Langmuir Films

or

Insoluble Monolayers at the Air Water Interface

Benjamin Franklin   -   1706 -1790

*From a letter to William Brownrigg 1773*

Dear Sir: I thank you for the remarks of your learned friend at Carlisle. I had, when a youth, read and smiled at Pliny's account of a practice among the seamen of his time, to still the waves in a storm by pouring oil into the sea; which he mentions as well as the use made of oil by the divers; but the stilling a tempest by throwing vinegar into the air had escaped me. I think with your friend that it has been of late too much the mode to slight the learning of the ancients. The learned, too, are apt to slight too much the knowledge of the vulgar. The cooling by evaporation was long an instance of the latter. The art of smoothing the waves by oil is an instance of both. ….

Recounting to the Royal Society an Experiment on Clapham Common (London), 1774

"At length being at Clapham, where there is on the common a large pond which I observed one day to be very rough with the wind, 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; 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 greatest; 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 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."

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Triolein (main component of olive oil)
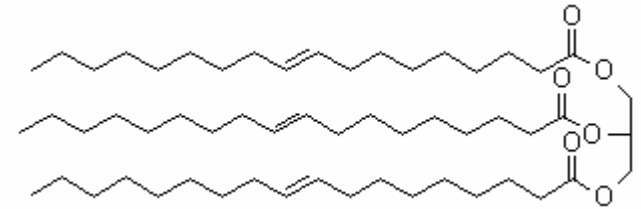
1 teaspoon has a volume ~ 5 ml   = 5 cm^3 = 5×10^{-6} m^3
1/2 acre ~ 2×10^3 m^2

Assuming once it spread it retains the same total volume, V= Area * Thickness

Then its final thickness = 5×10^{-6} m^3 / 2×10^3 m^2 = 2.5×10^{-9} m = 2.5 nm

Why did the molecules spread on the surface – and not dissolve ?

What is the implication of the final film thickness?

Why did Franklin not draw this conclusion?

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1862-1935

1842-1919

Agnes Pockels

John William Strutt (Lord Rayleigh)

I shall be obliged if you can find space for the accompanying translation of an interesting letter which I have received from a German lady, who with very homely appliances has arrived at valuable results respecting the behaviour of contaminated water surfaces. The earlier part of Miss Pockel's letter covers nearly the same ground as some of my own recent work, and in the main harmonizes with it. The later sections seem to me very suggestive, raising, if they do not fully answer, many important questions. I hope soon to find opportunity for repeating some of Miss Pockels' experiments. --- RAYLEIGH, March 2. *Nature* 1891

Surface Film Balance – introduced by Pockels

A rectangular tin trough, 70 cm. long, 5 cm. wide, 2 cm. high, is filled with water to the brim, and a strip of tin about 1.5 cm. laid across it perpendicular to its length, so that the underside of the strip is in contact with the surface of the water, and divides it into two halves. By shifting this partition to the right or the left, the surface on either side can be lengthened or shortened in any proportion, and the amount of the displacement may be read off on a scale held along the front of the trough.


Rayleigh –repeated Franklins experiment and concluded that the films were only a single molecule thick

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Langmuir 1881-1957

Nobel Prize 1932 - start of "surface chemistry" and it was for his efforts in this area that he became the first non-academic chemist to receive the Nobel Prize.

Along with **Dr. Katherine Burr Blodgett (1898 - 1979)** he studied thin films and how substances are adsorbed on surfaces.
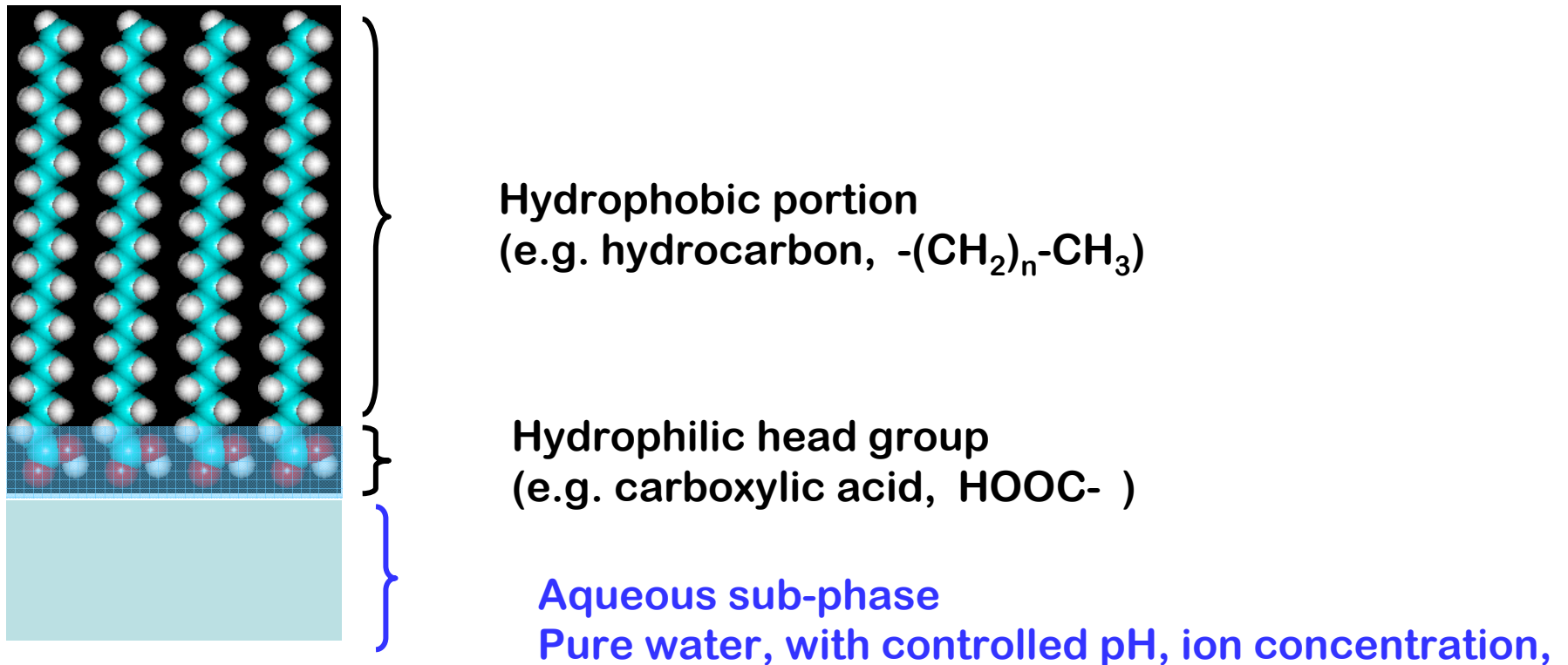
Their studies led to clarification of the true nature of surface adsorption and established the existence of **monolayers**.
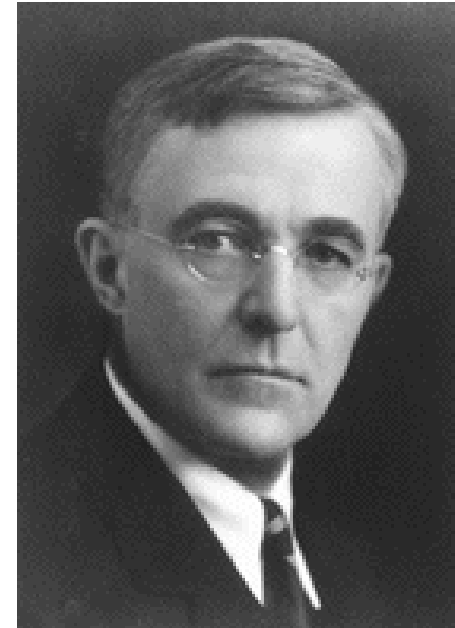
Langmuir demonstrated that long chain fatty acid molecules displayed the same area per molecules irrespective of the number of carbon atoms (~ 20 $Å^2$) – from such observations he deduced that the films were monolayer thick, and were oriented at the water surface with their polar head groups in the water and the hydrocarbon chains nearly normal to the surface.

Langmuir Film (Monolayer)

Amphiphilic molecules – contain both hydrophobic (water hating) and hydrophilic (water loving) portions

**Hydrophobic portion
(e.g. hydrocarbon, $-(CH_2)_n-CH_3$)**

**Hydrophilic head group
(e.g. carboxylic acid, HOOC-)**

**Aqueous sub-phase
Pure water, with controlled pH, ion concentration,**

The hydrophobic part must be large enough to make the molecule insoluble in the sub-phase whilst the hydrophilic head-group must have sufficient attraction to the water to keep the molecules anchored at the interface – and prevent thick film build-up.

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To spread a film at the air-water interface

The molecules are usually dissolved in a small amount of volatile solvent (eg hexane, chloroform,..) –with a positive spreading coefficient.

A few drops are placed at the air-water interface – this expands rapidly spreading the amphiphiles across the surface.

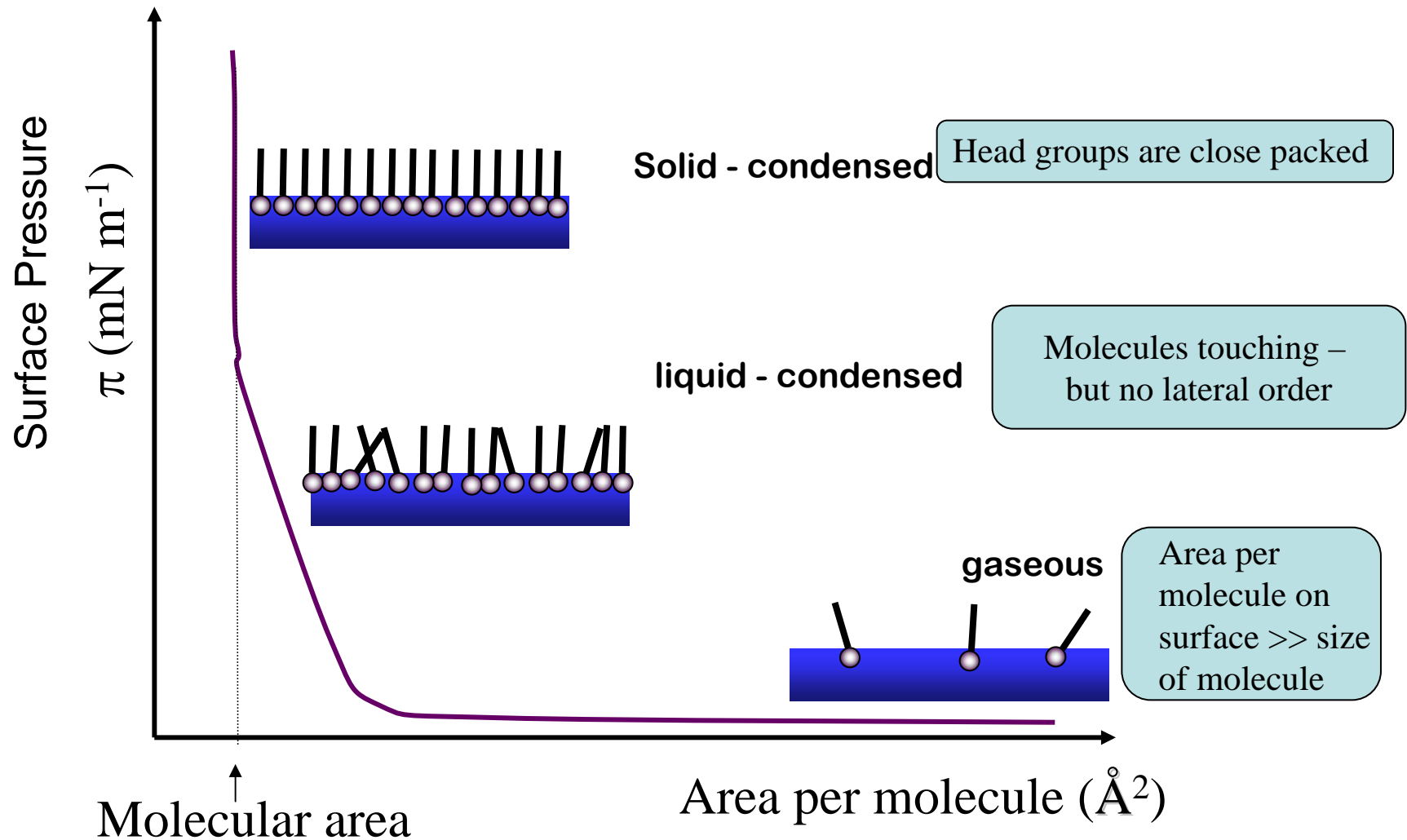The solvent evaporates – leaving the monolayer

Compression of the monolayer

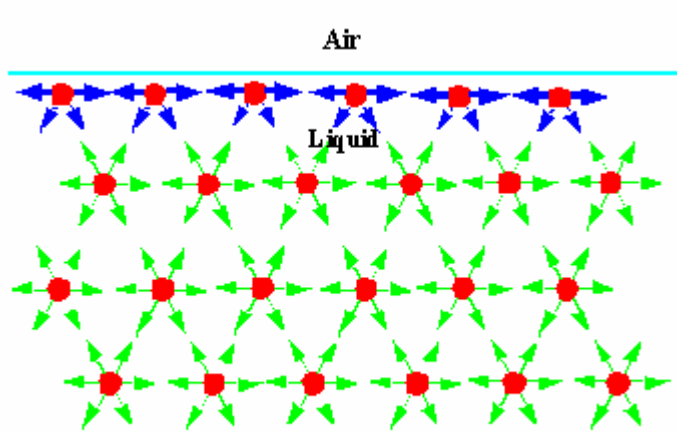The monolayer is gradually compressed using the movable barrier - to reduce the area available per molecule.

Movable barrier
Wilhelmy plate
Monolayer

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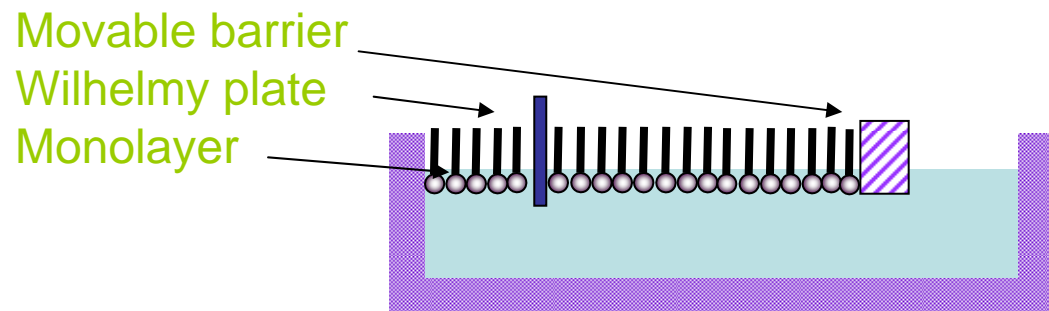
Surface Pressure vs. Area Isotherms

Displays 2-D analogues of gaseous, liquid and solid phases

Surface Pressure π (mN m^{-1})

Solid - condensed

Head groups are close packed

liquid - condensed

Molecules touching – but no lateral order

gaseous

Area per molecule on surface >> size of molecule

Area per molecule (Å^2)

Molecular area

Surface Tension & Surface Pressure

Molecules at interfaces –
Cohesive interaction stronger at surface.

Surface tension of water is 72.8 mNm^{-1} (dynes/cm)

E.g. water hoppers, floating needles,

Surfactants act to decrease surface tension.

The surface pressure, π, is defined as the difference between the surface tension of the bare subphase, γ_o, and the surface tension of the subphase covered by amphiphiles, γ.

$$\pi = \gamma_o - \gamma$$

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Wilhelmy Plate Method

At equilibrium
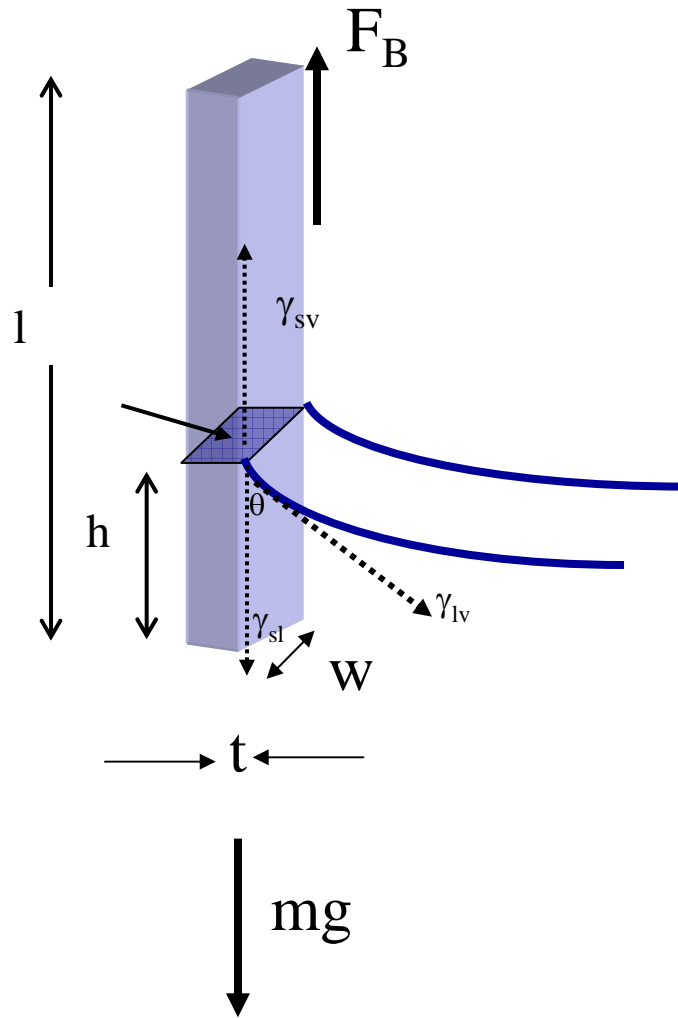
A thin plate (perimeter about 40 mm) is lowered to the surface of a liquid and the downward force directed to the plate is measured.

Surface tension is directly the force divided by the perimeter of the plate.

A couple of very important points

1. The plate must be completely wetted before the measurement to ensure that the contact angle between the plate and the liquid is zero.

2. The position of the plate must be correct, meaning that the lower end of the plate is exactly on the same level than the surface of the liquid. Otherwise the buoyancy effect must be calculated separately.

If we consider the forces acting on the plate

$$F = F_G + \gamma_{lv} \cos \theta \cdot P - F_B$$

Net force = gravity + surface tension - buoyancy
term   term   term

$$= mg + \gamma_{lv} \cos \theta \cdot P - m_l g$$

m= mass of plate
m_l = mass of fluid displaced
P= perimeter of plate

$$F = \rho_p . l . w . t . g + \gamma_{lv} \cos \theta .2(t + w) - \rho_l . h . w . t . g$$

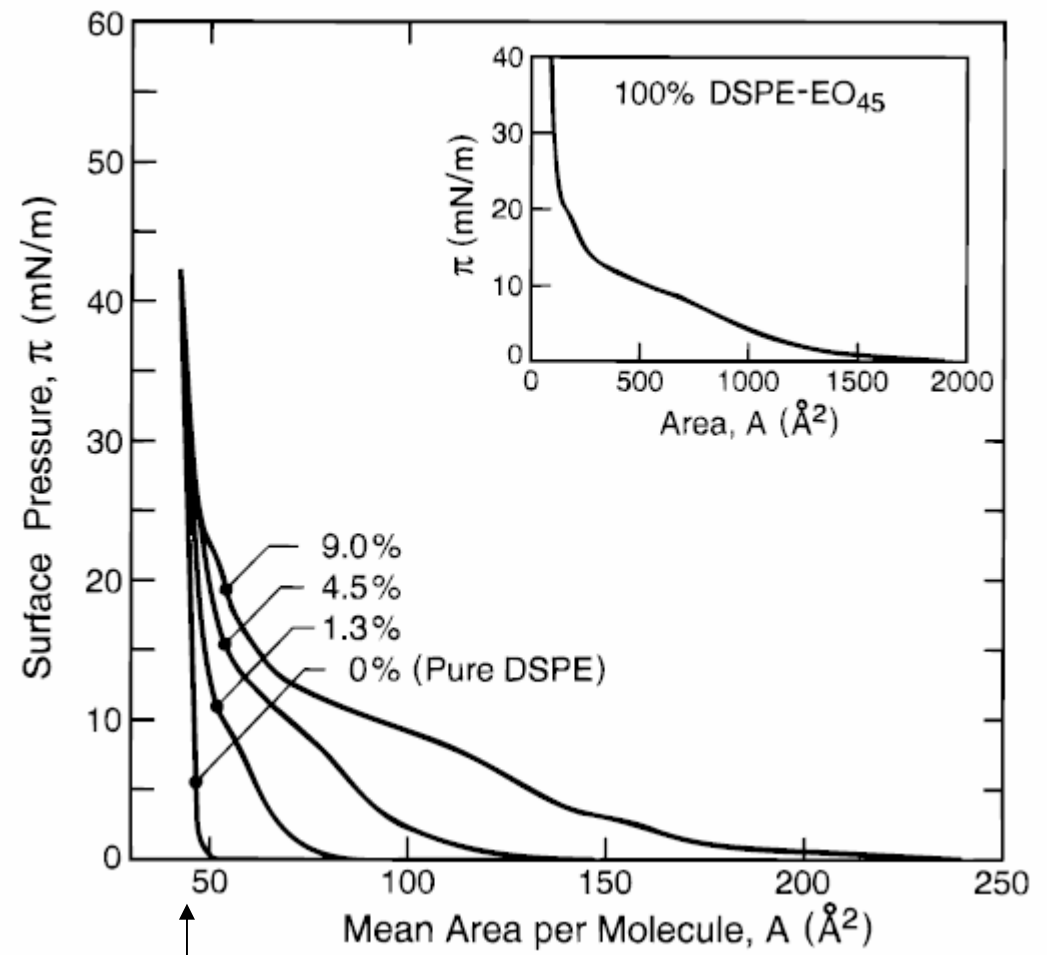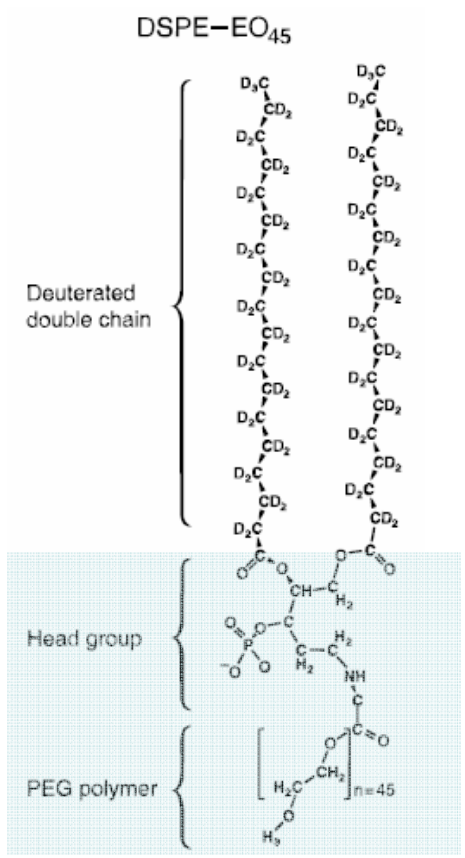If plate completely wetted then $\theta = 0$.

$$\frac{dF}{d\gamma} = 2(t + w)$$

Differentiate w.r.t γ 1st and last terms
are constant and hence drop out

$$\Delta\gamma = \frac{\Delta F}{2(t + w)} \approx \frac{\Delta F}{2w}$$

Re-arrange, and let t + w -> w

$$\pi = -\Delta\gamma = -\left(\frac{\Delta F}{2w} \right)$$

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Example – phospholipid behaviour - with attached poylmer

DSPE−EO45

Deuterated double chain

Head group

PEG polymer

100% DSPE-EO45

9.0%
4.5%
1.3%
0% (Pure DSPE)

DSPE

PEG

Water
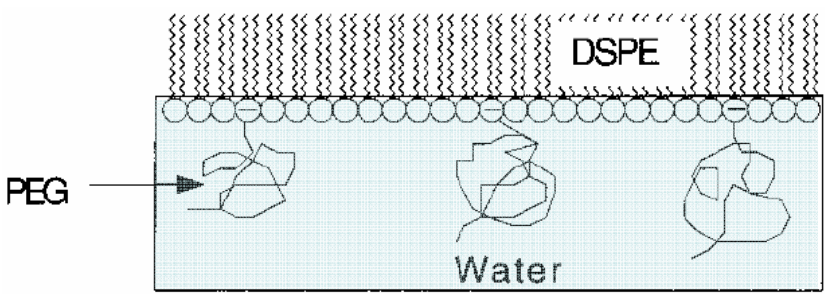
Nb area per molecule ~ 2x that for standard alkyl chain (because there are to chains per molecule)

Israelachvili et al

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Experimental Techniques for Investigating Monolayers

Surface Potential
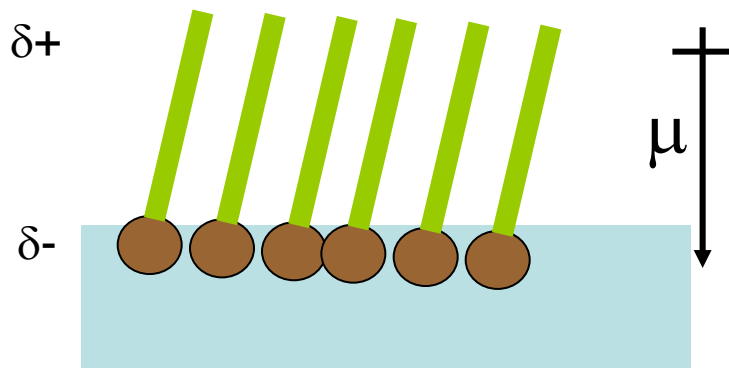
The molecules forming the monolayer are generally polar, i.e. have a net dipole moment, μ. When aligned at the surface they give rise to a double layer of charge – and a net potential called the Volta potential.

$\delta+$

μ

$\delta-$

The change in the Volta potential between the clean water surface and the monolayer coated surface is called the surface potential, ΔV.

$$\Delta V = \frac{\mu}{A \varepsilon \varepsilon_0}$$

Where A is the area per molecule

Measuring the surface potential can provide information on:
Molecular orientation and the net dipole per molecule

Surface potential is measured in one of two ways –
i)   Vibrating probe (Kelvin Probe) method
ii) Ionizing electrode method

Question: write a paragraph with figure outlining each of these methods

X-Ray Reflectivity and Diffraction
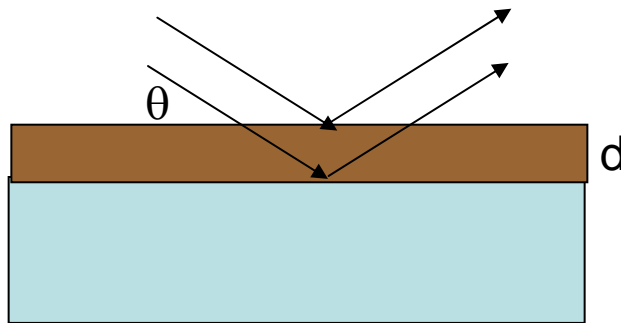
X-rays interact with electrons in a material
Reflectivity curves as function of angle –
gives series of maxima whenever

$$n\lambda = 2\, d \sin \theta$$

Good for determining film thickness
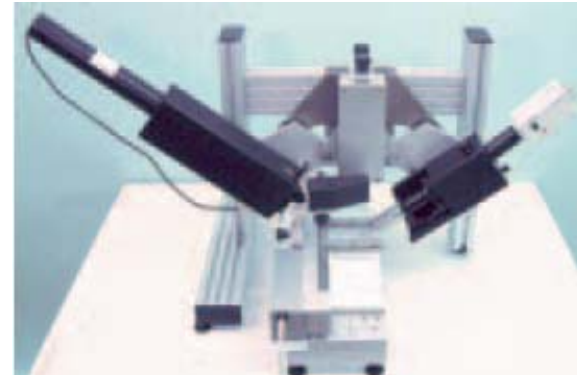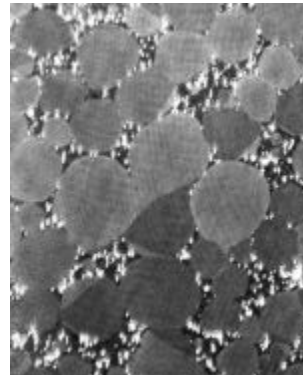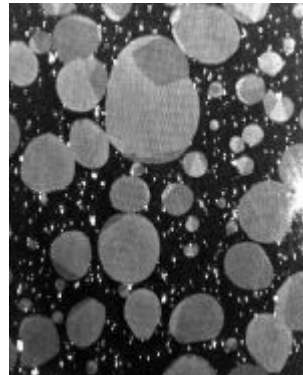
Diffraction – gives information re in-plane order
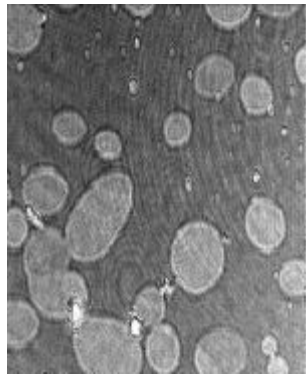
14

Brewster Angle Microscopy
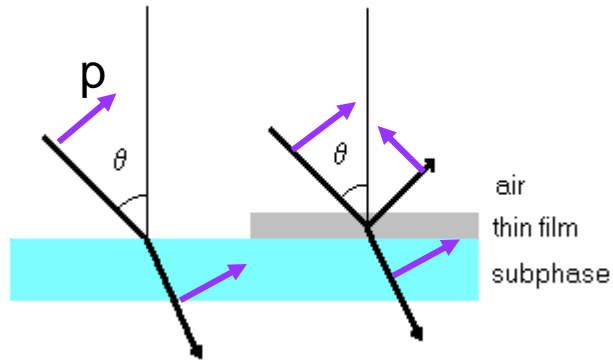
P-polarised light
Clean surface - no reflection at θ_B
Thin film – change in reflection

Images differences in film thickness /composition

Langmuir-Blodgett Films

Langmuir-Blodgett (LB) Films

Katharine Burr Blodgett

1898 - 1979

Langmuir-Blodgett (LB) films ordered molecular assemblies formed by the transfer of molecules from the air-water interface onto solid supports.

1. Spread material.

2. Compressed film to desired surface pressure.

3. Maintain a constant surface pressure while moving a solid support through the interface.

$$\textbf{Deposition Ratio} = \frac{\text{decrease in surface area of trough}}{\text{area of sample moved through interface}}$$
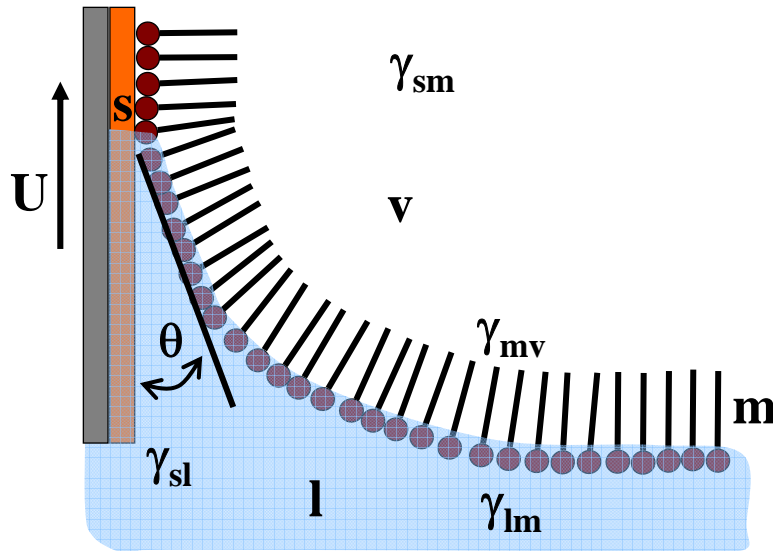
Deposition dependent on:

pH of subphase
temperature
Deposition speed, U.

(contact angle)

γ_{sm}
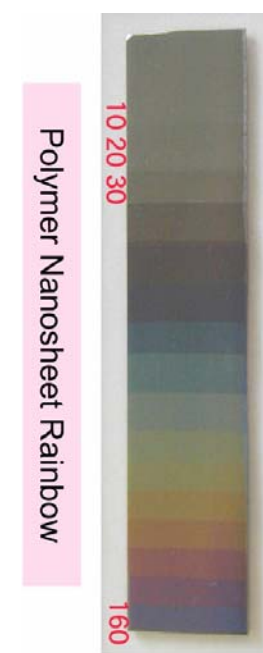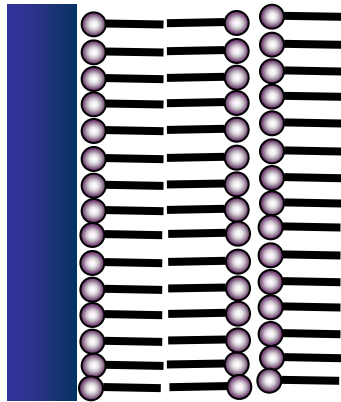
γ_{mv}

γ_{sl}

γ_{lm}

U

s

v

m

l

θ

LB Trough

tensiometer

barrier

sample

Polymer Nanosheet Rainbow

10 20 30

160

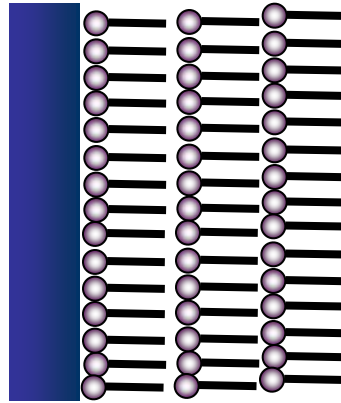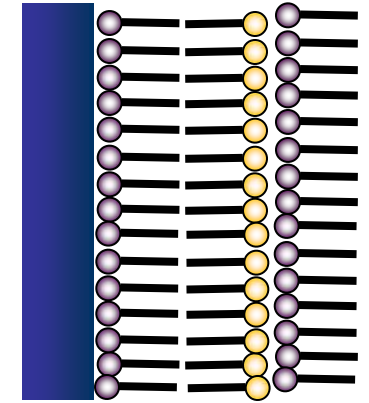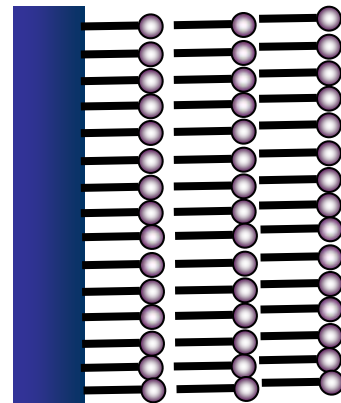# Multilayers

Y-type   X- and Z- type   Super lattices

Centro-symmetric or non-centro symmetric structures

Control at molecular level (20Å)

Insulators, semiconductors, (conductors?)

Applications include: non-linear optics, gas sensing, nanotechnology

Advantages

- Centro-symmetric or non-centro symmetric structures

- Control at molecular level (20Å)

- Insulators, semiconductors, conductors

- Applications include: non-linear optics, gas sensing, nanotechnology

Disadvantages

- Slow to fabricate thick films – drying time required after each layer

- Mechanical and Chemical stability poor

- Requires clean room

Hybrid silicon–organic nanoparticle memory device

S. Kolliopoulou, P. Dimitrakis, and P. Normand
Institute of Microelectronics, NCSR Demokritos, 15310 Aghia Paraskevi, Greece

Hao-Li Zhang, Nicola Cant, and Stephen D. Evans
Department of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, United Kingdom

S. Paul, C. Pearson, A. Molloy, and M. C. Petty
Centre for Molecular and Nanoscale Electronics, University of Durham, Durham DH1 3LE, United Kingdom

D. Tsoukalas[a]
Institute of Microelectronics, NCSR Demokritos, 15310 Aghia Paraskevi and Department of Applied Sciences, National Technical University of Athens, 15780 Zografou, Greece
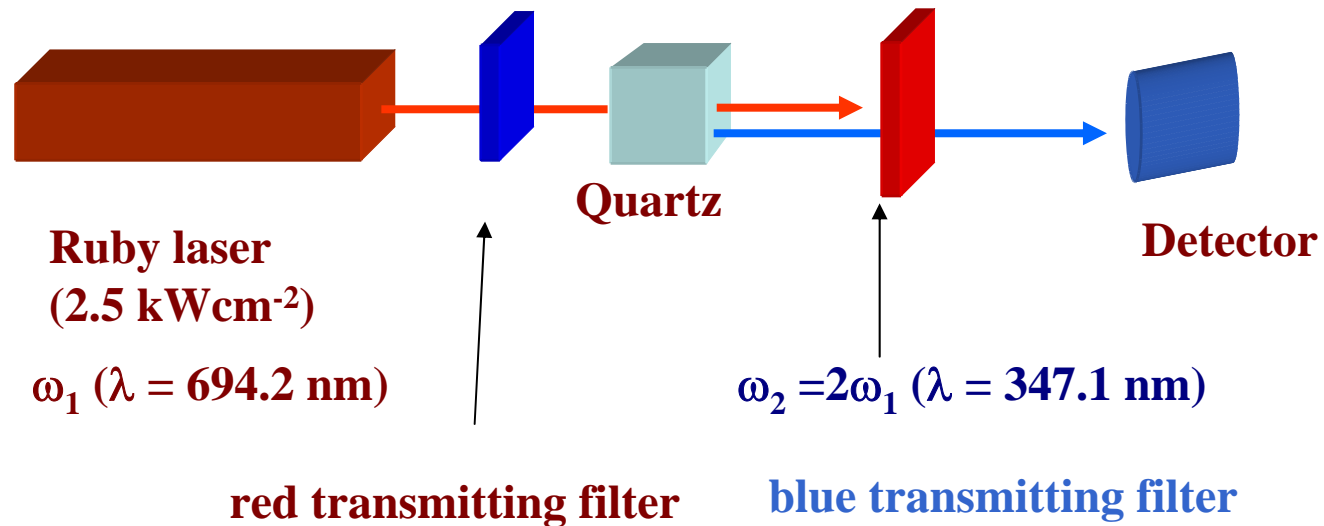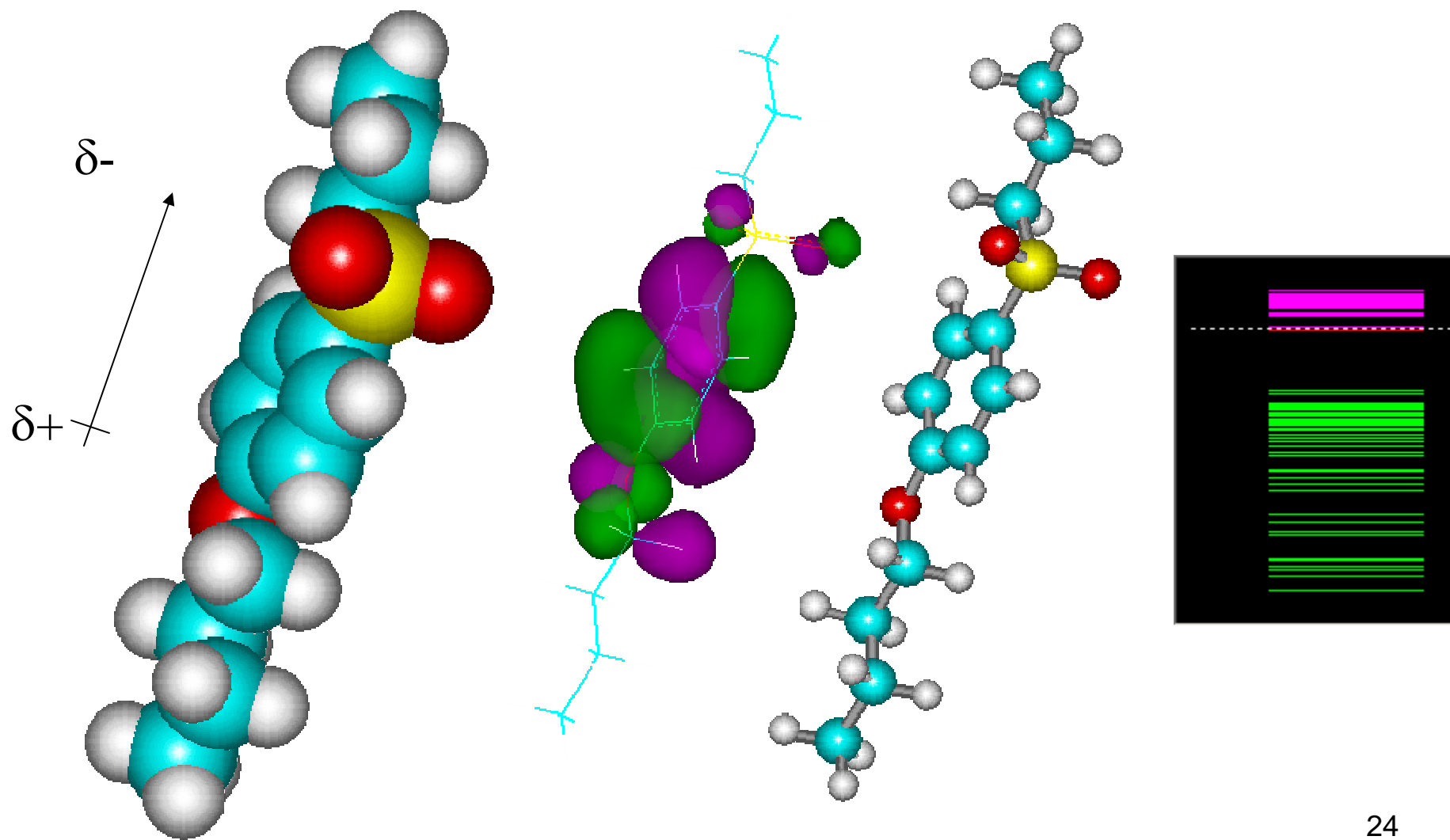
22
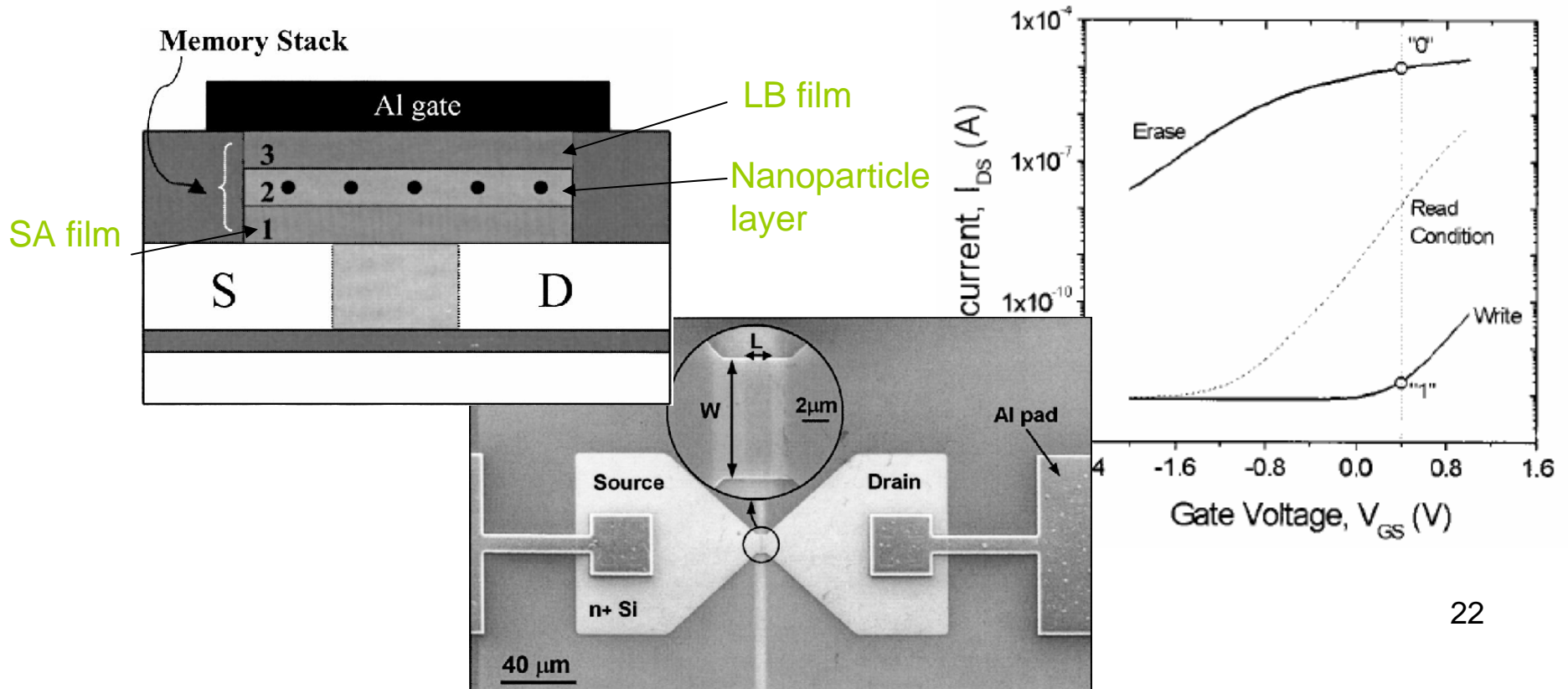
Nonlinear Optics

Franken's Experiment (The Birth of Nonlinear Optics)

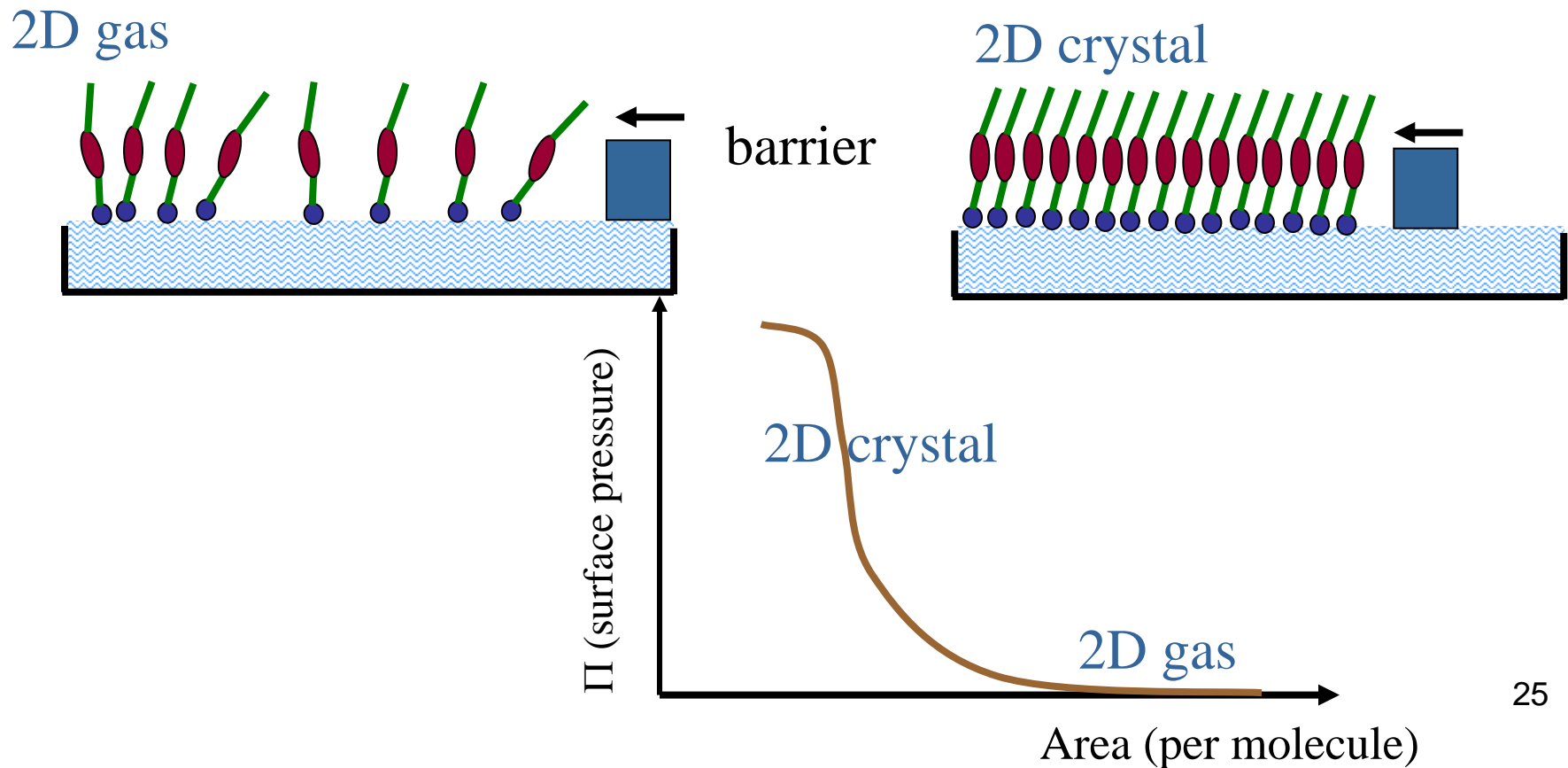P.A. Franken, A. H. Hill, C.W. Peters, G. Weinreich

Phys. Rev. Lett. 7, 118, 1961

Quartz

Detector

Ruby laser
(2.5 kWcm^{-2})

ω_1 ($\lambda = 694.2$ nm)

$\omega_2 = 2\omega_1$ ($\lambda = 347.1$ nm)

red transmitting filter

blue transmitting filter
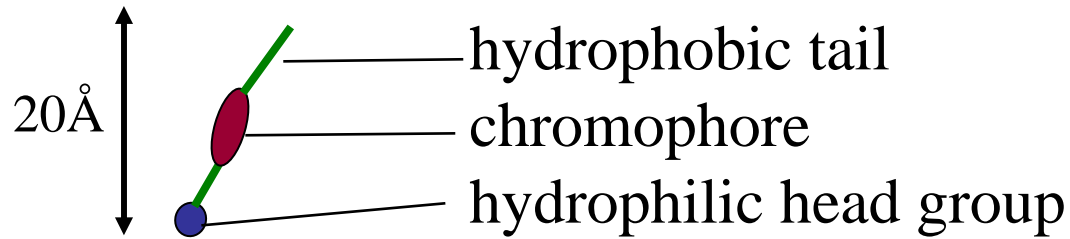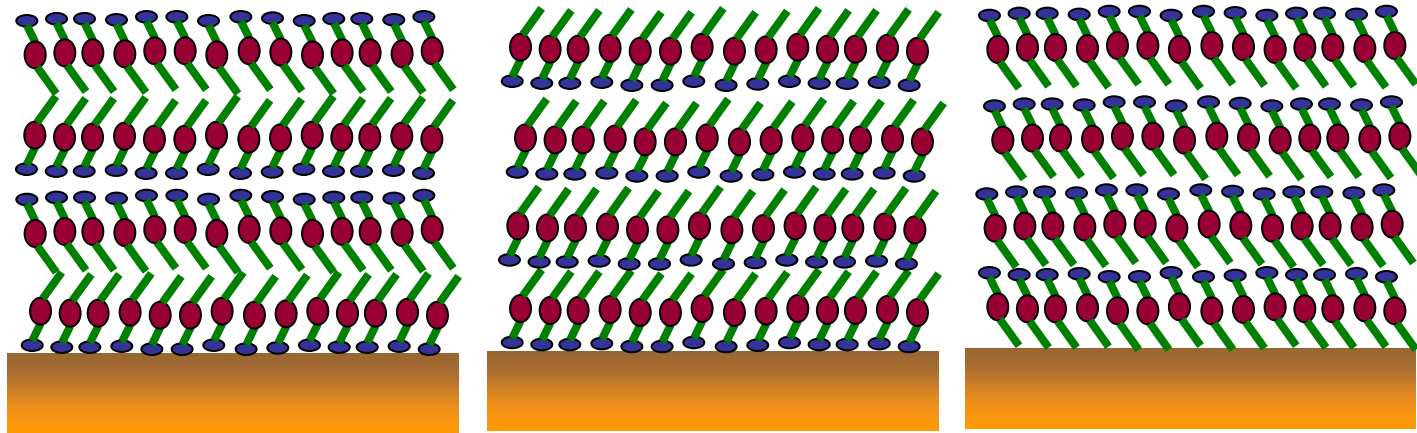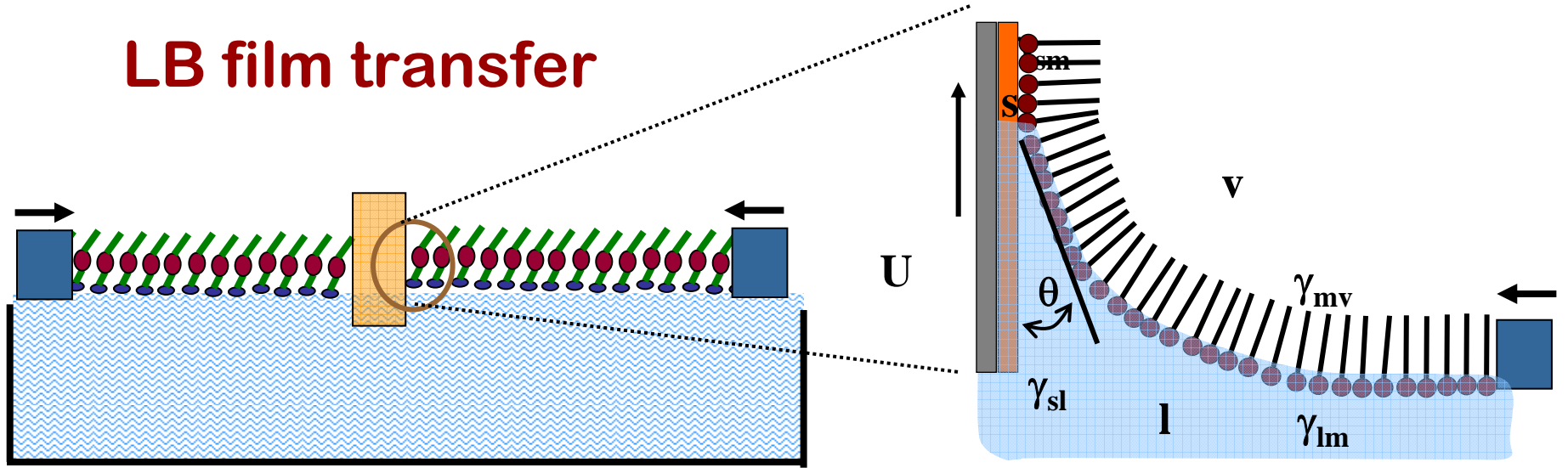
Typically, have molecules with conjugated (delocalised) electronic systems coupled donor-acceptor groups (to provide a highly polarised 1st excited state.

$\delta-$

$\delta+$

Langmuir-Blodgett (LB) Films

20Å — hydrophobic tail, chromophore, hydrophilic head group

2D gas — barrier — 2D crystal

Π (surface pressure) vs Area (per molecule): 2D crystal, 2D gas

LB film transfer

U

γ_{sm}
s
θ
γ_{mv}
v
γ_{sl}
l
γ_{lm}

Y-type

(X- and Z- type)

Virtue

Franklin sought to cultivate his character by a plan of thirteen virtues, which he developed at age 20 (in 1726) and continued to practice in some form for the rest of his life. His autobiography (see references below) lists his thirteen virtues as:

"TEMPERANCE. Eat not to dullness; drink not to elevation."
"SILENCE. Speak not but what may benefit others or yourself; avoid trifling conversation."
"ORDER. Let all your things have their places; let each part of your business have its time."
"RESOLUTION. Resolve to perform what you ought; perform without fail what you resolve."
"FRUGALITY. Make no expense but to do good to others or yourself; i.e., waste nothing."
"INDUSTRY. Lose no time; be always employ'd in something useful; cut off all unnecessary actions."
"SINCERITY. Use no hurtful deceit; think innocently and justly, and, if you speak, speak accordingly."
"JUSTICE. Wrong none by doing injuries, or omitting the benefits that are your duty."
"MODERATION. Avoid extremes; forbear resenting injuries so much as you think they deserve."
"CLEANLINESS. Tolerate no uncleanliness in body, cloaths, or habitation."
"TRANQUILLITY. Be not disturbed at trifles, or at accidents common or unavoidable."
"CHASTITY. Rarely use venery but for health or offspring, never to dullness, weakness, or the injury of your own or another's peace or reputation."
"HUMILITY. Imitate Jesus and Socrates."