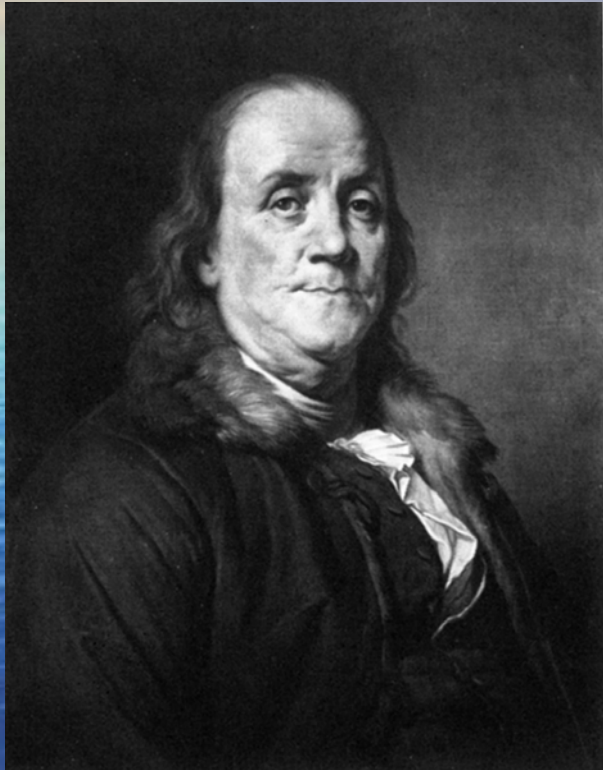


Franklin and the Future

From Franklin's Oil-Drop Experiment to Self-Assembled Monolayer Structures

Geraldine Richmond
University of Oregon

Stilling the Waves, Oil on Water: Benjamin Franklin



1757

Outline

- Oil on water
- Monolayers on water surfaces
- Monolayers on solid surfaces
- Self assembled monolayers
- Oil on water

Past current and future
perspectives

Inspiration from:



- Writings of Pliny the Elder
(AD 23-79)



- Observations during his travels that ships in back have smoother sailing than in front.
- Ship captain: "The cooks have, I suppose, been just emptying their greasy water through the scuppers, which has greased the sides of those ships a little."

Experiments on a pond at Clapham

“I fetched out a cruet of oil and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface... Though not more than a teaspoonful, produced an instant calm over a space several yards square which spread amazingly and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass.”

“After this I contrived to take with me, whenever I went into the country, a little oil in the upper hollow joint of my bamboo cane, with which I might repeat the experiment and I found it constantly to succeed.”

More Experiments



Does oil make
dead flies come
back to life?

“Mr. Jessop was about to clean a little cup in which he kept oil, and he threw upon the water some flies that had been drowned in the oil.

These flies presently began to move and turned around on the water very rapidly as if they were vigorously alive, though on examination he found they were not so.”

“I immediately concluded that the motion was occasioned by the power of the repulsion and that the oil issuing gradually from the spongy body of the fly continued the motion.”

Findings were published in *Philosophical Transactions* in 1774, one of the world's 1st scientific journals

Measuring Surface Properties :



www.physik.uni-frankfurt.de/~jr/physpicold.html

- Repeated Franklin's oil on water experiment in 1890.
- Made a calculation of the thickness of the oil layer.
- Nobel Prize in physics in 1904 for investigations of the densities of the most important gases and for his discovery of argon.

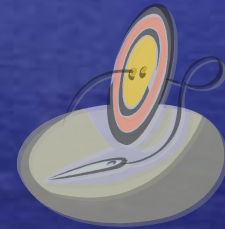
Lord Rayleigh

1842 - 1919

Pioneering Surface Tension Measurements:



- Conducted surface tension measurements in her kitchen by attaching a floating button to a balance.



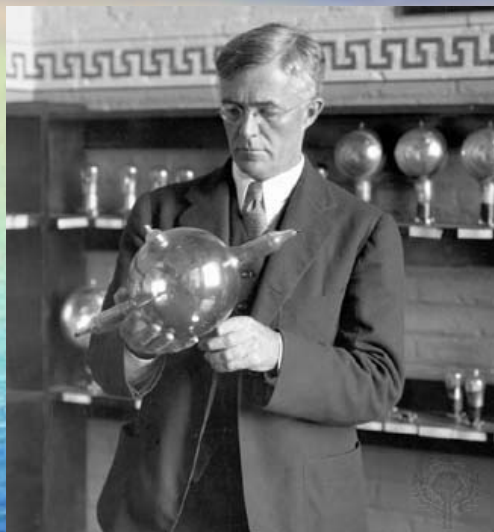
Agnes Pockels

1862-1935

www.muenster.org/.../bedeut/inhalt/pockels.htm

- Developed the slide trough to measure surface films that would later become the Langmuir trough.
- Results published in *Nature* in 1891 at the request of Lord Rayleigh.

Forming Monolayers on Water

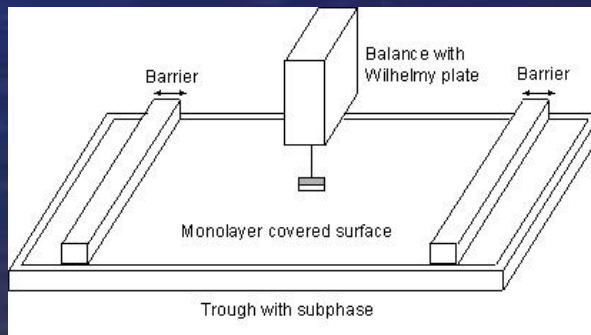


© Schenectady Museum; Hall of Electricians
History Foundation/Corbis

Irving Langmuir

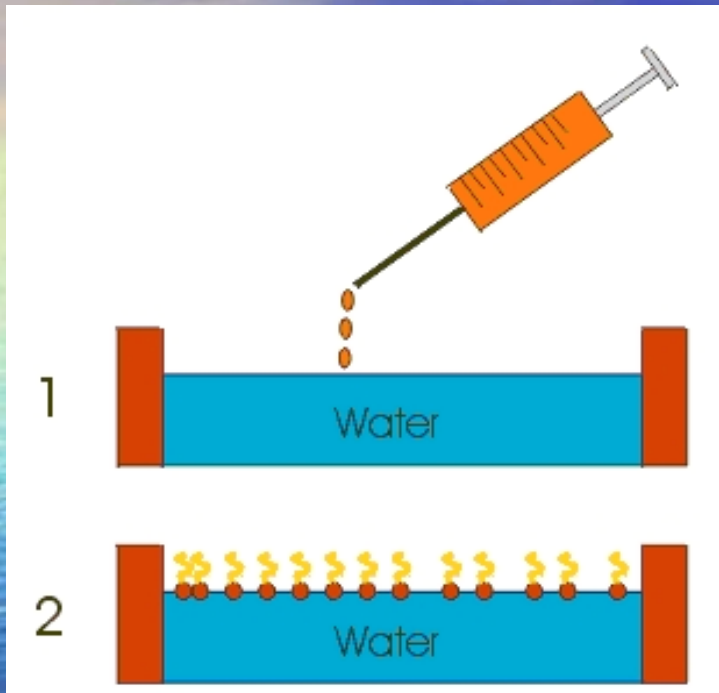
1881 - 1957

- Studied thin films and surface adsorption at General Electric.
- In 1917 he “introduced” the concept of a monolayer and the 2D physics that describe a surface.
- 1932 Nobel Prize in chemistry for discoveries and investigations in surface chemistry.



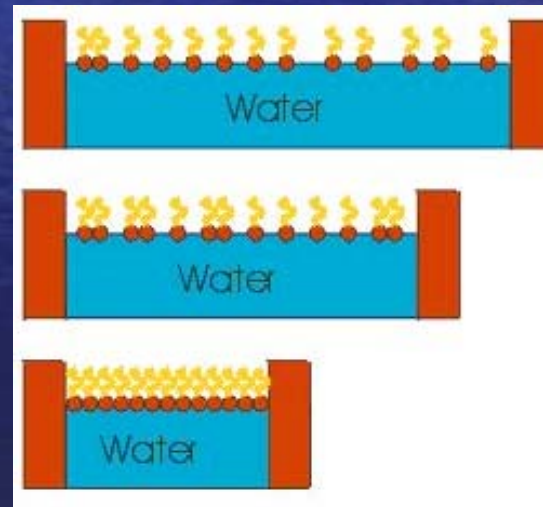
“Langmuir”
or
“Pockels”
trough?

Langmuir Monolayers



Hydrocarbon tail (oil or air seeking)

Polar headgroup (water seeking)



Gas phase

Liquid phase

Solid phase

Applications of Monolayer Technology:



Katherine
Blodgett

1898 - 1979

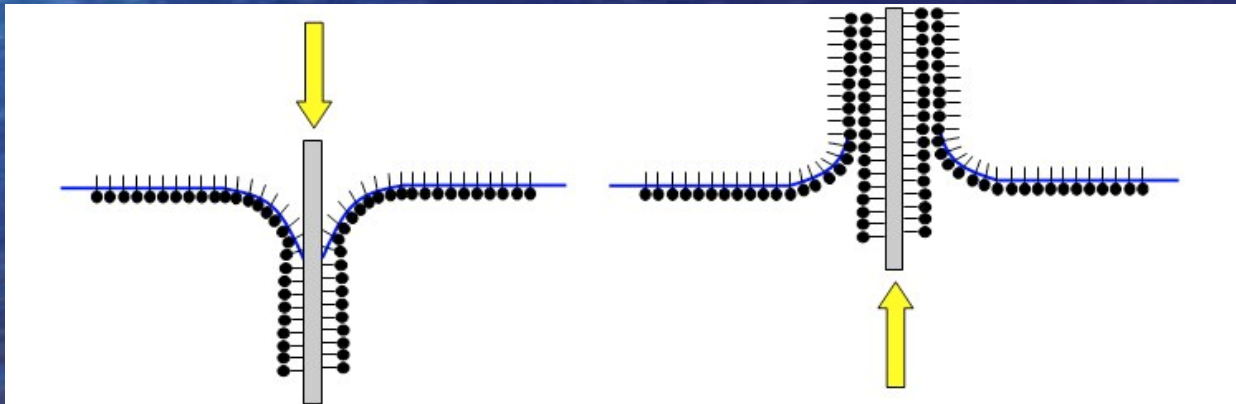
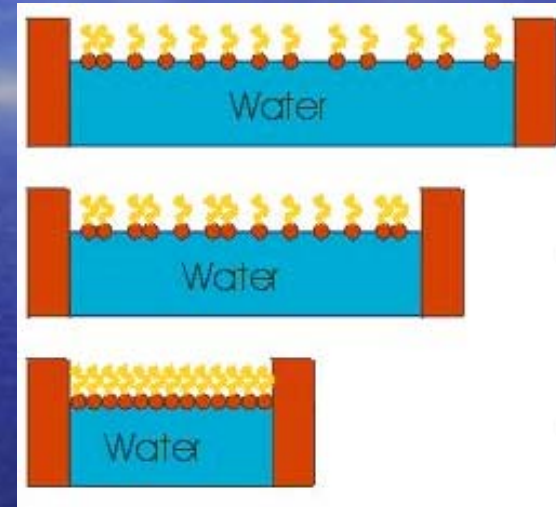
<http://home.frognet.net/~ejcov/blodgett2.jpg>

- In 1917 she became the first female scientist to be hired at GE.
- Assisted Langmuir in his Nobel award winning work on adsorption of monolayers on surfaces.
- Used this technology to coat glass to reduce glare and distortion for many practical applications using lenses.
- Developed a method to measure the thickness of these films ("color gauge"). Lead to first 100% transparent glass.

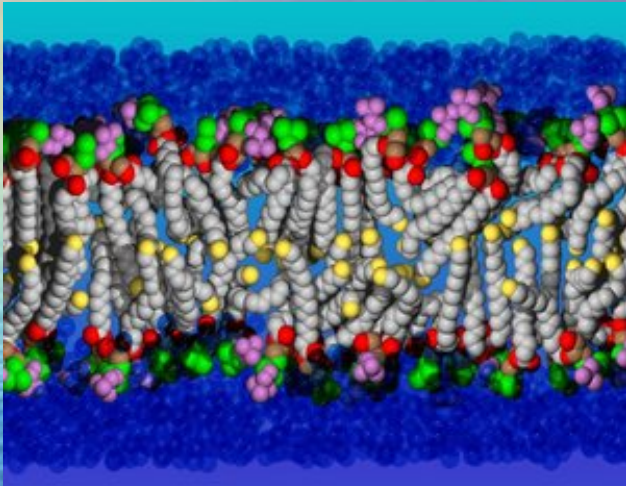


Langmuir-Blodgett Films

Monolayers on
solid substrates



Extending Surface Measurements to Medicine:



http://content.answers.com/main/content/wp/en/thumb/c/cf/300px-Lipid_Bilayer.jpg

Evert Gorter

1881 - 1954

- Measured surface pressure of lipid molecules from red blood cells using a trough similar to Langmuir's.
- Demonstrated that they could form both a bilayer and a monolayer.
- Conclude that cells are surrounded by a fatty layer two molecules thick.

Early Physiological Applications:



Charles Ernest
Overton

1865-1933

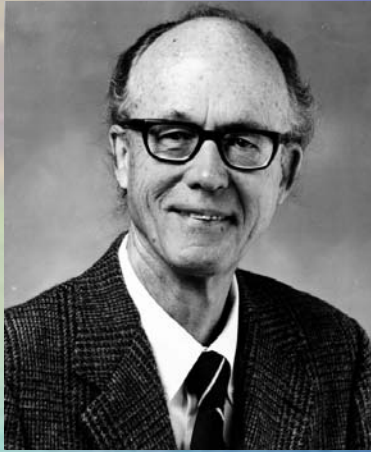
<http://www.unipublic.unizh.ch/magazin/gesundheit/2001/0366/>

- An educated botanist.
- Discovered, accidentally, some important properties of membranes.
- Hypothesized that there were similarities between cell membranes and fatty liquids (olive oil) and transport through membranes depended on the polarity of the substance.



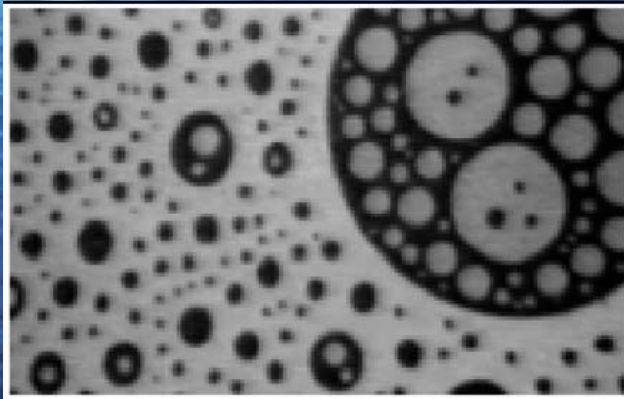
http://www.chem.uwa.edu.au/enrolled_students/BIC_sect3/sect3.2.1.html

And the field has grown:

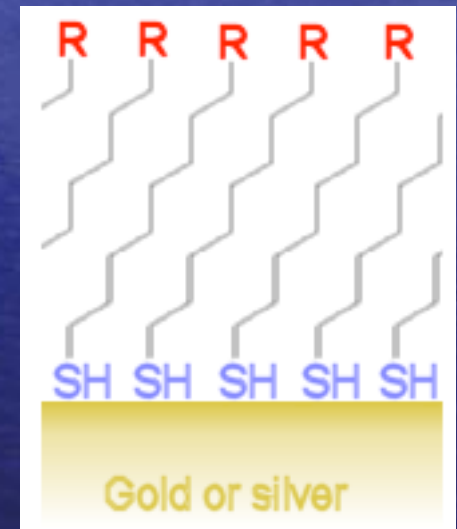
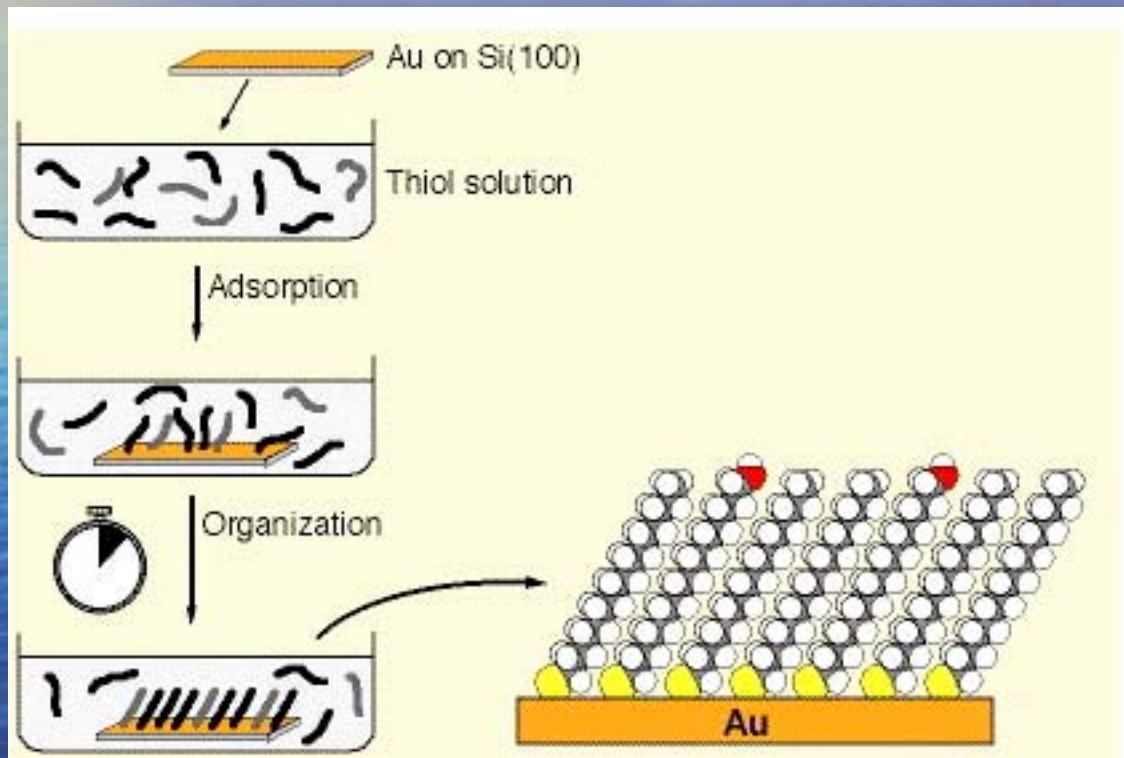


Harden McConnell
and others

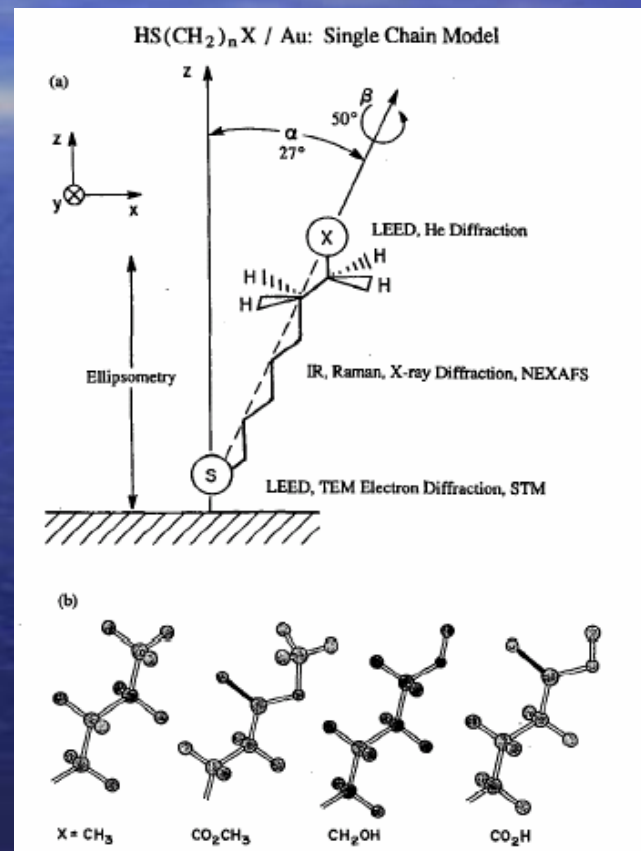
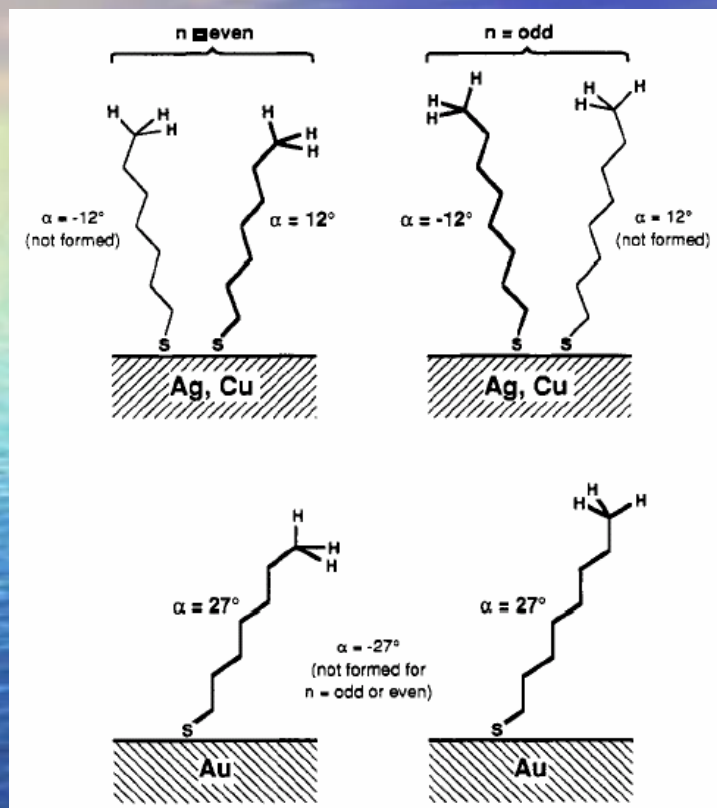
- Focuses on behavior of cholesterol in cell membranes
- Studies properties of monomolecular films on the surface of water to look at cholesterol-phospholipid interactions



Self Assembled Monolayers



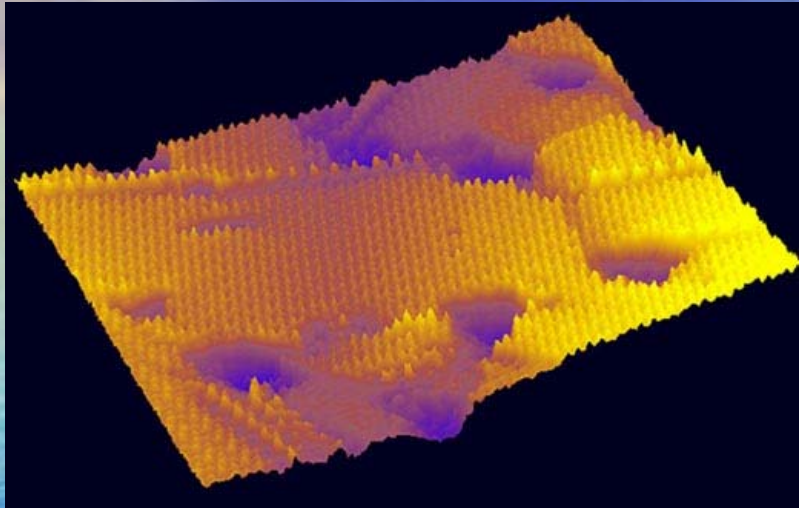
Self-Assembled Monolayers



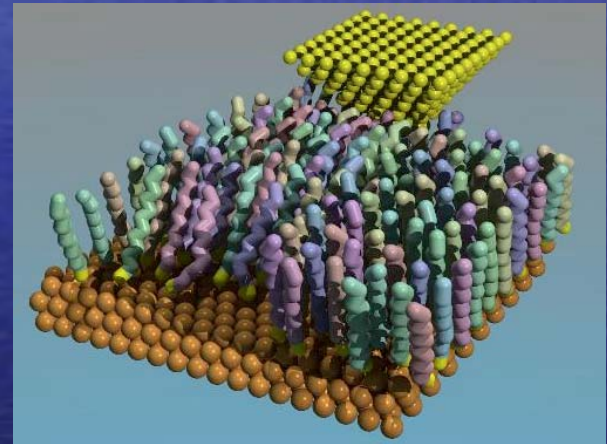
Folkers, John P.; et al. *Langmuir* **1995**, *11*, 813.

Laibinis, Paul E.; Whitesides, G. M.; et al. *J. Am. Chem. Soc.* **1991**, *113*, 152.

Self Assembled Monolayers



STM Image of a SAM

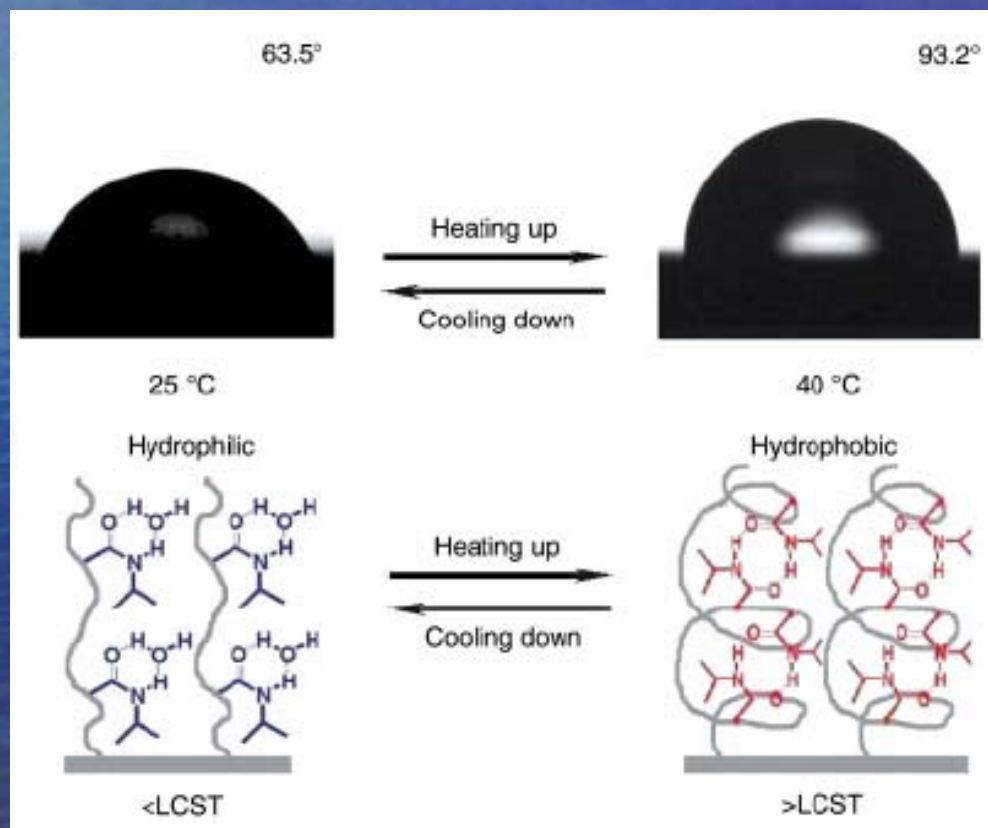


STM Modeling

T. Bonner, A. Baratoff, and H.-J. Güntherodt. MD-Simulations of Scanning Force Microscopy on Self-Assembled Monolayers. *Helv. Phys. Acta*, 68:199, 1995.

Self-Assembled Monolayers

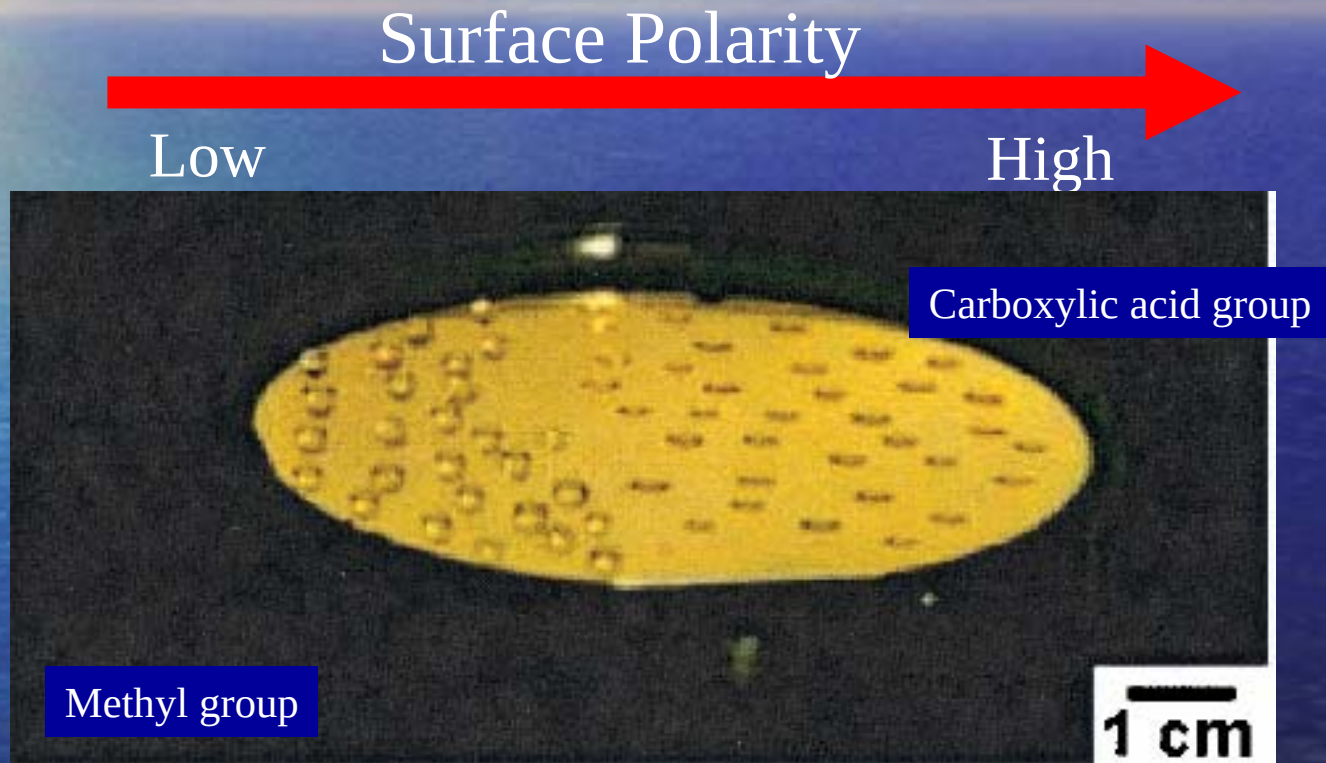
Controlling Wettability



Sun, T., et.al., *Angew. Chem.* 2004, 116, 361.

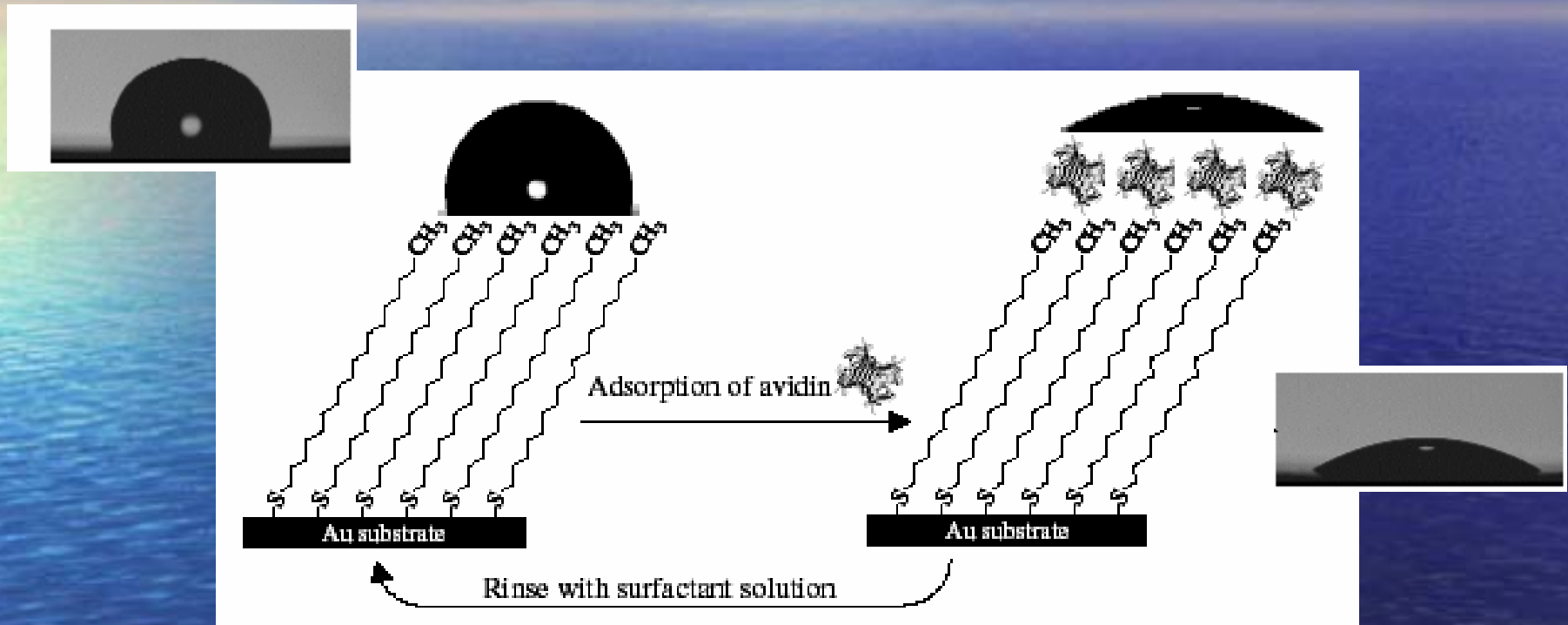
Self-Assembled Monolayers

Changing Functional Groups



Self-Assembled Monolayers

Reversible Hydrophobic/Hydrophilic Surfaces



Deval, J., et al., *J. Micromech. Microeng.* **2004**, 14, 91.

Nature's Examples

Nelumbo nucifera

Stenocara sp.

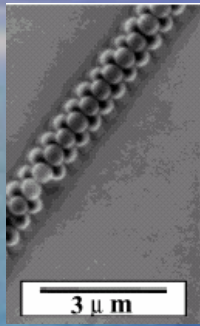


Parker, A., et al., *Nature*. 2001, 414, 33.



Self-Assembled Monolayers

SAMs for Particle Wire Formation

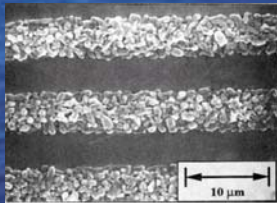


Masuda, Y., et al., *Langmuir*. 2003, 19, 5179.

Patterned Culture



Nuzzo, R., *Nat. Mater.* 2003, 2, 207.



Crystallized LiClO_4

Crystal growth on SAMs

Kumar, A., et al.,
Langmuir. 1994, 10, 1498

- Electronic transport through molecular wires
- Attaching proteins to monolayer surfaces
- Coating of nanoparticles
- Printing patterned SAMs via soft lithography
-

Soft Lithography: Masters and Stamps

Patterning Techniques

E-Beam	FIB (Focused Ion Beam)
Photolithography	Micromachining
Holography	SPM lithography

Poly(dimethylsiloxane)

Transparent

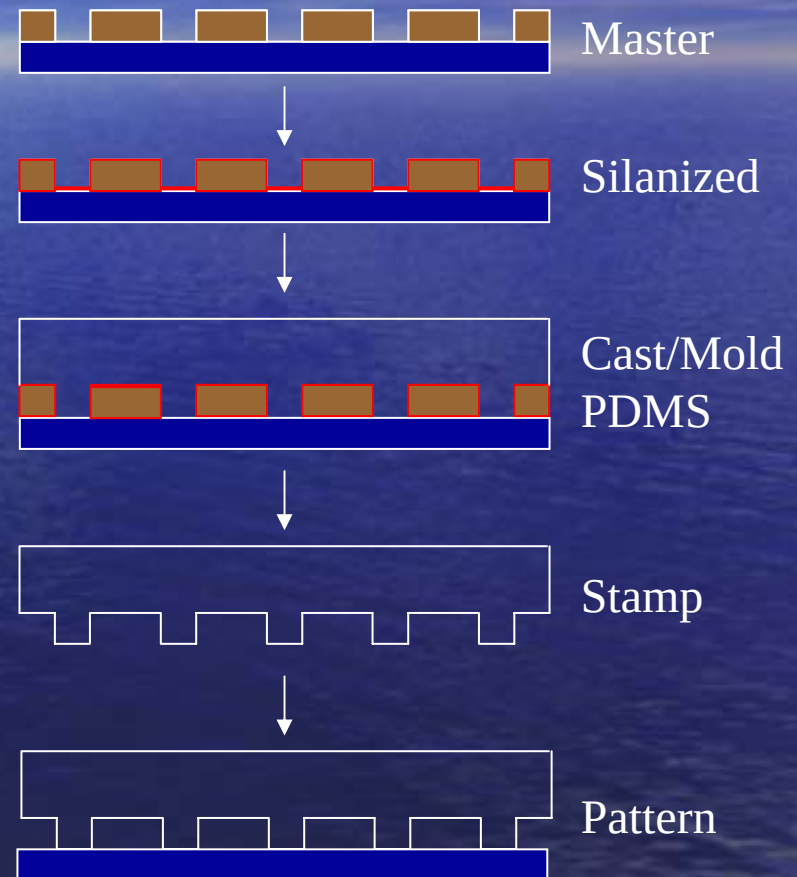
Low (but finite) Thermal Expansion

Chemically Inert

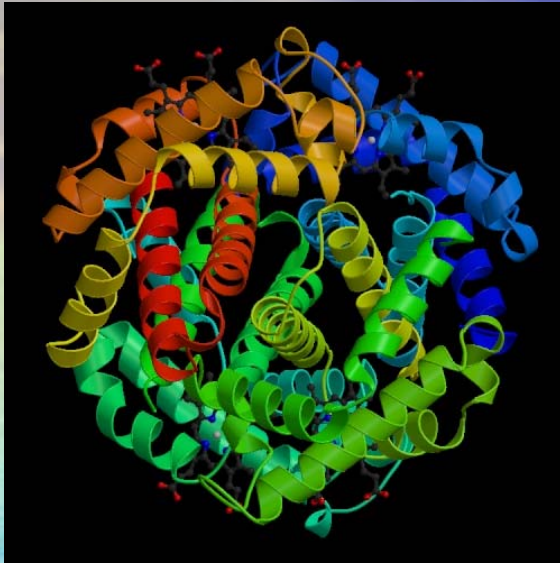
Environmentally Safe

Reusable for patterning

Record Resolution: ~30 nm



What's Next?



[www1.fzk.de/biostruct/ Assets/1a00x500.jpg](http://www1.fzk.de/biostruct/Assets/1a00x500.jpg)

SAMs were a model/lesson about the scientific challenges that are implicit in using assembly as a strategy to organize the structure of matter at all length scales.

It is a starting point that teaches us about thermodynamically directed assembly--structure in this sense is like the 3D case represented by protein folding--you squeeze out entropy and go to an energy minimum.

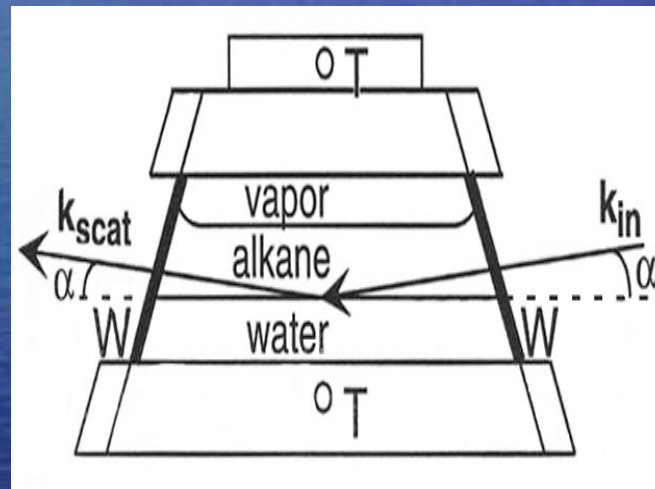
Life uses dynamics in conjunction with this form of assembly to make the really interesting things that make life possible.

That's the future challenge.

Other Challenges of Oil-Water Interfaces: Coming Full Circle

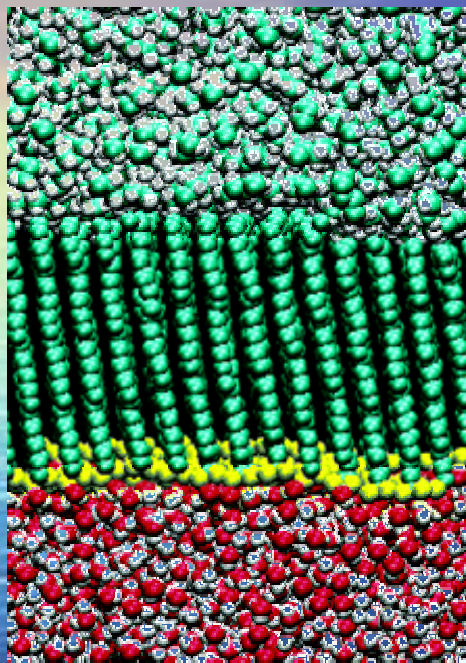
- What are the interfacial molecular properties?
- Is there a mixed interfacial region? A “drying” region?
- How does the oil (organic) affect the interfacial water structure and bonding?
- What interactions occur between water and the oil at the interface and how do these vary with the molecular characteristics of the organic molecules?
- How do adsorbates (including nanoparticles) assemble and react at these interfaces?

New directions in probing these issues: X-ray and Neutron Scattering



Li, M.; Tikhonov, A. M.; Schlossman, M. L.
Europhys. Lett. **2002**, 58, 80.

X-ray

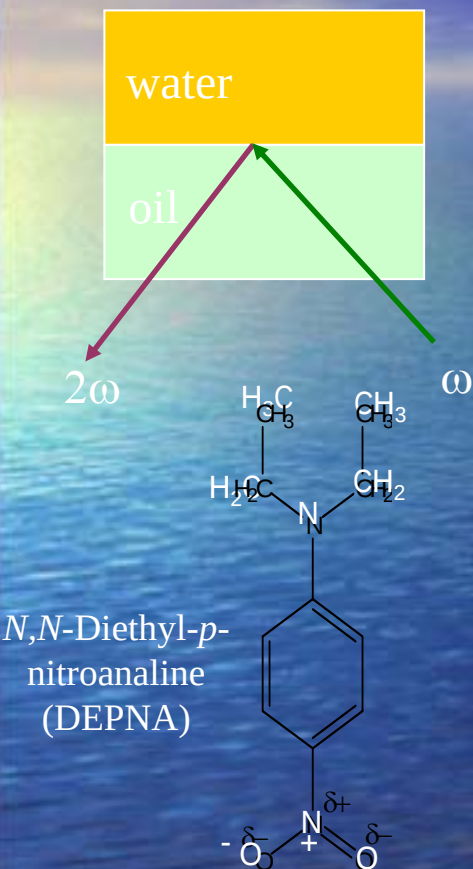


Aleksey M. Tikhonov, Harshit Patel, Shekhar Garde, and Mark L. Schlossman
J. Phys. Chem. B, **110** (39), 19093 -19096,
2006.

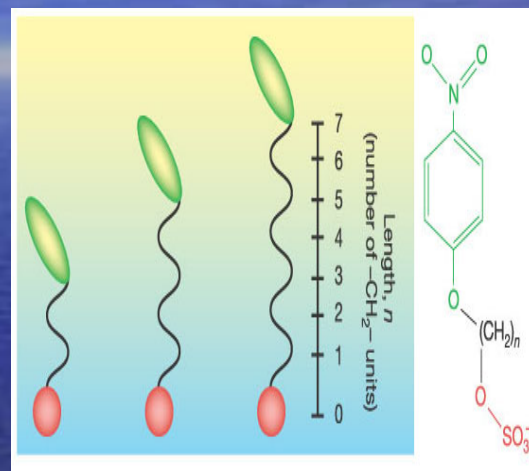
Recent Studies:

- Surfactant ordering at oil-water interfaces
- Ion distributions at liquid interfaces (ITIES)
- Temperature dependent structure of liquid-liquid interfaces

Second Harmonic Generation Development of an Interfacial Polarity Scale and Interfacial Width



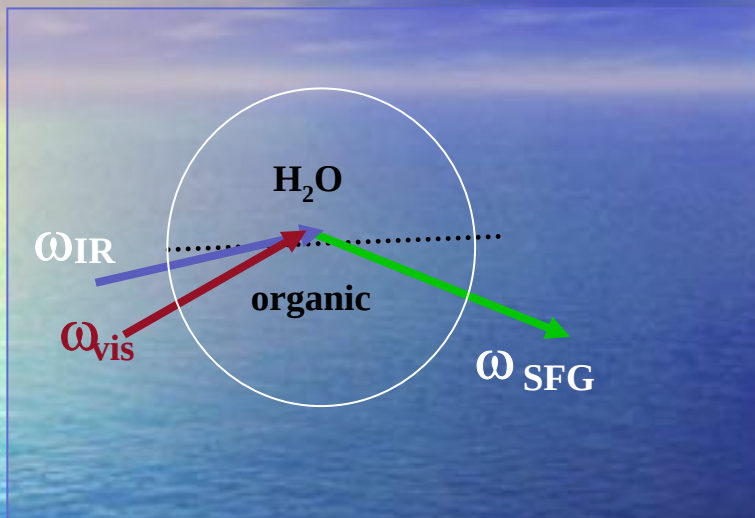
- Used polarity indicator molecules to study polarity of DCE/water and chlorobenzene/water interfaces



- Used *p*-nitro-anisole of different chain lengths to measure distance required to change solvent polarity

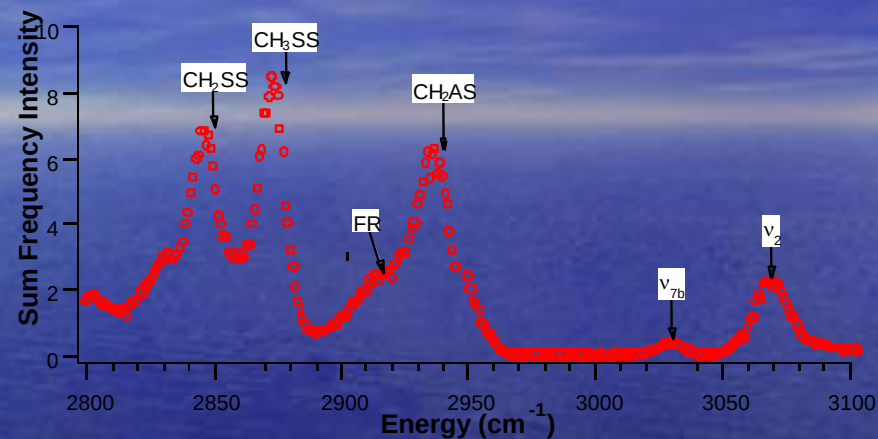
Surfactant Assembly at Oil/Water Interfaces

Vibrational Sum Frequency Spectroscopy

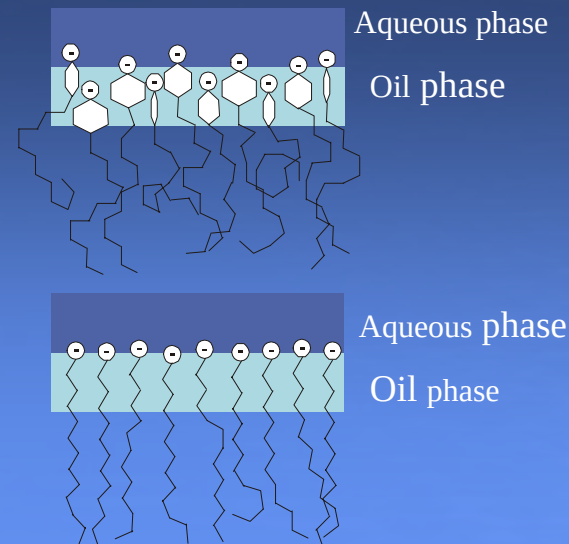


Conboy, Messmer, Richmond, *J. Am. Chem. Soc.*, 117 (8040) 1995.

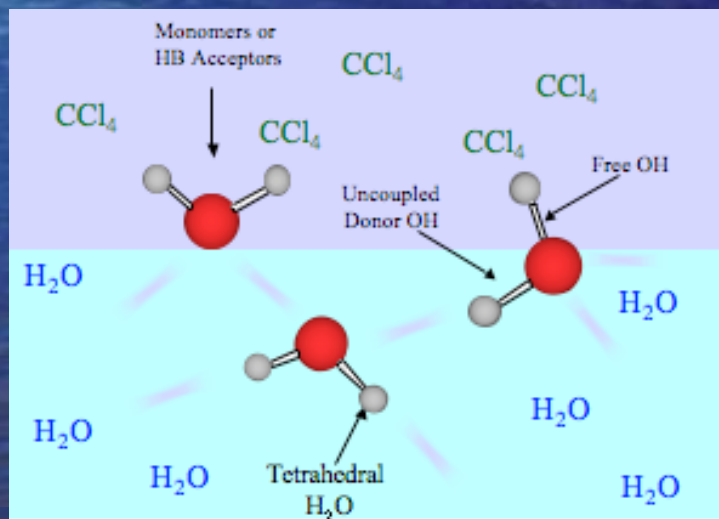
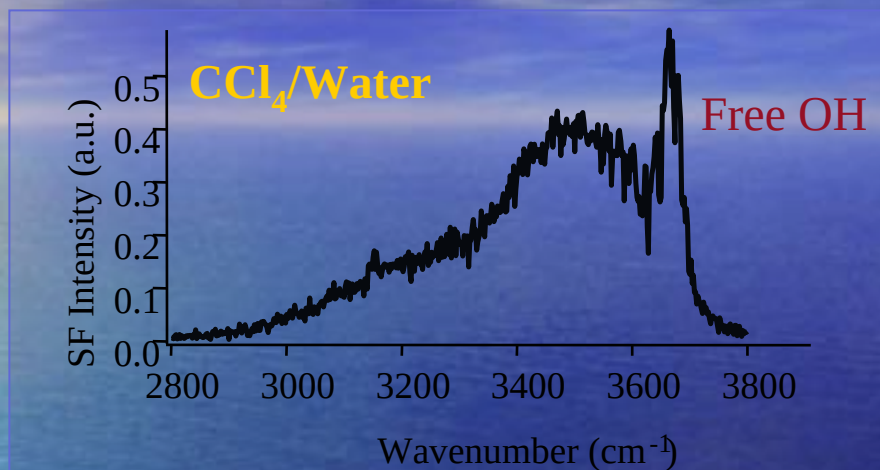
Knock, M. M.; Bell, G. R.; Hill, E. K.; Turner, H. J.; Bain, C. D. *J. Phys. Chem. B* **2003**, 107, 10801.



Comparison of LDS and DBS Order



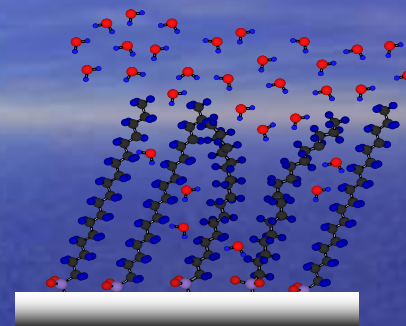
Spectroscopy of Interfacial Water



L.F. Scatena and G.L. Richmond,
Science, 292 (908-911) 2001.

Water-Organic Interactions

	Free OH	
Vapor/H ₂ O	3705 cm ⁻¹	(± 2)
F-Monolayer/SiO ₂	3694 cm ⁻¹	(± 3)
H-Monolayer/ SiO ₂	3674 cm ⁻¹	(± 2)
Hexane, Octane Nonane	3674 cm ⁻¹	(± 3)
CCl ₄ / H ₂ O	3669 cm ⁻¹	(± 2)
CDCl ₃ / H ₂ O	3650 cm ⁻¹	(± 3)

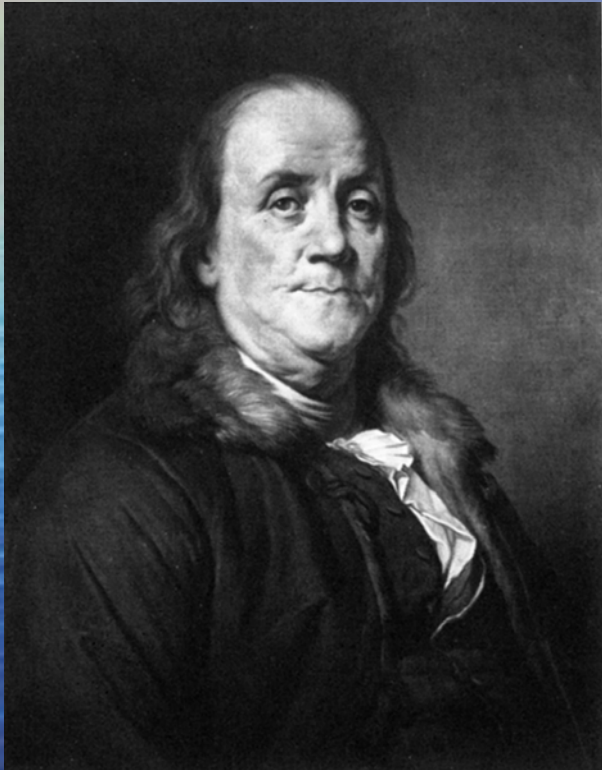


Monolayer/
water



Organic/water

Benjamin Franklin

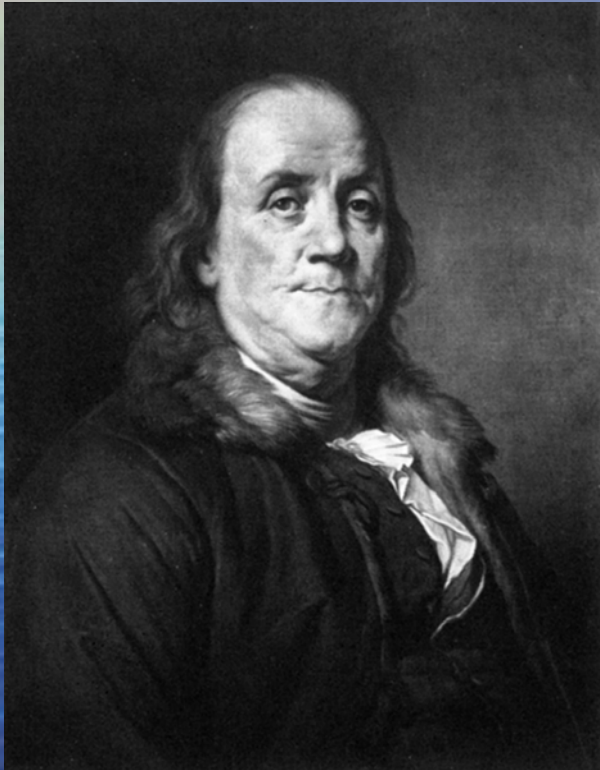


From stilling the raging seas...

to monolayers that are all the rage.

His legacy continues.

Benjamin Franklin



Ben Franklin Stilled the Waves by Charles Tanford

Thanks to:
Cathryn McFearin
Prof. Ralph Nuzzo