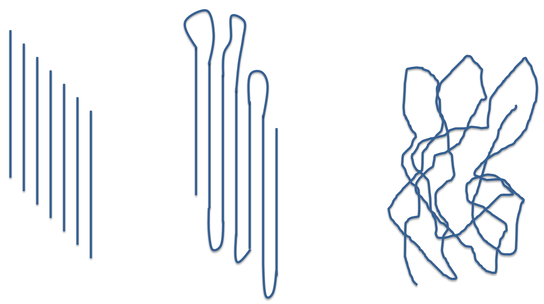
CHEMISTRY
TEXAS A&M UNIVERSITY

Wide Angle Scattering (WAXS) (Powder Diffraction)

How do we do

XRDLab TAMU
CUM VIDEBIMUS LUMEN

The Solid State



Crystalline Semi crystalline Amorphous
Long range order short range order only

"For most crystallographers it is long-range order that sets crystals apart from glasses and amorphous solids. But condensed-matter physicists have recognized that there is a structural continuum between ideal crystals and amorphous solids." . Gautam Desiraju : Nature 2013

Interaction of X-ray radiation with solids

- Collision of the X-ray photon with a charged particle causes the component of the particle to oscillate with the same frequency.
- The oscillating particle returns to the resting state by emitting a photon that travels outward.

The Math

Debye's Equation describes the interaction of radiation between two identical "atoms" i and j separated by the distance r_{ij}

- $\boldsymbol{I(s) = \sum_{i=1}^{2}\sum_{j=1}^{2} f_i(s) f_j(s) \frac{\sin 2\pi s r_{ij}}{2\pi s r_{ij}}}$
- Where $s = 2\sin\theta/\lambda$ and $f(s)=\sum ae^{-bs^2} + c$

a, b, c are the Cromer–Mann coefficients for a given element

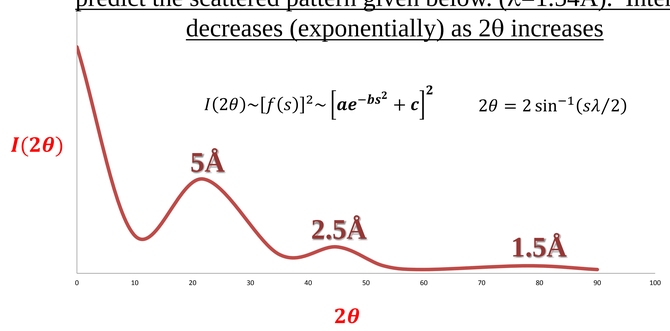
For a diatomic molecule of the same element the maxima for Debye's equation will be ~ $r_{ij}s_m = 1.23$ given s $= 2\sin\theta/\lambda$ then :

$$\boldsymbol{K\lambda = 2r_m \sin\theta_m \quad K = 1.23}$$

Debye's Equation [$I(s) = \sum_{i=1}^{N}\sum_{j=1}^{N} f_i(s) f_j(s) \frac{\sin 2\pi s r_{ij}}{2\pi s r_{ij}}$]describes the

Amorphous WAXS in general terms.

For a VERY simple system (all orientations are present) where the average contact distances are near 1.5, 2.5 and 5 Å we can predict the scattered pattern given below. (λ=1.54Å). Intensity decreases (exponentially) as 2θ increases

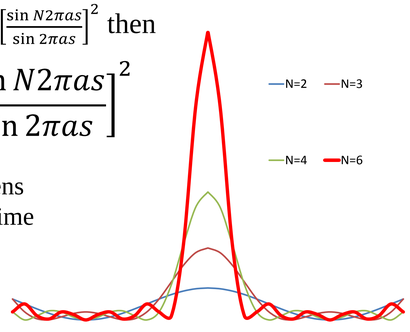


For a linear ordered system where the same element (atom) is spaced at equal distance(s) of a **N>2** times then

$$I(s) = \left[fe^{2\pi isr} + fe^{2\pi is(r+a)} + \cdots fe^{2\pi is(r+Na)}\right]^2 \mathrm{x}\left[\frac{\sin N2\pi as}{N2\pi as}\right]^2$$

given : $\left[\frac{\sin N2\pi as}{N2\pi as}\right]^2 \sim \frac{1}{N^2}\left[\frac{\sin N2\pi as}{\sin 2\pi as}\right]^2$ then

$$I(s) \sim f^2\left[\frac{\sin N2\pi as}{\sin 2\pi as}\right]^2$$



As N increases the peak sharpens until N>1000 atoms at which time you reach the line width of the instrument.

For a 3D ordered system (Crystalline)

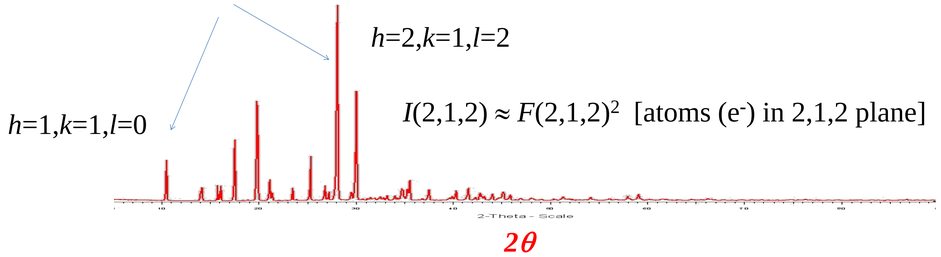
$F(s) = \sum_1^N f_n(s)e^{2\pi isr}$ $\quad r = xa + yb + zc$ (unit cell as vectors)

$F(s) = \sum_1^N f_n(s)e^{2\pi is(xa+yb+zc)}$ Given $s\cdot a = h, s\cdot b = k, s\cdot c = l$

$F(s) = \sum_1^N f_n(s)e^{2\pi i(hx+ky+lz)}$ and $\boldsymbol{I(s) \approx |F(s)|^2}$

For the 3D ordered systems $I(s)$ will have maxima at discrete positions

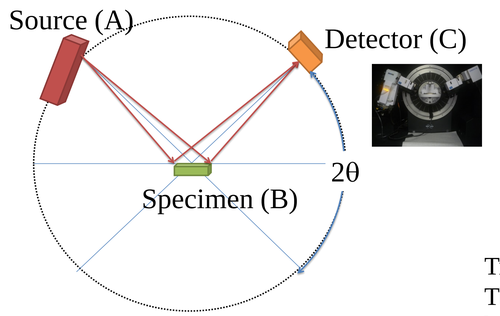
$\boldsymbol{hx + ky + lz \Rightarrow 2\theta_{hkl}}$ $\quad 2\theta_{hkl} = 2\times\sin^{-1}\left((a^{*2}h^2 + b^{*2}k^2 + c^{*2}l^2 + 2b^*c^*kl\cos\alpha^* + 2a^*c^*hl\cos\beta^* + 2a^*b^*hk\cos\gamma^*)^{1/2}/2\right)$



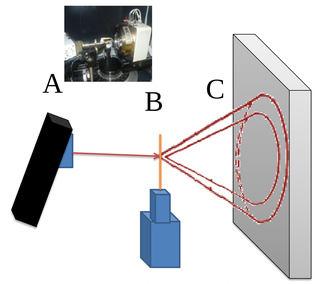
$I(2,1,2) \approx F(2,1,2)^2$ [atoms (e^-) in 2,1,2 plane]

Data Collection

X-rays diverge from the source (A) strike the specimen (B) and converge back to the detector (C) .

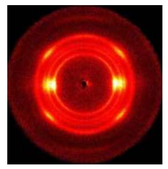


BRAGG BRENTANO :The detector is positioned at 2θ angle to collect the data. The number of X-rays counted by the detector is proportional to the intensity (I) of the scattered X-ray

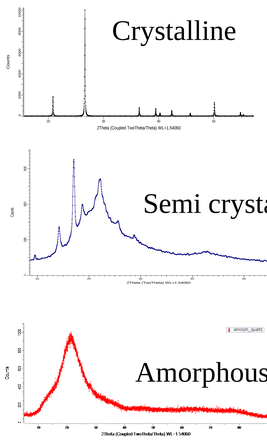


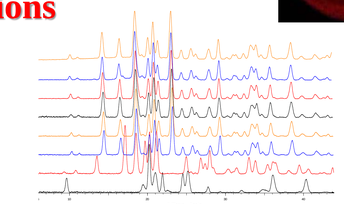
Transmission with Area detection.
The area (2D) detector is positioned behind the sample. X-rays travel; through the sample and are collected at the detector

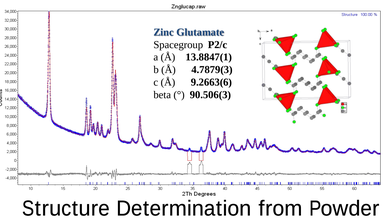
Fiber Diffraction



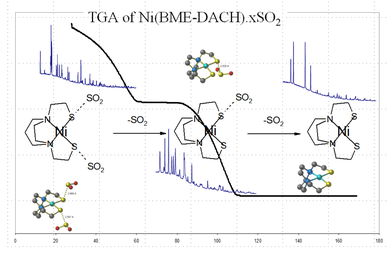
Applications

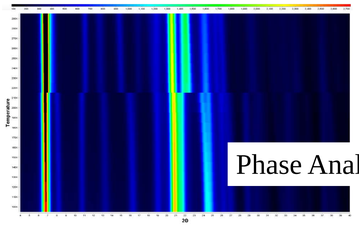


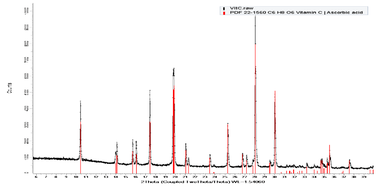




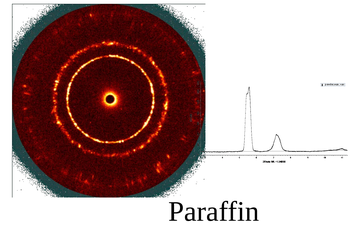
Structure Determination from Powder Data and Rietveld Refinement







Qualitative Analysis



Paraffin