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

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

“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:

- 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

www.physik.uni-frankfurt.de/~jr/physpicold.html
Pioneering Surface Tension Measurements:

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

- 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.

Agnes Pockels
1862-1935

www.muenster.org/.../bedeut/inhalt/pockels.htm
Forming Monolayers on Water

- 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.

Irving Langmuir
1881 - 1957

“Langmuir” or “Pockels” trough?

http://www.ksvltltd.com/pix/keywords_html_58a73608.jpg
Langmuir Monolayers

1. Water

2. Polar headgroup (water seeking)
   - Hydrocarbon tail (oil or air seeking)

Gas phase
Liquid phase
Solid phase
Applications of Monolayer Technology:

- 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.

Katherine Blodgett

1898 - 1979

http://home.frognet.net/~ejcov/blodgett2.jpg
Langmuir-Blodgett Films

Monolayers on solid substrates
Extending Surface Measurements to Medicine:

- 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.

Evert Gorter
1881 - 1954
Early Physiological Applications:

- 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.

Charles Ernest Overton
1865-1933

http://www.unipublic.unizh.ch/magazin/gesundheit/2001/0366/
And the field has grown:

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

Harden M. McConnell, Arun Radhakrishnan
Biochimica et Biophysica Acta 1610 (2003) 159–173
Self Assembled Monolayers
Self-Assembled Monolayers


Self Assembled Monolayers

STM Modeling

Self-Assembled Monolayers

Controlling Wettability

Self-Assembled Monolayers

Changing Functional Groups

Surface Polarity

Low

High

Carboxylic acid group

Methyl group

Self-Assembled Monolayers

Reversible Hydrophobic/Hydrophilic Surfaces

Nature’s Examples

*Nelumbo nucifera*

*Stenocara sp.*

10 mm

Self-Assembled Monolayers

SAMs for Particle Wire Formation

Patterned Culture

Crystal growth on SAMS

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

**Poly(dimethylsiloxane)**

- Transparent
- Low (but finite) Thermal Expansion
- Chemically Inert
- Environmentally Safe
- Reusable for patterning
- Record Resolution: \(~30\) nm
What’s Next?

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.
Recent Studies:

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

Aleksey M. Tikhonov, Harshit Patel, Shekhar Garde, and Mark L. Schlossman

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 measured distance required to change solvent polarity


Surfactant Assembly at Oil/Water Interfaces

Vibrational Sum Frequency Spectroscopy


Spectroscopy of Interfacial Water

## Water-Organcic Interactions

<table>
<thead>
<tr>
<th></th>
<th>Free OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor/H$_2$O</td>
<td>3705 cm$^{-1}$ (± 2)</td>
</tr>
<tr>
<td>F-Monolayer/SiO$_2$</td>
<td>3694 cm$^{-1}$ (± 3)</td>
</tr>
<tr>
<td>H-Monolayer/ SiO$_2$</td>
<td>3674 cm$^{-1}$ (± 2)</td>
</tr>
<tr>
<td>Hexane, Octane</td>
<td>3674 cm$^{-1}$ (± 3)</td>
</tr>
<tr>
<td>Nonane</td>
<td></td>
</tr>
<tr>
<td>CCl$_4$/ H$_2$O</td>
<td>3669 cm$^{-1}$ (± 2)</td>
</tr>
<tr>
<td>CDCI$_3$/ H$_2$O</td>
<td>3650 cm$^{-1}$ (± 3)</td>
</tr>
</tbody>
</table>
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