

# Crystal Structure and Dynamics

*Paolo G. Radaelli*, Michaelmas Term 2014

## *Part 2: Scattering theory and experiments*

### *Lectures 6-8*

Web Site:

<http://www2.physics.ox.ac.uk/students/course-materials/c3-condensed-matter-major-option>

---

### Bibliography

- **B.E. Warren**, *X-ray diffraction* Dover Publications, Inc., New York, 2nd Ed. 1990. is a rather old book with a very dated notation, but somehow I always find myself going back to it. Some of the explanations are very clear.
- **G.L. Squires** *Introduction to thermal neutron scattering* Dover Publications, Cambridge, New York, 1978 is a classic introductory book, and has all the basic derivations of nuclear and magnetic cross sections.
- **John D. Jackson** '*Classical Electrodynamics* John Wiley & sons, New York, Chichester, Brisbane, Toronto, Singapore, (1975). This book provides detailed derivation of the classical X-ray scattering cross section. It is a very complete compendium of electrodynamics, although not always easy to digest...
- **Stephen W. Lovesey**, *Theory of neutron scattering from condensed matter*, Oxford Science Publications, Clarendon Press, Oxford (1984) — in 2 volumes. This is “the” textbook on the theory of neutron scattering and related matters.
- **E. H. Kisi** *Applications of neutron powder diffraction* Oxford University Press, Oxford, New York, 2008 is a more recent book on neutron diffraction, focussing on the powder method.
- **André Authier** *Dynamical Theory of X-ray Diffraction*, International Union of Crystallography, Oxford University Press (Oxford, New York), 2001. This is a very complete book on the dynamical theory of X-ray scattering. It has a good historical introduction and some simple explanations of the phenomena.
- **P.J. Grundy & G.A. Jones** *Electron Microscopy in the Study of Materials*, (Edward Arnold Ltd. London: UK, 1976). A handy booklet on electron microscopy, a bit old but still useful to understand how dislocations can be imaged.
- **S.J.L. Billinge & M.F. Thorpe** *Local structure from diffraction*, Kluwer Academic Publishers New York, Boston, Dordrecht, London, Moscow, 2002. A good collection of articles on diffuse scattering and scattering from disordered materials.

# Contents

<b>1</b>	<b>Lecture 6 — Scattering from individual atoms and spins</b>	<b>3</b>
1.1	Thomson scattering of X-rays from a single electron . . . . .	3
1.2	Thomson scattering from many quasi-free electrons . . . . .	5
1.3	X-ray scattering from bound electrons — anomalous scattering . . . . .	7
1.4	Thermal neutron scattering from atoms and spins . . . . .	8
<b>2</b>	<b>Lecture 7 - Scattering from crystals</b>	<b>11</b>
2.1	Cross section for a “small” perfect single crystal . . . . .	11
2.2	Laue and Bragg equations . . . . .	14
2.3	The effect of atomic vibrations — the Debye-Waller factor . . . . .	15
2.4	Finite size effects . . . . .	17
<b>3</b>	<b>Lecture 8 - Diffraction experiments and data analysis</b>	<b>19</b>
3.1	Geometries for diffraction experiments - single crystal diffraction . . . . .	19
3.1.1	Scattering triangles for elastic scattering and the Ewald construction . . .	19
3.2	Scattering triangles for inelastic scattering . . . . .	20
3.3	Powder diffraction and the Debye-Scherrer cones . . . . .	22
3.4	Integrated Intensities . . . . .	22
3.5	Structural solution from diffraction data . . . . .	24
3.5.1	The phase problem . . . . .	24
3.5.2	The Patterson method . . . . .	25
3.5.3	Structural optimisation: least-square refinements . . . . .	26

# 1 Lecture 6 — Scattering from individual atoms and spins

In order to extract information about the *atomic* structure of a crystal, liquid or glass by diffraction, **the wavelength of the probe must be comparable or smaller than the interatomic distances**, which are typically a few Ångstroms ( $10^{-10}$  m, or  $10^{-1}$  nm). Tab. 1 illustrates the typical wavelengths and energies employed for X-ray, neutron and electron diffraction.

Table 1: Typical wavelengths and energies employed for X-ray, neutron and electron diffraction. For electromagnetic radiation,  $E = hc/\lambda$ , with  $hc = 12.4$  KeV · Å; for a non-relativistic particle beam,  $E = \frac{2\pi^2\hbar^2}{m\lambda^2}$ , where  $\frac{2\pi^2\hbar^2}{m} = 82$  meV · Å<sup>2</sup> for neutrons and  $150$  eV · Å<sup>2</sup> for electrons. A typical Transmission Electron Microscope (TEM) can operate at 200 KV raising the electron velocity to 70 % of the speed of light, and some state-of-the-art microscopes can reach the MV range; therefore, relativistic effects need to be taken into account in converting between energy and wavelength.

	$\lambda$	$E$
X-rays	0.1–6 Å	2–150 KeV
neutrons	0.3–10 Å	1–1000 meV
electrons	0.02–3 Å	20 eV–200 KeV

Powerful X-ray, neutron and electron sources and diffraction instruments are available to the experimentalists. For more detail, see the Supplementary Material.

## 1.1 Thomson scattering of X-rays from a single electron

- Bragg diffraction of X-rays is primarily due to the scattering from electrons bound to the atoms of the crystal structure. It is generally a very good approximation to employ the so-called Thomson formula (from J.J. Thomson, Nobel Prize 1906) to calculate the relevant scattering amplitudes and cross sections. This is a bit of a paradox, since the Thomson formula assumes *free* electrons<sup>1</sup>, but the agreement with experiments is nonetheless very good. The Thomson formula is valid in the non-relativistic limit (velocity of the particle  $\ll c$ ).
- By using classical electrodynamics, we can calculate the time-dependent amplitude of the electric field generated at a distance  $R$  from an electron that has been accelerated by an electromagnetic plane wave.

<sup>1</sup>A description of the scattering process beyond the free electron approximation is contained in the Supplementary Material.

- If the time-dependent electric field at the position of the electron is

$$\mathbf{E} = \epsilon E_0 e^{-i\omega t} \quad (1)$$

and the incident polarisation (see fig. 1) is

$$\epsilon = \cos \xi \epsilon_\sigma + \sin \xi \epsilon_\pi \quad (2)$$

then<sup>2</sup>

$$\mathbf{E}(\mathbf{R}, t) = -r_0 \mathbf{E}_0 \frac{e^{i(\mathbf{kR}-\omega t)}}{R} [\cos \xi \epsilon'_\sigma + \sin \xi \cos \gamma \epsilon'_\pi] \quad (3)$$

where

$$r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 2.82 \times 10^{-15} \text{ m} \quad (4)$$

is the *classical radius of the electron*.

- The *scattering angle*  $\gamma$  is the angle between the incident and scattered wavevector (this angle is also known, by longstanding diffraction convention, as  $2\theta$ ). Based on eq. 3, we can make the following observations:

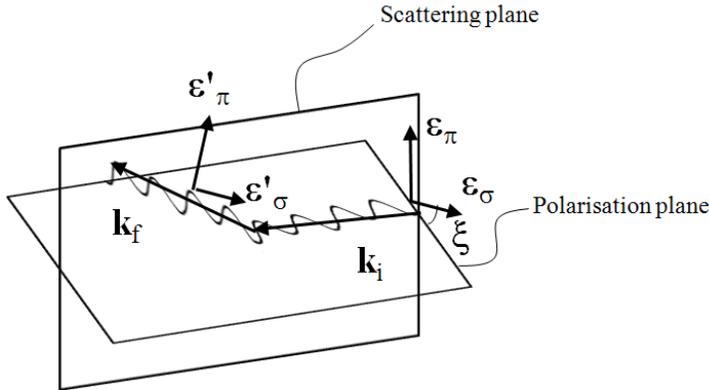


Figure 1: Diagram illustrating the conventional  $\sigma$  and  $\pi$  reference directions for the incident and scattered polarisation. Note that  $\epsilon_\sigma \cdot \epsilon'_\sigma = 1$  *always*. Conversely,  $\epsilon_\pi \cdot \epsilon'_\pi = \cos \gamma$  **depends on the scattering angle**  $\gamma$ , and **vanishes** for  $\gamma = \pi/2$ .

- A plane wave impinging on a quasi-free charge produces a scattered *spherical* wave  $\frac{e^{i(kR-\omega t)}}{R}$ , with an amplitude that in general depends on the scattering angle  $\gamma$ .

<sup>2</sup>See Supplementary Material for a complete derivation.

- If the incident wave is  $\sigma$ -polarised, the scattered wave is  $\sigma'$ -polarised, and has amplitude  $\frac{r_0}{R} E_0$ .
- If the incident wave is  $\pi$ -polarised, the scattered wave is  $\pi'$ -polarised, and has amplitude  $\frac{r_0}{R} E_0 \cos \gamma$ .
- The intensity of the scattered wave is zero for scattering of  $\pi$  polarisation at  $90^\circ$ .
- The scattered wave has a phase shift of  $\pi$  upon scattering (*minus* sign).
- For generic incident polarisation, the *scattering amplitude* (amplitude of the spherical wave) in each scattered polarisation can be written as:

$$A = r_0[\epsilon \cdot \epsilon'] \quad (5)$$

- The *cross section* is defined as the average power radiated per unit solid angle divided by the average incident power per unit area (power flux,  $\Phi$ )
- For an *unpolarised* X-ray beam, all the angles  $\xi$  are equally represented (i.e., there will be photons with all polarisations). The cross section in this case is

$$\boxed{\frac{d\sigma}{d\Omega} = r_0^2 \left[ \frac{1 + \cos^2 \gamma}{2} \right]} \quad (6)$$

## 1.2 Thomson scattering from many quasi-free electrons

- When many electrons are in close proximity to each other, the spherical waves emitted by them will interfere.
- The combined effect of these waves can be calculated in the following approximations:
  - ◊ The amplitude of the motion of the electrons is much smaller than the wavelength.
  - ◊ The distance at which the process is observed is also much larger than the distance between electrons (Fraunhofer diffraction or far-field limit).
  - ◊ The distribution of electrons can be considered continuous, with number density  $\rho(\mathbf{x})$  [electrons/m<sup>3</sup>].

With these approximations, which are always obeyed for the electron cloud around an atom and reasonable values of the electric field)

$$\mathbf{E}(\mathbf{R}, t) = -r_0 \mathbf{E}_0 \frac{e^{i(\mathbf{kR} - \omega t)}}{R} [\cos \xi \epsilon'_\sigma + \sin \xi \cos \gamma \epsilon'_\pi] \int \rho(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} d\mathbf{x} \quad (7)$$

- The vector  $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$  is the **scattering vector** and  $\mathbf{k}_i$  and  $\mathbf{k}_f$  are the incident and scattered wavevectors.
- Note the important formula, valid for elastic scattering (we recall that  $\gamma = 2\theta$ ):

$$q = |\mathbf{q}| = \frac{4\pi \sin \theta}{\lambda} \quad (8)$$

Eq. 8 is illustrated graphically in fig. 2

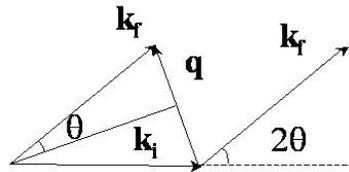


Figure 2: Scattering triangle for elastic scattering.

- The integral

$$f(\mathbf{q}) = \int \rho(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} d\mathbf{x} \quad (9)$$

is known as the **atomic scattering factor or form factor**.

We have arrived here at an important result: **the scattering amplitude for many quasi-free electrons is proportional to the Fourier transform of the charge density**. Note that the integral for  $\mathbf{q} = 0$  is the **total charge**, which for an atom is the atomic number  $Z$  (fig. 3).

**A key fact to remember: the more spread out the charge is around the atom, the faster  $f(\mathbf{q})$  will decay at high  $\mathbf{q}$ .**

**High  $\mathbf{q} \equiv$  high scattering angles, short wavelengths.**

- The cross sections are obtained in the same way as for a single charge — for instance, the unpolarised cross section for an atom is:

$$\left(\frac{d\sigma}{d\Omega}\right)_{atom} = r_0^2 |f(\mathbf{q})|^2 \left[\frac{1 + \cos^2 \gamma}{2}\right] \quad (10)$$

which, in forward scattering, becomes:

$$\left(\frac{d\sigma}{d\Omega}\right)_{atom} = r_0^2 Z^2 \quad (11)$$

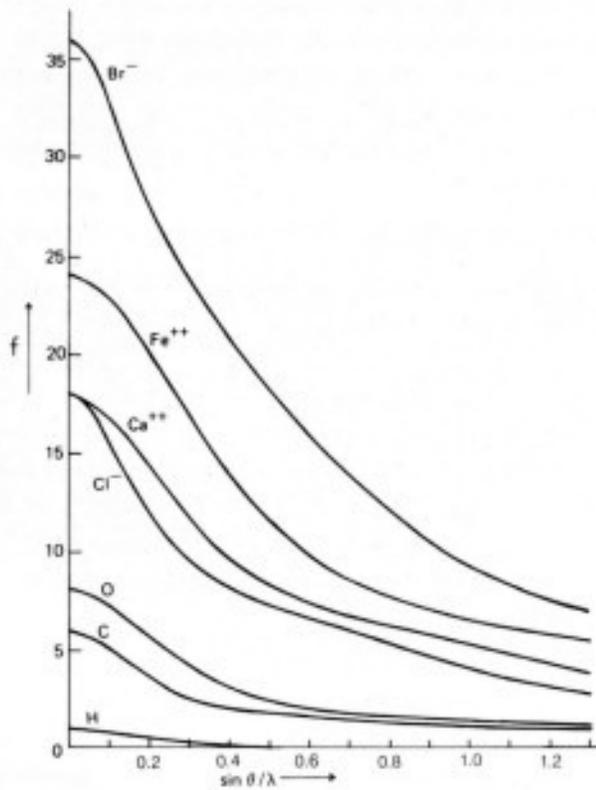


Figure 3: Atomic scattering factors (form factors) for selected neutral atoms and ions. Note that  $\sin \theta/\lambda = q/4\pi$ .

- One can find tabulated values of the form factors for neutral and ionised atoms in the International Tables for Crystallography, volume C, p 555 and p 566, respectively.

### 1.3 X-ray scattering from bound electrons — anomalous scattering

- Truly “free” electrons (e.g., conduction electrons in a metal) hardly contribute to the scattering of X-rays, because their probability distribution

extends a long way throughout the crystal, and, from eq. 9, the form factor decays very rapidly away from forward scattering (fig. 3).

- The largest contribution to X-ray scattering from atoms is given by “core” electrons, which are close to the nucleus and have slowly decaying form factors — but these electrons are certainly not free!
- There are large departures from the Thomson scattering formula near *atomic resonances*, where the energy of the photon is just sufficient to eject an electron from a core state into the continuum. Away from resonances, the Thomson formula can be corrected to a very good approximation by replacing the form factor by the *complex* quantity

$$f(\mathbf{q}) = f_{\text{Thom}}(\mathbf{q}) + f'(\hbar\omega) + if''(\hbar\omega) \quad (12)$$

where the so-called *anomalous terms*,  $f'$  and  $f''$ , away from atomic resonances do not depend on  $q$  and are weak functions of the photon energy<sup>3</sup>.

**It can be shown, as a consequence of the so-called optical theorem, that *the imaginary part of the scattering factor is proportional to the linear absorption coefficient due to the photoelectric effect.***

$$f''(\hbar\omega) = \frac{\omega}{4\pi r_0 c N_a} \mu \quad (13)$$

where  $N_a$  is the number of atoms per unit volume, and the other symbols have the usual meaning. The quantity  $\mu$  is the *linear absorption coefficient*, defined as:

$$I = I_0 e^{-\mu L} \quad (14)$$

## 1.4 Thermal neutron scattering from atoms and spins

- As in the case of X-rays, the neutron scattering process generates a *spherical wave*, the *squared* amplitude of which is proportional to the cross section.
- *Thermal neutrons*, with energies in the meV range, are commonly used to probe condensed matter. Their properties can be summarised as follows:
  - ◊ Free neutrons are unstable, with half-life  $\tau = 10.6$  min. ( $\beta$ -decay)

<sup>3</sup>See Supplementary Material for more details about resonant X-ray scattering.

- ◇ Neutrons bound in nuclei are (generally) stable.
- ◇ Mass:  $1.67492729(28) \times 10^{-27}$  kg
- ◇ Electric dipole moment  $D < 10^{-25}$  (e cm)
- ◇ Spin:  $s = \frac{1}{2}$  — neutrons are *fermions*.
- ◇ Magnetic dipole moment:  $\mu = -1.9130418 \mu_N$ , where  $\mu_N = \frac{e\hbar}{2m_p} = 5.05078324(13) \times 10^{-27}$  JT<sup>-1</sup> is the **nuclear magneton**.

Table 2: Neutron wavelenghts and kinetic energies in different “slow” ranges. The thermal energy per particle at room temperature is 25 meV.

	$\lambda$ (Å)	$E$ (meV)
Cold	3–30	0.1-10
Thermal	1–3	10–100
Hot	0.4–1	100–500
Epithermal	< 0.4	> 500

- Neutrons are elastically or inelastically scattered by the condensed matter through two completely different mechanisms, but, as it turns out, yielding comparable scattering lengths.
  1. By **nuclear interaction with the atomic nuclei**.
  2. By **dipole interaction with the unpaired spin and orbital magnetic moments of the atoms**. This is only present if the atom or ion has a magnetic moment.
- A summary of the key results is provided here below<sup>4</sup>.

---

<sup>4</sup>See Supplementary Material for a complete derivation of the nuclear and magnetic neutron cross sections

### Neutron-nuclear interaction

- The neutron-nuclear interaction is **isotope and elements specific**, and **depends on the mutual orientation of the neutron and the nuclear spin**.
- As far as neutron crystallography is concerned, **the key parameter is the scattering amplitude averaged over the nuclear spin states**, known as the **coherent scattering amplitude**.
- The neutron nuclear coherent scattering amplitude **is independent on  $q$**  — it carries **no form factor**, and is therefore expressed by a single number, known as the **Fermi length**.
- **Fermi lengths can be positive or negative, depending on whether the neutron-nuclear interaction is attractive or repulsive**. For typical nuclei, they are of the order of a few fm ( $10^{-15}$  m) (see fig 4), which means that they **are comparable to the classical electron radius**. However, atoms have a single nucleus and many electrons, so X-ray scattering cross sections in the *forward* direction are typically much larger than neutron cross sections (X-ray cross sections decay at high  $q$  due to the form factor).
- Fermi lengths do not vary in a systematic way across the periodic table (fig 4), which means that **with respect to X-rays, neutrons are uniquely sensitive to some light elements** — **notably oxygen**. The different scattering lengths of different isotopes is also widely exploited in the so-called **contrast variation techniques**.

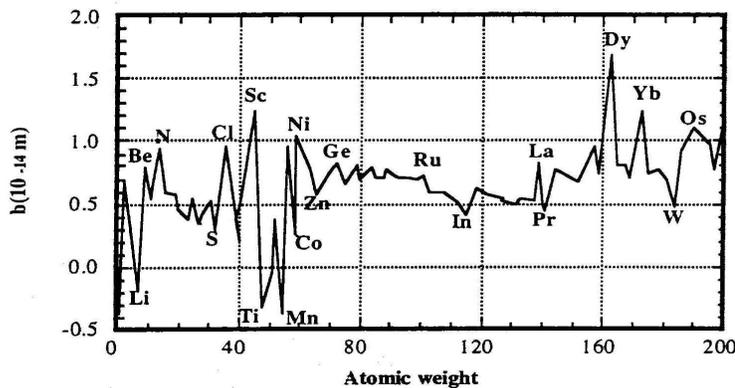


Figure 4: Variation of the Fermi length as a function of atomic weight.

### Neutron-magnetic interaction

- When the scatterer carries a magnetic moment, in addition to the normal nuclear interaction, neutrons are also scattered by dipole-dipole interaction from the magnetic moment of the atom.
- Magnetic scattering of neutrons is governed by the following **vector** scattering amplitude.

$$\mathbf{A}_n = \gamma_N r_0 f_m(\mathbf{q}) \mathbf{M}_\perp \quad (15)$$

where  $\gamma_N$  is the neutron gyromagnetic ratio ( $-1.9130418$ ),  $r_0$  is the familiar **classical electron radius** and  $\mathbf{M}_\perp$  is the **projection of the atomic magnetic moment perpendicular to the wavevector transfer  $\mathbf{q}$** , and is expressed in **Bohr magnetons**.

- The quantity  $f_m(\mathbf{q})$  is known as the **neutron magnetic form factor**, and is normalised so that  $f_m(0) = 1$ . It is similar to the X-ray form factor, except for the fact that it only includes the more extended **density of unpaired electrons**. Therefore **magnetic neutron scattering decays very rapidly at high  $q$** .
- From eq. 15 one can obtain a **number of cross sections**, accounting for the different orientations of the neutron spin with respect to the atomic magnetic moment (**neutron polarisation**). The most important cross section is the **unpolarised neutron cross section** (averaged over all the possible neutron polarisations), which, for a *single* atom, is:

$$\frac{d\sigma}{d\Omega} = \gamma_N^2 r_0^2 f_m^2(\mathbf{q}) |\mathbf{M}_\perp|^2 = \gamma_N^2 r_0^2 f_m^2(\mathbf{q}) M^2 \sin^2 \alpha \quad (16)$$

where  $\alpha$  is the angle between  $\mathbf{M}$  and  $\mathbf{q}$ . Note that **the cross section is zero if  $\mathbf{q}$  is parallel to  $\mathbf{M}$** .

- Typical magnetic moments for atoms and ions are **a few Bohr magnetons**. Therefore, from eq. 16, one finds that **neutron nuclear and magnetic scattering cross sections are typically comparable in magnitude for magnetic atoms**.

## 2 Lecture 7 - Scattering from crystals

### 2.1 Cross section for a “small” perfect single crystal

- We want to calculate the scattering cross section from a “small” single crystal. Here, “small” means that we can ignore multiple scattering events. We still consider the crystal as perfectly periodic.
- We will employ the same approximations that we have used for the scattering from many quasi-free electrons (the far-field approximation is not obeyed in some relevant cases, but we will not concern ourselves with them).
- We will consider the case of X-rays, but the calculation is analogous for neutrons. The scattering amplitude in each final polarisation direction is obtained by integrating over the whole crystal (instead that around an atom, as for eq. 7):

$$A(\mathbf{q}) = r_0 \int_{\text{Crystal}} d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'] \quad (17)$$

- We can exploit the fact that the charge density is periodic, so that, if  $\mathbf{r}_i$  is a lattice translation and  $\mathbf{x}$  is restricted to the unit cell containing the origin:

$$\rho(\mathbf{r}) = \rho(\mathbf{r}_i + \mathbf{x}) = \rho(\mathbf{x}) \quad (18)$$

whence the scattering amplitude becomes

$$\begin{aligned} A(\mathbf{q}) &= r_0 \sum_i \int_{\text{Unit Cell}} d\mathbf{x} \rho(\mathbf{x}) e^{-i\mathbf{q}\cdot(\mathbf{r}_i+\mathbf{x})} [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'] \\ &= r_0 \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} \int_{\text{Unit Cell}} d\mathbf{x} \rho(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}} [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'] \end{aligned} \quad (19)$$

where the summation runs over all the unit cells in the crystal. The expression

$$F(\mathbf{q}) = r_0 \int_{\text{Unit Cell}} d\mathbf{x} \rho(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}} \quad (20)$$

is known as the **structure factor**. Note the close analogy with eq. 32, Part I.

**The structure factor is proportional to the Fourier transform of the charge density (or, more in general, scattering density) integrated over the unit cell.**

- If the electron density  $\rho(\mathbf{r})$  is a superposition of atomic-like electron densities (i.e., a series of  $\delta$  functions),  $F(\mathbf{q})$  can be written as

$$F(\mathbf{q}) = r_0 \sum_n f_n(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{x}_n} \quad (21)$$

where the sum runs over all the atoms in the unit cell and  $f_n(\mathbf{q})$  are the form factors of each species and  $\mathbf{x}_n$  are their positions within the unit cell.

- We can now calculate the **cross section**:

$$\frac{d\sigma}{d\Omega} = A(\mathbf{q}) \mathbf{A}^*(\mathbf{q}) = \left( \sum_j \sum_i e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right) |\mathbf{F}(\mathbf{q})|^2 [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}']^2 \quad (22)$$

- We now introduce the fact that the double summation in parentheses can be considered as running over an infinite lattice. Consequently, all the summations over  $i$  labelled by  $\mathbf{r}_j$  are the same (they only differ by a shift in origin), and the summation over  $j$  can be replaced by multiplication by  $N_c$  — the number of unit cells in the crystal ( $\rightarrow \infty$ ).
- The remaining single summation is only non-zero when  $\mathbf{q}$  is a  $RL$  vector. If  $\mathbf{q}$  is restricted to the first Brillouin zone, we can write:

$$\delta(\mathbf{q}) = \frac{1}{(2\pi)^3} \int d\mathbf{x} e^{-i\mathbf{q} \cdot \mathbf{x}} \simeq \frac{v_0}{(2\pi)^3} \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} \quad (23)$$

where  $v_0$  is the unit cell volume. For an unrestricted  $\mathbf{q}$ , the same expression holds with the left-hand member replaced by a sum of delta functions centred at all reciprocal lattice nodes, indicated with  $\boldsymbol{\tau}$  in the remainder. With this, we can write the final expression for the cross section:

$$\frac{d\sigma}{d\Omega} = N_c \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta(\mathbf{q} - \boldsymbol{\tau}) |F(\boldsymbol{\tau})|^2 [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}']^2 \quad (24)$$

- The term  $[\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}']^2$  needs to be averaged over all this incident and scattered polarisations, yielding a **polarisation factor**  $\mathcal{P}(\gamma)$ , which depends on the experimental setting. For example, for an unpolarised incident beam and no polarisation analysis:

$$\mathcal{P}(\gamma) = \left[ \frac{1 + \cos^2 \gamma}{2} \right] \text{ unpolarised beam} \quad (25)$$

- The final general expression for the average cross section is:

$$\frac{d\sigma}{d\Omega} = N_c \frac{(2\pi)^3}{v_0} \sum_{\tau} \delta(\mathbf{q} - \tau) |F(\tau)|^2 \mathcal{P}(\gamma) \quad (26)$$

Let's recap the key points to remember:

- ◇ **The cross section is proportional to the number of unit cells in the crystal. The bigger the crystal, the more photons or particles will be scattered. We can clearly see that this result *must* involve an approximation: the scattered intensity must reach a limit when all the particles in the beam are scattered.**
- ◇ **The cross section is proportional to the squared modulus of the structure factor (no surprises here — you should have learned this last year).**
- ◇ **Scattering only occurs at the nodes of the *RL*. For a perfect, infinite crystal, this is in the form of delta functions.**
- ◇ **The cross section contains the unit-cell volume in the denominator. This is necessary for dimensional reasons, but it could perhaps cause surprise. After all, we could arbitrarily decide to *double* the size of the unit cell by introducing a “basis”. The answer is, naturally, that the  $|F(\tau)|^2$  term exactly compensates for this.**

- The limitations of the *small crystal approximation* can be overcome by complete description of the scattering process, including *multiple scattering*, in what is known as **dynamical theory of diffraction** (see extended version of the notes for a very short introduction).

## 2.2 Laue and Bragg equations

- The  $\delta$  function in eq. 24 expresses the fact that the cross section is zero unless  $\mathbf{q}$  is equal to one of the *RLV*.
- This is more traditionally expressed by the *Laue equations*:

$$\mathbf{q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (27)$$

$$\begin{aligned} \mathbf{q} \cdot \mathbf{a}_1 &= (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{a}_1 = 2\pi h \\ \mathbf{q} \cdot \mathbf{a}_2 &= (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{a}_2 = 2\pi k \\ \mathbf{q} \cdot \mathbf{a}_3 &= (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{a}_3 = 2\pi l \end{aligned} \quad (28)$$

- $h, k$  and  $l$  are the **Miller indices** that we have already encountered.
- The *modulus* of the scattering vector (fig. 2 and eq. 8) is:

$$q = |\mathbf{q}| = \frac{4\pi \sin \theta}{\lambda} \quad (29)$$

- Given a *RLV*  $\mathbf{q}$  with Miller indices  $hkl$ , it can be shown by simple geometry that there exist a family of *parallel real-lattice planes* perpendicular to it, and that the distance between two adjacent planes is  $d = 2\pi n/q$ , where  $n$  is the greatest common divisor of  $h, k$  and  $l$ .
- From this and eq. 29, one can deduce that the scattering process can be thought as a mirror reflection from this family of planes, with the addition of **Bragg law**:

$$2d \sin \theta = n\lambda \quad (30)$$

### 2.3 The effect of atomic vibrations — the Debye-Waller factor

- Atoms are always displaced away from their “ideal” positions, primarily due to thermal vibrations, but also due to crystal defects. This has an effect on the scattering cross section.
- We can re-write the expression of the scattering amplitude (eq. 19), taking into account the effect of these displacements (we omit the polarisation factor  $[\epsilon \cdot \epsilon']$  for simplicity):

$$A(\mathbf{q}) = r_0 \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} \sum_n f_n(\mathbf{q}) e^{-i\mathbf{q} \cdot (\mathbf{x}_n + \mathbf{u}_{n,i})} \quad (31)$$

where  $\mathbf{u}_{n,i}$  is the *displacement vector* characterising the position of the atom with label  $n$  in the  $i^{\text{th}}$  unit cell.

- Bragg scattering results from **time averaging of the scattering amplitude** (*not* the cross section). The effect of this is that<sup>5</sup>

---

<sup>5</sup>See Supplementary Material for a more complete derivation, including the temperature dependence of the D-W factors.

**Atomic vibrations “smear out” the scattering density, acting, in a sense as an additional “form factor”.**

- ◇ **The higher the temperature, the more the atoms will vibrate, the more the intensity will decay at high  $q$ . This is easily understood by analogy with the form factor  $f(q)$ : the more the atoms vibrate, the more “spread” out the scattering density will be, the faster the scattering will decay at high  $q$ .**
- ◇ **The *softer* the spring constants, the more the atoms will vibrate, the more the intensity will decay at high  $q$ .**
- ◇ **The *lighter* the atoms, the more the atoms will vibrate, the more the intensity will decay at high  $q$ .**

- The time averaging can be expressed as:

$$A(\mathbf{q}) = r_0 \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} \sum_n f_n(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{x}_n} \langle e^{-i\mathbf{q}\cdot\mathbf{u}_{n,i}} \rangle \quad (32)$$

- The term in  $\langle \rangle$  represents the time averaging and does not depend on the specific atomic site  $i$ . One can show (see extended version of the notes on web site) that

$$\langle e^{-i\mathbf{q}\cdot\mathbf{u}_{n,i}} \rangle = e^{-W(\mathbf{q},n)}. \quad (33)$$

where, in the simple isotropic case

$$W(\mathbf{q}, n) = U_n q^2 \quad (34)$$

- With this, we obtain the **general expression for the X-ray structure factor in the isotropic case**

$$F(\mathbf{q}) = r_0 \sum_n f_n(q) e^{-i\mathbf{q}\cdot\mathbf{x}_n} e^{-U_n q^2} \quad (35)$$

- A very similar expression is found for the **coherent neutron structure factors for nuclear scattering**.

$$F(\mathbf{q}) = \sum_n b_n e^{-i\mathbf{q}\cdot\mathbf{x}_n} e^{-U_n q^2} \quad (36)$$

- The corresponding formula for **magnetic scattering of neutrons from a collinear ferromagnet or antiferromagnet** is

$$F(\mathbf{q}) = \gamma_N r_0 \sum_n f_n(\mathbf{q}) M_n \sin \alpha e^{-i\mathbf{q} \cdot \mathbf{x}_n} e^{-U_n q^2} \quad (37)$$

where  $M_n$  (expressed in Bohr magnetons) reflects both the magnitude and the sign of the magnetic moment of atom  $n$ , and  $f_{m_n}(\mathbf{q})$  is the corresponding magnetic form factor and  $\alpha$  is the angle between  $\mathbf{M}$  and  $\mathbf{q}$

- Real crystals are not perfectly periodic, due to the presence of *defects*, *lattice vibrations* and, quite simply, the fact that they are of finite size.
- In scattering experiments, *deviation from perfect periodicity results in scattering outside the RL nodes*.
- *Static defects* produce elastic *elastic scattering*, known as *diffuse scattering* because of the fact that it not strongly peaked as Bragg scattering.
- *Dynamic effects* (such as lattice vibrations) produce *inelastic scattering*.
- In a diffraction experiment, one does not analyse the energy of the scattered particle, and both effects contribute to the diffuse scattering. Scattering from phonons is known as *thermal diffuse scattering*.
- *Extended defects* (involving planes or lines of defects) are described in the extended version of the notes.

## 2.4 Finite size effects

- In the case of an infinite perfect crystal, the cross section is a series of  $\delta$  functions centred at the *RL nodes*, This is a result of the infinite summation over all the real lattice nodes.
- If we carry out a *finite* summation instead, for example over  $N_1, N_2$  and  $N_3$  unit cell in the  $\mathbf{a}_1, \mathbf{a}_2$  and  $\mathbf{a}_3$  directions, and remembering that

$$\sum_{n=-N}^N e^{-inx} = \frac{\sin\left(\left(2N+1\right)\frac{x}{2}\right)}{\sin\frac{x}{2}} \quad (38)$$

we obtain (in each direction,  $x$  in eq. 38 is  $= \mathbf{q} \cdot \mathbf{a}_i$ )

$$\frac{d\sigma}{d\Omega} = \left[ \prod_i \frac{\sin^2\left(N_i \frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i\right)}{\sin^2\left(\frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i\right)} \right] |F(\mathbf{q})|^2 [\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}']^2 \quad (39)$$

- This oscillatory function will be in general smeared out by coherence effects (see long versions of the notes), and can be approximated as

$$\frac{d\sigma}{d\Omega} = N_c^2 \left[ \prod_i e^{-(N_i \frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i)^2 / \pi} \right] |F(\mathbf{q})|^2 [\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}']^2 \quad (40)$$

where the Gaussian functions have variance and FWHM

$$\begin{aligned} \sigma_i^2 &= \frac{2\pi}{N_i^2 a_i^2} \\ FWHM &= \frac{4\sqrt{\pi \ln 2}}{N_i a_i} \end{aligned} \quad (41)$$

- We can therefore conclude that:
  - ◊ The **cross section at a given  $\mathbf{q}$**  is proportional to  $N_c^2$ .
  - ◊ The **width** in  $\mathbf{q}$  is *inversely proportional to the number of unit cells along that direction*.
  - ◊ The **integrated cross section** in three dimensions (remember the Gaussian integral  $\sqrt{2\pi\sigma^2}$ ) is therefore proportional to  $N_c$ , which reproduces the result we obtained for the infinite crystal (eq. 8, lecture 6).

### 3 Lecture 8 - Diffraction experiments and data analysis

#### 3.1 Geometries for diffraction experiments - single crystal diffraction

In general, the experimental apparatus to perform a diffraction experiment on a single crystal or a collection of small crystals (powder diffraction) will consist of (fig. 5):

- ◇ An **incident beam**, which can be **monochromatic** or **polychromatic**.
- ◇ A **sample stage**, which enables the sample to be oriented and also incorporates the **sample environment** to control a variety of physical ( $P$ ,  $T$ ,  $H...$ ) and/or chemical parameters.
- ◇ A **detector**, which includes a detector of photons or particles. This is normally mounted on a separate arm, enabling the  $2\theta$  angular range to be varied.

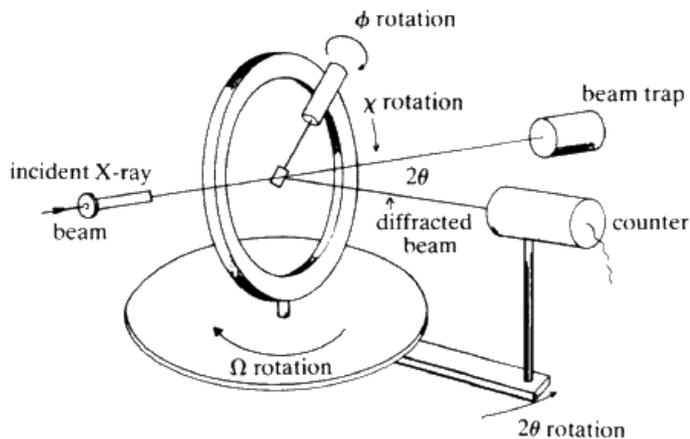


Figure 5: The geometry of a “four circle” single-crystal diffractometer. The “four circles” (actually four axes) are marked “ $\phi$ ”, “ $\chi$ ”, “ $\Omega$ ” and “ $2\theta$ ”. The  $2\theta$  and  $\Omega$  angles are also known as  $\gamma$  and  $\eta$ .

##### 3.1.1 Scattering triangles for elastic scattering and the Ewald construction

- As we have seen, the scattering cross section for a single crystal is a series of delta functions in reciprocal space, centred at the nodes of the reciprocal lattice.

- When a single crystal is illuminated with monochromatic radiation, the scattering conditions are satisfied only for particular orientations of the crystal itself — in essence, the specular (mirror-like) reflection from a family of lattice planes must satisfy Bragg law at the given wavelength.

**With monochromatic radiation, for a generic crystal orientation, no Bragg scattering will be observed at all.**

- Fig. 6 show the geometrical construction used to establish when the scattering conditions are satisfied. Note that here we employ the **diffraction convention**:  $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$  (see below for the inelastic conventions).
- A typical problem will state the wavelength  $\lambda$  of the incident and scattered radiation (which are the same, since the scattering is elastic), the symmetry and the lattice parameters of the material and the Bragg reflection to be measured (given in terms of the Miller indices  $hkl$ ). These data are sufficient to determine  $k_i = k_f = 2\pi/\lambda$  and  $q$  (for a right-angle lattice  $q = 2\pi\sqrt{h^2/a^2 + k^2/b^2 + l^2/c^2}$ ; see previous lectures for formulas to calculate  $q$  in the general case).
- Since all the sides of the scattering triangle are known, it is possible to determine all the angles — in particular the scattering angle  $\gamma = 2\theta$  and the orientation of the incident beam with respect to the lattice required to be in scattering condition.
- The circle shown in fig. 6 is actually a sphere in 3D, and defines the *locus* of all the possible scattering vectors for a given  $\mathbf{k}_i$ . This is known as the **Ewald sphere**, from the German physicist Paul Peter Ewald (1888, 1985).
- The maximum value of  $q$  is achieved for  $\gamma = 2\pi$  (*backscattering*), and is  $\mathbf{q} = -2\mathbf{k}_i$
- The nodes "accessible" by scattering are contained within a sphere of radius  $2k_i = 4\pi/\lambda$ , centered on the origin of reciprocal space, so that

$$0 \leq q \leq 2k_i \quad (42)$$

### 3.2 Scattering triangles for inelastic scattering

- For inelastic scattering, the **inelastic convention**:  $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$  is generally employed, so that  $\mathbf{q}_{\text{dif}} = -\mathbf{q}_{\text{ine}}$ .

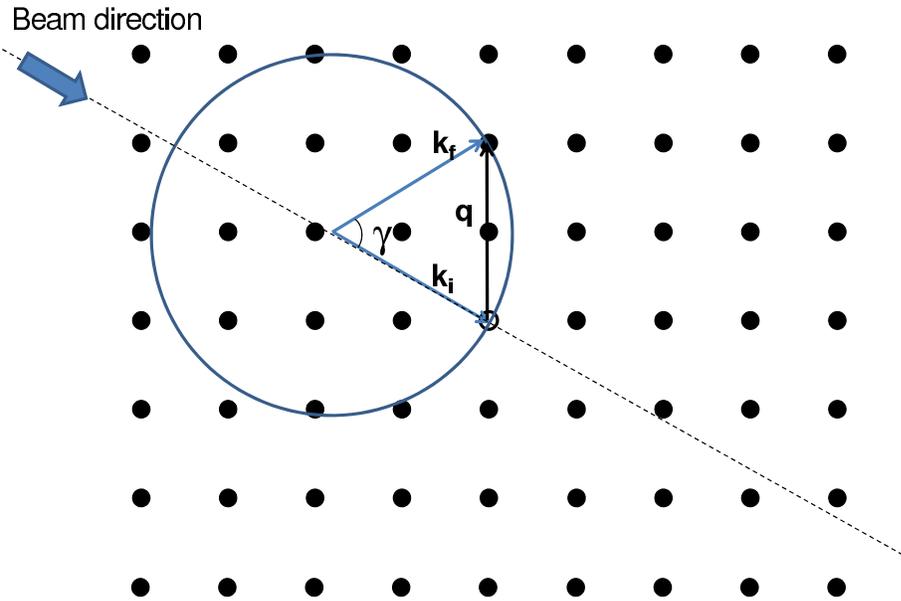


Figure 6: The procedure to construct the scattering triangle for elastic scattering.

- In an inelastic scattering experiment, the scattered particle loses (**energy loss scattering**) or gains (**energy gain scattering**) part of its energy, and a corresponding amount of energy is transferred to or from an excitation in the crystal such as a *phonon* or a *magnon*. In constructing the scattering triangle, we should therefore allow for the fact that  $k_f$  will be either larger or smaller than  $k_i$ .

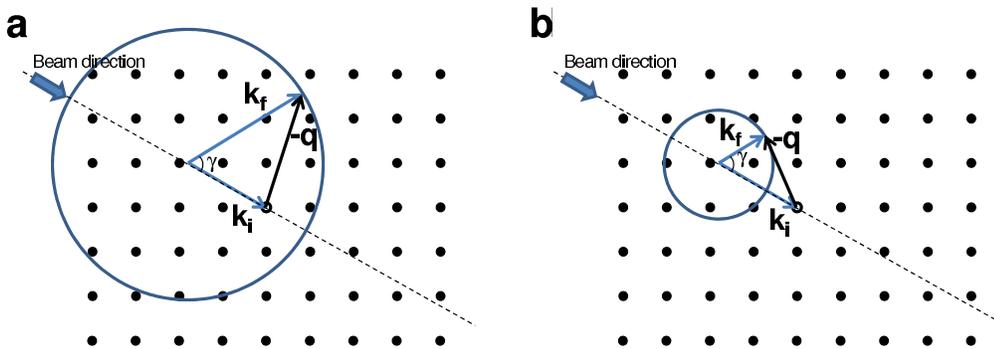


Figure 7: The procedure to construct the scattering triangle for inelastic scattering. (a) energy gain; (b) energy loss.

- The corresponding constructions are shown in 7. One can see that eq. 42 should be replaced by

$$|k_i - k_f| \leq q \leq k_i + k_f \quad (43)$$

- The region of reciprocal space "accessible" by scattering is bounded by

two spheres of radius  $k_i + k_f$  and  $|k_i - k_f|$ , centered on the origin of reciprocal space.

- Maximum and minimum  $q$  are achieved in backscattering and forward scattering, respectively.

### 3.3 Powder diffraction and the Debye-Scherrer cones

- A “powder” sample is a more or less “random” collection of small single crystals, known as “crystallites”.
- The cross section for the whole powder sample depends on the *modulus* of the scattering vector  $q$  but not on its direction. Therefore, when a powder sample is illuminated, scattering is always observed (unlike the case of a single crystal).
- For a monochromatic incident beam, the  $2\theta$  angle *between* the incident and scattered beam is fixed for a given Bragg reflection, but the angle *around* the incident beam is arbitrary. The *locus* of all the possible scattered beams is a **cone** around the direction of the incident beam (fig. 8).
- All the symmetry-equivalent  $RL$  nodes, having the same  $q$ , *contribute to the same D-S cone* (fig. 9).
- *Accidentally degenerate* reflections, having the same  $q$  but unrelated  $hkl$ 's, also contribute to the same D-S cone. This is the case for example, for reflections  $[333]$  and  $[115]$  in the cubic system, since  $3^2 + 3^2 + 3^2 = 1^2 + 1^2 + 5^2$ .

#### Key points to retain about powder diffraction

- ◇ In powder diffraction methods, the intensity around the D-S cones is *always integrated*, yielding a 1-dimensional pattern.
- ◇ Powder diffraction peaks are usually well-separated at low  $q$ , but become increasingly crowded at high  $q$  often becoming completely overlapped. This substantially reduce the amount of information available to solve or refine the structure precisely (see below).

### 3.4 Integrated Intensities

- Exam problems will not be concerned with peak fitting, and you will be given integrated intensities of some form. These intensities will be usually

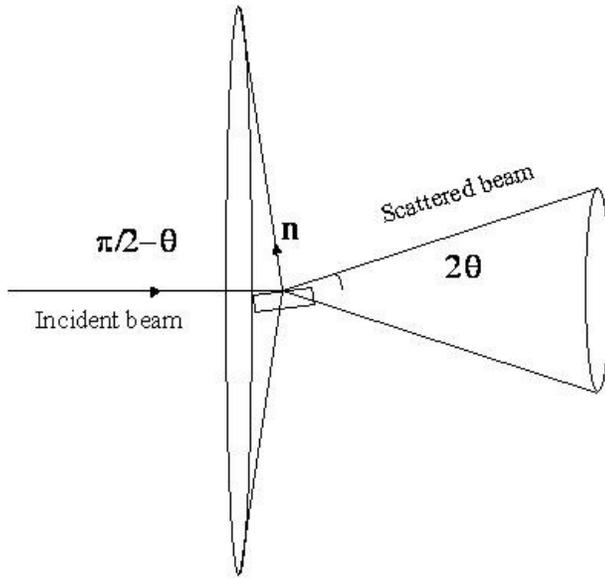


Figure 8: Debye-Scherrer cones and the orientations of the sets of Bragg planes generating them.

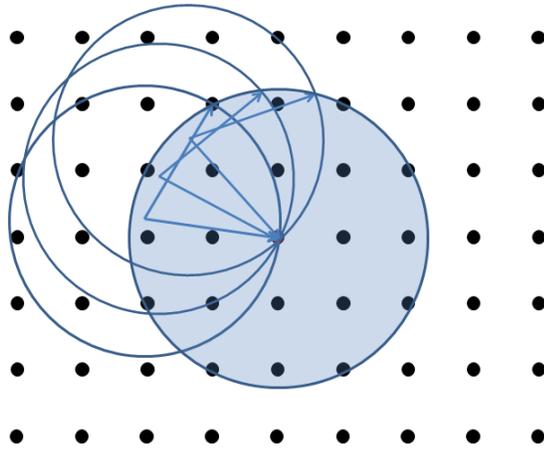


Figure 9: Ewald construction for powder diffraction, to represent the crystal being rotated randomly around the direction of the incident beam (the figure actually shows the opposite, for clarity). Note that many  $RL$  nodes are simultaneously in scattering — those that have the same  $|q|$ . Symmetry-equivalent reflections have the same  $|q|$  and also the same structure factor. The powder intensity is therefore multiplied by the number of symmetry-equivalent reflections, known as the *multiplicity*.

corrected for the Lorentz - polarisation (i.e.,  $\mathcal{P}(\gamma)$ ), angle-dependent attenuation (typically due to X-ray or neutron absorption) and incident flux terms, but the role these terms may be requested as part of the discussion. The integrated intensity can always be reduced to a dimensionless quantity (counts).

- The general expression for the integrated intensity (number of particles) is

$$P_{\tau} = N_c \left( \frac{d^3}{v_0} \right) m_{\tau} |F(\boldsymbol{\tau})|^2 \mathcal{P}(\gamma) \mathcal{L}(\gamma) \mathcal{A}_{\tau}(\lambda, \gamma) \mathcal{F}_{inc} \quad (44)$$

- $N_c$  is the number of unit cells in the sample.
  - $d$  is the d-spacing of the reflection.
  - $v_0$  is the unit-cell volume.
  - $m_{\tau}$  (powder diffraction only) is the *number of symmetry-equivalent reflections*. This accounts for the fact that in powder diffraction these reflections are not separable, and will always contribute to the same Bragg powder peak (see previous discussion and fig. 9).
  - $\mathcal{P}(\gamma)$  is the *polarisation factor* (dimensionless), which we have already introduced.
  - $\mathcal{L}(\gamma)$  is the so-called *Lorentz factor* (dimensionless), and contains all the experiment-specific geometrical factors arising from the  $\delta$ -function integration.
  - $\mathcal{A}_{\tau}(\lambda, \gamma)$  (dimensionless) is the *attenuation and extinction coefficient*, which account for the beam absorption and for dynamical effects.
  - $\mathcal{F}_{inc}$  is the incident time-integrated flux term (counts per square metre), which accounts for the strength of the incident beam and for the counting time.
- The product  $(d^3/v_0)\mathcal{P}(\gamma)\mathcal{L}(\gamma)\mathcal{A}_{\tau}(\lambda, \gamma)$ , is sometimes called the **LPGA factor** (Lorentz-Polarisation-Geometrical-Attenuation), and is used to correct the raw data. When absolute incident flux measurements are not available, one obtains a pattern where the intensities are proportional to the square of the structure factor, the proportionality constant being a *scale factor*.

## 3.5 Structural solution from diffraction data

### 3.5.1 The phase problem

- From eq. 20, we can see that **the structure factor is proportional to the Fourier transform of the charge density (or, more in general, scattering density) integrated over the unit cell**.
- By the elementary theory of the Fourier transform over a finite interval (extended to 3 dimensions) we can calculate the charge density given all the structure factors:

$$\rho(\mathbf{x}) = \frac{1}{r_0 v_0} \sum_{\tau} \mathbf{F}(\tau) e^{i\tau \cdot \mathbf{x}} \quad (45)$$

- From eq. 45 follows that *if we were able to measure all the structure factors, we could reconstruct the charge density exactly*. Clearly, it is impossible to measure all the infinite nodes of the reciprocal space, but it can be shown that it would be sufficient to measure up to a value of  $q_{max}$  to obtain a **Fourier map** with **resolution**  $2\pi/q_{max}$  in *real space*.
- However, direct reconstruction of the charge density from diffraction data is impossible, because only the *amplitudes* of the structure factors are known (through the term  $|F|^2$  in the cross section), while the *phases* are unknown. Solving a crystal structure is therefore equivalent to *phasing* the reflections.
- A set of mathematical methods, known as **direct methods**, have been developed to phase reflections without any *a priori* knowledge of the crystal structure. They exploit the fact that the *Fourier maps* are not completely arbitrary, but are *positive* (for X-rays) and *atomic-like*.

### 3.5.2 The Patterson method

- It is nonetheless possible to obtain some degree of information about scattering densities without any knowledge of the phases. Again, from eq. 20, we obtain:

$$|F(\mathbf{q})|^2 = r_0^2 \iint_{\text{unit cell}} d\mathbf{x} d\mathbf{x}' \rho(\mathbf{x}) \rho(\mathbf{x}') e^{-i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')} \quad (46)$$

With some manipulations we obtain:

$$\frac{1}{r_0^2 v_0} \sum_{\tau} |F(\tau)|^2 e^{i\tau \cdot \mathbf{x}} = \int_{\text{unit cell}} d\mathbf{x}' \rho(\mathbf{x}') \rho(\mathbf{x} + \mathbf{x}') = P(\mathbf{x}) \quad (47)$$

- The function defined in eq. 47 is known as the **Patterson function** (from Lindo Patterson, 1934). One can perhaps recognise in eq. 47 that the Patterson is *the autocorrelation function of the scattering density*.
- Patterson functions are 3-dimensional functions defined within one unit cell, and are usually presented in the form of 2-dimensional “slices”.

- Atomic-like scattering densities are *mostly zero*, except at the atomic positions. Therefore the Patterson function will be mostly zero as well, except at the *origin* ( $x = 0$ ) and *for values of  $x$  corresponding to vectors joining two atoms*. At these vectors, the Patterson function will have **peaks**.
- The integral of the  $x = 0$  peak is easily calculated to be  $\sum_i Z_i^2$ , where  $Z_i$  is the atomic number of atom  $i$  and the sum is over all atoms in the unit cell.
- Likewise, the integral of a peak corresponding to the interatomic distance  $r_{ij}$  is  $Z_i Z_j$ .

### 3.5.3 Structural optimisation: least-square refinements

- Most problems in physical crystallography involve determining subtle structural variations from well-known and rather simple structural motifs. Therefore, structural optimisation is usually the method of choice for the structural condensed-matter physicist.
- If one is reasonably close of the solution, with only a few free parameters left to determine, it is possible to *minimise the agreement between observed and calculated squared structure factors  $|F|^2$  as a function of the free parameters*. This is clearly a non-linear optimisation problem, and a number of strategies have been developed to solve it in a variety of cases.
- The best known structural optimisation method is known as the **Rietveld method**, and is applied to powder data.
- In the Rietveld method, one performs a nonlinear least-square fit *of the measured profile*, rather than of the  $|F|^2$  as in the single-crystal methods. This could appear more complicated, since one has to fit the microstructural and instrumental parameters controlling peak broadening and the background at the same time, but has the great advantage of *accounting automatically for peak overlap*.