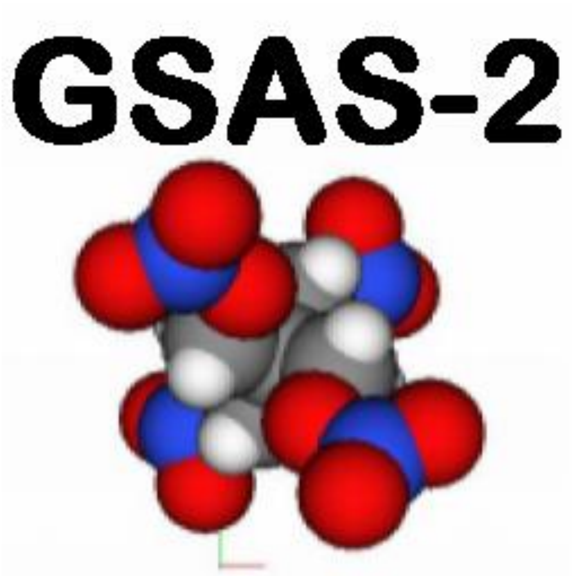
Argonne NATIONAL LABORATORY

GSAS-II BEYOND RIETVELD



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Saskatoon
June, 2024

2D IMAGE PROCESSING – FORGOTTEN OLD MATH

2D IMAGE DATA

Conic sections

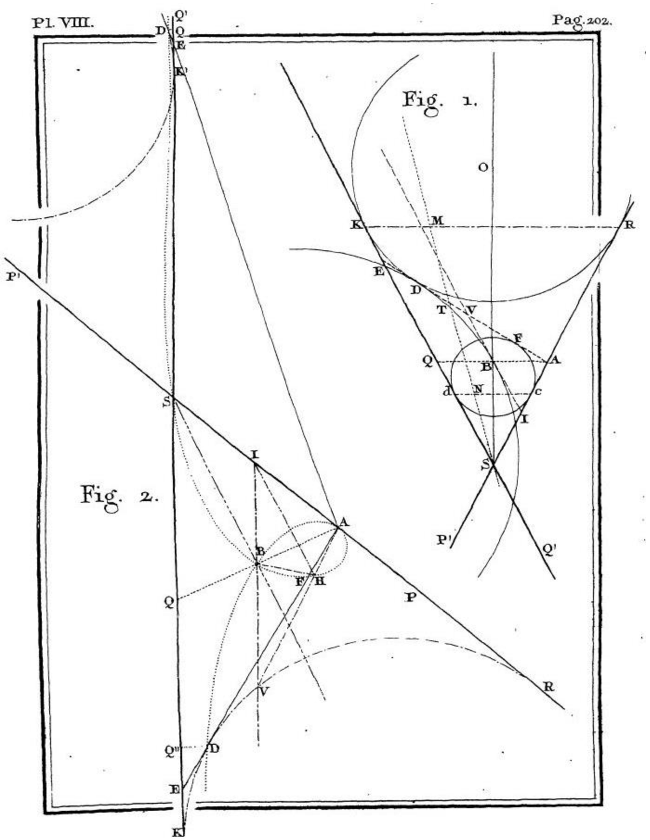
Where is the incident beam on the detector?

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

Analysis – G.P. Dandelin,

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

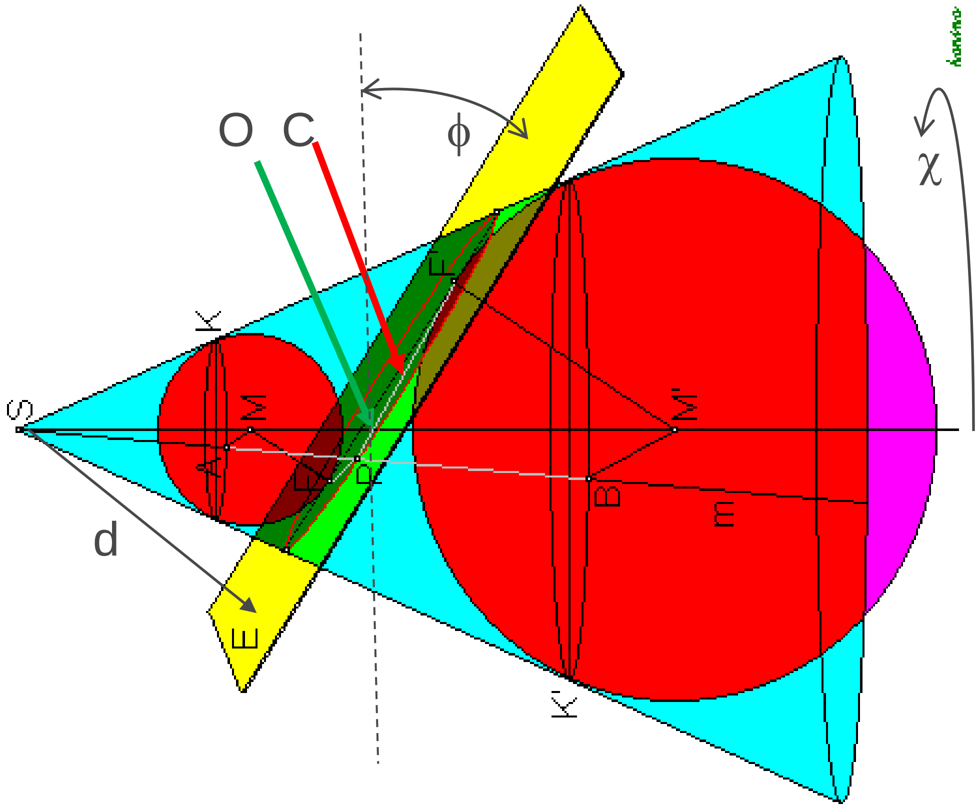
He refers to a work by M. Quetlet as having previously made this construction - source?

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

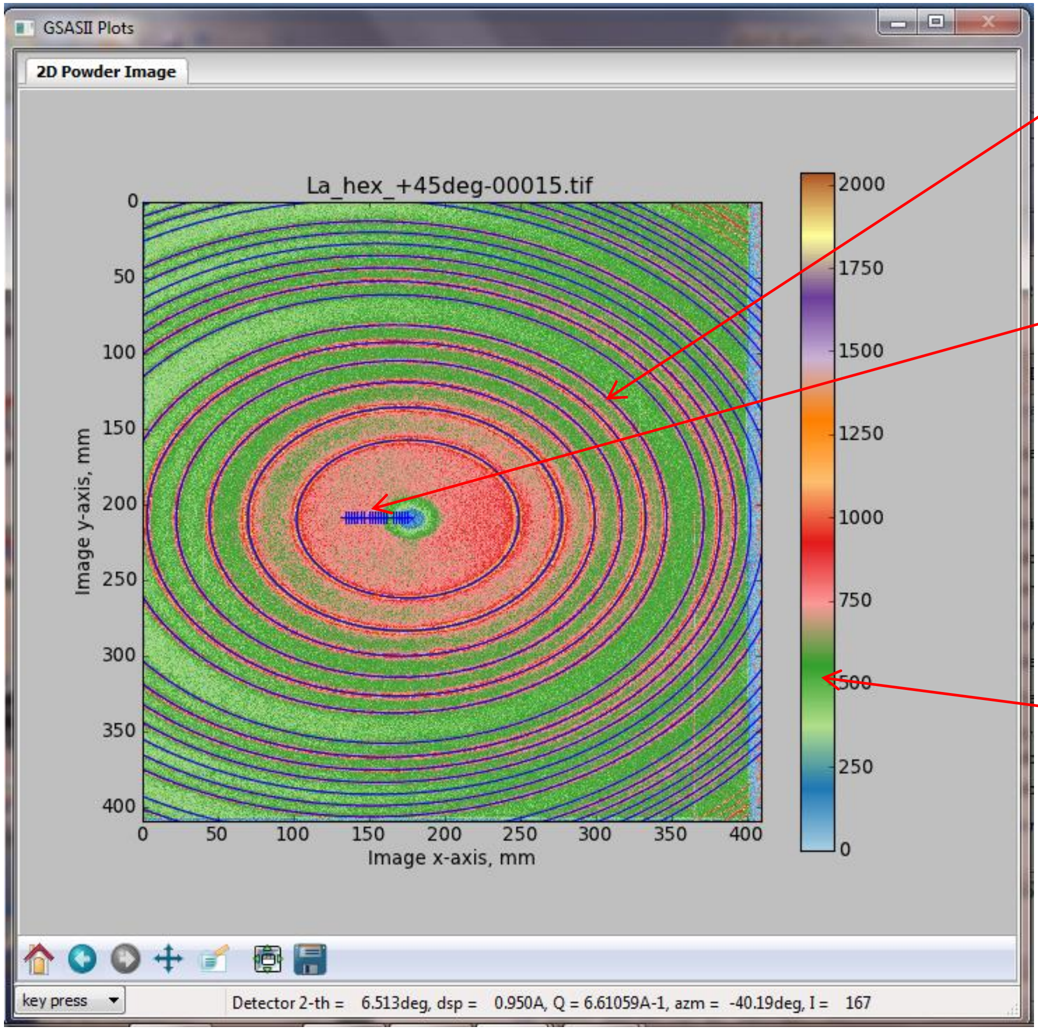


- Plane E is a tilted area detector
- The line SMM’ is the Bragg cone axis – incident beam direction & passes through centers of both spheres
- Spheres touch plane at foci (F & F’) of conic section (ellipse)
- Intersection of axis with plane (**O**) **not** at halfway point (**C**) between F & F’ (ellipse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

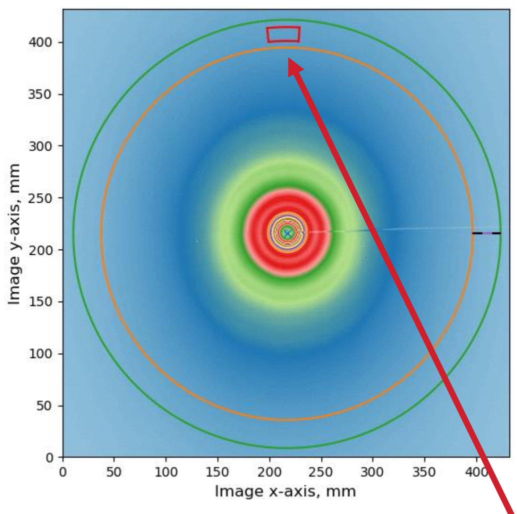
Fitting only requires material (LaB_6) and λ (e.g. don't need to know distance – get that from fit)

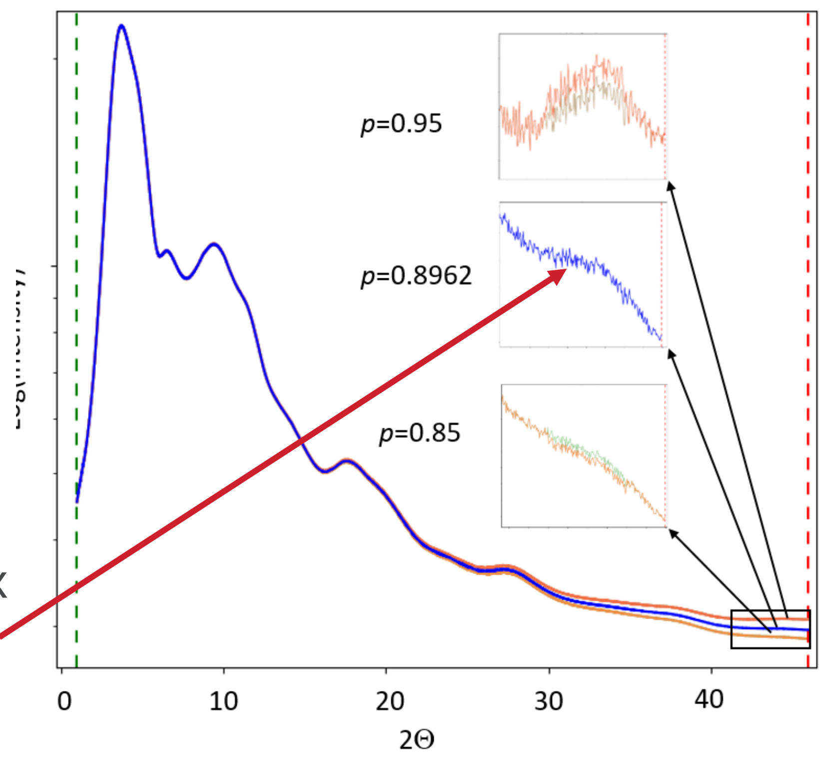
Choice of color scheme – "Paired" is shown

2D IMAGE POLARIZATION DETERMINATION

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

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

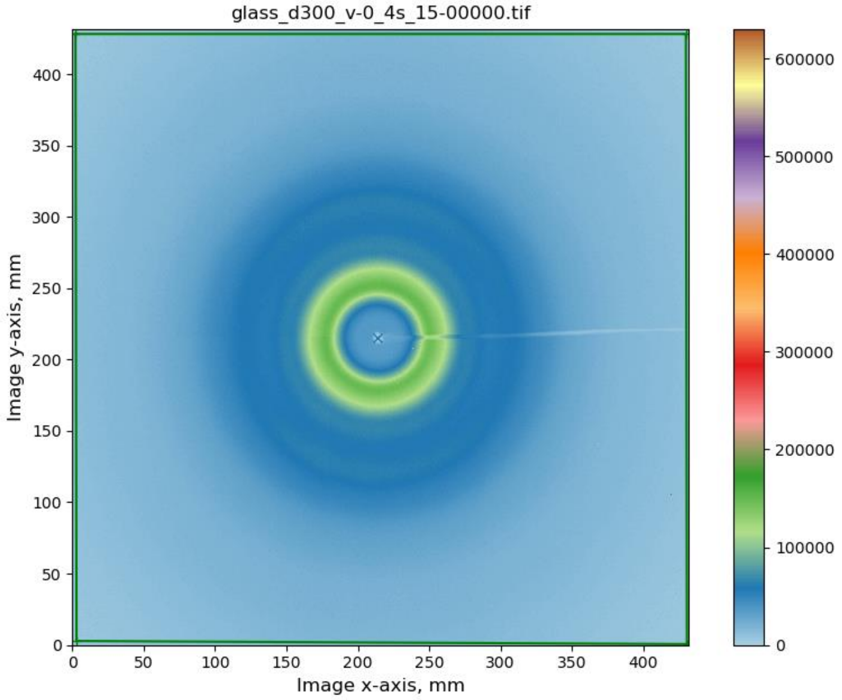


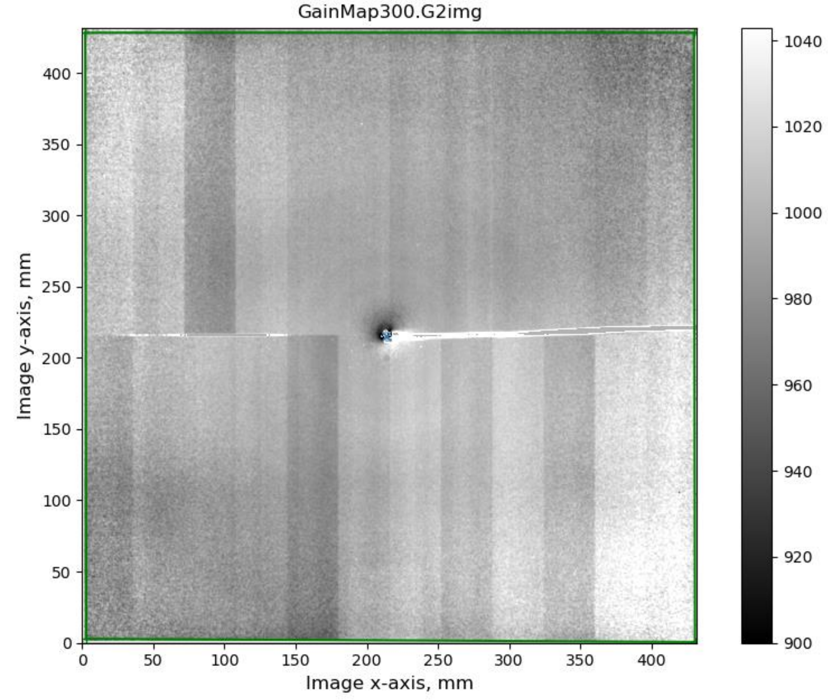


Integrate in band w/o mask box
Match if polarization is correct

2D DETECTOR GAIN MAP

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

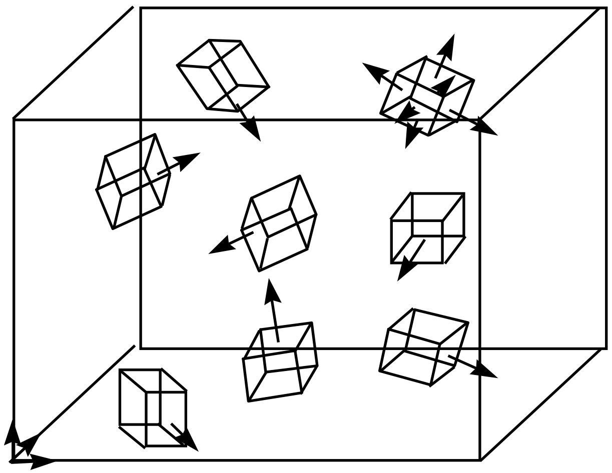




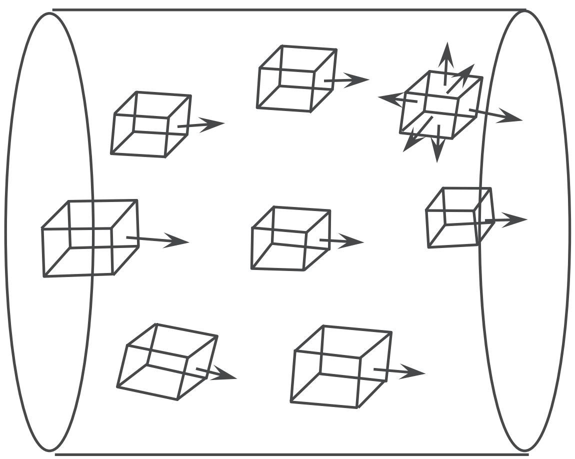
Integrate, compute ave image & subtract; residual is gain map (x1000)
Better with 3 offset images – clean up center spot

TEXTURE ANALYSIS

What is texture?
Nonrandom crystallite grain orientations

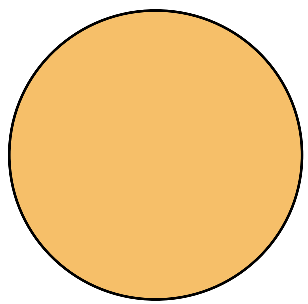


Loose powder

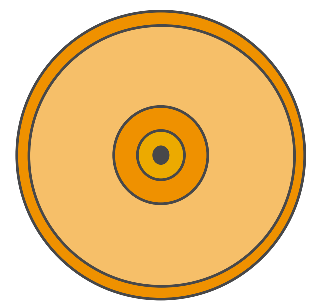


Metal wire

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

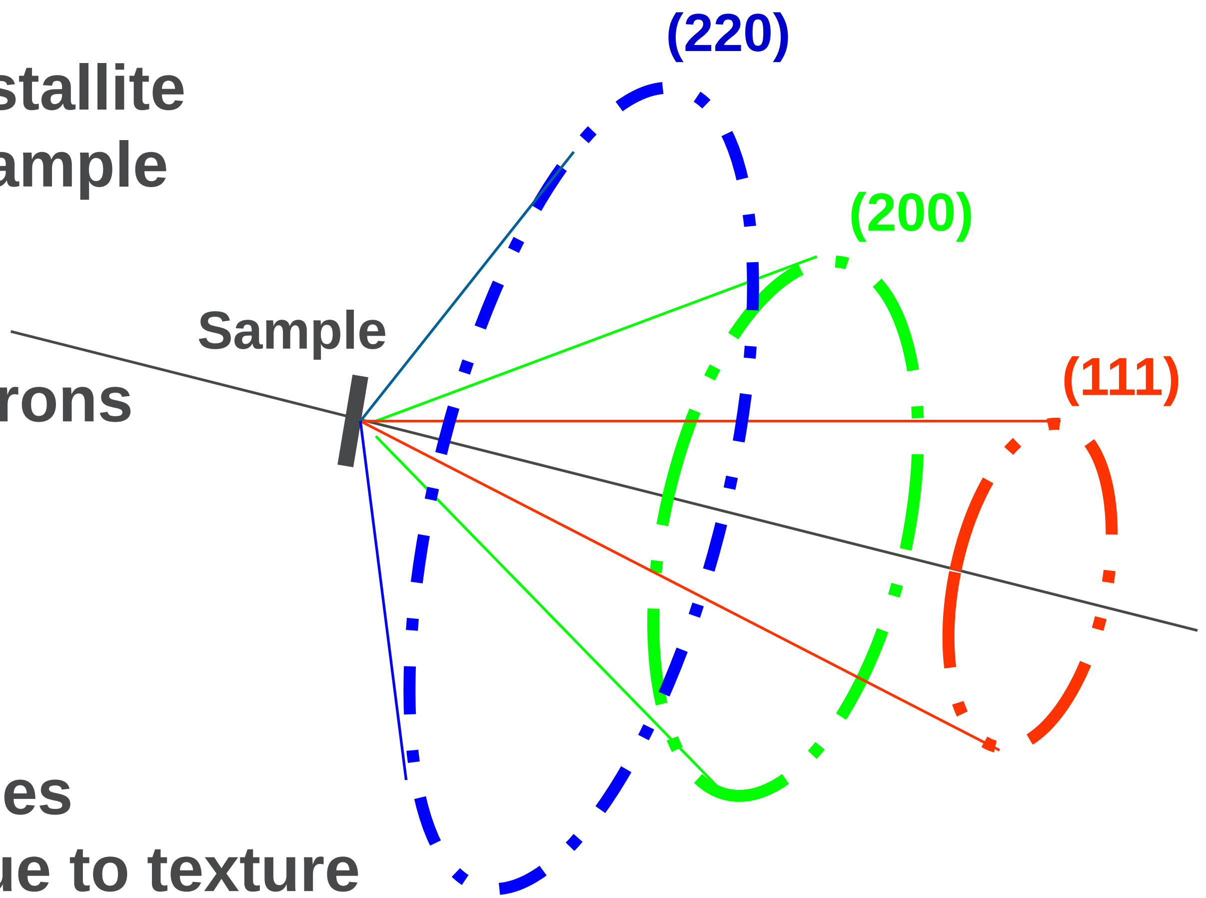
Crystallites oriented along wire axis - pole figure peaked in center and at the rim (100's are 90° apart)

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

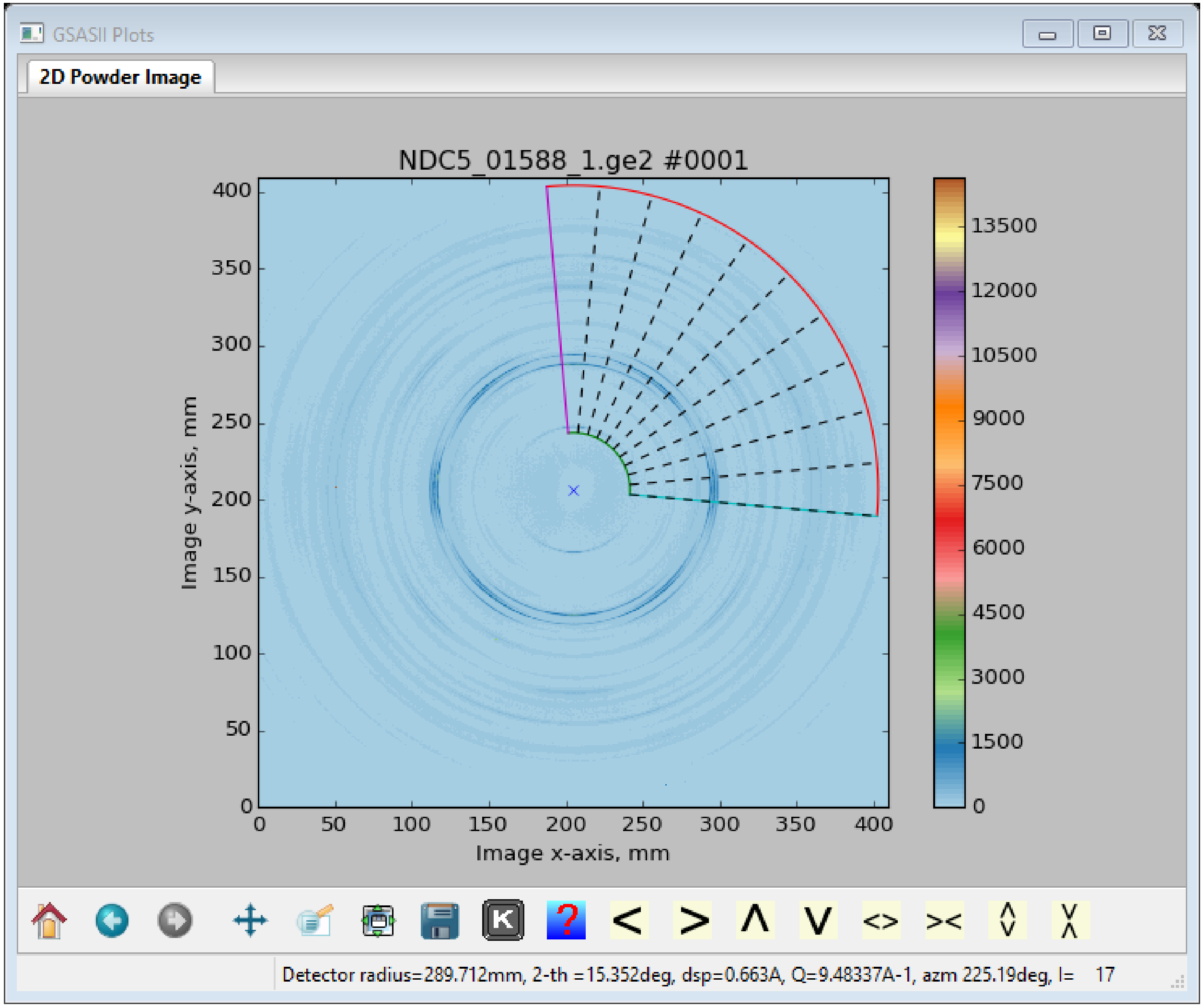
$$A(h,y) = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \sum_{n=-l}^{l} C_l^{mn} K_l^m(h) K_l^n(y)$$

- 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

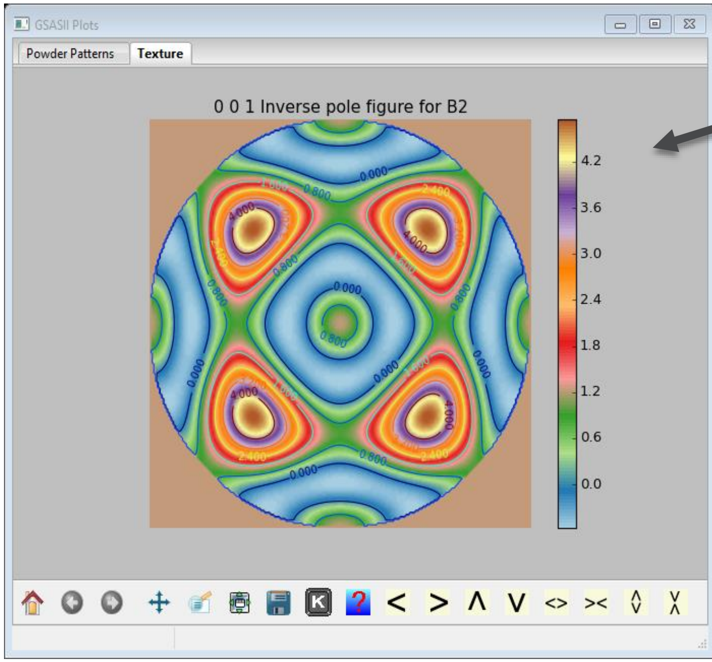
NiTi shape memory alloy wire: B2 & B19' phases

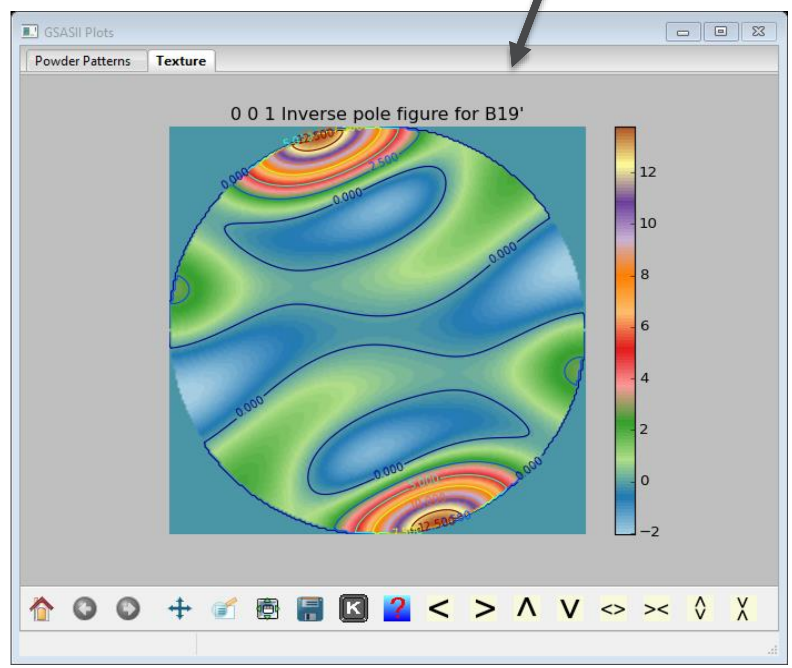


Sample – wire symmetry
Need only ¼ of image
Caked in 10° increments
Integration – PWDR patterns
Analyze for texture

GSAS-II TEXTURE ANALYSIS

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

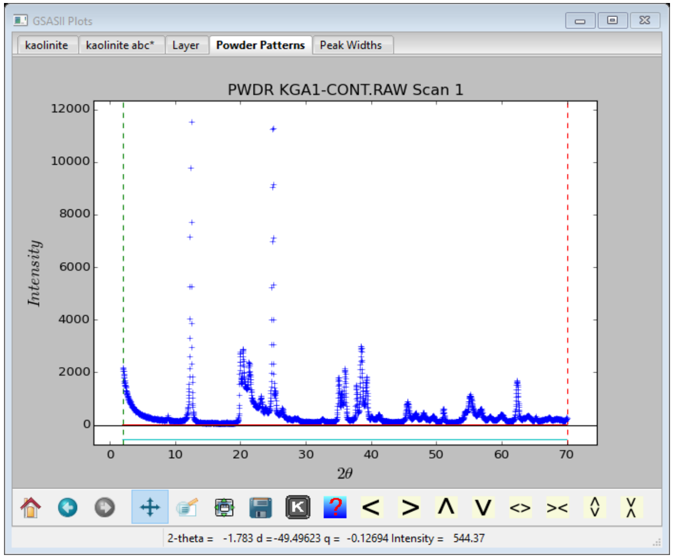


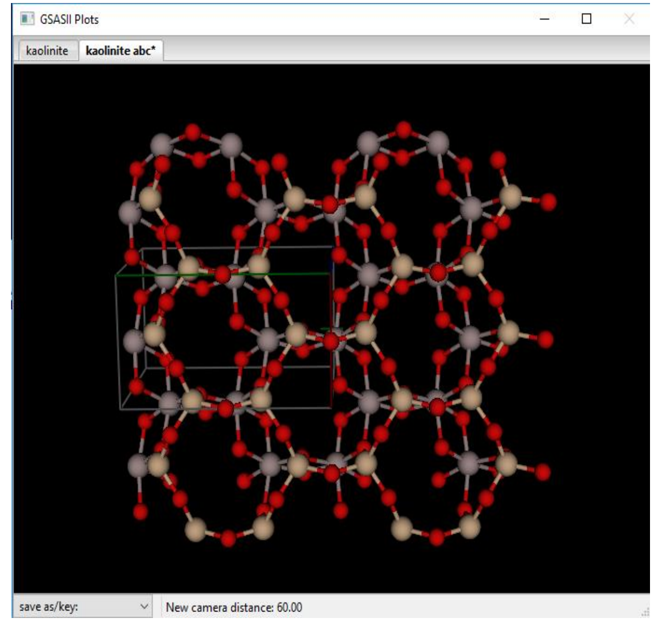


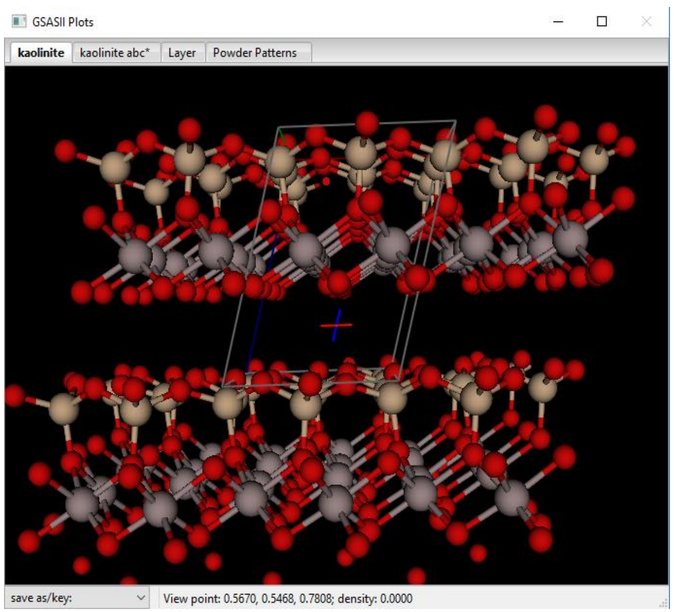
Pole figures – bulls eyes (boring)
GSAS-II → 3 methods for texture

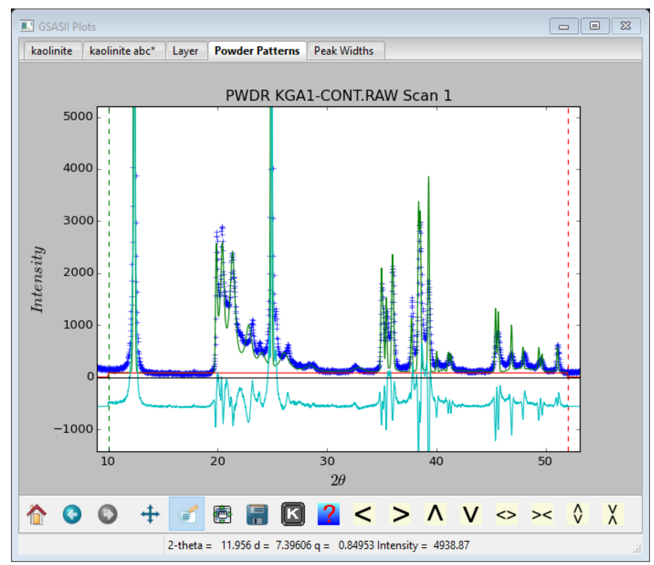
STACKING FAULTS – DIFFAX IN GSAS-II

STACKING FAULTS IN KAOLINITE $Al_2Si_2O_5(OH)_4$









SMALL ANGLE DATA ANALYSIS IN GSAS-II

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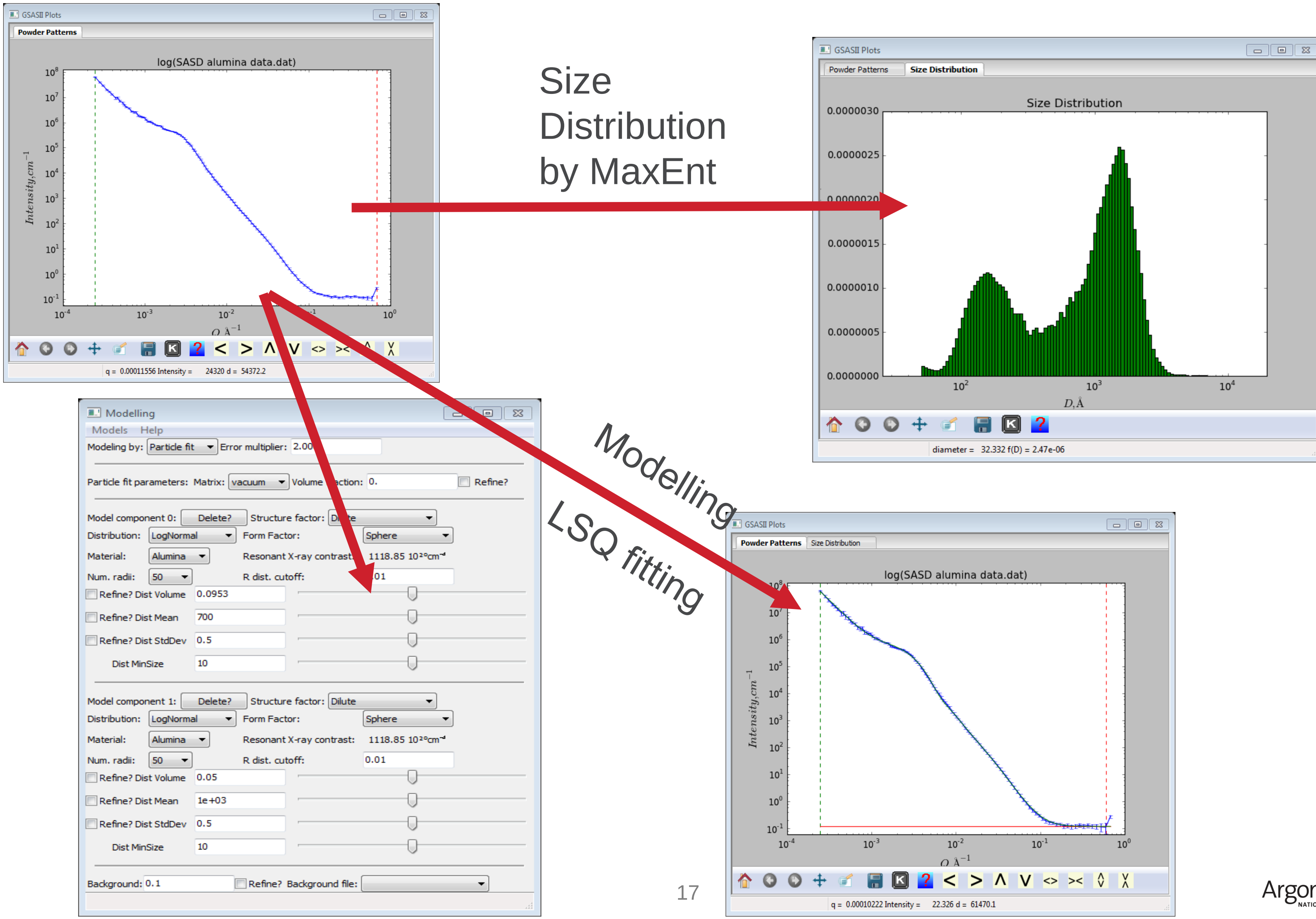
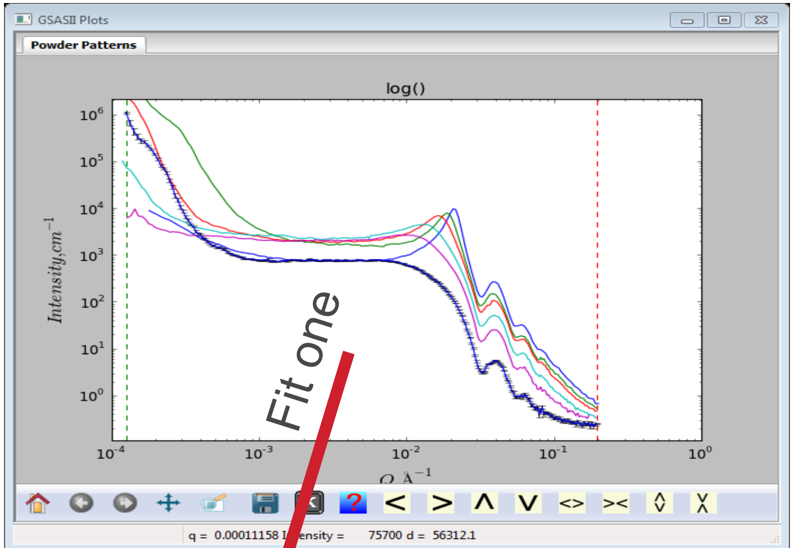
SMALL ANGLE SCATTERING

Range of tools

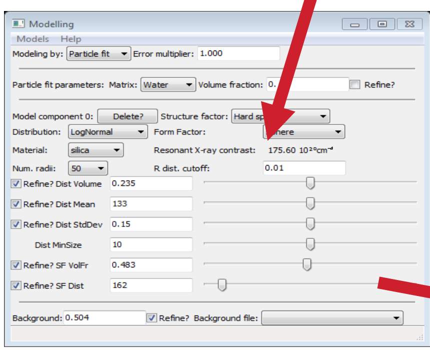


SEQUENTIAL ANALYSIS

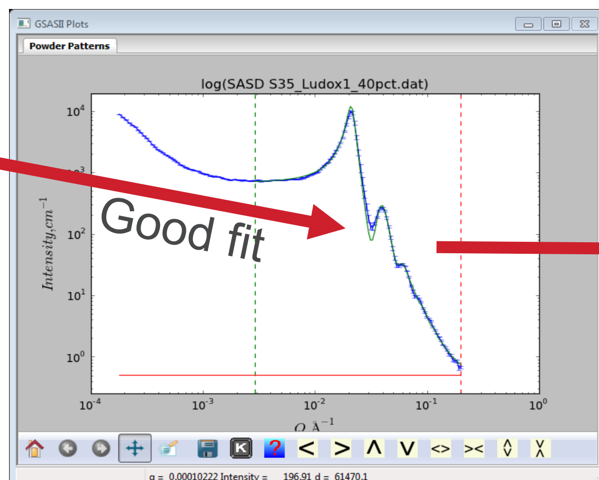
Series of experiments vs independent variable (e.g. composition)



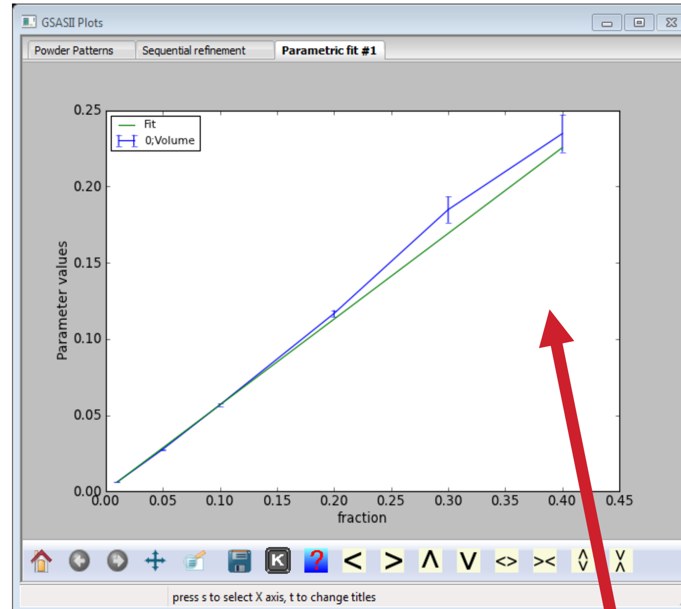
Fit one



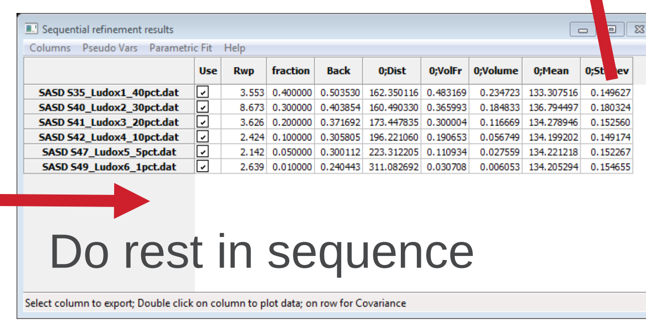
All inside GSAS-II



Good fit



Plot coeff. & fit to equation



	Use	Rwp	fraction	Back	0;Dist	0;VolFr	0;Volume	0;Mean	0;St[illegible]ev
SASD S35_Ludox1_40pct.dat	✓	3.553	0.400000	0.503530	162.350116	0.483169	0.234723	133.307516	0.149627
SASD S40_Ludox2_30pct.dat	✓	8.673	0.300000	0.403854	160.490330	0.365993	0.184833	136.794497	0.180324
SASD S41_Ludox3_20pct.dat	✓	3.626	0.200000	0.371692	173.447835	0.300004	0.116669	134.278946	0.152560
SASD S42_Ludox4_10pct.dat	✓	2.424	0.100000	0.305805	196.221060	0.190653	0.056749	134.199202	0.149174
SASD S47_Ludox5_5pct.dat	✓	2.142	0.050000	0.300112	223.312205	0.110934	0.027559	134.221218	0.152267
SASD S49_Ludox6_1pct.dat	✓	2.639	0.010000	0.240443	311.082692	0.030708	0.006053	134.205294	0.154655

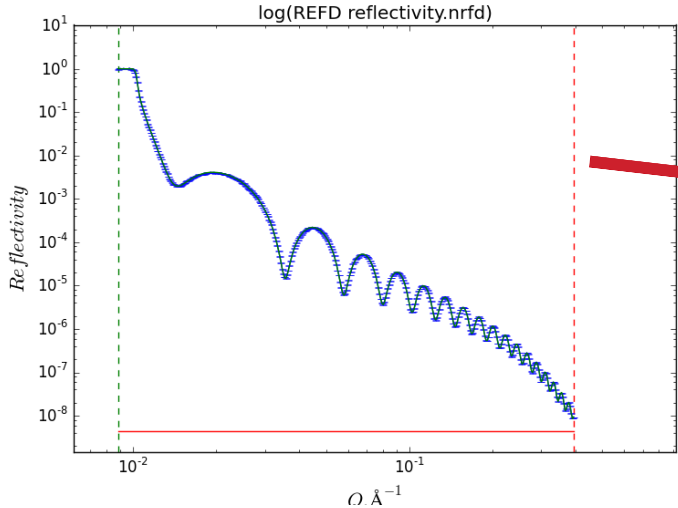
Select column to export; Double click on column to plot data; on row for Covariance

Do rest in sequence

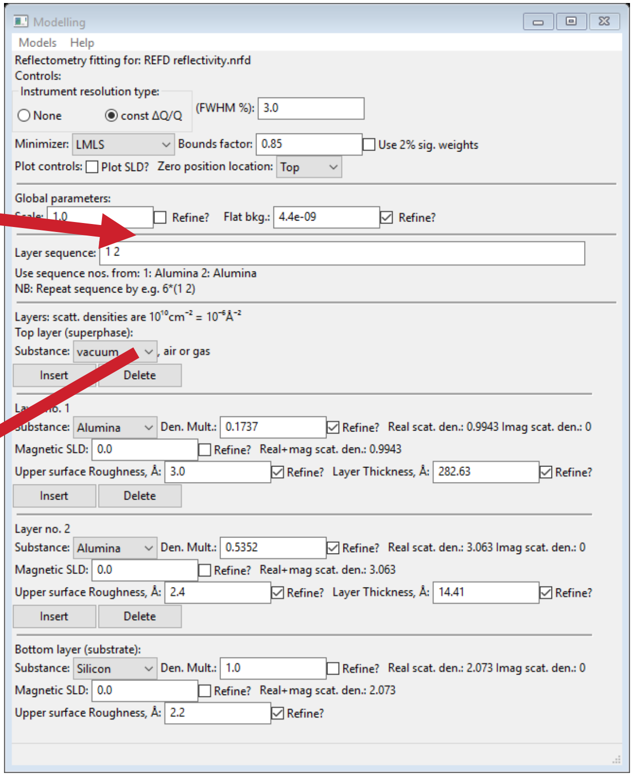
REFLECTOMETRY

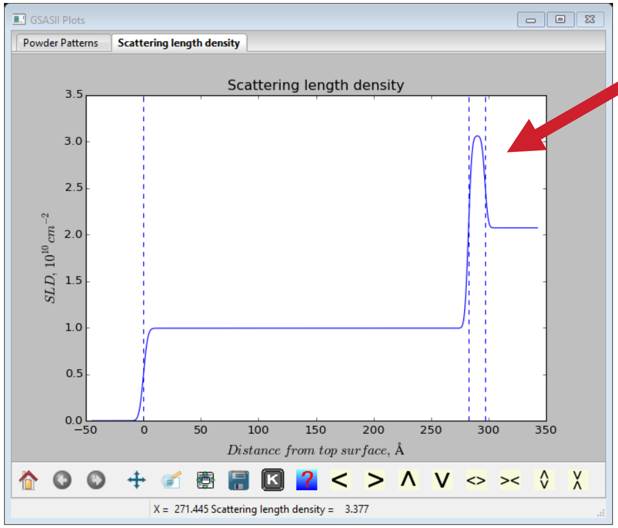
REFLECTOMETRY ANALYSIS IN GSAS-II

X-rays & Neutrons (CW at least)



Multilayer model
Scattering density

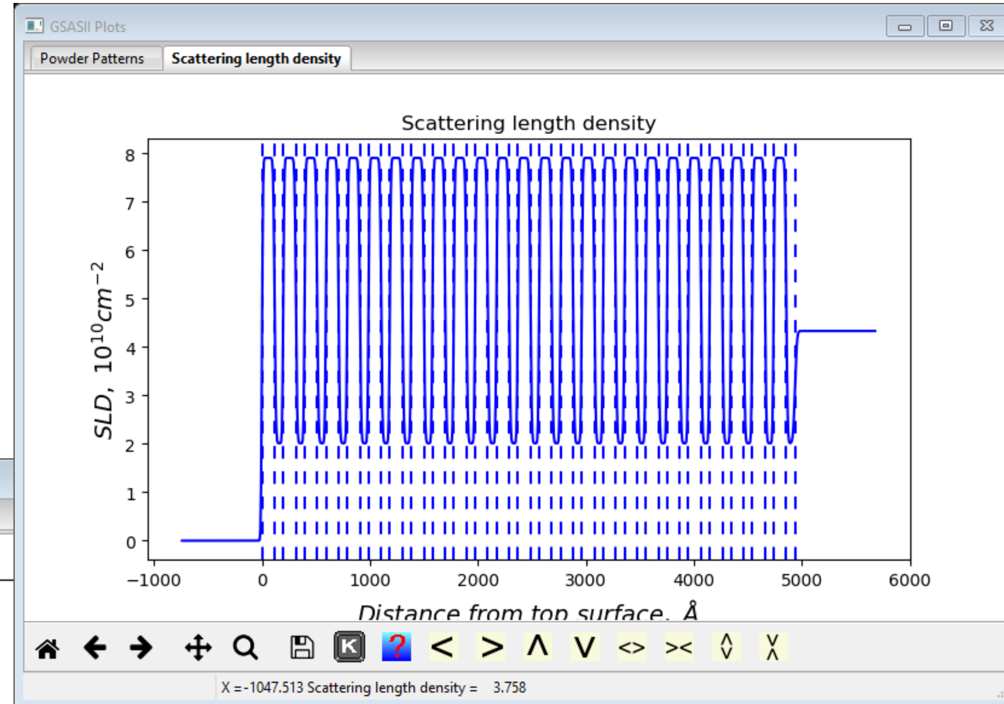


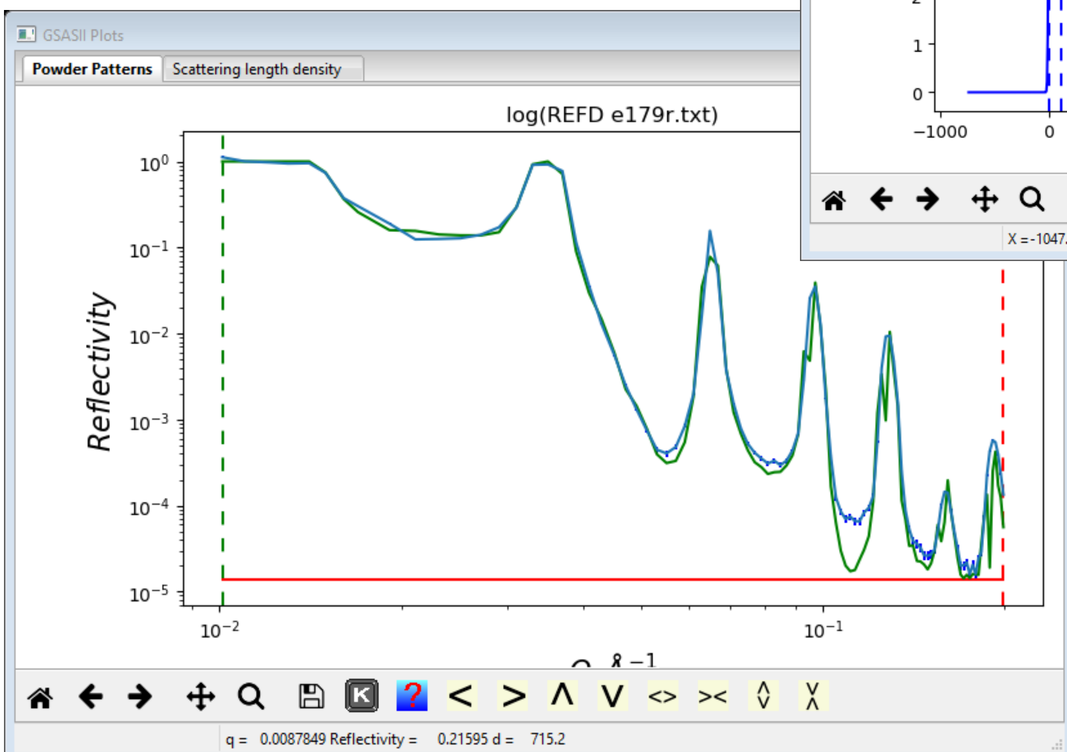


Define components, stacking sequence (can be repeated), thickness & "roughness"
Fit by LSQ, MC/SA & "basinhopping" (under development)

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

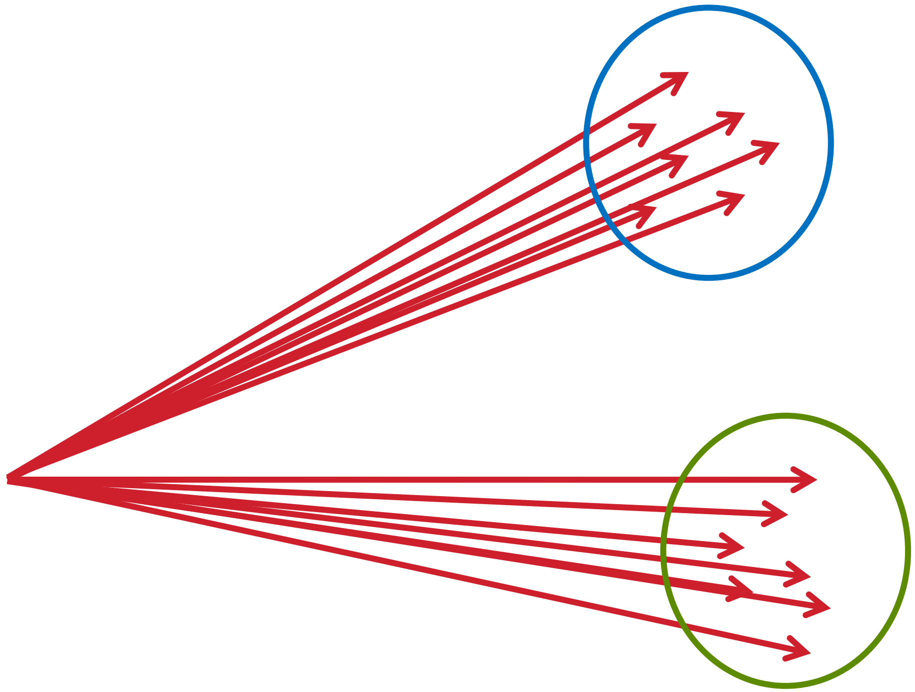
What to do?

- 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"



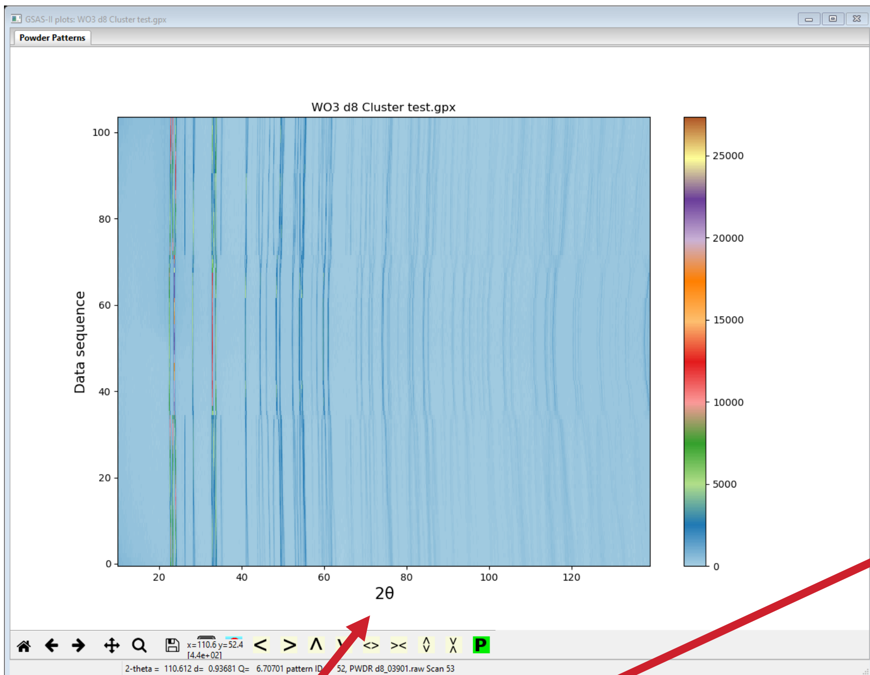
"Distance" in GSAS-II

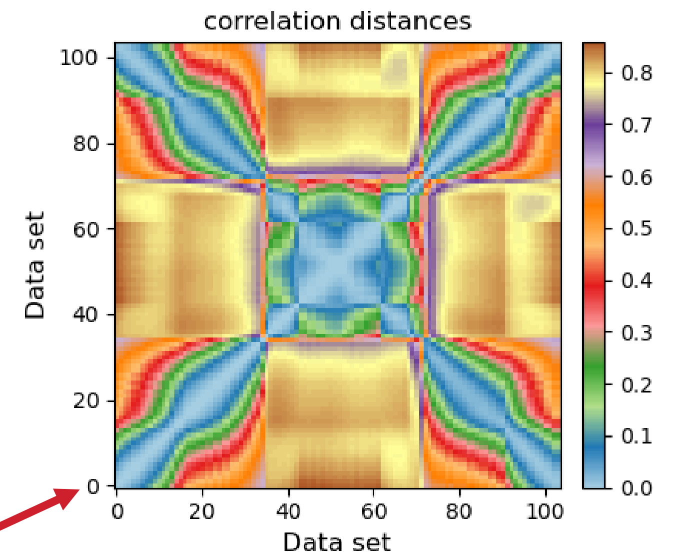
- Euclidian - shortest
- City block – steps along each axis (longer)
- Cosine – of angle between
- Correlation – coefficient
- Etc… - 11 methods; take your pick. Some are more contrasty than others

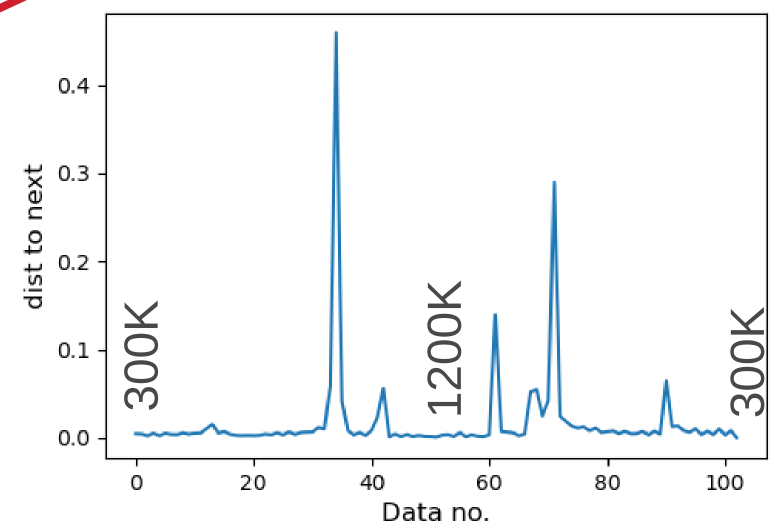
DISTANCES

Preliminary results – distance matrix & serial distances

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



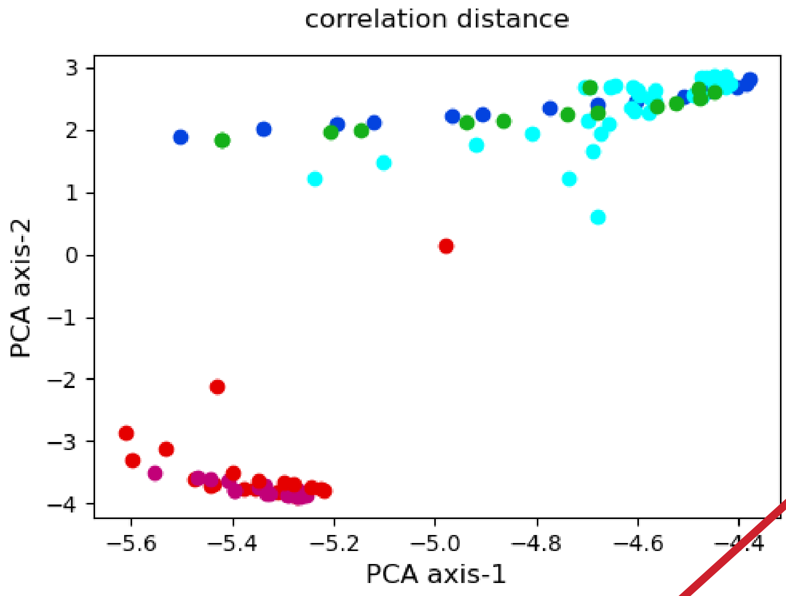




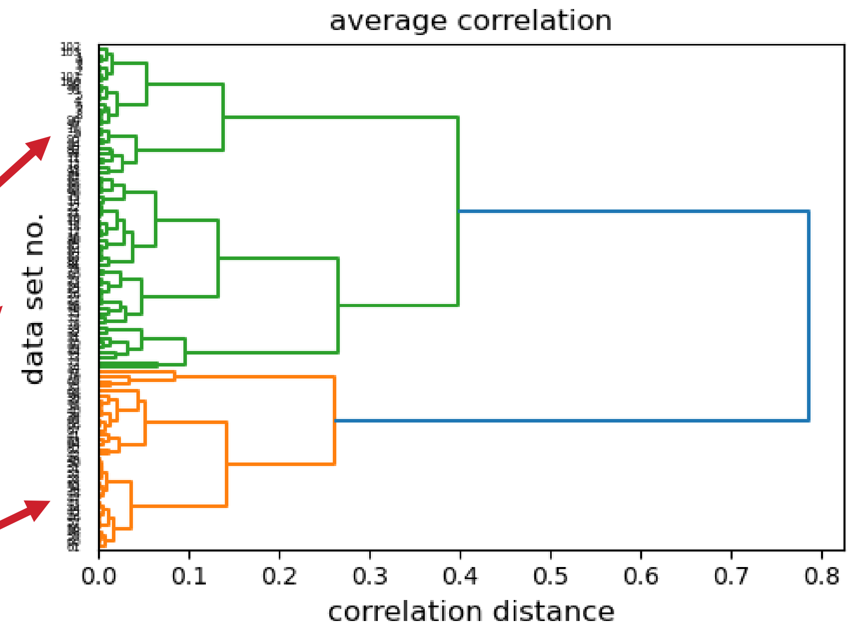
Powder data
Distance matrix
Serial distances
- n+1 vs n
- Peaks = Phase changes
- Not useful for random data

DISTANCES – PRINCIPAL COMPONENT ANALYSIS & DENDOGRAM

Most significant 2-3 dimensions – cluster analysis



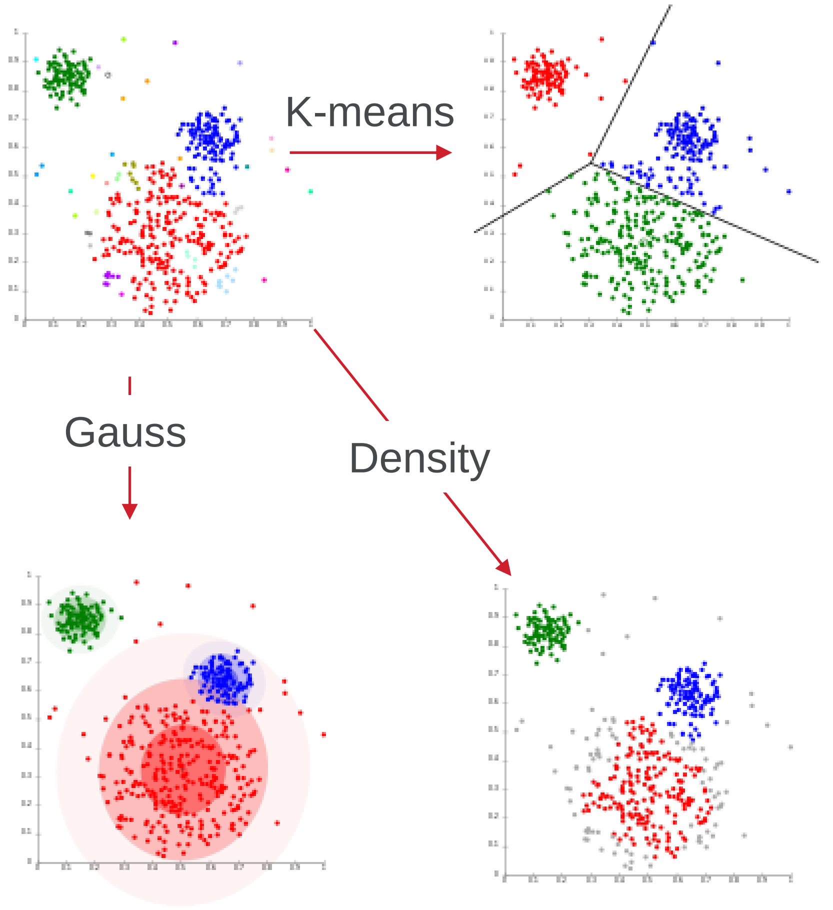
Temp variation – trails in PCA
→ Clusters ill defined in this case
Colored by "cluster"

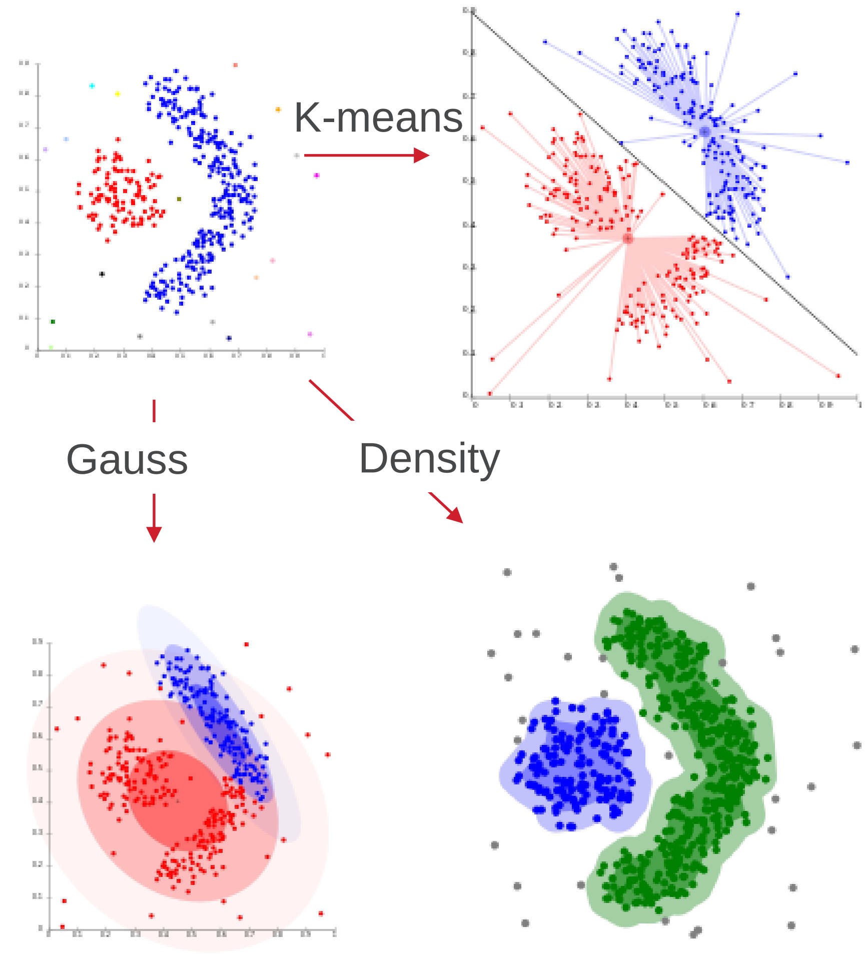


Dendogram
– hierarchy in data?
- Low T phase
- Intermediate T phases
- High T phase

THE CLUSTERING PROBLEM

Wide variations possible – 2 example PCAs & cluster algorithms



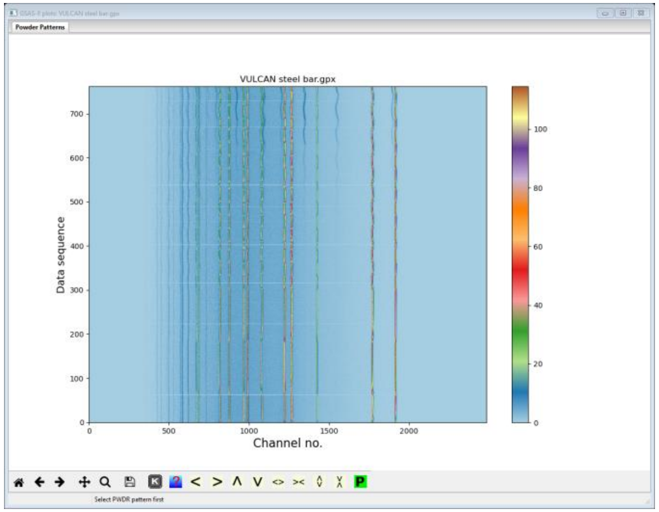


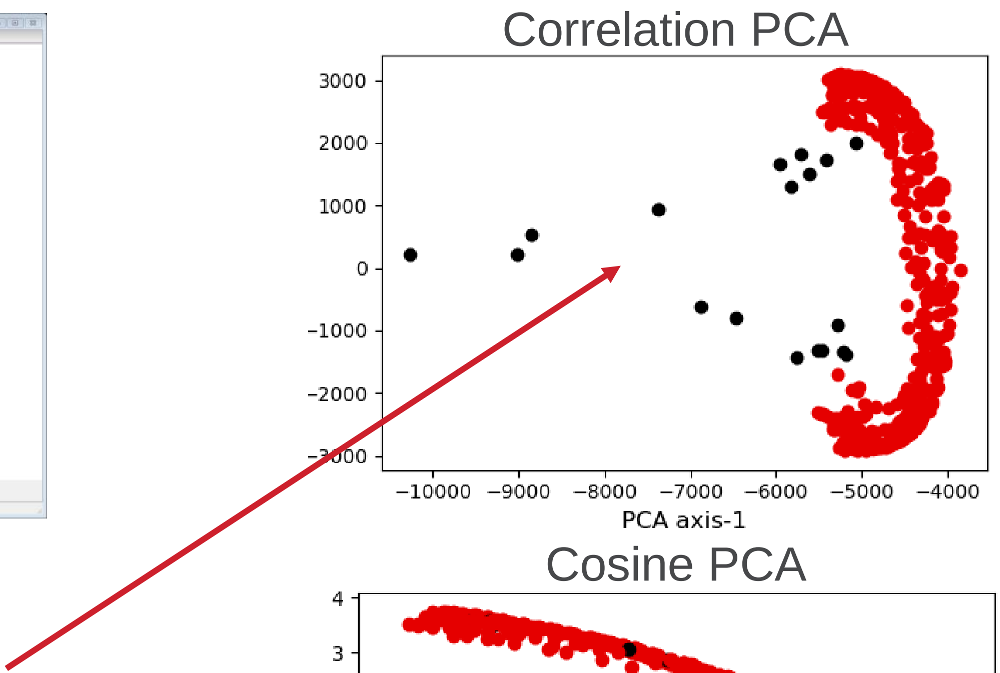
GSAS-II has 6 clustering algorithms – some require # of clusters

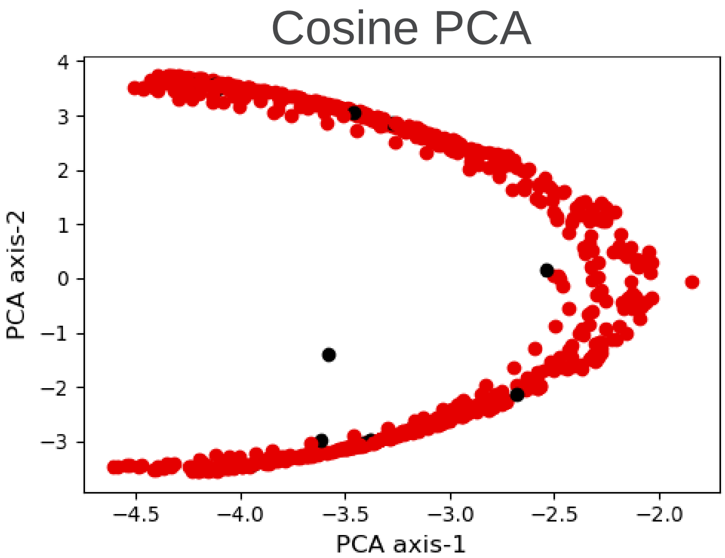
Taken from Wikipedia

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

THANK YOU

www.anl.gov