

Small box modelling using PDFGui

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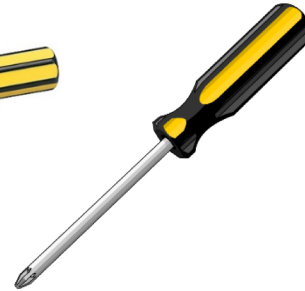
September 18, 2018

Outline

- Introductory notes on PDF approach
- On small box modelling in general and PDFgui in particular
- PDFgui parameters, concepts, and layout
- Agenda for hands-on part and examples to be covered

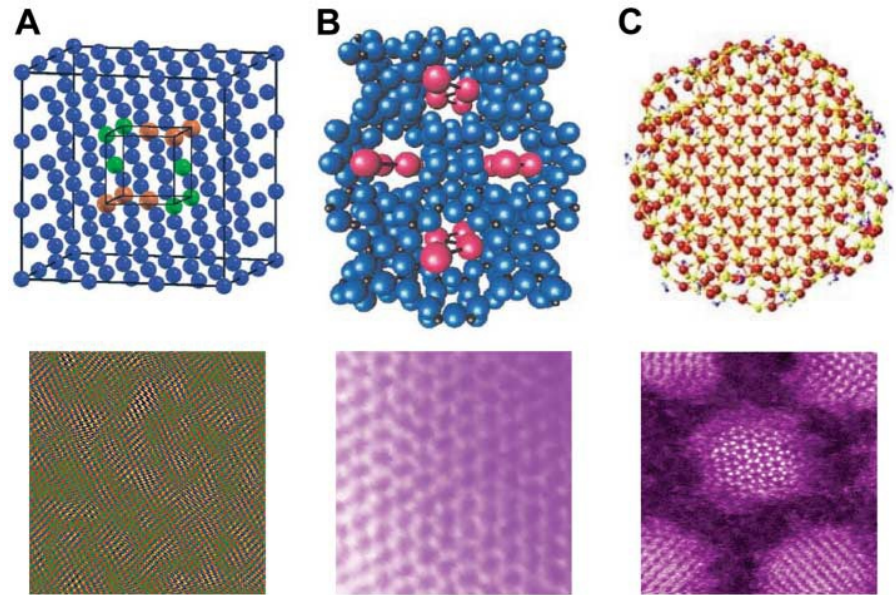
PDF approach

- Choosing the right tool for the problem



PDF approach

- Non crystalline materials
(liquids, amorphous solids, polymers)
- Nanoscale materials
- Disordered crystalline systems
with nanoscale heterogeneities



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



PDF approach

- Considering scattering contrast

hydrogen 1 H 1.00794	beryllium 4 Be 9.012182	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180	holmium 67 Ho 164.930	erbium 68 Er 167.255	thulium 69 Tm 168.930	ytterbium 70 Yb 173.054	lutetium 71 Lu 174.967	hafnium 72 Hf 178.49	tantalum 73 Ta 180.948	niobium 41 Nb 92.906	zirconium 40 Zr 91.224	yttrium 39 Y 88.906	strontium 38 Sr 87.62	rubidium 37 Rb 85.468	cesium 55 Cs 132.91	barium 56 Ba 137.33	* 57-70	* *	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.05	lutetium 71 Lu 174.97	berkelium 97 Bk 247.07	californium 98 Cf 251.08	americium 95 Am 243.06	einsteinium 99 Es 252.08	fermium 100 Fm 257.10	mendelevium 101 Md 258.10	nobelium 102 No 259.10	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbinium 112 Uub [273]	ununseptium 114 Uuq [284]	bohrium 107 Bh [264]	hassium 108 Hs [265]	meitnerium 109 Mt [266]	darmstadtium 110 Ds [267]	roentgenium 111 Rg [268]	copernicium 112 Cn [269]	tennessium 113 Ts [270]	oganesson 114 Og [271]	bohrium 107 Bh [264]	hassium 108 Hs [265]	meitnerium 109 Mt [266]	darmstadtium 110 Ds [267]	roentgenium 111 Rg [268]	copernicium 112 Cn [269]	tennessium 113 Ts [270]	oganesson 114 Og [271]
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- Considering absorption

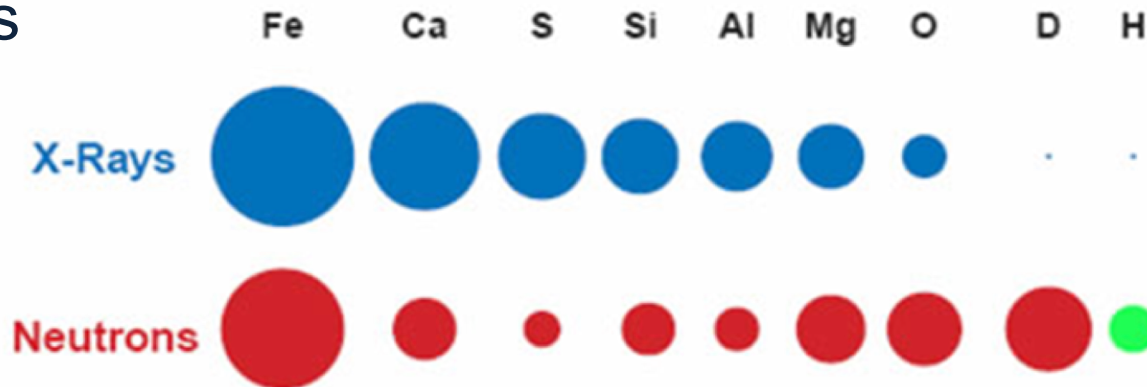
* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.05
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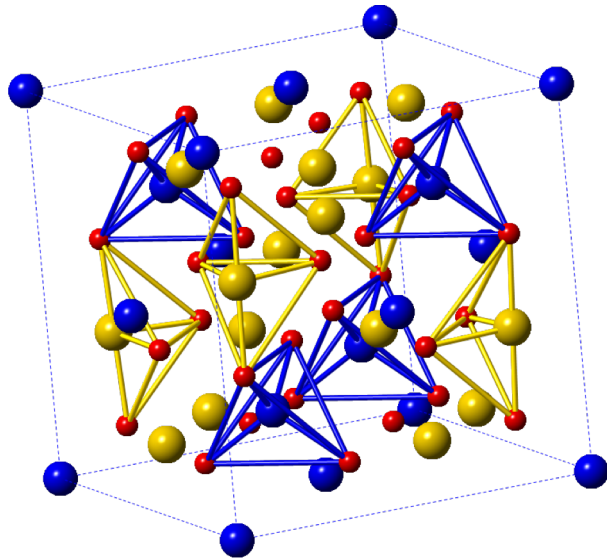
** Actinide series

actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]
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- Considering isotopes and resonances



PDF recap

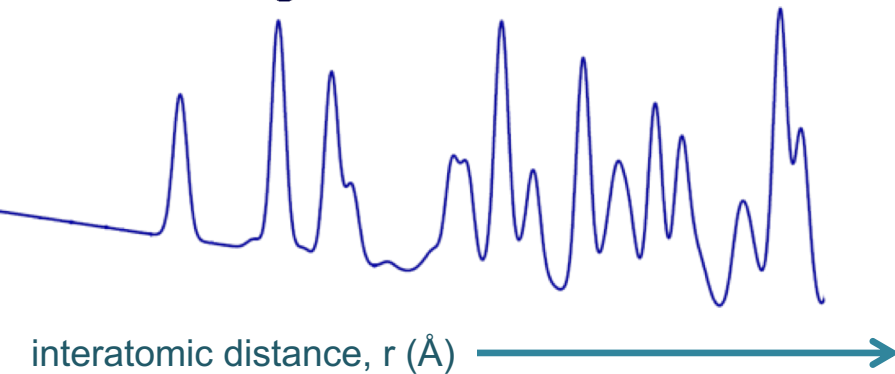


$$I_{tot} = I_{sam} + I_{bgrd}$$

$$I_{sam} = A \cdot P \cdot [C \cdot I_{coh} + I_{inc} + I_{mul}]$$

$$S(Q) = \frac{I_{coh}(Q) - \langle b^2 \rangle + \langle b \rangle^2}{\langle b \rangle^2} \quad Q = \frac{4\pi \sin \theta}{\lambda}$$

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



Raw data



Data reduction



PDF

Relationship to structure

$$G(r) = \frac{1}{Nr \langle b \rangle^2} \sum_{i \neq j} b_i b_j \delta(r - r_{ij}) - 4\pi r \rho_0$$



Atomic PDF skeleton

r_{ij} – interatomic distance between atoms i and j

Relationship to structure

$$G(r) = \frac{1}{N \langle b \rangle^2} \sum_{i \neq j} b_i b_j \delta(r - r_{ij}) - 4\pi r \rho_0$$

Annotations for the equation above:

- $\rho_0 = N/V$ average number density (number of atoms per unit volume)
- r – running variable (distance)

scattering “scale” for pair of atoms i and j
weighted by averaged scattering “strength”

Neutrons: b_{coh}
X-rays: $f(Q=0)$, effectively Z

Experimental setup limitations

Truncation effects in Fourier transform
(termination ripples, limited r -resolution)

$$G(r) = \frac{2}{\pi} \int_{Q_{\text{MIN}}}^{Q_{\text{MAX}}} Q (S(Q) - 1) \sin Qr \, dQ$$

Annotations for the equation above:

- Q_{MAX} (indicated with a red 'X') points to the upper limit of the integral.
- Q_{MIN} (indicated with a red 'X') points to the lower limit of the integral.

Ideally one would like to have

- broad Q -range
- good Q -resolution

Small angle scattering information is missing

This is not always essential!

PDFgui – awareness of various effects

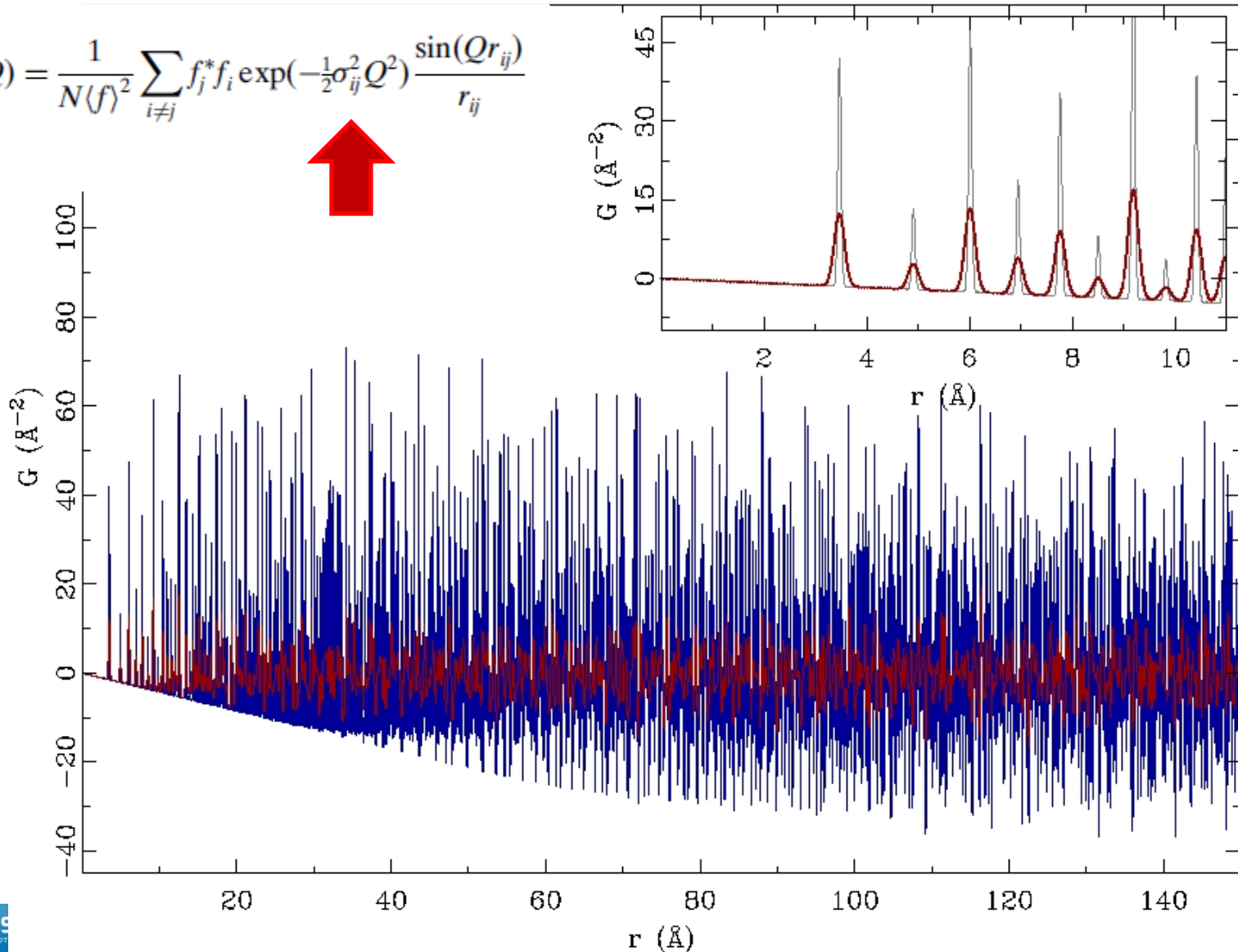
Some effects that should be accounted for

- Thermal broadening
- Correlated motion of nearest neighbours
- Finite Q_{MAX} (truncation)
- Limited Q-space resolution
- Particle size

PDF: effect of thermal broadening

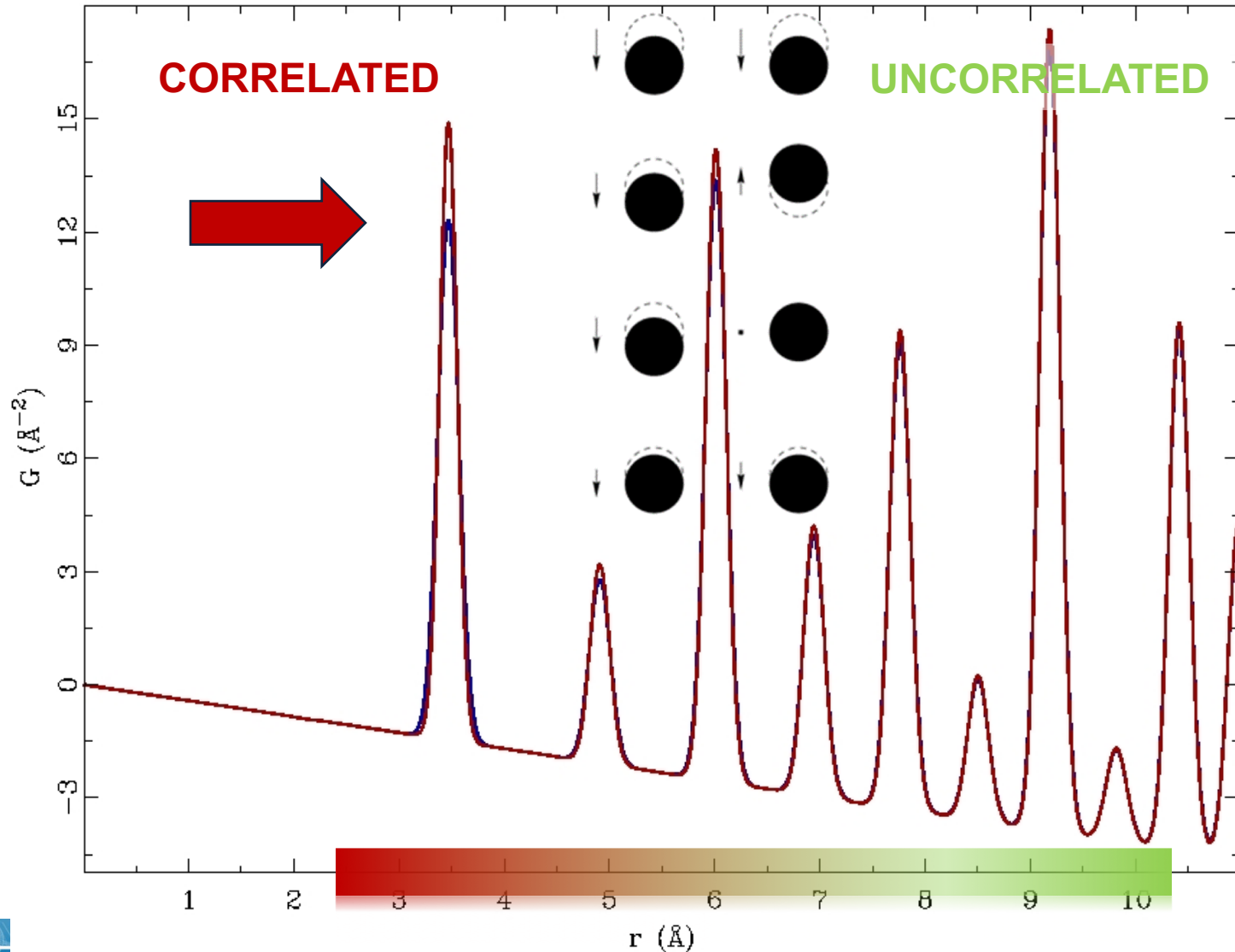
Effect of thermal motion U_{iso} on PDF
(thermal displacement parameters)

$$F(Q) = \frac{1}{N(f)^2} \sum_{i \neq j} f_j^* f_i \exp\left(-\frac{1}{2} \sigma_{ij}^2 Q^2\right) \frac{\sin(Qr_{ij})}{r_{ij}}$$

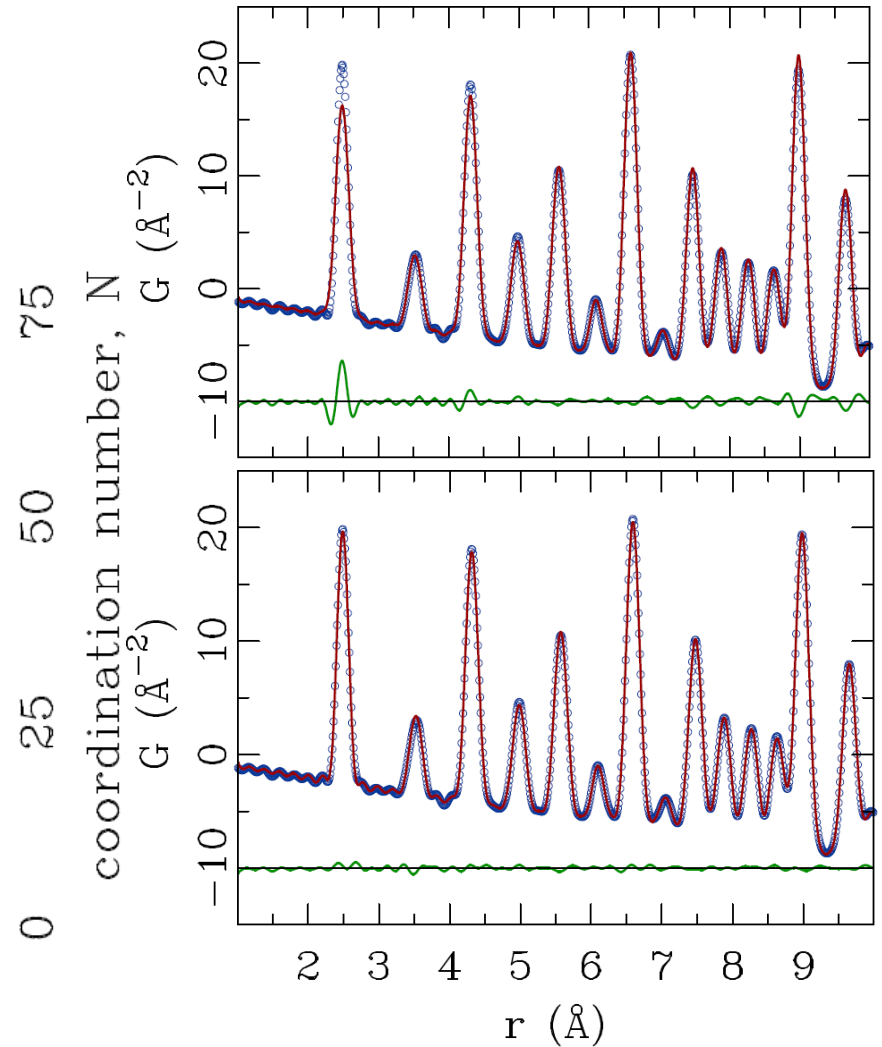
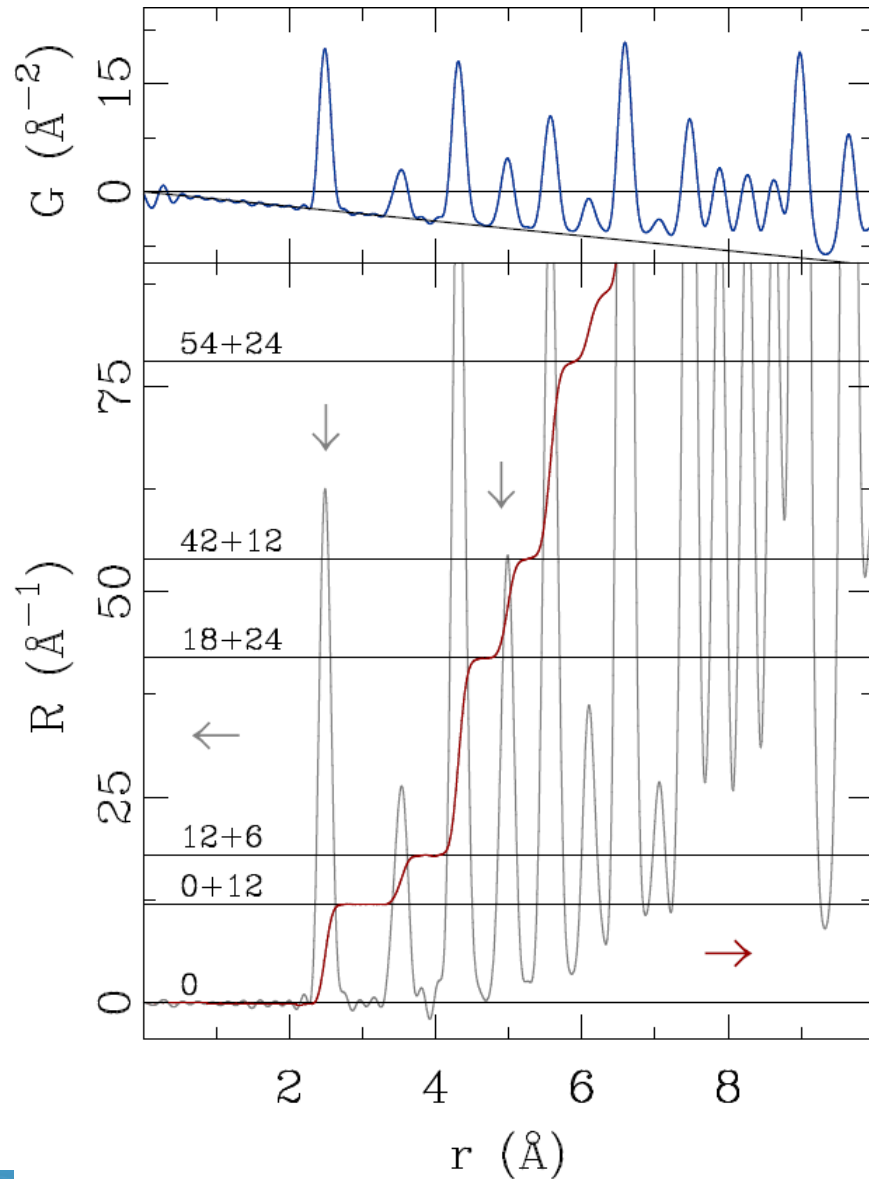


PDF: effect of correlated atomic motion

Effect of correlated atomic motion on PDF
(nearest neighbor peak SHARPENS)



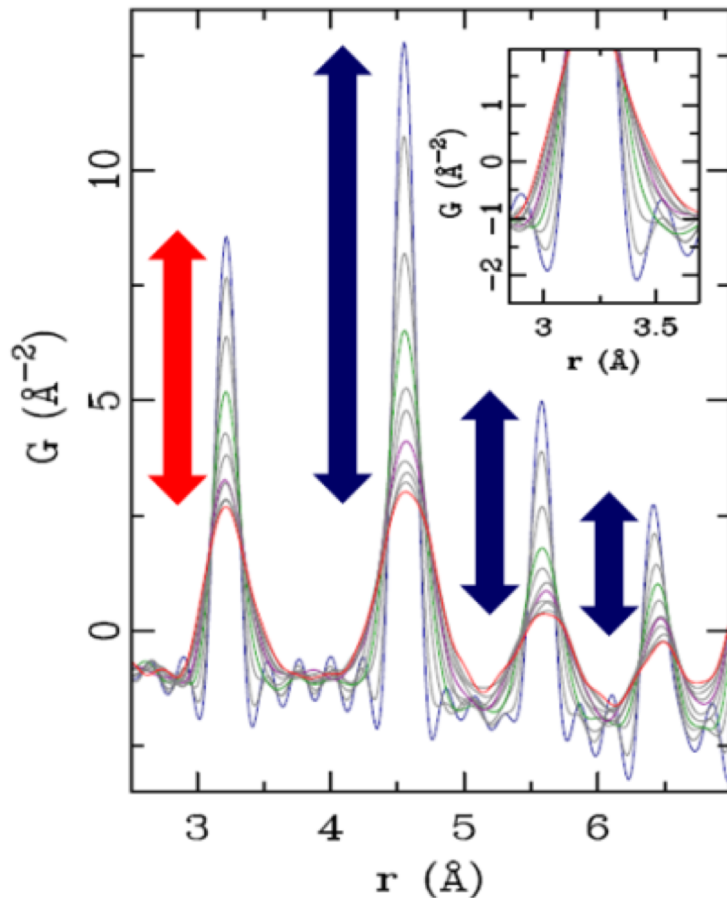
PDF: effect of correlated atomic motion



PDF: correlated atomic motion outlaws

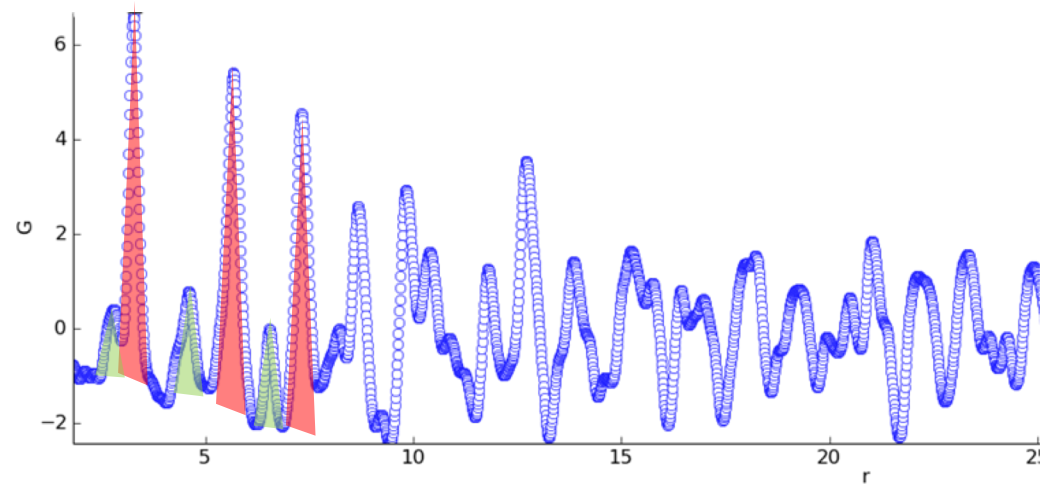
Weak effects
(e.g. PbTe)

break the rule



Strong effects
(e.g. in CeCoIn_5)

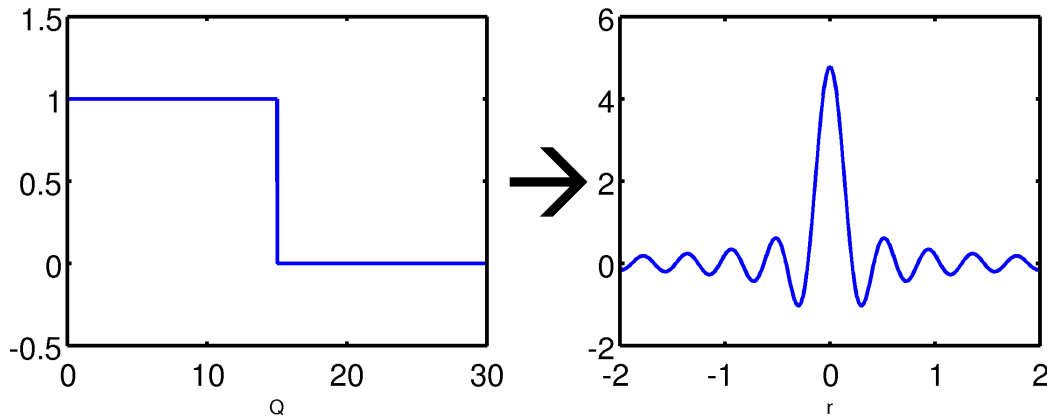
difficult to model



PDF: effect of finite Q_{\max} (truncation)

Effects from finite Q -range

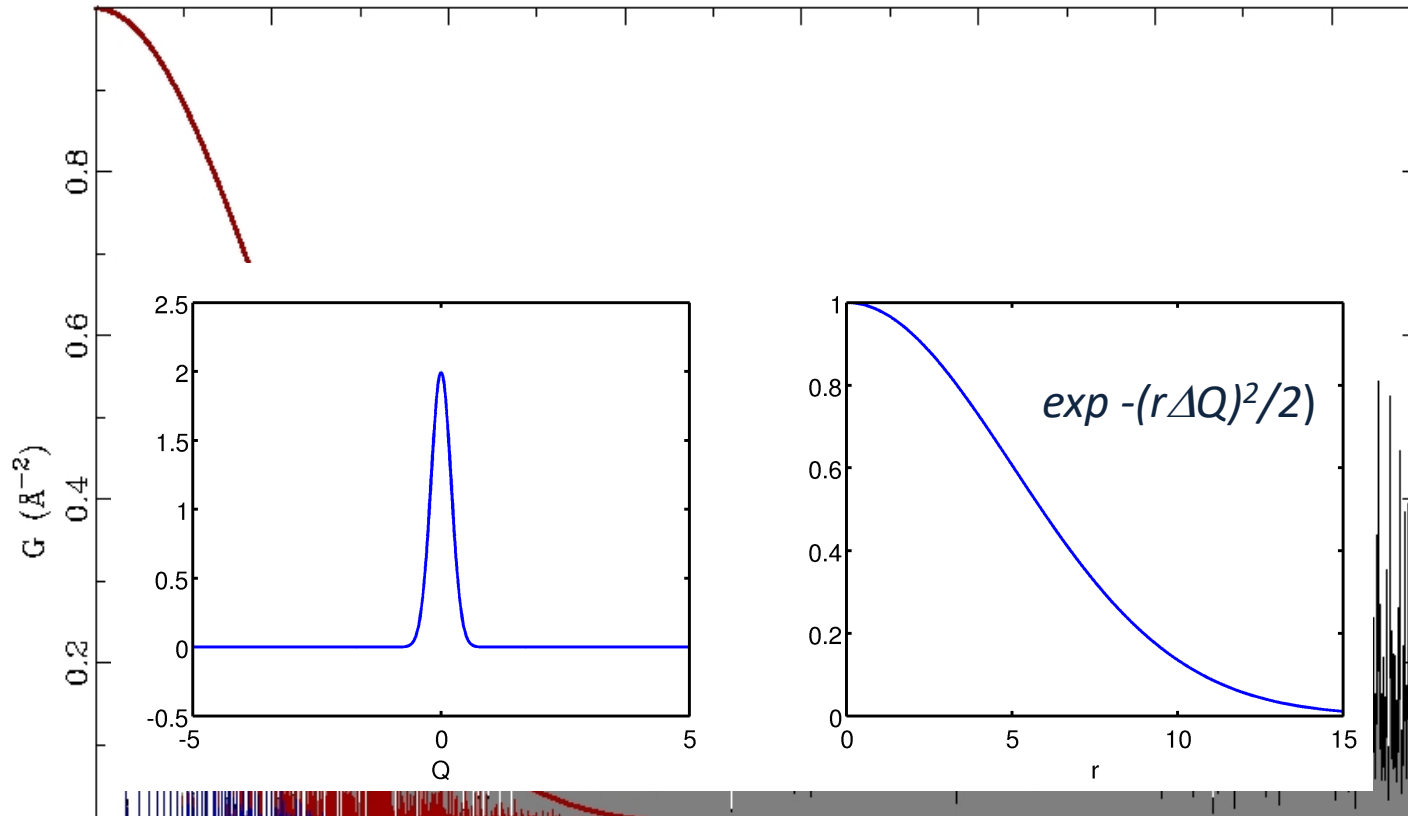
$$G(r) = \frac{2}{\pi} \int_0^{Q_{\max}} F(Q) \sin Qr \, dQ$$



- ideal $F(Q)$ is multiplied by a step function
- $G(r)$ gets convoluted with a sinc function $\text{sinc}(r) = \sin(Q_{\max} r) / r \rightarrow$
 r -resolution $\approx \pi/Q_{\max}$
- **good r -resolution of G requires large Q_{\max}**
 $Q = 4\pi \sin \theta/\lambda \rightarrow$ best results with TOF neutrons or high-energy x-rays

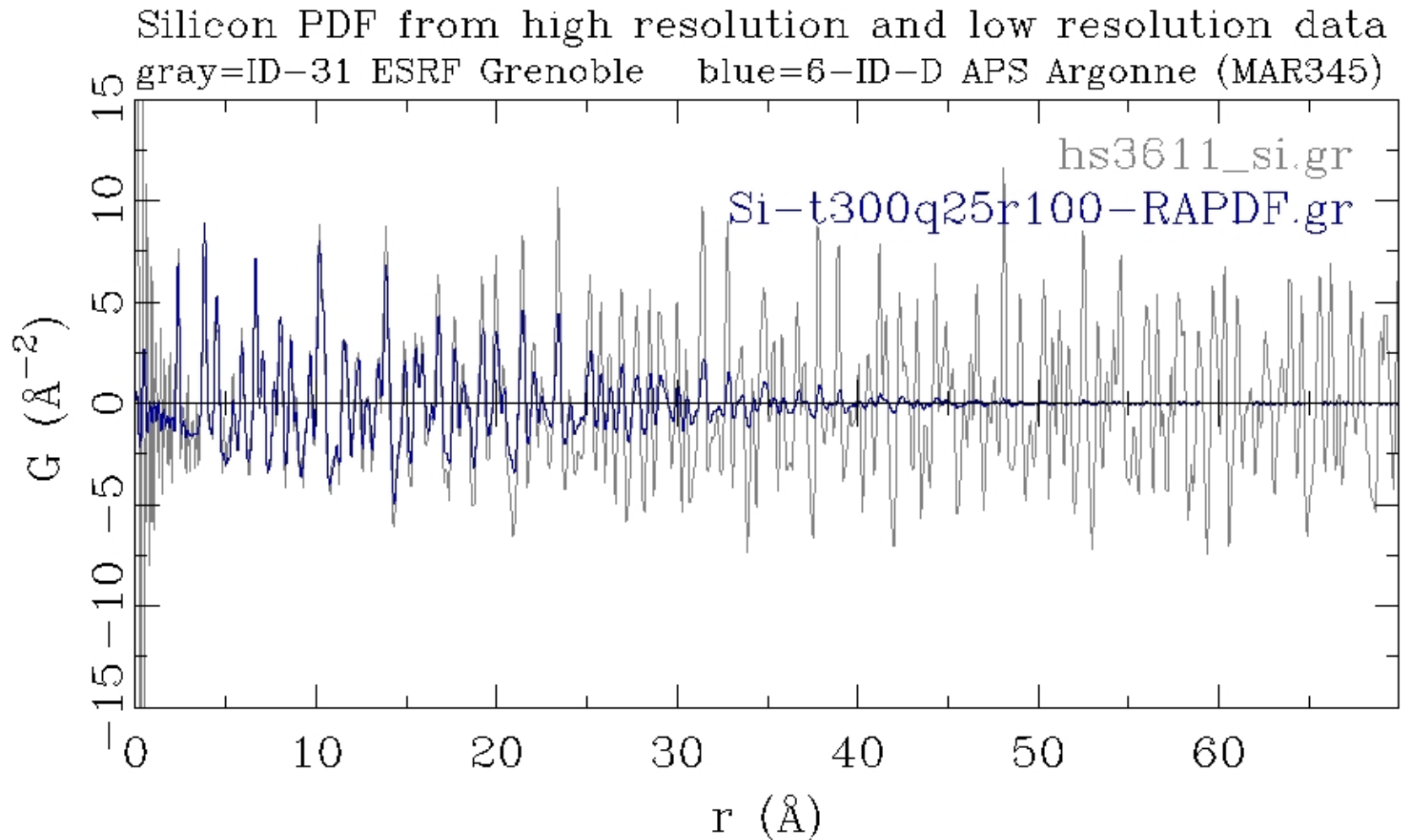
PDF: effect of the Q-space resolution

Effect of limited Q-resolution on PDF data

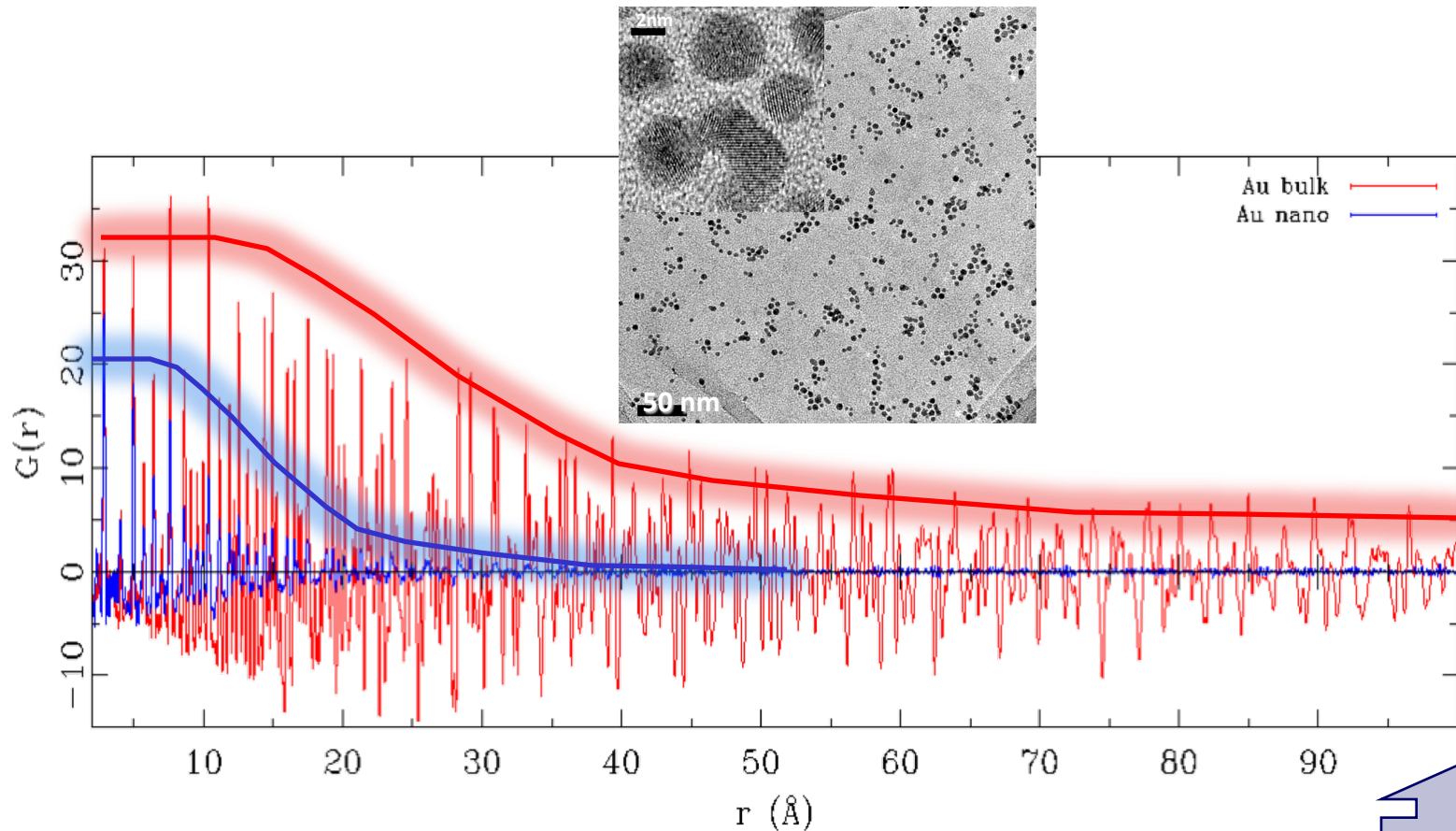


- ideal $F(Q)$ is convoluted by Gaussian to simulate finite Q resolution
- $G(r)$ gets multiplied by real-space Gaussian with reciprocal width
- For $G(r)$ to have good r -range high resolution in Q is required
Q-resolution defines PDF “field of view”

PDF: effect of the Q-space resolution



PDF: effect of the finite particle size – nano vs bulk



Experimental PDFs of gold nanoparticles and bulk gold, measured on NPDF.

K.L. Page *et al.*, *Chem. Phys. Lett.* **393**, 385 (2004).

After the PDF experiment ...

Now that you have collected your X-ray or neutron data and reduced it to PDF, what is the next step?

- It's time to harvest the information from PDF data, of course!
- Which approach to use depends on the problem at hand
- Good starting point (always) is to observe the PDF data in a model independent way, followed by modelling using the available tools, some of which are presented in this school
- Data inspection could provide valuable clues that would help modelling efforts/strategies tremendously at times

PDF data modeling

Small Models: Least Squares Refinement

Up to several hundreds of 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)

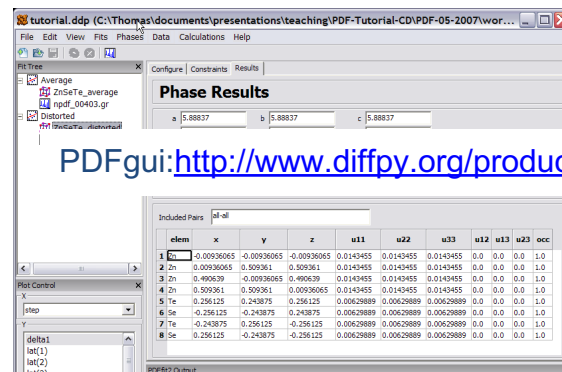
Example nanoparticle: *diameter, layer spacing, stacking fault probability*

Choose minimization scheme

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

Density Functional Theory

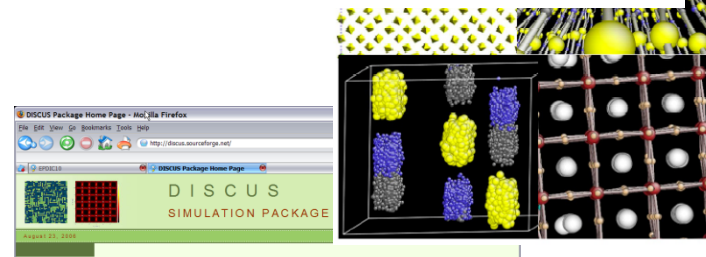
Molecular Dynamics



PDFgui: <http://www.diffpy.org/products/pdfgui>

RMCprofile: <http://www.isis2.isis.rl.ac.uk/rmc/>

EPSR: www.facebook.com/disord.matt



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

DiffPy-CMI: <http://www.diffpy.org/products/diffpycmi>

Include symmetry operations, Monte Carlo simulation capabilities and the generation of domain structure to name just a few.

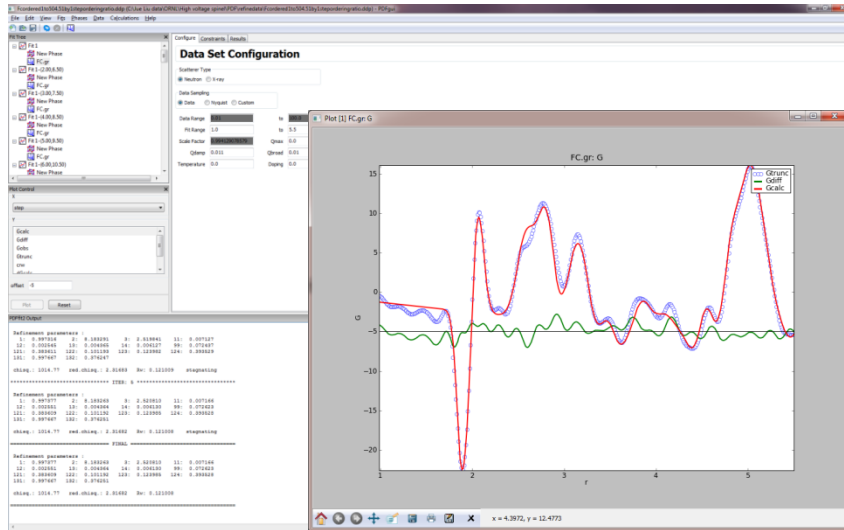
The second program is called PDFFIT. It is used for full profile refinements of the PDF based on an atomic structure. The program uses least squares and enforces a very powerful set of refinement constraints. Recently we have added a graphical users interface for simple refinements.

The third program is DIFFEV. This is a generic minimization program using an evolutionary algorithm. It is designed to work with the other programs in the package.

Finally the package contains a general plotting program called KUPLOT.

Thomas Proffen, Richard Heine, #14 Simon Billinge

“Small Box” software comparison



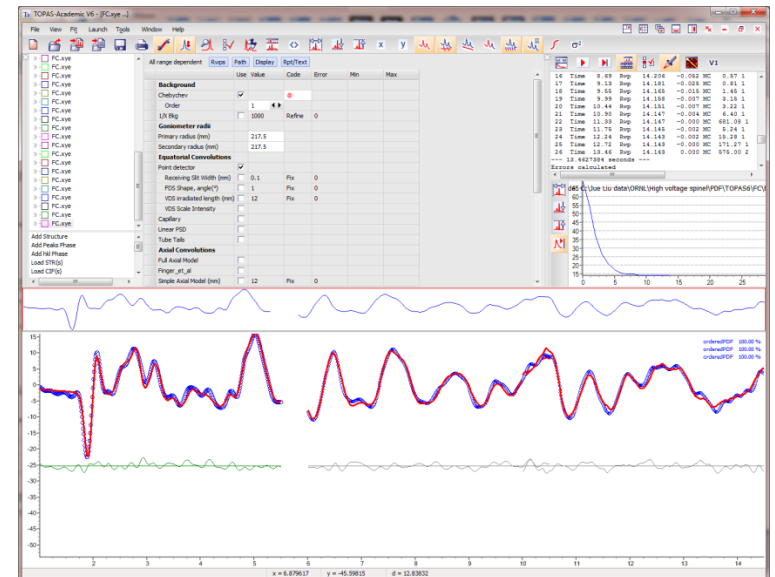
PDFgui <http://www.diffpy.org/>

- Slow refinement, e.g. for high- r
- Cumbersome outputs
- + Open Source and Free
- + GUI is Simple and User-friendly

TOPAS PDF

- Commercial
- Steeper learning curve
- Have to write your own macro
- + Super Fast
- + Easy manipulation of fitting parameters and plotting
- + Can easily customize output functions

<http://www.topas-academic.net>



Small box PDF modeling approach

- Small box: assumption of periodic boundary conditions (P1)
- Relatively small number of atoms (up to several hundred)
- Built-in symmetry constraints with symmetry equal or usually lower than the average crystal symmetry
- Involves least squares refinement over selected r -range (typically up to a few unit cells, translational symmetry not necessarily important as the box size mostly provides “metrics”)



Things needed ...

- PDF **data** (*sample.gr* files) and associated information such as Q_{\max} used, range of data, type of radiation, sample chemistry,
- In **small box modelling** approach, one typically starts from a **refinement** of a known/suspect structure, (thus reducing the volume of the parameter space as much as possible)
 - High- r region ~average structure
 - Low- r region ~local structure(biased view with bulk materials in mind)
- **Starting structure information**
 - space group and lattice parameters
 - fractional coordinates (asymmetric unit cell) & occupancies
 - having site-multiplicities handy may be helpful for crosschecking (e.g. PDFgui works with symmetrized cells)
 - Having an origin choice handy, if multiple are available, could matter

PDF modeling

- PDF is simulated from a known structure model

$$G_{calc}(r) = \frac{1}{Nr\langle b \rangle^2} \sum_{i \neq j} b_i b_j \frac{1}{\sqrt{2\pi}\sigma_{ij}} \exp \left[-\frac{(r - r_{ij})^2}{2\sigma_{ij}^2} \right] - 4\pi r \rho_0$$

- structure model is parameterized by a set of parameters p_i
- residuum R_w - difference between observed and simulated PDF

$$R_w(p_1, p_2, \dots) = \sqrt{\frac{\sum_n [G_{obs}(r_n) - G_{calc}(r_n)]^2}{\sum_n G_{obs}^2(r_n)}}$$

- least-squares refinement of p_i to minimize R_w
- Effects from setup (such as finite Q-resolution) or sample (correlated NN-motion) accounted for

$$B(r) = e^{-\frac{(rQ_{damp})^2}{2}}$$

$$\sigma_{ij} = \sigma'_{ij} \sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{broad}^2 r_{ij}^2}$$

PDFgui overview

- PDFgui is a **graphical interface built on the PDFfit2 engine**, which is a program as well as a library for real-space refinement of crystal structures based on the atomic pair distribution function (PDF) method.
- PDFgui organizes fits **and simplifies many data analysis tasks**, such as configuring and plotting multiple fits, **adding functionality** to script driven PDFfit2.
- PDFfit2 is capable of fitting a theoretical three dimensional structure to atomic pair distribution function data and is well suited for nanoscale investigations.
- The fit system accounts for lattice constants, atomic positions and anisotropic atomic displacement parameters, correlated atomic motion, as well as various experimental factors that may affect the data.
- The atomic positions and thermal coefficients can be constrained to follow symmetry requirements of an arbitrary space group. Limited restraints supported.
- The PDFfit2 engine is written in C++ and accessible via Python, and can also be prompt operated.

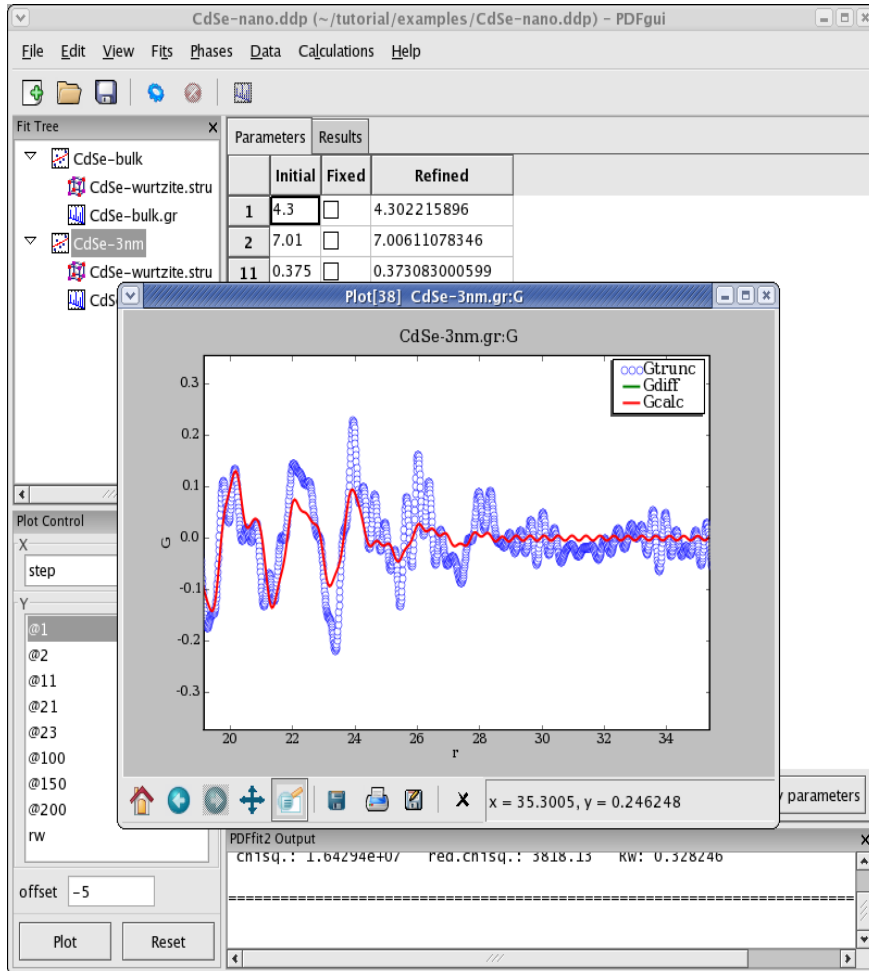
PDFgui

```
graph TD; PDFgui[PDFgui] --- PDFfit2[PDFfit2 engine];
```

PDFfit2 engine

PDFgui overview

PDFgui



- GUI interface to PDFfit2 is user friendly modelling environment that **can be used for quick simulations (useful for experiment planning and sensitivity tests)**
- can **organize** multiple related fits in a single project file (.ddp file) easily shareable with colleagues
- powerful **visualization facilities**
 - live plotting of refined PDF profiles
 - parametric plots of variables from multiple fits
 - 3D structure visualization (optional)
- **structure model manipulation**
 - supports xyz, PDF, CIF and PDFfit formats
 - supercell expansion
 - expansion of asymmetric unit
 - generation of symmetry constraints for coordinates and atomic displacement factors, ADPs (“thermals”)
- **wizards** for T-series, doping-series, r-series (smart extraction of meta-data from files)

Easy set up for “on the fly” refinements of incoming data helps making experimental decisions

PDFgui parameters and program structure

• PDFgui parameters associated with DATASET

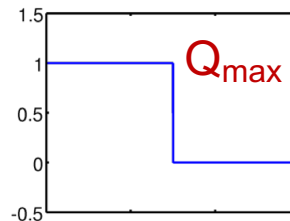
Fit range (r_{MIN} , r_{MAX})
fixed in refinement

user selected refinement r -range

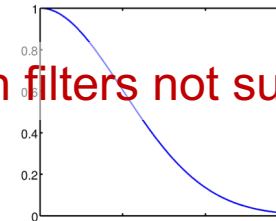
Q_{max}
fixed in refinement

upper limit of integration used in Fourier transform
defines r -space resolution, predetermined

Q_{damp}
refined for calibrant
fixed for sample



Lorch filters not supported



Gaussian dampening (due to limited Q -resolution)

Q_{broad}
refined for calibrant
fixed for sample

High- r peak broadening (due to increased refined intensity noise at high Q and other sources, only significant if r_{MAX} is large)

d_{scale}
refined

scale factor associated with dataset

PDFgui parameters and program structure

- PDFgui parameters associated with PHASE

pscale refined	phase scale factor NOTE: could be redundant/correlated with dscale
a, b, c, α , β , γ refined	lattice parameters
x[n]	x-position (fractional coordinates)
y[n]	y-position
z[n]	z-position
occ[n]	site occupancy
u[1..6,n] refined (per symmetry)	anisotropic displacement parameters U_{ij} [\AA^{-2}]

NOTE: Refinement parameters can be correlated, particularly when a model is refined over a narrow r-range of data. PDFgui reports on correlations $> |0.8|$

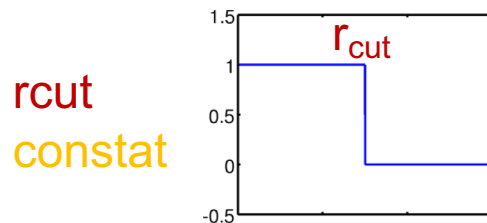
PDFgui parameters and program structure

- PDFgui parameters associated with PHASE for correlated atomic motion

delta1
refined 1/r contribution to peak sharpening [\AA^{-1}]

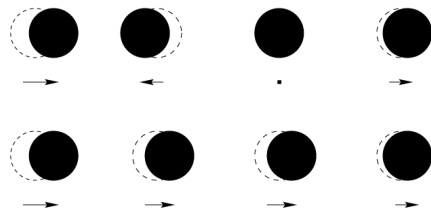
delta2
refined 1/r² contribution to the peak sharpening [\AA^{-2}]

sratio
refined peak width reduction for correlated motion
(special cases of rigid structural units)



r_cut
constat radius cutoff for applying the sratio
sharpening factor [\AA]

Note: Empirical correlated motion parameters are selected depending on material, they are **very strongly correlated** and affect other parameters

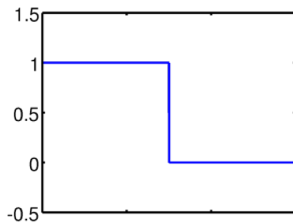


$$\sigma_{ij} = \sigma'_{ij} \sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{broad}^2 r_{ij}^2}$$

PDFgui parameters for nanoparticles

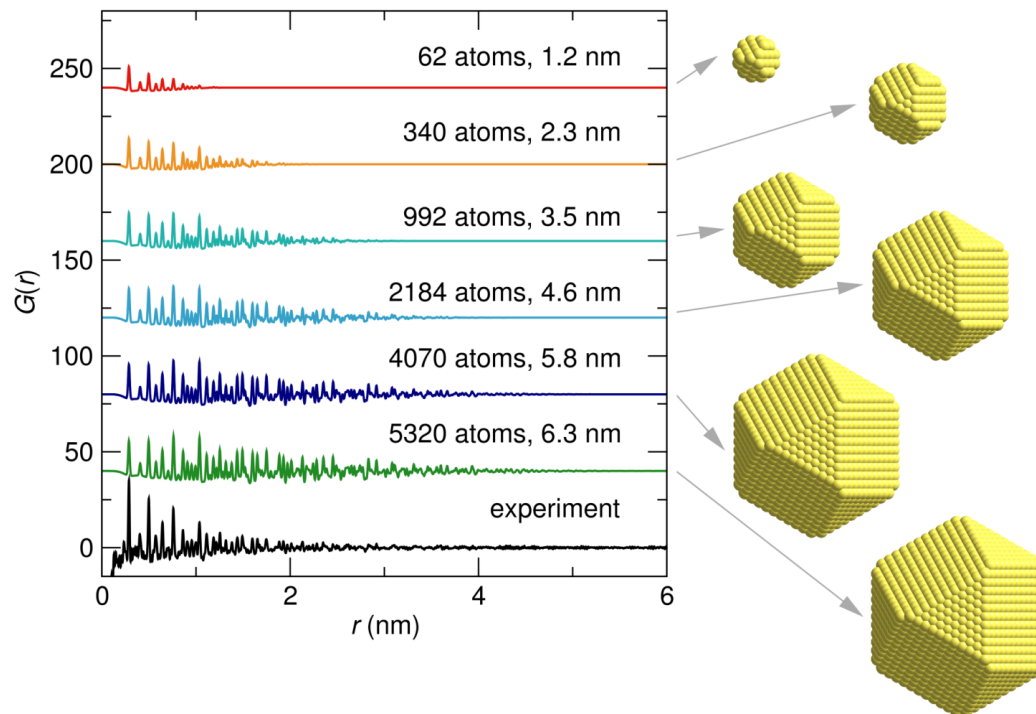
sp
diameter
refined

stepcut
constant



spherical particle diameter for PDF shape damping function [Å]

r value above which the PDF is truncated to zero [Å]



PDFgui parameters and program structure

- PDFgui declarations associated with PHASE

X
declaration

atom type associated with given site (all sites)
e.g. Ni/Ta/Ca (label used to read scattering info
from lookup tables of b_{coh} and Z).

- PDFgui declarations associated with DATASET

Neutron/X-ray
declaration

scatterer type
(used to determine lookup table)

NOTE: In rare instances one may experience the following

In case of X-ray radiation Z_X is used for element X. If ions present one can change X from original element to a fellow element with adequate electron count.

In case of neutron radiation b_{cohX} is used for element X. Lookup table contains information per natural isotope abundance. If isotope substitution is present, lookup table has to be modified with adequate b specified for a dummy element with made-up alphabetical code that will then be declared in the phase using that alphabetical code.

Parameters are assigned using the syntax **@pn**, where **pn** is the parameter number.

For example, **@1**, **@55**, **@321**, etc, numbers do not have to be consecutive.

Variables that are assigned the same parameter number will be described by the same parameter.

Caution should be exercised to avoid unintentional assignment of the same parameter number to incompatible variables (variables of different type)

PDFgui: quick start

PDFgui: Layout

The layout can be somewhat customized to create comfortable work environment

The screenshot shows the PDFgui software interface with several components labeled in red text:

- Menu Bar:** File Edit View Fits Phases Data Calculations Help
- Tool Bar:** Contains icons for file operations and a plot icon.
- Fit Tree:** A tree view showing the current fit configuration, including 'Fit 1' and 'ni.stru'.
- Plot Control:** A panel for controlling the plot, including X and Y axes, a dropdown menu (set to 'step'), an offset field (set to '-5'), and 'Plot' and 'Reset' buttons.
- Configure Panel:** Contains tabs for 'Configure', 'Constraints', and 'Results'. A red arrow points to these tabs with the label 'Tabs to panes'.
- Phase Configuration:** A section for setting phase parameters, including 'a', 'b', 'c', 'alpha', 'beta', and 'gamma'.
- Scale Factor:** A section for setting scale factors, including 'Scale Factor', 'delta1', 'delta2', 'spdiameter', 'sratio', 'rcut', and 'stepcut'.
- Included Pairs:** A section for selecting included pairs, with a dropdown menu set to 'all-all'.
- Current Action:** A table showing the current action parameters for the fit.
- PDFfit2 Output:** A panel at the bottom for displaying the output of the PDFfit2 algorithm.

	elem	x	y	z	u11	u22	u33	u12	u13	u23	occ
1	Ni	0.0	0.0	0.0	0.003	0.003	0.003	0.0	0.0	0.0	1.0
2	Ni	0.0	0.5	0.5	0.003	0.003	0.003	0.0	0.0	0.0	1.0
3	Ni	0.5	0.0	0.5	0.003	0.003	0.003	0.0	0.0	0.0	1.0
4	Ni	0.5	0.5	0.0	0.003	0.003	0.003	0.0	0.0	0.0	1.0

Creating a simple fit using a preexisting struct file

Appearance of a PDFgui window after a PDF dataset is loaded.

The screenshot displays the PDFgui software interface. The main window is titled 'PDFgui' and has a menu bar with 'File', 'Edit', 'View', 'Fits', 'Phases', 'Data', 'Calculations', and 'Help'. Below the menu bar is a toolbar with icons for file operations and a plot. The interface is divided into several panels:

- Fit Tree:** A tree view showing the loaded data and fits. It contains 'Fit 1', which includes 'Ni.stru' and 'Ni-xray.gr'.
- Plot Control:** A panel for controlling the plot. It has an 'X' axis dropdown set to 'step' and a 'Y' axis dropdown with options: 'Gcalc', 'Gdiff', 'Gobs', 'Gtrunc', 'crw', and 'dGcalc'. Below these is an 'offset' field set to '-5' and 'Plot' and 'Reset' buttons.
- Data Set Configuration:** A panel with tabs for 'Configure', 'Constraints', and 'Results'. It contains the following settings:
 - Scatterer Type:** Radio buttons for 'Neutron' and 'X-ray' (selected).
 - Data Sampling:** Radio buttons for 'Data' (selected), 'Nyquist', and 'Custom'.
 - Data Range:** Input fields for '0.01' to '20.0' with a 'spacing' of '0.01'.
 - Fit Range:** Input fields for '0.01' to '20.0' with a 'spacing' of '0.01'.
 - Scale Factor:** Input field for '1.0' and 'Qmax' input field for '40.0'.
 - Qdamp:** Input field for '0.001' and 'Qbroad' input field for '0.0'.
 - Temperature:** Input field for '300.0' and 'Doping' input field for '0.0'.
- PDFfit2 Output:** A panel at the bottom for displaying the output of the fit.

Creating a simple fit using a preexisting struct file

Adjusting data set related configuration.

The screenshot displays the PDFfit2 software interface. The main window is titled "PDFfit2 Output" and contains a "Fit Tree" on the left, a "Plot Control" section, and a "Data Set Configuration" panel. The "Fit Tree" shows a hierarchy: "Fit 1" containing "Ni.stru" and "Ni-xray.gr". The "Plot Control" section has an "X" axis set to "step" and a "Y" axis list with "Gcalc" selected. The "Data Set Configuration" panel is the central focus, with the "Configure" tab selected. It includes the following settings:

- Scatterer Type: Neutron, X-ray
- Data Sampling: Data, Nyquist, Custom
- Data Range: 0.01 to 20.0, spacing: 0.01
- Fit Range: 1.7 to 20.0, spacing: 0.01
- Scale Factor: 1.0, Qmax: 40.0
- Qdamp: 0.08, Qbroad: 0.0
- Temperature: 300.0, Doping: 0.0

The values 1.7, 40.0, and 0.08 are circled in red. The "Configure" tab label is also circled in red. The "PDFfit2 Output" window at the bottom is currently empty.

Creating a simple fit using a preexisting struct file

Setting up the refinement parameters and constraints: experimental parameters

The screenshot displays the PDFfit2 software interface. The main window has a menu bar (File, Edit, View, Fits, Phases, Data, Calculations, Help) and a toolbar. The 'Fit Tree' panel on the left shows a tree structure with 'Fit 1' expanded to show 'Ni.stru' and 'Ni-xray.gr'. The 'Plot Control' panel below it shows 'X' set to 'step' and 'Y' set to 'Gcalc'. The 'offset' is set to '-5'. The 'Constraints' tab is active, showing 'Data Set Constraints' with 'Scale Factor' set to '@1' and 'Qdamp' set to '@2', both circled in red. The 'Qbroad' field is empty. The 'PDFfit2 Output' panel at the bottom is empty.

Creating a simple fit using a preexisting structure file

Setting up the refinement parameters and constraints: model structure

The screenshot shows the PDFfit2 software interface with the 'Constraints' tab selected. The 'Phase Constraints' section contains the following parameters:

- a @3
- b @3
- c @3

The 'Included Pairs' section shows a table with the following data:

	elem	x	y	z	u11	u22	u33	u12	u13	u23	occ
1	Ni				@4	@4	@4				
2	Ni				@4	@4	@4				
3	Ni				@4	@4	@4				
4	Ni				@4	@4	@4				

The 'Fit Tree' on the left shows the following structure:

- Fit 1
 - Ni.stru
 - Ni-xray.gr

The 'Plot Control' section shows the X-axis set to 'step' and the Y-axis set to 'offset' with a value of -5. The 'PDFfit2 Output' window is empty.

Creating a simple fit using a preexisting struct file

Reviewing the fit parameters and conditions

The screenshot shows a software interface for reviewing fit parameters and conditions. The main window is titled "Fit Tree" and contains a tree view with the following structure:

- Fit 1
 - Ni.stru
 - Ni-xray.gr

The "Parameters" tab is selected, displaying a table with the following data:

	initial	Fixed	Refined
1	1.0	<input type="checkbox"/>	
2	0.08	<input type="checkbox"/>	
3	3.52	<input type="checkbox"/>	
4	0.0025	<input type="checkbox"/>	

The "Plot Control" panel is visible, showing a dropdown menu set to "step" and a list of fit components: @1, @2, @3, @4, and rw. The "offset" is set to -5. The "Plot" and "Reset" buttons are visible at the bottom of the panel. The "Apply parameters" button is located at the bottom right of the main window. The "PDFfit2 Output" window is visible at the bottom of the interface.

Creating a simple fit using a preexisting struct file

The refinement progress is displayed in the PDFfit2 Output panel.

The screenshot displays the PDFfit2 software interface. The 'Parameters' tab is active, showing a table of refinement parameters. The 'Refined' column values are circled in red. The 'PDFfit2 Output' panel at the bottom shows the current fit statistics, also circled in red.

	Initial	Fixed	Refined
1	1.0	<input type="checkbox"/>	0.7605115324
2	0.08	<input type="checkbox"/>	0.068831864865
3	3.52	<input type="checkbox"/>	3.53161588341
4	0.0025	<input type="checkbox"/>	0.00512432502226

PDFfit2 Output
chisq.: 236.817 red.chisq.: 0.129479 Rw: 0.0973844

Creating a simple fit using a preexisting struct file

Updating the set of initial values of refined parameters.

File Edit View Fits Phases Data Calculations Help

Fit Tree

- Fit 1
 - Ni.stru
 - Ni-xray.gr

	Initial	Fixed	Refined
1	1.0	<input type="checkbox"/>	0.7605115324
2	0.08	<input type="checkbox"/>	0.068831864865
3	3.52	<input type="checkbox"/>	3.53161588341
4	0.0025	<input type="checkbox"/>	0.0051243250222

Fix / Free
Copy Refined To Initial
Rename Parameters

Plot Control

X: step

Y: @1, @2, @3, @4, rw

offset: -5

Plot Reset

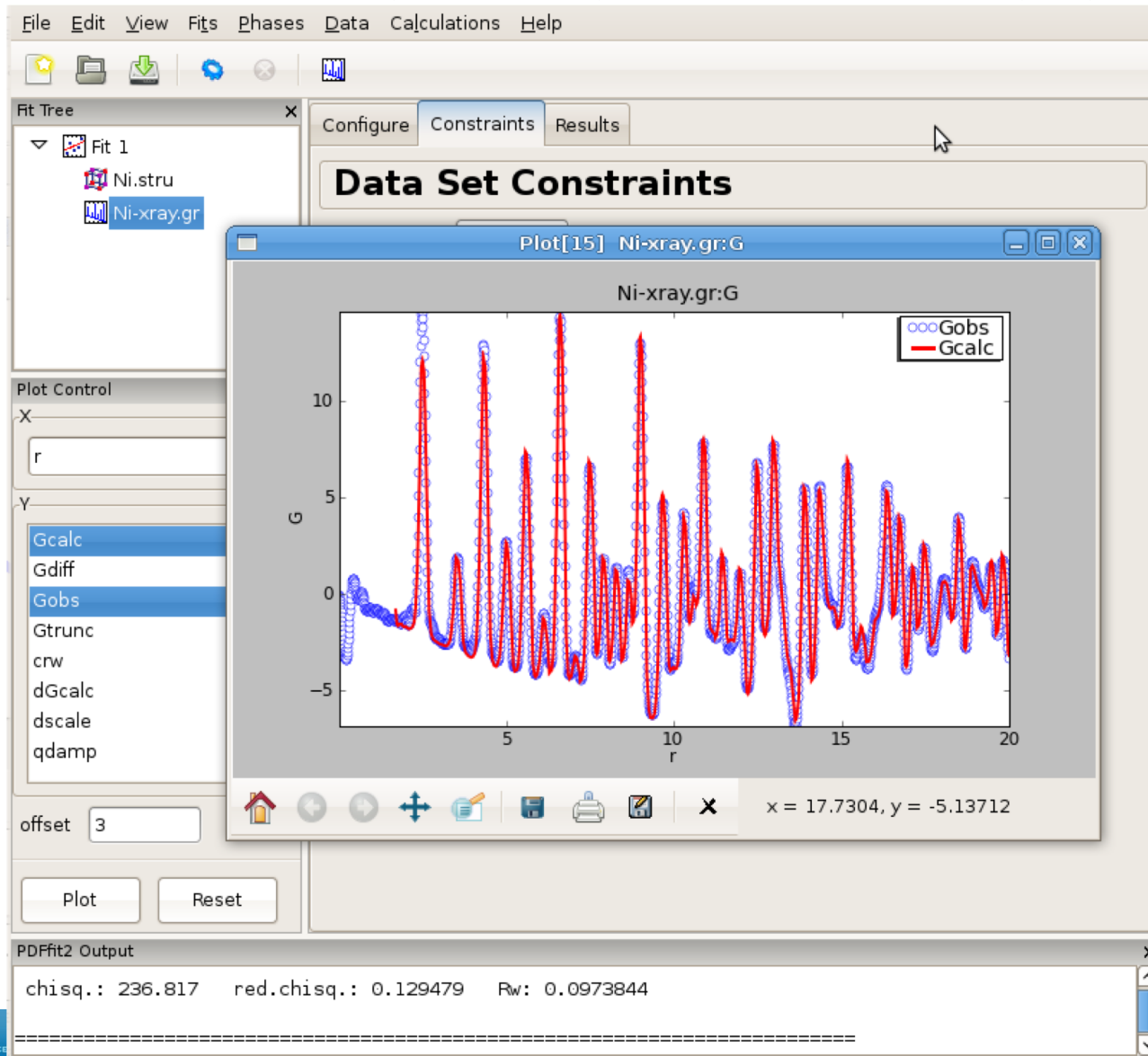
Apply parameters

PDFfit2 Output

chisq.: 236.817 red.chisq.: 0.129479 Rw: 0.0973844

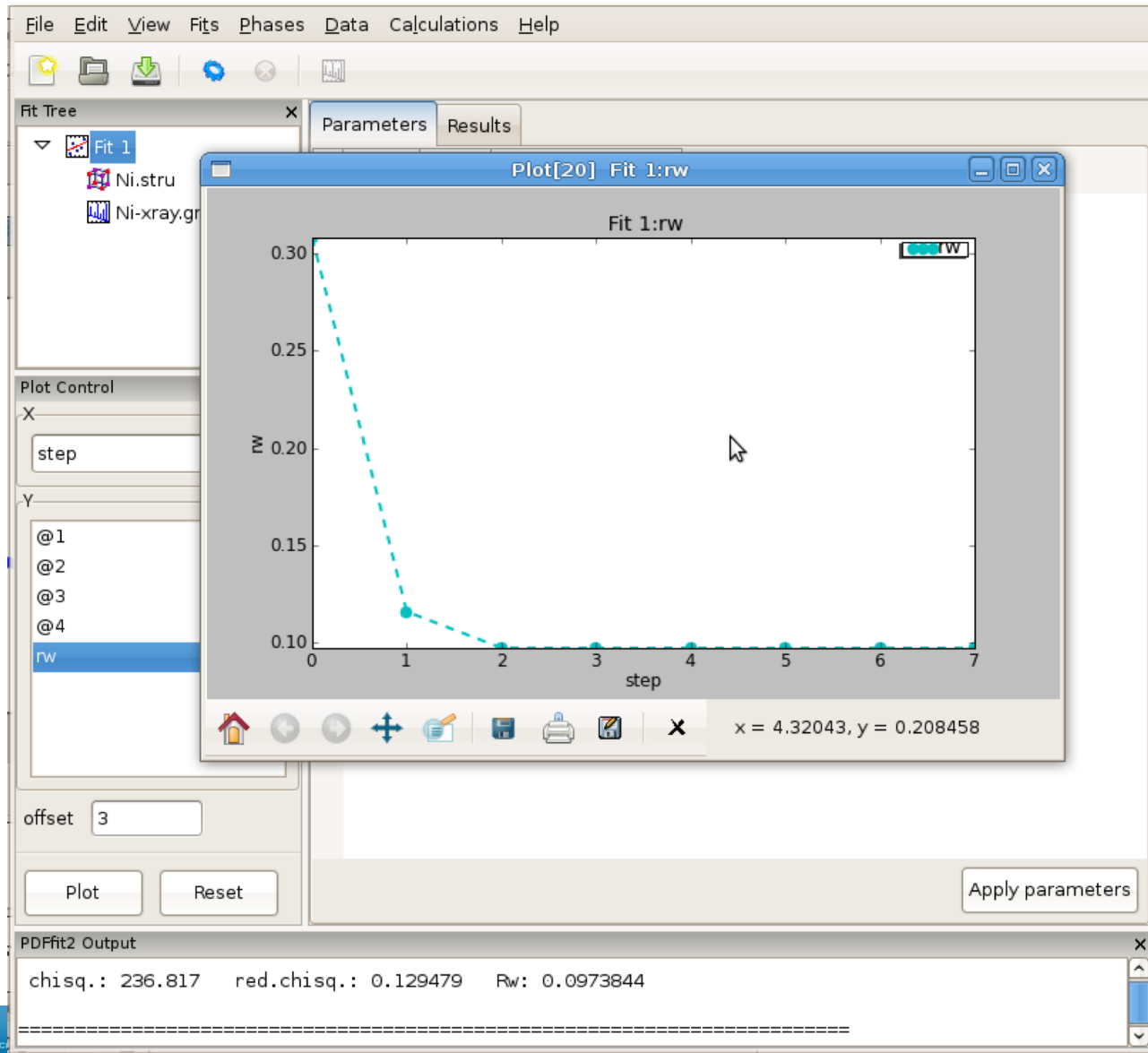
Creating a simple fit using a preexisting struct file

An example of PDFgui plotting capabilities: displaying a fit.



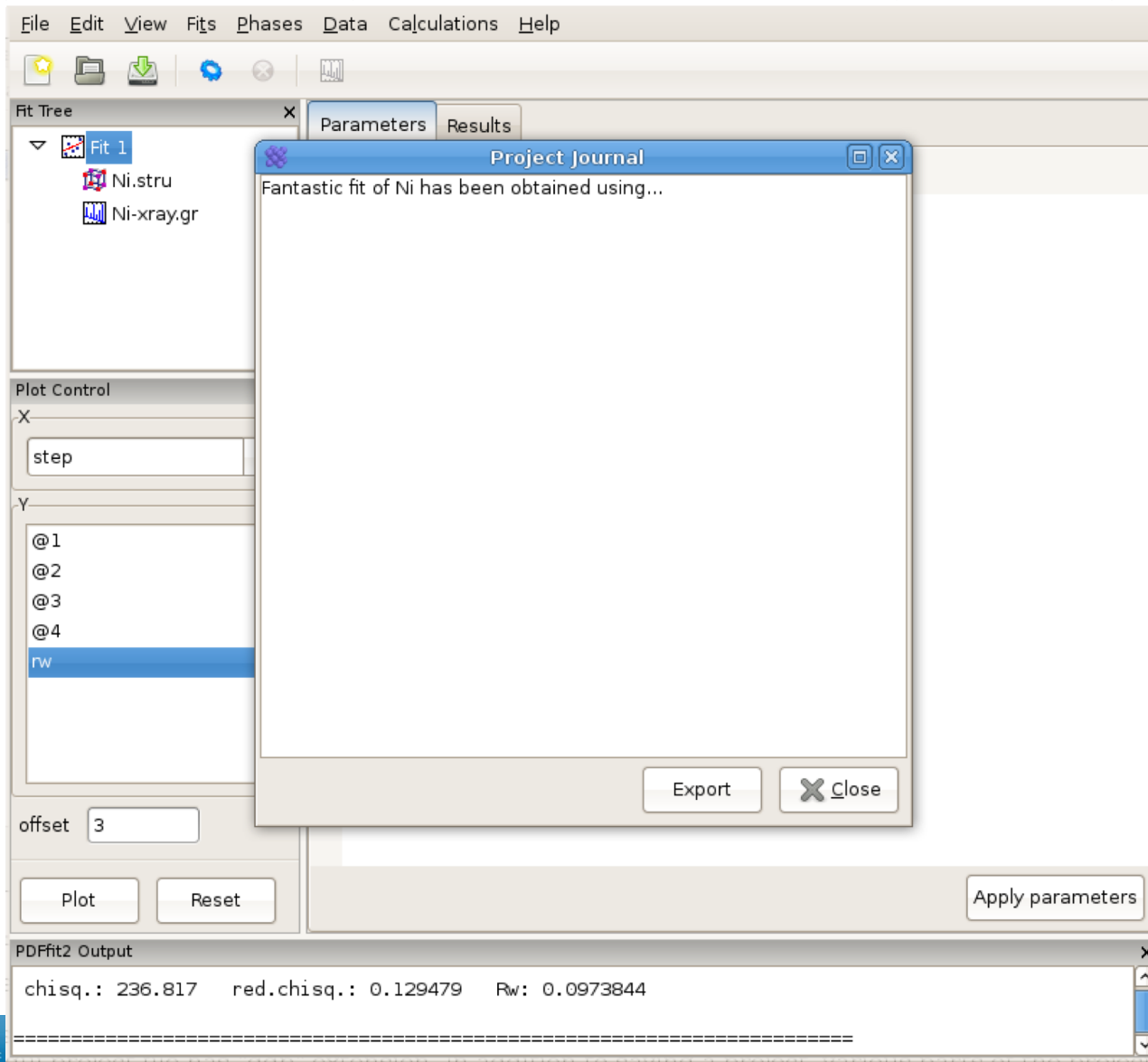
Creating a simple fit using a preexisting struct file

An example of PDFgui plotting capabilities: displaying a parameter.



Creating a simple fit using a preexisting struct file

Using “Journal” facility can be a convenient way for taking notes.



The screenshot displays a software interface with a menu bar (File, Edit, View, Fits, Phases, Data, Calculations, Help) and a toolbar. The main window is titled "Fit Tree" and contains a tree view with "Fit 1" expanded, showing "Ni.stru" and "Ni-xray.gr". Below the tree is a "Plot Control" section with an "X" axis set to "step" and a "Y" axis list containing "@1", "@2", "@3", "@4", and "rw" (selected). An "offset" field is set to "3". At the bottom of the plot control are "Plot" and "Reset" buttons. A "Project Journal" window is open in the foreground, displaying the text "Fantastic fit of Ni has been obtained using...". At the bottom of the journal window are "Export" and "Close" buttons. The bottom of the main window shows a "PDFfit2 Output" section with the text "chisq.: 236.817 red.chisq.: 0.129479 Rw: 0.0973844".

Building structure model using crystal symmetry

Expanding the **unit cell** using space group information.

The screenshot shows a software interface for building a structure model. The main window is titled "Phase Configuration" and has tabs for "Configure", "Constraints", and "Results". The "Configure" tab is active and shows unit cell parameters: a = 3.52, b = 3.52, c = 3.52, alpha = 90.0, beta = 90.0, gamma = 90.0. A "Space Group Expansion" dialog box is open, showing "Space Group Expansion" and "1 atom selected. Expanding to 4 positions." The dialog box has a "Space Group" dropdown menu set to "Fm-3m" and "Origin Offset" fields set to 0.0, 0.0, 0.0. The dialog box has "Cancel" and "OK" buttons. The main window also has a "Fit Tree" on the left showing "Ni from scratch" and "Ni fcc". A "Plot Control" panel is visible below the "Fit Tree" with a "step" dropdown and "Plot" and "Reset" buttons. The "PDFfit2 Output" panel is at the bottom.

File Edit View Fits Phases Data Calculations Help

Fit Tree

- Ni from scratch
 - Ni fcc

Plot Control

X

step

Y

offset 3

Plot Reset

PDFfit2 Output

Phase Configuration

Configure Constraints Results

a 3.52 b 3.52 c 3.52

alpha 90.0 beta 90.0 gamma 90.0

Space Group Expansion

Space Group Expansion

1 atom selected. Expanding to 4 positions.

Space Group Fm-3m

Origin Offset 0.0 0.0 0.0

Cancel OK

Building structure model using crystal symmetry

Setting up **symmetry constraints** to be used in a refinement.

The screenshot shows a software interface with a menu bar (File, Edit, View, Fits, Phases, Data, Calculations, Help) and a toolbar. The main window has three tabs: 'Configure', 'Constraints' (highlighted with a red circle), and 'Results'. The 'Constraints' tab is active, displaying the 'Phase Constraints' section with input fields for 'a', 'b', and 'c'. A 'Space Group Constraints' dialog box is open over the main window, showing '4 atoms selected.' and a 'Space Group' dropdown menu set to 'Fm-3m'. Below this, there are three 'Origin Offset' input fields, each containing '0.0'. Two checkboxes are checked: 'constrain positions' and 'constrain temperature factors'. At the bottom of the dialog are 'Cancel' and 'OK' buttons. On the left side of the main window, there is a 'Fit Tree' panel showing a tree structure with 'Ni from scratch' and 'Ni fcc'. Below it is a 'Plot Control' panel with a dropdown menu set to 'step' and an 'offset' field set to '3'. At the bottom of the main window is a 'PDFfit2 Output' panel.

Calculating PDF from a structure

An example of the calculation configuration panel.

The screenshot shows a software interface for calculating PDF from a structure. The main window has a menu bar with options: File, Edit, View, Fits, Phases, Data, Calculations, and Help. Below the menu bar is a toolbar with icons for home, save, download, settings, close, and a plot icon. The interface is divided into several panels:

- Fit Tree:** A tree view showing the project structure. It includes a folder icon for "Ni from scratch", a sub-item "Ni fcc", and a selected item "Calculation 1".
- Plot Control:** A panel for controlling the plot. It has an "X" axis dropdown menu with "r" selected, a "Y" axis dropdown menu with "Gcalc" selected, an "offset" input field with the value "3", and "Plot" and "Reset" buttons.
- Calculation Configuration:** A panel for configuring the calculation. It has a "Scatterer Type" section with radio buttons for "Neutron" (selected) and "X-ray". Below this are input fields for "Range" (0.01), "to" (50.0), "spacing" (0.01), "Scale Factor" (1.0), "Qmax" (25.0), "Qdamp" (0.08), and "Qbroad" (0.0).
- PDFfit2 Output:** A panel at the bottom for displaying the output of the PDFfit2 calculation.

Multistage fitting

Sequential refinement where fits are chronologically linked

File Edit View Fits Phases Data Calculations Help

Fit Tree

- lcmo-pbnm-550
 - LaMnO3-PBNM
 - 550K.gr
- lcmo-pbnm-650
 - LaMnO3-PBNM
 - 650K.gr

Plot Control

X: step

Y: @1

offset: 3

Plot Reset

Parameters Results

	Initial	Fixed	Refined
1	=lcmo-pbnm-550:1	<input type="checkbox"/>	5.54112301089
2	=lcmo-pbnm-550:2	<input type="checkbox"/>	5.7467340003
3	=lcmo-pbnm-550:3	<input type="checkbox"/>	7.68397896947
7	=lcmo-pbnm-550:7	<input type="checkbox"/>	0.00201860852715
8	=lcmo-pbnm-550:8	<input type="checkbox"/>	0.00217981215605
9	=lcmo-pbnm-550:9	<input type="checkbox"/>	0.00408078054004
10	=lcmo-pbnm-550:10	<input type="checkbox"/>	0.0044913862195
21	=lcmo-pbnm-550:21	<input type="checkbox"/>	-0.00837699376439
22	=lcmo-pbnm-550:22	<input type="checkbox"/>	0.0489062376597
23	=lcmo-pbnm-550:23	<input type="checkbox"/>	0.0742991663718
24	=lcmo-pbnm-550:24	<input type="checkbox"/>	0.487574732275
25	=lcmo-pbnm-550:25	<input type="checkbox"/>	0.725295010199
26	=lcmo-pbnm-550:26	<input type="checkbox"/>	0.305613295225
27	=lcmo-pbnm-550:27	<input type="checkbox"/>	0.039219781619

Apply parameters

PDFfit2 Output

Sequential fitting of incremental r-series

Appearance of the setup panel for specifying an incremental r-series fit conditions.

The screenshot shows a software window with a menu bar (File, Edit, View, Fits, Phases, Data, Calculations, Help) and a toolbar. The main area is divided into several panels:

- Fit Tree:** A tree view on the left showing a folder 'fit-Ni' containing 'Ni' and 'Ni_2-8.chi.gr'. A mouse cursor is pointing at the 'fit-Ni' folder.
- Plot Control:** A panel on the left with 'X' and 'Y' axes. The 'X' axis is set to 'step'. The 'Y' axis has a list of values: '@1', '@10', '@20', '@100'. Below this is an 'offset' field set to '3' and 'Plot' and 'Reset' buttons.
- Fit Parameters:** The main right-hand area contains instructions: "Select a fit from the tree on the left and set the first value, last value, and the step size of the maximum and/or minimum of the fit range below. If you have not set up a fit to be the template for the series, hit cancel and rerun this macro once a fit has been created." Below this are two sections: 'fit maximum' with input fields for 'first' (5), 'last' (20), and 'step' (5); and 'fit minimum' with empty input fields for 'first', 'last', and 'step'.
- Buttons:** 'OK' and 'Cancel' buttons are located at the bottom right of the main area.
- PDFfit2 Output:** A panel at the bottom of the window, currently empty.

Sequential fitting of temperature series

Setting up a T-series sequential refinement for LaMnO_3 .

Select a fit from the tree on the left then add datasets and assign temperatures below. If you have not set up a fit to be the template for the series, hit cancel and rerun this macro once a fit has been created.

Temperature	Data Set
550.0	.../550K.gr
650.0	.../650K.gr
700.0	.../700K.gr
720.0	.../720K.gr
730.0	.../730K.gr
740.0	.../740K.gr
750.0	.../750K.gr
800.0	.../800K.gr
880.0	.../880K.gr
980.0	.../980K.gr
1050.0	.../1050K.gr

Click header to sort by temperature

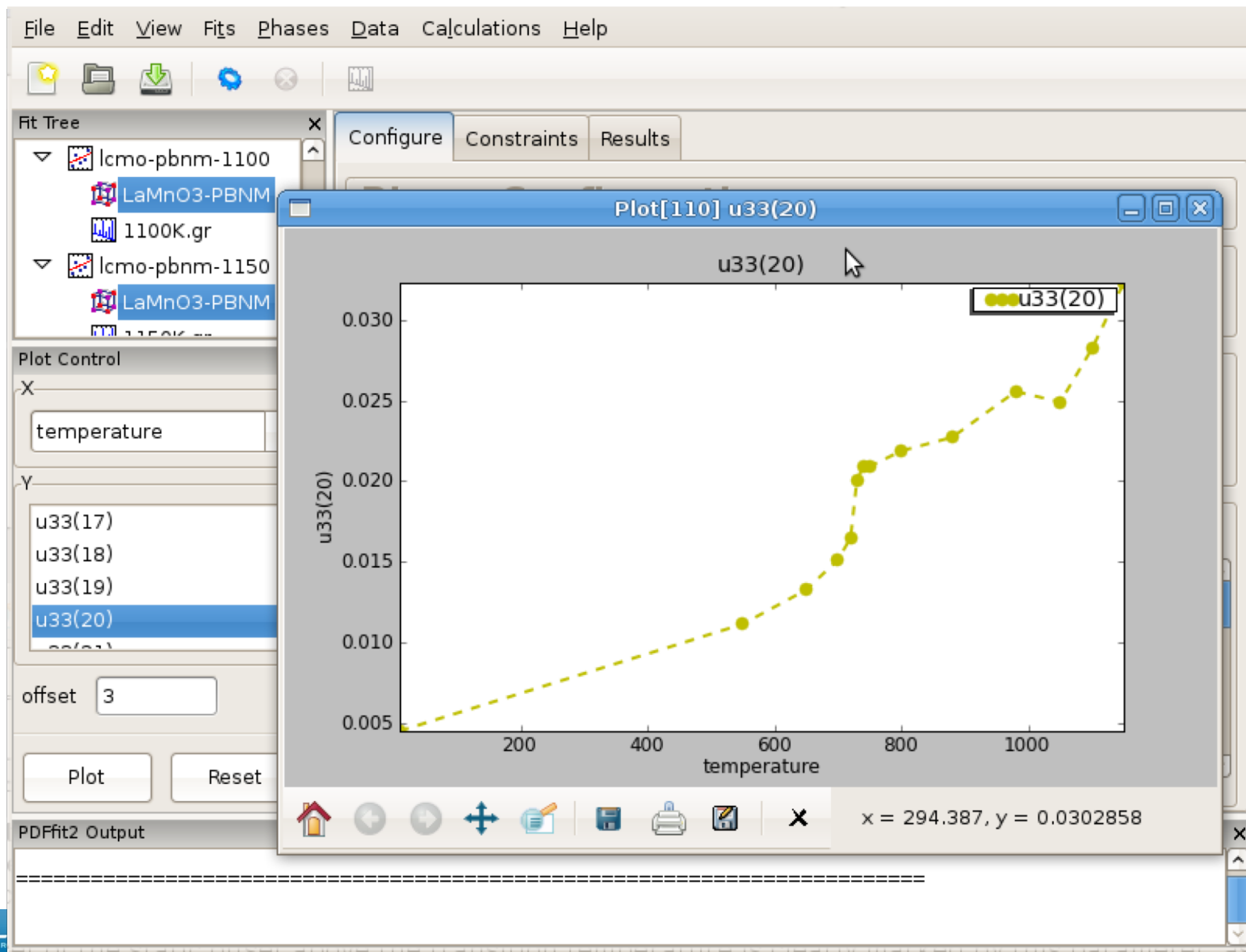
+ Add Delete

Plot Reset OK Cancel

Ordering by temperature will ensure that the fits are linked correctly!

Sequential fitting of temperature series

Displaying refinement results as a function of external parameter: T-series refinement



Sequential fitting of doping series

Loading of the Ca-doping data series of LaMnO₃ system.

Select a fit from the tree on the left then add datasets and assign doping elements and values below. If you have not set up a fit to be the template for the series, hit cancel and rerun this macro once a fit has been created.

Base element Dopant

Doping	Data Set
0.04	.../x004t010q35.gr
0.12	.../x012t010q35.gr
16.0	...
20.0	.../x020t010q35.gr
24.0	.../x024t010q35.gr
28.0	.../x028t010q35.gr

Click header to sort by doping

+ Add Delete

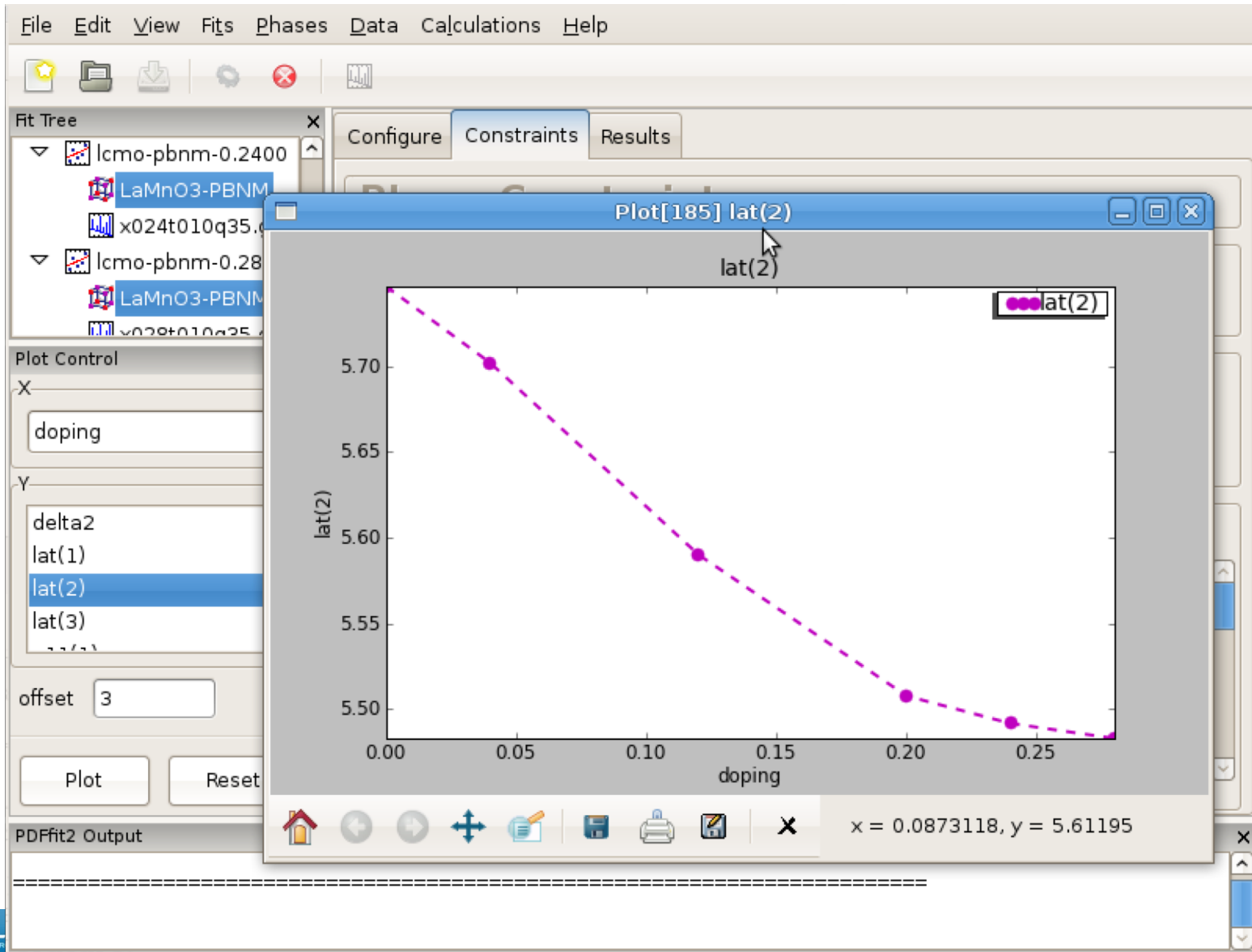
Plot Reset OK Cancel

PDFfit2 Output

Verify that proper doping assignment was carried out!

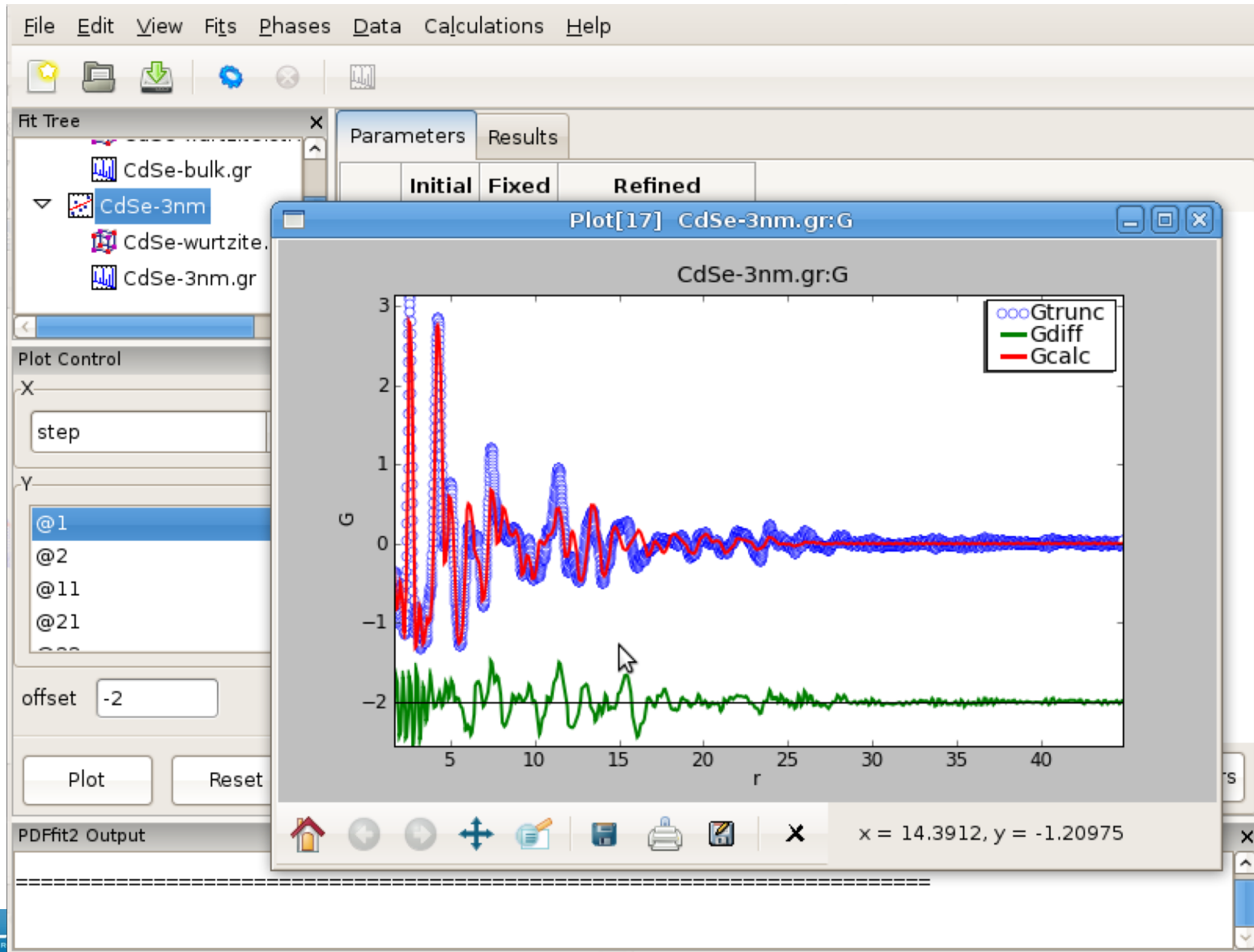
Sequential fitting of doping series

Displaying refinement results as a function of external parameter: doping series



Nanoparticle structure: spherical!

Fitting the structure of a nanoparticle: 3nm CdSe nanoparticle example



Displaying the structure

Using AtomEye functionality for 3D visualization of the initial and refined PDF structures

File Edit View Fits Phases Data Calculations Help

Fit Tree

- Fit 1
 - Ni.stru
 - Ni-xray.gr

Plot Control

X

step

Y

lat(1)

lat(2)

lat(3)

sratio

offset -2

Plot Reset

PDFfit2 Output

```
After pairwise/own_pair saving,
likely MAX(neighbor) = ( 13 ) atoms,
atom-atom list created.

Uncompressed atom-atom list: 32 entries,
max=8, min=4, avg=6.00 (46.2%), std.dev.=1.58

Compressed atom-atom list: 32 entries,
max=8, min=4, avg=6.00, std.dev.=1.58

All bin-related allocations freed.
----- Coordination Number Statistics -----
Coord. Count Percentage R G
12 32 100.00% 0.933 0.867
-----
average = 12, most populous = 12.

avg. M = | 1 0 0 |
| 0 1 0 |
| 0 0 1 |

avg. microscopic shear strain = 3.2049
This process has used up to 760 KB.
```

												occ
3	Ni	0.5	0.0	0.5	0.00126651	0.00126651	0.00126651	0.0	0.0	0.0	1.0	
4	Ni	0.5	0.5	0.0	0.00126651	0.00126651	0.00126651	0.0	0.0	0.0	1.0	

PDFgui tutorial content & agenda

- Plan is to cover different examples featuring various aspects of PDFgui functionality
- GOALS:
 - becoming familiar and comfortable with the program
 - building up basic expertise and awareness of various PDFgui capabilities
 - Exploring a few more complex examples
- Examples:
 - Simulating PDFs
 - Ni X-ray and neutron data refinement
 - Ni neutron-Xray corefinement
 - Ni/Si mixture refinement; phase analysis
 - Ni T-dependence sequential refinement

 - LaMnO₃ at 300 K - complex system
 - LaMnO₃ T-dependence sequential refinement
 - LaMnO₃ at 800 K r-dependent sequential refinement
 - La₂CuO₄ composition/doping-dependence sequential refinement