Argonne NATIONAL LABORATORY

GIXS: hands-on data analysis

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Beamline 8-ID-E

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Advanced Photon Source

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AMERICAN CRYSTALLOGRAPHIC ASSOCIATION ANNUAL MEETING

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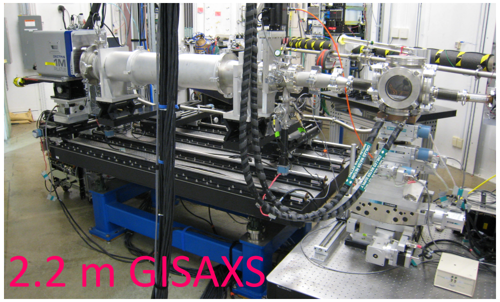
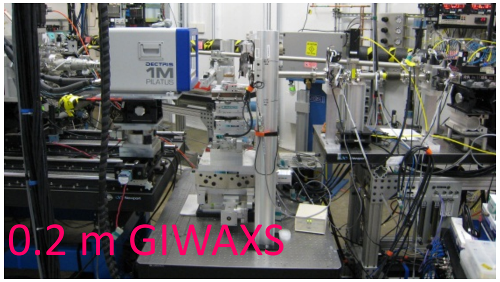
U.S. DEPARTMENT OF ENERGY

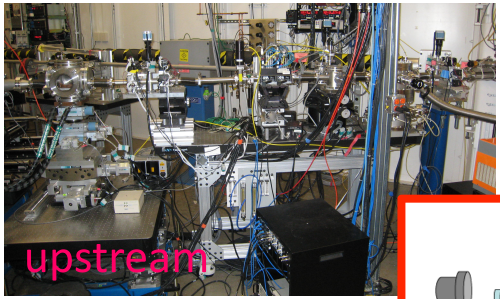
Outline

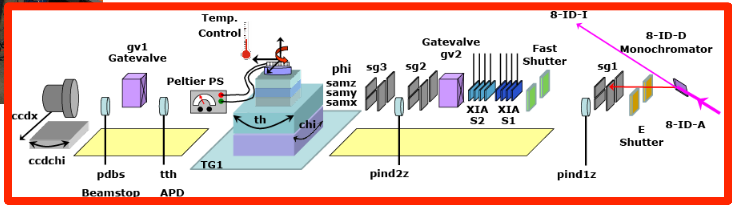
- GIXS at 8-ID-E of the APS
- GIWAXS by inspection: ordering and orientation
- GIWAXS linecuts: d-spacing and resolution
  - Also: paracrystallinity
- Different representations of GIWAXS data
- Determining texture and crystallinty
- Software: GIXSGUI
- Conclusions

GIXS at Beamline 8-ID-E of the APS









- Undulator-based (2 x APS Undulator A;)
- Single bounce monochromator (fixed E)
  - 7.35keV [Si(111)]
- No focusing, high q-space resolution
- Typical flux: 5×10^{10} photon/s 100 (h) x 50 (v) μm^2
- Transverse coherence length: 5 (h) x 140 (v) μm^2
  - XPCS with contrasts of ~40%
- GISAXS: Adjustable vacuum flight path length (1.5 – 2.2m) →qmax ≈ 0.14-0.2 $Å^{-1}$

- GIWAXS: mostly in air, 0.2 m, vacuum for thermal annealing (qz, qy < 2.2 $Å^{-1}$)
- Pilatus 1M fast option, 135 frames/sec
- High-resolution reflectivity for $q_z < 0.2$ $Å^{-1}$
- Sample environment
  - Vacuum sample chamber (-20 to 230 °C)
  - High-temperature oven (750 °C) in air
  - Humidity controlled chambers
  - Filmetrics UV for thickness monitor
- Liquid scattering geometry (tilt < 0.5°)
  - Langmuir trough

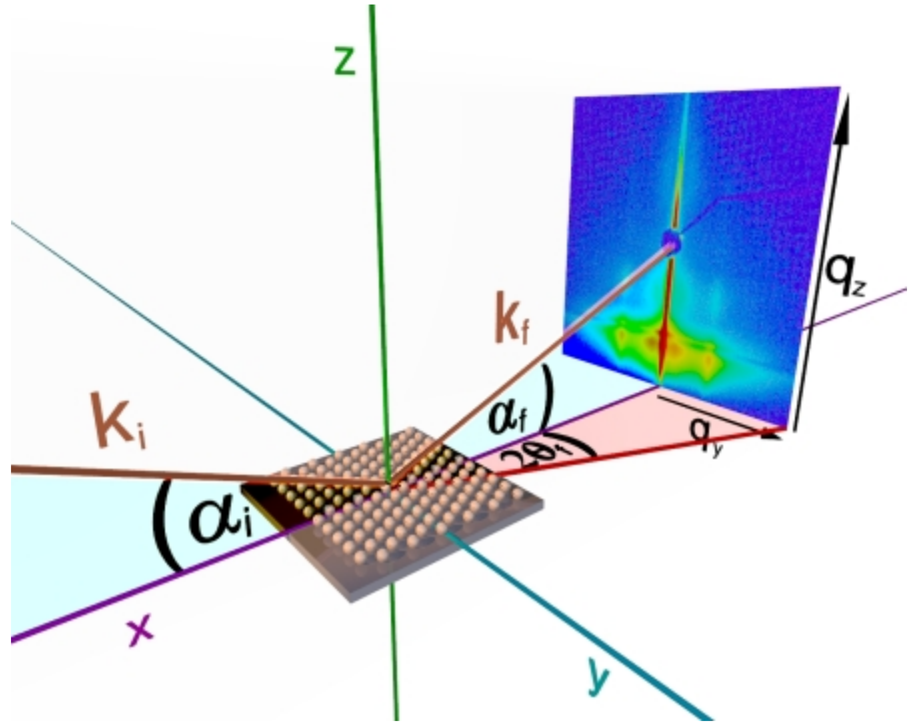
Z. Jiang, X. Li, J. Strzalka, *et al*; *J. Synchr. Rad.* **19** 627-636 (2012).

Grazing Incidence X-ray Scattering (GIXS) conventions

- area detector
- pixels ↔ q
- in-plane: q_y
- out-of-plane: q_z

Only for specular condition
$\alpha_f = \alpha_i$

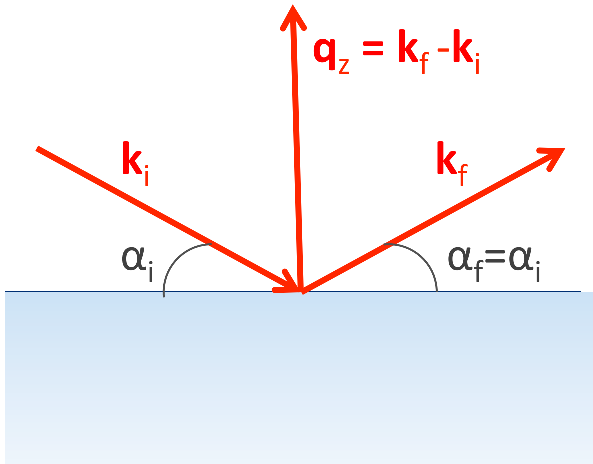
$$q_x = 0$$



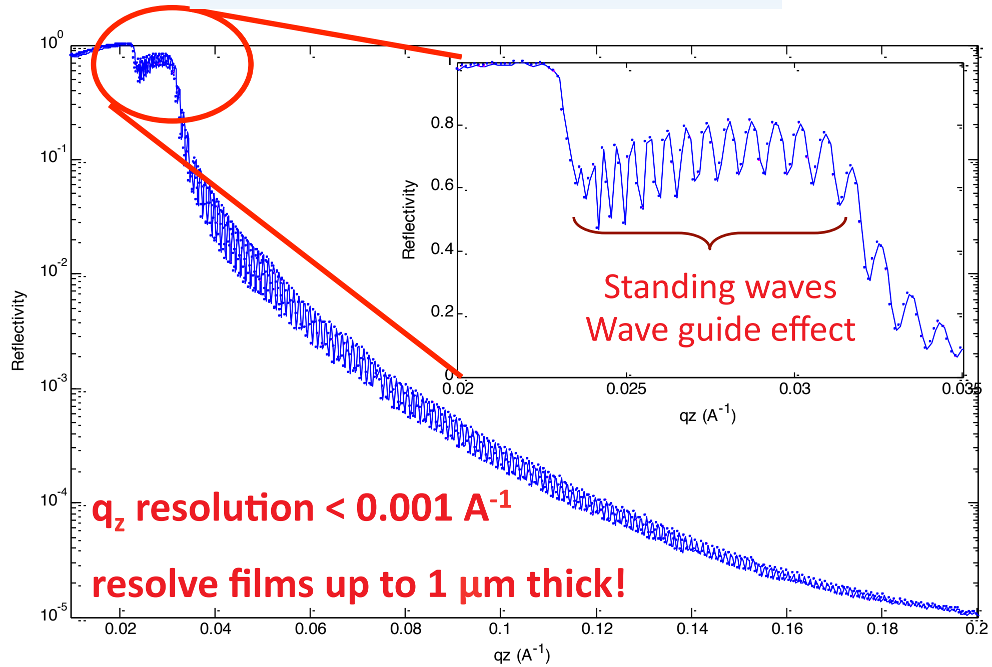
$$q_{x,y,z} = \frac{2\pi}{\lambda}\begin{bmatrix} \cos(\alpha_f)\cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f)\sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}$$

Images: Prof. Andreas Meyer, U. Hamburg,, www.gisaxs.de

8-ID-E also hosts high-resolution x-ray reflectivity

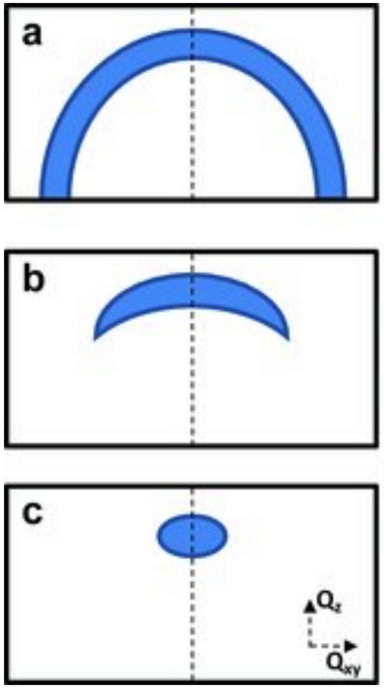


- Point detector and collimation measure strictly along $q_z = (4\pi/\lambda)\sin(\alpha)$
- Resolution constant over entire q-range



- Reflectivity from a ~800nm polymer film supported on Si
- Total external reflection occurs at small angles (grazing incidence)
  - One critical angle for the polymer film α_{cp}
  - One critical angle for the Si support α_{cSi}
  - GIXS usually $\alpha_{cp} < \alpha_i < \alpha_{cSi}$ (penetrate thin film but not substrate → surface sensitivity)

GIWAXS by Inspection: Ordering

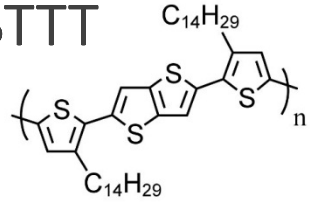


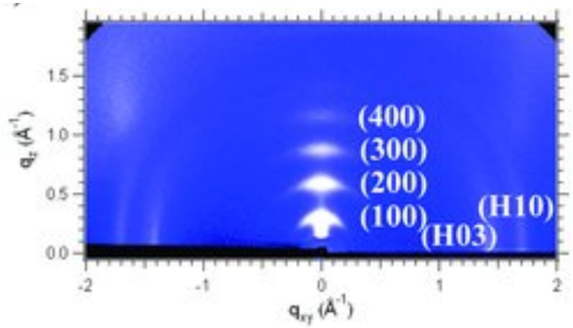
isotropic

textured/oriented
with broad distribution

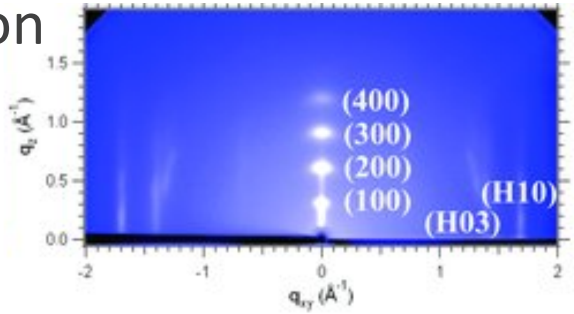
highly-oriented

GIWAXS from pBTTT





as cast

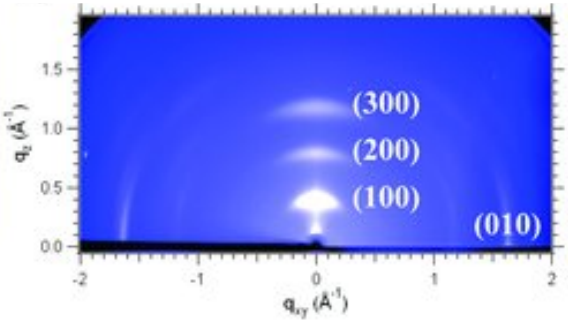


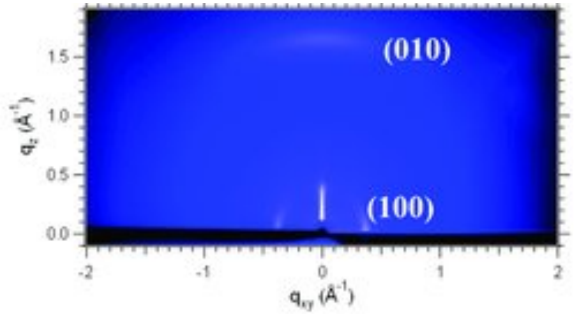
annealed

Adapted from DeLongchamp, Kline, Fisher, Richter, and Toney, *Adv. Mater.* **23** 319-337 (2011).

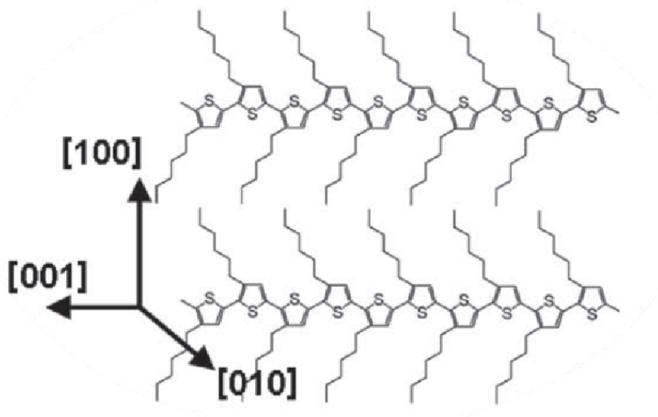
GIWAXS by Inspection: orientation

P3HT GIWAXS

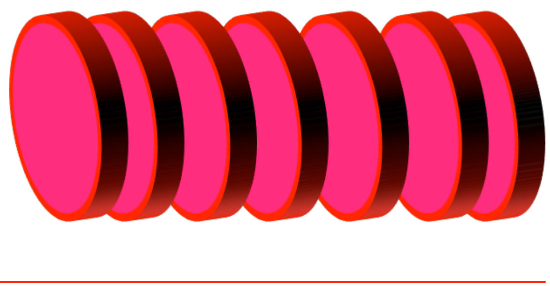




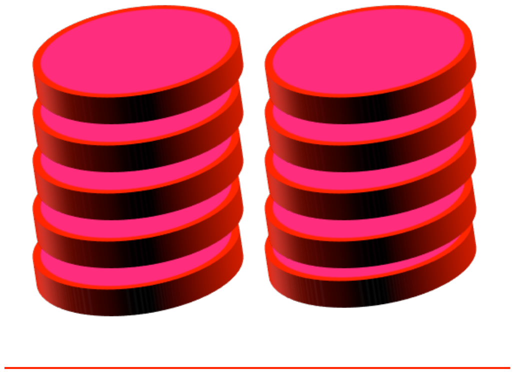
Crystal Structure



Edge-on



Face-on



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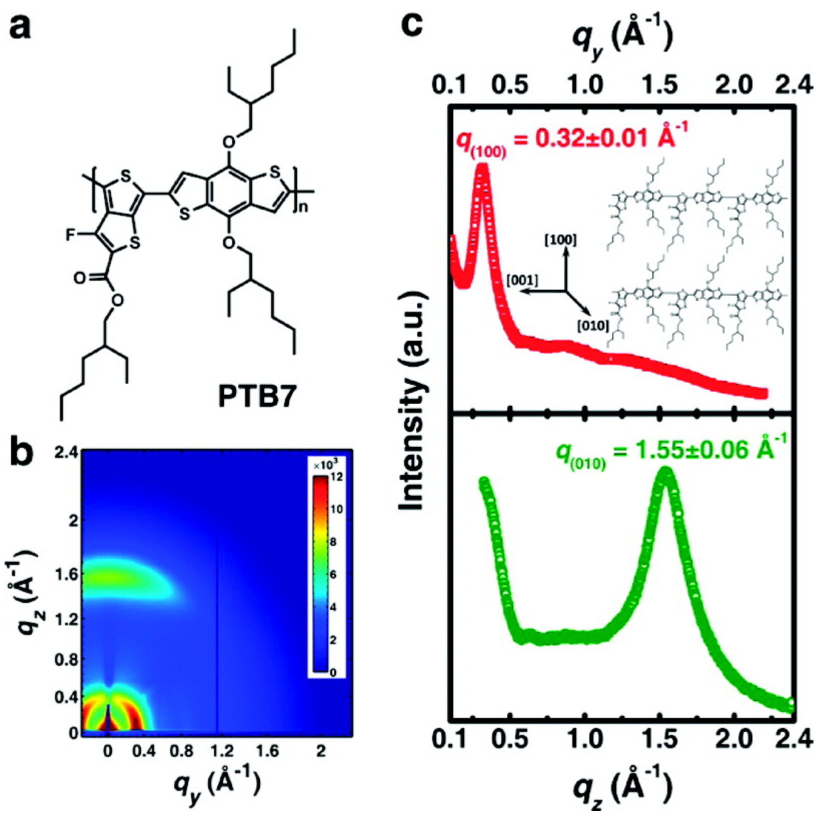
Linecuts in GIXS Patterns Quantify Structure



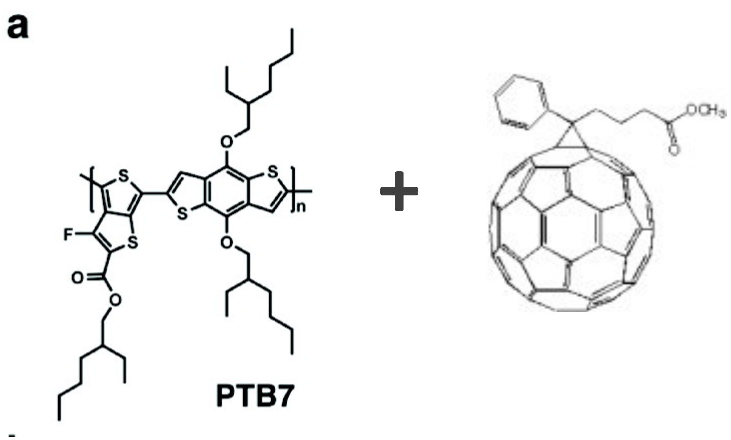
Vertical linecut → out of plane structure

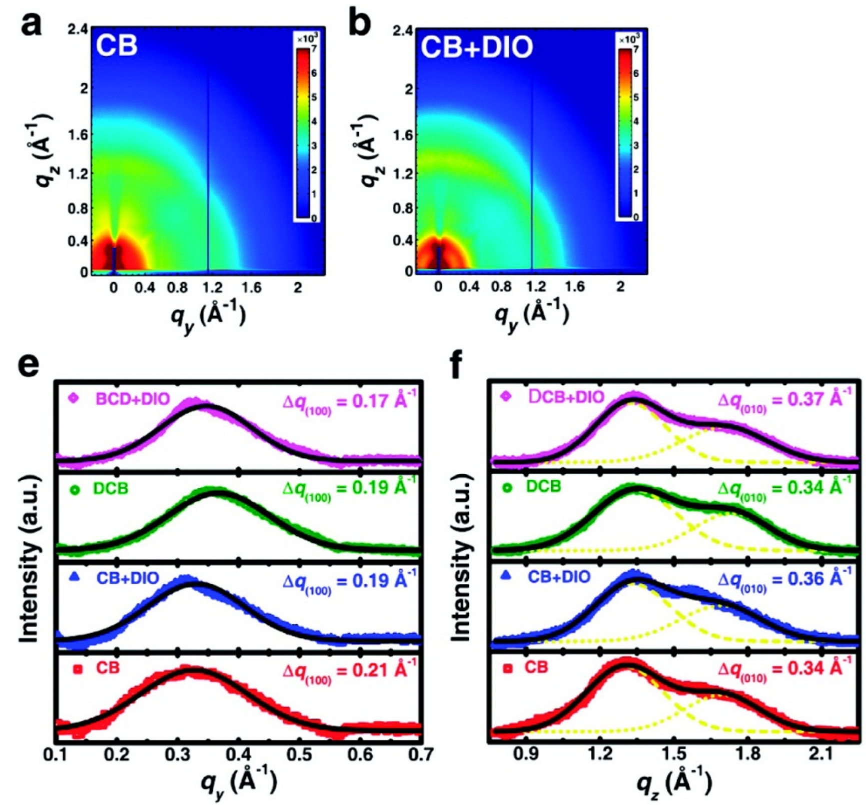
Horizontal linecut → in plane structure

Fits help quantify peak center, linewidth

Wei Chen *et al; Nano Lett.* **2011,** 11, 3707-3713.

Linecuts in GIXS Patterns Quantify Structure





Vertical linecut → out of plane structure

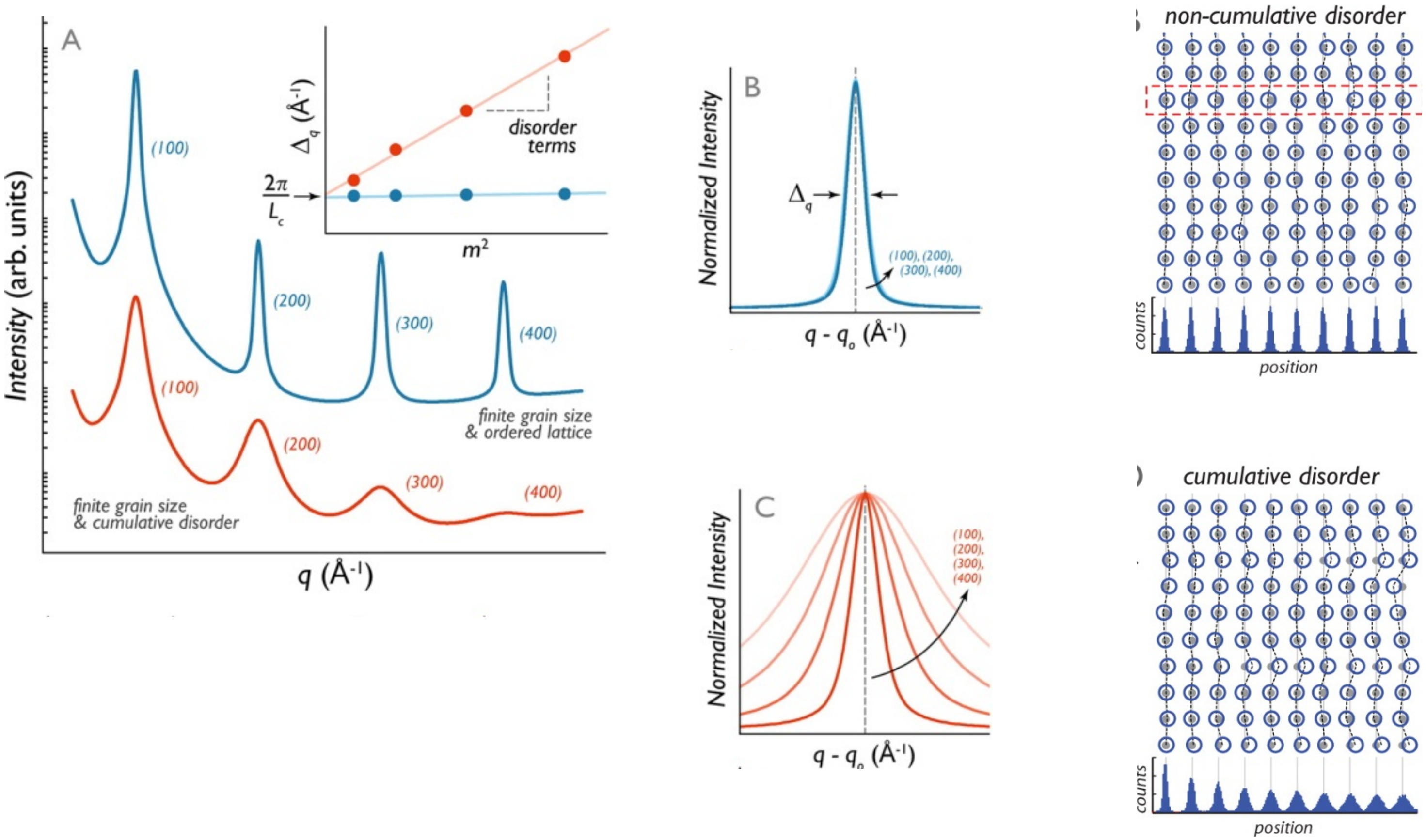
Horizontal linecut → in plane structure

Fits help quantify peak center, linewidth

Linewidths correspond to grain size, but can also be affected by disorder.

Wei Chen *et al*; *Nano Lett.* **2011,** 11, 3707-3713.

Lattice Disorder Affects Linewidths



Crystalline system (non-cumulative disorder): grain size determines linewidth.
Paracrystalline system (cumulative disorder): coherence length ≠ grain size.
Need to measure more than one order to determine grain size.

Rivnay; Mannsfeld; Miller; Salleo; Toney; *Chem. Rev.* **112,** 5488-5519 (2012)

Quantifying Linewidths on an Area Detector

The coherence length of a particular reflection (hkl)

$D_{hkl} = 2\pi K/\Delta q_{hkl}$

K: geometry-dependent constant (0.866 for lamellae)

λ: x-ray wavelength (1.6868 Å, 7.35 keV)

The experimental width, Δq_{exp}, must be corrected for the resolution Δq_{res}

$\Delta q_{hkl} = ((\Delta q_{exp})^2 - (\Delta q_{res})^2)^{1/2}$

The resolution is dominated by the geometry of the area detector, related to the angular resolution, $B_{res.}$ For q_z direction:

$\Delta q_{res} = (4\pi/\lambda)\cos(\alpha_f/2)(B_{res}/2)$

$B_{res} = B_{geo} = w \tan(\alpha_f)/L$

L: specimen-detector distance (204 mm)

α_f: scattering angle in the scattering plane

w: footprint on sample (~ 6 mm)

20 µm vertical slits (200 µm horizontal slits)

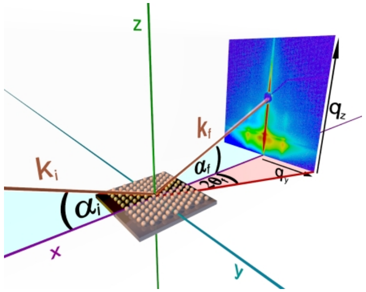
α_i: incident angle (0.2°)

w = 20 µm/sin(0.2°) ≈ 6 mm

Vertical slit size determines the resolution.

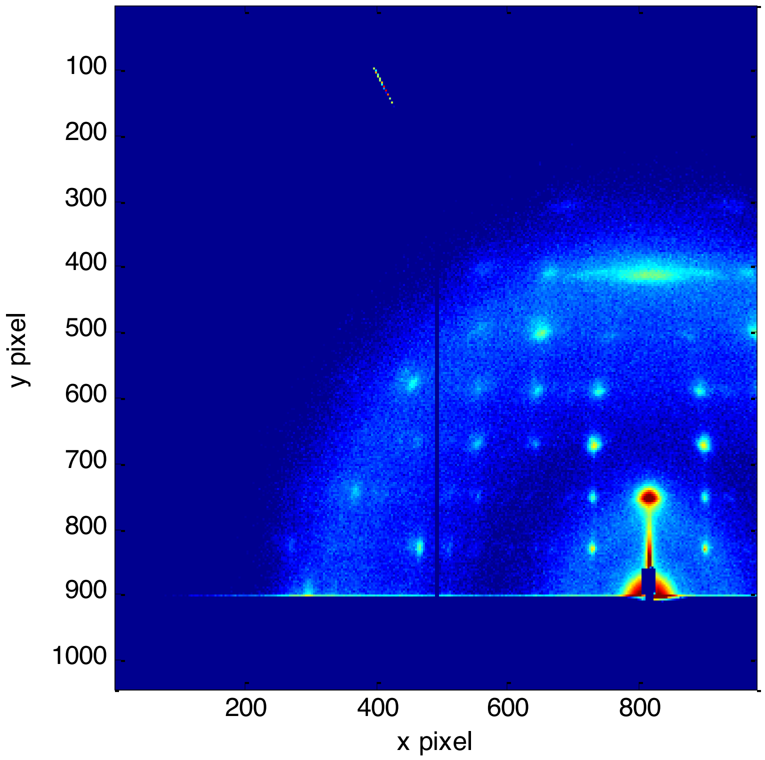
Smilgies, J. Appl. Cryst. **42** 1030-1034 (2009)

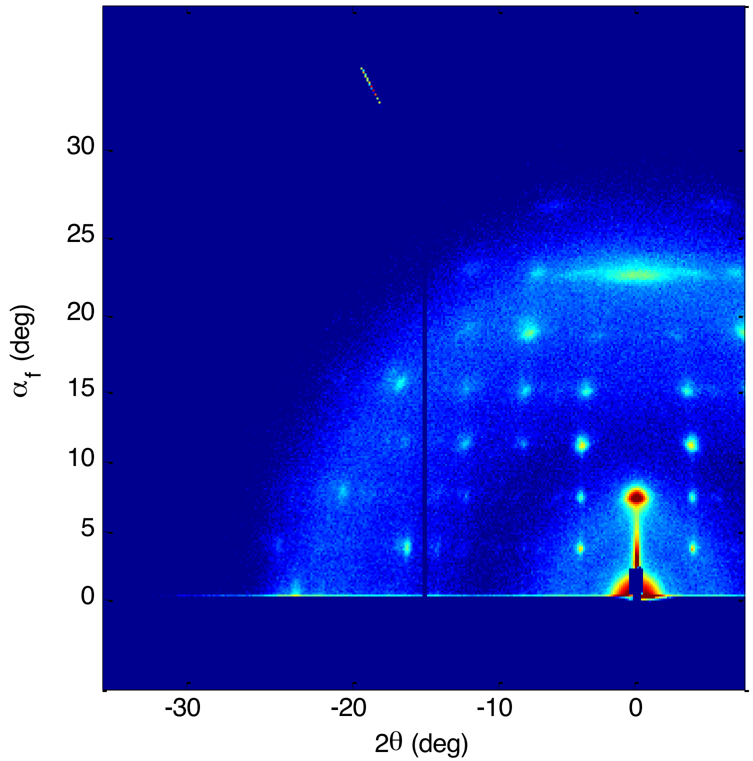
Representing GIWAXS data



$$q_{x,y,z} = \frac{2\pi}{\lambda} \begin{bmatrix} \cos(\alpha_f)\cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f)\sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}$$

Diagram: www.gisaxs.de
Prof. Andreas Meyer, U. Hamburg

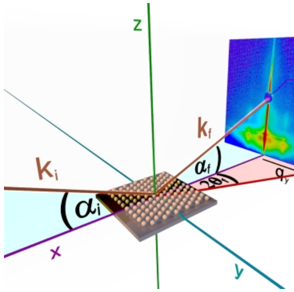




Data: Rafael Verduzco group, Rice University

Angle representation $I(2\theta, \alpha_f)$ correct, but limits information

Representing GIWAXS data



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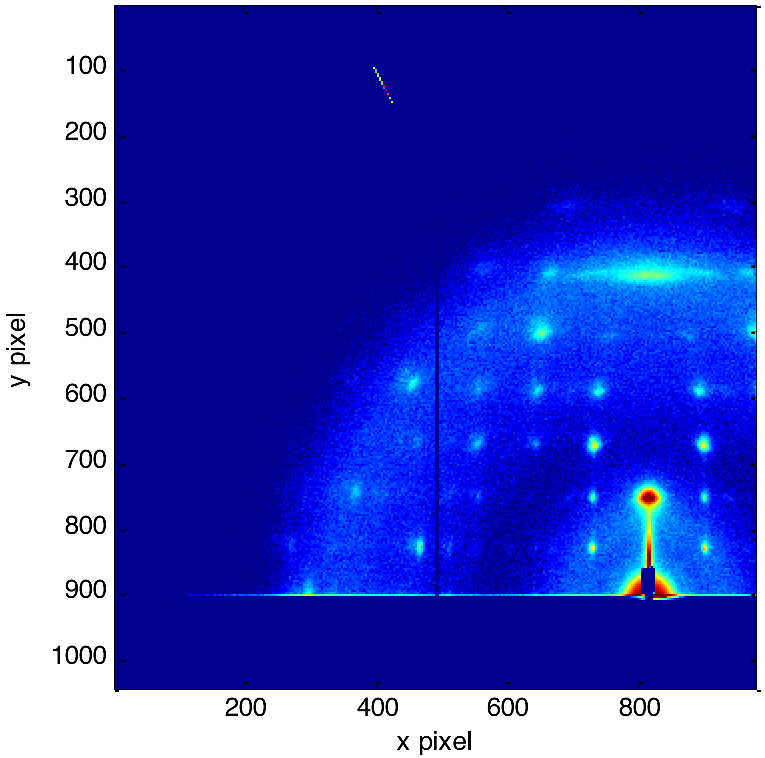
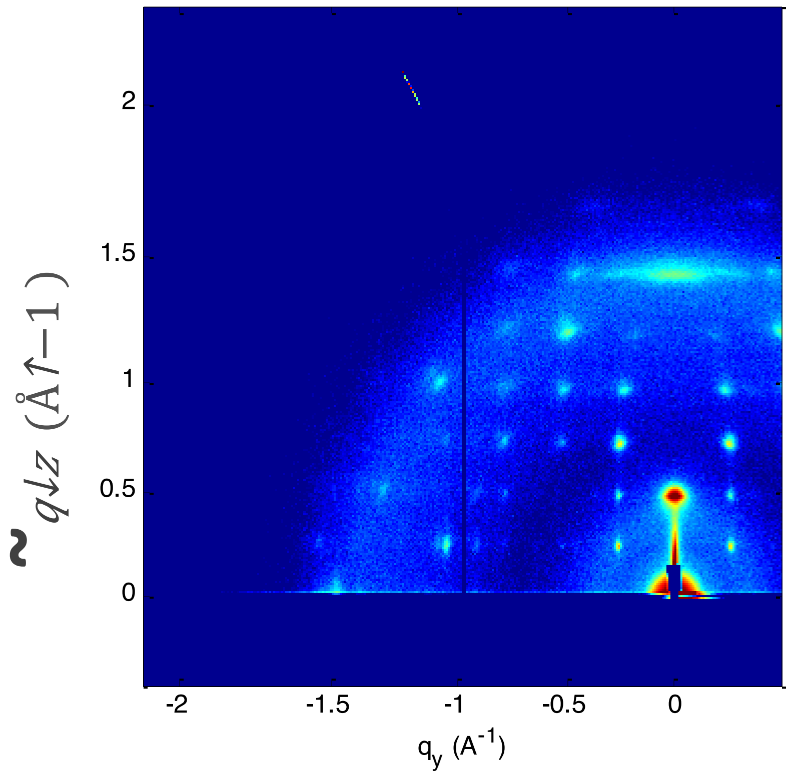
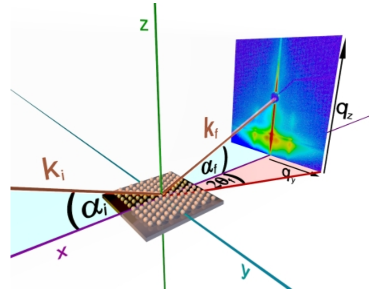




Q-space representation $I(q_y, q_z)$ often conventional, but not correct.

Representing GIWAXS data



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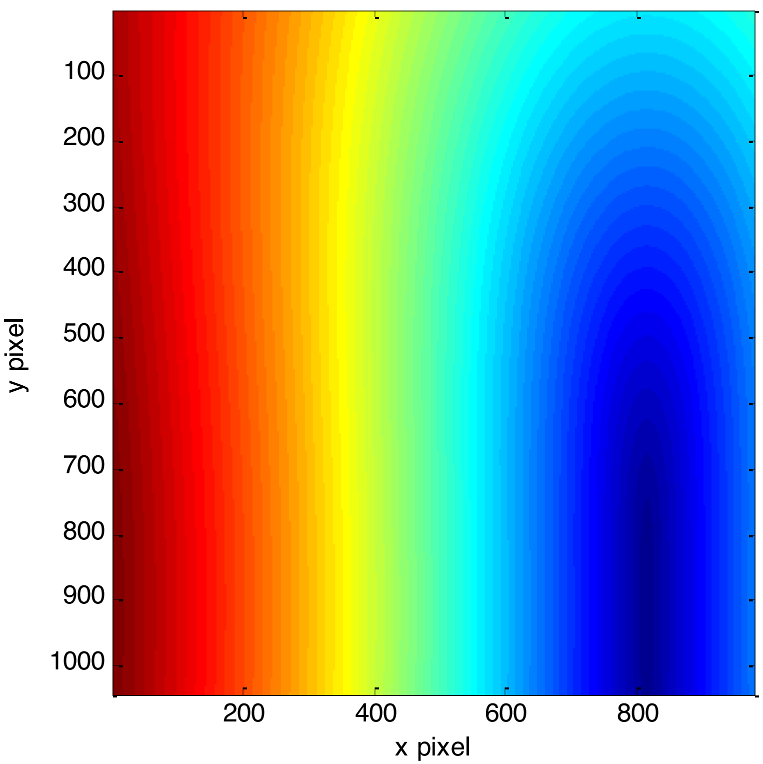
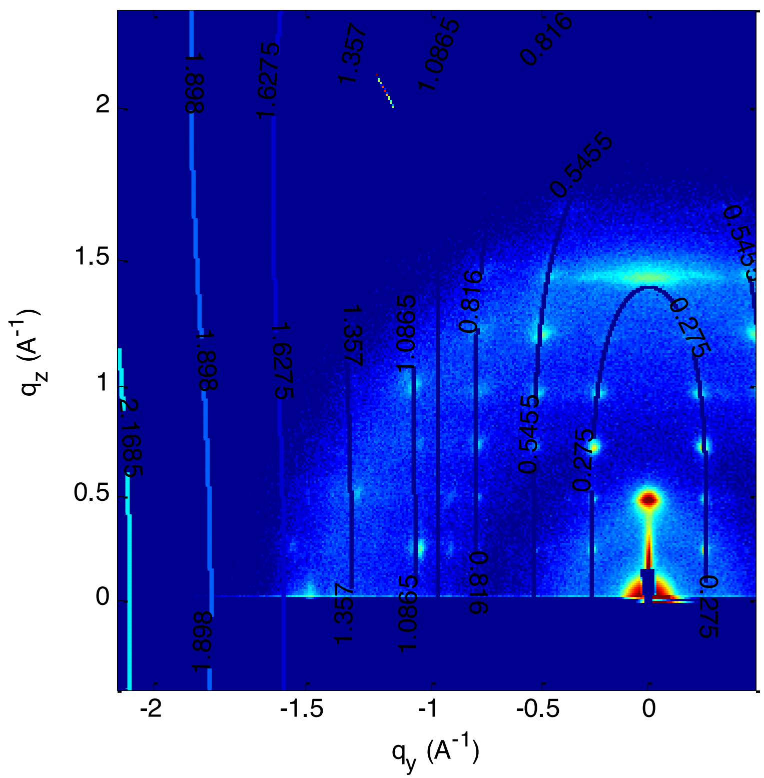
Prof. Andreas Meyer, U. Hamburg

Map of constant q_r values in pixel space.





Features follow contours of equal $q_r = \sqrt{q_x^2 + q_y^2}$

Representing GIWAXS data

Reshaping the data into I(qr, qz) makes relationship between reflections more clear.

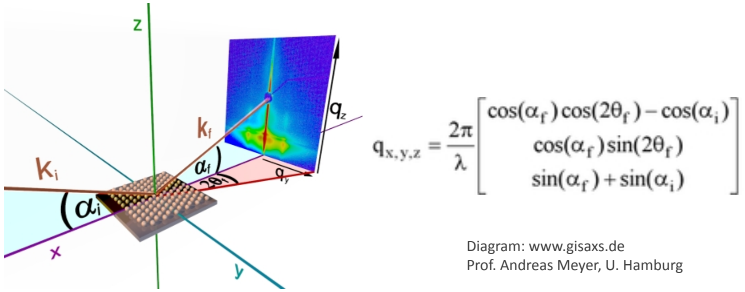
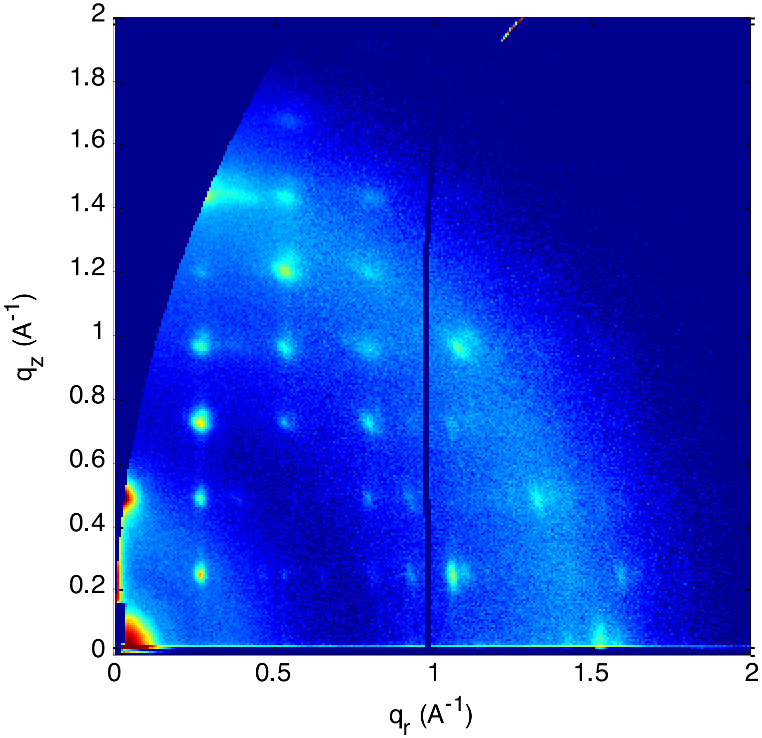
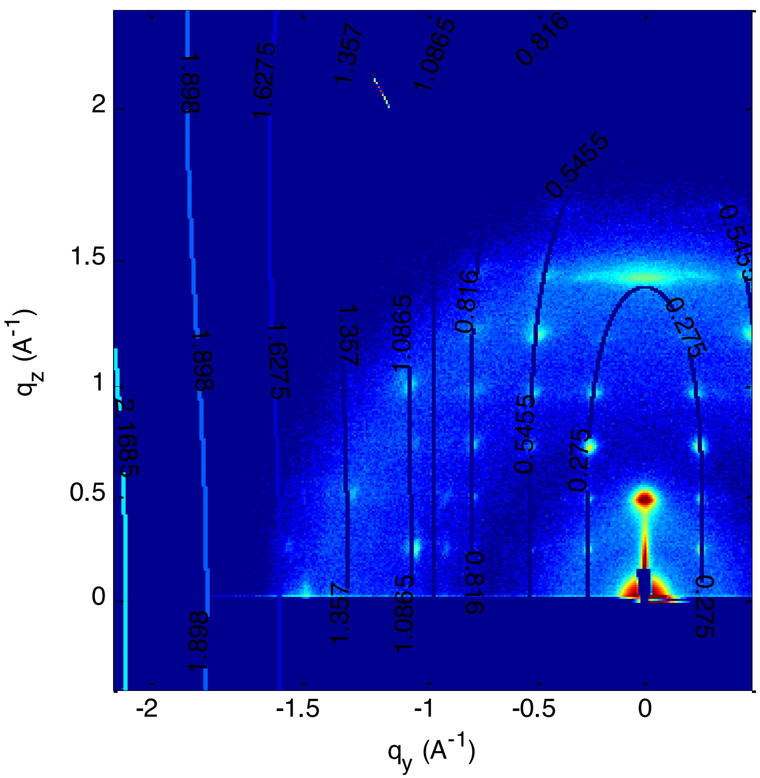


Diagram: www.gisaxs.de
Prof. Andreas Meyer, U. Hamburg



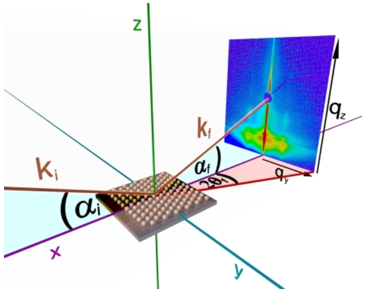


Features at constant q_r follow straight lines.

Features follow contours of equal $q_r = \sqrt{q_x^2 + q_y^2}$

Representing GIWAXS data

Further reshaping into I(χ,q) very useful for comparing arcing features



$$q_{x,y,z} = \frac{2\pi}{\lambda}\begin{bmatrix}\cos(\alpha_f)\cos(2\theta_f)-\cos(\alpha_i)\\ \cos(\alpha_f)\sin(2\theta_f)\\ \sin(\alpha_f)+\sin(\alpha_i)\end{bmatrix}$$

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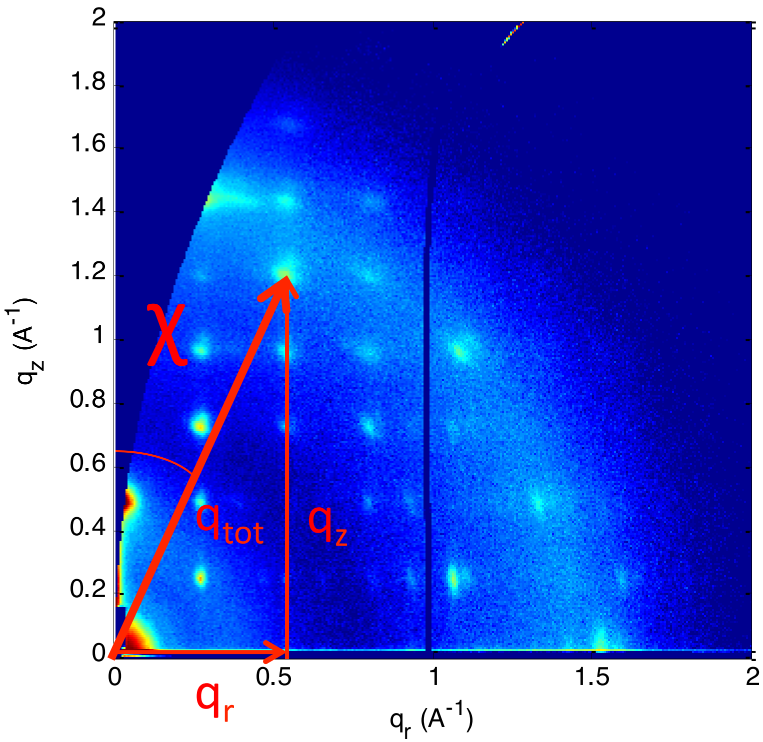
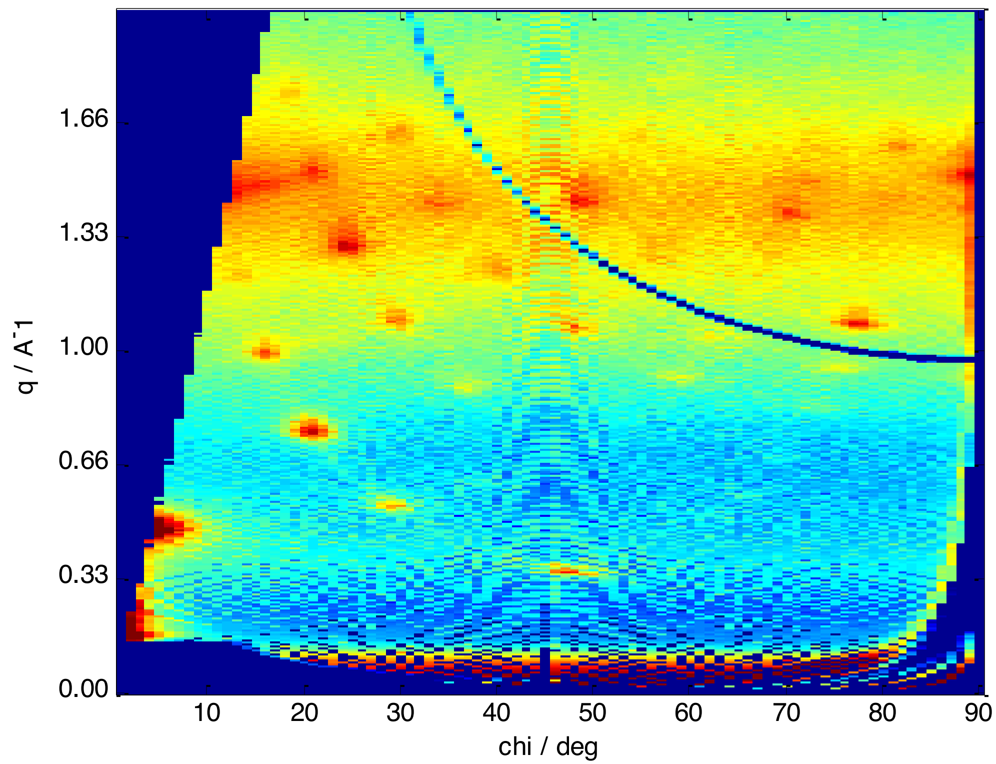
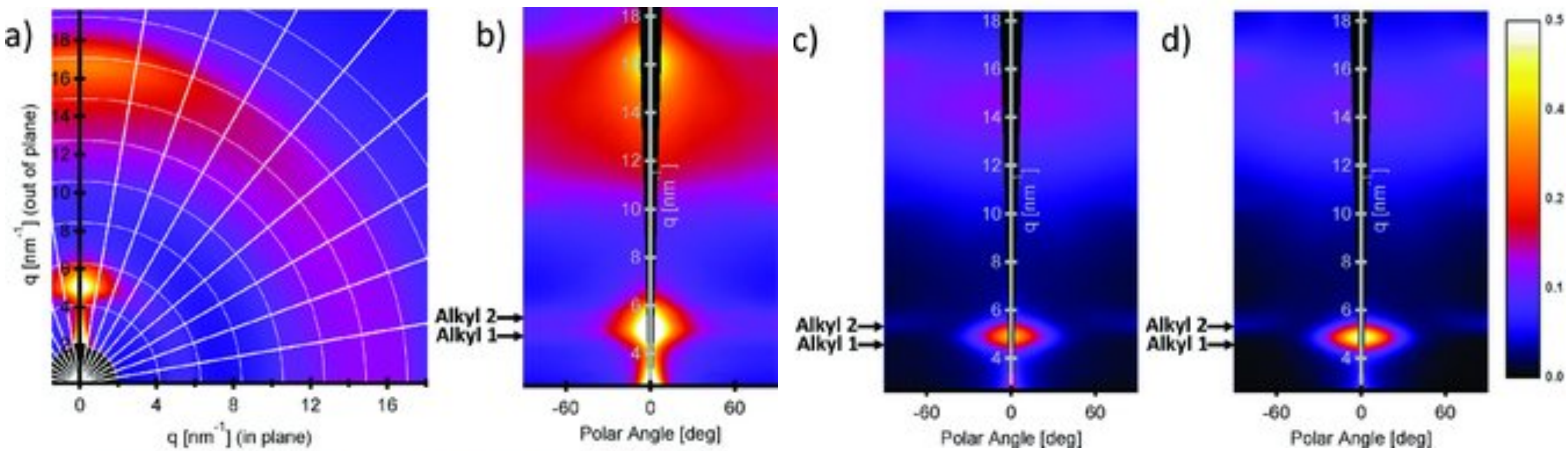




Ordinate is now

$$q_{tot} = \sqrt{q_r^2 + q_z^2}$$

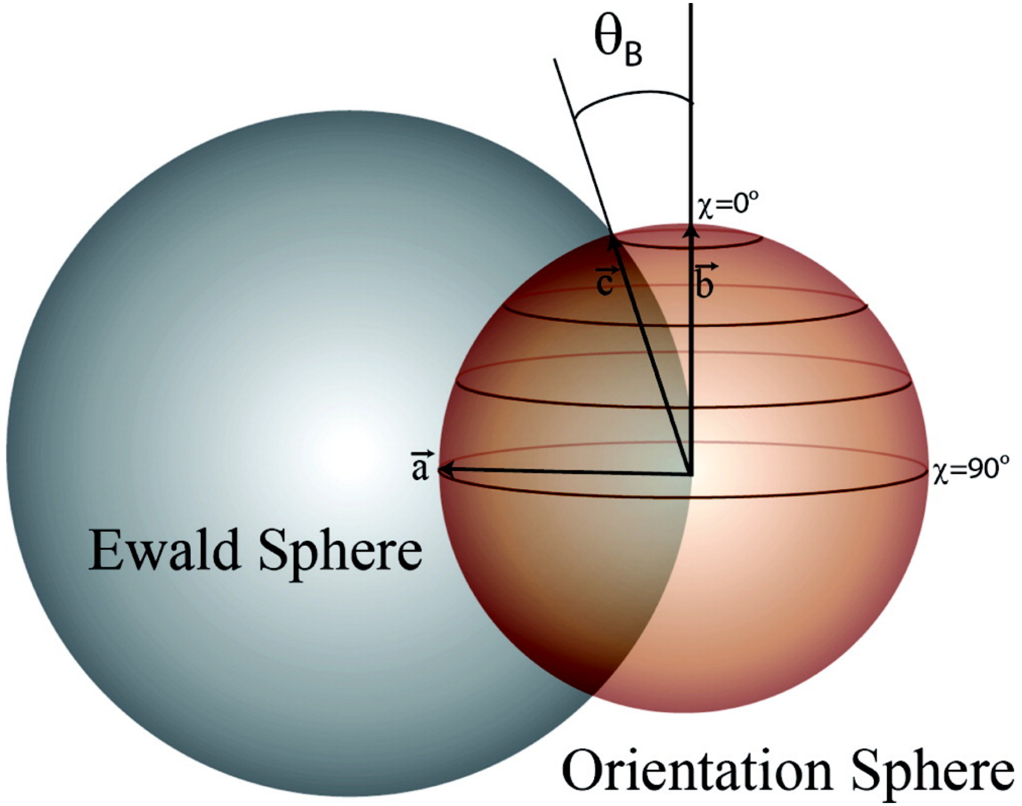
Representing GIWAXS data: sector plots



Sector plot shows different crystalline forms.

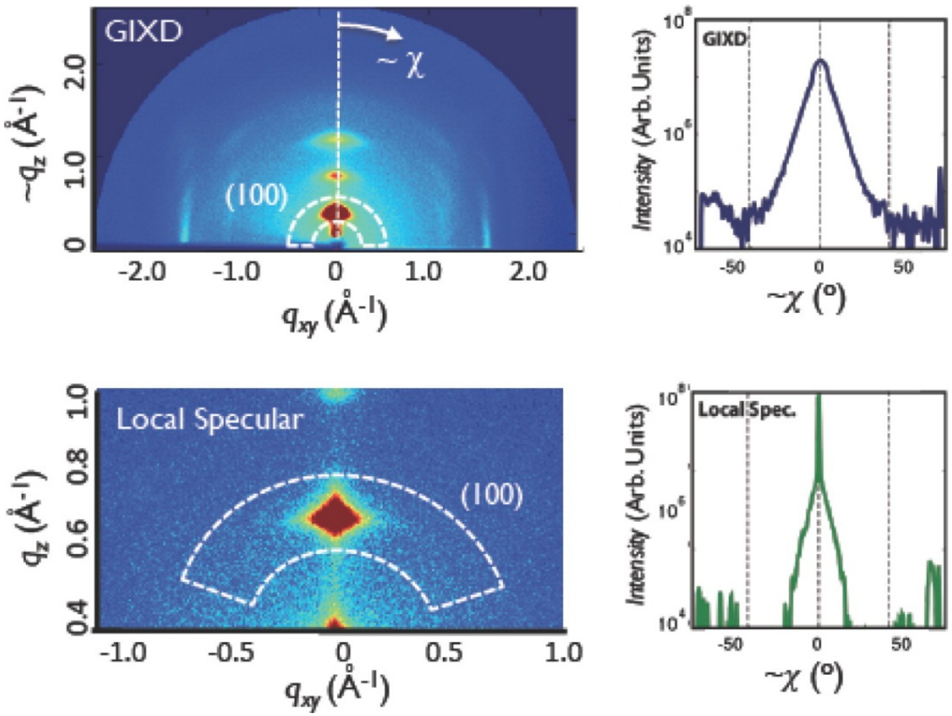
Rogers, Schmidt, Toney, Kramer, and Bazan, *Adv. Mater.* **23** 2284-2288 (2011).

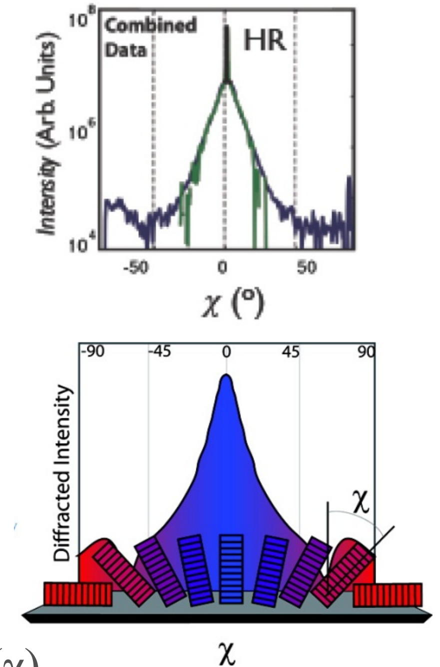
Filling in the GIWAXS "blind spot"



Baker; Jimison; Mannsfeld; Volkman; Yin; Subramanian; Salleo; Alivisatos; Toney; *Langmuir* **26**, 9146-9151 (2010).

Constructing Pole Figures



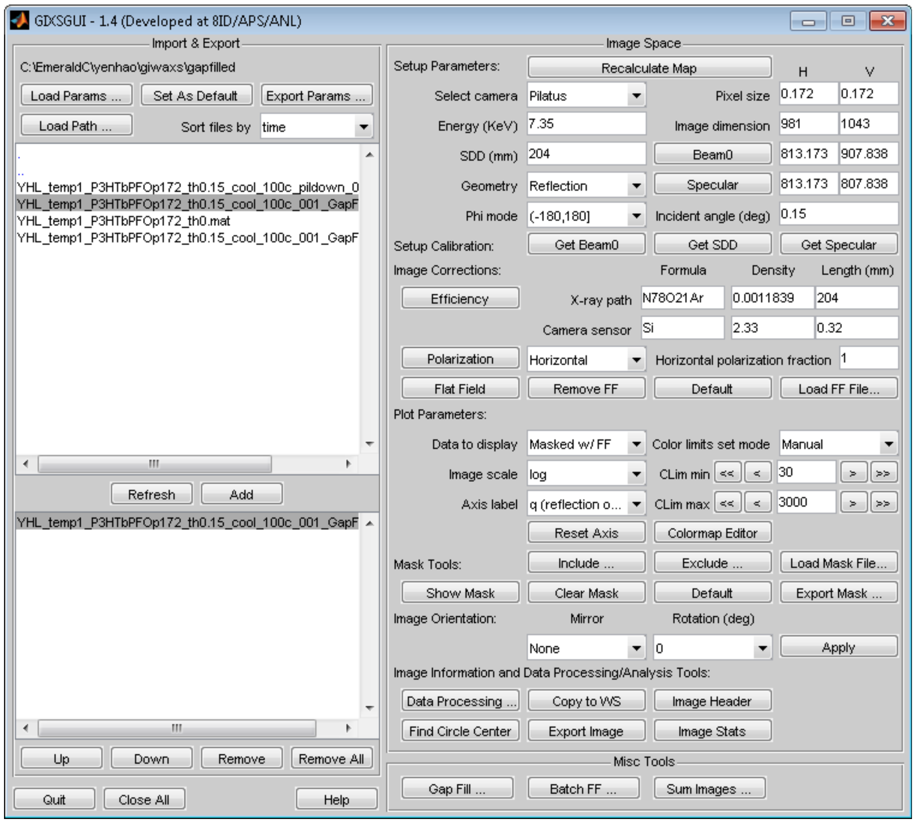


Stitch together linecuts
GIWAXS + specular + rocking curve → pole figure I(χ)
Integrating I(χ) gives Degree of Crystallinty

Baker *et al*; *Langmuir* **26**, 9146-9151 (2010)
Rivnay; Mannsfeld; Miller; Salleo; Toney; *Chem. Rev.* **112,** 5488-5519 (2012)

GIXSGUI software package

GIXSGUI by Zhang Jiang is a Matlab package for GIXS data visualization and reduction.



- Display 2-D data (pixel-, angle- or q-space)
- Apply corrections
- Calibrate detector distance from standard data
- Compute linecuts
- Sum/average 2-d files
- Interactive GUI
- Fully scriptable

Available for download (requires Matlab license to run): http://www.aps.anl.gov/Sectors/Sector8/Operations/GIXSGUI.html

GIXSGUI software package

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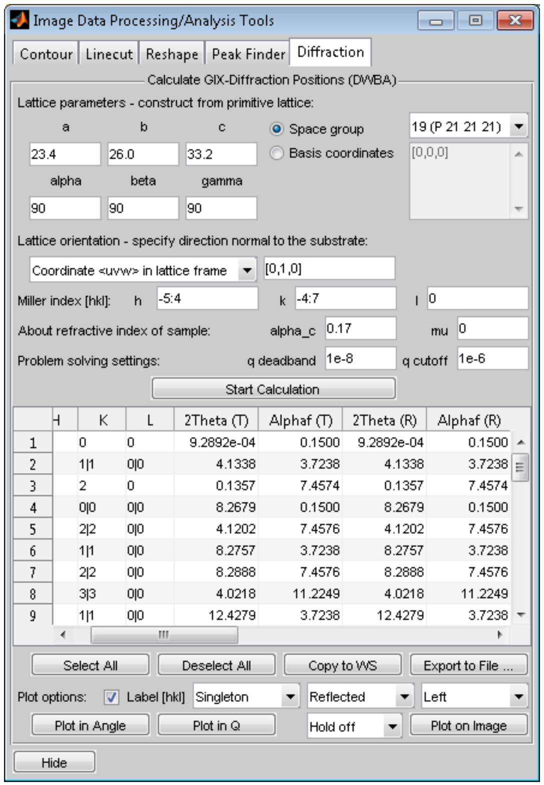
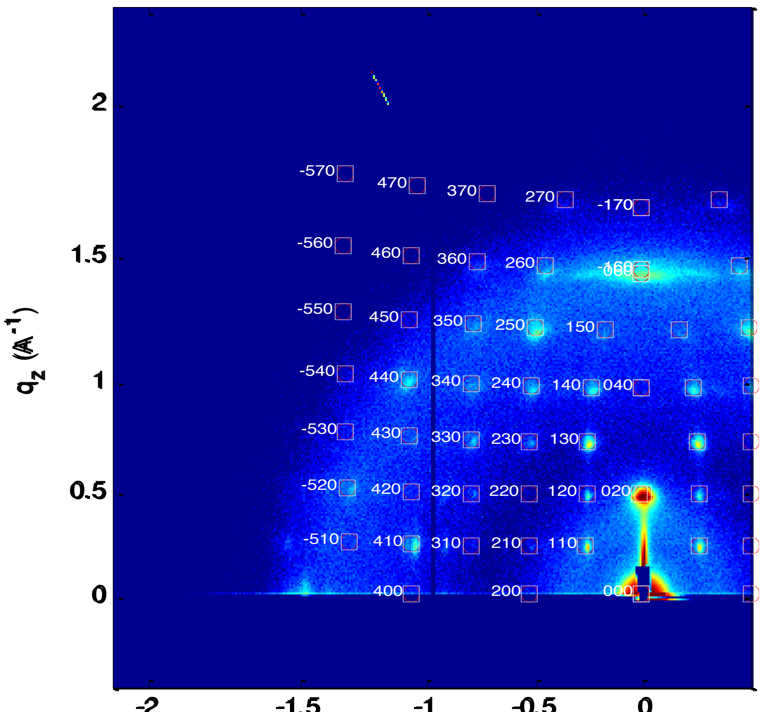


Under development:

- Reflection indexing



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References

- "Microstructural Characterization and Charge Transport in Thin Films of Conjugated Polymers," Alberto Salleo, R. Joseph Kline, Dean M. DeLongchamp, Michael L. Chabinyc
- "Molecular Characterization of Organic Electronic Films," Dean M. DeLongchamp, R. Joseph Kline, Daniel A. Fisher, Lee J. Richter, Michael F. Toney, *Adv. Mater.* **23**(3) 319-337 (2011)
- "Quantitative Determination of Organic Semiconductor Microstructure from the Molecular to the Device Scale," Jonathan Rivnay, Stefan C. B. Mannsfeld, Chad E. Miller, Alberto Salleo, Michael F. Toney, *Chem. Rev. ,* 112(10) 5488-5519 (2012).
- "Quantification of Thin Film Crystallographic Orientation Using X-ray Diffraction with an Area Detector," Jessy L. Baker, Leslie H. Jimison, Stefan Mannsfeld, Steven Volkman, Shong Yin, Vivek Subramanian, Alberto Salleo, A. Paul Alivisatos and Michael F. Toney, *Langmuir*, **26**(11) 9146-9151 (2010).
- "Structural Order in Bulk Heterojunction Films Prepared with Solvent Additives," James T. Rogers, Kristin Schmidt, Michael F. Toney, Edward J. Kramer and Guillermo C. Bazan, *Adv. Mater.* **23**(20**)** 2284-2288 (2011).
- "Scherrer grain-size analysis adapted to grazing-incidence scattering with area detectors," Detlef Smilgies, *J. Appl. Cryst.* **42** 1030-1034 (2009).
- "Hierarchical Nanomorphologies Promote Exciton Dissociation in Polymer/Fullerene Bulk Heterojunction Solar Cells," Wei Chen, Tao Xu, Feng He, Wei Wang, Cheng Wang, Joseph Strzalka, Yun Liu, Jianguo Wen, Dean J. Miller, Jihua Chen, Kunlun Hong, Luping Yu, Seth B. Darling, *Nano Lett.* **11**(9) 3707-3713 (2011).

Summary

- GIWAXS data reveal
  - Ordering
  - Orientation
  - d-spacing
  - (para)crystalline disorder and sometimes grain size
- GIWAXS supplemented with local specular data gives quantitative orientation distribution (pole figure)
- Reshaping the data highlights different aspects
- GIXSGUI (Zhang Jiang) is Matlab-based software for GIXS data visualization and reduction

Acknowledgments

Thanks to Zhang Jiang, Jin Wang, Alec Sandy, Suresh Narayanan. Collaborations and interactions with Prof. Ed Kramer (UCSB), Prof. Lin X Chen(Northwestern/Argonne), Dr. Seth Darling (CNM Argonne), Dr. Wei Chen (CNM Argonne), Prof. Rafael Verduzco (Rice) are gratefully acknowledged. Use of the APS is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Thank you for your attention!

Introduction to GIXSGUI

Joseph Strzalka
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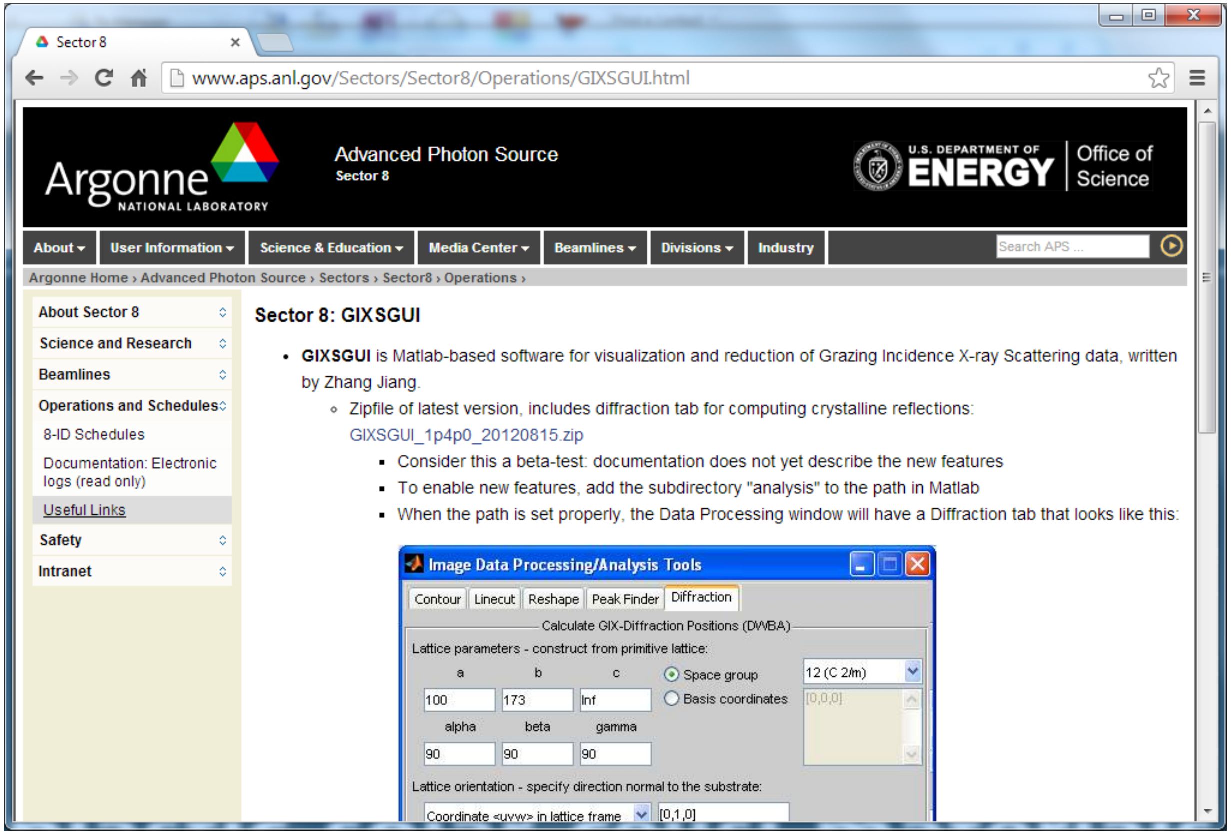
GIXSGUI by Zhang Jiang

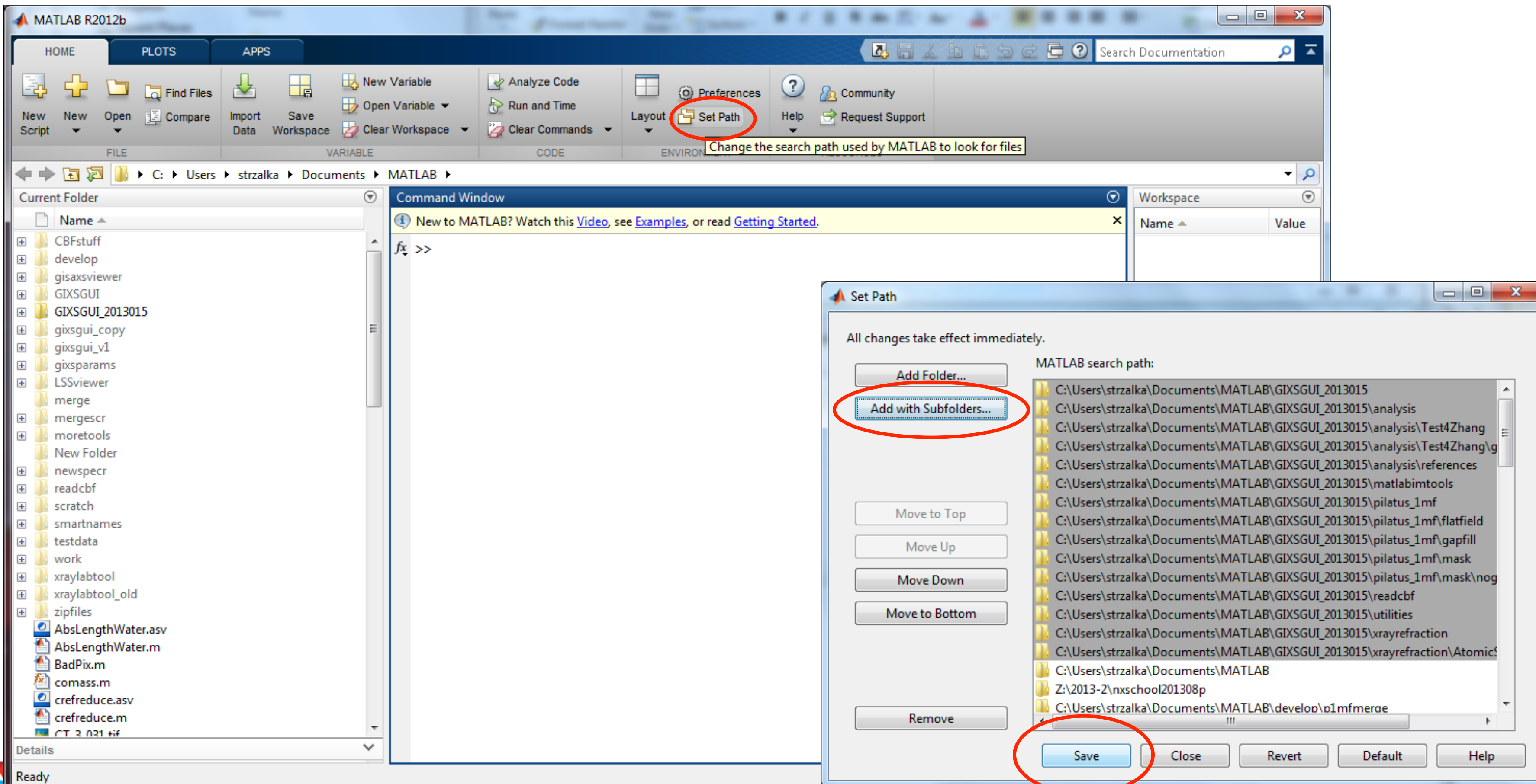
Downloading GIXSGUI

- GIXSGUI is a Matlab package available for download: www.aps.anl.gov/Sectors/Sector8/Operations/GIXSGUI.html
- Use requires license for Matlab (Distribution 2010a or newer).



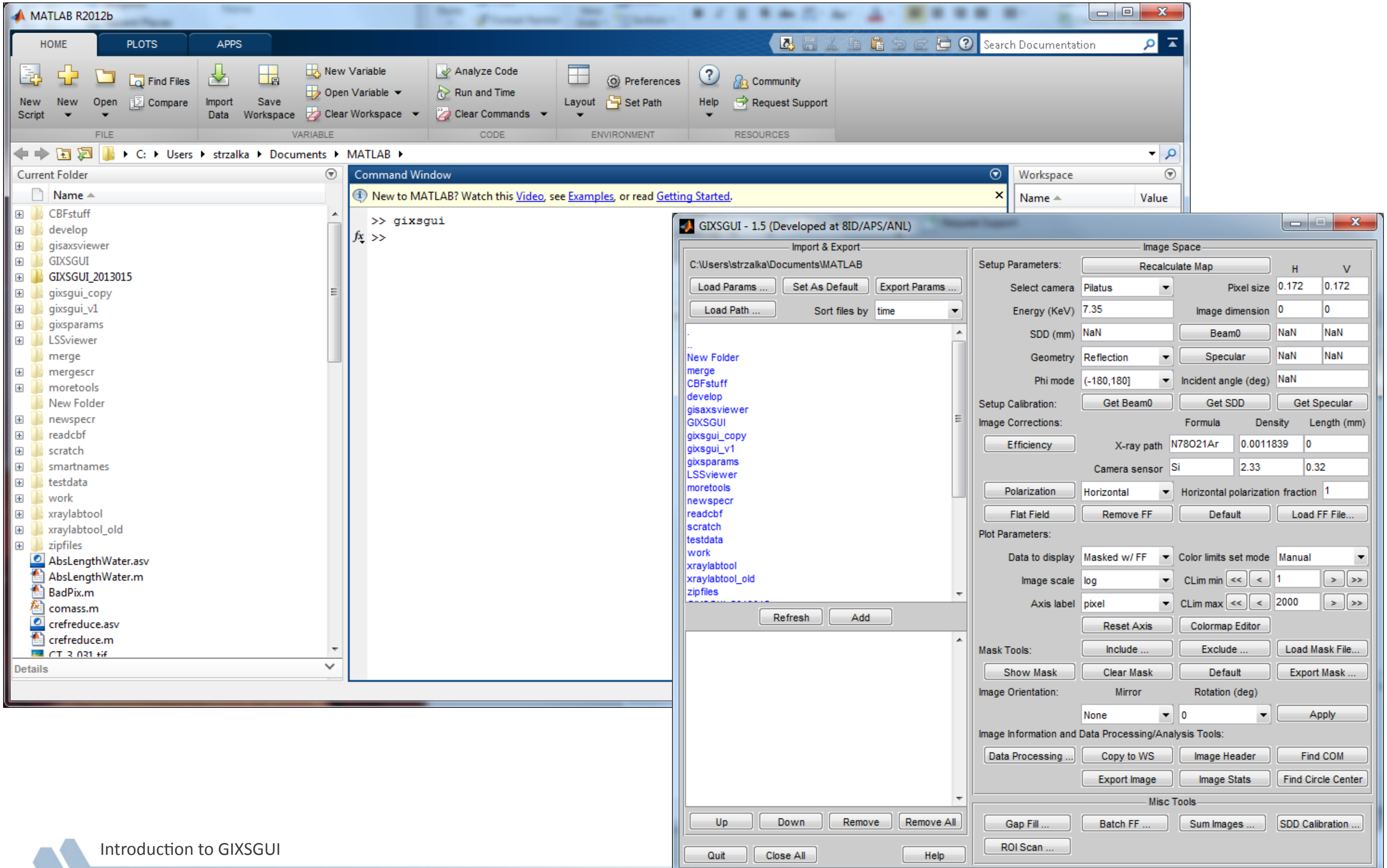
Setting up GIXSGUI

- Unzip the .zip file. The doc subfolder contains doc.pdf, documentation for GIXSGUI.
- Start Matlab.
- Modify your path: Set Path →Add with Subfolders → <Select the path for GIXSGUI> → Save



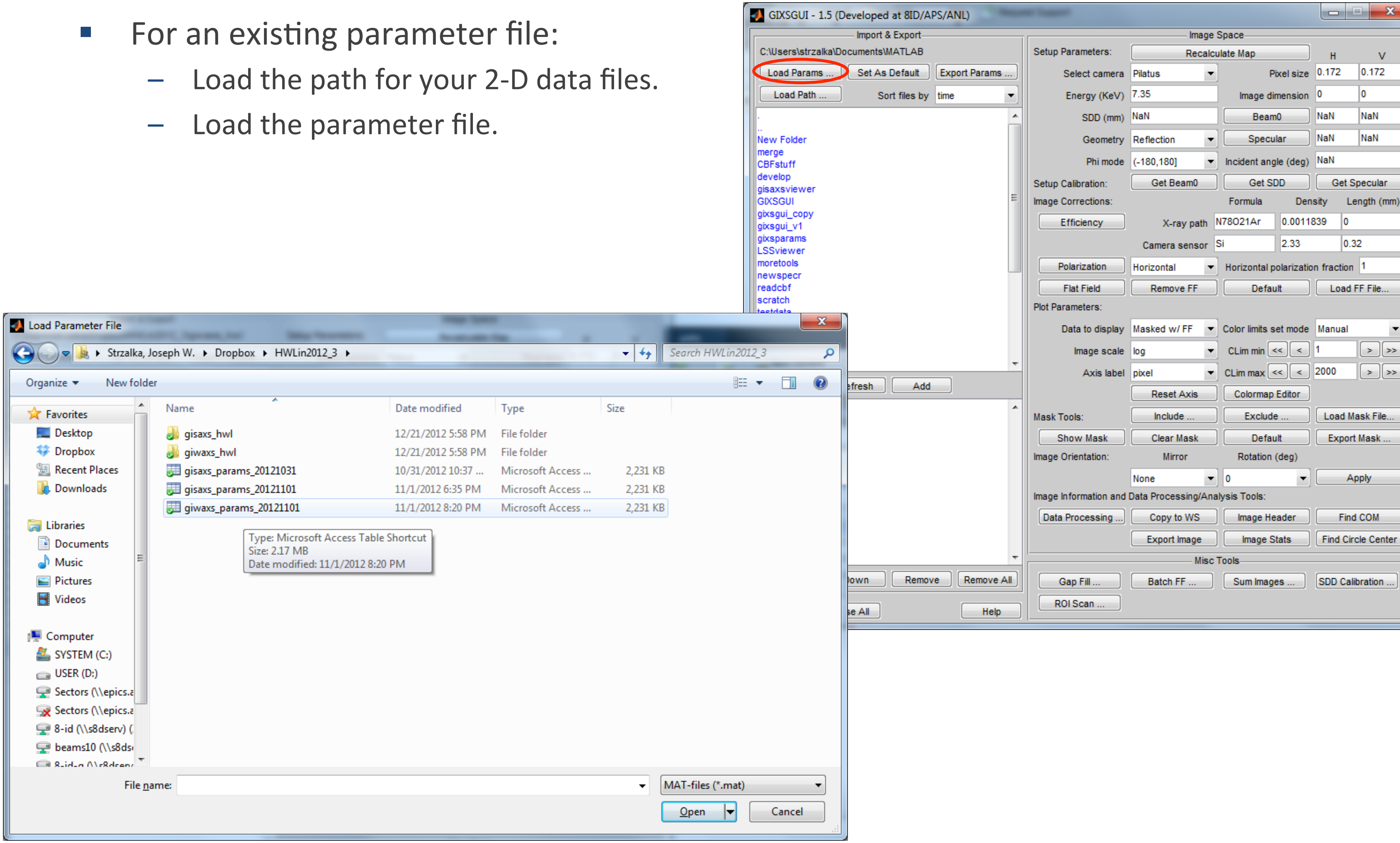
Starting GIXSGUI

- Enter `gixsgui` into the command window.



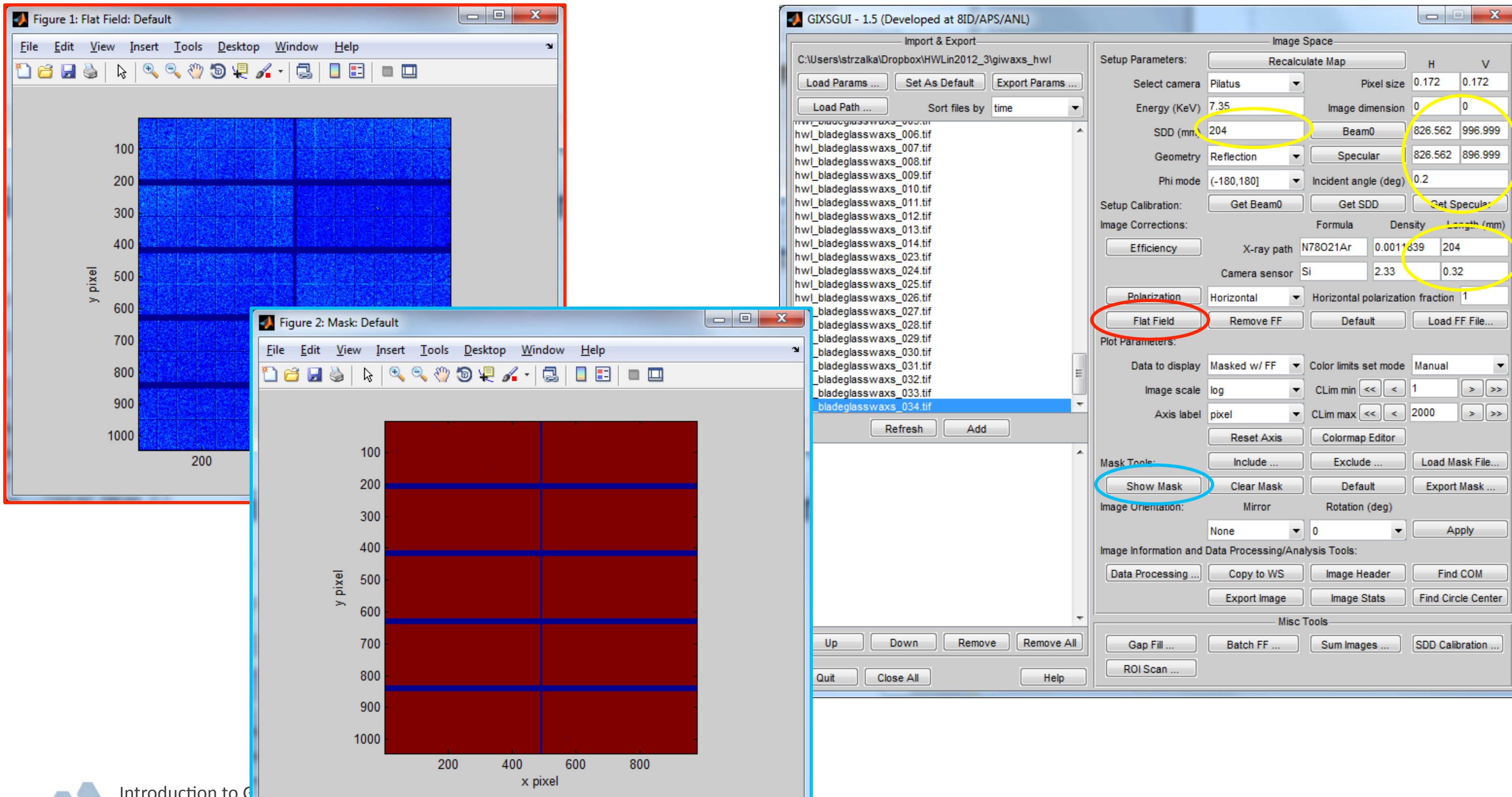
Loading GIXSGUI parameters from a file

- For an existing parameter file:
  - Load the path for your 2-D data files.
  - Load the parameter file.



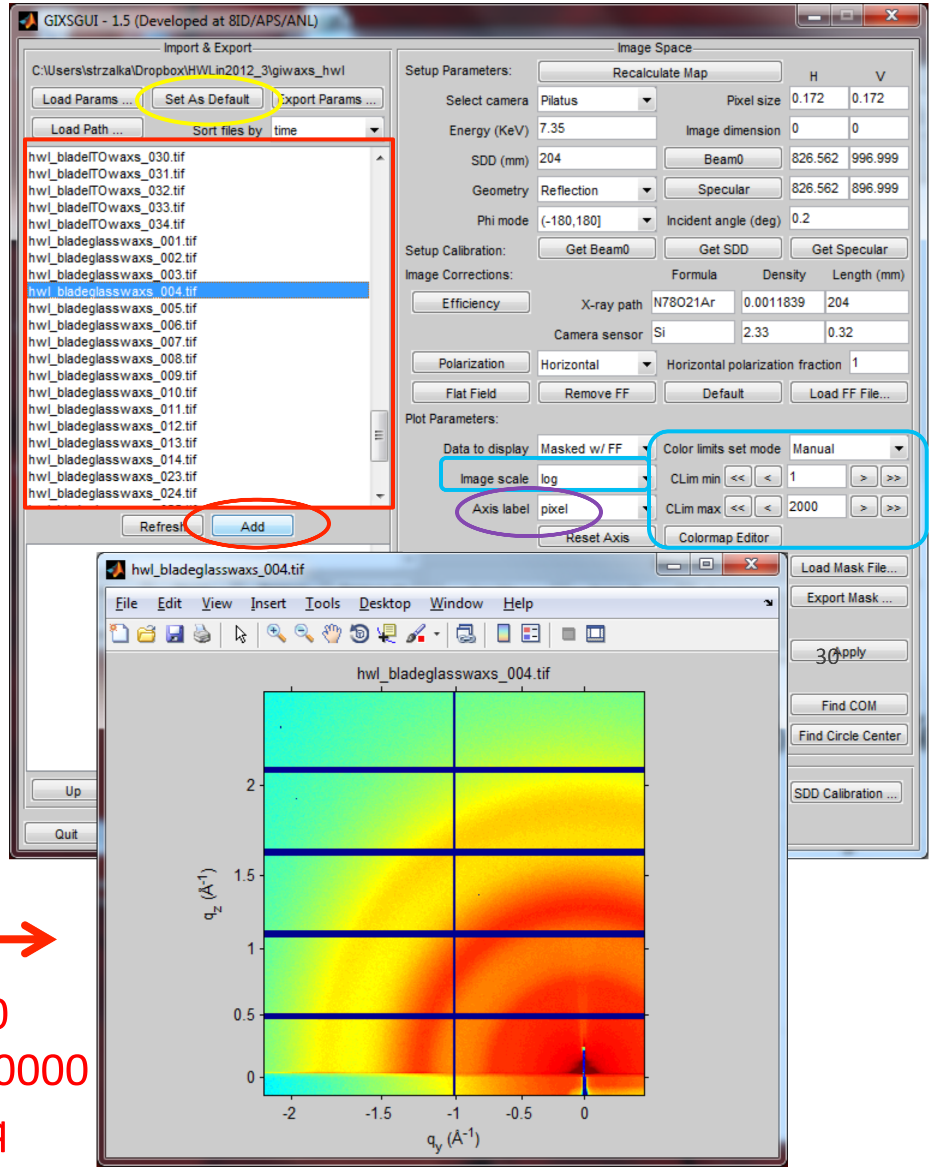
Loading GIXSGUI parameters from a file

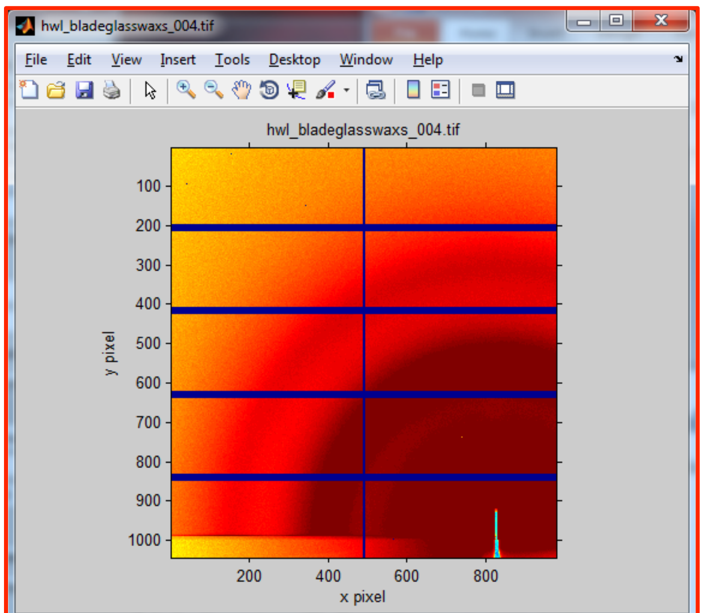
- After loading,
  - Parameters appear
  - Flat field data and mask data are read in



Displaying 2-D data in GIXSGUI

- Select a file in the path list box
  - Double click on the filename OR
  - Click the Add button
  - Image appears
  - Adjust color scale with controls
  - Control axes with Axis label menu
  - Make new settings default with Set as Default button

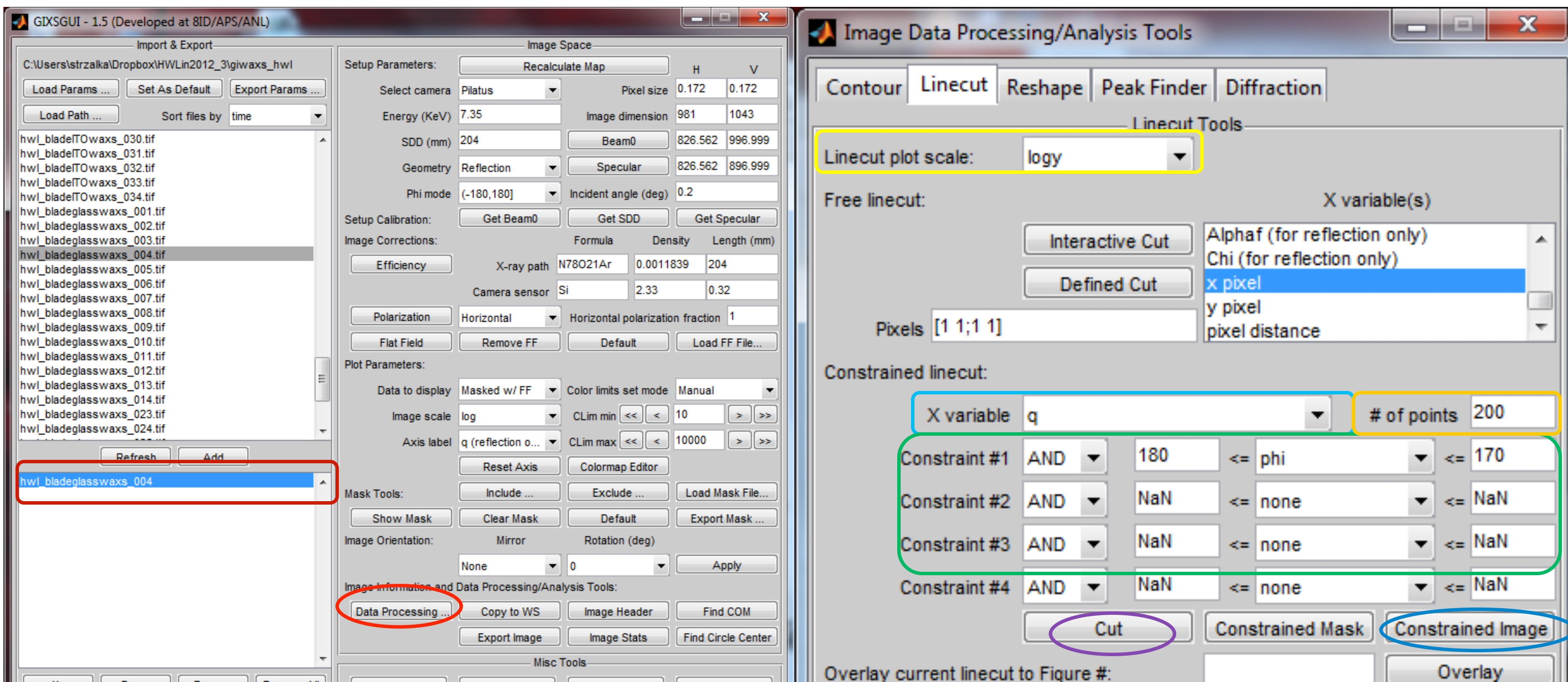




Clim min = 10
Clim max = 10000
Axis label = q

Applying simple linecuts

- Data processing button calls up new window
- For Constrained linecut, set X variable, Constraints, enter # of points in the result and set the Linecut plot scale
- Click Constrained Image to see the region included in the integration
- Click Cut to produce the linecut
- Note: linecut is performed on whichever image is selected in the list box.



Example Linecut

- Settings on previous slide produce the Constrained Image (left) and the linecut (right) below.