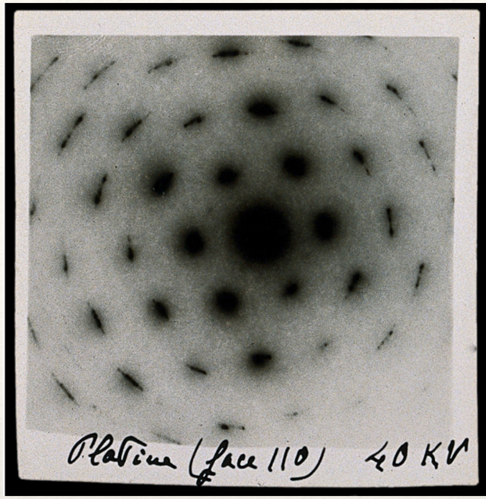

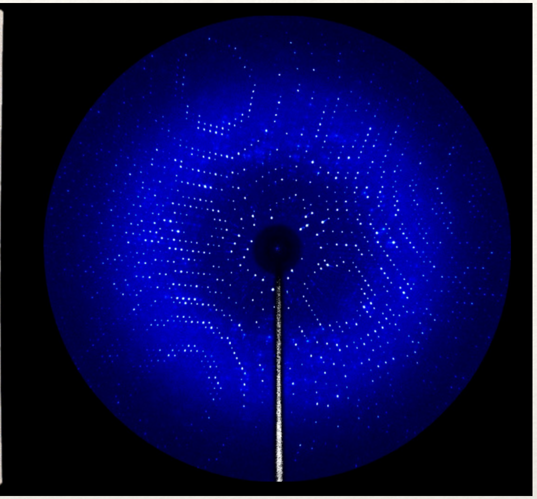

Structure of Solids - X-ray diffraction Studies (Bragg's Law)

Lecture 5

CHM 637

Chemistry & Physics of Materials

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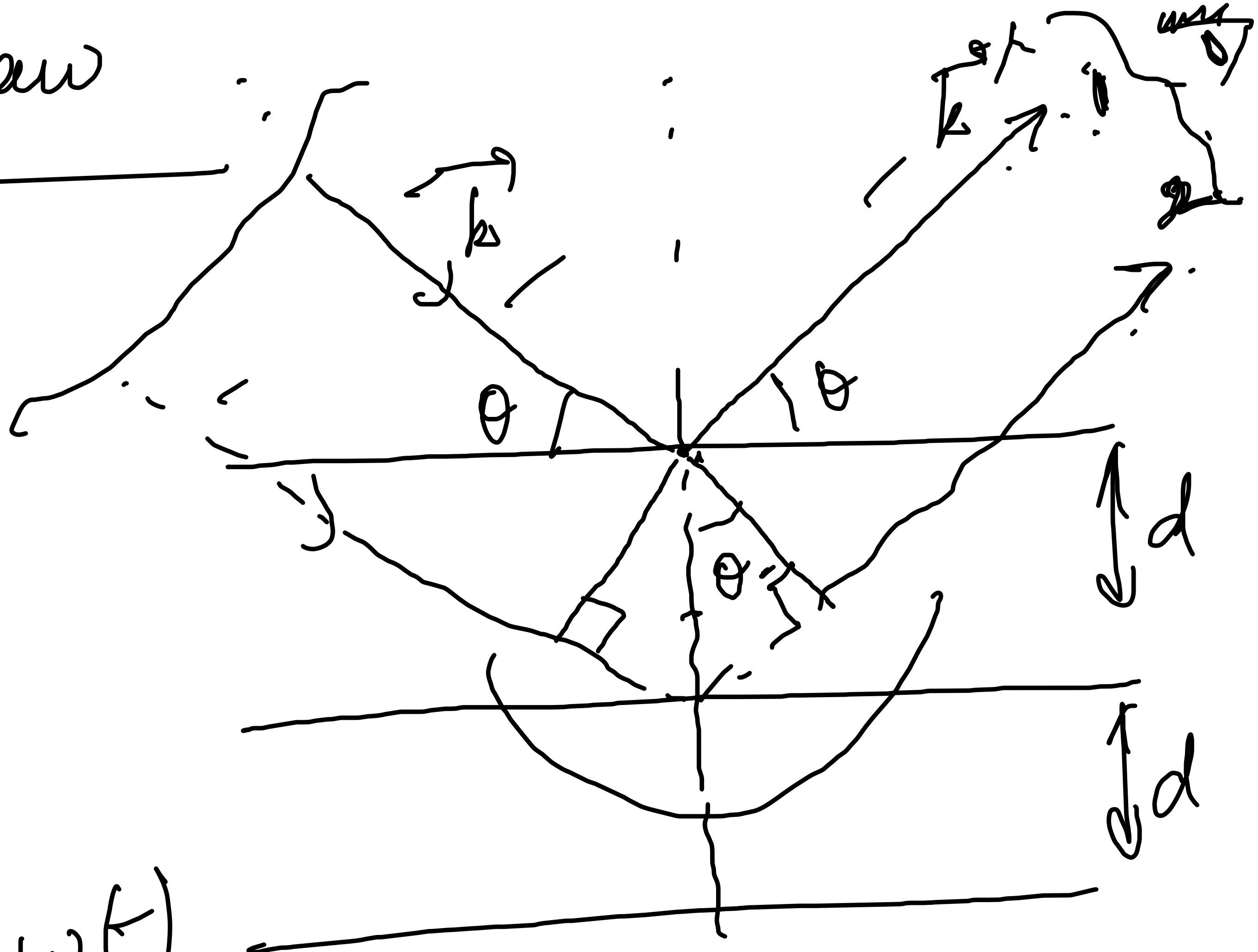
Lecture Plan

- Bragg's formulation of X-ray diffraction by crystals
- Scattering theory formulation

Bragg's Law

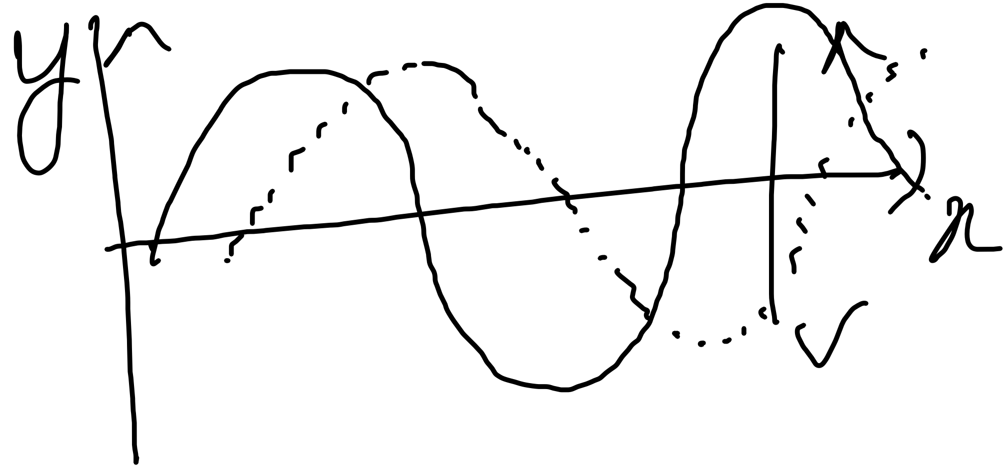
Elastic and coherent

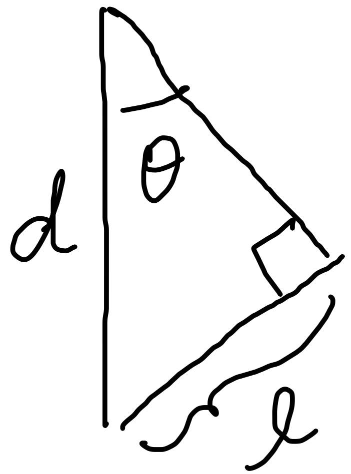


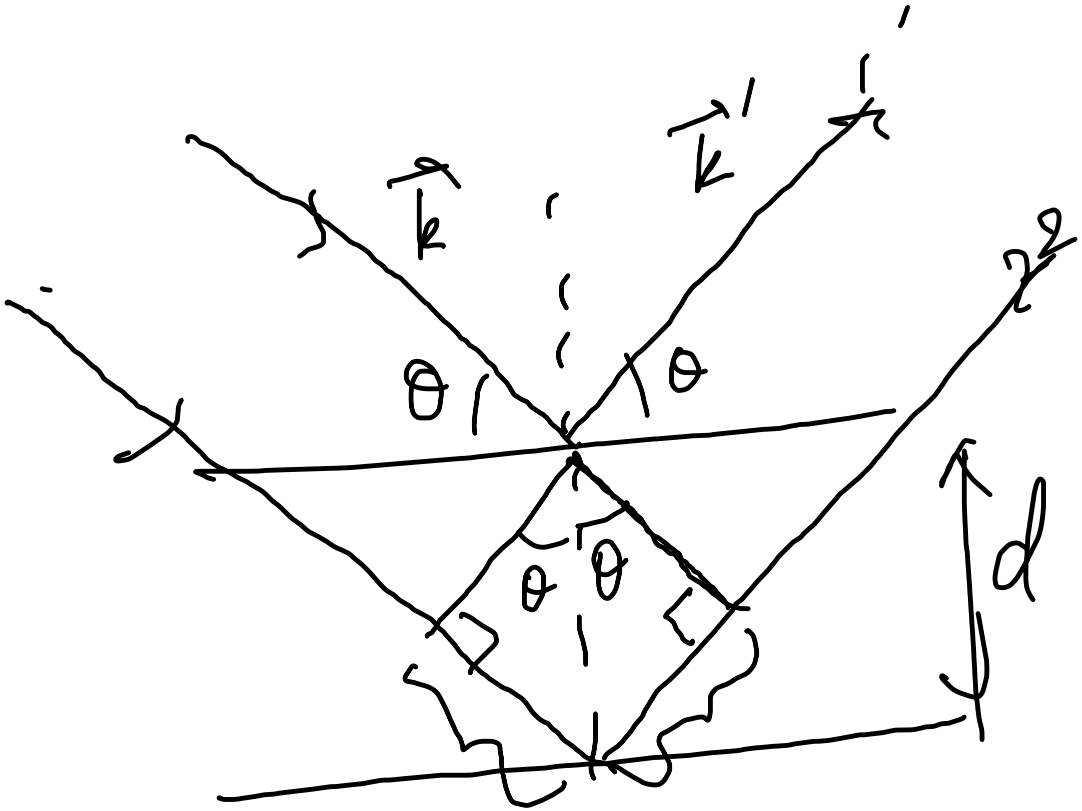
d_{hkl}

$$\vec{E} = E_0 \hat{\varepsilon} \sin(\vec{k}\cdot\vec{r} - \omega t)$$

$$\lambda \equiv 2\pi$$







$$l = d \sin\theta$$

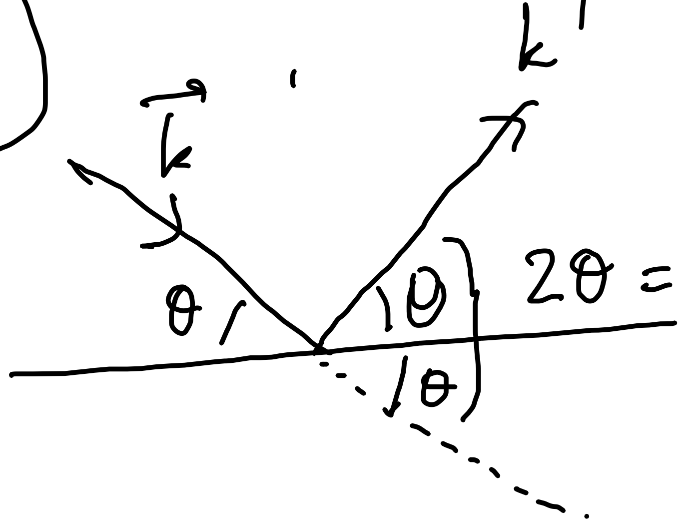
$\Rightarrow$ Path diff. betw. 2 & 1 $= 2l = 2d\sin\theta$

For constructive interference $2\pi n$ $\equiv$ $\boxed{n\lambda = 2d\sin\theta}$ Bragg formula

$n \in \mathbb{Z}$

$n = 1, 2, \ldots$

$$\boxed{2d\sin\theta = n\lambda}$$



$2\theta = \varphi$

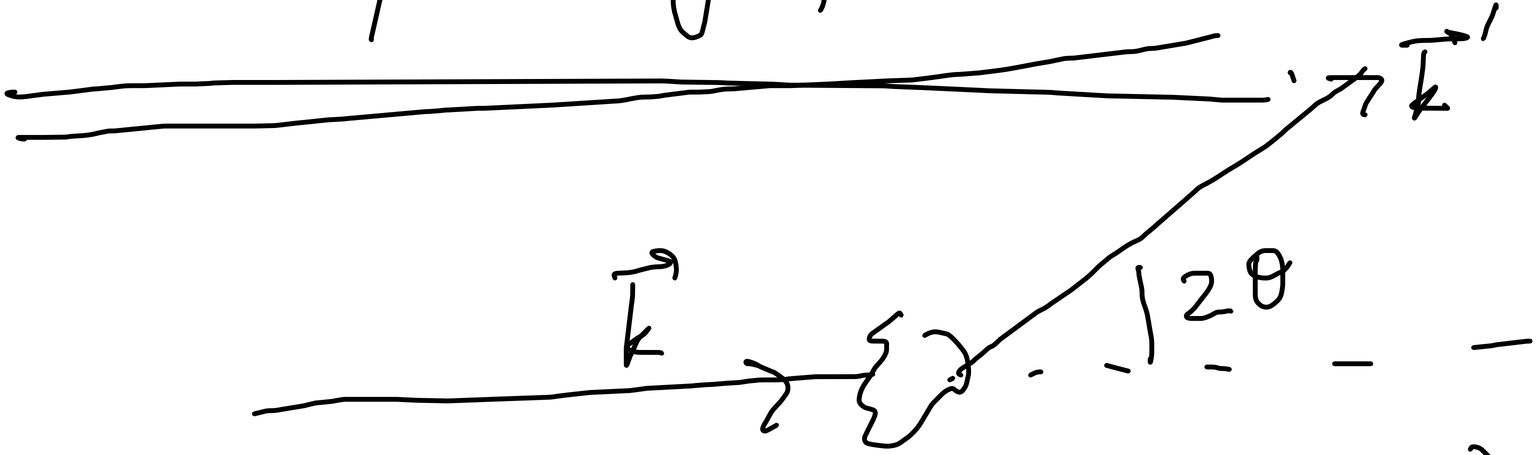
$$\vec{k}\cdot\vec{k}' = k^2\cos(2\theta)$$
$$= k^2\cos\varphi$$

$$\frac{2\pi}{\lambda} = k$$

$$\boxed{2k\sin\theta = n\left(\frac{2\pi}{d}\right) = nG_1}$$

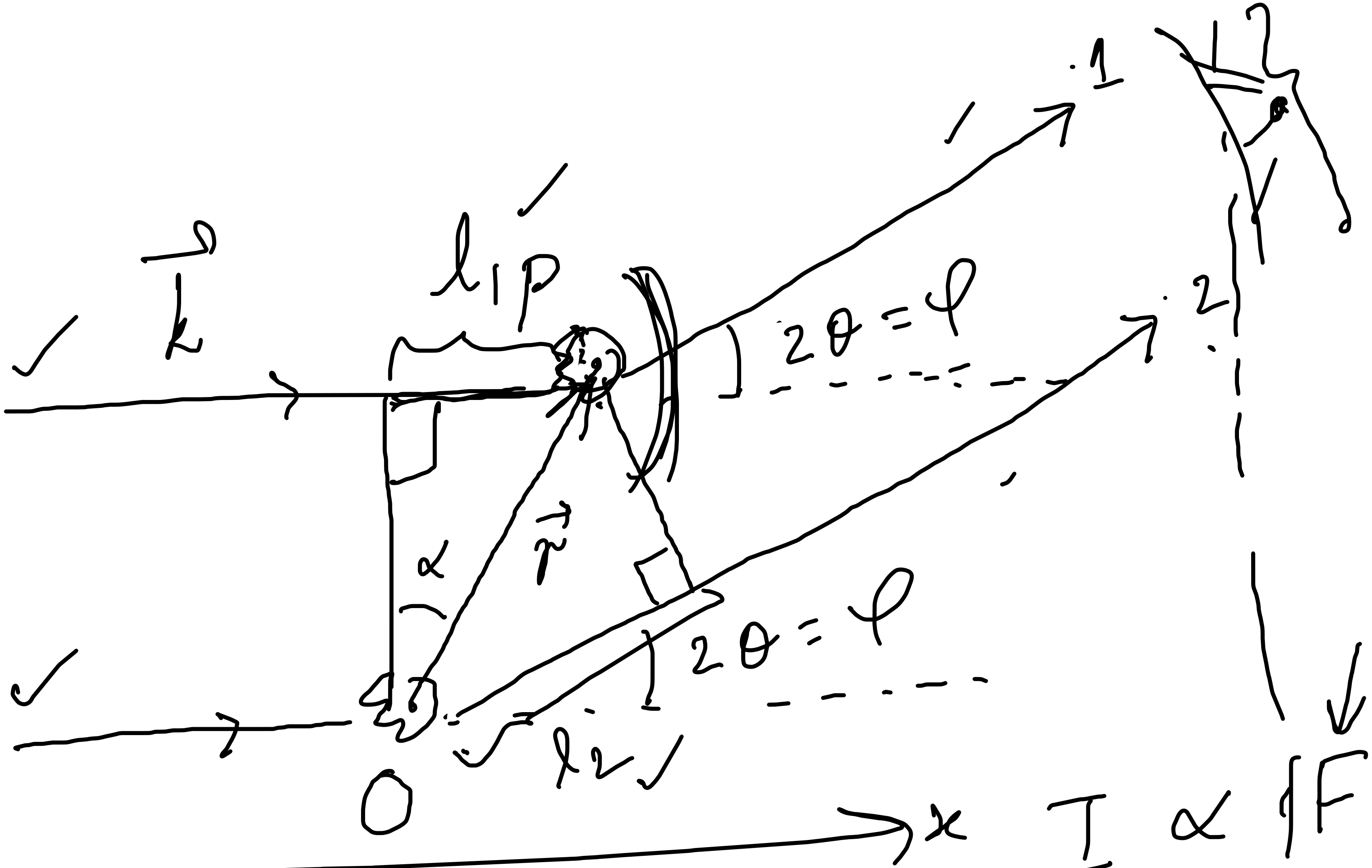
$$|\vec{G}_1| = 2\pi/d$$

Scattering Theory formulation



$$\frac{d\sigma}{d\Omega} = \frac{r_0^2}{2}\left(1 + \cos^2(2\theta)\right) = \frac{\langle dP/d\Omega \rangle}{\langle I_0 \rangle}$$

$$\left\langle \frac{dP}{d\Omega} \right\rangle = \langle I_0 \rangle \frac{d\sigma}{d\Omega}$$

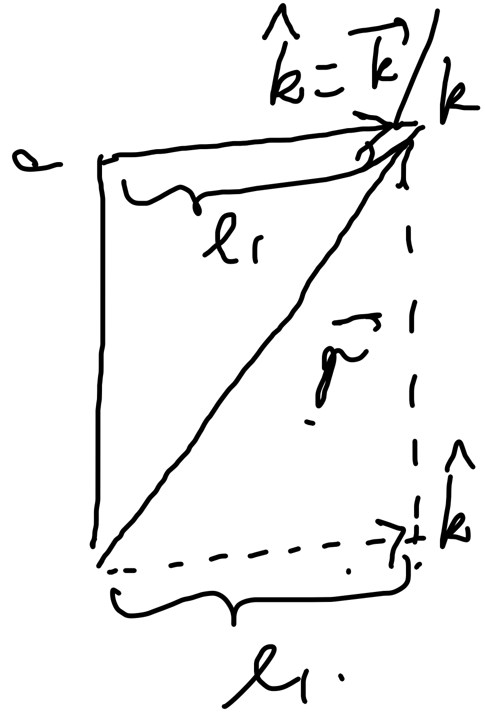


$I \propto |F|^2$

Before scattering: $d_{12}^{in} = l_1$

After scattering $d_{12}^{out} = -l_2$

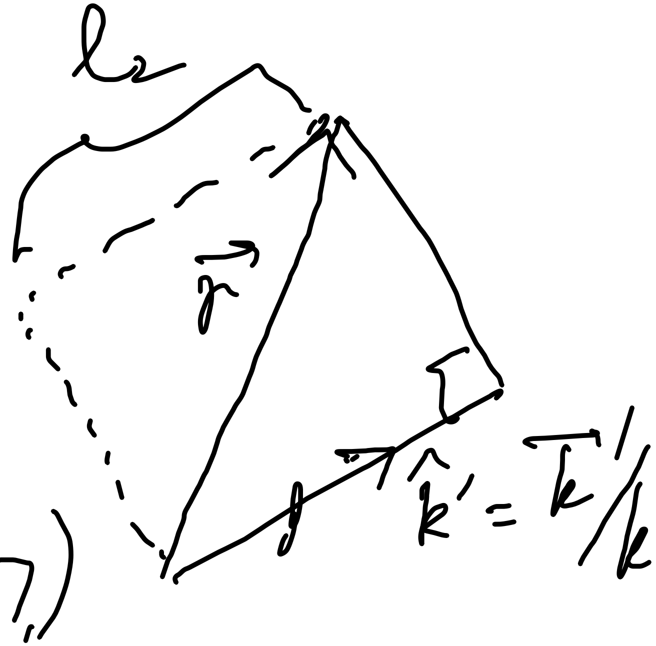
$$d_{12}^{in} = l_1 = \vec{r}\cdot\hat{k} = \frac{\vec{r}\cdot\vec{k}}{k}$$



$$d_{12}^{out} = -l_2$$

$$= -\frac{\vec{r}\cdot\vec{k}'}{k'} = \frac{\vec{r}\cdot\vec{k}'}{k}$$

= (elastic scattering)



Total p.d. between 1 & 2 is

$$d_{12} = d_{12}^{in} + d_{12}^{out} = \frac{(\vec{k} - \vec{k}') \cdot \vec{r}}{k}$$

Total phase diff. between 1 & 2 is

$$\delta_{12} = \frac{2\pi}{\lambda} d_{12} = (\vec{k} - \vec{k}') \cdot \vec{r}$$

because $k = 2\pi/\lambda$

$$= - \vec{q} \cdot \vec{r}$$

$\vec{q} \rightarrow$ scattering vector

Assuming that both incoming & outgoing radiation can be treated as plane waves.

Collection of scatterers:

$$\sum_i e^{-i\vec{q}\cdot\vec{r}_i}$$

$$n(\vec{r}) = |\psi(\vec{r})|^2$$

$n(\vec{r})$:

Total scattered amplitude :

$$f(\vec{q}) = \int d^3r\, n(\vec{r})\, e^{-i\vec{q}\cdot\vec{r}}$$

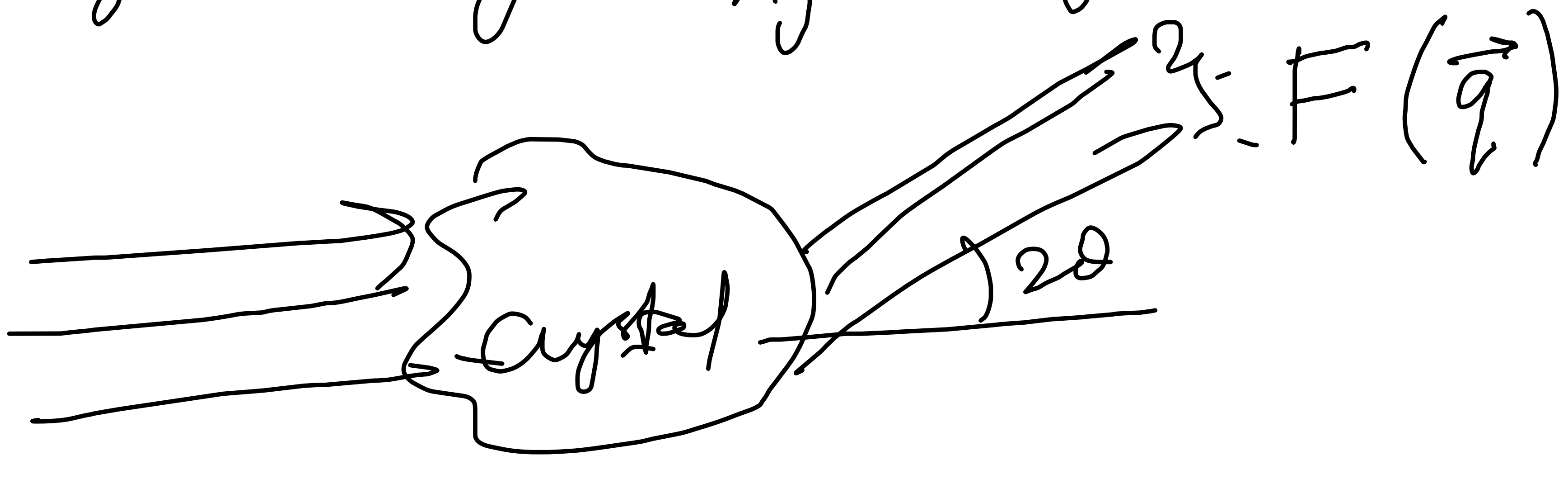
$\rightarrow$ Atomic form factor

$$f(0) = \int d^3r\, n(\vec{r}) = Z$$

$$\boxed{\frac{d\sigma}{d\Omega} = |f(\vec{q})|^2 \frac{r_0^2}{2}(1+\cos^2 2\theta)}$$

Scattering by a crystal : Consider a crystal w/ a Bravais lattice $\{\vec{R}\}$ and basis atoms $\{\vec{s}_i\}_{i=1,N_b}$

Then the position of the i^{th} basis atom in an arbitrary lattice pt. is given by: $\vec{A}_j = \vec{R}_j + \vec{s}_j$



Let $n(\vec{r}) = \sum_{\vec{R}} \sum_{j=1}^{N_b} n_j(\vec{r})$

$$n_{j\vec{R}}(\vec{r}) \equiv n(\vec{r} - \vec{A}_j)$$

i.e. we are assuming that the crystal density can be written as a sum of atomic densities.

$$F(\vec{q}) = \int d^3r\, n(\vec{r})\, e^{-i\vec{q}\cdot\vec{r}}$$

$$\simeq \sum_{j} \sum_{\vec{R}} \underbrace{\int d^3r\, \underline{n(\vec{r}-\vec{A}_j)}\, e^{-i\vec{q}\cdot\vec{r}}}$$

$$= \sum_{\vec{R}} \left(\underbrace{\sum_{j} \left[\int d^3r\, n(\vec{r}-\vec{A}_j)\, e^{-i\vec{q}\cdot(\vec{r}-\vec{A}_j)} \right]}_{f_j(\vec{q})} \times e^{-i\vec{q}\cdot\vec{A}_j} \right)$$

$$= \sum_{\vec{R}}' \sum_{j} f_j(\vec{q})\, e^{-i\underbrace{\vec{q}\cdot\vec{A}_j}}$$

$$= \sum_{\vec{R}}' \underbrace{\left(\sum_{j} f_j(\vec{q})\, e^{-i\vec{q}\cdot\vec{s}_j} \right)} e^{-i\vec{q}\cdot\vec{R}}$$

$$= \underbrace{\left(\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} \right)} \underbrace{\left(\sum_{j} f_j(\vec{q})\, e^{-i\vec{q}\cdot\vec{s}_j} \right)}$$

$$\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} = \sum_{\vec{R}} e^{-i\vec{q}\cdot(\vec{R}+\vec{R}')}$$

$$\Rightarrow \left(1 - e^{-i\vec{q}\cdot\vec{R}'}\right)\left(\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}}\right) = 0$$

either $\vec{q}\cdot\vec{R}' = 2\pi m \Rightarrow$ if $\vec{q}$ is a reciprocal lattice vector

or $\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} = 0$

i.e. $\vec{q} = \vec{G} \longrightarrow$ reciprocal lattice vector

in this case

$$\sum_{\vec{R}} e^{-i\vec{G}\cdot\vec{R}} = N \longrightarrow \text{no. of unit cells in the crystal}$$

$$\therefore \quad \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} = \begin{cases} 0 & \\ N & (\vec{q} = \vec{G}) \end{cases}$$

any reciprocal lattice vector

$$= N \sum_{\vec{G}}{}' \delta_{\vec{q},\vec{G}}$$

$$F(\vec{q}) = \underbrace{\left(N \sum_{\vec{G}} \delta_{\vec{q},\vec{G}} \right)} \times \underbrace{\Phi(\vec{q})}$$

$$\Phi(\vec{q}) = \sum_j f_j(\vec{q})\, e^{-i \vec{q} \cdot \vec{r}_j}$$

$$\frac{d\sigma}{d\Omega} = |F(\vec{q})|^2 \frac{r_0^2}{2} \left(1 + \cos^2 2\theta\right)$$

$$\propto N^2 \underbrace{\sum_{\vec{G}} \delta_{\vec{q},\vec{G}}} \underbrace{|\Phi(\vec{q})|^2}$$

when $\vec{q} = \vec{G} = \vec{k}' - \vec{k}$ ✓

$\Rightarrow -\hbar \vec{G}$ is the momentum change in the crystal

$$q = \frac{2p}{\hbar} \sin\left(\frac{\varphi}{2}\right) = 2k \sin(\theta)$$

$$|\vec{G}_1| = \frac{2\pi}{d}$$

$$\boxed{2k \sin\theta = \frac{2\pi}{d}}$$

$$\boxed{2k \sin\theta = G}$$

$$G = n|\vec{G}_1| = 2\pi n/d$$

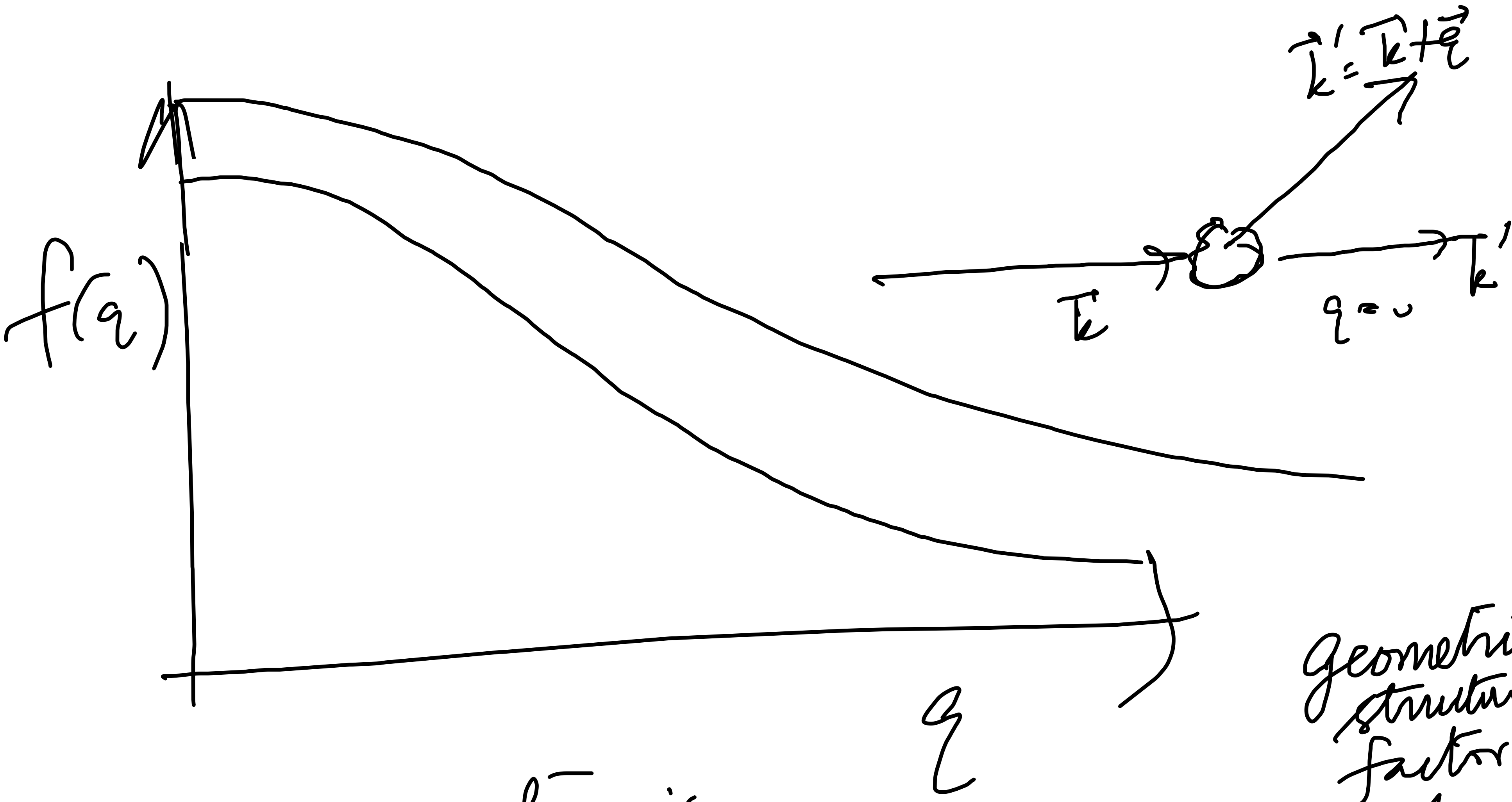
Atomic form factors:

$$f(\vec{q}) = \underbrace{\int d^3r \, n(\vec{r}) \, e^{-i\vec{q}\cdot\vec{r}}}_{\text{Fourier transform of density}}$$

$$\Rightarrow f(0) = Z$$

$\Rightarrow$ Large atoms will contribute more to the scattering of X-rays

e.g. $n(\vec{r}) = \dfrac{Z}{\pi a^3} e^{-2r/a} \Rightarrow \boxed{f(\vec{q}) \sim \dfrac{Z}{1 + \left(\frac{qa}{2}\right)^2}}$



For a monatomic crystal $\Rightarrow$ all f_j's are identical

$$\Phi(\vec{q}) = f(\vec{q})\, S(\vec{q})$$

where

$$\boxed{S(\vec{q}) = \sum_j e^{-i\vec{q}\cdot\vec{r}_j}}$$

geometric structure factor

For primitive lattices of monatomic crystals

$\longrightarrow$ all f_j's are the same

$\longrightarrow$ $N_b = 1$

$\Rightarrow S(\vec{q}) = 1$