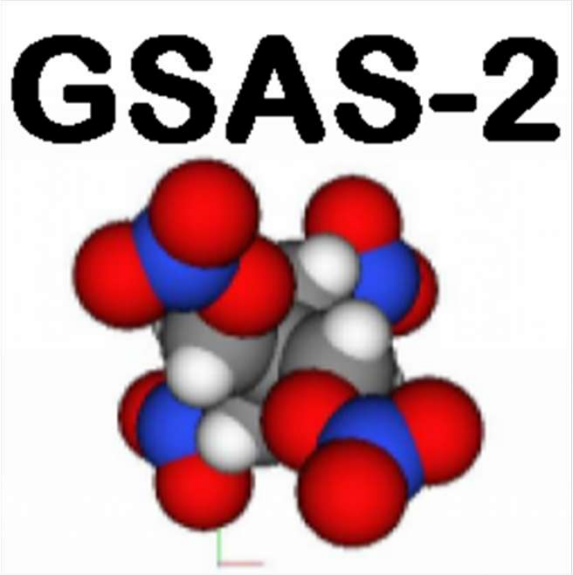
GSAS-II BEYOND RIETVELD



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Saskatoon
June, 2024

2D IMAGE PROCESSING – FORGOTTEN OLD MATH

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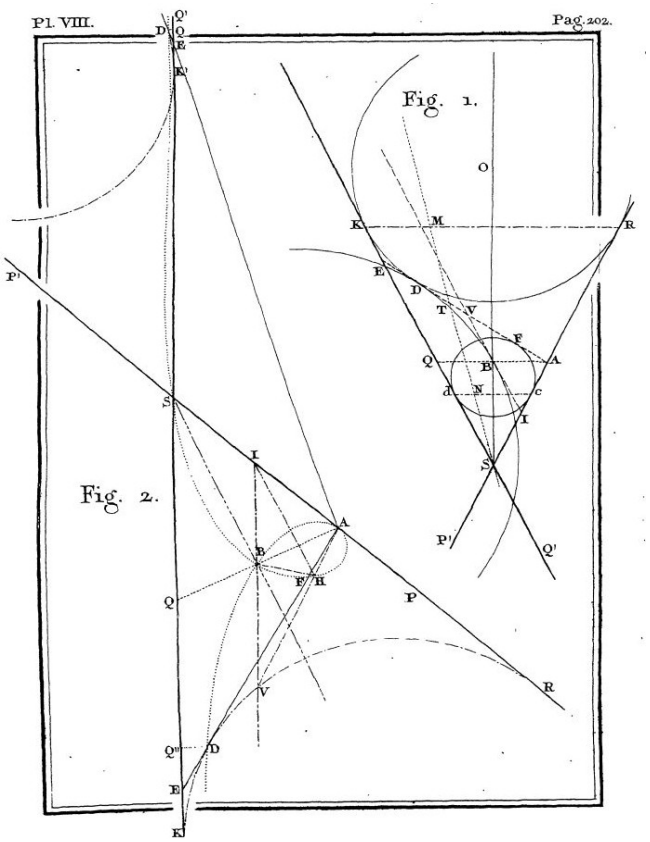
2D IMAGE DATA

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

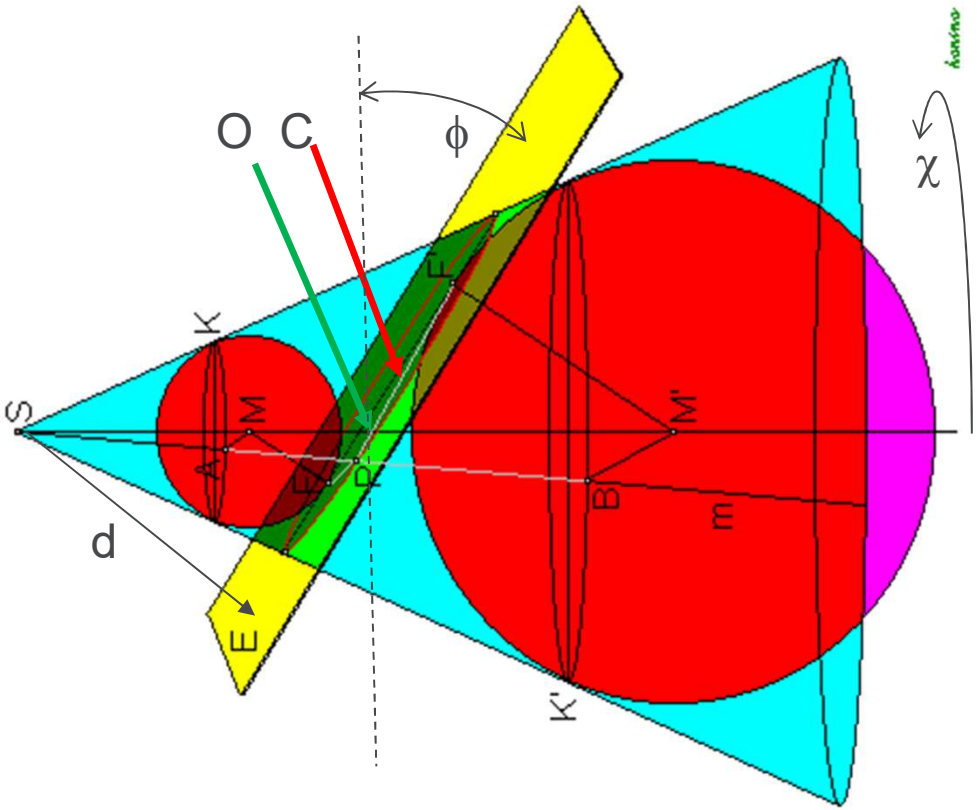
- line SO is cone axis
- F&D are the ellipse foci on the plane

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

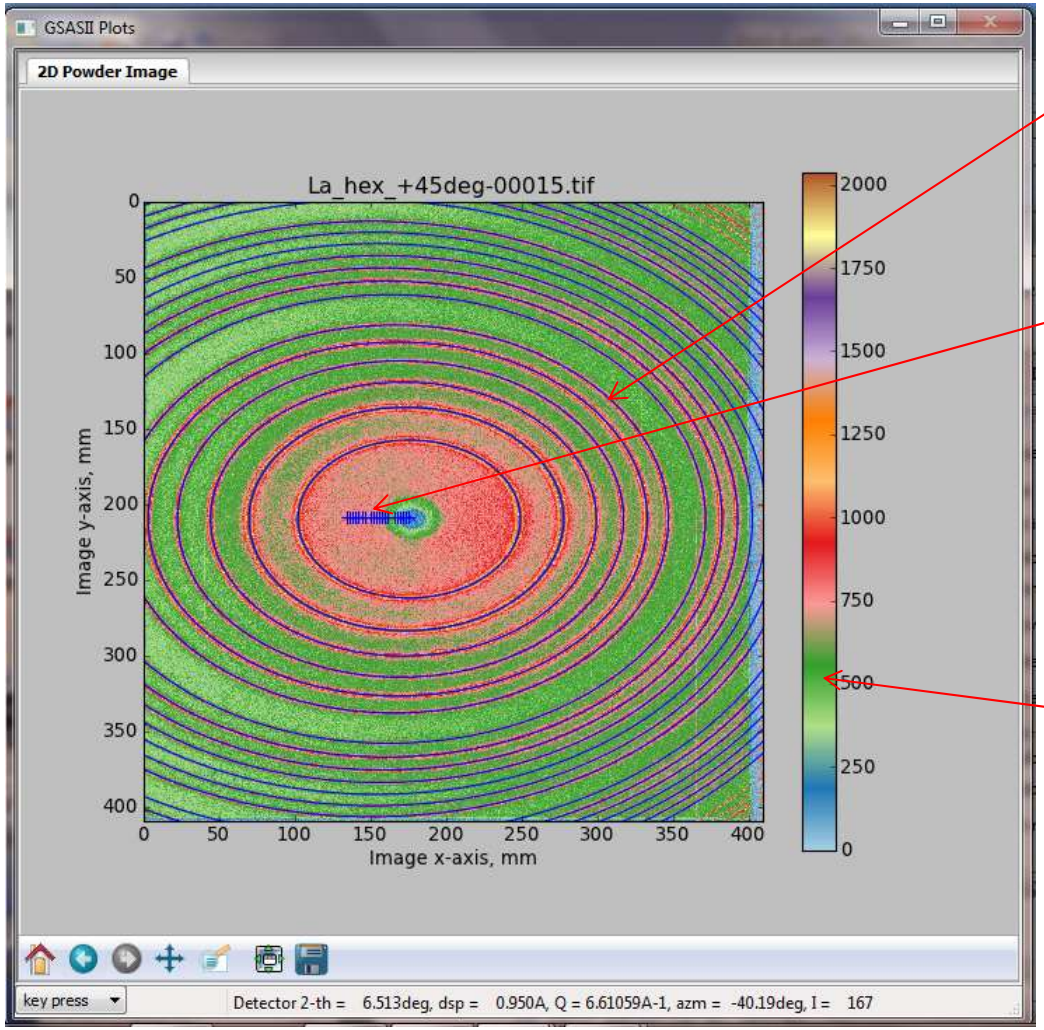


- Plane E is a tilted area detector
- The line SMM' is the Bragg cone axis – incident beam direction & passes through centers of both spheres
- Spheres touch plane at foci (F & F') of conic section (ellipse)
- Intersection of axis with plane (**O**) **not** at halfway point (**C**) between F & F' (ellipse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

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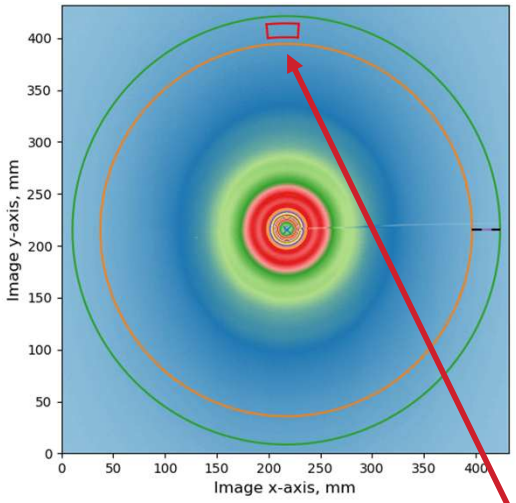
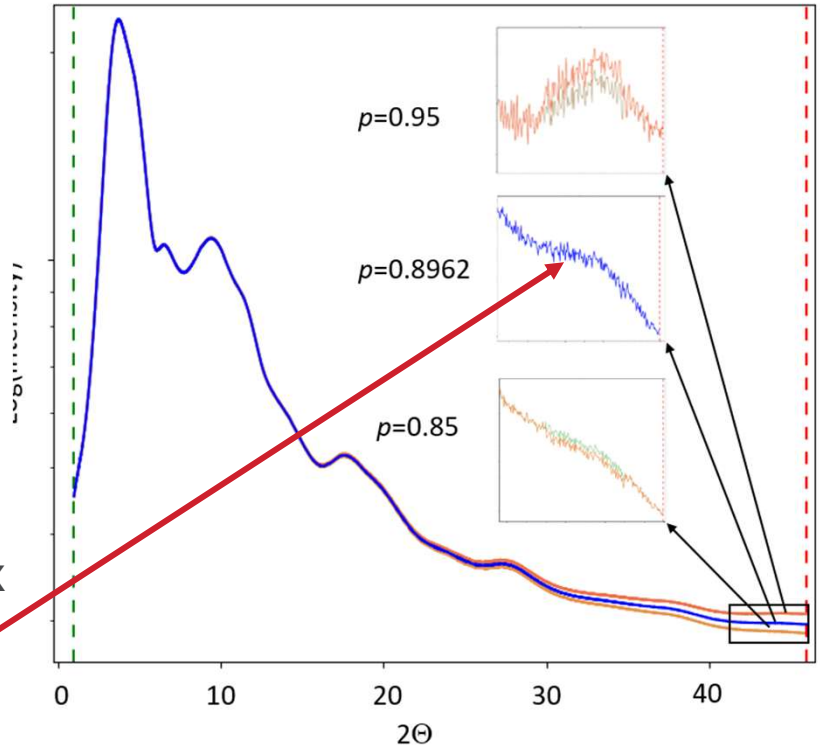
2D IMAGE POLARIZATION DETERMINATION

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

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

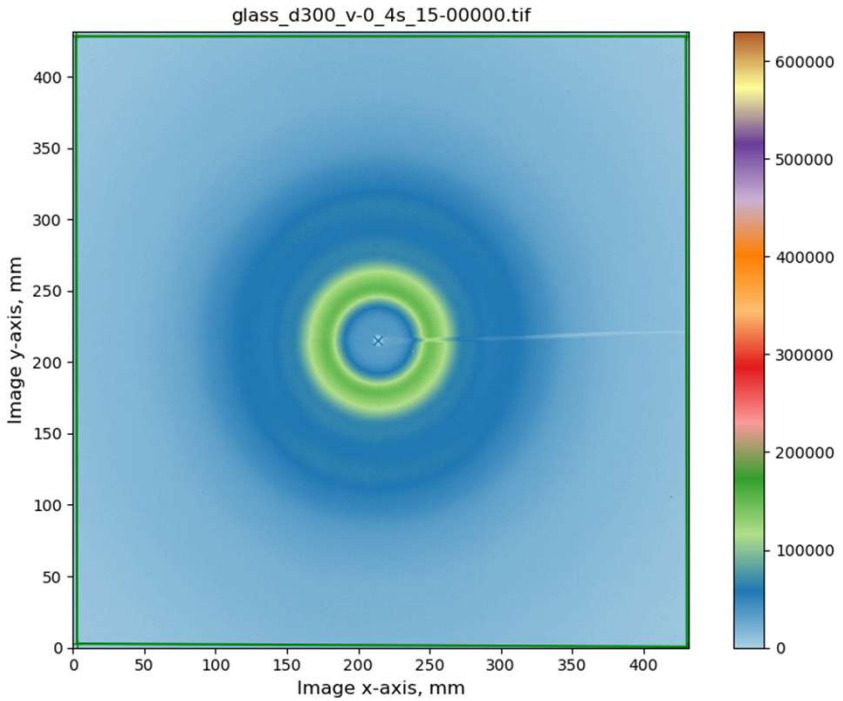


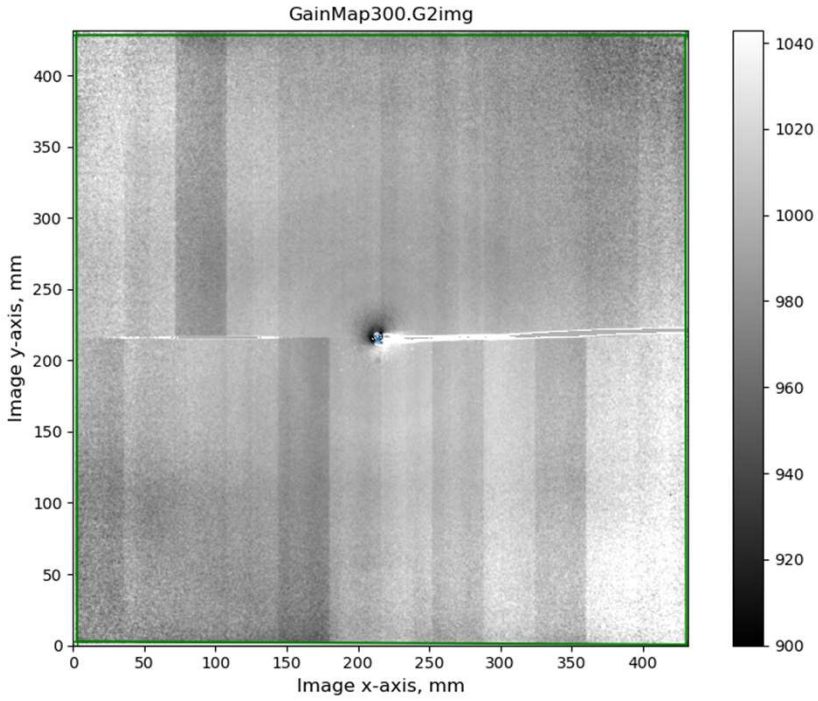


Integrate in band w/o mask box
Match if polarization is correct

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)
Better with 3 offset images – clean up center spot

TEXTURE ANALYSIS

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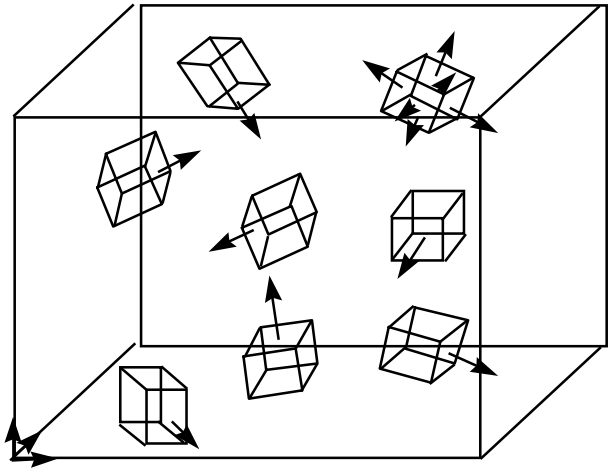
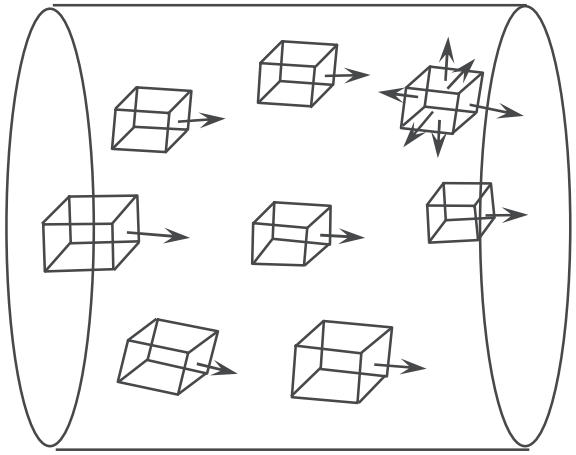
What is texture?

Nonrandom crystallite grain orientations



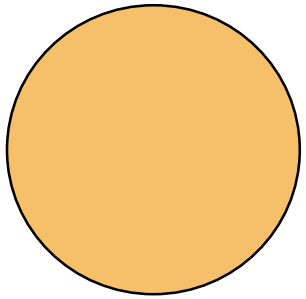
Loose powder



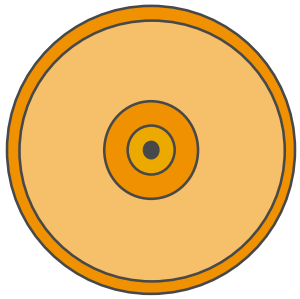
Metal wire

Random powder - all crystallite orientations equally probable - flat pole figure

Pole figure - stereographic projection of a crystal axis down some sample direction



(100) random texture



(100) wire texture

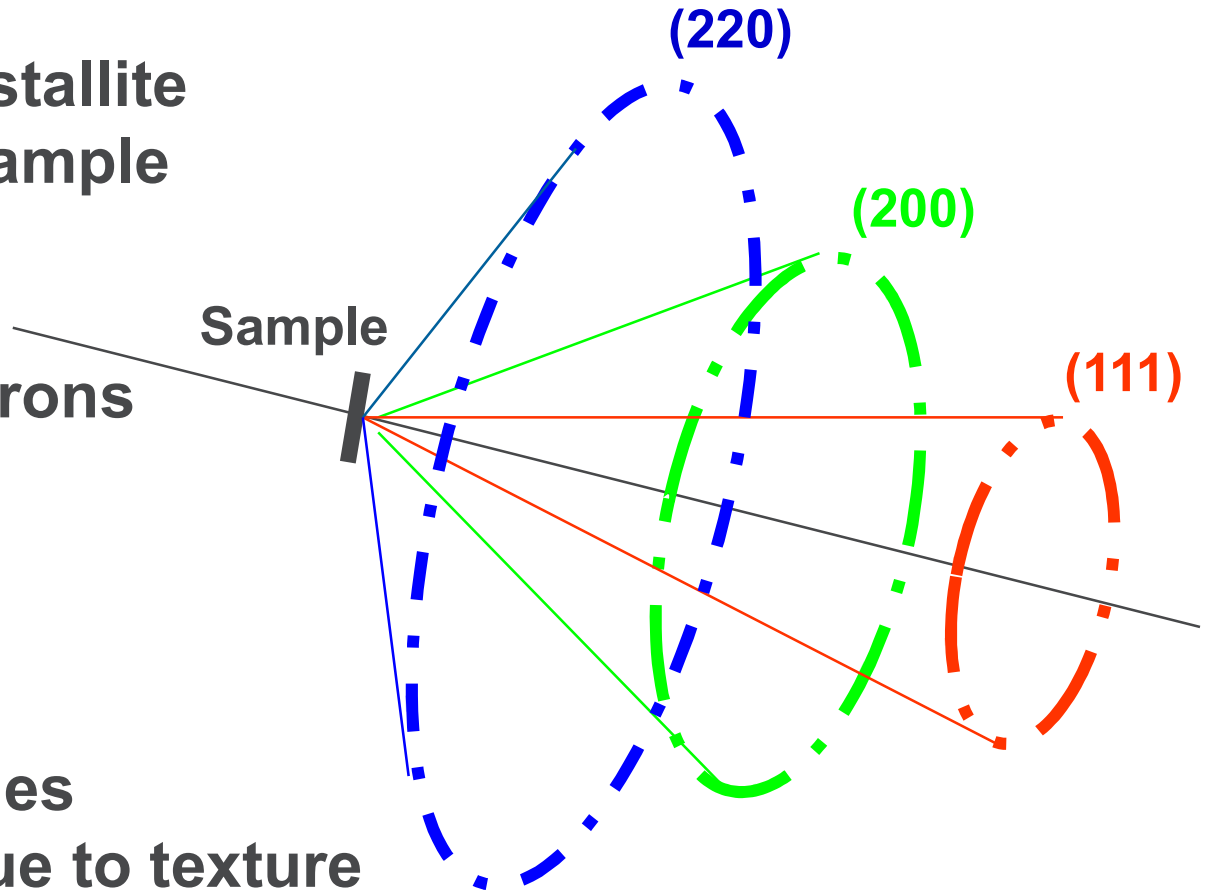
Crystallites oriented along wire axis - pole figure peaked in center and at the rim (100's are 90° apart)

Orientation Distribution Function - probability function for texture

Texture - measurement by diffraction

Non-random crystallite orientations in sample

Incident beam x-rays or neutrons



Debye-Scherrer cones

- uneven intensity due to texture
- also different pattern of unevenness for different hkl's
- Intensity pattern changes as sample is turned

Texture effect on reflection intensity – Sph. Harm. model

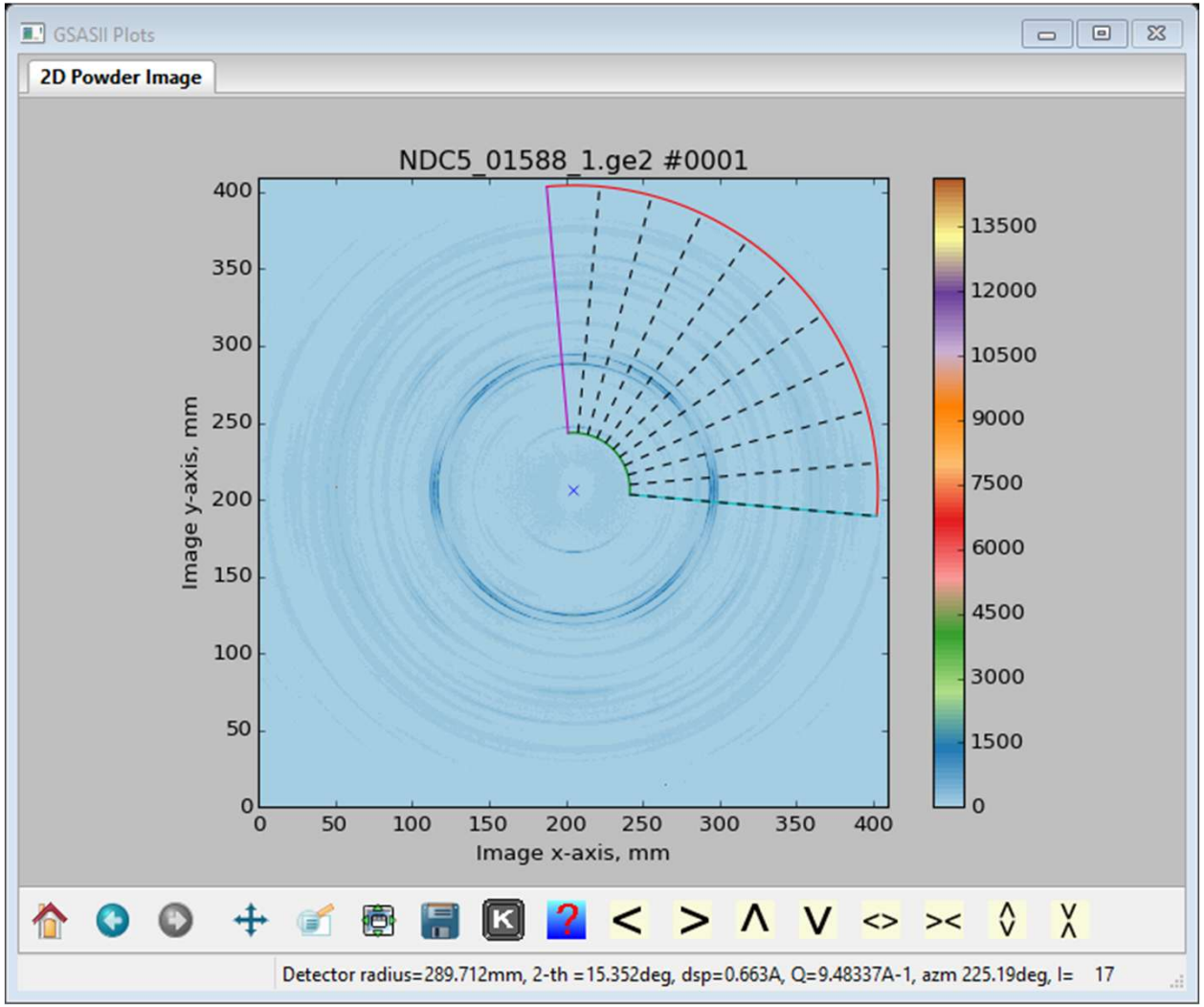
$$A(h,y) = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \sum_{n=-l}^{l} C_l^{mn} K_l^m(h) K_l^n(y)$$

- Projection of orientation distribution function for chosen reflection (h) and sample direction (y)
- *K* - symmetrized spherical harmonics - account for sample & crystal symmetry
- "Pole figure" - variation of single reflection intensity as fxn. of sample orientation - fixed h
- "Inverse pole figure" - modification of all reflection intensities by sample texture - fixed y - Ideally suited for neutron TOF diffraction
- Rietveld refinement of coefficients, C_l^{mn}, and 3 orientation angles - sample alignment

NB: In GSAS-II as correction & texture analysis

2D IMAGE

NiTi shape memory alloy wire: B2 & B19’ phases



Sample – wire symmetry
Need only ¼ of image
Caked in 10° increments
Integration – PWDR patterns
Analyze for texture

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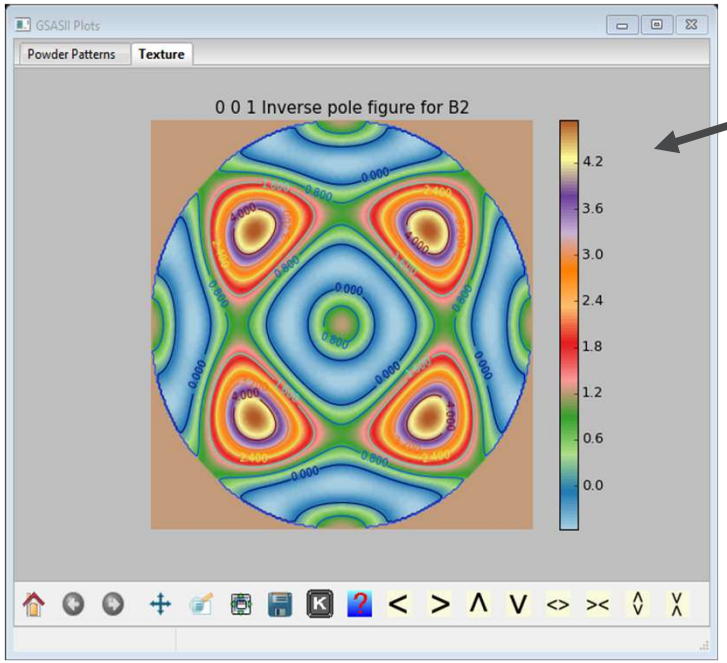
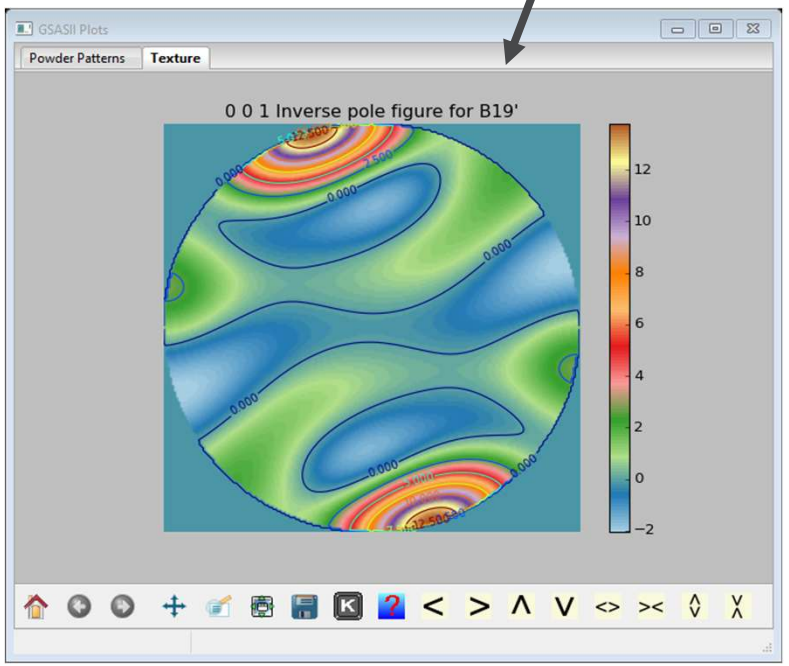
GSAS-II TEXTURE ANALYSIS

Fit C_L^{mn} & crystal structure stuff – inverse pole figures B2 & B19'





Pole figures – bullseyes (boring)
GSAS-II → 3 methods for texture

RMCPROFILE IN GSAS-II

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RMCPROFILE “BIG BOX” SIMULATION

GSAS-II interface development goals

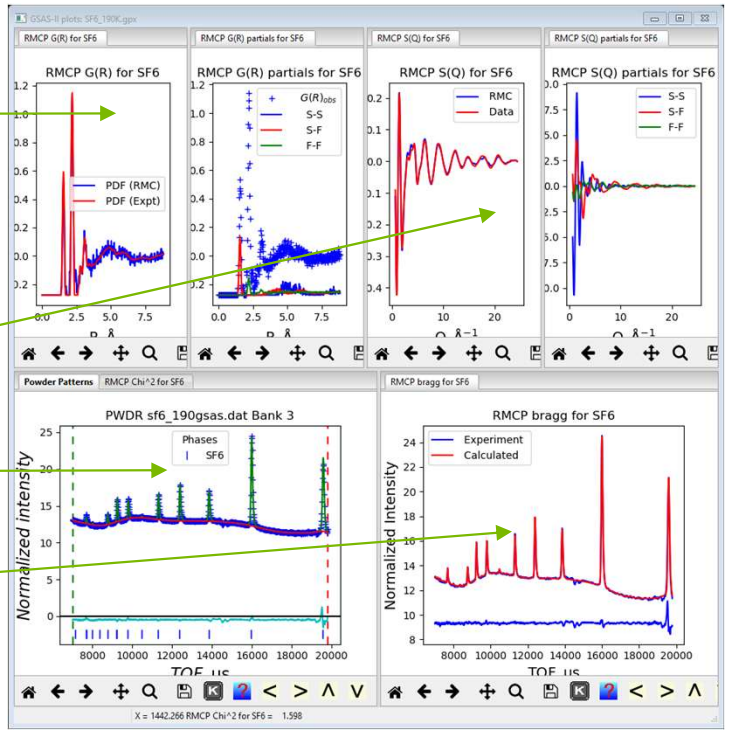
- Provide GUI interface to setup of RMCProfile - save setup controls for reuse
- Initiate independent RMCProfile execution – may run for hours
- Allow graphical display on intermediate results

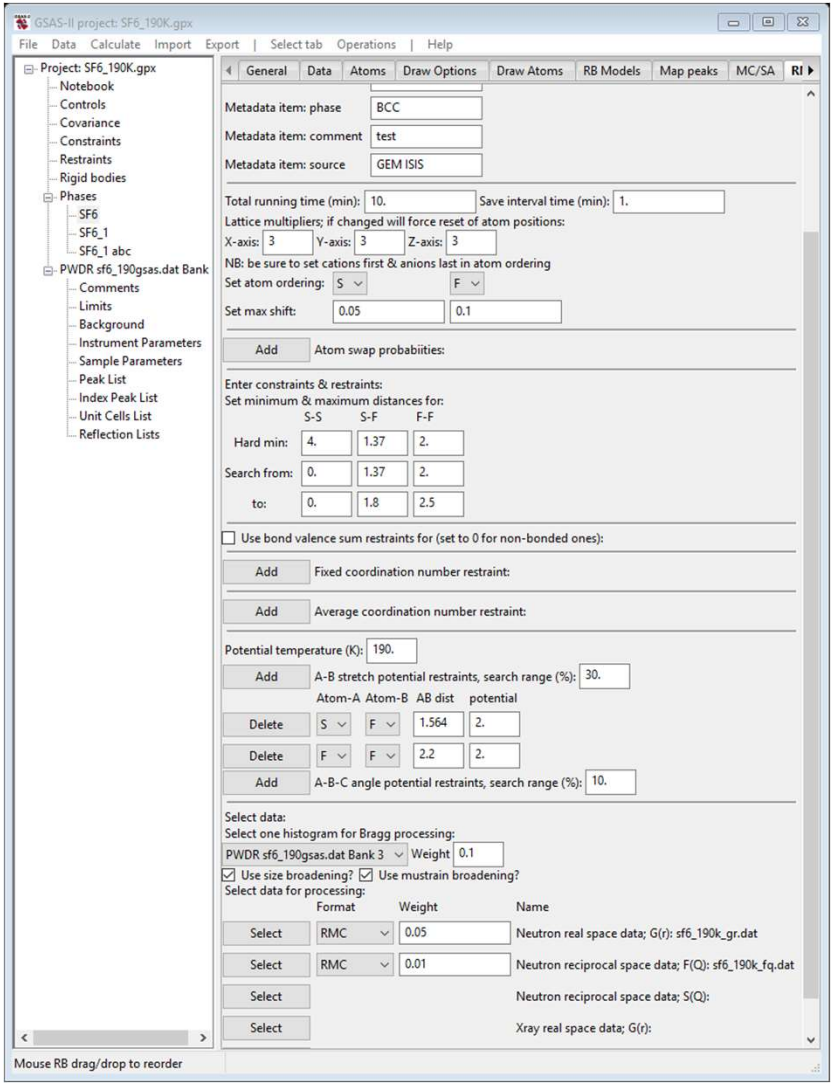
G(R) & partials

S(Q) & partials

RR result

PWDR simulation





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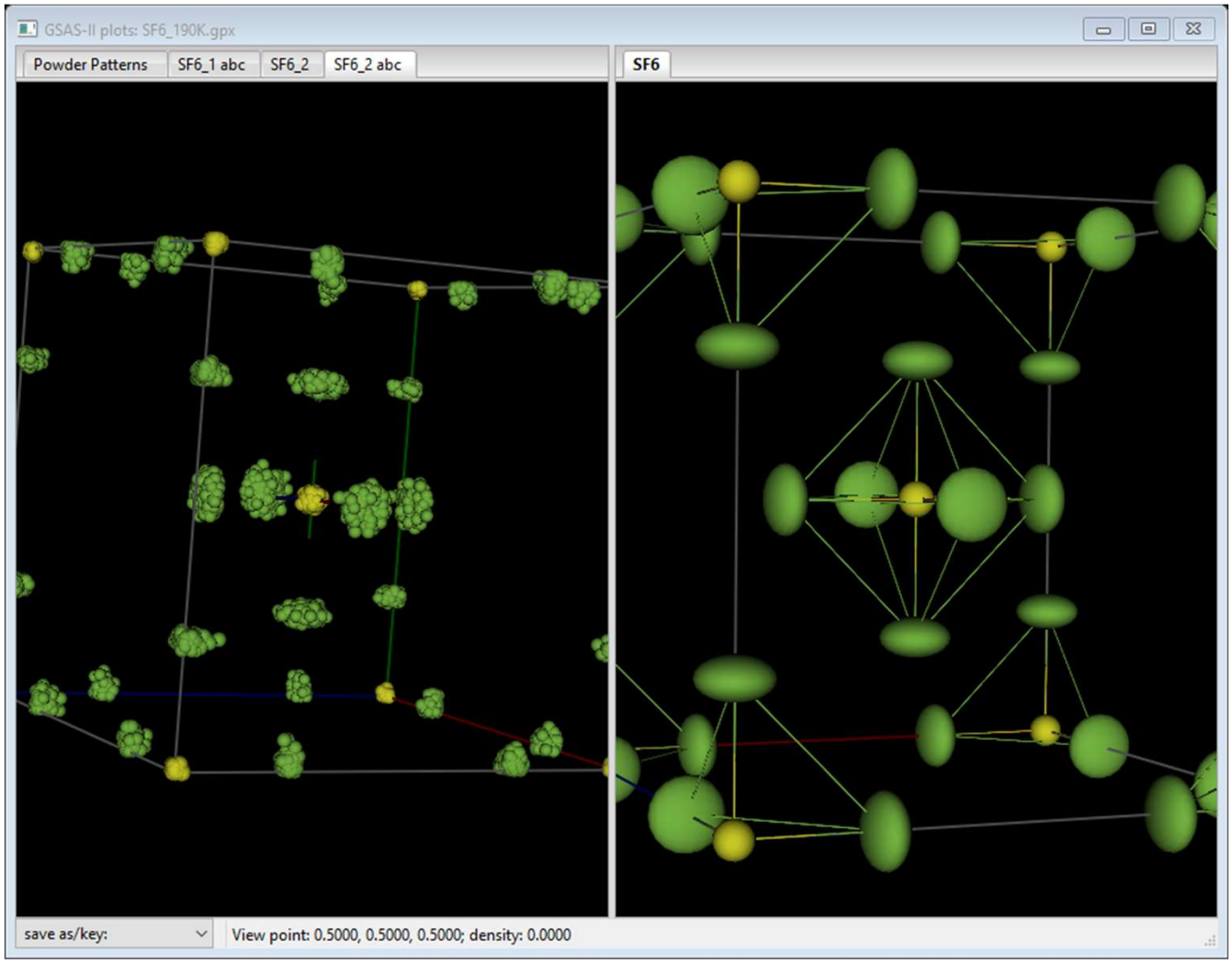
RMCPROFILE RESULT FOR SF_6

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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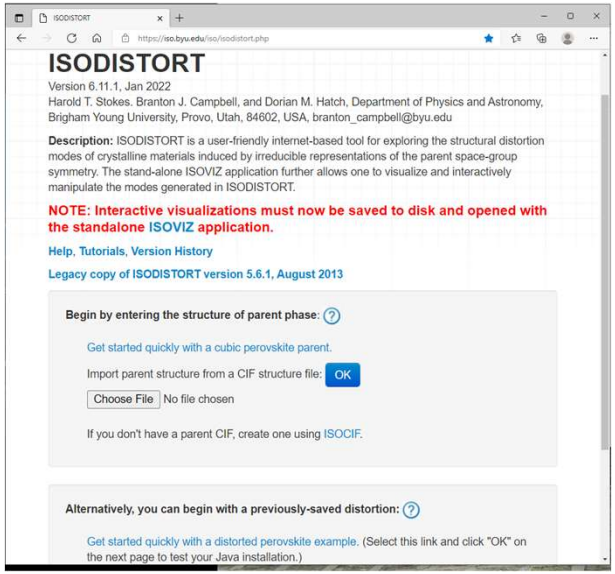
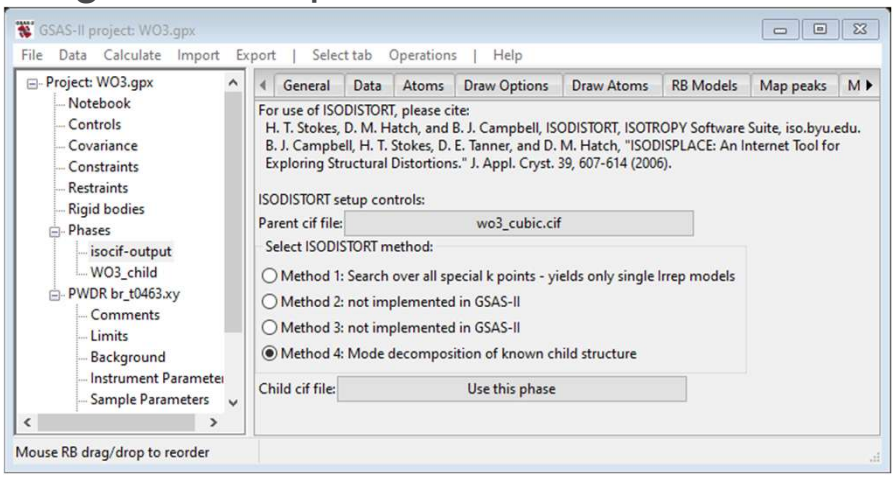
ISODISTORT

Implementation in GSAS-II

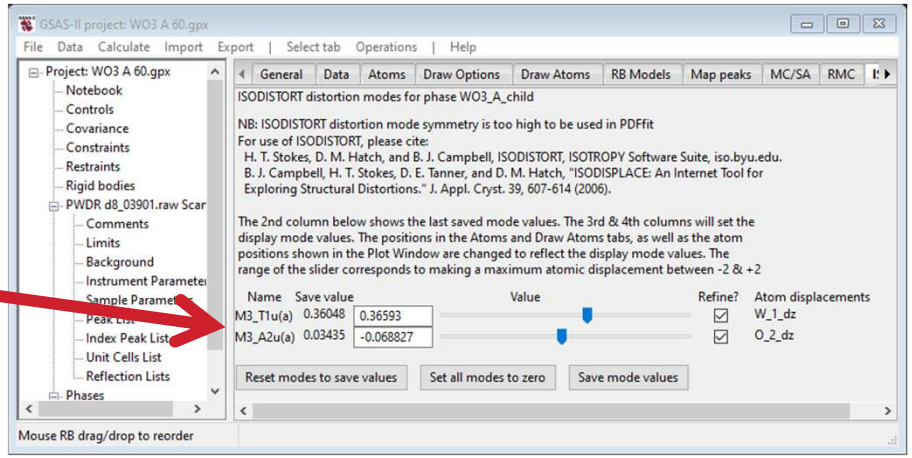
ISODISTORT: Web based tool for discerning mode displacements of atoms from an idealized parent structure



- 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



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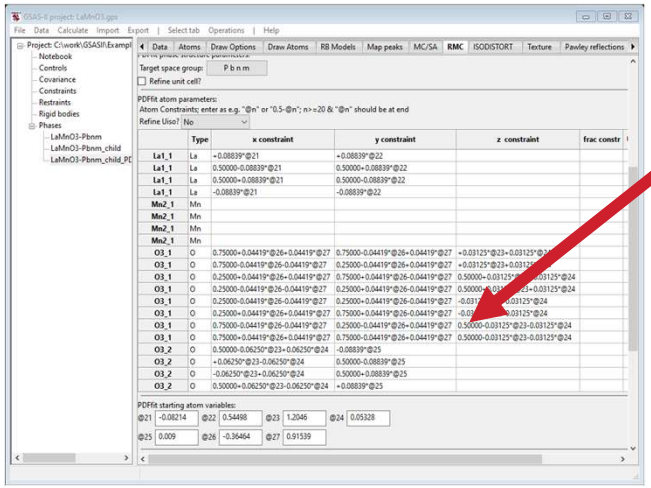
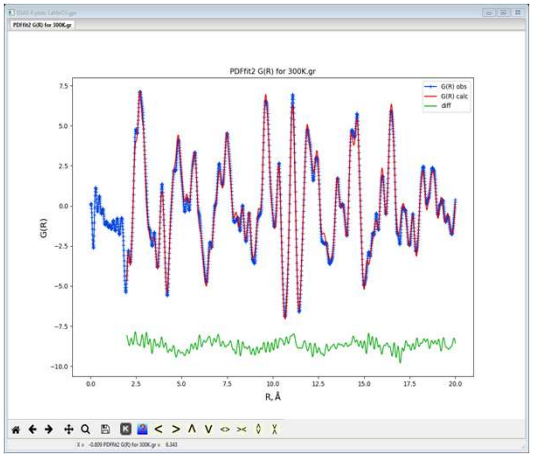
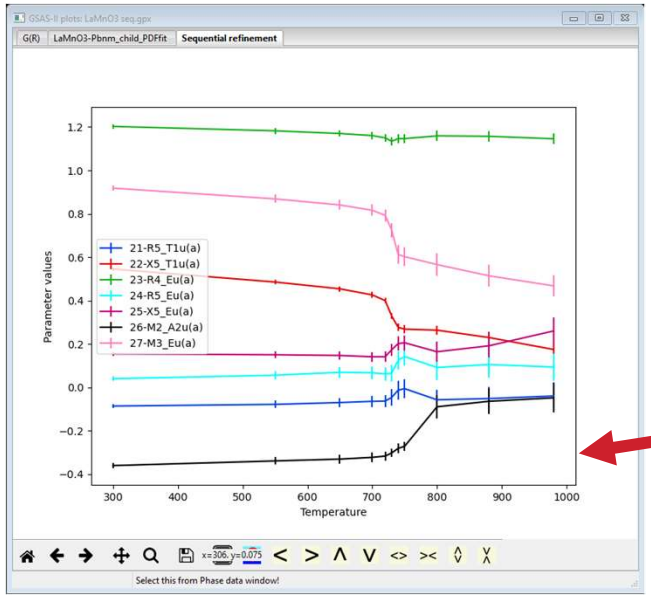
PDFFIT2 = “PDFfit” IN GSAS-II

“Small Box” modelling of pair distribution functions

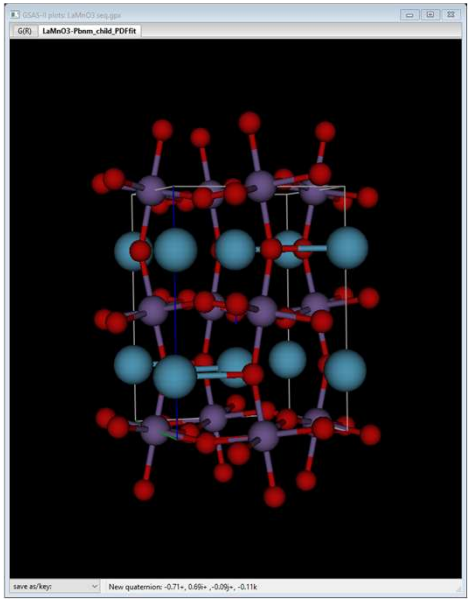
Use ISODISTORT – create the atom position constraints in new interface to PDFfit2







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



INCOMMENSURATE STRUCTURES IN GSAS-II

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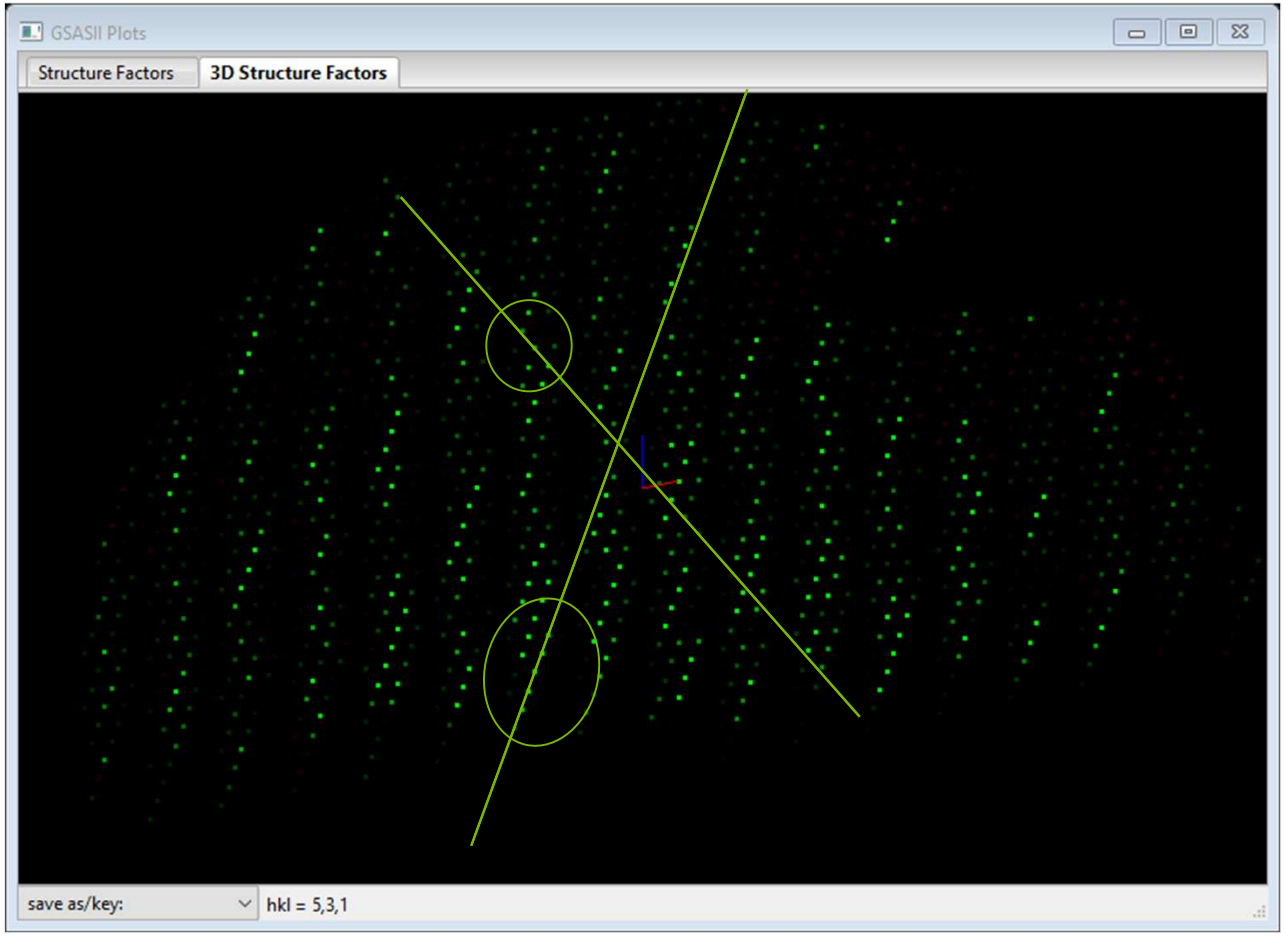
INCOMMENSURATE STRUCTURES N GSAS-II

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

INCOMMENSURATE STRUCTURES

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

- Space group + super symmetry symbol

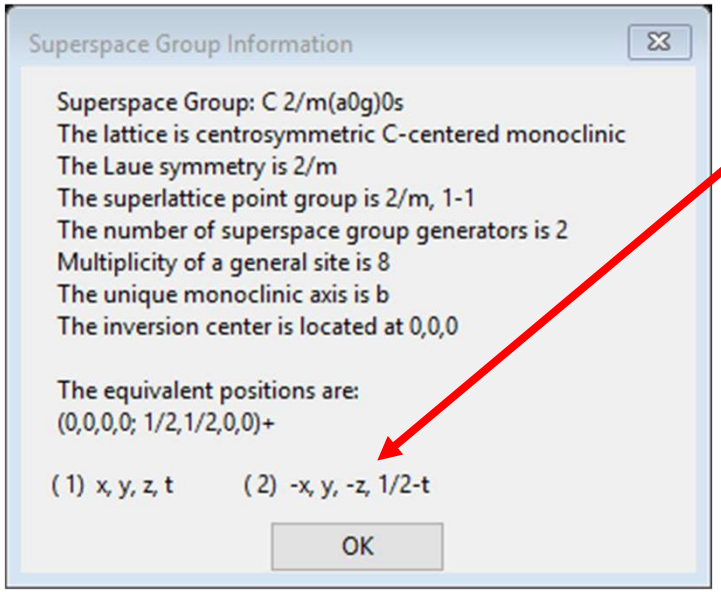
e.g. Na_2CO_3 – C2/m(α0γ)os

Space group

Modulation vector

Translation component

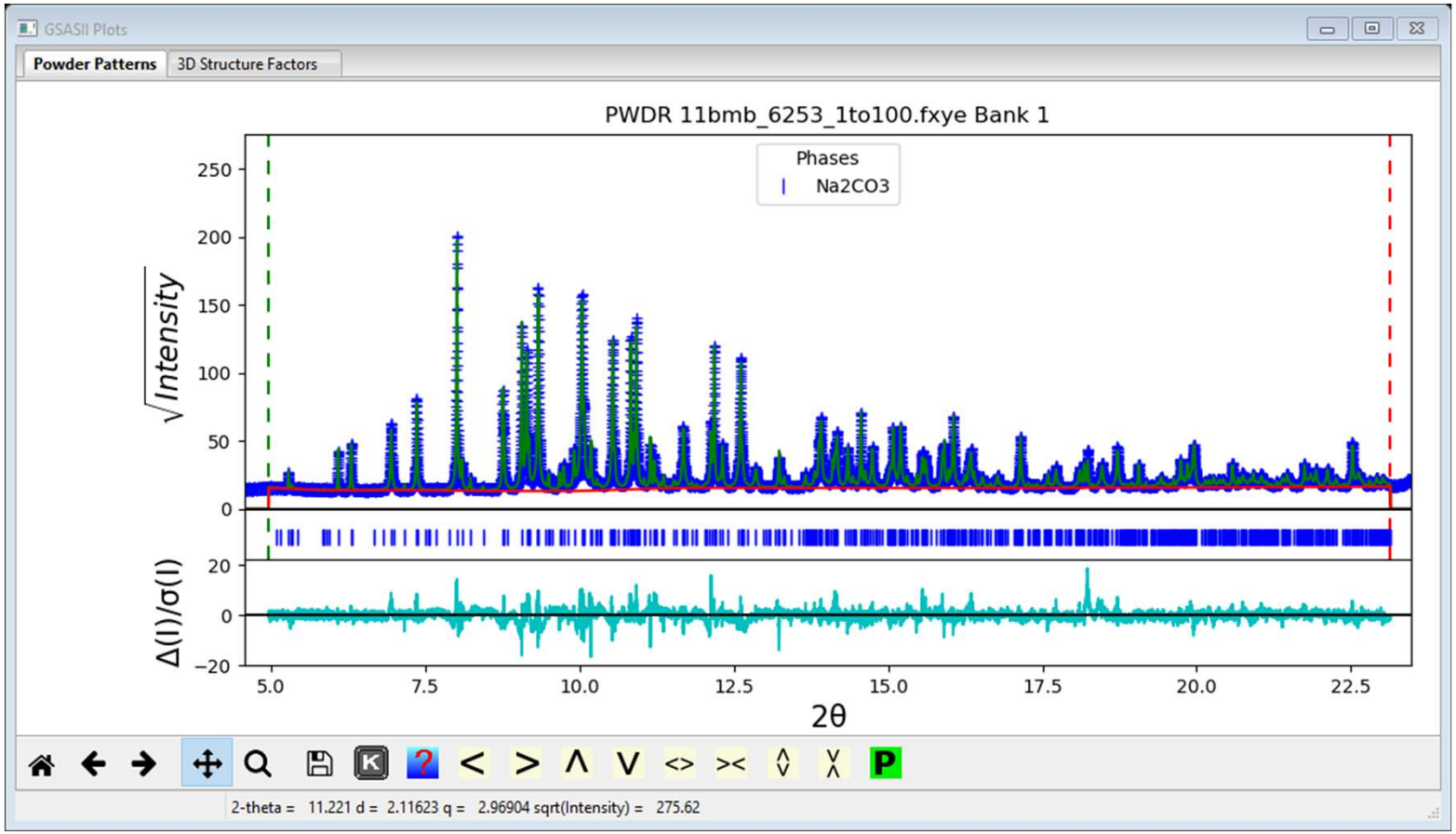
Operators: conventional space group & 4th dim component



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

POWDER DIFFRACTION

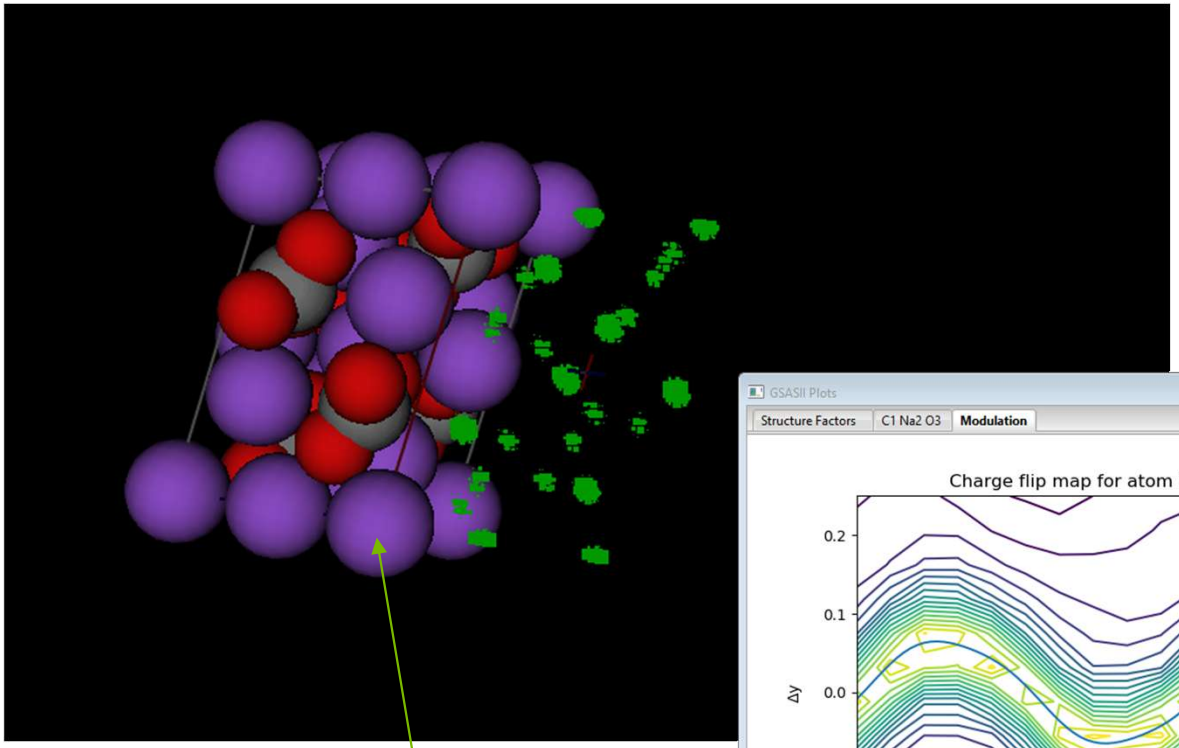
Na_2CO_3 – 11BM @ APS room temp.

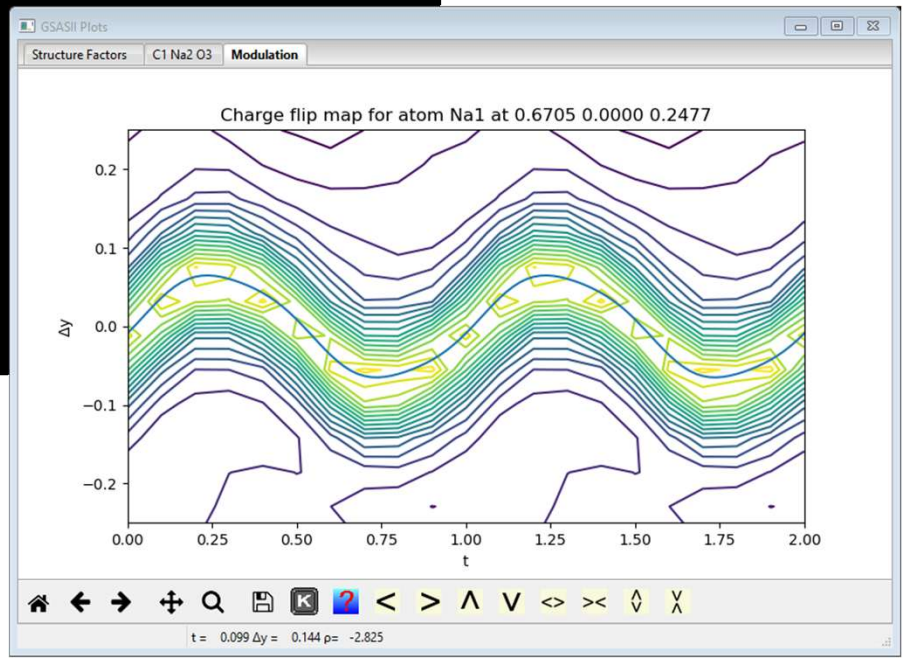


Includes m=-2,-1,1,2 superlattice reflections; Rietveld refinement includes 1st & 2nd order harmonics on position depending on atom

INCOMMENSURATE STRUCTURE SOLUTION

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

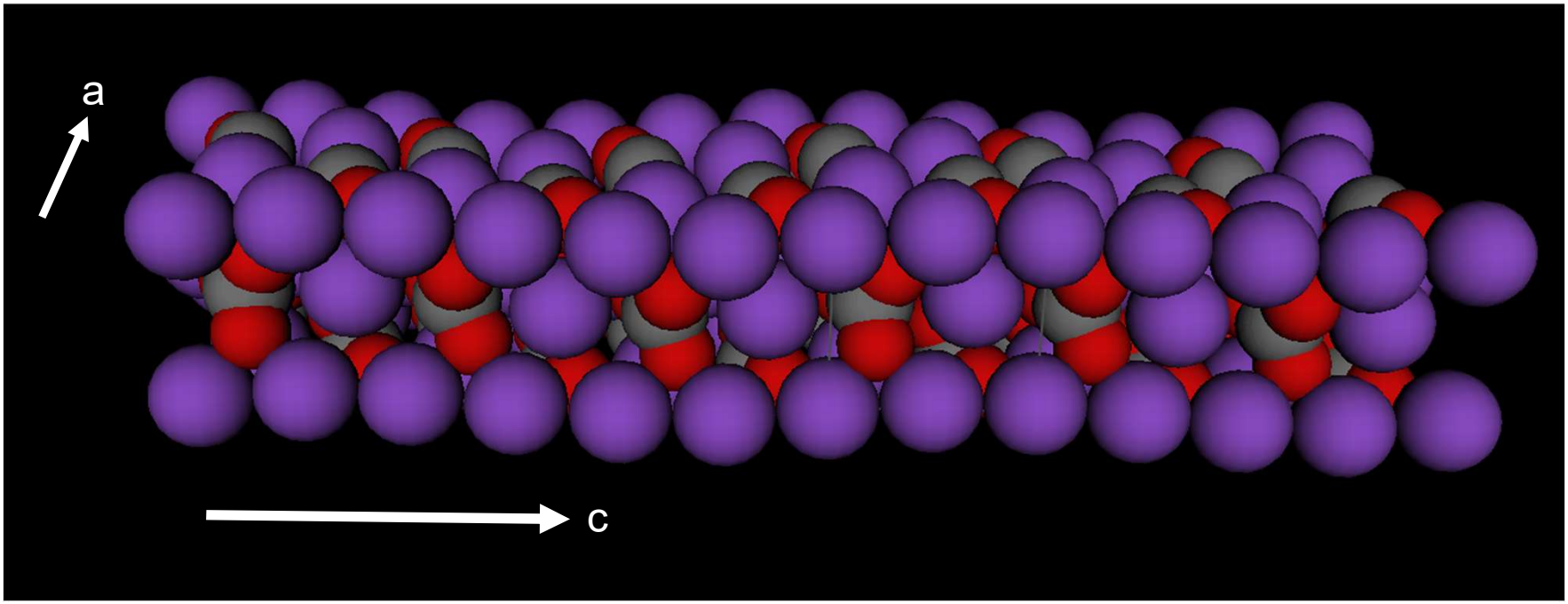




Modulation of atom positions (Na1-y)
Fit function – fourier series in tau

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)

STACKING FAULTS – DIFFAX IN GSAS-II

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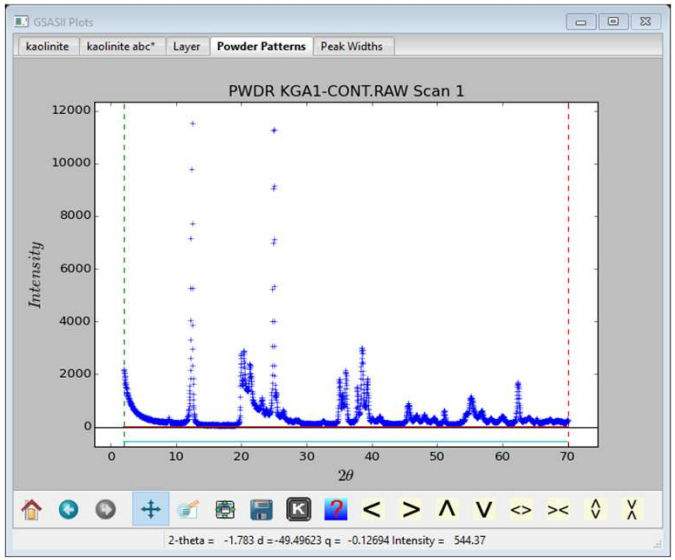
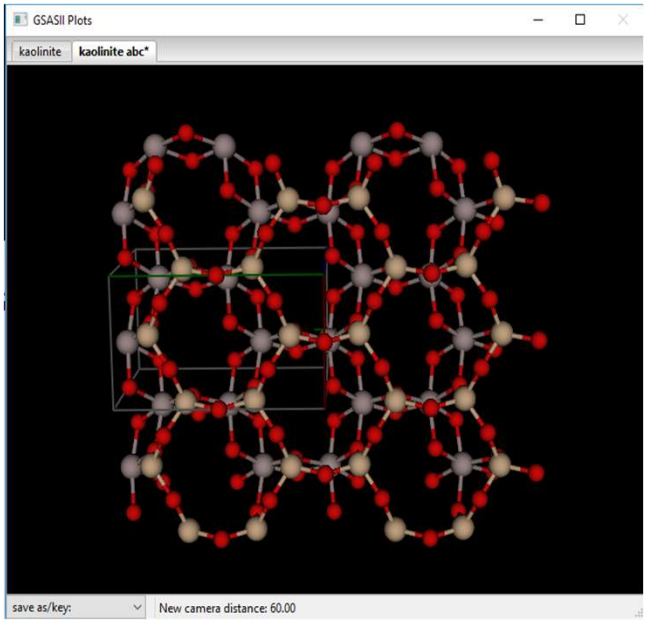
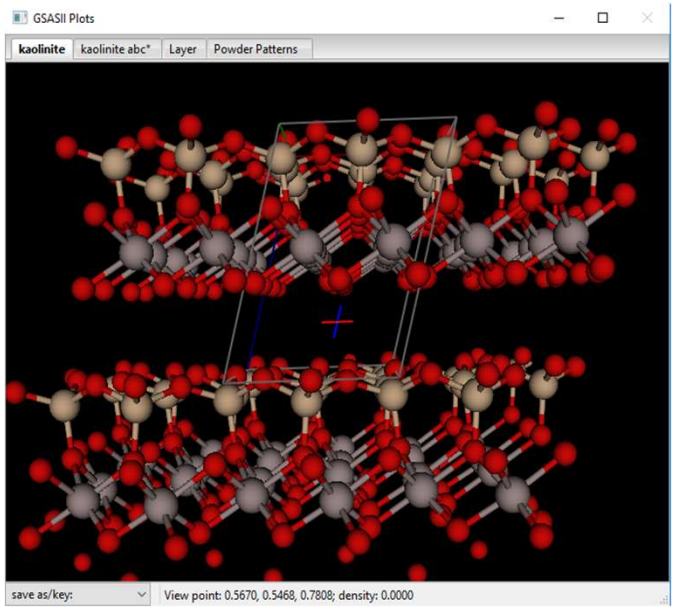
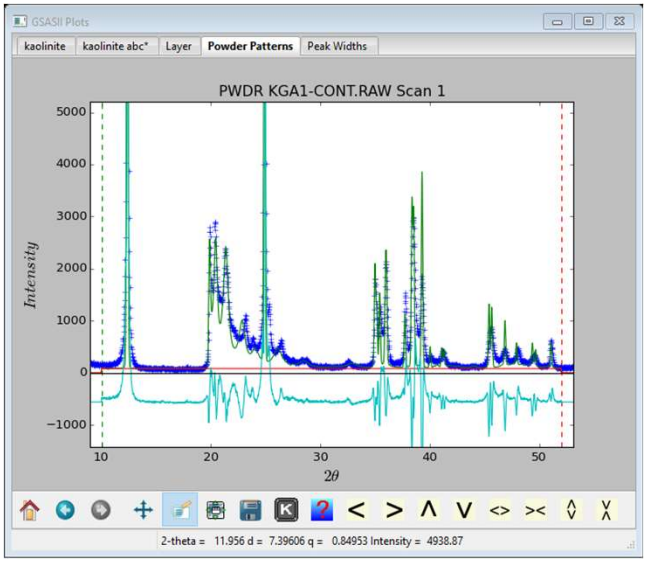
STACKING FAULTS IN KAOLINITE $Al_2Si_2O_5(OH)_4$









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SMALL ANGLE DATA ANALYSIS IN GSAS-II

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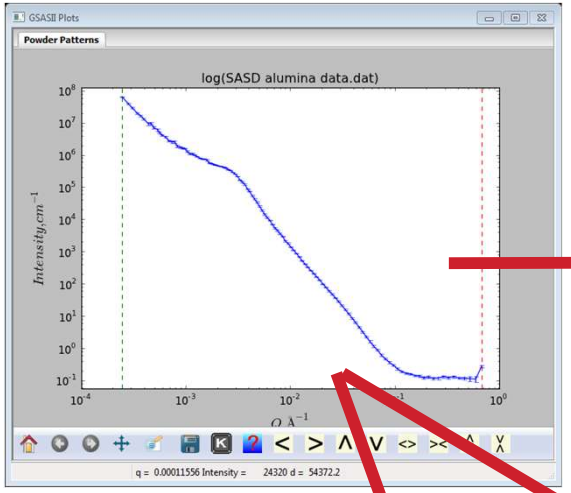
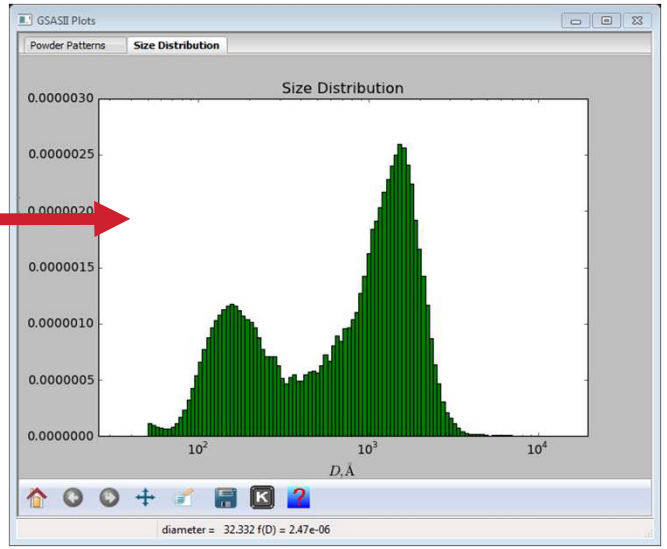
SMALL ANGLE SCATTERING

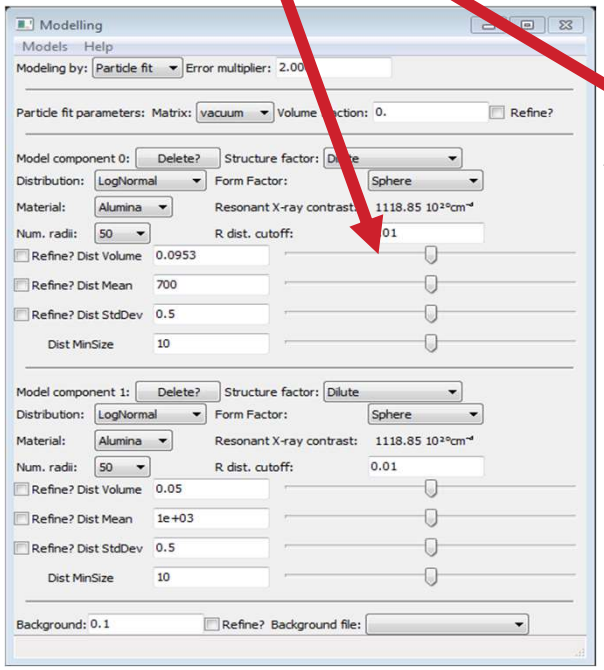
Range of tools

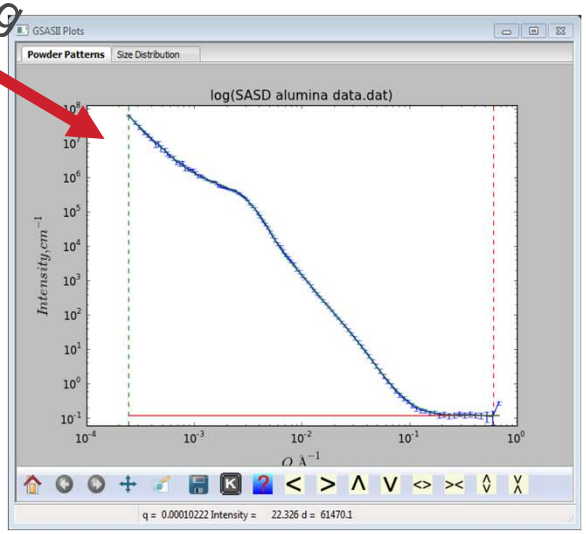


Size Distribution by MaxEnt



Modelling LSQ fitting





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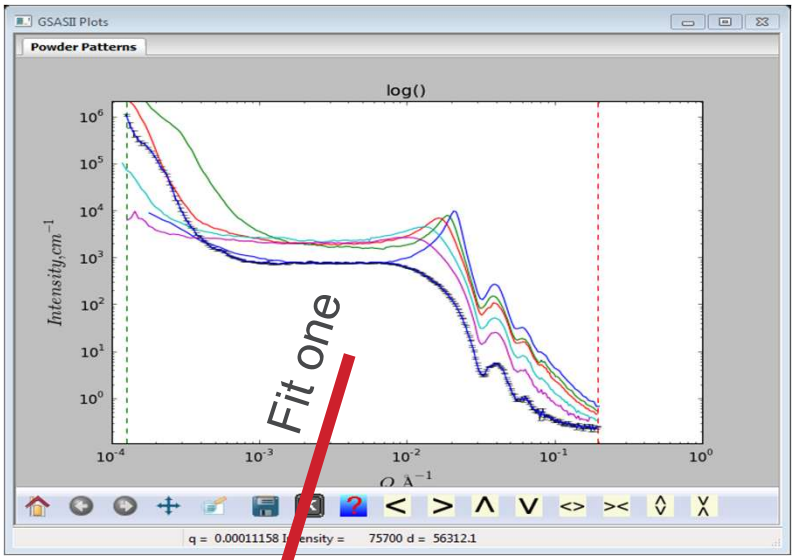
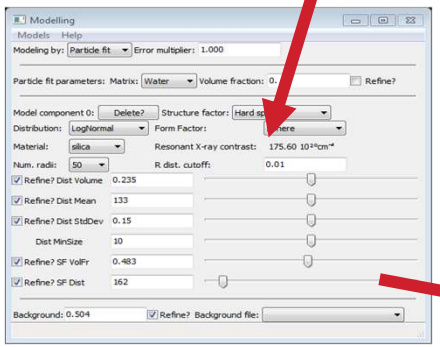
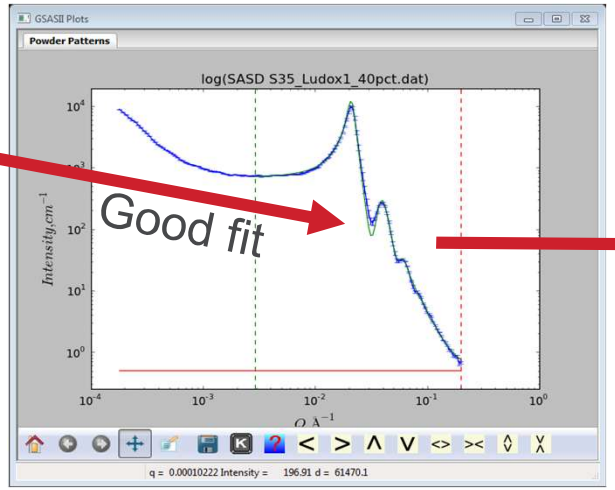
SEQUENTIAL ANALYSIS

Series of experiments vs independent variable (e.g. composition)

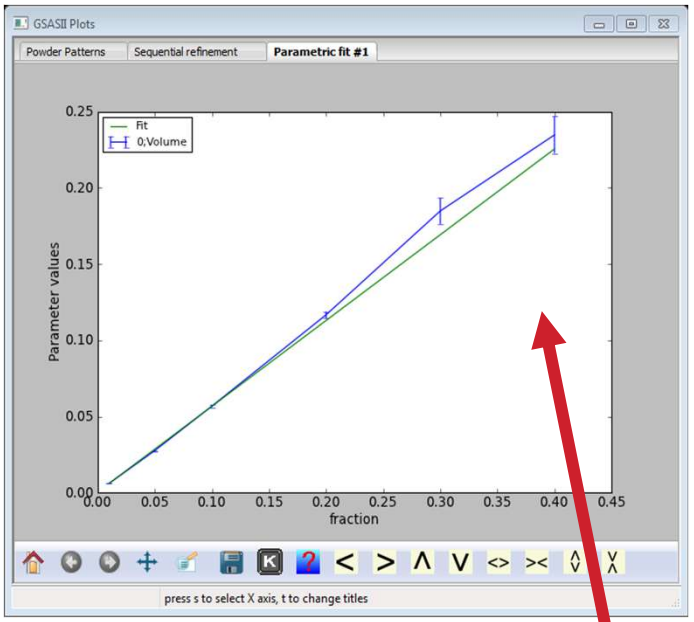


Fit one

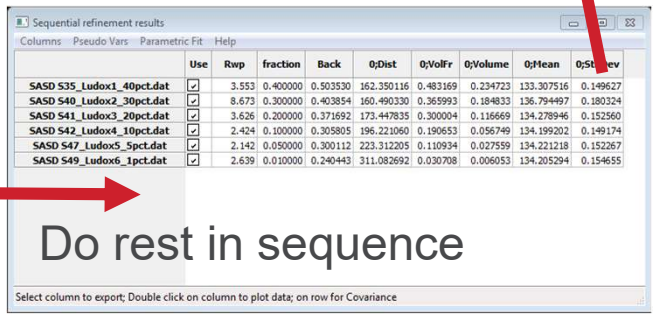




Good fit



Plot coeff. & fit to equation



Do rest in sequence

All inside GSAS-II

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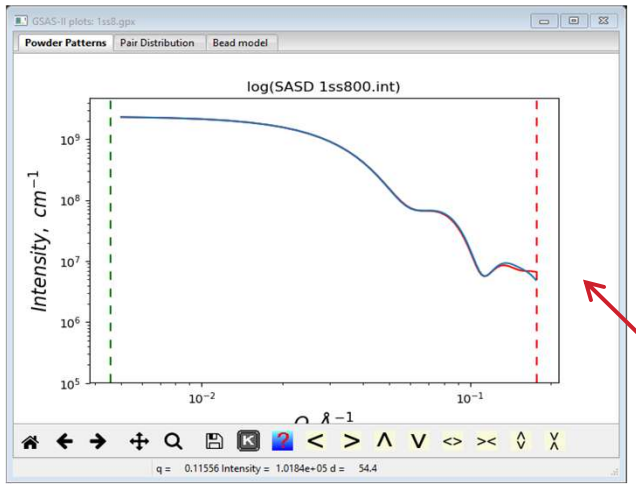
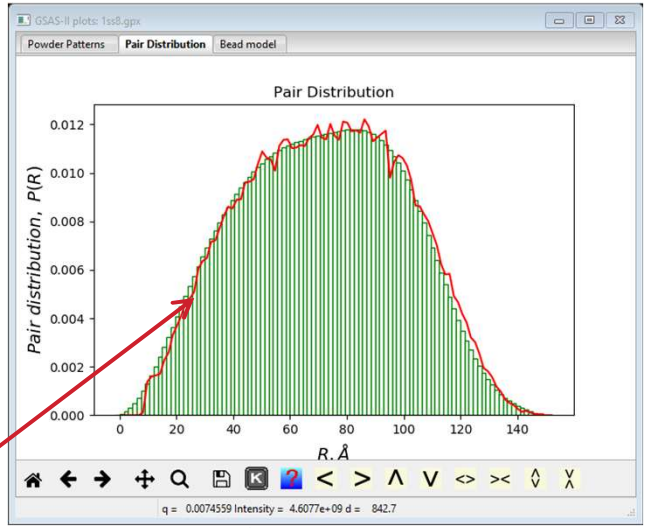
PROTEIN SMALL ANGLE MODELING IN GSAS-II

Bead models via SHAPES (alternative to DAMMIN in python)

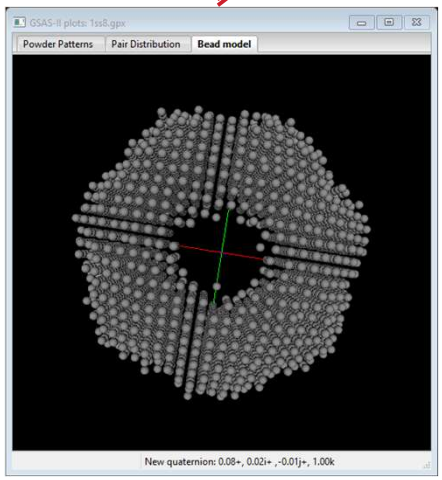


Make P(R)

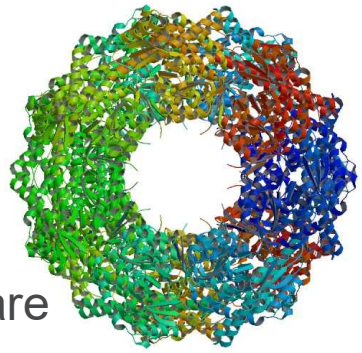


calc

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

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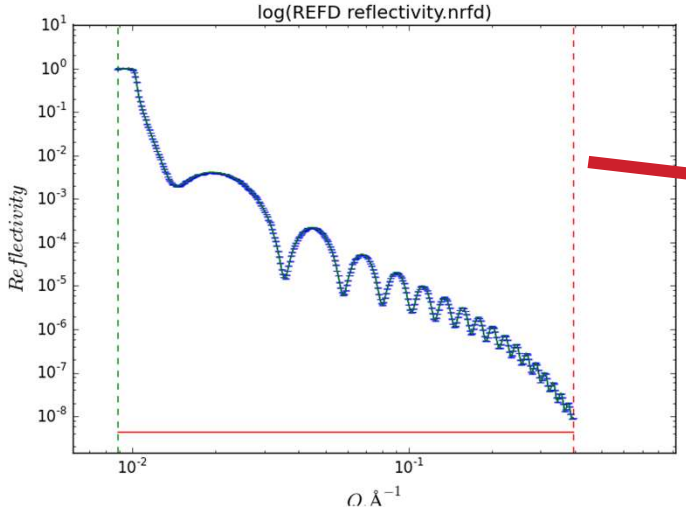
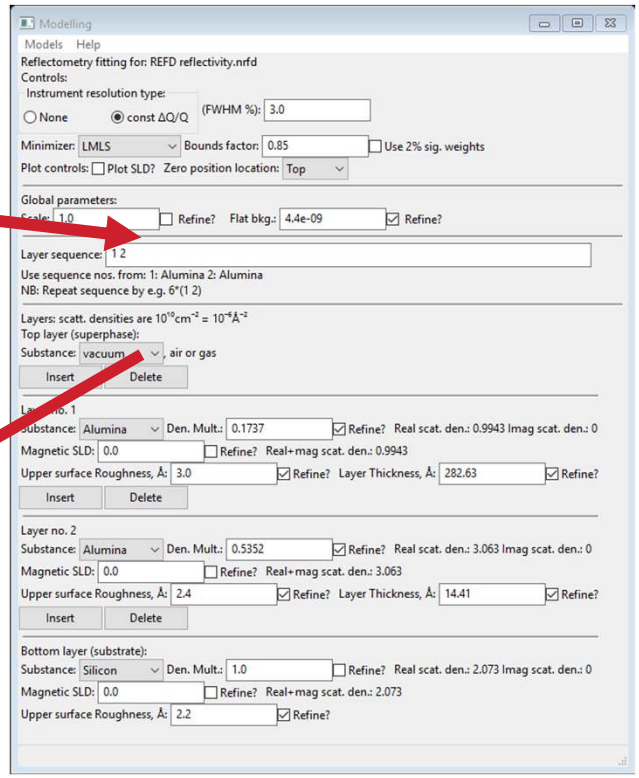
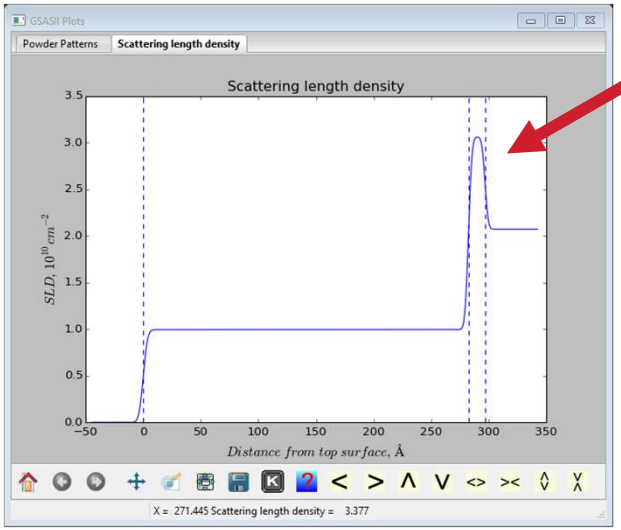
REFLECTOMETRY ANALYSIS IN GSAS-II

X-rays & Neutrons (CW at least)



Multilayer model
Scattering density

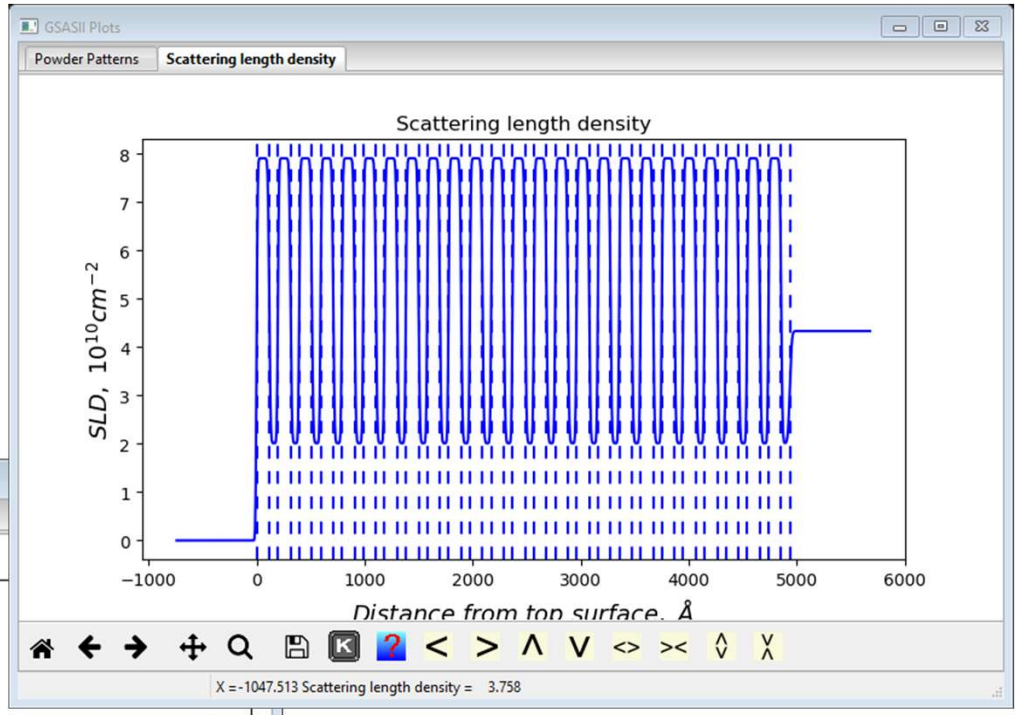


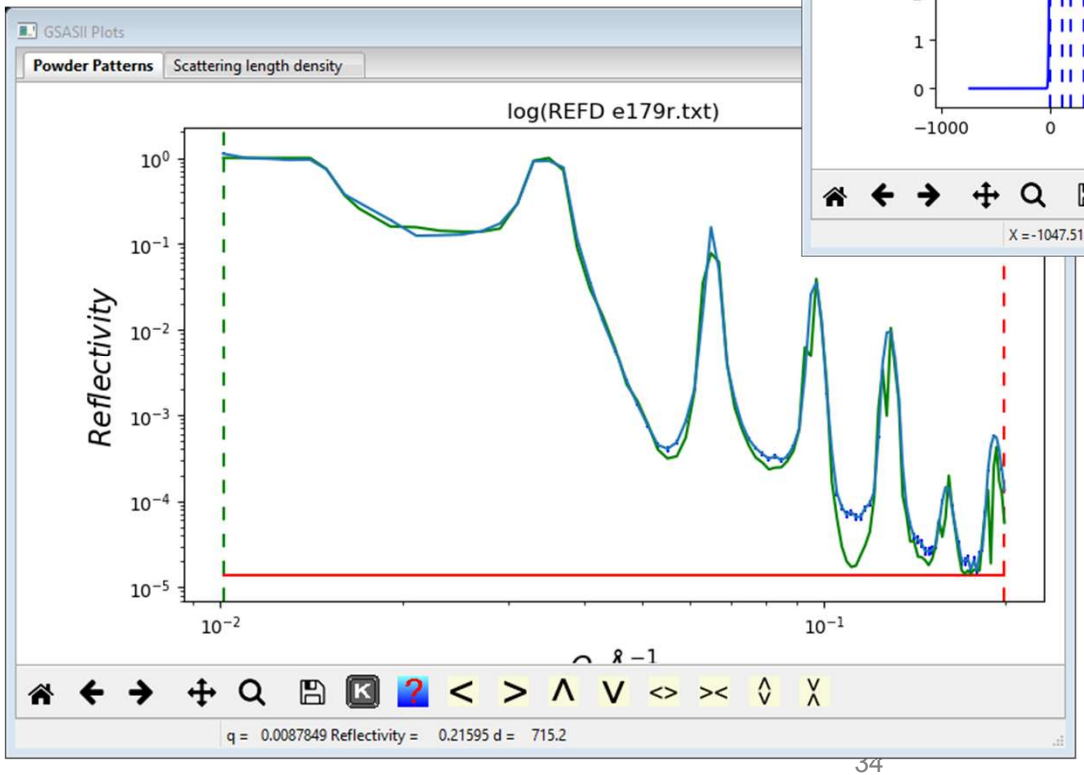


Define components, stacking sequence (can be repeated), thickness & “roughness”
Fit by LSQ, MC/SA & “basinhopping” (under development)

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

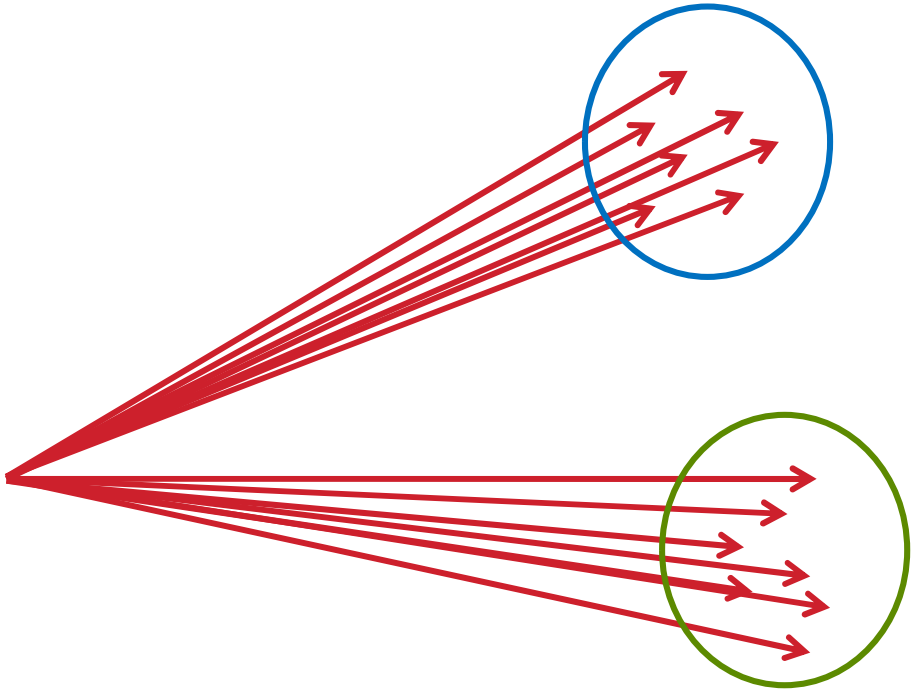
What to do?

- 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"



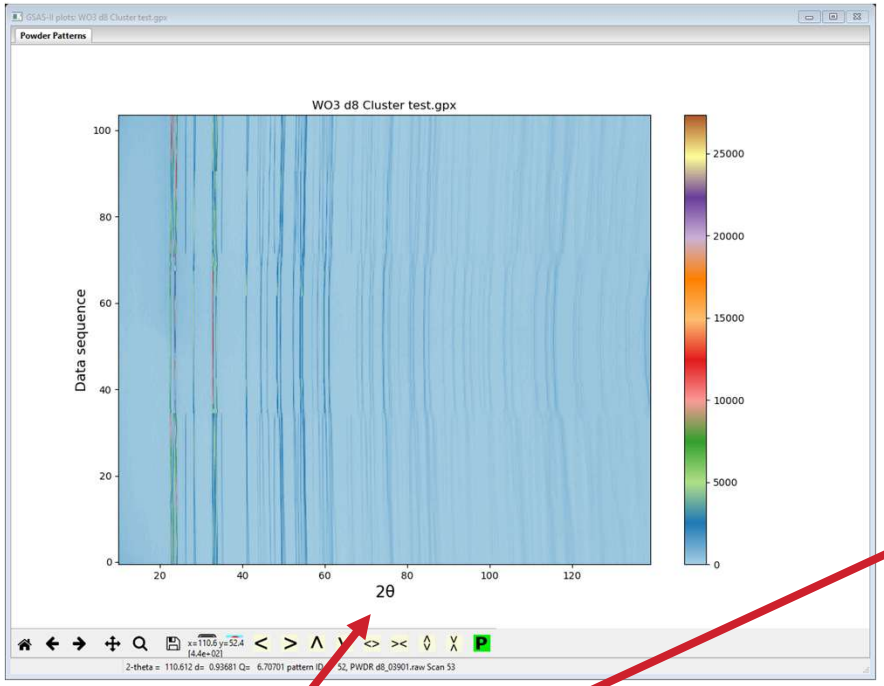
"Distance" in GSAS-II

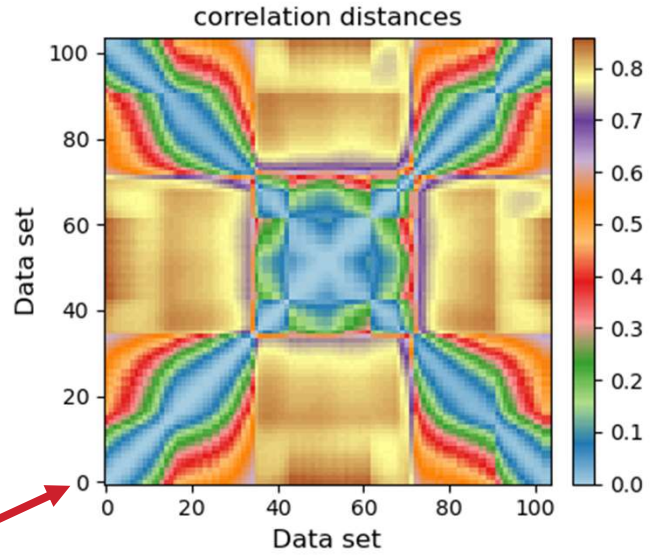
- Euclidian - shortest
- City block – steps along each axis (longer)
- Cosine – of angle between
- Correlation – coefficient
- Etc… - 11 methods; take your pick. Some are more contrasty than others

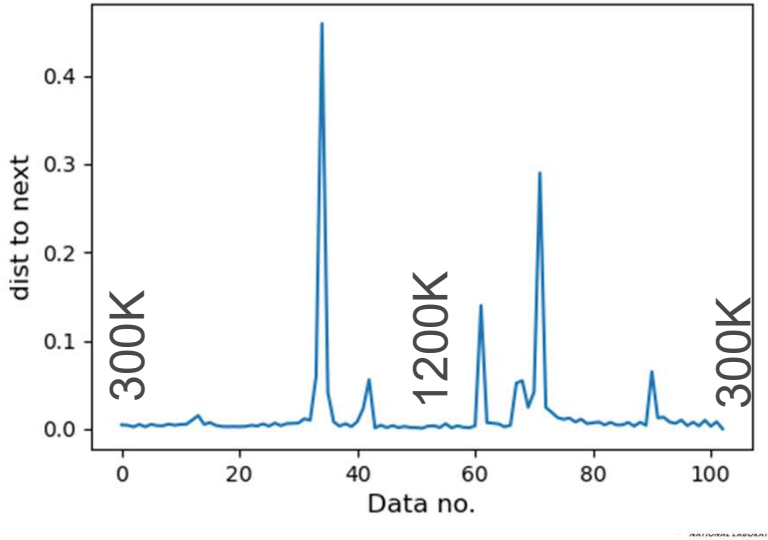
DISTANCES

Preliminary results – distance matrix & serial distances

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



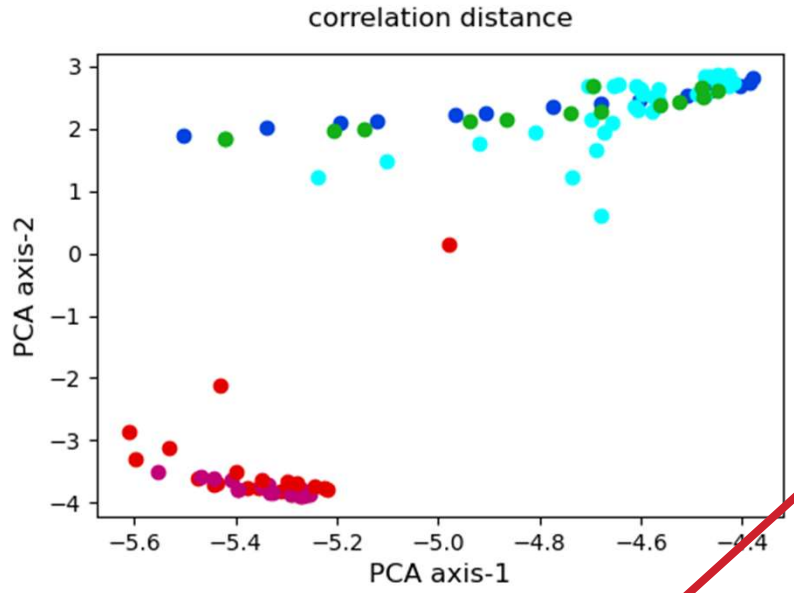




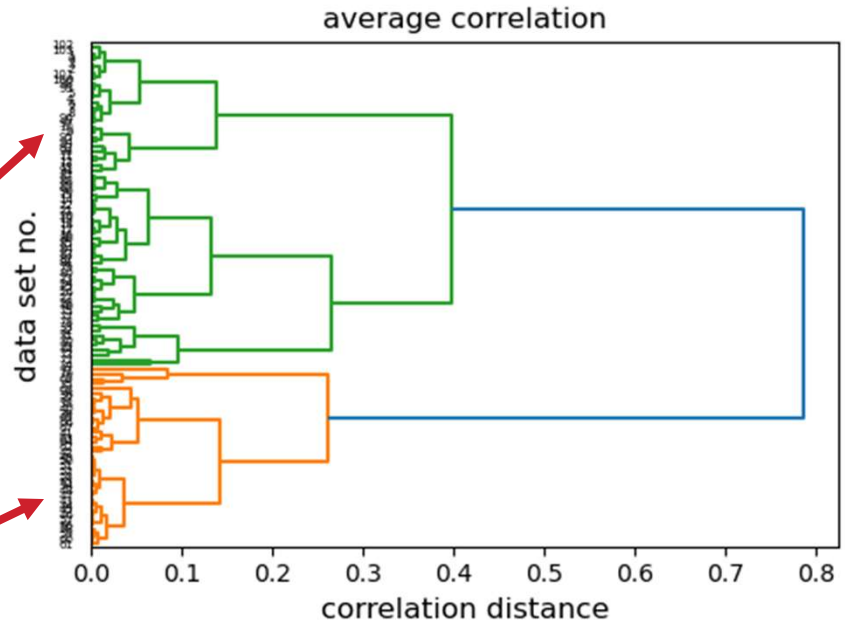
Powder data
Distance matrix
Serial distances
- n+1 vs n
- Peaks = Phase changes
- Not useful for random data

DISTANCES – PRINCIPAL COMPONENT ANALYSIS & DENDOGRAM

Most significant 2-3 dimensions – cluster analysis



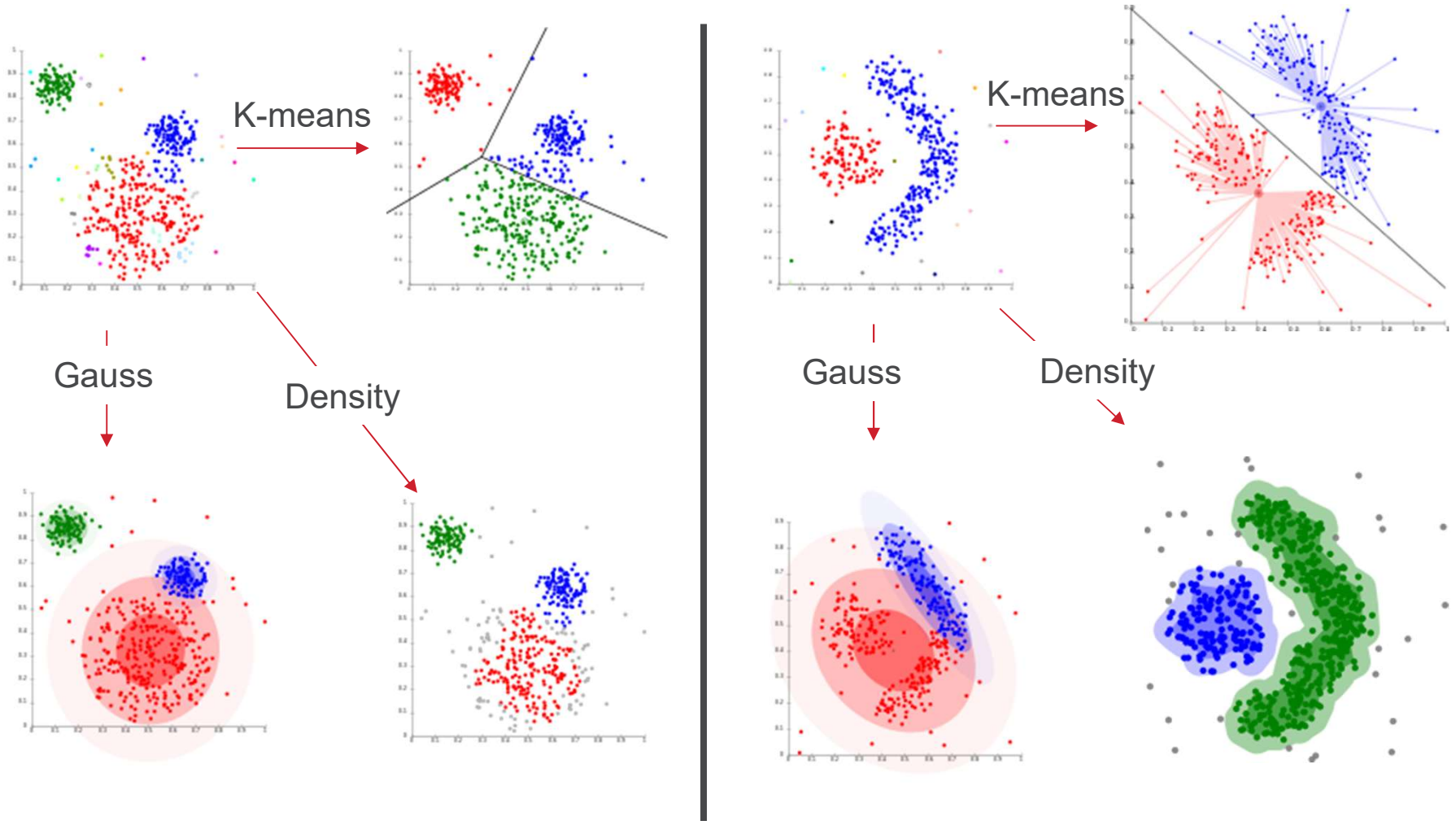
Temp variation – trails in PCA
→ Clusters ill defined in this case
Colored by “cluster”



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

THE CLUSTERING PROBLEM

Wide variations possible – 2 example PCAs & cluster algorithms

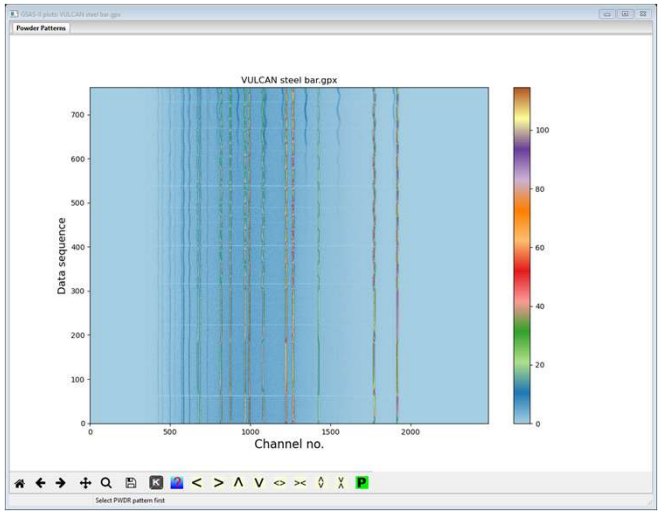


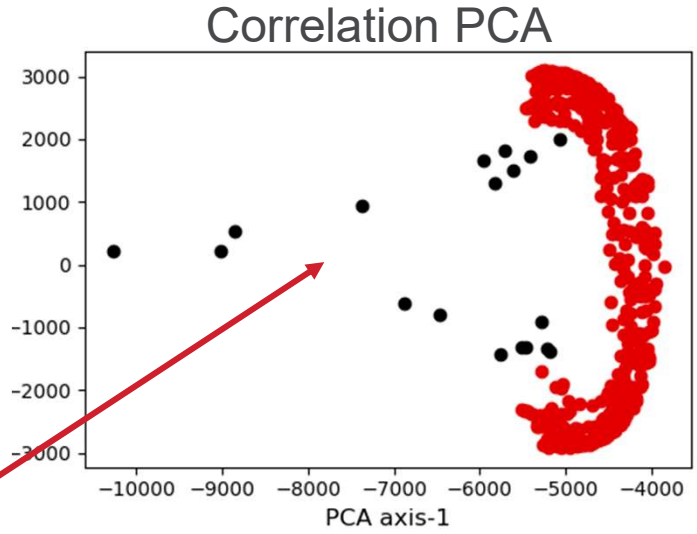
GSAS-II has 6 clustering algorithms – some require # of clusters

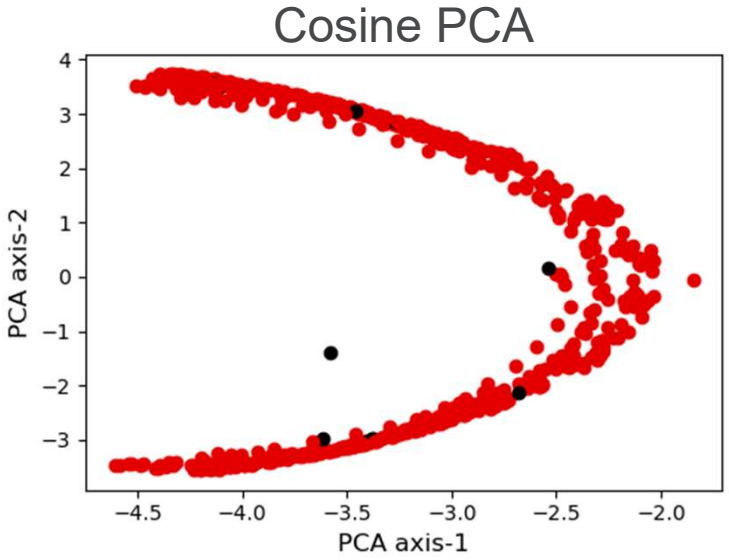
Taken from Wikipedia

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

CHARGE FLIPPING

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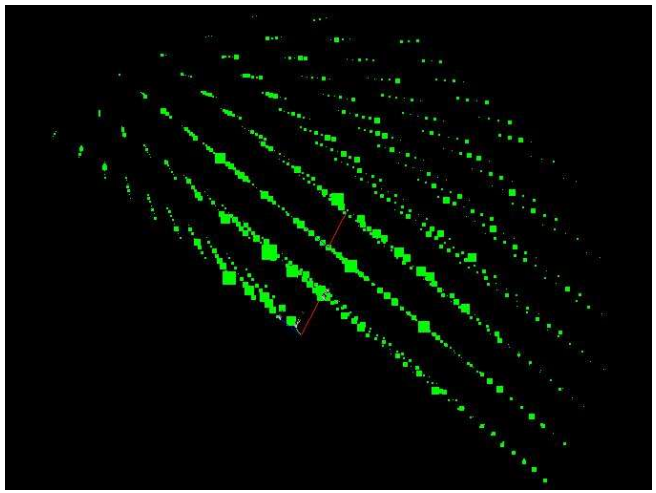
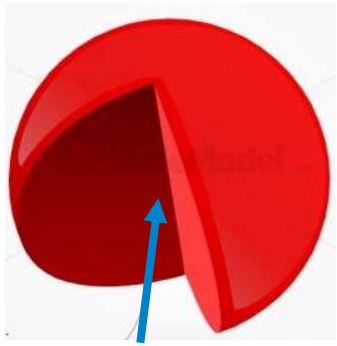
CHARGE FLIPPING

The algorithm set up:

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

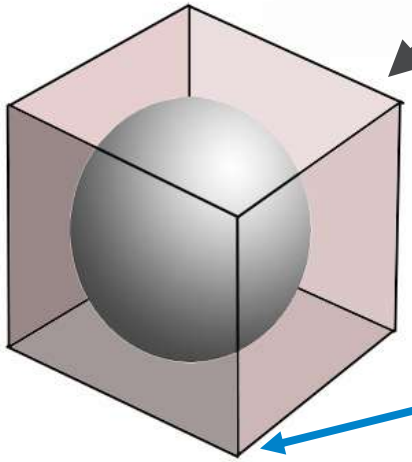


1D list

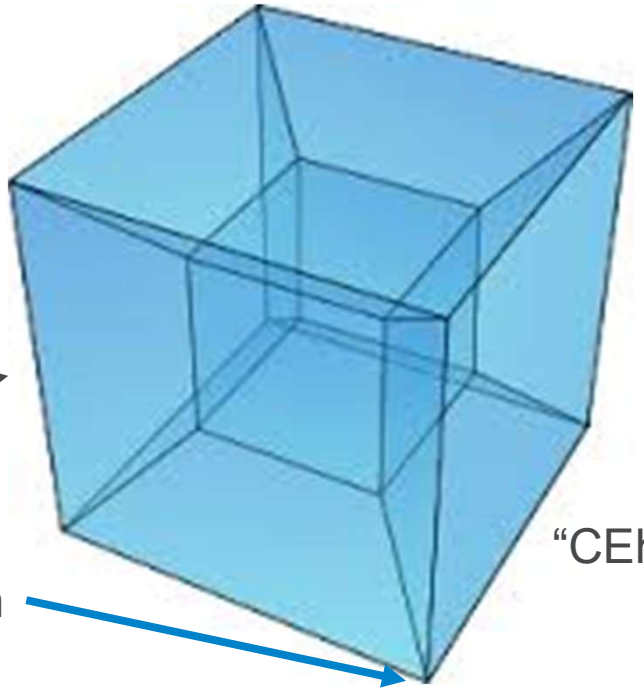


Origin @ F_{000}

1D list → 3D array



Expand
3D array

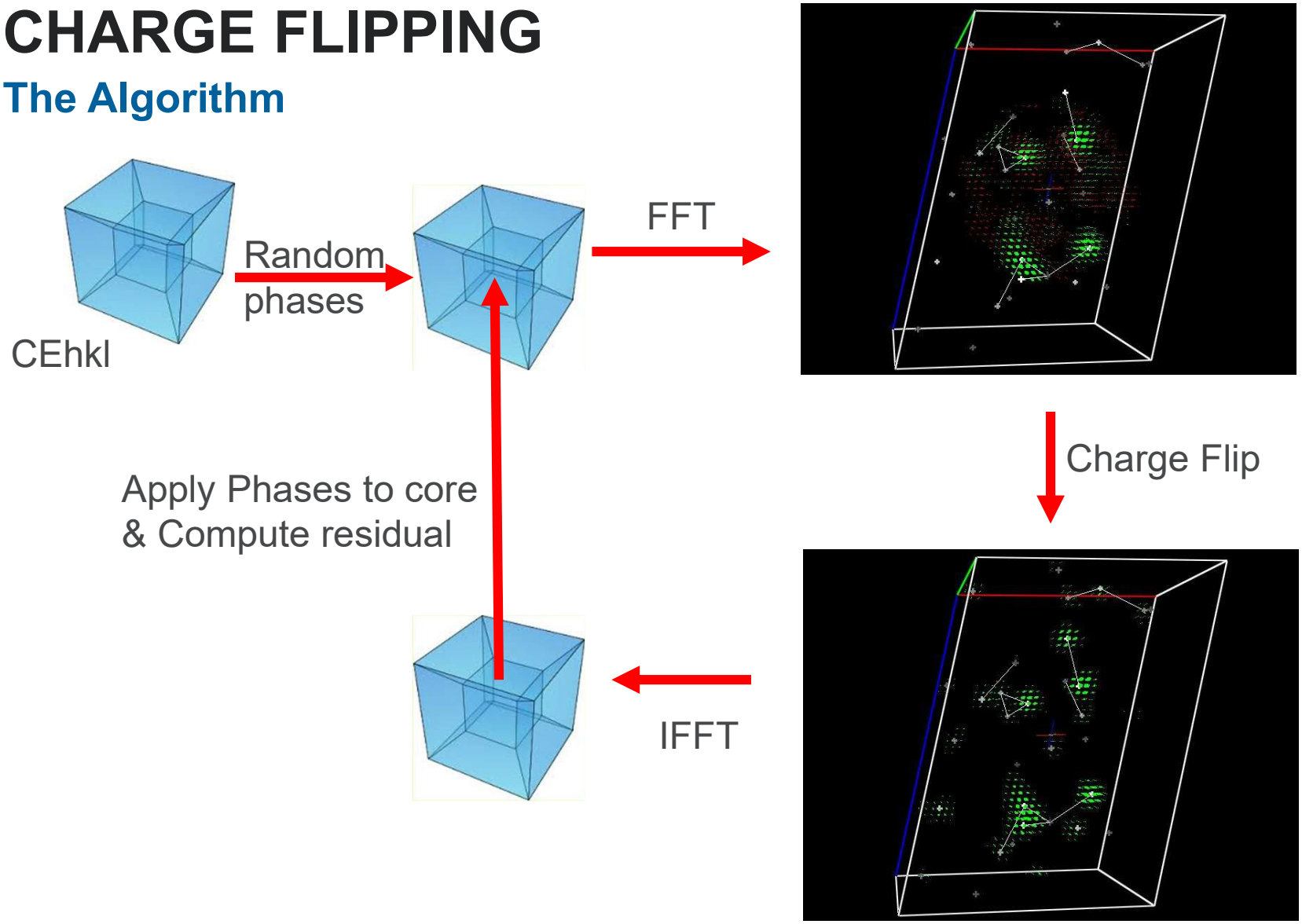


"CEhkl"

New origin

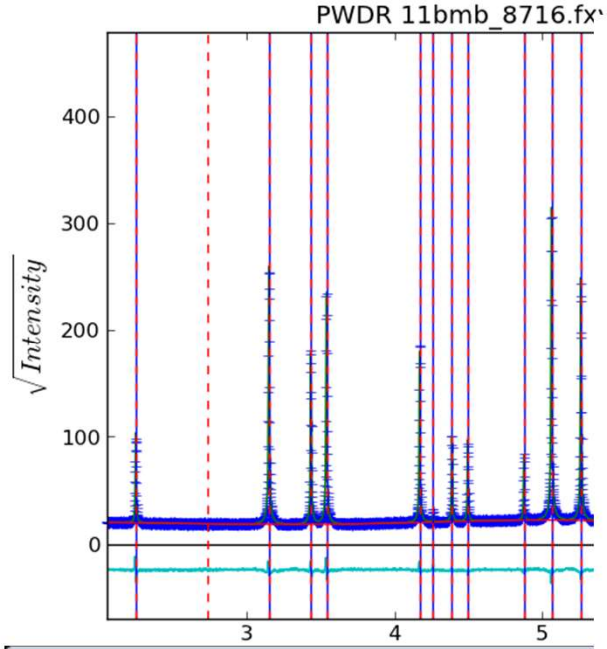
CHARGE FLIPPING

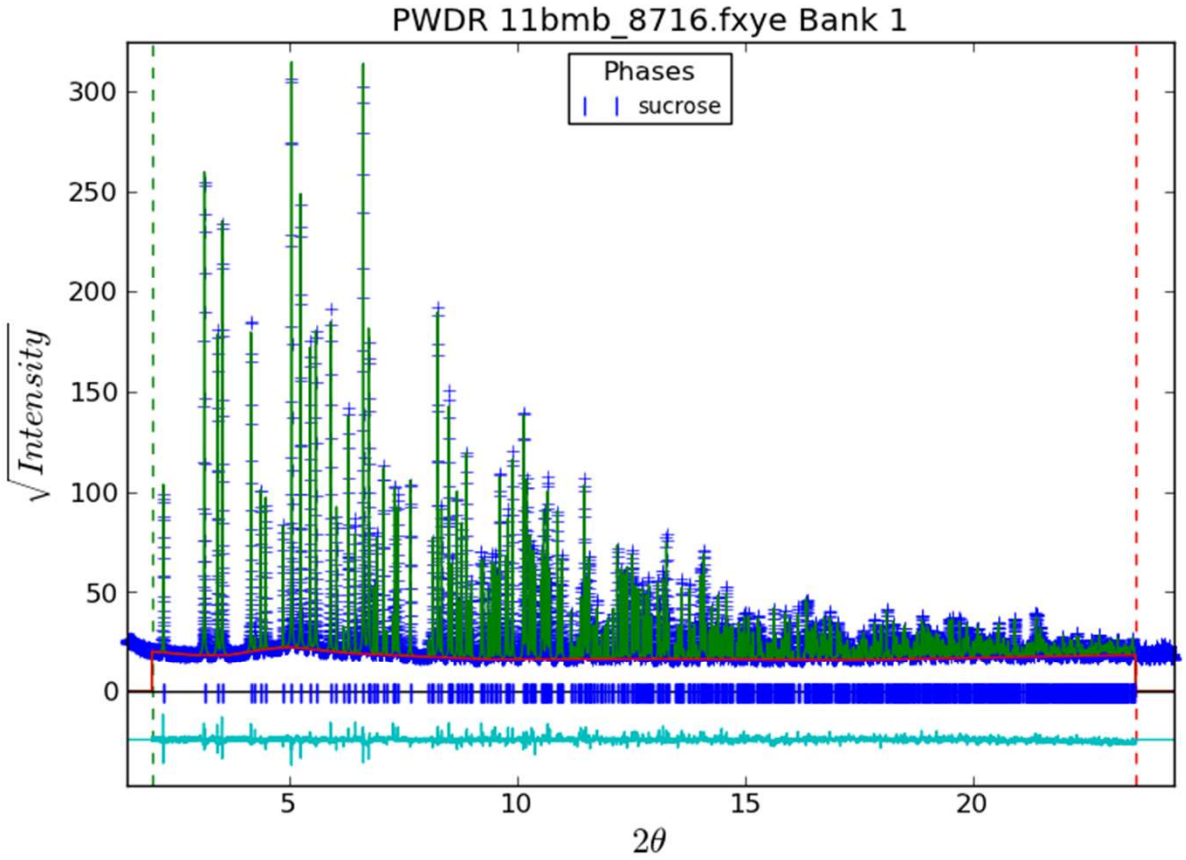
The Algorithm

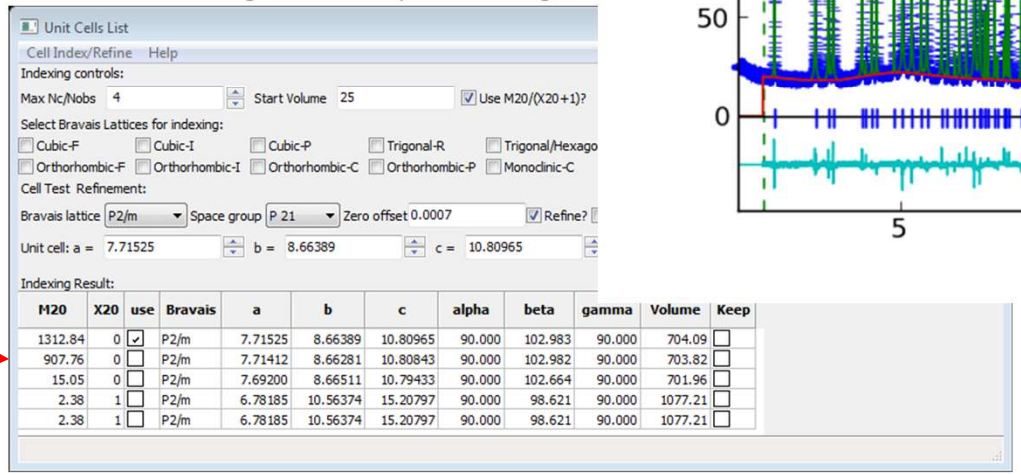


EXAMPLE – SUCROSE POWDER

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







781 unique hkl's
CF with 61440

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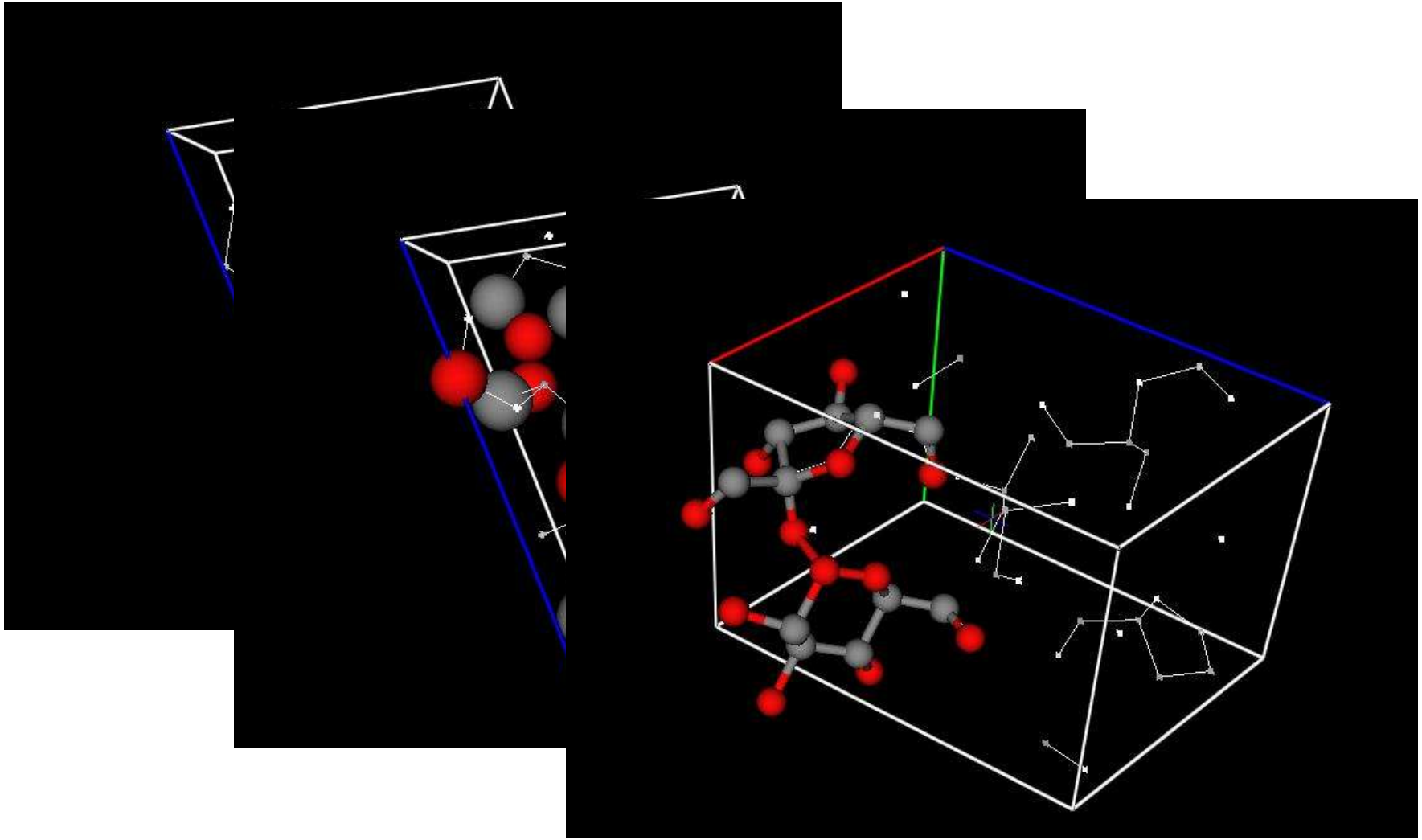
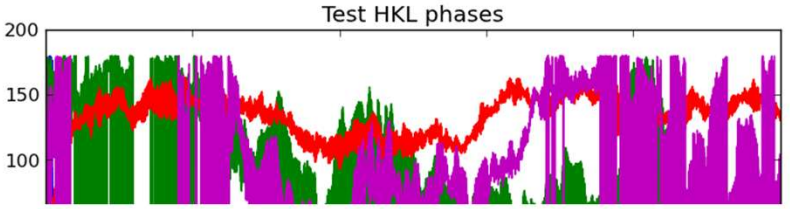
CHARGE FLIPPING SOLUTION

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

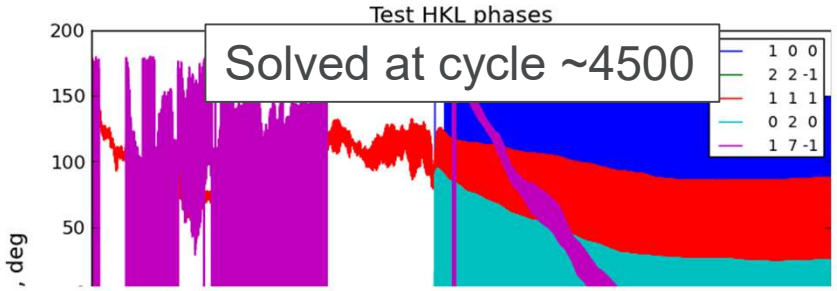


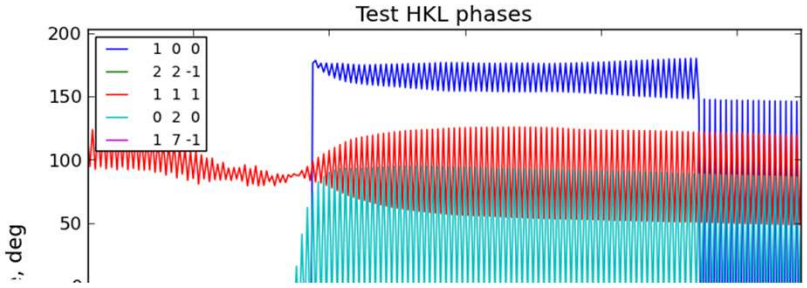
CHARGE FLIPPING – PHASES?

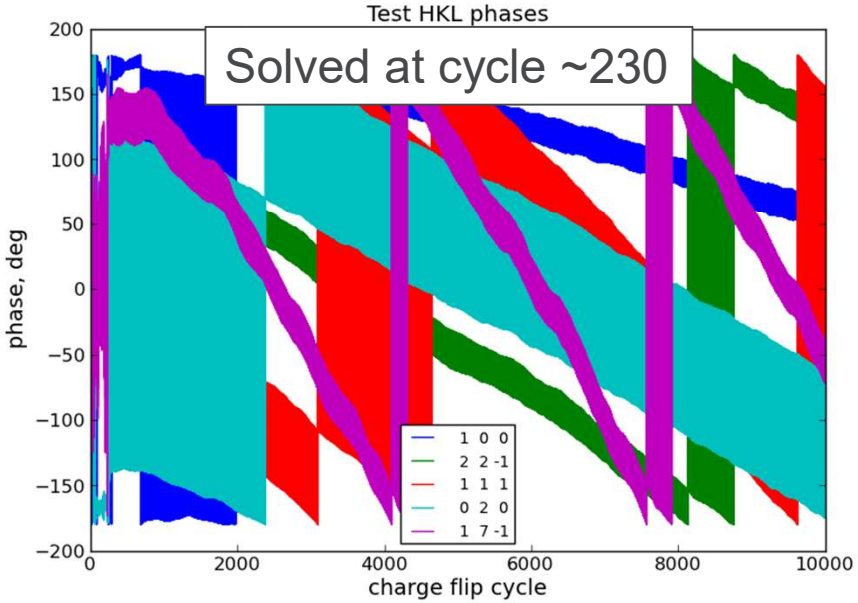
Track phases of 5 reflections – 10000 CF cycles

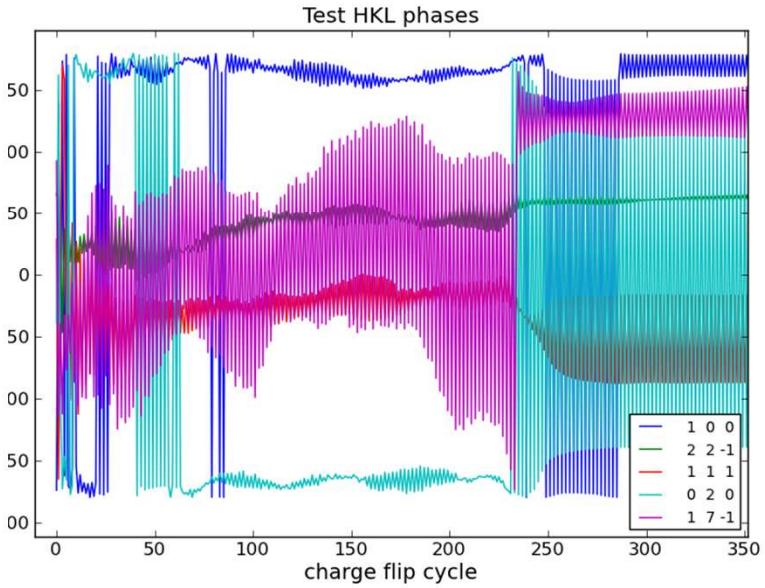


Not solved in 10000 cycles





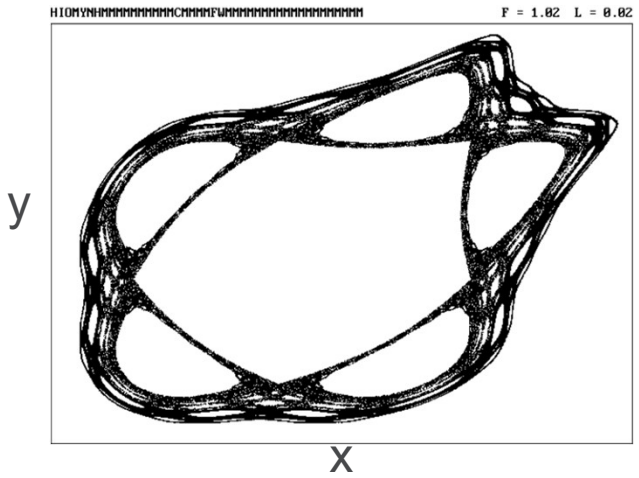


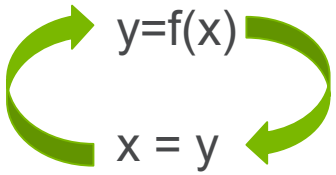


CHARGE FLIPPING – CHAOS MATHEMATICS?

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