Simulation of high energy electron diffraction patterns of organic crystals

Tarik Ronan Drevon, David Waterman & Eugene Krissinel

Science and Technology Facility Council, Scientific Computing Department, CCP4
tarik.drevon@stfc.ac.uk

Contribution

We provide a comparison of the 2 most popular methods used for simulating electron diffraction(ED), namely the multislice(MS) and blochwave(BW).
Dynamical diffraction is described by both methods while advantages and limitations of both approaches are highlighted and discussed.
As proof of concept, the multislice method is subsequently used to reproduce a continuous rotation experiment based on alpha glycine.

Motivations for ED simulations

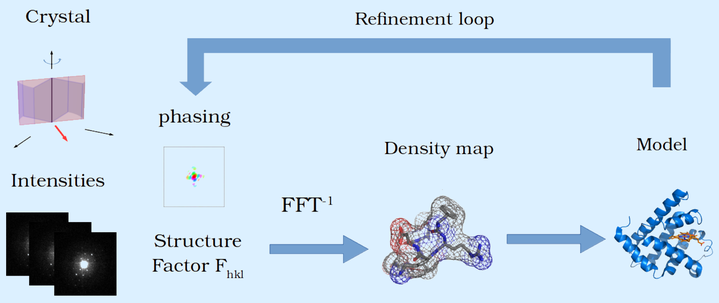
Macromolecular structures can be solved from ED patterns using standard macromolecular X-ray crystallographic(MX) techniques.
ED is attractive as it:

- Enables **solving structures from nanocrystals** due to the *strong electron-atom interaction.*
- Produces **high resolution maps** due to the very *small electronic wavelength 0.025A@200keV.*
- Resolves **atomic nucleus positions** through the *electrostatic potential map.*

However, **Rfactors obtained through ED remain larger than those of X-ray** due to a lack of theoretical understanding of *dynamical diffraction.*

Theoretical background

Standard MX pipeline



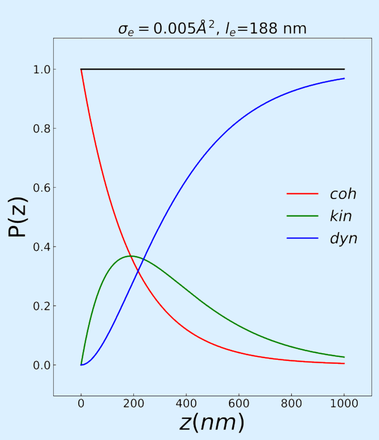
MX is based on the *kinematic theory of diffraction* due to the weak interaction between X-rays and the electron density. Kinematic theory can not rigorously be applied to ED.

Schrödinger fast electron wave equation

In ED, the structure factor is related to the electrostatic potential through :

$$\frac{\partial \Psi(x,y,z)}{\partial_z} = \left\{ \frac{i\lambda}{4\pi} \boldsymbol{\nabla}^2_{xy} + i\sigma V(x,y,z) \right\}$$

Particle oriented picture



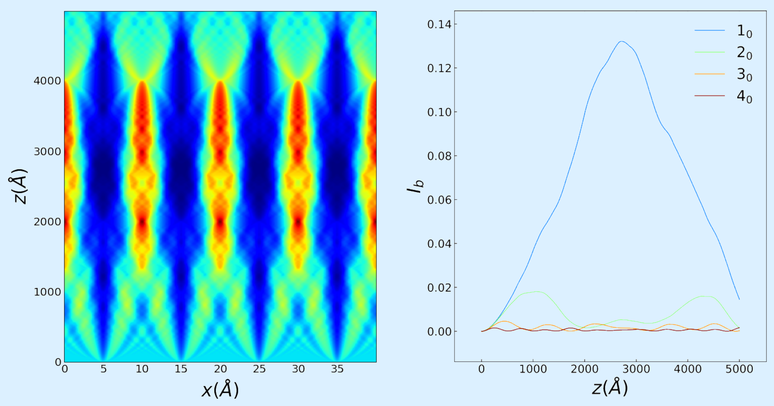
200keV electrons have typical elastic mean free path of 200nm in organic atoms. This results in an appreciable probability of multiple scattering in nanocrystals.

Multislice(MS) method [1]

The sample is **sliced in real space** into regular slices Δz and the solution is propagated from slice to slice through:

$$\Psi(z+\Delta z) = \mathcal{F}^{-1}\left\{ p(k_x,k_y)\mathcal{F}\left(e^{i\sigma\nu_{\Delta_z}(z)}\Psi(z)\right)\right\}$$

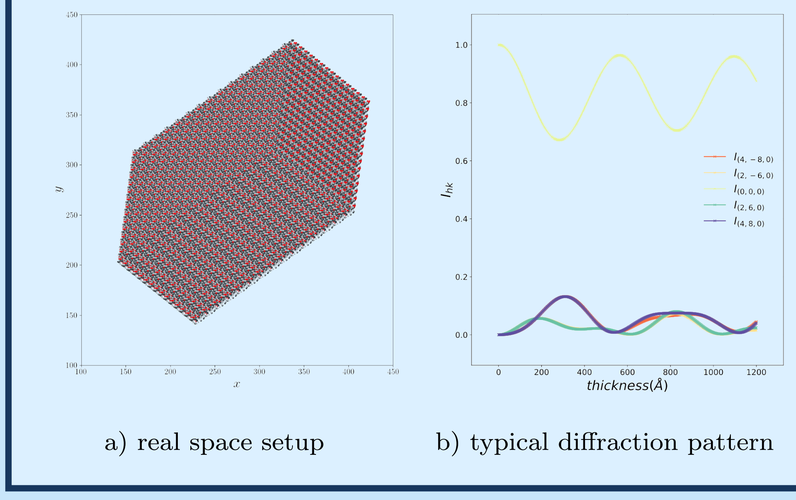
where the Fresnel propagator $p(k_x,k_y) = e^{-i\pi\lambda\Delta z(k_x^2+k_y^2)}$, $\nu_{\Delta_z} = \int_z^{z+\Delta z} V(x,y,z')dz'$ is the projected potential.



a) Typical $\Psi(x,z)$ b) Strong beams intensities

- The Discrete Fourier Transform $\mathcal{F}$ provides **fast and efficient** $N \log N$ **time complexity**.
- **Padding and large transverse super cells** necessary for non zone-axis orientations.
- Possiblity to model **solvent,inelastic scattering, disorder, partial coherency...**.

Padded simulation for a IRELOH :



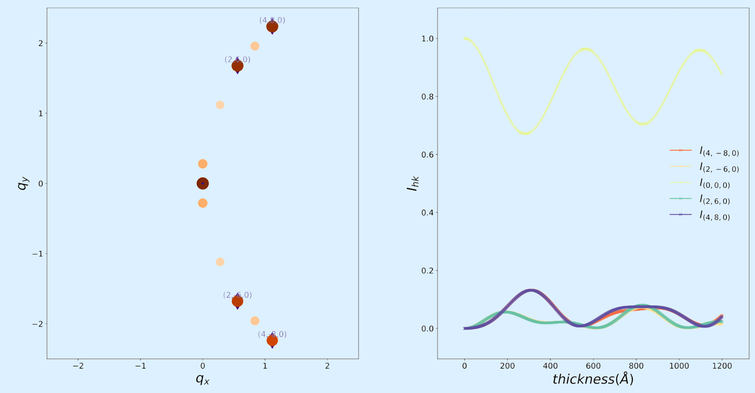
a) real space setup b) typical diffraction pattern

Blochwave(BW) approach [2]

The wave function is **solved in reciprocal space** by finding the eigen values γ_j and eigen vectors $C_{j,\mathbf{G}}$:

$$S_{\mathbf{G}}C_{j,\mathbf{G}} + \sum_{\mathbf{G}'} \frac{U_{\mathbf{G}-\mathbf{G}'}}{2k_0} C_{j,\mathbf{G}'} = \gamma_j C_{j,\mathbf{G}}$$

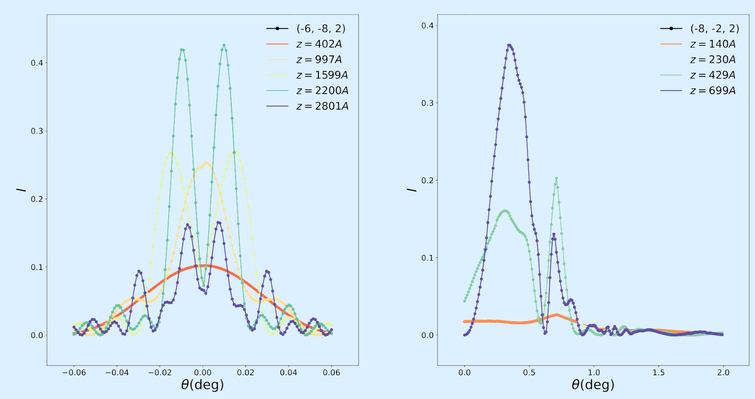
The diffracted intensities of the strong beams $\mathbf{G}$ (small excitation error $S_{\mathbf{G}}$) are computed for any thickness sample H with $I_{\mathbf{G}} = |\mathbf{C}\mathbf{e}^{2i\pi\boldsymbol{\gamma}_j H}\mathbf{C}^{-1}|^2$.



a) $S_{\mathbf{G}}$ and potential $U_{\mathbf{G}}$ b) Strong beams intensities $I_{\mathbf{G}}$

- Diagonalization **time complexity scales as** N^3 but **only strongest beams need be included**.
- **Random orientations of any lattice** can be simulated.
- Inelastic scattering can be modelled but **not solvent scattering, disorder and defects**.

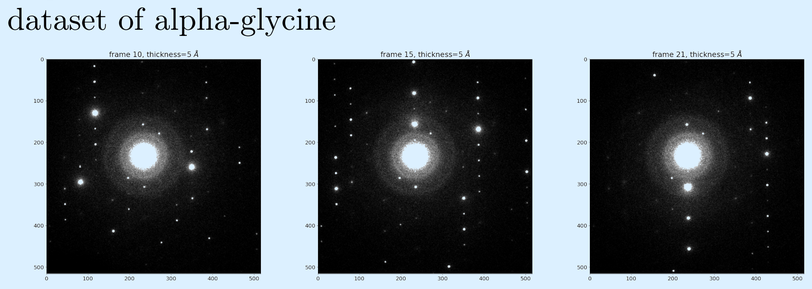
Rocking curves for diamond in different configurations :



a) 3 beam setup b) arbitrary orientation

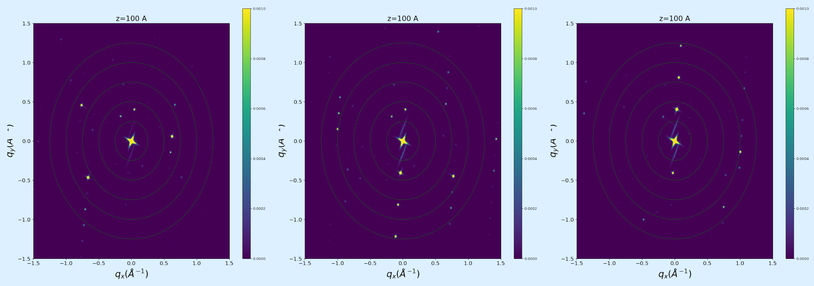
Application to alpha-glycine

Experimental continuous rotation electron diffraction dataset of alpha-glycine



a) frame 10 b) frame 15 c) frame 21

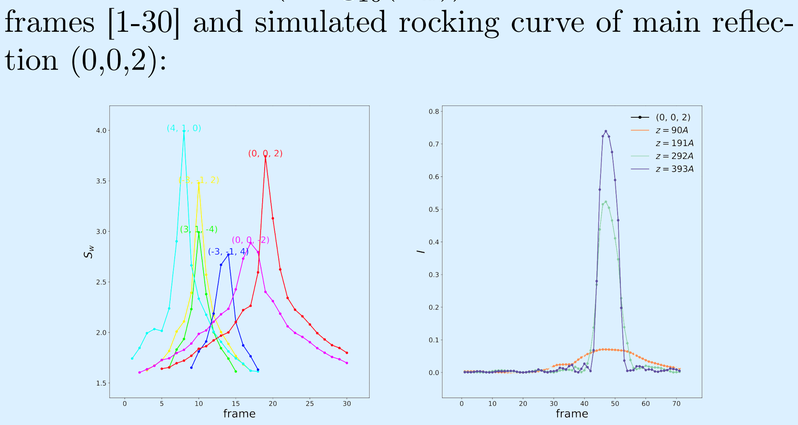
Simulated frames using multislice. Padding was used to simulate the experimental orientations as retrieved by data processing software PETS2(`http://pets.fzu.cz/`)



a) frame 10 b) frame 15 c) frame 21

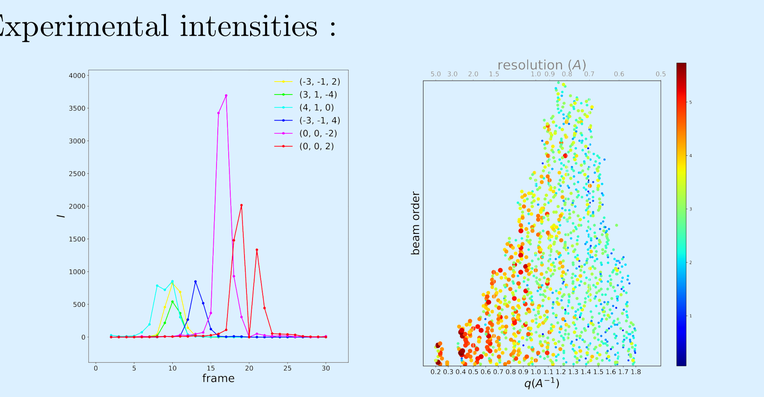
The main reflections are correctly predicted, although the patterns need to be rotated in the plane of the figure to get an exact match.

Excitation errors $(-\log_{10}(S_{\mathbf{G}}))$ of main beams over frames [1-30] and simulated rocking curve of main reflection (0,0,2):



a) Excitation error b) Rocking curve for (0,0,2)

Experimental intensities :



a) Experimental intensities b) Distribution with resolution

References

[1] E. J. Kirkland. *Advanced Computing in Electron Microscopy*. Springer, third edit edition, 2019.

[2] J. M. Zuo and A. L. Weickenmeier. *Ultramicroscopy*, 57(4):375–383, 1995.

Acknowledgements

This research was supported by BBSRC grant 4576434 WP4. The supports are gratefully acknowledged.