

GIXS: hands-on data analysis

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ALBUQUERQUE, NM

MAY 24-28, 2014

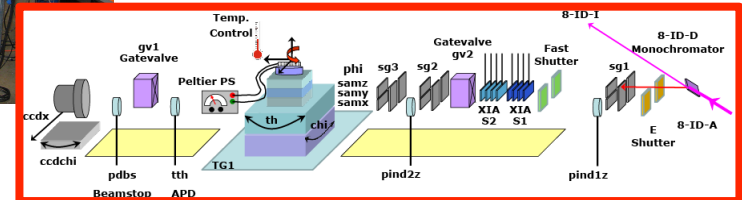
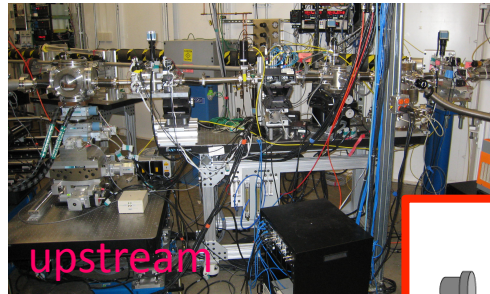
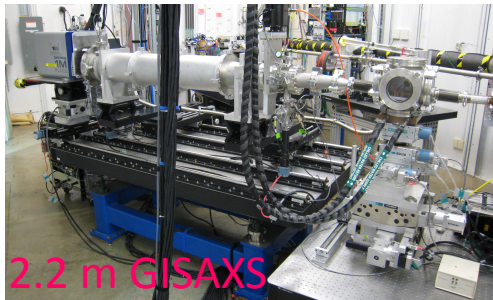


Outline

- 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 crystallinity
- Software: GIXSGUI
- Conclusions



GISAX 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 $\sim 40\%$
- GISAXS: Adjustable vacuum flight path length (1.5 – 2.2m) $\rightarrow q_{\text{max}} \approx 0.14\text{-}0.2 \text{ \AA}^{-1}$

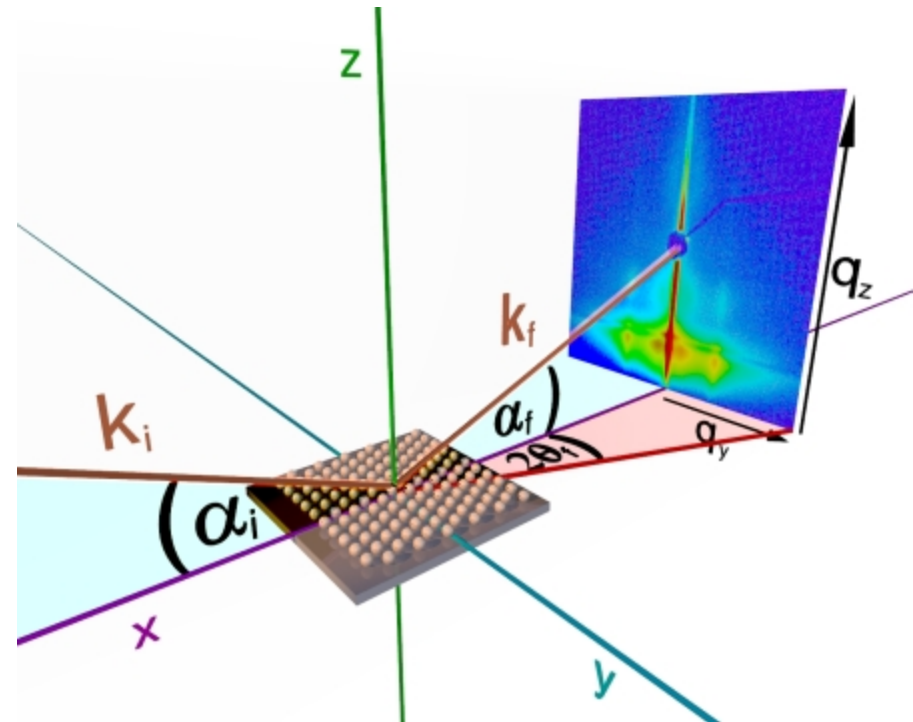
- GIWAXS: mostly in air, 0.2 m, vacuum for thermal annealing ($q_z, q_y < 2.2 \text{ \AA}^{-1}$)
- Pilatus 1M fast option, 135 frames/sec
- High-resolution reflectivity for $q_z < 0.2 \text{ \AA}^{-1}$
- Sample environment
 - Vacuum sample chamber (-20 to 230 °C)
 - High-temperature oven (750 °C) in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

Grazing Incidence X-ray Scattering (GISXS) conventions

- area detector
- pixels $\leftrightarrow q$
- in-plane: $q \downarrow y$
- out-of-plane: $q \downarrow z$

Only for specular condition
 $\alpha \downarrow f = \alpha \downarrow i$

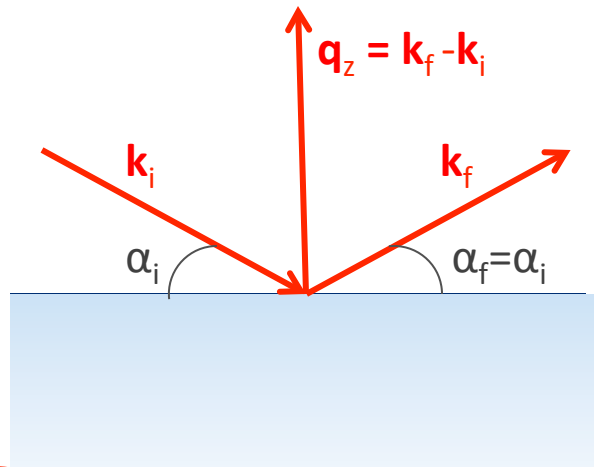
$$q \downarrow x = 0$$



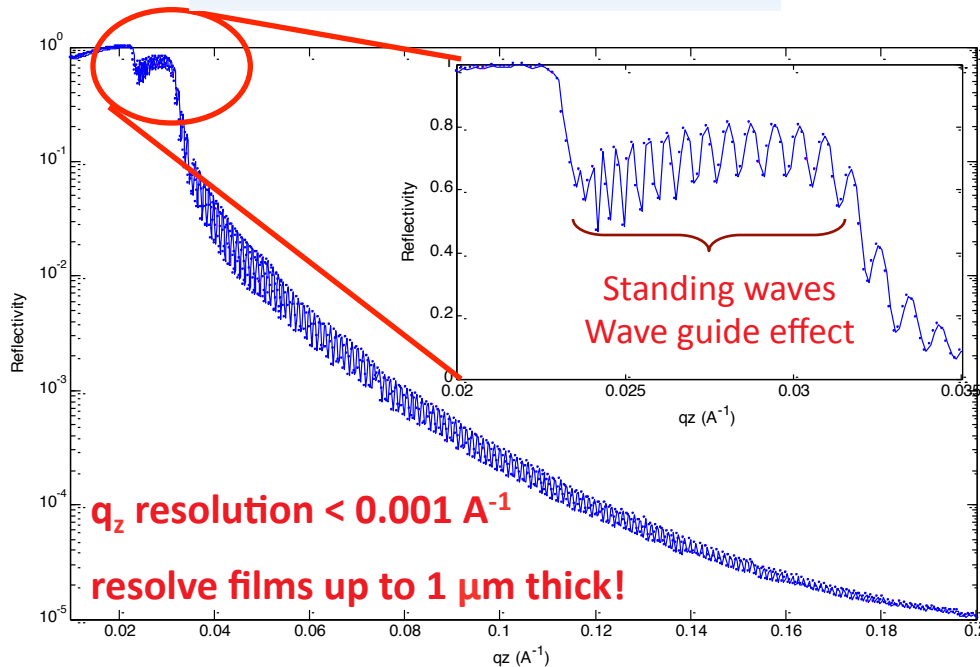
$$q_{x,y,z} = \frac{2\pi}{\lambda} \begin{bmatrix} \cos(\alpha_f) \cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f) \sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}$$

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

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

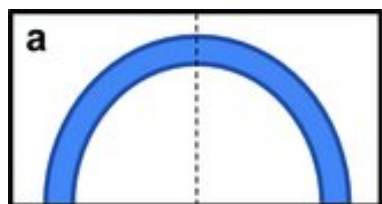


- Point detector and collimation measure strictly along $q_z = (4\pi/\lambda)\sin(\alpha)$
- Resolution constant over entire q -range

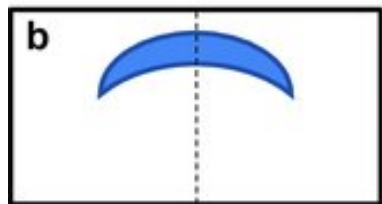


- Reflectivity from a $\sim 800\text{nm}$ polymer film supported on Si
- Total external reflection occurs at small angles (grazing incidence)
 - One critical angle for the polymer film α_{cp}
 - One critical angle for the Si support α_{cSi}
 - GIXS usually $\alpha_{cp} < \alpha_i < \alpha_{cSi}$ (penetrate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

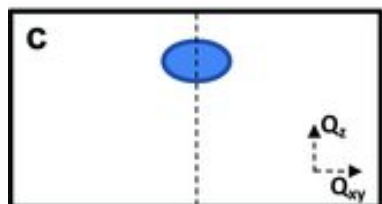
GIWAXS by Inspection: Ordering



isotropic

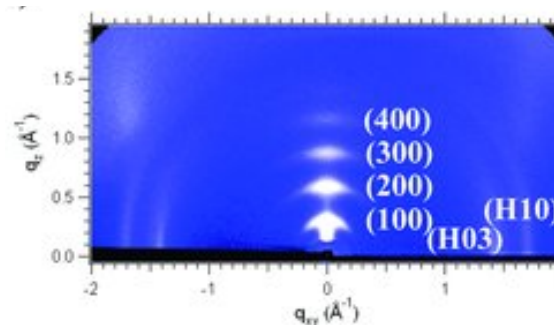
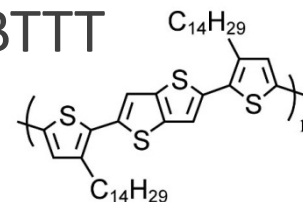


textured/oriented
with broad distribution

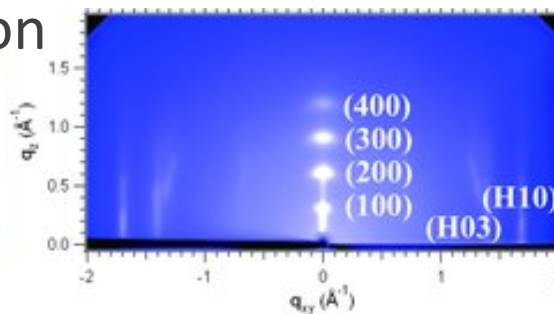


highly-oriented

GIWAXS from pBTTT



as cast



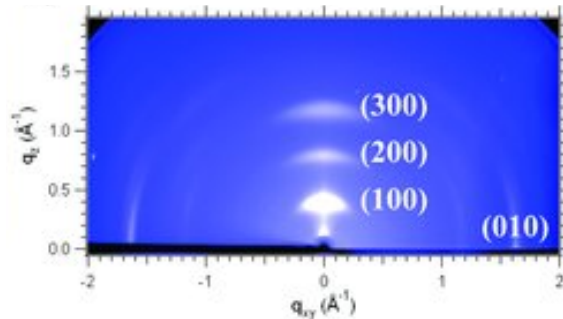
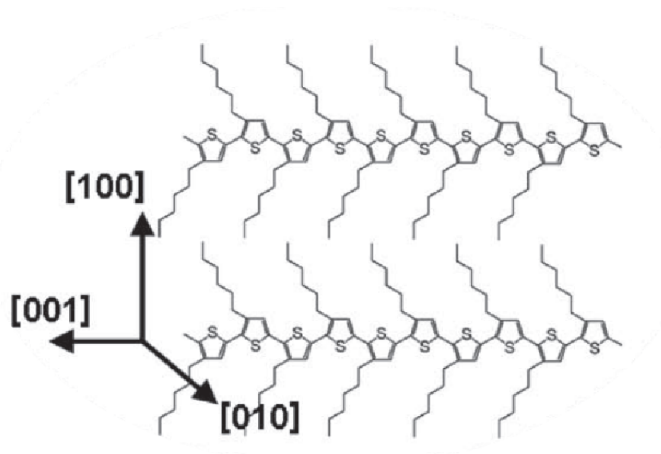
annealed

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

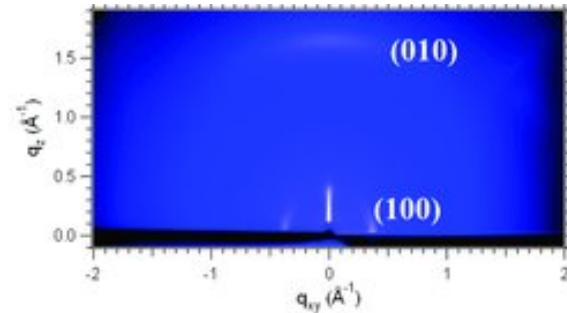
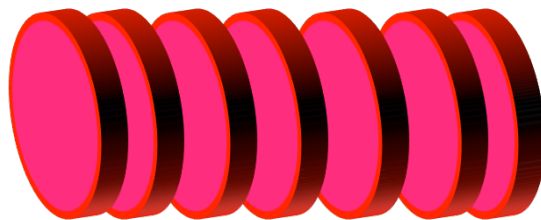
GIWAXS by Inspection: orientation

P3HT GIWAXS

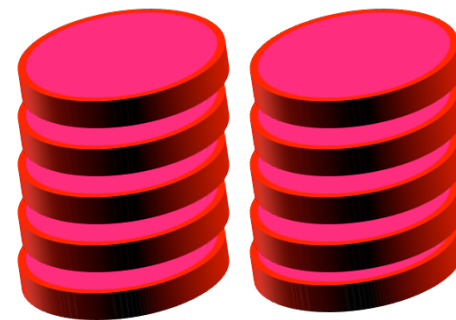
Crystal Structure



Edge-on

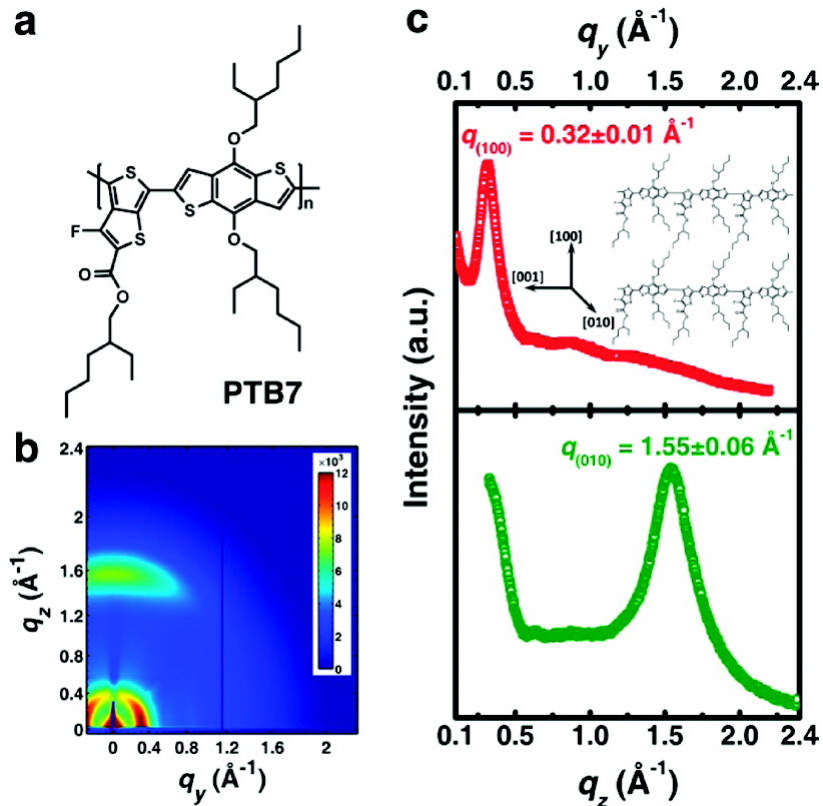


Face-on



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

Linecuts in GIXS Patterns Quantify Structure

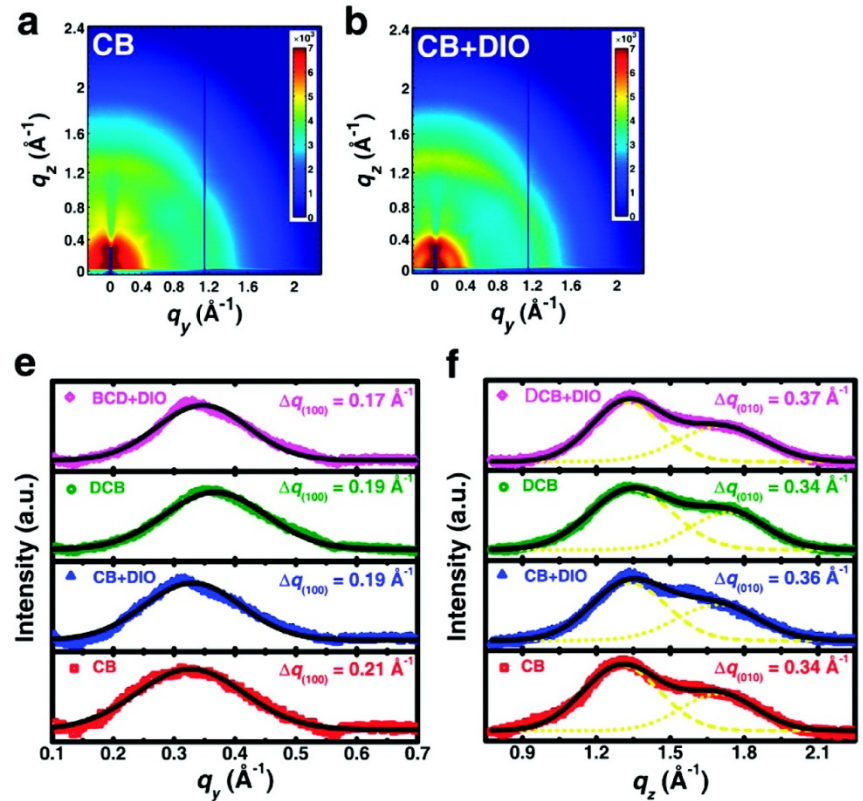
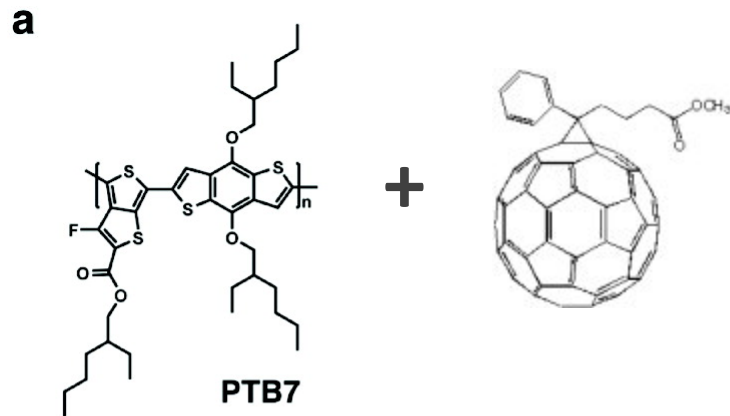


Vertical linecut → out of plane structure

Horizontal linecut → in plane structure

Fits help quantify peak center, linewidth

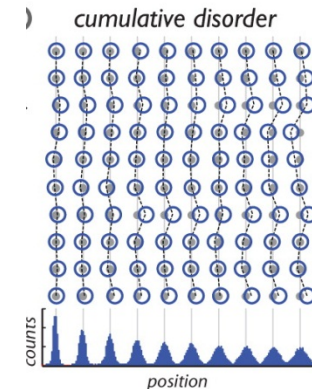
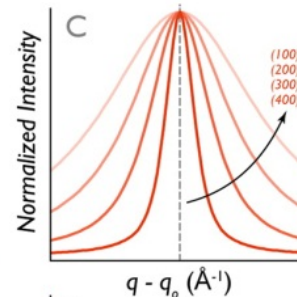
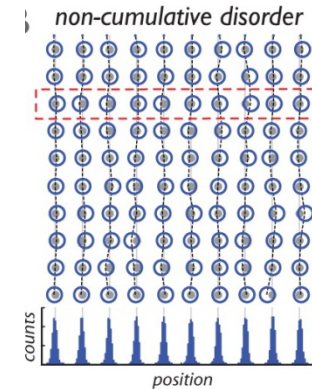
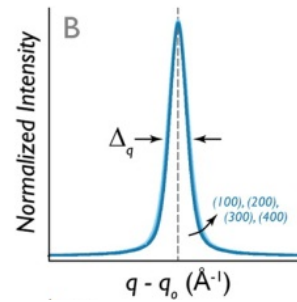
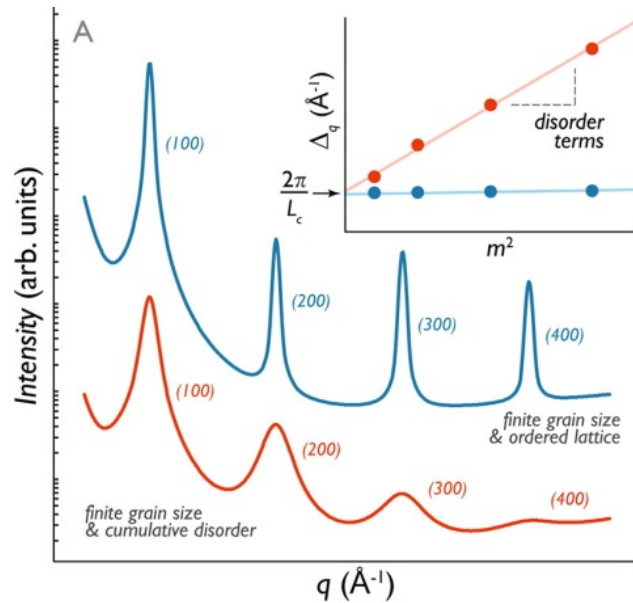
Linecuts in GIXS Patterns Quantify Structure



Vertical linecut \rightarrow out of plane structure
 Horizontal linecut \rightarrow in plane structure
 Fits help quantify peak center, linewidth

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

Lattice Disorder Affects Linewidths



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

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)

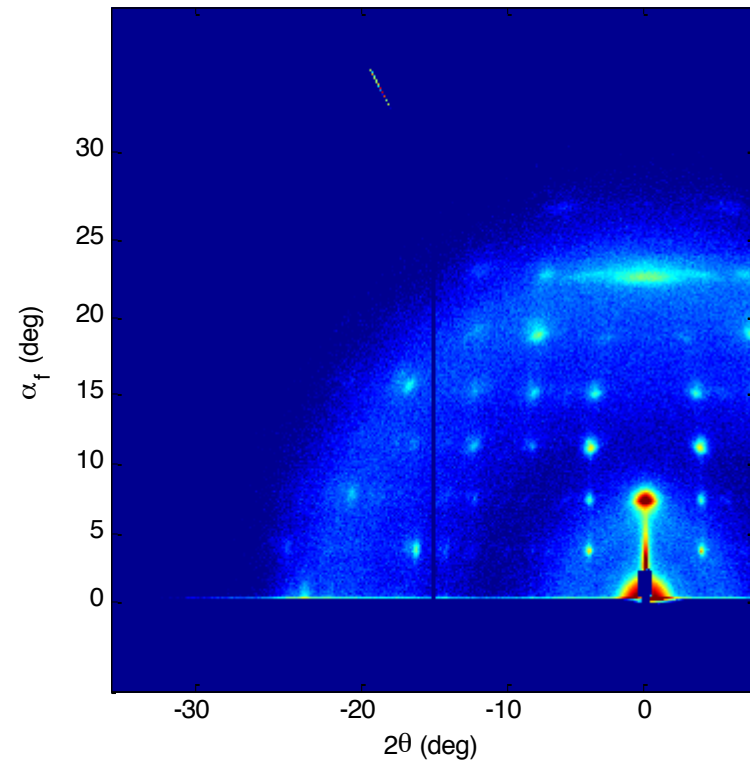
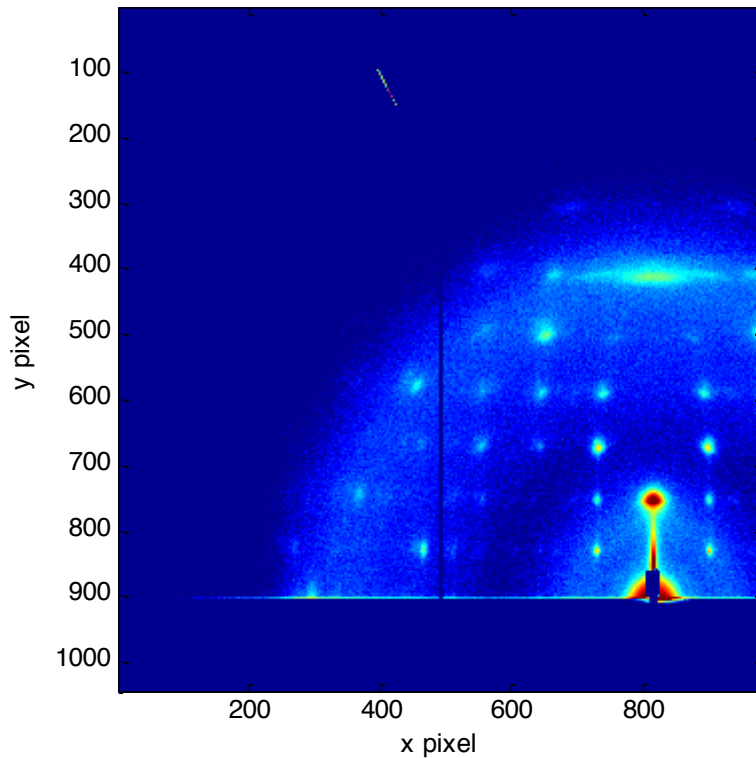
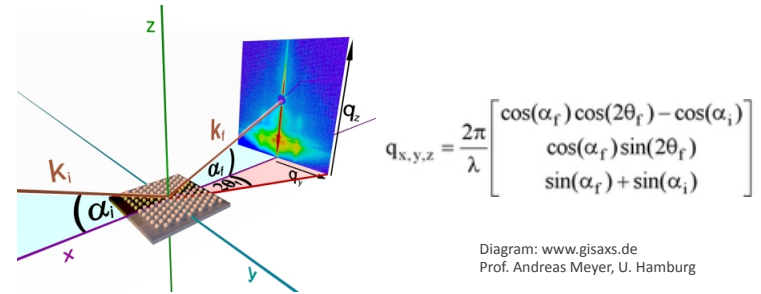
20 μ m vertical slits (200 μ m horizontal slits)

α_i : incident angle (0.2°)

$w = 20 \mu\text{m}/\sin(0.2^\circ) \approx 6 \text{ mm}$

Vertical slit size determines the resolution.

Representing GIWAXS data

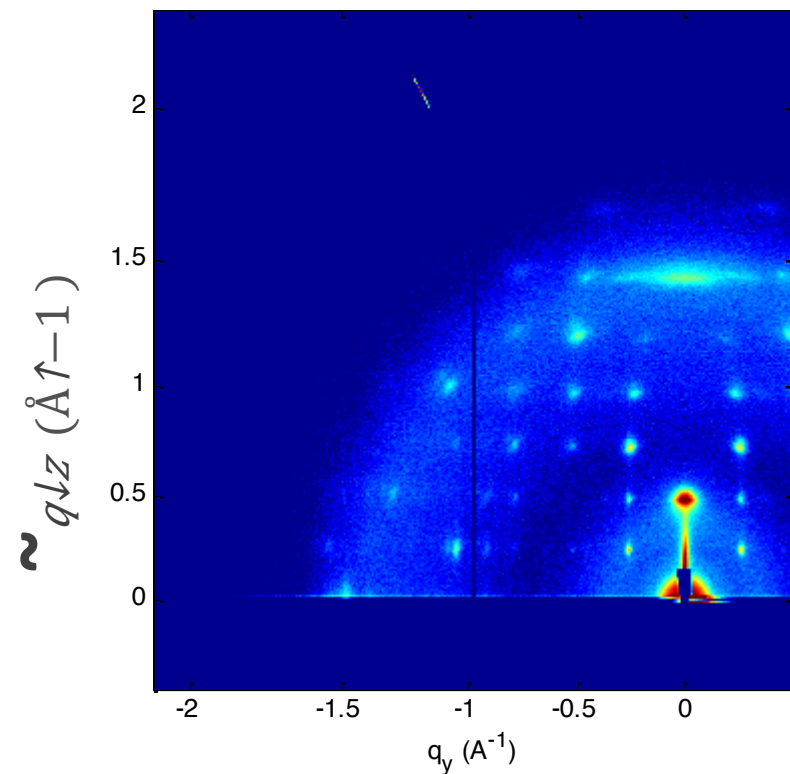
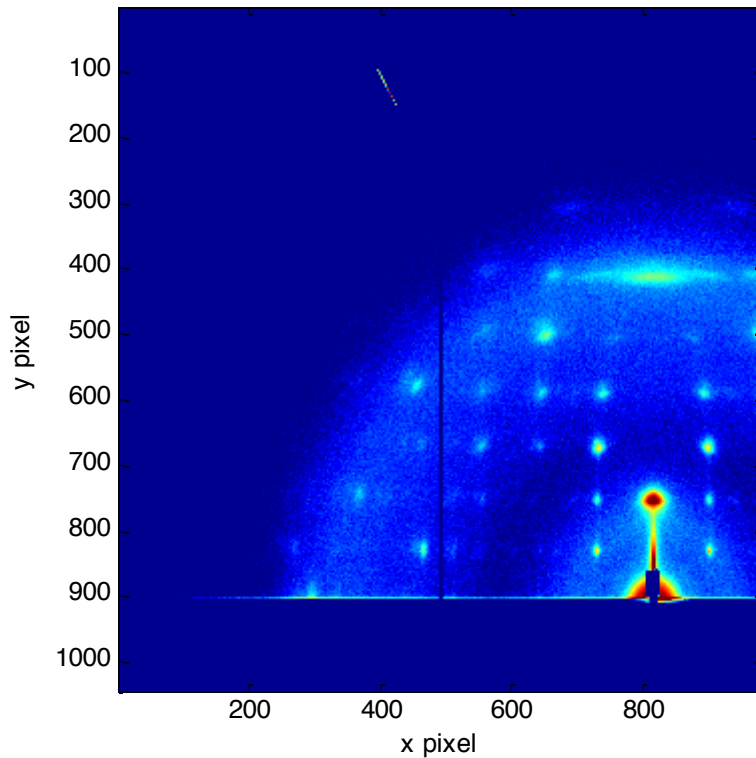
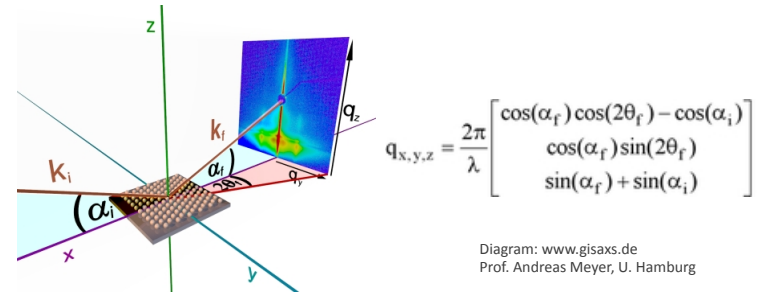


Data: Rafael Verduzco group, Rice University

2014 ACA Meeting: WK02 GISAXS Theory & Analysis

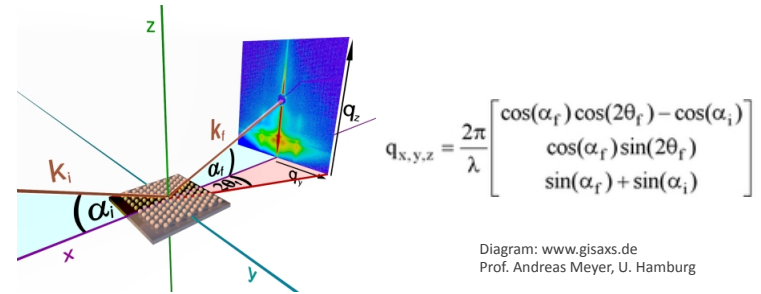
Angle representation $I(2\theta, \alpha_f)$ correct,
but limits information

Representing GIWAXS data

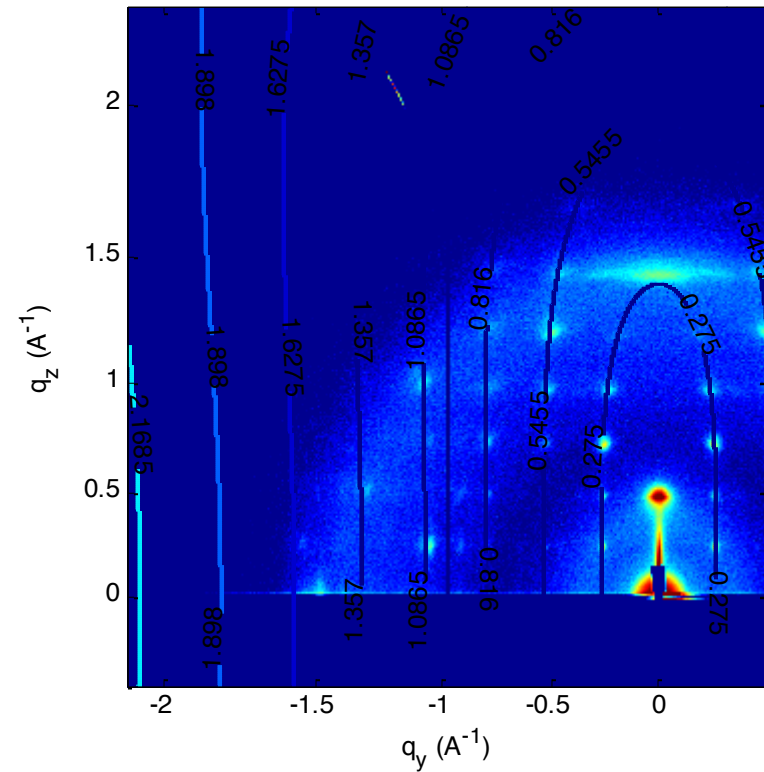
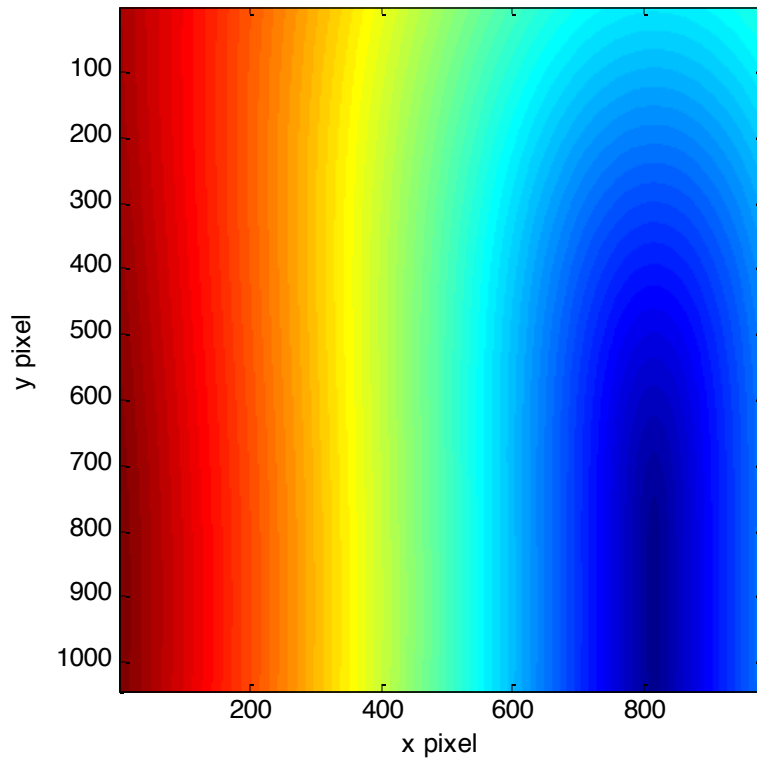


Q-space representation $I(q_y, q_z)$ often conventional, but not correct.

Representing GIWAXS data



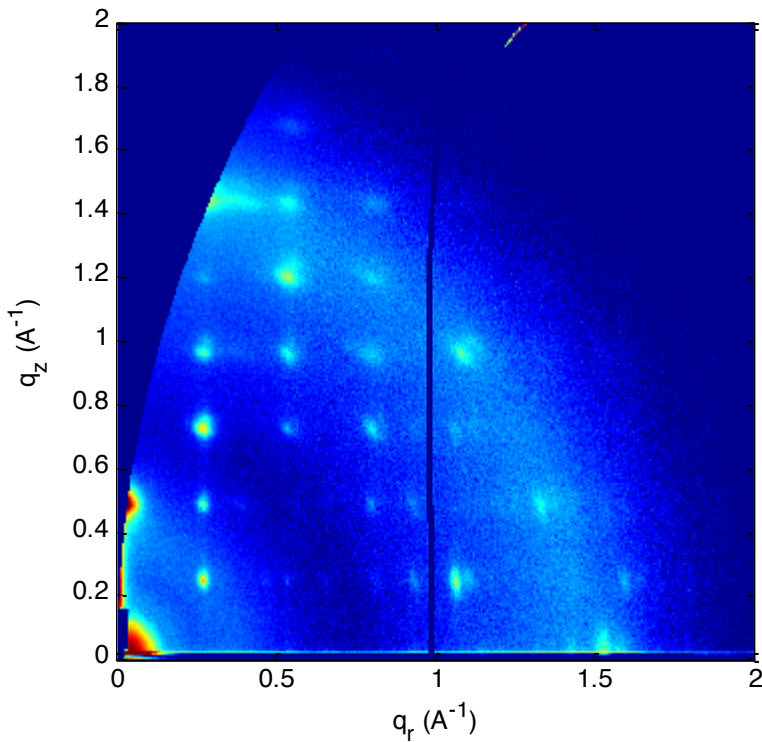
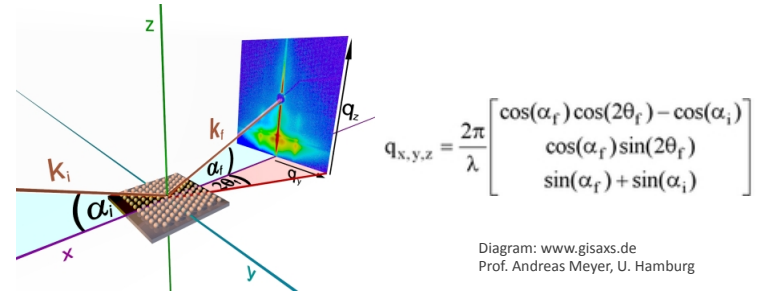
Map of constant q_r values in pixel space.



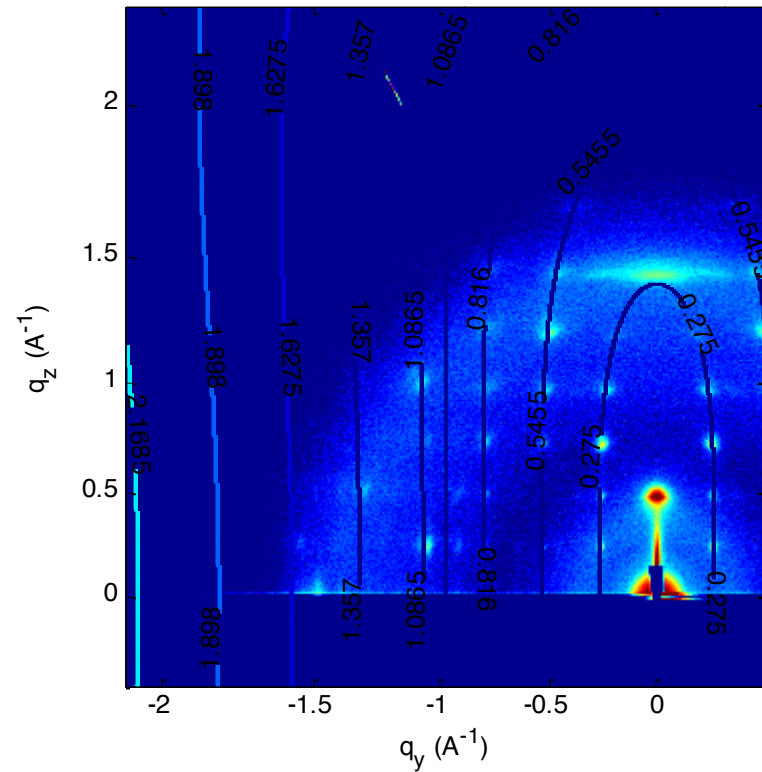
Features follow contours of equal $q_r = \sqrt{q_x^2 + q_y^2}$

Representing GIWAXS data

Reshaping the data into $I(q_r, q_z)$ makes relationship between reflections more clear.



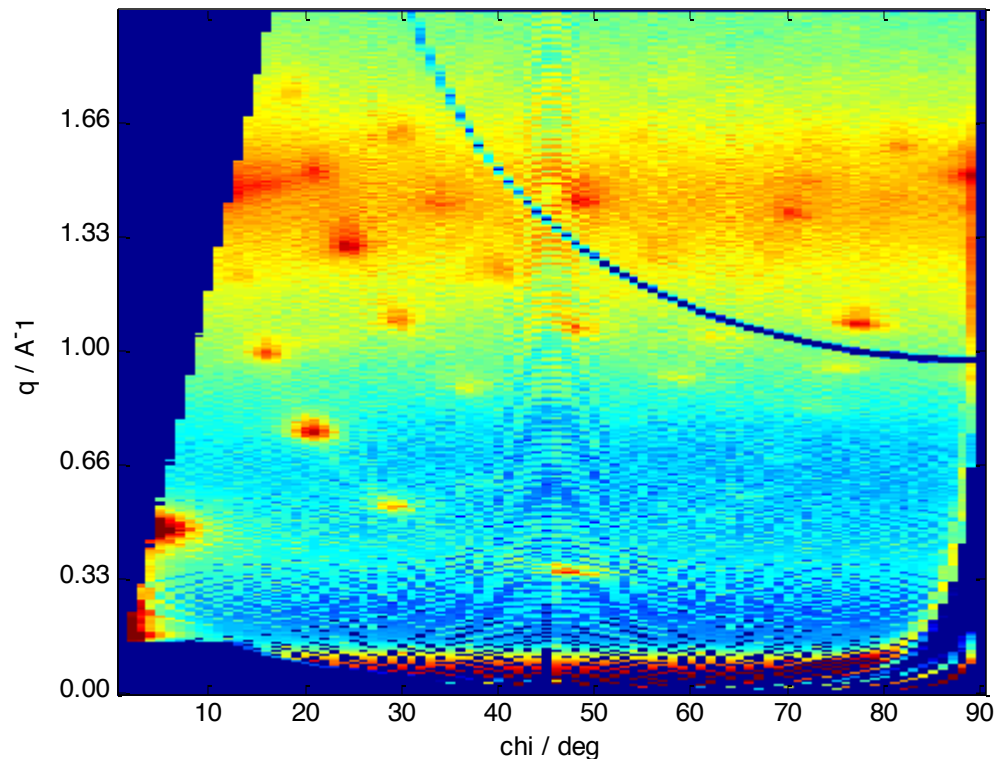
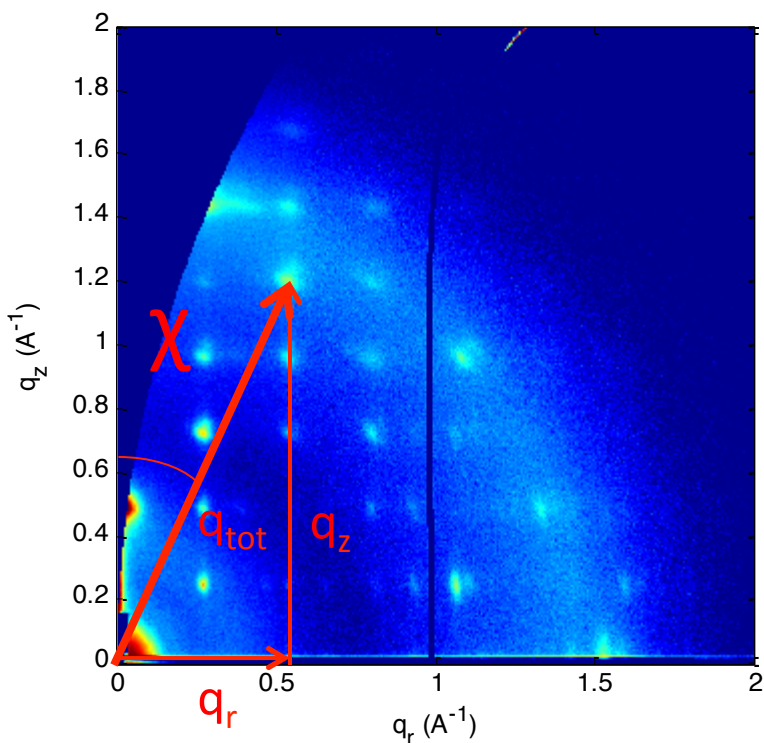
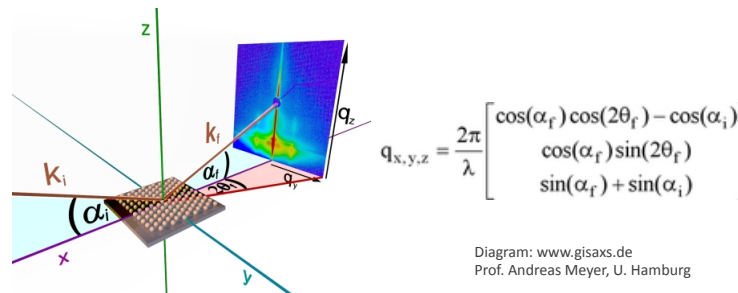
Features at constant q_r follow straight lines.



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

Representing GIWAXS data

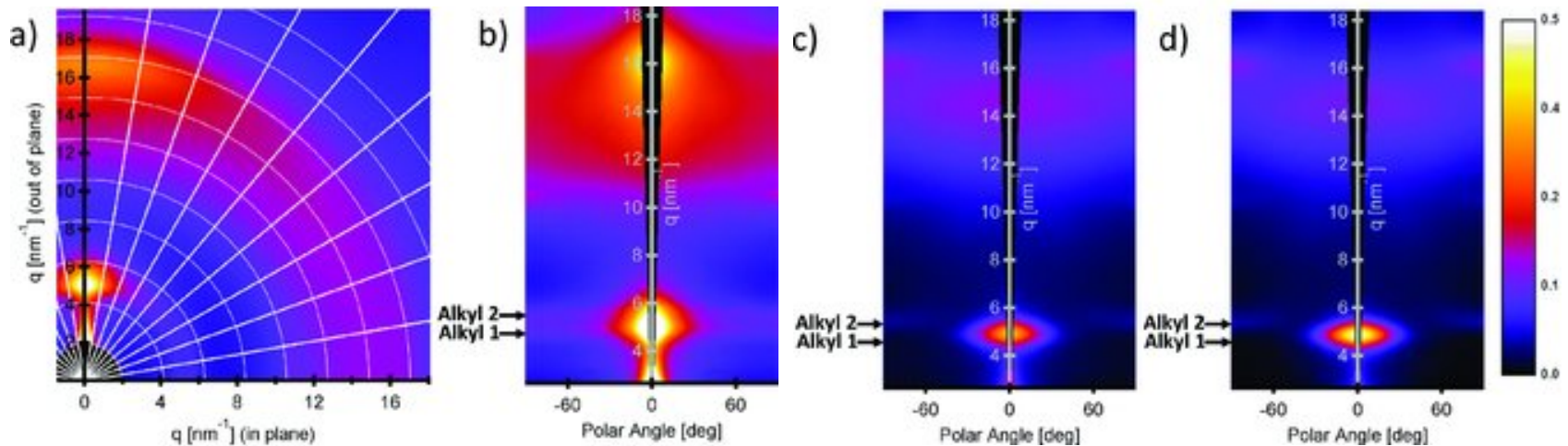
Further reshaping into $I(\chi, q)$ very useful for comparing arcing features



Ordinate is now

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

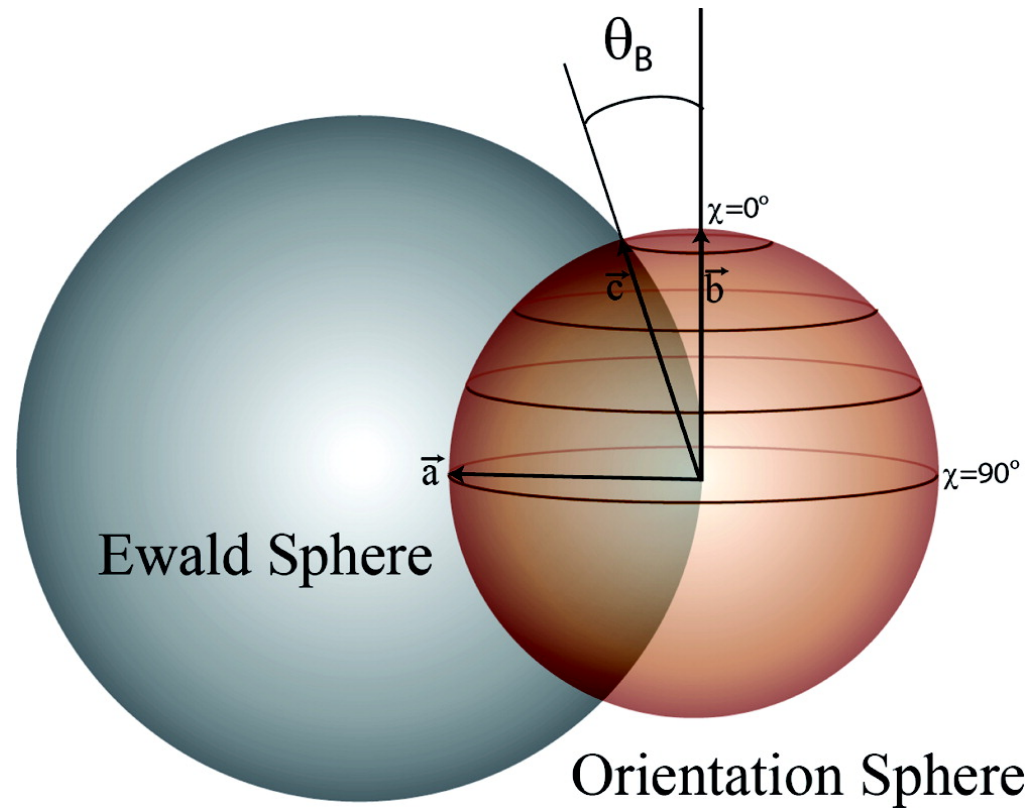
Representing GIWAXS data: sector plots



Sector plot shows different crystalline forms.

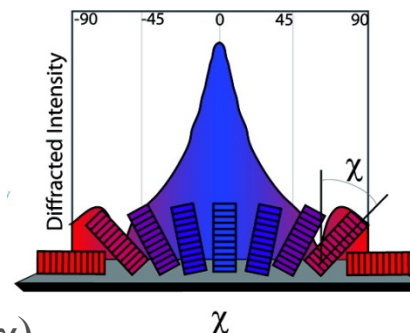
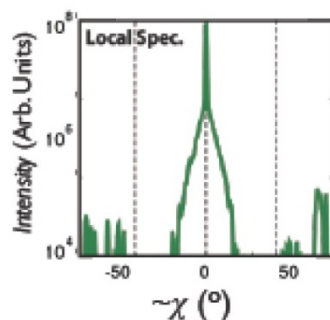
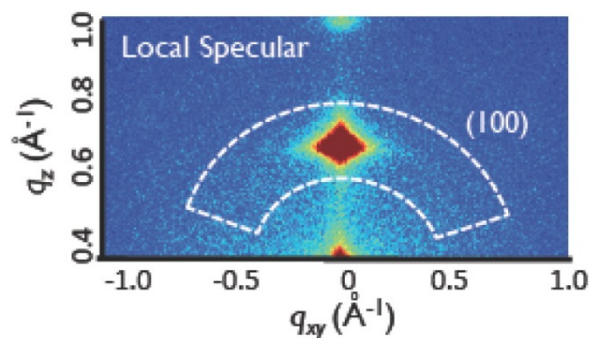
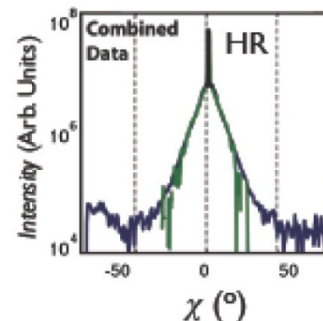
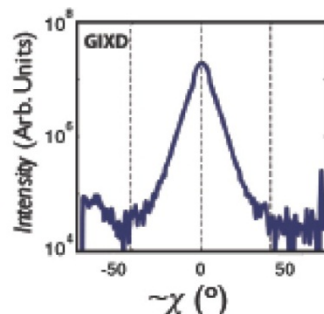
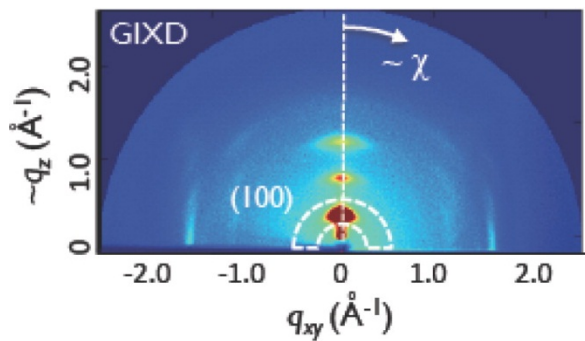
Rogers, Schmidt, Toney, Kramer, and Bazan, *Adv. Mater.* **23** 2284-2288 (2011).

Filling in the GIWAXS “blind spot”



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

Constructing Pole Figures



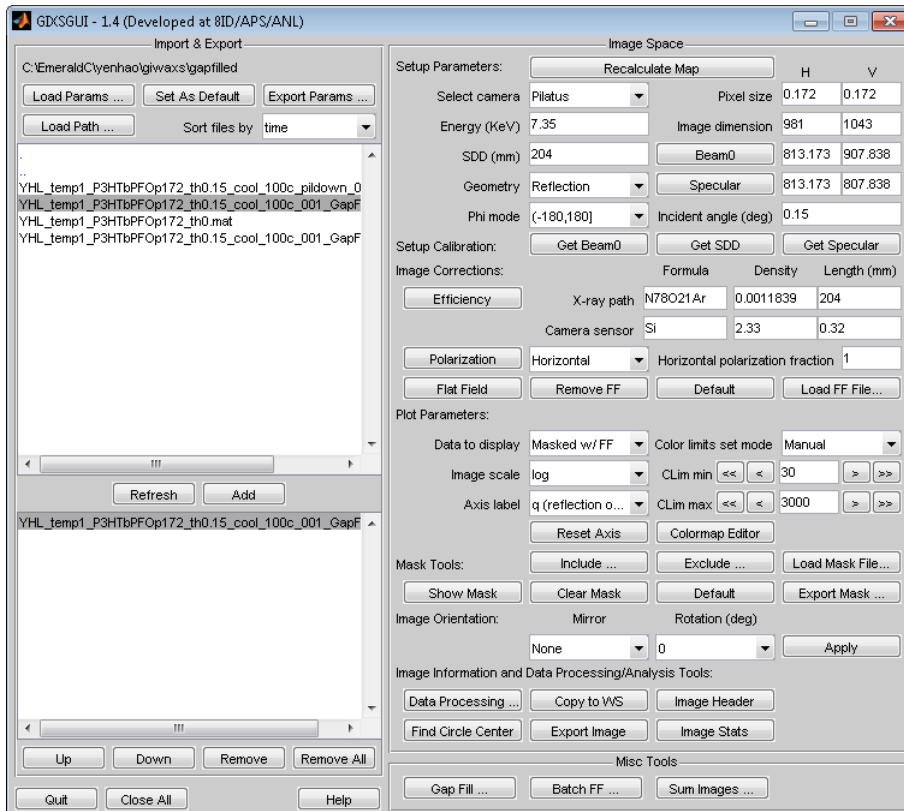
Stitch together linecuts
 GIWAXS + specular + rocking curve → pole figure $I(\chi)$
 Integrating $I(\chi)$ gives Degree of Crystallinity

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.

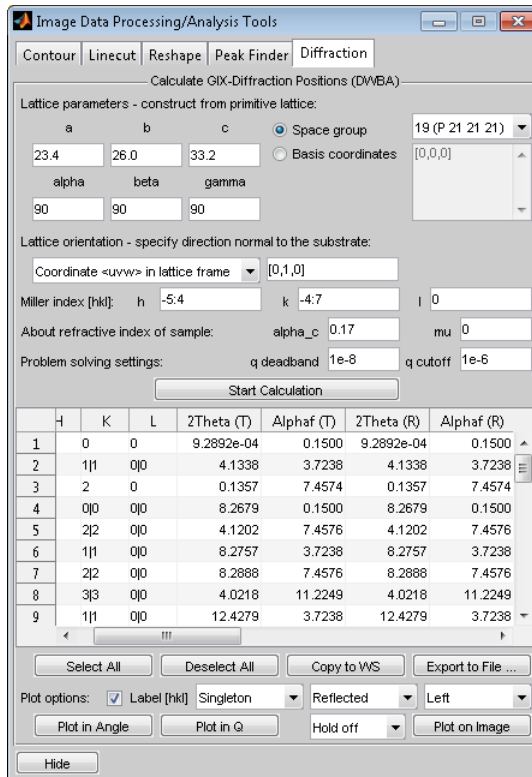


- Display 2-D data (pixel-, angle- or q-space)
- Apply corrections
- Calibrate detector distance from standard data
- Compute linecuts
- Sum/average 2-d files
- Interactive GUI
- Fully scriptable

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

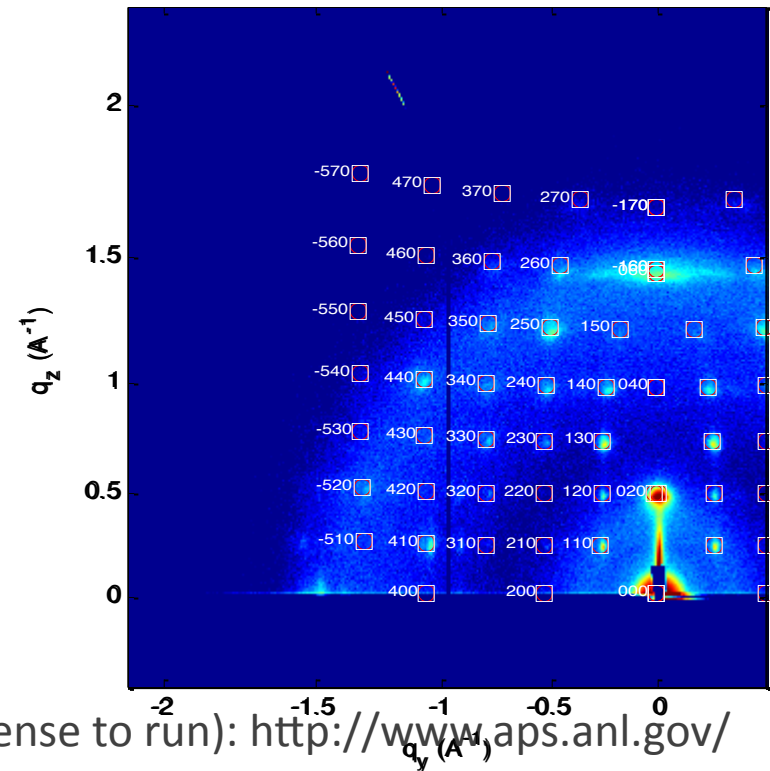
GIXSGUI software package

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



Under development:

- Reflection indexing



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

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

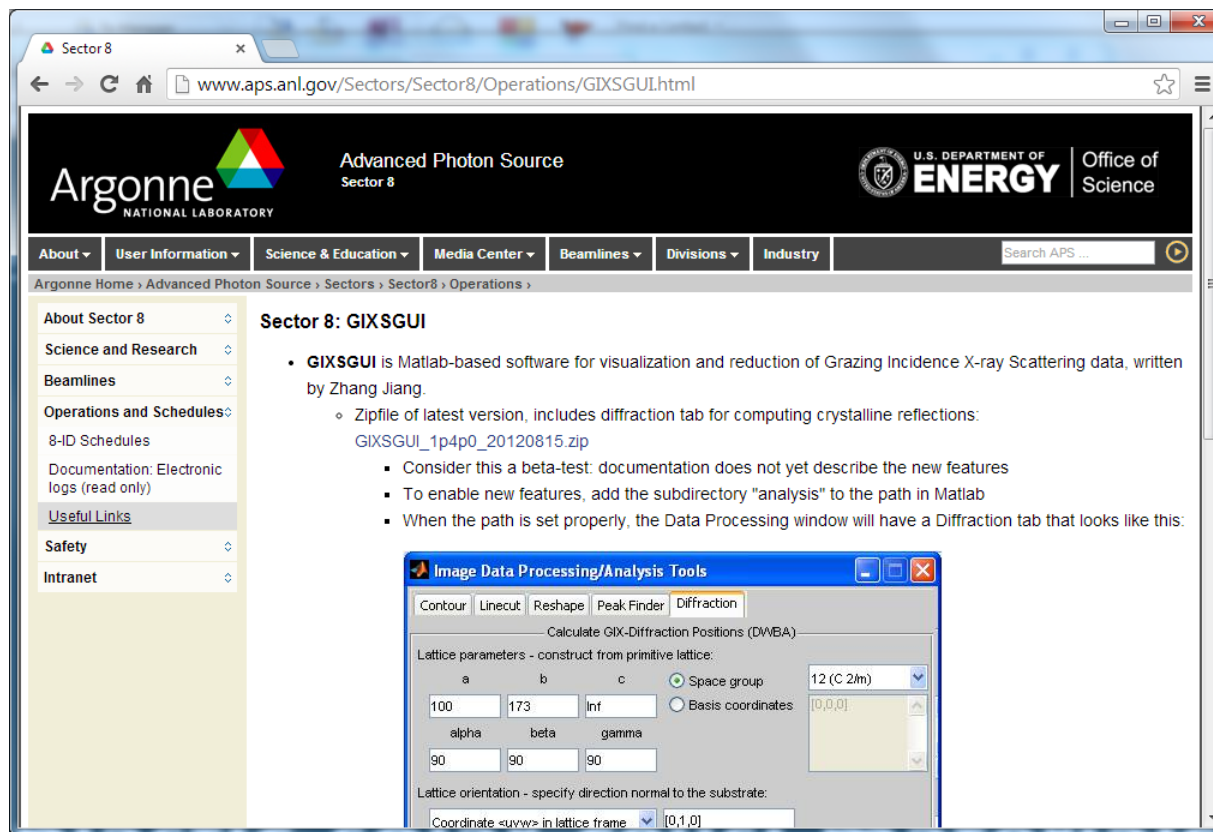
Joseph Strzalka

strzalka@aps.anl.gov

GIXSGUI by Zhang Jiang

Downloading GIXSGUI

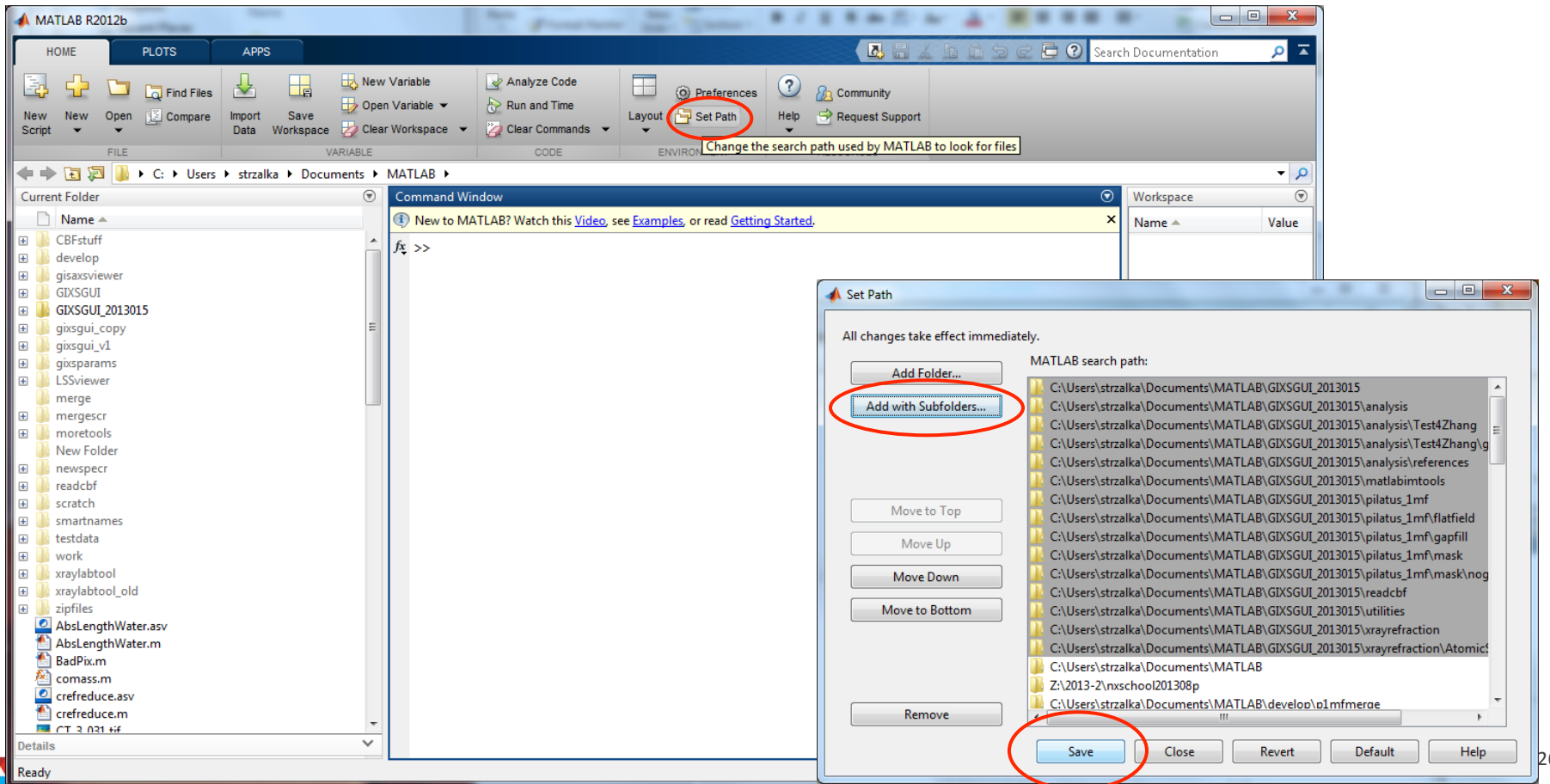
- GIXSGUI is a Matlab package available for download:
www.aps.anl.gov/Sectors/Sector8/Operations/GIXSGUI.html
- Use requires license for Matlab (Distribution 2010a or newer).



The screenshot shows a web browser window displaying the GIXSGUI page on the Argonne National Laboratory website. The page title is "Sector 8: GIXSGUI". The content includes a description of GIXSGUI as Matlab-based software for visualization and reduction of Grazing Incidence X-ray Scattering data, written by Zhang Jiang. It also provides a link to a zipfile of the latest version (GIXSGUI_1p4p0_20120815.zip) and lists two bullet points: "Consider this a beta-test: documentation does not yet describe the new features" and "To enable new features, add the subdirectory 'analysis' to the path in Matlab". A third bullet point states: "When the path is set properly, the Data Processing window will have a Diffraction tab that looks like this:". Below the text, a window titled "Image Data Processing/Analysis Tools" is shown. The window has tabs for "Contour", "Linecut", "Reshape", "Peak Finder", and "Diffraction". The "Diffraction" tab is active, showing a "Calculate GIX-Diffraction Positions (DWBA)" section. The "Lattice parameters - construct from primitive lattice:" section includes input fields for "a" (100), "b" (173), and "c" (inf), and a "Space group" dropdown menu set to "12 (C 2/m)". The "Lattice orientation - specify direction normal to the substrate:" section includes a "Coordinate <uvw> in lattice frame" dropdown menu set to "[0,1,0]".

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.

The screenshot displays the MATLAB R2012b environment. The Command Window shows the following commands:

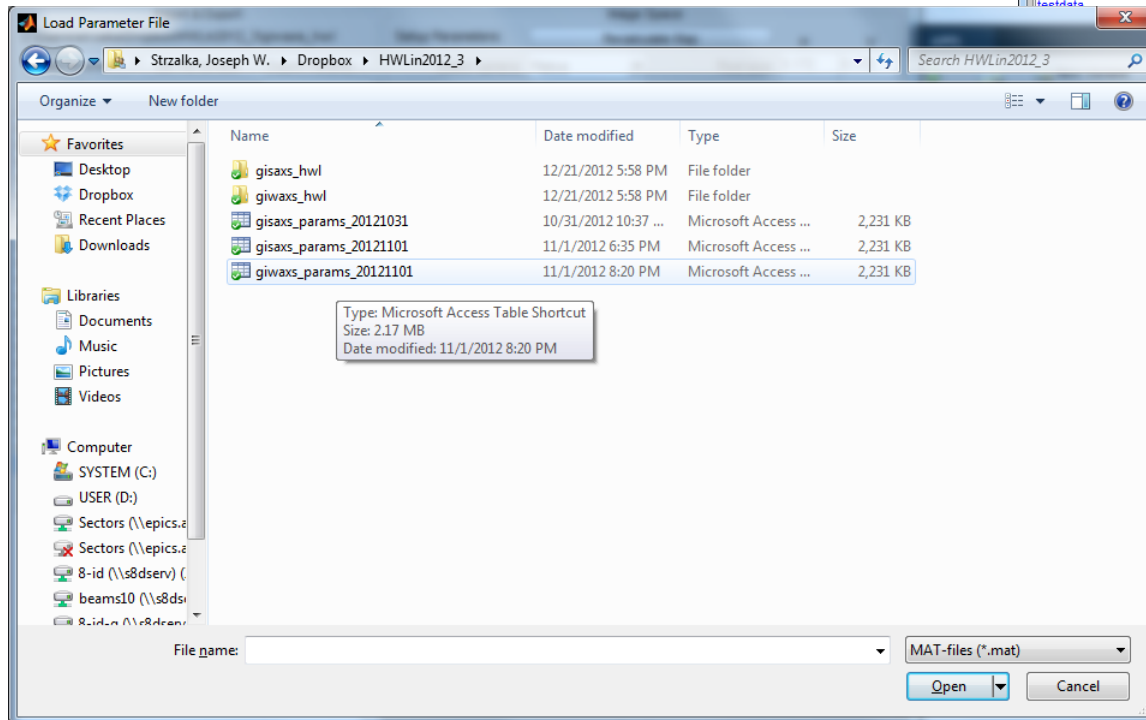
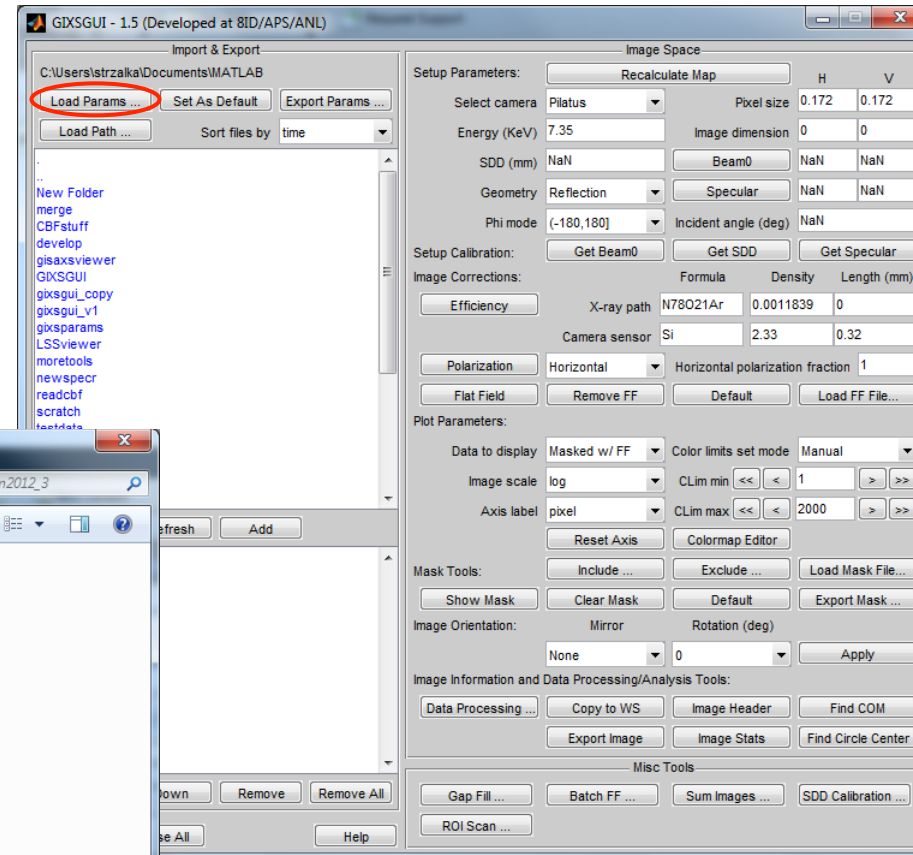
```
>> gixsgui
fx >>
```

The GIXSGUI - 1.5 (Developed at 8ID/APS/ANL) window is open, showing the following configuration options:

- Import & Export:** Load Params..., Set As Default, Export Params..., Load Path..., Sort files by: time
- Image Space:**
 - Setup Parameters: Recalculate Map, H, V
 - Select camera: Pilatus, Pixel size: 0.172, 0.172
 - Energy (KeV): 7.35, Image dimension: 0, 0
 - SDD (mm): NaN, Beam0, NaN, NaN
 - Geometry: Reflection, Specular, NaN, NaN
 - Phi mode: (-180, 180], Incident angle (deg): NaN
 - Setup Calibration: Get Beam0, Get SDD, Get Specular
 - Image Corrections: Efficiency, X-ray path: N78021Ar, Formula: 0.0011839, Density: 0, Length (mm): 0
 - Camera sensor: Si, 2.33, 0.32
 - Polarization: Horizontal, Horizontal polarization fraction: 1
 - Flat Field: Remove FF, Default, Load FF File...
- Plot Parameters:**
 - Data to display: Masked w/ FF, Color limits set mode: Manual
 - Image scale: log, CLim min: 1, CLim max: 2000
 - Axis label: pixel, CLim max: 2000
 - Buttons: Reset Axis, Colormap Editor
- Mask Tools:** Include..., Exclude..., Load Mask File..., Show Mask, Clear Mask, Default, Export Mask...
- Image Orientation:** Mirror, Rotation (deg): 0, Apply
- Image Information and Data Processing/Analysis Tools:** Data Processing..., Copy to WS, Image Header, Find COM, Export Image, Image Stats, Find Circle Center
- Misc Tools:** Gap Fill..., Batch FF..., Sum Images..., SDD Calibration..., ROI Scan...

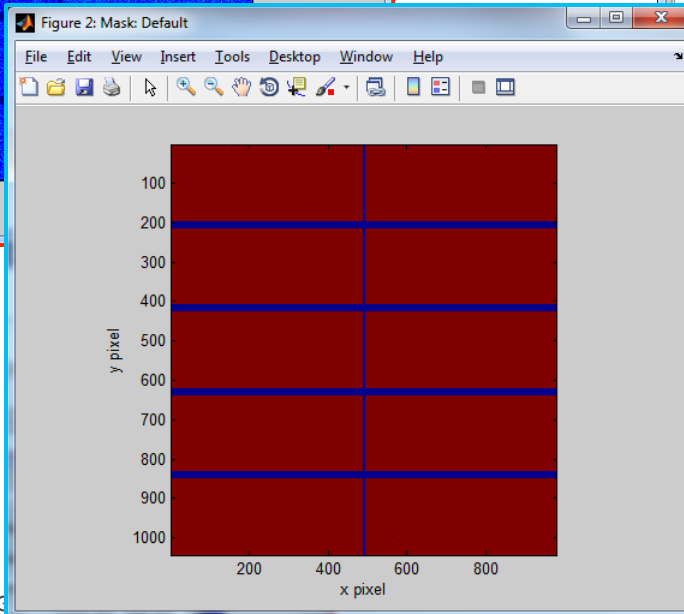
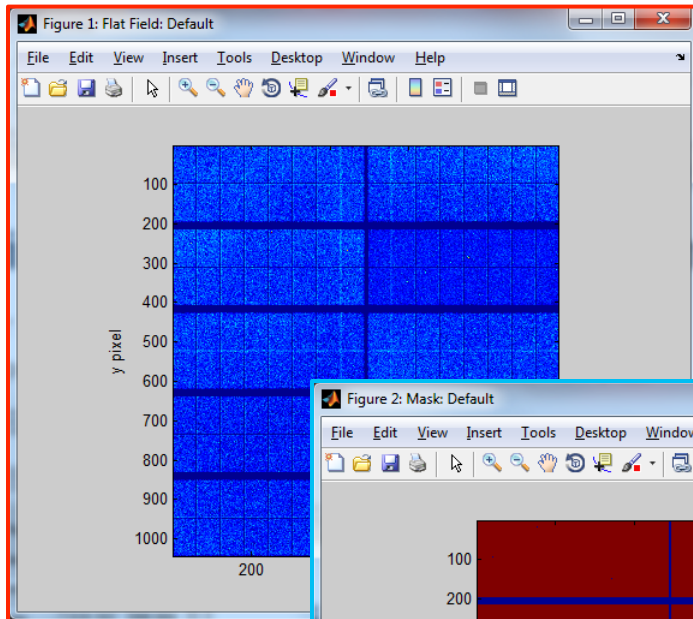
Loading GIXSGUI parameters from a file

- 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

GIXSGUI - 1.5 (Developed at 8ID/APS/ANL)

Import & Export

C:\Users\lstrzalka\Dropbox\Hwlin2012_3\giwaxs_hwl

Load Params ... **Set As Default** Export Params ...

Load Path ... Sort files by: time

- hwI_bladeITOWaxs_030.tif
- hwI_bladeITOWaxs_031.tif
- hwI_bladeITOWaxs_032.tif
- hwI_bladeITOWaxs_033.tif
- hwI_bladeITOWaxs_034.tif
- hwI_bladeglasswaxs_001.tif
- hwI_bladeglasswaxs_002.tif
- hwI_bladeglasswaxs_003.tif
- hwI_bladeglasswaxs_004.tif
- hwI_bladeglasswaxs_005.tif
- hwI_bladeglasswaxs_006.tif
- hwI_bladeglasswaxs_007.tif
- hwI_bladeglasswaxs_008.tif
- hwI_bladeglasswaxs_009.tif
- hwI_bladeglasswaxs_010.tif
- hwI_bladeglasswaxs_011.tif
- hwI_bladeglasswaxs_012.tif
- hwI_bladeglasswaxs_013.tif
- hwI_bladeglasswaxs_014.tif
- hwI_bladeglasswaxs_023.tif
- hwI_bladeglasswaxs_024.tif

Refresh Add

Image Space

Recalculate Map

Setup Parameters:

Select camera: Pilatus Pixel size: 0.172 0.172

Energy (KeV): 7.35 Image dimension: 826.562 996.999

SDD (mm): 204 Beam0: 826.562 896.999

Geometry: Reflection Specular

Phi mode: (-180, 180] Incident angle (deg): 0.2

Setup Calibration: Get Beam0 Get SDD Get Specular

Image Corrections: Formula Density Length (mm)

Efficiency X-ray path: N78021Ar 0.0011839 204

Polarization: Horizontal Camera sensor: Si 2.33 0.32

Flat Field: Remove FF Default Load FF File...

Plot Parameters:

Data to display: Masked w/ FF Color limits set mode: Manual

Image scale: log CLim min: 1 CLim max: 2000

Axis label: pixel

Reset Axis Colormap Editor

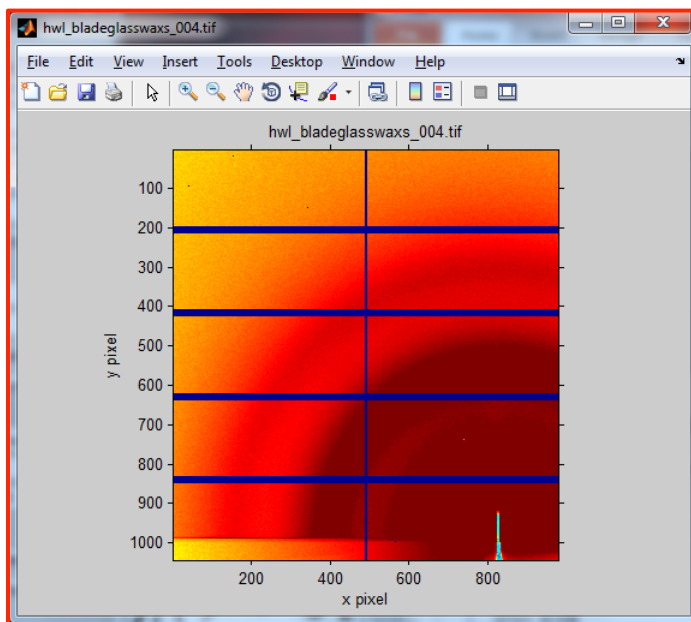
hwl_bladeglasswaxs_004.tif

File Edit View Insert Tools Desktop Window Help

hwl_bladeglasswaxs_004.tif

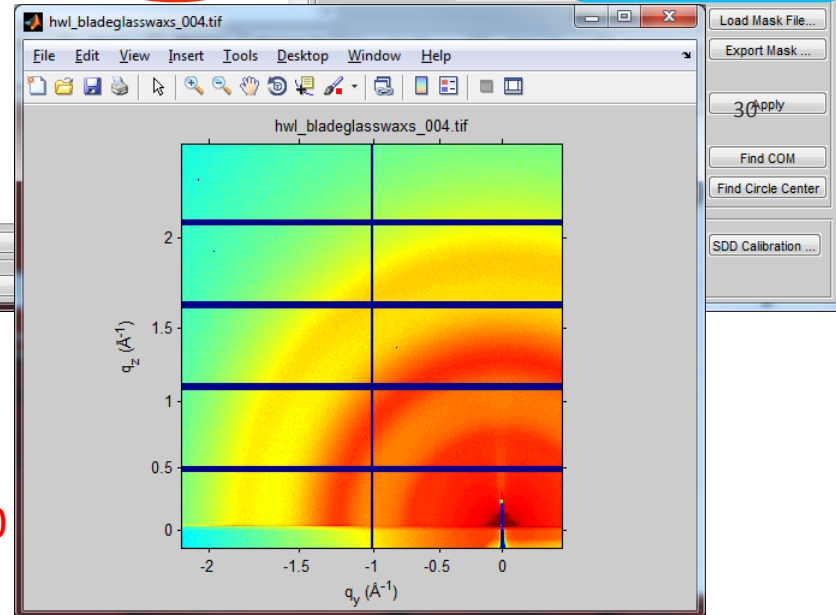
Up Quit

Load Mask File... Export Mask... Apply Find COM Find Circle Center SDD Calibration ...



→

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**.

The image shows two windows from the GIXSGUI software. The left window is the main application, titled 'GIXSGUI - 1.5 (Developed at 8ID/APS/ANL)'. It features a file list on the left with 'hwl_bladeglasswaxs_004.tif' selected. The main panel contains various setup parameters for an X-ray diffraction experiment, including camera type (Pilatus), energy (7.35 KeV), SDD (204 mm), and geometry (Reflection). At the bottom, the 'Data Processing/Analysis Tools' window is open, showing options for 'Linecut' and 'Constrained linecut'. The 'Linecut plot scale' is set to 'logy'. The 'X variable' is 'q' and the '# of points' is '200'. The 'Constrained linecut' section has four constraints defined. The 'Cut' button is highlighted with a purple circle, and the 'Constrained Image' button is highlighted with a blue circle.

Image Data Processing/Analysis Tools

Contour | **Linecut** | Reshape | Peak Finder | Diffraction

Linecut Tools

Linecut plot scale: logy

Free linecut: Interactive Cut | Defined Cut

X variable(s): Alphaf (for reflection only), Chi (for reflection only), x pixel, y pixel, pixel distance

Constrained linecut: X variable q | # of points 200

Constraint #	Operator	Value	Operator	Variable	Operator	Value
Constraint #1	AND	180	<=	phi	<=	170
Constraint #2	AND	NaN	<=	none	<=	NaN
Constraint #3	AND	NaN	<=	none	<=	NaN
Constraint #4	AND	NaN	<=	none	<=	NaN

Cut | Constrained Mask | **Constrained Image**

Overlay current linecut to Figure #: Overlay

Example Linecut

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

