Generating and Fitting a Pair Distribution Function

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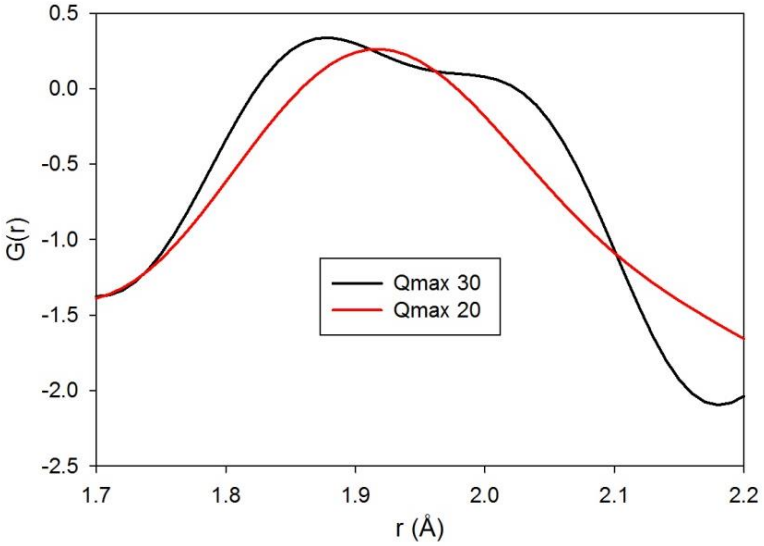
First Step: Decide on Experimental Conditions

- Deciding on the energy to use is an important step to make sure you can get the information you want from your data.
- For synchrotron PDF using an area detector there is a trade-off between the resolution in real space and the dampening rate of the PDF.
- First let’s review some instrumental considerations.

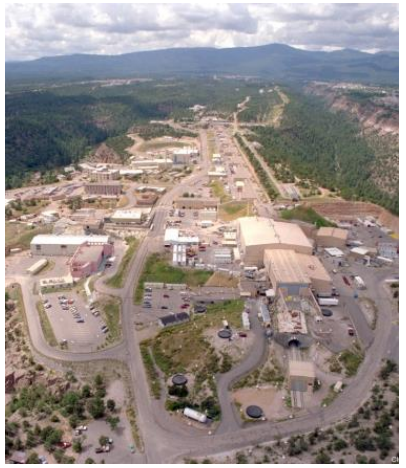
Experimental Consideration: Q_{max}

Higher Q_{max} = Better *r*-space resolution

A finite Q_{max} broadens the peaks. This can be minimized by collecting data to large Q values. Synchrotrons can typically achieve usable Q_{max} between about 20 to 34 $Å^{-1}$.



Neutron PDFs of Sr_2FeMnO_5 created with 2 different Q_{max} values.



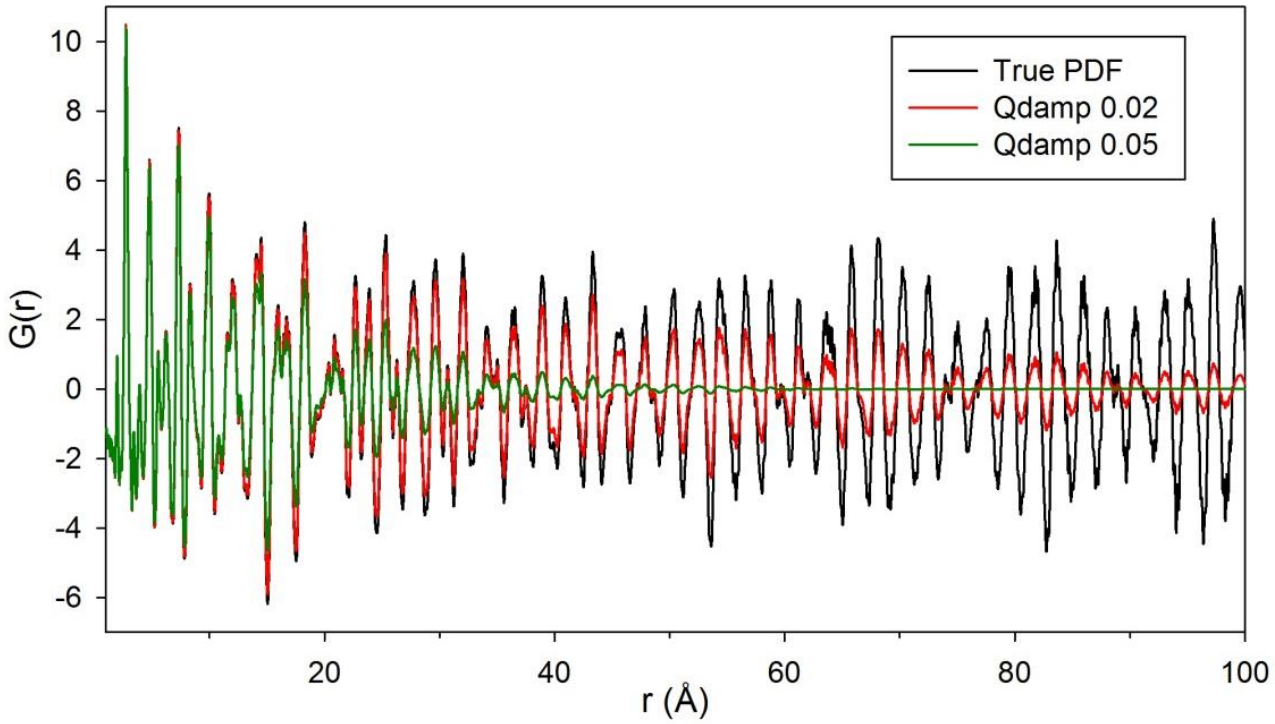
Typical Q_{max} values for different sources:
Cu X-ray tube ~8 $Å^{-1}$
Mo X-ray tube ~17 $Å^{-1}$
Ag X-ray tube ~ 22 $Å^{-1}$ *
Constant wavelength neutron ~6-12 $Å^{-1}$ *
Spallation neutron ~24-40 $Å^{-1}$

* Silver tubes have very low fluxes, requiring counting times of many hours or days. Hot neutron sources can give Q_{max} values up to ~35 $Å^{-1}$, but with lower resolution.

Experimental Consideration: Resolution

Better resolution = Less intensity dampening at high *r*

The intensity of G(*r*) is dampened by: $\exp(-(r\Delta Q)^2/2))$.



Experimental Consideration: Statistics

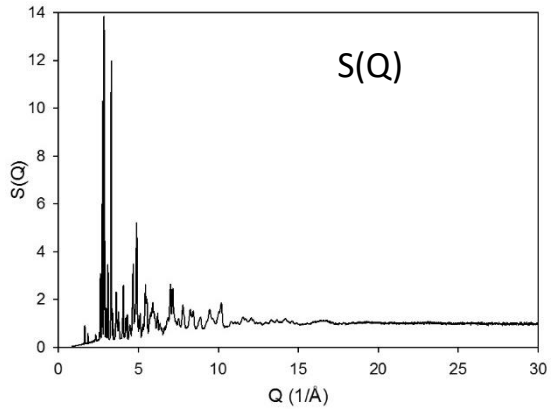
Since it is Q(S(Q)-1) that is Fourier transformed, the noise at high Q gets amplified, making the quality of the data at high Q particularly important.

Choice of Q_{max} a trade off:

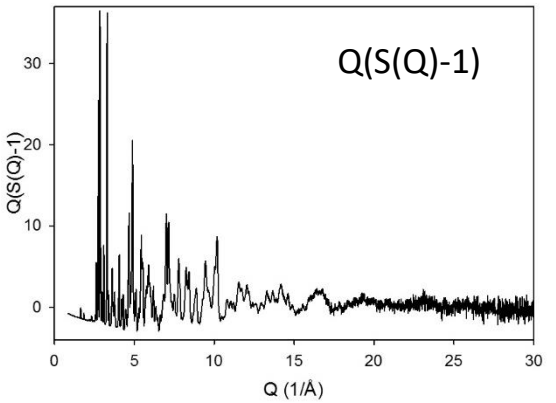
Low Q_{max} = less noise in data.

Q

High Q_{max} = good *r*-space resolution.



The full Q range collected is not always used as the noise for the highest Q data is too large. A decision must be made as to when the extra resolution from more Q no longer outweighs the additional noise.



Deciding on the Energy

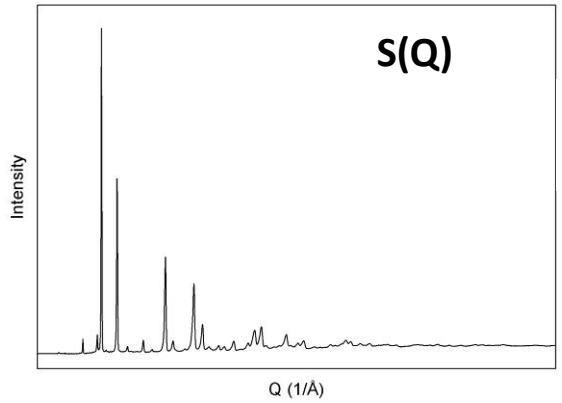
- High energy photons (~55-90 keV) are used as they produce high Q_{max} data. Several factors should be taken into account when deciding exactly how high to go.
- Higher energy equals higher Q_{max} but also lower resolution (faster dampening).
- There is lower flux at higher energies.
- The PDFs of amorphous solids or liquids fall off quickly anyway, so resolution is not an issue. For crystalline materials the PDF dampening should be a consideration.
- If only interested in nearest neighbor distances get the best Q_{max}, if interested in medium range features you might not want the PDF to dampen too quickly.
- If you have nano-particles with a known structure but want to look at their shape and size, use lower energy.
- For weakly scattering materials you may not be able to use too high an energy and still get a reasonable signal.

Typical usable Q_{max} values at common energies on the Brockhouse High Energy beamline.

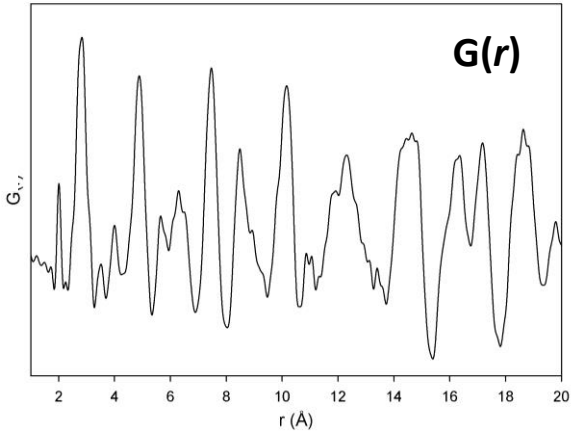
60 keV: 20-24 $Å^{-1}$ 65 keV: 22-26 $Å^{-1}$ 80 keV: 28-34 $Å^{-1}$

General Procedure for Producing a PDF

- Subtract container and instrumental background.
- Apply corrections such as absorption, multiple scattering, detector dead-time, inelastic scattering, etc.. (the exact corrections depend on the experimental conditions).
- Normalize so that S(Q) goes to 1 at high Q. For X-rays the data needs to be divided by the average form factor while for neutrons it is simpler.
- Fourier transform F(Q), which is Q(S(Q)-1), to get G(r).



$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ$$



Software for PDF Production and Analysis

- GSAS-II (2D data integration, Rietveld, basic production of PDFs)
- FIT2D (older software for 2D integration)
- PDFgetX2 and PDFgetX3 (PDF generation, xPDFsuite is a commercial package based on these)
- GudrunX (PDF generation)
- PDFgui (Fitting PDFs using a unit cell-like description)
- TOPAS (Can also fit PDFs)
- RMCProfile (for Reverse Monte Carlo modeling of PDF data)

Methods to Model a PDF

Small Box Method:

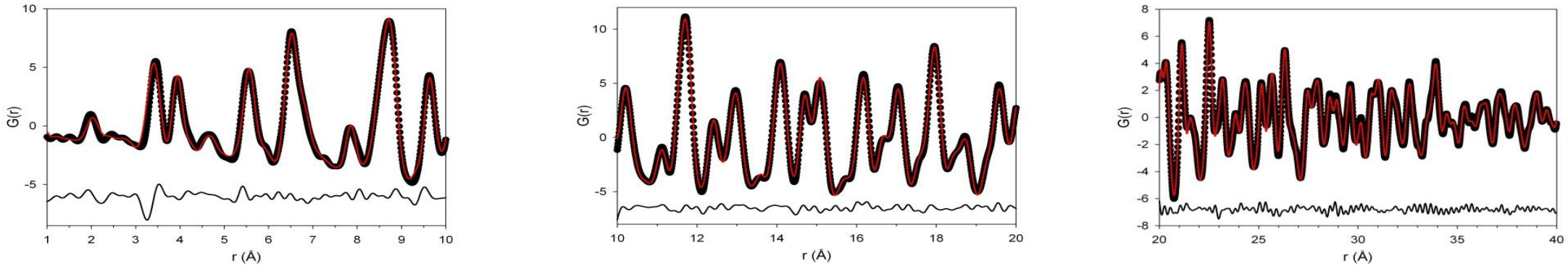
- Uses a unit cell-like description for Rietveld-like refinement in real space.
- Can refine cell dimensions, atomic positions, and displacement parameters.
- Uses each inter-atomic distance as the center of peak, which has a Gaussian shape with the width proportional to the thermal parameter.
- Refinements are quick and easy to interpret. Some systems have too many local environments to be modeled this way.

Large Box Reverse Monte Carlo (RMC) method:

- Uses a supercell containing ~10,000-20,000 atoms to model the PDF.
- Cell parameters fixed, no peak broadening as there are enough distances to create the peak shapes.
- Very flexible and less dependent on starting model, can give detailed information but caution is needed.
- Takes hours to days to do one refinement.
- Can be used for amorphous materials, getting a good starting model is more difficult in this case.

Small Box Fitting

- Often the first step in modeling as it is quick and can easily compare average and local structure.
- Corrections such as Q dependent broadening and dampening can be modeled.
- Often local distortions do not correlate very far, so one model is needed to fit the low-*r* region of the PDF and the average structure is needed to fit the high-*r* region.

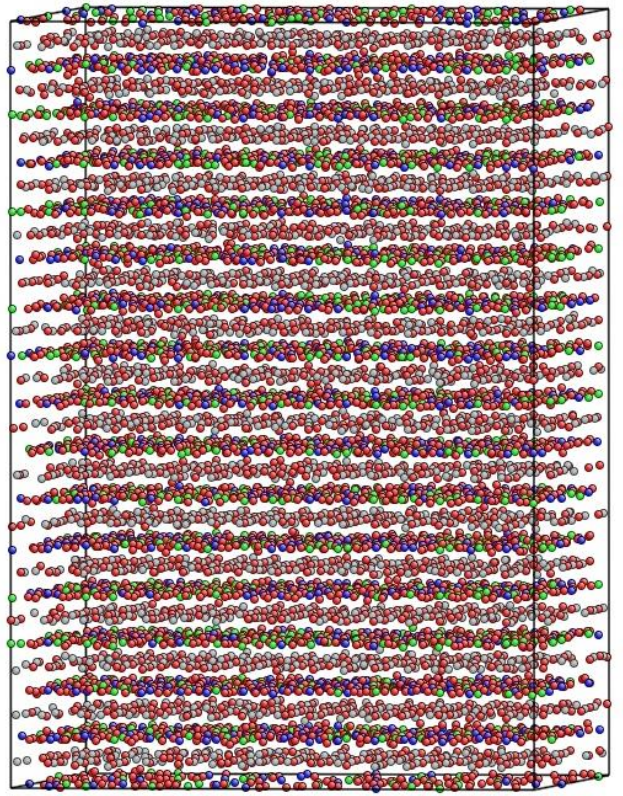


A PDF fit with an average structure model over three *r*-ranges. Notice how the average structure does not fit the low-*r* region well but does fit the high-*r* regions well.

The Reverse Monte Carlo Method

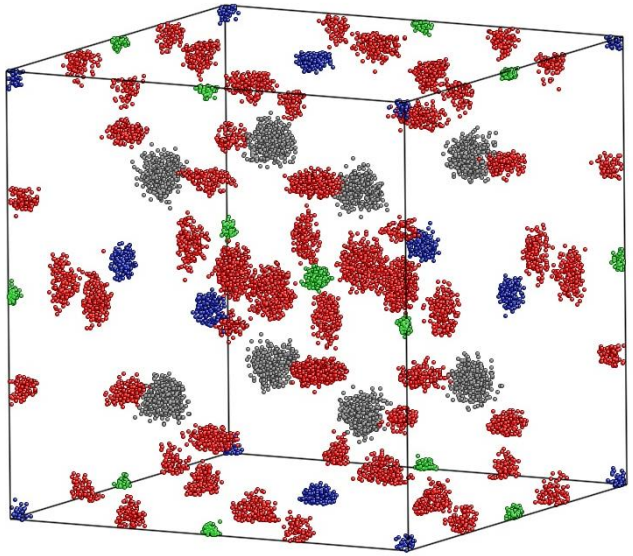
Process:

- Generate supercell (10^4 atoms), usually by expanding the unit cell.
- A random atom is moved by a small amount.
- If the fit is improved the move is accepted. If the fit gets worse it is sometimes accepted. The chance of a worse fit move getting accepted depends on a user defined value σ.
- Repeat millions of times.
- Constraints such as potentials or bond valence sums can be used to help guide it. Need to be weighted carefully.



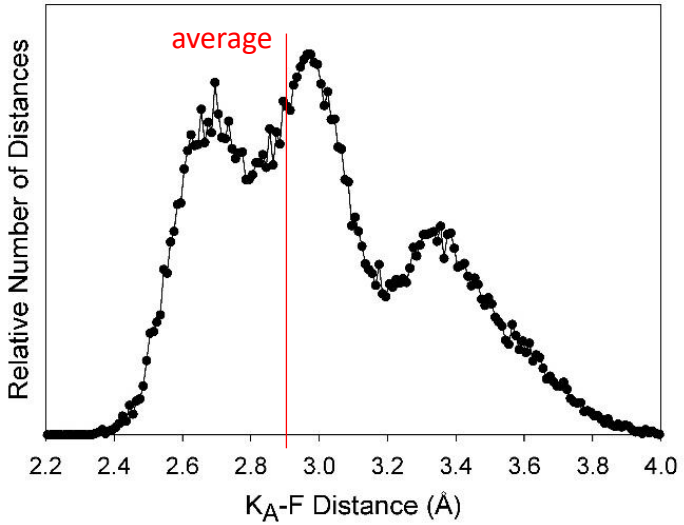
RMC Output

Example for the “cubic” HT form of perovskite K_3AlF_6

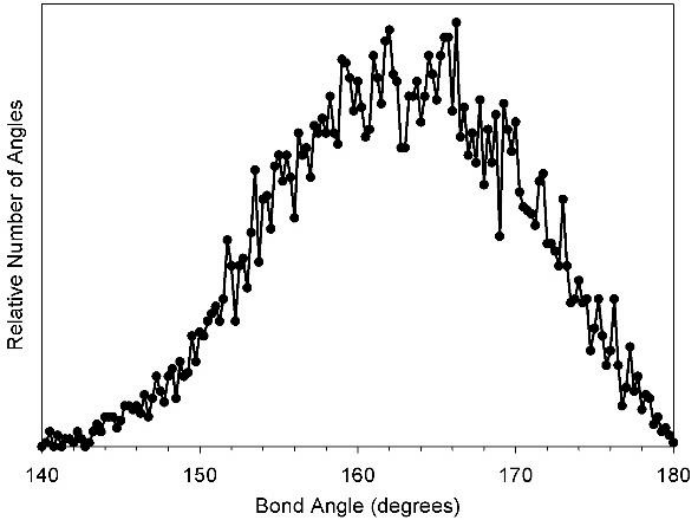


The final RMC configuration folded back into a single unit cell to show “clouds” of atoms.

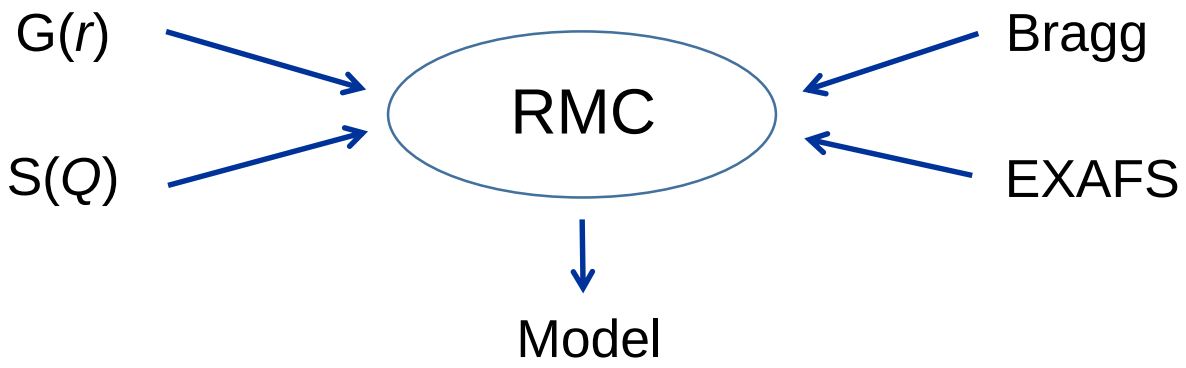
Bond length distributions



Bond angle distributions

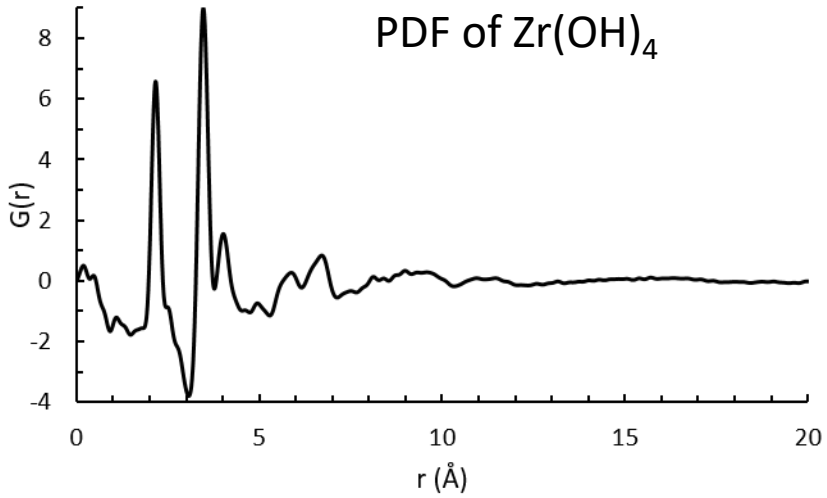


RMC as a multi-scale multi-data method.



By fitting G(*r*), S(Q), and the Bragg peaks an atomic configuration is obtained which is simultaneously consistent with the short, medium, and long range structural features of the material. A complete structural description.

Extracting Information for PDFs of Amorphous Materials



- Bond distances can be assigned based on peak positions.
- The area of the first peak(s) can be integrated to get the coordination number.
- RMC modeling can be done. Creating a starting model is a bit tricky and may involve several steps.

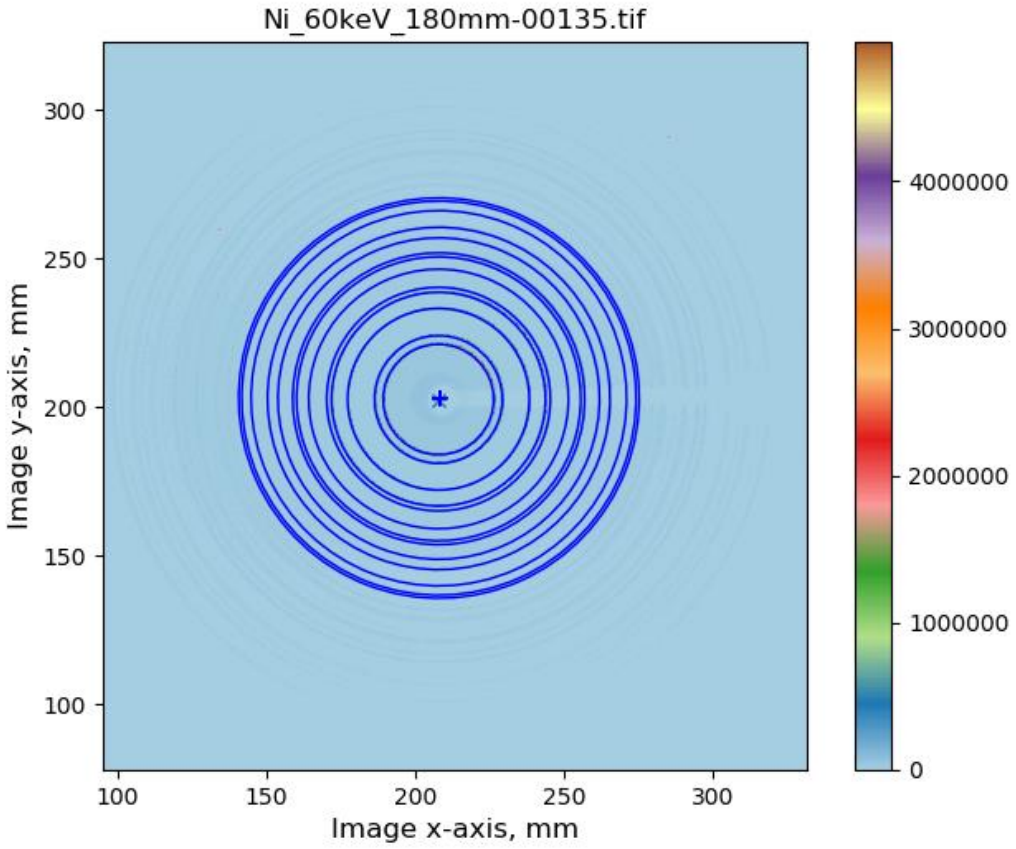
Ni Example Step 1: Calibrate Detector

Import ⟶ Image ⟶ TIFF

Step 1:
Set X 207, Y 203
Set distance 180
wavelength 0.20664
Tilt and tilt rotation 0
Min-d 0.65
Ring I/Ib 5
Pixel search range 5
Refine X, Y, distance

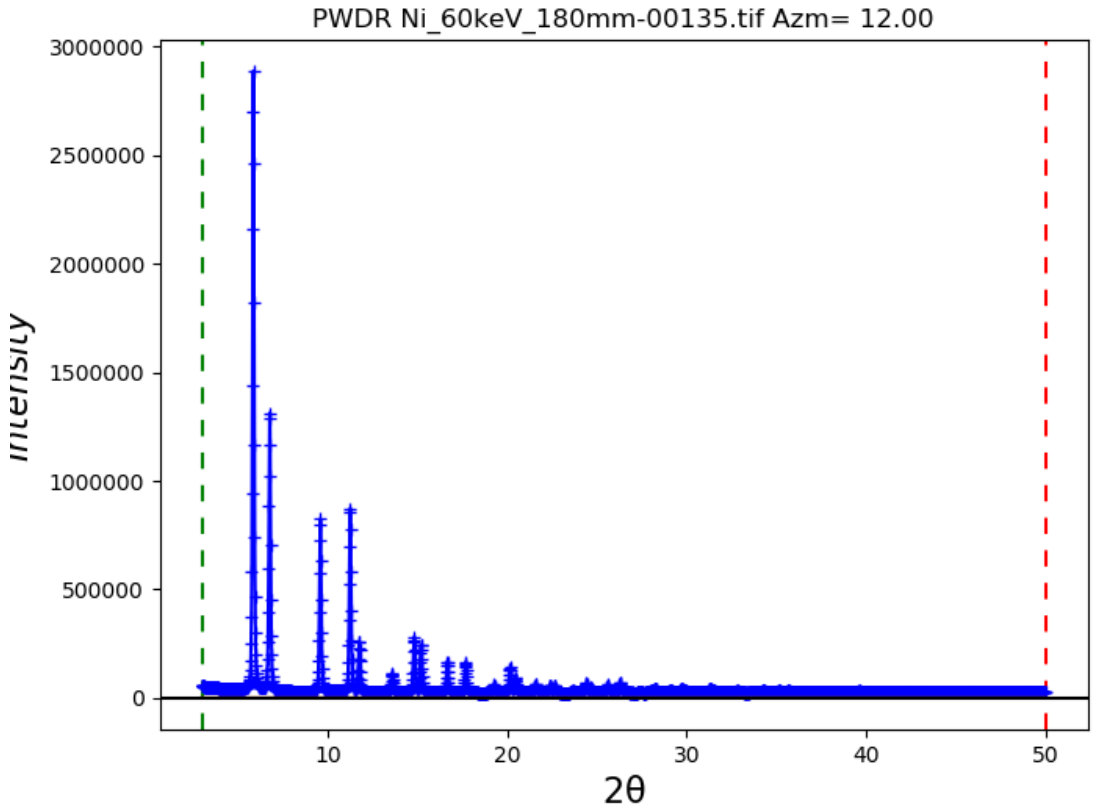
Step 2:
Min-d 0.57
Ring I/Ib 2
Pixel search range 2
Add tilt and tilt rotation to refine.

Step 3:
Once stabilized the wavelength can be refined as well.



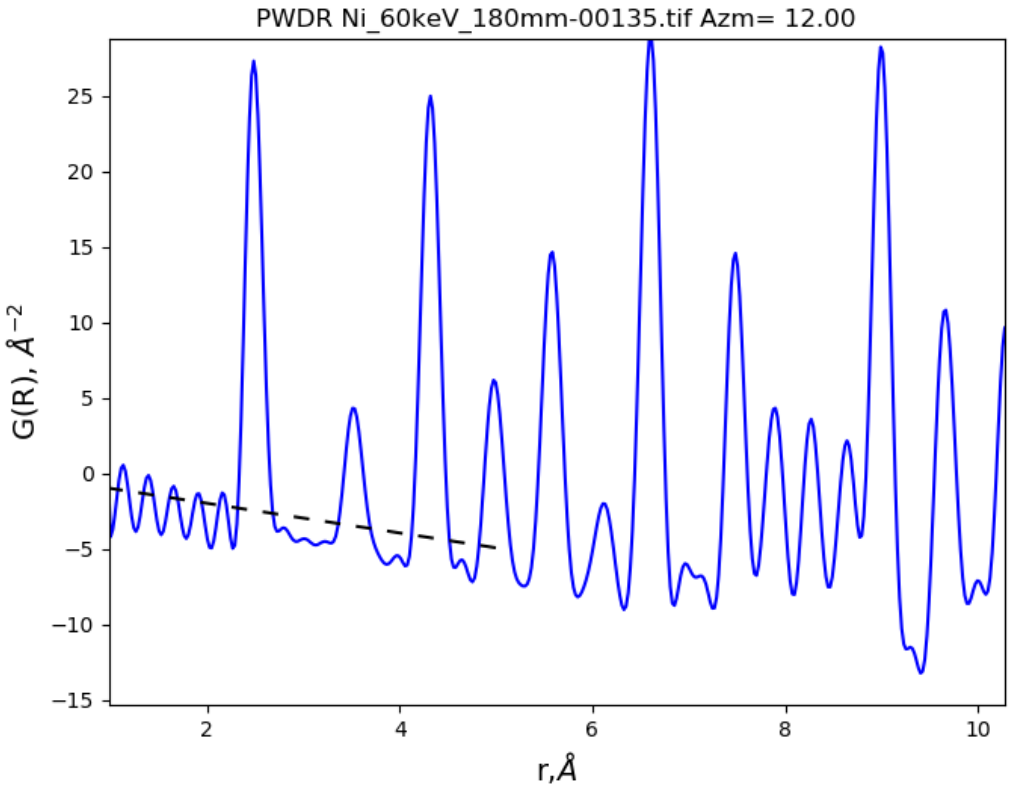
Ni Example Step 2: Integrate Data

- Clicking “Show integration limit” can be helpful
- Unclick “Do full intergration”
- Inner/Outer 2-theta range should be 3-50
- Can keep 2500 bins (for amorphous materials with broad features this can be reduced to 1600-2000) for better statistics)
- Change azimuthal range to 12-350 to exclude beamstop
- Integrate
- Load Kapton TIFF, copy controls from Ni to Kapton, integrate Kapton



Ni Example Step 3: Generate PDF

- Go to “Setup PDF” and select the Ni (not Kapton yet)
- Define chemical formula (just Ni)
- Capillary diameter is 0.63
- Choose the Kapton for sample holder, scale to 0.99
- Cut Qmax to 24 to get rid of detector edge effects
- Optimize several times until parameters stabilize



Now Time for a Live Demo of PDFgui