1.

Scattering of X-rays from layered structure

"1 dimensional xtal":

Scattered intensity:

$$I_{sc} \propto I_0 \, |G(\theta)|^2 \, L_p(\theta) \, S(\theta)$$

I_0: incoming intensity

$|G(\theta)|^2$: (unit cell structure factor)^2

$L_p(\theta)$: Lorentz-polarization factor

$S(\theta)$: interference function

Unit cell structure factor:

$$G(\theta) = \sum_j n_j f_j(\theta) \cos\left(4\pi z_j \frac{\sin\theta}{\lambda}\right)$$

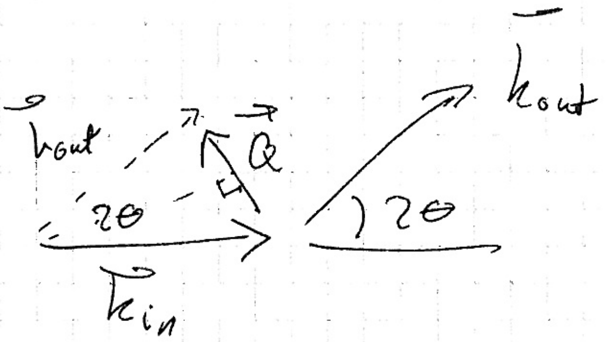
z_j: position z_j of element j

$f_j(\theta)$: atomic form factor

n_j: # of element type j at position z_j

$\sum_j$: sum over all atoms in unit cell

2.



elastic scattering $|\vec{k}_{in}| = |\vec{k}_{out}| = \frac{2\pi}{\lambda}$

Scattering angle 2θ

$\vec{Q}$ scattering vector

$$\frac{|\vec{Q}|}{2} = \sin\theta \, |\vec{k}| = \frac{2\pi}{\lambda} \sin\theta$$

$$\Rightarrow |\vec{Q}| = Q = \frac{4\pi}{\lambda} \sin\theta$$

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atomic form factor:

$$f_j(\theta) = f_j^0 \, \underbrace{e^{-B_T^j \left(\frac{\sin\theta}{\lambda}\right)^2}}$$

atomic form factor of element type j at rest
$\equiv$ scattering strength of element type j.

Debye-Waller factor due to lattice vibrations around eq. positions

$$B_T^j = 8\pi^2 \underbrace{\langle u_j^2 \rangle}_{\text{mean square displacement of atom } j}$$

3.

Lorentz polarization factor

$$L_p(\theta) = \frac{P(\theta)}{\sin 2\theta \, \sin^\beta \theta}$$

$P(\theta)$ = polarization factor

depends on source (synchrotron or anode)

$$P(\theta) = \begin{cases} 1 & \text{— vertical scattering plane synchrotron} \\ \cos^2 2\theta & \text{— horizontal scattering plane synchrotron} \\ \frac{1}{2}(1+\cos^2 2\theta) & \text{— unpolarized source} \end{cases}$$

Lorentz factor $\frac{1}{\sin 2\theta \sin^\beta \theta}$ is a

geometrical factor depending on scattering ~~geometry~~ and on how many crystallites ~~[illegible]~~ contributes to the scattering

$$\beta = \begin{cases} 0 & \text{for perfect crystal} \\ \text{intermediate} & \text{for other cases} \\ 1 & \text{for perfect powder} \end{cases}$$

i.e. many crystallites with random orientations

β is a free parameter to be fitted in the general case

4b.

Interference function:

$$S(\theta) = \frac{\sin^2(Nx)}{\sin^2(x)} \xrightarrow[N\to\infty]{} \delta(x)$$

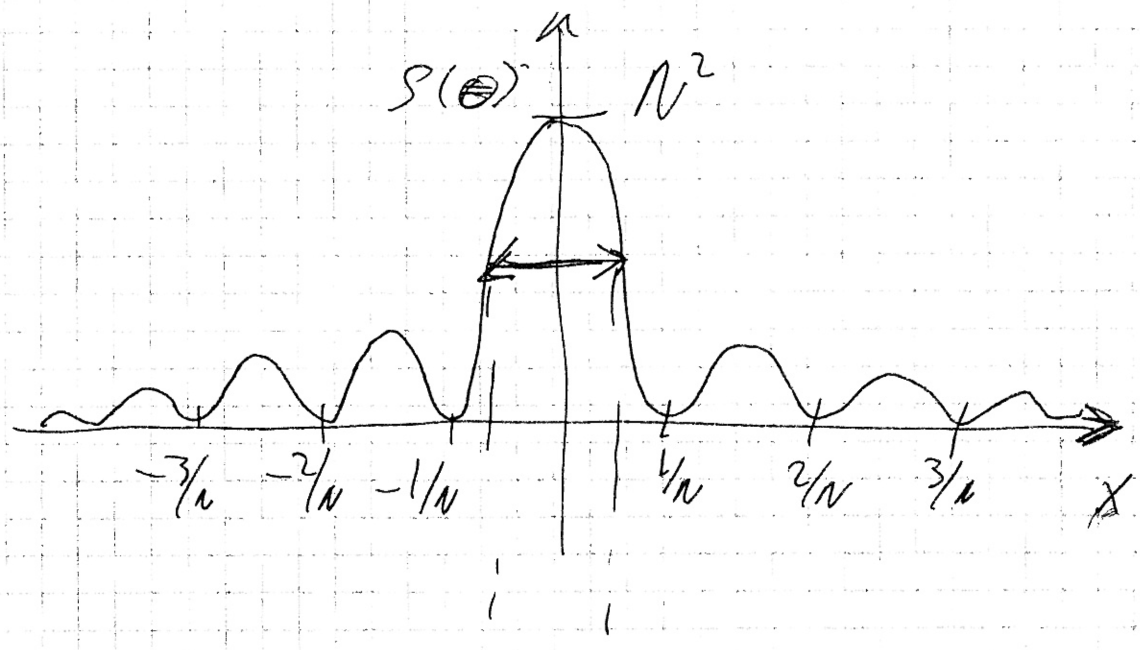
N: # lattice planes

$$x = \left(\frac{2d}{\lambda}\sin\theta - n\right)\pi = \frac{d}{2}\frac{4\pi}{\lambda}\sin\theta - n\pi$$

n: integer

$$= \frac{qd}{2} - n\pi$$

$x = 0 \Rightarrow$ Bragg's law



$\frac{0.88}{N}$ = FWHM

In reality:

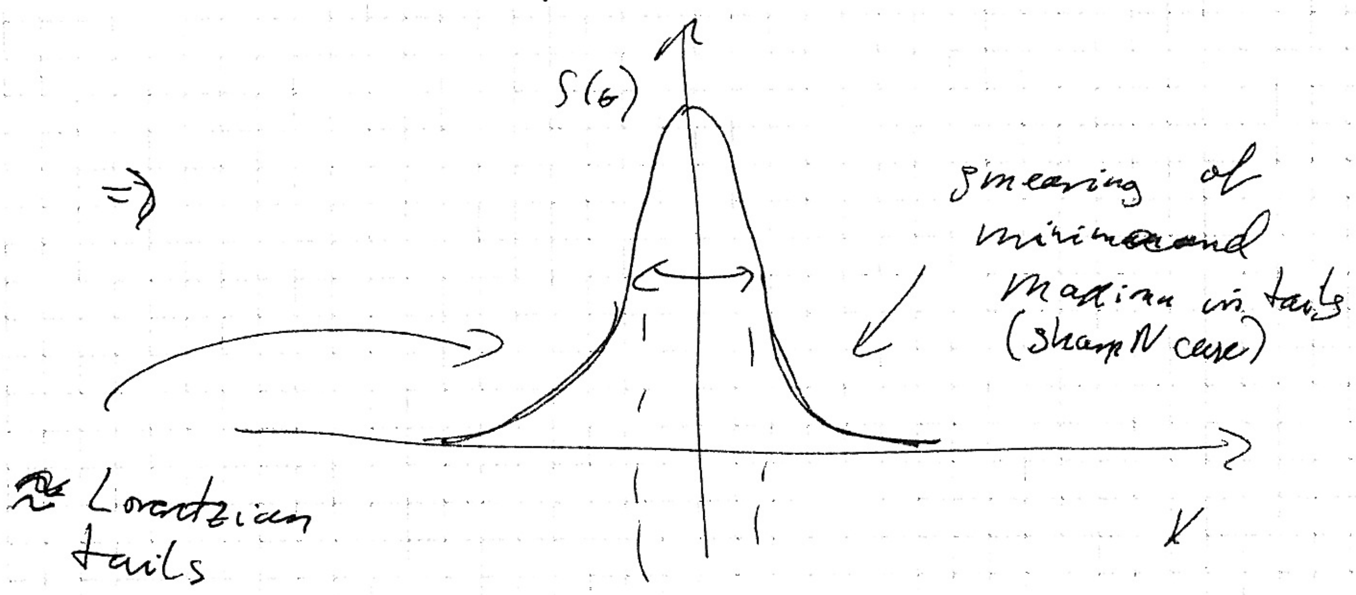
$\underbrace{N_1 < N < N_2}$

Several Xtals contribute, N not sharp

$\Rightarrow$ distribution of N = $p(N)$

$$\Rightarrow \quad S(\theta) = \sum_{N=N_1}^{N=N_2} P(N) \frac{\sin^2(Nx)}{\sin^2 x}$$

$\Rightarrow$



Lorentzian peak form
$$\frac{A}{\left(\frac{FWHM}{2}\right)^2 + x^2}$$

$FWHM \sim \frac{0.88}{N_{average}}$

$N \to \infty$ δ – Bragg peaks

N finite $\Rightarrow$ Finite width Bragg peaks $\sim FWHM \sim \frac{1}{N_{av}}$

$x = \frac{1}{2} q d \quad \Rightarrow \quad \Delta q \sim \frac{2\Delta x}{d} \sim \frac{2}{d N_{av}} \sim \frac{2}{\text{average Xtal thickness}}$

6.

Braggs law:

$2d\sin\theta = n\lambda$

Assume d unsharp $\Rightarrow$ $d \pm \frac{\Delta d}{2}$

$$d = \frac{n\lambda}{2\sin\theta} \Rightarrow \Delta d = \frac{n\lambda}{2}\frac{\cos\theta}{\sin^2\theta}\Delta\theta$$

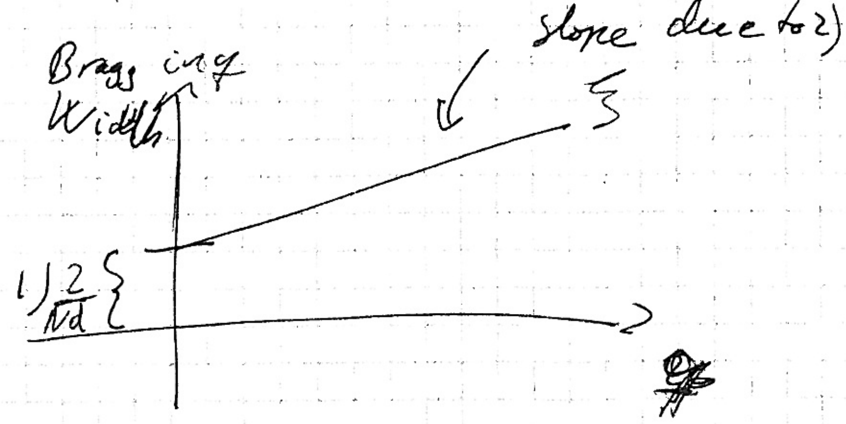
$$\Rightarrow \frac{\Delta d}{d} = \frac{\Delta\theta}{\tan\theta} \Rightarrow \underline{\Delta\theta = \frac{\Delta d}{d}\tan\theta}$$

$$\frac{\Delta q}{q} = \frac{\Delta d}{d} \Rightarrow \Delta q = \xi q$$

$\Rightarrow$ Contributions to finite width Bragg peaks:

1) Finite N (~ 100 in our case)

2) $\frac{\Delta d}{d}$

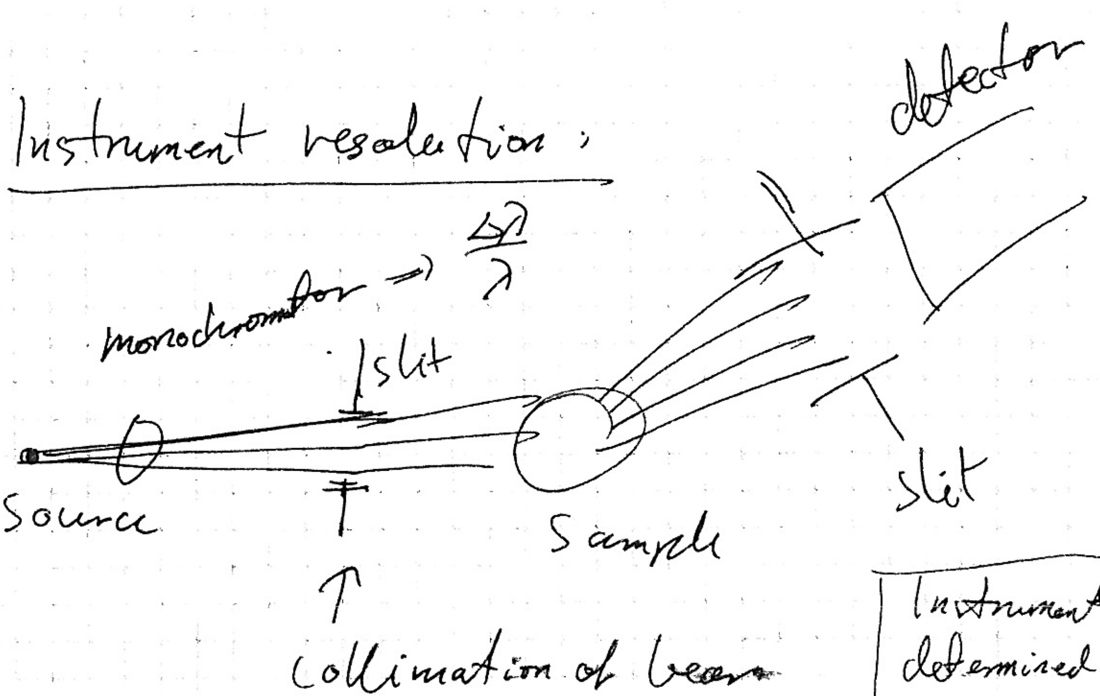


Williamson-Hall analysis.

3) Temperature (Debye-Waller) can be neglected in our case.

7.

Instrument resolution:

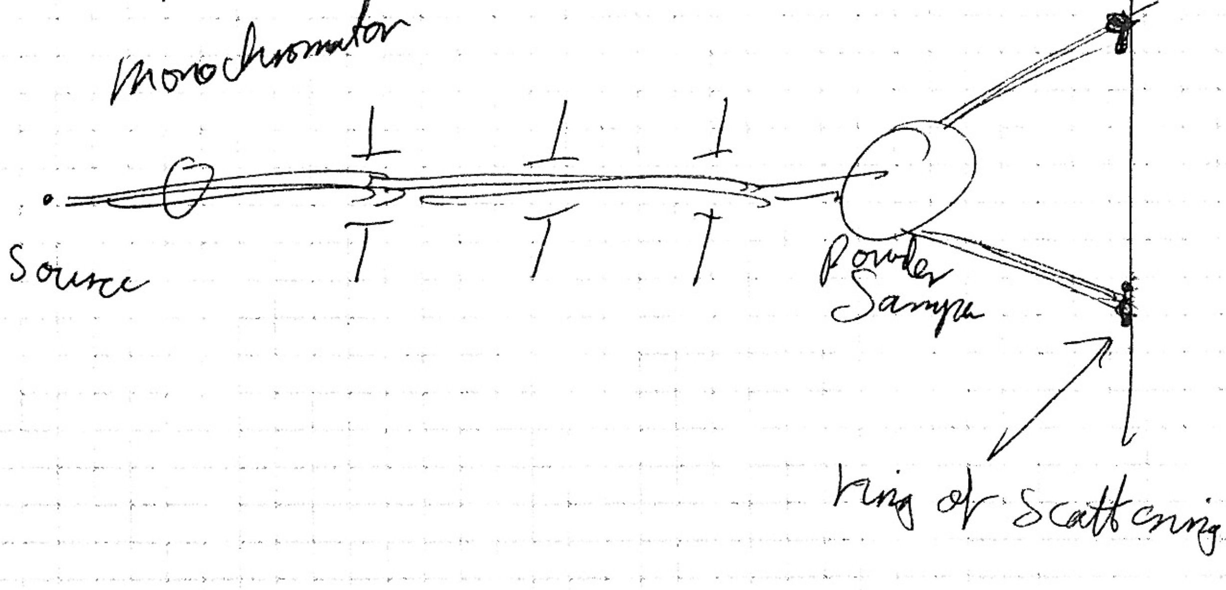


Instrument width determined from monochromator + slit widths

"Perfect" scattering sample i.e. δ-peak Bragg

$\Rightarrow$ Measures resolution function of the instrument $I_{instrument}$

In our lab-case:
2d detector, i.e. no slit after sample



8.

convolution = amount of overlap as Instrument is moved through I_{sc}.

$$I_{measured} = I_{sc} \otimes I_{instrument}$$

Lorentzian empirically

$$\frac{A}{\left(\frac{FWHM}{2}\right)^2 + (x - x_c)^2}$$

Gaussian empirically

$$A e^{-\frac{(x-x_c)^2}{2\sigma^2}}$$

If I_{sc} = δ function $\Rightarrow I_{measured} = I_{instrument}$

$$I_{measured} = \int_0^t I_{sc}(\tau)\, I_{instrument}(t-\tau)\, d\tau$$

convolution

$\Rightarrow$ Need to deconvolute in order to get I_{sc} ~~from~~ I measured when I instrument is known.

If width of $I_{instrument} \ll I_{sc} \Rightarrow$

$\hookrightarrow I_{measured} \approx I_{sc}$

9.

Deconvolution "difficult":

$\Rightarrow$ Approximation:

<u>Pseudo-Voigt analysis:</u>

Approximation to convolution of $\underbrace{\text{Gaussian}}_{\text{Instrument}}$ and $\underbrace{\text{Lorentzian}}_{\text{Sample}}$

$$S(q) = S(q)$$

$$= \frac{2\eta}{\pi\Gamma(1+4(q-q_c)^2)} + 2\,\frac{1-\eta}{\Gamma}\left(\frac{\ln 2}{\pi}\right)^{1/2} e^{-\frac{4\ln 2}{\Gamma^2}(q-q_c)^2}$$

$$\Gamma = \left(\Omega_g^5 + 2.7\,\Omega_g^4\Omega_L + 2.43\,\Omega_g^3\Omega_L^2 + 4.5\,\Omega_g^2\Omega_L^3 + 0.08\,\Omega_g\Omega_L^4 + \Omega_L^5\right)^{1/5}$$

$$\eta = 1.4\,\frac{\Omega_L}{\Gamma} - 0.5\,\frac{\Omega_L^2}{\Gamma^2} + 0.11\,\frac{\Omega_L^3}{\Gamma^3}$$

Ω_g - instrumental width

$$\Omega_L = \underbrace{\frac{2\pi}{N_{av}d}}_{\substack{\text{Finite}\\ \text{size}}} + \underbrace{\xi q}_{\frac{\Delta d}{d} q}$$

10 NTNU:

Stationary source (X-ray tube)
+ $\underbrace{\text{SAXS Nanostar system}}_{\text{Bruker}}$

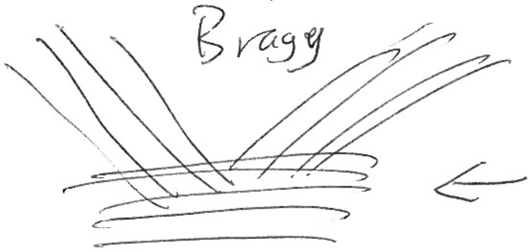
Traditional
Stationary source: 1.5 kW ← 1mm² spot
replaced 2009 by new generation
X-ray source: 30 W ← 1μm² spot

5-6 times higher flux then traditional source

CuKα radiation: $\lambda = 1.5418 Å$

Monochromating and collimating (curved) multilayer mirror

Bragg



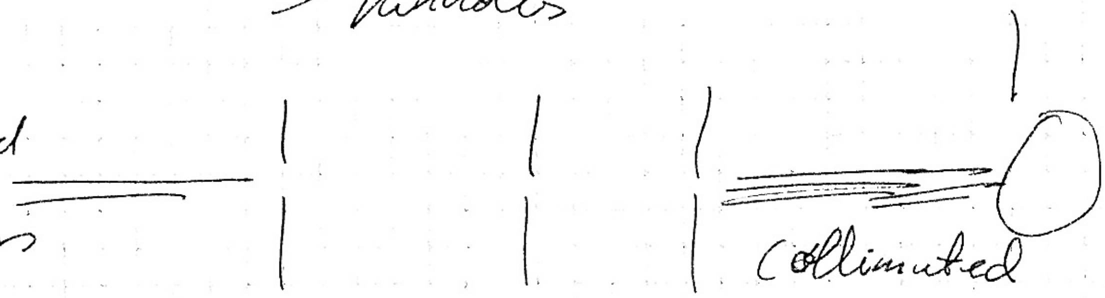
← selects CuKα only

⇒ Out from mirror comes
∥ monochromatic X-rays

finite sample length

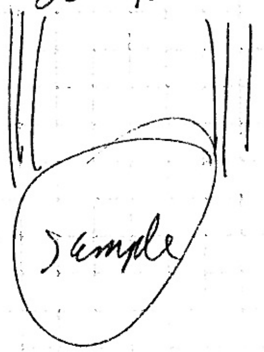
3 pinholes

Göbel mirrors



collimated
0.4 mm
beamspot on sample

Finite sample length + $\frac{\Delta\lambda}{\lambda}$ + divergence of incoming beam



$\Downarrow$

Instrumental resolution function in this case

Detector:

Multiwire grid

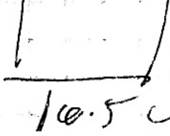
Xe-gas detector

ionized by incoming scattered x-rays

$\Rightarrow$ charged Xe hits grid

14 bit location in xy

$\Rightarrow$ 1024 × 1024 pixel resolution



10.5 cm } detector size

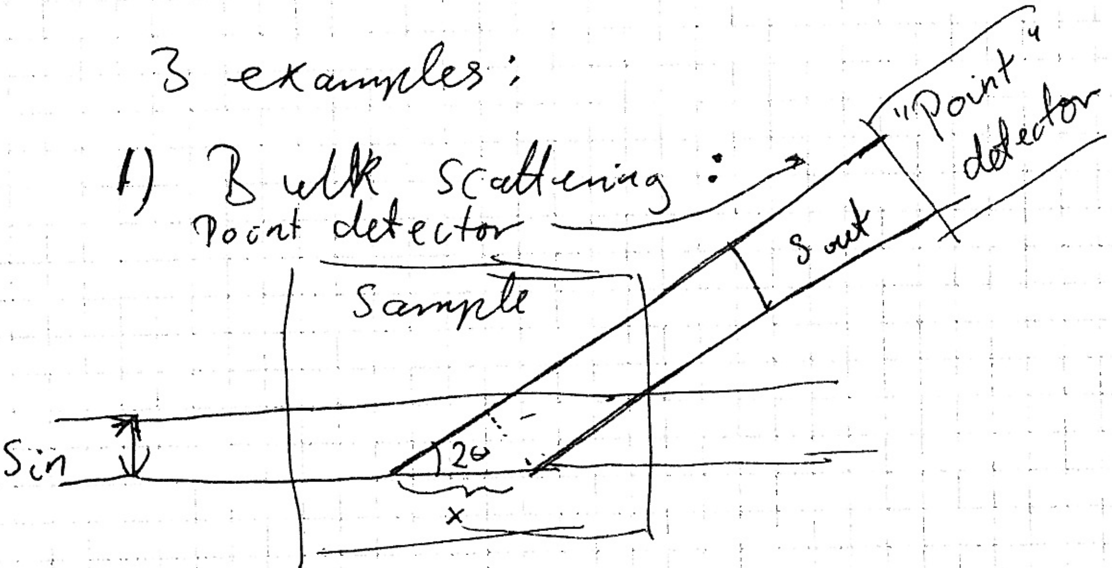
10.5 cm

Corrections due to scattering volume:

Measured $I \propto N$ = # of scatterers in $\underbrace{\text{Scattering volume}}_{\text{may change with } \theta}$.

3 examples:

1) Bulk scattering: Point detector



S_{in} and S_{out} — incoming and outgoing slits

$$\sin 2\theta = \frac{S_{out}}{x}$$

$$\Rightarrow N \propto V_{scattering} = \underset{\substack{\uparrow \\ \text{horizontal} \\ \text{width of beam}}}{W} \cdot x\, S_{in} = W \frac{S_{in} S_{out}}{\sin 2\theta}$$

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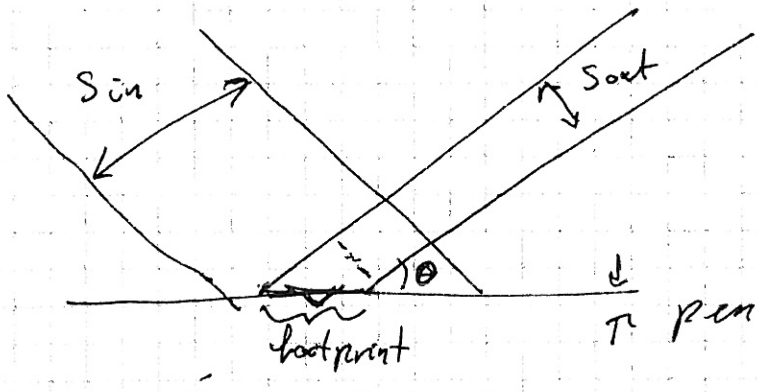
2) Surface scattering (reflection):
Point detector



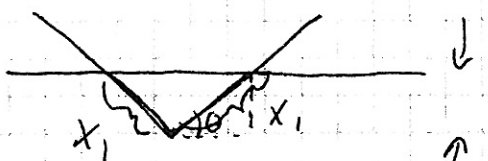
Sample

$N \propto V_{scattering} \sim w \cdot \text{footprint} \cdot \text{penetration depth}$

Footprint determined from narrowest slit (Sin or Sout) $S_{narrowest}$

$$\text{footprint} = \frac{S_{narrowest}}{\sin\theta}$$

$I = I_0 e^{-\mu x}$ ← absorption coeff.



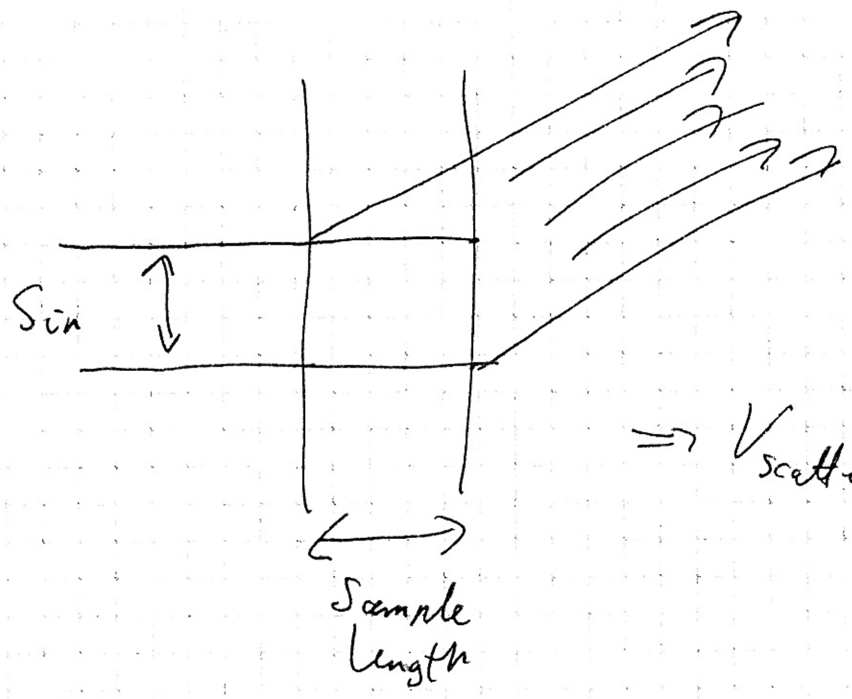
penetration depth $\sim x_1 \sin\theta$

$\sim \frac{1}{2\mu} \sin\theta$

$2x_1 \sim \mu$

$\Rightarrow V_{scattering} \sim w \cdot \frac{1}{2\mu} S_{narrowest}$

3) Area detector, no S_{out}



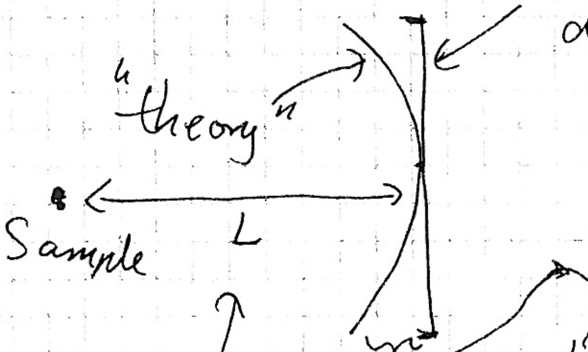
$$\Rightarrow V_{scattering} \sim S_{in} \times \frac{\text{Sample}}{\text{length}}$$

Special corrections for 2d detectors (area detectors):

1) Correction for pixel variations

   => Division by calibration image

2) Correction for "flatness"

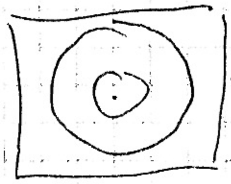


depends on

Sample - detector distance determines ~~[illegible]~~ "importance of" flatness correction.

3) Powder samples => Rings

   => Integration



← Detector image

$$I_{\text{integration}} = \frac{\sum \text{pixel values}}{2\pi r} = \frac{\sum \text{pixels}}{2\pi L \, tg 2\theta}$$