Fundamentals of diffraction

Incident **beam**: plane wave propagating in the direction of the unit vector $\hat{\boldsymbol{k}}$

wavelength: λ;   wave vector: $\boldsymbol{k} = k\hat{\boldsymbol{k}} = \dfrac{1}{\lambda}\hat{\boldsymbol{k}}$

amplitude: $A(\boldsymbol{r}) = \sqrt{I_0}\,e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}}$;   intensity: $I(\boldsymbol{r}) = |A(\boldsymbol{r})|^2 = I_0$ $[\mathrm{Js^{-1}m^{-2}}]$

An **atom** is a *point** scatterer, that scatters *coherently* and *elastically*:
it absorbs a plane wave of wavelength λ and emits a spherical wave of wavelength λ.
The power it absorbs is equal to the incident intensity times the atom's

coherent elastic scattering **cross section** : σ

We define also the

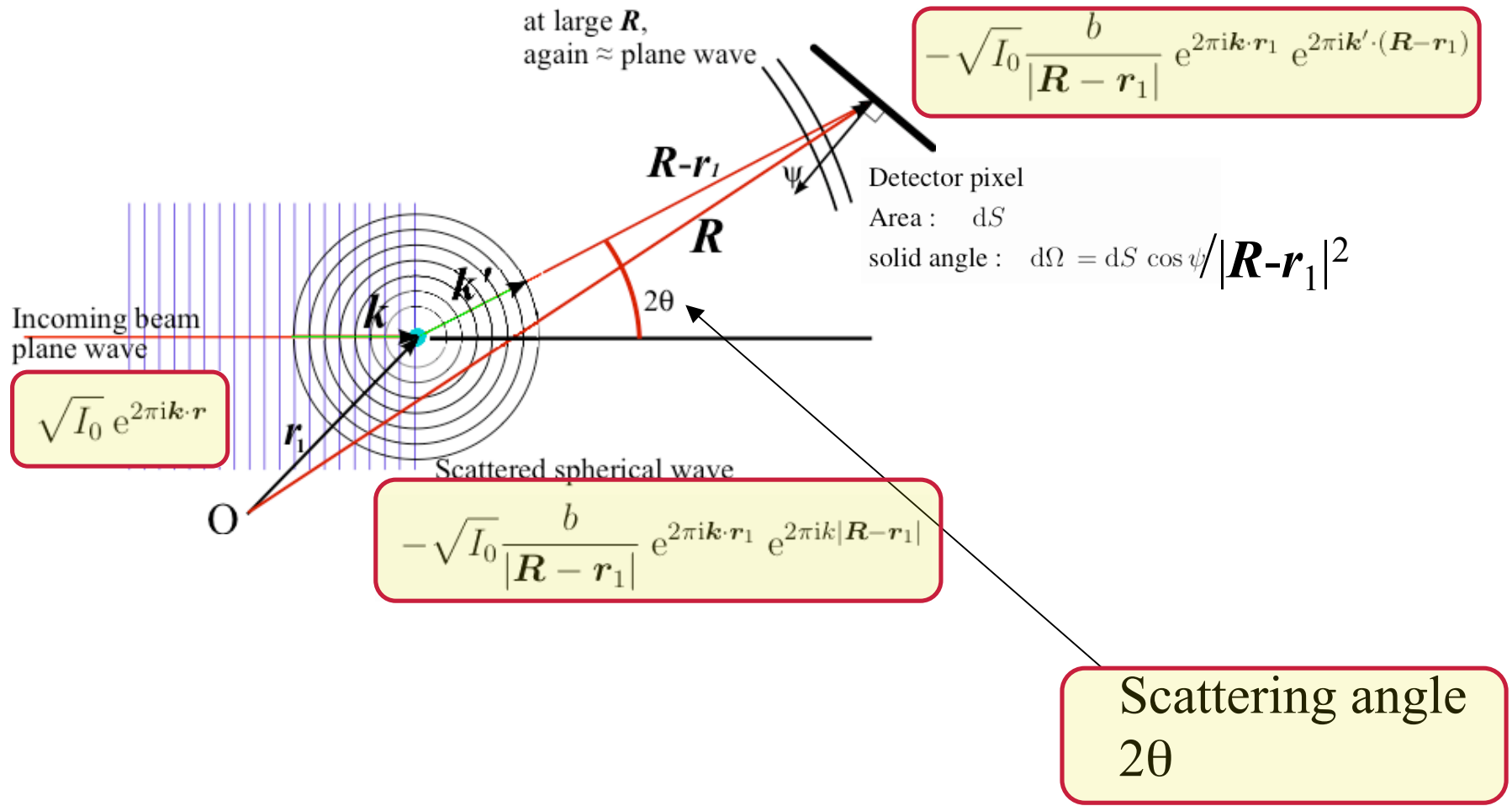coherent elastic **scattering length** : b such that: $\sigma = 4\pi b^2$

If the atom is at position $\boldsymbol{r}_1$, then the scattered spherical wave is

$$S(\boldsymbol{r}) = -\sqrt{I_0}\,\frac{b}{|\boldsymbol{r} - \boldsymbol{r}_1|}\,e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}_1}\,e^{2\pi i k|\boldsymbol{r}-\boldsymbol{r}_1|}$$

The emitted power on a spherical wave surface is is equal to the incident power:

$$4\pi|\boldsymbol{r} - \boldsymbol{r}_1||S(\boldsymbol{r})|^2 = 4\pi b^2 I_0 = \sigma I_0$$

* We will remove this simplification later.

at large $\boldsymbol{R}$,
again $\approx$ plane wave

$$-\sqrt{I_0}\,\frac{b}{|\boldsymbol{R}-\boldsymbol{r}_1|}\,\mathrm{e}^{2\pi \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_1}\,\mathrm{e}^{2\pi \mathrm{i}\boldsymbol{k}'\cdot(\boldsymbol{R}-\boldsymbol{r}_1)}$$

$\boldsymbol{R}$-$\boldsymbol{r}_1$

ψ

$\boldsymbol{R}$

Detector pixel

Area : $\mathrm{d}S$

solid angle : $\mathrm{d}\Omega = \mathrm{d}S\,\cos\psi\,/\,|\boldsymbol{R}\text{-}\boldsymbol{r}_1|^2$

$\boldsymbol{k}'$

$\boldsymbol{k}$

2θ

Incoming beam
plane wave

$$\sqrt{I_0}\,\mathrm{e}^{2\pi \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}$$

$\boldsymbol{r}_1$

Scattered spherical wave

$$-\sqrt{I_0}\,\frac{b}{|\boldsymbol{R}-\boldsymbol{r}_1|}\,\mathrm{e}^{2\pi \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_1}\,\mathrm{e}^{2\pi \mathrm{i}\mathrm{k}|\boldsymbol{R}-\boldsymbol{r}_1|}$$

O

Scattering angle
2θ

The energy we measure in 1 second on the detector is

$$\mathrm{d}W = \left| -\sqrt{I_0}\frac{b}{|\boldsymbol{R}-\boldsymbol{r}_1|}\,\mathrm{e}^{2\pi\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_1}\,\mathrm{e}^{2\pi\mathrm{i}\boldsymbol{k}'\cdot(\boldsymbol{R}-\boldsymbol{r}_1)} \right|^2 \mathrm{d}S\,\cos\psi = I_0\,b^2\frac{\mathrm{d}S\,\cos\psi}{|\boldsymbol{R}-\boldsymbol{r}_1|^2} = I_0\,b^2\mathrm{d}\Omega$$

For a more 'absolute' quantity we define the **differential cross section** as

$$\frac{\partial\sigma}{\partial\Omega} \equiv \frac{\mathrm{d}W}{I_0\mathrm{d}\Omega} = b^2 \qquad \text{[in this simple case!]}$$

with

$$\int \mathrm{d}\Omega\,\frac{\partial\sigma}{\partial\Omega} = 4\pi b^2 = \sigma$$

Many atoms case

Now we have N atoms in the sample, at positions $\boldsymbol{r}_j$, with scattering lengths b_j.
We **sum the amplitudes** of the diffracted waves:

$$\Psi = -\sqrt{I_0} \sum_{j=1}^{N} \frac{b_j}{|\boldsymbol{R} - \boldsymbol{r}_j|} \, e^{2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_j} \, e^{2\pi i \boldsymbol{k}' \cdot (\boldsymbol{R} - \boldsymbol{r}_j)}$$

$$\approx -\sqrt{I_0} \, \frac{e^{2\pi i \boldsymbol{k}' \cdot \boldsymbol{R}}}{|\boldsymbol{R}|} \sum_{j=1}^{N} b_j \, e^{-2\pi i (\boldsymbol{k}' - \boldsymbol{k}) \cdot \boldsymbol{r}_j}$$

Here we used the fact that $|\boldsymbol{R}| >> |\boldsymbol{r}_j|$ (meters to nanometers) so $1/|\boldsymbol{R} - \boldsymbol{r}_j| \approx 1/|\boldsymbol{R}|$.

We define the transferred momentum vector

$$\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k} \qquad (\boldsymbol{Q} = 2\pi \boldsymbol{q} \quad \text{is also often used!})$$

As $k = |\boldsymbol{k}| = |\boldsymbol{k}'| = 1/\lambda$ and 2θ is the diffraction angle (between $\boldsymbol{k}'$ and $\boldsymbol{k}$) :

$$q = |\boldsymbol{q}| = 2k \sin(\theta) = 2\frac{\sin(\theta)}{\lambda}$$

and so the scattered power on the detector pixel is

$$|\Psi|^2 \mathrm{d}S \, \cos\psi = I_0 \frac{\mathrm{d}S \, \cos\psi}{R^2} \left| \sum_{j=1}^{N} b_j \, e^{-2\pi i (\boldsymbol{k}' - \boldsymbol{k}) \cdot \boldsymbol{r}_j} \right|^2 = I_0 \mathrm{d}\Omega \left| \sum_{j=1}^{N} b_j \, e^{-2\pi i (\boldsymbol{k}' - \boldsymbol{k}) \cdot \boldsymbol{r}_j} \right|^2$$

and

$$\frac{\partial \sigma}{\partial \Omega} = \left| \sum_{j=1}^{N} b_j \, e^{-2\pi i \boldsymbol{q} \cdot \boldsymbol{r}_j} \right|^2 = \sum_{j=1}^{N} b_j^2 + 2 \sum_{j>i=1}^{N} b_j b_i \cos\left(2\pi \boldsymbol{q} \cdot (\boldsymbol{r}_j - \boldsymbol{r}_i)\right)$$

This is the distance between a pair of atoms, we will denote it as d_{ij}
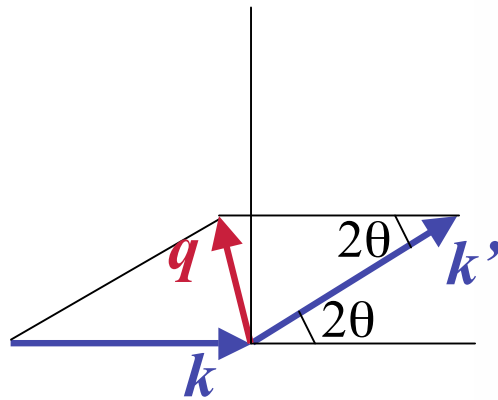
Powder diffraction:

many identical particles, in all possible 3D orientations, isotropically distributed!

We need the **spherical average** of the differential cross section.

$$\left\langle \frac{\partial \sigma}{\partial \Omega} \right\rangle_{orient.} = \frac{1}{4\pi} \int_0^{2\pi} \mathrm{d}\beta \int_0^{\pi} \sin(\phi)\mathrm{d}\phi \, \frac{\partial \sigma}{\partial \Omega}$$

Now, for each cosine, we take the polar axis along $\boldsymbol{q}$:

$$\frac{1}{4\pi} \int_0^{2\pi} \mathrm{d}\beta \int_0^{\pi} \sin(\phi)\mathrm{d}\phi \, \cos\left(2\pi d_{ij} q \cos(\phi)\right) = \frac{\sin(2\pi d_{ij} q)}{2\pi d_{ij} q}$$

and

$$\left\langle \frac{\partial \sigma}{\partial \Omega} \right\rangle_{orient.} = \sum_{j=1}^{N} b_j^2 + 2 \sum_{j>i=1}^{N} b_j b_i \frac{\sin(2\pi d_{ij} q)}{2\pi d_{ij} q}$$

Debye's formula

Peter Debye,
Ann. Phys. 1915, **46**,809.

Remark:

What relates detector counts to the differential cross sections?

At most a constant scale factor. In fact:

we always normalize to a constant detector solid angle and unit efficiency (often using a flat-field correction);

we normalize to unit I_0 and acquisition time (using a monitor).

After that, the detector counts are simply proportional to the differential cross section.

Remark:

Which correction factors do we need?

Lorentz factor: no. This is a factor needed to convert the differential cross section profile (powder pattern) to integrated intensity of Bragg peaks. We do not consider Bragg peaks here.

Polarization factor: depending on the source. Synchrotrons and neutrons sources can be built so that they do not need it; anode X-ray sources yes.

Absorption correction: depending ... If the sample is not too thick and too strongly absorbing for the incident radiation, no, otherwise yes. Such correction - if needed - is strongly dependent on the sample / detector geometry.

Instrumental resolution function: depending ... If the pattern of your sample is much smoother than the IRF, you do not need to bother.

More precisely…

1) **Atoms are not always point-like scatterers.**

$\lambda \sim 1$ Å typically (on the order of interatomic distances)

Neutrons: scattered by **nuclei**. Diameter of a nucleus $\sim 10^{-4}$ Å: atoms *are* point-like scatterers!

X-rays: scattered by **electrons**. Atomic electrons are spread over a "cloud" of ~ 1 Å: atoms *are not* point-like scatterers!

However, the electron cloud is $\sim$ spherically isotropic. Therefore we simply substitute constant scattering lengths b_j with atomic form factors $f_j(q)$. Those are tabulated and/or analytical approximations are known (also for ions).

Plot of $f(q)$ for all elements

D. Waasmaier and A. Kirfel,
Acta Cryst. A 51(1995) 416-431
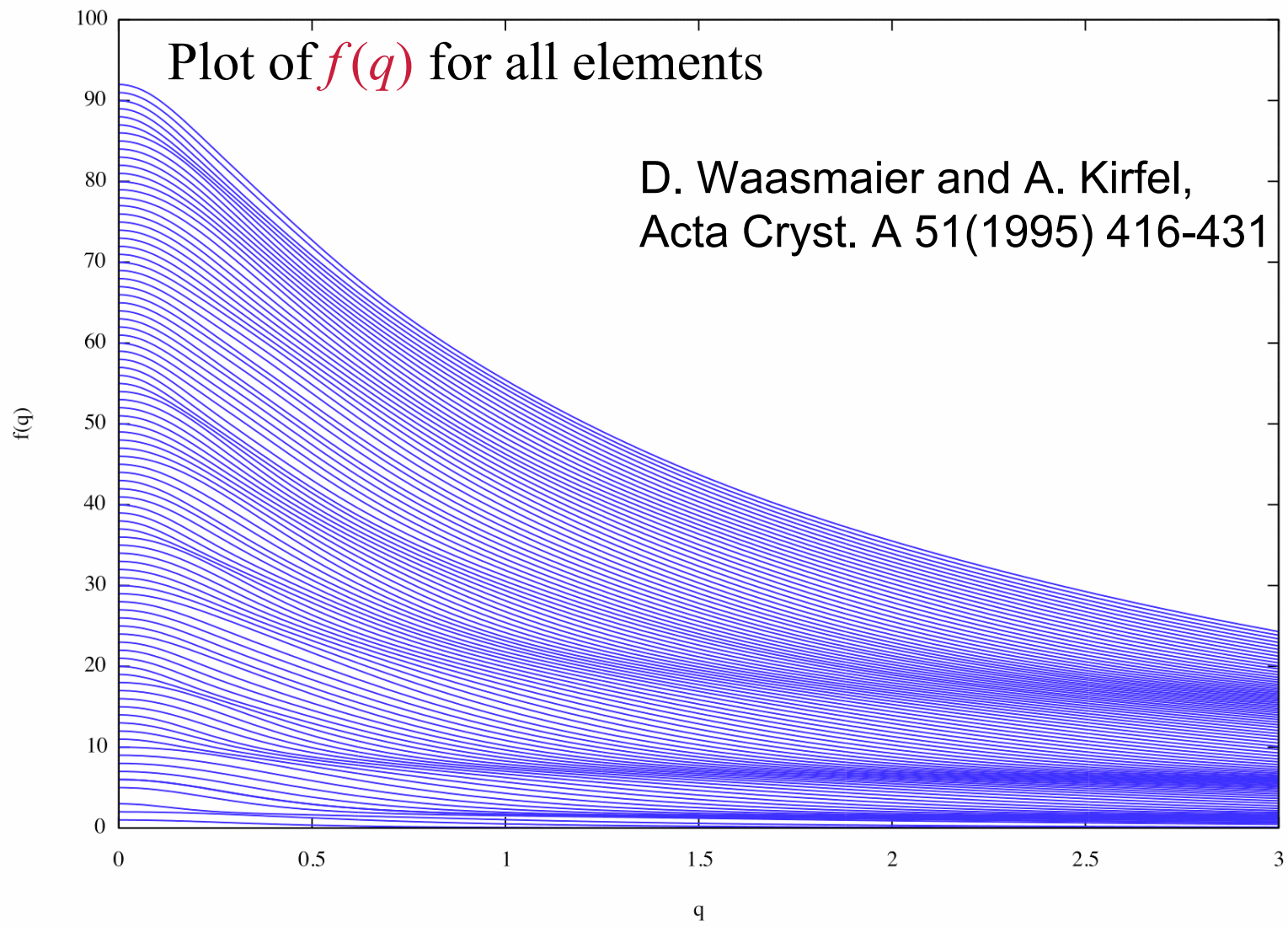
More precisely…

2) **Atoms are not stationary : thermal motion.**

Assumption (most often sufficient): thermal motion is harmonic and isotropic around the average position. It is then fully described by its **mean-square amplitude** $<u^2>$. Crystallographers use $B = 8\pi^2 <u^2>$.

The scattering length must be multiplied by

$T(q) = \exp(-Bq^2/4)$. Of course this concerns only pairs of different atoms!

$$\left\langle \frac{\partial \sigma}{\partial \Omega} \right\rangle_{orient.} = \sum_{j=1}^{N} f_j(q)^2 + 2 \sum_{j>i=1}^{N} f_j(q) f_i(q) T_j(q) T_i(q) \frac{\sin{(2\pi d_{ij} q)}}{2\pi d_{ij} q}$$

More precisely…

3) **Atoms may not be always there: site occupancies.**

Many "identical" particles are needed to form a powder diffraction pattern. In some of them some atoms may be absent. Or some atom may have two or more sites where it may choose to be. To kake this into account,

-we consider all possible *atomic sites* and multiply the associated scattering length by the *site occupancy o* (or the probability that an atom is actually there; 0<*o*<1).

- if two site are to be occupied in alternative (e.g. when their distance is too short) we shift their contribution to the first sum (without the sinc term)

$$\left\langle \frac{\partial \sigma}{\partial \Omega} \right\rangle_{orient.} = \sum_{j=1}^{N} f_j(q)^2 o_j^2 + 2 \sum_{j>i=1}^{N} f_j(q) f_i(q) T_j(q) T_i(q) o_j o_i \frac{\sin (2\pi d_{ij} q)}{2\pi d_{ij} q}$$