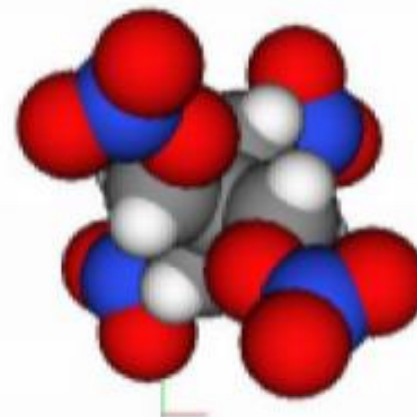


GSAS-II BEYOND RIETVELD

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CSX/XSD/APS
vondreele@anl.gov

Saskatoon
June, 2024

GSAS-2



2D IMAGE PROCESSING – FORGOTTEN OLD MATH

2D IMAGE DATA

Conic sections

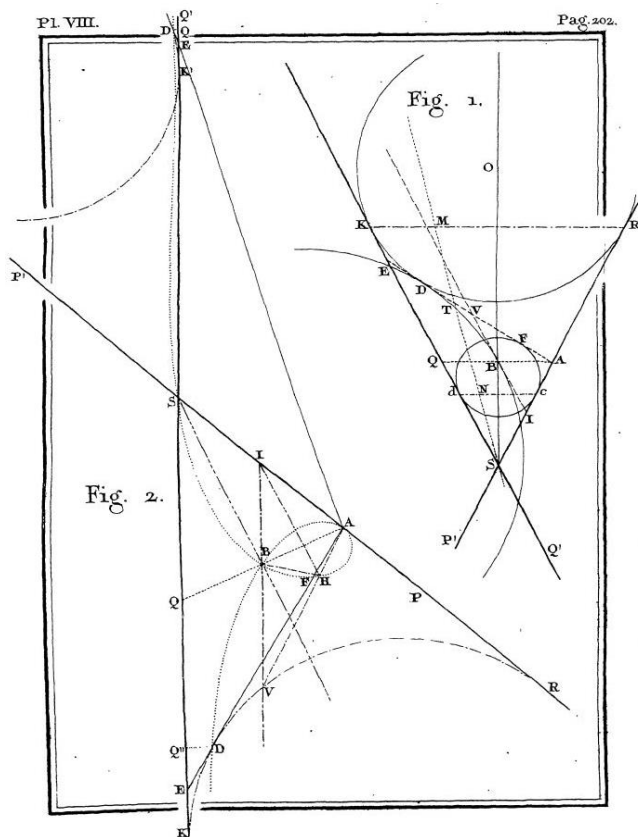
Where is the incident beam on the detector?

Fit2D (& DataSqueeze) – assumes center of the diffraction ellipse - **False**

Analysis – G.P. Dandelin,

Nouveaux memories de l'Academie royal de Bruxelles, 2, 171-202 (1822)

Drawing by Dandelin p.202



Taken from Dandelin's original paper
Fig. 1: Shows the 2 spheres in contact with plane EA

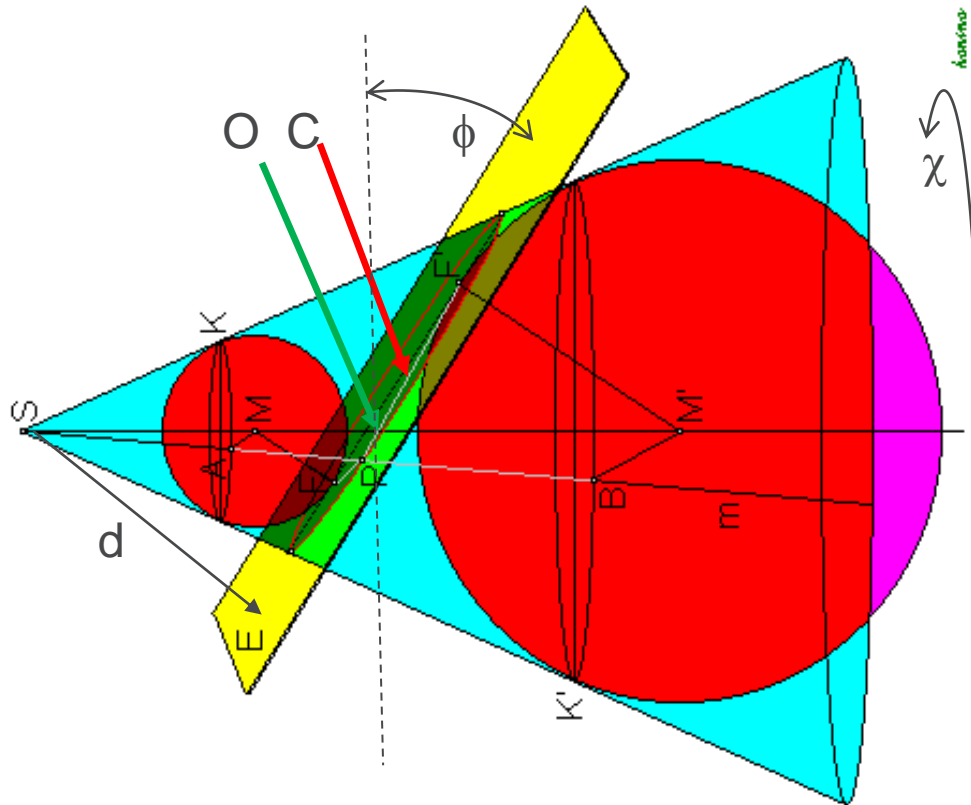
- line SO is cone axis
 - F&D are the ellipse foci on the plane
- He refers to a work by M. Quetlet as having previously made this construction - source?

This is not something new!

Dandelin sphere construction is used in GSAS-II for image plate orientation calibration

NB: Irena & pyFAI get this right

GSAS-II IMAGE DETECTOR CALIBRATION VIA DANDELIN SPHERES

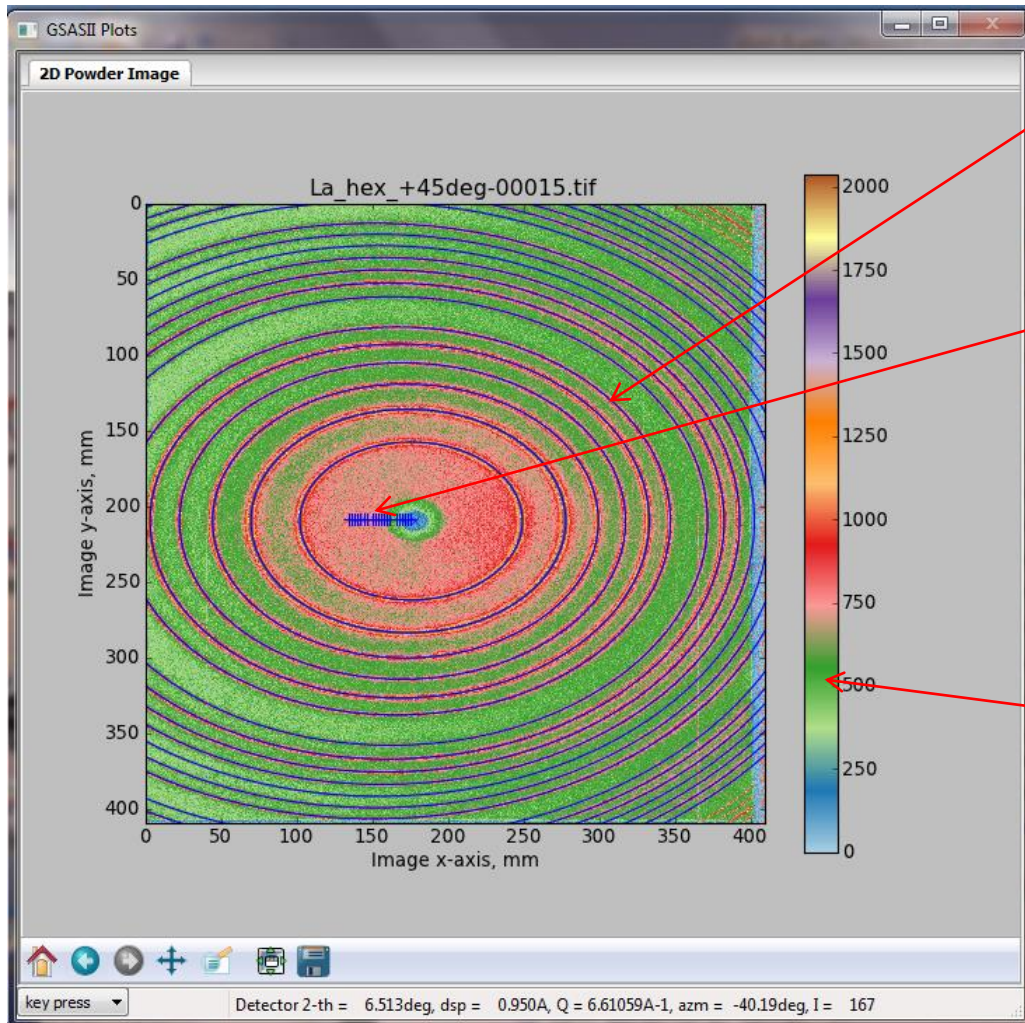


- Plane E is a tilted area detector
- The line SMM' is the Bragg cone axis – incident beam direction & passes through centers of both spheres
- Spheres touch plane at foci (F & F') of conic section (ellipse)
- Intersection of axis with plane (**O**) not at halfway point (**C**) between F & F' (ellipse center) – note similar triangles MFO & M'F'O of different sizes
- If plane is perpendicular to cone axis then conic section is a circle and O & C coincide
- GSAS-II parameters:
 - d – sample-detector plane distance
 - ϕ – detector tilt angle ($= 2\Theta_{\text{detector}}$)
 - χ – tilt azimuth angle
 - x_o, y_o – beam position @ **O** on detector

This is just geometry

2D IMAGES IN GSAS-II:

Calibration – tilted detector (e.g. 45° about vertical axis)



Ellipses – sections of Debye-Scherrer cones

Ellipse centers – not on beam center!

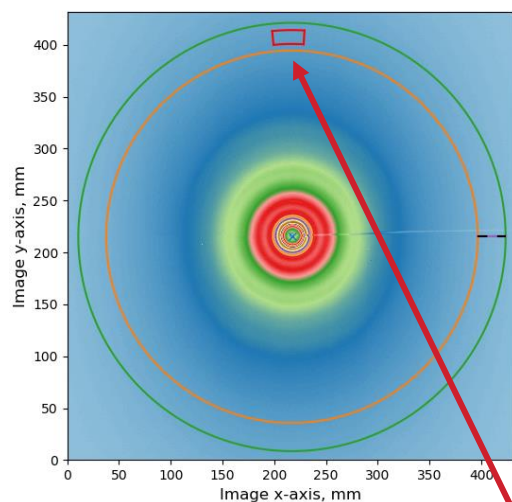
Fitting only requires material (LaB_6) and λ (e.g. don't need to know distance – get that from fit)

Choice of color scheme – “Paired” is shown

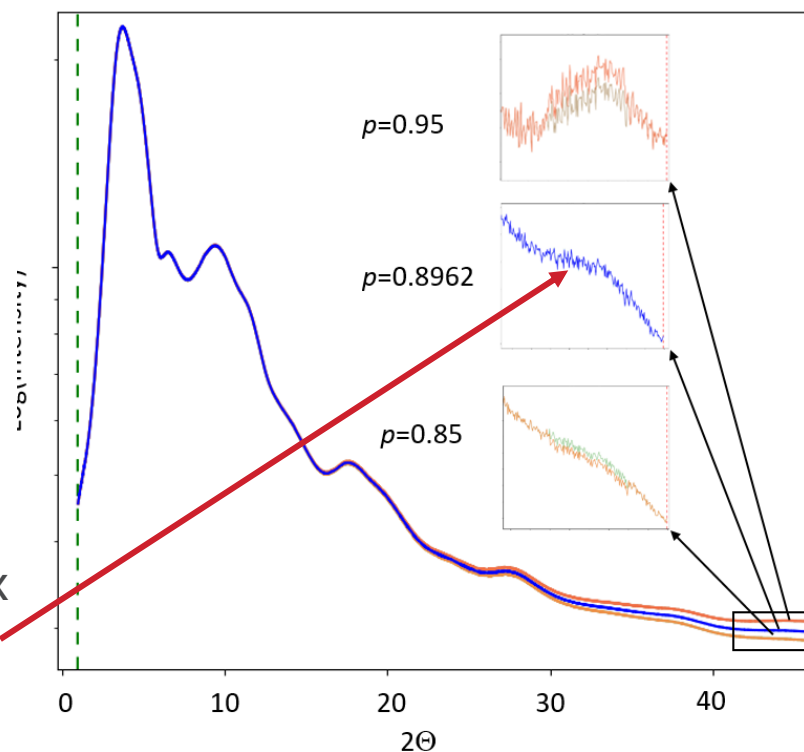
2D IMAGE POLARIZATION DETERMINATION

Sample – glass microscope slide – purely amorphous & isotropic
Polarization correction: azimuth (φ) dependent

$$P = [(1 - p)\cos^2\varphi + p\sin^2\varphi]\cos^2 2\Theta + (1 - p)\sin^2\varphi + p\cos^2\varphi$$

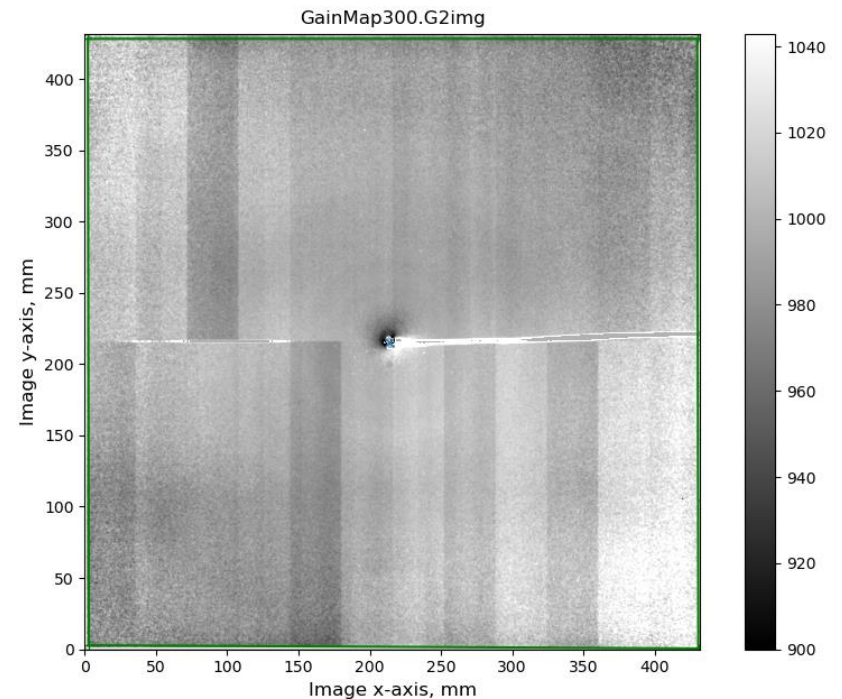
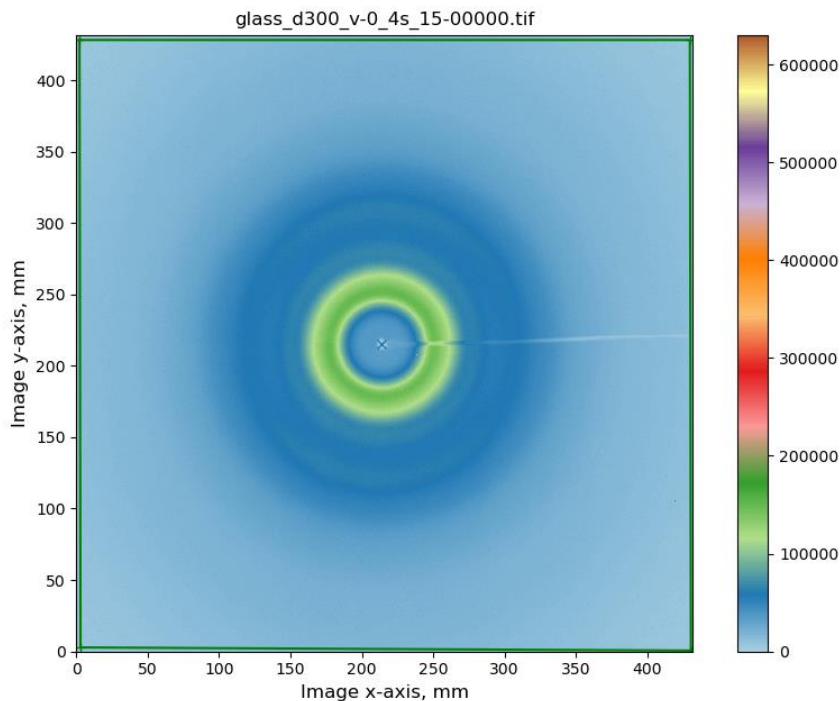


Integrate in band w/o mask box
Match if polarization is correct



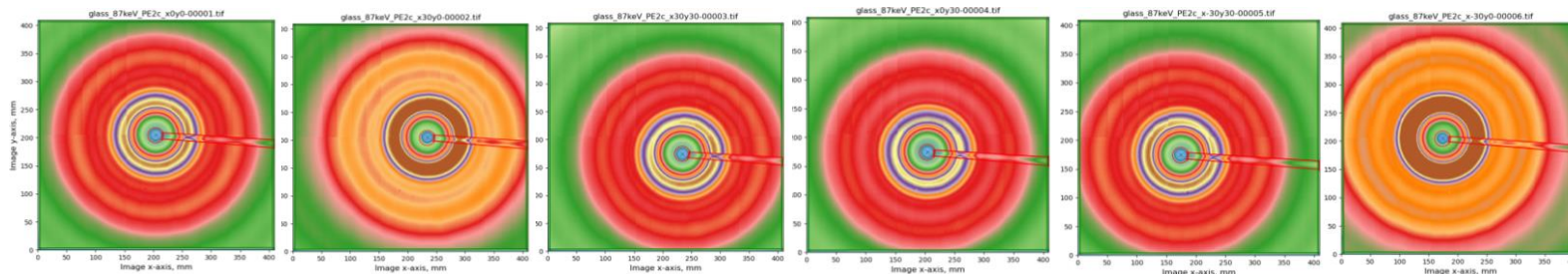
2D DETECTOR GAIN MAP

Sample – glass microscope slide – purely amorphous & isotropic
Image corrected for polarization (automatic in GSAS-II)



Integrate, compute ave image & subtract; residual is gain map (x1000)
Still have beam stop shadow

MULTI-IMAGE GAIN MAP – BETTER



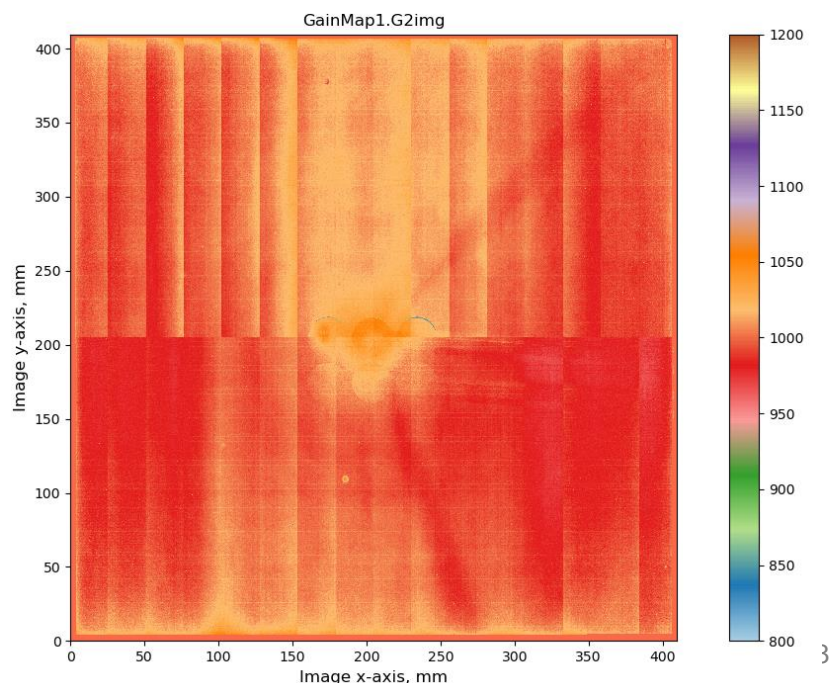
Shift 0



Multiple exposures – shift on x & y; calibrate each

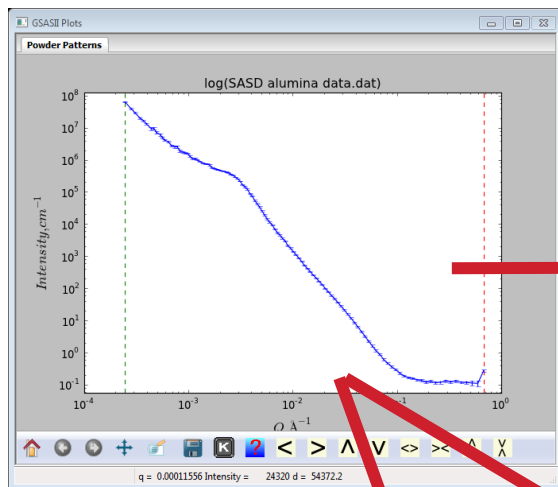
Mask undesireables – beam stop & arm, etc.

Combine to one gain map

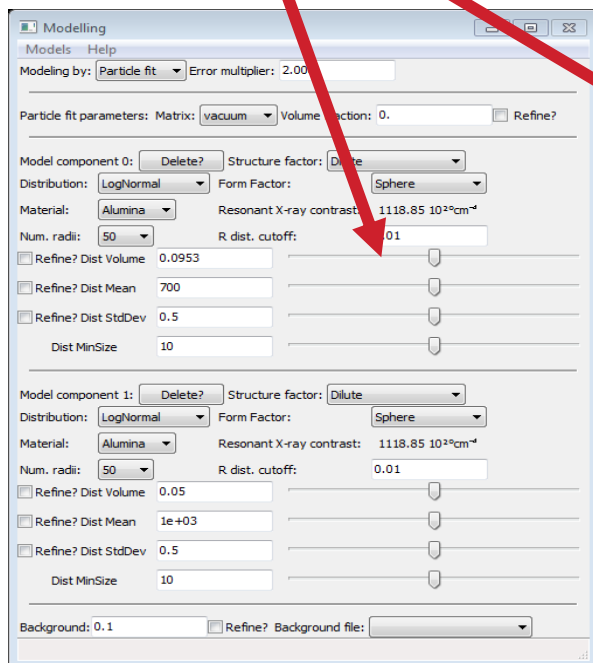
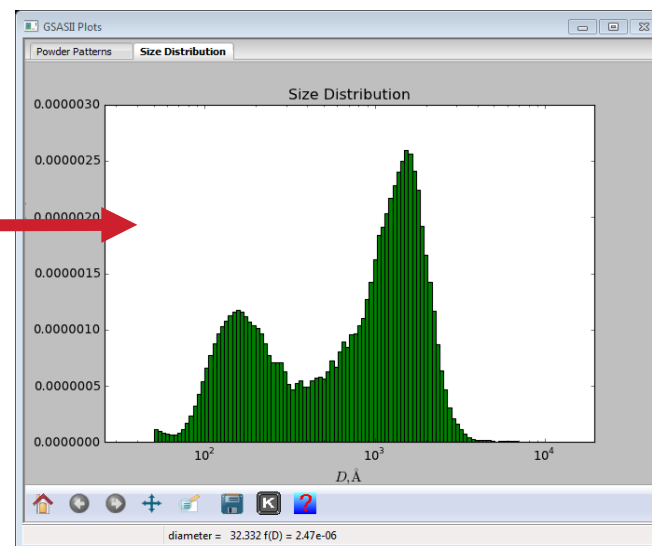


SMALL ANGLE SCATTERING

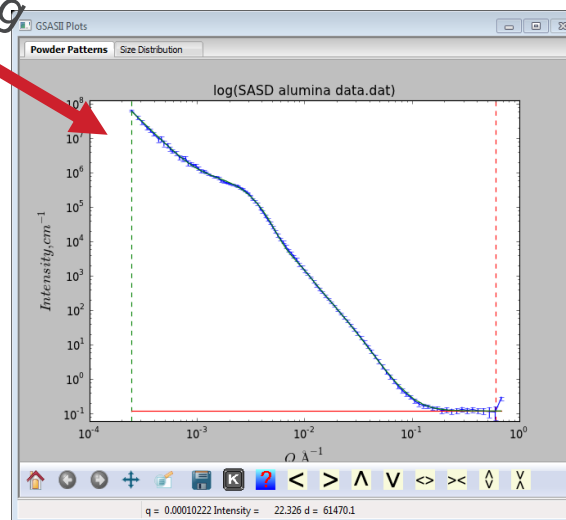
Range of tools



Size
Distribution
by MaxEnt

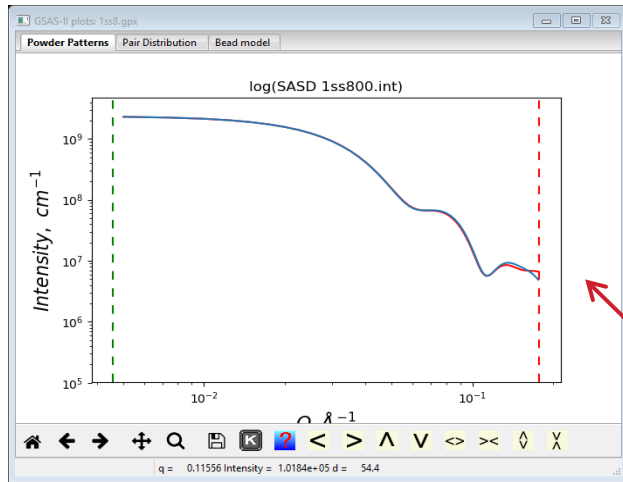


Modelling
LSQ fitting

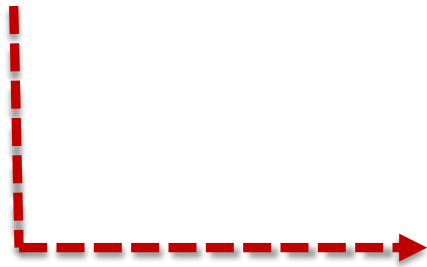


PROTEIN SMALL ANGLE MODELING IN GSAS-II

Bead models via SHAPES (alternative to DAMMIN in python)

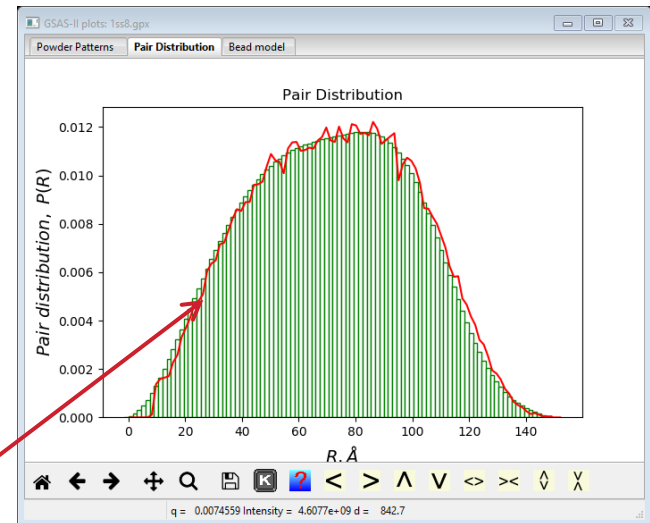


Data (simulated) from PDB 1ss8
3668 AA, 7-fold rot. symm.
E. Coli chaperonin GroEL

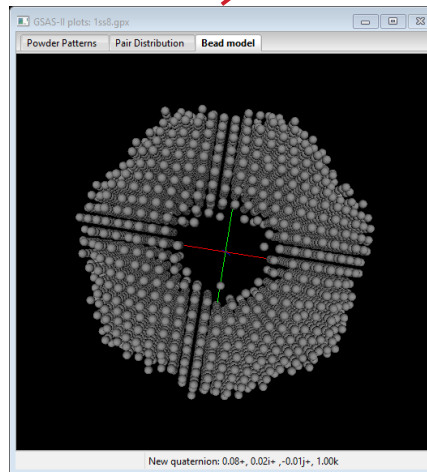


Direct fit?
(In development)

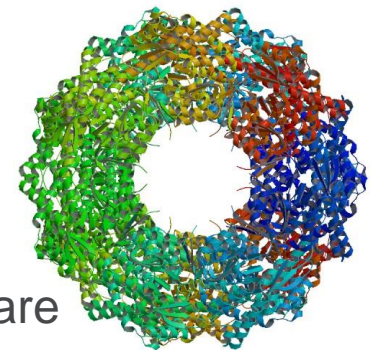
Make $P(R)$



calc



Run SHAPES
Make bead model



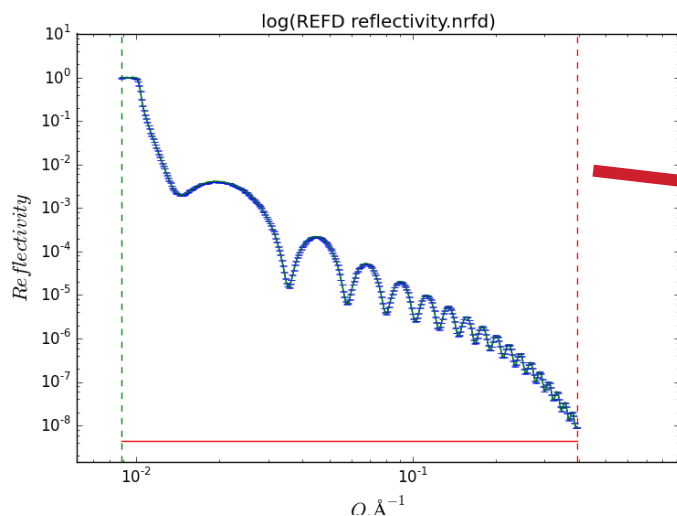
compare

“SHAPES”, J. Badger, J. Appl. Cryst 52, 937-944 (2019)

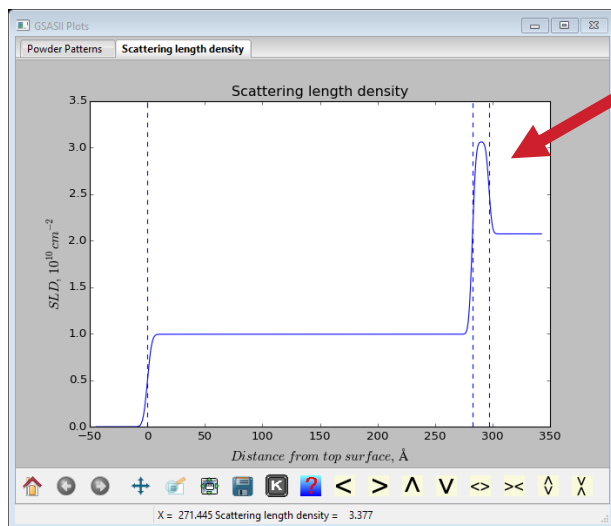
REFLECTOMETRY

REFLECTOMETRY ANALYSIS IN GSAS-II

X-rays & Neutrons (CW at least)



Multilayer model
Scattering density

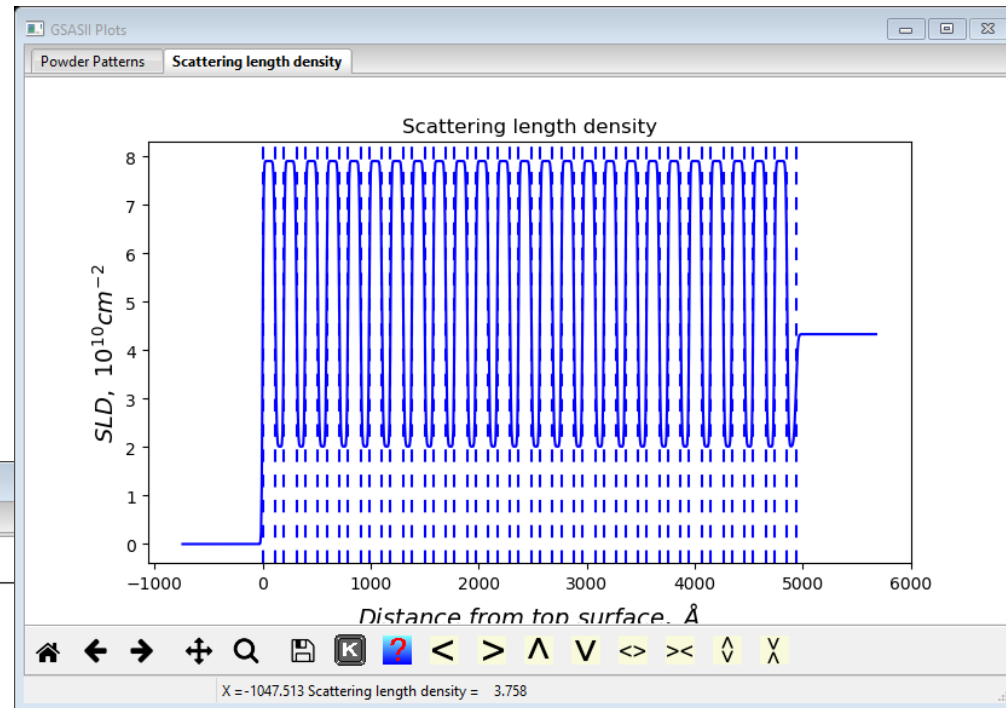
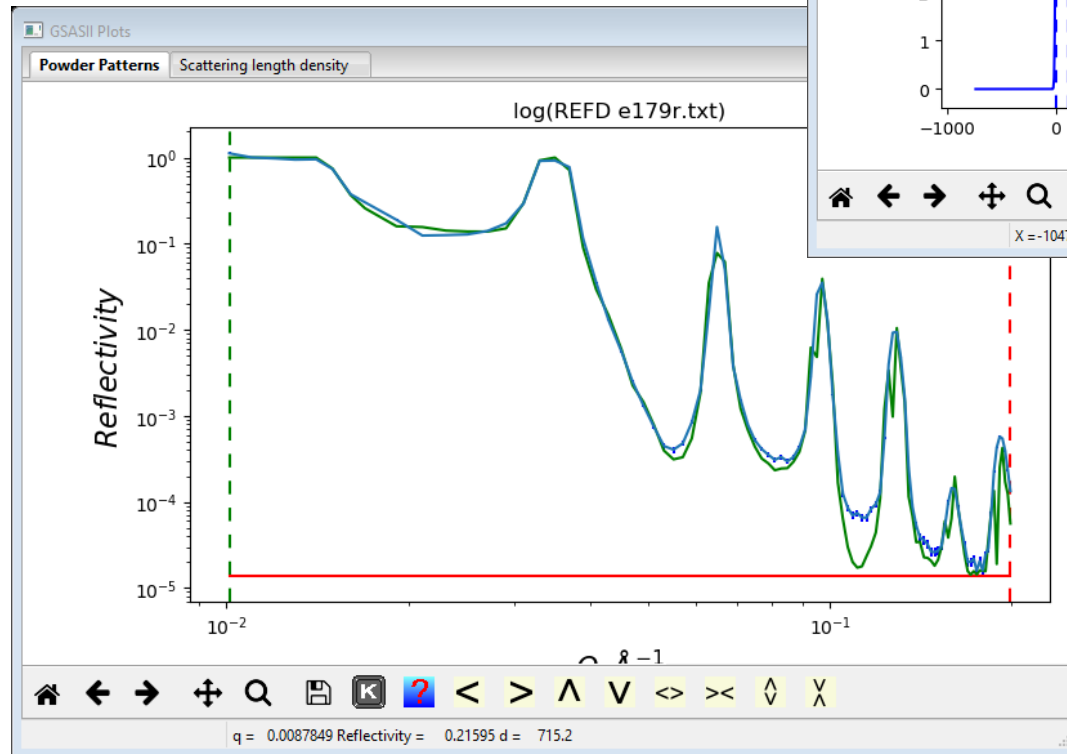


The "Modelling" window in GSAS-II shows the Reflectometry fitting for REFD reflectivity.nrfd. The controls include Instrument resolution type (const $\Delta Q/Q$), Minimizer (LMLS), Bounds factor (0.85), and Plot controls (Plot SLD?, Zero position location: Top). The Global parameters section shows Scales (1.0) and Flat bkg. (4.4e-09). The Layer sequence is 1 2. The Use sequence nos. from: 1: Alumina 2: Alumina. The NB: Repeat sequence by e.g. 6*(1 2). The Layers: scatt. densities are $10^{10} \text{ cm}^{-2} = 10^{-4} \text{ Å}^{-2}$. The Top layer (superphase) is vacuum. The Layer no. 1 parameters are Substance: Alumina, Den. Mult.: 0.1737, Real scat. den.: 0.9943, Imag scat. den.: 0, Magnetic SLD: 0.0, Upper surface Roughness, Å: 3.0, Layer Thickness, Å: 282.63. The Layer no. 2 parameters are Substance: Alumina, Den. Mult.: 0.5352, Real scat. den.: 3.063, Imag scat. den.: 0, Magnetic SLD: 0.0, Upper surface Roughness, Å: 2.4, Layer Thickness, Å: 14.41. The Bottom layer (substrate) is Silicon, Den. Mult.: 1.0, Real scat. den.: 2.073, Imag scat. den.: 0, Magnetic SLD: 0.0, Upper surface Roughness, Å: 2.2.

Define components, stacking sequence
(can be repeated), thickness & "roughness"
Fit by LSQ, MC/SA & "basinhopping"
(under development)

MULTILAYER REFLECTIVITY

25 layers on a substrate
Common thickness & contrast



CLUSTER ANALYSIS

CLUSTER ANALYSIS?

“Unsupervised Machine Learning”, “Pattern Recognition”, etc.

Faced with (say) 1000 powder patterns collected as a survey of some object

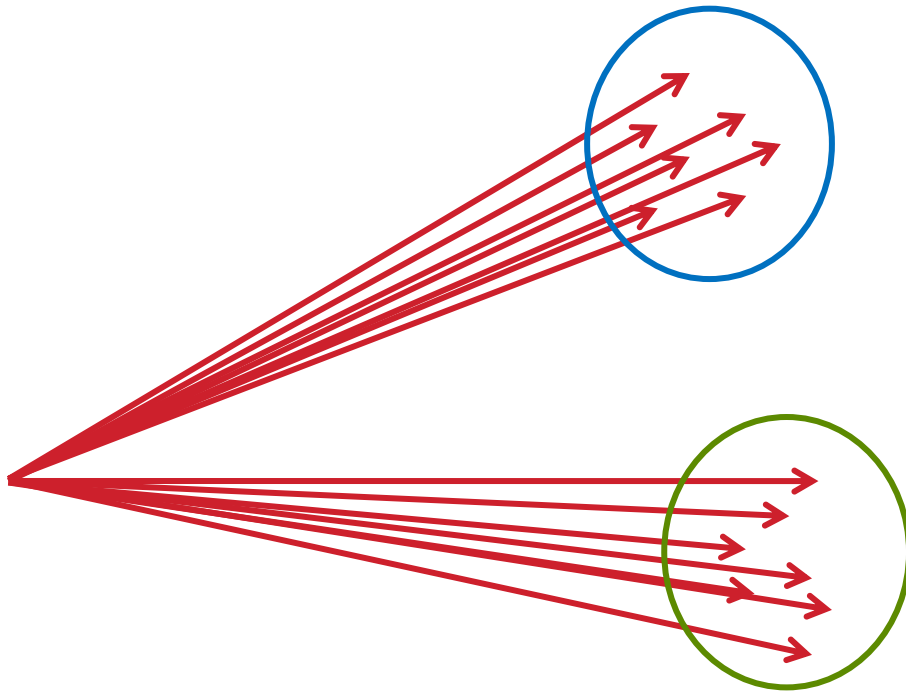
What to do?

- Group “similar” data
- Somehow different from other data
 - May be other clusters each with own “similar” data
 - Some may be “outliers” (“bad” data?)
- Start knowing “nothing” about the entire suite of data (no preconceived notions)
- Not a single method! Iterative exploration to find useful result.
- Fast – can do 100’s-1000’s of data sets in few seconds
- GSAS-II – will do cluster analysis on powder patterns & pair distribution functions (PDF); NB: not images
- Some requirements:
 - Don’t want to compare “apples & oranges” so data collections (e.g. powder data) must all be done the same way (span, #steps, radiation wavelength, etc.)
 - Don’t mix x-rays & neutrons.
 - Otherwise, cluster analysis will pick out these differences first (& not what you’re after).

PROCESS

Comparison method?

- Each pattern – vector (1000's of dimensions)
- Cluster similar vectors (data sets) by “distance”



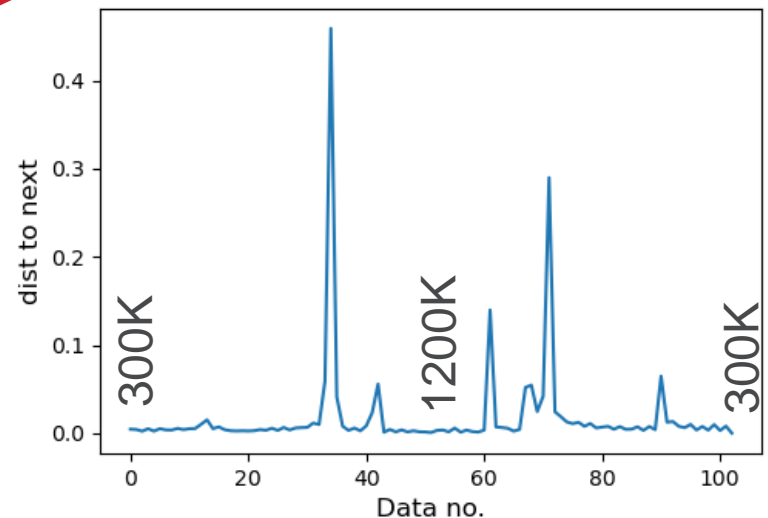
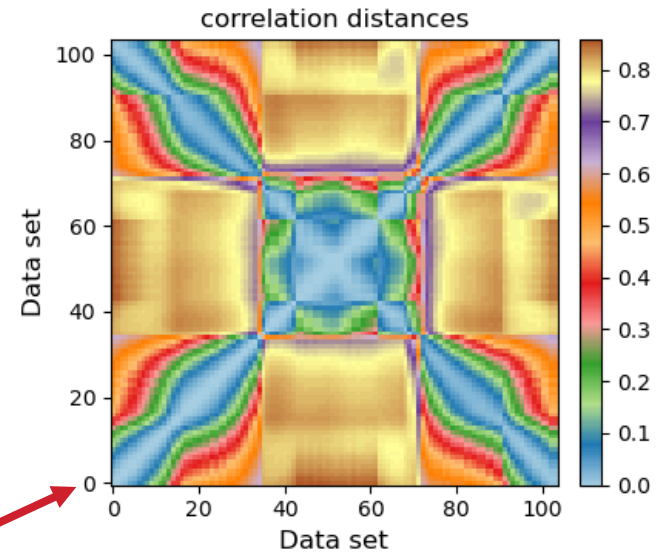
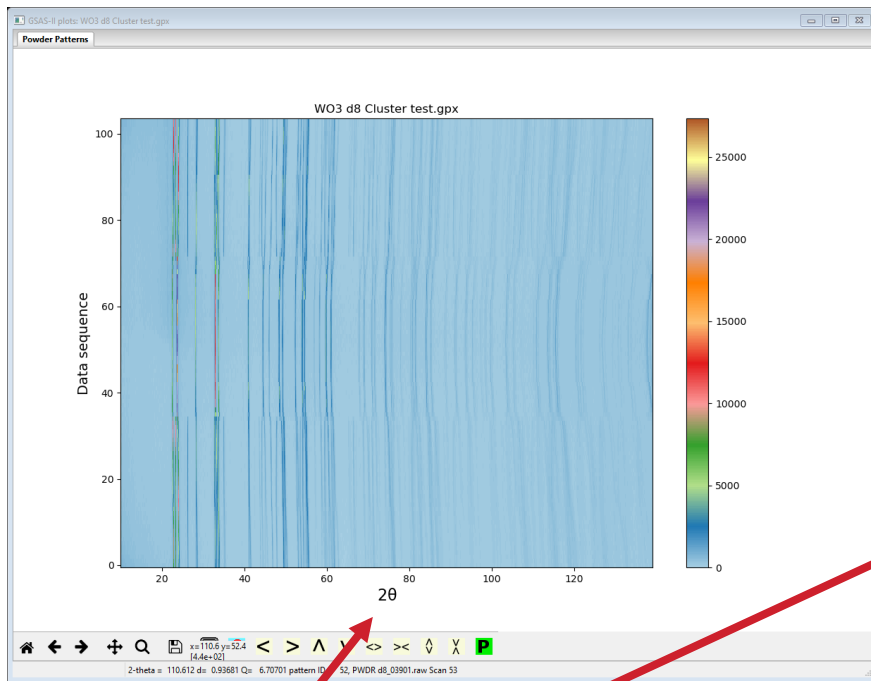
“Distance” in GSAS-II

- Euclidian - shortest
- City block – steps along each axis (longer)
- Cosine – of angle between
- Correlation – coefficient
- Etc... - 11 methods; take your pick. Some are more contrasty than others

DISTANCES

Preliminary results – distance matrix & serial distances

- Example – WO_3 x-ray data 300-1200K & back; 108 powder patterns (integrated from images).



Powder data
Distance matrix
Serial distances

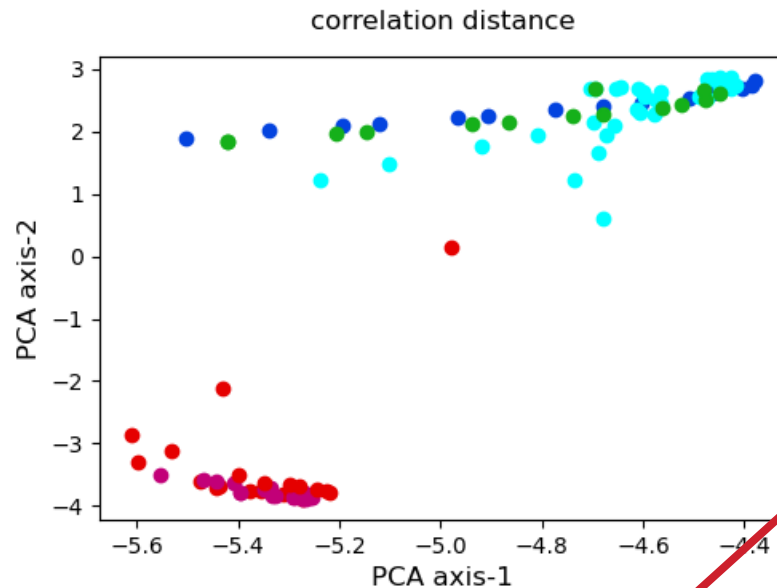
n+1 vs n

Peaks = Phase changes

Not useful for random data

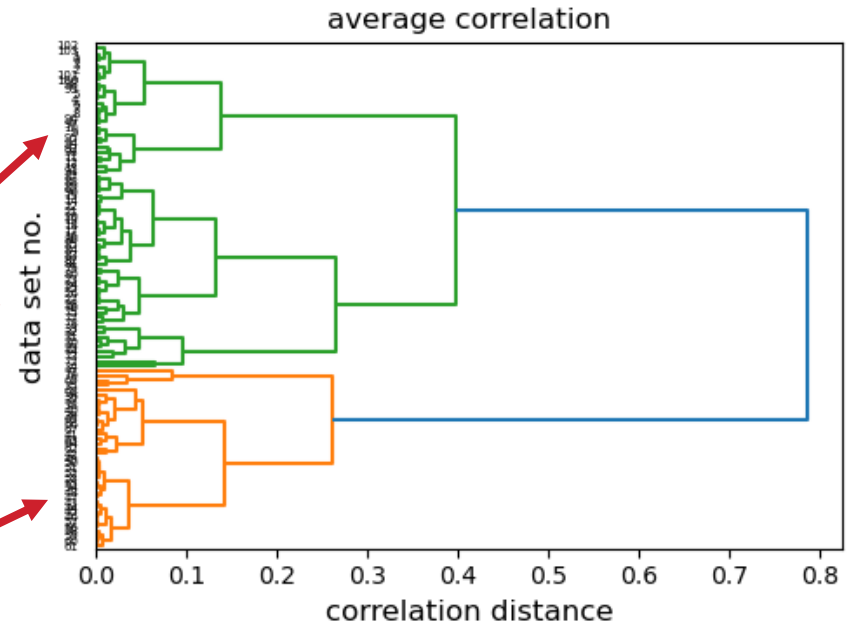
DISTANCES – PRINCIPAL COMPONENT ANALYSIS & DENDOGRAM

Most significant 2-3 dimensions – cluster analysis



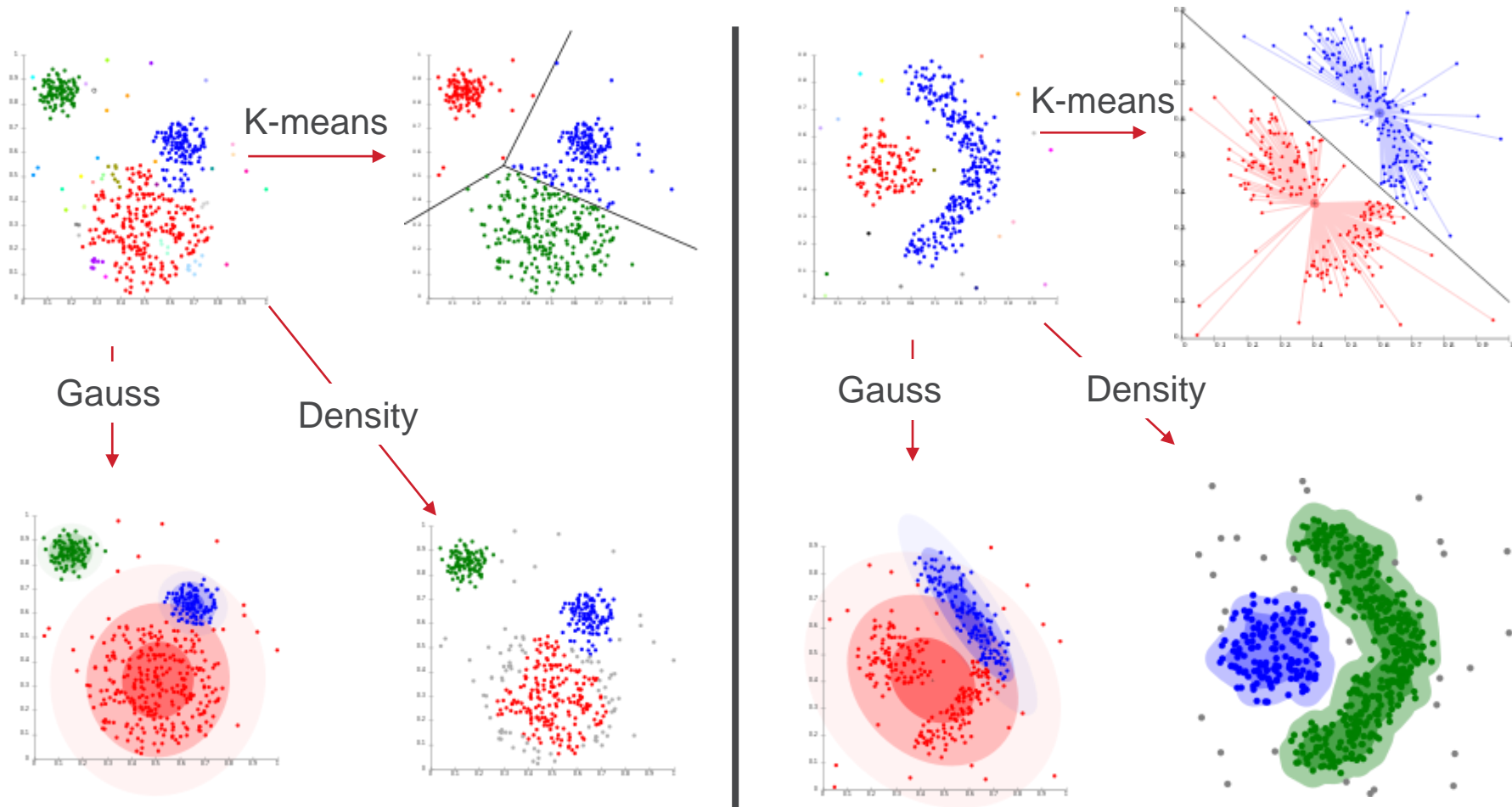
Temp variation – trails in PCA
→ Clusters ill defined in this case
Colored by “cluster”

Dendrogram
– hierarchy in data?
Low T phase
Intermediate T phases
High T phase



THE CLUSTERING PROBLEM

Wide variations possible – 2 example PCAs & cluster algorithms

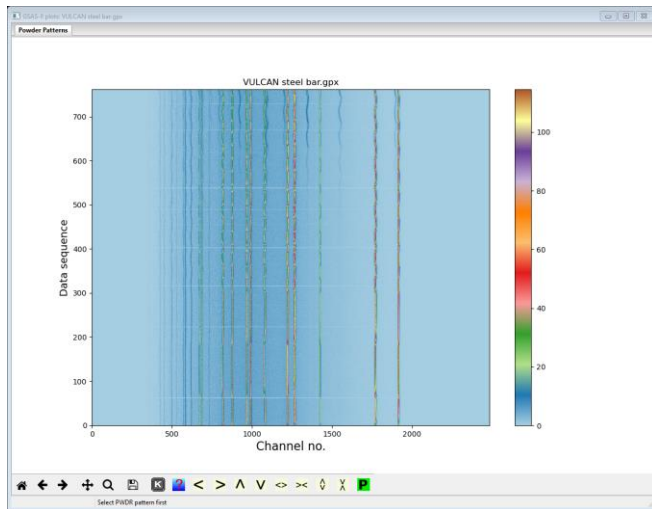


GSAS-II has 6 clustering algorithms – some require # of clusters

Taken from Wikipedia

OUTLIER ANALYSIS IN GSAS-II

Find “bad data”: Steel bar – repeated stress (TOF neutron)



800 patterns

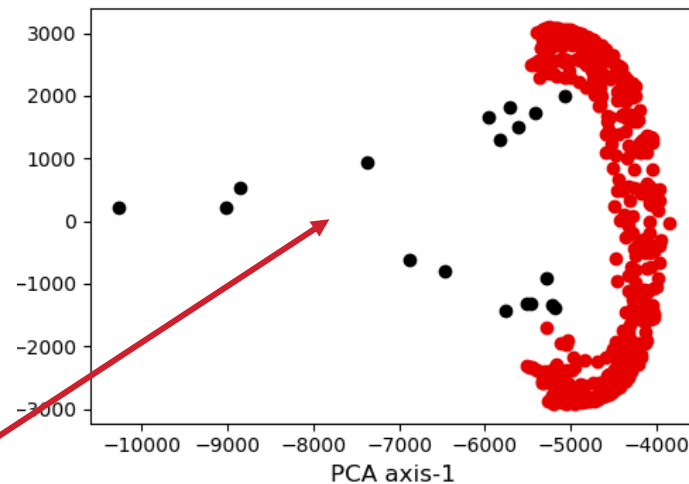
There were beam dropouts!

3 outlier algorithms in GSAS-II

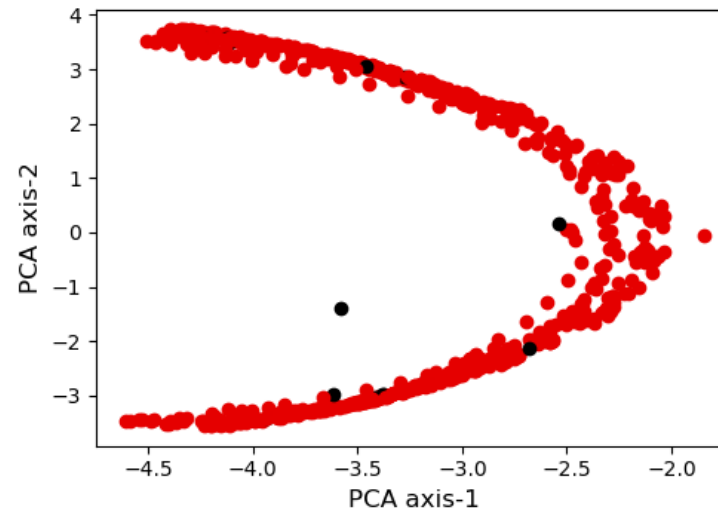
Depends on distance algorithm

GUI will show list of bad data

Correlation PCA



Cosine PCA



RMCPROFILE IN GSAS-II

RMCPROFILE “BIG BOX” SIMULATION

GSAS-II interface development goals

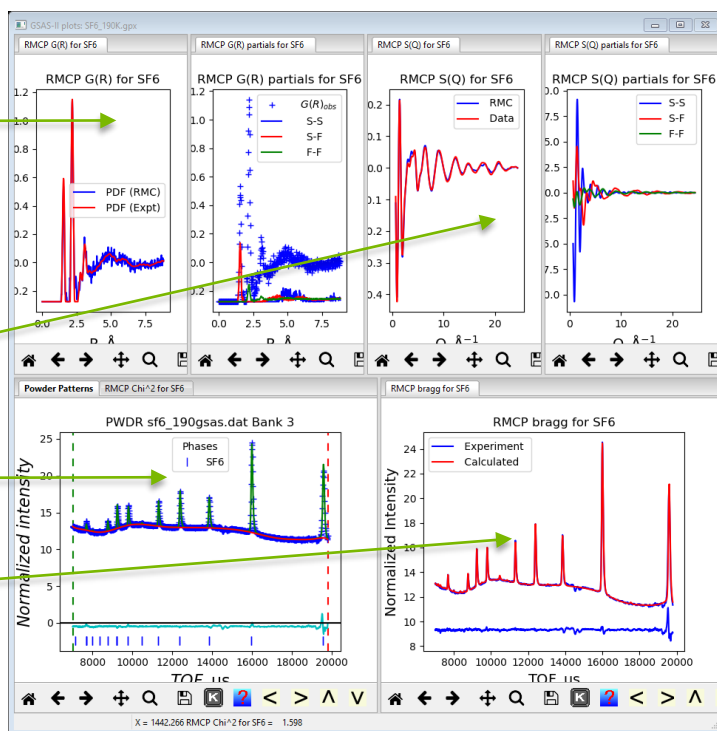
- Provide GUI interface to setup of RMCPProfile - save setup controls for reuse
- Initiate independent RMCPProfile execution – may run for hours
- Allow graphical display on intermediate results

G(R) & partials

S(Q) & partials

RR result

PWDR simulation



Project: SF6_190K.gpx

File Data Calculate Import Export Select tab Operations Help

Project: SF6_190K.gpx

- ◻ Notebook
 - ◻ Controls
 - ◻ Covariance
 - ◻ Constraints
 - ◻ Restraints
 - ◻ Rigid bodies
- ◻ Phases
 - ◻ SF6
 - ◻ SF6_1
 - ◻ SF6_1 abc
- ◻ PWDR sf6_190gsas.dat Bank
 - ◻ Comments
 - ◻ Limits
 - ◻ Background
 - ◻ Instrument Parameters
 - ◻ Sample Parameters
 - ◻ Peak List
 - ◻ Index Peak List
 - ◻ Unit Cells List
 - ◻ Reflection Lists

General Data Atoms Draw Options Draw Atoms RB Models Map peaks MC/SA RI

Metadata item: phase BCC

Metadata item: comment test

Metadata item: source GEM ISIS

Total running time (min): 10. Save interval time (min): 1.

Lattice multipliers; if changed will force reset of atom positions:

X-axis: 3 Y-axis: 3 Z-axis: 3

NB: be sure to set cations first & anions last in atom ordering

Set atom ordering: S F

Set max shift: 0.05 0.1

Add Atom swap probabilities:

Enter constraints & restraints:

Set minimum & maximum distances for:

	S-S	S-F	F-F
Hard min:	4.	1.37	2.
Search from:	0.	1.37	2.
to:	0.	1.8	2.5

☐ 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	F	1.564	2.
Delete	F	F	2.2	2.

Add A-B-C angle potential restraints, search range (%): 10.

Select data:

Select one histogram for Bragg processing:

PWDR sf6_190gsas.dat Bank 3 Weight 0.1

☒ Use size broadening? ☒ Use mustrain broadening?

Select data for processing:

	Format	Weight	Name
Select	RMC	0.05	Neutron real space data; G(r): sf6_190k_gr.dat
Select	RMC	0.01	Neutron reciprocal space data; F(Q): sf6_190k_fq.dat
Select			Neutron reciprocal space data; S(Q):
Select			X-ray real space data; G(r):

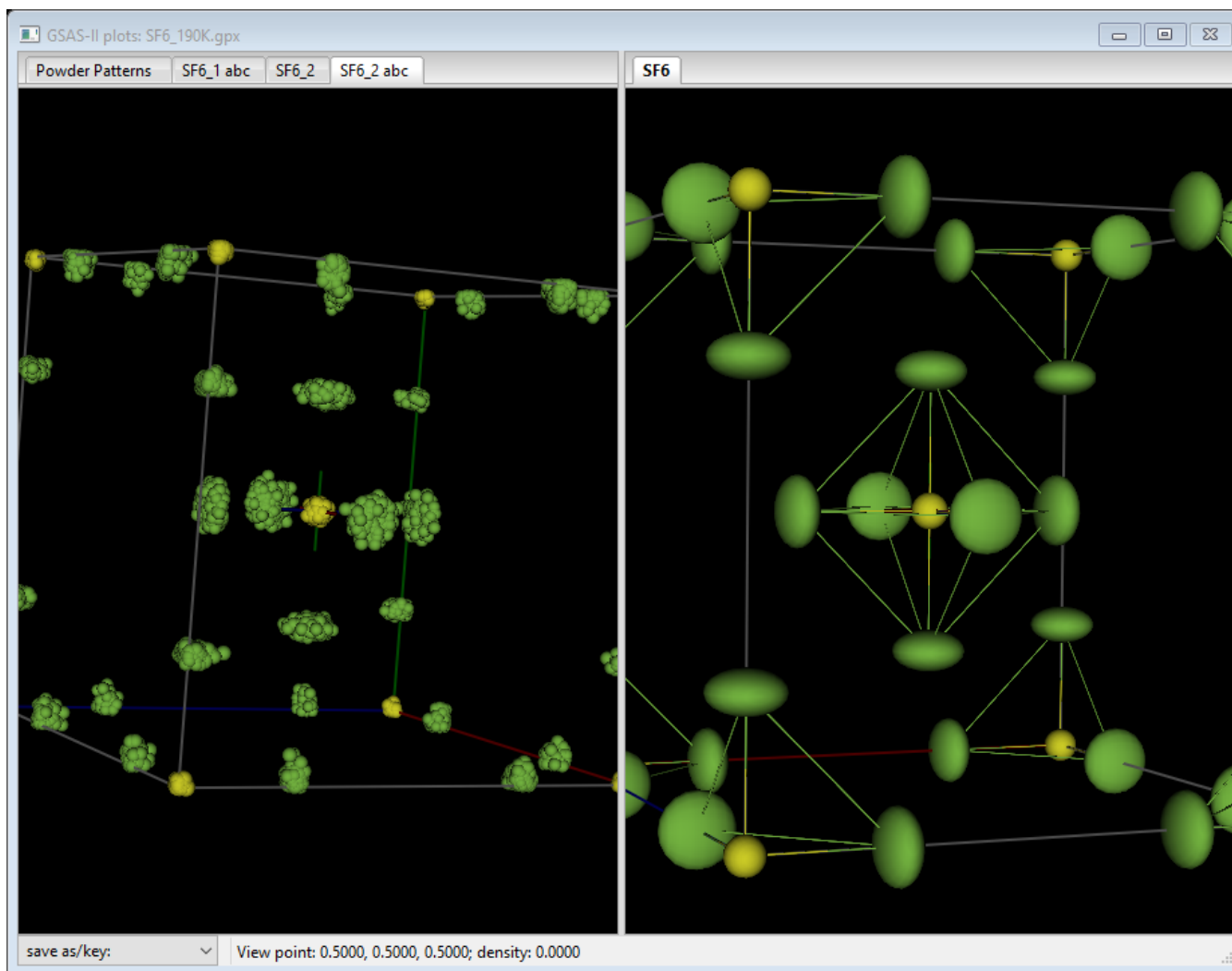
Mouse RB drag/drop to reorder

RMCPROFILE RESULT FOR SF₆

10x10x10 unit cell box – transform back to original

See disordered atom distribution

– compare to Rietveld U_{aniso} for F atom

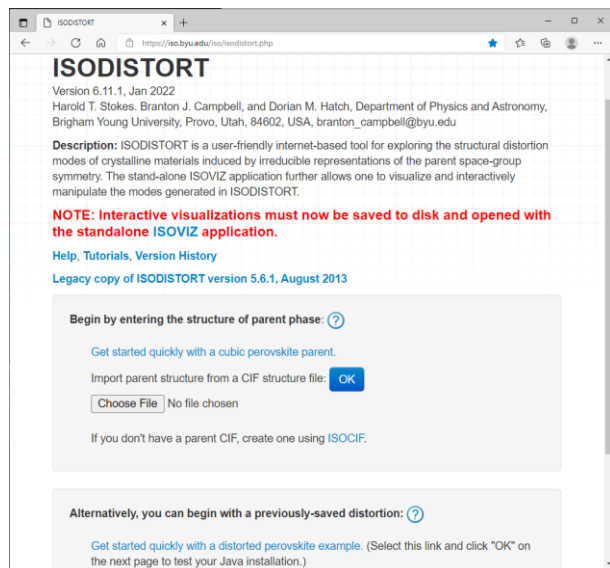


PDFFIT & ISODISTORT

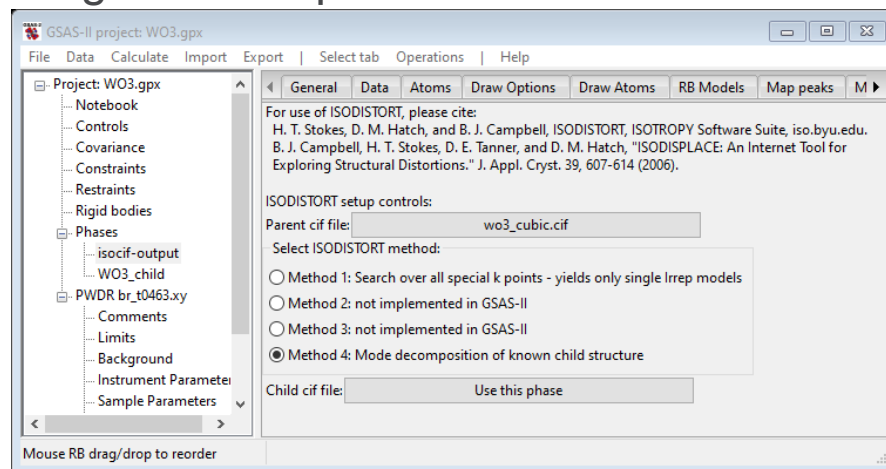
ISODISTORT

Implementation in GSAS-II

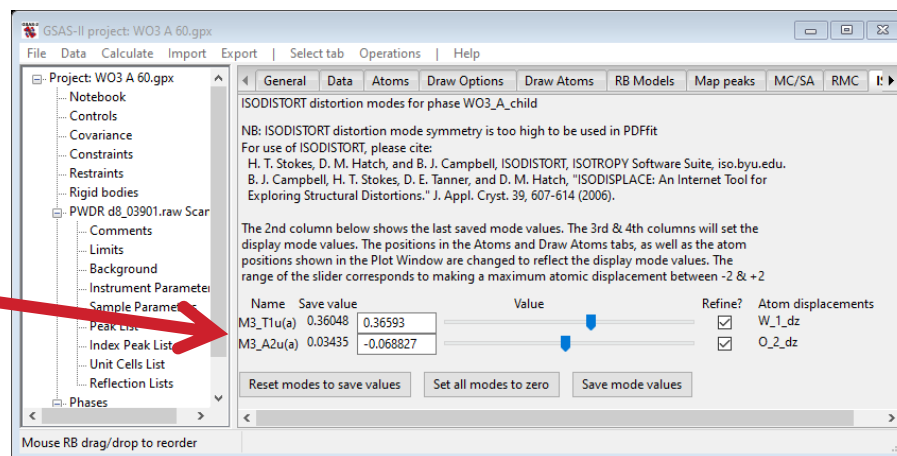
ISODISTORT: Web based tool for discerning mode displacements of atoms from an idealized parent structure



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



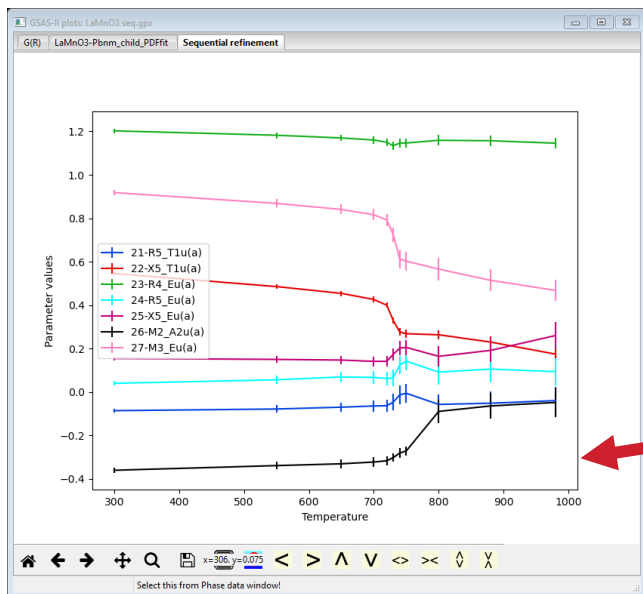
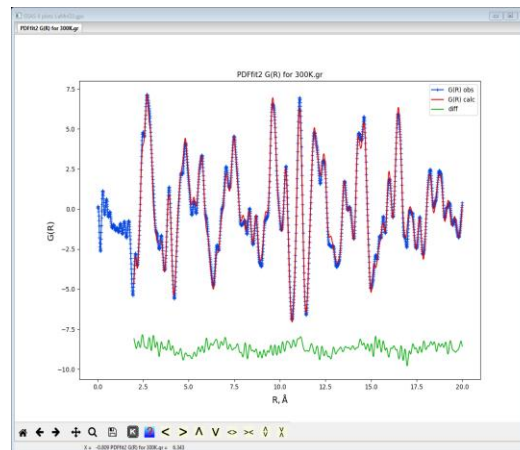
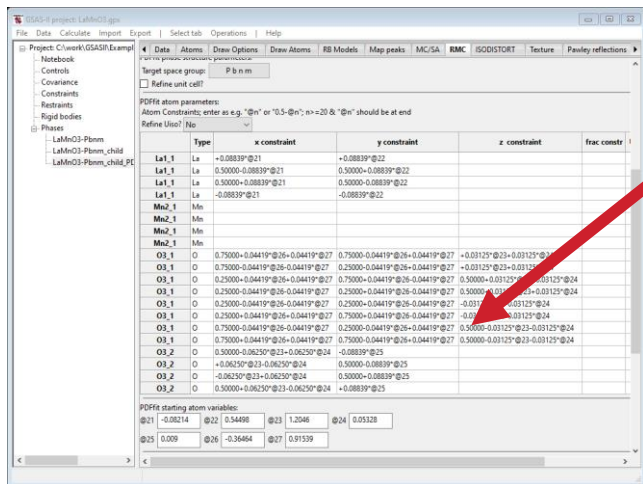
- New implementation – direct interaction between GSAS-II & ISODISTORT; simplified operation



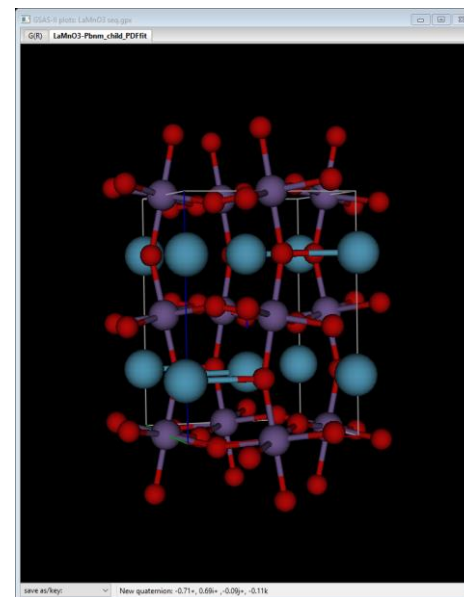
PDFFIT2 = “PDFfit” IN GSAS-II

“Small Box” modelling of pair distribution functions

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



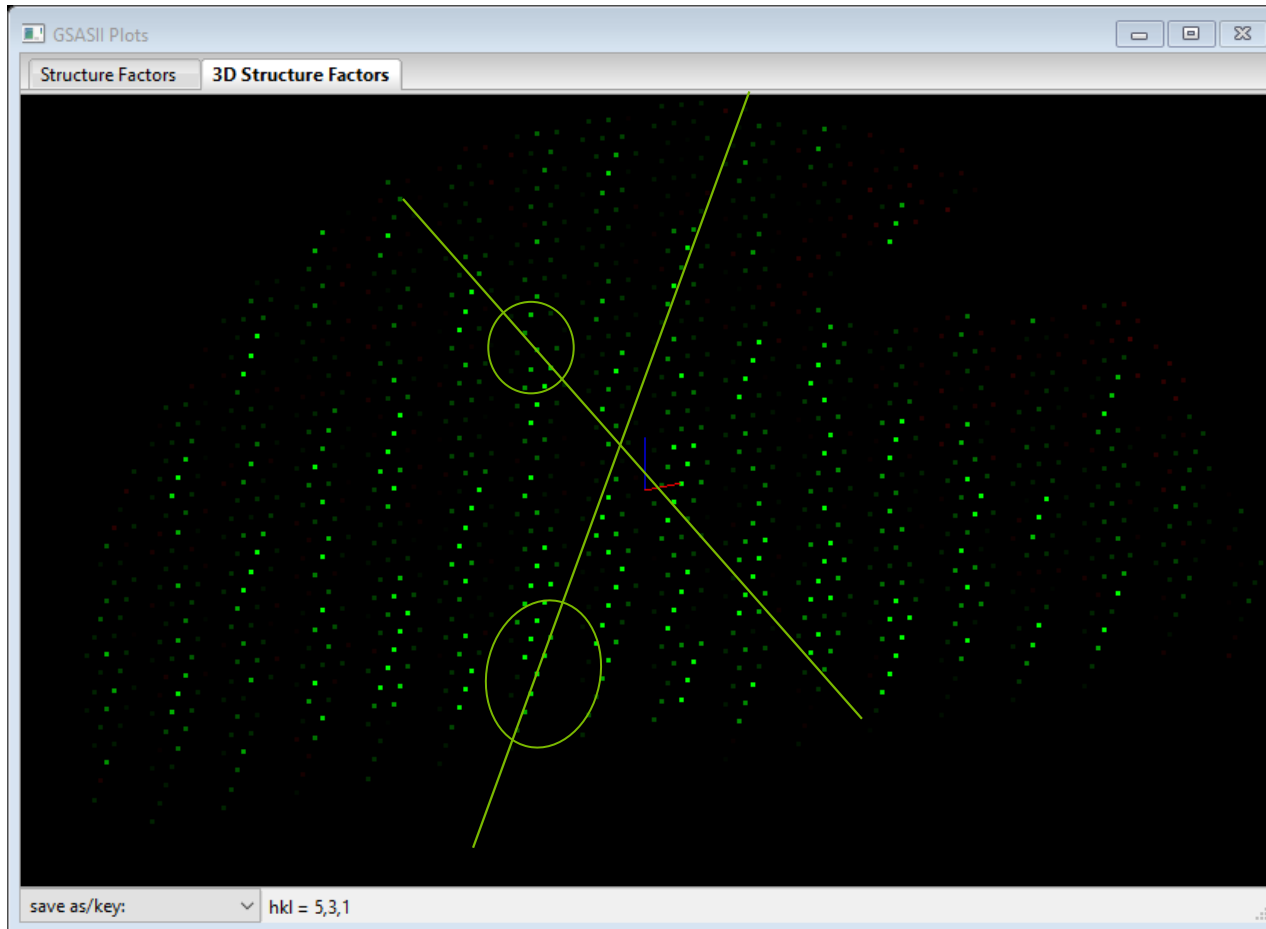
Parameters: mode displacements (Å)
Can be fit for sequence of T



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

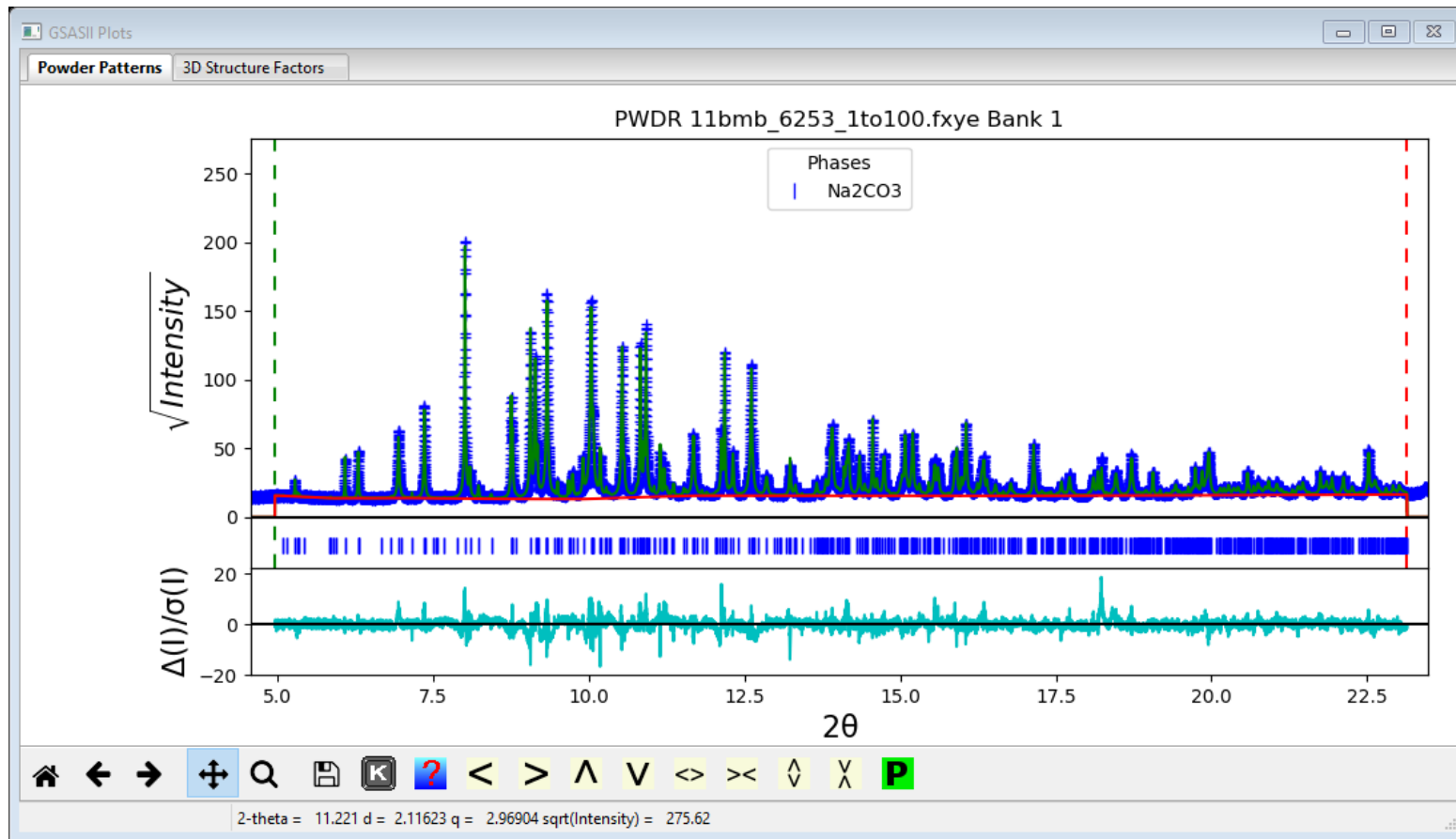
For Na_2CO_3
 $q = 0.183, 0, .319$

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

Na_2CO_3 – single crystal X-ray data – h0l zone → rows of spots don't line up

POWDER DIFFRACTION

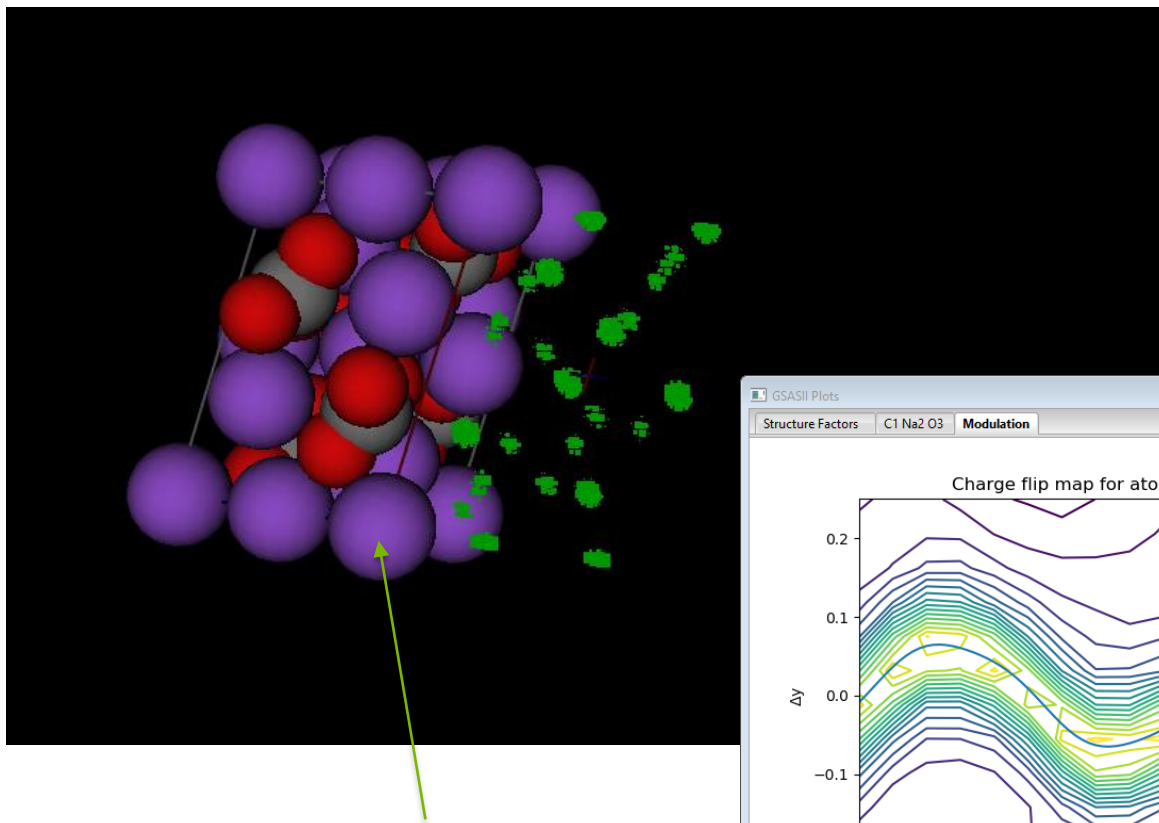
Na_2CO_3 – 11BM @ APS room temp.



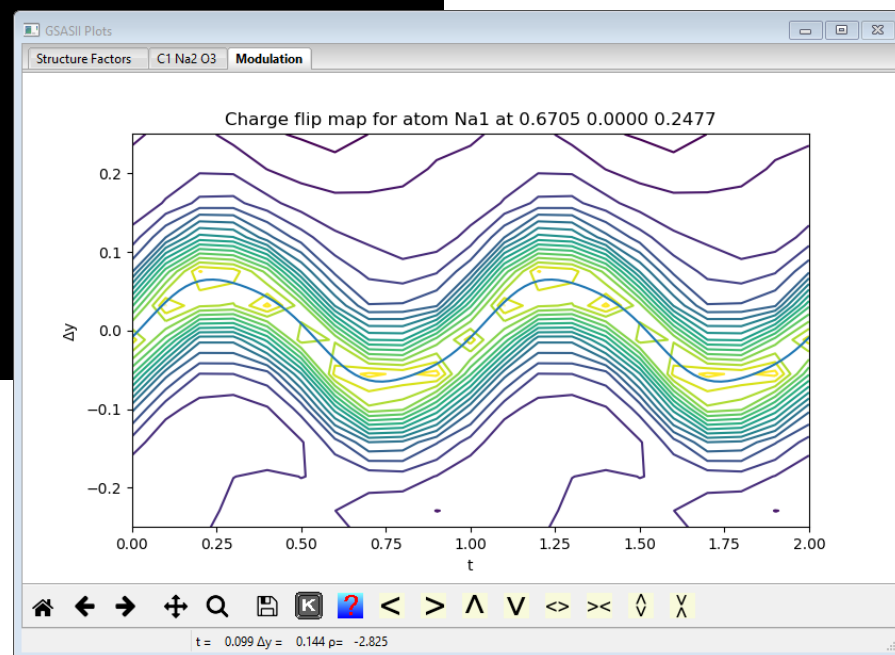
Includes $m=-2,-1,1,2$ superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom

INCOMMENSURATE STRUCTURE SOLUTION

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

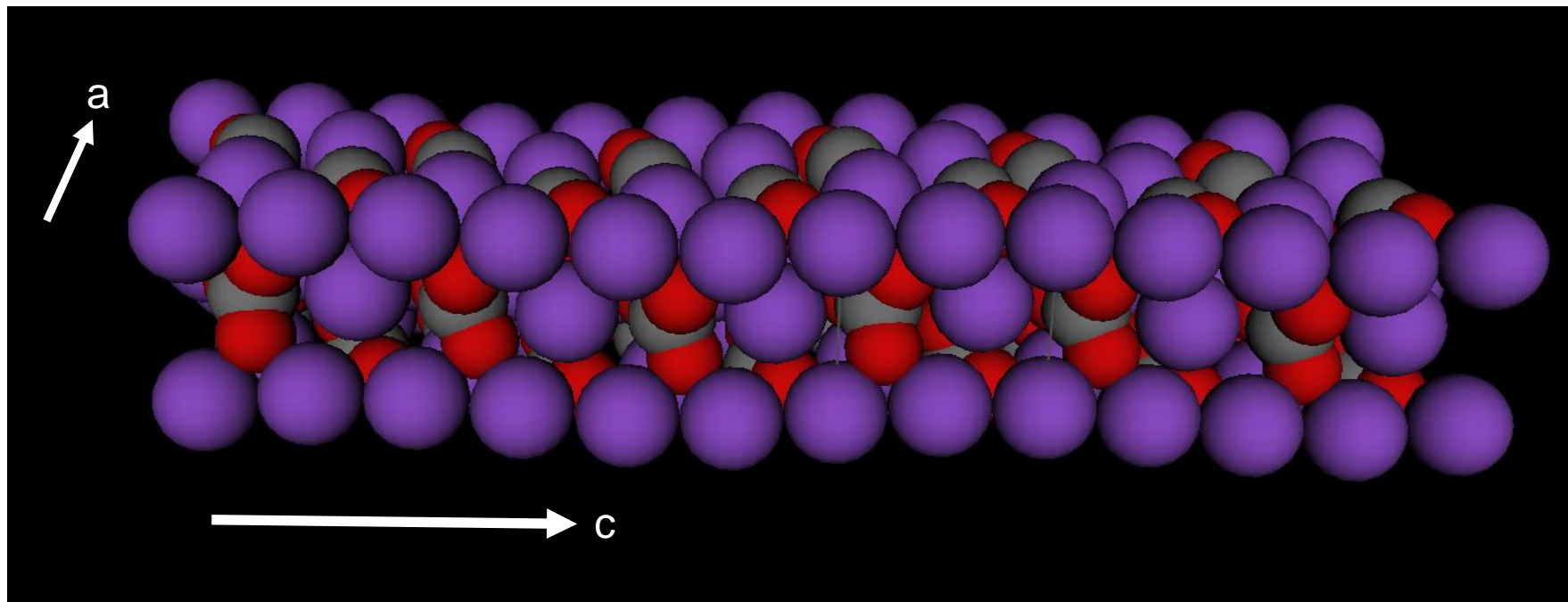


Modulation of atom positions (Na1-y)
Fit function – fourier series in τ



LATTICE MODULATION

Na_2CO_3 – single crystal data



Coordinated wave motion – Na lattice y motion/ CO_3 rocking motion

Recall $q = 0.183, 0, 319$ so period $\sim 6-7$ on x & ~ 3 on z

Possible modulations: positions, thermal parameters, site fractions
(& magnetic moments)

INCOMMENSURATE STRUCTURES

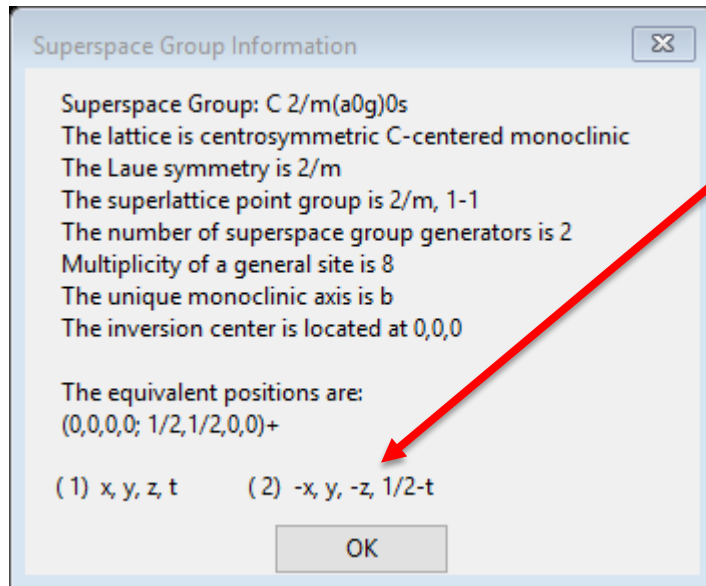
Symmetry symbols – interpreted by GSAS-II (not lookup)

- Space group + super symmetry symbol

e.g. $\text{Na}_2\text{CO}_3 - \text{C}2/m(\alpha 0 \gamma)os$

Space group Modulation vector Translation component

Operators: conventional space group & 4th dim component



Possible modulation vectors:
e.g. $\alpha\beta\gamma$, $\alpha 0 \gamma$, $0\beta 0$, $\alpha^{1/2}\gamma$, $\frac{1}{2}\beta 0$

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)

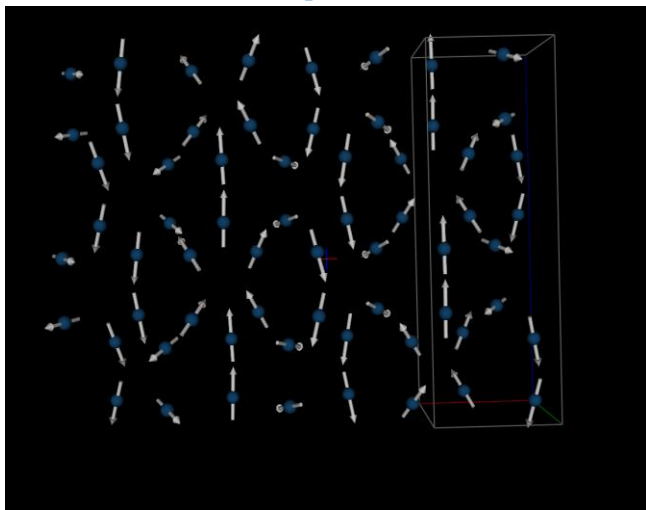
INCOMMENSURATE STRUCTURES

Cases not allowed in GSAS-II

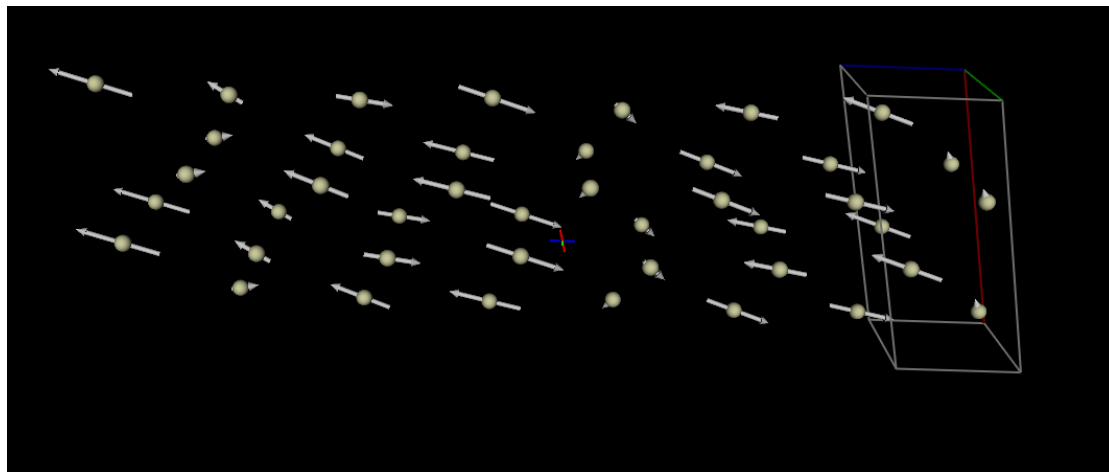
- 3+2 & 3+3 not allowed in GSAS-II
 - Too complex to deal with easily
 - 3-D 230 SG
 - For 3+1: 4,783 possible SG
 - For 3+2: 222,018 possible SG
 - For 3+3: 28,927,922 possible SG
 - But only a handful found – not worth the hassle
- Ad hoc centering not allowed
 - ‘X’ space groups – all have equivalent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

MAGNETIC INCOMMENSURATE STRUCTURES

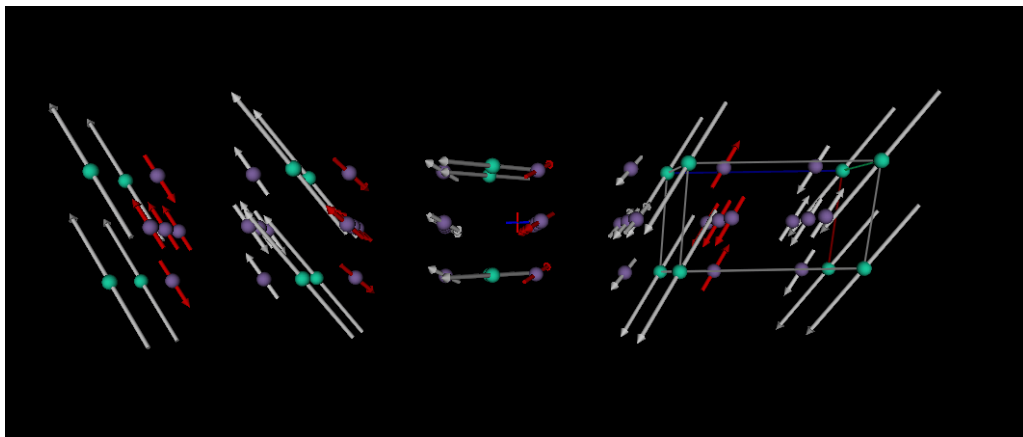
Some examples:



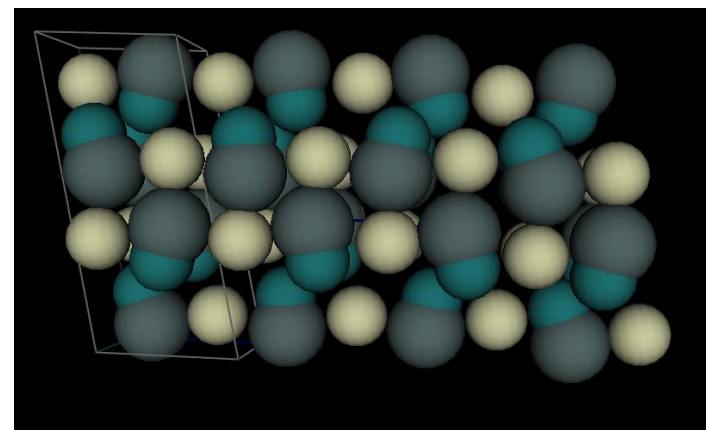
β -Li₂IrO₃



CeRuSn – Ce moment



DyMn₆Ge₆ – residual moment



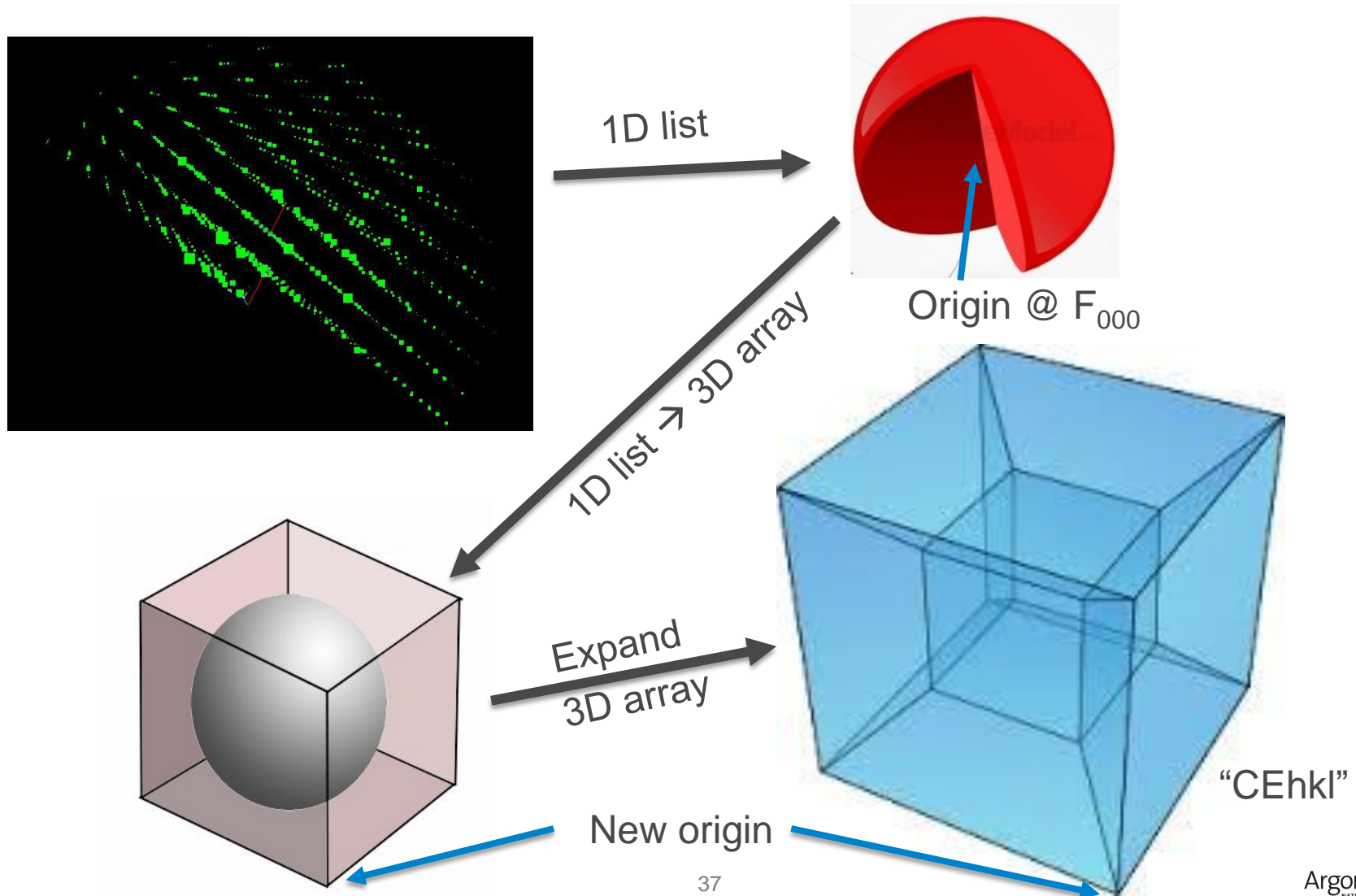
CeRuSn –
structure modulation

CHARGE FLIPPING

CHARGE FLIPPING

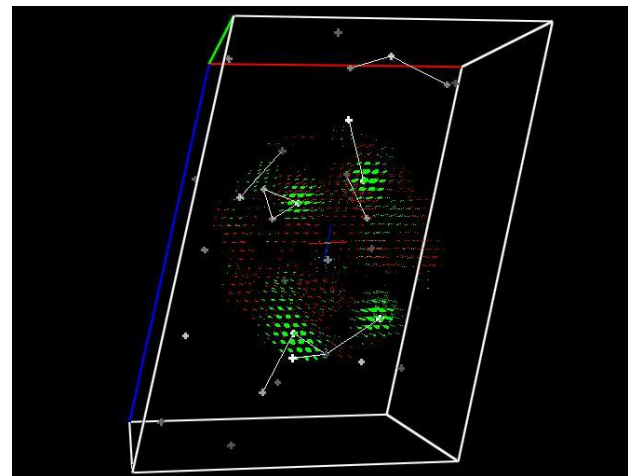
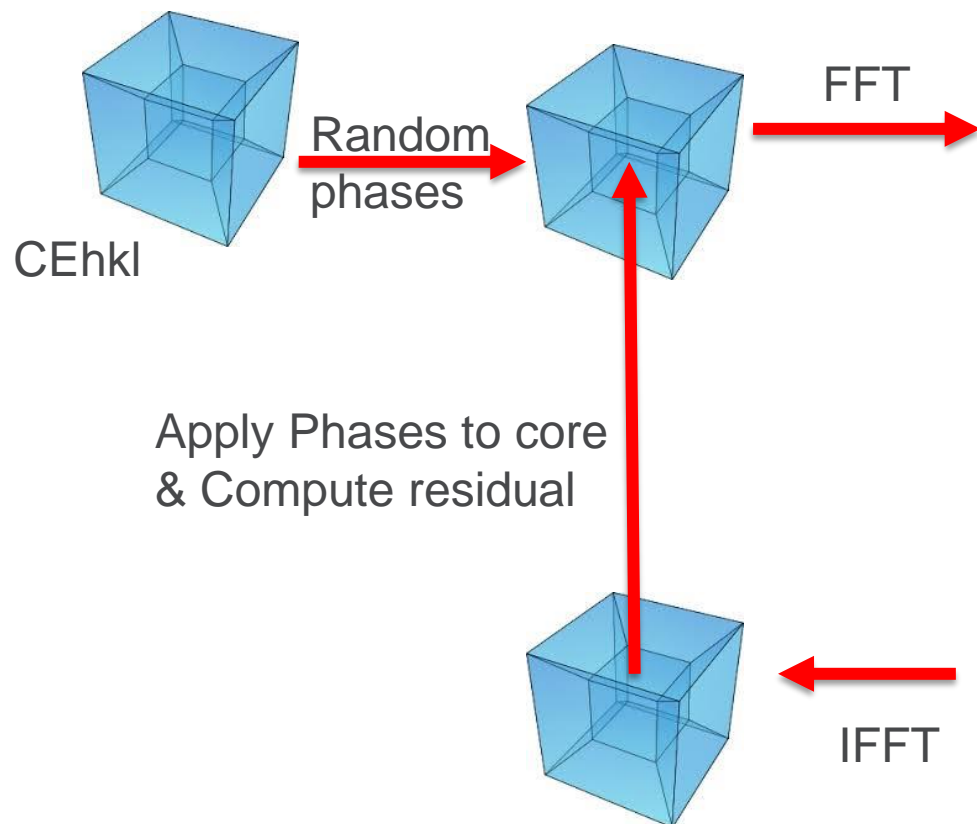
The algorithm set up:

~1Å unique reflections → sphere → box → 0.5Å box

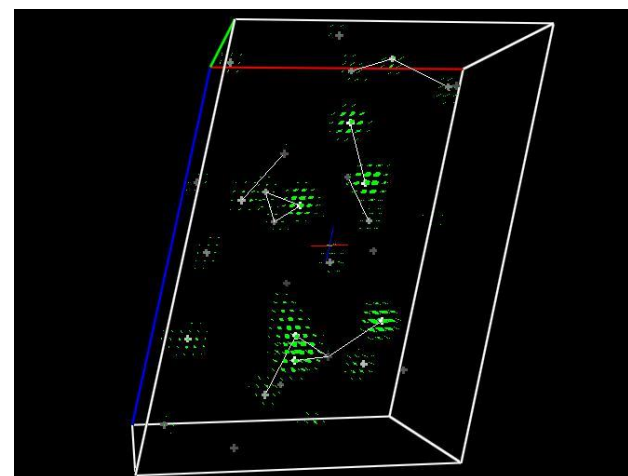


CHARGE FLIPPING

The Algorithm



Charge Flip



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 → ρ(xyz)
CEsig = np.std(CErho)                                       #get σ(ρ)
CFrho = np.where(np.real(CErho) >= flipData['k-factor']*CEsig,CErho,-CErho)  #CF ρ → ρ'
CFrho = np.where(np.real(CErho) <= flipData['k-Max']*CEsig,CFrho,-CFrho)      #U atom CF!
CFhkl = fft.ifftshift(fft.ifftn(CFrho))                    #fft ρ'(xyz) → F'(hkl)
CFhkl = np.where(CFhkl,CFhkl,1.0)                          #avoid divide by zero
phase = CFhkl/np.absolute(CFhkl)                          #get φ(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=Emask))    #Σ F
DEhkl = np.absolute(np.absolute(Ehkl)/sumE-np.absolute(CFhkl)/sumCF)  #Σ |DF|
Rcf = min(100.,np.sum(ma.array(DEhkl,mask=Emask)*100.))    #residual
```

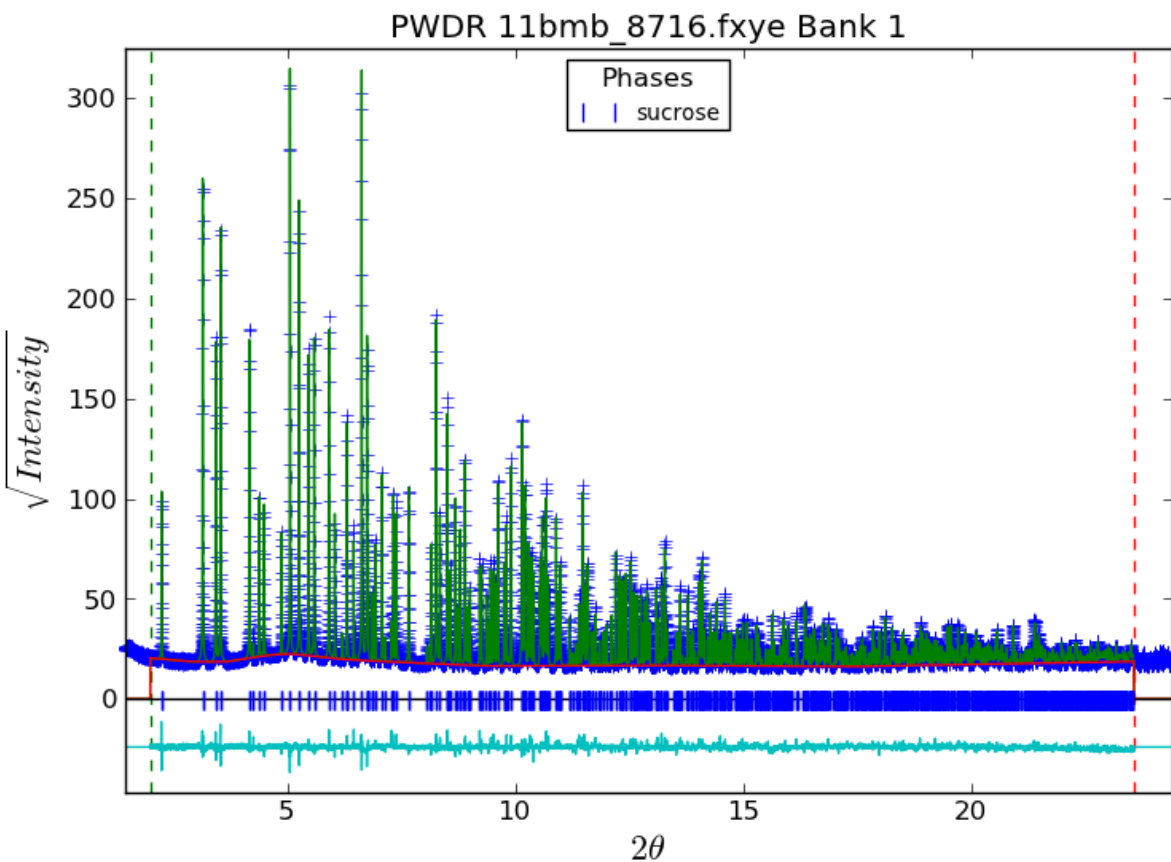
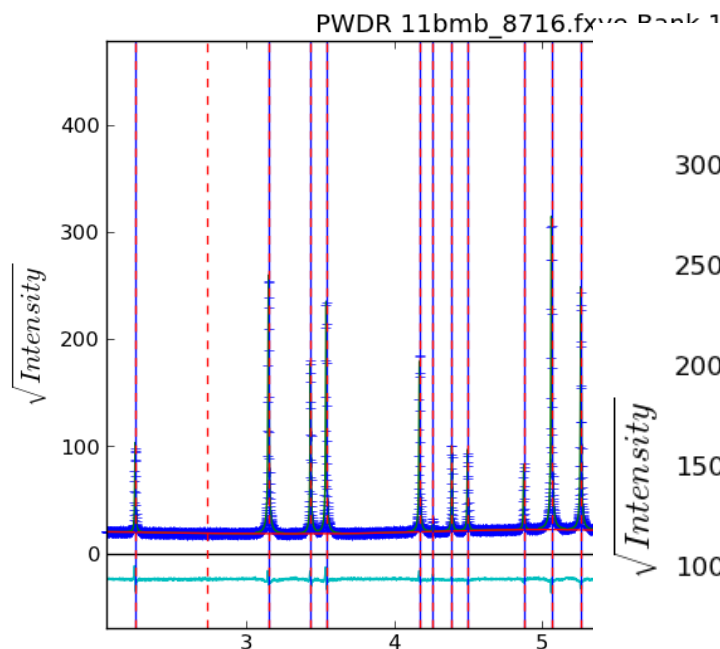
After user break:

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



Unit Cells List

Cell Index/Refine Help

Indexing controls:

Max Nc/Nobs 4 Start Volume 25 ☒ Use M20/(X20+1)?

Select Bravais Lattices for indexing:

☐ Cubic-F ☐ Cubic-I ☐ Cubic-P ☐ Trigonal-R ☐ Trigonal/Hexago
☐ Orthorhombic-F ☐ Orthorhombic-I ☐ Orthorhombic-C ☐ Orthorhombic-P ☐ Monoclinic-C

Cell Test Refinement:

Bravais lattice **P2/m** Space group **P 21** Zero offset 0.0007 ☒ Refine?

Unit cell: a = 7.71525 b = 8.66389 c = 10.80965

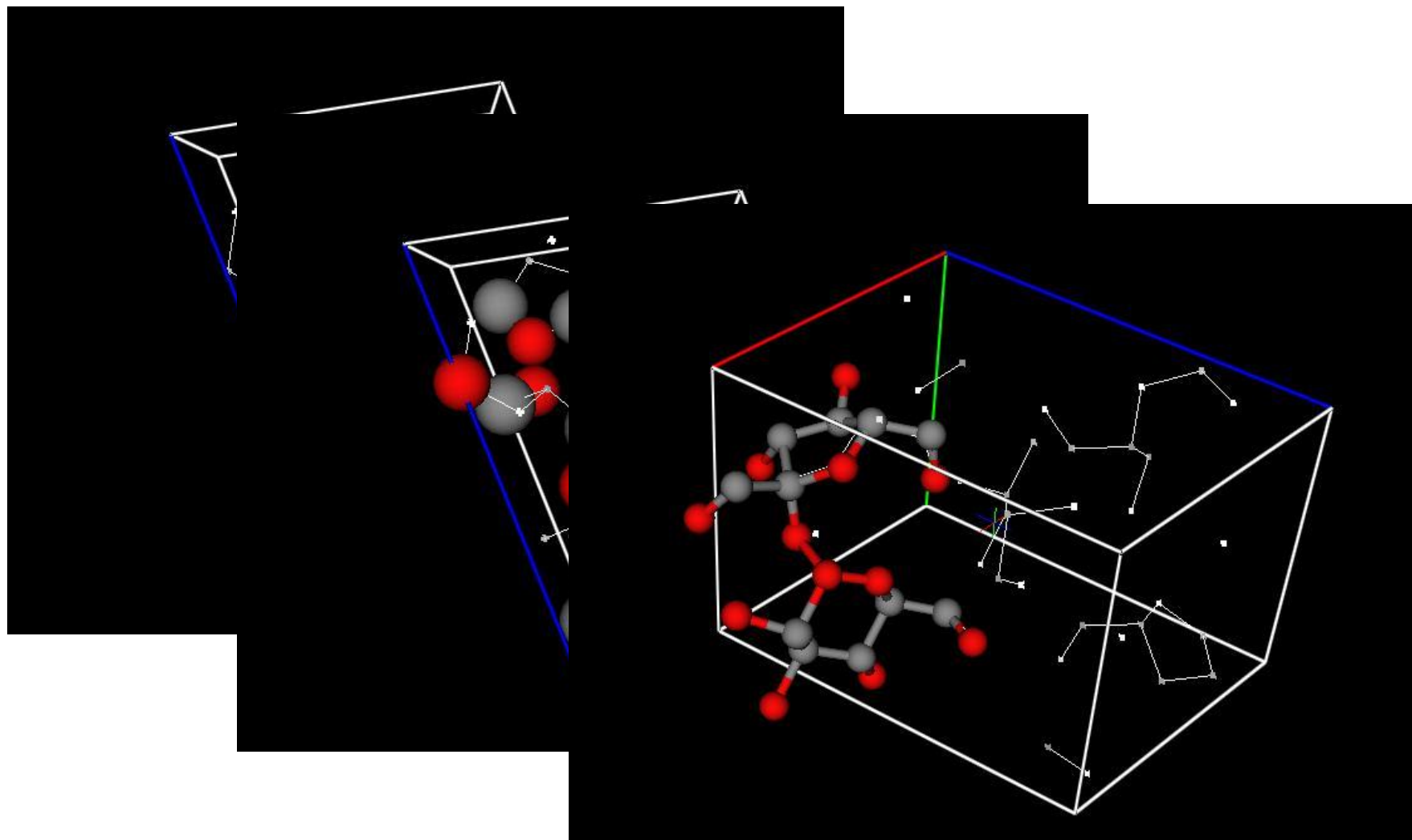
Indexing Result:

M20	X20	use	Bravais	a	b	c	alpha	beta	gamma	Volume	Keep
1312.84	0	<input checked="" type="checkbox"/>	P2/m	7.71525	8.66389	10.80965	90.000	102.983	90.000	704.09	<input type="checkbox"/>
907.76	0	<input type="checkbox"/>	P2/m	7.71412	8.66281	10.80843	90.000	102.982	90.000	703.82	<input type="checkbox"/>
15.05	0	<input type="checkbox"/>	P2/m	7.69200	8.66511	10.79433	90.000	102.664	90.000	701.96	<input type="checkbox"/>
2.38	1	<input type="checkbox"/>	P2/m	6.78185	10.56374	15.20797	90.000	98.621	90.000	1077.21	<input type="checkbox"/>
2.38	1	<input type="checkbox"/>	P2/m	6.78185	10.56374	15.20797	90.000	98.621	90.000	1077.21	<input type="checkbox"/>

781 unique hkl's
CF with 61440

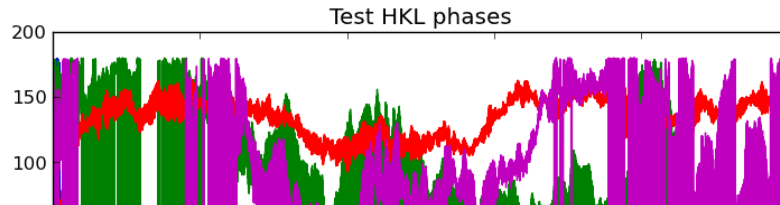
CHARGE FLIPPING SOLUTION

Residual ~45% → ~17% & 46 peaks in cell (NB: sucrose $C_{12}H_{22}O_{11}$)
Map peaks – unique set & select – identify atoms – make molecule

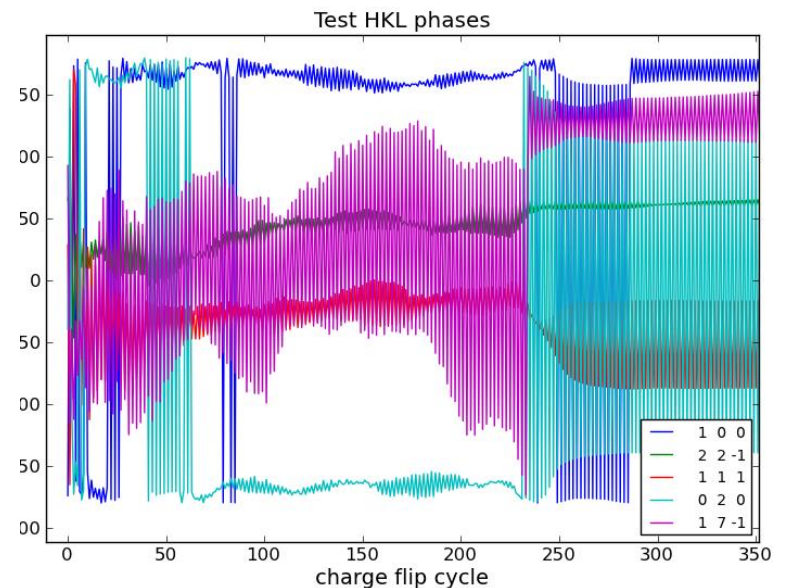
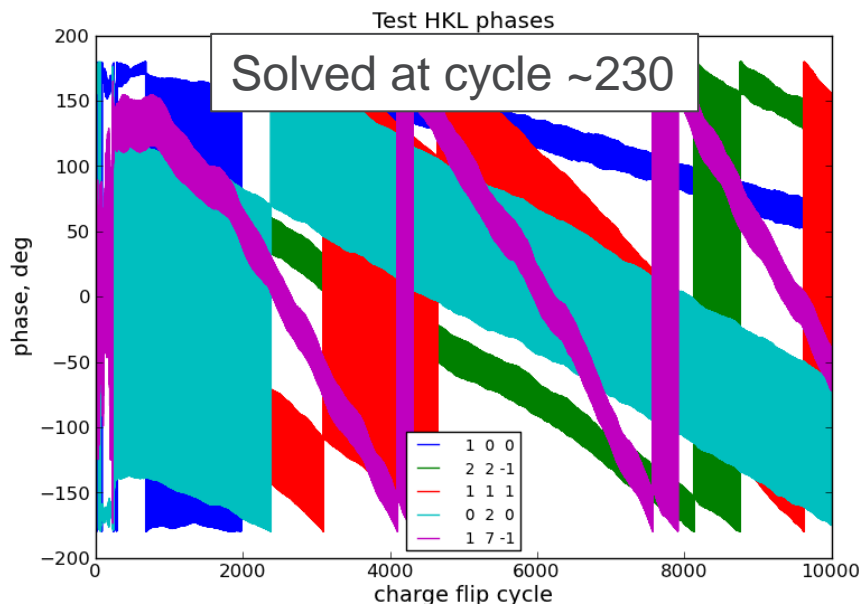
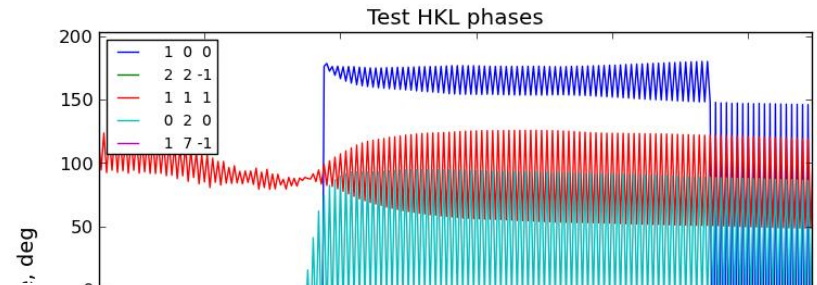
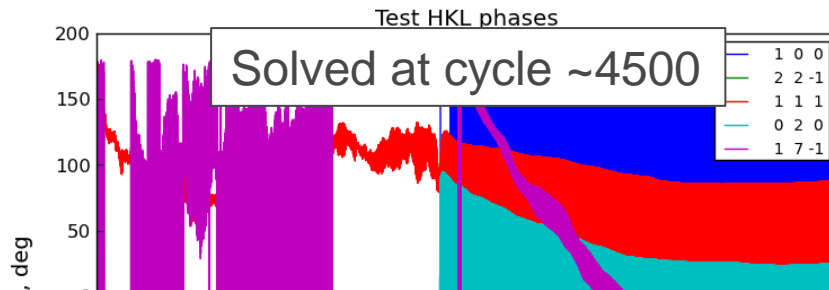


CHARGE FLIPPING – PHASES?

Track phases of 5 reflections – 10000 CF cycles

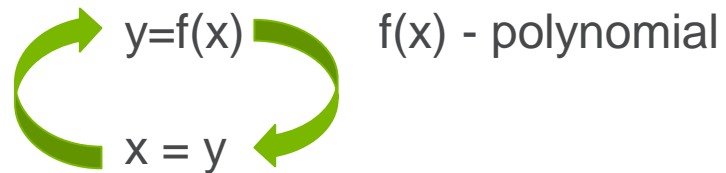


Not solved in 10000 cycles



CHARGE FLIPPING – CHAOS MATHEMATICS?

- 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 – “symplectic” or “non-symplectic” strange attractors?
- Is there a “basin of attraction”?
- Does this really matter?

An aerial photograph of the Argonne National Laboratory campus, showing various buildings, parking lots, and a large circular structure, all overlaid with a semi-transparent blue filter.

THANK YOU