Software for PDF analysis

Overview

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Experimental considerations

or

What makes a good PDF ?

What is required to obtain high quality PDFs ?

The PDF (similar to the Patterson) is obtained via Fourier transform of the normalized total scattering S(Q):

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

Requirements to obtain 'good' PDF:

- High momentum transfer, Q_{max}.
- High Q-resolution.
- Good counting statistics @ high Q.
- Low instrument and stable background

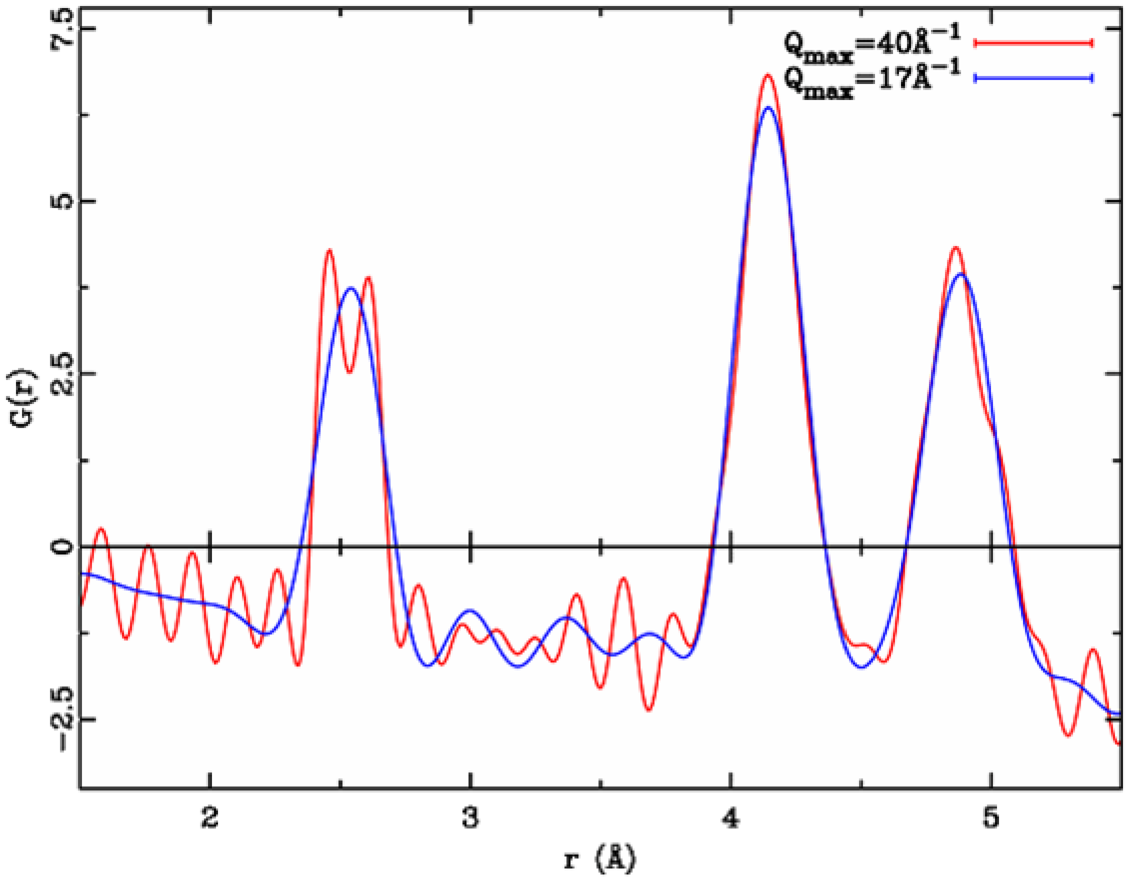
Where ?

Synchrotron sources (high energy X-rays)

or

spallation neutron sources
(reactor neutron energies are too low)

What makes a good PDF: Influence of Q_{max} …



Termination of integral at Q_{max} results in convolution of G(r) with $\sin(Q_{max}\, r)/r$.

$ZnSe_{0.5}Te_{0.5}$ data collected on GEM terminated at 40 $Å^{-1}$ and 17 $Å^{-1}$

NN split unresolved at 17 $Å^{-1}$!

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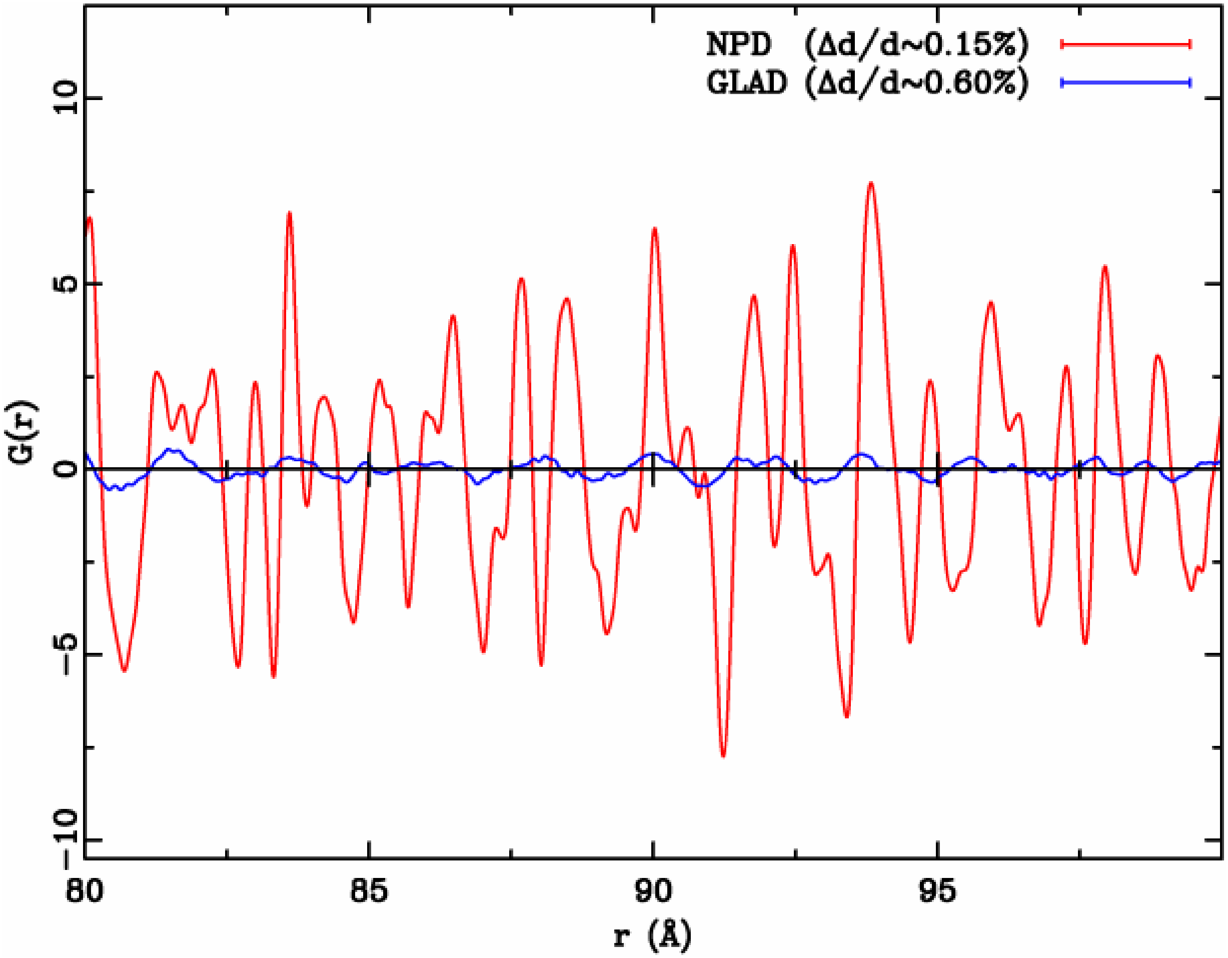
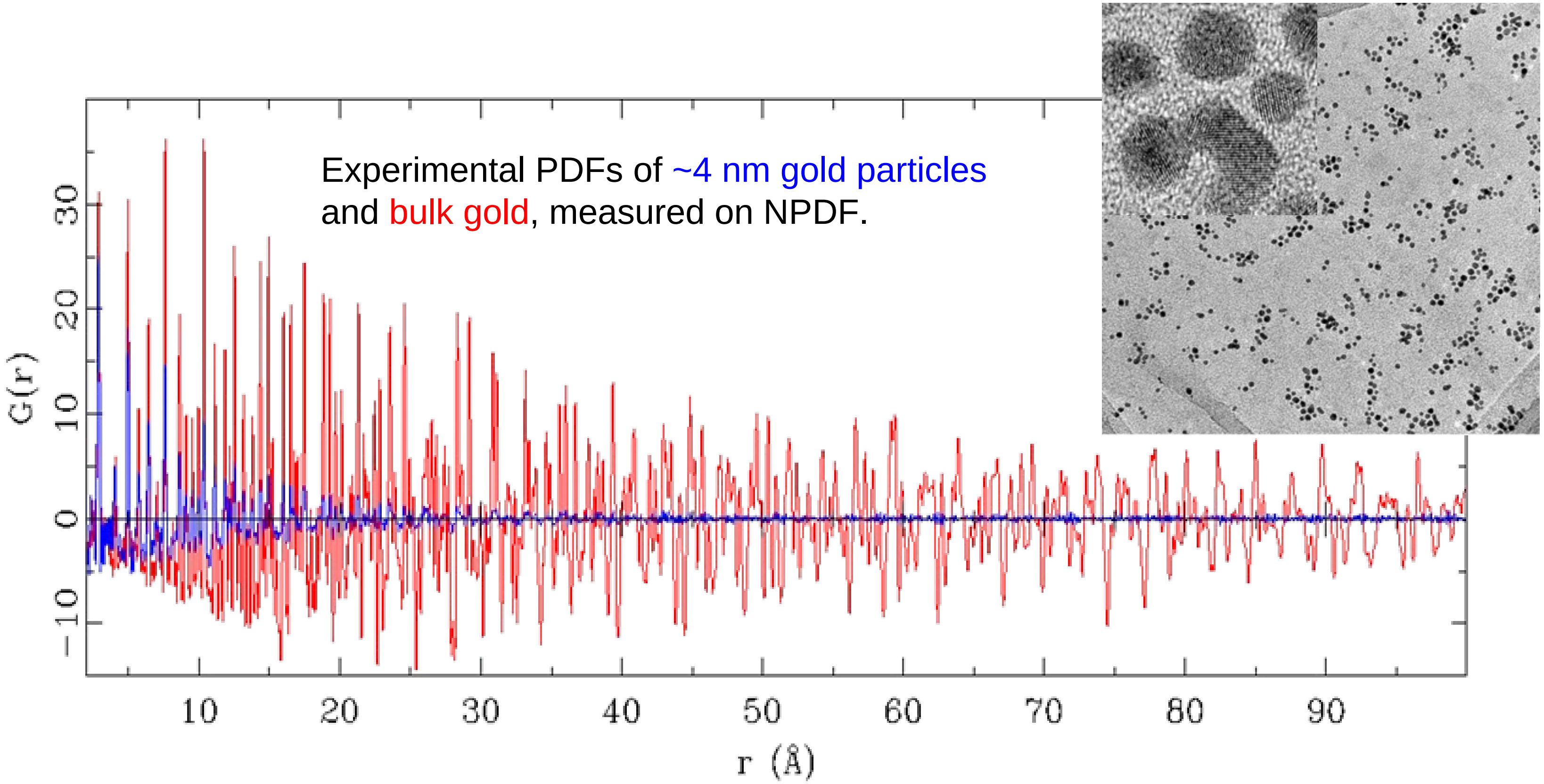
What makes a good PDF: Influence of Q resolution …



High Q resolution: Large *r* range (PDF dampened by *exp* $-(r\Delta Q)^2/2)$)

Nano-PDF: Example gold nanoparticles



K.L. 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).

PDF workshop – October 22-23, 2007

Data Reduction

or

How difficult is the processing of total scattering data ?

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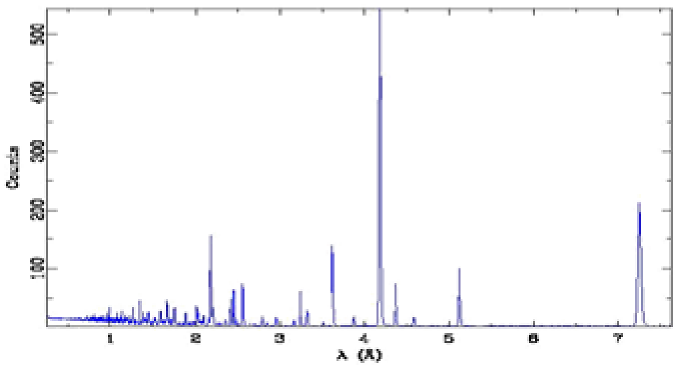
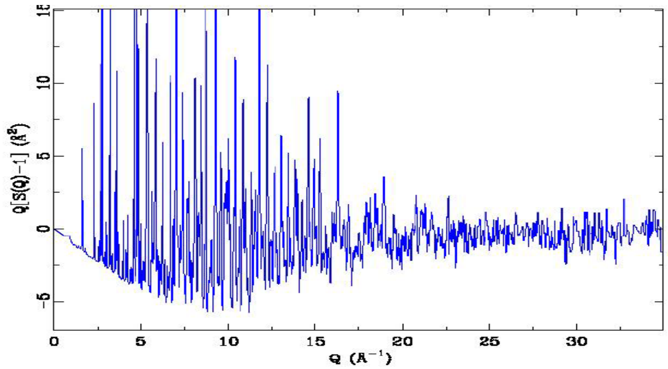
Neutron data processing

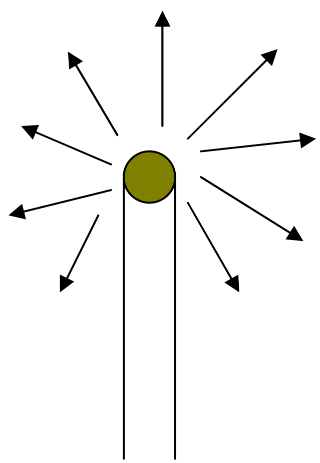


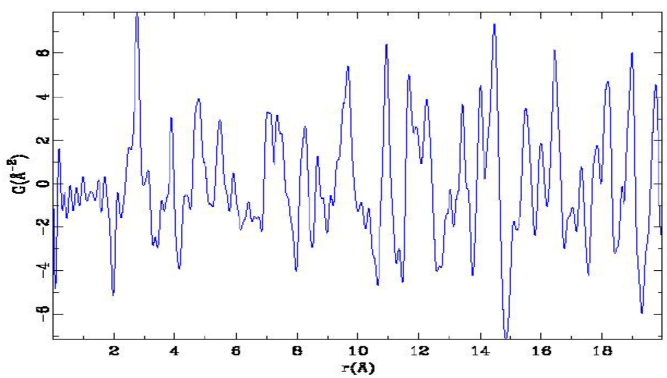
Corrections



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

Cylindrical Time-Of-Flight geometry (energy dispersive)





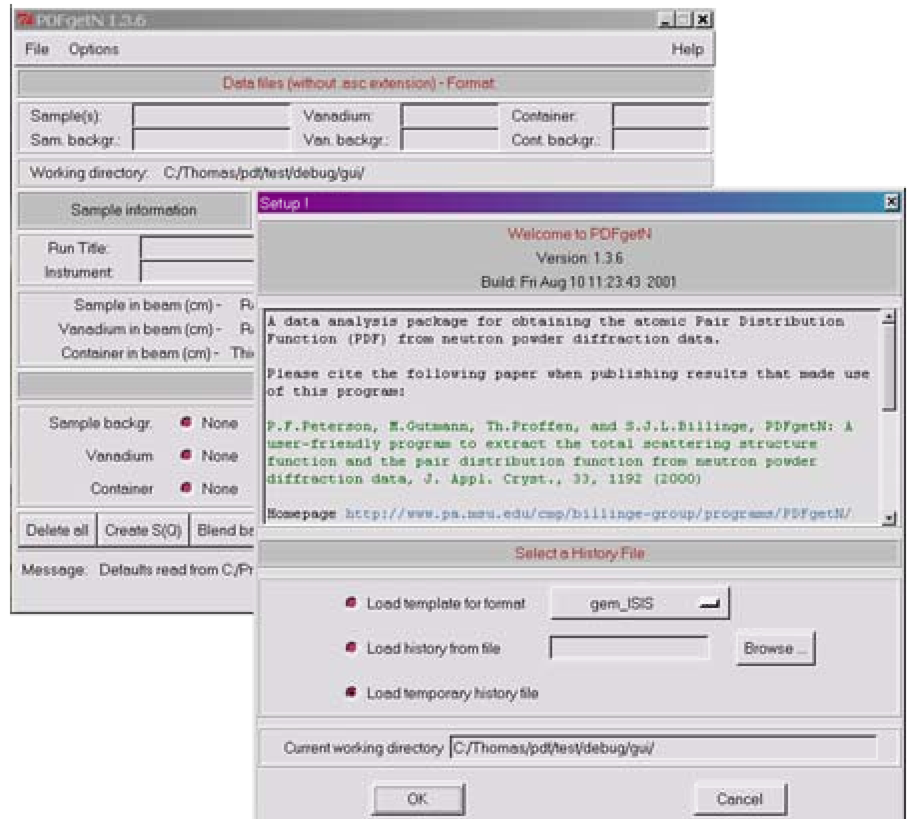
Typical characterization runs

- Empty instrument (B)
- Empty Container (C)
- Empty Container background (CB)
- Vanadium (V)
- Vanadium background (VB)
- Sample (S)

S_{corr}=[(S-SB)-α(C-CB)]/[V-VB]

Software: PDFgetN

- Based on GLASS package.
- Graphical users interface & integrated plotting.
- Supports most TOF neutron powder file formats.
- Records all processing parameters as part of output files G(r) and S(Q).
- Runs on Windows 95/98/NT/2000 and UNIX

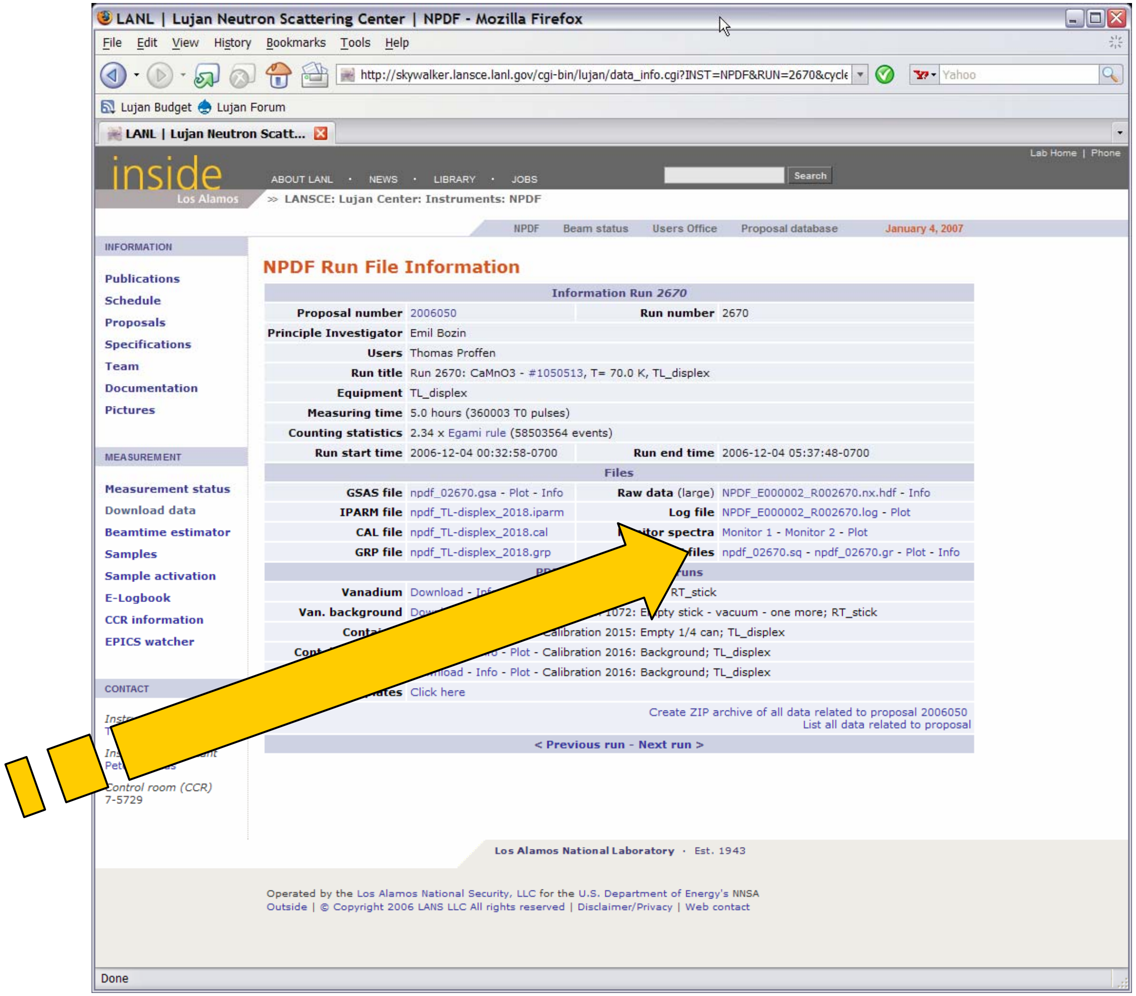


http://pdfgetn.sourceforge.net

P.F. Peterson, M. Gutmann, Th. Proffen and S.J.L. Billinge, **PDFgetN: A User-Friendly Program ..**, *J. Appl. Cryst.* **33**, 1192 (2000).

Software: NPDF creates PDF automatically !

- S(Q) and G(r) automatically generated.
- Access via instrument web site.
- Click PDF information



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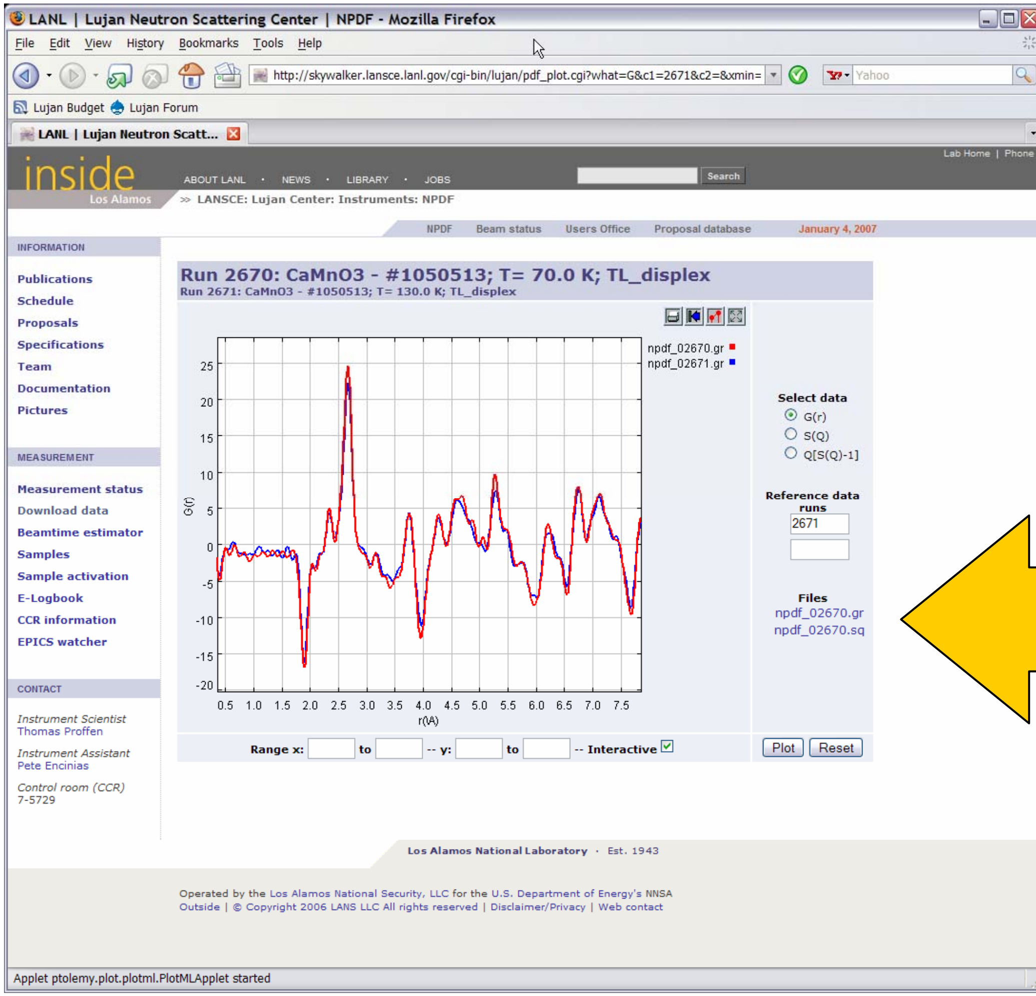
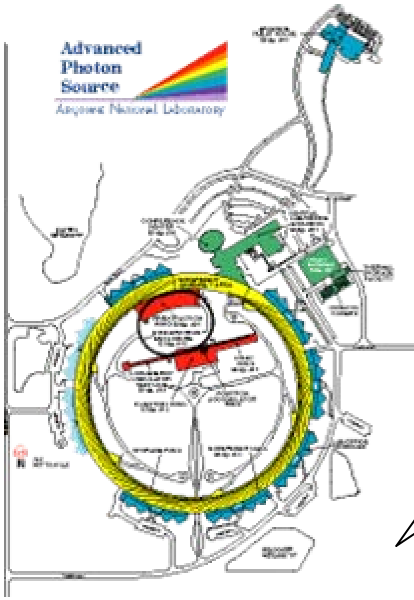
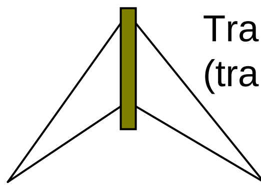
Software: NPDF creates PDF automatically !



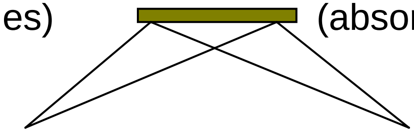
X-ray data processing



- **In house X-ray experiments**:
  - Easy.
  - Low *r* resolution, slow (and/or poor statistics).
  - *Mo*: Q_{max} ~ 17Å^{-1}, *Ag*: Q_{max} ~ 20Å^{-1}.
  - Flat plate transmission or reflection geometry.



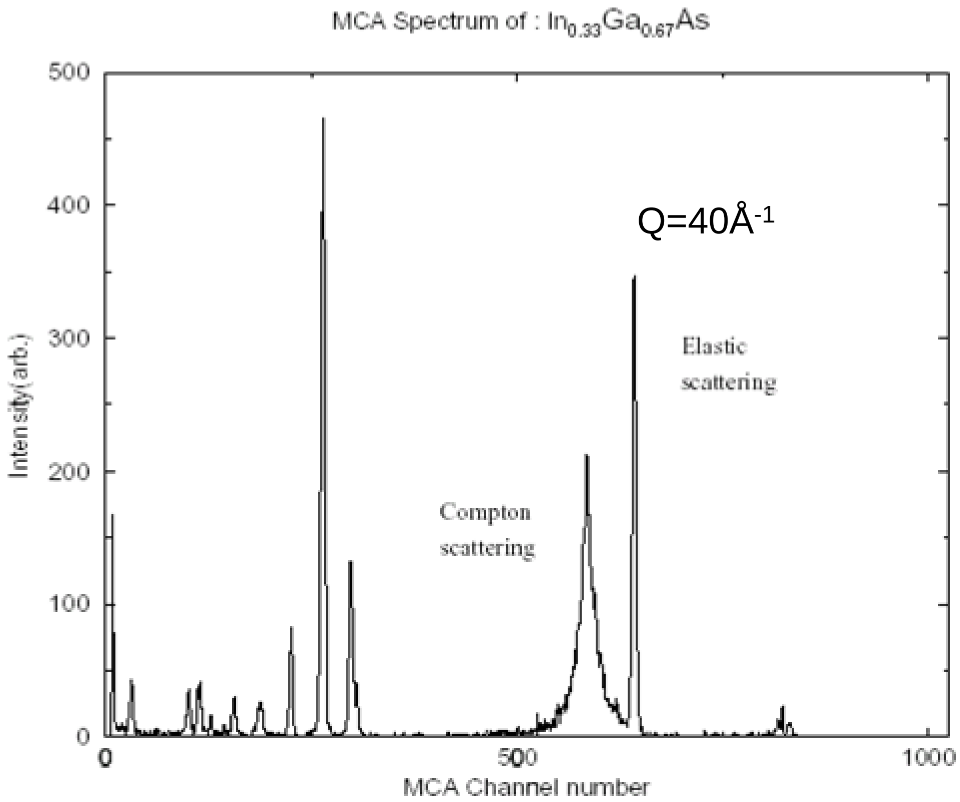
Transmission
(transparent samples)



Reflection
(absorbing samples)

- **Synchrotron experiments**:
  - Little precious beamtime.
  - High energy X-rays (Q_{max} > 60Å^{-1}).
  - High intensity (x 10,000 times stronger).
  - Parallel beam optics.
  - Generally flat plate transmission geometry.
  - New rapid PDF setup (PDF in seconds).

X-ray corrections: Removal of Compton scattering

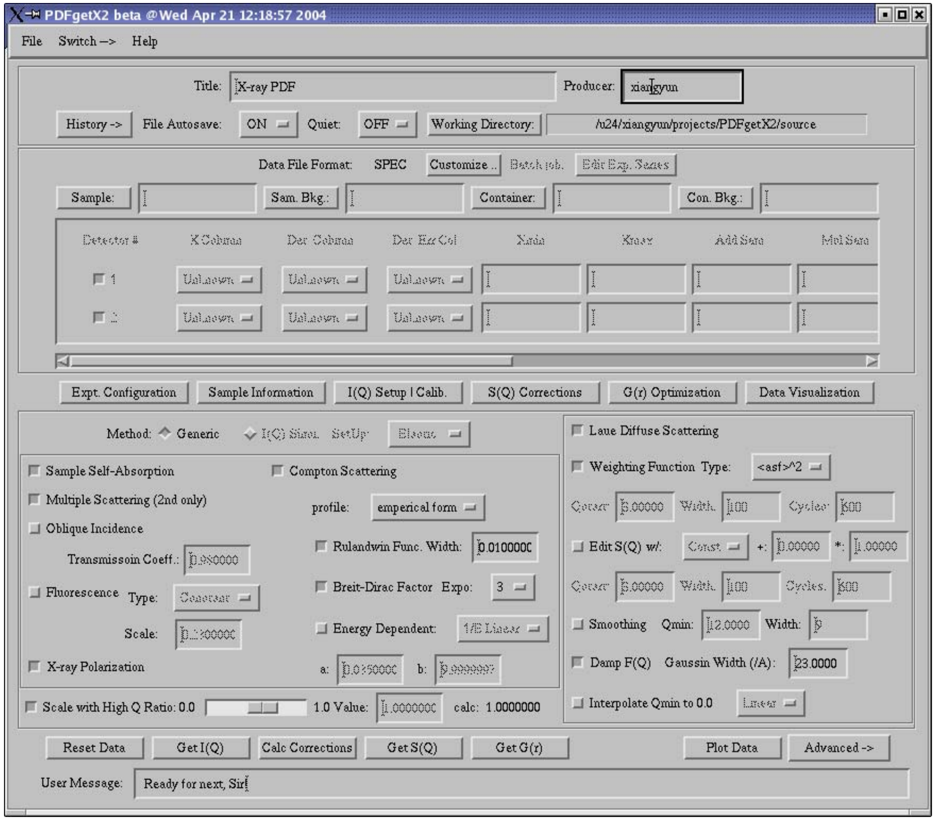


- Energy sensitive detector (e.g. Ge detector) allows separation of Compton scattering at higher Q.
- **Modes:**
  - SCA: Electronic windows to separate elastic channel
  - MCA: recording of complete spectrum at each measured point → software integration.

Software: PDFgetX2

X. Qiu, J. W. Thompson, and S. J. L. Billinge, *J. Appl. Cryst.* **37**, 678-678

- Reads SPEC files.
- Supports MCA and SCA data.
- Integrated plotting of various corrections applied.
- Tools for merging scans.
- Runs on Windows and UNIX. Based on IDL.



http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/

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What to do with your PDF ?

Outline

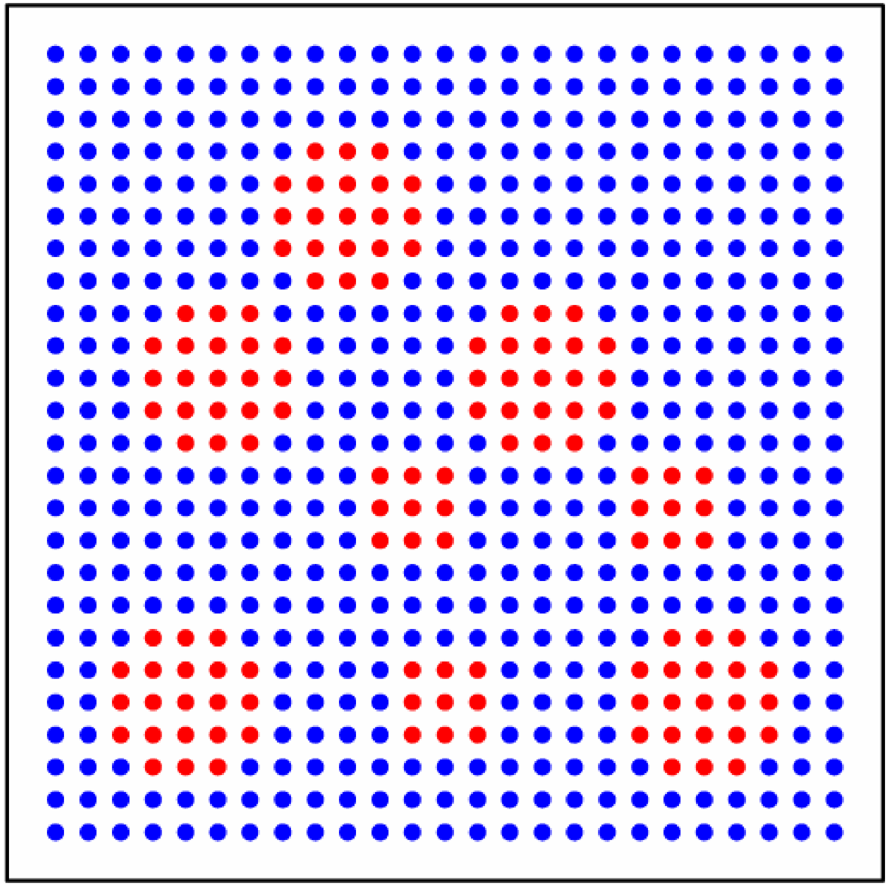
- What to do with your PDF ?

- Give it to your favorite theorist.

- Try ‘experimentalists’ modeling

  - Modeling base on a structural model
    - A new parameter – *r*
    - Small models: Least square refinements
    - Large models: Reverse Monte Carlo
    - Any model: Evolutionary Algorithms

Refinement range – length scales in structure

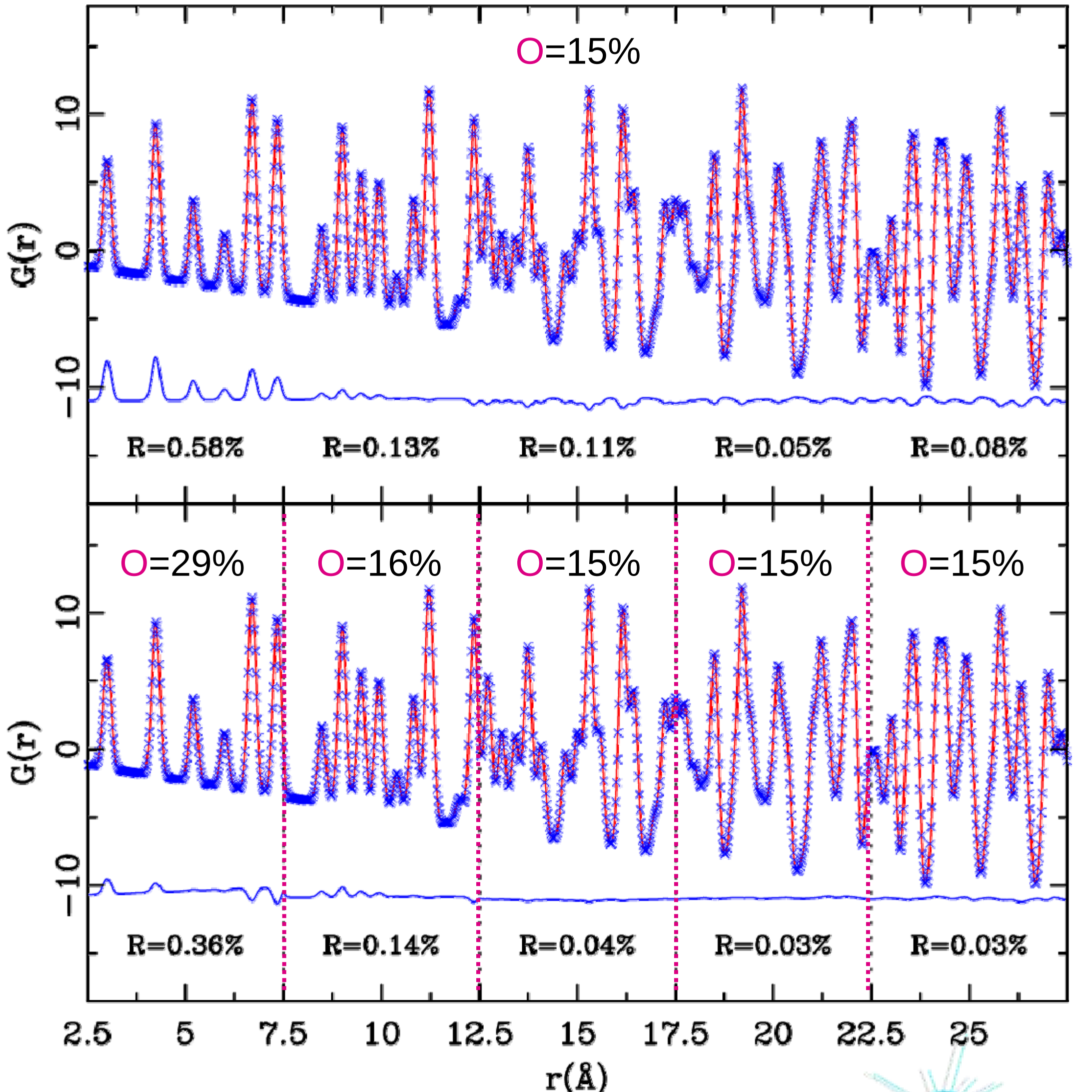


- Simulated structure of 20x20x20 unit cells.
- Matrix (M): blue atoms
- Domains (D): red atoms, spherical shape, d=15Å.
- Simulated using DISCUS.

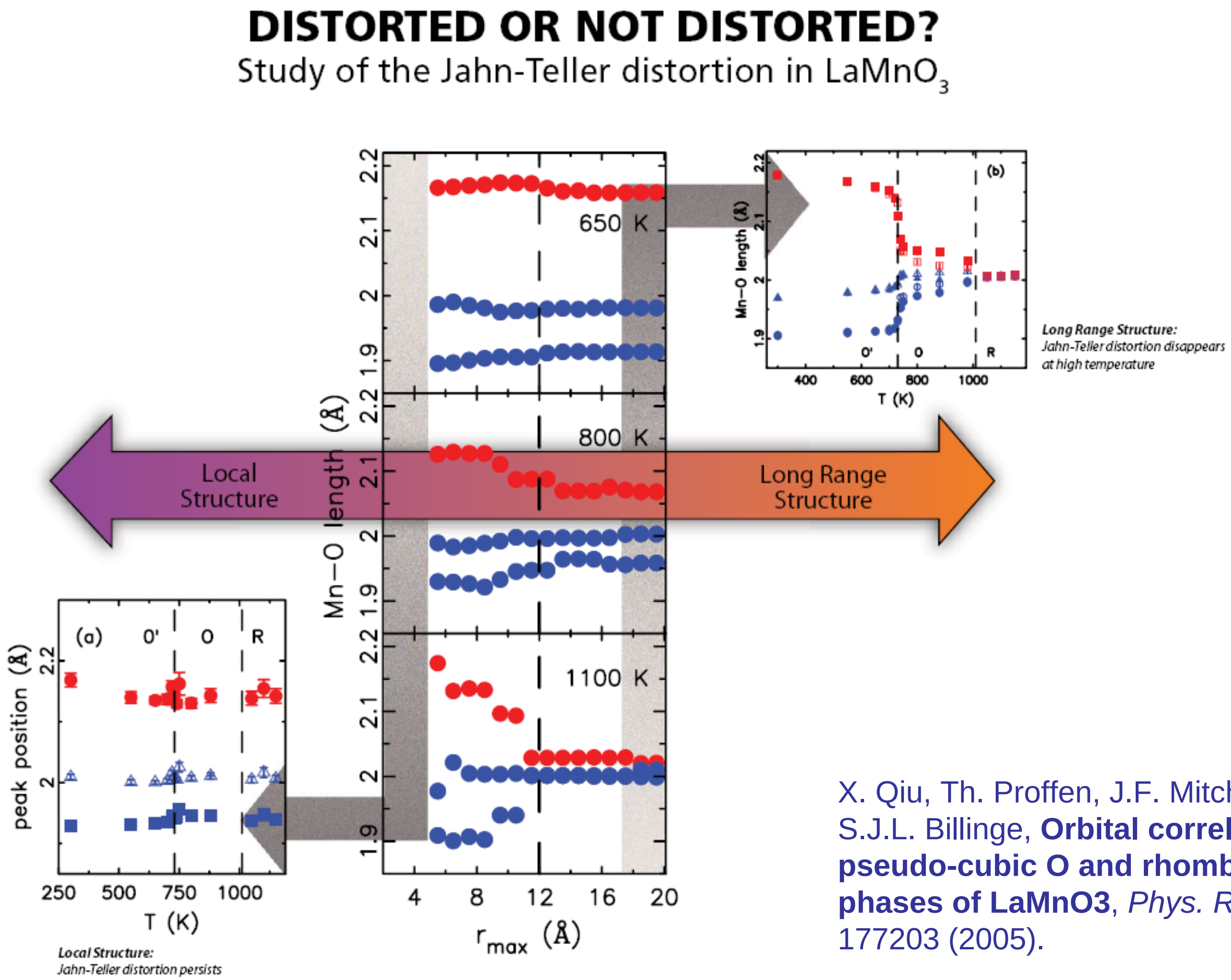
Th. Proffen and K.L. Page, **Obtaining Structural Information from the Atomic Pair Distribution Function**, *Z. Krist.* **219**, 130-135 (2004).

Refinement range – length scales in structure

- *Top*: Single-phase model with blue/red fractional occupancies (O).
- *Bottom*: Refinement of same model for 5Å wide sections.
- Extensions:
  - Multi phase models
  - Modeling of boundary
  - R-dependent refinable mixing parameters



Refinement range – the mystery of $LaMnO_3$



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).

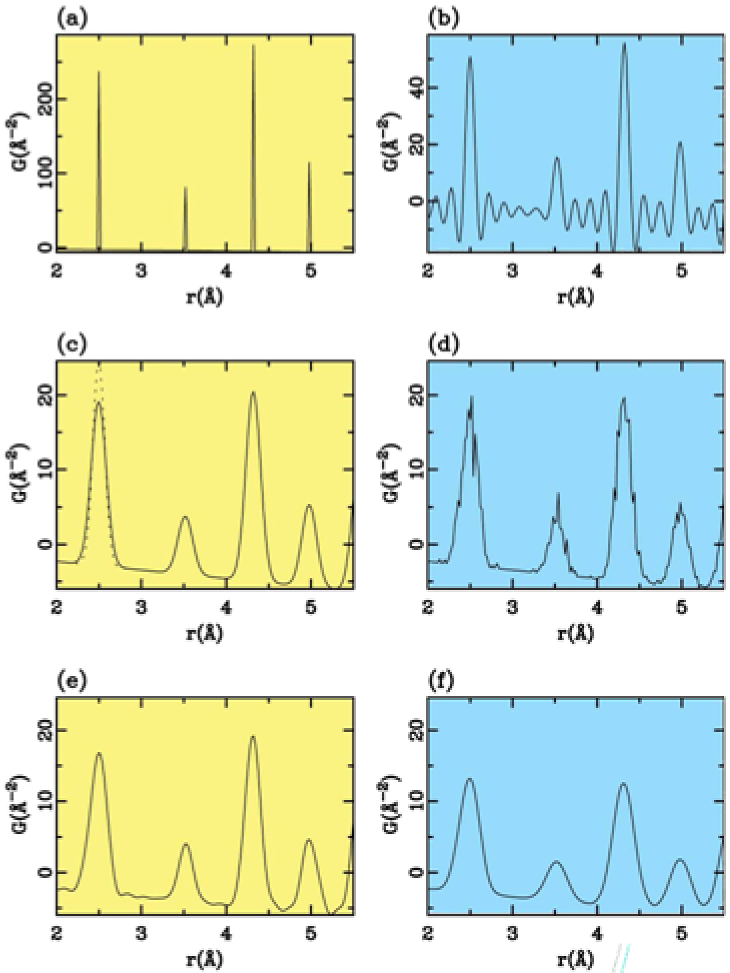
Calculating a PDF ..

- Calculating a PDF from a structural 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 crystal ⇒ convolution of $\delta(r-r_{ij})$ with distribution function (*PDFFIT*)
  - Large crystal ⇒ actual displacements & ensemble average (*DISCUS*)

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



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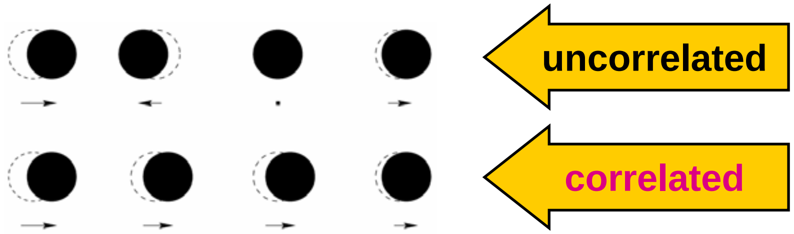
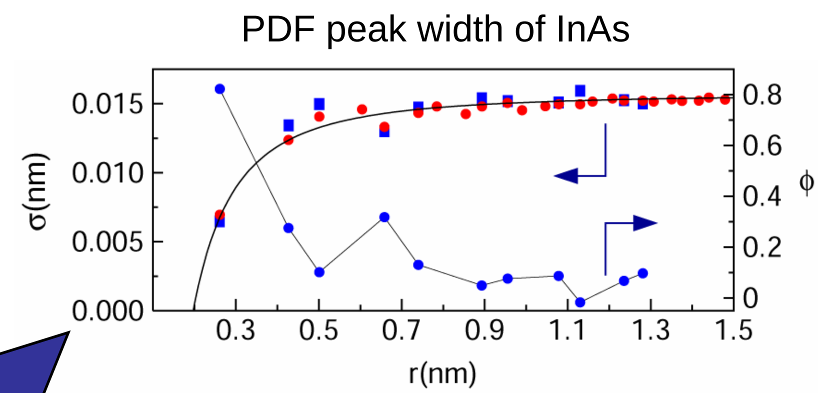
PDF analysis: Analysis of individual peaks

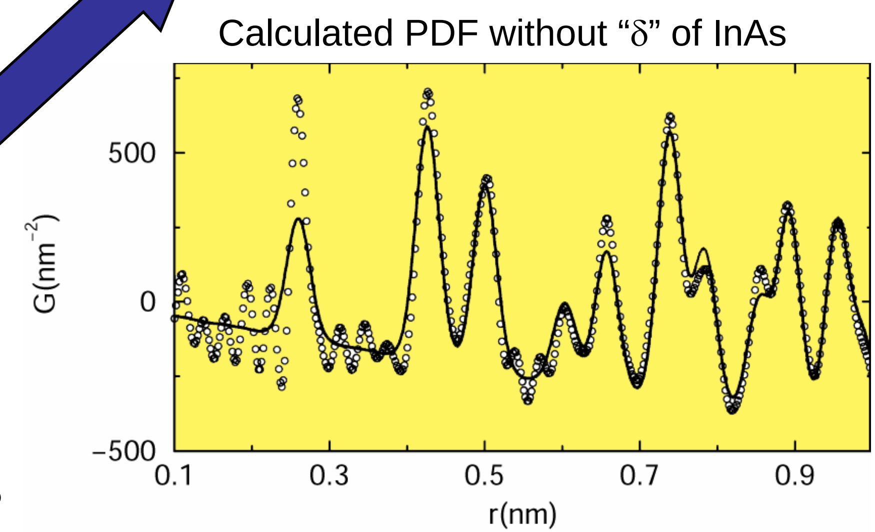




- Correlated motion results in sharpening of near neighbor PDF peaks.

- Empirical correction

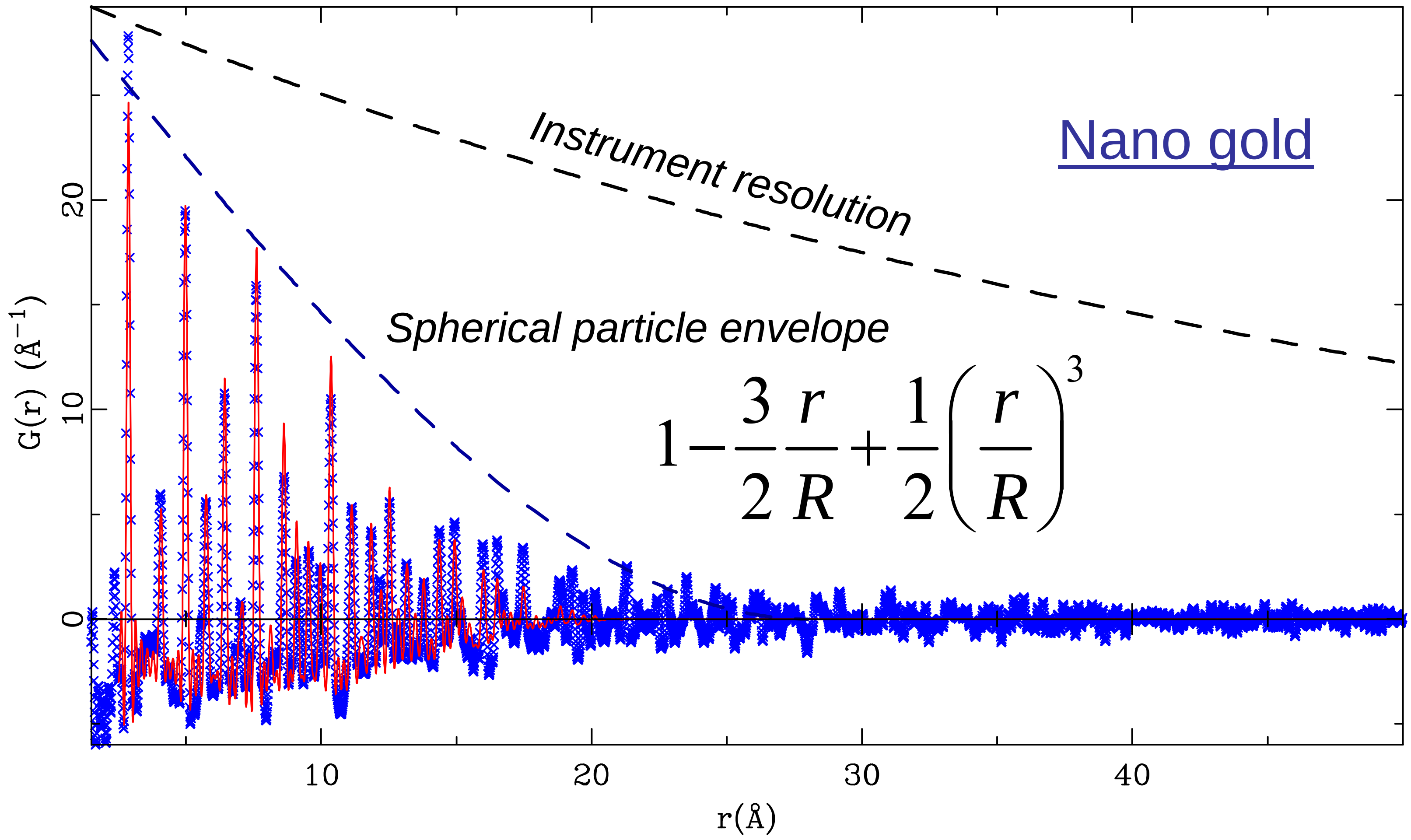
$$\sigma_c = \sqrt{\sigma_0 - \delta / r^2 - \gamma / r}$$



- *Future*: Extraction of phonons ??

Jeong et al., *J. Phys. Chem. A* **103**, 921 (1999)

Nanoparticles: Particle size



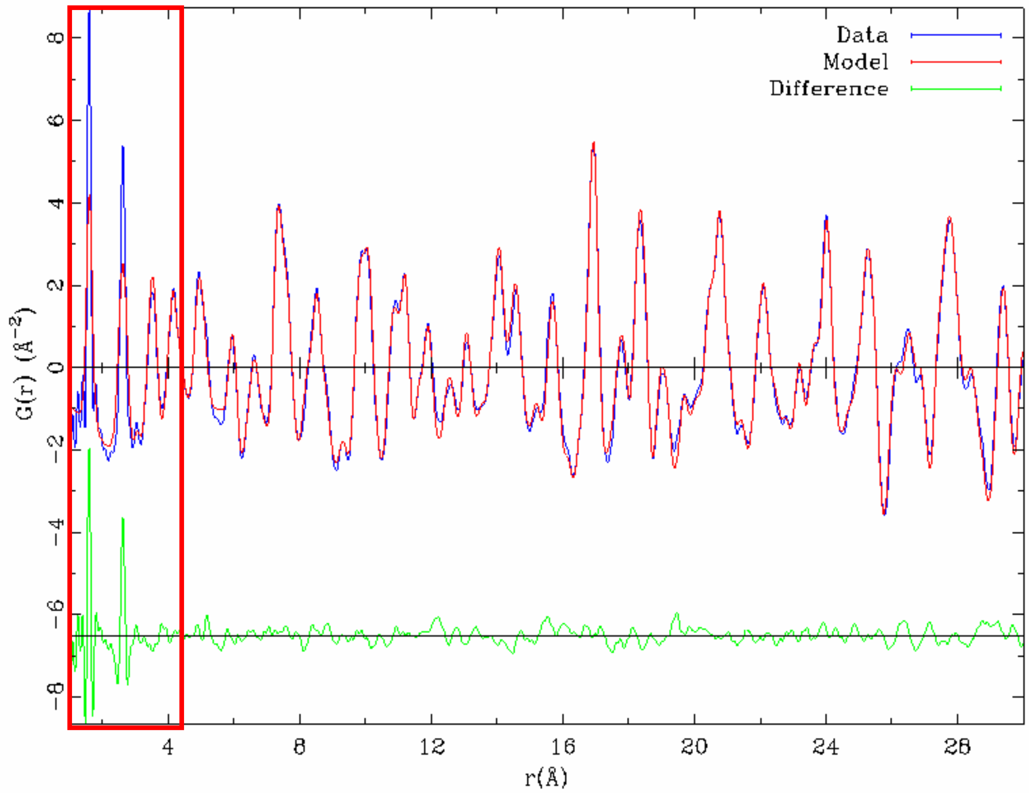
PDFfit

Refining a small structural model to the PDF

PDFfit: Refinement of a small structural model

- “Real space Rietveld”
- Refinement of structural parameters: *lattice parameters, atom positions, occupancies, adp’s, ..*
- Small models (<200 atoms).
- Corrections for Q_{max}, *instrument resolution, correlated motion.*
- Software: *PDFfit, PDFfit2 and PDFGui.*

Example: Is sandstone simply quartz ?



K.L. Page, Th. Proffen, S.E. McLain, T.W. Darling and J.A. TenCate, **Local Atomic Structure of Fontainebleau Sandstone: Evidence for an Amorphous Phase ?**, *Geophys. Res. Lett.* **31**, L24606 (2004).

Calculating a PDF: PDFfit

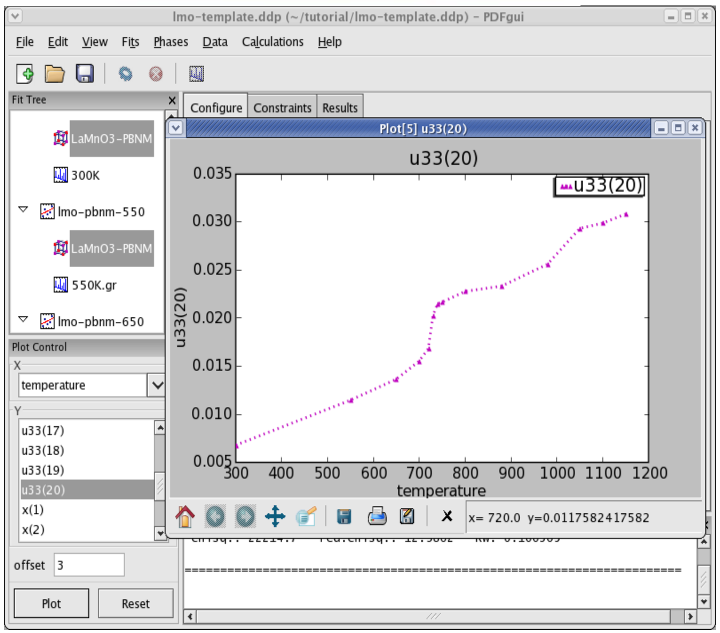
PDF calculated according to

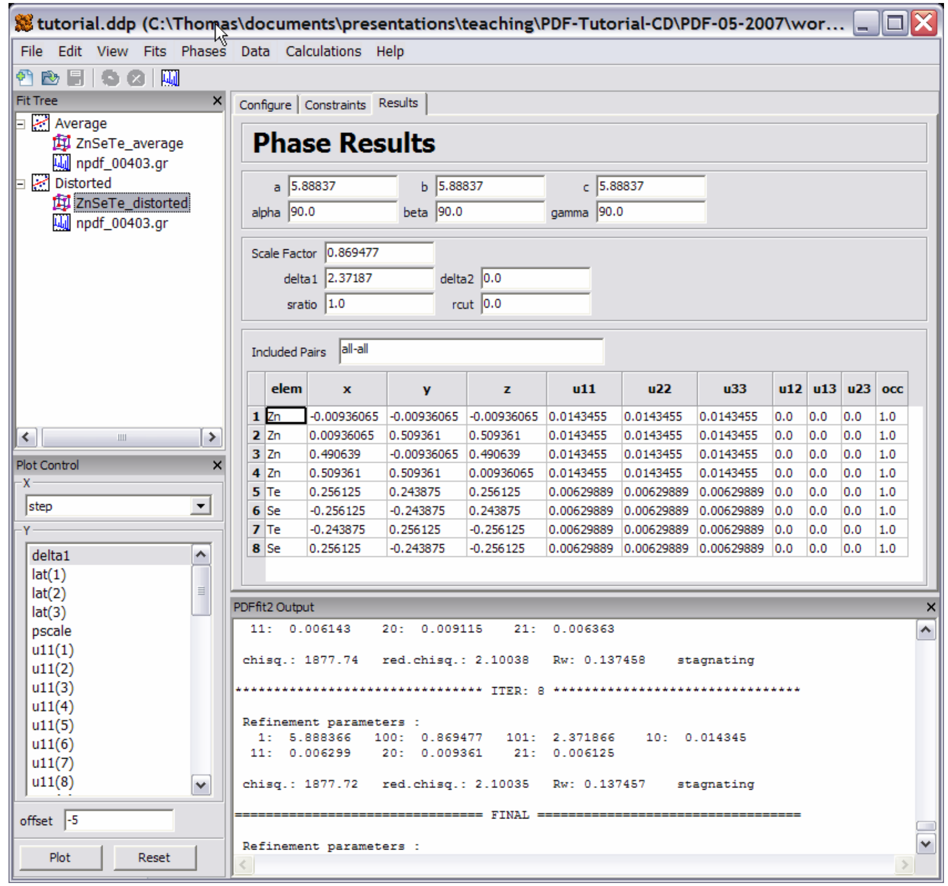
$$G(r) = \sum_{ij} \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

In more detail

$$\begin{aligned}
G(r_k, s) &= f_s B_k(s) \sum_{p=1}^{P} f_p G_p(r_k, s) \\
G_p(r_k, s) &= \frac{1}{N_p r_k} \sum_i \sum_j [A_{ij}(p) \cdot T_{ij}(r_k, p)] \\
&\quad -4\pi r_k \rho_0(p) \\
B_k(s) &= \exp\left[-\frac{(r_k \sigma_Q(s))^2}{2} \right] \\
A_{ij}(p) &= \frac{c_i(p) c_j(p) b_i b_j}{\langle b \rangle^2} \\
T_{ij}(r_k, p) &= \frac{1}{\sqrt{2\pi}\sigma_{ij}(p)} \exp\left[-\frac{(r_k - r_{ij}(p))^2}{2\sigma_{ij}^2(p)} \right]
\end{aligned}$$

PDFgui – looks cool ..





http://www.diffpy.org

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RMC

Shaking a big box of atoms.

Courtesy of M. Tucker, ISIS

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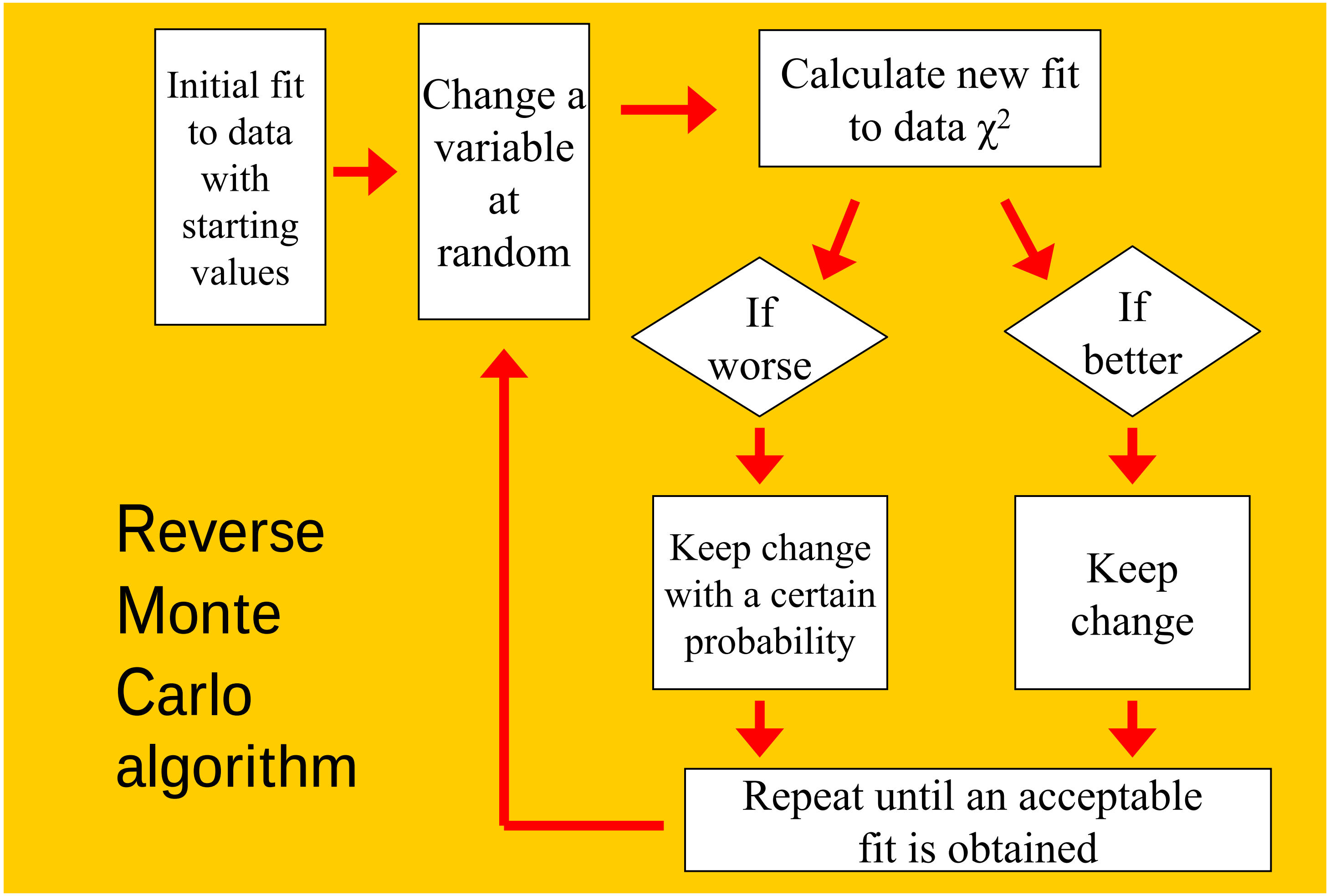
Reverse Monte Carlo

- Commonly used to model glasses and liquids (no long range order).
- Recently applied to disordered crystalline materials.
- Large model structures.
- Importance of constrains.
- Uniqueness of solution ?

R.L. McGreevy and L. Pusztai, **Reverse Monte Carlo Simulation: a New Technique for the Determination of Disordered Structures** , *Mol. Simul.* **1**, 359-367 (1988).

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).

RMC: How does it work ?

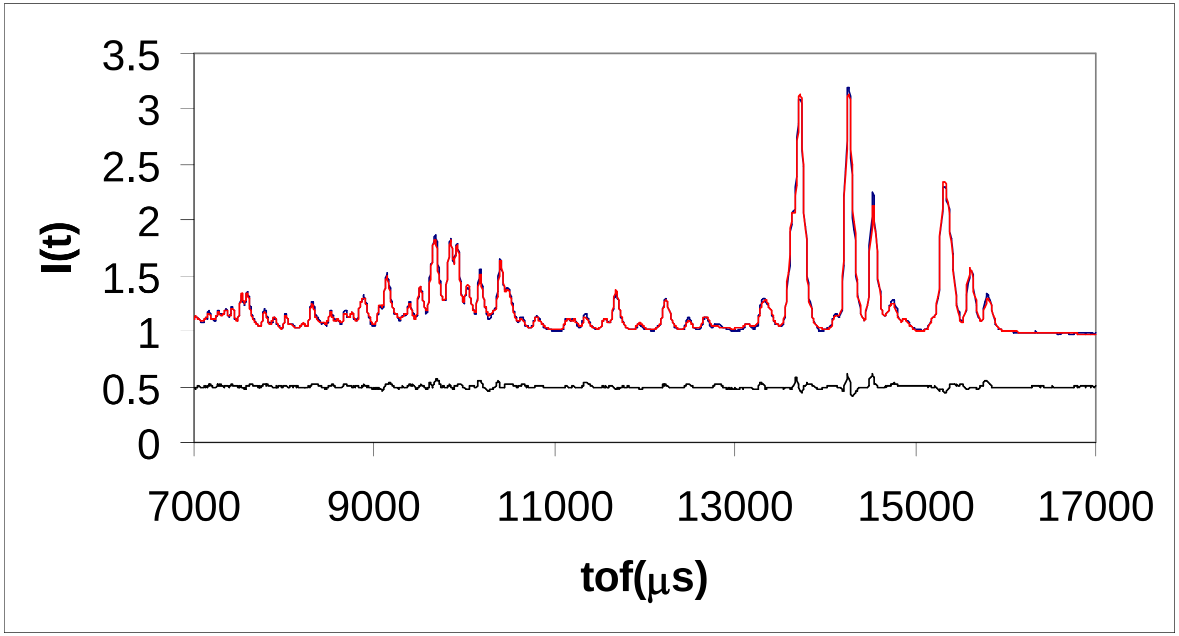


Include Bragg intensities ..

Use GSAS to fit :
Peak shape
Background
Lattice parameters

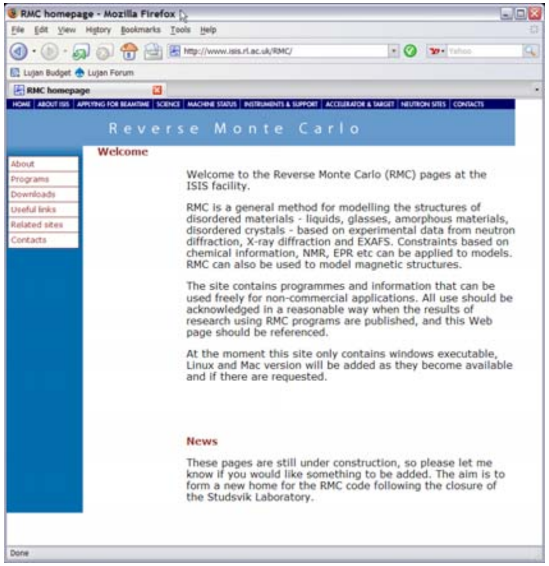
RMCProfile calculates the intensities and then produces the profile.

$$+\sum_j |I_{\text{expt}}(t_j) - sI_{\text{calc}}(t_j)|^2 / \sigma^2_{I(t_j)}$$



Software: RMCprofile and DISCUS

- RMCprofile
  - Atomic configurations ~600 to 20000+ atoms
  - Fit both X-ray and neutron F(Q)
  - Fit G(r)
  - Fit Bragg profile (GSAS tof 1,2 & 3)
  - Polyhedral restraints
  - Coordination constraints
  - Closest approach constraints



- Produce a static 3-D model of the structure (a snap-shot in time)
- Link: http://www.isis.rl.ac.uk/RMC

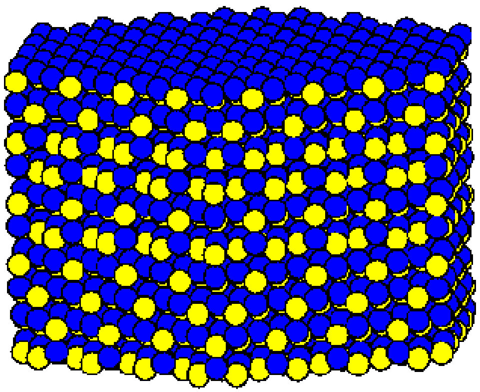
DIFFEV

Refining parameters of a disordered particle/crystal

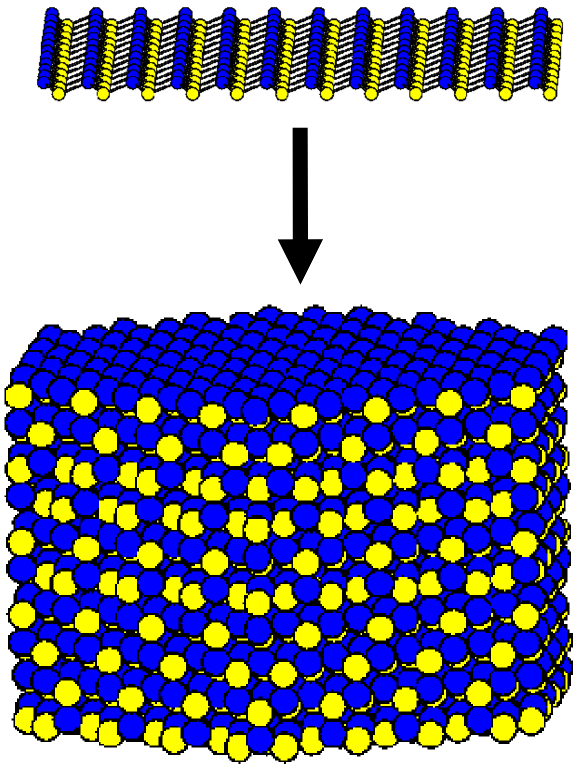
Courtesy of R.B. Neder, U Würzburg

DIFFEV: Refining model parameters

- PDFfit and RMC
  - Refine structure directly in terms of atom coordinates etc ..
  - Difficult for complex systems
- Alternative
  - Refine parameters of a structural model and not each atom.
  - Example nanoparticle: *diameter, atom spacing, stacking fault probability, …*
  - Choose minimization – here DIFFEV



Example: ZnSe nanoparticles - Model



{110} and {001}

create a large single Wurtzite layer A/B

Stack along c (with faults)

Cut to proper size

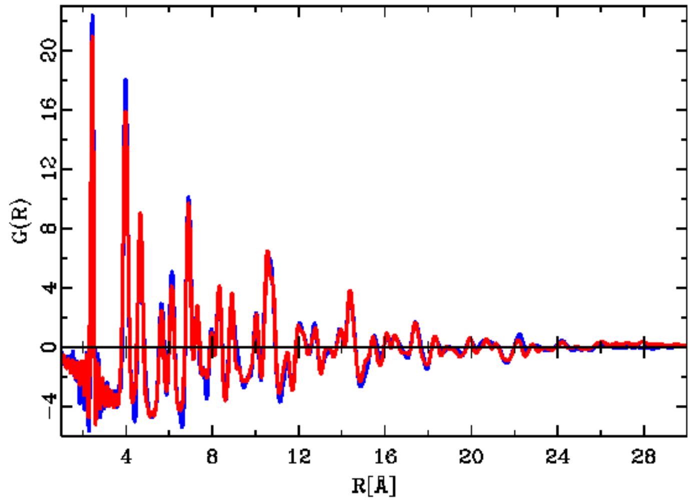
Calculate PDF / powder pattern

Repeat and average

Repeat with new set of parameter using a Differential Evolutionary Scheme

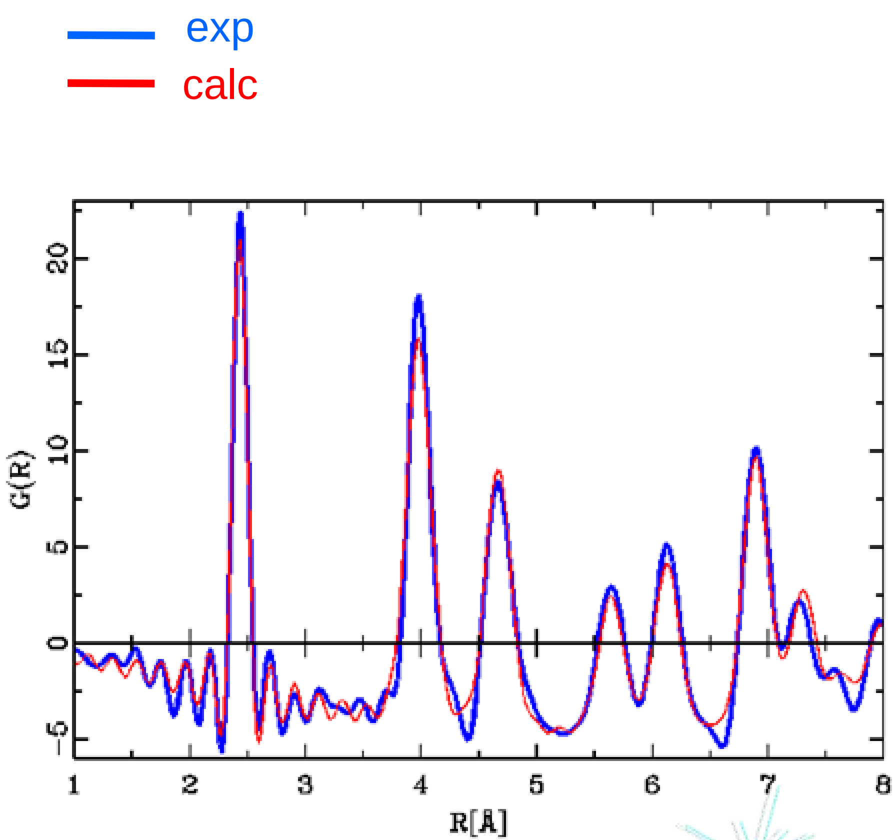
Software: DISCUS and DIFFEV

Example: ZnSe nanoparticles - Results



C. Kumpf, R.B. Neder et al., **Structure determination of CdS and ZnS nanoparticles: Direct modeling of synchrotron-radiation diffraction data**, *J. Chem. Phys.* **123**, 224707 (2005).

- Results:
  - a=3.973Å, c=6.494Å
  - Diameter ~26Å
  - Stacking fault prob. 70%



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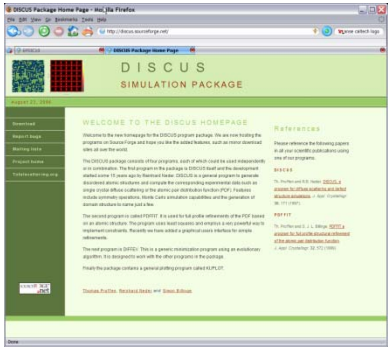
Diffuse package: DISCUS, PDFfit and DIFFEV

- PDFfit
  - User defined relation between parameters and refinement variables.
  - Multiple structural phases and data sets (neutron and X-ray) supported.
- DISCUS
  - Calculation of Fourier transform, inverse and difference Fourier.
  - Expand structure from asymmetric unit and space group symbol.
  - Structure “statistics”: correlations, real space lots, ...
  - PDF calculations.
  - Monte Carlo simulations.
  - Reverse Monte Carlo simulations – diffuse scattering & PDF.
  - Symmetry & unit cell transformations.
- DIFFEV: General minimization using evolutionary algorithms
- KUPLOT: General plotting program
- Common features
  - Command language including loops and IF statements.
  - Online help function
  - UNIX or Windows operating system.
  - Binary or source code distribution.
  - Written in FORTRAN-77 (and some C).
- Link: http://discus.sourceforge.net



Th. Proffen and R.B. Neder, *J. Appl. Cryst.* **30**, 171-175 (1997).
Th. Proffen and S.J.L. Billinge, *J. Appl. Cryst.* **32**, 572-575 (1999).

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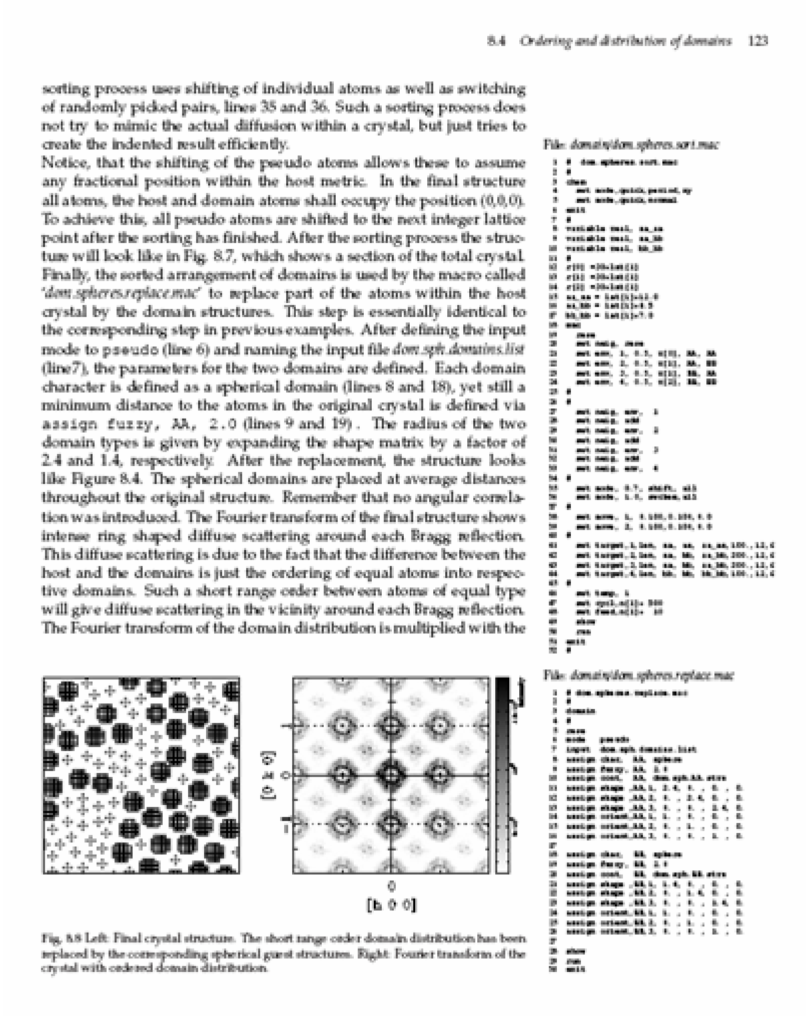
The DISCUS cook book – coming soon !

- To be published by Oxford University Press as IUCr text.
- Includes CDROM with many examples.
- Summer 2008



8.4 *Ordering and distribution of domains* 123

sorting process uses shifting of individual atoms as well as switching of randomly picked pairs, lines 35 and 36. Such a sorting process does not try to mimic the actual diffusion within a crystal, but just tries to create the indented result efficiently.
Notice, that the shifting of the pseudo atoms allows these to assume any fractional position within the host metric. In the final structure all atoms, the host and domain atoms shall occupy the position (0,0,0). To achieve this, all pseudo atoms are shifted to the next integer lattice point after the sorting has finished. After the sorting process the structure will look like in Fig. 8.7, which shows a section of the total crystal. Finally, the sorted arrangement of domains is used by the macro called '*dom.spheres.replace.mac*' to replace part of the atoms within the host crystal by the domain structures. This step is essentially identical to the corresponding step in previous examples. After defining the input mode to `pseudo` (line 6) and naming the input file *dom.sph.domains.list* (line7), the parameters for the two domains are defined. Each domain character is defined as a spherical domain (lines 8 and 18), yet still a minimum distance to the atoms in the original crystal is defined via `assign fuzzy, AA, 2.0` (lines 9 and 19). The radius of the two domain types is given by expanding the shape matrix by a factor of 2.4 and 1.4, respectively. After the replacement, the structure looks like Figure 8.4. The spherical domains are placed at average distances throughout the original structure. Remember that no angular correlation was introduced. The Fourier transform of the final structure shows intense ring shaped diffuse scattering around each Bragg reflection. This diffuse scattering is due to the fact that the difference between the host and the domains is just the ordering of equal atoms into respective domains. Such a short range order between atoms of equal type will give diffuse scattering in the vicinity around each Bragg reflection. The Fourier transform of the domain distribution is multiplied with the

File: *domain/dom.spheres.sort.mac*

File: *domain/dom.spheres.replace.mac*

Fig. 8.8 Left: Final crystal structure. The short range order domain distribution has been replaced by the corresponding spherical guest structures. Right: Fourier transform of the crystal with ordered domain distribution.

Summary and more information

- Refinement of structural models based on PDF is becoming more routine.
- PDF refinements as function of ‘r’ give structural information as function of length scale.
- Software is out there.
- More great software is coming ..
- ***Involve your favorite theorist !***

http://www.totalscattering.org


Thank you