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.

Canadian Light Source
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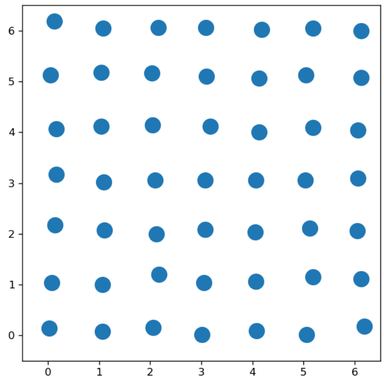
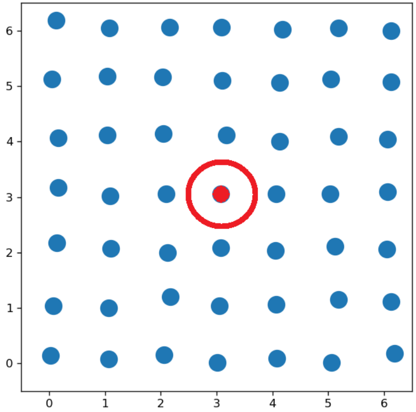
Overview

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

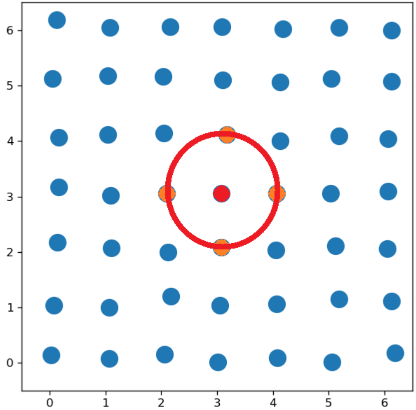
Atomic Model

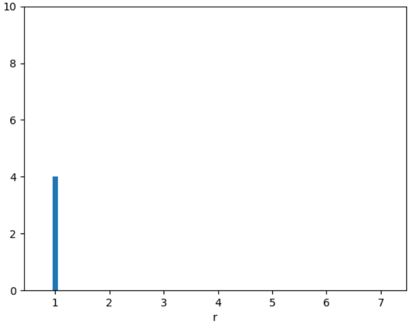


Atomic Model

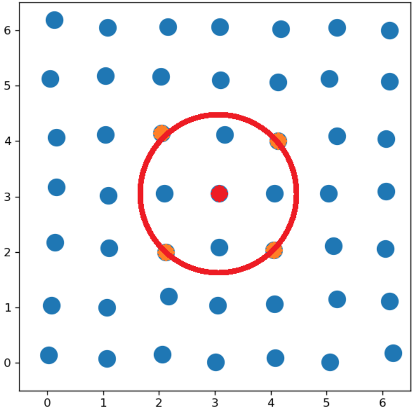


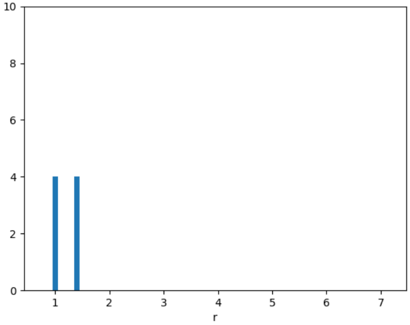
Atomic Model



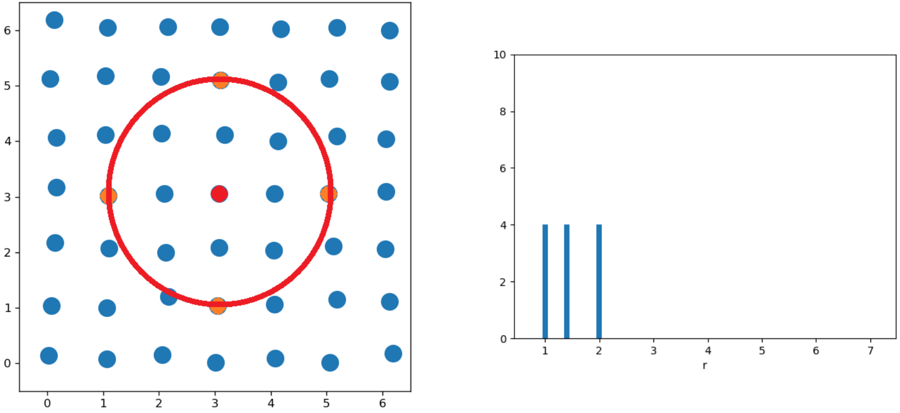


Atomic Model

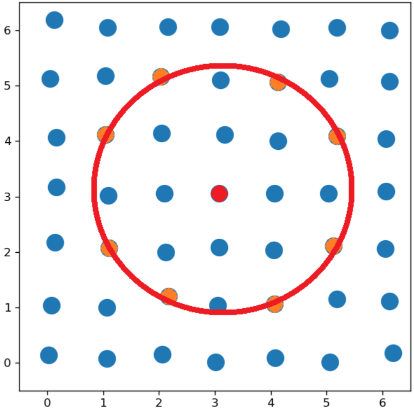


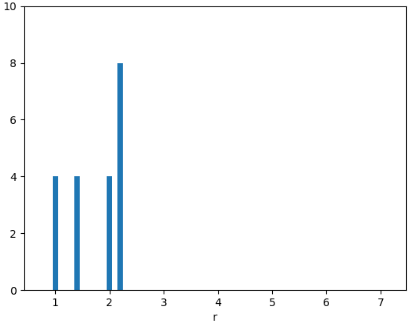


Atomic Model

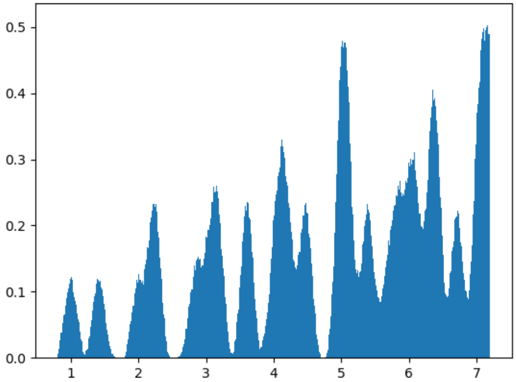


Atomic Model





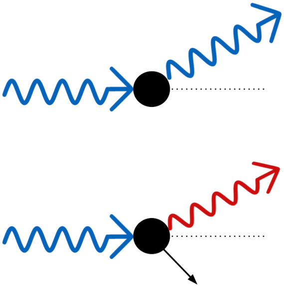
Atomic Model



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



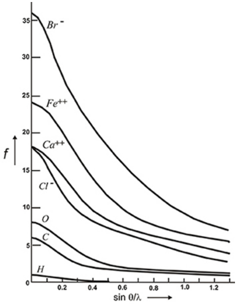
Elastic Scattering

- 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



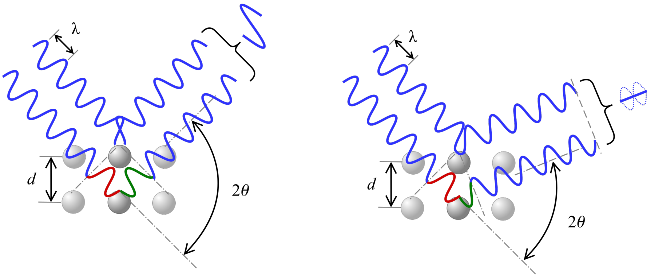
Momenum Transfer

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

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

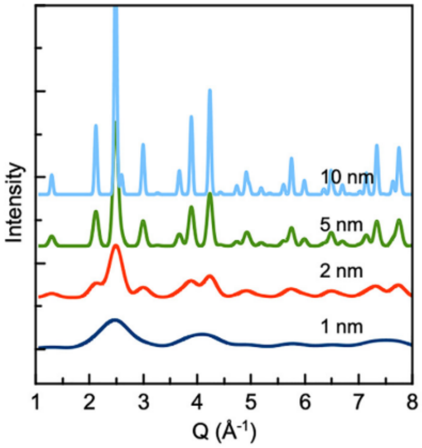
Diffraction with X-rays



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

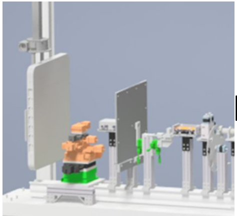
Non-crystalline scattering

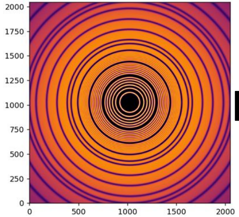
- Amorphous materials don't have repeating unit cells
- No longer have nearly infinite planes leading to sharp bragg peaks
- Diffuse scattering is the consistent short range ordering causing weak diffraction

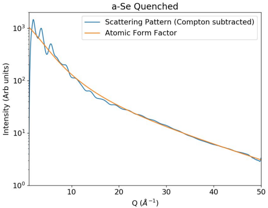


Simulated XRD of Fe_3O_4

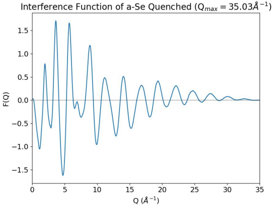
Measurement process







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

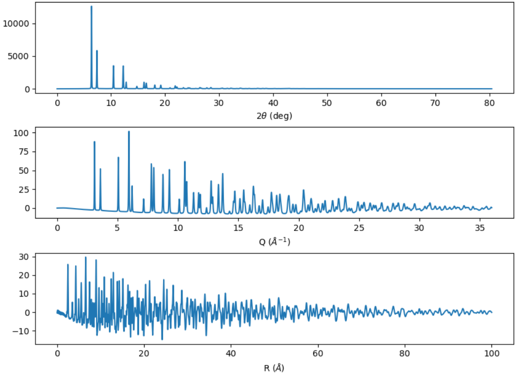


$$F(Q) = Q(S(Q) - 1)$$

The Pair Distribution Function

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

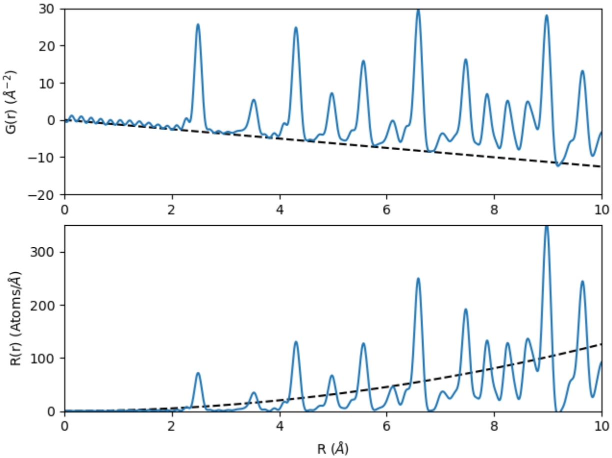
$$Q = \frac{4\pi}{\lambda} \sin\left(\frac{2\theta}{2}\right)$$



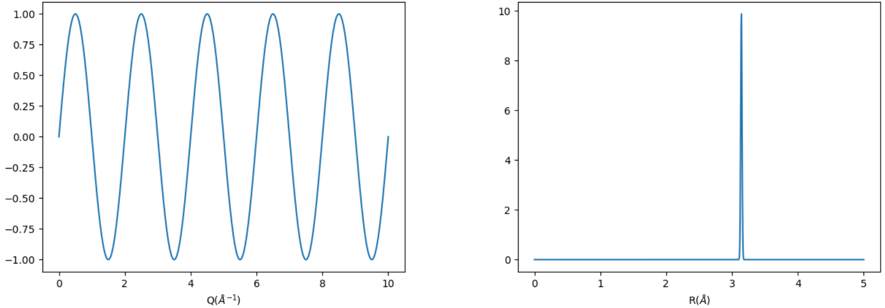
Other Forms

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

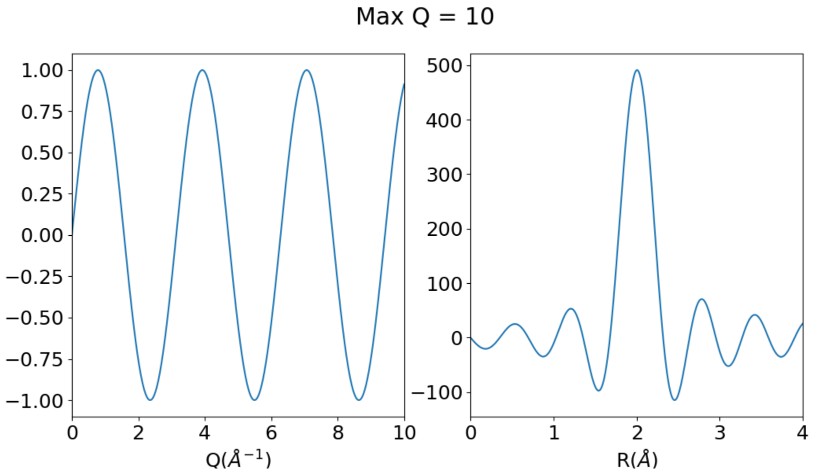
$$R(r) = 4\pi r^2 \rho_0 g(r)$$



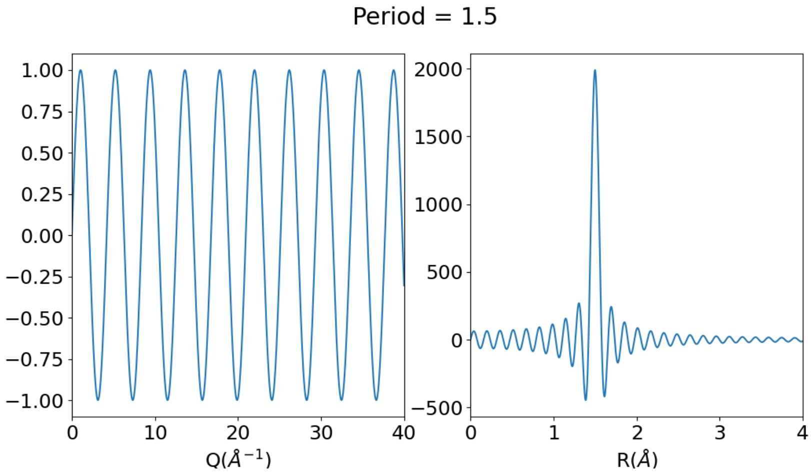
Reciprocal and Real Space



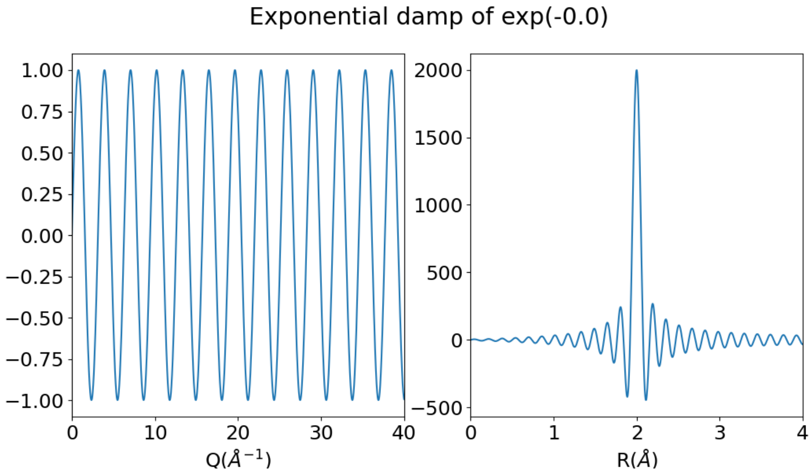
Effects of Finite limit of Reciprocal Space



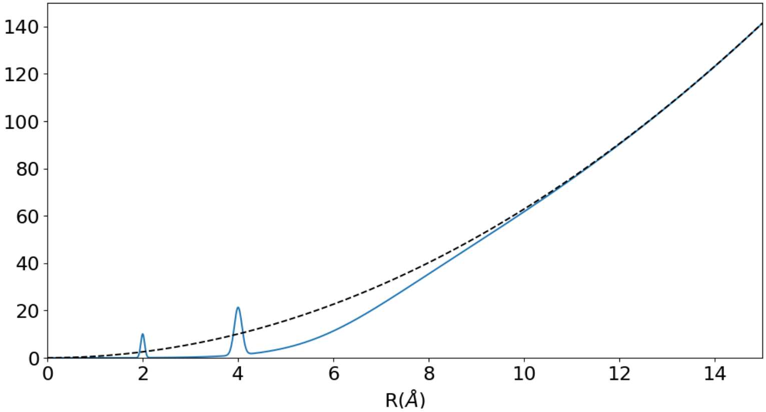
Period and Peak Position



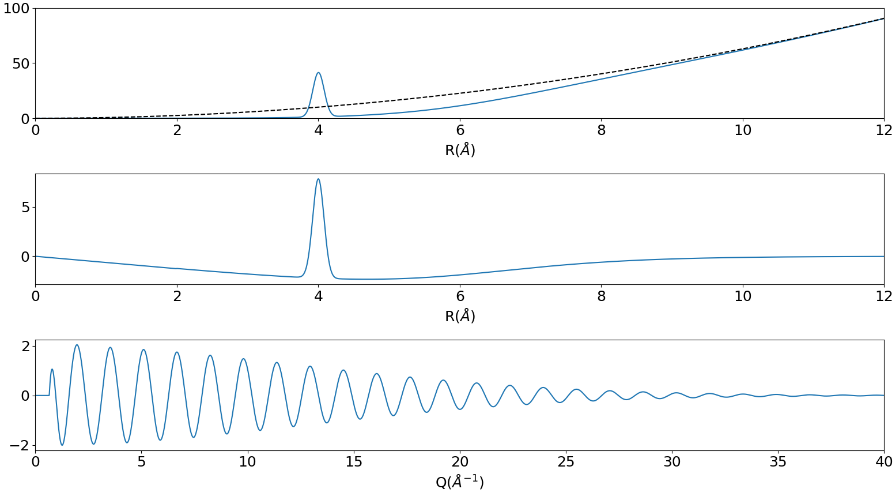
Adding a Damp



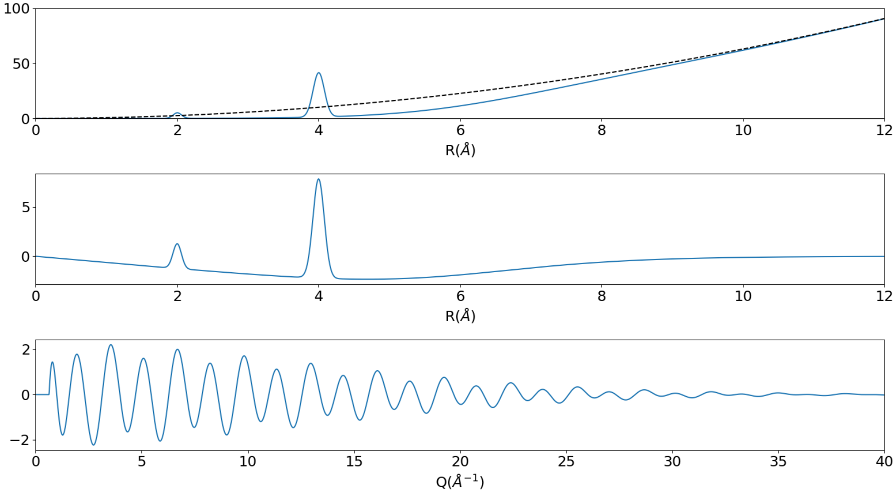
How Real Space correlates to Reciprocal Space



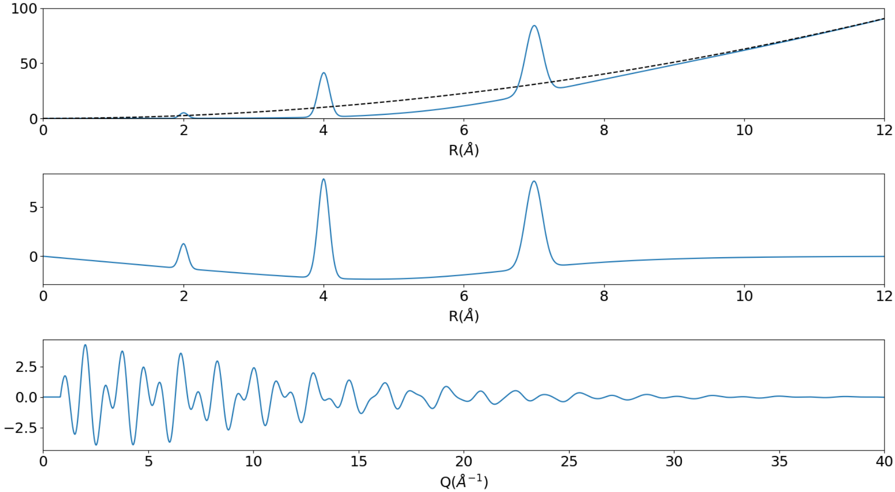
Single Peak


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})

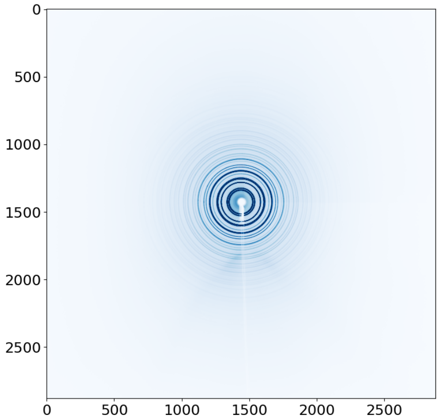
Two Peaks


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)

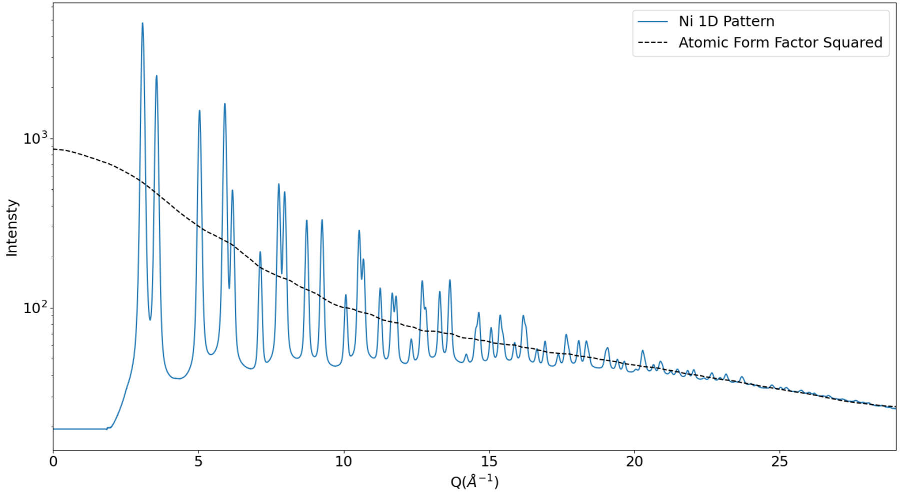
Three Peaks


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)

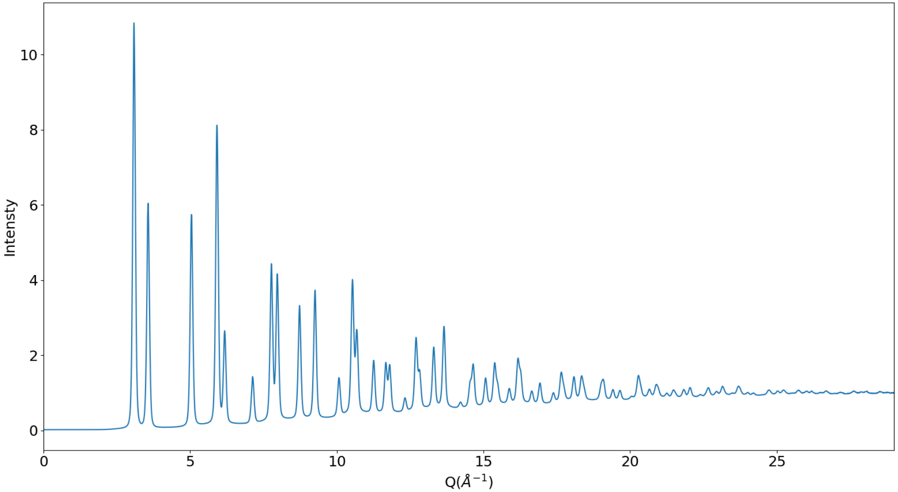
Raw Data



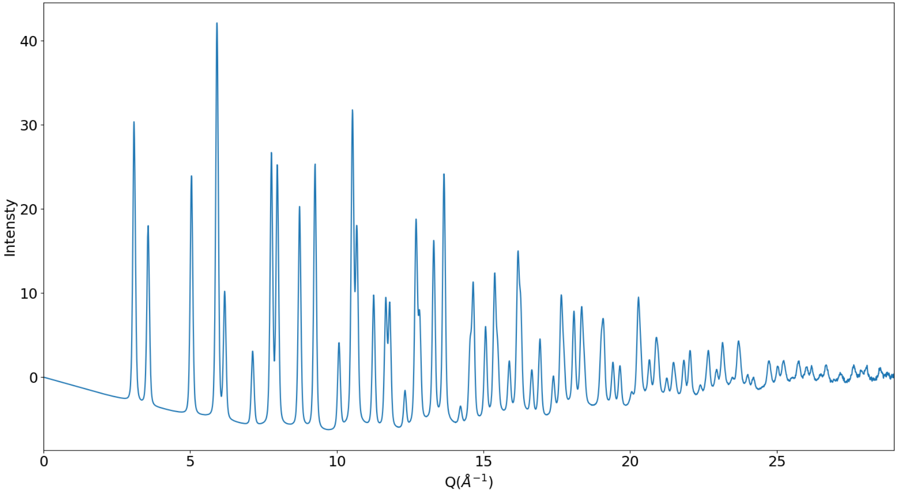
Integrated Data



Normalizing to Atomic Form Factor



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



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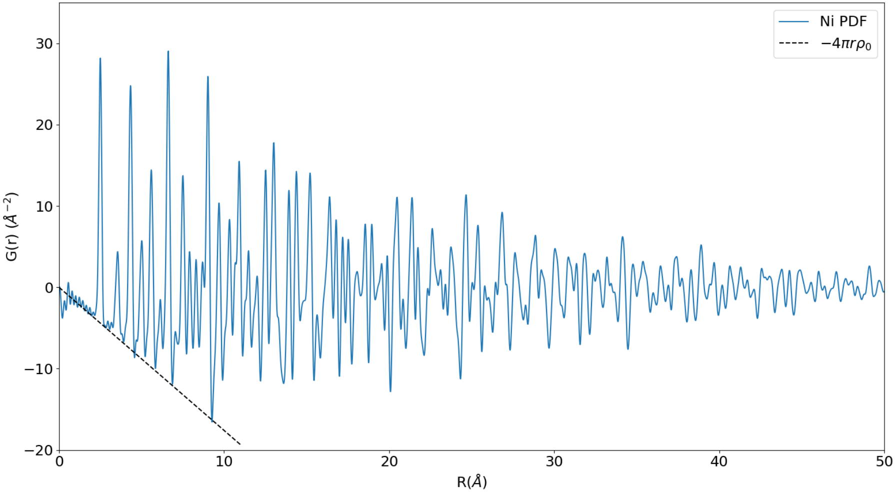
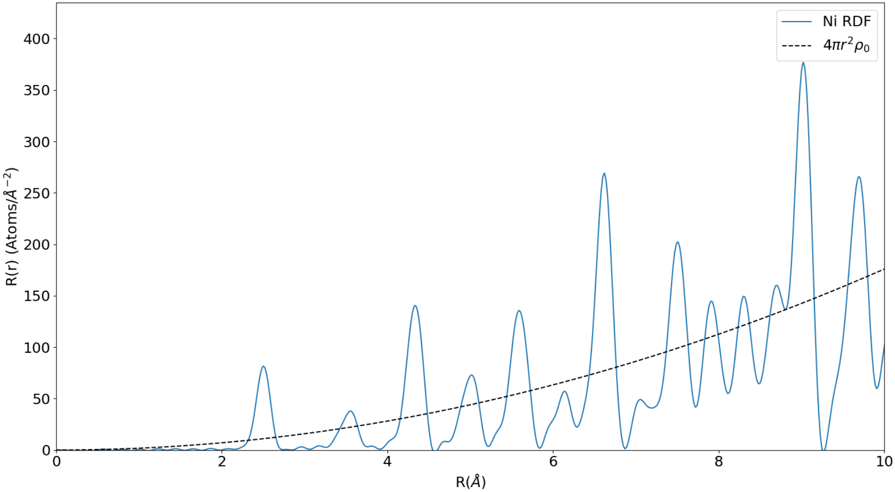
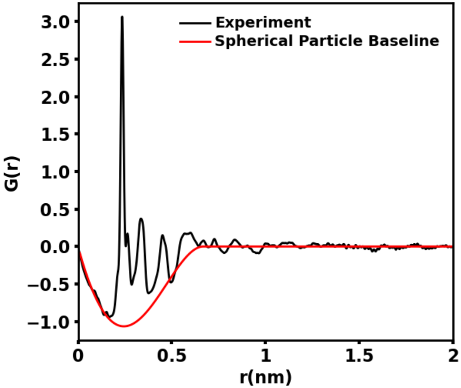
$F(Q) \rightarrow G(r) = \frac{2}{\pi}\int F(Q)\sin(Qr)dQ$



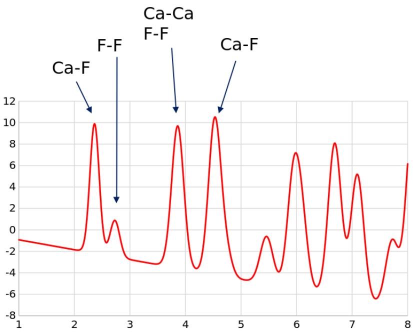
G(r) $\rightarrow$ R(r) = rG(r) + $4\pi\rho_0 r^2$

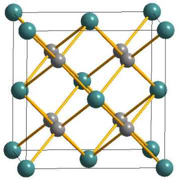


Nanoparticles



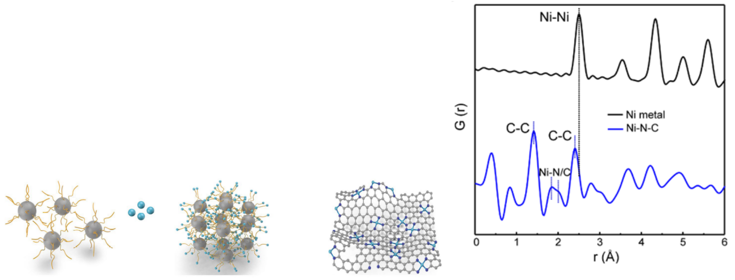
Local Ordering





CaF_2

Single Atom Catalysts



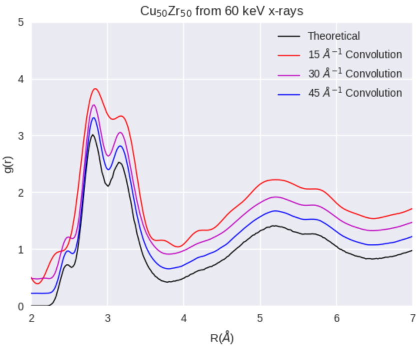
Synthesizing single atoms catalysts has been developed using cross linked graphene quantum dots as the support. Absence of Ni-Ni bonds in PDF confirm Ni dispersed atomically and not aggregates.

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

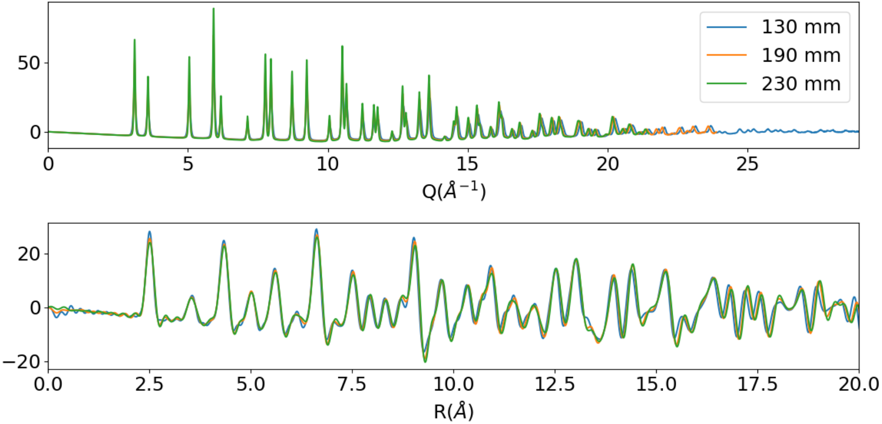
Experimental Challenges

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

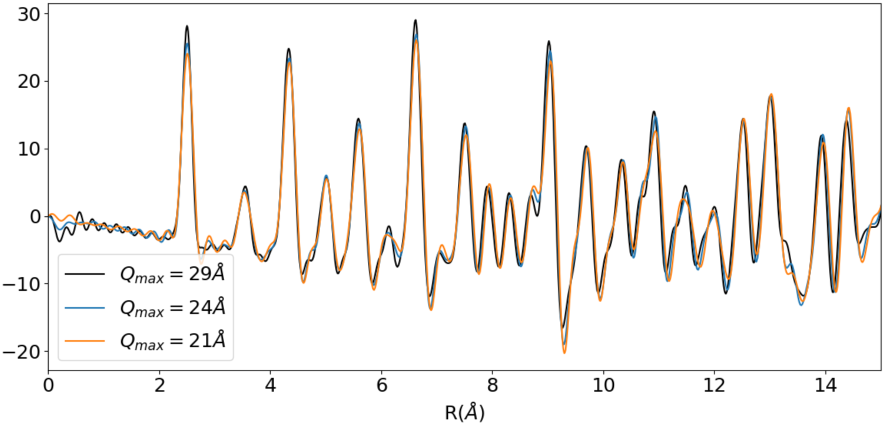
The Q Problem



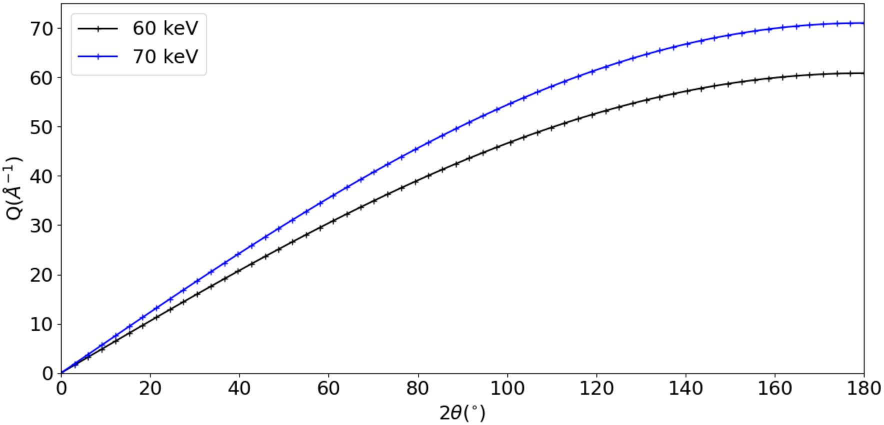
Sample-Detector Distance



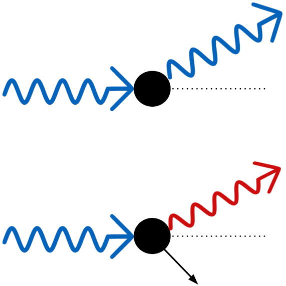
Sample-Detector Distance

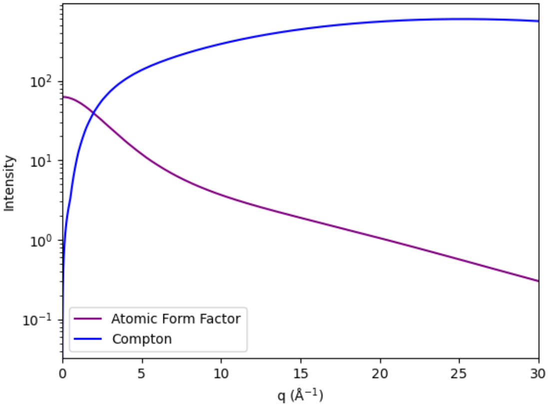


Q Related to Angle and Energy

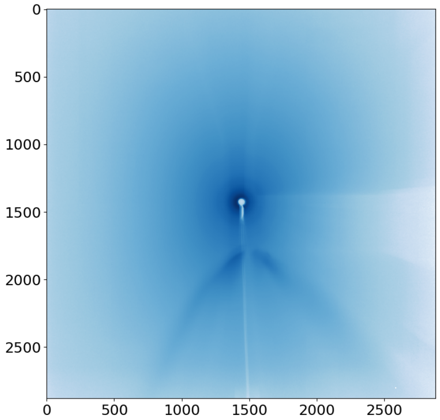


Compton Scattering





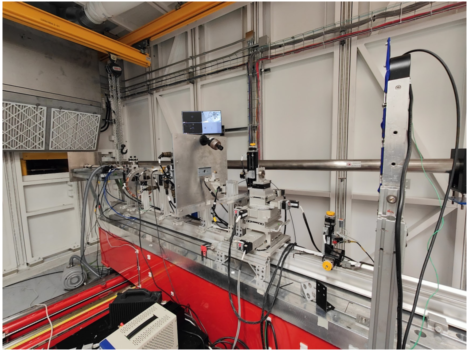
Non-Sample Signal



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

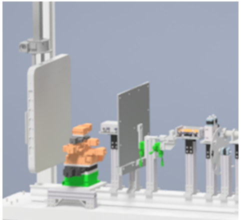
High Energy Wiggler Beamline (BXDS-WHE)

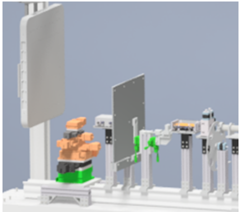


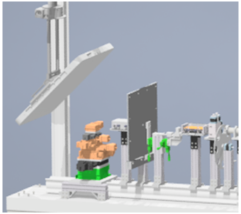
Details

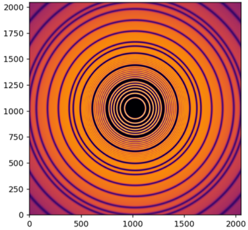
- 20-95 keV
- Rapid Powder XRD
- Pair Distribution Function Measurement
- High Pressure XRD
- Resistive furnace cells with gas flow for in-situ measurements ($RT \leq T \leq 1000C$)
- Cold air stream ($80\ K \leq T \leq 500\ K$)

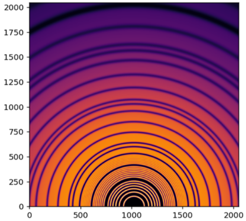
Improving PDF Collection

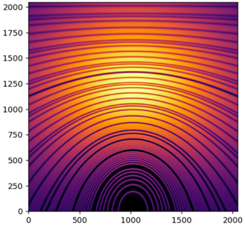




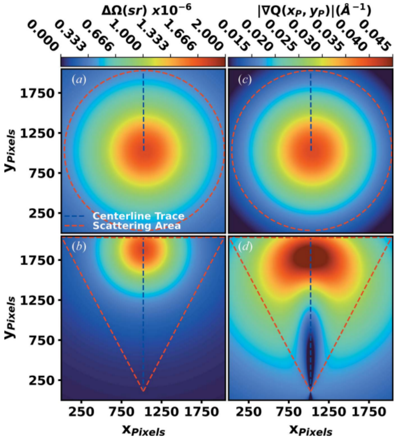








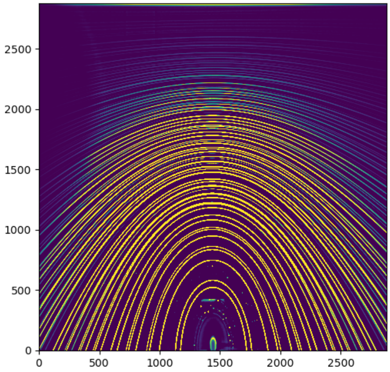
Inclined Geometry



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

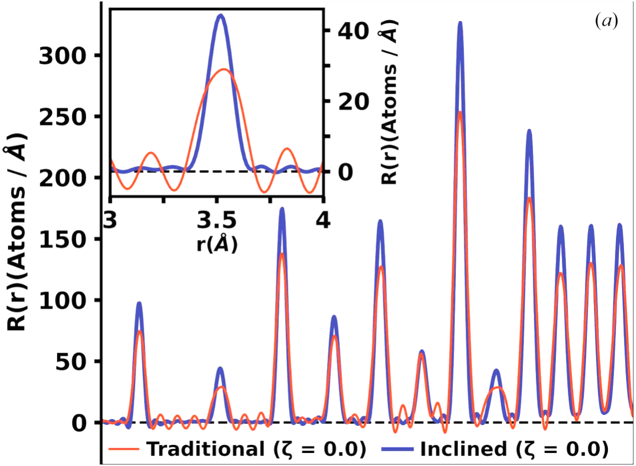
Inclined Geometry



Disadvantages

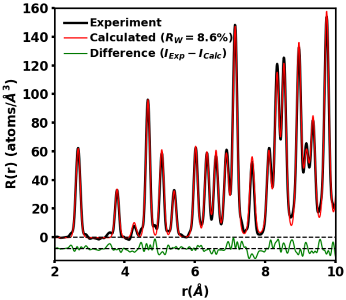
- Geometry calibration much harder
- High Q signal very weak – noise can easily get convoluted
- New software needed to accurately work in these extremes
- No averaging over full rings – need good smooth samples
- Background measurements needed more frequently

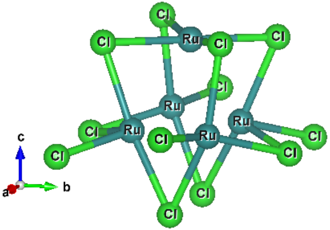
Comparison



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

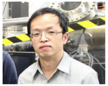
Brockhouse Team

Stefan Kycia
Professor, U. Guelph
Beamteam Leader

Al Rahemtulla

Narayan Appathurai

Beatriz Diaz Moreno
Beamline Responsible



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Joel Reid

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- Brockhouse website – `http://www.brockhouse.lightsource.ca`

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`