpha \beta}^0 \) is (for an RPM electrolyte)

\[
c_{\alpha \beta}^0(r, r') = 0 \quad |r - r'| > R \tag{6.4.9}
\]

together with the exact condition

\[
h_{\alpha \beta}(r, r') = -1 \quad |r - r'| < R . \tag{6.4.10}
\]

Eq. (6.4.4) then becomes

\[
F_{\alpha}(r) = -z_{\alpha} e \nabla_r \psi(r) + kT \lim_{r' \to r} \{ \psi(r)[\beta z_{\alpha}^2 e^2 G^{c}(r, r') - c_{\alpha \alpha}^0(r, r')] \}
\]

\[
+ kT \int_V dr' \Sigma_{\beta} \{ \nabla_r c_{\alpha \beta}^0(r, r') \} \rho_\beta(r'), \tag{6.4.11}
\]

where \( V \) is the volume of a sphere of radius \( R \) about \( r \). Eq. (6.4.11) can be immediately integrated (using Eq. (6.4.8)) to give

\[
W_{\alpha}(r) = z_{\alpha} e \psi(r) - \frac{1}{2} kT \left[ \lim_{r' \to r} \{ \beta z_{\alpha}^2 e^2 G^{c}(r, r') - c_{\alpha \alpha}^0(r, r') \} + \frac{1}{2} \end{array}ight.
\]

\[
+ kT \int_V dr' \Sigma_{\beta} \{ c_{\alpha \beta}^0(r, r') \} \rho_\beta(r') - c_{\alpha \beta}^{obulk}(|r - r'|) \rho_\beta \} . \tag{6.4.12}
\]

To implement Eq. (6.4.12), we would have to use Eqs. (6.4.9), (6.4.10) and (6.4.1) to determine \( c_{\alpha \beta}^0(r, r') \). From this we could determine \( h_{\alpha \beta}(r, r') \), which does not appear explicitly in Eq. (6.4.12), and so check the local electroneutrality condition. It seems clear from Chapter 3 that, since \( c_{\alpha \beta}^0(r, r') \approx -\beta e^2 z_{\alpha} z_{\beta} G(r, r') \) and provided \( h_{\alpha \beta}(r, r') \) is calculated from \( c_{\alpha \beta}^0(r, r') \) via the non-uniform Ornstein-Zernike equation, local electroneutrality (as well as Eq. (3.3.24))
will be satisfied. Also, since

\[ h_{\alpha\beta}(r, r') \rightarrow h_{\alpha\beta}^{MSA}(|r - r'|) \quad \text{as} \quad r, r' \rightarrow \infty \]  

(6.4.13)

the contact condition is satisfied with \( p = p^{MSA} \). Unfortunately, the chances of finding \( c_{\alpha\beta}^0(r, r') \) through the coupled equations (6.4.1) and (6.4.12) seem remote.

A cruder approximation would be the further assumption (neglecting image effects)

\[ c_{\alpha\beta}^0(r, r') = c_{\alpha\beta}^{MSA}(|r - r'|) \quad |r - r'| < R. \]  

(6.4.14)

This assumption is inconsistent with Eqs. (6.4.1), (6.4.9) and (6.4.10) so that we must either discard the core condition Eq. (6.4.10), the condition given by Eq. (6.4.9) or the connection between \( h \) and \( c \) given by Eq. (6.4.1). If we retain the core condition and the large-\( r \) behaviour of \( c_{\alpha\beta}^0(r, r') \) then we must accept that \( h \) and \( c \) are no longer related through Eq. (6.4.1) and so local electro-neutrality is no longer obeyed. Similarly, it is no longer true that \( h_{\alpha\beta}(r, r') \) necessarily tends to a bulk distribution function, so that the contact condition is no longer satisfied.

In this case, the approximation Eq. (6.4.14) implies that the second term on the right hand side of Eq. (6.4.12) vanishes and we recover

\[ \hat{W}_{\alpha}(r) = \sum_{\beta} e \psi(r) - kT \int dV \Sigma \rho_{\beta}^{MSA} c_{\alpha\beta}^{MSA}(|r - r'|) h_{\beta}(r'), \]  

(6.4.15)

i.e. the HNC/MSA equations. The preceding comments explain why the HNC/MSA equations do not obey the exact contact condition but instead obey Eq. (4.1.28).
The approximation given by Eq. (4.3.2) contains most of the defects of Eq. (6.4.14) but retains the effects due to local ionic activity contained in the second term of Eq. (6.4.12). For example, the use of $c^\text{MSA}_{ij}(|\mathbf{r} - \mathbf{r}'|; \mathbf{p})$ produces a term (from $c^\text{c}(\mathbf{r})$)

$$\frac{z^2 e^2}{\epsilon R} (B - B_{\text{bulk}}) \rightarrow \frac{z^2 e^2}{2\epsilon} (\kappa + \kappa_{\text{bulk}}) \quad \text{as } R \rightarrow 0,$$

(6.4.16)

where $B$ is given in Chapter 4. This is clearly the same term that is included in the MPB theory as $(F - F_{\text{bulk}})$ (see Eq. (6.3.24)). It describes the changes in the electrostatic component of the local ionic activity, since

$$\langle \ln \gamma^\text{ES}_{\alpha} \rangle^\text{MSA} = \frac{z^2 e^2}{\epsilon R} B,$$

(6.4.17)

and it serves to attract ions to the surface. Another term (from $c^\text{PYHS}(\mathbf{r})$) due to hard sphere interactions does not appear to have such a simple interpretation.

In this chapter we have outlined several theories of the double layer and clarified the strengths and weaknesses of the MPB and HNC/MSA equations. Our attempt to generalize the HNC/MSA equations so as to include image and local ionic activity effects has been largely unsuccessful, because of the difficulty of solving the non-uniform Ornstein-Zernike equation. On this disappointing note, we end our study of PM electrolytes against charged surfaces, and start our investigation of effects due to solvent structure.
REFERENCES


CHAPTER 7
ION/DIPOLAR MIXTURES AGAINST A CHARGED SURFACE IN THE MSA

7.1 ION/DIPOLAR MODEL OF ELECTROLYTES

For the remainder of this thesis, we investigate the effects of solvent structure on the double layer. From the start, we consider only a simple bulk-level model of the electrolyte. The ions are modeled as hard spheres with embedded point charges and the solvent is taken to be a fluid of hard spheres with embedded permanent point dipoles. The dipole solvent properties are determined by specifying the solvent's quadrupole moments on the basis that the contributions of the dipolar solvent are discussed in Chapter 2. Otherwise, all higher multipoles, as well as electronic polarizability effects, are neglected. The cell is taken to be hard, uniformly charged but with $\varepsilon_0 = 1$.

We shall further restrict our model by taking the solvent mixture to be hard spheres of equal diameter $R$, another diameter $d_{\text{ion}}$, and valencies $z_1, z_2, \ldots$, which satisfy the bulk electroneutrality condition

$$\sum_{i=1}^{\infty} z_i = 0.$$ 

The solvent is modeled as a fluid of hard spheres of radius $d_2$ with embedded permanent point dipoles of dipole moment $d$. The intermolecular potential has the form
CHAPTER 7
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7.1 ION/DIPOLE MODEL OF ELECTROLYTES

For the remainder of this thesis, we investigate the effects of solvent structure on the double layer. From the start, we consider only a simple BO-level model of the electrolyte. The ions are modelled as hard spheres with embedded point charges and the solvent is taken to be a fluid of hard spheres with embedded permanent point dipoles. The dielectric constant of the solvent is determined by specifying the molecular properties of the dipolar fluid. The effects of permanent water-like quadrupole moments on the bulk thermodynamics of the dipolar solvent are discussed in Chapter 9. Otherwise, all higher multipole moments, as well as electronic polarizability effects, are neglected. The wall is taken to be hard, uniformly charged but with $\varepsilon_w = 1$.

We shall further restrict our model by taking the ionic solutes to be hard spheres of equal diameter $R_1$, number densities $\rho_1, \rho_j, \ldots$ and valencies $z_1, z_j, \ldots$ which satisfy the bulk electroneutrality condition

$$\sum \rho_i z_i = 0 . \quad (7.1.1)$$

The solvent is modelled as a fluid of hard spheres of number density $\rho_d$, diameter $R_2$, with embedded permanent point dipole of dipole moment $\mu$. The intermolecular potentials have the form:
ion-ion:

\[
    u_{ij}(r) = \begin{cases} 
        \infty & , \quad r < R_1 \\
        \frac{z_i z_j e^2}{r} & , \quad r > R_1
    \end{cases}
\]  

(7.1.2)

ion-dipole:

\[
    u_{id}(r, \omega) = \begin{cases} 
        \infty & , \quad r < R_{12} \equiv \frac{1}{2}(R_1 + R_2) \\
        -\frac{z_i e \mu(\omega)}{r^2} & , \quad r > R_{12}
    \end{cases}
\]  

(7.1.3)

dipole-dipole:

\[
    u_{dd}(\omega_1, \omega_2) = \begin{cases} 
        \infty & , \quad r < R_2 \\
        -\frac{\mu^2 D_{12}}{r^3} & , \quad r > R_2
    \end{cases}
\]  

(7.1.4)

and

\[
    D_{12} \equiv \hat{\mu}(\omega_1) \cdot \left(3\hat{\mu}(\omega_2) - \frac{1}{2} I \right) \hat{\mu}(\omega_2)
\]  

(7.1.5)

where \( e \) is the protonic charge and \( I \) the 3 x 3 unit tensor. \( \hat{\mu}(\omega) \) is a unit vector in the direction of the dipole moment whose orientation is specified by the angular variable \( \omega = (\theta, \phi) \) with \( \int d\omega = 4\pi \). The subscripts \( i, j, k, \ldots \) will hereafter be reserved for ionic quantities and the subscript \( d \) for dipoles.

The structure of this ion-dipole mixture at a uniformly charged planar surface is obtained by first considering the structure about a single spherical colloidal particle of diameter \( R_0 \gg R_1 \) and valence \( z_0 \). The structure at a planar surface is then recovered by taking the limit \( R_0 \to \infty, z_0 \to \infty \) but at constant surface charge density \( \sigma_0 = z_0 e/\pi R_0^2 \). This limit is only taken when it is "safe" to do so without causing any divergences. The interaction potentials between the surface and the ions and dipoles are:
surface-ion:

\[ u_{0j}(r) = \begin{cases} \infty, & r < R_{10} = \frac{1}{2}(R_1 + R_2) \\ \frac{z_iz_je^{2}}{r}, & r > R_{10} \end{cases} \]  \hspace{1cm} (7.1.6)

surface-dipole:

\[ u_{0d}(r, \omega) = \begin{cases} \infty, & r < R_{20} = \frac{1}{2}(R_2 + R_0) \\ \frac{Z_0 e^{i\omega \cdot \hat{r}}}{r^2}, & r > R_{20} \end{cases} \]  \hspace{1cm} (7.1.7)

with the subscript 0 referring to quantities associated with the surface.

Integral equation theories of non-simple fluids, whose molecules interact via angle-dependent potentials, are based on the Ornstein-Zernike equation (written here in matrix form)

\[ h(x_1, x_2) = c(x_1, x_2) + \frac{1}{8\pi^2} \int d\omega_3 \int_3 c(x_1, x_3) \rho(\omega) h(x_3, x_2), \]  \hspace{1cm} (7.1.8)

where the \((\alpha, \beta)\) component of \(h\) or \(c\) is the total or direct correlation function between species \(\alpha\) and \(\beta\), and \(\rho\) is a diagonal matrix with elements \(\rho_{\alpha} \delta_{\alpha\beta}\) with \(\rho_{\alpha}\) being the density of species \(\alpha\).

The coordinate \(x = (r, \omega)\) denotes both the position vector \(r\) as well as the set of Euler angles \(\omega = (\theta, \phi, \chi)\) of each molecule. By appealing to translational and rotational invariance of the bulk fluid we can use the following expansion to separate radial and orientational behaviour in any function \(f_\| (= h \; \text{or} \; c) [1]\)

\[ f_\| (x_1, x_2) = \sum_{mnL} \int_{\mu\nu} f_{\ell\mu\nu}^{mnL}(r) \phi_{\mu\nu}^{mnL}(\omega_1, \omega_2, \hat{r}). \]  \hspace{1cm} (7.1.9)

In this expansion, the functions \(f_{\ell\mu\nu}^{mnL}(r)\) depend only on the scalar distance, \(r\), between the molecules. The rotational invariants \(\phi_{\mu\nu}^{mnL}\)
are functions only of the orientation variables of the molecules $\omega_1, \omega_2$ and the direction of the intermolecular axis, $\hat{r}$, relative to the laboratory frame. The orientation-independent term in Eq. (7.1.9) is just $f_{000}^{000}(r)$ since $\psi_{00}^{000}(\omega_1, \omega_2, \hat{r}) = 1$.

The hard sphere condition then becomes

$$h_{000}^{000}(r) = -1, \quad r < R_{\alpha\beta}$$

$$h_{\mu\nu}^{\alpha\beta}(r) = 0, \quad r < R_{\alpha\beta}, \text{ all other } (\alpha\beta, \mu\nu),$$

where $f$ denotes the $(\alpha, \beta)$ component of $\hat{r}$.

The MSA closure between $c$ and $h$ is

$$c(x_1, x_2) = -\beta u(x_1, x_2), \quad r > R$$

which becomes

$$c_{\mu\nu}^{\alpha\beta}(r) = -\beta u_{\mu\nu}^{\alpha\beta}(r), \quad r > R_{\alpha\beta}$$

upon using the expansion

$$u(x_1, x_2) = \sum_{\mu\nu} u_{\mu\nu}^{\alpha\beta}(r) \phi^{\mu\nu}_{\alpha\beta}(\omega_1, \omega_2, \hat{r}).$$

It turns out that in the MSA theories of polar fluids [2-8], Eq. (7.1.12) ensures that only a finite, manageable small subset of the components $f_{\mu\nu}^{\alpha\beta}(r)$ are non-vanishing.

The HNC closure between $c(x_1, x_2)$ and $h(x_1, x_2)$ is

$$c(x_1, x_2) = -\beta u(x_1, x_2) + h(x_1, x_2) - 2n[1 + h(x_1, x_2)]$$

$$= -\beta u(x_1, x_2) + h(x_1, x_2) - 2n[1 + f_{000}^{000}(r) + h'(x_1, x_2)],$$

where

$$h'(x_1, x_2) = h_{000}(x_1, x_2) - f_{000}^{000}(r).$$

The non-linear term on the right hand side of Eq. (7.1.14) entails
that each component, $C_{\mu \nu}^{mn}(r)$, is coupled to an infinite series of the other components. A suggestion due to Patey [9] is to expand the logarithmic term about $\ln[1 + h_{00}^{00}(r)]$. If only the term linear in $h'(x_1, x_2)$ is retained, we have the linearized HNC (LHNC) equations [9]

$$c_{00}^{00}(r) = -\beta u_{00}^{00}(r) + h_{00}^{00}(r) - \ln[1 + h_{00}^{00}(r)], \quad r > R_{d\beta}$$

$$c_{\mu \nu}^{mn}(r) = -\beta u_{\mu \nu}^{mn}(r) + \left( \frac{h_{00}^{00}(r)}{1 + h_{00}^{00}(r)} \right) h_{\mu \nu}^{mn}(r), \quad r > R_{d\beta}, \quad \text{all other } (mn, \mu \nu)$$

(7.1.16)

If the next term in the expression is also retained, we have the quadratic HNC (QHNC) approximation [10]. A further restriction is necessary to make these theories tractable — only the components that appear in the MSA solution are considered. In the MSA and LHNC theories, all contributions to this set of components appearing in the MSA come from within the same set, i.e. the set is closed. In the QHNC, however, there are contributions to the MSA set from components outside the set which have been arbitrarily neglected. In this sense, the QHNC theory is inconsistent.

For model fluids consisting of equal size hard spheres with embedded dipoles or higher multipoles, the three approximations have qualitatively different features. In the MSA [2,6], the angle-independent correlation function decouples entirely from the angle-dependent functions and is just the Percus-Yevick hard sphere correlation function. The angle-dependent correlation functions are independent of $h_{00}^{00}(r)$. In the LHNC, the angle-independent function is just the HNC hard sphere correlation function but the angle-dependent functions are now coupled to $h_{00}^{00}(r)$. Only in the QHNC is $h_{00}^{00}(r)$ dependent on the electrostatic interactions. Both the angle-independent and angle-dependent correlation functions must be found
simultaneously. Thus only the QHNC contains the possibility of reproducing the observation (from Monte Carlo calculations on a quadrupolar system) that $h^{000}_{00}(r)$ differs appreciably from the hard sphere correlation function [11].

For our case, ion-dipole mixtures, we can simplify the general formalism. The factor $8\pi^2$ in Eq. (7.1.8) becomes $4\pi^2$ and the only angular functions that appear are [6] $D_{12}$ (given in Eq. (7.1.5)),

$$E_i = \hat{\mathcal{G}}(\omega_1) \cdot \hat{r}$$

and

$$\Delta_{12} = \hat{\mathcal{G}}(\omega_1) \cdot \mathcal{G}(\omega_2).$$

These angular functions are proportional to $\phi^{112}_{00}(\omega_1, \omega_2, \hat{r})$, $\phi^{101}_{00}(\omega_1, \omega_2, \hat{r})$ and $\phi^{110}_{00}(\omega_1, \omega_2, \hat{r})$, respectively. Throughout Chapters 7 and 8, therefore, we use only the components $f^{000}_{00}(r)$, $f^E(r)$, $f^D(r)$ and $f^A(r)$. When considering quadrupolar effects in Chapter 9, we return to the more general formalism of Eq. (7.1.9).

The main statistical mechanical problem is to evaluate the density distribution of ionic species $\rho_{oi}(r) \equiv \rho_{oi} [1 + h_{oi}(r)]$ and dipolar species $\rho_{od}(r, \omega) \equiv \rho_d [1 + h_{od}(r, \omega)]$ around the colloidal particle. Here $h_{oi}(r)$ is the surface (or colloidal particle) — ion indirect correlation function at a distance $r$ from the centre of the colloidal particle and $h_{od}(r, \omega)$ is the indirect correlation function between the surface and a dipole at position $r$ and orientation $\omega$. All thermodynamic quantities associated with the surface can be written in terms of $h_{oi}(r)$ and $h_{od}(r, \omega)$.

The Ornstein-Zernike equation for the surface-particle correlation functions is
where the summation is over all ionic and dipolar species. The bulk correlation functions $c_{\alpha\beta}$ are assumed to be known. The use of Eq. (7.1.19) and a simple closure on $c_{\alpha\alpha}(x_1,x_2)$ will lead to a poor treatment of lateral interactions close to the surface, just as in Chapter 5. For this reason we cannot expect any surface charge saturation phenomena to be present in theories based on Eq. (7.1.19). Any observed saturation will be an artifact of linearization. From the results of Chapter 6, we can see that such theories will neglect effects due to local ionic activity.

Our choice for the bulk correlation functions $c_{\alpha\beta}$ is not wide since at the time this work was done, no LHNC results for ion-dipole mixtures at finite concentrations had been reported. MSA correlation functions were thus the natural choice. Previous study of the MSA ion-dipole mixture [6] has shown that the experimentally observed turning point in $\ln \gamma^+$, the mean ionic activity coefficient, as a function of ionic concentration is not reproduced in the model fluid. We can avoid this unrealistic behaviour of the model electrolyte by restricting our attention to the regime of low ionic concentrations, since the MSA ion-dipole mixture does reproduce the Debye-Hückel limiting law.

We now have a choice of closures between $h_{\alpha\alpha}(x_1,x_2)$ and $c_{\alpha\alpha}(x_1,x_2)$. One interesting feature of the ion-dipole mixture is that the image forces due to the dielectric discontinuity ($\varepsilon_u = 1$ and $\varepsilon$ defined by the molecular properties of the dipole) are completely described by the pair potentials Eqs. (7.1.2) - (7.1.7). In a PM electrolyte, three-body potentials are required to describe the same
image forces. For any other choice of $\varepsilon_w$, however, three-body potentials are necessary at both levels of description. It is clear that the MSA closure neglects the image forces since the $h^{000}_0(r)$ functions decouple from the angle-dependent interactions. Both the LHNC and QHNC contain terms due to image interactions with the QHNC retaining more of these terms than the LHNC.

For the sake of obtaining analytic results, we use the MSA closure on $h_{00}$ and $c_{00}$

$$h_{00}(x_1,x_2) = -1, \quad r < R_{00} \tag{7.1.20}$$

and

$$c_{00}(x_1,x_2) = -\beta u_{00}(x_1,x_2), \quad r > R_{00}. \tag{7.1.21}$$

As in the RPM case discussed in the Appendix of Chapter 5, this closure ensures a linear relationship between $\psi_0$ and $\sigma_0$. Our results are therefore restricted to the regime of low surface charge densities, where linearization is not a serious defect.

In the next section we present the requisite analysis for the bulk MSA ion-dipole mixture, which we use in Section 7.3 when we solve for the surface correlation functions and thermodynamic quantities. In Section 7.4 we present our results in a simple form and discuss their implications.

7.2 BULK MSA ION-DIPOLE MIXTURE

Our method of solution is based on Ref. 6 which in turn uses techniques developed by Wertheim [2] and Baxter [12]. The Ornstein-Zernike equations for the ion-dipole mixture are explicitly
\[ h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int d\mathbf{r}' c_{ik}(|r-r'|) h_{kj}(r') \]
\[ + \frac{\rho_d}{4\pi} \int d\omega_3 d\mathbf{r}' c_{id}(r-r',\omega_3) h_{dj}(\omega_3,r') \quad (7.2.1a) \]

\[ h_{id}(r,\omega_2) = c_{id}(r,\omega_2) + \sum_k \rho_k \int d\mathbf{r}' c_{ik}(|r-r'|) h_{kd}(r',\omega_2) \]
\[ + \frac{\rho_d}{4\pi} \int d\omega_3 d\mathbf{r}' c_{id}(r-r',\omega_3) h_{dd}(\omega_3,r',\omega_2) \quad (7.2.1b) \]

\[ h_{di}(\omega_1, r) = c_{di}(\omega_1, r) + \sum_k \rho_k \int d\mathbf{r}' c_{dk}(\omega_1, r-r') h_{ki}(r') \]
\[ + \frac{\rho_d}{4\pi} \int d\omega_3 d\mathbf{r}' c_{di}(\omega_1, r-r',\omega_3) h_{di}(\omega_3, r') \quad (7.2.1c) \]

and

\[ h_{dd}(\omega_1, r, \omega_2) = c_{dd}(\omega_1, r, \omega_2) + \sum_k \rho_k \int d\mathbf{r}' c_{dk}(\omega_1, r-r') h_{kd}(r', \omega_2) \]
\[ + \frac{\rho_d}{4\pi} \int d\omega_3 d\mathbf{r}' c_{dd}(\omega_1, r-r', \omega_3) h_{dd}(\omega_3, r', \omega_2) \]
\[ \quad (7.2.1d) \]

where the summation is over all ionic species.

The exact hard core conditions are

\[ c_{ij}(r) = - \frac{\beta e^2 z_i z_j}{r}, \quad r > R_i \quad (7.2.2a) \]

\[ c_{id}(r, \omega_1) = \frac{z_i \beta e^\mu}{r^3} E_2, \quad r > R_i \quad (7.2.2b) \]

\[ c_{di}(\omega_1, r) = - \frac{z_i \beta e^\mu}{r^3} E_1, \quad r > R_i \quad (7.2.2c) \]

and

\[ c_{dd}(\omega_1, r, \omega_2) = \frac{\beta e^2}{r^3} D_{12}, \quad r > R_2 \quad (7.2.2d) \]

where we have used the convention that the vector \( r \) in Eqs. (7.2.2b) and (7.2.2c) is directed from the first particle towards the second.

The exact hard core conditions are
It is shown in Ref. 6 that the angular functions $l$, $E_i$, $\Delta_{12}$ and $D_{12}$ form a closed set under angular convolution and are the only components appearing. For the case of equal ion size, the decomposition

\begin{align*}
  f_{ij}(r) &= f^{1s}_{11}(r) + z_1 z_j f^{C}_{11}(r) 
\end{align*}

\begin{align*}
  f_{id}(r, \omega_2) &= f^{1s}_{12}(r) + z_1 f^{E}_{12}(r) E_2 
\end{align*}

\begin{align*}
  f_{di}(\omega_1, r) &= f^{1s}_{21}(r) + z_1 f^{E}_{21}(r) E_1 
\end{align*}

\begin{align*}
  f_{dd}(\omega_1, \omega_2, r) &= f^{1s}_{22}(r) + f^{A}_{12} + f^{D}_{12} D_{12} 
\end{align*}

is valid. From symmetry considerations, we see that

\begin{align*}
  f^{1s}_{12}(r) &= f^{1s}_{21}(r) 
\end{align*}

\begin{align*}
  f^{E}_{12}(r) &= -f^{E}_{21}(r) .
\end{align*}

Eq. (7.2.4) simplifies the analysis greatly -- for unequal ion sizes, the methods of Blum [5] are required.

Eqs. (7.2.1) are in Fourier convolution form and on Fourier transformation become

\begin{align*}
  \tilde{h}_{ij}(k) &= \tilde{c}_{ij}(k) + \sum_k \rho_k \tilde{c}_{ik}(k) \tilde{h}_{kj}(k) \\
  &+ \frac{\rho_d}{4\pi} \int d\omega_3 \tilde{e}_{id}(k, \omega_3) \tilde{h}_{dj}(\omega_3, k)
\end{align*}
\[ \tilde{h}_{id}(k, \omega_2) = \tilde{c}_{id}(k, \omega_2) + \sum_k \rho_k \tilde{c}_{ik}(k) \tilde{h}_{kd}(k, \omega_2) \]
\[ + \frac{\rho_d}{4\pi} \int d\omega_3 \tilde{c}_{id}(k, \omega_3) \tilde{h}_{dd}(\omega_3, k, \omega_2) \]  
\[ (7.2.6b) \]
\[ \tilde{h}_{di}(\omega_1, k) = \tilde{c}_{di}(\omega_1, k) + \sum_k \rho_k \tilde{c}_{dk}(\omega_1, k) \tilde{h}_{ki}(k) \]
\[ + \frac{\rho_d}{4\pi} \int d\omega_3 \tilde{c}_{di}(\omega_1, \omega_3) \tilde{h}_{dd}(\omega_3, k) \]  
\[ (7.2.6c) \]
\[ \tilde{h}_{dd}(\omega_1, k, \omega_2) = \tilde{c}_{dd}(\omega_1, k, \omega_2) + \sum_k \rho_k \tilde{c}_{dk}(\omega_1, k) \tilde{h}_{kd}(k, \omega_2) \]
\[ + \frac{\rho_d}{4\pi} \int d\omega_3 \tilde{c}_{dd}(\omega_1, \omega_3, k) \tilde{h}_{dd}(\omega_3, k) \]  
\[ (7.2.6d) \]

where
\[ \tilde{r}(k) = \int dr e^{-ikr} \tilde{r}(r) \]  
\[ (7.2.7) \]

Eqs. (7.2.7) and (7.2.4) then entail
\[ \tilde{r}_{ij}(k) = \tilde{r}^{HS}_{ij}(k) + \tilde{z}_i \tilde{z}_j \tilde{r}^C_{ij}(k) \]  
\[ (7.2.8a) \]
\[ \tilde{r}_{id}(k, \omega_2) = \tilde{r}^{HS}_{id}(k) + \tilde{z}_i \tilde{r}^E_{id}(k) \]  
\[ (7.2.8b) \]
\[ \tilde{r}_{di}(\omega_1, k) = \tilde{r}^{HS}_{di}(k) + \tilde{z}_i \tilde{r}^E_{di}(k) \]  
\[ (7.2.8c) \]
\[ \tilde{r}_{dd}(\omega_1, k, \omega_2) = \tilde{r}^{HS}_{dd}(k) + \tilde{r}^{A}_{dd}(k) \Delta_{12} + \tilde{r}^{D}_{dd}(k) \tilde{D}_{12} \]  
\[ (7.2.8d) \]

where
\[ \tilde{E}_i = \hat{\mu}(\omega_i) \hat{k} \]  
\[ (7.2.9a) \]
and
\[ \tilde{D}_{12} = \hat{\mu}(\omega_1) (3 \hat{k} \hat{k} - 1) \hat{\mu}(\omega_2) \]  
\[ (7.2.9b) \]

The transformed components in Eq. (7.2.8) are related to the original components of Eq. (7.2.4) by
\[ r^D(k) = -4\pi \int_0^\infty dr r^2 j_2(kr) r^D(r) \]  
\[ (7.2.10a) \]
\[ r^E(k) = -4\pi i \int_0^\infty dr r^2 j_1(kr) r^E(r) \]  
\[ (7.2.10b) \]
and

\[ \tilde{f}(k) = 4\pi \int_0^\infty d r^2 j_0(kr) f(r) , \]  

(7.2.10c)

where \( \tilde{f} \) is \( \tilde{f}^\Delta \), \( \tilde{f}^C \) or \( \tilde{f}^C \) and \( j_n(x) \) is the spherical Bessel function.

The closed set of angular functions 1, E, \( \Delta \) and D, obeys the multiplication table under angular convolution given in Table 1.

Substituting Eq. (7.2.8) into Eq. (7.2.6) and using the multiplication table, we obtain nine distinct equations which decouple into three separate groups.

The hard sphere functions decouple entirely and become

\[ \tilde{h}_{11}^{HS}(k) = c_{11}^{HS}(k) + \rho_1 c_{21}^{HS}(k) \tilde{h}_{11}^{HS}(k) + \rho_2 c_{12}^{HS}(k) \tilde{h}_{12}^{HS}(k) \]  

(7.2.11a)

\[ \tilde{h}_{12}^{HS}(k) = c_{12}^{HS}(k) + \rho_1 c_{21}^{HS}(k) \tilde{h}_{12}^{HS}(k) + \rho_2 c_{11}^{HS}(k) \tilde{h}_{11}^{HS}(k) \]  

(7.2.11b)

\[ \tilde{h}_{21}^{HS}(k) = c_{21}^{HS}(k) + \rho_1 c_{12}^{HS}(k) \tilde{h}_{21}^{HS}(k) + \rho_2 c_{22}^{HS}(k) \tilde{h}_{22}^{HS}(k) \]  

(7.2.11c)

\[ \tilde{h}_{22}^{HS}(k) = c_{22}^{HS}(k) + \rho_1 c_{21}^{HS}(k) \tilde{h}_{22}^{HS}(k) + \rho_2 c_{11}^{HS}(k) \tilde{h}_{12}^{HS}(k) \]  

(7.2.11d)

where

\[ \rho_1 = \sum_i \rho_i \]  

(7.2.12a)

and

\[ \rho_2 = \rho_d . \]  

(7.2.12b)

From Eqs. (7.2.3) and (7.2.4) it is evident that the hard sphere and MSA closure conditions on \( \tilde{f}^{HS}(r) \) are just

\[ \tilde{h}_{\alpha\beta}^{HS}(r) = -1 , \quad r < R_{\alpha\beta} \quad (\alpha, \beta = 1 \text{ or } 2) \]  

(7.2.13a)

and

\[ \tilde{c}_{\alpha\beta}^{HS}(r) = 0 , \quad r > R_{\alpha\beta} \]  

(7.2.13b)

so that \( \tilde{h}_{\alpha\beta}^{HS}(r) \) are just the Percus-Yevick hard sphere correlation functions for a mixture of hard spheres of diameter \( R_i \) at density \( \sum \rho_i \).
with hard spheres of diameter $R_z$ at density $\rho_d$.

The remaining two groups of equations are comprised of the electrostatic components of $h$ and $c$. One group consists of the four equations

\begin{align*}
\tilde{h}^c_{11}(k) &= \tilde{c}^c_{11}(k) + \rho_1 \tilde{c}^c_{11}(k) \tilde{h}^c_{11}(k) + \rho_2 \tilde{c}^E_{12}(k) \tilde{h}^E_{21}(k) \quad (7.2.14a) \\
\tilde{h}^E_{12}(k) &= \tilde{c}^E_{12}(k) + \rho_1 \tilde{c}^c_{11}(k) \tilde{h}^E_{12}(k) + \rho_2 \tilde{c}^E_{12}(k) \tilde{h}^c_{12}(k) \quad (7.2.14b) \\
\tilde{h}^c_{21}(k) &= \tilde{c}^E_{21}(k) + \rho_1 \tilde{c}^E_{21}(k) \tilde{h}^c_{11}(k) + \rho_2 \tilde{c}^+_{12}(k) \tilde{h}^E_{21}(k) \quad (7.2.14c) \\
\tilde{h}^+(k) &= \tilde{c}^+(k) + \rho_1 \tilde{c}^E_{21}(k) \tilde{h}^E_{12}(k) + \rho_2 \tilde{c}^+(k) \tilde{h}^E_{21}(k) \quad (7.2.14d)
\end{align*}

where

\begin{align*}
\tilde{t}^+(k) &= \tilde{t}^+(k) + 2\tilde{t}^D(k) \quad (7.2.15) \\
\rho_1^c &= \Sigma \rho_1 z_i^2 \quad (7.2.16a) \\
\rho_2^c &= \frac{\rho_d}{3} \quad (7.2.16b)
\end{align*}

The one remaining equation is

\begin{equation}
\tilde{h}^-(k) = \tilde{c}^-(k) + \rho_2 \tilde{c}^-(k) \tilde{h}^-(k) \quad (7.2.17)
\end{equation}

where

\begin{equation}
\tilde{t}^-(k) = \tilde{t}^A(k) - \tilde{t}^D(k) \quad (7.2.18)
\end{equation}

Eq. (7.2.17) is the same as the corresponding equation for the pure dipolar fluid [2]. For this reason, it is possible to follow Wertheim's method and show that $h^-$ and $c^-$ must have the same functional form as in the pure dipolar case. In particular,

\begin{equation}
1 - \rho_2 \tilde{c}^-(0) = K(-\xi) \quad (7.2.19)
\end{equation}

where

\begin{equation}
K(\eta) = \frac{(1 + 2\eta)^2}{(1 - \eta)^4} \quad (7.2.20)
\end{equation}

and $\xi$ is a parameter that is proportional to the contribution to the
internal energy due to dipole-dipole interactions, viz.

\[ \zeta \propto \int_{R}^{\infty} \frac{h_D(r)}{r} \, dr. \]  

(7.2.21)

Eq. (7.2.17) couples to Eq. (7.2.14) only through Eq. (7.2.2d).

A solution for MSA ion-dipole mixture thermodynamics therefore hinges on the solution of Eq. (7.2.14). We now drop the superscripts in Eq. (7.2.14) and write \( \tilde{f}^+(k) \) as \( \tilde{f}_{22}(k) \). Since from Eq. (7.2.10) \( \tilde{c}_{11}(k) \) and \( \tilde{c}_{22}(k) \) are even functions of \( k \), \( \tilde{c}_{12}(k) \) and \( \tilde{c}_{21}(k) \) are odd functions of \( k \) and Eq. (7.2.5b) holds, we see that the matrix \( \tilde{c}(k) \) given by

\[ \tilde{c}(k) = \begin{pmatrix} \tilde{c}_{11}(k) & \tilde{c}_{12}(k) \\ \tilde{c}_{21}(k) & \tilde{c}_{22}(k) \end{pmatrix} \]  

satisfies the condition

\[ \tilde{c}^T(-k) = \tilde{c}(k) \]  

(7.2.23)

necessary for the application of Baxter's factorization method.

As in the RPM electrolyte case described in the appendix to Chapter 5, we only require \( Q_{\alpha\beta}(r) \) (\( \alpha, \beta = 1 \) or 2) in order to describe the bulk thermodynamic properties and direct correlation functions.

The specification of \( Q_{\alpha\beta}(r) \) is the goal of this section.

The Baxter factorization leads to the equations (\( \alpha, \beta = 1 \) or 2)

\[ \tilde{c}_{\alpha\beta}(k) = \tilde{q}_{\alpha\beta}(k) + \tilde{q}_{\beta\alpha}(-k) - \sum_{\gamma=1,2} \rho_{\gamma} \tilde{q}_{\gamma\alpha}(k) \tilde{q}_{\gamma\beta}(-k). \]  

(7.2.24)

Now, from Eqs. (7.2.8) and (7.2.2), \( \tilde{c}_{\alpha\beta}(k) \) have the following behaviour around \( k = 0 \),

\[ \tilde{c}_{11}(k) = -\frac{4\pi \beta e^2}{k^2} \]  

(7.2.25a)

\[ \tilde{c}_{12}(k) = -\tilde{c}_{21}(k) = -\frac{4\pi i \beta e \mu}{k} \]  

(7.2.25b)
\[ \tilde{\tau}_{22}(k) = \tilde{\tau}_{22}(0), \quad \text{a constant.} \] (7.2.25c)

This behaviour around \( k = 0 \) leads to the following properties of \( Q_{\alpha \beta}(r) \)

\[
Q_{11}(r) = -A_{11}, \quad r > R_1
\]
\[= 0, \quad r < 0 \] (7.2.26a)

\[
Q_{21}(r) = -A_{21}, \quad r > R_{12}
\]
\[= 0, \quad r < S_{21} \] (7.2.26b)

\[
Q_{12}(r) = 0, \quad r > R_{12}, r < S_{12} \] (7.2.27a)

\[
Q_{22}(r) = 0, \quad r > R_2, r < 0. \] (7.2.27b)

At this stage, it is convenient to introduce the notation for the moments of \( Q_{\alpha \beta}(r) \)

\[
M^{(n)}_{\alpha \beta} = \int_{r_{\alpha \beta}}^{R_{\alpha \beta}} (R_{\alpha \beta} - r)^n Q_{\alpha \beta}(r) \, dr \quad (7.2.28)
\]

and the definitions

\[
a_2 = 1 - \rho_2 M^{(0)}_{22} \]
(7.2.29a)

\[
a_1 = 1 - \rho_1 M^{(0)}_{11} \]
(7.2.29b)

\[
s = R_2 - \rho_2 M^{(1)}_{22} \quad . \] (7.2.29c)

Matching coefficients of \( k^{-1} \) in Eq. (7.2.24) then leads to the results

\[
4\pi \beta \epsilon = \rho_1 A_{11}^2 + \rho_2 A_{21}^2 \quad (7.2.30)
\]

\[
4\pi \beta \mu = A_{21}a_2 - \rho_1 A_{11} M^{(0)}_{12} \quad . \] (7.2.31)

Another equation comes from Eq. (7.2.2d), which can be written

\[
\tilde{\tau}^{D}(0) = -\frac{4\pi \beta \mu^2}{3} \quad (7.2.32)
\]

or

\[
4\pi \beta \rho_2 \mu^2 = [1 - \rho_2 \tilde{\tau}^+(0)] - [1 - \rho_2 \tilde{\tau}^-(0)] \quad (7.2.33)
\]

which becomes, using Eqs. (7.2.24) and (7.2.19),
The determination of \( Q_{\alpha\beta}(r) \) follows from the equation

\[
H_{\alpha\beta}(r) = Q_{\alpha\beta}(r) + \sum_{\gamma} \rho_{\gamma} \int_{S_{\alpha\gamma}} ds Q_{\gamma\gamma}(s) H_{\gamma\beta}(r-s),
\]

where

\[
F(r) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk e^{-ikr} \tilde{f}(k).
\]

Eqs. (7.2.36) and (7.2.10) then show that

\[
F^D(r) = 2\pi \int_{|r|}^{\infty} ds \, s \, \rho_{1}(r) \tilde{f}^D(s),
\]

\[
F^E(r) = 2\pi \int_{|r|}^{\infty} ds \, s \, \rho_{1}(r) \tilde{f}^E(s),
\]

and

\[
F(r) = 2\pi \int_{|r|}^{\infty} ds \, \rho_{0}(r) \tilde{f}(s),
\]

where \( f \) is \( f_{HS} \), \( f^C \) or \( f^A \). In the RPM electrolyte all functions transform as in Eq. (7.2.37c).

The hard sphere conditions show that

\[
h_{\alpha\beta}(r) = 0, \quad S_{\alpha\beta} < r < R_{\alpha\beta}
\]

so that

\[
H_{11}(r) = 2\pi \int_{R_1}^{\infty} ds \, h_{11}(s) \equiv H_{11}, \quad r < R_1
\]

\[
H_{21}(r) = 2\pi \int_{R_1}^{\infty} ds \, h_{21}(s) \equiv rH_{21}, \quad r < R_{21}
\]

and

\[
H_{22}(r) = r^2 \left\{ \frac{12\varepsilon}{\rho_{2}R_2^3} \right\} + H_{22}, \quad r < R_2.
\]

We now proceed as in the RPM electrolyte, by differentiating each equation of Eq. (7.2.35) and using Eqs. (7.2.38) and (7.2.39) to express \( Q_{\alpha\beta}(r) \) in terms of the 11 constants \( A_{11}, A_{21}, H_{11}, H_{21}, a_i \).
By differentiation of Eqs. (7.2.34) we find

\[ Q_{11}(r) = -A_{11} \quad \text{, } r > R_1 \]  
\[ Q_{21}(r) = -A_{21} \quad \text{, } r > R_{21} \]  
\[ Q_{12}(r) = 0 \quad \text{, } r > R_{12} \]  
\[ Q_{22}(r) = 0 \quad \text{, } r > R_2 \]

Evaluation of the H-Q equation leads to the equations (the first two from \( H_{11} - Q_{11} \), the next two from \( H_{21} - Q_{21} \), then \( H_{12} - Q_{12} \) and \( H_{22} - Q_{22} \))

\[ H_{11}a_1 = -\frac{24\xi}{\rho_2 R_2^3} a_2 - \frac{24\xi}{\rho_2 R_2^3} M_{12}'(0) \quad (7.2.41a) \]

\[ 1 - a_1 = -\rho_2 H_{12} M_{12}'(0) + S_{12} M_{12}'(0) \quad (7.2.41b) \]

\[ H_{21} [s + S_{12} a_2] = -\frac{24\xi}{\rho_2 R_2^3} a_2 + \frac{24\xi}{\rho_2 R_2^3} M_{12}'(0) \quad (7.2.41c) \]
\[ M_{21}^{(0)} = -A_{21}R_1 - \frac{bR_1^2}{3} \left( \rho_{11}A_{21}H_{11} + H_{11}a_2 \right) \]  

(7.2.41d)

\[ M_{12}^{(0)} = \frac{bR_2^2H_{21}}{(1 - 2\xi)^2} \left\{ a_1 - \rho_{11}A_{11} \left( \frac{1}{3} R_2 (1 + \xi) + S_{12} \right) \right\} \]  

(7.2.41e)

\[ M_{12}^{(1)} = -\frac{bR_2^2H_{21}}{(1 - 2\xi)^2} \left\{ \frac{1}{3} a_1 (\xi - 2) + \rho_{11}A_{11} \left( \frac{1}{4} R_2 + \frac{1}{3} S_{12} (\xi - 2) \right) \right\} \]  

(7.2.41f)

\[ a_2 = \frac{1 + 4\xi}{(1 - 2\xi)^2} + \frac{b\rho_{11}\rho_{21}R_2^2H_{21}}{(1 - 2\xi)^2} \left\{ M_{21}^{(0)} + \frac{1}{3} A_{21} \left( R_2 (1 + \xi) + S_{12} \right) \right\} \]  

(7.2.41g)

\[ \frac{s}{R_2} = \frac{1 + \xi}{(1 - 2\xi)^2} + \frac{b\rho_{11}\rho_{21}R_2^2H_{21}}{(1 - 2\xi)^2} \left\{ \frac{1}{3} M_{21}^{(0)} (2 - \xi) + A_{21} \left( \frac{1}{4} R_2 + \frac{1}{3} S_{12} (2 - \xi) \right) \right\} \]  

(7.2.41h)

For arbitrary concentration, the 11 equations Eqs. (7.2.30), (7.2.31), (7.2.34) and (7.2.41) must be solved numerically. We are interested mainly in the low concentration regime, and so a perturbation expansion in \( \kappa R_1 \) gives us the following quantities to order \( \kappa R_1 \) or equivalently to order \( \rho_1^{1/2} \):

\[ a_2 = q_+^{1/2} \]  

(7.2.42a)

\[ \rho_{11}A_{11} = \kappa \left( 1 + \frac{\gamma(\gamma - 1)}{4q_+^{1/2}} \right) \]  

(7.2.42b)

\[ a_1 = 1 + \kappa R_1 \]  

(7.2.42c)

\[ A_{21} = \frac{4\pi\beta\epsilon\mu}{q_+^{1/2}} \left( 1 - \frac{\gamma R_2}{4q_+^{1/2}} \right) \]  

(7.2.42d)

\[ M_{12}^{(0)} = \frac{-\pi\beta\epsilon\gamma R_2}{q_+^{1/2}} \]  

(7.2.42e)

\[ M_{21}^{(0)} = \frac{-4\pi\beta\epsilon\gamma R_1}{q_+^{1/2}} \left( 1 - \frac{\gamma R_1}{4R_2} \right), \]  

(7.2.42f)

where

\[ \gamma = \frac{R_2}{R_2 (1 + \xi) + S_{12} (1 + 4\xi)} \]  

(7.2.43)

\[ q_+ = K(2\xi) = \frac{(1 + 4\xi)^2}{(1 - 2\xi)^n}. \]  

(7.2.44)
In Eqs. (7.2.42) - (7.2.44) $\xi$ has the same numerical value as for the pure dipolar fluid (at least to order $(\kappa R)$) since $\xi$ is the solution of

$$4\pi \beta \rho_2 u^2 = K(2\xi) - K(-\xi) \tag{7.2.45}$$

which is just Eq. (7.2.34) to order $(\kappa R)$. The dielectric constant $\varepsilon$ appearing explicitly and implicitly via $\kappa$ in Eq. (7.2.42) is the pure dipolar fluid dielectric constant, given by

$$\varepsilon = \frac{K(2\xi)}{K(-\xi)} = \frac{(1 + 4\xi)^2(1 + \xi)^6}{(1 - 2\xi)^6}. \tag{7.2.46}$$

The fact that $\xi$ is unchanged from the pure dipolar fluid value to order $(\kappa R)$ is reflected in the result that $\varepsilon$ is similarly unchanged.

With these results, we now turn to the problem of solving for the surface-particle correlation functions.

7.3 ION-DIPOLE MIXTURE AT A CHARGED WALL

As stated in Section 7.1, the thermodynamic properties of the double layer can be expressed in terms of the ion-wall correlation function, $h_{i0}(r)$, and the dipole-wall correlation function $h_{d0}(\omega_1, r)$. The wall-particle Ornstein-Zernike equations are

$$h_{i0}(r) = c_{i0}(r) + \sum_k \rho_k \int dr' c_{ik}(|r - r'|) h_{ko}(r')$$

$$+ \frac{\rho_d}{4\pi} \int d\omega_3 dr' c_{i1d}(\omega_3, r - r', \omega_3) h_{d0}(\omega_3, r') \tag{7.3.1a}$$

$$h_{d0}(\omega_1, r) = c_{d0}(\omega_1, r) + \sum_k \rho_k \int dr' c_{dk}(\omega_1, \omega_3, r - r') h_{ko}(r')$$

$$+ \frac{\rho_d}{4\pi} \int d\omega_3 dr' c_{dd}(\omega_1, \omega_3, r - r', \omega_3) h_{d0}(\omega_3, r') \tag{7.3.1b}$$

where at this stage the wall is a spherical colloidal particle with charge $z_0$ and diameter $R_0$. The MSA closure is just
\[ h_{10}(r) = -1, \quad r < R_{10} \quad (7.3.2a) \]

\[ h_{d0}(\omega_1, r) = -1, \quad r < R_{20} \quad (7.3.2b) \]

and, from Eqs. (7.1.6) and (7.1.7)

\[ c_{10}(r) = -\frac{\beta z \zeta e^2}{r}, \quad r > R_{10} \quad (7.3.3a) \]

\[ c_{d0}(\omega_1, r) = -\frac{\beta \zeta e}{r^2} E_1, \quad r > R_{20} . \quad (7.3.3b) \]

Using the decomposition

\[ f_{d0}(\omega_1, r) = f_{d20}(r) + f_{d20}(r) E_1 \quad (7.3.4) \]

we now follow the procedure of the RPM electrolyte example and write

\[ \frac{1}{\rho_1} h_{10}(r) = \sum \frac{\rho_1 h_{10}(r)}{\rho_1} \quad (7.3.5a) \]

\[ \frac{1}{\rho_1} h_{10}(r) = \sum \frac{\rho_1 z h_{10}(r)}{\rho_1} . \quad (7.3.5b) \]

As in the bulk problem, we now get two groups of two equations each.

The hard sphere functions form the first group.

\[ \tilde{h}_{10}(k) = \tilde{c}_{10}(k) + \rho_1 \tilde{h}_{10}(k) + \rho_2 \tilde{h}_{12}(k) \tilde{h}_{20}(k) \quad (7.3.6a) \]

\[ \tilde{h}_{20}(k) = \tilde{c}_{20}(k) + \rho_1 \tilde{c}_{21}(k) + \rho_2 \tilde{c}_{22}(k) \tilde{h}_{20}(k) \quad (7.3.6b) \]

subject to, from Eqs. (7.3.2) - (7.3.5)

\[ \tilde{h}_{10}(k) = -1, \quad r < R_{10} \quad (7.3.7a) \]

\[ \tilde{h}_{20}(r) = -1, \quad r < R_{20} \quad (7.3.7b) \]

and

\[ \tilde{c}_{10}(r) = 0, \quad r > R_{10} \quad (7.3.8a) \]

\[ \tilde{c}_{20}(r) = 0, \quad r > R_{20} . \quad (7.3.8b) \]
As before, the functions $f^{\text{HS}}_{10}(r)$ and $f^{\text{HS}}_{20}(r)$ are the Percus-Yevick hard sphere correlation functions of a two-component hard sphere fluid of densities $\sum_{i} \rho_{i}$ and $\rho_{d}$ and diameters $R_{1}$ and $R_{2}$ at a hard wall. In the MSA these functions describe the density profile at the surface. This unsatisfactory feature of the MSA is due to its failure to properly account for the angle averaged potential and image effects which also affect the density profiles. The electrostatic properties of the interface are determined by $f^{C}_{10}(r)$ and $f^{E}_{20}(r)$ which we shall study in detail.

The second group of equations involves these electrostatic components.

\begin{align*}
\tilde{h}^{C}_{10}(r) &= \tilde{c}^{C}_{10}(r) + \rho_{1} \tilde{c}^{C}_{11}(k) \tilde{h}^{C}_{10}(k) + \rho_{2} \tilde{c}^{C}_{12}(k) \tilde{h}^{E}_{10}(k) \quad (7.3.9a) \\
\tilde{h}^{E}_{20}(r) &= \tilde{c}^{E}_{20}(r) + \rho_{1} \tilde{c}^{E}_{21}(k) \tilde{h}^{C}_{10}(k) + \rho_{2} \tilde{c}^{*}(k) \tilde{h}^{E}_{20}(k) \quad (7.3.9b)
\end{align*}

subject to

\begin{align*}
h^{C}_{10}(r) &= 0, \quad r < R_{1} \quad (7.3.10a) \\
h^{E}_{20}(r) &= 0, \quad r < R_{2} \quad (7.3.10b)
\end{align*}

and

\begin{align*}
c^{C}_{10}(r) &= -\frac{\beta z_{0} e^{2}}{r}, \quad r > R_{1} \quad (7.3.11a) \\
c^{E}_{20}(r) &= -\frac{\beta_{z} e^{2}}{r^{2}}, \quad r > R_{2} \quad (7.3.11b)
\end{align*}

Once again, Baxter's factorization method can be used and we drop superscripts and set $f^{+} = f^{2}$. The auxiliary functions then obey

\[
\tilde{c}_{\alpha\alpha}(k) = \tilde{q}_{\alpha\alpha}(k) + \tilde{q}_{\alpha\alpha}(-k) - \sum_{\gamma=1}^{2} \tilde{q}_{\gamma\alpha}(k) \tilde{q}_{\gamma\alpha}(-k), \quad (\alpha = 1, 2). \quad (7.3.12)
\]

The long-range behaviour of $c_{\alpha\alpha}(r)$

\[
\tilde{c}_{10}(k) = -\frac{4\pi \beta e^{2} z_{0}}{k^{2}} \quad (7.3.13a)
\]
leads to the results

\[ Q_{10}(r) = -\Lambda_{10}, \quad r > R_{10} \]  
\[ = 0, \quad r < S_{10} \]  
\[ Q_{20}(r) = -\Lambda_{20}, \quad r > R_{20} \]  
\[ = 0, \quad r < S_{20} \]  

where

\[ \Lambda_{10} = z_{0} \Lambda_{11} \]  
\[ \Lambda_{20} = z_{0} \Lambda_{21} \]  

The correlation functions are again found from the equation

\[ H_{\alpha 0}(r) = Q_{\alpha 0}(r) + \sum_{\gamma=1,2} \rho_{\gamma} \int_{S_{\alpha \gamma}}^{\infty} Q_{\alpha \gamma}(s) H_{\gamma 0}(r-s), \]  

where, as before

\[ H_{10}(r) = 2\pi \int_{|r|}^{\infty} ds s P_{0} \left( \frac{r}{s} \right) h_{10}(s) \]  
\[ H_{20}(r) = 2\pi \int_{|r|}^{\infty} ds s P_{1} \left( \frac{r}{s} \right) h_{20}(s) \]  

so that, from Eq. (7.3.10),

\[ H_{10}(r) = 2\pi \int_{R_{10}}^{\infty} ds h_{10}(s) = H_{10}, \quad r < R_{10} \]  
\[ H_{20}(r) = 2\pi r \int_{R_{20}}^{\infty} ds h_{20}(s) = rH_{20}, \quad r < R_{20}. \]  

We differentiate Eq. (7.3.16) and use Eq. (7.3.18) to find

\[ Q_{10}(r) = -\Lambda_{10}, \quad r > R_{10} \]  
\[ = [\rho_{1} A_{11} H_{10}^{(0)} - \rho_{2} H_{20} H_{12}] (r - R_{10}) - \Lambda_{10}, \quad S_{10} < r < R_{10} \]  
\[ Q_{20}(r) = -\Lambda_{20}, \quad r > R_{20} \]  
\[ = [H_{20} a_{2} + \rho_{1} A_{21} H_{12}] (r - R_{20}) - \Lambda_{20}, \quad S_{20} < r < R_{20}. \]
By evaluating Eq. (7.3.16) at \( r = R \) and using Eqs. (7.3.18) and (7.3.19) we can show that the constants \( H_{1o} \) and \( H_{2o} \) satisfy the equations

\[
-H_{1o} (a_1 - \rho_1 A_{11} S_{1o}) + H_{2o} \rho_2 (M_{12}^{(1)} - S_{2o} M_{12}^{(0)}) = \frac{1}{2} z_q A_{11}
\]  
\[
H_{1o} \rho_1 (M_{21}^{(0)} + S_{1o} A_{21}) - H_{2o} [R_{2o} - \rho_2 (M_{22}^{(1)} - S_{2o} M_{22}^{(0)})] = \frac{1}{2} z_q A_{21}.
\]

Eqs. (7.3.15), (7.3.19) and (7.3.20) provide the solution for the correlation functions of the MSA ion-dipole mixture against a hard charged wall. In the next section, we use these results to find the surface thermodynamic properties of the double layer.

7.4 RESULTS AND DISCUSSION

As stated in Section 7.1, the MSA treatment of an ion-dipole mixture at a charged surface is a linear theory. Even so, we can only obtain simple analytical results in the limit of a dilute electrolyte, that is when \( \kappa R_1 \ll 1 \), where \( \kappa^{-1} \) is the Debye screening length. Before we present results in this regime, it is useful to briefly recapitulate the classical Debye-Hückel result for the purpose of comparison with and interpretation of our new results.

Consider the classical Stern picture in Fig. 3 Chapter 1 where a Stern layer of thickness \( d \) and dielectric constant \( \varepsilon_s \) has been set up adjacent to a planar surface with uniform surface density \( \sigma_0 \) and surface potential \( \psi_0 \). The ionic solution is confined in the region \( x > 0 \) where the dielectric constant is \( \varepsilon \). In the Debye-Hückel theory the relation between the surface charge \( \sigma_0 \) and surface potential \( \psi_0 \) is

\[
\psi_0 = \frac{4 \pi \sigma_0}{\varepsilon k} \left( 1 + \frac{\varepsilon}{\varepsilon_s} \kappa d \right).
\]
The adjustable parameter in this model is the capacitance (per unit area) $C_s$ of the Stern layer given by

$$C_s = \frac{e_s}{4\pi d}. \quad (7.4.2)$$

The capacitance of the diffuse part of the double layer is

$$C_{dl} = \frac{eK}{4\pi}. \quad (7.4.3)$$

Another macroscopic quantity which contains information about the structure of solvents in the double layer is the polarization density or dipole moment per unit volume $P(x)$. This is a measure of the degree of polarization or orientation of the solvent molecules due to the presence of the charged surface. In the macroscopic continuum theory $P_{\text{mac}}(x)$ is given by

$$P_{\text{mac}}(x) = \left( \frac{e - 1}{4\pi} \right) E(x) = \left( \frac{e - 1}{4\pi} \right) \left( - \frac{\partial \psi}{\partial x} \right)$$

$$= \left( \frac{e - 1}{e} \right) \sigma_0 e^{-\kappa x}, \quad x \geq 0 \quad (7.4.4)$$

since the potential profile is given by

$$\psi(x) = \frac{4\pi \sigma_0}{eK} e^{-\kappa x}, \quad x \geq 0. \quad (7.4.5)$$

Having stated these familiar results we can examine the corresponding quantities for the ion-dipole mixture at a charged surface.

(i) Surface Charge vs. Surface Potential

An important quantity in electrical double layer problems is the relationship between the surface charge and surface potential. The statistical mechanical definition of the surface potential of a spherical colloidal particle of diameter $R_o$ is
where we have chosen the origin of the co-ordinate system to be at the centre of the colloidal particle. The origin of the three terms in Eq. (7.4.6) is as follows. The first term is the direct Coulomb potential due to the colloidal particle. The second term accounts for the potential due to the charge distribution about the colloidal particle. The expression for the charge density $\rho_i z_i e^{-\frac{1}{h_0(r)}}$ follows from the definition of the local ionic concentration, viz.

$\rho_i [1 + h_0(r)]$ and the bulk electroneutrality condition. Contributions to the surface potential from the dipolar species are given by the third term on the right hand side of Eq. (7.4.6). Although the number density of dipoles at position $\mathbf{r}$ with orientation $\mathbf{h}$ is $\rho_d [1 + h_0(r,\mathbf{h})]$, the constant term vanishes because of the angular integration.

Using the definitions given by Eqs. (7.4.6) and (7.3.10) the surface potential $\psi_0$ can be written as

$$\psi_0 = \frac{2z_0 e}{R_0} + 2\rho_1 eH_1 - 2\rho_2 \mu H_2 .$$

(7.4.7)

We can solve for $H_1$ and $H_2$ by using Eq. (7.3.20). In the planar limit $R_0 \to \infty$, $z_0 \to \infty$, $\sigma_0 = \frac{2z_0 e}{\pi R_0^2}$, we find

$$\psi_0 = \frac{4\pi \sigma_0}{e} \{ e[a_2 (a_1 - h_0 A_{12})] - \rho_1 \rho_2 M_{12}^{(0)} (N_{21}^{(0)} + h R_1 A_{21}) \}
\cdot \{ \rho_2 A_{11} A_2 + \rho_1 \rho_2 A_{21} M_{12}^{(0)} \}^{-1} .$$

(7.4.8)

Eq. (7.4.8) is the general expression for the surface potential of an MSA ion-dipole mixture against a uniformly charged hard planar wall and is valid for all ionic concentrations and ion-dipole size ratios. However, analytic expressions for the bulk MSA constants can only be
found for low ionic concentrations. Using Eqs. (7.2.42) - (7.2.44) we find, correct to order \((\kappa R_1)\) and \((\kappa R_2)\),

\[
\psi_0 = \frac{4\pi \sigma_x}{\varepsilon \kappa} \left( 1 + h_1 \kappa R_1 + h_2 \kappa R_2 \frac{\varepsilon_0 - 1}{\lambda} \right). \tag{7.4.9}
\]

The dimensionless constant \(\lambda\) is only a function of the properties of the pure dipolar fluid and its value is given by

\[
\lambda = \left( 1 + \frac{4\varepsilon_0}{1 - 2\varepsilon} \right) \geq 1 \tag{7.4.10}
\]

or more simply in terms of the dielectric constant

\[
\lambda^2(1 + \lambda)^n = 16\varepsilon \tag{7.4.11}
\]

(cf. Eq. (7.2.46)). This constant is related to the scale length \(R_s\) encountered earlier in the MSA expression for the Born energy of an ion in a dipolar solvent [6]:

\[
2R_s^2 = \frac{R_2}{\lambda} \leq R_2. \tag{7.4.12}
\]

To begin our discussion of the physical significance of Eq. (7.4.9) and its relation to classical theory we note that in the limit of point ions and dipoles \((R_1, R_2 \to 0)\) we recover the Debye-Hückel result without the Stern correction (cf. Eq. (7.4.1) with \(d = 0\)). We can also recover the "primitive" model result by letting \(R_2 \to 0\) to get

\[
\psi_0 = \frac{4\pi \sigma_x}{\varepsilon \kappa} (1 + h_1 \kappa R_1) \tag{7.4.13}
\]

(cf. Eq. (7.4.1) with \(\varepsilon_s = \varepsilon\)). We recognise that this is the Debye-Hückel result with a modification to exclude ionic centres from a layer one ionic radius \((h R_1)\) thick adjacent to the surface. To lowest order in \(\kappa R_1\) this is the correction to the Debye-Hückel result due to finite ion size. To the same order in ionic concentrations this result also coincides with the MSA expression for a "primitive" model.
electrolyte at a charged surface [13]. However, for an ion-dipole mixture of finite particle sizes Eq. (7.4.9) indicates that in addition to the capacitance due to the diffuse part of the electrical double layer, Eq. (7.4.3), there are separate contributions to the total double layer capacitance from the ions:

$$C_{\text{ion}} = \frac{e}{2\pi R_1^2}$$  \hspace{1cm} (7.4.14)

and from the dipolar solvent:

$$C_{\text{solv}} = \left(\frac{e}{e - 1}\right) \left(\frac{\lambda}{2\pi R_2^2}\right).$$  \hspace{1cm} (7.4.15)

The contribution corresponding to $C_{\text{solv}}$ will give an additional term to the entropy of the double layer due to solvent structuring. However, for small values of $\kappa R_2$ this is not a very large effect.

We now attempt to relate our surface charge-surface potential relationship derived for an ion-dipole mixture at a charged surface to the Stern result.

For simplicity we consider the special case of equal size ions and dipoles and so set $R_1 = R_2 = R$ in Eq. (7.4.9). On comparing this with the Stern result in Eq. (7.4.1) we can make the formal identification

$$\frac{d}{\varepsilon_S} = \frac{R}{2\varepsilon} \left(1 + \frac{\varepsilon - 1}{\lambda}\right).$$  \hspace{1cm} (7.4.16)

Now, we have two possible ways of identifying the thickness $d$ and dielectric constant $\varepsilon_S$ of the effective Stern layer of the ion-dipole mixture.

(a) If we choose the thickness $d$ of the Stern layer to be a molecular diameter, i.e. $d = R/2$, then we would expect $\varepsilon_S = 1$, since the centres of all molecules (ions and dipoles) are excluded from the
region within \( \frac{1}{2}R \) of the surface. However, Eq. (7.4.16) gives, for \( d = R/2 \), a dielectric constant

\[
\varepsilon_s = \frac{\varepsilon}{1 + \frac{\varepsilon - 1}{\lambda}}. \tag{7.4.17}
\]

For \( \varepsilon = 80 \), Eqs. (7.4.11) and (7.4.17) give \( \varepsilon_s = 2.6 \). Thus, in this interpretation, the effect of solvent structure in the region \( x \geq 0 \) is to increase the dielectric constant of the Stern layer above unity.

(b) If, on the other hand, we choose to fix the dielectric constant of the Stern layer to be unity, then Eq. (7.4.16) gives the thickness of the Stern layer to be

\[
d = \frac{R}{2\varepsilon} \left( 1 + \frac{\varepsilon - 1}{\lambda} \right) \leq \frac{R}{2}, \tag{7.4.18}
\]

where the last inequality follows from Eqs. (7.4.10) and (7.4.11). In other words, as a result of solvent structure the region of unit dielectric constant from which all ions and dipoles are excluded appears thinner than the molecular radius.

As we shall see in the next section, both interpretations arise from the attempt to model the complex dielectric response of a structured region of ions and solvent molecules adjacent to the surface by an equivalent system consisting of regions of uniform dielectric constant. (In this respect, the Stern picture is analogous to the Gibbs dividing surface construction in adsorption problems.) In particular, a region of high local dielectric constant near \( x = 0 \) could give rise to interpretations (a) and (b). To examine more closely the structure at the interface, we now investigate the polarization density, charge density and electrostatic potential.
(ii) Polarization Density, Charge Density and Potential

The polarization density or dipole moment per unit volume is a measure of the local dielectric response or orientational order of the dipolar solvent in an applied field. The statistical mechanical definition of the polarization density around the spherical colloidal particle \( P(r) = P(r) \hat{r} \) is

\[
P(r) = \frac{\rho_d}{4\pi} \int d\omega h_{od}(r, \omega) [\mu(\omega) \cdot \hat{r}]
\]

\[= -\rho_d h_{20}(r)
\]

while the charge density becomes

\[
\rho_{CH}(r) = \sum_i \rho_i z_i e h_{10}(r)
\]

\[= \rho_{1e} h_{10}(r).
\]

The functions \( h_{10}(r) \) and \( h_{20}(r) \) can be obtained by differentiating Eq. (7.3.16). The polarization density \( P(x) \) and charge density \( \rho_{CH}(x) \) at a planar charged surface are obtained by taking the limit of an infinitely large colloidal particle, \( R_0 \to \infty \).

If we define

\[
h_1(x') = h_{10}(R_{10} + x')
\]

\[
h_2(x) = h_{20}(R_{20} + x),
\]

where

\[
r = R_{10} + x' = R_{20} + x
\]

so that

\[
x' = x + S_{21}
\]

we can take the planar limit \( R_0 \to \infty, z_0 \to \infty \) with \( \sigma_0 = \frac{z_0 e}{\pi R_0^2} \) constant to get...
\[ h_1(x') = -A_{11} \left( \frac{\sigma_0}{e} \right) - \rho_1 A_{11} \int_0^{x'} h_1(y) \, dy + \rho_2 \int_{S_{12}}^{R_{12}} Q_{12}^0(y) h_2(x-y) \, dy \]

\[ + \rho_1 \int_0^{R_1} Q_{11}^0(y) h_1(x' - y) \, dy \]  \hspace{1cm} (7.4.26)

\[ h_2(x) = -A_{21} \left( \frac{\sigma_0}{e} \right) - \rho_1 A_{21} \int_0^x h_1(y) \, dy + \rho_2 \int_0^{R_2} Q_{22}^0(y) h_2(x-y) \, dy \]

\[ + \rho_1 \int_{S_{21}}^{R_{21}} Q_{21}^0(y) h_1(x' - y) \, dy, \]  \hspace{1cm} (7.4.27)

where

\[ Q_{ij}^0(r) = Q_{ij}(r) + A_{ij}, \quad S_{ij} < r < R_{ij} \]

\[ = 0, \quad r > R_{ij}. \]  \hspace{1cm} (7.4.28)

Eqs. (7.4.26) - (7.4.28) are the general equations for the charge density and polarization density away from the planar charged wall for arbitrary ionic concentrations. Since we only have analytic expressions for \( Q_{ij}(r) \) for low ionic concentrations, we examine the behaviour of Eqs. (7.4.26) - (7.4.28) for dilute solutions. At this stage, we take \( R_1 = R_2 = R \) for simplicity. Careful analysis shows that, to lowest order in \( \kappa R \), Eqs. (7.4.26) and (7.4.27) then become

\[ h_1(x) = -A_{11} \left( \frac{\sigma_0}{e} \right) - \rho_1 A_{11} \int_0^x h_1(y) \, dy \]  \hspace{1cm} (7.4.29)

and

\[ h_2(x) = -A_{21} \left( \frac{\sigma_0}{e} \right) - \rho_1 A_{21} \int_0^x h_1(y) \, dy + \rho_2 \int_0^R Q_{22}^0(y) h_2(x-y) \, dy. \]  \hspace{1cm} (7.4.30)

The solution of Eq. (7.4.29) is

\[ h_1(x) = -\frac{\kappa \sigma_0}{\rho_1 e} e^{-\kappa x} \]  \hspace{1cm} (7.4.31)

so that

\[ \rho_{CI}^H(x) = \rho_1 e h_1(x) = -\kappa \sigma_0 e^{-\kappa x}, \]  \hspace{1cm} (7.4.32)

i.e. the Debye-Hückel result. This leads to
\[ h_2(x) = -A_2 \frac{\sigma}{e} e^{-\kappa x} + \rho_2 \int_0^R Q_{22}^0(y) h_2(x-y) \, dy, \quad (7.4.33) \]

where the only terms to be retained to this order in \( Q_{22}^0(y) \) are

\[ Q_{22}^0(r) = \frac{12 \varepsilon a_2}{\rho_2 R^3} (r^2 - R^2) - \frac{24 \varepsilon}{\rho_2 R^3} (Ra_2 - s)(r - R). \quad (7.4.34) \]

Eq. (7.4.33) can be solved numerically by Perram's method [14] to give Fig. 1, or analytically by Laplace Transform methods. Such analytic investigation shows that the inverse decay length of the charge density from the surface has the form \( \kappa[1 + \alpha(\kappa R)^2] \) just as is the case for the MSA bulk primitive model electrolyte. Similarly, corrections to the asymptotic forms of the charge and polarization densities have no terms of order \( \kappa R \). This is consistent with the observation that to order \( \kappa R \) the dielectric constant of the ion-dipole mixture is the same as that for the pure dipolar fluid.

In Fig. 1 we plot the ratio \( P(x)/P_{\text{mac}}(x) \) (see Eq. (7.4.4)) as a function of the distance \( x \) from the charged surface for \( \varepsilon = 80.5 \). The same quantity is given in Fig. 2 for the cases \( \varepsilon = 20 \) and \( \varepsilon = 7.8 \). In all cases \( P(x) \) is calculated to lowest order in \( \kappa R \). It is clear that both the range and magnitude of the oscillations decrease as the dielectric constant of the solvent decreases. For the case \( \varepsilon = 80.5 \), there are significant deviations in \( P(x) \) from the macroscopic result over 3-4 molecular diameters from the surface. Although the magnitude of the oscillations may be overestimated due to the linear nature of the MSA, the oscillatory nature of \( P(x)/P_{\text{mac}}(x) \) indicates the strong co-operative alignment of dipolar molecules that are located near the surface. This oscillatory form of \( P(x)/P_{\text{mac}}(x) \), which can only come from a discrete (rather than continuum) treatment of the solvent, is similar to the polarization density around a single ion in a dipolar
Fig. 1: Polarization density at the surface, for the case $R_1 = R_2 = 3 \, \text{Å}$, $\varepsilon = 80.5$, $T = 298 \, \text{K}$, $\rho_d R^3 = 0.8$, $\kappa R = 0.1$. 
Fig. 2: Polarization density at the surface for $\varepsilon = 20$ (---), $\varepsilon = 7.8$ (---), other details as in Fig. 1.
solvent [6]. In the regime $\kappa R \ll 1$, the form of $P(x)$ is insensitive to the electrolyte concentration, since it is determined mainly by the properties of the dipolar fluid. Effects of the electrolyte can only be important at distances $\sim \kappa^{-1}$ from the surface (i.e. for low concentrations, at distances much greater than $R$).

For the results in Figs. 1 and 2, the total polarization

$$\int_0^\infty P(x) \, dx$$

is in excess of that given by macroscopic theory. That is, a discrete treatment of the solvent allows for the possibility of a larger depolarizing field due to the dipoles. Consequently, if we were to use some sort of "local" dielectric constant to characterize the dielectric response of the solvent near the surface, this local dielectric constant would be larger than the bulk value.

The results in Figs. 1 and 2 also show the difficulties in justifying the use of a position-dependent local dielectric constant. Since our model, which has no such local dielectric constant, still reproduces the Stern layer form for the $\psi_0 - \sigma_0$ relationship, the ability to mimic thermodynamic properties of the surface is, by itself, no justification for a particular choice of the form of a local dielectric constant.

We can clarify the relationship between the oscillatory polarization density and the Stern-like $\psi_0 - \sigma_0$ equation by considering the electrostatic potential as a function of position in the double layer. The potential is just

$$\psi(x) = 4\pi \rho_1 e \int_x^\infty (x - y) \, h_1(y) \, dy + 4\pi \rho_2 \mu \int_x^\infty h_2(y) \, dy. \quad (7.4.35)$$

By using Eq. (7.4.31) and the solution of Eq. (7.4.33), we can generate the potential throughout the double layer.
In Figs. 3-5 we show the results for $\psi(x)$ for different values of $\varepsilon$ and $\kappa R$. The oscillations in polarization density exhibited in Figs. 1 and 2 are reflected in oscillations in the electrostatic potential of opposite phase. As is the case for $P(x)$, the oscillations decrease in both magnitude and range as the dielectric constant of the solvent is decreased. In contrast to the insensitivity of $P(x)/P_{\text{mac}}(x)$ to $\kappa R$, the oscillations in potential also decrease as $\kappa R$ is decreased. This is because the macroscopic form for $\psi(x)$ (see Eq. (7.4.5)) is inversely proportional to $\kappa R$, whereas the contribution to the potential from the oscillations in polarization density remains constant for $\kappa R < 0.1$. The enhanced total polarization shown in Figs. 1 and 2 leads to a decrease in $\psi_B$ (for the case $\varepsilon = 80.45$, $\kappa R = 0.1$, $\psi_B$ becomes negative) which could again be interpreted as a local increase in dielectric constant near the surface.

For the case of equal ions and dipole size, the region between the wall and the plane $x = 0$ is just vacuum so that

$$\psi_0 = \psi_B + 4\pi\sigma_0 \frac{\psi}{\varepsilon K}.$$  \hspace{1cm} (7.4.36)

If we take the potential to be described by the macroscopic result up to the plane $x = 0$, we would have

$$\psi_0 = \frac{4\pi\sigma_0}{\varepsilon K} \left(1 + \frac{1}{\kappa R} \frac{\varepsilon - 1}{\lambda} - \varepsilon\right).$$ \hspace{1cm} (7.4.37)

which is larger than the result for the MSA ion-dipole mixture, Eq. (7.4.9). This discrepancy is due to the lower value of $\psi_B$ for the ion-dipole mixture, namely

$$\psi_B = \frac{4\pi\sigma_0}{\varepsilon K} \left(1 + \frac{1}{\kappa R} \left(1 + \frac{\varepsilon - 1}{\lambda} - \varepsilon\right)\right).$$ \hspace{1cm} (7.4.38)

which is caused by the increased total polarization in the double
Fig. 3: Electrostatic potential near the surface for the parameters given in Fig. 1 for both macroscopic (monotonic) and ion-dipole mixture (oscillatory) models. The dashed line indicates the potential described by the classical Stern layer theory with $d=\frac{\varepsilon}{kT}$, $\varepsilon_s$ given in Eq. (7.4.17).

$\sigma_0$ has been chosen so that $e\psi^\text{mac}_B/kT = 1$. 

$e\psi/kT$ vs $x/R$
Fig. 4: Electrostatic potential near the surface as in Fig. 3 but with \( \kappa R = 0.01 \) and \( \sigma_0 \) chosen so that \( e\psi_{\text{mac}} / kT = 1 \).
Fig. 5: Electrostatic potential near the surface with parameters as in Fig. 1 but \( \varepsilon = 20 \) (———) and \( \varepsilon = 7.8 \) (— —).
layer. If we insist on retaining the macroscopic description for \( x > 0 \) we must interpret the lower than expected surface potential by positing an increase in dielectric constant in the region \( -\frac{R}{2} < x < 0 \). The dashed line in Figs. 3 and 4 represents the electrostatic potential envisaged in such an interpretation. The actual potential variation with distance is much more complicated than such a picture but the results for \( \psi_0 \) are the same in both cases.

The work presented in this chapter is the first attempt to derive an expression for the Stern layer capacitance and other surface properties of the electrical double layer from a well-defined model fluid including both ionic and solvent structure. The major limitations of the results are due to the use of the MSA ion-dipole mixture. This model fluid gives the correct limiting-law behaviour at low concentrations but the inaccuracy of \( \ln \gamma_+ \) at higher concentrations indicates an inherent deficiency of the model.

Now that bulk correlation functions of LHNC ion-dipole mixtures [14] are available, an obvious extension would be the use of the LHNC closure on all interactions. The resultant equations are derived in the next chapter. Such an approach will still only partially treat image forces and will not give analytic results, so the equations of this chapter are still of interest.

The most important conclusion is that even though the Stern layer model of double layer capacitance is undoubtedly successful, it can be produced in a model solely from solvent structure rather than from dielectric saturation or hydrogen-bonding effects. Also, the idea of a position-dependent local dielectric constant is a tenuous one and the ability of such theories to model surface thermodynamic properties
does not give validity to the microscopic picture envisaged in these theories. The Stern layer model is a useful parametrization of the surface properties of the double layer but is actually an attempt to model a complex double layer structure by discrete regions of uniform dielectric constant.

REFERENCES

Table 1

Multiplication table for the angular convolution

\[
\frac{1}{4\pi} \int A(\omega_1, \omega_3) \ B(\omega_3, \omega_2) \ d\omega_3
\]

<table>
<thead>
<tr>
<th>$A(\omega_1, \omega_3)$</th>
<th>1</th>
<th>$\Delta_{32}$</th>
<th>$D_{32}$</th>
<th>$E_3     $</th>
<th>$E_2     $</th>
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</thead>
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<tr>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$E_2 \phantom{1}$</td>
</tr>
<tr>
<td>$\Delta_{13}$</td>
<td>0</td>
<td>$\frac{1}{3} \Delta_{12}$</td>
<td>$\frac{1}{3} D_{12}$</td>
<td>$\frac{1}{3} E_1$</td>
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<tr>
<td>$D_{13}$</td>
<td>0</td>
<td>$\frac{1}{3} D_{12}$</td>
<td>$\frac{1}{3} (D_{12} + 2\Delta_{12})$</td>
<td>$\frac{2}{3} E_1$</td>
<td>0</td>
</tr>
<tr>
<td>$E_3$</td>
<td>0</td>
<td>$\frac{1}{3} E_2$</td>
<td>$\frac{2}{3} E_2$</td>
<td>$\frac{1}{3}$</td>
<td>0</td>
</tr>
<tr>
<td>$E_1$</td>
<td>$E_1$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{3} (D_{12} + \Delta_{12})$</td>
</tr>
</tbody>
</table>

The solutions for ionic and dipolar adsorption onto a uniformly charged planar wall is also given, but the TDC equations are not solved.

We again consider an ion-dipole mixture, defined by the interaction potential given in Eq. (7.45)
CHAPTER 8
IONIC AND DIPOLAR ADSORPTION
FROM AN ION-DIPOLE MIXTURE

8.1 IONIC AND DIPOLAR ADSORPTION
VIA BAXTER'S STICKY POTENTIAL

In this chapter we extend the methods of Chapter 7 to consider ionic and dipolar adsorption (modelled by Baxter's sticky potential [1]) from an MSA ion-dipole mixture. In addition to dipolar adsorption, the dipoles at the surface can be made to preferentially orient, by the inclusion of an angle-dependent sticky potential. We treat in detail only the case of adsorption onto a neutral surface since there are many interesting new features in this simple system. The extension to adsorption onto a uniformly charged surface is straightforward and the solution is given in Section 8.4. A derivation of the LHNC equations for ionic and dipolar adsorption onto a uniformly charged planar wall is also given, but the LHNC equations are not solved.

We again consider an ion-dipole mixture, defined by the intermolecular potentials given in Eqs. (7.1.2) - (7.1.5). In the wall-particle HNC closure,

\[ 1 + h_{10}(r) = e^{-\beta u_{10}^s(r)} \exp[h_{10}(r) - c_{10}(r)] \]
\[ 1 + h_{do}(\omega, r) = e^{-\beta u_{do}^s(\omega, r)} \exp[h_{do}(\omega, r) - c_{do}(\omega, r)] \]
we can linearize the factor \( \exp(h - c) \) to obtain the Percus-Yevick (PY) closure

\[
1 + h_{10}(r) = e^{-\beta u^{S}_{10}(r)} \left[ 1 + h_{10}(r) - c_{10}(r) \right] \tag{8.1.2a}
\]

\[
1 + h_{do}(\omega_1, r) = e^{-\beta u^{S}_{do}(\omega_1, r)} \left[ 1 + h_{do}(\omega_1, r) - c_{do}(\omega_1, r) \right]. \tag{8.1.2b}
\]

\( u^{S}_{10}(r) \) and \( u^{S}_{do}(\omega_1, r) \) are the short-ranged potentials between the neutral wall and the ions and dipoles, respectively.

As in Chapter 5 we take the ion-wall short-range potential to have the form of Baxter's sticky potential [1]

\[
e^{-\beta u^{S}_{10}(r)} = a_{i} \delta(r - R_{10}), \quad r < R_{10}
\]

\[
e^{-\beta u^{S}_{10}(r)} = 1, \quad r > R_{10}
\]  

so that, using Eqs. (8.1.2) and (8.1.3),

\[
h_{10}(r) = b_{i} \delta(r - R_{10}) + h^{*}_{10}(r)
\]

\[
c_{10}(r) = b_{i} \delta(r - R_{10}) + c^{*}_{10}(r)
\]  

where the starred functions have no delta function behaviour.

Equating coefficients of \( \delta(r - R_{10}) \) in Eq. (8.1.2a) we find

\[
b_{i} = a_{i} [1 + h_{10}(R_{10}^{+})]
\]  

as before.

Since we wish to incorporate the feature of preferential orientation of the dipoles adsorbed at the surface, we require an angle-dependent short-range wall-dipole potential. We choose the form

\[
e^{-\beta u^{S}_{do}(\omega_1, r)} = a_{d} \delta(r - R_{20}) + a_{E} \delta(r - R_{20}) E_{1}, \quad r < R_{20}
\]

\[
e^{-\beta u^{S}_{do}(\omega_1, r)} = 1, \quad r > R_{20}
\]  

where \( \omega_1 \) is the dipole orientation angle.
Since both the factor

\[ -\beta \hat{u}_{do}^s(\omega_1, r) \]

and the angle-averaged quantity

\[ \int d\omega_1 \ e^{-\beta \hat{u}_{do}^s(\omega_1, r)} \]

must be positive we have the restrictions

\[
\begin{align*}
    a_d & \geq 0 \\
    |a_E| & \leq a_d
\end{align*}
\]  

\[ (8.1.7) \]

The form of potential given in Eq. (8.1.6) enables the orientation with the dipole moment pointing towards (away from) the wall to be energetically favoured by choosing \( a_d \) to be positive (negative). (Remember that \( E_1 = \hat{u}(\omega_1) \cdot \hat{r} \), where \( \hat{r} \) points from the dipole to the wall.) The orientation with the dipole moment parallel to the wall will always be intermediate in energy. In order to preferentially orient the dipoles in the plane-parallel configuration, we would need to associate with the wall a dipole moment fixed at some angle to the plane of the surface, as has been done in some studies of dipolar adsorption [2,3]. We would then require more complex angular functions (e.g. \( \Lambda_{12} \) or \( D_{12} \)) in our short-range dipole-wall potential.

Eq. (8.1.6) together with Eq. (8.1.2b) implies

\[
\begin{align*}
    h_{do}(\omega_1, r) = b_d \ \delta(r - R_{20}) + b_E \ \delta(r - R_{20}) \ E_1 + h_{20}^{*HS}(r) + h_{20}^{*E}(r) \ E_1 \\
    c_{do}(\omega_1, r) = b_d \ \delta(r - R_{20}) + b_E \ \delta(r - R_{20}) \ E_1 + c_{20}^{*HS}(r) + c_{20}^{*E}(r) \ E_1
\end{align*}
\]

\[ (8.1.8) \]

where again starred functions have no delta function behaviour.

Substituting Eq. (8.1.8) into Eq. (8.1.2), we can integrate over \( \omega_1 \)
and find

\[ b_d = a_d \left[ 1 + h_{20}^{\text{HS}}(R_{20}) \right] + \frac{1}{3} a_E h_{20}^{\text{E}}(R_{20}) . \]  \hspace{1cm} (8.1.9)

We can also multiply Eq. (8.1.2) by \( E_1 \) and integrate over \( \omega_1 \) to get

\[ b_E = a_d h_{20}^{\text{E}}(R_{20}) + a_E \left[ 1 + h_{20}^{\text{HS}}(R_{20}) \right] . \]  \hspace{1cm} (8.1.10)

Eqs. (8.1.5), (8.1.9) and (8.1.10) are used to find the ionic and dipolar adsorption isotherms.

8.2 ADSORPTION ONTO A NEUTRAL SURFACE IN THE MSA

The surface thermodynamic properties can be found in a very similar fashion to that described in Section 7.3, so that we only outline the various steps required. The wall-particle Ornstein-Zernike equations are given by Eq. (7.3.1), but on this occasion with the closures

\[ h_{i0}(r) = -1 + b_1 \delta(r - R_{i0}) , \quad r < R_{i0} \]  \hspace{1cm} (8.2.1a)

\[ h_{d0}(\omega_1, r) = -1 + b_d \delta(r - R_{20}) + b_E \delta(r - R_{20}) E_1 , \quad r < R_{20} \]  \hspace{1cm} (8.2.1b)

and

\[ c_{i0}(r) = 0 , \quad r > R_{i0} \]  \hspace{1cm} (8.2.2a)

\[ c_{d0}(\omega_1, r) = 0 , \quad r > R_{20} . \]  \hspace{1cm} (8.2.2b)

As before we define

\[ h_{i0}^{\text{HS}}(r) = \frac{\sum \rho_1 h_{i0}(r)}{\rho_1} \]  \hspace{1cm} (8.2.3a)

\[ h_{i0}^{\text{C}}(r) = \frac{\sum \rho_1 h_{i0}(r)}{\rho_1} \]  \hspace{1cm} (8.2.3b)

and use the decomposition Eq. (7.3.4) to find two groups of equations. The first group is
These are just the Percus-Yevick equations for a mixture of hard spheres of diameter $R_1$ and $R_2$, density $\Sigma \rho_i$ and $\rho_d$ against a wall to which they adhere via Baxter's sticky potential with adhesion parameters $\Sigma \rho_i b_i / \Sigma \rho_i$ and $b_d$. These equations have a known solution [4,5] and, as in Chapter 7, do not affect the electrostatic properties of the double layer.

The second group of equations is

$$
\hat{h}_{10}^C(k) = \hat{c}_{10}^{C}(k) + \rho_1 \hat{c}_{11}^{C}(k) \hat{h}_{10}^C(k) + \rho_2 \hat{c}_{12}^{C}(k) \hat{h}_{20}^C(k)
$$

subject to

$$
\hat{h}_{10}^C(r) = \frac{\Sigma \rho_i b_i}{\rho_1} \delta(r - R_{10}), \quad r < R_{10}
$$

$$
\hat{h}_{20}^C(r) = b_d \delta(r - R_{20}), \quad r < R_{20}
$$

and

$$
\hat{c}_{10}^{E}(r) = 0, \quad r > R_{10}
$$

$$
\hat{c}_{20}^{E}(r) = 0, \quad r > R_{20}
$$

These methods of the solution of the Percus-Yevick equation are the Baxter equations for a mixture of hard spheres, and they satisfy the same properties of interest derived only for hard spheres subject to the Baxter equation for a mixture of hard spheres.
\[ c_{10}^{C}(r) = 0, \quad r > R_{10} \quad (8.2.9a) \]

\[ c_{20}^{E}(r) = 0, \quad r > R_{20} \quad (8.2.9b) \]

Since all the thermodynamic properties of interest depend only on \( h_{10}(r) \) and \( h_{20}^{E}(r) \) we henceforth drop all superscripts. Using the methods of the appendix to Chapter 5, and Chapter 7, we can perform the Baxter factorization of Eq. (8.2.7) and show that

\[ Q_{10}(r) = 0, \quad r < S_{10}, \quad r > R_{10} \quad (8.2.10a) \]

\[ = [\rho_{1}A_{1}H_{10} - \rho_{2}H_{12}(0)](r - R_{10}) + B_{10}, \quad S_{10} < r < R_{10} \]

and

\[ Q_{20}(r) = 0, \quad r < S_{20}, \quad r > R_{20} \quad (8.2.10b) \]

\[ = [H_{20}a_{2} + \rho_{1}A_{2}H_{10}](r - R_{20}) + B_{20}, \quad S_{20} < r < R_{20}, \]

where

\[ B_{10} = \frac{2\pi\sigma_{c}}{c\rho_{1}} R_{10} \quad (8.2.11a) \]

\[ B_{20} = 2\pi b_{E} R_{20} \quad (8.2.11b) \]

and now

\[ H_{10} \equiv 2\pi \int_{R_{10}}^{\infty} ds s h_{10}(s) \quad (8.2.12a) \]

\[ = 2\pi \int_{R_{10}}^{\infty} ds s h_{10}^{*}(s) + B_{10} \]

and

\[ H_{20} \equiv 2\pi \int_{R_{20}}^{\infty} ds h_{20}(s) \quad (8.2.12b) \]

\[ = 2\pi \int_{R_{20}}^{\infty} ds h_{20}^{*}(s) + \frac{B_{20}}{R_{20}}. \]

The constants \( H_{10} \) and \( H_{20} \) can be found from the \( Q_{\alpha 0} - H_{\alpha 0} \) equations (see Eq. (7.3.16)) and satisfy the equations...
At this stage, however, we do not know the constants $\sigma_\beta$ and $b_E$ in terms of the adsorption parameters $a_1$, $a_d$ and $a_E$. We therefore need to evaluate the functions on the right hand side of Eqs. (8.1.5), (8.1.9) and (8.1.10).

We first consider the contributions to the adsorption isotherms from hard sphere interactions. Since we can write

$$1 + h_{10}^H(R_{10}^+) = 1 + h_{10}^{HS}(R_{10}^+) + z_1 h_{10}^C(R_{10}^+)$$

in Eq. (8.1.5), and because of the form of Eqs. (8.1.9) and (8.1.10), we need to evaluate $1 + h_{10}^{HS}(R_{10}^+)$, $\alpha = 1, 2$. We can perform the Baxter factorization [6] for the two-component mixture of hard spheres adsorbing to the wall in much the same way as in the derivation of Eq. (5.A.73). On defining

$$h_{10}^{HS}(x' + R_{10}) = h_{10}^{HS}(x')$$

we find that

$$h_{10}^{HS}(x') = (\Sigma_j \rho_j b_j) Q_{11}^{HS}(x') + \rho_1 \int_0^{R_1} Q_{11}^{HS}(y) h_1^{HS}(x' - y) dy + \rho_d b_d Q_{12}^{HS}(x) + \rho_d \int_{S_{12}}^{R_{12}} Q_{12}^{HS}(y) h_2^{HS}(x - y) dy$$

$$h_{20}^{HS}(x + R_{20}) = h_{20}^{HS}(x),$$

we find that

$$h_{10}^{HS}(x') = (\Sigma_j \rho_j b_j) Q_{11}^{HS}(x') + \rho_1 \int_0^{R_1} Q_{11}^{HS}(y) h_1^{HS}(x' - y) dy + \rho_d b_d Q_{12}^{HS}(x) + \rho_d \int_{S_{12}}^{R_{12}} Q_{12}^{HS}(y) h_2^{HS}(x - y) dy$$

$$h_{20}^{HS}(x) = (\Sigma_j \rho_j b_j) Q_{21}^{HS}(x') + \rho_1 \int_{S_{21}}^{R_{21}} Q_{21}^{HS}(y) h_1^{HS}(x' - y) dy + \rho_d b_d Q_{22}^{HS}(x) + \rho_d \int_0^{R_2} Q_{22}^{HS}(y) h_2^{HS}(x - y) dy.$$
It then follows that

\[ 1 + h_{10}^{HS}(R_{10}) = 1 - \rho_1 \int_0^{R_1} q_{11}^{HS}(y) \, dy - \rho_d \int_{S_{12}}^{R_{12}} q_{12}^{HS}(y) \, dy \]
\[ + (\sum_j \rho_j b_j) q_{11}^{HS}(0) + \rho_d b_d q_{12}^{HS}(S_{12}) \]  
(8.2.17a)

\[ 1 + h_{20}^{HS}(R_{20}) = 1 - \rho_1 \int_{S_{21}}^{R_{21}} q_{21}^{HS}(y) \, dy - \rho_d \int_0^{R_{22}} q_{22}^{HS}(y) \, dy \]
\[ + (\sum_j \rho_j b_j) q_{21}^{HS}(S_{21}) + \rho_d b_d q_{22}^{HS}(0) . \]  
(8.2.17b)

Using the known formulae for \( Q_{\alpha\beta}(r) \) for Percus-Yevick hard spheres we eventually find

\[ 1 + h_{10}^{HS}(R_{10}) = \frac{1 - \eta + 3R_1 \xi_2}{(1 - \eta)^2} - \frac{\pi R_1^2}{(1 - \eta)} \sum_j \rho_j b_j - \frac{\pi R_{12}^2}{(1 - \eta)} \rho_d b_d \]  
(8.2.18a)

\[ 1 + h_{20}^{HS}(R_{20}) = \frac{1 - \eta + 3R_2 \xi_2}{(1 - \eta)^2} - \frac{\pi R_{12}^2}{(1 - \eta)} \sum_j \rho_j b_j - \frac{\pi R_{22}^2}{(1 - \eta)} \rho_d b_d \]  
(8.2.18b)

where

\[ \eta = \pi \frac{2}{6} \sum_{\alpha=1}^S \rho_\alpha R_\alpha^3 \]  
(8.2.19a)

and

\[ \xi_2 = \pi \frac{2}{6} \sum_{\alpha=1}^S \rho_\alpha R_\alpha^2 . \]  
(8.2.19b)

The remaining contributions to the adsorption isotherms come from the charge density and polarization density at the surface. If we define (dropping superscripts from electrostatic components)

\[ h_{10}^C(x' + R_{10}) = h_1(x') \]  
(8.2.20a)

\[ h_{20}^E(x + R_{20}) = h_2(x) , \]  
(8.2.20b)

then the charge density and polarization density from the wall are
given simply by
\[
\rho^{CH}(x') = \rho_1 \, \epsilon \, h_1(x') \quad (8.2.21a)
\]
\[
P(x) = -\rho_2 \, \mu \, h_1(x) . \quad (8.2.21b)
\]

By following the methods of Chapters 5 and 7, we can show that
\[
h_1(x') = \frac{\sigma \beta}{\epsilon} Q_{11}(x') + \rho_1 \int_{0}^{R_1} Q_{11}^0(y) \, h_1(x' - y) \, dy - \rho_1 A_{11} \int_{0}^{0} h_1(y) \, dy
\]
\[+ \rho_2 \, b_E \, Q_{12}(x) + \rho_2 \int_{S_{12}}^{R_{12}} Q_{12}(y) \, h_2(x - y) \, dy \quad (8.2.22a)
\]
\[
h_2(x) = \frac{\sigma \beta}{\epsilon} Q_{21}(x') + \rho_1 \int_{S_{21}}^{R_{21}} Q_{21}^0(y) \, h_1(x' - y) \, dy - \rho_1 A_{21} \int_{0}^{X} h_1(y) \, dy
\]
\[+ \rho_2 \, b_E \, Q_{22}(x) + \rho_2 \int_{0}^{R_2} Q_{22}(y) \, h_2(x - y) \, dy, \quad (8.2.22b)
\]

where the \( Q_{\alpha\beta}(r) \) are given in Eq. (7.2.40). From Eq. (8.2.22) it follows that
\[
h_1(0^+) = \frac{\sigma \beta}{\epsilon} Q_{11}(0) + \rho_2 \, b_E \, Q_{12}(S_{12}) \quad (8.2.23a)
\]
\[
h_2(0^+) = \frac{\sigma \beta}{\epsilon} Q_{21}(S_{21}) + \rho_2 \, b_E \, Q_{22}(0) . \quad (8.2.23b)
\]

Upon evaluation of Eq. (8.2.23) (neglecting terms of \( O(\kappa R) \) or higher) and substitution into Eqs. (8.1.9), (8.1.10) and (8.2.14), the adsorption isotherms are
\[
\frac{b_i}{a_i} = \frac{1 - \eta + 5R_1 \xi_2}{(1 - \eta)^2} - \frac{\pi R_2^2}{(1 - \eta)^2} \sum_j \rho_j b_j \, \frac{\pi R_1 R_2}{(1 - \eta)} \rho_d b_d
\]
\[\frac{\kappa}{\rho_1} \frac{\sigma \beta}{\epsilon} \, z_i \left(1 - \kappa \rho_1 R_1 \left(1 + \frac{\epsilon - 1}{\tau^2}\right) + \kappa \epsilon \frac{\epsilon - 1}{\lambda^2}\right)
\]
\[\frac{- z_i \rho_2 \, b_E}{\rho_2} \frac{4\pi \alpha \epsilon \mu}{\sqrt{\lambda^2}} \quad (8.2.24a)
\]
\[
\frac{b_d}{a_d} = \frac{1 - \eta + 3R_2 \xi_2}{(1 - \eta)^2} - \frac{\pi R_1 R_2}{(1 - \eta)} \sum_j \rho_j b_j - \frac{\pi R_2^2}{(1 - \eta)} \rho_d b_d
\]
\[
- \frac{1}{3} \frac{a}{a_d} \left( \frac{\sigma \beta}{e} \frac{4 \pi \beta e u}{q_+^2} + 2 \frac{b E}{R_2} (\lambda - 1) \right)
\]

\[
\frac{b_E}{a_E} = \frac{1 - \eta + 3R_2 \xi_2}{(1 - \eta)^2} - \frac{\pi R_1 R_2}{(1 - \eta)} \sum_j \rho_j b_j - \frac{\pi R_2^2}{(1 - \eta)} \rho_d b_d
\]
\[
- \frac{a}{a_d} \left( \frac{\sigma \beta}{e} \frac{4 \pi \beta e u}{q_+^2} + 2 \frac{b E}{R_2} (\lambda - 1) \right)
\]

where
\[
\tau = 1 + \lambda \frac{R_1}{R_2}.
\]

Eq. (8.2.24) therefore completes the specification of the thermodynamic quantities (e.g. \(H_{10}\)) in terms of the adsorption parameters \(\{a_1, a_d, a_E\}\).

The surface potential \(\psi_0\) (= \(\psi(\min(R_{10}^-, R_{20}^-))\)) is given by
\[
\psi_0 = 2 \rho_1 e H_{10} + 2 \rho_2 \mu H_{20}.
\]

The potential has a discontinuity due to the adsorbed dipole layer at \(R_{20}\) so that, using Eq. (8.2.12b) we have
\[
\psi(R_{20}^+) = \psi(R_{20}^-) - 4 \pi \rho_2 \mu b_E.
\]

No such discontinuity arises from the adsorbed layer of charge. By solving for \(H_{10}\) and \(H_{20}\) from Eq. (8.2.13) and taking the limit \(R_0 \rightarrow \infty\), we find
\[
\psi_0 = 4 \pi \left\{ \sigma \beta \left[ a_2 - \frac{\rho_2 \mu A_{21}}{e} \right] + b_E \left( \rho_1 \rho_2 \mu A_{11} + \rho_1 \rho_2 e M_{12}^{(1)} \right) \right\}
\]
\[
\times \left( \rho_1 A_{11} a_2 + \rho_1 \rho_2 A_{21} M_{12}^{(0)} \right)^{-1},
\]

an expression which is valid for all concentrations and ion/dipole size ratios. To lowest order in \(\kappa R_1\) and \(\kappa R_2\), we find
In the next section we investigate the implications of Eqs. (8.2.22), (8.2.24) and (8.2.29).

8.3 RESULTS FOR ADSORPTION ONTO A NEUTRAL SURFACE

It is evident from Eqs. (8.2.22) and (8.2.29) that the electrostatic properties of the double layer depend in a relatively simple way on the parameters $\sigma_B$ and $b_E$. $\sigma_B$ is simply the adsorbed surface charge density whereas $b_E$ provides a measure of the net orientation in the adsorbed dipole layer – as can be seen from Eq. (8.2.27). It should be emphasized that the discontinuity in potential (proportional to $b_E$) exists only when the dipoles specifically adsorb onto the plane $x=0$ – the distribution of dipoles near the surface in Chapter 7 does not lead to such an effect.

In order to examine each new feature of Eqs. (8.2.22), (8.2.24) and (8.2.29) separately, and so obtain more physical understanding of the behaviour near the surface, we investigate the following simplified cases.

Case A: $b_E = 0$. Dipoles do not adsorb into the plane $x=0$, and we can then compare directly with the results of Chapter 7.

Case B: $\sigma_B = 0$. We examine the polarization density and electrostatic potential caused solely by preferential orientation of the dipoles adsorbed from a MSA pure dipolar fluid – the behaviour is substantially unchanged when (indifferent) electrolyte is added.

Case C: $\sigma_B, b_E \neq 0$. The simplest case containing contributions from both $\sigma_B$ and $b_E$ arises when dipoles adsorb (but do not...
preferentially orient via $a_E$ into the plane of adsorbed ions. The field created by the surface charge orients the dipole layer and hence leads to a finite value of $b_E$.

In addition, we briefly discuss the effect of the addition of specific dipolar orientation (via $a_E$) on the behaviour of Case C.

For each case, we discuss the role of the adsorption parameters $\{a_i\}, a_d, a_E$ in specifying the controlling parameters $\{b_i\}, b_d, b_E$.

Case A: $b_E = 0$

By setting $a_d = 0$, we prevent the formation of a dipole layer and so eliminate any separate contribution to the surface potential due solely to the dipoles. The potential at the plane of charge is then

$$
\psi_B = \frac{4\pi \sigma_B}{\varepsilon \kappa} \left( 1 + \frac{1}{\nu_1 R_2} \right) \left( \frac{\varepsilon - 1}{\lambda \tau} \right)
$$

(8.3.1)

which we can compare directly with Eq. (7.4.9). The absence in Eq. (8.3.1) of any inner layer capacitance attributable to the ions (see Eq. (7.4.14)) is due to the fact that non-adsorbing ions can approach arbitrarily close to the plane of charge. The same effect has been noted in the corresponding Primitive Model calculation [7].

Another new feature in Eq. (8.3.1) is the appearance of a factor $\tau$ in the term due to solvent effects. For point ions, $\tau = 1$ and we recover Eq. (7.4.9) with $\sigma_0 = \sigma_B$ and $R_1 = 0$. This is because the dipoles, just as in Chapter 7, can approach no closer than $b R_2$ to the plane of charge. The factor $\tau$ thus reflects the degree to which solvent molecules can interpenetrate the layer of surface charge. We can use interpretation (a) of Chapter 7 (i.e. $d = R_2 / 2$) to determine an effective Stern layer dielectric constant.
\[ \varepsilon_s = \lambda \tau. \] (8.3.2)

It is clear that \( \tau \) causes an appreciable change in \( \varepsilon_s \) compared to the value found from Eq. (7.4.17). For example, for \( R_1 = R_2 \), we have from Eq. (8.3.2), \( \varepsilon_s = 9.8 \) for \( \varepsilon = 80 \). This is substantially larger than the value \( \varepsilon_s = 2.6 \) given by Eq. (7.4.17).

The formula
\[ C_s (\mu F/cm^2) = \frac{8.85 \varepsilon_s}{d(\AA)} \] (8.3.3)
shows that, taking \( R_1 = R_2 = 3 \, \AA \), the inner layer capacitance corresponding to \( \varepsilon_s = 9.8 \) is 58 \( \mu F/cm^2 \), compared to 15 \( \mu F/cm^2 \) for the result of Chapter 7. (The value at small surface charges for aqueous solutions at the mercury electrode is 25-30 \( \mu F/cm^2 \) at room temperature [8]). The larger value of \( \varepsilon_s \) reflects the closer resemblance to bulk solvent of the solvent near the plane of charge, since solvent molecules can penetrate the surface layer of charge.

For the simplifying case of one adsorbing ion (species \( v \)) in a symmetric electrolyte the ionic adsorption isotherm can be written as
\[ \sigma_b = \rho_v e z_v b_v \]
\[ = \frac{\rho_v e z_v a_v}{1 + \rho_v a_v \left[ \frac{\pi R_1^2}{1 - \eta} + \frac{4 \pi \varepsilon_0^2 R_2^2}{\varepsilon \kappa} \left( 1 - \frac{\varepsilon - 1}{\varepsilon + 1} \right) + \frac{\varepsilon - 1}{\lambda T} \right]} \] (8.3.4)

Since \( \eta \) is now dominated by \( \frac{\pi}{6} \rho_d R_2^3 \), the excluded volume effects are much more significant than in Eq. (5.2.17). For the same values of \( \rho_v \) and \( a_v \), the surface charge density is increased roughly fivefold over the result for adsorption from a PM electrolyte. This reflects the increased pressure in the bulk electrolyte when finite size solvent effects are included.
In addition, extra electrostatic terms due to ion-dipole interactions can be seen in the denominator of Eq. (8.3.4). If we set the terms involving \( \tau \) to zero, we recover the primitive model result, since \( B = -\frac{\kappa R}{2} + 0(\kappa R)^2 \) in Eq. (5.2.17). Notice that the term \( \frac{\kappa R}{\lambda} \) still contributes in the limit of point ions.

As in Chapter 5, the adsorption isotherm derived from the MSA equations shows an artificial saturation in surface charge density as \( a \nu \to \infty \). It is necessary to make the restriction \( a \nu / R < 10 \) in order to ensure that we are not in this artificial regime.

By setting \( b_E = 0 \), and noting from Eq. (8.3.4) that \( \sigma_\beta = 0(\rho_1) \), Eq. (8.2.22) becomes, to lowest order in \( \kappa R \) \( (R_1 = R_2 = R) \),

\[
\begin{align*}
\h_1(x) &= \frac{\sigma_\beta}{e} A_1 - \rho_1 A_1 \int_0^x h_1(y) \, dy \\
\h_2(x) &= \frac{\sigma_\beta}{e} Q_{21}(x) - \rho_1 A_2 \int_0^x h_1(y) \, dy + \rho_2 \int_0^{R_2} Q_{22}(y) h_2(x - y) \, dy .
\end{align*}
\]

As in Chapter 7, Eq. (8.3.5a) can be solved immediately

\[
\h_1(x) = -\frac{\kappa \sigma_\beta}{\rho_1 e} e^{-\kappa x}
\]

(8.3.6)

to yield the Debye-Hückel charge density

\[
\rho_{\text{CH}}(x) = -\kappa \sigma_\beta e^{-\kappa x} .
\]

(8.3.7)

Using Eq. (8.3.6), \( \h_2(x) \) is then given by

\[
\begin{align*}
\h_2(x) &= -A_2 \frac{\sigma_\beta}{e} e^{-\kappa x} + \frac{\sigma_\beta}{e} Q_{21}^0(x) + \rho_2 \int_0^{R_2} Q_{22}(y) h_2(x - y) \, dy ,
\end{align*}
\]

(8.3.8)

where, to this order in \( \kappa R \), \( Q_{22}(x) \) is given by Eq. (7.4.34) and

\[
\begin{align*}
Q_{21}^0(x) &= H_{21} a_2(x - R) , \quad 0 < x < R \\
&= 0 \quad x > R .
\end{align*}
\]

(8.3.9)
The novel feature of Eq. (8.3.8) is the second term – one which directly contributes only in the first diameter from the surface. In the next section we shall see that such a term is due to ion-dipole interactions. In particular, the cavity potential caused by the displacement of ion-dipole interactions in vacuum from the sphere of radius \( R \) contributes to such a term. For the moment, we just note that

\[
Q^0_{21}(x) = \frac{2\pi \varepsilon_0 \varepsilon}{R^2} \frac{(1 - 2\varepsilon)^2}{(1 + \varepsilon)} \left( 1 - \frac{x}{R} \right), \quad 0 < x < R \tag{8.3.10}
\]

which leads to an increase in \( h_2(x) \) near the surface.

We have calculated the polarization density at the surface by applying Perram's method [9] to Eq. (8.3.8). In Fig. 1 we compare the results with the polarization density found in Chapter 7. As in Chapter 5, the cusp in \( h_2(x) \) at \( x = R \) is due to our use of the MSA and an adsorption potential with delta function behaviour. The effect of \( \frac{\partial}{\varepsilon} Q^0_{21}(x) \) is to dramatically increase \( h_2(x) \) (and so reduce \( P(x) \)) in the region \( 0 < x < \frac{3}{2}R \). This effect propagates via the integral equation and \( P(x) \) shows much smaller oscillations about the macroscopic result than does the corresponding curve from Chapter 7. Just as in the previous chapter, the range and magnitude of the oscillations may be further reduced by decreasing the value of \( \varepsilon \).

In Chapter 7, the dipoles at the surface are physically separated from the plane of charge and so feel an electric field directed normal to the surface. The dipoles align strongly with the field and so cause a large depolarizing field \( P(x) \) near the surface. In Case A, dipoles are present in amongst the adsorbed ions, the tendency to align is greatly reduced and the depolarizing field is not as strong.

Since we have
Fig. 1: Polarization density at the surface for an ion-dipole mixture against a hard wall with only intrinsic surface charge $\sigma_0$ (---) and with only adsorbed surface charge $\sigma_\beta$ (-----), where $\sigma_0 = \sigma_\beta$. Other parameters as in Fig. 1, Chapter 7.
\[ \psi(x) = 4\pi \rho_1 e \int_x^\infty (x - y) h_1(y) \, dy + 4\pi \rho_2 \mu \int_x^\infty h_2(y) \, dy, \quad (8.3.11) \]

the reduced polarization density at the surface is reflected in a larger electrostatic potential near the surface, as shown in Fig. 2. Since the total polarization \( \int_y^\infty P(y) \, dy \) is now smaller than the macroscopic result, the surface potential is higher. Eq. (8.3.1) therefore reflects a real increase in electrostatic potential near the surface and not the more complicated situation shown in Fig. 3 of Chapter 7.

Case B: \( \sigma_B = 0 \)

For simplicity, we consider the case of MSA pure dipolar fluid both adsorbing and preferentially orienting at the surface. Both a potential discontinuity at \( x = 0 \) and a potential distribution extending into the solvent arise from the finite value of \( b_E \). The surface potential inside the dipole layer is

\[ \psi_B^- = \frac{4\pi \rho_2 \mu b_E}{q_+^{1/2}} \quad (8.3.12a) \]

and the potential just outside \( x = 0 \) is

\[ \psi_B^+ = \frac{4\pi \rho_2 \mu b_E}{q_+^{1/2}} (1 - q_+^{1/2}) \quad (8.3.12b) \]

Since \( q_+^{1/2} = 4.15 \) for \( \varepsilon = 80 \), one interesting consequence of Eq. (8.3.12) is that the error caused by neglecting both components of the dipole potential is only \( \sim 30\% \) of that caused by the neglect of just the potential discontinuity. Note also that the potentials inside and outside the plane \( x = 0 \) are of opposite sign.

The parameters \( b_d \) and \( b_E \) are given by
Fig. 2: Electrostatic potential resulting from the polarization density given in Fig. 1, for intrinsic surface charge $\sigma_0$ (---) and adsorbed surface charge $\sigma_\beta$ (-----).
\[
\frac{b_d}{R} = \frac{1 + 2\eta}{(1 - \eta)^2} \left[ \frac{a_d}{R} + 2(\lambda - 1) \left( \frac{a_d}{R^2} - \frac{1}{3} \left( \frac{a_E}{R} \right)^2 \right) \right]
\]  
(8.3.13)

\[
\frac{b_E}{R} = \frac{1 + 2\eta}{(1 - \eta)^2} \frac{a_E}{R} \Delta,
\]  
(8.3.14)

where
\[
\Delta = 1 + \frac{a_d}{R} \left[ \frac{6\eta}{1 - \eta} + 2(\lambda - 1) \right] + \frac{12\eta}{1 - \eta} (\lambda - 1) \left( \frac{a_d}{R^2} - \frac{1}{3} \left( \frac{a_E}{R} \right)^2 \right).
\]  
(8.3.15)

The restrictions given in Eq. (8.1.7) imply that \( \Delta \) and \( b_d \) are always positive. The monolayer density per unit area of the adsorbed dipole layer must be less than the close-packed density. This requires that
\[
\frac{\pi}{4} \rho_d R^3 \frac{b_d}{R} < \frac{\pi}{2\sqrt{3}} = 0.91.
\]  
(8.3.16)

The sticky sphere adsorption isotherm has the fortuitous property [10] that the monolayer surface density saturates to the value
\[
\frac{\pi}{4} \rho_d R^3 \frac{b_d}{R} \rightarrow \frac{1 + 2\eta}{4(1 - \eta)} = 0.79 \quad \text{for} \quad \rho_d R^3 = 0.8
\]  
(8.3.17)
as \( a_d \to \infty \). We have usually taken \( a_d/R = 1 \) in our calculations, but Eq. (8.3.17) ensures that any value for \( a_d/R \) will still keep realistic surface densities. From Eq. (8.3.14) we see that positive values of \( a_E \) (dipoles pointing towards the wall) lead to positive values of \( b_E \) and hence a decrease in potential across the plane \( x = 0 \), as expected.

For the pure dipolar fluid, Eq. (8.2.22) reduces to
\[
h_2(x) = \rho_2 b_E Q_{22}(x) + \rho_2 \int_0^R Q_{22}(y) h_2(x - y) \, dy,
\]  
(8.3.18)

where \( Q_{22}(x) \) is given by Eq. (7.3.34). We have solved Eq. (8.3.18) by Perram's method and the results are shown in Fig. 3 for two values of \( \varepsilon \). The corresponding graphs of \( \psi(x) \) are shown in Fig. 4.
Fig. 3: Electrostatic component of the wall-dipole total correlation function for a dipolar hard sphere fluid with $R = 3 \text{ Å}$, $\rho_d R^3 = 0.8$, $\varepsilon = 80.5$ (---) or 12.5 (---) adsorbing to the wall with parameter $b_E/R = 0.01$. 
Fig. 4: Electrostatic potential resulting from the polarization density given in Fig. 3, for cases $\varepsilon = 80.5$ (— —) or 12.5 (— —).
is just the electric field in the dipolar fluid near the surface, since
\[ \psi(x) = 4\pi\rho_2\mu \int_x^\infty h_2(y) \, dy. \] (8.3.19)

The potential (and hence the field) is short-ranged, extending only to 3 diameters from the surface for \( \varepsilon = 80 \). Since the net orientation of the dipole layer is given by \( 4\pi\rho_2\mu b_E \), the net fraction of dipoles oriented towards the wall is
\[ f = \frac{1}{3} \frac{b_E}{b_d}. \] (8.3.20)

A monolayer with net 3% of dipoles aligned towards the wall will therefore correspond to \( b_E \sim 0.07 \) (using Eq. (8.3.17)). The potential discontinuity then has a value \( \sim 200 \text{ mV} \) (see Ref. 11) but the surface potential \( \psi_b^- \) is only \( \sim 50 \text{ mV} \).

Case C: \( \sigma_b, b_E \neq 0 \)

We consider the case where both ions and dipoles adsorb onto the surface but dipoles do not specifically orient at the surface. There is a net orientation of the dipole layer caused by the field from the adsorbed surface charge. The potential is given by Eq. (8.2.29) where the separate terms have been discussed previously.

The expression for the surface charge density \( \sigma_b^- \) is much the same as in Case A, the main difference being a factor (provided \( R_1 = R_2 \))
\[ \alpha = \left( 1 + \frac{\pi R^2 \rho_d a_d}{1 - \eta} \right)^{-1} \] (8.3.21)
in the numerator. This factor serves to reduce \( \sigma_b^- \) because of the competition between the adsorbing ions and dipoles. \( b_E \) is given by
A positive surface charge will therefore yield a value of $b_E$ that corresponds to dipoles pointing away from the wall, i.e. the dipoles align with the field emanating from the surface charge.

To lowest order in $\kappa R$ the charge density is just the Debye-Hückel result, i.e. the same as in Case A. The polarization density is described by the equation

$$h_2(x) = -\Lambda_2 \frac{q}{e} e^{-\kappa x} + \frac{\sigma}{e} Q_{21}(x) + \rho_2 b_E Q_{22}(x) + \rho_2 \int_{e}^{R} Q_{22}(y) h_2(x - y) \, dy. \quad (8.3.23)$$

The adsorbed layer of dipoles introduces the new term $\rho_2 b_E Q_{22}(x)$, the effect of which can be seen in Figs. 5 and 6. The fact that the dipoles align with the field at the surface effectively increases the magnitude of the surface charge and so increases the potential. As in Case B, the effect of the dipole layer is short-ranged, vanishing after a few molecular diameters.

The introduction of specific dipolar orientation via $a_E$ simply has the effect of changing $b_E$ in a complicated way through Eq. (8.2.24). By varying $a_E$ (subject to Eq. (8.1.7)), we can tune $b_E$ and vary the potential about the dashed curve in Fig. 6. In the next section, we discuss the adsorption of ions and dipoles onto a charged surface.
Fig. 5: Polarization density for an ion-dipole mixture against a surface with adsorbed surface charge $\sigma_S = 0.64 \ \mu\text{C/cm}^2$, for the cases without dipole adsorption, $b_E = 0$ (-----) and with dipole adsorption, $b_E/R = -10 \ \sigma_S R^2/e$ (---). Other parameters as in Fig. 1, Chapter 7.
Fig. 6: Electrostatic potential resulting from the polarization density in Fig. 5, for the cases without (——) and with (—) dipole adsorption.
8.4 ADSORPTION ONTO A CHARGED SURFACE

MSA Results

The solution of the MSA equations for ionic and dipolar adsorption onto a uniformly charged surface may be found by using the methods of Sections 7.3 and 8.2. Since the MSA is a linear theory, the expression for \( \psi_0 (\Xi \psi(hR_0)) \) is just given by the sum of Eqs. (7.4.8) and (8.2.28) in general, i.e. to order \( \kappa R_1 \) and \( \kappa R_2 \),

\[
\psi_0 = \frac{4\pi\sigma_0}{\varepsilon\kappa} \left( 1 + \frac{\kappa R_1}{\varepsilon} + \frac{\kappa R_2}{\varepsilon} \right) + \frac{4\pi\sigma_0}{\varepsilon\kappa} \left( 1 + \frac{\kappa R_2}{\varepsilon} \right) \frac{\varepsilon - 1}{\lambda^2} \\
+ 4\pi\sigma_0 \frac{\mu_b}{q_+} \frac{E}{b} \left( 1 - \frac{\kappa R_2}{\lambda^2} \right). \tag{8.4.1}
\]

The adsorption isotherms are changed slightly from the results of Section 8.2. To the right hand side of Eqs. (8.2.22a) and (8.2.23a) is added the term \(- \frac{\sigma_0}{e} A_{11}\) and to Eqs. (8.2.22b) and (8.2.23b) is added \(- \frac{\sigma_0}{e} A_{21}\). The necessary changes to Eq. (8.2.24) immediately follow.

For the case of dipoles adsorbing to a charged surface and where \( \sigma_\beta \) and \( a_E = 0 \), the dipole layer is aligned by the field at the surface, as in Case C. The parameter \( b_E \) is given by

\[
b_E = -a_d \sigma_0 \frac{4\pi\beta\mu}{q_+^b \left( 1 + \frac{a_d}{R} \frac{\lambda - 1}{\lambda} \right)} \tag{8.4.2}
\]

Comparison with Eq. (8.3.22) reveals the quantitative difference — once again the factor \( \tau \) represents the amount of solvent penetration into the plane surface charge. The dipole layer is oriented more completely when the source of the surface field lies behind the plane \( x = 0 \). As before this can be interpreted as an effective increase in the surface charge density and so the potential near the surface is
increased over that given in Chapter 7.

The more complete situation with $\sigma_\theta$, $\sigma_\beta$, $b_E$ and $a_E$ all $\neq 0$ is complex to analyse but the new features that appear have been elucidated in this and the previous sections. At this stage, we leave the MSA solution and investigate the LHNC equations.

**LHNC Theory**

We now derive the equations for ionic and dipolar adsorption onto a uniformly charged surface for the case where ion-wall and dipole-wall interactions are treated using the LHNC closure, and bulk interactions are left unspecified. These equations are the simplest generalization of the HNC/bulk equations of ionic adsorption from a PM electrolyte (Eq. (5.1.19)) so as to include solvent structure. The LHNC treatment has the advantage of recovering the correct non-linear dependence on surface charge but only gives a partial treatment of image forces. For simplicity, we take $R_1 = R_2$.

We start with the wall-particle Ornstein-Zernike equations Eq. (7.3.1). We write

$$ u_{10}(r) = u^S_{10}(r) + u^C_{10}(r) $$

(8.4.3a)

$$ u_{do} (\omega, r) = u^S_{do} (\omega, r) + u^C_{do} (\omega, r) $$

(8.4.3b)

and use the HNC closure for wall-ion interactions to obtain

$$ 1 + h_{10}(r) = e^{-\beta u^S_{10}(r)} \exp[-\beta u^C_{10}(r) + h_{10}(r) - c_{10}(r)]. $$

(8.4.4)

As in Chapter 5, we parametrize the short-range interaction by Baxter's sticky potential,
which implies that
\[ h_{10}(r) = b_1 \delta(r - R_{10}) + h_{10}^*(r) \]  

(8.4.6)

where
\[ b_1 = a_1 [1 + h_{10}(R_{10})] . \]  

(8.4.7)

The wall-ion Ornstein-Zernike equation Eq. (7.3.1a) then becomes
\[
\ln[1 + h_{10}^*(r)] = -\beta \mu_{10}^c(r) + \sum_j \rho_j \int dr' c_i j(|r - r'|) h_{10}(r') \\
+ \rho_d \int d\omega_3 dr' c_{id}(r - r', \omega_3) h_{d0}(\omega_3, r').
\]  

(8.4.8)

We can follow the same procedure for the wall-dipole equation. By using Eq. (8.1.6) for the short-range interaction we recover Eqs. (8.1.8) - (8.1.10). Eq. (7.3.16) is then
\[
\ln[1 + h_{d0}^*(\omega_1, r)] = -\beta \mu_{d0}^c(\omega_1, r) + \sum_j \rho_j \int dr' c_{d j}(\omega_1, r - r') h_{j0}(r') \\
+ \rho_d \int d\omega_3 dr' c_{dd}(\omega_1, r - r', \omega_3) h_{d0}(\omega_3, r').
\]  

(8.4.9)

At this stage, we need to use the decomposition given in Eq. (7.3.4) and
\[
f_{id}(r, \omega_2) = f_{12}^{HS}(r) + f_{12}^E(r) E_2 \]  

(8.4.10a)

\[
f_{di}(\omega_1, r) = f_{2i}^{HS}(r) + f_{2i}^E(r) E_1 \]  

(8.4.10b)

\[
f_{dd}(\omega_1, r, \omega_2) = f_{22}^{HS}(r) + f_{12}^D(r) \Lambda_{12} + f_{12}^D(r) D_{12} . \]  

(8.4.10c)

Eq. (8.4.10) is used in the LHNC and QHNC treatments of bulk ion-dipole mixtures [12]. We can now integrate over \( \omega_3 \) in Eq. (8.4.8) to obtain
\[ \ln [1 + h_{10}^*(r)] = -\beta u_{10}^c(r) + \sum_j \rho_j \int \frac{dr'}{r'} c_{ij}(|r - r'|) h_{j0}(r') \]
\[ + \rho_d \int \frac{dr'}{r'} c_{12}^{HS}(|r - r'|) h_{20}^{HS}(r') \]
\[ + \rho_2^c \int \frac{dr'}{r'} c_{i2}^E(|r - r'|) h_i^E(r') \hat{r} \cdot \hat{r}' . \tag{8.4.11} \]

Using Eq. (7.3.4) we expand the left hand side of Eq. (8.4.8) and retain only linear terms and so we find
\[ \ln [1 + h_{20}^{*HS}(r)] = \sum_j \rho_j \int \frac{dr'}{r'} c_{2j}^{HS}(|r - r'|) h_{j0}(r') \]
\[ + \rho_d \int \frac{dr'}{r'} c_{22}^{HS}(|r - r'|) h_{20}^{HS}(r') \tag{8.4.12} \]
and
\[ \frac{h_{20}^{HS}(r)}{h_{20}(r)} = -\beta u_{20}^c(r) + \sum_j \rho_j \int \frac{dr'}{r'} c_{2j}^E(|r - r'|) h_{j0}(r') \hat{r} \cdot \hat{r}' \]
\[ + \rho_2^c \int \frac{dr'}{r'} h_{20}^E(r') \{ c^A(|r - r'|) \hat{r} \cdot \hat{r}' \]
\[ + c^D(|r - r'|) \hat{r} \cdot 3 \hat{r} \cdot \hat{r}' + \hat{r}' - \hat{r} \cdot \hat{r}' \} \tag{8.4.13} \]

Notice that the correlation functions \( h_{10}(r) \) on the right hand side of Eqs. (8.4.11) - (8.4.13) still have delta function behaviour.

We proceed as in Chapters 4 and 5 and write
\[ c_{ij}(r) = -\beta u_{ij}(r) + c_{ij}^O(r) \tag{8.4.14a} \]
\[ c_{i2}^E(r) = -\beta u_{i2}^E(r) + c_{i2}^O E(r) \tag{8.4.14b} \]
\[ c_{2j}(r) = -\beta u_{2j}^E(r) + c_{2j}^O E(r) \tag{8.4.14c} \]
\[ c_{22}^D(r) = -\beta u_{22}^E(r) + c_{22}^O D(r) , \tag{8.4.14d} \]
where the appropriate potentials are given in Eq. (7.1.2) - (7.1.7).

By using the definition of the mean electrostatic potential
\[ \psi(r) = \frac{z_0 e}{r} + \int dr' \frac{\Sigma \rho_{j} z_{j} e h_{j_{0}}(r')}{|r - r'|} + \frac{\rho_{d} \mu}{4\pi} \int dw_3 dw' \frac{h_{0d}(r', \omega) \hat{\mu}(\omega) \tilde{r}}{|r - r'|^2} \]

we can then write Eq. (8.4.11) as

\[ \ln[1 + h_{10}^*(r)] = -\beta z_1 e \psi(r) + \sum_i \rho_i \int dr' c_{i}^{0j}(|r - r'|) h_{j_{0}}(r') + \rho_{d} \int dr' c_{12}^{E}(|r - r'|) h_{2_{0}}^{E}(r') \]

which now has the correct non-linear dependence between \( g_{j_{0}}(r) \) and the mean electrostatic potential. The potential of mean force on an ion is then just the mean electrostatic potential plus terms due to short-range direct correlations. The LHNC treatment will therefore reduce to Gouy-Chapman theory if short-range direct correlations are set to zero.

We now perform the angular integrals in Eqs. (8.4.12), (8.4.13) and (8.4.16) to obtain the one-dimensional forms

\[ \ln[1 + h_{1}(x)] = -\beta z_1 e \psi(x) + \sum_i \rho_i \int_{-\infty}^{\infty} c_{i}^{0j}(x - y) h_{j_{0}}(y) dy + \sum_i \rho_i b_i c_{i}^{0j}(x) \]

\[ \ln[1 + h_{2}^{HS}(x)] = \sum_i \rho_i \int_{-\infty}^{\infty} c_{i}^{2j}(x - y) h_{2_{0}}^{HS}(y) dy + \sum_i \rho_i b_i c_{i}^{2j}(x) \]
\[
\frac{h_2(x)}{g_2(x)} = -4\pi\beta \mu \left\{ \int_0^x \sum_j \rho_j z_j e_h(y) \, dy \right\} \\
+ \sum_j \rho_j \int_{-\infty}^{\infty} C^{\text{OE}}_j(x-y) \, dy + \sum_j \rho_j b_j C^{\text{OE}}_j(x) \\
+ \rho_2^c \int_{-\infty}^{\infty} C^{+}_j(x-y) \, dy + \rho_2^b C^{+}(x), \tag{8.4.19}
\]

where we have defined

\[
\begin{align*}
  h^*_i(x + R_1) &= h_i(x) \\
  h^*_E(x + R_1) &= h_i(x) \\
  h^*_H(x + R_1) &= h_i(x)
\end{align*}
\tag{8.4.20}
\]

and

\[
\begin{align*}
  C^{\text{HS}}_{\alpha\beta}(x) &= 2\pi \int_{-\infty}^{\infty} ds s \left( \int_{|x|}^\infty \frac{d|x|}{s} \right) C^{\text{HS}}_{\alpha\beta}(s) \\
  C^{\text{ij}}_{\alpha\beta}(x) &= 2\pi \int_{-\infty}^{\infty} ds s \left( \int_{|x|}^\infty \frac{d|x|}{s} \right) C^{\text{ij}}_{\alpha\beta}(s) \\
  C^{\text{OE}}_{\alpha\beta}(x) &= 2\pi \int_{-\infty}^{\infty} ds s \left( \int_{|x|}^\infty \frac{d|x|}{s} \right) C^{\text{OE}}_{\alpha\beta}(s) \\
  C^{+}(x) &= 2\pi \int_{|x|}^{\infty} ds s \left( \int_{|x|}^\infty \frac{d|x|}{s} \right) C^{+}(s) + 2 \rho_2 \left( \int_{|x|}^\infty \frac{d|x|}{s} \right) C^{+}(s).
\end{align*}
\tag{8.4.21}
\]

Eqs. (8.4.17) - (8.4.21) are the LHNC/bulk equations for adsorbing ion-dipole mixtures against a uniformly charged surface.

The functions given in Eq. (8.4.20) can be computed from bulk direct correlation functions — at this stage, only MSA and LHNC results are available for finite ionic concentrations. In the MSA, for the case \( R_1 = R_2 = R \), \( C^{\text{ij}}_{\alpha\beta}(x) \) can be written

\[
C^{\text{ij}}_{\alpha\beta}(x) = C^{\text{HS}}_{\alpha\beta}(x) + z_i z_j C^{\text{c}}_{\alpha\beta}(x). \tag{8.4.22}
\]

In addition
\[ C_{1j}^{OE}(x) = z_j C_{21}^{OE}(x) \]  
(8.4.23)

\[ C_{2j}^{HS}(x) = C_{21}^{HS}(x), \quad \text{for all } j, \]

where \( C_{\alpha\beta}^{HS}(x) \) \((\alpha, \beta = 1, 2)\) is given by Eq. (4.2.3) except that

\[ \eta = \frac{n}{6} \left[ \sum_i \rho_i + \rho_d \right] R^3. \]  
(8.4.24)

\( C_{11}^{C}(x) \) is given, to lowest order in ionic concentration, by

\[ C_{11}^{C}(x) = \frac{2\pi \beta e^2}{\varepsilon} R \left\{ (\varepsilon - 1) \left( \frac{1}{3} \frac{\lambda}{1 + \lambda} \right)^2 \left( 1 - \frac{x^3}{R^3} \right) - \frac{\lambda}{1 + \lambda} \left( 1 - \frac{x^2}{R^2} \right) + \varepsilon \left( 1 - \frac{x}{R} \right) \right\}. \]  
(8.4.25)

The last term on the right hand side is just the cavity term describing the exclusion of ion-ion interactions in vacuum from the sphere of radius \( R \) centred at \( x \). The first two terms are corrections due to ion-dipole interactions. A cavity term for ion-dipole interactions of the form

\[ 2\pi \beta e \left( 1 - \frac{x}{R} \right) \]  
(8.4.26)

also appears in \( C_{21}^{OE}(x) \).

Eq. (8.4.25) can be compared with the primitive model result, to lowest order in \( \kappa R \),

\[ C_{11}^{C}(x) = \frac{2\pi \beta e^2}{\varepsilon} R \left( 1 - \frac{x}{R} \right). \]  
(8.4.27)

This is just the cavity term of Eq. (8.4.25) but reduced by a factor \( \varepsilon \) because of the continuum solvent. In Chapter 5 we showed that the term responsible for Levine's discrete-ion effects [13] - \( W_1^{ad(2b)}(0) \) - is just \( \sigma / e z_i C_{11}^{C}(0) \). For adsorption from a primitive model electrolyte we use Eq. (8.4.27) to obtain a term smaller than Levine's by roughly \( \varepsilon / \varepsilon_s \). It is interesting to see that the same term in Eq.
(8.4.17) for non-linear adsorption from an MSA ion-dipole mixture is just

\[ \frac{\sigma_B}{e} z_i c_{11}(0) = z_i \frac{2\pi e^2}{\varepsilon_{\text{eff}}} R \frac{\sigma_B}{e}, \]  

(8.4.28)

where

\[ \varepsilon_{\text{eff}} = 2.5 \quad \text{for} \quad \varepsilon = 80. \]  

(8.4.29)

The discrete-ion effects will therefore be much more important in adsorption from an ion-dipole mixture than from a primitive model electrolyte, and their magnitude will be closer to that described by Levine et al. [13].

An additional discrete-ion effect arises in adsorption from ion-dipole mixtures – the cavity terms between the adsorbed ions and non-adsorbed dipoles. Such terms are found in \( \sigma_B/e \sigma_{21}^{OE}(x) \) and correspond to the term \( \sigma_B/e Q_{21}^O(x) \) given in Eq. (8.3.10). The larger values of \( h_2(x) \) (and hence \( \psi(x) \)) near the surface for Case A compared with the values in Chapter 7 are due to these new discrete-ion effects.

When an oriented dipole layer is present, additional adsorption terms appear \( \rho_d \rho_{\text{d}}^{C_{12}(x)}, \rho_d \rho_{\text{d}}^{C_{22}(x)} \) in Eq. (8.4.17), \( \rho_d \rho_{\text{d}}^{C_{12}(x)} \) in Eq. (8.4.18) and \( \rho_d \rho_{\text{d}}^{C_{22}(x)} \) in Eq. (8.4.19)). In the MSA/MSA expressions these effects are included, albeit with \( C(x) \) replaced by \( Q(x) \). Their importance is shown in Figs. 3-6.

At this point we conclude our investigation of adsorption from ion-dipole mixtures. To obtain more reliable results, particularly for larger values of surface charge density, it would be desirable to solve Eqs. (8.4.17) - (8.4.21), preferably using UNIC values of \( C_{12}(x) \) [12].
REFERENCES

CHAPTER 9
TETRAHEDRAL QUADRUPOlar EFFECTS
ON THE DIPOLAR HARD SPHERE FLUID

9.1 GENERAL FORMALISM OF MULTIPOLAR FLUIDS

The ion-dipole mixture model of the electrolyte that was used in the previous two chapters has the advantage of simplicity with the concomitant ease of interpretation of new effects. However, the most interesting solvent, water, has many features not included in the ion-dipole mixture model — quadrupolar effects, polarizability, hydrogen-bonding, etc. In this chapter we examine the effects on the dipolar solvent of a water-like quadrupole moment. We also investigate the formalism necessary for incorporating water-like quadrupole effects into the theory of electrolytes (and hence, eventually, double-layer theory).

The general formalism of multipolar fluids has been developed in studies based on cluster expansions [1], integral equation methods [2-4] and perturbation techniques [5,6]. For the cases of dipolar fluids [7,8] and ion-dipole mixtures [9-14], we can use the simplifying notation of Chapters 7 and 8. Once quadrupolar effects are included, however, we require the general formalism in order to proceed.

Only recently have quadrupolar interactions been considered [5,6, 15,16]. In all cases, however, the molecules are assumed to possess a quadrupole tensor of the form
which can be generated by a linear arrangement of charges along the z molecular axis, e.g. as in the HCl molecule. Hence this is known as a linear quadrupole. A non-linear quadrupole of interest is one that resembles the quadrupole tensor of water which has a form close to

\[
\begin{pmatrix}
0_T & 0 & 0 \\
0 & -0_T & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

when referred to the centre of mass of the water molecule [17]. Such a quadrupole tensor can be obtained by putting two positive charges and two negative charges of equal magnitude at the vertices of a regular tetrahedron. We therefore call this a tetrahedral quadrupole.

In this section, we outline the requisite formalism and rederive some necessary results of Blum et al. [2-4]. The properties of some special functions encountered in this section are summarized in Appendix 1. In the next section, we apply the formalism to a mixture of ions - modelled as hard spheres with embedded point charges - and a hard sphere solvent containing both dipole and tetrahedral-quadrupole moments. The main result of this section is the demonstration of a mathematical correspondence between this system and the same mixture with the tetrahedral quadrupole replaced by a linear quadrupole. As an application of our analysis, in section 9.3 we obtain the analytical MSA solution for a pure hard sphere tetrahedral quadrupolar fluid. Some transformations used in this section are detailed in Appendix 2. In section 9.4 we employ thermodynamic perturbation
theory to study the model solvent consisting of hard spheres which have both dipole and tetrahedral quadrupole moments.

The formalism outlined in this section is similar to that of Jepsen and Friedman [1] and Blum et al. [2-4]. We consider the general case of a multi-component mixture of hard spheres of equal diameters in which all components may possess a point charge, dipole moment and quadrupole moment. But more specifically we envisage a system in which some species only carry charges (the ions) and others only carry a dipole and quadrupole moment (the solvent). Our goal is to give a simple derivation of Eq. (2.33) of Ref. 3.

The Ornstein-Zernike equation for a multi-component mixture is just that given in Chapter 7,

\[
h(x_1, x_2) = c(x_1, x_2) + \frac{1}{8\pi^2} \int d\omega_1 \int d\omega_2 c(x_1, \omega_1) \varrho h(\omega_1, \omega_2, x_2). \tag{9.1.3}
\]

As stated before, by appealing to translational and rotational invariance of the bulk fluid, we can expand any function \( f = h \) or \( c \) [1]

\[
f(x_1, x_2) = \sum_{\mu, \nu, \lambda} \phi_{\mu, \nu, \lambda}^{mn}(r) \varphi_{\mu, \nu, \lambda}^{mn}(\omega_1, \omega_2, \hat{r}). \tag{9.1.4}
\]

The functions \( \phi_{\mu, \nu, \lambda}^{mn}(r) \) depend only on the intermolecular separation, \( r \), and the rotational invariants \( \varphi_{\mu, \nu, \lambda}^{mn} \) are given by

\[
\phi_{\mu, \nu, \lambda}^{mn} = \sum_{\mu', \nu', \lambda'} (-1)^{\mu'} \left( \begin{array}{ccc} m & n & \ell \\ -\mu & \nu & \lambda' \end{array} \right) \varphi_{\mu', \nu', \lambda'}^{n*}(\omega_1) \varphi_{\nu, \nu, \lambda}^{n*}(\omega_2) D_{\mu, \nu, \lambda}^{\ell}(\hat{r}). \tag{9.1.5}
\]

in which \( \left( \begin{array}{ccc} m & n & \ell \\ -\mu & \nu & \lambda' \end{array} \right) \) is a Wigner 3-j symbol and \( D_{\mu, \nu, \lambda}^{\ell}(\omega) \) is a generalized spherical harmonic. The important properties of these quantities and the manner in which they limit the range of summations in Eqs. (9.1.4) and (9.1.5) are given in Appendix 1 and Refs. 18 and
19. Our definition of the rotational invariant is the same as that in Ref. 1 while that of Blum [2-4] (denoted by a carat) is given by

\[ \hat{\phi}_{\mu \nu}^{mn} (\omega_1, \omega_2, \hat{r}) = (-1)^{\mu} \left( (2m+1)(2n+1) \right)^{1/2} \phi_{\mu, \nu}^{mn} (\omega_1, \omega_2, \hat{r}) . \] (9.1.6)

For an isotropic fluid, Eq. (9.1.3) is a convolution form in the variables \( r_1 - r_2, r_2 - r_3, r_3 - r_1 \) so that its three-dimensional Fourier transform is

\[ \tilde{\omega}(\omega_1, \omega_2, k) = \tilde{\omega}(\omega_1, \omega_2, k) + \frac{1}{8\pi^2} \int d\omega_3 \tilde{c}(\omega_1, \omega_3, k) \tilde{h}(\omega_3, \omega_2, k) , \] (9.1.7)

where

\[ \tilde{h}(\omega_1, \omega_2, k) = \sum_{mnL} \frac{1}{8\pi^2} \int d\omega_3 \tilde{c}(\omega_1, \omega_3, k) \tilde{h}(\omega_3, \omega_2, k) \] (9.1.8)

and \( j_L(kr) \) is a spherical Bessel function of order \( L \) (see Eq. (9.A.2.1)). There is also a similar set of transformations for \( \tilde{c} \). We can construct a multiplication table for the angular convolution in Eq. (9.1.7) using the result

\[ \frac{1}{8\pi^2} \int d\omega_3 \phi_{\mu \nu}^{mn} (\omega_1, \omega_3, \hat{r}) \phi_{\mu', \nu'}^{m'n'} (\omega_3, \omega_2, \hat{r}) \] (9.1.10)

\[ = \delta_{mn} \delta_{\nu \nu'} (-1)^{m+n+n'} \sum_L \left( \begin{array}{ccc} L' & L & \ell' \\ m & n & \ell \end{array} \right) \left( \begin{array}{ccc} \ell' & \ell & L \\ 0 & 0 & 0 \end{array} \right) \phi_{\mu \nu}^{mn \ell} (\omega_1, \omega_2, \hat{r}) . \]

The range of the sum over \( L \) is limited by the properties of the Wigner 6-j symbol \( \left( \ell', \ell, L \right) \) summarized in Appendix 1. We substitute Eq. (9.1.8) into Eq. (9.1.7) and use Eq. (9.1.10) together with the orthogonality condition (see Appendix 1)

\[ \frac{1}{(8\pi^2)^3} \int \frac{d\omega_1}{d\omega_2} \int d\hat{r} \phi_{\mu \nu}^{mn} (\omega_1, \omega_2, \hat{r}) \phi_{\mu', \nu'}^{m'n'} (\omega_1, \omega_2, \hat{r}) \] (9.1.11)
to obtain
\[ \tilde{h}_{nmn'}^{\mu \nu}(k) = \tilde{h}_{mn}^{\mu \nu}(k) + \sum_{n''} (-1)^{m+n+n''} \left( \begin{array}{ccc} n'' & n' & n \\ l'' & l' & l \end{array} \right) \left( \begin{array}{ccc} 2l+1 \\ 2l''+1 \end{array} \right) \tilde{h}_{n''n''}^{l''l''l''}(k) \]

which is equivalent to Eqs. (2.18) - (2.21) of Ref. 3. Following Blum [3] we define the linear combinations (see Eq. (9.A.2.2))

\[ \tilde{h}_{mn}^{\mu \nu}(k) = (-1)^{\chi} \sum_{l} \left( \begin{array}{ccc} m & n & n' \\ \chi & \chi & 0 \end{array} \right) \tilde{h}_{\chi \chi \mu \nu}(k) \]

and use the properties of the 6-j symbol, Eq. (9.A.1.10), to get

\[ \tilde{h}_{nm}^{\mu \nu}(k) = \tilde{h}_{mn}^{\mu \nu}(k) + \sum_{n'} \frac{1}{2n'+1} \tilde{h}_{nmn'}^{\mu \nu}(k) \tilde{h}_{n'n'}^{\mu \nu}(k), \]

where \( n' \geq \chi \) and \( |\nu'| \leq n' \). Eq. (9.1.14), which is equivalent to Eq. (2.33) of Ref. 3, is a general result which resembles the Ornstein-Zernike equations for a simple fluid mixture since all angular variables have been removed and the functions only depend on the magnitude of the wave vector.

The transformation in Eq. (9.1.13) is a generalization of Wertheim's choice of \( h^+ \) and \( h^- \) as a linear combination of \( h^D \) and \( h^A \) for the case of dipolar fluids [7]. For each allowed value of \( \chi \), Eq. (9.1.14) separates into a series of simpler equations of the usual Ornstein-Zernike form with block matrix structure. For example, the highest value of \( \chi \) gives a single scalar equation for one element of \( \tilde{h}_{\chi \chi \mu \nu} \) and \( \tilde{c}_{\chi \chi} \); the next lower value of \( \chi \) gives a \( 2 \times 2 \) matrix equation for three independent functions, and so on. We shall give a more detailed discussion of Eq. (9.1.14) for an ion-dipole-quadrupole mixture in the next section.
Before we discuss the solution of the Ornstein-Zernike equations for an ion-dipole-quadrupole mixture, let us recall the form of the multipole expansion of the electrostatic interaction between two non-overlapping charge distributions \[18,19\]

\[
U(r, \omega_1, \omega_2) = \sum_{m\mu} (-1)^{m+\mu} \frac{(2\mu+1)!}{(2m)! (2n)!} \left( \frac{\hat{Q}^\mu_m(\hat{1}) \hat{Q}^\nu_n(\hat{2})}{r^{\mu+1}} \right) \phi_{m\nu}^{\mu\nu}(\omega_1, \omega_2, \hat{r}),
\]

where \( \hat{r} = m+n \), \( r \) is the distance between the centres of the two charge distributions and the angular variables \( \omega_1 \), \( \omega_2 \) and \( \hat{r} \) specify the orientation of the two molecular axis systems and the intermolecular axis with respect to the laboratory frame. The multipole moments \( \hat{Q}^\mu_m \) are defined by

\[
\hat{Q}^\mu_m(\hat{1}) = \sum_{\alpha} q_{\alpha} \hat{r}^m_{\alpha} \delta_{0\mu}^{\alpha} (\hat{\theta}_{\alpha}, \hat{\phi}_{\alpha}),
\]

where the co-ordinate of the charge \( q_{\alpha} \) is \((\hat{r}_{\alpha}, \hat{\phi}_{\alpha}, \hat{\theta}_{\alpha})\) in the molecular axis system. The relationship between \( \hat{Q}^\mu_m \) and the multipole moments \( Q^\mu_m \) of Eq. (12.1-18a) of Ref. 19 is

\[
\hat{Q}^\mu_m(\hat{1}) = i^{\mu-m} \frac{1}{(m+|\mu|)!} \frac{1}{(m-|\mu|)!} \left( 2m + |\mu| \right)! \left( 2m - |\mu| \right)! \left( 2m \right)! \left( 2n \right)! \left( 2\mu+1 \right)! \left( 2\mu+3 \right)! \left( 2m+2\mu+2 \right)! \left( 2n+2\mu+2 \right)! \sum_{\mu} Q^\mu_m(\hat{1}),
\]

For quadrupoles, the connection between these multipole moments and the more familiar definition of the quadrupole tensor

\[
\theta_{ij} = \frac{4}{3} Q_{ij} = \frac{1}{2} \sum_{\alpha} q_{\alpha} \left( r_{i\alpha} r_{j\alpha} - r^2 \delta_{ij} \right)
\]

is given by Eqs. (12.1-16), (12.1-22) - (12.1-24) of Ref. 19. For example, \( Q^2_0 = q \) is the net charge on the molecule; and if the molecule has a dipole moment, \( \mu \) along the \( z \) molecular axis; \( Q^2_z = \mu \).
In general, the number of coefficients in Eq. (9.1.4) is restricted by the symmetry of the intermolecular potential [2]. In particular, for axisymmetric molecules such as dipoles or linear quadrupoles we only have \( \mu = 0 = \nu \). For molecules with \( C_{2v} \) symmetry such as water or tetrahedral quadrupoles we only need \( \mu,\nu = -2, 0, +2 \) so that for a given set \((mnl)\) the nine functions \( f_{\pm \mu \pm \nu}^{mnl}(r) \), where \( f \) stands for any element of \( h \) or \( \tilde{c} \), are all equal. For molecules with tetrahedral symmetry (e.g. tetrahedral quadrupoles or a charge distribution consisting of two positive and two negative charges of equal magnitude at the vertices of a regular tetrahedron) there is a further symmetry property: \( f(x_1, x_2) \) is invariant under the rotation of both molecules by \( \pi/2 \) about the \( z \)-axis of the molecular frame. This operation, which is equivalent to reversing the signs of the charges on each molecule, implies \( \mu + \nu = -4, 0, +4 \) so that the only coefficients that survive in Eq. (9.1.4) are \( f_{00}^{mnl}(r) \) and \( f_{\pm 2\pm 2}^{mnl}(r) \).

So far we have considered how the general symmetry properties of the intermolecular potential can be used to eliminate some of the coefficients in Eq. (9.1.4). One possible approximation in the treatment of multipolar fluids is to retain only the set of rotational invariants appearing in the interaction potential together with any further invariants that are needed to complete the angular convolution multiplication table generated by Eq. (9.1.10). In the MSA the solution of the Ornstein-Zernike equations can be represented in terms of this subset. In the LHNC approximation, the usual HNC closure is linearized which ensures that the retention of only those rotational invariants that are members of this subset is self-consistent.

Let us examine in more detail this subset for ion-dipole-quadrupole mixtures. If we are dealing with a linear quadrupole the
only non-zero multipole moments in Eq. (9.2.1) are \( Q_0^0 = q \) the net charge, \( Q_1^1 = \mu \) the dipole moment and \( Q_2^2 = Q_{zz} = -Q_L \) the linear quadrupole moment (cf. Eq. (9.1.1)). Explicit expressions for the multipole potentials are:

**charge-charge**

\[
U_{CC} = q^2 \phi_{000}^0 (\omega_1, \omega_2, \mathbf{r}) \mathbf{r}^{-1} = q^2 \frac{1}{r^1} \tag{9.2.5}
\]

**charge-dipole**

\[
U_{CD} = 3^{1/2} q \mu \phi_{011}^1 (\omega_1, \omega_2, \mathbf{r}) \mathbf{r}^{-2} \tag{9.2.6}
\]

**dipole-dipole**

\[
U_{DD} = -30^{1/2} \mu^2 \phi_{112}^2 (\omega_1, \omega_2, \mathbf{r}) \mathbf{r}^{-3} \tag{9.2.7}
\]

**charge-quadrupole**

\[
U_{CQ_L} = 5^{1/2} q Q_L \phi_{022}^2 (\omega_1, \omega_2, \mathbf{r}) \mathbf{r}^{-3} \tag{9.2.8}
\]

**dipole-quadrupole**

\[
U_{DQ_L} = -105^{1/2} \mu Q_L \phi_{123}^3 (\omega_1, \omega_2, \mathbf{r}) \mathbf{r}^{-4} \tag{9.2.9}
\]

**quadrupole-quadrupole**

\[
U_{Q_LQ_L} = 3(70)^{1/2} Q_L^2 \phi_{022}^2 (\omega_1, \omega_2, \mathbf{r}) \mathbf{r}^{-5} \tag{9.2.10}
\]

In Eqs. (9.2.6), (9.2.8) and (9.2.9) the position vector \( \mathbf{r} \) is directed towards the higher multipole. We note that for this ion-dipole-linear quadrupole system the molecules have axial symmetry so we always have \( \mu = 0 = \nu \). The six rotational invariants which appear in Eqs. (9.2.5) - (9.2.10) require four additional functions to form a multiplication table under the angular convolution in the Ornstein-Zernike equation. These ten functions are:
$\phi_{00}^{00}$  

hard sphere and charge-charge interactions

$\phi_{00}^{11} (=-\phi_{00}^{011})$  

charge-dipole (= $E$ of Ref. 11 and Chapters 7 and 8)

$\phi_{00}^{20} (=-\phi_{00}^{022})$ 

charge-quadrupole

$\phi_{00}^{11} , \phi_{00}^{112}$  

dipole-dipole (= $A$ and $D$ of Ref. 7 and Chapters 7 and 8)

$\phi_{00}^{211} (=-\phi_{00}^{121}) , \phi_{00}^{123} (-=\phi_{00}^{213})$  

dipole-quadrupole

$\phi_{00}^{220} , \phi_{00}^{222} , \phi_{00}^{224}$  

quadrupole-quadrupole.

There will of course be ten independent matrix functions of $r$ corresponding to this set of ten angular functions.

We now examine the similar subset of rotational invariants for an ion-dipole-tetrahedral quadrupole mixture. In Eq. (9.2.1), the non-zero multipole moments are $\tilde{Q}_1^2 = q$, $\tilde{Q}_1^0 = \mu$ and

$$\tilde{Q}_2^4 = (24)^{-1/2} Q_2^4 = \left(\frac{2}{5}\right)^{1/2} \tilde{Q}_1^4 .$$

Consequently the charge-charge, charge-dipole and dipole-dipole interactions for this case are the same as that given by Eqs. (9.2.5) - (9.2.7). Interactions involving the tetrahedral quadrupole are of the form:

charge-quadrupole

$$U_{CQT} = (10/3)^{1/2} q \Theta_T \phi^{022} (\omega_1, \omega_2, \vec{r}) \, r^{-3}$$

(9.2.12)

dipole-quadrupole

$$U_{DQT} = -70^{1/2} \mu \Theta_T \phi^{123} (\omega_1, \omega_2, \vec{r}) \, r^{-4}$$

(9.2.13)
quadrupole-quadrupole

\[ U_{Q_1Q_2} = 2(70)^{1/2} \zeta_T^2 \Phi^{224}(\omega_1, \omega_2, \zeta) r^{-5} \]  

(9.2.14)

with

\[ \Phi^{022} \equiv \Phi^{022}_{0-2} + \Phi^{022}_{02} \]  

(9.2.15)

\[ \Phi^{123} \equiv \Phi^{123}_{0-2} + \Phi^{123}_{02} \]  

(9.2.16)

\[ \Phi^{224} \equiv \Phi^{224}_{2-2} + \Phi^{224}_{02} + \Phi^{224}_{22} + \Phi^{224}_{-2-2}. \]  

(9.2.17)

Thus by comparing Eqs. (9.2.8) - (9.2.10) with Eqs. (9.2.12) - (9.2.14) we see that the potentials involving the tetrahedral quadrupole can be obtained from those for the linear quadrupole by the substitution

\[ \Theta_L \rightarrow \left(\frac{2}{3}\right)^{1/2} \Theta_T \]  

(9.2.18)

\[ \phi_{00}^{mn\lambda} \rightarrow \Phi^{mn\lambda}. \]

Therefore, the subset of rotational invariants for an ion-dipole-linear quadrupole system is very similar to that for an ion-dipole-tetrahedral quadrupole system except where \( m(n) = 2 \) we have \( \mu(v) = \pm 2 \) instead of 0. So although the tetrahedral case requires more rotational invariants as a result of the general symmetry of tetrahedral quadrupoles discussed earlier, the same number (10) of independent matrix functions of \( r \) are needed for the linear or tetrahedral system. We note parenthetically that in the quadratic hypernetted chain (QHNC) treatment of a dipole-linear quadrupole fluid the results do not reduce to the QHNC dipolar fluid when the quadrupole moment is set to zero. However, because rotational invariants with indices \((\mu, v) = (0, 0)\) are not involved in describing interactions involving tetrahedral quadrupoles the QHNC approximation for a dipole-tetrahedral quadrupole fluid will reduce to a QHNC dipolar fluid when
the quadrupole moment is set to zero.

In the remainder of this section we shall consider the MSA or LHNC closure for a mixture of ionic species – hard spheres with point charges – of number density \( \rho_i \), \( i = 1, 2, \ldots, n \) and one solvent species at number density \( \rho_s \) – hard spheres with point dipoles and tetrahedral quadrupoles. This is a simple model of an electrolyte in which the molecular nature of the ions and solvent are treated on an equal basis. Furthermore, the solvent can be made to mimic the low multipoles of water. We assume the hard sphere diameters of the ions and solvent to be the same value, \( R \), and call this the Restricted Civilized Model electrolyte. In the MSA or LHNC, the solution of the Ornstein-Zernike equations for this system can be represented by the set of ten rotational invariants generated by the multipole potentials and the angular convolution integral. These are \( \phi_{000}^0, \phi_{001}^{10} (= -\phi_{001}^{01}) \), \( \phi_{110}^{11}, \phi_{002}^{20} (= \phi_{020}^{02}) \), \( \phi_{211}^{211} (= -\phi_{121}^{121}) \), \( \phi_{123}^{123} (= -\phi_{223}^{223}) \), \( \phi_{222}^{222} \) and \( \phi_{224}^{224} \); and there will, of course, be ten matrix functions of \( r \) to specify \( \mathbf{h} \) or \( \mathbf{c} \). However, we can see from this set of rotational invariants that for a fixed value of \( (m, n, \ell) \) these functions are identical for all allowed values of \( (\mu, \nu) \), hence hereafter we can suppress the indices \( (\mu, \nu) \).

The exact hard core condition implies

\[
\begin{align*}
\mathbf{h}_{000}^0(r) &= -1, \quad r < R \\
\mathbf{h}_{mn\ell}^\ell(r) &= 0, \quad r < R, \quad \text{all other (mn\ell)}. 
\end{align*}
\]  

(9.2.19)

In the MSA we have \( (\beta = 1/kT) \)

\[
\mathbf{c}_{mn\ell}^\ell(r) = -\beta \mathbf{u}_{mn\ell}^\ell(r), \quad r > R
\]  

(9.2.20)

and in the LHNC
\[
c^{000}(r) = -\beta u^{000}(r) + h^{000}(r) - 2n[1 + h^{000}(r)], \quad r > R \tag{9.2.21}
\]

and for \((mn\ell) \neq (000)\)

\[
c^{mn\ell}(r) = -\beta u^{mn\ell}(r) + \left( \frac{h^{000}(r)}{1 + h^{000}(r)} \right) h^{mn\ell}(r), \quad r > R, \tag{9.2.22}
\]

where \(h\) or \(c\) denotes any element of the matrix \(h\) or \(c\) and the functions \(u^{mn\ell}(r)\) are given by Eqs. (9.2.5) - (9.2.7) and (9.2.12) - (9.2.14).

The Ornstein-Zernike equations for the various components of the correlation functions can be obtained from Eq. (9.1.14). For the case \(\chi = 2\) we have a single scalar equation for the function \(h_2^{22}(k)\) which from Eq. (9.1.13), is a linear combination of \(h_2^{20}\), \(h_2^{22}\) and \(h_2^{24}\).

This equation, which only describes quadrupole-quadrupole interactions between the solvent molecules has the appearance of an Ornstein-Zernike equation for a one-component fluid of density \(\rho Q_T = 2\rho_s / 5\)

\[
h_2^{22}(k) = 2c_2^{22}(k) + \rho Q_T c_2^{22}(k) h_2^{22}(k). \tag{9.2.23}
\]

For \(\chi = 1\), Eq. (9.1.14) results in a \(2 \times 2\) matrix equation for \(h_1^{mn}(k)\), \(m,n = 1,2\). From Eq. (9.1.13) it is easy to see that this equation describes dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions between the solvent molecules. The equation for \(h_1^{mn}(k)\) between solvent molecules is

\[
h_1^{mn}(k) = \tilde{c}_1^{mn}(k) + \sum_{n'=1,2} \tilde{c}_1^{mn'}(k) \rho_{n'}^{-1} h_1^{n'n}(k), \tag{9.2.24}
\]

where \(\rho_1 = \rho_s / 3\), \(\rho_2 = 2\rho_s / 5\). Eq. (9.2.24) is therefore the Ornstein-Zernike equation for a two-component mixture where the densities of the components are \(\rho_D = 2\rho_s / 5\) and \(\rho Q_T\).

For \(\chi = 0\), Eq. (9.1.14) describes ion-ion, ion-solvent and...
solvent-solvent interactions and can be written as an \((n+3)\)-component 
Ornstein-Zernike equation with densities of components \(\{\rho_1, \ldots, \rho_n\}\), 
\(\rho_s\), \(\rho_D\) and \(\rho_{QT}\). Alternatively, it can be written as a three-component 
Ornstein-Zernike equation for \(\hat{h}_{mn}^{\text{nn}}(k)\), \(m, n = 0, 1, 2\), provided one 
formally regards the matrix \(\hat{h}_{s}^{00}(k)\) as a single element.

An important point to note is that if one carries through the 
identical analysis for an ion-dipole-linear quadrupole system, one 
would obtain an identical set of equations with \(\rho_{QT}\) replaced by 
\(\rho_s = \rho_D / 5\) and \(\Theta_T\) replaced by \((3/2)^{1/2} \Theta_s\). Consequently, existing 
programs which solve the LHNC equations for an ion-dipole-linear 
quadrupole system only require the above minor modification to handle 
an ion-dipole-tetrahedral quadrupole mixture.

9.3 TETRAHEDRAL QUADRUPOULAR FLUID IN THE MSA

As an example of the application of the results of the previous 
section we consider the MSA solution for a fluid consisting of hard 
spheres (diameter \(R\), density \(\rho\)) with embedded point tetrahedral 
quadrupoles of magnitude \(\Theta_T\) — see Eq. (9.1.2). The solution of the 
Ornstein-Zernike equation for this problem can be written in terms of 
four rotational invariants: \(\Phi^{000}, \Phi^{220}, \Phi^{222}\) and \(\Phi^{224}\). Hence only 
four independent functions of \(r\) are needed: \(h_{00}^{00}(r)\) and \(h_{\mu\nu}^{22\ell}(r)\), 
\(\ell = 0, 2, 4\), where \(h_{\mu\nu}^{22\ell}(r)\) is independent of the values of \((\mu, \nu) = (\pm 2, \pm 2)\). From Eq. (9.1.14) we see that one of these functions obeys the 
equation (in k-space) \(\chi = 0\), \(m = n = 0\)

\[
\hat{h}_{00}^{00}(k) = \tilde{c}_{00}^{00}(k) + \rho \tilde{c}_{00}^{00}(k) \hat{h}_{00}^{00}(k) \quad (9.3.1)
\]
since from Eq. (9.1.13)

\[
\tilde{h}_{00}^{00}(k) = \hat{h}_{0,00}^{00}(k) \quad (9.3.2)
\]
and similarly for $\tilde{c}_{000}^{000}$. The boundary conditions for Eq. (9.3.1) are

$$h_{000}^{000}(r) = -1, \quad r < R$$

$$c_{000}^{000}(r) = 0, \quad r > R$$

so that Eq. (9.3.1) is just the Percus-Yevick equation for hard spheres which has a known solution [20].

For the remaining three functions $h_{\mu\nu}^{22\lambda}(r), \lambda = 0, 2, 4$, we have from Eq. (9.1.14)

$$\tilde{h}_{\chi}(k) = \tilde{c}_{\chi}(k) + \frac{2\rho}{5} \tilde{c}_{\chi}(k) \tilde{h}_{\chi}(k), \quad \chi = 0, 1, 2, \quad (9.3.4)$$

where

$$\tilde{h}_{\chi}(k) = (-1)^\chi \sum_{\ell=0,2,4} \left( \begin{array}{ccc} 2 & 2 & \ell \\ \chi & -\chi & 0 \end{array} \right) \tilde{h}_{\mu\nu}^{22\ell}(k), \quad \mu, \nu = \pm 2 \quad (9.3.5)$$

with a similar definition for $\tilde{c}_{\chi}(k)$. Again we note that $\tilde{h}_{\chi}(k)$ is independent of $(\mu, \nu)$. The boundary conditions for Eq. (9.3.4) are

$$h_{\mu\nu}^{22\lambda}(r) = 0, \quad \lambda = 0, 2, 4 \quad (9.3.6a)$$

$$c_{\mu\nu}^{220}(r) = c_{\mu\nu}^{222}(r) = 0, \quad r > R \quad (9.3.6b)$$

$$c_{\mu\nu}^{224}(r) = -2(70)^{\frac{1}{2}} \tilde{\beta} \hat{\alpha}^2 r^{-5}, \quad r > R \quad (9.3.6c)$$

Eqs. (9.3.4) and (9.3.6) can be solved by Baxter's Wiener-Hopf factorization method [21]. The auxiliary functions $\tilde{q}_{\chi}(k)$ are given by

$$\tilde{c}_{\chi}(k) = \tilde{q}_{\chi}(k) + \tilde{q}_{\chi}(-k) - \frac{2\rho}{5} \tilde{q}_{\chi}(k) \tilde{q}_{\chi}(-k). \quad (9.3.7)$$

As in previous chapters, we proceed by defining the one-dimensional inverses, $F_{\chi}(r)$

$$F_{\chi}(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \ e^{-ikr} \tilde{f}_{\chi}(k), \quad (f = h, c \text{ or } q) \quad (9.3.8)$$

and so obtain...
\[ C_\chi(r) = Q_\chi(r) - \frac{2\alpha}{5} \int_0^\infty Q_\chi(r+s) Q_\chi(s) \, ds \quad (9.3.9) \]

\[ H_\chi(r) = Q_\chi(r) + \frac{2\alpha}{5} \int_0^\infty Q_\chi(s) H_\chi(r-s) \, ds . \quad (9.3.10) \]

From Eqs. (9.1.9) and (9.3.8) it follows that \((F=H, C \text{ or } Q)\)

\[ F_\chi(r) = 2\pi (-1)^\chi \sum_{\lambda=0,2,4} \left( \begin{array}{c} 2 \\ \lambda \\ \chi - \lambda \end{array} \right) \int_0^\infty ds \, s \, P_\lambda \left( \frac{r}{s} \right) s^{2\lambda} \left( \frac{\partial^2}{\partial \mu \partial \nu} \right) (s) \quad (9.3.11) \]

where \(P_\lambda(x)\) is a Legendre polynomial of degree \(\lambda\).

The large \(r\) behaviour of \(Q_\chi(r)\) can be found for the present case from boundary conditions on \(C_\chi(r)\) using Eq. (9.3.6). For an ion-dipole-quadrupole mixture, the methods of Chapter 7 for obtaining the asymptotic behaviour of \(Q_\chi(r)\) at large \(r\) by considering the singularity at \(k = 0\) in Eq. (9.3.7) must be used.

For a tetrahedral quadrupolar fluid the only contribution to \(C_\chi(r)\) for \(r > R\) is from \(C_{\mu \nu}^{2,2,4}(r)\). But since

\[ \int_{-1}^1 ds \, s^{-\lambda} \int s \, \left( \begin{array}{c} 2 \\ \lambda \end{array} \right) P_\lambda (x) = 0 , \quad \lambda \geq 2 \quad (9.3.12) \]

we have from Eqs. (9.3.6b,c) and (9.3.11)

\[ C_\chi(r) = 0 , \quad r > R \quad (\chi = 0,1,2) \quad (9.3.13) \]

and so

\[ Q_\chi(r) = 0 , \quad r > R \quad (\chi = 0,1,2) . \quad (9.3.14) \]

For \(r < R\), we see from Eqs. (9.3.6a) and (9.3.11) that \(H_\chi(r)\) is of the form

\[ H_\chi(r) = H_4 \chi \, r^4 + H_2 \chi \, r^2 + H_0 \chi , \quad r < R \quad (\chi = 0,1,2) , \quad (9.3.15) \]

where the coefficients of this quartic polynomial are...
for $\chi = 0, 1, 2$, and we have to determine the value of the six moments of $h^{22\ell}_{\mu\nu}(r)$ in Eq. (9.3.16), these being independent of the value of $(\mu, \nu)$. To do so, we use the inverse transformation of Eq. (9.3.11).

\[
2\pi c^{22\ell}_{\mu\nu}(r) = \frac{22\ell + 1}{2\ell + 1} \sum_{|\chi| = 0} (-1)^{\chi} \left[ \begin{array}{c} 2 \\ 2 \\ \ell \\
\chi \\ -\chi \\ 0 \end{array} \right] \left[ -\frac{1}{r} C^\prime(r) + \frac{P^\prime_{\ell}(1)}{r^{\ell + 1/2}} C(r) \right] - \frac{1}{r^3} \int_0^R ds P_{\ell}(r) C(\chi(s)), \quad \ell = 0, 2, 4
\]  

(9.3.17)
Three other equations for the six moments can be obtained from the fact that \( Q_X(r) \) is continuous at \( r = R \), that is

\[
Q_X(R) = 0, \quad \chi = 0,1,2. \tag{9.3.22}
\]

The remaining task is to relate the constants \( H_{iX} (i = 0,2,4) \) to the integrals of \( C_X \) in Eqs. (9.3.19) - (9.3.21). We observe from Eq. (9.3.10) that since \( H_{iX}(r) \) is a quartic polynomial in \( r \) for \( r < R \), \( Q_X(r) \) must also be a quartic polynomial for \( r < R \). This polynomial can be specified in terms of its four moments

\[
M_{iX}(H_4X, H_2X, H_0X) \equiv \int_0^R ds \, s^i \, Q_X(s), \quad i = 0,1,2,3 \tag{9.3.23}
\]

which can in turn be related to the constants \( H_{iX} (i = 0,2,4) \) using Eqs. (9.3.10), (9.3.15). Finally using Eq. (9.3.9) we have the desired results

\[
\int_0^R ds \, C_X(s) = M_{0X} - \frac{\rho}{5} M_{0X}^2 \tag{9.3.24}
\]

and

\[
\int_0^R ds \, s^2 \, C_X(s) = M_{2X} + \frac{2\rho}{5} \left[ M_{1X}^2 - M_{0X} M_{2X} \right] \tag{9.3.25}
\]

for the right hand side of Eqs. (9.3.19) - (9.3.21).

The MSA solution of a hard sphere tetrahedral quadrupolar fluid has been reduced to solving a set of coupled algebraic equations, Eqs. (9.3.19) - (9.3.25) for the three constants \( H_{iX} (i = 0,2,4) \). For instance, the excess free energy per particle over the hard sphere reference system is
Also once $Q_x(r)$ is known the total correlation function can be determined from Eq. (9.3.9).

A comparison between the usefulness of the transformation given by Eq. (9.3.8), which was also used in Refs. 11 and 12, and in Chapters 7 and 8, and that used in Refs. 3 and 7 is given in Appendix 2.

9.4 THERMODYNAMIC PERTURBATION THEORY OF DIPOLE-TETRAHEDRAL QUADRUPOLE FLUIDS

The method of thermodynamic perturbation theory has enjoyed remarkable success in predicting the thermodynamic properties of dipolar hard sphere fluids [22]. For hard spheres with dipoles and linear quadrupoles the results are equally encouraging [16]. Therefore we can gain some insight into the relative importance of dipole-quadrupole and quadrupole-quadrupole interaction in a fluid of hard spheres with dipoles and tetrahedral quadrupoles. The application of thermodynamic perturbation theory to systems with tetrahedral quadrupoles is a straightforward extension of earlier work [23-25] which was restricted to axisymmetric molecules. We briefly outline the derivation.

Consider a system for which the Hamiltonian is of the form

$$H_x = H_0 + \lambda V,$$

(9.4.1)

where $H_0$ is the Hamiltonian of a suitably chosen reference, $V$ is the
perturbation potential and the coupling constant $\lambda$ provides a means by which we can keep track of the order of the perturbation. The excess free energy of the system at state $\lambda$ relative to the reference state $\lambda = 0$ is given by the identity

$$F^{\text{ex}}_\lambda = F_\lambda - F_0 = \int_0^\lambda d\lambda' \frac{\partial F(\lambda')}{\partial \lambda},$$

(9.4.2)

where

$$\beta F(\lambda) = -\ln \left\{ \frac{1}{N!} \int d\chi^N e^{-\beta H_0 - \lambda \beta V} \right\}$$

(9.4.3)

with $\chi = (r, \omega)$ denoting both the spatial and angular co-ordinates of the $N$ molecules. The result we want is obtained by setting $\lambda = 1$. Combining Eqs. (9.4.2) and (9.4.3) we obtain the general expansion

$$F^{\text{ex}}_\lambda = \lambda \langle V \rangle_0 + \frac{1}{2} \lambda^2 \beta [\langle V \rangle_0^2 - \langle V^2 \rangle_0]$$

$$+ \frac{1}{3} \lambda^3 \beta^2 \left\{ \langle V \rangle_0^3 - \frac{3}{2} \langle V \rangle_0 \langle V^2 \rangle_0 + \frac{1}{2} \langle V^3 \rangle_0 \right\} + O(\lambda^4),$$

(9.4.4)

where

$$\langle V^n \rangle_0 = \left\{ \frac{\int d\chi^N \langle V^n \rangle_0 e^{-\beta H_0}}{\int d\chi^N e^{-\beta H_0}} \right\}, \quad n = 1, 2, 3$$

(9.4.5)

is the expectation value taken with respect to the reference Hamiltonian.

If the intermolecular potentials in the reference system is independent of the molecular orientations and the perturbation potential $V$ is the pair-wise sum of multipolar potentials as in Eq. (9.2.1), we have

$$\langle V \rangle_0 = 0$$

(9.4.6)

because of the angular integrations. Consequently Eq. (9.4.4) simplifies to
For most reasonable values of the multipole moment Eq. (9.4.7) shows no signs of convergence. However, it has been found that a Padé approximant formed by treating the right hand side of Eq. (9.4.7) as the first two terms of a geometric series in $\lambda$

$$F_{\lambda}^{\text{ex}} = -\frac{1}{2} \lambda^2 \beta \langle V^2 \rangle_0 + \frac{1}{6} \lambda^3 \beta^2 \langle V^3 \rangle_0 + O(\lambda^4). \quad (9.4.7)$$

For most reasonable values of the multipole moment Eq. (9.4.7) shows no signs of convergence. However, it has been found that a Padé approximant formed by treating the right hand side of Eq. (9.4.7) as the first two terms of a geometric series in $\lambda$

$$F_{\lambda, \text{Padé}}^{\text{ex}} = \frac{-\frac{1}{2} \lambda^2 \beta \langle V^2 \rangle_0}{1 + \frac{1}{3} \lambda \beta \frac{\langle V^3 \rangle_0}{\langle V^2 \rangle_0}} \quad (9.4.8)$$

provides remarkably good descriptions of the properties of dipolar hard spheres [22] and dipole-linear quadrupolar hard sphere fluids [16]. This serendipitous construction is motivated by intuitions based upon a study of the MSA result for dipolar fluids and upon Onsager's observation that the ground state energy must be linear in the coupling constant [23-25].

The remaining task is to obtain expressions for the expectation values of the perturbation potential $\langle V^2 \rangle_0$ and $\langle V^3 \rangle_0$. For a fluid of hard spheres with embedded dipoles and linear quadrupoles the perturbation potential is of the form

$$V = \frac{1}{2} \sum_{i,j} U(i,j)$$

$$= \frac{1}{2} \sum_{i,j} \{U_{DD}(i,j) + U_{DQ_L}(i,j) + U_{QLQ_L}(i,j)\}, \quad (9.4.9)$$

where the dipole-dipole $U_{DD}$, dipole-quadrupole $U_{DQ_L}$ and quadrupole-quadrupole $U_{QLQ_L}$ potentials are given by Eqs. (9.2.7), (9.2.9) and (9.2.10). The arguments $i,j$ in Eq. (9.4.9) stands for the spatial and orientation co-ordinates $x_i$ and $x_j$. Combining Eqs. (9.4.7), (9.4.9)
and the expressions for the pair potentials we find

\[
\langle V^2 \rangle_0 = \frac{1}{2} \left( \frac{\rho}{8\pi^2} \right)^2 \int d^3 \rho \, g^{(2)}_0(1,2) \left\{ U_{DD}^2(1,2) + 2U_{DQL}^2(1,2) + U_{QLQ_L}^2(1,2) \right\}
\]

\[
= \left( \frac{N}{\beta^2} \right) \rho^* \left[ \frac{1}{3} \mu^* I_6 + \mu^* \beta I_8 + \frac{7}{5} \beta I_{10} \right] \quad (9.4.10)
\]

\[
\langle V^3 \rangle_0 = \frac{1}{4} \left( \frac{\rho}{8\pi^2} \right)^3 \int d^3 \rho \, g^{(3)}_0(1,2) \left\{ U_{DD}^3(1,2) U_{Q_LQ_L}(1,2) \right\}
\]

\[
+ \frac{3}{4} \left( \frac{\rho}{8\pi^2} \right)^3 \int d^3 \rho \, g^{(3)}_0(1,2,3) \left\{ U_{DD}(1,2) U_{DD}(2,3) U_{DD}(3,1) \right\}
\]

\[
+ \frac{3}{4} \left( \frac{\rho}{8\pi^2} \right)^3 \int d^3 \rho \, g^{(3)}_0(1,2) \left\{ U_{DQL}^3(1,2) U_{Q_LQ_L}(2,3) U_{Q_LD}(3,1) \right\}
\]

\[
+ \frac{3}{4} \left( \frac{\rho}{8\pi^2} \right)^3 \int d^3 \rho \, g^{(3)}_0(1,2) \left\{ U_{Q_LQ_L}(1,2) U_{Q_LQ_L}(2,3) U_{Q_LD}(3,1) \right\}
\]

\[
+ \frac{3}{4} \left( \frac{\rho}{8\pi^2} \right)^3 \int d^3 \rho \, g^{(3)}_0(1,2) \left\{ U_{Q_LQ_L}(1,2) U_{Q_LQ_L}(2,3) U_{Q_LD}(3,1) \right\}
\]

\[
= \left( \frac{6N}{5\beta^3} \right) \rho^* \left[ \frac{1}{54} \mu^* I_{DDD} + \frac{1}{480} \mu^* I_{DDQ} + \frac{\mu^* \beta I_{DQ} + \beta I_{QQQ} \right] \quad (9.4.11)
\]

In the above results \( g^{(2)}_0 \) and \( g^{(3)}_0 \) are, respectively, the pair and triplet distribution function of the reference system. We see that to order \( \lambda^3 \) there are two- and three-body contributions to \( \langle V^3 \rangle_0 \). The dimensionless quantities have the following definitions

\[
\rho^* = \rho R^3
\]

\[
\mu^* = \beta \mu^2 / R^3 \quad (9.4.12)
\]

\[
\beta^* = \beta \beta^2 / R^3
\]

where \( R \) is the hard sphere diameter and \( \rho \) is the number density. The quantities \( I_n \) and \( I_{\alpha\beta\gamma} \) are defined by
\[ I_n = 4\pi \int_0^\infty dr \, r^{2-n} \, g^{(2)}_0(r) \tag{9.4.13} \]

\[ I_{\alpha\beta\gamma} = \int dr \, ds \, g^{(3)}_0(r,s) \, W_{\alpha\beta\gamma}(r,s), \tag{9.4.14} \]

where \( W_{\alpha\beta\gamma} \) is the three-body potential function found in the theory of dispersion forces [26].

We now give the results for \( \langle V^2 \rangle_0 \) and \( \langle V^3 \rangle_0 \) for the case of hard spheres plus dipoles and tetrahedral quadrupoles for which the dipole-quadrupole \( U_{DQ_T} \) and quadrupole-quadrupole \( U_{QQ_T} \) potentials are given by Eqs. (9.2.13) - (9.2.17). Using these expressions in Eq. (9.4.7) and (9.4.9) we get

\[ \langle V^2 \rangle_0 = \frac{1}{2} \left( \frac{\rho}{8\pi^2} \right)^2 \int \ld d2 \, g^{(2)}_0(1,2) \left\{ U_{DD}^2(1,2) + 2U_{DQ_T}^2(1,2) + U_{QQ_T}^2(1,2) \right\} \]

\[ = \left( \frac{2N}{3\Omega^2} \right) \rho^* \left( \frac{1}{2} \mu^* \theta_0 + 2\mu^* Q^* \theta_0 + \frac{56}{15} \mu^* \theta_0 \right) \left( \frac{1}{2} \mu^* \theta_0 + 2\mu^* Q^* \theta_0 + \frac{56}{15} \mu^* \theta_0 \right) \tag{9.4.15} \]

and

\[ \langle V^3 \rangle_0 = \frac{3}{4} \left( \frac{\rho}{8\pi^2} \right)^3 \int \ld d2d3 \, g^{(3)}_0(1,2,3) \left\{ U_{DD}^2(1,2) U_{DD}^2(2,3) U_{DD}^2(3,1) \right\} \]

\[ + 3U_{DD}^2(1,2) U_{DQ_T}(2,3) U_{QQ_T}(3,1) + 3U_{DQ_T}(1,2) U_{QQ_T}(2,3) U_{QQ_T}(3,1) \]

\[ + U_{QQ_T}(1,2) U_{QQ_T}(2,3) U_{QQ_T}(3,1) \}

\[ = \left( \frac{6N}{8\Omega^3} \right) \rho^* \left( \frac{1}{54} \mu^* \theta_0 \left( \frac{1}{360} \theta_0 + \frac{1}{360} \theta_0 \right) + \frac{1}{2700} \theta_0 \right) \left( \frac{1}{54} \mu^* \theta_0 \left( \frac{1}{360} \theta_0 + \frac{1}{360} \theta_0 \right) + \frac{1}{2700} \theta_0 \right) \tag{9.4.16} \]

On comparing Eqs. (9.4.11) and (9.4.16) we see that only three-body terms contribute to \( \langle V^3 \rangle_0 \) for the dipole-tetrahedral quadrupole system.

To obtain numerical results we must specify the reference system.

A fluid of hard spheres at the same density and diameter is the obvious candidate. For the hard sphere reference system, the integrals \( I_n \) and \( I_{\alpha\beta\gamma} \) are only functions of the density and simple
accurate representations of these functions have been compiled [25].

We now proceed to study two cases: a pure tetrahedral quadrupolar fluid and a dipole-tetrahedral quadrupolar fluid.

Consider first a pure tetrahedral fluid for which the results from thermodynamic perturbation theory can be obtained by setting \( \mu^* = 0 \) in Eqs. (9.4.15) and (9.4.16). In Fig. 1 we compare the excess free energy, \( F^\text{ex} \), obtained from the series expansion, including terms of order \( \lambda^3 \), Eq. (9.4.7) with that obtained from using the Padé approximant, \( F^\text{ex}_{\text{Padé}} \), Eq. (9.4.8). The close agreement between the two results in the range \( 0 < \Theta^* \tau^2 < 1 \) indicates that in this regime terms of order \( \lambda^3 \) and higher are relatively unimportant. We note that \( \Theta^* \tau^2 \) for water at room temperature is \( \approx 0.62 \) if we use \( R = 3 \) Å, and \( \approx 1.05 \) for \( R = 2.7 \) Å. In Fig. 2 we compare the internal energy obtained from the MSA, Eq. (9.3.26), with that obtained from the perturbation theory by differentiating the Padé free energy, \( F^\text{ex}_{\text{Padé}} \), Eq. (9.4.8). The disagreement between the two theories is not unexpected since the MSA is essentially equivalent to replacing the distribution functions \( g_0^{(2)} \) and \( g_0^{(3)} \) required in the perturbation theory by unit step functions [24]. It is interesting to note that the two-body term of order \( (\lambda^3 \Theta^* \tau^6) \) in \( \langle V^3 \rangle_0 \) which is omitted in the MSA, turns out to be zero for tetrahedral quadrupoles. In the MSA the internal energy per unit volume is only a function of the product \( (\rho^* \Theta^* \tau^2) \). This is not true in general. In Fig. 3 we compare the universal curve from the MSA with the Padé internal energy at different densities. The Padé and MSA results coincide only for \( \rho^* \ll 1 \).

We now turn to the case of a dipole-tetrahedral quadrupolar hard sphere fluid. We have chosen for our input data
Fig. 1: Excess free energy per molecule of a tetrahedral quadrupolar hard sphere fluid at $\rho^* = 0.8$ from perturbation theory. (A) $F_{\text{ex}}^{\text{Padé}}$ (left hand scale), (B) the ratio $\left( F_{\text{ex}}^{\text{series}} / F_{\text{Padé}} \right)$ (right hand scale).
Fig. 2: Excess internal energy per molecule of a tetrahedral quadrupolar hard sphere fluid at $\rho^* = 0.8$. (A) Padé version of perturbation theory, (B) MSA.
Fig. 3: Excess internal energy per unit volume of a tetrahedral quadrupolar hard sphere fluid. Padé version of perturbation theory at (A) $\rho^* = 0.8$, (B) 0.5, (C) MSA-independent of $\rho^*$. 
\[ \mu = 1.84 \times 10^{-18} \text{ esu-cm} \]
\[ \Theta_T = 2.5 \times 10^{-26} \text{ esu-cm}^2 \]  
(9.4.17)

\[ R = 3 \text{ Å} \]

which to a good approximation, are the dipole and tetrahedral quadrupole moments of water. Unlike the case of pure tetrahedral quadrupoles, there is considerable difference between the Padé (Eq. (9.4.8)) and series expansion (Eq. (9.4.7)) of the free energy (Fig. 4). It is obvious that this is due to the presence of the dipolar contribution. Hereafter we shall use the Padé version of the perturbation theory because it gives quite reasonable agreement with Monte Carlo results for the dipole-linear quadrupole hard sphere fluid [16]. In Figs. 5-7 we show the excess free energy, excess internal energy and the excess compressibility factor \((\beta p^\text{ex}/\rho)\) as a function of temperature. The latter two properties are obtained by appropriate differentiations of the Padé free energy. By comparison with the curves obtained by setting \(u^* = 0\) or \(\Theta_T^* = 0\) we can see that the dipole-quadrupole interaction gives an important contribution to the thermodynamic properties of such fluids. We note that at \(\rho^* = 0.8\) \((\beta p^\text{ex}/\rho)\) for water-like values of \(u^*\) and \(\Theta_T^*\) is -6.6 at room temperature. This almost cancels the reference value \((\beta p_0/\rho) = 7.74\) for a hard sphere system and gives a fairly low pressure at room temperature.

With these results we conclude our investigation into tetrahedral quadrupolar effects on the dipolar hard sphere fluid. The tetrahedral quadrupole appears to be a useful way of representing the quadrupole tensor of water, in that the Ornstein-Zernike equation (in the MSA, LHNC or QHNC theories) can be obtained by trivial changes to existing
Fig. 4: A comparison of the excess free energy per molecule for a dipole-tetrahedral quadrupolar hard sphere fluid at $\rho^* = 0.8$ (see Eq. (9.4.17) for data) obtained from the series and Padé versions of the perturbation theory.
Fig. 5: Excess free energy per molecule of a dipole-tetrahedral quadrupolar hard sphere fluid at \( \rho^* = 0.8 \) (see Eq. (9.4.17) for data). Results for a pure tetrahedral quadrupolar fluid \( (\Theta^* = 0) \) and a pure dipolar fluid \( (\Theta^*_T = 0) \) are also shown.
Fig. 6: Excess internal energy per molecule of a hard sphere fluid at $\rho^* = 0.8$ with (A) dipole and tetrahedral quadrupole moments, (B) only a dipole moment and (C) only a tetrahedral quadrupole moment — see Eq. (9.4.17) for data.
Fig. 7: Excess compressibility factor for a dipole-tetrahedral quadrupolar hard sphere fluid at $\rho^* = 0.8$ (see Eq. (9.4.17) for data). Results for a pure dipolar fluid ($\Theta^* = 0$) and a pure tetrahedral quadrupolar fluid ($\mu^* = 0$) are also shown.
programs which have been designed to study similar systems with linear quadrupoles. We have obtained an analytic solution of a pure tetrahedral quadrupolar fluid in the MSA and it is clear that, although the same treatment could be applied to an ion-dipole-quadrupole mixture, the algebraic effort that has to be expended probably far outweighs the accuracy which the MSA will return. Similarly, the results of Chapters 7 and 8 are only perspicuous because of the particularly simple form for $\varepsilon$ in the MSA dipolar fluid. Such a feature will be lost when quadrupolar effects are included. Our studies using thermodynamic perturbation theory suggest that dipole-quadrupole interactions in this water-like hard sphere dipole-tetrahedral quadrupolar fluid can be far from negligible. It seems that the effects of such interactions on the structure of the double layer will require extensive numerical computations — either using integral equations or perturbation theory.

APPENDIX 1

PROPERTIES OF 3-j, 6-j SYMBOLS AND $D_{mn}^{\ell}(\omega)$

A. The Wigner 3-j and 6-j symbols are discussed and tabulated in Rotenberg et al. [27]. The useful properties of the 3-j symbol are the following:

\[(1) \quad \begin{vmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{vmatrix} = 0 \quad \text{if } m_1 > j_1 \text{ for any } i.\quad (9.A.1.1)\]

This condition restricts the sum on the right hand side of Eq. (9.1.13), e.g. for $\chi = 2$, only terms with $(m,n) = (2,2)$ appear.
Thus the sum over $\lambda'$ in Eq. (9.1.5) is only symbolic.

This implies

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 0 \text{ unless } m_1 + m_2 + m_3 = 0.$$  (9.A.1.2)

unless $j_1 + j_2 + j_3$ is even which helps to restrict the range of the sum on the right hand side of Eq. (9.1.10).

(4) Orthogonality conditions

$$\sum_{j_3 m_3} (2j_3 + 1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3' \end{pmatrix} = \delta_{m_1 m_1'} \delta_{m_2 m_2'}.$$  (9.A.1.8)

and

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \frac{1}{2j_3 + 1} \delta_{j_3 j_3'} \delta_{m_3 m_3'}.$$  (9.A.1.9)

These are used in the derivation of Eq. (9.1.14) from Eq. (9.1.12).
B. The 6-j symbols have the following properties:

1. \( \{ j_1 \ j_2 \ j_3 \ \mid \ \begin{array}{ll} m_1 & m_2 \\ m_3 & \end{array} \} \) is invariant under the interchange of columns and under the interchange of any two numbers in the bottom row with the corresponding two numbers in the top row. This property is used in the derivation of Eqs. (9.1.10) and (9.1.14).

2. \( \{ j_1 \ j_2 \ j_3 \ \mid \ \begin{array}{ll} m_1 & m_2 \\ m_3 & \end{array} \} = 0 \) unless the triplets \( (j_1 j_2 j_3) \), \( (j_1 j_2 m_3) \), \( (j_1 m_2 j_3) \), \( (m_1 j_2 j_3) \) all satisfy the triangle inequality (Eq. (9.A.1.7)). This completes the restriction of the sum in Eq. (9.1.10).

3. \( \sum (-1)^S \begin{pmatrix} j_1 & \ell_2 & \ell_3 \\ m_1 & n_2 & -n_3 \end{pmatrix} \begin{pmatrix} \ell_1 & j_2 & j_3 \\ -n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \),

where \( S = \ell_1 + \ell_2 + \ell_3 + n_1 + n_2 + n_3 \). This equation is used in the derivation of Eqs. (9.1.10) and (9.1.14).

C. The generalized spherical harmonic \( D^\lambda_{nm}(\omega) \) can be written as

\[
D^\lambda_{nm}(\omega) = e^{i \gamma} \lambda d^\lambda_{nm}(\cos \theta) e^{i m \phi},
\]

where we have used the Euler angles \((\theta, \phi, \gamma)\) as given in Ref. 19. Eq. (9.A.1.11) denotes the index-to-angle convention of Ref. 19. Edmonds [18] has a different convention but this makes little practical difference. \( d^\lambda_{nm}(\cos \theta) \) can be written as a Jacobi polynomial [18] but the only properties we need are

1. \( D^\lambda_{nm}(\omega) = \left( \frac{4\pi}{2\lambda + 1} \right)^{1/2} \frac{\lambda}{m} Y^\lambda_m(\theta, \phi) \)

\[
= i |m| \left[ \frac{\lambda - |m|}{\lambda + |m|} \right]^{1/2} \frac{\lambda}{m} Y^\lambda_m(\cos \theta) e^{i m \phi}.
\]
where $p^m_\lambda(\cos \theta)$ is an associated Legendre function and $Y^m_\lambda(\theta, \phi)$ is a spherical harmonic.

\begin{equation}
(2) \quad D^{\ell *}_{nm}(\omega) = (-1)^{n-m} D^{\ell}_{-n,-m}(\omega)
\end{equation}

\begin{equation}
(3) \quad D^\ell_{mn}(\omega) D^{\ell^*}_{m_1n_1}(\omega) = \sum_{L,M} (2L+1) D^{L^*}_{MN}(\omega) \begin{pmatrix} \ell & \ell^* & L \\ m & m_1 & M \\ n & n_1 & N \end{pmatrix}
\end{equation}

This equation is needed for the derivation of Eqs. (9.1.10) and (9.4.10), (9.4.11), (9.4.15) and (9.4.16).

\begin{equation}
(4) \quad \sum_{m_1 n_1} D^\ell_{mn}(\omega) D^{\ell^*}_{m_1n_1}(\omega) \begin{pmatrix} \ell & \ell_1 & L \\ m & m_1 & M \\ n & n_1 & N \end{pmatrix} = \frac{\delta_{LL'}}{2L+1} D^{L'}_{MN}(\omega)
\end{equation}

\begin{equation}
(5) \quad \frac{2L+1}{8\pi^2} \int d\omega D^\ell_{mn}(\omega) D^{\ell^*}_{m_1n_1}(\omega) = \delta_{mn_1} \delta_{m_1n_1} \delta_{\ell\ell^*}
\end{equation}

which is used in the derivation of Eqs. (9.1.10), (9.1.11), and (9.4.10).

\begin{equation}
(6) \quad \frac{1}{8\pi^2} \int d\omega D^{\ell^*}_{m_1n_1}(\omega) D^{\ell^*}_{m_2n_2}(\omega) D^{\ell^*}_{m_3n_3}(\omega) = \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{pmatrix}
\end{equation}

which is used in the derivation of Eqs. (9.4.10), (9.4.11), (9.4.15) and (9.4.16).

APPENDIX 2

TRANSFORMATIONS USED IN SECTION 9.3

The various transformations used in this chapter and earlier works [2-4,7] are summarized in Fig. 8 and the relation between our notation and that of Blum [4] is shown in Table 1.
Fig. 8: Transformation scheme for the coefficient functions in the Ornstein-Zernike equation – indices \((\mu, \nu)\) have been suppressed.
Table 1

Notational difference between this work and Blum [4]

<table>
<thead>
<tr>
<th>Notation of this Chapter</th>
<th>Notation of Ref. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{mn}(r)$</td>
<td>$h_{mn}(r)$</td>
</tr>
<tr>
<td>$h_{mn}^*(k)$</td>
<td>$h_{mn}^*(k)$</td>
</tr>
<tr>
<td>$c_{mn}(r)$</td>
<td>$c_{mn}(r)$</td>
</tr>
<tr>
<td>$c_{mn}^*(k)$</td>
<td>$c_{mn}^*(k)$</td>
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<td>$h_{mn}(r)$</td>
<td>$h_{mn}(r)$</td>
</tr>
<tr>
<td>$h_{mn}^e(r) + h_{mn}^o(r)$</td>
<td>$h_{mn}^e(r) + h_{mn}^o(r)$</td>
</tr>
</tbody>
</table>

From Table 1, we observe the following differences in notation:

- $h_{mn}(r)$ and $h_{mn}(r)$ are equivalent.
- $h_{mn}^*(k)$ and $h_{mn}^*(k)$ are equivalent.
- $c_{mn}(r)$ and $c_{mn}(r)$ are equivalent.
- $c_{mn}^*(k)$ and $c_{mn}^*(k)$ are equivalent.
- $h_{mn}(r)$ and $h_{mn}(r)$ are equivalent.
- $h_{mn}(r)$ and $h_{mn}(r)$ are equivalent.
- $h_{mn}^e(r) + h_{mn}^o(r)$ and $h_{mn}^e(r) + h_{mn}^o(r)$ are equivalent.

These differences highlight the notational choices made by the authors of this work and Blum [4].
We start with the real coefficient functions \((f = h \text{ or } c)\) from Eq. (9.1.4). On Fourier-transforming in three dimensions we get the transform pair \((\mu \text{ and } \nu \text{ are suppressed in this appendix})\)

\[
\tilde{f}^{mn\lambda}(r) = \left(\frac{-i}{2\pi^2}\right) \int_0^\infty dk \, k^2 \, j_{\lambda}(kr) \, \tilde{f}^{mn\lambda}(k) \\
\tilde{f}^{mn\lambda}(k) = 4\pi i {\lambda} \int_0^\infty dr \, r^2 \, j_{\lambda}(kr) \, f^{mn\lambda}(r)
\]

(9.1.2.1)

We then take the linear combination of \(\tilde{f}^{mn\lambda}(k)\) which simplifies the matrix structure of the Ornstein-Zernike equation

\[
\tilde{f}^{mn\lambda}(k) = \sum_{\chi} \left(\frac{-1}{2}\right)^{\chi} \begin{pmatrix} m & n \\ \chi & -\chi & 0 \end{pmatrix} \tilde{f}^{mn\lambda}(k)
\]

(9.1.2.2)

Following Blum [4], we could then transform back to real space via the transform

\[
\hat{f}^{mn\lambda}(r) = \frac{1}{2\pi^2} \int_0^\infty dk \, k^2 \, \left\{ \begin{array}{l} j_{0}(kr) \\ -ij_{1}(kr) \end{array} \right\} \tilde{f}^{mn\lambda}(k)
\]

\[
\hat{f}^{mn\lambda}(k) = 4\pi \int_0^\infty dr \, r^2 \, \left\{ \begin{array}{l} j_{0}(kr) \\ ij_{1}(kr) \end{array} \right\} \tilde{f}^{mn\lambda}(r)
\]

(9.1.2.3)

where \(\lambda\) is \{even, odd\}. The chief disadvantage of this method is the need to use different transforms depending on the parity of \(\lambda\). For a dipolar fluid, this complication does not arise and Wertheim [7] introduced \(\hat{f}^{110}(r)\) and \(\hat{f}^{112}(r)\) directly, without passing through Fourier space. (His use of the carat is the origin of our notation for these functions.) They are related to the original functions by
\[ f^{mn\ell}(r) = \int_0^\infty ds \ s^2 \ f^{mn\ell}(s) \ \theta_\ell(s,r) \]  
(9.A.2.4)

\[ f^{mn\ell}(r) = \int_0^\infty ds \ s^2 \ \hat{f}^{mn\ell}(s) \ \theta_\ell(r,s) \ , \]

where

\[ \theta_\ell(r,s) = \frac{2}{\pi} \int_0^\infty ds \ k^2 \ j_\ell(kr) \left\{ \frac{j_0(ks)}{i j_1(ks)} \right\} \]

for \( \ell \{\text{even}\} \). A general expression for \( \theta_\ell(r,s) \) is given in Ref. 4 Eqs. (2.13) - (2.17) and explicit expressions for \( \ell = 2,4 \) in Ref. 3 Eqs. (3.13) and (3.14).

An alternative route is to follow Baxter [21] and take a one-dimensional Fourier transform back to real space

\[ f^{mn\ell}(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \ e^{-ikr} \ f^{mn\ell}(k) \]  
(9.A.2.5)

\[ \hat{f}^{mn\ell}(k) = \int_{-\infty}^{\infty} dr \ e^{ikr} \ f^{mn\ell}(r) \ . \]

The advantage of this method is that the distinction between even and odd \( \ell \) does not arise. These new functions are related to the original ones by

\[ f^{mn\ell}(r) = 2\pi \int_0^r ds \ s \ f^{mn\ell}(s) \ P_\ell\left(\frac{r}{s}\right) \]

\[ 2\pi r f^{mn\ell}(r) = -\frac{d}{dr} f^{mn\ell}(r) + \frac{P_\ell(1)}{r} f^{mn\ell}(r) \]  
(9.A.2.6)

\[ -\frac{1}{r^2} \int_0^r ds \ P_\ell\left(\frac{s}{r}\right) f^{mn\ell}(s) \ , \]

where \( P_\ell(x) \) is a Legendre polynomial.

The two sets of functions \( F, \hat{f} \) are in turn related by
\[
\hat{f}_{mn\lambda}(r) = 2\pi \int_{|r|}^{\infty} ds \left\{ \frac{s}{r} \right\} \hat{f}_{mn\lambda}(s)
\]

\[
2\pi r \hat{f}_{mn\lambda}(r) = \begin{cases} 
-\frac{d}{dr} & \text{for } \lambda \in \{\text{even}\} \\
\frac{1}{r} - \frac{d}{dr} & \text{for } \lambda \in \{\text{odd}\}
\end{cases}
\]

which just follows from Eqs. (9.A.2.3) and (9.A.2.5).

For analytical work (viz. the MSA), both sets of functions \(F\) and \(\hat{f}\) have the necessary properties for solution by Baxter's method [21] (i.e. we could have obtained the results of Section 9.3 by following Wertheim's solution for dipoles [7]) and since the transform (9.A.2.6) does not depend on \(\lambda\), it seems to be the preferred method. For numerical work, however (e.g. LHNC, QHNC), the transform from \(\hat{f}_{mn\lambda}(r)\) back to \(f_{mn\lambda}(r)\) involves only integrals whereas the transform from \(f_{mn\lambda}(r)\) to \(\hat{f}_{mn\lambda}(r)\) involves a differentiation. This seems to make the set \(\hat{f}_{mn\lambda}(r)\) preferable for numerical work.

REFERENCES


