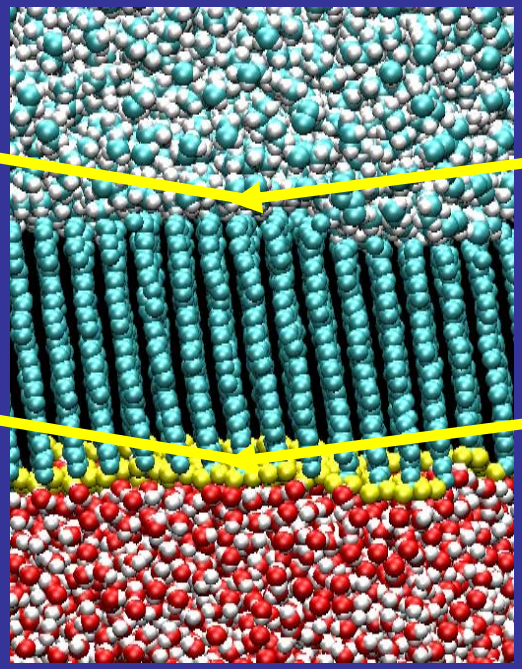
Some Scientific Opportunities in the Field of Liquid Surface Scattering

Mark Schlossman, University of Illinois at Chicago

Bulk Phase 1 - oil, vapor

Interface -
ordered & disordered
molecular assemblies

Bulk Phase 2 - water, oil



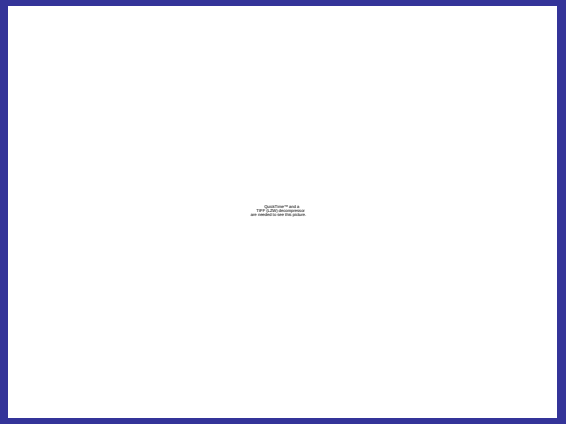
X-rays

J.Phys.Chem.B **110**, 19093(2006)

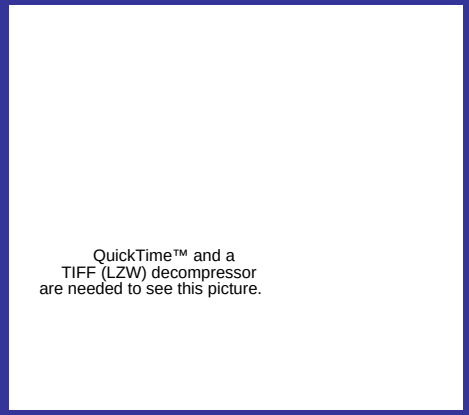
Molecular ordering at the surface or interface determines the variation of electron density. X-ray surface scattering probes this electron density, either within the interfacial plane or out of (perpendicular to) the interfacial plane.

Thanks to NSF and DOE for funding my research.

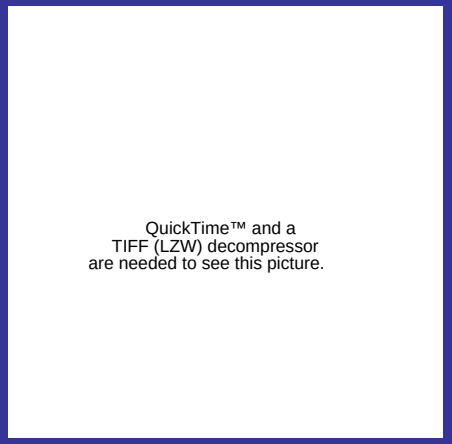
Capillarity
The Study of Liquid-Liquid and Liquid-Gas Interfaces



Capillary Rise
web.mit.edu/nnf/education
/wettability/gravity.html



Water Drop
middle_fork.org



Soap Bubble
The Forces of Nature
Messrs. Macmillan

Early studies recognized that capillary phenomena provided insight into the cohesive, or intermolecular, forces that hold materials together.

These effects are often determined by molecular layers at the interface.

Synchrotron X-ray surface scattering provides a probe of the molecular basis for macroscopic capillary phenomena.

Scientific Communities Interested in Liquid Surface Scattering

Many common scientific and industrial applications utilize liquid interfaces.

middle_fork.org

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

Wetting/de-wetting

liquids-on-liquids, liquids-on-solids (coatings, paints)

biological cells on wet surfaces

Communities: Chemical engineers, industrial chemists and materials scientists, environmental scientists.

Complex fluids

Surfactant assemblies at interfaces, many domestic products (soaps, detergents, emulsions), oil industry

Communities: Chemical engineers, industrial chemists, materials scientists, and soft matter physicists.

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

Biomembrane processes

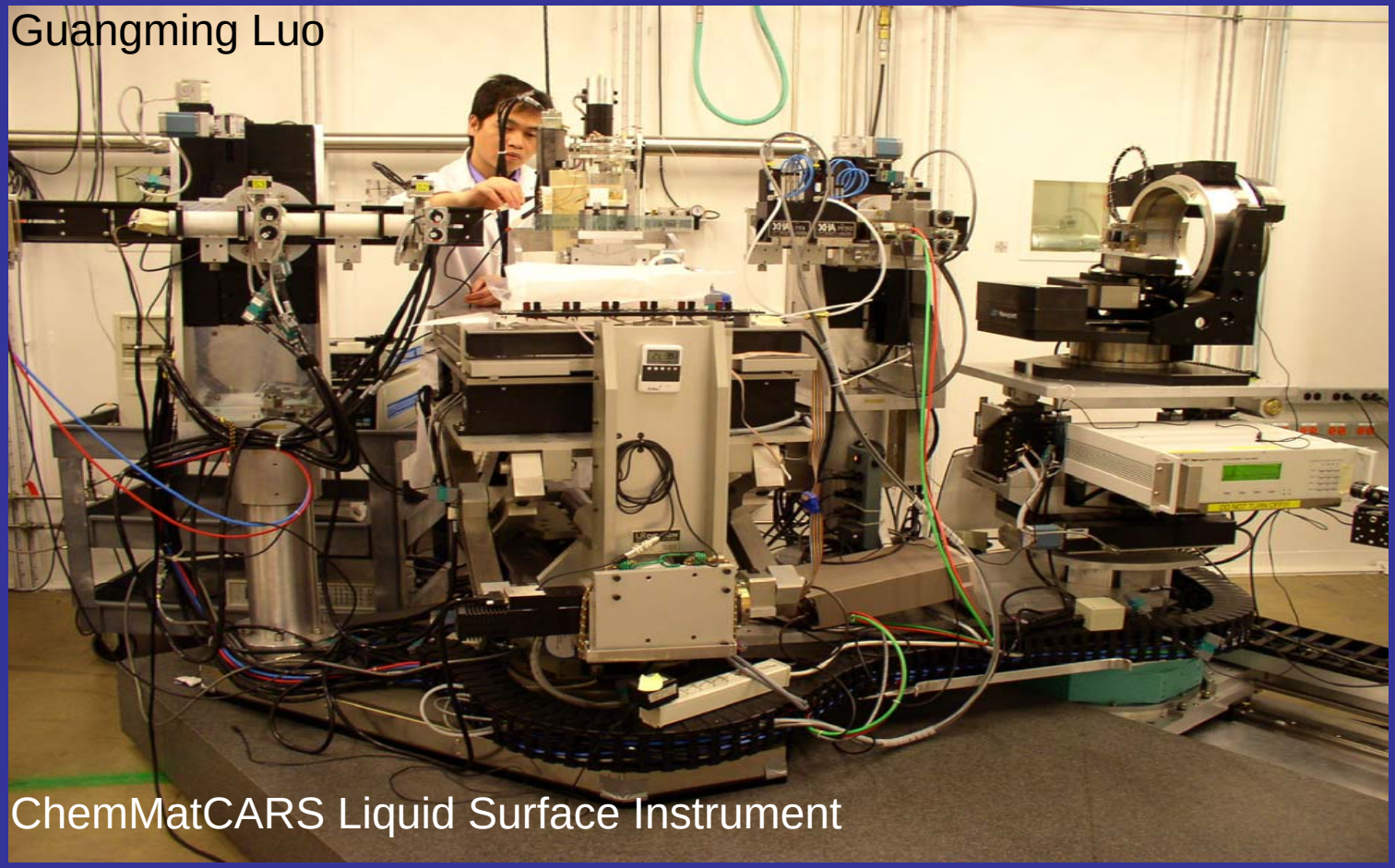
lipid-lipid and protein lipid interactions, cell biology

ion transport, disease treatment and mechanisms

Communities: bio-engineers, biochemists, drug industry, biophysicists

The liquid surface community is poised for growth into new areas IF
New facilities can extend current work to more complex samples AND
Well staffed facilities cater to some "perpetually novice" users.

Custom Instrument is Required for Liquid Surface Scattering



ChemMatCARS Liquid Surface Instrument, Advanced Photon Source

Argonne National Lab

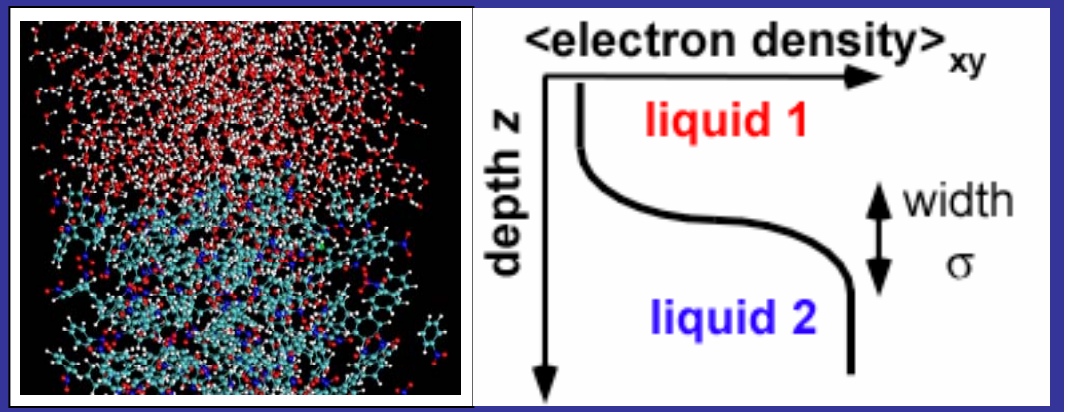
Binhua Lin, Mati Meron, Jeff Sundwall,Jeff Gebhardt, Tim Graber, Harold Brewer, Frank Westferro, P. James Viccaro

Rev. Sci. Instrum. **68**, 4372-4384 (1997); Physica B, **336**, 75 (2003)

Funded by NSF Chemistry & DOE BES

Liquid Interfaces Fluctuate
(thermally driven, not mechanical)

MD simulation (Ilan Benjamin)



Nitrobenzene/water interface

Interfacial fluctuations lead to an interfacial width σ.

Measure σ with x-ray reflectivity.

Interfacial fluctuations and widths are determined by interfacial elastic properties.

$\sigma \propto \sqrt{k_B T / \gamma}$

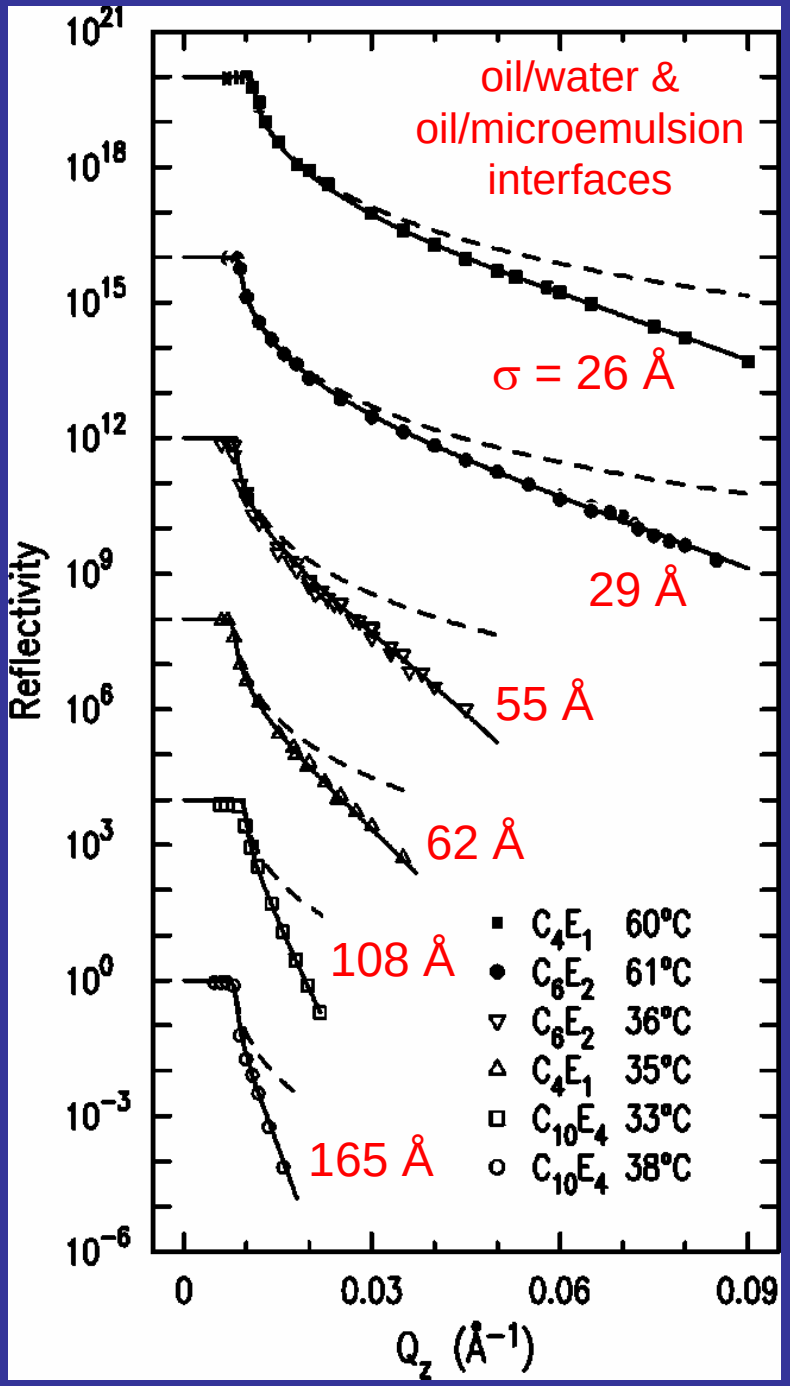
γ is the interfacial tension

σ~1 Å liquid metal surfaces, γ~500 mN/m

σ~3 Å water surface, 70 mN/m

σ~4 to 165 Å water/oil interfaces 0.03 to 50 mN/m

Phys.Rev.E 63, 021601 (2001)

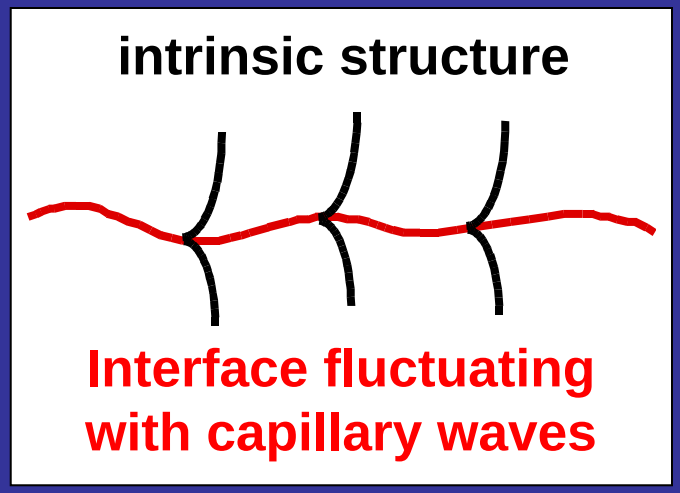


More on Interfacial Fluctuations

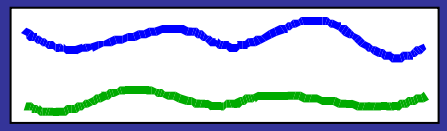
Probe height-height correlation functions $\langle \zeta(0)\,\zeta(r) \rangle$ with x-ray diffuse scattering

Other issues (current research areas):

- **Molecular (intrinsic) structure near the interface contributes to the width.**
- **Short wavelength capillary waves. How to correctly describe and measure? Do they distort the intrinsic structure?**
- **Types of fluctuations near interfaces: bulk and interface position fluctuations.**



- **Multiple interfaces that interact as they fluctuate.**



- **Role of intermolecular forces in determining interfacial elastic properties and fluctuations.**

Diffuse scattering and reflectivity from rough interfaces are both weak

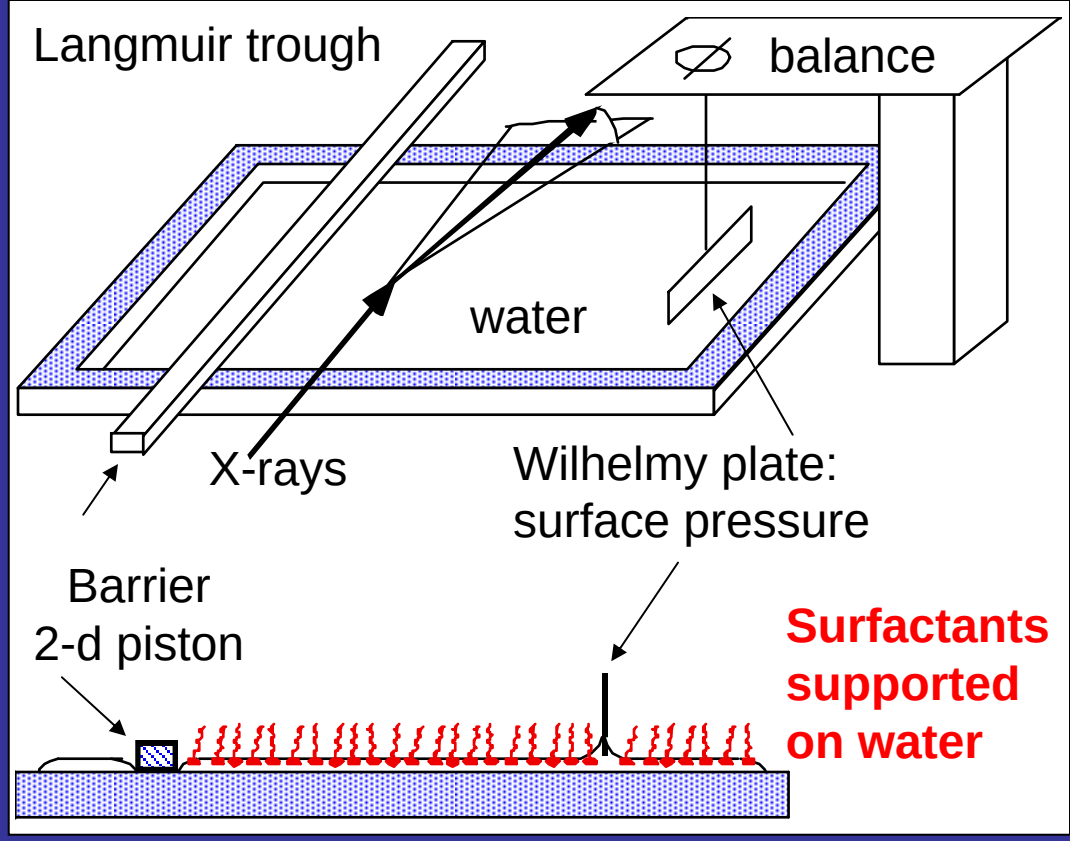
- 3rd generation sources have significantly advanced these studies

Molecular Ordering – The Kingdom of Langmuir Monolayers

Insoluble surfactants - confined to the surface of water.

Science: Probe molecular ordering of quasi-2-dimensional assemblies of molecules and particles. Surface density and surface pressure can be varied.

Originally used by Langmuir to probe molecular sizes, conformation and orientation of surfactants.

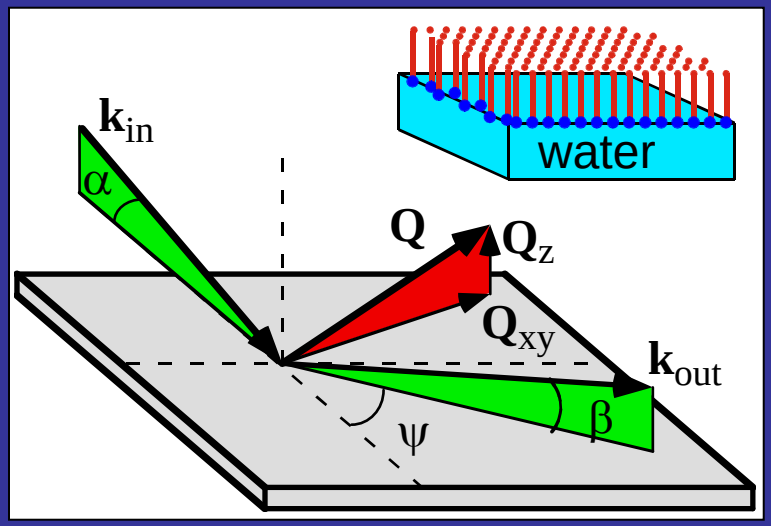


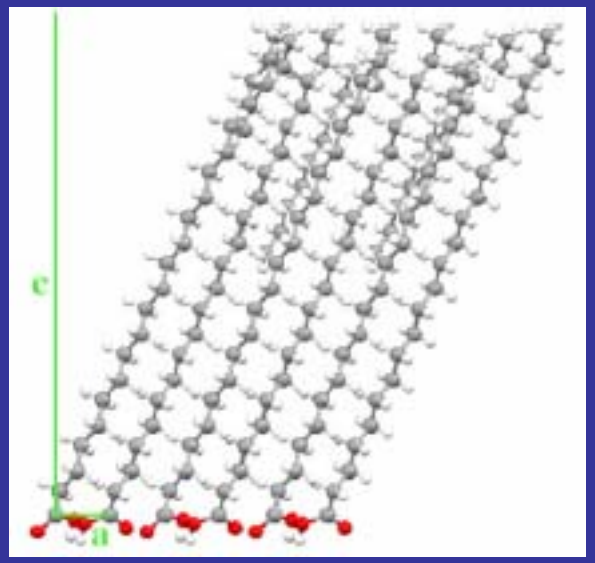
Currently used to mimic many scientific processes, such as

- ***biomolecular interactions with lipid monolayers (bilayer mimic)***
- ***mineralization from a prepared 2-dimensional nucleation site***
- ***2-d phase behavior that may be of relevance for complex fluids***

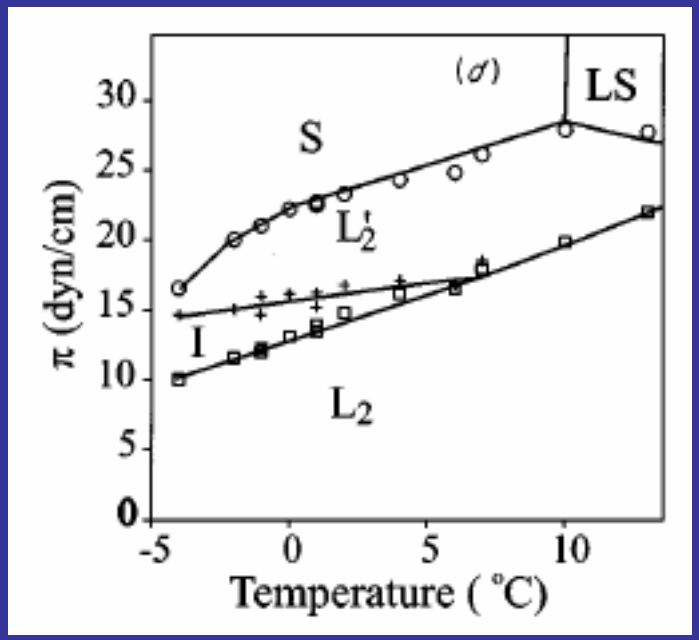
Applications: Monolayers can be transferred to solid surfaces to make Langmuir-Blodgett films useful for non-linear optical, piezoelectric, pyro-electric, dielectric, photoelectric, chromic, and biological properties, among other properties, in sensors and devices.

Grazing Incidence X-ray Diffraction of Langmuir Monolayers probes in-plane order





Thin Solid Films 515, 5691 (2007)



Rev.Mod.Phys.71, 779 (1999)

Studies of long chain surfactants yield

Headgroup ordering

Tailgroup ordering, including presence of defects

Unit cell parameters

Polar and azimuthal tilt angles of molecules

Phase diagrams

Fundamental questions remain on

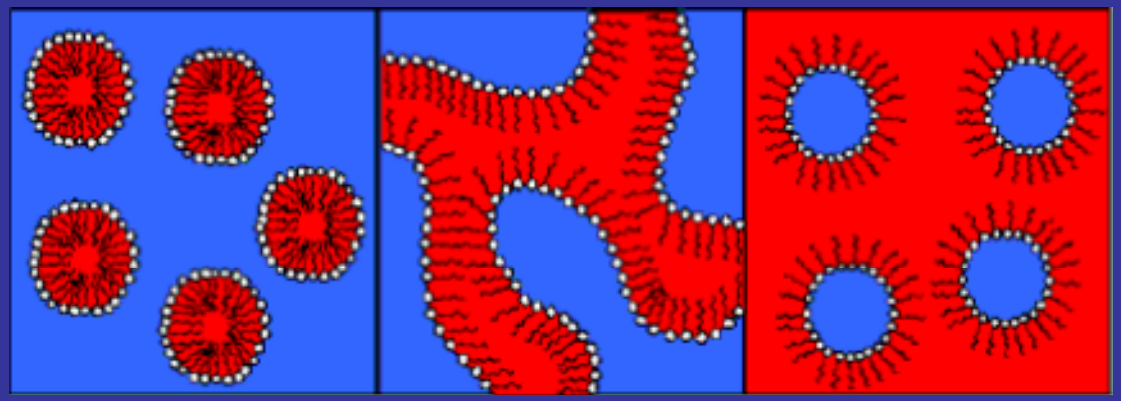
The form of in-plane molecular correlations

Kinetic and dynamic processes in monolayers

Behavior of multi-component monolayers

Surfactants and Interfaces in Complex Fluids

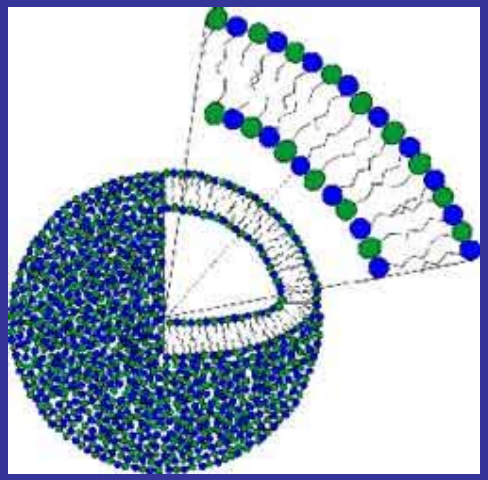
Surfactants bring incompatible materials together on the molecular scale



Oil
Water
Surfactant

Or separate regions of materials that would otherwise mix

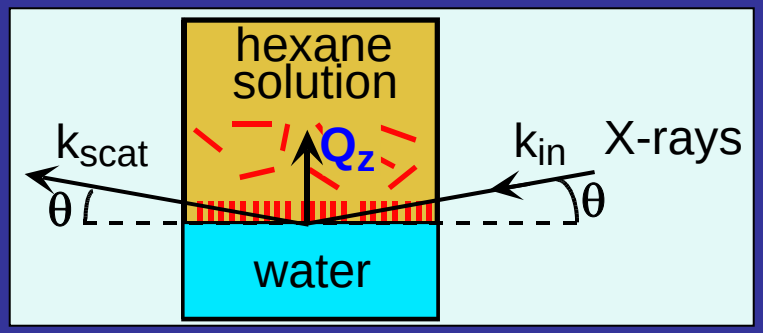
Water is inside and outside

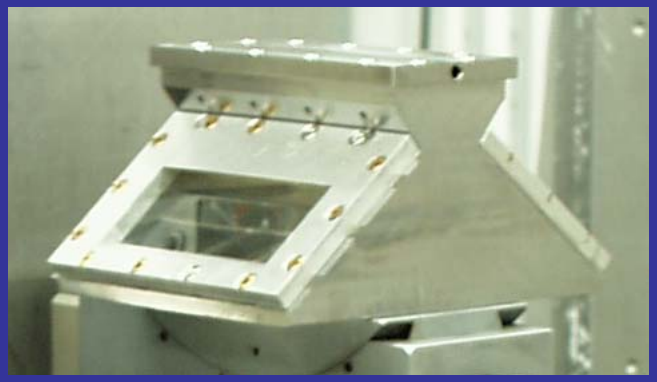


These are soluble surfactants, in contrast with those used in Langmuir monolayers.
Small angle scattering can be used to study the morphology of the internal structures.

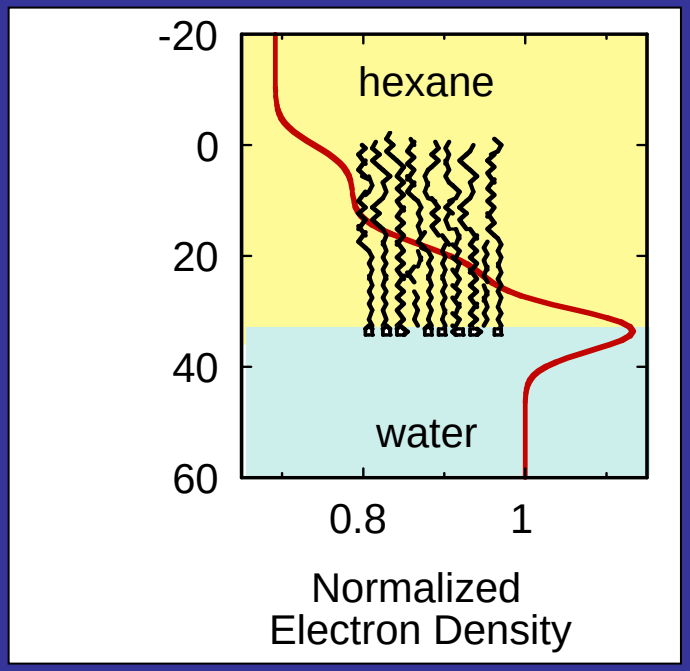
Images from Eric Kaler's website, U. of Delaware

Gibbs Monolayers (of soluble surfactants) at the Water-Oil Interface

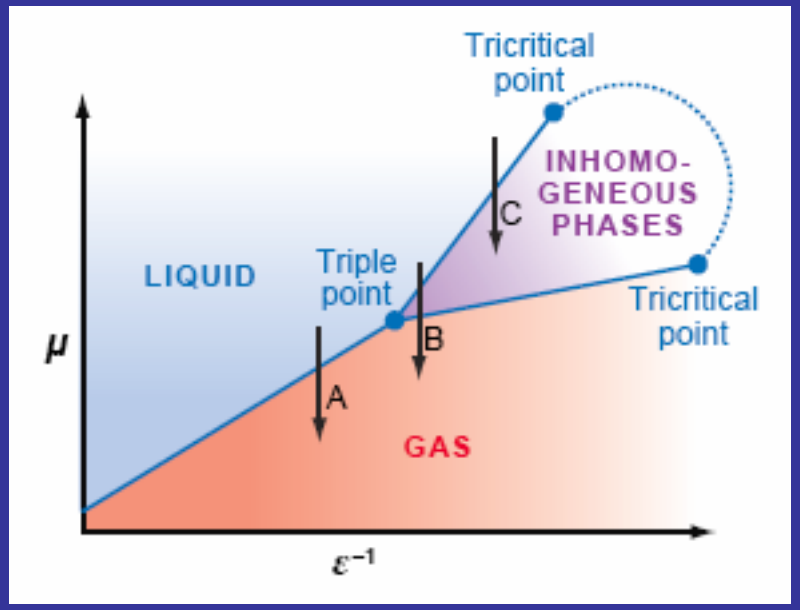




J. Phys. Chem. B, **107**, 3344 (2003)



Ann.Rev.Phys.Chem.59, 153 (2008)



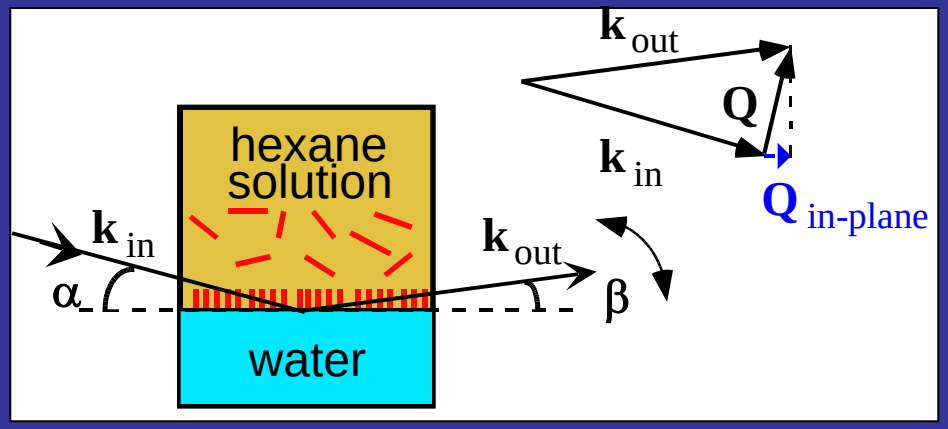
Long-chain alkanol surfactants
disordered at water-hexane interface
ordered at water-vapor interface

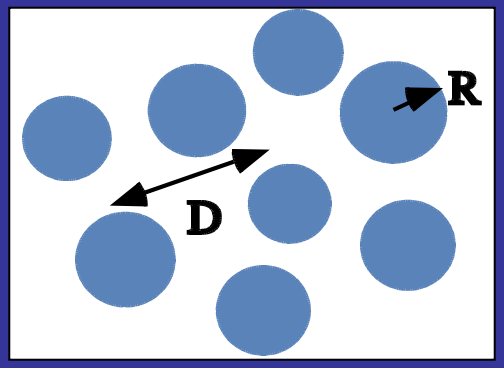
Correct phase diagram?
Misses solid monolayer phases!

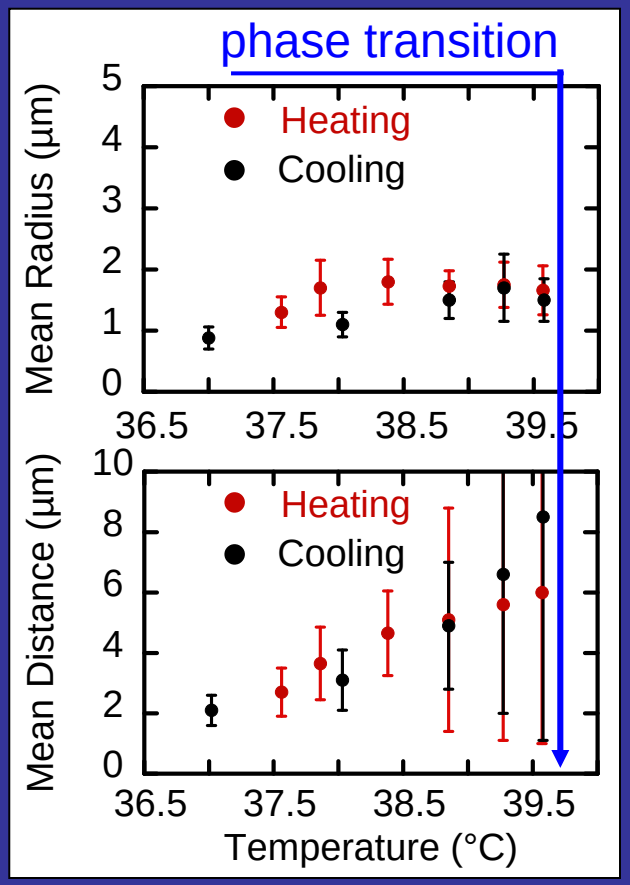
Inhomogeneous Surface Phases and Diffuse Scattering (GISAXS)

Interfaces are often spatially inhomogeneous.

Since reflectivity probes the electron density averaged over the interface, and surface diffraction picks out the ordered regions of the interface, the overall inhomogeneity of the interface may be missed.







Surfactants form interfacial domains.

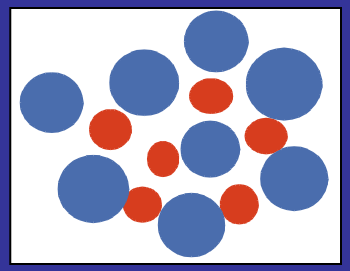
Surface "small angle scattering" can probe them.

Constant radius, but interfacial density varies by a factor of 20

Creation/annihilation of domains

How will a new facility benefit the study of monolayers?

Mixed surfactant interfacial systems - common industrially and biologically



bio-membrane mimics exhibit phase coexistence
thermodynamic studies indicate non-ideal mixing
complex interfacial morphology
(multiple types of domains) likely

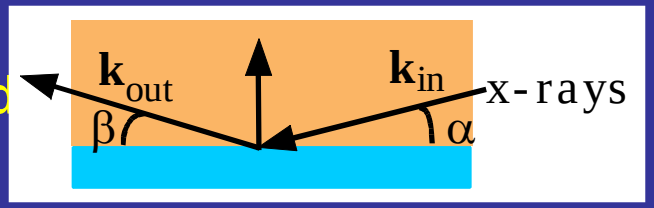
At NSLS, scattering studies of such systems are difficult to interpret because the domain sizes are similar to the transverse coherence length in the plane of the interface.

At NSLS2, greatly improved coherence will help address this problem.

Incorporation of Brewster angle microscopy (optical imaging) or x-ray microscopy into x-ray instrument will provide complementary information.

Reflectivity measurement at buried interfaces is time consuming (24 hours)

Higher energy (decreased x-ray absorption) and higher brilliance reduce the measurement time.



Higher energy will also allow different interfaces to be studied by allowing penetration through higher absorbing bulk materials

More advantages of a new facility - Time resolution

Scientific:

biomembrane lipids and proteins often fragile - limit x-ray exposure

kinetics and dynamics of biological interface processes

- interfacial protein layer formation
- biomineralization film growth
- mechanism of destruction of lipid layers by antimicrobial peptides
- binding dynamics of proteins, toxins, etc. to lipid layers

"pump-probe" processes

- response of photo-sensitive interfaces to light (electron/ion transfer)
- response of interfacial electrostatic processes to DC/AC electric fields

Measurement duration:

Reflectivity - hours; Grazing incidence diffraction (GID) - 1/2 hour

Diffuse scattering - hour

New Facility

Higher brilliance and fast linear or area detector will reduce GID peaks and diffuse scattering to minutes.

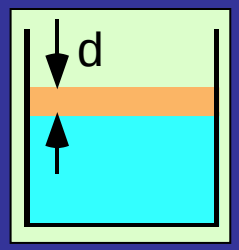
Low resolution Q_z information in diffuse scattering.

Fast reflectivity will require new design - fast energy scanning OR energy dispersive (to milliseconds) - simplest with fast, spectroscopic, pixel detector

The Tyranny of Monolayers Overthrown - Multi-molecular Layers and Wetting Transitions

Wetting of liquid on a solid or liquid substrate

Free energy of a film of thickness d:



$$F(d) = \gamma_{liquid/vapor} + \gamma_{liquid/substrate} + \Delta G(d)$$

$\Delta G(d)$ ***depends upon long range interactions between molecules in the film and the substrate***

middle_fork.org

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

The form of $\Delta G(d)$ ***will produce***

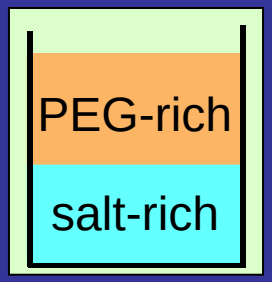
- ***total wetting (complete spreading of a drop on a substrate)***
- ***incomplete wetting (coexistence of drop and bare substrate)***
- ***pseudo-partial wetting (coexistence of drop and thin film)***

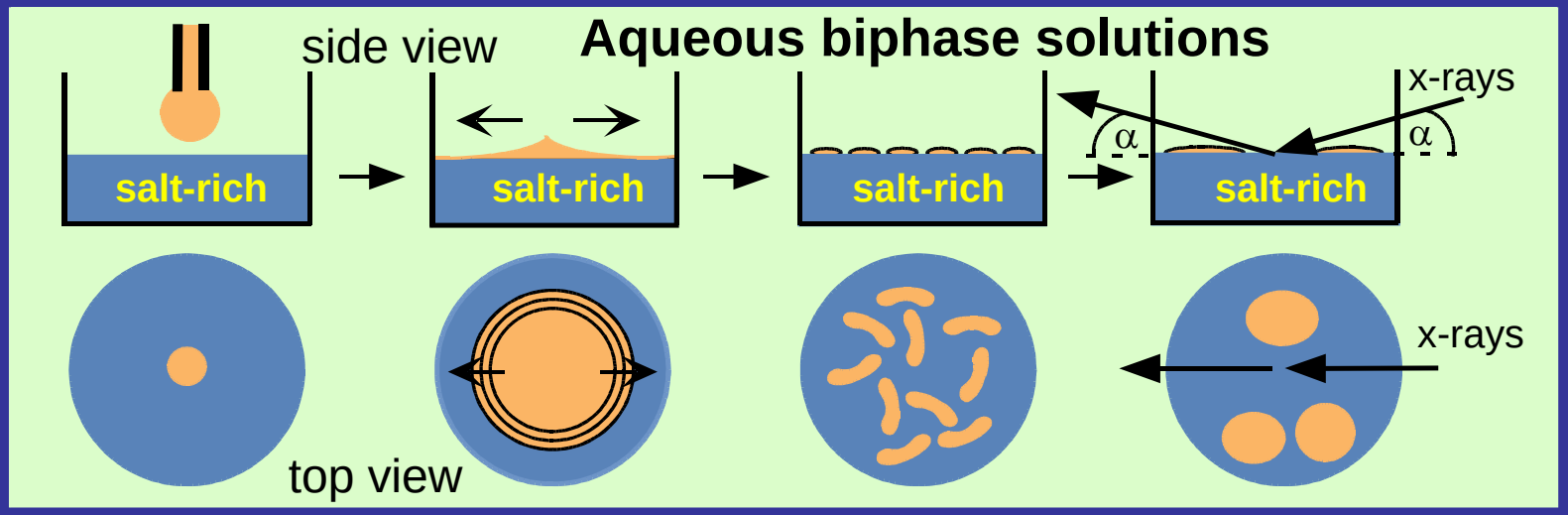
Wetting films are often very thin (1 to 100's of molecules thick) interfacial structure, roughness, and fluctuations are important for wetting and the formation of wetting layers - ideal for x-ray studies.

Many applications:

coatings, paint, lubrication, stopping a car on a rainy road (dewetting of water within 1 ms), cell adsorption/motion, and many industrial

Example of an X-ray Study of Pseudo-Partial Wetting





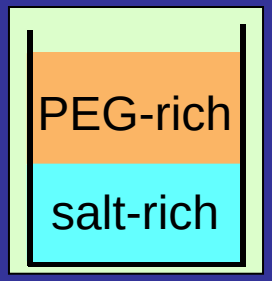
Polyethylene Glycol, Potassium Phosphates, Water

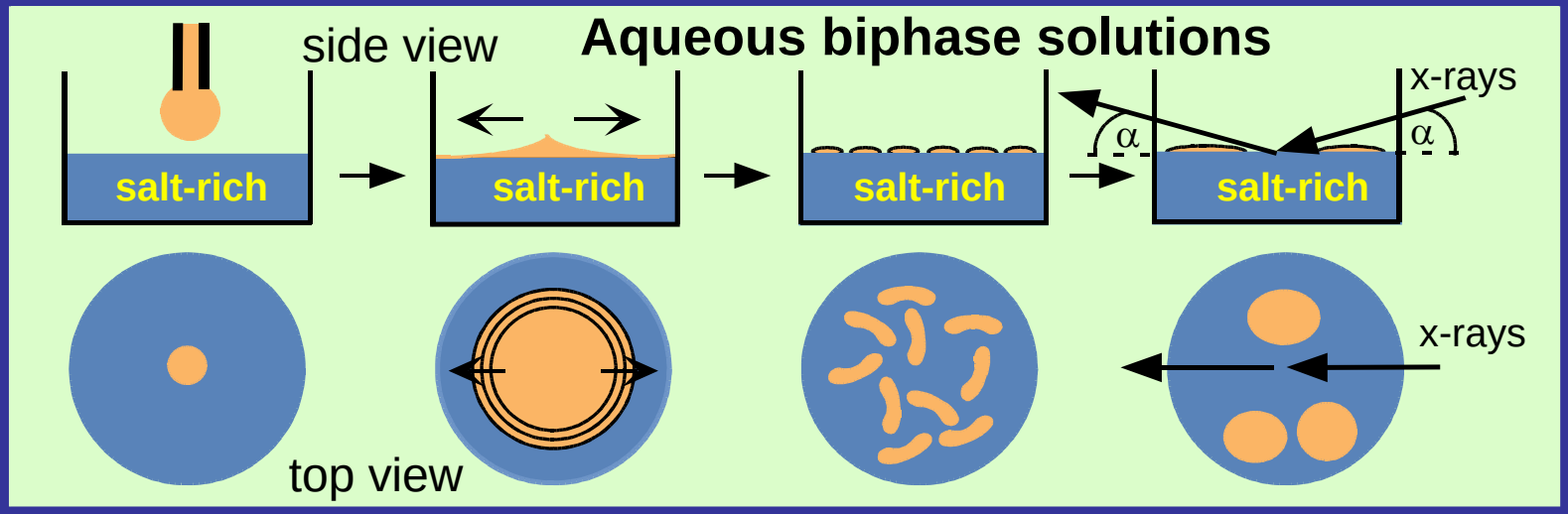
Dynamics of this spreading process are illustrative of many dynamical interfacial phenomena in liquid systems.

Large spreading coefficient indicates that a thick drop spreads completely, but once the layer is thinned the long range forces dominate to create pseudo partial wetting.

This hypothesis could be tested with fast reflectivity measurements. As of now, we can only investigate the final equilibrium state.

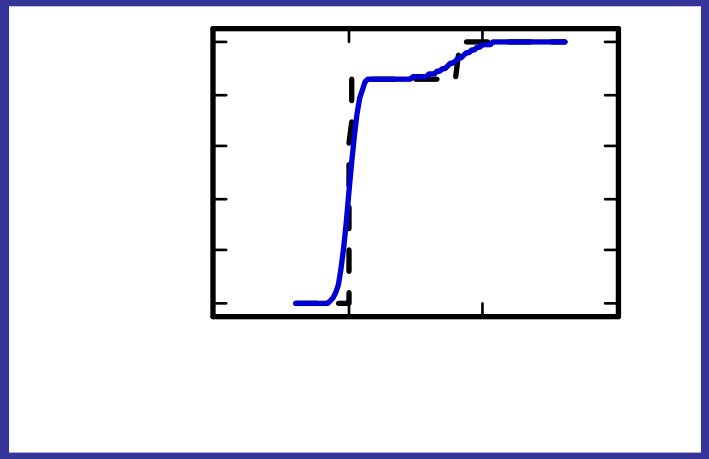
Example of an X-ray Study of Pseudo-Partial Wetting

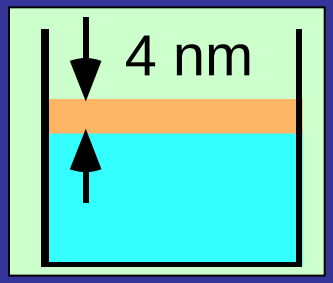




Polyethylene Glycol, Potassium Phosphates, Water

X-ray Reflectivity Probe of Film Thickness and Interfacial Width





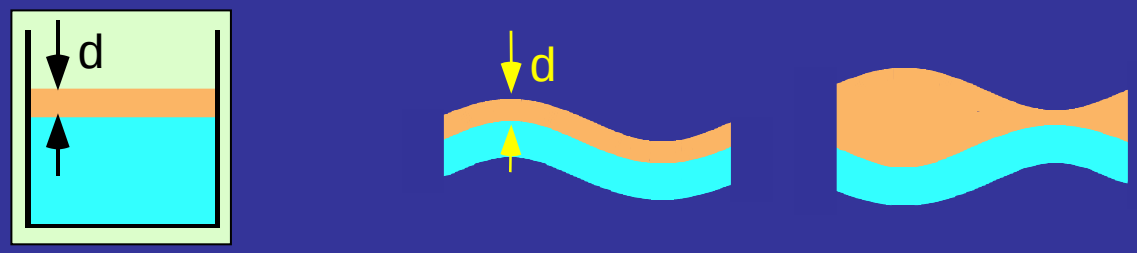
Film thickness d = 42 Å

Interfacial widths: $\sigma_{PEG\text{-}rich/vapor}$ = 2.9 Å

$\sigma_{salt\text{-}rich/PEG\text{-}rich}$ = 7.9 Å

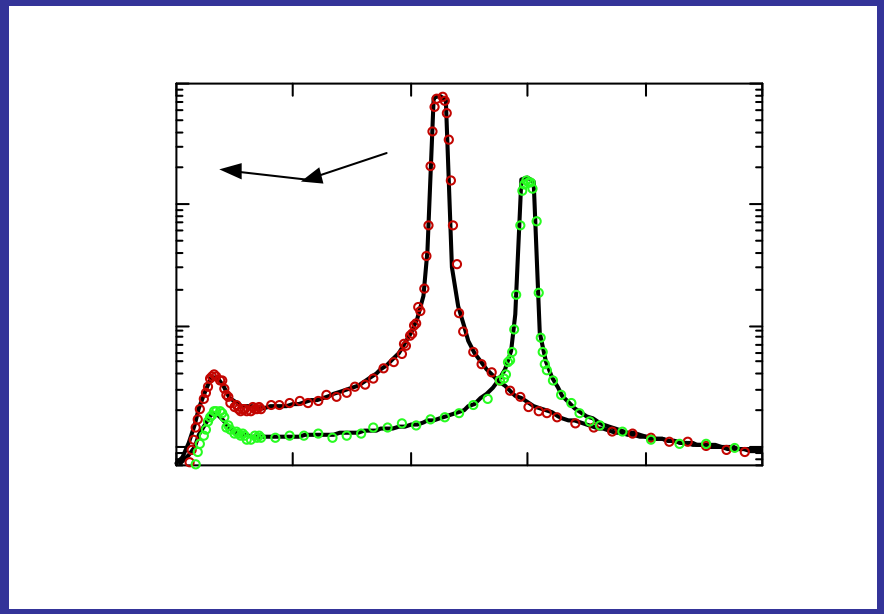
Phys.Rev.Lett. 86,5934 (21001)
J.Phys.Chem.B 107,9079 (2003)

Film Fluctuations - Coupled Capillary Waves on Two Interfaces



$$H = \int d^2 s \left\{ \sum_{i=1,2} \left[\frac{1}{2}\gamma_i \left(|\nabla \zeta_i|^2 + \left(\frac{\zeta_i}{\xi_{\parallel,cw}} \right)^2 \right) \right] + \frac{1}{2} B \left(\zeta_1 - \zeta_2 \right)^2 \right\}$$

Phys.Rev.Lett. 86,5934 (2001)



$$B = 1.4^{+1.6}_{-0.8} \times 10^{11}\, J / m^4$$

(PEG:K_2HPO_4&KH_2PO_4:H_2O -- 13.2:28.9:57.9 wt%)

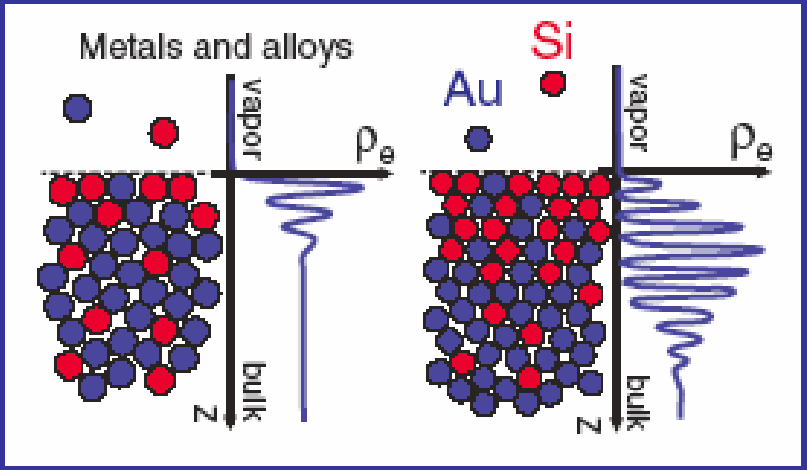
Measure coupling constant: Coupling is intermediate between stacks of flexible lipid membranes and stacks of stiff lamellar liquid crystals.

Can also determine ΔG(d) in free energy of film

Surface Ordering Arising from Termination of Bulk Phases

Liquid metals -

- ***particle interactions change from metallic to insulating across surface***
- ***surface atomic layering in pure metals***
- ***surface layering and segregation in alloys***



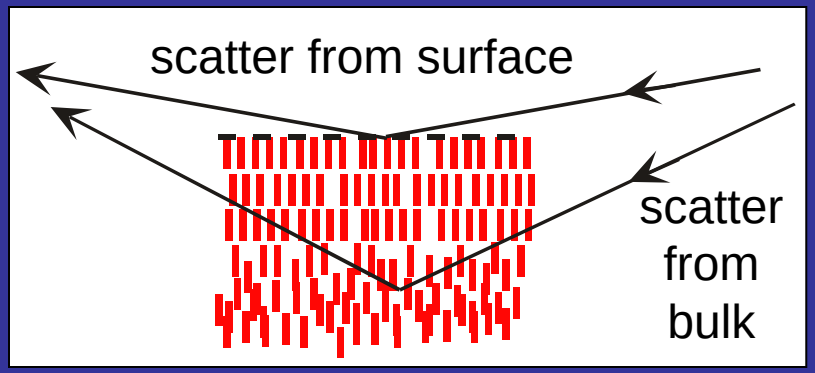
Science 313, 77 (2006)

Surface segregation is predicted by Gibbs adsorption equation

$$d\gamma = S_a^{\sigma} dT - \sum_i \Gamma_i d\mu_i$$

Liquid crystals (one of many examples) -

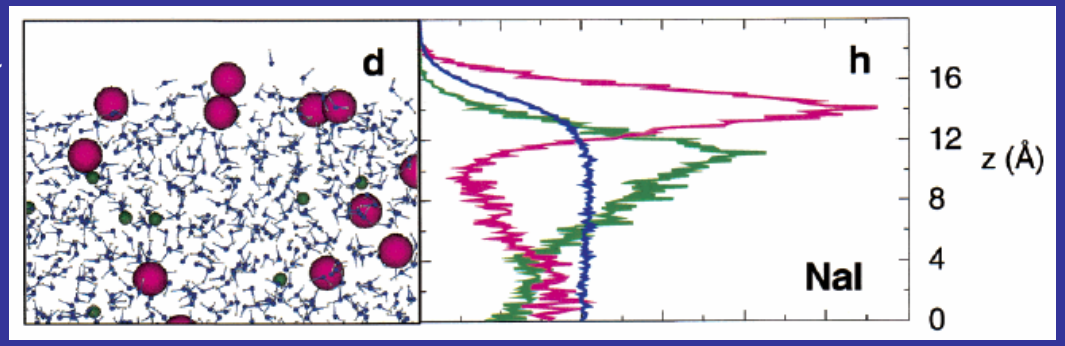
- ***develop smectic surface order from nematic bulk order***
- ***vary temperature to approach the bulk nematic to smectic transition, thickness of surface smectic layers corresponds to bulk smectic correlation length***



P.S. Pershan's group

Ion Surface Segregation in Electrolyte Solutions

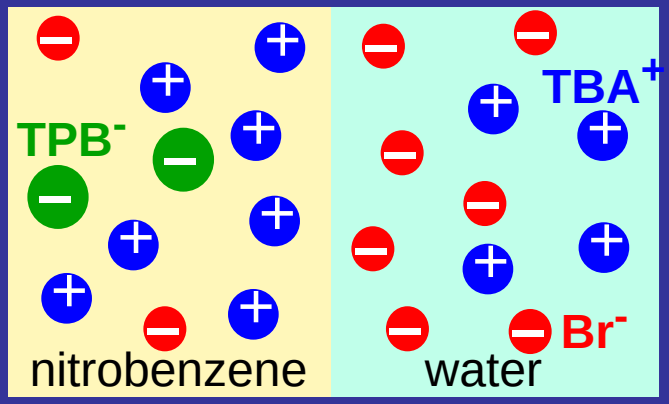
JPCB 105, 10468 (2001)



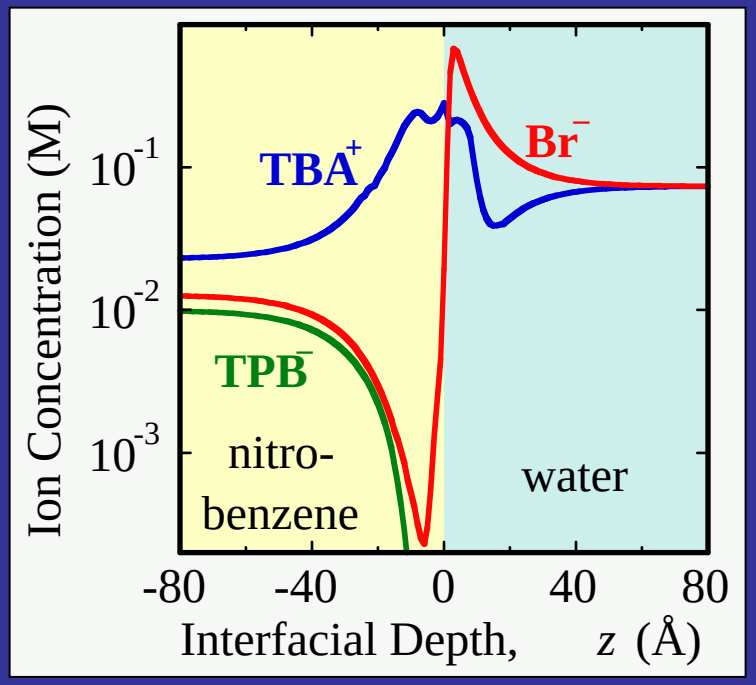
Important at the water-vapor interface for chemical reactions in the atmosphere on the surface of aerosols.

Segregation of I^- at water surface

Ion distributions develop at water-oil interfaces.



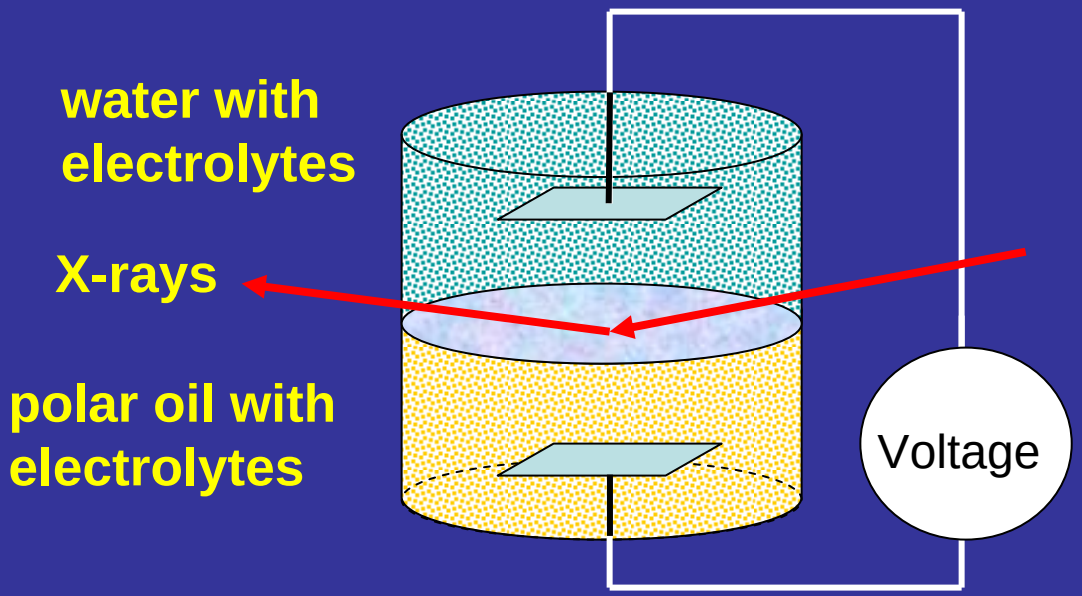
TBA^+ Br^- in water
TBA^+ TPB^- in nitrobenzene

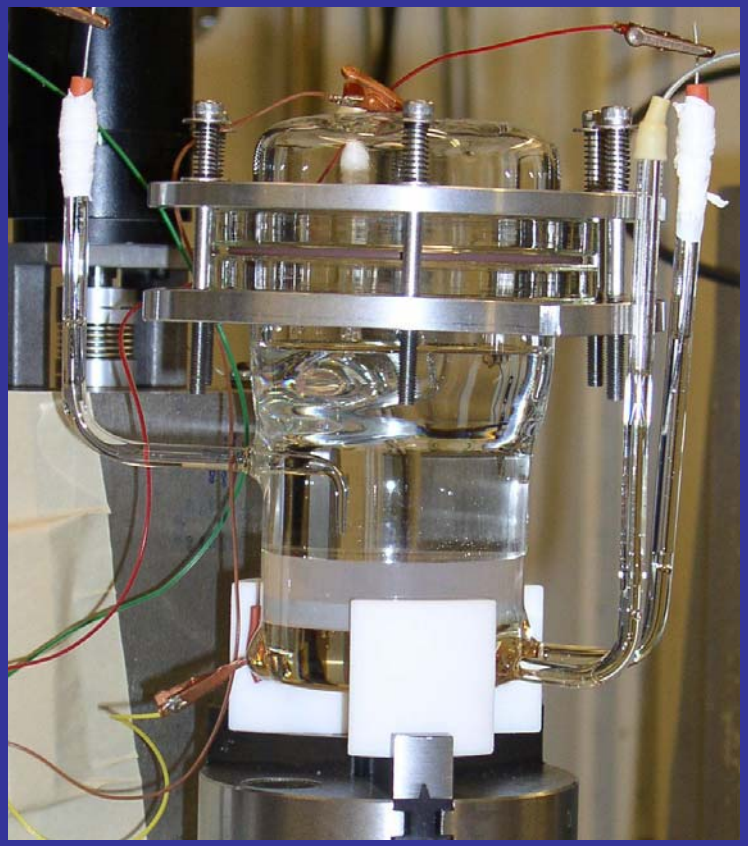


Science 311, 216 (2006)

Control of Electrical Potential Across the Water-Oil Interface

Alter concentration and species of ions at interface
Change physical properties of interface
Control molecular transport through interface
Investigate electrostatically controlled interfacial processes





Requires an interface between two polar liquids - small potential (~0.1 V) yields large electric field across interface ~10^8 V/m

20 to 30 keV high brilliance required (NSLS-II experiment)

Many Biomolecular Phenomena Occur at Interfaces

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

www.tech.gunma-u.ac.jp/gakka/hirai/Intro(English).files/image008.gif

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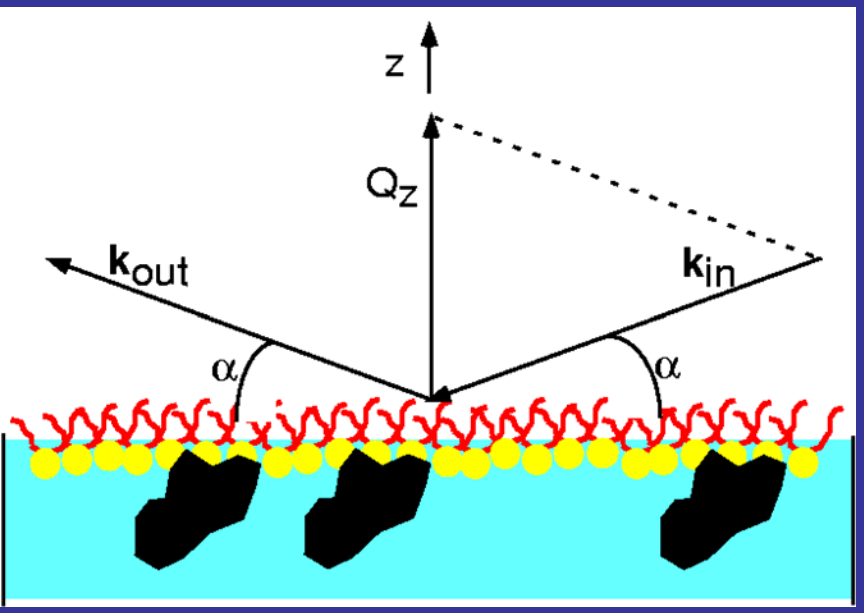
These interfaces are very disordered, with structural properties that cannot be adequately addressed by crystallography.

Many biomembrane phenomena are being studied with surface scattering. These include the ordering of proteins, peptides and toxins at lipid monolayers supported on water, and the ordering of lipid bilayers supported on solid surfaces.

Biomaterials applications at interfaces are also abundant, which rely on the interaction of cell surfaces with a synthetic environment.

One Example: Protein Adsorption to Lipid Monolayers on Water



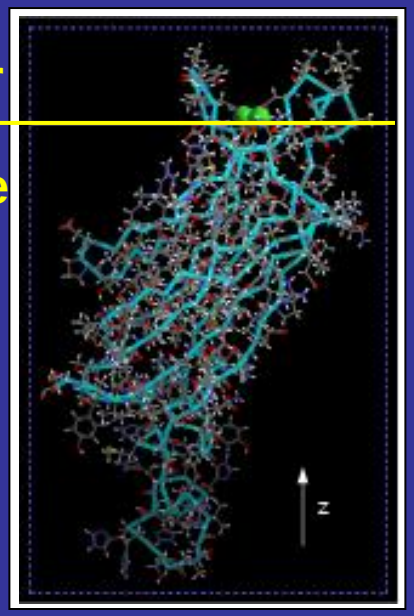
Peripheral membrane proteins important for cell signaling, biocatalysis.
Interactions with the membrane are poorly understood.

Cytosolic phospholipase A_2 ($cPLA_2$) is an enzyme (protein) that catalyzes the production of arachidonic acid from membrane phospholipids.
$cPLA_2$ consists of 2 domains,
the C2 domain is responsible for membrane binding.
Similar C2 domains are present in many signaling proteins.

Most C2 domains are highly positively charged, require Ca^{++} to bind to negatively charged membrane lipids. Binding mechanism is electrostatic.
The cPLA2α-C2 domain binds to neutral lipids - how?
Reflectivity provides useful structural information.

Reflectivity Model for $cPLA_2$-C2 Domains Adsorbed to SOPC monolayer

Model $cPLA_2$-C2 electron density with x-ray crystallography structure and use to fit reflectivity.



Biophys. J. 89, 1861 (2005)

Reflectivity data determines

- **orientation of protein**
- **depth of penetration of protein into lipid layer**
- **changes in thickness and electron density of headgroup and tailgroup region of the lipid layer.**

Structural Conclusions and Relevance to Binding Mechanism

- **Ca^{++} ions are located close to the phosphate $RR'PO_4^-$ in lipid headgroups**
  Electrostatic interactions are important
- **Hydrophobic residues on binding loops are located in lipid tailgroups**
  van der Waals or hydrophobic interactions are important
- **>5 water molecules leave the lipids for each bound protein**
  Entropy important for binding

Many dynamical bio-interfacial phenomena involve binding, rearrangement of the bio-membrane, and subsequent biochemical reactions.

Time-resolved and resonant anomalous surface scattering could have an impact in this area

Some Scientific Opportunities in the Field of Liquid Surface Scattering

**A very wide range of liquid interfacial phenomena,
of interest to physicists, chemists, biologists, and engineers
can be studied with x-ray surface scattering techniques.**

I have provided only a few examples of the possibilities.

**The higher brilliance, coherence, and energy of NSLS-II,
and the opportunity to develop new instruments
optimized to take advantage of these source properties,
optimized for fast surface scattering measurements,
and catering to users from “perpetual novices” to experts,
will allow for new types of experiments and
growth of the liquid surface scattering community.**