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Introduction to Pair Distribution Functions (PDF)

Dr. Al Rahemtulla

Associate Scientist at Brockhouse X-ray Diffraction & Scattering (BXDS) Sector

July 15, 2026



What is the PDF Technique?

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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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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



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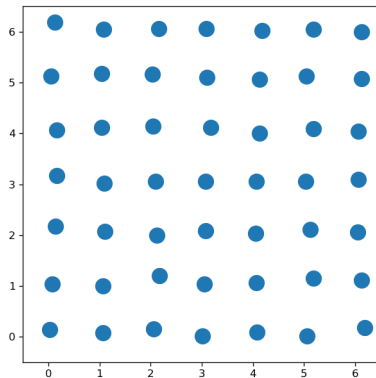
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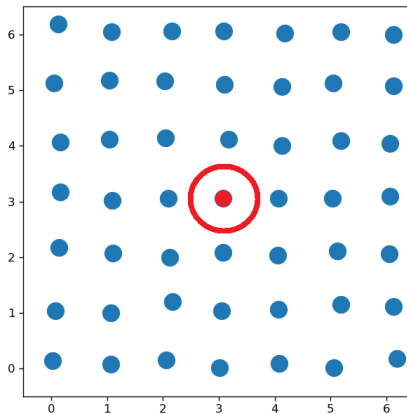
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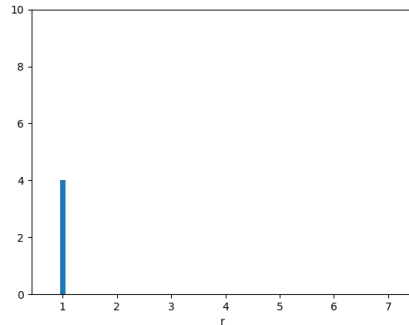
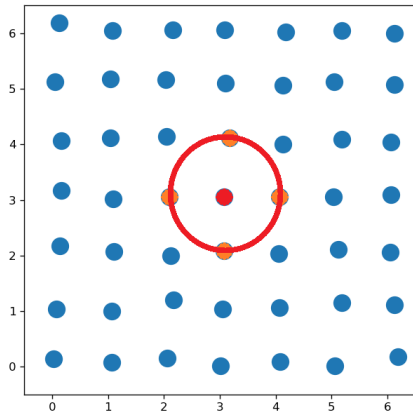
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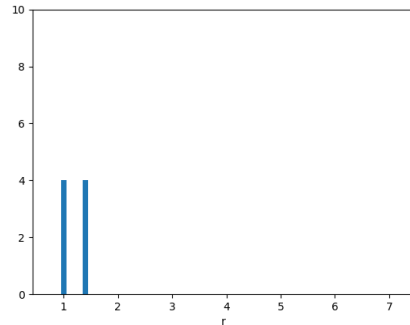
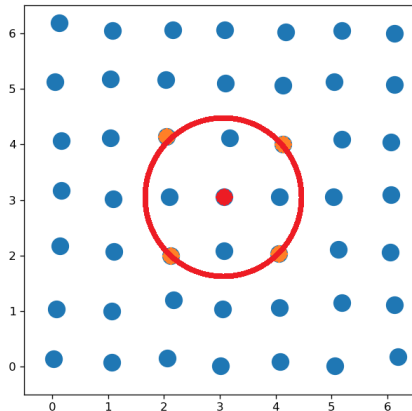
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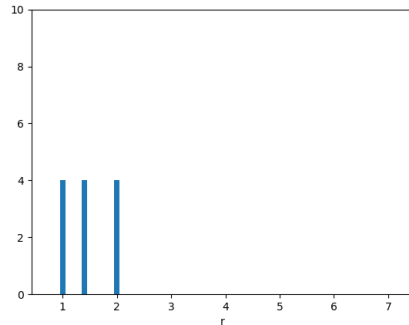
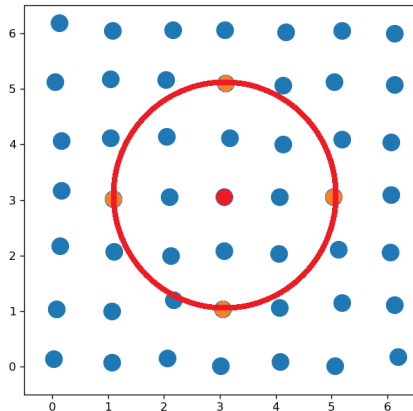
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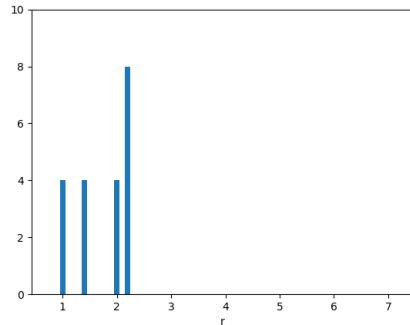
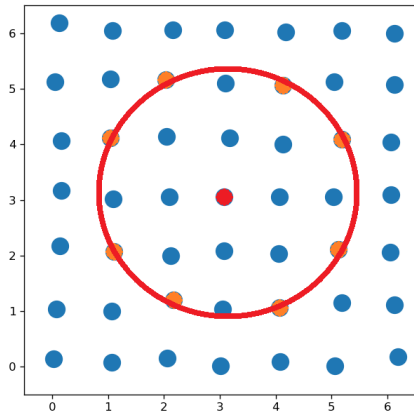
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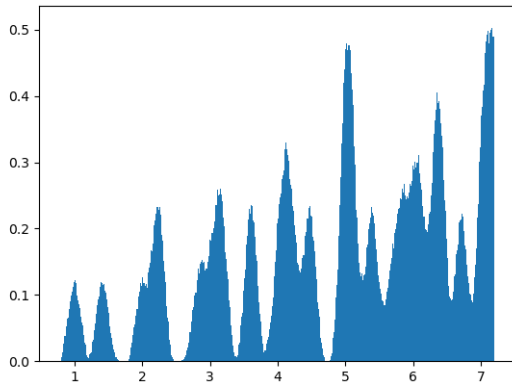
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A Brief History of x-ray Scattering

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- ▶ 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

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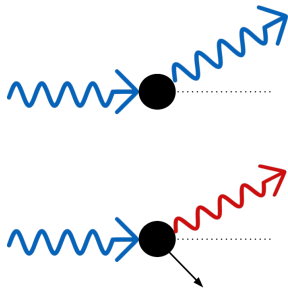
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Elastic Scattering

- ▶ 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

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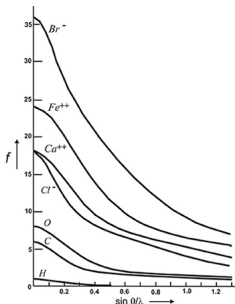
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Atomic Form Factor

- ▶ 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

Momentum Transfer

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



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Diffraction with X-rays

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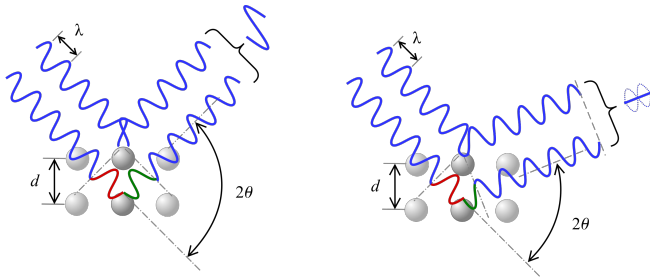
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$$n\lambda = 2d \sin(\theta)$$



Non-crystalline scattering

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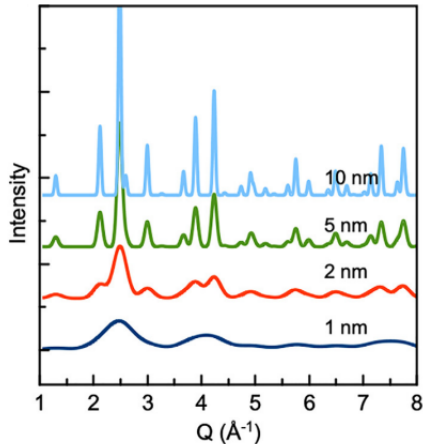
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- ▶ Amorphous materials don't have repeating unit cells
- ▶ No longer have nearly infinite planes leading to sharp bragg peaks
- ▶ Diffuse scattering is the consistent short range ordering causing weak diffraction



Simulated XRD of Fe_3O_4



Measurement process

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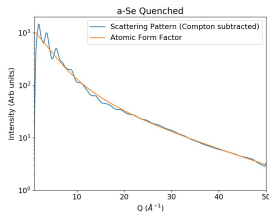
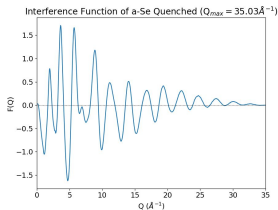
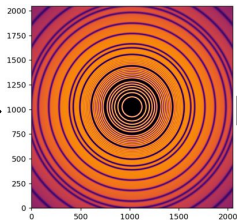
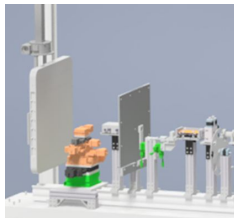
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$$F(Q) = Q(S(Q) - 1)$$

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



The Pair Distribution Function

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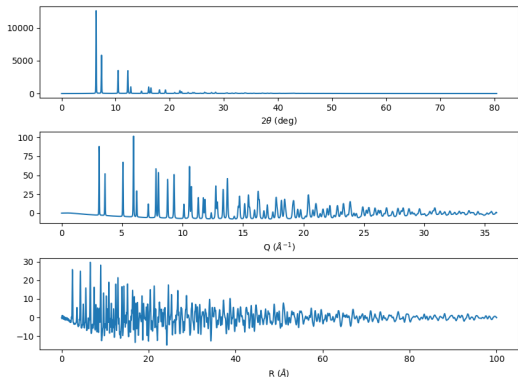
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$$G(r) = \frac{2}{\pi} \int Q(S(Q) - 1) \sin(Qr) dQ$$

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





Other Forms

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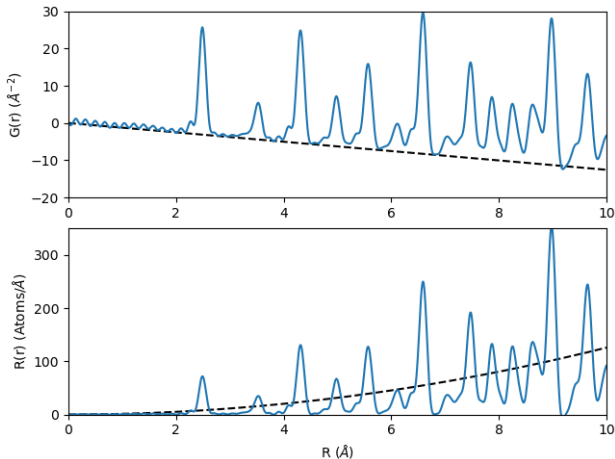
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Summary

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

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





Reciprocal and Real Space

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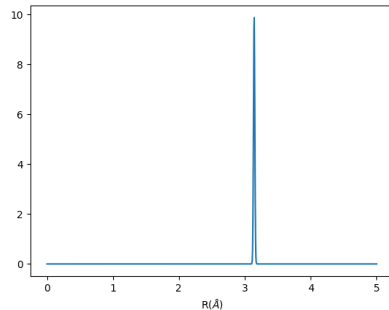
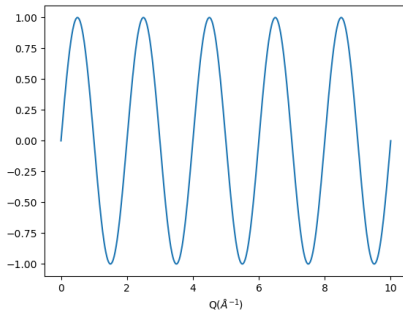
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Effects of Finite limit of Reciprocal Space

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How Real Space correlates to Reciprocal Space

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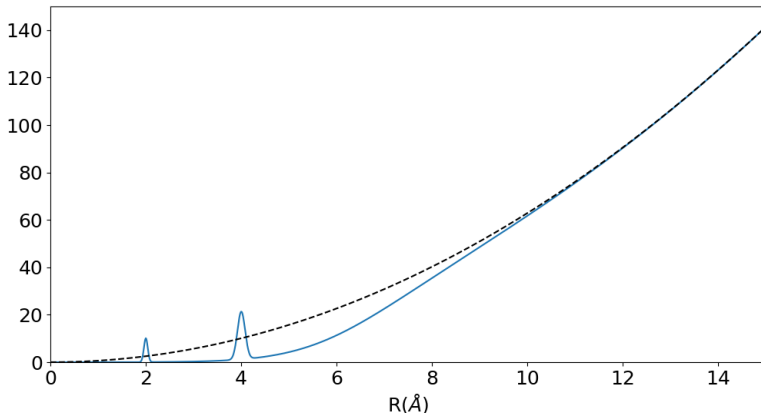
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Single Peak

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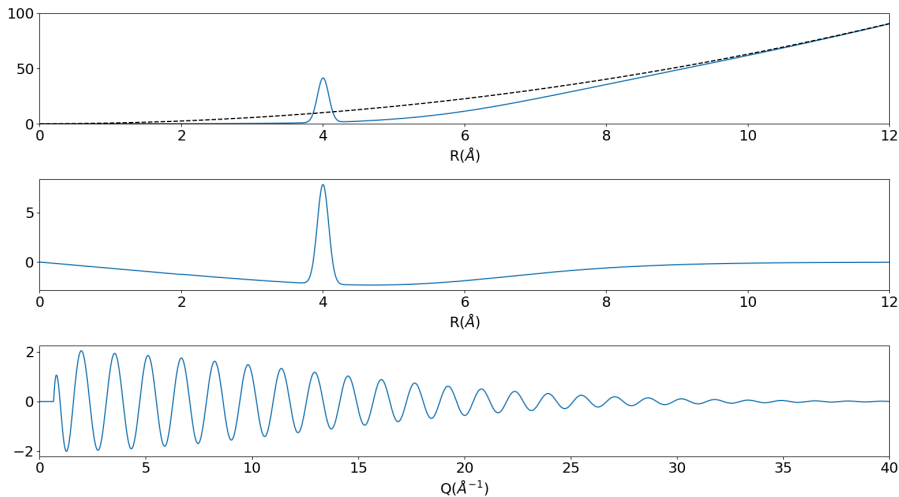
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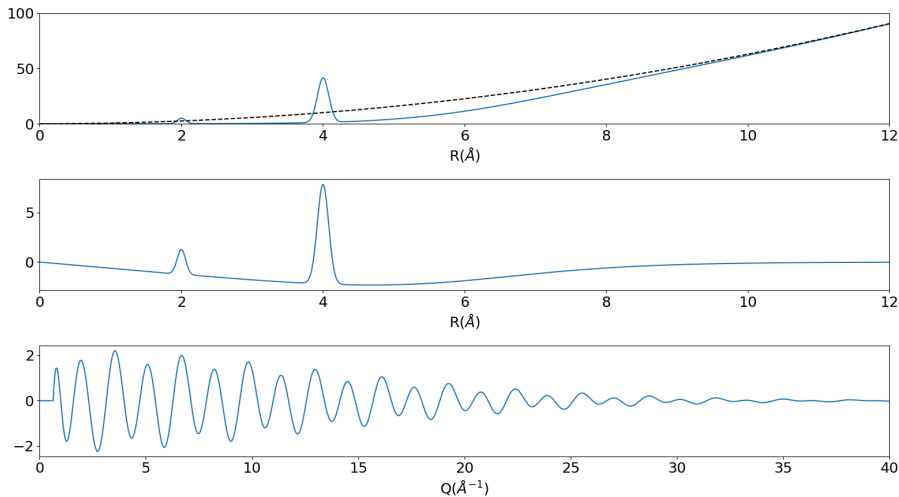
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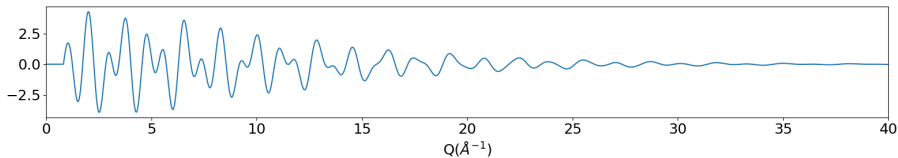
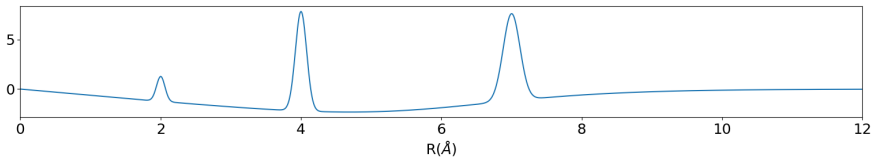
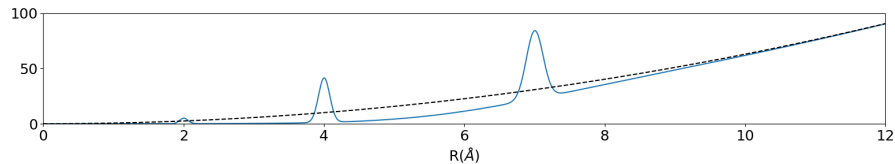
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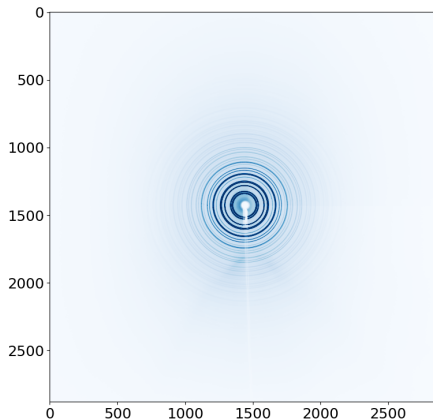
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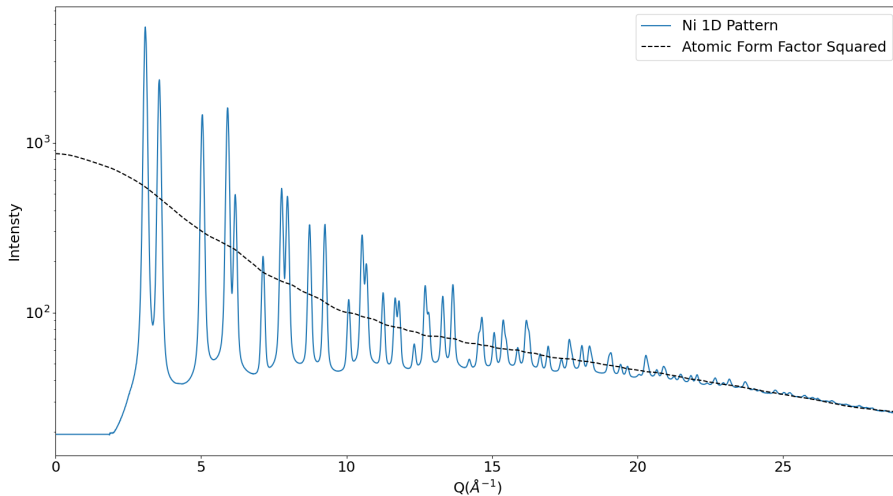
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Normalizing to Atomic Form Factor

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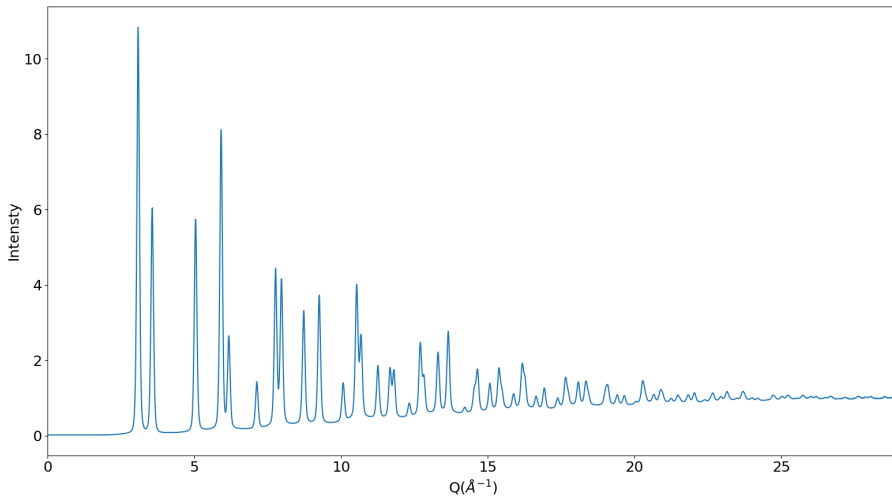
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$$S(Q) \rightarrow F(Q) = Q(S(Q) - 1)$$

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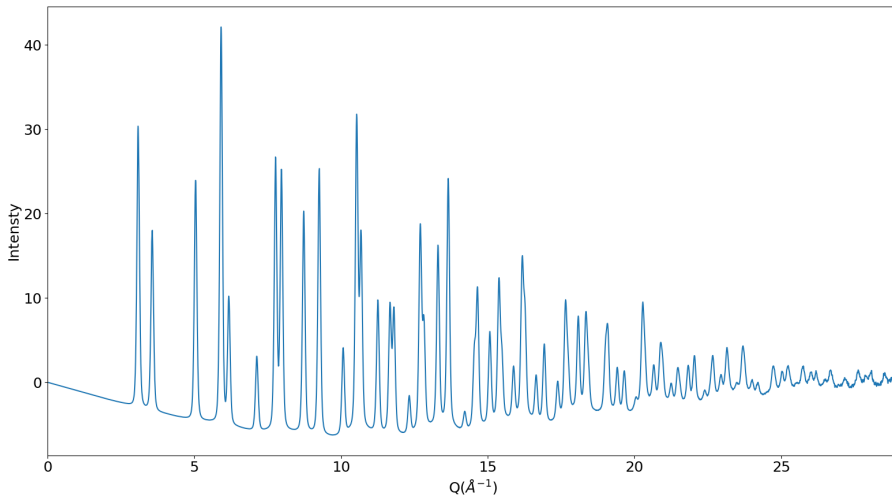
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$$F(Q) \rightarrow G(r) = \frac{2}{\pi} \int F(Q) \sin(Qr) dQ$$

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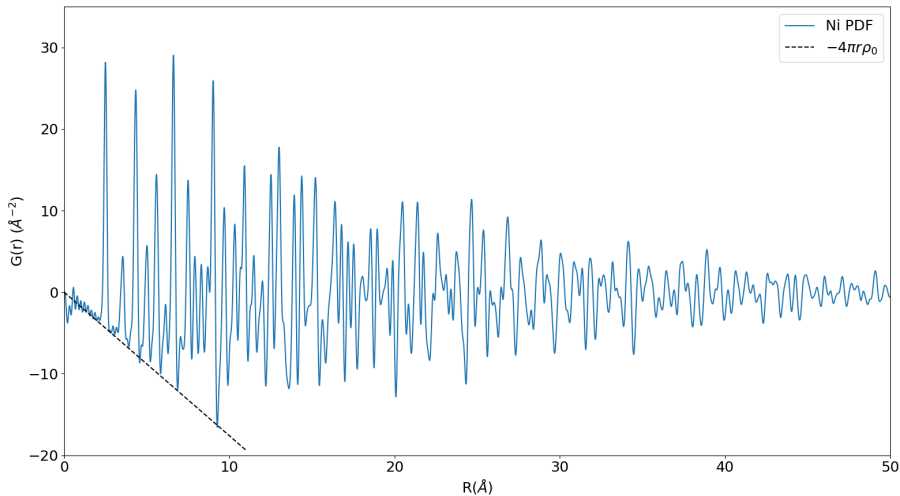
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$$G(r) \rightarrow R(r) = rG(r) + 4\pi\rho_0 r^2$$

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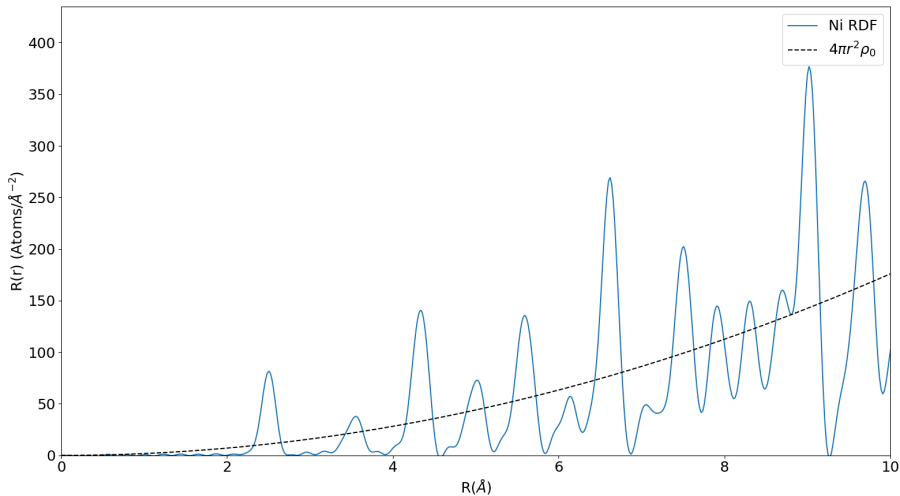
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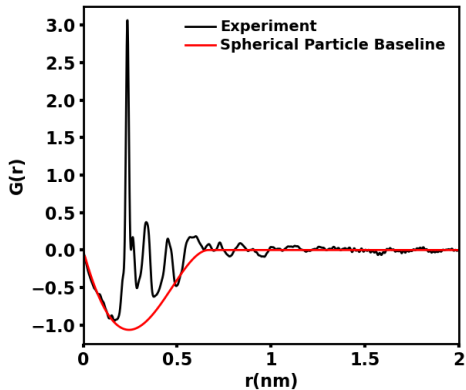
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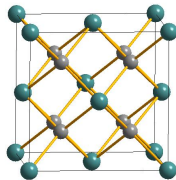
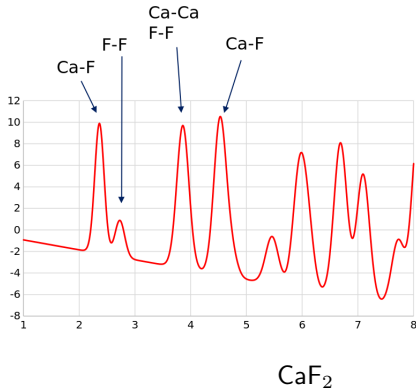
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Single Atom Catalysts

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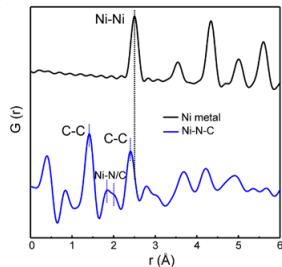
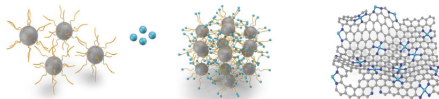
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Synthesizing single atoms catalysts has been developed using cross linked graphene quantum dots as the support. Absence of Ni-Ni bonds in PDF confirm Ni dispersed atomically and not aggregates.

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

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Q max vs resolution

Unwanted Photons

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



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The Q Problem

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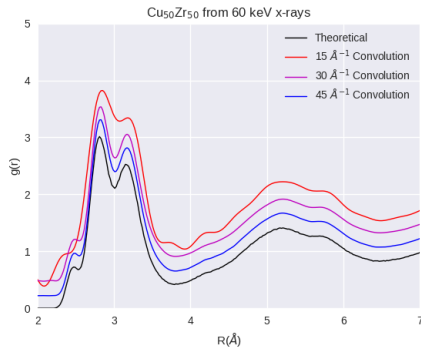
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Sample-Detector Distance

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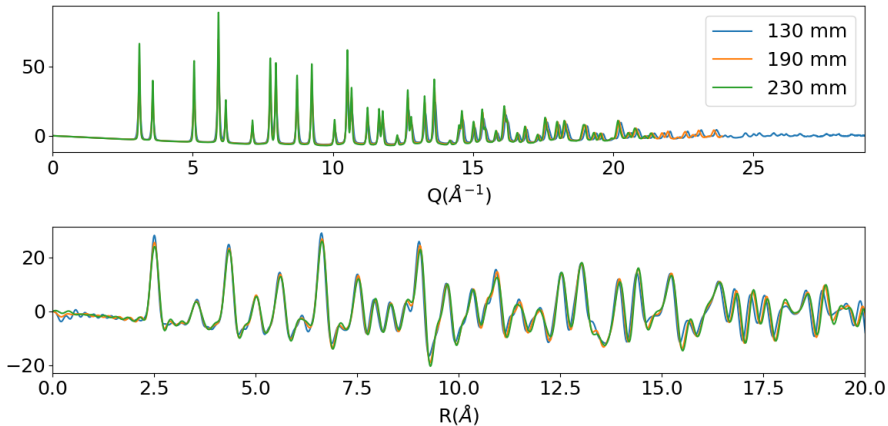
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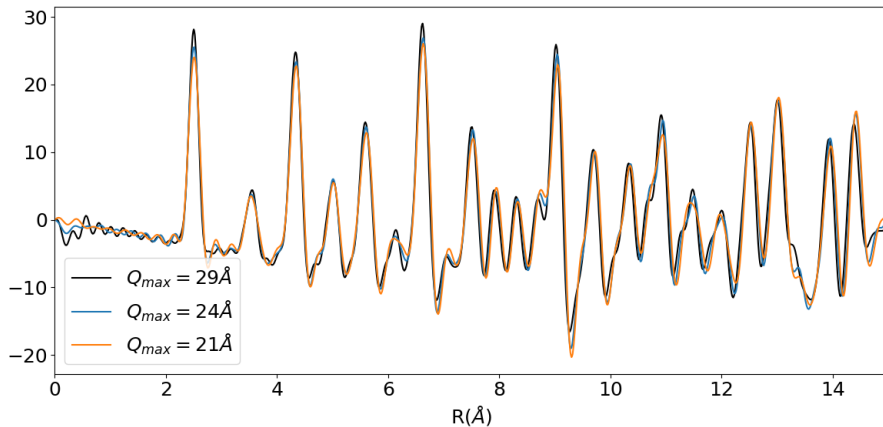
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Q Related to Angle and Energy

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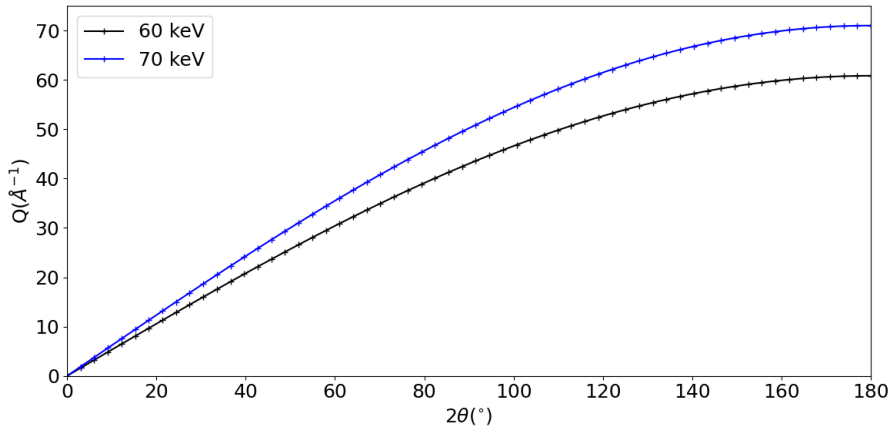
Unwanted Photons

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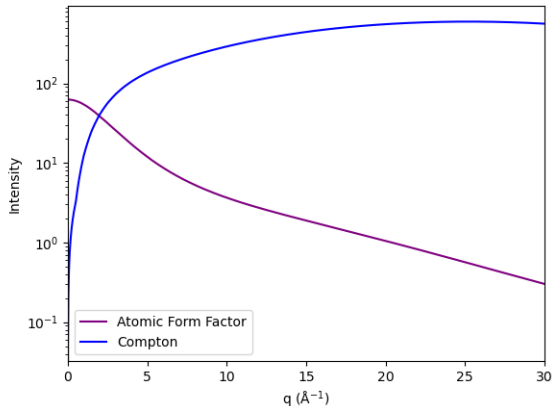
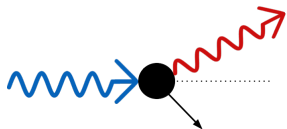
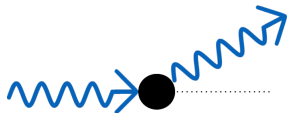
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Non-Sample Signal

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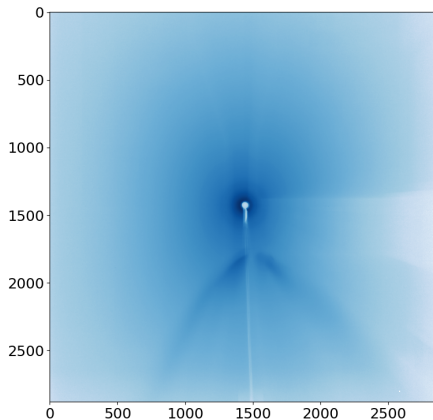
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- ▶ What are you hoping to resolve?
 - ▶ Short range structure
 - ▶ Medium range ordering
 - ▶ Comparative changes (*in situ/ in operando*)
 - ▶ Modeling
- ▶ Is there low Q or high Q signal?
- ▶ Be aware of the experimental parameters
 - ▶ Choice of 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)

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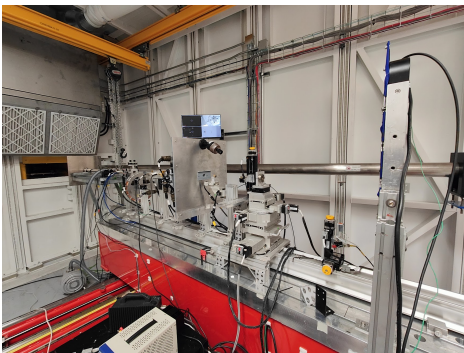
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Details

- ▶ 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 ($80 K \leq T \leq 500 K$)



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Improving PDF Collection

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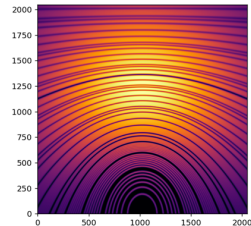
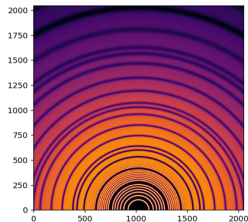
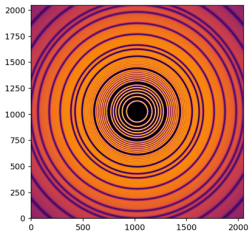
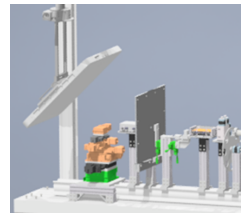
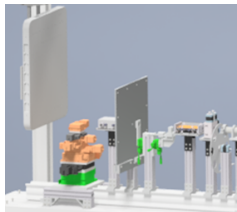
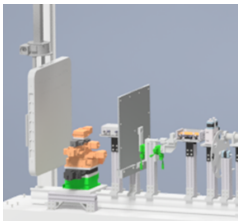
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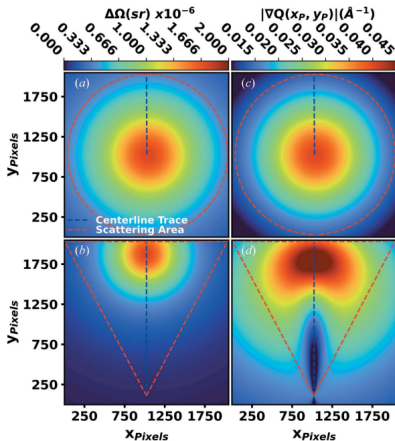
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Advantages

- 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



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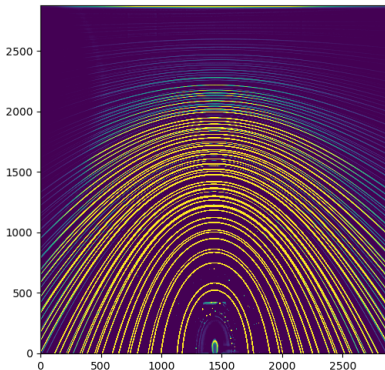
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Disadvantages

- ▶ 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

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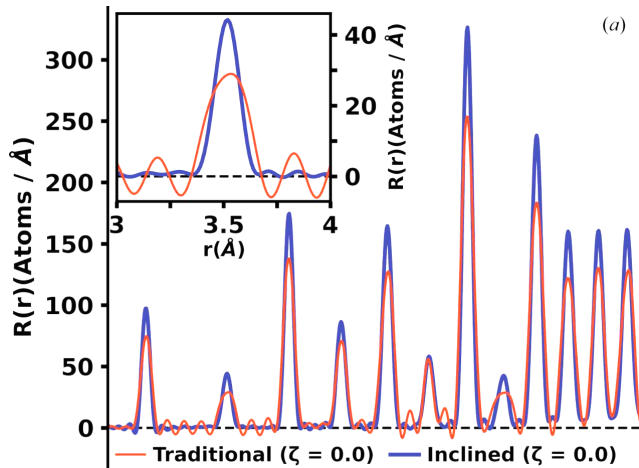
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N. Burns *et al.*, Journal of Applied Crystallography 2023, 56, 510.



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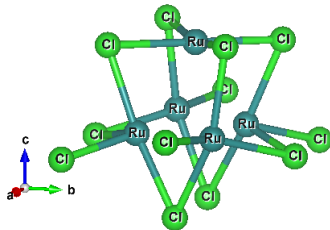
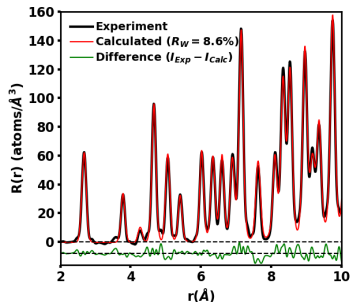
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Summary

- ▶ 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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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>