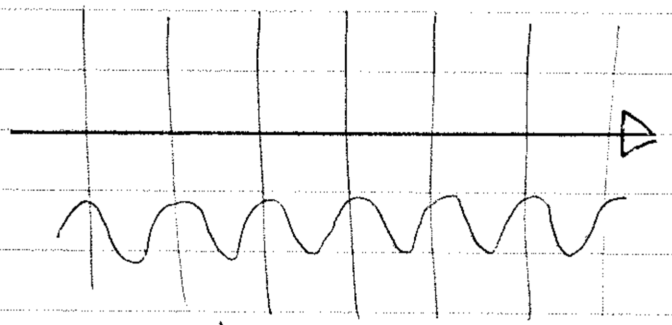
Scattering theory by pictures.

1/ Waves, wavevectors and phase.

- Scattering is all about using wave-like radiation (light, X-rays, neutrons, etc) to probe the structure of a material.

- We will look at theory for weak scattering (i.e. ignore multiple scattering events). The maths is basically the same whichever radiation is used.



- We describe a wave by its <u>amplitude</u> (how big are the oscillations) and its <u>phase</u> (a measure of how many oscillations there are).
  Phase is an angle, measured in radians (so, one complete oscillation is 2π radians). Examples of mathematical functions describing a wave are:

$$A = \underbrace{A_0}_{\text{amplitude}} \cos(\underbrace{kx - \omega t}_{\text{phase}})$$

$$A = A_0 e^{i(kx - \omega t)}$$

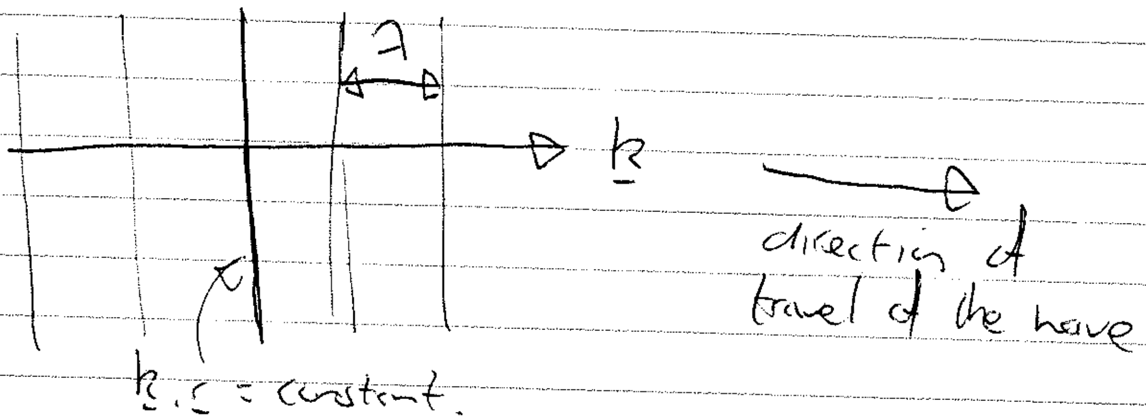
(we often use complex numbers in scattering theory)

- The phase of a wave varies with time (ωt, where ω is the angular frequency), we don't usually concern ourselves with this part in static scattering; it cancels out in the maths.

- The phase also depends on position. For a wave in 3D space we define a wavevector $\underline{k}$. The phase of the wave varies in space as

$$\phi = \underline{k} \cdot \underline{r} \qquad \underline{k} = \text{wavevector}$$
$$\underline{r} = \text{position.}$$

All points with the same $\underline{k}\cdot\underline{r}$ have the same phase. This gives planes perpendicular to $\underline{k}$.



One complete oscillation of the wave corresponds to a change in phase of 2π. This gives a separation λ between planes.. λ is the wavelength.

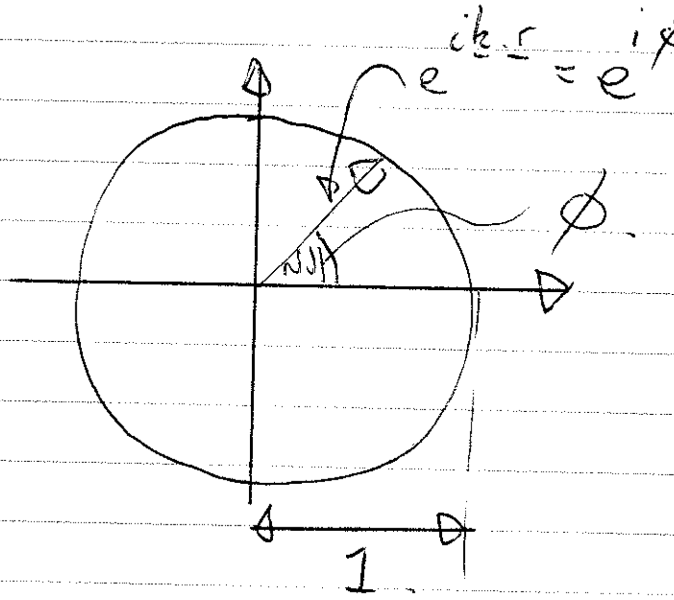
$$\Delta\phi = 2\pi = |\underline{k}|\lambda$$

So... $$\boxed{|\underline{k}| = \frac{2\pi}{\lambda}}$$

- We usually use the mathematical function $e^{i\phi} = e^{i\underline{k}.\underline{r}}$ to describe a wave, ie,

$$A = A_0 e^{i\underline{k}.\underline{r}}$$

You can think of the function $e^{i\underline{k}.\underline{r}}$ a bit like an anticlockwise clock:



As ϕ increases, the hand on the clock moves round a circle of radius 1, in an anticlockwise direction. A phase change of 2π takes the hand back to where it started.

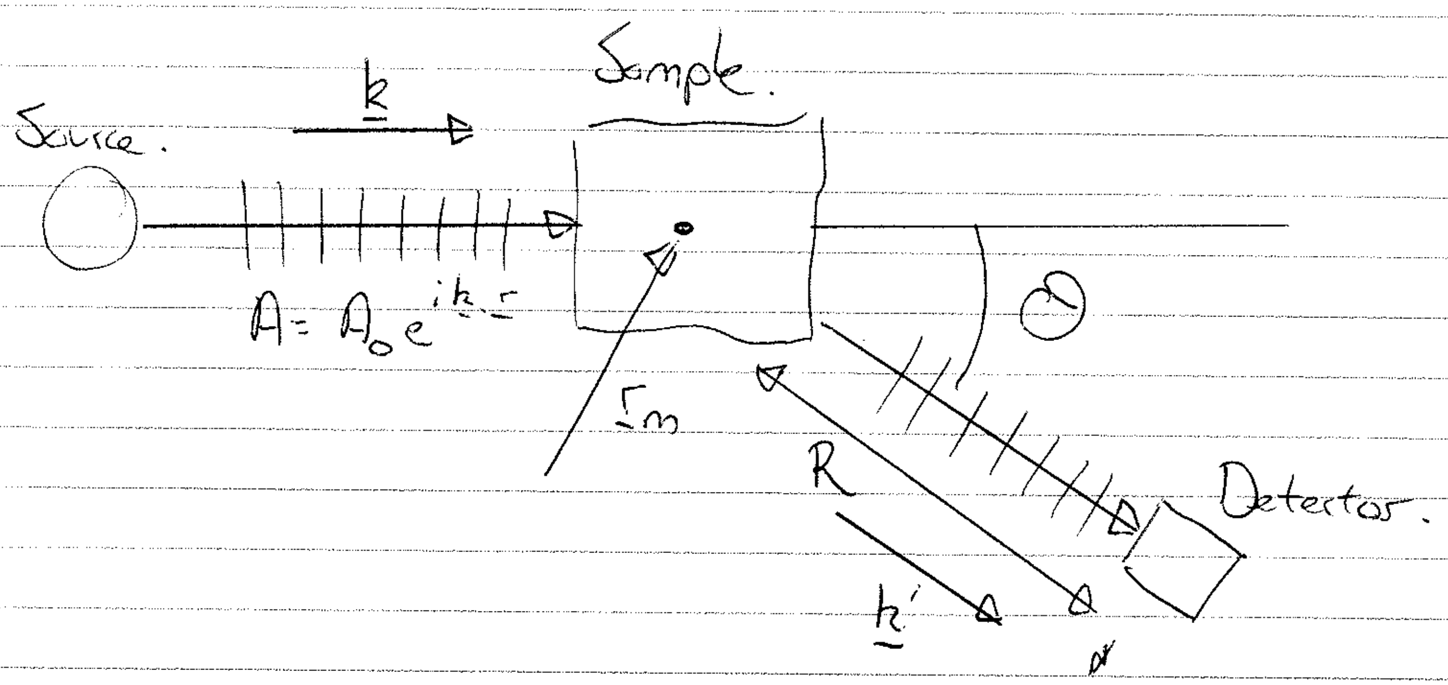
If we multiply $e^{i\phi}$ by an amplitude A ... we just make the arm on the clock longer.

THIS PICTURE WILL BE VERY HELPFUL IN UNDERSTANDING SCATTERING!!

(I hope)

2. Geometry of a scattering experiment.

A scattering experiment looks like this:



- A_0 = amplitude of radiation from source (intensity $= I_0 = A_0^2$)
- θ = scattering angle to detector
- R = distance to detector
- $\underline{k}$ = wavevector of incident radiation
  $\underline{k}'$ = wavevector of scattered radiation.

Imagine scattering from particle at position $\underline{r}_m$

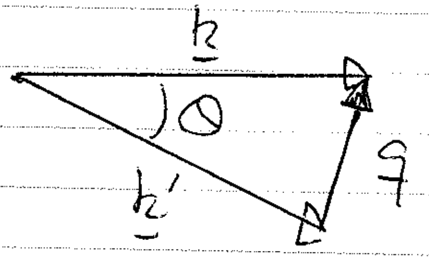
- Phase of incident wave at $\underline{r}_m$ is: $\phi_1 = \underline{k}.\underline{r}_m$
- Phase change from particle to detector at position $\underline{x}$ is: $\phi_2 = \underline{k}'.(\underline{x} - \underline{r}_m)$

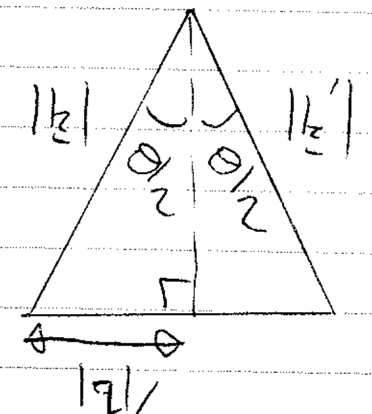
So, total phase change from source to detector is

$$\phi = \phi_1 + \phi_2$$
$$= \underline{k} \cdot \underline{r}_m + \underline{k}' \cdot (\underline{x} - \underline{r}_m)$$
$$= \underbrace{\underline{k}' \cdot \underline{x}}_{\substack{\text{contribution from} \\ \text{detector position:} \\ \text{same for all particles}}} + \underbrace{(\underline{k} - \underline{k}') \cdot \underline{r}_m}_{\substack{\text{the bit which depends} \\ \text{on particle position.}}} = \underline{k}' \cdot \underline{x} + \underline{q} \cdot \underline{r}_m$$

- The vector $\underline{q} = \underline{k} - \underline{k}'$ is called the <u>scattering wavevector</u>.

- All particles with the same value of $\underline{q} \cdot \underline{r}_m$ scatter with the same phase.





- From the diagram, $\frac{|\underline{q}|}{2} = |\underline{k}| \sin\theta/2$ (Isosceles Δ)

$$|\underline{q}| = 2|\underline{k}| \sin\theta/2 = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}.$$

- Large $|\underline{q}|$ probes small structures, small $|\underline{q}|$ probes larger structures.

Scattered wave at detector from particle at $\underline{r}_m$ is:

$$A_m = \frac{A_0}{R}\, b_m\, e^{i\underline{q}\cdot\underline{r}_m}$$

$\frac{1}{R}$ gives inverse square law for intensity.

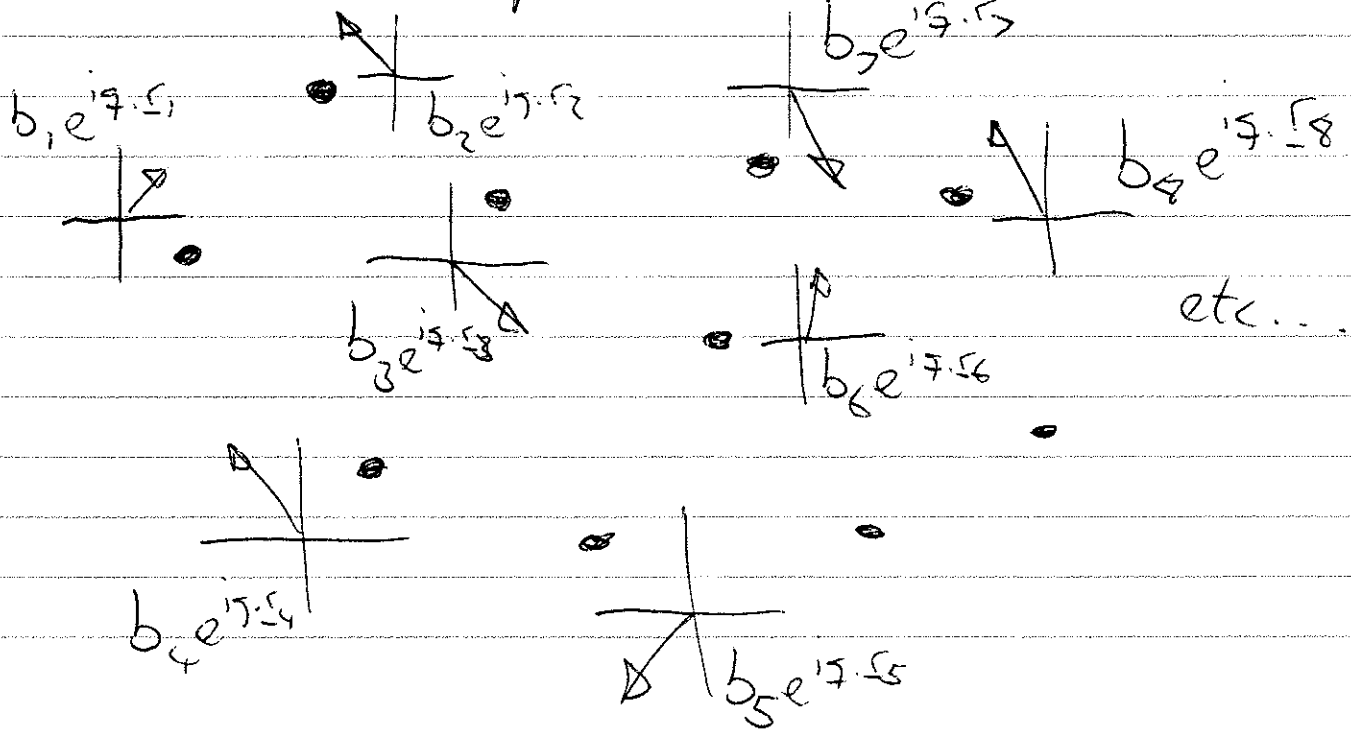
scattering length

phase function (anticlockwise clock).

Total amplitude from many particles:

$$A_{detector} = \frac{A_0}{R} \underbrace{\sum_m b_m\, e^{i\underline{q}\cdot\underline{r}_m}}$$

we can think of this as summing up all the little "clocks" representing scattering from each particle:



- In practice, the detector measures intensity:

$$I = |A_{detector}|^2$$
$$= \frac{A_0^2}{R^2} \left| \sum_m b_m e^{i\underline{q}\cdot\underline{r}_m} \right|^2 \qquad (A_0^2 = I_0)$$

- If the volume of the sample is V, we often report:

$$\frac{I R^2}{I_0 V} = \text{normalised scattering}$$

(removes all details of experimental set-up, so result just depends on sample).

- So, the important quantity for us to calculate is

$$I_{norm} = \frac{1}{V} \left| \sum_m b_m e^{i\underline{q}\cdot\underline{r}_m} \right|^2.$$

(scattering from particles)

Sometimes we think of scattering off a density which varies continuously ... then scattering length in volume ΔV is $b = \rho(\underline{r}) \Delta V$

$$\Rightarrow I_{norm} = \frac{1}{V} \left| \sum_m \rho(\underline{r}) \Delta V_m e^{i\underline{q}\cdot\underline{r}_m} \right|^2$$
$$= \frac{1}{V} \left| \int \rho(\underline{r}) e^{i\underline{q}\cdot\underline{r}_m} d^3\underline{r} \right|^2.$$

FOURIER TRANSFORM.

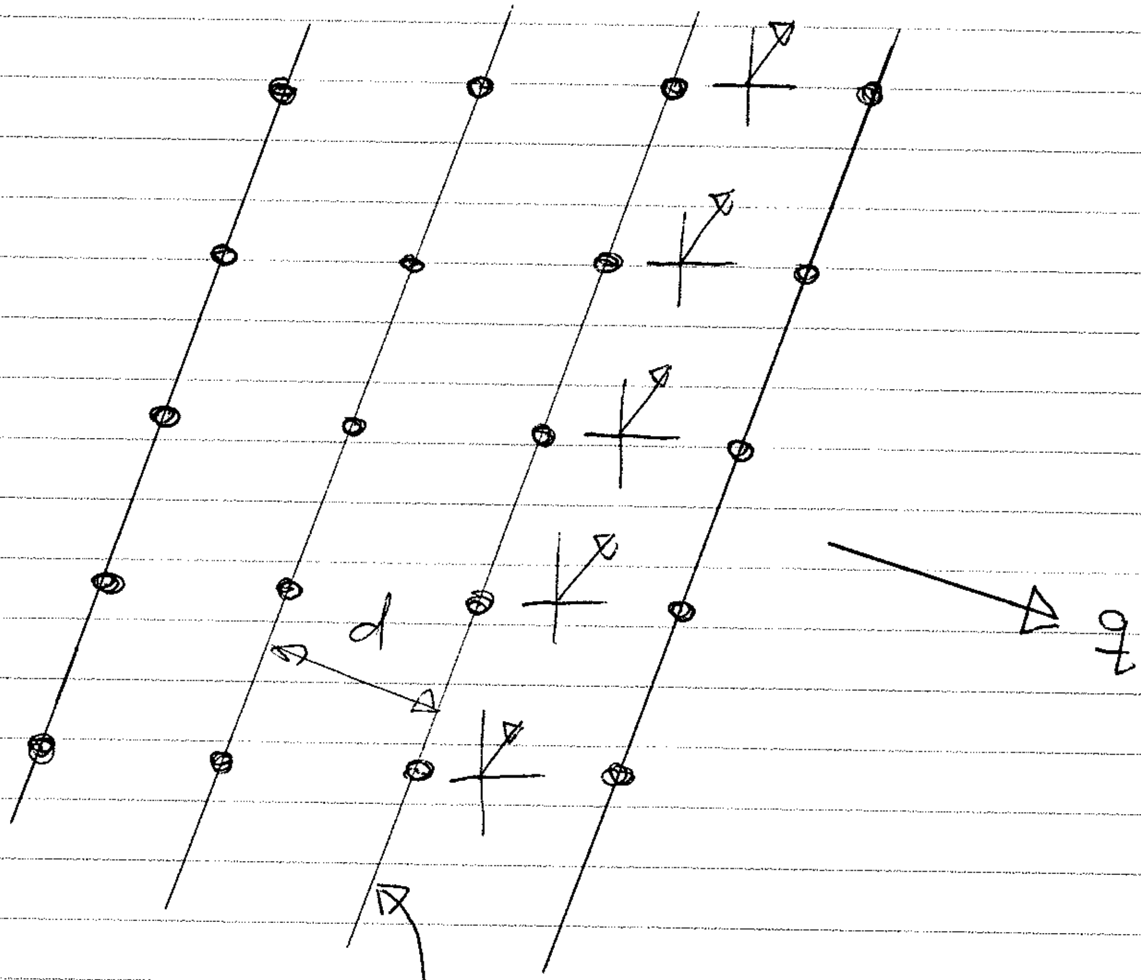
So... in summary... we want to calculate

$$\sum_m b_m e^{i\underline{q}\cdot\underline{r}_m}$$

Which we interpret as adding up all the little "phase clocks"

3) Bragg scattering from crystals.

- This is the example you will be most familiar with.
- Suppose all particles lie in crystal planes:



$\underline{q}\cdot\underline{r} = \text{constant}$

$\Rightarrow$ ALL clocks have same phase!

- IF the planes are perpendicular to $\underline{q}$ then $\underline{q} \cdot \underline{r}$ is constant along the plane
  $\Rightarrow$ all clocks in the plane have the same phase.

- IF the distance between planes is d, then the change in phase from one plane to the next is

$$\Delta\phi = |\underline{q}|\, d$$

AND if $\Delta\phi = 2n\pi$ (a multiple of 2π)

then from one plane to the next, the "clock" goes round "n" times (i.e. the clock looks the same!)

This gives lots of scattering(!) because all the clocks point in the same direction. (so $\left|\sum_m b_m e^{i\underline{q}\cdot\underline{r}_m}\right| = Nb$)

$\Rightarrow$ Bragg law for scattering!

$$|\underline{q}|.d = 2n\pi.$$

$$\frac{4\pi}{\lambda}\sin\frac{\theta}{2}.d = 2n\pi.$$

$$\underline{\underline{2d\sin\frac{\theta}{2} = n\lambda.}}$$

This gives a set of "peaks" at specific scattering angles, which allow you to determine the spacing of the crystal planes, and the type of crystal structure'.

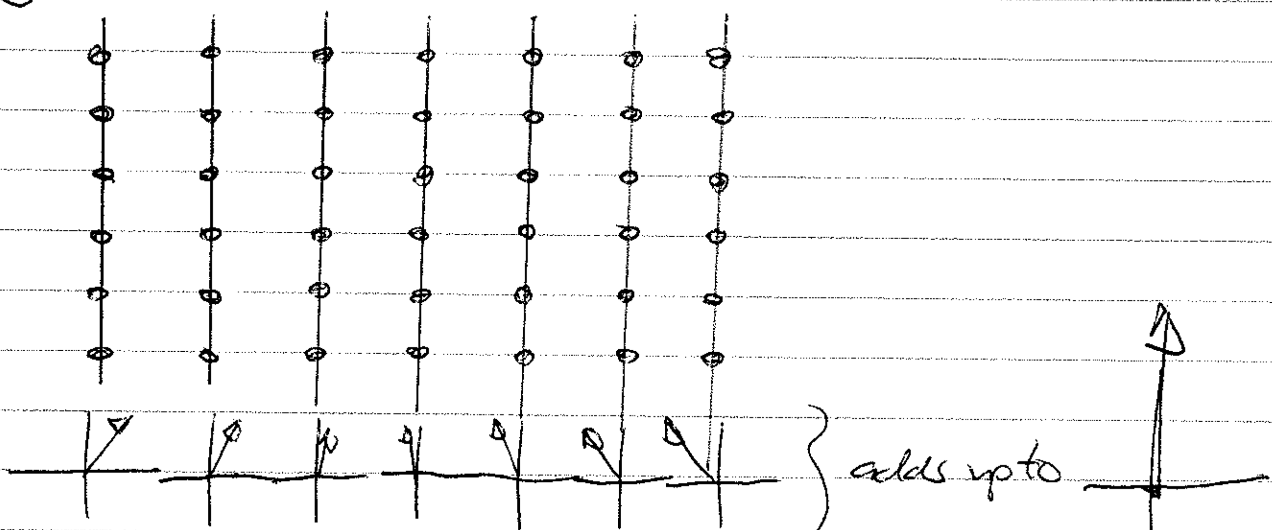
lamellae: $q_0, 2q_0, 3q_0, 4q_0$

hexagonal: $q_0, \sqrt{3}q_0, \sqrt{4}q_0, \sqrt{7}q_0$

b.c.c. : $q_0, \sqrt{2}q_0, \sqrt{3}q_0, \sqrt{4}q_0, \sqrt{5}q_0 \ldots$

Note on finite crystals.

- For an infinite crystal, all of the clocks need to exactly align for scattering to happen.
- For a finite crystal, if we are close to the Bragg scattering condition, then the clocks do not get far out of alignment across the crystal... you still get some scattering.

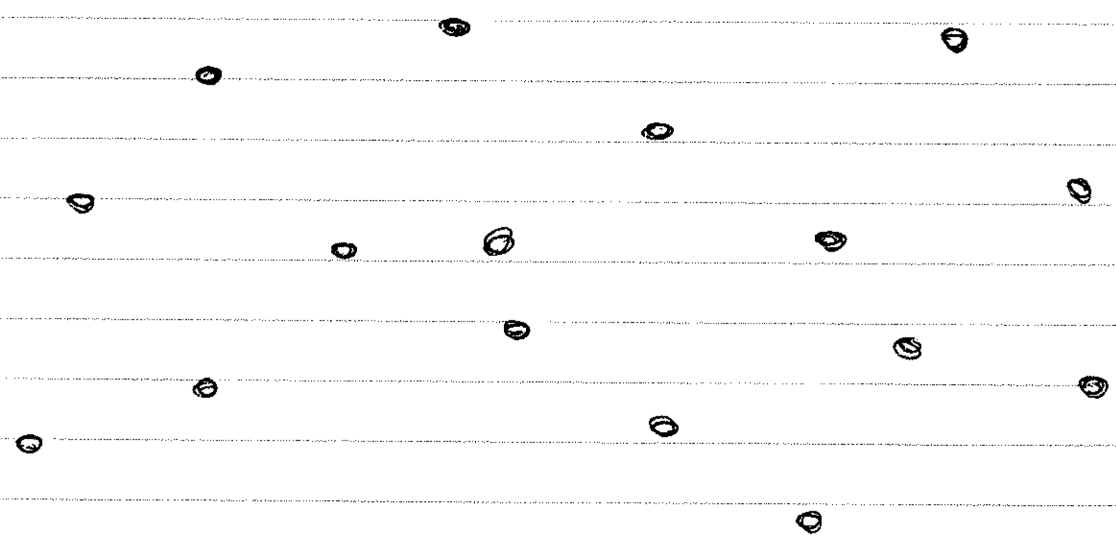


- bigger crystals, or further distance from Bragg condition, makes alligment worse.

So ... width of scattering peak is a measure of size of crystals!

4/ <u>Scattering from randomly placed particles.</u>

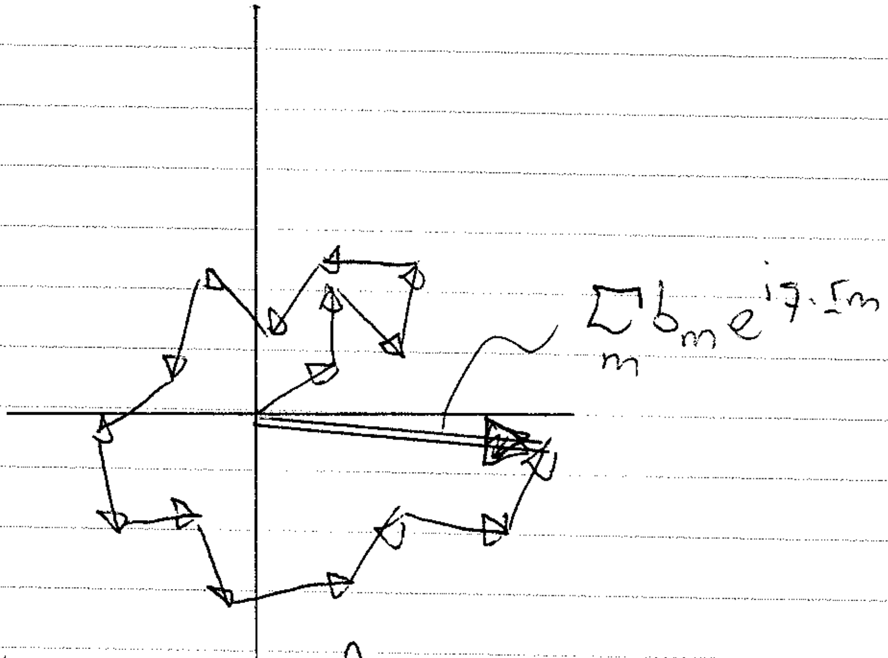
Bragg's law requires all the particles to be on regularly spaced crystal planes. What happens if all particles are in random positions?



THEN the "clock" for each particle will have essentially a random direction.

So $\sum_m b_m e^{i\underline{q}\cdot\underline{r}_m}$ $\equiv$ a sum over randomly directed arrows, each of size b

$\equiv$ RANDOM WALK!!!



But, you know that for a random walk with N steps, the result is $\langle R^2 \rangle = N b^2$.

So, by analogy:

$$\left\langle \left| \sum_m b_m e^{i\underline{q}\cdot\underline{r}_m} \right|^2 \right\rangle = N b^2$$

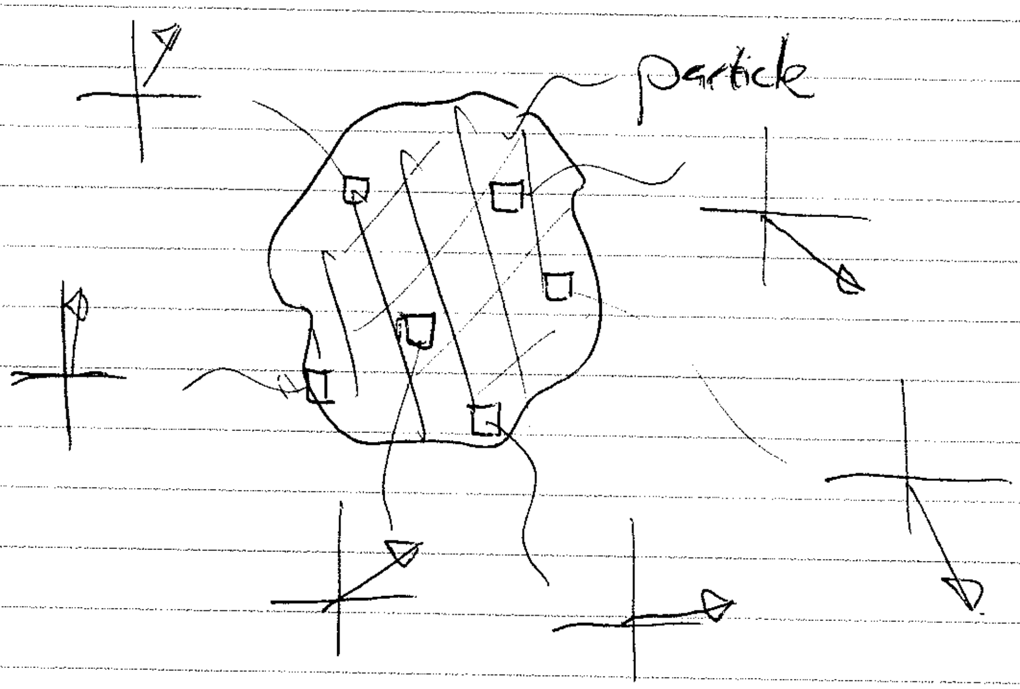
number of particles

square of scattering length.

This gives a "flat" scattering profile (ie, the result does not depend on $|\underline{q}|$).

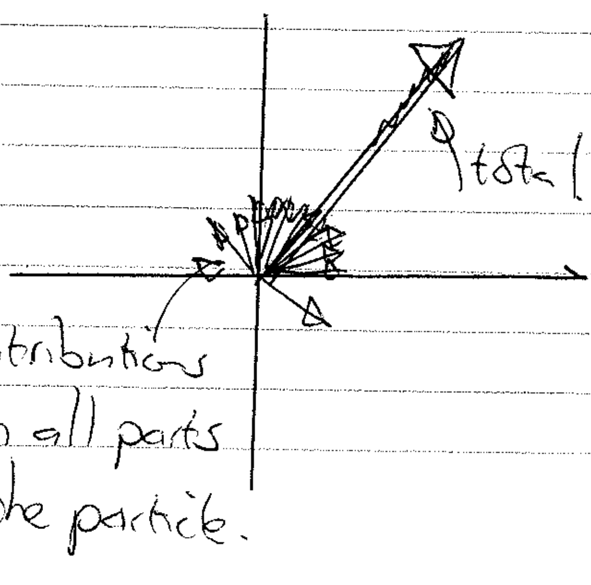
5) "Structure factor" and "Form factor".

- In all the above, "particles" were treated as point-like objects
- Suppose the particles are not points... but that the scattered phase changes across one particle!



Then the scattering sum for a single particle looks like:

$$\sum_{\substack{m \text{ in} \\ \text{particle}}} b_m e^{i\underline{q}\cdot\underline{r}_m} =$$



- So, the total scattering from one particle is a sum over all the small contributions (with phases) from each part of the particle.

- We define

$$P(q) = \Big| \sum_{\substack{m \\ \text{in particle}}} b_m e^{i q \cdot r_m} \Big|^2$$

$\equiv$ FORM FACTOR for particle.

- If $|q|$ is small, or size of particle is small so that

$|q| \times$ particle size $\ll 1$

then the phase does not change much across the particle and form factor is large.

If this is not true, then phase changes across the particle and so form factor is smaller.

In general, for small q and isotropic particles:

$$P(q) = P_0 \left(1 - \frac{q^2 R_g^2}{3} + \dots \right)$$

$R_g \equiv$ "radius of gyration".

$P_0 = \Big| \sum_m b_m \Big|^2 \propto (\text{Mass})^2$ of particle.

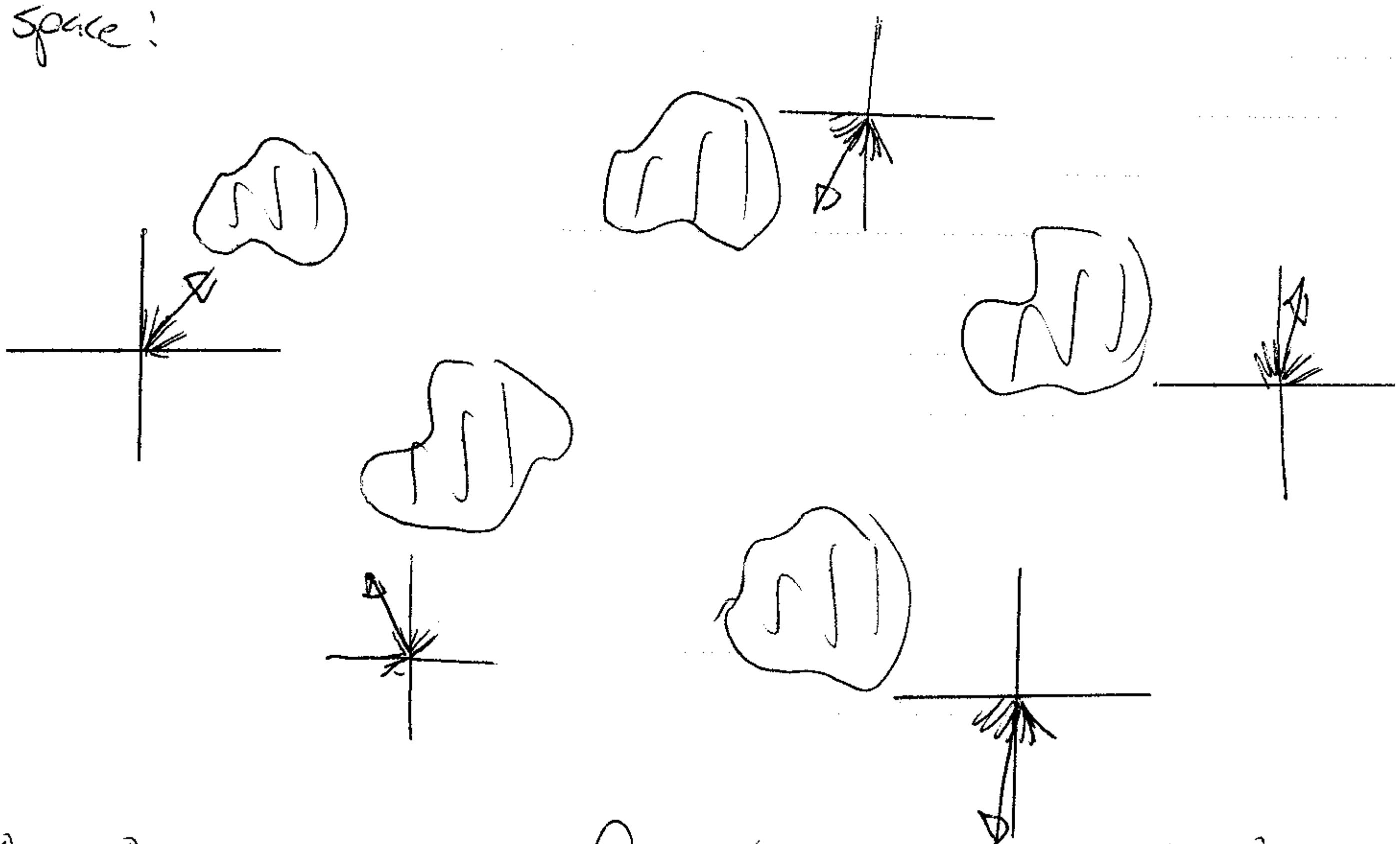
These are exact results for different shapes, e.g.
form factor of a sphere is:

$$P(q) = \frac{(4\pi \rho a^3)^2}{Q^6}\left(\sin(Q) - Q\cos(Q)\right)^2$$

$Q = qa$

a = sphere radius.

Now... if the particles are at different points in space:



then the scattering sum for each particle will be the same, but rotated around the clock depending on where the particle is placed.

Then:

$$\left| \sum_{m} b_m e^{i\underline{q}\cdot\underline{r}_m} \right|^2 = \left| \sum_{\substack{\text{particles} \\ i}} \sum_{\substack{m \\ \text{in } i}} b_m e^{i\underline{q}\cdot\underline{r}_m} \right|^2$$

all scattering points in this sum

sum of scattering in one particle

$$= \left| \sum_{\substack{\text{particles} \\ i}} e^{i\underline{q}\cdot\underline{r}_i} \right|^2 P(q)$$

centre of mass of particle i

form factor

$$= S(q)\, P(q)$$

structure factor

The STRUCTURE FACTOR gives the contribution to the scattering from the arrangement of particles.

The FORM FACTOR gives the contribution from the shape of particles.

e.g. 1. If particles are on a crystal lattice then

$S(q)$ gives Bragg peaks

$P(q)$ changes the peak intensity.

e.g. 2. If particles are randomly distributed, then:

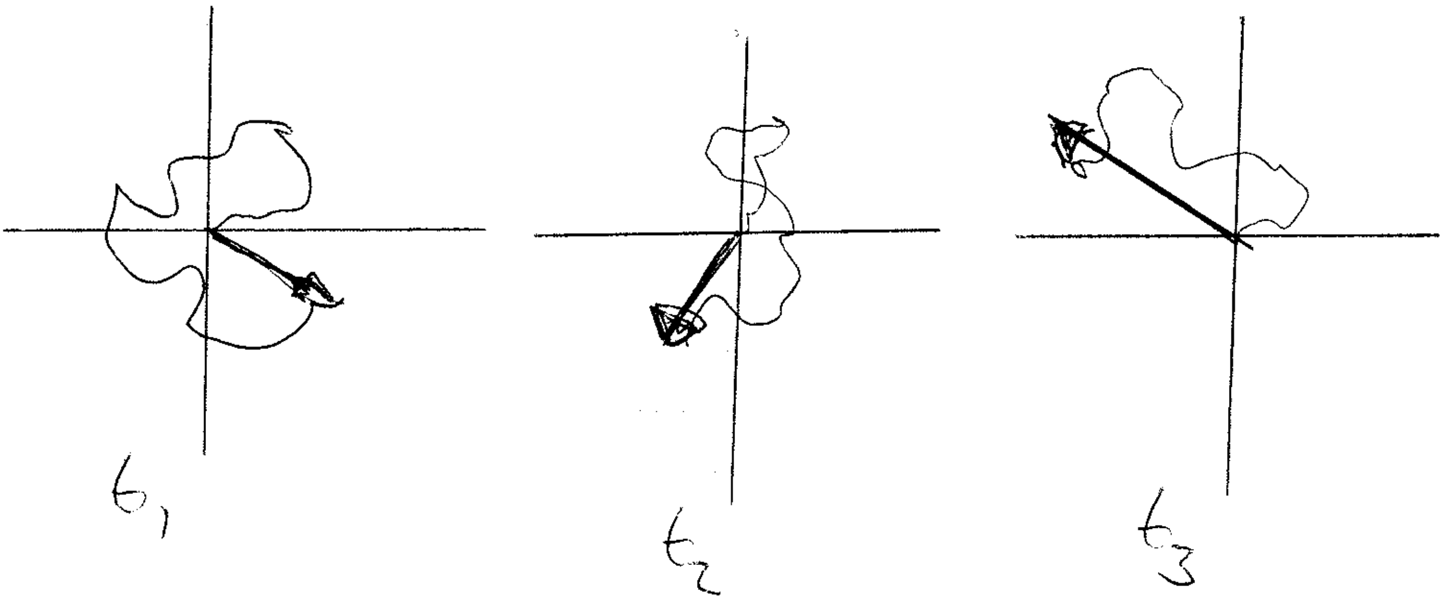
$$S(q) = N \quad (\text{no. of particles})$$

$$P(q) = P_0 \left(1 - \frac{q^2 R_g^2}{3} + \dots\right)$$

So, scattering measures $\underset{\substack{\uparrow \\ \text{size}}}{R_g}$ and $\underset{\substack{\uparrow \\ \text{mass}}}{P_0}$.

6/ Dynamic light scattering. (DLS)

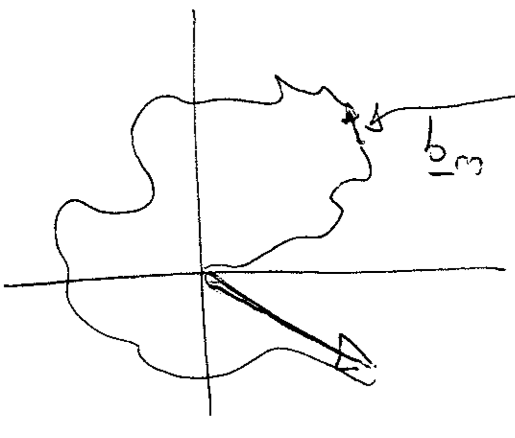
Think back to §4. – scattering from a random distribution of particles. Now, imagine doing the experiment where you measure scattered intensity as a function of time. Each time, the particles move a bit, and you get a different random set of phases.



the intensity at time t is proportional to:

$$I(t) = \left| \sum_m b_m e^{i \underline{q} \cdot \underline{r}_m} \right|^2$$

$$= \left| \sum_m \underline{b}_m(t) \right|^2$$ where $\underline{b}_m \equiv$ vector in 2D plane above from particle m.



The dynamics of the intensity depends on the dynamics of each $\underline{b}_m$.

Detailed calculation.... (for those interested)

DLS measures the correlation in intensity between times separated by τ.

$$\langle I(t+\tau)I(t)\rangle = \left\langle \left|\sum_m \underline{b}_m(\tau)\right|^2 \left|\sum_n \underline{b}_n(0)\right|^2 \right\rangle$$

to calculate $\left|\sum_m b_m(\tau)\right|^2$ we need the dot product!

$$\sum_l \underline{b}_l(\tau) \cdot \sum_m \underline{b}_m(\tau)$$

$$= \sum_{l,m} \left[b_{x,l}(\tau) b_{x,m}(\tau) + b_{y,l}(\tau) b_{y,m}(\tau) \right]$$

So, we need to calculate (splitting $\underline{b}$ into x, y components)

$$\langle I(\tau) I(0)\rangle$$

$$= \left\langle \sum_{l,m}\left(b_{x,l}(\tau) b_{x,m}(\tau) + b_{y,l}(\tau) b_{y,m}(\tau)\right) \times \sum_{k,n}\left(b_{x,k}(0) b_{x,n}(0) + b_{y,k}(0) b_{y,n}(0)\right) \right\rangle$$

This looks big and complicated, but most terms are zero. x and y directions are not correlated, and different particles have randomly different phases. The only non-zero terms come when l, m, k, n count same particles.... (this is a bit like the random walks calculation)

There are N^2 terms with $l=m$ and $k=n$, giving:

$$N^2\left(\langle(b_x^2+b_y^2)\rangle\langle(b_x^2+b_y^2)\rangle\right)$$

$$= N^2 b^4 = \langle I(t)\rangle^2$$

There are N^2 terms with $l=k$ and $m=n$ giving:

$$N^2\left(\langle b_x(\tau)b_x(0)\rangle^2+\langle b_y(\tau)b_y(0)\rangle^2\right)$$

$$= 2N^2\left(\langle b_x(\tau)b_x(0)\rangle^2\right)$$

There are also N^2 terms with $l=n$, $m=k$ also giving

$$2N^2\left(\langle b_x(\tau)b_x(0)\rangle^2\right)$$

and since $\langle b_x(\tau)b_x(0)\rangle = \langle b_y(\tau)b_y(0)\rangle$

$$\langle b_x(\tau)b_x(0)\rangle = \frac{1}{2}\langle \underline{b}_p(\tau)\cdot\underline{b}_p(0)\rangle$$

$\underline{b}$ for same particle at two times.

So: $$\boxed{\langle I(\tau)I(0)\rangle = N^2\left(b^4+\langle\underline{b}(\tau)\cdot\underline{b}(0)\rangle^2\right)}$$

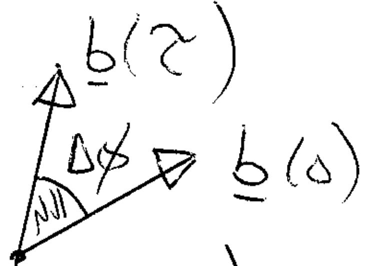
(there are order N corrections).

This depends on how a particle moves.

So, we need to calculate:

$\langle \underline{b}(\tau).\underline{b}(0) \rangle$ for a particle, which is a measure of HOW MUCH DID THE PHASE CLOCK CHANGE in time τ?

$\underline{b}(\tau).\underline{b}(0) = b^2 \cos \Delta\phi$



where $\Delta\phi = \underline{q}.(\underline{r}(\tau) - \underline{r}(0)) = \underline{q}.\Delta\underline{r}$

For diffusing particles:

$$P(\Delta\underline{r}) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(\frac{-\Delta\underline{r}^2}{4Dt}\right)$$

$$\begin{aligned}
\text{So } \langle \underline{b}(\tau).\underline{b}(0) \rangle &= b^2 \langle \cos \Delta\phi \rangle \left(= b^2 \exp\left(-\frac{\langle \Delta\phi^2 \rangle}{2}\right)\right) \\
&= b^2 \int \cos(\underline{q}.\Delta\underline{r}) P(\Delta\underline{r})\, d^3(\Delta\underline{r}) \\
&= b^2 \exp\left(-q^2 Dt\right)
\end{aligned}$$

$$\begin{aligned}
\Rightarrow \langle I(\tau) I(0) \rangle &= N^2 b^4 \left(1 + \exp(-2q^2 Dt)\right) \\
&= \langle I \rangle^2 \left(1 + \exp(-2q^2 Dt)\right)
\end{aligned}$$