4. Other diffraction techniques

4.1 Reflection High Energy Electron Diffraction (RHEED)

Setup:
- Grazing-incidence high energy electron beam (3-5 keV: MEED, <100 keV: RHEED)
- Diffraction pattern measured in forward scattering geometry
- Retarding grid filters inelastic electrons

Diffraction pattern:
- Very large Ewald sphere crosses many points, but few in grazing exit angles (θ small)
- Often only the (00) and one arc of (0n) beams measured → restricted information on surface unit-cell
- Finite-size rods lead to streaky spots

Dynamic RHEED?
- No, because poor data quality large $l_{\text{max}}$ badly defined spot intensity
Major (sole?) RHEED application: film growth

- RHEED geometry very suitable for MBE/MOCVD setups
- Intensities very sensitive to surface roughness

→ „RHEED oscillations“
4.2 Surface X-ray Diffraction (SXRD)

Setup:
- Collimated X-ray beam (~ keV) directed at sample at grazing incidence $\alpha_i < 1^\circ$: total internal reflection ensures surface sensitivity
  large illuminated area requires high photon flux: synchrotron
- Diffraeted X-ray beam measured at exit angle $\alpha_f$, corresponding to specific momentum transfer $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$

Modes of operation:

i) in-plane measurements ($\alpha_f \sim 0^\circ$: $q_\perp \approx 0$)
- $q_\parallel$-mapping by systematic variation of detector position and sample rotation
- high required angular precision of X-ray diffractometer (0.001°)
  a) spot arrangement (→ LEED pattern): $h$-, $k$-scans
     surface symmetry and surface unit-cell
     spot width: lateral order
  b) in-plane sensitivity of fractional-order spots
     projected electron density of overlayer

ii) out-of-plane measurements ($\alpha_f > 0^\circ$: $q_\perp \neq 0$)
- intensity variations along reciprocal rods by similar detector and sample rotations as in in-plane case: Ewald sphere cuts rods at different heights (→ $I(V)$-spectra)
  a) fractional order spots: rod scans, $l$-scans
     out-of-plane structure of reconstructed overlayer
  b) integer order spots: crystal truncation rods (CTRs)
     registry of overlayer to substrate
     surface roughness
4.4.1. Kinematic scattering theory

- Coherent scattering from a free electron: spherical wave (Thomson scattering)

- If not close to an absorption edge (resonance), X-rays can’t distinguish between a free electron and an electron bound to an atom

- Scattering cross section for X-rays is very small, i.e. single-scattering approximation works well:

  Scattering from one atom with charge density $\rho_{\text{atom}}(\mathbf{r})$:
  $$ f_{\text{atom}}(\mathbf{q}) = \int \rho_{\text{atom}}(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) \, d^3r, \quad \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i $$

  Atomic form factor (→ „$t$-matrix“)

  Scattering from one unit-cell with charge density $\rho_{\text{unit}}(\mathbf{r})$:
  $$ F_{\text{struc}}(\mathbf{q}) = \int \rho_{\text{unit}}(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) \, d^3r, \quad \text{Structure factor} $$

  Scattering from crystal with charge density $\rho(\mathbf{r})$:
  $$ A(\mathbf{q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) \, d^3r $$

- Can exploit Fourier-transform theory to analyse the scattering, e.g.

  $\text{FT}[f(r-r_0)](\mathbf{q}) = \text{FT}[f(r)] \exp(i\mathbf{q} \cdot \mathbf{r}_0)$ \quad \text{Shift theorem}

  $\text{FT}[f \otimes g](\mathbf{q}) = \text{FT}[f] \times \text{FT}[g]$ \quad \text{Convolution theorems}

  $\text{FT}[fg](\mathbf{q}) = \text{FT}[f] \otimes \text{FT}[g]$ \quad \text{with } f(r) \otimes g(r) = \int f(r') g(r-r')$

  \[ \rightarrow A(\mathbf{q}) = \text{FT}[\rho(\mathbf{r})] = \text{FT} \left[ \sum_{\text{unit-cells}} \delta(\mathbf{r} - \mathbf{r}_u) \right] \cdot \text{FT} \left[ \sum_{\text{atoms}} \delta(\mathbf{r} - \mathbf{r}_a) \right] \cdot \text{FT}[\rho_{\text{atom}}(\mathbf{r})] = \sum_{\text{unit-cells}} e^{i\mathbf{q} \cdot \mathbf{r}_u} F_{\text{struc}}(\mathbf{q}) \]

- Infinite 3D bulk: $A(\mathbf{q}) = \sum_{\text{cells}} \delta(\mathbf{q} - g_{\text{hkl}}) F_{\text{struc}}(\mathbf{hkl})$ \quad and \quad $I_{\text{hkl}} = |F_{\text{hkl}}|^2$

- Straightforward retrieval of structural data not possible by Fourier-backtransform, because we can only measure the intensity („phase problem in X-ray crystallography“)

- Exploit arsenal of inversion methods developed in crystallography (trial&error, anomalous scattering, heavy atom method, max. entropy…). Most prominently: Patterson function (auto-correlation function)
  $$ P(\mathbf{r}) = \text{FT}^{-1}[I(\mathbf{q})] = \text{FT}^{-1}[A(\mathbf{q}) A^*(\mathbf{q})] = \text{FT}^{-1}[A(\mathbf{q})] \otimes \text{FT}^{-1}[A^*(\mathbf{q})] = \rho(\mathbf{r}) \otimes \rho(\mathbf{r}) = |\rho(\mathbf{r})|^2 \delta(\mathbf{r}) \otimes \rho(\mathbf{r}) = \int_{\mathbf{r}'} |\rho(\mathbf{r})|^2 \delta(\mathbf{r} - \mathbf{r}') d^3r'$$
4.4.2. Application to surface scattering

i) In-plane diffraction pattern
- spots at reciprocal lattice positions: size and symmetry of surface unit-cell
- spot width related to lateral correlation length: domains, order (finite Fourier-transform!), „rocking scans“

ii) Fractional order spots
- intensity exclusively due to X-ray scattering from reconstructed surface fringe: highly surface sensitive, but need high fluxes
- no information about registry of overlayer to substrate
- in-plane (\(q_{\perp}=0\)): \(z\)-projected Patterson function of overlayer (distorted due to missing integer-order intensities)
- rod-scans: out-of-plane structure and periodicity (films!) of overlayer

iii) Integer order spots (crystal truncation rods)
- intensity due to X-ray scattering from bulk and surface
- truncation at the surface leads to finite intensity between Bragg spots along the rod
  \[
  \rho_{\text{semi-inf}}(r) = \rho_{\text{inf}}(r) \cdot \theta(z) \rightarrow A_{\text{semi-inf}}(\mathbf{q}) = \text{FT}[\rho_{\text{inf}}(r)] \otimes \text{FT}[\theta(z)] = A_{\text{inf}}(\mathbf{q}) \otimes i/q_{\perp} \sum_{\text{hkl}} \delta(q_{\parallel} - g_{hk}) \frac{F_{hk}(q_{\perp})}{q_{\perp} - g_{l}}
  \]
- minimum of CTRs mostly influenced by relaxation (unsymmetric) and roughness (symmetric)

4.4.3. Pros and cons

+ Very versatile information contained in SXRD intensities
  Symmetry and size of surface/adsorbate unit cell (in-plane pattern)
  Surface order, steps, domains, roughness (spot width, rocking scans, CTRs)
  Atomic structure in surface fringe (in-plane intensities, out-of-plane rod scans)
Comparably simple theoretical analysis with kinematic scattering theory (Patterson function…)
Works in any environment, particularly at high-pressure
Works for both insulators and conductors
May be used to study buried interfaces (if suitably reconstructed)

─ Very expensive instrumentation (diffractometer, synchrotron)
  Tedious data acquisition
  Lower structural precision compared to LEED

![Structural diagram of K/Ag(001)-(2x1) reconstruction](image)
4.5 Exploiting photoelectron excitation for structural analysis

4.5.1. X-ray photoelectron diffraction (XPD or PED)

Setup:
- Incident X-rays excite photoelectrons in solid
- Photoelectrons diffract on way back to the detector (= LEED with internal source)
- Measure diffuse diffraction pattern with angular variations like in LEED

- Diffraction pattern contains structural information about local environment of emitting atom

- Structure retrieval in principle possible just like in LEED (multiple scattering analysis), but

  complex emitted wave (not simple plane wave like in LEED): strong variation of photoelectron cross-section with energy
  overshadows diffracted intensity variations
  multiple emitting atoms in different environments
  \( \rightarrow \) works best for adsorbates
4.5.2. Extended X-ray Absorption Fine Structure (EXAFS)

- X-ray absorption characterized by series of "absorption edges" whenever ionization of a core level becomes possible.
- In condensed matter, small intensity variations (fine structure) appear above the edge that do not occur for isolated atoms.
- Total X-ray absorption is measured, and the EXAFS contains structural information about the environment of the emitting atom.

Theory:

- Absorption coefficient $\alpha(h\nu) = |<\Psi_f|\mu|\Psi_i>|^2$ depends on final state wave function $\Psi_f$, i.e., on photo-excited atom AND emitted photoelectron.
- Interference of outgoing electron wave with itself when backscattered by neighboring atoms leads to amplitude variations, changing the final state and thus modulating the absorption coefficient.
- Neglecting multiple scattering, for $N$ neighbors at distance $R$, the so-called fine-structure function can be written as

$$
\chi(k) = (I - I_{atom})/I_{atom} \sim 1 + (N/R^2) |f(\pi,k)| \exp(-2R/\lambda_{inel}) \cos(2kR + \phi(k)),
$$

i.e., apart from the unknown phase shift $\phi(k)$, period of oscillation between constructive and destructive interference is just twice the distance $R$.
- Modulations dominated by nearest neighbors, and amplitude scales with nearest-neighbor coordination.

$\rightarrow$ EXAFS highly sensitive to short-range order (works for amorphous, polycrystalline, glassy materials and liquids!!)
- In energy range >50-100 eV above absorption edge back-scattering is so small that single-scattering approximation works
  → replot absorption spectrum $I(h\nu)$ as $\chi(k)$, and Fourier-transform oscillations

- For energy range ~0-50 eV need multiple scattering analysis
  → near-edge extended X-ray absorption fine structure (NEXAFS or XANES)
  → contains most oscillations and best signal/noise

- EXAFS not intrinsically surface-sensitive (bulk-technique), but
  choose absorption edge of adsorbate species
  use grazing incidence
  measure total photoelectron, secondary electron yield
  → SEXAFS

Pros & cons:

+ accurate nearest-neighbor distances and coordination needs only short-range order
  simple data analysis in EXAFS part

- requires energy tunable Xrays (synchrotron)
  long data collection times (weak signal)
  most information contained in NEXAFS part, which requires dynamical analysis