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International Centre for Theoretical Physics

United Nations
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International Atomic
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SMR.1825 - 6

Advanced Workshop on

Recent Developments in Nanomaterials

15 - 19 January, 2007, ICTP, Trieste, Italy

Total Scattering: A "Complete" Structural Fingerprint of Nanoparticles Modeling

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Total Scattering and Nanomaterials

Modeling

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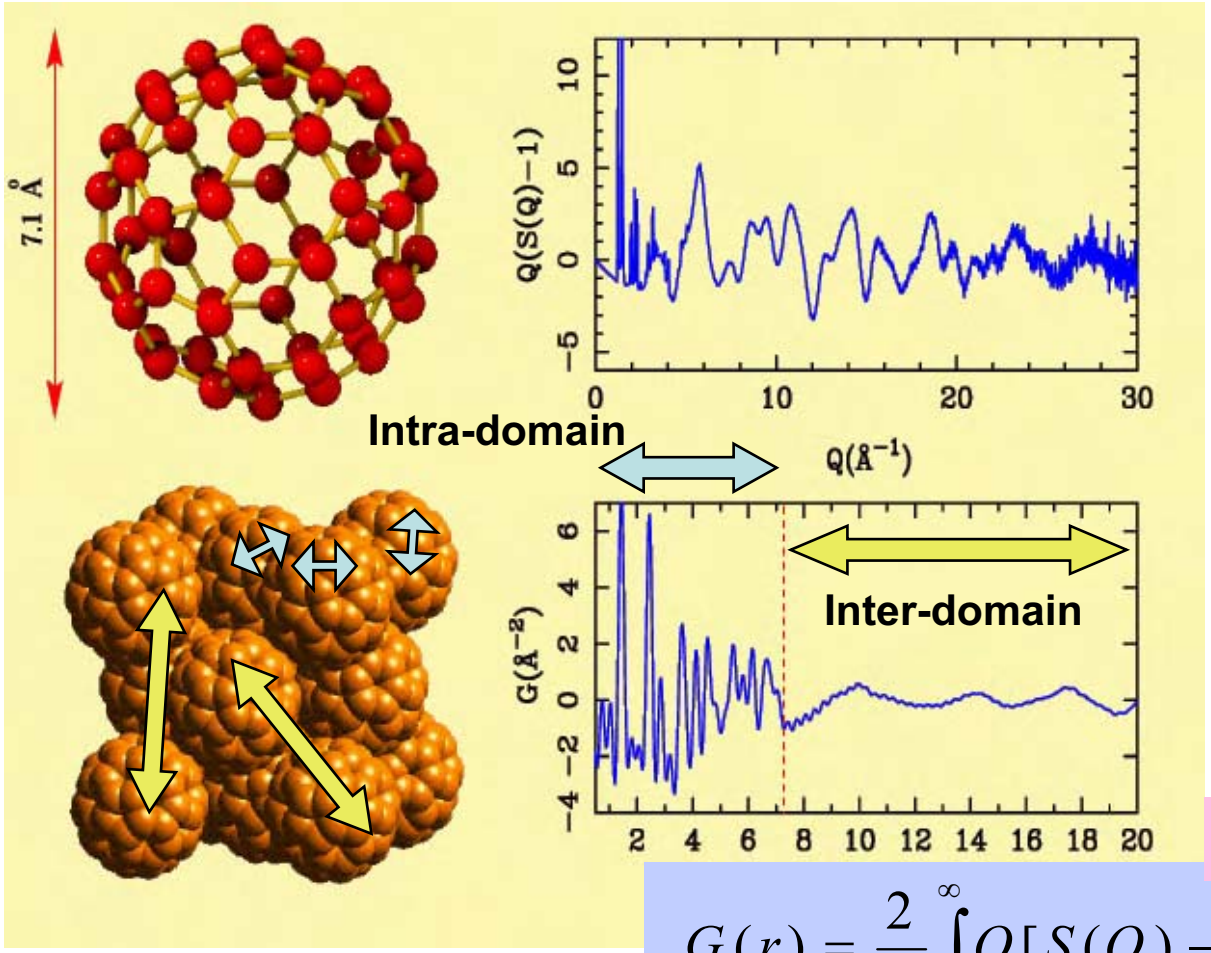
Outline

- What to do with your PDF ?
- Modeling base on a structural model
  - A new parameter – *r*
  - Small models: Least square refinements
  - Large models: Reverse Monte Carlo
  - Any model: Evolutionary Algorithms

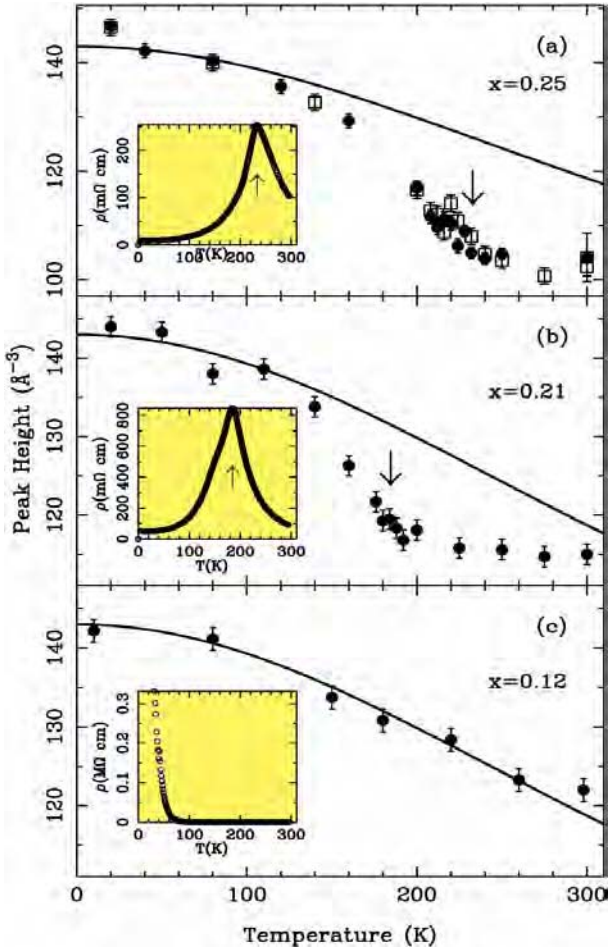
REMINDER: What is a PDF?



$$Q = 4\pi \sin\theta / \lambda$$

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

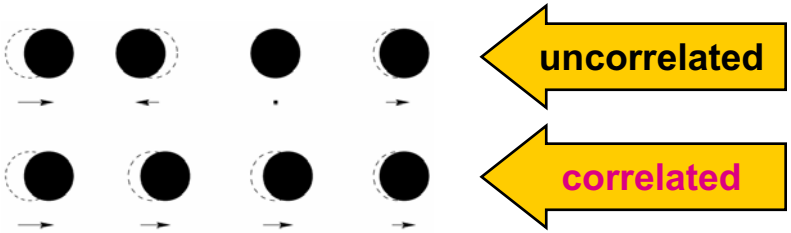
PDF analysis: Analysis of individual peaks



- Temperature dependence of PDF O-O peak height of $La_{1-x}Ca_xMnO_3$ at *r = 2.75Å*.
- Peak height is inverse of peak width (assuming constant number of neighbors).
- Sharper/higher PDF peak corresponds to regular octahedra ⇒ PDF peak height is *relative measure of proportion of sample in delocalized Z phase.*

Billinge et al., *Phys. Rev. Lett.* **77**, 715 (1996)

PDF analysis: Analysis of individual peaks

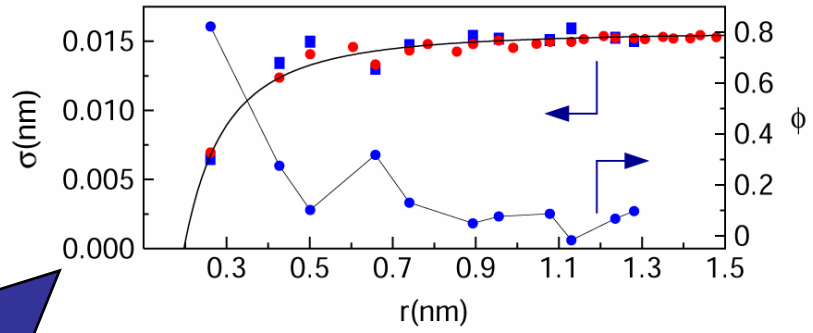


- Correlated motion results in sharpening of near neighbor PDF peaks.
- Empirical correction

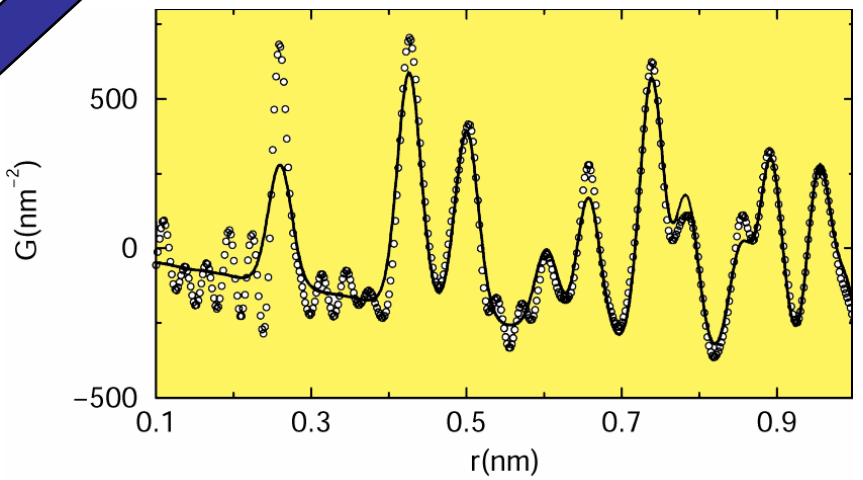
$$\sigma_c = \sqrt{\sigma_0 - \delta / r^2 - \gamma / r}$$

- *Future*: Extraction of phonons ??

PDF peak width of InAs



Calculated PDF without "δ" of InAs

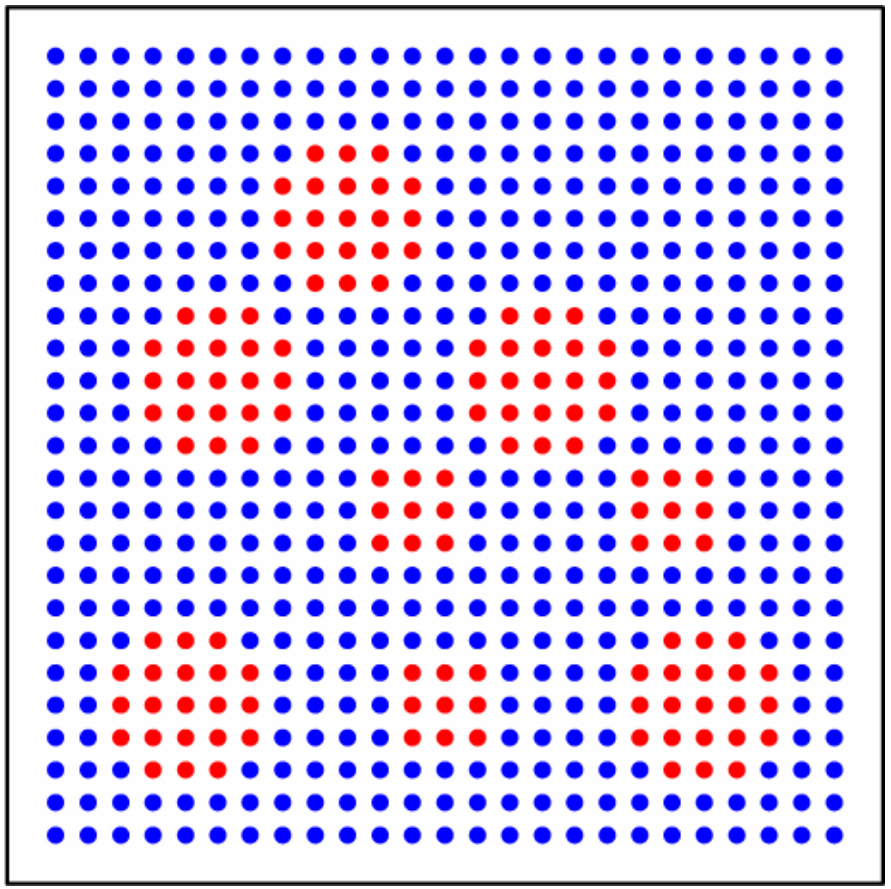


Jeong et al., *J. Phys. Chem. A* **103**, 921 (1999)

A new parameter

Refinement range *r*

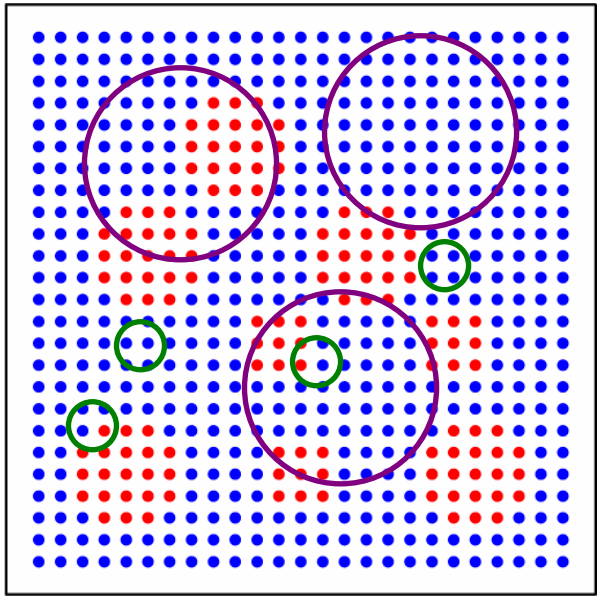
Refinement range – length scales in structure

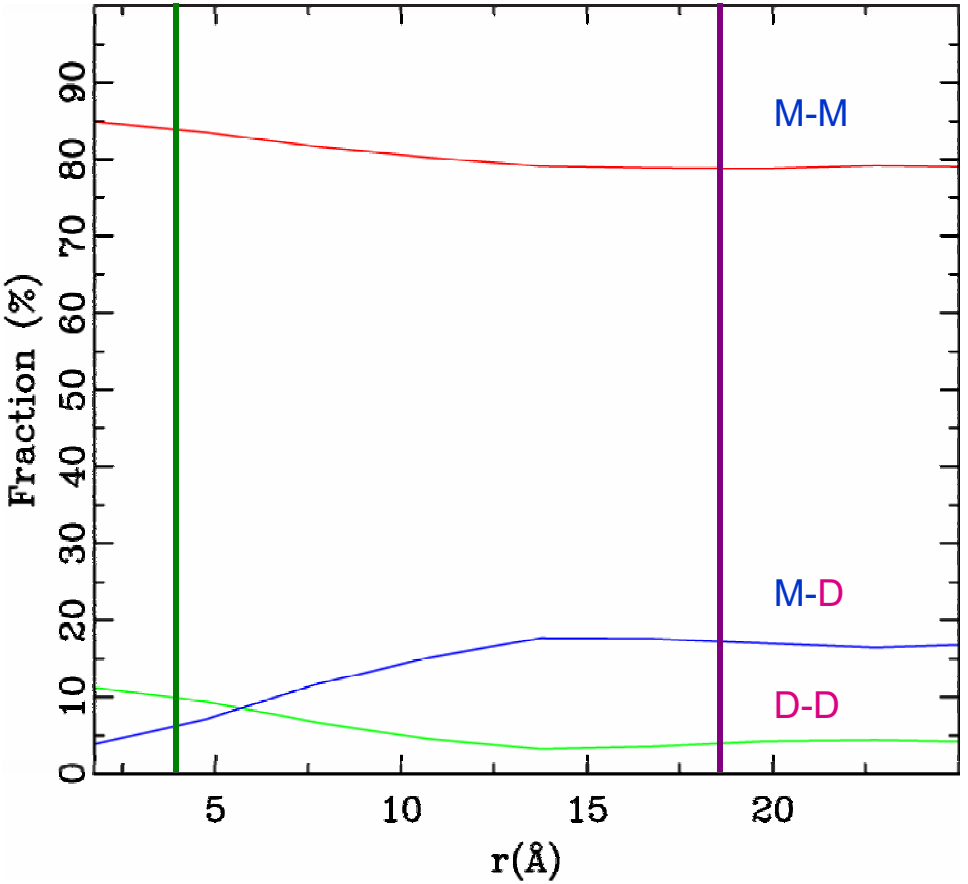


- Simulated structure of 20x20x20 unit cells.
- Matrix (M): blue atoms
- Domains (D): red atoms, spherical shape, d=15Å.
- Simulated using DISCUS.

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



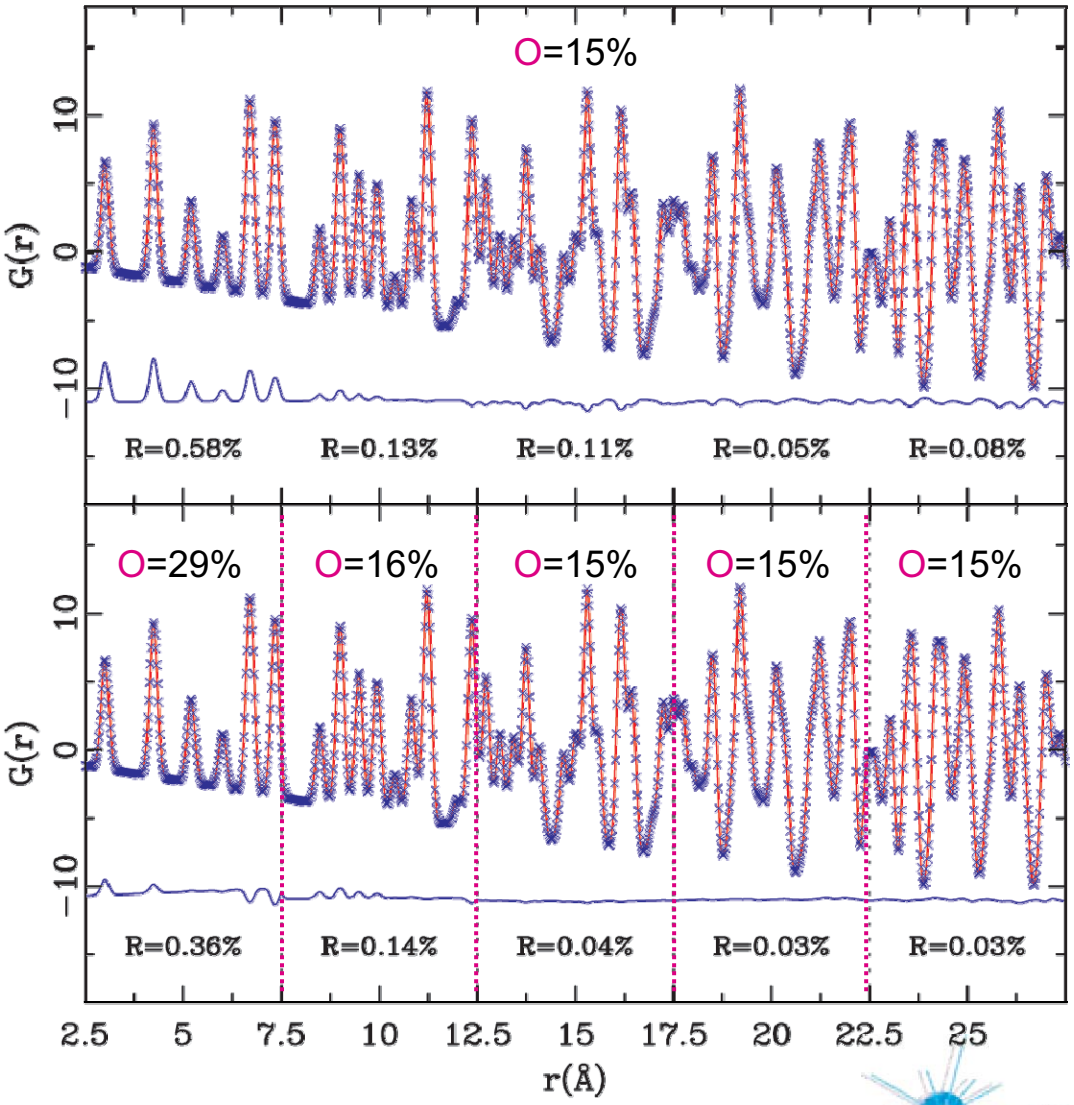


r < r>Domain size:
Many D-D and M-D pairs

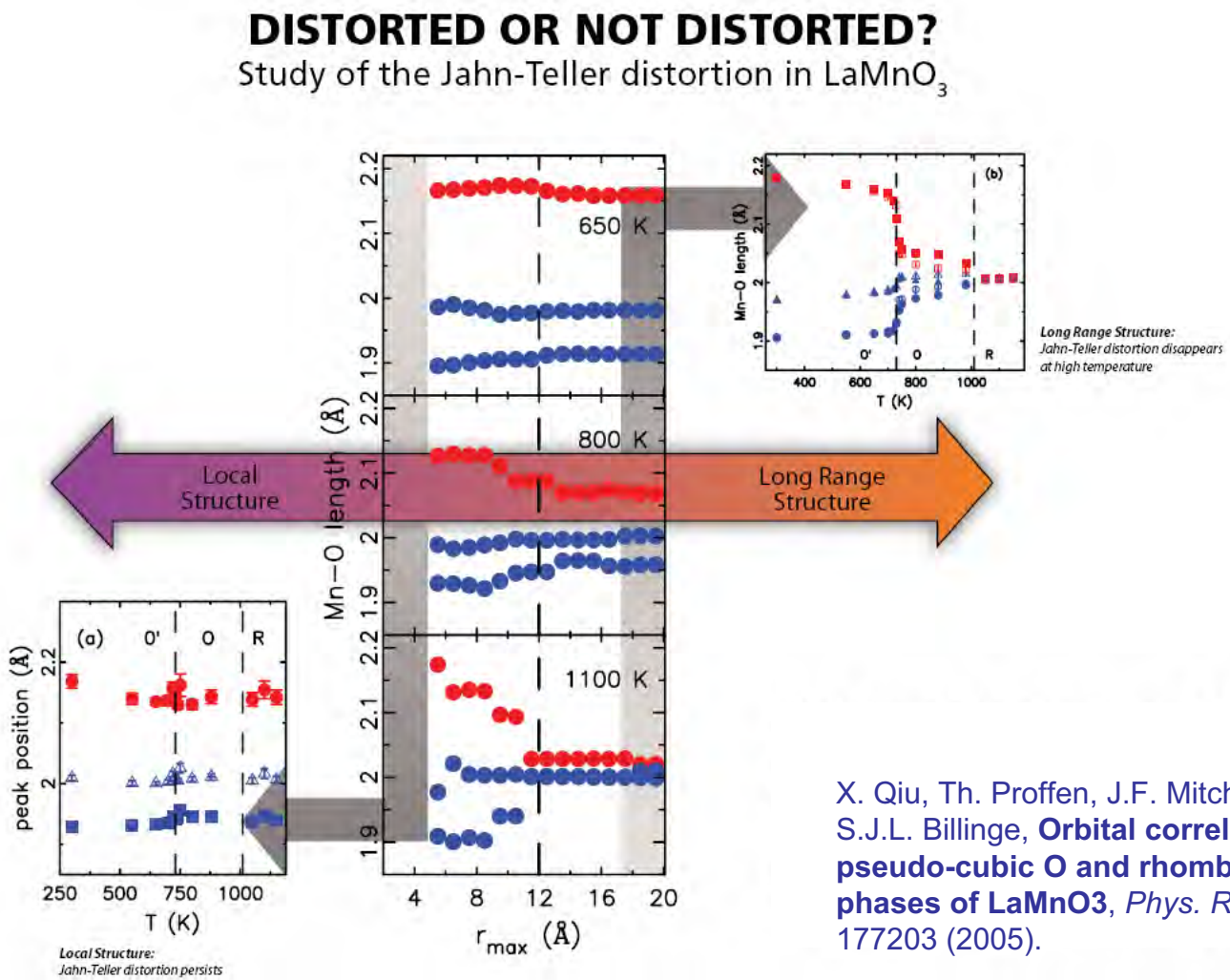
r > Domain size:
NO D-D contribution

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 the PDF from a structural model

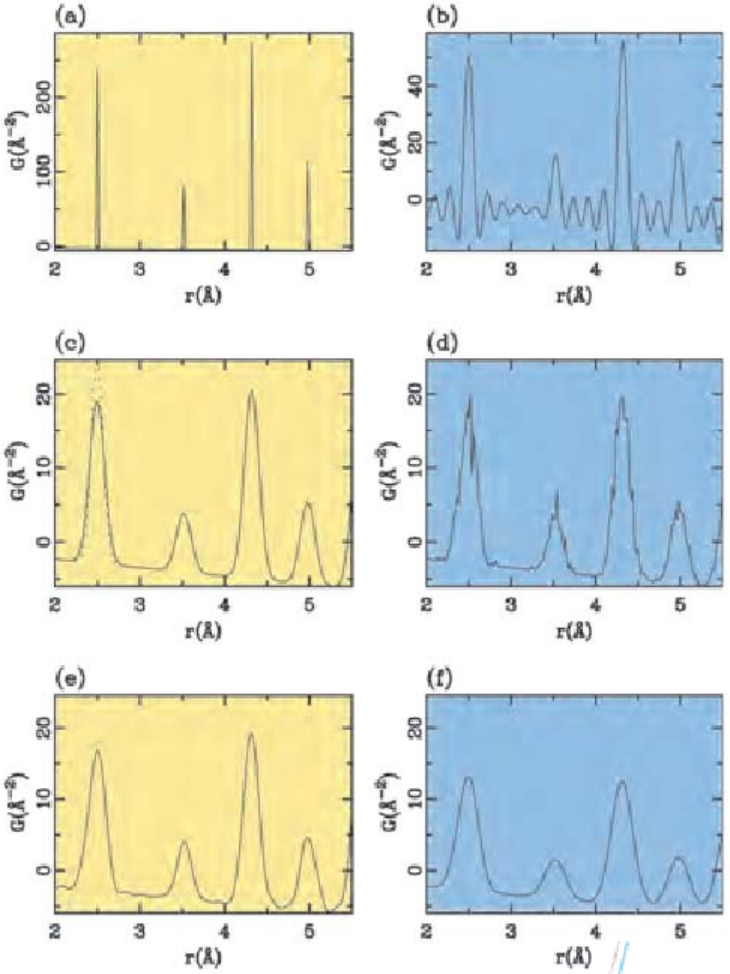
Calculating a PDF ..

- Calculating a PDF from a structural model:

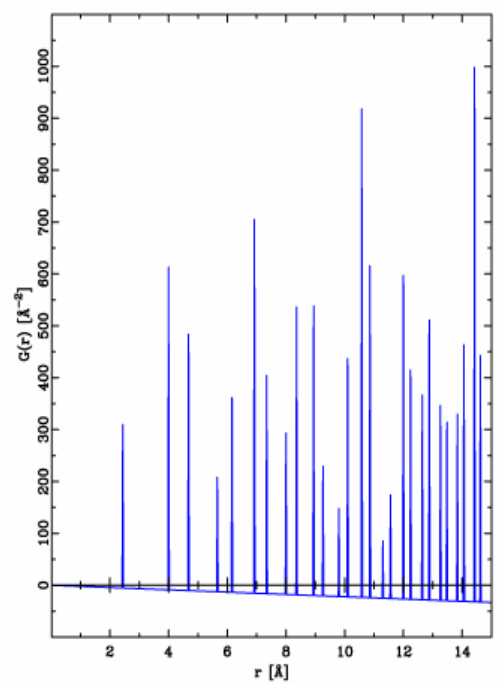
$$G(r) = \sum_{ij}\left[\frac{b_i b_j}{\langle b\rangle^2}\delta(r - r_{ij})\right] - 4\pi r\rho_0$$

- Thermal motion
  - Small crystal ⇒ convolution of $\delta(r\text{-}r_{ij})$ with distribution function (*PDFFIT*)
  - Large crystal ⇒ actual displacements & ensemble average (*DISCUS*)

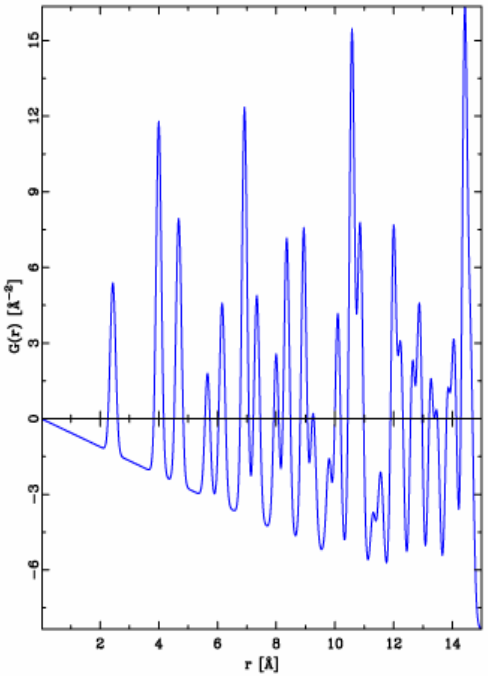
- Termination ripples
  - Multiplication with step function in reciprocal space gives convolution with $\sin(Q_{max}r)/r$ in real space.



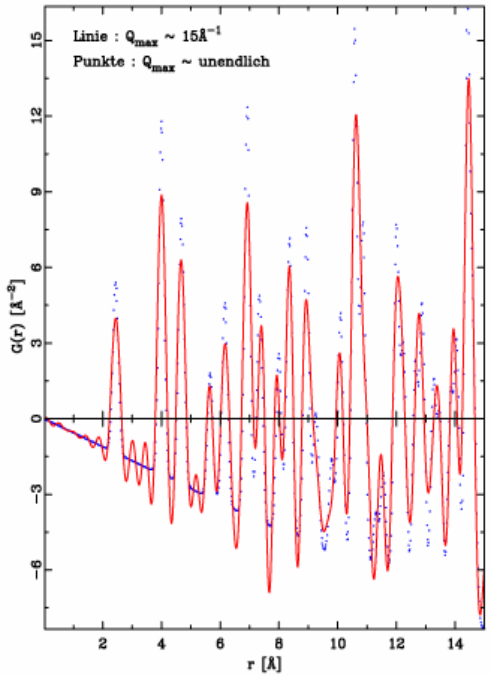
Calculating a PDF: thermal motion



'perfect'

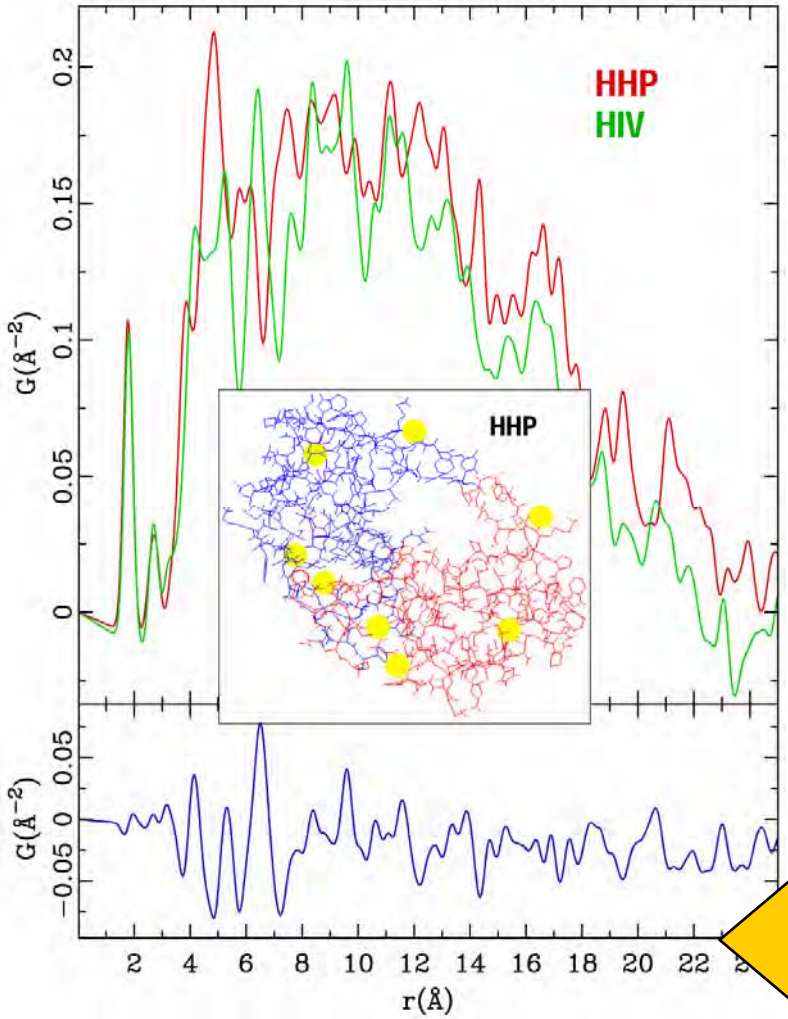


thermal motion



termination ripples

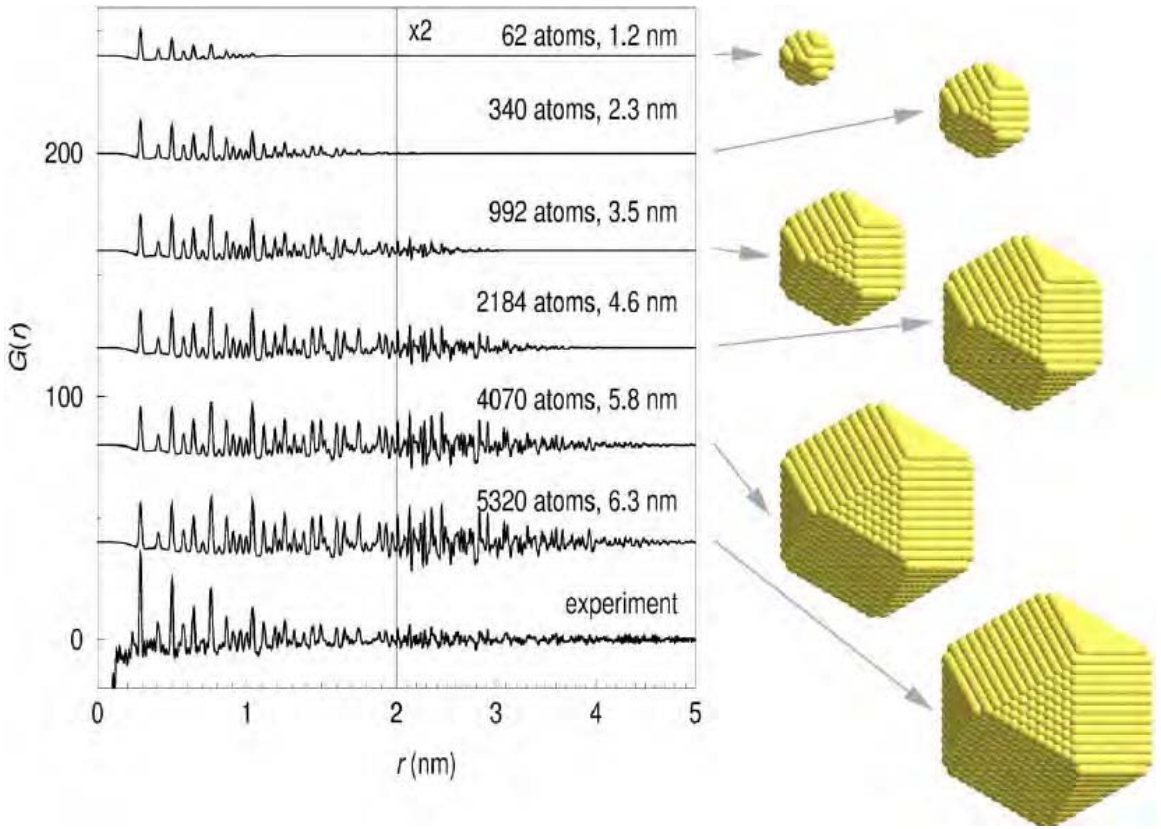
Calculating the PDF ..



- **Calculation of PDFs of any kind of structure.**
- **Applications:**
  - 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, ..)

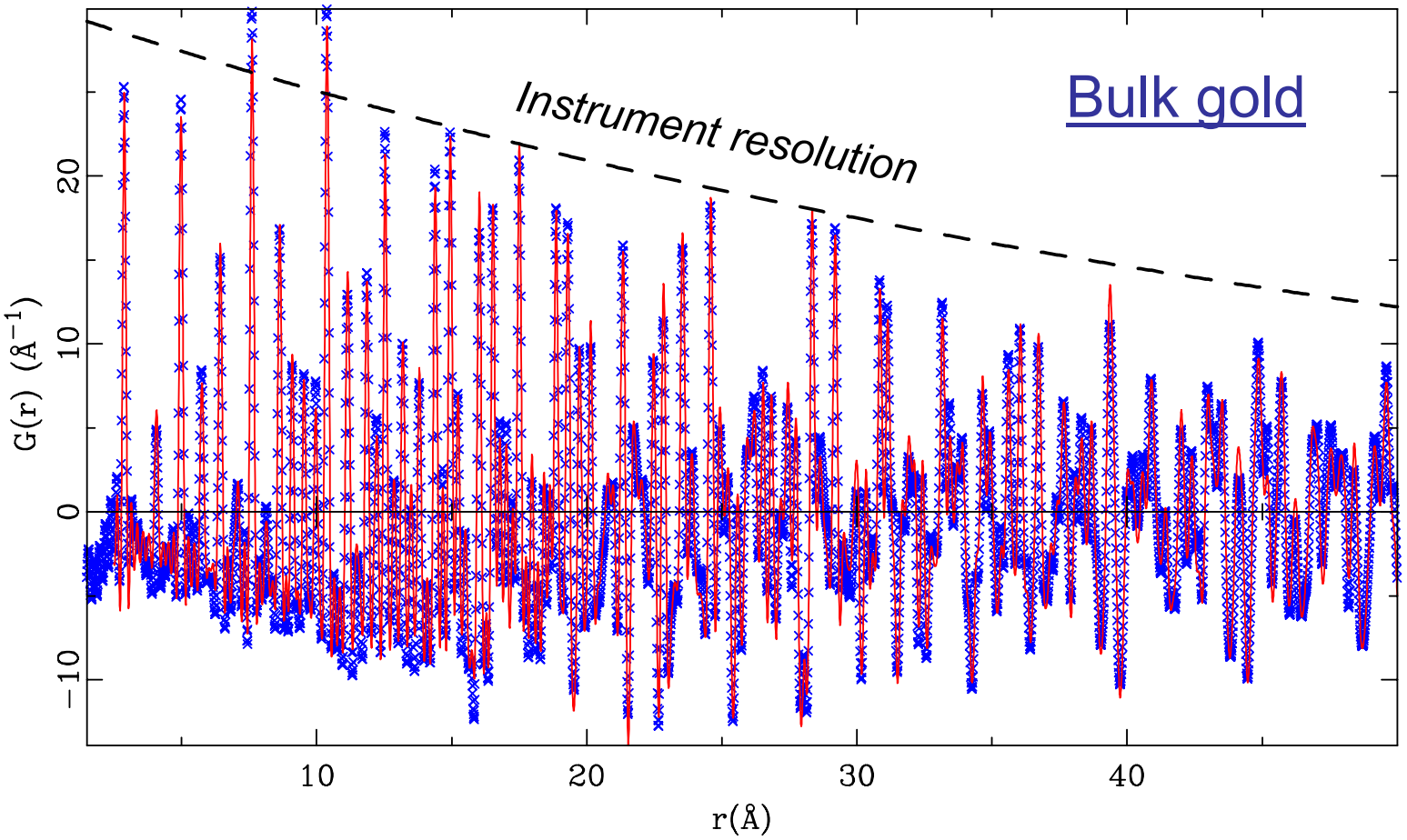
***Se* differential PDF of HIV protease with flaps closed and open !**

Nanoparticles: Particle size

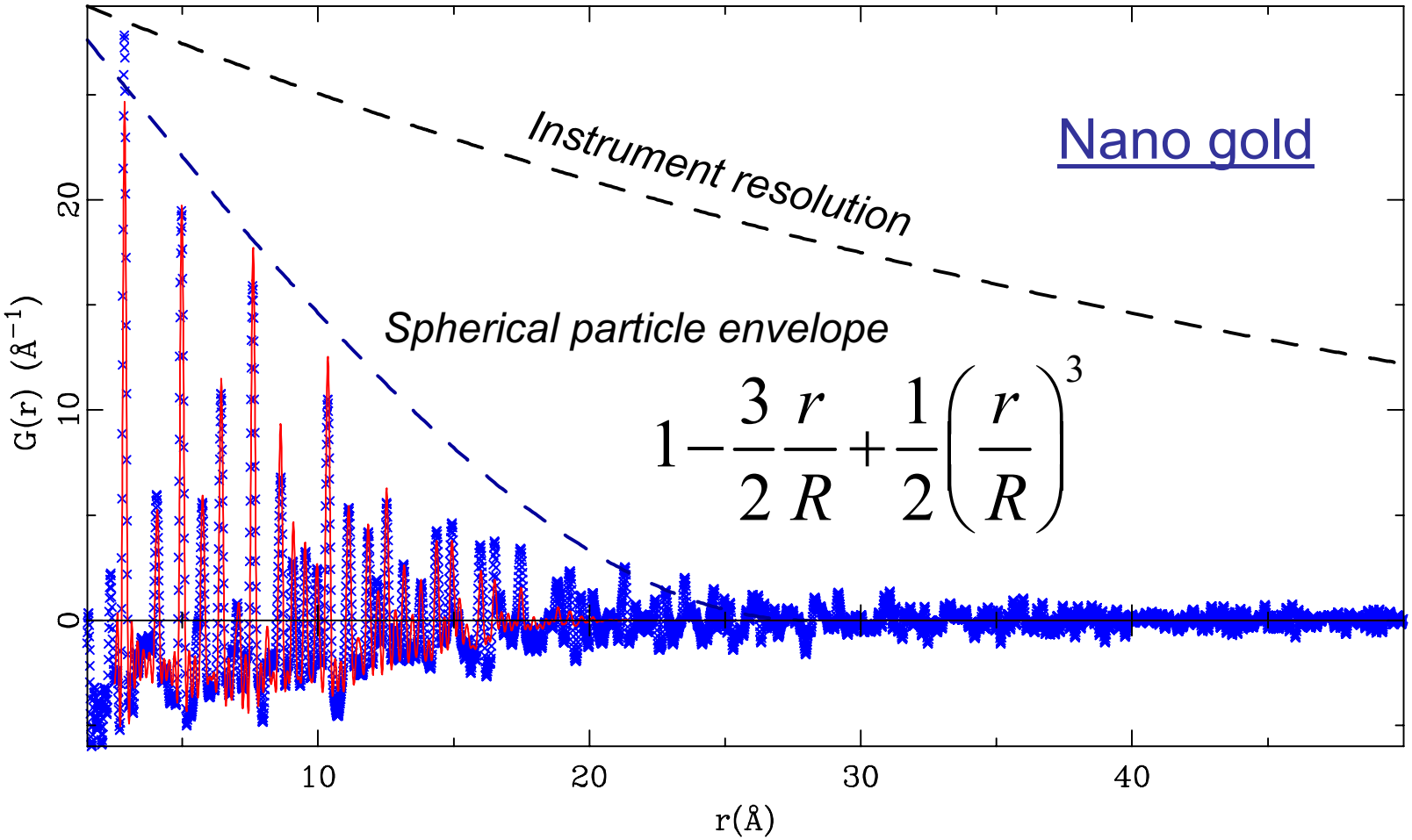


We're dealing with a length scale that can be simulated on an atom by atom basis, perhaps opening the door to extremely detailed refinements.

Nanoparticles: Particle size



Nanoparticles: Particle size



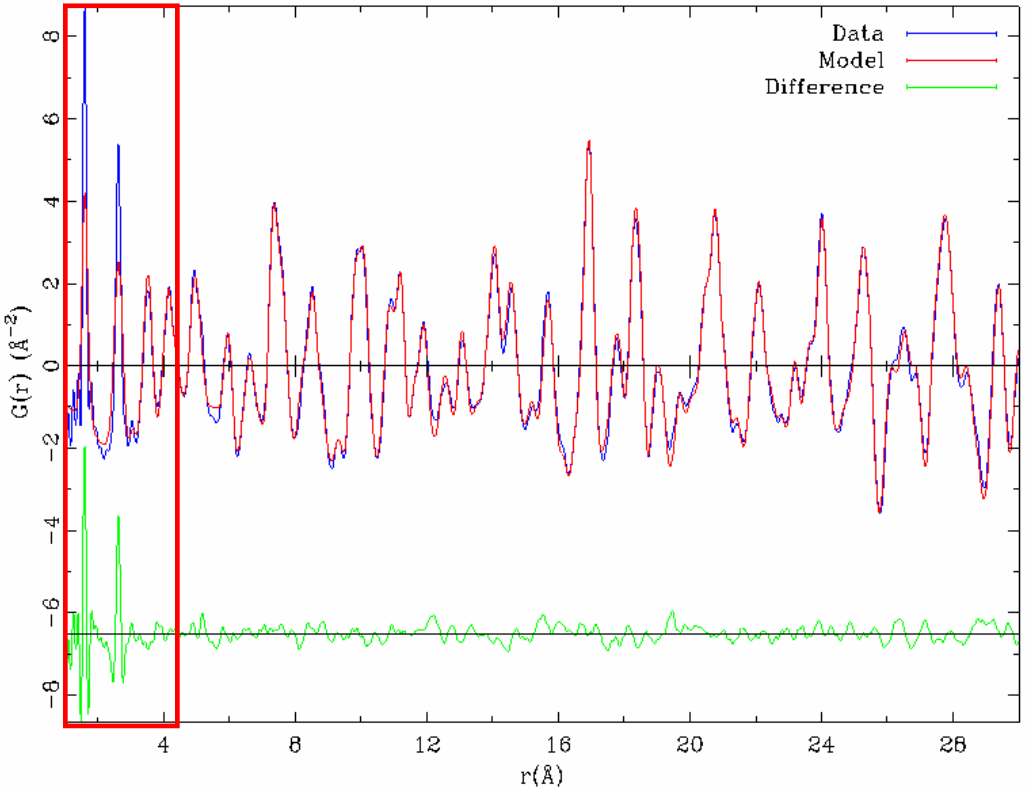
PDFfit

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

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

PDFfit – refinable parameters

Structural	for each phase p
`lat[1..6]`	Lattice parameters $a, b, c, \alpha, \beta, \gamma)$
`delt[p]`	Dynamic correlation factor δ
`srat[p]`	Peak width ratio for $r < r_{cut}$
`csca[p]`	Scale factor f_p
Per atom	for each atom n in phase p
`x[n]`	x-position (fractional coordinates)
`y[n]`	y-position
`z[n]`	z-position
`o[n]`	Occupancy
`u[1..6,n]`	Anisotropic thermal parameter U_{ij}
Experimental	for each data set s
`dsca[s]`	Overall scale factor f_s
`qsig[s]`	Resolution factor σ_Q

PDFfit – parameter coding

There is no predefined relation between structural variables and refinement parameters `p[i]`

Example:

Consider rigid molecule consisting of two atoms, one at $(\frac{1}{4}, 0, 0)$ and one at $(-\frac{1}{4}, 0, 0)$. The rotation of the molecule around the z-axis through the center of the molecule (conveniently located at $(0, 0, 0)$) shall be modeled by a single refinement parameter, the rotation angle ψ. This rotation can be described by the following matrix

$$R = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

PDFfit – parameter coding

```
 1 r[1]=x[1]
 2 r[2]=y[1]
 3 r[3]=x[2]
 4 r[4]=y[2]
 5 #
 6 par x[1]=    r[1]*cosd(p[5])+r[2]*sind(p[5]),-1.*r[1]*sind(p[5])+r[2]*cosd(p[5])
 7 par y[1]=-1.*r[1]*sind(p[5])+r[2]*cosd(p[5]),-1.*r[1]*cosd(p[5])-r[2]*sind(p[5])
 8 par x[2]=    r[3]*cosd(p[5])+r[4]*sind(p[5]),-1.*r[3]*sind(p[5])+r[4]*cosd(p[5])
 9 par y[2]=-1.*r[3]*sind(p[5])+r[4]*cosd(p[5]),-1.*r[3]*cosd(p[5])-r[4]*sind(p[5])
10 #
11 p[5]=4.5
```

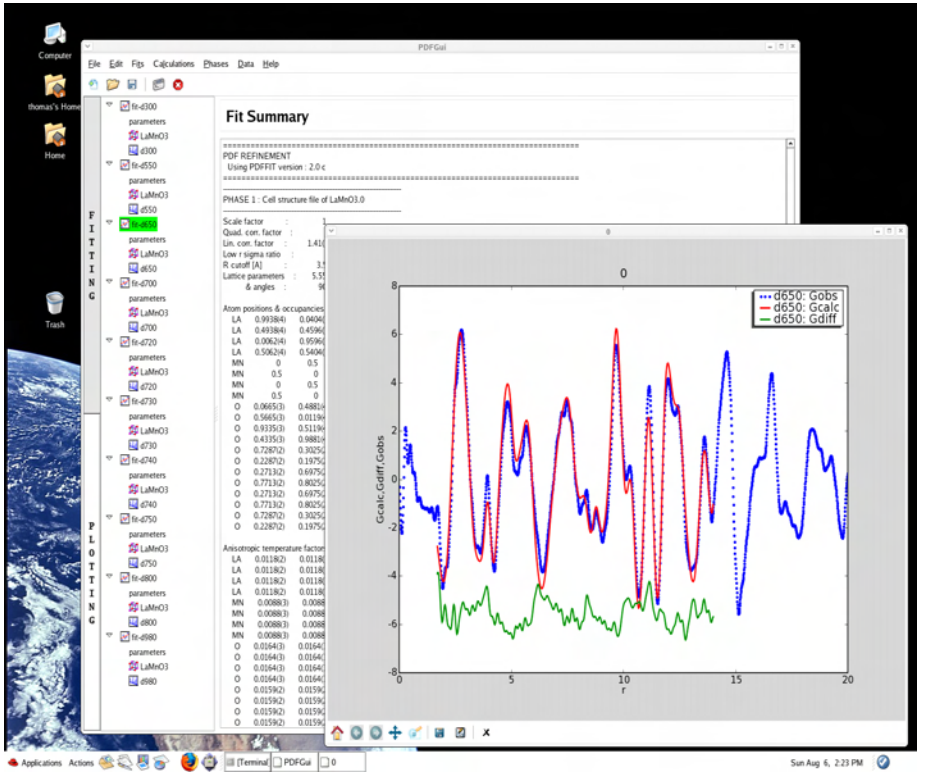
Diffuse package: DISCUS, PDFfit and DIFFEV

- 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).

Next generation PDFfit (under development)

- PDFfit2 and PDFgui
- Part of the DANSE project.
- NSF award of ~$12M.
- Contact: *Simon Billinge*



- Link: http://wiki.cacr.caltech.edu/danse/index.php/Main_Page

RMC

Shaking a big box of atoms.

Courtesy of M. Tucker, ISIS

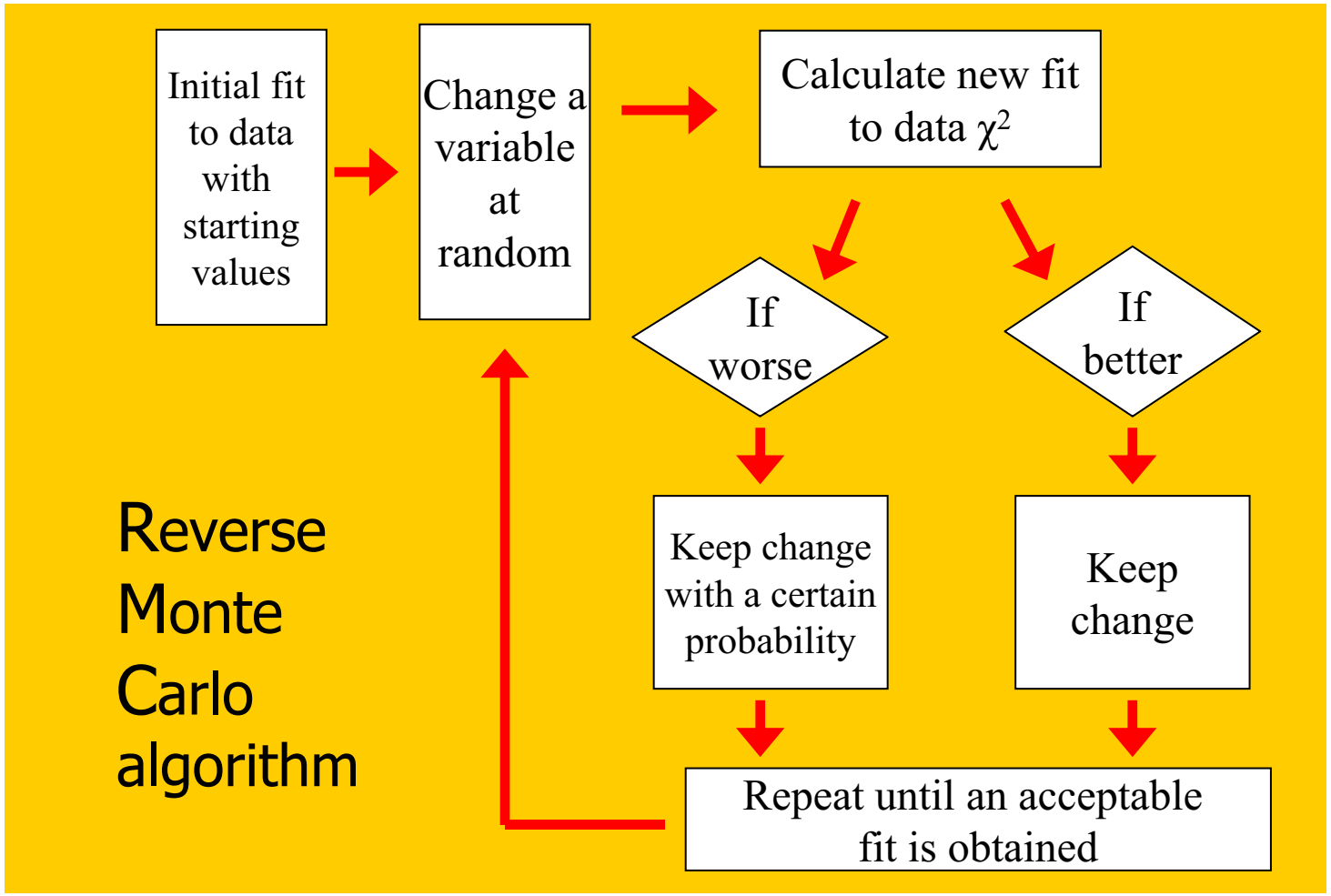
Reverse Monte Carlo

- 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 ?



Adding constraints

$$\chi^2 = \sum_j \left| F_{\text{calc}}(Q_i) - F_{\text{expt}}(Q_i) \right|^2 / \sigma^2_{F(Q_j)} + \sum_j \left| T_{\text{calc}}(r_i) - T_{\text{expt}}(r_i) \right|^2 / \sigma^2_{T(r_j)} + \sum_{\text{Si–O}} \left| r_{\text{Si-O}} - R_{\text{Si-O}} \right|^2 / \sigma^2_{\text{Si-O}} + \sum_{\text{O–Si–O}} \left| \theta_{\text{O-Si-O}} - \Theta_{\text{O-Si-O}} \right|^2 / \sigma^2_{\text{O-Si-O}} + \sum_j \left| I_{\text{expt}}(t_j) - sI_{\text{calc}}(t_j) \right|^2 / \sigma^2_{I(t_j)}$$

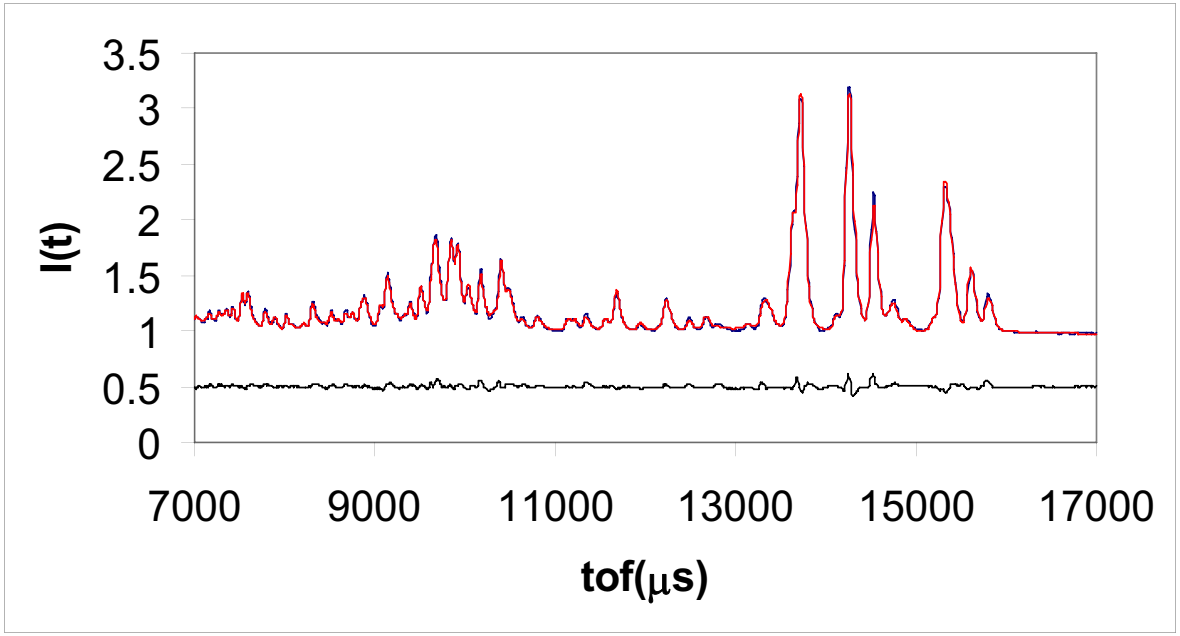
+ anything else you can calculate from the configuration of atoms

Include Bragg intensities ..

Use GSAS to fit :
Peak shape
Background
Lattice parameters

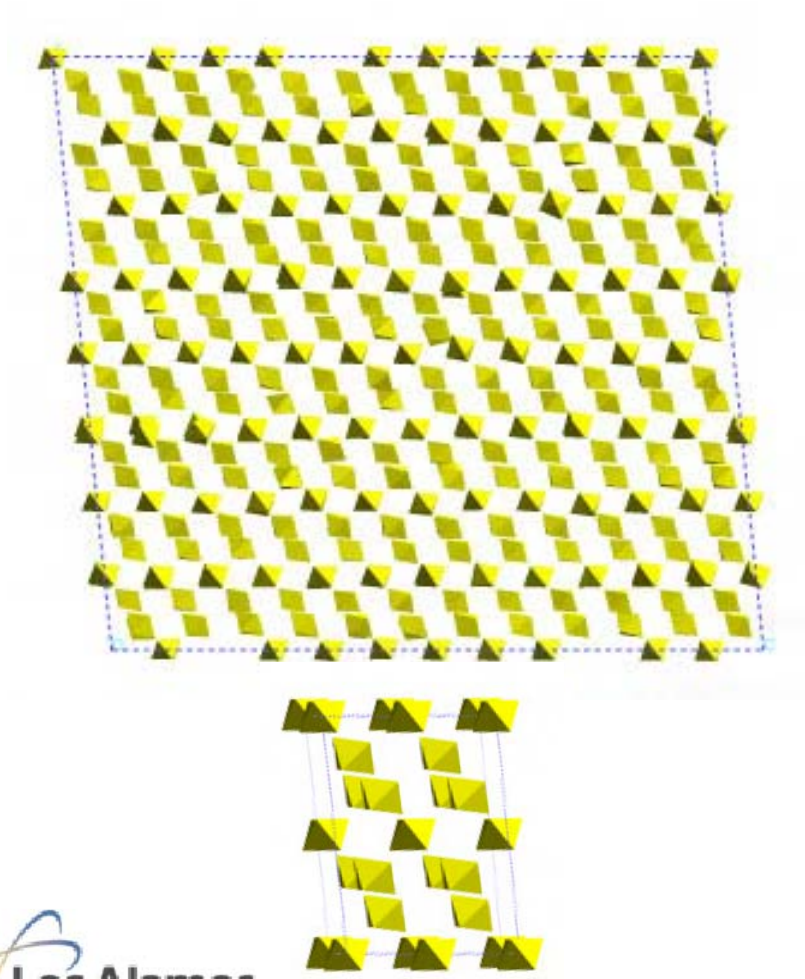
RMCProfile calculates the intensities and then produces the profile.

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

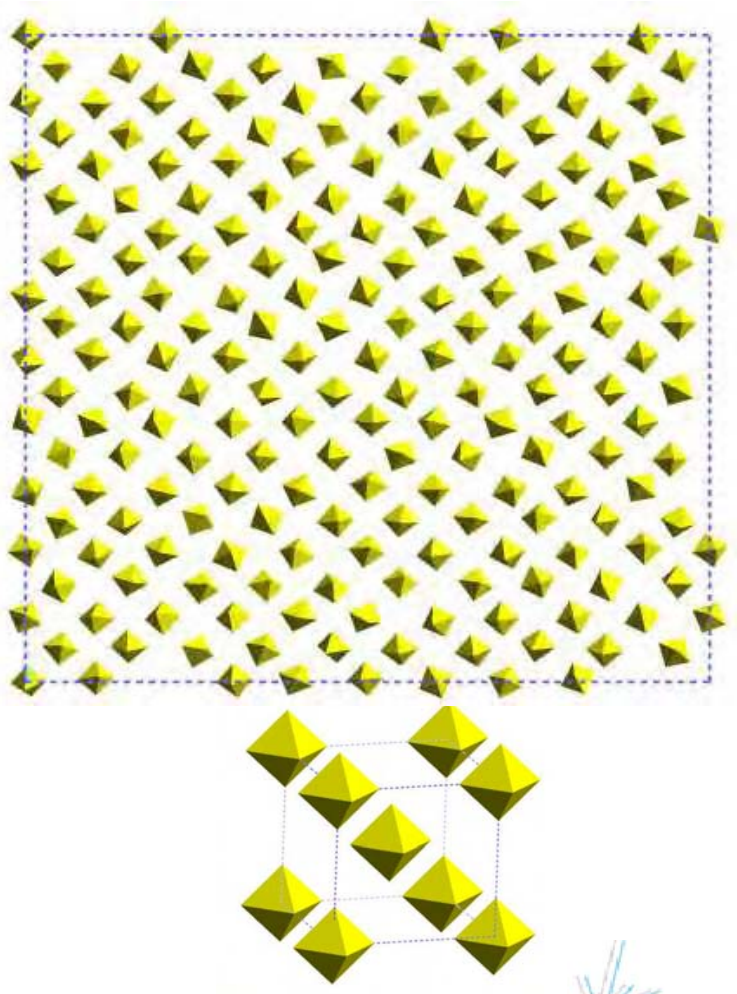


Example: SF_6

(010) Section of SF_6 at 50K



(010) Section of SF_6 at 190K



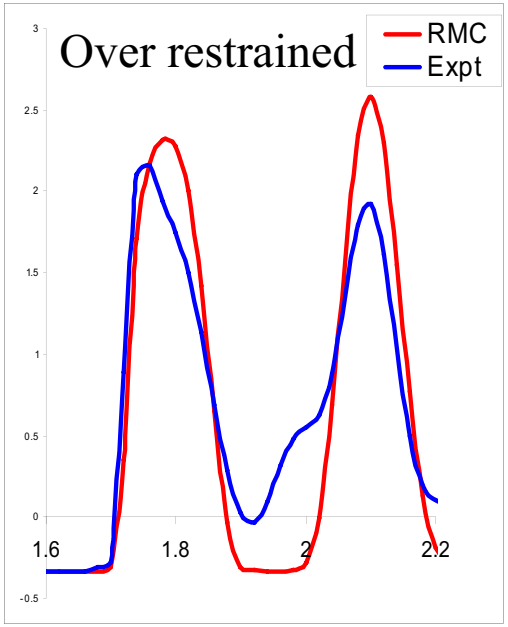
Polyhedral Restraints

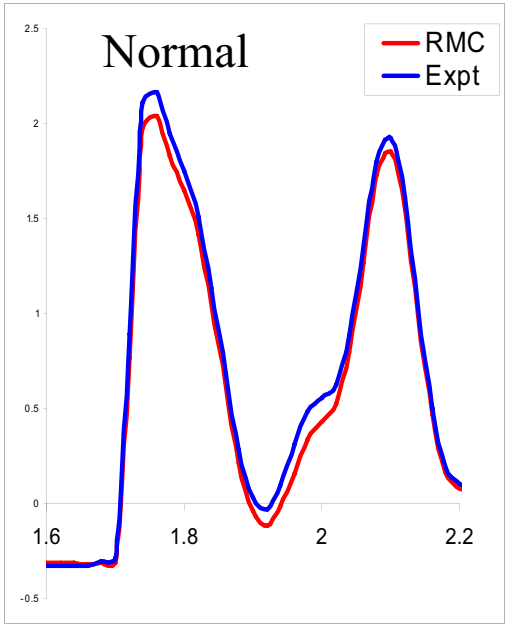
- Tetrahedra
- Octahedra
- Tetrahedra & Octahedra
- Chains
- Triangles
- Tether
- and more

$$+ \sum_{\text{Si–O}} \left| r_{\text{Si}-\text{O}} - R_{\text{Si}-\text{O}} \right|^2 / \sigma^2_{\text{Si}-\text{O}}$$

$$+ \sum_{\text{O–Si–O}} \left| \theta_{\text{O}-\text{Si}-\text{O}} - \Theta_{\text{O}-\text{Si}-\text{O}} \right|^2 / \sigma^2_{\text{O}-\text{Si}-\text{O}}$$

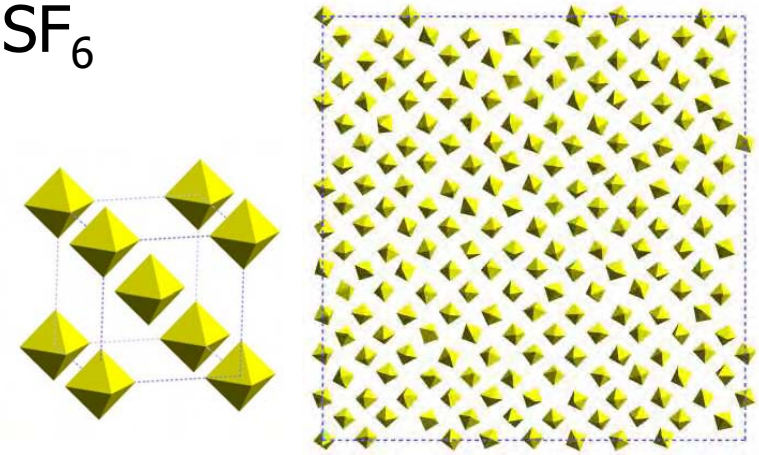
Weighting is weak
to hold things
together while the data
chooses the final shape



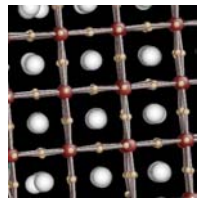


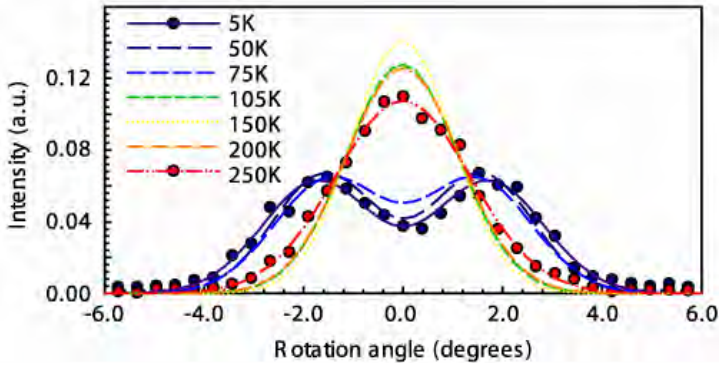
RMC: Examples

SF_6

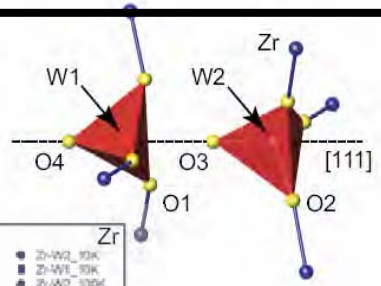


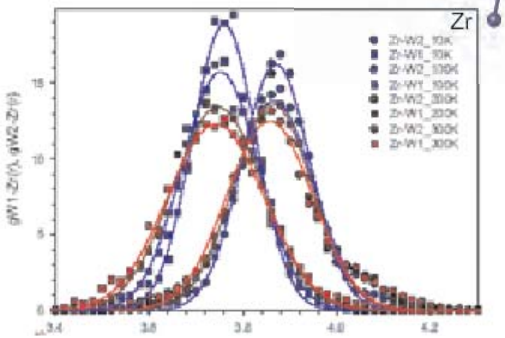
$SrTiO_3$



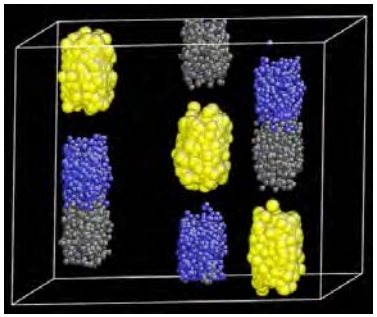


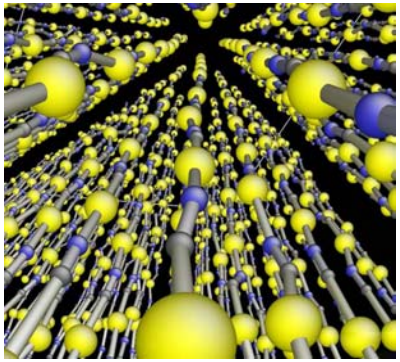
ZrW_2O_8





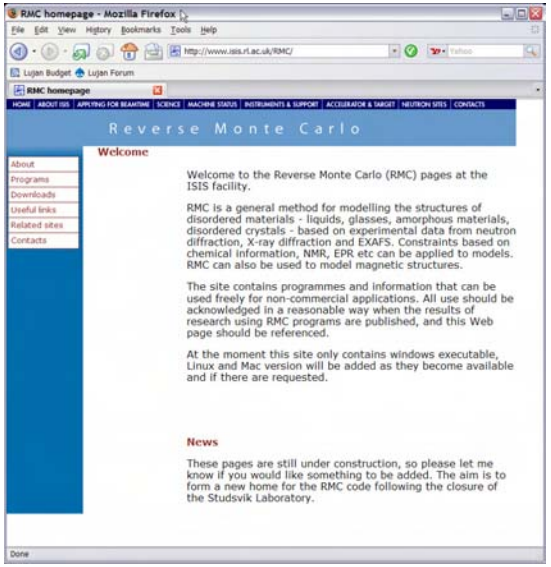
AuCN





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



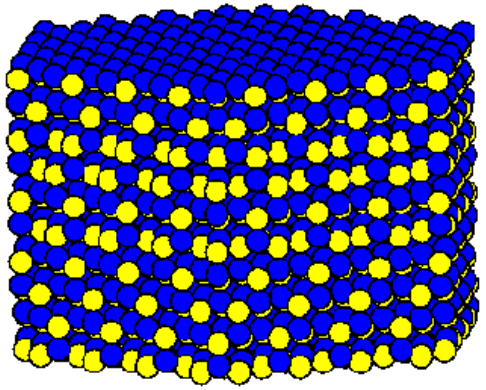
DIFFEV

Refining parameters of a disordered particle/crystal

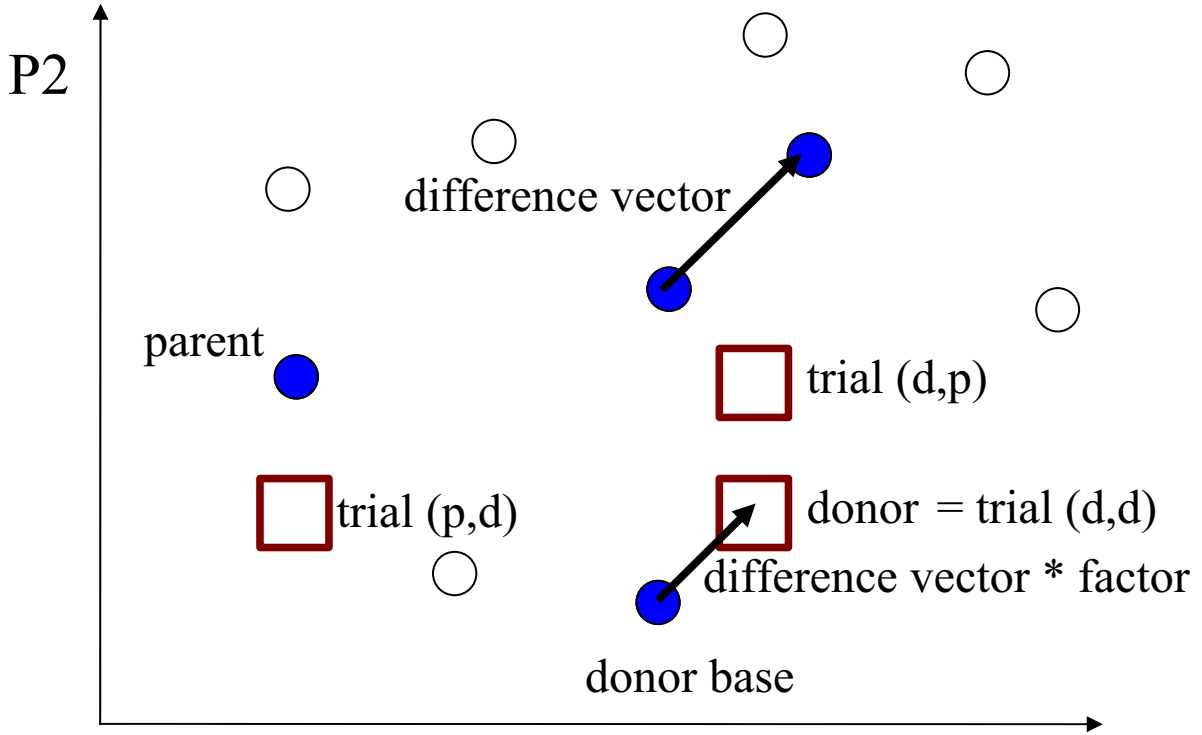
Courtesy of R.B. Neder,
U Würzburg

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

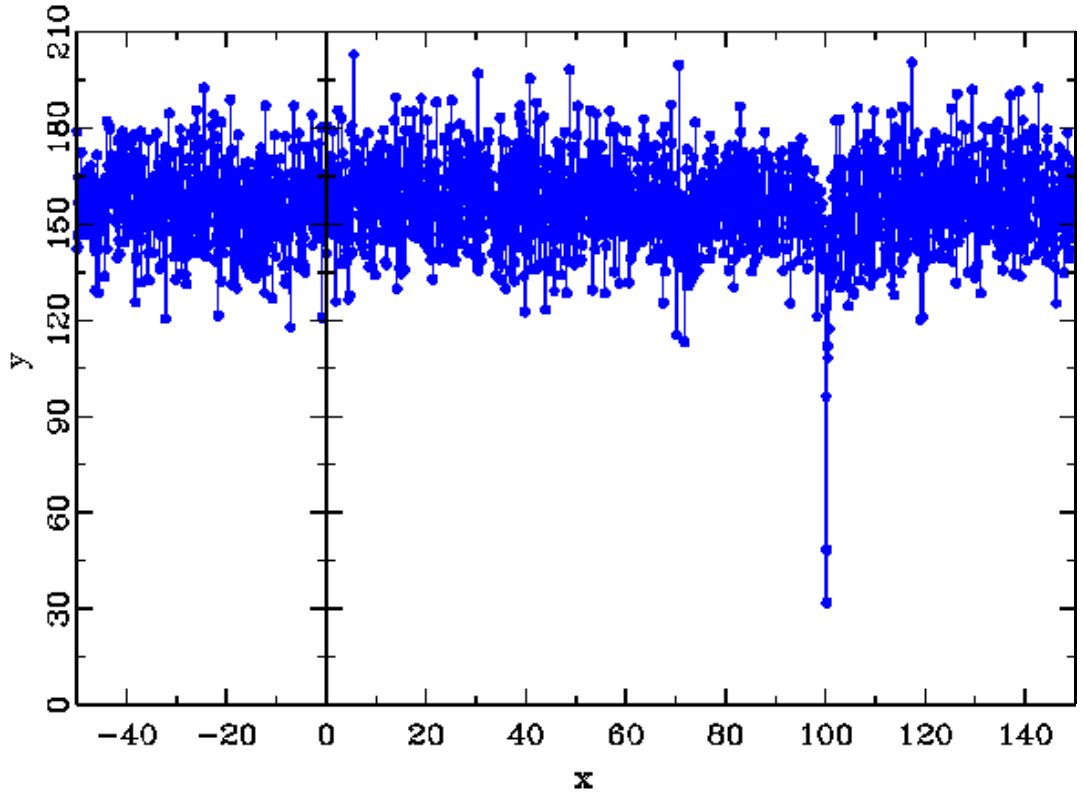


Differential Evolution



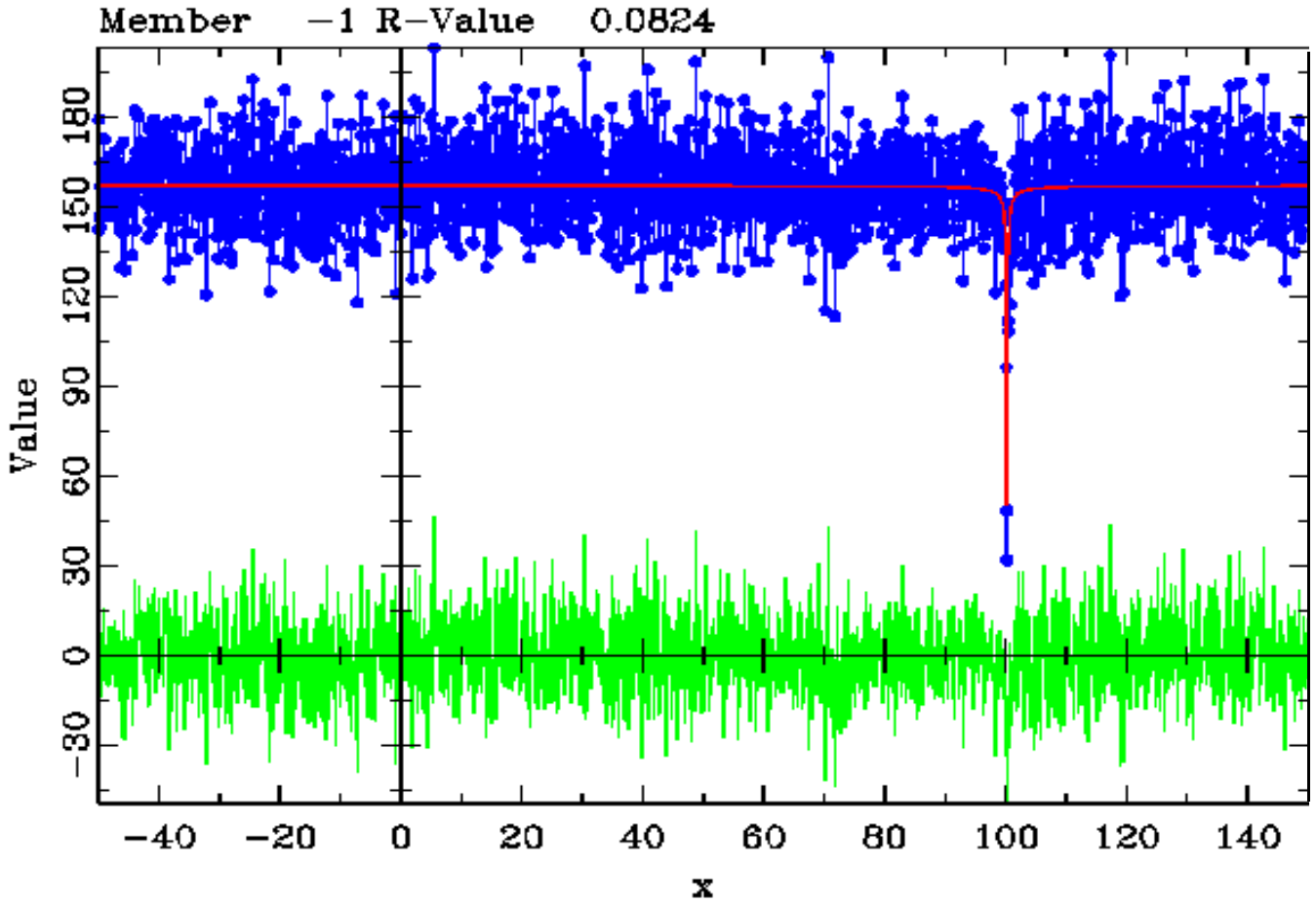
choose parent
choose difference vector
add to donor base to get donor
cross-over between parent and donor
compute cost function, keep better of parent/trial

Example: Nasty function



$$100 * \arctan\left(\frac{|\ x - 100.23\ |}{0.05}\right) + \text{noise}$$

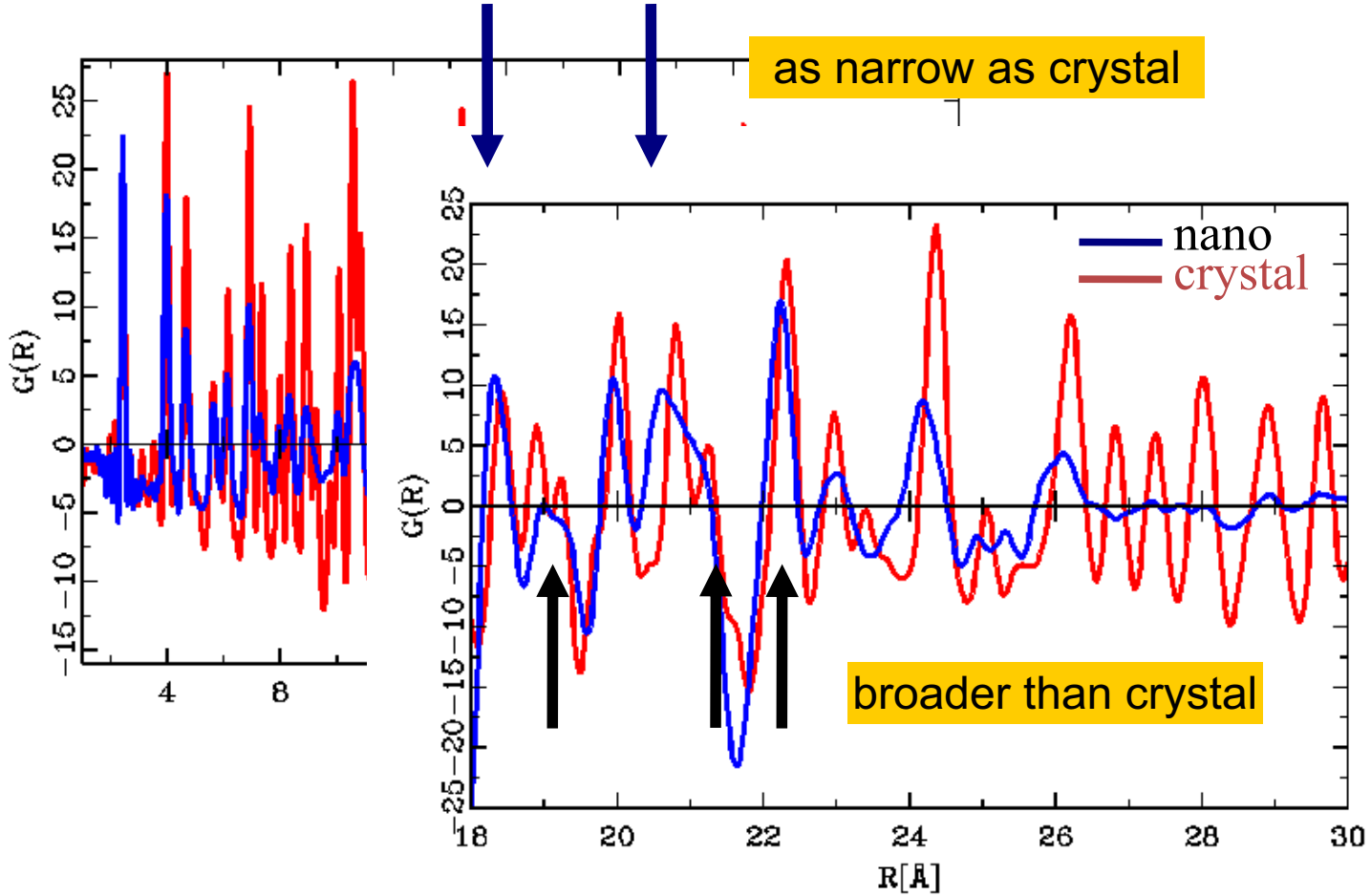
Example: Nasty function



$$99.93 * \arctan\left(\frac{\left| x - 100.23 \right|}{0.049}\right)$$

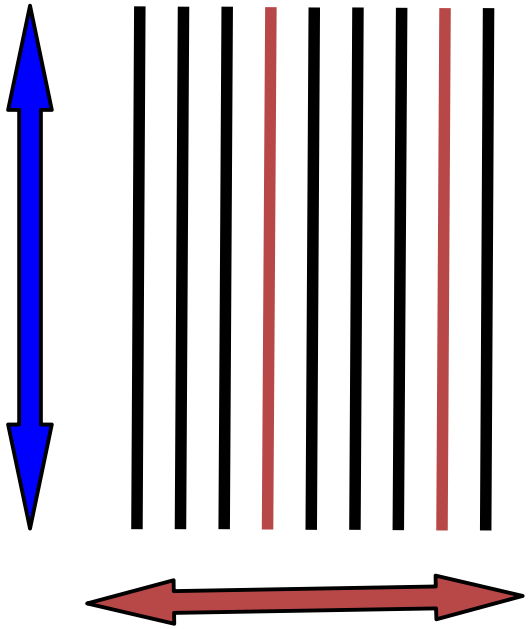
Example: ZnSe nanoparticles

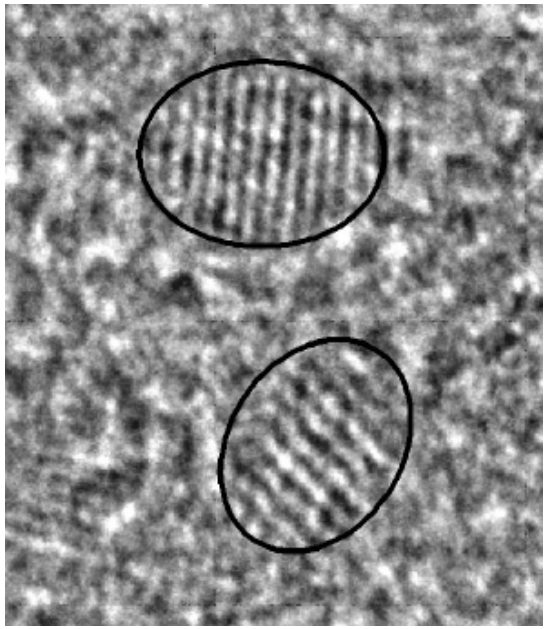
nanocrystalline ZnSe
crystalline ZnSe



Example: ZnSe nanoparticles

structural coherence

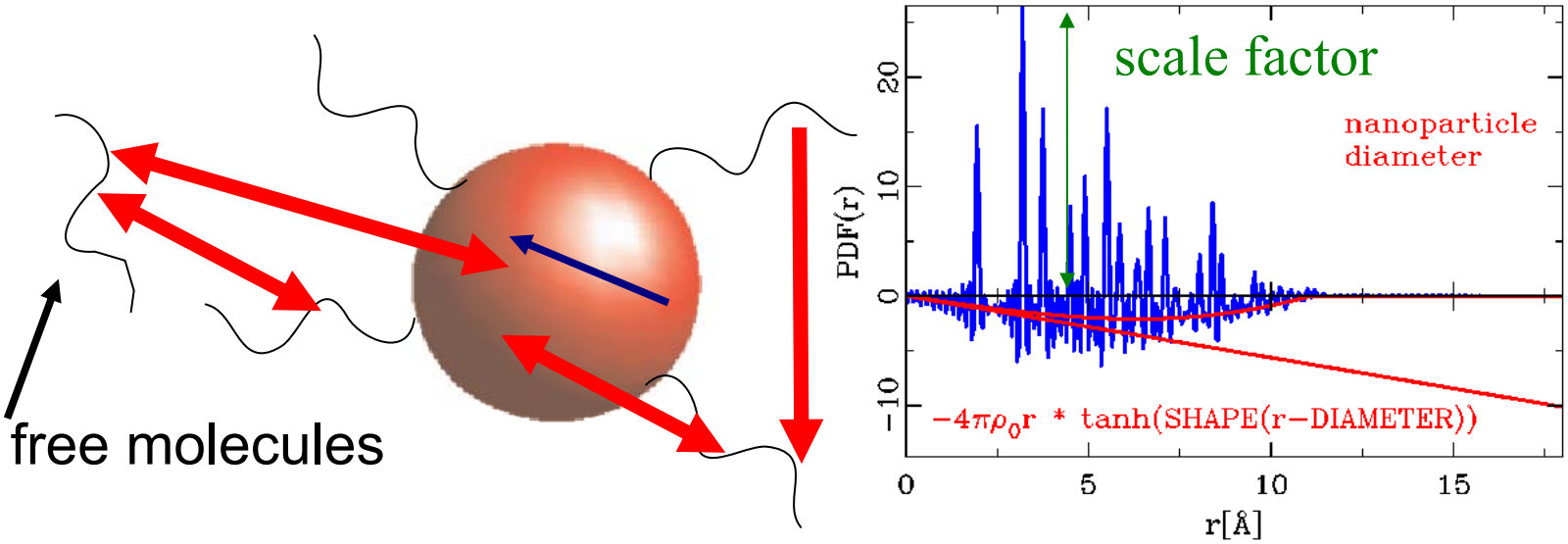




loss of coherence due to stacking faults

PDF of nanoparticles

Nanoparticle with core and stabilizing molecules

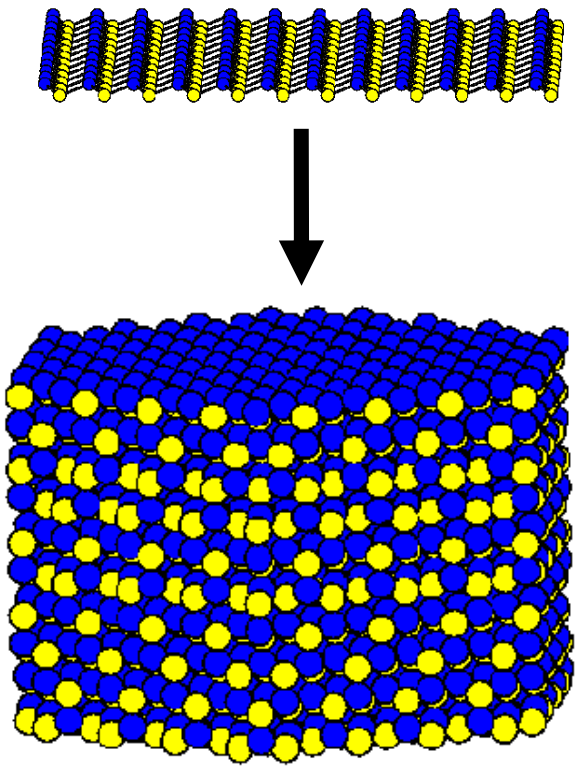


Vectors within core defined by model structure

ill defined vectors

volume ratio

Example: ZnSe nanoparticles - Model



{110} and {001}

create a large single Wurtzite layer A/B

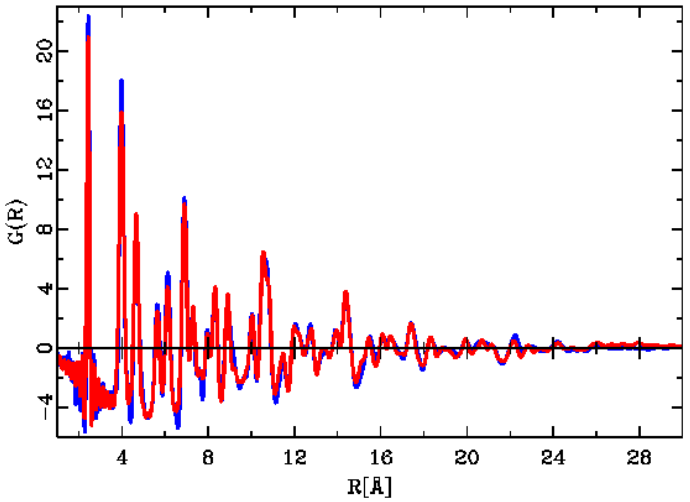
- Stack along c (with faults)
- Cut to proper size
- Calculate PDF / powder pattern

Repeat and average

Repeat with new set of parameter
using a Differential Evolutionary Scheme

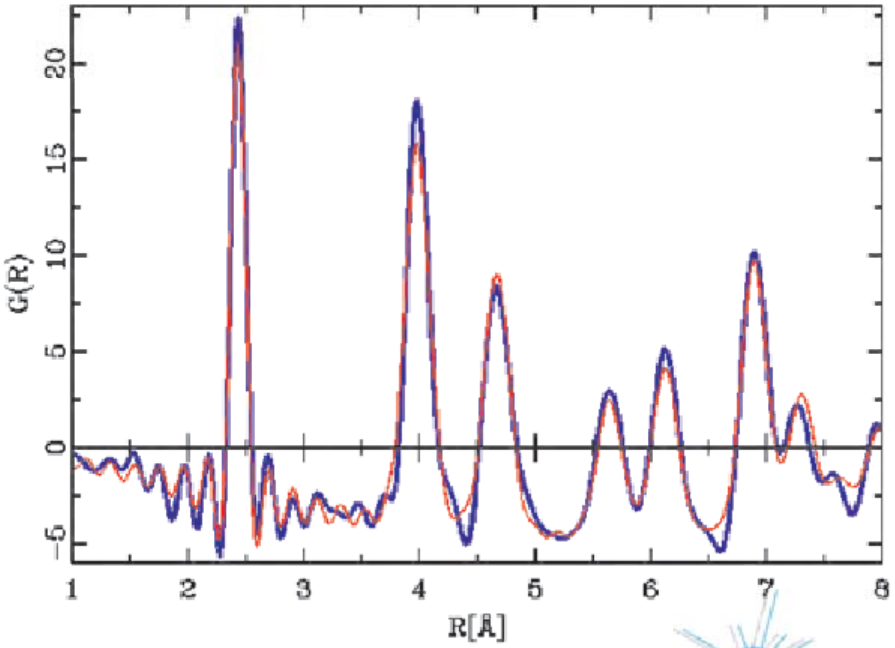
Software: DISCUS and DIFFEV

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).

exp
calc



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

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 again