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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

12 April - 18 June 1982

NEUTRON AND X-RAY DIFFRACTION STUDIES

(Transparencies)

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Multicomponent liquids and amorphous solids

- these are more common than pure liquids, often technically of interest

- examples include: glasses, liquid and amorphous semiconductors, water, molten salt, ionic solutions, organic liquids ....

- often, pair-wise potentials not sufficient.

$$A(k) = A_1 \sum_{j=1}^{N_1} e^{i\underline{k}\cdot\underline{r}_{1j}} + A_2 \sum_{k=1}^{N_2} e^{i\underline{k}\cdot\underline{r}_{2k}} + \cdots$$

$$N_1 + N_2 + \cdots = N$$

For X-rays $A_i = f(k)$

Neutrons $A_i = f \equiv$ constant

$$c_1 = \frac{N_1}{N_1 + N_2 + \cdots}$$

$$I = \langle A A^* \rangle \qquad \frac{\underline{I}}{Nf^2} = \underline{\underline{S}}(k)$$

$$= c_1 f_1^2 + c_2 f_2^2 + \cdots + F(k)$$

$$F(k) = c_1^2 f_1^2 S_{11} + c_2^2 f_2^2 S_{22} + \cdots + 2 c_1 c_2 \underbrace{f_1 f_2}_{k} S_{12} + \cdots$$

$$S_{11} = 1 + \frac{4\pi\rho}{k} \int (g_{11} - 1) r \sin kr \, dr$$

$$S_{22} = 1 + \frac{4\pi\rho}{k} \int (g_{22} - 1) r \sin kr \, dr$$

$$\vdots \qquad\qquad \vdots$$

$$S_{\alpha\beta} = 1 + \frac{4\pi\rho}{k} \int (g_{\alpha\beta} - 1) r \sin kr \, dr$$

$\{S\}$ = Faber-Ziman structure factors

For Neutrons

$I(\theta) \Rightarrow F(k) = \sum' FT(g_{ij}) f_i f_j$

For X-rays

$I(\theta) \Rightarrow F(k) = \sum FT(S_{ij})$ combined with $f_i f_j(k)$

This is the central problem

Note for → 2 chemical species ≡ 3 S_{ij}
glasses
Metals Salts → 3 .. - ≡ 6
main → 4 .. - ≡ 10
Sub structure → 5
ionic solutions

$\frac{n(n+1)}{2}$

Two types of experimental solutions have been suggested

A/ Change f_i, without changing anything else

B/ EXAFS (Sayers et al 1971)

Method A

1. Neutron Diffraction with isotopes (Enderby, North & Egelstaff, 1966)

2. X-ray, neutron & electron (Masumoto et al 1978)

3. Anomalous X-ray scattering (Waseda, Masumoto and Tanaka 1977)

Two component Case

Matrix form (Edwards, Enderby, Howe + Page 1975)

$$[A][X(k)] = [F(k)]$$

$$[A] = \begin{bmatrix} c_a^2 f_a^2 & c_b^2 f_b^2 & 2c_a c_b f_a f_b \\ c_a^2 (f_a')^2 & c_b^2 f_b'^2 & 2c_a c_b (f_a' f_b) \\ c_a (f_a'')^2 & c_b^2 f_b'^2 & 2c_a c_b (f_a'' f_b) \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

$$[X] = \begin{bmatrix} S_{aa} - 1 \\ S_{bb} - 1 \\ S_{ab} - 1 \end{bmatrix} = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix}$$

$$[F] = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix} \equiv \text{measures}$$

Formal Solution

$$[X] = [A]^{-1}[F]$$

Unique if $|A| \neq 0$

But errors in $[F]$, we must test the condition of the equation

Edwards et al consider

$$|A_n|,$$

i.e. a 'normalised determinant':

divide each row by

$$\left[\sum_{j=1}^{3} a_{ij}^2 \right]^{1/2}$$

$|A_n| \sim 1$, very well conditioned ~ direct solution possible. In practice $|A_n| \sim 0.05$!! for method A1 + much less for A2 + A3 ($\sim 10^{-4}$ or less!!)

However, we know some properties of $S_{\alpha\beta}$

1. $S_{\alpha\beta}(k) \to 1$ for $k \to \infty$
2. $S_{\alpha\beta}(0) = n k_B T \chi_T +$ mixing term $(\partial^2 G / \partial c^2)$
3. $\int (S_{11}-1) k^2 dk = \int (S_{22}-1) k^2 dk = \int (S_{12}-1) k^2 dk = -2\pi^2 \rho$

4. $C_a + C_a^2 (S_{aa}-1) > 0$

   $C_b + C_b^2 (S_{bb}-1) > 0$

5. $C_b + C_b^2 (S_{bb}-1) - \dfrac{C_a^2 C_b^2 (S_{ab}-1)^2}{C_a + C_a^2 (S_{aa}-1)} > 0$

Algorithm $\times \begin{bmatrix} S_{11}-1 \\ S_{22}-1 \end{bmatrix}$

1. Solve $[x] = [A]^{-1}[f]$
   ↑ error in $F(k)$

   Allow $[f]$ to vary subject to the condition that new components of $X \pm x$ violate the condition 4 + 5

2. Find a smooth S_{aa} which satisfies 3, 2 + 1

3. Now solve for S_{bb} and S_{ab}

[$|A_n| \sim 0.4$ if $f_a + f_a''$ are used]

4. Test S_{ab} for 1, 2, 3. If O.K find S_{bb}

1. Test S_{bb}. If satisfactory, reconstruct F_a $F_2 + F_3$; otherwise return to step 2.

In practice, two iterations have been found to be sufficient.

Current work at Bristol aims to find the minimum value of $|A_n|$. Our estimate is ~ 0.003, but more work needed.

Other tests (Turing Nº) have been proposed

to the *radial distribution functions* for one atom type with respect to another atom type $g_{\alpha\beta}$ by

$$S_{\alpha\beta} = 1 + \frac{4\pi N}{VQ}\int (g_{\alpha\beta} - 1) r \sin Qr\, dr$$

where $\alpha, \beta = a$ or b.

It is now accepted that the aim of structural analyses on two-component systems should be to extract $S_{\alpha\beta}$ rather than $F(Q)$. This can be done by varying the scattering lengths of one or both components in such a way as to provide three total structure factors F_1, F_2 and F_3 which are sufficiently different to enable three linear equations to be solved for S_{aa}, S_{bb} and S_{ab}. In these experiments, the variation in f was achieved by isotopic substitution of the chlorine. In table 1 we show the isotopes used in this work, together with the degrees of enrichment and the relevant scattering lengths.

Table 1.

Isotope	Enrichment	Coherent scattering length ($\times 10^{-12}$ cm)
^{35}Cl	99·3%	1·18
^{37}Cl	90·4%	0·349
Cl (mixture)	(37) 41 %–(35) 59%	0·799
Na	(natural)	0·351

The total structure factors $F(Q)$ (figure 1) were determined by the methods described by North *et al* (1968), and a summary of the experimental conditions is given in table 2.

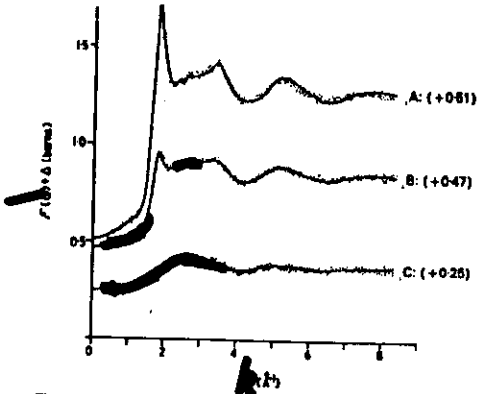


Figure 1. $F(Q)$ data for liquid $Na^{35}Cl$ (curve A), NaCl (curve B) and $Na^{37}Cl$ (curve C) at 875°C. The points are experimental and the curves are derived from the structure factors shown in figure 4. ($A = c_a f_a^2 + c_b f_b^2$).

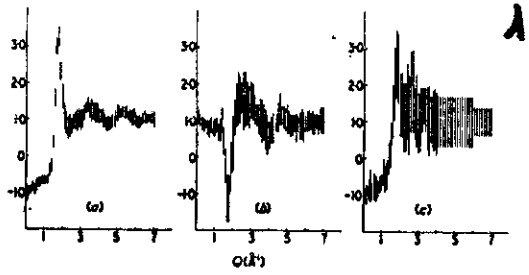


Figure 3. Partial structure factors relating to (*a*) Cl–Cl, (*b*) Na–Cl and (*c*) Na–Na derived from the direct solution of equation (1); the error band reflects the uncertainties in the experimental data shown in figure 1.

in S_{ab} is only $\pm 0{\cdot}2$. We can therefore test whether an S_{ab} can be found which satisfies, as it must, the same sum rule as S_{aa}.

(iii) If it does, S_{bb} is evaluated immediately. If it does not, S_{ab} is adjusted and the process started again at step (ii).

The final S_{aa}, S_{ab} and S_{bb} are shown in figure 4. We have demonstrated numerically that our procedure leads to a unique solution within the error bands given. These errors represent the variation allowed in any one of the partial structure factors as the other two are held constant.

Numerical inversion of the broken curves through S_{ab} to yield the two-body radial distribution functions shown in figure 5 was carried out by standard procedures (North

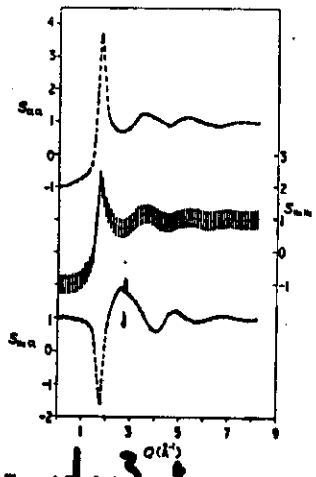


Figure 4. The final partial structure factors for liquid NaCl. The meaning of the error bars is explained in the text.

et al (1968). We have checked that the S_{ab} shown generate the original data within experimental error (figure 1).

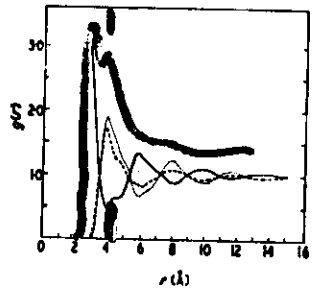


Figure 5. The radial distribution functions for molten NaCl: ——— g_{NaNa}; ····· g_{ClCl}; —— g_{NaCl}.

4. Discussion

The experimental work reported here enables some definite conclusions to be drawn

A1 Neutron Diffraction + Isotopes

- good where suitable isotopes exist
- techniques now well established
- has been applied to liquid alloys, molten salts, liquid semiconductors, solutions, [metallic glasses]
- future application planned for biological systems, organic liquids, glasses ....

Examples of f (10^{-12} cm)

H	−0.372	^{56}Fe	1.01
D	0.670	^{57}Fe	0.23
^{6}Li	0.18	^{58}Ni	1.44
^{7}Li	−0.21	^{62}Ni	−0.87
^{12}C	0.665		
^{13}C	0.600		
^{14}N	0.94		
^{15}N	0.65		
^{35}Cl	1.17		
^{37}Cl	0.308		
^{40}Ca	0.49		
^{44}Ca	0.18		

Newer Ones

S, Ge Se Sr

Te ? } at present under investigation
Hg ? }

- Demanding preparation
- Access to neutrons
- Large initial investment in isotopes (but can be reused)

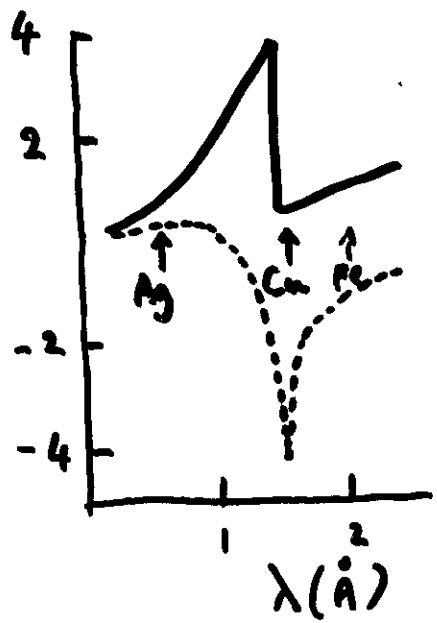
A2 X-ray/Neutron/electron

- |Anl: poor
- practical difficulty
- theoretical problem

A3 Anomalous Scattering (X-rays)

Near an edge, f is of the form

$$f = f^0 + f' + if''$$



Wasada et al applied this technique to Ni P $\langle A A^* \rangle \equiv F(k)$ using laboratory sources.

Difficulties appear to be

- very small determinant. [Not given by Wasada but estimated at $\sim 10^{-4}$]
- For Co K_α, $k_{max} \sim 7\ Å^{-1}$ ∴ matching difficulties

- Fluorescence induced by white rad?
Difficult to resolve in scattered beam by a monochromator

eg $Cu_{K\alpha}$ with Ni alloy

$Ni K\beta$

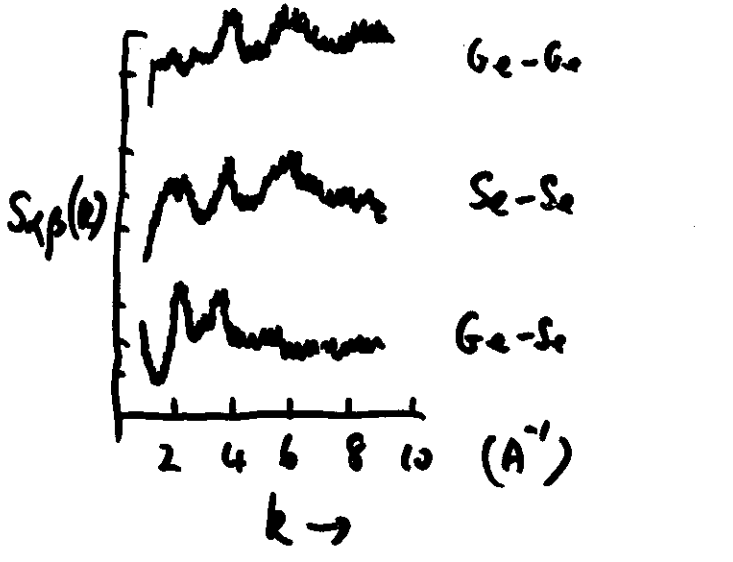
$Mo K\alpha$ with Zr alloy

$Zr K\beta$

With a synchrotron source, technique looks more promising

- tunable : means to edge
- intense : monochromator in incident beam

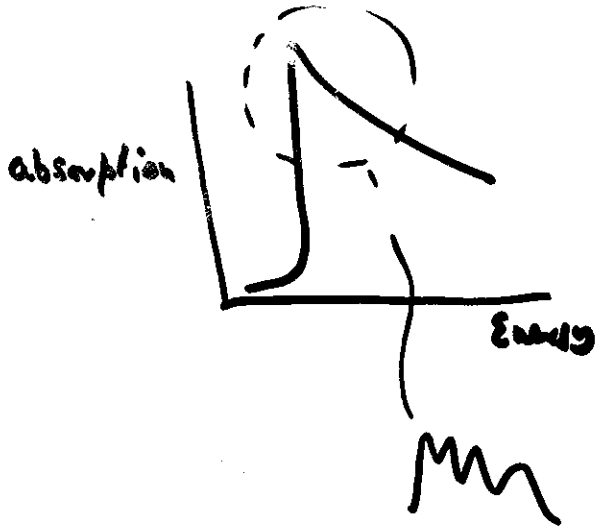
Fuoss, Warburton and Bienenstock (1980) applied technique to GeSe (a)



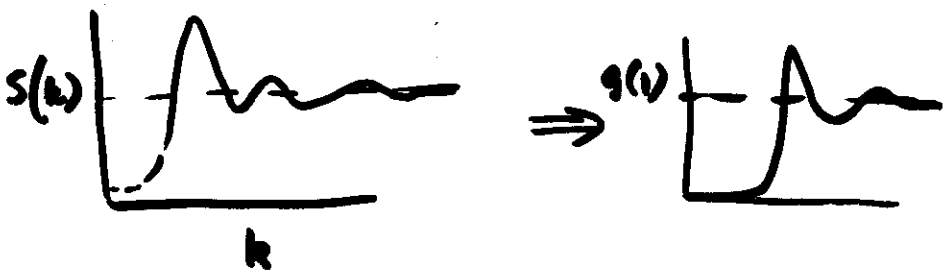
EXAFS

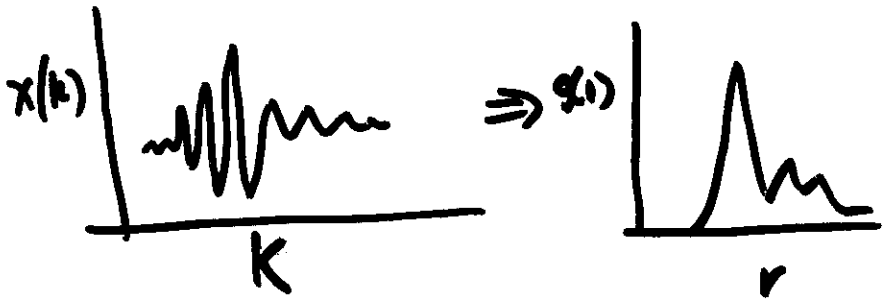
Extended
X-ray
Absorption
Fine Structure

Sayers Stern Lytle 1971



"Text Book"

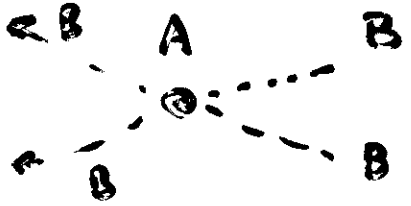




$$\chi(K) = -\frac{1}{K} \sum_J \frac{N_J}{r_J} t_J(2K) \exp(-2r_J/\lambda)$$
$$\times \sin 2(Kr_J + \delta_J) \exp(-2k^2\sigma_J^2)$$

$$K = [2m(E-E_0)/\hbar^2]^{1/2}$$

r_J, N_J distances and coordination numbers of the J-atom from the absorbing atom



λ = m f p of the photoelectron
δ_J = phase shift
σ_J^2 = "Debye Waller" factor

δ_j (no counterpart in X-ray or neutron) obtained empirically $S(k) \to g(r)$ $k \to \delta$

- Several demonstration experiments have now been performed. Consensus view is that method is good for near-neighbour interaction

- On one or two systems, EXAFS results were 'new'. But for molten $ZnCl_2$ r_{ZnCl} was wrong

- much more work required both theoretical and experimental before real value of the method can be assessed.

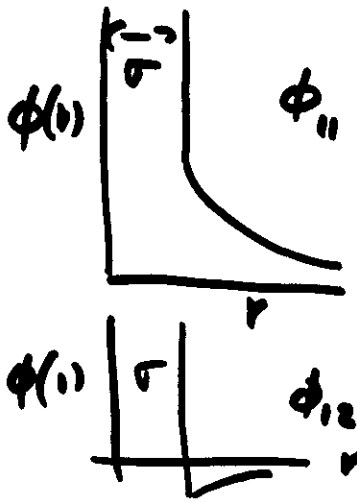
Mean Spherical Approximation

Hard Spheres + Coulomb tail

$$\phi_{ij} = \infty \quad \text{for } 0 \le r \le \sigma$$

$$= \lambda \left(\frac{z_i z_j e^2}{r} \right) \quad r \ge \sigma$$

$z_1 = -z_2 = 1$



EXACT: $g(r) = 0$ for $r \leq \sigma$

$$c(r) = -\frac{\phi}{k_B T} \quad \text{for } r \geq \sigma$$

Combined with

$$h(1) = c(r) + \rho \int h(|\underset{\sim}{r} - \underset{\sim}{r}'|) c(\underset{\sim}{r}') d\underset{\sim}{r}'$$

Allows one to get

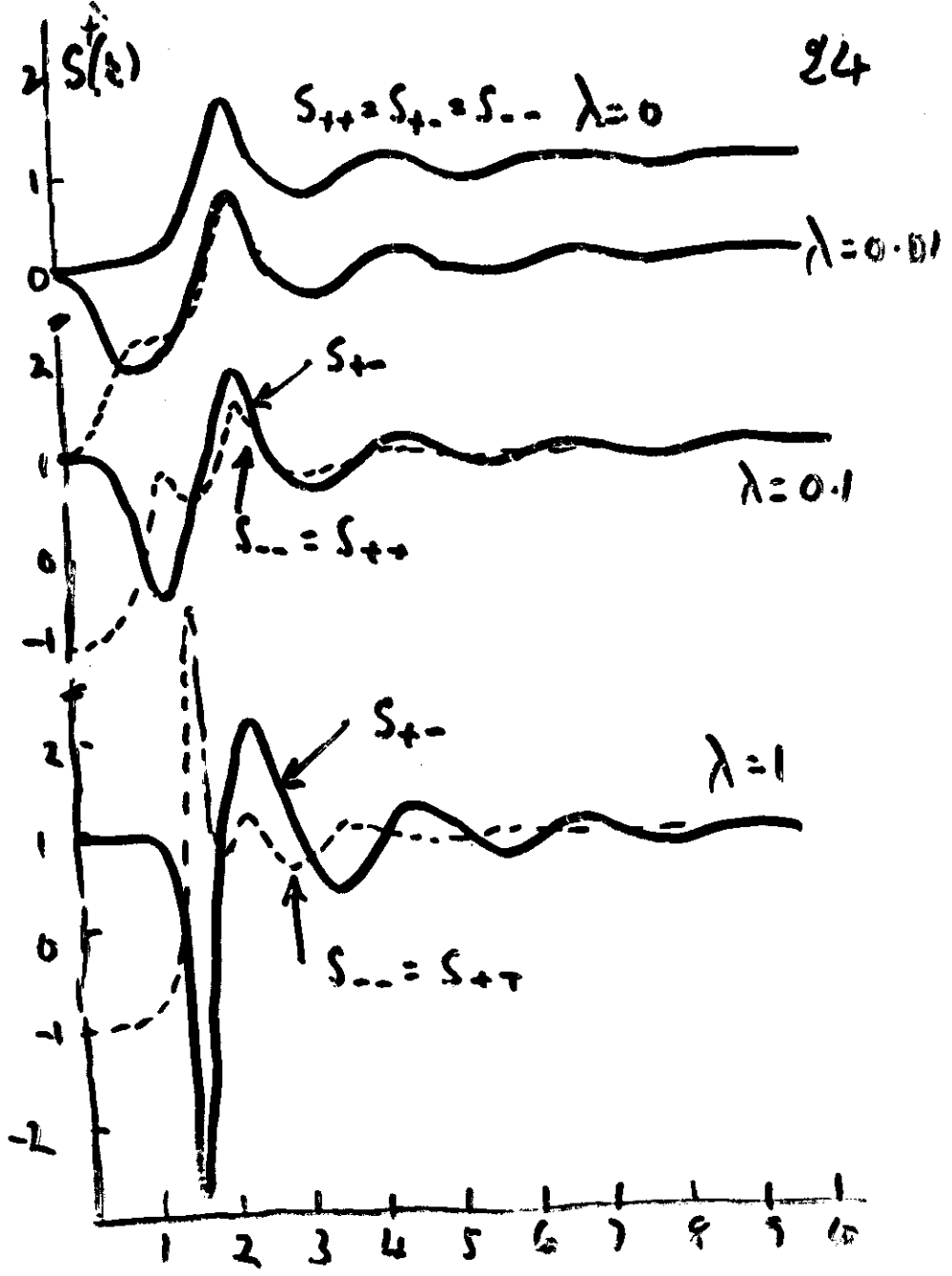
$g_{11}(1) = g_{22}(1)$

& $g_{12}(1)$

$S_{11}(k) = S_{22}(k)$

& $S_{12}(k)$

IN CLOSED FORM

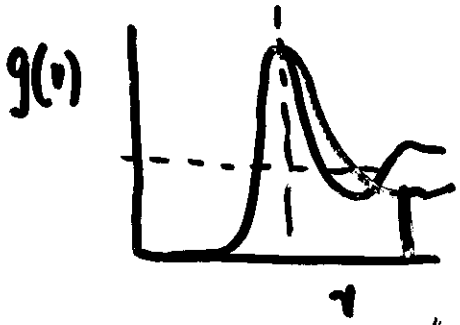


MSA for diff. values of λ

	r_{+-} (Å)	r_{++}	r_{--}	n_{+-} (a)	n_{+-} (b)	n_{++}	n_{--}
NaCl	2·78	3·91	3·96	3·9	5·3	13·0	13·0
KCl	3·1	4·8	(4·9)	–	6·1	16·0	16·0
RbCl	3·2	4·9	4·8	3·8	6·9	13·0	14·0
CsCl	3·4	3·9	3·9	–	6·0	13·0	13·0
CuCl	2·3	3·4	3·8	–	–	–	–
AgCl	2·6	3·2	(3·2)	–	2·7	4·1	2·7
$ZnCl_2$	2·29	3·8	3·71	4·3	4·3	4·7	8·6
$CaCl_2$	2·78	3·6	3·73	5·3	5·4	4·2	7·8
$SrCl_2$	2·94	5·0	3·8	5·1	6·8	6·8	9·3
$BaCl_2$	3·10	4·9	3·86	6·4	7·7	14·0	7·0

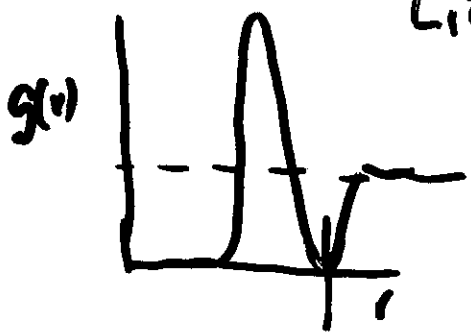
Coordination Number

- no statistical mechanical significance
- useful if well-defined local chemical effects are present
- required for approximate theories for thermodynamics



No stray local conformation

Liquid



Clear local conformation

Four methods to find $\bar{n}$

$$\bar{n} = 4\pi\rho \int_0^{r_1} g(r)\, r^2\, dr$$

1. $[r\,g(r)]_{sym}$
2. $[r^2 g(r)]_{sym}$
3. β min in $g(r)$
4. min in $r^2 g(r)$

1 ⇒ justified by Coulson and Rushbrooke for solid-like local order

Also:

$$\bar{n}(\text{liquid}) = \bar{n}(\text{solid})\left(\frac{V_s}{V_l}\right)\left(\frac{\bar{r}(\text{solid})}{\bar{r}(\text{liquid})}\right)^{-3}$$

		$[r\,g(r)]_{sym}$	$[r^2 g(r)]_{sym}$	min in $g(r)$
NaCl	$g_{+-}(r)$	3.9	4.0	5.3
(0.95 Å)	$G_{total}(r)$	4.0	4.1	4.5
$BaCl_2$	$g_{+-}(r)$	6.4	6.3	7.0
(1.35 Å)	$G_{total}(r)$	15	16	26

	Cationic radius (Å)	$\left(\bar{n}_{+-}(r)\right)_{sym}$	$\bar{n}$ (formula)
$ZnCl_2$	0.74	4.3	3.5
NaCl	0.95	3.9	4.0
$CaCl_2$	0.99	5.3	5.8
$SrCl_2$	1.12	(5.1)	6.5
KCl	1.33	4.1	4.1
$BaCl_2$	1.35	6.4	7.5
RbCl	1.47	3.5	3.8

SUMMARY

Molten Salts - Use of X-rays for structure

- penetration of first coordination sphere by LIKE ions increases as cation size increases

- X-rays (total) measure a (convoluted) average of all three partial structure factors

- $\int_{K}^{+-} \; --\; ++$

- X-rays reliable for SMALL cations for $\bar{r}$ and $\bar{n}$ provided latter is calculated by the $[r\,g(r)]_{sym}$ method

- Small cations include

Li^+ Na^+ Mg^{2+} Zn^{2+} $\underbrace{Ni^{2+}\ Mn^{2+}}$

d-band effects!

- if no other method available, use

$$\bar{n}(\text{liquid}) = \bar{n}(\text{solid})\left(\frac{V_s}{V_l}\right)\left(\frac{\bar{r}(\text{liq})}{\bar{r}(\text{solid})}\right)^3$$

as a good estimate of $\bar{n}$ for quasi-chemical treatment of molten salts

- large cations, partial structure factors essential
- chemical effects, particularly for d-band materials also need care.

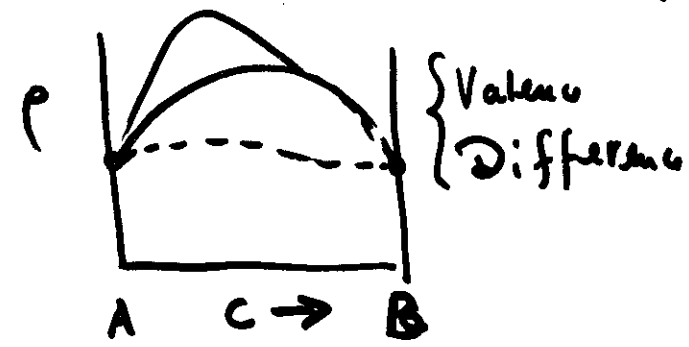
Electrical Properties of Liquids

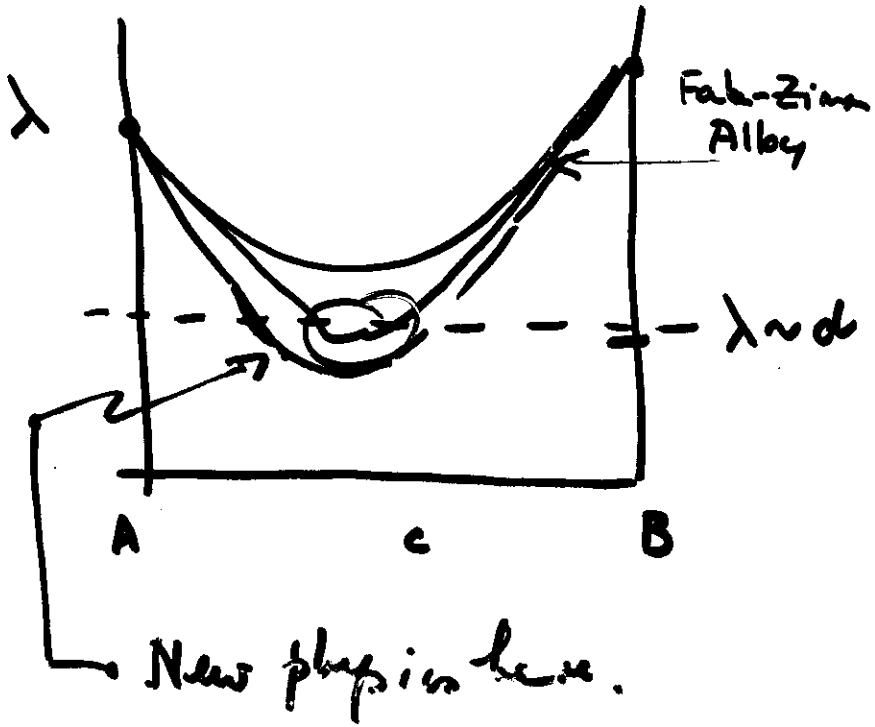
$\rho \propto \langle \delta U^2 \rangle$ — in fact

provided $\lambda > d$ (The Ziman limit)

For alloys:

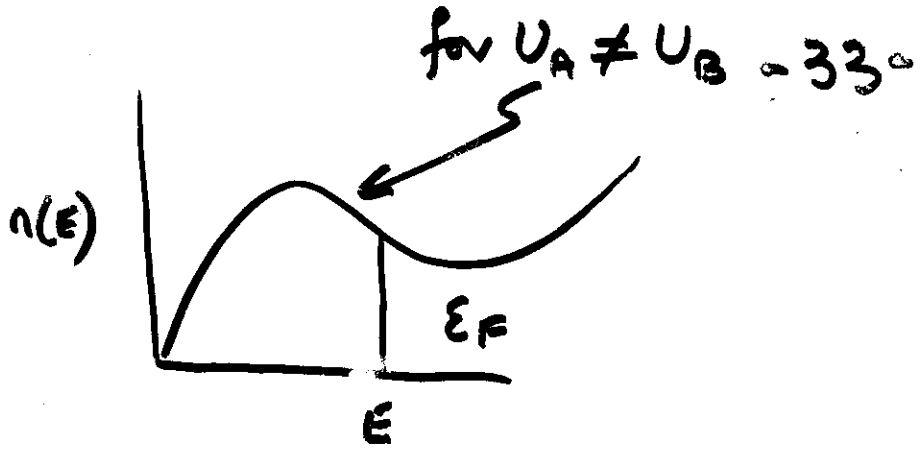
$\rho \propto c_1 U_1^2 + c_2 U_2^2 - \langle \delta_{ep} U_{ep}^2 \rangle$





——— ρ not depended on $n(E_F)$

——— ρ depends on $n(E_F)$?



Thus
if U_A very different from U_B
- structure introduced into $n(E_F)$
- λ made shorter & may approach Ziman limit.
- charge transfer favoured

$\bar{n}$ $\quad$ $\bar{r}$ (Å)

	M-M	M-Te	Te-Te	M-M	Te-M	Te-Te
N_6Te	2·9 ±0·4	4·5 ± 0·5	14 ± 3	2·54* ±0·03	? ± ?	?
N_6Te_2	1·6 ±0·4	4·6 ±0·3	11 ± 3	2·91 ± ?	? ± ?	?
$CuTe$	3·6 ±0·4	2·9 ±0·3	10 ± 3	2·92[b] ± ?	? ± ?	?

* solid 2.68 Å

[b] solid 2.63 Å

Distances etc for liquid Tl_2Te

$\overline{r}$

$r_{TeTe}^{(1)}$ (Tl_2Te and Te_2) $r_{TlTl}^{(1)}$

9.6 ± 0.2 (a)

3.41 ± 0.02 11.0 ± 0.2 (b) 4.24 ± 0.03

F-Space structure of Tl_2Te

- $\overline{F}$ for $g_{TeTe}^{(r)}$ should be [illegible]

smaller than $\overline{F}_{Te^+}$ and $\overline{F}_{Te^{2-}}$

~ 3.5 Å cf 3.41 obs

- $\overline{F}_{TeTe} / \overline{F}_{TlTl}$ should

correspond to [illegible]

for $Bi_2(Te_3)$

Tl_2Te	$Bi_2(Te_3)$
0.82	0.79

Calculate fractional charge (in %)
ionic bonds [illegible] anions
and cations

Schulte et al (J.R II, 3808 (1975))

PbS_x		$PbTe_x$	
Pb	S	Pb	Te
21	79	25	75
20	80	20	80
$\Delta\chi = 0.8$		$\Delta\chi = 0.5$	

$\Delta\chi$ for Thin = 0.6

Simple ionic model

Ionic Solutions

- physics
- chemistry
- biology
- electrochemistry
- crystal growth

MX_n in H_2O

Cations (valence) — Anions

eg LiCl in H_2O
NiCl$_2$ in H_2O
etc

Key Questions are

- how does the water structure around $M^{(n)+}$? } HYDRATION
- around X^- ?
- how do $M^{(n)+}$ ions affect around $M^{(n)+}$? } ION-ION
- around X^- ?
- X^- around X^- ?
- how is the bulk structure modified ?
- how does the static structure alone evolve with time

There are ten structure factors and ten rdf's

- M-O
- M-H
- X-O
- X-H

} hydration

- M-M
- X-X
- M-X

} ion-ion

O-O, H-H, C-H

WATER

Scattering, when corrected ... to

$$\langle A(r)\, ?(r) \rangle$$

$$= \sum_{\alpha} \sum_{\beta} c_\alpha c_\beta f_\alpha f_\beta (S_{\alpha\beta}(k) - 1)$$ [illegible]

Sum over not possible ... [16] ...

Suppose, however, that two experiments are carried out on samples identical in all respects except for the isotopic state of α

eg $^{nat}Cl \longrightarrow {}^{37}Cl$

$$(\alpha - \alpha')_{diff} = c_\alpha [f_\alpha - f_{\alpha'}] \sum_{\beta \neq \alpha} c_\beta f_\beta (S_{\alpha\beta} - 1)$$

$$+ c_\alpha^2 [f_\alpha^2 - f_{\alpha'}^2](S_{\alpha\alpha} - 1)$$

i.e. 4 terms

This is known as a **FIRST ORDER DIFFERENCE** (Soper, Neilson, Enderby & Howe 1977)

Advantages

- 4 terms, two of which are very small & in fact only $S_{\alpha O}$ and $S_{\alpha D}$ matter
- **No** contribution from O-O, O-D and D-D
- Placzek corrections eliminated

-eg-

$$^{N}NiCl_2 \longrightarrow {}^{62}NiCl_2$$

$$\Delta G(r) = 0.277\, g_{NiO} + 0.637\, g_{NiD} + 0.089\, g_{NiCl} + 0.005\, g_{NiNi}$$

Time dependent effects

Outer Shell coordination

$$A(k,t) = \sum_i f_i \, e^{-i\vec{k}\cdot\vec{r}_i(t)}$$

$$\langle A(k,t) A^*(k,0) \rangle < \sum_i \sum_{i'} f_i f_{i'} e^{i\vec{k}\cdot[\vec{r}_i(t) - \vec{r}_{i'}(0)]} >$$

The measured quantity is the frequency spectrum

$$\int dt \, e^{i\omega t} \langle \quad \rangle$$

$$= \sum c_\alpha \langle f_\alpha^2 \rangle S_\alpha^s(k,\omega) + \sum_{\alpha\beta} \sum c_\alpha c_\beta \cdots$$

$$\simeq \sum c_\alpha \langle f_\alpha^2 \rangle S_\alpha^s(k,\omega)$$

for solutions, at small k

For $t > 10^{-11}$ sec

(a) $G_H^s(r,t) = (4\pi D_H t)^{-3/2} \exp\left(-r^2/4 D_H t\right)$

(b) $D_H = D_{ion}$ if $\tau_b > 10^{-11}$ sec

(protons follow the ions)

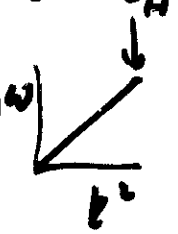
(a) only valid for $t > 10^{-11}$ sec

($\tau_{rot} \sim 8$ ps)

$D_H^2 k^2 \ll 1/\tau_{rot}$ $\therefore$ $k \ll 1 \text{Å}^{-1}$ } IN10

$\delta\mathcal{E}\,\delta t \sim \hbar$ $\quad \delta\mathcal{E} \sim 10^{-4}$ eV

FT of (a) is $\frac{1}{\pi} \frac{D_H k^2}{D_H k^2 + \omega^2}$



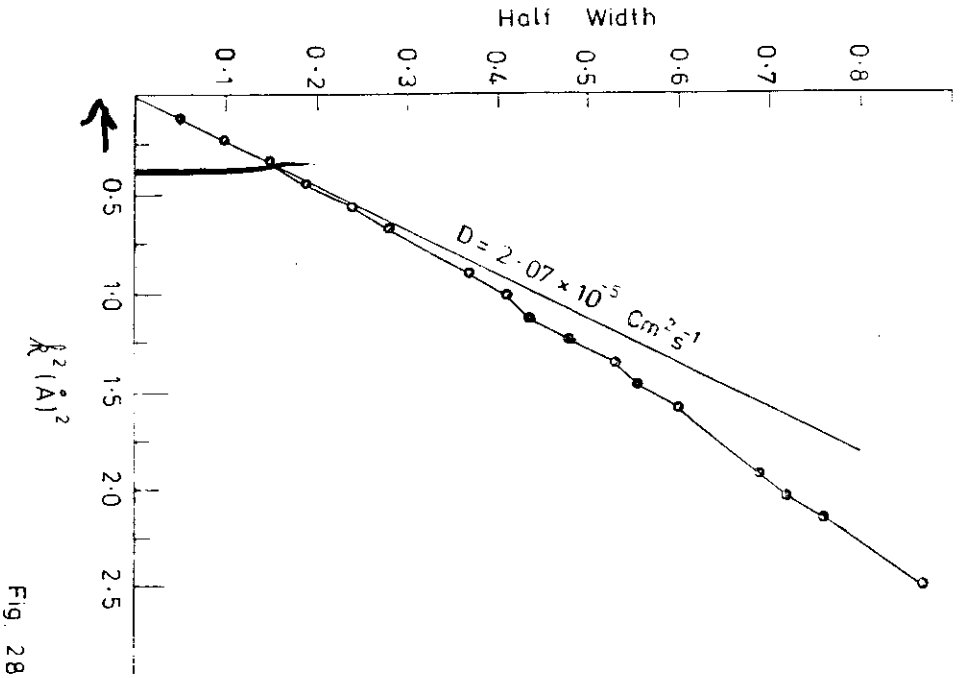


Fig 28

Fast Exchange: $\tau_b < 10^{-10}$ secs

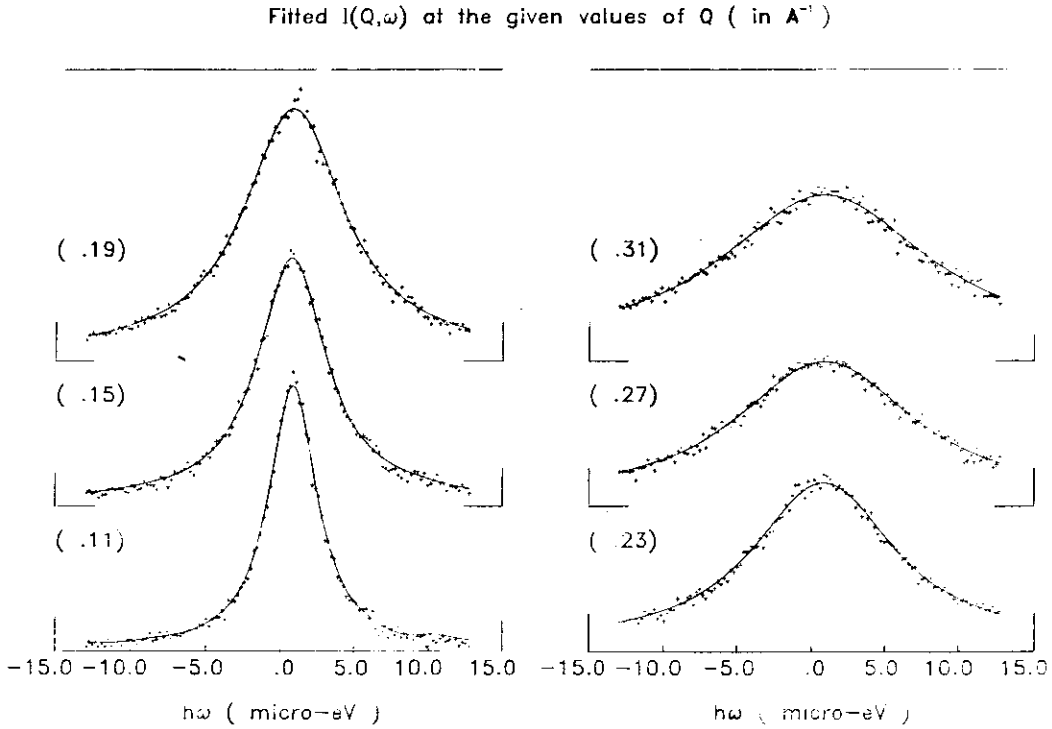


Fig 8.4.3 Single peak fit for 5m LiCl

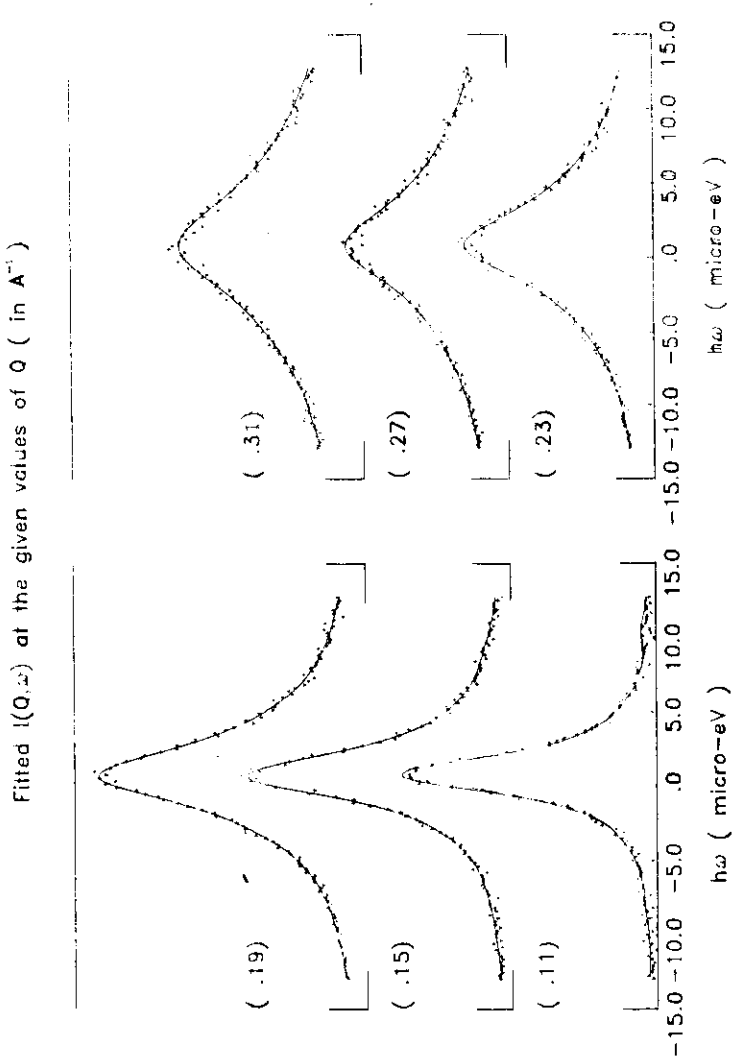


Fig 8.3:2 Two peak fit for 2m NiC.

Hewish Enderby Howells

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right experimental conditions.[3] The incident wavelength was 6.27 Å and the corrections due to multiple scattering need considerable care. However, the sample thickness was ~2 mm or less so that a Monte Carlo method could be used to make the appropriate correction. Several tests were carried out to check that the method was sufficiently accurate for the present purposes, the most stringent of which was a detailed investigation of a 5*m* solution of LiCl [Fig. 1(a)]. This is a complex liquid but is characterized by a proton population which is in the fast-exchange limit. We therefore expect that (i) $S_H^s(k,\omega)$ at each value of k will be a *single* Lorentzian, (ii) the half-width of Lorentzians should be strictly proportional to k^2, and (iii) the value of the mean diffusion coefficient D predicted by these data should agree exactly with that derived from NMR spin-echo techniques. This is because both sets of data refer to the fast-exchange limit. Inspection of Figs. 1(a) and 1(b) shows that (i) and (ii) are indeed satisfied. The slope of half-width versus k^2 yields a value for D of $(1.30 \pm 0.05) \times 10^{-9}$ m^2 sec^{-1} which agrees, within experimental error, with the spin-echo value of $(1.23 \pm 0.05) \times 10^{-9}$ m^2 sec^{-1}.

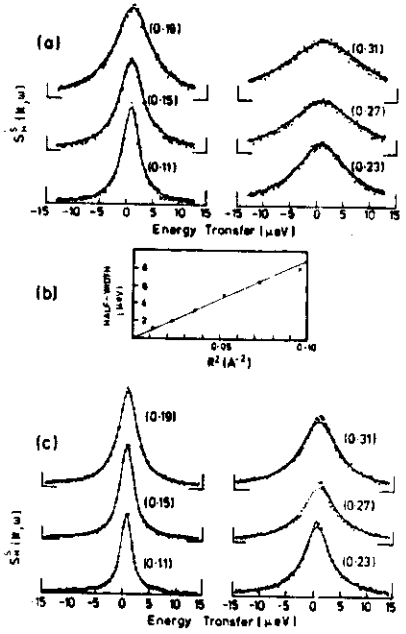

FIG. 1. (a) The neutron spectra for a 5*m* solution of LiCl in H_2O fitted by a single Lorentzian, with k values shown in brackets (in inverse angstroms). (b) The half-width of the Lorentzians in (a) as a function of k^2. The slope corresponds to an effective diffusion coefficient of $(1.30 \pm 0.05) \times 10^{-9}$ m^2 sec^{-1}. (c) An attempt to fit the neutron spectra for a 3*m* solution of $NiCl_2$ in H_2O by a single Lorentzian. The data were treated in exactly the same way as those shown in (a).

Consider now the situation in which i types of water molecule can be distinguished on the time scale of the experiment. For this case, $S_H^s(k,\omega)$ can be written as

$$S_H^s(k,\omega) = \sum (c_i/\pi) D_i k^2 / [(D_i k^2)^2 + \omega^2], \qquad (2)$$

where D_i and c_i are the diffusion coefficients and the atomic fraction, respectively, of the ith type. Specifically, for two types of water,

$$S_H^s(k,\omega) = \frac{1}{\pi}\left[\frac{c_1 D_1 k^2}{(D_1 k^2)^2 + \omega^2} + \frac{c_2 D_2 k^2}{(D_2 k^2)^2 + \omega^2}\right]. \qquad (3)$$

We focus attention on Fig. 1(c), which shows $S_H^s(k,\omega)$ at various k values for 3*m* solution of $NiCl_2$. These data were corrected for multiple scattering *in the same way* as those for the LiCl solutions referred to above. However, in this case a single Lorentzian [Fig. 1(c)] does not reproduce the experimental data (note especially the deviation for $k = 0.31$ Å^{-1}) and this result shows that there are at least two relevant diffusion coefficients (D_1 and D_2). For the first shell of Ni^{2+} we know, from a variety of studies,[4] that the IN10 experiment refers to the "slow-exchange" limit, i.e., the time scale of the measurement (~10^{-9} sec) is much shorter than the binding time of water molecules τ_0 (~10^{-6} sec). Moreover, since for binding times greater than 10^{-11} sec the diffusion coefficients of the ion and the attached water molecules are essentially equal, we can set $D_1 = D_{ion}$, a quantity accessible independently through tracer measurements. Reliable values of D_{ion} as a function of concentration are available for both Ni^{2+} and Mg^{2+} in chloride solution and are shown in Fig. 2. The first-order difference method[5] has shown that for Ni^{2+} there are six water molecules in the first hydration shell.[6] We can therefore calculate, *without adjustable parameters*, the first term in Eq. (3).

Water molecules in the second zone are in the "fast-exchange" limit with bulk water so that the

$\tau_R \geq 10^{-6}$ sec $\tilde{\tau}_m \sim 10^{-10}$ sec

total contribution to the scattering law will be a single Lorentzian characterized by a mean diffusion coefficient D_2, given by

$$D_2 = (c_{sec}D_{sec} + c_0 D_0)/c_2,$$

where D_{sec} and c_{sec} are the diffusion coefficient and the atomic fraction of water molecules in the second zone and D_0 and c_0 are the corresponding quantities for the bulk water molecules. The first-order difference method yields a value of 15 ± 2 water molecules in the second zone[4] so that c_{sec} and c_0 are known, and experiments on pure water yield D_0. Once again, therefore, we can, without adjustable parameters, find D_{sec} by fitting the observed $S_H^S(k,\omega)$ with two Lorentzians [Fig. 3(a)]. The results for D_{sec} are shown in Fig. 2 for the case of $NiCl_2$ solutions. Similar results were obtained for $MgCl_2$ solutions (Fig. 2). We have carried out a number of checks on these data to confirm the basis of our analysis. In Fig. 3(b) we show that two Lorentzians with $D_1 = D_{ion}$ and $D_2 = D_0$ fail to fit the experiment results. This failure to fit with D_1 and D_0 is a *direct* demonstration that there are water molecules, other than those in the first shell, whose dynamical properties are affected by the presence of the cations. In this respect our results contradict those of Sakuma, Hishino, and Fujii[5] which, in our view, were obtained in the wrong region of (k,ω) space.

The value of D_0 [$(2.30 \pm 0.03) \times 10^{-9}$ m^2 sec^{-1}] used for the fits was taken from our own measurements on samples of pure water for a range of thicknesses between 1.3 and 2.4 mm; this value agrees exactly with the accepted value of $(2.30 \pm 0.05) \times 10^{-9}$ m^2 sec^{-1} derived from the work of Mills.[7] This agreement constitutes a further proof that the multiple scattering effects are being properly allowed for. The value of D_{ion} was taken from Mills *et al.*[8] The accuracy of D_{ion} is $\sim \pm \frac{1}{2}\%$ but we have shown [Fig. 3(b)] that even if

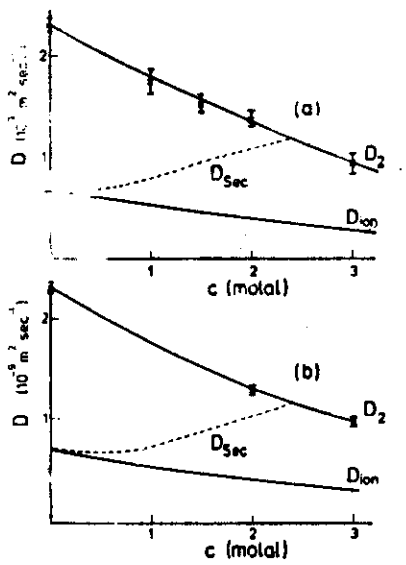

FIG. 2. The cationic diffusion coefficient D_{ion}, together with the fitted values for D_2 and calculated values for D_{sec} for the two solutions studied. (a) $NiCl_2$ solutions. (b) $MgCl_2$ solutions. Data from NMR measurements were used in addition to the neutron results to produce the curve for D_2.

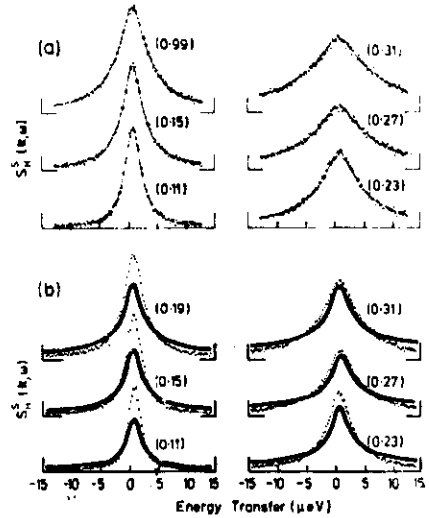

FIG. 3. Attempts to fit a theoretical curve to the neutron spectra for various values of k for $NiCl_2$ solutions. The fitted functions were (a) two Lorentzian peaks, the narrow peak width determined by D_{ion} (concentration: $2m$); (b) two Lorentzian peaks, with both widths fixed to correspond to D_0 and D_{ion} and with six water molecules bound to Ni^{2+}, the rest considered free. A range of D_{ion} values from 0.21 to 0.26×10^{-9} m^2 sec^{-1} were tried and the resulting curves are all contained within the band shown (concentration: $3m$).