

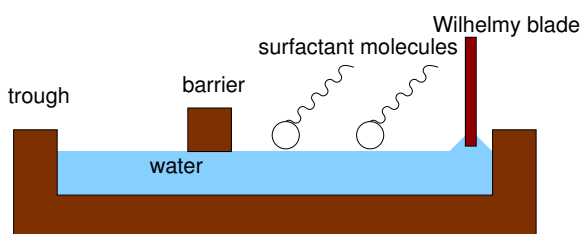
## MATRL 265 Class 3: Langmuir and Self-Assembled Monolayers

Franklin performed a number of experiments on the spreading of oil on water surfaces. Here is what Franklin writes (*Philos. Trans.* 64 (1774) 445-460) [Downloadable at [www.jstor.org](http://www.jstor.org)]: "I fetched out a cruet of oil, and dropt a little of it on the water. I saw it spread itself with surprising swiftness upon the surface; ... making all that quarter of the pond, perhaps half an acre, as smooth as a looking-glass"

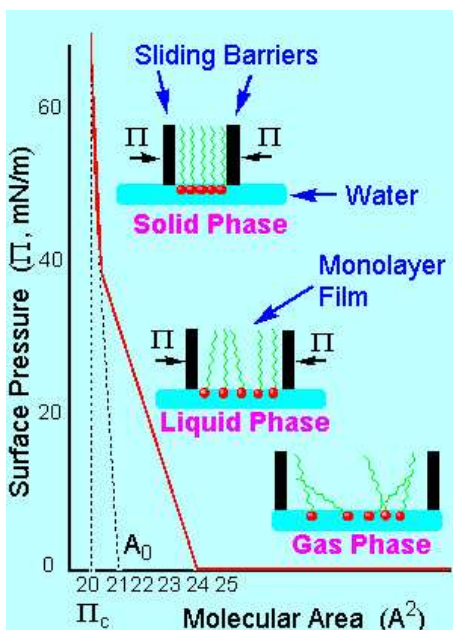
The first detailed experiments on the spreading of surfactants on the air-water interface were performed by Agnes Pockels (1862-1935), some of which were described in *Nature* 43 (1891) 437.

Today, the technique of spreading surfactants at the air-water interface is performed using a so-called Langmuir trough, and the films so-formed are called Langmuir monolayers.

**The modern Langmuir trough** is usually constructed from teflon, and a teflon barrier (often connected to a precise positioner) is used to compress the monolayer.



The surface tension of the compressed film is obtained using the force on the Wilhelmy blade. Isotherms of the surface tension  $\pi$  can be plotted against surface area per surfactant molecule, to obtain  $\pi - A$  isotherms that resemble the  $p - V$  isotherms of a real gas.

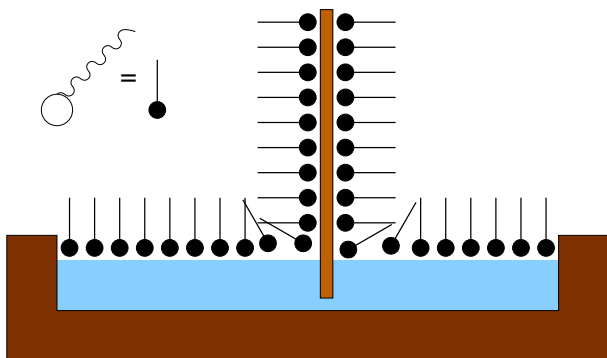


From the school of Chemistry at Tel-Aviv University: <http://www.tau.ac.il/physchem>

When each molecule (typically a long-chain carboxylic acid) has lots of area, the phase is gas-like. Compression converts this first into a liquid, and then a solid. Typically, surfactant molecules, when close-packed, occupy between 25 and 30 Å<sup>2</sup> of surface area. There are actually more phases than depicted here, and there can be coexistence of phases.

Some years ago, it was shown that one does not really require surfactants. Most insoluble molecules will close-pack. See *Nature* 367 (1994) 151-153 ([DOI](#)).

**Langmuir-Blodgett films** are formed when a solid substrate is dipped into a compressed monolayer at the air-water interface, and pulled out. There are a number of ways of doing this. L-B films are somewhat robust and can be used as substrates to do other things.



**Self-Assembled Monolayers** Please read the following articles:

1. D. K. Schwartz, Mechanisms and kinetics of self-assembled monolayer formation, *Annu. Rev. Phys. Chem.* **52** (2001) 107-137 ([DOI](#)).
2. A. Badia, R. B. Lennox, and L. Reven, A dynamic view of self-assembled monolayers, *Acc. Chem. Res.* **33** (2000) 475-481 ([DOI](#)).
3. G.-Y. Liu, S. Xu, and Y. Qian, Nanofabrication of self-assembled monolayers using scanning probe lithography, *Acc. Chem. Res.* **33** (2000) 457-466 ([DOI](#)).