X-Ray Diffraction as a key to the Structure of Materials
Interpretation of scattering patterns in real and reciprocal space

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1. “Internal” structure of materials – macroscopic characteristics: importance of experimental physics to understand fundamental properties

   The dilemma of x-ray optics

2. X-rays in structural analysis: diffraction as a sensing parameter for inter-atomic distances

3. Introduction to diffraction and reciprocal space

4. Limits of reciprocal space

5. Getting the most out of real and reciprocal space, How can we get the holy grail?
We know.
Glass is brittle, (-experiment)
Shape cannot be changed easily

Metals are much less brittle can be formed/deformed,

Metals conduct well electricity and heat

Glass is transparent and electrically insulating and a poor heat conductor

Mechanical properties    Optical properties    Electrical properties
Novoselov & Geim Nobel Price 2010:
Using scotch tape to lift of one atomic layer of Graphene,
With outstanding mechanical and electrical properties

2010: single layers of MoS$_2$ turn out to have outstanding electronic properties.
Atomic distances typically 0.1 nm (1 Å)

X-ray wavelength (typical)
\[ \lambda = 0.01 \ldots 0.1 \text{ nm} \]

Light \( \lambda \sim 500\text{nm} \)

Resolution \( \Delta x \) of a light microscope:
\[ \Delta x = \frac{1.22 \lambda}{2 \text{NA}} \sim \frac{0.6 \lambda}{n \sin \alpha} \]

High resolution means small wavelengths and large apertures (large collection angles)
MAGNIFICATION AND RESOLUTION

Be careful with “1000-times magnification” Microscopes

Magnification: geometrical optics (no reasonable limits, everything is allowed)
Resolution (=Δx): real information: limited (at least) by quantum mechanics
X-RAY OPTICS: THE DILEMMA OF REFRACTION

interaction of electromagnetic waves (light!) and matter (~electron clouds)
The refractive index is expressed as \( n = 1 - \delta + i\beta = \sqrt{\varepsilon \mu} \approx \sqrt{\varepsilon} = \sqrt{\varepsilon_0 (1 + \chi)} \)

\( n \approx 1 + \chi \quad \chi = \text{polarizability} \)

The polarizability \( \chi \) describes the polarization \( P \) as a function of a field \( E \):
\( P \sim \chi E \); in the mechanical equivalent, \( 1/\chi \) is similar to a spring constant

\[
\rho_m \ddot{s}(t) + B s(t) = \rho_e E(t)
\]

Inertia Spring constant driving force

Driven oscillator equivalent to simple mechanical model

We replace \( s(t) \) by the Polarization \( P(t) = \rho_e s \)

Damping factor (friction): \( \phi \) (we ignore the origin)

\[
\ddot{P}(t) + \omega_0^2 P(t) + \phi \dot{P}(t) = \frac{\rho_e^2}{\rho_m} E(t)
\]
SOLUTION OF “EQUATION OF MOTION”

\[
\rho \approx \sqrt{1 + \chi}
\]

With \( P \sim \chi \)

\[
\ddot{P}(t) + \omega_0^2 P(t) + \phi \dot{P}(t) = \frac{\rho^2_e}{\rho_m} E(t)
\]

What else can we interpret from the mechanical equivalent?

Amplitude

\[
X_0 \equiv P \propto \frac{\omega_0^2}{\left(\omega_0^2 - \omega^2\right)^2 + \phi^2 \omega^2}
\]

For \( \omega \ll \omega_0 \): \( P \approx \text{const.} \) (does hardly vary with \( \omega \))

For \( \omega \gg \omega_0 \): \( P \approx \frac{1}{\omega^2} \), thus \( P \to 0 \)

Refraction in the x-ray regime is very weak and highly chromatic!!

\[ n \approx 0.99999 \]
Lens surfaces must be paraboloids of rotation

parameters for Be lenses:

\[ R = 50 \text{ to } 1500 \mu m \]
\[ 2R_0 = 0.45 \text{ to } 2.5 \text{ mm} \]
\[ d \text{ below } 30 \mu m \]

Resolution \[ \Delta x = 1.22 \frac{\lambda}{2NA} \approx 0.6 \frac{\lambda}{(n \sin \alpha)} \]

parabolic profile: no spherical aberration

focusing in full plane

=>$ \text{ excellent imaging optics}$
At the observation point we record

\[ I = \langle \left| \sum_{j=1}^{N} \hat{A}_j e^{i(k_f - k_i) \cdot r_j} e^{i\omega t} \right|^2 \rangle_t = \left| \int \rho(r) e^{iQ \cdot r} \cdot dr \right|^2 \]

We admit that only the time averaged Intensity can be measured and that the point scatterers can be described as

\[ \rho(r) = \sum_{j=1}^{N} \hat{A}_j \delta(r_j) \]
Young's experiment

\[ \text{Path difference} = n^*\lambda = d^*\sin\alpha \]
Angular distance of the peaks $\leftrightarrow$ determines distances of the slits (grating parameter)

The width of the peaks (FWHM) depends on the number $p$ of illuminated slits

$\text{FWHM} \sim \frac{1}{p}$

The envelope of the peaks determines the width $A$ of one slit.

$\text{FWHM} \sim \frac{1}{A}$
STRUCTURE RESOLUTION IN RECIPROCAL SPACE

Crystal

“Unit cell” (smallest repetitive building block)

Envelope->

Information about the atomic arrangement inside the unit cell.

Scattering pattern

“Bragg-peaks” corresponding to different net planes)
COMPLEX MOLECULE: INSULIN
Plane wave approach
\[ \hat{A} e^{i(-k_i \cdot r + \omega t)} \]

At the observation point we record
\[
I = \langle \left| \sum_{j=1}^{N} \hat{A}_j e^{i(k_f - k_i) \cdot r_j} e^{i\omega t} \right|^2 \rangle_t = \left| \int \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} \, d\mathbf{r} \right|^2
\]

We admit that only the time averaged intensity can be measured and that the point scatterers can be described as
\[
\rho(\mathbf{r}) = \sum_{j=1}^{N} \hat{A}_j \delta(\mathbf{r}_j)
\]
FOURIER TRANSFORM: USEFUL RELATIONS

\[ I = \langle | \sum_{j=1}^{N} \hat{A}_j e^{i \mathbf{k}_f - \mathbf{k}_i \cdot \mathbf{r}_j} e^{i \omega t} |^2 \rangle_t = \left| \int \rho(\mathbf{r}) e^{i \mathbf{Q} \cdot \mathbf{r}} \cdot d\mathbf{r} \right|^2 \]

1. Linearity: The FT of \( \rho(\mathbf{r}) = f(\mathbf{r}) + g(\mathbf{r}) \) is

\[ \text{FT} [f(\mathbf{r}) + g(\mathbf{r})] = \text{FT} [f(\mathbf{r})] + \text{FT} [g(\mathbf{r})] \]

2. Convolution:

\[ \rho(\mathbf{r}) = \int f(\mathbf{\xi}) g(\mathbf{r} - \mathbf{\xi}) d\mathbf{\xi} \]

\[ \text{FT} [f(\mathbf{r}) \ast g(\mathbf{r})] = \text{FT} [f(\mathbf{r})] \ast \text{FT} [g(\mathbf{r})] \]

FT “converts” a convolution in a product and vice versa
Big Crystals-sharp peaks, small crystals broad peaks. Peak intensities depend on the structure factor.
Miller indices “naming of Bragg peaks”: \((hkl)\)-peak” means that the considered netplanes intercept the unit cell axes at positions \(a/h, b/k, c/l\) or \(x/h, y/k, z/l\). Higher indices \(\rightarrow\) closer net-plane spacings \(\rightarrow\) higher Q-values.
USEFUL RELATIONS IN (RECIPROCAL) Q-SPACE:

Bragg's law: \( \sin \theta = \frac{\lambda}{2d} \)

\[
Q = \frac{4\pi \sin \theta}{\lambda}
\]
with \( k = \frac{2\pi}{\lambda} \)

Peak width \( \Delta Q \)

Useful relations:
1) Lattice spacing: \( d_{hkl} = \frac{2\pi}{Q_{hkl}} \)
2) Particle size: \( D = \frac{2\pi}{\Delta Q} \)
SIZE BROADENING AND STRAIN BROADENING

Strain may lead to lattice parameter changes or gradients within one crystal.

Assuming a $d$-spacing change $\Delta d$:

\[
Q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d}, \quad \frac{\Delta Q}{\Delta d} = -\frac{2\pi}{d^2}
\]

Strain broadening

\[
\Delta Q(\Delta d) = -\frac{\Delta d}{d} \cdot \frac{2\pi}{d} = -\frac{\Delta d}{d^2} Q
\]

Depends on $Q$ itself

Particle size ($D$) broadening:

\[
\Delta Q(D) = \frac{2\pi}{D}
\]

No $Q$-dependence

(100) (200) (300) Size broadening

(100) (200) (300) Strain broadening
Q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d}

Resolution only limited by well-definition of the wavelength \( \lambda \) and beam divergence.

Typical absolute resolution of 10^{-4}-10^{-5} possible without too much effort.

Simple structure resolution may not require that. But in order to separate different phases or in order to measure small perturbations in perfect crystals (strain) this is important.
Most of diffraction experiments use “big and homogeneous” samples, like Homogeneous ensembles of nanostructures, chemical solutions or 2D “infinite” structures as surfaces, thin films, ...
Presence of multiple materials on different lengths scales: new strategy required.

In many interesting systems, heterogeneity happens to be on the “mesoscale” (not atomic scale).

Beams of 100 nm can be produced by x-ray optics.
Radiography vs. Diffraction

Imaging: full field technique with spatial resolution ~sub mm (traditional sources)

Diffraction: spatial resolution limited in any case and traded in for angular resolution
**DIFFRACTION AND SCATTERING: ADVANTAGES**

Objects can be far away (leaves a lot of space around the sample)

Angular resolution obtained by diffraction leads to spatial **information** below $\lambda$ -> “interferometric” technique (~0.0001 nm for Bragg diffraction in crystals)

Limits: requires spatially homogeneous samples

Position 1: interatomic distance $a$

Position 2: interatomic distance $b$

In many interesting systems, heterogeneity happens to be on the “mesoscale” (not atomic scale).

Combining small x-ray beams with diffraction
Use of focused beam/ scanning technique.

Resolution limited by beam spot Sub 100 nm are possible.
STRUCTURED THIN FILM: TYPICAL FOR A DEVICE

- $\text{Si}_{0.8}\text{Ge}_{0.2}$ layer grown on a Si (001) substrate patterned by focused ion beam (FIB) to draw the ESRF logo.
STRAIN AND ORIENTATION

- Determine the degree of strain:
  - Fully strained: the lattice parameters of the film are strained to fit to the substrate

- Tilts appears as perpendicular shifts

- The Bragg peak position in reciprocal space is essential for retrieving all information related to strain and/or tilts in the structure.

G.CHAHINE – K-Mapping /SOCS at ID01
Full treatment allows to image lattice tilts and strain

Relative strain levels of $\Delta a/a \ 10^{-6}$ can trace a landscape (= we can “see” a $\Delta T$ of a few K potentially in buried systems working devices)

Spatial resolution: 100 nm

DIFFRACTION IMAGING: CROSS HATCHES IN GRADED BUFFERS

- Light interference microscopy
- Scanning x-ray diffraction microscopy: Tilt maps

Zöllner, Richard, Chahine: Appl. Mat.&Interf. 2015

Surface roughness
Lattice undulations
Full field technique

Resolution limited by
Detector pixel size and detector distance
and numerical aperture of the optics

Sub 100 nm possible

Real potential needs long detector arms
SETUP

Detector

100 cm

Polymer CRLs

8 cm

Slits

Incoming X-rays

Sample

~9 m

Focusing Monochromator

~34 m
Full field technique

Resolution ultimately limited by numerical aperture of the imaging optics
Sub 100 nm within reach
Coherent Diffraction Imaging:
Theory of optics is very well known. 
-> Measure all emitted rays from the sample and replace the lens by a computer to calculate the image

The physics of resolution remains the same

\[
\Delta x = \frac{1.22*\lambda}{2*n*sin\alpha}
\]

Instead of the lens we need a detector with a large opening angle.

We need perfect detectors: A noisy detector is like a sandblasted lens. And we need single photon detection at near 100% efficiency
Another Problem: Waves have amplitudes and phases; they interfere to form an image;

Refraction (as in a real lens) preserves the phase information, crucial for the image
Detection measures only the intensity (number of photons) and not their phase

From a quantum mechanical point of view, refraction (preserves $\Delta p$) by a lens cannot be replaced by detection (destroys $\Delta p$): Equivalence between Abbé and Heisenberg.

The loss of phase information cannot be recovered by a computer. We have thus to know the phase beforehand. The sample has to be illuminated with photons that are all in phase with each other. This is the definition of a coherent beam.
PHASE OF PHOTONS AND COHERENT BEAMS

Marathon: photons=runners
Phase depends on the exact departure time of the runners
We have to select one single phase. The rest of the runners cannot be used for the experiment.

We select the “coherent fraction” (Runners that all have roughly the same departure time).
ESRF coherent fraction: <1%

Flux available for “normal” light imaging and coherent diffraction x-ray imaging:
5 Watt LED: $10^{19}$ photons/second (incoherent but with optics we can use them all)

ESRF coherent flux: $10^{11}$ photons/second (@ 8keV ) -> $10^{19}$ photons in 1 year

X-ray tube coh. flux: few photons/second,$10^{19}$ photons in $10^{10}$ years (the age of this world)
Use of focused beam/ scanning technique.

Resolution below beam spot size possible by reconstruction of scattering pattern.

Limits imposed by coherent flux vs. stability of the sample and sample/beam stability in general and detector surface (numerical aperture).

Resolution below 10 nm possible.