Survey of OPLS

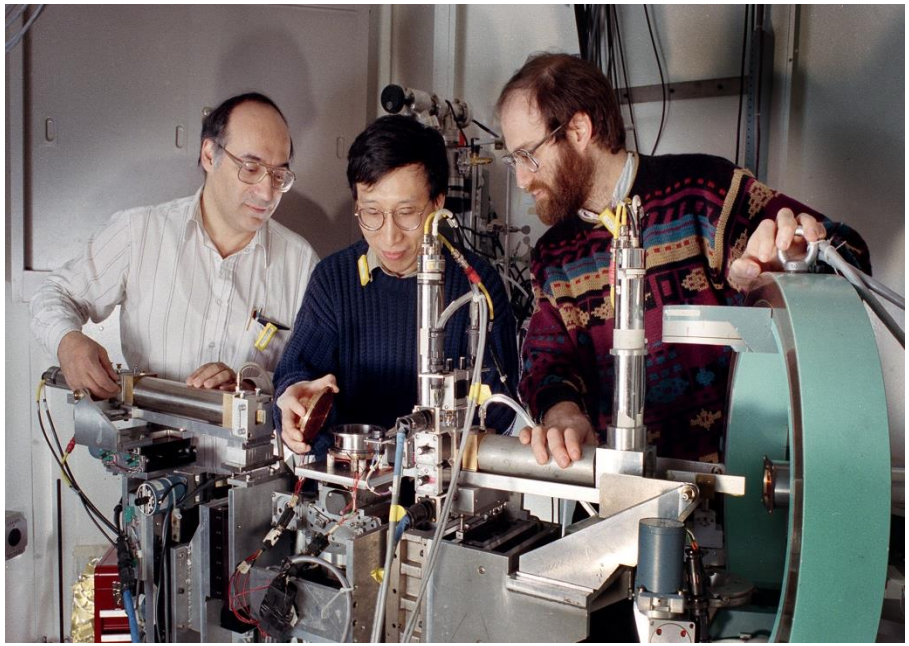
Ben Ocko (NSLS II @ BNL)
Dec 10,2024

Agenda

1. Video Tour and discussion of the OPLS beamline at NSLS II.
    a. Highlight features, detectors, sample cells.
2. Decide date and discussion leader for March meeting, possibly March 18 or 25.
3. Possible other discussions
    a. Plans for a tender XR liquids instrument at SMI using the GISAXS in vacuum instrument using Pseudo XR.
    b. Software for Pseudo XR, how can we develop a universal software platform.
    c. New developments at other facilities

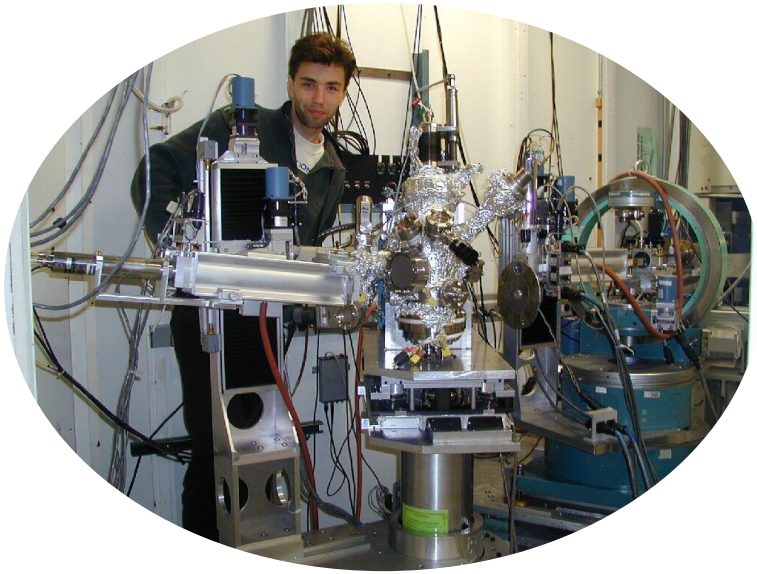

Birth of Liquid Surface X-ray Science (~40 years ago)
Peter Pershan and Jen Als-Nielsen at D4 (DORIS)

Photos from the NSLS liquids Instruments (closed in 2014)
Liquids program started in 1986 at NSLS with Prof. Peter Pershan



~1993

Moshe Deutsch, Xiao Zhong Wu & Ben Ocko
taken soon after the discovery of surface freezing



~2000
Improved Instrument
Can support heavy chambers
Oleg Shpyrko (liquid metal surface)

NSLS-II scattering beamlines under Complex Scattering Program

(Masa Fukuto is the Group Leader)

4-ID ISR: In-situ & Resonant X-ray Studies

- Hard & tender x-ray resonant scattering
- Time-resolved scattering

10-ID IXS: Inelastic X-ray Scattering

11-ID CHX: Coherent Hard X-ray Scattering

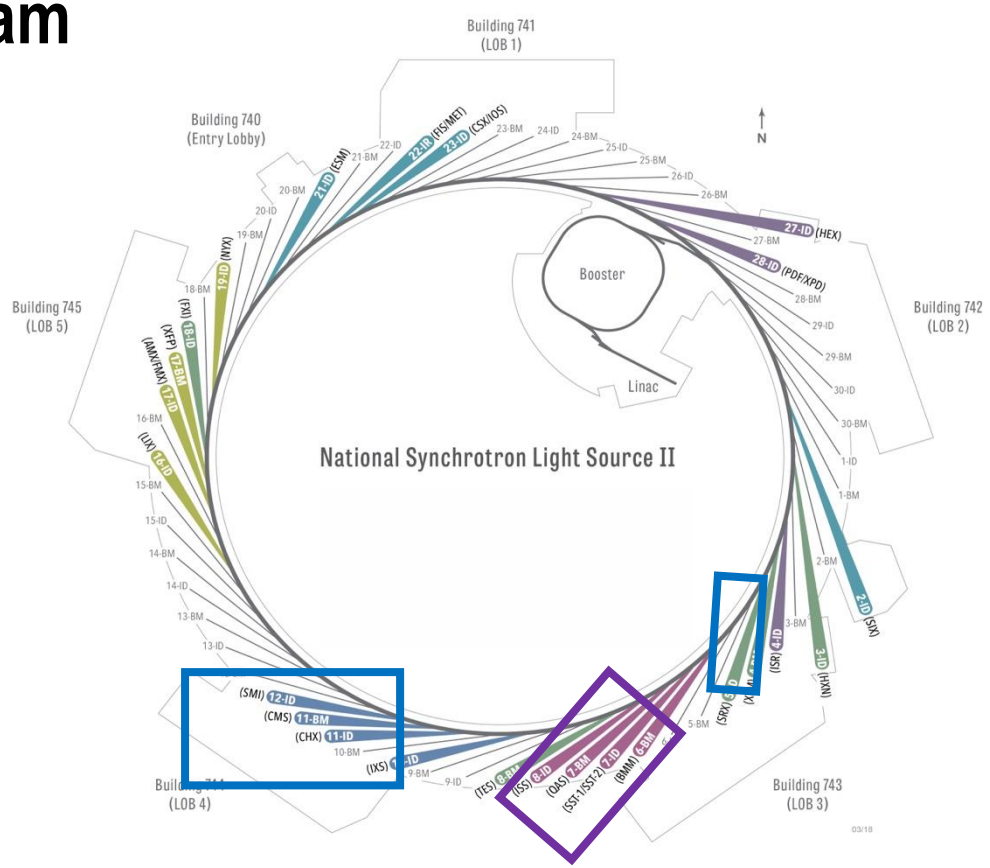
- X-ray photon correlation spectroscopy (XPCS)

11-BM CMS: Complex Materials Scattering

- High-throughput (GI)SAXS/WAXS

12-ID SMI: Soft Matter Interfaces

- High q-resolution, time-resolved (GI)SAXS/WAXS
- Microbeam SAXS/WAXS
- Hard & tender x-ray resonant SAXS/WAXS
- Liquid-surface scattering

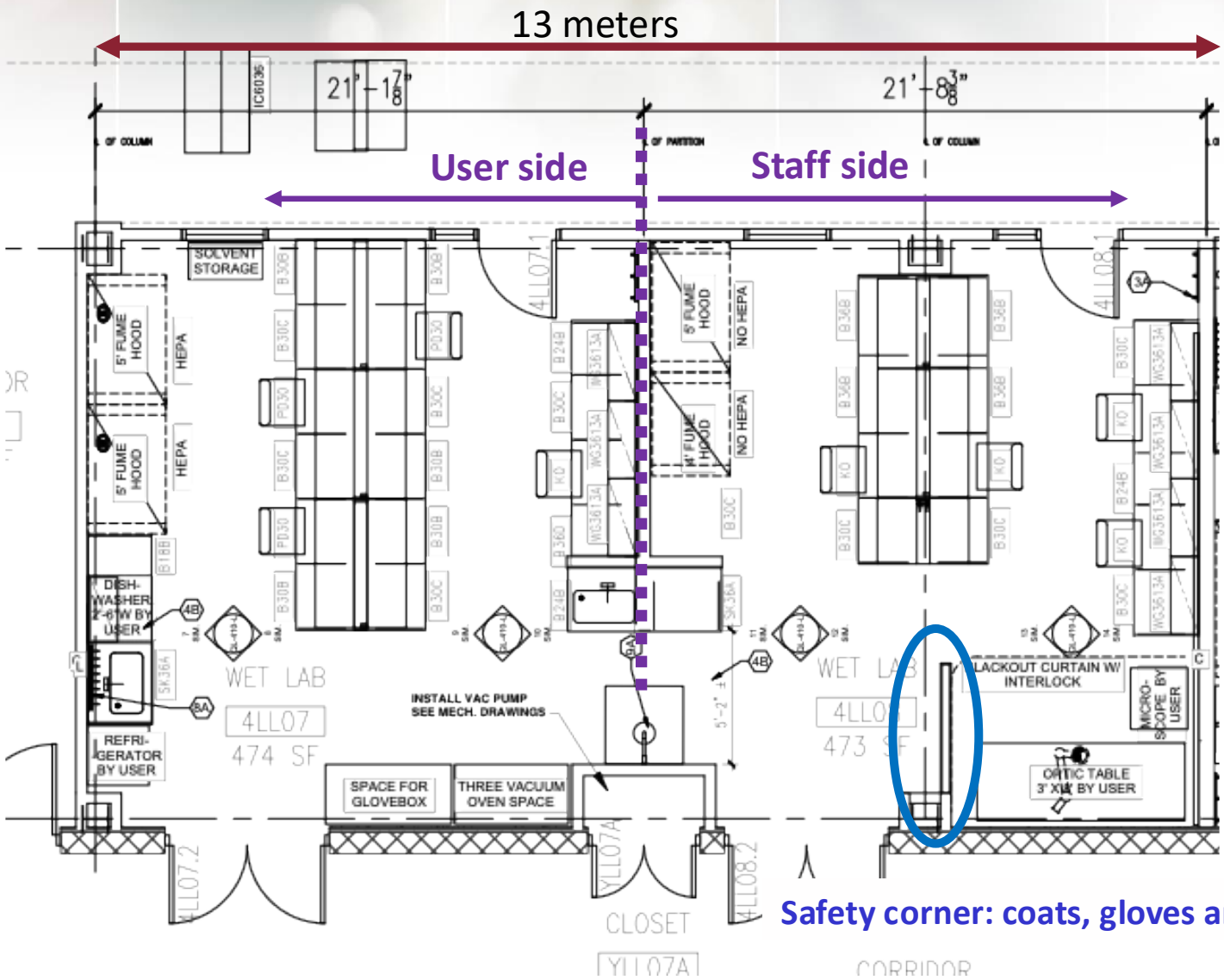


Operated by NIST

7-ID-1 SST: Spectroscopy Soft & Tender (NIST)

- Resonant soft x-ray scattering (RSoXS)

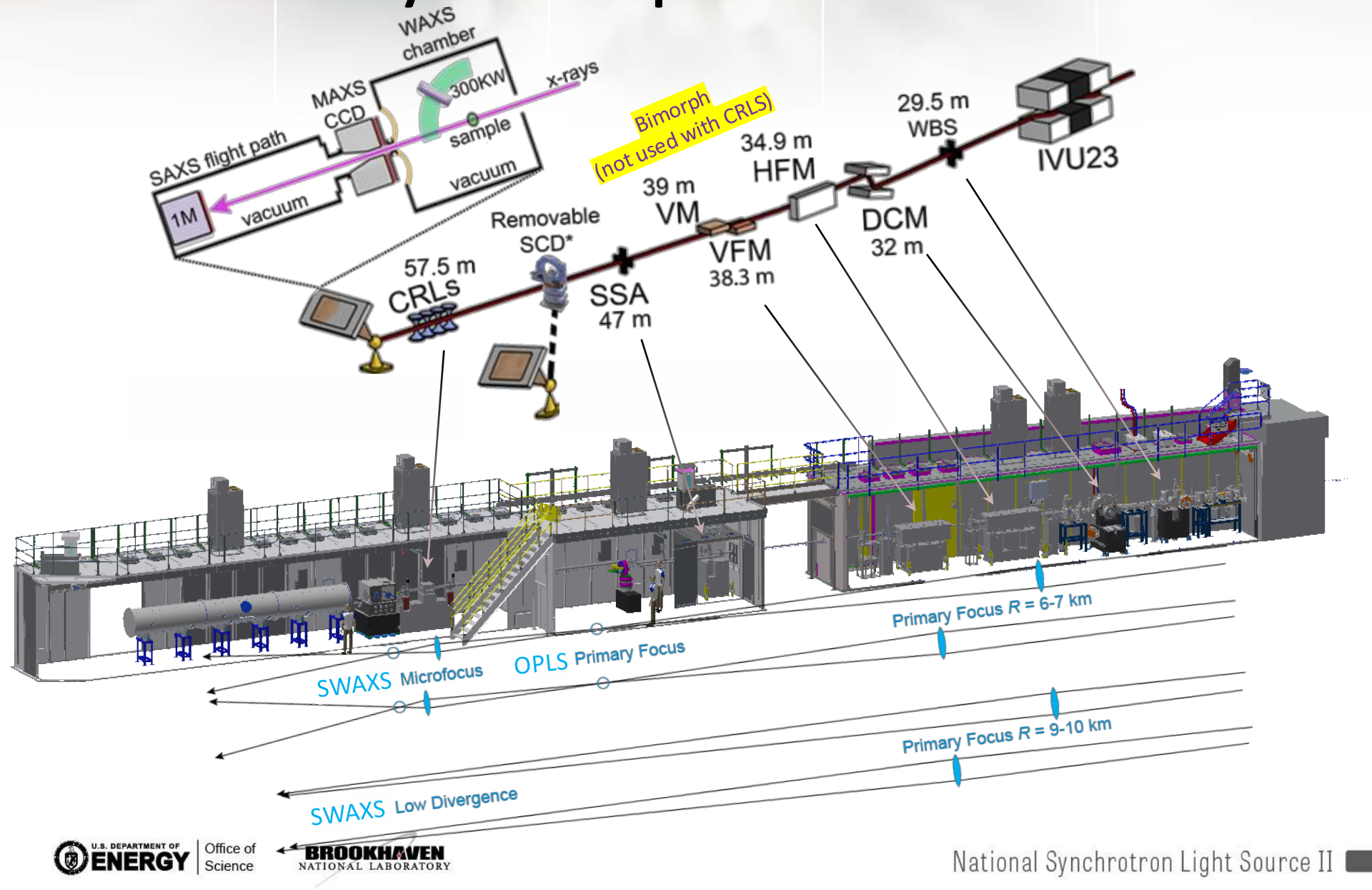
Huge Chemistry Lab for Soft Matter Science (4 hoods)



Safety corner: coats, gloves and eyewear

Glove box, spin coater, vacuum ovens, …

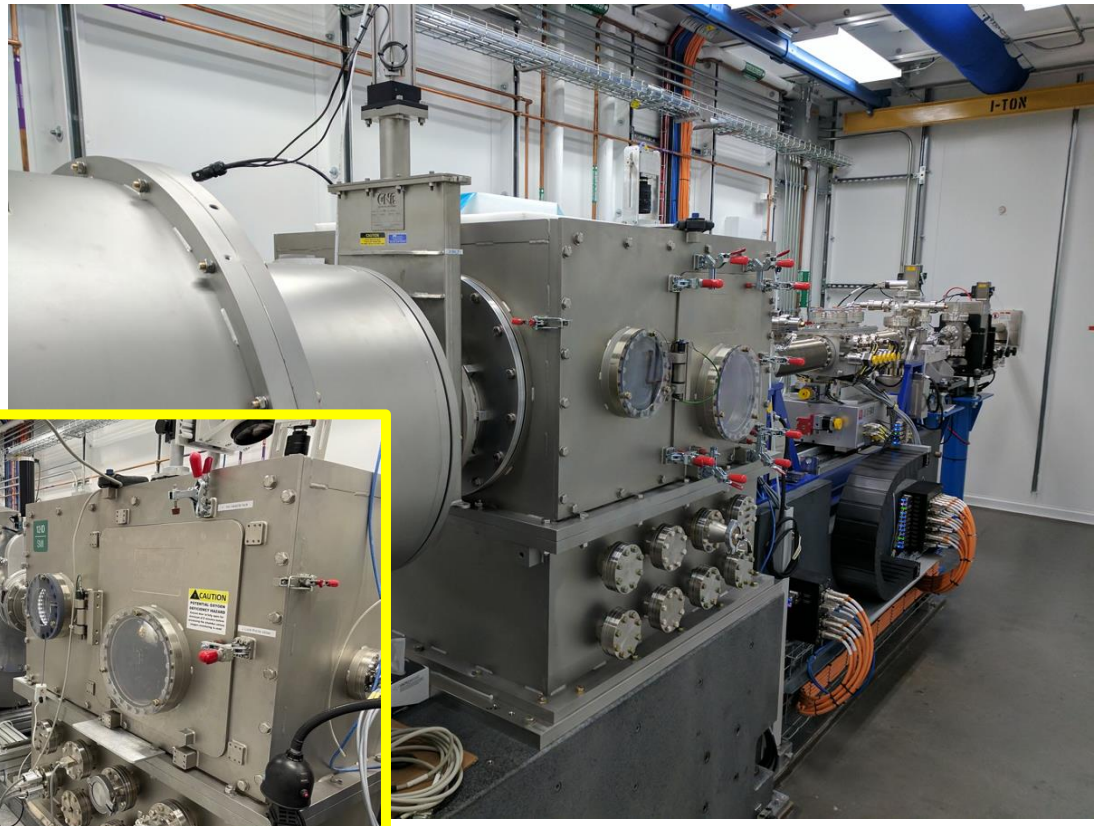
SMI 12-ID layout and optical scheme



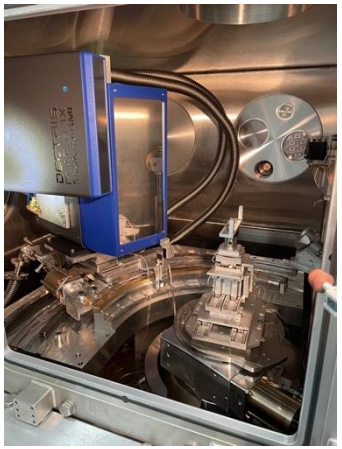
SMI-SWAXS: Small and Wide Angle X-ray Scattering

A Versatile X-ray Scattering Instrument (vacuum sample and detector environment)

- X-ray Scattering angles from <0.01 degrees – 90 degrees
- Low divergence mode (25 x 200 microns) or microfocus (2 x 20 microns)
- Energies from 2.1 to 24 keV – Tender and Hard X-ray resonant scattering



Plans are to use for liquid surfaces experiments with a single bounce down mirror.



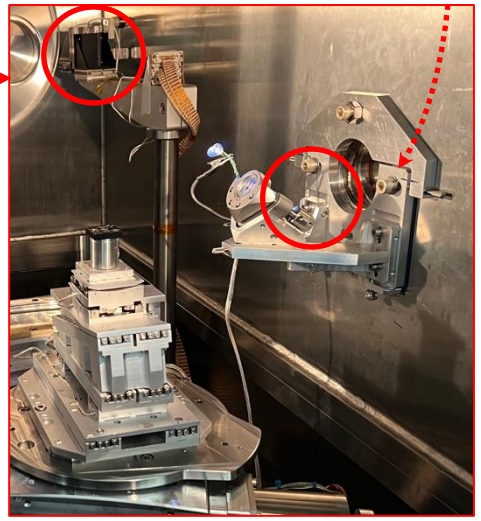
SMI-SWAXS: Tender X-ray Reflectivity from Liquid Surfaces

Use a bounce down mirror in the front of the chamber

- **Installed and ready for use**
- **Pseudo XR method to get the XR**

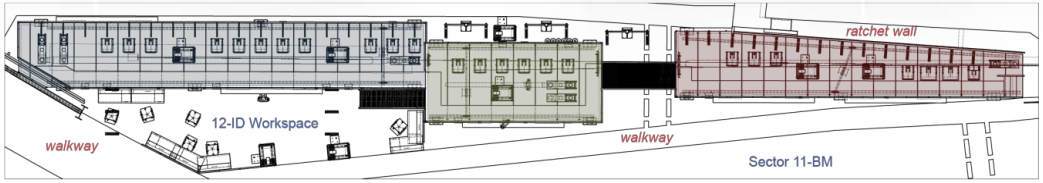
Large chamber door open

Bounce down mirror,
Translator & tilt stages
Rotate post to put in position



- For tender operations the chamber is evacuated or in Helium.
- Proposed tender energy liquid surface chamber would be wet He interior and vacuum on the outside.
- Experience with tender energy humidity cells.

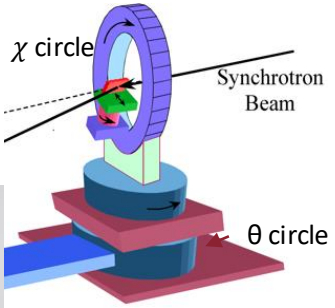
NSLS II Liquid Surfaces Instrument
SMI-OPLS: Open Platform Liquid Surfaces

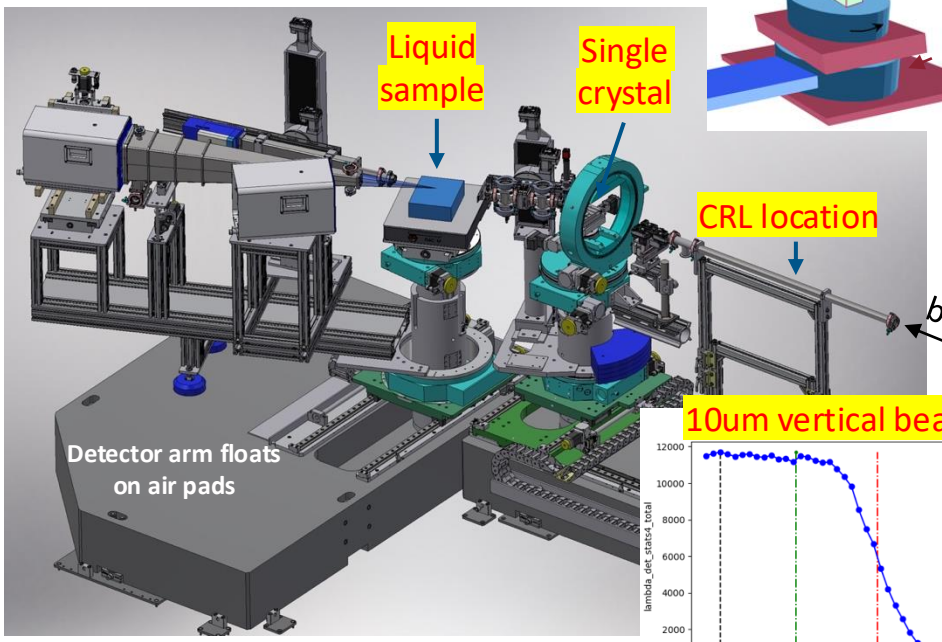


- SMI-OPLS: Suited for probing molecular and nanoscale structures at vapor/liquid and liquid/liquid interfaces.

- A deflector crystal, Ge (111), is used to adjust the incident angles downward.
- Ge(111) asymmetrically cut to broaden beam

- Beam characteristics:
  - 8-24 keV
  - 10^{12}/sec
  - 10 μm vertical focus via CRL
  - (two vertical mirrors are removed)



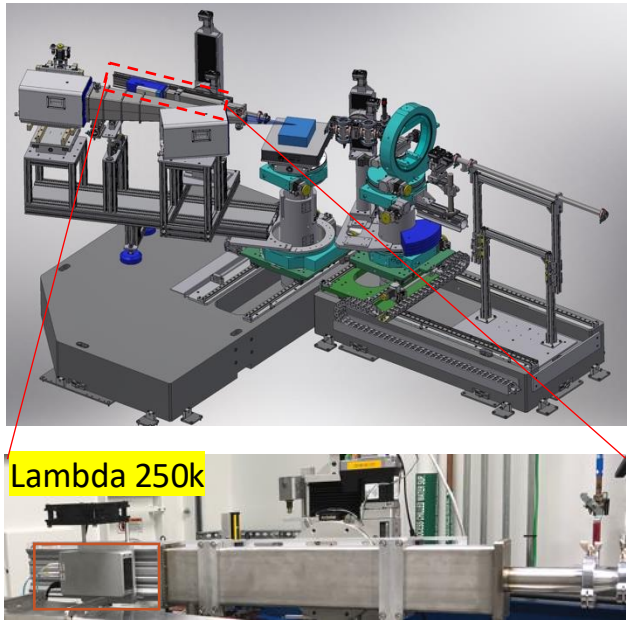


Techniques

- X-ray reflectivity (XRR)
  - Lambda Detector
- Grazing-incidence diffraction

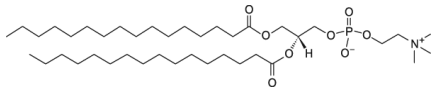
  Pilatus100k with Soller Slits
- Grazing Incidence small-angle X-ray scattering (GID, GISAXS)
  - Pilatus 1m
- Grazing-incidence X-ray fluorescence (XRF)
  - Vortex silicon drift detector (EX90)
- Pseudo X-ray Reflectivity
  - Same Pilatus 100k as with the Sollers

Specular XRR to determine surface-normal electron density profile

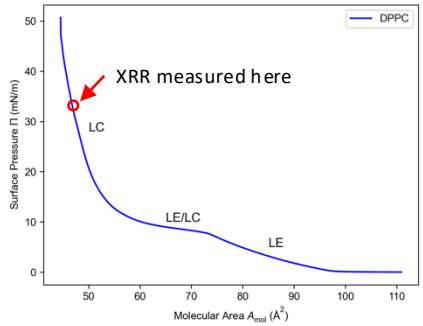


- Pixel size: 55 µm
- 1000 mm from sample
- GaAs high-E % at 24 keV
- High count rates
- Compact

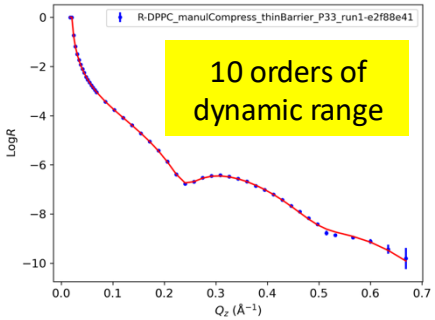
1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) monolayer



Isotherm



XRR



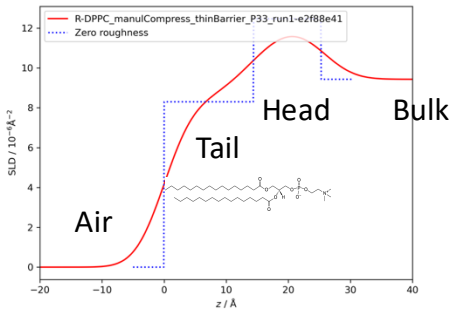
$$\frac{R(Q_z)}{R_F(Q_z)} = \frac{1}{\rho_\infty^2}\left|\int_{-\infty}^{\infty}\frac{d\langle\rho(z)\rangle}{dz}e^{iQ_z z}dz\right|^2$$

$$Re(SLD) = r_e\rho(z)$$

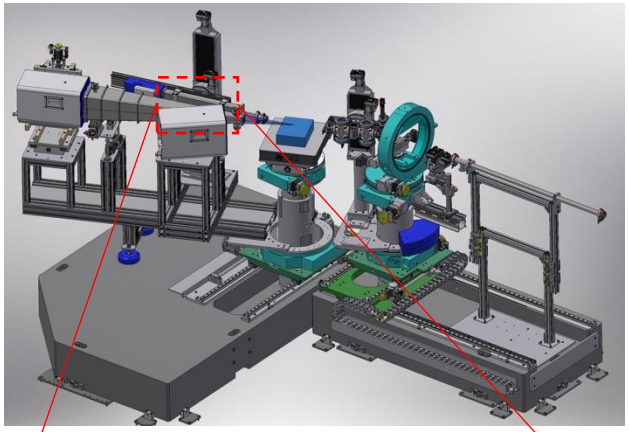
$\rho(z)$: electron density

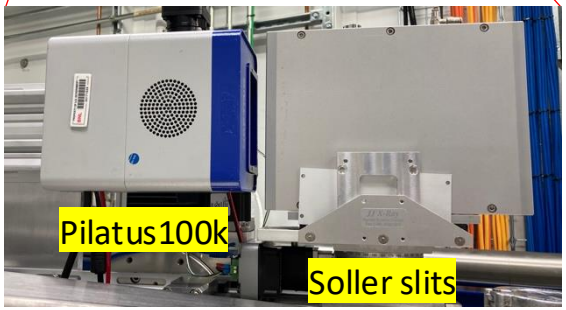
SLD: scattering length density

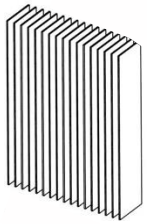
Scattering length density



Grazing incidence diffraction (GID) to reveal lateral structures (with Soller Slits)



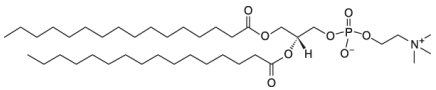




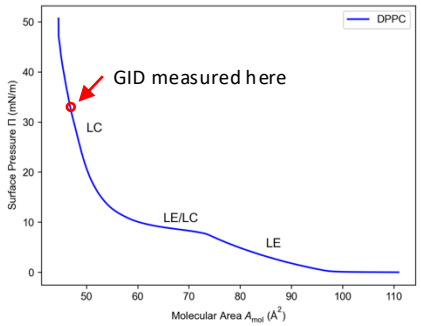
4 mrad (0.25 deg)

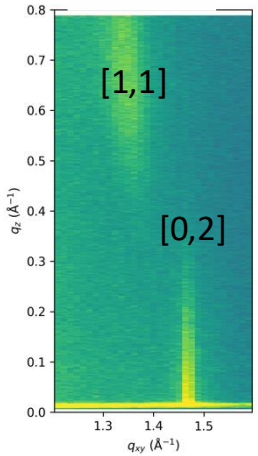
Can be translated out of the way for pseudo XR

1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) monolayer



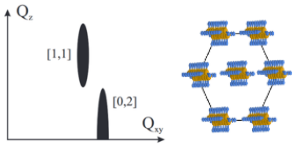
Isotherm





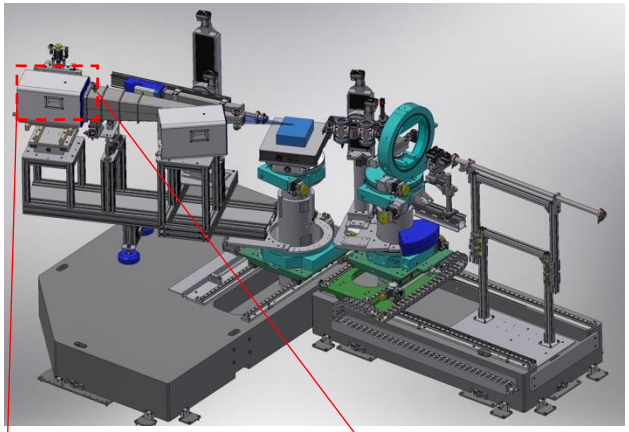
Nearest neighbor (NN) tilt

Centered rectangular structure

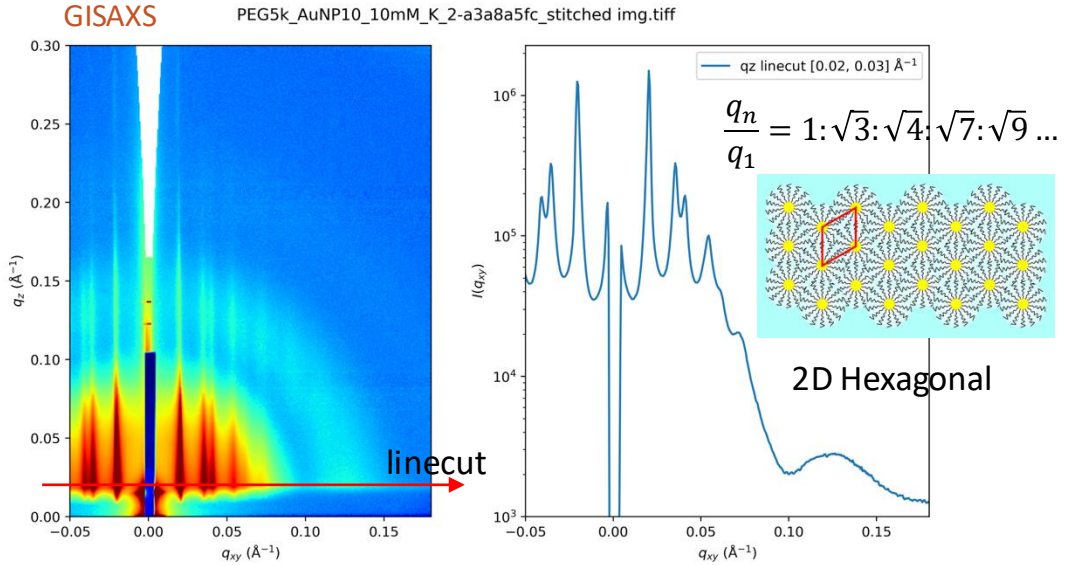


Grazing-incidence GISAXS) of self-assembled nanostructures

- 2D hexagonal lattices of PEG-coated nanoparticles (10nm) self-assembled on water surface



- Samp-to-Det: 1.5m
- Q_{min}= 0.005 A^{-1}



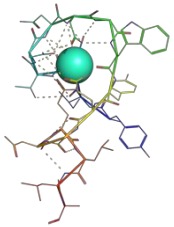
Grazing Incident X-ray Fluorescence

***Example:Bio-surfactants for Lanthanide recovery* (CCNY)**

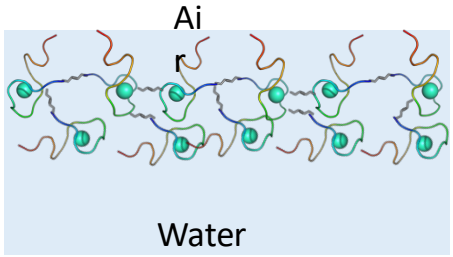
- Detector fits in slot (cell cover)
- Vortex 90 (Hitachi) with Xspress 3
- Detector remains fixed when sample translated

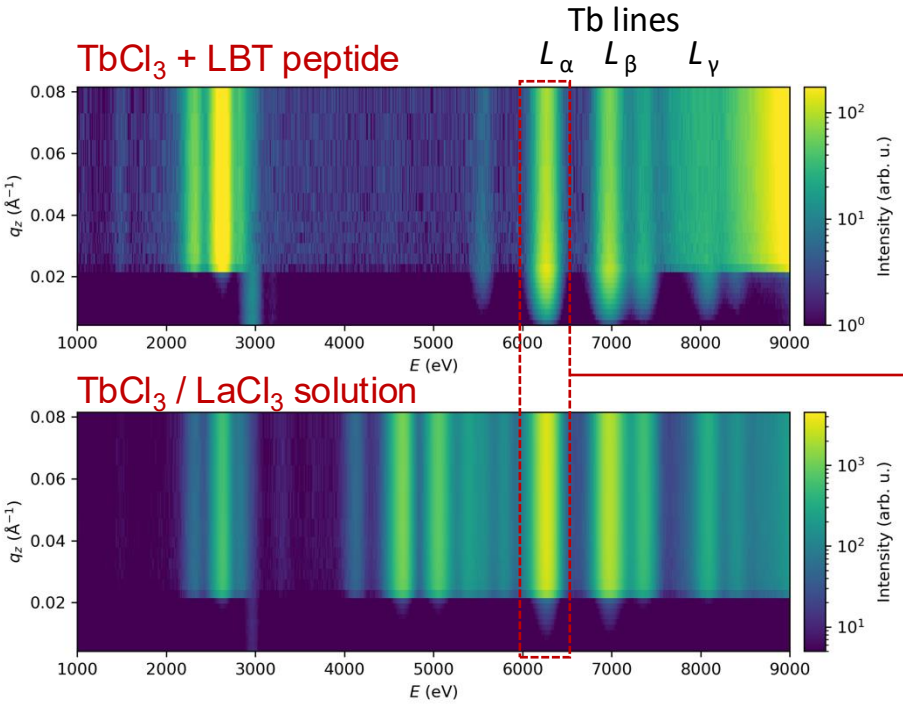
Charles Maldarelli

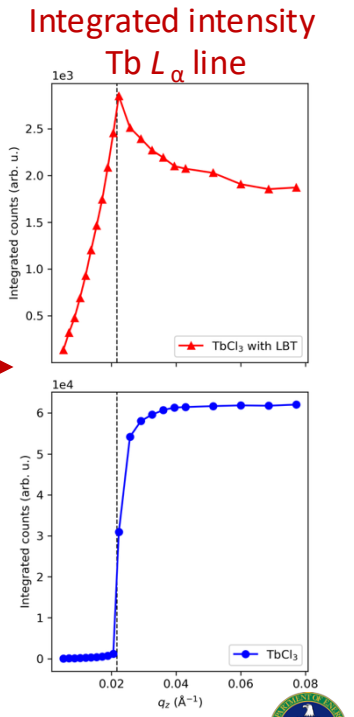
Raymond S. Tu



Lanthanide Binding Tag (LBT) peptide







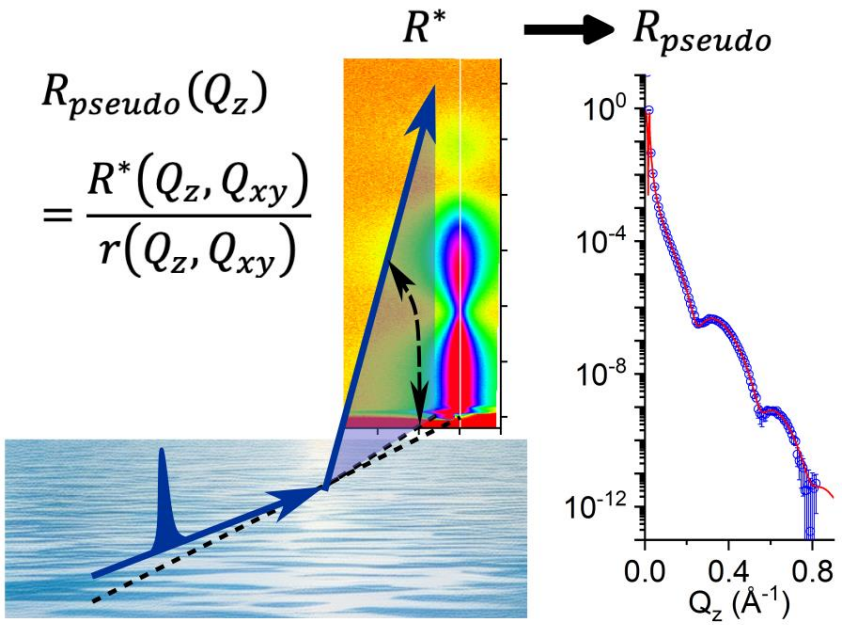
Ortuno Macias L. E.; Zhang, H.; Ocko, B. M.; Stebe, K. J.; Maldarelli1, C.; Tu, R. S, J. Colloids and Int (2025)

Vary the incident angle to distinguish surface and bulk ions

GIOXS: Pseudo XR

direct comparison with Specular XR on the same instrument

$$R_{pseudo}(Q_z) = \frac{R^*(Q_z, Q_{xy})}{r(Q_z, Q_{xy})}$$



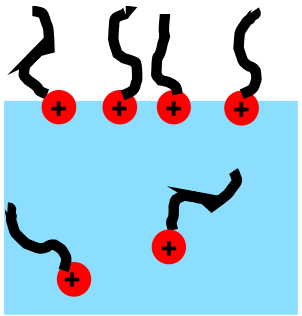
- Exact expression of diffuse scattering including stiffness
- Back calculation to XR: allows use of typical XRR analysis software.
- Directly compare with Specular XR

Chen Shen, Honghu Zhang, and Benjamin M. Ocko. "Reconstructing the reflectivity of liquid surfaces from grazing incidence X-ray off-specular scattering data." *Journal of Applied Crystallography* (2024).

Example 1: Langmuir Gibbs Films, low bending rigidity

CTAB Gibbs layer at 19degC
Below the CMC

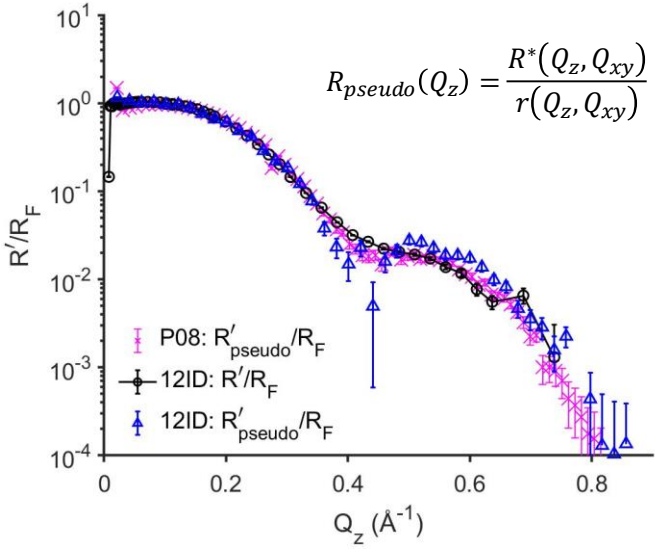
GIXOS & XRR @12ID-OPLS, NSLS-II
GIXOS @P08, PETRA III



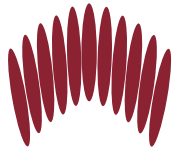
CTAB: Cationic, quatenary ammonium surfactant, C16

Eli Sloutskin et al., *Langmuir* **38**, 12356 (2022)

pseudo reflectivity: calculated reflectivity from R*



Simple surfaces like water are not stiff



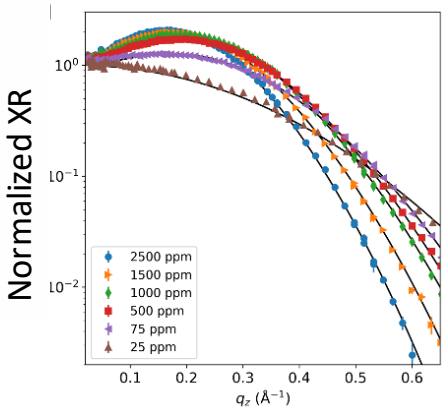
Rod like molecules more likely to be stiff, ie bending rigidity

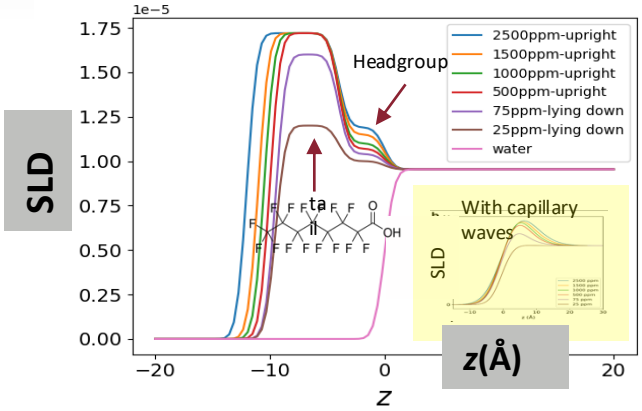
Works well for soft liquid surfaces…
What about a stiff thin film on the surface?

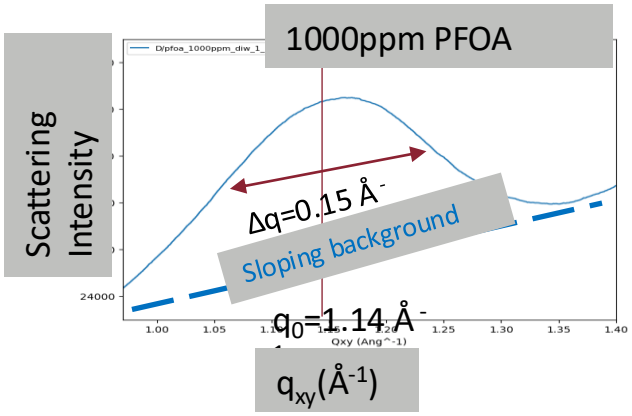
Shen, Chen, Honghu Zhang, and Benjamin M. Ocko. "Reconstructing the reflectivity of liquid surfaces from grazing incidence X-ray off-specular scattering data." *Journal of Applied Crystallography* (2024).

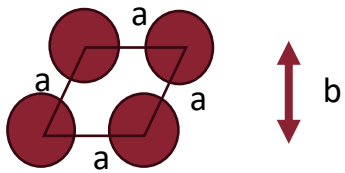
Example 3: Characterization of PFAS monolayer via XR and GIWAXS (Forever chemicals)

- PFAS remediation is a major societal issue.
- Bubblers can be used to bring PFAS to the surface
- Surface activity of PFAS modifies the x-ray reflectivity of pure water
- Differences in electron density in the surface layer modifies the X-ray Reflectivity (XR) profiles
- Varying bulk PFAS conc. result in different surface PFAS excesses hence different XR profiles.









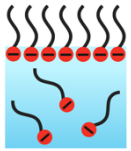
a=2pi/sqrt(3)//q_0
Area= a^2*sqrt(3)/2

q_0=1.14 Å^{-1}, a=6.34 Å
Area =34.8 Å^2/molecule

Well-packed monolayer 28.5 Å.^{2}

Peak is from In-plane "diffraction"
Broad peak is from liquid-like correlations
Only a few nearest neighbors.

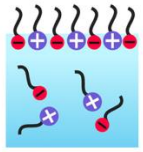
Example 3: Direct Comparison between pseudo and specular XR on PFOA samples



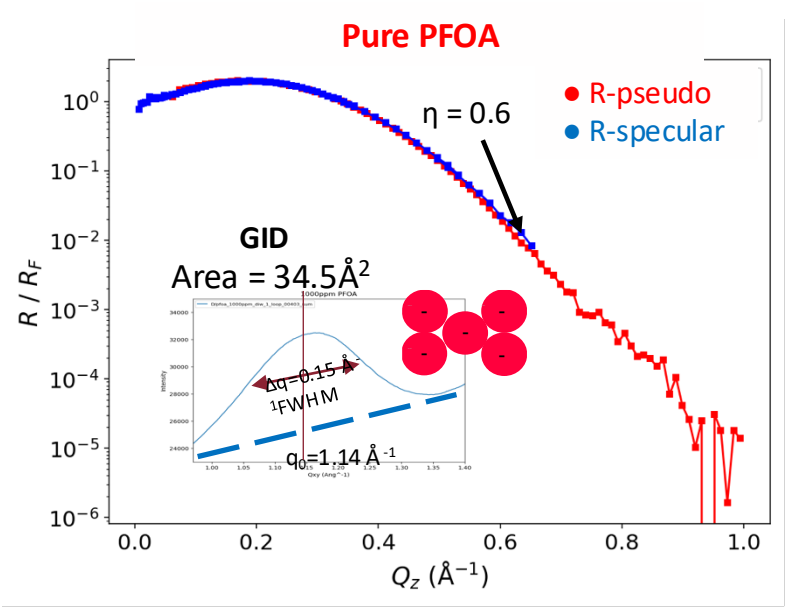
Medium concentration

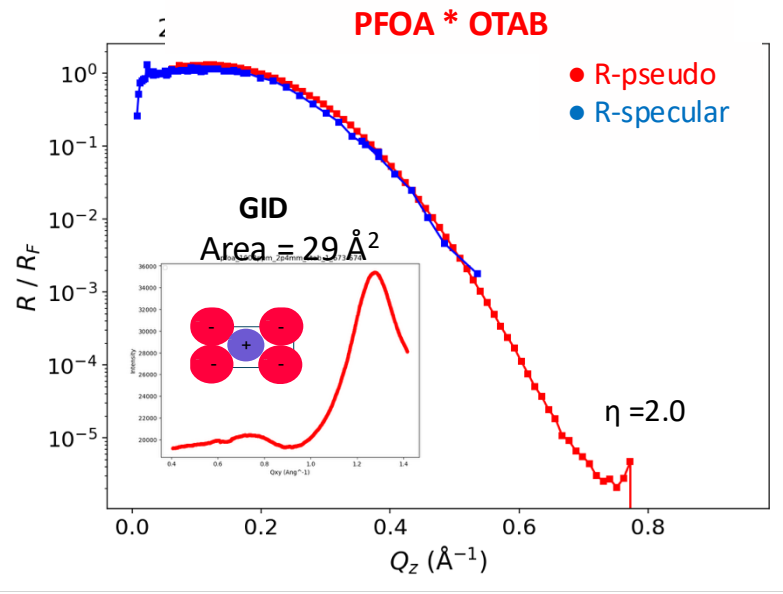
γ=35.6 mN/m,
η = 2 @ 1.05Å^{-1}

$$\eta = \frac{k_B T}{2\pi\gamma} Q_z^2$$



γ=16 mN/m,
η = 2 @ 0.78Å^{-1}
Bending modulus (7 kT)





Same sample, different instrument but very stable Langmuir-Gibbs films

(not published)

Decide date and discussion leader for March meeting, possibly March 18 or 25

Practical matters of writing code for pseudo XR analysis (Chen Shen)