

IONICITY AND COVALENCY IN THE STRUCTURE
OF CLASSICAL CHARGED BINARY LIQUIDS

Thesis submitted for the degree of
Doctor of Philosophy
of the University of London

by

LUTFUL BARI BHUIYAN

Theoretical Solid State
Department of Physics
The Blackett Laboratory
Imperial College of Science and Technology
London. S.W.7.
October 1977.

ABSTRACT

This thesis is primarily concerned with the effects of ionicity versus covalency in the structure of classical binary liquids. There is an interest in liquid UO_2 from the point of view of testing and safety aspects of nuclear reactors, and therefore a major part of the work has been concerned with this liquid. Two models are explored, and from them the partial structure factors and the corresponding radial distribution (pair correlation) functions are derived. In the first model, the ionic picture is adopted, and represented by charged hard spheres with diameters appropriate to positive uranium ions and negative oxygen ions. While it seems likely that the fully ionic picture U^{4+} , O^{2-} is quite appropriate, the influence of ionic charge on the structure of the liquid just above its melting point is explored. In contrast, a molecular model is examined in which the liquid is assumed to be built up from UO_2 units. The main conclusion from the ionic picture is that there is considerable short range order in the liquid. On the other hand the molecular model leads to results which show shielding of the uranium atoms by the oxygen atoms and a structure factor for U-U correlations which is rather featureless. High temperature neutron diffraction experiments would be of considerable interest therefore, on liquid UO_2 , or on an ionic liquid with similar ionic diameters.

Whereas in UO_2 the weight of evidence favours an ionic picture for the liquid, in HgCl_2 the ionic conductivity in the liquid near its melting point is a factor 10^{-4} - 10^{-5} less than that of a molten alkali halide. Therefore the molecular fluid model referred to above would seem to be appropriate for liquid HgCl_2 . Again, the main feature

that emerges is a rather structureless partial structure factor for the Hg-Hg correlations, due to shielding of Hg by the Cl atoms.

Finally, a model is examined in which the influence on liquid structure of the ratio of delocalized to localized electrons is simulated by a mixture of charged hard spheres, point ions and a non-responsive, neutralizing uniform background. From this model it is demonstrated that the structure is sensitive to variation of delocalized to localized charges. The behaviour found appears to correspond qualitatively to that in liquid Te. Some aspects of the strong coupling limit of this model are briefly discussed.

ACKNOWLEDGEMENTS

The work presented in this thesis was carried out in the Theoretical Solid State Group of the Department of Physics, Imperial College of Science and Technology, under the supervision of Professor N. H. March.

I am deeply indebted to Professor March for suggesting the problem and innumerable discussions on it. His interest in the work and constant encouragement coupled with a very sympathetic attitude have been a source of great inspiration for me throughout the course of this research.

It is a pleasure to thank Dr. P.J. Grout who was always willing to help and advise; I am grateful to him for his invaluable assistance with computing in general and for many fruitful discussions and help with regard to the work in Chapter 3 in particular.

I am grateful to Professors A.B. Bhatia and M.P. Tosi for illuminating discussions and their comments on my work during their visits to Imperial College.

I would like to thank Drs. Lidiard, Gillan and Rae of the Theoretical Physics Division, AERE, Harwell, for their interest in the work on liquid UO_2 ; Professor D. Chandler and Dr. Lowden for helpful correspondence, and Drs. Gillan and Lowden for sending me copies of their computer programs.

I am also thankful to Drs. M. Parrinello, C. Caccamo, G. Pizzimenti, M.C. Abramo and P. Giaquinta of the Solid State Group, Istituto di Fisica, University of Messina, Italy, for their generous hospitality accorded to me during my visit to Messina in connection with the work in Chapter 2, and for stimulating discussions about it.

I gratefully acknowledge the award of a Commonwealth Scholarship and a study-travel grant (which made the visit to Messina possible) by the Commonwealth Scholarship Commission (UK).

I should like to thank Mrs. T. Wright for her speedy typing of this thesis.

And finally, I am grateful to my parents, who from a distance of over five thousand miles have always stood by me, inspired me and given me moral support.

CONTENTS

	<u>Page</u>
ABSTRACT	i
ACKNOWLEDGEMENTS	iii
INTRODUCTION	1
<u>CHAPTER 1 :</u> <u>STATIC STRUCTURE</u>	6
<u>FACTORS AND RADIAL DISTRIBUTION</u>	
<u>FUNCTIONS IN BINARY CLASSICAL LIQUIDS</u>	
1.1 Definition of pair correlation function and structure factor in terms of distribution functions	6
1.2 Relation to X-ray scattering intensity	9
1.3 Long wave length limit of structure factor	10
1.4 Ornstein-Zernike direct correlation function	13
1.5 Generalization to two component systems	14
1.6 Summary	16
<u>CHAPTER 2 :</u> <u>PARTIAL STRUCTURE FACTORS AND RADIAL</u>	17
<u>DISTRIBUTION FUNCTIONS OF AN IONIC MODEL</u>	
<u>OF LIQUID UO₂</u>	
2.1 Introduction	17
2.2 The Mean Spherical Approximation	19
2.3 Solution of the Mean Spherical Approximation	20
2.3.1 Solution for uncharged hard spheres	21
2.3.2 Partial structure factors	22
2.3.3 Charge and density fluctuations	24
2.4 Method of numerical solution and the physical parameters used	25
2.5 Results	27
2.6 Comparison of results with crystalline structure	45
2.7 Conclusions	49

	<u>Page</u>
<u>CHAPTER 3 :</u> <u>STRUCTURAL DIFFERENCES BETWEEN IONIC AND</u>	50
<u>MOLECULAR FLUID MODELS OF LIQUID UO₂</u>	
3.1 Introduction	50
3.2 The Reference Interaction Site Model	51
3.2.1 Partial structure factors	56
3.3 Method of numerical solution	56
3.3.1 Model of UO ₂ molecule and the physical parameters used	57
3.4 Results	58
3.5 Comparison of partial structure factors of liquid UO ₂ in ionic and molecular fluid models	63
3.6 Conclusions	65
<u>CHAPTER 4 :</u> <u>MOLECULAR FLUID MODEL OF MOLTEN HgCl₂</u>	67
4.1 Introduction	67
4.2 Physical parameters used in the calculations	68
4.3 Partial structure factors	68
4.4 Effects of ionicity versus covalency on the structure of classical binary liquids	72
<u>CHAPTER 5 :</u> <u>STRUCTURE OF CLASSICAL FLUID OF CHARGED HARD</u>	80
<u>SPHERES AND POINT IONS IN THE PERTURBATION OF</u>	
<u>A SMALL, NON-RESPONSIVE UNIFORM BACKGROUND</u>	
<u>DENSITY</u>	
5.1 Introduction	80
5.2 The model	81
5.2.1 Solution for the coefficients	83
5.2.2 Data used in the calculations	84
5.3 Results	85
5.4 Conclusions	89

	<u>Page</u>
APPENDIX 2.1 : Fourier-transforms of the direct correlation functions	91
APPENDIX 2.2 : Summary of the numerical procedure to solve for the Waisman-Lebowitz coefficients in the Mean Spherical Approximation solutions	95
APPENDIX 3.1 : Numerical solution of Reference Interaction Site Model equations using a non-linear optimization routine	98
APPENDIX 5.1 : Form of the direct correlation functions	104
APPENDIX 5.2 : Summary of the singularities method of solution for the coefficients in the direct correlation functions	110
APPENDIX 5.3 : Fourier transforms of the direct correlation functions	113
APPENDIX 5.4 : Strong coupling properties of the Classical One Component Plasma	116
REFERENCES	122

INTRODUCTION

Of the three states of matter, the liquid phase remains the least understood. Primarily this is because, unlike solids and gases, there is no such thing as an 'ideal liquid' which can be used as a reference system for further theoretical development. In the description of crystalline solids, the structural order is emphasized and configurational processes are important. The underlying idea in the theory of gases is the randomness of particle positions and therefore in this case kinetic processes dominate. But in liquids both kinetic and configurational contributions to the total energy are important. Thus in describing liquids either as dense gases or disordered solids, there is always the possibility of leaning too heavily on either side.

Experimental information about structure in liquids comes mainly from the X-ray and neutron scattering experiments performed on these. The intensity of the scattered rays reveals the existence of a short range order in this state. Besides these, over the past few years the techniques of computer simulations have added immensely to our knowledge on liquid structure.

From a theoretical point of view, the physicist's goal is to explain the observed phenomena of structure in simple physical terms. Though in very recent work, three-body forces have been studied to some extent, still the most common assumption made is that the total potential energy in a classical liquid can be expressed as a sum of pairwise additive potentials $\phi(r)$. The main problem in the equilibrium structure of the liquid then is to obtain the pair correlation function $g(r)$ from $\phi(r)$. (The $g(r)$ is related to the probability of finding a molecule at a distance r from another chosen at the origin). The usual approach is to solve one of the so-called approximate integral equations, e.g. Percus-Yevick, Born-Green, Hypernetted chain, etc. (1a). This necessitates assuming a specific form of the pair potential. One

thus has models of the liquid state depending upon the choice of $\phi(r)$, e.g. hard-sphere, square well, Lennard-Jones etc.. From a knowledge of $g(r)$, other thermodynamic properties such as the internal energy and the equation of state for the liquid may be calculated (2a). The fourier transform of $g(r)$ is known as the liquid structure factor $S(q)$, and is the quantity directly measurable through the scattering experiments. In two-component liquids, static structure is described in terms of three pair correlation functions $g_{ij}(r)$ ($i,j = 1,2$), and three partial structure factors $S_{ij}(q)$.

It is important to realize that the models referred to above could be solved exactly through 'Monte-Carlo' simulations on the computer. From the point of view of physics, however, consideration of such models becomes worthwhile in the sense that one can relate the correlation functions and other thermodynamic properties of the system to model characteristics such as the number density of the particles, temperature, etc..

Binary charged liquids are important from a practical point of view as these encompass a vast range of two component molten salts and electrolytes. A considerable amount of work, both theoretical and experimental, on the structure of such systems has been reported (3-21). The existing literature which constitutes 'experimental' information in this area may be conveniently classified into two main groups:

- (a) results of scattering experiments, e.g. neutron diffraction studies of molten NaCl by Edwards et al (17), of molten CuCl by Page and Mika (8) etc.,
- (b) results of machine simulations, e.g. Monte-Carlo studies of molten alkali halides by Woodcock and Singer (9), Lewis et al (16), molecular dynamics of molten NaCl by Lantelme et al (14) etc..

Viewed as ionic melts, molten salts are interesting physically because of the presence of long range coulomb interactions. Important

theoretical progress in this field based on the model of charged hard spheres has been made by Rasaiah and Friedman (3,6), Waisman and Lebowitz (7,11), Gillan et al (19) and Abramo et al (20,21). This model is attractive not only because of its simplicity, but also because it retains the principal features of coulomb systems.

Parallel to the work on charged fluids, extensive studies on the structure of classical molecular liquids have also been made. For example, Lowden and Chandler (22,23) have made theoretical studies of liquid N_2 , CCl_4 , CS_2 , CSe_2 and C_6H_6 while Hsu et al (24) report results for N_2 , O_2 and Br_2 . For these liquids on the 'experimental' side neutron diffraction results are available for CS_2 , CSe_2 (Suzuki and Egelstaff (25)), CCl_4 (Egelstaff et al (26)), N_2 , O_2 (Dore et al (27)), X-ray diffraction for C_6H_6 (O'Malley and Narten (28)), while molecular dynamics results exist for liquid N_2 (Barojas et al (29)).

A comparative study of the structure in these two broad classes of liquids leads one to consider the interesting question: how is the structure of a binary classical liquid influenced by ionicity versus covalency assumptions? To take a specific example, molten $CuCl$, various approaches have been studied; for instance, an ionic model in the limit of a very large difference in ionic diameters (19), and with appropriate ratio of diameters for $CuCl$ (20) and, in contrast, a molecular fluid model (30,31). In both types of models, the partial structure factors exhibit some of the main features of those determined experimentally (8). This situation obtains in spite of firm evidence for ionicity in molten $CuCl$ from nuclear magnetic resonance (32) and from electrical conductivity (33) results which show a conductivity comparable to that in molten alkali halides.

In this thesis we consider the above question in particular relation to liquid UO_2 . The motivation for this choice is the extensive use of UO_2 in high temperature nuclear reactors. This

points to the need to understand not only the solid fuel, but also for design and testing purposes, some of the physical properties of molten

UO_2 . To this end, a certain amount of work has been done on the thermodynamic properties in the liquid state. For example, compressibility ⁽³⁴⁾, vapour-pressure and enthalpy ⁽³⁵⁾ measurements have recently been made. Based on these Fischer et al ⁽³⁶⁾ have obtained a refined equation of state. It was felt that, even though experimental measurement of the partial structure factors is probably a long way off in such a high melting point substance as UO_2 , it would be a useful step forward to study the structure away from the long wave-length limit.

After introducing the concepts commonly used in the equilibrium structural description of fluids in Chapter 1, we examine the structure of liquid UO_2 in an ionic model in Chapter 2. The model used is that of the classical fluid of charged hard spheres with appropriate radius ratio for the U and O⁻ ions. This model is, of course, exactly solvable through computer simulation, but our work is based on the Mean Spherical Approximation (MSA) (see, for example, Reference (11)) to the model. An important reason for this is the relative success of the MSA in predicting the structural properties of binary ionic liquids and molten salts ^(19,20,21). In Chapter 3, we study the structure of liquid UO_2 in a molecular fluid picture. Though the weight of evidence for UO_2 would seem to favour an ionic model for the liquid, we thought it of interest to study the opposite extreme of a molecular fluid model to assess how sensitive the structure is to ionicity versus covalency considerations. In this picture the liquid is assumed to be made up of UO_2 units. For the solution of this model we have used the Reference Interaction Site Model (RISM) theory (see, for instance, Reference (22)) for classical molecular liquids. In support of the RISM we can cite its remarkable success in predicting equilibrium structural and thermodynamic properties of several molecular liquids ^(22,23,24)

In Chapter 4 we apply the molecular fluid model to molten HgCl_2 . For this case, experimental measurements of electrical conductivity shows it to be a factor 10^{-4} - 10^{-5} times less than that of a molten alkali halide (33,37,38). It appears therefore that a molecular model might well be appropriate for the molten salt.

In the final chapter we examine the influence on the structure of a two-component charged fluid of delocalizing some fraction of localized electrons initially in covalent bonds. The situation is simulated in a model of charged hard spheres, point charges (classical electrons), all moving in a small, non-responsive, neutralizing background density. Such a model might have relevance for liquid Te for which the model of Cabane and Friedel (39) is based on the coexistence of a network of strong covalent bonds with a metallic like electron gas.

Much of the work presented in this thesis has been published in the following papers :

- (i) "Structure of classical fluid of charged hard spheres and point ions in the perturbation of a small, non-responsive, uniform background density" by L.B. Bhuiyan and N.H. March; "Physics and Chemistry of liquids" (in the press).
- (ii) "Partial structure factors of an ionic model of liquid UO_2 " by L.B. Bhuiyan, N.H. March, M.C. Abramo, C. Caccamo and G. Pizzimenti; Mol.Phys. 34, 755 (1977).
- (iii) "Structural differences between ionic and molecular fluid models of liquid UO_2 " by L.B. Bhuiyan, P.J. Grout and N.H. March; "Physics and Chemistry of liquids" (in the press).
- (iv) "Partial structure factors of molten HgCl_2 in a molecular fluid model" by L.B. Bhuiyan; "Physics and Chemistry of liquids" (in the press).

CHAPTER 1

STATIC STRUCTURE FACTORS AND RADIAL DISTRIBUTION

FUNCTIONS IN BINARY CLASSICAL LIQUIDS

The basic characteristic which distinguishes a liquid from a crystalline solid is the absence of long range order, and from a low density gas is the presence of short range interactions. Thus the central problem in the equilibrium structural description of liquids is the arrangement of molecules and the correlations between their positions. Formally, this may be treated using the distribution function theories of statistical mechanics. This approach allows one not only to obtain a complete microscopic structural description of the system, but also to consider equilibrium properties of the liquid state. In the following section we introduce some of the basic concepts used to describe the structure of a classical liquid from distribution function theory. In Section 1.2 we establish contact with experiment and see how the short range order in a liquid is reflected in the intensity of its X-ray diffraction patterns. Initially, we consider the case of monatomic (single component) liquids; generalization to two component cases is done in later sections.

1.1 Definition of pair correlation function and structure factor in terms of distribution functions

Supposing our system consists of N identical particles in a volume V and temperature T ; then in the canonical ensemble the normalized probability density is

$$f(\underline{r}_1 \dots \underline{r}_N, \underline{p}_1 \dots \underline{p}_N) = \frac{e^{-\beta H(\underline{r}_1 \dots \underline{r}_N, \underline{p}_1 \dots \underline{p}_N)}}{N! h^{3N} Q_N} \quad (1.1)$$

Here $\beta = \frac{1}{k_B T}$, k_B is Boltzman constant; h is Planck's constant and H is the classical hamiltonian given by

$$H = \sum_i \frac{p_i^2}{2mv} + \Phi(\underline{r}_1 \dots \underline{r}_N) \quad (1.2)$$

where m is the particle mass; $\underline{p}_i$ the momentum of the i th particle and $\Phi(\underline{r}_1 \dots \underline{r}_N)$ the potential energy of the system. Q_N is the canonical partition function

$$Q_N = \frac{1}{N! h^{3N}} \int d\underline{r}_1 \dots d\underline{r}_N d\underline{p}_1 \dots d\underline{p}_N e^{-\beta H} \quad (1.3)$$

Since the hamiltonian is separable, this probability density in phase space factorizes into a momenta part and a configurational part which depends only on the positions of the particles in coordinate space.

As our interest is in the correlation between positions of particles we shall be concerned only with the latter.

The probability $p^{(N)}(\underline{r}_1 \dots \underline{r}_N)$ that particle 1 is in volume element $d\underline{r}_1$, particle 2 in $d\underline{r}_2$, etc. may be defined (2b,40) as

$$p^{(N)}(\underline{r}_1 \dots \underline{r}_N) d\underline{r}_1 \dots d\underline{r}_N = \frac{1}{Z_N} e^{-\beta \Phi(\underline{r}_1 \dots \underline{r}_N)} d\underline{r}_1 \dots d\underline{r}_N \quad (1.4)$$

where

$$Z_N = \int d\underline{r}_1 \dots d\underline{r}_N e^{-\beta \Phi(\underline{r}_1 \dots \underline{r}_N)} \quad (1.5)$$

is now called the configurational partition function. Evidently

$p^{(N)}(\underline{r}_1 \dots \underline{r}_N)$ has the normalization

$$\int d\underline{r}_1 \dots d\underline{r}_N p^{(N)}(\underline{r}_1 \dots \underline{r}_N) = 1 \quad (1.6)$$

From (1.4) we can obtain the n -particle probability distribution $n \leq N$, by integrating over the remaining coordinates $\underline{r}_{n+1}$ to $\underline{r}_N$

$$p^{(n)}(\underline{r}_1 \dots \underline{r}_n) d\underline{r}_1 \dots d\underline{r}_n = \frac{1}{Z_N} \left[\int d\underline{r}_{n+1} \dots d\underline{r}_N e^{-\beta \Phi(\underline{r}_1 \dots \underline{r}_N)} \right] d\underline{r}_1 \dots d\underline{r}_n \quad (1.7)$$

Sometimes it is more convenient to define n -particle densities $\rho^{(n)}$, by

$$\rho^{(n)} = \frac{N!}{(N-n)!} p^{(n)} \quad (1.8)$$

The factor $N!/(N-n)!$ takes into account the indistinguishability of particles.

$\rho^{(n)}(\underline{r}_1 \dots \underline{r}_n)$ has the normalization

$$\int d\underline{r}_1 \dots d\underline{r}_n \rho^{(n)}(\underline{r}_1 \dots \underline{r}_n) = \frac{N!}{(N-n)!} \quad (1.9)$$

One can now see why $\rho^{(n)}$ is more convenient than $p^{(N)}$. In a fluid with zero interparticle forces, $p^{(1)} = \frac{1}{V}$ and thus

$\rho^{(1)}(\underline{r}_1) = \frac{N}{V} = \rho$ — the uniform average density. In general

$$\rho^{(n)} = \frac{N!}{(N-n)!} \frac{1}{V^n} \quad (1.10)$$

These relations hold in case of real fluids in the limit when all the particles are far apart; in such case as $N \rightarrow \infty$ we have from (1.10), $\rho^{(n)} \rightarrow \rho^n$.

The important distribution functions used in the structural description of fluids are single particle and pair functions. We define the two-particle distribution function

$$g(\underline{r}_1, \underline{r}_2) = \rho^{(2)}(\underline{r}_1, \underline{r}_2) / \rho^2 \quad (1.11)$$

In an isotropic fluid $g(\underline{r}_1, \underline{r}_2)$ depends only on $|\underline{r}_1 - \underline{r}_2| = |\underline{r}_{12}|$ such that

$$g(\underline{r}_1, \underline{r}_2) = g(|\underline{r}_1 - \underline{r}_2|) \quad (1.12)$$

The $g(r)$ is called the radial distribution or the pair correlation function. As r gets large we see from (1.11) $g(r) \rightarrow 1$. From a physical standpoint $4\pi\rho g(r) r^2 dr$ represents the number of atoms within a spherical shell of width dr at a distance r from the atom at the origin. The liquid structure factor $S(q)$ is formally defined as

$$S(q) = 1 + \rho \int d\underline{r} [g(\underline{r}) - 1] e^{-i\underline{q} \cdot \underline{r}} \quad (1.13)$$

Since in a liquid $g(\underline{r}) = g(|\underline{r}|)$, we can do the angular integrations in (1.13) to obtain

$$S(q) = 1 + 4\pi\rho \int_0^\infty dr r^2 \frac{\sin qr}{qr} [g(r) - 1] \quad (1.14)$$

From (1.13) and (1.14) we notice analogous to $g(r)$, $S(q)$ also goes to unity for large values of the wave vector q .

1.2 Relation to X-ray scattering intensity

We will now see how the above definition of structure factor is in accord with the short range order reflected in the intensity of the X-rays scattered from a liquid.

It can be shown ⁽⁴¹⁾ that this X-ray scattering intensity is given by

$$I(q) = N f^2 \left[1 + \sum_{i \neq j} \frac{\sin q r_{ij}}{q r_{ij}} \right] \quad (1.15)$$

with $q = \frac{4\pi \sin \theta}{\lambda}$

where λ is the wavelength of the radiation and θ is $\frac{1}{2}$ the scattering angle. $f(q)$ is the atomic scattering factor and r_{ij} the distance between i th and j th atoms. The second term in the right hand side

of (1.15) reveals an interference pattern between scattered waves from pairs of atoms.

Using the idea of radial distribution function $g(r)$ introduced in the previous section, the density $\rho(r)$ at a distance r from the atom at the origin is $\rho(r) = \rho g(r)$. Now replacing the summation in (1.15) by an integration we obtain

$$I(q) = Nf^2 \left[1 + \rho \int_0^R dr 4\pi r^2 \frac{\sin qr}{qr} [g(r)-1] + \rho \int_0^R dr 4\pi r^2 \frac{\sin qr}{qr} \right] \quad (1.16)$$

In the limit of infinite liquid sample, the radius $R \rightarrow \infty$, the final term in (1.16) becomes a delta function at $q = 0$ and represents scattering from a uniform density. Neglecting this delta function contribution we get

$$I(q) = Nf^2 \left[1 + \rho \int_0^\infty dr 4\pi r^2 \frac{\sin qr}{qr} (g(r)-1) \right] \quad (1.17)$$

The quantity in square brackets is just the structure factor defined in Equation (1.14). In fact in X-ray scattering from liquids, the structure factor is operationally defined by the relation

$$S(q) = \frac{I(q)}{Nf^2} \quad (1.18)$$

In a crystal $g(r)$ is a sum of delta functions centred on lattice sites. Therefore from (1.17), $S(q)$ has non-zero value only when $\underline{q}$ is a reciprocal lattice vector. But in an isotropic liquid the absence of long range order no longer leads to sharp Bragg reflections and hence $S(q)$ is non-zero for all q .

1.3 Long wave-length limit of structure factor

In X-ray scattering it is difficult to measure the intensity when the scattering takes place through very small angles. Fortunately there is an exact thermodynamic result which relates the long wave length limit of the structure factor to the isothermal compressibility of the liquid.

We proceed to derive this interesting relation below. We shall work in the grand canonical ensemble. Extending the definition of n-particle densities (Equations (1.7) and (1.8)) to this case we obtain

$$\rho_{Gc}^{(n)}(\underline{r}_1 \dots \underline{r}_n) = \frac{1}{\Xi} \sum_{N \geq n} \frac{N!}{(N-n)!} \frac{1}{h^{3N}} e^{\beta \mu N} \int d\underline{r}_{n+1} \dots d\underline{r}_N d\underline{p}_1 \dots d\underline{p}_N e^{-\beta H(\underline{r}_1 \dots \underline{r}_N, \underline{p}_1 \dots \underline{p}_N)} \quad (1.19)$$

where μ is the chemical potential, and Ξ is the grand canonical partition function given by

$$\Xi = \sum_N \frac{e^{\beta \mu N}}{N! h^{3N}} \int d\underline{r}_1 \dots d\underline{r}_N d\underline{p}_1 \dots d\underline{p}_N e^{-\beta H(\underline{r}_1 \dots \underline{r}_N, \underline{p}_1 \dots \underline{p}_N)} \quad (1.20)$$

Separating the hamiltonian in (1.19) into kinetic and potential energy parts and integrating over the momenta we have

$$\rho_{Gc}^{(n)}(\underline{r}_1 \dots \underline{r}_n) = \frac{1}{\Xi} \sum_{N \geq n} \frac{1}{(N-n)!} \left(\frac{e^{\beta \mu}}{\lambda^3} \right)^N \int d\underline{r}_{n+1} \dots d\underline{r}_N e^{-\beta \Phi(\underline{r}_1 \dots \underline{r}_N)} \quad (1.21)$$

with $\lambda = \left[\frac{h^2}{2\pi m k_B T} \right]^{1/2}$ being the thermal de-Broglie wave-length. The normalization of $\rho_{Gc}^{(n)}(\underline{r}_1 \dots \underline{r}_n)$ is

$$\int d\underline{r}_1 \dots d\underline{r}_n \rho_{Gc}^{(n)}(\underline{r}_1 \dots \underline{r}_n) = \left\langle \frac{N!}{(N-n)!} \right\rangle \quad (1.22)$$

the $\langle \dots \rangle$ now denoting average over the total number of particles in the ensemble. Thus

$$\int d\underline{r}_1 \rho_{Gc}^{(1)}(\underline{r}_1) = \langle N \rangle \quad (1.23)$$

$$\text{and } \int d\underline{r}_1 d\underline{r}_2 \rho_{Gc}^{(2)}(\underline{r}_1, \underline{r}_2) = \langle N^2 \rangle - \langle N \rangle \quad (1.24)$$

For fluids we can replace $\rho_{Gc}^{(2)}(\underline{r}_1, \underline{r}_2)$ by $\rho^2 g(|\underline{r}_1 - \underline{r}_2|)$ and

$\rho_{Gc}^{(1)}(\underline{r}_1)$ by ρ . Then from Equations (1.23) and (1.24) it follows

$$\rho^2 \int d\mathbf{r}_1 d\mathbf{r}_2 [g(|\mathbf{r}_1 - \mathbf{r}_2|) - 1] = \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2$$

or $\rho^2 V \int d\mathbf{r} [g(r) - 1] = \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2$

or $\rho \int d\mathbf{r} [g(r) - 1] = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} - 1$

That is

$$1 + \rho \int d\mathbf{r} [g(r) - 1] = \lim_{q \rightarrow 0} S(q) = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \quad (1.25)$$

We thus see from above that the long wave-length limit of the structure factor is related to the particle number fluctuations in the system.

We can rewrite the partition function in the grand canonical ensemble (Equation (1.20)) as

$$\Xi = \sum_N e^{\beta \mu N} Q_N \quad (1.26)$$

From this one immediately obtains

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \Xi}{\partial \mu} \quad (1.27)$$

and

$$\langle N^2 \rangle = \frac{1}{\beta^2} \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial \mu^2} \quad (1.28)$$

Therefore

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \frac{\partial^2 \ln \Xi}{\partial \mu^2} = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} \quad (1.29)$$

We now make use of the thermodynamic relation (1b)

$$\begin{aligned} \left(\frac{\partial \mu}{\partial N} \right)_{V,T} &= -\frac{1}{\rho^2} \left(\frac{\partial P}{\partial V} \right)_{T,N} \quad (P \text{ is the pressure}) \\ &= \frac{1}{\rho^2 V K_T} \end{aligned} \quad (1.30)$$

where $K_T \equiv \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ is the isothermal compressibility. Remembering

that all N must now refer to the average value $\langle N \rangle$, combining (1.29)

and (1.30) we obtain the equation

$$\lim_{q \rightarrow 0} S(q) = \rho k_B T K_T \quad (1.31)$$

which relates the liquid structure factor as $q \rightarrow 0$ to the isothermal

compressibility of the system.

1.4 Ornstein-Zernike direct correlation function

A frequently used and useful concept in the theory of equilibrium structure of fluids is the direct correlation function $c(r)$. This is defined by the Ornstein-Zernike relation ⁽⁴²⁾.

$$h(r) = c(r) + \rho \int c(|\underline{r} - \underline{r}'|) h(|\underline{r}'|) d\underline{r}' \quad (1.32)$$

Here $h(r) = [g(r) - 1]$ is called the total correlation function and represents the deviation from the probability $g = 1.0$ (i.e. no structure) of finding a particle at a distance r from the particle at the origin.

To obtain a physical interpretation of Equation (1.32) we may rewrite it as

$$h(12) = c(12) + \rho \int c(13) h(23) d\underline{3} \quad (1.33)$$

(1.33) now tells us that the total correlation between two particles 1 and 2 consists of two parts. The first is the direct correlation between 1 and 2; the second is an indirect part due to some average effect of a particle 3 which is correlated to 2. Unlike $g(r)$, $c(r)$ has no direct physical meaning; but it can be shown ^(2c), asymptotically $c(r) \sim \frac{-\phi(r)}{k_B T}$, where $\phi(r)$ is the pair potential.

An important reason why the concept of the direct correlation function is important in the theory of liquids is that it is directly accessible to experiment. For example, defining the fourier-transform $\tilde{c}(q)$ of $c(r)$

$$\tilde{c}(q) = \int d\underline{r} e^{-i \underline{q} \cdot \underline{r}} c(r) \quad (1.34)$$

etc., we rewrite Equation (1.32) in q -space as

$$\tilde{h}(q) = \tilde{c}(q) + \tilde{c}(q) \tilde{h}(q) \quad (1.35)$$

$$\text{or } \tilde{c}(q) = \frac{\tilde{h}(q)}{1 + \tilde{h}(q)} \quad (1.36)$$

Note that from Equation (1.14), $\tilde{h}(q) = S(q) - 1$.

$$\text{Therefore } S(q) = \frac{1}{1 - \tilde{c}(q)} \quad (1.37)$$

relating $\tilde{c}(q)$ and the structure factor.

Equations(1.37) and (1.34) now give

$$c(r) = \frac{1}{2\pi^2\rho} \int_0^\infty dq q^2 \frac{\sin qr}{q^3} \left\{ \frac{S(q)-1}{S(q)} \right\} \quad (1.38)$$

Thus knowing $S(q)$ experimentally we can determine both $g(r)$ and $c(r)$.

1.5 Generalization to two component systems

The concepts introduced thus far may be easily generalized to two-component liquid mixtures. Obviously now one needs three pair correlation functions for a complete structural description of the system.

In analogy to Equation (1.14) the partial structure factors $S_{ij}(q)$ ($i, j = 1, 2$) are defined as

$$S_{ij}(q) = \delta_{ij} + 4\pi(\rho_i\rho_j)^{1/2} \int_0^\infty dr r^2 \frac{\sin qr}{q^3} [g_{ij}(r)-1] \quad (1.39)$$

$$= \delta_{ij} + \tilde{h}_{ij}(q) \quad (1.40)$$

where we have used $h_{ij}(r) = g_{ij}(r)-1$.

ρ_i, ρ_j are now the average densities of the components. It is to be noted $S_{12}(q)$ is normalized to zero at large q . Fourier inversion of (1.39) yields

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2(\rho_i\rho_j)^{1/2}} \int_0^\infty dq q^2 \frac{\sin qr}{q^3} [S_{ij}(q) - \delta_{ij}] \quad (1.41)$$

Likewise the Ornstein-Zernike equation appropriate to a binary mixture may be written as

$$h_{ij}(r) = c_{ij}(r) + \sum_{l=1}^2 \rho_l \int d\underline{r}' c_{il}(|\underline{r}-\underline{r}'|) h_{lj}(|\underline{r}'|) \quad (1.42)$$

The long wave length limits of the partial structure factors satisfy the compressibility sum rule (43)

$$\lim_{q \rightarrow 0} S_{ij}(q) = (\rho_i\rho_j)^{1/2} k_B T \kappa_T \quad (1.43)$$

For a charged fluid, overall electroneutrality is an important condition, and is given by

$$\sum_i \rho_i z_i = 0 \quad (1.44)$$

z_i being the valence of the i th type of ion. In such cases, the charge neutrality simply relates the long wave length limits of the three partial structure factors. This is expected since in a charged fluid the particle number fluctuations must be such that overall neutrality is maintained. To show this note around a cation (denoted by subscript 1), cations are distributed as $(z_1 e) \rho_1 g_{11}(r)$ and anions (denoted by subscript 2) are distributed as $-(z_2 e) \rho_2 g_{12}(r)$. Charge neutrality implies

$$\left[(z_1 e) \rho_1 \int d\mathbf{r} g_{11}(r) - (z_2 e) \rho_2 \int d\mathbf{r} g_{12}(r) \right] = -z_1 e \quad (1.45)$$

Similarly around an anion, anions are distributed as $-(z_2 e) \rho_2 g_{22}(r)$ and cations are $(z_1 e) \rho_1 g_{12}(r)$. Again from neutrality

$$\left[(z_1 e) \rho_1 \int d\mathbf{r} g_{12}(r) - (z_2 e) \rho_2 \int d\mathbf{r} g_{22}(r) \right] = z_2 e \quad (1.46)$$

From Equation (1.39) we obtain

$$\lim_{q \rightarrow 0} \frac{d}{dq} S_{11}(q) = 1 + \rho_1 \int d\mathbf{r} [g_{11}(r) - 1] \quad (1.47)$$

$$\lim_{q \rightarrow 0} \frac{d}{dq} S_{22}(q) = 1 + \rho_2 \int d\mathbf{r} [g_{22}(r) - 1] \quad (1.48)$$

$$\lim_{q \rightarrow 0} \frac{d}{dq} S_{12}(q) = (\rho_1 \rho_2)^{1/2} \int d\mathbf{r} [g_{12}(r) - 1] \quad (1.49)$$

Using now Equations (1.45) and (1.47) it can be easily shown

$$z_1 \left[\lim_{q \rightarrow 0} \frac{d}{dq} S_{11}(q) \right] = (z_1 z_2)^{1/2} \left[\lim_{q \rightarrow 0} \frac{d}{dq} S_{12}(q) \right] \quad (1.50)$$

Similarly from Equations (1.46) and (1.48) it follows

$$z_2 \left[\lim_{q \rightarrow 0} \frac{d}{dq} S_{22}(q) \right] = (z_1 z_2)^{1/2} \left[\lim_{q \rightarrow 0} \frac{d}{dq} S_{12}(q) \right] \quad (1.51)$$

Combining (1.50) and (1.51) we get the desired relation

$$z_1 \left[\lim_{q \rightarrow 0} \frac{d}{dq} S_{11}(q) \right] = (z_1 z_2)^{1/2} \left[\lim_{q \rightarrow 0} \frac{d}{dq} S_{12}(q) \right] = z_2 \left[\lim_{q \rightarrow 0} \frac{d}{dq} S_{22}(q) \right] \quad (1.52)$$

1.6 Summary

In this chapter we have introduced the basic concepts used in the equilibrium structural description of fluids. Starting from distribution function theory the pair correlation function and its fourier transform - the structure factor were defined. The latter quantity is directly measurable in the X-ray or neutron scattering from liquids and reflects the short-range order therein. The long wave length limit of the structure factor bears a simple relationship to the particle number fluctuation in the system. In binary liquids one needs three pair correlations and correspondingly three partial structure factors. For charged systems, the long wave length limits of the partial structure factors reveal the charge neutrality of the system. All these concepts will be used in the later chapters.

CHAPTER 2

PARTIAL STRUCTURE FACTORS AND RADIAL DISTRIBUTION

FUNCTIONS OF AN IONIC MODEL OF LIQUID UO_2

2.1 Introduction

In this chapter we begin our study of the effects of ionicity versus covalency on the structure of classical two-component liquids by examining the structure of liquid UO_2 (at just above its melting temperature) in an ionic model.

The method used here is to treat the liquid as an ionic melt and simulate interionic interactions by replacing the ions by oppositely charged hard spheres with appropriate diameters. Thus in this model, often referred to in the literature as the 'primitive model of electrolytes' ⁽⁶⁾, the short range repulsive part of the interparticle pair potential is approximated by an infinite hard sphere repulsion and the long range attractive part by a coulombic tail. Mathematically we have

$$\begin{aligned} \phi_{ij} &= \infty \quad \dots \dots r < \sigma_{ij} \\ &= \frac{e_i e_j}{\epsilon r} \quad \dots \dots r > \sigma_{ij} \end{aligned} \quad (2.1)$$

Here $\phi_{ij}(r)$ is the interaction potential between species i and j ; e_i, e_j are the charges on the species, ϵ the appropriate dielectric constant and σ_{ij} is the diameter for the interaction. σ_{ij} is usually taken to satisfy the additivity condition.

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (2.2)$$

σ_i, σ_j being the diameters of the individual hard spheres. Thus σ_{ij} is the distance of closest approach between two ions of type i and j . The overall charge neutrality condition (Eqn.(1.44)) in this case is

$$\sum_i p_i e_i = 0 \quad (2.3)$$

with the summation being taken over the total number of species.

For the particular case of liquid UO_2 therefore, we would have a binary mixture of positively charged uranium and negatively charged oxygen ions. As regards the magnitudes of these charges, the present evidence points to U^{4+} and O^{2-} . But it must be pointed out that this evidence is for solid UO_2 and basing on this we assume the liquid to be ionic with the same charge magnitudes. Regarding the evidence for ionicity of solid UO_2 , we may cite* :

- (i) the cohesive energy is correctly given by the Born-Mayer model with ionic charges $Z_{\text{U}} = 4$, $Z_{\text{O}} = 2$ ⁽⁴⁴⁾,
- (ii) the phonon dispersion curves are well described in terms of a shell model with an ionic charge of the same magnitude as in (i) above ⁽⁴⁵⁾.

However, we also examine the influence of charging on structure by considering the partially ionic case, i.e. U^{2+} and O^- . As a special case of above, in the extreme limit when the charges are switched off, we have the neutral hard sphere model. This limit is useful in that it reflects solely size (radius ratio) effects on the structure, and acts as a reference set of structure factors from which to assess the effects of charging.

For the solution of this ionic model we have employed the MSA using the procedure developed for arbitrary diameter ratio by Abramo et al ⁽⁴⁶⁾. When the ionic charges are zero, MSA reduces exactly to the Percus-Yevick (PY) theory ^(47,48) for a multicomponent hard sphere fluid mixture. In the latter case, exact solutions for a binary mixture have been given by Lebowitz ⁽⁴⁸⁾ and we have utilized these results for the solution of our corresponding model.

The layout of this chapter is as follows: in the next section the MSA is briefly discussed. In Section 2.3 the general solutions of the MSA and in 2.4 the method of its numerical solution and the physical parameters used are presented. The partial structure factors and the

* The author is grateful to Dr. M.J. Gillan of AERE, Harwell, for making the points (i) and (ii) below.

corresponding radial distribution functions are given and discussed in Section 2.5. In 2.6 some comparison of the results is made with the crystalline structure, in the absence of non-zero wave number information from experiment on the liquid. Finally in Section 2.7 some comments are made on the results.

2.2 The Mean Spherical Approximation

The Mean Spherical Approximation for a classical liquid mixture of hard spheres consists of the following statements :

- (a) the radial distribution functions $g_{ij}(r)$ vanish inside the hard cores

$$g_{ij}(r) = 0 \quad \dots \quad r < \sigma_{ij} \quad (2.4a)$$

This is of course an exact consequence of the assumption that the short range part of the pair potential is given by a hard sphere repulsion.

- (b) outside the repulsive cores, the direct correlation functions $c_{ij}(r)$ and the interaction potential $\phi_{ij}(r)$ bear the relationship

$$c_{ij}(r) = -\beta \phi_{ij}(r) \quad \dots \quad r > \sigma_{ij} \quad (2.4b)$$

This is the approximation in the theory.

In our case $\phi_{ij}(r)$ is purely coulombic outside the cores (see Equation (2.1)). It is easy to see from Equations (2.1) and (2.4b) that by setting $e_i, e_j = 0$, the Equations (2.4) become

$$\left. \begin{aligned} g_{ij}(r) &= 0 & \dots & r < \sigma_{ij} \\ c_{ij}(r) &= 0 & \dots & r > \sigma_{ij} \end{aligned} \right\} \quad (2.5)$$

This is now exactly the PY theory for a classical fluid mixture of uncharged (neutral) hard spheres*. In this case too, the first of

* The PY approximate equation for a multi-component fluid mixture is given by

$$g_{ij}(r) [e^{-\beta \phi_{ij}(r)} - 1] = e^{-\beta \phi_{ij}(r)} c_{ij}(r)$$

In particular for a mixture of neutral hard spheres, i.e. $\phi_{ij}(r) = \infty$ for $r < \sigma_{ij}$ and zero for $r > \sigma_{ij}$, the above reduces to the Equations (2.5).

Equations(2.5) is an exact condition for hard sphere interaction, the approximation is contained in the second.

For classical fluids the $g_{ij}(r)$ and the $c_{ij}(r)$ are related through the Ornstein-Zernike relation (Equation (1.32)). For a multi-component system this is

$$h_{ij}(r) = c_{ij}(r) + \sum_l \rho_l \int d\mathbf{r}' c_{il}(|\mathbf{r}-\mathbf{r}'|) h_{lj}(|\mathbf{r}'|) \quad (2.6)$$

Thus the essential problem of solving the MSA (as also the PY theory) is to determine the form of $g_{ij}(r)$ outside the hard core and of $c_{ij}(r)$ inside it. This is to be achieved by using Equation (2.6) together with the closure relations (2.4) and (2.5) for charged and uncharged hard sphere cases respectively.

2.3 Solution of the Mean Spherical Approximation

The formal solutions of the MSA (Equations (2.4)) for a binary charged hard sphere fluid have been obtained by Waisman and Lebowitz ⁽¹¹⁾; these may be written in the form ⁽²¹⁾

$$\begin{aligned} -c_{ii}(r) &= \left(a_i - \frac{\pi \beta V_{ii}}{3\eta_i} \right) + \frac{M_{ii}}{12\eta_i} r + \frac{1}{2} (\eta_1 a_1 + \eta_2 a_2) r^3 \dots r < \sigma_i \\ &= \frac{\beta e_i^2}{\epsilon r} \dots r > \sigma_i \end{aligned} \quad (2.7a)$$

$$\begin{aligned} -c_{12}(r) &= -c_{21}(r) \\ &= a_1 + \frac{\pi \beta V_{22}}{3\eta_1} \dots r \leq \lambda \\ &= \left(a_1 + \frac{\pi \beta V_{22}}{3\eta_1} \right) + \frac{M_{21}}{12(\eta_1 \eta_2)^{1/2}} \frac{(r-\lambda)^2}{r} + 2\lambda (\eta_1 a_1 + \eta_2 a_2) \frac{(r-\lambda)^3}{r} \\ &\quad + \frac{1}{2} (\eta_1 a_1 + \eta_2 a_2) \frac{(r-\lambda)^4}{r} \dots \lambda < r < \sigma_{12} \\ &= \frac{\beta e_1 e_2}{\epsilon r} \dots r > \sigma_{12} \end{aligned} \quad (2.7b)$$

Here $\eta_i = \frac{\pi}{6} \rho_i$, $\lambda = \frac{1}{2}(\sigma_2 - \sigma_1)$ (we have arbitrarily chosen $\sigma_2 > \sigma_1$)

While V_{11} and V_{22} are defined by

$$V_{ij} = \frac{72}{\pi} (\eta_i \eta_j)^{1/2} e_j \sum_{l=1}^2 \eta_l e_l \int_{\sigma_{il}}^{\infty} dx x g_{il}(x) \quad (2.8)$$

Exact analytic solutions for the seven coefficients in Equations (2.7), viz. a_1 , a_2 , M_{11} , M_{12} , M_{22} , V_{11} and V_{22} in terms of system parameters such as packing fraction, valences, radius ratio are available only in the special case where the radii of the ions are equal - the 'restricted primitive model' (RPM) ⁽⁷⁾. In the other limit of vanishing radius ratio, the solutions obtained by Gillan et al ⁽¹⁹⁾ are partly analytical and partly numerical. For the general case of arbitrary radius ratio, a numerical solution has been obtained by Abramo and co-workers ⁽²⁰⁾.

2.3.1 Solution for uncharged hard spheres

In this case the exact solutions of the PY equations (2.5) for a two-component fluid mixture (Lebowitz ⁽⁴⁸⁾) are

$$\begin{aligned} -c_{ij}(r) &= a_i + b_i r + d r^3 \quad \dots \quad r < \sigma_i \\ -c_{12}(r) &= -c_{21}(r) \end{aligned} \quad (2.9a)$$

$$\begin{aligned} &= a_1 \quad \dots \quad r \leq \lambda \\ &= a_1 + \left\{ b(r-\lambda)^2 + 4 \lambda d(r-\lambda)^3 + d(r-\lambda)^4 \right\} / r \\ &\quad \dots \quad \lambda < r < \sigma_{12} \end{aligned} \quad (2.9b)$$

The various coefficients in the above equations are given by

$$a_i = \frac{\partial}{\partial e_i} \left[\beta P(e_1, e_2) \right] \quad (2.10)$$

$$b_i = -\pi \left[e_i \sigma_i^2 g_{ii}'(\sigma_i) + e_2 \sigma_{i2}^2 g_{i2}'(\sigma_{i2}) \right] \quad (2.11)$$

$$b = -\pi \left[e_1 \sigma_1 g_{11}(\sigma_1) + e_2 \sigma_2 g_{22}(\sigma_2) \right] \sigma_{12} g_{12}(\sigma_{12}) \quad (2.12)$$

$$d = \frac{\pi}{12} \left[e_1 a_1 + e_2 a_2 \right] \quad (2.13)$$

$$\beta P = \left[(\rho_1 + \rho_2) (1 + \eta + \eta^2) - \frac{\pi}{2} \rho_1 \rho_2 (\sigma_2 - \sigma_1)^2 \left\{ (\sigma_1 + \sigma_2) + \sigma_1 \sigma_2 \frac{\pi}{6} (\rho_1 \sigma_1^2 + \rho_2 \sigma_2^2) \right\} \right] / (1 - \eta)^3 \quad (2.14)$$

$$g_{11}(\sigma_1) = \left[(1 + \eta/2) + \frac{\pi}{4} \rho_2 \sigma_2^2 (\sigma_1 - \sigma_2) \right] / (1 - \eta)^2 \quad (2.15)$$

$$g_{12}(\sigma_{12}) = \left[\sigma_2 g_{11}(\sigma_1) + \sigma_1 g_{22}(\sigma_2) \right] / 2 \sigma_{12} \quad (2.16)$$

with $\eta = \frac{\pi}{6} \rho_1 \sigma_1^3 + \frac{\pi}{6} \rho_2 \sigma_2^3$, being the total packing fraction; $b_2, g_{22}(\sigma_2)$ can be obtained from $b_1, g_{11}(\sigma_1)$ by the interchange $\rho_1 \leftrightarrow \rho_2, \sigma_1 \leftrightarrow \sigma_2$.

2.3.2 Partial structure factors

Starting from the above solutions, i.e. Equations (2.9), Ashcroft and Langreth ⁽⁴⁹⁾ and Enderby and North ⁽⁵⁰⁾ have numerically evaluated the partial structure factors $S_{ij}(q)$ for a binary Percus-Yevick hard sphere mixture. Here we follow similar techniques, which are also applicable to the more general case of two component charged liquids.

First we define the fourier transform of $c_{ij}(r)$ and $h_{ij}(r)$ as

$$\tilde{c}_{ij}(q) = (\rho_i \rho_j)^{1/2} \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} c_{ij}(r) \quad (2.17a)$$

$$= 4\pi (\rho_i \rho_j)^{1/2} \int_0^\infty dr r^2 \frac{\sin qr}{qr} c_{ij}(r) \quad (2.17b)$$

and similarly

$$\tilde{h}_{ij}(q) = 4\pi(\rho_i \rho_j)^{1/2} \int_0^\infty dr r^2 \frac{\sin qr}{qr} h_{ij}(r) \quad (2.18)$$

$$= S_{ij}(q) - \delta_{ij} \quad (2.19)$$

where in writing the last equality we have used Equation (1.40) of Chapter 1.

Using $c_{ij}(r)$ as given by the solutions of the MSA (Equations (2.7)), and of the PY theory (Equations (2.9)), $\tilde{c}_{ij}(q)$'s are easily evaluated and are collected in Appendix 2.1.

Writing the Ornstein-Zernike relation (Equation (1.42)) explicitly we have,

$$h_{ij}(r) = c_{ij}(r) + \rho_1 \int d\mathbf{r}' c_{i1}(|\mathbf{r}-\mathbf{r}'|) h_{1j}(|\mathbf{r}'|) + \rho_2 \int d\mathbf{r}' c_{i2}(|\mathbf{r}-\mathbf{r}'|) h_{2j}(|\mathbf{r}'|) \quad (2.20)$$

Using definitions (2.17) and (2.18), and the convolution theorem we now Fourier transform the above equation to obtain

$$\tilde{h}_{ij}(q) = \tilde{c}_{ij}(q) + \tilde{c}_{i1}(q) \tilde{h}_{1j}(q) + \tilde{c}_{i2}(q) \tilde{h}_{2j}(q). \quad (2.21)$$

Solutions of Equations (2.21) are now immediate; expressed in terms of $S_{ij}(q)$ and $\tilde{c}_{ij}(q)$ these are the so-called Pearson-Rushbrooke equations⁽⁵¹⁾ for a binary classical fluid.

$$\begin{aligned} S_{11}(q) &= \frac{1 - \tilde{c}_{22}(q)}{(1 - \tilde{c}_{11}(q))(1 - \tilde{c}_{22}(q)) - \tilde{c}_{12}^2(q)} \\ S_{22}(q) &= \frac{1 - \tilde{c}_{11}(q)}{(1 - \tilde{c}_{11}(q))(1 - \tilde{c}_{22}(q)) - \tilde{c}_{12}^2(q)} \\ S_{12}(q) &= \frac{\tilde{c}_{12}(q)}{(1 - \tilde{c}_{11}(q))(1 - \tilde{c}_{22}(q)) - \tilde{c}_{12}^2(q)} \end{aligned} \quad (2.22)$$

It is of course an advantage of the MSA (as also the PY theory) that the partial structure factors are related through a set of simple equations

to the fourier transforms of the direct correlation functions and hence to solution of the model itself. Thus comparison between model and any experimentally determined structure factors is a relatively straightforward task.

The partial radial distribution functions $g_{ij}(r)$ were evaluated using the fourier inversion formulae, (1.41).

2.3.3 Charge and density fluctuations

In the structural description of binary liquid mixtures, it is often convenient to introduce structure factors that describe correlation between fluctuations of physical quantities like concentration, number and charge densities etc.^(1c). These structure factors are defined in terms of linear combinations of $S_{ij}(q)$; for a charged liquid system, useful such quantities are number-number $S_{NN}(q)$, number-charge $S_{NQ}(q)$, and charge-charge $S_{QQ}(q)$ structure factors. These are defined as ⁽⁵²⁾

$$\begin{aligned} \rho_t S_{NN}(q) &= \rho_1 S_{11}(q) + 2(\rho_1 \rho_2)^{1/2} S_{12}(q) + \rho_2 S_{22}(q) \\ \rho_t S_{NQ}(q) &= \rho_1 Z_1 \left\{ S_{11}(q) + \left((\rho_2/\rho_1)^{1/2} - (\rho_1/\rho_2)^{1/2} \right) S_{12}(q) - S_{22}(q) \right\} \\ \rho_t S_{QQ}(q) &= (\rho_1 Z_1)^2 \left\{ S_{11}(q) \rho_1^{-1} - 2 S_{12}(q) (\rho_1 \rho_2)^{-1/2} + S_{22}(q) \rho_2^{-1} \right\} \quad (2.23) \end{aligned}$$

Here $\rho_t (= \rho_1 + \rho_2)$ is the total number density. From the overall electrical neutrality condition

$$Z_1 \rho_1 = Z_2 \rho_2 \quad (2.24)$$

$$\text{or} \quad \rho_1 / \rho_2 = Z_2 / Z_1 = Z \quad (2.25)$$

where Z is defined as the ratio of charges.

$$\begin{aligned} \text{Thus} \quad \rho_t &= \rho_1 + \rho_2 \\ &= Z \rho_2 + \rho_2 \\ &= (Z+1) \rho_2 \end{aligned} \quad (2.26)$$

Hence on substituting the above result for ρ_t in Equations (2.23) we get

$$\begin{aligned}
S_{NN}(q) &= \frac{Z}{Z+1} \left[S_{11}(q) + Z^{-1} S_{22}(q) + 2 Z^{-1/2} S_{12}(q) \right] \\
S_{NQ}(q) &= \frac{ZZ_1}{Z+1} \left[S_{11}(q) - S_{22}(q) + (Z^{-1/2} - Z^{1/2}) S_{12}(q) \right] \\
S_{QQ}(q) &= \frac{(ZZ_1)^2}{Z+1} \left[S_{11}(q) + Z S_{22}(q) - 2 Z^{1/2} S_{12}(q) \right]
\end{aligned} \tag{2.27}$$

It is to be noted here that $S_{QQ}(q) \rightarrow (ZZ_1)^2$ at large q so that dividing through by this quantity we can normalize $S_{QQ}(q)$ to unity.

2.4 Method of numerical solution and the physical parameters used

In order to facilitate numerical calculations, the following dimensionless variables were introduced. We chose subscript 1 for uranium and 2 for oxygen. The variables were

$$\alpha = \frac{\sigma_1}{\sigma_2}, \text{ the ratio of two diameters}$$

$$\eta = \left(\frac{\pi}{6} \rho_1 \sigma_1^3 + \frac{\pi}{6} \rho_2 \sigma_2^3 \right), \text{ the total packing fraction}$$

$$Z = \frac{z_2}{z_1}, \text{ the charge ratio}$$

$$\chi = \frac{\rho_2}{\rho_1 + \rho_2}, \text{ the concentration of larger hard spheres.}$$

$$\Gamma = \frac{z_2^2 |e|^2}{\epsilon k_B T \sigma_2}, \text{ the plasma parameter (the coupling constant)}$$

describing the strength of the coulomb interaction and hence is a measure of the ionicity of the system.

These dimensionless quantities completely specify the model and were the physical (system) parameters that entered the computer programs. Details of the numerical routines used to solve for the Waisman-Lebowitz coefficients in the MSA solutions (Equations (2.7)) are summarized in Appendix 2.2. Here we give the data used in the different sets of calculations.

(a) Charged hard spheres

Two broad sets of calculations were carried out. The first of these corresponded to the choice of diameters for uranium and oxygen ions

from Pauling radii. The second set allowed variation of these diameters, but with constant ratio, until the experimental compressibility K_T (36) for liquid UO_2 was reproduced on passing to the long wave-length limit of the structure factors.

(I) System parameters without fitting compressibility

For the first set of calculations, the Pauling diameters for uranium and oxygen were taken to be $\sigma_1 = 1.94 \text{ \AA}$ and $\sigma_2 = 2.8 \text{ \AA}$ (53). These then yielded $\alpha = 0.69$, $\eta = 0.5225$. Also $z = 0.5$, $\chi = 0.66$, $T = 3073^\circ\text{K}$, $\rho_1 = 0.01949 \text{ \AA}^{-3}$, $\rho_2 = 0.03897 \text{ \AA}^{-3}$ (the number densities were calculated from the density 8.74 gm/cm^3 (54a) of molten UO_2 at its melting temperature $\sim 3073^\circ\text{K}$). For Γ we chose two values :

- (i) the charges were taken as U^{4+} and O^{2-} which yielded $\Gamma = 77.6$,
- (ii) the ionic charges were reduced in order to examine the influence on structure; the second choice we adopted was U^{2+} and O^- , the corresponding Γ being 19.4.

(II) System parameters with fitting to experimental compressibility

The experimental isothermal compressibility of liquid UO_2 at $\sim 3133\text{K}$ is $4.4 \times 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$ (34,36). We sought to fit this using the compressibility sum rule, (Equation (1.43)), following the procedure of Abramo et al (21) (see Appendix 2.2 for details). Two different sets of calculations were performed :

- (i) the number density ρ_t was extrapolated to the temperature at which the compressibility was measured. This yielded $\rho_t = 0.0194 \text{ \AA}^{-3}$; also for this case T is actually 3138°K and $\sigma_2 = 2.36 \text{ \AA}$. It follows that $\Gamma = 90.1$ (for the completely ionic picture U^{4+}, O^{2-}) and $\Gamma = 22.5$ for the partially ionic case U^{2+}, O^- , while $\eta = 0.31$;
- (ii) here we assumed the same values of T and ρ_t as in (I) and obtained $\sigma_2 = 2.3 \text{ \AA}$, and hence $\eta = 0.289$, $\Gamma = 94.5$ (U^{4+}, O^{2-}) and 23.6 (U^{2+}, O^-).

It is worthwhile to mention here that there is a physical basis for the model hard sphere diameters being smaller than their values in

the crystal. In the latter case these are fixed so as to give the minimum of the cohesive energy. But in a hard sphere model with infinitely repulsive cores, the values of σ_{ij} closer to the zero of the potential would be more reasonable.

(b) Uncharged hard spheres

In this case the only parameters needed to describe the system are α , η and χ . We took $\alpha = 0.69$, $\chi = 0.66$ and $\eta = 0.5225$, the same as their values in (I) corresponding to the choice of Pauling diameters for uranium and oxygen. It should be noted that consistent with our assumption of a mixture of neutral U and O atoms, the choice of neutral atomic diameters for the corresponding hard spheres would seem more appropriate for this model. However, we have chosen the above diameters in order to make the calculations consistent with the charged hard sphere case and hence make comparison possible.

2.5 Results

The general features of the structure of molten UO_2 are evident from the sets of figures (2.1a) to (2.7a) which show the partial structure factors $S_{ij}(q)$. The corresponding radial distribution (pair correlation) functions $g_{ij}(r)$ are shown in figures (2.1b) to (2.7b). Actually in q -space the basic variable used is $y = q\sigma_2$ while the unit of length chosen in the r -space plots is σ_2 . The curves (2.3) to (2.6) correspond to the case where the experimental compressibility has been fitted and (2.2), (2.4) and (2.6) are for the partially ionic case, i.e. U^{2+} , O^- . The $S_{ij}(q)$ and $g_{ij}(r)$ in the limit $\Gamma \rightarrow 0$ corresponding to the neutral hard sphere case are shown in figures (2.7a) and (2.7b) respectively.

The overall structure in liquid UO_2 seems to be strongly influenced by the correlation of charges round the uranium ions induced by the high charges especially for the completely ionic model. This view is supported by the sharp first peak in $S_{QQ}(y)$ shown in figure (2.8) for the completely ionic case. As can be seen from figure (2.9) for the partially ionic case, this peak is reduced.

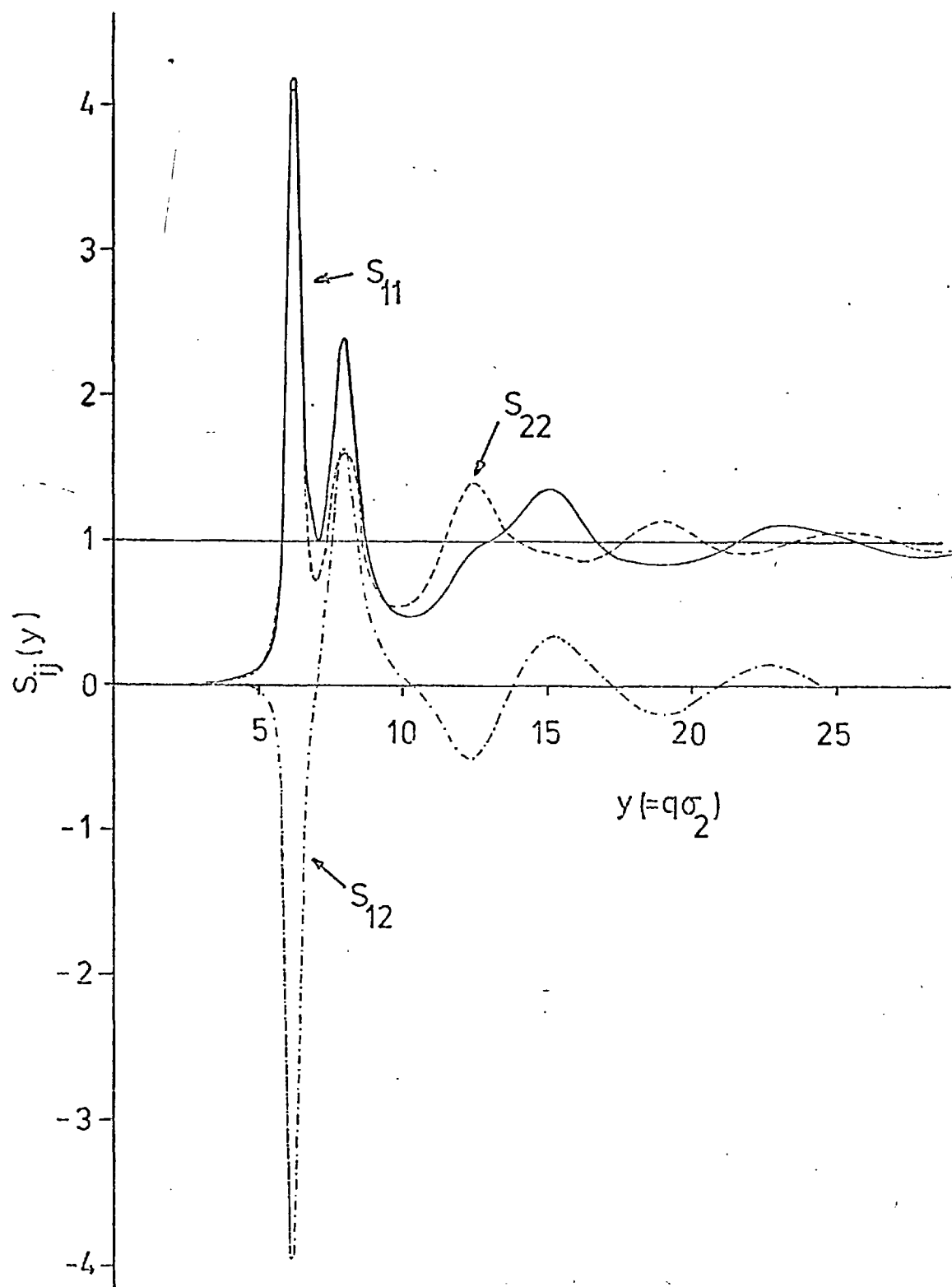


Figure 2.1a

Partial structure factors $S_{ij}(q)$ with the coupling constant $\Gamma = 77.6$ corresponding to completely ionic model U^{4+}, O^{2-} . Actual variable plotted is $y = q\sigma_2$ where $\sigma_2 = 2.8\text{\AA}$ is the diameter of the oxygen ion.

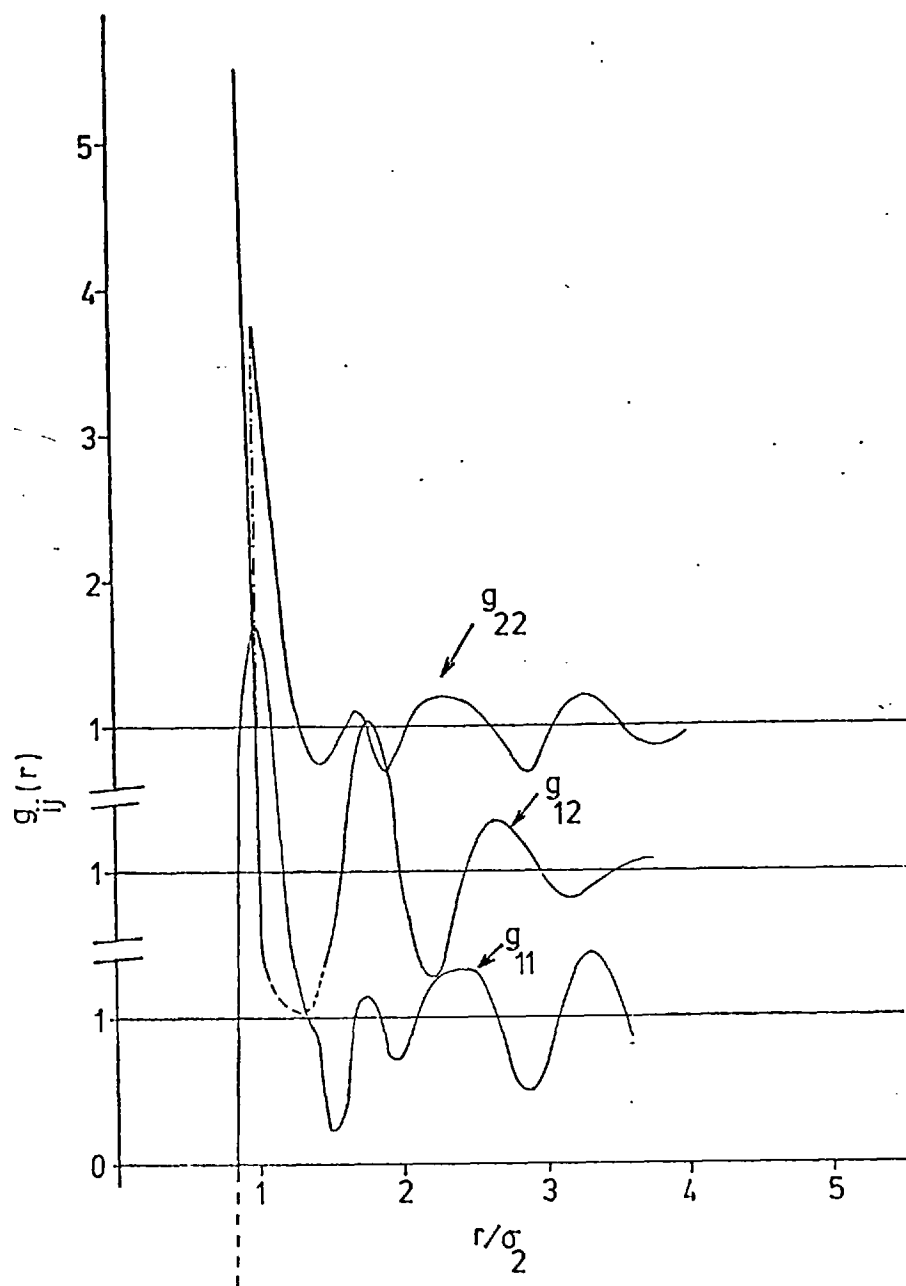


Figure 2.1b

Radial distribution (pair correlation) functions $g_{ij}(r)$ corresponding to the partial structure factors in Fig.2.1a; $\Gamma = 77.6$. As plotted $\sigma_2 = 2.8\text{\AA}$ is the unit of length.

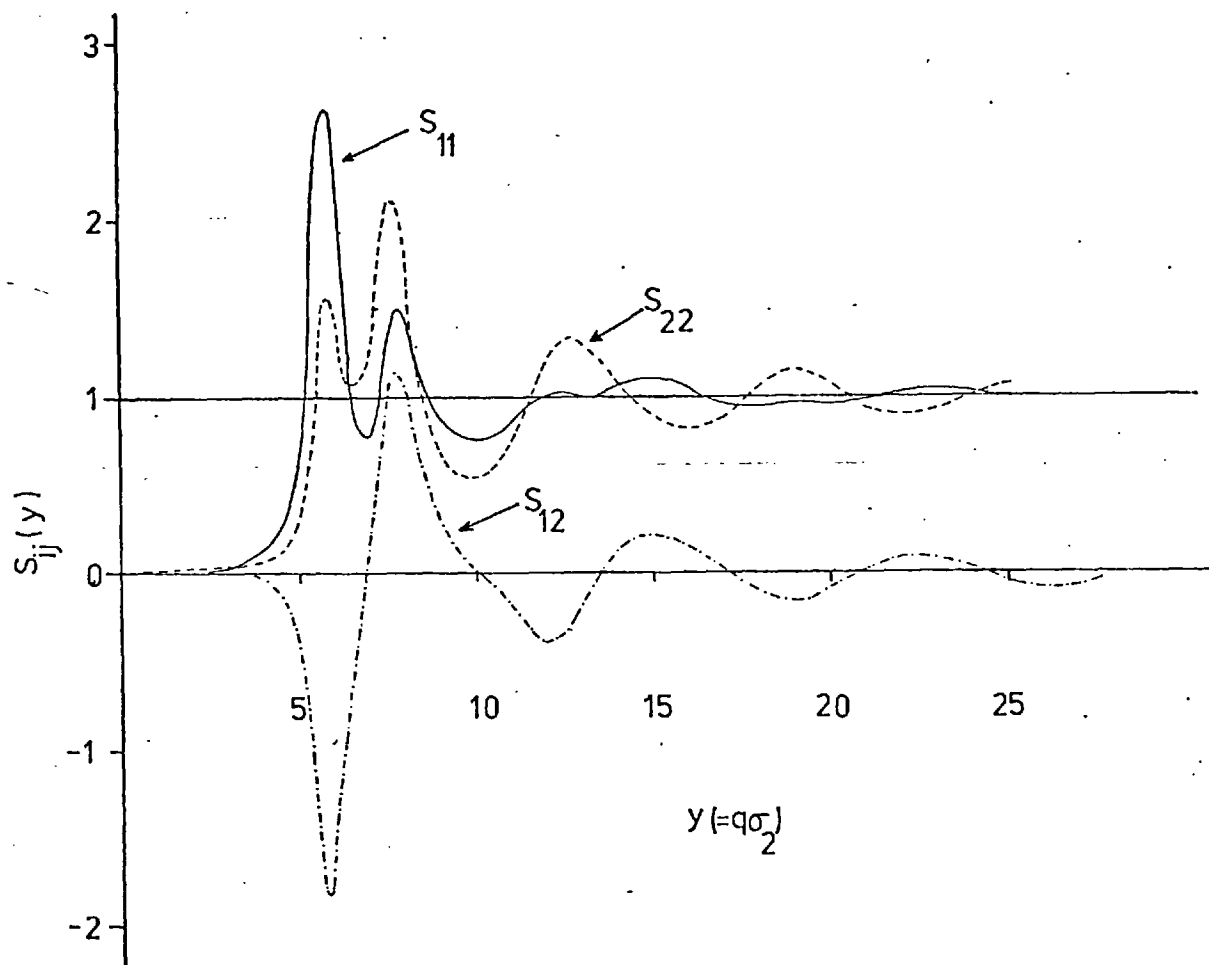


Figure 2.2a

Partial structure factors $S_{ij}(q)$ with the coupling constant $\Gamma = 19.4$ corresponding to partially ionic model U^{2+} , O^{-} . The variable plotted is $y = q\sigma_2$ where $\sigma_2 = 2.8\text{\AA}$ is the diameter of the oxygen ion.

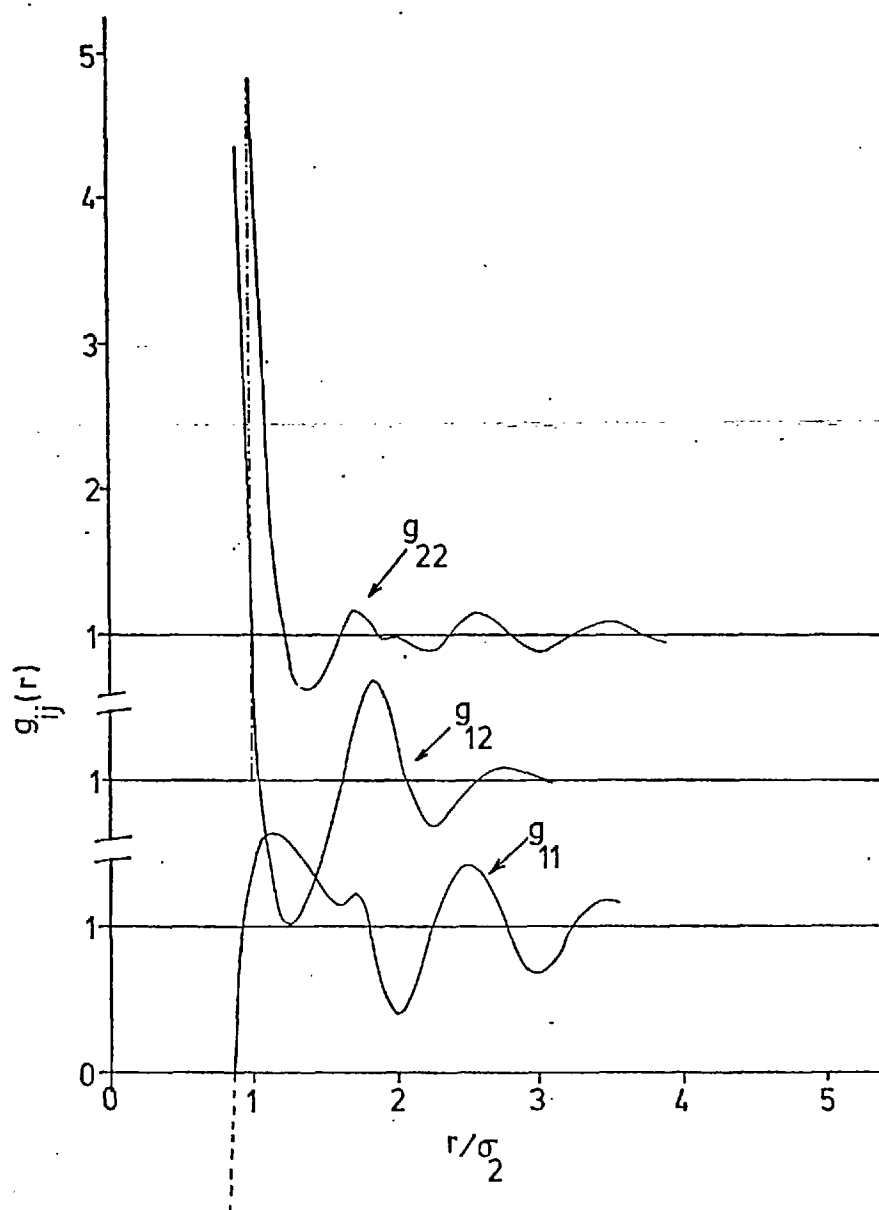


Figure 2.2b

Radial distribution functions $g_{ij}(r)$ corresponding to the partial structure factors in Fig.2.2a; $\Gamma = 19.4$. As plotted $\sigma_2 = 2.8\text{\AA}$ is the unit of length.

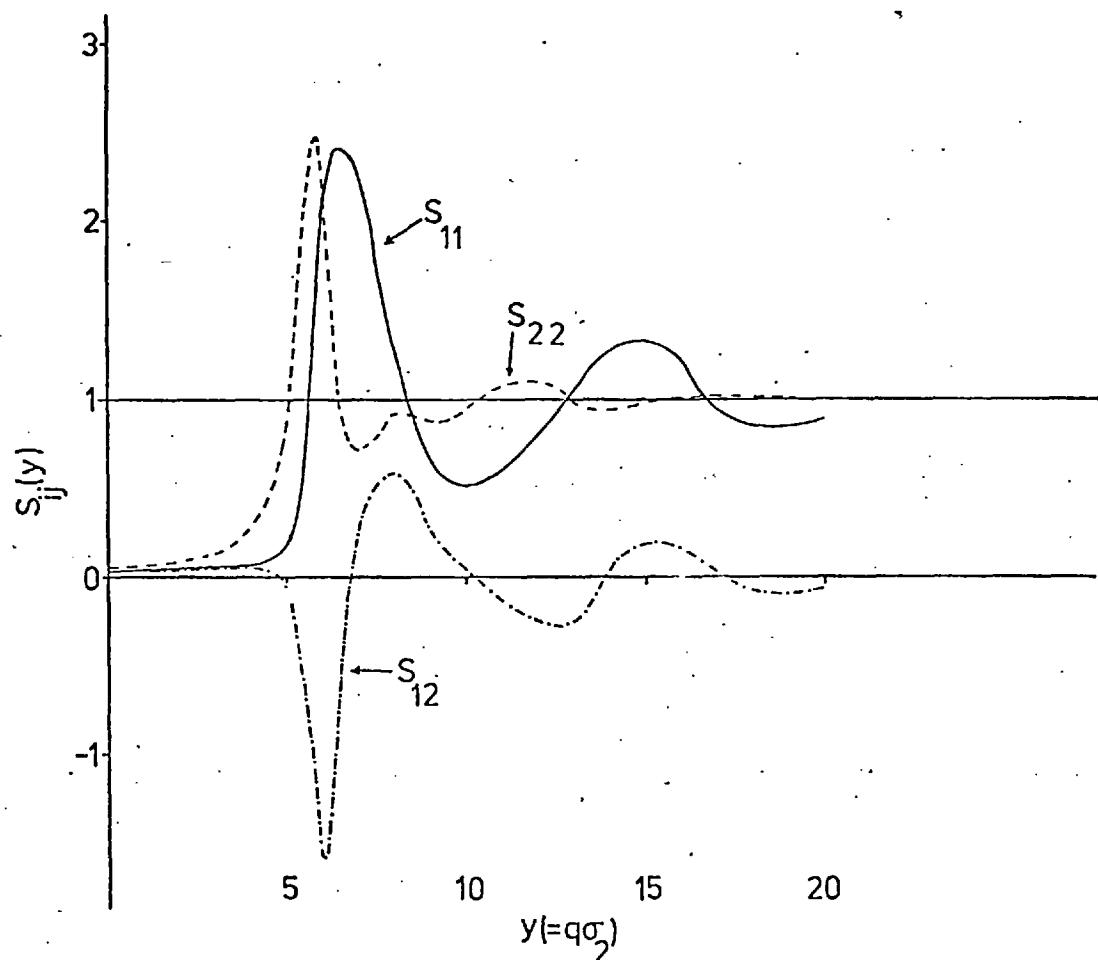


Figure 2.3a

Partial structure factors $S_{ij}(q)$ with $\Gamma = 90.1$ (U^{4+}, O^{2-}). The curves are fitted to experimental isothermal compressibility. (cf. calculation (i) of II, Section 2.4). The variable plotted is $y = q\sigma_2$, where σ_2 is the diameter of the oxygen ion. In this calculation $\sigma_2 = 2.36 \text{ \AA}$.

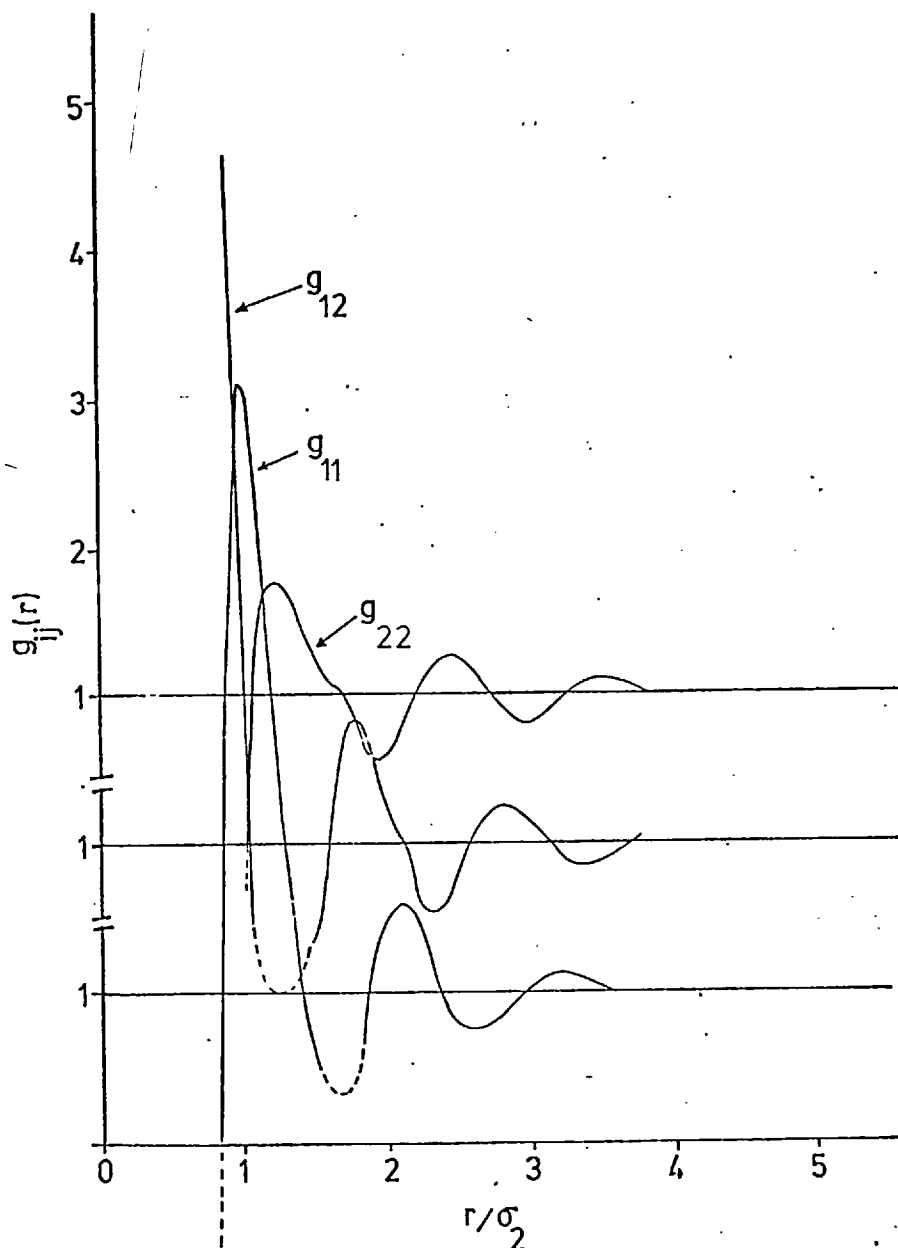


Figure 2.3b

Radial distribution functions $g_{ij}(r)$ corresponding to the partial structure factor in Fig.2.3a; $\Gamma = 90.1$. The unit of length is $\sigma_2 = 2.36 \text{ \AA}$.

N.B.

The small dashed regions in g_{11} and g_{12} are schematic as small negative values arise here in practice. These negative values are unphysical.

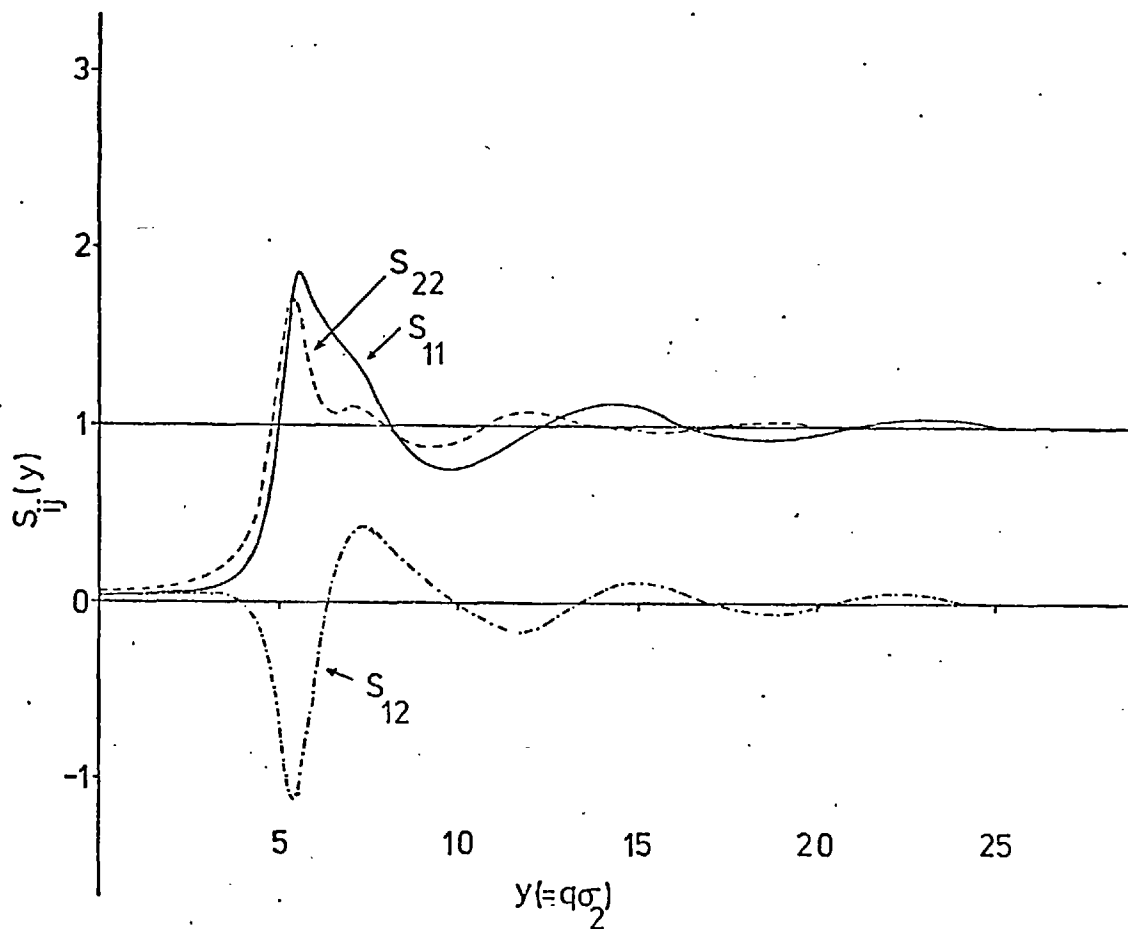


Figure 2.4a

Partial structure factors $S_{ij}(q)$ with $\Gamma = 22.5$ ($\text{U}^{2+}, \text{O}^{2-}$). The curves are fitted to experimental isothermal compressibility. (cf. calculation set (i) of II, Section 2.4). The variable plotted is $y = q\sigma_2$, where σ_2 is the diameter of oxygen ion. In this calculation $\sigma_2 = 2.36 \text{ \AA}$.

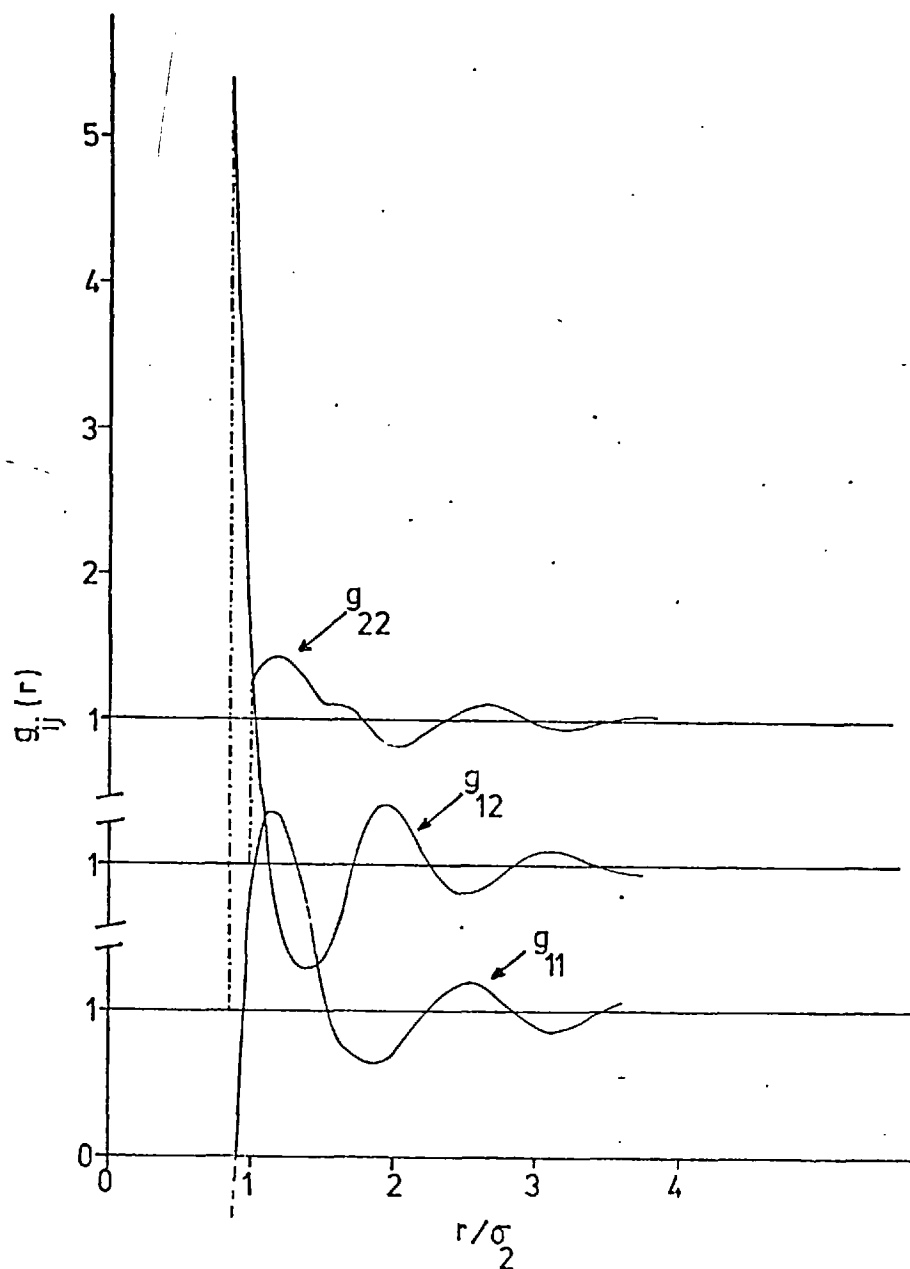


Figure 2.4b

Radial distribution functions $g_{ij}(r)$ corresponding to the partial structure factors in Fig.2.4a; $\Gamma = 22.5$. The unit of length is $\sigma_2 = 2.36 \text{ \AA}$.

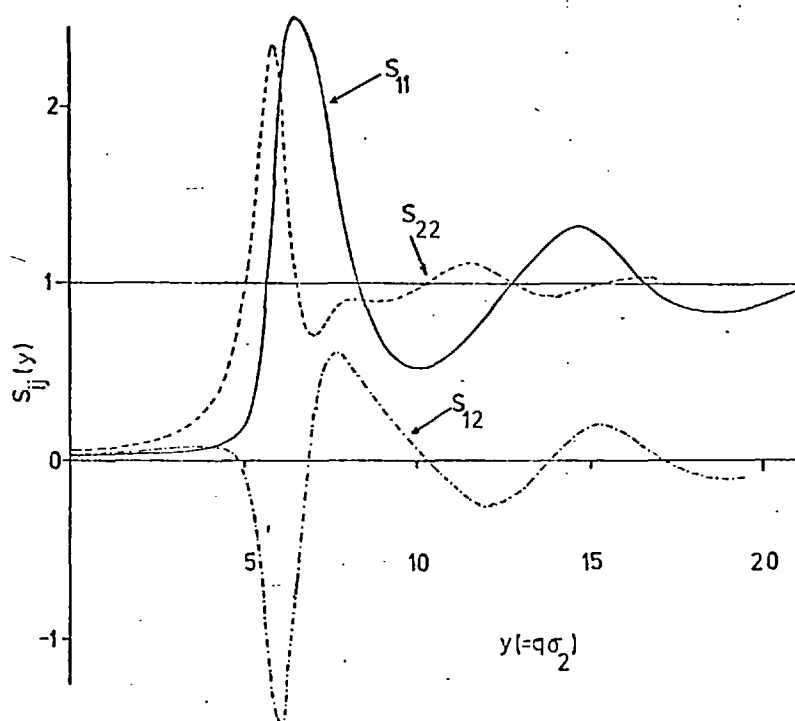


Figure 2.5a

Partial structure factors $S_{ij}(q)$ with $\Gamma = 94.5$ (U^{4+}, O^{2-}). The curves are fitted to experimental isothermal compressibility (cf. calculation set (ii) of II, Section 2.4). The variable plotted is $y = q\sigma_2$, where σ_2 is the diameter of the oxygen ion. In this calculation $\sigma_2 = 2.3\text{\AA}$.

N.B.

Notice that there is very little difference between these curves and those in Figure 2.3a.

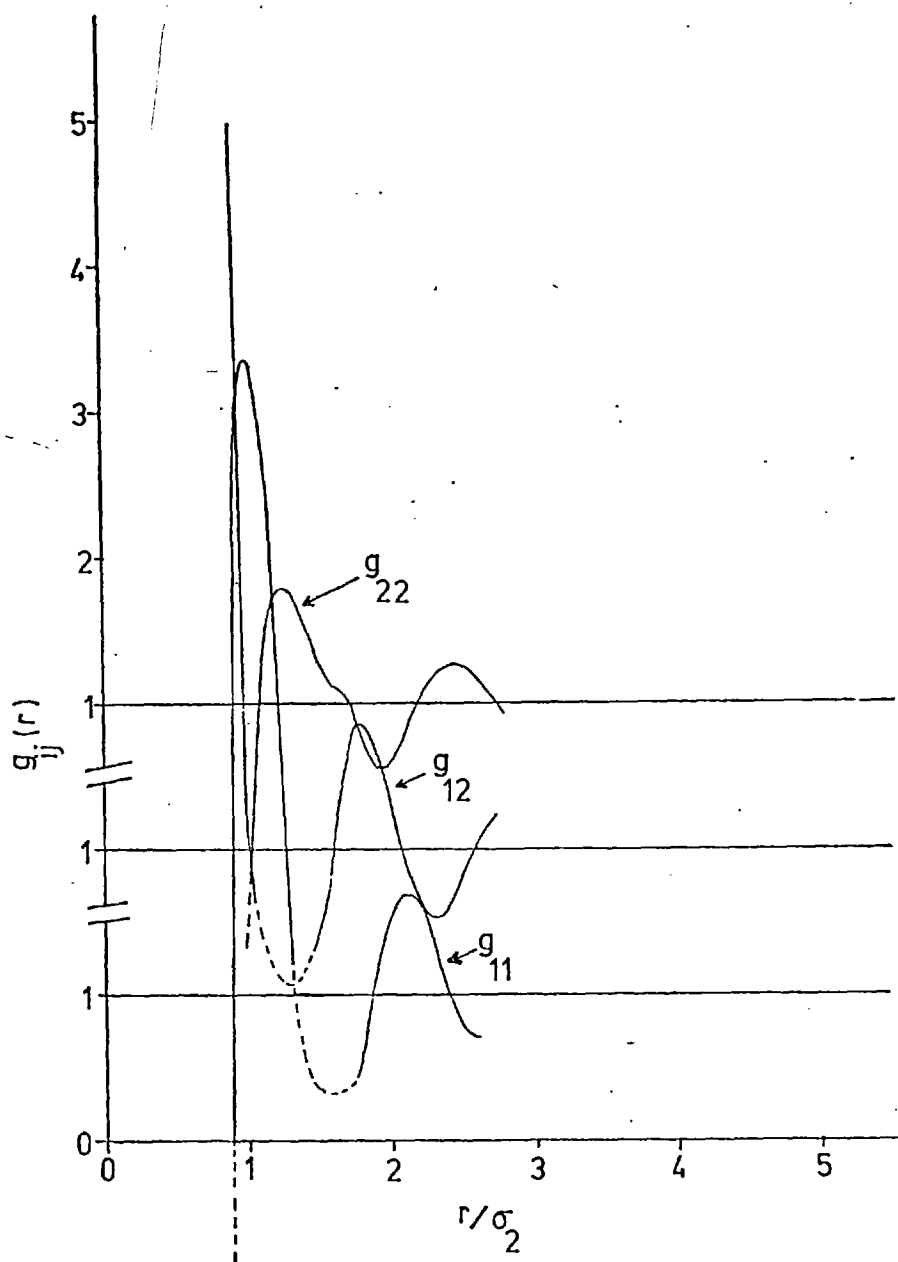


Figure 2.5b

Radial distribution functions $g_{ij}(r)$ corresponding to the partial structure factors in Fig.2.5a; $\Gamma = 94.5$. The unit of length is $\sigma_2 = 2.3\text{\AA}$.

N.B.

Again the small dashed regions in g_{11} and g_{12} are schematic as small negative values arise here in practice. These negative values are unphysical.

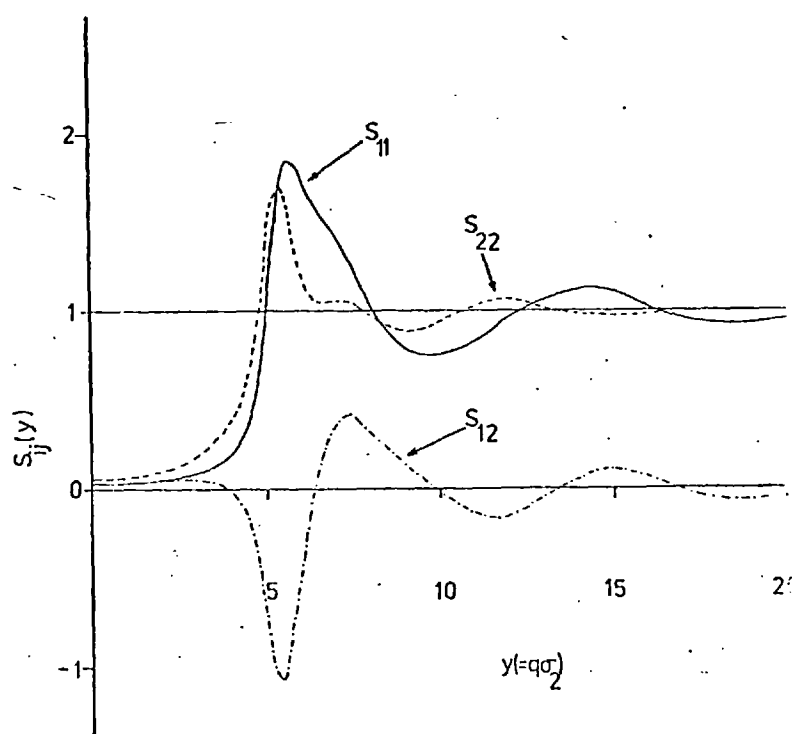


Figure 2.6a

Partial structure factors $S_{ij}(q)$ with $\Gamma = 23.6$ (U^{2+}, O^-). The curves are fitted to experimental isothermal compressibility (cf. calculation set (ii) of II, Section 2.4). The variable plotted is $y = q\sigma_2$, where σ_2 is the diameter of the oxygen ion. In this calculation $\sigma_2 = 2.3\text{\AA}$.

N.B.

Notice again that there is very little difference between these curves and those in Fig. 2.4a.

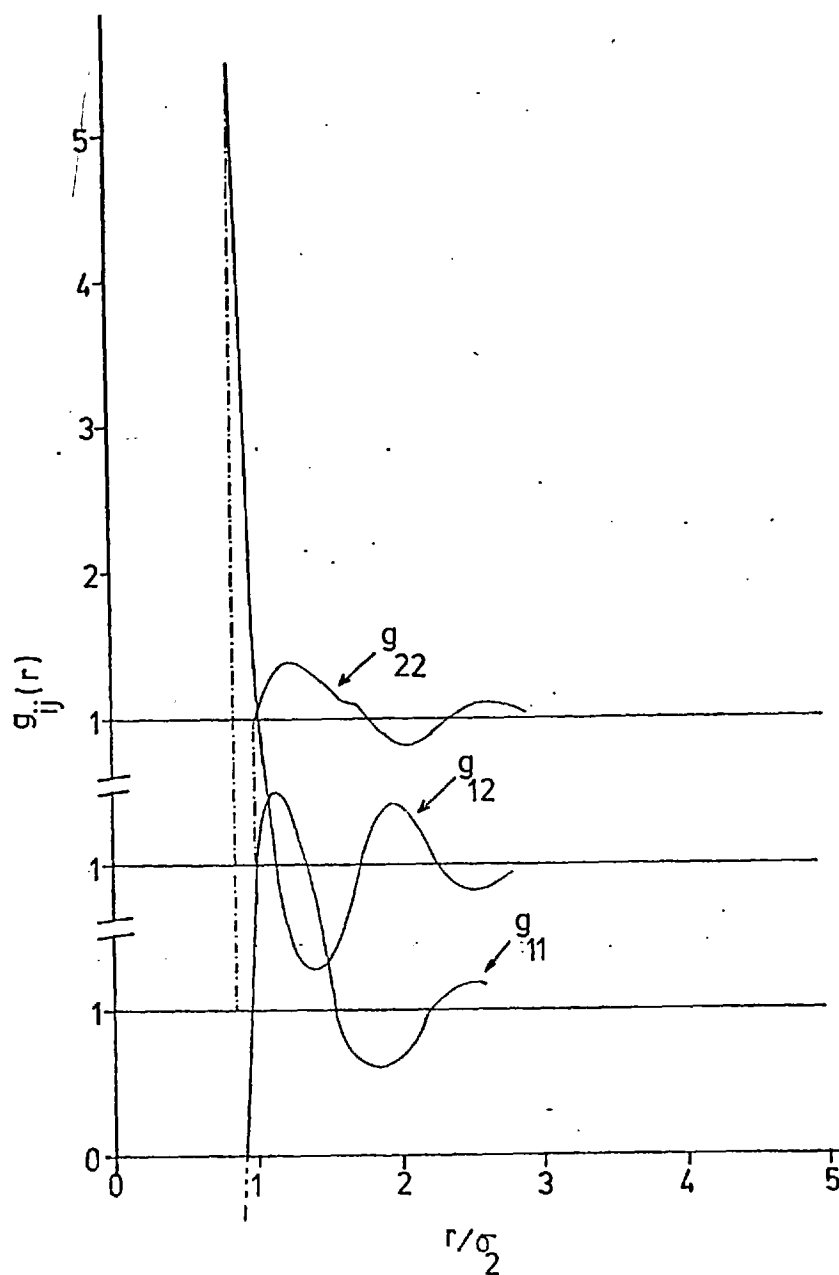


Figure 2.6b

Radial distribution functions $g_{ij}(r)$ corresponding to the partial structure factors in Fig. 2.6a; $\Gamma = 23.6$. The unit of length is $\sigma_2 = 2.3 \text{ \AA}$.

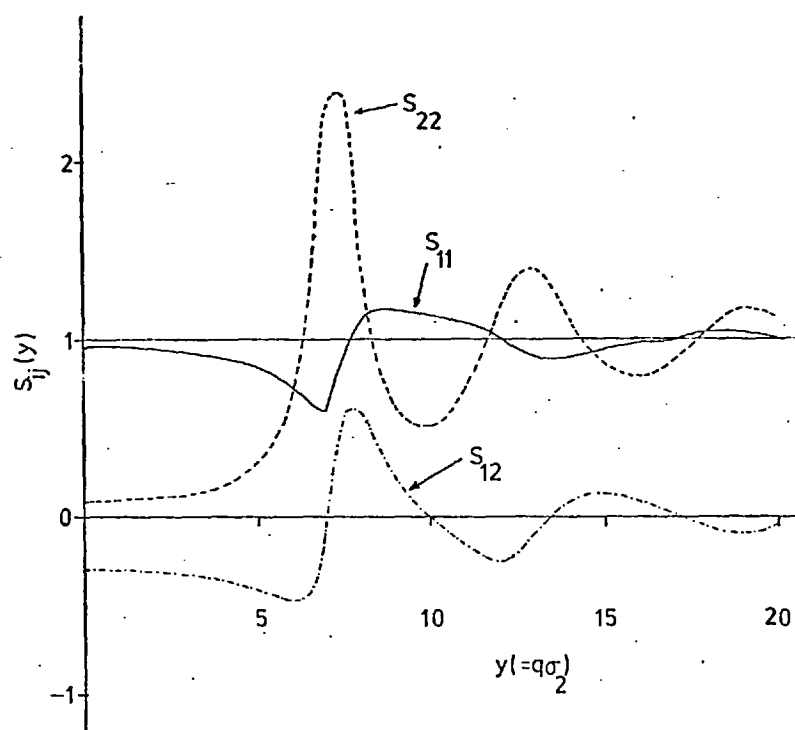


Figure 2.7a

Partial structure factors $S_{ij}(q)$ with $\Gamma = 0$ corresponding to a mixture of neutral uranium and oxygen atoms (uncharged hard spheres). The variable plotted is $y = q\sigma_2$ with $\sigma_2 = 2.8\text{\AA}$.

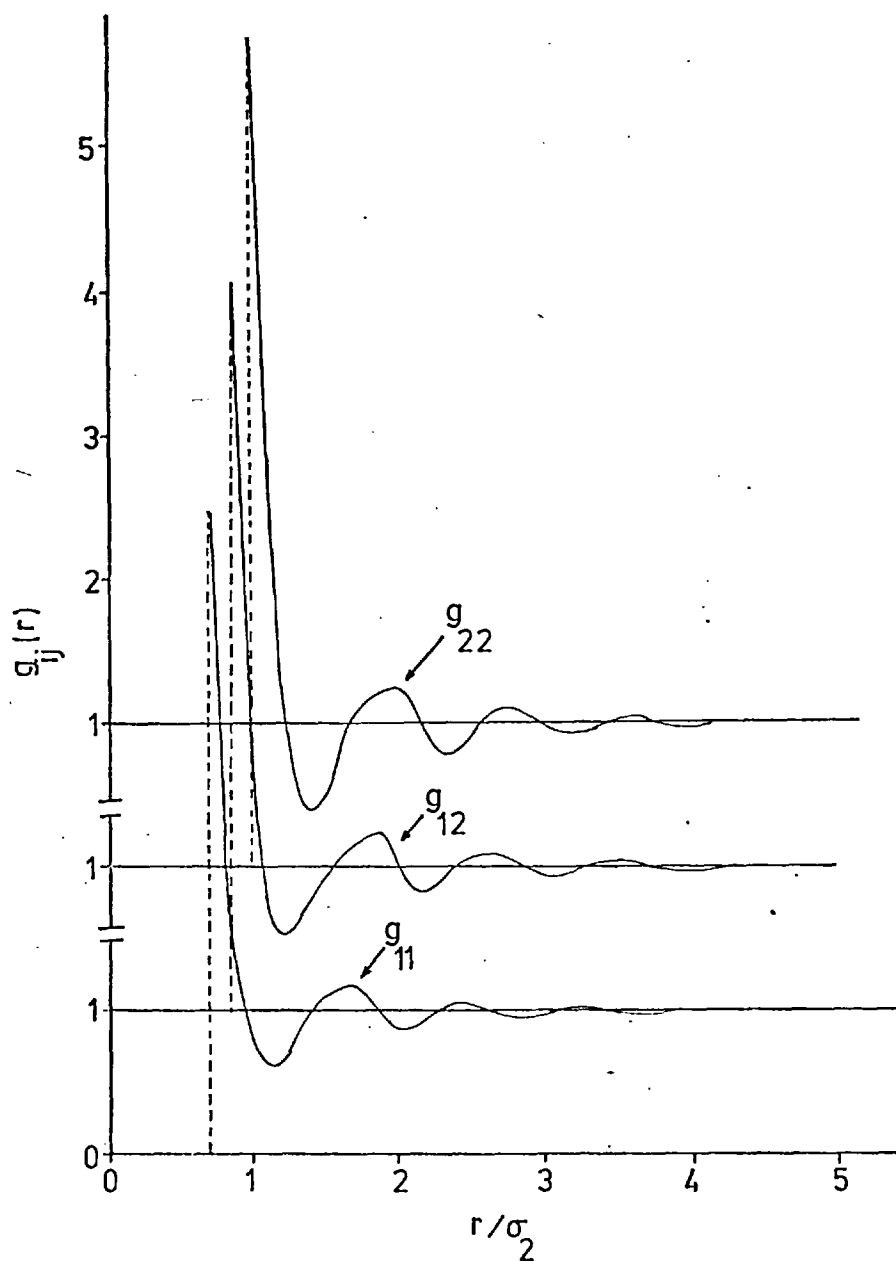


Figure 2.7b

Radial distribution functions $g_{ij}(r)$ corresponding to the partial structure factors of Fig. 2.7a; $\Gamma = 0$. The unit of length is $\sigma_2 = 2.8\text{\AA}$.

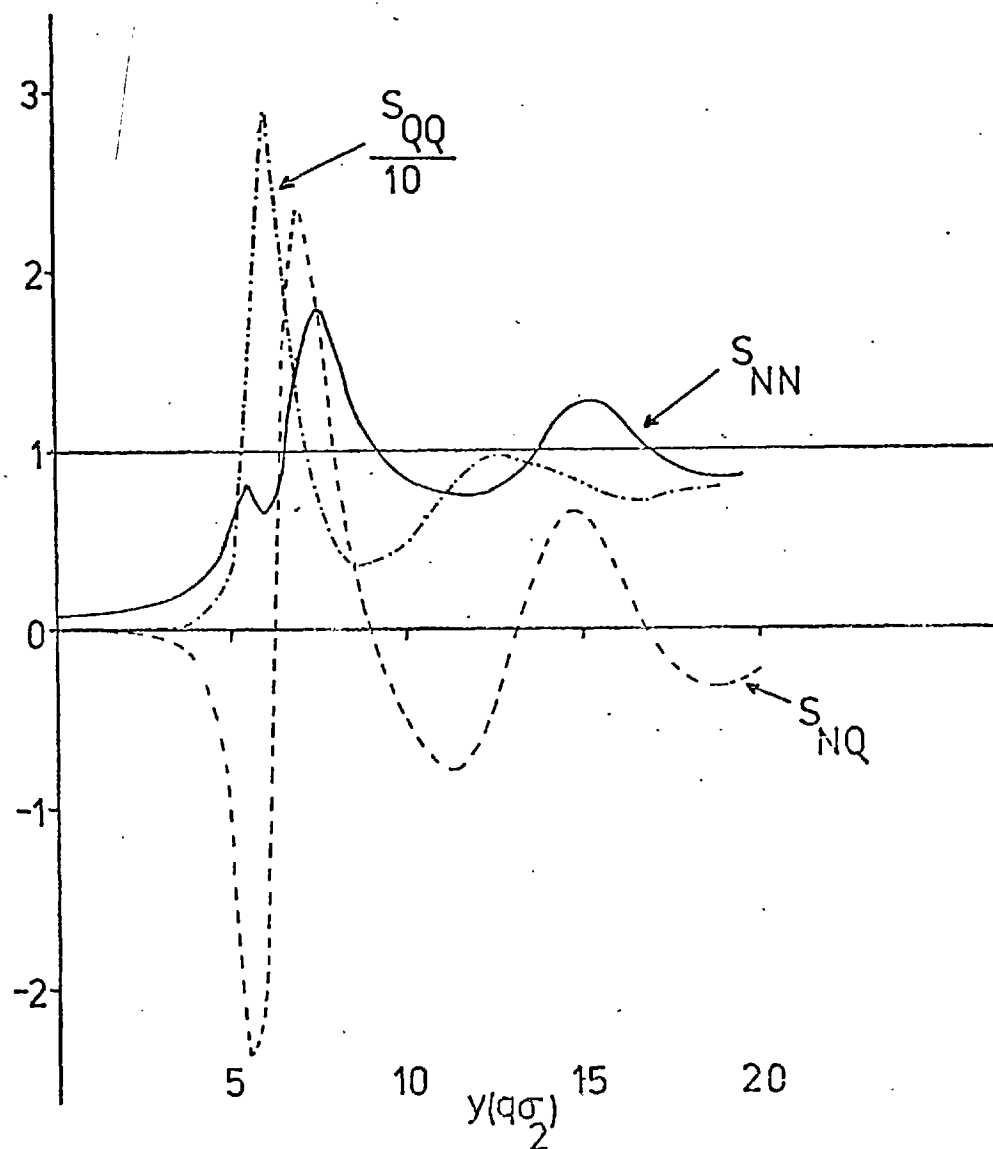


Figure 2.8

Number-charge fluctuations corresponding to the completely ionic model $\Gamma = 90.1$ (U^{4+} , O^{2-}). The variable plotted is $y = q\sigma_2$, $\sigma_2 = 2.36\text{\AA}$.

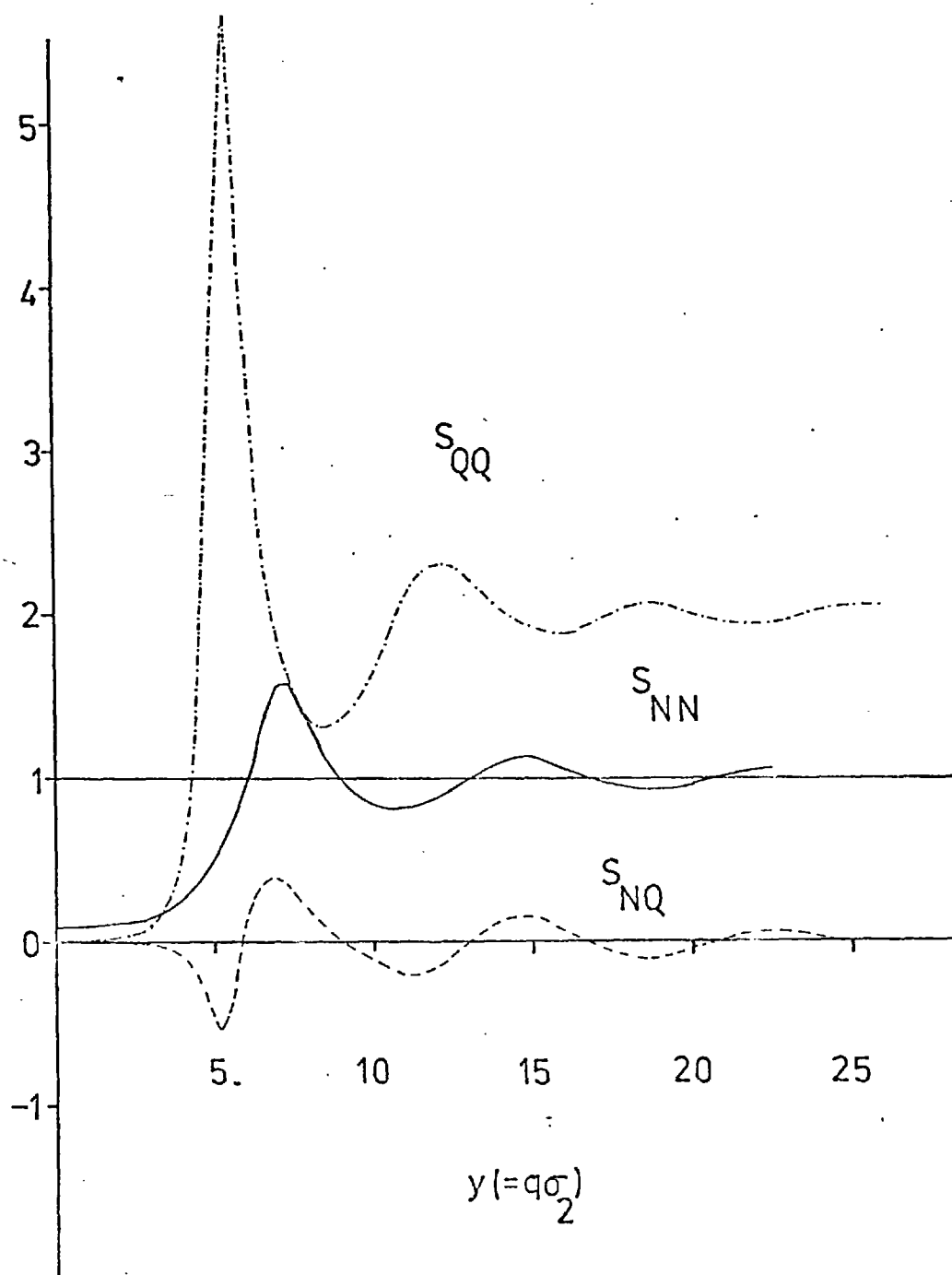


Figure 2.9

Number-charge fluctuations corresponding to the partially ionic model $\Gamma = 22.5$, (U^{2+}, O^-) . The variable plotted is $y = q\sigma_2$, $\sigma_2 = 2.36\text{\AA}$.

In the set of calculations corresponding to Pauling diameters for uranium and oxygen ions, for $\Gamma = 77.6$ (U^{4+} , O^{2-}), considerable short range order is reflected in the oscillations at large r in $g_{ij}(r)$ and an isolated low- y peak in $S_{ij}(y)$. In the cross-correlation function S_{12} the first minimum is very deep ~ -4 and the width of the trough very narrow. This is suggestive of a U-O correlation extending considerably into r -space. These trends are the same for $\Gamma = 19.4$ (U^{2+} , O^{2-}) but as expected, the effects are much less pronounced.

It is interesting to note the changes in the structure factors when the experimental compressibility is fitted. The striking feature is both the $S_{ij}(y)$'s and the $g_{ij}(r)$'s are much smoother, but in place of the isolated low- y peak we now notice the shoulder shown in figures (2.3a) to (2.6a). Also in this case there is little difference in $S_{ij}(y)$'s for $\Gamma = 94.5$ or 90.1 or between 23.6 and 22.5 . The same is true for $g_{ij}(r)$. It thus appears that the structure is not sensitive to small changes in Γ around the region where the long wave-length limits of $S_{ij}(y)$ are related to the experimental compressibility.

Going over to the limit $\Gamma \rightarrow 0$, i.e. the uncharged hard sphere case, (figure (2.7)), the most important feature is the relative structurelessness of S_{11} , in fact it is ~ 1 . S_{22} resembles that of a pure, simple liquid. Correspondingly in the $g_{ij}(r)$'s we have g_{22} showing considerable oscillations while g_{11} is the most damped. Another noticeable feature is the difference in the long wave length limits of the three $S_{ij}(y)$'s; $S_{11}(0) \sim 1$, $S_{12}(0) < 0$ and $S_{22}(0)$ goes to a very small positive value $\sim 10^{-2}$. It appears therefore when the charges are switched off, the relative sizes of the species is of considerable influence in determining structure. In the present case it is mainly due to O-O correlations. As oxygen is the larger species with larger concentration this is physically reasonable.

One other quantity which depends on charging is the contact value of $g_{ij}(r)$. For g_{22} it decreases as Γ increases from zero (a

selection of contact values of $g_{ij}(r)$ are given in Table 2.1). This is an immediate consequence of the coulombic repulsion. But for g_{12} , the trend is the reverse, this time because of the coulombic attractions. g_{11} at contact is negative for $\Gamma \neq 0$, also for high Γ (94.5; 90.1) g_{22} is negative. This unphysical feature is a well known general defect of the MSA (see, for example, Gillan et al (19), Abramo et al (21)).

2.6 Comparison of results with crystalline structure

In the absence of experimental structural data on the liquid with which to compare our partial structure factors, we shall consider what relations our results bear to the crystalline structure of the solid. We keep this discussion mainly to the $S_{ij}(y)$ for which the experimental compressibility has been fitted commenting on the Pauling diameter choice only when significantly different features are apparent.

The crystal structure of solid UO_2 at the stoichiometric composition is face-centred cubic with respect to the uranium atoms, with oxygen atoms occupying positions $\pm 1/4, \pm 1/4, \pm 1/4$ (54b). The structure is the fluorite lattice and is equivalent to that displayed in Figure (2.10) where the uranium atoms occupy alternate cube centres.

Taking the unit of length as σ_2 , the oxygen ion diameter, we take the distance between the O-atoms along a cube edge as unity. In this unit the distance between two uranium atoms in alternate cube centres is 2, but 1.4 going diagonally, as shown. It should be noted that this is the distance between the uranium atoms at the face centre and at the cube corner on the same face. We first consider the $S_{ij}(y)$ shown in Figure (2.4a), corresponding to $\Gamma = 22.5$.

(a) In S_{12} , the period is about 7.4, which corresponds to a correlation distance $2\pi/7.4 \sim 0.85$ in g_{12} . This is the r at contact value and we recognize it to be the distance between the uranium atom at the centre of a cube and an oxygen atom at the corner as shown in Figure (2.10). The same features are present in S_{12} and g_{12} for $\Gamma = 90.1$ in Figure (2.3a) but are much sharper.

TABLE 2.1

A Selection of Contact Values of $g_{ij}(r)$

	Positions at contact (Å)		Contact Value
$\Gamma = 0$	g_{11}	1.94	4.62
	g_{12}	2.36	5.08
	g_{22}	2.8	5.75
$\Gamma = 19.4$	g_{11}	1.94	-5.43
	g_{12}	2.36	8.07
	g_{22}	2.8	4.82
$\Gamma = 77.6$	g_{11}	1.94	-17.61
	g_{12}	2.36	11.60
	g_{22}	2.8	3.74
$\Gamma = 22.5$	g_{12}	1.99	6.40
	g_{22}	2.36	1.22
$\Gamma = 90.1$	g_{12}	1.99	11.34
	g_{22}	2.36	-0.32
$\Gamma = 23.6$	g_{11}	1.59	-12.22
	g_{12}	1.94	6.51
	g_{22}	2.3	0.94
$\Gamma = 94.5$	g_{11}	1.59	-29.92
	g_{12}	1.94	11.74
	g_{22}	2.3	-0.66

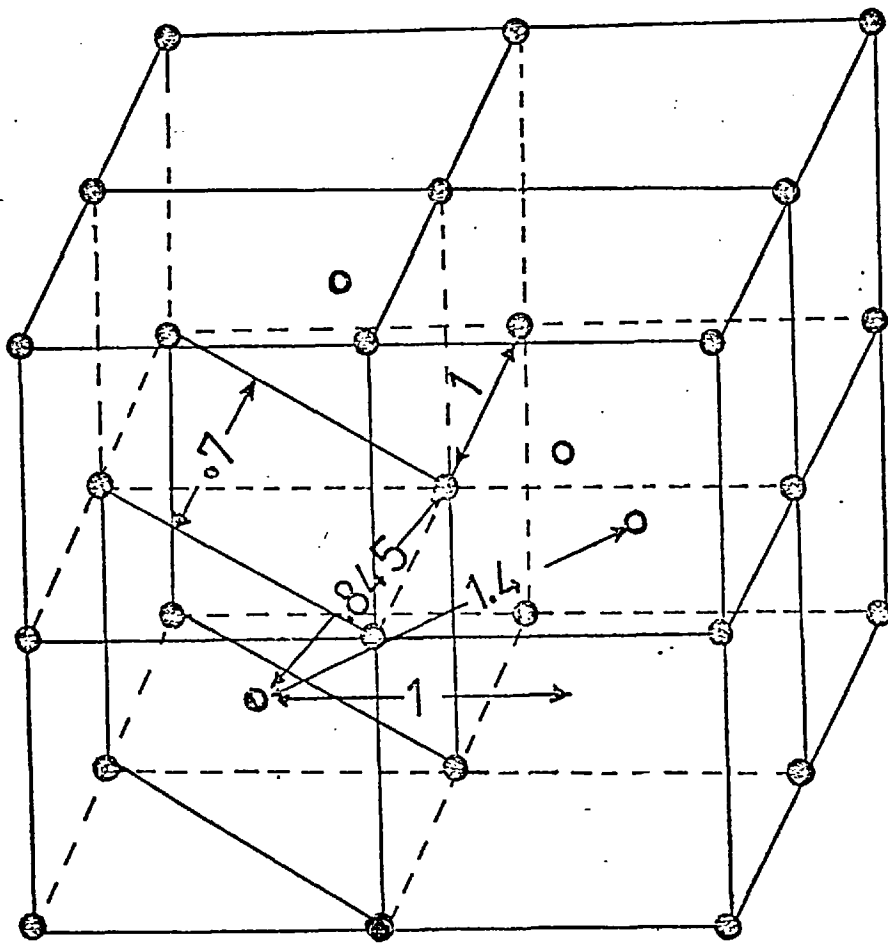


Figure 2.10 Crystalline structure of UO_2 :
 Filled circles - oxygen.
 Open circles - uranium.

(b) In S_{22} , $\Gamma = 22.5$, the period is about 6.3, which corresponds to the correlation distance $2\pi/6.3 \sim 1$ in g_{22} where it is recognized to be the first peak position, the contact distance for g_{22} . This is obviously the distance between two oxygen atoms along a cube edge in Figure (2.10). Besides sharpening up for $\Gamma = 90.1$ this first peak in S_{22} shifts slightly to the right, the above distances thus remaining more or less the same. There is however a shoulder at about $y = 8$ in S_{22} for $\Gamma = 22.5$, which disappears for the higher Γ . Without compressibility fitting it was found that the shoulder for the low Γ developed into an isolated peak which was still evident for the larger Γ . The isolated peak for the low Γ was responsible for oscillations of period ~ 0.7 which we observed in g_{22} . In the crystal structure this distance may be related to the distance between planes as shown in Figure (2.10). Thus, without compressibility fitting, it seems that substantial short-range ordering of the oxygen atoms is preserved on melting.

(c) In S_{11} , for $\Gamma = 22.5$, an oscillation of period ~ 8 is seen. Another oscillation of period ~ 6.2 , clearly in evidence without compressibility fitting, is barely discernible for $\Gamma = 22.5$. The period ~ 6.2 is seen to be the peak position in g_{11} at $2\pi/6.2 \sim 1$ and that with period ~ 8 must then correspond to the contact distance for g_{11} , that is $\tau/\sigma_2 = \sigma_1/\sigma_2 = 0.69$, where g_{11} is negative. Referring again to the crystal structure, the distance between the cube centres is 1 so that uranium atoms must now be taken to be occupying all cube centres but now with probability 0.5.

It is somewhat surprising however that no such distance ~ 0.7 occurs between uranium atoms in such a structure, the only other distance is twice this value, i.e. 1.4 between uranium atoms in diagonal cubes. However, we emphasize that this distance, while prominent without compressibility fitting, plays only a minor role with the correct compressibility built in.

It is relevant to note that in their calculation on NaCl Abramo et al (21) noticed also the appearance of a non-periodic isolated peak and shoulder in $S_{ij}(y)$ before and after fitting the experimental compressibility. It is thus tempting to conclude that the appearance of such an isolated peak in like partial structure is a characteristic of classical charged hard-sphere liquids. However, it is not obvious what kind of structure such peak/shoulder are reflecting for these systems. One plausible explanation might be to think of this low- y isolated peak as heralding substantial correlations extending well out into r space; this finds support in the fact that as soon as it disappears $g_{ij}(r)$ becomes smoother at large r .

2.7 Conclusions

In this chapter we have obtained the partial structure factors and the radial distribution functions in an ionic model of liquid UO_2 . The main conclusion that emerges from this ionic picture is that there is substantial short range ordering in the liquid extending well out into r -space. This situation persists even with considerably reduced ionicity (U^{2+} , O^-) that we have considered. In the uncharged hard sphere case, size effects are important in determining structure, which is now mainly due to O-O correlations.

In the absence of any experimental information on the structure of molten UO_2 , there can be few direct checks on the predicted partial structure factors from the model. However the agreement of our $S_{ij}(y)$'s with some of the features of crystalline UO_2 suggests that the present results should afford a useful starting point for subsequent refined work on the structure of molten UO_2 . Since a neutron diffraction experiment to obtain the partial structure factors of a high melting point substance like UO_2 is probably still a long way off, it would be of considerable interest if such an experiment could be carried out on a lower melting point ionic substance with similar ionic diameter ratio to that for UO_2 .

CHAPTER 3

STRUCTURAL DIFFERENCES BETWEEN IONIC AND MOLECULAR FLUID MODELS OF LIQUID UO_2

3.1 Introduction

In the preceding chapter we worked out the structure of liquid UO_2 in an ionic model based primarily on a mixture of U^{4+} and O^{2-} , though variations of the structure with degree of ionicity were also explored. The model was that of 'primitive model of electrolytes' and the MSA was used for its solution. This leaves uncertainties because the theory is valid for small and intermediate coupling constants, whereas in UO_2 , as we have seen, with a fully ionic model (U^{4+} , O^{2-}), this coupling constant is rather large.

It will therefore be of interest to compare and contrast the partial structure factors obtained by the above route with the opposite model which takes UO_2 as a molecular fluid. We want to emphasize that the weight of evidence is in favour of the ionic model of UO_2 (see Chapter 2). Although this evidence is for the solid, and since cases are known (e.g. AlCl_3 ⁽⁵⁸⁾) for which ionic materials in the solid state show negligible ionic conductivity in the liquid, this is by no means decisive. But the unresolved problem of the structure of molten UO_2 seems to be of sufficient practical importance to examine what common features, if any, might exist between two such different models as ionic and molecular.

The approximate theory we employ in the present chapter to solve the molecular model is the RISM theory for molecular fluids. It is noteworthy here that most of the previous applications of the RISM have been exclusively to classical molecular liquids (22,23,24). In contrast, for our case of UO_2 , as remarked above, the available evidence points towards an ionic model of the liquid. However, we recall here, the interesting case of CuCl (see Introduction), where in spite of firm

evidence for ionicity in the liquid state, a useful structural description seems still to be afforded by a molecular fluid picture within the framework of the RISM theory.

3.2 The Reference Interaction Site Model

In the RISM theory for molecular fluids proposed by Chandler and Andersen ⁽⁵⁹⁾ (see also Chandler ⁽⁶⁰⁾), each constituent molecule in the liquid has m interaction sites. These sites are usually taken to centre on the nuclei in the molecule, though this is not necessary. The position of the α th interaction site on the i th molecule is given by

$$\underline{r}_i^\alpha = \underline{R}_i + \underline{l}_i^\alpha \quad (3.1)$$

where $\underline{R}_i$ is the position of the centre of the i th molecule and $\underline{l}_i^\alpha$ the position of the α th site from the centre.

The molecules are assumed to be rigid. Thus the relative orientations of different $\underline{l}_i^\alpha$ vectors within the same molecule are constant.

The total potential energy of the system is a sum of the inter-molecular pair potentials

$$E = \frac{1}{2} \sum_{i,j}^N \phi(i,j) \quad (3.2)$$

where N is the total number of molecules in the liquid. The pair potential $\phi(i,j)$ between molecules i and j is a sum of site-site interactions

$$\phi(i,j) = \sum_{\alpha=1}^m \sum_{\beta=1}^m \varphi_{\alpha\beta}(|\underline{r}_i^\alpha - \underline{r}_j^\beta|) \quad (3.3)$$

where $\varphi_{\alpha\beta}(r)$ is a hard sphere potential

$$\varphi_{\alpha\beta}(r) = \begin{cases} \infty & \dots\dots r < \sigma_{\alpha\beta} \\ 0 & \dots\dots r > \sigma_{\alpha\beta} \end{cases} \quad (3.4)$$

The hard sphere diameters $\sigma_{\alpha\beta}$ are usually taken to satisfy the additivity condition

$$\sigma_{\alpha\beta} = \frac{1}{2} (\sigma_\alpha + \sigma_\beta)$$

Thus an RISM molecule may be pictured as a cluster of rigidly fused

hard spheres with overlapping diameters (see Figure (3.1)).

Two types of pair-correlation functions enter the theory. The first is the inter-molecular site-site pair-correlation (the site-site radial distribution) functions $g_{\alpha\beta}(r)$

$$g_{\alpha\beta}(r) = \frac{1}{\rho^2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \left\langle \delta(\underline{r}_i^\alpha) \delta(\underline{r}_j^\beta - \underline{r}) \right\rangle \quad (3.5)$$

Here $\langle \dots \rangle$ denotes an ensemble average. $\rho = \frac{N}{V}$ is the mean molecular number density, with V the volume of the system. It should be emphasized that $g_{\alpha\beta}(r)$ is the distribution function between sites α and β on different molecules. Thus physically $4\pi\rho g_{\alpha\beta}(r)r^2$ represents the probability distribution for finding the β th interaction site on one molecule at a distance r from a site α on another molecule located at the origin.

The other is the intra-molecular pair correlation function

$$\begin{aligned} \omega_{\alpha\beta}(\underline{r} - \underline{r}') &= \omega_{\alpha\beta}(|\underline{r}' - \underline{r}|) \\ &= \frac{1}{\rho} \sum_{i=1}^N \left\langle \delta(\underline{r} - \underline{r}_i^\alpha) \delta(\underline{r}' - \underline{r}_i^\beta) \right\rangle \end{aligned} \quad (3.6)$$

Defining now an inter-molecular site-site correlation function

$$h_{\alpha\beta}(r) = (g_{\alpha\beta}(r) - 1) \quad (3.7)$$

it is then important to the approach to introduce a site-site direct correlation function $c_{\alpha\beta}(r)$ through the Ornstein-Zernike like matrix equation

$$\tilde{h}(q) = \tilde{\omega}(q) \tilde{c}(q) \left[I - \rho \tilde{\omega}(q) \tilde{c}(q) \right]^{-1} \tilde{\omega}(q) \quad (3.8)$$

Here $\tilde{h}(q)$, $\tilde{\omega}(q)$, $\tilde{c}(q)$ are matrices with elements $\tilde{h}_{\alpha\beta}(q)$ etc.; I is the unit matrix. The 'tilde' denotes fourier-transform, viz.

$$\tilde{h}_{\alpha\beta}(q) = \int d\underline{r} e^{-i \underline{q} \cdot \underline{r}} h_{\alpha\beta}(r) \quad (3.9)$$

In particular we have,

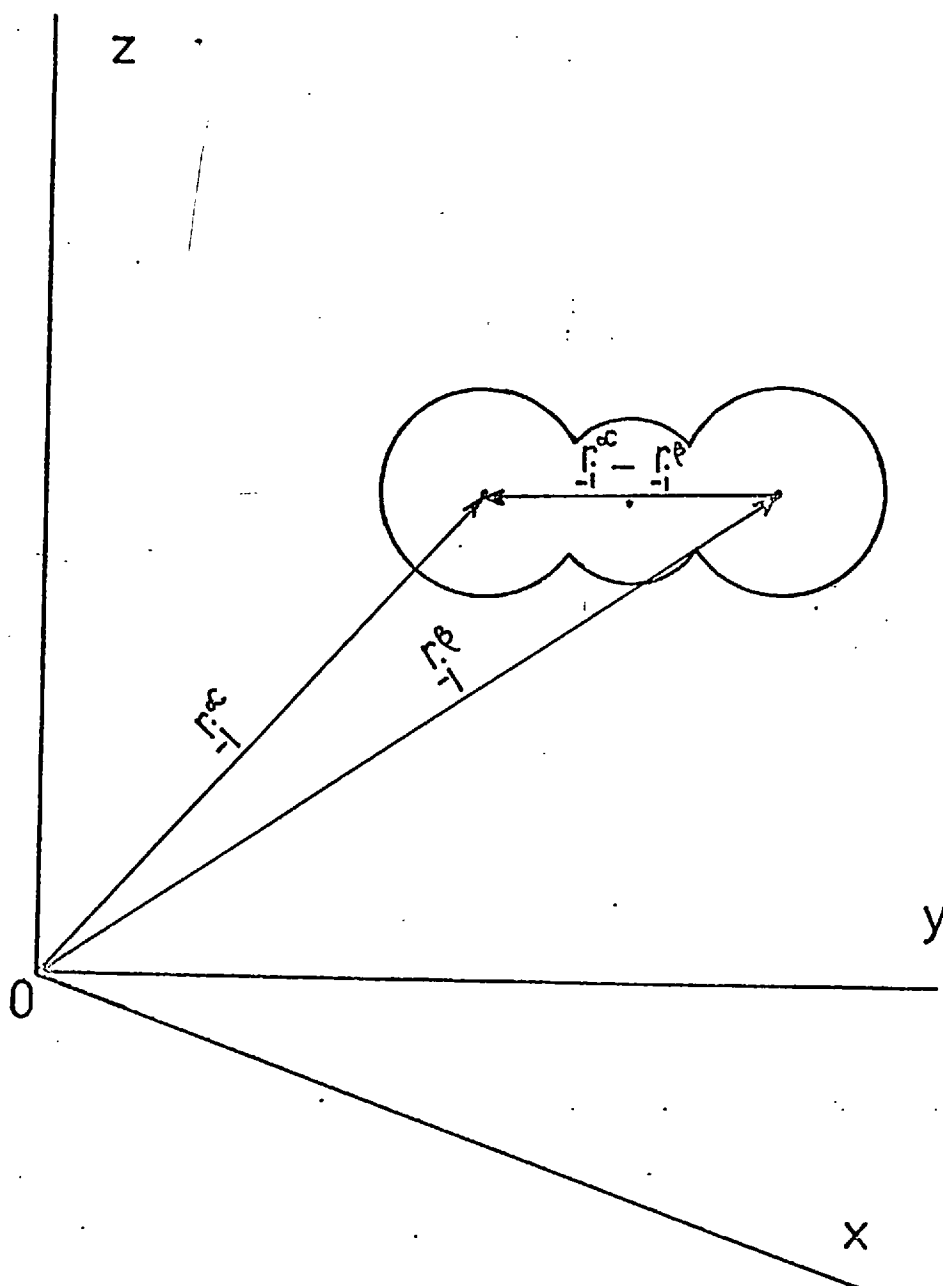


Figure 3.1

An RISM Molecule.

$$\begin{aligned}
\tilde{w}_{\alpha\beta}(q) &= \int d(\underline{r}' - \underline{r}) e^{-i\mathbf{q} \cdot (\underline{r}' - \underline{r})} \frac{1}{\rho} \sum_{i=1}^N \left\langle \delta(\underline{r} - \underline{r}_i^{\alpha}) \delta(\underline{r}' - \underline{r}_i^{\beta}) \right\rangle \\
&= \frac{1}{\rho} \sum_{i=1}^N \frac{1}{V} \left\langle \int d\underline{r} d\underline{r}' e^{-i\mathbf{q} \cdot (\underline{r}' - \underline{r})} \delta(\underline{r} - \underline{r}_i^{\alpha}) \delta(\underline{r}' - \underline{r}_i^{\beta}) \right\rangle \\
&= \frac{1}{\rho} \sum_{i=1}^N \frac{1}{V} \left\langle e^{i\mathbf{q} \cdot (\underline{r}_i^{\alpha} - \underline{r}_i^{\beta})} \right\rangle \\
&= \left\langle e^{i\mathbf{q} \cdot (\underline{r}_i^{\alpha} - \underline{r}_i^{\beta})} \right\rangle
\end{aligned} \tag{3.10}$$

where in writing the last equality we have used $\rho = \frac{N}{V}$.

Utilizing now the assumption of rigid molecules, the ensemble average can be easily performed. We denote the distance between the sites α and β on a molecule by $l_{\alpha\beta} = |\underline{r}_i^{\alpha} - \underline{r}_i^{\beta}|$

Thus

$$\begin{aligned}
\tilde{w}_{\alpha\beta}(q) &= \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta e^{iql_{\alpha\beta}\cos\theta} \\
&= \frac{1}{2} \int_{-1}^1 d(\cos\theta) e^{iql_{\alpha\beta}\cos\theta} \\
&= \frac{1}{2} \frac{1}{(iql_{\alpha\beta})} \left[e^{iql_{\alpha\beta}} - e^{-iql_{\alpha\beta}} \right] \\
&= \frac{\sin ql_{\alpha\beta}}{ql_{\alpha\beta}}
\end{aligned} \tag{3.11}$$

This is sometimes called the 'internal structure factor' ⁽⁶⁰⁾. Thus

in the $\tilde{w}(q)$ matrix, the elements on the principal diagonal are all unity while the off diagonal elements are the fourier transforms of the intra-molecular pair correlation functions. Also since $\tilde{w}_{\alpha\beta}(q) = \tilde{w}_{\beta\alpha}(q)$, $\tilde{w}(q)$ is a symmetric matrix.

Following the Percus-Yevick closure relations (cf. Equation (2.5)),

Chandler and Andersen add the following closure for Equation (3.8).

$$g_{\alpha\beta}(r) = 0 \quad \dots r < \sigma_{\alpha\beta} \quad (3.12a)$$

$$c_{\alpha\beta}(r) = 0 \quad \dots r > \sigma_{\alpha\beta} \quad (3.12b)$$

Equation (3.8) together with (3.12) form the RISM theory. Equation (3.12a) is an exact condition for hard-sphere interaction, approximations are contained in (3.12b).

Thus the problem the RISM presents is the solution of the coupled non-linear integral Equations (3.8) and (3.12) for $c_{\alpha\beta}(r)$ inside the hard core, and for $g_{\alpha\beta}(r)$ outside it.

The following limiting cases of RISM may be noted :

(a) when all the interaction sites on a molecule lie on one point, the RISM reduces exactly to the PY theory for a single component hard sphere fluid;

(b) in order to account for the presence of attractive forces in a real molecular liquid perturbation techniques are employed (59). The site-site pair potential is written

$$\phi_{\alpha\beta}(r) = u_{\alpha\beta}^0(r) + u_{\alpha\beta}(r) \quad (3.13)$$

where $u_{\alpha\beta}^0(r)$ is the interaction (hard sphere potential) in the reference system, i.e. the RISM, and $u_{\alpha\beta}(r)$ represents the perturbations.

The integral equation for $g_{\alpha\beta}(r)$ is shown to be

$$\begin{aligned} & (g_{\alpha\beta}(r) - 1) \\ &= h_{\alpha\beta}(r) \\ &= \frac{1}{(2\pi)^3} \int d\mathbf{q} e^{i\mathbf{q} \cdot \mathbf{r}} \left\{ \tilde{w}(\mathbf{q}) \tilde{c}(\mathbf{q}) \left[I - \rho \tilde{w}(\mathbf{q}) \tilde{c}(\mathbf{q}) \right]^{-1} \tilde{w}(\mathbf{q}) \right\}_{\alpha\beta} \end{aligned} \quad (3.14)$$

with the closure

$$g_{\alpha\beta}(r) = 0 \quad \dots r < \sigma_{\alpha\beta} \quad (3.15a)$$

$$c_{\alpha\beta}(r) = -\frac{1}{k_B T} u_{\alpha\beta}(r) \quad \dots r > \sigma_{\alpha\beta} \quad (3.15b)$$

Thus again when the sites within a molecule are concentric, this Interaction Site Model (ISM) reduces to the MSA of charged hard spheres of equal diameters.

3.2.1 Partial structure factors

The liquid partial structure factors are defined by

$$S_{\alpha\beta}(q) = \frac{1}{N} \sum_{i,j}^N \left\langle e^{i \underline{q} \cdot (\underline{r}_i^\alpha - \underline{r}_j^\beta)} \right\rangle \quad (3.16)$$

If the sites $\underline{r}_i^\alpha$ and $\underline{r}_j^\beta$ coincide with the nuclei, these are precisely the quantities determined by neutron-scattering experiments (8).

We can formally perform the average in Equation (3.16);

$$S_{\alpha\beta}(q) = \frac{1}{N} \sum_i^N \left\langle e^{i \underline{q} \cdot (\underline{r}_i^\alpha - \underline{r}_i^\beta)} \right\rangle + \frac{1}{N} \sum_{i \neq j}^N \left\langle e^{i \underline{q} \cdot (\underline{r}_i^\alpha - \underline{r}_j^\beta)} \right\rangle \quad (3.17)$$

Now writing $g_{\alpha\beta}(r)$ in the form

$$g_{\alpha\beta}(|\underline{r}-\underline{r}'|) = \frac{1}{\rho^2} \sum_i^N \sum_{\substack{j \\ (i \neq j)}}^N \left\langle \delta(\underline{r} - \underline{r}_i^\alpha) \delta(\underline{r}' - \underline{r}_j^\beta) \right\rangle \quad (3.18)$$

and taking its fourier-transform, also using Equations (3.10) and (3.11), we can express (3.17) as

$$S_{\alpha\beta}(q) = \tilde{w}_{\alpha\beta}(q) + \rho \tilde{h}_{\alpha\beta}(q) \quad (3.19)$$

$\tilde{w}(q)$ and $\tilde{h}(q)$ being given by Equations (3.11) and (3.8).

3.3 Method of numerical solution

For physical parameters appropriate to the two cases discussed below, the RISM Equations (3.8) and (3.12) were solved by use of the computer programs (61) and an independent verification of the solutions

was carried out using programs ⁽⁶²⁾ which treated the problem as one in non-linear optimization theory. Details of the latter method are given in Appendix 3.1. The radial distribution functions $g_{\alpha\beta}(r)$ were obtained by the fourier inversion of Equation (3.8).

3.3.1 Model of UO_2 molecule and the physical parameters used

We are not aware of direct experimental data on the geometry and bond-lengths of the UO_2 'molecule' in the liquid state. We therefore assume at the outset that based on the crystalline structure ^(54b), each uranium atom associated with its two nearest neighbour oxygen atoms forms a linear UO_2 molecule, the identity of which is preserved in the liquid. Consequently the "bond-length" used in the calculation is just the crystalline U-O distance. Two sets of calculations were carried out :

- (I) with the Pauling diameters for uranium and oxygen,
- (II) with the hard sphere diameters that reproduced the experimentally observed compressibility ^(34,36) in the ionic model of the preceding chapter. This was done mainly to examine the influence of relative sizes of the hard-spheres on the structure in the RISM. The parameters employed in (I) and (II) are collected in Table 3.1.

TABLE 3.1

Parameters used in the two cases studied

	I	II
U-O bond length	2.37 Å	2.37 Å
σ_{U}	1.94 Å	1.63 Å
σ_{O}	2.8 Å	2.36 Å
ρ	0.0195 Å ⁻³	0.0194 Å ⁻³

3.4 Results

The partial structure factors $S_{\alpha\beta}(q)$ and the pair correlation functions $g_{\alpha\beta}(r)$ are shown in Figures (3.2) and (3.3). Figures (3.2) corresponds to case I and (3.3) to case II. The variable q has been expressed in terms of the dimensionless quantity $y = q\sigma_0$, while in r -space we have measured distances in units of σ_0 .

The most striking feature in the $S_{\alpha\beta}(y)$'s is the presence of troughs on the long wave length side of the first peak in S_{UU} and S_{OO} . These troughs occur in both sets of calculations. It should be noted that in his work on CuCl, Gillan ⁽³¹⁾ also observed such a trough in S_{CuCu} .

In general, the $S_{\alpha\beta}(y)$ would imply that the structure in liquid UO_2 , in this molecular picture, is primarily determined by the O-O correlations. Apart from the presence of the trough referred to above, S_{UU} is almost featureless. In S_{OU} , the depth of the first minimum is small and the width of the trough large. This, in turn, would imply a weak O-U correlation. These points of view are supported by the behaviour of the site-site distribution functions. The oscillations are maximum for g_{OO} while these die away rapidly in g_{UU} . The contact values of $g_{\alpha\beta}(r)$ are again maximum for g_{OO} and minimum for g_{UU} . In all the $g_{\alpha\beta}(r)$'s 'cusps' i.e. discontinuities in slopes are observed; these appear to be a general feature in the RISM theory due to the hard-core interactions among the molecules ⁽²³⁾.

The differences in the structure factors and the distribution functions between the two sets of calculations are considerable. In set II the oscillations in $S_{\alpha\beta}(y)$ are heavily damped; the troughs in S_{OO} and S_{UU} are broadened out. Correspondingly in the $g_{\alpha\beta}(r)$'s also, the oscillations are more damped and the contact values lower than those in set I. Positions of the peaks and the phases of oscillations in $S_{\alpha\beta}(y)$ for the two cases are again different. In

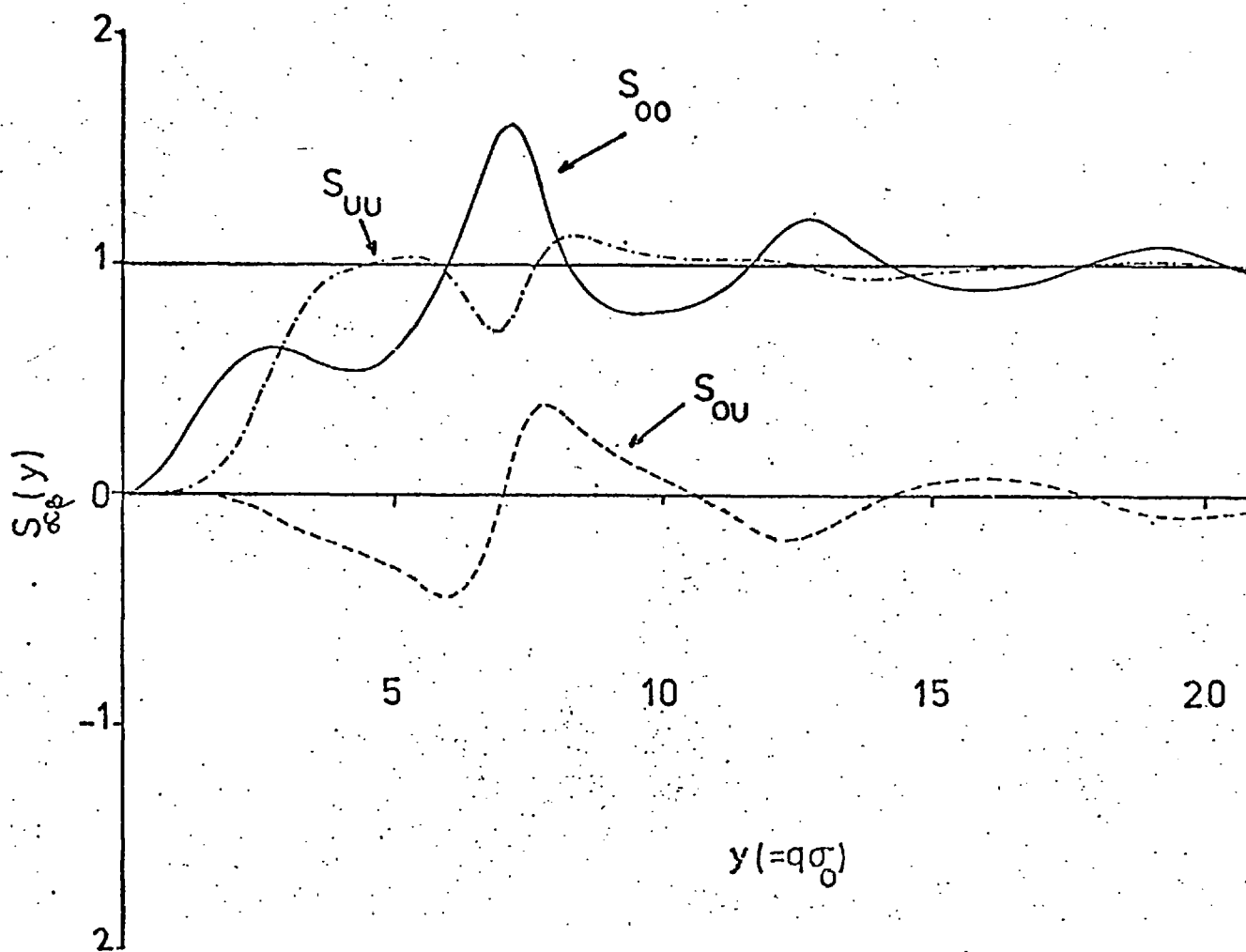


Figure 3.2a

Partial structure factors using Pauling diameters (model (I)). The variable plotted is $y = q\sigma_0$, with $\sigma_0 = 2.8\text{\AA}$.

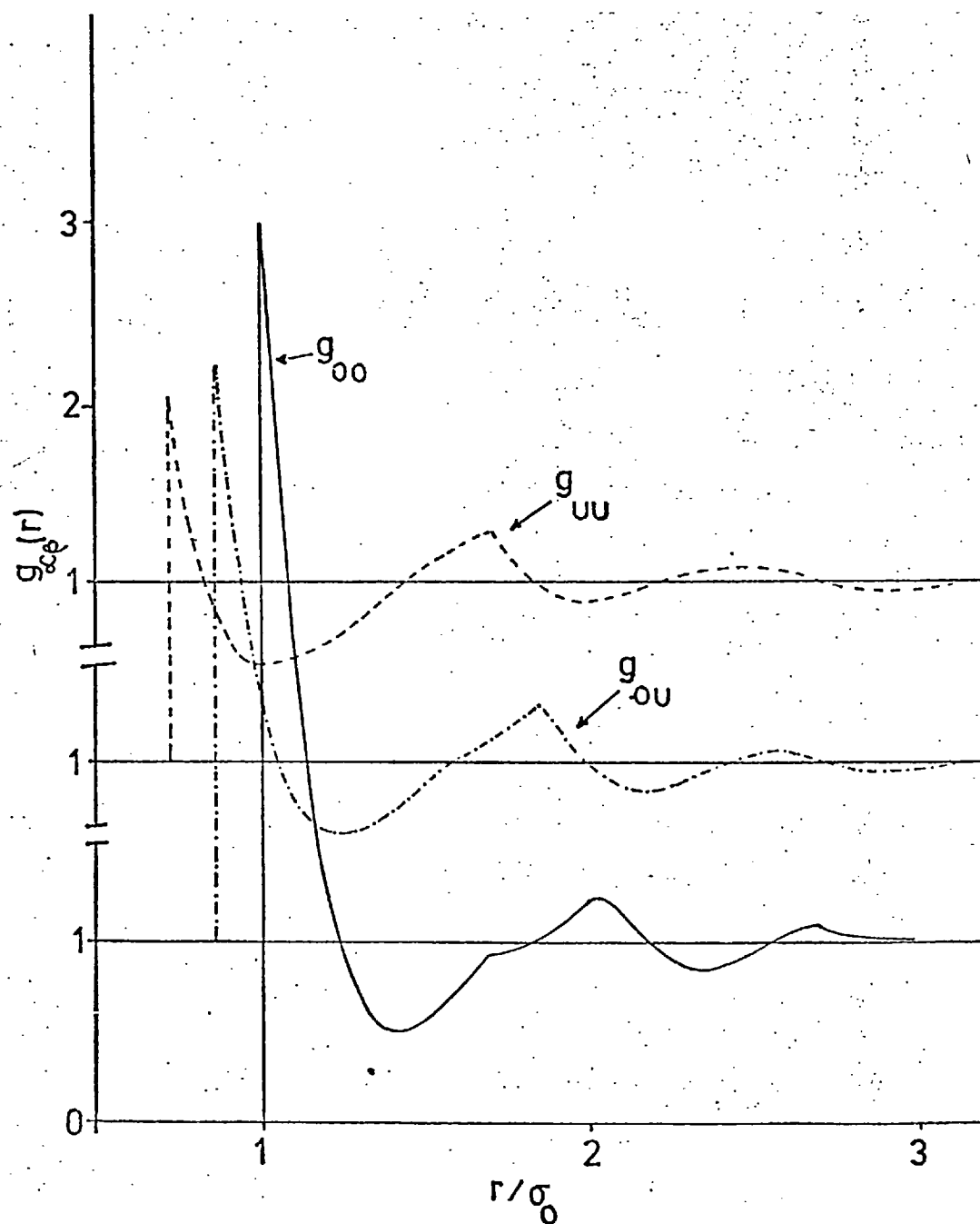


Figure 3.2b

Radial distribution functions for model (I).
The unit of length is $\sigma_0 = 2.8\text{\AA}$.

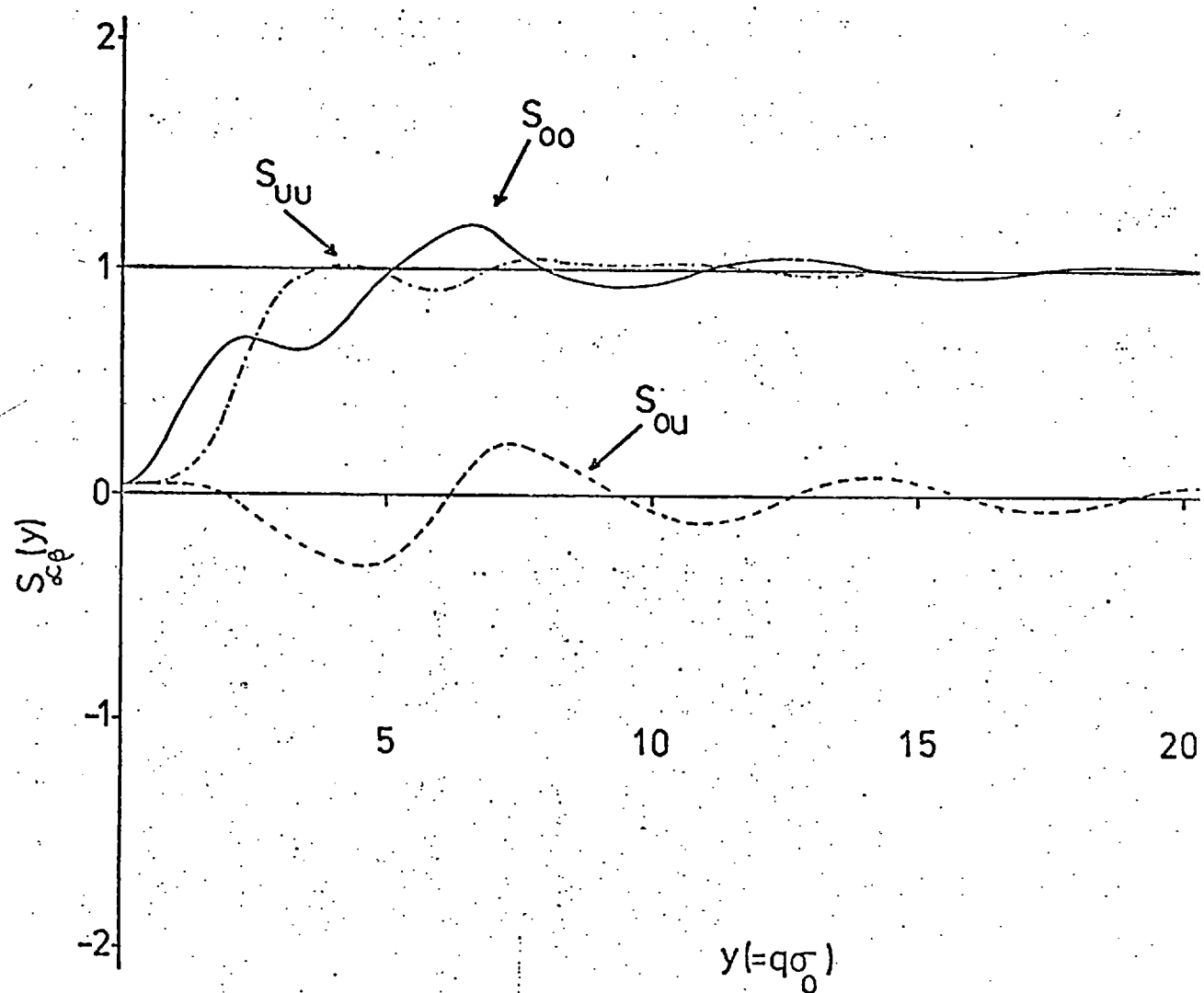


Figure 3.3a

Partial structure factors for model (II).
 The variable plotted is $y = q\sigma_0$,
 $\sigma_0 = 2.36\text{\AA}$.

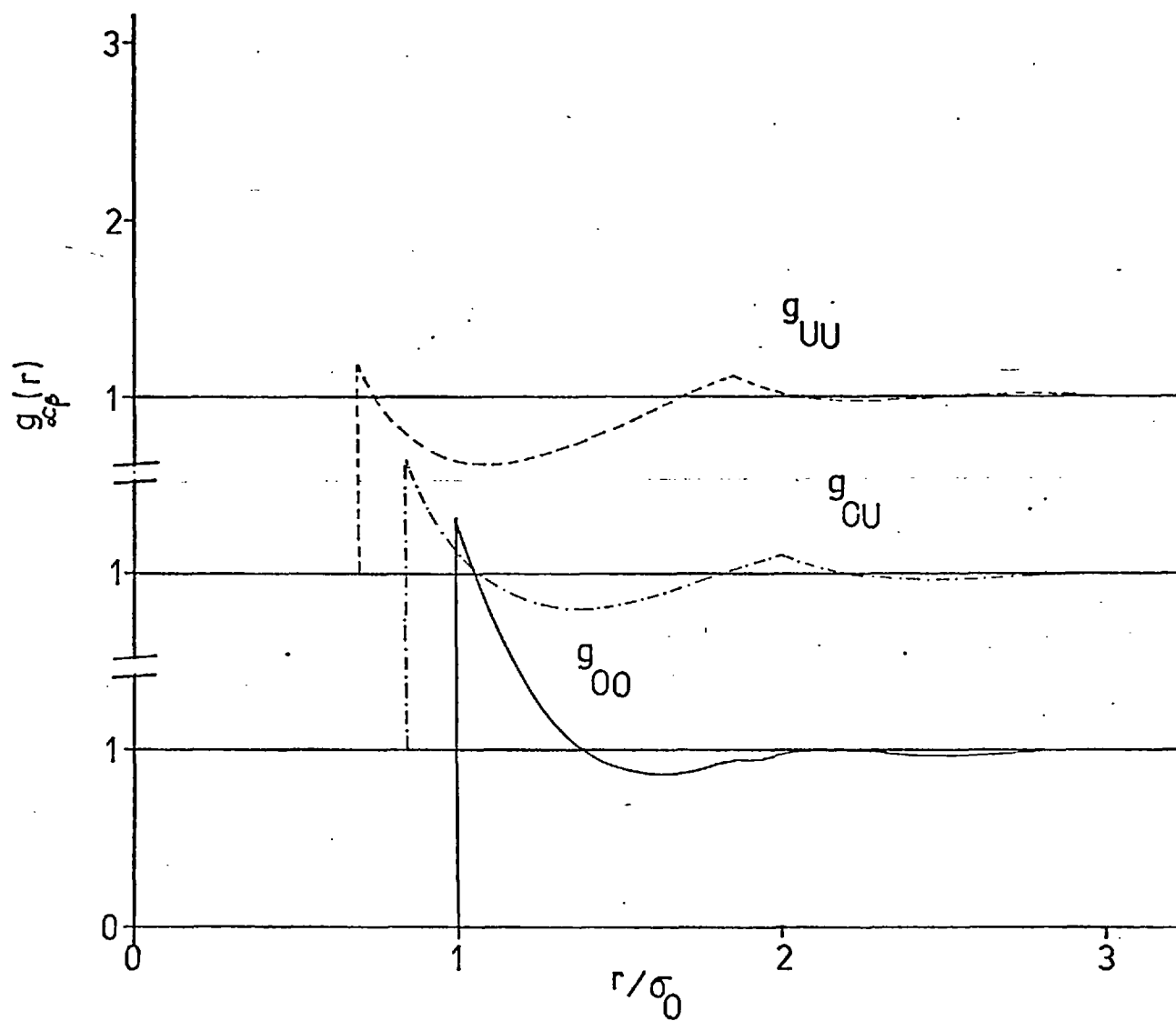


Figure 3.3b

Radial distribution functions for model (II).
The unit of length is $\sigma_0 = 2.36\text{\AA}$.

S_{00} for case I, the first peak occurs at $y \sim 7.5$, and the first minimum at $y \sim 10$ while for case II, these positions are $y \sim 7$ and $y \sim 9$ respectively. Height of the peak and the depth of the minimum are also lower in the second case. In S_{UU} the trough occurs at $y \sim 7.3$ in set I while in set II its position is $y \sim 6$. In the latter case the depth of the trough is smaller and the oscillations are barely discernible beyond $y \gtrsim 10$. Finally, in S_{OU} , the position of the first minimum shifts from $y \sim 6$ in case I to $y \sim 4.9$ in II. The principal maximum similarly shifts to the long wave-length side as we go from case I to II.

3.5 Comparison of partial structure factors of liquid UO_2 in ionic and molecular fluid models

We shall now compare the partial structure factors of molten UO_2 obtained in this chapter in a molecular fluid model with those obtained from the ionic model in Chapter 2.

A noticeable difference overall is in the sharpness of the oscillations of the structure factors. While in the MSA applied to the ionic model, these oscillations are fairly sharp even with the compressibility fitting, in the RISM these are rather damped implying weak correlations.

Comparing the partial structure factors in more detail with those corresponding to the partially ionic case (with fitting to the experimental compressibility) in Chapter 2 (cf. Figure (2.4a), the following features are observed :

- (1) the troughs observed on the long wave-length side of the first peak in S_{UU} and S_{00} in the RISM are absent in the MSA to the ionic model,
- (2) the amplitudes and phases of the structure factors are different; the height of the first peak in S_{00} is nearly the same, but the S_{UU}

peak is lower in the molecular fluid picture than in the MSA to the ionic model.

- 3) the shoulder observed in the S_{00} in the MSA is absent in the RISM, and in the MSA for large y the oscillations are less pronounced;
- 4) apart from the trough at $y \sim 7$, S_{UU} is relatively structureless in the RISM;
- 5) in the cross-correlation function S_{OU} , although the positions of the first minimum and maximum are the same in both the models, their widths are not and in general the results differ beyond $y \gtrsim 10$ both in phase and amplitude;
- 6) the depth of the first minimum in S_{OU} is smaller in the RISM than in the MSA and the width of the trough is large;
- 7) the long wave-length limits of the structure factors satisfy the charge neutrality condition, Equation (1.52), while in the RISM these are all equal. This follows from Equation (3.19), since for $q = 0$, all $\tilde{h}_{\alpha\beta}(q)$ and $\tilde{w}_{\alpha\beta}(q)$ are equal.

The points (4) and (6) clearly imply that the correlations for U-U and U-O in the MSA to the ionic model extending well into r -space are much weaker in the molecular picture. As we mentioned earlier in Section 3.4, the partial structure factors in this picture themselves suggest weak U-U and O-U correlations. We might say that the O-atoms are effectively shielding the U-atoms in the RISM. This is consistent with the observation that the oscillations in the pair-correlation functions are much more damped in the RISM than in the MSA to the ionic model.

Another feature which supports the above discussion is the similarity between the molecular fluid picture and the neutral hard sphere results for liquid UO_2 . Thus, in both the structure factors and the radial distribution functions the peak positions and the phases are the same although in RISM the oscillations in $g_{\alpha\beta}(r)$ are somewhat

more damped; the contact values of $g_{\alpha\beta}(r)$ are also lowered.

However, a major difference occurs between the molecular fluid results and the neutral hard sphere case in the long wave-length limits of the structure factors. Thus for neutral hard spheres $S_{UU}(0)$ is ~ 1 while $S_{OU}(0) < 0$, only $S_{OO}(0)$ being very small and positive. But in the RISM the $S_{\alpha\beta}(0)$ are all equal, positive and tend to values $\sim 10^{-2}$.

3.6 Conclusions

An immediate conclusion from the present chapter is that the considerable short-range order given by the MSA to the ionic model of molten UO_2 is no longer present in a molecular fluid picture. Indeed one very characteristic feature of an ionic model is the charge neutrality condition, which relates the phases in the oscillations of the three partial structure factors.

In contrast, the shielding of the U-atom by the O-atoms is done in the RISM, it would seem, too effectively. Similarities between the molecular fluid results for $S_{\alpha\beta}(y)$ and $g_{\alpha\beta}(r)$ with those from the neutral hard sphere theory support this point of view. The presence of troughs in $S_{\alpha\beta}(y)$ is not, as far as we can see, easily discussed in simple physical terms.

From the previous work on the RISM it has been shown that by varying the size of the atoms it is possible to bring theory and either experiment or computer simulation into agreement. The absence of such information for liquid UO_2 precludes such a procedure, with the consequence that, in all likelihood, the present structural calculations can at best be semi-quantitative.

It is important to re-emphasize that, while modelling the structure has been of interest in this chapter, we are well aware that the weight of evidence is in favour of an ionic picture of liquid UO_2 . A difficult point in any simulation of structure by a molecular fluid model must

therefore be that made above; i.e. the choice of sizes of the O and U atoms. There is considerable uncertainty on the 'best' way to make this choice on a priori grounds in a molecular fluid model; and yet comparison of calculations between cases I and II shows that the structure is very appreciably influenced by the choice of sizes.

Nevertheless, the results of the preceding chapter, in conjunction with those presented here, should be useful in interpreting structural properties of liquid UO_2 when eventually neutron diffraction data and/or computer simulation results become available.

CHAPTER 4

MOLECULAR FLUID MODEL OF MOLTEN HgCl_2

4.1 Introduction

In this chapter we continue our discussion of the effects of covalency on the structure of a classical binary liquid by looking at the structure of molten HgCl_2 (at slightly above its melting temperature) in a molecular fluid model.

In the preceding chapter we studied the structure of molten UO_2 assuming a molecular picture for the liquid. In view of the fact that no 'experimental' information is yet available on the structure of this liquid, it was of interest to compare and contrast the structural predictions from two different models - ionic and molecular.

Whereas in UO_2 the weight of evidence favours an ionic model, in HgCl_2 the electrical conductivity in the liquid near its melting point is a factor 10^{-4} - 10^{-5} times less than that of a molten alkali halide. For example, in their extensive measurements of electrical conductance of the molten halides of group IIA and IIB of the Periodic Table, Bockris et al. ⁽³⁸⁾ show HgCl_2 has a specific conductance κ , of $3.223 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 280.4°C . This conductance increases slightly as the temperature is increased. Grantham and Yosim ⁽³³⁾ have reported a value $3.42 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ for κ at 286°C . These authors have also shown that the conductivities in molten HgCl_2 and HgBr_2 exhibit a maxima in κ vs T curves. For HgCl_2 this occurs at 480°C . These maxima are attributed to increased covalency, i.e. increased ionic association with decreasing density at higher temperatures. The chief conclusion from these works is that molten mercuric halides are primarily covalent or molecular in character.

In the work of Darnell and McCollum ⁽⁶⁴⁾, it was found that the electrical conductivities of molten HgCl_2 and HgI_2 increase with pressure.

This is explained as being due to greater ionic dissociation at higher pressures. However, for ordinary pressures, the very low values of conductivity of molten HgCl_2 compared to those of the molten alkali halides suggest a structural description of the molten salt based on a molecular fluid model might be appropriate. As in the case of liquid UO_2 , in the present case too, for the solution of the model we use the RISM theory for molecular liquids.

The mathematical formalism of the RISM and the method of its numerical solution were given in Chapter 3 (see also Appendix 3.1). Therefore in the following section we shall only give the physical data used in the present calculations. The partial structure factors are presented and discussed in Section 4.3. In Section 4.4 we present a discussion of our study of the effects of ionicity versus covalency on the structure of classical binary liquids.

4.2 Physical parameters used in the calculations

For hard sphere diameters σ_{Hg} and σ_{Cl} we took values 2.2 Å and 3.62 Å respectively ⁽⁶⁵⁾; these are the Pauling diameters for these ions. The mean molecular number density ρ was taken as 0.00985 Å^{-3} ; this was calculated from the liquid density $d = 4.44 \text{ gm cm}^{-3}$ at 280°C ⁽⁶⁵⁾ using the formula

$$\rho = \frac{d}{(M/N_0)} \quad (4.1)$$

where M is the molecular weight in gms. and N_0 is Avogadro's number. For HgCl_2 , M is 271.5 gms. ⁽⁶⁵⁾. Electron diffraction experiments on gaseous HgCl_2 show it to be a linear molecule with mercury-chlorine bond length $\ell_{\text{Hg-Cl}} = 2.29 \text{ Å}$ ⁽⁶⁶⁾, and thus $\ell_{\text{Cl-Cl}} = 4.58 \text{ Å}$.

4.3 Partial structure factors

The partial structure factors $S_{\alpha\beta}(q)$ and the site-site radial distribution (pair correlation) functions $g_{\alpha\beta}(r)$ are shown in Figures (4.1a) and (4.1b) respectively. For the $S_{\alpha\beta}(q)$'s the actual variable

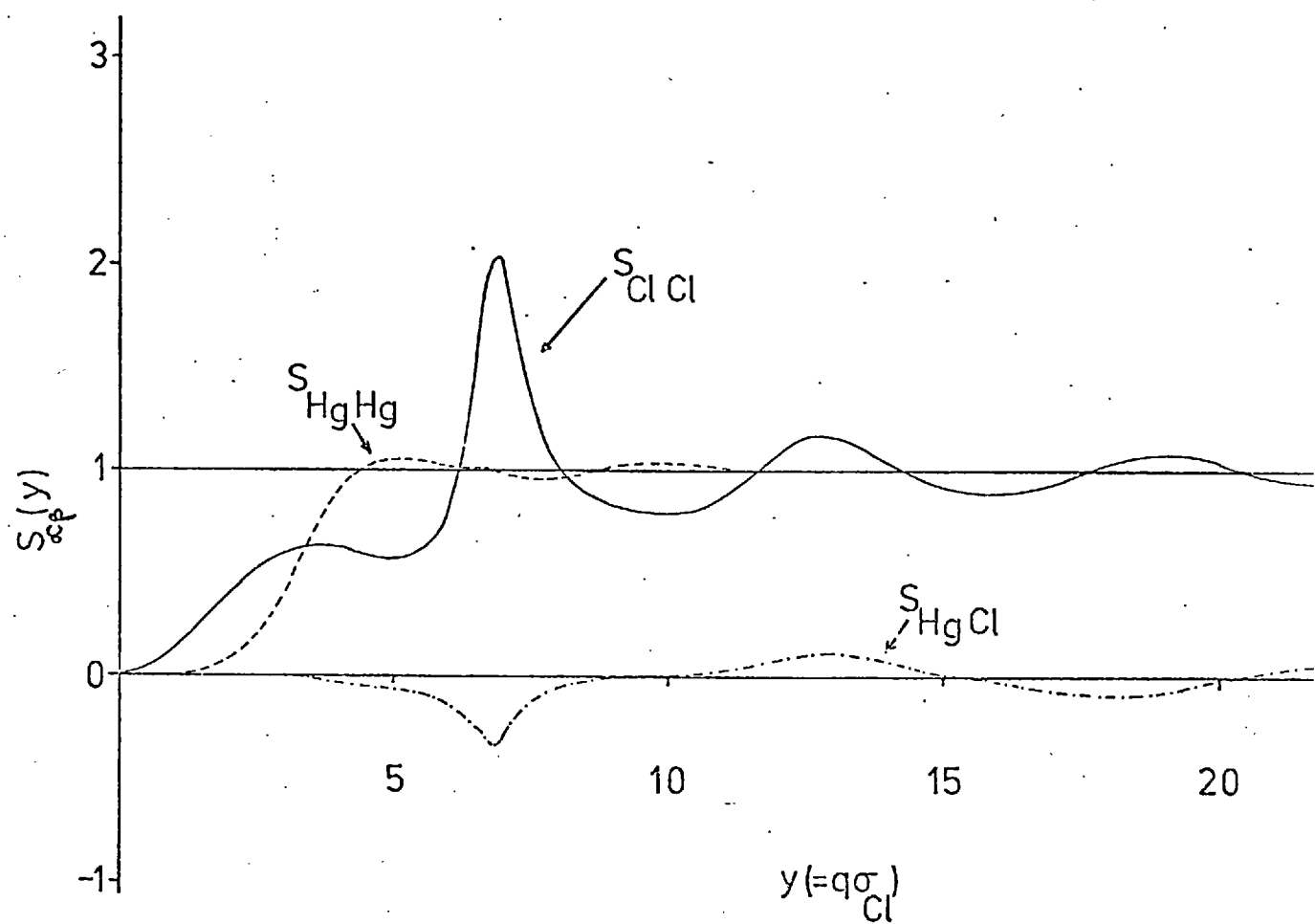


Figure 4.1a

Partial structure factors for liquid $HgCl_2$ at $280^\circ C$.
 The variable plotted is $y = q\sigma_{Cl}$, with $\sigma_{Cl} = 3.62\text{\AA}$.

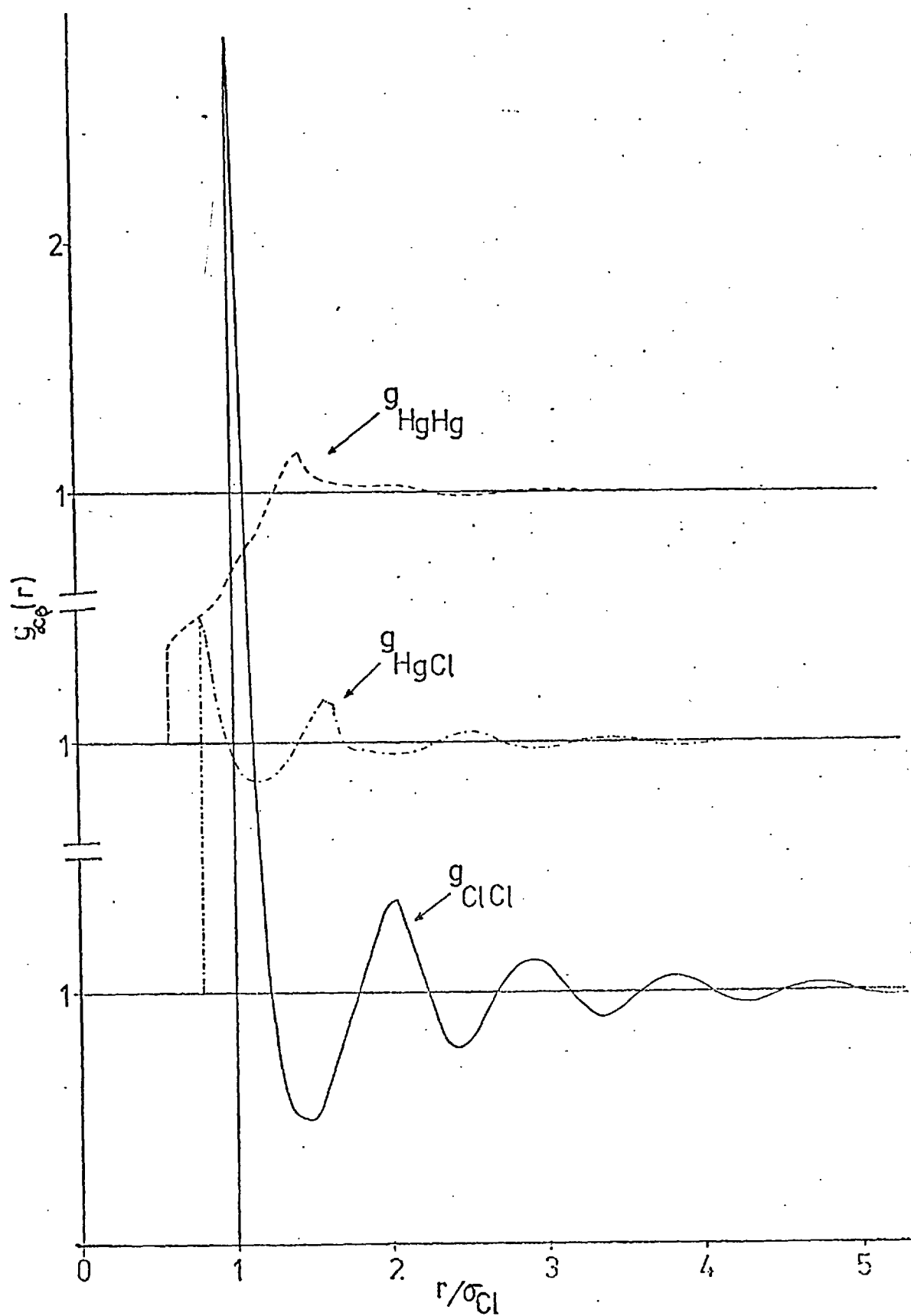


Figure 4.1b Radial distribution functions for liquid HgCl_2 at 280°C .
The unit of length is $\sigma_{\text{Cl}} = 3.62\text{\AA}$.

plotted is $y = q\sigma_{Cl}$ while in r -space lengths are expressed in units of σ_{Cl} .

The most important features we notice in the above curves are the following :

- (a) apart from the presence of a broad shoulder on the long wavelength side of the first peak at $y \sim 7$, the S_{Cl-Cl} resembles that for a simple liquid. In both $S_{\alpha\beta}(y)$ and $g_{\alpha\beta}(r)$, the oscillations in S_{Cl-Cl} and g_{Cl-Cl} are more pronounced than the other two correlations: in g_{Cl-Cl} in particular, oscillations extending well out into the r -space are observed;
- (b) in S_{Hg-Cl} , the depth of the first minimum is rather small and the width of the trough large; the oscillations in g_{Hg-Cl} are damped and beyond $r/\sigma_{Cl} \gtrsim 3.5$ these are barely recognizable;
- (c) S_{Hg-Hg} is almost structureless; also g_{Hg-Hg} is the most damped of the three g 's, going very rapidly to its asymptotic value of unity.

As before in the case of liquid UO_2 (Chapter 3), in the present case too, we notice 'cusps' in all the $g_{\alpha\beta}(r)$'s. The presence of the broad shoulder in S_{Cl-Cl} is, however, not immediately explicable physically.

It would seem from the above discussion that in a molecular fluid model, the structure in liquid $HgCl_2$ is dominated by correlations among chlorine atoms, the other correlations, viz. those among $Hg-Cl$ and $Hg-Hg$ being rather weak. A plausible explanation might be in this RISM theory the Hg -atom is very strongly shielded by the Cl -atom. It is worthwhile to recall here that in applying the RISM to liquid UO_2 we also observed relatively weak $U-U$ and $U-O$ correlations; in this case too, the UO_2 molecule was assumed linear and symmetric.

Appropriate choice of diameters for the constituent hard spheres in the molecule is a crucial feature of the RISM theory. As we saw earlier in the case of liquid UO_2 , this choice of sizes significantly

affects structure. Absence of such information for HgCl_2 is clearly a disadvantage in this connection. Our results must therefore be viewed in this light and at this stage can only be qualitative. Subsequently, when experimental results do become available it might be necessary to supplement this work by taking into account this variation of the sizes of Hg and Cl atoms.

4.4 Effects of ionicity versus covalency on the structure of classical binary liquids

One of the chief aims of the work described so far has been to examine the effects of ionicity versus covalency on the structure of classical two component liquids. Liquid UO_2 has an obvious interest for nuclear technology and therefore much of the work was concerned with this liquid.

The effects of ionicity on structure were examined in Chapter 2. There we obtained the partial structure factors and the corresponding radial distribution functions in an ionic model of liquid UO_2 . The principal conclusions that emerged from the various sets of $S_{ij}(q)$ were (a) the dominance of the structure by charge correlations and (b) the presence of considerable short range order in the liquid. The former was more clearly so in the case of $S_{ij}(q)$ where the experimental compressibility was not fitted. The high and very sharp first peak in the charge fluctuations $S_{QQ}(q)$ supported this. A further evidence which was indicative of substantial charge ordering was the way the principal peaks in like $g(r)$ lay corresponding to the troughs (minima) in unlike $g(r)$. Likewise in the $S_{ij}(q)$'s the phases of the oscillations were related by the overall charge neutrality condition. In particular the long wave length ($q \rightarrow 0$) limits of the three partial structure factors satisfied

$$\lim_{q \rightarrow 0} \left[Z_1 S_{11}(q) = (Z_1 Z_2)^{1/2} S_{12}(q) = Z_2 S_{22}(q) \right]$$

In light of the above, a basic ingredient in the structural description of an ionic liquid system must be the magnitudes of the ionic charges. In the case of liquid UO_2 , in the absence of information to the contrary, a fully ionic picture $\text{U}^{4+}, \text{O}^{2-}$ seemed to be the appropriate assumption. However, examination of the partially ionic case, $\text{U}^{2+}, \text{O}^-$, and the neutral hard sphere limit showed the effect of increased ionicity on charge correlations and consequently on the structure. An example of this was the sharpening up of the features of the $S_{ij}(q)$'s on going from the neutral model to the $\text{U}^{2+}, \text{O}^-$ case and then finally to the completely ionic model.

Comparison of the $S_{ij}(q)$'s in the ionic and the neutral hard sphere models brings out essentially two important points :

- (i) the size and concentration effects of the uncharged hard spheres on the structure, and
- (ii) the role of long range coulomb forces on the structure of a charged hard sphere fluid.

Regarding (i) we notice how the structure in the neutral hard sphere model of liquid UO_2 is mainly due to the O-O correlations. The structure factor for the U-U correlations is relatively featureless. As explained in Chapter 2, this is due to the larger size and concentration of the oxygen atoms. Ashcroft and Langreth ⁽⁴⁹⁾ have evaluated the structure factors in a binary hard sphere liquid mixture for various combinations of η , α and κ . Their results also lend support to the above conclusion.

Point (ii) is interesting in that it is well known ^(67,68,69) that in simple liquids the structure is primarily determined by the harshly varying repulsive forces. The effect of the more slowly varying long range attractive forces is small. But as can be seen in liquid UO_2 , on passing from an uncharged to a charged hard sphere system, by turning on the charges, the structure undergoes appreciable changes.

It thus appears in an ionic liquid model (with the ions being charged hard spheres) where the interactions are purely coulombic outside the ion cores, high charge ordering plays a significant role in determining structure. Considerable short range ordering of the various ion pairs extending well out into r -space is induced by charge correlations around the ions. Increasing the magnitude of the charges on the ions has the effect of increasing this charge correlations. Whereas for neutral hard spheres only the radius ratio and concentration come in, for the charged hard sphere case there is a competition between two effects on structure - this radius ratio of hard spheres and charge correlations; the latter dominates with increasing ionicity.

At this stage it is worthwhile to consider how our conclusions so far compare with the available literature on the structural description of charged fluids. In the $S_{ij}(q)$'s of molten KBr and NaCl obtained by Abramo et al ⁽⁷⁰⁾ from the Monte Carlo determinations of the $g_{ij}(r)$'s by Lewis et al ⁽¹⁶⁾, good short range ordering is reflected in the sharp first peaks. This is also borne out by the considerable oscillations in the $g_{ij}(r)$. The same is also true of liquid KCl obtained by similar Monte Carlo method by Woodcock and Singer ⁽⁹⁾. Of more interest are the $S_{QQ}(q)$'s (calculated by Abramo et al ⁽⁷⁰⁾) for molten KBr and NaCl. Here too, we notice rather sharp first peaks, again indicating substantial charge ordering. Neutron diffraction structure factors (and corresponding pair correlation functions) of molten NaCl obtained by Edwards et al ⁽¹⁷⁾ also show fairly good short range order. Similar studies of the structure of liquid CuCl by Page and Mike ⁽⁸⁾ are interesting. The measured $S_{ij}(q)$'s reveal good ordering for Cu-Cl and Cl-Cl but the correlation for Cu-Cu is weak. It is relevant to note here that the size of the copper ion is rather small compared to that of chlorine. MSA calculations by Gillan et al ⁽¹⁹⁾ for vanishing radius ratio bring out the salient features of

the above structure factors. The agreement is better in the later calculations of Abramo et al ⁽²⁰⁾ with the correct radius ratio of Cu and Cl ions.

It is important to emphasize here this discussion has been based on the results for the structure of an ionic model of liquid UO_2 within the framework of the MSA. A few comments on the relative merits and demerits of this approximation are therefore called for. From a physicist's point of view, perhaps the main attraction of the theory is that in spite of its simplicity it affords a general insight into the properties of electrolytes and molten salts. It is thus useful as a first approximation for the structural studies of such systems. When the interactions are purely hard sphere repulsions, the MSA is analytically tractable. This is true also with charges present but this time only when the sizes of the ions are equal. For arbitrary radius ratio of the ions we have to resort to numerical methods. Finally, as mentioned before, the MSA has the advantage that the partial structure factors are directly related to its solution. Thus comparison with any available 'experimental' partial structure factors is essentially a simple task.

Notwithstanding these merits of the MSA, some of its limitations are of significance. Perhaps the most obvious of these is the fact that the pair correlation functions for the like ions show negative values at contact, especially when the coupling constant is large. In equating the direct correlation function to its asymptotic value outside the hard core, a drastic approximation is introduced. Again, in real fluids the short-range repulsions are smoothly varying instead of the infinite step as in the theory. 'Softness' corrections to the hard core might be crucial in many cases. A comparison of the partial structure factors and the radial distribution functions in the work of Gillan et al ⁽¹⁹⁾ for the two coupling constants with those from the Monte-Carlo calculations shows that

- (i) the MSA is fairly good at low to intermediate coupling constants; the polymerization observed in the Monte-Carlo results is inexplicable in the approximation;
- (ii) in so far as thermodynamic quantities are concerned the MSA is only semi-quantitative.

In view of (i) and the fact that with a fully ionic model the coupling constant for liquid UO_2 was rather large, it might be revealing to do 'Monte-Carlo' simulations for this model. We also noticed, prior to fitting the experimental compressibility, the long wave length limits of the partial structure factors were underestimated. With such fitting, however, as Abramo et al observed in case of molten NaCl , agreement of the predicted structure factors with the corresponding 'experimental' results was remarkably good. The thermodynamic inaccuracies of the MSA have been well accounted for in the recently developed Generalized Mean Spherical Approximation (GMSA) ^(71,72,73). The latter theory has the advantage that thermodynamic consistency is automatically built into it.

Turning now to the effects of covalency on structure the most prominent feature in the structure factors of a molecular fluid model of liquid UO_2 (Chapter 3) was the damped oscillations. This led to the natural conclusion that the substantial short range ordering observed in the MSA to the ionic model was now absent. It would therefore seem that correlations among ions in a charged fluid are stronger than those among constituent atoms in a molecular liquid where the building blocks are neutral molecules. For UO_2 , however, as remarked earlier, the weight of evidence favours an ionic model for the liquid. As a result there might be some questions as to the relevance of the molecular fluid model for this case, at least in principle. It is worthwhile in this connection to refer again to Gillan's ⁽³¹⁾ work on the structure of liquid CuCl based on the RISM. There the partial structure factors agree fairly well with those measured experimentally by Page and Mika ⁽⁸⁾,

although in this case definite evidence for ionicity exists.

In the present chapter the structure factors of liquid HgCl_2 again indicate loose correlations for the Hg-Hg and Hg-Cl pairs. But now the very low values of the experimentally measured ionic conductivity indicate a molecular picture to be indeed appropriate. The physical explanation of the lack of structure in S_{UU} and $S_{\text{Hg-Hg}}$ is not difficult to find. Both HgCl_2 and UO_2 are linear molecules*, with the result the middle atoms Hg and U are considerably shielded by the two outer Cl and O atoms. Consequently, the structure factors for the Hg-Hg and O-O correlations are relatively featureless. Structure in these liquids is thus basically determined by the correlations between the outer atoms in the molecules.

The RISM stems from the idea, originally demonstrated in the work of Barker and Henderson (74,75), Verlet (76), Longuet-Higgins and Widom (77) etc., that structure of dense fluids is basically due to the repulsive forces. Since it is a repulsive hard sphere fluid theory, comparison between this and the uncharged hard sphere (PY theory) results for liquid UO_2 is interesting. Both show weak U-U correlations though S_{UU} in the RISM is more damped. Physically the difference between the two models is in the RISM, the neutral UO_2 molecules are the basic units whereas in the other these are neutral U and O atoms. As the sizes of both U and O and their respective concentrations were the same in both models, relatively weaker U-U correlations in the RISM look to be due to the shielding explained above. But if we have a charged hard sphere fluid with known ionicity, the important question seems to be how well the structure is predicted by the RISM. Unfortunately

* It ought to be mentioned though, in the absence of experimental information, we assumed UO_2 to be a linear molecule from the crystal structure (see Chapter 3).

in the absence of experimental information an answer for liquid UO_2 is currently not possible. Gillan's work for CuCl shows the answer to be "fairly well" for this case. But as he rightly comments it is difficult to reconcile the idea of undissociated CuCl molecules in the liquid state with the fact it has got such a high ionic conductivity. Without pressing this point any further, we feel, to answer this question in general there is clearly a need to do 'experiments' for structural information on classical binary liquid systems such as UO_2 .

The RISM is essentially an attempt to model realistic molecular liquids by choosing a reference fluid in which only rapidly varying short range repulsive forces act. Once the structure in this reference system is known, the slowly varying long range attractions may be treated as perturbations ⁽⁵⁹⁾. Surprisingly by incorporating even modest Coulomb effects for liquid CuCl , Gillan found the agreement of the structure factors with those of experiment worsened. This is puzzling. A priori knowledge of structure either through diffraction experiments and/or machine simulations, is, of course, very helpful in using the RISM, when available. Hard sphere diameters can then be varied until the best possible agreement with 'experiment' is obtained. When such information is lacking, predictions of the theory must contain a degree of uncertainty. The use of auxiliary interaction sites in the RISM molecules ⁽²⁴⁾ is another feature which is difficult to justify on physical grounds.

To sum up this discussion we note below the principal conclusions:

- (1) in classical binary charged liquids, charge correlations among the ions significantly influence structure,
- (2) when charges are switched off, the relative sizes and concentration of the species (i.e. the ions of (1) but now neutral) dominate the structure,
- (3) in a picture of covalent molecules forming the liquid, some of

the species in the molecule might get shielded owing to its particular geometry. In such situations the partial structure factors for those species show weak correlations.

CHAPTER 5

STRUCTURE OF CLASSICAL FLUID OF CHARGED HARD SPHERES AND POINT IONS IN THE PERTURBATION OF A SMALL, NON-RESPONSIVE UNIFORM BACKGROUND DENSITY

5.1 Introduction

For the Gillan et al ⁽¹⁹⁾ model of charged hard spheres and point ions, the most interesting conclusion drawn from the Monte-Carlo calculations was that at strong coupling the system polymerizes. The linear chains thus formed arising of course, from a purely classical description, leads one to enquire whether the model might have further utility in a different area of fluid structure, namely to simulate chemical bonds in a monatomic fluid.

There are then only very few fluids to which such a model would have relevance, one of which is liquid Te. Here Cabane and Friedel⁽³⁹⁾ describe the short range order at high temperature (900°C) by a structure where most atoms have 3 first neighbours, joined by strong bonds similar to the covalent bonds of the chains in solid Te. Such a network of covalent bonds coexists with delocalized electrons forming a metallic-like electron gas.

We have gone into the case of liquid Te, not because the model set out in the following section can hope to quantitatively simulate such a situation, but in order to motivate the study of the influence on structure of delocalizing some fraction of electrons initially in covalent bonds. The focus of this chapter is therefore on this point; it would be premature with such a crude model to attempt any detailed comparison with experiment.

Even this simple model studied here appears to be soluble exactly by machine calculations. Therefore we shall again employ the MSA. As

remarked previously the MSA becomes increasingly less accurate as the coupling strength increases. Thus, it may subsequently be necessary to supplement the present treatment by computer simulation.

5.2 The Model

The model we consider here consists of positively charged hard spheres, plus point classical electrons, but now all moving in a background of non-responsive negative neutralizing charge to simulate some 'delocalized' electrons. The overall electrical neutrality condition may be expressed as

$$\rho_1 e_1 + \rho_2 e_2 + \rho_3 e_3 = 0 \quad (5.1)$$

where ρ_1 is the number density of the point electrons, ρ_2 that of the charged hard spheres while ρ_3 is the background density; e_1, e_2, e_3 are the respective charges. In this case $|e_1| = |e_2| = |e_3| = e$, the electronic charge. The background, we emphasize again, is taken as not allowed to respond to ionic motions. Mathematically, this implies there is no correlation involving the background particles

$$g_{13}(r) = g_{23}(r) = g_{33}(r) = 1 \quad (5.2)$$

Following the same techniques as Waisman and Lebowitz ⁽¹¹⁾ and Palmer and Weeks ⁽⁷⁸⁾, the MSA Equations (2.4) for the above model were solved. Details are given in Appendix 5.1. The r-space forms of the direct correlation functions $c_{ij}(r)$ for $r < \sigma_{ij}$ are

$$-c_{11}(r) = \frac{\beta e_1^2}{\epsilon r} \quad \text{all } r \quad (5.3)$$

$$\begin{aligned} -c_{22}(r) &= \left[a_2 - \frac{2\beta V_2}{\rho_2} \right] + b_2(r/\sigma) + c'_2(r/\sigma)^2 \\ &\quad + d_2(r/\sigma)^3 + f_2(r/\sigma)^5 \quad \dots \quad r < \sigma \\ &= \frac{\beta e_2^2}{\epsilon r} \quad \dots \quad r > \sigma \end{aligned} \quad (5.4)$$

$$\begin{aligned}
-c_{21}(r) &= -c_{12}(r) \\
&= \left[a_1 + \frac{2\beta V_2}{\rho_1} \left(1 + \frac{\rho_3 e_3}{\rho_2 e_2} \right) \right] + c_2 (r/\sigma)^2 \quad \dots \quad r < \sigma/2 \\
&= \frac{\beta e_1 e_2}{\epsilon r} \quad \dots \quad r > \sigma/2
\end{aligned} \tag{5.5}$$

It is to be noted σ actually refers to the charged hard sphere diameter σ_2 . Since in this model this is the only hard sphere diameter, we have dropped the subscript 2.

In the above equations

$$v_2 = \frac{\rho_1}{2\beta(1 + \frac{\rho_3 e_3}{\rho_2 e_2})} \xi^{-1} \left[a_1(1 - \xi) - 1 + 3\xi \left(x - \frac{c_2}{2\sigma} \right) \right] \tag{5.6}$$

$$-c'_2 = c_2 = -4x\xi(1 - y) \tag{5.7}$$

$$\text{and } d_2 = \frac{\xi}{2} \left(a_2 + y a_1 + \frac{\rho_3}{\rho_2} \right) \tag{5.8}$$

The system parameters ξ , x and y are given by

$$\begin{aligned}
\xi &= \frac{\pi}{6} \rho_2 \sigma^3 && \text{(packing fraction)} \\
x &= \beta \frac{e_1 e_2}{\sigma} && \text{(dimensionless coupling parameter)} \\
y &= \rho_1 / \rho_2
\end{aligned} \tag{5.9}$$

In the limit $\rho_3 \rightarrow 0$, $y \rightarrow 1$ so that c_2, c'_2 vanish as also must f_2 in order to reduce to the form given by Gillan et al (19).

Thus putting $f_2 \propto \rho_3$ and taking the limit $\rho_3 \rightarrow 0$, the above $c_{ij}(r)$'s reduce exactly to those given by Gillan et al. The coefficients to be determined are now a_1, a_2, b_2 and f_2 . This is done in the following section.

5.2.1 Solution for the coefficients

We follow here the 'singularities method', see for example, (Gillan et al ⁽¹⁹⁾) by requiring that the coefficients of q^{-4} , q^{-6} , q^{-8} and q^{-10} in the large q -expansion of the structure factor $S_{22}(q)$ be zero. The method is summarized in Appendix 5.2. Before doing this it is necessary to evaluate the fourier transforms $\tilde{c}_{ij}(q)$'s of the functions $c_{ij}(r)$'s. This can be done by straightforward algebra using the defining Equations (2.17) and the $c_{ij}(r)$'s as given in the Equations (5.3) to (5.5). The $\tilde{c}_{ij}(q)$'s are given in Appendix 5.3. The partial structure factors are now obtained using the Pearson-Rushbrooke Equations (2.22).

The singularities method of solution gave four extremely complicated equations for the four unknowns. It is worthy of note that the q^{-10} equation (that is the equation obtained by equating the coefficients of q^{-10} terms to zero), though rather too long, is the simplest in that it is linear in f_2 . In the Gillan et al case, the q^{-8} equation is linear in b_2 . In principle then, these equations can be solved by first solving for f_2 , then substituting this value in q^{-8} equation (quadratic in b_2) to solve for b_2 and so on. But in practice it turned out beyond solving for f_2 , the equations became increasingly long, complex and involved to handle. In order to simplify these we carried out a process of linearization, to yield

$$\begin{aligned} a_1 &\simeq a_1^0 + \rho_3 A_1 (a_1^0, a_2^0, b_2^0) \\ a_2 &\simeq a_2^0 + \rho_3 A_2 (a_1^0, a_2^0, b_2^0) \\ b_2 &\simeq b_2^0 + \rho_3 B_2 (a_1^0, a_2^0, b_2^0) \\ f_2 &\simeq \rho_3 F_2 (a_1^0, a_2^0, b_2^0) \end{aligned} \tag{5.10}$$

where a_1^0 etc. are the corresponding constants in the model of Gillan

et al with no background charge. As f_2 is the new constant appearing in the present case of non-zero background it is calculated only to first order in ρ_3 . The quantities A_1 etc. involve a_1^0 etc. as indicated.

The linearization programme was extended to calculate the partial structure factors according to

$$S_{ij}(q) \simeq S_{ij}^0(q) + (\rho_3/\rho_2) \Delta S_{ij}(q) \quad (5.11)$$

and correspondingly the radial distribution functions according to

$$g_{ij}(r) \simeq g_{ij}^0(r) + (\rho_3/\rho_2) \Delta g_{ij}(r) \quad (5.12)$$

The quantities $\Delta S_{ij}(q)$ and $\Delta g_{ij}(r)$ involve the constants a_1^0 , a_2^0 , b_2^0 and the physical parameters.

According to the procedure outlined above, it is thus possible to evaluate $S_{ij}(q)$ and the $g_{ij}(r)$ by treating the background density only upto the first order. Since the linearization is about the Gillan et al limit our solution is intimately connected to this case. In fact to be able to apply our model, a knowledge of the solution of Gillan et al limiting case for the same system parameters is an essential pre-requisite.

It may be recalled the final step of the solution of the Gillan et al model involves the solution for the roots of a 10th order polynomial for the coefficient a_1^0 . We used numerical routines to do this. Knowing a_1^0 for a particular set, programs were then written to calculate $S_{ij}^0(q)$ and hence $S_{ij}(q)$ and their fourier transforms $g_{ij}^0(r)$ and $g_{ij}(r)$.

5.2.2 Data used in the calculations

For the dimensionless variables defined in Section 5.2 we used the values $\xi = 0.30$ and $\chi = -20.0$, and the ratios of background to the localized charge ρ_3/ρ_2 used was varied but kept small $\sim 10^{-3}$. $y = \rho_1/\rho_2$ was fixed by the value of ρ_3/ρ_2 .

5.3 Results

Results for the partial structure factors for $\rho_3/\rho_2 = 5.236 \times 10^{-3}$ are shown in Figure (5.1). It is to be noted the actual variable plotted in the wave-vector space is the dimensionless quantity $y' = q\sigma$ while in r-space it is r/σ . In order to see the changes in the structure factors due to the background, the $S_{ij}^0(q)$'s appropriate to the Gillan et al. model, i.e. $\rho_3/\rho_2 = 0$ are shown in Figure 5.2. In particular, Figure (5.3a) shows $S_{22}(q)$ for the Gillan et al. model and for the degree of delocalization as above. Corresponding results for $g_{22}(r)$ are shown in Figure (5.3b). The quantities $\Delta S_{22}(q)$ and $\Delta g_{22}(r)$ are shown in Figures (5.4a) and (5.4b).

Comparison of Figures (5.1) and (5.2) shows even for a small ratio of delocalized to localized electrons (1/200) the change in structure is very substantial. While such a pronounced effect may well be an artefact of MSA in part, it seems clear that such a delocalization has a quite definite effect on structure.

If we look at the model of Gillan et al as one that simulates a fluid where the point electrons are in the chemical bonds then the quantity of interest is the hard sphere structure factor $S_{22}(q)$. Our results (Figure (5.3a)) then reveal as some of these electrons are smeared into the background how this undergoes appreciable changes. With $\rho_3/\rho_2 \sim 1/200$, the height of the first peak increases from 1.5 to 1.7 and that of the second from 1.10 to 1.15. The contact values of $g_{22}(r)$ also change; these are given in Table 5.1.

TABLE 5.1

Contact values of $g_{22}(r)$ for different ratios of ρ_3/ρ_2

ρ_3/ρ_2	$g_{22}(\sigma)$
0.0	2.058
5.236×10^{-3}	2.954
8.727×10^{-3}	3.550

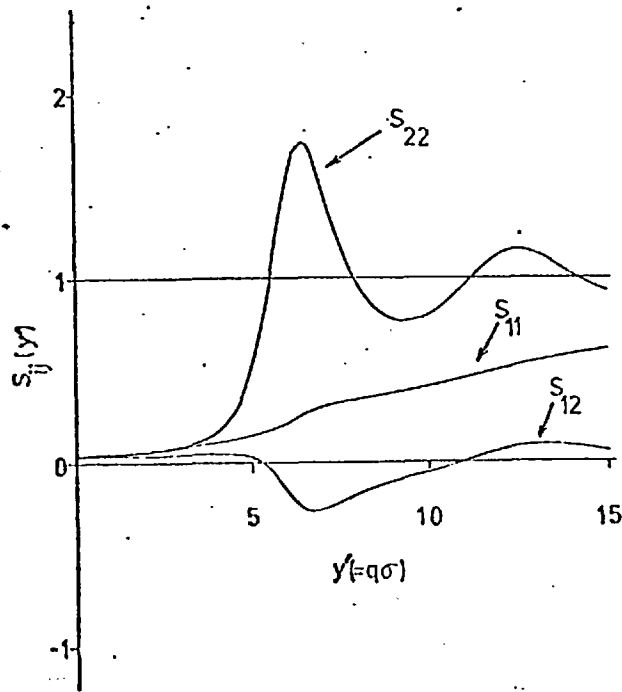


Figure 5.1

Partial structure factors $S_{ij}(q)$ for $\rho_3/\rho_2 = 5.236 \times 10^{-3}$. The variable plotted is $y' = q\sigma$, where σ is the charged hard sphere diameter. The packing fraction $\xi = 0.3$, while the coupling parameter $\chi = -20.0$.

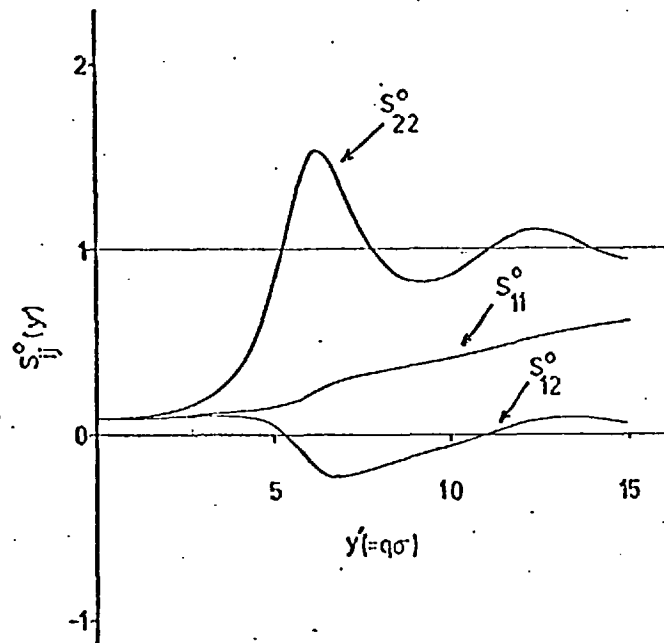


Figure 5.2

Partial structure factors $S_{ij}^0(q)$ for $\rho_3/\rho_2 = 0$ (limit of Gillan et al⁽¹⁹⁾). The variable plotted is $y' = q\sigma$, where σ is the charged hard sphere diameter. The packing fraction $\xi = 0.3$, while the coupling parameter $\chi = -20.0$.

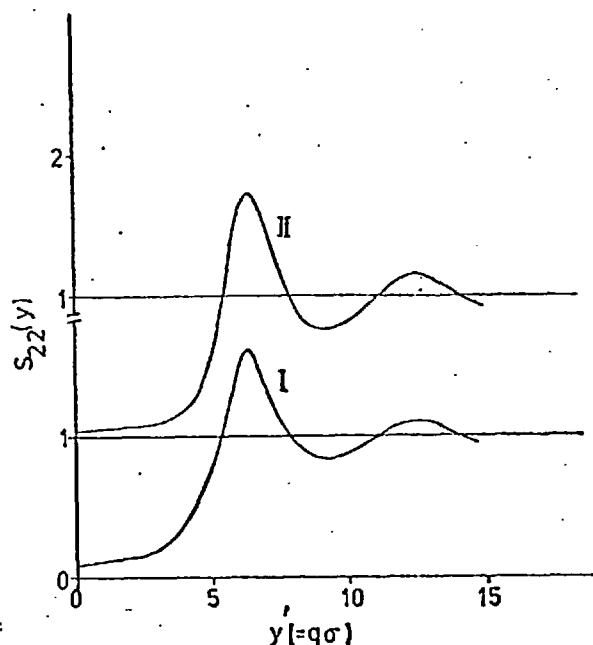


Figure 5.3a

Charged hard sphere structure factor $S_{22}(q)$.

Curve (i) $\rho_3/\rho_2 = 0$ (limit of Gillan et al (19)),

Curve (ii) with small delocalized background charge given by $\rho_3/\rho_2 = 5.236 \times 10^{-3}$. Note that the height

of the first peak is significantly enhanced by even this small background density. The actual variable plotted is $y' = q\sigma$, being the charged hard sphere diameter.

Also the packing fraction $\xi = 0.3$ and coupling parameter $\chi = -20.0$.

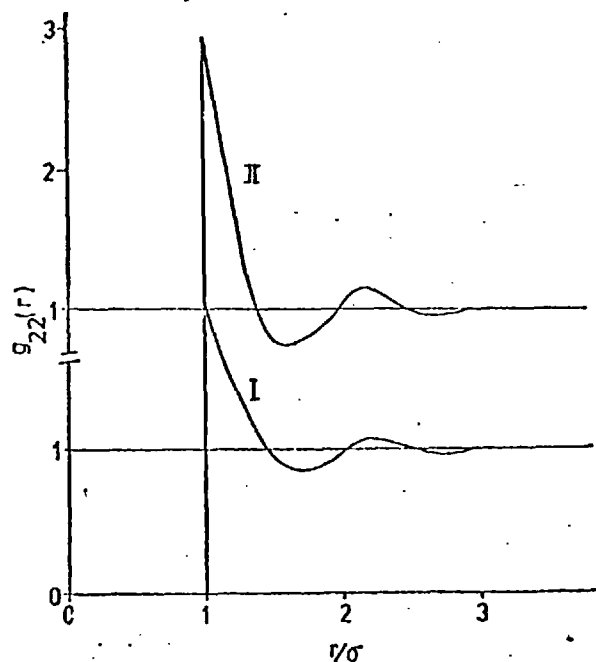


Figure 5.3b

Pair correlation function $g_{22}(r)$ corresponding to the structure factor $S_{22}(q)$ in Fig. 5.3a. Curve (I) :

$\rho_3/\rho_2 = 0$ (limit of Gillan et al (19)); Curve (II): $\rho_3/\rho_2 = 5.236 \times 10^{-3}$.

Note again the substantial increase in contact value $g_{22}(\sigma)$ due to the small degree of delocalization. The unit of length is σ (the charged hard sphere diameter).

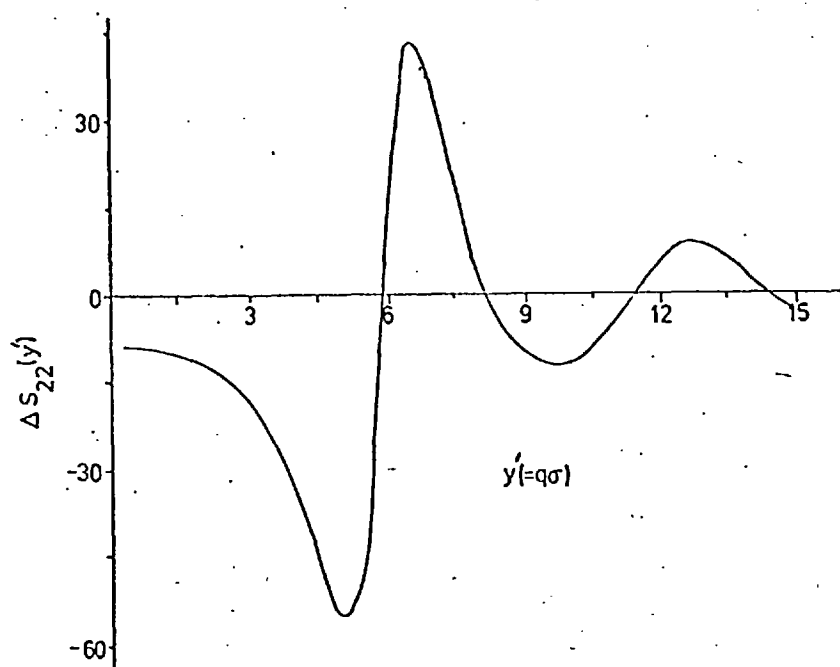


Figure 5.4a Change $\Delta S_{22}(q)$ in structure factor for charged hard sphere as defined in Equation (5.11).

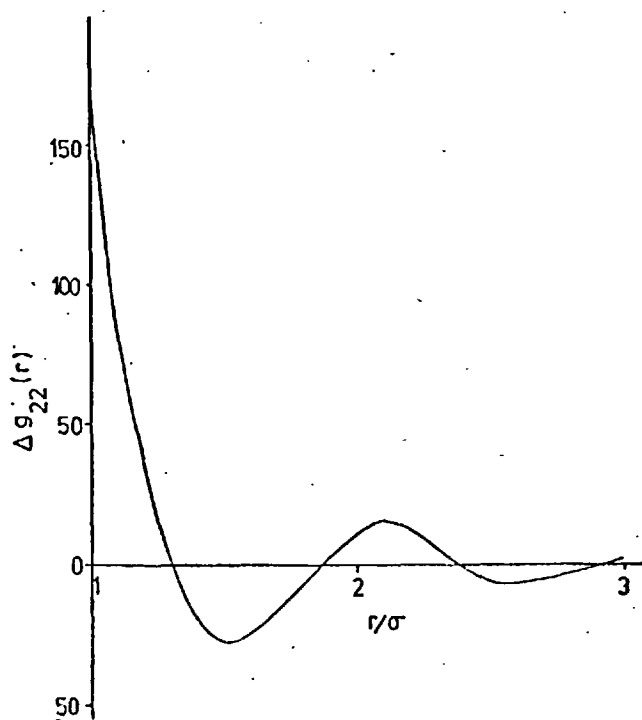


Figure 5.4b Change $\Delta g_{22}(r)$ in pair function for charged hard sphere as defined in Equation (5.12).

5.4 Conclusions

The main achievement of this chapter has been to observe the influence on structure of the ratio of delocalized to localized electrons in a classical fluid of charged hard spheres, point ions and a non-responsive, neutralizing uniform background.

Our principal conclusion is that the structure is very sensitive to the variation of delocalized to localized charge. In particular the changes $\Delta S_{22}(q)$ and $\Delta g_{22}(r)$ in the hard sphere structure factor and the pair-correlation functions from their values when the background density is zero are substantial. The magnitude of the change may be exaggerated in the MSA; it is certainly rather large for such a small ratio of background to localized electron density. Also it may be that the linearization is exaggerating the effect at the ratios discussed.

It is tempting to enquire whether such a behaviour is qualitatively relevant to liquid Te. When one examines the behaviour of the first peak in $g(r)$ with temperature, one finds that whereas, at first the height of the principal peak decreases with increasing temperature, this trend reverses as the temperature increases ⁽⁷⁹⁾. As there is a trend for the number of conduction electrons to increase with increasing temperature, it seems that this behaviour is consistent with the prediction from the present, admittedly grossly simplified, model.

One difficulty we faced in the course of calculations was the enormity of the 'singularities' equations. This forced us to resort to linearization. Unfortunately, results were possible only for a very small range of ρ_3/ρ_2 around the limit of Gillan et al. Monte-Carlo simulations are therefore proposed on this model for a wider range of ρ_3/ρ_2 . This would be of interest especially in view of the fact that solutions for the two limiting cases $\rho_3/\rho_2 = 0$ and 1 are known. The latter limit was solved by Palmer and Weeks ⁽⁷⁸⁾; in this case

for $\beta \rightarrow 0$ we have the Classical One Component Plasma (COCP). We consider briefly some of the implications of the COCP in the strong coupling regime in Appendix 5.3: the interest here being to transcend the MSA, which is not valid in the strong coupling regime (e.g. MSA does not predict crystallization in the COCP (80,81), nor polymerization in the Gillan et al model).

APPENDIX 2.1

Fourier Transforms of the direct correlation functions

We evaluate here the fourier transforms $\tilde{c}_{ij}(q)$ of the direct correlation functions $c_{ij}(r)$ as given by the solutions of the MSA and the PY theory in Chapter 2 (see Equations (2.7) and (2.9)). The Equations (2.17) define $\tilde{c}_{ij}(q)$.

The $c_{ij}(r)$'s occurring in the solution of the MSA (and the PY theory) are of the general form

$$\begin{aligned} c(r) &= A + B(r/\sigma) + C(r/\sigma)^2 + D(r/\sigma)^3 \quad \dots r < \sigma \\ &= \frac{E}{r} \quad \dots r > \sigma \end{aligned} \quad (\text{A2.1.1})$$

where $A, B, C, \dots$ etc are constants.

For $r < \sigma$, we substitute the above expression in Equation (2.17b); a typical integral that appears is

$$\text{Const.} \int_0^\sigma dr r^2 \frac{\sin qr}{qr} \left(\frac{r}{\sigma}\right)^m$$

where $m \geq 0$.

To evaluate this consider the integral

$$I_{n+1} = \frac{1}{q} \int_0^\sigma dr r \sin qr \left(\frac{r}{\sigma}\right)^n \quad \text{for } n \geq 1 \quad (\text{A2.1.2})$$

Integrating repeatedly by parts we get the recurrence relation

$$I_{n+1} = -\frac{\sigma \cos q\sigma}{q^2} + \frac{(n+1)}{q^3} \sin q\sigma - \frac{n(n+1)}{q^2 \sigma^2} I_{n-1} \quad (\text{A2.1.3})$$

$$\begin{aligned} \text{Also } I_1 &= \frac{1}{q} \int_0^\sigma dr r \sin qr \\ &= -\frac{\sigma \cos q\sigma}{q^2} + \frac{\sin q\sigma}{q^3} \end{aligned} \quad (\text{A2.1.4})$$

$$\begin{aligned} \text{And } I_0 &= \frac{\sigma}{q} \int_0^\sigma dr \sin qr \\ &= -\frac{\sigma}{q^2} [\cos q\sigma - 1] \end{aligned} \quad (\text{A2.1.5})$$

For $r > \sigma$, using (A2.1.1) in (2.17a) we get the well known fourier transform result

$$\tilde{c}(q) = \frac{\text{Const.}}{q^2} \cos q\sigma \quad (\text{A2.1.6})$$

Using now the results (A2.1.3) to (A2.1.6), the fourier transforms $\tilde{c}_{ij}(q)$'s of $c_{ij}(r)$'s are easily obtained.

(a) Charged hard spheres

$$\tilde{c}_{ii}(q) = \frac{4\pi\rho_i\sigma_i^3}{(q\sigma_i)^2} \left\{ A_i(q) \cos q\sigma_i - B_i(q) \frac{\sin q\sigma_i}{q\sigma_i} + \frac{C_i(q)}{(q\sigma_i)^2} \right\} \quad (\text{A2.1.7})$$

$$\begin{aligned} \tilde{c}_{12}(q) &= \tilde{c}_{21}(q)^{1/2} \\ &= \frac{4\pi(\rho_1\rho_2)^{1/2}}{(q\sigma_{12})^2} \left\{ A(q) \cos q\sigma_{12} - B(q) \frac{\sin q\sigma_{12}}{q\sigma_{12}} \right. \\ &\quad \left. + D(q) \frac{\sin q\lambda}{q\lambda} + E(q) \frac{\cos q\lambda}{(q\sigma_{12})^2} \right\} \end{aligned} \quad (\text{A2.1.8})$$

$$\begin{aligned} \text{where } A_i(q) &= \left(\alpha_i + \beta_i + c_i - \frac{\beta e_i^2}{\epsilon\sigma_i} \right) - \frac{(2\beta_i + 12c_i)}{(q\sigma_i)^2} \\ &\quad + \frac{24c_i}{(q\sigma_i)^4} \end{aligned}$$

$$B_i(q) = (\alpha_i + 2\beta_i + 4c_i) - \frac{24c_i}{(q\sigma_i)^2}$$

$$C_i(q) = 2\beta_i - \frac{24c_i}{(q\sigma_i)^2} \quad (\text{A2.1.9})$$

$$\text{with } \alpha_i = \left(a_i - \frac{2\beta V_{ii}}{\rho_i} \right), \quad \beta_i = \frac{M_{ii}\sigma_i}{2\pi\rho_i}$$

$$c_i = \frac{\pi\sigma_i^3}{12} (\rho_1 a_1 + \rho_2 a_2) \quad (\text{A2.1.10})$$

$$\text{Also } A(q) = \left\{ (a + b + c + d) - \frac{\beta e_1 e_2}{\epsilon \sigma_{12}} \right\} - \frac{1}{(q \sigma_{12})^2} (2b + 12c) + \frac{24c}{(q \sigma_{12})^4}$$

$$B(q) = (a + 2b + 4c) - \frac{24c}{(q \sigma_{12})^2}$$

$$D(q) = -\frac{24c\lambda}{\sigma_{12}(q \sigma_{12})^2}, \quad E(q) = 2b + 12c \left(\frac{\lambda}{\sigma_{12}} \right)^2 - \frac{24c}{(q \sigma_{12})^2}$$

(A2.1.11)

$$\text{and } \mathcal{L} = \left(a_1 + \frac{2\beta V_{22}}{\rho_1} \right) + \frac{\lambda}{\pi(\rho_1 \rho_2)^{1/2}} \left[-M_{21} + \frac{2}{3} \lambda^2 \pi^2 (\rho_1 \rho_2)^{1/2} (\rho_1 a_1 + \rho_2 a_2) \right]$$

$$b = \frac{\sigma_{12}}{2\pi(\rho_1 \rho_2)^{1/2}} \left[M_{21} - \pi^2 \lambda^2 (\rho_1 \rho_2)^{1/2} (\rho_1 a_1 + \rho_2 a_2) \right]$$

$$c = \frac{\pi \sigma_{12}^3}{12} (\rho_1 a_1 + \rho_2 a_2)$$

$$d = \frac{\lambda^2}{2\pi \sigma_{12} (\rho_1 \rho_2)^{1/2}} \left[M_{21} - \frac{\pi^2}{2} \lambda^2 (\rho_1 \rho_2)^{1/2} (\rho_1 a_1 + \rho_2 a_2) \right]$$

(A2.1.12)

(b) Uncharged hard spheres

$$\tilde{c}_{ii}(q) = \frac{4\pi \rho_i \sigma_i^3}{(q \sigma_i)^2} \left[A_i(q) \cos q \sigma_i - B_i(q) \frac{\sin q \sigma_i}{q \sigma_i} + \frac{C_i(q)}{(q \sigma_i)^2} \right]$$

(A2.1.13)

$$\begin{aligned} \tilde{c}_{12}(q) &= \tilde{c}_{21}(q) \\ &= \frac{4\pi(\rho_1 \rho_2)^{1/2} \sigma_1^3}{(q \sigma_1)^2} \left[\cos q \lambda \left\{ \frac{2b \sigma_1}{(q \sigma_1)^2} - \frac{24d \sigma_1^3}{(q \sigma_1)^4} \right\} \right. \\ &\quad - \frac{\sin q \lambda}{(q \sigma_1)} \left\{ \frac{24d \lambda \sigma_1^2}{(q \sigma_1)^2} \right\} + \cos q \sigma_{12} \left\{ a_1 \left(\frac{\sigma_{12}}{\sigma_1} \right) \right. \\ &\quad \left. \left. + b \sigma_1 - \frac{2b \sigma_1}{(q \sigma_1)^2} + 4d \lambda \sigma_1^2 - \frac{24d \lambda \sigma_1^2}{(q \sigma_1)^2} + d \sigma_1^3 \right\} \right] \end{aligned}$$

$$\begin{aligned}
 & - \frac{12d\sigma_i^3}{(q\sigma_i)^2} + \frac{24d\sigma_i^3}{(q\sigma_i)^4} \} - \frac{\sin q\sigma_{i2}}{(q\sigma_i)} \left\{ a_i + 2b_i\sigma_i \right. \\
 & \left. + 12d\lambda\sigma_i^2 - \frac{24d\lambda\sigma_i^2}{(q\sigma_i)^2} + 4d\sigma_i^3 - \frac{24d\sigma_i^3}{(q\sigma_i)^2} \right\} \quad (A2.1.14)
 \end{aligned}$$

where now

$$\begin{aligned}
 A_i(q) &= (a_i + b_i\sigma_i + d\sigma_i^3) - \frac{2b_i\sigma_i + 12d\sigma_i^3}{(q\sigma_i)^2} \\
 &\quad + \frac{24d\sigma_i^3}{(q\sigma_i)^4} \\
 B_i(q) &= (a_i + 2b_i\sigma_i + 4d\sigma_i^3) - \frac{24d\sigma_i^3}{(q\sigma_i)^2} \\
 C_i(q) &= 2b_i\sigma_i - \frac{24d\sigma_i^3}{(q\sigma_i)^2} \quad (A2.1.15)
 \end{aligned}$$

APPENDIX 2.2

Summary of the numerical procedure to solve for the Waisman-Lebowitz coefficients in the Mean Spherical Approximation solutions

The formal solutions of the MSA given by Waisman and Lebowitz ⁽¹¹⁾ involve seven unknown coefficients: a_1 , a_2 , M_{11} , M_{12} , M_{22} , V_{11} and V_{22} . (cf. Equations (2.7), Chapter 2). To obtain the complete solution one has to solve for these coefficients in terms of system parameters. To see how this could be done numerically ⁽⁴⁶⁾, note Waisman and Lebowitz show these unknowns are related by seven quadratic equations. Of these five are independent because of the symmetry of the problem, viz. $\sigma_1 \leftrightarrow \sigma_2$. The two other equations needed follow from the defining relation

$$a_j = 1 - 4\pi \sum_l \rho_l \int_0^{\sigma_{lj}} dr r^2 c_{lj}^{(0)}(r) \quad (A2.2.1)$$

$$\text{with } c_{ij}^{(0)}(r) \equiv \left[c_{ij}(r) + \beta \frac{e_i e_j}{\epsilon r} \right] \quad (A2.2.2)$$

being the reduced direct correlation function which vanishes for $r > \sigma_{ij}$. (A2.2.1) gives two linear equations in seven unknowns. We thus have to solve for a system of five quadratic and two linear equations.

The computer program used was a CERN library routine ⁽⁵⁷⁾. This calculates the solutions, i.e. the Waisman-Lebowitz coefficients, corresponding to a set of η , Γ and α starting from an input solution corresponding to a different set of these parameters, the constraint being that the two sets must lie close to each other. We performed the calculations by varying α ; starting from the equal diameter ($\alpha=1$) case (with η and Γ appropriate to the particular calculation) α was decreased in steps of 0.001 until the required value was reached. At every step the coefficients obtained were substituted back into the equations and these were satisfied to a precision $\sim 10^{-10}$. During programming the following different limiting cases of the MSA for which solutions are known proved useful:

- (i) $\alpha\mathcal{C} = 1, \Gamma = 0$ uncharged one component hard sphere liquid (55,56)
- (ii) $0 \leq \alpha\mathcal{C} \leq 1, \Gamma = 0$ uncharged hard sphere (two component mixture)
with arbitrary diameter ratio (48)
- (iii) $\alpha\mathcal{C} = 1, \Gamma \geq 0$ charged hard spheres (binary mixture) with equal
diameters(RPM) (7)
- (iv) $\alpha\mathcal{C} = 0, \Gamma \geq 0$ binary charged hard sphere mixture with vanishing
diameter ratio (19).

In the programs, to check the consistency of the calculations, a few additional checking criteria were used :

- (1) 'cross-checkings' were done; by fixing η and $\alpha\mathcal{C}$, Γ was increased in small steps from 0 and thereby the identity of solutions for the same set of η , Γ and $\alpha\mathcal{C}$ was satisfied.
- (2) the $S_{ij}(q)$'s obtained by setting $\Gamma = 0$, were checked for consistency against those calculated independently from the Lebowitz solutions of the PY theory (neutral hard sphere mixture) for the same η , $\alpha\mathcal{C}$ and κ .
- (3) the overall electroneutrality condition in terms of the long wave-length limit of $S_{ij}(q)$'s (cf. Equation (1.52)) was satisfied.
- (4) the coefficients a_1, a_2 appearing in the Waisman-Lebowitz solutions relate to the partial molar volumes per particle through

$$a_i = \beta \frac{\overline{v}_i}{K_T} \quad (19) \quad (\text{A2.2.3})$$

From the neutrality condition

$$\rho_1 z_1 = \rho_2 z_2 \quad (\text{A2.2.4})$$

the compressibility sum rule (Equation (1.43)), and the condition

$$\rho_1 \overline{v}_1 + \rho_2 \overline{v}_2 = 1 \quad (\text{A2.2.5})$$

it is easy to prove

$$\left(a_1 + \frac{a_2}{z}\right)^{-1} = \lim_{q \rightarrow 0} S_{11}(q) \quad (\text{A2.2.6})$$

$$\text{and } (a_1 z + a_2)^{-1} = \lim_{q \rightarrow 0} \frac{d}{dq} S_{22}(q) \quad (\text{A2.2.7})$$

These relations were satisfied in our programs.

It is relevant to mention here that the above equations were also used to fit the experimental compressibility. For example, knowing K_T , ρ_1 , ρ_2 and T , $S_{11}(0)$ and $S_{22}(0)$ were fixed. We now varied σ_2 (keeping α constant), and hence η and Γ , until these equations were satisfied.

APPENDIX 3.1

Numerical solution of Reference Interaction Site Model equations using a non-linear optimization routine

Lowden and Chandler ⁽²³⁾ have shown that the solution of the RISM equations (cf. Chapter 3) corresponds to the solution of the variational problem

$$\frac{\delta I_{\text{RISM}}}{\delta c_{\alpha\beta}(r)} = 0 \quad (\text{A3.1.1})$$

where

$$\begin{aligned} I_{\text{RISM}} = & \rho \sum_{\alpha, \beta}^m \int d\mathbf{r} \left[c_{\alpha\beta}(r) + \frac{1}{2} c_{\alpha\beta}^2(r) \right] \\ & - \frac{1}{(2\pi)^3} \int d\mathbf{q} \text{Tr} \left\{ \rho \tilde{w}(\mathbf{q}) \tilde{c}(\mathbf{q}) + \frac{1}{2} \rho^2 \tilde{c}^2(\mathbf{q}) \right\} \\ & + \ln \det \left[I - \rho \tilde{w}(\mathbf{q}) \tilde{c}(\mathbf{q}) \right] \end{aligned} \quad (\text{A3.1.2})$$

By choosing

$$c_{\alpha\beta}(r) = \Theta(\sigma_{\alpha\beta} - r) \sum_{i=1}^4 a_i^{\alpha\beta} \left(r/\sigma_{\alpha\beta} - 1 \right)^{i-1} \quad * \quad (\text{A3.1.3})$$

where

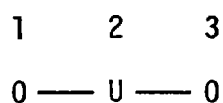
$$\begin{aligned} \Theta(x) &= 0 & \dots & x < 0 \\ &= 1 & \dots & x \geq 0 \end{aligned}$$

reduces the above variational problem to one that involves solution of the coupled algebraic equations for the coefficients $a_i^{\alpha\beta}$

$$\frac{\partial I_{\text{RISM}}}{\partial a_i^{\alpha\beta}} = 0 \quad (\text{A3.1.4})$$

* In principle one can choose the upper index in the summation higher than 4, but as Lowden and Chandler have shown, 4 gives sufficiently accurate results for most cases.

In case of UO_2 , numbering the atoms in the molecule as



we have from symmetry

$$\begin{aligned} c_{11} &= c_{13} = c_{31} = c_{33} \\ c_{12} &= c_{21} = c_{23} = c_{32} \\ c_{22} & \end{aligned} \quad (A3.1.5)$$

Thus there are only 3 independent $c_{\alpha\beta}(r)$'s; also the index in Equation (A3.1.2) is 3.

We now amalgamate indices $\alpha\beta$ and i in $a_i^{\alpha\beta}$ into j such that j runs from 1 to 12, viz:

$$\begin{array}{ccc} a_1^{11} \rightarrow a_1 & a_1^{12} \rightarrow a_5 & a_1^{22} \rightarrow a_9 \\ \vdots & \vdots & \vdots \\ a_4^{11} \rightarrow a_4 & a_4^{12} \rightarrow a_8 & a_4^{22} \rightarrow a_{12} \end{array}$$

The problem then is to solve 12 coupled algebraic equations for a_j 's.

$$\frac{\partial I_{\text{RISM}}}{\partial a_j} = 0, \quad j = 1, \dots, 12 \quad (A3.1.6)$$

This was done numerically using a non-linear optimization routine (62), which first calculates

$$\frac{\partial I_{\text{RISM}}}{\partial a_j} = F_j \quad (A3.1.7)$$

corresponding to a given initial set of values of a_j 's. It then evaluates $\sum_{j=1}^{12} |F_j|^2$ and optimizes the parameters until the sum is

a minimum, zero, to a specified numerical precision, 'EPS' (say). Clearly

then each $F_j = 0$. We chose EPS to be 10^{-8} . In what follows we shall describe briefly the techniques used to evaluate $\partial I_{\text{RISM}} / \partial a_j$ before programming was done.

From the form of I_{RISM} (Equation (A3.1.2)), it is clear that the evaluation of $\partial I_{\text{RISM}} / \partial a_j$ may be divided into three distinct parts. The first is

$$\frac{\partial}{\partial a_j} \left\{ \rho \sum_{\alpha, \beta}^3 \int d\underline{r} \left[c_{\alpha\beta}(r) + \frac{1}{2} c_{\alpha\beta}^2(r) \right] \right\}$$

Expanding and using symmetry conditions, also doing the angular integrations the above expression within $\{\dots\}$ becomes

$$4\pi\rho \int_0^\infty dr r^2 \left[\left\{ 4c_{11}(r) + 2c_{11}^2(r) \right\} + \left\{ 4c_{12}(r) + 2c_{12}^2(r) \right\} + \left\{ c_{22}(r) + \frac{1}{2} c_{22}^2(r) \right\} \right] = J_1 \quad (\text{say}) \quad (\text{A3.1.8})$$

From Equation (A3.1.3), we can write $c_{11}(r)$ as

$$c_{11}(r) = (a_1 - a_2 + a_3 - a_4) + (a_2 - 2a_3 + 3a_4)(r/\sigma_{11}) + (a_3 - 3a_4)(r/\sigma_{11})^2 + a_4(r/\sigma_{11})^3 \quad (\text{A3.1.9})$$

with similar expressions for $c_{12}(r)$ and $c_{22}(r)$.

Thus

$$c_{11}(r) = AA_{11} + BB_{11}(r/\sigma_{11}) + CC_{11}(r/\sigma_{11})^2 + DD_{11}(r/\sigma_{11})^3 \quad (\text{A3.1.10})$$

$c_{12}(r)$, $c_{22}(r)$ may be obtained by replacing subscript 11 by 12, 22, etc.. In above

$$\begin{aligned}
 AA_{11} &= a_1 - a_2 + a_3 - a_4 \\
 BB_{11} &= a_2 - 2a_3 + 3a_4 \\
 CC_{11} &= a_3 - 3a_4 \\
 DD_{11} &= a_4
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} AA_{11} \\ BB_{11} \\ CC_{11} \\ DD_{11} \end{aligned}} \right\} \quad (A3.1.11)$$

etc.. the quantities $\partial J_1 / \partial a_j$ were now obtained by straightforward differentiation followed by integration.

The second part is

$$\begin{aligned}
 \frac{\partial}{\partial a_j} \left\{ -\frac{1}{(2\pi)^3 \rho} \int d\mathbf{q} \left[\text{Tr} \left\{ \rho \tilde{\omega}(\mathbf{q}) \tilde{c}(\mathbf{q}) + \frac{1}{2} \rho^2 \tilde{c}^2(\mathbf{q}) \right\} \right] \right\} \\
 = \frac{\partial J_2}{\partial a_j} \quad (\text{say})
 \end{aligned}
 \quad (A3.1.12)$$

To evaluate above we first have to calculate the fourier transforms

$$\tilde{\omega}_{\alpha\beta}(\mathbf{q}) \quad \text{and} \quad \tilde{c}_{\alpha\beta}(\mathbf{q}). \quad \text{From Equation (3.11),}$$

$$\tilde{\omega}'_{\alpha\beta}(\mathbf{q}) = \frac{\sin \mathbf{q} l_{\alpha\beta}}{q l_{\alpha\beta}}$$

There are two lengths $l_{\alpha\beta}$ in the problem. Therefore.

$$\tilde{\omega}_{11}(\mathbf{q}) = 1$$

$$\tilde{\omega}_{12}(\mathbf{q}) = \frac{\sin ql}{ql} \quad (A3.1.13)$$

$$\tilde{\omega}_{13}(\mathbf{q}) = \frac{\sin qm}{qm}$$

Others are immediately obtained from symmetry. To obtain $\tilde{c}_{\alpha\beta}(\mathbf{q})$, we use the form of $c_{\alpha\beta}(r)$ given in (A3.1.10). Now using the same methods as in Appendix 2.1, one easily gets

$$\tilde{c}_{11}(\mathbf{q}) = \frac{4\pi \sigma_{11}^3}{(q \sigma_{11})^2} \left[L_{11}(\mathbf{q}) \cos q \sigma_{11} - M_{11}(\mathbf{q}) \frac{\sin q \sigma_{11}}{q \sigma_{11}} + \frac{N_{11}(\mathbf{q})}{(q \sigma_{11})^2} \right] \quad (A3.1.14)$$

Similarly for $\tilde{c}_{12}(q)$ and $\tilde{c}_{22}(q)$.

in (A3.1.14),

$$\begin{aligned} L_{11}(q) &= -a_1 + \frac{1}{(q\sigma_{11})^2} (2a_2 + 2a_3) - \frac{24a_4}{(q\sigma_{11})^4} \\ M_{11}(q) &= -(a_1 + a_2) + (6a_3 + 6a_4)/(q\sigma_{11})^2 \\ N_{11}(q) &= -2a_2 + 4a_3 - 6a_4 + 24a_4/(q\sigma_{11})^2 \end{aligned}$$

(A3.1.15)

We can now evaluate the traces in (A3.1.14). In particular

$$\begin{aligned} &\text{Tr} \left\{ \rho \tilde{\omega}(q) \tilde{c}(q) \right\} \\ &= \rho \sum_{i,j=1}^3 \tilde{\omega}_{ij}(q) \tilde{c}_{ji}(q) \\ &= \rho \left[2\tilde{c}_{11}(q) (1 + \tilde{\omega}_{13}(q)) + 4\tilde{\omega}_{12}(q) \tilde{c}_{12}(q) + \tilde{c}_{22}(q) \right] \end{aligned}$$

(A3.1.16)

using symmetry.

Similarly

$$\begin{aligned} &\text{Tr} \left\{ \frac{1}{2} \rho^2 \tilde{c}^2(q) \right\} \\ &= \frac{1}{2} \rho^2 \sum_{i,j=1}^3 \left\{ \tilde{c}_{ij}(q) \tilde{c}_{ji}(q) \right\} \\ &= \frac{1}{2} \rho^2 \left[4\tilde{c}_{11}^2(q) + 4\tilde{c}_{12}^2(q) + \tilde{c}_{22}^2(q) \right] \end{aligned}$$

(A3.1.17)

Calculations of $-\partial J_2 / \partial a_j$ were now done.

The final part is

$$\frac{\partial}{\partial a_j} \left[-\frac{1}{(2\pi)^3 \rho} \int \frac{dq}{q} \ln \det \left[I - \rho \tilde{\omega}(q) \tilde{c}(q) \right] \right] = \frac{\partial J_3}{\partial a_j} \quad (\text{say})$$

(A3.1.18)

Knowing $\tilde{\omega}_{\alpha\beta}(q)$ and $\tilde{c}_{\alpha\beta}(q)$ from the second part above, and after some lengthy algebra (A3.1.18) was evaluated. The final form of $\det [I - \rho \tilde{\omega}(q) \tilde{c}(q)]$ is

$$\det [I - \rho \tilde{\omega}(q) \tilde{c}(q)] \equiv X = \begin{vmatrix} x_1 & x_2 & x_3 \\ x_4 & x_5 & x_6 \\ x_7 & x_8 & x_9 \end{vmatrix} \quad (\text{A3.1.19})$$

where

$$\begin{aligned} x_1 = x_9 &= [1 - \rho \{ \tilde{c}_{11}(q)(1 + \tilde{\omega}_{13}(q)) + \tilde{c}_{12}(q) \tilde{\omega}_{12}(q) \}] \\ x_2 = x_8 &= [-\rho \{ \tilde{c}_{12}(q)(1 + \tilde{\omega}_{13}(q)) + \tilde{c}_{22}(q) \tilde{\omega}_{12}(q) \}] \\ x_4 = x_6 &= [-\rho \{ 2\tilde{c}_{11}(q) \tilde{\omega}_{12}(q) + \tilde{c}_{12}(q) \}] \\ x_3 = x_7 &= [-\rho \{ \tilde{c}_{11}(q)(1 + \tilde{\omega}_{13}(q)) + \tilde{c}_{12}(q) \tilde{\omega}_{12}(q) \}] \\ x_5 &= [1 - \rho \{ 2\tilde{c}_{12}(q) \tilde{\omega}_{12}(q) + \tilde{c}_{22}(q) \}] \end{aligned} \quad (\text{A3.1.20})$$

The integrations involved in $\partial J_2 / \partial a_j$ and $\partial J_3 / \partial a_j$ were done numerically using a CERN library routine (63).

APPENDIX 5.1

Form of the direct correlation functions

We follow here closely the methods of Waisman and Lebowitz (11), and Palmer and Weeks (78).

Recall the definition of the reduced direct correlation function $c_{ij}^{(0)}(r)$ (cf. Equation (A2.2.1))

$$c_{ij}^{(0)}(r) = c_{ij}(r) + \beta \frac{e_i e_j}{\epsilon r}$$

Substitution of $c_{ij}^{(0)}(r)$ into the Ornstein-Zernike relation (Equation (2.6)) yields

$$\begin{aligned} h_{ij}(r) - c_{ij}^{(0)}(r) &= \sum_{l=1}^3 \rho_l \int d\underline{r}' h_{il}(|\underline{r}'|) c_{lj}^{(0)}(|\underline{r} - \underline{r}'|) \\ &= -\beta \frac{e_i e_j}{\epsilon r} - \left(\frac{\beta}{\epsilon}\right) \sum_{l=1}^3 \rho_l e_l e_j \int d\underline{r}' \frac{h_{il}(|\underline{r}'|)}{|\underline{r} - \underline{r}'|} \end{aligned} \quad (\text{A5.1.1})$$

We evaluate first the angular integration in the R.H.S. of above.

Let $|\underline{r}'| = x$, then

$$|\underline{r} - \underline{r}'| = (r^2 + x^2 - 2rx \cos \theta)^{1/2}, \text{ and the volume element } |d\underline{r}'| = x^2 dx \sin \theta d\theta d\phi$$

Therefore

$$\begin{aligned} \int d\underline{r}' \frac{h_{il}(|\underline{r}'|)}{|\underline{r} - \underline{r}'|} &= \int_0^\infty dx \int_0^\pi d\theta \int_0^{2\pi} d\phi \frac{h_{il}(x) x^2 \sin \theta}{(r^2 + x^2 - 2rx \cos \theta)^{1/2}} \\ &= 2\pi \int_0^\infty dx \int_0^\pi d\theta \frac{h_{il}(x) x^2 \sin \theta}{(x^2 + r^2 - 2rx \cos \theta)^{1/2}} \\ &= 2\pi \int_0^\infty dx \int_{-1}^1 dz \frac{h_{il}(x) x^2}{(x^2 + r^2 - 2rxz)^{1/2}} \end{aligned} \quad \text{Let } \cos \theta = z$$

$$\begin{aligned}
&= -2\pi \int_0^\infty dx x^2 h_{il}(x) \left| \frac{(r^2 + x^2 - 2rx)^{1/2}}{rx} \right|_{-1}^1 \\
&= -2\pi \int_0^r dx h_{il}(x) \frac{x}{r} \{ (r-x) - (r+x) \} \\
&\quad - 2\pi \int_r^\infty dx h_{il}(x) \frac{x}{r} \{ (x-r) - (r+x) \} \\
&= \frac{4\pi}{r} \int_0^r dx x^2 h_{il}(x) + 4\pi \int_r^\infty dx x h_{il}(x)
\end{aligned}$$

Thus Equation (A5.1.1) becomes

$$\begin{aligned}
h_{ij}(r) - c_{ij}^{(0)}(r) &= \sum_{l=1}^3 \rho_l \int d\underline{r}' h_{il}(|\underline{r}'|) c_{lj}^{(0)}(|\underline{r} - \underline{r}'|) \\
&= -\beta \frac{e_i e_j}{\epsilon r} - \frac{4\pi\beta}{\epsilon} \sum_{l=1}^3 \rho_l e_l e_j \left\{ \frac{1}{r} \int_0^r dx h_{il}(x) x^2 + \int_r^\infty dx x h_{il}(x) \right\} \\
&= \left[-\frac{\beta e_i e_j}{\epsilon r} - \frac{4\pi\beta}{\epsilon} \sum_{l=1}^3 \rho_l e_l e_j \int_0^\infty dx x^2 h_{il}(x) \right] \\
&\quad - \frac{4\pi\beta}{\epsilon} \sum_{l=1}^3 \rho_l e_l e_j \left\{ -\frac{1}{r} \int_r^\infty dx x^2 h_{il}(x) + \int_r^\infty dx x h_{il}(x) \right\}
\end{aligned} \tag{A5.1.2}$$

Now from the Stillinger and Lovett ⁽⁴⁾ zeroth moment relation for an electrolyte

$$4\pi \int_0^\infty dr \sum_l \rho_l e_l g_{il}(r) r^2 = -e_i \tag{A5.1.3}$$

for each i ; the quantity within square brackets in (A5.1.2) vanishes.

Therefore we obtain

$$\begin{aligned}
 h_{ij}(r) - c_{ij}^{(0)}(r) &= \sum_{\ell=1}^2 \rho_{\ell} \int d\underline{r}' h_{i\ell}(|\underline{r}'|) c_{ij}^{(0)}(|\underline{r} - \underline{r}'|) \\
 &= \frac{1}{2} \gamma^2 \sum_{\ell=1}^2 \rho_{\ell} e_{\ell} e_j \left(\frac{1}{r} \int_r^{\infty} dx x^2 h_{i\ell}(x) - \int_r^{\infty} dx x h_{i\ell}(x) \right)
 \end{aligned}
 \tag{A5.1.4}$$

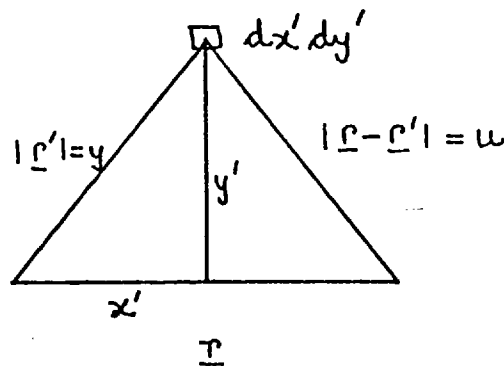
where $\gamma^2 = 8\pi\beta/\epsilon$

Notice because from Equation (5.2), $h_{13} = 0$ etc. $\sum_{\ell}$ is only over 1 and 2 components.

We now define a matrix $W_{ij}(r)$ by the relations

$$\begin{aligned}
 \left[12(\eta_i \eta_j)^{1/2} r \right]^{-1} W_{ij}(r) &= -c_{ij}^{(0)}(r) \quad \text{for } r < \sigma_{ij} \\
 &= g_{ij}(r) \quad \text{for } r > \sigma_{ij}
 \end{aligned}
 \tag{A5.1.5}$$

with $\eta_i = \frac{\pi}{6} \rho_i$



Employing bipolar coordinates for the third term in the L.H.S. of (A5.1.4), using the definition (A5.1.5), we obtain after some algebraic manipulations

$$W_{ij}(r) = A_{ij}(r) + \sum_{\ell=1}^2 \int_{y \geq \sigma_{i\ell}}^{\infty} dy w_{i\ell}(y) \int_{u=|r-y|}^{\min(r+y, \sigma_{\ell j})} du w_{\ell j}(u)$$

$$\begin{aligned}
&= -\frac{\gamma^2}{2} r \sum_{\ell=1}^2 \mathcal{D}_{\ell j} \int_{\max(r, \sigma_{i\ell})}^{\infty} dx w_{i\ell}(x) + \frac{\gamma^2}{2} \sum_{\ell=1}^2 \mathcal{D}_{\ell j} \\
&\quad \int_{\max(r, \sigma_{i\ell})}^{\infty} dx x w_{i\ell}(x) - \gamma^2 (\eta_i \eta_j)^{1/2} \sum_{\ell=1}^2 \rho_{\ell} e_{\ell} r^3
\end{aligned}
\tag{A5.1.6}$$

In the L.H.S. the lower limit $u = |r-y| < \sigma_{\ell j}$ implies that the integral vanishes for $|r-y| \geq \sigma_{\ell j}$. $\mathcal{D}_{ij} = (\rho_i \rho_j)^{1/2} e_i e_j$, and $A_{ij}(r) = 2\pi (\rho_i \rho_j)^{1/2} a_j$ with a_j defined as in Equation (A2.2.1).

Consider now the quantity

$$\sum_{\ell=1}^2 \int_{y \geq \sigma_{i\ell}}^{\infty} dy w_{i\ell}(y) \int_{u = |r-y| < \sigma_{\ell j}}^{\min(r+y, \sigma_{\ell j})} du w_{\ell j}(u)$$

for $\ell = 1$. In the model we consider (cf. Section 5.2), $\sigma_1 \rightarrow 0$ and $\sigma_2 = \sigma$. Therefore for $j = 1$, $i = 2$ and for $r = \sigma/2$, we have

$$|r-y| = \left| \frac{\sigma}{2} - \frac{\sigma}{2} \right| = 0 = \sigma_1.$$

Similarly for $\ell = 2$.

$$|r-y| = \left| \frac{\sigma}{2} - \sigma \right| = \frac{\sigma}{2} = \sigma_{12}$$

We thus have $|r-y| = \sigma_{\ell i}$ ($\ell = 1, 2$) for $r = \sigma/2$. But this is the extreme case, and obviously for $r < \sigma/2$,

$$|r-y| > \sigma_{\ell i}, \quad \ell = 1, 2$$

Therefore the integral in the L.H.S. of (A5.1.6) vanishes.

Hence

$$W_{12}(r) = W_{21}(r)$$

$$= \frac{\gamma^2}{2} \sum_{\ell} \mathcal{D}_{\ell 1} \int_{\sigma_{2\ell}}^{\infty} dx x w_{2\ell}(x)$$

$$+ \left[A_{21} - \frac{\gamma^2}{2} \sum_l D_{l1} \int_{\sigma_{2l}}^{\infty} dx \sigma_{2l}(x) \right] r - \left[\gamma^2 (\eta_1 \eta_2)^{1/2} (e_1 e_1 + e_2 e_2) \right] r^3 \dots r \ll \frac{\sigma}{2} \quad (A5.1.7)$$

$$\begin{aligned} \text{Now } & \frac{\gamma^2}{2} \sum_l D_{l1} \int_{\sigma_{2l}}^{\infty} dx x w_{2l}(x) \\ &= \frac{\gamma^2}{2} \sum_l D_{l1} \int_{\sigma_{2l}}^{\infty} dx x^2 \frac{1}{2} (\eta_2 \eta_l)^{1/2} g_{2l}(x) \\ &= \frac{\gamma^2}{2} \sum_l (p_1 p_l)^{1/2} e_1 e_l \int_{\sigma_{2l}}^{\infty} dx x^2 4\pi (p_2 p_l)^{1/2} g_{2l}(x) \\ &= \frac{\gamma^2}{4} (p_1 p_2)^{1/2} e_1 \left[4\pi \sum_l p_l e_l \int_{\sigma_{2l}}^{\infty} dx x^2 g_{2l}(x) \right] \\ &= -\frac{\gamma^2}{4} (p_1 p_2)^{1/2} e_1 e_2 \quad \text{using (A5.1.3)} \\ &= -\frac{\gamma^2}{4} D_{21} \quad (A5.1.8) \end{aligned}$$

Also defining

$$V_{ij} = \sum_l D_{lj} \int_{\sigma_{il}}^{\infty} dx \sigma_{il}(x) \quad (A5.1.9)$$

we finally get

$$\begin{aligned} W_{12}(r) &= W_{21}(r) \\ &= -\frac{\gamma^2}{4} D_{21} + \left[A_{21} - \frac{\gamma^2}{2} V_{21} \right] r - \gamma^2 e_1 (p_1 e_1 + p_2 e_2) (\eta_1 \eta_2)^{1/2} r^3 \\ &\dots r \ll \frac{\sigma}{2} \quad (A5.1.10) \end{aligned}$$

Dividing the above equation throughout by $12(\eta_1\eta_2)^{1/2}r$, the form $c_{12}(r)$ given in Equation (5.5) follows. To obtain $c_{22}(r)$, we rewrite Equation (A5.1.6) with subscript ii. Laplace transform can then be taken when it reduces to the form of the corresponding equation given in Palmer and Weeks ⁽⁷⁸⁾; following now the method given there we get the form of $c_{22}(r)$ for $r < \sigma$ as in Equation (5.4). $c_{11}(r)$ follows from $c_{22}(r)$ from symmetry, and as $\sigma_1 \rightarrow 0$ we get the form (5.3).

APPENDIX 5.2

Summary of the singularities method of solution for the coefficients in the direct correlation functions

In this method the coefficients appearing in the direct correlation functions, $c_{ij}(r)$ are determined by studying the singularities in these functions.

Consider the $c(r)$ given by the exact solution of PY theory for one component hard sphere fluid (55,56),

$$\begin{aligned} c(r) &= \alpha_0 + \beta_0(r/\sigma) + \gamma_0(r/\sigma)^3 & \dots & r < \sigma \\ &= 0 & \dots & r > \sigma \end{aligned} \quad (\text{A5.2.1})$$

where $\alpha_0, \beta_0, \gamma_0$ are functions of the packing fraction $\eta = \frac{\pi}{6} \rho \sigma^3$

Because of the singularities at $r = 0$ and $r = \sigma$ in $c(r)$, its fourier transform

$$\tilde{c}(q) = 4\pi\rho \int_0^\infty dr r^2 \frac{\sin qr}{qr} c(r)$$

contains for large q

- (i) terms of the type q^{-4}, q^{-6} proportional to β_0 and γ_0 , and
- (ii) terms of the type $\frac{\cos q\sigma}{(q\sigma)^{2n}}$ and $\frac{\sin q\sigma}{(q\sigma)^{2n+1}}$ (cf. the fourier

transforms calculated in Appendices 2.1 and 5.3 show these two points explicitly).

For a single-component fluid we have

$$S(q) = [1 - \tilde{c}(q)]^{-1} \quad (\text{A5.2.2})$$

as $|\tilde{c}(q)| < 1$, we can perform the expansion to obtain

$$S(q) = 1 + \tilde{c}(q) + \tilde{c}^2(q) + \tilde{c}^3(q) + \dots \quad (\text{A5.2.3})$$

Now since $S(q)$ and $g(r)$ are related by

$$g(r)-1 = \frac{1}{2\pi^2\rho} \int_0^\infty dq q^2 \frac{\sin qr}{qr} (S(q)-1) \quad (\text{A5.2.4})$$

From the above arguments (points (i) and (ii)) we see that the presence of q^{-2n} terms for large q in $S(q)$ would immediately indicate the presence of $r^{(2n-3)}$ terms in $[g(r)-1]$ for small r . But the physical condition $g(r) = 0$ for $r < \sigma$ for hard spheres implies such terms cannot be present in a hard sphere pair function. We therefore conclude terms behaving as q^{-2n} must not be present in the asymptotic form of $S(q)$.

Alternatively doing small r expansion of $\sin qr$ in the right hand side of Equation (A5.2.4) we obtain

$$[g(r)-1] = \frac{1}{2\pi^2\rho} \int_0^\infty dq q^2 [S(q)-1] \left[1 - \frac{q^2 r^2}{3!} + \frac{q^4 r^4}{5!} - \dots \right] \quad (\text{A5.2.5})$$

Obviously in the above a general term of the type,

coeff $\times \int_0^\infty [S(q)-1] q^{2n+2} dq$ converges for all n only if $[S(q)-1]$ decays exponentially.

We can rewrite (A5.2.5) as

$$[g(r)-1] = \text{constant} + c_1 r^2 + c_2 r^4 + c_3 r^6 + \dots \quad (\text{for small } r) \quad (\text{A5.2.6})$$

Note no term containing odd powers of r appears. The only way the coefficients of $r^2, r^4, \dots$ terms can diverge is if $[S(q)-1]$ contains $q^{-4}, q^{-6}, \dots$ terms etc..

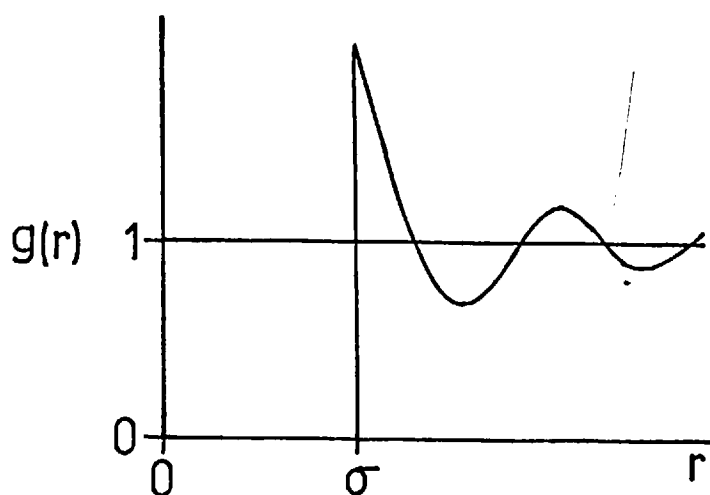


Figure A5.1.1

Physically too, in a hard sphere model $g(r)$ is flat and zero within the hard core (see Figure (A5.1.1)). Thus terms proportional to r, r^3 cannot be present in such a hard sphere pair correlation function.

To summarize the singularities method consists in

- Step 1 taking fourier transforms of $c(r)$ to obtain $\tilde{c}(q)$
- Step 2 using $\tilde{c}(q)$ to determine asymptotic expansion of $S(q)$.

In general this may be easily done by using the Pearson-Rushbrooke equations

- Step 3 using conditions that coefficients of $\frac{1}{q^4}, \frac{1}{q^6}, \frac{1}{q^8}, \dots$ unless multiplied by $\sin q\sigma$ or $\cos q\sigma$ vanish in the expansion (step 2) to obtain equations which determine the coefficients in $c(r)$.

APPENDIX 5.3

Fourier transforms of the direct correlation functions

To obtain the fourier transforms $\tilde{c}_{ij}(q)$ of the direct correlation functions $c_{ij}(r)$ we follow exactly the same techniques as given in Appendix 2.1.

For the present case, from the Equations (5.3) to (5.5) (and the definition (2.17)), we obtain

$$\tilde{c}_{11}(q) = -4\pi\rho\rho_1 e_1^2/q^2 \quad (\text{A5.3.1})$$

$$\tilde{c}_{22}(q) = \frac{4\pi\rho_2\sigma^3}{(q\sigma)^2} \left[L(q) \cos q\sigma - M(q) \frac{\sin q\sigma}{q\sigma} + \frac{N(q)}{(q\sigma)^2} \right] \quad (\text{A5.3.2})$$

$$\tilde{c}_{12}(q) = \tilde{c}_{21}(q)$$

$$= \frac{2\pi(\rho_1\rho_2)^{1/2}\sigma^3}{(q\sigma)^2} \left[P(q) \cos \frac{q\sigma}{2} - Q(q) \frac{\sin \frac{q\sigma}{2}}{(q\sigma)/2} \right] \quad (\text{A5.3.3})$$

where

$$L(q) = (\alpha + b_2 + c_2' + d_2 + f_2) - \frac{1}{(q\sigma)^2} (2b_2 + 6c_2' + 12d_2 + 30f_2) \\ + \frac{1}{(q\sigma)^4} (24d_2 + 360f_2) - \frac{720f_2}{(q\sigma)^6} - \frac{\rho e_2^2}{\sigma}$$

$$M(q) = (\alpha + 2b_2 + 3c_2' + 4d_2 + 6f_2) - \frac{1}{(q\sigma)^2} (6c_2' + 24d_2 + 120f_2) \\ + \frac{720f_2}{(q\sigma)^4}$$

$$N(q) = 2b_2 - \frac{24d_2}{(q\sigma)^2} + \frac{720f_2}{(q\sigma)^4} \quad (\text{A5.3.4})$$

$$P(q) = \left\{ a_1 + \frac{2\beta V_2}{\rho_1} \left(1 + \frac{\rho_3 e_3}{\rho_2 e_2} \right) \right\} + \frac{c_2}{4} - \frac{6c_2}{(q\sigma)^2} - \frac{2\beta e_1 e_2}{\sigma}$$

$$Q(q) = \left\{ a_1 + \frac{2\beta V_2}{\rho_1} \left(1 + \frac{\rho_3 e_3}{\rho_2 e_2} \right) \right\} + \frac{3}{4} c_2 - \frac{6c_2}{(q\sigma)^2} \quad (\text{A5.3.5})$$

$$\text{with } \alpha \equiv a_2 - \frac{2\beta V_2}{\rho_2} \quad (\text{A5.3.6})$$

It is easy to check the limits of the above fourier transforms when $\rho_3 \rightarrow 0$, i.e. no background. For example, in the limit $\rho_3 \rightarrow 0$,

$$c_2, c'_2 \rightarrow 0 \text{ and } f_2 \rightarrow 0$$

then

$$\tilde{c}_{11}^0(q) = -\frac{4\pi\beta\rho_1 e_1^2}{q^2} \quad (\text{A5.3.7})$$

$$\tilde{c}_{22}^0(q) = \frac{4\pi\rho_2\sigma^3}{(q\sigma)^2} \left[L^0(q) \cos q\sigma - M^0(q) \frac{\sin q\sigma}{q\sigma} + \frac{N^0(q)}{(q\sigma)^2} \right] \quad (\text{A5.3.8})$$

with

$$L^0(q) = \left\{ \left(a_2^0 - \frac{2\beta V_2^0}{\rho_2} \right) + b_2^0 + d_2^0 \right\} - \frac{2b_2^0 + 12d_2^0}{(q\sigma)^2} \\ + \frac{24d_2^0}{(q\sigma)^4} - \frac{\beta e_2^2}{\sigma}$$

$$M^0(q) = \left\{ \left(a_2^0 - \frac{2\beta V_2^0}{\rho_2} \right) + 2b_2^0 + 4d_2^0 \right\} - \frac{24d_2^0}{(q\sigma)^2}$$

$$N^0(q) = 2b_2^0 - \frac{24d_2^0}{(q\sigma)^2} \quad (\text{A5.3.9})$$

and

$$\begin{aligned}
 \tilde{c}_{12}^0(q) &= \tilde{c}_{21}^0(q) \\
 &= \frac{2\pi(\rho_1 \rho_2)^{1/2} \sigma^3}{(q\sigma)^2} \left[p^0(q) \cos \frac{q\sigma}{2} - Q^0(q) \right. \\
 &\quad \left. \frac{\sin \frac{q\sigma}{2}}{(q\sigma)/2} \right]
 \end{aligned} \tag{A5.3.10}$$

with

$$\begin{aligned}
 p^0(q) &= (a_1^0 + \frac{2\beta v_2^0}{\rho_1}) - \frac{2\beta e_1 e_2}{\sigma} \\
 Q^0(q) &= (a_1^0 + \frac{2\beta v_2^0}{\rho_1})
 \end{aligned} \tag{A5.3.11}$$

which are precisely the quantities in Gillan et al (19).

APPENDIX 5.4

Strong Coupling Properties of the Classical

One Component Plasma

The classical one component plasma (COCP) may be formally defined as a system of identical point like charges (of magnitude e) embedded in a uniform neutralizing background of opposite charge. Theoretically such a system has been of great interest as a model for complicated coulomb systems such as electrolytes. It also simulates many features of dense and completely ionized matter, and thus has important relevance for astrophysics.

The properties of the COCP are usually described in terms of a dimensionless coupling constant

$$\Gamma = \frac{e^2}{a k_B T} \quad (\text{A5.4.1})$$

where 'a' is the mean separation between the charges

$$a = \left[\frac{4}{3} \pi \rho \right]^{-1/3} \quad (\text{A5.4.2})$$

Physically Γ is the ratio of average potential energy to the average kinetic energy per particle.

'Experimental' information on the properties of the COCP primarily comes from the extensive computer simulations such as those by Brush et al⁽⁸⁰⁾, Hansen⁽⁸¹⁾, Pollock and Hansen⁽⁸²⁾, Hansen et al⁽⁸³⁾, etc.. Their results for the radial distribution function $g(r)$ corresponding to different values of Γ are interesting. For $\Gamma \lesssim 2$, $g(r)$ is a monotonic function of r , for higher values of Γ oscillations are seen. These oscillations indicate the onset of short range order in the system. Around $\Gamma \sim 155$, transition to an ordered solid phase is observed.

Unfortunately, on the theoretical side, a theory capable of describing the observed properties of the structure of the COCP for the range of Γ

upto and including the critical value 155, is still lacking. The first theory was provided by the pioneering work of Debye and Hückel ⁽⁸⁴⁾ in the field of electrolytes. Their result for the pair correlation function is

$$g_{DH}(r) = 1 - \frac{e^2}{k_B T r} e^{-\chi r} \quad (A5.4.3)$$

where $\chi = [(4\pi \rho e^2)/k_B T]^{1/2}$ is the inverse Debye-Hückel screening length. The principal defect of this result is that at small distances we get the non-physical result of negative probabilities. For example, it is easy to see from (A5.4.3) that at $r \rightarrow 0$, $g_{DH}(r) \rightarrow -\infty$. Nonetheless, the Debye-Hückel theory introduces the important idea of 'screening' in charged systems. The above equation tells us that the particle correlation is screened out at distances $\sim \frac{1}{\chi}$. Quantitatively the theory is good for describing the structure only for $\Gamma \ll 1$.

Approximate integral equations of liquid structure have also been applied to the COCP. For example, Springer et al ⁽⁸⁵⁾ have numerically solved the Hypernetted chain equation for upto $\Gamma = 50$. The results are in reasonable agreement with the computer experiments. Gillan ⁽⁸⁶⁾ has obtained results for $g(r)$ based on the MSA upto $\Gamma \sim 120$; but in this case departure from the Monte-Carlo results for $\Gamma > 50$ are considerable.

In the following discussion we consider some implications of the Monte-Carlo data for the COCP obtained by Hansen ⁽⁸¹⁾.

Let us consider the direct correlation function $c(r)$ tabulated for $\Gamma = 2, 3$ and 4. We have plotted these as functions of r in Figure (A5.4.1). It is noticeable that the curves are almost flat and parallel to each other for small r . In Figure (A5.4.2) we have plotted the 'universal' curves $c(r)/\Gamma$ versus r for the same Γ values as above. It is interesting to observe now, that apart from the small

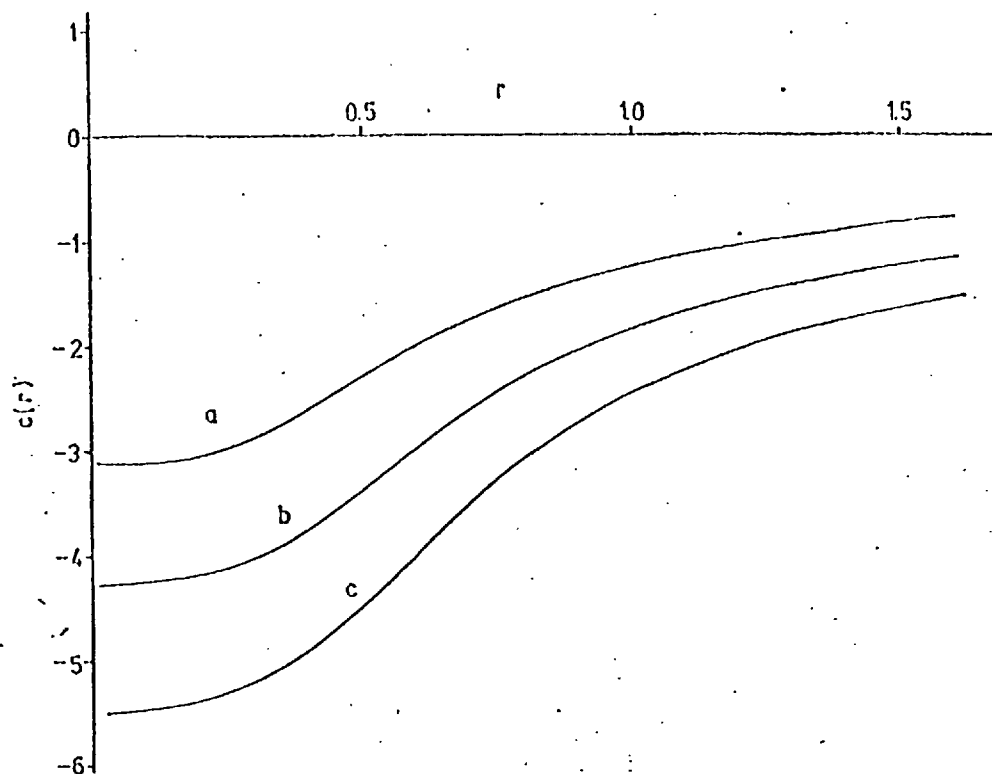


Figure A5.4.1

Direct correlation function $c(r)$ as given by the 'Monte-Carlo' simulation of Hansen (81).

Curve (a) : $\Gamma = 2$.

Curve (b) : $\Gamma = 3$.

Curve (c) : $\Gamma = 4$.

r is in units of $\rho^{-1/3}$.

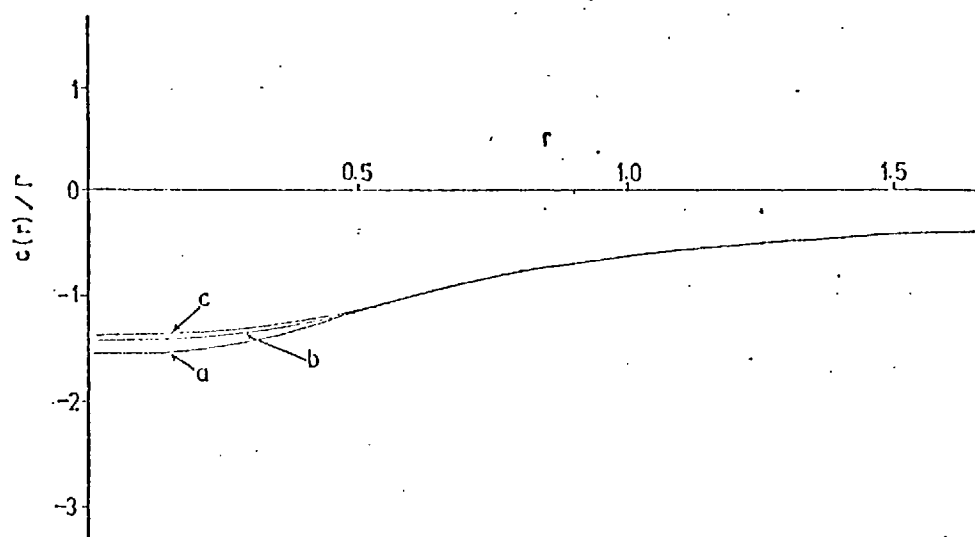


Figure A5.4.2

'Universal' plot $c(r)/\Gamma$ of the direct correlation function in Fig.A5.4.1.

Curve (a) : $\Gamma = 2$.

Curve (b) : $\Gamma = 3$.

Curve (c) : $\Gamma = 4$.

r is in units of $\rho^{-1/3}$.

region near $r = 0$, the curves converge together for large r . Indeed as Hansen ⁽⁸¹⁾ points out, all $c(r)$'s given by his Monte Carlo data tend towards their Debye-Hückel limit as $r \rightarrow \infty$

$$c_{DH}(r) = -\frac{e^2}{k_B T r} \quad (A5.4.4)$$

The behaviour of $c(r)$ in the above figures prompted us to assume the following form for it for small r :

$$-c(r) = A_0 + A_2 r^2 \quad (A5.4.5)$$

where A_0 and A_2 are constants.

Now

$$\begin{aligned} c(r) &= \frac{1}{(2\pi)^3 \rho} \int d\mathbf{q} e^{i \mathbf{q} \cdot \mathbf{r}} \tilde{c}(\mathbf{q}) \\ &= \frac{1}{2\pi^2 \rho} \int_0^\infty dq q^2 \frac{\sin qr}{qr} \tilde{c}(q) \end{aligned} \quad (A5.4.6)$$

Expanding $\sin qr$ for small r , we get

$$c(r) \simeq \frac{1}{2\pi^2 \rho} \int_0^\infty dq q^2 \tilde{c}(q) - \frac{r^2}{12\pi^2 \rho} \int_0^\infty dq q^4 \tilde{c}(q) \quad (A5.4.7)$$

Comparing Equations (A5.4.5) and (A5.4.7) we have

$$\begin{aligned} A_0 &= -\frac{1}{2\pi^2 \rho} \int_0^\infty dq q^2 \tilde{c}(q) \\ \text{and } A_2 &= \frac{1}{12\pi^2 \rho} \int_0^\infty dq q^4 \tilde{c}(q) \end{aligned} \quad (A5.4.8)$$

Obviously for our assumption (A5.4.5) to be true, the integral $\int_0^\infty dq q^2 \tilde{c}(q)$ and $\int_0^\infty dq q^4 \tilde{c}(q)$ must exist. In particular from fourier transform arguments if there is no r term in $c(r)$, $\tilde{c}(q)$ must fall off faster than as q^{-4} .

We evaluated the above integrals numerically using the data given in Hansen for $\Gamma = 4, 10, 100$ and 140 . $q^2 \tilde{c}(q)$ converged for large q

and interestingly we noticed $A_0/r \simeq \text{const.}$ But unfortunately, with the available data for large q values of $\tilde{c}(q)$, convergence of $q^4 \tilde{c}(q)$ was not good and consequently the result for $\int_0^\infty dq q^4 \tilde{c}(q)$ is unreliable.

The Monte-Carlo data provides interesting results for small q behaviour of $\tilde{c}(q)$ and the structure factor $S(q)$ for the COCP. Since all $c(r) \rightarrow \frac{-e^2}{k_B T r}$ for large r , it immediately follows its fourier transform

$$\tilde{c}(q) \simeq -\frac{4\pi \rho e^2}{k_B T q^2} \quad \text{for small } q \quad (\text{A5.4.9})$$

Substituting this result in Equation (1.37) we get

$$S(q) \simeq \frac{k_B T q^2}{4\pi \rho e^2}$$

$$\text{i.e.} \quad S(q) \simeq \text{Const. } q^2 \quad \text{for small } q \quad (\text{A5.4.10})$$

Consequently

$$\lim_{q \rightarrow 0} [S(q)] = 0 \quad (\text{A5.4.11})$$

It is important to note that these relations may also be obtained by applying the Stillinger - Lovett ⁽⁴⁾ moment relations for coulomb fluids to the COCP. For example, using the neutrality condition

$\sum \rho_e e_e = 0$ in the zeroth moment relation (Equation (A5.1.3)) we have

$$4\pi \sum_e \rho_e e_e \int_0^\infty dr r^2 h_{i1}(r) = -e_i \quad (\text{A5.4.12})$$

For the one component plasma this becomes

$$4\pi \rho e \int_0^\infty dr r^2 h(r) = -e$$

$$\text{or } \lim_{q \rightarrow 0} \left[\rho \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} h(r) \right] = -1$$

$$\text{or } \lim_{q \rightarrow 0} [S(q) - 1] = -1$$

$$\text{i.e. } \lim_{q \rightarrow 0} [S(q)] = 0$$

The second moment relation is

$$4\pi \int_0^\infty dr \left\{ \sum_{\ell, m} \rho_\ell \rho_m e_\ell e_m g_{\ell m}(r) r^4 \right\} = -6 \sum_\ell \rho_\ell e_\ell^2 / \Lambda^2 \quad (\text{A5.4.13})$$

where

$$\Lambda^2 = \frac{4\pi}{k_B T} \sum_\ell \rho_\ell e_\ell^2$$

Again for the one component plasma this can be written as

$$4\pi \int_0^\infty dr \rho^2 e^2 h(r) r^4 = -6 \rho e^2 / \frac{4\pi \rho e^2}{k_B T} \quad (\text{A5.4.14})$$

where we have again used the neutrality condition. It now follows

$$\rho e^2 \cdot 4\pi \rho \int_0^\infty dr r^4 h(r) = -\frac{3 k_B T}{2\pi}$$

or $\nabla_{-q}^2 \left\{ \rho \int dr e^{-i \underline{q} \cdot \underline{r}} h(r) \right\} \Big|_{q=0} = \frac{3 k_B T}{2\pi \rho e^2}$

or $\nabla_{-q}^2 S(q) \Big|_{q=0} = \frac{3 k_B T}{2\pi \rho e^2} \quad (\text{A5.4.15})$

From this we again see

$$S(q) \sim \text{Const. } q^2 \quad \text{for } q \rightarrow 0$$

Clearly what is required is a general form of $c(r)$ which will contain within itself the possibility of a transition to an ordered state at a critical coupling strength. The linear relation between $c(r)$ and the pair interaction $\phi(r)$ of the MSA must clearly be transcended, e.g. at sufficiently low density $c(r)$ should reduce to the Mayer function⁽⁸⁷⁾ $(e^{-\phi(r)/k_B T} - 1)$. While this function obeys the MSA at large r its non-linearity seems to be a crucial feature for a transition.

REFERENCES

- (1) March, N.H. and Tosi, M.P., Atomic Dynamics in Liquids, Macmillan Press, London (1976), (1a, p.18), (1b, p.7), (1c, p.101).
- (2) Theory of Condensed Matter, Proceedings of an international course held at the International Centre for Theoretical Physics, Trieste 1967; International Atomic Energy Agency, Vienna (1968).
(2a, p.96), (2b, p.93), (2c, p.107).
- (3) Rasaiah, J.C. and Friedman, H.L., J.Chem.Phys. 48, 2742 (1968).
- (4) Stillinger, Jr., F.H. and Lovett, R., J.Chem.Phys. 49, 1991 (1968).
- (5) Outhwaite, C.W., J.Chem.Phys. 50, 2277 (1969).
- (6) Rasaiah, J.C. and Friedman, H.L., J.Chem.Phys. 50, 3965 (1969).
- (7) Waisman, E. and Lebowitz, J.L., J.Chem.Phys. 52, 4307 (1970).
- (8) Page, D.I. and Mika, K., J.Phys. C4, 3034 (1971).
- (9) Woodcock, L.V. and Singer, K., Trans.Faraday Soc. 67, 12 (1971).
- (10) Rasaiah, J.C., Card, D.N. and Valleau, J.P., J.Chem.Phys. 56, 248 (1972).
- (11) Waisman, E. and Lebowitz, J.L., J.Chem.Phys. 56, 3086, 3093 (1972).
- (12) Andersen, H.C. and Chandler, D., J.Chem.Phys. 57, 1918 (1972).
- (13) Larsen, B., Report of workshop on ionic liquids, CACAM (1974).
- (14) Lantelme, F., Turq, P., Quentrec, B. and Lewis, J.W.E.
Mol.Phys. 28, 1537 (1974).
- (15) Larsen, B., Chem.Phys.Lett. 27, 47 (1974).
- (16) Lewis, J.W.E., Woodcock, L.V. and Singer, K., J.Chem.Soc.Faraday Trans.II, 71, 301 (1975).
- (17) Edwards, F.G., Enderby, J.E., Howe, R.A. and Page, D.I.
J.Phys. C8, 3483 (1975).
- (18) Derrien, J.Y. and Dupuy, J., J.Physique 36, 191 (1975).
- (19) Gillan, M., Larsen, B., Tosi, M.P. and March, N.H., J.Phys. C9, 889 (1976).
- (20) Abramo, M.C., Caccamo, C., Pizzimenti, G., Parrinello, M. and Tosi, M.P., J.Phys. C9, L593 (1976).

- (21) Abramo, M.C., Caccamo, C. and Pizzimenti, G., Phys. and Chem. of Liquids (1977) (In the Press).
- (22) Lowden, L.J. and Chandler, D., J.Chem.Phys. 59, 6587 (1973).
- (23) Lowden, L.J. and Chandler, D., J.Chem.Phys. 61, 5228 (1974).
- (24) Hsu, C.S., Chandler, D. and Lowden, L.J., Chem.Phys. 14, 213 (1976).
- (25) Suzuki, K. and Egelstaff, P.A., Can.J.Phys. 52, 241 (1974).
- (26) Egelstaff, P.A., Page, D.I. and Powles, J.G., Mol.Phys. 20, 881 (1971).
- (27) Dore, J.C., Walford, G. and Page, D.I., Mol.Phys. 29, 565 (1975).
- (28) O'Malley, J.A. and Narten, A.H., "X-ray Diffraction Data on Liquid Benzene at 25⁰C" ORNL-4166, July 1967.
- (29) Barojas, J., Levesque, D. and Quentrec, B., Phys.Rev. A7, 1092 (1973).
- (30) Powles, J.G., J.Phys. C8, 895 (1975).
- (31) Gillan, M.J., J.Phys. C9, 2261 (1976).
- (32) Boyce, J.B. and Mikkelsen, J.C., J.Phys. C10, L41 (1977).
- (33) Grantham, L.F. and Yosim, S.J., J.Chem.Phys. 45, 1192 (1966).
- (34) Slagle, O.D. and Nelson, R.P., J.Nucl.Mater. 40, 349 (1971).
- (35) Ohse, R.W., Berrie, P.G., Bogensberger, H.G. and Fischer, E.A., J.Nucl.Mater. 59, 112 (1976).
- (36) Fischer, E.A., Kinsman, P.R. and Ohse, R.W., J.Nucl.Mater, 59, 125 (1976).
- (37) Landölt-Bornstein, 6th edition 1960, Vol.II, Pt.7, p.4. (Springer-Verlag, Berlin).
- (38) Bockris, J. O'M., Crook, E.H., Bloom, H. and Richards, N.E., Proc.Roy.Soc.(London), A255, 558 (1960).
- (39) Cabane, B. and Friedel, J., J.Physique 32, 73 (1971).
- (40) Hansen, J.P. and McDonald, I.R., Theory of Simple Liquids, Academic Press, London (1976), Chapter 2.
- (41) March, N.H., Liquid Metals, Pergamon Press, Oxford (1968), p.6.

- (42) Ornstein, L.S. and Zernike, F., Proc.Acad.Sci.Amsterdam, 17, 793 (1914).
- (43) Tosi, M.P., Parrinello, M. and March. N.H., Nuovo Cimento 23B, 135 (1974).
- (44) Benson, G.C., Freeman, P.I. and Dempsey, E., J.Am.Ceram.Soc. 46, 43 (1963).
- (45) Dolling, G., Cowley, R.A. and Woods, A.B.D., Can.J.Phys. 43, 1397 (1965).
- (46) Abramo, M.C., Caccamo, C. and Pizzimenti, G., Internal Report No.1 (1977), Istituto di Fisica and GNSM of CNR, Messina, Italy.
- (47) Percus, J.K. and Yevick, G.J., Phys.Rev. 110, 1 (1958).
- (48) Lebowitz, J.L., Phys.Rev. 133, A895 (1964).
- (49) Ashcroft, N.W. and Langreth, D.C., Phys.Rev. 156, 685 (1967).
- (50) Enderby, J.E. and North, D.M., Phys. and Chem. of Liquids, 1, 1 (1968).
- (51) Pearson, F.J. and Rushbrooke, G.S., Proc.Roy.Soc. (Edinburgh), A64, 305 (1957).
- (52) Price, D.L. and Copley, J.R.D., Phys.Rev. A11, 2124 (1975).
- (53) Tables of Physical and Chemical Constants, Longman, London, 14th edition (1973).
- (54) Cordfunke, E.H.P., The Chemistry of Uranium including its applications in Nuclear Technology, Elsevier, Amsterdam (1968). (54a, p.77), (54b, p.68).
- (55) Wartheim, M., Phys.Rev.Letters 10, 321 (1963).
- (56) Thiele, E., J.Chem.Phys. 39, 474 (1963).
- (57) Gerrad, M., CERN Computer 6000 Series, Prog.Library C400 (1971).
- (58) Ubbelohde, A.R. Melting and Crystal Structure, Clarendon Press, Oxford (1965), p.147.
- (59) Chandler, D. and Andersen, H.C., J.Chem.Phys. 57, 1930 (1972).
- (60) Chandler, D., J.Chem.Phys. 59, 2742 (1973).

- (61) Lowden, L.J., RISM, RISMGR, RISMSK, Program No.QCPE 306, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana 47401, U.S.A.
- (62) Powell, M.J.D., Harwell subroutine, No. VA05A.
- (63) Kölbig, K.S., CERN Computer Centre, Program No. D103.
- (64) Darnell, A.J. and McCollum, W.A., J.Chem.Phys. 55, 116 (1971).
- (65) Handbook of Chemistry and Physics, Cleveland Ohio (Chemical Rubber Company), 53rd edition, 1972-1973.
- (66) Tables of interatomic distances and configuration in molecules and ions. Special publication No.18, the Chemical Society, London. (Supplement 1956-1959).
- (67) Weeks, J.D., Chandler, D. and Andersen, H.C., J.Chem.Phys. 54, 5237 (1971).
- (68) Weeks, J.D., Chandler, D. and Andersen, H.C., J.Chem.Phys. 55, 5422 (1971).
- (69) Andersen, H.C., Chandler, D. and Weeks, J.D., J.Chem.Phys. 56, 3812 (1972).
- (70) Abramo, M.C., Parrinello, M. and Tosi, M.P., J.Nonmetals 2, 57 (1973).
- (71) Høye, J.S., Lebowitz, J.L. and Stell, G., J.Chem.Phys. 61, 3253 (1974).
- (72) Stell, G. and Sun, S.F., J.Chem.Phys. 63, 5333 (1975).
- (73) Henderson, D. and Blum, L., Mol.Phys. 32, 1627 (1976).
- (74) Barker, J.A. and Henderson, D., J.Chem.Phys. 47, 2856 (1967).
- (75) Barker, J.A. and Henderson, D., J.Chem.Phys. 47, 4714 (1967).
- (76) Verlet, L., Phys.Rev. 165, 201 (1968).
- (77) Longuet-Higgins, H.C. and Widom, B., Mol.Phys. 8, 549 (1964).
- (78) Palmer, R.G. and Weeks, J.D., J.Chem.Phys. 58, 4171 (1973).
- (79) Tourand, G. and Breuil, M. J.Physique, 32, 813 (1971).
- (80) Brush, S.G., Sahlin, H.L. and Teller, E., J.Chem.Phys. 45, 2102 (1966).
- (81) Hansen, J.P., Phys.Rev. A8, 3096 (1973).
- (82) Pollock, E.L. and Hansen, J.P., Phys.Rev. A8, 3110 (1973).

- (83) Hansen, J.P., McDonald, I.R. and Pollock, E.L., Phys.Rev.A11, 1025 (1975).
- (84) Debye, P. and Hückel, E., Z.Physik, 24, 185 (1923).
- (85) Springer, J.F., Pokrant, M.A. and Stevens, F.A., J.Chem.Phys., 58, 4863 (1973).
- (86) Gillan, M.J., J.Phys. C7, L1 (1974).
- (87) Mayer, J.E. and Mayer, M.G., Statistical Mechanics, John Wiley and Sons, New York, 1940.