

THE STRUCTURE OF AQUEOUS SOLUTIONS

BY

Alan K. Soper

A thesis submitted for the degree of

Doctor of Philosophy

University of Leicester, 1977.

THESIS
521913
31 3 77



PREFACE

The work presented in this thesis would not have been possible without the assistance, both physically and morally, of a large number of people in various establishments, and I am extremely grateful to all these people, whether they are mentioned here or not. In particular, Professor Enderby, my supervisor, must be thanked for his inspiring enthusiasm and sense of humour - without them I think I would have given up long ago. I should like to thank Dr. Neilson for many interesting 'arguments', and for much help in the presentation of the nickel chloride data. My thanks are also due to Dr. Howe for much useful discussion and advice, and to Dr. Nguyen for permission to quote his data on liquid iron, and liquid nickel-telluride alloys.

The experiments were performed at I.L.L., Grenoble, and Dr. Howells as local contact played a major part in ensuring the smooth running of the experiments : I wish to thank him for his very generous hospitality. I am also grateful to Drs. Knoll, Chieux and Egger, for their excellent maintenance of the D4 diffractometer, and their continual readiness to help at awkward moments.

Computing was an essential part of the data analysis: I should like to thank the staff of the computer laboratories at I.L.L. and Leicester for the considerable use of their respective machines.

The samples were provided by the Science Research Council, and sample preparation was aided considerably by the cooperation of Messrs. Les Bint and Dave McGahan of the Chemistry Division at Harwell.

I am greatly indebted to the Theoretical Physics group at Leicester, especially Nick Quirke and Professor Beeby, for many illuminating discussions. I must thank the S.R.C. for their Research Studentship, and their very generous support whilst in Grenoble. In the later stages, my parents and family were wonderful in providing a warm friendly home, a whole feast of excellent grub, and endless cups of coffee. I thank myself for laboriously typing the text.

STATISTICAL MECHANICS AND NEUTRON SCATTERING1) Distribution Functions

Progress in the structure of liquids has generally been achieved as an interplay between theory and experiment, and it is necessary to define a quantity which relates to both. Distribution functions form the building blocks of statistical mechanical theories, (1) and (2), and can be obtained from experiment, at least in principle.

In terms of the γ -space, each particle j is given a momentum vector \underline{p}_j and a position vector \underline{r}_j . There are N particles in the system and we represent the entire system by $3N$ dimensional vectors $\underline{p}^{(N)}$ and $\underline{r}^{(N)}$, where, for example, $\underline{r}^{(N)} = \sum_j \underline{r}_j$. Quantum mechanics applies to the system, so we define an elemental volume of phase space as $h^{-3N} d\underline{p}^{(N)} d\underline{r}^{(N)}$, where h is Planck's constant, and $d\underline{p}^{(N)} = \prod d\underline{p}_j$. We then define a generic distribution function $F(\underline{p}^{(N)}, \underline{r}^{(N)})$ for a system with identical particles such that

$$h^{-3N} F(\underline{p}^{(N)}, \underline{r}^{(N)}) d\underline{p}^{(N)} d\underline{r}^{(N)} \quad \dots 1.1$$

is the probability that any one of the N particles will be found within $d\underline{p}_1 d\underline{r}_1$ at $\underline{p}_1, \underline{r}_1$, while simultaneously any other particle will be found within $d\underline{p}_2 d\underline{r}_2$ at $\underline{p}_2, \underline{r}_2$, etc.

There are $N!$ ways of distributing the particles in the system, which places a normalizing condition on the distribution:

$$h^{-3N} \int \dots \int F(\underline{p}^{(N)}, \underline{r}^{(N)}) \prod_{j=1}^N d\underline{p}_j d\underline{r}_j = N! \quad \dots 1.2$$

In the same way we define the distribution for a subset of $k \leq N$ particles as:

$$F^{(k)}(\underline{p}^{(k)}, \underline{r}^{(k)}) = \frac{1}{(N-k)!} \int \dots \int F(\underline{p}^{(N)}, \underline{r}^{(N)}) \prod_{j=1}^N d\underline{p}_j d\underline{r}_j \quad \dots 1.3$$

The factor $1/(N-k)!$ arises because there are $(N-k)!$ ways of introducing the $N-k$ remaining particles to the system.

Hence this subset has the normalizing condition:

$$1/h^{3N} \int F^{(k)}(\underline{p}^{(k)}, \underline{r}^{(k)}) \prod_{j=1}^k dp_j dr_j = \frac{N}{(N-k)!} \quad \dots 1.4 \quad 2.$$

and phase distributions of consecutive order are related, from 1.3,

by

$$F^{(k)}(\underline{p}^{(k)}, \underline{r}^{(k)}) = 1/(N-k) \int F^{(k+1)}(\underline{p}^{(k+1)}, \underline{r}^{(k+1)}) dp_{k+1} dr_{k+1} \quad \dots 1.5$$

An important quantity, derived from the phase distribution, is the configuration distribution, obtained by integrating over all momenta:

$$n^k g^{(k)}(\underline{r}^{(k)}) = 1/h^{3N} \int F^{(k)}(\underline{p}^{(k)}, \underline{r}^{(k)}) d\underline{p}^{(k)}, \quad k \leq N \quad \dots 1.6$$

where n is the average number of particles per unit volume of configurational space. So defined, $g^{(k)}(\underline{r}^{(k)})$ is the probability of finding any particle within $d\underline{r}_1$ at \underline{r}_1 , whilst simultaneously finding any other particle within $d\underline{r}_2$ at \underline{r}_2 , etc. Consecutive distributions are obtained from (1.5):

$$g^{(k)}(\underline{r}^{(k)}) = \frac{n}{(N-k)} \int g^{(k+1)}(\underline{r}^{(k+1)}) d\underline{r}_{k+1} \quad \dots 1.7$$

Thus, for example, the pair and triplet correlation functions are given by:

$$n^2 g^{(2)}(\underline{r}_1, \underline{r}_2) = \frac{n^N}{(N-2)!} \int \dots \int g^{(N)}(\underline{r}^{(N)}) \prod_{j=3}^N d\underline{r}_j \quad \dots 1.8a$$

$$n^3 g^{(3)}(\underline{r}_1, \underline{r}_2, \underline{r}_3) = \frac{n^N}{(N-3)!} \int \dots \int g^{(N)}(\underline{r}^{(N)}) \prod_{j=4}^N d\underline{r}_j \quad \dots 1.8b$$

and from 1.7

$$g^{(2)}(\underline{r}_1, \underline{r}_2) = \frac{n}{(N-2)} g^{(3)}(\underline{r}_1, \underline{r}_2, \underline{r}_3) d\underline{r}_3 \quad \dots 1.9$$

Combining 1.6, 1.7 and 1.4, we have the important normalization condition:

$$\int n^2 g^{(2)}(\underline{r}_1, \underline{r}_2) d\underline{r}_1 d\underline{r}_2 = \frac{N!}{(N-2)!} = N(N-1) \quad \dots 1.10$$

The next stage in the problem is to relate the phase distributions to macroscopic variables. This is done by means of ensembles.

2) Ensembles

The idea of a cloud of points in γ -space, each point representing a complete system, leads to the concept of an ensemble of

systems in thermal and numerical contact. The entire ensemble, however, is isolated so that although the energy and number of particles may vary from one system to another, the totals for the ensemble remain constant. This is called the Grand Canonical form. The usual procedure is to assume energy fluctuations are small, so the average distribution is used as the most probable distribution. Moreover, the time average of a function of the system is set equal to the average over the ensemble.

For a one component system, the probability distribution,

F_G , is defined as :

$$F_G(\underline{p}^{(N)}, \underline{r}^{(N)}) = \frac{1}{\Xi} \exp\left(\frac{\mu N - H(\underline{p}^{(N)}, \underline{r}^{(N)})}{k_B T}\right) \quad \dots 1.11$$

where μ is to be associated with the thermodynamic chemical potential, H is the Hamiltonian for the system with N particles, k_B is Boltzmann's constant, and T is the absolute temperature. Ξ is the Grand partition function for the ensemble - it forms a normalizing function for F_G .

$$\Xi = \sum_{N \geq 0} \exp\left(\frac{\mu N}{k_B T}\right) \exp\left(\frac{-H(\underline{p}^{(N)}, \underline{r}^{(N)})}{k_B T}\right) \quad \dots 1.12$$

This may be written in the form:

$$\Xi = \sum_{N \geq 0} \lambda^N Z(N) \quad \dots 1.13$$

where λ , the absolute activity coefficient, is given by

$$= \exp\left(\frac{\mu}{k_B T}\right) \quad \dots 1.14$$

and $Z(N)$ is the Canonical partition function.

The link with thermodynamics is made via the entropy, S :-

$$\begin{aligned} S &= -k \langle \ln F_G \rangle \\ &= k \ln \Xi + \frac{\langle H \rangle}{T} - \frac{\mu \langle N \rangle}{T} \end{aligned} \quad \dots 1.15$$

The brackets $\langle \dots \rangle$ represent the average over the ensemble. We associate $\langle H \rangle$ with the internal energy of the system, and the similarity of this equation with the thermodynamic equation for the

Helmholtz free energy, (see, for example, ref. (3)):-

$$F = U - TS,$$

suggests we associate the Helmholtz free energy with Z :

$$F = k_B^T \ln Z + N k_B^T \ln \lambda \quad \dots 1.16$$

3) Multi-component systems

If we introduce more than one atomic species to the system, then, in general, each species will have its own chemical potential, and the phase distribution is now expressed in the form

$$F_G(\underline{p}^{(N)}, \underline{r}^{(N)}) = \frac{1}{Z} \exp\left(\frac{\underline{\mu} \cdot \underline{N} - H(\underline{p}^{(N)}, \underline{r}^{(N)})}{k_B^T}\right) \quad \dots 1.17$$

where $\underline{\mu} \cdot \underline{N} = \sum_a \mu_a N_a$, and μ_a , N_a are the chemical potential and number of atoms respectively of species a .

There is no effect on the meaning of the overall distribution functions, $f^{(N)}$. As an obvious example of a multi-component system, however, consider the electrical resistivity of binary alloys. in the formalism of Faber and Ziman (4). Since different species of atom have different scattering properties for the electron, the resistivity is dependent on the atomic distribution.

The overall distribution function is split into a series of partial distributions, according to their respective scattering properties. This can be complicated if we have to consider the triplet or higher order correlations, but for pair correlation the total is represented by a sum:

$$g^{(2)}(\underline{r}_1, \underline{r}_2) = \sum_a \sum_b c_a c_b g_{ab}^{(2)}(\underline{r}_1, \underline{r}_2) \quad \dots 1.18$$

where the sums over a and b are each over all the atomic species, and c_a is the atomic fraction of a atoms. The partial distribution, $g_{ab}^{(2)}(\underline{r}_1, \underline{r}_2)$, represents the probability of finding an atom of species a at \underline{r}_1 , and an atom of species b at \underline{r}_2 .

Another reason for this choice of separation is based

on the normalizing condition, 1.10. We can represent the total number of particles in the system as

$$N = \sum_a N_a \quad \dots 1.19$$

$$\text{Then } N(N-1) = \sum_a N_a \left(\sum_b N_b - 1 \right)$$

$$= \sum_a N_a (N_a - 1) + \sum_a \sum_{b \neq a} N_a N_b \quad \dots 1.20$$

Hence we have a normalizing condition for the partial distributions:

$$n^2 c_a^2 \int g_{aa}^{(2)}(\underline{r}_1, \underline{r}_2) d\underline{r}_1 d\underline{r}_2 = N_a (N_a - 1) \quad \dots 1.21a$$

$$n^2 c_a c_b \int g_{ab}^{(2)}(\underline{r}_1, \underline{r}_2) d\underline{r}_1 d\underline{r}_2 = N_a N_b \quad a \neq b \quad \dots 1.21b$$

4) Neutron Scattering

Various descriptions of the theory in relation to liquids are available, references (5) - (12). Van Hove (6) is generally invoked in the course of these discussions. The scattering process of the neutron is intimately bound up with its wave-particle duality. The fact that a single neutron can set up a series of scattered waves from an array of scattering centres, which then combine, coherently or incoherently, to form a single neutron, is incomprehensible on any classical basis, and the quantum mechanical approach, therefore, is to consider each neutron as being scattered by the entire array of nuclei available to it.

The neutron is given an initial wave vector, \underline{Q}_0 , so its initial momentum is $\hbar \underline{Q}_0$, where \hbar is Planck's constant/ 2π , and a scattered wave vector \underline{Q}_1 . The momentum transferred to the system in scattering the neutron is

$$\hbar \underline{Q}_0 = \hbar \underline{Q}_0 - \hbar \underline{Q}_1 \quad \dots 1.22$$

and the energy transfer is

$$w = \hbar^2 (Q_1^2 - Q_0^2) / 2m \quad \dots 1.23$$

m being the mass of the neutron.

When a neutron strikes a nucleus it is affected by three influences:

i) the neutron-nuclear potential - this is generally very short range (10^{-14} m) compared with the wavelength of the neutron (10^{-10} m) - hence the assumption of s-wave scattering only (i.e. no angular momentum interaction),

ii) the mass of the nucleus - this affects the recoil of the nucleus and hence the energy transferred to it by the neutron,

iii) the forces holding the nucleus in position, principally due to the surrounding electrons and nuclei. These also determine whether any vibrational modes in the bonds may be excited.

Scattering characteristics are expressed in terms of cross-sections. Thus, for an incident flux of N neutrons per unit area, the number scattered into solid angle $d\Omega$ is $N \left(\frac{d\sigma}{d\Omega} \right) d\Omega$, where $\frac{d\sigma}{d\Omega}$ is the differential scattering cross-section. As, in general, there will be an energy transfer, then a partial differential scattering cross-section is defined such that $N \left(\frac{d^2\sigma}{d\Omega dw} \right)$ is the number of neutrons scattered into solid angle $d\Omega$ with an energy gain of dw .

5) Inelastic Scattering Cross-section

In appendix 1 is derived an expression for the partial differential cross-section (equation A1.10). For neutrons, assumption (i) above implies a δ -function for $V_j(\underline{r} - \underline{R}_j)$ - the Fermi pseudo-potential (13) :

$$V_j(\underline{r} - \underline{R}_j) = \frac{2\pi b_j}{m} \delta(\underline{r} - \underline{R}_j) \quad \dots 1.24$$

and the Fourier component of a δ -function is a constant, $\frac{2\pi b_j}{m}$.

b_j is called the coherent bound scattering length for atom j (by

analogy with scattering from rigid spheres)

6) Elastic Scattering

If all the atoms were rigidly bound, neutrons would have the same energy after scattering as before. The Fourier transform over w is then performed immediately, giving a $\delta(t)$ function for the time dependence. This leaves

$$\frac{d\sigma}{d\Omega} = \sum_j \sum_k b_j b_k \exp(-i\mathbf{Q} \cdot \mathbf{R}_j(0)) \exp(i\mathbf{Q} \cdot \mathbf{R}_k(0)). \quad \dots 1.25$$

The cases for $j=k$ and $j \neq k$ separate:

$$\sum_j b_j^2 + \sum_{j \neq k} b_j b_k \exp(i\mathbf{Q} \cdot (\mathbf{R}_k - \mathbf{R}_j)) \quad \dots 1.26$$

The second summation in 1.26 is considered in appendix 2. For powder diffractometry and liquids the cross-section is averaged over all directions of the incident \mathbf{Q} vector, and we see only the radial distribution function. Introducing partial structure factors in the Faber-Ziman formulation, i.e.

$$a_{ab}(Q) = 1 + 4\pi n \int (g_{ab}(r) - 1) \frac{\sin(Qr)}{Qr} r^2 dr \quad \dots 1.27$$

and atomic fractions

$$c_a = \frac{N_a}{N} \quad \dots 1.28$$

we finally obtain for the scattering cross-section

$$\frac{d\sigma}{d\Omega} = N F(Q),$$

where

$$F(Q) = \sum_a c_a b_a^2 + \sum_a c_a^2 b_a^2 (a_{aa}(Q) - 1) + 2 \sum_a \sum_{b \neq a} c_a c_b b_a b_b (a_{ab}(Q) - 1) \quad \dots 1.29$$

Here we have made use of the definition A2.8, so that $g_{ab}(r)$ is invariant in the order of a, b , i.e. $g_{ab}(r) = g_{ba}(r)$.

7) Isotopes in Neutron scattering

There are two scattering lengths for each isotope with spin, and the isotopes are distributed randomly among the atoms of a given element.

The summations in equation 1.29 must first be performed over all the spin and isotope states of each element, but the partial structure factors are left outside such averages:-

$$F(Q) = \sum_a c_a \langle b_a^2 \rangle + \sum_a c_a^2 (a_{aa}(Q) - 1) \langle b_a \rangle^2 + 2 \sum_a \sum_{b>a} c_a c_b (a_{ab}(Q) - 1) \langle b_a b_b \rangle \dots 1.30$$

where the averages are performed over spin and isotope. The coherent bound scattering length of an element is then

$$b_a = \langle b_a \rangle_{\text{isotope, spin}} \dots 1.31$$

and the isotope bound scattering length is

$$b_{ia} = \langle b_{ia} \rangle_{\text{spin}} \dots 1.32$$

8) Isotopic Substitution

It is seen from tables (for example (14) and (15)) that scattering lengths show quite wide variations with isotope, and some are negative. This affords a method of extracting partial structure factors (Enderby (10)), assuming suitable isotopes are available. It would be impossible with X-rays, where the form factors are independent of isotope.

The first term in equation 1.30 represents the total scattering cross-section of the sample. In general, since the atoms are not rigidly bound, it depends on the neutron energy and the atomic environment. For heavy elements the measured cross-section is close to the bound value, but for light elements, such as hydrogen and deuterium, there is considerable recoil. In the present experiment the total cross-section was calculated as the average of that for

the water molecule, (see (16)), plus the bound cross-section of the two ions.

This total scattering cross-section also affects the choice of isotopes. Hydrogen, for example, has a much larger total cross-section than its coherent scattering, so is unsuitable: for accurate structure factors, the second and third terms in equation 1.30 should predominate. As a result, heavy water is used for the solvent. For the choice of solute, sodium chloride was readily available with chlorine isotopes, which have a suitable range of scattering lengths.

A solution of sodium chloride in heavy water presents to neutrons a four-component system, D, O, Na, Cl, having ten partial structure factors. Examination of 1.30 shows that just two chlorine substitutions (mass numbers 35 and 37), and a subtraction, produces:-

$$F_{35}(Q) - F_{37}(Q) - \Delta = c_{Cl}^2 (b_{35}^2 - b_{37}^2) (a_{ClCl} - 1) + 2c_{Cl} (b_{35} - b_{37}) \\ c_D b_D (a_{ClD} - 1) + c_O b_O (a_{ClO} - 1) + \\ c_{Na} b_{Na} (a_{ClNa} - 1) \quad \dots 1.33$$

where $\Delta = c_{Cl} (\langle b_{35}^2 \rangle - \langle b_{37}^2 \rangle)$,

and a third substitution (natural chlorine) with further subtractions gives

$$a_{ClCl} - 1 = \frac{1}{c_{Cl}^2 (b_{nat} - b_{35})} \left[\frac{F_{nat} - F_{37} - \Delta_1}{(b_{nat} - b_{37})} - \frac{F_{35} - F_{37} - \Delta_2}{(b_{35} - b_{37})} \right] \quad \dots 1.34$$

Equation 1.33 represents the environment surrounding the chlorine ion, and it will be dominated by the D - Cl and O - Cl terms, because of

the concentration factors. A Fourier transform of this equation produces a similarly weighted sum of the radial distributions, and so is a picture of the hydrated water molecules. Equation 1.34 represents the distribution of the chlorine ions in the solution.

$$G_2^{ij} = G_0^{ij} \frac{h^2}{M_i M_j} \frac{h^2 Q^4}{4} + (\underline{P}_i \cdot \underline{Q})(\underline{P}_j \cdot \underline{Q}) \left(\exp i \underline{Q} \cdot (\underline{r}_i - \underline{r}_j) \right)$$

The second term in the square brackets represents the correlation of momentum of the different nuclei. For classical statistics there is no such correlation, and this is usually treated as negligible.

Equations 1.35 and 1.36 may be combined, and the subtraction of 1.37 repeated here, after introducing the partial structure factors in exactly the same way as before.

For the self terms this produces to first order:

$$\left(b_{35}^2 - b_{37}^2 \right) \left(1 - \frac{m}{M_{Cl}} \left(4 \sin^2 \frac{\theta}{2} - \frac{1}{3E_0} K_{av} \right) + \dots \right) \quad \dots 1.39$$

If K_{av} is assumed to be of the order $k_B T$, and E_0 is 0.16 eV (for $\lambda = 0.69 \text{ \AA}$), the third term at $T = 293^\circ \text{ K}$ is 0.006, so it is reasonable to ignore it compared to $4 \sin^2 \frac{\theta}{2}$. m is the mass of the neutron.

For $\theta = 180^\circ$, the overall correction is -0.114, so we should expect a small fall in the term with increasing angle. It is not possible to employ this formula as the detector efficiency is not known.

However, in appendix 3 it is shown that there is a straightforward method for correcting any fall in the value of Δ .

For the interference terms, G_1^{ij} disappears, and so the second order corrections must be considered. The terms obtained are:

$$c_{Cl}^2 (a_{ClCl} - 1) (b_{35}^2 - b_{37}^2) \left(1 - \frac{m^2}{M_{Cl}^2} F_{ClCl}(\theta) \right) + 2c_{Cl} (b_{35} - b_{37}) \left[\right.$$

$$\left. c_D b_D (a_{ClD} - 1) \left(1 - \frac{m^2}{M_{Cl} M_D} F_{ClD}(\theta) \right) + \text{similar terms.} \right]$$

... 1.40

where $F_{ij}(\theta)$ is a function of a_{ij} and its derivatives which cannot, in general, be calculated (although the possibility of applying the correction iteratively has apparently not been

investigated), and momentum correlations are ignored. The important result is that the a_{DD} and a_{D0} terms and their troublesome Placzek corrections have disappeared.

CHAPTER 2THE STRUCTURE OF AQUEOUS SOLUTIONS1) Early Concepts of Dissociation

Modern electrolyte theory has evolved from several discoveries which were made in 1887. Gibbs (17) had previously developed a system of thermodynamics so that measurements of elevation of boiling point, lowering of freezing point, vapour pressure of solvent, solubility, osmotic pressure, conductivities, on solutions could all be related to a single thermodynamic quantity - the chemical potential. Raoult (18) showed that the lowering of vapour pressure of the solvent is proportional to the mole fraction of the solute. Van't Hoff (19) subsequently showed this to be proportional to the number of solute particles present. For example, from Raoult's Law it is possible to estimate the molecular weight of the solute, Dreisbach (20). The molecular weight of KCl in solution, as determined by this method, turns out to be nearly half its actual value of 75, implying that the solute molecule is dissociated into two particles. Another example is that the osmotic pressure of a 1-1 electrolyte is approximately double that of a sucrose solution of the same molality.

The electrical properties of dissociated solutions (mostly acid, base and salt solutions) had already been extensively studied: the concept of ions as charge carriers was introduced, and it was known that at low concentrations the equivalent conductivity of a solution was a maximum at infinite dilution. Arrhenius (21) proposed that when these substances dissolved in water they dissociated into positive and negative charged ions, and the degree of dissociation, α , was related

to the equivalent conductivity, Λ , by

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}} \quad \dots 2.1$$

where Λ_{∞} is the equivalent conductivity at infinite dilution. The implication was that the ions moved at a constant speed, independent of the concentration and inter-ionic forces.

The dissociation constant could also be defined from the Ostwald Dilution Law (21) in terms of the ionization constant, and discrepancies between the two definitions led to increasing support for a theory which allowed the solute to be completely dissociated, even at high concentrations, and the reduction in mobility of the ions was then attributed to their electrostatic attraction: the actual behaviour of osmotic coefficients, activity coefficients, and equivalent conductivities was quite unlike that predicted from the Arrhenius theory.

2) Debye-Huckel Theory (23)

The method of Debye and Huckel is to solve the Poisson-Boltzmann equation for a distribution of equal numbers of positive and negative charges. It invokes two major approximations (24):

(i) The potential of mean force between a pair of ions ignores all short range repulsive effects, and is simply the Coulomb interaction due to the charges on each ion. The effect of the solvent appears only in the dielectric constant, ϵ , of the medium in which the ions are situated.

Thus the potential energy of ion j, with charge q_j , due to ion i a distance r away is represented by

$$w_{ij}(r) = q_j \phi_i(r) \quad \dots 2.2$$

where $\varphi_i(\underline{r})$ is the electrostatic potential due to the charge q_i .

(ii) The quantity $w_{ij}(\underline{r})$ is assumed very small compared to $k_B T$, so that the distribution function between ions i and j may be approximated to

$$\begin{aligned} g_{ij}(\underline{r}) &= \exp\left(-\frac{w_{ij}(\underline{r})}{k_B T}\right) \\ &\approx 1 - \frac{q_j \varphi_i(\underline{r})}{k_B T} \end{aligned} \quad \dots 2.3$$

Neither approximation can work if the ions approach each other closely, so the resulting formulation can only work for extremely dilute solutions. Assuming a spherically symmetric charge distribution, the potential is

$$\varphi_i(\underline{r}) = \frac{q_i}{\epsilon} \frac{\exp(-kr)}{r} \quad \dots 2.4$$

where k , the reciprocal Debye length, is defined by

$$k^2 = \frac{4}{\epsilon k_B T} \sum_s n_s q_s^2 \quad \dots 2.5$$

and n_s is the number density of ions with charge q_s .

Subsequent modifications to the theory included the introduction of an ionic diameter, a , representing the distance of closest approach. Bjerrum (25) considered a 1-1 electrolyte to be associated if the ions approached within a distance of $\frac{1}{2} \frac{q^2}{\epsilon k_B T}$, and defined this as the closest distance of approach.

The success of the theory and its modifications is by now very well established. However it does only apply to very dilute solutions, typically 0.001 molar or less for 1-1 electrolytes. For 2-1 electrolytes the approximation, equation 2.3, when substituted into the Poisson-Boltzmann equation, is much less satisfactory, and the theory will apply to an even smaller range of concentration, Robinson and Stokes (26).

3) Modern Electrolyte Theory

There have been many semi-empirical attempts to extend the Debye-Huckel approach to higher concentrations, (26) and (27), and at least one major attempt to give electrolyte theory a rigorous statistical mechanical background, Friedman (28). The aim is to calculate thermodynamic quantities as functions of concentration and then make a comparison with experiment. The calculations are performed either with Monte Carlo / Molecular Dynamics simulations, or by approximation theories, such as the Percus Yevick or Hypernetted Chain approaches, Rasaiah (29). The former are time consuming and expensive, but act as standards with which to judge the more approximate results. A potential of mean force between ion pairs is modelled, and thermodynamic properties are evaluated from the radial distribution which is generated from the potential. Friedman (30) discusses a typical form for the potential between ions i and j :-

$$U_{ij}(r) = \text{COUL}_{ij} + \text{COR}_{ij} + \text{CAV}_{ij} + \text{GUR}_{ij} . \quad \dots 2.6$$

COUL_{ij} represents the electrostatic potential. COR_{ij} is the hard core repulsive potential, and assumes either an inverse power or exponential form. CAV_{ij} represents the polarization of the cavity in the dielectric medium containing the ion, which results in a force pushing the cavity toward a region of lower field. GUR_{ij} is an adjustable parameter, introduced to represent the overlap of the cospheres of the hydrated solvent, Gurney (31).

This latter effect is the extent to which the solvent is usually considered in all the theories: it appears as a structureless medium, whose dielectric constant is modified only in the proximity of an ion. Nonetheless, the behaviour of activity coefficients for the models, is a considerable improvement over that for the Debye-Huckel formulation. The concentration for which agreement with experiment is satisfactory is now as high as 1 molar. Unfortunately at higher concentrations

the agreement becomes worse again, and Rasaiah attributes this to the absence, in the models, of any reference to solvent granularity: detailed calculations which include solvent - solvent and solvent - solute interactions have yet to be performed.

The statistical mechanical approach was established by MacMillan and Mayer (32): it regards the ions as a gas of finite charged particles moving in a structureless medium. This is the justification for the use of the traditional Percus-Yevick or Hyper-netted Chain equations. However, interest in the original Debye-Huckel method has been renewed recently by Bennetto and Spitzer (33). They argue that 'any positive contribution to the free energy function arising from the (hard core) repulsions (between the ions) is also intrinsic to the standard state, and does not, therefore, contribute to the non-ideality.' For high concentrations the Debye-Huckel assumption of a spherically symmetric charge distribution around an ion becomes inadequate, and instead the cloud is allowed to be polarized by the neighbouring charges: this contributes additional multipole interactions. Unfortunately, detailed comparison with experiment is left to another paper which has not appeared yet, although the authors claim the behaviour of activity coefficients, derived from their treatment, with concentration is 'realistic'. They also claim they can recover the cube root dependence of activity coefficients on molality - this dependence has been the subject of some controversy.

The cube root "law", previously examined by Ghosh (34) and Frank and Thompson (35), has been interpreted by Bahe and Parker (36) in terms of a lattice model of the solution. The solvent appears as a continuous dielectric, but solvation is introduced as a dielectric gradient over a range of 1.5 to 5 Å from the centre of the ion. Beyond this distance the dielectric constant assumes the bulk value of the solvent. When a second ion is brought up to a first, polarization

of the dielectric gradient produces a $\frac{1}{r^3}$ (repulsive) term to the electrostatic potential energy, additional to the Coulomb interaction. Bahe assumes the ions are on a lattice, and then performs a Madelung-type energy sum over the ion distribution. However, Quirke (Ph.D. Thesis, Leicester University, 1977) argues that such a sum is invalid because the energies of the induced dipoles are not pair-wise additive. Moreover the authors seem unaware of all the recent X-ray and neutron scattering data on aqueous solutions.

As an overall view, it is clear that there is no unique theory for the structure of concentrated aqueous solutions. One of the difficulties of all the approaches is that they calculate thermodynamic properties, which are likely to be insensitive to the microscopic arrangement of the solution, and hence to the detailed form of the ion-ion and ion-solvent forces.

4) Evidence from X-ray Diffraction

Since the review of X-ray scattering data on aqueous solutions by Safford and Leung (37), there has been a considerable literature on the subject, and a lot of work published in Zhurnal Strukturnoi Khimii is now available in English translation.

For water, a tetrahedral near-neighbour configuration of water molecules, with some interstitial positions, which increase in number as the temperature is raised, has emerged as the most likely model. There is some disagreement over which precise disordered lattice model is used: Narten (38) proposes a disordered Ice I lattice with interstitial molecules, whereas O'Reilly (39) favours a mixture of Ice Ic and Ice VII lattices. However, because of the high degree of disorder beyond

Figure 2.1

List of principal contributors to structure of aqueous solutions,
using X-ray diffraction.

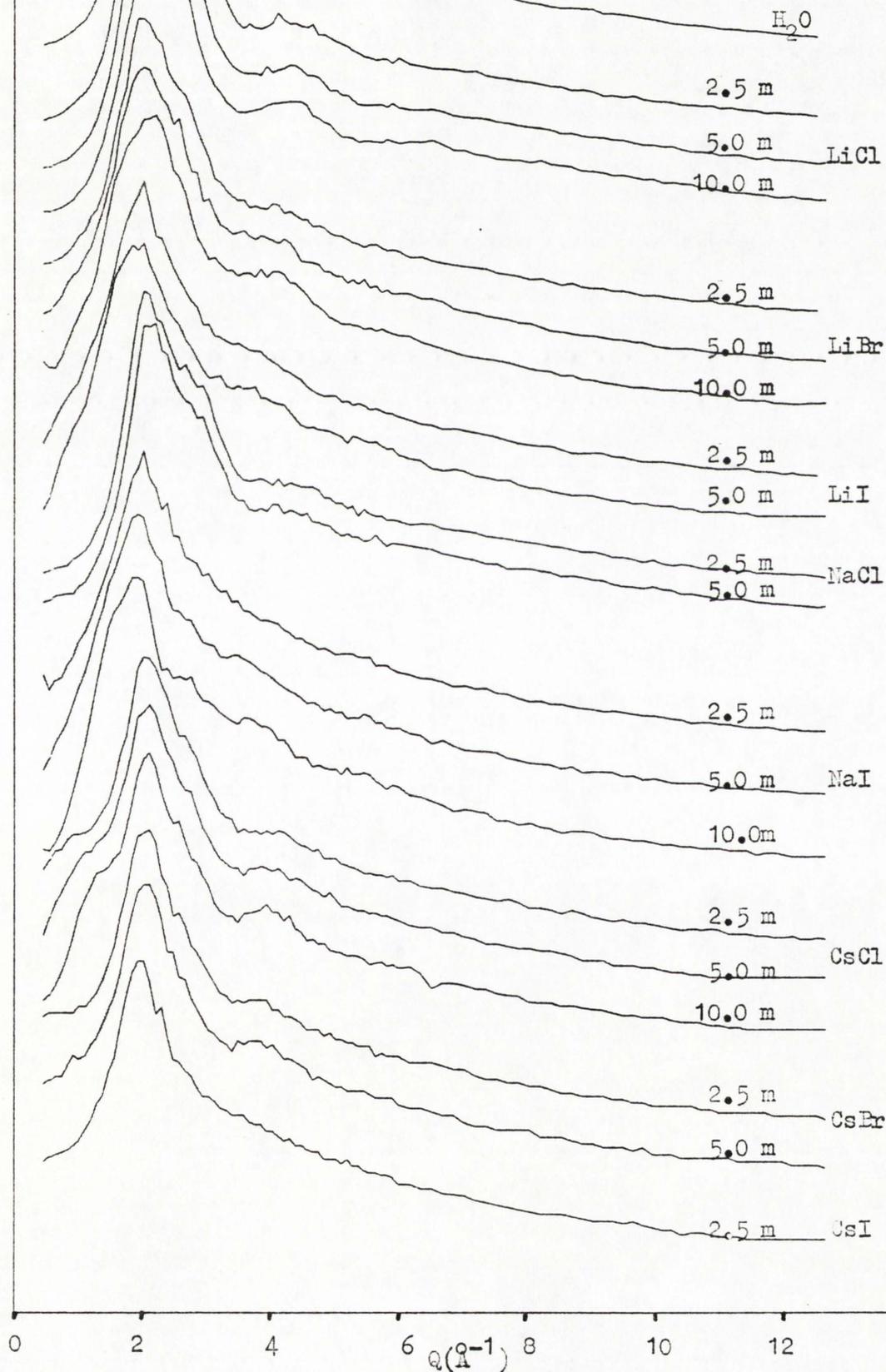
Author(s)	Ref.	Solute
Brady, Krause	42	KOH, KCl
Brady	43	KOH, LiCl
Brady	44	FeCl ₃
Strauss	45	LiI
Kruh, Standley	46	ZnCl ₂
Shapovalov, Radchenko, Lesovitskaya	47	K ₂ SO ₄ , Na ₂ SO ₄ , Li ₂ SO ₄
Ryss, Radchenko	47a	NaBF ₄
Dorosh, Skryshevskii	48	MgCl ₂ , NiCl ₂
Radchenko, Ryss	49	NH ₄ BF ₄ , LiBF ₄
Wertz, Lawrence, Kruh	50	ZnBr ₂
Namasivayam	51	HCl
Lawrence, Kruh	52	Alkali-metal halides
Dorosh, Skryshevskii	53	MgCl ₂ , CaCl ₂ , CoCl ₂ , NiCl ₂ , CuCl ₂ & CdCl ₂
Wertz, Kruh	54	CoCl ₂
Terekhova, Radchenko	55	NH ₄ Cl, KCl
Terekhova, Ryss, Radchenko	56	NH ₄ F, KF
Shapovalov, Radchenko	57	H ₂ SO ₄
Narten	58	Ammonium Halides
Shapovalov, Radchenko, Lesovitskaya	59	CoSO ₄ , NiSO ₄
Albright	60	Alkaline-earth Halides
Fishkis, Soboleva	61	KI, LiI
Narten, Vaslow, Levy	62	LiCl
Licheri, Piccaluga, Pinna	63	Alkali Halides
Wertz, Bell	64	ZnCl ₂ /HCl
Bell, Tyvoll, Wertz	65	CuCl ₂
Fishkis, Zhmak	66	CuSO ₄
Cristini, Licheri, Piccaluga, Pinna	67	Cr(H ₂ O) ₆ Cl ₃
Alves Marques, De Barros Marques	68	2-1, 1-2, & 1-3 electrolytes
Bertagnolli, Weidner, Zimmermann	69	CsF
Triolo, Narten	70	HCl
Licheri, Piccaluga, Pinna	71, 72, 73	LiBr, CaBr ₂ , CaCl ₂ respectively

the first near-neighbour shell, the models are essentially in agreement, and they are both supported by the molecular dynamics model for liquid water, Stillinger and Rahman(40).

For solutions, the general method is to generate a composite X-ray radial distribution, and assign different peaks to solute and solvent interactions, often using a model of the structure. On the assumption that the scattering from the water molecule is dominated by the spherical part of the molecular form factor, Blum (41), the composite distribution will be the sum of six partial distributions, and so the assignment must inevitably be ambiguous. The majority of the information derived from the technique concerns the coordination of water molecules around the ions, and a summary of this information is presented in Appendix 5. The hydration numbers show variations, depending on the solute studied, and on the authors performing the data analysis, and only in LiCl (62) has any attempt been made to assign orientations to the hydrated water molecules: this latter experiment was performed in conjunction with neutron scattering.

The other important information derived from X-ray scattering concerns the ion-ion distribution. The existence of a longer range structure beyond the ionic hydration shells is considered to be indicated by a maximum in the scattering pattern for a scattering vector in the region of 1 \AA^{-1} , Neilson, Enderby, and Howe (74). Previously, Dorosh and Skryshevskii (53) had come to a similar conclusion when considering X-ray scattering from solutions of MgCl_2 , CaCl_2 , CoCl_2 , NiCl_2 , CuCl_2 , CdCl_2 . Alves Marques and De Barros Marques (68) have successfully attributed low angle maxima to a lattice structure of cation complexes, which involve water molecules and anions, in solutions of BeCl_2 , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, MgBr_2 , AlCl_3 , AlBr_3 , $\text{Al}(\text{NO}_3)_3$, InCl_3 . For CaCl_2 , they find a low angle feature, but could not construct a model to explain it:

Fig. 2.2 X-ray Scattering intensities from
alkali-halide aqueous solutions (R.M.
Lawrence, private communication).
The units are arbitrary.



Licheri, Ficcaluga and Pinna (72) find no such feature (although their presentation of the data may obscure it), but both authors agree that it disappears in CaBr_2 solutions (73). It is not clear whether this is a true effect, or simply an artefact of the increased X-ray scattering amplitude of bromine.

For 1-1 electrolytes there is very little evidence for long range structure. Only for concentrated LiCl solutions has Beck (75) suggested a structure related to the crystalline hydrate, whilst Marten (62) finds no evidence for this structure at all. In figure 2.2 are shown the X-ray intensity curves obtained by Lawrence and Kruh (52) for a variety of alkali - halide solutions. Only for CsCl is there suggestion of a low angle feature, although its presence could also be hinted at in concentrated lithium and sodium iodide solutions. Bertagnolli, Weidner and Zimmermann (69) consider the Cs ions in CsF solutions to be arranged only in the cavities of a disordered β -tridymite lattice.

There has been some work on solutions in organic solvents. Hertz, Tutsch and Bowman (76) have remarked that 'water has a strong tendency to form its own structure, so part of the force exerted by an ion's electric field is needed to break down the proper structure of water. Consequently, solvation structure stabilization is known to be stronger in non-aqueous solvents, where proper solvent structures are absent or less developed'. There have been studies of ferric chloride in methanol (77) and magnesium, calcium, cobalt and nickel chlorides in methanol, ethanol, and dimethylformamide, (78) and (79). In all these solutions the hydration phenomena are more pronounced than in the equivalent aqueous solutions. The divalent cations are six-fold coordinated with solvent molecules, for dilute solutions: at higher concentrations this is reduced to four, with anions entering the first shell of molecules. For the solutions in

alcohol, the low angle maximum is much more prominent, indicating enhanced long-range ordering of the ions. For the dimethylformamide solutions the low angle maximum disappears.

5) Evidence from Neutron Scattering

The number of neutron scattering experiments on aqueous solutions is small. Apart from the work of Marten, the major contribution has come from Enderby (80). This work has given quantitative information about the nickel-nickel partial structure factor in nickel chloride solutions, and confirmed the idea of a lattice structure. There is also the inelastic neutron scattering work of Safford, Leung, Neumann and Schaffer (81). The inelastic spectra will contain contributions from all the molecular motions in the solutions, and so interpretation can only be qualitative at best: their main conclusion is that small highly charged ions disrupt the water structure and form locally ordered complexes.

6) Molecular Dynamics and Monte Carlo Calculations

Since the successful application of molecular dynamics to liquid water (40), the technique has been applied to aqueous solutions, although limitations in computer size and time have so far prevented a simulation with a large number of solute particles. However valuable information about the hydration of ions can be obtained. So far the calculations have been limited to alkali-metal and halogen ions. Either the ST2 model of the water molecule or Hartree-Fock calculations are used to obtain the ion-water and water-water potentials. The hydration numbers and ion-water distances are shown in Appendix 6. These papers also contain much information about the orientation of the water molecules. Rahman (91) has demonstrated the formation of hydration spheres around a pair of positive and negative ions surrounded by water molecules.

Figure 2.3

List of Monte Carlo / Molecular Dynamics calculations on the hydration of ions by water molecules.

Author(s)	Method	Ref.	Ion
Heinzinger, Vogel	MD	82	Li^+, Cl^-
Vogel, Heinzinger	MD	83	Cs^+, Cl^-
Heinzinger, Vogel	MD	84	$\text{Li}^+, \text{Na}^+, \text{Cs}^+, \text{I}^-, \text{Cl}^-, \text{F}^-$
Vogel, Heinzinger	MD	85	Na^+, Cl^-
Kistenmacher, Popkie, Clementi	MC	86	$\text{Li}^+, \text{Na}^+, \text{K}^+, \text{F}^-, \text{Cl}^-$
Fromm, Clementi, Watts	MC	87	Li^+, F^-
Watts	MC	88	$\text{Li}^+, \text{K}^+, \text{F}^-, \text{Cl}^-$
Briant, Burton	MD	89	$\text{Na}^+, \text{Rb}^+, \text{Cs}^+, \text{F}^-, \text{Br}^-, \text{I}^-$
Mruzik, Abraham, Schreiber, & Fould	MC	90	$\text{Li}^+, \text{K}^+, \text{Cl}^-, \text{F}^-$

7) Conclusion

There is a wide literature on the structure of aqueous solutions. Since the successful Debye-Hückel theory, ideas have diverged along several paths which represent a considerable improvement at higher concentrations, but development of a rigorous theory is unlikely until detailed knowledge of ion-solvent and ion-ion interactions is available. X-ray diffraction data and molecular dynamics calculations have supplied some of this, but discrepancies occur between different experiments on the same solution. The X-ray data is, however, quite consistent in assigning ion-water distances to the hydration spheres.

A variety of other techniques have been applied to the problem of ion hydration. Infra-red absorption, Raman spectroscopy, and nuclear magnetic resonance have supplied some information - see, for example, Irish (92), the series of papers by James et al. (93), and those by Hertz et al. (77). However because of the complex interpretation required for the latter experiments only general conclusions are usually drawn about the structure making and structure breaking properties of ions.

The neutron diffraction experiment presented in subsequent chapters is a source of reliable, quantitative information on the hydration of specific ions, and ion-ion interactions, and should eventually enable a major advance in both theory and interpretation of data from other experimental techniques to be made.

CHAPTER 3THE NEUTRON EXPERIMENT1) Introduction

Examination of the structure of liquids is usually accomplished using the Debye - Scherrer powder technique. There are two differences: the liquid structure pattern is considerably more diffuse than the crystal one, and peak intensities are much smaller. Hence a large incident flux is required to produce observable scattering, and it is not necessary to have the high resolution of a crystal diffractometer.

2) Neutron Diffractometer

Figure 3.1 shows a schematic diagram of the D4 liquids diffractometer at Institut Laue - Langevin, Grenoble, France. The principle of neutron diffraction has been described by Bacon (8). Samples were mounted in zirconium - titanium cans, fig. 3.2a. This is a random alloy, so that, because the titanium scattering length is negative, then, with appropriate choice of concentration, the alloy could be made with nearly zero coherent scattering. The sample was mounted on a metal candle at the centre of the vacuum chamber, and centred with a micrometer gauge: when completely central, rotating the sample produced no movement on the gauge. The incident beam was collimated to 50 mm high, and 20 mm wide, and cadmium shields on the sample container lowered the beam height to 31.4 mm. The wavelength used was 0.69 Å throughout, and was checked regularly by I.L.L. staff. Typical counting times were two days per sample; there was a count rate of ~ 360 per sec at the main peak in the total scattering pattern. The data were recorded on magnetic tape or paper tape for computer analysis.

Fig. 3.1 Schematic Diagram of the Geometry of D4 Liquids Diffractometer, I.L.L. Grenoble.

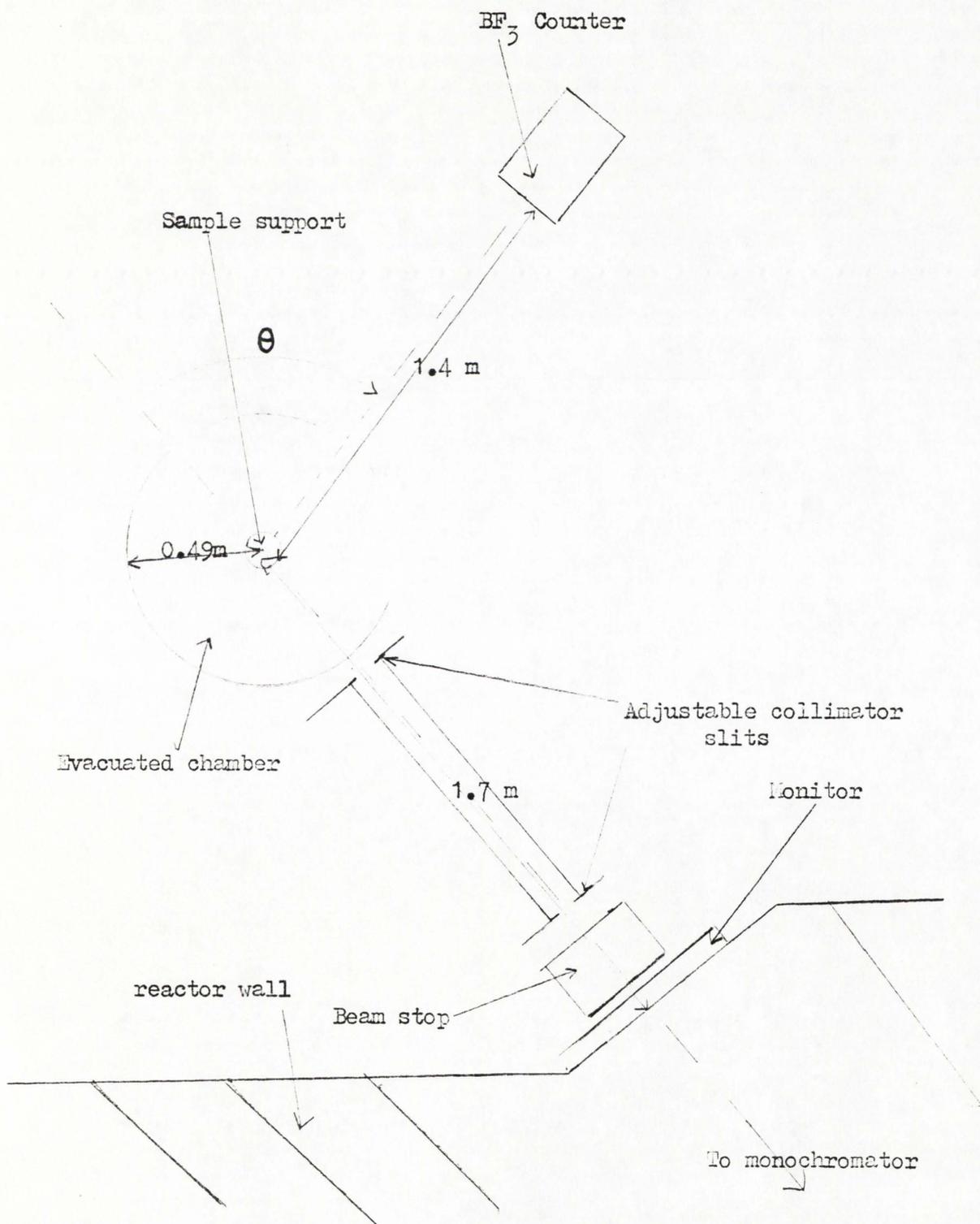


Fig. 3.2a Scale diagram of zirconium - titanium zero alloy sample can.

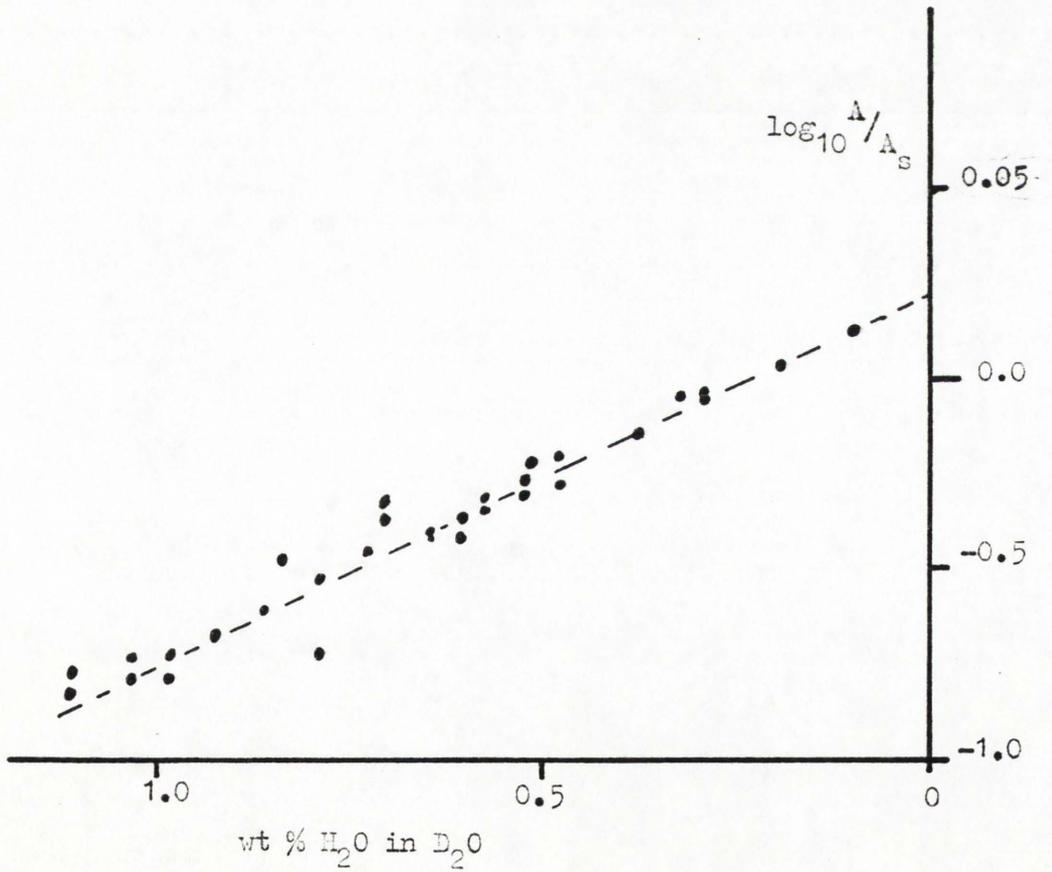
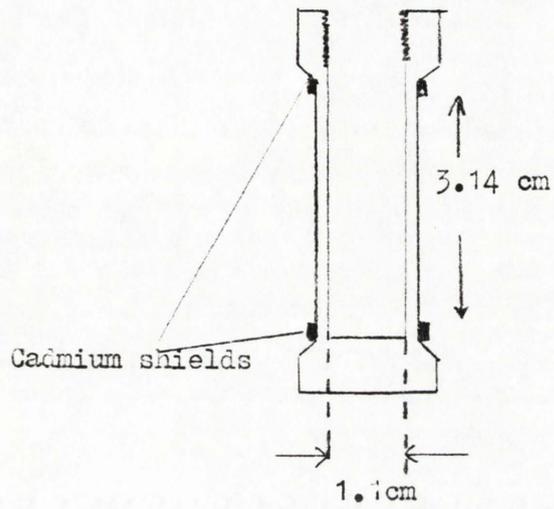


Fig 3.2b. Infra-red calibration curve, which demonstrates the Beer-Lambert Law

3) Sample Preparation

Several of the earlier experiments were not reproducible, and it emerged that this was due to varying amounts of light water in the samples. Dr. Neilson suggested the use of an infra-red spectrometer to monitor the hydrogen content. This spectrometer (a Perkin - Elmer infra-red spectrometer) produces a graph of the variation of infra-red absorption with wavelength. The sample is contained between calcium fluoride glass windows 0.1 mm apart. An absorption feature due to an O - H bond excitation at 3400 cm^{-1} was selected for the purpose. The absorption, A , is given by the Beer-Lambert law as a function of the concentration, c , in atoms per unit volume, of the component causing the absorption:

$$\log_{10} A = -kc, \quad \dots 3.1$$

where k is a sample cell constant. The procedure was to compare the absorption of the sample with that of a sheet of standard glass by taking the ratio

$$\log_{10} \frac{A}{A_s} = -kc + k_s c_s \quad \dots 3.2$$

where the suffix s applies to the standard. This equation was used to calibrate the spectrometer and sample cell, fig. 3.2b. The sodium chloride solutions were tested in a similar way and compared using the calibration curve. The important aim was to prepare all the samples with the same light water content. The heavy water used was normally 99.9 wt% D_2O ; it was possible to prepare samples with absorption the same as 99.2 to 99.7 wt % D_2O , and the three samples could be made the same within ± 0.05 wt % D_2O .

They were prepared in 5 or 10 ml Pyrex volumetric flasks with air-tight glass stoppers. To reduce the H_2O content, the sodium chloride was initially baked at $\sim 150^\circ \text{C}$ for several hours. Subsequently, in solution, if the content was still too high, the

solution was evaporated over gentle heat and the solute re-baked. The long neck of the flask prevented any loss of solute in the drying process, and it was generally not necessary to repeat the process more than three times.

Figure 3.3

Data Analysis (See Paalman and Pings (94) , and Elech and Averbach (95) , Placzek (5))

1. Subtract background counts from empty container, vanadium, and sample counts.
2. Correct vanadium counts for absorption, multiple scattering, and inelastic effects. From the known incoherent cross-section of vanadium, calculate a calibration constant, CVAN.
3. Calculate the Paalman and Pings quantities $A_{s,sc}$, $A_{c,sc}$, and $A_{c,c}$, and the multiple scattering cross-section, σ_m , for the sample.

4. Generate the corrected data as function of Θ :

$$I_s(\Theta) = I_{c+s}(\Theta) \frac{1}{A_{s,sc}} - I_c(\Theta) \frac{A_{c,sc}}{A_{s,sc} A_{c,c}}$$

where $I_{c+s}(\Theta)$ is the scattering from sample plus container, and $I_c(\Theta)$ is the scattering from the empty container.

5. Normalize $I_s(\Theta)$ to units of differential cross-section, and subtract the multiple scattering:

$$F(\Theta) = \frac{I_s(\Theta)}{CVAN} - \sigma_m$$

6. Convert values of scattering angle Θ to momentum transfer, Q :

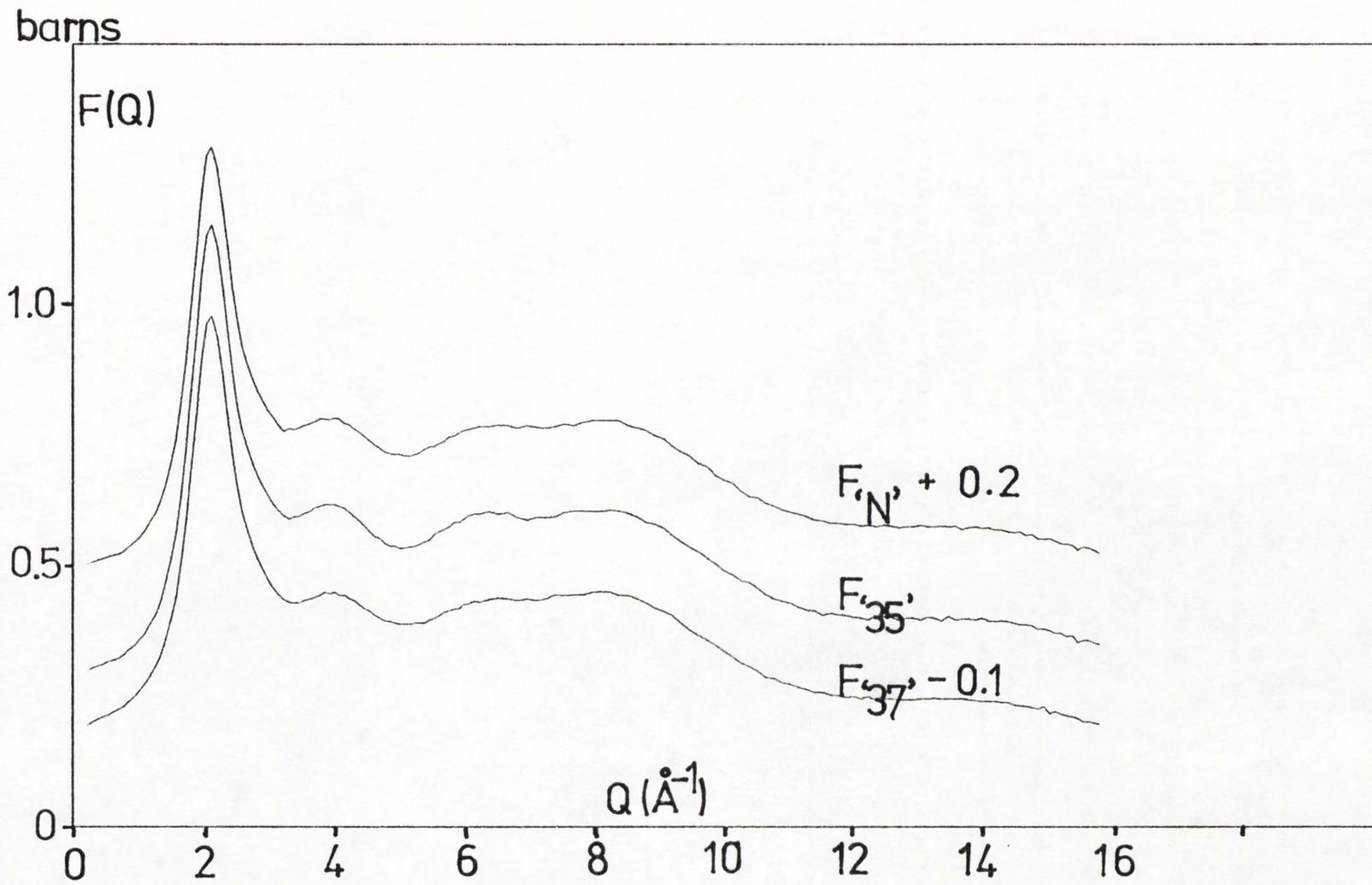
$$Q = \frac{4\pi \sin \frac{\Theta}{2}}{\lambda}$$

where λ is the wavelength of the neutrons.

4) Data Analysis

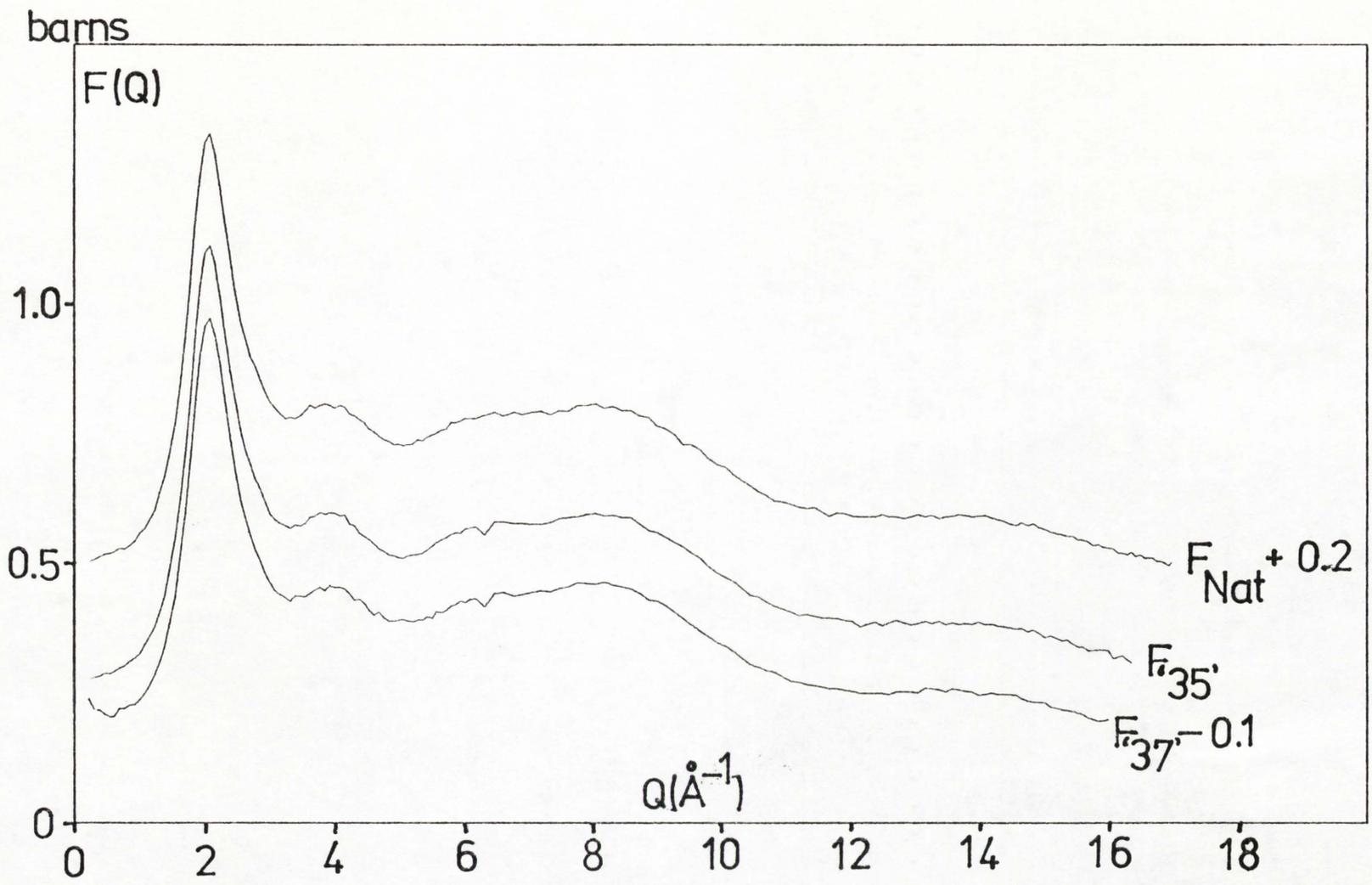
Data were taken for the background (i.e. no sample or container), empty container, vanadium rod of dimensions similar to the sample, and sample in the container. These were corrected for absorption, according to Paalman and Pings (94), and for multiple scattering, according to Blech and Averbach (95). See figure 3.3. The multiple scattering was assumed to be isotropic with scattering angle. Vanadium has virtually zero coherent scattering and so is used to calibrate the neutron counter.

This approach is open to some criticism. The Paalman and Pings work was originally derived for X-rays, in which photon capture is the predominant form of absorption, and scattering causes negligible attenuation. Hence multiple scattering is usually ignored for X-rays. For neutrons, in the present samples, scattering is the primary form of attenuation, and neutron capture is usually quite small. Multiply scattered neutrons contribute to $\sim 20\%$ of the total scattering. Thus it is not clear whether the Paalman and Pings approach is applicable in this instance: a more rigorous treatment should include both multiple scattering and absorption under the same formalism. In the past this procedure has been used quite satisfactorily with monatomic and binary liquids, where the degree of accuracy required is the same order of a magnitude as the errors in the absorption correction. In the next chapter, however, it will be seen that errors of 1.0 % can lead to a completely misleading picture of the ion-ion structure pattern. Paalman and Pings is used here in the absence of a more acceptable formalism: for the first order differences at least, the data go to approximately the correct limits.

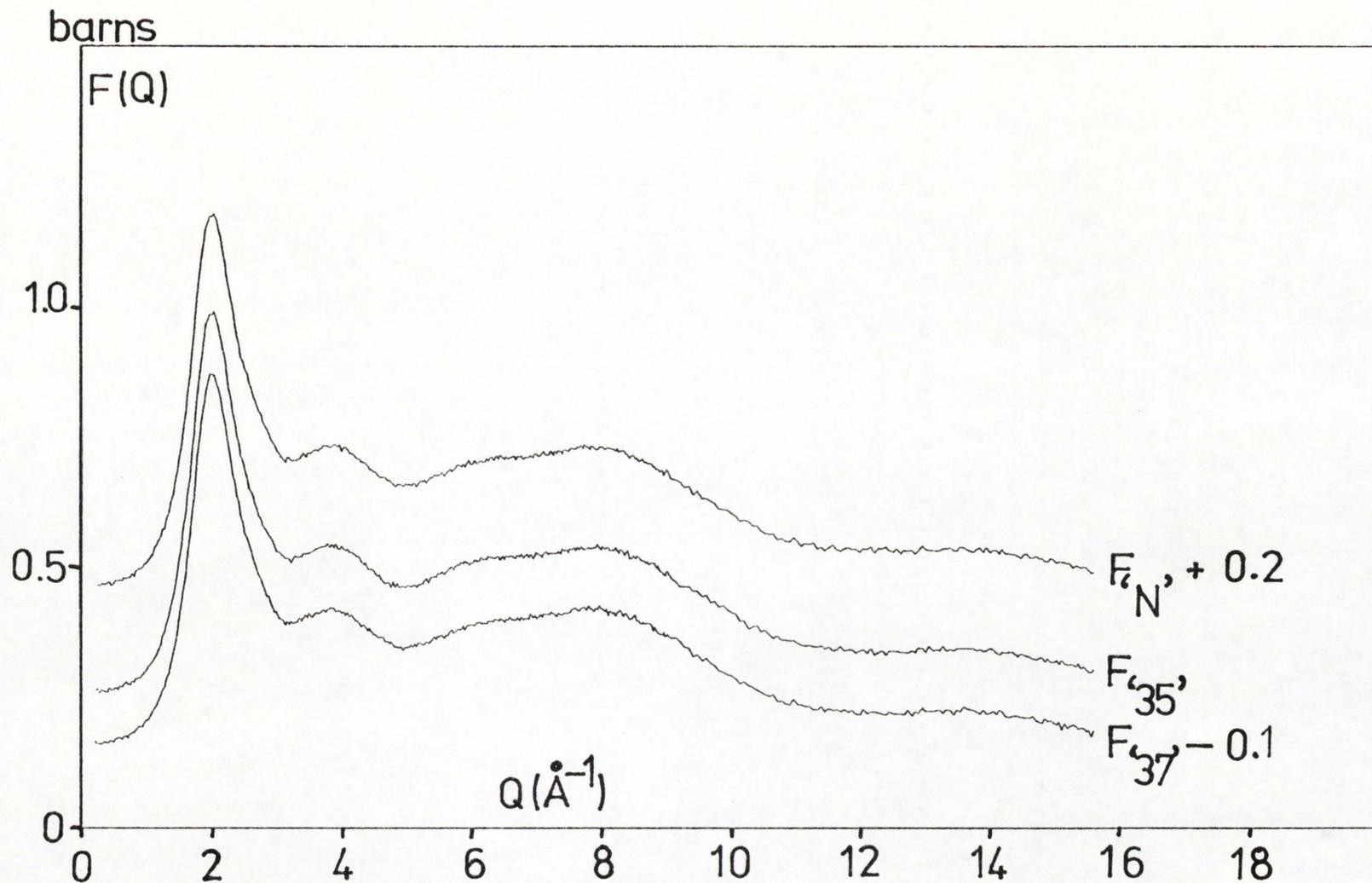


NACL 5.32 MOLAL. TOTAL F(Q) S

FIG. 3.4



NACL 2.99 MOLAL. TOTAL F(Q) S



NACL 1.49 MOLAL. TOTAL F(Q) S

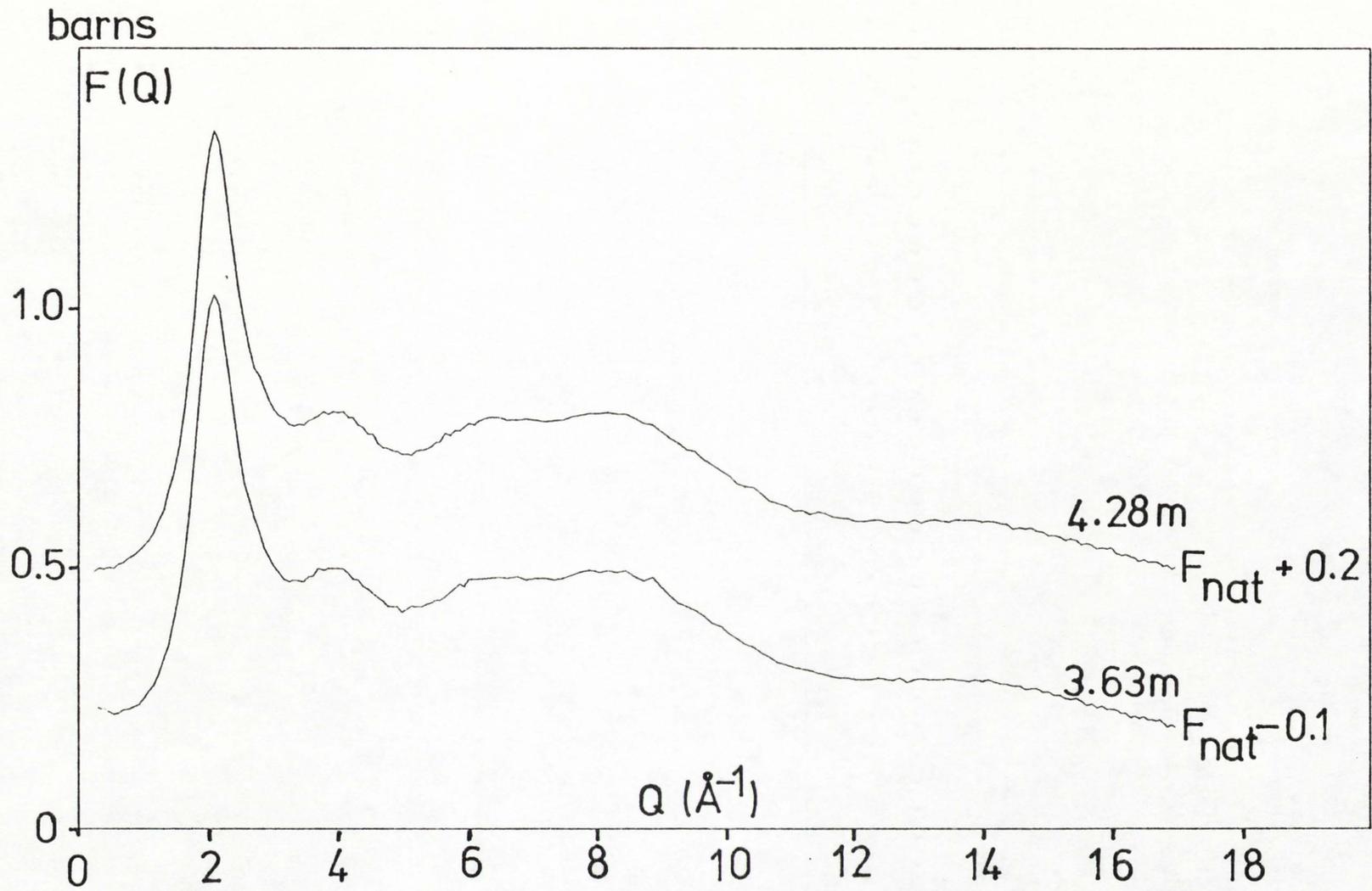
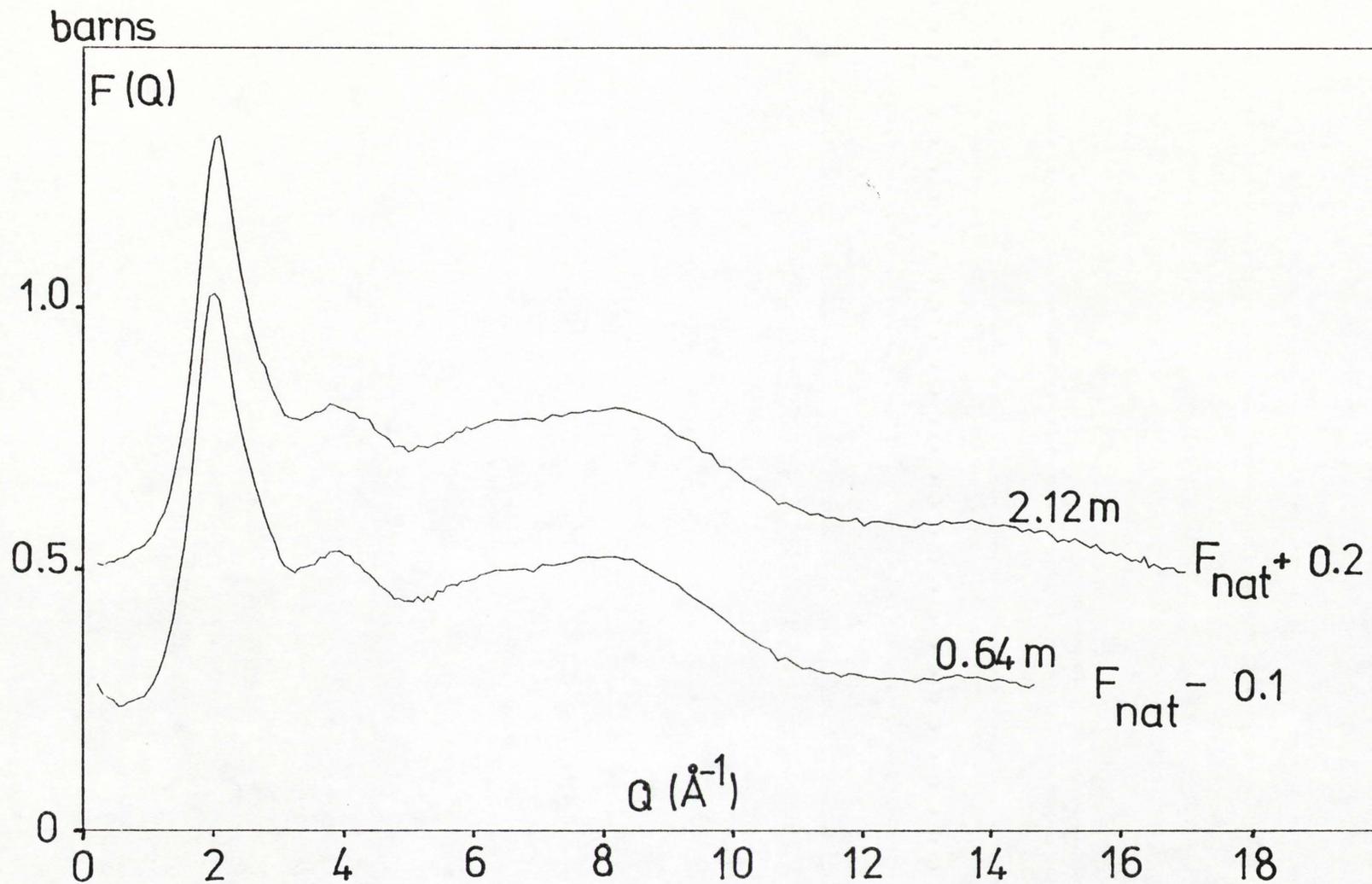


FIG. 5.7

NACL 4.279 Å 3.63 MOLAL. TOTAL F(Q)



NACL 2.12 ! 0.641 MOLAL. TOTAL F(Q) S

5) Correction Procedure

The first order differences were generated according to equation 1.33, and smoothed using the Fourier analysis technique described in Appendix 3. The latter considerably reduces the statistical noise in the data, but it was evident from the outset that systematic errors remaining in the data were sufficiently large to prevent a direct second subtraction to obtain the chlorine-chlorine distribution. This problem has arisen previously in partial structure factor analysis, and Edwards, Enderby, Howe and Page (96), have used an algorithm to remove as much of the systematic error as possible. Their method relies on the fact that the partial structure factors must lie within certain limits, and they allow the function $F(Q)$ for each isotope to vary between ± 0.01 barns for $0 < Q < 2 \text{ \AA}^{-1}$, and $(1 \pm 0.05)F(Q)$ for $Q > 2 \text{ \AA}^{-1}$. Table 3.1 gives the scattering lengths for the isotopes used in the present experiments. If these are substituted in equation 1.34, it will be seen that for a variation in $F_{\text{nat}}(Q)$ of 0.01 barns, and $c_{\text{Cl}} = 0.0331$ (corresponding to a 5.32 molal solution), then the value of a_{ClCl} generated will change by 53. The conditioning becomes even worse at greater dilutions.

Consider the first order differences from equation 1.33:-

$$\begin{aligned} D1 &= F_{\text{nat}}(Q) - F_{37}(Q) - \Delta_1 \\ D2 &= F_{35}(Q) - F_{37}(Q) - \Delta_2 \end{aligned} \quad \dots 3.3$$

The systematic and random errors are represented by δ_1, δ_2 respectively, and equation 3.3 is rewritten in the form

$$\begin{aligned} D1 &= c_{1X} X + c_{1Y} Y + \delta_1 \\ D2 &= c_{2X} X + c_{2Y} Y + \delta_2 \end{aligned} \quad \dots 3.4$$

$$\text{where } X = (a_{ClCl} - 1) \quad \dots 3.5a$$

$$Y = 2c_D b_D (a_{ClD} - 1) + 2c_O b_O (a_{ClO} - 1) + 2c_{Na} b_{Na} (a_{ClNa} - 1), \quad \dots 3.5b$$

$$\begin{aligned} \text{and } c_{1X} &= c_{Cl}^2 (b_{nat}^2 - b_{37}^2) \\ c_{2X} &= c_{Cl}^2 (b_{35}^2 - b_{37}^2) \\ c_{1Y} &= c_{Cl} (b_{nat} - b_{37}) \\ c_{2Y} &= c_{Cl} (b_{35} - b_{37}). \end{aligned} \quad \dots 3.6$$

There are two conditions on which the data ^{are} sensitive to errors:

$$SUM_X = a_X D1 + D2 = (a_X c_{1X} + c_{2X}) X + CORR_X \quad \dots 3.7$$

$$SUM_Y = a_Y D1 + D2 = (a_Y c_{1Y} + c_{2Y}) Y + CORR_Y \quad \dots 3.8$$

$$\text{where } a_X = -\frac{c_{2Y}}{c_{1Y}}, \text{ and } a_Y = -\frac{c_{2X}}{c_{1X}}, \quad \dots 3.9$$

$$CORR_X = a_X \delta_1 + \delta_2, \text{ and } CORR_Y = a_Y \delta_1 + \delta_2.$$

Because X and Y must lie within certain limits, then SUM_X and SUM_Y must also lie within limits L_X^{\pm} and L_Y^{\pm} respectively, and these define maximum and minimum values for $CORR_X$, $CORR_Y$:

$$\begin{aligned} CORR_X^{\max} &= L_X^+ - SUM_X \\ CORR_X^{\min} &= L_X^- - SUM_X \\ CORR_Y^{\max} &= L_Y^+ - SUM_Y \\ CORR_Y^{\min} &= L_Y^- - SUM_Y \end{aligned} \quad \dots 3.10$$

The procedure is to allow $CORR_X$ to vary between $CORR_X^{\max}$ and $CORR_X^{\min}$, while $CORR_Y$ simultaneously varies between $CORR_Y^{\max}$ and $CORR_Y^{\min}$, and for each pair of values $CORR_X$, $CORR_Y$, the corrections δ_1, δ_2 are computed from equation 3.9. A pair of values of δ_1, δ_2 are selected such that

$$\delta = |\delta_1| + |\delta_2| \quad \dots 3.11$$

is a minimum, i.e. the corrected curves are to lie as close as possible

to the original. To check the consistency of the procedure, a third difference may be defined:

$$D3 = D1 - D2,$$

and the analysis repeated for each of the pairs D1, D3 and D2, D3.

The corrected differences are then Fourier transformed to the weighted sum of radial distribution functions, and the analysis repeated, with of course different limits for SUM_X , SUM_Y .

The corrected first order differences are shown alongside the originals in figures 3.9 to 3.14. The correction is not usually greater than 0.01 barns - indeed it is an order of magnitude less than this for most of the Q range. The exception occurs in the range $0 < Q < 0.5 \text{ \AA}^{-1}$, which is difficult to measure experimentally. With this exception, the present corrected data lie well within the systematic error limits proposed by Edwards et al.

To describe the allowed limits for SUM_Y , an average sum of the partial distributions in equation 3.5b was defined as

$$Y_{av} = \frac{Y}{(2c_D b_D + 2c_O b_O + 2c_{Na} b_{Na})} \quad \dots 3.12$$

The limits on X and Y_{av} are shown in Table 3.2. The data indicate the limits on Y_{av} since this term dominates the first order difference. The limits on X are not well defined. However the thermodynamic limit of a_{ClCl} at $Q=0$, i.e. $a_{ClCl}(0)$, can be computed, and the limits for X were defined to be $\pm 1.5 (a_{ClCl}(0) - 1)$, (see Appendix 4).

For the radial distributions, it is known that none of the partial distributions can be negative, and atomic packing prevents any liquid radial distribution function going above ~ 4 for $r > 2 \text{ \AA}$. In fact the limits of the radial distribution function of X were larger than those which could be physically allowed, as the data retained large

truncation oscillations.

In general if the scattering lengths or the limits on SUM_X , SUM_Y have been wrongly chosen, then the corrected data lie further from the original than they would with correct values. This provides an inherent check on the scattering lengths.

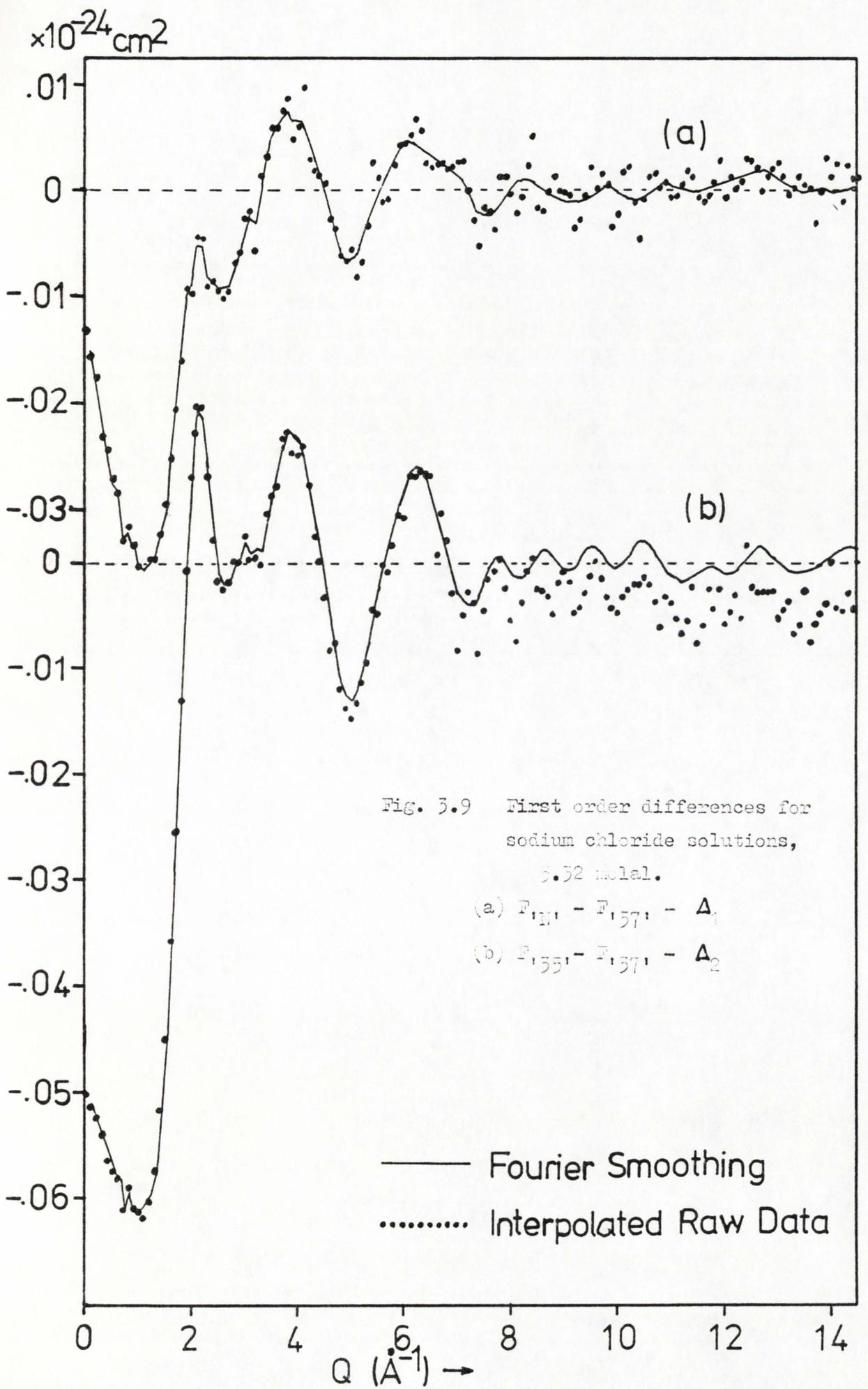


Fig. 3.9 First order differences for sodium chloride solutions, 5.32 mlal.

(a) $F_{111} - F_{157} - \Delta_1$

(b) $F_{155} - F_{157} - \Delta_2$

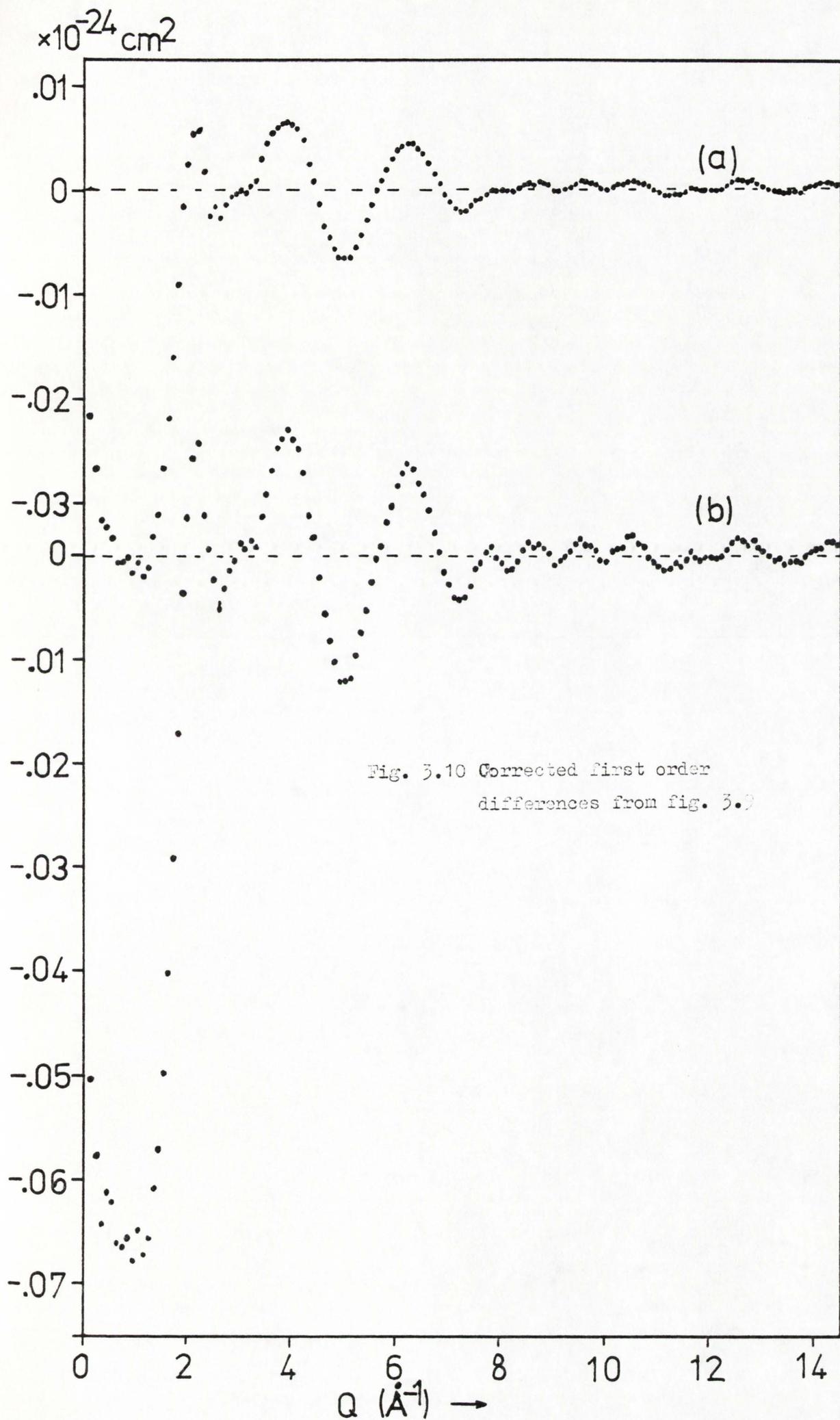
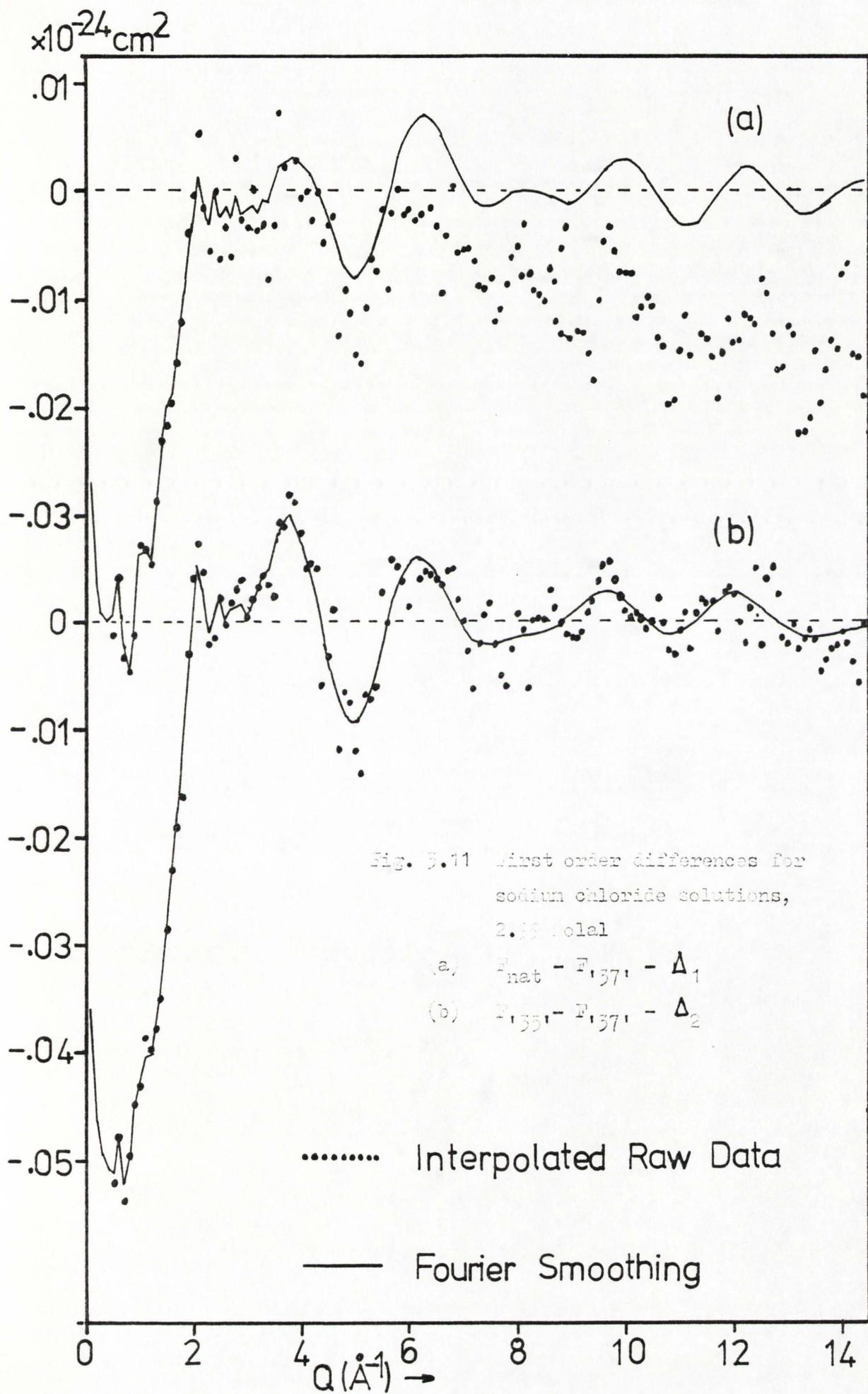


Fig. 3.10 Corrected first order differences from fig. 3.9



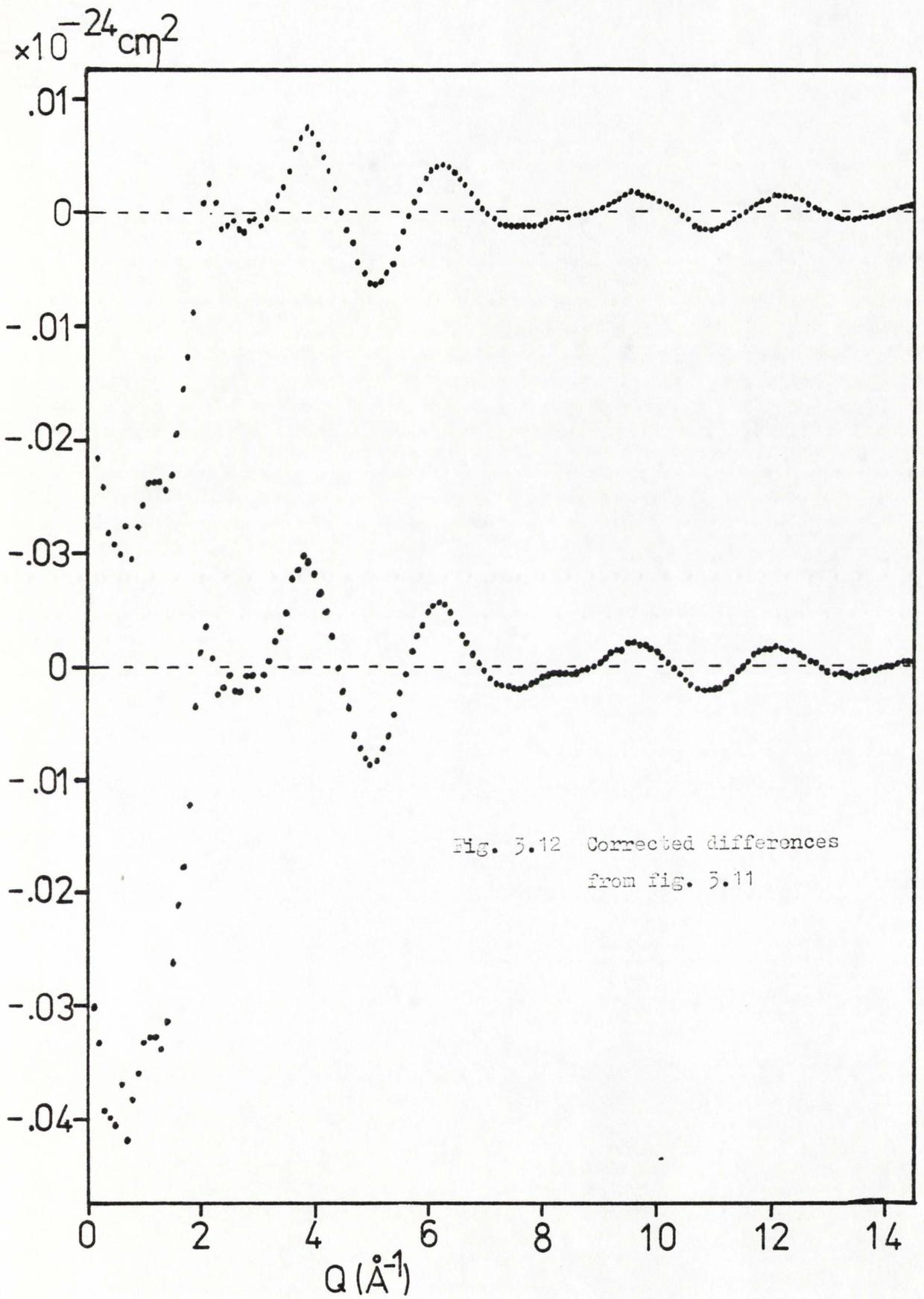
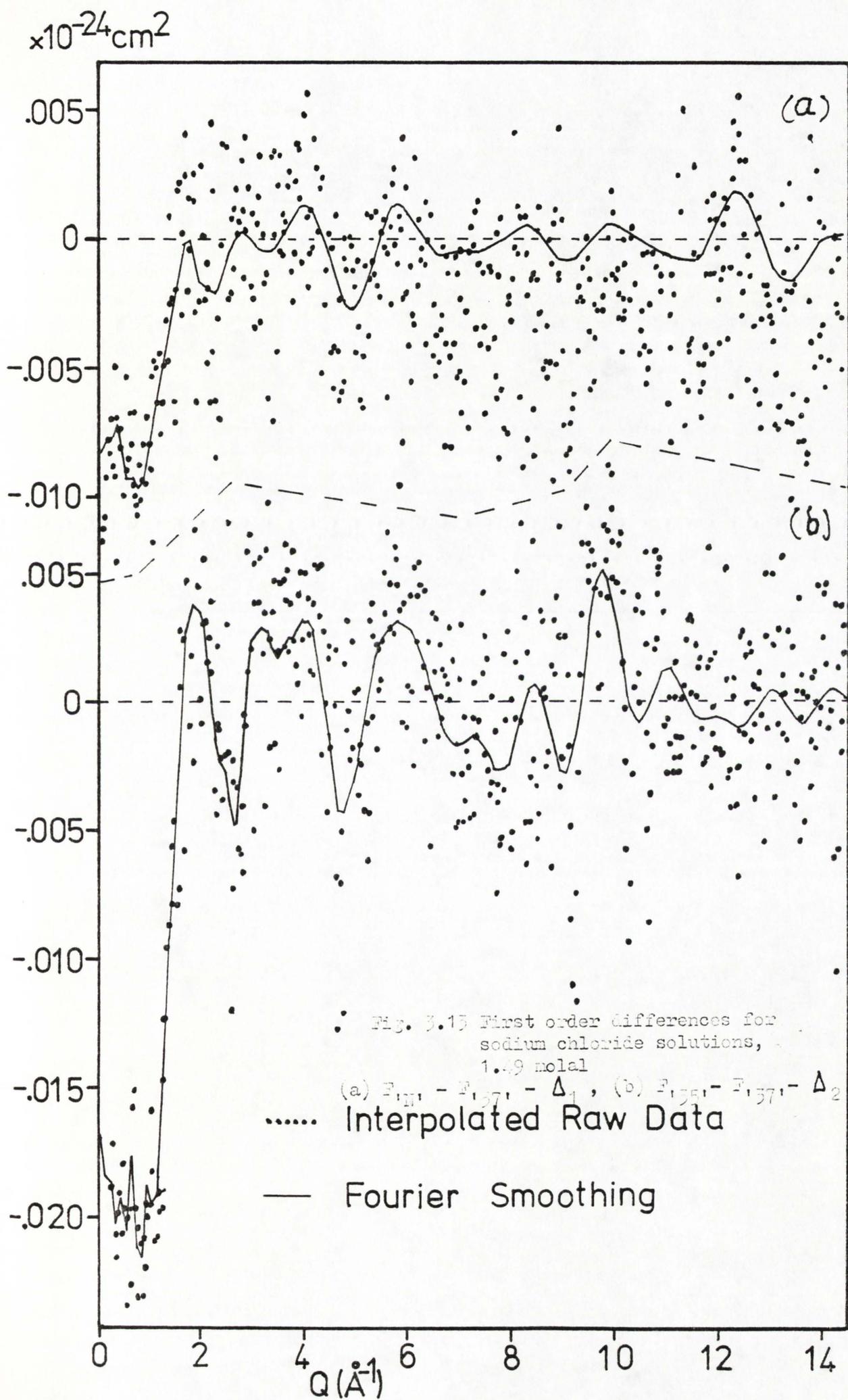
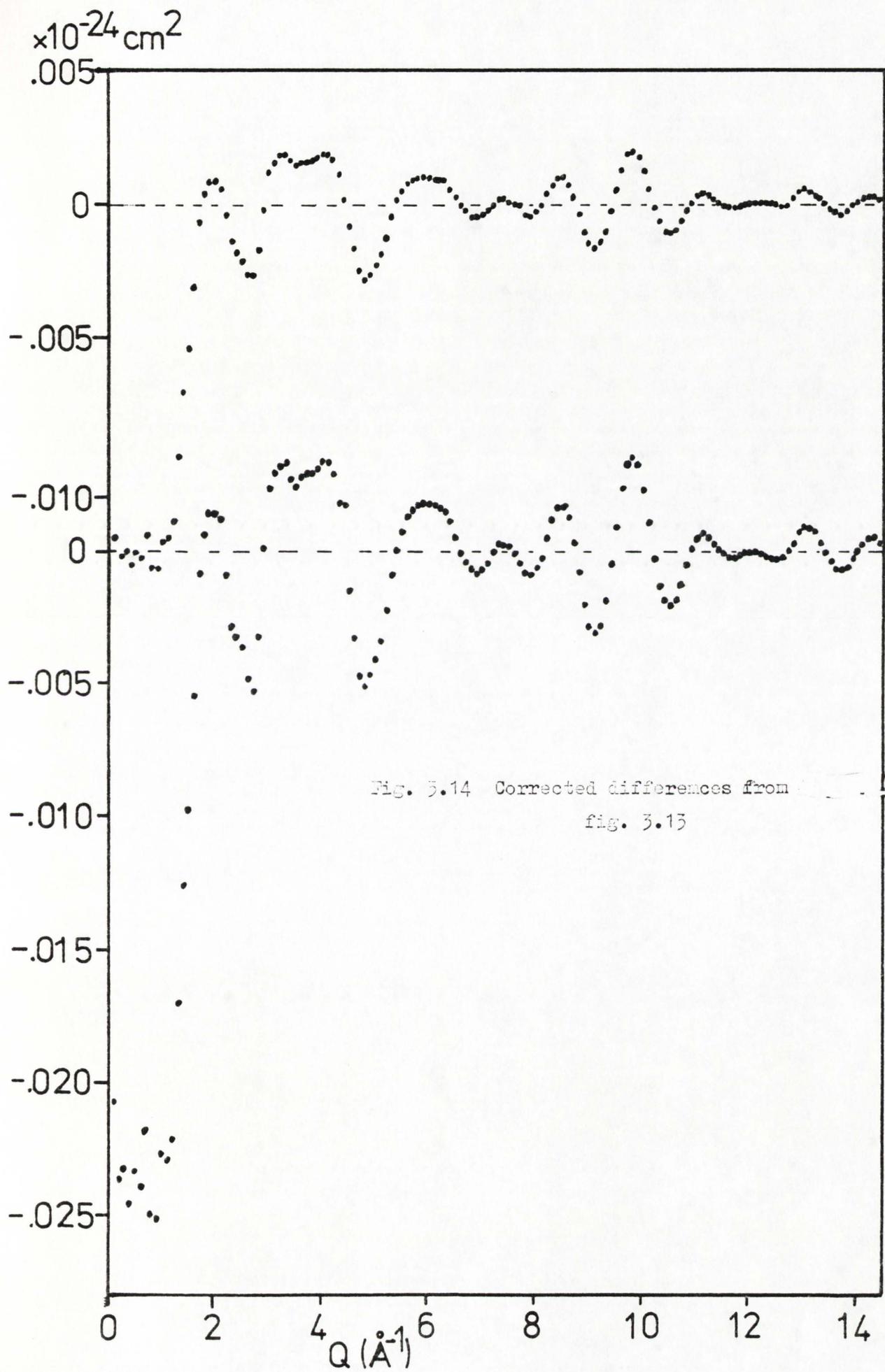


Fig. 3.12 Corrected differences
from fig. 3.11





CHAPTER 4RESULTS1) The Chlorine Hydration Sphere

The function $Y(Q)$ in equation 3.5b represents a weighted sum of Cl - D, Cl - O and Cl - Na partial structure factors, and can be extracted according to equation 3.8 (figs. 4.1 - 4.2). Fourier transform of this function yields $Y(r)$, (figs. 4.3 - 4.5), where

$$\begin{aligned}
 Y(r) &= \frac{1}{2\pi^2 nr} \int Y(Q) Q \sin(Qr) dQ \\
 &= 2c_D b_D (g_{ClD} - 1) + 2c_O b_O (g_{ClO} - 1) + 2c_{Na} b_{Na} (g_{ClNa} - 1)
 \end{aligned}$$

... 4.1

The figures show that statistical noise remains in the data as well as truncation errors caused by $Y(Q)$ being measurable to only finite values of Q ($< 15 \text{ \AA}^{-1}$). To identify true structural features, a window function (see for example (107)) was applied to $Y(Q)$. The form of the window function was

$$Y_w(Q) = Y(Q) \frac{(1 + \cos \frac{\pi Q}{T})}{2}$$

... 4.2

with $T = 15 \text{ \AA}^{-1}$, and $Y_w(Q) = 0$ for $Q > 15 \text{ \AA}^{-1}$.

Since $Y(r)$ is dominated by the Cl - D and Cl - O terms, it is immediately evident that the chlorine ion is strongly coordinated with water molecules, and beyond the hydration sphere there is practically no ordering of the water molecules. The double peak in $Y(r)$ implies that the water molecules have a definite orientation around the ion. The depth of the minimum between the two peaks indicates that the rate of exchange of hydrated water molecules with the unhydrated molecules is small, (but see Chapter 6 for a discussion of this).

However it is not clear whether the first peak consists entirely of deuterium atoms, or partly of deuterium and partly oxygen.

The coordination numbers are obtained by integrating over the first peak:

$$4\pi n \int_0^{R_{MIN}} (Y(r) + \Delta) r^2 dr = 2b_D N_D + 2b_O N_O + 2b_{Na} N_{Na} \quad \dots 4.3$$

$$\text{where } \Delta = 2c_D b_D + 2c_O b_O + 2c_{Na} b_{Na},$$

N_D , N_O , N_{Na} are the respective coordination numbers of D, O, Na, and R_{MIN} is the position of the minimum. Table 4.1 shows the results of the integration for the three cases when the first peak consists (i) entirely of deuterium ($N_O = N_{Na} = 0$), (ii) of equal numbers of deuterium and oxygen ($N_D = N_O$, $N_{Na} = 0$), and (iii) entirely of D_2O molecules ($N_D = 2N_O$, $N_{Na} = 0$).

2) Model of the Hydration Sphere

To obtain a more specific representation of the structure, a model of the hydration sphere was developed on the lines given in the previous paragraph. N_c is the number of water molecules coordinated to the ion: the total number of atoms in the hydration sphere is then $3N_c + 1$. If n_c is the total number density of D, O, and Na atoms in the bulk liquid, then the mean volume per atom is $\frac{1}{n_c}$, and so the volume occupied by the hydration sphere is $\frac{3N_c + 1}{n_c}$, which enables

a mean radius of the hydration sphere to be defined as

$$r_c = \sqrt[3]{\frac{3(3N_c + 1)}{4\pi n_c}}. \quad \dots 4.4$$

In the model, the continuum radial distribution function is assumed to be flat beyond this radius, and zero within it. As the transition from hydration sphere to continuum is unlikely to be truly 'hard', a small width, w , is placed on the continuum radial distribution function:

$$g_c(r) = 0, \quad r < r_c - w$$

$$g_c(r) = \frac{(r_c + w)^2}{r^2} \left(1 - \sin\left(\frac{\pi(r_c - r)}{2w}\right) \right), \quad r_c - w \leq r \leq r_c + w \quad \dots 4.5$$

$$g_c(r) = 1, \quad r > r_c + w$$

For the coordinated molecules, the spherical polar coordinates of the ion with respect to the oxygen atom of a water molecule were defined according to figure 4.6a, and the distance of each deuterium and oxygen atom from the chlorine ion calculated. The O - D bond length was set at 0.94 Å, and the D - O - D angle set at 104.5° (see Franks (97)). To account for thermal motion, a normalized Gaussian profile of width w was placed on each distance and weighted according to the neutron factors. This produces an hydrated radial distribution function:

$$g_h(r) = \frac{1}{4\pi nr^2} 2c_D b_D \sum_D \frac{N_D}{\sqrt{2\pi} w} \exp\left(\frac{-(r - r_D)^2}{2w}\right) +$$

$$+ 2c_O b_O \sum_O \frac{N_O}{\sqrt{2\pi} w} \exp\left(\frac{-(r - r_O)^2}{2w}\right) \quad \dots 4.6$$

Here, N_D , N_O are the numbers of deuterium and oxygen atoms at distances r_D , r_O respectively. The summations are performed over all the atoms in the hydration sphere. The weighted radial distribution for the model is finally defined as

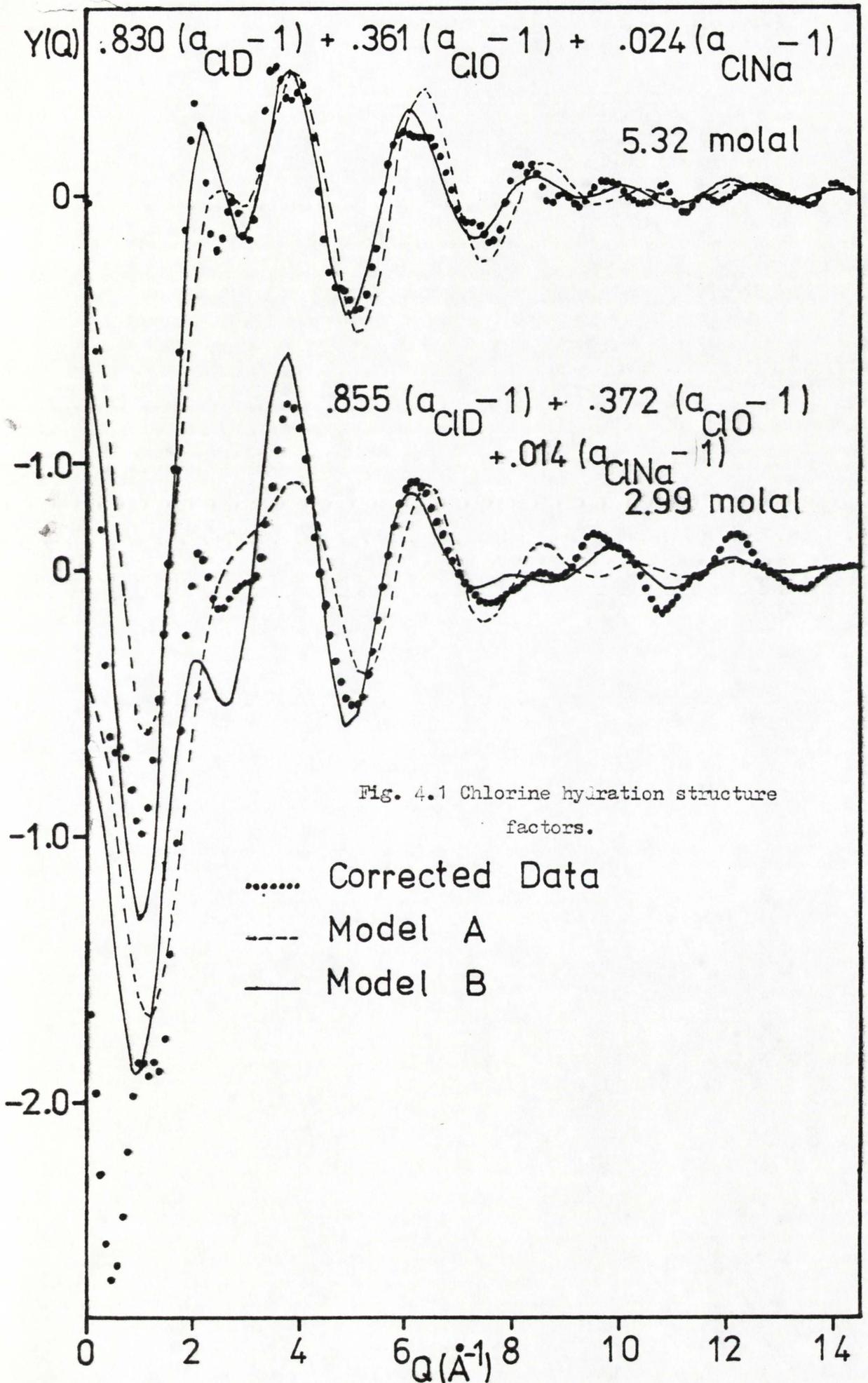
$$Y_{\text{model}}(r) = g_h(r) + \Delta g_c(r) - \Delta \quad \dots 4.7$$

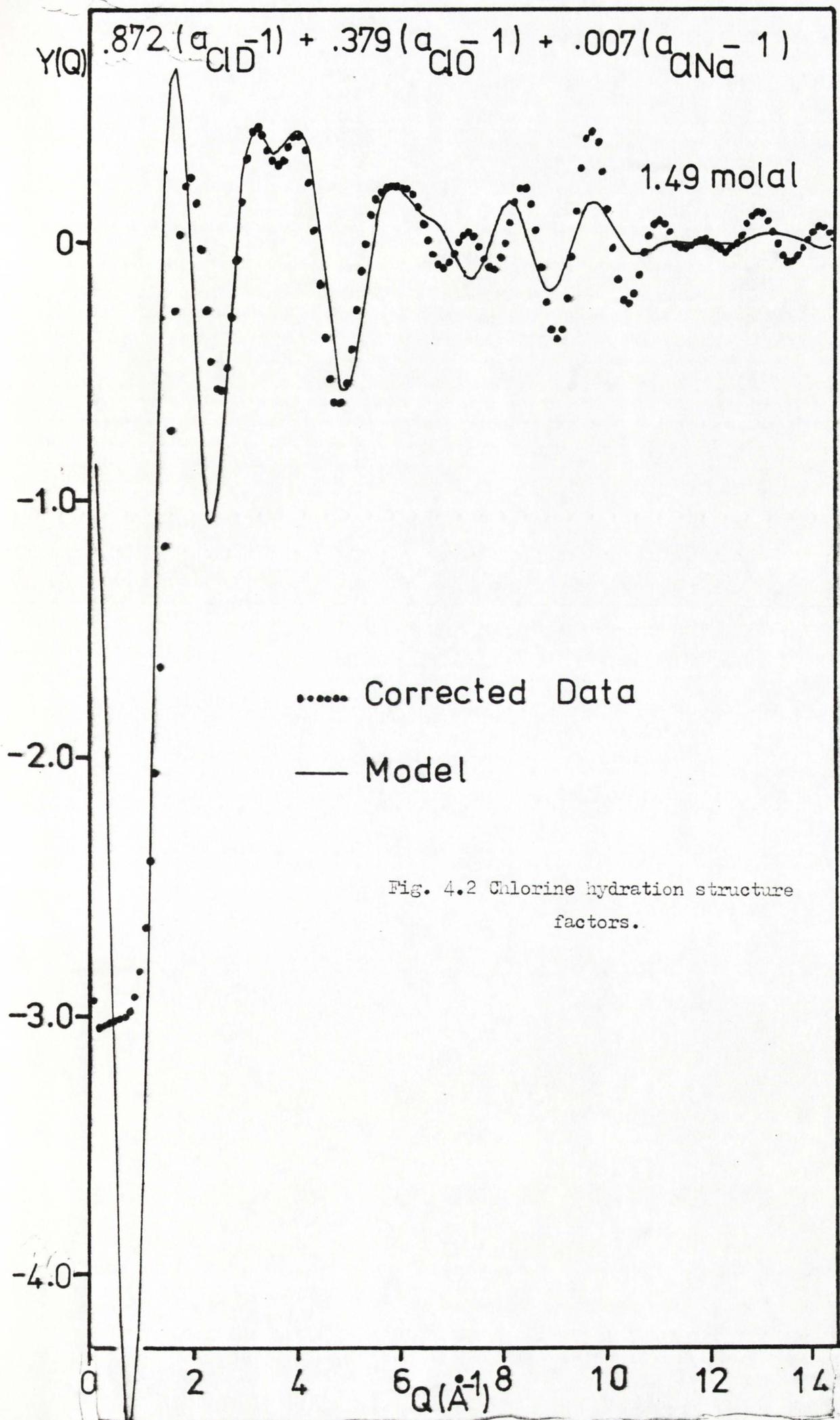
At concentrations 5.32 and 2.99 molal, two models emerged, (figs. 4.6b and 4.7a, and Table 4.2). It was not necessary to define more than two Cl - O distances. In model A, one of the O - D bonds in the water molecule lies nearly parallel to the Cl - O axis - there is only one hydration sphere. In model B the two deuterium atoms lie equidistant from the chlorine ion, and there is a second layer of water molecules, similarly orientated, which overlaps with the continuum.

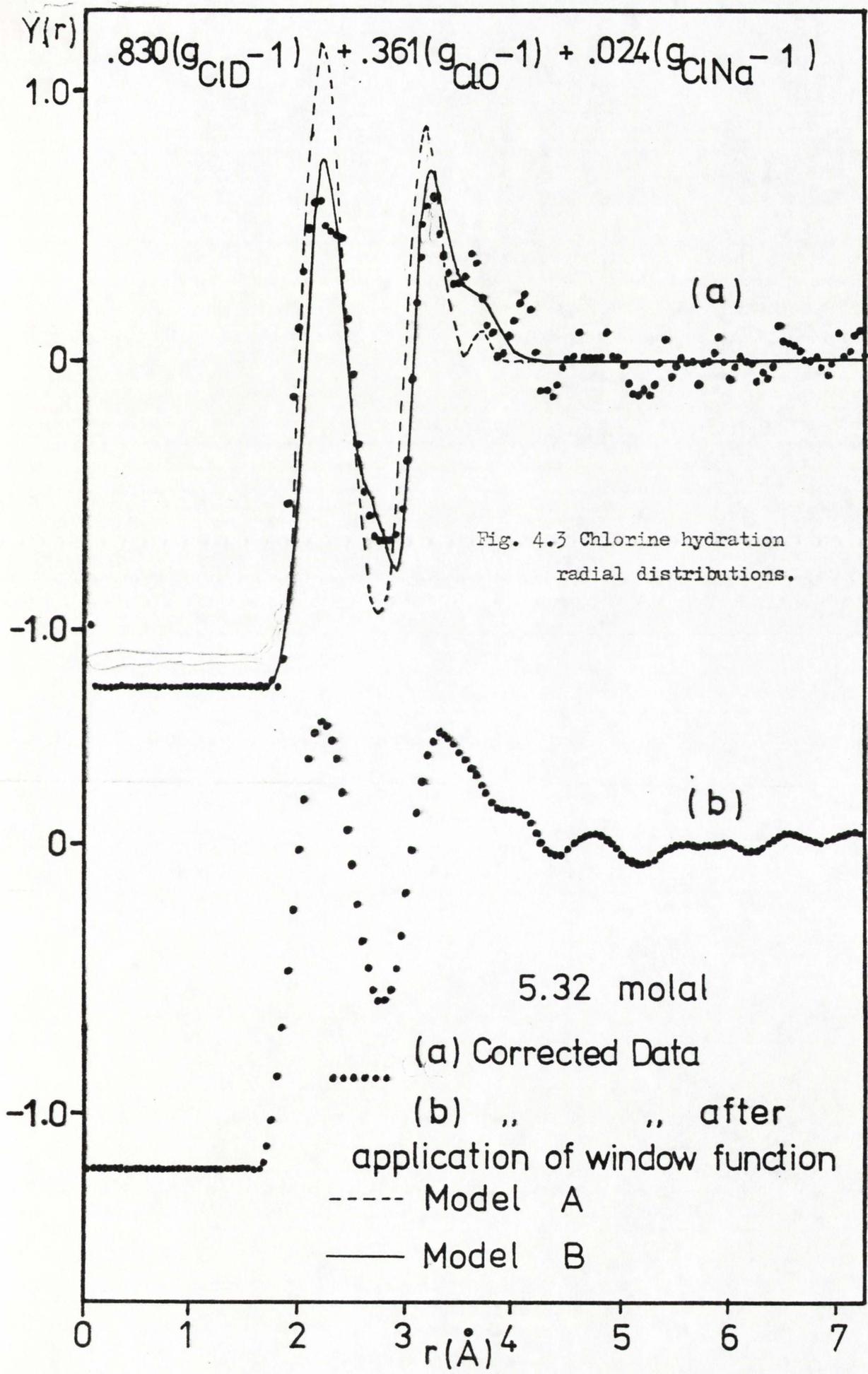
At a concentration of 1.49 molal, two models again emerged, and one of these (B) is shown in fig. 4.7b. The model A had a first shell similar to the model A of the higher concentrations, and a second hydration shell similar to the 1.49 molal model B. At this concentration, the small signal to noise ratio makes the analysis open to much greater ambiguity, but for both models at this concentration, unlike at the higher concentrations, a second shell of orientated water molecules is definitely needed to regenerate the experimental data.

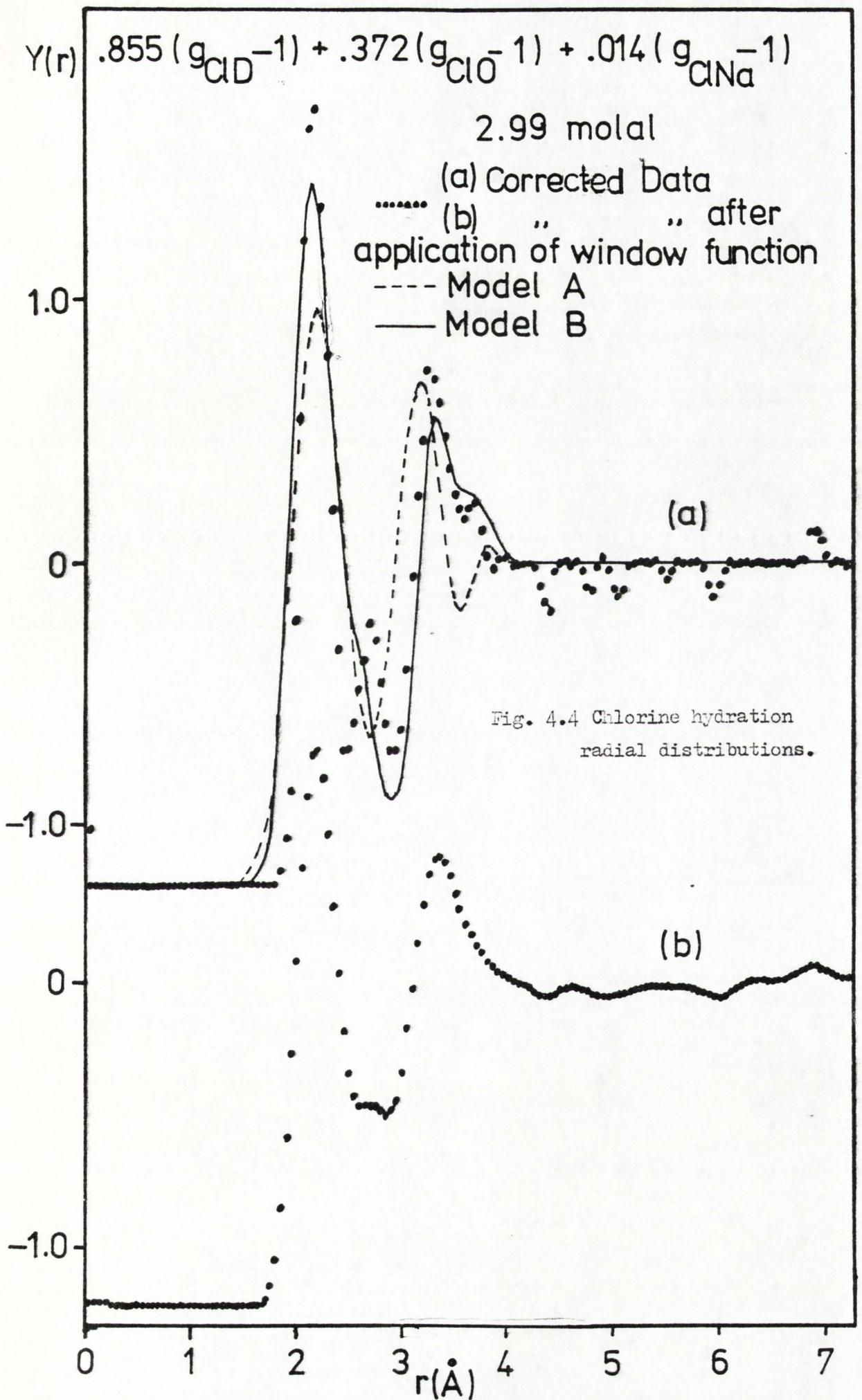
The models were analysed in terms of their mean square deviation from the experimental data, and results of this are shown in table 4.3. For concentrations 5.32 and 2.99 molal, model B emerges as giving the better fit of the two, despite the fact that it entails a Cl - O distance shorter than that observed in any X-ray experiment, appendix 5, and an orientation different from that observed in the molecular dynamics simulations. In the past, the orientation as in model A has been accepted as the most likely configuration. This discrepancy may well represent a short-coming in the modelling technique, but Marten, Vaslov and Levy (62) used the same type of model to obtain the hydration of chlorine ions in LiCl solutions, and there have been very few X-ray experiments on NaCl solutions. However one wouldn't expect the hydration of Cl in the two solutions to be very different.

Finally, it should be noted that the sodium ions are not included in the models as they contribute less than 3 % to the composite pattern.









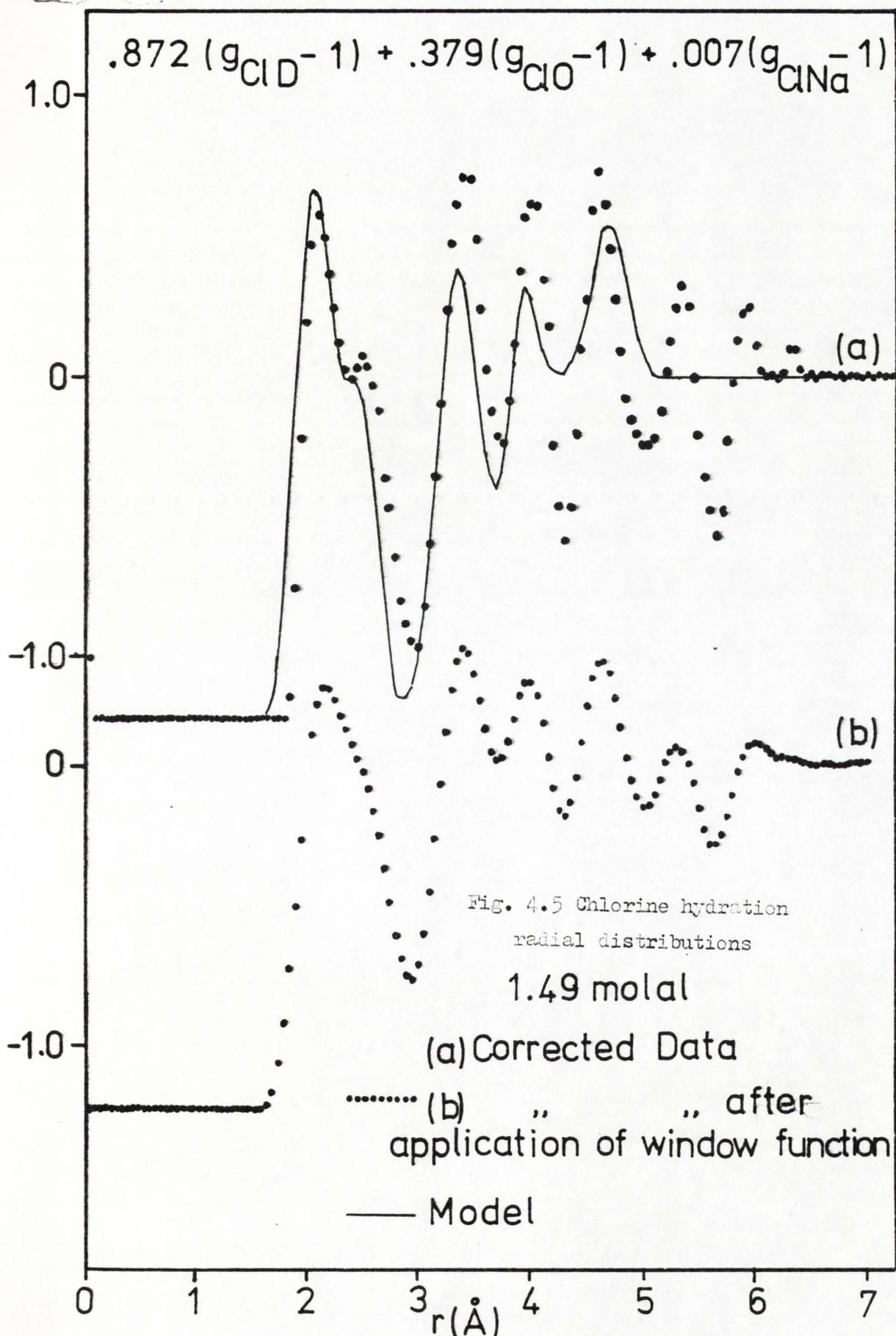
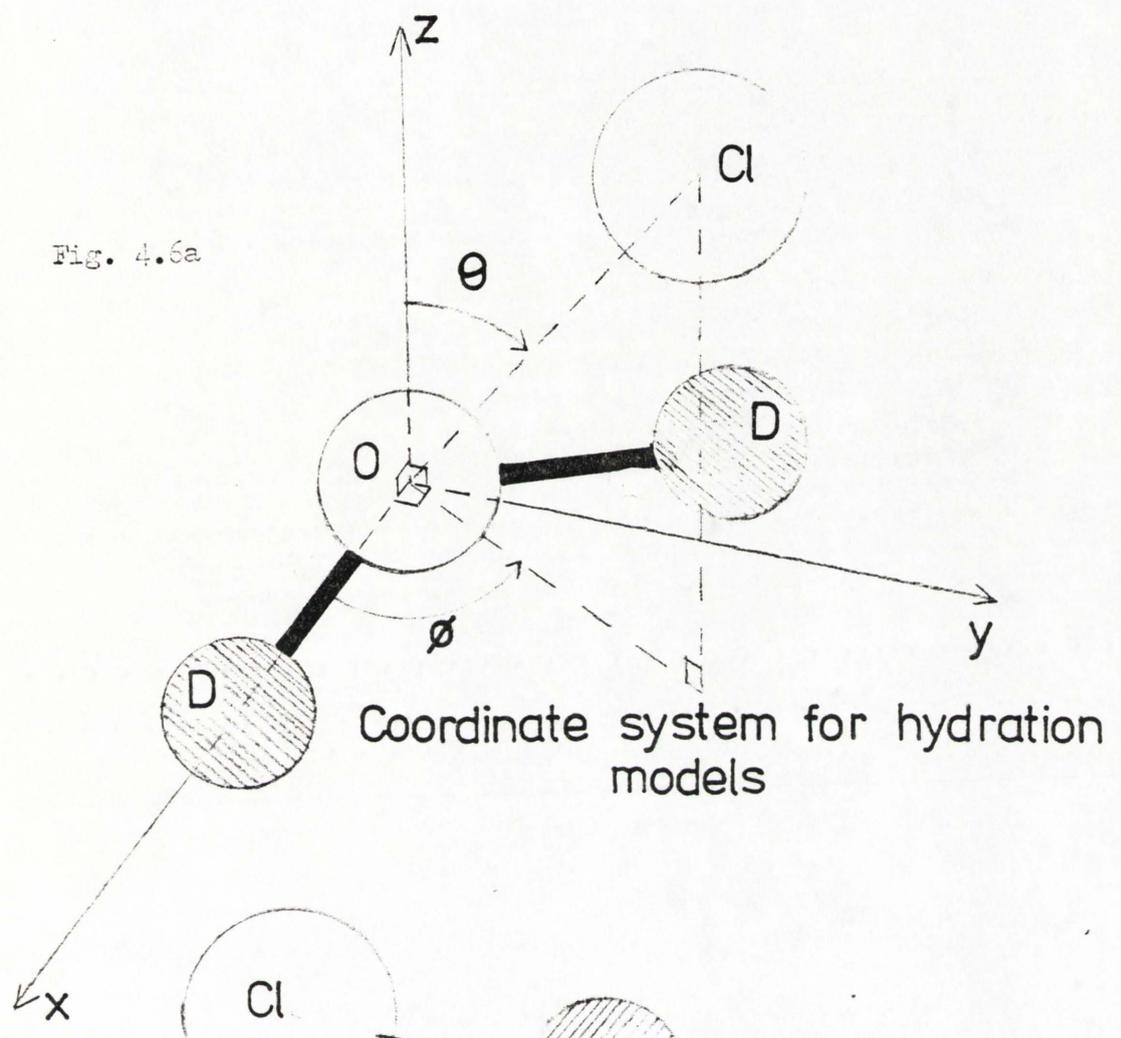
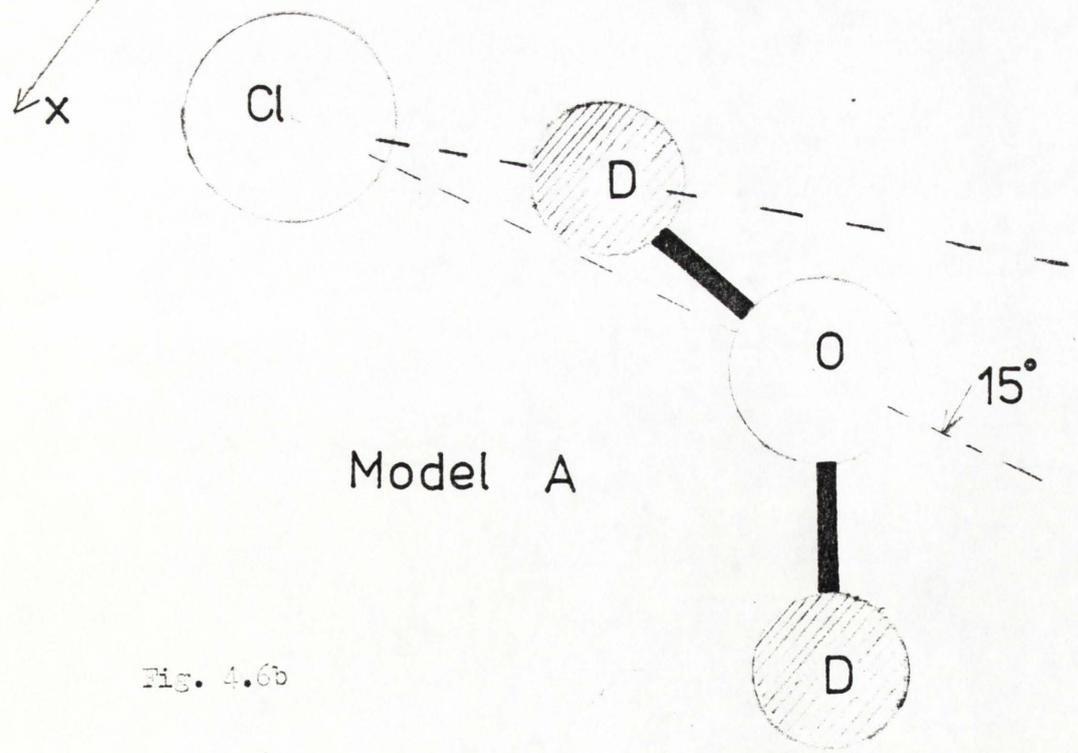


Fig. 4.6a

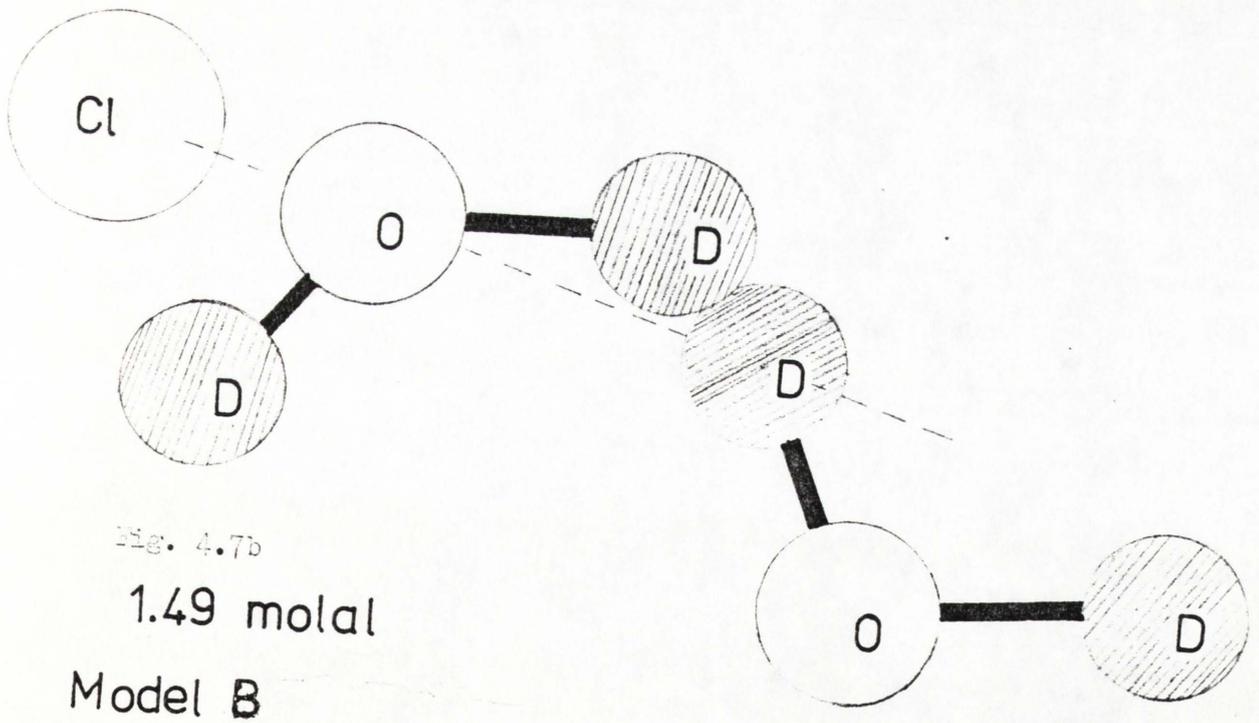
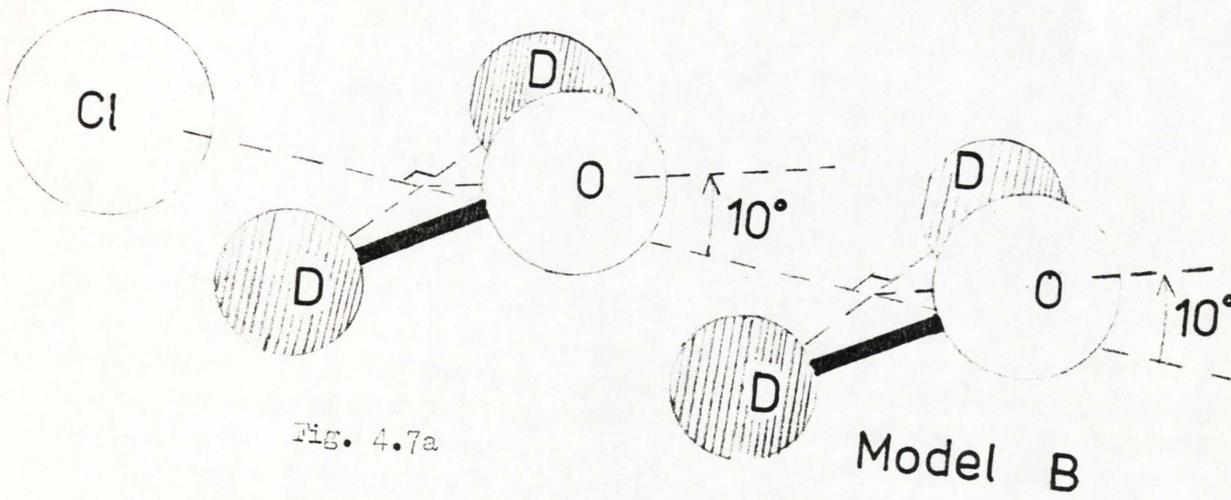


Coordinate system for hydration models



Model A

Fig. 4.6b



3) Chlorine Partial Structure Factors and Radial Distributions

The chlorine partial structure factors were extracted according to equation 3.7 from the corrected differences. Direct Fourier transform of the partials yielded a $g(r)$ which had large oscillations of period $\sim 1 \text{ \AA}$ in the range $2 - 10 \text{ \AA}$, and virtually structure-less beyond. Such a distribution is difficult to justify physically. The molten sodium chloride data (Edwards et al. (96)) shows that the chlorine ions do not approach any closer than 3 \AA in the liquid state, and the period of oscillation in the Cl - Cl radial distribution of the fused salt is $\sim 4 \text{ \AA}$. Hence the large oscillations were treated as truncation errors, and the oscillations in $a_{\text{ClCl}}(Q)$ were similarly found to be due to $g(r)$ values beyond 20 \AA . Assuming the $g(r)$ cannot have a period of oscillation less than 1.8 \AA , then $(a_{\text{ClCl}} - 1)$ should be substantially zero for Q values greater than $2\pi/1.8 \text{ \AA}^{-1}$, i.e. 3.5 \AA^{-1} . At the same time, the resolution of the D4 diffractometer at I.L.L., Grenoble is usually quoted as 0.2 \AA^{-1} at $Q = 1 \text{ \AA}^{-1}$, so it is difficult to observe oscillations of period 0.3 \AA^{-1} or less. This implies a restriction on the maximum radius value to which information can be obtained : $r_{\text{max}} \doteq 2\pi/0.3 = 20.9 \text{ \AA}$. The window function, equation 4.2, was applied to $a_{\text{ClCl}}(Q) - 1$ with $T = 3.5 \text{ \AA}^{-1}$, and to $s_{\text{ClCl}} - 1$ with $T = 20 \text{ \AA}$. Finally, because the data for $Q < 0.4 \text{ \AA}^{-1}$ is unreliable, this region was approximated by drawing a straight line between the thermodynamic value (Appendix 4) at $Q = 0$, and the value at $Q = 0.4 \text{ \AA}^{-1}$. In $g_{\text{ClCl}}(r)$, all values for $r < 3 \text{ \AA}$ were set to zero.

The partial structure factors obtained are shown in fig 4.8 : the band of error shows the amplitude of the oscillations in the raw data. Obviously with such large error bars at the lower

concentrations, it is difficult to justify the radial distribution curves presented in fig. 4.9. The apparent increase in structure with dilution is probably an effect of the increased statistical uncertainty in the partial, although there is some justification in terms of structuring of the ions by water molecules (see Chapter 6) at lower concentrations.

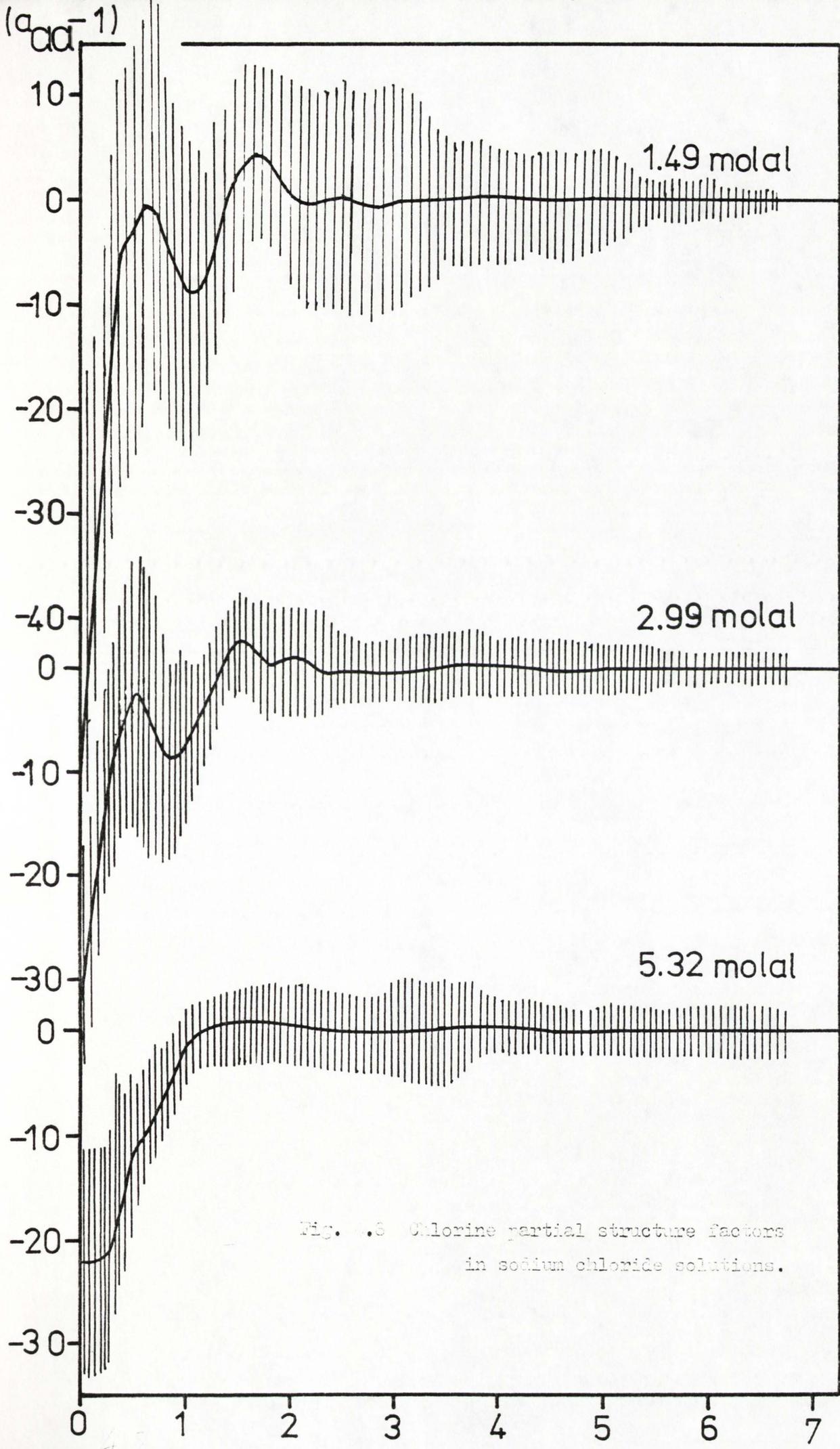
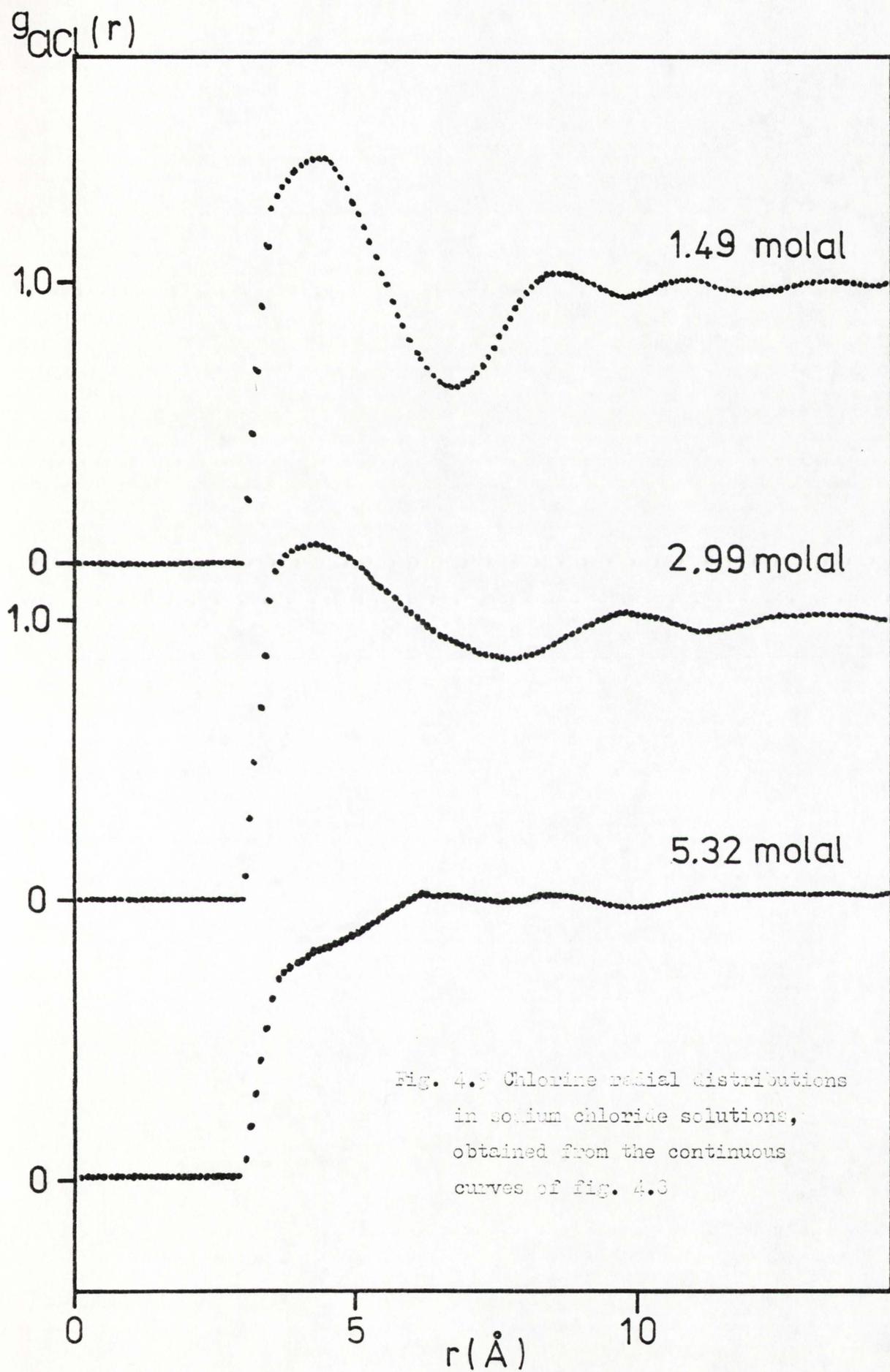


Fig. 4.6 Chlorine partial structure factors in sodium chloride solutions.



4) Nickel Chloride Aqueous Solutions

A study of nickel chloride aqueous solutions was performed concurrently with the present experiment, using nickel isotopes. This work was performed by Dr. Neilson, and so is only presented in outline here. The experimental method was identical with that for sodium chloride solutions. The nickel isotopes used were: natural nickel, nickel '62', and nickel 'zero', the latter consisting of a mixture of natural and '62' (which has a negative scattering length) such that the scattering length is nearly zero, (see Table 4.4). The equations relating to the structure functions are exactly analogous to those already described, and the figures contain all the relevant information. At present, application of the correction procedure described in Chapter 3, has not been completed, and so there are no $Y(Q)$ or $Y(r)$ curves for the data. Instead, the second order subtraction was performed directly; no reliable radial distribution has been obtained from this data. However the first order difference curves have been Fourier transformed, and yield important information concerning the nickel hydration sphere.

The total $F(Q)$ curves show a small feature in the region of 1.0 \AA^{-1} for the natural isotope, which moves inwards at lower concentrations: this movement has been interpreted in terms of a lattice model of the solution, Neilson, Enderby and Howe (74). The feature does not appear in the 'zero' or '62' isotope curves, and only very weakly in the first order difference curve, $F_{62} - F_{\text{zero}}$, where despite the negative scattering length of the nickel isotope, it would still appear as a positive feature if it were solely due to the Ni-Ni partial structure factor. This suggests that a major

contribution to the peak is from one of the terms a_{NiD} , a_{NiO} , a_{NiCl} . Thus the identification of the movement of the pre-peak in the total $F(Q)$ pattern with the movement of the main peak in the Ni-Ni partial structure factor has yet to be verified by partial structure factor analysis at lower concentrations. The existence of the feature and its movement contrasts strongly with the sodium chloride solutions, where no such feature is observed.

The radial distribution curves, fig. 4.18 - 4.20, indicate that the water molecules are tightly bound to the nickel ion. The coordination numbers were obtained by a similar integration to equation 4.3, and are shown in Table 4.5. Least squares analysis in terms of models has not been performed, but it is clear that only the orientation of the water molecules shown in fig. 4.22 would fit the data at all dilutions. Thus the existence of a cation complex, as suggested by X-ray diffraction data (Chapter 2), is confirmed, and the depth and width of the minimum between the double peak and subsequent features implies that the rate of exchange of hydrated water molecules with the surroundings is small. This again contrasts with the sodium chloride data, where the orientation of hydrated water molecules around the chlorine ion is open to ambiguity, and the hydration sphere merges continuously with its environment.

Fig. 4.10 $F(Q)$ curves for nickel chloride solutions:
4.41 molal

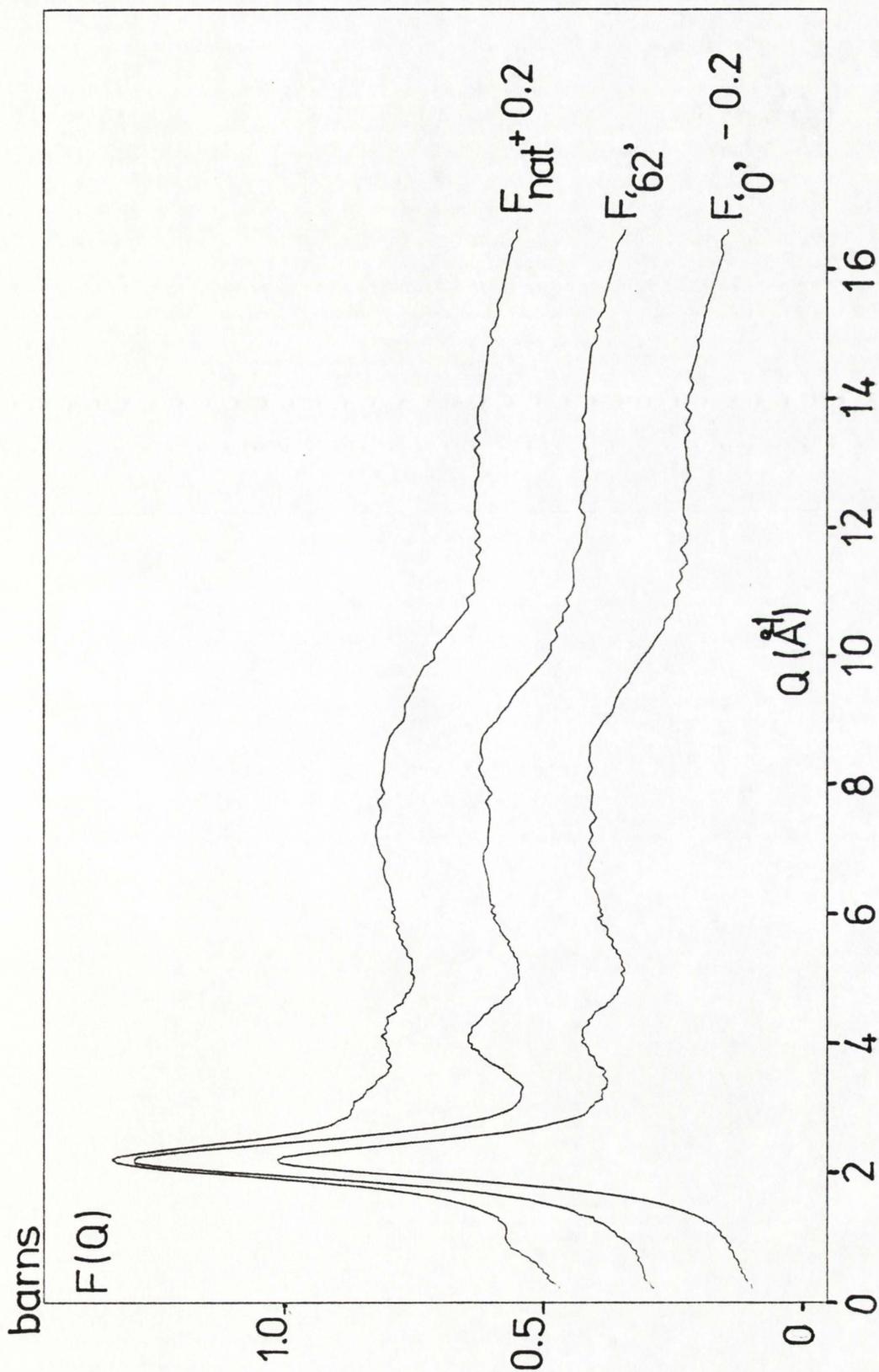


Fig. 4.11 $F(Q)$ curves for nickel chloride solutions:
3.02 molal

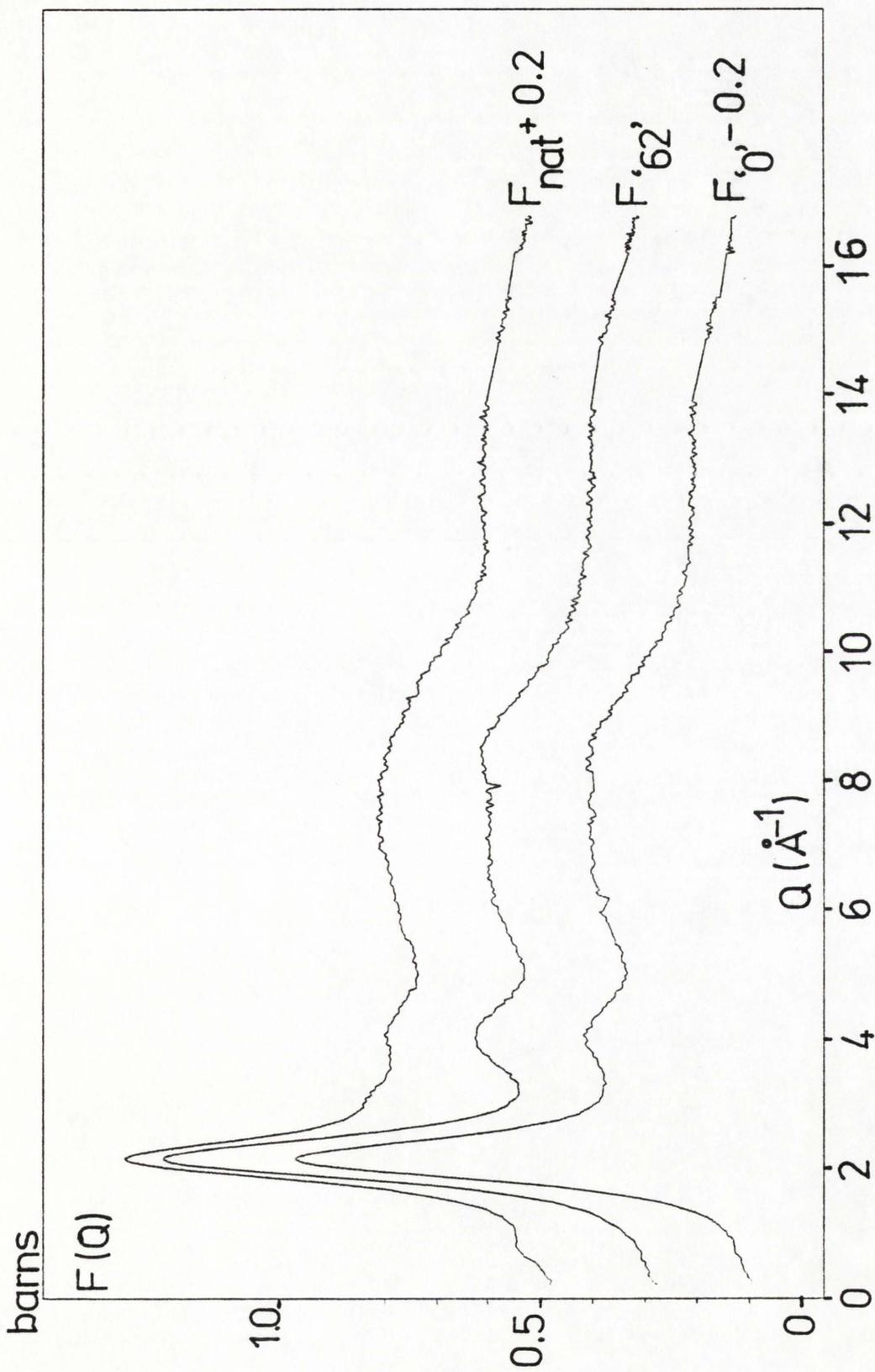


Fig. 4.12 $F(Q)$ curves for nickel chloride solutions:
1.45 molal

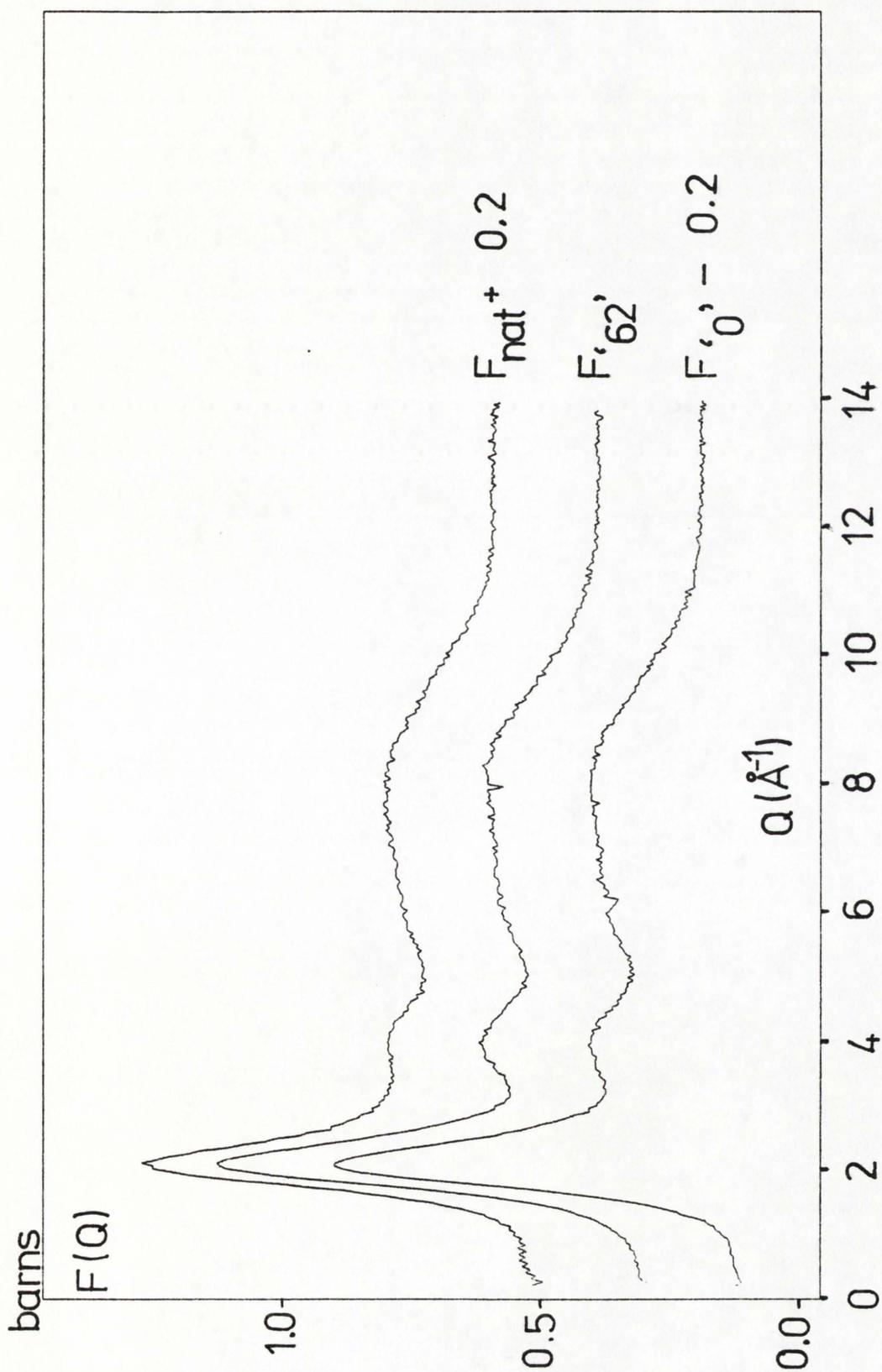


Fig. 4.13 $F(Q)$ curves for nickel chloride solutions.

0.68 molal

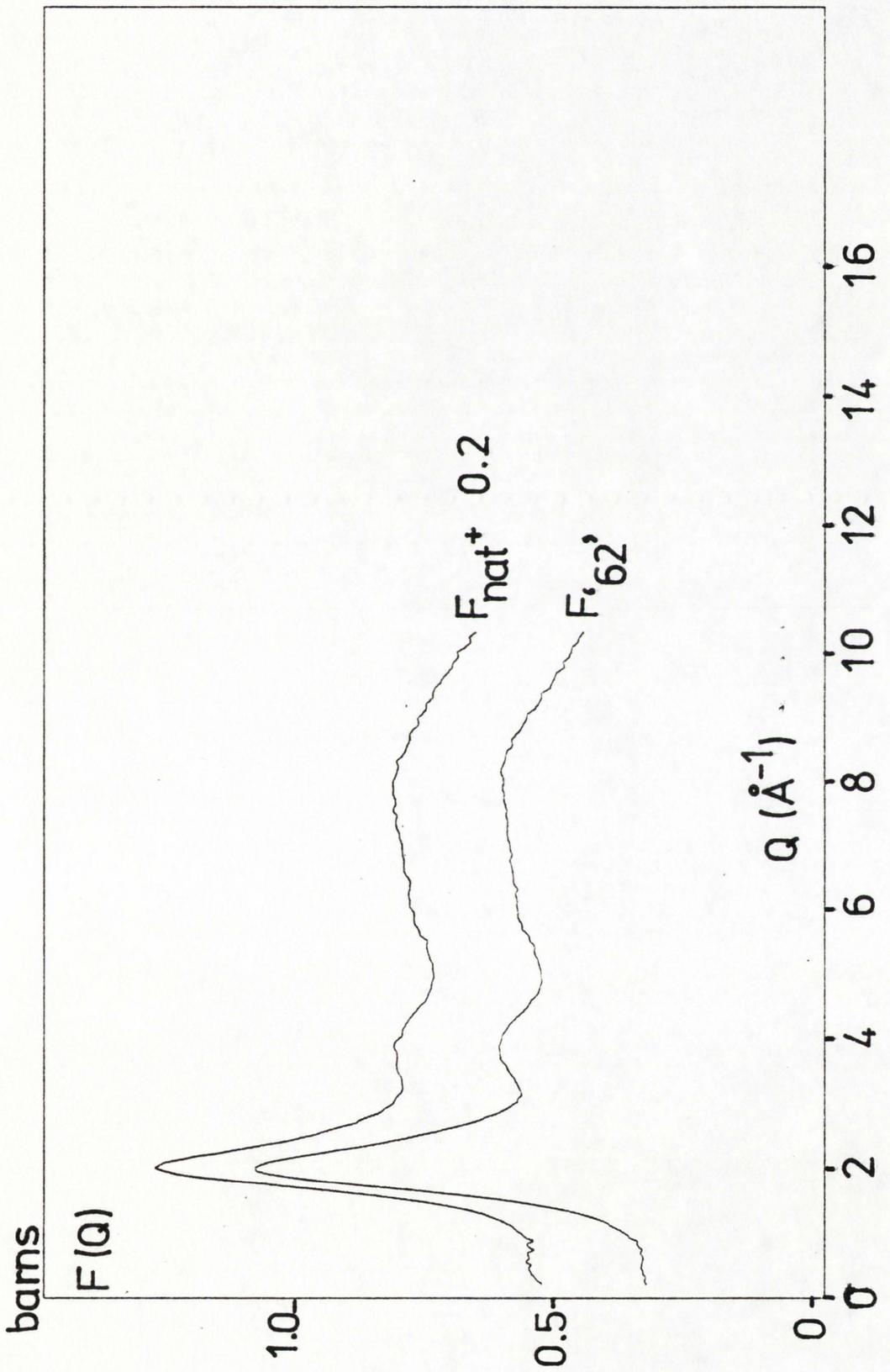
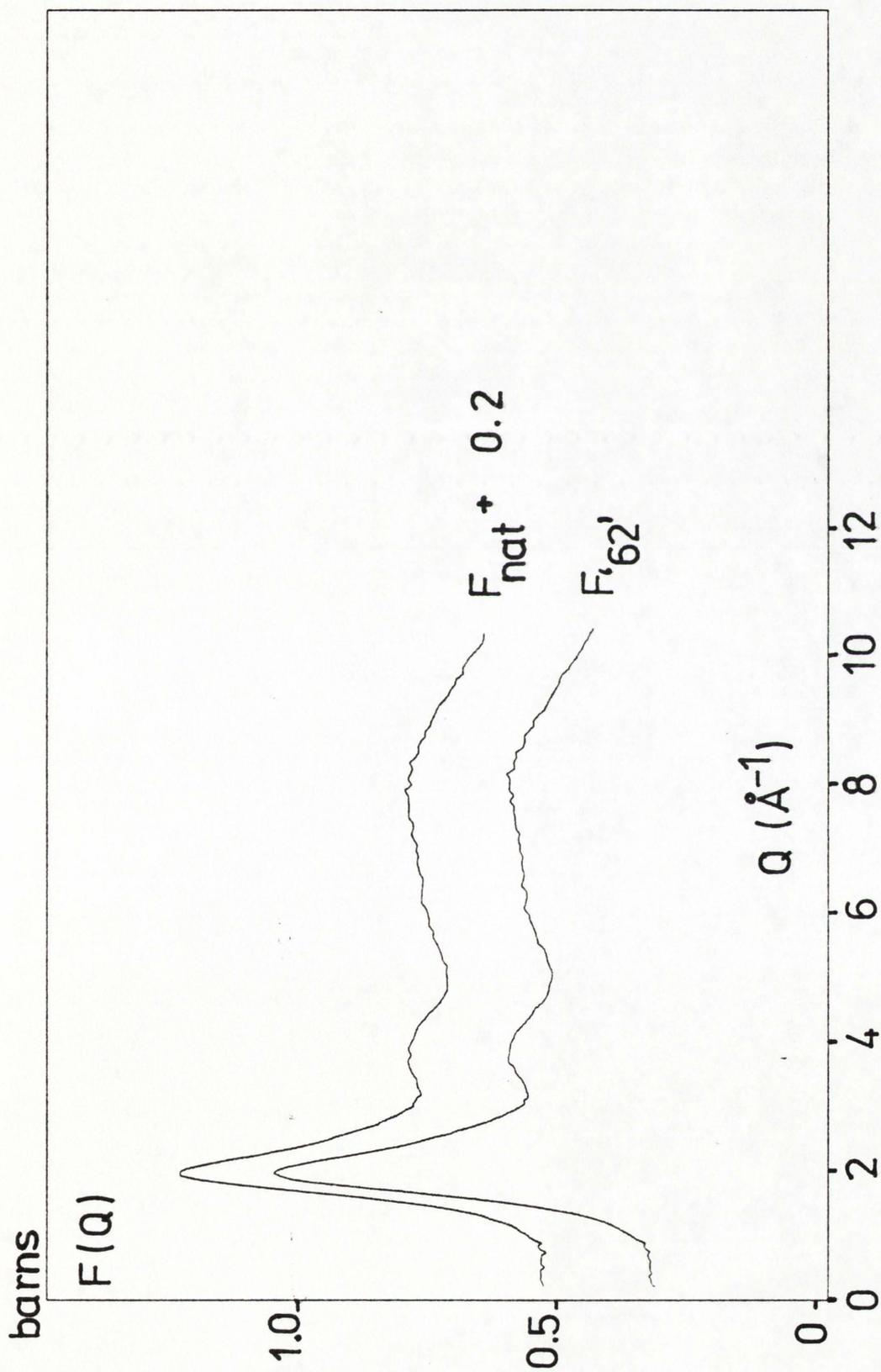
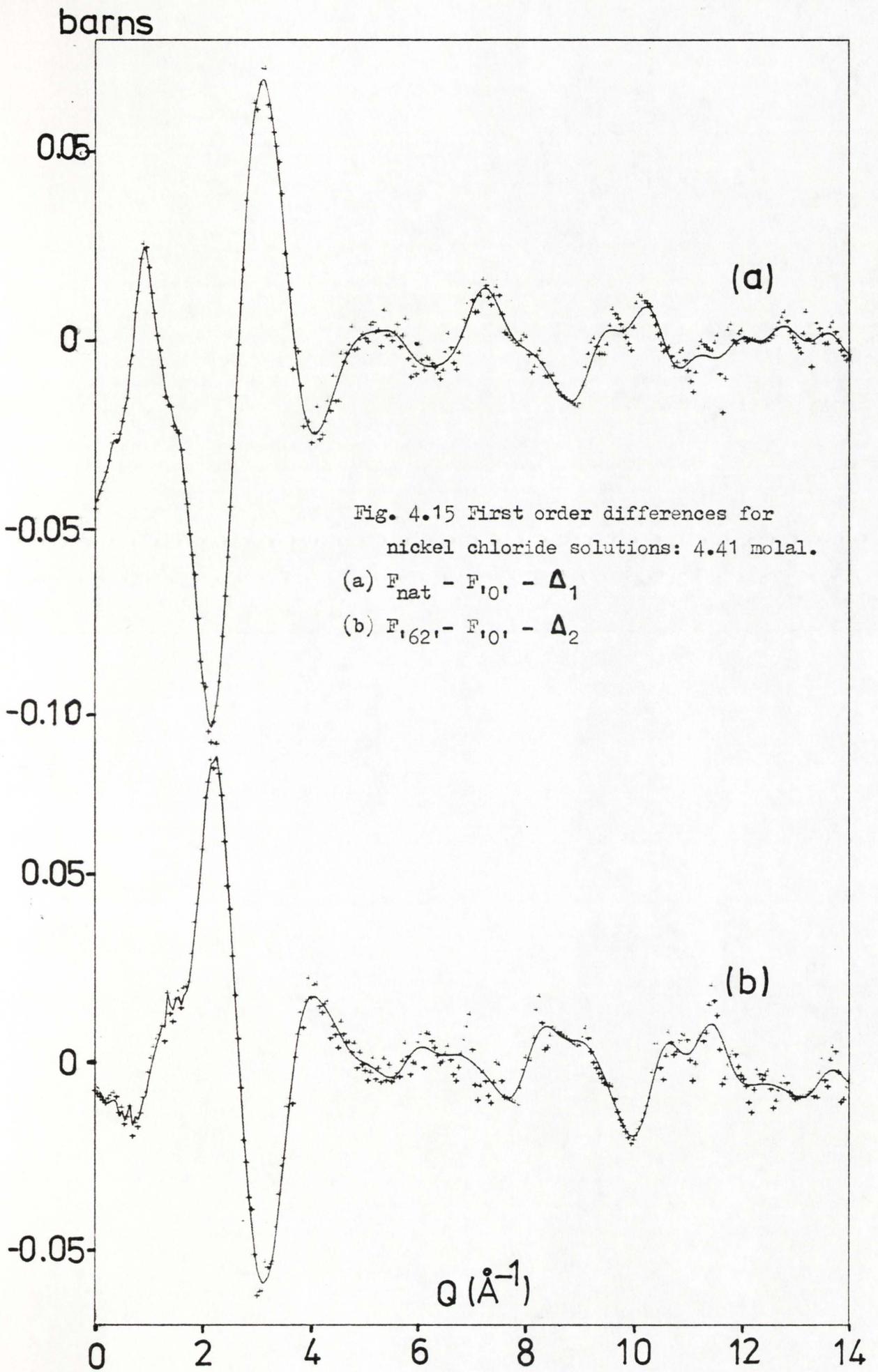
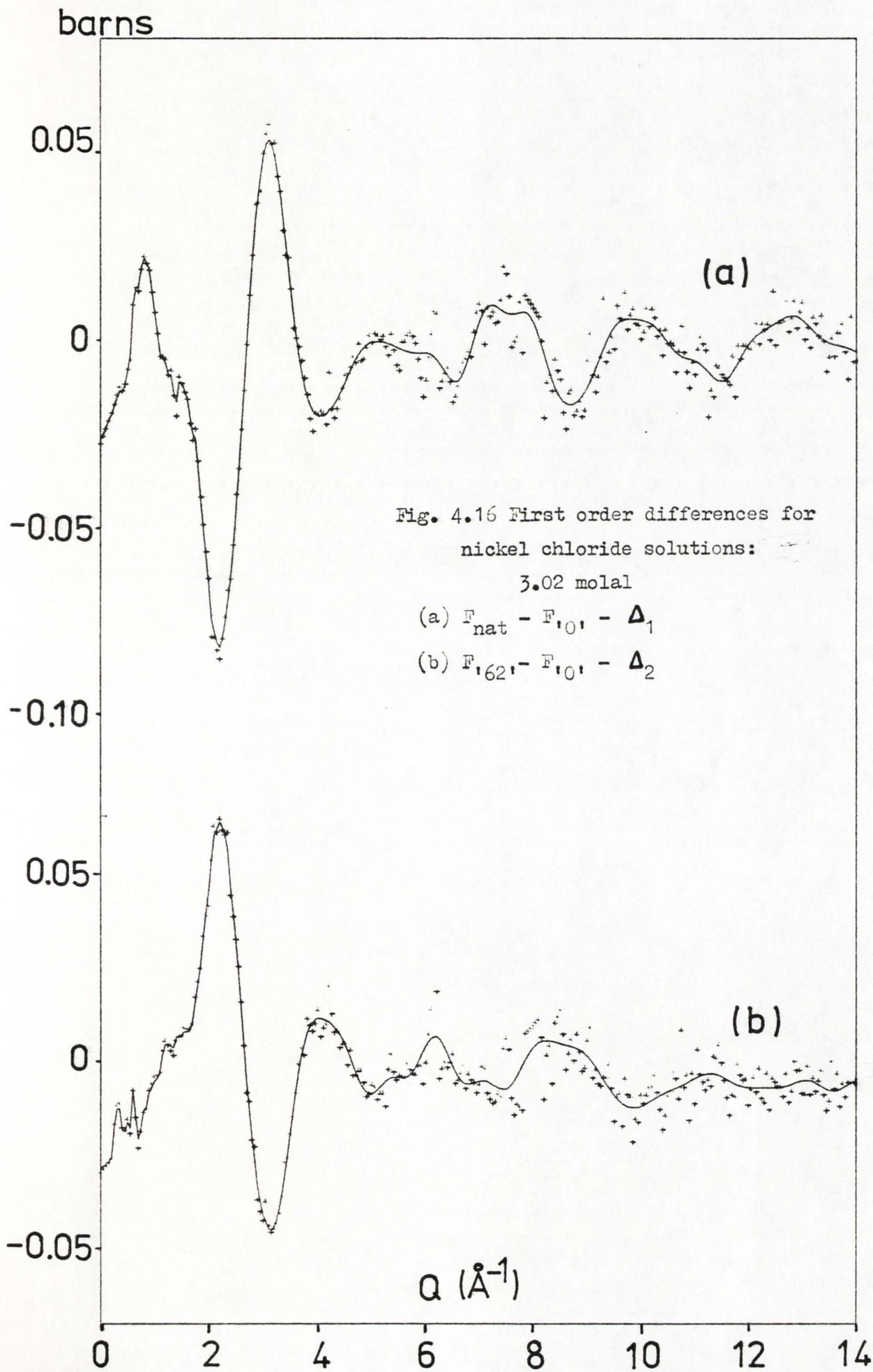


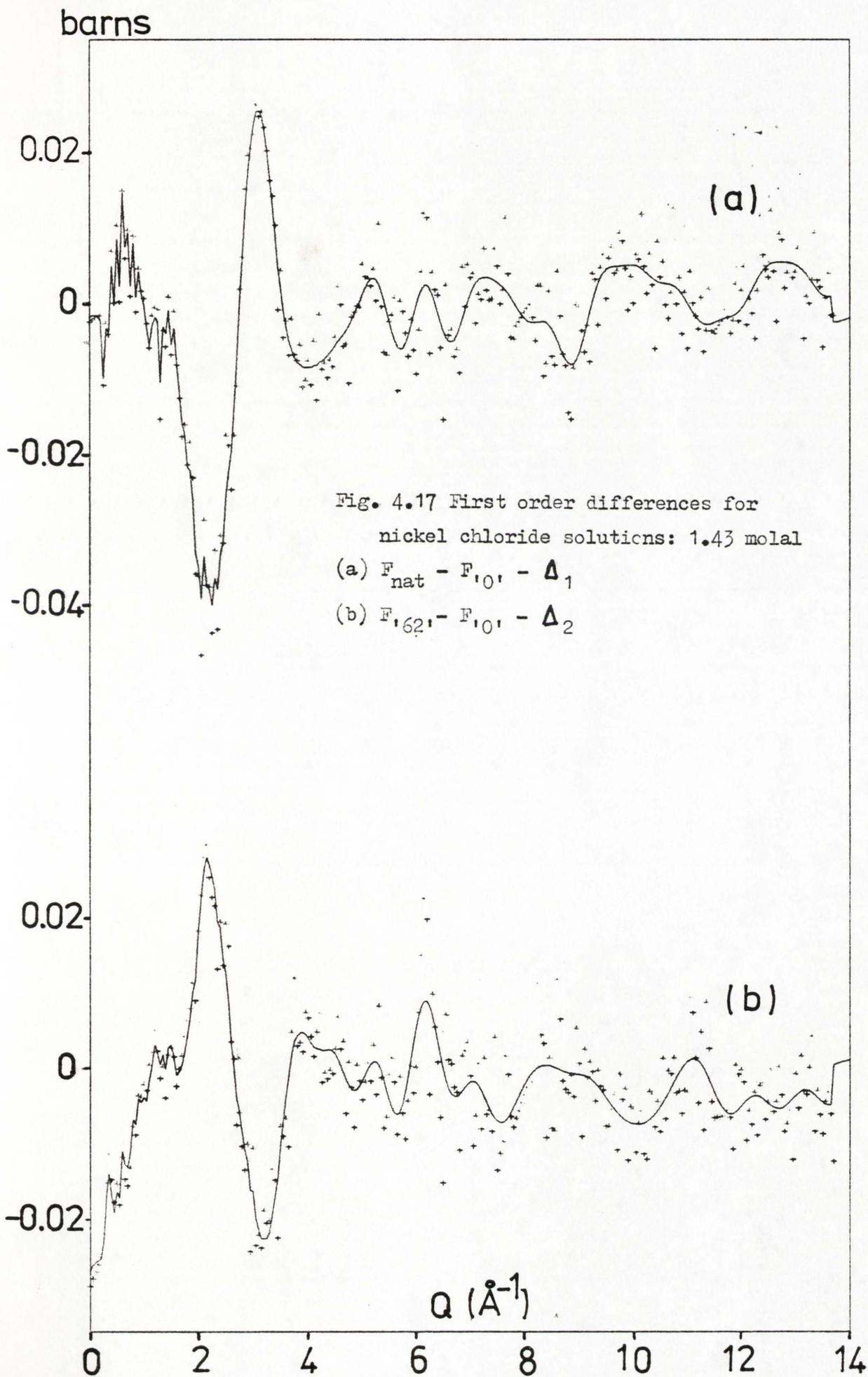
Fig. 4.14 $F(Q)$ curves for nickel chloride solutions:

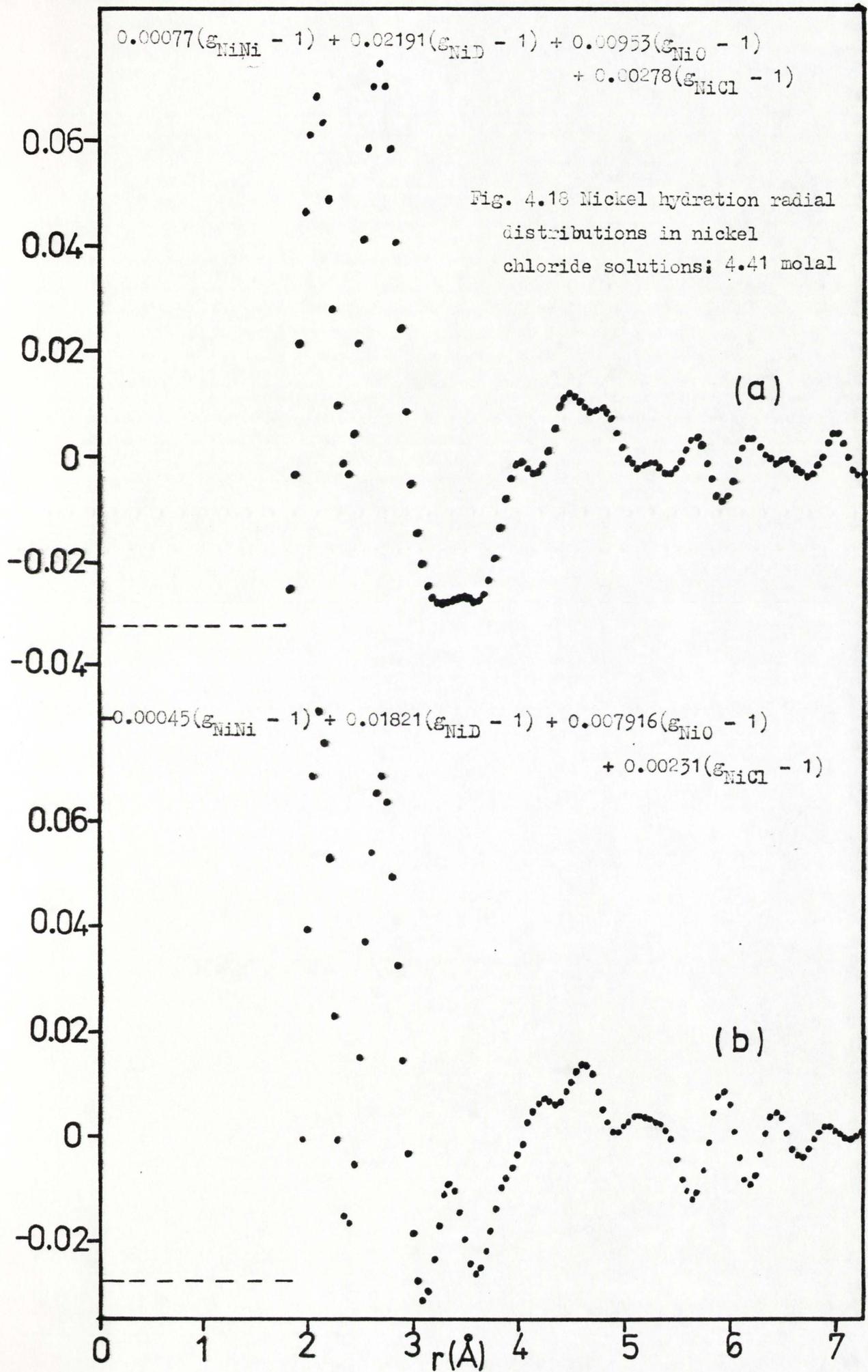
0.44 molal

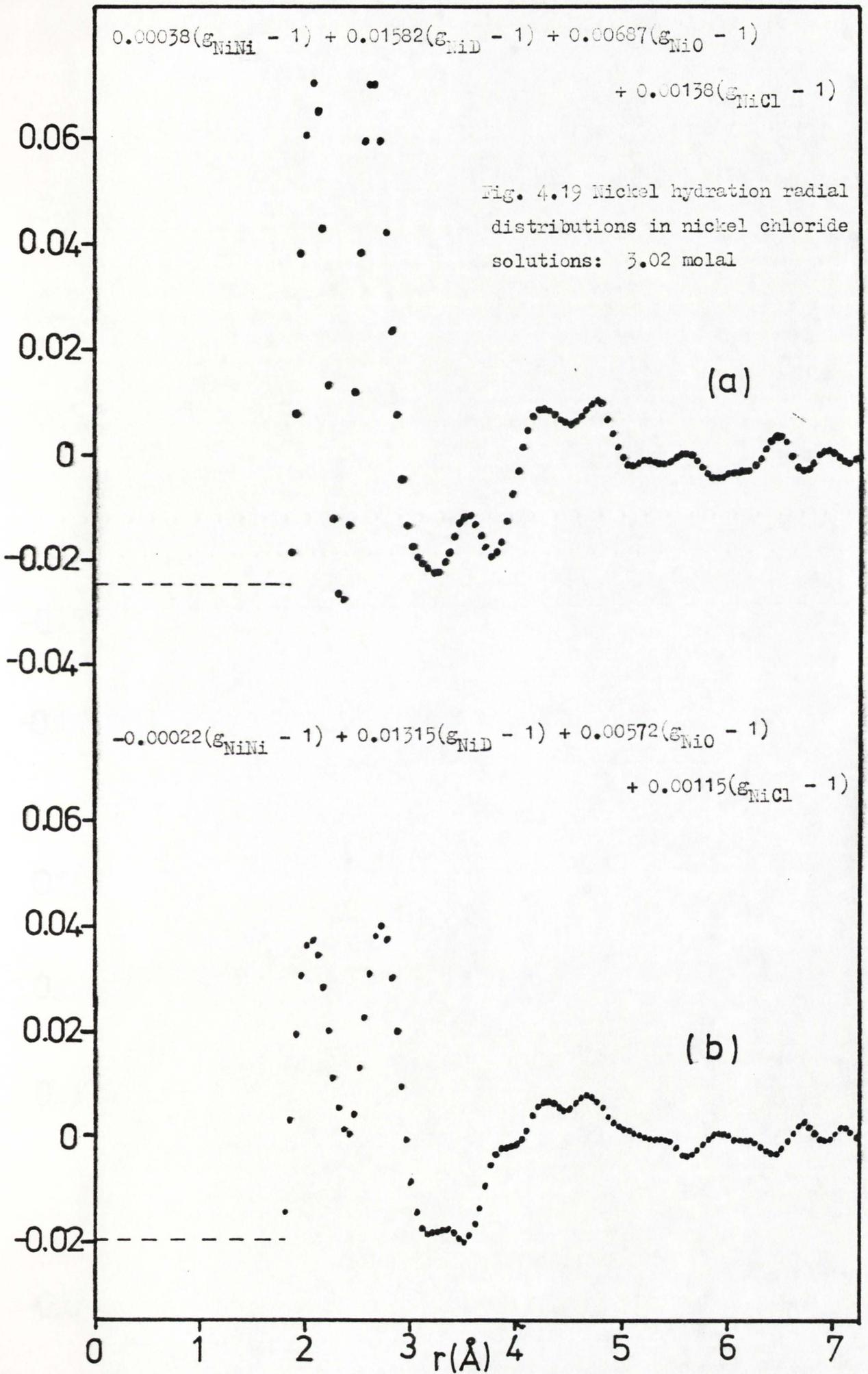


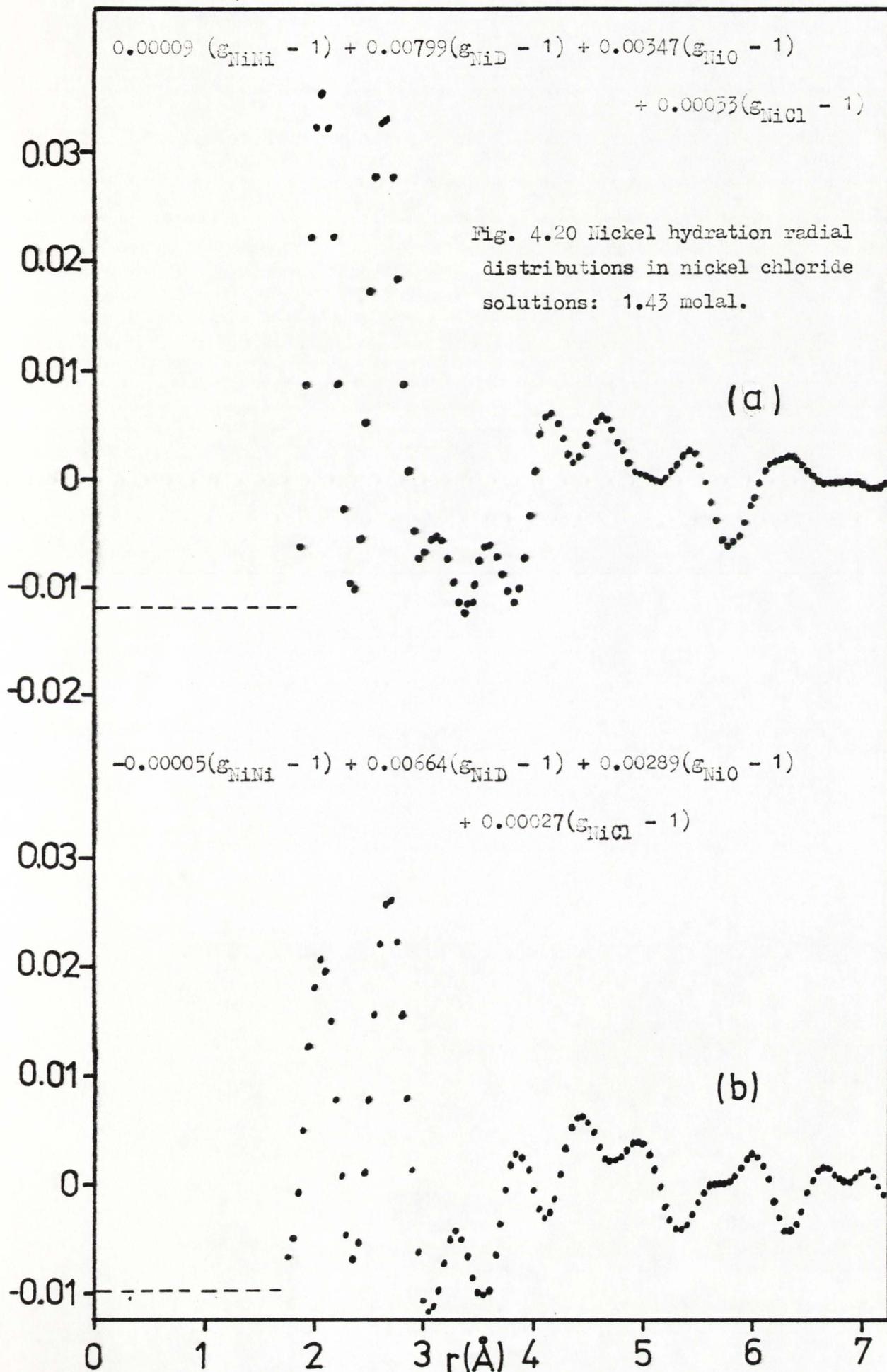












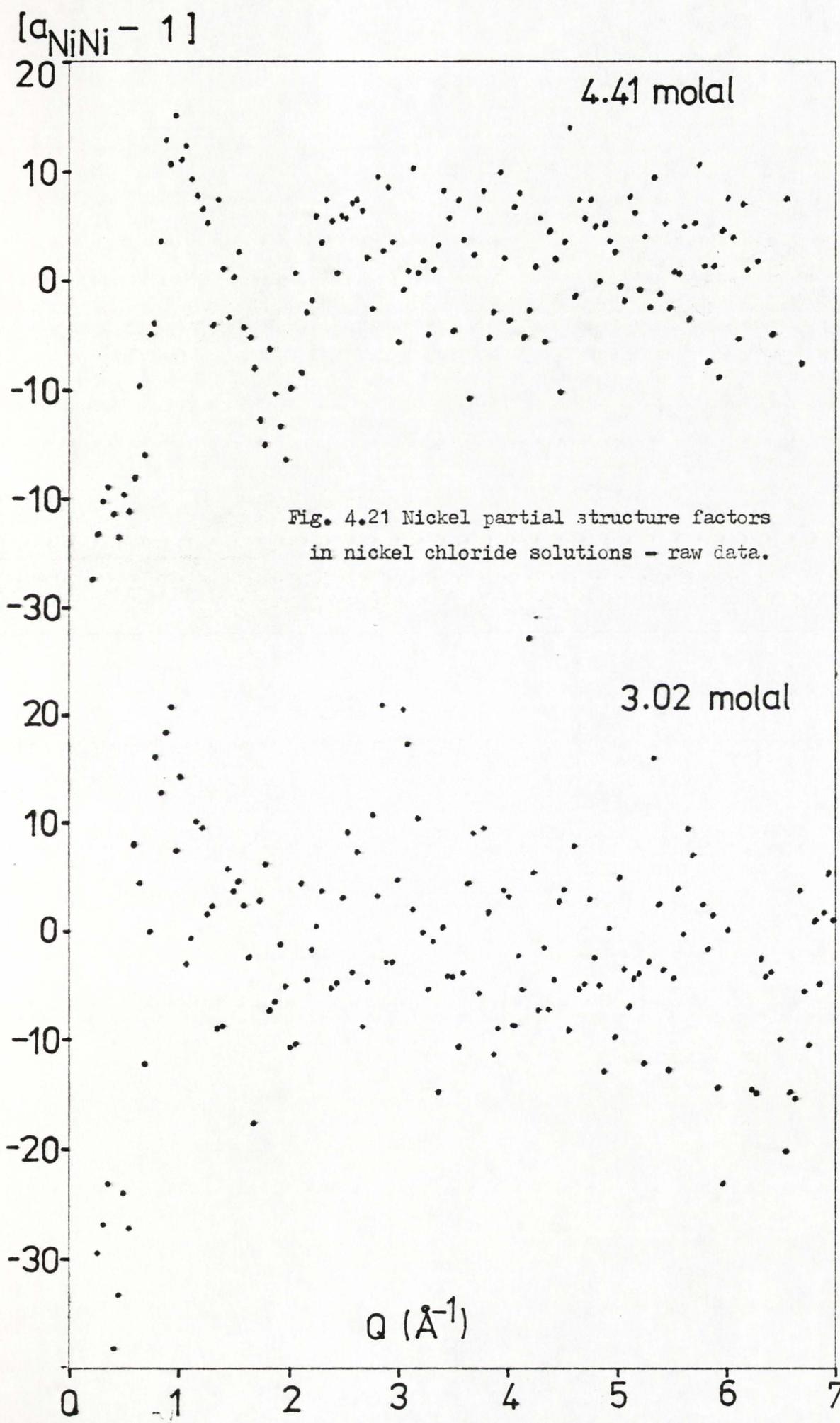
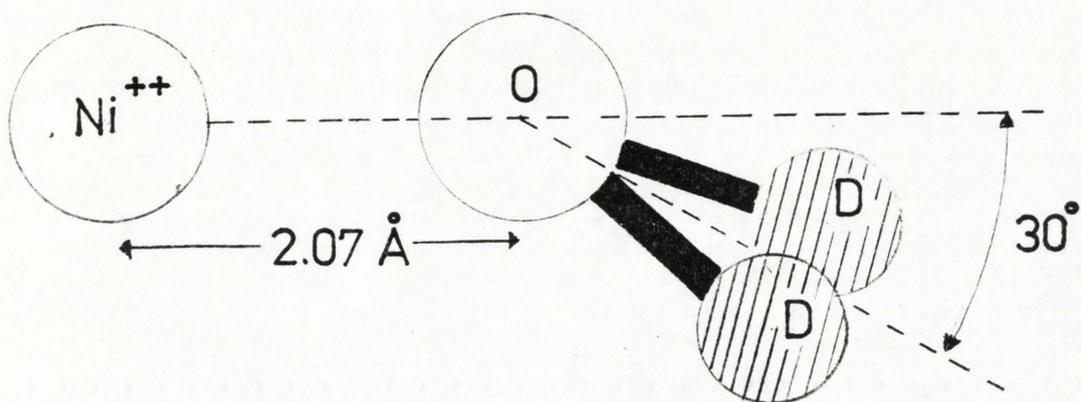


Fig. 4.21 Nickel partial structure factors in nickel chloride solutions - raw data.

Fig. 4.22 Orientation of water molecules around the nickel ion



MODELS OF LIQUIDS1) Introduction

In the discussion in Chapter 2, it emerged that some authors have suggested the existence of a quasi-lattice structure of the ions dissolved in an aqueous solution. This has prompted two questions: how lattice-like is the structure, and do other liquids not show similar features? There is also the question of whether the structure can be predicted by a non-lattice model.

For aqueous solutions we have the following information concerning the ion-ion distribution. The structure factor for chlorine ions in sodium chloride shows no ordering in the radial distribution. For nickel chloride, there is considerably more evidence for ordering in the Ni - Ni partial structure factor. In addition, a small peak in the total scattering pattern, associated with the first peak in the nickel partial, is seen to move linearly with $n_{Ni}^{\frac{1}{3}}$, where n_{Ni} is the number density of nickel atoms (74).

An attempt is made here to answer the questions by presenting some calculations on disordered lattices, and comparing them with the results of a hard-sphere simulation.

PART A - Disordered Lattices2) Setting Up the Disordered Lattice

The lattice model of liquids, both theoretically and experimentally, is well-known. Kaplow, Strong and Averbach (98)

and (99) have found good agreement between the disordered lattices of magnesium, lead and gold-tin alloys and their corresponding liquid structure. Narten (38) was able to obtain good agreement between a disordered Ice I model of water and experiment, although O'Reilly (39) showed an Ice Ic-VII model to be equally satisfactory. Most approaches use a large number of adjustable parameters to fit their models, leading to a confusing picture of the real liquid structure. In the present study, a simple model is used to compare a variety of liquids, showing the extent of the lattice-like behaviour, and gaining insight into the physical meaning of the liquid structure factor.

The radial distribution function for a crystal lattice is represented by a distribution of δ -functions, whose heights corresponds to the number of atoms at each radius value from a given origin. Thermal broadening, the Debye-Waller factor, reduces the height of the peaks, but the area under each still represents the number of atoms. For the liquid model, the broadening is allowed to increase considerably so that the peaks overlap and the distribution becomes continuous.

There are two types of distribution to be discussed:

$g(r)$ is the probability function discussed in Chapter 1. $G(r)dr$ is the number of atoms found within dr at r , and is equal to $4\pi nr^2 g(r)dr$. It is necessary to generate $G(r)$ before $g(r)$ can be calculated. The method for disordering a crystal structure therefore falls into three stages:-

- 1) Obtain $G(r)$ for the solid lattice.
- 2) Disorder this and then divide by $4\pi nr^2$ to obtain $g(r)$.

3) Perform a Fourier transform to obtain $a(Q)$.

The third stage is included since experimental data comes as $a(Q)$, and it is possible to avoid termination errors in the simulated data by generating $g(r)$ to large values of r . A general computer algorithm was written for any crystal lattice which can be described by a repeated unit cell, for the $G(r)$ in stage 1. See figure (5.1).

For step 2, the width of the 'i'th peak, σ_i , is described by the equation

$$\sigma_i = a x_i, \quad \dots 5.1$$

where x_i is the position of the peak, and a is the width constant. Other broadening terms were tried. A constant term was unsatisfactory, a square-root term did not produce sufficient disorder at large r , and a quadratic term was too strong: the linear function is the maximum broadening possible while keeping the distribution meaningful.

However, Frenkel (100) argues from statistical mechanics that the width should increase as $\sqrt{x_i}$. Indeed the linear term is not perfectly satisfactory. But in the real liquid there are interstitial positions, on account of the atomic motion, which are not possible in the solid, and this produces broadening additional to Frenkel's simple kinetic term.

Another effect, not mentioned by Frenkel, is that disordering a lattice with increasing peak widths increases the number density of the final $G(r)$. The amount will depend on the value of a , and the peak shape. Hence it is necessary to integrate the disordered $G(r)$ to obtain the new mean number density. This integral is awkward for the Gaussian probability curve usually

Figure 5.1

Algorithm for generating radial distribution of a crystal.

1. Input the dimensions and angles of the unit cell, the coordinates of the atoms within the cell, and their lattice site probabilities.
2. Define the maximum radius to which atoms are to be counted, and define a parallelepiped containing an integer number of unit cells, and sides parallel to the unit cell vectors, sufficiently large to contain a sphere of this radius.
3. Step through the parallelepiped, stopping at each unit cell.
4. At each unit cell, generate the coordinates of each atom in turn, and convert to Cartesian coordinates with respect to the centre of the parallelepiped. Measure the distance of the atom from this origin: compare with the previous values of such distances. If there are already atoms at this distance add the present lattice site probability to the existing value. If there are no atoms previously at this distance, generate a new lattice distance and probability, and place this in the array in order of increasing distance. If the distance is greater than the radius of the sphere, then ignore the lattice site.
5. When the stepping is complete, there will be two arrays, one containing all the distances from the origin at which a lattice site may be found, and the other contains the total number of atoms to be found at each distance, given that some or all of the sites are not filled for 100 % of the time.

associated with this type of disorder, so a simpler function for the peak shape is used here:-

$$F_i(r) = \frac{1}{\sigma_i} \left[1 + \cos\left(\frac{2(r-x_i)}{\sigma_i}\right) \right], \quad \dots 5.2$$

for $(x_i - \frac{\sigma_i}{2}) \leq r \leq (x_i + \frac{\sigma_i}{2})$, and zero for r outside these limits. The $\frac{1}{\sigma_i}$ factor is introduced so that the integral of the function over the allowed range of r is unity; this integral is analytic.

The disordered $G(r)$ is represented by the sum

$$G(r) = \sum_i N_i F_i(r) \quad \dots 5.3$$

where N_i is the number of atoms at radius x_i in the original lattice.

3) Results

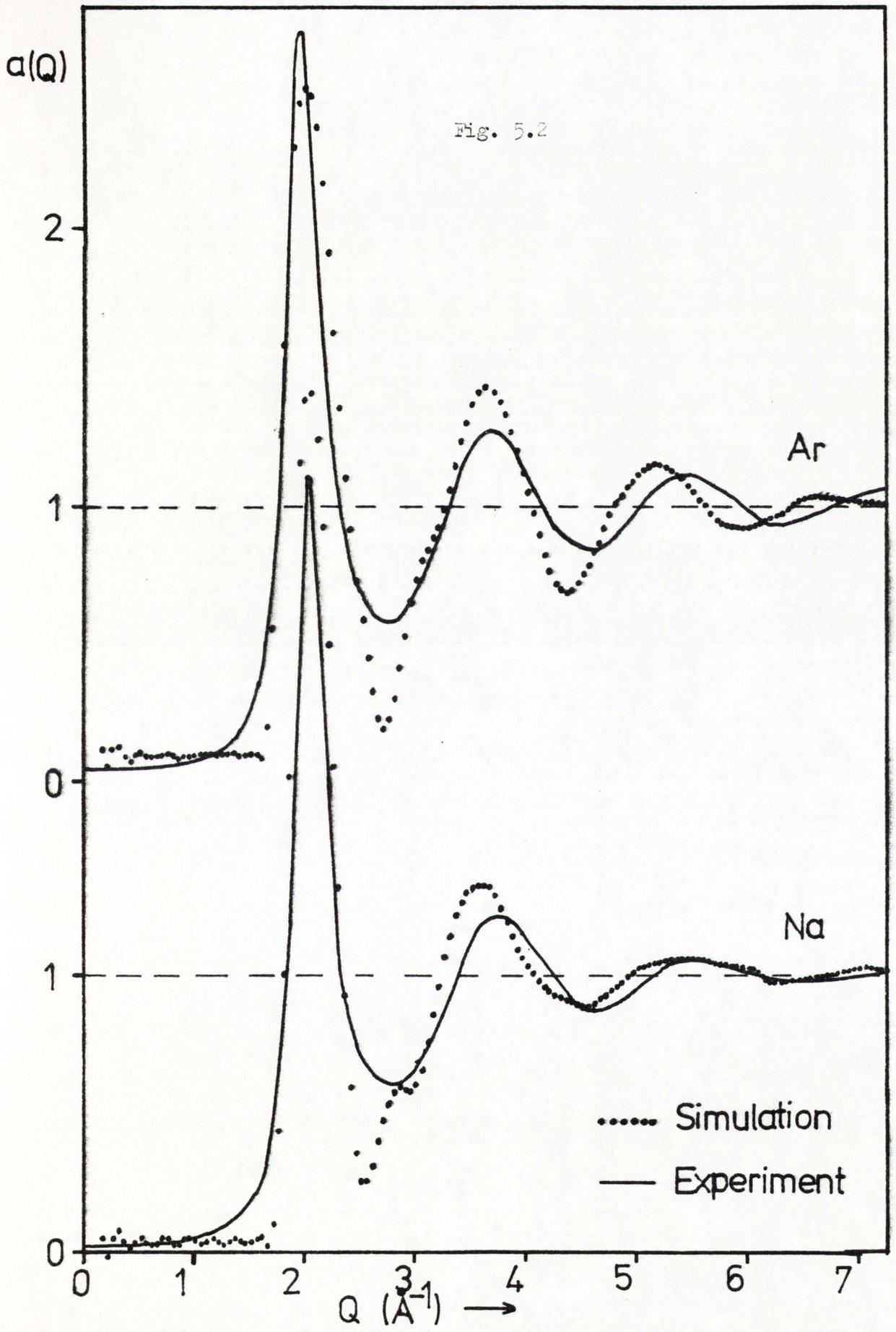
a) Monatomic Liquids.

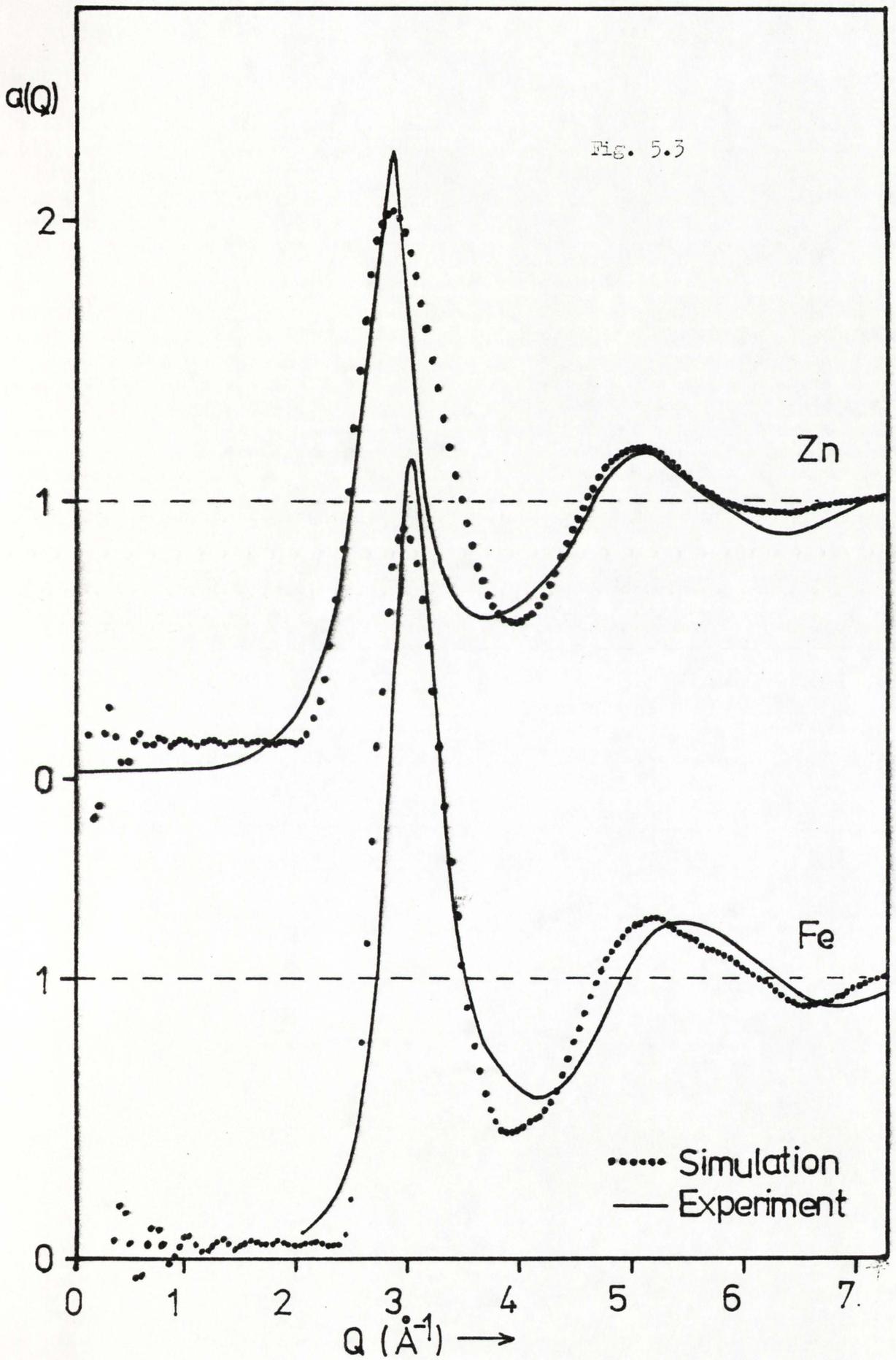
There is a wide literature for the structure factors of monatomic liquids. Comparison of the disordered solid-state structure with the liquid structure factors is shown in figs. 5.2, to 5.4. Table 5.1 gives the parameters used in the simulation. No attempt was made to obtain a least-squares fit: the amount of fitting was kept to an absolute minimum. The guiding criteria were, to obtain a near-neighbour distance, atomic number density and peak width constant, consistent with an $a(Q)$ close to experiment.

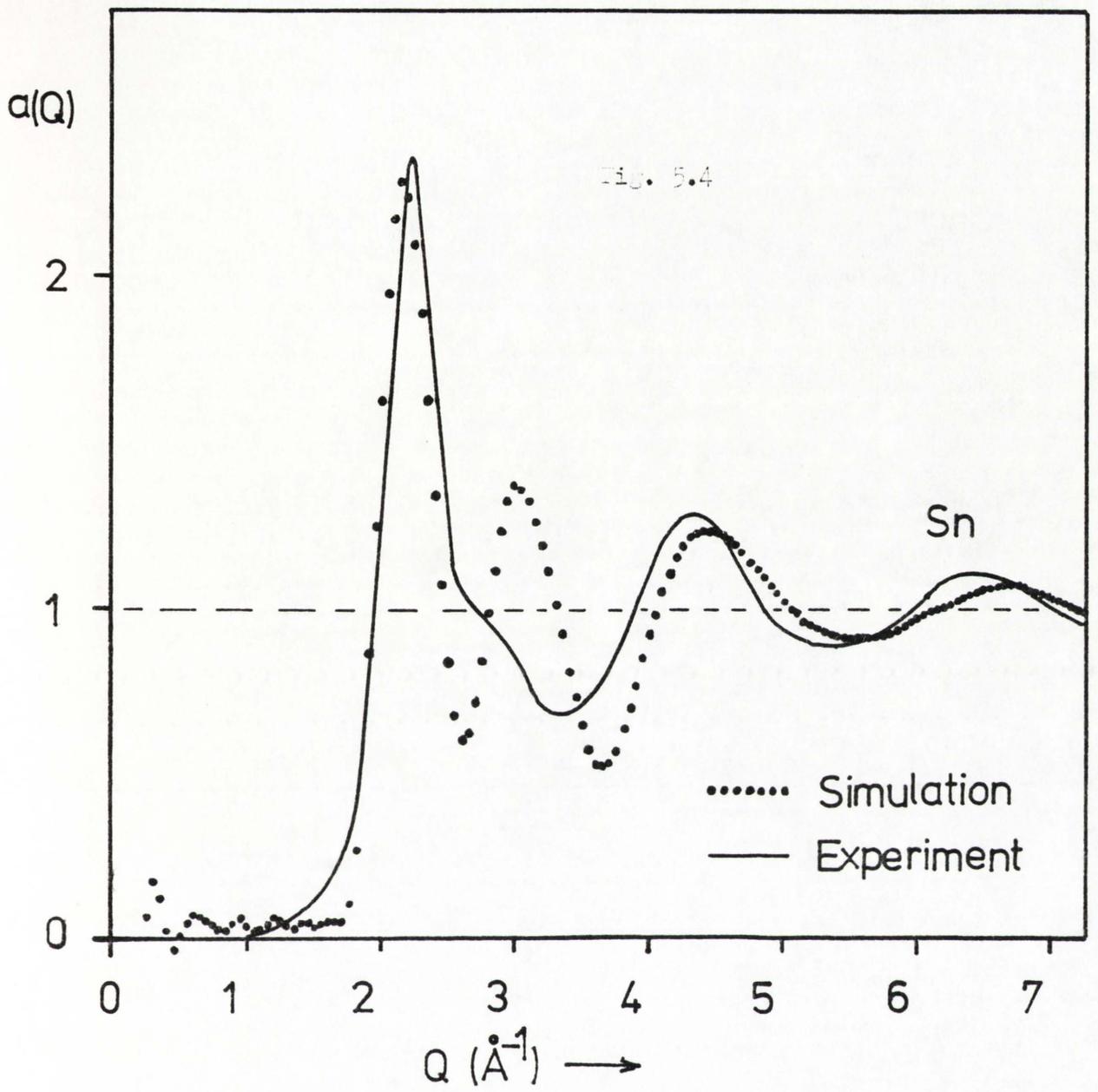
The following points emerge from the comparison:-

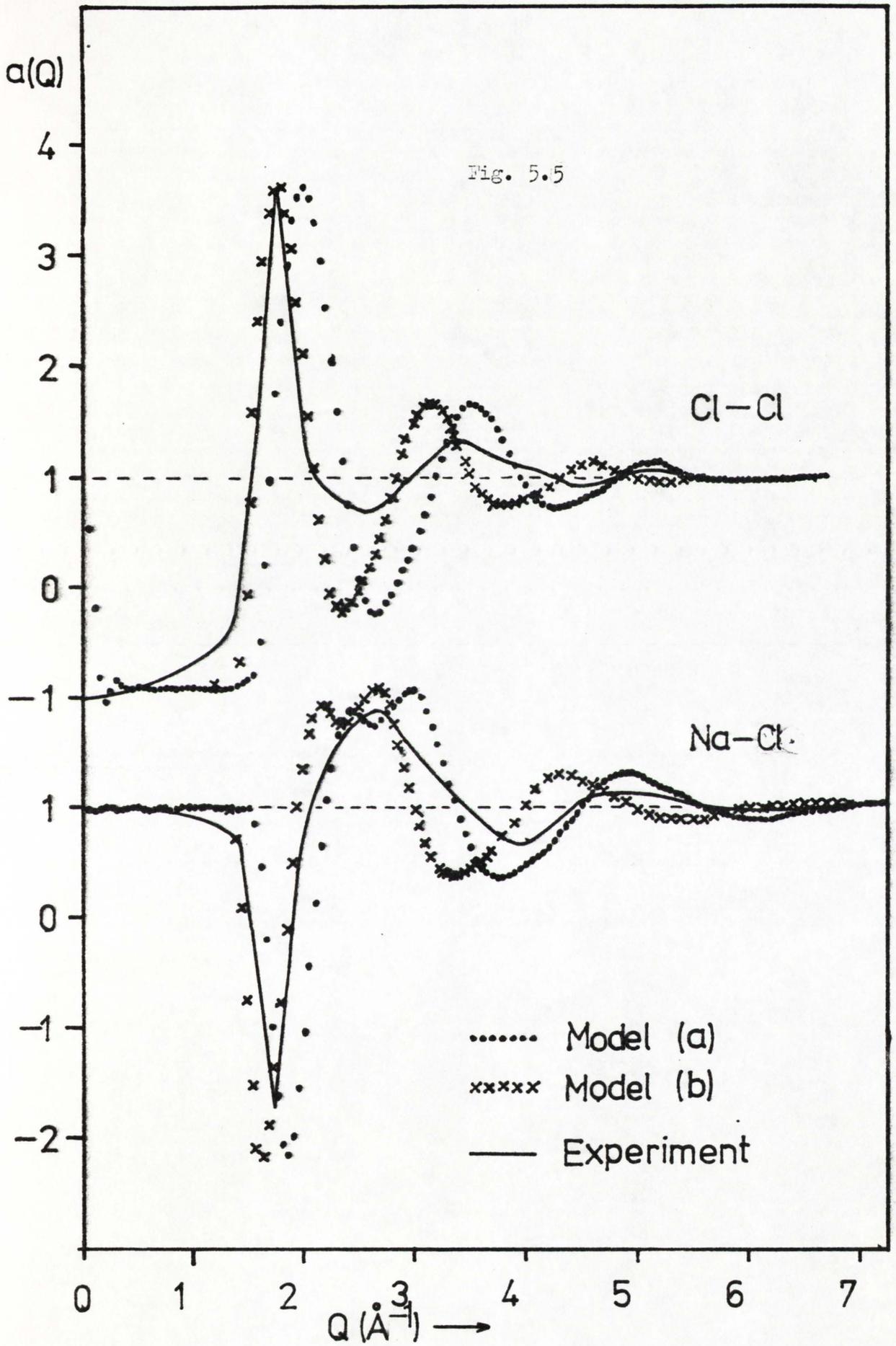
1) Except for zinc and tin, the near-neighbour distances of the simulation are too large. For zinc and tin they are too small.

2) Except for zinc and tin the second and subsequent peaks of the simulated data are at too low a value of Q . For tin they are at too large a value, for zinc they are approximately correct.









3) All the simulated number densities are too large, despite three out of five of the near-neighbour distances being too large.

The conclusion is that the second and subsequent peaks in the structure factor are more representative of the near-neighbour distance than the first peak, and that the liquid has vacancies in the solid state lattice. The liquid structure does resemble the solid lattice: it would, for example, be quite impossible to fit either of the cubic structures to liquid tin. To this extent the liquid may be described as lattice-like.

b) Molten Sodium Chloride

Reliable partial structure factors have been obtained for this system (Edwards, Enderby, Howe, and Page (96)), and these are compared in fig. (5.5) with a disordered F.C.C. lattice. See Table 5.2. Once again, number densities are too large; the lattice sites are only 75% occupied.

If the position, Q_0 , of a feature in a structure factor represents the near-neighbour distance, d , then we would expect the product $Q_0 d$ to be constant as d alters from real liquid to model. This product for the first and second peaks in the real liquid is compared with the simulated values in Table 5.3. The two models agree closely with each other, which is expected as model (b) is a scaled up version of model (a). Yet neither model represents the true liquid, as deduced from the structure factor, and it is seen that the second peak/minimum has the more direct relationship with the near-neighbour distance.

c) Liquids Based on the Nickel Arsenide Structure

Examples of these liquids are: Au-Sn, Ni-Te, Cu-Sn, Ni-Te, Cu_2Te , Cu-Te. They are all binary alloys. In the nickel arsenide structure (see Wyckoff (105)), metalloid (As) atoms form a close-packed hexagonal arrangement, and the metal sites are octahedrally coordinated by metalloid atoms. In terms of the unit cell vectors, the atomic coordinates are:-

$$\text{Ni} : \quad (\text{i}) \quad (0,0,0) \quad (\text{ii}) \quad (0,0,\frac{1}{2})$$

$$\text{As} : \quad (\text{i}) \quad (\frac{1}{3},\frac{2}{3},\frac{1}{4}) \quad (\text{ii}) \quad (\frac{2}{3},\frac{1}{3},\frac{3}{4})$$

These substances often show a variable composition. For compounds of the form Ni_2As an additional set of Ni sites occur at:-

$$\text{Ni} : \quad (\text{iii}) \quad (\frac{1}{3},\frac{2}{3},\frac{3}{4}) \quad (\text{iv}) \quad (\frac{2}{3},\frac{1}{3},\frac{1}{4})$$

For compounds of the form NiAs_2 , only site (i) is occupied.

A related structure, for Cu_2Te , is the iron arsenide structure, Fe_2As , which has a tetragonal unit cell, containing two molecules:-

$$\text{Fe} : \quad (\text{i}) \quad (0,0,0) \quad (\text{ii}) \quad (\frac{1}{2},\frac{1}{2},0)$$

$$\quad (\text{iii}) \quad (0,\frac{1}{2},u) \quad (\text{iv}) \quad (\frac{1}{2},0,\bar{u})$$

$$\text{As} : \quad (\text{i}) \quad (0,\frac{1}{2},u) \quad (\text{ii}) \quad (\frac{1}{2},0,\bar{u})$$

For Cu_2Te $u(\text{Cu}) = 0.27$, and $u(\text{Te}) = -0.285$; effectively this means a treble plane of Cu atoms sandwiched with a double layer of Te atoms.

Neutron data are available for Ni-Te, Ni-Te_3 (106), and Cu-Te, $\text{Cu}_2\text{-Te}$ (106), and here the total scattering functions, $F(Q)$, are compared (see equation 1.29), as these are more sensitive to errors in the partial structure factors. See Table 5.4 and figs.(5.6) and (5.7). For Ni-Te_3 , the abundance of tellurium over copper is represented by decreasing the lattice site probabilities of the copper to one third of those of the

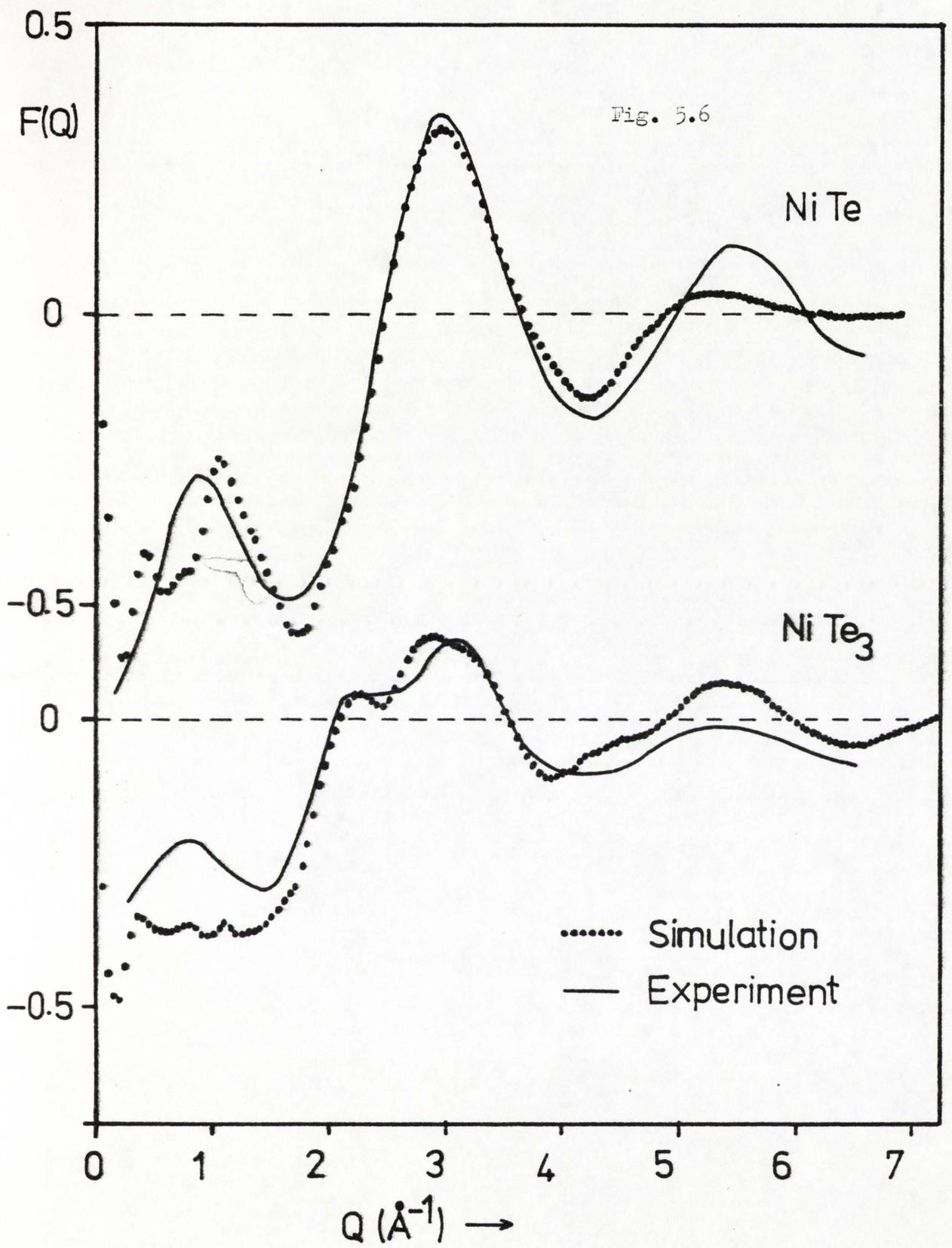
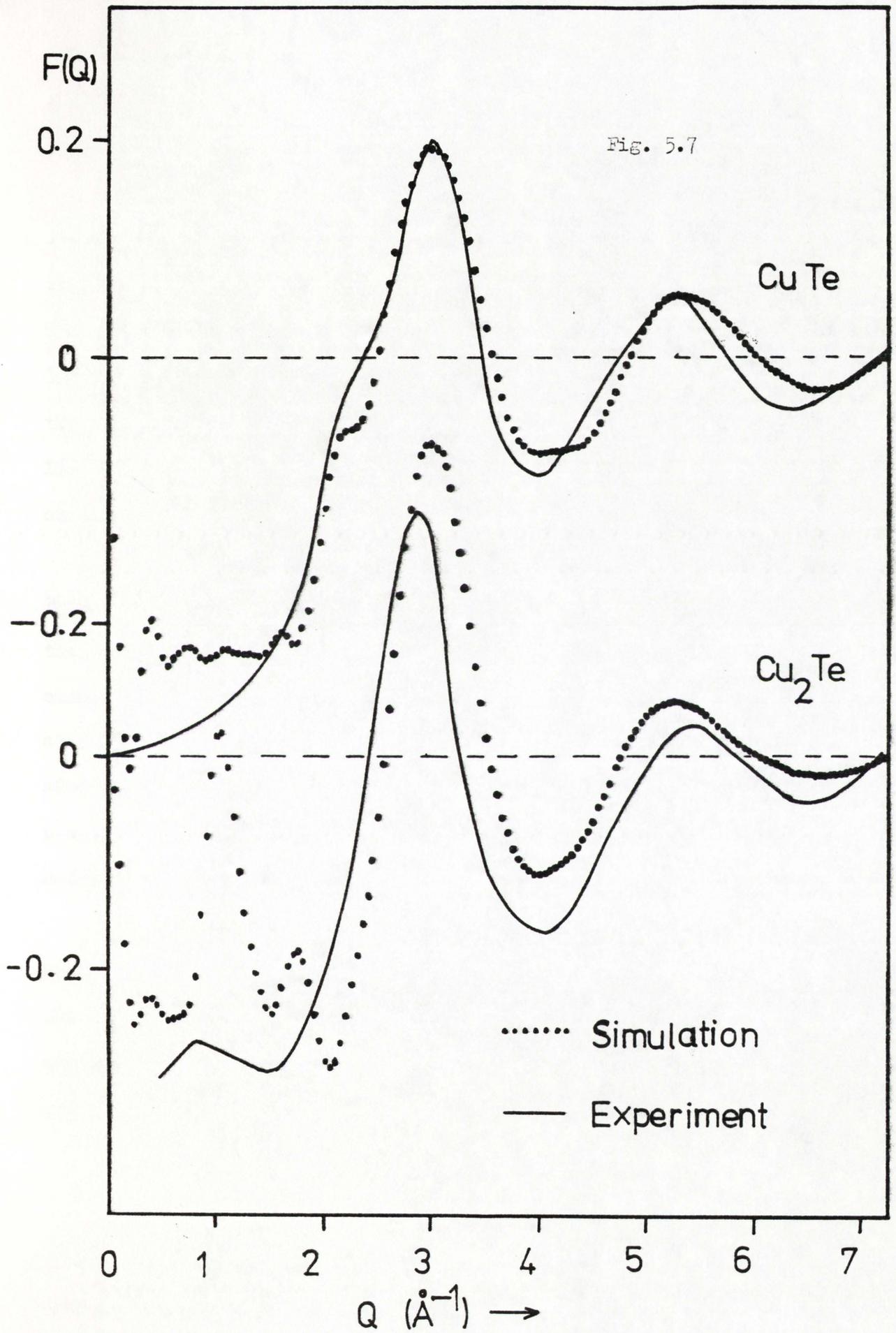


Fig. 5.7



tellurium. Crystal data are taken from Wyckopf, who is, however, silent on the structure of Cu-Te: the nickel arsenide structure has been assumed here.

Cu_2Te exhibits two structural forms - a low temperature Fe_2As structure, and a high temperature form, analogous to nickel arsenide, in which the metal atoms form planes with tellurium between. The simulation shown in the figure is for the former structure, as the latter produced a considerable peak at 2 \AA^{-1} . It is important that the experimental data show a peak at 0.8 \AA^{-1} , and both the high and low temperature simulations show a significant first peak at $\sim 1 \text{ \AA}^{-1}$, on account of the layered structure of these lattices.

The same point is made in the NiTe and NiTe_3 simulations. Both the experimental curves show a peak in the low Q region. In the simulated data, in which, for both liquids, the models are identical except for the lattice site probabilities and peak widths, the pre-peak at 1.05 \AA^{-1} is introduced by reducing the probability of site (ii) compared to (i). For NiTe_3 , the two sites have equal probability, and no pre-peak is observed. Hence the pre-peak is created in the disordered model by emphasizing the planes of nickel atoms.

In all these simulated structures, the nickel and copper near-neighbour distances remain near 2.6 \AA . The conclusion is that the first peak does not necessarily represent this distance, as the monatomic liquids already studied have a similar distance of closest approach, but there is no peak in the structure pattern at 1 \AA^{-1} .

d) Nickel Chloride Aqueous Solutions

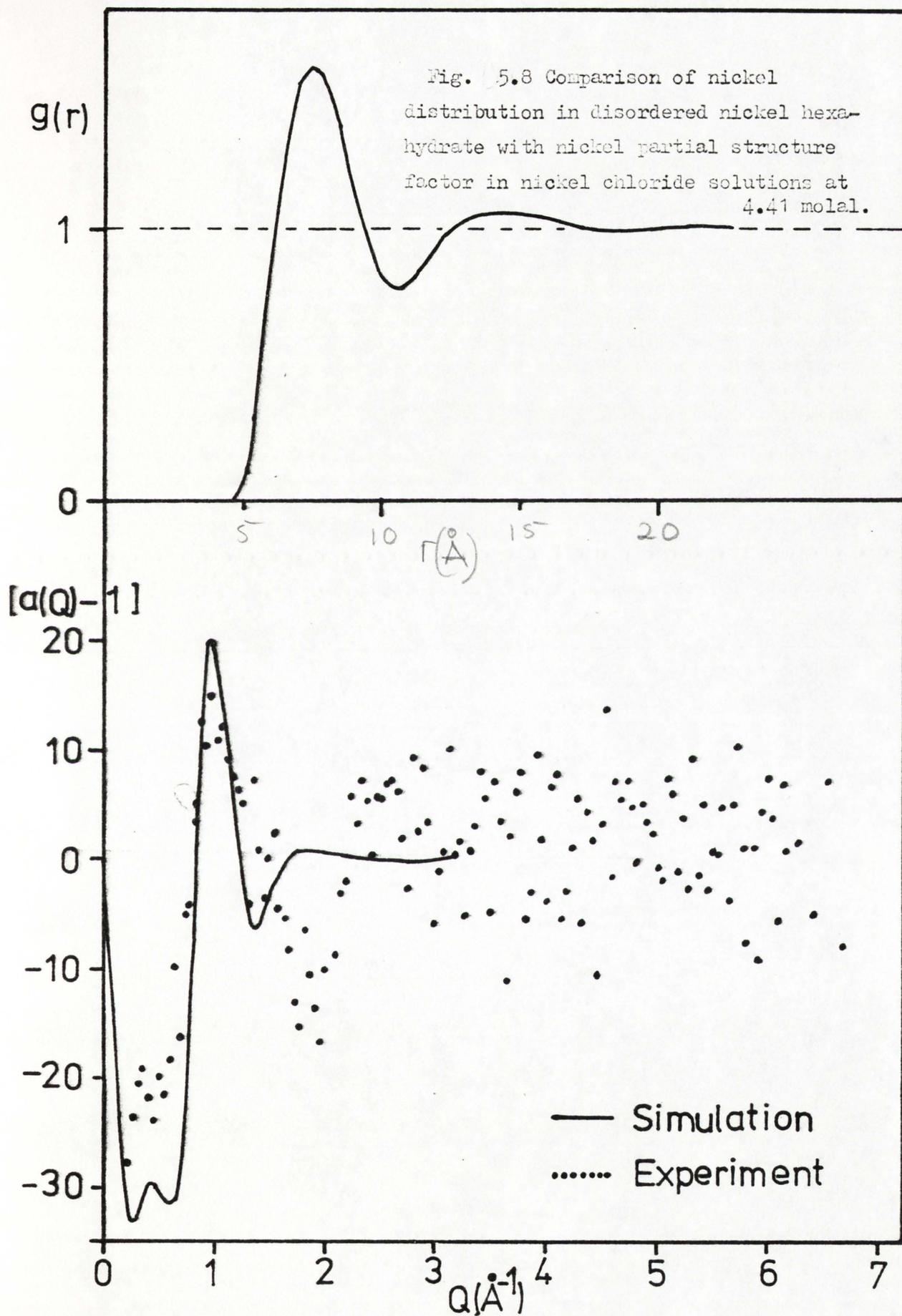
In the solid state nickel chloride hexahydrate forms a monoclinic structure consisting of planes of nickel atoms, along which the crystal cleaves easily (108). The disordered nickel distribution

and partial structure factor for this lattice, expanded to give a first peak in the structure factor at 1 \AA^{-1} , are shown in fig. 5.8. The amount of disordering necessary, (width constant $a = 0.8$), is substantially more than that used for the previous liquids, although the simulated peak is still too large. The comparison indicates that a lattice - type ordering of the ions is reasonable, but with greater disorder than found in one- and two- component liquids.

e) Sodium Chloride Aqueous Solutions

Although the chlorine partial structure factor, fig. 4.8 indicates no ordering of the chlorine ions, it has been seen, from the simulation of fused sodium chloride, that a peak in the Cl-Cl structure factor coincides with a sharp minimum from the Na-Cl structure factor, and when added together with the appropriate neutron factors the two features might cancel each other. Hence a suitably expanded F.C.C. lattice has been disordered (with $a = 0.8$) and the Cl-Cl and Na-Cl structure factors added together with the neutron factors appropriate to the $F_{35} - F_{37}$ first order difference at 5.32 molal, fig 5.9. For the disordered lattice there remains a significant peak at 1 \AA^{-1} , and the absence of such a sharp feature in the raw first order difference confirms our earlier conclusion that there is negligible ordering of the ions in the solution.

Fig. 5.8 Comparison of nickel distribution in disordered nickel hexahydrate with nickel partial structure factor in nickel chloride solutions at 4.41 molal.



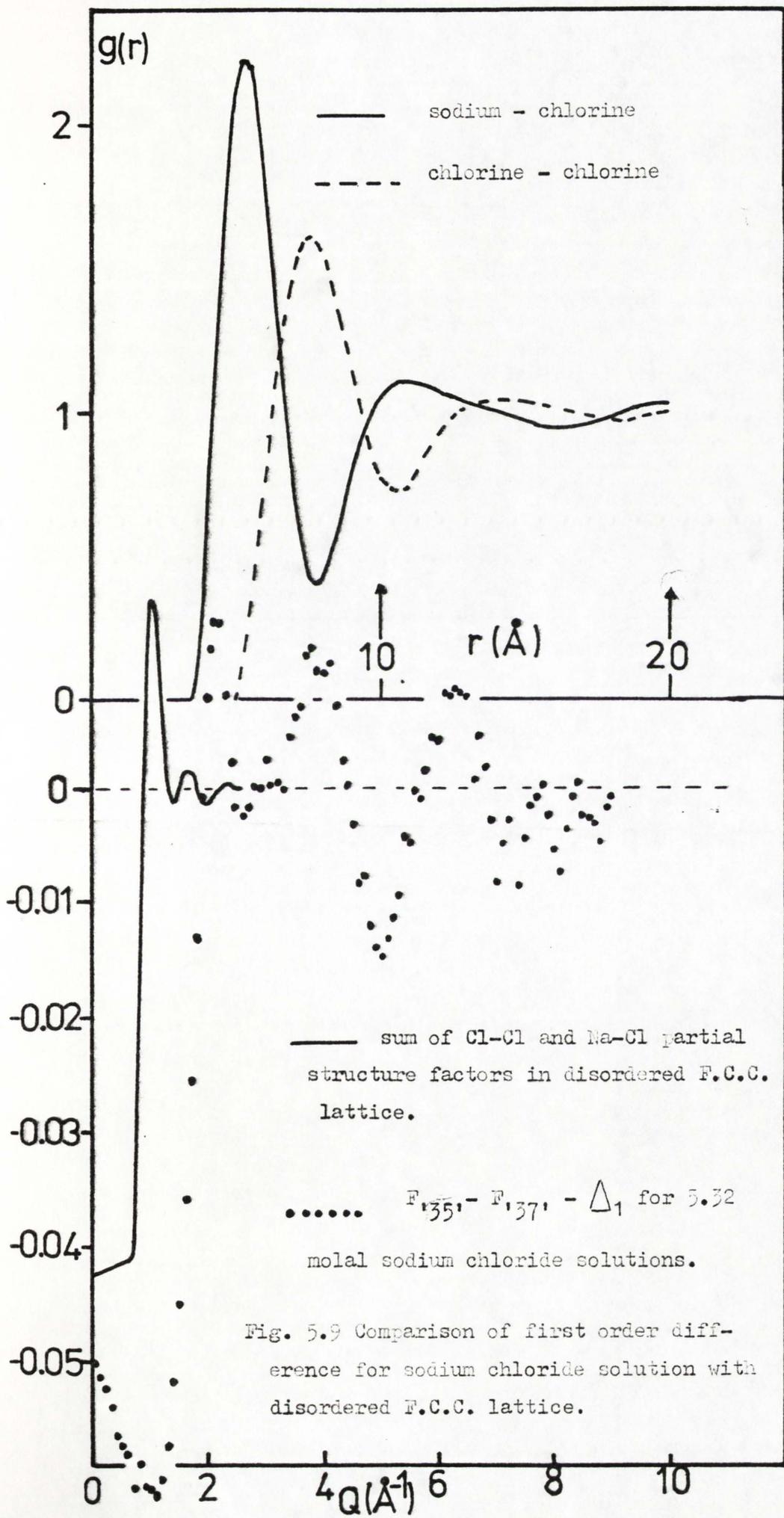


Fig. 5.9 Comparison of first order difference for sodium chloride solution with disordered F.C.C. lattice.

PART B - Hard Sphere Calculations

4) Baxter's Equations

The present neutron experiments on aqueous solutions indicate the strongly hydrated nature of the ions. This has prompted the idea of treating the hydrated ions as hard spheres, Quirke and Soper (109). Using a factorization procedure, Baxter (110) has derived a straightforward technique for generating multi-component, hard sphere radial distributions, in the Percus-Yevick approximation, without recourse to the usual Fourier inversion method. Perram (111) demonstrated that a stepwise solution is possible, and a program was written to perform this for the multi-component system. The computing time for the six partial distributions in a three component system, out to 35 \AA , and at a step of 0.05 \AA , was 2 minutes. The Fourier transform was then performed as described in Appendix 3.

5) One and Two Component Systems

As a check that the program worked correctly, the one-component distributions, with a hard sphere diameter of 1 \AA , were compared with those of Throop and Bearman (112), for a wide range of concentrations; the agreement was to within 0.1 % in all cases. Although the near-neighbour distance remains constant as the concentration decreases, the subsequent peaks in the radial distribution move to greater r values, and this is represented in the structure factor by movement in the position of the first peak, fig 5.10a.

The analysis was repeated for a two-component system with hard sphere diameters fixed at 5.6 \AA and 4.3 \AA for nickel and chlorine ions respectively. Again movements of the first peak are seen, especially at the higher concentration, fig 5.10b.

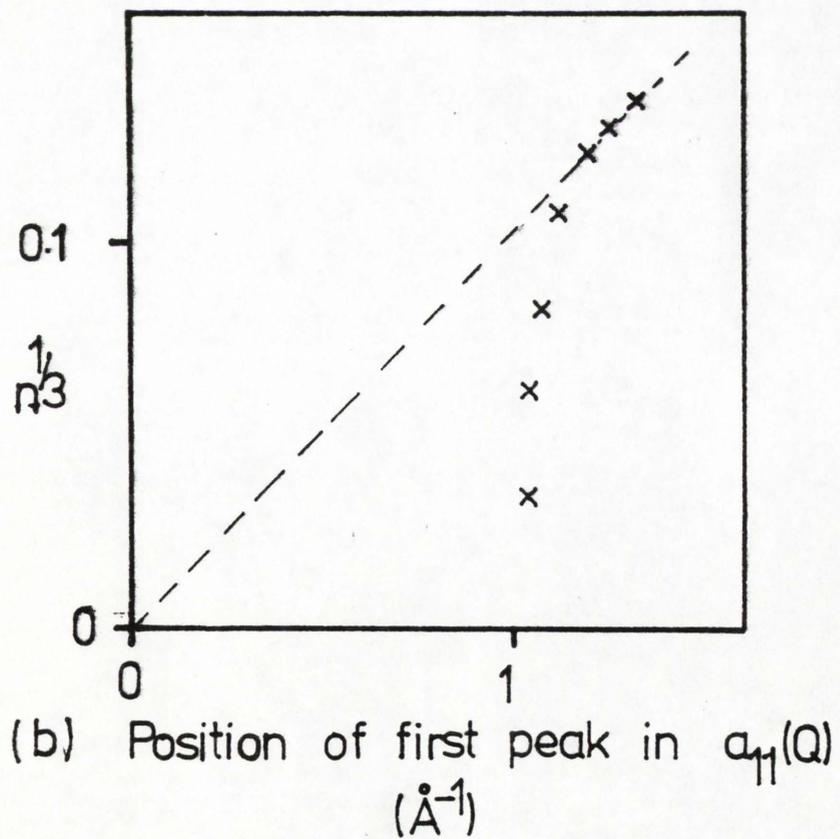
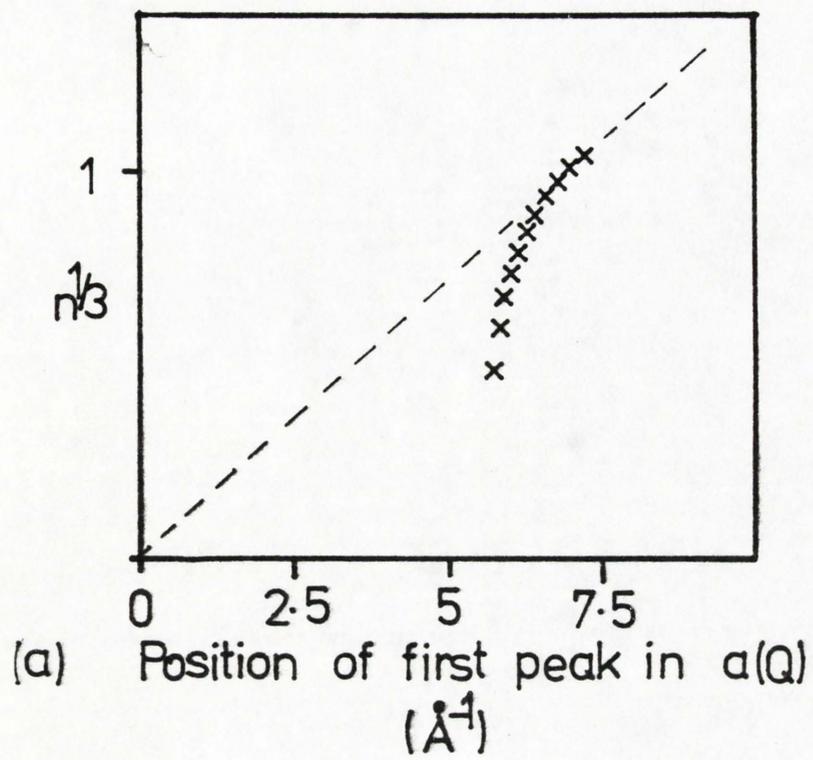
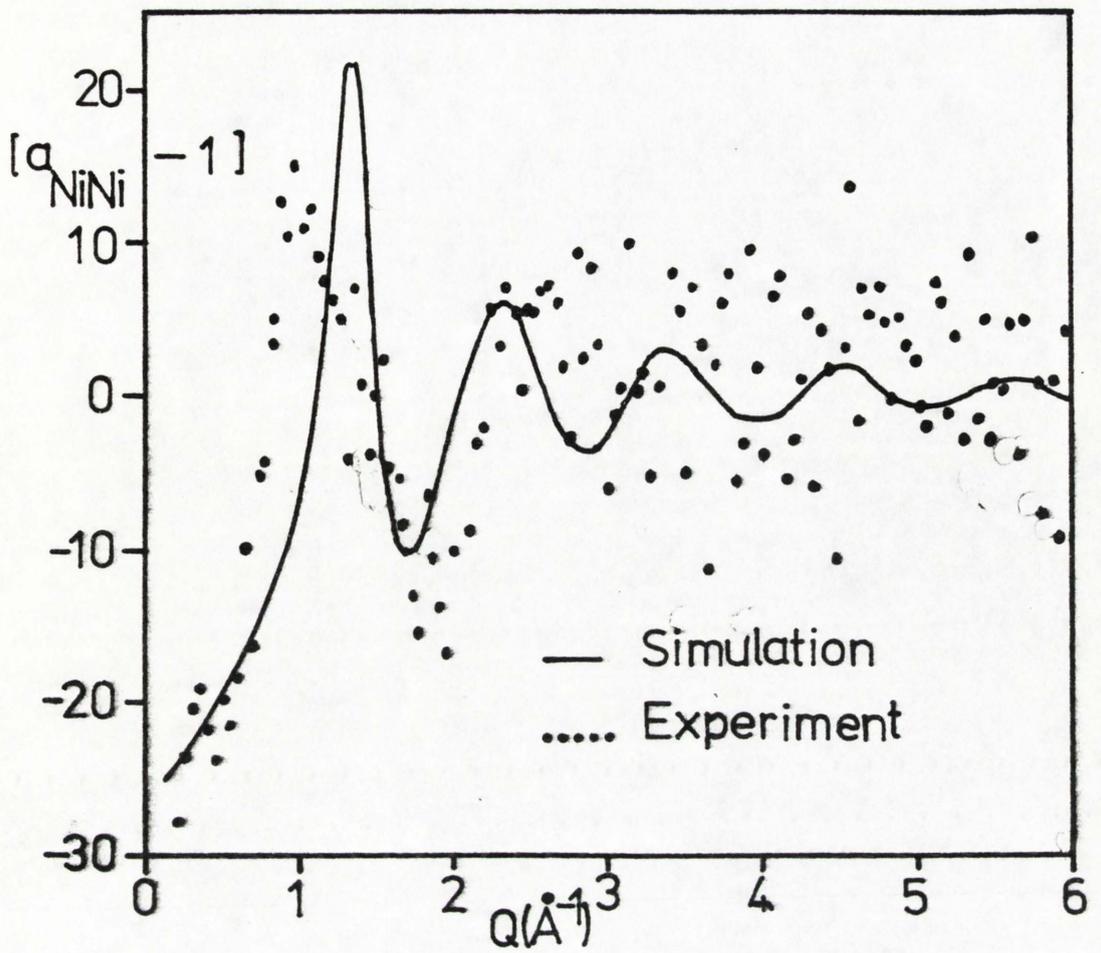
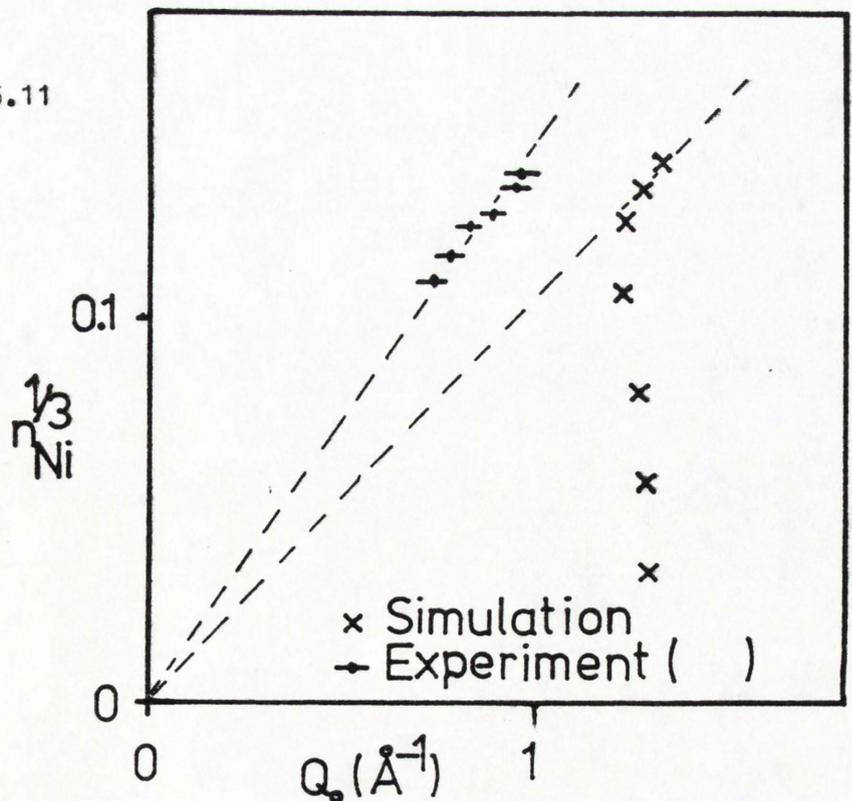


Fig 5.10 Movements of the first peak of hard sphere structure functions for (a) one-component (b) two-component systems.



(a) Comparison of Hard sphere structure function with nickel partial structure factor in solution, for 4.41 molal.

Fig. 5.11



(b) Movement of the first peak in nickel-nickel structure factor for the three-component model

6) Three Component Model

In the three component model, a more detailed description of the effect of hydration on the hard sphere diameter of the ions is given. For the concentrated solutions most of the water is bound, and free water molecules are only introduced after the maximum amount of water has been absorbed into the hydration spheres. The nickel diameter and hydration number are held at 5.6 Å and 6.0 respectively at all concentrations. At present no chlorine substitution has been carried out in NiCl_2 solutions, and both the both the magnitude and variation with concentration of the chlorine hydration number are unknown. In order to make progress we shall assume all the remaining water molecules are bound to the chlorine ion at 4.41 molal - this gives a chlorine hydration number of 2.3. This number is allowed to increase to 6 at 2.0 molal, after which it remains constant, Table 5.5.

The movement of Q_0 with number density is shown in fig 5.11b. (Q_0 is the position of the first peak in the Ni-Ni partial structure factor.) The region over which Q_0 moves linearly with $n_{\text{Ni}}^{\frac{1}{3}}$ is small in comparison to the experimental points; the gradients of the two lines are different. Also, the three component model deviates more rapidly from the linear behaviour than does the two component model, indicating that the free water molecules have their own structuring effect. Q_0 for the model partial structure factor is different from that found experimentally, but the magnitude of the partial is correct, so, judged solely from the magnitude of the experimental partial, there is no evidence for any more ionic ordering than found in a hard sphere fluid.

PART C - Argument from the Zero Limits

From the results of the previous two sections it is possible to draw some simple conclusions about the liquid structure factor:

(i) The first peak does not necessarily represent the near-neighbour distance of the atoms, but is more representative of the longer range structure.

(ii) The clue to the behaviour of the near-neighbour distance as the density of the liquid varies is in the second or subsequent peaks.

(iii) The magnitude of the first peak is not simply an indication of the extent of the order, since it is also proportional to the number density used in the structure factor definition, and the scaling effect of the size of the particles.

A necessary, but not sufficient, condition for the validity of a particular model, is that the low Q structure factor should go to the thermodynamic limit. These limits have been calculated according to the Beeby formulation, Appendix 4, for concentrations of nickel and sodium chlorides appropriate to the experiments, and comparison is made with the simple lattice and hard sphere models of nickel chloride in fig 5.12.

For a salt, AB_x , which completely dissociates in to $1+x$ ions on dissolving, the Beeby formula gives, for the zero limit in a very dilute solution:

$$S_{AA}(0) - 1 = nk_B^{\text{TH}} - \frac{1}{c_A} \left(\frac{x}{1+x} \right) \quad \dots 5.7$$

where n is the total number of atoms per unit volume, c_A is the atomic fraction of A ions, and the other symbols have the same meaning as those in the appendix. This result can be seen immediately by invoking the Landau-Lifshitz formula for the chemical potential

of the solvent in a dilute strong electrolyte (113). Hence, since $x > 0$, the limit goes to $-\infty$ at zero concentration, and is a general result for all systems which dissociate into ionized particles on dissolving.

It is interesting to compare this behaviour with that of the Debye-Huckel limiting law, which applies at low concentrations. The radial distribution about an ion in the theory is given by (see Chapter 2)

$$\epsilon_{ij}(r) = 1 - \frac{q_i q_j}{k_B T \epsilon} \frac{\exp(-kr)}{r} \quad \dots 5.8$$

where ϵ is the dielectric constant of the solvent and k is the reciprocal Debye length. Fourier transform of equation 5.8 at $Q=0$ gives immediately

$$a_{ij}(0) - 1 = - \frac{4\pi n}{k_B T} \frac{q_i q_j}{\epsilon} \frac{1}{k^2} = - \frac{q_i q_j}{\sum_i c_i q_i^2} \quad \dots 5.9$$

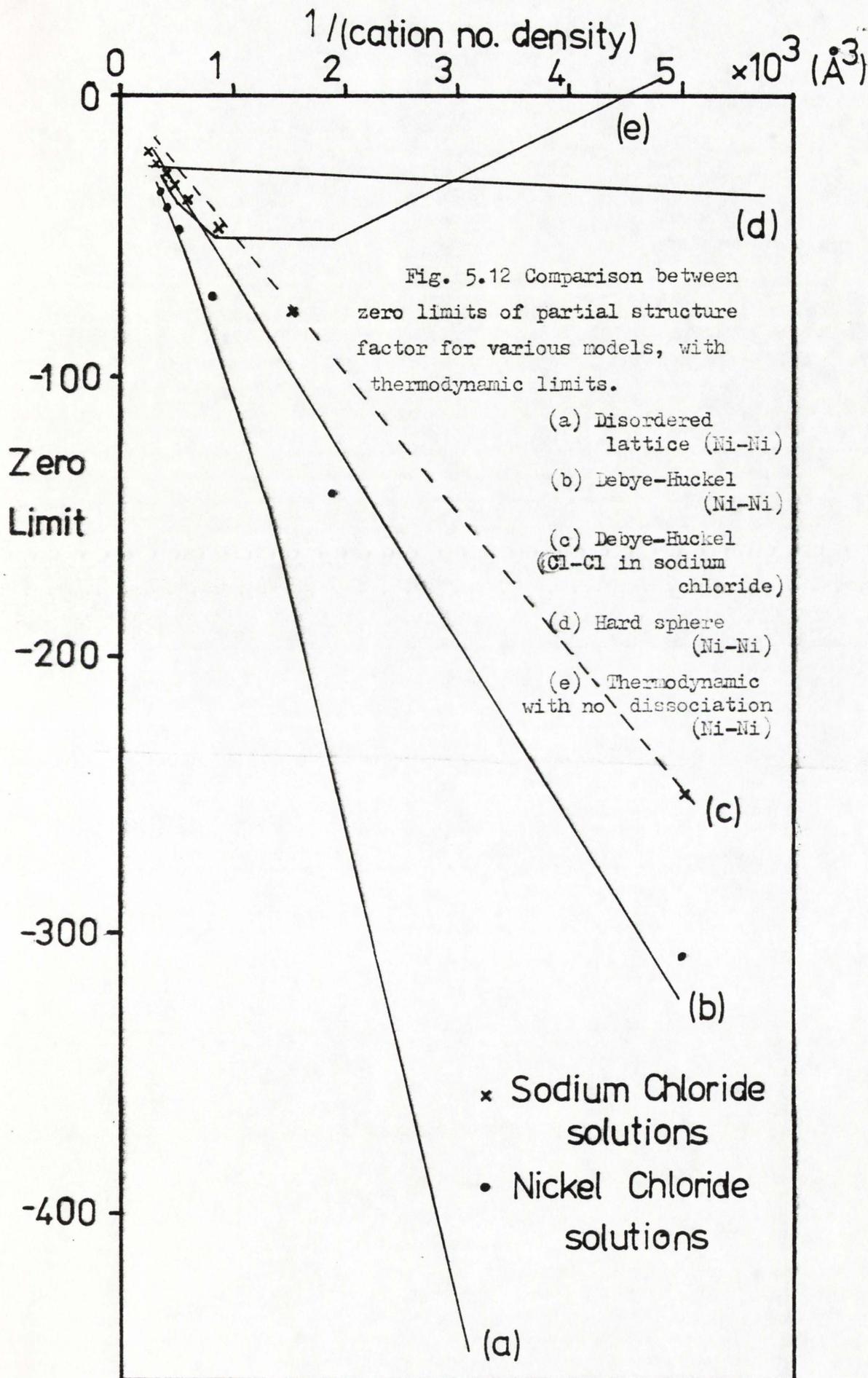
where c_i is the atomic fraction of species i .

For a molecule of the form AB_x , A is assumed to have a charge x units compared to B , then, for charge neutrality, the ion B will have an atomic fraction xc_A , if c_A is the atomic fraction of A . Substituted in 5.9, these results give

$$a_{AA}(0) - 1 = - \frac{1}{c_A} \left(\frac{x}{1+x} \right) \quad \dots 5.10$$

The only difference between this and equation 5.7 is the compressibility term, which represents the fact that the solvent is not a true continuum at any dilution. However this term is small, and, as fig 5. shows, the model fits the low Q limits for both sodium and nickel chlorides more accurately than the other models. The agreement is especially good for sodium chloride.

The importance of this result may be seen in the following way. In the Debye-Huckel theory, the quantity $\frac{1}{k}$ represents



the distance of the maximum in the charge cloud density from an ion, and it varies as $1/\sqrt{n_i}$. Hence, as the concentration decreases, the charge cloud expands away from the ion. The similarity between the thermodynamic limits of the real solutions and those of the Debye-Huckel theory suggests that such an expansion also occurs in the real solution. The absence of Coulomb forces in the hard sphere model is no doubt one reason why the model gives only approximate agreement with experiment, and then only at high concentrations, when atomic packing of the hydration spheres has a decisive role. Yet the Debye-Huckel charge cloud has no 'structure' in terms of peaks in the radial distribution function, equation 5.8. Combining the two approaches, the observed structure in nickel chloride solutions is an effect of hard sphere interactions between strongly hydrated nickel ions, but the movement of peaks with concentration is dominated by the Coulomb forces. A full three component simulation, which included electrostatic forces between the ions, has yet to be performed. The success or failure of such a simulation would confirm or disprove the ideas proposed here.

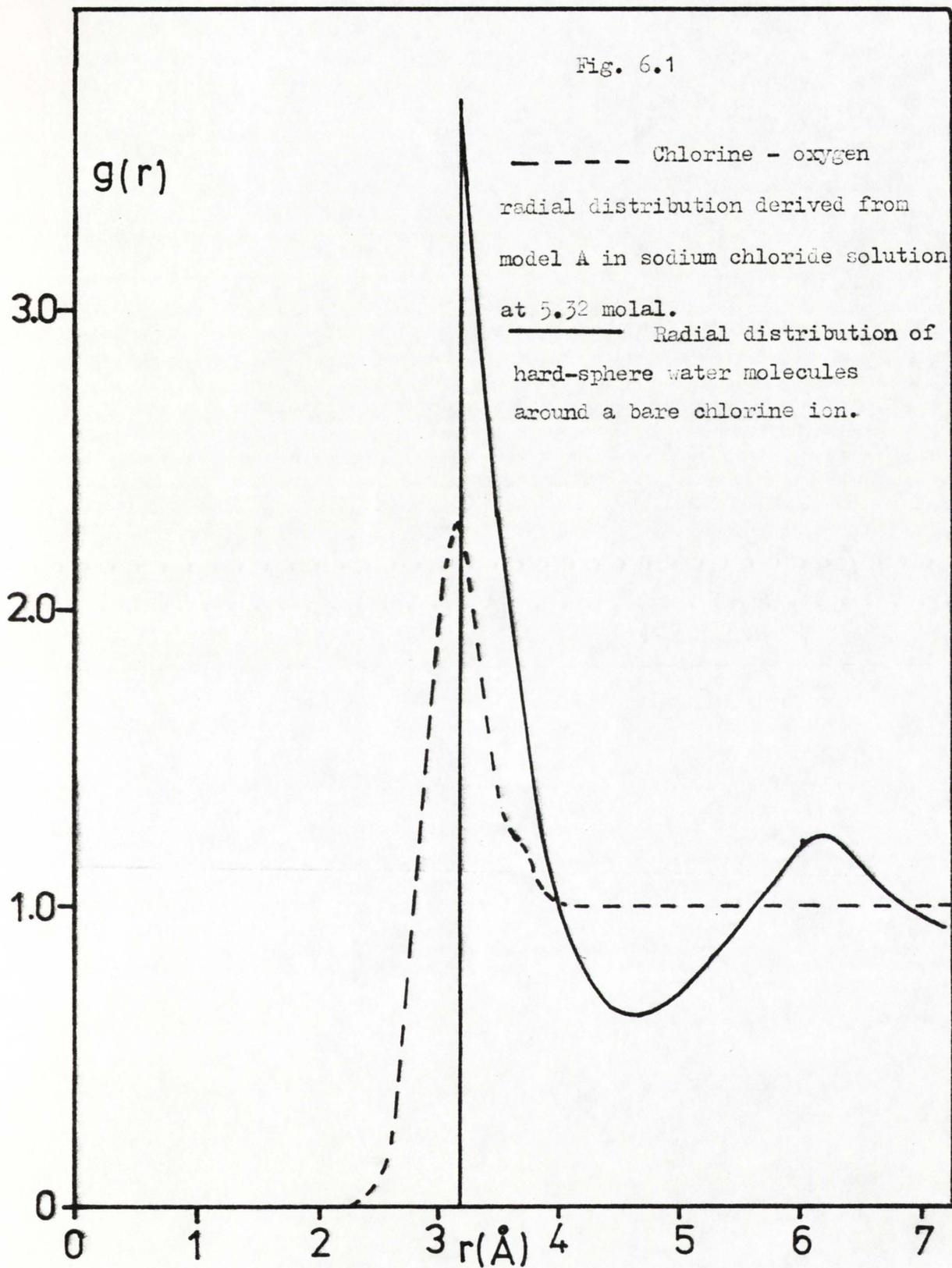
On the same argument, the absence of any structure in the distribution of chlorine ions in sodium chloride solutions, might suggest that the hydrated water molecules are not bound tightly to that ion, although the neutron evidence requires that they are strongly orientated towards it when approaching closely. The lack of structure could equally be an effect of the packing of non-spherical hydrated ions.

CHAPTER 6CONCLUSION

In the previous Chapter, we have seen how the hard-sphere simulation is a useful reference system with which to judge the real solution. The tightness of the binding between an ion and its hydration molecules will be represented by the sharpness of the first peak in the ion-oxygen radial distribution, but even a bare ion surrounded by water molecules with only hard sphere repulsions present, will show a significant peak, due to the atomic packing. Hence, the true extent of binding is determined by comparison with the hard sphere situation. Neutron data cannot at present supply information about the ion-oxygen partial distribution. Nonetheless, a model which fits the data must generate a reasonably accurate ion-oxygen distribution, and so in fig 6.1 comparison is made between the chlorine - oxygen partial obtained from model A in sodium chloride at 5.32 molal, with the same distribution function from a mixture of hard sphere water molecules (diameter 2.8 \AA , number density $0.0299 / \text{\AA}^3$), sodium ions (diameter 1.90 \AA , number density $0.00318 / \text{\AA}^3$), and chlorine ions (diameter 3.6 \AA , number density $0.00318 / \text{\AA}^3$), at the same concentration. Clearly, for the chlorine ion, the water molecules are no more tightly bound than in the hard sphere solution, and probably less so. In addition, the ion-water potential is much 'softer' than a hard sphere potential. Hence the hydration of water molecules around the chlorine ion is confirmed to be an orientation effect, but the role of binding between the ion and its hydration sphere is at present unclear.

. Samoilov (114), by considering the activation energy

Fig. 6.1

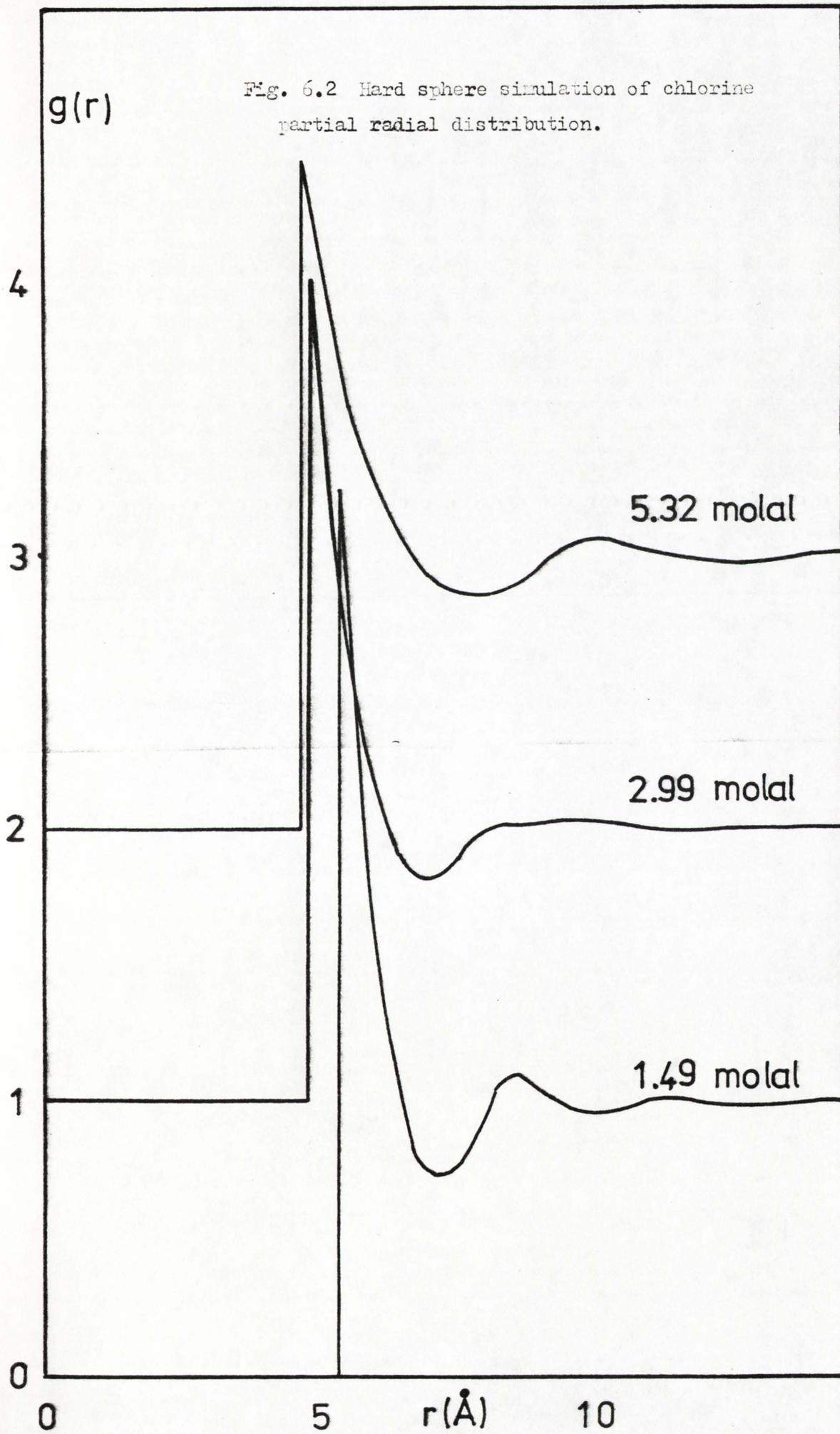


needed to replace a water molecule in the hydration sphere, argues that, for ions like K^+ , Cs^+ , Cl^- , Br^- , I^- , the rate of exchange of water molecules around the ions is greater than the rate for those around a water molecule in pure water, i.e. the ion actually 'lubricates' the motion of the water molecules. The present data agrees with this interpretation, although there is marked orientation of the water molecules near the ion.

As no model has been developed, so far, for the nickel hydration sphere, it is not possible to make the same comparison, although the height and sharpness of the features in figs 4.18 to 4.20 strongly suggest that binding does occur.

There are no previous experimental data on the distribution of chlorine ions in the solution, and all the simulations have been carried out at concentrations below 2.0 molal - these invariably ignore the finite size of the solvent particles. However, Stell and Sun (115) quote some Monte Carlo results, for a series of solutions up to 1.968 molar, for a two-component system of charged hard spheres, and Lantelme and Friedman (116) performed a simulation of a 1.0 molar solution, by treating the motion of the charged particles as Brownian motion in a viscous medium. Neither of the simulations shows 'structure' in the distributions, but it is unfair to compare them with the chlorine partial at 5.32 molal, which, as we saw earlier, of the three concentrations for which a partial structure factor is available, is least likely to contain experimental error.

Finally, a hard-sphere simulation of sodium chloride solutions, analogous to the one for nickel chloride, is presented in fig 6.2 - see Table 6.1. Although it is unrepresentative of the real solution, since we now know that the ion-solvent potential is not 'hard', the increasing role of the solvent



in structuring the ions is clearly demonstrated by these curves. Hence the result in fig 4.9 , where there appeared an increase in structure with dilution, could be interpreted as such an effect.

APPENDIX 1

We define the Hamiltonian for the unperturbed system as H_0 , and for the neutron interaction we then add the Hamiltonian of the particle to be scattered and the interaction potential:-

$$H = H_0 + \frac{Q_0^2}{2m} + \sum_j V_j(\underline{r} - \underline{R}_j) \quad \dots A1.1$$

where \underline{R}_j is the position of the j^{th} nucleus, and the sum is taken over all the scattering centres. $V_j(\underline{r} - \underline{R}_j)$ is the scattering potential.

Born approximation tells us the partial differential cross-section:-

$$\frac{d^2\sigma}{d\Omega dw} = \frac{Q_0^2}{Q_0} \left(\frac{m}{2\pi}\right)^2 \left| \langle f | \int d\underline{r} \exp(i\underline{Q}\cdot\underline{r}) \sum_j V_j(\underline{r} - \underline{R}_j) | i \rangle \right|^2 \delta(E_f - E_i - w) \quad \dots A1.2$$

where i and f represent the initial and final states, and E is the energy of the system. The δ -function expresses conservation of energy.

If we let $\underline{R} = \underline{r} - \underline{R}_j$, then the integral can be written as

$$\sum_j \int d\underline{R} V_j(\underline{R}) \exp(i\underline{Q}\cdot(\underline{R} + \underline{R}_j)) = \sum_j V_j(\underline{Q}) \exp(i\underline{Q}\cdot\underline{R}_j) \quad \dots A1.3$$

$V_j(\underline{Q})$ is the Fourier component of $V_j(\underline{R})$.

The cross-section must be averaged over all initial and final states. The average over the initial states simply is a thermal average. The distribution of final states is governed by the unperturbed Hamiltonian acting on the final states.

First we note the Fourier expansion of a δ -function:

$$\delta(E_f - E_i - w) = \frac{1}{2\pi} \int dt \exp(i(E_f - E_i - w)t) \quad \dots A1.4$$

In the Heisenberg representation

$$\exp(-i H_0 t) | i \rangle = \exp(-i E_i t) | i \rangle \quad \dots A1.5$$

$$\text{and } \langle f | \exp(i H_0 t) = \langle f | \exp(i E_f t) \quad \dots A1.6$$

Furthermore we note the following operation on a function of the system, f :

$$\exp(i H_0 t) f(0) \exp(-i H_0 t) = f(t). \quad \dots A1.7$$

Finally, to make use of these results, we replace the term within the modulus sign squared by the expression

$$\langle i | \sum_j v_j^+(\underline{Q}) \exp(-i\underline{Q} \cdot \underline{R}_j) | f \rangle \langle f | \sum_k v_k(\underline{Q}) \exp(i\underline{Q} \cdot \underline{R}_k) | i \rangle, \quad \dots A1.8$$

where

$$v_j^+(\underline{Q}) = \int d\underline{R} v_j(\underline{R}) \exp(-i\underline{Q} \cdot \underline{R}). \quad \dots A1.9$$

Note that $v_j^+(\underline{Q})$, $v_j(\underline{Q})$ are independent of operations of the Hamiltonian and time. Combining all the previous equations, we obtain

$$\frac{d^2 \sigma}{d\underline{\Omega} d\underline{\omega}} = \frac{Q_1}{Q_0} \left(\frac{m}{2\pi} \right)^2 \frac{1}{2\pi} \int dt \exp(-i\underline{\omega} t) \sum_j \sum_k v_j^+(\underline{Q}) v_k(\underline{Q}) * \exp(-i\underline{Q} \cdot \underline{R}_j(0)) \exp(i\underline{Q} \cdot \underline{R}_k(t)). \quad \dots A1.10$$

Here the thermal average has been assumed.

APPENDIX 2

In equation 1.26 we have the sum:

$$\sum_j \sum_{k \neq j} b_j b_k \exp(i\mathbf{Q} \cdot (\mathbf{R}_k - \mathbf{R}_j)) \quad \dots \text{A2.1}$$

Setting $\mathbf{R}_m = \mathbf{R}_k - \mathbf{R}_j$, this is rewritten:

$$\sum_j \sum_m b_j b_m (\exp(i\mathbf{Q} \cdot \mathbf{R}_m) - \delta(\mathbf{R}_m)) \quad \dots \text{A2.2}$$

The sum over j is performed immediately

$$\sum_j b_j = \sum_a N_a b_a \quad \dots \text{A2.3}$$

For the sum over m , let $\rho_{ab}(\mathbf{r})$ represent the density of particles 'b' with an 'a' particle at the origin.

$$\rho_{ab}(\mathbf{r}) = \sum_m \delta(\mathbf{r} - \mathbf{R}_m) \quad \dots \text{A2.4}$$

$$\text{so } \int \rho_{ab}(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} = \sum_m \exp(i\mathbf{Q} \cdot \mathbf{R}_m). \quad \dots \text{A2.5}$$

$$\text{Also note that } \sum_k \delta(\mathbf{R}_k) = \sum_b N_b \int \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \quad \dots \text{A2.6}$$

The sum over m now becomes

$$\sum_b b_b \int (\rho_{ab}(\mathbf{r}) - N_b) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \quad \dots \text{A2.7}$$

Using the partial distributions of equation 1.18, we write

$$g_{ab}(\mathbf{r}) = \frac{\rho_{ab}(\mathbf{r})}{n c_b}, \quad \dots \text{A2.8}$$

and A2.1 finally becomes

$$N_n \sum_a \sum_b c_a c_b b_a b_b \int (g_{ab}(\mathbf{r}) - 1) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r}. \quad \dots \text{A2.9}$$

APPENDIX 3SMOOTHING BY FOURIER ANALYSIS

The standard method of smoothing noisy data by Fourier analysis is to set up a Fourier series through the data. The higher frequency harmonics are then deleted since they correspond, principally, to the noise in the data, and 'smoothed' data regenerated from a reduced number of harmonics. Such a procedure applied to a structure function is open to an important criticism.

For the Fourier analysis, we take n data points, and set up a second set so that the combined set is an EVEN function, i.e.

$$I_j = I_{2n-j} \quad \text{for} \quad 0 \leq j \leq n, \quad \dots \text{A3.1}$$

then on Fourier analysis the sine coefficients disappear, and the data are expressed as a series of cosine coefficients:

$$I(Q_j) = \sum_{k=0}^{2n-1} a_k \cos\left(\frac{\pi jk}{n}\right) \quad \dots \text{A3.2}$$

where

$$a_k = \frac{1}{n} \sum_{j=0}^{2n-1} I(Q_j) \cos\left(\frac{\pi jk}{n}\right) \quad \dots \text{A3.3}$$

The Fourier transform of $I(Q)$ is in general defined by

$$G(r) = \frac{1}{2\pi^2 n_a r} \int_0^\infty Q I(Q) \sin(Qr) dQ, \quad \dots \text{A3.4}$$

where n_a is the total number density of atoms.

For a finite number of discrete data points, the definition, A 3.4,

can be rewritten as

$$G(r_m) = \frac{1}{2\pi^2 n_a r_m} \Delta Q \sum_{j=0}^{2n-1} Q_j I(Q_j) \sin(Q_j r_m) \quad \dots \text{A3.5}$$

where ΔQ is the step in Q -space between data points, so that

$Q_j = j \Delta Q$. Q_{MAX} is the maximum value of Q , so that $n = Q_{MAX} / \Delta Q$,

and $r_m = \frac{m\pi}{Q_{MAX}}$. This form of representation is used because the

fast-Fourier transform algorithm of Cooley and Tukey (117) was employed to evaluate equations A3.3 and A3.5.

For the transform A3.5 we need the sine coefficients,

so the function $Q_j I(Q_j)$ is made ODD, i.e. $Q_j I(Q_j) = -Q_{2n-j} I(Q_{2n-j})$ for $n < j < 2n$. Combining A3.2 and A3.5, after reordering the terms, gives

$$G(r_m) = \frac{1}{2\pi^2 n_a} \frac{1}{r_m} \sum_{k=0}^{2n-1} a_k \Delta Q \sum_{j=0}^{2n-1} Q_j \cos(Q_j r_k) \sin(Q_j r_m) \quad \dots \text{A3.6}$$

The bracketed term represents the Fourier analysis of the function

$Q_j \cos(Q_j r_k)$, and is given by

$$b_{km} = \pm \frac{Q_{MAX}^2 2m}{\pi (k^2 - m^2)} \quad \text{for } m \neq k \quad \begin{array}{l} \text{+ve for } k+m \text{ EVEN} \\ \text{-ve for } k-m \text{ ODD} \end{array} \quad \dots \text{A3.7a}$$

$$b_{km} = - \frac{Q_{MAX}^2}{2\pi k} \quad \text{for } m = k, \quad \dots \text{A3.7b}$$

assuming $n \gg k+m$. The cases for when $k=0$ and $n \approx k+m$ are also straightforward to derive. It is clear that values of b_{km} , for $m \neq k$, are large in the region $k \approx m$. Thus if we delete coefficients a_k for k greater than a value k' , say, then we similarly deleting most of the information about $G(r_m)$ for $r_m > r_{k'}$.

The point is demonstrated in fig. A3.1, where the Fourier coefficients (curve (c)), from the structure factor of a disordered F.C.C. lattice (see chapter 5), are compared with the radial distribution function (curve (a)) derived from the same structure factor: the two curves bear considerable resemblance to one another. Curve (b) shows the radial distribution function after terminating the Fourier coefficients at 3 \AA . Although this last curve may exaggerate the effect, it is clear that simply deleting coefficients is not a satisfactory way of obtaining a radial distribution.

Curve (d) shows the Fourier coefficients obtained from the first order difference $I_{35} - I_{37}$, (fig. 3.9b), after inter-

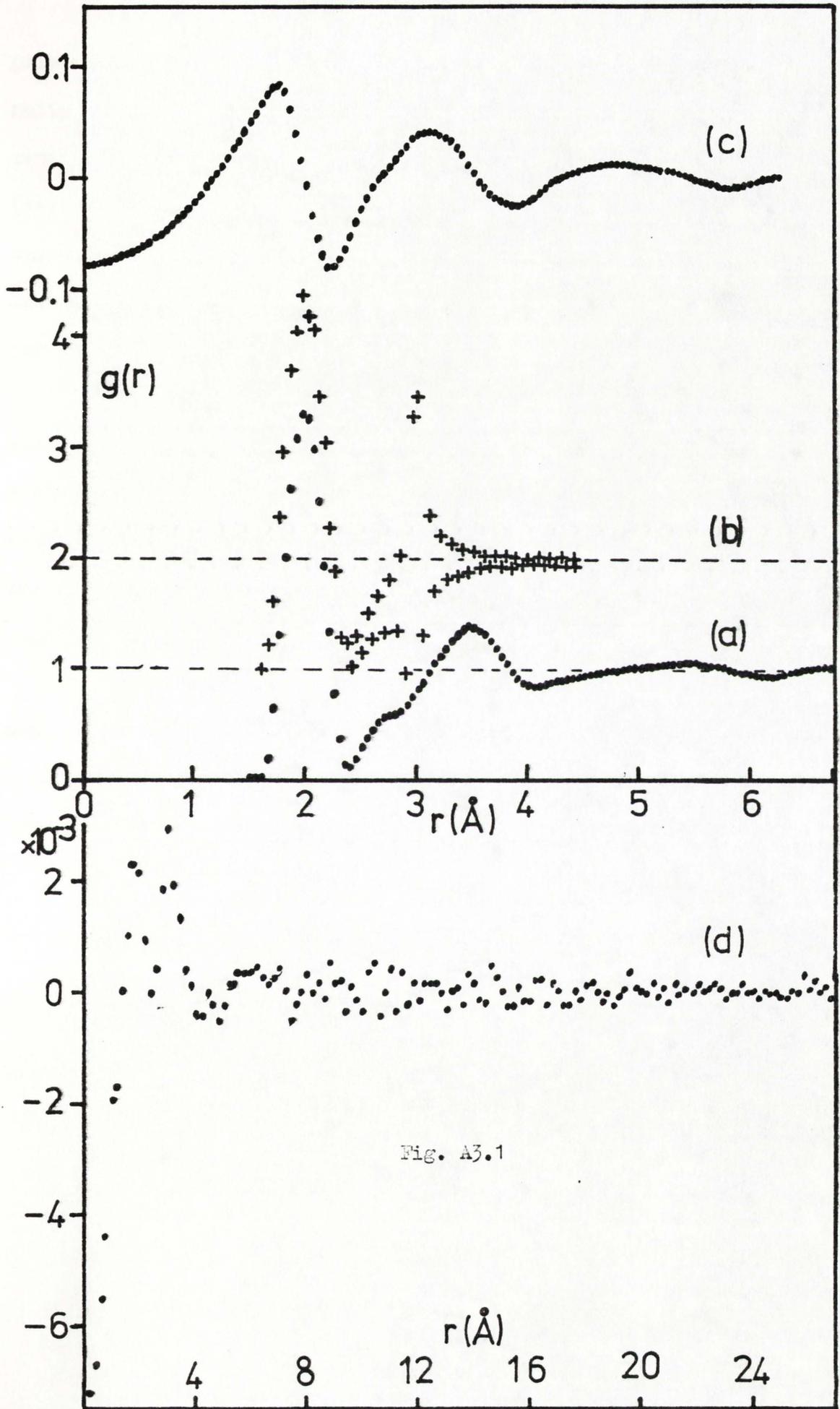


Fig. A3.1

polating the raw data to a step of 0.015 \AA^{-1} . This is the least noisy of all the difference curves, but the Fourier coefficients retain considerable noise: this noise persists over all radius values, (see Wertheim (118)), but has a maximum in the region of 10 \AA . The curve appears flat beyond 8 \AA , but there is no justification for assuming this, especially as the long range interaction, the Cl - Cl partial distribution, contributes only 5% to the total.

In the absence of a more satisfactory method, the problem was overcome in the present work by smoothing the coefficients using a simple averaging procedure, i.e. the value of coefficient a_n was replaced by $\frac{1}{4}(a_{n-1} + 2a_n + a_{n+1})$. The amount of averaging was kept to a minimum and restricted to regions where the Fourier coefficients displayed no or only slowly varying structure.

The Fourier analysis technique also enables us to correct any fall in the data due to Placzek effects on the self terms (section 9, Chapter 1.). To first order this correction is of the form

$$\Delta(Q)_{\text{actual}} = \Delta_0 (1 - bQ^2) \quad \dots \text{A3.8}$$

where Δ_0 is the ideal, elastic value, and b is a constant.

Fourier coefficients of $\Delta(Q)$ are, for $k \ll n$,

$$a_k = \Delta_0 Q_{\text{MAX}}^2 b^2 \frac{4}{\pi^2 k^2} (-1)^{k+1} \quad \dots \text{A3.9}$$

Hence the coefficients rise sharply for small k . By subtracting a curve of the form A3.9 from the coefficients at small values of k , the Placzek correction to the self terms can be completely eliminated. In practice, the effect occurs only within the first 5 coefficients of the first order differences.

APPENDIX 4ZERO LIMIT CALCULATIONS

Beeby (119) has derived expressions for the zero limits to the partial structure factors in an aqueous solution consisting of N_b solute molecules dissolved in N_a solvent molecules, in a volume V , in terms of the fluctuations $\Delta N_a, \Delta N_b$. These fluctuations are in turn related to the isothermal compressibility, H , and the derivative of the osmotic pressure $\frac{dP}{dc}$ with respect to molecular fraction, $c = \frac{N_b}{N_a + N_b}$.

Tabulated data usually give the practical osmotic coefficient, ϕ , which represents the deviation of the osmotic pressure from its ideal (van't Hoff) value, as a function of molality, m . The osmotic pressure is then given by (Robinson and Stokes (26))

$$P = \frac{vN_0 k_B T M_1}{1000 \bar{v}_a} m \phi$$

where N_0 is Avogadro's number, v is the number of ions which the solute dissociates into, M_1 is the molecular mass of the solvent, and \bar{v}_a is the average of the partial molar volume of the solvent, on either side of the membrane. In practice this number does not change significantly, and so it is treated simply as the partial molar volume of the solvent.

In terms of molality

$$m = \frac{c}{1-c} \frac{1000}{M_1}, \quad \frac{dm}{dc} = \frac{1}{(1-c)^2} \frac{1000}{M_1}$$

and so

$$\frac{dP}{dc} = \frac{vN_0 k_B T}{\bar{v}_a} \frac{1}{(1-c)^2} \left(\phi + m \frac{d\phi}{dm} \right).$$

There is a slight confusion about dimensions in Beeby's paper. The partial molar volumes are defined as

$$v_i = \left(\frac{\partial V}{\partial N_i} \right)_{P, N_k}$$

implying that N_i refers to the number of gram molecules of substance i , whereas the relations for the zero limits apply to the fluctuations in the number of molecules. For the present we shall keep the latter notation, so the partial molar volume becomes

$$v_i = N_0 \left(\frac{\partial V}{\partial N_i} \right)_{P, N_k},$$

and everywhere in Beeby's paper we replace v_i by $\frac{v_i}{N_0}$.

With this notation the fluctuations are

$$\frac{\langle \Delta N_a^2 \rangle}{\langle N_a \rangle} = \frac{N}{V} (k_B T (1-c) H + \frac{c}{(1-c)} \frac{N}{V} \frac{v_b^2}{N_0^2 v P_1})$$

$$\frac{\langle \Delta N_b^2 \rangle}{\langle N_b \rangle} = \frac{N}{V} (k_B T c H + \frac{N}{V} \frac{v_a^2}{N_0^2 v P_1})$$

$$\frac{\langle \Delta N_a \Delta N_b \rangle}{\langle N_b \rangle} = \frac{N}{V} (k_B T (1-c) H + \frac{N}{V} \frac{v_a v_b}{N_0^2 v P_1})$$

where $N = N_a + N_b$, and $P_1 = \frac{1}{(1-c)^2} (\phi + m \frac{d\phi}{dm})$

Osmotic coefficient data were taken from Growther and Dunlop (120) for sodium chloride, and from Robinson and Stokes (26) for nickel chloride. Strictly these values apply to light water solutions, but the conversion to D₂O does not affect the values very appreciably, Robinson (121).

APPENDIX 5

Hydration of ions in aqueous solutions - ion-water distances and coordination numbers obtained from X-ray diffraction. If more than one value of either parameter is given, this indicates the uncertainty of the particular experiment.

Ion	Ref.	Solute	Ion-Water(Oxygen) Distance Å	Hydration Number	Molality (gm moles per 1000g H ₂ O)
Li ⁺	47	Li ₂ SO ₄	2.08	4	2.22
	49	LiBF ₄	2.14	6	10.40
	61	LiI	-	2.6	5.53
				3.4	0.43
	62	LiCl	2.25	4 [±] 1	18.50
			1.95	4 [±] 1	6.90
	63	LiCl	2.1	-	-
71	LiBr	2.16	4,6	6.60	
		2.25	4,6	2.22	
Na ⁺	47	Na ₂ SO ₄	2.38	4	2.22
	47a	NaBF ₄	2.4	6	9.05
					2.65
K ⁺	42	KOH	2.9	4,6	2.02
					5.51
	47	K ₂ SO ₄	2.8	4	0.55
	61	KI	2.9	1.7	6.61
				3.2	0.51
Cs ⁺	52	CsCl	3.15	2.9,6.2	2.5
				2.8,4.2	5.0
				2.0,3.0	10.0
		CsBr	3.15	5.1,6.0	2.5
				1.9,3.0	5.0
		CsI	3.15	2.3,2.7	2.5
NH ₄ ⁺	49	NH ₄ BF ₄	3.00	4.5	2.78
	58	NH ₄ F	2.88	4.4	15.56
		NH ₄ Cl	2.80,	4.4	6.51
		NH ₄ Br	2.82	4.4	7.31
		NH ₄ I	2.91	4.4	6.78

APPENDIX 5 (cont'd)

Ion	Ref.	Solute	Ion-Water(Oxygen) Distance	Hydration Number	Molality			
Mg ⁺⁺	48	MgCl ₂	2.0	6	2.22			
	53	MgCl ₂	-	6	1.39			
				6	2.22			
				6	3.15			
	60	MgCl ₂	2.1	8.1	5.65			
				7.9	4.27			
	68	MgCl ₂	2.1	6	5.72			
					2.78			
					Mg(NO ₃) ₂	2.1	6	4.75
					2.13			
	MgBr ₂	2.1	6	5.72				
				2.52				
Ca ⁺⁺	53	CaCl ₂	-	6	2.22			
					1.38			
	60	CaCl ₂	2.4	8.0	5.22			
					8.2	3.26		
	72	CaBr ₂	2.44	6	2.14			
					2.40	1.26		
	73	CaCl ₂	2.42	6	4.52			
					2.41	2.08		
2.42					1.00			
Sr ⁺⁺	60	SrCl ₂	2.61	3.2,8	2.57			
Ba ⁺⁺	60	BaCl ₂	2.9	9.6	1.54			
Co ⁺⁺	53	CoCl ₂	-	6	3.83			
					2.22			
					1.39			
	54	CoCl ₂	2.1	6	3.75			
Ni ⁺⁺	48	NiCl ₂	2.1	6	2.22			
					3.15			
	53	NiCl ₂	-	6	2.22			
					1.39			
Cu ⁺⁺	53	CuCl ₂	-	4? 2 Cl ions	4.51			
				4 also coord-	2.22			
				6 inated	1.39			

APPENDIX 5 (cont'd)

Ion	Ref.	Solute	Ion-Water(Oxygen) Distance	Hydration Number	Molality
Cu ⁺⁺ (cont'd)	65	CuCl ₂	1.93	Cu ₃ Cl ₆ (H ₂ O) ₆ clusters	5.10
				Cu ₅ Cl ₁₀ (H ₂ O) ₁₂ clusters	3.55
	66	CuSO ₄	2.1,2.3	4,6	0.74 0.45
Zn ⁺⁺	46	ZnCl ₂	2.05	1 (3 Cl atoms are coord- inated at the same distance.)	27.5 8.5 5.0
	50	ZnBr ₂	2.1?	2 (2 Br atoms are coord- inated at the same distance.)	17.7 8.9 4.4
	64	ZnCl ₂ /HCl	2.05,2.15	2	3.5
Cd ⁺⁺	53	CdCl ₂	-	1,2 (2 or 3 Cl atoms coordinated as well)	2.22
					1.39
Al ⁺⁺⁺	68	AlCl ₃	1.9	6	3.38 1.63
		AlBr ₃	-	6?	2.42
In ⁺⁺⁺	68	InCl ₃	2.35	6	6.9 2.9
Cr ⁺⁺⁺	67	CrCl ₃	1.90	6	0.25

The coordination of anions is not well defined for solutes with di-valent or tri-valent cations, because the anion is frequently considered to form part of a cation complex.

OH ⁻	42	KOH	2.9	1,6	4.48 2.01				
					43	KOH	2.9	6	17.50
Cl ⁻	42	KCl	3.16	5.4,7.2	5.51				
					43	LiCl	3.24	8,9	6.86
									48
	52	LiCl	3.20	3.20	6.5,7.3	2.22 10.0			
						3.20	5.4,8.7	5.0	
			3.15	6.2,11.0	2.5				
54		CoCl ₂	3.1	-	3.75				

Ion	Ref.	Solute	Ion-Water(Oxygen) Distance	Hydration Number	Molality
Cl ⁻ (cont'd)	58	NH ₄ Cl	3.2	6 - may include NH ₄ ⁺ ions	6.51
	60	MgCl ₂	3.2	8.2	5.65
				8.9	4.27
		CaCl ₂	3.2	7.9	5.22
				8.0	3.26
	62	LiCl	3.19	6 [±] 1	18.5
				3.10	6 [±] 1
	63	LiCl	3.25	8.2,9.1	8.62
				7.1,10.2	3.99
				8.0	2.27
	70	HCl	3.13	4	13.9-0.58
	73	CaCl ₂	3.15	6	4.52
				3.14	2.09
3.14				1.00	
Br ⁻	52	LiBr	3.43	7.2,8.9	10.0
			3.37	6.6,8.3	5.0
			3.40	6.7,7.2	2.5
	58	NH ₄ Br	3.36	6 - may include NH ₄ ⁺ ions	7.3
	63	LiBr	3.40	7.4,9.5	4.26
	71	LiBr	3.29	6	6.60
					2.22
72	CaBr ₂	-	6	2.14	
				1.26	
I ⁻	52	LiI	3.76	6.1,8.9	10.0
			3.65	6.7,8.0	5.0
			3.69	8.8,9.4	2.5
	58	NH ₄ I	3.64 [±] 0.04	6	6.77
	61	KI	3.7	9.6	6.61
				4.2	0.51
	LiI	3.7	9.6	5.56	
			4.2	0.43	

Hydration numbers and ion-water distances derived from Molecular Dynamics and Monte Carlo calculations on ion-water clusters.

Ion	Ref.	Method	Ion - O Distance Å	Hydration number
Li ⁺	82 - 85	MD	2.08	5.7 [±] 0.2
	86	MC	1.9-2.0	4
	87	MC	1.75	4,5,6
	88	MC	2	5
	90	MC	2	-
Na ⁺	84,85	MD	2.31	6.6 (2.2 molal) 7.3 (0.55 molal)
	86	MC	2.3-2.4	5,6
	89	MD	2.3	5
K ⁺	86	MC	2.7-2.8	5,7
	88	MC	2.9	5
	90	MC	2.8	-
Rb ⁺	89	MD	2.4	5
Cs ⁺	83	MD	3.1	7.3 [±] 0.7 (anion:F ⁻) 8.2 [±] 0.8 (anion:Cl ⁻)
F ⁻	83	MD	2.22	6.3 [±] 0.1
	86	MC	2.7-2.8	4,6
	87	MC	2.2,2.3	3,4
	88	MC	2.7	5.5
	89	MD	2.3	6.5
	90	MC	2.5-2.6	-
Cl ⁻	82 - 85	MD	2.67	7.4 [±] 0.4 (anion: Li ⁺) 6.7 [±] 0.3 (anion: Na ⁺) 7.9 [±] 0.3 (anion: Cs ⁺)
	86	MC	3.4,3.5	6,7
	88	MC	3.5	6
	90	MC	3.3	-
Br ⁻	89	MD	2.9	5
I ⁻	84	MD	3.02	7.1 [±] 0.1
	89	MD	3.8	5

TABLE 3.1 Experimental Conditions for Sodium Chloride Solutions.

a) Isotopic Composition (Chlorine Isotopes) and Scattering Lengths

Sample	At. % ^{35}Cl	At. % ^{37}Cl	Coherent Scattering Length (10^{-12}cm)
Natural	75.5	24.5	0.96
'N'	59.3	40.7	0.81
'35'	99.4	0.7	1.17
'37'	9.6	90.4	0.35

b) Solution Composition and Scattering Cross-Sections.

Molality gm moles per 1000 gm D_2O	Density* gm/cc	Atomic Fraction	Scattering cross-section per atom barns			
			Natural	'N'	'35'	'37'
5.32	1.30	0.0331	-	4.09	4.31	3.82
2.99	1.22	0.0192	4.03	-	4.11	3.82
1.49	1.16	0.0097	-	3.91	3.97	3.83

* measured in the course of the experiments. The likely error is ± 0.01 gm/cc.

c) Hydrogen Contents.

Molality	Hydrogen content, expressed as the wt % of H_2O in pure D_2O which had the same absorption as the solution.			
	Natural	'N'	'35'	'37'
5.32	-	0.8	0.8	0.8
2.99	0.5	-	0.2	0.2
1.49	-	0.4	0.3	0.4

TABLE 3.2 Limits on Partial Structure Factors and Radial Distributions.

Molality	Partial Structure Factors				Partial Radial Distributions									
	X		Y_{av}		X		Y_{av}							
	Max	Min	Max	Min	Max	Min	Max	Min						
5.32	30	-30	1	-3	1	-3	-1	-1	3	-3	-1	-1	2	-1
2.99	40	-40	1	-4	1	-1	-1	-1	3	-3	-1	-1	2	-1
1.49	70	-70	1	-3	0.8	-0.8	-1	-1	3	-3	-1	-1	2	-1

TABLE 4.1 Hydration Numbers of Chlorine Ion in NaCl Solutions.

Molality	(i)	(ii)	(iii)
	All Deuterium atoms	Equal numbers of deuterium and oxygen atoms	All D ₂ O molecules
5.32	5.4	2.9	1.9
2.99	6.6	3.5	2.4
1.49	6.4	3.3	2.2

TABLE 4.2 Parameters for hydration sphere models drawn in figs. 4.1 to 4.7.

Molality	Model A - Cl - O				N ₀	w			
	Cl - O (Å)	θ (°)	φ (°)						
5.32	3.15	90	15	5.5	0.26				
2.99	3.15	90	15	6.0	0.24				
Model B	1st Hydration Sphere				2nd Hydration Sphere				
	Cl - O (Å)	θ (°)	φ (°)	N ₀	Cl - O (Å)	θ (°)	φ (°)	N ₀	w (Å)
5.32	2.7	80	52	2	3.7	80	52	1.5	0.18
2.99	2.6	80	52	2.5	3.7	80	52	1.5	0.18
1.49	2.5	60	-48	3	3.8	90	-60	4.5	0.16

TABLE 4.3 Optimum Parameters of the Hydration Sphere Models.

Molality	1st Hydration Sphere				2nd Hydration Sphere				r.m.s. deviation per point for Y(r)	r.m.s. deviation per point for Y(Q)	w (Å)
	Cl - 0 (Å)	N ₀	θ (°)	φ (°)	Cl - 0 (Å)	N ₀	θ (°)	φ (°)			
Model A											
5.32	3.2 [±] 0.02	5.5 [±] 0.1	80 [±] 3	12 [±] 2	-	-	-	-	0.173	0.178	0.26
2.99	3.2 [±] 0.05	6.0 [±] 0.2	90 [±] 10	10 [±] 5	-	-	-	-	0.303	0.353	0.24
1.49	3.25 [±] 0.05	6.0 [±] 0.2	80 [±] 10	5 [±] 5	4.0 [±] 0.1	5.9 [±] 0.2	25 [±] 15	-80 [±] 25	0.279	0.419	0.26
Model B											
5.32	2.68 [±] 0.04	2.1 [±] 0.1	82 [±] 4	46 [±] 2	3.7 [±] 0.1	1.3 [±] 0.2	90 [±] 40	52 [±] 8	0.154	0.121	0.18
2.99	2.65 [±] 0.03	2.2 [±] 0.2	85 [±] 10	52 [±] 4	3.5 [±] 0.1	1.6 [±] 0.2	55 [±] 25	45 [±] 25	0.228	0.270	0.18
1.49	2.6 [±] 0.1	3.0 [±] 0.2	55 [±] 20	-40 [±] 10	3.8 [±] 0.1	4.5 [±] 0.2	70 [±] 20	-60 [±] 10	0.234	0.445	0.16

The errors shown indicate approximately the range over which the mean square deviation varies

within 10 % of the minimum value.

TABLE 4.4 Composition of Nickel Chloride Aqueous Solutions.

Molality	Density gm/cc	Nickel Atomic Fraction	Scattering cross-section per atom (barns)		
			Natural	'62'	'zero'
4.41	1.53	0.027	4.61	4.39	4.36
3.02	1.41	0.019	4.43	4.29	4.26
1.43	1.25	0.009	4.33	4.29	4.26

Scattering Lengths:

Ni (Natural) 1.03×10^{-12} cmNi ('62') -0.79×10^{-12} cmNi ('zero') 0.04×10^{-12} cmTABLE 4.5 Hydration Numbers of Nickel Ion in Nickel Chloride

Solutions (assuming the double peak in figs. 4.18 - 4.20 consists solely of D₂O molecules) .

Molality	Hydration Number
4.41	5.8 ± 0.1
3.02	6.0 ± 0.2
1.43	6.1 ± 0.4

TABLE 5.1Parameters for Monatomic Liquids.

Liquid	Crystal Structure	Near-neighbour Distance (\AA)		Number Density (per \AA^3)		Width constant (\AA^{-1})	Reference No.
		Expt.	Model	Expt.	Model		
Ar	F.C.C.	3.71	3.88	0.0212	0.0237	0.4	101
Na	B.C.C.	3.7	3.83	0.0244	0.0253	0.42	102
Zn	H.C.P.	2.75	2.68	0.0622	0.0708	0.6	103
Fe	B.C.C.	2.54	2.61	0.0756	0.0796	0.5039	104
Sn	Tetragon.	3.18	3.07	0.0355	0.0371	0.42	103

TABLE 5.2Parameters for Molten Sodium Chloride

Partial	Near-neighbour Distance (\AA)			Number Density (per \AA^3)			Width Constant (\AA^{-1})
	Expt.	Model(a)	Model(b)	Expt.	Model(a)	Model(b)	
Cl-Cl	4.1	3.89	4.38				0.5
Na-Na	4.1	3.82	4.35	0.0311	0.0467	0.033	0.55
Na-Cl	2.6	2.75	3.08				0.525

TABLE 5.3Molten Sodium Chloride - Comparison of Peak Positions

Partial	Product $Q_0 d$					
	First peak/minimum			Second peak/minimum		
	Expt.	(a) Model	(b)	Expt.	(a) Model	(b)
Cl-Cl	7.17	7.78	7.80	13.94	13.69	13.88
Na-Cl	4.55	5.09	5.17	10.32	10.31	10.41

TABLE 5.4 Parameters for liquids with Nickel Arsenide-type Structures

Liquid	Structure	Metal-metal near-neighbour distance (Å)		Total no. density of model (per Å ³)	Width constants (Å ⁻¹)		
		Expt.	Model		Metal-metal	Metalloid-metal	Metalloid-metalloid
NiTe	NiAs	2.5	2.58	0.055	0.7	0.7	0.7
NiTe ₃	NiAs	-	2.64	0.055	0.4	0.4	0.7
CuTe	NiAs	2.78	2.61	0.055	0.55	0.45	0.5
Cu ₂ Te	Fe ₂ As	2.63	2.58	0.031	0.6	0.5	0.5

TABLE 5.5 Hydration Numbers and Free Water Molecule Concentration for Three Component Hard Sphere del

Molality	D ₂ O no. density (per Å ³)	Ni no. density (per Å ³)	Cl hydration number.	Hydrated diameter. (Å)	Remaining free D ₂ O no. density. (per Å ³)
4.27	0.02926	0.00274	2.3	4.3	-
3.71	0.02976	0.00239	3.2	4.45	-
3.05	0.03026	0.00197	4.7	4.75	-
1.87	0.03147	0.00123	6.0	5.0	0.00933
0.81	0.03237	0.00053	6.0	5.0	0.02283
0.31	0.03183	0.00020	6.0	5.0	0.02923
0.06	0.03289	0.00004	6.0	5.0	0.03217

Hydrated nickel diameter = 5.6 Å, water molecule diameter = 6.0 Å

Nickel hydration number = 6.0

TABLE 6.1 Hard Sphere Model of Sodium Chloride Solutions

Molality	D ₂ O no. density (per Å ³)	Na no. density (per Å ³)	Cl Hydration Number	Hydrated diameter	Remaining free D ₂ O no. density (per Å ³)
5.32	0.02988	0.00318	4.5	4.77	-
2.99	0.03109	0.00186	5.0	4.86	0.01265
1.49	0.03203	0.00095	7.5	5.31	0.02019

Na hydration number = 5.0, Na hydrated diameter = 4.15 Å.

1) 5.32 molal Sodium Chloride.

$\frac{Q}{(Q-1)}$	'N'	'35'	'37'
0.00000	.29198	.28636	.27833
.10000	.29623	.29181	.28488
.20000	.30047	.29726	.29144
.30000	.30464	.30477	.30069
.40000	.30911	.30858	.30685
.50000	.31234	.31335	.31258
.60000	.31680	.31836	.31845
.70000	.31928	.32233	.32546
.80000	.32633	.33029	.33115
.90000	.33759	.34413	.34413
1.00000	.34812	.35351	.35676
1.10000	.36231	.36772	.37170
1.20000	.38257	.38839	.39042
1.30000	.40625	.41508	.41415
1.40000	.43939	.45147	.44497
1.50000	.48481	.50056	.48745
1.60000	.55028	.57113	.54841
1.70000	.64325	.66960	.63691
1.80000	.76183	.79613	.75112
1.90000	.90367	.94347	.88615
2.00000	1.02785	1.07737	1.01077
2.10000	1.13828	1.14171	1.06877
2.20000	1.20255	1.12007	1.04733
2.30000	1.23472	1.03302	.96688
2.40000	1.28104	.92340	.88274
2.50000	1.79149	.83068	.77428
2.60000	2.23133	.75223	.70638
2.70000	2.63377	.71507	.66588
2.80000	2.93377	.68521	.62391
2.90000	3.17397	.65431	.59675
3.00000	3.35588	.63232	.57174
3.10000	3.47770	.61124	.55230
3.20000	3.56045	.59974	.53917
3.30000	3.58826	.58885	.53066
3.40000	3.55843	.57908	.52281
3.50000	3.46243	.57096	.51614
3.60000	3.27655	.56394	.51063
3.70000	2.93677	.55813	.50613
3.80000	2.47823	.56300	.50260
3.90000	1.88466	.61522	.54679
4.00000	1.1717	.61531	.54725
4.10000	.78722	.61096	.54190
4.20000	.6948	.63499	.53977
4.30000	.56164	.65934	.53230
4.40000	.32241	.68318	.52421
4.50000	.12711	.70700	.51511
4.60000	.158	.73115	.50774
4.70000	.23222	.75500	.49996
4.80000	.11482	.77840	.49398
4.90000	.11266	.80119	.48916
5.00000	.10299	.82334	.48897
5.10000	.7226	.84529	.48858
5.20000	.8440	.86685	.48811
5.30000	1.3110	.88818	.48933
5.40000	1.9533	.90931	.48937
5.50000	2.4388	.93025	.49630
5.60000	2.8338	.95108	.49633
5.70000	3.3611	.97174	.51006
5.80000	4.3395	.99228	.51453
5.90000	4.8997	1.01268	.51788
6.00000	5.5998	1.03295	.52463
6.10000	5.9919	1.05316	.52701
6.20000	6.3351	1.07334	.52984
6.30000	6.6438	1.09346	.53182
6.40000	6.9438	1.11347	.53499
6.50000	7.2222	1.13344	.53729
6.60000	7.4755	1.15338	.53967
6.70000	7.7055	1.17328	.54211
6.80000	7.9119	1.19313	.54463
6.90000	8.0933	1.21293	.54723
7.00000	8.2438	1.23268	.54991
7.10000	8.3624	1.25238	.55266
7.20000	8.4506	1.27202	.55548
7.30000	8.5088	1.29161	.55837
7.40000	8.5364	1.31115	.56133
7.50000	8.5333	1.33064	.56436
7.60000	8.4988	1.35008	.56746
7.70000	8.4333	1.36947	.57063
7.80000	8.3373	1.38881	.57387
7.90000	8.2111	1.40810	.57718
8.00000	8.0556	1.42734	.58056
8.10000	7.8711	1.44653	.58401
8.20000	7.6588	1.46567	.58753
8.30000	7.4288	1.48476	.59112
8.40000	7.1822	1.50380	.59478
8.50000	6.9200	1.52279	.59851
8.60000	6.6433	1.54174	.60231
8.70000	6.3522	1.56064	.60617
8.80000	6.0477	1.57949	.61010
8.90000	5.7311	1.59829	.61409
9.00000	5.4033	1.61704	.61815
9.10000	5.0655	1.63574	.62228
9.20000	4.7188	1.65439	.62648
9.30000	4.3633	1.67299	.63075
9.40000	3.9988	1.69154	.63509
9.50000	3.6255	1.71004	.63950
9.60000	3.2433	1.72849	.64397
9.70000	2.8522	1.74689	.64851
9.80000	2.4533	1.76524	.65312
9.90000	2.0466	1.78354	.65779
10.00000	1.6333	1.80179	.66253

(A-1)

'N'

'35'

'37'

7.300000
 7.400000
 7.500000
 7.600000
 7.700000
 7.800000
 7.900000
 8.000000
 8.100000
 8.200000
 8.300000
 8.400000
 8.500000
 8.600000
 8.700000
 8.800000
 8.900000
 9.000000
 9.100000
 9.200000
 9.300000
 9.400000
 9.500000
 9.600000
 9.700000
 9.800000
 9.900000
 10.000000
 10.100000
 10.200000
 10.300000
 10.400000
 10.500000
 10.600000
 10.700000
 10.800000
 10.900000
 11.000000
 11.100000
 11.200000
 11.300000
 11.400000
 11.500000
 11.600000
 11.700000
 11.800000
 11.900000
 12.000000
 12.100000
 12.200000
 12.300000
 12.400000
 12.500000
 12.600000
 12.700000
 12.800000
 12.900000
 13.000000
 13.100000
 13.200000
 13.300000
 13.400000
 13.500000
 13.600000
 13.700000
 13.800000
 13.900000
 14.000000
 14.100000
 14.200000
 14.300000
 14.400000
 14.500000

.56285
 .56508
 .56834
 .56837
 .56748
 .57202
 .57429
 .57529
 .57524
 .57594
 .57610
 .57491
 .56773
 .56345
 .56003
 .55613
 .54867
 .54266
 .53689
 .52776
 .51902
 .51169
 .50511
 .49527
 .48900
 .48021
 .46869
 .46181
 .45742
 .44836
 .43762
 .43308
 .42799
 .42169
 .41490
 .41089
 .40514
 .40142
 .39790
 .39431
 .39083
 .38635
 .38394
 .38110
 .37927
 .37911
 .37785
 .37717
 .37496
 .37516
 .37435
 .37287
 .37471
 .37454
 .37126
 .37169
 .37246
 .37449
 .37376
 .37239
 .37308
 .37324
 .37290
 .37267
 .36857
 .37097
 .37236
 .36912
 .37005
 .36537
 .36574
 .36244
 .36164

.59062
 .59097
 .59657
 .60006
 .60184
 .60201
 .60162
 .60123
 .60120
 .60360
 .60373
 .60142
 .59826
 .59391
 .58826
 .58092
 .57798
 .57336
 .56670
 .55751
 .54866
 .54038
 .53281
 .52643
 .51708
 .50776
 .49914
 .49022
 .48333
 .47557
 .46818
 .46597
 .45865
 .44951
 .44116
 .43574
 .42221
 .42936
 .42407
 .41801
 .41460
 .41402
 .40810
 .40758
 .40803
 .40517
 .40344
 .40148
 .40023
 .39792
 .39934
 .40257
 .40059
 .40038
 .39642
 .39880
 .39752
 .39915
 .40016
 .39722
 .39703
 .40104
 .39586
 .39731
 .39713
 .39652
 .39916
 .39942
 .39364
 .39443
 .39193
 .38914

.53869
 .54335
 .54286
 .54345
 .54438
 .54364
 .54592
 .54871
 .55051
 .54947
 .54655
 .54285
 .54247
 .53860
 .53332
 .52787
 .52170
 .51603
 .51057
 .50446
 .49492
 .48511
 .47589
 .46807
 .46046
 .45289
 .44523
 .43770
 .42886
 .41932
 .41196
 .40789
 .40188
 .39341
 .38640
 .38381
 .37748
 .37496
 .37150
 .36675
 .36204
 .35804
 .35772
 .35544
 .35236
 .35131
 .34790
 .34939
 .34692
 .34798
 .34649
 .34285
 .34473
 .34535
 .34428
 .34363
 .34327
 .34476
 .34546
 .34586
 .34599
 .34488
 .34548
 .34551
 .34488
 .34408
 .34235
 .34107
 .34051
 .34018
 .33935
 .33828
 .33401

(A-1)	'N'	'35'	'37'
14.60000	.36116	.38641	.33193
14.70000	.35726	.38603	.33030
14.80000	.35481	.38184	.32838
14.90000	.34963	.37840	.32873
15.00000	.34920	.37706	.32332
15.10000	.34583	.37165	.32046
15.20000	.34110	.37031	.31732
15.30000	.33952	.36465	.31325
15.40000	.33546	.36326	.31169

$\left(\frac{\rho}{A-1}\right)$	nat	'55'	'57'
0.00000	.28941	.26396	.34613
.10000	.29339	.26887	.34231
.20000	.29858	.27377	.33948
.30000	.30455	.27969	.33242
.40000	.31113	.28209	.31549
.50000	.31627	.28761	.30751
.60000	.31920	.28964	.30501
.70000	.32561	.29372	.31877
.80000	.32642	.30418	.32212
.90000	.33577	.31450	.32688
1.00000	.35276	.32491	.33569
1.10000	.36594	.34299	.34904
1.20000	.38733	.36505	.37208
1.30000	.42155	.39463	.40008
1.40000	.46201	.43233	.43492
1.50000	.52200	.49715	.49367
1.60000	.60363	.58262	.57317
1.70000	.71209	.69139	.67800
1.80000	.84163	.81980	.80377
1.90000	.98207	.96553	.93595
2.00000	1.08529	1.07212	1.03560
2.10000	1.12375	1.10827	1.06851
2.20000	1.07064	1.05948	1.02229
2.30000	.98595	.97160	.94160
2.40000	.89368	.87459	.84360
2.50000	.80678	.79820	.76324
2.60000	.74966	.73511	.70309
2.70000	.70437	.69463	.66051
2.80000	.67503	.66576	.62219
2.90000	.66422	.65314	.60951
3.00000	.66139	.65397	.60674
3.10000	.65963	.65307	.60597
3.20000	.65832	.65241	.60591
3.30000	.65761	.65261	.60520
3.40000	.65787	.65203	.60405
3.50000	.65818	.65199	.60350
3.60000	.65947	.65199	.60338
3.70000	.65995	.65199	.60338
3.80000	.66006	.65199	.60338
3.90000	.66023	.65199	.60338
4.00000	.66071	.65199	.60338
4.10000	.66000	.65199	.60338
4.20000	.65924	.65199	.60338
4.30000	.65820	.65199	.60338
4.40000	.65742	.65199	.60338
4.50000	.65633	.65199	.60338
4.60000	.65507	.65199	.60338
4.70000	.65413	.65199	.60338
4.80000	.65331	.65199	.60338
4.90000	.65260	.65199	.60338
5.00000	.65240	.65199	.60338
5.10000	.65261	.65199	.60338
5.20000	.65335	.65199	.60338
5.30000	.65493	.65199	.60338
5.40000	.65418	.65199	.60338
5.50000	.65468	.65199	.60338
5.60000	.65537	.65199	.60338
5.70000	.65645	.65199	.60338
5.80000	.65677	.65199	.60338
5.90000	.65722	.65199	.60338
6.00000	.65755	.65199	.60338
6.10000	.65754	.65199	.60338
6.20000	.65799	.65199	.60338
6.30000	.65846	.65199	.60338
6.40000	.65874	.65199	.60338
6.50000	.65819	.65199	.60338
6.60000	.65846	.65199	.60338
6.70000	.65871	.65199	.60338
6.80000	.65833	.65199	.60338
6.90000	.65858	.65199	.60338
7.00000	.65843	.65199	.60338
7.10000	.65898	.65199	.60338
7.20000	.65898	.65199	.60338

(A-1)	Nat	'55'	'57'
7.300000	.58531	.57447	.54427
7.400000	.58676	.57887	.54532
7.500000	.59179	.58411	.54972
7.600000	.59046	.58484	.55263
7.700000	.59605	.58557	.55730
7.800000	.60163	.58731	.56060
7.900000	.60136	.59127	.55941
8.000000	.60345	.59241	.55821
8.100000	.60181	.59143	.55975
8.200000	.59707	.58908	.56288
8.300000	.59336	.59022	.55756
8.400000	.59491	.58749	.55449
8.500000	.59155	.58464	.55201
8.600000	.59178	.58440	.55490
8.700000	.58406	.57636	.54255
8.800000	.57943	.57123	.53477
8.900000	.57476	.56913	.52786
9.000000	.56249	.55729	.52642
9.100000	.55707	.55090	.52007
9.200000	.55067	.54363	.51218
9.300000	.54148	.53631	.50353
9.400000	.52758	.52974	.49488
9.500000	.52469	.52176	.48513
9.600000	.52072	.51333	.47558
9.700000	.51264	.50430	.46648
9.800000	.49940	.49282	.45778
9.900000	.49028	.48332	.44908
10.000000	.48435	.47577	.44224
10.100000	.47854	.46933	.43544
10.200000	.46812	.46308	.42993
10.300000	.45928	.45316	.42055
10.400000	.45112	.44314	.41129
10.500000	.44293	.43361	.40362
10.600000	.43468	.42330	.39841
10.700000	.42905	.42259	.39354
10.800000	.42076	.41197	.39058
10.900000	.41657	.41466	.38536
11.000000	.41432	.40999	.37833
11.100000	.41049	.40533	.37204
11.200000	.40549	.40004	.37051
11.300000	.40347	.40001	.36670
11.400000	.40339	.39887	.36419
11.500000	.40113	.39671	.36249
11.600000	.39498	.39491	.36044
11.700000	.38825	.39397	.35758
11.800000	.39318	.39333	.35809
11.900000	.39360	.39121	.35560
12.000000	.39005	.38899	.35406
12.100000	.38726	.38321	.35121
12.200000	.38685	.37861	.34827
12.300000	.38675	.38233	.34857
12.400000	.38624	.38605	.34871
12.500000	.39030	.37873	.34851
12.600000	.38802	.38396	.34760
12.700000	.38682	.38324	.35072
12.800000	.38461	.38646	.35136
12.900000	.38498	.38210	.35138
13.000000	.38934	.38164	.35139
13.100000	.39012	.38569	.35361
13.200000	.38762	.38723	.35879
13.300000	.38906	.38434	.35744
13.400000	.38454	.38725	.35558
13.500000	.38710	.38262	.35207
13.600000	.38833	.38568	.35783
13.700000	.39181	.38229	.35578
13.800000	.38993	.38371	.35373
13.900000	.38659	.38140	.35133
14.000000	.38817	.38608	.34591
14.100000	.39008	.38114	.34679
14.200000	.38532	.38219	.35059
14.300000	.38172	.37860	.34713
14.400000	.37817	.37683	.34714
14.500000	.37396	.37394	.34639

(A-1)	Nat	'35'	'37'
14.60000	.37194	.37207	.34430
14.70000	.37418	.37186	.33776
14.80000	.37174	.36901	.33393
14.90000	.36907	.36750	.33221
15.00000	.36455	.35966	.33098
15.10000	.35800	.35933	.32534
15.20000	.35572	.35558	.32155
15.30000	.35335	.35054	.31873
15.40000	.34939	.34832	.31646
15.50000	.34677	.34056	.31335
15.60000	.34239	.33724	.30915
15.70000	.33963	.33110	.30190
15.80000	.33304	.33185	.29824
15.90000	.33119	.33236	.29699

.40.UCLP, 22,

0.252 KLNS.

(A ⁻¹)	'N'	'55'	'37'
0.000000	.26314	.25489	.26630
.100000	.26451	.25769	.26655
.200000	.26587	.26049	.26680
.300000	.26723	.25988	.26705
.400000	.26859	.25990	.26730
.500000	.26995	.26391	.26755
.600000	.27131	.27002	.27234
.700000	.27267	.27926	.27692
.800000	.27403	.28794	.28179
.900000	.27539	.28711	.29319
1.000000	.30424	.30071	.30359
1.100000	.31924	.31656	.31946
1.200000	.34618	.33763	.34029
1.300000	.37227	.37564	.37049
1.400000	.42509	.42570	.41746
1.500000	.43933	.43400	.44815
1.600000	.58888	.58888	.57044
1.700000	.69564	.70501	.68573
1.800000	.82081	.82879	.81255
1.900000	.92642	.94016	.91373
2.000000	.96991	.96236	.96537
2.100000	.95395	.96354	.96219
2.200000	.88788	.90059	.88301
2.300000	.81245	.82188	.80225
2.400000	.73306	.74640	.73138
2.500000	.68511	.69488	.67334
2.600000	.64361	.64316	.63535
2.700000	.60766	.60970	.59585
2.800000	.57595	.57557	.56566
2.900000	.54881	.55595	.53983
3.000000	.52461	.53117	.51132
3.100000	.50480	.51816	.49759
3.200000	.50590	.51287	.49114
3.300000	.50155	.51750	.49256
3.400000	.51148	.51836	.49973
3.500000	.51492	.52303	.50644
3.600000	.52124	.53033	.51038
3.700000	.52233	.53353	.51393
3.800000	.52895	.53949	.51785
3.900000	.53050	.53787	.51657
4.000000	.52145	.53491	.51277
4.100000	.52294	.53302	.51009
4.200000	.51110	.52202	.49923
4.300000	.50150	.51070	.48724
4.400000	.49220	.49668	.47835
4.500000	.48053	.49044	.47110
4.600000	.46647	.48003	.46404
4.700000	.45487	.46803	.45685
4.800000	.45480	.46687	.45007
4.900000	.45439	.46041	.44436
5.000000	.45628	.46099	.44456
5.100000	.45738	.46202	.44647
5.200000	.45738	.46432	.44534
5.300000	.46201	.47403	.45291
5.400000	.46874	.47834	.45890
5.500000	.47342	.48556	.46543
5.600000	.47553	.48631	.46647
5.700000	.48224	.49780	.47773
5.800000	.49222	.50003	.47896
5.900000	.49254	.50622	.48202
6.000000	.49644	.50942	.48807
6.100000	.49736	.50647	.49196
6.200000	.49933	.51202	.49192
6.300000	.50743	.51454	.49602
6.400000	.50835	.51677	.49827
6.500000	.50504	.51355	.49477
6.600000	.50743	.51800	.50008
6.700000	.50657	.51757	.50000
6.800000	.50393	.51489	.49300
6.900000	.50951	.51777	.50339
7.000000	.51334	.52381	.50247
7.100000	.51682	.51917	.50597
7.200000	.51369	.52326	.50865

3) cont'd

	'N'	'55'	'37'
7.300000	.518099	.523377	.506610
7.400000	.516444	.522819	.508812
7.500000	.518700	.522735	.512218
7.600000	.523360	.533153	.519332
7.700000	.522878	.533574	.520661
7.800000	.526599	.533365	.522214
7.900000	.525561	.533464	.515664
8.000000	.522770	.533232	.520933
8.100000	.524444	.533417	.515422
8.200000	.522102	.522973	.511163
8.300000	.518088	.522712	.516330
8.400000	.513422	.522469	.510466
8.500000	.510930	.511669	.502078
8.600000	.501300	.495588	.495542
8.700000	.499728	.516333	.491664
8.800000	.492218	.505500	.483312
8.900000	.485177	.493844	.472666
9.000000	.476988	.482269	.467664
9.100000	.467288	.477714	.462662
9.200000	.462100	.465554	.459833
9.300000	.450866	.460061	.446617
9.400000	.445033	.455787	.433637
9.500000	.441112	.452291	.430660
9.600000	.428224	.443668	.421116
9.700000	.423676	.443299	.416111
9.800000	.414566	.429755	.406333
9.900000	.407466	.424833	.398835
10.000000	.402899	.414933	.391966
10.100000	.394988	.409961	.385332
10.200000	.385833	.395722	.378330
10.300000	.383688	.379833	.372664
10.400000	.375449	.385551	.365559
10.500000	.365688	.375688	.358851
10.600000	.360355	.371233	.352922
10.700000	.356722	.366421	.351363
10.800000	.351733	.360932	.341663
10.900000	.345900	.355912	.336566
11.000000	.352247	.358088	.344229
11.100000	.340400	.351599	.336604
11.200000	.342003	.349334	.332996
11.300000	.343677	.347700	.327433
11.400000	.334661	.347433	.329533
11.500000	.333012	.342633	.323667
11.600000	.333754	.340336	.325111
11.700000	.329477	.334373	.324766
11.800000	.332248	.339330	.325033
11.900000	.331588	.340221	.324228
12.000000	.322838	.336557	.317455
12.100000	.331755	.338661	.324227
12.200000	.334495	.341044	.322099
12.300000	.330055	.333662	.320557
12.400000	.333387	.336188	.317554
12.500000	.323884	.337997	.321422
12.600000	.332622	.337995	.318887
12.700000	.322812	.335556	.317433
12.800000	.322831	.336447	.319433
12.900000	.324446	.337688	.321188
13.000000	.336746	.340335	.327900
13.100000	.330055	.346004	.322443
13.200000	.327877	.340771	.324400
13.300000	.333144	.343330	.321633
13.400000	.333755	.339664	.325366
13.500000	.322925	.339997	.320655
13.600000	.334622	.342003	.326199
13.700000	.336088	.341887	.326799
13.800000	.322739	.340095	.322357
13.900000	.332449	.340333	.320338
14.000000	.332204	.340225	.319088
14.100000	.329188	.338779	.321884
14.200000	.325337	.333194	.323661
14.300000	.323333	.334778	.312777
14.400000	.322097	.334414	.313166
14.500000	.316933	.330036	.312533

3) cont'd

	'H'	'35'	'37'
(A-1)			
14.60000	.32328	.32755	.31087
14.70000	.31503	.32291	.31332
14.80000	.31403	.32434	.30208
14.90000	.30849	.32015	.30672
15.00000	.31163	.31716	.30289
15.10000	.30692	.31449	.30157
15.20000	.30583	.31275	.29715
15.30000	.29907	.31176	.29636
15.40000	.29944	.31264	.28910

15.UCLP, 22, 0.252 KLNS.

4) 4.41 molal nickel chloride

	Nat	'62'	'0'
0.00000	.25479	.27116	.27402
.10000	.26677	.27743	.28173
.20000	.27875	.28369	.28944
.30000	.29307	.29302	.29694
.40000	.30186	.30076	.30498
.50000	.31234	.30877	.31116
.60000	.32426	.31248	.31769
.70000	.34238	.31923	.32586
.80000	.36154	.33055	.33495
.90000	.37739	.34825	.34678
1.00000	.38372	.36274	.35557
1.10000	.38196	.37880	.36863
1.20000	.38639	.39948	.39084
1.30000	.42519	.43566	.42065
1.40000	.44572	.47647	.45810
1.50000	.45850	.52980	.51340
1.60000	.57912	.61854	.59722
1.70000	.68934	.71398	.71089
1.80000	.81522	.90068	.86002
1.90000	.96493	1.07834	1.02438
2.00000	1.13560	1.22687	1.15782
2.10000	1.09097	1.27717	1.15477
2.20000	1.09997	1.22173	1.15068
2.30000	1.99226	1.08692	1.03179
2.40000	.88553	.94378	.90435
2.50000	.79920	.81145	.79205
2.60000	.73679	.70599	.70819
2.70000	.70654	.66345	.65402
2.80000	.68238	.58408	.61450
2.90000	.67730	.55294	.60352
3.00000	.67333	.55409	.60051
3.10000	.65561	.55368	.58078
3.20000	.64554	.55345	.57706
3.30000	.63147	.55430	.57003
3.40000	.61747	.55587	.57728
3.50000	.60861	.55720	.57671
3.60000	.60997	.55965	.59169
3.70000	.60720	.61309	.59775
3.80000	.60843	.62244	.60655
3.90000	.61229	.63499	.61601
4.00000	.62155	.63897	.61700
4.10000	.61537	.63258	.61728
4.20000	.60998	.62213	.60410
4.30000	.61045	.61086	.59884
4.40000	.59543	.59966	.58958
4.50000	.58537	.58095	.57062
4.60000	.57733	.56669	.55836
4.70000	.56776	.55579	.54986
4.80000	.55615	.54732	.54135
4.90000	.55932	.54060	.53879
5.00000	.56445	.54220	.54083
5.10000	.56415	.54191	.54209
5.20000	.56441	.54456	.54547
5.30000	.57339	.55227	.55278
5.40000	.58063	.55988	.56069
5.50000	.58537	.56262	.56165
5.60000	.59075	.57365	.56967
5.70000	.58990	.57840	.57338
5.80000	.59793	.58751	.58394
5.90000	.60075	.58993	.58167
6.00000	.59389	.58830	.58581
6.10000	.60127	.59638	.58619
6.20000	.60391	.59973	.59022
6.30000	.60652	.59906	.59556
6.40000	.61252	.60097	.59538
6.50000	.61734	.60326	.59897
6.60000	.61876	.60607	.60634
6.70000	.61556	.60961	.60102
6.80000	.62163	.60897	.59571
6.90000	.62747	.60046	.59002
7.00000	.63098	.59935	.60438
7.10000	.63284	.60005	.59868

	(\AA^{-1})	Nat	'62'	'0'
	7.300000	.63254	.59948	.60250
	7.400000	.62845	.59708	.59808
	7.500000	.62379	.59647	.59328
	7.600000	.62328	.59711	.60013
	7.700000	.62828	.59393	.60013
	7.800000	.62243	.59805	.59891
	7.900000	.61908	.59691	.59914
	8.000000	.62246	.60046	.60017
	8.100000	.61943	.60110	.60069
	8.200000	.61741	.60168	.60093
	8.300000	.61641	.60145	.60017
	8.400000	.61579	.60116	.60044
	8.500000	.61465	.60148	.60028
	8.600000	.61122	.60139	.60032
	8.700000	.60742	.60114	.59969
	8.800000	.60064	.60050	.59895
	8.900000	.59909	.59946	.59822
	9.000000	.59795	.59818	.59742
	9.100000	.59763	.59741	.59625
	9.200000	.59713	.59638	.59576
	9.300000	.59722	.59559	.59535
	9.400000	.59650	.59482	.59482
	9.500000	.59599	.59333	.59401
	9.600000	.59557	.59266	.59285
	9.700000	.59492	.59163	.59241
	9.800000	.59427	.59050	.59161
	9.900000	.59296	.58933	.59076
1	10.000000	.59221	.58841	.58984
11	10.100000	.59133	.58738	.58891
11	10.200000	.59045	.58635	.58806
11	10.300000	.58957	.58531	.58722
11	10.400000	.58869	.58427	.58639
11	10.500000	.58781	.58323	.58556
11	10.600000	.58693	.58219	.58473
11	10.700000	.58605	.58115	.58390
11	10.800000	.58517	.58011	.58307
11	10.900000	.58429	.57907	.58224
11	11.000000	.58341	.57803	.58141
11	11.100000	.58253	.57699	.58058
11	11.200000	.58165	.57595	.57975
11	11.300000	.58077	.57491	.57892
11	11.400000	.57989	.57387	.57809
11	11.500000	.57901	.57283	.57726
11	11.600000	.57813	.57179	.57643
11	11.700000	.57725	.57075	.57560
11	11.800000	.57637	.56971	.57477
11	11.900000	.57549	.56867	.57394
12	12.000000	.57461	.56763	.57311
12	12.100000	.57373	.56659	.57228
12	12.200000	.57285	.56555	.57145
12	12.300000	.57197	.56451	.57062
12	12.400000	.57109	.56347	.56979
12	12.500000	.57021	.56243	.56896
12	12.600000	.56933	.56139	.56813
12	12.700000	.56845	.56035	.56730
12	12.800000	.56757	.55931	.56647
12	12.900000	.56669	.55827	.56564
13	13.000000	.56581	.55723	.56481
13	13.100000	.56493	.55619	.56398
13	13.200000	.56405	.55515	.56315
13	13.300000	.56317	.55411	.56232
13	13.400000	.56229	.55307	.56149
13	13.500000	.56141	.55203	.56066
13	13.600000	.56053	.55099	.55983
13	13.700000	.55965	.54995	.55900
13	13.800000	.55877	.54891	.55817
13	13.900000	.55789	.54787	.55734
14	14.000000	.55701	.54683	.55651
14	14.100000	.55613	.54579	.55568
14	14.200000	.55525	.54475	.55485
14	14.300000	.55437	.54371	.55402
14	14.400000	.55349	.54267	.55319
14	14.500000	.55261	.54163	.55236
14	14.600000	.55173	.54059	.55153
14	14.700000	.55085	.53955	.55070
14	14.800000	.55000	.53851	.54987
14	14.900000	.54912	.53747	.54904
14	15.000000	.54824	.53643	.54821
14	15.100000	.54736	.53539	.54738
14	15.200000	.54648	.53435	.54655
14	15.300000	.54560	.53331	.54572
14	15.400000	.54472	.53227	.54489
14	15.500000	.54384	.53123	.54406
14	15.600000	.54296	.53019	.54323
14	15.700000	.54208	.52915	.54240
14	15.800000	.54120	.52811	.54157
14	15.900000	.54032	.52707	.54074
14	16.000000	.53944	.52603	.53991
14	16.100000	.53856	.52499	.53908
14	16.200000	.53768	.52395	.53825
14	16.300000	.53680	.52291	.53742
14	16.400000	.53592	.52187	.53659
14	16.500000	.53504	.52083	.53576
14	16.600000	.53416	.51979	.53493
14	16.700000	.53328	.51875	.53410
14	16.800000	.53240	.51771	.53327
14	16.900000	.53152	.51667	.53244
14	17.000000	.53064	.51563	.53161
14	17.100000	.52976	.51459	.53078
14	17.200000	.52888	.51355	.52995
14	17.300000	.52800	.51251	.52912
14	17.400000	.52712	.51147	.52829
14	17.500000	.52624	.51043	.52746
14	17.600000	.52536	.50939	.52663
14	17.700000	.52448	.50835	.52580
14	17.800000	.52360	.50731	.52497
14	17.900000	.52272	.50627	.52414
14	18.000000	.52184	.50523	.52331
14	18.100000	.52096	.50419	.52248
14	18.200000	.52008	.50315	.52165
14	18.300000	.51920	.50211	.52082
14	18.400000	.51832	.50107	.52000
14	18.500000	.51744	.50003	.51917
14	18.600000	.51656	.49899	.51834
14	18.700000	.51568	.49795	.51751
14	18.800000	.51480	.49691	.51668
14	18.900000	.51392	.49587	.51585
14	19.000000	.51304	.49483	.51502
14	19.100000	.51216	.49379	.51419
14	19.200000	.51128	.49275	.51336
14	19.300000	.51040	.49171	.51253
14	19.400000	.50952	.49067	.51170
14	19.500000	.50864	.48963	.51087
14	19.600000	.50776	.48859	.51004
14	19.700000	.50688	.48755	.50921
14	19.800000	.50600	.48651	.50838
14	19.900000	.50512	.48547	.50755
14	20.000000	.50424	.48443	.50672
14	20.100000	.50336	.48339	.50589
14	20.200000	.50248	.48235	.50506
14	20.300000	.50160	.48131	.50423
14	20.400000	.50072	.48027	.50340
14	20.500000	.50000	.47923	.50257
14	20.600000	.49912	.47819	.50174
14	20.700000	.49824	.47715	.50091
14	20.800000	.49736	.47611	.50008
14	20.900000	.49648	.47507	.49925
14	21.000000	.49560	.47403	.49842
14	21.100000	.49472	.47299	.49759
14	21.200000	.49384	.47195	.49676
14	21.300000	.49296	.47091	.49593
14	21.400000	.49208	.46987	.49510
14	21.500000	.49120	.46883	.49427
14	21.600000	.49032	.46779	.49344
14	21.700000	.48944	.46675	.49261
14	21.800000	.48856	.46571	.49178
14	21.900000	.48768	.46467	.49095
14	22.000000	.48680	.46363	.49012
14	22.100000	.48592	.46259	.48929
14	22.200000	.48504	.46155	.48846
14	22.300000	.48416	.46051	.48763
14	22.400000	.48328	.45947	.48680
14	22.500000	.48240	.45843	.48597
14	22.600000	.48152	.45739	.48514
14	22.700000	.48064	.45635	.48431
14	22.800000	.47976	.45531	.48348
14	22.900000	.47888	.45427	.48265
14	23.000000	.47800	.45323	.48182
14	23.100000	.47712	.45219	.48099
14	23.200000	.47624	.45115	.48016
14	23.300000	.47536	.45011	.47933
14	23.400000	.47448	.44907	.47850
14	23.500000	.47360	.44803	.47767
14	23.600000	.47272	.44699	.47684
14	23.700000	.47184	.44595	.47601
14	23.800000	.47096	.44491	.47518
14	23.900000	.47008	.44387	.47435
14	24.000000	.46920	.44283	.47352
14	24.100000	.46832	.44179	.47269
14	24.200000	.46744	.44075	.47186
14	24.300000	.46656	.43971	.47103
14	24.400000	.46568	.43867	.47020
14	24.500000	.46480	.43763	.46937
14	24.600000	.46392	.43659	.46854
14	24.700000	.46304	.43555	.46771
14	24.800000	.46216	.43451	.46688
14	24.900000	.46128	.43347	.46605
14	25.000000	.46040	.43243	.46522
14	25.100000	.45952	.43139	.46439
14	25.200000	.45864	.43035	.46356
14	25.300000	.45776	.42931	.46273
14	25.400000	.45688	.42827	.46190
14	25.500000	.45600	.42723	.46107
14	25.600000	.45512	.42619	.46024
14	25.700000	.45424	.42515	.45941
14	25.800000	.45336	.42411	.45858
14	25.900000	.45248	.42307	.45775
14	26.000000	.45160	.42203	.45692
14	26.100000	.45072	.42099	.45609
14	26.200000	.44984	.41995	.45526
14	26.300000	.44896	.41891	.45443
14	26.400000	.44808	.41787	.45360
14	26.500000	.44720	.41683	.45277
14	26.600000	.44632	.41579	.45194
14	26.700000	.44544	.41475	.45111
14	26.800000	.44456	.41371	.45028
14	26.900000	.44368	.41267	.44945
14	27.000000	.44280	.41163	.44862
14	27.100000	.44192	.41059	.44779
14	27.200000	.44104	.40955	.44696
14	27.300000	.44016	.40851	.44613
14	27.400000	.43928	.40747	.44530
14	27.500000	.43840	.40643	.44447
14	27.600000	.43752	.40539	.44364
14	27.700000	.43664	.40435	.44281
14	27.800000	.43576	.40331	.44198
14	27.900000	.43488	.40227	.44115
14	28.000000	.43400	.40123	.44032
14	28.100000	.43312	.40019	.43949
14	28.200000	.43224	.39915	.43866
14	28.300000	.43136	.39811	.43783
14	28.400000	.43048	.39707	.43700
14	28.500000	.42960	.39603	.43617
14	28.600000	.42872	.39499	.43534
14	28.700000	.42784	.39395	.43451
14	28.800000	.42696	.39291	.43368
14	28.900000	.42608	.39187	.43285
14	29.000000	.42520	.39083	.43202
14	29.100000	.42432	.38979	.43119
14	29.200000	.42344	.38875	.43036</

(A)	Net	'62'	'0'
14.60000	.41854	.40423	.40011
14.70000	.41707	.40271	.39659
14.80000	.41550	.40119	.39306
14.90000	.40680	.39201	.39472
15.00000	.41151	.39144	.38774
15.10000	.40575	.38907	.38628
15.20000	.40003	.39951	.38278
15.30000	.39700	.38261	.38067
15.40000	.39846	.37627	.37806
15.50000	.39653	.37784	.37424
15.60000	.39035	.37568	.37025
15.70000	.38786	.37209	.36636
15.80000	.38537	.36849	.36247
15.90000	.38288	.36490	.35858
16.00000	.38039	.36130	.35469
16.10000	.37790	.35771	.35079
16.20000	.37541	.35411	.34690
16.30000	.37110	.35422	.34815
16.40000	.36935	.35090	.34894

5) 3.02 molal nickel chloride.

(A)	Nat	'62'	'01'
0.000000	.26028	.24892	.27108
.100000	.26859	.25528	.27580
.200000	.27689	.26164	.28052
.300000	.28133	.27416	.28067
.400000	.29048	.27712	.28881
.500000	.30033	.28391	.29368
.600000	.31726	.29265	.29566
.700000	.33290	.29165	.30806
.800000	.34294	.30204	.31011
.900000	.34199	.30922	.31230
1.000000	.34453	.32487	.32471
1.100000	.34746	.33914	.33775
1.200000	.36227	.36170	.35323
1.300000	.38450	.38450	.37820
1.400000	.41155	.42444	.41574
1.500000	.46496	.47116	.46152
1.600000	.53450	.54614	.53479
1.700000	.61608	.63856	.62605
1.800000	.73689	.77395	.75158
1.900000	.86904	.93158	.89860
2.000000	1.00464	1.08704	1.04694
2.100000	1.18242	1.19705	1.13864
2.200000	1.36688	1.20808	1.14789
2.300000	1.55278	1.13082	1.07427
2.400000	1.73555	1.01016	.96763
2.500000	1.83156	.88635	.85411
2.600000	1.75134	.77627	.75865
2.700000	1.70039	.68437	.68852
2.800000	1.68548	.61779	.63231
2.900000	1.64631	.57301	.60014
3.000000	1.63342	.55473	.58305
3.100000	1.62154	.53271	.56671
3.200000	1.60762	.52820	.55957
3.300000	1.59456	.51463	.55137
3.400000	1.58890	.50504	.55371
3.500000	1.58674	.50699	.55727
3.600000	1.58464	.50827	.55931
3.700000	1.58450	.50973	.56369
3.800000	1.58817	.51000	.56959
3.900000	1.59026	.51000	.57432
4.000000	1.59198	.51072	.57973
4.100000	1.59446	.51048	.58362
4.200000	1.59789	.50941	.58654
4.300000	1.59966	.50709	.58906
4.400000	1.59922	.50618	.59029
4.500000	1.59955	.50463	.59333
4.600000	1.59894	.50336	.59778
4.700000	1.59811	.50276	.59964
4.800000	1.59728	.50201	.59963
4.900000	1.59637	.50170	.59882
5.000000	1.59532	.50158	.59894
5.100000	1.59408	.50122	.59959
5.200000	1.59289	.50082	.59963
5.300000	1.59198	.50044	.59984
5.400000	1.59159	.50011	.59922
5.500000	1.59101	.50038	.59800
5.600000	1.59032	.50042	.59732
5.700000	1.58950	.50020	.59635
5.800000	1.58850	.50006	.59515
5.900000	1.58730	.50000	.59351
6.000000	1.58590	.50000	.59166
6.100000	1.58430	.50000	.58956
6.200000	1.58250	.50000	.58719
6.300000	1.58050	.50000	.58454
6.400000	1.57830	.50000	.58161
6.500000	1.57590	.50000	.57835
6.600000	1.57330	.50000	.57471
6.700000	1.57050	.50000	.57066
6.800000	1.56750	.50000	.56621
6.900000	1.56430	.50000	.56135
7.000000	1.56090	.50000	.55606
7.100000	1.55730	.50000	.55031
7.200000	1.55350	.50000	.54406
7.300000	1.54950	.50000	.53731
7.400000	1.54530	.50000	.53006
7.500000	1.54090	.50000	.52231
7.600000	1.53630	.50000	.51406
7.700000	1.53150	.50000	.50531
7.800000	1.52650	.50000	.49606
7.900000	1.52130	.50000	.48631
8.000000	1.51590	.50000	.47606
8.100000	1.51030	.50000	.46531
8.200000	1.50450	.50000	.45406
8.300000	1.49850	.50000	.44231
8.400000	1.49230	.50000	.43006
8.500000	1.48590	.50000	.41731
8.600000	1.47930	.50000	.40406
8.700000	1.47250	.50000	.39031
8.800000	1.46550	.50000	.37606
8.900000	1.45830	.50000	.36131
9.000000	1.45090	.50000	.34606
9.100000	1.44330	.50000	.33031
9.200000	1.43550	.50000	.31406
9.300000	1.42750	.50000	.29731
9.400000	1.41930	.50000	.28006
9.500000	1.41090	.50000	.26231
9.600000	1.40230	.50000	.24406
9.700000	1.39350	.50000	.22531
9.800000	1.38450	.50000	.20606
9.900000	1.37530	.50000	.18631
10.000000	1.36590	.50000	.16606

5) cont'd

λ (\AA^{-1})	Nat	'62'	'0'
14.60000	.38252	.37431	.37275
14.70000	.37993	.37248	.36995
14.80000	.37734	.36991	.36715
14.90000	.37816	.37310	.36371
15.00000	.37840	.36068	.35534
15.10000	.36990	.35835	.35883
15.20000	.36946	.35392	.35663
15.30000	.36493	.35353	.35383
15.40000	.36114	.34776	.34862
15.50000	.36171	.34640	.34574
15.60000	.35790	.34454	.33610
15.70000	.35533	.33991	.33429
15.80000	.35396	.33529	.33247
15.90000	.35198	.33066	.33066
16.00000	.35001	.32604	.32885
16.10000	.34804	.32141	.32703
16.20000	.34607	.31679	.32522
16.30000	.33326	.31605	.31949
16.40000	.32778	.31562	.31781

6) 1.43 molal nickel chloride.

	(A-1)	Nat	'62'	'0'
0.	00000	.29576	.27265	.29333
.10	00000	.29820	.27649	.29536
.20	00000	.30063	.28034	.29739
.30	00000	.30307	.28419	.29942
.40	00000	.30551	.28804	.30145
.50	00000	.30795	.29189	.30348
.60	00000	.31039	.29574	.30551
.70	00000	.31283	.29959	.30754
.80	00000	.31527	.30344	.30957
.90	00000	.31771	.30729	.31160
1.	00000	.32015	.31114	.31363
1.	10000	.32259	.31499	.31566
1.	20000	.32503	.31884	.31769
1.	30000	.32747	.32269	.31972
1.	40000	.32991	.32654	.32175
1.	50000	.33235	.33039	.32378
1.	60000	.33479	.33424	.32581
1.	70000	.33723	.33809	.32784
1.	80000	.33967	.34194	.32987
1.	90000	.34211	.34579	.33190
2.	00000	.34455	.34964	.33393
2.	10000	.34699	.35349	.33596
2.	20000	.34943	.35734	.33799
2.	30000	.35187	.36119	.34002
2.	40000	.35431	.36504	.34205
2.	50000	.35675	.36889	.34408
2.	60000	.35919	.37274	.34611
2.	70000	.36163	.37659	.34814
2.	80000	.36407	.38044	.35017
2.	90000	.36651	.38429	.35220
3.	00000	.36895	.38814	.35423
3.	10000	.37139	.39199	.35626
3.	20000	.37383	.39584	.35829
3.	30000	.37627	.39969	.36032
3.	40000	.37871	.40354	.36235
3.	50000	.38115	.40739	.36438
3.	60000	.38359	.41124	.36641
3.	70000	.38603	.41509	.36844
3.	80000	.38847	.41894	.37047
3.	90000	.39091	.42279	.37250
4.	00000	.39335	.42664	.37453
4.	10000	.39579	.43049	.37656
4.	20000	.39823	.43434	.37859
4.	30000	.40067	.43819	.38062
4.	40000	.40311	.44204	.38265
4.	50000	.40555	.44589	.38468
4.	60000	.40799	.44974	.38671
4.	70000	.41043	.45359	.38874
4.	80000	.41287	.45744	.39077
4.	90000	.41531	.46129	.39280
5.	00000	.41775	.46514	.39483
5.	10000	.42019	.46899	.39686
5.	20000	.42263	.47284	.39889
5.	30000	.42507	.47669	.40092
5.	40000	.42751	.48054	.40295
5.	50000	.42995	.48439	.40498
5.	60000	.43239	.48824	.40701
5.	70000	.43483	.49209	.40904
5.	80000	.43727	.49594	.41107
5.	90000	.43971	.49979	.41310
6.	00000	.44215	.50364	.41513
6.	10000	.44459	.50749	.41716
6.	20000	.44703	.51134	.41919
6.	30000	.44947	.51519	.42122
6.	40000	.45191	.51904	.42325
6.	50000	.45435	.52289	.42528
6.	60000	.45679	.52674	.42731
6.	70000	.45923	.53059	.42934
6.	80000	.46167	.53444	.43137
6.	90000	.46411	.53829	.43340
7.	00000	.46655	.54214	.43543
7.	10000	.46899	.54599	.43746
7.	20000	.47143	.54984	.43949
7.	30000	.47387	.55369	.44152
7.	40000	.47631	.55754	.44355
7.	50000	.47875	.56139	.44558
7.	60000	.48119	.56524	.44761
7.	70000	.48363	.56909	.44964
7.	80000	.48607	.57294	.45167
7.	90000	.48851	.57679	.45370
7.	00000	.49095	.58064	.45573
7.	10000	.49339	.58449	.45776
7.	20000	.49583	.58834	.45979
7.	30000	.49827	.59219	.46182
7.	40000	.50071	.59604	.46385
7.	50000	.50315	.59989	.46588
7.	60000	.50559	.60374	.46791
7.	70000	.50803	.60759	.46994
7.	80000	.51047	.61144	.47197
7.	90000	.51291	.61529	.47400
7.	00000	.51535	.61914	.47603
7.	10000	.51779	.62299	.47806
7.	20000	.52023	.62684	.48009
7.	30000	.52267	.63069	.48212
7.	40000	.52511	.63454	.48415
7.	50000	.52755	.63839	.48618
7.	60000	.52999	.64224	.48821
7.	70000	.53243	.64609	.49024
7.	80000	.53487	.64994	.49227
7.	90000	.53731	.65379	.49430
7.	00000	.53975	.65764	.49633
7.	10000	.54219	.66149	.49836
7.	20000	.54463	.66534	.50039
7.	30000	.54707	.66919	.50242
7.	40000	.54951	.67304	.50445
7.	50000	.55195	.67689	.50648
7.	60000	.55439	.68074	.50851
7.	70000	.55683	.68459	.51054
7.	80000	.55927	.68844	.51257
7.	90000	.56171	.69229	.51460
7.	00000	.56415	.69614	.51663
7.	10000	.56659	.70000	.51866
7.	20000	.56903	.70385	.52069
7.	30000	.57147	.70770	.52272
7.	40000	.57391	.71155	.52475
7.	50000	.57635	.71540	.52678
7.	60000	.57879	.71925	.52881
7.	70000	.58123	.72310	.53084
7.	80000	.58367	.72695	.53287
7.	90000	.58611	.73080	.53490
7.	00000	.58855	.73465	.53693
7.	10000	.59099	.73850	.53896
7.	20000	.59343	.74235	.54099
7.	30000	.59587	.74620	.54302
7.	40000	.59831	.75005	.54505
7.	50000	.60075	.75390	.54708
7.	60000	.60319	.75775	.54911
7.	70000	.60563	.76160	.55114
7.	80000	.60807	.76545	.55317
7.	90000	.61051	.76930	.55520
7.	00000	.61295	.77315	.55723
7.	10000	.61539	.77700	.55926
7.	20000	.61783	.78085	.56129
7.	30000	.62027	.78470	.56332
7.	40000	.62271	.78855	.56535
7.	50000	.62515	.79240	.56738
7.	60000	.62759	.79625	.56941
7.	70000	.63003	.80010	.57144
7.	80000	.63247	.80395	.57347
7.	90000	.63491	.80780	.57550
7.	00000	.63735	.81165	.57753
7.	10000	.63979	.81550	.57956
7.	20000	.64223	.81935	.58159
7.	30000	.64467	.82320	.58362
7.	40000	.64711	.82705	.58565
7.	50000	.64955	.83090	.58768
7.	60000	.65199	.83475	.58971
7.	70000	.65443	.83860	.59174
7.	80000	.65687	.84245	.59377
7.	90000	.65931	.84630	.59580
7.	00000	.66175	.85015	.59783
7.	10000	.66419	.85400	.59986
7.	20000	.66663	.85785	.60189
7.	30000	.66907	.86170	.60392
7.	40000	.67151	.86555	.60595
7.	50000	.67395	.86940	.60798
7.	60000	.67639	.87325	.61001
7.	70000	.67883	.87710	.61204
7.	80000	.68127	.88095	.61407
7.	90000	.68371	.88480	.61610
7.	00000	.68615	.88865	.61813
7.	10000	.68859	.89250	.62016
7.	20000	.69103	.89635	.62219
7.	30000	.69347	.90020	.62422
7.	40000	.69591	.90405	.62625
7.	50000	.69835	.90790	.62828
7.	60000	.70079	.91175	.63031
7.	70000	.70323	.91560	.63234
7.	80000	.70567	.91945	.63437
7.	90000	.70811	.92330	.63640
7.	00000	.71055	.92715	.63843
7.	10000	.71299	.93100	.64046
7.	20000	.71543	.93485	.64249
7.	30000	.71787	.93870	.64452
7.	40000	.72031	.94255	.64655
7.	50000	.72275	.94640	.64858
7.	60000	.72519	.95025	.65061
7.	70000	.72763	.95410	.65264
7.	80000	.73007	.95795	.65467
7.	90000	.73251	.96180	.65670
7.	00000	.73495	.96565	.65873
7.	10000	.73739	.96950	.66076
7.	20000	.73983	.97335	.66279
7.	30000	.74227	.97720	.66482
7.	40000	.74471	.98105	.66685
7.	50000	.74715	.98490	.66888
7.	60000	.74959	.98875	.67091
7.	70000	.75203	.99260	.67294
7.	80000	.75447	.99645	.67497
7.	90000	.75691	.10000	.67700

6) cont'd

(A-1)	Nat	'52'	'0'
7.300000	.57845	.57263	.57207
7.400000	.57741	.57059	.57221
7.500000	.58699	.57711	.57758
7.600000	.58250	.57346	.57625
7.700000	.58346	.58055	.57506
7.800000	.57751	.57882	.57927
7.900000	.57750	.57319	.58156
8.000000	.53502	.53229	.53066
8.100000	.58421	.58225	.57977
8.200000	.57947	.58593	.57934
8.300000	.58027	.58375	.57339
8.400000	.57342	.57737	.57611
8.500000	.57131	.57224	.57357
8.600000	.56335	.57778	.56070
8.700000	.55841	.56545	.55989
8.800000	.54830	.56026	.55706
8.900000	.54377	.55497	.54705
9.000000	.54347	.55392	.55365
9.100000	.52245	.55345	.55259
9.200000	.51764	.55227	.55200
9.300000	.51500	.55099	.55073
9.400000	.50968	.55046	.55005
9.500000	.50290	.49665	.49753
9.600000	.49999	.48868	.48756
9.700000	.49561	.48729	.48683
9.800000	.48255	.47224	.47004
9.900000	.47078	.46175	.46688
10.000000	.46388	.46022	.45910
10.100000	.45455	.44378	.44436
10.200000	.44940	.44357	.44007
10.300000	.44394	.44319	.42859
10.400000	.42459	.42443	.42541
10.500000	.42738	.41780	.41938
10.600000	.41831	.41371	.41371
10.700000	.41247	.41200	.40642
10.800000	.40466	.40318	.39999
10.900000	.40005	.39997	.39904
11.000000	.39467	.39887	.39546
11.100000	.38909	.39479	.38832
11.200000	.38425	.38848	.38274
11.300000	.38328	.38313	.38447
11.400000	.38581	.38797	.37931
11.500000	.38570	.38356	.37832
11.600000	.37954	.38224	.37486
11.700000	.37649	.37332	.37260
11.800000	.37851	.37764	.37748
11.900000	.37716	.37665	.37006
12.000000	.37570	.37537	.36936
12.100000	.37768	.37287	.37557
12.200000	.37633	.37214	.37282
12.300000	.37855	.37025	.37226
12.400000	.37864	.37226	.36736
12.500000	.38048	.37311	.37107
12.600000	.37749	.36966	.36876
12.700000	.37875	.37184	.36546
12.800000	.37552	.36743	.36898
12.900000	.37623	.36758	.36655
13.000000	.37429	.37120	.36566
13.100000	.38404	.37120	.36349
13.200000	.37613	.37354	.37055
13.300000	.37290	.37548	.36531
13.400000	.37671	.37258	.36912

BIBLIOGRAPHY

- 1) G.H.A. Cole, 'Introduction to Statistical Mechanics of Simple Dense Fluids' Pergamon (1967)
- 2) T.L. Hill, 'Statistical Mechanics: Principles and Selected Applications' McGraw-Hill (1956)
- 3) Te Haar, Wengeland, 'Introduction to Thermodynamics', Addison-Wesley (1968)
- 4) T.E. Faber, J.M. Ziman, Phil. Mag. 11, 153 (1965)
- 5) G. Flaczek, Phys. Rev. 86, 577 (1952)
- 6) L. Van Hove, Phys. Rev. 95, 249 (1954)
- 7) P.G. De Gennes, Physica 25, 825 (1959)
- 8) G.E. Bacon 'Neutron Diffraction' O.U.P. (1968)
- 9) F.A. Egelstaff, 'Introduction to the Liquid State', Academic Press (1967)
- 10) J.E. Enderby, Chapter 14 of 'Physics of Simple Liquids' ed. H.N.V. Temperly, et al., North-Holland, (1968)
- 11) W. Marshall, S.W. Lovesey, 'Theory of Thermal Neutron Scattering' O.U.P. (1971)
- 12) J.G. Powles, Adv. Phys. 22, 1 (1975)
- 13) E. Fermi, Ricerca. Scient., 1, 13 (1936)
- 14) G.E. Bacon, Acta. Cryst. A 28, 7 (1972)
- 15) G.E. Bacon, Acta. Cryst. A 30, 847 (1974)
- 16) Scattering cross-sections are reported in many volumes of ENL - 325 (1958, 1960, 1964, 1966), published by Brookhaven National Laboratory. For absorption cross-sections, see 'Handbook of American Institute of Physics', 3rd edition, McGraw-Hill (1972)
- 17) J.W. Gibbs, Trans. of Connecticut Acad. Sciences., 2, 309, 382 (1873) and 2, 108, 343 (1875-1878)
- 18) F.M. Raoult, Comptes Rendus, 104, 1430 (1887); Z. Physik. Chem. 2, 353 (1888)
- 19) J.H. van't Hoff, Z. Physik. Chem. 1, 481 (1887)
- 20) D. Dreisbach, 'Liquids and Solutions', Houghton Mifflin Co., Boston (1966)
- 21) S. Arrhenius, Z. Physik. Chem. 1, 351 (1887)
- 22) W. Ostwald, Z. Physik. Chem. 2, 270 (1888)

- 23) F.J.W. Debye, E. Huckel, Physik. Z., 24, 185 (1923)
- 24) D.A. McQuarrie, 'Statistical Mechanics', Harper & Row (1976)
- 25) N. Bjerrum, K. danske. vidensk. Selsk., 7 (9) (1926)
- 26) R.A. Robinson, R.H. Stokes, 'Electrolyte Solutions' Butterworth, (1959)
- 27) H.S. Harned, B.B. Owen, 'Physical Chemistry of Electrolyte Solutions', Reinhold, New York, (1958)
- 28) H.L. Friedman, 'Ionic Solution Theory', Interscience, (1962)
- 29) J.C. Rasaiah, J.Sol Chem. 2, 301 (1973)
- 30) H.L. Friedman, C.V. Krishnan, C. Jolicoeur, Ann. N.Y. Acad. Sci. 204, 79 (1973)
- 31) R.W. Gurney, 'Ionic processes in Solution', Dover, New York (1953)
- 32) W.G. Millan, J.E. Mayer, J.Chem. Phys. 13, 276 (1945)
- 33) H.P. Bennetto, J.J. Spitzer, J.Chem.Soc. Farad. Trans. I. 72, 2108 (1976)
- 34) G.C. Ghosh, J.Chem. Soc. 113, 449, 627, 707, 790 (1918)
- 35) H.S. Frank, P.T. Thompson 'Structure of Electrolyte Solutions', W.J. Hamer, Ed., Wiley, New York (1959)
- 36) L.W. Bahe, D. Parker, J. Am. Chem. Soc. 97, 5664 (1975)
- see also L.W. Bahe, J. Phys. Chem. 76, 1062 (1972)
- 37) G.J. Safford, P.S. Leung, 'Techniques of Electrochemistry' ed. E. Yeager, A.J. Salkind, vol II, p173, Wiley (1973)
- 38) A.H. Marten, H.A. Levy, Science 165, 447 (1969)
- 39) D.E. O'Reilly, J. Chem. Phys. 63, 5432 (1975)
- 40) F.H. Stillinger, A. Rahman, J.Chem Phys. 60, 1545 (1974)
- 41) L.Blum, J. Comput. Phys. 7, 592 (1971)
- 42) G.W. Brady, J.T. Krause, J.Chem. Phys. 27, 304 (1957)
- 43) G.W. Brady, J. Chem Phys. 28, 464 (1958)
- 44) G.W. Brady, J. Chem Phys. 29, 1371 (1958)
- 45) M.A. Strauss, Dissertation Abstracts 21, 751 (1960)
- 46) R.F. Kruh, C.L. Standley, Inorg. Chem. 1, 941 (1962)
- 47) I.M. Shapolov, I.V. Radchenko, I.K. Lesovitskaya, Zh. Strukt. Khim. 4, 10 (1963)
- 47a) A.I. Ryss, I.V. Radchenko Zh. Strukt. Khim. 5, 489 (1964)
- 48) A.K. Dorosh, A.F. Skryshevskii, Zh. Strukt. Khim. 5, 911 (1964)

- 49) I.V. Radchenko, A.I. Ryss, Zh. Strukt. Khim. 6, 182 (1965)
- 50) D.L. Wertz, R.M. Lawrence, R.F. Kruh, J. Chem Phys. 43, 2165 (1965)
- 51) R. Namasivayan, J. Annamalai Univ., Pt. B 26, 10 (1965)
- 52) R.M. Lawrence, R.F. Kruh, J. Chem Phys. 47, 4758 (1967)
- 53) A.K. Dorosh, A.F. Skryshevskii, Zh. Strukt. Khim. 8, 348 (1967)
- 54) D.L. Wertz, R.F. Kruh, J. Chem. Phys. 50, 4513 (1969)
- 55) D.S. Terekhova, I.V. Radchenko, Zh. Strukt. Khim. 10, 1102 (1969)
- 56) D.S. Terekhova, A.I. Ryss, I.V. Radchenko, Zh. Strukt. Khim.
10, 923 (1969)
- 57) I.M. Shapolov, I.V. Radchenko, Zh. Strukt. Khim. 10, 921 (1969)
- 58) A.H. Narten, J. Phys. Chem. 74, 765 (1970)
- 59) I.M. Shapovalov, I.V. Radchenko, M.K. Lesovitskaya,
Zh. Strukt. Khim. 13, 140
- 60) J.N. Albright, J. Chem. Phys. 56, 3783 (1972)
- 61) M.Ya. Fishkis, T.E. Soboleva, Zh. Strukt. Khim. 15, 186 (1974)
- 62) A.H. Narten, F. Vaslov, H.A. Levy, J. Chem. Phys. 58, 5017 (1973)
- 63) G. Licheri, G. Piccaluga, G. Pinna, J. Appl. Cryst. 6, 392 (1973)
- 64) D.L. Wertz, J.R. Bell, J. Inorg. Nucl. Chem. 35, 137 (1973)
35, 861 (1973)
- 65) J.R. Bell, J.L. Tyvoll, D.L. Wertz, J. Am. Chem. Soc.
95, 1456 (1973)
- 66) M.Ya. Fishkis, V.A. Zhmak, Zh. Strukt. Khim. 15, 3 (1974)
- 67) A. Cristini, G. Licheri, G. Piccaluga, G. Pinna, Chem. Phys. Lett.
24, 289 (1974)
- 68) M. Alves Marques, M.I. De Barros Marques, Proc. Koninklijke
Nethlandze Akademy Wetenschappen, series B 77, 286 (1974)
- 69) V.H. Bertagnolli, J.U. Weidner, H.W. Zimmermann. Ber. Dunsen.
Gesel. 78, 1 (1974)
- 70) R. Eriolo, A.H. Narten, J. Chem. Phys. 63, 3624 (1975)
- 71) G. Licheri, G. Piccaluga, G. Pinna, Chem. Phys. Lett. 35, 119 (1975)
- 72) ditto J. Chem. Phys. 63, 4412 (1975)
- 73) ditto J. Chem. Phys. 64, 2437 (1976)
- 74) G.W. Neilson, J.E. Enderby, R.A. Howe, Chem. Phys. Lett.
33, 284 (1975)

- 75) J. Beck, Phys. Z. 40, 474 (1939)
- 76) G. Hertz, R. Tutsch, N.S. Bowman, J. Phys. Chem. 80(4) (1976)
- 77) D.L. Wertz, R.F. Kruh, J. Chem. Phys. 50, 4013 (1969)
- 78) A.M. Golub, V.I. Golovorushkin, A.K. Dorosh, A.F. Skryshevskii, V.Ya Proshko, Zh. Strukt. Khim. 15, 14 (1974)
- 79) ditto Zh. Strukt. Khim. 14, 973 (1973)
- 80) J.E. Enderby, Proc. R. Soc. London A345, 107 (1975)
- 81) G.J. Safford, P.S. Leung, A.W. Naumann, P.C. Schaffer, J. Chem Phys. 50, 4444 (1969)
- 82) K. Heinzinger, P.C. Vogel, Z. Naturforsch 29a, 1164 (1974)
- 83) P.C. Vogel, K. Heinzinger, Ibid 30a, 789 (1975)
- 84) K. Heinzinger, P.C. Vogel, Ibid 31a, 463 (1976)
- 85) P.C. Vogel, K. Heinzinger, Ibid 31a, 476 (1976)
- 86) H. Kistenmacher, H. Popkie, E. Clementi, J. Chem. Phys. 61, 799 (1974)
- 87) J. Fromm, E. Clementi, R.O. Watts, J. Chem. Phys. 62, 1388 (1975)
- 88) R.O. Watts, Mol. Phys. 32, 659 (1976)
- 89) C.L. Briant, J.J. Burton, J. Chem. Phys. 64, 2888 (1976)
- 90) M.R. Mruzik, F.F. Abraham, D.E. Schreiber, G.M. Pound, J. Chem. Phys. 64, 481 (1976)
- 91) A. Rahman, CECAM Report of Workshop on Ionic Liquids, p263 (1974)
- 92) D.E. Irish, 'Ionic Interactions' ed. S. Petrucci, vol II, p187 (1971)
- 93) D.W. James, R.F. Armishaw, Aust. J. Chem. 28, 1179 (1975)
- 94) H.H. Paalman, C.J. Pings, J. Appl. Phys. 33, 2635 (1962)
- 95) I.A. Blech, B.L. Averbach, Phys. Rev. 137A, 1113 (1965)
- 96) F.G. Edwards, J.E. Enderby, R.A. Howe, D.I. Page, J. Phys. C 8, 3483 (1975)
- 97) F. Franks, 'Water: a Comprehensive Treatise', Vol. 1, Plenum, New York, (1973)
- 98) R. Kaplow, S.L. Strong, B.L. Averbach, 'Local Atomic Arrangements studied by X-ray Diffraction', Chap. 5, Gordon & Breach (1966)
- 99) ditto Phys. Rev. 138, 1386 (1965)

- 100) J. Frenkel 'Kinetic Theory of Liquids' Dover (1955)
- 101) J.L. Yarnell, M.J. Katz, R.G. Wenzel, S.H. Koenig,
Phys. Rev. A7 , 2130 (1973)
- 102) A.J. Greenfield, J. Wellendorf, Phys. Rev. A4 , 1607 (1971)
- 103) D.M. North, J.E. Enderby, P.A. Egelstaff, J. Phys. C. Ser 2,
2 , 1075 (1968)
- 104) V.T. Nguyen, private communication.
- 105) R.W.G. Wyckoff 'Crystal Structures' Wiley-Interscience (1963)
- 106) V.T. Nguyen, private communication.
- 107) I. Hawker, Ph.D. Thesis, Leicester University (1974)
- 108) J. Mizuno, J. Phys. Soc. Japan 16, 1574 (1961)
- 109) N.P. Quirke, A.K. Soper, J. Phys. C, to be published.
- 110) R.J. Baxter, J. Chem. Phys. 52 , 4559 (1970)
- 111) J.W. Ferram, Mol. Phys. 30 , 1505 (1975)
- 112) G.J. Throop, R.J. Bearman, J. Chem Phys. 42 , 2408 (1965)
- 113) L.D. Landau, E.M. Lifshitz, 'Statistical Physics', London,
Pergamon, (1959)
- 114) O.Ya Samoilov, Disc. Farad Soc. 24 , 141 (1957)
- 115) G. Stell, S.F. Sun, J. Chem Phys. 63 , 5333 (1975)
- 116) F. Lantelme, P. Turq, H.L. Friedman, CECAM Report of workshop
on Ionic Liquids, p208 (1974)
- 117) J.W. Cooley, J.W. Tukey, Math. Comput. 19, 297 (1965)
- 118) G.K. Wertheim, J. Electron Spectroscopy and Related Phenomena
6 , 239 (1975)
- 119) J.L. Beeby, J. Phys. C 6 , 2262 (1973)
- 120) N.P. Crowther, P. Dunlop, J. Chem. Thermodynamics, 4 , 255 (1972)
- 121) R.A. Robinson, J. Chem. Thermodynamics 5 , 819 (1973)

ABSTRACT

In the introductory chapters, some of the theoretical and experimental evidence for the structure of aqueous solutions is reviewed. A neutron diffraction experiment is described, which employs isotopic substitution, from which information concerning the hydration of ions in solution, and their distribution, can be obtained. The results for sodium chloride solutions, with chlorine isotopes, at concentrations of 5.32, 2.99, and 1.49 molal, and the accompanying data analysis are presented in detail, whilst data from nickel chloride solutions, with nickel isotopes, are presented in outline.

Both chlorine and nickel ions are strongly hydrated, but for the chlorine ion the binding may be weak: the hydration appears as marked orientation of water molecules towards the ion. With the accepted orientation of water molecules around the chlorine ion, the optimum coordination number for a model of the hydration sphere is 5.5 ± 0.1 at 5.32 molal, increasing to 6.0 ± 0.2 at lower concentrations - at 1.49 molal a second hydration sphere is suggested by the data. The nickel hydration sphere is more tightly bound, with a hydration number of 5.8 ± 0.1 which remains essentially constant with dilution.

The ionic distributions are discussed in terms of lattice and hard-sphere models. The chlorine distribution in sodium chloride is apparently structureless, whilst the distribution of nickel ions in nickel chloride has a much more ordered character, but the models give only a qualitative representation of the nickel structure function.