

## Molecules at the air-water interface: The work of Franklin

At length being at CLAPHAM where there is, on the common, a large pond, which I observed to be one day very rough with the wind, I fetched out a cruet of oil, and dropt a little of it on the water. I saw it spread itself with surprizing swiftness upon the surface; but the effect of smoothing the waves was not produced; for I had applied it first on the leeward side of the pond, where the waves were largest, and the wind drove my oil back upon the shore. I then went to the windward side, where they began to form; and there the oil, though not more than a tea spoonful, 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.

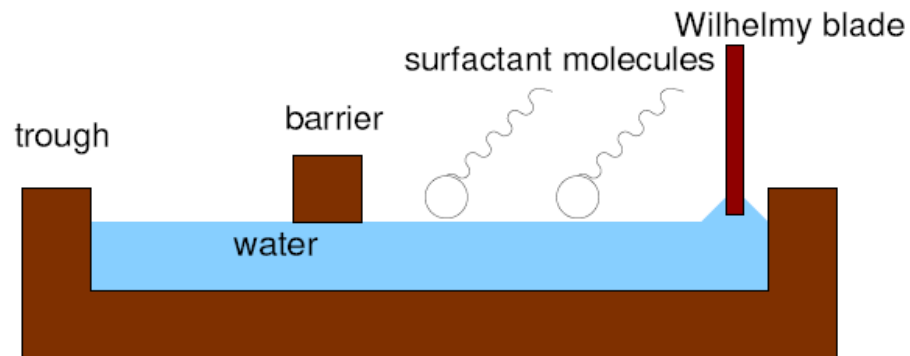
Here is what Franklin writes (*Philos. Trans.* 64 (1774) 445-460).

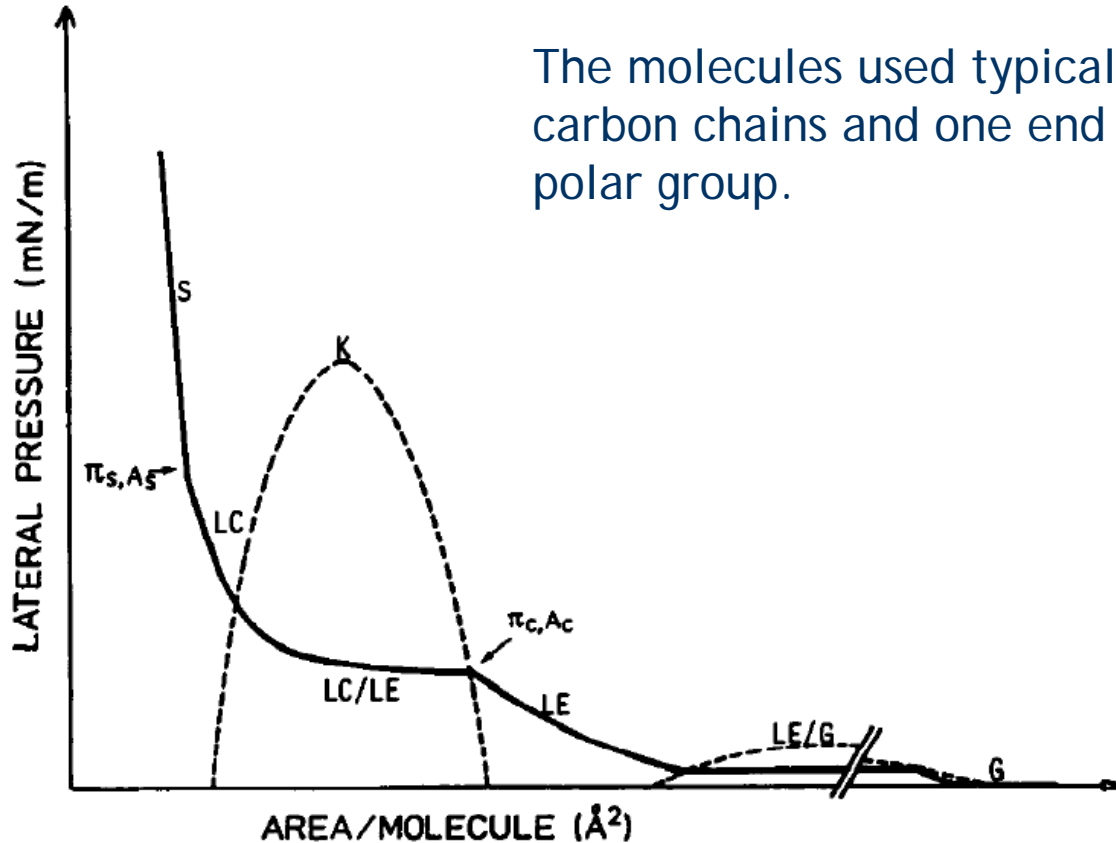
The experiment can be extended to estimate the typical sizes of molecules if one recognizes that the oil forms a monolayer, no thicker than one molecule.

## Molecules at the air-water interface: The work of Agnes Pockels

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.

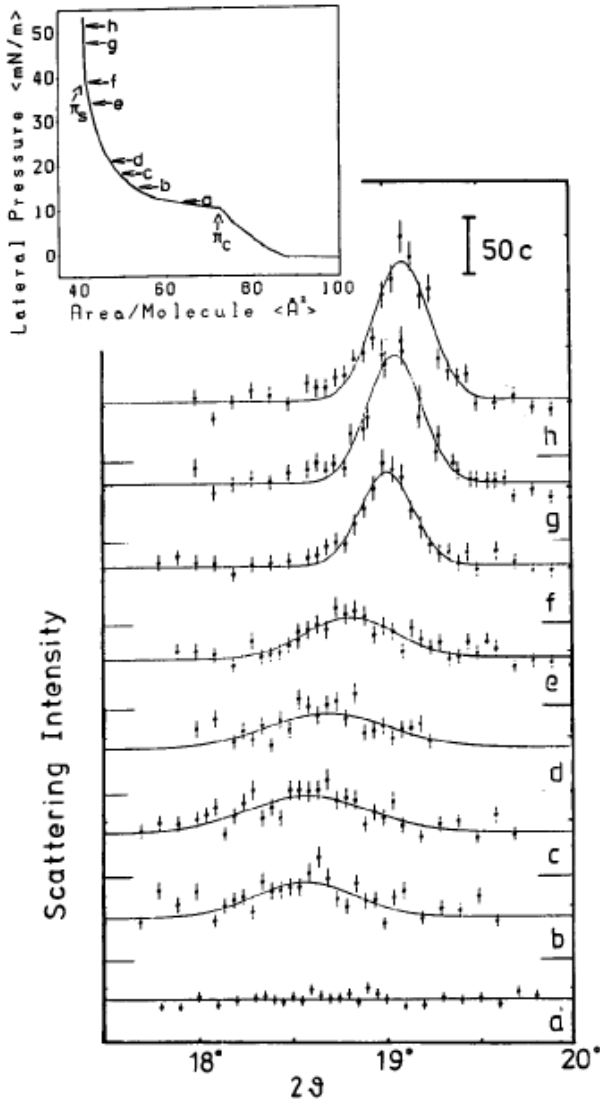


Molecules at the air-water interface:  $\pi$ -A isotherms

The molecules used typically have at least 12-18 carbon chains and one end of the molecules have a polar group.

Figure 3 Monolayer phases going along an isotherm. The dashed lines mark coexistence ranges of the LE and gaseous (G) phases and of the LE and LC phases.

Molecules at the air-water interface:  $\pi$ -A isotherms



X-ray reflectivity studies allow the separations of the molecules within the monolayer to be monitored as a function of the area per molecule.

## Molecules at the air-water interface: Non-amphiphiles and excluded volume interactions

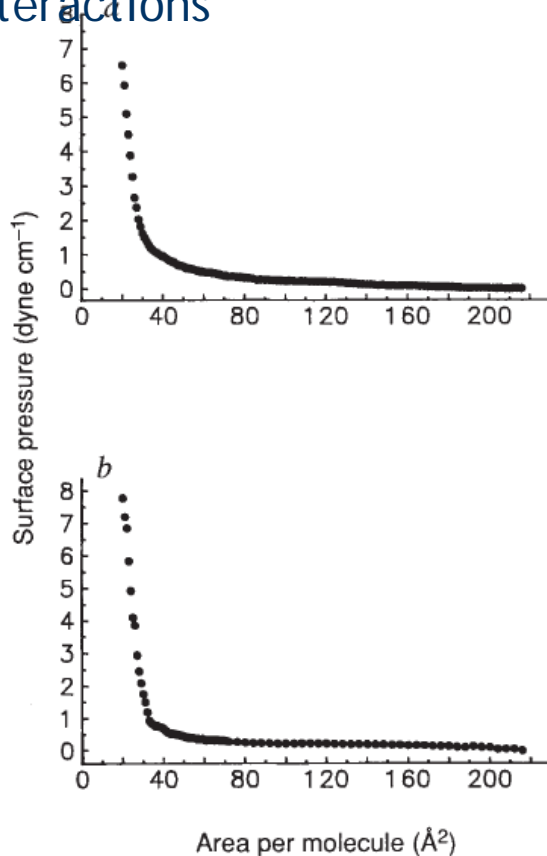


FIG. 1 Isotherms of the perfluoro-*n*-eicosane monolayer on water at 4 °C (a) and 20 °C (b). The surface pressure was measured with a precision of  $\pm 0.05$  dyne  $\text{cm}^{-1}$  and an accuracy of  $\pm 0.5$  dyne  $\text{cm}^{-1}$ . The rate of monolayer compression varied along the isotherm to allow for surface pressure relaxation; the compression rate used was everywhere  $< 2 \text{ \AA}^2 \text{ min}^{-1}$  per molecule.

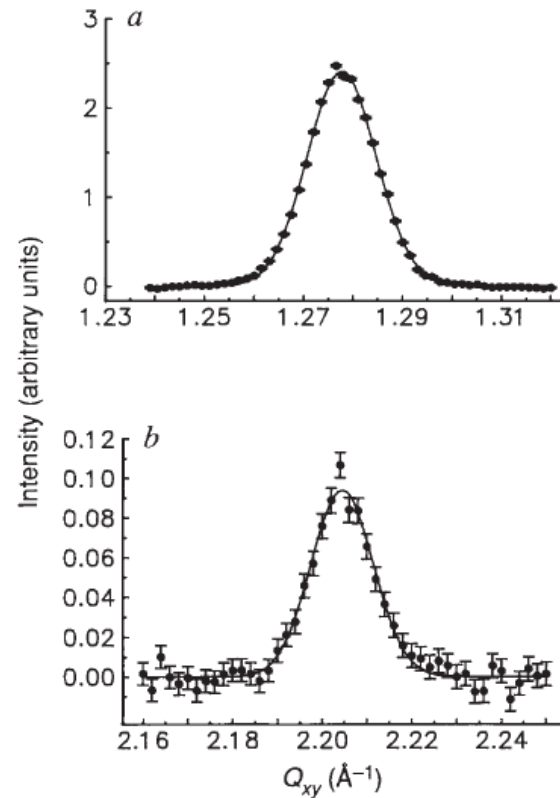


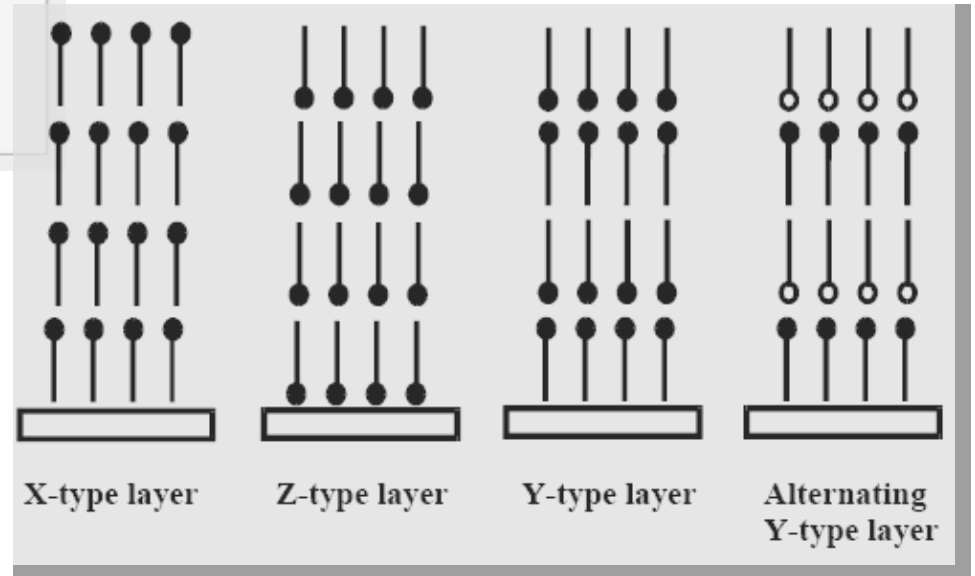
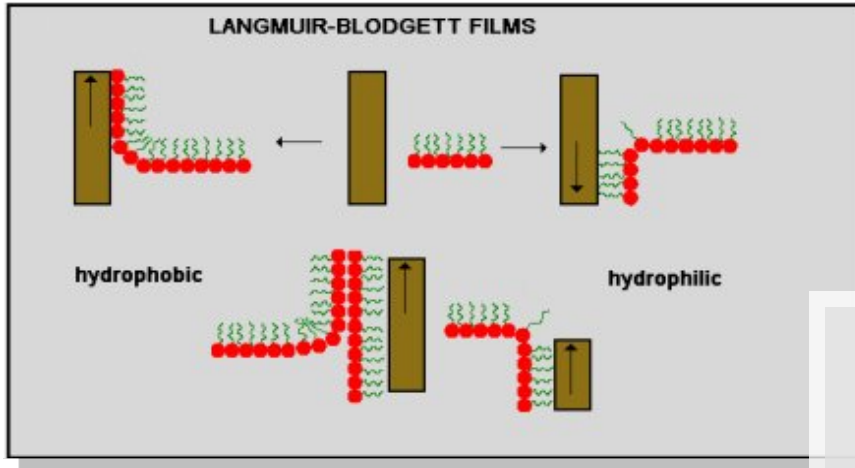
FIG. 2 In-plane diffraction peaks (near  $Q_z=0$ ) of the perfluoro-*n*-eicosane monolayer at 25 °C on water at a reciprocal surface density of  $42.7 \text{ \AA}^2$  per molecule. The dots with statistical error-bars represent the experimental data. The lines are gaussian fits to the experimental data. a, First-order diffraction peak. b, Second-order diffraction peak. ( $Q_{xy} = (Q_x^2 + Q_y^2)^{0.5}$  is the magnitude of the in-plane momentum transfer).

Perfluoro-*n*-eicosane

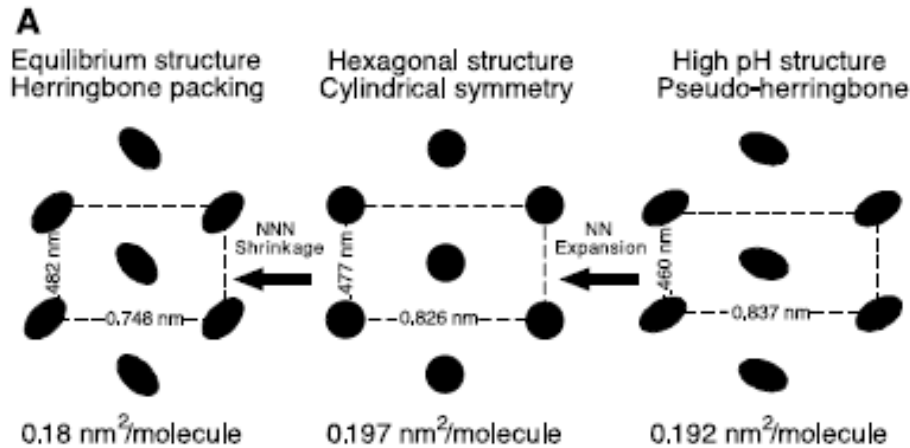
Formation of an ordered Langmuir monolayer by a non-polar chain molecule, Li, Acero, Huang & Rice, *Nature* 367 (1994) 151.

# Ultrathin Organic Films

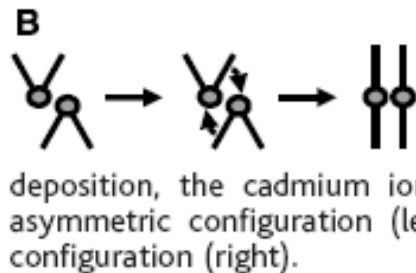
Langmuir-Blodgett films: Monolayers are transferred from the air-water interface on to a solid substrate.



Langmuir-Blodgett films: Monolayers are transferred from the air-water interface on to a solid substrate. Cadmium arachidate at different pH:



**Fig. 2. (A)** The three lattice structures of cadmium arachidate. The hexagonal structure is that present at the air-water interface at pH 7 and in monolayers deposited from pH 7. The equilibrium structure is present in three-dimensional crystals of cadmium arachidate and in multilayer Langmuir-Blodgett films deposited from pH 7 subphases. The high pH structure is present at the air-



water interface at pH >8.5 and has a different orientational ordering of the alkane chains. For this structure to transform into the equilibrium structure, the lattice must expand in the NN direction and go through the hexagonal packing. (B) Whenever a headgroup-headgroup (shaded circles) interface is formed during

## Stable Ordering in Langmuir-Blodgett Films

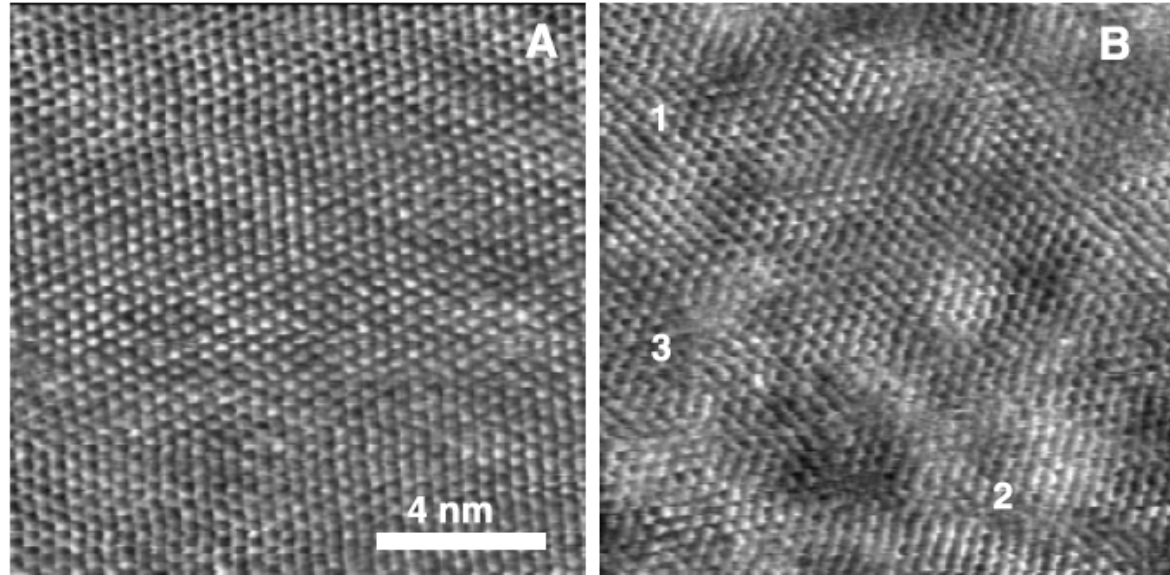
Dawn Y. Takamoto, *et al.*

*Science* **293**, 1292 (2001);

DOI: 10.1126/science.1060018

Langmuir-Blodgett films: Monolayers are transferred from the air-water interface on to a solid substrate.

**Fig. 4.** Molecular-resolution AFM images (14 nm by 14 nm) of five-layer CdA<sub>2</sub> films on silicon. (A) Film deposited at pH 7 shows only one crystal grain with measured lattice parameters,  $d_{02} = 0.375 \pm 0.004$  nm and  $d_{11} = 0.406 \pm 0.004$  nm, consistent with the herringbone structure (Fig. 2A). AFM and electron diffraction



show that the typical grain size at pH 7 is of order 10 to 100  $\mu\text{m}$ . (B) Film deposited at pH 8.8 shows numerous small crystallites. The nanocrystal labeled 1 has the herringbone packing, with measured  $d_{02} = 0.375$  nm and  $d_{11} = 0.406$  nm (12). The nanocrystal labeled 2 is hexagonal, with  $d$  spacings of 0.411, 0.416, and 0.412 nm, which compare well to the expected  $d_{02} = d_{11} = 0.41$  nm for the hexagonal phase (12). Nanocrystal 3 has measured  $d_{02} = 0.391$  nm and  $d_{11} = 0.415$  nm (5, 6). The error in the measured  $d$  spacing is the small size of the nanocrystals.

## Stable Ordering in Langmuir-Blodgett Films

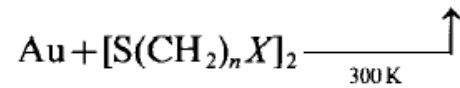
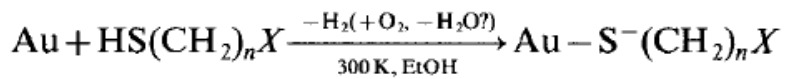
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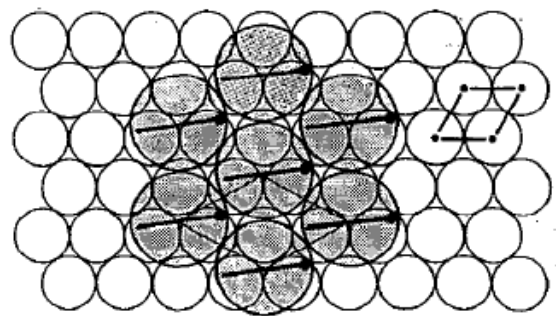
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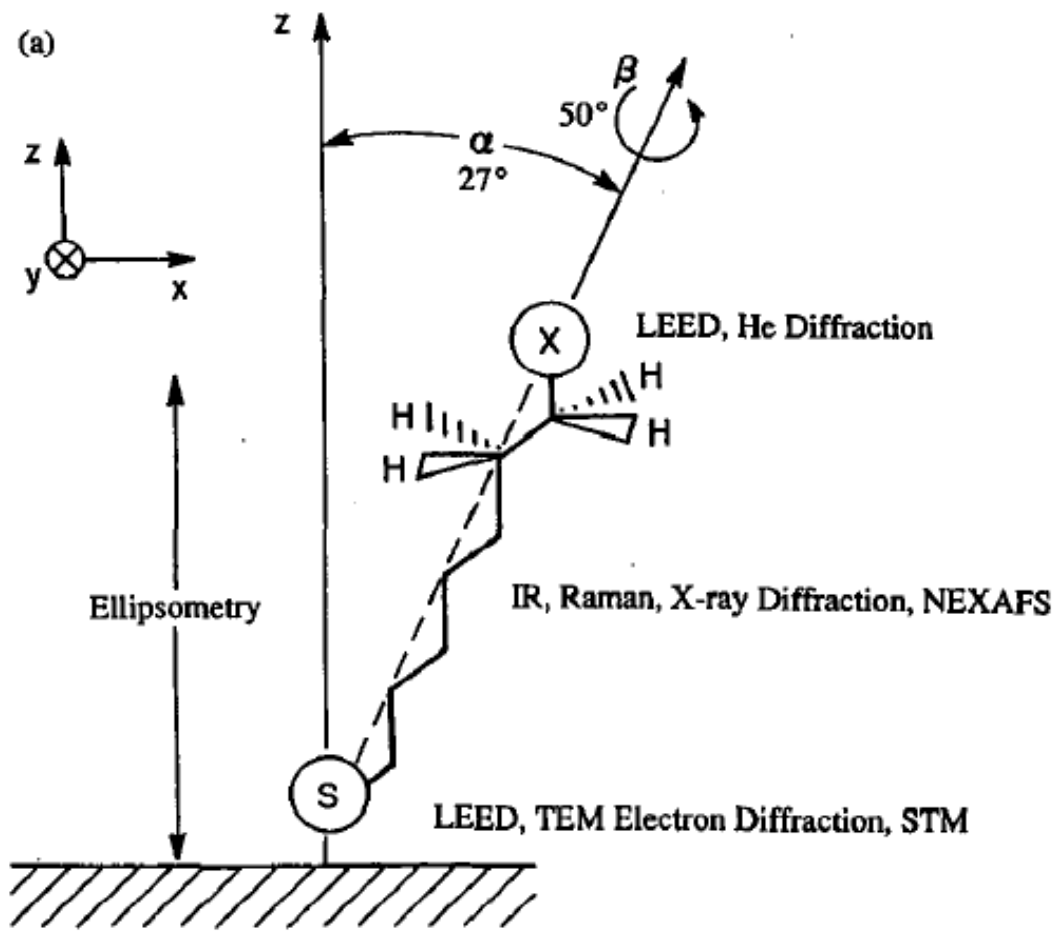
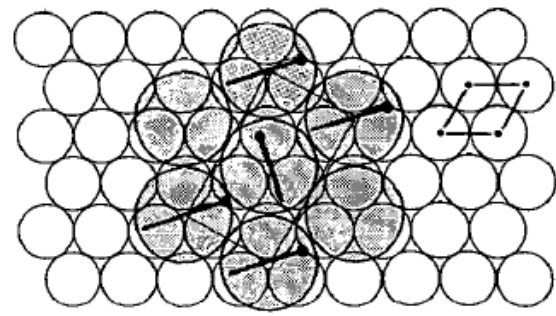
Self-assembled monolayers: Thiols on gold



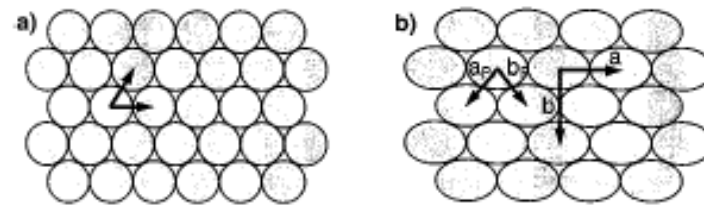
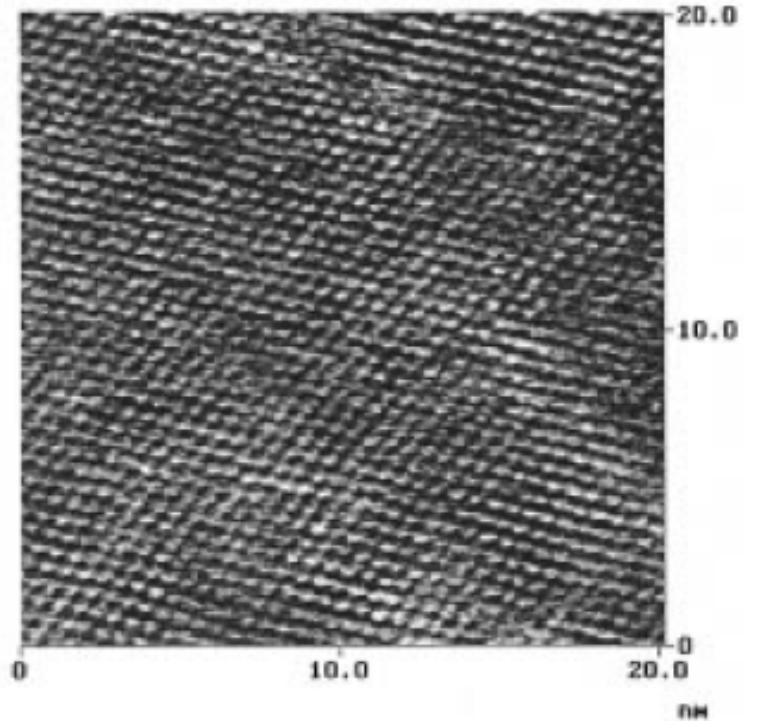
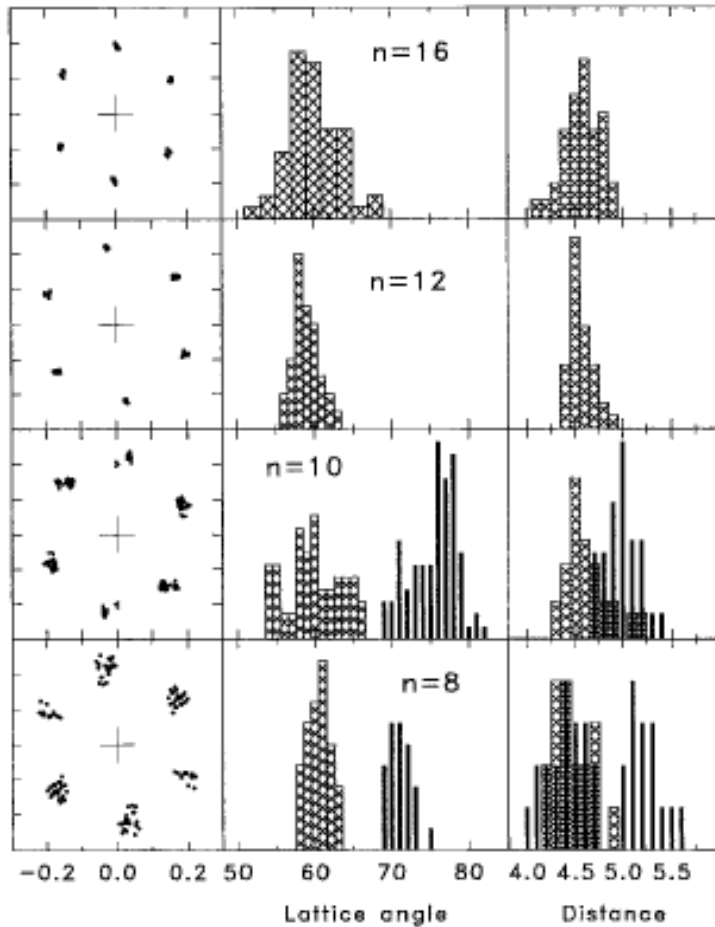
(a)  $(\sqrt{3} \times \sqrt{3})R30^\circ$



(b)  $(\sqrt{3} \times 2\sqrt{3})R30^\circ$



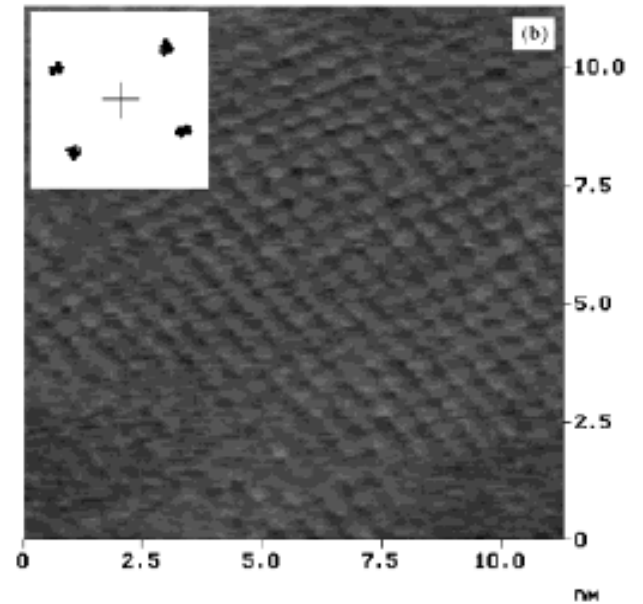
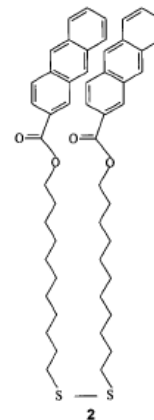
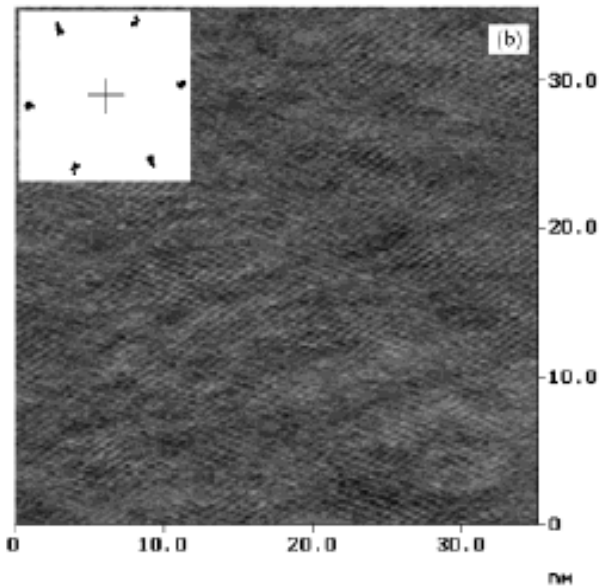
Self-assembled monolayers: Thiols on gold



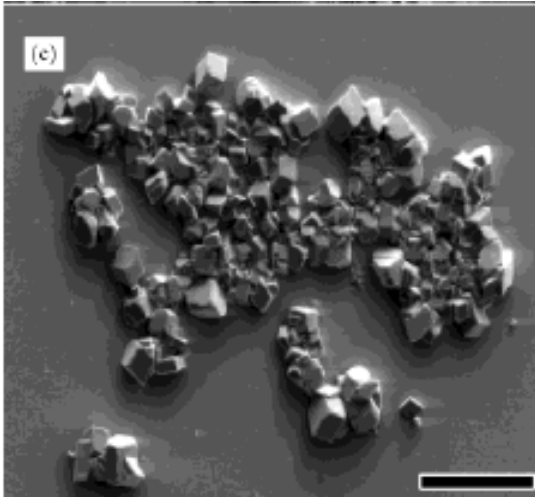
Self-assembled monolayers:

Also carboxylic acids on many metal surfaces, amines ...

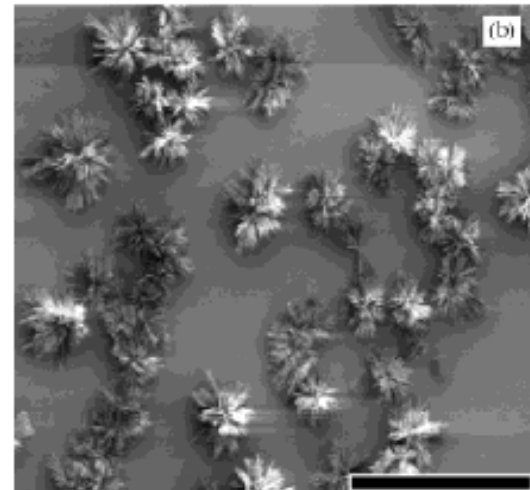
Self-assembled monolayers: templating growth of crystals



Self-assembled monolayers: templating growth of crystals



Calcite on the hexagonal monolayer



Aragonite on the hexagonal monolayer