

GSAS-II SPECIAL TOPICS



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CONSTRAINTS & RESTRAINTS



CONSTRAINTS & RESTRAINTS - "WHAT TO DO WHEN YOU HAVE TOO MANY PARAMETERS & NOT ENOUGH DATA"

Constraints – reduce no. of parameters

Derivative vector Derivative vector $\rightarrow \frac{\partial F}{\partial v_i} = R_{il} U_{lk} S_{kj}$ **Before constraints** After constraints **Rectangular matrices Rigid body User Symmetry** χ_2 t_{xvz} χ_1 3 Argonne

QUATERNIONS – SIR WILLIAM ROWAN HAMILTON 1843



Broome Bridge, Dublin

Here as he walked by on the 16th of October 1843 Sir William Rowan Hamilton in a flash of genius discovered the fundamental formula for quaternion multiplication $i^2 = j^2 = k^2 = ijk = -1$ & cut it on a stone of this bridge.

Here as be walked by on the 16th of October 1843 Sie William Rowan Rentwo In a flash of genitis cliscovered the fendamental archita for enaternion mail collection

"Quaternions came from Hamilton after his really good work had been done; and, though beautifully ingenious, have been an unmixed evil to those who have touched them in any way, including <u>Clerk Maxwell</u>." — <u>Lord Kelvin</u>, 1892.

NB: W.R. Hamilton is the H in $H\Psi = E\Psi$



Q_{IJK} – QUATERNION TO REPRESENT ROTATIONS IN GSAS-II

- In GSAS-II defined as: Q_{ijk} = r+ai+bj+ck 4D complex number – 1 real + 3 imaginary components
- Normalization: $r^2+a^2+b^2+c^2 = 1$
- Rotation vector: $v = a_x + b_y + c_z$; $u = (a_x + b_y + c_z)/sin(\alpha/2)$
- Rotation angle: $r^2 = cos^2(\alpha/2)$; $a^2+b^2+c^2 = sin^2(\alpha/2)$
- Quaternion product: $Q_{ab} = Q_a * Q_b \neq Q_b * Q_a$
- Quaternion vector transformation: v' = QvQ⁻¹
- Uses: RB rotations, structure drawings, etc.
- No gimbel lock as with Eulerian angles $@ \chi = 0$



FULL MINIMIZATION FUNCTION + RESTRAINTS: ADDITIONAL "DATA"

Least-squares – nonlinear; transcendental functions

 $M = f_Y \sum w_i (Y_{oi} - Y_{ci})^2$ $+ f_a \sum w_i (a_{oi} - a_{ci})^2$ $+ f_d \sum w_i (d_{oi} - d_{ci})^2$ $+f_t \sum w_i (-t_{ci})^4$ $+ f_{p} \sum w_{i} (-p_{ci})^{2}$ $+ f_{v} \sum W_{i} (v_{oi} - v_{ci})^{4}$ $+ f_h \sum w_i (h_{oi} - h_{ci})^2$ $+ f_x \sum w_i (x_{oi} - x_{ci})^2$ $+f_R \sum W_i (-R_{ci})^4$

Powder profile (Rietveld)/Single crystal F_{hkl} **Bond angles Bond distances** Torsion angle pseudopotentials **Plane RMS displacements** van der Waals distances (if $v_{oi} < v_{ci}$) Hydrogen bonds **Chiral volumes** "φ/ψ" pseudopotential

NB: May be 1,000's of these terms for e.g. proteins



RMCPROFILE IN GSAS-II



RMCPROFILE "BIG BOX" SIMULATION

GSAS-II interface development goals

- Provide GUI interface to setup of RMCProfile - save setup controls for reuse
- Initiate independent RMCProfile execution - may run for hours
- Allow graphical display on intermediate



🐝 GSAS-II project: SF6_190K.gpx													
File Data Calculate Import Ex	port Select tab Operations Help												
Project: SF6_190K.gpx	✓ General Data Atoms Draw Options Draw Atoms RB Models Map peaks MC/SA RI ►												
Notebook	A												
Covariance	Metadata item: phase BCC												
Constraints	Metadata item: comment test												
Restraints	Metadata item: source GEM ISIS												
Rigid bodies													
- Phases	Total running time (min): 10. Save interval time (min): 1.												
	Lattice multipliers; if changed will force reset of atom positions:												
SF6_1 abc	X-axis: 3 Y-axis: 3 Z-axis: 3												
PWDR sf6_190gsas.dat Bank	No: be sure to set cations first of anions last in atom ordering												
Comments													
Background	Set max shift: 0.05 0.1												
- Instrument Parameters	Add Atom swap probabilities:												
Sample Parameters													
Index Peak List	Enter constraints & restraints: Set minimum & maximum dictances for:												
Unit Cells List	S-S S-F F-F												
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	Search from: 0. 1.37 2.												
	try 0 18 25												
	Use bond valence sum restraints for (set to 0 for non-bonded ones):												
	Add Fixed coordination number restraint:												
	Add Average coordination number restraint:												
	Potential temperature (K): 190.												
	Add A-B stretch potential restraints, search range (%): 30.												
	Atom-A Atom-B AB dist potential												
	Delete S v F v 1.564 2.												
	Delete F v F v 2.2 2.												
	Add A-B-C angle potential restraints, search range (%): 10.												
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	Select data for processing:												
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	Select RMC V 0.01 Neutron reciprocal space data; F(Q): sf6_190k_fq.dat												
	Select Neutron reciprocal space data; S(Q):												
< >	Select Xray real space data; G(r):												
Mouse RB drag/drop to reorder	h.												



RMCPROFILE RESULT FOR SF₆

10x10x10 unit cell box – transform back to original See disordered atom distribution

- compare to Rietveld U_{aniso} for F atom





PDFFIT & ISODISTORT



ISODISTORT Implementation in GSAS-II

ISODISTORT: Web based tool for discerning mode displacements of atoms

from an idealized parent structure

Isodistori x +			-		×
← → C A https://iso.byu.edu/iso/isodistort.php	*	£^≡	¢	۲	
ISODISTORT					^
Version 6.11.1, Jan 2022					
Harold T. Stokes. Branton J. Campbell, and Dorian M. Hatch, Department of Physics and	d As	trono	my,		
Brigham Young University, Provo, Utah, 84602, USA, branton_campbell@byu.edu					- 1
Description: ISODISTORT is a user-friendly internet-based tool for exploring the struct	ural (distor	tion		
modes of crystalline materials induced by irreducible representations of the parent space symmetry. The stand-alone ISOVIZ application further allows one to visualize and intera	e-gro	oup			
manipulate the modes generated in ISODISTORT.	oure	,			- 1
NOTE: Interactive visualizations must now be saved to disk and or	ben	ed w	ith		
the standalone ISOVIZ application.					
Help, Tutorials, Version History					
Legacy copy of ISODISTORT version 5.6.1, August 2013					
Begin by entering the structure of parent phase: 🥜					
Get started quickly with a cubic perovskite parent.					
Import parent structure from a CIF structure file: OK					
Choose File No file chosen					
If you don't have a parent CIF, create one using ISOCIF.					
Alternatively, you can begin with a previously-saved distortion: (?)					
Get started quickly with a distorted perovskite example. (Select this link and click	k "Ol	K" on			
the next page to test your Java installation.)	-	-	Train and	1000	-

 To use: a multistep process → a cif file with modes; can be imported into GSAS-II with new variables for the modes.



 New implementation – direct interaction between GSAS-II & ISODISTORT; simplified operation





PDFFIT2 = "PDFfit" IN GSAS-II "Small Box" modelling of pair distribution functions

Use ISODISTORT – create the atom position constraints in new interface to PDFfit2

Project: C:\work\GSASII\Exampl Notebook Controls Covariance Constraints Restraints Rigid bodies Digit bodies Covariance Constraints Restraints	4 D	late At	oms	Draw Options	Drav	Atoms	RB Models	Map peaks	MC/SA	RMC	ISODISTORT	Texture P	swley reflection	•	
	Tenatorea areas											^			
	Refine unit cell?														
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	(03_1	0	0.75000+0.04419*@26+0.04419*@27			0.75000	0.75000-0.04419*@26+0.04419*@27 0.5000				23-0.03125*@24			
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Parameters: mode displacements (Å) Can be fit for sequence of T





INCOMMENSURATE STRUCTURES IN GSAS-II



INCOMMENSURATE STRUCTURES N GSAS-II

Book: "Incommensurate Crystallography" S. van Smaalen



H=G+mq

G: substructure hkl m: +/- small integers q: modulation vector

For Na₂CO₃ q= 0.183,0,.319

Each reflection: hklm m=0 sublattice m≠0 superlattice

 $Na_2CO_3 - single crystal X-ray data - h0l zone \rightarrow rows of spots don't line up$



POWDER DIFFRACTION

Na₂CO₃ – 11BM @ APS room temp.



Includes m=-2,-1,1,2 superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom



INCOMMENSURATE STRUCTURE SOLUTION

4D charge flipping; single crystal & powders (e.g. Pawley refinement)



Modulation of atom positions (Na1-y) Fit function – fourier series in tau





LATTICE MODULATION

Na₂CO₃ – single crystal data



Coordinated wave motion – Na lattice y motion/ CO_3 rocking motion Recall q= 0.183,0,319 so period ~6-7 on x & ~3 on z Possible modulations: positions, thermal parameters, site fractions (& magnetic moments)



INCOMMENSURATE STRUCTURES

Symmetry symbols – interpreted by GSAS-II (not lookup)

Space group + super symmetry symbol

e.g. $Na_2CO_3 - C2/m(\alpha 0\gamma)os$ Space group Modulation vector

Operators: conventional space group & 4th dim component



Possible modulation vectors: e.g. $\alpha\beta\gamma$, $\alpha0\gamma$, $0\beta0$, $\alpha1/2\gamma$, $1/2\beta0$ Translations: 0,s,t,q,h 1-4 of these Depend on space group GSAS-II shows legal choices



MODULATION MODELS

Position, thermal motion, site fraction & magnetic moment

- Position: on x,y,z
 - Fourier series sin & cos- symmetry allowed choices
 - Zigzag, sawtooth & block just 1, add Fourier for more terms



- Thermal motion:
 - Fourier series
- Site fraction:
 - Fourier series
 - Crenel like block but 0/1 (not +/- x)
- Magnetic moment
 - Fourier (odd terms only generally just 1)



INCOMMENSURATE STRUCTURES

Cases not allowed in GSAS-II

- 3+2 & 3+3 not allowed in GSAS-II
 - Too complex to deal with easily
 - 3-D 230 SG
 - For 3+1: 4,783 possible SG
 - For 3+2: 222,018 possible SG
 - For 3+3: 28,927,922 possible SG
 - But only a handful found not worth the hassle
- Ad hoc centering not allowed
 - 'X' space groups all have equivalent legal ones with transformation
- Other odd cases found in cif files not allowed
 - e.g. R-centered monoclinic



MAGNETIC INCOMMENSURATE STRUCTURES

Some examples:





CeRuSn - Ce moment

$\beta\text{-Li}_2\text{IrO}_3$



 $DyMn_6Ge_6$ – residual moment



CeRuSn – structure modulation



CURRENT STATUS

GSAS-II & incommensurate/magnetic structures – still to be done!

- Incommensurate magnetic structures
 - Structure factor & derivatives math & refinement
 - Site symmetry rules for allowed Fourier coefficients
- Incommensurate structures
 - Certain high symmetry site symmetry rules (in tetragonal, trigonal & hexagonal)
 - Refinement of non Fourier functions (derivative issues)
 - Cif file output?
- Magnetic structures
 - Structure solving aids i.e. selection of magnetic cell & space group from observed data
 - Output mcif files TBD
 - 1st tutorial now available Simple Magnetic Structures



CHARGE FLIPPING



CHARGE FLIPPING

The algorithm set up: ~1Å unique reflections \rightarrow sphere \rightarrow box \rightarrow 0.5Å box







CHARGE FLIPPING – 3D & 4D

Python loop – all double precision; start random phases for CEhkl

CErho = np.real(fft.fftn(fft.fftshift(CEhkl)))*(1.+0j)	#fft Fhkl $\rightarrow \rho(xyz)$	
CEsig = np.std(CErho)	#get σ(ρ)	
CFrho = np.where(np.real(CErho) >= flipData['k-factor']*C	Esig,CErho,-CErho)	$\#CF \rho \not \rightarrow \rho'$
CFrho = np.where(np.real(CErho) <= flipData['k-Max']*CE	sig,CFrho,-CFrho)	#U atom CF!
CFhkl = fft.ifftshift(fft.ifftn(CFrho))	$\# {\it fft} \ \rho`(xyz) \twoheadrightarrow {\sf F}`(hkl)$	
CFhkl = np.where(CFhkl,CFhkl,1.0)	#avoid divide by zero)
phase = CFhkl/np.absolute(CFhkl)	#get $\phi(hkl)$ from F'	
CEhkl = np.absolute(CEhkl)*phase	#apply ϕ to F	
Ncyc += 1	#count tries	
sumCF = np.sum(ma.array(np.absolute(CFhkl),mask=Em	#Σ F	
DEhkl = np.absolute(np.absolute(Ehkl)/sumE-np.absolute	$\#\Sigma DF $	
Rcf = min(100.,np.sum(ma.array(DEhkl,mask=Emask)*10)0.))	#residual

After user break: Repeat 1st line to get result map Find origin; search for peaks & display result



EXAMPLE – SUCROSE POWDER

11BM @ APS - 1st steps – peak fitting/indexing/Pawley refinement



CHARGE FLIPPING SOLUTION

Residual ~45% \rightarrow ~17% & 46 peaks in cell (NB: sucrose C₁₂H₂₂O₁₁) Map peaks – unique set & select – identify atoms – make molecule





CHARGE FLIPPING – PHASES?

Track phases of 5 reflections – 10000 CF cycles



CHARGE FLIPPING – CHAOS MATHEMATICS?

Strange attractors? Cantor dust? Butterfly effect? Basin of attraction?

- Cyclic algorithm successive iteration stable solution (apparently?)
- Chaotic phase behavior but deterministic (Butterfly effect?)
- Hyper dimensionality ~7680-D for sucrose example (NB: no symmetry used)
- Infinite phase possibilities >> Infinite phase sets for recognizable atoms (Cantor dust?)



- Phase oscillation & drift "<u>sympletic</u>" or "non-sympletic" strange attractors?
- Is there a "basin of attraction"?
- Does this really matter?

(picture from "Strange Attractors: Creating Patterns in Chaos" by J. C. Sprott)



THANK YOU

