Studies on the structure and thermodynamics of electrolyte solutions

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by

Pelin Gevher Özler

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1 INTRODUCTION

There are mainly two methods for the prediction of the thermodynamic properties of fluid mixtures. A common chemical engineering approach is to employ empirical or semiempirical methods that involve several experimentally determined parameters. However, it is impracticable to obtain a large amount of experimental data to evaluate the adjustable parameters for pure substances and certain empirical mixing rules have to be involved to predict the properties of mixtures. Although the existing results are useful in correlation or interpolation, it is generally not possible to extrapolate them. Serious errors may occur if it is attempted to extrapolate the results to temperatures and pressures beyond the experimental range. Also, this method has proved difficult to apply to systems containing highly polar or associating molecules or to very high pressures. On the other hand, it may be possible to overcome some of the above mentioned difficulties by using theoretical methods that are based on statistical thermodynamics.

Theoretical studies on electrolyte solutions aim to develop a relationship between the intermolecular potential and various thermodynamic properties such as internal energy, compressibility, chemical potential or structural properties such as the distribution of ions or solvent molecules in solution. These methods may require certain general assumptions about the electrolyte model:
1. The rigid molecule assumption: The intermolecular potential energy depends only on the positions of the centers of mass and on the orientations of the molecules.

2. The classical fluid assumption: The quantum effects in the translational and rotational motions of the molecules are negligible.

3. Pairwise additivity assumption: The total intermolecular potential energy is the sum of the intermolecular potentials for each pair of molecules (effective pair potential).

4. Nature of the solvent molecules: In some studies the discrete nature of the solvent molecules is omitted.

In addition to these, an assumption about a higher order distribution function must be made. This step is called a 'closure approximation' in integral equation theories and a 'superposition approximation' in perturbation theories. Therefore, when theoretical results are compared with experimental results, it is difficult to conclude whether the source of the discrepancy is a weakness in the potential model or the particular closure approximation employed in the calculations. Computer simulation methods, which do not involve any further mathematical approximation beyond the potential model, provide a connection between theory and experiment. A comparison between theoretical and simulation results gives information about the validity of the mathematical approximations made in the theoretical methods. A comparison between experimental and simulation results shows how realistic the potential model is for certain types of fluids.
Also, it is possible to produce thermodynamic or structural data with computer simulations which are not possible by experimental methods.
2 PREVIOUS WORK

2.1 Continuum Solvent Models

Statistical theory of ionic solutions began with the classic work of Debye and Hückel in 1923 (1). In that study, ions are assumed to be randomly distributed in the solution and are represented by points with a positive or negative charge. The solvent is represented by a continuous medium of uniform dielectric constant, \( \varepsilon_0 \). It is assumed that the ions are composed of the same dielectric continua as the solvent. In the prediction of the activity coefficients as a function of ionic strength, Debye-Hückel theory provides an exact limiting law for very dilute electrolyte solutions. For concentrations greater than 0.01 M, the type and size of the short range interactions become important, and almost all electrolytes show either positive or negative deviations from the limiting law. Debye-Hückel theory has been reviewed and modified by Mayer (2), who extended the applicability of the results up to 0.4 M, at least for 1-1 electrolytes. Mayer developed a general ionic cluster theory which gives the Debye-Hückel results as a limiting case, by neglecting some of the interaction terms.

The simplest model based on the Debye-Hückel theory is the primitive model. In contrast to Debye-Hückel theory, short range interactions are represented by the hard sphere potential. For the primitive model of an electrolyte solution, the pair
potential energy is given by;

\[
U_{\alpha\beta} = \begin{cases} 
\infty & r < (\sigma_+ + \sigma_-)/2 \\
\frac{q_+q_-}{\epsilon_0 r} & r > (\sigma_+ + \sigma_-)/2
\end{cases}
\]  

(2.1)

where \( q_+ \) and \( q_- \) are the charges on the positive and negative ions and \( \sigma_+ \) and \( \sigma_- \) are the ionic diameters respectively. The model is known as the restricted primitive model if all the ions are assumed to have the same diameter.

Integral equation methods have been applied to the primitive and the restricted primitive model of electrolyte solutions. These methods involve the simultaneous solution of the Ornstein-Zernike equation with a closure approximation such as the Percus-Yevick equation (PY), hypernetted chain equation (HNC), or mean spherical approximation (MSA). Numerical solutions of the PY and HNC equations have been obtained by Rasaiah and Friedman, who obtained a number of properties including the internal energy, the osmotic pressure and the ionic distribution functions (3-6). It has been found that the HNC equation is superior to the PY equation, at least for a 1-1 aqueous electrolyte at concentrations up to 1 M. When these results are compared with the Monte Carlo simulation results of the primitive model obtained by Card and Valleau (7), it can be said that the general agreement is quite good up to 2 M solutions. Waisman and Lebowitz have solved the MSA for the restricted primitive model analytically (8-10). For the case of no charges on spheres, this model reduces to the PY approximation for hard spheres. When the hard sphere diameter is zero, it reduces to the Debye-Hückel theory.

Another approach is an expansion for the Helmholtz free energy of a system of particles in terms of pair potentials and multibody distribution functions. The
potential energy of the system is assumed to be composed of two parts, a reference system potential and a perturbation potential. This technique has been applied to electrolyte solutions by Andersen and Chandler (11-13). The system potential is Fourier transformed and is expressed as an infinite series,

$$A = A_0 + A_1 + A_2 + A_3 + \ldots$$

(2.2)

where $A_0$ is the excess free energy of the reference system and higher order terms are determined by the perturbation potential and the distribution functions (two, three and higher order) of the reference system. This technique has been used in the calculation of the thermodynamic properties of the restricted primitive model of 1-1 electrolytes by Andersen and Chandler. Their reference potential is a hard sphere potential and the perturbation is a Coulombic potential. It has been found that the rate of convergence of the expansion integrals depends upon the type and magnitude of the perturbation potential. For smaller magnitude of perturbations, the convergence of the series is quite fast. The numerical results obtained with this approach are compared with the integral equation results of Rasaiah and Friedman (3,4), Rasaiah (5,6) and the Monte Carlo results of Card and Valleau (7). Results are found to be in good agreement, but it is noted that for high values of the ionic charge, the convergence of the expansion is not fast. Stell and Lebowitz have obtained a similar expression in terms of Debye screening length (14). The expansion is valid in the high temperature or low density limit.

Monte Carlo simulation results for electrolyte solutions have been given by Card and Valleau (7) and by Vorontsov - Vel’yaminov and El’yashevich (15,16). Most of the simulation work has been done for the restricted primitive model, the exception being that of Rasaiah and Friedman who examined the square well poten-
tial with Coulomb interactions (3-6). When theoretical results are compared with simulation results, the HNC equation, which gives good results for 1-1, 2-1, 3-1, 3-2 electrolytes for concentrations up to 2 M, seems to be the most useful approximation. However, there are slight discrepancies between the osmotic pressure data, especially at high concentrations. For 2-2 electrolytes in the primitive model, it is found that the deviations from the Debye-Hückel limiting law are in the same direction as the experimental results, although the opposite is true for 4-1 electrolytes such as $Na_4Fe(CN)_6$ unless the value of the hard sphere diameter is increased. This suggests that the short range potential may be responsible for deviations from the limiting law. In general, the PY approximation is not particularly good for electrolytes, but MSA results, if obtained from the energy equation, are in good agreement with simulation results, at least in a restricted range of concentrations. However, the MSA results obtained with the pressure equation are not good and the perturbation theory provides an excellent approximation for the primitive model electrolyte solutions.

On the other hand, when these results, including the exact Monte Carlo results for the primitive model, are compared with the experiment, the results are quite poor above concentrations greater than 0.2 M. There have been several attempts to modify the primitive model, by introducing adjustable parameters into the integral equation solutions of the primitive model. In a study by Ramanathan and Friedman, the ion-ion interaction has been modeled as a usual Coulomb term plus other terms which contain some empirical parameters that account for the short range repulsion, dielectric polarization and soft core interaction or overlapping (17). They solved the HNC equation for the primitive model and found good agreement with experimental
data for various salt solutions up to concentrations of 1 M. In another attempt to modify the primitive model, Triolo et al. introduced a density dependent dielectric constant and a density dependent ionic hard core diameter (18). The MSA equation is solved in the primitive model and satisfactory results have been reported which reproduce the experimental data for 16 alkali halides in the concentration range of 0.2-2.0 M.

In fact, the empirical parameters utilized in the interaction potential force the primitive model to predict the experimental results in an artificial way. Although it is possible to obtain good results using the primitive model with the above mentioned modifications, it does not reflect the physics of electrolyte solutions. The most important assumption involved is that the molecular nature of the solvent-solvent and solvent-ion interactions is ignored in the primitive model. This assumption may be applicable for the solutions where the sizes of the ions are much bigger than that of the solvent molecules. However, it is not valid for the case where the ions and the solvent molecules have comparable sizes.

2.2 Discrete Solvent Models

Recently there has been considerable interest in developing models for electrolyte solutions in which both the ions and the solvent molecules are treated on a molecular basis. The solvent may be water or any other highly polar substance.

2.2.1 Integral equation theory

Integral equation methods have been applied to predict the structural and thermodynamic properties of pure multipolar fluids. These efforts have been extended
to obtain a solution of the Ornstein-Zernike equation for a mixture of ions and multipoles. This equation is written as

$$h_{ij}(12) - c_{ij}(12) = \sum_k \rho_k \int c_{ik}(23) h_{kj}(13) d3$$  \hspace{1cm} (2.3)

where the subscripts stand for the mixture components. $h(12)$ is the total correlation function, which is assumed to be composed of two parts: $c(12)$ is the direct correlation function and the convolution integral is the indirect correlation function. $d3$ indicates that the integration is to be taken over the position and angular coordinates of particle three.

According to the mean spherical approximation (MSA)

$$h_{ij}(12) = \begin{cases} -1 & r_{12} < \sigma \\ c_{ij}(12) = \frac{U_{ij}(12)}{kT} & r_{12} > \sigma. \end{cases}$$  \hspace{1cm} (2.4)

In the Percus-Yevick (PY) closure

$$h_{ij}(12) = \begin{cases} 1 & r_{12} < \sigma \\ c_{ij}(12) = (h_{ij}(12) + 1)(1 - e^{-\frac{U_{ij}(12)}{kT}}) \end{cases}$$  \hspace{1cm} (2.5)

In the hypernetted-chain (HNC) closure

$$h_{ij}(12) = \begin{cases} -1 & r_{12} < \sigma \\ h_{ij}(12) = c_{ij}(12) + ln(h_{ij}(12) + 1) - \frac{U_{ij}(12)}{kT} \end{cases}$$  \hspace{1cm} (2.6)

Analytic solutions of the Ornstein-Zernike equation with the MSA closure have been obtained by Blum (19-21), Vericat and Blum (22), Hernandez and Blum (23)
and also by Adelman and Deutch (24) for a mixture of ions and dipoles with equal diameters. This method was then extended to spheres with unequal diameters by Vericat and Blum (25).

Analytic solutions of the OZ equation with HNC closure have not been found yet, but numerical solutions have been obtained for a number of polar fluids as well as primitive model electrolyte solutions. Solution of the full HNC equation for molecular fluids with angle dependent pair potentials has been described. Application of this method requires that the pair potential and the correlation functions are expandable in rotational invariants. This method was applied to pure dipolar solvents (26) and liquid crystals (27). Linearized HNC and quadratic HNC approximations, which can be obtained by making simplifying expansions of the HNC closure equation, were solved for a mixture of ions and dipoles at infinite dilution (28) and finite concentration of ions (29) by Levesque, Weis and Patey who have solved the same approximation for pure polar fluids (30-32). The direct and total pair correlation functions in eqn. (2.3) are expanded in terms of rotational invariants $\Phi^{mnl}(12)$ which are functions of the mutual angles of orientation and are expressed as;

$$
\Phi^{000}(12) = 1, \\
\Phi^{101}(12) = \hat{s}_1 \cdot \hat{r}, \\
\Phi^{011}(12) = \hat{s}_2 \cdot \hat{r}, \\
\Phi^{112}(12) = 3(\hat{s}_1 \cdot \hat{r})(\hat{s}_2 \cdot \hat{r}) - \hat{s}_1 \cdot \hat{s}_2, \\
\Phi^{110}(12) = \hat{s}_1 \cdot \hat{s}_2
$$

(2.7)

where $\hat{s}_1$ and $\hat{s}_2$ are the unit vectors in the directions of dipoles 1 and 2 and $\hat{r}$ is
the unit vector joining two particles. The result for an ion-dipole mixture is

\[ h(12) = h^{000} \Phi^{000}(12) + h^{101}(r) \Phi^{101}(12) + h^{011}(r) \Phi^{011}(12) + h^{110}(r) \Phi^{110}(12) + h^{112}(r) \Phi^{112}(12) + \ldots \]  

(2.8)

with an analogous equation for \( c(12) \). The Fourier transform of the OZ equation with the spherical harmonic expansions for the direct and indirect pair correlation functions becomes

\[ \tilde{h}_{ij} - \tilde{c}_{ij} = \sum_n \rho_n \tilde{h}_{in} c_{nj} + \rho_s \tilde{h}_{is} \tilde{c}_{js} - \frac{1}{3} \rho_s \tilde{h}_{is} \tilde{c}_{js}, \]  

(2.9)

\[ \tilde{h}_{000} - \tilde{c}_{000} = \sum_n \rho_n \tilde{h}_{in} \tilde{c}_{ns} + \rho_s \tilde{h}_{is} \tilde{c}_{ss}, \]  

(2.10)

\[ \tilde{h}_{000} - \tilde{c}_{000} = \sum_n \rho_n \tilde{h}_{in} \tilde{c}_{ns} + \rho_s \tilde{h}_{is} \tilde{c}_{ss}, \]  

(2.11)

\[ \tilde{h}_{011} - \tilde{c}_{011} = \sum_n \rho_n \tilde{h}_{in} \tilde{c}_{ns} + \frac{1}{3} \rho_s \tilde{h}_{is} \tilde{c}_{ss} + \tilde{c}_{112}, \]  

(2.12)

\[ \tilde{h}_{110} - \tilde{c}_{110} = -\frac{1}{3} \sum_n \rho_n \tilde{h}_{in} \tilde{c}_{ns} + \frac{1}{3} \rho_s (\tilde{h}_{is} \tilde{c}_{ss} + \tilde{c}_{112} \tilde{c}_{ss}), \]  

(2.13)

\[ \tilde{h}_{112} - \tilde{c}_{112} = -\frac{1}{3} \sum_n \rho_n \tilde{h}_{in} \tilde{c}_{ns} + \frac{1}{3} \rho_s (\tilde{h}_{is} \tilde{c}_{ss} + \tilde{c}_{112} \tilde{c}_{ss}), \]  

(2.14)

where \( i \) and \( j \) represent either positive or negative ions and the sum on \( n \) is over the subscripts \( + \) and \( - \). The tilde denotes the Hankel transform,

\[ \tilde{h}^{mn}(k) = 4\pi i \int_0^\infty r^2 j_i(kr) h^{mnl}(r) dr \]  

(2.15)
where \( j_l(kr) \) is the spherical Bessel function. LHNC approximation is obtained by expanding the logarithmic term in the HNC closure, i.e., eqn. (2.6), and retaining only the first order terms. The final expressions for ion-dipole mixtures are

\[
c_{\alpha\beta}^{000}(r) = e^{\gamma_{\alpha\beta}^{000}(r)} - \gamma_{\alpha\beta}^{000}(r) - 1 - \gamma_{\alpha\beta}(r) \\
\quad r < \sigma
\]

\[
c_{is}^{011}(r) = g_{is}^{000}(r)(-3\gamma_{is}^{011}(r) + \gamma_{is}^{011}(r)) - \gamma_{is}^{011} \\
\quad r < \sigma
\]

where:

\[
\gamma_{\alpha\beta}(r) = h_{\alpha\beta}(r) - c_{\alpha\beta}(r). \tag{2.20}
\]

Numerical results of LHNC theory will be compared with simulation results in Chapter 6. For the case of ion-dipole mixtures at finite ion concentrations, the solvation structure and various thermodynamic and dielectric properties were determined. It has been found that, at low ion concentrations the solution is dominated by solvated ions. This condition is more pronounced at higher ionic charges, with a decrease in the first maximum and an increase in the second maximum of the oppositely signed ion pair correlation functions. This prediction is in contrast with the primitive model solutions in which ion clustering increases with the charge of the ions.
2.2.2 Perturbation theory

Within the context of perturbation theory intermolecular forces have been usefully separated in two groups: Short range repulsive and long range attractive forces. At higher densities, the structure of the fluids is determined by short range repulsive forces, at least for simple and multipolar fluids. Perturbation theory has been used to relate the properties of a liquid to those of a purely repulsive reference fluid. Thermodynamic and structural properties such as the Helmholtz free energy, internal energy or pair correlation function of the given system are expanded in Taylor series about this reference system with known properties.

Application of the perturbation theory to the statistical mechanics of liquids started with attempts to model particles with the Lennard-Jones potential. The main question is to separate the reference and perturbation parts of the potential. The separation method adopted by McQuarrie and Katz is especially useful at high temperatures (33)

\[ U_{\text{ref}} = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} \]
\[ U_{\text{per}} = -4\varepsilon \left( \frac{\sigma}{r} \right)^6. \]

However, at low temperatures and low densities the results are not in agreement with exact results for the full Lennard Jones potential obtained with computer simulation. The error is attributed to the fact that the reference potential is much softer than the full LJ potential.

Barker and Henderson were the first to get some successful results by applying a second order perturbation expansion of the Helmholtz free energy to an LJ liquid,
where the reference and perturbation are described as (34)

\[
\begin{align*}
U_{\text{ref}} &= 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} & r < \sigma \\
&= 0 & r > \sigma \\
U_{\text{per}} &= 0 & r < \sigma \\
&= 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} & r > \sigma.
\end{align*}
\]

(2.22)

In this case the entire positive portion of the LJ potential forms the reference whereas the perturbation is the negative portion of the potential. The three body and four body distribution functions of the hard sphere fluid that appear in the second order term are replaced by pair distribution functions using the superposition approximation (35)

\[
g(123) = g(12)g(13)g(23)
\]

(2.23)

and the resulting integrals are evaluated numerically. The method has an important disadvantage of providing a very slowly converging series. It is found that the rapidly varying portion of the potential, that remains in the perturbation part, and thus puts too much emphasize on the second order term, is responsible for the slow convergence. The rate of convergence of the method was increased by Weeks, Chandler and Andersen, who considered a first order theory with the repulsive part of the LJ fluid as the reference system (36)

\[
\begin{align*}
U_{\text{ref}} &= v(r) + U_{\text{per}} & r < r_m \\
&= 0 & r > r_m \\
U_{\text{per}} &= -\varepsilon & r < r_m \\
&= v(r) & r > r_m
\end{align*}
\]

(2.24)
where

\[
\begin{align*}
-\frac{dv(r)}{dr} & > 0 & r < r_m \\
-\frac{dv(r)}{dr} & < 0 & r > r_m \\
v(r) = 4\varepsilon \left[ (\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6 \right],
\end{align*}
\]

(2.25)

\(r_m = 2^{1/6}\sigma\) is the location of the minimum of the potential function and \(\varepsilon\) is the depth of the potential well. Thus WCA separation of the potential gives rise to a rapidly convergent perturbation theory of the LJ fluid.

The development of perturbation expansions for molecular fluids is due to Barker (37) and Pople (38,39). Barker expanded the partition function for a polar fluid using an atomic fluid as the reference system. The choice of the reference system brings the advantage that the first order term in the free energy expansion vanishes. Also the higher order terms can easily be simplified. He derives an expression for the second order free energy term for a dipolar perturbation. Pople worked out the free energy terms for multipolar interaction up to quadrupoles. Barker extended his work to include polarizable dipoles (37) and Pople presented an expression for an intermolecular potential of the general multipolar form (38). The comparison of the Barker-Pople approach for the free energy, with the computer simulations and experiments has been done. Expansion to third order for a multipolar fluid yields

\[
\frac{2\beta}{N}(A - A_{ref}) = -3\rho \int d2g_{r_{ef}}(12)U_{per}(12) \\
-\frac{3^2\rho^2}{3} \int d2 \int d3g_{r_{ef}}(123)U_{per}(13).
\]

(2.26)

where \(\beta\) is the inverse of Boltzmann constant times the absolute temperature. A
third order expansion gives good results for moderately polar fluids (e.g., HCl) but diverges in the case of strong dipoles (e.g., H₂O, NH₃, acetone) and quadrupoles. The slow convergence of the series led Stell et al. to suggest a simple Padé approximant for the free energy (40). Assuming that the entire expansion forms a geometric series

\[ A = A_0 + \frac{A_2}{1 - \frac{A_3}{A_2}}. \]  

(2.27)

This approximation is found to give excellent results for very high dipole and quadrupole moments.

The perturbation expansion can also be applied to distribution functions. An exact expression for the first order perturbation term in the expansion of distribution functions of order \( m \) was first derived by Buff and Schindler (41). Weeks et al. (36), Weeks and Chandler (42) considered high density systems where attractive forces were negligible. Perturbation expansions of \( g(r) \) for a fluid having both attractive and repulsive potentials have been studied by Smith et al. (43) and Gubbins et al. (44). Later, using an approach similar to that of Pople's, a perturbation theory for the angular pair correlation function \( g(r, \omega_1, \omega_2) \) was developed by Gubbins and Gray (45).

Gubbins and Twu developed a theory for generalized Stockmayer fluids, where the reference is an LJ fluid and the perturbation includes multipolar and overlap terms. Using a Padé approximant, they obtained a number of thermodynamic properties and equilibrium phase diagrams for various fluids and fluid mixtures (46).

Thermodynamic perturbation theory with a Padé approximant has been used by Larsen and coworkers to predict the excess properties and coexistence curve for
dipolar, quadrupolar and polarizable hard spheres (47). Larsen et al. considered a perturbation theory for pure charged hard spheres at low concentrations and suggested that a mixture of ions and polarizable multipolar molecules will provide a satisfactory description of real ionic solutions. It has been noted by Henderson and Blum that rearrangement of terms in second order perturbation theory for pure charged hard spheres may give rise to some convergent results, but numerical results have not been obtained yet (48).

Henderson et al. derived a third order perturbation theory for a mixture of ions and dipolar hard spheres (49). It has been noted that the resulting expression has a form similar to the analytic results derived by Blum using the MSA at low concentrations (19-23). The expression reduces to the Stell-Lebowitz expansion for pure charged hard spheres at vanishing dipole concentrations (14). However, no numerical results for this theory have been presented yet. In Chapter 5, the theory developed by HBT (Henderson-Blum-Tani) will be examined in more details.

2.2.3 Computer experiments

Computer simulation studies for polar liquids have been performed starting from the very simple to more sophisticated models. McDonald made Monte Carlo calculations for polar molecules interacting with the Stockmayer potential; he also examined the effect of polarizability of the molecules (50). Patey and Valleau made similar studies for dipolar and quadrupolar hard spheres (51). Morris (52), Isbister and Morris (53) have studied the dielectric properties of a polar diatomic fluid with a Monte Carlo simulation method. The solvent particles are modeled as two fused hard spheres with a point charge on each site. This model is considered to be the
simplest one which includes the effect of shape and higher order multipolar moments. The long range nature of the electrostatic interactions have been taken into account by means of the Ewald summation technique (54). It has been concluded that the choice of the dielectric constant of the continuum that surrounds the simulation sample, $\varepsilon'$, has a large effect on the dielectric constant of the medium. At $\varepsilon' = 1$ it is found that the dielectric constant decreases with elongation of the diatomic, while at $\varepsilon' = \infty$ it increases with elongation.

More elaborate models intended to represent water have been studied by molecular dynamics (55-58) and Monte Carlo (59-64) methods. The ST2 water model developed by Stillinger and Rahman (56-58), consists of four point charges located in a tetrahedral geometry around an oxygen atom. The positive charges represent the hydrogen atoms and are placed at a distance of 0.1 nm from the oxygen atom center, which is assumed to be the real distance in a water molecule. The negative charges are located at the remaining two corners of the tetrahedron so as to provide the actual dipole and quadrupole moments of the water molecule. This arrangement also allows the formation of hydrogen bonds in the right direction. The short range interactions are represented by an LJ potential placed at the center of the oxygen atom. The central force (CF) model developed by Lemberg and Stillinger (65) consist of oxygen and hydrogen centers and its geometry depends on the choice of the oxygen-hydrogen and hydrogen-hydrogen pair potentials.

McDonald and Rasaiah studied, by Monte Carlo methods, the average force between ions in a Stockmayer solvent (66). Patey and Valleau made similar studies for charged hard spheres in a dipolar hard sphere solvent (67). Heinzinger and Vogel (68-71) and Heinzinger and Palinkas (72) used molecular dynamics methods to
study the solvation characteristics of various salts including LiF, LiCl, NaCl, CsCl, CsF in ST2 water model. In these simulations 216 particles with 8 anions and 8 cations are employed. These simulations are performed to study the effect of anion and cation size and concentration on the structure of water. Some qualitative conclusions obtained are: a) water molecules rotate faster in the first hydration shell of the ions compared with the bulk water; b) the structure of the ionic solution shows similarities with pure water at high temperature or pressure, in terms of solvent-solvent geometry; c) the hydration shell structure becomes broken with increasing ion size and decreasing size of counterions; d) in solutions with larger anions, deviations in the average dipole moment of the solution is more pronounced as compared with pure water; e) at lower concentrations of the solute, the hydration shell of the ions is not broken, especially for smaller ions.

Several Monte Carlo (73) and molecular dynamics (74,75) studies at infinite dilution of ions have been performed. These simulations involve a single positive or negative ion and several hundred solvent molecules. Molecular dynamics studies aim to investigate the dynamic aspects of ion solvation and find answers to questions such as the reason for the experimentally observed increased fluidity of the aqueous solutions of various salts compared to pure water. Frank and Wen (76) suggested a concentric shell model of ionic hydration where the water surrounding the ion is examined in three regions. The primary region water molecules are strongly affected by the ions and are immobilized. In the secondary region water structure is broken to a small extent since the water molecules are weakly oriented by the ions. In the third region which is far from the ion, structure is the same as in the bulk water. The ions are classified as structure makers or structure breakers according to the relative
thickness of the primary and secondary regions. Generally smaller ions are structure makers and larger ions are structure breakers because they destroy the hydrogen-bond structure of pure water and have higher mobilities in solution. Gurney (77) has noted that, for special combinations of ionic size and charge, the thickness of the secondary layer increases and extends up to the surface of the ions. The dependence of the mechanism of ion solvation on the charge of the ions is considered by Geiger et al. (78). In another work by Geiger a model experiment has been developed in which an uncharged sphere in a dipolar solvent is charged step-by-step from \( q = 0 \) to \( q = +2 \). At \( q = 0 \), hydrophobic hydration or water structure promotion is observed (75). The structure of the solvent is destroyed continuously as the ionic charge increases. The dipole-ion-dipole distribution function shows that there is a marked structuring which favors small angles, at \( q = 0 \) and \( q = +2 \), but at \( q = +1 \) this structuring vanishes. It is concluded that at low ionic charges hydrogen bonding is responsible for the structure formation. At intermediate charges the effect of hydrogen bonding is neutralized by the ion-dipole interaction forces, resulting in increased orientational disorder and mobility of the solvent. At high ionic charges, the only mechanism responsible for the structure is the ion-dipole interactions.
3 SCIENTIFIC OBJECTIVES

The primitive or restricted primitive models do not provide a realistic description for the thermodynamic properties of electrolyte solutions in a wide range of concentrations. Also it is not possible to obtain any reliable information about the structural properties with these models. The computer simulations with discrete solvent models that employ sophisticated potentials, which consider the molecular shape and higher order multipoles for the solvent particles, give reasonable results when compared with experiments. These simulation studies involve only one or a small number of ions. Therefore they do not provide detailed information about the solvation structure including ion clustering. Even structural results for the ion-solvent geometry as reported contain large statistical uncertainties (68-72). Also, it is practically very difficult to incorporate these models into theory, to obtain a predictive description. It has been noted that a simpler model consisting of polarizable hard spheres with embedded point dipoles and quadrupoles is sufficient to predict the anomalously high dielectric constant of liquid water (79-81). This prediction provided a motivation for several theoretical studies of electrolyte solutions, involving such simple solvent models, to be conducted (28,29,49). However, not many corresponding simulation studies have been reported to test the accuracy of the theoretical methods. This comparison is an essential step in the development
of a predictive description of electrolytes.

The current work is designed to provide a better understanding of the structural and thermodynamic properties of electrolyte solutions at finite dilution. The objectives of this work can be listed as follows:

1. By using exact Monte Carlo simulation methods, to obtain results that will provide a basis of comparison for the theoretical techniques that employ discrete solvent models. The models to be studied are chosen to be sufficiently simple to be mathematically tractable. The potential models used to describe the solvent particles in electrolyte solution include

   - point-dipolar hard spheres
   - hard spheres with point dipoles and linear quadrupoles
   - dipolar diatomics

while ions are described as either positively or negatively charged hard spheres.

2. To investigate the solvation geometry of the ions and solvent particles in solution by means of the pair distribution functions for the ion-solvent, ion-ion and solvent-solvent interactions, three body distribution functions for the ions and spherical harmonic coefficients that describe the orientational structure of the solvent molecules. These calculations are important in learning more about the mechanisms involved in ion solvation.

3. To calculate various thermodynamic and dielectric properties including the internal configurational energy, compressibility, specific heat and dielectric constant.
4. To examine the effect of state variables such as the charge and concentration of the ions on the structural and thermodynamic properties of electrolyte solutions.

5. To test the quality of the existing theories with discrete solvent models including

- integral equation theory with the MSA and LHNC closures
- perturbation theory developed by Henderson, Blum and Tani.

and consider various modifications and alternatives to the existing theories.
4 APPLICATION OF COMPUTER SIMULATION TECHNIQUES TO ELECTROLYTES

There are two widely used simulation techniques in the literature of the statistical mechanics of fluids: 1. Monte Carlo (MC) methods which involve evaluation of ensemble averages in the sense of statistical mechanics, and 2. the molecular dynamics (MD) methods, which consider the solution of the equation of motion for a system of particles and time averaging of trajectories to obtain dynamic properties. The choice of the method depends on the type of problem to be solved. Molecular dynamics gives dynamical information about a system and can be used to study time dependent phenomena. On the other hand, Monte Carlo methods can yield certain thermodynamic properties which cannot easily be obtained from molecular dynamics.

In the present study, Monte Carlo method, which refers to the use of random sampling techniques to estimate averages or integrals, is used. This method has been introduced into classical statistical mechanics by Metropolis et al. in 1953 (82). Most MC calculations have been performed using the canonical \((T,V,N)\) ensemble in which the temperature \(T\), the volume \(V\) and the number of molecules \(N\) are fixed. The equilibrium distribution of configurations for a finite number of particles enclosed in a cubic cell is calculated. Statistical uncertainties in the results
can be reduced by employing a large number of ions and solvent molecules. It has been noted that several hundred particles of the same kind are necessary to obtain statistically acceptable results (83). On the other hand, the number of particles employed is subject to optimization to keep the computational requirements at a reasonable level. A sequence of configurations is generated such that the probability of any particular configuration with energy $U$ is proportional to the Boltzmann factor or the exponential of $-U/kT$. Estimation of equilibrium properties, such as correlation functions and thermodynamic properties, is done by sampling over a random sequence of configurations. The initial condition for the ions and solvent molecules is a lattice configuration. To generate a new configuration each particle is made to move one at a time in a random way. Then the variation in the potential energy is calculated. If it is found to be negative, the jump is allowed to occur. Otherwise, it is accepted with a probability proportional to $-\Delta U$, where $\Delta U$ is the change in the potential energy for that step. Problems due to the long range nature of the interaction potential and surface effects that arise, because of the limited number of particles in a fixed volume of the cell, are eliminated by assuming imaginary cells with the same configuration around the cell in consideration. Thus, when a particle leaves the cell an equivalent particle enters through the opposite boundary. Therefore, interactions due to imaginary particles in neighboring cells are also considered (84-87). The overall interaction energy is approximated with periodic boundary conditions using one of three methods:

1. Truncation of intermolecular forces: A simple approximation that is applicable to models with fairly short-ranged forces such as the LJ fluid is to truncate the intermolecular potential. Only the interaction of particles separated by
less than some finite range is calculated. Periodic boundary conditions are applied. In the minimum image method the potential function is truncated at the surface of a cube centered at the particle in consideration. In the cutoff method the truncation is at the surface of a sphere. Therefore only the nearest image of all particles is included in the energy calculation.

2. Reaction field: In this method the cutoff sphere is surrounded by a polarizable continuum. The potential energy of a particle includes direct interaction with all the other particles within the sphere and also the interaction with the reaction field caused by all particles in the sphere.

3. Total periodic boundary conditions: This method in which all the images of every particle in the imaginary cells are included in the energy calculation will be explained in more detail in section 4.1.2.

4.1 The Internal Energy

4.1.1 Interaction potential

Calculation of the internal energy is the most important part of the MC simulation. For the discrete solvent models considered in this study, the total interaction potential is given by the summation of pair interaction potentials of the solute and solvent particles

\[
U = \sum_{i \neq j} U_{ij} \quad \text{for } r_{ij} > \sigma
\]

\[
U = \infty \quad \text{for } r_{ij} < \sigma
\]  

(4.1)
where $r_{ij}$ is the interparticle separation and $\sigma$ is the particle diameter. The ion-ion, ion-dipole, dipole-dipole and ion-quadrupole interaction potentials are given as:

\[
U_{ii}(r_{ij}) = q_i q_j |r_{ij}|^{-1} \quad (4.2)
\]

\[
U_{id}(r_{ij}) = -q_i \vec{\mu}_j \cdot \nabla (1/ |r_{ij}|) \quad (4.3)
\]

\[
U_{dd}(r_{ij}) = -((\vec{\mu}_i \cdot \nabla)(\vec{\mu}_j \cdot \nabla))(1/ |r_{ij}|) \quad (4.4)
\]

\[
U_{iq}(r_{ij}) = -q_i \vec{Q}_j \cdot \nabla \nabla (1/ |r_{ij}|) \quad (4.5)
\]

where $q, \vec{\mu}, \vec{Q}$ represent the ionic charge, dipole moment and quadrupole moment respectively. The ion-dipole, dipole-dipole, ion-quadrupole, dipole-quadrupole and quadrupole-quadrupole potentials for a mixture of ions and linear multipoles are expressed as

\[
U_{id} = -\frac{q_i \mu_j}{r^2} (\hat{s}_1 \cdot \hat{r}) \quad (4.6)
\]

\[
U_{dd} = -\frac{\mu_i \mu_j}{r^3} (3(\hat{s}_1 \cdot \hat{r})(\hat{s}_2 \cdot \hat{r}) - \hat{s}_1 \cdot \hat{s}_2) \quad (4.7)
\]

\[
U_{iq} = \frac{q_i Q_j}{2r^3} (1 - 3(\hat{r} \cdot \hat{s}_1)^2) \quad (4.8)
\]

\[
U_{dq} = \frac{3\mu_i Q_j}{2r^4} (5(\hat{s}_1 \cdot \hat{r})(\hat{s}_2 \cdot \hat{r})^2 - (\hat{s}_1 \cdot \hat{r})^2 - 2(\hat{s}_1 \cdot \hat{s}_2)(\hat{s}_2 \cdot \hat{r})) \quad (4.9)
\]

\[
U_{qq} = \frac{3 Q_i Q_j}{4r^5} (1 - 5(\hat{s}_1 \cdot \hat{r})^2 - 5(\hat{s}_2 \cdot \hat{r})^2 + 2(\hat{s}_1 \cdot \hat{s}_2)^2 + 35(\hat{s}_1 \cdot \hat{r})^2(\hat{s}_2 \cdot \hat{r})^2 - 2(\hat{s}_1 \cdot \hat{s}_2)(\hat{s}_1 \cdot \hat{r})(\hat{s}_2 \cdot \hat{r})) \quad (4.10)
\]

where $\hat{s}_1$ and $\hat{s}_2$ are the unit vectors along the multipoles and $\hat{r}$ is the unit vector joining intermolecular centers in the space fixed frame (88).
4.1.2 Ewald summation technique

If the potential energy between two particles $i$ and $j$ is written as a product of a strength parameter $\xi_{ij}$ and an inverse power of the interparticle separation $r_{ij}$ as

$$U_{ij} = \frac{\xi_{ij}}{r_{ij}^m} \quad (4.11)$$

then the total potential energy of $N$ particles in the MC system with periodic boundary conditions is represented by the infinite sum

$$U_{ij,MC} = \frac{1}{2} \sum_{\vec{n}} \left( \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\xi_{ij}}{|\vec{r}_{ij} + \vec{n}L|^m} \right) \quad (4.12)$$

Eqn. (4.12) assumes that the charge neutrality condition exists in the solution. $\vec{n}$ represents all cubic lattice points with integer coordinates and the prime on the first summation indicates that if $i = j$ the $\vec{n} = \vec{0}$ term is to be omitted. $L$ is the length of the side of the cubic simulation cell that contains $N$ particles. The self-energy arising from the interaction of a particle with all its periodic images has to be subtracted from eqn. (4.12). Self-energy is a constant quantity and need not be included explicitly in the MC calculation. If the interaction potential of two different types of particles is considered, this term is not present.

For large values ($m > 6$) of the exponent $m$, the lattice sum in eqn. (4.12), converges very rapidly. For smaller $m$ the sum converges less rapidly and for $m \leq 3$ it is conditionally convergent. The problem of transforming lattice sums into rapidly convergent series has received attention from mathematical physicists beginning with the work of Madelung (89) and Ewald (90) on ionic crystals.

In these methods each term in the conditionally convergent sum is multiplied with a convergence factor which is a function of the lattice vector and a variable $s$
related to the system shape (54). For the summation of spherical shells, the factor

\[ f = e^{-s\vec{n} \cdot \vec{n}} \]  

(4.13)
is appropriate. At the end of the analysis the limit as \( s \) approaches zero is taken to give a unique solution of the lattice sum as

\[ U = \lim_{s \to 0} \sum_{\vec{n}} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\epsilon_{ij} e^{-s\vec{n} \cdot \vec{n}}}{|\vec{r}_{ij} + \vec{n}L|}. \]  

(4.14)

Since this sum is absolutely and uniformly convergent, it is possible to change the order of summation. The following three identities are needed in the lattice sum evaluations

\[ \frac{1}{x} = \frac{1}{\Gamma(1/2)} \int_{0}^{\infty} t^{-1/2} e^{-tx^2} dt, \]  

(4.15)

\[ -(s + t) \left| \vec{n} + \frac{t\vec{r}}{t+s} \right|^2 \left| \vec{n} \right|^2 = s \left| \vec{n} + \frac{t\vec{r}}{t+s} \right|^2 - \frac{s \left| \vec{r} \right|^2}{s + t}, \]  

(4.16)

\[ e^{-t|\vec{n}+\vec{r}|^2} = \frac{\pi}{t} \frac{1}{t} \sum_{\vec{n}} e^{-\pi^2 \frac{|\vec{n}|^2}{t} + 2\pi i \vec{n} \cdot \vec{r}}. \]  

(4.17)
The first identity can be obtained from the definition of the gamma function, \( \Gamma(x) \). The second identity is derived by arranging the terms on the left hand side of eqn. (4.16). The third identity can be proved by expanding the function \( f(x) = e^{-tx^2} \), in terms of a Fourier series.

\[ f(x) = \sum_{-\infty}^{\infty} a_n e^{2\pi i nx} \]  

(4.18)

where

\[ a_n = \int_{0}^{1} dx f(x) e^{-2\pi i nx} \]  

(4.19)
and
\[ g(x) = \sum_{-\infty}^{\infty} f(x + n). \quad (4.20) \]

Using eqn. (4.15) the summation over the lattice vectors \( \bar{n} \) becomes
\[ \bar{U} = \frac{1}{\sqrt{\pi}} \int_{0}^{\infty} t^{-1/2} \left[ \sum_{\bar{n}} e^{-t|\bar{r} + \bar{n}|^2/2} - s|\bar{n}|^2 \right] dt. \quad (4.21) \]

In the limit \( s \to 0 \), the function \( \bar{U} \) may be singular. Therefore the integral is split into two parts, one on \([0, \alpha^2]\) and one on \([\alpha^2, \infty]\). The parameter \( \alpha \) is chosen so as to optimize the rate of convergence of both parts.
\[ \bar{U} = \frac{1}{\sqrt{\pi}} \int_{0}^{\alpha^2} t^{-1/2} \left[ \sum_{\bar{n}} e^{-t|\bar{r} + \bar{n}|^2/2} \right] dt + \int_{\alpha^2}^{\infty} t^{-1/2} \left[ \sum_{\bar{n}} e^{-t|\bar{r} + \bar{n}|^2/2 - s|\bar{n}|^2} \right] dt. \quad (4.22) \]

Substituting the identity given into eqn. (4.16) to eqn. (4.21) and considering only the integral from 0 to \( \alpha^2 \)
\[ I_1(0, \alpha^2) = \frac{1}{\sqrt{\pi}} \int_{0}^{\alpha^2} t^{-1/2} \sum_{\bar{n}} e^{-(s+t)|\bar{n} + t\bar{r}/t-s|^2/2 - st|\bar{r}|^2/2} dt. \quad (4.23) \]

If the identity given in eqn. (4.17) is introduced and the terms with \( \bar{n} = 0 \) are written separately, eqn. (4.22) takes the form
\[ \bar{U} = \frac{1}{\sqrt{\pi}} \int_{0}^{\alpha^2} \frac{\pi^{3/2}}{(t(t + s)^2)^{1/2}} \sum_{\bar{n} \neq 0} e^{-\frac{\pi^2|\bar{n}|^2}{(t+s)^2} - \frac{2\pi i\bar{n} \cdot \bar{r}}{(t+s)} - \frac{st|\bar{r}|^2}{(s+t)}} dt + \int_{0}^{\alpha^2} \frac{\pi^{3/2}}{(t(t + s)^2)^{1/2}} \frac{st|\bar{r}|^2}{(s+t)} dt + \sum_{\bar{n}} \frac{1}{\sqrt{\pi}} \int_{\alpha^2}^{\infty} t^{-1/2} e^{-s|\bar{n}|^2 - t|\bar{r} + \bar{n}|^2} dt. \quad (4.24) \]
After some rearrangement, the integral from $\alpha^2$ to $\infty$ takes the form

$$I_2(\alpha^2, \infty) = \sum_{\vec{n}} e^{-s|\vec{n}|^2} \frac{erfc(\alpha \sqrt{\vec{r} + \vec{n}})}{|\vec{r} + \vec{n}|},$$  

(4.25)

where $erfc(x)$ is the complementary error function defined as

$$erfc(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-s^2} ds = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-s^2} ds.$$  

(4.26)

From eqn. (4.14)

$$U = \lim_{s \to 0} \sum_{i=1}^N \sum_{j=1}^N (I_1(0, \alpha^2) + I_2(\alpha^2, \infty))$$  

(4.27)

where

$$\lim_{s \to 0} I_2(\alpha^2, \infty) = \sum_{\vec{n}} \frac{erfc(\alpha \sqrt{\vec{r} + \vec{n}})}{|\vec{r} + \vec{n}|}.$$  

(4.28)

Defining the variable

$$v^2 = \frac{t}{(s + t)} |\pi \vec{n} + i s \vec{r}|^2,$$  

(4.29)

the integral from 0 to $\alpha^2$ becomes

$$I_1(0, \alpha^2) = \sum_{\vec{n} \neq 0} \frac{2\pi s^{-1/2} e^{-\pi^2 |\vec{n}|^2}}{|\pi \vec{n} + i s \vec{r}|} \int_{s}^{x} e^{v^2} dv$$  

(4.30)

where

$$w = \frac{\alpha |\pi \vec{n} + i s \vec{r}|}{(\alpha^2 + s)^{1/2}}.$$  

(4.31)

However, the integral diverges because of the singularity at the upper limit. A new variable is defined as

$$v = \frac{w}{s} - \frac{u \sqrt{s}}{2w}$$  

(4.32)
and is substituted into the integral in eqn. (4.30) to give

$$\int_0^\infty e^{\nu^2/s} \frac{2w^2/s}{2w} e^{-u} du = \frac{\sqrt{s}e^{w^2/s}}{2w} \int_0^\infty e^{2w^2/s} e^{-u} du.$$  \hspace{2cm} (4.33)

For the small values of the argument, $e^{(s u^2/4 w^2)}$ can be expanded in a power series in $s$ and integrated term by term,

$$\int_0^\infty e^{\nu^2/s} \frac{2w^2/s}{2w} e^{-u} du = \frac{\sqrt{s}e^{w^2/s}}{2w} \sum_{n=0}^\infty \frac{1}{n!} \left(\frac{s}{4w^2}\right)^n \int_0^\infty u^{2n} e^{-u} du - \int_0^\infty \frac{2w^2}{s} e^{-u} du $$

$$= \frac{\sqrt{s}e^{w^2/s}}{2w} \sum_{n=0}^\infty \frac{1}{n!} \left(\frac{s}{4w^2}\right)^n \left[\Gamma(2n+1) - \Gamma(2n+1, \frac{2w^2}{s})\right]$$

$$= \frac{\sqrt{s}e^{w^2/s}}{2w} \sum_{n=0}^\infty \frac{1}{n!} \left(\frac{s}{4w^2}\right)^n \left[(2n)! - \left(\frac{2w^2}{s}\right)2n e^{-2w^2/s}\right]$$

$$= \frac{\sqrt{s}e^{w^2/s}}{2w} \left[1 + \frac{s}{2w^2} + o(s^2)\right] \hspace{2cm} (4.34)$$

where only the $n = 0$ and $n = 1$ terms are considered in the last expression.

Substituting this result into eqn. (4.30)

$$I_1(0, \alpha^2) = \sum_{n \neq 0} \frac{\pi}{w |\vec{n} + i \vec{r}|} e^{-\left(\frac{n^2}{s} + \frac{w^2}{s}\right)\left(1 + \frac{s}{2w^2}\right)} \hspace{2cm} (4.35)$$

and taking the limit $s \to 0$

$$\lim_{s \to 0} I_1(0, \alpha^2) = \sum_{n \neq 0} \frac{1}{\pi |\vec{n}|^2} e^{-\left(\frac{n^2}{\alpha^2} + 2\pi i n \cdot \vec{r}\right)} \hspace{2cm} (4.36)$$

Considering the integral in eqn. (4.24) where $\vec{n} = \vec{0}$

$$I_1(0, \alpha^2) \mid_{\vec{n} = \vec{0}} = \frac{1}{\sqrt{\pi}} \int_0^\alpha \frac{\pi^{3/2}}{(t(s + t)^3)^{1/2}} e^{-\frac{st|\vec{r}|^2}{(s + t)}} dt \hspace{2cm} (4.37)$$
and defining
\[ u = \frac{t}{s + t}. \]  
(4.38)

Eqn. (4.37) becomes
\[ I_1(0, \alpha^2) \bigg|_{\vec{n} = 0} = \int_0^{\alpha^2/(\alpha^2 + s)} \frac{\pi}{s} u_{-1/2} e^{-su}\vec{n}^2 du. \]  
(4.39)

Similar to the procedure applied before, \( e^{-su}\vec{n}^2 \) is expanded in a power series in \( s \) and integrated term by term. If the first two terms in the expansion are considered
\[ I_1(0, \alpha^2) \bigg|_{\vec{n} = 0} = \pi \left( -\frac{2}{s} \left( \frac{\alpha^2}{\alpha^2 + s} \right)^{1/2} - \frac{2}{3} \mid \vec{r} \mid^2 \left( \frac{\alpha^2}{\alpha^2 + s} \right)^{3/2} \right). \]  
(4.40)

The charge neutrality condition requires that
\[ \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j = 0. \]  
(4.41)

Therefore, the first term in eqn. (4.40) is zero. Taking the limit as \( s \to 0 \) it becomes
\[ \lim_{s \to 0} I_1(0, \alpha^2) \bigg|_{\vec{n} = 0} = -\frac{2\pi}{3} \sum_{i=1}^{N} q_i \vec{r}_i \mid^2. \]  
(4.42)

In order to calculate the interaction of a particle with its own images in the other periodic cells, i.e., \( (\vec{n} \neq \vec{0}, \vec{r}_{ij} = \vec{0}) \), a similar procedure is adopted. Using eqn. (4.15)
\[ \sum_{\vec{n} \neq \vec{0}} \frac{1}{\mid \vec{n} \mid} e^{-s\mid \vec{n} \mid^2} = \frac{1}{\sqrt{\pi}} \int_0^{\infty} e^{-(s+t)} \mid \vec{n} \mid^2 t^{-1/2} dt \]
\[ = \frac{1}{\sqrt{\pi}} \int_0^{\alpha^2} \sum_{\vec{n} \neq \vec{0}} e^{-(s+t)} \mid \vec{n} \mid^2 t^{-1/2} dt \]
\[ + \frac{1}{\sqrt{\pi}} \int_0^{\alpha^2} \sum_{\vec{n}} e^{-(s+t)} \mid \vec{n} \mid^2 t^{-1/2} dt \]
\[ - \frac{1}{\sqrt{\pi}} \int_0^{\alpha^2} t^{-1/2} dt. \]  
(4.43)
Using eqn. (4.17) in the integral from 0 to $\alpha^2$ and eqn. (4.26) in the integral from $\alpha^2$ to $\infty$

\[
\sum_{\vec{n} \neq 0} \frac{1}{|\vec{n}|} e^{-s|\vec{n}|^2} = \sum_{\vec{n} \neq 0} \frac{\text{erfc}(\alpha |\vec{n}|)}{|\vec{n}|} e^{-s|\vec{n}|^2} + \pi \int_0^{\alpha^2} (t(s+t)^3)^{-1/2} e^{-\pi^2|\vec{n}|^2/(s+t)} dt - \frac{2\alpha}{\sqrt{\pi}}. \tag{4.44}
\]

Defining

\[
v^2 = \frac{t}{s(t-s)} \pi^2 |\vec{n}|^2 \tag{4.45}
\]

and substituting into the integral in eqn. (4.44)

\[
I_1(0, \alpha^2) |_{\vec{n}, \vec{r}, \vec{v}} = 0 = \sum_{\vec{n}} \frac{2}{|\vec{n}| \sqrt{s}} \int_0^{w/\sqrt{s}} e^{v^2} dv \tag{4.46}
\]

where

\[
w = \frac{\alpha \pi |\vec{n}|}{(\alpha^2 + s)^{1/2}}. \tag{4.47}
\]

The variable defined by eqn. (4.32) is substituted into eqn. (4.46), which then becomes

\[
\int_0^{w/\sqrt{s}} e^{v^2} dv = \sum_{\vec{n}} e^{-\left(\frac{\pi^2|\vec{n}|^2}{s} + \frac{w^2}{s}\right)} \int_0^{2w^2/s} e^{-u} u^{2s/4w^2} du
\]

\[
= \sum_{\vec{n}} e^{-\left(\frac{\pi^2|\vec{n}|^2}{s} + \frac{w^2}{s}\right)} (1 + \frac{s}{2w^2} + 0(s^2)) \tag{4.48}
\]

where the last form is obtained by expanding $e^{(su^2/4w^2)}$ in power series. Then

\[
\lim_{s \to 0} \sum_{\vec{n} \neq 0} \frac{1}{|\vec{n}|} e^{-s|\vec{n}|^2} = \sum_{\vec{n} \neq 0} \frac{\text{erfc}(\alpha |\vec{n}|)}{|\vec{n}|} + \sum_{\vec{n}} \frac{e^{-\left(\frac{\pi^2|\vec{n}|^2}{2\alpha^2}\right)}}{\pi |\vec{n}|^2} - \frac{2\alpha}{\sqrt{\pi}}. \tag{4.49}
\]
According to De Moivre's theorem;

\[ e^{ix} = \cos x + isinx. \]  \hspace{1cm} (4.50)

So the real part of eqn. (4.36) is

\[ I_1(0, \alpha^2) = \sum_{\vec{n} \neq 0} \frac{1}{\pi |\vec{n}|^2} (-\frac{\pi^2 |\vec{n}|^2}{\alpha^2}) \cos(2\pi \vec{n} \cdot \vec{r}_{ij}) \]  \hspace{1cm} (4.51)

where \( \vec{r}_{ij} \) is the intermolecular vector

\[ \vec{r}_{ij} = \vec{r}_j - \vec{r}_i. \]  \hspace{1cm} (4.52)

In space fixed coordinates

\[ I_1(0, \alpha^2) = \sum_{\vec{n} \neq 0} \frac{1}{\pi |\vec{n}|^2} (-\frac{\pi^2 |\vec{n}|^2}{\alpha^2}) \left( \cos^2(2\pi \vec{n} \cdot \vec{r}_i) + \sin^2(2\pi \vec{n} \cdot \vec{r}_j) \right). \]  \hspace{1cm} (4.53)

Combining eqns. (4.42), (4.44) and (4.53)

\[ \frac{U_{ij}}{NkT} = \frac{2}{N} (\sigma L) q^2 \left( \sum_{i=1}^{N_i} \sum_{j=i}^{N_j} z_i z_j \frac{\text{erfc}(\alpha |\vec{r}_{ij}|/\sqrt{2})}{|\vec{r}_{ij}|} \right. \]

\[ + \left. \frac{1}{2\pi} \sum_{\vec{n} \neq 0} \frac{e^{-\pi^2 n^2 / \alpha^2}}{|\vec{n}|^2} \left[ \left( \sum_{i=1}^{N_i} z_i \cos(\pi \vec{n} \cdot \vec{r}_i) \right)^2 \right. \]

\[ + \left. \left( \sum_{i=1}^{N_i} z_i \sin(\pi \vec{n} \cdot \vec{r}_i) \right)^2 - \frac{\alpha N_i}{N \sqrt{\pi} (\sigma L) q^2} \right] \]  \hspace{1cm} (4.54)

where the dimensionless variables are defined as

\[ r_{ij}^* = \frac{2r_{ij}}{L} \]  \hspace{1cm} (4.55)

\[ q^2 = \frac{q^2}{\sigma kT}. \]  \hspace{1cm} (4.56)
\( z_i \) is the sign of the ionic charge, and \( N_i \) the number of ions of type \( i \). The ion-dipole energy is calculated from eqn. (4.3) as

\[
U_{id} = - \sum_{i=1}^{N_i} \sum_{j=1}^{N_d} \frac{q_i \mu_j}{L} \nabla \left[ \sum_{\tilde{n}} \frac{\text{erfc}(\alpha | \tilde{r} + \tilde{n} | / L)}{\tilde{r} + \tilde{n}} \right] \\
+ \frac{1}{\pi} \sum_{\tilde{n} \neq 0} e^{-\pi^2 |\tilde{n}|^2 / \alpha^2} \frac{2 \pi i \tilde{n} \cdot \tilde{r}}{L}, \tag{4.57}
\]

\[
\nabla \sum_{\tilde{n}} \frac{\text{erfc}(\alpha | \tilde{r} + \tilde{n} | / L)}{\tilde{r} + \tilde{n}} = \sum_{\tilde{n}} \frac{-2 \alpha (\tilde{r} + \tilde{n})}{\sqrt{\pi} | \tilde{r} + \tilde{n} |} e^{-\frac{\alpha^2 |\tilde{r} + \tilde{n}|^2}{L^2}} \\
- \frac{(\tilde{r} + \tilde{n}) L}{| \tilde{r} + \tilde{n} |^3 \text{erfc}(\alpha | \tilde{r} + \tilde{n} | / L)}, \tag{4.58}
\]

\[
\nabla \sum_{\tilde{n} \neq 0} e^{-\pi^2 |\tilde{n}|^2 / \alpha^2} \frac{2 \pi i \tilde{n} \cdot \tilde{r}}{L} = \frac{2 i \tilde{n}}{L} | \tilde{n} |^2 e^{-\pi^2 |\tilde{n}|^2 / \alpha^2} e^{\frac{2 \pi i \tilde{n} \cdot \tilde{r}}{L}}. \tag{4.59}
\]

where \( N_d \) is the number of dipoles. Substituting eqns. (4.58) and (4.59) into eqn (4.57)

\[
\frac{U_{id}}{NkT} = \frac{4}{N} \left( \frac{\sigma}{L} \right)^2 q^* \mu^* \left[ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{z_j (\tilde{s}_i \cdot \tilde{r}_{ij}^*)}{| \tilde{r}_{ij}^* |^3} \text{erfc}(\alpha | \tilde{r}_{ij}^* | / 2) \\
+ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{z_j \alpha (\tilde{r}_{ij}^* \cdot \tilde{s}_i)}{\sqrt{\pi} | \tilde{r}_{ij}^* |^2} e^{-\alpha^2 |\tilde{r}_{ij}^*|^2 / 4} \\
- \frac{i}{2} \sum_{\tilde{n} \neq 0} \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{z_j (\tilde{s}_i \cdot \tilde{n})}{| \tilde{n} |^2} e^{-\pi^2 |\tilde{n}|^2 / \alpha^2} e^{2 \pi i \tilde{n} \cdot \tilde{r}_{ij}^*} \right] \tag{4.60}
\]

where

\[
\mu^* = \frac{\mu^2}{\sigma^2 kT} \tag{4.61}
\]

\[
\tilde{\mu} = \mu \tilde{s} \tag{4.62}
\]

\[
q = | q | z. \tag{4.63}
\]
According to De Moivre's theorem

\[ -ie^{x} = -\cos x + \sin x. \]  

(4.64)

Considering only the real part

\[ -ie^{(\pi i \vec{n} \cdot \vec{r}_{ij}^* \cdot x)} = \sin(\pi \vec{n} \cdot \vec{r}_{ij}^* \cdot x). \]  

(4.65)

Using the identity

\[ \sin(\pi \vec{n} \cdot \vec{r}_{ij}^*) = \sin(\pi \vec{n} \cdot \vec{r}_{j}^*) \cos(\pi \vec{n} \cdot \vec{r}_{i}^*) - \cos(\pi \vec{n} \cdot \vec{r}_{j}^*) \sin(\pi \vec{n} \cdot \vec{r}_{i}^*). \]  

(4.66)

Substituting eqn. (4.66) into eqn. (4.60), the ion-dipole energy is expressed as

\[
\begin{align*}
U_{id} &= \frac{4 \pi}{NkT} \left[ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{(\vec{s}_i \cdot \vec{r}_{ij}^*) \cdot (\vec{n_i} \cdot \vec{r}_{ij}^*)}{|\vec{r}_{ij}^*|^2} \right] \\
&\quad + \frac{\alpha}{\sqrt{\pi}} \left[ e^{-\frac{\pi^2 |\vec{n}|^2}{\alpha}} \right] \left[ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} [\vec{s}_i \cdot \vec{n}_k] \cos(\pi \vec{n} \cdot \vec{r}_{ij}^*) \right] \\
&\quad + \frac{2i}{L} \left[ \sum_{\vec{n} \neq \vec{0}} \frac{e^{-\pi^2 |\vec{n}|^2/\alpha^2} / \sqrt{\pi}}{|\vec{n}|^2} \right] \left[ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{(\vec{s}_i \cdot \vec{r}_{ij}^*) \cdot (\vec{n}_j \cdot \vec{r}_{ij}^*)}{|\vec{r}_{ij}^*|^2} \right] \\
&= \frac{4 \pi}{NkT} \left[ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{(\vec{s}_i \cdot \vec{r}_{ij}^*) \cdot (\vec{n}_j \cdot \vec{r}_{ij}^*)}{|\vec{r}_{ij}^*|^2} \right] \\
&\quad + \frac{\alpha}{\sqrt{\pi}} \left[ e^{-\frac{\pi^2 |\vec{n}|^2}{\alpha}} \right] \left[ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} [\vec{s}_i \cdot \vec{n}_k] \cos(\pi \vec{n} \cdot \vec{r}_{ij}^*) \right] \\
&\quad + \frac{2i}{L} \left[ \sum_{\vec{n} \neq \vec{0}} \frac{e^{-\pi^2 |\vec{n}|^2/\alpha^2} / \sqrt{\pi}}{|\vec{n}|^2} \right] \left[ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{(\vec{s}_i \cdot \vec{r}_{ij}^*) \cdot (\vec{n}_j \cdot \vec{r}_{ij}^*)}{|\vec{r}_{ij}^*|^2} \right].
\end{align*}
\]  

(4.67)

The dipole-dipole energy was given in eqn. (4.4). So

\[
U_{dd} = -\frac{1}{L} \sum_{i=1}^{N_d} \sum_{j>i}^{N_d} \vec{\mu}_i \cdot \vec{\mu}_j \cdot \nabla \left[ \frac{2\alpha}{\sqrt{\pi}} \sum_{\vec{n}} \frac{(\vec{r} + \vec{n})}{|\vec{r} + \vec{n}|^2} \right] - \frac{\alpha^2 |\vec{r} + \vec{n}|^2}{L^2} \]
\[
- \frac{L}{\sqrt{\pi}} \sum_{\vec{n}} \frac{(\vec{r} + \vec{n})}{|\vec{r} + \vec{n}|^3} e^{-\frac{\pi^2 |\vec{n}|^2}{\alpha^2} / \sqrt{\pi}} \left[ \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{(\vec{s}_i \cdot \vec{r}_{ij}^*) \cdot (\vec{n}_j \cdot \vec{r}_{ij}^*)}{|\vec{r}_{ij}^*|^2} \right] \\
+ \frac{2i}{L} \sum_{\vec{n} \neq \vec{0}} \frac{e^{-\pi^2 |\vec{n}|^2/\alpha^2} / \sqrt{\pi}}{|\vec{n}|^2} \left( \sum_{i=1}^{N_d} \sum_{j=1}^{N_i} \frac{(\vec{s}_i \cdot \vec{r}_{ij}^*) \cdot (\vec{n}_j \cdot \vec{r}_{ij}^*)}{|\vec{r}_{ij}^*|^2} \right). 
\]  

(4.68)
After evaluating the gradient;

\[
U_{dd} = -\frac{1}{L^2} \sum_{i=1}^{N_d} \sum_{j>i}^N \vec{\mu}_i \cdot \vec{\mu}_j : [-L \sum_{n} \text{erf}(\alpha |\vec{r} + \vec{n}|)\left(\frac{\vec{I}}{|\vec{r} + \vec{n}|^3} - 3(\vec{r} + \vec{n})(\vec{r} + \vec{n}) \right)
\]

\[
-2\alpha \frac{e^{-\frac{1}{2} |\vec{r} + \vec{n}|^2}}{L^2} \left(\frac{\vec{I}}{|\vec{r} + \vec{n}|^2} - 3(\vec{r} + \vec{n})(\vec{r} + \vec{n}) \right)
\]

\[
+ \frac{4c^2}{\sqrt{\pi} L^2} \sum_{n} \frac{(\vec{r} + \vec{n})(\vec{r} + \vec{n})}{|\vec{r} + \vec{n}|^2} e^{-\frac{4}{\alpha^2}|\vec{r} + \vec{n}|^2/L^2}
\]

\[
- \frac{4\pi}{L^2} \sum_{\vec{n} \neq \vec{0}} \vec{n} \cdot \vec{r} \frac{-\pi^2 |\vec{n}|^2 / \alpha^2}{|\vec{n}|} \frac{e^{2\pi i \vec{n} \cdot \vec{r}}}{L}
\]

The real part of the last term is

\[
e^{\pi i \vec{n} \cdot \vec{r}_{ij}} = \cos(\pi \vec{n} \cdot \vec{r}_{ij}^*).
\]

\(\vec{I}\) is the identity tensor. Eqn. (4.69), expressed in space-fixed coordinates with the
dimensionless variables defined previously, becomes

\[
\frac{U_{dd}}{NkT} = \frac{8\mu_*^2}{N} (\frac{\sigma}{L})^3 \sum_{i=1}^{N_d} \sum_{j>i}^N \text{erf}(\alpha |\vec{r}_{ij}^*| / 2) + \frac{\alpha |\vec{r}_{ij}^*|}{\sqrt{\pi}} e^{-\alpha^2 |\vec{r}_{ij}^*|^2/4} \cdot
\]

\[
\left(\frac{\hat{s}_i \cdot \hat{s}_j}{\vec{r}_{ij}^*} \right)^3 - 3(\hat{s}_i \cdot \vec{r}_{ij}^*)(\hat{s}_j \cdot \vec{r}_{ij}^*) - \frac{2\pi^2 |\vec{n}|^2 / \alpha^2}{|\vec{r}_{ij}^*|} \cdot
\]

\[
+ \frac{\alpha}{2} \sum_{\vec{n} \neq \vec{0}} \frac{e^{-\pi^2 |\vec{n}|^2 / \alpha^2}}{|\vec{n}|^2} \left[ \sum_{i=1}^{N_d} (\hat{s}_i \cdot \vec{n}_k) \cos(\pi \vec{n}_k \cdot \vec{r}_{ij}^*) \right]^2
\]

\[
+ \frac{N_d}{3} \sum_{i=1}^{N_d} \sum_{i=1}^{N} \sum_{j>i}^N \frac{1}{|\vec{r}_{ij}^*|} - \frac{3(\hat{s}_i \cdot \hat{s}_j)^2}{|\vec{r}_{ij}^*|^3}
\]

Similarly, the ion-quadrupole energy given in eqn. (4.5) is expressed as

\[
\frac{U_{iq}}{NkT} = \frac{q^* Q^*}{2} (\frac{2\sigma}{L})^3 \sum_{j=1}^{N_q} \sum_{i=1}^{N_i} \frac{z_i}{|\vec{r}_{ij}^*|^3} - \frac{3(\hat{s}_i \cdot \vec{r}_{ij}^*)^2}{|\vec{r}_{ij}^*|^3}
\]
where $N_q$ is the number of the quadrupoles.

\section*{4.2 The Compressibility Factor}

The pressure of a fluid enclosed in a fixed volume is calculated by averaging the virial function defined as

\[ \vartheta = \sum_{i=1}^{N} \vec{F}_i \cdot \vec{r}_i \]  

(4.73)

where $F_i$ is the total force acting on the $i$-th particle and $r_i$ is its position vector. The virial function can be separated into two parts: $\vartheta_{int}$ is associated with the interparticle forces and $\vartheta_{ext}$ is associated with external forces due to the pressure exerted by the container. If the fluid is enclosed in a cubic box, the contribution of external forces to the virial is $-3PV$, and the time averaged total virial is $-3NkT$. Therefore

\[ -3NkT = -3PV + \sum_{i=1}^{N} \vec{r}_i \cdot \nabla_i U_N \]  

(4.74)

or

\[ \frac{3P}{\rho} = 1 - \frac{3}{N} \sum_{i=1}^{N} \vec{r}_i \cdot \nabla_i U_N \]  

(4.75)
where $\beta$ is the inverse of Boltzmann constant times the absolute temperature and $\rho$ is the total density. The canonical ensemble average of the compressibility factor is evaluated as

$$\frac{3P}{\rho} = 1 - \frac{\beta(N-1)}{3Z_N} \int e^{-\beta U_N} \sum_{i=1}^{N} \vec{r}_i \cdot \nabla_i \sum_{j \neq i}^{N} U_{ij} d\vec{r}^N d\Omega^N$$

(4.76)

where the partition function $Z_N$ is given as

$$Z_N = \int e^{-\beta U_N} d\vec{r}^N d\Omega^N / \Omega^N$$

(4.77)

and $\Omega$ is the set of Euler angles needed to describe the orientation of the $N$ nonspherical particles. Defining the pair distribution function for $\alpha$ and $\beta$ type particles as

$$g_{\alpha,\beta} = \frac{\Omega_\alpha \Omega_\beta}{\rho_\alpha \rho_\beta} \frac{N_\alpha (V_\beta - \delta_{\alpha,\beta})}{Z_N} \int e^{-\beta U_N} d\vec{r}_3 \ldots d\vec{r}_N d\Omega_3 \ldots d\Omega_N$$

(4.78)

The compressibility equation becomes

$$\frac{3P}{\rho} = 1 - \frac{3\rho}{6} \int g(\vec{r}_{12}, \omega_1, \omega_2) r_{12} \frac{\partial U(\vec{r}_{12}, \omega_1, \omega_2)}{\partial r_{12}}
\times g_{\alpha,\beta}(\vec{r}_{12}, \omega_1, \omega_2) d\vec{r}_1 d\vec{r}_2 d\omega_1 d\omega_2
= 1 - \frac{2\pi \rho \beta}{3} \int_0^\infty g(\vec{r}_{12}, \omega_1, \omega_2) r_{12}^2 \frac{\partial U(\vec{r}_{12}, \omega_1, \omega_2)}{\partial r_{12}} d\vec{r}_{12}.$$ 

(4.79)

For the case of a pure hard sphere fluid the compressibility can be calculated analytically from eqn. (4.79) as

$$\frac{3P}{\rho} \bigg|_{HS} = 1 + \frac{2\pi \rho \beta}{3} g(\sigma).$$

(4.80)

g(\sigma) is the value of the pair distribution function in the limit as $r \rightarrow \sigma$, the hard sphere diameter.
The canonical ensemble average of the overall interaction potential gives the internal energy of the system as

$$\frac{U}{NkT} = \frac{3}{2} + 2\pi \rho_3 \int_0^\infty U(\vec{r}_{12}, \omega_1, \omega_2) g_{\alpha\beta}(\vec{r}_{12}, \omega_1, \omega_2) r_{12}^2 dr_{12} \quad (4.81)$$

where $3/2$ corresponds to the internal energy of an ideal gas and the second term on the right hand side is the contribution due to the interaction between particles. A comparison of eqns. (4.79) and (4.81) gives a general expression for the contribution to compressibility of the various ionic and/or multipolar interactions as

$$\frac{3P_{nm}}{\rho} = \frac{U_{nm} C_{nm}}{3} \quad (4.82)$$

where the subscripts represent the type of the interaction, i.e., ion, dipole, quadrupole, and $C_{nm}$ is a constant due to an $n - m$ type interaction. For the case of an ionic solution consisting of ions and hard spheres with embedded point dipoles and linear quadrupoles, the expression for the compressibility becomes

$$\frac{P}{\rho kT} = 1 + \frac{2\pi}{3} \left( \rho_i^* \frac{\rho_i^*}{\rho^*} g_{++}(\sigma) + \rho_i^* \frac{\rho_i^*}{\rho^*} g_{-+}(\sigma) + \frac{2\rho_i^*}{\rho^*} g_{+-}(\sigma) \right)$$

$$+ \frac{2\rho_i^* \rho_s^*}{\rho^*} g_{+s}(\sigma) + \frac{2\rho_i^* \rho_s^*}{\rho^*} g_{-s}(\sigma) + \frac{\rho_s^*}{\rho^*} g_{ss}(\sigma)$$

$$+ \frac{1}{3} < U_{ii}^* > + \frac{2}{3} < U_{id}^* > + < U_{dd}^* >$$

$$+ \frac{4}{3} < U_{dq}^* > + \frac{5}{3} < U_{qq}^* > + < U_{iq}^* > \quad (4.83)$$

where

$$U^* = \frac{U}{NkT}, \quad \rho^* = \rho \sigma^3 \quad (4.84)$$

The subscripts $i, d, q,$ and $s$ represent the ion, dipole, quadrupole and solvent respectively. If the last three terms are omitted in eqn. (4.83), it reduces to the
compressibility expression for an ionic solution described as a mixture of ions and linear dipoles embedded in hard spheres.

4.3 The Specific Heat and the Dielectric Constant

Certain thermodynamic and dielectric properties are related to the mean square deviation or fluctuation of given quantities from their average value. Examples are the specific heat and the static component of the dielectric constant.

A second order Taylor expansion of the energy distribution function of a system gives

$$f(U) \sim e^{-\Delta U^2/(2kT^2C_v)}.$$  \hspace{1cm} (4.86)

On comparison of this expression with the standard form of the Gaussian distribution for a quantity $U$

$$f(U) = \frac{1}{(2\pi\sigma_u^2)^{1/2}} e^{-\Delta U^2/2\sigma_u^2}.$$  \hspace{1cm} (4.87)

It can be seen that the mean square energy fluctuation $\sigma_u^2$ is given by

$$\sigma_u^2 = kT^2C_v.$$  \hspace{1cm} (4.88)

Considering the ideal gas contribution, the expression for the specific heat at constant volume becomes

$$\frac{C_v}{Nk} = \frac{3}{2} + N\sigma_u^2$$  \hspace{1cm} (4.89)

where

$$\sigma_u = \frac{<U'^2> - <U^2>/N}{N}.$$  \hspace{1cm} (4.90)
A second order phase transition is characterized by a sharp discontinuity in the specific heat versus one of the state variables.

In MC simulation the system is visualized as a large spherical sample composed of periodic replications of the simulation cell contained in an annulus of dielectric continuum with dielectric constant $\varepsilon'$, which is contained in a vacuum. The static component of the dielectric constant is determined from the Kirkwood g-factor with

$$\frac{(\varepsilon - 1)(2\varepsilon' + 1)}{3(2\varepsilon' + \varepsilon)} = yg(\varepsilon') \quad (4.91)$$

where $g(\varepsilon')$ is the mean square deviation in the dipole moment vector in a canonical ensemble of particles

$$g(\varepsilon') = \frac{< \vec{\mu}^2 > - < \vec{\mu} >^2}{N\mu^2} \quad (4.92)$$

and the dipole moment vector of the central simulation cell is

$$\vec{\mu} = \sum_i \vec{\mu}_i. \quad (4.93)$$

$y$ is a dimensionless quantity given as

$$y = \frac{4\pi}{9} \rho^* \mu^* 2. \quad (4.94)$$

It has been proven for an infinite system that $\varepsilon$ is independent of the value of $\varepsilon'$ (54). For systems of finite size, the dielectric constant obtained using $\varepsilon''$ differs from that obtained with $\varepsilon'$ by terms of order $(1/N)$, $N$ being the number of particles. However, the coefficient of this $(1/N)$ order term is also important in determining $\varepsilon$ (52).

If $\varepsilon'$ is chosen to be infinity, the expression for the dielectric constant simplifies to

$$\varepsilon = 1 + 3yg(\infty). \quad (4.95)$$
4.4 Distribution Functions and the Coordination Number

The importance of distribution functions stem from the fact that they play an important role in the prediction of equilibrium macroscopic properties of fluids in theoretical methods. The local order that exists in an electrolyte solution can be visualized by the help of pair and multibody distribution functions. Experimental studies on monatomic fluids show that the positions of two arbitrary particles are radially correlated in space. The probability of simultaneously finding particle 1 in a volume \( d\vec{r}_1 \) around \( \vec{r}_1 \) and particle 2 in \( d\vec{r}_2 \) around \( \vec{r}_2 \) is expressed by the probability density in the form

\[
P^{(N)}(\vec{r}_1, \ldots \vec{r}_N) d\vec{r}_1 d\vec{r}_N = \frac{1}{Z_N} e^{-\beta U_N(\vec{r}_1 \ldots \vec{r}_N)} d\vec{r}_1 \ldots d\vec{r}_N \quad (4.96)
\]

The \( n \)-body probability density \( P^{(n)}_N \) is obtained from \( P^{(N)}_N \) by integrating over the coordinates of the remaining \( N - n \) particles as

\[
P^{(n)}_N(\vec{r}_1 \ldots \vec{r}_N) = \int \ldots \int P^{(N)}_N(\vec{r}_1 \ldots \vec{r}_N) d\vec{r}_{N+1} \ldots d\vec{r}_N \quad (4.97)
\]

For the case of very low densities, the mutual distances between the \( n \) particles increase and the correlation between their positions are expected to decrease. Finally in the limit \( |r_i - r_j| \to \infty \) for all \( 1 \leq i, j \leq n \), the \( n \)-particle probability density will factorize into the product of \( n \) single particle probability densities,

\[
P^{(n)}_N(\vec{r}_1 \ldots \vec{r}_n) \approx P^{(1)}_N(\vec{r}_1) \ldots P^{(1)}_N(\vec{r}_N) \quad (4.98)
\]

In this limit the position of each of the \( n \) particles is independent of the positions of the remaining \( n-1 \) particles. Therefore \( n \)-particle distribution function is defined
as,

\[ g_N^{(n)}(\vec{r}_1, \ldots \vec{r}_n) = \frac{P_N^{(n)}(\vec{r}_1, \ldots \vec{r}_n)}{\prod_{i=1}^{n} P_N^{(1)}(\vec{r}_i)} \]  

(4.99)

\[ g_N^{(n)}(\vec{r}_n) \to 1 \] for all \( n \) as the mutual distances between the \( n \)-particles increase indefinitely. For systems of macroscopic size, the asymptotic limit is reached for all practical purposes when \( |r_i - r_j| \simeq V^{1/3} \), the distance \( V^{1/3} \) being many orders of magnitude larger than typical interatomic distances. In a homogeneous system,

\[ P_N^{(1)}(\vec{r}_1) = \frac{1}{V} \]  

(4.100)

Therefore;

\[ g_N^{(n)} = V^n P_N^{(n)}(\vec{r}_n) \]  

(4.101)

For the present case,

\[ g_N^{(2)}(\vec{r}_1, \vec{r}_2) = V^2 P_N^{(2)}(\vec{r}_1, \vec{r}_2) \]

\[ = \frac{V^2}{Z_N} \int \ldots \int e^{-\beta U_N(\vec{r}_N)} d\vec{r}_3 \ldots d\vec{r}_N \]  

(4.102)

If the system is isotropic,

\[ g_N^{(2)}(\vec{r}_1, \vec{r}_2) = g(|\vec{r}_1 - \vec{r}_2|) \]  

(4.103)

where the quantity \( g(r) \) is the radial distribution function. \( g(r) \to 1 \) as \( r \to \infty \).

In the case of molecular fluids the interaction potential depends upon the angles of orientation as well as the position and the angular pair correlation function is defined as,

\[ g_N^{(2)}(\vec{r}_1, \vec{r}_2, \omega_1, \omega_2) = \frac{V^2}{Z_N} \int \ldots \int e^{-\beta U(\vec{r}_N)} d\vec{r}_3 \ldots d\vec{r}_N d\omega_3 \ldots d\omega_N \]  

(4.104)
Therefore a pair distribution function $g_{\alpha\beta}(r)$ is related to the probability of finding a particle of type $\beta$ at a distance $r$ when an $\alpha$-type particle is placed at the origin. A three body distribution function $g_{\alpha\beta\beta}(r_1, r_2, \theta)$ is related to the joint probability of finding two $\beta$-type particles at distances $r_1$ and $r_2$, and separated by an angle of $\theta$ when an $\alpha$-type particle is placed at the origin. Pair and triplet distribution functions are obtained by sampling a large system of particles having the same macroscopic properties. There are several experimental techniques, such as the neutron scattering method, to determine pair distribution functions [91]. Although triple and higher order distribution functions may be calculated from multiple scattering experiments, certain difficulties are encountered. A major obstacle is the problem of obtaining a beam of radiation with sufficient intensity so that the multiply scattered radiation is comparable with the radiation which is scattered from only one molecule. Another problem is to analyze binary, ternary and higher order scattering separately and accurately [91]. On the other hand, it is also possible to compute $g_3(r_{12}, r_{13}, \theta)$ directly from the computer simulation of a fluid with a given potential model. Several MC and MD studies for monatomic fluids such as the LJ fluid have been reported [91,92].

In the simulation pair distribution functions are calculated with eqn. (4.96).

$$g_2(r) = \frac{V}{\Delta V_i \kappa} \sum_i \sigma_i$$  \hspace{1cm} (4.105)$$

where;

$$\sigma_i = \begin{cases} 1 & \text{if } r_i - \frac{\Delta r}{2} < r < r_i + \frac{\Delta r}{2} \\ 0 & \text{otherwise} \end{cases}$$

$$\kappa = NH(N - 1)/2,$$
\begin{equation}
V = N / \rho^*,
\end{equation}
\begin{equation}
\Delta V_i = 4\pi (r_i^2 \Delta r + \Delta r^3 / 12),
\end{equation}
in which \( V \) is the total volume of the cell, \( \Delta V_i \) is the volume of the shell of thickness \( \Delta r \) and located at \( r_i \), \( r \) is the interparticle separation, \( N \) is the number of particles, and \( N_H \) is the number of histogram samplings. The triple distribution function is calculated with the following equation.
\begin{equation}
g_3(r_1, r_2, \theta) = \frac{V^2}{\Delta V_i \Delta V_j} \frac{1}{\kappa \Delta \cos \theta} \sum_k \sum_i \sum_j \sigma_i \sigma_j \sigma_k
\end{equation}
where
\begin{align}
k &= N_H (N - 1) N^2 / 2,

\sigma_k &= 1 \quad \text{if} \quad \cos \theta_k + \Delta \cos \theta / 2 < \cos \theta < \cos \theta_k - \Delta \cos \theta / 2

\sigma_i &= 1 \quad \text{if} \quad r_i - \Delta r / 2 < r_1 < r_i + \Delta r / 2

\sigma_j &= 1 \quad \text{if} \quad r_j - \Delta r / 2 < r_2 < r_j + \Delta r / 2

\end{align}

Another useful quantity to describe the microscopic nature of fluids is the coordination number. Since the density and intermolecular distances in a liquid are comparable in magnitude with those in solids, liquid structure can be visualized as a loosely joined lattice structure and the same tools used in solid state analysis have
been used to characterize the liquids. Consequently, the coordination number (CN), used to describe the lattice structure for solids, has been applied to visualize the liquid structure. It must be considered that CN for liquids gives only an approximate picture of the arrangement of particles, since these particles are in continuous motion. CN for liquids and dense gases is defined as

\[ CN = 4\pi \rho \int_{\sigma}^{r_{\text{min}}} g(r)r^2 dr \]

(4.109)

where the integration is carried out between the particle surface and the first minimum that follows the first peak of the pair distribution function. CN represents the number of nearest neighbors around a given particle. This method is quite reliable for dense fluids. However, for moderately dense fluids the first minimum is broad and it is difficult to estimate the CN accurately (84).
5 THEORETICAL MODELLING OF ELECTROLYTES

5.1 Mean Spherical Approximation (MSA)

The analytic solution of the OZ equation with the simplest closure, i.e., MSA, has been obtained for the primitive model of electrolytes as well as for a mixture of ions and dipoles (93). For 1-1 electrolytes in the primitive model it has been found that

\[ c_{ij}(r) = c_{ij}^0(r) - (2B - B^2 \frac{r}{\sigma}) \frac{q_i q_j \beta}{\epsilon_0 \sigma} \quad r < \sigma \]

\[ = -\frac{\beta q_i q_j}{\epsilon_0 r} \quad r > \sigma \quad (5.1) \]

where \( c_{ij}^0(r) \) is the direct correlation function of a system of uncharged hard spheres, \( \sigma \) is the diameter of the ions, \( \epsilon_0 \) the dielectric constant, \( \beta \) is the inverse of Boltzmann constant times absolute temperature and

\[ B = x^{-2} \left[x^2 + x - x(1 + 2x)^{1/2}\right] \quad (5.2) \]

where

\[ x^2 = \frac{4\pi \beta}{\epsilon} \sum_i \rho_i q_i^2 \sigma^2. \quad (5.3) \]
The solution given by eqn. (5.1) is valid provided that the global charge neutrality is maintained as

$$\sum_i \rho_i q_i = 0.$$  \hspace{1cm} (5.4)

Waisman and Lebowitz (9,10) show that $c_{ij}(r)$ can be used directly to give the potential energy and Helmholtz free energy as

$$U - U^0 = -\frac{x^2 + x - x(1 + 2x)^{1/2}}{4\pi \beta \sigma^3},$$  \hspace{1cm} (5.5)

$$3(A - A^0)V = -\frac{1}{12\pi \sigma^3}(6x + 3x^2 + 2 - 2(1 + 2x)^{3/2})$$  \hspace{1cm} (5.6)

where $U^0$ and $A^0$ are the reference potential and Helmholtz free energies, respectively. The model can also be used to describe a molten salt if the dielectric constant is taken equal to unity (e.s.u). The results obtained are in good agreement with the MC calculations on the RPM corresponding to electrolytes at low ionic charge and concentration (94), but the method fails for molten salts (47).

The nonprimitive model for a 1-1 electrolyte in a dipolar solvent has been solved for the case of equal particle sizes and also for the more general case of a mixture of ions with different charges in a dipolar solvent, with all the species of different diameters. The problem was solved by Blum (19-21) using the Baxter factorization method (95) and independently by Adelman and Deutch (24) who utilized Laplace transforms. The results of these works are not in complete agreement for all concentrations of the electrolyte, except for low concentrations. A summary of Blum's method is given below.

The method of solution of the MSA for a mixture of ion and dipoles is an extension of the method employed for the case of neutral hard spheres with an
arbitrary electrical charge distribution (96-98). In Fourier space, the OZ equation can be reduced to a set of algebraic equations. This is achieved by expanding the correlation functions $h_{ij}(12)$ and $c_{ij}(12)$ in a set of rotational invariants as

$$h_{ij}(12) = \sum h_{ij}^{mn}(r)\phi^{mn}(12), \quad (5.7)$$

$$c_{ij}(12) = \sum c_{ij}^{mn}(r)\phi^{mn}(12). \quad (5.8)$$

Only a finite number of terms is usually sufficient to determine the thermodynamic and dielectric properties of the system. The coefficients for $h^{000}, h^{011}, h^{112}$ and $h^{110}$ are required in the present case. The three component system is reduced to a binary system with the following definitions

$$h^{000}(r) = h^{000}_{++}(r) + h^{000}_{+-}(r), \quad (5.9)$$

$$h^{011}(r) = h^{011}_{++}(r) + h^{011}_{+-}(r). \quad (5.10)$$

$h^{000}$ is the expansion coefficient of the total pair correlation function, for the combination of similar and oppositely charged ions. $h^{011}$ is the coefficient for the net effect of ion-dipole interactions. Similar definitions are needed for the direct correlation functions. Then in transform space the OZ equation, becomes a matrix equation,

$$[I + H(k)][I - C(k)] = I \quad (5.11)$$

where the matrices $H(k)$ and $C(k)$ are given by;

$$H(k) = \begin{pmatrix} \tilde{h}_{ii}(k) & \tilde{h}_{is}(k) \\ \tilde{h}_{si}(k) & \tilde{h}_{ss}(k) \end{pmatrix}, \quad (5.12)$$
\[ C(k) = \begin{pmatrix} \tilde{c}_{ii}(k) & \tilde{c}_{is}(k) \\ \tilde{c}_{si}(k) & \tilde{c}_{ss}(k) \end{pmatrix}. \] (5.13)

and \( I \) is the identity matrix. The transforms of the direct correlation function, \( \tilde{c}(k) \) for ion-ion and ion-dipole interactions has a singularity at the origin. These singularities can be eliminated by an exponential damping factor which is set to one at the end of the calculations. Then the matrix \([I - C(k)]\) can be factorized according to Baxter's method as

\[ [I - C(k)] = Q(k)Q^T(-k). \] (5.14)

In this way the original OZ equation is split into two coupled equations: An explicit equation which relates \( Q \) to the moments of \( h(r) \) and a nonlinear equation for the moments of \( c(r) \). The inverse transform of \( Q(k) \) is a second order matrix polynomial of the form

\[ Q(r) = Q_0 + rQ_1 + r^2Q_2. \] (5.15)

Defining the function

\[ J(r) = \begin{pmatrix} b_0 & 0 \\ 0 & b'_0 \end{pmatrix} + \begin{pmatrix} 0 & b_1 \\ -b_1 & 0 \end{pmatrix} r + \begin{pmatrix} 0 & 0 \\ 0 & b_2 \end{pmatrix} r^2 \] (5.16)

where \( b_0, b_1, b_2 \) and \( b'_0 \) are functions of the correlation functions \( h^{000}(r) \), \( h^{011}(r) \) and \( h^{112}(r) \) respectively. Then the excess interaction energy matrix is given by

\[ J(r) = Q(r) + \int_0^r dr_1 J(r - r_1)Q(r_1) + \int_r^1 dr_1 J(r_1 - r)Q(r_1) + \frac{1}{2} \begin{pmatrix} a_1 & 0 \\ 0 & 0 \end{pmatrix} + \int_0^{1-r} dr_1 J^T(r_1).A, \] (5.17)
with

\[ A = \begin{pmatrix} a_1 & a_2 \\ 0 & 0 \end{pmatrix}. \]  

(5.18)

An analysis of the discontinuity at the hard core diameter yields the following boundary conditions for the problem

\[ Q(1) = -A, \]

\[ a_1^2 + a_2^2 = 4\pi\beta q^2 \rho_i, \]

\[ -a_1 K_{10} + a_2 (1 - K_{11}) = 4\pi\beta q \mu \left( \frac{\rho_d \rho_i}{3} \right)^{1/2}, \]

\[ K_{10}^2 + (1 - K_{11})^2 = \frac{4}{3} \pi \beta \rho_d \rho_i^2 + \frac{(1 - b_2/6)^2}{(1 + b_2/12)^4} \]  

(5.19)

where

\[ K_{ij} = \int_0^1 dr Q_{ij}(r). \]  

(5.20)

Eqn. (5.17) is then solved explicitly for \( Q(r) \) yielding a set of equations relating \( a_1, a_2, K_{10}, K_{11} \) to \( b_0, b_1, b_2 \). Simultaneous solution of these nonlinear equations with the boundary conditions listed above gives numerical values for \( b_0, b_1 \) and \( b_2 \) which are related to ion-ion, ion-dipole and dipole-dipole energies, respectively. Finally, the dimensionless free energy for a mixture of ions and dipoles is expressed as follows

\[ U_{\text{tot}}^* = U_{ii}^* + U_{id}^* + U_{dd}^* \]

\[ = \frac{\sigma^3}{\rho^*} [b_0 q^2 \rho_i^* - 2b_1 q^* \mu^* \left( \frac{\rho_i^* \rho_d^*}{3} \right)^{1/2} \]

\[ - \frac{2b_2 \mu^* \rho_d^*}{3}]. \]  

(5.21)
Defining the dimensionless parameters

\[ \xi^* = \frac{b_2 \sigma^3}{12}, \quad (5.22) \]
\[ H_1^* = \frac{3 \sigma^3 b_1}{2 \sqrt{\rho_d^*}}, \quad (5.23) \]
\[ H_0^* = \frac{b_0 \sigma^3}{2^{3/2} \sqrt{\rho_d^* q_i^* 2}}, \quad (5.24) \]

\[ U_{tot}^* = \frac{\lambda^* 3 H_0^*}{\rho^*} - \frac{2 \lambda^* 2 H_1^* \mu^* \rho_d^*}{3 \rho^*} - \frac{8 \rho_d^* \mu^* 2 \xi^*}{\rho^*}, \quad (5.25) \]

where

\[ U^* = U/NkT, \quad (5.26) \]
\[ \rho^* = \rho \sigma^3, \quad (5.27) \]
\[ \mu^* 2 = \mu^2/(\sigma^3 kT), \quad (5.28) \]
\[ q_i^* 2 = q_i^2/(\sigma kT), \quad (5.29) \]
\[ \lambda^* 2 = \sum_i \rho_i^* q_i^* 2. \quad (5.30) \]

The parameters \( H_0^*, H_1^* \) and \( \xi^* \) can be obtained by the simultaneous solution of the following set of ten nonlinear equations:

\[ 4\pi = A_1^* 2 + \frac{A_2^* \rho_d^*}{3}, \quad (5.31) \]
\[ 4\pi \mu^* = \lambda^* A_1^* Q_1^* - A_2^* Q_2^*, \quad (5.32) \]
\[ \frac{4\pi \mu^* 2 \rho_d^*}{3} = Q_2^* 2 + \frac{\lambda^* 2 \rho_d^* Q_1^* 2}{3} - Q^*, \quad (5.33) \]
\[ Q^* = \frac{(1 - 2\xi^*)^2}{(1 + \xi^*)^4}, \]  
(5.34)

\[ ((1 - 2\xi^*)^2 + B^*)Q_2^* = 1 + 4\xi^* - \frac{\lambda^* \rho^*_d H^*_1 A^*_2}{36} (3\lambda^* H^*_0 + 4 - \xi^*), \]  
(5.35)

\[ ((1 - 2\xi^*)^2 + B^*)Q_1^* = \frac{H^*_1}{12} (2\lambda^* A^*_1 (2 - \xi^*) + 3\lambda^* \rho^*_d H^*_0 - 6), \]  
(5.36)

\[ X^* A_1^* = \frac{\lambda^* \rho^*_d H^*_1}{9} (2 - \xi^*) - 2H^*_0 (1 - \xi^*)^2, \]  
(5.37)

\[ B^* = \frac{\lambda^* \rho^*_d H^*_1}{12} \]  
(5.38)

\[ X^* A_2^* = \lambda^* H^*_0 H^*_1 (1 + 4\xi^*) + H^*_1 (1 + 4\xi^*) + H^*_1 (1 - 2\xi^* + \frac{2}{3} B^*), \]  
(5.39)

\[ X^* = \frac{2}{3} \lambda^* B^* H^*_0 (1 - 2\xi^*) + \frac{\lambda^* \rho^*_d H^*_1}{18} \left[ 1 - 2\xi^* - \frac{B^*}{6} \right] - (1 + \lambda^* H^*_0)^2 (1 - 2\xi^*)^2. \]  
(5.40)

The solution of these equations has been discussed in the literature (99,100). Blum and Vericat (99) recommended a rapidly converging approximation scheme which gives reasonable results for concentrations below 0.2 M Garisto et al. (100) obtained the solution at infinite dilution by expanding all the parameters in terms of power series and truncating these series after the second order terms. In this study
solutions at finite concentrations are obtained by an iterative procedure based on Newton-Raphson method. A disadvantage of the method may be the relative sensitivity of the rate of convergence to the initial estimate. The initial estimate for the ten parameters is obtained from the ion-ion, ion-dipole, dipole-dipole energies calculated from the simulation. A new estimate is calculated from an old estimate according to:

\[ X'_i = X_i - \sum (J^{-1})_{ij} f_j(X_i) \]  

(5.41)

where \( J_{ij} \) is the \((10 \times 10)\) Jacobian matrix:

\[ J_{ij} = \frac{\partial f_i}{\partial X_j}. \]  

(5.42)

The functions \( f_j(j = 1, \ldots, 10) \), are given in eqns. (5.31-5.40) and the variables \( X_i(i = 1, \ldots, 10) \) correspond to \( A_1^*, A_2^*, Q_1^*, Q_2^*, Q^*, \xi^*, B^*, H_1^*, H_0^* \) and \( X^* \) respectively. The dielectric constant of the solution is calculated as follows

\[ \epsilon = 1 + \frac{4\pi \mu^*}{3} \rho d^*(1 + \xi^*)^4 (1 - 2\xi^*)^2. \]  

(5.43)

The results of these calculations will be given in Chapter 6.

5.2 HBT Theory for an Ion-dipole Mixture

The solution of the OZ equation with the MSA closure is analytic but implicit. The results can only be obtained with a trial and error procedure. On the other hand, perturbation theory (PT) is a simple and explicit theory to predict the thermodynamic properties of the fluids. It has been successfully applied to pure and mixed multipolar fluids and to pure ionic solutions in the primitive model. The theory has been applied to a mixture of ions and dipoles recently (49).
In the theory developed by Henderson and coworkers, the pure hard sphere fluid is considered as the reference and ion-ion, ion-dipole, dipole-dipole interactions as the disturbance. Then the Helmholtz free energy of the system is expanded in powers of $\beta = 1/kT$ up to third order terms. The result after taking the orientational average of the pair interaction potential is

$$\frac{\beta(A - A_0)}{N} = -\frac{K_0^4}{16\pi\rho} \int_0^\infty g_0(r) dr - \frac{3K_0^2y}{8\pi\rho} \int_0^\infty \frac{g_0(r) dr}{r^2} - \frac{27y^2}{8\pi\rho} \int_0^\infty \frac{g_0(r) dr}{r^4}$$

$$+ \frac{K_0^6}{6(4\pi)^3\rho} \int_{r_{ij} \geq \sigma} \frac{g_0(123) dr_2 dr_3}{r_1^2 r_2^2 r_3^2}$$

$$+ \frac{3K_0^4y^2}{2(4\pi)^3\rho} \int_{r_{ij} \geq \sigma} \frac{g_0(123) \cos \theta_2 \cos \theta_3}{r_1^2 r_2^2 r_3^2} dr_2 dr_3$$

$$+ \frac{9K_0^2y^2}{(4\pi)^3\rho} \int_{r_{ij} \geq \sigma} \frac{g_0(123) \cos(\theta_2 - \theta_3) + \cos \theta_2 \cos \theta_3}{r_1^2 r_2^2 r_3^2} dr_2 dr_3$$

$$+ \frac{27y^3}{2(4\pi)^3\rho} \int_{r_{ij} \geq \sigma} \frac{g_0(123) [1 + 3\cos \theta_1 \cos \theta_2 \cos \theta_3]}{r_1^2 r_2^2 r_3^2} dr_2 dr_3 \quad (5.44)$$

where

$$K_0^2 = 4\pi\beta q^2 \rho_i, \quad (5.45)$$

$$y = \frac{4\pi}{9} \beta \mu^2 \rho_d. \quad (5.46)$$

$A_0$ is the free energy of the reference hard sphere system and $g_0(12)$ and $g_0(123)$ are the reference pair and triplet correlation functions for a pair or triplet of hard spheres. The first, fourth and fifth terms in this expansion are divergent. The divergence of the pair integrals is caused by $g_0(r)$ approaching one at very large values of $r$. The divergence of the fifth integral also arises because $g_0(123)$ tends
to unity when all three hard spheres are far apart. The divergence of the fourth integral is caused by the asymptotic form of $g_0(123)$ when two spheres are far apart.

5.2.1 Resummation of the divergent integrals

The procedure used to eliminate the divergent integrals that arise from the long range nature of the ion-ion and ion-dipole interactions is to take the Fourier transform of these integrals and resum them into a single term which can be back-transformed easily. Introducing

$$h_0(r) = g_0(r) - 1,$$  \hspace{1cm} (5.47)

the expansion becomes

$$\beta \left( \mathcal{A} - \mathcal{A}_0 \right) \frac{1}{N} = - \frac{K_0^4}{16\pi\rho} \int_0^\infty dr + \frac{K_0^6}{6(4\pi)^3\rho} \int_{r_{ij} \geq 0} \frac{dr_2 dr_3}{r_{12}r_{13}r_{23}}$$

$$+ \frac{3K_0^4y}{2(4\pi)^3\rho} \int_{r_{ij} \geq 0} \cos \theta_2 \frac{dr_2 dr_3}{r_{12}r_{13}r_{23}} + \ldots$$  \hspace{1cm} (5.48)

The $\beta$ derivative of this expression after some rearrangement gives the internal energy $U$ as

$$\frac{\beta(U - U_0)}{N} = - \frac{K_0^4}{8\pi\rho} (1 - 9y) \int_{r_{ij} \geq 0} \left[ \frac{1}{r_{12}} - \frac{[K_0(1 - 1.5y)]^2}{4\pi} \right] \frac{dr_3}{r_{12}^2r_{13}r_{23}} + \ldots$$  \hspace{1cm} (5.49)

Then the Fourier transform of the terms in the integral are taken and summed as

$$\Gamma(k) = \frac{4\pi}{k^2 + [(K_0(1 - 1.5y)]^2}.$$  \hspace{1cm} (5.50)
When the inverse Fourier transform of eqn. (5.50) is substituted into eqn. (5.49)

\[
\frac{\beta(U - U_0)}{N} = -\frac{K_0^4}{8\pi\rho}(1 - 9y) \int_0^\infty e^{x\sqrt{-K_0(1 - 1.5y)r}} |dr = -\frac{K_0^3}{8\pi\rho}(1 - 7.5y) + \ldots 
\]

(5.51)

Integrating w.r.t. \( \beta \),

\[
\frac{\beta(A - A_0)}{N} = -\frac{K_0^3}{12\pi\rho}(1 - 4.5y) + \ldots 
\]

(5.52)

and using the superposition approximation,

\[
h_0(123) = g_0(123) - 1 - h_0(12) - h_0(13) - h_0(23),
\]

(5.53)

the expression for the Helmholtz free energy for a mixture of equal diameter ions and dipoles is obtained as,

\[
\frac{\beta(A - A_0)}{N} = -\frac{K_0^3}{12\pi\rho}(1 - 4.5y) - \frac{K_0^4}{16\pi\rho} \frac{\sigma I_{cc}}{\rho} + \\
\frac{K_0^6}{8\pi}\left[\frac{\sigma^2 I_{ccc}}{8\pi} + \frac{3I_{ccc}'}{8\pi} + \frac{3K_0^2 y \sigma I_{ccd}}{8\pi}\right] + \\
\frac{3\sigma I_{cc}}{8\pi} - \frac{3K_0^2 y I_{cd}}{8\pi\rho} - \frac{27y^2 I_{dd}}{8\pi\rho^2} + \\
\frac{9K_0^3y^2 I_{cdd}}{8\pi\rho} + \frac{27y^3 I_{ddd}}{16\pi\rho^3}
\]

(5.54)

where

\[
I_{cc} = \frac{1}{\sigma}\int_0^\infty h_0(r) dr,
\]

(5.55)

\[
I_{cc}' = \frac{1}{\sigma^2}\int_0^\infty rh_0(r) dr,
\]

(5.56)

\[
I_{cc}'' = \frac{1}{\sigma^3}\int_0^\infty r^2h_0(r) dr,
\]

(5.57)
\[ I_{cd} = \sigma \int_0^\infty \frac{g_0(r)}{r^2} dr, \quad (5.58) \]

\[ I_{dd} = \sigma^3 \int_0^\infty \frac{g_0(r)}{r^4} dr, \quad (5.59) \]

\[ I_{ccc} = \frac{1}{\sigma^3} \int_0^\infty dr_{12} \int_0^\infty dr_{13} \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} h_0(123) dr_{23}, \quad (5.60) \]

\[ I'_{ccc} = 2 \int_0^\infty r h_0(r) dr \int_0^\infty ds - \int_0^\infty r^2 h_0(r) dr, \quad (5.61) \]

\[ I_{ccd} = \frac{1}{\sigma} \int_0^\infty dr_{12} \int_0^\infty dr_{13} \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} h_0(123) \frac{\cos \theta_3}{r_{23}} dr_{23}, \quad (5.62) \]

\[ I_{cdd} = \sigma \int_0^\infty \frac{dr_{12}}{r_{12}} \int_0^\infty \frac{dr_{13}}{r_{13}} \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} g_0(123) \frac{\cos(\theta_2 - \theta_3) + \cos \theta_2 \cos \theta_3}{r_{23}^2} dr_{23}, \quad (5.63) \]

\[ I_{ddd} = \sigma^3 \int_0^\infty \frac{dr_{12}}{r_{12}^2} \int_0^\infty \frac{dr_{13}}{r_{13}^2} \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} g_0(123) \frac{1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3}{r_{23}^2} dr_{23}. \quad (5.64) \]

\(I'_{ccc}\) is also a divergent integral. However, it is not easy to perform a resummation with a small number of terms. The series is compared with the Stell-Lebowitz expansion for pure charged hard spheres and the low density MSA free energy results for a charged hard sphere and dipolar hard sphere mixture. As a result it is assumed that a truncated perturbation expansion correctly identifies all the terms but does not give the correct values for some of the coefficients because of resummed contributions from higher order terms. The procedure used is to replace the coefficients of the pair integrals of order \(K_0^5\) and and \(K_0^6\) from the Stell-Lebowitz
series and the pair terms of order $K_0^2 y^2$ and $K_0^4 y$ from the low density expansion of the MSA free energy for the charged hard sphere-dipolar hard sphere mixture. The result is

$$\frac{\beta(A - A_0)}{N} = \frac{K_0^*}{12\pi \rho^*} - \frac{K_0^{*4} I_{cc}}{16\pi \rho^*} - \frac{3K_0^{*2} y^* I_{cd}}{8\pi \rho^*}$$

$$- \frac{27y^*2 I_{dd}}{8\pi \rho^*} + \frac{K_0^{*5} I'_{cc}}{8\pi \rho^*} + \frac{3K_0^{*3} y^*}{8\pi \rho^*}$$

$$- \frac{K_0^{*6}}{8\pi \rho^*} (I''_{cc} - \frac{1}{6} I_{ccc})$$

$$+ \frac{K_0^{*4} y^*}{16\pi \rho^*} \left( \frac{23}{3} I_{cc} + 3I_{ccd} \right)$$

$$+ \frac{3K_0^{*2} y^*2}{8\pi \rho^*} \left[ -1.2155 I_{cd} + 3I_{cdd} \right]$$

$$+ \frac{27y^*3 I_{dd}}{16\pi \rho^*}$$  \hspace{1cm} (5.65)$$

where

$$K_0^{*2} = 4\pi q^2 \rho_i^* = K_0^2 \sigma^2, \hspace{1cm} (5.66)$$

$$y^* = \frac{4\pi}{9} \mu^*2\rho_d^* = y. \hspace{1cm} (5.67)$$

The derivatives of the variables $K_0^*$ and $y^*$ w.r.t. $\beta$ are given as

$$\frac{\partial K_0^{*n}}{\partial \beta} = \frac{n}{2} K_0^{*n}, \hspace{1cm} (5.68)$$

$$\frac{\partial y^*n}{\partial \beta} = ny^*n. \hspace{1cm} (5.69)$$

The $\beta$ derivative of the Helmholtz free energy expression gives the internal energy as

$$\frac{\beta(U - U_0)}{N} = \frac{\partial}{\partial \beta} \left[ \frac{\beta(A - A_0)}{N} \right]$$
For high values of ionic charge or dipole moment of the solvent, the results obtained with this equation are divergent.

5.2.2 Padé approximation

In many applications of perturbation theory the series calculated up to second or third order terms is found to diverge, but it is possible to recover results by forming a Padé approximation. In the case of an ion-dipole mixture this procedure is more complicated. It has been noted that the Padé approximant suggested by Henderson et al., assuming a geometric series in terms of the square of temperature, has singularities at certain combinations of the ionic charge and concentration.

In the present work, an alternative Padé approximation is suggested. This approximation consists of a separate treatment of the ion-ion, ion-dipole and dipole-dipole energies. Instead of forming a single temperature expansion, the perturbation series is treated as a sum of four different series in terms of either ionic charge squared or dipole moment squared; A 4-2 Padé approximation, which was found to be successful for pure ionic solutions by Stell et al. (40), is used to represent the

\[ \text{For high values of ionic charge or dipole moment of the solvent, the results obtained with this equation are divergent.} \]

5.2.2 Padé approximation

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sum of the terms for ion-ion energy

\[
U_{ii}^* = -\frac{K_0^{*3}}{8\pi \rho^*} - \frac{K_0^{*4} I_{cc}}{8\pi \rho^*} + \frac{5K_0^{*5} I_{cc}'}{16\pi \rho^*} - \frac{3K_0^{*6}}{8\pi \rho^*}(I_{cc}'' - \frac{1}{6} I_{ccc})
= \frac{a_0 + a_1 K_0^* + a_2 K_0^{*2} + a_3 K_0^{*3} + a_4 K_0^{*4}}{1 + b_1 K_0^* + b_2 K_0^{*2}},
\tag{5.71}
\]

with

\[
\begin{align*}
a_0 &= 0, \\
a_1 &= 0, \\
a_2 &= 0, \\
a_3 &= \xi, \\
a_4 &= \alpha + b_1 \xi, \\
b_1 &= \frac{\alpha \beta - \gamma \xi}{\beta \xi - \alpha^2}, \\
b_2 &= -\frac{(\beta + \alpha b_1)}{\xi},
\end{align*}
\tag{5.72}
\]

and

\[
\begin{align*}
\xi &= -1/(8\pi \rho^*), \\
\alpha &= -I_{cc}/(8\pi \rho^*), \\
\beta &= 5I_{cc}'/(16\pi \rho^*), \\
\gamma &= -3(I_{cc}'' - \frac{I_{ccc}}{6})/(8\pi \rho^*).
\end{align*}
\tag{5.73}
\]

A 2-1 Padé approximation that represents well the pure dipolar fluids is used to represent the dipole-dipole energy terms.

\[
U_{dd}^* = -\frac{27y^*2 I_{dd}}{4\pi \rho^*} + \frac{81I_{dd}y^*3}{16\pi \rho^*}
= \frac{a_0' + a_1' y^* + a_2' y^*2}{1 + b_1' y^*},
\tag{5.74}
\]
where

\[
\begin{align*}
\alpha' & = 0, \\
\alpha' & = 0, \\
\alpha' & = \alpha', \\
b_1' & = -\beta'/\alpha', \\
\alpha' & = -27I_{dd}/(4\pi\rho^*), \\
\beta' & = 81I_{ddd}/(16\pi\rho^*),
\end{align*}
\]

(5.75)

The ion-dipole cross terms are expressed in two different series: A geometric series in powers of ionic charge at constant power of dipole moment of the solvent and a series in powers of dipole moment of the solvent at constant power of ionic charge.

\[
U_{id}^* = U_{id,1}^* + U_{id,2}^*.
\]  

(5.76)

\[
\begin{align*}
U_{id,1}^* & = -\frac{3K_0^*y^*I_{cd}}{8\pi\rho^*} - \frac{15K_0^*3y^*}{16\pi\rho^*} + \frac{3K_0^*4y^*}{16\pi\rho^*}(\frac{23}{3}I_{cc} + 3I_{ccd}). \\
U_{id,2}^* & = -\frac{3K_0^*y^*I_{cd}}{8\pi\rho^*} - \frac{6K_0^*2y^*I_{cd}}{8\pi\rho^*} \\
& \quad + \frac{9K_0^*2y^*2}{8\pi\rho^*}(-1.2155I_{cd} + 3I_{cd}).
\end{align*}
\]  

(5.77)

(5.78)

A 3-1 Padé approximation is assumed for the first group of terms, but it is found that these terms form a divergent series and are discarded.

\[
\begin{align*}
U_{id,1}^* & = \frac{a_{0}y^* + a_{1}K_0^*y^* + a_{2}K_0^*2y^* + a_{3}K_0^*3y^*}{1 - b_{1}K_0^*} \\
& = \frac{\alpha'K_0^*2 + (\beta' - \alpha'2\gamma')K_0^*3}{1 - \frac{2\gamma'}{3\gamma'}K_0^*},
\end{align*}
\]  

(5.79)
where

\[
\begin{align*}
    a''_0 & = a''_1 = 0, \\
    a''_2 & = \alpha'' \\
    a''_3 & = \beta'' - \frac{\alpha'' \gamma''}{\beta''} \\
    b''_1 & = -\frac{\gamma''}{\beta''} \\
    \alpha'' & = -\frac{3K_0^* 2y^* I_{cd}}{8\pi \rho^*} \\
    \beta'' & = \frac{15y^*}{16\pi \rho^*}, \\
    \gamma'' & = \frac{3y^*}{16\pi \rho^*} \left[ \frac{23I_{cc}}{3} + 3I_{cd} \right].
\end{align*}
\]

(5.80)

A 2-2 Padé approximation is formed with the second group of terms.

\[
U_{id,2}^{*} = \frac{a'''' + a''''' y^*}{1 + b''''' y^*}
= \frac{\alpha''''' y^*}{1 - \beta''''' y^*/\alpha''''},
\]

(5.81)

where

\[
\begin{align*}
    a''''_0 & = 0, \\
    \alpha''''' & = -\frac{3K_0^* 2I_{cd}}{8\pi \rho^*}, \\
    \beta''''' & = \frac{3K_0^* 2}{8\pi \rho^*} \left[ -1.2155I_{cd} + 3I_{cdd} \right].
\end{align*}
\]

(5.82)

The resulting series is found to be free of singularities.
5.3 An Alternative to HBT Theory

HBT theory has some disadvantages. First of all, the resummation of the divergent integrals resulting from the treatment of the Coulombic potential as a perturbation complicates the formation of a Padé approximant for the free energy. As a result, some of the terms are neglected to obtain convergent results and the method is restricted to low ionic charges and concentrations. Another disadvantage of the method is related to the choice of the reference and perturbation potentials. In successful applications of perturbation theory, the reference potential is the structure determining part of the system potential and has thermodynamic and structural properties very similar to the overall system. It is seen in Tables 6.4 and 6.5 that the thermodynamic properties of an electrolyte solution are very sensitive to changes in ionic concentration and charge. On the other hand, a comparison of the first rows in Tables 6.4 and 6.5 shows that the thermodynamic properties of a mixture of hard spheres and point dipoles are not too different from those of a pure dipolar hard sphere fluid. The pair correlation functions, shown in Figure 5.1, demonstrate the similarity in structure of the pure hard sphere fluid (lower solid line) and the dipole-dipole correlations in the ionic solution. The latter is shown as dash-dot curves corresponding to four different ionic concentrations between 0.4 to 2.0 M at fixed total density. The upper solid curve is the distribution function for the pure solvent. Clearly, the solvent pair structure is insensitive to ionic strength and quite well represented by the pure hard sphere function. In contrast, the charged hard sphere structure is quite different from that of the pure hard sphere fluid. All these results indicate that a perturbation theory based on a hard sphere plus charged sphere reference system and multipolar interactions as the perturbation will be promising for electrolyte solutions.
Figure 5.1: The structure of the solution compared with the pure hard sphere reference fluid (The dash-dot lines correspond to ion-dipole mixtures from 0.4 M to 2.0 M)
5.3.1 Derivation of an expression for the free energy

The Helmholtz free energy of a mixture of ions and dipoles is expanded in a Taylor series in terms of two variables, an ion-ion perturbation parameter \( \lambda_q \) and an ion-dipole perturbation parameter \( \lambda_\mu \) as

\[
-\beta A_c = \beta A \bigg|_{\lambda_q=\lambda_\mu=0} + \lambda_q \frac{\partial A}{\partial \lambda_q} \bigg|_{\lambda_q=\lambda_\mu=0} \lambda_q \lambda_\mu + \lambda_\mu \frac{\partial A}{\partial \lambda_\mu} \bigg|_{\lambda_q=\lambda_\mu=0} \lambda_q \lambda_\mu + \lambda_q \lambda_\mu + \frac{1}{2!} \left[ \lambda_q^2 \frac{\partial^2 A}{\partial \lambda_q^2} \bigg|_{\lambda_q=\lambda_\mu=0} + 2 \lambda_q \lambda_\mu \frac{\partial^2 A}{\partial \lambda_q \partial \lambda_\mu} \bigg|_{\lambda_q=\lambda_\mu=0} + \lambda_\mu^2 \frac{\partial^2 A}{\partial \lambda_\mu^2} \bigg|_{\lambda_q=\lambda_\mu=0} \right] \\
+ \frac{1}{3!} \left[ \lambda_q^3 \frac{\partial^3 A}{\partial \lambda_q^3} \bigg|_{\lambda_q=\lambda_\mu=0} + 3 \lambda_q^2 \lambda_\mu \frac{\partial^3 A}{\partial \lambda_q^2 \partial \lambda_\mu} \bigg|_{\lambda_q=\lambda_\mu=0} \right]
\]

The series is truncated after the third order terms. The first order derivatives are zero since they involve integrals of a single spherical harmonic. Some of the second order and third order derivatives are neglected for the same reason. The Helmholtz free energy is related to the canonical ensemble configurational partition function \( Z \) as

\[
-\beta A_c = \ln Z. \tag{5.84}
\]

Substituting into the previous equation gives

\[
-\beta \Delta A_c = \frac{1}{2} \frac{\partial^2 Z}{\partial \lambda_q^2} \bigg|_{\lambda_q=\lambda_\mu=0} + \frac{1}{2} \frac{\partial^2 Z}{\partial \lambda_\mu^2} \bigg|_{\lambda_q=\lambda_\mu=0} + \frac{1}{2} \frac{\partial^3 Z}{\partial \lambda_q \partial \lambda_\mu \partial \lambda_q} \bigg|_{\lambda_q=\lambda_\mu=0} + \frac{1}{6} \frac{\partial^3 Z}{\partial \lambda_\mu^3} \bigg|_{\lambda_q=\lambda_\mu=0}. \tag{5.85}
\]
The configurational partition function is expressed in terms of intermolecular potential as

\[
Z = \frac{1}{\Omega^N} \int dr_1 \ldots dr_N \int d\omega_1 \ldots d\omega_N e^{[-\beta(\lambda q U_{13} + \lambda q U_{23})]}
\]

\[
e^{-\beta \lambda \mu U_{33}} e^{(-\beta(U_{11} + U_{12} + U_{22} + U_{13}^0 + U_{23}^0 + U_{33}^0))}. \tag{5.86}
\]

\(\omega_N\) is a set of Euler angles used to describe the orientation of particles 1 to N. \(\Omega = 4\pi\) for a linear molecule. The subscripts 1, 2 and 3 represent positive ions, negative ions and dipoles, respectively. The superscript 0 shows that the interaction potential is the reference potential. The canonical pair distribution function for a pair of molecules \(\alpha\) and \(\beta\) is given by:

\[
g_{\alpha\beta}^0 = \frac{\Omega_\alpha \Omega_\beta}{\rho_\alpha \rho_\beta} N_\alpha (N_\beta - \delta_{\alpha\beta}) \int dr_1^{-} dr_2^{-} d\Omega_1 d\Omega_2 U_{13}^0 g_{13}^0 \tag{5.87}
\]

where \(\delta_{\alpha\beta}\) is the Kronecker delta. In eqn. (5.87)

\[
U_{13}^0 = U_{11} + U_{12} + U_{22} + U_{13}^0 + U_{23}^0 + U_{33}^0. \tag{5.88}
\]

The derivatives in eqn. (5.83) are

\[
\frac{1}{Z} \frac{\partial^2 Z}{\partial \lambda_q^2} |_{\lambda_q = \lambda_q = 0} = \frac{\rho_1 \rho_3}{\Omega^2} \int dr_1^{-} dr_2^{-} d\Omega_1 d\Omega_2 U_{13}^0 g_{13}^0 \tag{5.89}
\]

\[
+ \frac{\rho_1 \rho_3}{\Omega^3} \int dr_1^{-} dr_2^{-} dr_3^{-} d\Omega_1 d\Omega_2 d\Omega_3 U_{13} U_{13}^0 g_{13}^{0}\tag{5.90}
\]

\[
+ \frac{2 \rho_1 \rho_2 \rho_3}{\Omega^3} \int dr_1^{-} dr_2^{-} dr_3^{-} d\Omega_1 d\Omega_2 d\Omega_3 U_{13} U_{13}^0 g_{13}^{0}\tag{5.90}
\]

\[
+ \frac{2 \rho_1 \rho_2 \rho_3}{\Omega^3} \int dr_1^{-} dr_2^{-} dr_3^{-} d\Omega_1 d\Omega_2 d\Omega_3 U_{13} U_{13}^0 g_{13}^{0}\tag{5.90}
\]
The general expression for the spherical harmonic expansion of the potential in the intermolecular frame with the polar axis along \( r \) is given by the following expression

\[
\frac{1}{Z} \frac{\partial^3 Z}{\partial \lambda_q \partial \lambda_\mu} \bigg|_{\lambda_q = \lambda_\mu = 0} = -\frac{\beta^3}{2 \Omega^3} \rho_1 \rho_2^2 \frac{1}{\rho_3} \int dr_1^2 dr_2^3 dr_3^4 d\Omega_1 d\Omega_2 d\Omega_3 \left[ C_{1333}^{(123)}(12) U_{13}^{(13)}(13) U_{33}^{(23)}(23) \right] + \frac{\rho_1^2 \rho_2^2}{\Omega^4} \int dr_1^2 dr_2^3 dr_3^4 d\Omega_1 d\Omega_2 d\Omega_3 d\Omega_4 \left[ C_{0331}^{(123)}(12) U_{13}^{(13)}(13) U_{23}^{(13)}(23) U_{33}^{(34)}(34) \right] + \frac{\rho_3^2}{\Omega^4} \int dr_1^2 dr_2^3 dr_3^4 d\Omega_1 d\Omega_2 d\Omega_3 d\Omega_4 \left[ C_{2333}^{(123)}(12) U_{23}^{(13)}(12) U_{23}^{(13)}(13) U_{33}^{(34)}(34) \right].
\]

The general expression for the spherical harmonic expansion with the polar axis along \( r \) is given by the following expression

\[
\frac{1}{Z} \frac{\partial^3 Z}{\partial \lambda_q \partial \lambda_\mu} = -\frac{\beta^3}{2 \Omega^3} \rho_1 \rho_2^2 \frac{1}{\rho_3} \int dr_1^2 dr_2^3 dr_3^4 d\Omega_1 d\Omega_2 d\Omega_3 \left[ C_{33}^{(123)}(123) U_{33}^{(12)}(12) U_{33}^{(13)}(13) U_{33}^{(23)}(23) U_{33}^{(34)}(34) \right].
\]

The general expression for the spherical harmonic expansion of the potential in the intermolecular frame with the polar axis along \( r \) is given by the following expression

\[
U_{1l_2} = A_{l_1 l_2} \left( \frac{2l_1 + 1}{4\pi} \right)^{1/2} \left( \frac{Q_{l_1} Q_{l_2}}{r^{l_1 + 1}} \right) \sum_m C(l_1 l_2; m m 0) Y_{l_1 m}(\omega_1) Y_{l_2 m}(\omega_2)
\]

where

\[
A_{l_1 l_2} = \frac{(-1)^{l_2}}{2l + 1} \frac{(4\pi)^3 (2l + 1)!}{(2l_1 + 1)!(2l_2 + 1)!}^{1/2}.
\]

\( Q_{l_1} \), \( Q_{l_2} \) are the multipole moments, \( C(l_1 l_2; m m 0) \) is the Clebsch-Gordan coefficient. \( Y_{l_1 m} \), \( Y_{l_2 m} \) are the spherical harmonic coefficients. For ions, \( l = 1 \), for dipoles,
l=2 and for quadrupoles, l=3, etc. The Clebsch-Gordan coefficients are related to Wigner 3-j symbols with

$$\begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} = (-1)^{l_1+l_2+m(2l+1)} -^{1/2} C(l_1l_2l; m_1m_2m). \quad (5.95)$$

The dipole-dipole and ion-dipole energies are expressed as

$$U_{33}(12) = -\frac{4\pi\mu^2}{r_{12}^3} Y_1^1(\Omega_1) Y_1^1(\Omega_2), \quad (5.96)$$

$$U_{23}(12) = -\frac{4\pi}{3} q_2 \mu \frac{r_{12}^3}{r_{12}^4} Y_1^0(\Omega_1), \quad (5.97)$$

$$U_{13}(12) = \frac{4\pi}{3} q_2 \mu \frac{r_{12}^3}{r_{12}^4} Y_1^0(\Omega_1). \quad (5.98)$$

The spherical harmonic coefficients used to represent a mixture of ion-dipole are

$$Y_{00}(\omega_{12}) = \left[\frac{1}{4\pi}\right]^{1/2}, \quad (5.99)$$

$$Y_{10}(\omega_{12}) = \left[\frac{3}{4\pi}\right]^{1/2} \cos \theta, \quad (5.100)$$

$$Y_{11}(\omega_{12}) = \left[\frac{3}{8\pi}\right]^{1/2} \sin \theta e^{i\phi}. \quad (5.101)$$

Substituting eqns. (5.96-5.101) in the derivatives in eqn. (5.83) and rearranging, an expression for the Helmholtz free energy for the mixture is obtained as

$$-\beta(A_c - A_0) = k_1 \rho_3^2 \beta^2 \mu \rho \int g_{33}^0 r^{-6} d\tilde{r}_1 d\tilde{r}_2 + k_2 \rho_2^2 \beta^2 \mu \rho \int g_{13}^0 r^{-4} d\tilde{r}_1 d\tilde{r}_2 + \rho_2 \rho_3 \int g_{23}^0 r^{-4} d\tilde{r}_1 d\tilde{r}_2$$

$$+ k_3 \beta^2 \mu^2 (\rho \rho_3^2 \int f_{131}^0 r^{-4} d\tilde{r}_1 d\tilde{r}_2 d\tilde{r}_3 + \rho_1 \rho_2 \rho_3 \int f_{232}^0 r^{-4} d\tilde{r}_1 d\tilde{r}_2 d\tilde{r}_3)$$

$$+ k_4 \beta^3 \rho_3^6 \int f_{333}^0 r^{-4} d\tilde{r}_1 d\tilde{r}_2 d\tilde{r}_3$$
\[ + k_5 \beta^3 q^2 \mu^4 (\rho_1 \rho_3^2 \int f_3 g_{133}^0 d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 + \rho_2 \rho_3^2 \int f_3 g_{233}^0 d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3) \]
\[ + k_6 \beta^3 q^2 \mu^4 \rho_3^2 (\rho_1^2 \int g_{1331}^0 f_4 d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 + \rho_2^2 \int g_{2332}^0 f_4 d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4). \] (5.102)

The functions \( f_1 \) to \( f_4 \) represent the orientational averages and are given by the following equations

\[ f_1 = \frac{\cos \theta_1}{r_{12}^2 r_{23}^2}, \] (5.103)
\[ f_2 = \frac{(1 + 3 \cos \theta_1 \theta_2 \theta_3)}{r_{12}^3 r_{23}^3 r_{13}^3}, \] (5.104)
\[ f_3 = \frac{\cos \theta_2 \cos \theta_3 + \cos (\theta_2 - \theta_3)}{r_{12}^2 r_{23}^2 r_{13}^3}, \] (5.105)
\[ f_4 = \frac{2 \cos \theta_1 \cos \theta_2 \cos \theta_3 - \sin \theta_1 \sin \theta_2 \cos (\phi_{13} - \phi_{24})}{r_{13}^3 r_{24}^3 r_{34}^3}. \] (5.106)

where \( \theta_1, \theta_2, \theta_3 \) are the interior angles of the triangle formed between the three particles. \( \theta_{23}, \theta_{24} \) are the polar angles, \( \phi_{13} \) and \( \phi_{24} \) are the azimuthal angles for the four particle system. The constant \( k_1 \) to \( k_6 \) are given by

\[ k_1 = \frac{2\pi}{3}, \]
\[ k_2 = 2\pi, \]
\[ k_3 = \frac{1}{8\pi}, \]
\[ k_4 = \sqrt{\frac{10}{3}}, \]
\[ k_5 = \frac{8\pi^2}{25}, \]
\[ k_6 = \frac{1}{36\sqrt{5}\pi}. \] (5.107)
$g_{ij}^0$, $g_{ijk}^0$ and $g_{ijkl}^0$ are the two, three and four body distribution functions for a mixture of ions and hard spheres. The three and four body distribution functions are calculated with the superposition approximation as

$$g_{ijk}^0(123) = g_{ij}^0(12)g_{ik}^0(13)g_{jk}^0(23), \quad (5.108)$$

$$g_{ijkl}^0(1234) = g_{ij}^0(12)g_{ik}^0(13)g_{il}^0(14)g_{jk}^0(24)g_{jl}^0(23)g_{kl}^0(34). \quad (5.109)$$

where $i,j,k$ and $l$ represent different combinations of anions, cations and dipoles.

5.3.2 Evaluation of multibody integrals

The integrals involving two body pair correlation functions are evaluated in the spherical polar coordinate system, using the trapezoidal rule.

$$\int dr_1^2 \cdots = \frac{N}{\rho} 4\pi \int_0^\infty \frac{d}{dr_1} \frac{r_1^2}{12} \cdots$$

$$= \frac{\Delta x}{2} \sum_{i=1}^n (f(i) + f(i + 1)) \quad (5.110)$$

where $f$ is the function to be integrated. The increment size and the upper limit of integration are chosen as $0.05\sigma$ and $12\sigma$, respectively, to provide acceptable accuracy with minimum computational effort.

It is more convenient to calculate the triple vector integrals involving 3-body distribution functions in the bipolar coordinate system.

$$\int dr_1^2 dr_2 dr_3 \cdots = \frac{N}{\rho} 8\pi 2 \int_0^\infty r_{12}^2 dr_{12} \int_0^\infty r_{13}^2 dr_{13} \int |r_{12} + r_{13}| dr_{23} \cdots$$

$$= \frac{N}{\rho} 8\pi 2 \int_0^\infty r_{12}^2 dr_{12} \int_0^\infty r_{13}^2 dr_{13} \int |r_{12} + r_{13}| r_{23}^2 dr_{23} \cdots \quad (5.111)$$

where $r_{12}, r_{13}$ and $r_{23}$ are intermolecular distances between the three particles.

For the case of hard spheres the integral over $r_{13}$ and $r_{23}$ has been written as the
sum of two terms within the interval $1 \leq r_{12} \leq 2$ and as the sum of three terms in
the range $2 \leq r_{12} < \infty$ (40). The integral limits are given as follows:

Region Ia

\begin{align*}
1 \leq r_{13} & \leq r_{12} + 1 \\
1 \leq r_{23} & \leq r_{12} + r_{13} \\
1 \leq r_{12} & \leq 2. \\
\end{align*} \tag{5.112}

Region Ib

\begin{align*}
r_{12} + 1 \leq r_{13} & \leq T + 1 \\
r_{13} - r_{12} \leq r_{23} & \leq r_{12} + r_{13} \\
1 \leq r_{12} & \leq 2. \\
\end{align*} \tag{5.113}

Region IIa

\begin{align*}
1 \leq r_{13} & \leq r_{12} - 1 \\
r_{12} - r_{13} \leq r_{23} & \leq r_{12} + r_{13} \\
2 \leq r_{12} & \leq T. \\
\end{align*} \tag{5.114}

Region IIb

\begin{align*}
r_{12} - 1 \leq r_{13} & \leq r_{12} + 1 \\
1 \leq r_{23} & \leq r_{12} + r_{13} \\
2 \leq r_{12} & \leq T. \\
\end{align*} \tag{5.115}

Region IIc

\begin{align*}
r_{12} + 1 \leq r_{13} & \leq T + 1
\end{align*}
\[ r_{13} - r_{12} \leq r_{23} \leq r_{12} + r_{13} \]
\[ 2 \leq r_{12} \leq T. \]  
(5.116)

where \( T \) is used to represent the truncation distance. The same procedure is applied for the ion-dipole mixture. The integration step size and truncation distance are chosen as the same with the two body integrals. Using the cosine theorem, functions \( f_1 \) to \( f_3 \) are expressed as

\[
f_1 = \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{13}^3},
\]

\[
f_2 = \frac{r_{12}^2r_{13}^2r_{23}^2 + 3(r_{12}^2 + r_{13}^2 - r_{23}^2)(r_{12}^2 + r_{23}^2 - r_{13}^2)(r_{23}^2 + r_{13}^2 - r_{12}^2)}{8r_{12}^3r_{13}^5r_{23}},
\]

\[
f_3 = \frac{2(r_{23}^2 + r_{12}^2 - r_{13}^2)(r_{12}^2 + r_{23}^2 - r_{13}^2)}{4r_{12}^3r_{13}^3r_{23}^5} + \frac{[4r_{23}^2r_{12}^2 - (r_{23}^2 + r_{12}^2 - r_{13}^2)^2][4r_{13}^2r_{23}^2 - (r_{13}^2 + r_{23}^2 - r_{12}^2)^2]^{1/2}}{4r_{12}^3r_{13}^3r_{23}^5}
\]

(5.117)

The triple integrals are evaluated with the 3-dimensional trapezoidal rule

\[
I_{\text{triple}} = \frac{\Delta x \Delta y \Delta z}{8} f(x_0, y_0, z_0) + \frac{\Delta x \Delta y \Delta z}{8} f(x_N, y_N, z_N)
+ \frac{\Delta x \Delta y \Delta z}{8} f(x_0, y_N, z_0) + \frac{\Delta x \Delta y \Delta z}{8} f(x_N, y_N, z_0)
+ \frac{\Delta x \Delta y \Delta z}{8} f(x_N, y_0, z_N) + \frac{\Delta x \Delta y \Delta z}{8} f(x_0, y_0, z_N)
+ \frac{\Delta x \Delta y \Delta z}{8} f(x_0, y_0, z_0) + \frac{\Delta x \Delta y \Delta z}{8} f(x_N, y_0, z_0)
+ \frac{\Delta x \Delta y \Delta z}{4} \sum_{j=1}^{N-1} f(x_0, y_j, z_0) + \frac{\Delta x \Delta y \Delta z}{4} \sum_{j=1}^{N-1} f(x_N, y_j, z_N)
+ \frac{\Delta x \Delta y \Delta z}{4} \sum_{j=1}^{N-1} f(x_0, y_j, z_N) + \frac{\Delta x \Delta y \Delta z}{4} \sum_{j=1}^{N-1} f(x_N, y_j, z_j)
\]
\[
\int f_{ijkl}^{0}d\rho_{1}d\rho_{2}d\rho_{3}d\rho_{4} = \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} f_{ijkl}^{0}r_{12}^{2}\rho_{13}^{2}\rho_{14}^{2}\sin\theta_{23}\sin\theta_{24}dr_{12}dr_{13}dr_{14}d\theta_{23}d\theta_{24}d\phi_{13}d\phi_{24}
\]

(5.118)

where \(x, y, z\) are used for \(r_{12}, r_{13}\) and \(r_{23}\), and the subscripts 0 and \(N\) stand for the lower and upper limits of integration, respectively.

The evaluation of four dimensional vector integrals requires twelve dimensions in a spherical polar coordinate system. The dimensions can be reduced to seven by placing one particle at the origin of the reference frame and another one on the z-axis.

\[
\int f_{ijkl}^{0}d\rho_{1}d\rho_{2}d\rho_{3}d\rho_{4} = \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} f_{ijkl}^{0}r_{12}^{2}\rho_{13}^{2}\rho_{14}^{2}\sin\theta_{23}\sin\theta_{24}dr_{12}dr_{13}dr_{14}d\theta_{23}d\theta_{24}d\phi_{13}d\phi_{24}
\]

(5.119)
where $f_4$ is given by eqn. (5.106). In order to calculate the four body distribution function $g_{ijkl}^0$ in the spherical polar coordinate system with the superposition approximation, the interparticle separation must be calculated using the cosine theorem

$$r_{23} = (r_2^2 + r_3^2 - 2r_2r_3\cos\theta_{23})^{1/2}. \quad (5.120)$$

$$r_{24} = (r_2^2 + r_4^2 - 2r_2r_4\cos\theta_{24})^{1/2}. \quad (5.121)$$

$$r_{34} = (r_3^2 + r_4^2 - 2r_3r_4(\cos\theta_{23}\cos\theta_{24} + \cos\Delta\phi_{34}\sin\theta_{23}\sin\theta_{24}))^{1/2}. \quad (5.122)$$

The three dimensional trapezoidal rule can be extended to six dimensions, however this approach requires large amount of calculations for a successful approximation. As an alternative approximate integration by a Monte Carlo method is preferred.

In this method, the value of the multi-dimensional integral is calculated approximately by a sampling procedure.

$$I = \int_a^b f(x)dx = \frac{b-a}{N_s} \sum_{i=1}^{N_s} f(x_i) \quad (5.123)$$

where $N_s$ is the number of samples and $x_i$ are random values of $x$ in the interval $(a, b)$. The law of large numbers requires that;

$$\text{probability}(\lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{n} f(x_i) = I) = 1. \quad (5.124)$$

Therefore the accuracy of integration is proportional to the number of the sampling steps, but depends upon the nature of the function to be integrated. If the function is symmetrical w.r.t. all variables and the integral limits are the same, only a
relatively small number of samples may be sufficient. But for highly unsymmetrical functions and with different integration limits, a large number of samples is required.

One of the questions associated with the application of the MC method is how to generate a random sequence of numbers. It is possible to use sequences of numbers prepared in advance or to connect up the computer to a physical process with a random feature in it. In practice, these are not done. The first requires too much storage. The second has the poor feature that the numbers can not be duplicated easily and, hence, a computation can not be readily checked. In practice, so-called pseudorandom sequence of numbers are generated and used. A pseudorandom sequence of numbers is a deterministic sequence of numbers, each of which are unpredictable by themselves which satisfies certain statistical tests depending on the uses to which the sequence is to be put. These tests include tests for uniform distribution, for independence of successive numbers, and for autocorrelation between consecutive numbers.

Pseudorandom sequences are most commonly generated by the power residue method, since this method satisfies the above mentioned tests. The integers $x_1, x_2, \ldots$ are defined recursively by means of

$$x_{n+1} = ax_n (mod[m]). \quad (5.125)$$

Hence a and m are certain integers, such that $x_{n+1}$ is the remainder when $ax_n$ is divided by m. Since division by m can produce at most m different reminders, the sequence $x_0, x_1, \ldots$ will be a periodic sequence whose period can not exceed m. Therefore, a and m must be selected to produce a period that is large relative to the number of random numbers required in a computation.
The computer code used in these simulations has been developed by G.P. Morriss for dipolar diatomic fluids. It has been modified to simulate mixtures of ions and solvent molecules. In all the simulations, ions are described as hard spheres with positive or negative point charges. The state points simulated in which the solvent molecules are represented as hard spheres with embedded point dipoles, hard spheres with embedded point dipoles and linear quadrupoles, and dipolar diatomics with a point charge on each site are shown in Tables 6.1, 6.2 and 6.3 respectively.

### 6.1 Simulations with the First Solvent Model

The first set of simulations have been performed to study the effect of ionic charge and concentration on the structure and thermodynamics of electrolyte solutions. The effect of ion concentration on the structure is shown in Figures 6.1-6.3, where the dipole-dipole, dipole-ion and unlike ion pair correlation functions are plotted as a function of the dimensionless distance and in Table 6.4, where the coordination numbers for different kind of ions and solvent molecules are shown.

It can be seen in Figure 6.1 that the ion concentration has a significant effect on the solvent structure as far as the immediate neighborhood of each solvent particle is considered. When the ion concentration increases in the range 0.4-2.0
Table 6.1: State points simulated with the first solvent model

<table>
<thead>
<tr>
<th>Run</th>
<th>M</th>
<th>$q^*^2$</th>
<th>$N_i$</th>
<th>$N_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>40.0</td>
<td>192</td>
<td>1536</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>160.0</td>
<td>192</td>
<td>1536</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>160.0</td>
<td>76</td>
<td>1652</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>40.0</td>
<td>76</td>
<td>1652</td>
</tr>
<tr>
<td>5</td>
<td>1.6</td>
<td>160.0</td>
<td>128</td>
<td>601</td>
</tr>
<tr>
<td>6</td>
<td>2.0</td>
<td>160.0</td>
<td>160</td>
<td>569</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>0.0</td>
<td>56</td>
<td>456</td>
</tr>
</tbody>
</table>

The reduced charge $q^*^2 = q^2/\sigma kT$, the approximate Molarity M, (assuming an ionic diameter of 0.425nm), the number of solvent particles $N_s$ and ions $N_i$ are shown. In all runs the reduced dipole moment $\mu^*^2 = 2.5$.

Table 6.2: State points simulated with the second solvent model

<table>
<thead>
<tr>
<th>Run</th>
<th>M</th>
<th>$\Theta^*^2$</th>
<th>$N_i$</th>
<th>$N_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1.0</td>
<td>0.5</td>
<td>192</td>
<td>1536</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>1.0</td>
<td>192</td>
<td>1536</td>
</tr>
</tbody>
</table>

The reduced charge $q^*^2 = 160.0$ and the reduced dipole moment $\mu^*^2 = 2.5$. $\Theta^*^2 = \Theta^2/\sigma^5 kT$ is the reduced quadrupole moment of the solvent molecules.

Table 6.3: State points simulated with the third solvent model

<table>
<thead>
<tr>
<th>Run</th>
<th>M</th>
<th>$q^*^2$</th>
<th>$N_i$</th>
<th>$N_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.0</td>
<td>40.0</td>
<td>112</td>
<td>888</td>
</tr>
<tr>
<td>11</td>
<td>1.0</td>
<td>160.0</td>
<td>112</td>
<td>888</td>
</tr>
<tr>
<td>12</td>
<td>0.4</td>
<td>160.0</td>
<td>44</td>
<td>956</td>
</tr>
</tbody>
</table>

The reduced dipole moment $\mu^*^2 = 2.5$ and the elongation of the two fused hard spheres forming the solvent molecules, $l/\sigma = 0.5$.

Table 6.4: Coordination numbers versus concentration at $q^*^2 = 160$

<table>
<thead>
<tr>
<th>conc.</th>
<th>$(++)$ ions</th>
<th>$(-)$ ions</th>
<th>$(+-)$ ions</th>
<th>solv.-solv.</th>
<th>solv.-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4 M</td>
<td>0.05</td>
<td>0.06</td>
<td>0.68</td>
<td>11.69</td>
<td>6.36</td>
</tr>
<tr>
<td>1.0 M</td>
<td>0.16</td>
<td>0.25</td>
<td>1.20</td>
<td>11.21</td>
<td>6.03</td>
</tr>
<tr>
<td>1.6 M</td>
<td>1.19</td>
<td>0.95</td>
<td>1.51</td>
<td>9.18</td>
<td>6.02</td>
</tr>
<tr>
<td>2.0 M</td>
<td>2.33</td>
<td>2.20</td>
<td>1.86</td>
<td>8.70</td>
<td>5.32</td>
</tr>
</tbody>
</table>
M, at a fixed ion charge \((q^* = 160.0)\), the coordination of solvent molecules with other solvent molecules decreases about 25 percent. The second peak at \(r = 2\sigma\) of the solvent-solvent pair distribution function indicates that the three neighboring solvent particles, or the solvent particles separated by one anion or cation, form linear geometry. The effect of ionic concentration on this structure is negligible.

The ion-dipole geometry is affected by ion concentration. A larger number of solvent molecules are involved in the solvation of ions at low ionic concentrations as is shown in Table 6.4. The structure is enhanced at lower ionic concentrations, with higher contact value and second maximum of the ion-solvent pair correlation function as shown in Figure 6.2. The shape of the ion-solvent pair distribution function suggests that the triplets formed by ion and solvent particles, separated by another solvent or ion of opposite charge are linear. This structure becomes slightly less dominant at higher ionic concentrations. For the case of 2 M solution, a shoulder appears at approximately \(1.4\sigma\), which is roughly the length of the diagonal of a square formed by four equal sized ions and dipoles at the opposite corners. This means that at high concentrations large ionic clusters, which include some solvent particles, exist. In general, shoulders at \(\sqrt{2}\sigma\) and \(\sqrt{3}\sigma\) can be attributed to an fcc type lattice structure. But a single peak at \(\sqrt{2}\sigma\) suggests that the form of the ion-solvent clusters is a polyhedra with square faces.

At low ionic concentrations unlike ion structure is also affected in the same way. A higher contact value and an increase in the height of the second maximum in the unlike ion pair correlation function at \(r = 2\sigma\) occurs, as can be seen in Figure 6.3. The magnitude of the second maximum indicates that there is a significant increase in the amount of solvent separated ion pairs at low ionic concentrations. An increase
in the contact value of the pair distribution function might indicate more ion pairs at low ionic concentrations. However, the first coordination number for oppositely signed ions is found to increase as ion concentration increases, which seems to be in contradiction with the high contact values of the pair distribution functions at low concentrations. Therefore, it is concluded that at low ionic concentrations the ion pairs are more strongly bound to each other than at higher concentrations. It is essential to make higher order analyses to determine the relative numbers of ion pairs and the contribution of bigger ionic clusters to the pair distribution function.

The first coordination number is zero for similarly charged ions, since the first minimum of the pair distribution function is located at the origin. The integral of the pair distribution function to the minimum point following the first maximum corresponds to the second coordination number and gives an idea about the number of similar particles screened, partially or totally, by one other particle. This may be either an oppositely charged ion or a solvent particle. The second coordination number for the same type of ions is also found to increase with ionic concentration, but because of the statistical uncertainties involved in the similar ion distribution function, location of the minimum may not be very accurate in this case. Since the size and charge magnitude of both types of ions in the purely dipolar solvent are the same, symmetry requires that

\[ g_{++}(r) = g_{--}(r). \]  

(6.1)

This is found to be a difficult criterion to satisfy, even with the very large system sizes and number of sampling steps employed in the simulations.

After the initial lattice structure melts into a liquid like state, which corresponds to approximately 1.2-2 million configurations in the MC calculations, the
sampling procedure is carried out for the next 9-18 million configurations. At the end of the first few million steps, the statistics for the similar type ion distribution functions are found to be quite poor, especially at low ionic concentrations (i.e., 0.4 M). The reason for the slow convergence of eqn. (6.1) may be due to insufficient initial equilibration steps. Although the randomness in the orientation and positions of the solvent particles and nondecaying configurational energies indicate a stable liquid state point, the distribution of ions may not attain equilibrium. Large ionic clusters may exist at the beginning of the simulation and a very large number of steps may be required to break them down. At higher ionic charges the situation is even more critical. A larger number of initial equilibration steps is needed to obtain stable energies. It is concluded that, the convergence of eqn. (6.1) is strongly dependent on the system size and the number of sampling steps and extremely large systems of particles must be considered in order to obtain better statistics than those reported here.

Anion and cation distribution functions for the first seven runs are presented in Figures 6.4-6.10. At low ionic concentrations a maximum occurs close to \( r = 2\sigma \), indicating that ionic triplets or solvent separated similar ions are linear or close to linear in shape. At higher concentrations, a maximum lies between \( r = 1.2\sigma \) and \( r = 1.8\sigma \), which means that similar ions are only partially screened by a solvent particle or an ion of opposite charge. The structure of the ionic clusters is further examined by calculating the triplet ion distribution functions, as described below.

Besides the symmetry of anion and cation pair distribution functions, the variation in properties like specific heat and static component of the dielectric constant may give an idea about the amount of statistical error in the results and may be
Table 6.5: Thermodynamic properties versus ionic concentration at $q^2 = 160$

<table>
<thead>
<tr>
<th>$M^a$</th>
<th>$U^*$</th>
<th>$Z$</th>
<th>$C_{v^*}$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-3.127</td>
<td>2.7</td>
<td>3.9</td>
<td>31</td>
</tr>
<tr>
<td>0.4</td>
<td>-8.736</td>
<td>2.6</td>
<td>5.1-5.3</td>
<td>10.7-11.2</td>
</tr>
<tr>
<td>1.0</td>
<td>-16.922</td>
<td>1.2</td>
<td>15.4-15.8</td>
<td>6.2-6.4</td>
</tr>
<tr>
<td>1.6</td>
<td>-24.689</td>
<td>-0.14</td>
<td>10.5</td>
<td>4.5</td>
</tr>
<tr>
<td>2.0</td>
<td>-29.963</td>
<td>-1.08</td>
<td>18.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

$a$ The reduced internal potential energy $U^* = U/NkT$, the compressibility factor $Z$, the reduced specific heat $C_{v^*} = C_v/Nk$ and the static component of the dielectric constant $\epsilon$ are shown.

used as a stopping criterion. In Figure 6.11 the variation in the static component of the solution dielectric is shown for runs 1-3 as the simulation proceeds. The dependence of thermodynamic properties on ionic concentration is shown in Table 6.5. The specific heat of the solution is found to increase with concentration while the internal potential energy, compressibility factor and the static component of the dielectric constant decrease. The discontinuity in the specific heat between 1 M and 1.6 M solutions, and the negative values of the compressibility factor, indicate that a phase change occurs between 1 M and 1.6 M for this solution.

The effect of ionic charge on the solution structure is shown in Figures 6.12-6.17. Figures 6.12 and 6.13 show that the ionic charge has a larger effect on the solvent-solvent geometry for the 1 M solution than for the 0.4 M solution. At higher ionic charges, the contact value of the solvent-solvent pair correlation function and the height of the second maximum slightly decrease. The effect of ionic charge on the structure formed by linear solvent triplets or linear ion separated solvent particles is negligible. There are slightly larger numbers of other solvent molecules in the first coordination shell of each solvent molecule at low ionic charges.
Table 6.6: Coordination numbers versus ionic charge for the 1 M solution

<table>
<thead>
<tr>
<th>$q^\pm$</th>
<th>$(\text{++})$ ions</th>
<th>$(\text{--})$ ions</th>
<th>$(\text{+-})$ ions</th>
<th>solv.-solv.</th>
<th>solv.-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.215</td>
<td>0.262</td>
<td>0.266</td>
<td>9.58</td>
<td>6.60</td>
</tr>
<tr>
<td>40.0</td>
<td>0.540</td>
<td>0.682</td>
<td>0.987</td>
<td>10.07</td>
<td>7.40</td>
</tr>
<tr>
<td>160.0</td>
<td>0.163</td>
<td>0.246</td>
<td>1.187</td>
<td>11.21</td>
<td>6.03</td>
</tr>
</tbody>
</table>

The effect of ionic charge on ion-dipole structure is shown in Figures 6.14, 6.15 and Table 6.6 where the CN is higher at $q^\pm = 40$. At high ionic charge, there are fewer solvent particles in the first solvation shell of the ions, but these solvent particles are very tightly bound to the ions. The higher contact values and sharper decay of the pair correlation functions for $q^\pm = 160$ and relatively lower contact value but slower decay for $q^\pm = 40$, shown in Figures 6.14 and 6.15 indicate that at low ionic charge the ions are coordinated with a larger number of solvent particles which are loosely bound to the ions.

The ionic charge has a very important effect on the ion-ion geometry. At higher values of the ionic charge, the contact value of the oppositely signed ion pair correlation function and the coordination number increase significantly, as can be seen in Figures 6.16, 6.17 and Table 6.7. There are more ion pairs, or larger ionic clusters, at higher ionic charge. The increase in the amount of solvent separated ion pairs is significant as the ionic charge increases.

An increase in ionic charge has an effect similar to an increase in ionic concentration, on the thermodynamic properties of the solution. The total potential energy, compressibility and dielectric constant decrease while the specific heat increases with ionic charge. However, for the case of 0.4 M solution, there is a slight decrease in the specific heat at a higher ionic charge. These effects are shown in
Table 6.7: Thermodynamic properties versus ionic charge for the 1 M solution

<table>
<thead>
<tr>
<th>$q^*$</th>
<th>$U^*$</th>
<th>$Z$</th>
<th>$C_v^*$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-2.879</td>
<td>3.80</td>
<td>3.0</td>
<td>19.7</td>
</tr>
<tr>
<td>40.0</td>
<td>-6.311</td>
<td>3.17</td>
<td>2.5</td>
<td>12.6</td>
</tr>
<tr>
<td>160.0</td>
<td>-16.922</td>
<td>1.20</td>
<td>15.4-15.8</td>
<td>6.2-6.4</td>
</tr>
</tbody>
</table>

Table 6.8: Thermodynamic properties versus ionic charge for the 0.4 M solution

<table>
<thead>
<tr>
<th>$q^*$</th>
<th>$U^*$</th>
<th>$Z$</th>
<th>$C_v^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>-4.515</td>
<td>3.4</td>
<td>6.3</td>
</tr>
<tr>
<td>160.0</td>
<td>-8.736</td>
<td>2.6</td>
<td>5.1-5.3</td>
</tr>
</tbody>
</table>

Table 6.7 and 6.8.

The triplet distribution function $g_3(r_{12}, r_{13}, \theta)$ for oppositely charged ions (+-) is calculated. In Figure 6.18 $g_3(1.025, 1.025, \theta)$ at different ionic concentrations is shown. At a relatively lower ionic concentration, e.g., 0.4 M, there are fewer triplets than at higher concentrations and the most favorable angle formed by these three ions is approximately $120-138^\circ$. When this result is compared with the high contact value of the oppositely charged ion distribution function at low concentrations, it can be concluded that the solution is dominated by pairs of ions and single ions at 0.4 M. At a concentration of 1 M, there are more triplets and bigger clusters of ions in the solution. A peak at $180^\circ$ corresponds to linear triplets, while a second peak at $90^\circ$ shows that there are quadruplets or bigger clusters in the solution. The maximum at $180^\circ$ vanishes and a single peak at $90-105^\circ$ is observed at 1.6 M and 2.0 M solutions. This means that the solution is dominated by quadruplets and bigger clusters. However, the decrease in the contact value of the pair distribution, and the value of the triplet distribution function at $r = 1.025\sigma$, with increasing concentration above 1 M, suggests that the amount of solvated ions increases with concentration as well.
This may be attributed to big nonneutral clusters accompanied by single ions in highly concentrated solutions. It may also be concluded that bigger clusters are less tightly packed than the smaller ones. The effect of ionic charge on $g_2(1.025,1.025,\theta)$ is presented in Figure 6.19 where, at zero ionic charge, there is no cluster formation and the amount of ionic clustering increases as ion charge increases.

In order to provide additional information about ionic cluster formation, the number of ions involved in clusters of different sizes are counted and averaged over several configurations. The results for the first four runs are given in Figure 6.20. The neighborhood for pairs of ions is chosen to be $1.2\sigma$. Figure 6.20 gives further evidence that, at low ionic charges and concentrations, the solution is dominated by solvated ions and pairs of ions to a lesser degree. At higher charges and concentrations, larger ionic clusters appear and increase in amount.

The spherical harmonic coefficients $g_{1s}^{101}(r)$, $g_{3s}^{110}(r)$ and $g_{3s}^{112}(r)$ that are defined in section 2.2.1 are calculated in the simulation. These functions are the projections of the pair distribution functions and can be viewed as a quantitative measure of the response of each particle to the electric field set up by the rest of the particles. The results for the first four runs are given in Figures 6.21-6.23. $g_{1s}^{101}(r)$ is closely related to the ion-dipole energy and is proportional to the cosine of the angle between the dipole moment vector and the unit vector joining the centers of the ion and solvent particles. $g_{1s}^{101}(r)$ is symmetrical w.r.t. both type of ions within statistical error. A dipole in the vicinity of an anion is expected to orient itself so that the dipole moment vector points toward the negative ion, and turns $180^0$ from a cation. These configurations represent minimum interaction energies. However, the complexity of the ionic clusters formed in the solution makes this configuration
difficult to maintain. For the case of low ionic concentration and charge, where the
majority of the ions are solvated, dipoles are oriented strongly to minimize the inter-
action energy when they are close to ions. At high ionic charge and concentration,
where larger ionic clusters exist, orientation of dipoles becomes weaker.

\( g_{ss}^{110}(r) \) is related to the static component of the dielectric constant and is
proportional to the cosine of the angle between the dipole moment vectors of the
two dipoles. \( g_{ss}^{112}(r) \) is related to the dipole-dipole energy and is a function of
the relative orientations of two dipoles. In order to provide the minimum energy
orientation, two dipoles must be lined up, head-to-tail in the same direction. In
the immediate vicinity of a dipole, there is a strong electric field which induces an
alignment of other dipoles. The magnitude of the ionic charge has a slight effect in
destroying this structure. At higher ionic concentrations the electric field generated
by ions has a slightly larger influence on the orientation of dipoles.

6.2 Comparison with the Theory and Primitive Model Simulations

The first set of simulations provided an opportunity to test the quality of
integral equation theories for a mixture of ions and dipoles and the continuum
solvent model. In Figures 6.24-6.39, the structure of an ion-dipole mixture predicted
by MSA and LHNC theories (where available) are compared with the simulation
results. The solvent-solvent pair distribution functions are predicted well by MSA,
but the ion-solvent distribution functions are very different from both LHNC and
MC results. For the relatively lower ionic charge and concentration, LHNC theory
gives satisfactory results for the ion-solvent structure. The nonzero contact values
of the similar ion pair distribution functions predicted by MSA and LHNC theories
at the low ionic charge and concentration don’t seem to be realistic. The position of the maximum, at approximately \( r = 1.75\sigma \), is predicted as \( 1.4\sigma \) by the LHNC theory and \( 2\sigma \) by the MSA. This doesn’t reflect the actual ion-ion geometry. Both theories underestimate the oppositely charged ion distribution function at small \( r \). The second maximum of the function is underestimated by MSA and overestimated by LHNC.

In Figures 6.28-6.39, the spherical harmonic coefficients \( g_{33}^{112}(r) \), \( g_{33}^{110}(r) \) and \( g_{1s}^{101}(r) \) of the pair distribution functions obtained from MSA are compared with MC simulation results for the first four runs. For the case of \( g_{33}^{112}(r) \) and \( g_{33}^{110}(r) \), MSA underestimates both the short range structure and the second maximum at \( r = 2\sigma \). Agreement between the MSA and MC results is not very satisfactory for \( g_{1s}^{101}(r) \) either. The pair contact value and the second maximum are either underestimated or overestimated by the theory at different state points.

The static component of the dielectric constant calculated from MSA theory is fairly close to simulation results at \( q^* = 160 \), as shown in Figure 6.40. At \( q^* = 40 \) and 0.4 M solution, the magnitude of the oscillation in the static dielectric constant was important even after ten million sampling steps of MC simulation and this point is not included in Figure 6.41. It is concluded that a larger number of sampling steps must be considered to obtain a reliable simulation result for the static dielectric constant at this state point. Although the concentration dependence of the static dielectric constant predicted by MSA and LHNC theories show trends similar to the MC results, the discrepancy is between 5 and 30 per cent.

The compressibility factor predicted by the LHNC theory is in good agreement with simulation results at \( q^* = 40 \), except at 0.4 M, but MSA results for the com-
pressibility factor are very poor. These comparisons are shown in Figure 6.42. The internal configurational energy and its components, as predicted by LHNC theory at $q^{*2} = 40$, are compared with simulation results in Figure 6.43. Except for the ion-dipole energy, which is slightly underestimated at higher ionic concentrations, the agreement between LHNC and simulation is very good. In Figures 6.44 and 6.45, MSA results for the internal energy as a function of ionic concentration at $q^{*2} = 160$ and ionic charge for the 1 M solution are presented. The agreement is quite satisfactory, except for the ion-dipole energy which is overestimated by the theory.

Thermodynamic perturbation theory as developed by Henderson et al. was examined and singularities at certain combinations of ionic charge and concentration were observed. As described in Chapter 5, the singular terms are removed and a new Padé approximation is suggested. The dimensionless internal configurational energy, and its components predicted by the modified version of the HBT theory (MHBT), are plotted w.r.t. ionic concentration and charge in Figures 6.46 and 6.47, respectively. Although the ion-ion energy and the total energy are predicted well, the dipole-dipole energy is underestimated and the ion-dipole energy is overestimated. The theory neglects the coupling effect of ionic interactions on the dipole-dipole energy or vice versa and is therefore restricted to low ionic charges and concentrations. For the case of highly polar solvents, it may not give the correct ion-ion energies.

Oppositely charged ion pair distribution functions, obtained for mixtures of ions and dipoles, are compared with continuum solvent model results for 0.4 M and 1 M solutions in Figures 6.48 and 6.49, respectively. In the primitive model, the solution
Table 6.9: Comparison of ion-ion energies with different methods

<table>
<thead>
<tr>
<th>M</th>
<th>$U_{ii}(\text{sim})$</th>
<th>$U_{ii}(\text{MSA})$</th>
<th>$U_{ii}(\text{MHBT})$</th>
<th>$U_{ii}(\text{RPM})$</th>
<th>$U_{ii}(\text{MRPM})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-8.744</td>
<td>-10.133</td>
<td>-10.531</td>
<td>-2.126</td>
<td>-9.413</td>
</tr>
<tr>
<td>0.4</td>
<td>2.672</td>
<td>-3.150</td>
<td>-3.520</td>
<td>-1.765</td>
<td>-2.386</td>
</tr>
</tbody>
</table>

is represented by a single property, the dielectric constant. In most applications, the dielectric constant of the pure solvent is employed since that of the solution is not known. The effect of the electric field generated by the ions, which has a strong orientational influence on the solvent particles, is neglected. The thermodynamics of the solution is expected to be strongly dependent on the orientational and structural properties of the solution. To demonstrate the importance of this effect, two versions of the restricted primitive model with the dielectric constant of the pure solvent and the solution are compared with the discrete solvent model results obtained in the MC simulation. Although the pair contact values obtained with the modified restricted primitive model (MRPM) are much closer to the discrete solvent model result, the second maximum of the pair distribution function is not predicted at all by either versions of the primitive model. However, there is a big improvement in the ion-ion energies predicted by the MRPM, in comparison with the simulation results and other theoretical methods at the same state point. These results are tabulated in Table 6.9, where $q^* = 160$ and $\mu^* = 2.5$ at the state point considered.

6.3 Simulations with the Second and Third Solvent Models

Most solvents have non-zero quadrupole moments. As mentioned in Chapter 3, it has been found that a proper account of the dielectric properties of water requires that both dipolar and quadrupolar interactions be considered (79,80). This
important observation suggests promise for the development of a realistic model of ionic solutions which is sufficiently simple to be theoretically tractable. Three additional MC simulation studies are performed with the pure dipolar plus quadrupolar solvent, with $\mu^* = 2.5$ and $\Theta^* = 0.0, 0.1, 1.0$ at a total density of $\rho^* = 0.678$. The effect of the magnitude of the quadrupole moment on the structure of the pure solvent is shown in Figure 6.50. At a high quadrupole moment, solvent-solvent coordination improves and slight shoulders appear at approximately $r = 1.4\sigma$ and $r = 1.8\sigma$ of the pair correlation function. This may suggest a packed and ordered structure in the form of an fcc type lattice structure. This observation is consistent with previous studies on pure dipolar and quadrupolar solutions (101).

The second set of simulations are intended to study the effect of the quadrupolar nature of the solvent molecules on the solvation geometry. The most important observation is that the hydration properties of positive and negative ions, which are identical in purely dipolar solvents, are found to be dissimilar in the dipolar plus quadrupolar solvent model. This prediction is in agreement with experimentally observed results for the solvation of various anions and cations in water. It has been noted that, when oppositely charged ions are solvated in water, heats of solvation of cations are greater than those of anions with the same ionic radius and absolute ionic charge (102). This shows that cations have better solvation properties than anions with the same diameter in water. As water molecules have a negative net quadrupole moment, it is expected that negative ions are solvated more in solvents with positive quadrupole moments, as in the case of the present simulation results. These results are plotted in Figures 6.51-6.53. In Figure 6.51, where $\Theta^* = 0.0$, there is a symmetry between solvent-positive ion and solvent-negative ion pair correlation.
functions with small statistical uncertainties. In Figures 6.52 and 6.53, where the reduced quadrupole moment is equal to 0.5 and 1.0, respectively, this symmetry vanishes. In a dipolar plus quadrupolar solvent, negative ions have a larger number of solvent molecules in their first coordination shell, as can be seen from Table 6.10, and these solvent particles are more tightly bound to the negative ions than to the positive ions. The higher contact value and sharper decay of the solvent-anion pair correlation function, and relatively lower contact value and slower decay of the solvent-cation pair correlation function in Figures 6.52 and 6.53, suggest this structure.

The solvation characteristics of both kinds of ions are improved by the addition of a quadrupole moment. This is observed by an increase in the contact value of the ion-solvent correlation functions as the strength of the quadrupole moment increases in Figures 6.55 and 6.56. The enhancement is more significant for the negative ions. In the case of dipolar-quadrupolar solvent, the second maximum in the solvent ion pair correlation function, corresponding to the second coordination shell, splits into three parts: A slight shoulder at $1.4\sigma$, another shoulder at $r = 1.7\sigma$ and a peak at $r = 2\sigma$. This is more clearly observed in the case of negative ions at higher quadrupole moment, i.e., $Q^2 = 1.0$. At higher quadrupole moments, the second maximum in the solvent-cation pair correlation function becomes less pronounced, while it becomes more pronounced in the case of solvent-anion pair correlation. The appearance of shoulders and a decrease in the magnitude of the second peak suggests that solvent-anion pairs form a more packed and dense structure in the form of an fcc-type lattice for the case of a dipolar plus quadrupolar solvent.

The solvent-solvent pair distribution function is more structured with a higher
contact value and a second maximum at higher values of the quadrupole moment, as can be seen in Figure 6.54. Although the solvent-solvent coordination number is smaller for the quadrupolar solvents, these molecules are more tightly bound to each other. The higher contact value and sharp decay of the pair distribution function for the purely dipolar solvent and the lower contact value but slower decay for the dipolar plus quadrupolar solvent suggests this structure. The magnitude of the second maximum in the solvent-solvent pair correlation function increases as the quadrupole moment increases.

Unlike ion pair formation increases while the groups formed by unlike ions separated by one solvent molecule vanish with an increase in the quadrupole moment of the solvent, as is seen in Figure 6.57. There is an increase in the pair contact value and a disappearance of the second maximum of the function.

Although the like ion pair correlation functions contain a great amount of statistical uncertainty, it can still be observed from Figures 6.58 and 6.59 that the maximum, at approximately $r = 2\sigma$, of the pair correlation function is highest at an intermediate quadrupole moment, i.e., $\Theta^* = 0.5$. This means that either the number of linear ion triplets in the form of $(- + -)$ or the number of solvent separated like ions is largest at this state point. Figure 6.59 shows that, at $\Theta^* = 1$, the number of linear ion triplets in the form of $(+ - +)$ or the number of solvent separated like ions is largest. The nonzero contact values of the functions indicate that associated anions exist in the solution at $\Theta^* = 0.5$. But at a higher quadrupole moment these groups decay.

The triplet ion distribution function $g_3(1.025, 1.025, 0)$ and cluster size distribution at different values of the quadrupole moment of the solvent are presented
Table 6.10: Coordination numbers versus quadrupole moment of the solvent

<table>
<thead>
<tr>
<th>$\Theta^*^2$</th>
<th>(++)</th>
<th>(--)</th>
<th>(+-)</th>
<th>solv-solv</th>
<th>solv-(+</th>
<th>solv-(–)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.16</td>
<td>0.25</td>
<td>1.19</td>
<td>11.21</td>
<td>6.03</td>
<td>6.03</td>
</tr>
<tr>
<td>0.5</td>
<td>0.02</td>
<td>0.04</td>
<td>1.53</td>
<td>8.41</td>
<td>6.63</td>
<td>8.10</td>
</tr>
<tr>
<td>1.0</td>
<td>0.03</td>
<td>0.05</td>
<td>1.34</td>
<td>7.90</td>
<td>7.38</td>
<td>8.33</td>
</tr>
</tbody>
</table>

* In all runs $q^2 = 160.0$, $\mu^2 = 2.5$ and the solution is approximately 1 M.

in Figures 6.60 and 6.61. When the quadrupole moment of the solvent is different from zero the number of associated ions increases, but these ionic clusters form close to linear or linear configurations. This suggests a decrease in the cluster size. The actual cluster counting shows that at $\Theta^*^2 = 0$, there is a large number of solvated ions and large-size ionic clusters. At $\Theta^*^2 = 0.5$, the number of solvated ions and large clusters decreases significantly and medium-size ionic clusters are dominant in the solution. At $\Theta^*^2 = 1.0$, some of the intermediate size clusters break down into solvated ions and pairs of ions.

The harmonic functions $g_{10}^{11}(r)$, $g_{10}^{110}(r)$ and $g_{11}^{112}(r)$ are plotted in Figures 6.62-6.63. The addition of a quadrupole moment enhances the alignment of the dipoles in the direction of the electric field for negative ions. For the case of positive ions, the quadrupole moment of the solvent particles causes the dipoles to orient in a way different from their minimum energy orientation in the vicinity of the positive ions. As a result, the solvation energies of anions and cations are different and anions are solvated better than cations in the dipolar plus quadrupolar solvent used in this study. The functions $g_{10}^{110}(r)$ and $g_{11}^{112}(r)$ become less structured with dipole moment vectors oriented at angles greater than 0° w.r.t. each other in a dipolar plus quadrupolar solvent, which is of course different from the minimum
Table 6.11: Thermodynamic properties versus quadrupole moment of the solvent

<table>
<thead>
<tr>
<th>$\Theta^*2$</th>
<th>$U^*$</th>
<th>$Z$</th>
<th>$C_v^*$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-16.922</td>
<td>1.20</td>
<td>15.4-15.8</td>
<td>6.2-6.4</td>
</tr>
<tr>
<td>0.5</td>
<td>-19.296</td>
<td>1.33</td>
<td>14.7</td>
<td>4.4</td>
</tr>
<tr>
<td>1.0</td>
<td>-22.170</td>
<td>-0.35</td>
<td>4.9</td>
<td>5.4</td>
</tr>
</tbody>
</table>

$^a \mu^* = 2.5$ and the concentration of ions is approximately 1 M.

energy orientation for two dipoles.

Variations in the thermodynamic properties of the solution with the quadrupole moment of the solvent are given in Table 6.11. The sharp decrease in the specific heat suggests that a phase change takes place between $\Theta^*2 = 0.5$ and $\Theta^*2 = 1.0$. The negative pressure of the solution at $\Theta^*2 = 1.0$ supports this. Some differences are observed in the nature and mechanism of this phase change from the one observed with dipolar solvent between 1 M and 1.6 M solutions, in which most of the ions are collected together in the form of a metastable or unstable solid phase. After the phase change, i.e., at the 2 M solution, some solvent particles are included in the solid phase forming a polyhedra type structure with ions and solvent particles. In the present case, such large ionic clusters did not appear. This may be interpreted in two ways. Either the solid phase contains solvent particles as well as ions during the phase transition or a liquid-liquid type phase transformation takes place which seems to be quite unlikely at the very low temperature considered. Also the appearance of shoulders in the solvent-ion pair correlation function when the phase transition takes place suggests the formation of an fcc-type solid lattice involving ions and solvent particles.

In the case of electrolytes involving highly anisotropic solvent molecules, the idealized multipolar hard sphere model may not be sufficient to predict the orien-
Table 6.12: Specific heat and dielectric constant of the solution with the dipolar diatomic solvent model

<table>
<thead>
<tr>
<th>$q^2$</th>
<th>M</th>
<th>$C_v^*$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>1.0</td>
<td>5.48</td>
<td>20.0</td>
</tr>
<tr>
<td>160.0</td>
<td>1.0</td>
<td>29.56</td>
<td>16.2</td>
</tr>
<tr>
<td>160.0</td>
<td>0.4</td>
<td>9.39</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Table 6.13: The internal configurational energy and its components with the dipolar diatomic solvent model

<table>
<thead>
<tr>
<th>$q^2$</th>
<th>M</th>
<th>$U_{ii}^*$</th>
<th>$U_{dd}^*$</th>
<th>$U_{id}^*$</th>
<th>$U_{tot}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.0</td>
<td>1.0</td>
<td>-1.718</td>
<td>-1.013</td>
<td>-2.269</td>
<td>-5.003</td>
</tr>
<tr>
<td>160.0</td>
<td>1.0</td>
<td>-8.147</td>
<td>-0.017</td>
<td>-6.369</td>
<td>-14.530</td>
</tr>
<tr>
<td>160.0</td>
<td>0.4</td>
<td>-2.507</td>
<td>-0.751</td>
<td>-3.738</td>
<td>-6.999</td>
</tr>
</tbody>
</table>

tational correlation between molecules. The third solvent model, where the solvent particles are described as fused hard spheres with a point charge on each site, is studied to consider shape anisotropies. The effects of ionic concentration, charge and the type of the solvent model on the structure of the solution are shown in Figures 6.65-6.73. It is observed that the oppositely charged ions have higher contact values in dipolar diatomic solvents than in the corresponding point dipolar solvents. This means that the degree of unlike ion pair formation is more important in dipolar diatomic solvents. The amount of ion pair formation is found to increase with increasing ionic charge and decreasing ionic concentration. The solvent-ion pair distribution functions show the same trend as found in the spherical core solvent: An increase in coordination of ions with solvent molecules at higher ionic charges and lower concentrations. Since the elongation of the two fused hard spheres is chosen to be 0.5$\sigma$, the maximum of the pair distribution function is shifted to 1.25$\sigma$, which was 1$\sigma$ for the point dipolar solvent, and the second maximum disappears
Solvent-solvent coordination is not affected very much by changes in ion density or charge. In general, the total internal configurational energy, the specific heat of the solution and the static dielectric constant of the solution are higher in a dipolar diatomic solvent than in a corresponding point dipolar solvent. These results are shown in Tables 6.12 and 6.13.
Figure 6.1: Variation in solvent-solvent pair correlation function with ion concentration where the solvent molecules are modeled as hard spheres plus embedded dipoles ($\mu^* = 2.5$ for all runs).
Figure 6.2: Variation in solvent-ion pair correlation function with ion concentration where the solvent molecules are modeled as hard spheres plus embedded dipoles ($\mu^2 = 2.5$ for all runs)
Figure 6.3: Variation in oppositely signed ion pair correlation function with ion concentration where the solvent molecules are modeled as hard spheres plus embedded dipoles ($\mu^2 = 2.5$ for all runs)
Figure 6.4: Like ion pair distribution functions for run 3

\( q^{*2} = 160 \ 0.4m \)

- ○ anions
- △ cations
Figure 6.5: Like ion distribution functions for run 2
Figure 6.6: Like ion distribution functions for run 5
Figure 6.7: Like ion distribution functions for run 6

$q^2 = 160 \ 2.0m$

△ anions
○ cations
Figure 6.8: Like ion distribution functions for run 1
Figure 6.9: Like ion distribution functions for run 4
Figure 6.10: Like ion distribution functions for run 7
Figure 6.11: Variations in the static component of the solution dielectric with the equilibrium sampling steps
Figure 6.12: Variation in solvent-solvent pair correlation function with ionic charge at 1 M solution (the solvent molecules are modeled as hard spheres plus embedded dipoles and $\mu^2 = 2.5$ for all runs)
Figure 6.13: Variation in solvent-solvent pair correlation function with ionic charge at 0.4 M solution (the solvent molecules are modeled as hard spheres plus embedded dipoles and $\mu^{*2} = 2.5$ for all runs)
Figure 6.14: Variation in solvent-ion pair correlation function with ionic charge at 1 M solution (the solvent molecules are modeled as hard spheres plus embedded dipoles and $\mu^2 = 2.5$ for all runs)
Figure 6.15: Variation in solvent-ion pair correlation function with ionic charge at 0.4 M solution (the solvent molecules are modeled as hard spheres plus embedded dipoles and $\mu^2 = 2.5$ for all runs)
Figure 6.16: Variation in oppositely signed ion pair correlation function with ionic charge at 1 M solution (the solvent molecules are modeled as hard spheres plus embedded dipoles and $\mu^{*2} = 2.5$ for all runs)
Figure 6.17: Variations in oppositely signed ion pair correlation function with ionic charge at 0.4 M solution (the solvent molecules are modeled as hard spheres plus embedded dipoles and $\mu^2 = 2.5$ for all runs)
The triplet distribution function $g_{3}(1.025,1.025,\theta)$ at different ionic concentrations ($Q^{2} = 160, \mu^{2} = 2.5, \Theta^{2} = 0$ in all runs).

Figure 6.18: The triplet distribution function $g_{3}(1.025,1.025,\theta)$ at different ionic concentrations ($Q^{2} = 160, \mu^{2} = 2.5, \Theta^{2} = 0$ in all runs)
Figure 6.19: The triplet distribution function $g_\alpha(1.025, 1.025, \theta)$ at different ionic charges (the solution is approximately 1 M, $\mu^{*2} = 2.5$, $\Theta^{*2} = 0.0$ in all runs)
Figure 6.20: The ionic charge and concentration dependence of the ionic cluster size
Figure 6.21: The ionic charge and concentration dependence of $g_{is}^{101}(r)$
Figure 6.22: The ionic charge and concentration dependence of $g_{110}^{ss}(r)$
Figure 6.23: The ionic charge and concentration dependence of $g_{12}^{112}(r)$
Figure 6.24: Comparison of the solvent-solvent pair correlation function at $q^2 = 40$ and 1 M solution.
Figure 6.25: Comparison of the solvent-ion pair correlation function at $q^2 = 40$ and 0.1 M solution.
Figure 6.26: Comparison of the similar ion pair correlation function at $q^* = 40$ and 1 M solution
Figure 6.27: Comparison of the oppositely charged ion pair correlation function at $q^*^2 = 40$ and 1 M solution

- MC
- LHNC
- MSA
Figure 6.28: Comparison of $g^{112}(r)$ with the MSA results for the state point of run 1
Figure 6.29: Comparison of $g^{112}(r)$ with the MSA results for the state point of run 2.
Figure 6.30: Comparison of $g_{ss}^{112}(r)$ with the MSA results for the state point of run 3.
Figure 6.31: Comparison of $g^{12}(r)$ with the MSA results for the state point of run 4.
Figure 6.32: Comparison of $g_1^{10}(r)$ with the MSA results for the state point of run 4
Figure 6.33: Comparison of $g_{is}^{110}(r)$ with the MSA results for the state point of run 3.
Figure 6.34: Comparison of $g_{110}(r)$ with the MSA results for the state point of run 2.
Figure 6.35: Comparison of $g_{ss}^{110}(r)$ with the MSA results for the state point of run 1
Figure 6.36: Comparison of $g_{i^0}(r)$ with the MSA results for the state point of run 4.
Figure 6.37: Comparison of $g^{101}_s(r)$ with the MSA results for the state point of run 3.
Figure 6.38: Comparison of $g_{10}^{10}(r)$ with the MSA results for the state point of run 2.
Figure 6.39: Comparison of $g_{101}^{\text{MC}}(r)$ with the MSA results for the state point of run 1.
Figure 6.40: Comparison of MSA dielectric constant with MC results at $q^2 = 160$
Figure 6.41: Comparison of MSA and LHNC dielectric constants with MC results at $q^2 = 40$
Figure 6.42: Comparison of the compressibility factor at $q^2 = 40$
Figure 6.43: Variation of internal configurational energy and its components with the ionic concentration; comparison of LHNC and MC results
Figure 6.44: Variation of internal configurational energy and its components with the ionic concentration; comparison of MSA and MC results.
Figure 6.45: Variation of internal configurational energy and its components with the ionic charge; comparison of MSA and MC results.
Figure 6.46: Variation of internal configurational energy and its components with the ionic concentration; comparison of HBT perturbation theory with the new Padé approximation and MC results.
Figure 6.47: Variation of internal configurational energy and its components with the ionic charge; comparison of HBT perturbation theory with the new Padé approximation and MC results.
Figure 6.48: Comparison of the oppositely charged ion structure for the restricted primitive model and a mixture of ions and dipoles at high ionic concentration.
Figure 6.49: Comparison of the oppositely charged ion structure for the restricted primitive model and a mixture of ions and dipoles at low ionic concentration.
Figure 6.50: Variation in the pair correlation function with the quadrupole moment of the pure solvent
Figure 6.51: Pair distribution functions for solvent-ion interaction where the solvent molecules are modeled as hard spheres plus embedded dipoles with $\mu^2 = 2.5$.
Figure 6.52: Pair distribution functions for solvent-ion interaction where the solvent molecules are modeled as hard spheres plus embedded dipoles and linear quadrupoles with $\mu^* = 2.5$, $\Theta^* = 0.5$. 
Figure 6.53: Pair distribution functions for solvent-ion interaction where the solvent molecules are modeled as hard spheres plus embedded dipoles and linear quadrupoles with $\mu^{*2} = 2.5$, $\Theta^{*2} = 1.0$.
Figure 6.54: Variation in solvent-solvent pair correlation function with the quadrupole moment of the solvent (the solvent molecules are modeled as hard spheres plus embedded dipoles and linear quadrupoles, $\mu^2 = 2.5$)
Figure 6.55: Variation in solvent-anion pair correlation function with the quadrupole moment of the solvent (the solvent molecules are modeled as hard spheres plus embedded dipoles and linear quadrupoles, $\mu^{*2} = 2.5$)
Figure 6.56: Variation in solvent-cation pair correlation function with the quadrupole moment of the solvent (the solvent molecules are modeled as hard spheres plus embedded dipoles and linear quadrupoles, $\mu^q = 2.5$)
Figure 6.57: Variation in oppositely signed ion pair correlation function with the quadrupole moment of the solvent (the solvent molecules are modeled as hard spheres plus embedded dipoles and linear quadrupoles, $\mu^{*2} = 2.5$)

$q^{*2}=160 \ (1 \ M)$

$\Theta^{*2}=0.0$ ———

$\Theta^{*2}=0.5$ ———

$\Theta^{*2}=1.0$ ———
Figure 6.58: Variation in anion-anion pair correlation function with the quadrupole moment of the solvent (the solvent molecules are modeled as hard spheres plus embedded dipoles and linear quadrupoles, $\mu^2 = 2.5$)
Figure 6.59: Variation in cation-cation pair correlation function with the quadrupole moment of the solvent (the solvent molecules are modeled as hard spheres plus embedded dipoles and linear quadrupoles, $\mu^2 = 2.5$)
Figure 6.60: The triplet distribution function $g_3(1.025,1.025,\theta)$ at different quadrupole moments of the solvent (the solution is approximately 1 M and $q^{\pi^2} = 160, \mu^{\pi^2} = 2.5, \Theta^{\pi^2} = 0$ in all runs)
Figure 6.61: Dependence of the ionic cluster size on the quadrupole moment of the solvent
Figure 6.62: Dependence of $g_{ij}^{101}(r)$ on the quadrupole moment of the solvent
Figure 6.63: Dependence of $g_{ss}^{110}(r)$ on the quadrupole moment of the solvent
Figure 6.64: Dependence of $g_{ss}^{112}(r)$ on the quadrupole moment of the solvent.
Figure 6.65: The solvent-solvent pair distribution function at different ionic concentrations where the solvent is modeled as dipolar diatomics ($q^2 = 160$ dds,

$1 \, M$ ———

$0.4 \, M$ ———

$g_{ss}(r)$

$r/\sigma$

Figure 6.65: The solvent-solvent pair distribution function at different ionic concentrations where the solvent is modeled as dipolar diatomics ($q^2 = 160$, $\mu^2 = 2.5$ in all runs)
Figure 6.66: The solvent-ion pair distribution function at different ionic concentrations where the solvent is modeled as dipolar diatomics ($q^{*2} = 160$, $\mu^{*2} = 2.5$ in all runs).
Figure 6.67: Oppositely signed ion pair distribution function at different ionic concentrations where the solvent is modeled as dipolar diatomics ($q^{*2}$ =160, $\mu^{*2}$ =2.5 in all runs)
Figure 6.68: The solvent-solvent pair distribution function at different ionic charges where the solvent is modeled as dipolar diatomics (the solution is approximately 1 M and $\mu^2 : 2.5$ in all runs)
Figure 6.69: The solvent-ion pair distribution function at different ionic charges where the solvent is modeled as dipolar diatomics (the solution is approximately 1 M and $\mu^2 = 2.5$ in all runs)
Figure 6.70: Oppositely signed ion pair distribution function at different ionic charges where the solvent is modeled as dipolar diatomics (the solution is approximately 1 M and $\mu^{*2} \approx 2.5$ in all runs)
Figure 6.71: The solvent-solvent pair distribution function for two different solvent models: hard spheres with point dipoles and dipolar diatomics (the solution is approximately 1 M $q^2 = 160$)
Figure 6.72: The solvent-ion pair distribution function for two different solvent models; hard spheres with point dipoles and dipolar diatomics (the solution is approximately 1 M $q^*^2 = 160$ and $\mu^*^2 = 2.5$ in all runs)
Figure 6.73: Oppositely signed ion pair distribution function for two different solvent models; hard spheres with point dipoles and dipolar diatomics (the solution is approximately 1 M $q^* = 160$ and $\mu^* = 2.5$ in all runs)
7 CONCLUSIONS

To summarize the main conclusions drawn from this study;

1. Monte Carlo method is used to obtain exact results for the structure and thermodynamics of electrolytes, which are used to compare with integral equation and thermodynamic perturbation theories.

2. It is found that ion clustering in electrolytes is very sensitive to the model used to describe the ions and solvent particles. In a dipolar hard sphere solvent the solution is dominated by single ions and pairs of ions at low ionic charges and concentrations. At high concentrations, the size of the clusters increase. In a dipolar plus quadrupolar solvent number of ion pairs and triplets increase but the amount of clusters with larger number of ions is less significant.

3. The solvation properties of anions and cations, which are found to be exactly the same in a dipolar solvent, are dissimilar in a dipolar plus quadrupolar solvent.

4. Total internal configurational energy, compressibility and the static component of the dielectric constant decrease while the specific heat increase with ionic charge and concentration. In the case of 1 M solution at $q^2 = 160$, a phase transition is observed between 1 M and 1.6 M.
5. Continuum solvent model is found to be inadequate in predicting the structure of the electrolyte solutions. However, the ion-ion energies predicted by the restricted primitive model are very similar to discrete solvent model results, if the dielectric constant of the solution is employed in the model.

6. Analytic solution of the Ornstein-Zernike equation with the mean spherical approximation for a mixture of hard ions and dipoles is used to obtain thermodynamic and structural information. Total internal configurational energy and its components are found to be in good agreement with the Monte Carlo simulation results, except for the ion-dipole energy, which is overestimated by the theory. The solution dielectric shows a similar trend as the MC results, but the compressibility factor and structural results are very poor except the dipole-dipole pair distribution function which is well predicted by MSA.

7. The LHNC theory results given in the literature are compared with the simulation. The internal configurational energy and its components, the compressibility factor and some of the structural results obtained from LHNC theory are in good agreement with MC results.

8. Thermodynamic perturbation theory developed by Henderson et al. is examined. A new padé approximation is suggested which is found to give satisfactory results for the total internal configurational energy and the ion-ion energy.

9. The similarity between the structure and thermodynamic properties of a dipolar fluid and a hard sphere fluid suggests that a new reference system should be employed in the thermodynamic perturbation theory.
8 NOMENCLATURE

$A$  Helmholtz free energy

c($r$)  Direct correlation function

$C(k)$  A matrix composed of Hankel transforms of the direct correlation functions for an ion-dipole mixture

$CN$  Coordination number

$C_v$  Specific heat

g  Kirkwood g-factor

$g_{\alpha\beta}(r)$  Pair distribution function

$g_{\alpha\beta\gamma}(r)$  Triplet distribution function

$h(r)$  Total correlation function

$H(k)$  A matrix composed of Hankel transforms of total correlation functions for an ion-dipole mixture

$I_{\alpha\beta\gamma}$  Various integrals of pair and triplet distribution functions, the type of which is specified by the subscript

$k$  Boltzmann constant

$K_0^2$  A parameter related to the ionic charge and density, defined by eqn. (5.45)

$L$  Length of a side of the simulation cell
I elongation of the two fused hard spheres in the dipolar diatomic solvent model

\[ M \] Approximate molarity of the solution

\[ \vec{n} \] Lattice vector

\[ N \] Number of the particles

\[ N_H \] Number of histogram sampling

\[ P \] Pressure

\[ q \] Ionic charge

\[ r_{\alpha\beta} \] Interparticle separation

\[ \hat{r} \] Unit vector joining the center of mass of the particles

\[ \hat{s} \] Unit vector in the direction of the dipoles

\[ T \] Absolute temperature

\[ U \] Internal configurational energy

\[ V \] Volume of the simulation cell

\[ y \] A parameter related to dipole moment and density of the solvent

\[ Y_{\alpha\beta}(\varphi_{12}) \] Spherical harmonic coefficient

\[ Z \] Compressibility factor

\[ Z_N \] Canonical ensemble partition function
Greek letters:

$\alpha$  Limit of integration used to separate the Ewald sum into two parts

$\beta$  Boltzmann factor $= 1/kT$

$\varepsilon$  Depth of the potential well in the Lennard-Jones fluid

$\varepsilon_0$  Dielectric constant of the solvent

$\varepsilon_{sol}$  Dielectric constant of the solution

$\varepsilon'$  Dielectric constant of the surrounding medium

$\theta$  Angle formed between three particles

$\vartheta$  Virial function

$\Delta$  Difference

$\Theta$  Magnitude of the quadrupole moment

$\lambda_q$  Ion-ion perturbation parameter

$\lambda_\mu$  Ion-dipole perturbation parameter

$\mu$  Magnitude of the dipole moment

$\rho$  Number density

$\sigma$  Particle diameter

$\sigma_u^2$  Mean square energy fluctuation

$\Phi$  Azimuthal angle in the spherical polar coordinate system

$\Phi^{\alpha,\beta,\gamma}$  Coefficients for the rotational invariant expansion

$\Omega$  A set of Euler angles used to describe the orientation of the particles
Subscripts:

\[ i \] Ion
\[ ii \] Ion-ion interaction
\[ id \] Ion-dipole interaction
\[ iq \] Ion-quadrupole interaction
\[ is \] Ion-solvent interaction
\[ d \] Dipole
\[ dd \] Dipole-dipole interaction
\[ dq \] Dipole-quadrupole interaction
\[ per \] Perturbation property
\[ qq \] Quadrupole-quadrupole interaction
\[ ref \] Reference property
\[ s \] Solvent
\[ ss \] Solvent-solvent interaction
\[ \mu \] Dipole
\[ + \] Cations
\[ ++ \] Cation-cation interaction
\[ +s \] Cation-solvent interaction
\[ - \] Anions
\[ -- \] Anion-anion interaction
\[ -s \] Anion-solvent interaction
\[ +- \] Anion-cation interaction
Superscripts:

* Dimensionless variable
0 Reference property
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