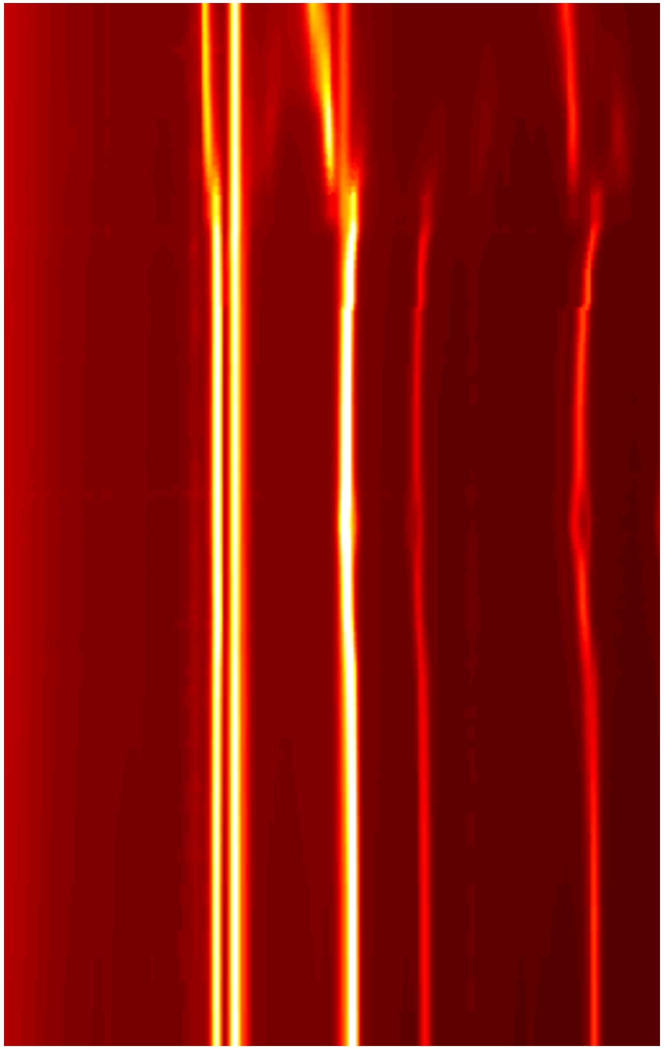
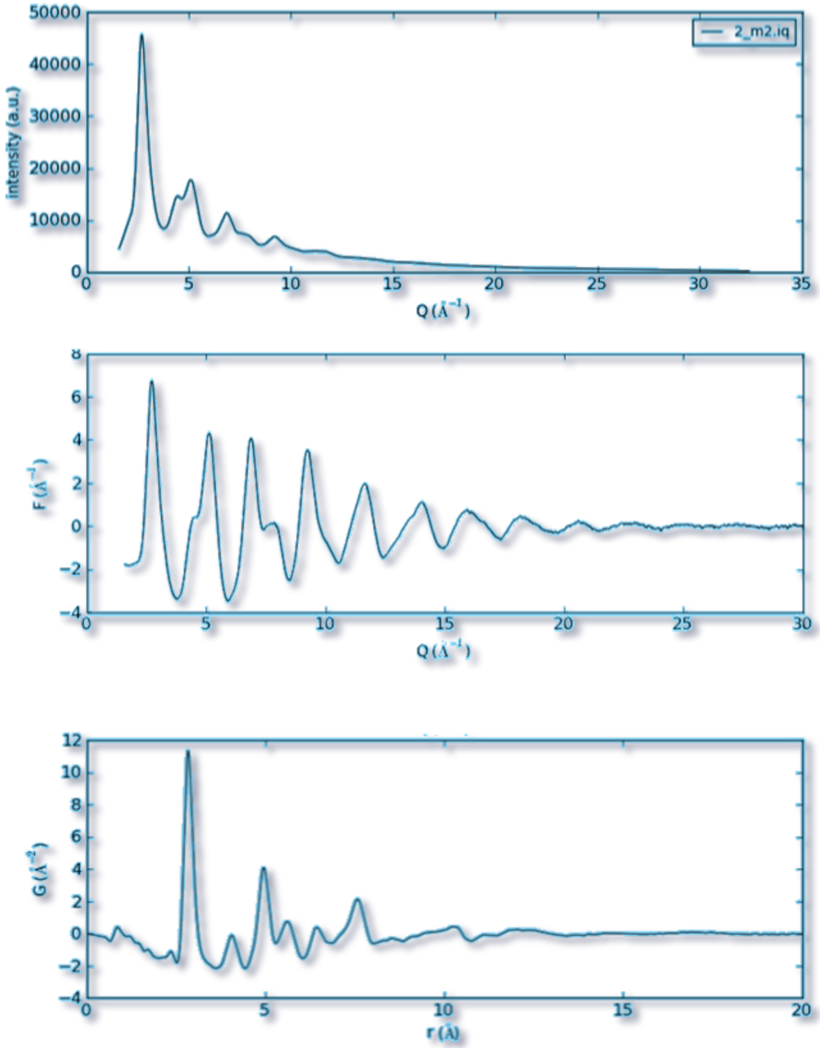
ESRF | The European Synchrotron



Synchrotron PDF Data Acquistion and Reduction

G. Vaughan & S. Checchia

GETTING THE PDF FROM THE DIFFRACTION DATA



$$S(q) = \frac{I(q) - \langle f(q)^2 \rangle}{\langle f(q) \rangle^2} + 1$$

$$F(q) = q(S(q) - 1)$$

Debye Equation:

$$F(q) = \frac{1}{N\langle f(q) \rangle^2} \sum_{i \neq j} f_i(q)\, f_j(q) \frac{\sin q r_{ij}}{r_{ij}}$$

$$G(r) = \frac{2}{\pi} \int_{q_{min}}^{q_{max}} F(q) \sin qr \, dq$$

$$G(r) = \frac{1}{rN\langle f \rangle^2} \sum_{i \neq j} f_i\, f_j \delta(r - r_{ij}) \; - 4\pi r \rho_0$$

DATA ACQUISITION

Continuous Transform on finite data

- High q – implies high energy

Good statistics

- Particularly at high q; contrary to form factor behaviour

Low/well characterized background

- Minimize inelastic scattering
  - avoid absorption edges (W, Pb, …)
  - using energy discrimination
- Clean background – minimize parasitic scattering
  - sample environment
  - tomographic methods

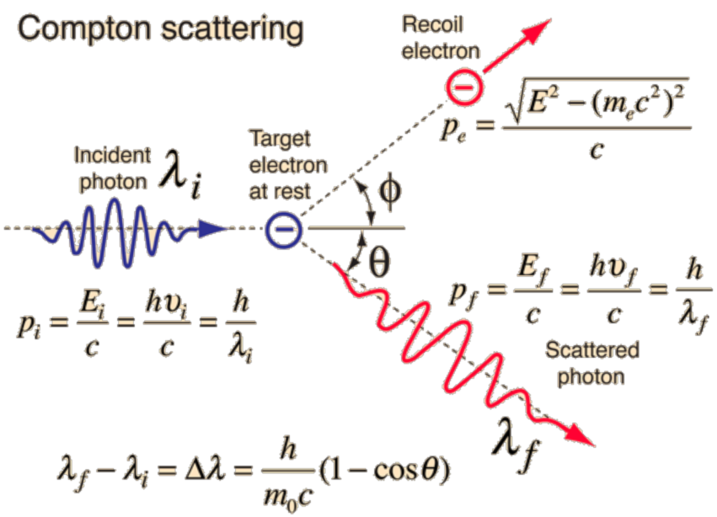
In the case of X-ray diffraction, only the elastic scattering is modeled (essentially the scattering from valance electrons ≡ atomic positions. Scattering from the nucleus and bonding electrons is generally neglected).

$$I = I_e + I_{ie} + I_p$$

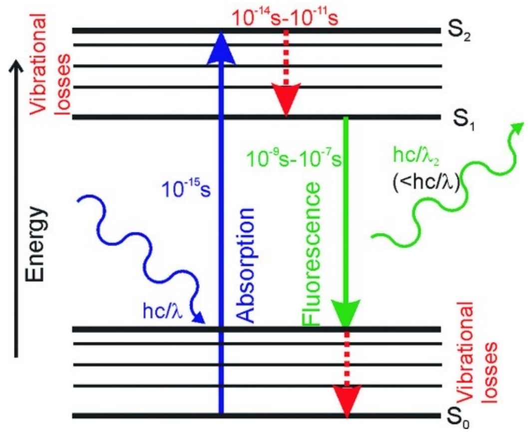
$$I = I_e + \left(I_{istruct} + I_{Comp} + I_{Fluo}\right) + I_p$$

Fluorescence comes from all absorption edges below the incident energy
Fluorescence can be 80% of the signal at high Q

Compton scattering has a spatial and energy distribution

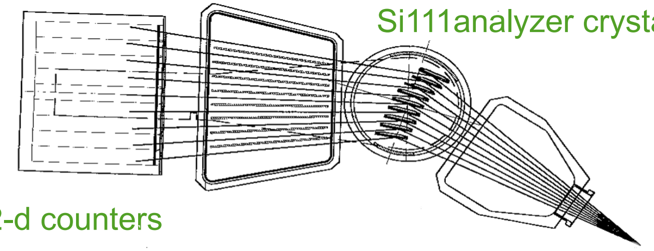


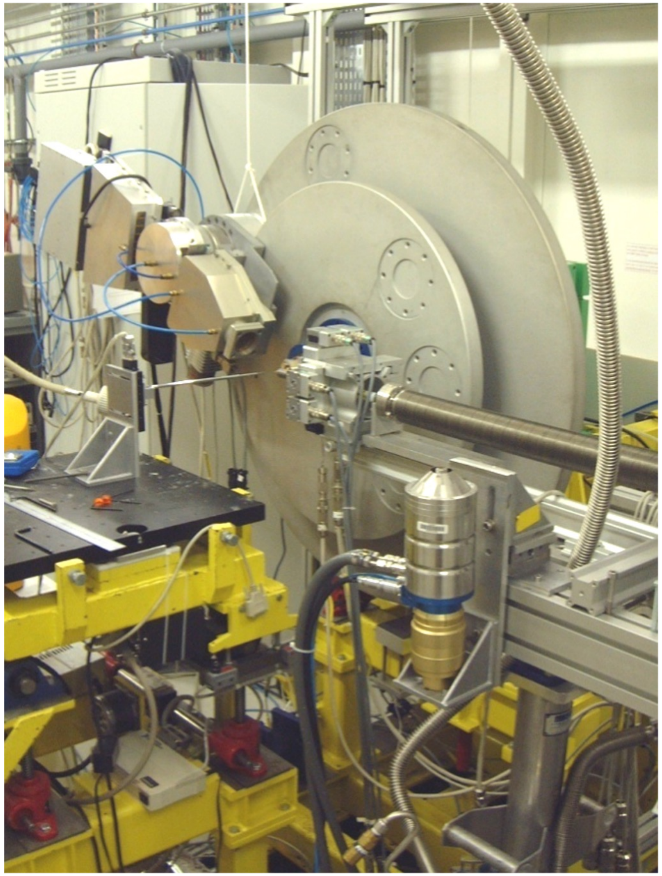
Jablonksi diagram depicting simple 1 photon excitation fluorescence



Scintillators and PMT

- Angle sensitive
  - Energy discrimination
  - Background elimination
- Good dynamic range
- Photon counting
- Very high angular resolution
  - Accurate lattice parameters
  - Ideal for structure refinement
- Slow

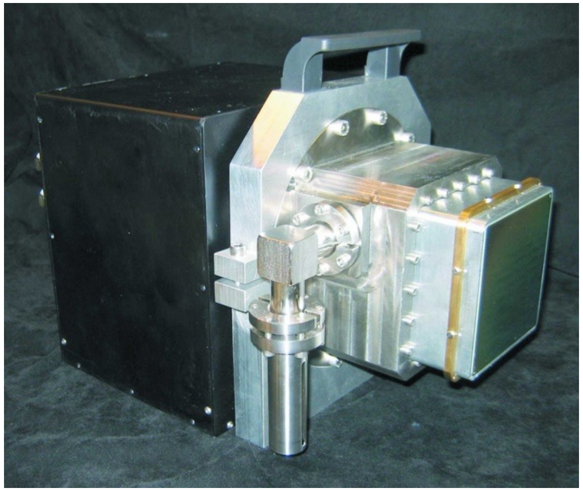




ID22

Mostly Developed for Medical Imaging

- Image plates
- Flat panel detectors
- CCD/CMOS cameras coupled to scintillators
- Hybrid Pixel detectors



2D DETECTORS

	Advantages	Disadvantages
CCD/CMOS Cameras Phosphor optical fiber or lens coupled	Stable Background Stable Flat Field Stable Distortion	High Background Limited Dynamic Range Large PSF Low Sensitivity Integrating Large corrections
Flat Panel	High Sensitivity Stable Flat Field No PSF Cheap	Very High Background Variable Background Integrating
Hybrid Pixel Detectors	High Dynamic Range High Sensitivity Photon Counting Zero Background Energy Discrimination Stable Flat Field “No” PSF	Price

STATISTICAL EFFECT OF ELECTRONIC NOISE

$$I = (I_0 - D)R$$

$$I = (I_0 - D)\frac{\langle R \rangle}{R_i}$$

If D is constant:

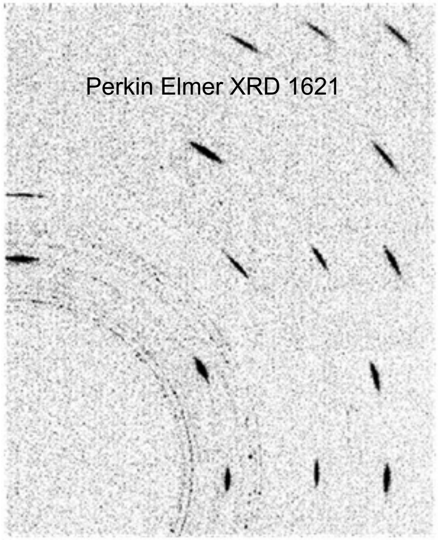
$$D = \frac{1}{N_D}\sum D_j = \frac{n_D}{N_D}\sum I_{0,j} = n_D I_0$$

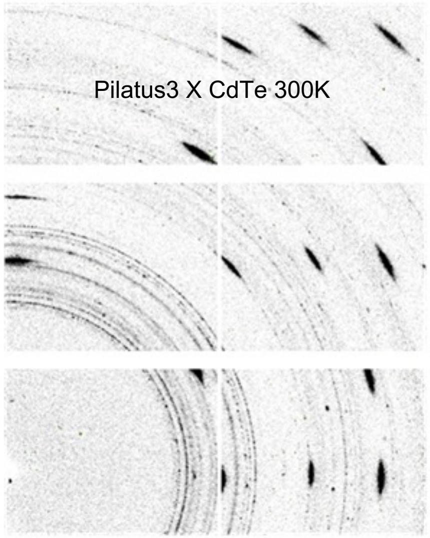
$$\sigma_I^2 \cong \sigma_{I_0}^2 \left[1 + \frac{n_D}{N_D} + \frac{(1-n_D)^2}{n_R N_R} \right]$$

$$\begin{aligned} \sigma_{\langle R \rangle}^2 &= \left(\frac{1}{N}\right)^2 N \sigma_{R_i}^2 \\ &= \left(\frac{\sigma_{R_i}^2}{N}\right) \\ &\approx 0 \end{aligned}$$

COMPARISON OF FLAT PANEL AND PIXEL DETECTOR

	Pilatus3 X CdTe 2M	Perkin Elmer XRD 1621
Detection technology	Hybrid photon counting	Flat panel
Sensor material	CdTe	CsI
Pixel size [μm²]	172×172	200×200
Total number of pixels (H × V)	1475×1679	2024×2024
Maximum frame rate[Hz]	250 (500 with ROI)	15 (30 with 2×2binning)
Point Spread Function (FWHM)	1 pixel	2 pixels
Energy threshold [keV]	8-40	none
Maximum count rate [ph/s/pixel]	5×10^6	Integrating detector
Non linearity	<2% at 10^6 counts/s/pixel	
Counter depth	20 bit	16 bit
Dynamic range	20 bit	12.8 bit
Minimum exposure [ns]	200	33000000
Image lag	0	~1% after 100ms



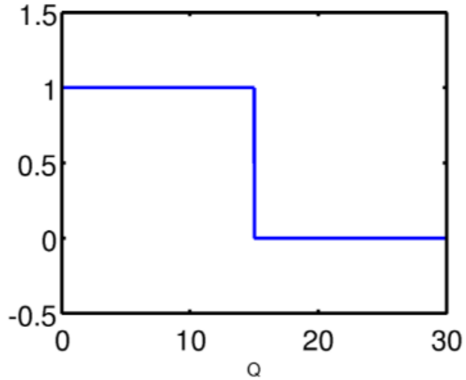


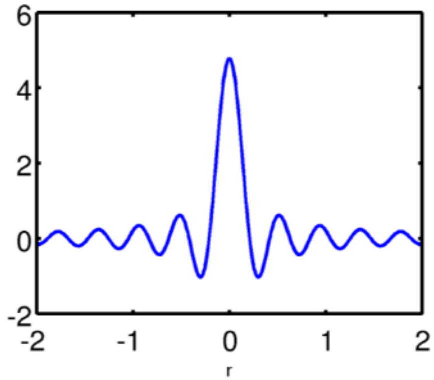
Superconducting filament, Ø50 μm, measured at 50 keV, with exposure time of 100ms with a Perkin Elmer XRD 1621 flat panel detector (left) and with the Dectris Pilatus3 X CdTe 300K prototype

Effect of finite Q-range (truncation)

$$G(r) = \frac{2}{\pi}\int_{Q_{min}}^{Q_{max}} F(Q)\sin(Qr)\,dQ$$

Emil showed

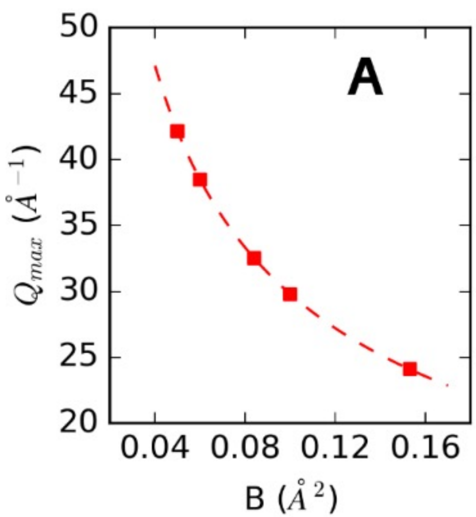


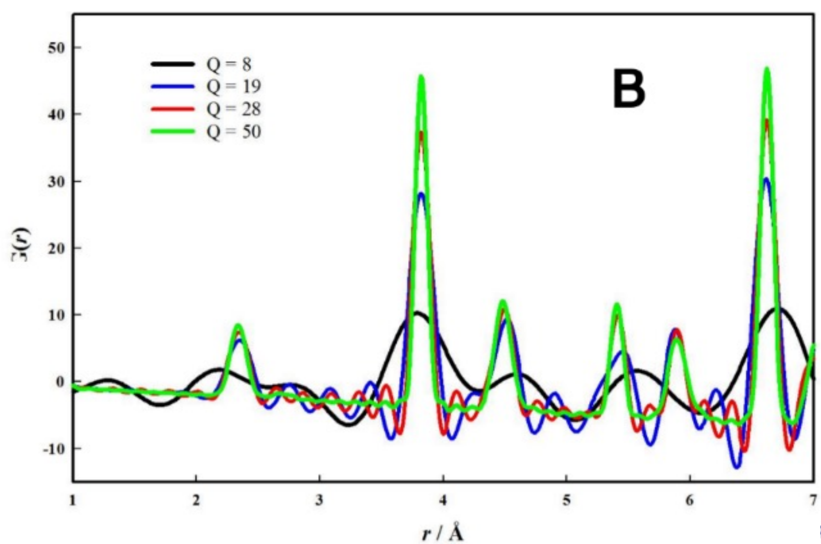


$$\frac{\sin(Q_{max}\,\Delta r)}{\Delta r}$$

G(r) is convoluted with a sinc function: PDF resolution ≈ π/Q_{max}

- peak breadth = resolution + thermal broadening
- Use highest available Q containing useful signal





Effects of Q-resolution and particle size

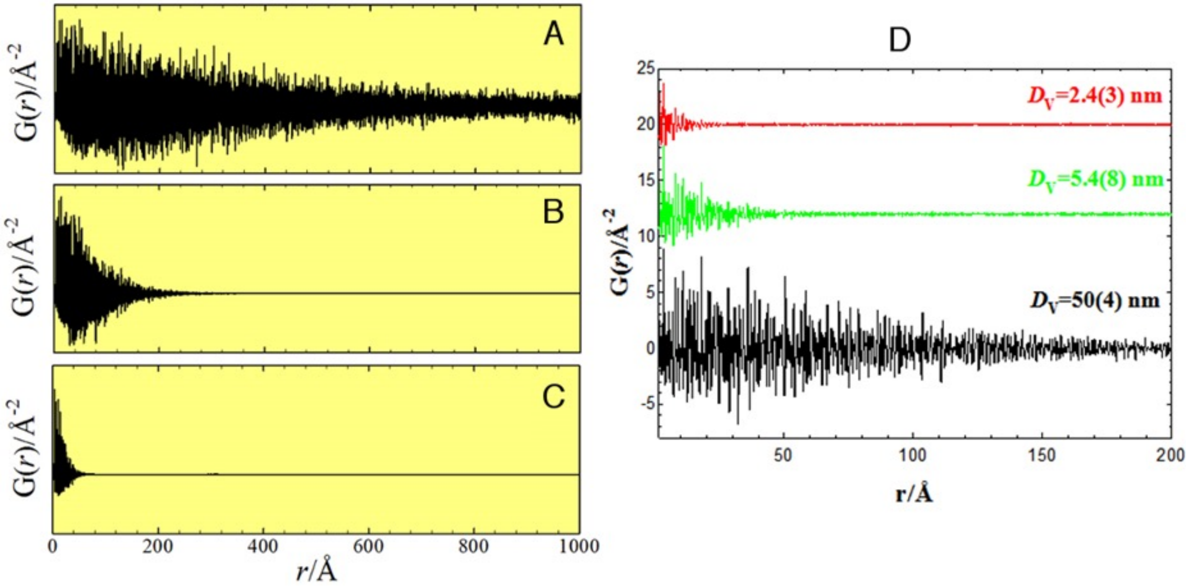
G(r) intensity falloff:

- Sample independent Q-space resolution [$\approx e^{-(r\Delta q)^2}$]
- Sample-dependent particle size

$\Delta d/d \approx 10^{-4}$

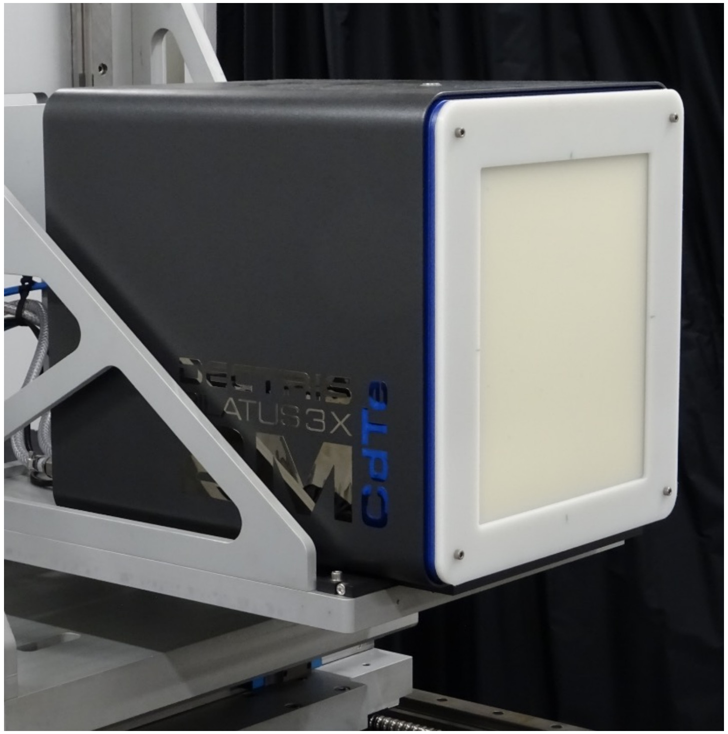
$\Delta d/d \approx 10^{-3}$

$\Delta d/d \approx 10^{-2}$



EXPERIMENTAL SET-UP

Pilatus3X 2M CdTe

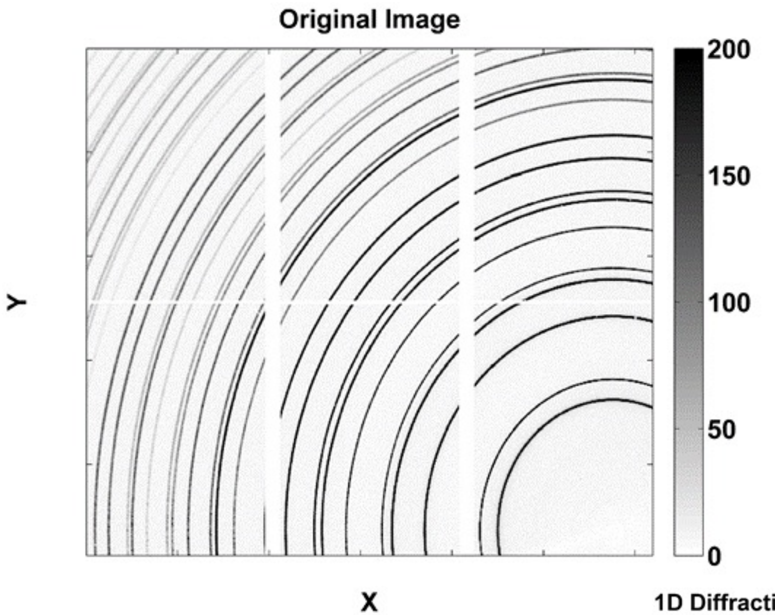


- Pixel size 172μm x 172μm
- Single photon counting
- 20-bit dynamic range
- Linear up to more than 1Mcps
- Maximum frame rate 250Hz (500 with ROI)

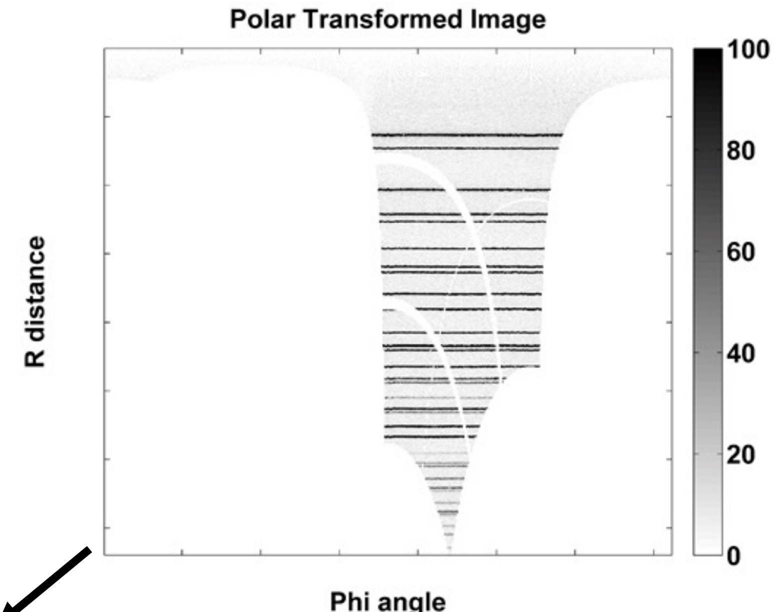
Sample Environments: Heating, cooling, pressure, chemical potential (gases, liquids), mechanical modification

Experimental geometry (sample-detector distance, beam centre, tilts) calibrated using a standard sample

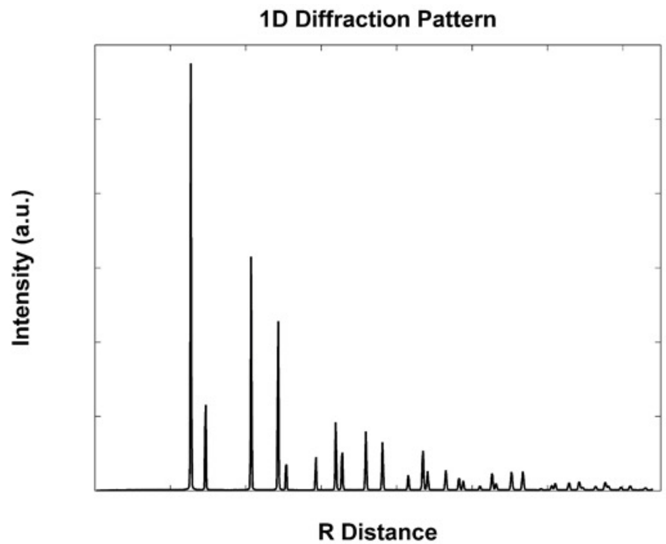
REDUCTION OF XRD DATA



Geometric corrections

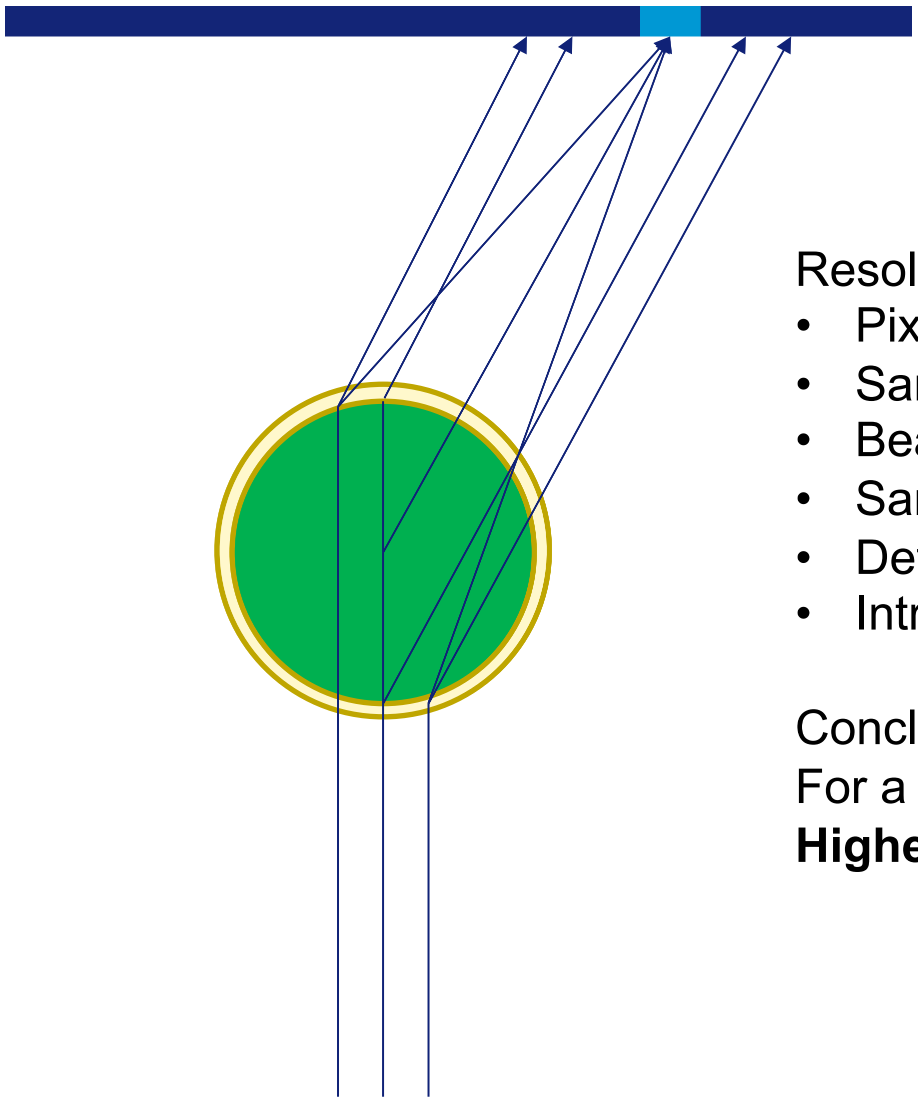


Cylindrical symmetry, i.e., a perfect powder, is implicit



- *Outlier rejection (spots, cosmic rays)*
- *Masking of bad pixels*
- *Flood, polarization and spatial corrections*

EFFECTS OF SAMPLE GEOMETRY - BROADENING



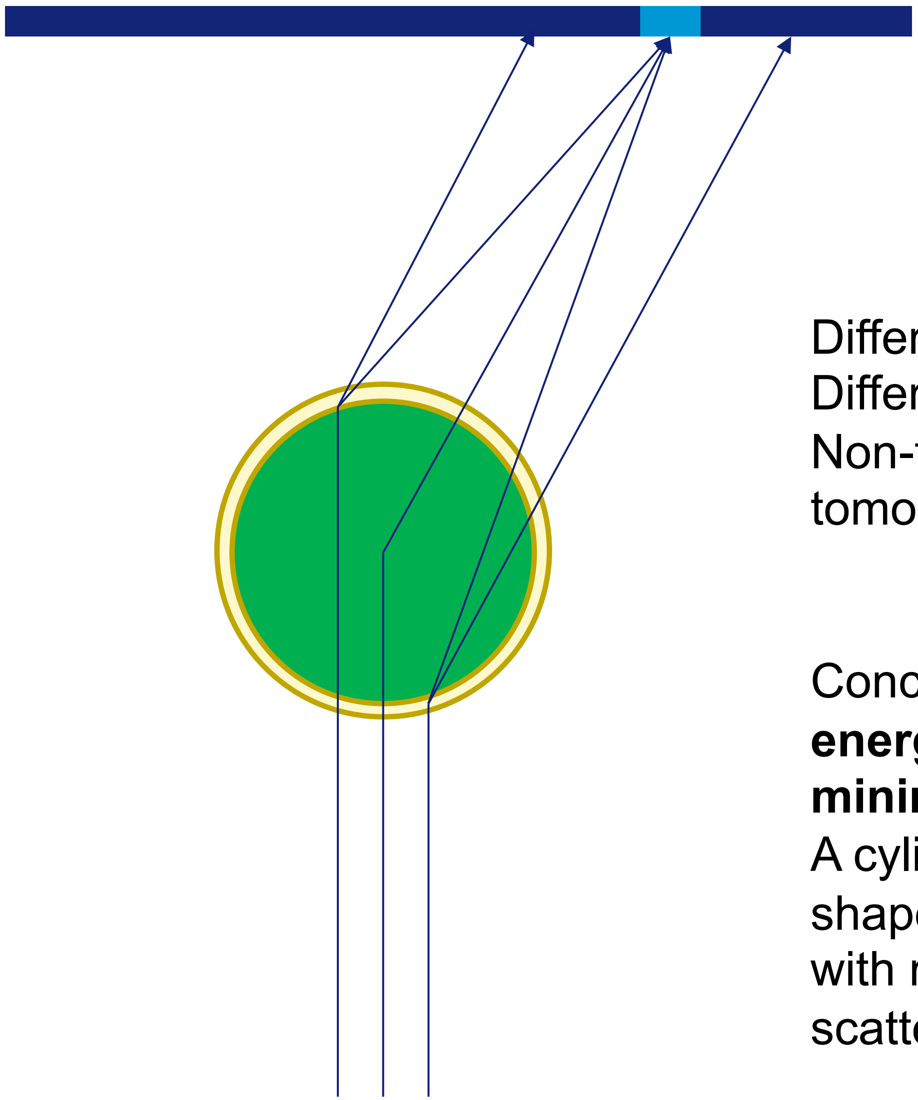
Resolution dependent on

- Pixel Size
- Sample – Detector Distance
- Beam Size
- Sample Size
- Detector Transparency
- Intrinsic Broadening

Conclusion:

For a given Q-range, best to use **Higher Energy/further distance**

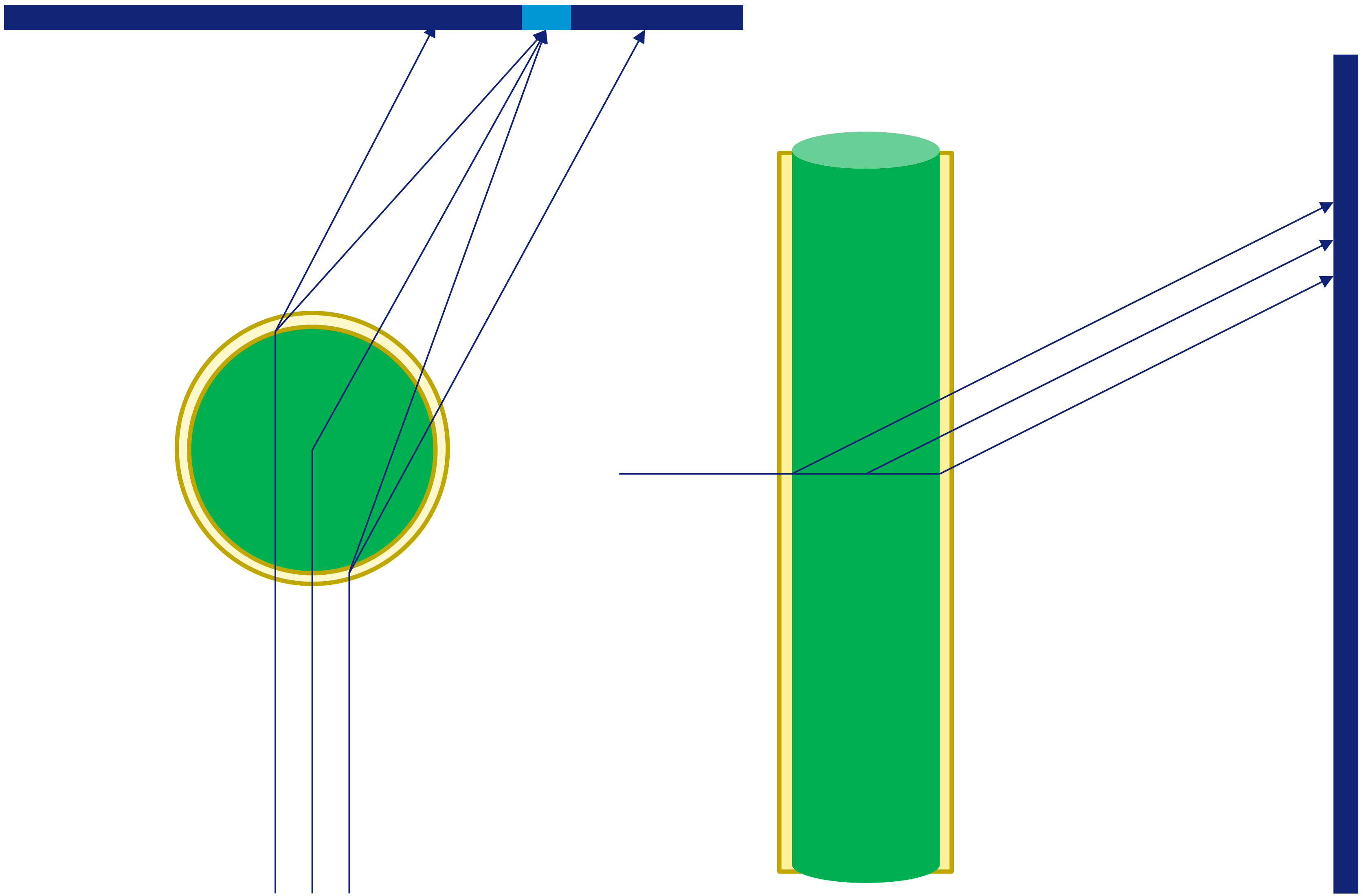
EFFECTS OF SAMPLE GEOMETRY – ABSORPTION



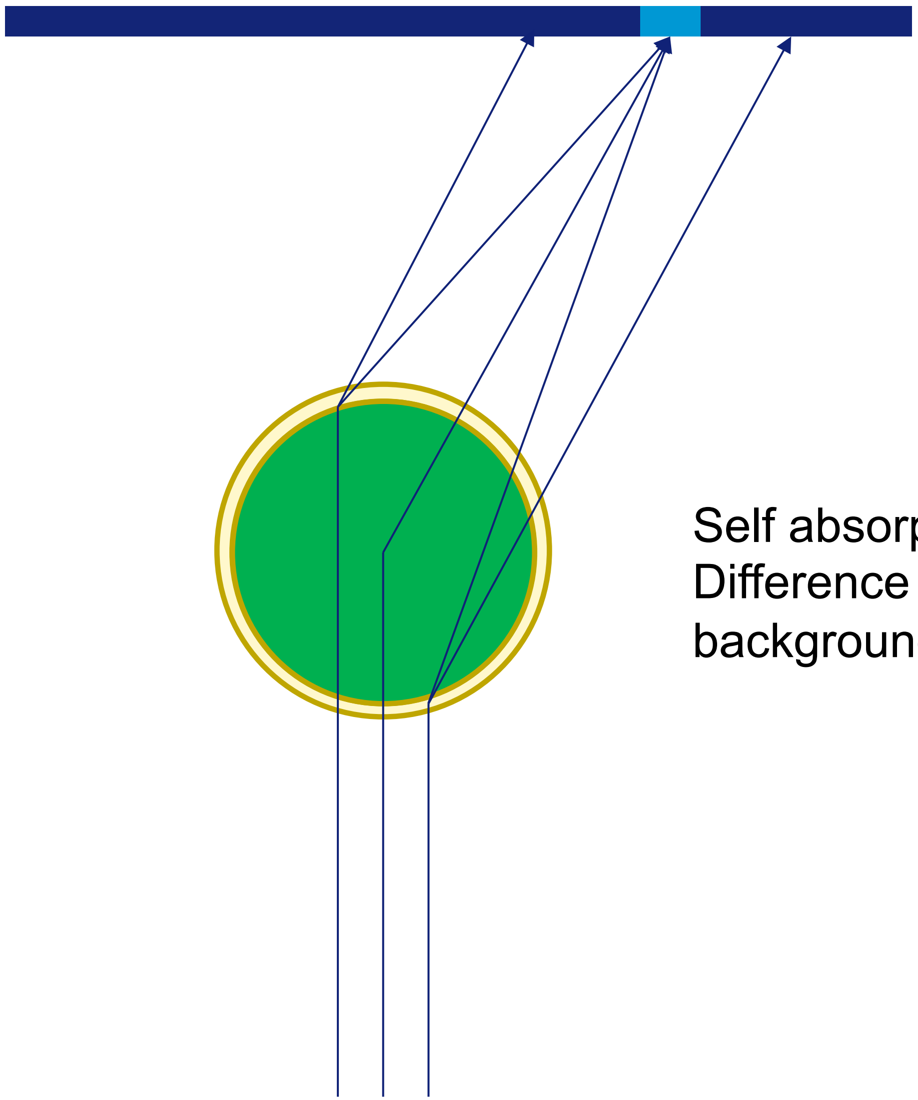
Different rays have different path lengths
Different angles have different signals
Non-trivial absorption correction (needs tomographic reconstruction)

Conclusion: **Use high enough energy/thin enough sample to minimize absorption**
A cylindrical capillary is not a good shape for use with 2d detectors (also with respect to in-plane/out-of-plane scattering)

EFFECTS OF SAMPLE GEOMETRY – 2D CASE



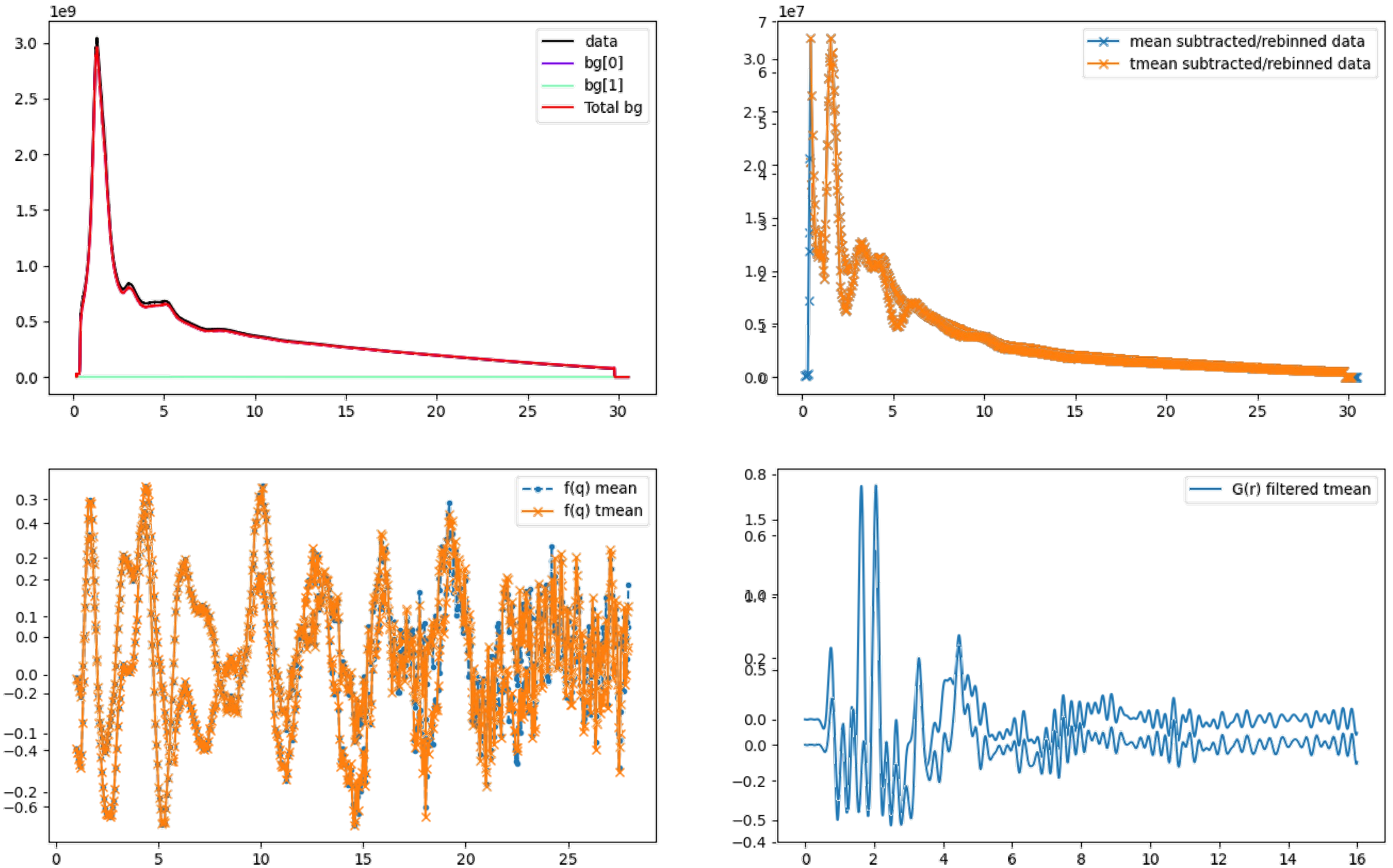
EFFECTS OF SAMPLE GEOMETRY – BACKGROUND SUBTRACTION

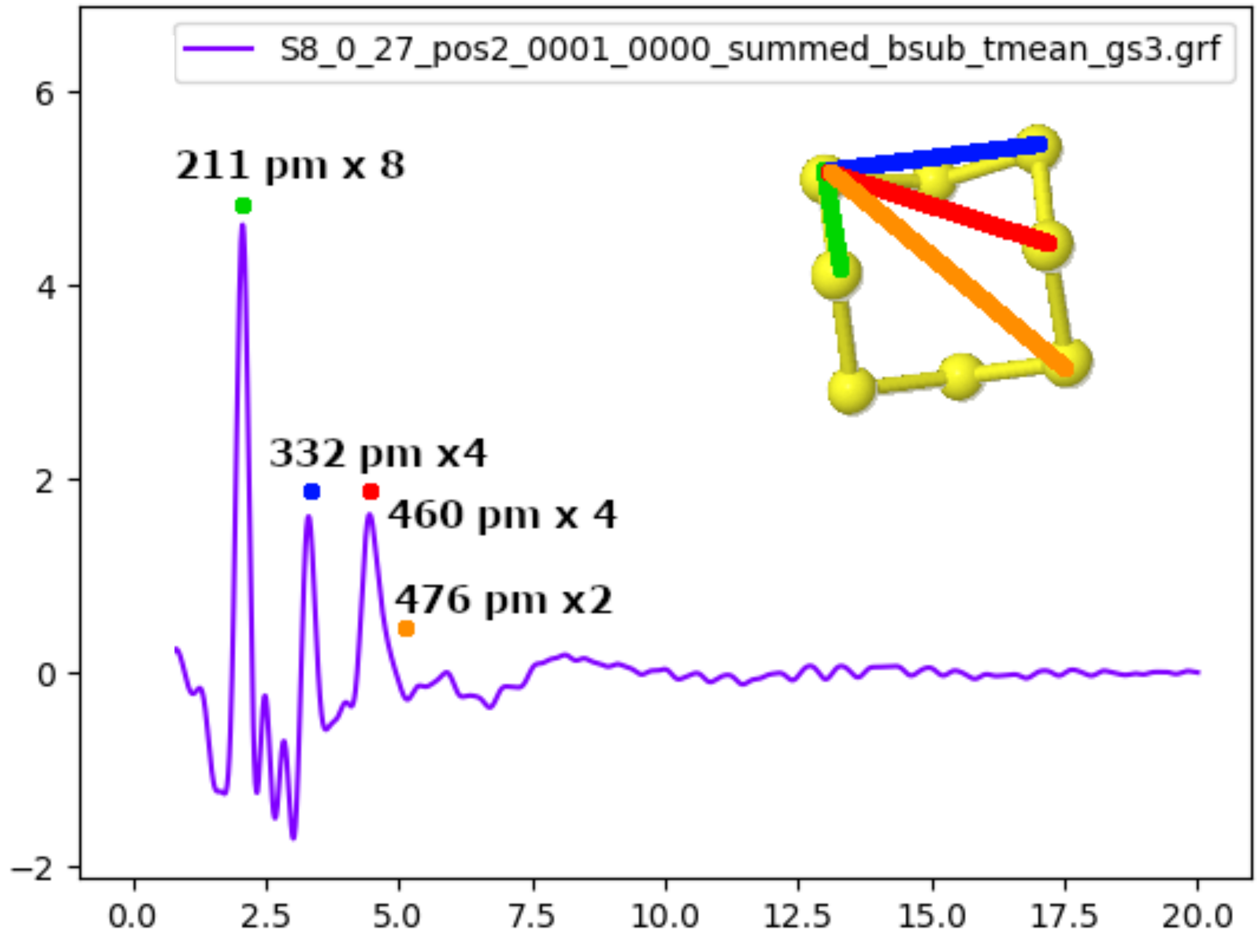


Self absorption affects background subtraction
Difference pattern will slightly over-subtract background contribution

CAREFUL BACKGROUND SUBTRACTION

0.3 mol/L S_8 in Toluene





S8_0_27_pos2_0001_0000_summed_bsub_tmean_gs3.grf
211 pm x 8
332 pm x4
460 pm x 4
476 pm x2
6
4
2
0
−2
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0

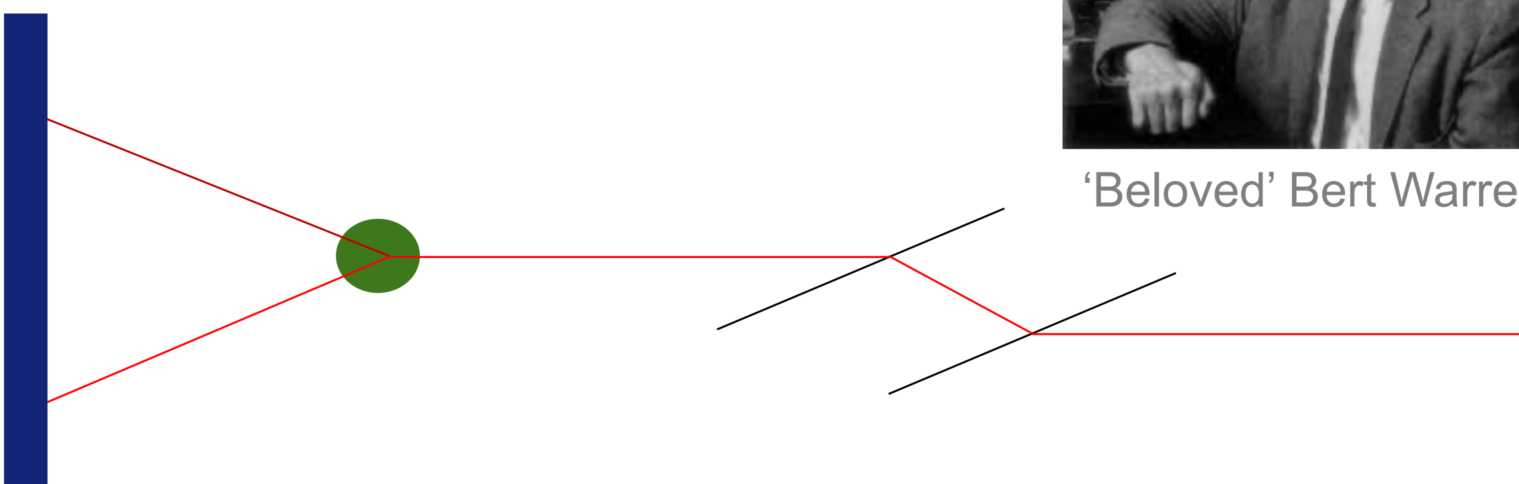
POLARIZATION CORRECTOIN

Polarization correction depends on

- **Scattering angle**
- **Azimuthal angle (synchrotron plane polarized)**
- **Optical and sample configuration**
  - Every scattering event affects the polarization
  - Right/left symmetry broken by sample scattering

Every talk on powder diffraction must feature this picture of me

'Beloved' Bert Warren



EFFECT OF SAMPLE GEOMETRY

Sample Geometry affects

- Angular Resolution
- Absorption correction
- Background subtraction

Convolution of (rapidly-varying) scattering pattern means that a proper treatment would require ray-tracing (algebraic reconstruction)

Achievable but not in general plausible

- Tomographic data collection
- Iterative computation

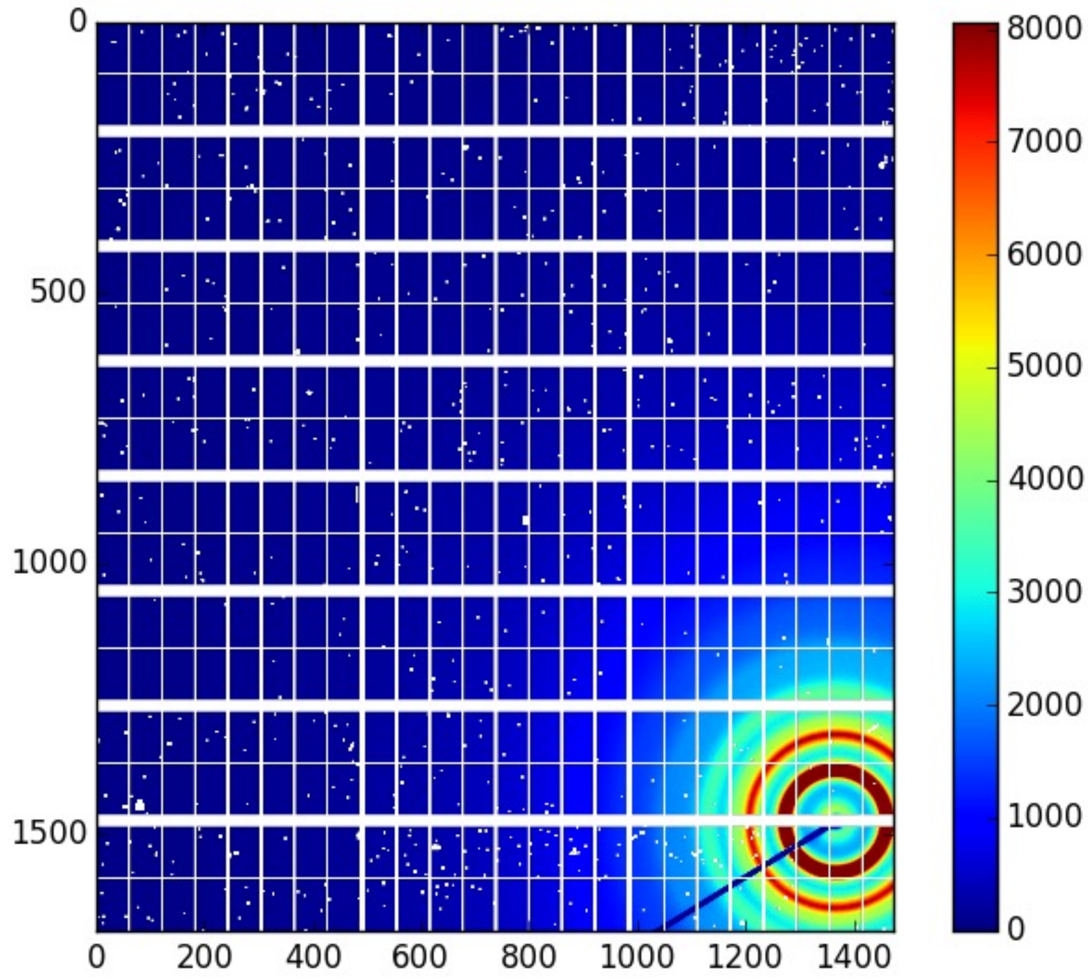
Precise polarization correction difficult to implement

- This can be seen with noiseless detectors and good statistics at high Q

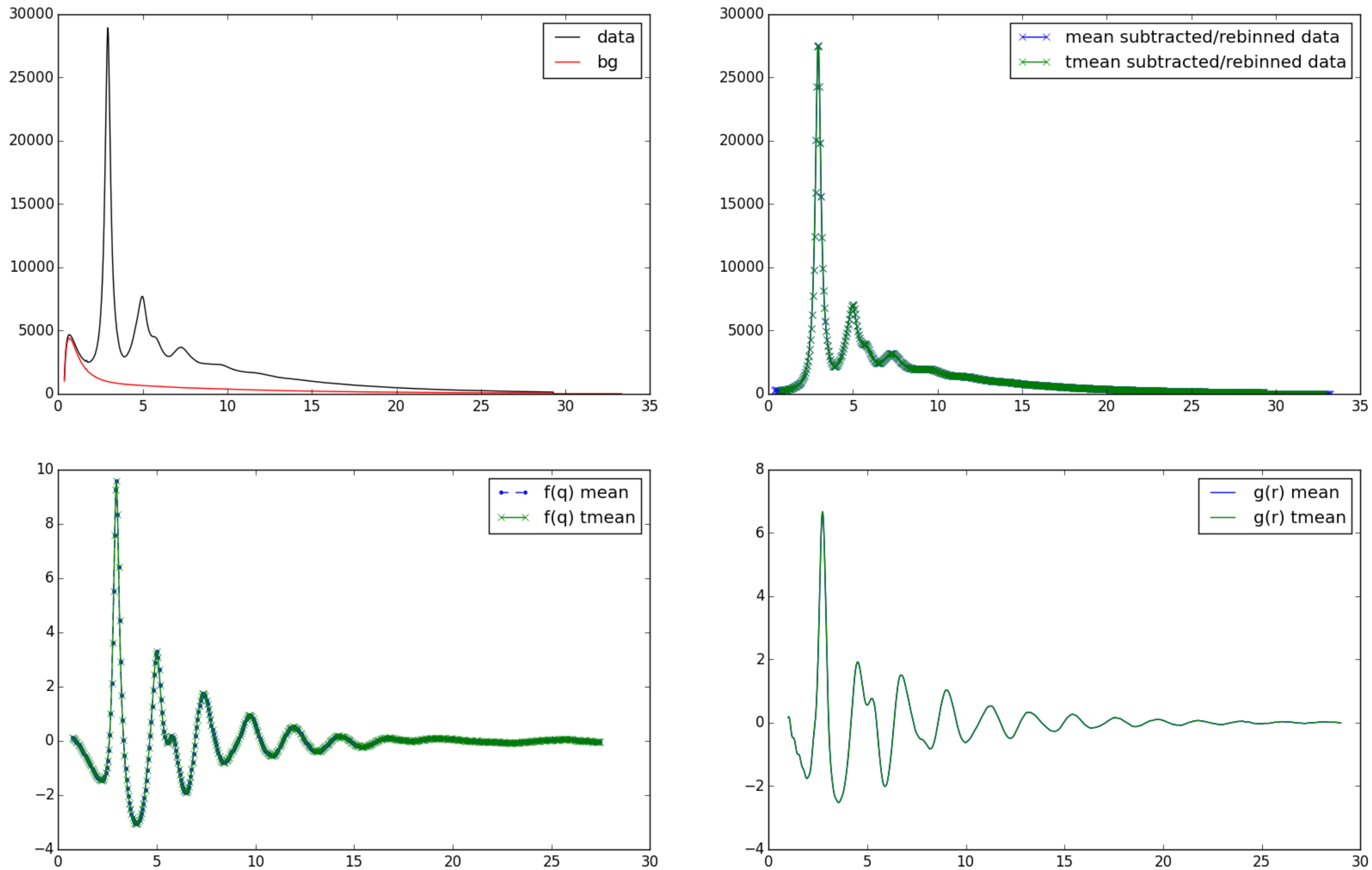
"Solution" ← i.e., work-around to hide the problems

- Use either 90 or 360 azimuthal degrees

EXAMPLE OF A BMG - MASKING

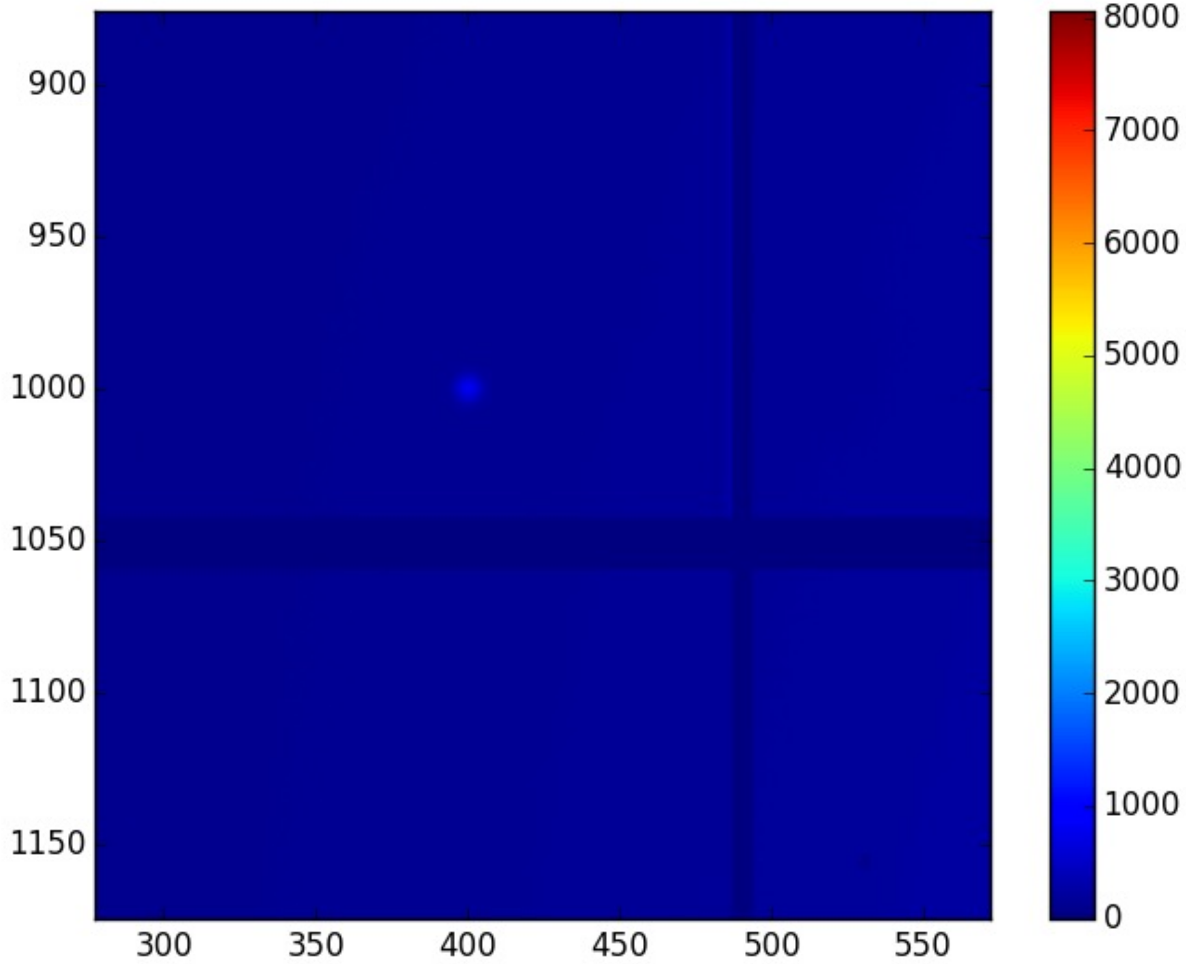


BMG

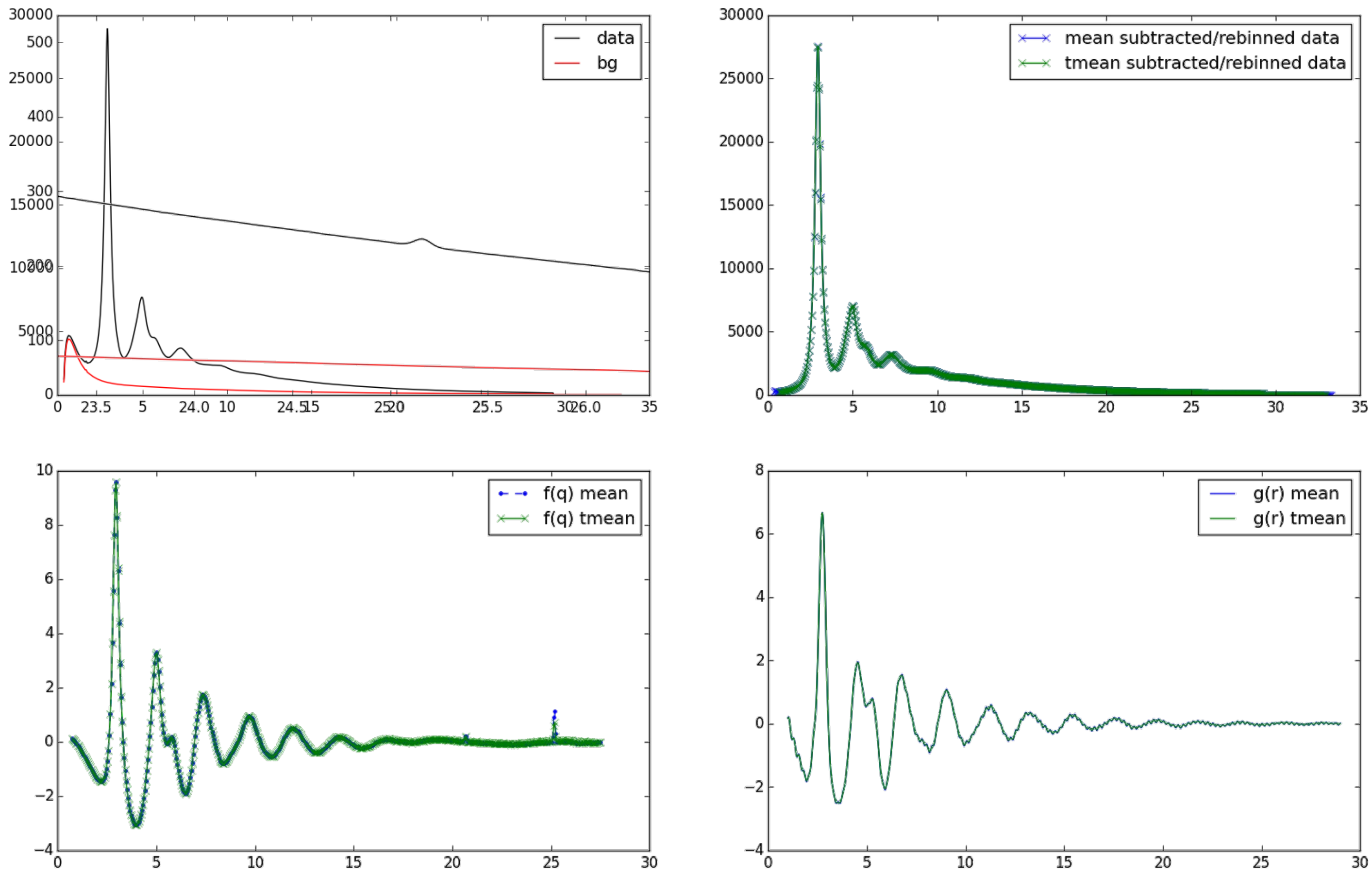


data
bg
mean subtracted/rebinned data
tmean subtracted/rebinned data
f(q) mean
f(q) tmean
g(r) mean
g(r) tmean

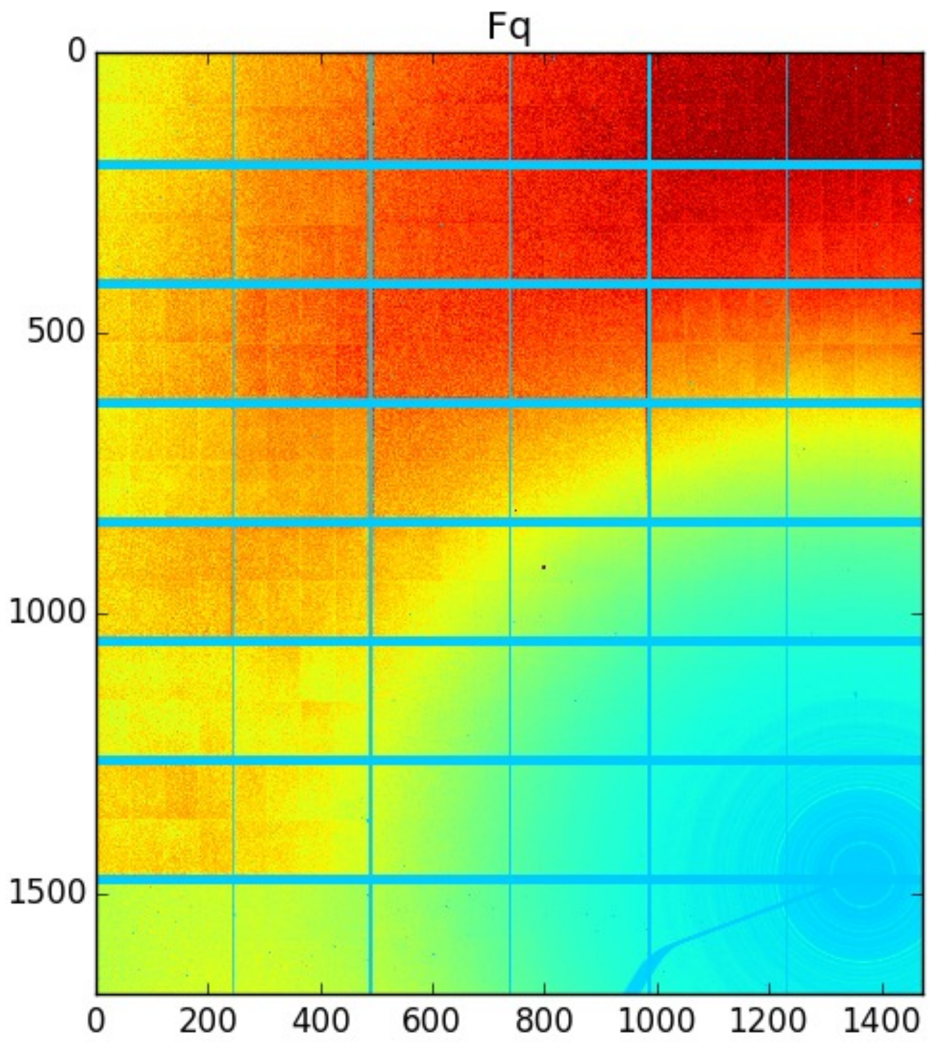
EFFECT OF NOISE ON G(R)



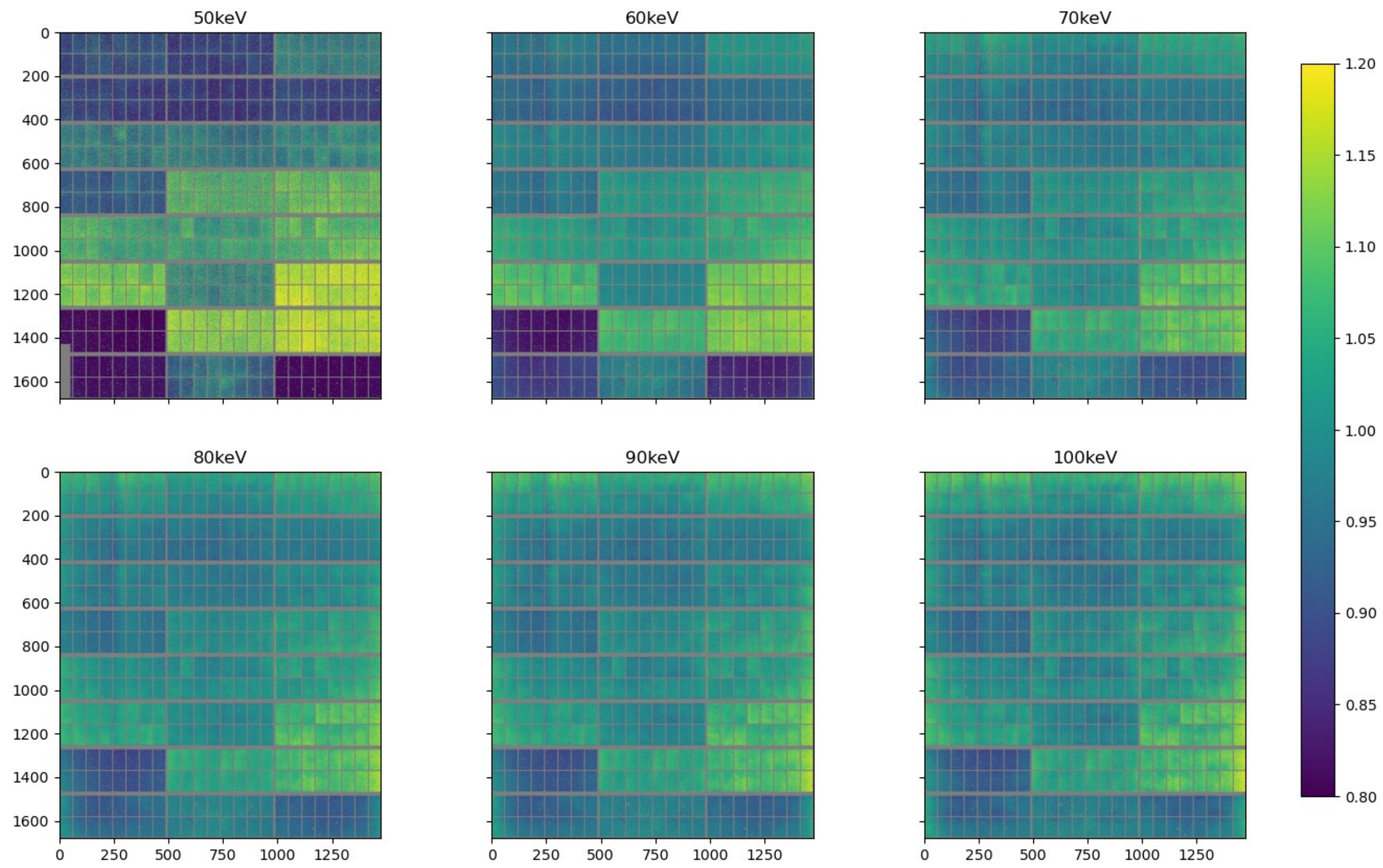
EFFECT OF NOISE ON G(R)



THE DREADFUL F(Q) ISSUE

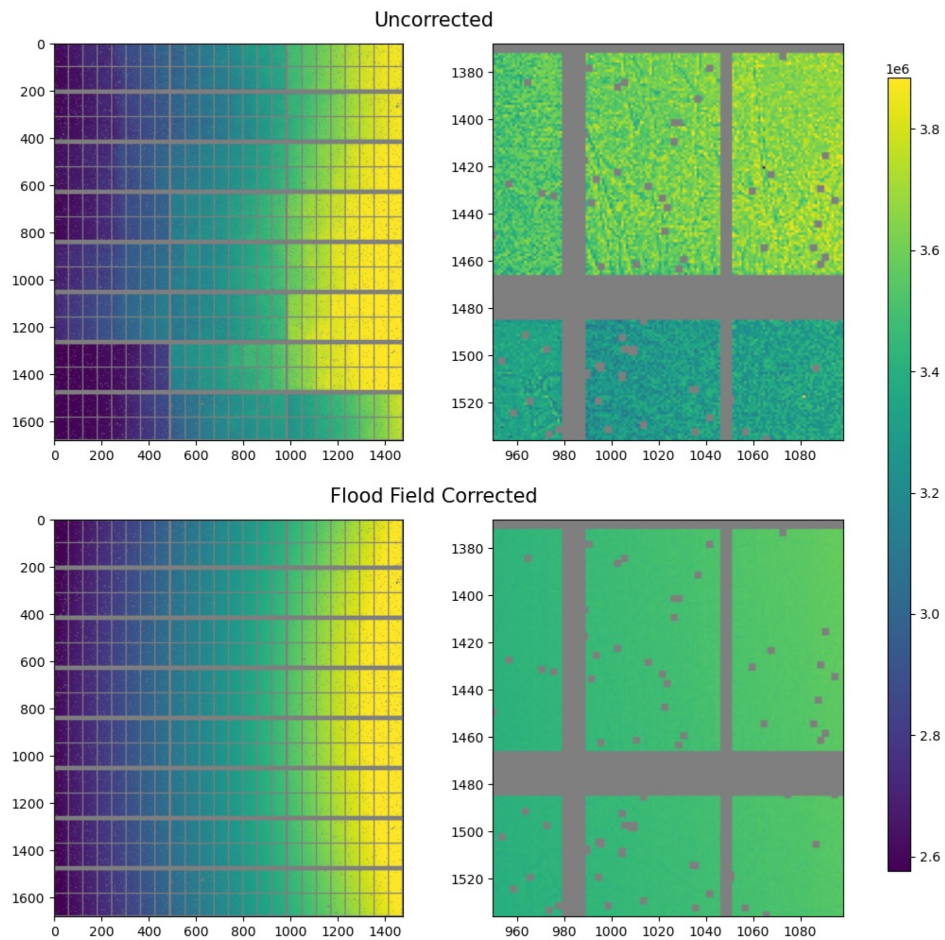


FLOOD FIELD

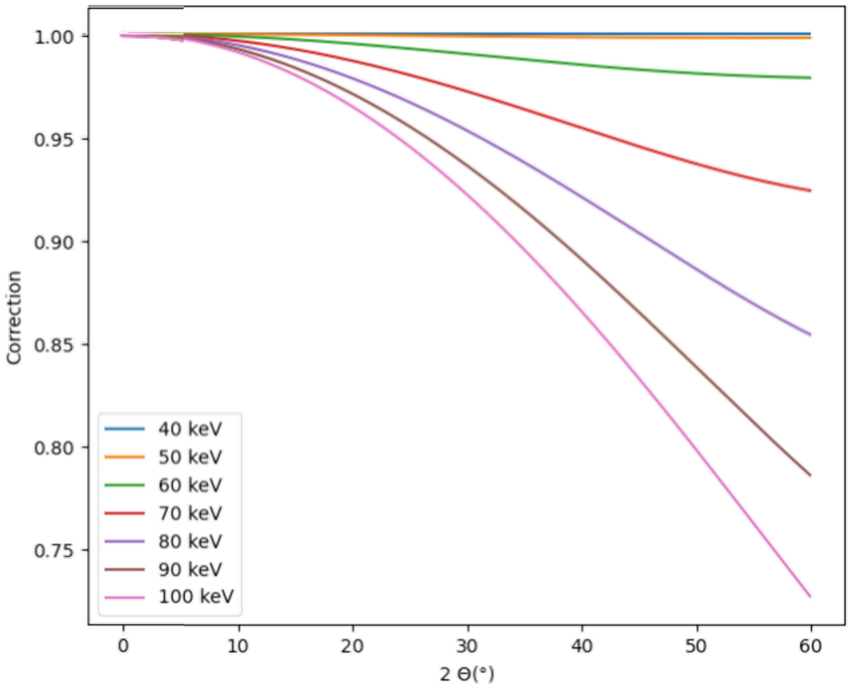


50keV
60keV
70keV
80keV
90keV
100keV
0
200
400
600
800
1000
1200
1400
1600
0
250
500
750
1000
1250
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
0.80

FLOOD FIELD

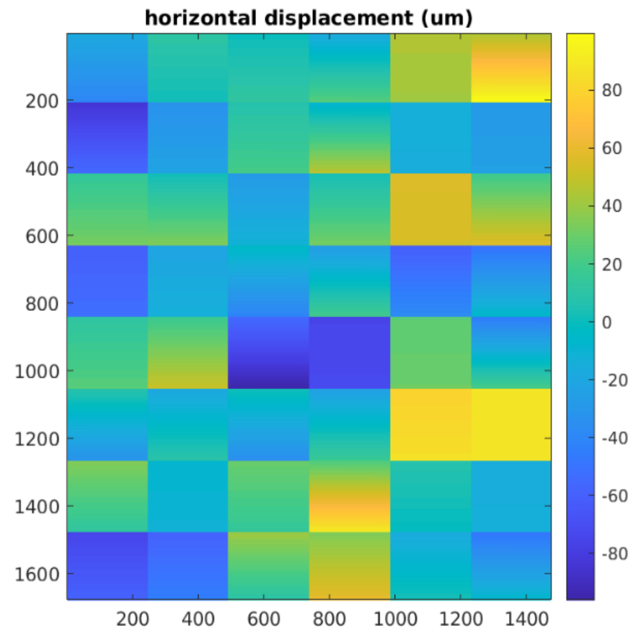


Detector transparency



The precise correction would consider the path length in adjacent pixels, but this effect is swamped by others

Module Misalignment

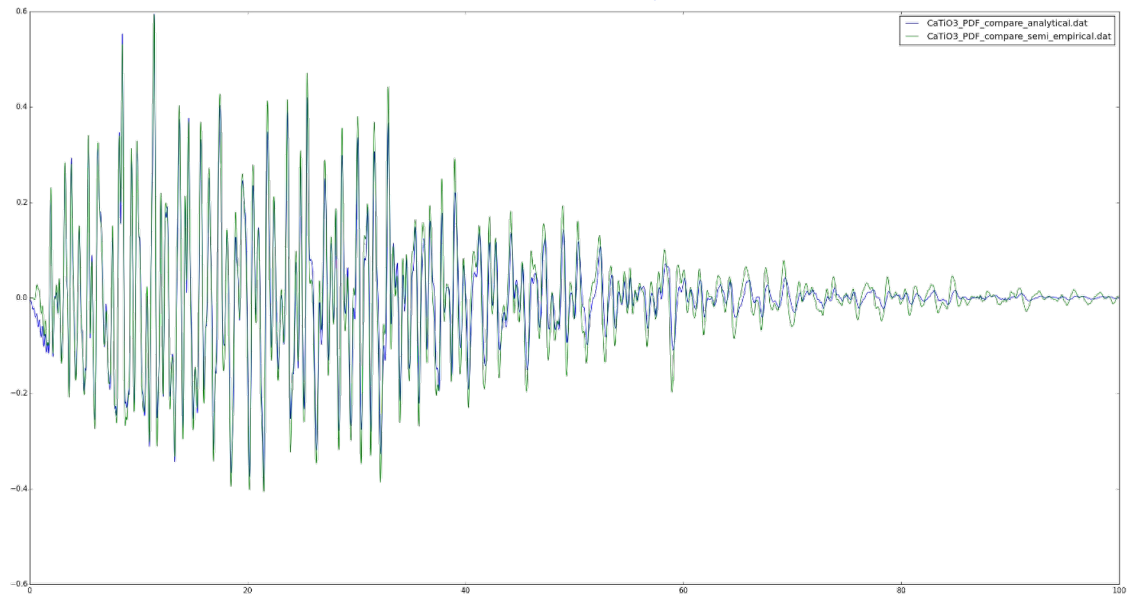


Other sorts of detectos (i.e., fibre-optic coupled CCD cameras) have spherical abberation

ANALYTICAL VS. SEMI-EMPIRICAL BACKGROUND SUBTRACTION

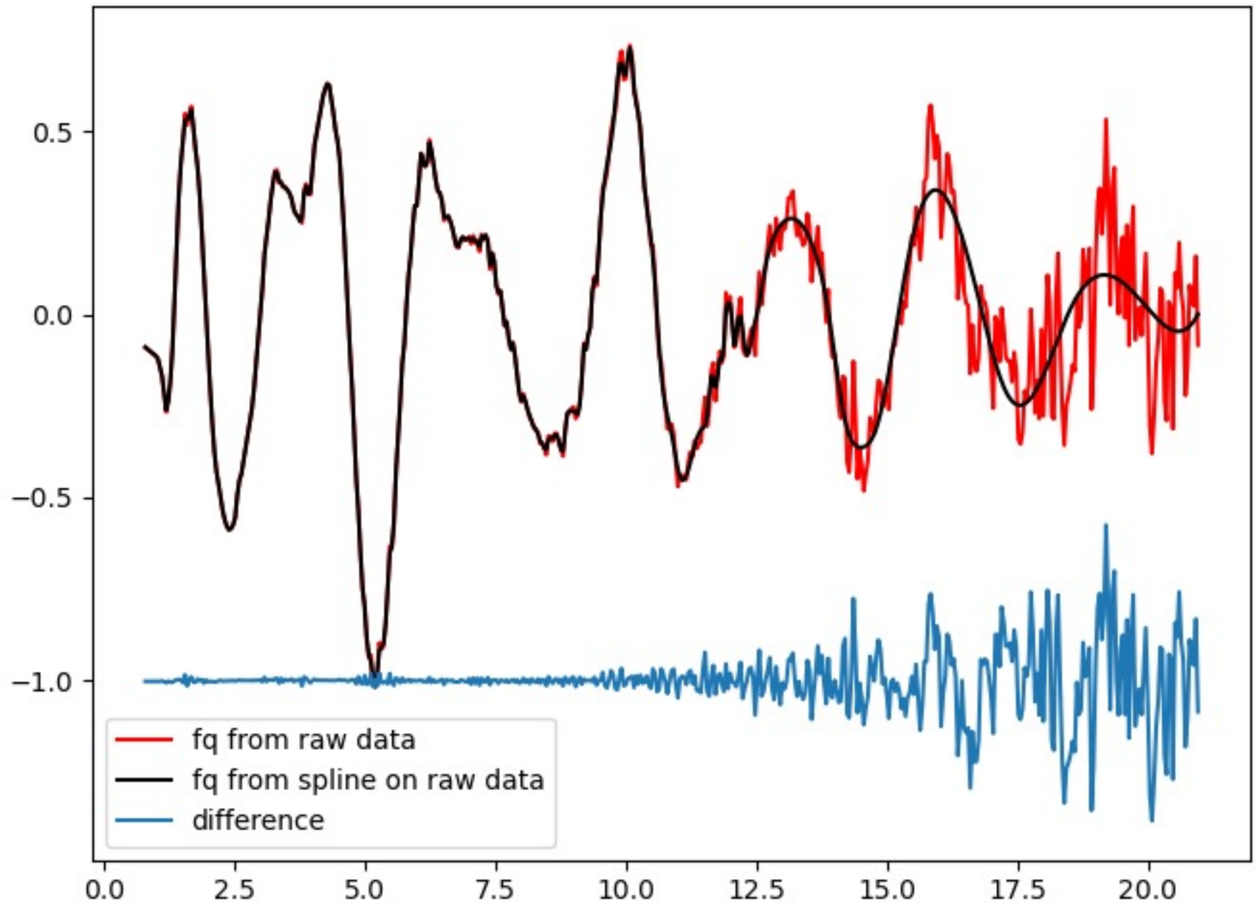
Inelastic Backgrounds can be subtracted by either

- **Analytical**
  - Correct form calculated and removed
- **Semi-Empirical**
  - Polynomial or spline representation for the effects
  - Form of the function respects analytical form

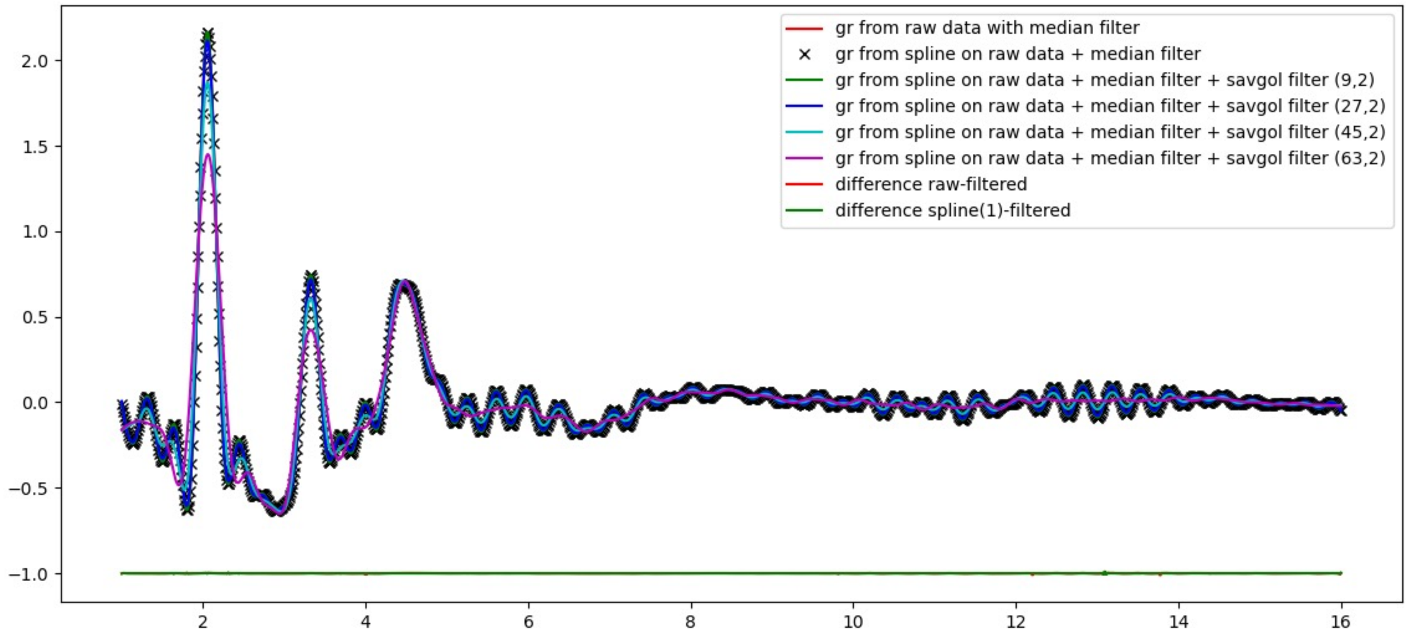


- Backgrounds (Compton) from detectors with energy cutoff can be difficult to model
- 10^6 diffraction patterns can be time consuming to model

EXTRACT G(R) FROM SPLINE ON RAW DATA

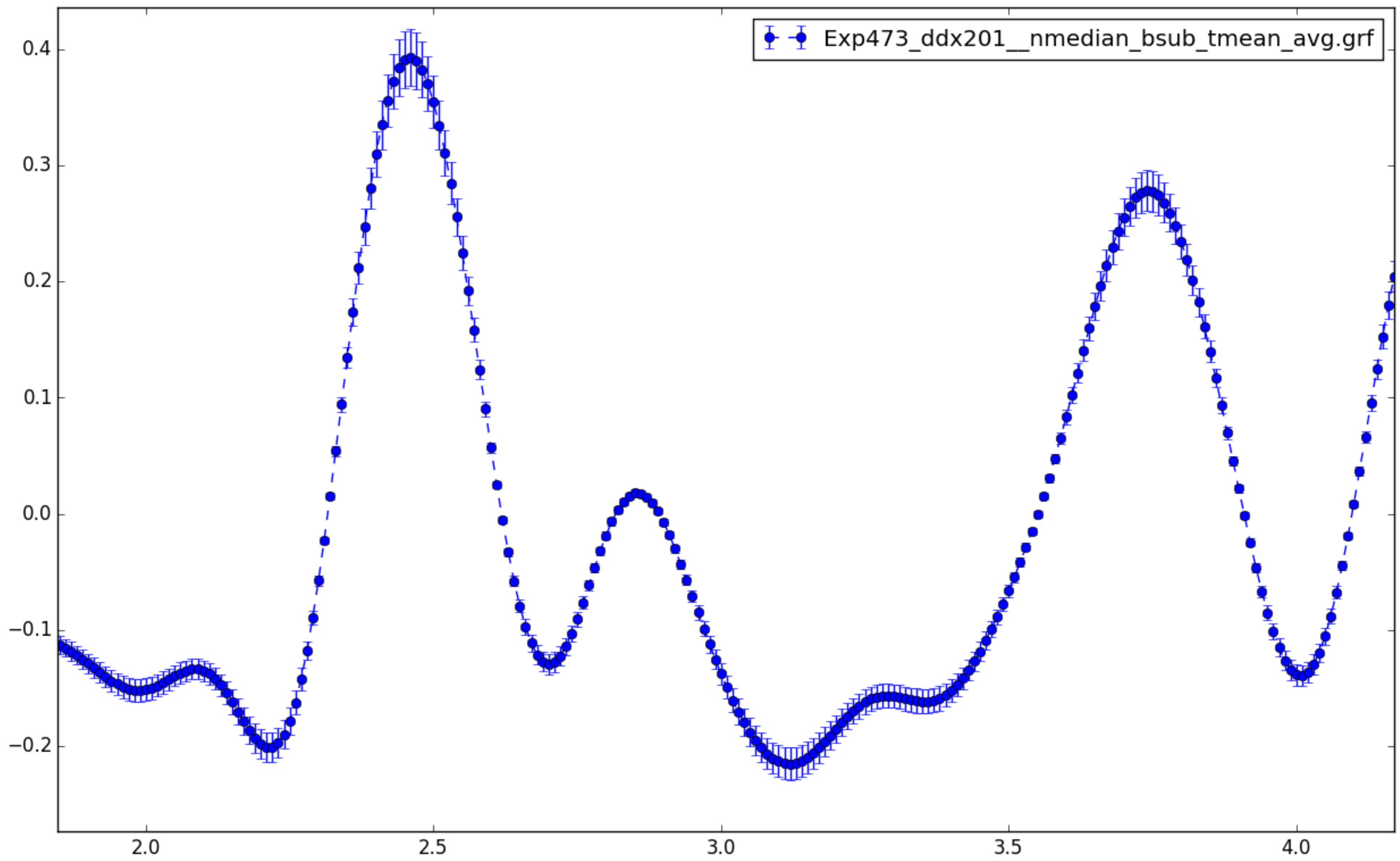


FILTER ON G(R)



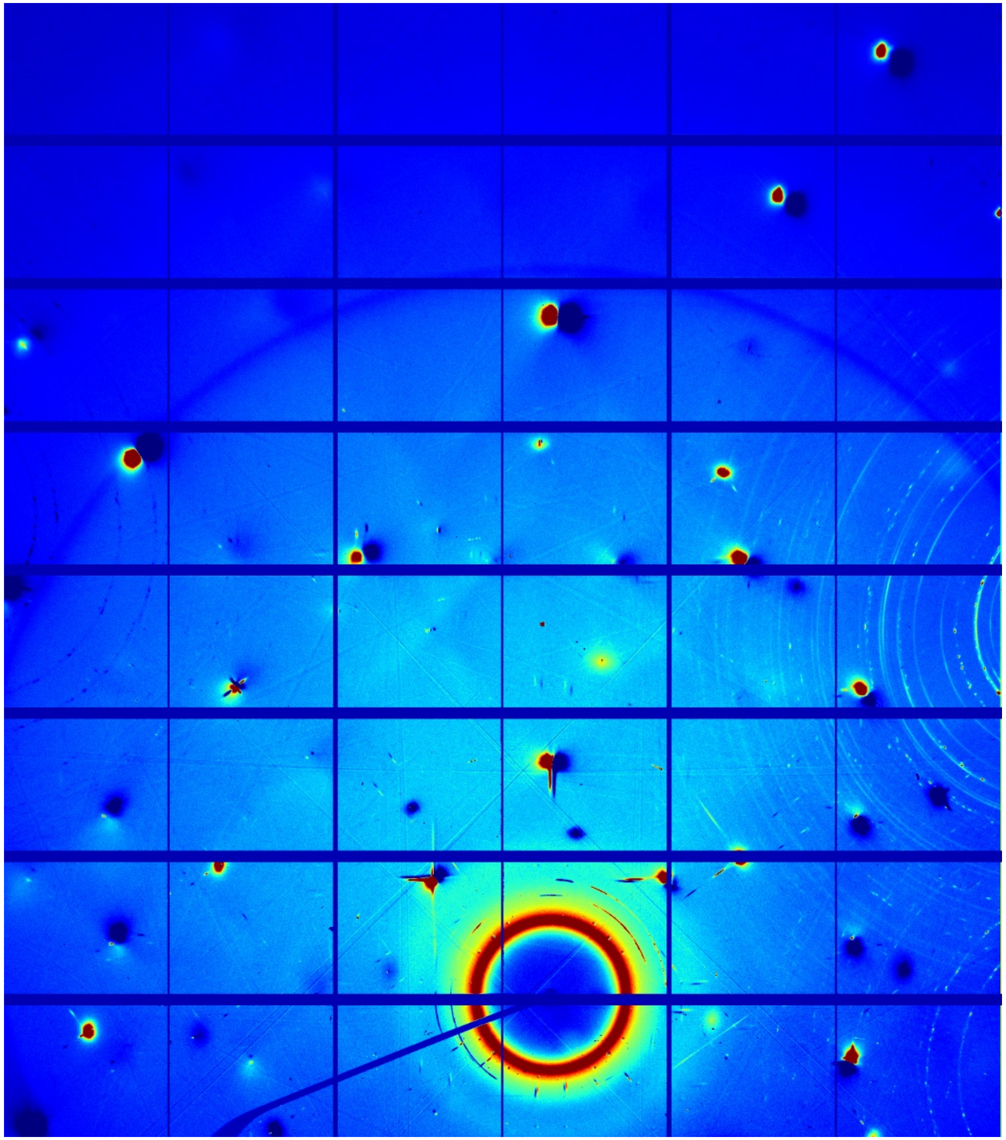
Savitzky-Golay filter of proper width

G(R) UNCERTAINTIES

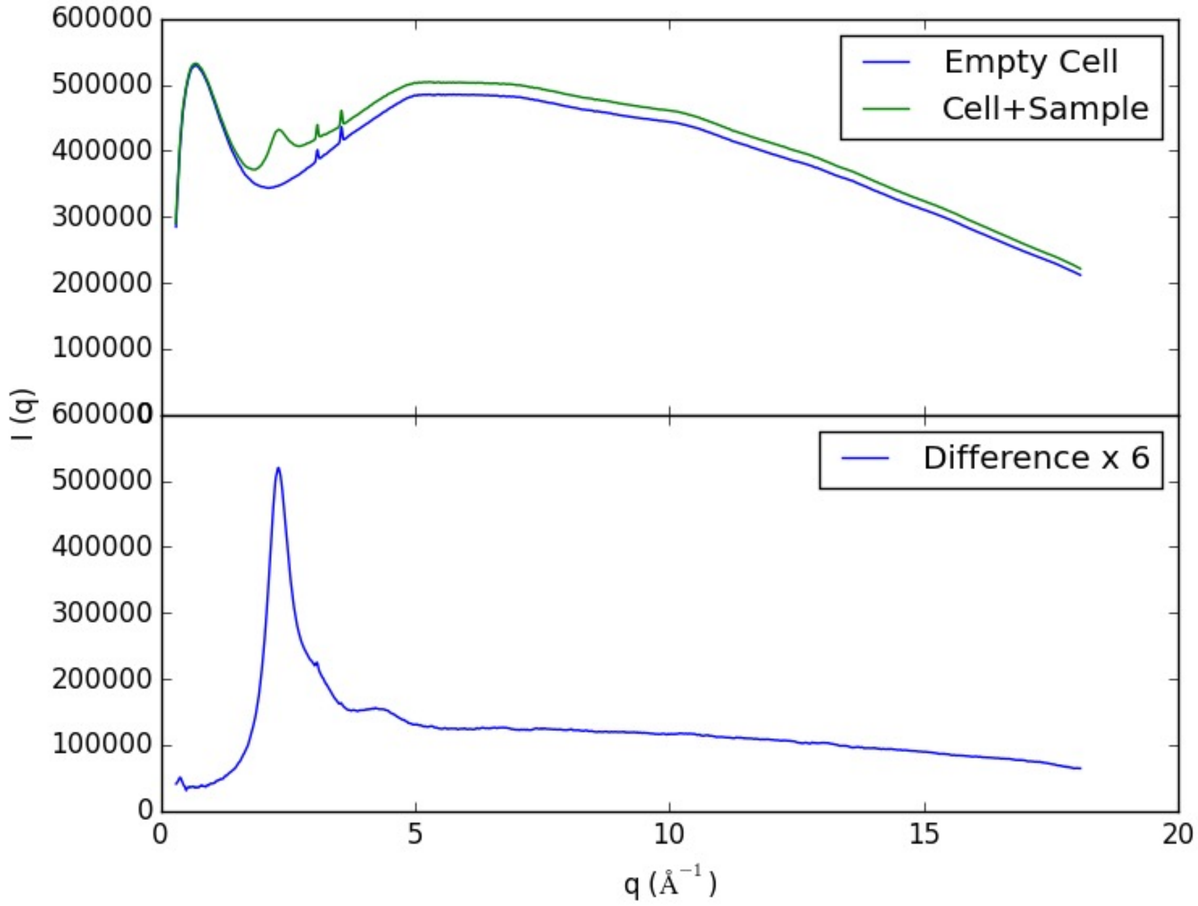


Calculate statistics on G(r) from repeated measurments or weighted simulations

PDF IN DIFFICULT CIRCUMSTANCES

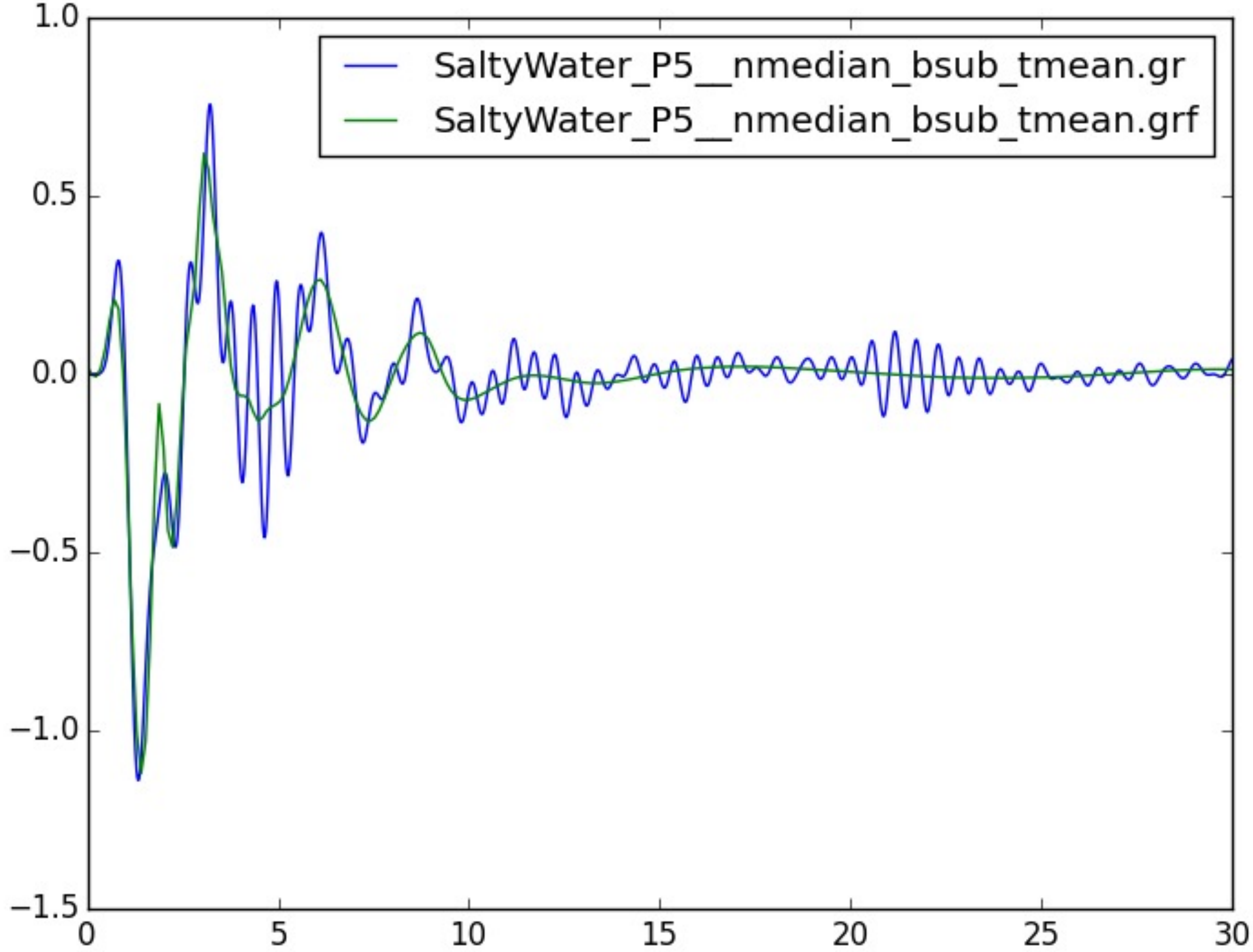


PDF IN DACS

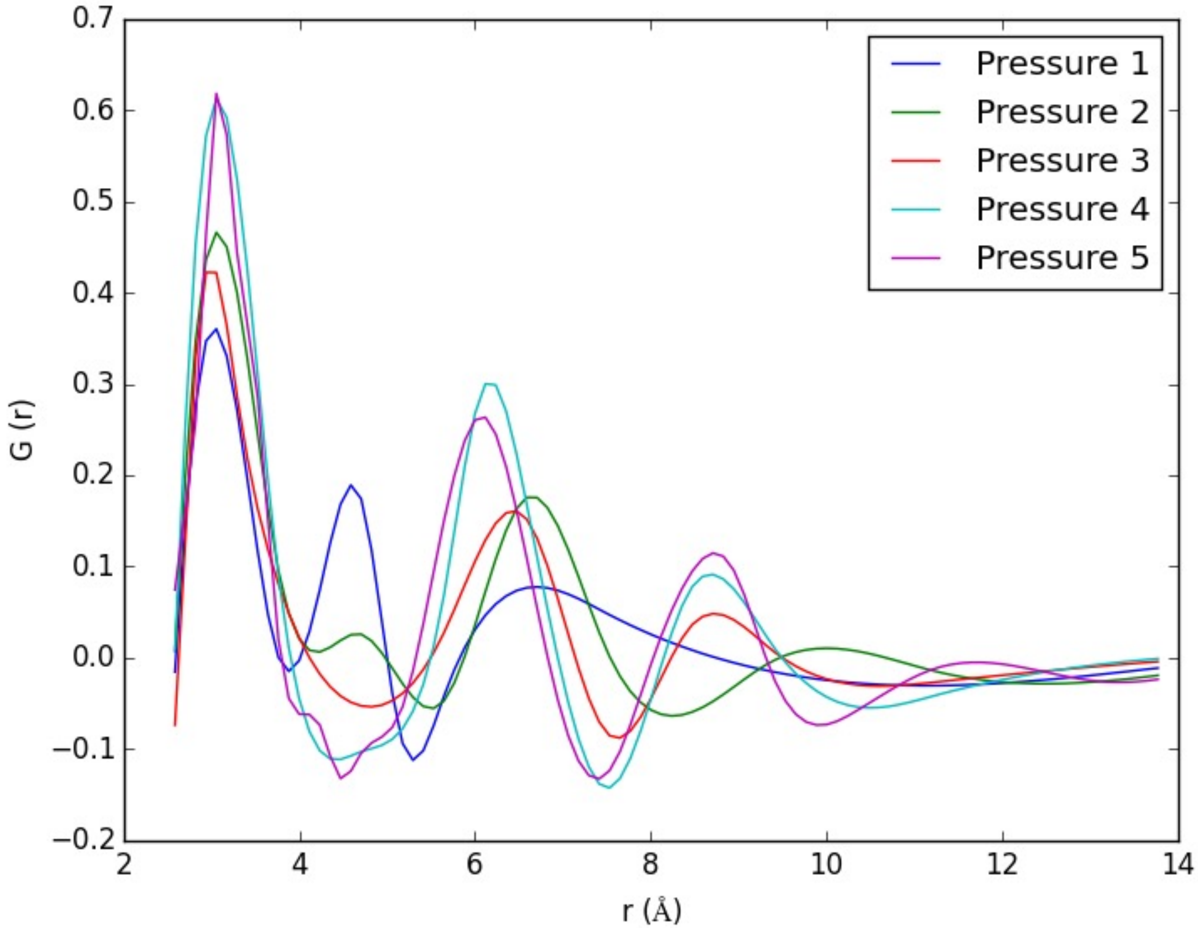


Signal from the material of interest is a small fraction of the total signal

SPLINES TO DATA

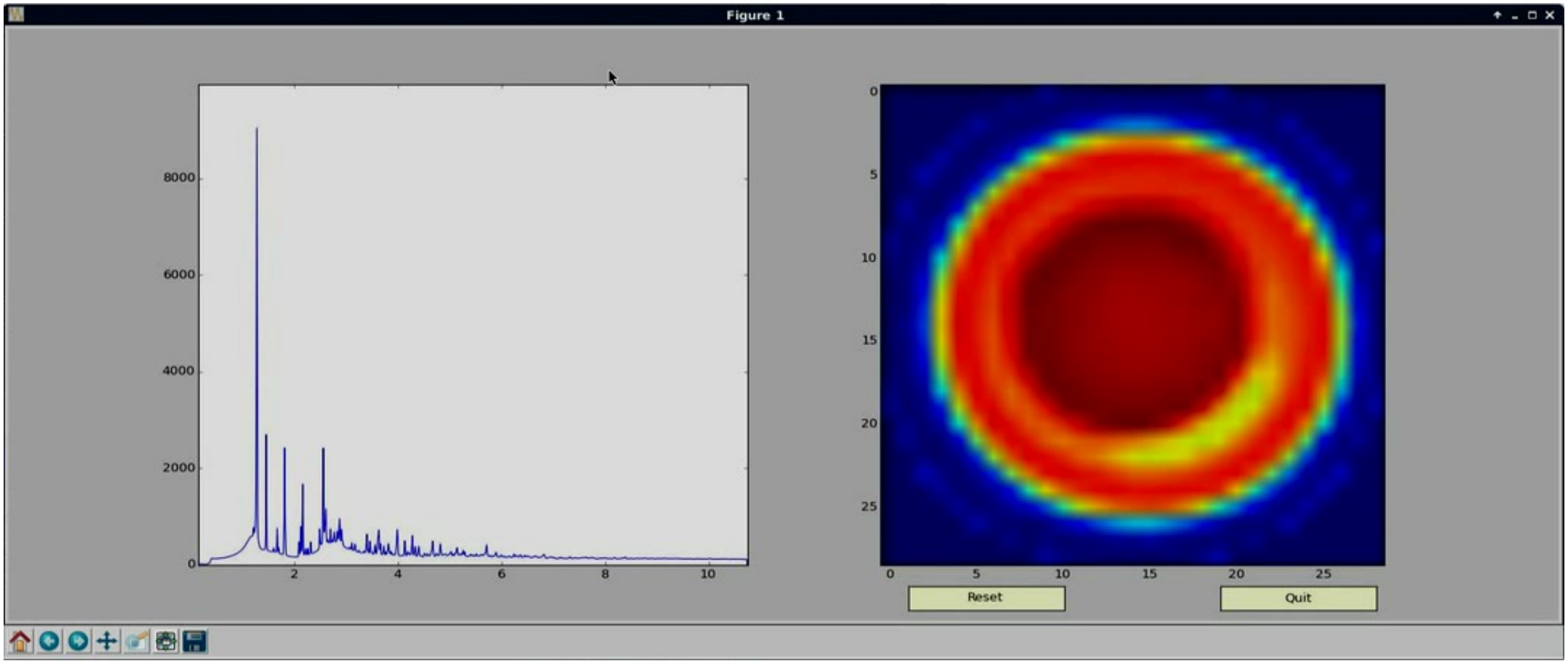


PDF OF SALTY WATER IN A DAC



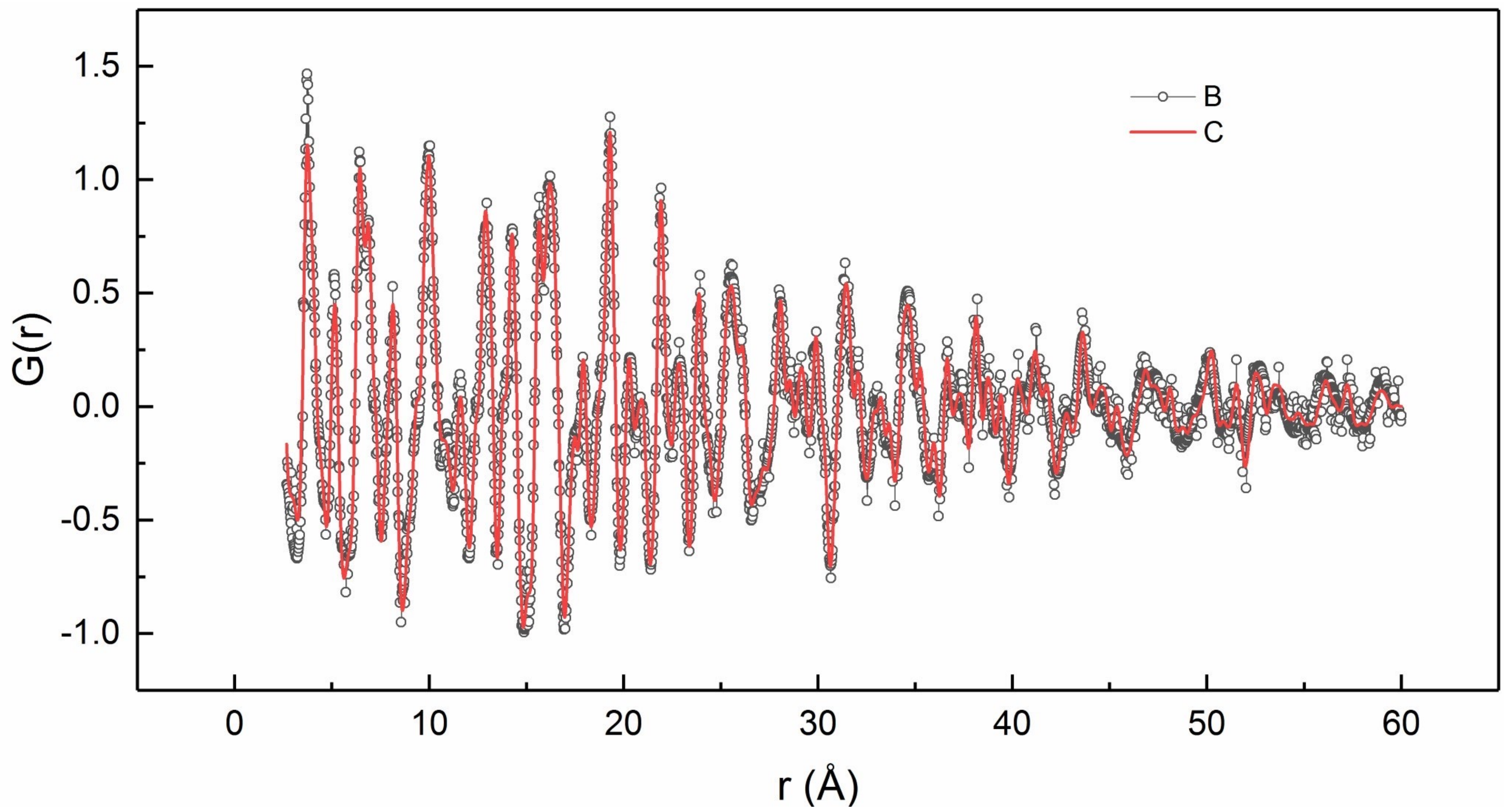
Clear changes in local environment can be seen with pressure

3D RECONSTRUCTION OF WORKING BATTERY



Liu et al, submitted to Nature Comm.

FIT TO G(R) IN RECONSTRUCTED VOXEL (6 PHASES/MORPHOLOGIES)



Wragg et al. PCCP in press

CONCLUSION

- **Every new advance in data quality reveals new problems to resolve**
- **Data quality from 2d detectors is now approaching that of point detectors/analyser crystal**
  - ms resolution is now possible
  - Sub-micron resolution already achieved