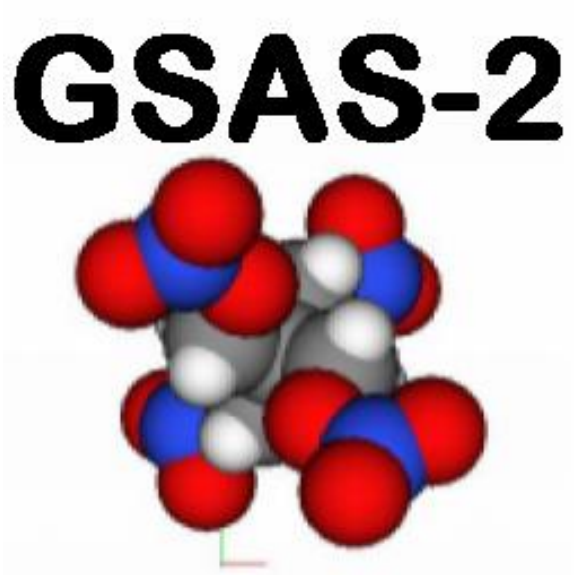
GSAS-II BEYOND RIETVELD



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vondreele@anl.gov

Saskatoon
June, 2024

2D IMAGE PROCESSING – FORGOTTEN OLD MATH

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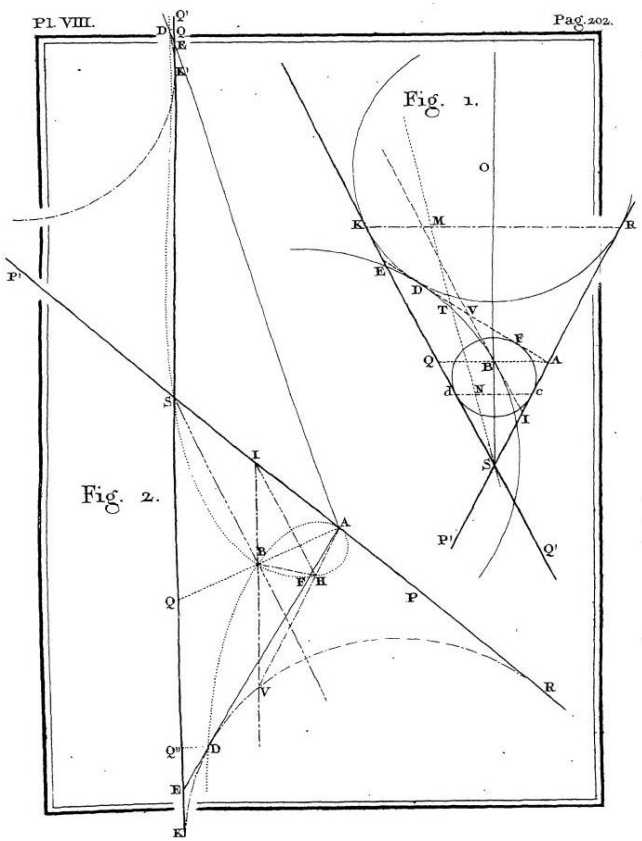
2D IMAGE DATA

Conic sections

Where is the incident beam on the detector?
Fit2D (& DataSqueeze) – assumes center of the diffraction ellipse - **False**
Analysis – G.P. Dandelin,
Noveaux 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

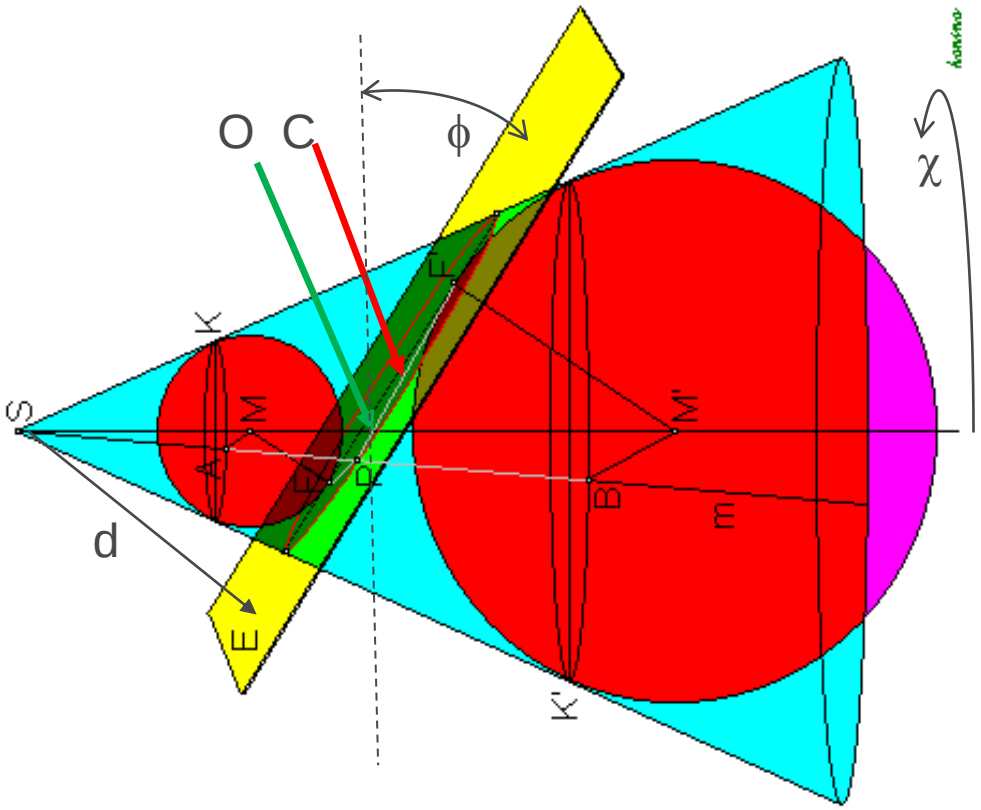
- line SO is cone axis
- F&D are the ellipse foci on the plane

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

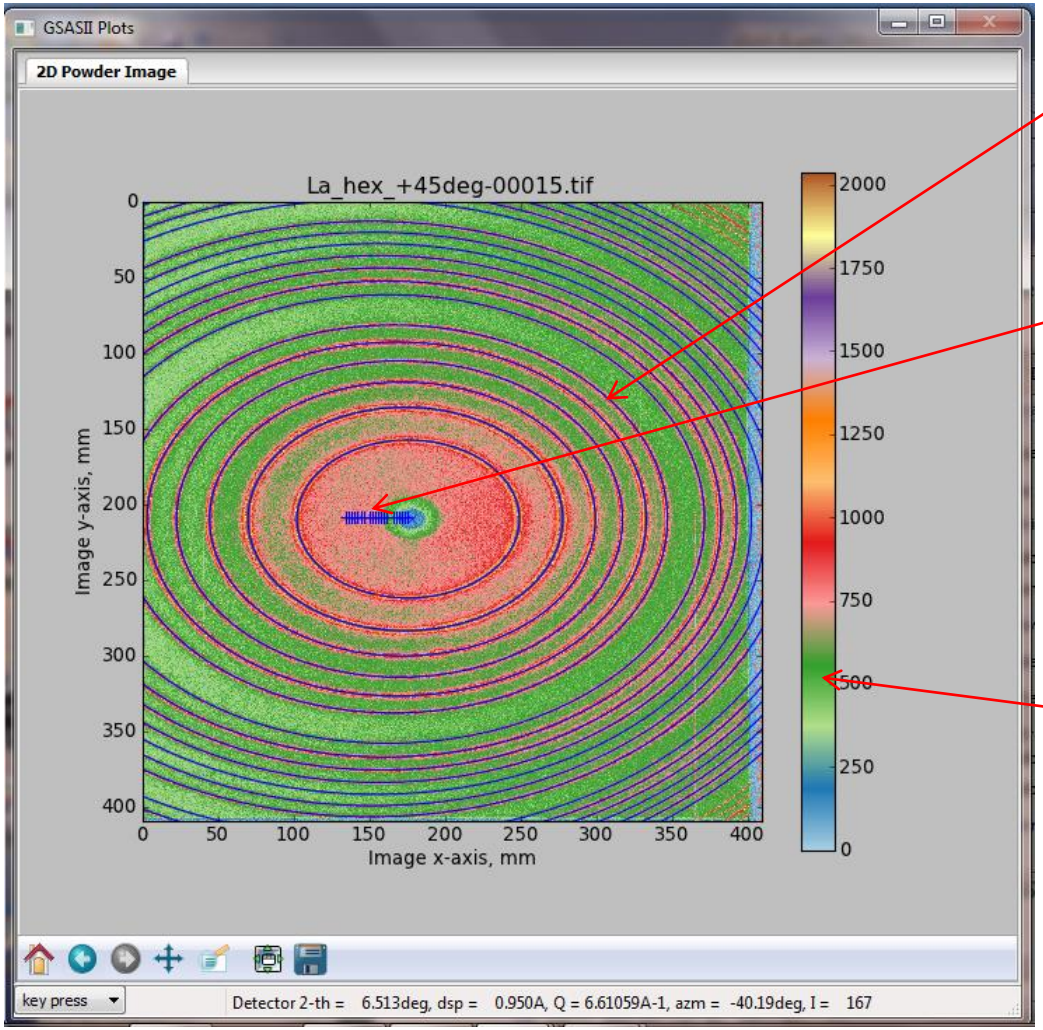


- Plane E is a tilted area detector
- The line SMM' is the Bragg cone axis – incident beam direction & passes through centers of both spheres
- Spheres touch plane at foci (F & F') of conic section (ellipse)
- Intersection of axis with plane (**O**) **not** at halfway point (**C**) between F & F' (ellipse 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 (= $2\Theta_{detector}$)
  - 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!

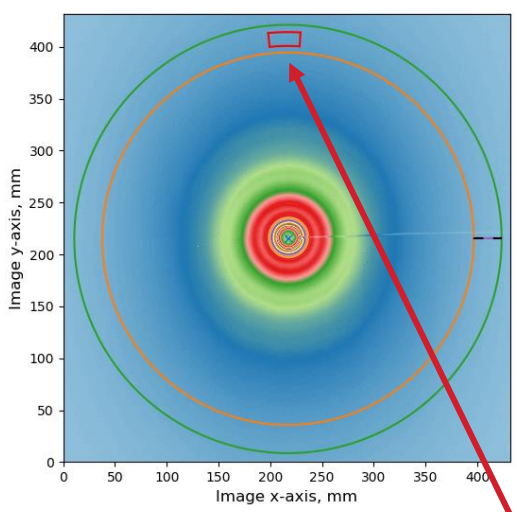
Fitting only requires material (LaB_6) and λ (e.g. don't need to know distance – get that from fit)

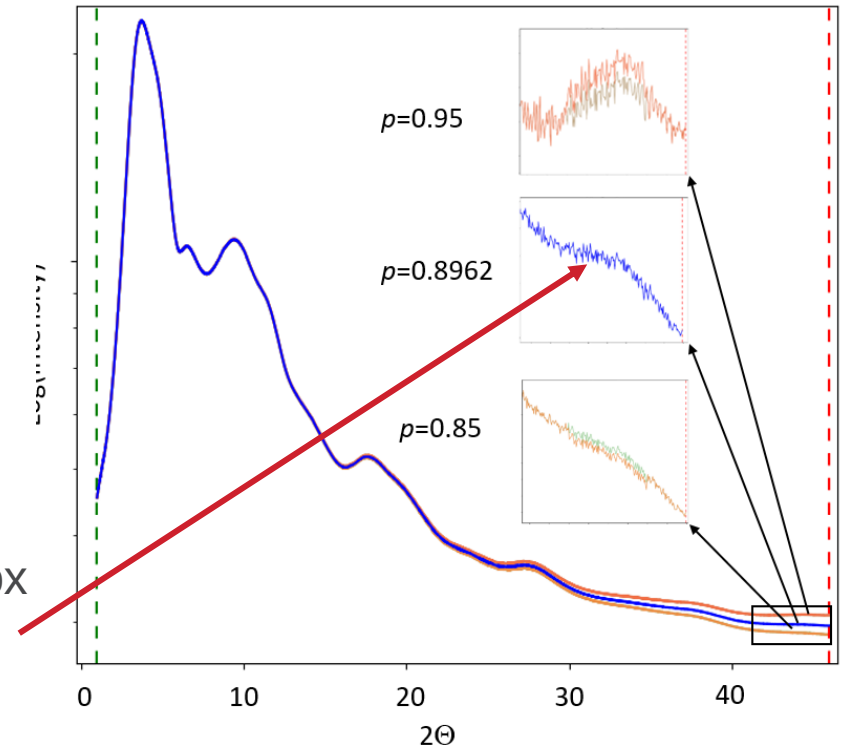
Choice of color scheme – "Paired" is shown

2D IMAGE POLARIZATION DETERMINATION

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

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

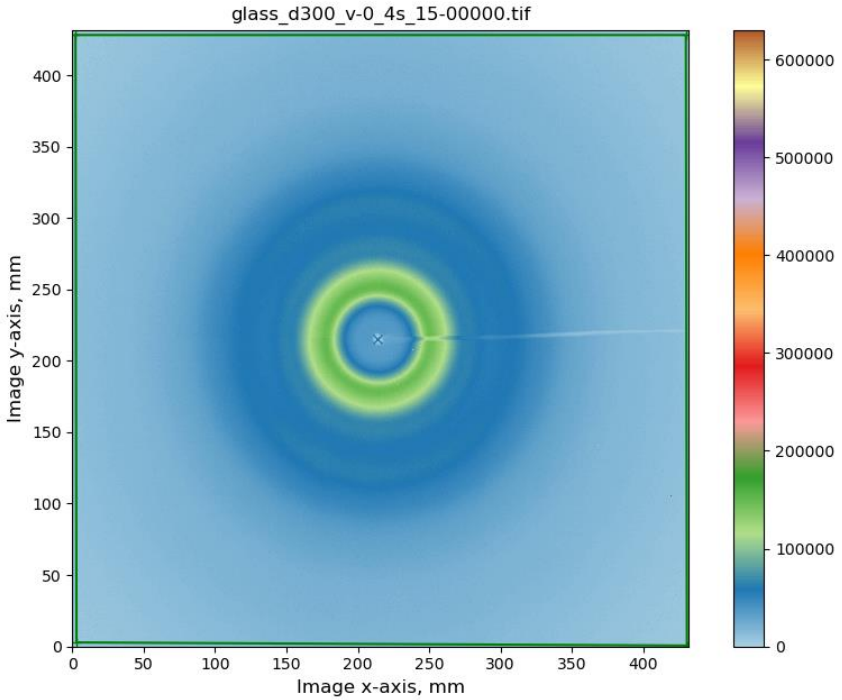


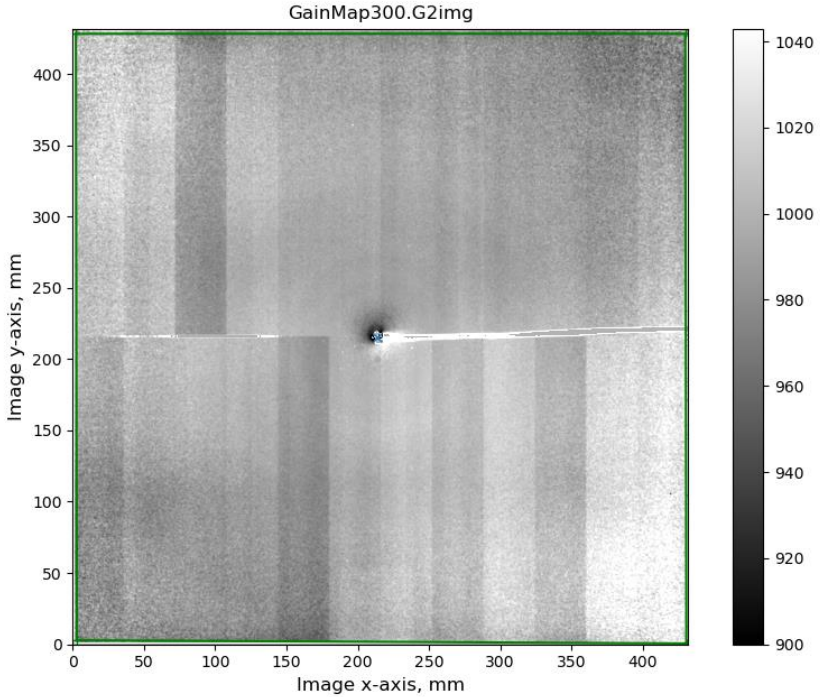


Integrate in band w/o mask box
Match if polarization is correct

2D DETECTOR GAIN MAP

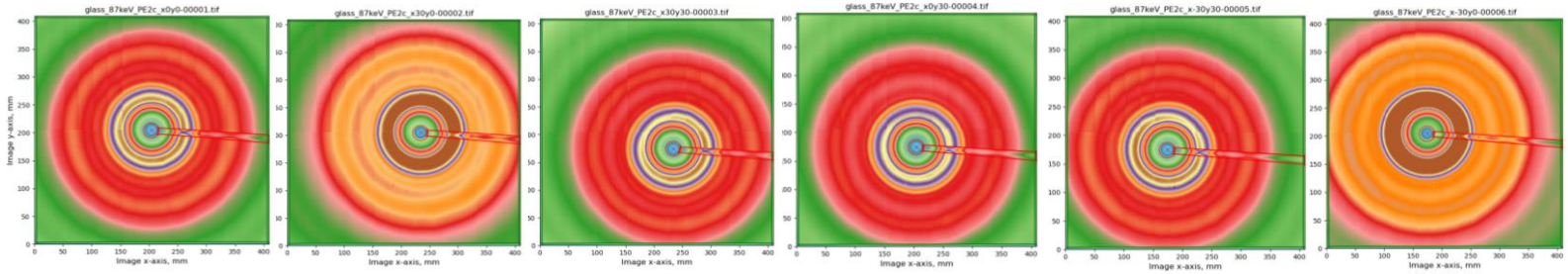
Sample – glass microscope slide – purely amorphous & isotropic
Image corrected for polarization (automatic in GSAS-II)





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

MULTI-IMAGE GAIN MAP – BETTER

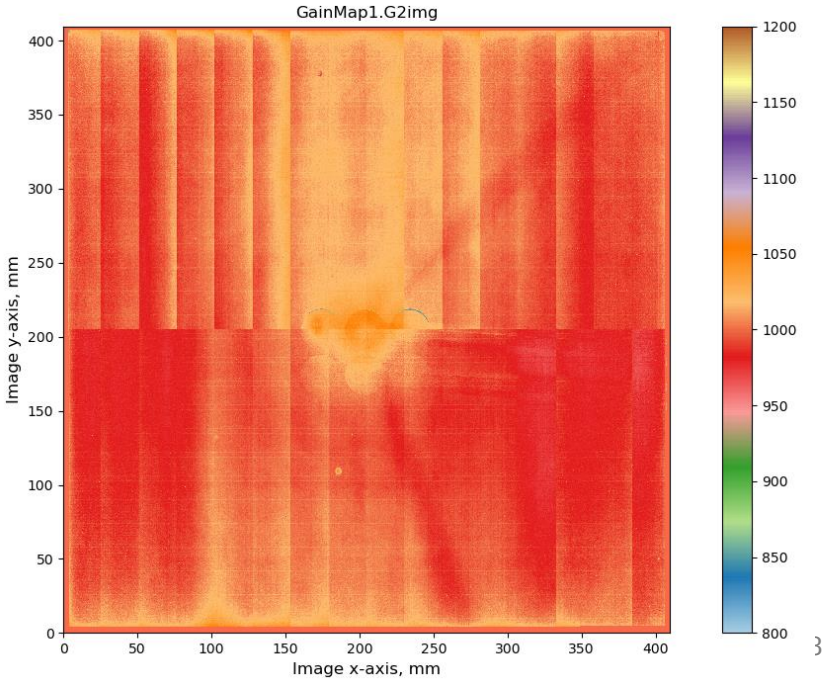


Shift 0 → ↓ ← ← ↑

Multiple exposures – shift on x & y; calibrate each

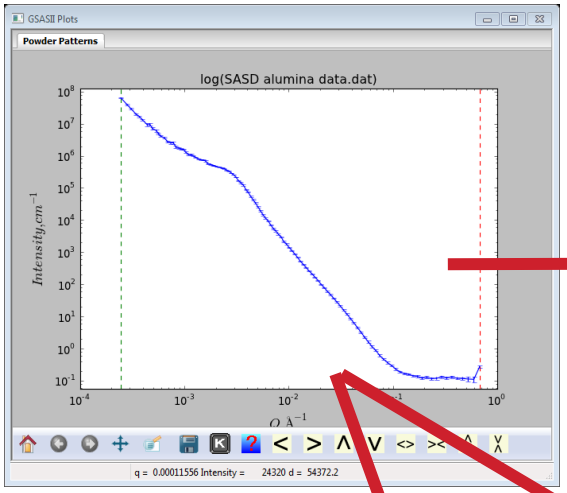
Mask undesireables – beam stop & arm, etc.

Combine to one gain map

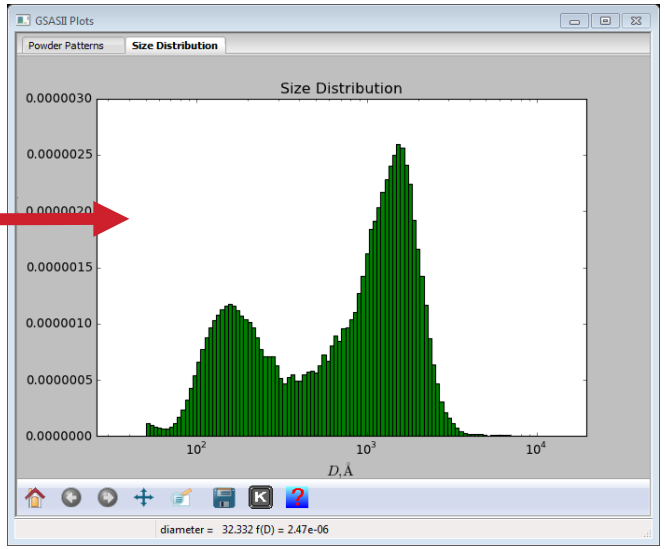


SMALL ANGLE SCATTERING

Range of tools

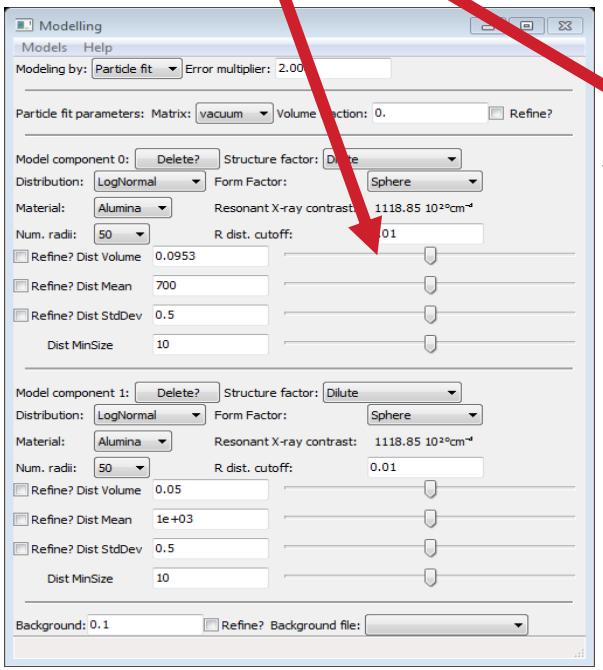


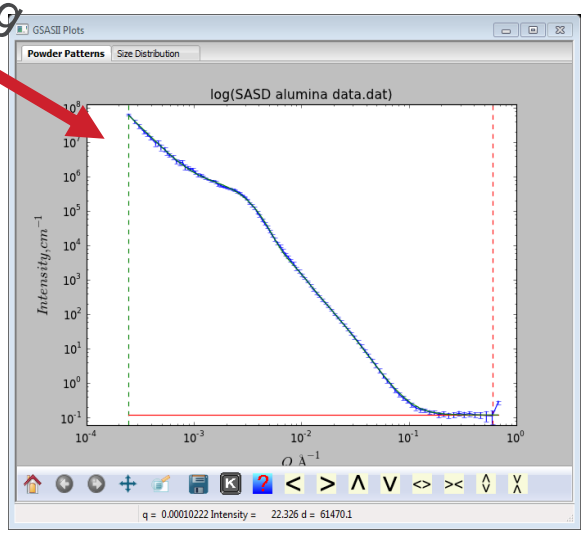
Size Distribution by MaxEnt



Modelling

LSQ fitting





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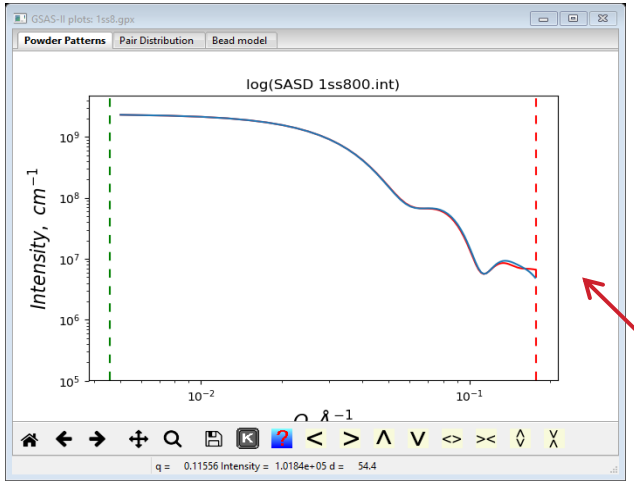
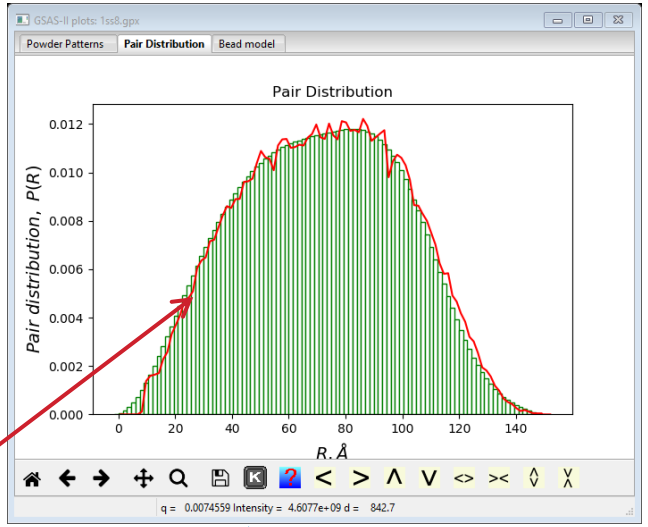
PROTEIN SMALL ANGLE MODELING IN GSAS-II

Bead models via SHAPES (alternative to DAMMIN in python)

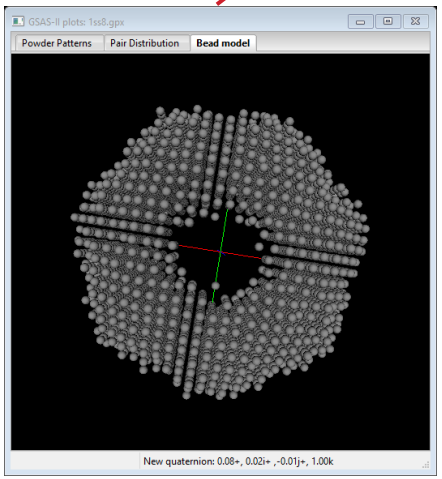


Make P(R)

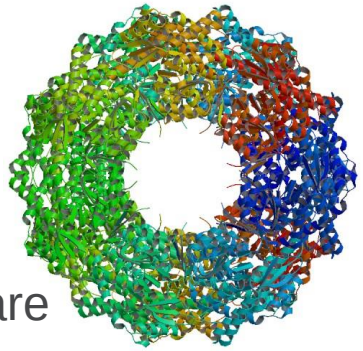


calc

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



Run SHAPES
Make bead model



compare

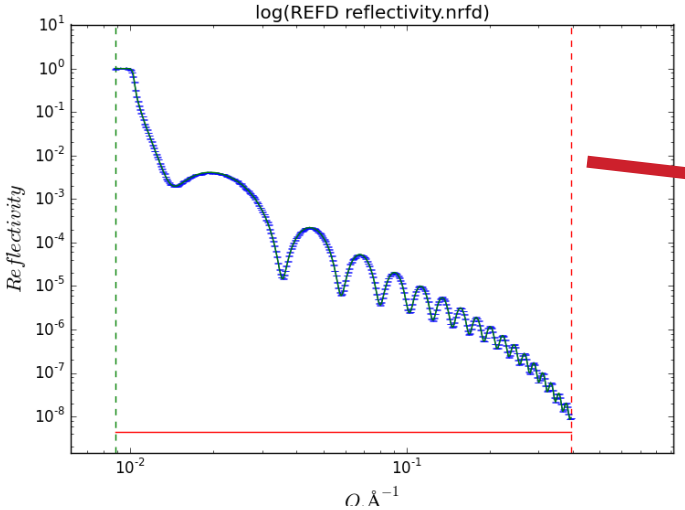
Direct fit?
(In development)

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

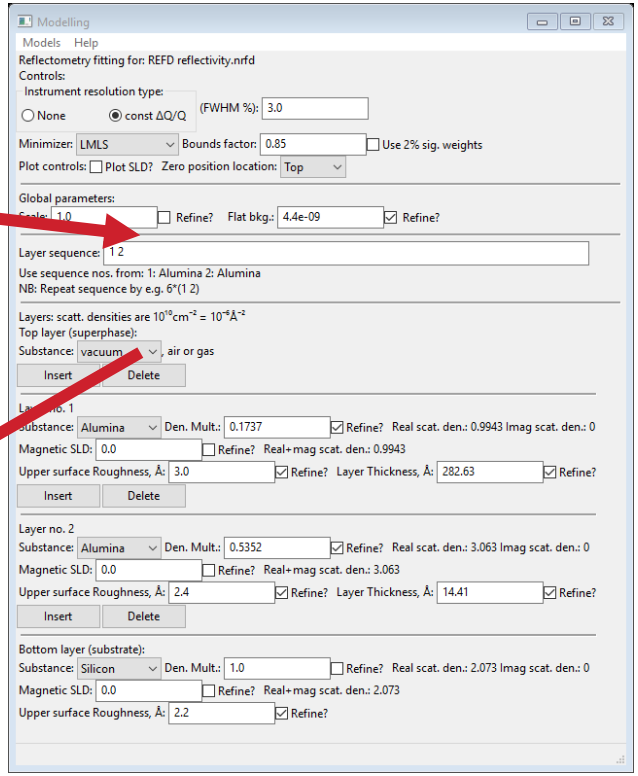
REFLECTOMETRY

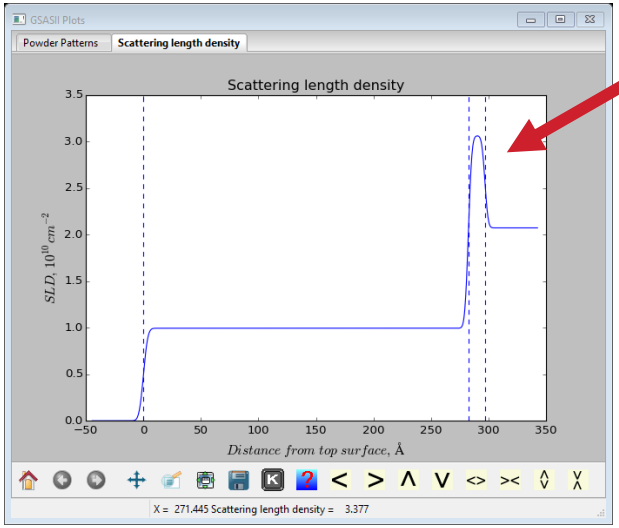
REFLECTOMETRY ANALYSIS IN GSAS-II

X-rays & Neutrons (CW at least)



Multilayer model
Scattering density





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

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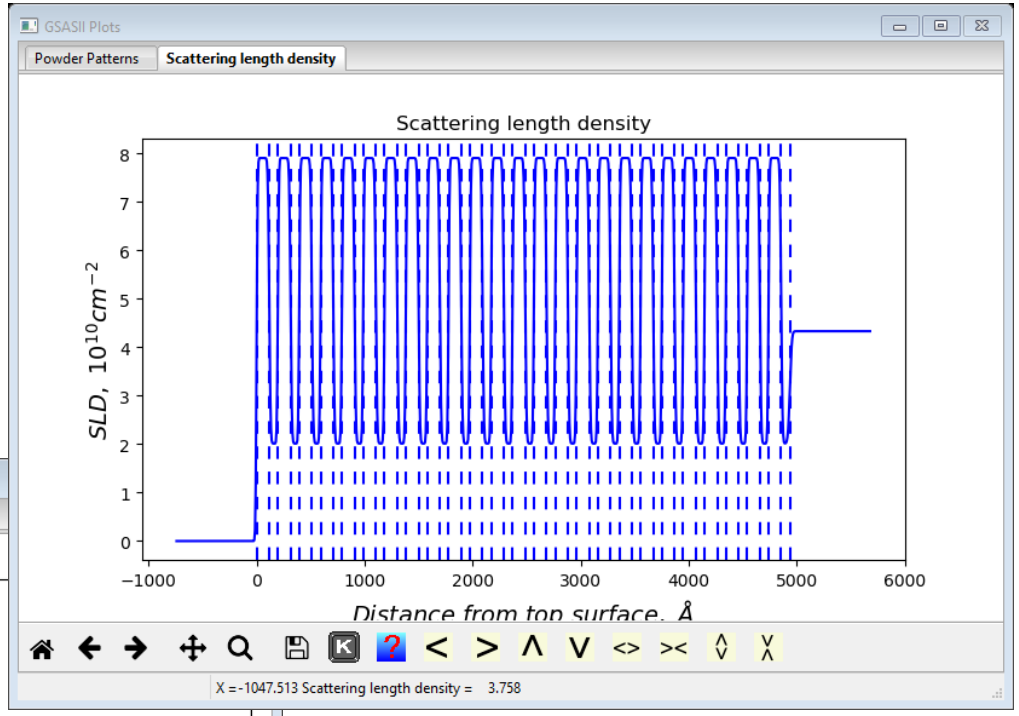
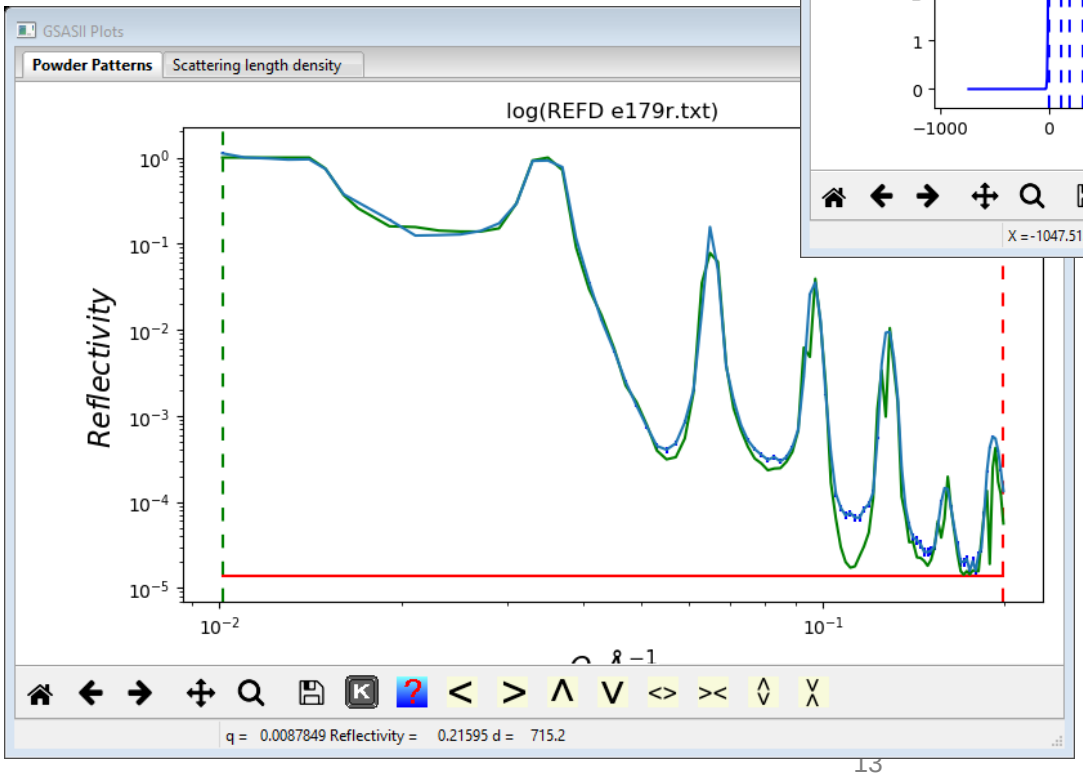
MULTILAYER REFLECTIVITY

25 layers on a substrate
Common thickness & contrast





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CLUSTER ANALYSIS

CLUSTER ANALYSIS?

"Unsupervised Machine Learning", "Pattern Recognition", etc.

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

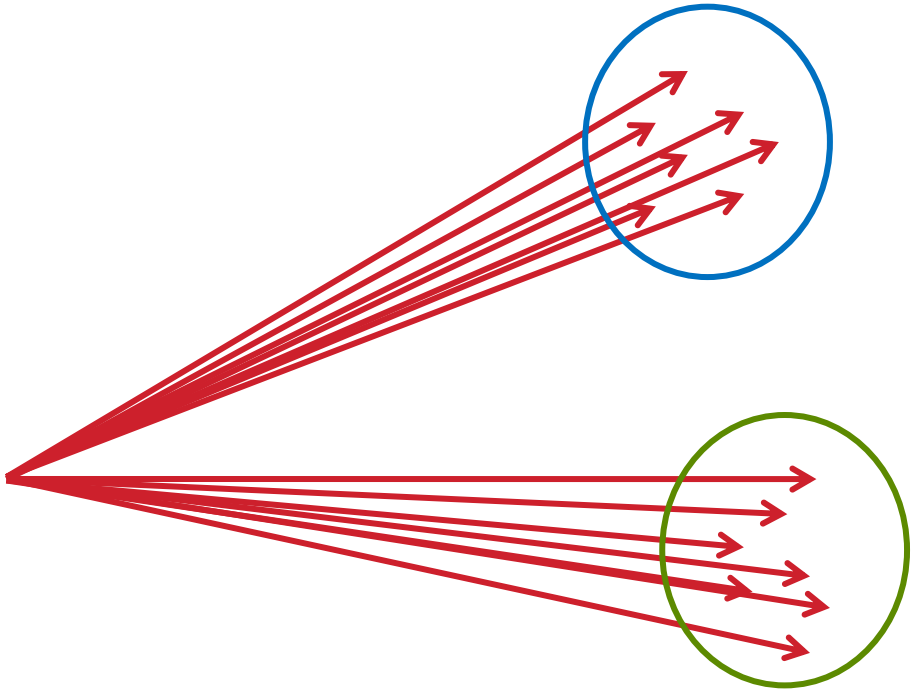
What to do?

- 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"



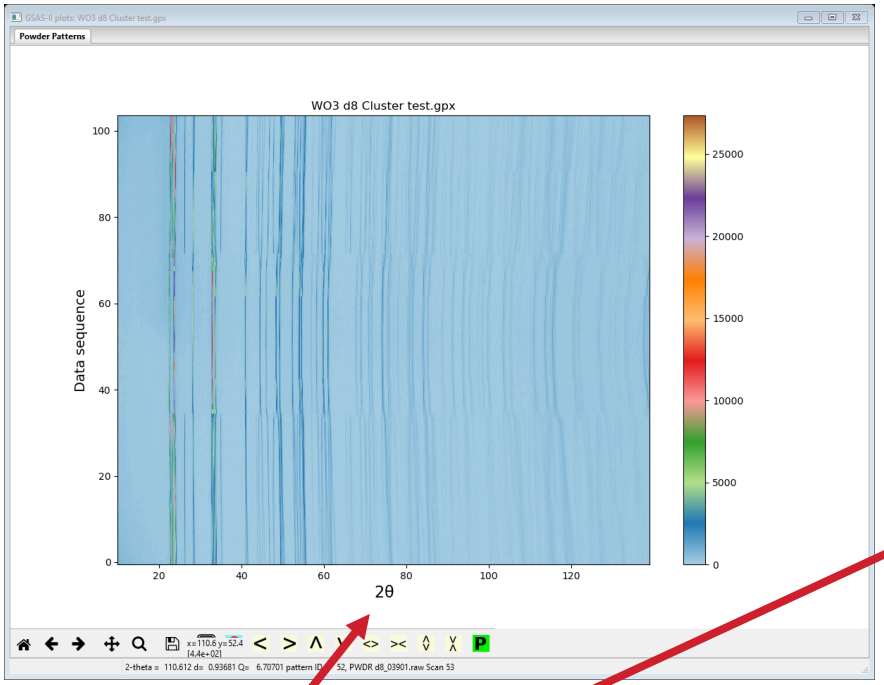
"Distance" in GSAS-II

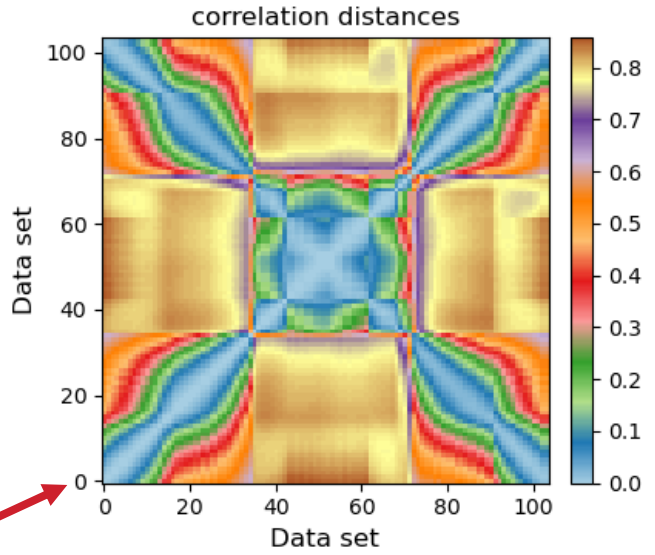
- Euclidian - shortest
- City block – steps along each axis (longer)
- Cosine – of angle between
- Correlation – coefficient
- Etc… - 11 methods; take your pick. Some are more contrasty than others

DISTANCES

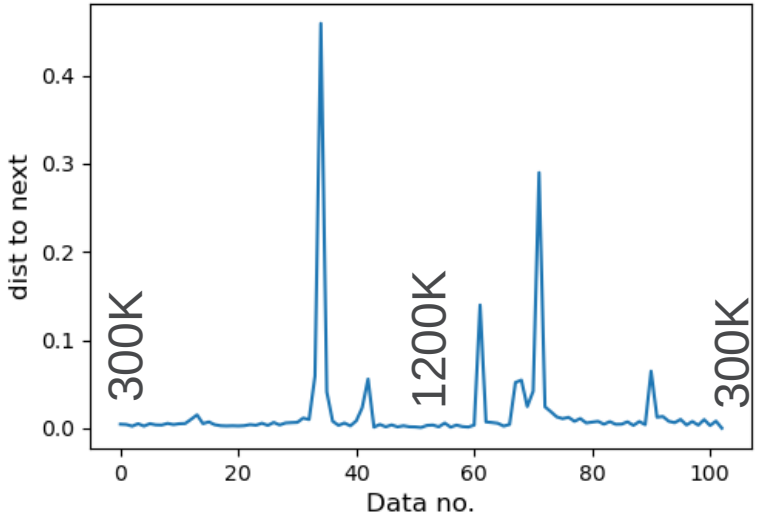
Preliminary results – distance matrix & serial distances

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



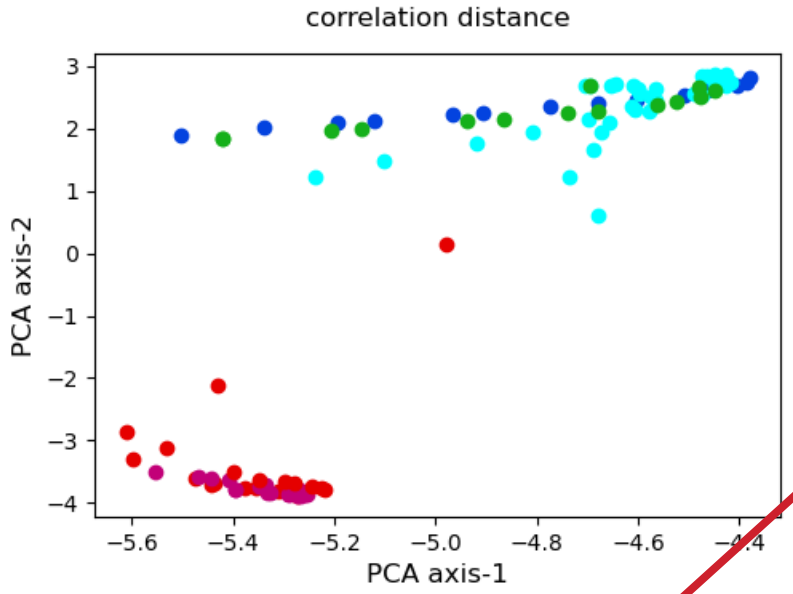


Powder data
Distance matrix
Serial distances
- n+1 vs n
- Peaks = Phase changes
- Not useful for random data

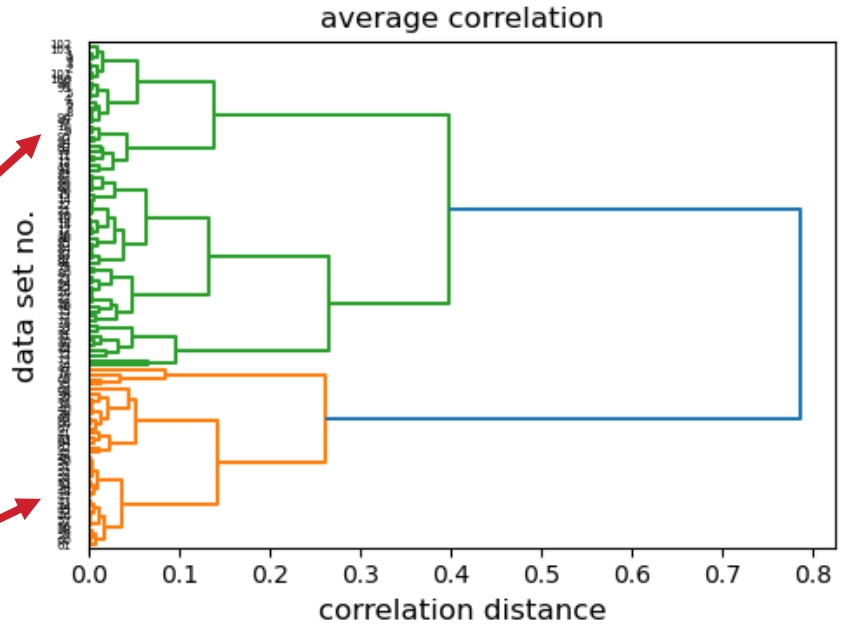


DISTANCES – PRINCIPAL COMPONENT ANALYSIS & DENDOGRAM

Most significant 2-3 dimensions – cluster analysis



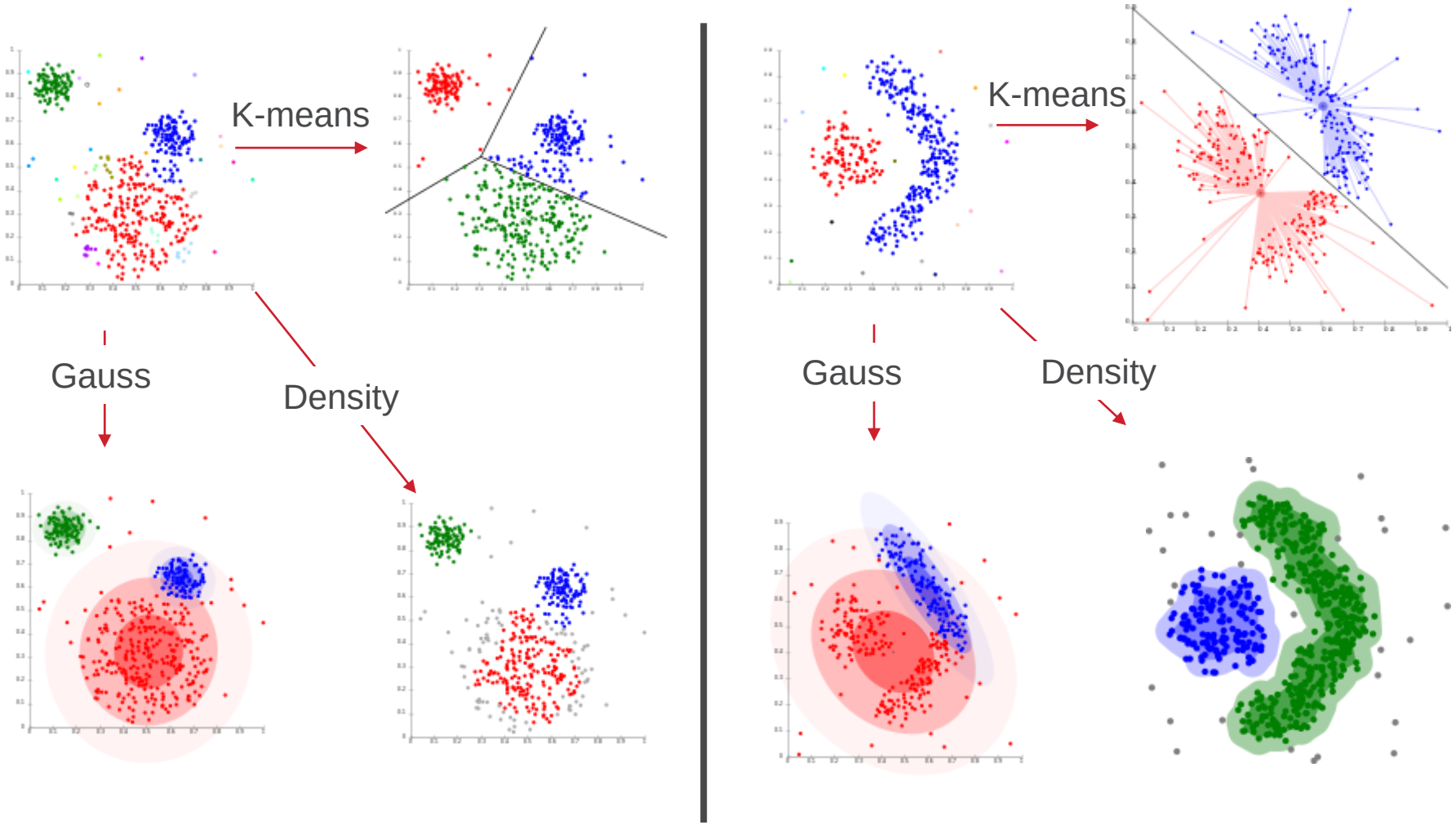
Temp variation – trails in PCA
→ Clusters ill defined in this case
Colored by “cluster”



Dendogram
– hierarchy in data?
- Low T phase
- Intermediate T phases
- High T phase

THE CLUSTERING PROBLEM

Wide variations possible – 2 example PCAs & cluster algorithms

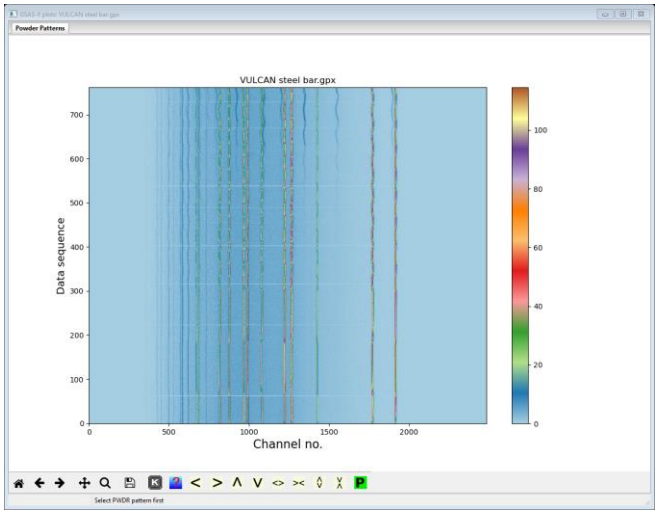


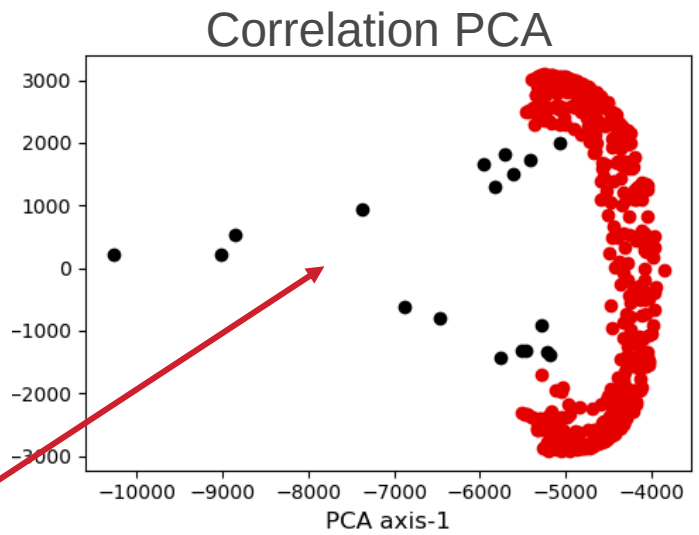
GSAS-II has 6 clustering algorithms – some require # of clusters

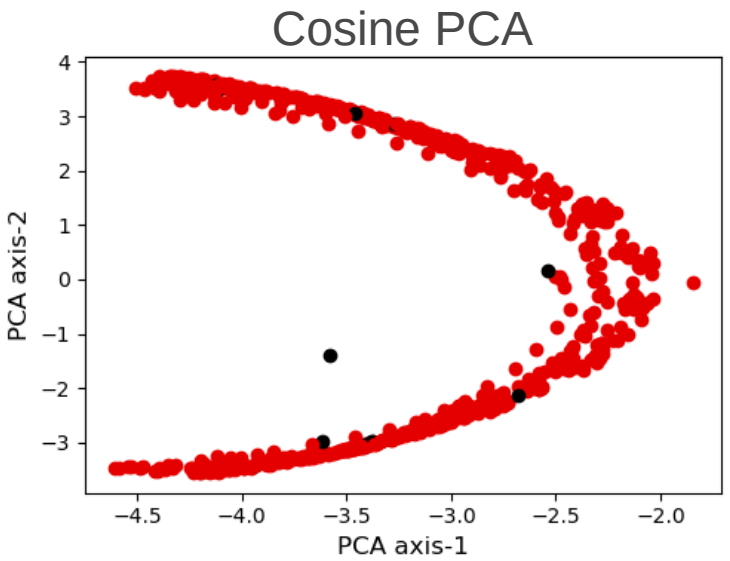
Taken from Wikipedia

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

RMCPROFILE IN GSAS-II

RMCPROFILE “BIG BOX” SIMULATION

GSAS-II interface development goals

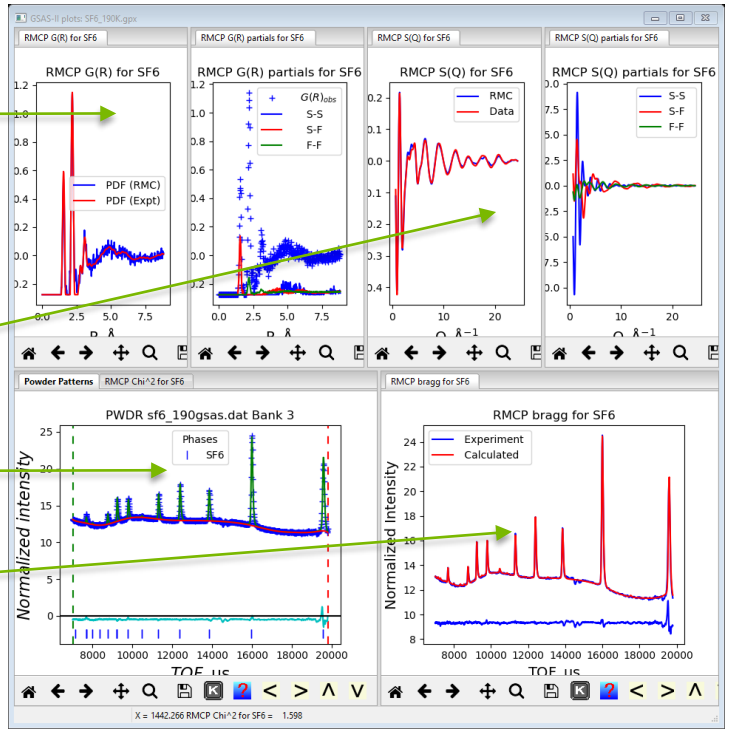
- Provide GUI interface to setup of RMCProfile - save setup controls for reuse
- Initiate independent RMCProfile execution – may run for hours
- Allow graphical display on intermediate results

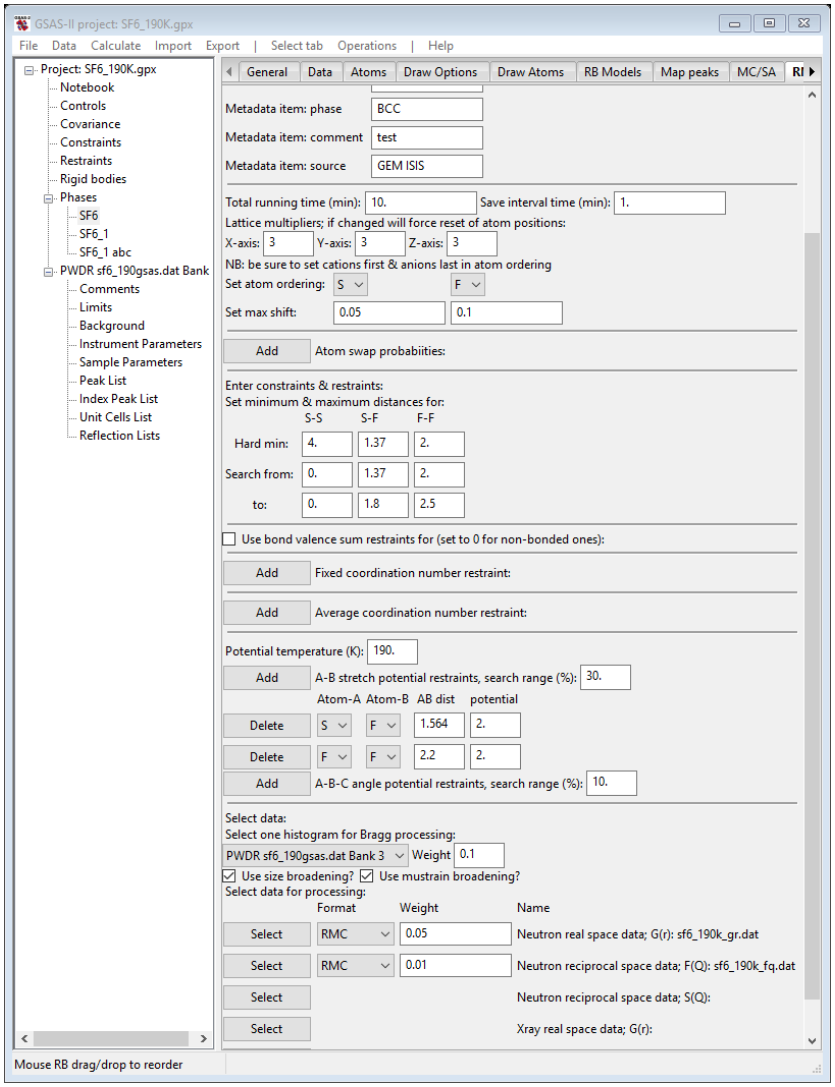
G(R) & partials

S(Q) & partials

RR result

PWDR simulation



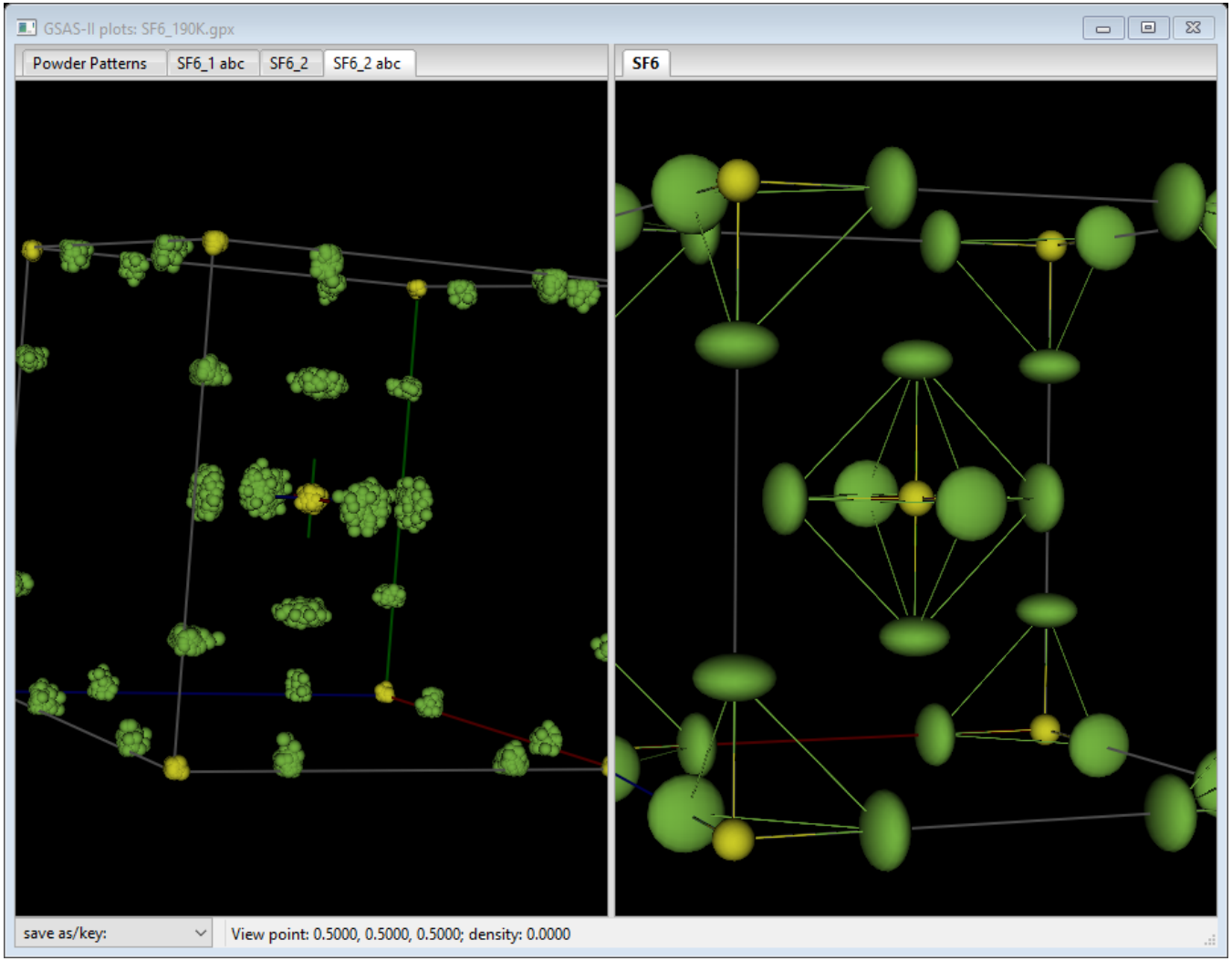


RMCPROFILE RESULT FOR SF_6

10x10x10 unit cell box – transform back to original

See disordered atom distribution

– compare to Rietveld U_{aniso} for F atom



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PDFFIT & ISODISTORT

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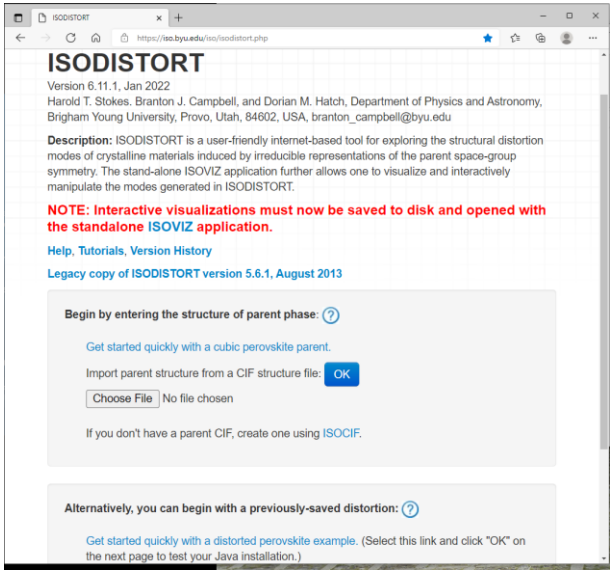
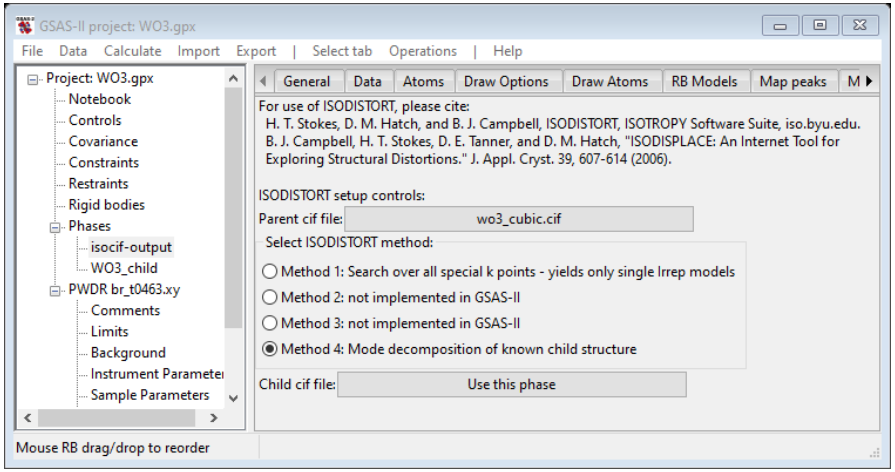
ISODISTORT

Implementation in GSAS-II

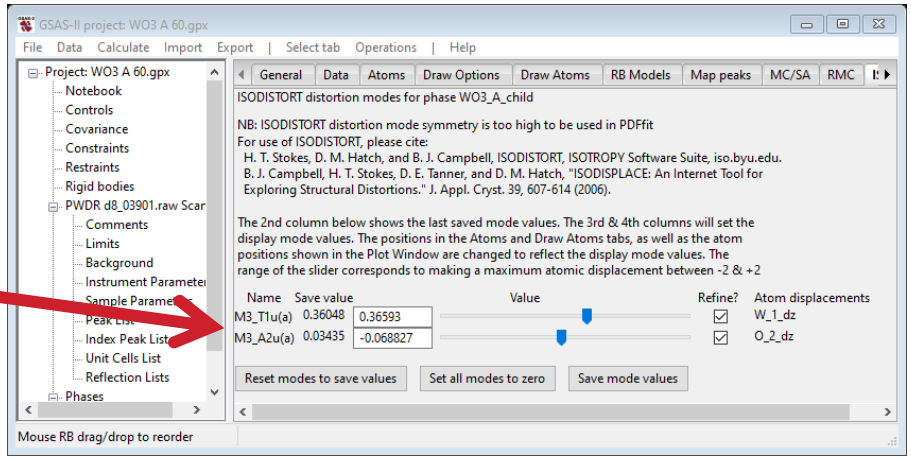
ISODISTORT: Web based tool for discerning mode displacements of atoms from an idealized parent structure





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

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



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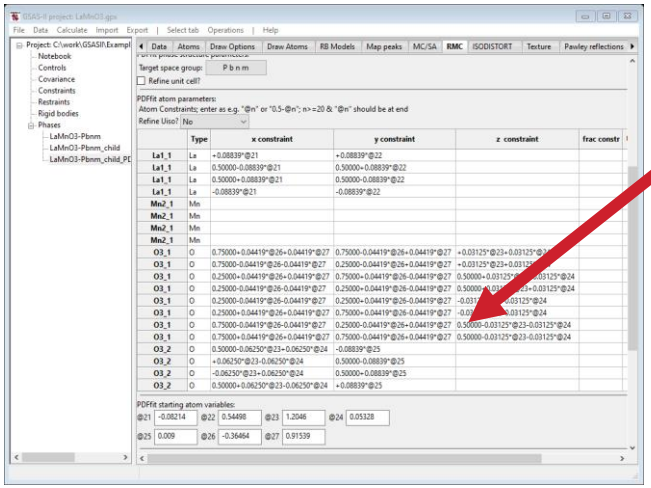
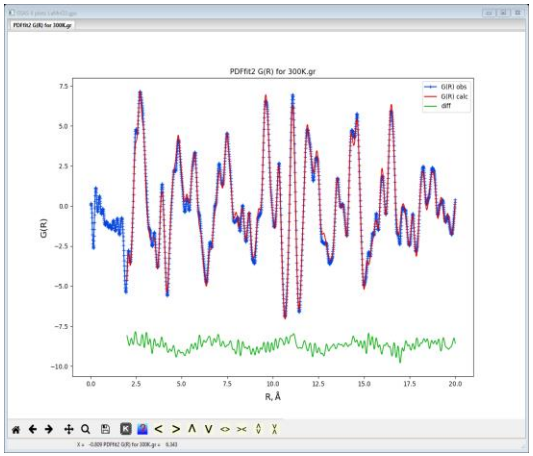
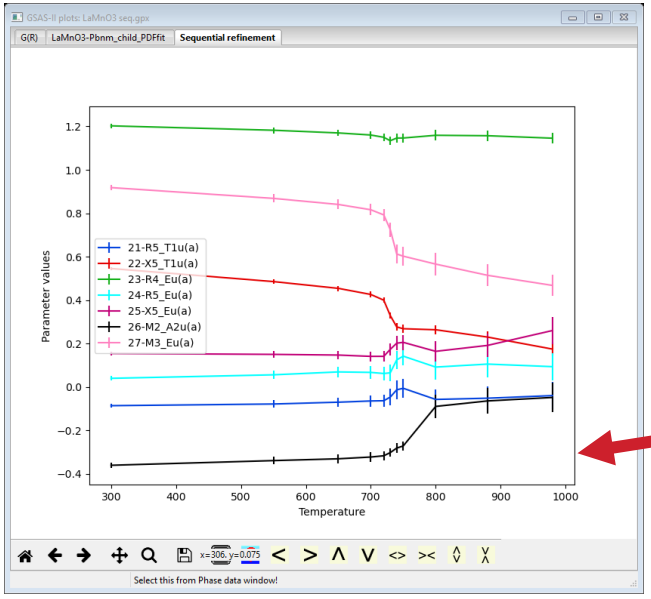
PDFFIT2 = “PDFfit” IN GSAS-II

“Small Box” modelling of pair distribution functions

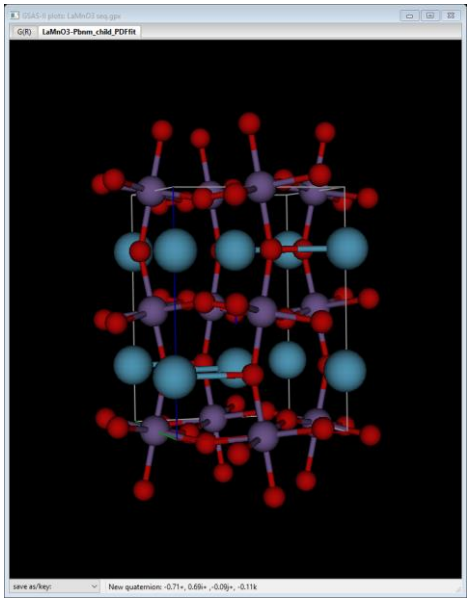
Use ISODISTORT – create the atom position constraints in new interface to PDFfit2







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



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INCOMMENSURATE STRUCTURES IN GSAS-II

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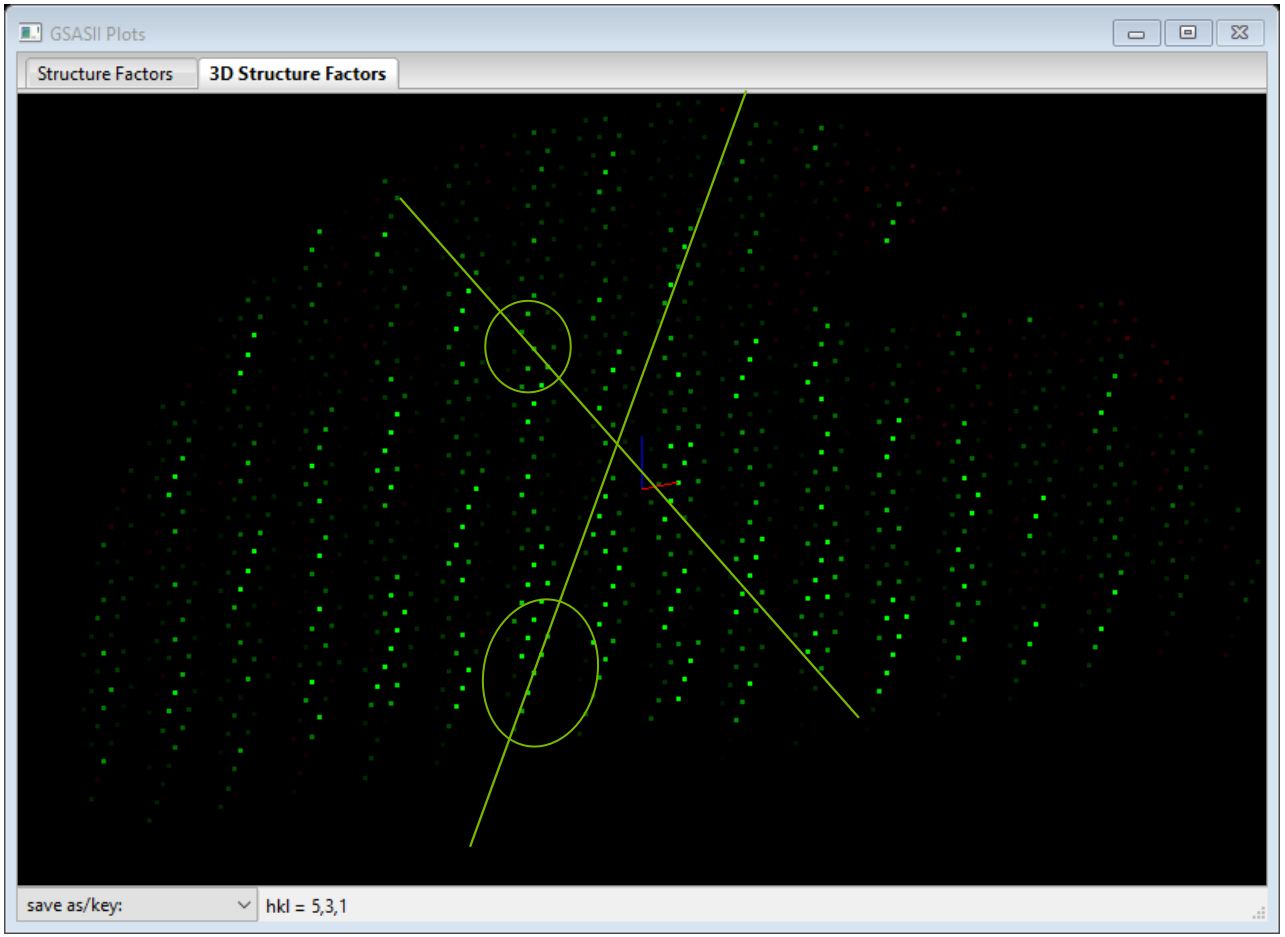
INCOMMENSURATE STRUCTURES N GSAS-II

Book: “Incommensurate Crystallography” S. van Smaalen



H=G+mq

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

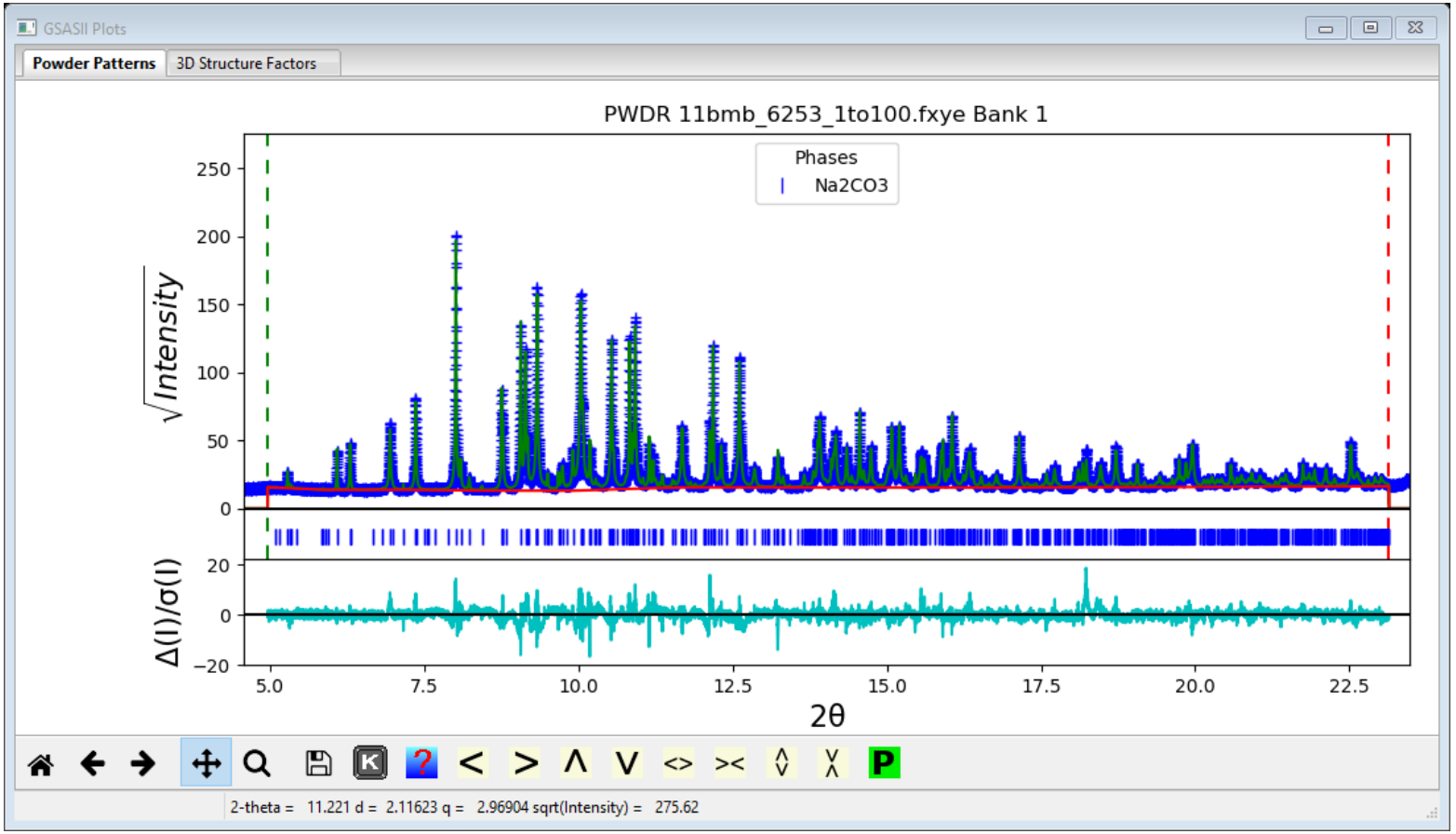
For Na_2CO_3
q= 0.183,0,.319

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

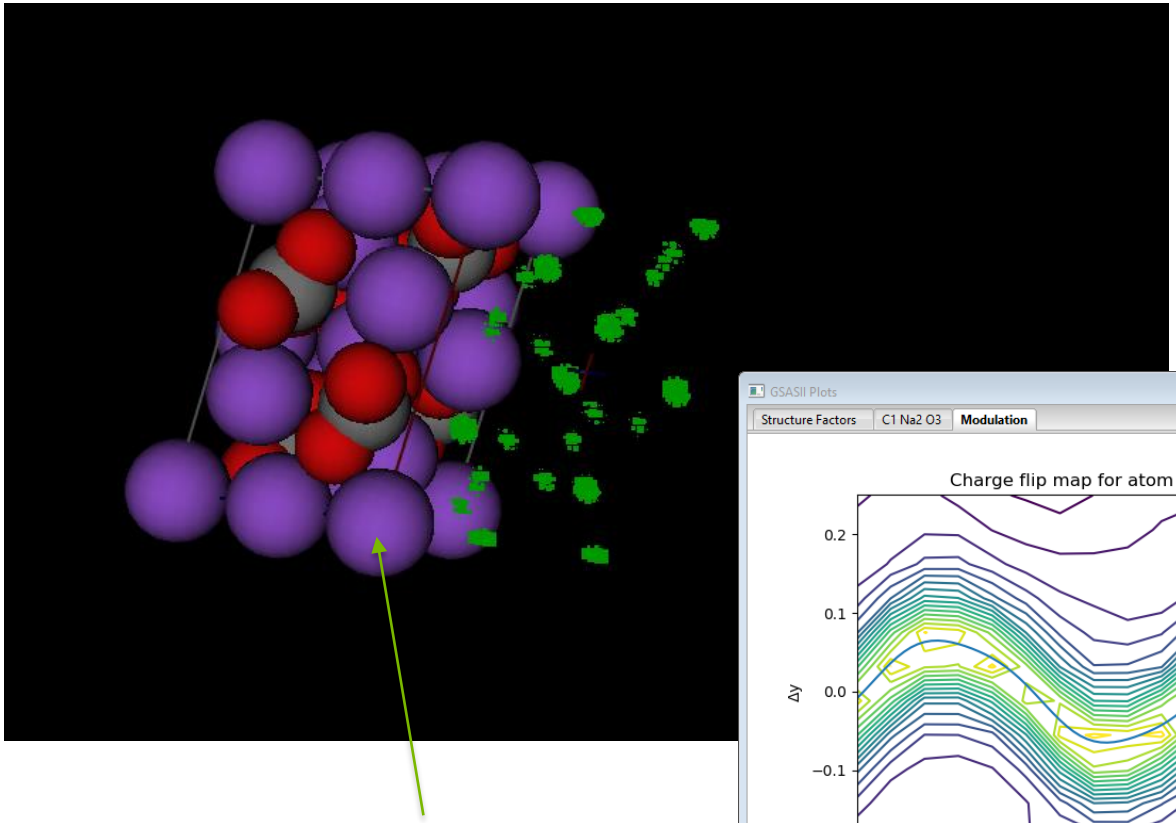
Na_2CO_3 – 11BM @ APS room temp.

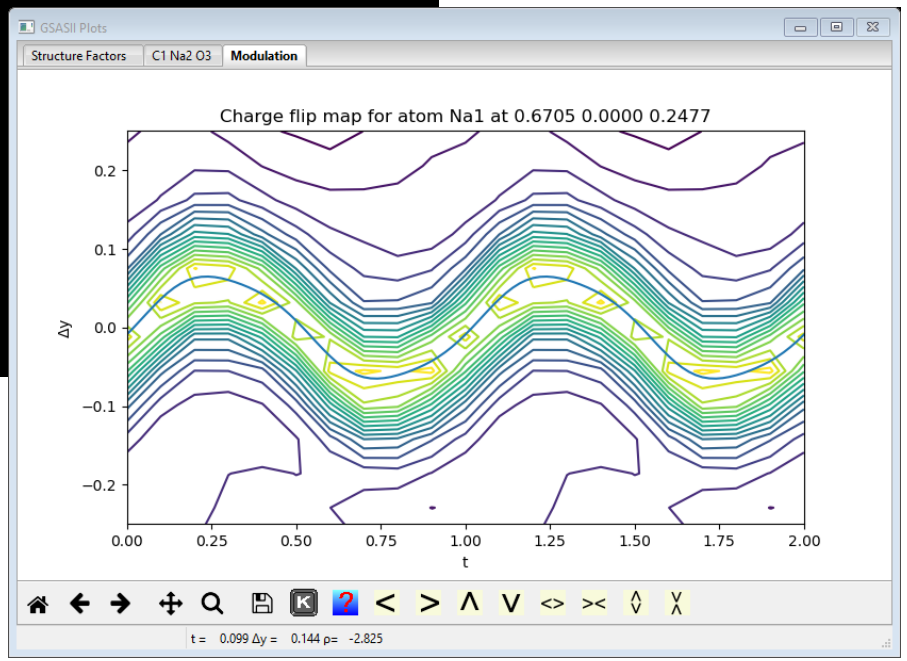


Includes m=-2,-1,1,2 superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom

INCOMMENSURATE STRUCTURE SOLUTION

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

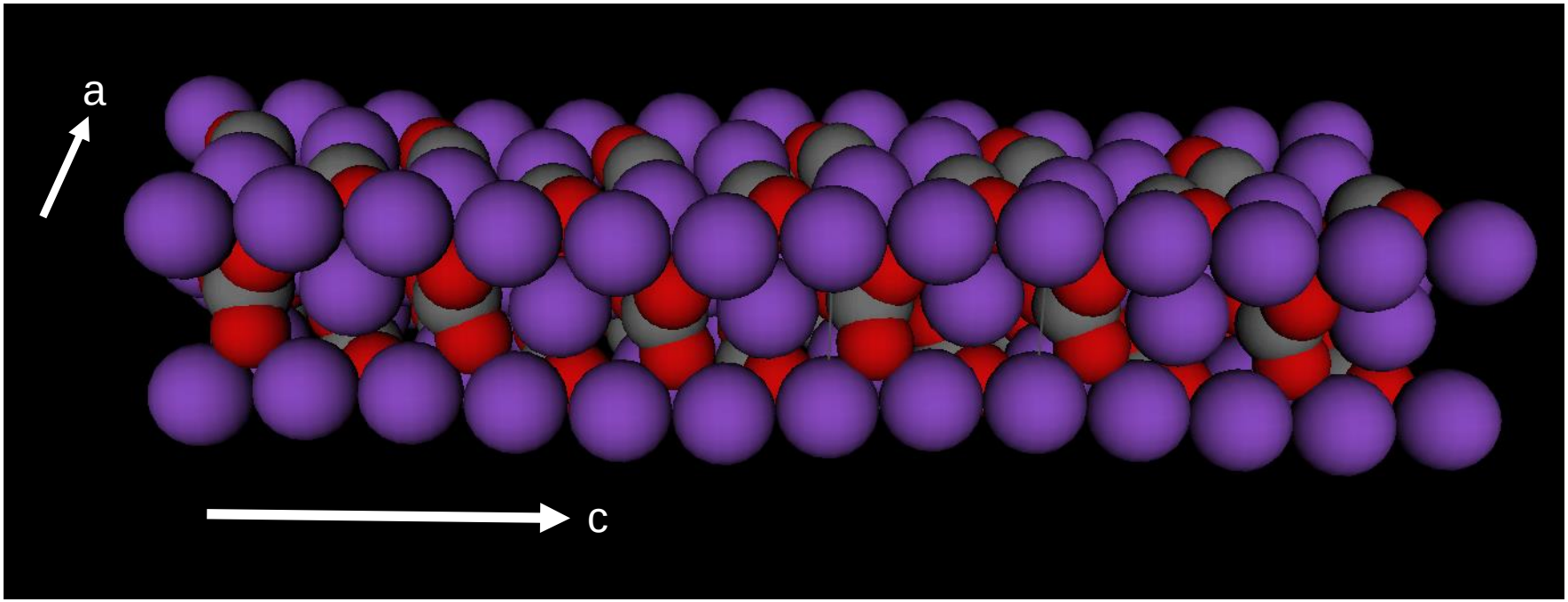




Modulation of atom positions (Na1-y)
Fit function – fourier series in tau

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 ~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

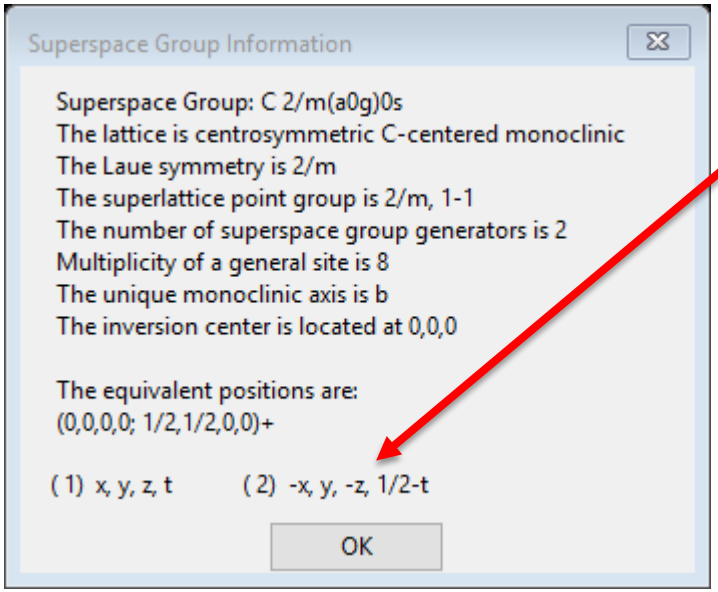
e.g. Na_2CO_3 – C2/m(α0γ)os

Space group

Modulation vector

Translation component

Operators: conventional space group & 4th dim component



Possible modulation vectors:
e.g. αβγ, α0γ, 0β0, α½γ, ½β0
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)

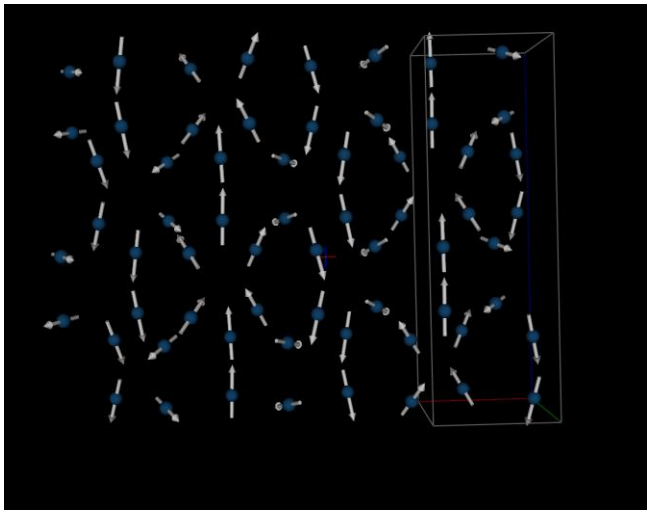
INCOMMENSURATE STRUCTURES

Cases not allowed in GSAS-II

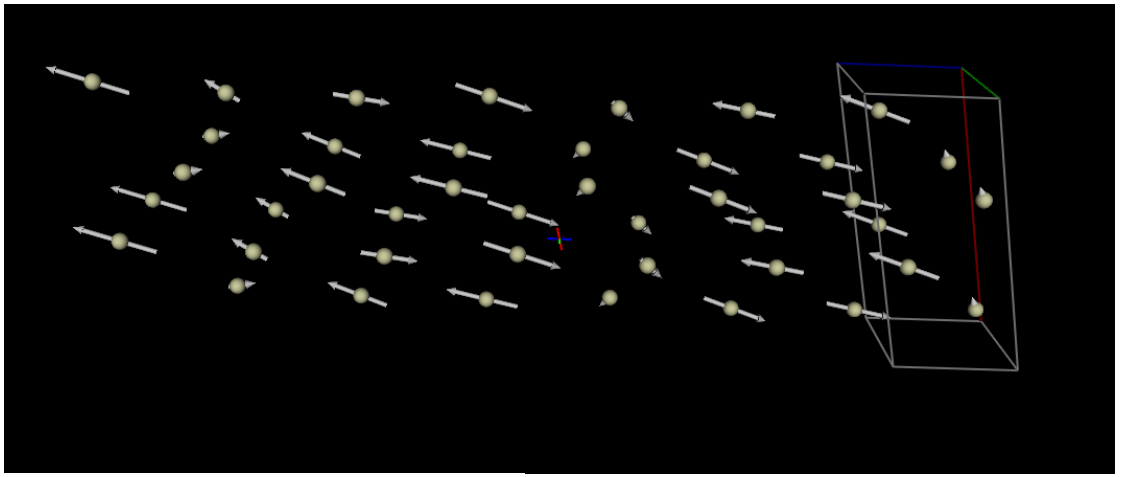
- 3+2 & 3+3 not allowed in GSAS-II
  - Too complex to deal with easily
  - 3-D 230 SG
  - For 3+1: 4,783 possible SG
  - For 3+2: 222,018 possible SG
  - For 3+3: 28,927,922 possible SG
  - But only a handful found – not worth the hassle
- Ad hoc centering not allowed
  - ‘X’ space groups – all have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

MAGNETIC INCOMMENSURATE STRUCTURES

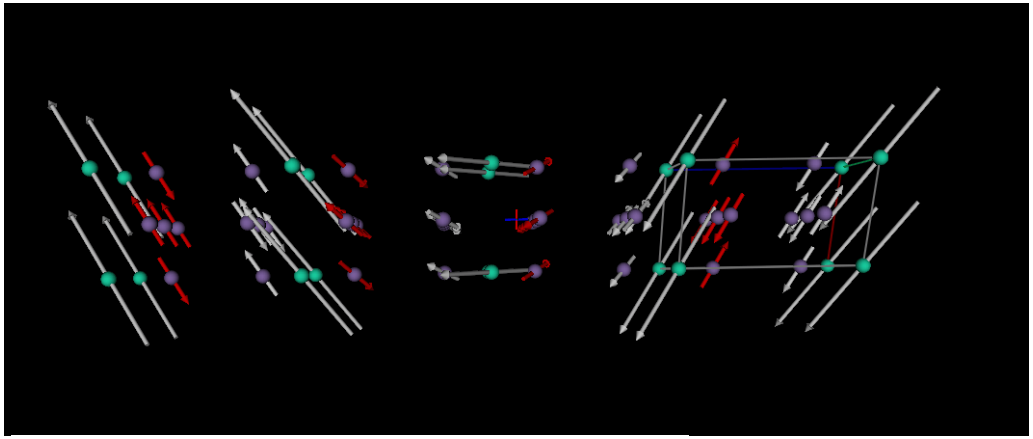
Some examples:



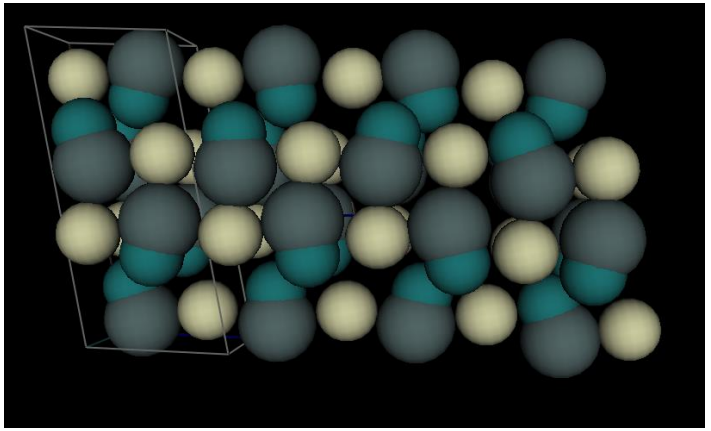
β-Li_2IrO_3



CeRuSn – Ce moment



$DyMn_6Ge_6$ – residual moment

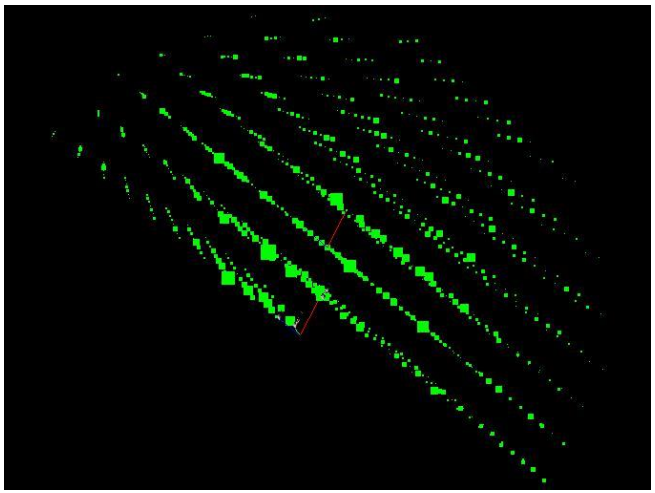


CeRuSn –
structure modulation

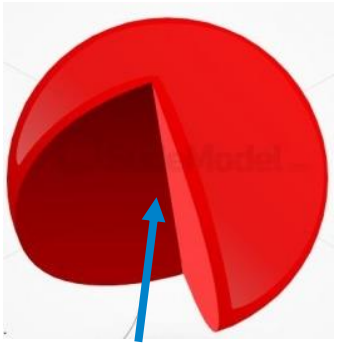
CHARGE FLIPPING

CHARGE FLIPPING

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

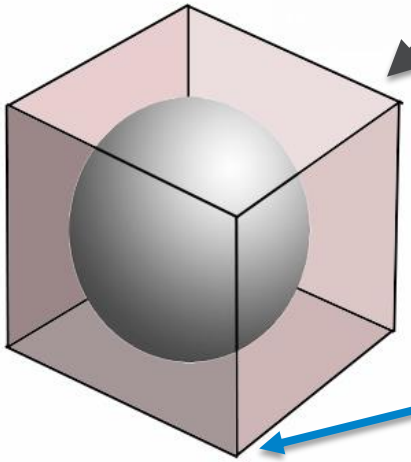


1D list

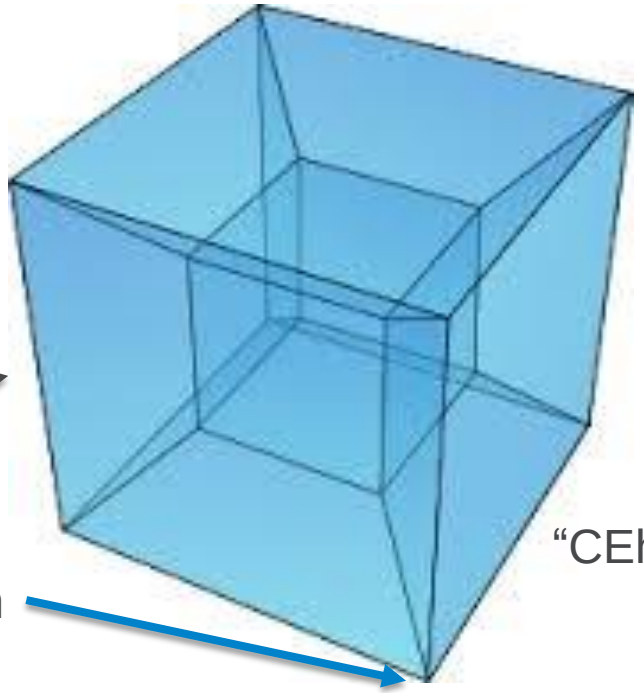


Origin @ F_{000}

1D list → 3D array



Expand 3D array

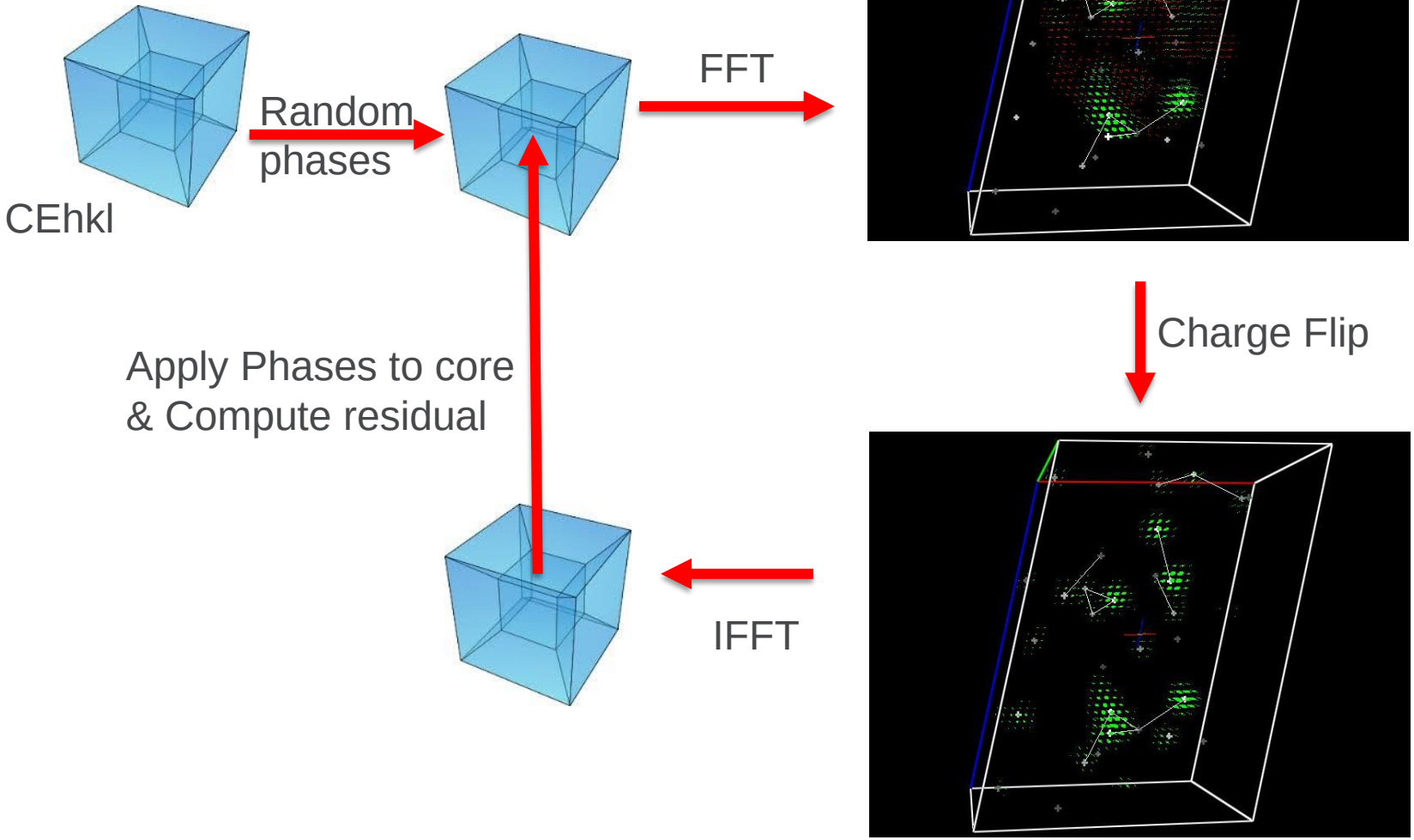


"CEhkl"

New origin

CHARGE FLIPPING

The Algorithm



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
```

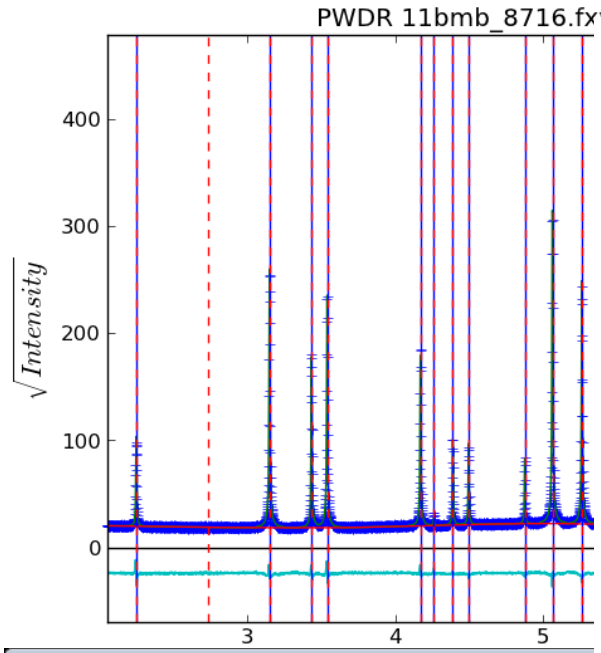
After user break:

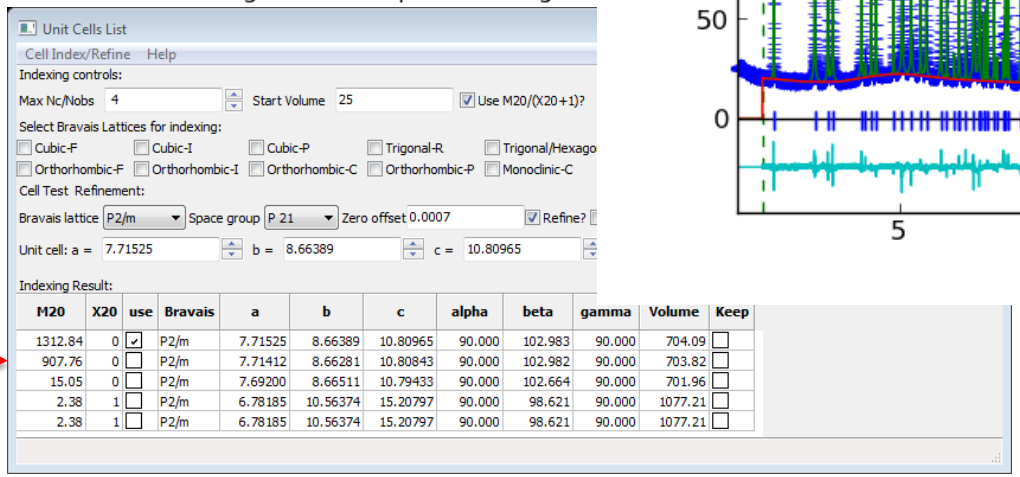
Repeat 1st line to get result map

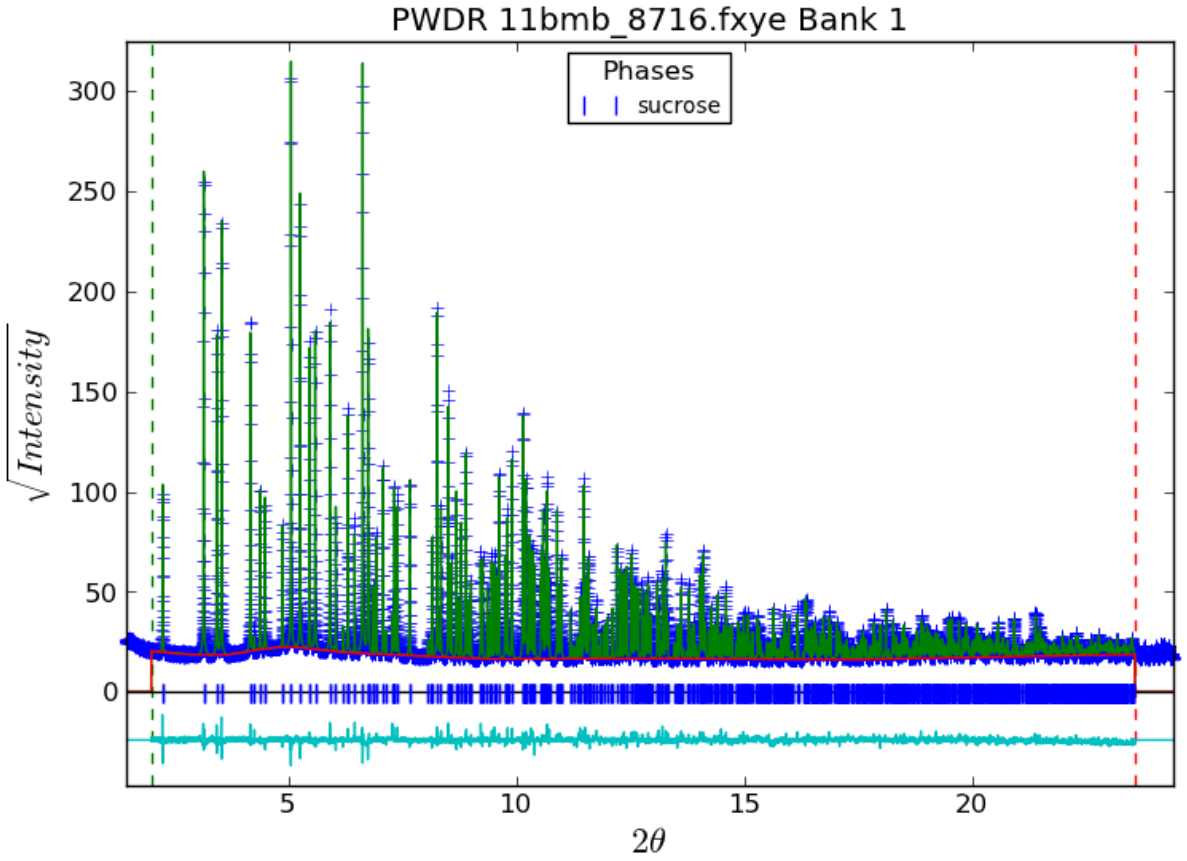
Find origin; search for peaks & display result

EXAMPLE – SUCROSE POWDER

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





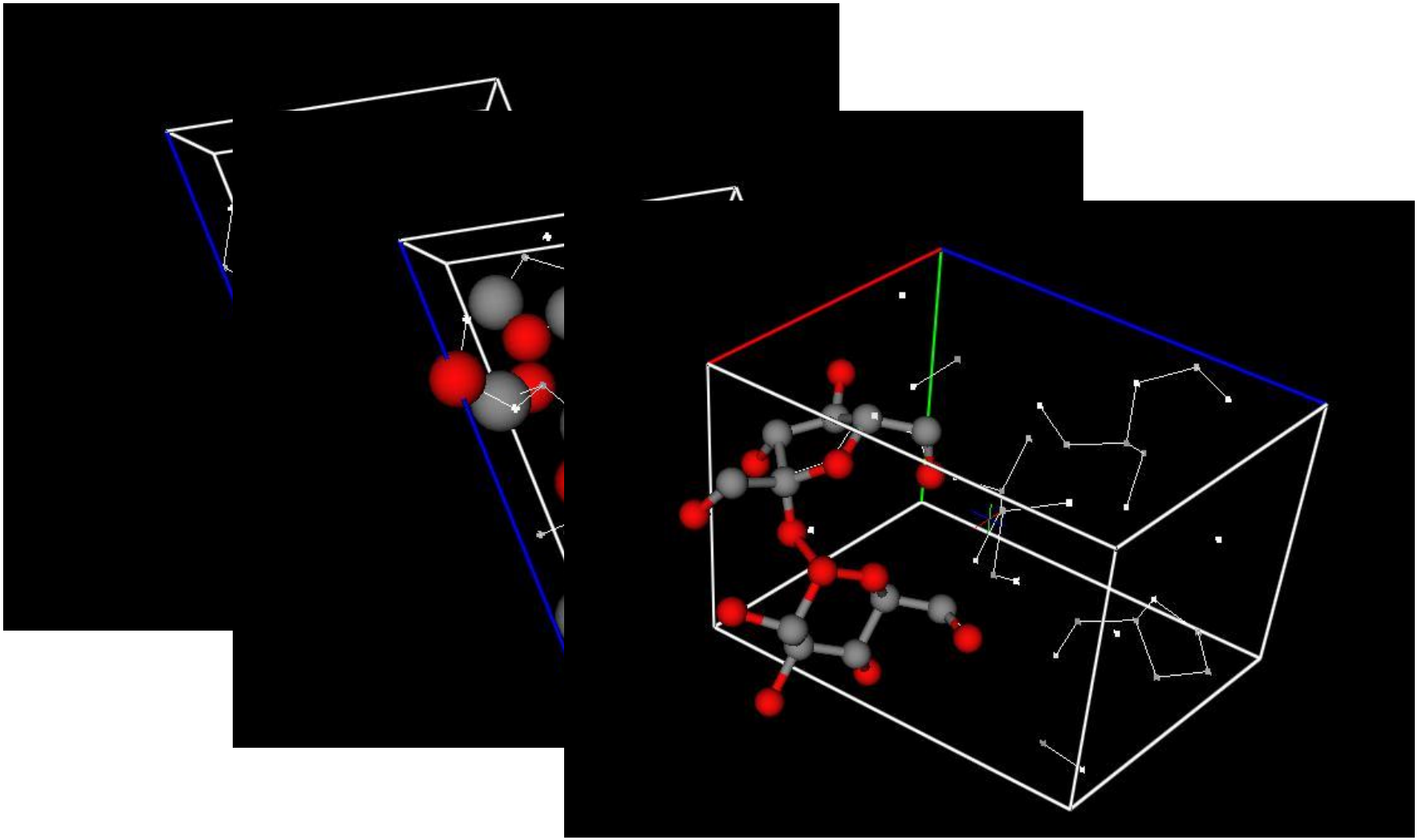


781 unique hkl's
CF with 61440

Argonne NATIONAL LABORATORY

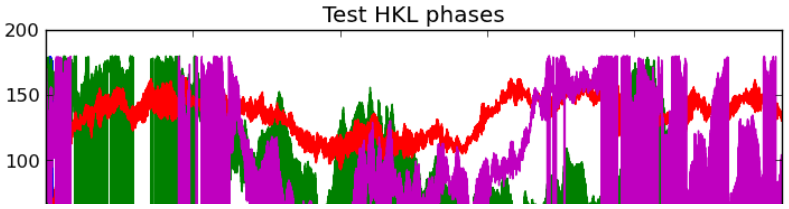
CHARGE FLIPPING SOLUTION

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

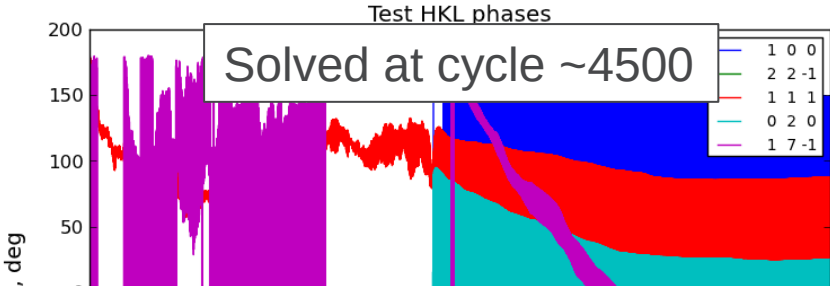


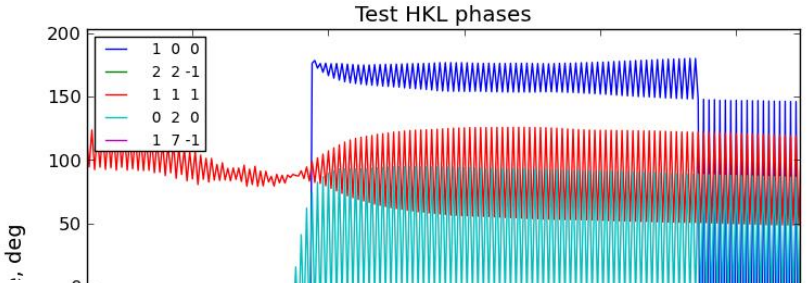
CHARGE FLIPPING – PHASES?

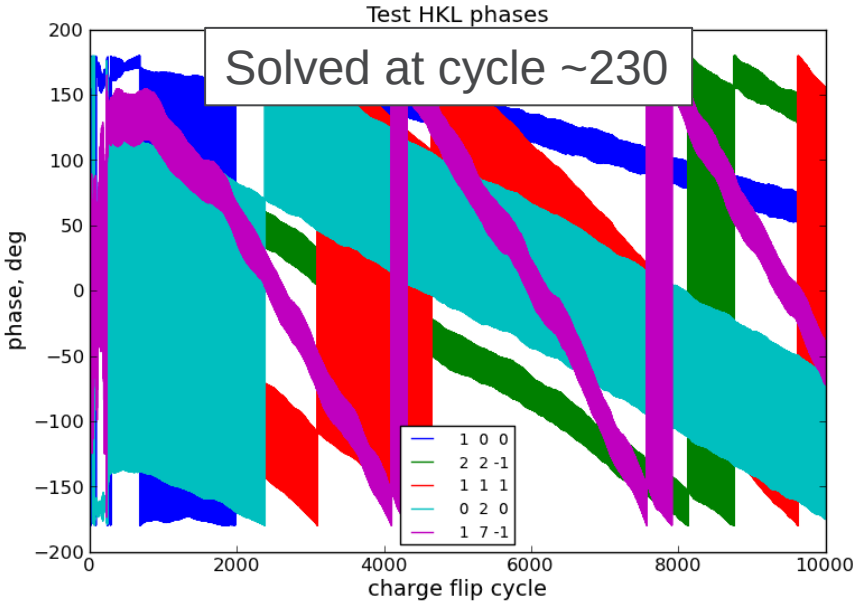
Track phases of 5 reflections – 10000 CF cycles

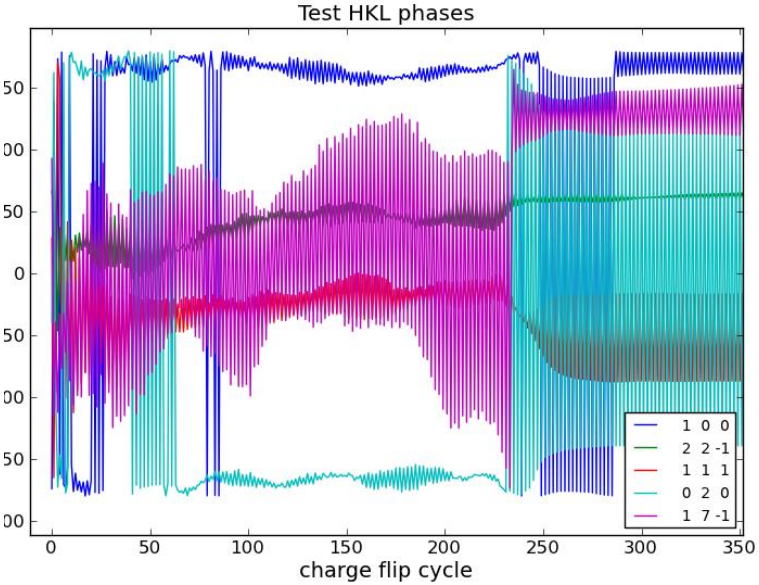


Not solved in 10000 cycles





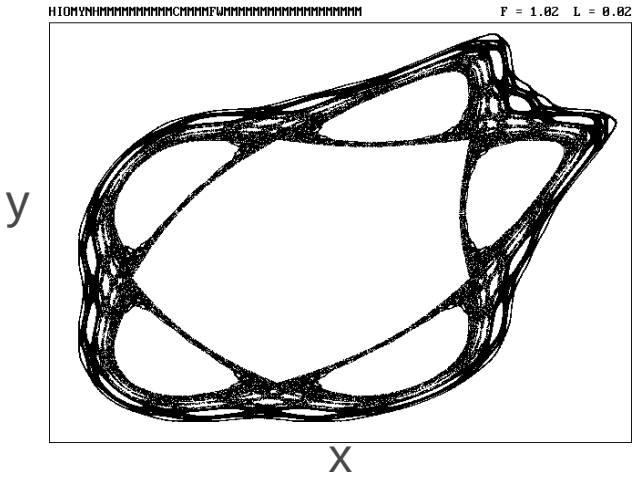


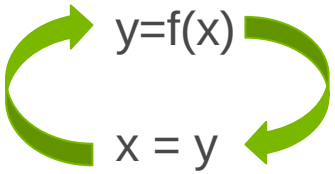


CHARGE FLIPPING – CHAOS MATHEMATICS?

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?)





f(x) - polynomial

- Phase oscillation & drift – "sympletic" 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