Introduction to Pair Distribution Functions (PDF)

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What is the PDF Technique?

The PDF method is a **total scattering** technique for determining local order in materials using the fourier relationship of scattering from materials in **momentum space** to the **real space** correlation of atoms.

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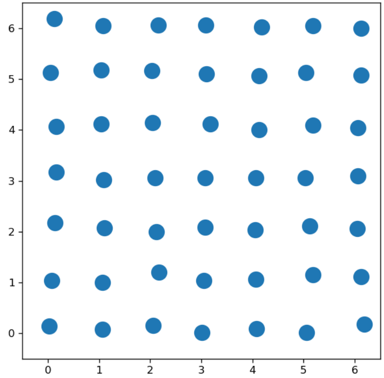
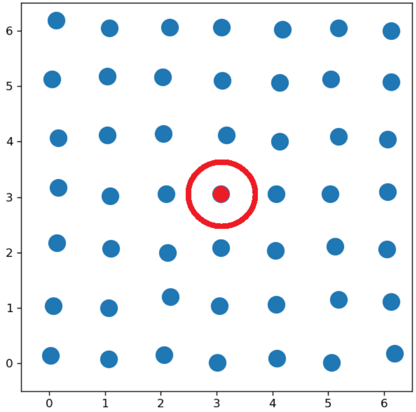
Overview

1. Describing atomic ordering
2. Brief history of PDFs
3. How x-rays scatter through matter
4. X-ray diffraction
5. Pair Distribution Function Technique
6. Real Space - Fourier Relationship
7. PDF Data Collection
8. Experimental Considerations
9. Developments in PDFs at BXDS-WHE
10. Final Remarks

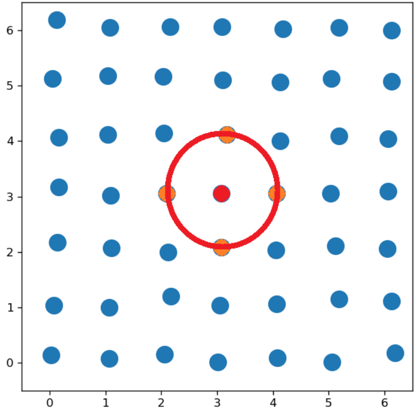
Atomic Model

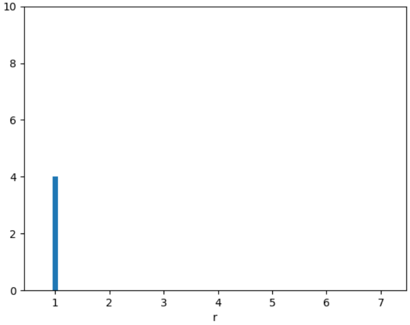


Atomic Model

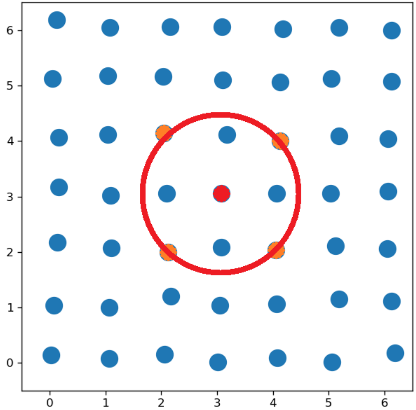


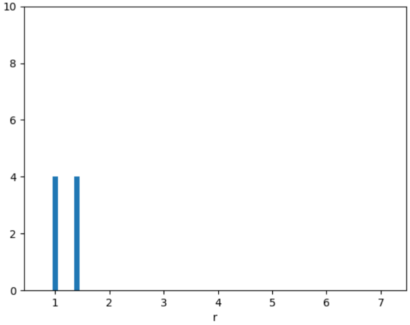
Atomic Model



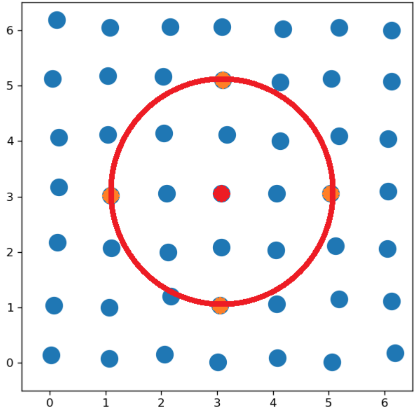


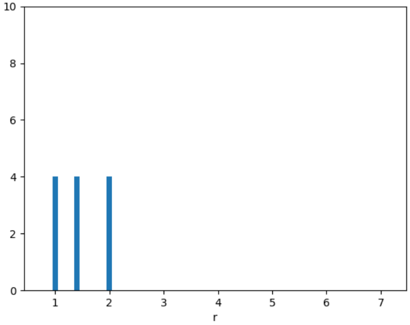
Atomic Model



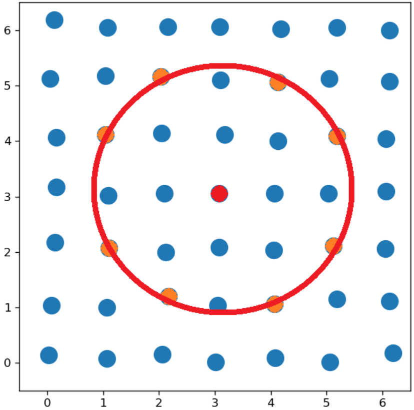


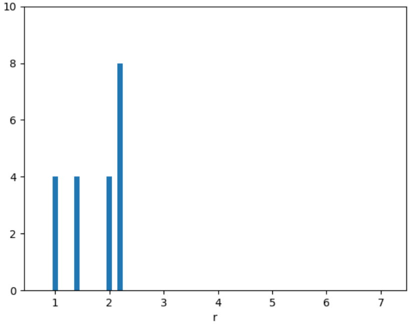
Atomic Model



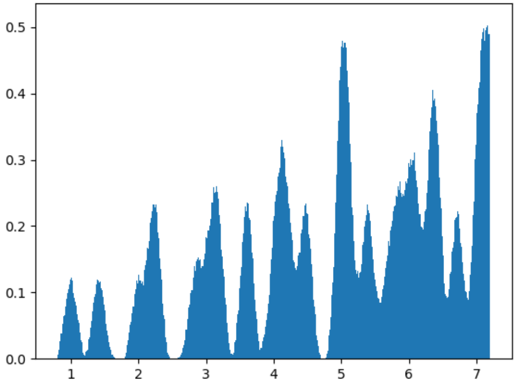


Atomic Model





Atomic Model



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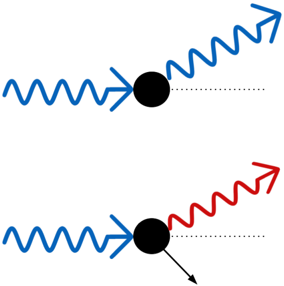
A Brief History of x-ray Scattering

- x-ray diffraction laws → Lawrence & William Henry Bragg (1912)
  - Won Nobel Prize is 1914
- Powder x-ray diffraction measurements → Peter Debye & Paul Scherrer in Germany (1916) **and** Albert Hull in the United States (1917)
- Fourier Relationship between Debye scattering equation and real-space pair density derived → Zernicke & Prins (1927)
- First Pair Distribution Function (PDF) measurement → Debye & Menke (1930)
- First Synchrotron PDF measurement → Takeshi Egami (1986)
  - Datasets took ~ 12 hours to collect after days of setup
  - Energy sensitive point detector used
- PDF Measurements collected with an area detector → Peter Chupas & Xiangyun Qiu (2003)
  - PDF measurements are now done in the order of **seconds**

X-ray Scattering on Electrons



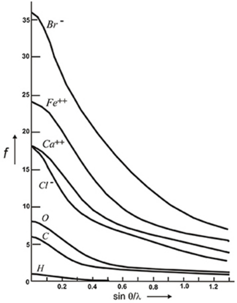
Elastic Scattering

- Coherently scattered photon has same phase and wavelength

Compton Scattering

- Photon imparts energy into the electron causing it to move
- Scattered Photon loses energy and has a larger wavelength
- Not useful for this work

X-ray Scattering on Atoms



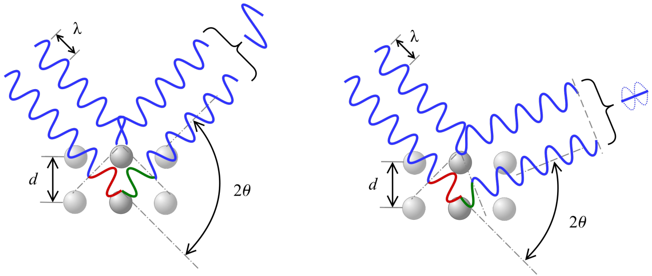
Momenum Transfer

$$Q = 4\pi \sin(\frac{2\theta}{2})/\lambda$$

Atomic Form Factor

- Photons scatter off the electron cloud
- Fewer scattering events with increasing momentum transfer
- Higher Z materials scatter x-rays more
- Distribution known as Atomic Form Factor
- The ratio of the coherent amplitude of waves scattered by an atom to that of a single electron

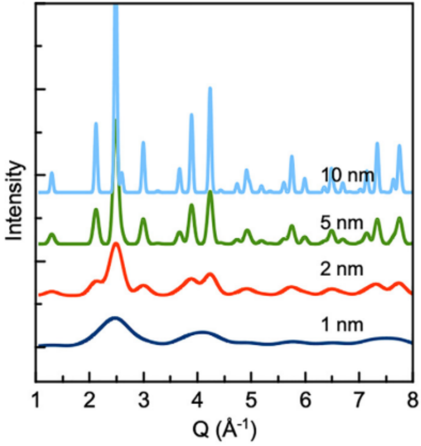
Diffraction with X-rays



$$n\lambda = 2d\sin(\theta)$$

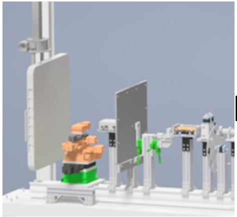
Non-crystalline scattering

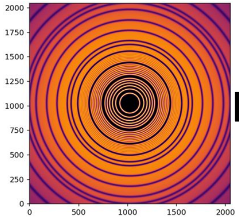
- Amorphous materials don't have repeating unit cells
- No longer have nearly infinite planes leading to sharp bragg peaks
- Diffuse scattering is the consistent short range ordering causing weak diffraction

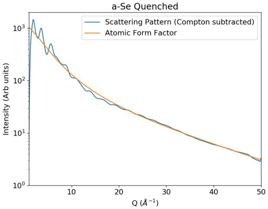


Simulated XRD of Fe_3O_4

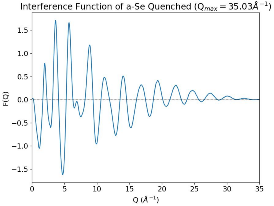
Measurement process







$$Q = 4\pi \frac{\sin\theta}{\lambda}$$

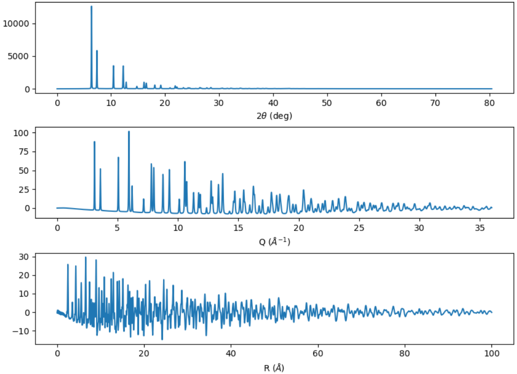


$$F(Q) = Q(S(Q) - 1)$$

The Pair Distribution Function

$$G(r) = \frac{2}{\pi}\int \mathrm{Q}(S(\mathrm{Q})-1)\sin(\mathrm{Qr})\mathrm{dQ}$$

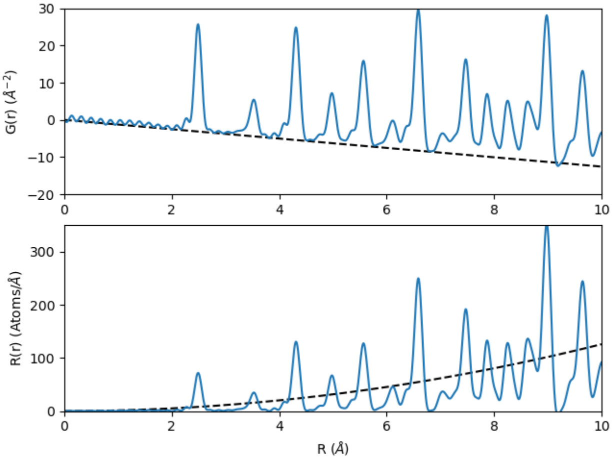
$$Q = \frac{4\pi}{\lambda}\sin\left(\frac{2\theta}{2}\right)$$



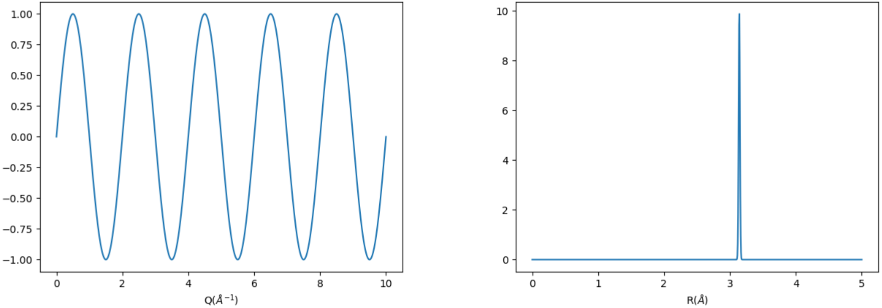
Other Forms

$$G(r) = 4\pi r \rho_0 (g(r) - 1)$$

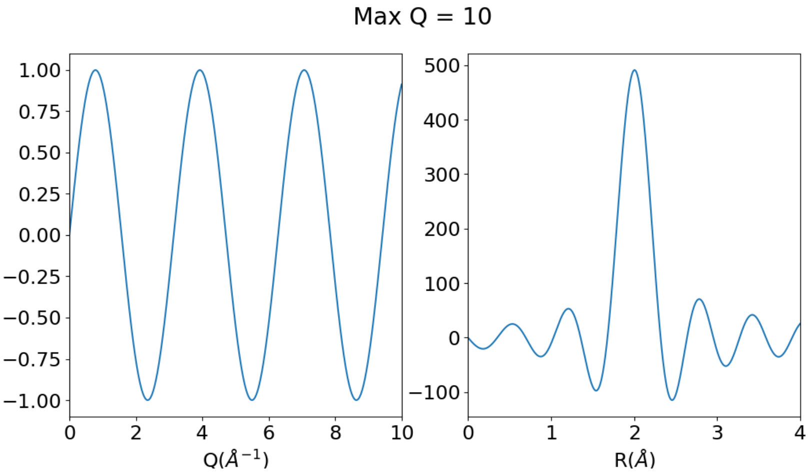
$$R(r) = 4\pi r^2 \rho_0 g(r)$$



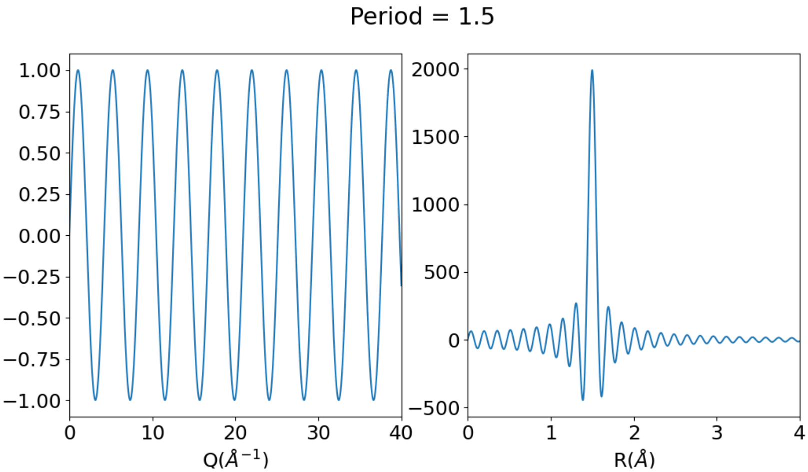
Reciprocal and Real Space



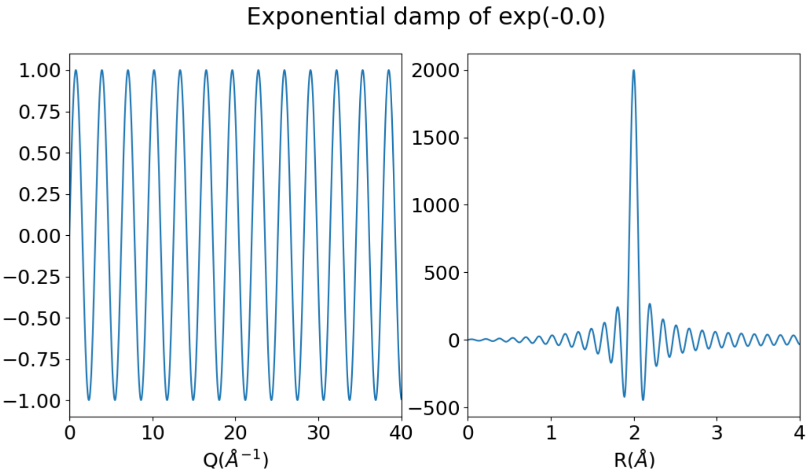
Effects of Finite limit of Reciprocal Space



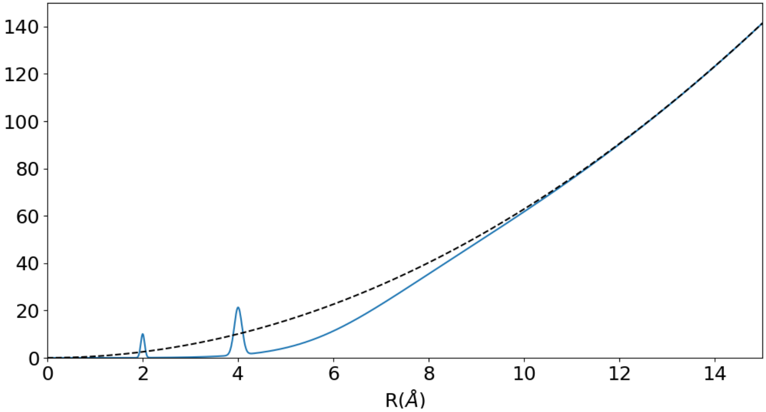
Period and Peak Position



Adding a Damp



How Real Space correlates to Reciprocal Space



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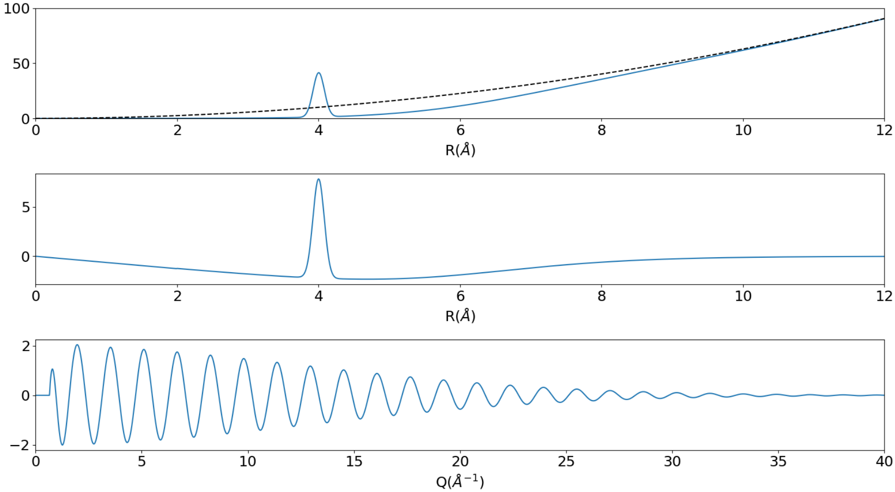
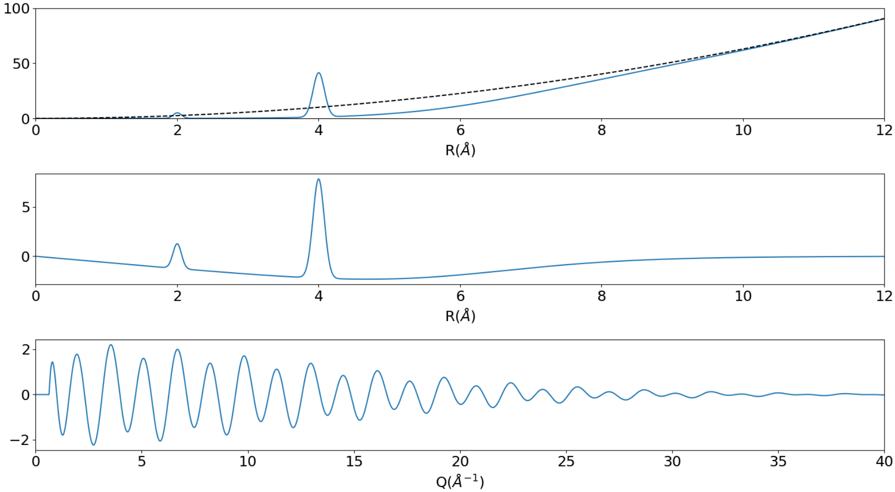
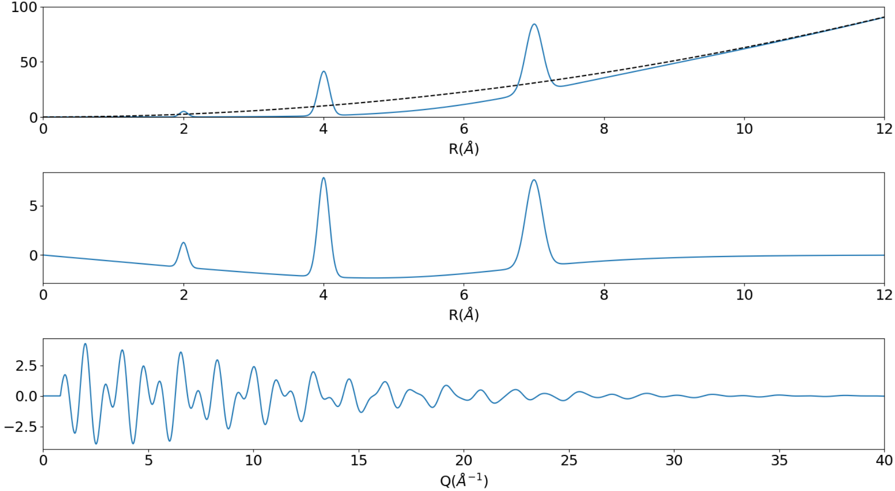
Single Peak



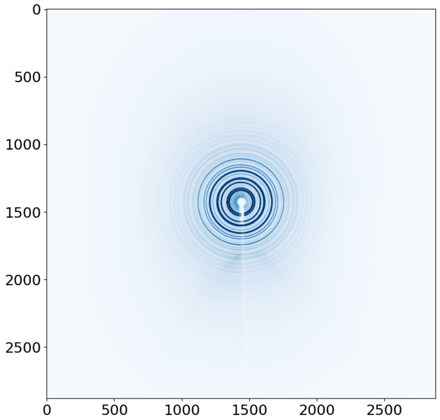
Two Peaks


100
50
0
0
2
4
6
8
10
12
R(Å)
5
0
0
2
4
6
8
10
12
R(Å)
2
0
−2
0
5
10
15
20
25
30
35
40
Q(Å⁻¹)

Three Peaks


100
50
0
0
2
4
6
8
10
12
R(Å)
5
0
0
2
4
6
8
10
12
R(Å)
2.5
0.0
−2.5
0
5
10
15
20
25
30
35
40
Q(Å^{-1})

Raw Data



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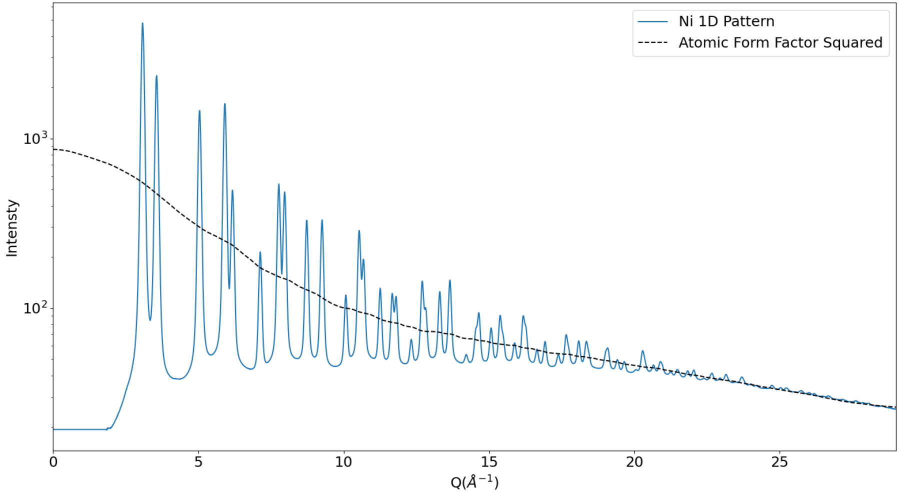
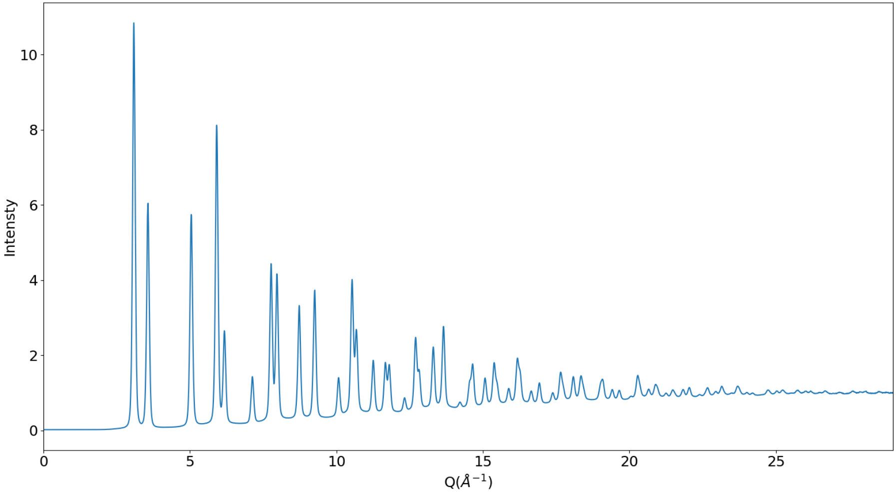
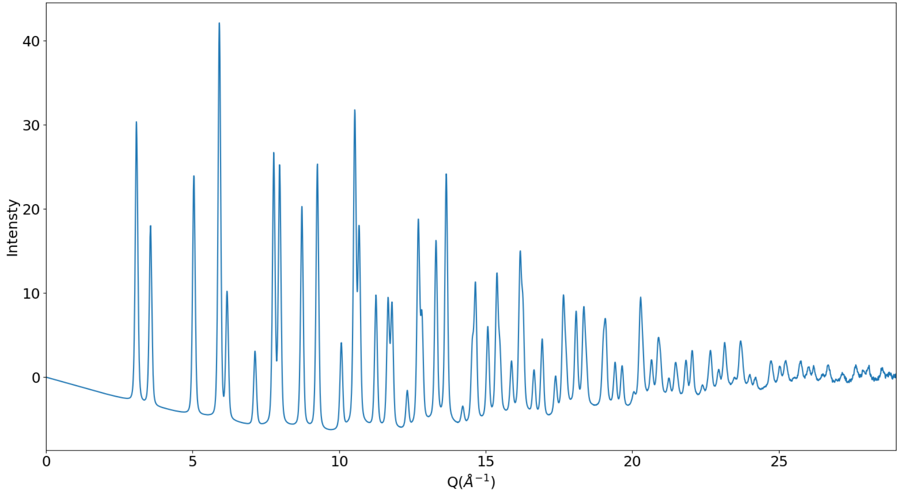
Integrated Data



Normalizing to Atomic Form Factor



$S(Q) \rightarrow F(Q) = Q(S(Q) - 1)$



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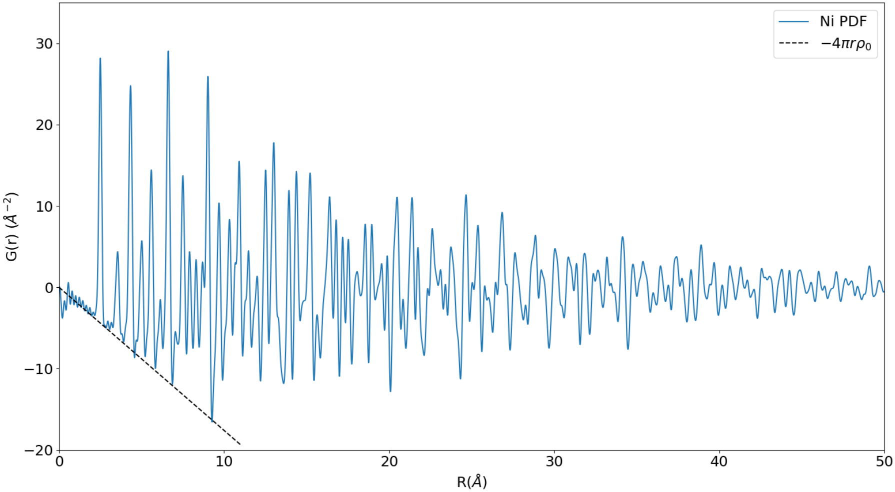
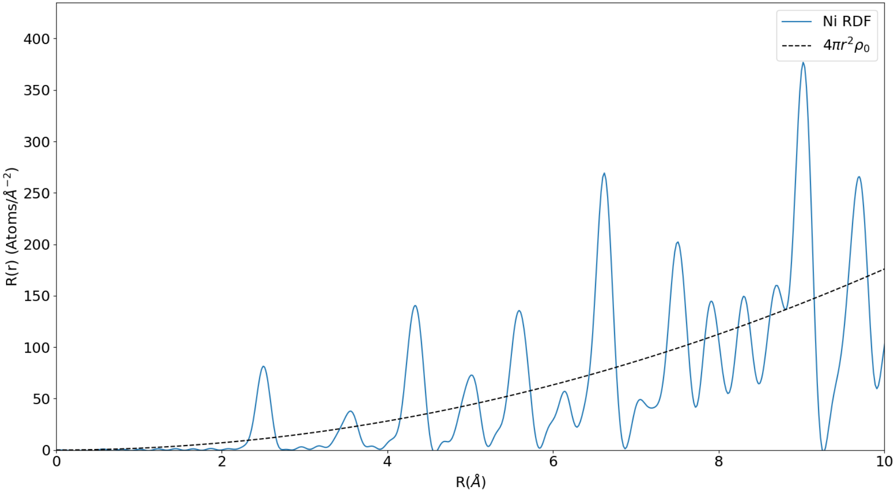
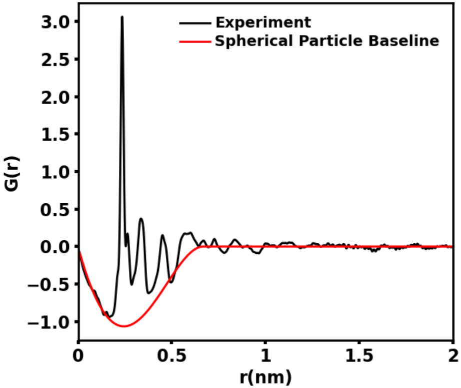
$F(Q) \rightarrow G(r) = \frac{2}{\pi} \int F(Q)\sin(Qr)dQ$



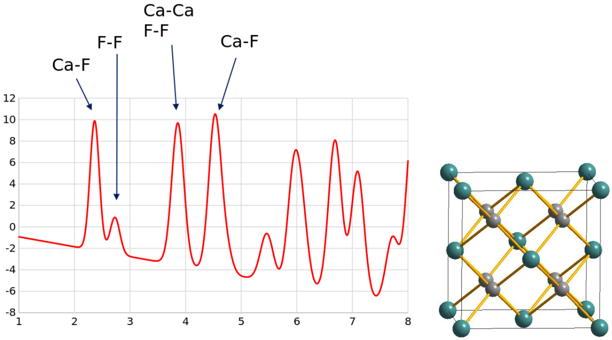
$\mathrm{G(r)} \rightarrow \mathrm{R(r)} = \mathrm{rG(r)} + 4\pi\rho_0 r^2$



Nanoparticles

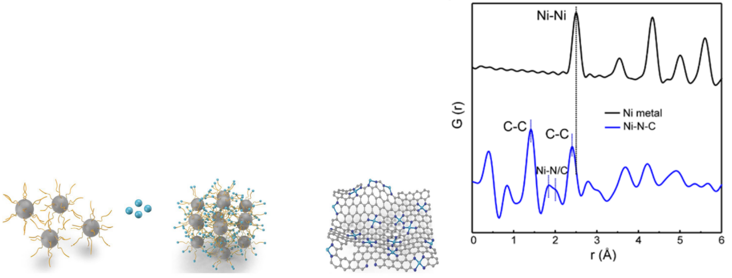


Local Ordering



CaF_2

Single Atom Catalysts



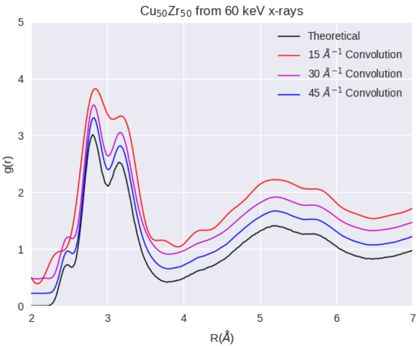
Synthesizing single atoms catalysts has been developed using cross linked graphene quantum dots as the support. Absence of Ni-Ni bonds in PDF confirm Ni dispersed atomically and not aggregates.

Xia, C. *et al.* General synthesis of single-atom catalysts with high metal loading using graphene quantum dots. Nature Chemistry (2021) 13, 887-894.

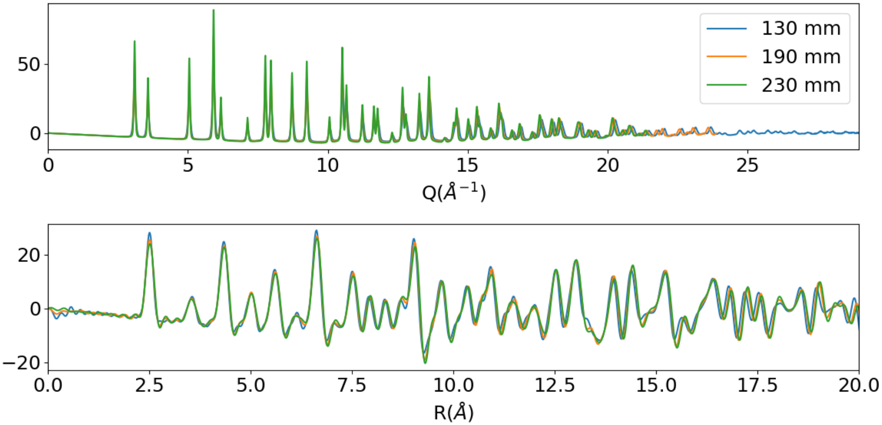
Experimental Challenges

- Q-range & Q-resolution
- Sample quality
- Compton Scattering
- Non-sample coherent scattering
- Detector noise

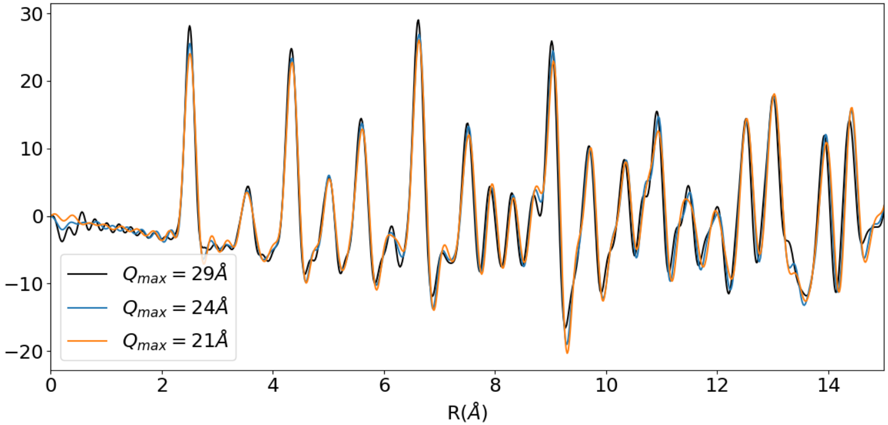
The Q Problem



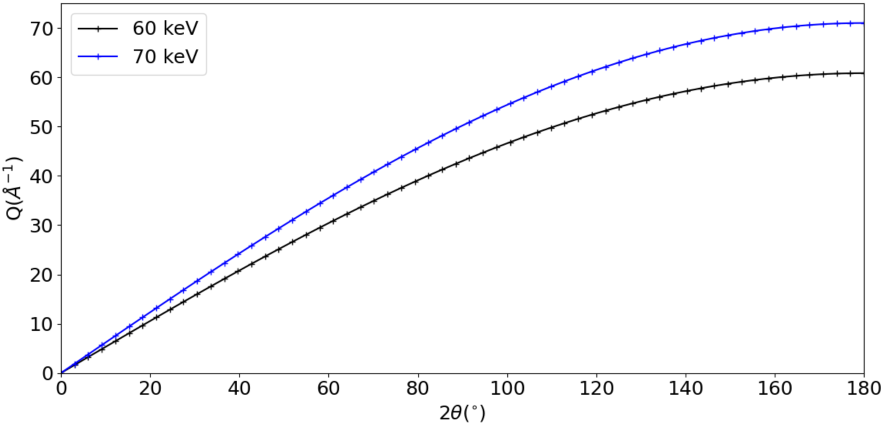
Sample-Detector Distance



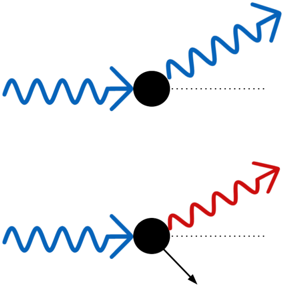
Sample-Detector Distance

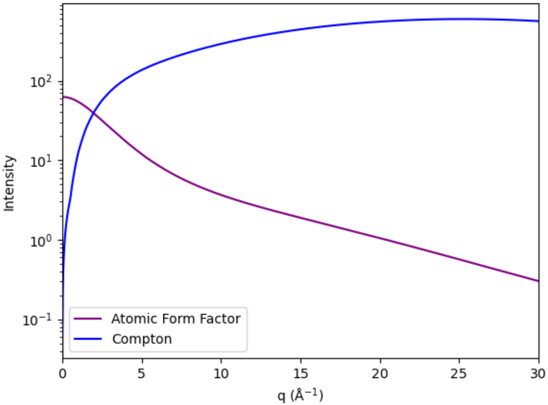


Q Related to Angle and Energy

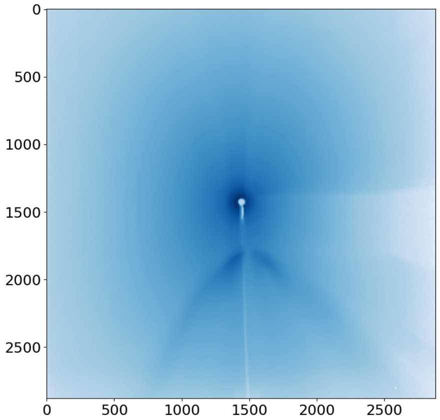


Compton Scattering





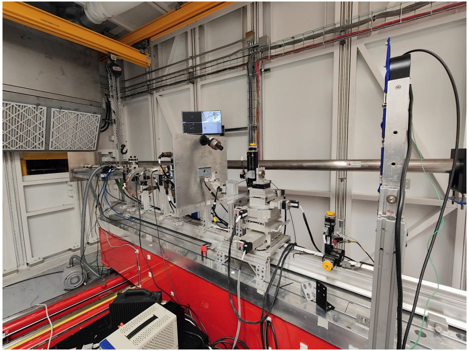
Non-Sample Signal



User Pro Tips

- What are you hoping to resolve?
  - Short range structure
  - Medium range ordering
  - Comparitive changes (*in situ/ in operando*)
  - Modeling
- Is there low Q or high Q signal?
- Be aware of the experimental parameters
  - Choice of energy vs flux and Q
  - Area detector being used
    - Pixel Size
    - Afterglow
    - Dark current
    - Flatfield
    - Saturation levels
  - Beam size
- Collect more subtractive images than you need!
- Keep it simple

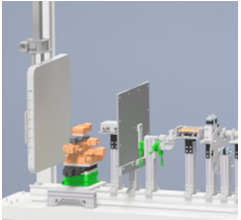
High Energy Wiggler Beamline (BXDS-WHE)

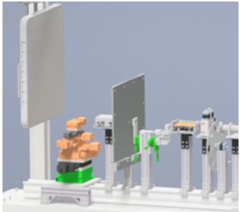


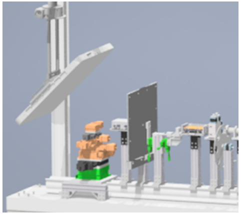
Details

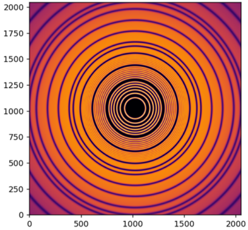
- 20-95 keV
- Rapid Powder XRD
- Pair Distribution Function Measurement
- High Pressure XRD
- Resistive furnace cells with gas flow for in-situ measurements (RT $\leq$ T $\leq$ 1000C)
- Cold air stream (80 K $\leq$ T $\leq$ 500 K)

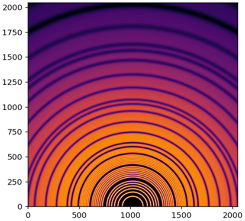
Improving PDF Collection

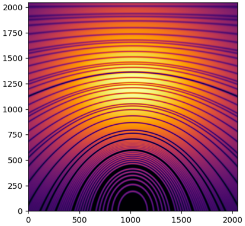












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CPDW18

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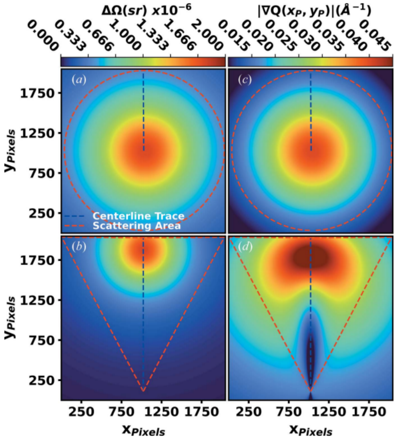
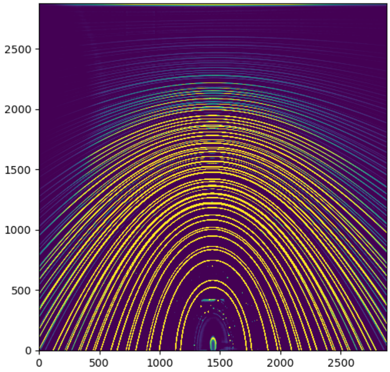
Inclined Geometry



Advantages

- Higher Q accessed
- Better Q resolution for low angle peaks & lower resolution for high angle peaks improves dynamic range
- Can use much lower x-ray energies for equivalent Q

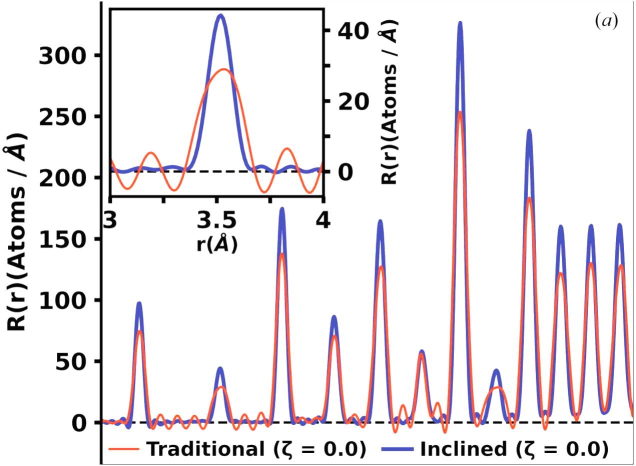
Inclined Geometry



Disadvantages

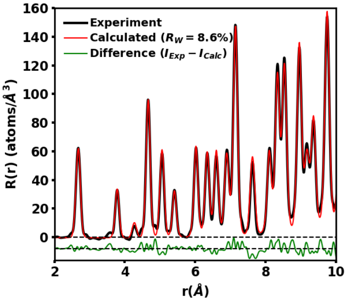
- Geometry calibration much harder
- High Q signal very weak – noise can easily get convoluted
- New software needed to accurately work in these extremes
- No averaging over full rings – need good smooth samples
- Background measurements needed more frequently

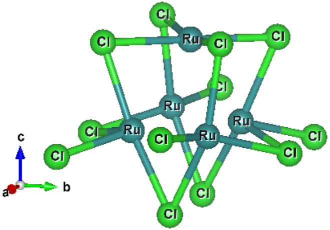
Comparison



N. Burns *et al.*, Journal of Applied Crystallography 2023, 56, 510.

Ru_5Cl_{12} Nanoparticle PDF Measurement





Summary

- PDF is a powerful tool that can probe local structure regardless of crystallinity
- With synchrotrons data collection is fast to observe structural changes as they happen
- PDF methods are improving and provide a way of seeing local structure nanoparticle structure
- GSAS-II very useful for PDF generation but it's not difficult to make your own code

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Thank You

Resources

- X-Ray Diffraction – B. E. Warren (1990)
- Elements of X-Ray Diffraction – B. D. Cullity (2001)
- The rise of the X-ray atomic pair distribution function method: a series of fortunate events – S. Billinge https://doi.org/10.1098/rsta.2018.0413
- An inclined detector geometry for improved X-ray total scattering measurements – N. Burns *et al* https://doi.org/10.1107/S1600576723001747
- GSAS-II – https://subversion.xray.aps.anl.gov/trac/pyGSAS