PDFgui – a small box modelling platform for nanoscale structure analysis

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October 17, 2022





A reflection on PDFgui usage: increasing popularity

PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals

Farrow, CL; Juhas, P; (...); Billinge, SJL 3rd Workshop on Reverse Monte Carlo Methods

Aug 22 2007 JOURNAL OF PHYSICS-CONDENSED MATTER 19 (33)

PDFfit2 is a program as well as a library for real-space refinement of crystal structures. It is capable of fitting a theoretical three-dimensional (3D) structure to atomic pair distribution function data and is ideal for nanoscale investigations. The fit system accounts for lattice constants, atomic p ... Show more

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Clarivate

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Overview

- Small box modelling and PDFgui
- Notes of relevance for PDF analysis
- PDFgui parameters & program structure
- Illustrative PDFgui-based science example



• 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 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 Models: 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







slide courtesy of Katharine Page

PDF data modeling

0.....

PDFgui

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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 to 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 relevant for narrow range fits, when box size effectively provides "metrics")



Considering scattering contrast

Considering absorption

| hydrogen | 1 | | | | | | | | | | | | | | | | 2 | helium |
|--|---|-----------------------------|---|---|--|---|--|--|---|--|--|---|--|---|---|---|--|--|
| | | | | | | | | | | | | | | | | | | 2 |
| н | | | | | | | | | | | | | | | | | | He |
| 1.0079 filbium | bendlium | 1 | | | | | | | | | | ſ | boron | | nitrogan | 0000000 | fluorino | 4.0026 |
| 3 | 4 | | | | | | | | | | | | 5 | 6 | 7 | 8 | 9 | 10 |
| Li | Be | | | | | | | | | | | | В | C | N | 0 | F | Ne |
| 6,941 | 9.0122 | | | | | | | | | | | | 10.811 | 12.011 | 14.007 | 15.999 | 18.998 | 20,180 |
| sodium 11 | magnesium 12 | | | | | | | | | | | | aluminium | slicon 14 | phosphorus 15 | sulfur 16 | chlorine 17 | argon 19 |
| NIE | N/L av | | | | | | | | | | | | Å | 0: | D | | ő | A |
| Na | IVIG | | | | | | | | | | | | AI | 51 | Р | Э | CI. | Ar |
| 22.990 notassium | 24.305 coleium | | scondium | titonium | vanadium | chromium | mongonoso | iron | coball | nickel | conner | zine | 26.982 collium | 28.086 | 30.974 presente | 32.065 solonium | 35.453 bromino | 39,948 keynton |
| 19 | 20 | | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 |
| 1/ | Ca | | C - | T : | 1/ | 0 | B./ | Fa | Co | NI: | C | Zn | Co | Go | Ac | Sa | Dr | 1/m |
| n | Ua l | | SC | | V | UC I | IVIN | ге | 60 | | Gu | | Ga | Ge | AS | Se | DI | N |
| N 39.098 | 40.078 | | 3C 44.966 | 47.867 | V 50.942 | 51.996 | 1VIN 54.938 | 55.845 | 58.933 | 58.693 | 63.546 | 65.39 | 69.723 | 72.61 | A5 74.922 | 3e 78.96 | DI 79.904 | 83.90 |
| 29.098 rubidium 27 | 40.078 stronlium 38 | | 3C 44.966 yttrium 30 | 47.867 zirconium | 50.942 nicbium | 51.996 molybdenum | 54.938 technetium | 55.845 ruthenium | 58.933 rhodium | 58.693 palladium | 63.546 silver 47 | 65.39 cadmium | 69.723 Indium | 72.61 tin 50 | A5 74.922 antimony 51 | 3e 78.96 tellurium 52 | 79.904 Iodine | 83.90 xenon 54 |
| 839.098 rubidium 37 | 40.078 strontium 38 | | 30 39 | 47.867 zirconium 40 | 50.942 nicolum 41 | 51.996 molybdenum 42 | 54.938 technetium 43 | 55.845 ruthenium 44 | 58.933 rhodium 45 | 58.693 palladium 46 | 63.546 silver 47 | 65.39 cadmium 48 | 69.723 indium 49 | 72.61 tin 50 | A3 74.922 antimony 51 | 78.96 tellurium 52 | 79.904 iodine 53 | xenon 54 |
| n 39.098 rutidium 37 Rb | 40.078 stronlium 38 Sr | | 39 Yttrium | 47.867 zirconium 40 Zr | 50.942 nicolium 41 Nb | 61.996 motybdenum 42 Mo | technetium 43 TC | re 55.845 ruthenium 44 Ru | 58.933 flocium 45 Rh | ^{58.693} pattadium 46 Pd | 63.546 silver 47 Ag | ^{65,39} cadmium 48 Cd | 69,723 Indium 49 In | 72.61 Un 50 Sn | AS 74.922 antimony 51 Sb | 5e 78.96 tellurium 52 Te | 79.904 Iodine 53 | xenon 54 Xe |
| 39.098 rutvdium 37 Rb 85.468 | 40.078 stronflum 38 Sr 87.62 badum | | 39 Yttium 39 Y 88.906 | 47.867 ztrconium 40 Zr 91.224 badejum | 50.942 nicblum 41 Nb 92.906 tantakum | 51.996 molybdenum 42 Mo 95.94 hunnslan | 43 1981 1981 1981 1981 | 55.845 ruthenium 44 Ru 101.07 | 58.933 modium 45 Rh 102.91 | 58.693 palladium 46 Pd 106.42 | 63,546 silver 47 Ag 107,87 | 65.39 cadmium 48 Cd 112.41 | 69.723 indium 49 In 114.82 thallum | 72.61 Un 50 Sn 118.71 | AS 74.922 antimony 51 Sb 121.76 bismuth | 52 78.96 52 Te 127.60 | 53 126.90 astatino | 83.80 xenon 54 Xe 131.29 |
| 39,098 rubidium 37 Rb 85,468 caesium 55 | 40.078 stronlium 38 Sr 87.62 barlum 56 | 57-70 | 39 Ytthum 39 Y 88,906 Iutetium 71 | 47.867 zirconium 40 Zr 91.224 hafnium 72 | V 50.942 nicolium 41 Nb 92.906 tantalum 73 | 51.996 molybdenum 42 MO 95.94 tungsten 74 | 43 54.938 technetium 43 TC [98] fhenium 75 | ruthenium 44 Ru 101.07 osmium 76 | 58,933 rhodium 45 Rh 102,91 ridium 77 | 58.693 patladkum 46 Pd 106.42 platinum 78 | 63,546 silver 47 Ag 107,87 gold 79 | 48 Cd 112.41 80 | 69.723 indium 49 In 114.82 thallium 81 | 72.61 tin 50 Sn 118.71 lead 82 | AS 74.922 antimony 51 Sb 121.76 bismuth 83 | 52 Te 127.60 polonium 84 | 126.90 astatine 85 | 83.80 xenon 54 Xe 131.29 radon 86 |
| 85,468 caesium 55 Cs | 40.078 stronilum 38 Sr 87.62 barlum 56 Ba | 57-70 X | 39 yttrium 39 Y 88.906 hutelium 71 Lu | 47.867 zirconium 40 Zr 91.224 hafnium 72 Hf | v 50.942 nicolum 41 Nb 92.906 tantalum 73 Ta | 51.996 molybdenum 42 Mo 95.94 lungsten 74 W | technetium 43 Tc 1981 fbenhum 75 Re | 55.845 ruthen/um 44 Ru 101.07 osm/um 76 Os | 58.933 rhodum 45 Rh 102.91 ridium 77 Ir | palladium 46 Pd 106.42 platirum 78 Pt | 63.546 silver 47 Ag 107.87 gold 79 Au | 48 Cd 112.41 B0 Hg | 69.723 indium 49 In 114.82 thailium 81 TI | 72.61 Un 50 Sn 118.71 Head 82 Pb | AS 74.922 antimony 51 Sb 121.76 bismuth 83 Bi | 52 Te 127.60 pokenium 84 PO | 79.904 iodine 53 1 126.90 astatine 85 At | xenon 54 Xee 131.29 radon 86 Rn |
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| *Lanthanida carias | lanthanum 57 | cerium 58 | praseodymium 59 | neodymium 60 | promethium 61 | samarium 62 | europium 63 | gadolinium 64 | terbium 65 | dysprosium 66 | holmium 67 | erbium 68 | thulium 69 | ytterbium 70 |
|---------------------|-----------------|--------------|--------------------|-----------------|------------------|----------------|----------------|------------------|---------------|------------------|---------------|--------------|---------------|-----------------|
| Lantinannue series | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb |
| | 138.91 | 140.12 | 140.91 | 144.24 | [145] | 150.36 | 151.96 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 168.93 | 173.04 |
| | actinium | thorium | protactinium | uranium | neptunium | plutonium | americium | curium | berkelium | californium | einsteinium | fermium | mendelevium | nobelium |
| * * Actinide series | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 |
| | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No |
| ~~ | [227] | 232.04 | 231.04 | 238.03 | [237] | [244] | [243] | [247] | [247] | [251] | [252] | [257] | [258] | [259] |

Considering isotopes and resonances









PDFgui – awareness of various effects

Some effects that should be accounted for in data modelling

- Thermal broadening
- Correlated motion of nearest neighbors
- Finite Q_{max} (truncation)
- Limited Q-space resolution (field of view)
- Particle size



Effect of thermal broadening





Effect of correlated atomic motion





Effect of correlated atomic motion





PDF correlated atomic motion outlaws





Effect of finite data range (Q_{max} truncation)



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

Effect of the Q-space resolution

- 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**"



Effect of the Q-space resolution



PDFgui accounts for the effect



Effects of the finite particle size – nano vs bulk





Experimental PDFs of gold nanoparticles and bulk gold, measured on NPDF. Signal damping depends on both **shape & size**!

PDFgui accounts for spherical shapes only



Things needed for small box modeling ...

- 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

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

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

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

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

$$B(r) = e^{-\frac{(rQ_{damp})^2}{2}} \qquad \sigma_{ij} = \sigma'_{ij}\sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{broad}^2 r_{ij}^2}$$

ADP



PDFgui overview

- PDFgui is a graphical interface (modeling platform) built on the PDFfit2 engine
- The PDFfit2 engine written in C++, Python accessible, can be prompt operated
- PDFgui organizes fits and simplifies many data analysis tasks, such as configuring, exectuing, and plotting multiple fits, adding functionality to script driven PDFfit2
- PDFfit2 calculates & fits a theoretical 3D-structure to PDF data (does all the work!)
- The fit system accounts for lattice constants, atomic positions and anisotropic ADPs, correlated atomic motion, as well as standard experimental factors affecting the data
- The atomic positions amd thermal coefficients can be constrained to follow symmetry requirements of an arbitrary space group, enabling studies of local broken symmetry





PDFgui overview

| ✓ CdSe-nano.ddp (~/tutorial/examples/CdSe-nano.ddp) - PDFgui = □ x | | | | | |
|--|--------------------|---------------------|--------------------|------------------------|------------|
| <u>F</u> ile <u>E</u> dit <u>V</u> iew Fi <u>t</u> s <u>P</u> ha | ses <u>D</u> ata C | a <u>l</u> culation | is <u>H</u> elp | | |
| 3 📄 🖬 💊 🥝 | | | | | |
| Fit Tree | Parameters | Results | | | |
| CdSe-bulk | Initia | l Fixed | Refined | | |
| CdSe-bulk.gr | 1 4.3 | | 4.302215896 | | |
| ▽ 🔣 CdSe-3nm | 2 7.01 | | 7.00611078346 | | |
| 🛱 CdSe-wurtzite.stru | 11 0.375 | | 0.373083000599 | | |
| Cds 🕑 | | Plo | t[38] CdSe-3nm.gr: | G | |
| | | | CdSe-3nm.gr:C | 3 | |
| 0.3 | 1 1 | 1 | | Gdiff | |
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| offset –5 | | | | | |
| Plot Reset | | | | | × |
| | 4 | | | | > |

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, with **journal facility**
- powerful visualization facilities
 - live plotting of refined PDF profiles
 - · parametric plots of variables from multiple fits
 - 3D structure visualization (optional connection to structure plotting)
- 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 associated with DATASET

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

Q_{max} fixed in refinement

Q_{damp} refined for calibrant fixed for sample

Q_{broad} refined for calibrant fixed for sample

dscale refined user selected refinement r-range

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



Gaussian dampening (due to limited Q-resolution)

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

scale factor associated with dataset



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] y[n] z[n] occ[n] u[16,n] refined (per symmetry) | x-position (fractional coordinates) y-position z-position site occupancy anisotropic displacement parameters U _{ij} [Å ⁻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 associated with PHASE for correlated atomic motion



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





PDFgui parameters for nanoparticles





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 | scatterer type |
|---------------|----------------------------------|
| declaration | (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 by the handle syntax **@pn**, where **pn** is the parameter number

For example, @1, @55, @321, etc, note that numbers do not have to be consecutive

Variables that are assigned the same handle 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)

...more details at the tutorial ©



Illustrative example: emerging state in AgGaTe₂



Why is lattice thermal conductivity at high temperature Ultralow, and smaller in Ag- than in the Cu-variants?

CuGaTe, CulnTe₂ AgGaTe, _{K_} (Wm⁻¹K⁻¹) 0.2 900 300 450600 750 Temperature (K)



Diamondoid structures (zincblende doubled along c-axis) of intense interest in high-performance thermoelectricity

Illustrative example: emerging state in AgGaTe₂



Atomic ADPs of **Ag** are abnormally enlarged in the ab-plane (perp. to c-axis) indicating in-plane nanoscale disorder!

Rietveld finds that in average structure c-axis of **Ag-variant** has negative thermal expansion (**NTE**) while **Cu-variant** behaves normally. Why?





Illustrative example: emerging state in AgGaTe₂



PDFgui modeling evidences short-range distortion of AgTe₄ tetrahedra, correlated over nanometer length-scale!



- discovery via elaborate PDFgui modeling
- distortion involves local AgTe₄ rotations leading to global NTE effect
- continuous emergence on warming

Brookhaven

• NTE a macroscopic measure of nanoscale distortion and its evolution on warming

Hongyao Xie et al, Adv. Mater. **34**, 2202255 (2022)