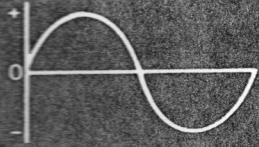


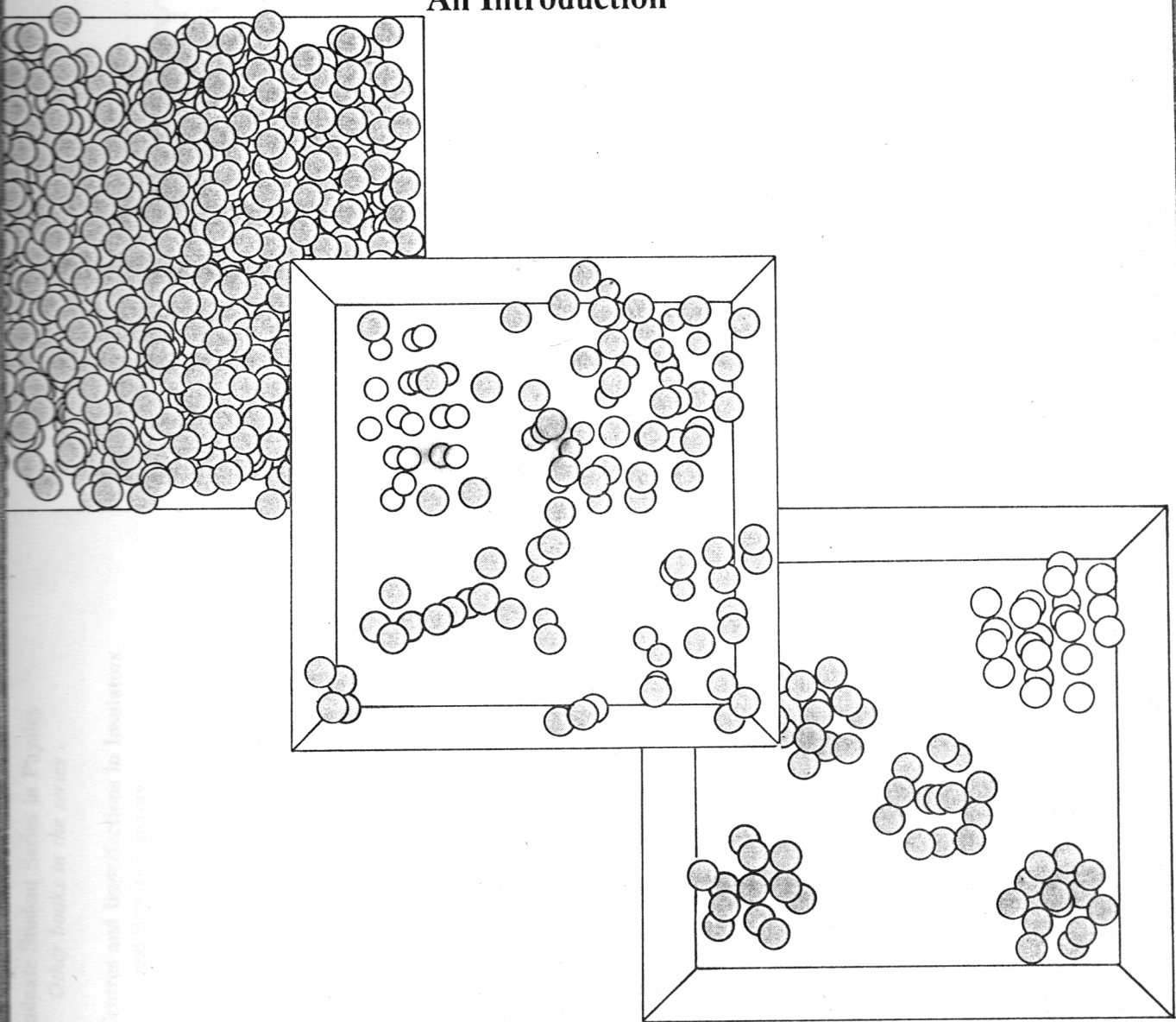
GRADUATE STUDENT SERIES IN PHYSICS



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The Physics of Structurally Disordered Matter

An Introduction



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THE EXPERIMENTAL INVESTIGATION OF DISORDERED STRUCTURES

In order to discover the distribution functions of §2.3 or to test the applicability of the models in §§2.5 and 2.6 the structure of real matter must be studied experimentally. This is almost always done by scattering experiments which are interpreted with diffraction theory. There are many standard works and valuable articles concerning this field (James 1962, Guinier 1963, Waseda 1980, Guinier and Fournet 1955, Lovesey 1984, Pings 1968, Bacon 1975, *International Tables for X-ray Crystallography* 1962, Howe 1978) and this chapter is intended to introduce the main ideas.

3.1 Scattered intensity

Some essential quantities can be defined with the help of figure 3.1. hk_i , hk_f are the momenta of the photons, electrons or neutrons scattered by scattering centres inside the sample. One of these is chosen as the origin O; another is at P, distant R_P from O. We immediately make some assumptions, namely, the scattering is elastic so $|k_i| = |k_f|$; more than one scattering event in the sample is so improbable that only single scattering need be considered. These assumptions by no means always hold but the formulae resulting from them are indispensable starting points. We define as follows the momentum transfer vector, Q , and the connection with the scattering angle, θ :

$$\hbar Q \equiv \hbar(k_i - k_f) \quad |Q| = 2k \sin \frac{1}{2}\theta. \quad (3.1)$$

We assume the incident waves are unpolarised.

If there is an isolated scattering centre at O the scattered wave has the form $(f(\theta)/r) \exp[i(kr - \omega t)]$ where r is the distance in the θ -direction. Waves from P and other scattering centres arrive at the distant detector with different phases because of their various path lengths. The phase difference for waves from O and P is $Q \cdot R_P$, consequently the intensity at the detector is

$$I(Q) = A \left| \sum f_P(Q) \exp(iQ \cdot R_P) \right|^2 \quad (3.2)$$

where the sum is over all the scattering centres such as P, and Q is used as a variable instead of θ ; A is a proportionality constant. The quantity $|f(\theta)|^2$ is a cross section and will depend on the nature of the incoming waves and of the scattering centre; $f(\theta)$ is a *scattering amplitude*.

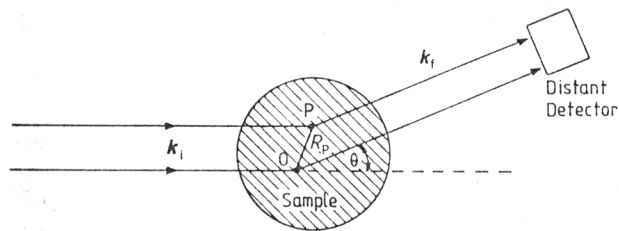


Figure 3.1 Definitions of quantities for the coherent scattering calculation.

3.2 X-rays

X-ray radiation is scattered by electrons and it is conventional to express $I(\mathbf{Q})$ in terms of the intensity scattered by a single electron. A single electron at O would give

$$I_c(\mathbf{Q}) = A |f_c(\mathbf{Q})|^2 \quad (3.3)$$

where $|f_c(\mathbf{Q})|^2$ is the known cross section for an electron.

What, for x-rays, is to be regarded as a 'scattering centre'? Since electron wavefunctions give a continuous distribution of position probability it is reasonable to take a volume element of sample, dr , containing electron charge $en_c(\mathbf{r}) dr$, as the scattering centre and replace the sum in equation (3.2) by an integral over the sample. The scattering from dr then has amplitude proportional to $f_c(\mathbf{Q})n_c(\mathbf{r}) dr$ and, using equation (3.3), we have

$$I_{cu}(\mathbf{Q}) \equiv I(\mathbf{Q})/I_c(\mathbf{Q}) = \left| \int n_c(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \right|^2 \quad (3.4)$$

where $n_c(\mathbf{r})$ is the total electron number density and the quantity in equation (3.4) is called the intensity in the \mathbf{Q} -direction in electron units.

Even in metals, where the conduction electron wavefunctions permeate the entire sample, the charge density still resembles that of a set of separate atoms to a very good approximation. We therefore divide expression (3.4) into contributions from N identical fixed spherical atoms with centres at $\{\mathbf{R}_i\}$. Then

$$n_c(\mathbf{r}) \rightarrow \sum_{i=1}^N n_{ca}(\mathbf{r} - \mathbf{R}_i) \quad (3.5)$$

where $n_{ca}(\mathbf{r} - \mathbf{R}_i)$ is the electron density in the i th atom at a distance $(\mathbf{r} - \mathbf{R}_i)$ from its centre and

$$I_{cu}(\mathbf{Q}) = \left| \int \sum_{i=1}^N n_{ca}(\mathbf{r} - \mathbf{R}_i) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \right|^2 \quad (3.6a)$$

If we multiply and divide under the summation by $\exp(i\mathbf{Q} \cdot \mathbf{R}_i)$, this becomes

$$I_{cu}(\mathbf{Q}) = \left| \sum_{i=1}^N \exp(i\mathbf{Q} \cdot \mathbf{R}_i) \right|^2 |f_a(\mathbf{Q})|^2 \quad (3.6b)$$

where

$$f_a(\mathbf{Q}) \equiv \int_{\text{atom}} n_{ca}(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r}. \quad (3.6c)$$

$f_a(\mathbf{Q})$ is an important quantity known as the atomic scattering factor in electron units. It is known and tabulated (*International Tables for X-ray Crystallography* 1962) and will not be discussed in detail (see figure 3.2).

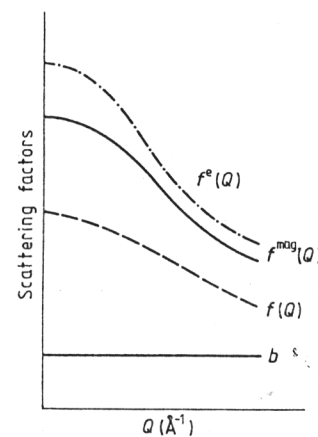


Figure 3.2 Single-centre scattering factors for: electrons by atoms (f^e), neutrons by magnetic ions (f^{mag}), x-rays by atoms (f), and neutrons by nuclei (b) (from Waseda 1980).

Equation (3.6) achieves a separation of the intensity into two factors one characteristic of the atoms and the other depending on where they are. The latter factor may be written as

$$\left| \sum_{i=1}^N \exp(i\mathbf{Q} \cdot \mathbf{R}_i) \right|^2 \equiv NS(\mathbf{Q}) \quad (3.7)$$

which defines $S(\mathbf{Q})$, the structure factor. $S(\mathbf{Q})$ will claim a lot of attention. Let us first relate it to equation (2.2a) for $v^{(1)}(\mathbf{r})$. Since $v^{(1)}$ is the density function we expect, in analogy with equation (3.4), that

$$I_{cu}(\mathbf{Q}) = |f_a(\mathbf{Q})|^2 \left| \int v^{(1)}(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \right|^2 \quad (3.8a)$$

and from equations (3.6b) and (3.7)

$$NS(\mathbf{Q}) = \int v^{(1)}(\mathbf{r}_1) \exp(i\mathbf{Q} \cdot \mathbf{r}_1) d\mathbf{r}_1 \times \int v^{(1)}(\mathbf{r}_2) \exp(-i\mathbf{Q} \cdot \mathbf{r}_2) d\mathbf{r}_2. \quad (3.8b)$$

By substituting equation (2.2a) into (3.8b), equation (3.7) is readily recapitulated. If we now rewrite equation (3.8b) as

$$NS(\mathbf{Q}) = \int v^{(1)}(\mathbf{r}_1)v^{(1)}(\mathbf{r}_2) \exp[i\mathbf{Q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2$$

and change the variables so that $\mathbf{r}_2 \rightarrow \mathbf{r}'$, $\mathbf{r}_1 - \mathbf{r}_2 \rightarrow \mathbf{r}$ we have

$$NS(\mathbf{Q}) = \int P_a(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \quad (3.9a)$$

where

$$P_a(\mathbf{r}) \equiv \int v^{(1)}(\mathbf{r} + \mathbf{r}')v^{(1)}(\mathbf{r}') d\mathbf{r}'. \quad (3.9b)$$

$P_a(\mathbf{r})$ is called the autocorrelation function of the atomic positions.

There is no statistical mechanics in this so far. The structure, represented by $S(\mathbf{Q})$, is that of a fixed array. We could calculate $S(\mathbf{Q})$ from $\{\mathbf{R}_i\}$, taking the $\{\mathbf{R}_i\}$ from one of the models in the previous chapter. Model $S(\mathbf{Q})$ have been found this way. If the model is big enough it will contain many different local configurations and its $S(\mathbf{Q})$ will approximate more or less to the configuration average which a scattering experiment would obtain for a real material.

3.3 The average $S(\mathbf{Q})$ for a real sample

To find the ensemble or configuration average of $S(\mathbf{Q})$ we need that of $P_a(\mathbf{r})$ for use in equation (3.9a). We now show that $\langle P_a(\mathbf{r}) \rangle$ is related to the $g(\mathbf{r})$ of equation (2.7).

Now, from equations (3.9b) and (2.2a) we have

$$P_a(\mathbf{r}) = \int \sum_i \delta(\mathbf{r} + \mathbf{r}' - \mathbf{R}_i) \sum_j \delta(\mathbf{r}' - \mathbf{R}_j) d\mathbf{r}' = \sum_{i,j} \delta(\mathbf{r} + \mathbf{R}_j - \mathbf{R}_i).$$

Put $\mathbf{R}_j = \mathbf{R}_1$ and sum over i using \mathbf{R}_1 as origin (see figure 3.3). This gives $\sum_i \delta(\mathbf{r} - \mathbf{R}_i)$ which is the density function at a distance \mathbf{r} away from the point $\mathbf{R}_1 - \mathbf{a}$ at which there is also a particle. The average of this is exactly the function $z(\mathbf{r})$ in equation (2.8). Similarly for $\mathbf{R}_j = \mathbf{R}_2, \mathbf{R}_j = \mathbf{R}_3$ etc, giving N

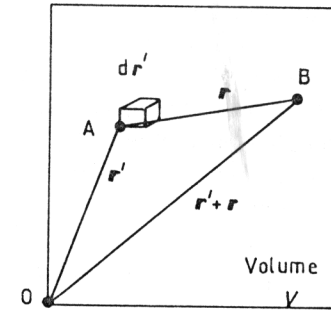


Figure 3.3 Definitions of quantities.

similar terms. Thus finally,

$$\begin{aligned} \langle P_a(\mathbf{r}) \rangle &= N(n_0g(\mathbf{r}) + \delta(\mathbf{r})) \\ \langle S(\mathbf{Q}) \rangle &= N^{-1} \int_V \langle P_a(\mathbf{r}) \rangle \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \\ &= \int [n_0(g(\mathbf{r}) - 1) + n_0 + \delta(\mathbf{r})] \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \\ &= n_0 \int_V (g(\mathbf{r}) - 1) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} + (2\pi)^3 n_0 \delta(\mathbf{Q}) + 1. \quad (3.10) \end{aligned}$$

To reach equation (3.10) we have used the properties of the δ -function, notably

$$\delta(\mathbf{Q}) = (2\pi)^{-3} \int \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r}.$$

There is also a tacit assumption that the volume V is a representative subsection of an infinite volume with uniform properties rather than a finite sample with a bounding surface. The $\delta(\mathbf{Q})$ term implies a strong scattering intensity in the forward direction with $|\mathbf{Q}| = 0 = \theta$. This peak would fall in the incident beam and not be observed in practice but should in any case be replaced by another term which arises as follows. Strictly, when $d\mathbf{r}'$ goes over the sample volume during integration, $v^{(1)}(\mathbf{r}' + \mathbf{r})$ falls to zero outside the body and the exact value of integral depends on the shape and size of the sample. In Guinier (1963) it is shown that the second term of equation (3.10) becomes

$$n_0 V^{-1} \left| \int \sigma(\mathbf{r}) \exp(i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{r} \right|^2$$

where $\sigma(\mathbf{r}) = 1$ inside and 0 outside the sample. This term does not contain information about the structure and it is negligible unless \mathbf{Q} is very small in which event θ would be too near the incident direction for observation. Thus

to a very good approximation

$$\langle S(\mathbf{Q}) \rangle = 1 + n_0 \int (g(r) - 1) \exp(i\mathbf{Q} \cdot \mathbf{r}) \, d\mathbf{r}. \quad (3.11a)$$

For an isotropic material—which most disordered substances are— $\langle S(\mathbf{Q}) \rangle \rightarrow \langle S|\mathbf{Q}| \rangle$ which is often written $S(Q)$ with the averaging bracket tacitly assumed, $g(\mathbf{r}) \rightarrow g(r)$, and

$$S(Q) = 1 + n_0 \int_0^\infty (g(r) - 1) \frac{\sin Qr}{Qr} 4\pi r^2 \, dr. \quad (3.11b)$$

Finally,

$$I_{\text{cu}}(Q) = N |f_a|^2 S(Q) \quad (3.11c)$$

and

$$S(Q) \rightarrow 1 \text{ as } Q \rightarrow \infty. \quad (3.11d)$$

3.4 The importance of the structure factor

In crystals, $S(\mathbf{Q})$ gives the Bragg peaks and is at the foundations of crystallography. For materials without LRO, equation (3.11b) enables $g(r)$ to be found if $S(Q)$ is inferred from the observed intensity—though this inference is not without difficulty (§3.8). In any event, the Fourier transformation of equation (3.11b) gives

$$g(r) = 1 + \frac{1}{8\pi^3 n_0} \int_0^\infty (S(Q) - 1) \frac{\sin Qr}{Qr} 4\pi Q^2 \, dQ. \quad (3.12)$$

The structure factor is therefore the route to the pair distribution, the RDF and the coordination number.

$S(Q)$ and $g(r)$ have strong connections with many theoretical functions in statistical mechanics, e.g., in liquid state theory the pressure is

$$p = n_0 k_B T - \frac{1}{6} n_0^2 \int g(r) \frac{d\varphi(r)}{d \ln r} \, dr \quad (3.13)$$

where $\varphi(r)$ is the interatomic potential (§4.3).

As we have already seen $S(Q)$ can be calculated for computer or other models in order to compare with observed $S(Q)$. In theories of electronic and many other properties of liquid metals or semiconductors, $S(Q)$ is almost invariably required and its measured value is used for numerical calculations.

In all these applications $S(Q)$ or $g(r)$ —which we have seen to be interchangeable—carry the structural information. Because of the single-scattering assumption and the use of diffraction theory only the interparticle distance vectors were involved in the intensity expression, equation (3.2). Because

there are no periodicities or preferred directions in the structure, only the distribution of interparticle distances, i.e. $g(r)$, can be inferred. Scattering experiments do not determine $g^{(3)}$, $g^{(4)}$ etc. This is a considerable limitation.

Before giving examples of the practical use of these formulae two generalisations are required, firstly to mixtures of different atomic species and secondly to waves other than x-rays.

3.5 Formulae for binary mixtures

Returning to the amplitude summation in equation (3.2) and treating the atoms as scattering centres we may rewrite it for a binary system as

$$I(Q) = A \left| \sum_k f_A(Q) \exp(i\mathbf{Q} \cdot \mathbf{R}_k^{(A)}) + \sum_l f_B(Q) \exp(i\mathbf{Q} \cdot \mathbf{R}_l^{(B)}) \right|^2 \quad (3.14)$$

where two types of atom, A and B, each have their characteristic scattering factors. The two sums are over the N_A A atoms and N_B B atoms respectively. It is clear that the intensity will have terms in f_A^2 , f_B^2 and $2f_A f_B$ associated with A-type, B-type and AB-type structure factors. These terms introduce *partial structure factors* S_{ij} , which are related by a Fourier transformation like equation (3.12) to the partial pair distributions introduced in §2.4. The results for a homogeneous isotropic binary material follow from the same reasoning as that of §§3.2 and 3.3 and are:

$$I_{\text{cu}}(Q) = N F(Q) \quad (3.15a)$$

$$F(Q) \equiv f_A^2 (c_A c_B + c_A^2 S_{AA}(Q)) + f_B^2 (c_A c_B + c_B^2 S_{BB}(Q)) + 2f_A f_B c_A c_B (S_{AB}(Q) - 1) \quad (3.15b)$$

$$S_{ij} \equiv 1 + n_0 \int_0^\infty (g_{ij}(r) - 1) \frac{\sin Qr}{Qr} 4\pi r^2 \, dr \quad (3.15c)$$

$$g_{ij}(r) = 1 + \frac{1}{8\pi^3 n_0} \int (S_{ij}(Q) - 1) \frac{\sin Qr}{Qr} 4\pi Q^2 \, dQ \quad (3.15d)$$

$$S_{AB} = S_{BA} \quad (3.15e)$$

$$n_0 \equiv (N_A + N_B)/V \quad c_i \equiv N_i/N \quad i, j = A \text{ or } B. \quad (3.15f)$$

When $c_A = 1$, $c_B = 0$, equation (3.15) reduces to the formulae of §3.3. Equation (3.15c) is the definition of the partial structure factor in terms of the partial pair distribution and leads to the expression (3.15b) for the intensity. Other definitions of the partial structure factors are conceivable with corresponding intensity formulae (see §3.12). Equation (3.15e) results from equation (2.14b).

3.6 Incoherent and inelastic scattering

Scattering can be coherent or incoherent, elastic or inelastic. Coherent scattering is that for which the angular dependence of the intensity is determined by the interference of scattered wavelets from different scattering centres. It depends on the structure factors. The incoherent scattering has an angular dependence affected only by the intrinsic cross sections of the scattering centres and not by their relative positions. Let us label EC, IC, EI and II the pairings elastic-coherent, inelastic-coherent, elastic-incoherent and inelastic-incoherent, respectively.

The x-ray scattering in equation (3.11c) is type EC. In equation (3.15) for the binary system there are EC-type and EI-type terms. The latter may be written $c_A c_B (f_A - f_B)^2$ or $\langle\langle f^2 \rangle\rangle - \langle\langle f \rangle\rangle^2$ where $\langle\langle x \rangle\rangle \equiv c_A x_A + c_B x_B$. X-rays are subject to Compton scattering which can be shown to be of type II.

For measuring structure factors, incoherent and inelastic scattering have a certain amount of nuisance value though they are interesting in their own right. For example, Compton scattering has to be subtracted from the observed intensity before processing the data. This point recurs in neutron scattering.

3.7 Neutron and electron scattering

An aspect of nuclear reactor technology is the provision of monoenergetic neutron beams in wavelengths suitable for crystallography. The formulae of the preceding sections are used except that the atomic scattering factor $f_a(Q)$ is replaced by an appropriate quantity representing neutron scattering by the nucleus. This quantity is the scattering length, b , which is related to the bound-atom cross section, σ_s , by $\sigma_s = 4\pi b^2$. Only s-wave scattering is important at the energies involved (Bacon 1975) and this is isotropic (figure 3.2).

Neutron scattering is considerably more complicated than x-ray scattering, however. A chemically pure sample is not necessarily isotopically pure. If there were two isotopes with scattering lengths b_1, b_2 , we should expect an equation like (3.15b) to apply. However, there would be only one structure factor to consider since the atomic distribution is determined by chemical not nuclear effects. The three S -terms therefore reduce to $\langle\langle b \rangle\rangle^2 S$ and the incoherent term to $\langle\langle b^2 \rangle\rangle - \langle\langle b \rangle\rangle^2$. In other words a weighted mean scattering length deals with isotopic mixtures. However, the incoherent term will be present even in an isotopically pure sample because the system (nucleus + neutron) can exist in two spin states with different b . An incoherent term of the form $\langle\langle b^2 \rangle\rangle - \langle\langle b \rangle\rangle^2$ arises from the relative weight of the two spin states. The meaning of b , written without brackets, will therefore be extended to stand for a mean scattering length weighted for both isotopic mixture and spin states. $\langle\langle b \rangle\rangle$ will mean $c_A b_A + c_B b_B$ as in §3.6.

More serious still is the inelasticity of neutron scattering. The important quantity is not really $S(Q)$ but $S(Q, \omega)$ where $\hbar\omega$ is the energy lost by the neutron in its collision. Mechanics gives

$$Q^2 = 2k_i^2 \left[1 - \frac{m\omega}{\hbar k_i^2} - \left(1 - \frac{2m\omega}{\hbar k_i^2} \right)^{1/2} \cos \theta \right] \quad (3.16)$$

where $\hbar k_i$ is the initial momentum of the neutron. If $\omega = 0$ and $k_f = k_i$, equation (3.16) reduces to equation (3.1), and this is valid for x-radiation because the energy transfers are very small. In neutron practice, however, θ alone does not define Q uniquely and a detector receiving at an angle θ records a coherent intensity, *not* $Nb^2 S(Q)$ in analogy with equation (3.11c), but

$$I(\theta) = Nb^2 \int_{-\infty}^{E_i/\hbar} D(k_f) \frac{k_f}{k_i} S(Q, \omega) d\omega \quad (3.17)$$

where the integral has the following meaning. It integrates over all the energies of the incoming neutrons with a weighting factor, $D(k_f)$, expressing the efficiency of the detector as a function of neutron speed. Since the observable is the counting rate, the factor k_f/k_i is required because the rate is proportional to the speed of arrival. If the effective spread of ω were small enough for k_f to be essentially constant—the so called static approximation—the coherent intensity from an element becomes proportional to $Nb^2 S(Q)$. This is not really good enough in practice and there are methods of correcting for inelastic scattering. In the terms of §3.6, neutron scattering has EC, IC, EI and II contributions. The underlying theory can be pursued in Lovesey (1984) and Howe (1978).

Because of its magnetic moment a neutron can also be scattered by a magnetic interaction with unpaired electron states or spins. The cross section for this resembles f_a in that it depends on the atomic structure (figure 3.2).

Electrons are scattered by the screened Coulomb fields of the atoms. The scattering factor, $f_{ei}(Q)$, is related to the $f_a(Q)$ for x-rays because of the electrostatic connection between field and charge density (see figure 3.2). The relation is

$$f_{ei}(Q) = \frac{8\pi^2 m e^2}{h^2} \left(\frac{Z - f_a(Q)}{Q^2} \right). \quad (3.18)$$

Electrons are subject to inelastic and multiple scattering especially in higher- Z elements. They are suited to measurements on thin amorphous layers. An example with a technical description is given in Leung and Wright (1974).

3.8 Some experimental considerations. Pure samples

The preceding sections show that the single scattering cross section and the structure factors are two of the influences that determine the observed

intensity. A third influence is a whole variety of extraneous phenomena that have to be corrected for as part of the data processing. Exactly how to do the corrections has to be thought out for each experiment and can be found in original papers. The problem is merely illustrated by the following discussion which is far from exhaustive.

Consider the following formulae for x-ray, neutron and electron observed intensities:

$$I^{\text{obs}}(Q) \text{ (x-ray)} = \alpha\beta N(f_a^2 S(Q) + f_c^2(Q) + \Delta) \quad (3.19a)$$

$$I^{\text{obs}}(Q) \text{ (neutrons)} = \alpha\beta N\{[b_{\text{coh}}^2(S(Q) + p(Q)) + b_{\text{inc}}^2(1 + p(Q))] + \Delta\} \quad (3.19b)$$

$$I^{\text{obs}}(Q) \text{ (electrons)} = \alpha\beta N(f_{\text{el}}^2 S(Q) + f_{\text{in}}^2 + \Delta) + I_{\text{substrate}} \quad (3.19c)$$

The factor α corrects for the effect on the intensity of absorption in the sample and its container if any. It depends on the material and geometry and is well known for standard cases, e.g. cylindrical samples in cylindrical cells (Waseda 1980). P refers to the polarisation of x-rays and depends on whatever reflections are imposed on the rays by the instrumental design.

f_c refers to the inelastic incoherent Compton scattering and its known theoretical value can be inserted. f_{in}^2 , referring to the inelastic scattering of electrons, must also be inserted. In both cases the effect is not necessarily very large and can be removed by extra instrumentation, e.g. by putting a velocity filter or monochromator in the scattered beam to reject electrons or photons which have lost energy.

Δ is for multiple scattering which was excluded from the discussion in §3.1. It is small and is sometimes neglected for x-rays, but it is more serious with electrons and neutrons. In neutron scattering Δ is isotropic and can be subtracted (Howe 1978). The factors $p(Q)$ in equation (3.19b) are the corrections for inelastic neutron scattering. These are small for heavy elements but are serious at low Z (Howe 1978, Dahlberg and Kunsch 1983). $I_{\text{substrate}}$ in equation (3.19c) is the intensity scattered from the foil or substrate on which the very thin samples required in electron diffraction are often supported.

There remains the product βN which converts the factors f^2 and b^2 which are expressed in absolute units into the observed counting rates. This is quite a difficult matter. $S(Q) \rightarrow 1$ as $Q \rightarrow \infty$ and it will be seen in §3.12 that $S(0) = n_0 \kappa_T k_B T$ where κ_T is the isothermal compressibility. If either or both these limiting values were inserted in equation (3.19) with the observed value of $I(Q)$ for very large or very small Q , βN could be calculated. This is somewhat unsatisfactory because high- and low- Q are the ranges in which $I(Q)$ is least accurate: with x-rays and electrons the scattered intensity is small at high Q . Nevertheless versions of this method have been used one of

which is, from equation (3.19a),

$$\beta N = \int_{Q_1}^{Q_2} (f_a^2 + f_c^2 + \Delta) dQ \left((\alpha P)^{-1} \int_{Q_1}^{Q_2} I^{\text{obs}}(Q) dQ \right)^{-1} \quad (3.20a)$$

where Q_1 is a fairly high value, say, 8 \AA^{-1} , and Q_2 is the observed upper limit of Q which might be 15 \AA^{-1} . $S(Q) \simeq 1$ in the numerator. Alternatively, use can be made of the fact that the Fourier transform of $S(Q)$ is $g(r)$ (equation (3.12)) and that for $r \rightarrow 0$, $g(r) = 0$ because of the mutual impenetrability of atoms. This leads to (Waseda 1980, Pings 1968)

$$\beta N = \int_0^{Q_2} [Q^2(f_a^2 + f_c^2 + \Delta) dQ - 2\pi^2 n_0] \left((\alpha P)^{-1} \int_0^{Q_2} I^{\text{obs}}(Q) dQ \right)^{-1} \quad (3.20b)$$

In neutron experiments this problem can be solved another way because the scattering from the element vanadium is over 99 % incoherent and is consequently isotropic. A solid vanadium replica substituted for the sample will give scattering according to equation (3.19b) with N and b^2 known and the coherent term negligible. This gives β which will apply also to the sample. N and b^2 for the latter must be known to extract $S(Q)$ from the sample scattering (North *et al* 1968).

These numerous corrections, and others not referred to, are applied to intensities observed in either reflection or transmission with diffraction equipment or, if $S(Q, \omega)$ is required, with neutron spectrometers (see figure 3.4). Typically, unless special measures are taken, $\sim 0.5 < Q < \sim 12 \text{ \AA}^{-1}$. Good measurements of $S(Q)$ might achieve an overall accuracy at the first peak of about $\pm 2\%$: there are examples in §3.11. Modern radiation sources, like synchrotrons for x-rays and spallation neutron sources, are extending observable Q -values to 40 \AA^{-1} and more (White and Windsor 1984, Biggin 1986).

3.9 From $S(Q)$ to $g(r)$

Assuming the best $S(Q)$ has been extracted from $I^{\text{obs}}(Q)$, one use for it is to obtain $g(r)$ from equation (3.12). Computing a Fourier transform is a routine procedure but errors in $g(r)$ result from the limited range of Q over which $S(Q)$ can be measured and from the errors in $S(Q)$ itself. Probably the most serious matter is the truncation of $S(Q)$ at Q_{max} . This means that equations like (3.12) and (3.15d) have in their integrands a factor $M(Q)$ which is a step function of magnitude unity which cuts off to zero at $Q = Q_{\text{max}}$. The implication is that the transform will be a distorted $g(r)$ containing spurious ripples particularly noticeable below the first peak and

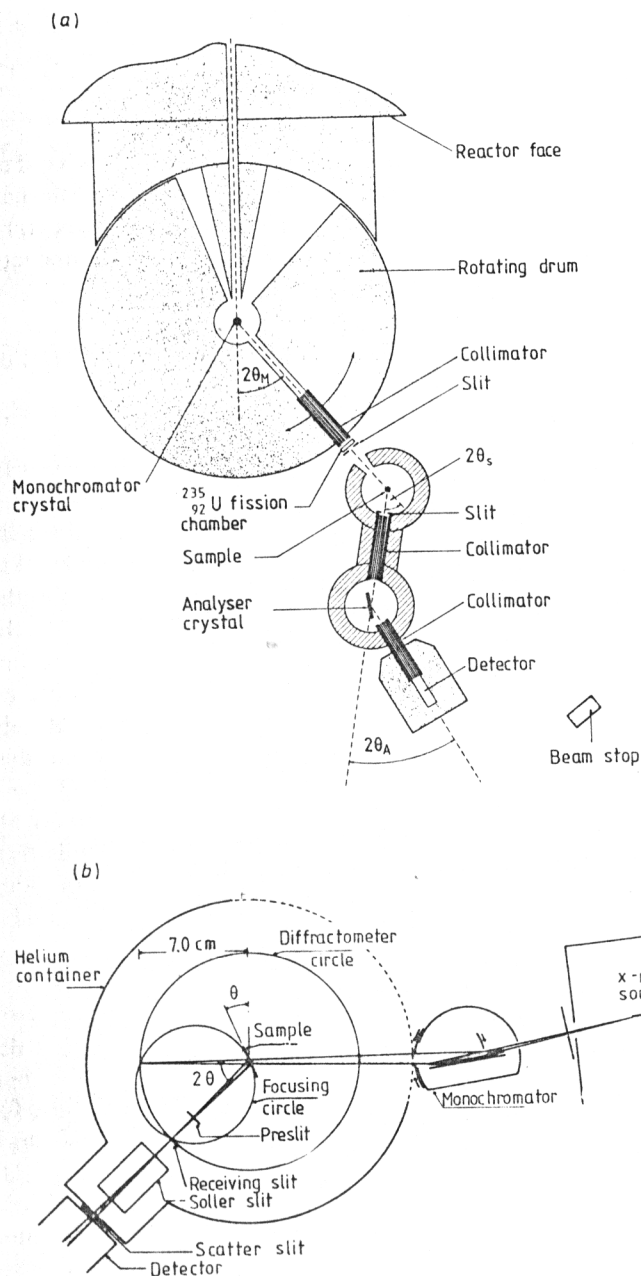


Figure 3.4 (a) Layout of a triple-axis neutron spectrometer for measuring $S(Q, \omega)$ (for details see White and Windsor 1984; Biggin 1986). (b) Layout of equipment for measuring $S(Q)$ by transmitted x-rays (from Van der Lugt 1979).

these can lead to erroneous structural inferences. Error analysis and correction techniques have been devised (Kaplow *et al* 1965, Wright 1974). One of these involves transforming $S(Q)$ and $g(r)$ cyclically into one another and removing obvious truncation errors from $g(r)$. This operation continues until $g(r)$ is zero and devoid of spurious ripples at small r , but will also transform into an $S(Q)$ which agrees with the observed one within experimental error. However, this is not the only approach and may be criticised on the grounds that $g(r)$ is not necessarily zero at small r if inferred from x-rays scattered by electrons. There is really no substitute for non-existent data and the removal of spurious ripples from $g(r)$ can only be achieved by sacrificing something elsewhere. Some workers prefer to do this by using an $M(Q)$ which is not a step function but a more gentle cut-off such as

$$M(Q) = \sin(\pi Q/Q_{\max})/(\pi Q/Q_{\max}).$$

This certainly reduces spurious ripples but broadens somewhat the peaks in the transform, i.e., it spoils the resolution.

3.10 Binary systems and isotopic substitution

It is possible to Fourier transform the intensity from the binary system to obtain a total pair distribution function, $g_T(r)$. From equations (3.15b) and (3.15d),

$$F(Q) - \langle\langle f^2 \rangle\rangle = \sum_{i,j} c_i c_j f_i f_j (S_{ij} - 1) \quad (3.21a)$$

and if we Fourier transform this according to equation (3.15d) there results

$$\frac{1}{8\pi^3 n_0} \int (F(Q) - \langle\langle f^2 \rangle\rangle) \frac{\sin Qr}{Qr} 4\pi Q^2 dQ = \sum_{i,j} c_i c_j f_i f_j (g_{ij} - 1). \quad (3.21b)$$

Let us define $g_T(r)$ by

$$\langle\langle f^2 \rangle\rangle (g_T(r) - 1) \equiv \sum_{i,j} c_i c_j f_i f_j (g_{ij} - 1). \quad (3.21c)$$

Equation (3.21b) then shows how $g_T(r)$ can be found from the observed $F(Q)$.

It is by no means impossible to make useful inferences from $g_T(r)$ obtained in this way but it would clearly reveal more if the three g_{ij} 's could be measured separately.

Since the three S_{ij} are independent, three separate determinations of $F(Q)$ are required to measure them with three distinctly different ratios of f_A to f_B . Varying c_A, c_B is not an alternative because in general S_{ij} varies with c . Except for the special case of anomalous dispersion (Waseda 1980), $f(Q)$ for x-rays is not itself open to variation though one could substitute one or both

elements by others which do not affect the structure. This is 'isomorphous substitution', e.g., substitute Zr for Hf in amorphous NiHf alloys (Wagner 1980). Alternatively three different radiations (x-rays, electrons, neutrons) could be used on the same mixture. A third possibility is to alter the neutron scattering lengths by changing the isotopic abundances in a mixture of fixed chemical composition (isotopic substitution).

This kind of programme was first envisaged by Keating in 1963, and first implemented by Enderby, North and Egelstaff in 1966 (Enderby *et al* 1966). Since then the method of isotopic substitution has been exploited, especially by Enderby and co-workers, to find S_{ij} and therefore g_{ij} in liquid and amorphous alloys and semiconductors, molten salts and solutions. Sometimes a combination of neutron, with x-ray or electron, scattering experiments is suitable.

Clearly the isotopic method is limited by the availability of suitable isotopes. The $F(Q)$ resulting from the three experiments must be sufficiently different to make the solution of the three simultaneous equations for S_{ij} a practical possibility (Edwards *et al* 1975, Biggin and Enderby 1982). All the errors and corrections involved in neutron scattering will be present, enhanced by the necessity of combining three results. There are some interesting possibilities to exploit however. Since scattering lengths can be negative, b for an element can be negative or zero and to some extent disposable if isotopes can be mixed. An example is given in §3.11.

3.11 Examples of structure investigations

A large number of examples are given in Waseda (1980). In this section a few are selected from the literature to illustrate the achievements possible with the methods outlined in the previous sections.

X-rays in transmission were used by Greenfield *et al* (1971) to provide accurate tabulated structure factors for liquid Na and K. Points with Q -values as low as 0.3 \AA^{-1} were observed and the result is shown in figure 3.5. Somewhat comparable work with neutrons on simple liquid metals is reported in North *et al* (1968) and these two papers provide an interesting comparison of two techniques. The x-ray work on a simple non-metallic liquid, Ar, over a large density range is described in Pings (1968) and part of this is shown in figure 3.6. This shows that as the density decreases the coordination number, defined as

$$2n_0 \int_0^{r(\text{peak})} \rho(r) dr$$

falls significantly. This reveals the important point that expansion reorganises the SRO, it does not merely increase the interatomic distances as it would in a crystal.

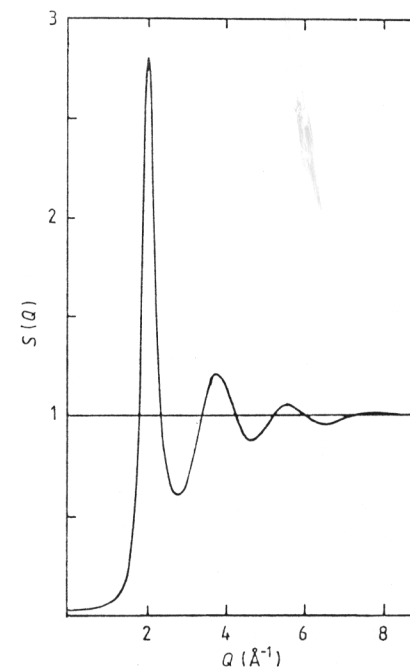


Figure 3.5 $S(Q)$ from Greenfield *et al* (1971) for liquid Na.

One type of non-simple liquid is molecular, like liquid CCl_4 . If the scattering from one isolated molecule is known—which is often so for simple molecules—this information must supply part of the content of $F(Q)$. An assumption about the relative orientation of molecules in the liquid will supply more. These two items, plus a single measurement of $F(Q)$, go some way towards distinguishing the three partial structure factors without requiring isotopic substitution (Egelstaff *et al* 1971a,b). The element Ti has a small negative scattering length for neutrons and this circumstance enables $g_T(r)$ of equation (3.21c) to be useful. For TiCl_4

$$g_T = 1 + 0.004(g_{\text{TiTi}} - 1) + 0.588(g_{\text{ClCl}} - 1) - 0.101(g_{\text{TiCl}} - 1).$$

Figure 3.7 from Enderby (1978) shows the effect of the g_{TiCl} term clearly with a Ti-Cl intramolecular separation of 2.17 \AA . The examples of CCl_4 and TiCl_4 illustrate inferences made without separate measurements of the partial structure factors in binary systems.

The study of molten salts was advanced by the application of the isotopic substitution method. Figure 3.8(a) shows $F(Q)$ of equation (3.15b) measured by Edwards *et al* (1975) for three liquid NaCl samples containing natural Na but three isotopically different Cl anions. Because of the different Cl scattering lengths, the curves are sufficiently different for the S_{ij} to be

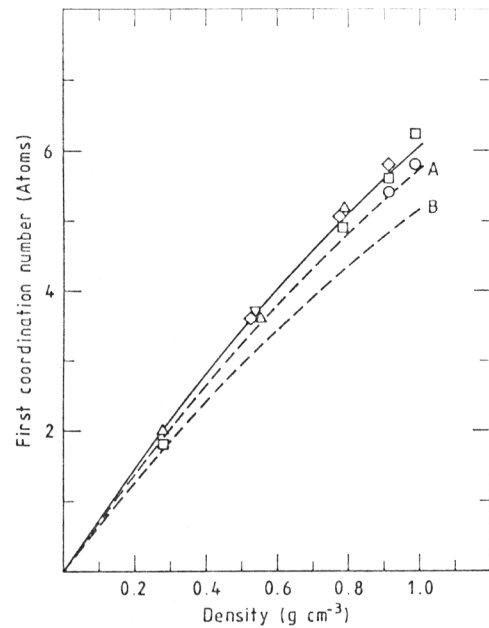


Figure 3.6 Data for Ar from Pings (1968) showing that the coordination number is a function of density. Broken curves are theoretical estimates from the LJ potential.

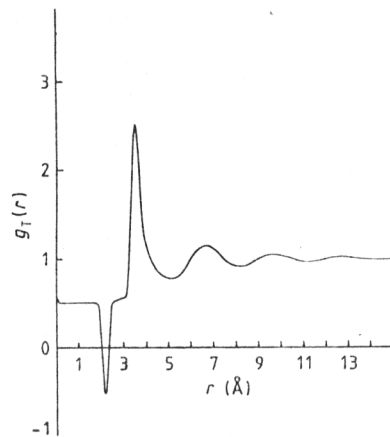


Figure 3.7 Enderby's total $g_T(r)$ for TiCl_4 (from Enderby 1978).

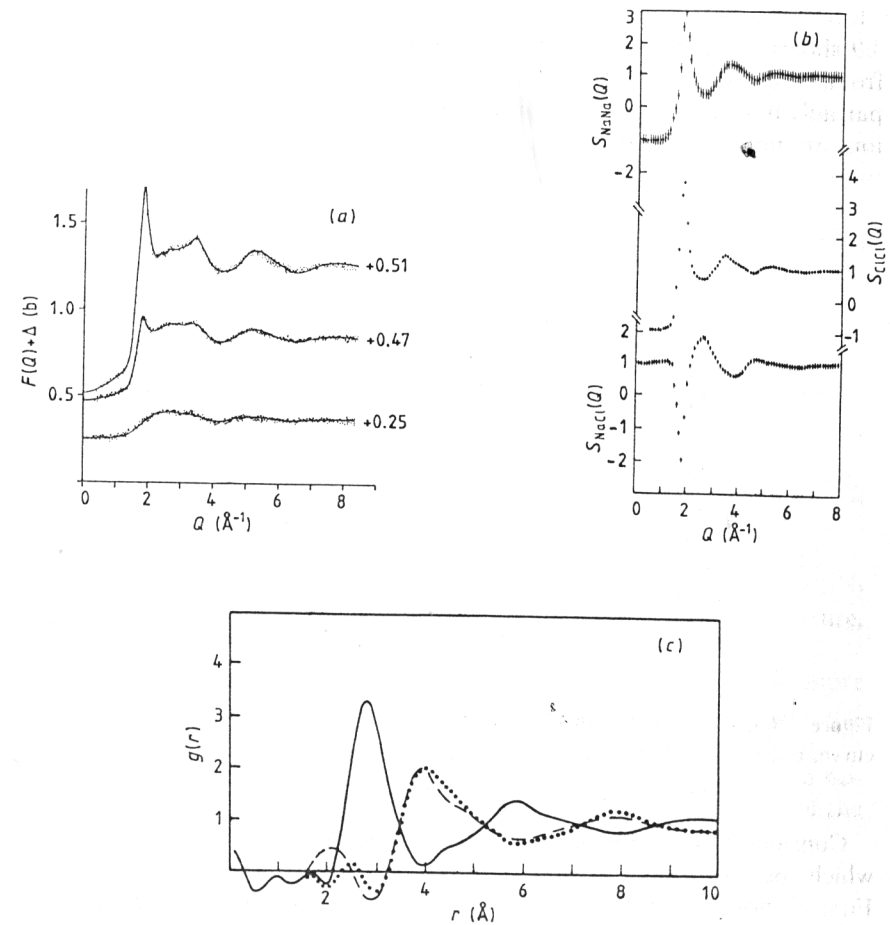


Figure 3.8 (a) $F(Q)$ from Edwards *et al* (1975) for neutron scattering by NaCl. Top curve, Na^{35}Cl ; middle curve, NaCl; bottom curve Na^{37}Cl . The points are observed. The lines are derived from the S_{ij} . $\Delta = c_a b_a^2 + c_b b_b^2$. (b) Partial structure factors S_{ij} for NaCl (from Edwards *et al* 1975). (c) Partial g_{ij} (from Biggin and Enderby 1982) from the data of (a) and (b). Full curve, $g_{\text{NaCl}}(r)$; broken curve, $g_{\text{NaNa}}(r)$; dotted curve, $g_{\text{ClCl}}(r)$.

resolved (figure 3.8(b)) and the S_{ij} can be transformed into g_{ij} (figure 3.8(c)). It is evident that the first shell of neighbours, given by the peak in g_{NaCl} , is of opposite electrical sign to that of the ion at the origin; the coordination number is 5.8 ± 0.1 . The g_{ClCl} and g_{NaNa} peaks coincide and contain 13.0 ± 0.5 second-nearest neighbours. Above 5 \AA the charges cancel one another. Similarities to and differences from crystalline NaCl are obvious.

Clearly it would be impossible to infer such things from a single $F(Q)$. Figure 3.9 shows the outcome for BaCl_2 (Edwards *et al* 1978). It is distinguished from NaCl especially in that the g_{BaBa} and g_{ClCl} curves are quite different, partially because of the ionic charge difference but probably also because the ions are not equally mobile.

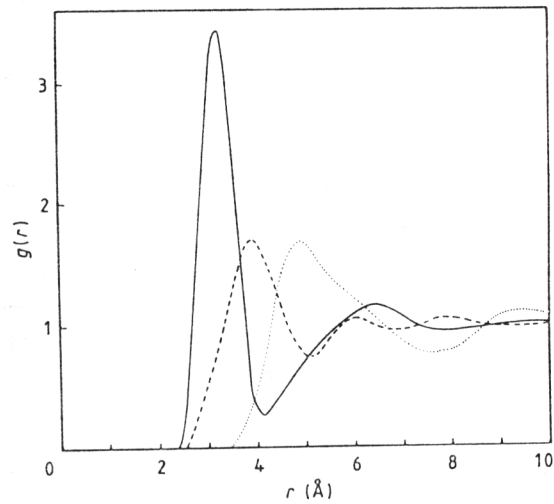


Figure 3.9 $g_{ij}(r)$ for BaCl_2 from Edwards *et al* (1978). Full curve, $g_{\text{BaCl}}(r)$; broken curve, $g_{\text{ClCl}}(r)$; dotted curve, $g_{\text{BaBa}}(r)$.

Consideration of amorphous alloys of Ni and Ti illustrates the way in which special expedients can be used to maximise the yield of information. First we note that both Ni and Ti have isotopes both with $b < 0$ and $b > 0$. In principle therefore isotopes could be mixed to give either $b_{\text{Ni}} = 0$ or $b_{\text{Ti}} = 0$; these are called null elements. With $b_{\text{Ni}} = 0$, equation (3.15b) shows that $F(Q)$ would give S_{TiTi} directly: similarly $b_{\text{Ti}} = 0$ would give S_{NiNi} . A zero alloy, i.e., one with $c_{\text{Ni}}b_{\text{Ni}} + c_{\text{Ti}}b_{\text{Ti}} = \langle\langle b \rangle\rangle = 0$, could also be prepared as could another alloy with $\Delta b = b_{\text{Ti}} - b_{\text{Ni}} = 0$. These last two alloys would yield $F(Q)$ which give directly the quantities called S_{cc} and S_{NN} which will be introduced in the next section and which, together with a third quantity, S_{Nc} , are altogether equivalent to the three S_{ij} . Between them, S_{TiTi} , S_{NiNi} , S_{cc} , S_{NN} give all the partial structure factors. At the time of writing this programme has not been realised but neutron and x-ray scattering from $\text{Ni}_{40}\text{Ti}_{60}$ has been observed (Wagner 1980). In this material, because of the relative sizes of the b , the x-ray $F(Q)$ was dominated by S_{NN} and the neutron $F(Q)$ by S_{cc} . S_{Nc} exerted so small an effect that it was sufficient to calculate it by an approximate theory. The result is shown in figure 3.10 and amounts to a very plausible solution of the partial structure factor

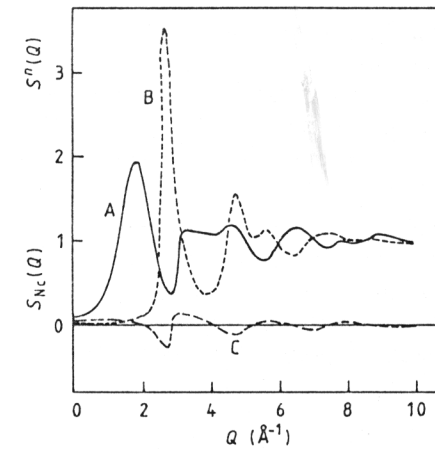


Figure 3.10 Bhatia-Thornton structure factors for amorphous $\text{Ni}_{40}\text{Ti}_{60}$. A, $S_{\text{cc}}(Q)/c_1c_2$; B, $S_{\text{NN}}(Q)$; C, $S_{\text{Nc}}(Q)_{\text{HS}}$ (from Wagner 1980).

problem in this alloy. From the corresponding g_{ij} it could be inferred that Ni had 9.3 Ti neighbours instead of the 7.7 it would have in a random mixture, i.e., SRO existed (see also §12.2).

As a final example we consider the archetypal glass, SiO_2 . One of the more recent of many experiments used a time-of-flight neutron spectrometer and a pulsed neutron source (Misawa *et al* 1980). This took the Q -value up to about 45 \AA^{-1} . Figure 3.11 shows the total radial distribution function obtained by Fourier transforming $(F(Q)/\langle\langle b^2 \rangle\rangle - 1)$. The interpretation of the

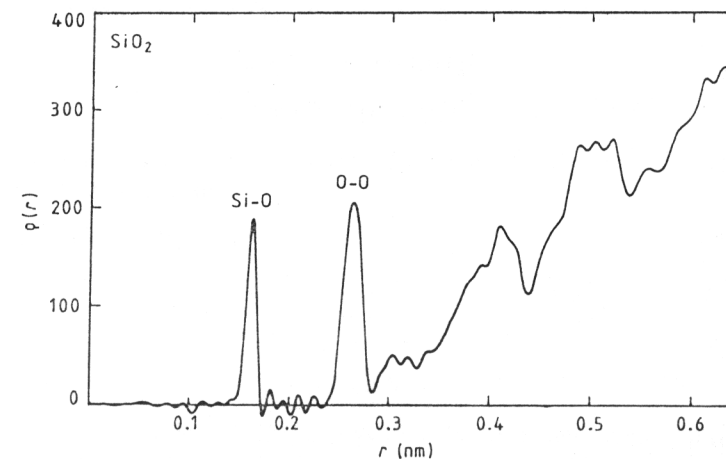


Figure 3.11 The radial distribution junction of vitreous silica derived from the scattering of neutrons from a spallation source (from Misawa *et al* 1980).

two prominent peaks is that they represent the Si-O and O-O distances of 0.1613 and 0.2628 nm respectively. The areas of the peaks lead to corresponding coordination numbers 4 and 2. The widths of the peaks indicate the variation in bond lengths. These results are clearly consistent with the Si-O tetrahedral unit and CRN of §2.6 (see also §10.6).

3.12 Different kinds of structure factor. Fluctuations

In §§3.5 and 3.11 it was mentioned in passing that the S_{ij} used so far are just one set of possible partial structure factors. In this section we introduce others and make the further points that when $Q = 0$ the structure factor is connected on the one hand with fluctuations and on the other with thermodynamic quantities.

It will be convenient to use previous notations except that the superscript will be dropped from the density function $v^{(i)}$. V now stands for a fixed volume within a much larger amount of binary mixture and we must differentiate between the fluctuating numbers N_A, N_B and N of atoms in V and their averages $\langle N_A \rangle$ etc. There will be corresponding instantaneous and average number densities v_A, n_A etc.

Let

$$\Delta v_A(\mathbf{r}) \equiv v_A(\mathbf{r}) - n_A = \sum_k \delta(\mathbf{r} - \mathbf{R}_k^{(A)}) - n_A \quad (3.22a)$$

and define the Fourier component $\Delta v_A(Q)$ by

$$\Delta v_A(Q) = V^{-1} \sum_Q v_A(Q) \exp(-iQ \cdot \mathbf{r}) \quad (3.22b)$$

then

$$\begin{aligned} \Delta v_A(Q) &= \int \exp(iQ \cdot \mathbf{r}) \Delta v_A(\mathbf{r}) \, d\mathbf{r} \\ &= \sum_k \exp(iQ \cdot \mathbf{R}_k^{(A)}) - n_A \int_V \exp(iQ \cdot \mathbf{r}) \, d\mathbf{r}. \end{aligned}$$

Similarly

$$\Delta v_B(Q) = \sum_l \exp(iQ \cdot \mathbf{R}_l^{(B)}) - n_B \int_V \exp(iQ \cdot \mathbf{r}) \, d\mathbf{r}$$

and

$$\Delta v(Q) \equiv \Delta v_A(Q) + \Delta v_B(Q) = \sum_{j=k,l} \exp(iQ \cdot \mathbf{R}_j) - n_0 \int_V \exp(iQ \cdot \mathbf{r}) \, d\mathbf{r}. \quad (3.22c)$$

The new partial structure factor $S_{NN}(Q)$ will now be defined by

$$S_{NN}(Q) \equiv \frac{1}{\langle N \rangle} \langle \Delta v(Q) * \Delta v(Q) \rangle. \quad (3.23)$$

For a homogeneous isotropic binary mixture $Q \rightarrow Q$. In the limit $Q = 0$, it follows from equation (3.22c) that

$$S_{NN}(0) = \frac{1}{\langle N \rangle} \langle (N - \langle N \rangle)^2 \rangle \equiv \frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} \quad (3.24)$$

which is a statement of the mean-square fluctuation in the number N .

Before discussing S_{NN} let us introduce S_{cc} and S_{Nc} . For this we require the definition

$$\Delta c(\mathbf{r}) \equiv (V/\langle N \rangle)(c_B \Delta v_A(\mathbf{r}) - c_A \Delta v_B(\mathbf{r})). \quad (3.25a)$$

Δc is an expression of the concentration fluctuations within V , and the definition is reasonable because it ensures that, if the density fluctuations, Δv , of each component were proportional to their respective average concentrations (i.e., the latter remain unchanged), $\Delta c(\mathbf{r})$ would vanish. $\Delta c(Q)$ is introduced by

$$\Delta c(\mathbf{r}) = \sum_Q \Delta c(Q) \exp(-iQ \cdot \mathbf{r}) \quad (3.25b)$$

and

$$\Delta c(Q) = V^{-1} \int_V \Delta c(\mathbf{r}) \exp(iQ \cdot \mathbf{r}) \, d\mathbf{r}. \quad (3.25c)$$

Two more new structure factors are now defined as follows:

$$S_{cc} \equiv \langle N \rangle \langle \Delta c(Q) * \Delta c(Q) \rangle \quad (3.26)$$

$$S_{Nc} \equiv \mathcal{R} \langle \Delta v(Q) * \Delta c(Q) \rangle. \quad (3.27)$$

Substitution into equations (3.26) and (3.27) from (3.22c) and (3.25c), taking the limit $Q \rightarrow 0$, leads to

$$S_{cc}(0) = \langle N \rangle \langle (\Delta c)^2 \rangle \quad (3.28a)$$

$$\Delta c = \langle N \rangle^{-1} [c_B(N_A - \langle N_A \rangle) - c_A(N_B - \langle N_B \rangle)] \quad (3.28b)$$

and

$$S_{Nc}(0) = \langle \Delta N \Delta c \rangle. \quad (3.29)$$

Inspection of equation (3.22c) shows that the three new structure factors contain the sum $\sum_{j=k,l} \exp(iQ \cdot \mathbf{R}_j)$ though it enters in different ways. Thus, the same positional information is carried that is in equation (3.14), leading to the structure factors S_{ij} . In fact, Bhatia and Thornton (1970), who

introduced S_{cc} , S_{NN} and S_{Nc} in 1970, showed that the latter are linear combinations of the S_{ij} . The linear relations with the arguments Q omitted are

$$S_{NN} = c_A^2 S_{AA} + c_B^2 S_{BB} + 2c_A c_B S_{AB} \quad (3.30a)$$

$$S_{Nc} = c_A c_B [c_A (S_{AA} - S_{AB}) - c_B (S_{BB} - S_{AB})] \quad (3.30b)$$

$$S_{cc} = c_A c_B [1 + c_A c_B (S_{AA} + S_{BB} - 2S_{AB})] \quad (3.30c)$$

conversely

$$c_A^2 S_{AA} = c_A^2 S_{NN} + 2c_A S_{Nc} + S_{cc} - c_A c_B \quad (3.31a)$$

$$c_B^2 S_{BB} = c_B^2 S_{NN} - 2c_B S_{Nc} + S_{cc} - c_A c_B \quad (3.31b)$$

$$c_A c_B S_{AB} = c_A c_B S_{NN} + (c_B - c_A) S_{Nc} - S_{cc} + c_A c_B \quad (3.31c)$$

The equivalence of these two sets of structure factors means that the scattering intensity in equation (3.15) could be re-expressed. Substituting equation (3.31) into (3.15b) leads to

$$F(Q) = \langle\langle f \rangle\rangle^2 S_{NN} + (\Delta f)^2 S_{cc} + 2\Delta f \langle\langle f \rangle\rangle S_{Nc} \quad (3.32a)$$

where

$$\Delta f \equiv f_A - f_B \quad (3.32b)$$

Equation (3.32) justifies the remarks about S_{cc} and S_{NN} in §3.11.

It is probably most readily seen from equation (3.30) that, at large Q , S_{NN} oscillates about and tends to one, S_{Nc} behaves similarly about zero and S_{cc} about $c_A c_B$. $S_{cc} = c_A c_B$ if $S_{AA} = S_{BB} = S_{AB}$.

At $Q = 0$, often called the long-wavelength limit, equations (3.24), (3.28a) and (3.29) show the connection with fluctuations. In a pure material, S_{cc} and S_{Nc} vanish and $S_{NN} \rightarrow S$. Thus $S(0)$ is $\langle(\Delta N)^2\rangle/\langle N\rangle$ for a pure material.

The fluctuation expressions can be connected with thermodynamic quantities. We shall demonstrate the simplest relation and quote the rest in table 3.2. For these purposes the thermodynamic symbols in table 3.1 will be useful.

Table 3.1 List of thermodynamic symbols.

Name or definition	Symbol
Isothermal compressibility	κ_T
Gibbs free energy	G
Activity of i th component	a_i
Number of moles or particles of i th component according to context	n_i
Partial molar Gibbs free energy of i th component or chemical potential $\equiv (\partial G/\partial n_i)_{T, p, n_j}$	μ_i
Partial molar volume $(\partial V/\partial n_i)_{T, p, n_j}$	v_i
$n_0(v_A - v_B)$	δ
Boltzmann's constant	k_B
$n_0 k_B T \kappa_T$	θ
Grand canonical partition function	\mathcal{Z}
Energy of j th state of a system	E_j

Table 3.2 The connection of fluctuation expressions with thermodynamic quantities. Note: $\langle\langle x \rangle\rangle \equiv c_A x_A + c_B x_B$.

Fluctuation expression	Structure factor for $Q = 0$	Thermodynamic expression
$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{\langle(\Delta N)^2\rangle}{\langle N \rangle}$	$S(0)$	$\theta \equiv n_0 k_B T \kappa_T$
$\frac{\langle(\Delta N)^2\rangle}{\langle N \rangle}$	$S_{NN}(0)$	$\theta + \delta^2 S_{cc}(0)$
$\langle N \rangle \langle(\Delta c)^2\rangle$	$S_{cc}(0)$	$\frac{RT}{(\partial^2 G/\partial c_A^2)_{T, p, N}} = \frac{k_B T(1 - c_A)}{(\partial \mu_A/\partial c_A)_{T, p, N}}$
$\langle \Delta N \Delta c \rangle$	$S_{Nc}(0)$	$-S_{cc}(0)$
$1 + \langle N \rangle \left(\frac{\langle N_A^2 \rangle - \langle N_A \rangle^2}{\langle N_A \rangle^2} \right)$	$S_{AA}(0)$	$\theta - \frac{c_B}{c_A} + \left(\frac{1}{c_A} - \delta \right)^2 S_{cc}(0)$
$1 + \langle N \rangle \left(\frac{\langle N_B^2 \rangle - \langle N_B \rangle^2}{\langle N_B \rangle^2} \right)$	$S_{BB}(0)$	$\theta - \frac{c_A}{c_B} + \left(\frac{1}{c_B} + \delta \right)^2 S_{cc}(0)$
$1 + \langle N \rangle \left(\frac{\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle}{\langle N_A \rangle \langle N_B \rangle} \right)$	$S_{AB}(0)$	$\theta + 1 - \left(\frac{1}{c_A} - \delta \right) \left(\frac{1}{c_B} + \delta \right) S_{cc}(0)$
	$F(0)$	$\theta \langle\langle f \rangle\rangle^2 + S_{cc} \langle\langle f \rangle\rangle^2 \left(\delta - \frac{f_A - f_B}{\langle\langle f \rangle\rangle} \right)^2$

We now show that $S(0) = \theta$. The way V has been used in this section indicates that V , T and μ (but not N) are the specified variables and the system in V is accordingly a member of a grand canonical ensemble. For a pure system the partition function is therefore

$$\mathcal{Z} = \sum_N \sum_j \exp\left(\frac{\mu N - E_j}{k_B T}\right) \quad (3.33a)$$

and the probability of a system having N particles and total energy E_j is

$$p(N, E_j) = \mathcal{Z}^{-1} \exp\frac{\mu N - E_j}{k_B T}. \quad (3.33b)$$

From the latter the average, $\langle X \rangle$, of any property X is obtainable as $\sum_{N,j} X p(N, E_j)$ and consequently

$$\begin{aligned} \langle (\Delta N)^2 \rangle &\equiv \langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 \\ &= (k_B T)^2 \left[\mathcal{Z}^{-1} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right)_{T,V} - \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)_{T,V}^2 \right] \\ &= k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \end{aligned} \quad (3.34)$$

Manipulation of the last derivative brings the required result for, by the chain rule,

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \left(\frac{\partial \langle N \rangle}{\partial n_0} \right)_{T,V} \left(\frac{\partial n_0}{\partial p} \right)_{T,V} \left(\frac{\partial p}{\partial \mu} \right)_{T,V}$$

where $n_0 \equiv \langle N \rangle / V$. Now

$$\left(\frac{\partial \langle N \rangle}{\partial n_0} \right)_{T,V} = V \quad \left(\frac{\partial n_0}{\partial p} \right)_{T,V} = -\frac{\langle N \rangle}{V^2} \left(\frac{\partial V}{\partial p} \right)_{T,N} \quad \left(\frac{\partial p}{\partial \mu} \right)_{T,V} = n_0$$

of these, the third relation follows from the thermodynamic equations $V = (\partial G / \partial p)_T$ and $G = \langle N \rangle \mu$. From equation (3.34)

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = -k_B T \frac{n_0}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = k_B T n_0 \kappa_T = 0 \quad (3.35a)$$

thus,

$$S(0) = \theta. \quad (3.35b)$$

Other connections between thermodynamic quantities and fluctuations can be demonstrated (Bhatia and Thornton 1970) (see table 3.2).

There are other structure factors—called the Ashcroft–Langreth—quite common in the literature and valuable for some purposes. Writing them

as $S_{ij}^{(AL)}(Q)$, their relation with others is,

$$S_{ij}^{(AL)} = \delta_{ij} + (c_i c_j)^{1/2} (S_{ij} - 1) \quad (3.36a)$$

$$S_{11}^{(AL)} = c_1 S_{NN} + S_{cc} / c_1 + 2 S_{Nc} \quad (3.36b)$$

$$S_{22}^{(AL)} = c_2 S_{NN} + S_{cc} / c_2 - 2 S_{Nc} \quad (3.36c)$$

$$S_{12}^{(AL)} = (c_1 c_2)^{1/2} S_{NN} - S_{cc} / (c_1 c_2)^{1/2} + [(c_2 / c_1)^{1/2} - (c_1 / c_2)^{1/2}] S_{Nc} \quad (3.36d)$$

$$S_{NN} = c_1 S_{11}^{(AL)} + c_2 S_{22}^{(AL)} + 2(c_1 c_2)^{1/2} S_{12}^{(AL)} \quad (3.36e)$$

$$S_{cc} = c_1 c_2 [c_2 S_{11} + c_1 S_{22}^{(AL)} - 2(c_1 c_2)^{1/2} S_{12}^{(AL)}] \quad (3.36f)$$

$$S_{Nc} = c_1 c_2 [S_{11}^{(AL)} - S_{22}^{(AL)} + (c_2 - c_1) S_{12}^{(AL)} / (c_1 c_2)^{1/2}]. \quad (3.36g)$$

The $S_{ij}^{(AL)}$ may be defined by

$$S_{ij}^{(AL)} = \delta_{ij} + (c_i c_j)^{1/2} n_0 \int (g_{ij}(r) - 1) \exp(-i\mathbf{Q} \cdot \mathbf{r}) \, dr. \quad (3.36h)$$

Since the new structure factors and the S_{ij} are mutually interconvertible it is a matter of convenience which is used. The Bhatia–Thornton ones connect more directly with fluctuations and the S_{ij} , often called Faber–Ziman structure factors, may be thought to arise more naturally in scattering discussions and in connection with the $g_{ij}(r)$. $S_{cc}(0)$ has featured in much discussion of liquid mixtures because, if $S_{cc}(0) \simeq 0$ for, say, $c_0 \neq c$, fluctuations are negligible and this signifies a stable compound with the composition c_0 . On the other hand if $S_{cc}(0)$ becomes very large then the large concentration fluctuations imply a tendency to phase separation or liquid immiscibility. It can be shown that $S_{cc}(0) = c_A c_B$ if A and B mix randomly without volume change or heat of mixing (see §6.9). As table 3.2 shows, $S_{cc}(0)$ is obtainable as a function of composition by thermodynamic measurements or from $F(0)$. Since scattering observations becomes impossible at very small Q , $F(0)$ has to be obtained by extrapolating the intensity to $Q = 0$. This should lead to the same values for $S_{cc}(0)$ as thermodynamic measurements and where this point has been tested the results are satisfactory though not accurate.

3.13 Other clues to structure. Triplet distribution

Although scattering studies are the major source of structural information, clues can be picked up elsewhere. Chemical knowledge of molecular structure or preferred bond orientations, or crystallographic knowledge of related crystal structures, may suggest hypotheses about SRO in liquids or glasses. Even bulk properties, like density, may eliminate some structures from consideration and the composition dependence of thermodynamic variables such as the heat of mixing may indicate that SRO of some kind—as distinct

from random mixing—may be occurring. However, ideally we require techniques in which the signal is affected by the number and disposition of the atoms round any one of them thought of as the origin. The reader's attention will now be drawn briefly to a few such techniques but it is one of the problems in the study of disordered matter that the inference of the structure from the signal is somewhat complex and indirect.

In x-ray absorption it is often noticed that on the high-energy side of the absorption edge the spectrum has a complex oscillatory form. This phenomenon is extended x-ray absorption fine structure, called EXAFS. X-ray absorption chiefly results from photoelectron emission and EXAFS stems from the fact that on its departure from its parent atom the photoelectron is backscattered by the neighbouring atoms. There is interference between the photoelectron wave and the backscattered wavelets and whether this is constructive or destructive depends on the photon energy. This is the origin of the ripples in the spectrum. The ripples must therefore depend also on how many neighbouring atoms there are, of what kind and how far away. In other words the partial radial distribution functions are involved. For a monatomic target, the theory (Lee *et al* 1981) leads to

$$\frac{\Delta\mu}{\mu_0} = -\left(\frac{3f(k, \pi)}{2k}\right) \int_0^\infty \frac{g(r) \exp(-r/L)}{r^2} \sin(2kr + \alpha(k)) dr \quad (3.37)$$

where $\Delta\mu/\mu_0$ is the fractional change in the absorption coefficient represented by the ripples; k is the photoelectron wavenumber, $f(k, \pi)$ is the backscattering amplitude, L is the photoelectron mean-free path, $\alpha(k)$ is the scattering phaseshift. Each element i in a binary mixture will have its own absorption edge and two partial distributions, g_{ii} and g_{ij} , will control the backscattering. Despite the difficulties of extracting anything about $g_{ij}(r)$ from EXAFS, methods of analysis have been evolved (Lee *et al* 1981, Teo and Joy 1981) and applications to liquids and glasses can be found in Lee *et al* (1981), Teo and Joy (1981) and Bianconi *et al* (1983). For example the EXAFS of Ni in an amorphous Ni–Mo alloy could be fitted accurately with equation (3.37) if Ni were assumed to have 3.6 Mo neighbours at 2.59 Å and 8.4 Ni neighbours at 2.36 Å. EXAFS has made significant contributions to the understanding of glass structures (§10.6).

The fields from neighbouring atoms affect the magnetic, quadrupole and Mössbauer resonances of nuclei. Therefore, these phenomena can also furnish clues about SRO. For example, a given environment results in a characteristic Mössbauer spectrum. In a disordered structure a range of environments will result in a range of superposed spectra. It may be possible to devise models of SRO which would result in the observed spectra. As with scattering and EXAFS, there is a considerable distance in data processing and interpretation to be traversed before structural inferences can be reached. An application of NMR to glassy solids is in §10.6.

It has several times been remarked that scattering experiments measure only $g(r)$ or $g_{ij}(r)$ and that this is a serious limitation. It should be added however that the triplet distribution is theoretically related to the variation with pressure of the pair distribution. Since scattering experiments can be performed at more than one pressure, $(\partial S(Q)/\partial p)_T$ can in principle tell us something about $g^{(3)}$. The theory and an experimental application are given in Egelstaff *et al* (1971a).

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MONTE CARLO AND MOLECULAR DYNAMICS METHODS

The complicated configuration of atoms in a disordered structure and our lack of detailed knowledge about it make the routine application of quantum mechanics and statistical mechanics very difficult. The partition function can be obtained only by approximate methods even if simplifications are used for the interparticle potentials. Approximate theoretical methods are not lacking but they have been supplemented since the 1950s by numerical calculations with computers. The two most important of these will be introduced in this chapter.

These numerical simulation methods may be a source of information about some things, such as the triplet distribution, which cannot be obtained from experiment. However their chief value probably lies in their ability to proceed from a well defined physical model to accurate numerical consequences. The latter can then be used to test approximate theories applied to the same physical model. In many ways this is better than testing the theory against observations on real matter because, even if there were no experimental errors, the assumed model might not suit the real sample.

Only the principles of these methods will be described. As with laboratory techniques, there are numerous tricks of the trade for which the specialist literature must be consulted.

The second object of this chapter will be to set out some results of the numerical methods which have particular relevance to the subjects in the rest of the book.

4.1 The Monte Carlo method

It will be convenient to recall first some formulae from statistical mechanics. If the systems in an ensemble have prescribed V , N and T the ensemble is canonical and the normalised probability that a system is in its i th quantum state with energy E_i is

$$P_i = \exp(-\beta E_i) / Z \quad (4.1a)$$

where

$$Z \equiv \sum_i \exp(-\beta E_i) \quad (4.1b)$$