Liquid Surface Spectrometer (LSS) at CMC

Ivan Kuzmenko

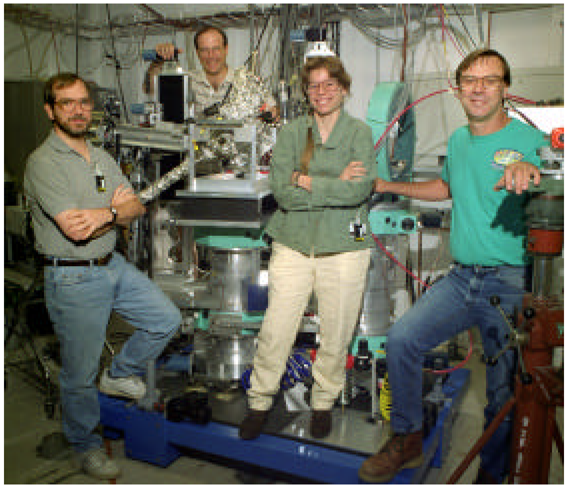
CMC

April 18, 2005

Who is involved?

- People involved in design construction and commissioning of LSS (1997-2001):

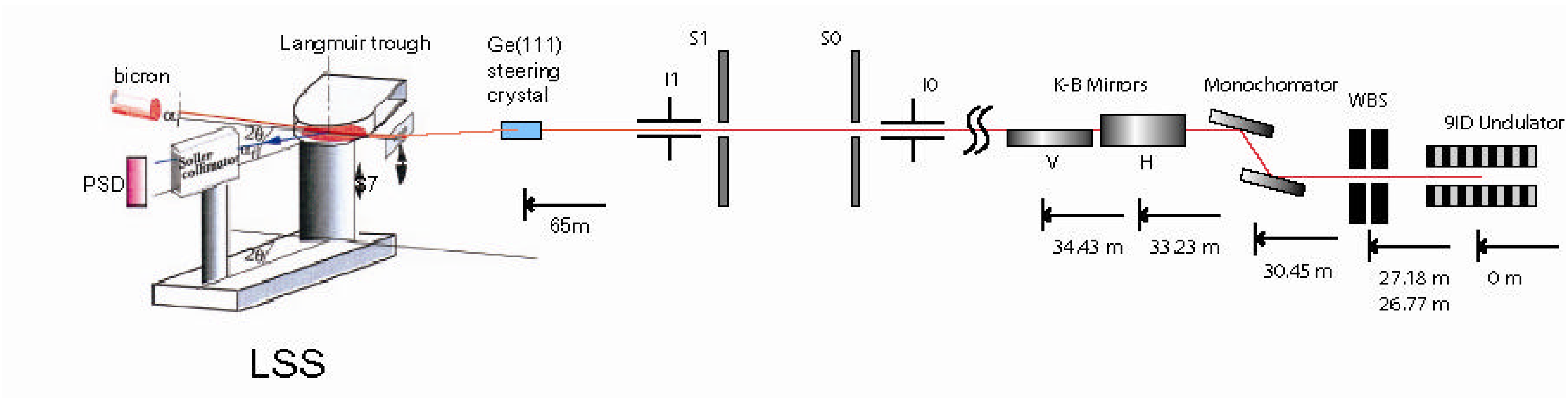
- Scott Coburn (BNL)
- Ben Ocko (BNL)
- Elaine DiMasi (BNL)
- Thomas Gog (CMC)
- Kent Blasie (UPENN)



- People currently involved in support and maintenance of LSS at 9-ID:

- Ivan Kuzmenko (CMC)
- Thomas Gog (CMC)
- Diego Casa (CMC)

Liquid Surface Spectrometer at 9-ID



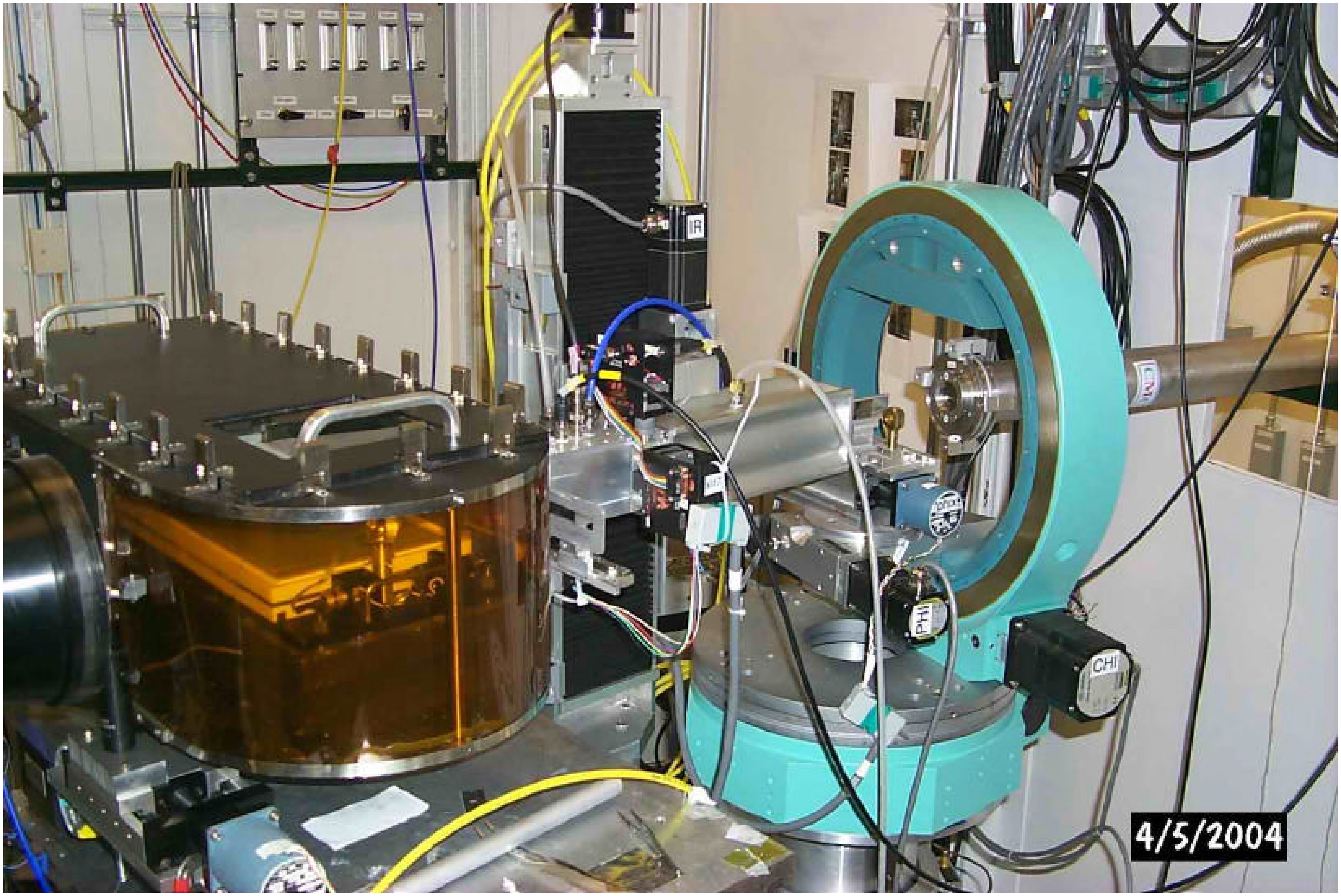
Liquid Spectrometer Capabilities

- Reflectivity and Grazing Incident X-ray measurements (8-25KeV, typically)
  - Reflectivity measures surface normal density profile
  - GIXD measures the in-plane structure
- Large angular range
  - Required for liquid metal measurements
- Precise tracking,
  - required for ultra high resolution, analyzer, anomalous
- Two detector set-up (Bicron and PSD with soller slits)
  - Allows easy switch between different measurements
  - Heavy Sample chambers (UHV), weights up to 250 LB
- Very bright beam, well focused in vert. and horiz
- Optimized motion control for fast operations

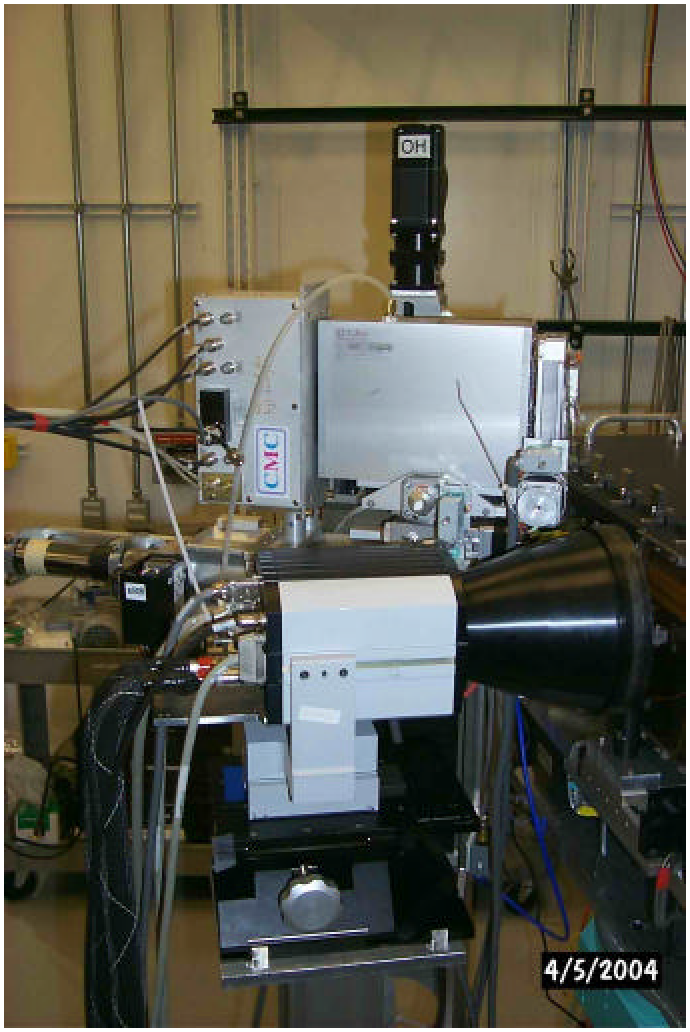
Some Recent Features

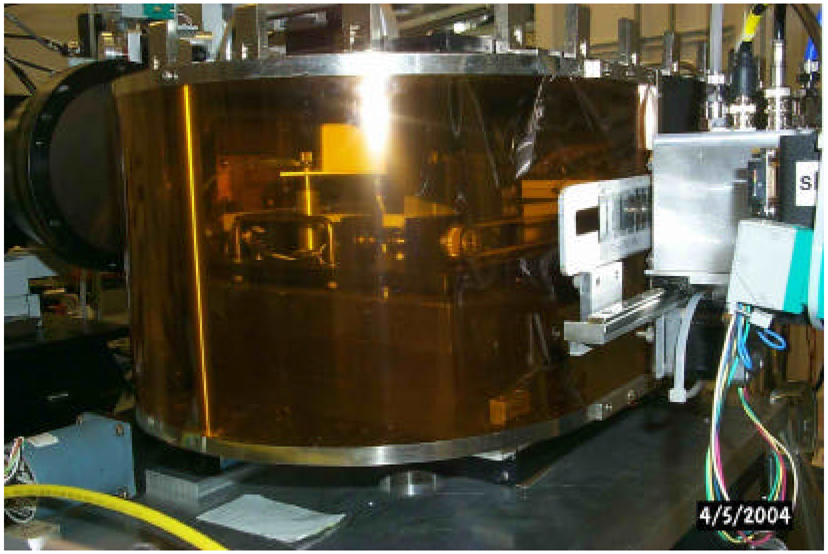
- Si (111) asymmetric crystal was designed and commissioned for λ=1.3 Å (E=9.54KeV) to defocus the incoming beam horizontally (10-fold) to avoid beam damage and improve sample statistics
- Ge (111) asymmetric crystal was designed and commissioned to overcome tracking problems at high energies (~25KeV)
- Two dimensional detector (Bruker CCD) now can be mounted for in-plane GIXD measurements
- Oxygen sensor was installed to control the oxygen level in the trough

LSS setup at CMC: pictures (1)

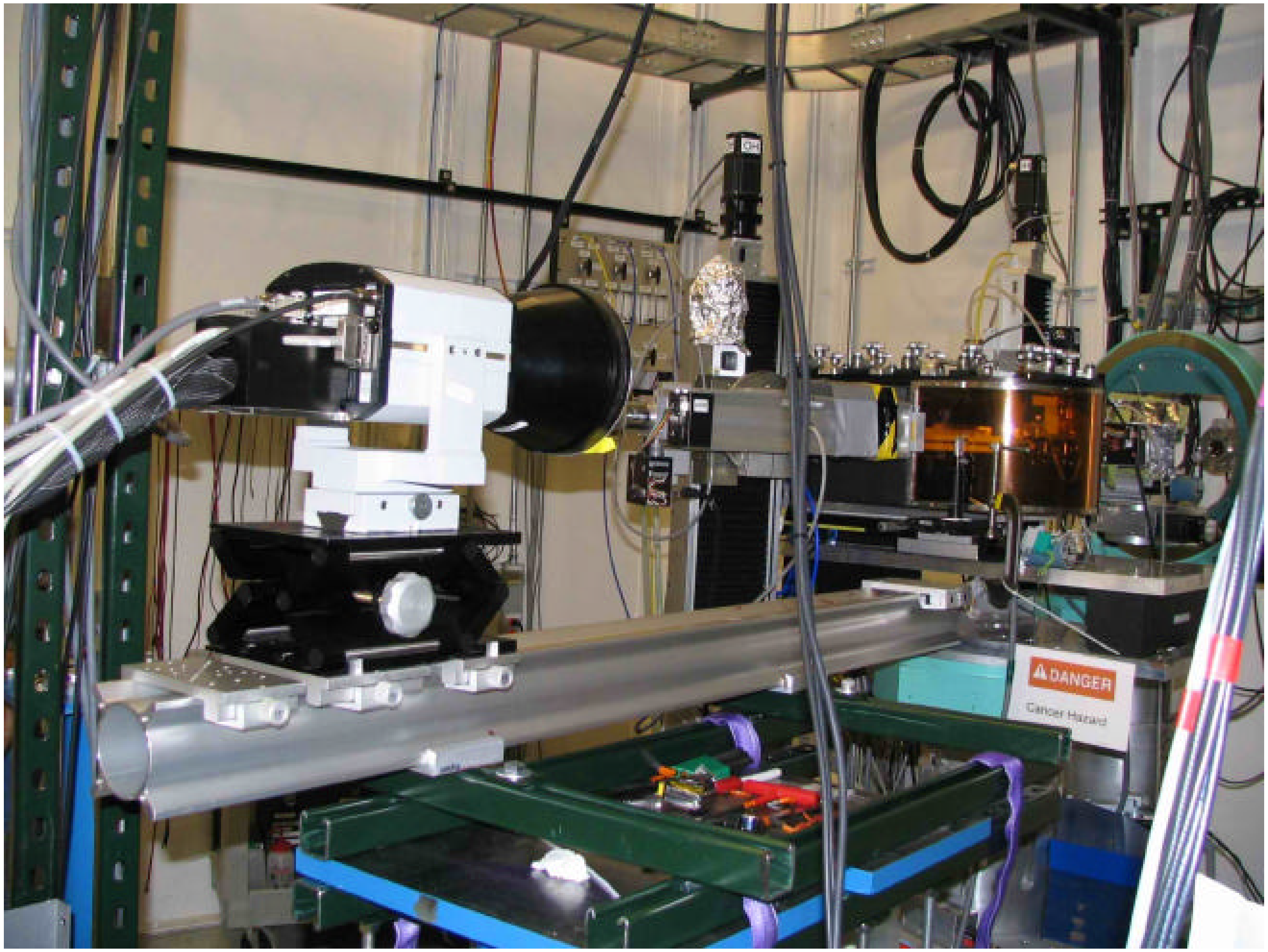


LSS setup at CMC: pictures (2)





LSS at CMC: some pictures (3)



Scientific topics and publications (1)

- **Surface structure of Liquids:**

  B. M. Ocko, Eric B. Sirota, M. Deutsch, E. DiMasi, S. Coburn, J. Strzalka, S. Zheng, A. Tronin, T. Gog, C. Venkataraman, **Positional order and thermal expansion of surface crystalline N-alkane monolayers**, Phys. Rev. E 63, 032602 (2001)

  O. Shpyrko, M. Fukuto, P. Pershan, B. Ocko, I. Kuzmenko, T. Gog, M. Deutsch, **Surface layering of liquids: The role of surface tension**, Phys. Rev. B 69, 245423 (2004)

  E. Sloutskin, B.M. Ocko, L. Tamam, I. Kuzmenko, T. Gog, and M. Deutsch, **Surface Layering in Ionic Liquids: An X-ray Reflectivity Study** (accepted for publication in JACS)

  Brown M, Uran S, Law B, Marschand L, Lurio L, Kuzmenko I, Gog T, **Ultra-stable oven designed for x-ray reflectometry and ellipsometry studies of liquid surfaces** Rev. Sci. Ins. S 75 (8): 2536-2540 (2004)

  L Marschand, M Brown, L B Lurio, B M Law, S Uran, I Kuzmenko, T Gog, **X-Ray specular reflectivity study of scaling in critical binary fluid mixtures in the strong surface field limit** (submitted for publication)

- **Geosciences:**

  E. DiMasi, J. O. Fossum, T. Gog, C. T. Venkataraman, **Orientational Order in Gravity Dispersed Clay Colloids: A Synchrotron X-ray Scattering Study of Na Fluorohectorite Suspensions**, Phys. Rev. E 64, 061704 (2001)

- **Structure of buried interfaces:**

  J Baumert, Michael Lefenfeld, E. Sloutskin, M. Deutsch, C. Nuckolls, B. Ocko **Direct Observation of a Molecular Junction using High-Energy X-ray Reflectometry** (work in progress)

Scientific topics and publications (2)

- **Langmuir Films (Non Biological):**

  Pao WJ, Zhang F, Heiney PA, Mitchell C, Cho WD, Percec V,
  Grazing-incidence x-ray diffraction study of Langmuir films of amphiphilic monodendrons Phys. Rev. E 67 (2), 021601 (2003)

  Strzalka J, DiMasi E, Kuzmenko I, Gog T, Blasie JK,
  Resonant x-ray reflectivity from a bromine-labeled fatty acid Langnmir monolayer
  Phys. Rev. E 70 (5), 051603 (2004)

- **Langmuir Films (Biological):**

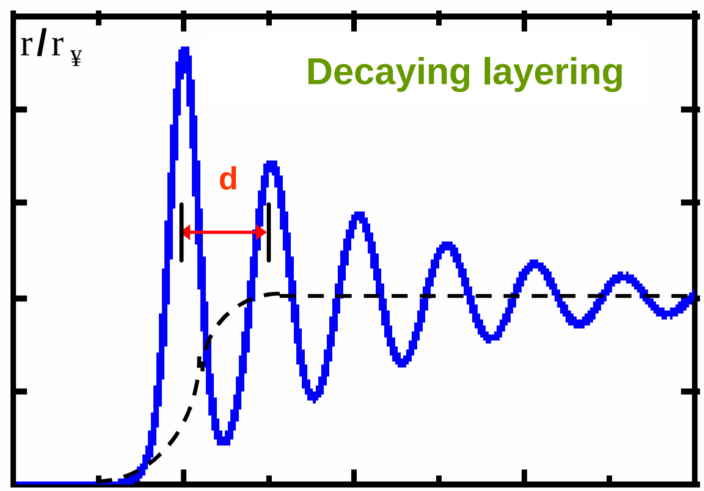
  Zheng S, Strzalka J, Jones DH, Opella SJ, Blasie JK
  Comparative structural studies of Vpu peptides in phospholipid monolayers by X-ray scattering Biophys. J. 84 (4): 2393 (2003)

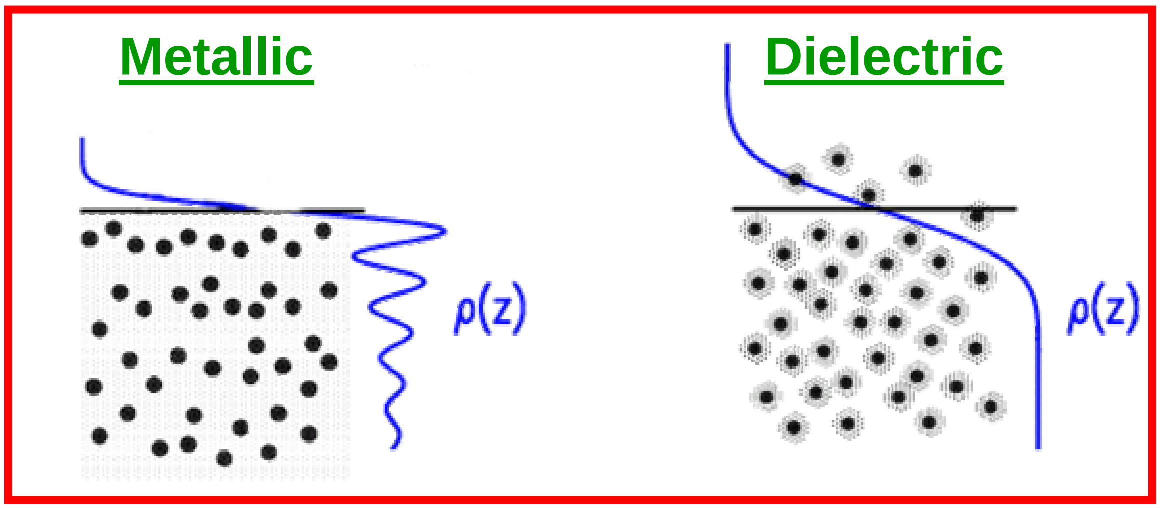
  M. S. Kent, H. Yim, D. Y. Sasaki, S. Satija, J. Majewski, T. Gog,
  Analysis of Myoglobin Adsorption to Cu(II)-IDA and Ni(II)-IDA Functionalized Langmuir Monolayers by Grazing Incidence Neutron and X-ray Techniques, Langmuir 20, 2819 (2004)

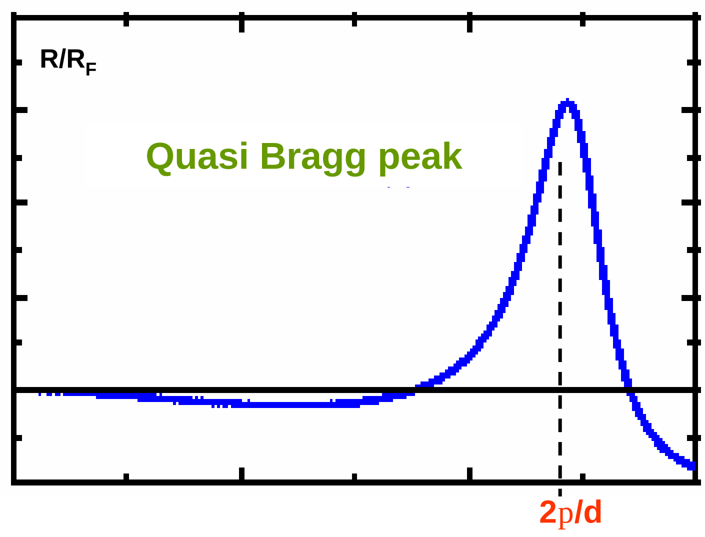
Liquid metals vs dielectric liquids

S. Rice *et al.* (1960-75) and others:

- Liquid metal: a strong variation in the interaction across the surface from conductor (bulk) to insulator (vapour).
- No such variation in a dielectric liquid, hence no layering should occur.



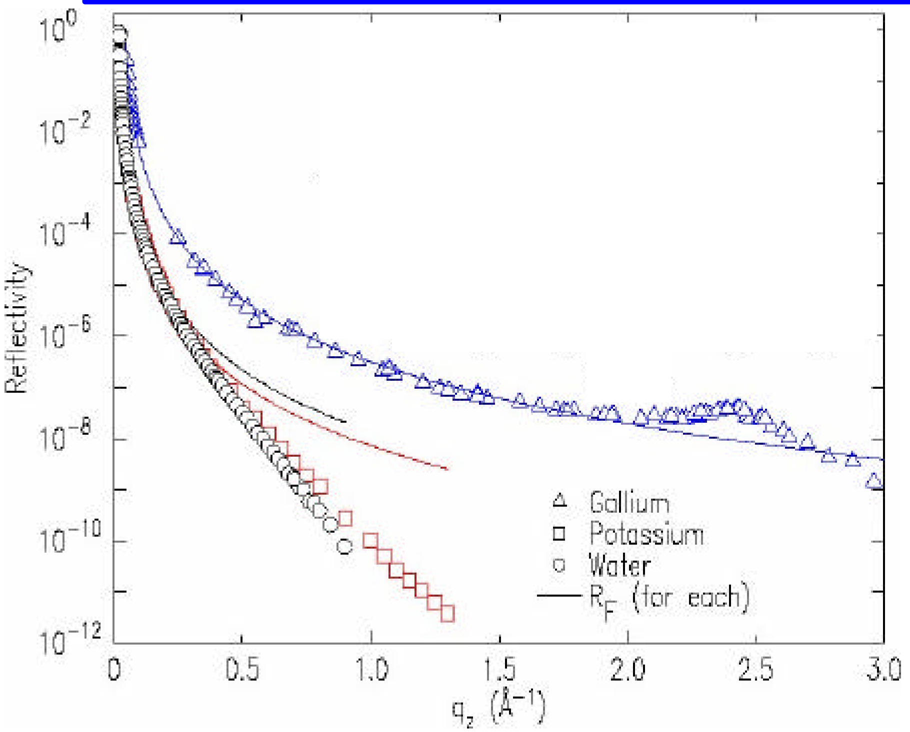


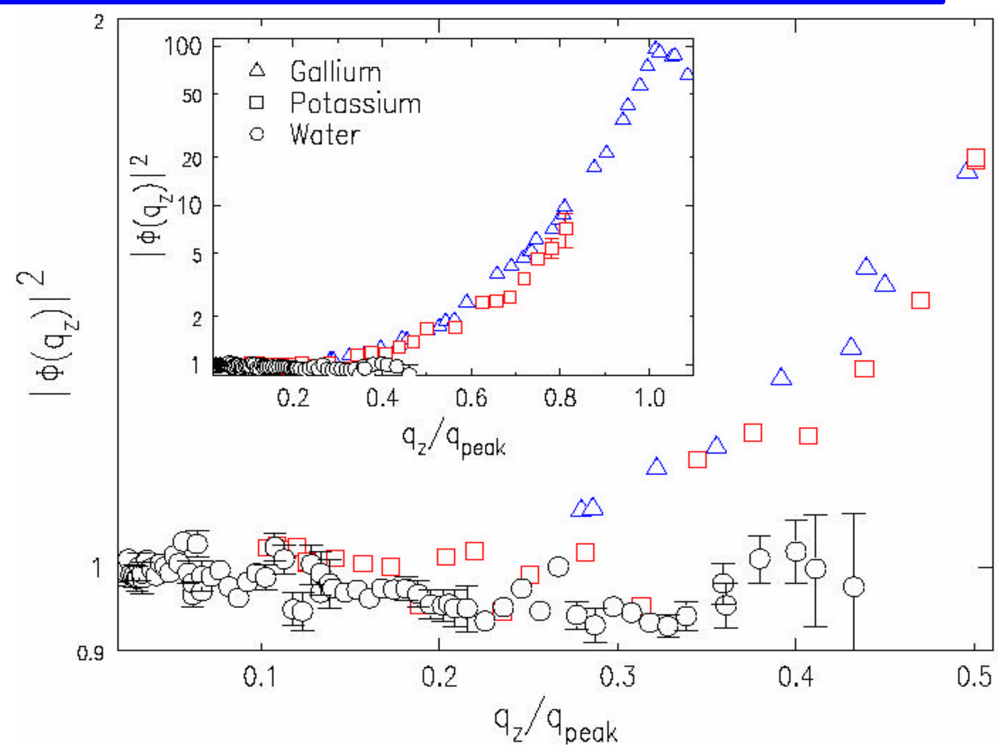


Are all liquid surfaces intrinsically layered ?

If K (γ=110 mN/m) is layered, why not also water (γ=72 mN/m) ?

Broader question: Is surface layering specific to liquid metals ?

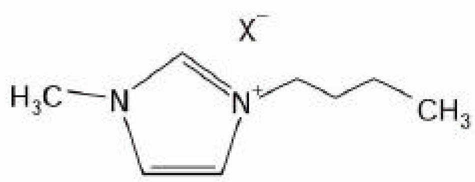




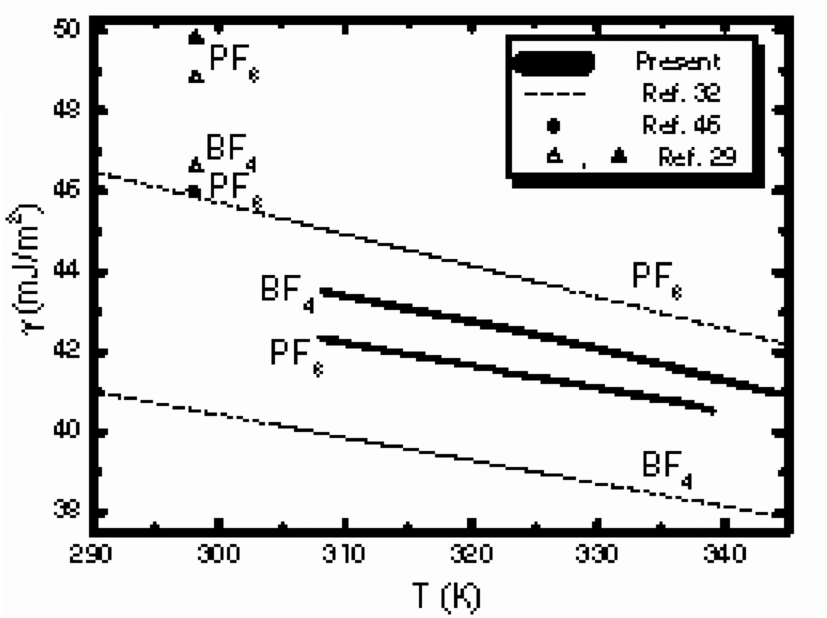
- **Seems to support Rice et al. : layering is specific to liquid metals.**
- **Chacón et al. : all liquids layer for $T/T_C \leq 0.2$, if T is still above T_m.**
- **For water: T_m/T_C=0.42 $\Rightarrow$ no layering expected and none indeed observed.**
  For Ga: T_m/T_C=0.043 $\Rightarrow$ layering is expected and indeed observed.
- **What about propane, 1-butene, where $T/T_C \leq 0.2$??**

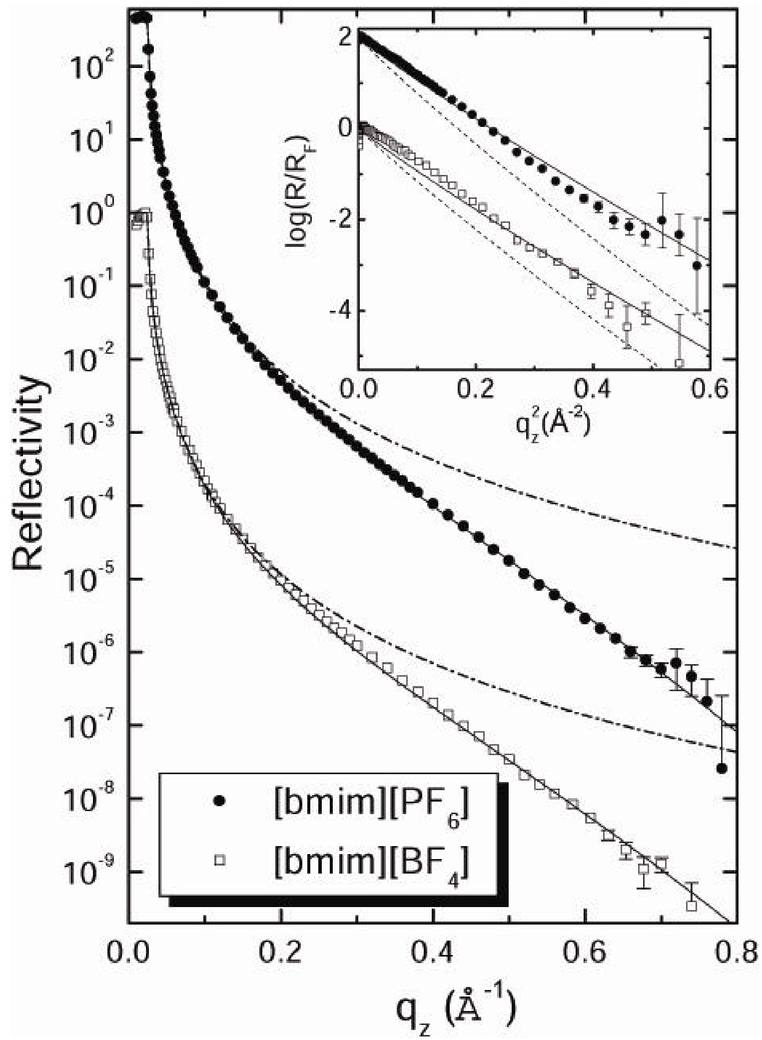
O. Shpyrko et al., PRB

Surface Lavering in Ionic Liquids (1)



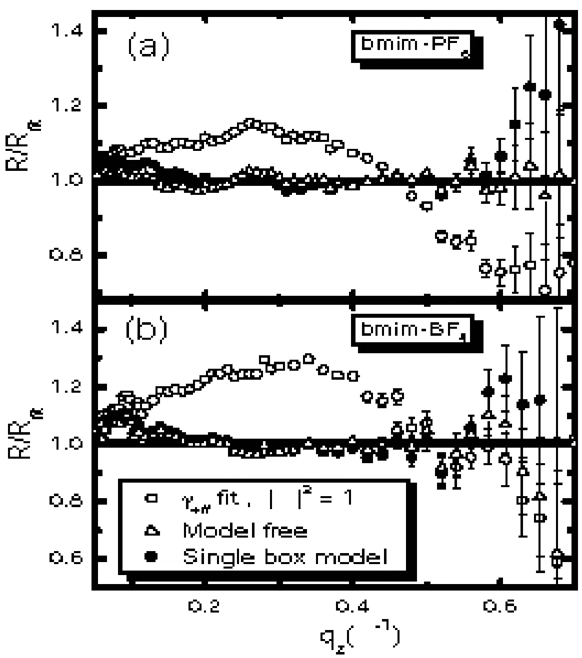
bmim

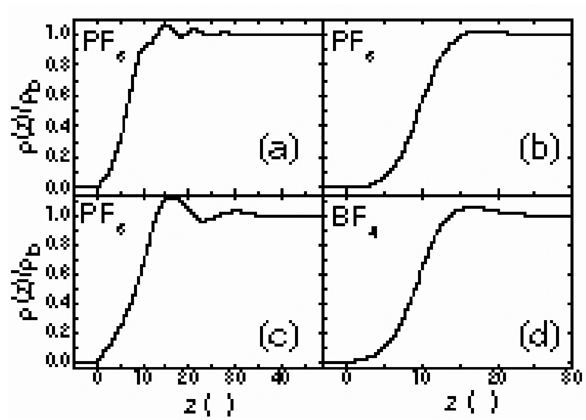


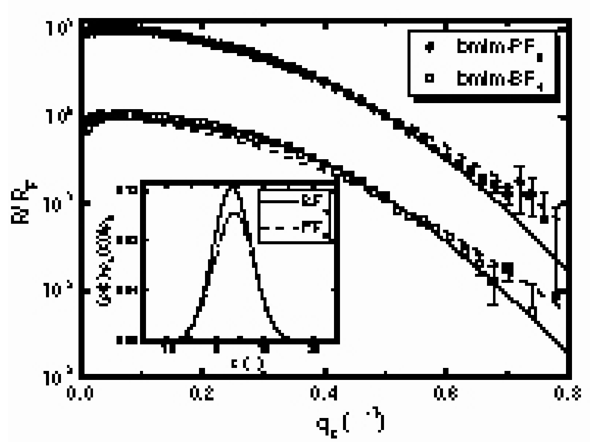


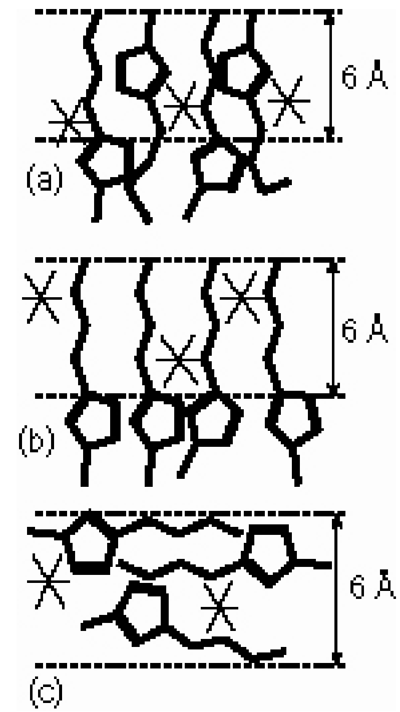
Slutskin et al (JACS)

Surface Layering in Ionic Liquids (2)





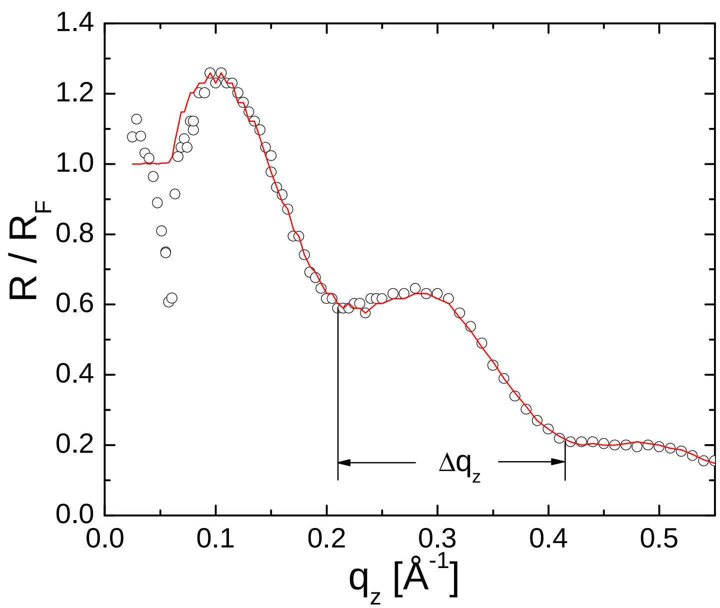




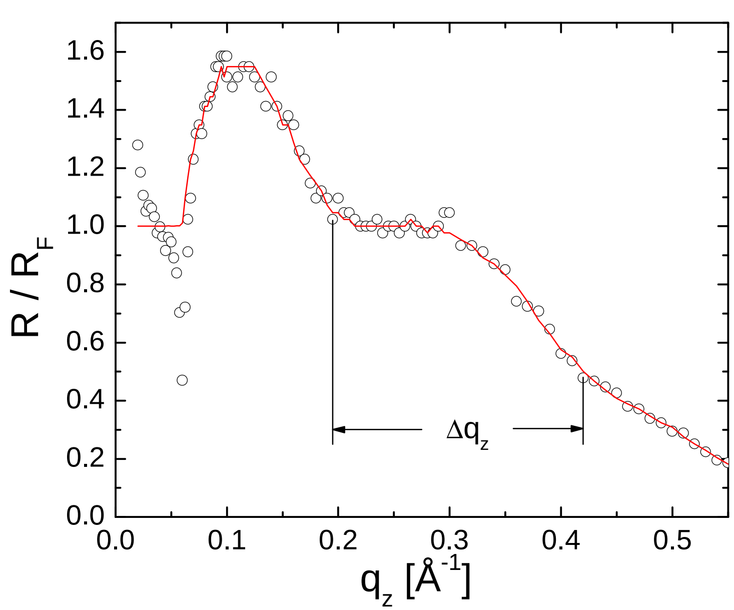
Slutskin et al (JACS)

Studies of buried interfaces (1)

Si - C_{18}SH - Hg



Si - OTS - Hg



“Kiessig” fringes clearly observable

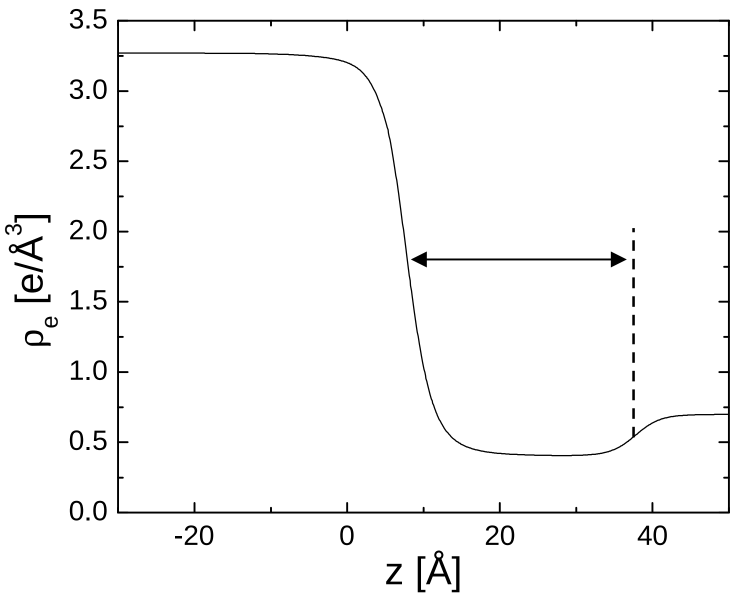
d ˜ 29.9 Å

d ˜ 27.3 Å

Julian Baumert et al (work in progress)

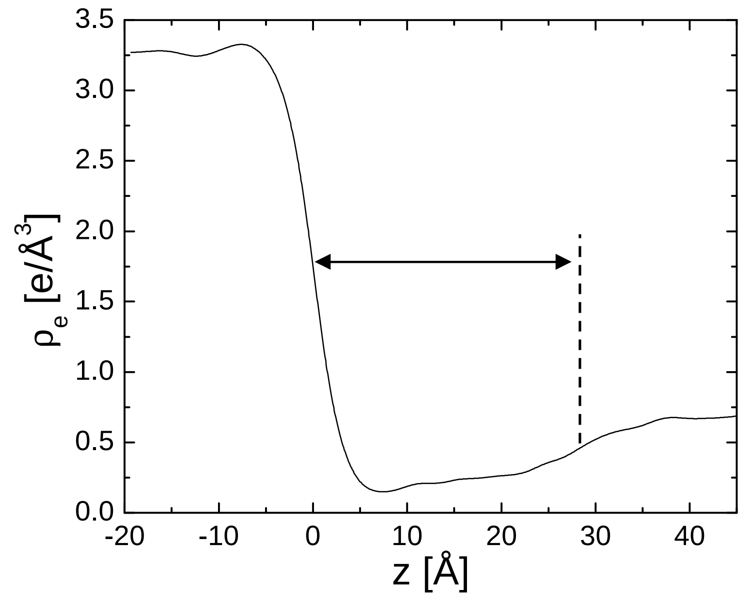
Studies of buried interfaces (2)

Si - C_{18}SH - Hg



- Electron density: ?$_e$ = 0.4 e/ Å^3
- Thickness: d = 29.6 Å

Si - OTS - Hg



- Electron density: ?$_e$ = 0.24 e/ Å^3
- Thickness: d = 28.4 Å

→ Densely packed monolayers in buried interfaces

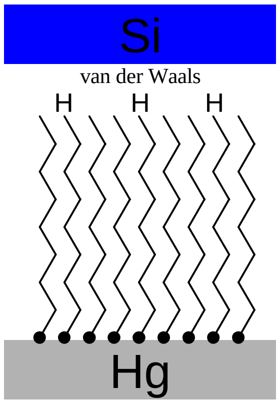
Julian Baumert et al (work in progress)

Structure of Buried Interfaces (3)

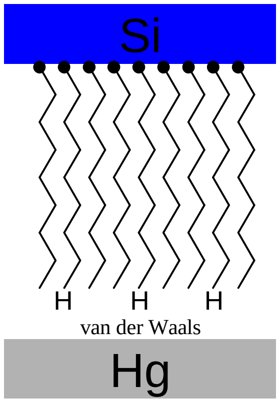
Si - C_{18}SH - Hg: d = 29.6 Å
Air - C_{18}SH - Hg: l = 25.2 Å

Si - OTS - Hg: d = 28.4 Å
Air - OTS - Si: l = 24.7 Å

C_{18}SH



OTS



•C_{18} – thiols and OTS molecular junctions are found to be 29.6Å and 28.4Å in length, consistently larger than monolayer thicknesses at the air interface.

•The terminal hydrogen atom and the van der Waals radii of the hydrogen and the contacting surface (Thiol 4.3Å, OTS 3.9Å) account for the additional length.

→ Thickness of Interface given by standing up molecules

Julian Baumert et al (work in progress)

Resonance Reflectivity (1)

X-Ray Reflectivity measures the profile structure ?(z) of Langmuir Monolayers

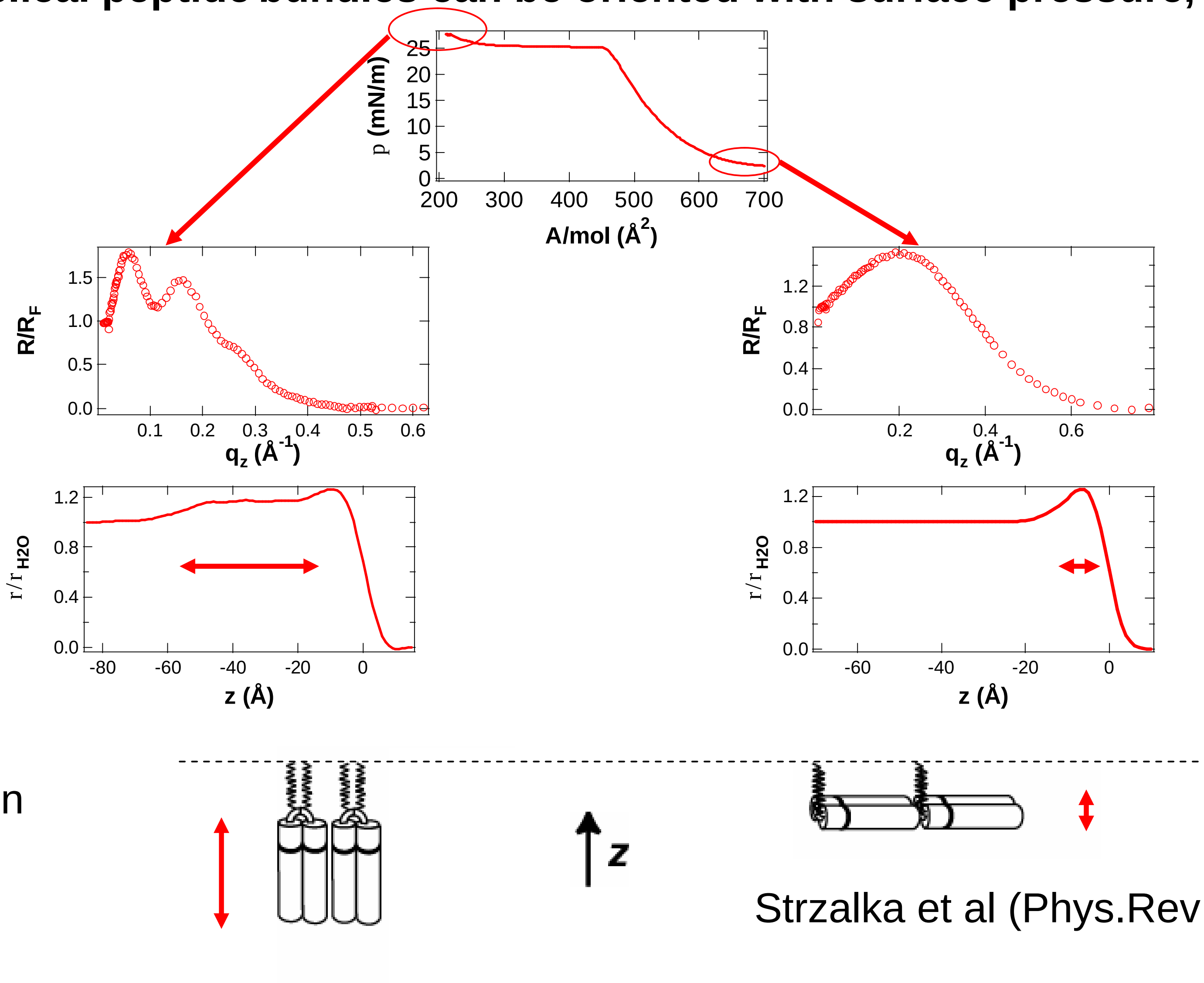
? shows a-helical peptide bundles can be oriented with surface pressure, p

Isotherm

XR data

Profiles:
?(z)

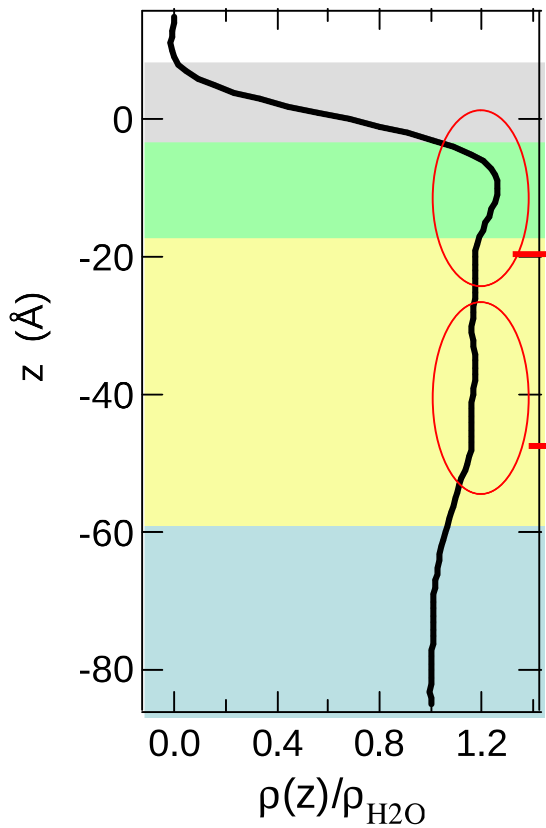
Interpretation



Strzalka et al (Phys.Rev.E)

Resonance Reflectivity (2)

X-Ray Reflectivity identifies regions, shapes, not specific groups



Assignments

Air (He)

Hydrocarbon chains

Phospholipid headgroups/ peptide

Peptide/water (a-helices)

Subphase

Unknowns

Where's His-24?

Strzalka et al (Phys.Rev.E)

Resonant X-ray Reflectivity (3): Fatty Acid

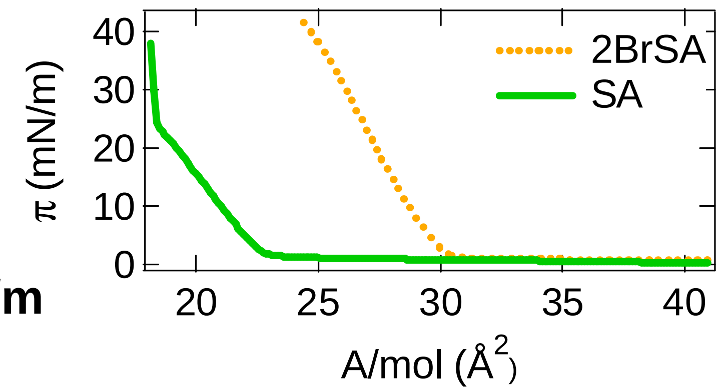
Methods

Samples: **2-Bromo-Stearic Acid (2BrSA)** **and** **Stearic Acid (SA)**

CH3(CH2)$_{15}$CBrHCOOH — **Br-labeled**

$CH_3(CH_2)_{16}COOH$ — **CONTROL**

Measurements: **13 474 eV (Br K edge)**
13 674 eV (Br K+d)
13 274 eV (Br K-d)
step sample 40µm between points



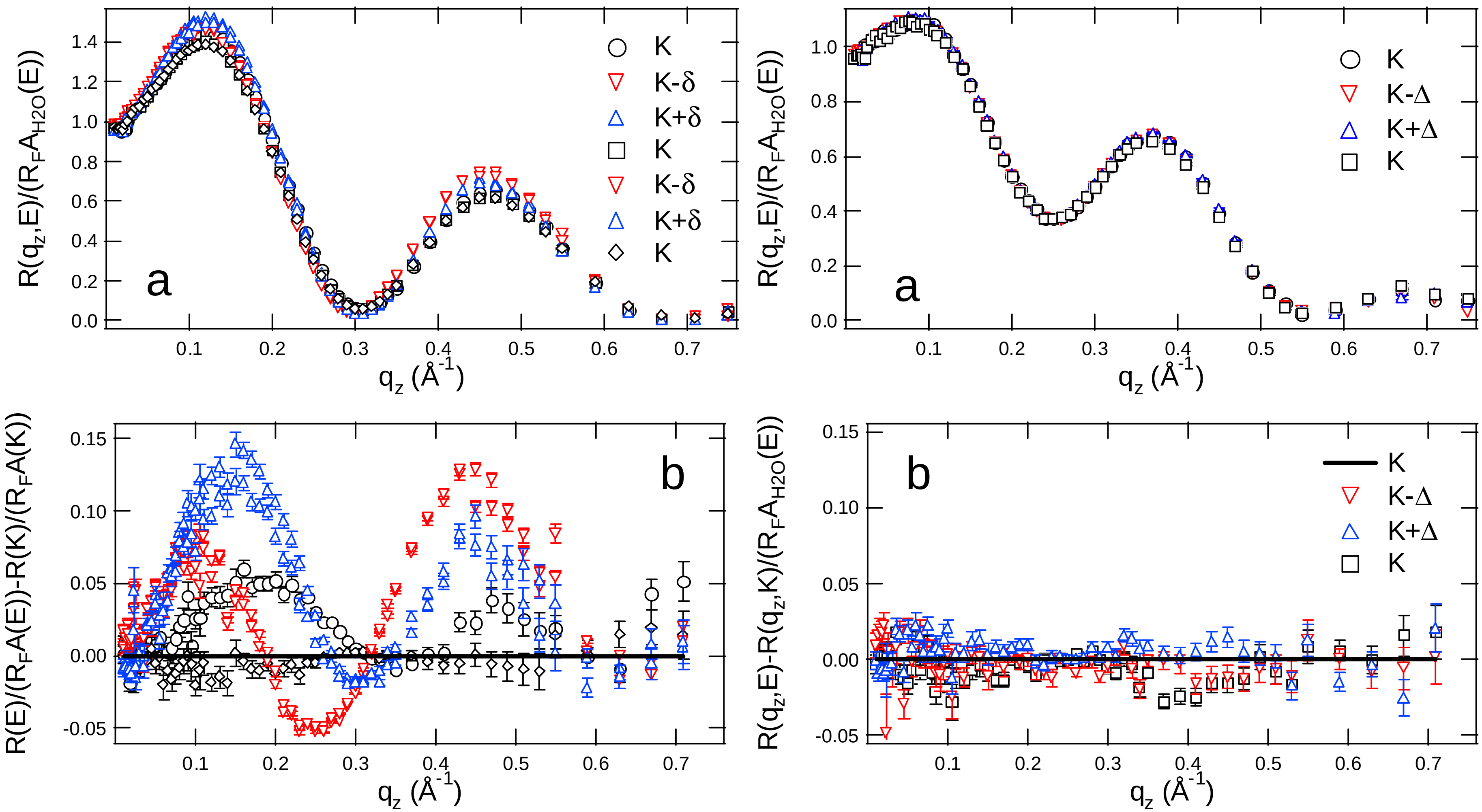
Monolayers: **pure 2BrSA or SA at p=5 mN/m**
MilliQ water, 5°C

X-rays: Liquid Surface Spectrometer at CMC CAT,
Sector 9 of Advanced Photon Source (Argonne, IL)

Strzalka et al (Phys.Rev.E)

Resonant X-ray Reflectivity (4): Fatty Acid

2-bromo-stearic acid (2BrSA) | **Control: stearic acid (SA)**



Strzalka et al (Phys.Rev.E)