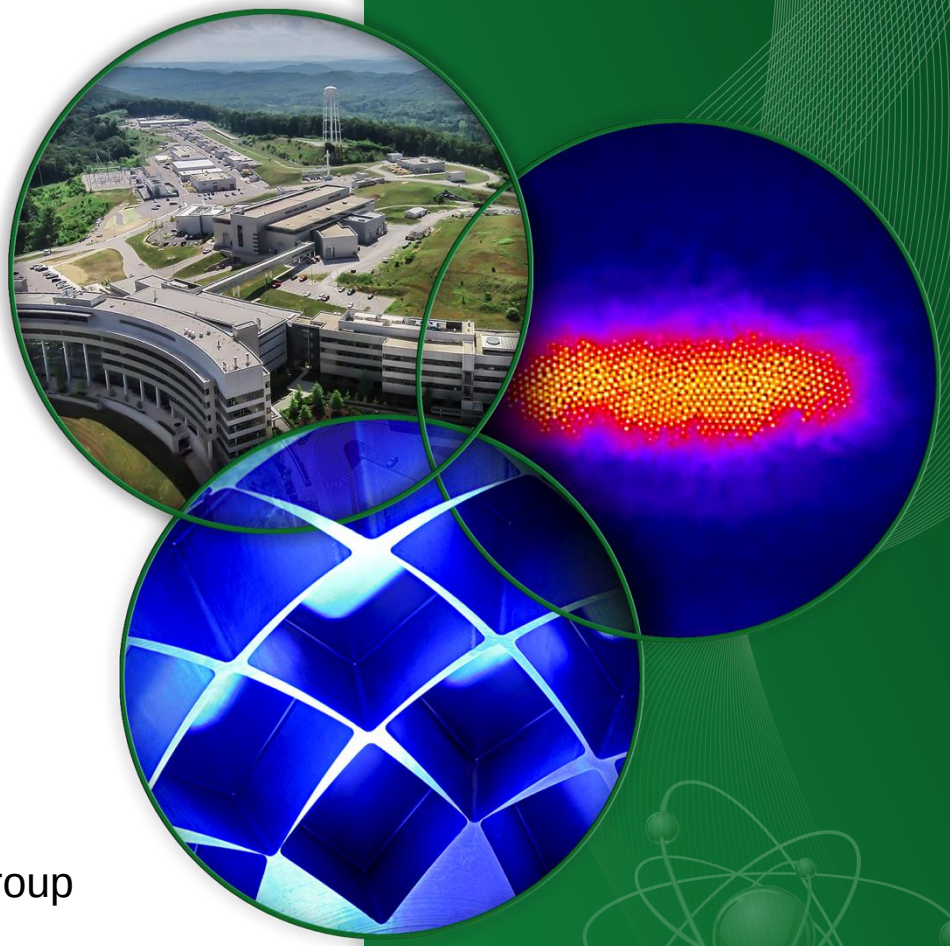
Neutron PDF for Local Structure Studies



Katharine Page
Instrument Scientist, Advanced Diffraction Group
Chemical and Engineering Materials Division
Oak Ridge National Laboratory
pagekl@ornl.gov

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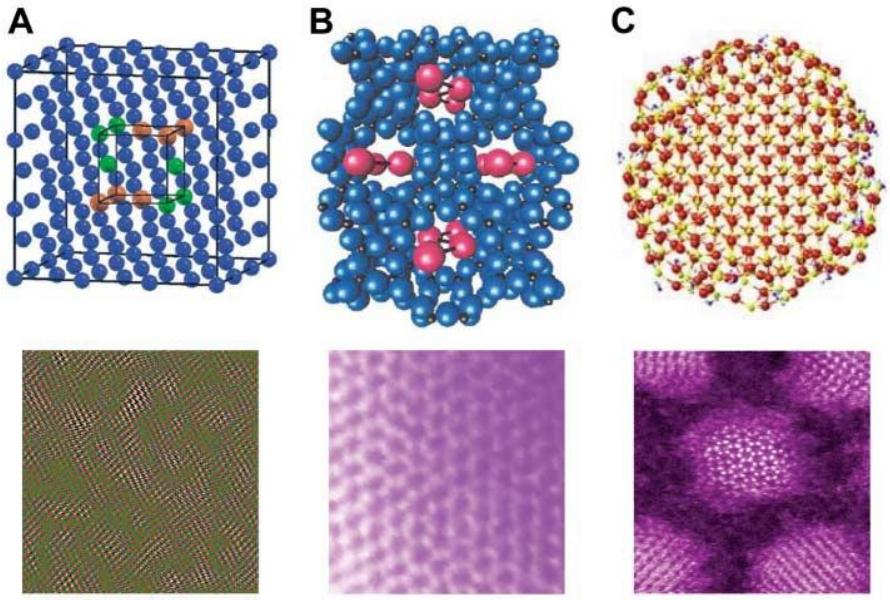
OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

What does one mean by *local structure*?

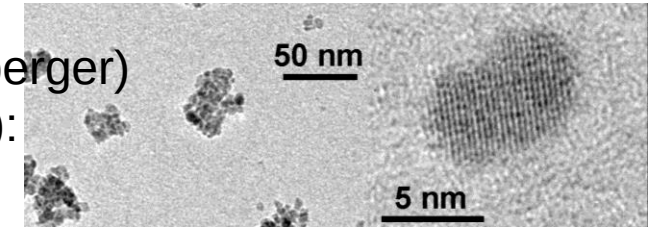
- **Non crystalline materials:** Amorphous solids and polymers
- **Disordered materials**: The interesting properties are often governed by the defects or local structure
- **Nanostructures**: Well defined local structure, but long-range order limited to few nanometers (poorly defined Bragg peaks)

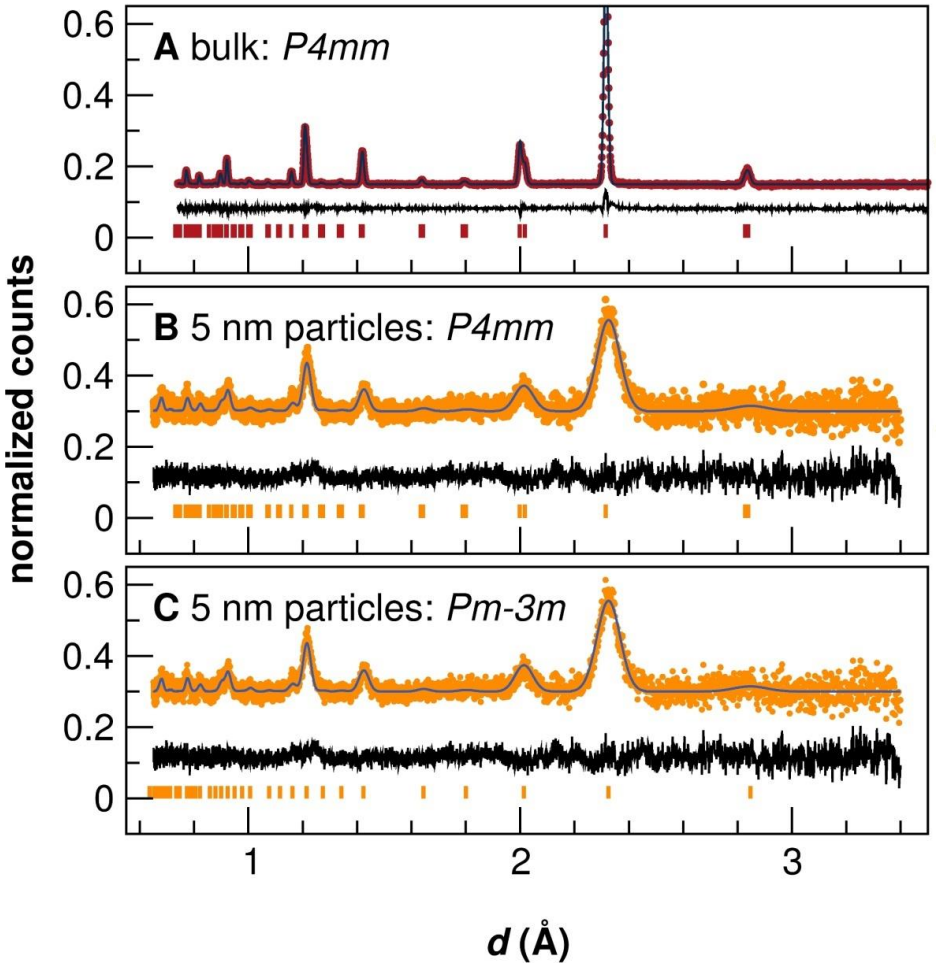


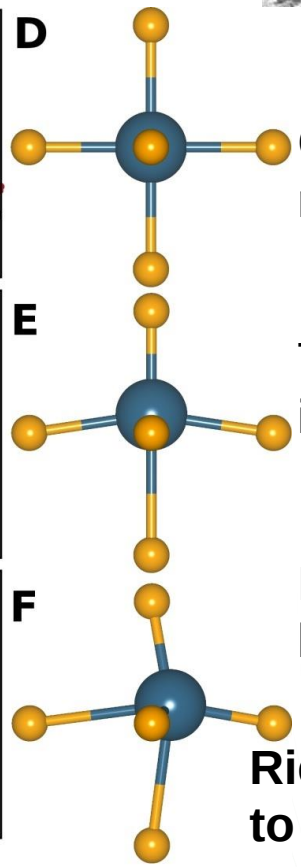
S.J.L. Billinge and I. Levin, **The Problem with Determining Atomic Structure at the Nanoscale**, *Science* **316**, 561 (2007).

Example: $BaTiO_3$ nanoparticle

Approx. 1 g samples of 5 nm $BaTiO_3$ (Markus Niederberger) studied by neutrons (NPDF, Los Alamos National Lab):







Cubic, high *T*, no dipole

Tetragonal, intermediate *T*, dipole

Rhombohedral, low *T*, dipole

Rietveld (*Q*-space) is unable to distinguish cubic from tetragonal at these sizes.

Total Scattering Structure Function

Structure function, determined from the scattering intensity/differential cross section:

coherent scattering intensity (corrected)

scattering length (neutrons) or atomic form factor (x-rays)

$$S(Q) = \frac{I_{coh}(Q) - \sum c_i |b_i|^2}{\left|\sum c_i b_i\right|^2} + 1 \qquad Q = \frac{4\pi \sin\theta}{\lambda}$$

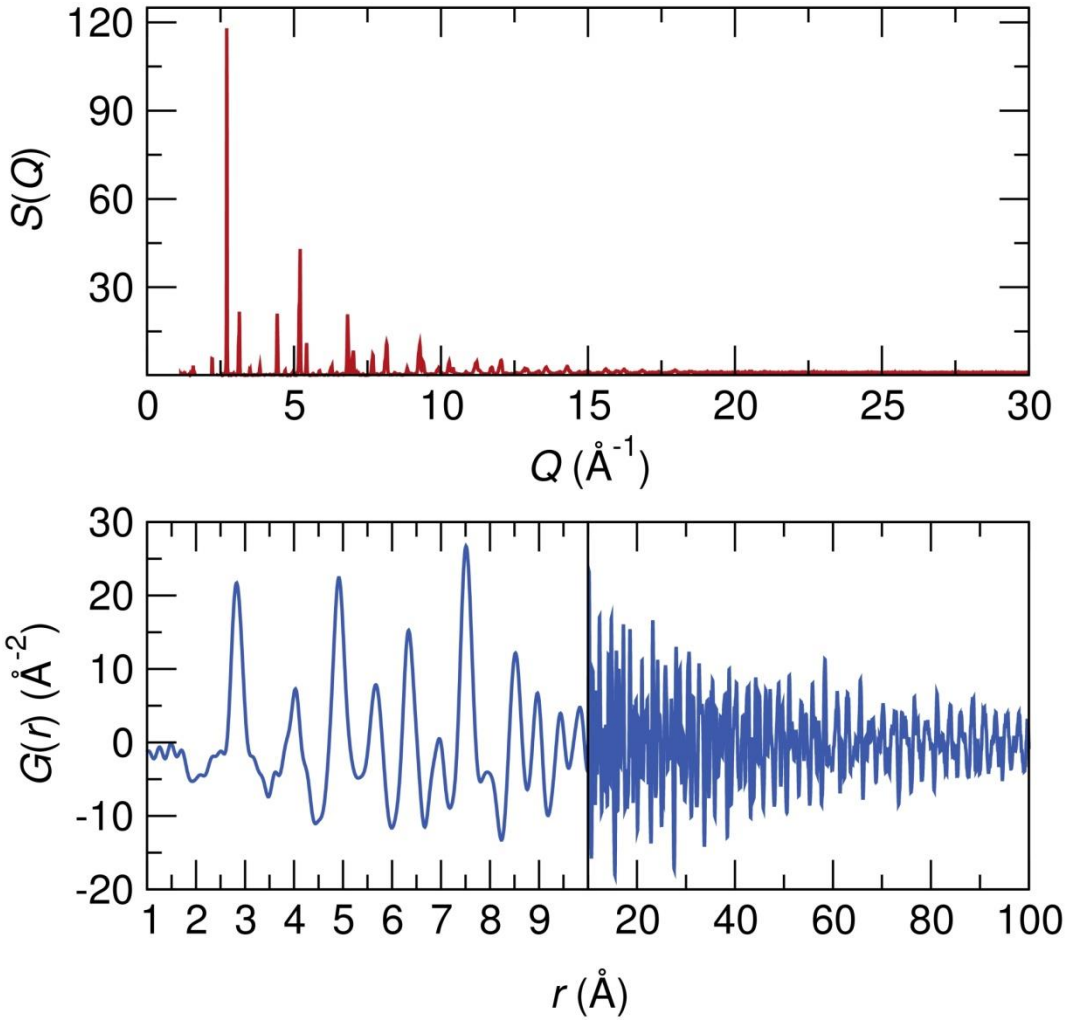
Corrected for: Container & background scattering, self-absorption, *etc.*
Normalized by: Incident flux, number of atoms, square of the scattering length/form factor

For unambiguous derivation of this derivation and relationship to other forms:

C. Farrow and S. J. L. Billinge, *Acta Cryst.* (2009) A65, 232–239.
D. A. Keen, *J. Appl. Cryst*. 34 (2001) 172-177.

The Experimental PDF

The Sine Fourier transform of the total (Bragg and diffuse) scattering



The total scattering structure factor: $S(Q)$

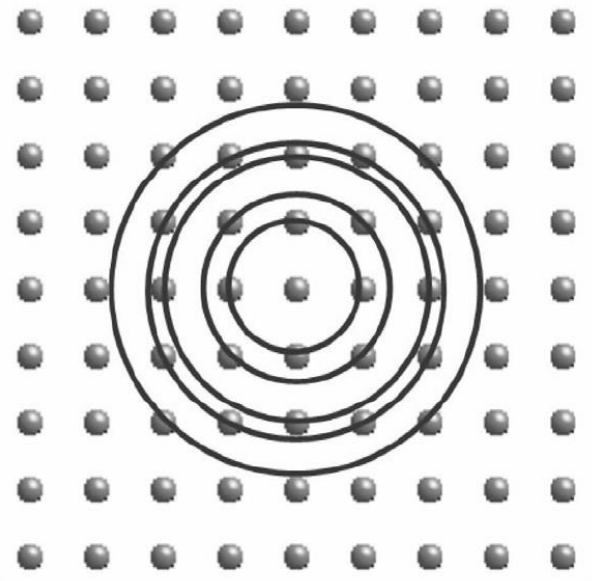
Sine Fourier transform

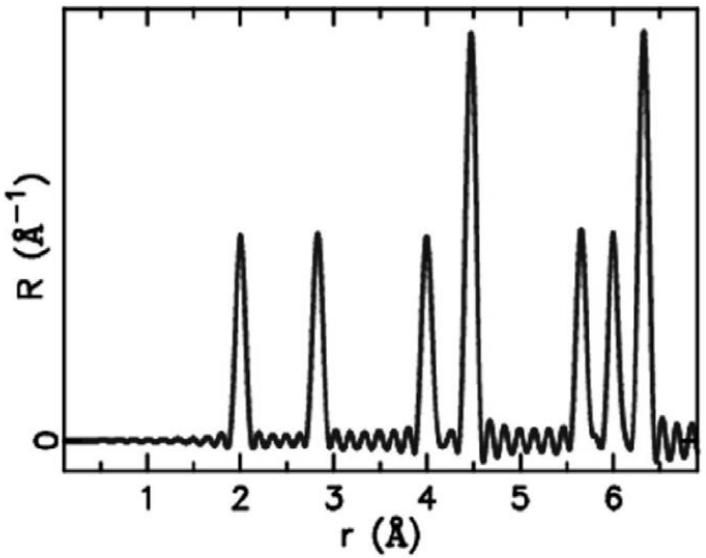
The Pair Distribution Function (PDF): $G(r)$

$$G(r) = \frac{2}{\pi}\int_{Q_{\min}}^{Q_{\max}} Q[S(Q)-1]\sin(Qr)dQ$$

Pair Distribution Function

Based on the *radial distribution function* (RDF):





Atomic PDF (PDFFIT notation):

S.J.L Billinge, *Z. Kristallogr. Suppl.*,26,17 (2007)

$$G(r) = 4\pi r\left[\rho(r) - \rho_0\right]$$

$$G(r) = \sum_{ij}\left[\frac{b_i b_j}{\langle b\rangle^2}\,\delta(r - r_{ij})\right] - 4\pi r\rho_0$$

atomic form factors (Z for x-rays, b for neutrons)

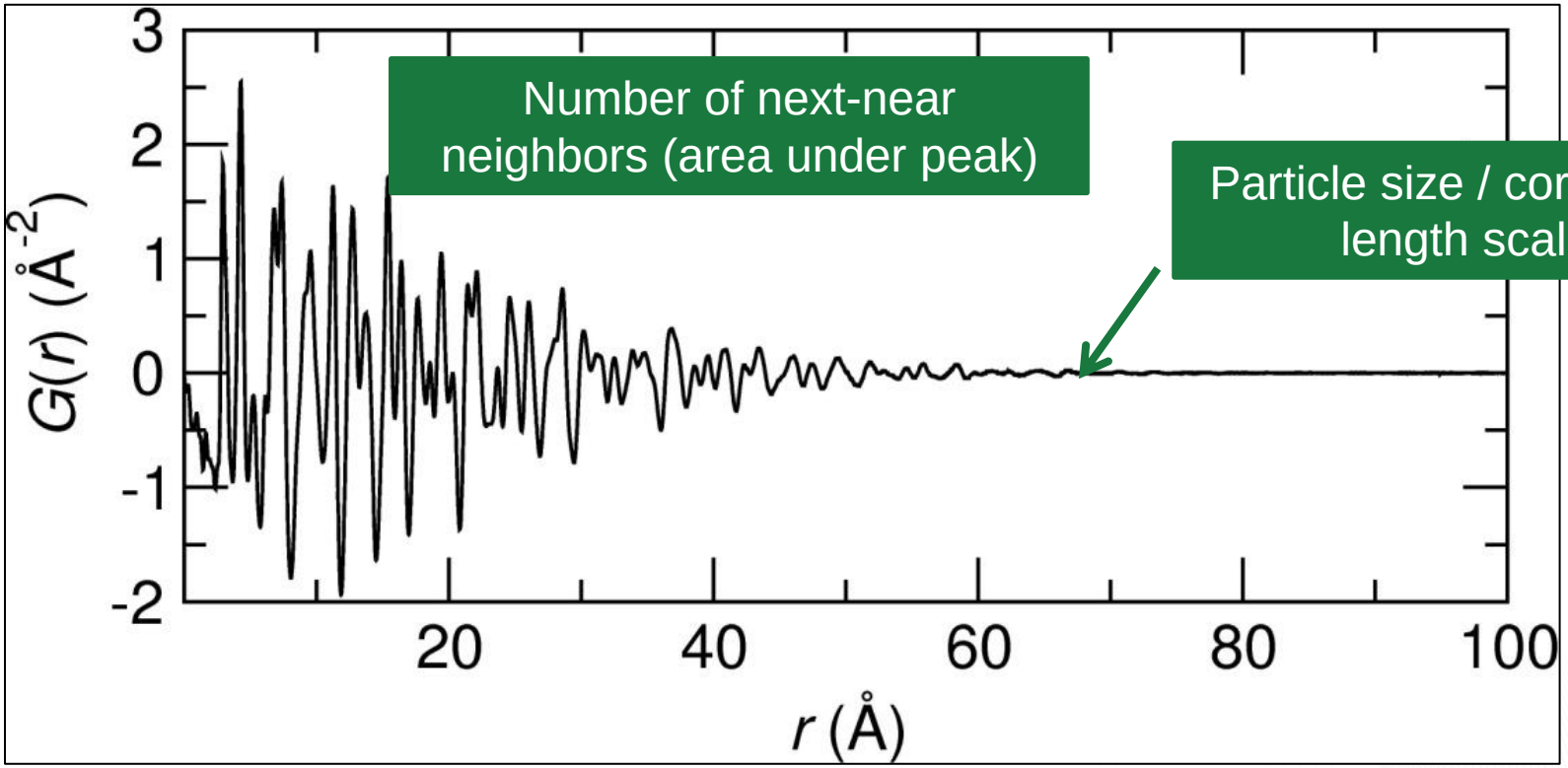
distance between i and j atoms

average density

sum over all atoms

Pair Distribution Function

Inter-atomic distances

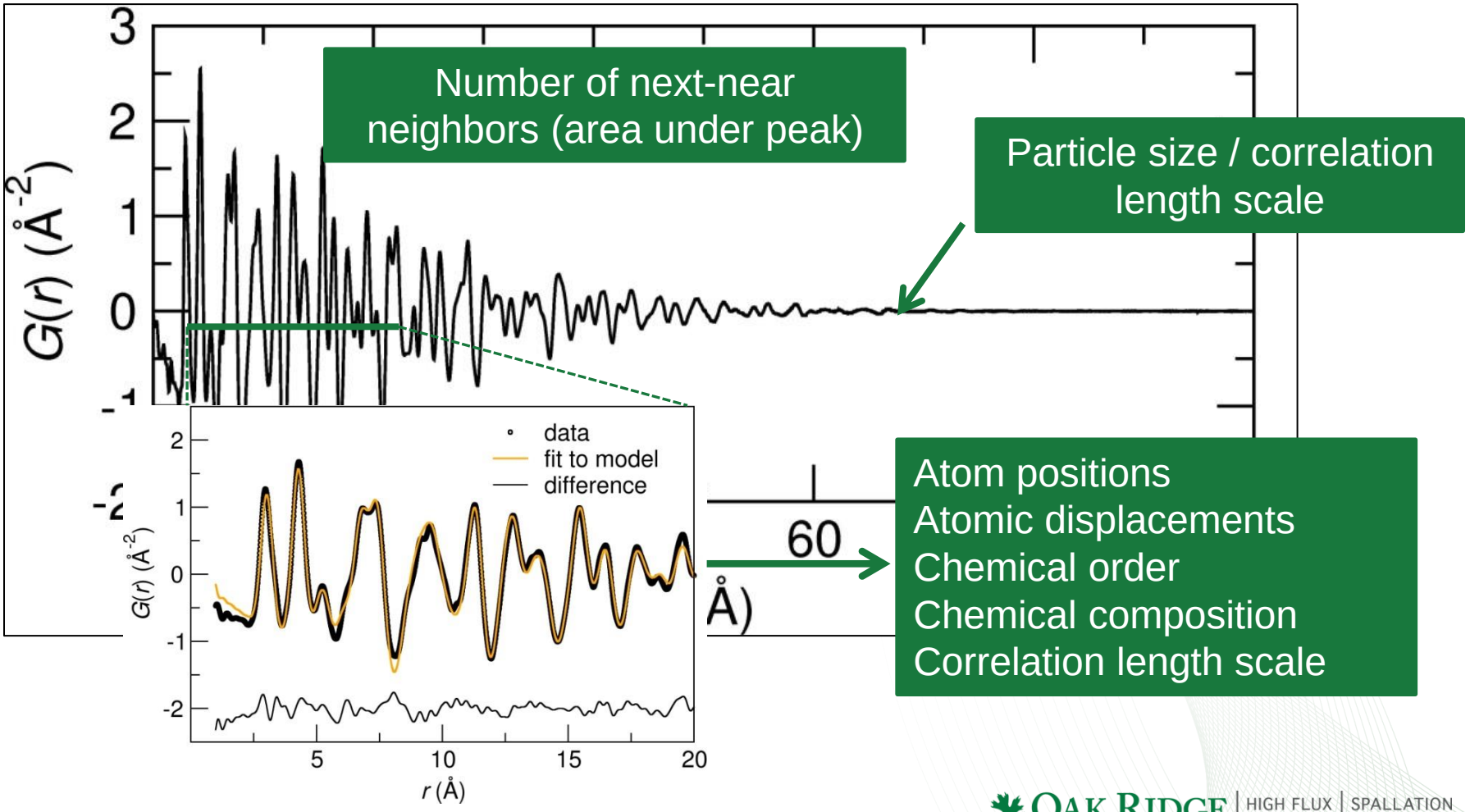


PDF analysis → Average and short-range structure for disordered crystalline materials, nanomaterials, and amorphous materials

Pair Distribution Function

Quantitative analysis: fitting a model to the data over specific ranges

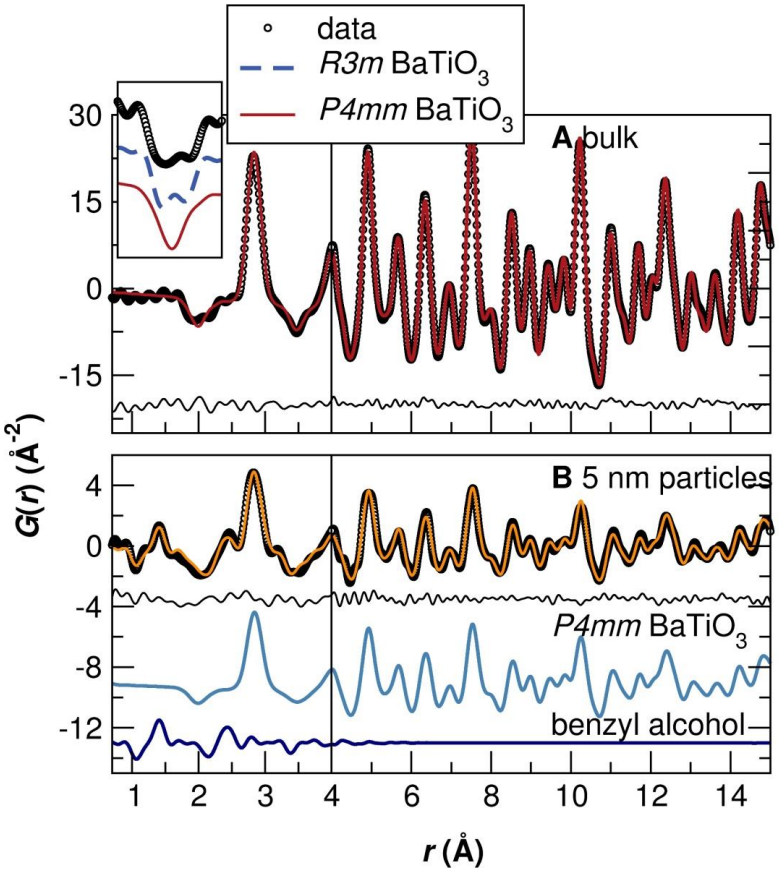
Inter-atomic distances

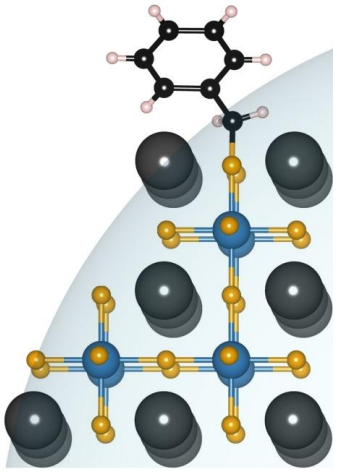


Atom positions
Atomic displacements
Chemical order
Chemical composition
Correlation length scale

Example: $BaTiO_3$ nanoparticle

The PDF: Bulk $BaTiO_3$ is tetragonal with a split (*R3m*) first Ti-O peak.
The 5 nm particles appear cubic but are *strongly* distorted.





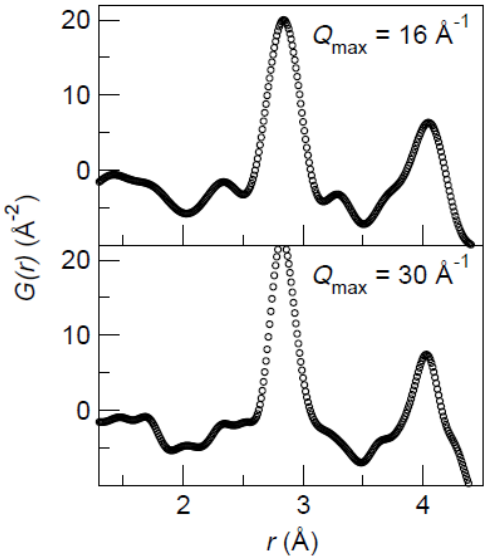
Capping groups observed by scattering for the first time (for any polydisperse nanoparticle system).

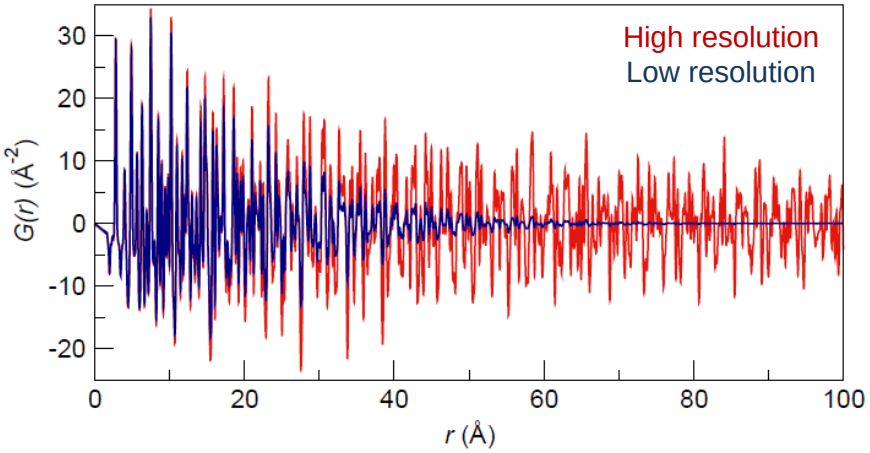
Phase ratios consistent with size, TGA *etc.*

K. Page, Th. Proffen, M. Niederberger, and R. Seshadri, Probing local dipoles and ligand structure in BaTiO3 nanoparticles, *Chem. Mater*. 22 (2010), 43864391.

Experiment considerations

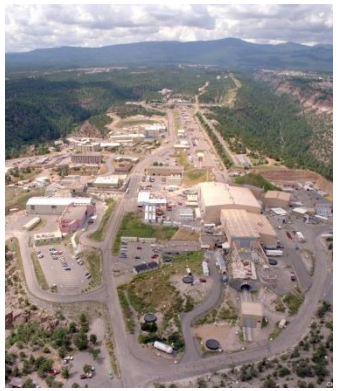
- High maximum momentum transfer (Q_{max}): convolution of G(r) with $sin(Q_{max}\ r)/r$
- Good Q-resolution: (PDF dampened by $exp\ -(r\Delta Q)^2/2$)
- Good counting statistics
- Low (and stable) instrument background





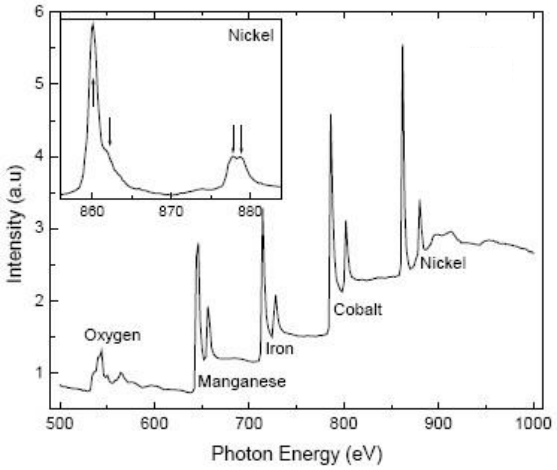
PDFgetN: http://pdfgetn.sourceforge.net
PDFgetX2: http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/

synchrotron and spallation neutron sources



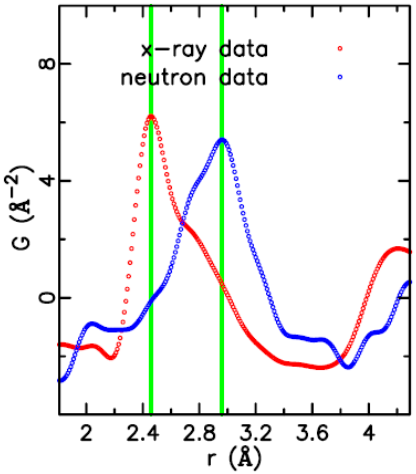
X-ray or Neutron?

X-ray Synchrotron
- Tunability of wavelengths (element specific information)
- Extreme high intensity (weak phenomena, tiny samples)
- Pulse structure (time-resolved studies)
- High energy (low absorption and extinction effects)



Neutrons
- Accurate location of light elements (most importantly H)
- Distinction of neighbored elements (3d transition metals, etc.)
- Distinction of different isotopes of one element
- Weak interaction with sample (highly penetrating, nondestructiv

Make intelligent use of neutrons and x-rays according to their unique properties and your scientific problems!



PDF of MgCo alloy showing Co and Mg nearest neighbor environment
(H.-J. Kim, Th. Proffen)

Calculating a PDF

Calculating a PDF from an atomistic model:

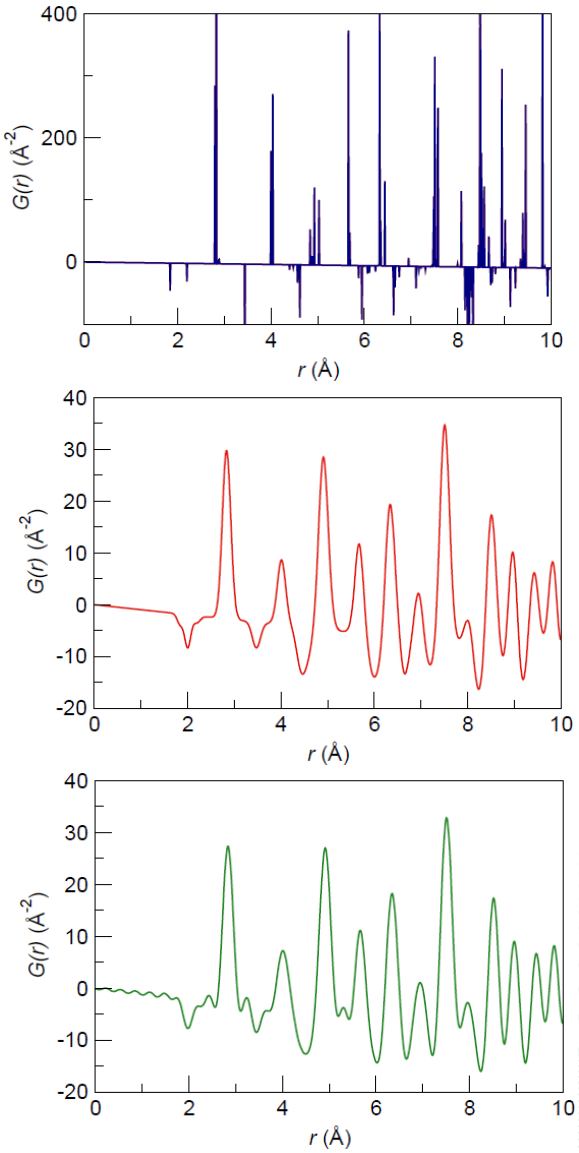
$$G(r) = \sum_{ij}\left[\frac{b_i b_j}{\langle b\rangle^2}\delta(r - r_{ij})\right] - 4\pi r\rho_0$$

Thermal motion

- Small model: convolution of $\delta(r-r_{ij})$ with distribution function (*PDFgui*)
- Large model: actual displacements and ensemble average (*RMCprofile*)

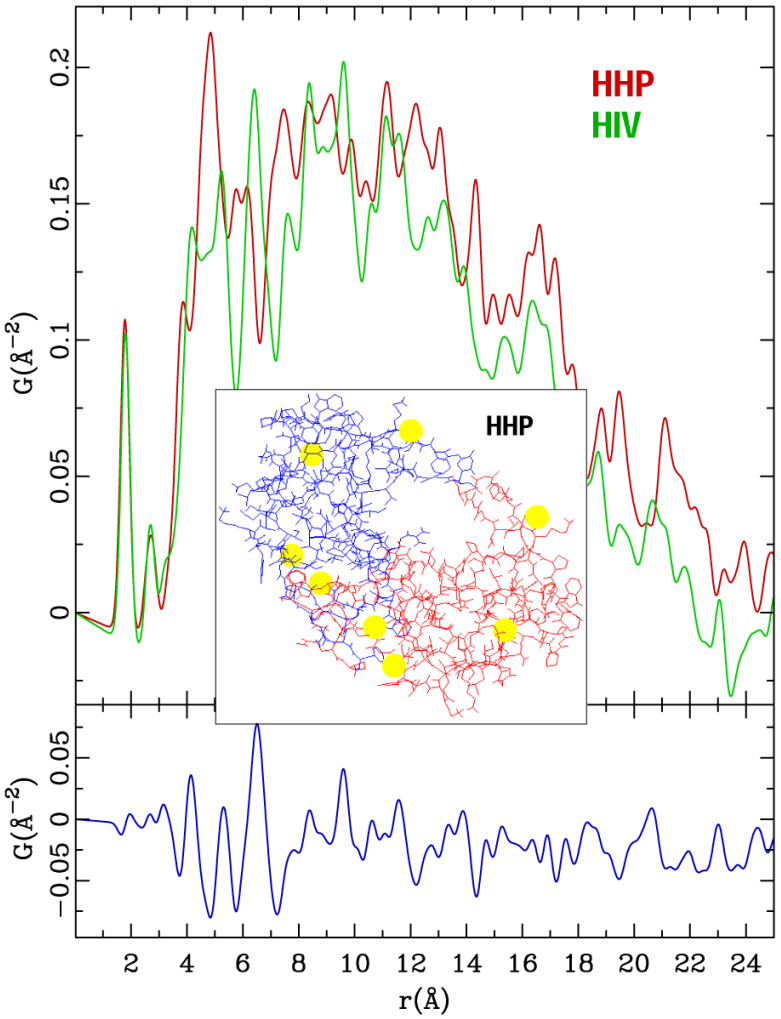
Termination ripples

- Multiplication with step function in reciprocal space gives convolution with $\sin(Q_{max}r)/r$ in real space



Calculating a PDF

Calculation of PDFs of any kind of structure.



T. Proffen, unpublished.

- Simple comparison with average structure.
- Local structure signature, e.g. to distinguish open and closed form of HIV protease.
- Differential PDFs allow one to be chemically sensitive (isotope substitution, anomalous scattering, ..)

Differential PDF of HIV protease with flaps closed and open !

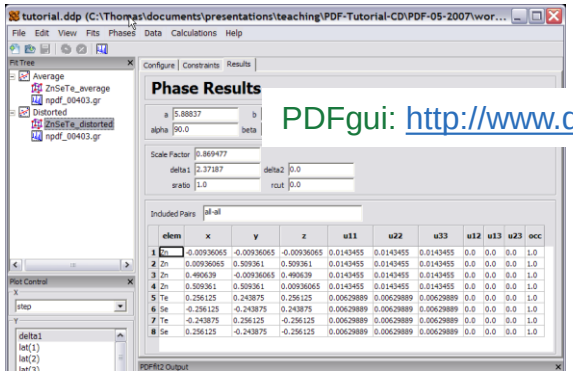
Atomic PDF Modeling

Small Models: Least Squares Refinement
Up to several hundred atoms
'Rietveld'-type parameters: *lattice parameters, atomic positions, displacement parameters, etc.*
Refinements as function of *r*-range

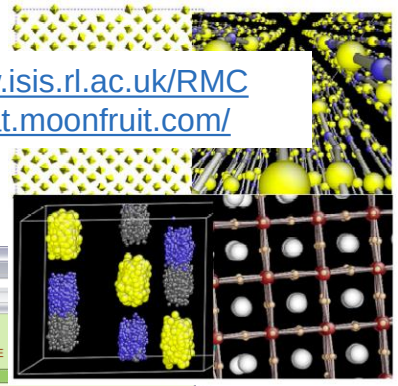
Large Model: Reverse Monte Carlo
20000 + atoms
Fit X-ray and neutron *F(Q), G(r)* , Bragg profile
Constraints utilized
Static 3-D model of the structure (a snap-shot)

Multi-level /Complex Modeling
Refine higher level parameters (not each atom)
Example nanoparticle: *diameter, atom spacing, stacking fault probability*
Choose minimization scheme

Emerging: *ab initio* and force-field based approaches
Density Functional Theory
Molecular Dynamics

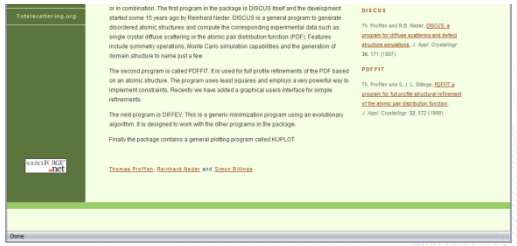


PDFgui: http://www.diffpy.org/



RMCprofile: http://www.isis.rl.ac.uk/RMC
EPSR: http://disordmat.moonfruit.com/

DIFFEV and DISCUS: http://discus.sourceforge.net



Neutron PDF Instruments

Instrument	Gem	HIPD	Nimrod	NOMAD	NOVA	NPDF
Country	UK	USA	UK	USA	Japan	USA
Moderator Type		Chilled Water at 283 K	Coupled cold hydrogen and water	Decoupled Hydrogen	Decoupled-poisoned H2	Chilled Water at 283 K
Moderator to Sample Distance (m)	17	9	20	19.5		32
Sample to detector distance (m)	1-2.9		1-7	0.5-3		1.5
Incident Wavelength Range (Å)		0.2 to 10	0.05 to 10	0.1-3	0.12 to 8.3	
Scattering Angle Coverage (°)	1.1 to 169.3	14, 40, 90, 153		3 to 175		45,90,119, 148
Flux on sample (neutrons cm^{-2} sec^{-1})				$1x10^{8}$		$8x10^{5}$
Highest Resolution (dQ/Q) %		0.3	0.5		0.35	0.15
Q- range ($Å^{-1}$)		0.2 to 40	0.02 to 100	0.04 to 100	0.01 to 100	0.8 to 50

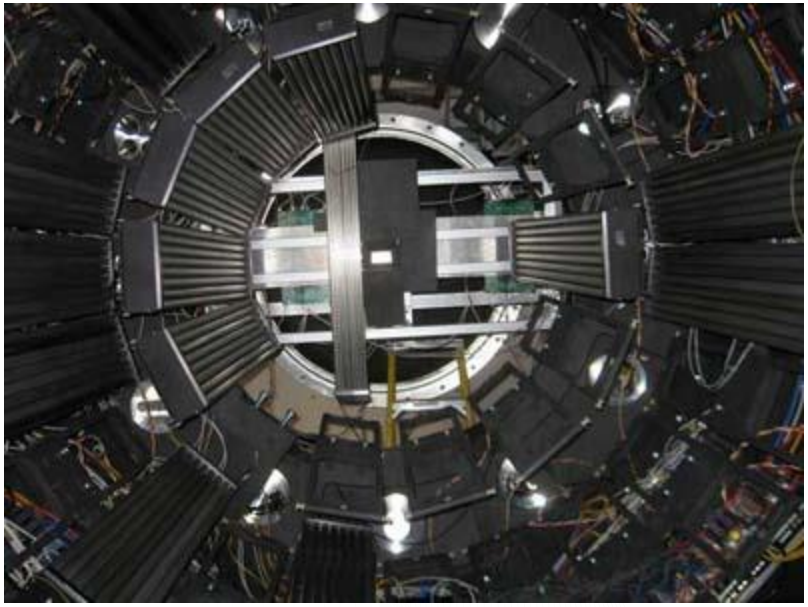
Spallation Neutron Source (SNS) at Oak Ridge National Laboratory
http://neutrons.ornl.gov/facilities/SNS/

Lujan Neutron Scattering Center at Los Alamos National Laboratory
http://lansce.lanl.gov/lujan

The Nanoscale-Ordered Materials Diffractometer

- Liquids
- Solutions
- Glasses
- Polymers
- Nanocrystalline materials
- Long-range-ordered crystals

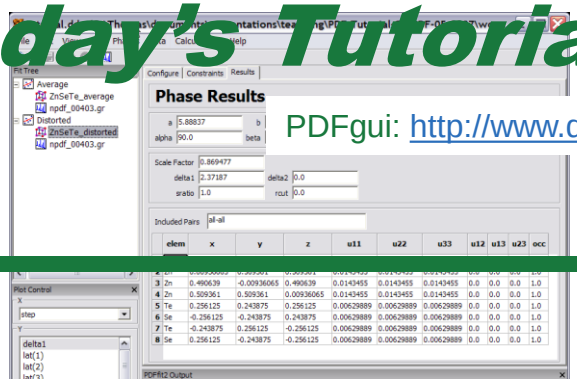
The enhanced neutron flux at SNS, coupled with the advanced neutron optics and detector features of NOMAD, allows for unprecedented access to high-resolution pair distribution functions, small-contrast isotope substitution experiments, small sample sizes, and parametric studies.



Atomic PDF Modeling

Small Models: Least Squares Refinement
Up to several hundred atoms
'Rietveld'-type parameters: *lattice parameters, atomic positions, displacement parameters, etc.*
Refinements as function of *r*-range

Today's Tutorial



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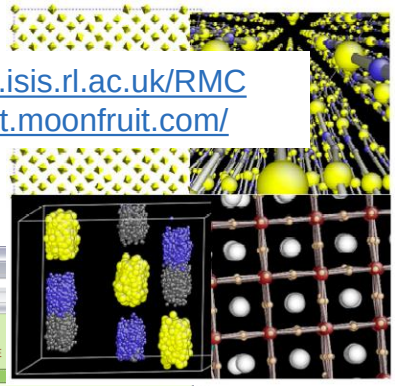

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Multi-level /Complex Modeling
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DIFFEV and DISCUS: http://discus.sourceforge.net

Emerging: *ab initio* and force-field based approaches
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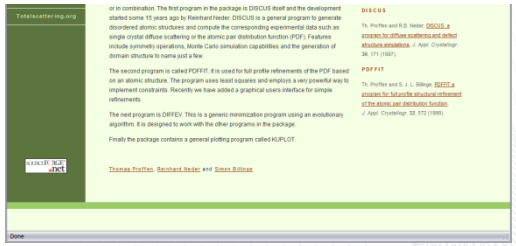
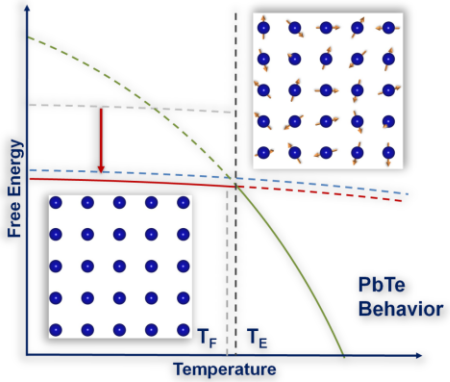
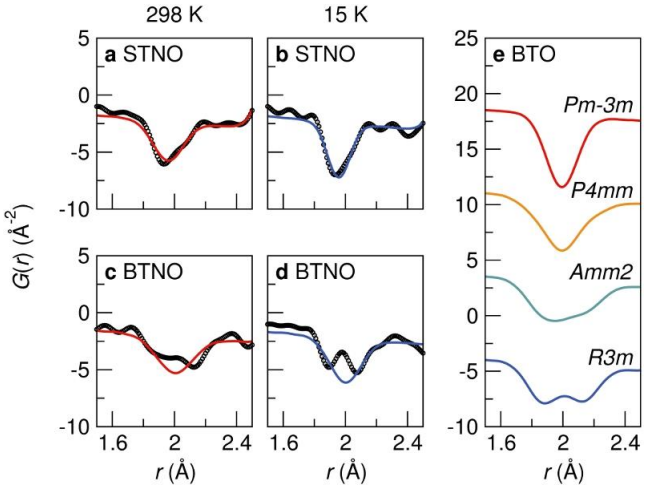


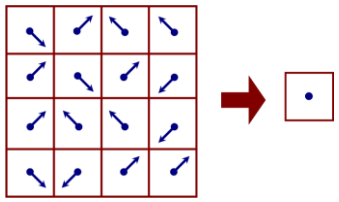
Examples: local distortions

Local Dipoles
Local Jahn-Teller Distortions
Frustrated Lattices
etc.

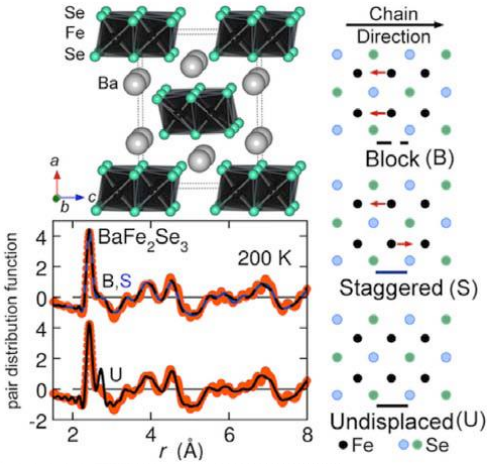


E. Bozin, *et al*., Entropically Stabilized Local Dipole Formation in Lead Chalcogenides, *Science* **330**, 1660 (2010).



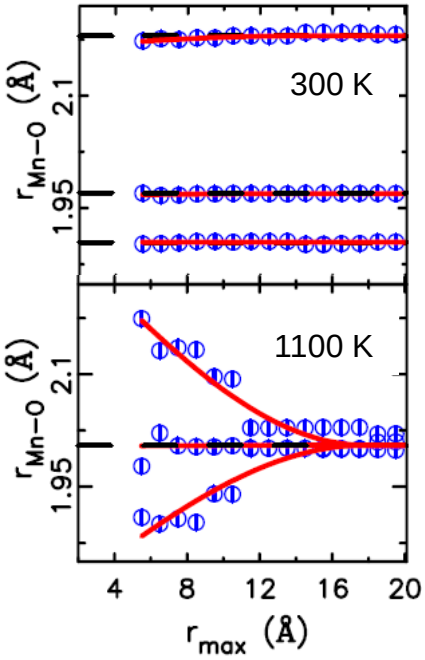


K. Page, *et al*., Distinct local structure of Nb-substituted SrTiO3 and BaTiO3 from total neutron scattering: implications for electronic properties, *Phys. Rev. Lett.* **101**, 205502 (2008).

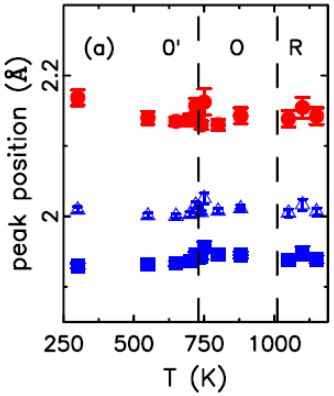


D. Louca, *et al.*, Suppression of superconductivity in Fe pnictides by annealing; a reverse effect to pressure, *Phys. Rev. B* **84**, 054522 (2011).

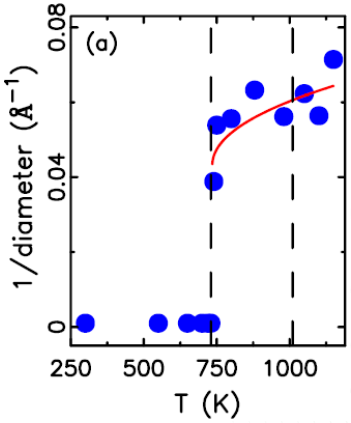
Examples: orbital ordering in $LaMnO_3$

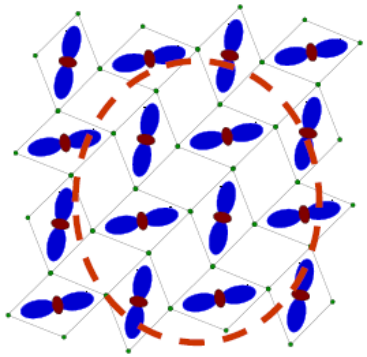


Nearest neighbor behavior shows locally atomic arrangements change little with temperature



Higher *r*-range gives information about the correlation of the JT distortions.





Nature and length scale of Jahn-Teller interactions in $LaMnO_3$

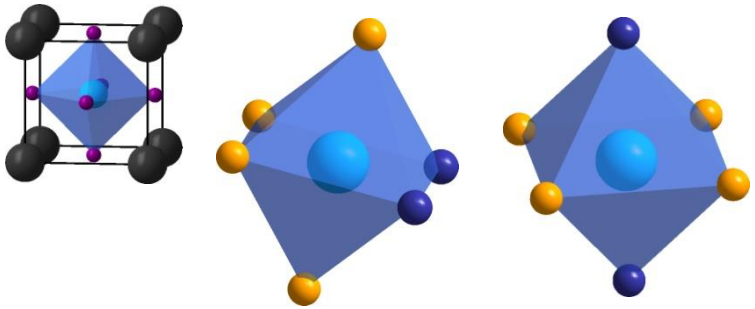
X. Qiu, Th. Proffen, J.F. Mitchell and S.J.L. Billinge, **Orbital correlations in the pseudo-cubic O and rhombohedral R phases of LaMnO3**, *Phys. Rev. Lett.* **94**, 177203 (2005).

***r*-range refinement**

Examples: chemical short-range order

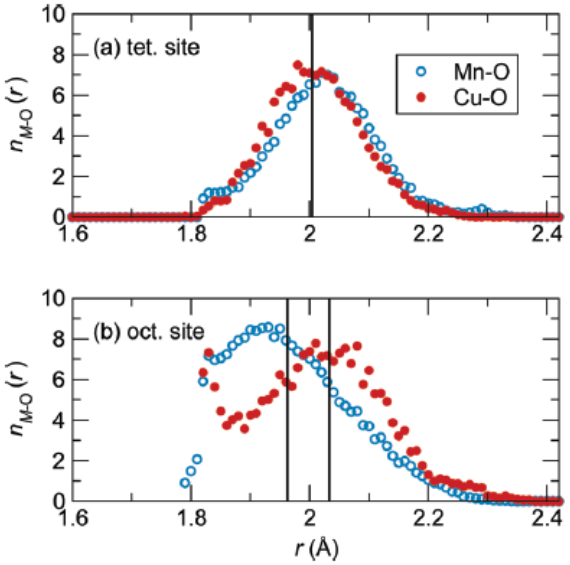
Substitution effects
Chemical clustering
Ion-specific local environments

K. Page, *et al*., Local atomic ordering in BaTaO2N studied by neutron pair distribution function analysis and density functional theory, *Chem. Mater.* **19** (2007) 4037-4042.



cis *trans*

D. P. Shoemaker, J. Li, and R. Seshadri, Unraveling Atomic Positions in an Oxide Spinel with Two Jahn-Teller Ions: Local Structure Investigation of CuMn2O4, *J. Am. Chem. Soc.* **131,** 11450 (2009).

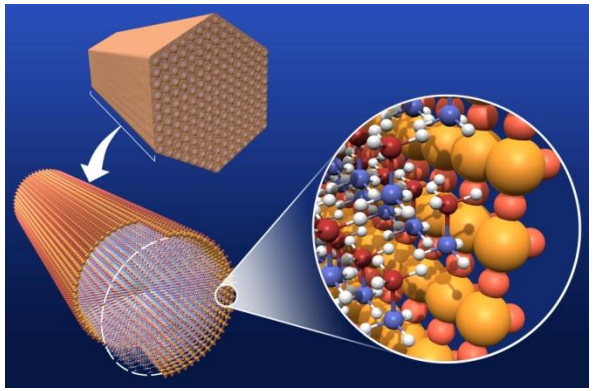


Examples: amorphous and nanoscale structure

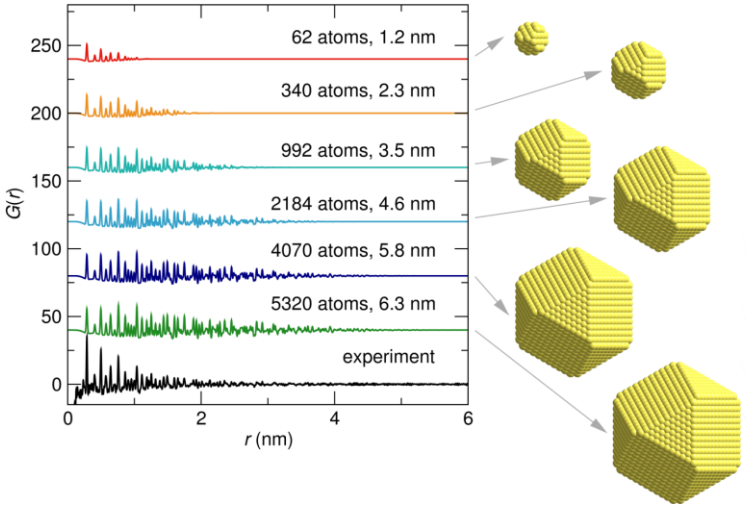
The PDF can be used to follow local atomic bonding configurations, intermediate structure, and correlation length scale- regardless of a material's long range structure

Surfaces and interfaces
Finite size effects

Glasses
Liquids
Concretes
etc.



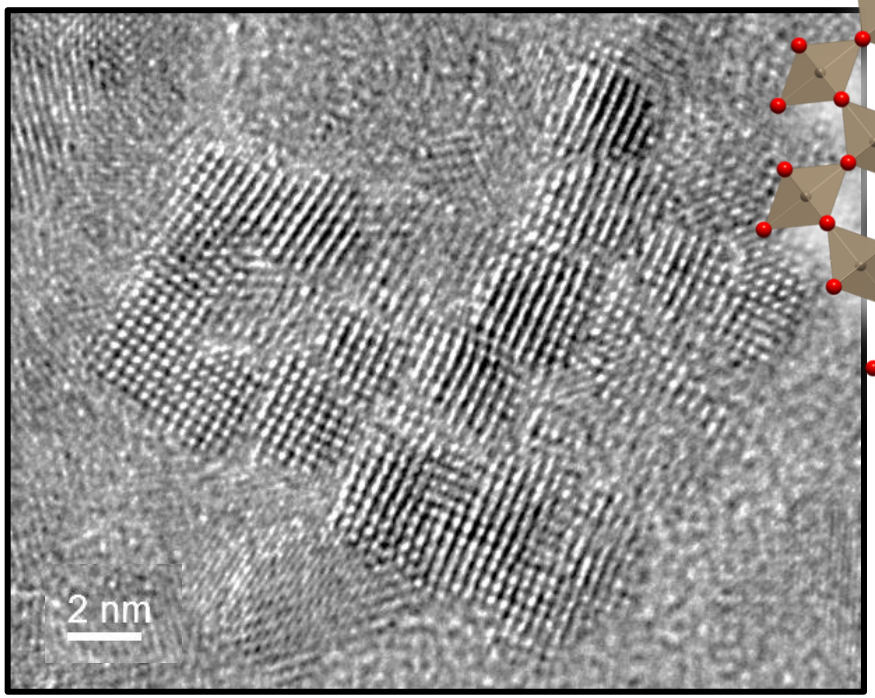
H. Kim *et al*., Determination of structure and phase transition of light element nanocomposites in mesoporous silica: case study of NH3BH3 in MCM-41, *J. Am. Chem. Soc.* 131, 13749-13755 (2009).

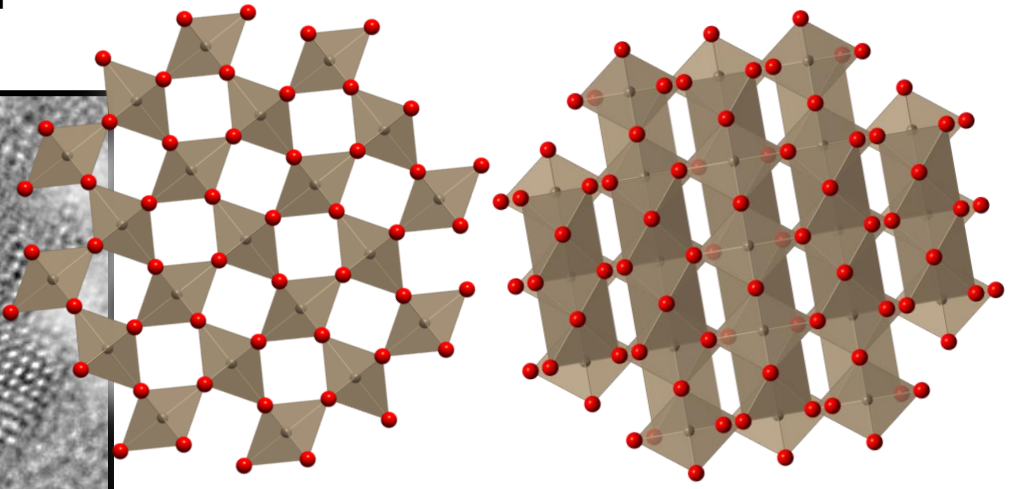


K. Page, Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri and A.K. Cheetham, Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction, *Chem. Phys. Lett.* **393**, 385-388 (2004).

Example: SnO_2 Nanocrystals

SnO_2 (cassiterite) nanocrystals capped with H_2O/OH or D_2O/OD groups





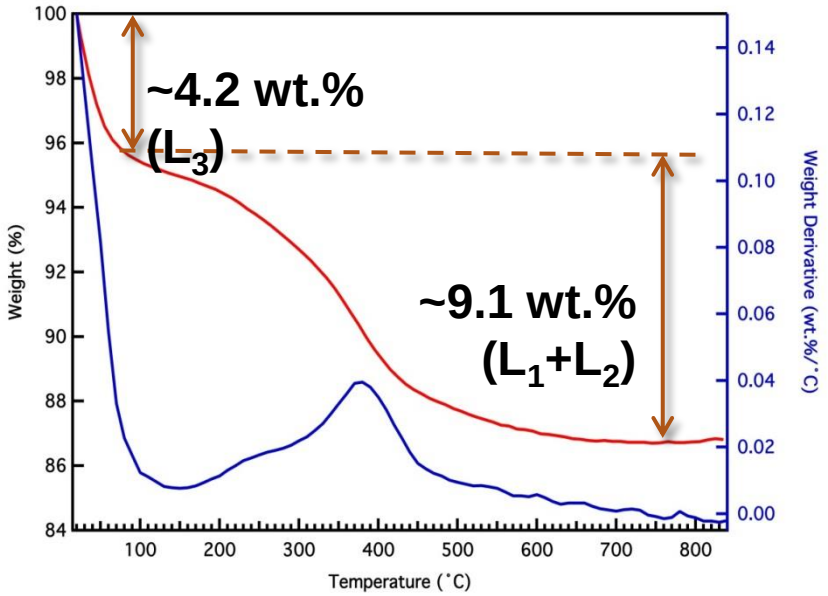
How many layers of water are actually formed?

What are the dynamics of dehydration?

How is water bonded to surfaces?

H.W. Wang, et al, *J. Am. Chem. Soc*., 2013, 135 , 6885–6895.

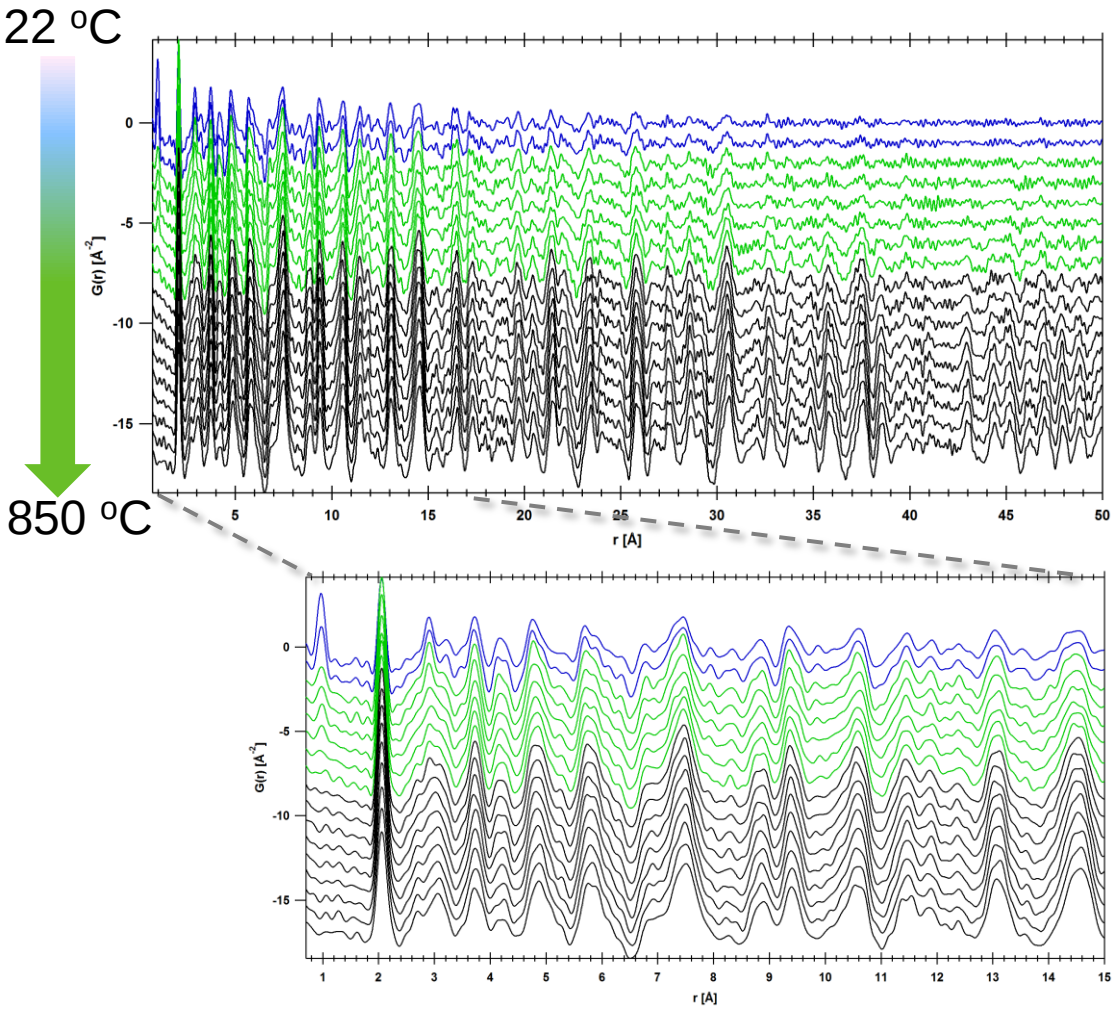
TGA suggests 2 steps dehydration



Example: SnO_2 Nanocrystals

In situ Dehydration, NOMAD, SNS

- Starting with full coverage ($L_1 + L_2 + L_3$)
- Blue lines: 22 and 50 ºC - $L_1 + L_2 + L_3$
- Green lines: 50 to 350 ºC (with 50 ºC increments) - $L_1 + L_2$
- Black lines: 400 to 850 ºC (with 50 ºC increments) – SnO_2 grain growth



H.W. Wang, et al, *J. Am. Chem. Soc.*, 2013, 135 , 6885–6895.

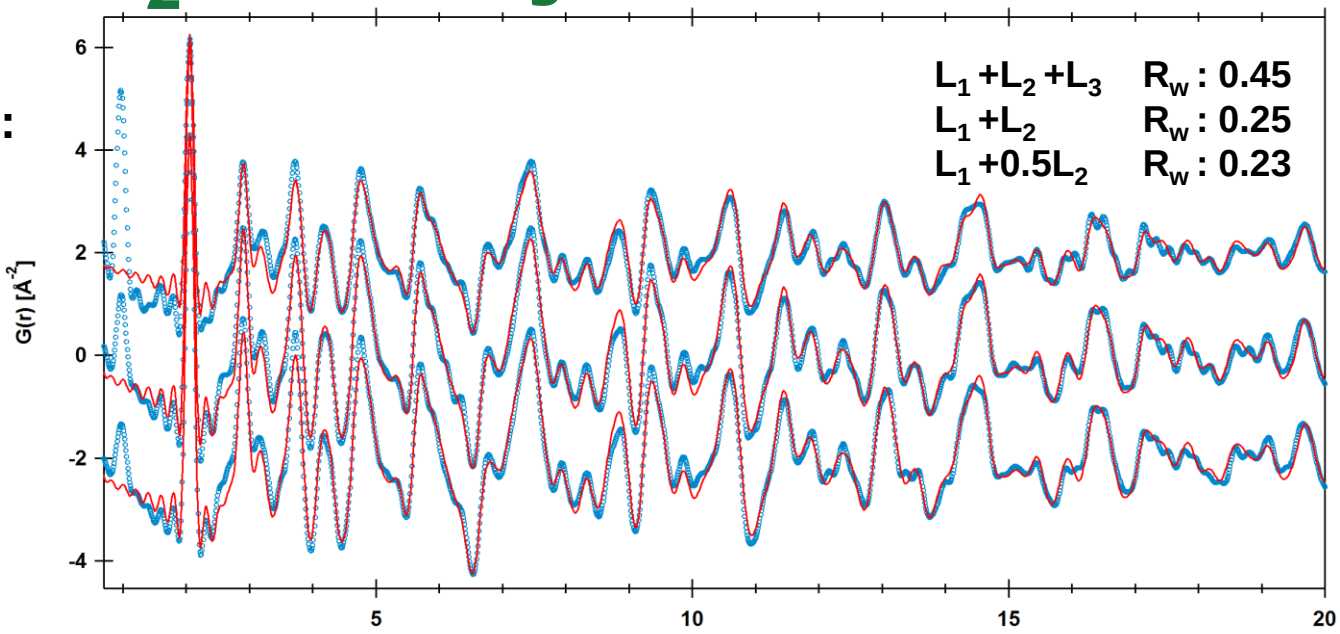
Example: SnO_2 Nanocrystals

Single phase model:

SnO_2 bulk structure,

refined particle

size = ~47 Å

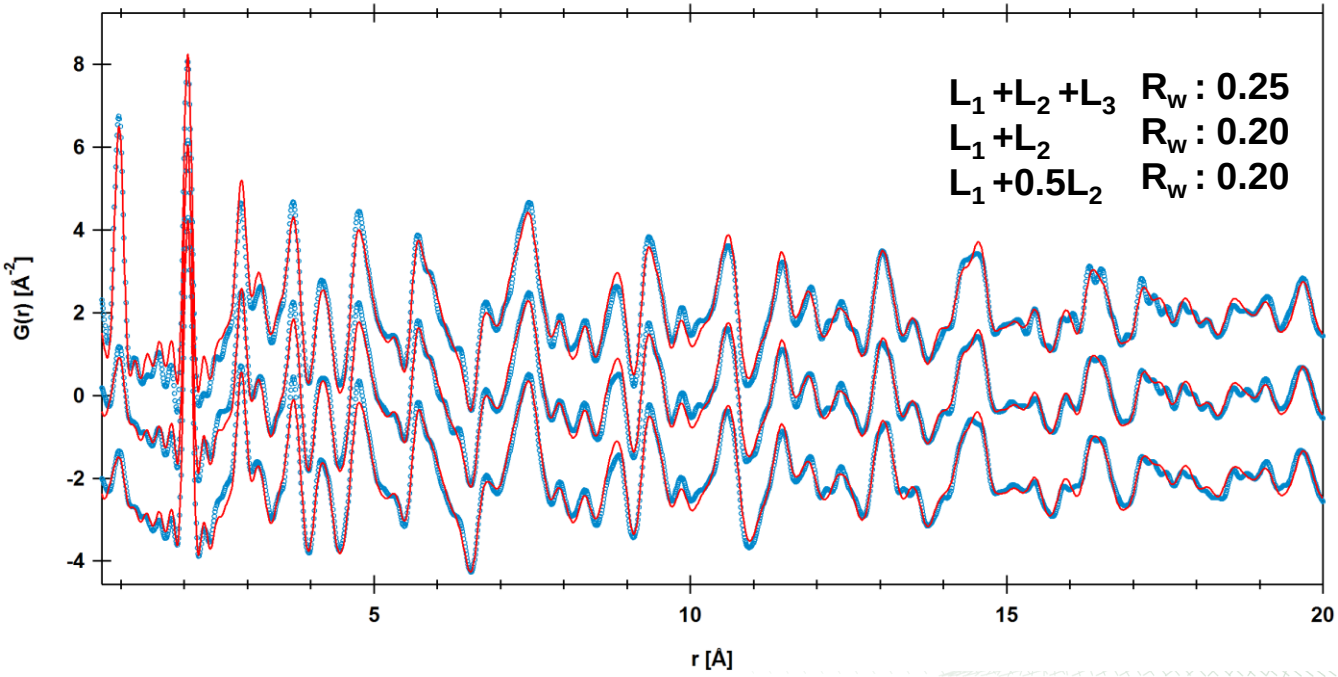


Two phase model:

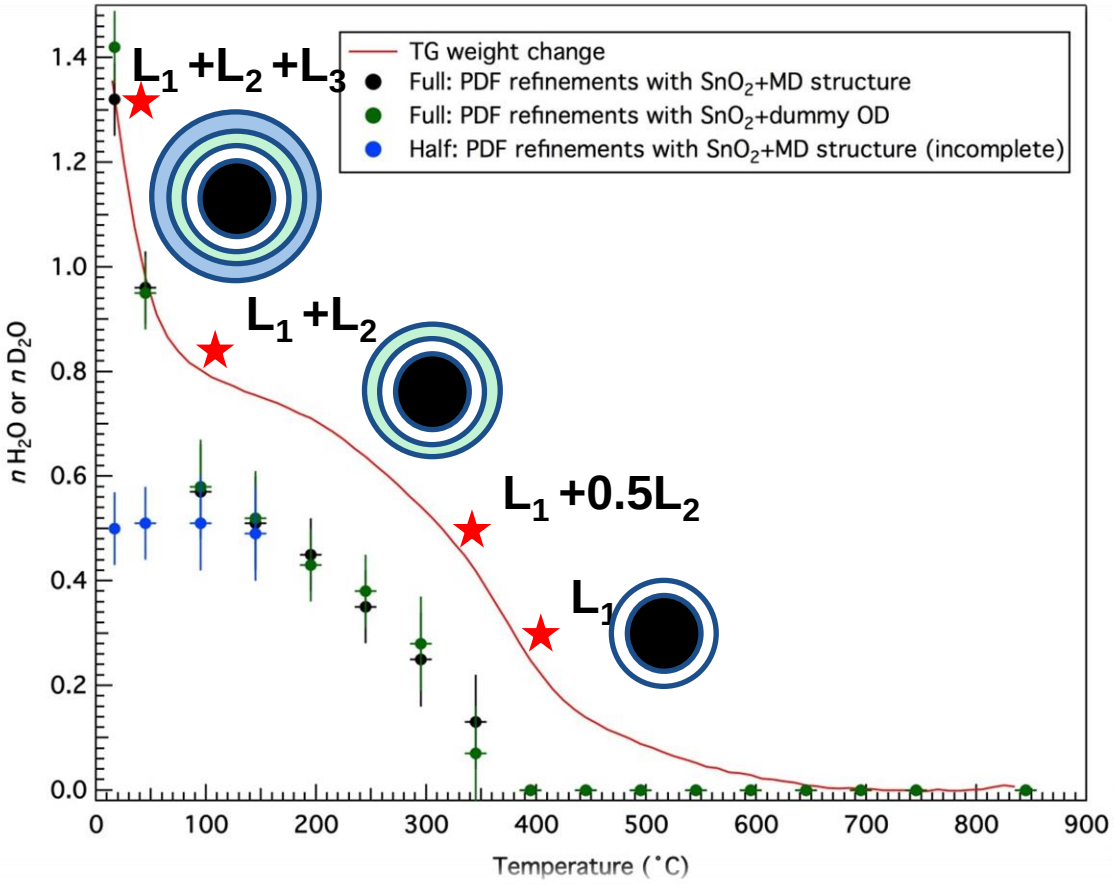
SnO_2 bulk +

layered MD water

structure



Example: SnO_2 Nanocrystals



Hsiu-Wen Wang

Wei Wang (synthesis)

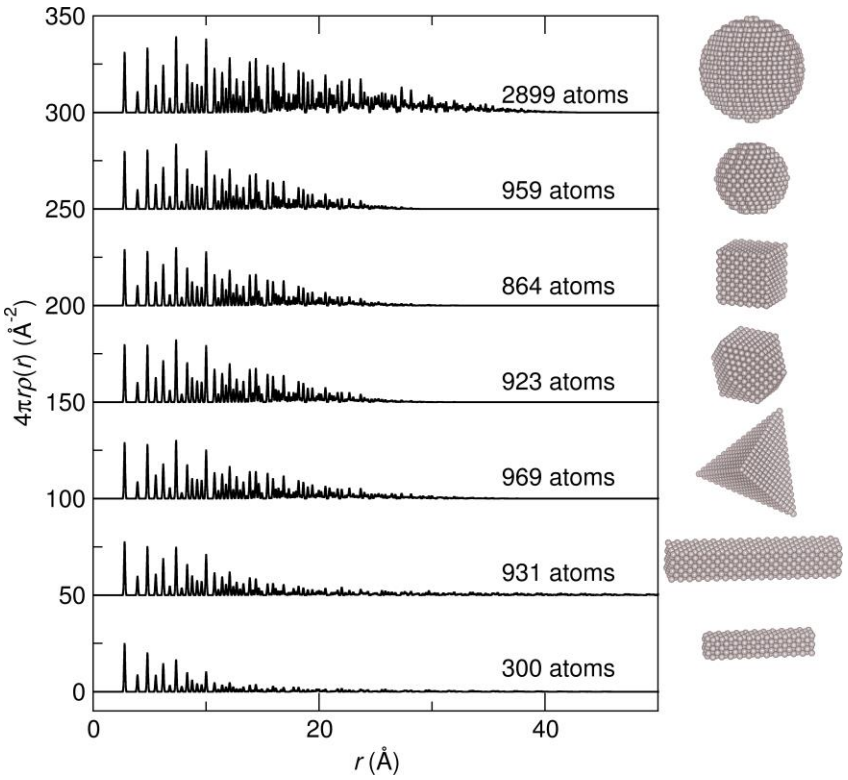
Thomas Proffen and Mikhail Feygenson (NOMAD-NPDF)

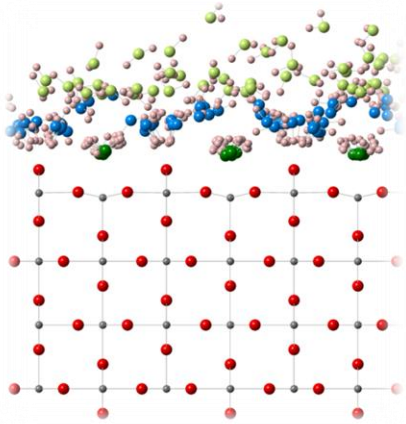
Alexander Kolesnikov and Dave Wesolowski (SEQUOIA-INS)

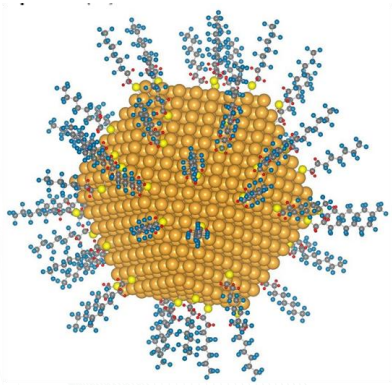
Lukas Vlcek (MD model), Lawrence Allard (TEM), and Lawrence Anovitz

New, high intensity sources are enabling studies with smaller samples, and on faster time-scales.

There are a few things that can't be done with small-box modeling….







Shapes, stacking faults, surface relaxation, ligand structure, etc.:

RMCprofile: http://www.isis.rl.ac.uk/RMC
DIFFEV: http://discus.sourceforge.net
EPSR: http://disordmat.moonfruit.com/

Some Resources and Programs

Data Collection	• Neutron: http://neutron.anl.gov/facilities.html • X-ray: http://www-als.lbl.gov/als/synchrotron_sources.html
Data Extraction	• PDFgetN: http://pdfgetn.sourceforge.net • PDFgetX2: http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/ • Gudrun: http://disordmat.moonfruit.com/
Data Modeling	• PDFgui: http://www.diffpy.org/ • RMCprofile: http://www.isis.rl.ac.uk/RMC • DIFFEV: http://discus.sourceforge.net • EPSR: http://disordmat.moonfruit.com/

Essential References

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R. Neder and Th. Proffen*, Diffuse Scattering and Defect Structure Simulation*, Oxford University Press, 2008.

M. G. Tucker, M. T. Dove, and D. A. Keen, Application of the reverse Monte Carlo method to crystalline materials, J. Appl. Cryst. 34, 630-638 (2001).

Conclusions

Atomic PDF from total (Bragg and diffuse) scattering data gives access to:

Departure from long range (average structure)

→Chemical short range order

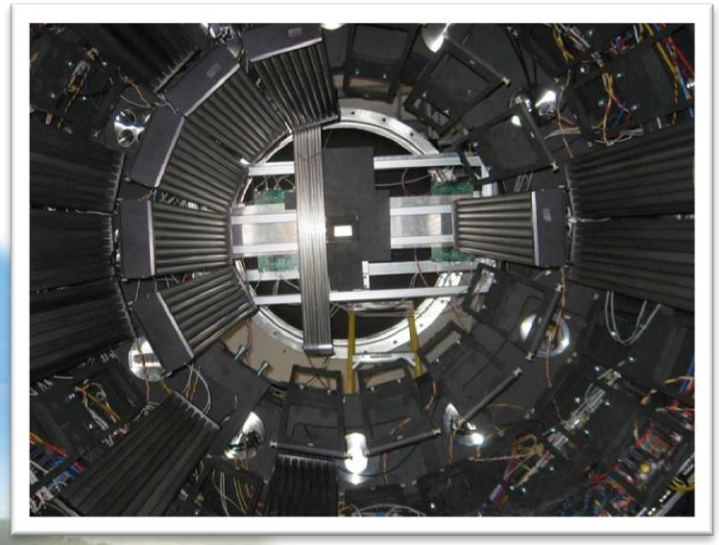
→Displacements

→Interstitials/vacancies

Amorphous and nanoscale structure

Correlation length scale (size)

Thank you!



We will be using the PDFgui Program

Do you have the program installed?

Download it from:

http://www.diffpy.org/

(or directly from the tutorial folder)

To install MAC/LINUX

The DiffPy components are registered at the Python Package Index (PyPI), therefore the most straightforward way to install is to execute easy_install MODULE_NAME. The easy_install command downloads, unzips and installs the required package together with its requirements, for example

easy_install diffpy.pdfgui

would install diffpy.pdfgui together with diffpy.pdffit2 and diffpy. The programs can be then started as pdfgui or pdffit2.

The easy_install command is a part of the Python setuptools library. If it is not available, install the "python-setuptools" package with the system package manager or use the ".tgz" archive below, which comes with easy_install included.

If you prefer to install from local files, download the latest **diffpy-VERSION.tgz** archive list below, unpack and run the enclosed easy_install script

tar -xzf diffpy-VERSION.tgz
cd diffpy-VERSION ./easy_install diffpy.pdfgui
For more detailed installation instructions see PDFgui manual.