

# Simulation of 2D perovskite X-ray diffraction pattern

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A program for 2D material diffraction simulation is introduced in this work. The sample is considered as crystallites with a Gaussian distribution in orientation in spherical coordinate  $(r, \theta, \phi)$ . The simulated diffraction pattern is in  $(q_x, q_y)$  plane which is designed to compare with WAXS(wide angle x-ray scattering) measurement. Thus Bragg peaks elongates in a ring pattern from their original positions in reciprocal space.

## I. THEORETICAL MODEL

### A. Gaussian Distribution of Orientated Crystallites

For 2D material, the crystallites are fully isotropic in 2-dimensions (x-y plane) and anisotropic in z-axis. If the crystal is grown to a consistent orientation according to its substrate, there would be a distinct pattern in the in-plane(xy) and out-of-plane(z) directions from GIWAXS image.. Here we consider a model of Gaussian distribution of orientation in polar angles. The possibility of a crystallite to be find in orientation direction  $(\theta, \phi)$  is:

$$P(\theta, \phi) = \frac{1}{2\pi\sigma_\theta\sigma_\phi} e^{-\frac{1}{2}\left(\frac{\theta-\theta_0}{\sigma_\theta}\right)^2} e^{-\frac{1}{2}\left(\frac{\phi-\phi_0}{\sigma_\phi}\right)^2} \quad (1)$$

where  $\theta_0$  and  $\phi_0$  are the center of crystal orientation which is 0 for the 2D perovskites case above.  $\sigma_\theta$  and  $\sigma_\phi$  are the peak widths which are typically related to the crystal formation dynamics. In x-y direction isotropic 2D materials,  $\sigma_\phi = \infty$ .

It should be noticed that this model is only well-defined in the region where  $\sigma_\theta \ll \theta - \theta_0$  since the Gaussian distribution is decouple in  $\theta$  and  $\phi$  which doesn't hold when  $\theta$  approaches zero. The distribution in  $\theta$  and  $\phi$  direction are no longer independent if  $\theta$  passes the polar  $(0, \pi)$  where  $\phi$  can be any value from 0 to  $2\pi$ .

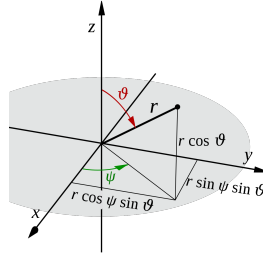


Figure 1: 3D spherical coordinate

### B. Diffraction Intensity

In reciprocal space, the Gaussian distribution in crystallites orientation results in a rotation for each Bragg peak. If we consider using an area detector to measure the diffraction intensity in  $q_z$   $q_x$  plane. It is a summation of all Bragg peaks with each of them has the same Gaussian width  $(\sigma_\theta, \sigma_\phi)$  centered in  $(q_x, q_y, q_z)$ :

$$I(q_z, q_x) = \sum_{h,k,l} \left| \sum_i f_i(\vec{Q}) e^{i\vec{Q} \cdot \vec{r}_i} \right|^2 e^{-\frac{1}{2} \frac{(\theta^I - \theta_0^B)^2}{\sigma_\theta^2}} e^{-\frac{1}{2} \frac{(\phi^I - \phi_0^B)^2}{\sigma_\phi^2}} e^{-\frac{1}{2} \frac{(q^I - q_0^B)^2}{\sigma_q^2}}$$

where  $(q^I, \theta^I, \phi^I)$  is the position of image plane  $(q_x, q_z)$  in spherical coordinate.

$$q = \sqrt{q_z^2 + q_x^2}, \quad \theta = \frac{\pi}{2} - \arctan \frac{q_z}{|q_x|}, \quad \phi = \begin{cases} 0, & x > 0 \\ \pi, & x < 0 \end{cases} \quad (2)$$

$\vec{Q}$  is the position of Brag peaks and (hkl) is Miller index.  $n$  indicate the atoms in the unit cell and  $r_n$  is the real space position of  $n$ th atom in the unit cell.

$$\vec{Q} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 \quad (3)$$

$(q_0^B, \theta_0^B, \phi_0^B)$  is the position of Brag peaks in reciprocal space converted to spherical coordinates:

$$q_0^B = |\vec{Q}|, \quad \theta_0^B = \arctan \frac{Q_z}{\sqrt{Q_x^2 + Q_y^2}}, \quad \phi_0^B = \arccos \frac{Q_y}{\sqrt{Q_x^2 + Q_y^2}} \quad (4)$$

It should be noticed that this is a theoretical result in  $(q_z, q_x)$  plane. Diffraction Ewald sphere is not considered here. Thus there is no 'missing wedge' as it always appears in GIWAXS. And a Gaussian profile in  $\hat{q}$  direction is added to make a finite peak width in 2D image plane. In real materials the line shape in  $\hat{q}$  is Lorentizian which depends on strain and crystallite size.

### C. Brag Peaks

Although we aim at 2D material in this proposal, a 3D crystal structure is needed to calculate the Brag peaks. If the position of atoms is described in 2D, we need to assume a lattice constant or d-spacing in z-direction. The single crystal Brag peaks are calculated from crystal structure file(.cif, POSCAR et. al) where lattice parameters and the positions of atoms in real space are provided.

The unit vector in real and reciprocal space are defined as:

$$\begin{aligned} \vec{a}_1 &= (a, 0, 0), & \vec{b}_1 &= \frac{2\pi}{V} \vec{a}_2 \times \vec{a}_3 \\ \vec{a}_2 &= (b \cos \gamma, b \sin \gamma, 0), & \vec{b}_2 &= \frac{2\pi}{V} \vec{a}_3 \times \vec{a}_1 \\ \vec{a}_3 &= (c \cos \beta, cn_2, c\sqrt{\sin^2 \beta + n_2^2}), & \vec{b}_3 &= \frac{2\pi}{V} \vec{a}_1 \times \vec{a}_2 \end{aligned} \quad (5)$$

where  $(a, b, c)$  and  $(\alpha, \beta, \gamma)$  are lattice constants and angles of unit cell,

$$n_2 = \frac{\cos \alpha - \cos \beta \cos \gamma}{\sin \gamma} \quad (6)$$

$$V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) \quad (7)$$

We also made a rotation matrix to help adjust the sample orientation if the it is not ideally given by in the crystal structure file:

$$M = \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix} = \begin{pmatrix} a & 0 & 0 \\ b \cos \gamma & b \sin \gamma & 0 \\ c \cos \beta & cn_2 & c\sqrt{\sin^2 \beta + n_2^2} \end{pmatrix} \quad (8)$$

$$\hat{q}, |\vec{q}|, \Delta E \quad (9)$$

$$E = \sqrt{m^2 c^4 + p^2 c^2} \quad (10)$$

$$R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix}, \quad R_y(\theta) = \begin{pmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{pmatrix} \quad (11)$$

Multiply Matrix M by  $R_x(\theta)$  or  $R_y(\theta)$  gives the rotated lattice vectors.

Position of Brag peaks with Miller index (hkl):

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 \quad (12)$$

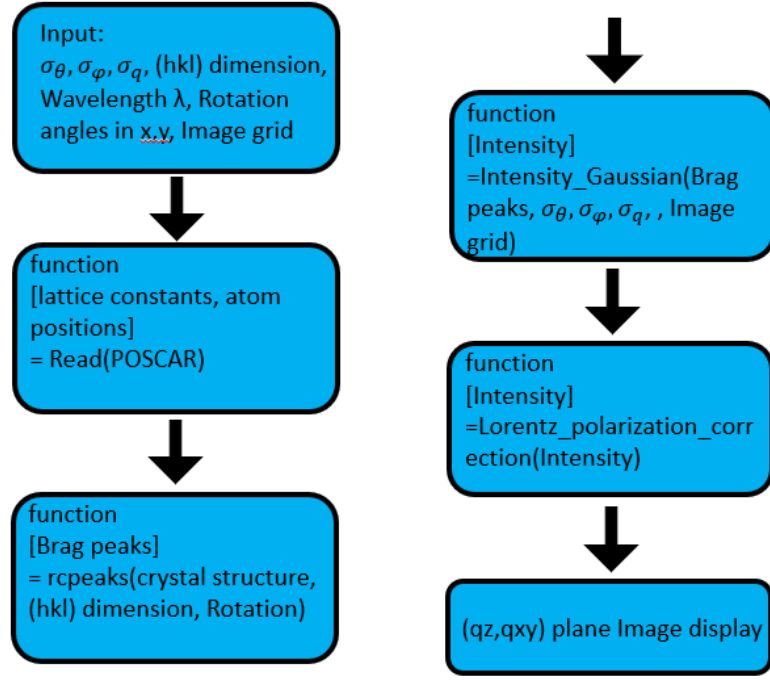


Figure 2: Program of 2D diffraction pattern simulation

#### D. Atomic Form Factor

The atomic form factor is the Fourier transform of the electron density of an atom. It is assumed that the electron density is spherically symmetric so that the value of the Fourier transform only depends on the distance from the origin in reciprocal space. The atomic form factor is well approximated by a sum of Gaussians of the form[1]:

$$f(q) = \sum_{i=1}^4 a_i \exp\left(-b_i \left(\frac{q}{4\pi}\right)^2\right) + c \quad (13)$$

#### E. Lorentz Polarization Factor

The Lorentz-polarization factor controls X-ray intensity with respect to diffraction angle. Its evaluation is essential to any analysis that depends on the intensities of X-ray diffraction maxima[2].

$$\Xi = \frac{1 - \cos^2 2\theta}{\sin 2\theta} \quad (14)$$

where  $(1 - \cos^2 2\theta)$  results from random polarized incoming X-ray and  $\frac{1}{\sin 2\theta}$  is the Lorentz factor for single crystals for the case of "equatorial" x-ray reflections[3].

$$\theta = \arcsin \frac{|q|\lambda}{4\pi} \quad (15)$$

## II. PROGRAM

The algorithm is realized on *Matlab* 2021b. Input POSCAR and .cif files are generated by *VESTA*.

### III. PRELIMINARY RESULTS

We tested this algorithm on graphite with DFT calculated lattice structure. An rotation of 90 degrees respect to x-axis is applied to check the hexagon pattern in  $(q_x, q_y)$  plane.

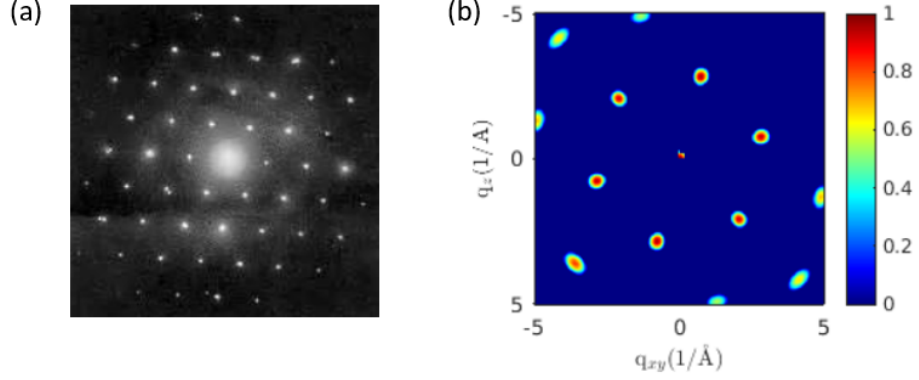


Figure 3: (a) Electron diffraction image and (b) 2D diffraction pattern simulation of single crystal graphite.

The 2D perovskites diffraction simulation shows a good agreement with GIWAXS experiment data except for some peaks in the out-of-plane direction which are contributed from intermediate states. The strong peaks of (002) (004) (012) and (014) gives exact same position as experiment. However, the elongated part shows a different geometry which indicates that the distribution of orientation is not a perfect Gaussian profile. Other models of crystallites distribution are still needed to implement to the program in future versions.

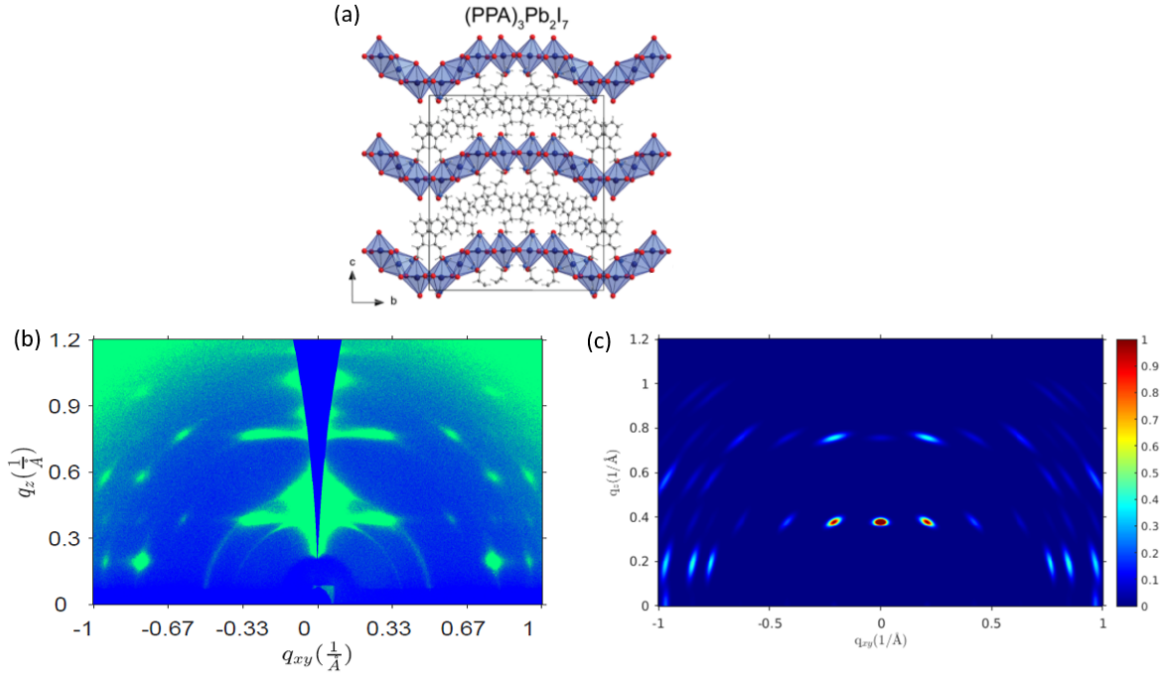


Figure 4:  $(\text{PPA})_2\text{Pb}_3\text{I}_7$  (a) crystal structure[4] (b) GIWAXS data (c) 2D diffraction pattern simulation.

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- [1] *International tables for crystallography*, <http://it.iucr.org/Cb/ch6o1v0001/>, accessed: 2021-05-01.
  - [2] R. C. Reynolds, *Clays and Clay Minerals* **34**, 359 (1986).
  - [3] C. Darwin, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **43**, 800 (1922).
  - [4] M. E. Kamminga, H.-H. Fang, M. R. Filip, F. Giustino, J. Baas, G. R. Blake, M. A. Loi, and T. T. M. Palstra, *Chemistry of Materials* **28**, 4554 (2016).