TOPICS IN THE STATISTICAL THEORY OF LIQUIDS

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This dissertation is an account of work carried out in the Department of Applied Mathematics, Research School of Physical Sciences, Australian National University and the Mathematics Institute, Odense University, Denmark, during the period February 1974 and April 1978 under the supervision of professor John W. Perram.

None of the material presented here has been submitted to any other institute of learning for any degree.
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The first chapter of this thesis is a discussion of the dielectric saturation effect in the vicinity of a charged metal interface immersed in an aqueous electrolyte medium. This effect is important in the study of electrode kinetics and the thermodynamics of adsorption at interfaces. The usual discontinuous two phase model of the electric double layer introduces singularities in the image potential of an ion within the double layer. These singularities may be overcome by assuming a smoothly varying dielectric profile across the entire double layer. The extent to which such profiles can be brought about through dielectric saturation of the solvent is investigated. A general statistical mechanical expression for the dependence of the dielectric constant of a dipolar liquid on field strengths is given and applied to the case of the aqueous electrolyte. Through a study of the Poisson-Boltzmann equation dielectric profiles are then calculated as a function of distance from the interface.

Chapter 2 studies the statistical mechanics of simple liquids. It is a discussion of the role of correlation functions and the various integral equation approximation theories for them. Solutions to the Ornstein-Zernike equation using both the Percus-Yevick (PY) and Mean Spherical Approximation (MSA) closures are given. In particular radial distribution functions for the MSA applied to a 1-1 restricted primitive model electrolyte are obtained. These functions have not been presented in detail before.
The third and final chapter is concerned with perturbation theory for the radial distribution function of simple liquids. The usual method of using the hard sphere reference system to obtain accurate radial distributions is surveyed and the possibility of introducing attractive forces into the reference system is then discussed. This was done using the "adhesive" hard sphere system in which the Boltzmann factor has a delta function at the particle diameter. Further investigations were made on a parametric "soft core" fluid. The solution of the PY equation for this is known accurately. This system provides a new way of obtaining accurate radial distribution functions for systems in which the interparticle potential contains soft core repulsions.
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CHAPTER 1

THE DIELECTRIC SATURATION EFFECT IN A DIFFUSE DOUBLE LAYER
1.1 Introduction

Electric Field in Vacuo

The concept of an electric field dates to the time of Coulomb [1]. He found that the force experienced by two charges, say \( q \) and \( q' \), was inversely proportional to the square of the distance between them.

This experimentally determined law may be written in vacuo as

\[
\mathbf{F} = \frac{qq'}{r^2} \hat{r}
\]

where \( \hat{r} \) is a unit vector along the line joining the two charges.

The electric field is now defined by

\[
\mathbf{E} = \lim_{q' \to 0} \frac{\mathbf{F}}{q'}
\]

and is the effect of the charge \( q \) on the environment of a test charge \( q' \).

Thus according to Coulomb's law the field \( \mathbf{E} \) at a distance \( r \) from a charge \( q \), due to the charge \( q \), is [2]

\[
\mathbf{E} = \frac{q}{r^2} \hat{r}
\]

or

\[
\mathbf{E} = -qV\left(\frac{1}{r}\right) \quad (1.1)
\]

where \( V \) is the gradient operator.

From equation (1.1) the electric flux through any surface \( S \) enclosing \( q \) is given by [2], [3]

\[
\oint_S \mathbf{E} \cdot d\mathbf{s} = 4\pi q
\]

This result may be extended to include any number of charges within some volume \( V \) enclosed by the surface \( S \). By the superposition principle the field at a point \( \mathbf{r} \) is the sum of the separate fields due to the individual point charges. Thus if \( \mathbf{Q} \)
is the total charge then
\[ \int_S \mathbf{E} \cdot d\mathbf{S} = 4\pi Q \]

The application of Gauss's Divergence theorem then yields
\[ \int_V \nabla \cdot \mathbf{E} \, d^3 \mathbf{r} = 4\pi Q \]

Replacing \( Q \) by an integral over the spatial charge density \( \rho(\mathbf{r}) \) then yields
\[ \nabla \cdot \mathbf{E} = 4\pi \rho(\mathbf{r}) \] (1.2)

As a further consequence of the superposition principle and equation (1.1) we have
\[ \nabla \times \mathbf{E} = 0 \] (1.3)

It follows at once that \( \mathbf{E} \) may be written as the gradient of a scalar potential function. Thus an electrostatic potential, \( \phi \), may be defined by
\[ \mathbf{E} = - \nabla \phi \]

Substituting into equation (1.2) now yields Poisson's equation
\[ \nabla \cdot (\nabla \phi) = \nabla^2 \phi = -4\pi \rho(\mathbf{r}) \] (1.4)

Equation (1.4) may be taken as a statement of the fundamental problem of electrostatics. That is, for given boundary conditions on \( \phi \) and a specified charge distribution \( \rho(\mathbf{r}) \), what is the solution \( \phi(\mathbf{r}) \) of Poisson's equation.

Dielectric Media: Polarization and the Dielectric Constant.

When the charges are no longer in free space but are immersed in a material medium, the basic equations governing the electric field and electrostatic potential are modified by the nature of
that medium [4], [5]. The source of the charge density in equation (1.4) can be separated into two parts. First, there is the true, movable charge \( \rho \) manifesting itself on the surface of say a piece of conducting material suspended between the plates of a charged capacitor and second, there is the so called polarization charge \( \rho_p \) normally assumed to be caused by dipoles present in the medium.

The Poisson source equation now becomes

\[
\nabla^2 \Phi = -\nabla \cdot E = -4\pi (\rho + \rho_p) \quad (1.5)
\]

where

\[
\rho_p = -\nabla \cdot P \quad (1.6)
\]

and \( P \) is the dipole moment per unit volume, that is, the polarization.

Using equation (1.6) we may rewrite equation (1.5) as

\[
\nabla \cdot (E + 4\pi P) = 4\pi \rho \quad (1.7)
\]

Thus when considering the electric field as calculated from the Maxwell source equation a displacement of the field due to polarization of the medium must be taken into account. This new field \( \vec{D} \), called the displacement field or displacement vector represents a partial field whose sources are the true, movable charges.

Thus

\[
\nabla \cdot \vec{D} = 4\pi \rho \quad (1.8)
\]

where

\[
\vec{D} = E + 4\pi \vec{P} \quad (1.9)
\]

To obtain the vector \( \vec{D} \) the manner in which \( \vec{P} \) depends on \( E \) must be known. For most substances it is assumed that \( \vec{P} \) is directly proportional to \( E \) and thus it follows from equation (1.9) that \( \vec{D} \) is porportional to \( E \).
We may then write

\[ D = \varepsilon S E \]  

(1.10)

where the constant of proportionality \( \varepsilon_S \) is called the dielectric constant.

The electric properties of most material or dielectric media are usually described in terms of their dielectric constants.

Rearranging (1.9) using (1.10) we get

\[ \varepsilon_S^{-1} = 4\pi |P| / |E| \]  

(1.11)

in an isotropic medium where \( P \) is parallel to \( E \).

From equation (1.11) we see that the dielectric constant is expressed in terms of the polarization which in turn depends on the microscopic response of the material to an electric field. Equation (1.11) provides the link between any microscopic theory of structure or intermolecular interactions and observed electrical properties of matter.

In the next section an expression for \( P \) and thus \( \varepsilon_S \) is derived in the case where the medium is a liquid composed of dipolar molecules. Having calculated a general expression for \( \varepsilon_S \) it is then applied to water using the tetrahedral model for the H\(_2\)O nearest neighbour structure. Finally, in sections (1.3) and (1.4), this approximate expression is applied to the problem of dielectric saturation near a metallic interface immersed in an aqueous electrolyte solution through a study of the Poisson-Boltzmann equation.
1.2 The Dielectric Constant in Dipolar Liquids

We consider a fluid medium the molecules of which have a permanent dipole moment \( \mu \). The usual method of calculating the polarization \( \mathcal{P} \) due to an external field \( \mathcal{E} \) is to select a spherical region \( S \) containing \( N \) molecules which are treated according to the laws of statistical mechanics and then to consider the remaining part of the fluid as a continuum dielectric medium characterized by a bulk dielectric constant \( \varepsilon \). \([6],[7]\).

To account for polarization due to electron configurations within the sphere \( S \), the dipoles are assumed to be embedded in a medium with dielectric constant \( n^2 \) where \( n \) is the optical refractive index. \([8]\)

The polarization of the sphere will now be the total average moment per unit volume due to the dipoles and induced by \( \mathcal{E} \), denoted by

\[
|\mathcal{P}| = \frac{M_E}{V}
\]

The dielectric constant \( \varepsilon \) is then related to \( M_E \) by the equation

\[
\varepsilon - n^2 = 4\pi \frac{M_E}{EV}
\]

The applied field acting on the spherical region will be the field \( \mathcal{G} \) due to a cavity with dielectric constant \( n^2 \) in a uniform medium of dielectric constant \( \varepsilon \). This cavity field is given by \([4],[5],[9]\)

\[
\mathcal{G} = \frac{3\varepsilon}{2\varepsilon+n^2} \mathcal{E}
\]

For the sake of brevity this may be approximated by

\[
\mathcal{G} = \frac{3}{2} \mathcal{E}
\]

since for most dipolar liquids and in the particular case of water discussed in the next section \( \varepsilon \gg n^2 \).
The potential energy of any configuration of the dipoles in S is given by
\[ P.E. = U_N - \tilde{M} \cdot \tilde{G} \]
where \( U_N \) is the potential energy due to the intermolecular forces for the whole dielectric medium and \( \tilde{M} \) is the total electric moment of the sphere S.

\[ \tilde{M} = \sum_{i=1}^{N} \mu_i \]

Hence, the average component of the permanent dipole moment of any dipole \( i \) in the direction of \( \hat{E} \) now may be written
\[ \overline{\mu_i} = \frac{\int \cdots \int (\mu_i \cdot \hat{e}) \exp[-\beta (U_N - \tilde{M} \cdot \tilde{G})] \, dx_1 \cdots dx_N}{\int \cdots \int \exp[-\beta (U_N - \tilde{M} \cdot \tilde{G})] \, dx_1 \cdots dx_N} \]
(1.12)

where \( \hat{e} \) is a unit vector in the field direction, \( x_i \) is the coordinate vector of the \( i \)'th dipole and \( \beta = 1/kT \) where \( k \) is Boltzmann's constant and \( T \) is the absolute temperature.

The integrands in equation (1.12) may be expanded and written in the form [8]
\[ \overline{\mu_i} = \frac{n_0 (3E/2kT)^n I(x: (\mu_i \cdot \hat{e}) (\tilde{M} \cdot \hat{e})^n)}{n!} \]
(1.13)

where \( I(x:f) \) is defined by
\[ I(x:f) = \int \cdots \int f \exp[-\beta U_N] \, dx_1 \cdots dx_N \]
(1.14)

To obtain the total contribution \( \overline{\mu_{E_i}} \) from the dipole \( i \) we must now average over all directions of the field. Thus from equation (1.13)
\[ \overline{\mu_{E_i}} = \frac{n_0 (3E/2kT)^{2n+1} I(x: (\mu_i \cdot \tilde{M})^{2n+1})}{n! (2n+1)! (2n+3)!} \]

Evaluation of the integrals in equation (1.14) may now be
carried out according to the method of Kirkwood [9]. We select a dipole with coordinates \( \mathbf{x}_i \) and first perform the integration of the other \( N-1 \) coordinate sets after which the \( dx_i \) integration is carried out. Thus we may write

\[
\mu_{E_i} = \frac{\sum_{n=0}^{\infty} (3E/2kT)^{2n+1}(\mathbf{\mu}_i \cdot A_i[M^{2n+1}])/(2n+1)!(2n+3)}{\sum_{n=0}^{\infty} (3E/2kT)^{2n} A_i[M^{2n}]/(2n+1)!}
\]

where

\[
A_i[f] = \frac{\int \cdots \int \exp[-\beta U_N] dx_i, \ldots, dx_{i-1} dx_{i+1} \ldots dx_N}{\int \cdots \int \exp[-\beta U_N] dx_i, \ldots, dx_{i-1} dx_{i+1} \ldots dx_N}
\]

The quantity \( A_i[f] \) is the average of \( f \) over the \( \mathbf{x}_j \), \( j \neq i \) for given values of \( \mathbf{x}_i \). In a liquid this average will depend on \( \mathbf{x}_i \) only in a thin boundary region \( V_B \) of the volume \( V \) of \( S \). If the volume \( V \) is assumed to be sufficiently large the ratio \( V_B/V \) can be made arbitrarily small. This means that the suffix \( i \) may be excluded in equation (1.15). The dielectric constant then may be written using equation (1.11) as

\[
\varepsilon = n^2 + \frac{4\pi N \sum_{n=0}^{\infty} (3E/2kT)^{2n+1}(\mathbf{\mu} \cdot A[M^{2n+1}])/(2n+1)!(2n+3)}{EV \sum_{n=0}^{\infty} (3E/2kT)^{2n} A[M^{2n}]/(2n+1)!}
\]

Equation (1.17) is a general expression relating \( \varepsilon \) to the strength of the external field and the strength of the permanent dipole moment of the molecules comprising the liquid. In general its exact evaluation is too difficult and in order to reduce its complexity further assumptions regarding the detailed structure of the liquid are needed.

The Onsager Equation

If we assume that the effect of the short range intermolecular interactions is negligible, then the surface of the sphere \( S \) may be reduced to the surface of a dipolar molecule giving \( M = \mathbf{\mu} \). The integrals \( A[.] \) of equation (1.17), (1.16) then may be
approximated by
\[ A[M^{2n}] = \mu^{2n} \; ; \; A[M^{2n+1}] = \mu^{2n+1} \]  
(1.18)

Substituting into equation (1.17) then yields
\[ \varepsilon = n^2 + \frac{4\pi n \mu}{\varepsilon \nu} \L (3\varepsilon u / 2kT) \]  
(1.19)

where \( \L[x] = \coth x - 1/x \)
is the Langevin function.

Equation (1.19) is the well known Onsager formula which is valid only for weak field strengths and neglects the effects of short range interactions. [10].

**The Dielectric Constant of Water**

In the case of water there is a high degree of short range structure due to the effects of hydrogen bonding. The interaction of a dipole with the other dipoles in its immediate environment will be influenced by this structure and thus the short ranged interactions no longer may be neglected.

To take account of the short ranged interactions the method of Kirkwood is used [9]. We assume that the only contributing interactions are those between a dipole and its first ring of nearest neighbours. Thus we consider ordering to be complete for nearest neighbours but vanishes for larger distances.

An exact calculation of these short ranged interactions relies on a detailed knowledge of the structure exhibited by a molecule and its first nearest neighbours. However, such structural information is not available and it is necessary to use a model.

To calculate the averages in equation (1.17) we adopt the tetrahedral model of water. (fig. 1.1). The H-O-H bond angle is taken to be 109° so that a regular tetrahedron is formed by a molecule
and its four nearest neighbours. The oxygen atom of the central molecule coincides with the centre, whilst the four other oxygen atoms form the corners of the tetrahedron. If the direction of the central dipole is fixed then the two molecules marked A and B in fig (1.1) will have 3 possible directions of their dipole moments, each pointing away from the cube. A dipole pointing towards the cube would necessitate a hydrogen bond being directed towards a hydrogen atom (i.e. \(-O-H-\ldots-H-O-\)) and thus must be excluded. Similarly the molecules marked C and D will have 3 possible dipole directions pointing towards the cube.

Fig 1.1 The tetrahedral model for the \(H_2O\) nearest neighbour structure

\[ (\mu \cdot A[M]) = \mu^2 (1 + 4 < \cos \gamma >) \]
and
\[ A[M^2] = \mu^2 (5 + 8 < \cos \gamma > + 12 < \cos \gamma'>) \]

where \(\gamma\) is the angle between dipole moments of nearest neighbours and \(\gamma'\) is the angle between the axes of the four nearest neighbours.
neighbours of a given molecule. The angular bracket $<\cdot>$ denotes an average over all angle coordinates.

Exclusion of non-nearest neighbour ordering means that the dipole directions of molecules $A$, $B$, $C$ and $D$ in fig. (1.1) can be considered equally probable. The only dipole directions contributing to the averages $<\cdot>$ in equation (1.19) will be those parallel to the central dipole. Thus we have

$$<\cos \gamma> = 1/3; \quad <\cos \gamma'> = 1/27$$

yielding for the first two moments of $\tilde{\gamma}$

$$\langle \mu \cdot \langle \tilde{\gamma} \rangle \rangle = \frac{7}{3} \mu^2$$

$$\langle \tilde{\gamma} \rangle = \frac{73}{9} \mu^2$$

In order to calculate the higher moments of $\tilde{\gamma}$ we make the further approximations [8]

$$A[\tilde{\gamma}^{2n}] = A^n[\tilde{\gamma}^2] = \left(\frac{73}{9}\right)^n \mu^{2n}$$

$$\mu \cdot A[\tilde{\gamma}^{2n+1}] = A[\mu \cdot \tilde{\gamma}] A^n[\tilde{\gamma}^2] = \left(\frac{7}{3}\right) \left(\frac{73}{9}\right)^n \mu^{2n+2}$$

(1.20)

Substituting equations (1.20) into the general expression (1.17) now yields for the dielectric constant of water

$$\varepsilon = n^2 + (28\pi N\mu/\sqrt{73EV})L[(BE/\sqrt{73/2kT})$$

(1.21)

If $\mu_\nu$ is the dipole moment in the vapour phase then we have [4]

$$\mu = \frac{(n^2+2)}{3} \mu_\nu$$

From which we have

$$\varepsilon = n^2 + \frac{A}{E}L(BE/kT)$$

(1.22)

where

$$A = (28\pi N\mu_\nu(n^2+2))/(3\sqrt{73V})$$

$$B = (\sqrt{73}(n^2+2)\mu_\nu)/6$$
1.3 Dielectric Saturation in a Diffuse Double Layer

We consider a charged metallic interface of infinite extent against an aqueous solution of 1-1 electrolyte. The classical picture of the electric double layer assumes that the solution has two separate regions of differing dielectric properties (fig. 1.2) [12], [13]. The dielectric constant $\varepsilon_1$ of the inner region or Stern layer is assumed to be less than the dielectric constant $\varepsilon_2$ of the outer diffuse layer. Both $\varepsilon_1$ and $\varepsilon_2$ are assumed to be constant over their respective regions with a discontinuous jump from $\varepsilon_1$ to $\varepsilon_2$ at a distance of about a hydrated ionic diameter from the interface.

Fig 1.2
Classical picture of the diffuse double layer

Capacitance measurements of the Mercury/Water interface indicate that a dielectric constant $\varepsilon_1 \approx 6$ is appropriate near the interface whilst the dielectric constant of the diffuse part is about 80. [14], [15].
The discontinuities implicit in this approach cause difficulties in the calculation of energies of ions approaching the interface. For point charges the electrostatic energy diverges at the discontinuity so that a cut off must be introduced into the Fourier integral of the image potential.

These singularities may be removed by assuming a continuous dielectric profile across the entire interface and calculating the Green's function $G(r,r')$ for a unit point charge in the interfacial region, [16] - [20]. In the following sections the extent to which such a profile can be brought about through dielectric saturation of the solvent is investigated. It is assumed that saturation can occur as a result of high field strengths in the vicinity of ions within the diffuse layer.
The Poisson-Boltzmann Equation with Saturation

The total potential at a point \( \vec{r} \) due to an ion at a point \( \vec{r}' \) in the interfacial region may be written [21]

\[
\phi(\vec{r}) = G(\vec{r},\vec{r}') + \psi(z)
\]

(1.22)

where \( G(\vec{r},\vec{r}') \) is the Green's function and \( \psi(z) \) is the potential due to a uniform surface charge density \( \sigma \), and is a function of \( z \) only. The plane interface is assumed to be infinite in extent and we may further suppose that

\[
|G(\vec{r},\vec{r}')| \ll |\psi(z)|
\]

(1.23)

The dependence of the solvent dielectric constant \( \varepsilon \) on field strengths is described by adopting equation (1.21) derived above.

That is

\[
\varepsilon(E) = n^2 + \frac{A}{E} L (BE/kT)
\]

(1.24)

where

\[
A = \pi N_o (n^2 + 2) \mu_v \frac{28/3}{\sqrt{73}}
\]

and

\[
B = \frac{\mu_v (n^2 + 2)}{\sqrt{73}}/6
\]

In view of equations (1.22) and (1.23) the field strength to be used in equation (1.24) at \( \vec{r} \) may be approximated by

\[
E = |\nabla \phi(\vec{r})| \approx |\frac{d\psi}{dz}|
\]

The dielectric constant is then considered to be a function of \( \frac{d\psi}{dz} \) (or implicitly of \( z \)) only.

The potential in the diffuse layer is assumed to satisfy the Poisson-Boltzmann equation which for our purposes takes the form

\[
\nabla \left[ \varepsilon \left( \frac{d\psi}{dz} \right) \nabla \phi(\vec{r}) \right] = 8\pi N_A q c \sinh \beta q \phi(\vec{r})
\]

(1.25)

where \( N_A \) is Avogadro's number, \( q \) is the proton charge and \( c \) is the concentration of the 1-1 electrolyte in moles/litre.
Substituting equation (1.22) into (1.25), expanding the hyperbolic sine function and retaining terms up to order $G$ then gives

\[ \nabla \left[ \varepsilon \left( \frac{d\psi}{dz} \right) \nabla G \right] + \frac{d}{dz} \left[ \varepsilon \left( \frac{d\psi}{dz} \right) \right] = 8\pi N A q^2 c \cosh(\beta q \psi) G + 8\pi N q c \sinh(\beta q \psi) \]

Equating orders of $G$ we then have

\[ \frac{d}{dz} \left[ \varepsilon \left( \frac{d\psi}{dz} \right) \right] = 8\pi N A q c \sinh(\beta q \psi) \quad (1.26) \]

\[ \nabla \left[ \varepsilon \nabla G \right] = \kappa_0^2 (\cosh(\beta q \psi)) G \quad (1.27) \]

where \[ \kappa_0^2 = 8\pi N A q^2 \beta c \]

To proceed with a calculation of $\varepsilon$ we must first solve equation (1.26) for $\psi(z)$ subject to the boundary conditions

\[ \psi(0) = \psi_0 \]

and \[ \psi(\infty) = 0 \quad (1.28) \]

Corrections to the full potential $\phi(x)$ are then obtained by solving (1.27) for $G(x, x')$. However, we have assumed that these corrections are small and that the dielectric saturation is caused solely by variations in $\psi(z)$ so that we need only solve equation (1.26).

Introducing the reduced potential

\[ y = \beta q \psi \]

and the non dimensional variable

\[ \xi = \kappa_0^2 z \]

equation (1.26) becomes

\[ \frac{d}{d\xi} \left[ \varepsilon(y')y' \right] = \sinh y \quad (1.29) \]
where \( y' = \frac{dy}{d\xi} \)

and

\[
\varepsilon(y') = n^2 + \frac{a}{y'} L[by'] 
\]

\[
a = \beta qA/\kappa_0 \\
b = \kappa_0 B/q
\]

Equation (1.29) may at once be rewritten as

\[
y' \frac{d}{dy}[\varepsilon(y')y'] = \sinh y
\]

Integrating from the point of zero potential at \( \xi = \infty \) to \( y \) then yields

\[
(y')^2 \varepsilon(y') - \int_0^{y'} y' \varepsilon(y')dy' = \cosh y - 1
\]

where we have used the fact that \( y' \to 0 \) when \( y \to 0 \) (i.e. when \( \xi \to \infty \)).

Substituting equation (1.30) into (1.31) and performing the integration with respect to \( y' \) then yields as the first integral of equation (1.29)

\[
(y')^2 \varepsilon(y') - \ln^2(y') - \frac{a}{b} \log \left\{ \frac{\sinh(by')}{by'} \right\} = \cosh y - 1
\]

We proceed by expanding the separate terms on the left hand side of equation (1.32) in powers of \( y' \).

For the dielectric constant we obtain

\[
\varepsilon(y') = n^2 + \frac{ab}{3} - \frac{ab^3}{45} (y')^2 + \frac{2ab^5}{945} (y')^4 + 0[(y')^6]
\]

and for the logarithmic term

\[
\log \left\{ \frac{\sinh(by')}{by'} \right\} = \frac{b^2}{6} (y')^2 - \frac{b^4}{180} (y')^4 - \frac{b^6}{2865} (y')^6 + 0[(y')^8]
\]

Substituting into equation (1.32) and retaining terms up to order 4 in \( y' \) only, we have

\[
(y')^2 \varepsilon_0 - \frac{ab^3}{30} (y')^4 = 2(\cosh y - 1)
\]
where
\[ \varepsilon_0 = \varepsilon(y' = 0) = n^2 + ab/3 \]

We now change to the more familiar coordinate
\[ \eta = \kappa z = \xi/\sqrt{\varepsilon_0} \]
where
\[ \kappa = \kappa_0/\sqrt{\varepsilon_0} \]
is the usual Debye parameter.

The final expression for the first integral of equation (1.29) now becomes
\[ (y')^2 - \frac{ab^3}{30\varepsilon_0^2} (y')^4 = 2(\text{cosh}y - 1) \quad (1.34) \]
where
\[ ab^3 = \beta\kappa_0^2 (\pi N_0 (n^2 + 2))^4 \mu_0^2 \cdot 14 \sqrt{73}/39 \]
and
\[ y' = \frac{dy}{d\eta} \]
Equation (1.34) contains the first correction to the Gouy-Chapman equation due to saturation of the dielectric constant [14], [15]. It can be seen that at low electrolyte concentration and/or low field strengths the deviations from the Gouy-Chapman theory should be small.

In order to integrate equation (1.34) we set \( v = y/2 \) which transforms it into the form
\[ \frac{1}{4} \Delta^2 (v')^4 - (v')^2 + \sinh^2 v = 0 \quad (1.35) \]
with
\[ \Delta^2 = 4ab^3/15\varepsilon_0^2. \]
From equation (1.35) we then have
\[ (v')^2 = \frac{1 - \sqrt{1 - 2\Delta^2 \sinh^2 v}}{\Delta^2 \sinh^2 v} \]
where the minus sign has been taken to ensure $v' > 0$ when $v > 0$ ($\eta \to \infty$). Thus we have

$$\frac{d\eta}{dv} = -\frac{\Delta}{\sqrt{1 - 1 - 2\Delta^2 \sinh^2 v}}$$  \hspace{1cm} (1.36)$$

or

$$\eta = \Delta \int_0^v \frac{dv}{\sqrt{1 - 1 - 2\Delta^2 \sinh^2 v}}$$  \hspace{1cm} (1.37)$$

The above integral is an elliptic integral. To cast it into a form involving standard elliptic integrals of the first, second, or third kinds we first introduce the variable $t$ by

$$t^2 = 1 - 2\Delta^2 \sinh^2 v$$  \hspace{1cm} (1.38a)$$

from which

$$\frac{dv}{dt} = -t/[\sqrt{(1-t^2)(1+2\Delta^2-t^2)}]$$  \hspace{1cm} (1.38b)$$

Equation (1.37) then becomes

$$\eta = \Delta \delta \int_{t_0}^t \frac{t \, dt}{\sqrt{(1-t)(1-t^2)(1-\delta^2 t^2)}}$$

where $\delta^2 = 1/(1+2\Delta^2) < 1$

Splitting the range of integration we may now write

$$\eta = \Delta [I(t) - I(t_0)]$$

where

$$I(t) = \delta \int_1^t \frac{t \, dt}{\sqrt{(1-t)(1-t^2)(1-\delta^2 t^2)}}$$  \hspace{1cm} (1.39)$$

To carry out the integration we now make the substitutions [22]

$$\sin^2 \psi = \frac{2\delta}{(1+\delta)(1+\delta t)}$$

and

$$\text{sn} \, u = \sin \psi$$

where $\text{sn} \, u$ is the Jacobi sn function with modulus
and argument
\[ u = F(\psi, k^2) \]
where \( F \) is the elliptic integral of the first kind. The integral (1.39) then becomes (see Appendix A).

\[ I(t) = \sqrt{\delta} \int_0^u \frac{1 - \alpha_1^2 \sn^2 u}{1 - \alpha_2^2 \sn^2 u} \, du \]

with \[ \alpha_1^2 = (1 + \delta)/2 \delta \]
and \[ \alpha_2^2 = (1 + \delta)^2/4\delta > 1 \]

Using the identity
\[ 1 - \alpha_1^2 \sn^2 u = \frac{\alpha_2^2}{\alpha_1^2} (1 - \alpha_2^2 \sn^2 u) + (1 - \frac{\alpha_1^2}{\alpha_2^2}) \]
we may now write

\[ I(t) = \sqrt{\delta} \left[ \frac{\alpha_2^2}{\alpha_1^2} u + (1 - \frac{\alpha_1^2}{\alpha_2^2}) \Pi(u, \alpha_1^2, k^2) \right] \]

where
\[ \Pi(u, \alpha_1^2, k^2) = \int_0^u \frac{du}{1 - \alpha_2^2 \sn^2 u} \]
is the elliptic integral of the third kind given by

\[ \Pi(u, \alpha_1^2, k^2) = \frac{-\alpha}{\sqrt{(\alpha_1^2 - 1)(\alpha_1^2 - k^2)}} \left[ u Z(A, k^2) - \Omega_4 \right] \]
with \[ Z(A, k^2) = E(A, k^2) - F(A, k^2)/ \]
\[ A = \sin^{-1}(1/\alpha) \]
\[ K = F(\frac{\pi}{2}, k^2) \]
\[ E = E(\frac{\pi}{2}, k^2) \]

where \( E(\psi, k^2) \) is the elliptic integral of the second kind and

\[ \Omega_4 = \frac{1}{2} \log \frac{\theta_1(w+v)}{\theta_1(w-v)} \]

where \( \theta_1 \) is the Jacobi theta function, and
\[ w = \pi F(A, k^2) / 2K \]
\[ v = \pi u / 2K \]

We thus have

\[ \eta = \Delta \sqrt{\frac{\delta}{2}} \left[ (1-\frac{\alpha^2}{\alpha^2+u^2}) \Pi(u, \alpha^2, k^2) - \frac{\alpha^2}{\alpha^2+u^2} u \right] u_o \]  

(1.40)

It is not possible to invert this expression to obtain the potential as a function of \( \eta \).

However, we may obtain the dielectric profile across the diffuse layer by iterating the potential down from the value \( v_o \) and at each step evaluate \( v' \) from equation (1.38b). Substituting into equation (1.30) then gives us the value of the dielectric constant corresponding to the value of \( \eta \) calculated from equation (1.40)
### 1.4 Dielectric Profiles in the Diffuse Layer

In this section are presented the dielectric profiles obtained by varying the potential across the interface.

The value of $v_o$ chosen is subject to the limitation imposed by equation (1.38). That is, we must have

$$v_o < v_o^{\text{max}} = \sinh^{-1}(1/\sqrt{2\Delta^2}) \quad (1.41)$$

The possible values of $v_o^{\text{max}}$ and the corresponding values of $\psi_o^{\text{max}} = 2v_o^{\text{max}}/\beta q$ are listed for various concentrations in Table (1.1):

<table>
<thead>
<tr>
<th>Concentration (Moles/litre)</th>
<th>$v_o^{\text{max}}$ (mV)</th>
<th>$\psi_o^{\text{max}}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.94</td>
<td>97</td>
</tr>
<tr>
<td>1.0</td>
<td>0.936</td>
<td>46.8</td>
</tr>
<tr>
<td>2.0</td>
<td>0.702</td>
<td>35.1</td>
</tr>
<tr>
<td>5.0</td>
<td>0.464</td>
<td>23.2</td>
</tr>
</tbody>
</table>

The calculations reported were done at $300^\circ\text{K}$ using a $\text{H}_2\text{O}$ dipole moment of 2 Debye, the optical refractive index of water being $n = 1.9416$. The bulk dielectric constant $\varepsilon_o = n^2 + \alpha \beta^3/3$ is then 76.6.

Because of the restriction (1.41) the maximum possible saturation occurs when $v' = 1/\Delta$. Using equation (1.30) we have

$$\varepsilon_{\text{min}} = n^2 + \frac{\Delta a}{2}[\coth(2b/\Delta) - \Delta/2b]$$

$$= n^2 + \frac{(\beta AB)^{3/2}}{\varepsilon_o \sqrt{15}} [\coth(\varepsilon_o \sqrt{15}/\sqrt{\beta AB}) - \sqrt{\beta AB}/\varepsilon_o \sqrt{15}]$$

This expression is independent of concentration. Yielding a value $\varepsilon_{\text{min}} \approx 60$

which is a 21% reduction in the bulk value.

In the following $v_o$ was chosen close to $v_o^{\text{max}}$ to show the maximum possible saturation and as a result all the dielectric...
profiles start at a value $\varepsilon = \varepsilon_{\text{min}}$. (Fig. (1.3) to (1.6)).

In general it was found that at all concentrations there was an initial sharp increase in the value of the dielectric constant from 60 to about 70 then a gradual increase to the bulk value 76.6. As to be expected the bulk value was approached more rapidly at the lower concentrations.

The potential profiles used to produce the saturation are shown above each of the dielectric profiles. To assess the overall importance of the saturation effect it is necessary to consider the dielectric profiles in the light of the potential curves.

For .1 molar electrolyte (fig. 1.3) the dielectric constant has already reached a value of 75 at $\eta = .5$ representing a reduction of only 1% below the bulk value. The value of the potential at this point is quite high being 47 mV. To produce further saturation it can be seen that much higher potentials must be invoked.

In the case of the 1 Molar electrolyte (fig. 1.4) we see that the saturation is more pronounced. The whole profile has been lowered. The value of $\varepsilon$ at $\eta = .5$ is now 73, a 4% reduction in the bulk value. However we now note that the potentials needed to cause the onset of saturation are much lower than they were in the previous case. The value of $\psi_0$ in this case was taken to be 46.7 mV, half as large as the value needed for .1 M electrolyte.

As we pass to higher concentrations [figs. (1.5) and (1.6)], both the dielectric and the corresponding potential profiles are lowered even further. That is the potentials necessary to produce saturation become lower.
From the above considerations we see that for concentrations above .1 Molar the value of the solvent dielectric constant can be reduced markedly from its bulk value. At the higher concentrations, a 21% reduction can be obtained from quite low values of potential $\Psi(z)$, well within those values experienced in the laboratory. Although the above treatment was by no means exact it does show that the effect could be important when considering the energies of ions as they approach an interface.
$\psi_0 = 96.9$

$C = 0.1$ Mole/litre

Fig 1.3 Dielectric profile across the diffuse layer at electrolyte concentration 0.1 molar
Fig 1.4 Dielectric profile across the diffuse layer at electrolyte concentration 1.0 molar
Fig 1.5 Dielectric profile across the diffuse layer at electrolyte concentration 2.0 molar
Fig 1.6 Dielectric profile across the diffuse layer at electrolyte concentration 5.0 molar
REFERENCES for Chapter 1

[1] Coulomb discovered this law in 1795 but it was in fact first discovered by Henry Cavendish much earlier and lay hidden in his notes until 1879.


CHAPTER 2

THE ROLE OF CORRELATION FUNCTIONS IN
THE STATISTICAL MECHANICS OF
SIMPLE LIQUIDS
2.1 Introduction

The processes of statistical mechanics concern the calculation of macroscopic thermodynamic properties of a system from a detailed consideration of the microscopic forces that govern the way the system behaves on a molecular level. In the case of gases and liquids, the forces, via the interparticle interactions potentials usually are assumed known and the macroscopic manifestations of these interactions occur in such measurable quantities as the pressure, internal energy and heat capacity.

However, this process is not in general one way as our knowledge of the interparticle interactions is by no means exact. Thus the passage from known macroscopic to unknown microscopic phenomena is of equal importance if we are to understand the detailed structure of matter.

2.1.1 The Grand Canonical Partition Function.

Consider a volume \( V \) of a gas or liquid in which the number of particles \( N \) is allowed to vary. The joint probability that the particle labelled \( i \), for \( i=1,\ldots,N \), will be located within the volume element \( (r_i^+dr_i, p_i^+dp_i) \) centred on the point \( (r_i, p_i) \) of phase space is given by [1]

\[
P dr_1, \ldots, dr_N, dp_1, \ldots, dp_N
\]

where \( P = (1/h^3N \xi) \exp [\beta(N\mu-e)] \) ................. (1.2)

In equation (1.2) \( \mu \) is the chemical potential, \( h \) is Planck's constant, \( \beta = 1/kT \) where \( k \) is Boltzmann's constant and \( T \) is the temperature, \( \xi \) is a normalization factor and \( E \) is the energy of a particular configuration of the \( N \) particles.

For the systems studied in this dissertation, the assumptions of no external field and additive two body interactions will be used. Thus the energy \( E \) may be written
\[ E = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j}^{N} u(r_{ij}) \]  

(1.3)

where \( r_{ij} = |\xi_i - \xi_j| \) is the distance between particles \( i \) and \( j \) and \( u(r_{ij}) \) is their interaction potential.

Any function \( f \) operating on the points of phase space may be averaged with respect to the probability density function defined in equation (1.2).

Thus \[ \bar{f} = \frac{1}{N!} \int \cdots \int f \rho \ d\xi_1 \cdots d\xi_N \ d\xi_1 \cdots d\xi_N \]  

(1.4)

To evaluate the normalization constant \( \Xi \) in equation (1.2) we integrate over the phase space coordinates.

Thus \[ \frac{1}{N!} \sum_{N=0}^{\infty} \frac{\rho^N}{N!} \int \cdots \int e^{-\frac{\beta E}{N}} \ d\xi_1 \cdots d\xi_N \ d\xi_1 \cdots d\xi_N = 1 \]  

Substituting equation (1.3) into this expression and performing the momentum integrations yields

\[ \Xi = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \cdots \int e^{-\sum_{i<j}^{N} \beta u(r_{ij})} \ d\xi_1 \cdots d\xi_N \cdots \]  

(1.4a)

where \[ z = \frac{1}{\hbar^3} (4\pi mkT)^{3/2} e^{\mu/kT} \]  

(1.4b)

and thus

\[ \Xi = \sum_{N=0}^{\infty} \frac{z}{N!} Q_N \]  

(1.5)

where

\[ Q_N = \frac{1}{N!} \int \cdots \int e^{-\sum_{i<j}^{N} \beta u(r_{ij})} \ d\xi_1 \cdots d\xi_N \cdots \]  

(1.6)

The constant \( \Xi \) is termed the Grand Canonical Partition function. The constant \( Q_N \) defined by equation (1.6) is termed the Canonical Partition function, and is the normalization factor for the distribution of particles in a system for which the number of particles \( N \) in the volume \( V \) remains fixed.
2.1.2 The L Body Distribution Functions

For a set of \( L \) particles the joint probability of finding the \( i \)th particle in the volume element \( V_i + \delta V_i \) centred on \( V_i \) for all \( i = 1, \ldots, L \) is given by [2]

\[
n^L(r_1, \ldots, r_L) \, \delta r_1 \cdots \delta r_L
\]

where \( n^L(r_1, \ldots, r_L) = \sum_{N=L}^{\infty} \frac{1}{(N-L)!} \int \cdots \int p \, \delta r_1 \cdots \delta r_N \, \delta p_1 \cdots \delta p_N \) (1.7)

Using equations (1.2) and (1.3) and performing the momentum integrations gives

\[
n^L(r_1 \ldots r_L) = \frac{1}{N!} \sum_{N=L}^{\infty} \frac{Z^N}{(N-L)!} \int \cdots \int e^{\delta \sum u(r_{ij})} \, \delta r_{L+1} \cdots \delta r_N \quad (1.8)
\]

The function \( n^L(r_1, \ldots, r_L) \) is called the \( L \)-body distribution function.

For the case \( L = 1 \)

\[
n'(r) = \frac{1}{N!} \sum_{N=1}^{\infty} \frac{Z^N}{(N-1)!} \int \cdots \int e^{\delta \sum u(r_{ij})} \, \delta r_2 \cdots \delta r_N
\]

\[
= \frac{N}{V} = \rho
\]

(1.9)

is the number density at \( r \).

The radial distribution function \( g(r_1, r_2) \), is defined in terms of the 2-body distribution function by the relation

\[
n^2(r_1, r_2) = \rho^2 \, g(r_1, r_2)
\]

(1.10)

Since the interactions considered in this discussion are assumed to be "central", that is, they depend only on the distance between two particles, the radial distribution function will be a function of \( r_{12} = |r_1 - r_2| \) only.
That is
\[ n^2(r_1, r_2) = \rho^2 g(r_{12}) \] .......
(1.11)

When the particles are far apart, their mutual interaction can be assumed to be negligible. This means that the probability of a particle being at \( r_1 \) will be unaffected by the presence of a particle at \( r_2 \) and thus
\[ n^2(r_1, r_2) = n^1(r_1) n^1(r_2) = \rho^2 \]

From equation (1.11) it follows that the radial distribution function has the property
\[ g(r_{12}) + 1 \quad \text{as} \quad r_{12} \to \infty \] .......
(1.12)

The total correlation function is defined by the relation
\[ h(r) = g(r) - 1 \] .........
(1.13)

The 3-dimensional Fourier transform of \( h(r) \) is simply related to the structure factor \( S(k) \) which measures the ratio of the correlated and uncorrelated intensities when x-rays or neutrons are scattered from the system
\[ S(|k|) = 1 + \rho \int \frac{ik \cdot r}{|r|} h(r) \, dr \] .......
(1.14)

Equations (1.13) and (1.14) show that \( h(r) \) and thus \( g(r) \) can be calculated from measurements of their Fourier transforms in scattering experiments.

To complete the array of functions needed in a discussion of liquids and gases, the Ornstein-Zernike (O.Z), equation (Ornstein and Zernike 1914) [3] is introduced. This equation defines the direct correlation functions \( c(r) \) by
\[ h(|r|) = c(|r|) + \rho \int c(|r-r_1|) h(|r_1|) \, dr_1 \] .........
(1.15)
The Fourier transform of the O.Z. equation is

\[ \hat{h}(k) = \hat{c}(k) + \rho \hat{h}(k) \hat{c}(k) \] ........... (1.16)

which may be re-arranged to

\[ (1-\rho \hat{c}(k)) (1+\rho \hat{h}(k)) = 1 \] ........... (1.17)

2.1.3 Thermodynamic Properties in terms of the Radial Distribution Function.

The microscopic and macroscopic properties of the system are related to the grand canonical partition function via the relation [1]

\[ \frac{PV}{kT} = \log \Xi \] (1.18)

From equations (1.4) to (1.6) it follows that

\[ \frac{\partial \log \Xi}{\partial \mu} = \frac{\bar{N}}{kT} \] (1.19)

and differentiating again gives

\[ \frac{\partial N}{\partial \mu} = \frac{\bar{N}^2 - \bar{N}}{kT} \] (1.20)

From equation (1.8) it follows that

\[ \int \nu n^1(r_1) dr = \bar{N} \]

and

\[ \int \int \nu n^2(r_1,r_2) dr_1 dr_2 = \frac{\bar{N}(\bar{N}-1)}{2} \]

Thus

\[ \int \int \nu (n^2(r_1,r_2) - n^1(r_1)n^1(r_2)) dr_1 dr_2 = \bar{N}^2 - \bar{N} \] (1.21)

From the definition of the isothermal compressibility, \( \kappa_T \), and using equations (1.9) and (1.18) then

\[ \kappa_T = kT \frac{\partial^2 \Xi}{\partial P^2} V, T = \frac{kT}{V} \left( \frac{\partial N}{\partial \log \Xi} \right) V, T \]

\[ = \left( \frac{\partial N}{\partial \log \Xi} \right) V, T \] ........... (1.22)
Combining this expression with equations (1.19) and (1.20) gives
\[ kT \frac{\partial \rho}{\partial p} V, T = \frac{N^2 - N^2}{N} \] \hspace{1cm} \text{(1.23)}

Now, using equation (1.21) the compressibility can be expressed in terms of the one and two particle distribution functions. That is
\[ kT = 1 + (N)^{-1} \int \left[ n^2(r_1, r_2) - n_1(r_1)n_1(r_2) \right] \, dr_1 \, dr_2 \]
and using (1.9) and (1.11)
\[ kT \equiv kT \left( \frac{\partial \rho}{\partial p} \right) V, T = 1 + \rho \int [g(r)-1] \, dr \] \hspace{1cm} \text{(1.24)}
which is the so-called compressibility equation.

The pressure may be calculated from equation (1.24) by integrating with respect to density.

An alternative equation for the pressure was derived by Born and Green [4]. If non-dimensional coordinates \( s_i = r_i V^{-1/3} \) are introduced in equation (1.4a) then
\[ \Xi = \sum_{N=0}^{\infty} N^N \int \cdots \int \exp \left[ -\beta \Sigma u(S_{ij} V^{1/3}) \right] \, ds_1 \cdots ds_N \] \hspace{1cm} \text{(1.25)}
where the integrations are now over some volume \( D \) which has a fixed surface boundary. This means that (1.25) may be integrated with respect to volume \( V \), yielding
\[ V \frac{\partial \Xi}{\partial V} = N - \frac{1}{3kT} \sum_{N=0}^{\infty} \frac{N^N}{N!} \int \cdots \int \frac{\partial u(V^{1/3} S_{ij})}{\partial (V^{1/3} S_{ij})} V^{1/3} S_{ij} \exp \left[ -\beta \Sigma u(V^{1/3} S_{ij}) \right] \] \hspace{1cm} \text{(1.26)}

The summation under the integral sign yields \( N(N-1)/2 \) identical terms. Thus, reverting to the \( r_i \) coordinates equation (1.26) may be written
\[ V \frac{\partial \Xi}{\partial V} = N - \frac{1}{6\beta kT} \sum \frac{N^N}{(N-2)!} \int \cdots \int \frac{\partial u(r_{12})}{\partial r_{12}} r_{12} \exp \left[ -\beta \Sigma u(r_{ij}) \right] \, dr_1 \cdots dr_N \]
Dividing by $V$ and using equations (1.9) and 1.10

$$\frac{PV}{kT} = \rho - \frac{\rho^2}{6kT} \int \frac{\partial u(r)}{\partial r} r g(r) \, dr$$

(1.27)

Equations (1.27) and (1.24) are exact and should give the same values for the pressure. They are useful when examining the accuracy of any approximate theories of the distribution functions.

As well as the pressure, the internal energy $U$ can be written conveniently in terms of the radial distribution function. It is usual to identify $U$ with the average of the energy $E$ given in equation (1.3). Thus using equations (1.2) and (1.4):

$$U = \sum_{N=0}^{\infty} \frac{N}{N!} \int \cdots \int \left( \frac{3}{2} NkT + kT \sum_{i<j} u(r_{ij}) \exp(-\beta \sum_{i<j} u(r_{ij})) \right) dr_1 \cdots dr_N$$

(1.28)

where again the momentum integrations have been carried out.

The sum in the brackets contributes $N(N-1)/2$ identical terms to $U$. Thus

$$U = \frac{3}{2} NkT + kT \sum_{N=0}^{\infty} \frac{N}{(N-2)!} \int \cdots \int u(r_{ij}) \exp(-\beta \sum_{i<j} u(r_{ij})) \, dr_1 \cdots dr_N$$

Using equations (1.8) to 1.11) and dividing by $N$ gives

$$\frac{U}{N} = \frac{3}{2} kT + 2\pi \rho kT \int u(r) g(r) \, dr$$

(1.29)

which is the energy equation.

Equations (1.29), (1.27) and (1.24) are the most common connections between microscopic theory and macroscopic thermodynamics.

2.2 Integral Equation Approximations

In the previous section expressions relating particle interactions to laboratory observables were obtained. Thus the problems
of statistical mechanics are mathematically well defined. However, evaluation of the expressions is far too difficult and it is necessary to resort to the various approximate theories that have evolved.

The nature of these theories is to provide a closure or second equation which supplements the Ornstein-Zernike equation giving, in a general sense, two equations that are to be solved for the unknown functions $c(r)$ and $h(r)$.

2.2.1 The Percus Yevick Approximation

The Percus Yevick approximation equation was originally derived in a somewhat involved way using the method of collective coordinates [5]. However, we present here for the sake of brevity its derivation using the techniques of functional differentiation [2], [6], [7].

We introduce a particle into the system at a fixed position $x_0$. This gives rise to an external field which perturbs the interaction energy. The resulting perturbed energy may be written

$$ U_N = \sum_{i=1}^{N} \phi(i) + \sum_{i<j} u(r_{ij}) \quad (2.1) $$

where the first sum arises from the interaction of the new particle with all others in the system. A change $\delta\phi(i)$ in the interaction energy causes a corresponding change in $\Xi$. Thus using equation (1.4a)

$$ \delta\Xi = -\beta \sum_{N=0}^{\infty} \frac{Z^N}{N!} \int \cdots \int \sum_{i=1}^{N} \delta\phi(i) \exp \left[-\beta \sum_{i=1}^{N} \phi(i) \right] \exp \left[-\beta \sum_{i<j} u(r_{ij}) \right] \, dr_1 \cdots dr_N $$

$$ = -\beta \sum_{N=0}^{\infty} \frac{Z^N}{N!} \int \cdots \int \delta\phi(1) \exp \left[-\beta \sum_{i=1}^{N} \phi(i) \right] \exp \left[-\beta \sum_{i<j} u(r_{ij}) \right] \, dr_1 \cdots dr_N $$

Now by the definition of the functional derivative (Appendix B)
\[
\frac{1}{\beta} \frac{\delta \mathcal{E}}{\delta \phi(1)} = -\beta n^1(r_1)
\]

\[
= \frac{\delta \log \mathcal{E}}{\delta \phi(1)} 
\]

(2.2)

Similarly a differentiation of \( n^1(r_1) \) with respect to \( \delta \phi(2) \) yields

\[
\frac{\delta n^1(r_1)}{\delta \phi(2)} = -\beta \{ n^2(r_1, r_2) - n^1(r_1)n^2(r_2) + n^1(r_1)\delta(r_1-r_2) \} \ldots (2.3)
\]

From equations (1.9), (1.10) and (1.13)

\[
h(r_{12}) = g(r_{12}) - 1 = \frac{n^2(r_1, r_2)}{n^1(r_1)n^2(r_2)} - 1
\]

and using (2.3)

\[
h(r_{12}) = -\frac{1}{\beta} \frac{\delta \log n^1(r_1)}{n^1(r_2)\delta \phi(2)} - \frac{\delta(r_1-r_2)}{n^1(r_1)} \ldots (2.4)
\]

If equation (2.4) is now substituted into the O.Z. equation then an expression for the direct correlation function is found to be

\[
c(r_{12}) = \beta \frac{\delta \phi(1)}{\delta n^1(r_2)} + \frac{\delta(r_1-r_2)}{n^1(r_2)} \ldots (2.5)
\]

Now consider the functional Taylor series of the functional \( n^1(r_0_1)\exp(\beta \phi(1)) \) with the perturbation

\[
\delta n^1(r_0_2) = n^1(r_0_2) - \rho \ldots (2.6)
\]

In equation (2.6) it should be understood that \( n^1(r_0_2) \) is the conditional probability of finding a particle at \( r_2 \) given that there is a particle at \( r_0 \). Thus if \( \phi(2) \) is zero there is no perturbation of particle 2 due to the particle at \( r_0 \) and

\[
n^1(r_0_2) = n^1(r_2) = \rho
\]
The chain rule for functional derivatives gives

\[ \frac{\delta n^1(r_{o1}) \exp(\beta \phi(1))}{\delta n^1(x_{o2})} = \exp(\beta \phi(1)) \frac{\delta n^1(r_{o1})}{\delta n^1(x_{o2})} + \beta \exp(\beta \phi(1)) n^1(r_{o1}) \frac{\delta \phi(1)}{\delta n^1(x_{o2})} \]

Thus to first order the Taylor series becomes

\[ n^1(z_{o1}) \exp(\beta \phi(1)) = n^1(z_1) + \int \left[ \delta(z_1 - z_2) + \beta n^1(z_1) \frac{\delta \phi(1)}{\delta n^1(z_2)} | \phi(1) = 0 \right] \times (n^1(r_{o2}) - \rho) \, dz_2 \] .... (2.7)

Now using equations (2.5) and (2.7) it can be shown that

\[ n^1(r_{o1}) \exp(\beta \phi(1)) = \rho (g(z_{o1}) - c(r_{o1})) \]

or

\[ g(z_{o1}) \exp(\beta u(r_{o1})) = g(r_{o1}) - c(r_{o1}) \] .... (2.8)

which is called the Percus-Yevick equation. (Hereafter: PY equation)

2.2.2 The Hypernetted Chain Equation

If the function \( \log[n(r_{o1}) \exp(\beta \phi(1))] \) is expanded in terms of \( n^1(r_{o2}) \) about \( \phi(1) = 0 \) then a different approximation called the hypernetted chain approximation is obtained \([1]\). That is

\[ c(r_{o1}) = h(r_{o1}) - \log[1 + h(r_{o1})] - \beta u(r_{o1}) \] .... (2.9)

2.2.3 The Mean Spherical Approximation

For large interparticle separations \( r \), the magnitude of the potential \( u(r) \) is small and the radial distribution function will be close to its limiting value of unity. It follows from the PY approximation (equation 2.8) that for large \( r \), \( c(r) \) is given by

\[ c(r) = - \beta u(r) \] .... (2.10)
If equation (2.10) is assumed valid for all interparticle separations then a new approximation, called the Mean Spherical Approximation (MSA), is obtained. [8]

For a system in which the particles are not allowed to overlap there is an additional requirement

\[ h(r) = -1 \quad r < R \quad (2.11) \]

where \( R \) is the particle diameter.

For the particular case of non-interacting hard spheres for which

\[ u(r) = 0 \quad r > R \]
\[ = \infty \quad r < R \quad \ldots \ldots \quad (2.12) \]

then the MSA, given by equations (2.10) and (2.11), becomes identical with the PY approximation. That is

\[ c(r) = 0 \quad r > R \]
\[ h(r) = -1 \quad r < R \quad (2.13) \]

### 2.3 Solutions of the Ornstein Zernicke Equation

#### 2.3.1 Finite Range Direct Correlation Functions

Recall that the Fourier transform of the O.Z. equation may be written

\[ [1 - \rho \hat{c}(k)][1 + \rho \hat{h}(k)] = 1 \quad (3.1) \]

where after performing the angle integrations

\[ \hat{h}(k) = 4\pi \int_0^\infty \text{d}r \cos kr H(r) \quad (3.2a) \]
\[ \hat{c}(k) = 4\pi \int_0^\infty \text{d}r \cos kr C(r) \quad (3.2b) \]

and

\[ C(r) = \int_r^\infty tc(t) \text{d}t \quad (3.3a) \]
\[ H(r) = \int_r^\infty th(t) \text{d}t \quad (3.3b) \]
For a disordered fluid $\hat{h}(k)$ remains finite for all real values of $k$. In the case that $c(r)$ is zero outside some finite range $R$ then from equations (3.1), (3.2b) and (3.3a) the function

$$\hat{A}(k) = 1 - 4\pi \rho \int_0^R \cos kr C(r) \, dr$$  \hspace{1cm} (3.4)

will have no zeros on the real axis.

Using the theory of Fourier Integrals it can be shown that $\hat{A}(k)$ then may be written [2,9]

$$\hat{A}(k) = \hat{Q}(k)\hat{Q}(-k)$$  \hspace{1cm} (3.5)

in some finite strip, $\text{Im}(k) < \varepsilon$, about the real axis where the function $\hat{Q}(k)$ is analytic and has no zeros in the region $\text{Im}(k) > -\varepsilon$.

Further, $1 - \hat{Q}(k)$, is Fourier integrable along the real axis and thus there exists a function $Q(r)$ such that

$$2\pi \rho Q(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikr} (1 - \hat{Q}(k)) \, dk$$  \hspace{1cm} (3.6)

It can be shown also that

$$Q(r) = 0 \text{ for } r > R, \, r < 0$$  \hspace{1cm} (3.7)

and so inverting equation (3.6)

$$\hat{Q}(k) = 1 - 2\pi \rho \int_0^R \cos kr Q(r) \, dr$$  \hspace{1cm} (3.8)

Substituting equations (3.8) and (3.4) into equation (3.5) and then performing the Fourier inversion leads to

$$C(r) = Q(r) - 2\pi \rho \int_0^R Q(t)Q(t-r) \, dt$$  \hspace{1cm} (3.9)

From equations (3.1) and (3.5)

$$\hat{Q}(k)[1 + \rho \hat{h}(k)] = 1/\hat{Q}(-k)$$  \hspace{1cm} (3.10)

Now, multiplying by $\exp(-ikr)$ and integrating from $-\infty$ to $\infty$ yields

$$H(r) = Q(r) + 2\pi \rho \int_0^R Q(t)H(|r-t|) \, dt$$  \hspace{1cm} (3.11) 

$r > 0$
Equations (3.9) and (3.11) represent a reformulation of the O.Z. equation in the case that \( c(r) = 0 \) for \( r > R \). If \( h(r) \) and thus \( H(r) \) are known for \( r < R \) then in principle equation (3.11) can be solved for \( Q(r) \), \( r < R \). Then substituting \( Q(r) \) into (3.9) and integrating yields \( C(r) \) for \( r < R \).

The main use of equation (3.11) however lies in the fact that if \( Q(r) \) is known for \( r < R \) then it can be used to generate the total correlation function \( h(r) \) to any desired distance \( r \) outside the range \( R \). [21]

Using equations (3.1), (3.4) and (3.5) a convenient expression for the compressibility may be obtained. Thus from (1.24)

\[
\frac{kT}{\gamma_p} \frac{\partial \varphi}{\partial \rho} = \frac{1}{[\hat{Q}(o)]^2}
\]  

(3.12)

2.3.2 Application to the Percus Yevick Equation

A consequence of the PY equation is that \( c(r) \) vanishes when the potential vanishes. Thus one might expect the method outlined in section (2.3.1) to be useful when considering this approximation.

Hard Spheres (Non-interacting)

For non-interacting hard spheres, using equations (3.11) and (2.13) it can be seen that \( Q(r) \) must be a quadratic polynomial continuous at \( R \). Thus

\[
Q(r) = \frac{1}{2} \alpha (r^2 - R^2) + \beta (r-R)
\]

(3.13)

where it is found that

\[
\hat{Q}(o) = \alpha = \frac{(1+2n)}{(1-n)^2}
\]

and

\[
\frac{\beta}{R} = \frac{3\eta}{2(1-n)^2}
\]

(3.14)

where

\[
\eta = \frac{\pi}{6} \rho R^3
\]

Integration of equation (3.12) using (3.13) and (3.14) now yields the compressibility pressure. [9]

\[
\beta P_{\text{comp}} = \frac{(1+n+n^2)}{(1-n)^3}
\]

(3.15)
Adhesive Hard Spheres

The PY equation has been solved also for a system of hard spheres in which the Boltzmann factor has a delta function at the particle diameter $R$ [10, 11, 2]. This corresponds to an infinitely narrow and infinitely deep square well potential. Such a system exhibits the desirable feature of a phase transition. In fact the compressibility equation of state for this system has the same qualitative behaviour as a system of particles interacting via the Lennard-Jones 6-12 potential [2, 12].

The Boltzmann factor may be written

$$e^{-\beta u(r)} = \frac{R}{12\tau} \delta(r-R) \quad r < R$$

$$= 1 \quad r > R$$

where $\tau$ is a temperature parameter.

By inspecting the virial cluster expansion of the total correlation function it is seen that $h(r)$ has the form

$$h(r) = -1 + \frac{\lambda R}{12} \delta(r-R) \quad \text{for } r < R \ldots$$

where $\lambda$ is a non-dimensional parameter.

Substitution of equation (3.16) into (3.11) indicates that $Q(r)$ has the form

$$Q(r) = \frac{1}{2} Ar^2 + Br + c \quad r < R$$

As $\lim_{r \to R^+} Q(r) = 0$, taking the limits $r \to R^+$ in (3.11) yields

$$c = \frac{\lambda R^2}{12} - \frac{1}{2}AR^2 - RB$$

Replacing $c$ by this expression in equation (3.17) and then substituting into equation (3.11) gives two equations for $A$ and $B$ which when solved yield

$$\hat{Q}(0) = A = \frac{(1+2n-\mu)/(1-n)^2}{2}$$

$$B = \frac{R}{2}(-3n+\mu)/(1-n)^2$$

where

$$\mu = \lambda n(1-n)$$
From equations (2.8) and (1.15) it can be seen that
\[ y(r) = g(r)e^{iu(r)} \]
is continuous at \( r = R \). From (3.16a) and (3.16) then
\[ y(R) = \lambda \tau \]
(3.20)

From the PY equation and equations (3.9) and (3.11) it can be shown that
\[ Ry(R) = R + 2\pi \rho \int_0^R Q(t)(R-t)h(R-t)dt \]
(3.21)

It is readily shown using (3.21) and (3.20) that
\[ \lambda \tau = \frac{(1+\eta/2)}{(1-\eta)^2} - \frac{\eta \lambda}{(1-\eta)} + \frac{\eta \lambda^2}{12} \]
(3.22)

This is a quadratic equation for \( \lambda \) in terms of \( \tau \) and \( \eta \) which admits solutions for all \( \eta \) provided
\[ \tau > \tau_c = (2-\sqrt{2})/6 \]
in which case the critical density calculated using (3.22) is
\[ \eta_c = (3\sqrt{2}-4)/2 \]

For temperatures below \( \tau_c \) there is an intermediate range of densities for which \( \lambda \) takes complex values so that the system undergoes a discontinuous first order phase transition between states of different densities.

There is another restriction on the solutions for \( \lambda \) given by the properties of \( \hat{Q}(k) \). From equation (3.8) it can be seen that \( \hat{Q}(k) \to 1 \) as \( k \to \infty \) on the positive imaginary axis and thus \( \hat{Q}(0) \) must be positive as \( \hat{Q}(k) \) has no zeros in \( \text{Im}(k) > -\varepsilon \)

Thus from equations (3.18) and (3.19) the condition \( (1+2\eta) > \mu \) must be satisfied.

As in the case of non-interacting hard spheres the compressibility pressure can be easily evaluated using (3.18) and (3.12). Thus
\[ \beta P_{\text{comp}} = \rho [1+\eta+\eta^2-\mu(1+\eta^2) + (\eta^{-1}\mu^3)/36]/(1-\eta)^3 \]
(3.23)
Potentials with a Soft Core

The discussion in the preceding two examples was for systems of particles with a hard core. The total correlation \( h(r) \) for \( r < R \) had a conveniently simple form and the solution followed with a minimum of effort. However, for the case in which the particles have a non-zero probability of overlapping and in which the potential rises to infinity continuously as \( r \to 0 \) no such simple expression exists. To take advantage of the finite range transformation it is therefore necessary to consider some parameterisation of \( h(r) \) keeping sufficient flexibility to enable a comparison with the known correlation functions from either computer simulations, scattering experiments, or perturbation theories.

Consider a system with a finite ranged potential in which the total correlation function may be represented by

\[
h(x) = -1 + \sum_{i=1}^{M} \alpha_i \lambda_i^2 \frac{\sinh \lambda_i x}{\lambda_i x} \frac{1}{\cosh \lambda_i} \quad x < 1 \tag{3.24}
\]

where \( x = r/R \); \( r \) being the distance between two particle and \( R \) the range of the potential.

Thus using equation (3.3b)

\[
H(x) = H_0 + \frac{1}{2} \gamma x^2 - \sum_{i=1}^{M} \Delta_i (\cosh \lambda_i x - 1) \quad x < 1 \tag{3.25}
\]

where

\[
\gamma = 1 + \sum_{i=1}^{M} \alpha_i \lambda_i^2 / \cosh \lambda_i
\]

\[
\Delta_i = \alpha_i / \cosh \lambda_i
\]

and

\[
H_0 = \int_{0}^{\infty} \theta(t) dt
\]

The \( 2M \) parameters \( \alpha_i, \lambda_i \) as yet are not specified.
From equation (3.25) it can be seen that \( H(x) \) is an even function of \( x \) and may be substituted into equation (3.11), the restriction of the modulus sign now being satisfied identically.

Changing the variable \( t \) to \( t/R \) in equation (3.11) and using (3.25) yields

\[
H_0 + \frac{1}{2} \gamma x^2 - \sum_{i=1}^{M} \Delta_i (\cosh \lambda_i x - 1) = Q(x)
\]

\[
+ 12 \eta \int_0^1 Q(t) [H_0 + \frac{1}{2} \gamma (x-t)^2 - \sum_{i=1}^{M} \Delta_i (\cosh \lambda_i (x-t) - 1)] dt
\]

for \( x < 1 \) \hspace{1cm} (3.26)

where \( \eta = \frac{\pi}{\rho R^3} \)

The above equation is a Fredholm integral equation with a separable kernel. The function \( Q(x) \) will have the form

\[
Q(x) = Q_1 + Q_2 x + Q_3 x^2 + \sum_{i=1}^{M} [Q_{i1} \cosh \lambda_i x + Q_{i2} \sinh \lambda_i x] \hspace{1cm} x < 1
\]

Equating coefficients in (3.26) now yields

\[
Q_2 - 12 \eta \gamma \int_0^1 t Q(t) dt = 0
\]

\[
2Q_3 + 12 \eta \gamma \int_0^1 Q(t) dt = \gamma
\]

\[
-Q_{i1} + 12 \eta \Delta_i \int_0^1 Q(t) \cosh \lambda_i t dt = \Delta_i \hspace{1cm} i = 1, \ldots, M
\]

\[
Q_{i2} + 12 \eta \Delta_i \int_0^1 Q(t) \sinh \lambda_i t dt = 0 \hspace{1cm} i = 1, \ldots, M \hspace{1cm} (3.26)
\]

The requirement that \( Q(x) \) be continuous at \( x = 1 \) yields a further equation

\[
Q_1 = -Q_2 - Q_3 - \sum_{i=1}^{M} [Q_{i1} \cosh \lambda_i + Q_{i2} \sinh \lambda_i]
\]

which when used in equations (3.26) yields a set of \( 2M+2 \) linear equations among the \( 2M+2 \) coefficients of \( Q(x) \) in terms of the parameters \( \alpha_i, \lambda_i \). Explicit expressions are given in appendices C and D and may be easily programmed on a computer to yield the function \( Q(x) \). The direct correlation function can be calculated in closed
form using equation (3.9) and then the potential function in the PY approximation is obtained from equation (2.8).

2.3.3 Mean Spherical Approximation for Electrolyte Solutions

The extension of the Ornstein-Zernike equation to the case of multi-component liquids such as electrolyte solutions is straightforward [19]. For an N component liquid in which the component i has number density $\rho_i$ and radius $R_i$ it takes the form

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^{N} \rho_k \int c_{ik}(r) h_{kj}(r'-r) dr'$$

(3.28)

which may be written as

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^{N} k(c_{ik} * h_{kj})(r)$$

(3.29)

where the * represents the convolution integral in equation (3.29). The functions $h_{ij}(r)$ and $c_{ij}(r)$ are respectively the total and direct correlations of a particle of type i with a particle of type j.

Similarly we may generalize the MSA for an N component system with additive hard cores as

$$h_{ij}(r) = -1 \quad r < R_{ij} = (R_i + R_j)/2$$

$$c_{ij}(r) = -\beta u_{ij}(r) \quad r > R_{ij}$$

(3.30)

The general case of an N component system in which the potential has the form

$$u_{ij}(r) = \beta z_i z_j q^2 e^{-\mu r/\epsilon r} \quad r > R_{ij}$$

(3.31)

has been solved using an extension of the finite transformation method of section (2.3.1)[13]. In equation (3.31) $z_i$ is the valency of component i, q is the unit of electronic change and $\epsilon$ is the dielectric constant of the intervening medium.
Taking the limit \( \mu \to 0 \) yields the MSA for electrolytes.

In the next section an alternative derivation of the solution is given for the special case of a restricted primitive model electrolyte. This solution reveals a simple method for calculating the correlation functions \( h_{ij}(r) \) that does not appear in the case of the general \( N \) component system. This method has also been used for calculating the correlation functions for a system in which the potential has a Yukawa tail [14].

**Restricted Primitive model Electrolyte**

In this case we have a 2 component mixture interacting via the potential in equation (3.31). We later take the limit \( \mu \to 0 \) to recover the usual Coulomb interaction. In addition we have that the particle diameters and the number densities of the two species are equal and that their charges are equal but opposite in sign. Thus we write

\[
R_1 = R_2 = R, \quad \rho_1 = \rho_2 = \frac{\rho}{2}, \quad z_1 = -z_2 = -1
\]

Because of symmetry we have

\[
\begin{align*}
h_{11}(r) &= h_{22}(r), & c_{11}(r) &= c_{12}(r) \\
h_{12}(r) &= h_{21}(r), & c_{12}(r) &= c_{21}(r)
\end{align*}
\]

The O.Z. equations defined in the expression (3.29) now reduce to two equations for the four different function \( h_{11}, h_{12}, c_{11}, c_{12} \). Namely,

\[
\begin{align*}
h_{11}(r) &= c_{11}(r) + \frac{\rho}{2}(c_{11}h_{11} + c_{12}h_{12})(r) & (3.32 \text{ a}) \\
h_{12}(r) &= c_{12}(r) + \frac{\rho}{2}(c_{11}h_{12} + c_{12}h_{11})(r) & (3.32 \text{ b})
\end{align*}
\]

The MSA closures for these equations now become
To proceed we define four new functions

\[ h_+(r) = \frac{1}{2}(h_{11}(r) + h_{12}(r)) \]
\[ h_-(r) = \frac{1}{2}(h_{11}(r) - h_{12}(r)) \]
\[ c_+(r) = \frac{1}{2}(c_{11}(r) + c_{12}(r)) \]
\[ c_-(r) = \frac{1}{2}(c_{11}(r) - c_{12}(r)) \] (3.34)

If we now add and subtract equations (3.32 a) and (3.32 b) and make use of the relations (3.34) together with the MSA closures we obtain

\[ h_+(r) = c_+(r) + \rho(c_+ h_+)(r) \] (3.35 a)

with \[ h_+(r) = -1 \quad r < R \]
and \[ c_+(r) = 0 \quad r > R \] (3.35 b)

\[ h_-(r) = c_-(r) + (c_- h_-)(r) \] (3.36 a)

with \[ h_-(r) = 0 \quad r < R \]
and \[ c_-(r) = -\beta q^2 e^{-\mu r/\epsilon r} \quad r > R \] (3.36 b)

Thus the equations (3.32a,b) have been decoupled into two separate equations; one for \( h_+(r) \) and \( c_+(r) \), the other for \( h_-(r) \) and \( c_-(r) \).

Equations (3.35a) and (3.35 b) for the functions \( h_+(r) \) and \( c_+(r) \) have the same form as the O.Z. and MSA equations for non-interacting hard spheres [see equations (2.12), (2.13) of section (2.2)]. The properties of \( h_+(r) \) with respect to Fourier transformation are the same as the properties of the hard sphere \( h(r) \), hence, we may apply directly the methods of section (2.3). At this stage we assume that equations (3.35a) and (3.35 b) already have been solved.

We now turn to the solution of equations (3.36 a) and...
(3.36 b) for the functions \( h_-(r) \) and \( c_-(r) \).

First define a new finite ranged correlation function by

\[
c_0(r) = c_-(r) + \beta q^2 \frac{e^{-ur}}{\epsilon r} \equiv 0 \quad r > R \tag{3.37}
\]

The Fourier transform of equation (3.36a) then may be written

\[
[1 - \rho \hat{c}_0(k) + \frac{\kappa^2}{k^2 + \mu^2}] [1 + \rho \hat{h}(k)] = 1 \tag{3.38}
\]

where we have defined

\[
\hat{c}_0(k) = \int_{-\infty}^{\infty} e^{ik \cdot r} c_0(r) \, dr = 4\pi \int_{-\infty}^{\infty} \cos kr \, c_0(r) \tag{3.38a}
\]

\[
\hat{h}(k) = \int_{-\infty}^{\infty} e^{ik \cdot r} h_(r) \, dr = 4\pi \int_{-\infty}^{\infty} \cos kr \, H(r) \, dr
\]

with

\[
C_0(r) = \int_{-\infty}^{\infty} c_0(t) \, dt
\]

and

\[
H(r) = \int_{-\infty}^{\infty} h_(t) \, dt
\]

The quantity \( \kappa \) is the usual Debye parameter given by

\[
\kappa^2 = 4\pi \beta q^2 \rho / \epsilon
\]

For a disordered fluid \( 1 + \rho \hat{h}(k) \) is finite for all \( \text{real} \ k \) and from equation (3.38) we infer that

\[
\hat{\Lambda}(k) = 1 - \rho \hat{c}_0(k) + \frac{\kappa^2}{k^2 + \mu^2} \tag{3.39}
\]

has no zeros in some finite strip \( |\text{Im}(k)| < \delta \) about the real axis. The function \( \hat{c}_0(k) \) as defined by equations (3.38a),(3.37) is a finite Fourier cosine transform and therefore is an entire function. From equation (3.39) it follows that \( \hat{\Lambda}(k) \) is analytic in the strip \( |\text{Im}(k)| < \delta < \mu \) about the real axis. Thus we may write

\[
\hat{\Lambda}(k) = \hat{Q}(k) \hat{Q}(-k) \tag{3.40}
\]
where $Q(k)$ is analytic and has no zeros for $\text{Im}(k) > -\delta > -\mu$
and is given by

$$\log \hat{Q}(k) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\log \hat{\Lambda}(k\omega)}{k\omega - k} \, dk \quad (3.41)$$

It follows from equation (3.41) that $\log \hat{Q}(k) \sim O(1/x)$
as $|x| \to \infty$, where $x = \text{Real}(k)$. This means $\hat{Q}(k) \sim 1 + O(1/x)$
as $|x| \to \infty$. Further, from equation (3.41) $\hat{Q}(k)$ and $\hat{Q}(-k)$
are complex conjugates. We may now define a real valued function $Q(r)$ by

$$2\pi \rho Q(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikr}(1-\hat{Q}(k)) \, dk \quad (3.42)$$

For $y > 0$, $\hat{Q}(k) \to 1$ as $k \to \infty$. If $r < 0$ we close the
integral of equation (3.42) in the upper half plane. Using
Cauchy's residue theorem and Jordan's lemma [15]

$$Q(r) = 0 \quad r < 0 \quad (3.43)$$

Consider now $r > R$. The continuation of $\hat{Q}(k)$ into the
lower half plane is given by

$$\hat{Q}(k) = \hat{\Lambda}(k)/\hat{Q}(-k) \quad (3.44)$$

We see then that for $y \to -\infty$, $\hat{Q}(k)$ and $\hat{\Lambda}(k)$ are asymptotic to $e^{ikR}$. If we now close the integral of equation (3.42)
in the lower half plane we get

$$2\pi \rho Q(r) = \frac{1}{2\pi} \int_{c} e^{-ikr}[1-(1-\rho \hat{c}_0(k)+\frac{k^2}{k^2+\mu^2}/\hat{Q}(-k)] \, dk$$

Where the contour $C$ is shown below
On the integrand approaches zero as \( k \to \infty \) and we have using the residue theorem [taking \( B \to \infty \)]

\[
2\pi \rho Q(r) = -a e^{-\mu r} \quad r > R
\]

where \( a = \kappa^2 / 2\mu \hat{Q}(i\mu) \)

Inverting equation (3.42) using (3.43) and (3.45) now yields

\[
\hat{Q}(k) = 1 - 2\pi \rho \int_0^R e^{ikr} Q(r) dr + a \int_0^\infty e^{-\mu r} e^{ikr} dr
\]  

(3.46)

It now follows from equation (3.46) that

\[
\lim_{\mu \to 0} \mu \hat{Q}(i\mu) = a/2
\]

Thus in the limit \( \mu \to 0 \)

\[
a^2 = \kappa^2
\]

(3.47)

Careful Fourier inversion of equations (3.39) and (3.40) using (3.46) yields

\[
c_0(|r|) = \frac{\kappa}{(k^2 + \mu^2) 2\mu 2\pi \rho} Q(r) - 2\pi \rho \int_0^R Q(t) Q(r+t) dt
\]

\[
- \frac{a^2}{2\pi \rho} e^{-\mu r} \theta(r-R) + a e^{-\mu r} \int_R^\infty Q(t) e^{-\mu t} dt - \frac{a^2}{2\pi \rho} e^{-\mu r} e^{-2\mu R}/2\mu
\]

Now taking the limit \( \mu \to 0 \) and noting the result of equation (3.47) yields \( c_0(r) \) in terms of \( Q(r) \)

\[
c_0(r) = Q(r) - 2\pi \rho \int_0^R Q(t) Q(r+t) dt - \frac{a}{2\pi \rho} \theta(r-R) + a \int_0^R Q(t) dt
\]

\[ r > 0 \]  

(3.48)

From equation (3.48) it is found that

\[
Q(R_-) = -\frac{a}{2\pi \rho}
\]

(3.49)

To obtain the relation between \( H(r) \) and \( Q(r) \) we return to equations (3.38) and (3.40) from which

\[
[1 + \rho \hat{h}(k)] \hat{Q}(k) = 1/\hat{Q}(-k)
\]
Multiplying this expression by $e^{-ikr}$ and integrating from $-\infty$ to $\infty$ yields [taking $\mu \to 0$]

$$H(|r|) = Q(r) + 2\pi \rho \int_0^R Q(t)H(|t-r|)dt - \frac{a}{2\pi \rho} \theta(r-R) - \frac{a}{8\pi} \int_{R-r}^\infty H(|t|)dt$$  \hspace{1cm} (3.50)

To ensure the convergence of the last integral in equation (3.50) we need the condition of overall charge neutrality. In general this states [16]

$$\sum_{k=1}^{N} 4\pi \rho \sum_{k} z_k \rho_k \int_0^\infty r^2 g_{kj}(r)dr = -z_j$$

which in the present case reduces to

$$H_0 = \int_0^\infty H(t)dt = -1/4\pi \rho$$

The final expression for $H(r)$ now becomes

$$H(|r|) = Q(r) + 2\pi \rho \int_0^R Q(t)H(|t-r|)dt - \frac{a}{2\pi \rho} \theta(r-R) + \frac{a}{4\pi \rho} + \frac{a}{\pi} \int_0^R H(|t|)dt$$  \hspace{1cm} (3.51)

For the range $0 < r < R$ we have

$$H(r) = \int_r^\infty \theta_-(t)dt$$

$$= \int_0^\infty \theta_-(t)dt - \int_0^R \theta_-(t)dt$$

$$= H_0 - \int_0^R \theta_-(t)dt$$

Using the MSA condition for $h_-(r)$ yields

$$H(r) = H_0 \quad 0 < r < R$$

This means that for $r < R$ $Q(r)$ is a linear polynomial and according to equation (3.51) it must take the form

$$Q(r) = \alpha (R-r) - \frac{a}{2\pi \rho} \quad r < R$$  \hspace{1cm} (3.52)

Substituting this into equation (3.51) and equating coefficients of $r$ gives two equations for the unknown constants $\alpha$
and \( H_0 \). In particular the coefficient of \( r \) yields

\[
\alpha = -\alpha H_0
\]

and the coefficient of \( r^0 \) then gives a quadratic equation for \( H_0 \).

\[
H_0^2(\pi \rho R^2 \alpha) + H_0(1+\alpha R) + \frac{\alpha}{4\pi \rho} = 0
\]

Thus

\[
H_0 = (-1-\alpha R \pm \sqrt{1+2\alpha R})/2\pi \rho R^2 \alpha \quad (3.53)
\]

Inserting \( \alpha = \kappa \) and taking the positive sign in equation (3.53) now yields the known result for the excess energy parameter \( B = 2\pi \rho R H_0 \). [17]

\[
B = (-1-\kappa R + \sqrt{1+2\kappa R})/\kappa R
\]

The thermodynamic properties of this solution have been discussed in detail elsewhere, [18,20]; however the correlation functions have not. Equations (3.51) and (3.48) allow simple calculation of these functions.

The numerical procedure used to calculate the correlation functions \( h_+ \) and \( h_- \) is a modified version of the Perram algorithm [21] . The functions \( h_+(r) \) are generated using a straightforward application of the hard sphere results. To obtain \( h_-(r) \) we first differentiate equation (3.51) yielding

\[
r h_-(r) = -Q'(r) + 2\pi \rho \int_0^R Q(t)(r-t)h_-(r-t)dt - aH_0 + a \int_0^R th_-(t)dt \quad r > 0
\]

(3.54)

For \( r < 2R \) the integrand of the last integral in equation (3.54) is zero, as required by the MSA. Again the hard sphere algorithm may be applied directly, the hard sphere \( Q \) function being replaced by the expression for \( Q(r) \) from equation (3.52). Thus \( h_-(r) \) for the interval \( R < r < 2R \) is calculated on a grid of 200 equally spaced points, using trapezoidal rule integration.
For $r > 2R$

$$\int_0^{r-R} th_-(t)dt = \int_R^{r-R} th_-(t)dt \quad (3.55)$$

from which it can be seen that at each new iteration of $r$

beginning at $r = 2R + \Delta r$, the integrand in equation (3.55)

contributes to the value of $h_-(r)$. However, the integral is only

over the range of the previously calculated values of $h_-(r)$ and

again the trapezoidal rule can be used to calculate its contribution.

Finally $h_{11}(r)$ and $h_{12}(r)$ are given by the decoupling formulae

$$h_{11}(r) = h_+(r) + h_-(r)$$

$$h_{12}(r) = h_+(r) - h_-(r)$$
Results for the Restricted Primitive Model Electrolyte

This section is devoted to numerical presentation and discussion of the MSA correlation functions $h_{11}(r)$ and $h_{12}(r)$ for a univalent primitive model electrolyte. Results are given for a wide range of temperatures and densities. It is found that the MSA is invalid at low densities and temperatures, because it predicts unphysical values of the correlation functions.

The results are expressed in terms of the one component plasma parameter

$$\Gamma = (2q^2)\eta^{1/3}/\varepsilon kT$$

where

$$\eta = \frac{\pi}{6}\rho R^3$$

is the usual reduced density. The more familiar Debye parameter $\kappa$ is then given by

$$\kappa R = 12\Gamma\eta^{2/3}$$

In the case of the 1-1 univalent electrolyte the MSA proves to be best at concentrations around 2 Molar at room temperature. For this state $\Gamma = 1.5$, $\eta = 0.1$ and $\kappa R = 1.97$. The MSA functions $h_{11}(r)$, $h_{12}(r)$ for this state are compared in figure (2.1) with the Monte Carlo simulation results for the primitive model taken from reference [22]. It can be seen that $h_{11}(r)$ lies within the error bounds of the Monte Carlo data for all separations. However, at small separations $h_{12}(r)$ underestimates the Monte Carlo results considerably, indicating the MSA to be deficient in treating the attractive interactions. Oscillations in the MSA charge density, indicated by changes in sign of the quantity $h_{11}(r)-h_{12}(r)$, occur at $r/R \approx 2.2$, in accordance with the simulation results.
We now look at the temperature dependence of the particle correlations. From the definition of the MSA (equation (2.10)), one would expect it to be most accurate at high temperature close to the hard sphere limit ($\Gamma \approx 0$). The failure of the MSA at low temperature can be seen by following the behaviour of $h_{11}(r)$ and $h_{12}(r)$ as the temperature is reduced at fixed density.

In figures (2.2) to (2.4), the temperature was reduced so that $\Gamma$ increased from 1.5 to 5 at fixed density $\eta = .1$. From these plots, we see the increasing importance of the Coulombic attraction in determining the liquid structure as temperature is reduced. The contact value of $h_{11}(r)$ is increased and the value of its first minimum is reduced. The increased presence of oppositely charged particles near the central particle is accompanied by an increased exclusion of like particles from that region as shown by the reduced contact value of $h_{11}(r)$ and the increased height of its first peak. This first peak can also be seen to move inward as the temperature is reduced. The increased charged density oscillations indicating an increase in structure can be seen in passing from figures (2.2) to (2.4).

In figure (2.4), we note unphysical values of $h_{11}(r)$ less than -1, indicating the failure of the MSA under these conditions. This type of behaviour of the MSA correlation functions has also been noted for angular dependent systems.[23]

A further example of the breakdown of the MSA for strong attractions is shown in figure (2.5). This state $\Gamma = 50$, $\eta = .35$ corresponds to a molten salt. Again there is strong coulombic attraction indicated by the high $h_{12}(r)$ peak and as before $h_{11}(r)$ has become less than -1.

The correct low density limit for $g_{\alpha\beta}(r)$ is $\exp[-\beta u_{\alpha\beta}(r)]$ whereas the MSA gives $1-\beta u_{\alpha\beta}(r)$ [18]. We may again illustrate this
breakdown by looking at the correlation functions. Figures (2.6) to (2.8) were obtained by fixing the temperature \( T = 298^\circ \text{K} \) and decreasing the density. At \( \eta = 0.05 \) the change oscillations have disappeared. (c.f. fig (2.6)). Reducing the density further moves the \( h_{12}(r) \) contact value up and the \( h_{11}(r) \) contact value down until at \( \eta = 0.01 \) it has become less than -1.

The above results indicate that the main failure of the MSA in describing the thermodynamics of electrolytes is due to its inability to describe the coulombic attractions. For those states in which the attraction is large the correlations between like particles become unphysical.

However, the MSA appears to give reasonable results for the correlation functions and thermodynamic properties for states appropriate to 1-1 electrolytes for concentrations between 1 and 2 Molar at room temperature, an important region from a practical physico-chemical point of view. We have shown that the correlation functions as well as the thermodynamics properties of the primitive model may be readily calculated for the MSA in this region.
Fig 2.1 Comparison of the MSA radial distribution functions with the Monte Carlo simulation results of Rasaiah, Card and Valleau [22] for the restricted primitive model

Concentration = 2.0 Molar
Ion diameter = 4.25 Å

$\Gamma = 1.5$
$\eta = 0.1$
Fig 2.2

\[ h_{11}(r) \]

\[ h_{12}(r) \]

\[ \eta = 0.1 \]
\[ \Gamma = 1.5 \]
$n = 0.1$

$\Gamma = 3.0$

Fig. 2.3
\( h(r) \)

\[ \eta = 0.1 \]

\[ R = 5.0 \]

\[ h_{12}(r) \]

\[ h_{11}(r) \]

Fig. 2.4
**Fig 2.5**

MSA correlation functions for the 1-1 primitive model electrolyte at a state typical of a molten salt

Γ = 50  η = 0.35
\[ n = 0.05 \]
\[ T = 298^\circ K \]

Fig 2.6
Fig 2.7

\[ h(r) \]

-1.5 \hspace{1cm} -1.0 \hspace{1cm} -0.5 \hspace{1cm} 0.0 \hspace{1cm} 0.5 \hspace{1cm} 1.0 \hspace{1cm} 1.5 \hspace{1cm} 2.0 \hspace{1cm} 2.5 \hspace{1cm} 3.0

-1.5 \hspace{1cm} -1.0 \hspace{1cm} -0.5 \hspace{1cm} 0.0 \hspace{1cm} 0.5 \hspace{1cm} 1.0 \hspace{1cm} 1.5 \hspace{1cm} 2.0 \hspace{1cm} 2.5 \hspace{1cm} 3.0

\[ h_{12}(r) \]

\[ h_{11}(r) \]

\[ n = 0.02 \]

\[ T = 298^\circ K \]
$n = 0.01$
$T = 298^\circ K$

$\frac{h_{12}(r)}{r/R}$

$\frac{h_{11}(r)}{r/R}$

Fig 2.8
CHAPTER 3

PERTURBATION THEORY FOR THE RADIAL DISTRIBUTION FUNCTION
3.1 Introduction

In the previous chapter it was seen how the seemingly impossible task of calculating two-body distribution functions may be effected. However, such functions may only be obtained for a few model interaction potentials and even then only within the bounds of the integral equation approximation theories. To proceed to a calculation of the radial distribution functions or the thermodynamic functions of a real system perturbation theories have been developed. In using these theories one looks at the dominant structural features of a real liquid and tries to relate them to a model reference system which best describes those particular features.

The basic procedure of the perturbation theories is to write the potential of the system in the form

\[ u(r) = u_0(r) + u_1(r) \]

where \( u_0(r) \) is the reference system potential and \( u_1(r) \) is considered as a perturbation term.

Zwanzig first used this idea to expand the Helmholtz free energy of a system of particles interacting via the Lennard Jones 6-12 potential given by [24]

\[ u(r) = 4\epsilon \left[ (6/r)^{12} - (6/r)^{6} \right] \]

about a hard sphere reference system with arbitrary diameter \( d \). His theory achieved moderate success in reproducing the then available data for Argon and Nitrogen but was accurate only in the high temperature, low density regime relevant to the gas phase.

Later treatments, notably those of Rowlinson and, McQuarrie and Katz improved the results of Zwanzig by reducing the lower
bound on the temperature range for which reasonable equations of state could be obtained for the 6-12 potential.

Rowlinson [25] expanded the canonical partition function for a potential of the form

$$u(r) = \varepsilon[(\sigma/r)^n - (\sigma/r)^{n/2}]$$

in powers of $1/n$ about the hard sphere limit $n = \infty$ and obtained good results for the 6-12 potential ($n=12$) at high temperatures and pressures. McQuarrie and Katz [26] combined the Zwanzig and Rowlinson methods by first expanding the free energy for the 6-12 potential about the reference potential $u_o = \varepsilon(\sigma/r)^{12}$ treating $u_1(r) = -\varepsilon(\sigma/r)^6$ as the perturbation, and then using the $1/n$ expansion to describe the reference system free energy. This procedure gave satisfactory results for reduced temperatures down to about 3.

Despite this their results were still restricted to the low density gas regime.

The first perturbation theory to give an accurate equation of state in the temperature and density range typical of a liquid was that of Barker and Henderson (H-B) [27, 28]. They showed that the main defects in the earlier theories were due to the detailed nature of the repulsive interactions.

The reference system in the B-H theory is that part of the potential up to the zero at $r = \sigma$. Thus they chose

$$u_o(r) = u(r) \quad r < \sigma$$

$$= 0 \quad r > \sigma$$
which is shown in fig 3.1

The most important consequence of equation (3.1) is that by choosing an equivalent hard sphere reference system with diameter \( d \) defined by

\[
d = \int_0^\sigma \left( e^{-\beta u(r)} - 1 \right) dr
\]  

(3.2)

then the zeroth order terms in both the free energy and correlation function expansions may be systematically approximated by

\[
A_0 = A_{HS}
\]

and

\[
g_0(r) = g_{HS}(r)
\]
In order to calculate accurate radial distribution functions using the B-H theory it is necessary to use the first order correction term, involving three and four body distribution functions, even at relatively high densities (see fig. 3.2). As the density is reduced it becomes necessary to calculate even higher order terms and the implementation of the B-H theory becomes more difficult. [28, 29]

**Fig. 3.2** Radial Distribution functions for 6-12 potential obtained from Barker-Henderson perturbation theory: --- zeroth order: —— first order .... Simulation results [29b]

The next step in the history of perturbation theories was the development due to Weeks, Chandler and Andersen [30],[31] (hereafter WCA). This theory takes the idea of the B-H theory one step further and assumes that the major structural features at high density are due to repulsive forces and not just the positive energy part of the potential. Thus WCA proposed that the potential be split in the following manner, which is shown in figure (3.3)
\[ u_0(r) = u(r) + \varepsilon \quad r < r_m \]
\[ = 0 \quad r > r_m \]
\[ u_1(r) = -\varepsilon \quad r < r_m \]
\[ = u(r) \quad r > r_m \]  
(3.3)

where \( \varepsilon = u(r_m) \) is the value of the potential at the first minimum and \( r_m \) is the position of the first minimum. In the case of the Lennard Jones 6-12 potential \( r_m = 2^{1/6}\sigma \).

**Fig. 3.3** The WCA choice of perturbation potential [30]

The reference system defined in equations (3.3) includes that part of the potential between \( r_m \) and \( \sigma \) neglected in the B-H theory. This part will certainly be important in determining the structure of the liquid because it plays a major role in balancing the tendency of two neighbouring molecules to be pushed together against their tendency to sit in the potential minimum.

The mathematical details of the WCA theory (to first order)
appear as a special case of the expansion derived in the next section. Briefly we obtain, to first order, that the Helmholtz free energy is

$$A = A_0 + \frac{1}{2}N_p \int u_1(r)g_o(r)d^3r$$  \hspace{1cm} (3.4)

where both $A_0$ and $g_o$ may be systematically approximated by

$$A_0 = A_{HS}$$

$$g_o = g_{HS}\exp(-\beta u_o(r))$$  \hspace{1cm} (3.5)

The diameter $d$ of the equivalent hard sphere reference system is given by

$$\int_{-\infty}^{\infty} y_{HS}(r) [\exp(-\beta u_{HS}(r)) - \exp(-\beta u_o(r))]r^2dr = 0$$  \hspace{1cm} (3.6)

where

$$y_{HS}(r) = g_{HS}(r)\exp(\beta u_{HS}(r))$$

Equation (3.6) defines both a density and temperature dependent hard sphere diameter whilst the B-H criterion, equation (3.2) defines a reference diameter that only depends on the temperature.
In the following sections we focus attention upon two unsatisfactory aspects of these perturbation theories.

When the contribution of the attractive forces is added to the reference system free energy via equation (3.4) the description of the liquid-vapour equilibrium is basically the same as that of the van der Waals theory. In section (3.3) we explore the possibility of including attractive forces in the reference system with a view to yielding a better description of phase equilibria. The second difficulty arises as the reference system potential becomes softer. The WCA prescription of employing the Percus-Yevick hard sphere $y_{HS}(r)$ becomes less accurate. On the other hand there is evidence that for soft-core finite range potentials the Percus-Yevick approximation is quite accurate. In section (3.4) we explore a new method for generating the radial distribution function for such potentials according to this approximation.
3.2 Expansion in terms of the Boltzmann Factor

In chapter 2 we saw how functional differentiation of both the grand canonical partition function and the grand canonical distribution functions could be carried out by introducing an extra particle into our system and considering its perturbing effect on the two body potential \( u(r_{1j}) \).

Now, instead of introducing this new particle we write the potential as

\[
u(r_{12}) = u_o(r_{12}) + u(r_{12}) - u_o(r_{12})
= u_o(r_{12}) + \delta u(r_{12})
\]  

(3.7)

and in a similar fashion we write the Boltzmann factor as

\[
\exp[-\beta u(r_{12})] = \exp[-\beta u_o(r_{12})] + \exp[-\beta u(r_{12})] - \exp[-\beta u_o(r_{12})]
= \exp[-\beta u(r_{12})] + \delta e(r_{12})
\]  

(3.8)

We make functional Taylor series expansions using both \( \delta u(r_{12}) \) and \( \delta e(r_{12}) \) as our perturbations.[32]

To compute the first functional derivative of \( A \), the Helmholtz free energy, with respect to \( u(r_{12}) \) we recall the results of chapter 2. In terms of the canonical partition function we have [see chapter 2 equation 1.6].

\[
A \equiv -kT \log Q_N
\]  

(3.10)

The derivative of \( \log Q_N \) with respect to \( u(r_{12}) \) is obtained by a method analogous to the derivation of equation (2.2) in chapter 2 for the grand canonical ensemble. Thus we find

\[
\frac{\delta \ln Q_N}{\delta u(r_{12})} = -\frac{1}{2} \beta n^1(r_{12}) - \beta \frac{\delta A}{\delta u(r_{12})}
\]  

(3.11)
We note at this stage that \( n^1(r_{12}) \) in equation (3.11) is the 2-body distribution function in the canonical ensemble.

That is
\[
n^1(r_{12}) = \frac{\Lambda^N}{Q^N(N-2)!} \int \cdots \int \exp[-\beta \sum_{i<j} u(r_{ij})] \, dr_3 \cdots dr_N
\]

where
\[
\Lambda = (4\pi mkT/h^2)^{3/2}
\]

Using equation (3.11) and the results of appendix B we have that to first order
\[
A = A_0 + \frac{1}{2} \int \int n^1(r_{12}) \delta u(r_{12}) \, dr_1 \, dr_2
\]
changing to relative coordinates and performing a volume integration yields
\[
A = A_0 + \frac{1}{2} Np \int g_o(r_{12}) \delta u(r_{12}) \, dr_{12}
\] (3.12)

A second expansion of \( A \) may be obtained in terms of the perturbation \( \delta e(r_{12}) \)

If we write
\[
e(r_{12}) = \exp[-\beta u(r_{12})]
\]
and use the function of a function rule for functional differentiation we have
\[
\frac{\delta}{\delta e(r_{12})} = \frac{\delta}{\delta u(r_{12})} \cdot \frac{\delta u(r_{12})}{\delta e(r_{12})}
\]
from which
\[
\frac{\delta u(r_{12})}{\delta e(r_{12})} = -1/[\beta e(r_{12})]
\] (3.13)
Thus to first order we may write

\[
A = A_0 + \int \int \frac{\delta A}{\delta e(r_{12})} \big|_0 \delta e(r_{12}) \, dr_1 \, dr_2
\]

\[
= A_0 - kT \int \left[ \int n_0(r_{12}) \frac{\delta e(r_{12})}{e_o(r_{12})} \right] \, dr_1 \, dr_2
\]

\[
= A_0 - kTN_0 \int g_o(r_{12}) \frac{\delta e(r_{12})}{e(r_{12})} \, dr_{12}
\]

which reduces to the expression

\[
A = A_o - kTN_0 \int y_0(r) \left[ \exp(-u(r)) - \exp(-u_o(r)) \right] \, dr
\]

where \( y_0(r) = g_o(r) \exp[\beta u_o(r)] \)

Equation (3.14) is referred to as the first order blip function expansion. The integrand in equation (3.14) viz.

\[
B(r) = y_0(r) \left[ \exp(-u(r)) - \exp(-u_o(r)) \right]
\]

is referred to as the blip function.

Equation (3.14) forms a basis for practical realization of the WCA theory outlined above. By choosing the second order term to vanish we have to second order that \([31]\)

\[
A = A_o
\]

Further it has been shown that if this is done then a good approximation to \( y(r) \) is

\[
y(r) = y_o(r)
\]

provided that \( \xi \), the interval over which \( B(r) \) is non zero is not too large. (see fig. 3.7)

The WCA procedure is to use equation (3.15) to relate the "repulsive force" reference system to an effective hard sphere reference system and the correction to the free energy due to the attraction is then given by equation (3.12).
In the following sections various model systems which were discussed in chapter 2 will be considered as reference systems in perturbation studies. Having decided on a reference system the radial distribution function of the real system will be approximated by first requiring that the free energies of both systems be the same to second order through the condition that

\[ \int B(r) \, dx = 0 \]  \hspace{1cm} (3.18)

and then adopting the zeroth order approximation given by equation (3.17). That is

\[ g(r) = y_0(r) \exp[-\beta u(r)] \]  \hspace{1cm} (3.19)
3.3 Adhesive Hard Sphere Reference System

The zeroth order WCA approximation for the radial distribution function gives excellent results for the Lennard-Jones system at reduced density $\rho^* = \rho_0^3$ above 0.7 in the liquid regime. This reflects the fact that the liquid structure at high densities is indeed dominated by repulsive forces. However, as the density is reduced the attractive interparticle interactions become more and more important and this simple approximation breaks down [50,51]. A rigorous many body theory, the Optimized Cluster theory, has been developed to correct this deficiency but the formalism is very cumbersome and is difficult to implement [33].

It would be interesting to have a reference system, the radial distribution function of which is known, that contains some information about the attractive forces and could be used successfully in the zeroth order approximation.

As a first step in a search for such a reference system we consider the adhesive hard spheres discussed in section 2.3.2 of chapter 2. It has already been pointed out that the Percus-Yevick solution for this system has a compressibility equation of state that is qualitatively similar to the compressibility equation of state for the Lennard-Jones 6-12 potential obtained from the numerical solution of the Percus-Yevick equation.

This suggests that it might well be useful as a starting point in a perturbation study since the phase transition would be already present in the reference system.

Thus the reference system we now use is described by the Boltzmann factor

$$e_{AS}(r) = \exp(-\beta u_{AS}(r)) = \begin{cases} \frac{R}{12r} \delta(r-R) & r < R \\ 0 & r > R \end{cases}$$

and is completely determined by assigning values to the
particle diameter \( R \), and the temperature parameter \( \tau \). The subscript "AS" hereafter refers to adhesive hard spheres.

Application to the Lennard-Jones 6-12 Potential

The first calculations presented for the 6-12 potential are the correlation functions obtained by choosing \( R \) and \( \tau \) in such a way as to have equation (3.18) satisfied together with the requirement that the second virial coefficients of the two systems be equivalent.

Equating virial coefficients we have

\[
\int_0^\infty r^2 \left[ \exp(-\beta u_{LJ}(r)) - 1 \right] dr = \int_0^\infty r^2 \left[ e_{AS}(r) - 1 \right] dr
\]

Substituting equation (3.20) into the right hand side of this expression and performing the integrations then yields

\[
\frac{1}{12\tau} = \frac{1}{3} + \left( \frac{\delta}{R} \right)^3 B_{2}^{LJ}
\]

where the non-dimensional quantity \( B_{2}^{LJ} \) is given by

\[
B_{2}^{LJ} = \int_0^\infty x^2 \left[ \exp(-\beta u_{LJ}(x)) - 1 \right] dx
\]

and

\[
u_{LJ}(x) = 4\epsilon \left[ \left( \frac{1}{x} \right)^{12} - \left( \frac{1}{x} \right)^6 \right]
\]

with \( x = r/\sigma \)

To obtain a more convenient expression for equation (3.19) we first rewrite it in the form

\[
\int_0^\infty r^2 y_{AS}(r) \left[ \exp(-\beta u_{LJ}(r)) - 1 \right] dr = \int_0^\infty r^2 y_{AS}(r) \left[ e_{AS}(r) - 1 \right] dr
\]

The adhesive hard sphere correlation functions are taken to be those given by the solution of the Percus-Yevick equation. (see chapter 2, section 2.3.2).
From the Percus-Yevick equation we have
\[ \gamma_{AS}(r) = g_{AS}(r) - c_{AS}(r) \]

For adhesive hard spheres
\[ g_{AS}(r) = \frac{\lambda R}{12} \delta(r-R) \quad r < R \]
and
\[ \gamma_{AS}(R) = \lambda \tau \quad \text{(finite)} \]
from which it is evident that in the neighbourhood of \( r = R \)
\[ c_{AS}(r) \sim \frac{\lambda R}{12} \delta(r-R) \]

Substituting equation (3.20) into equation (3.22) we obtain
\[ \int_0^\infty r^2 \gamma_{AS}(r)[\exp(-\beta u_{LJ}(r))-1]dr = -\int_0^\infty r^2 \gamma_{AS}(r)dr + R^3 \frac{\gamma_{AS}(R)}{12\tau} \]
This may be conveniently written in the form
\[ \int_0^\infty r^2 \gamma_{AS}[\exp(-\beta u_{LJ}(r))-1]dr = -\int_0^\infty r^2 \gamma_{AS}(r)dr + R^3 \frac{\lambda}{12} \]
From the PY equation
\[ \gamma_{AS}(r) = -c_{AS}(r) \quad r < R \]
\[ c_{AS}(r) = 0 \quad r > R \]
which now enables us to write
\[ \int_0^\infty r^2 \gamma_{AS}[\exp(-\beta u_{LJ}(r))-1]dr = \int_0^\infty r^2 c_{AS}(r)dr \quad (3.23) \]

To evaluate the right hand side of equation (3.23) we now recall the results of the Percus-Yevick solution.

If we define the function \( C_{AS}(r) \) by
\[ C_{AS}(r) = \int_r^\infty t c_{AS}(t) \, dt \]
then the three dimensional Fourier transform of \( c_{AS}(r) \) may be written
\[ \tilde{c}(k) = 4\pi \int_0^\infty dr \cos kr c_{AS}(r) \]
\[ = 4\pi \int_0^\infty dr \cos kr [\int_r^\infty t c_{AS}(t) dt] \]

Integrating by parts yields
\[ \hat{c}(k) = 4\pi \int_0^\infty \frac{\sin kr}{kr} r^2 c_{AS}(r) dr \]

Taking the limit \( k \to 0 \) we then have
\[ \hat{c}(0) = 4\pi \int_0^\infty r^2 c_{AS}(r) dr \]

From the finite transformation method (chapter 2, section 3.1) the function \( \hat{Q}(k) \) is related to \( \hat{c}(k) \) by
\[ \hat{Q}(k)\hat{Q}(-k) = 1 - \rho \hat{c}(k) \]

Thus
\[ [\hat{Q}(0)]^2 = 1 - \rho \hat{c}(0) \]
\[ = 1 - 4\pi \rho \int_0^\infty r^2 c_{AS}(r) dr \]

We may rearrange this to obtain
\[ \int_0^\infty r^2 c_{AS}(r) dr = [1-\hat{Q}(0)^2]/4\pi \rho \]

Substituting into equation (3.23) now yields
\[ \int_0^\infty r^2 y_{AS}[\exp(-\beta u_{LJ}(r))-1] dr = [1-A^2]/24\eta \quad (3.24) \]

where for the adhesive sphere system
\[ A = \hat{Q}(0) = (1+2\eta-\mu)/(1-\eta)^2 \]
\[ \mu = \lambda \eta(1-\eta) \]
\[ \eta = \frac{\pi}{6\rho R^3} \]

Equations (3.21) and (3.24) provide the two criteria necessary for relating \( R \) and \( \tau \) to the temperature \( T \) and the distance scaling parameter \( \sigma \) for the Lennard-Jones system.

Results for the Lennard-Jones 6-12 Potential

Figure (3.4) contains the radial distribution functions
\( g_{\text{LJ}}(r) \) obtained according to the above procedure for the Lennard Jones potential at reduced temperature \( T^* = 1.25 \).

The values of the density \( \rho^* = \rho_0^3 \) are indicated for each curve. Figure (3.5) shows the corresponding reference system radial distribution functions \( g_{\text{AS}}(r) \). The functions \( y_{\text{AS}}(r) \) are displayed in figure (3.6). The relevant parameters calculated so as to satisfy equations (3.21) and (3.24) are listed in table (3.1).

Table 3.1 Adhesive hard sphere reference system parameters calculated for the Lennard-Jones potential at \( T^* = 1.25 \)

<table>
<thead>
<tr>
<th>( R/\sigma )</th>
<th>( \tau )</th>
<th>( \eta )</th>
<th>( \rho^* )</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.152</td>
<td>.1087</td>
<td>.4803</td>
<td>.6</td>
<td>5.7</td>
</tr>
<tr>
<td>1.1004</td>
<td>.1033</td>
<td>.48837</td>
<td>.7</td>
<td>5.806</td>
</tr>
<tr>
<td>1.063</td>
<td>.0941</td>
<td>.503</td>
<td>.8</td>
<td>5.89</td>
</tr>
<tr>
<td>1.032</td>
<td>.089</td>
<td>.518</td>
<td>.9</td>
<td>5.98</td>
</tr>
</tbody>
</table>

The behaviour of the L-J radial distribution functions (fig 3.4) can be explained by looking more closely at the behaviour of the reference system.

In the reference system the average number of particles adhering to the central particle at \( r = 0 \) is given by [34]
\[ N_{AV} = \lim_{\epsilon \to 0} \left\{ 4\pi \int_{R-\epsilon}^{R+\epsilon} \rho r^2 g_{AS}(r) \, dr \right\} \]
\[ = 4\pi R^3 \rho \lambda /12 \]
\[ = 2\eta \lambda \]

From the values of \( \eta \) and \( \lambda \) in table 3.1, it can be seen that \( N_{AV} \) increases with increasing \( \rho^* \). This must be accompanied by an increase in the number of particles excluded from the vicinity of the central particle. Consequently the profile of \( g_{AS}(r) \) will be lowered near \( r = R/\sigma \) and lifted further out at the second ring of nearest neighbours near \( r = 1 + R/\sigma \). The resulting "rotation" of the \( g_{AS}(r) \) and \( y_{AS}(r) \) profiles can be seen in figures (3.5) and (3.6).

The effect of the increased adhesion on \( y_{AS}(r/\sigma) \) is to move the cusp at \( r = R/\sigma \) lower and inwards (fig. 3.6). This must happen since \( y_{AS}(r/\sigma) \) is continuous at \( r = R/\sigma \). The result of multiplying the \( y_{AS} \) functions by \( \exp[-\beta u_{LJ}(r)] \) is then to show a reduction in the height of the \( g_{LJ} \) peaks with density.

Thus it can be seen that for the density range considered the adhesive hard sphere reference system predicts the wrong density dependence of the radial distribution function. In reality the Lennard-Jones radial distribution function peaks increase with increasing density at constant temperature, the high density structure being dominated by the repulsive forces[30]. If the adhesive hard sphere system is to be useful in describing the Lennard-Jones structure with respect to density then the values of \( \tau \) found from equations (3.21) and (3.24) need to increase with density indicating a tendency toward the hard sphere limit (\( \tau = \infty \), \( \lambda = 0 \)).
Fig 3.4 Perturbation theory radial distribution functions for the Lennard-Jones 6-12 potential using the Ashesive Hard Sphere reference system.
Fig 3.5  Reference system radial distribution functions for fig 3.4,
(i.e. Adhesive Hard Spheres )

\[ g(r) \]

\[ r/\sigma \]

\[ \rho^* = 0.6 \]
\[ \rho^* = 0.7 \]
\[ \rho^* = 0.8 \]
\[ \rho^* = 0.9 \]

\[ T^* = 1.25 \]
Fig 3.6. The function $y_{AS}(r/\sigma)$ used in calculating the radial distribution functions in fig 3.4.

$T^* = 1.25$

$\rho^* = 0.6$  
$\rho^* = 0.7$  
$\rho^* = 0.8$  
$\rho^* = 0.9$
3.4 Perturbation Theory for Soft Core Potentials

For very soft potentials such as the inverse twelfth power potential [35], repulsive potentials characteristic of liquid metals and the "angle averaged" potentials arising in the perturbation theory of angle dependent systems [36], the hard sphere reference system has shown to be inadequate.

The reason for this is best seen by examining the bahaviour of the blip function \( B(r) \). In figure (3.7) \( B(r) \) is shown schematically for a harsh repulsive potential and a soft repulsive potential when the reference system is the hard sphere system. In both cases the parameters \( \xi \) represent the range over which \( B(r) \) is non-zero. WCA [31] showed that the first order corrections to equation (3.19) are of order \( \xi^2 \). For the case of the steep repulsive potential the Boltzmann factor rises from zero to one over a very short range. From the definition of the blip function it will be non-zero over a similarly short range. Thus the parameter \( \xi_H \) will be small and corrections to equation (3.19) unimportant. However, in the case of the softer potential the Boltzmann factor takes much longer to approach its limit value of 1. Consequently \( B(r) \) is non-zero over a much wider range \( \xi_S \). Increasing the softness increases the value of \( \xi_S \) and thus first order corrections to equation (3.19) become more significant.

Another source of error lies in the values of \( d \), the effective hard sphere diameter obtained from equation (3.18). The function \( B(r) \) in general encloses an area above and an area below the r-axis. Equation (3.18) is satisfied by the value of \( d \) making these two areas equal. For harsh repulsions such as the repulsive part of the Lannard Jones potential the Boltzmann factor is almost symmetric about the characteristic length scale...
Fig 3.7  Schematic representation of the blip function $B(r)$ for purely repulsive potentials using the hard sphere reference system.
\( \sigma \) and as a result \( d \) is found to be close to \( \sigma \). Thus the reduced density in the reference system and the real system are roughly the same. However, for softer repulsions (fig. 3.7b) the value of \( d \), needed to make the areas \( B \) and \( B' \) equal, is displaced to the right. This means that the reduced density in the reference system may be so large that the PY results cannot be used accurately. In the case of the inverse twelfth power potential the structure is grossly overestimated in comparison to the Monte Carlo simulations.[35], [37].

To improve the zeroth order results a more accurate treatment of the reference system is needed and it is to this problem we now turn. In order to proceed we adopt as the reference system the fluid defined by the parametric correlation function on page (44) of chapter 2. That is, the reference system indirect correlation function is taken to be

\[
 h_0(x) = -1 + \sum_{i=1}^{M} \alpha_i \lambda_i^2 \left\{ \frac{\sinh \lambda_i x}{\lambda_i x} - 1 \right\} / \cosh \lambda_i \quad x < 1 \quad (3.25)
\]

where \( x = r/R \)

We assume that the direct correlation \( c_o(x) \) vanishes for \( x > 1 \).

\[
 c_o(x) = 0 \quad x > 1 .
\]

The direct correlation for \( x < 1 \) and the indirect correlations for \( x > 1 \) are then obtained using the finite range transformation (Section 2.3.1 page 39). The potential for the reference system may then be approximated using the PY approximation

\[
 \beta \phi_o(x) = \log \left\{ 1 - c_o(x) / (1 + h_o(x)) \right\} \quad (3.26)
\]
Application to the Truncated Lennard Jones Potential

We first apply this system to the Lennard Jones potential truncated at its first zero given by

\[ u_{LJ}(r) = 4\varepsilon \{ (\sigma/r)^{12} - (\sigma/r)^6 \} \quad r < \sigma \]
\[ = 0 \quad r > \sigma \]

To describe this system we consider equation (3.25) with \( M = 1 \). There are now two parameters \( \alpha \) and \( \lambda \) which can be used to relate the two systems. For convenience we choose \( R = \sigma \) ensuring that the cusp in the real system and reference system correlation functions occur at the same point.

In order to determine \( \alpha \) and \( \lambda \) we must stipulate two conditions. The first is given by the blip function approximation, equation (3.18), thus giving us a thermodynamic link between the two systems. The second condition is provided by the finite range transformation, requiring \( h_0(x) \) to be continuous at \( x = 1 \). Recalling equation (3.11) on page 40 and differentiating we obtain after scaling with respect to \( R \)

\[ xh_0(x) = -Q'(x) + 12\pi \int_0^1 (x-t)h(|x-t|)Q(t)dt \quad (3.27) \]

where

\[ Q(x) = Q_1 + Q_2 x + Q_3 x^2 + Q_{11} \cosh \lambda x + Q_{12} \sinh \lambda x \]

the coefficients \( Q_i \) being functions of \( \alpha \) and \( \lambda \). Inspecting equation (3.27) and using the result \( Q'(x) = Q(x) = 0, x > 1 \) we see that \( h_0(x) \) will be continuous if and only if \( Q'(x) \) is continuous. This means we must have

\[ Q'(1) = 0 \quad (3.28) \]

The parameters \( \alpha \) and \( \lambda \) now may be determined by numerically solving equations (3.18) and (3.28).
The numerical method used to solve these equations is an iterative one. First a starting value \( \alpha \) is chosen then equation (3.28) is solved to obtain an initial value of \( \lambda \). This may be done using a Newton-Raphson technique. For each iteration of \( \lambda \) at given \( \alpha \) the coefficients \( Q_i \) may be determined by solving either equations C1 to C4 of appendix C or equations D2 to D5 of appendix D in the case that \( \lambda \) is large (typically greater than 12). This was done using a Gauss elimination process.

Having determined \( \lambda \) and thus \( Q_i \) for the initial value of \( \alpha \) the direct correlation function \( c_0(x) \) and the PY potential may be computed on a grid of \( N \) points on the interval \( 0 \leq x \leq 1 \). The blip function integral is then calculated numerically using Simpson's rule.

Selecting a new value of \( \alpha \) the process is repeated, comparing the blip function integral with zero at each step. Iterating so that the blip function integral differs from zero by less than \( 10^{-4} \) requires about 30 seconds c.p.u on an IMB 360 computer.

Having obtained the required values of \( \alpha \) and \( \lambda \) the indirect correlation function \( h_0(x) \) may be evaluated for \( x > 1 \) by applying the trapezoidal rule integration scheme of Perram [21] to equation (3.27) and \( c_0(x) \) is obtained analytically from equation (3.9) on page 40 of chapter 2.

The radial distribution function for the truncated Lennard Jones potential is then approximated by

\[
g_{LJ}(x) = (1+h_0(x))\exp(-u_{LJ}(x)) \quad x > 1
\]
\[
= -c_0(r)\exp(-u_{LJ}(x)) \quad x < 1
\]

(3.29)
Results for the Truncated Lennard Jones Potential

The radial distribution functions generated using the above procedure are displayed in figure (3.8) at reduced density \( \rho R^3 = 0.86 \). The reduced temperature for each curve is indicated. The corresponding values of the parameters \( \alpha \) and \( \lambda \) are listed in table (3.2).

Table 3.2  Values of the constants \( \alpha \) and \( \lambda \) used in calculating the correlations in figure (3.8) and satisfying equations (3.18) and (3.28)

<table>
<thead>
<tr>
<th>( T^* = kT/\varepsilon )</th>
<th>( \alpha )</th>
<th>( \lambda )</th>
<th>( \eta = 0.45 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>.1735</td>
<td>12.403</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>.1513</td>
<td>15.92</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>.1264</td>
<td>21.34</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>.09</td>
<td>34.55</td>
<td></td>
</tr>
</tbody>
</table>

For the range of temperatures given the values of \( \lambda \) were all found to be greater than 12. It was thus necessary to use the appendix D equations to evaluate the coefficients of the function \( Q(x) \) accurately.

It can be seen from figure (3.8) that the qualitative description of the truncated Lennard Jones system using the present method is correct. As \( T^* \) increases the first peak in \( g_{LJ}(r) \) decreases and the oscillations become less pronounced.

As a first indication of the quantitative accuracy we may look at the blip functions \( B(r) \) for each curve. These are shown in figure (3.9). From these plots it can be seen that the most accurate radial distribution functions should be those at the lower temperatures. For \( T^* < 2 \) corrections to the zeroth order
approximation, equation (3.29), should be in the second decimal place. As the temperature is increased the non-zero width of $B(r)$ increases indicating the increased importance of first order corrections.

The reason for this lies in the nature of the PY potentials for the reference system which are used to calculate $B(r)$. These are shown in figure (3.10).

For the higher temperatures they are too soft and should only be useful in describing potentials that are not as harshly repulsive as the truncated Lennard Jones potential. For example at $T^* = 3.2$ the Boltzmann factor for the Lennard Jones system at $r = 0.8R$ is $1.5 \times 10^{-6}$ so that the only non-zero contribution to $B(r)$ comes from the reference system in which the Boltzmann factor is $3 \times 10^{-2}$, too large for a description of harsh interparticle repulsions. However, at low temperature the width of $B(r)$ becomes smaller and the results of the zeroth order approximation should become more accurate.

To show the usefulness of this method at low temperatures we now look at the state $T^* = 1$ and $\rho^* = 0.85$ for which Monte Carlo results are available. For this state the reference system parameters are found to be $\alpha = 0.0885$ and $\lambda = 34.6$. The radial distribution function obtained using equation (3.29) is compared in figure (3.11) with the Monte Carlo simulation reported by Kohler, Perram and White [38]. The agreement is excellent.
Fig 3.8 Perturbation theory radial distribution functions for the Lennard-Jones potential (truncated) at reduced density $= 0.86$
Fig 3.9 Blip Functions $B(r)$ for the truncated Lennard-Jones potential using the parametric reference system (equation (3.25)) $\rho^* = 0.86$
Fig 3.10 Comparison of the reference system PY potentials with the truncated Lennard Jones potentials for the curves in figs. (3.8) and (3.9)
Circles 

(r) using eqn. (3).

At T*=1.0 and p*=0.85 for the perturbation theory for the above

The 3.11 results for the above

Monte Carlo results of Kohn's perturbation

Py hard sphere g(r) at p*=0.85 ref. [38]
REFERENCES for Chapters 2 and 3.


[21] Perram, J.W., Molecular Physics, 30, 1505 (1975)


[25] Rowlinson, J.S., Molecular Physics 8, 107 (1964)


Appendix A

\[ I(t) = \delta \int_{1}^{t} \frac{dt}{(1-t)\sqrt{(1-t^2)(1-\delta^2 t^2)}} \quad (A1) \]

Introducing the variable by

\[ \sin^2 \psi = \frac{2\delta}{1+\delta} \left[ \frac{1+t}{1+\delta t} \right] \]

we have

\[ dt = \left( \frac{1-\delta^2}{\delta^2} \right) \frac{\sin \psi \cos \psi \, d\psi}{\left[ 1-\left( \frac{1+\delta}{2} \right)^2 \sin^2 \psi \right]^2} \]

\[ 1+t = \left( \frac{1-\delta^2}{2\delta} \right) \frac{\sin^2 \psi}{\left[ 1-\left( \frac{1+\delta}{2} \right)^2 \sin^2 \psi \right]} \]

\[ 1-\delta t = \frac{(1+\delta) \cos^2 \psi}{\left[ 1-\left( \frac{1+\delta}{2} \right)^2 \sin^2 \psi \right]} \]

\[ 1+\delta t = \frac{(1-\delta)}{\left[ 1-\frac{1+\delta}{2} \sin^2 \psi \right]} \]

Substituting into the integral (A1) then yields

\[ I = \sqrt{\frac{\delta}{2}} \int_{0}^{\psi} \frac{[1 - \frac{1+\delta}{2\delta} \sin^2 \psi]}{\left[ 1-(1+\delta)^2 \sin^2 \psi \right]^{1/2} \left[ 1-(\frac{1+\delta}{2})^2 \sin^2 \psi \right]} \, d\psi \quad (A2) \]

This may be cast into a standard form via the transformation

\[ \sin \psi = sn(u,k^2) = sn u \]

where \( sn u \) is the Jacobi \( sn \) function with argument

\[ u = F(\psi,k^2) \]

and \( F(\psi,k^2) \) is the elliptic integral of the first kind with modulus

\[ k^2 = (1+\delta)/2 \]
Thus
\[ \cos \psi \, d\psi = \text{cn} \, u \, \text{dn} \, u \, du \]

where
\[ \text{cn} \, u = \sqrt{1-\text{sn}^2 u} = \cos \psi \]

and
\[ \text{dn} \, u = \sqrt{1-k^2 \text{sn}^2 u} \]

The integral \( A_2 \) now may be written
\[
I = \sqrt{\frac{\delta}{2}} \int_{0}^{u} \frac{1-\alpha^2 \text{sn}^2 u}{1-\alpha^2 \text{sn}^2 u} \, du \tag{A3}
\]

with
\[
\alpha_1^2 = \frac{(1+\delta)}{2\delta} \\
\alpha_2^2 = \frac{(1+\delta)^2}{4\delta}
\]
Functional Differentiation and Functional Taylor Series

If we consider the quantity

$$G = \int_{x_0}^{x_n} f(x, y(x)) \, dx$$

then we see that $G$ depends on the function $y(x)$ and all of its arguments, namely the infinity of $x$ values in the interval $[x_0, x_n]$. We say $G$ is a functional of $y$.

Any variation $\delta y(x)$ in the function $y(x)$ will cause a corresponding variation $\delta G$ in $G$ and we may write

$$G + \delta G = \int_{x_0}^{x_n} f(x, y(x) + \delta y(x)) \, dx \quad (B1)$$

If we consider a component of $f$ to be $f(x_i, y(x_i))$ evaluated at the point $x_i$ then we see there are infinitely many such components in the interval $[x_0, x_n]$. For each of these components we may form the Taylor series

$$f(x_i, y(x_i) + \delta y(x_i)) = f(x_i, y(x_i)) + \frac{\partial f}{\partial y} \bigg|_{y=y(x_i)} \delta y(x_i) + \ldots$$

Then from equation (B1)

$$G + \delta G = \int_{x_0}^{x_n} f(x, y(x)) \, dx + \int_{x_0}^{x_n} \frac{\partial f}{\partial y} \bigg|_{y=y(x)} \delta y(x) \, dx + \ldots$$

For an infinitesimal variation $\delta y(x)$ we have

$$\delta G = \int_{x_0}^{x_n} \frac{\partial f}{\partial y} \bigg|_{y=y(x)} \delta y(x) \, dx = \int_{x_0}^{x_n} \frac{\partial G}{\partial y} \delta y(x) \, dx$$

which defines the first functional derivative of $G$ with respect to $y(x)$ viz.
\[
\frac{\delta G}{\delta y(x)} = \frac{\delta f}{\delta y} \bigg|_{y=y(x)} \tag{B2}
\]

To obtain the functional of a functional rule let

\[
y(x) = \int_{t_0}^{t} g(t, z(t)) dt
\]

then

\[
\delta y(x) = \int_{t_0}^{t} \frac{\delta y(x)}{\delta z(t)} \delta z(t) dt
\]

and

\[
\delta G = \int_{x_0}^{x} \int_{t_0}^{t} \frac{\delta G}{\delta y(x)} \frac{\delta y(x)}{\delta t} \delta z(t) dt \ dx
\]

from which

\[
\frac{\delta G}{\delta z(t)} = \int_{x_0}^{x} \frac{\delta G}{\delta y(x)} \frac{\delta y(x)}{\delta z(t)} dx
\]

An important special case occurs if we let \( G = z(r) \) giving

\[
\delta z(r) = \int_{x_0}^{x} \int_{t_0}^{t} \frac{\delta G}{\delta y(x)} \frac{\delta y(x)}{\delta z(t)} \delta z(t) dt \ dx
\]

which implies that the Dirac delta function is given by

\[
\delta (r-t) = \int_{x_0}^{x} \delta r \frac{\delta x(r)}{\delta y(x)} \cdot \frac{\delta y(x)}{\delta z(t)} dt
\]

The notion of a functional Taylor series is a generalization of the Taylor series for a function of \( n \) variables \( f(x_1, \ldots, x_n) \) given by

\[
f(x_1, \ldots, x_n) = f(a_1, \ldots, a_n) + \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} \bigg|_{x=a} (x_i-a_i) + \ldots
\]

For a functional \( f \) of a function \( y(x) \) the summation of the \( n \) discrete vector components becomes an integral of the infinite number of components and the partial derivatives become functional derivatives. We thus have

\[
f(x, y(x) + \delta y(x)) = f(x, y(x)) + \int_{x_0}^{x} \frac{\delta f}{\delta y(x)} \bigg|_{y=y(x)} \delta y(x) \ dx + \ldots
\]
Appendix C

Explicit expressions for equations (3.26)

\[-Q_2 \left( \frac{1}{6} \gamma_1 \right) - \frac{1}{4} Q_3 + \sum_{j=1}^{M} \left[ Q_{j1} (C_j^1 - \frac{1}{2} \cosh \lambda_j) + Q_{j2} (S_j^1 - \frac{1}{2} \sinh \lambda_j) \right] = 0 \quad (C1)\]

\[-Q_2 + 2 \left( \frac{1}{6} - \frac{1}{3} \right) Q_3 + \sum_{j=1}^{M} \left[ Q_{j1} (C_j^0 - \cosh \lambda_j) + Q_{j2} (S_j^0 - \sinh \lambda_j) \right] = \frac{1}{12} \pi \quad (C2)\]

\[Q_2 (C_i^1 - C_i^0) + Q_3 (C_i^2 - C_i^0) + \sum_{j=1}^{M} \left[ Q_{j1} (C_j^i - \cosh \lambda_j C_i^0 - \frac{\delta_{ij}}{a_j}) + Q_{j2} (S_j^i - \sinh \lambda_j C_i^0) \right] = \frac{1}{12} \pi \quad i = 1, M \quad (C3)\]

\[Q_2 (S_i^1 - S_i^0) + Q_3 (S_i^2 - S_i^0) + \sum_{j=1}^{M} \left[ Q_{j1} (C_j^i - \cosh \lambda_j S_i^0) + Q_{j2} (S_j^i - \sinh \lambda_j S_i^0 + \frac{\delta_{ij}}{a_j}) \right] = 0 \quad i = 1, M \quad (C4)\]

where

\[
\begin{align*}
C_i^n & = \int_0^1 t^n \left\{ \cosh \lambda_i t \right\} dt \\
S_i^n & = \int_0^1 t^n \left\{ \sinh \lambda_i t \right\} dt
\end{align*}
\]

(C5)
and
\[
\begin{align*}
\mathbf{C}_{ij} & = \int_0^1 \begin{pmatrix} \cosh \lambda_j t & \cosh \lambda_i t \\ \cosh \lambda_i t & \sinh \lambda_j t \end{pmatrix} dt \\
\mathbf{S}_{ij} & = \begin{pmatrix} \sinh \lambda_i t & \sinh \lambda_j t \end{pmatrix} \\
\end{align*}
\]

\[a_i = 12\pi \Delta_i\]
\[\gamma_1 = 12\pi \gamma\]
\[\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}\]
Well conditioned form of equations c1 - c4 for large $\lambda$

For large $\lambda$ we have from equations c6 and c7 that

$$C_i^n \approx S_i^n$$

and

$$C_{ij}^i \approx CS_{ij}^i \approx SS_{ij}^i$$

In addition we see that the influence of $\delta_{ij}/a_j$ on the other terms in the coefficients where it appears in equations c3 and c4 is negligible. Consequently the coefficient of $Q_{j1}$ and $Q_{j2}$ in each of equations c1 to c4 become approximately equal resulting in a set of equations that is ill conditioned, the determinant being very close to zero. Thus for large $\lambda$ accurate solution using Gauss elimination is not possible.

To overcome this difficulty we may perform the following algebraic manipulations to transform the equations into a well conditioned set. The new equations are presented for the case $M = 1$.

First, we subtract equation c3 from equation c4 and then introduce the new variables $x$ and $y$ through

$$Q_{11} = x$$
$$Q_{12} = -x+y$$

Thus we obtain

$$Q_2 \left[ \frac{1}{\lambda} - \frac{1}{\lambda^2} e^{-\lambda} \right] + Q_3 \left[ \frac{1}{\lambda} \frac{2}{\lambda^2} + 2e^{-\lambda} (\frac{1}{\lambda} - 1) \right] + x \left( \frac{1}{2\lambda} e^{-\lambda} e^{-2\lambda} \right) + (e^\lambda y) \left[ \frac{1}{\lambda} \left( \frac{1}{12\eta} \right) - \frac{e^{-\lambda}}{2} (\frac{1}{2}) e^{-2\lambda} \frac{1}{12\eta} + \frac{1}{4\lambda} \right]$$

$$= - \frac{1}{12\eta}$$

(D2)
If we now add equations c3 and c4 and again use D1 and then divide by $e^\lambda$ we obtain

$$Q_2\left[\frac{1}{\lambda^2}e^{-\lambda}(1+\frac{1}{\lambda^2})\right]+Q_3\left[\frac{2}{\lambda^2}(\lambda-1)+e^{-\lambda}(1-\frac{2}{\lambda^2})\right]+x\left[\frac{1}{\lambda^2}\right]+e^{-\lambda}(1-\frac{1}{\lambda})+e^{-2\lambda}(1-\frac{1}{\lambda})$$

$$(\lambda+1\right)+e^{-3\lambda}(1-\frac{1}{\lambda})$$

$$= \frac{e^{-\lambda}}{12\eta} \quad (D3)$$

Introducing the new variables given by equation D1 into equations C1 and C2 then yields

$$Q_2\left(-\frac{1}{6}\right)-Q_3\left(\frac{1}{4}\right)+x\left[\frac{1}{\lambda^2}e^{-\lambda}(1+\frac{1}{\lambda^2}-\frac{1}{2})\right]+(e^\lambda x)^2\left[\frac{1}{2}(\frac{1}{\lambda^2}-\frac{1}{2})+\frac{e^{-2\lambda}}{2}(1+\frac{1}{\lambda^2})\right] = 0$$

$$Q_2\left(-\frac{1}{2}\right)+Q_3\left(\frac{1}{6}\right)+x\left[\frac{1}{\lambda^2}e^{-\lambda}(1+\frac{1}{\lambda})\right]+(e^\lambda x)^2\left[\frac{1}{2}(\lambda+1)\frac{e^{-\lambda}}{\lambda}+\frac{e^{-2\lambda}}{2}(1+\frac{1}{\lambda})\right] = \frac{1}{12\eta} \quad (D4)$$

We now have four equations which must be solved to obtain the quantities $Q_2$, $Q_3$, $x$ and $e^\lambda y$. By inspecting the coefficients we now see that for large $\lambda$ the determinant is no longer close to zero. Thus we may now employ the Gauss elimination method. In passing we note that the effect of a is no longer nullified as it was in the equations of appendix C. It now appears in the largest contribution to the coefficients of $e^\lambda y$ in equation D2 and $x$ in equation D3.

Further comment should be given here on the accurate calculation of $c_0(r)$. In order to evaluate the functions $Q(r)$ and $Q'(r)$ accurately it is now necessary to use the form

$$Q(r) = Q_1 + Q_2 r + Q_3 r^2 + x e^{-\lambda r} \frac{e^\lambda y}{2} (e^\lambda(r-1) - e^{-\lambda(r+1)}) \quad (D6)$$

The analytic form of $c_0(r)$ was then calculated by
substituting equation (D6) into equation (3.9) of chapter 2. This should be done in order to have accurate values of $c_o(r)$ and hence $y_o(r)$ in the vicinity of $r = R$ where the major contribution to the blip function integral occurs.