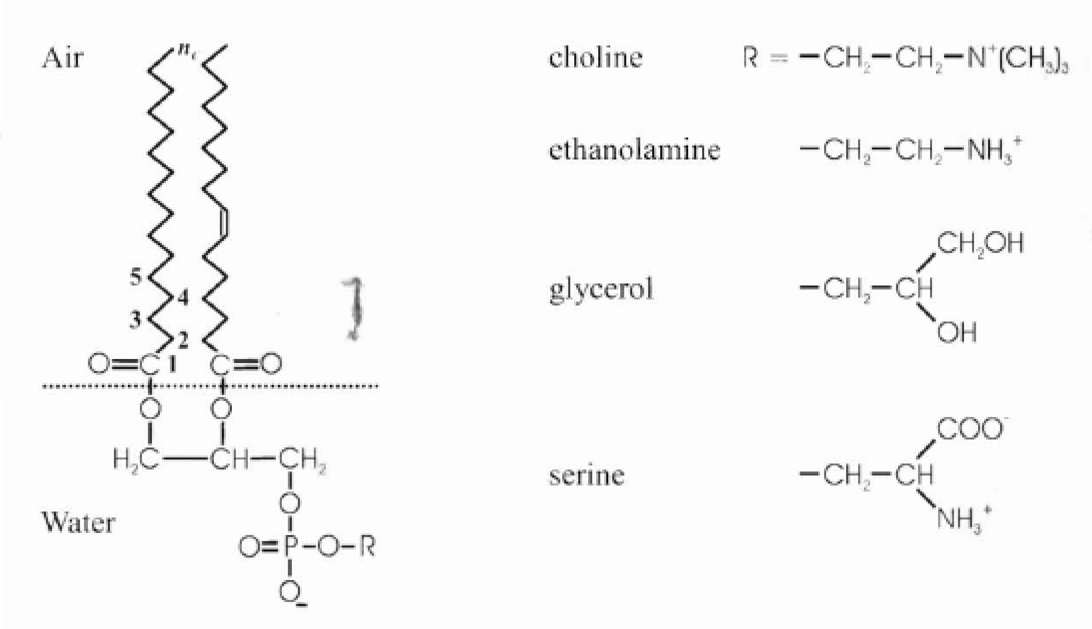
Lecture 4

Langmuir-Blodgett films. II.
Donnan Potential

Floating monolayers

- Generally, amphiphilic molecules adsorb on the liquid-air interface
- Insoluble amphiphiles can create a solid monolayer on a liquid surface

n_C	Prefix	Common abbreviation
12	Dilauroyl-	DLPC / DLPE
14	Dimyristoyl-	DMPC / DMPE
16	Dipalmitoyl-	DPPC / DPPE
18	Distearoyl-	DSPC / DSPE



Structure of a phospholipid

Formation of floating monolayer

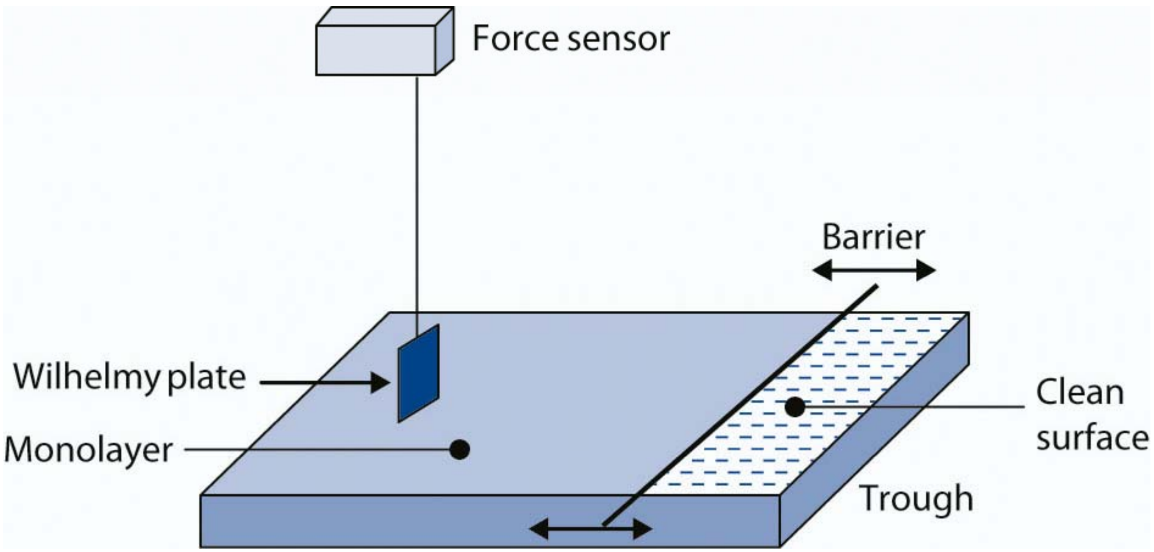
- monolayer can be spread in 2 ways:
  - depositing droplet of a pure substance on the surface, that spreads till equilibrium spreading pressure is reached
  - depositing substance in a volatile solvent with positive spreading pressure

- surface pressure

$$\Pi = \gamma_w - \gamma_f$$

- area per molecule

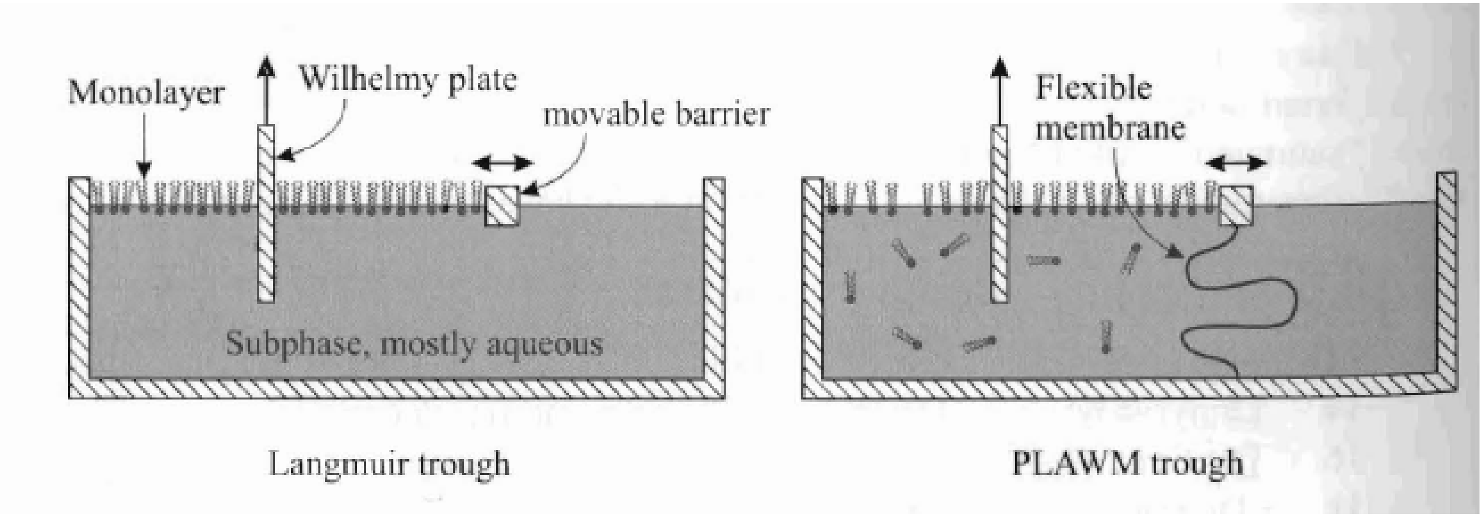
$$\sigma_A = A / N_M$$



Surface film balance (Langmuir trough)

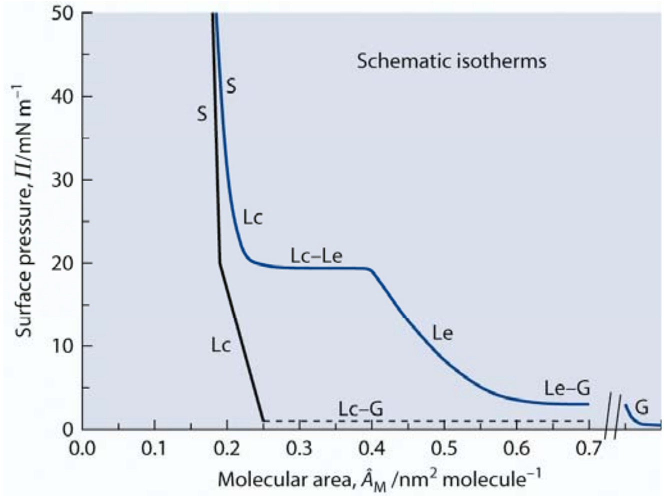
Formation of floating monolayers

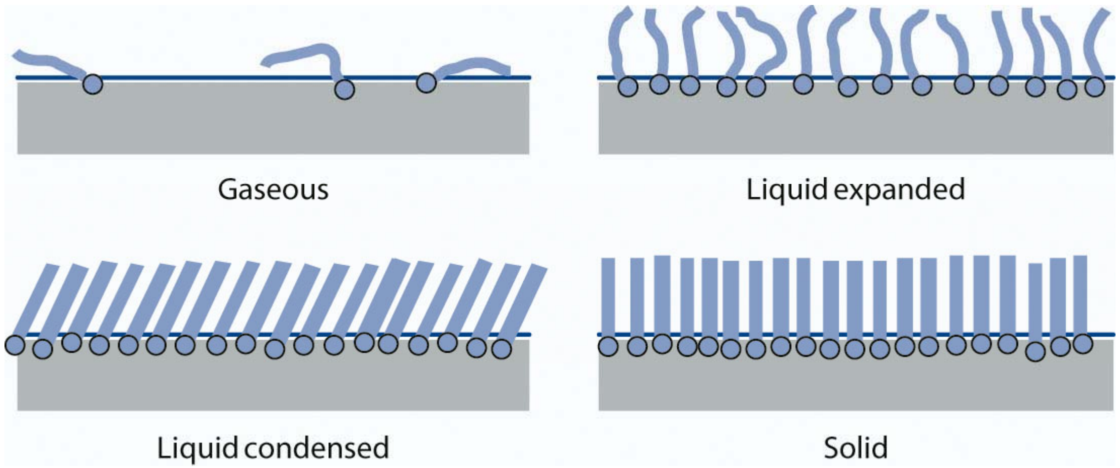
- Measurements on insoluble and soluble amphiphiles

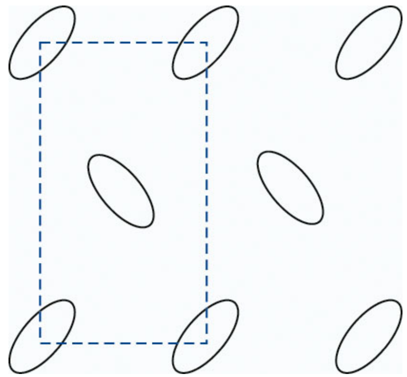


Principal monolayer phases

- S: Solid phase: low compressibility, vertical chains, rectangular (herringbone), A=0.192 nm^2/chain.
- LS: Super Liquid: vertical chains, hexagonal (rotator), A=0.198 nm^2/chain.







Principal monolayer phases

- **L_c**: liquid condensed: linear but less steep, probably fully extended chains but tilted, rotator, A=0.198 nm^2 per chain
- **L_e**: liquid expanded: chains disordered A>0.4 nm^2 per chain

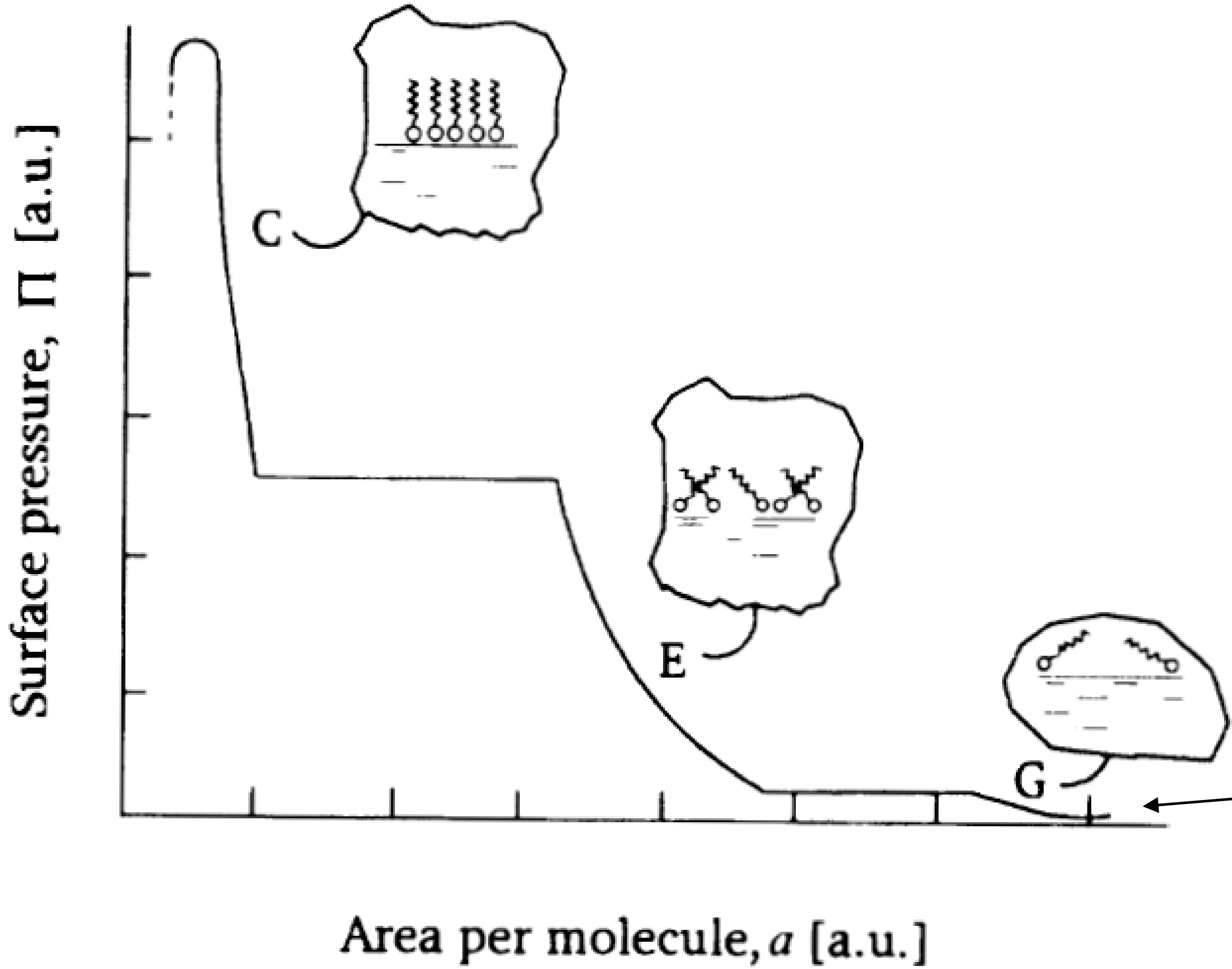
equation of state: $$\left(\Pi - \Pi_0\right)(A - A_0) = NkT$$

Amagat equation: $$\Pi(\hat{A} - \hat{A}^0) = qkT$$ (q<0)

- **G**: gaseous phase, molecules widely separated, move independently, A~ 8 nm^2 per chain

$$\Pi A = NkT$$

Surface pressure vs. area isotherms



$$\Pi\sigma_A = kT$$

$$\Gamma = -\frac{c}{RT}\frac{\partial\gamma}{\partial c}$$

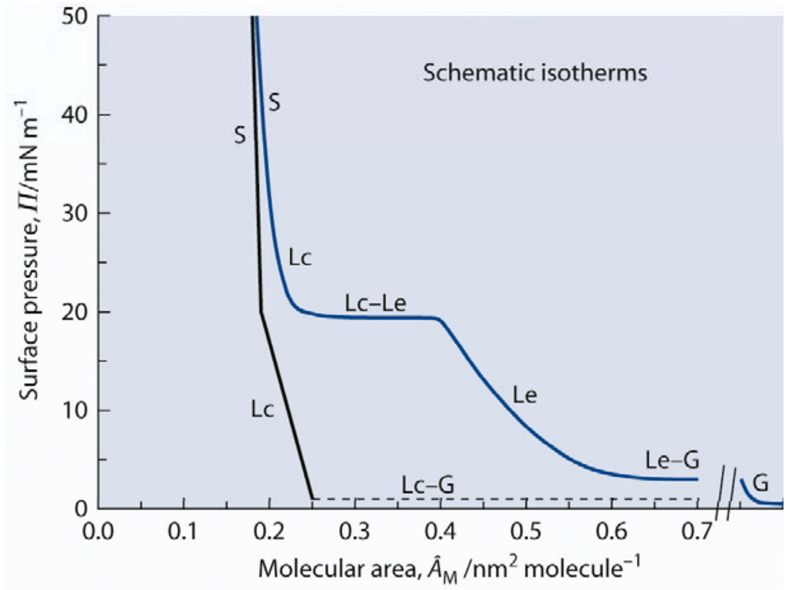
$$\gamma = \gamma_0 - bc$$

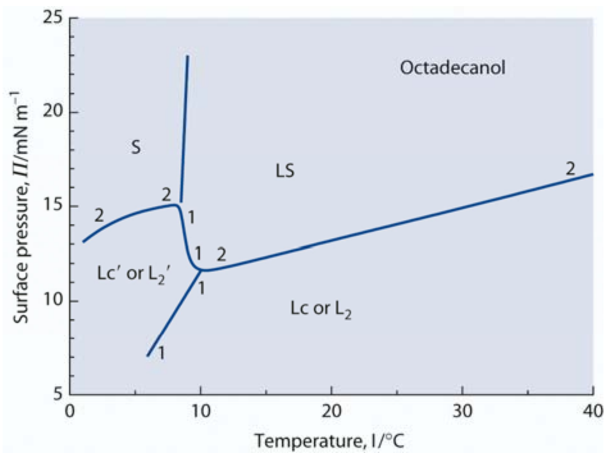
$$\Pi\sigma_A = kT$$

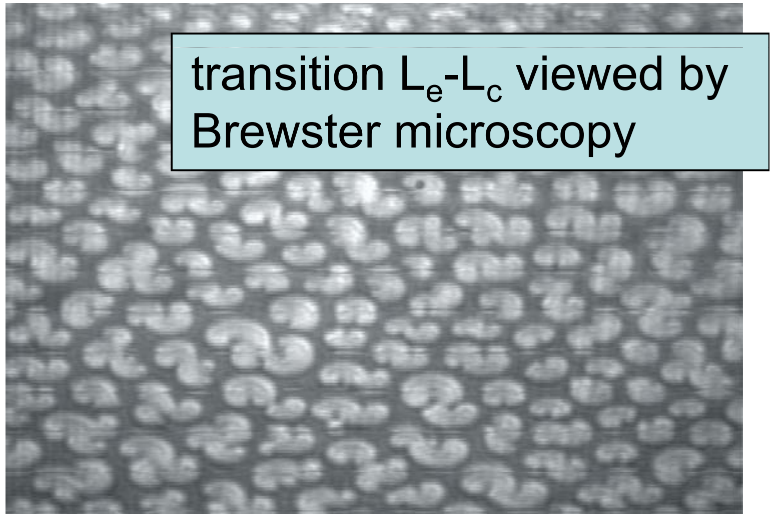
$$\left(\Pi + \frac{a}{\sigma_A^{\ 2}}\right)(\sigma_A - \sigma_0) = kT$$

Phase transitions

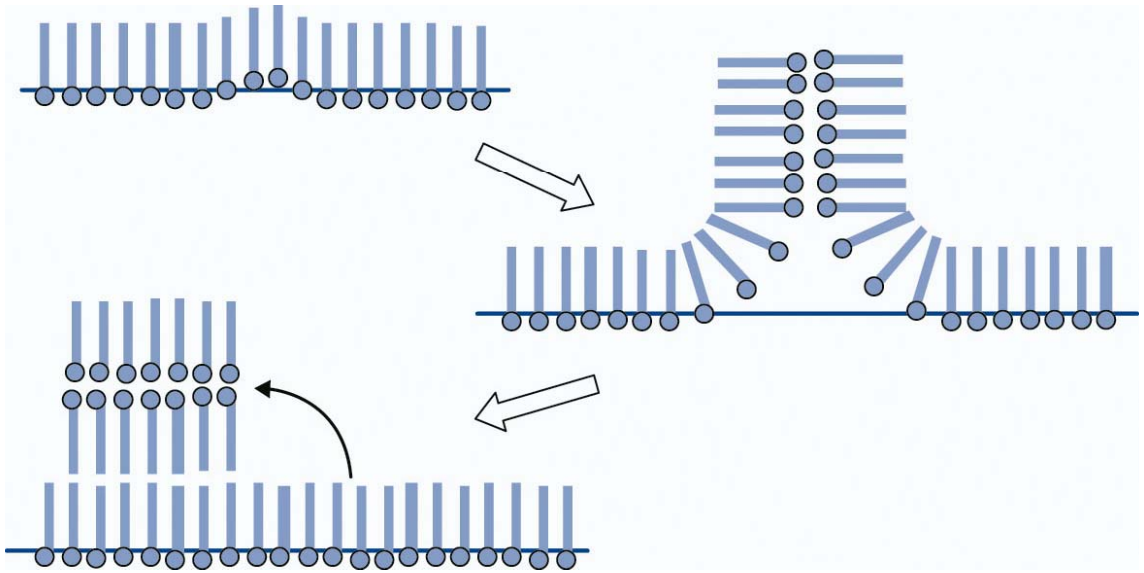
- First order transitions appear as constant pressure regions on the isotherm G->L_e, L_c, S
- First order (often without plateau) L_e->L_c, L_e->S
- Second order: L_c->S



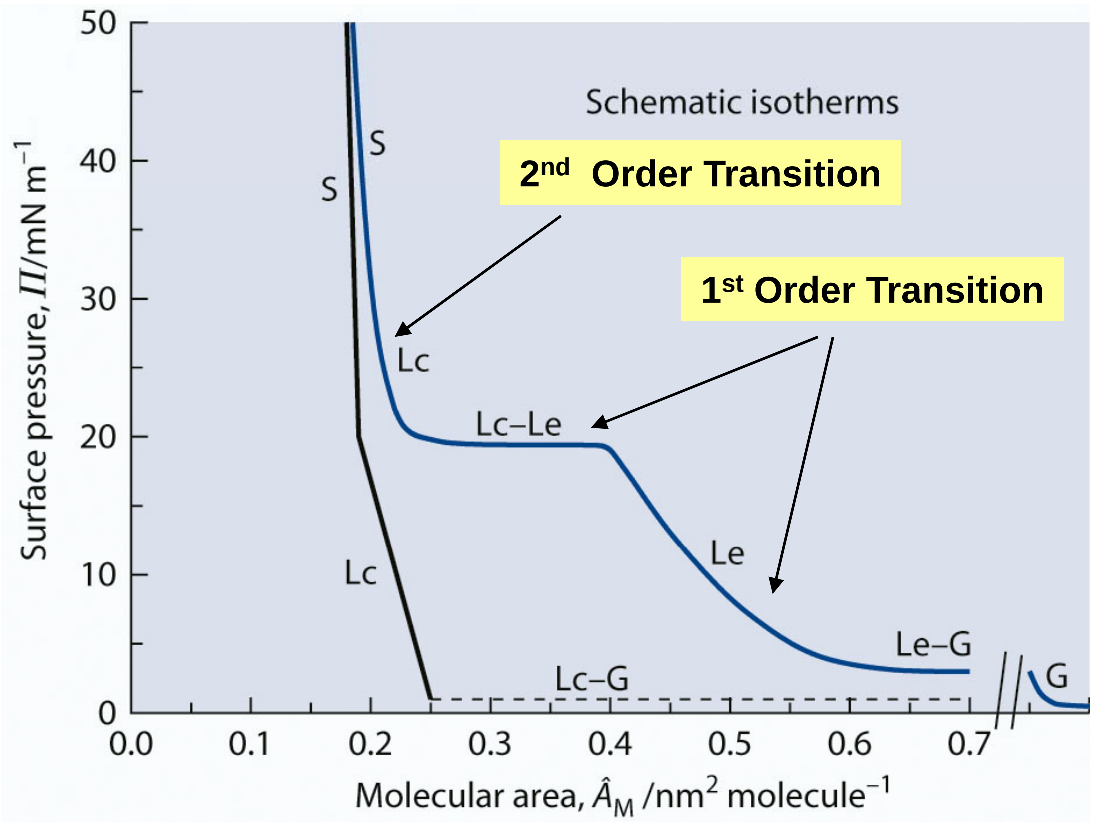




Monolayer collapse

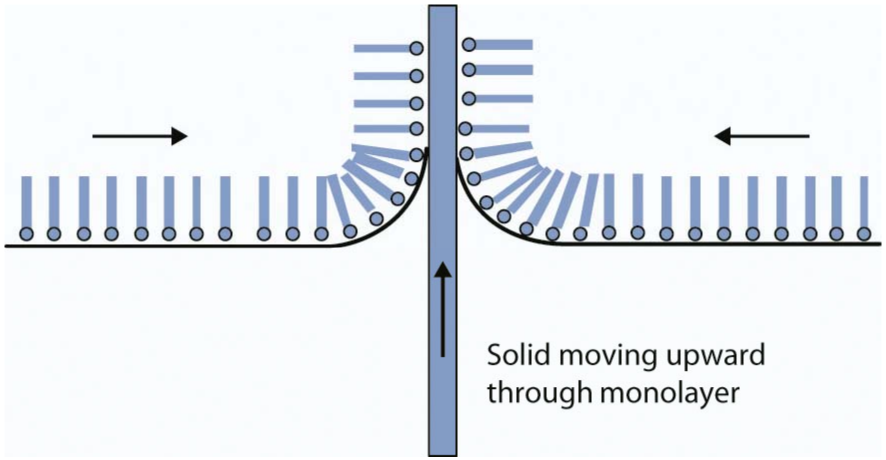


Surface pressure isotherms

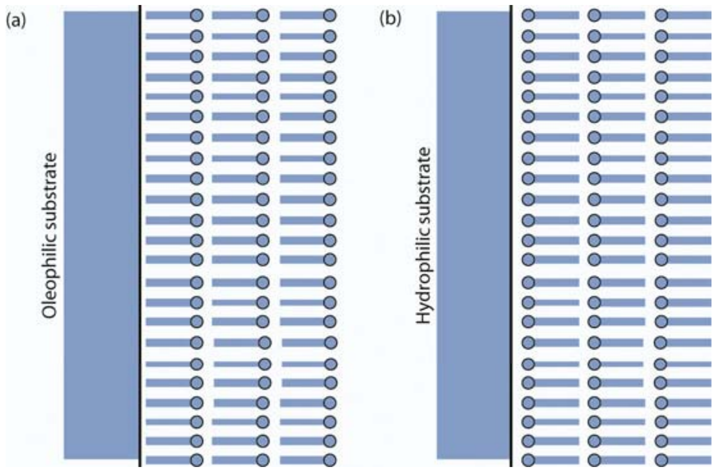


- gaseous phase (G)
- liquid expanded (L_e or L_1)
- liquid condensed (L_c or L_2)
- Solid phase (S)

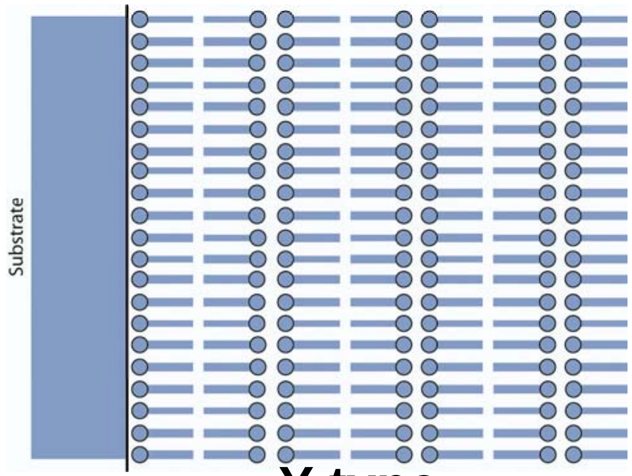
Deposition of Langmuir-Blodgett films



- efficiency of deposition - transfer ratio – ratio of area transferred to the solid to area decrease in the monolayer
- usual substrates (depends on application): mica, silicon, quartz etc.
- film quality depends on pH, ionic strength in subphase



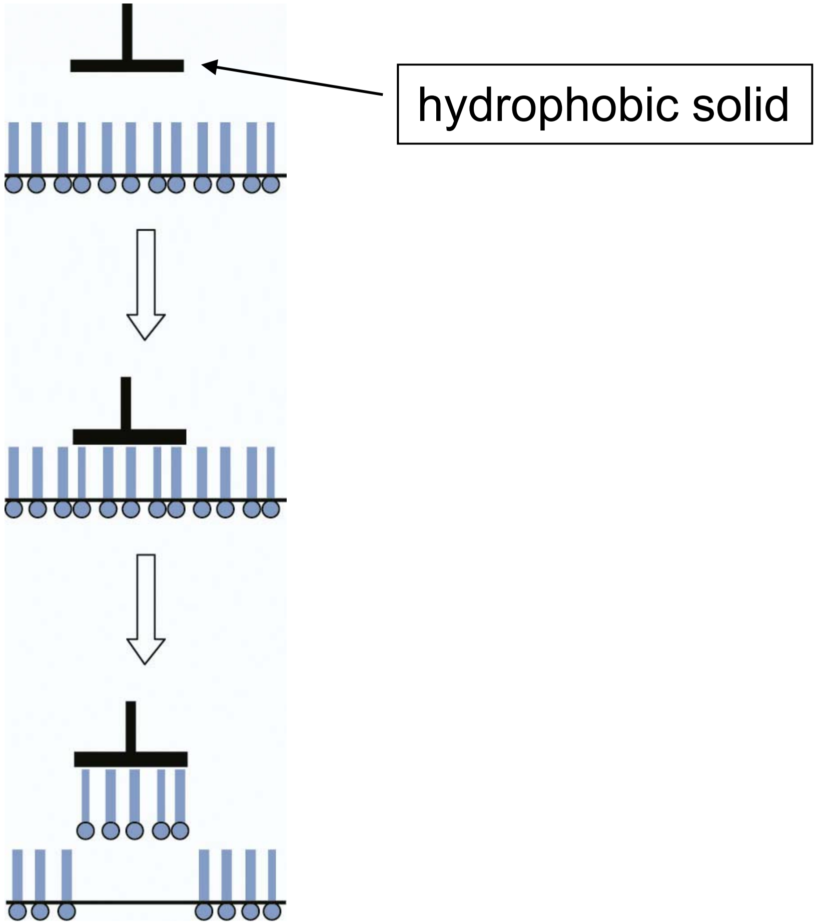
X-type **Z-type**



Y-type

Deposition of Langmuir-Blodgett films

- Langmuir-Shaefer technique (works for rigid monolayers, can be also used for SAMs)



Study of film structure

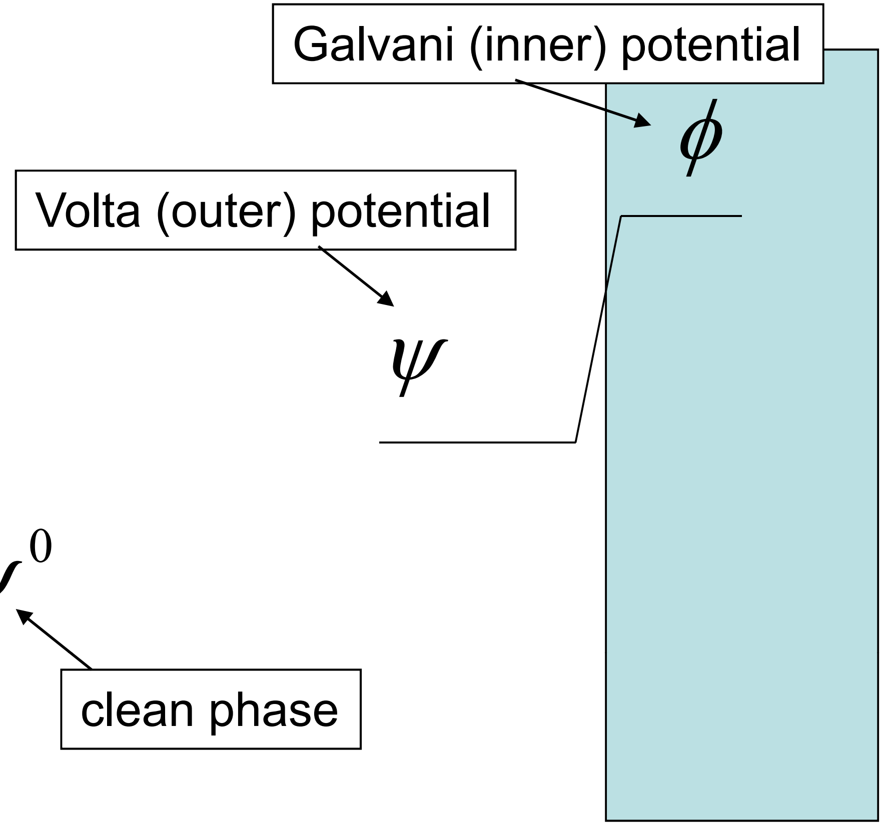
- surface film balance
- surface potential
  - using air electrode
  - vibrating plate technique

$$\phi = \psi + \chi$$

surface potential $$\Delta E = \psi^{m} - \psi^{0}$$

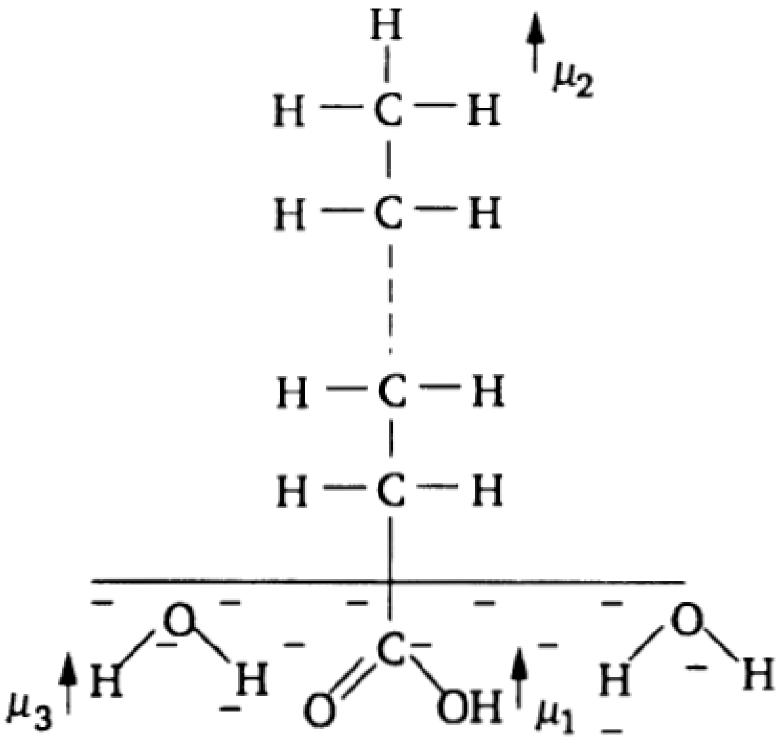
with monolayer

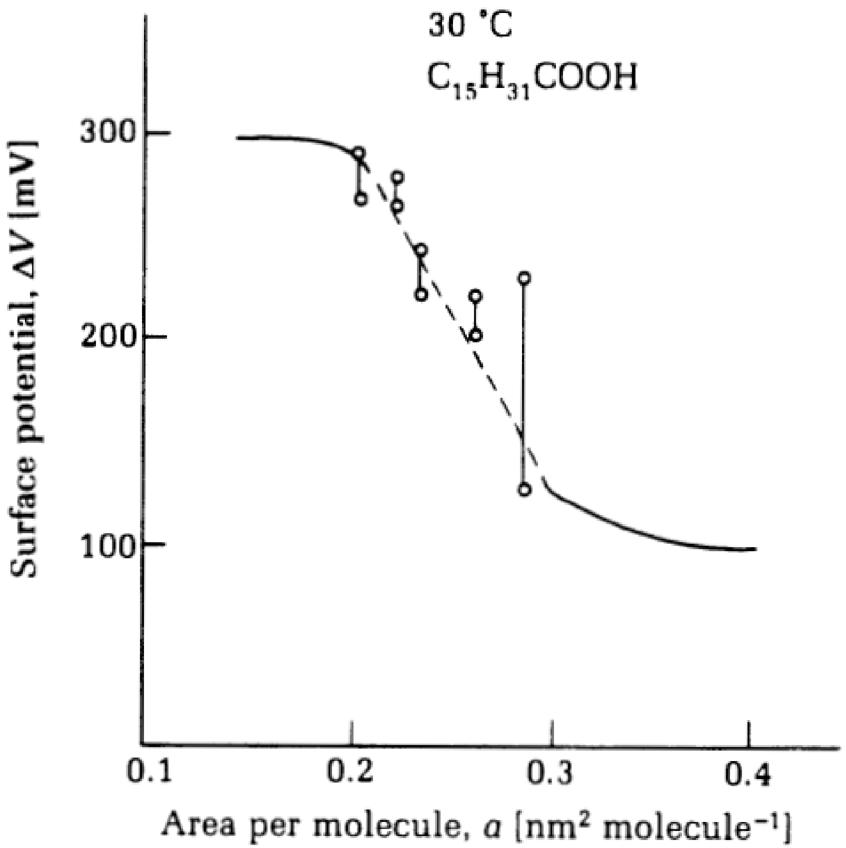
clean phase



- surface viscosity
  - shear viscosity
  - surface dilational modulus
  - dynamic modulus

Surface potential



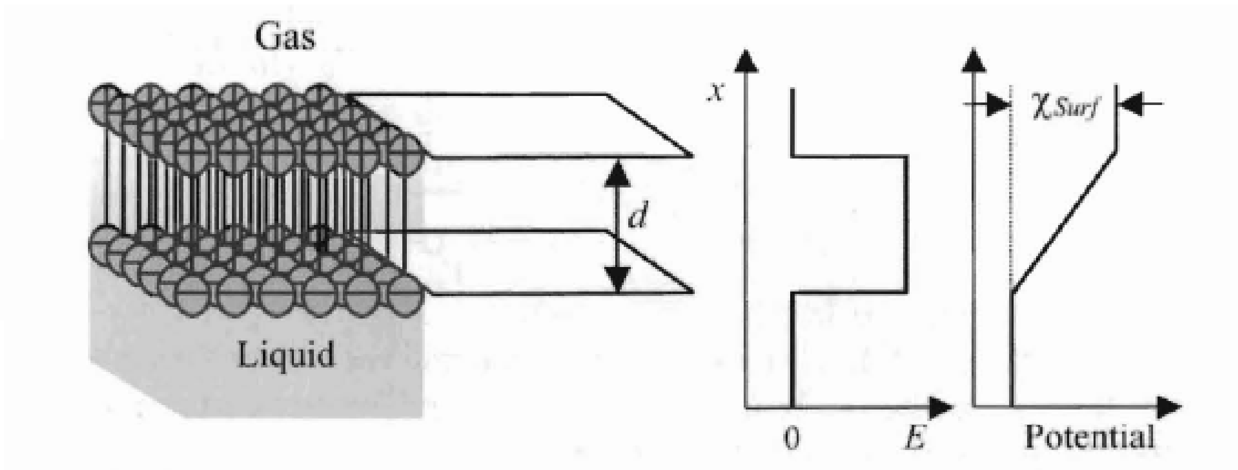


- Surface potential vs. area per molecule for n-hexadecanoic acid

Surface potential

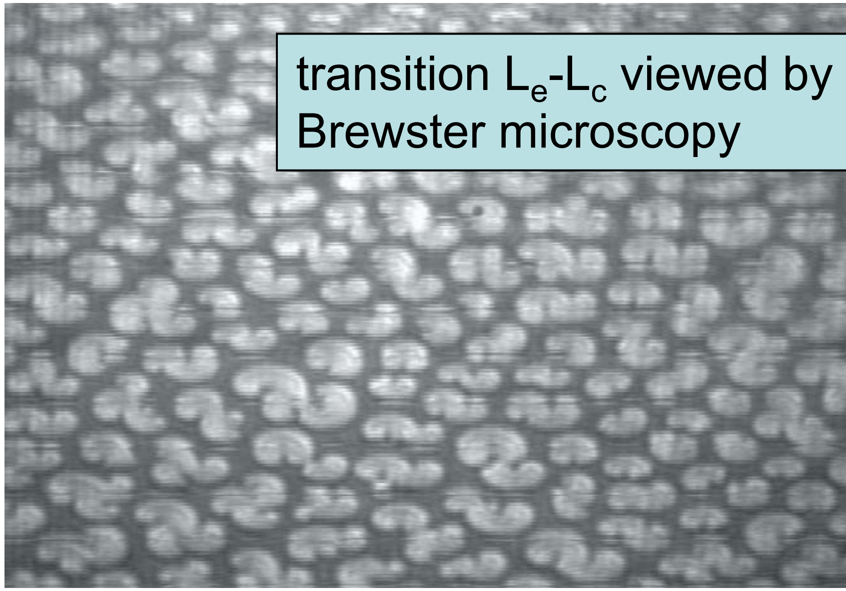
- measurement of surface potential

$$\chi_{Surf} = \frac{\mu_\perp}{\sigma_A \varepsilon \varepsilon_0}$$

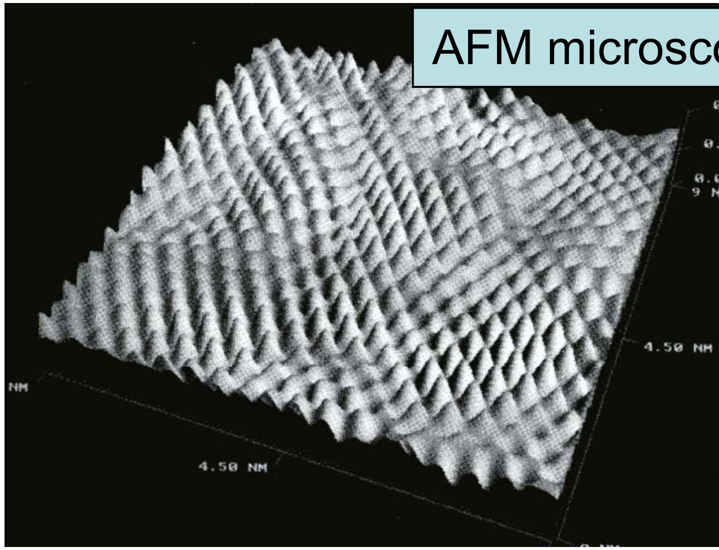


Study of film structure

- Electron diffraction
- Electron microscopy
- Ellipsometry
- Brewster angle microscopy
- Fluorescent microscopy
- Scanning probe microscopy
- Surface Plasmon Resonance



transition L_e-L_c viewed by Brewster microscopy

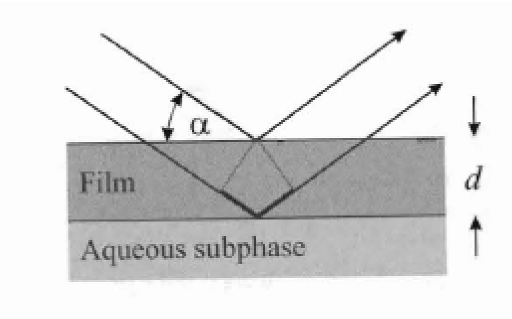


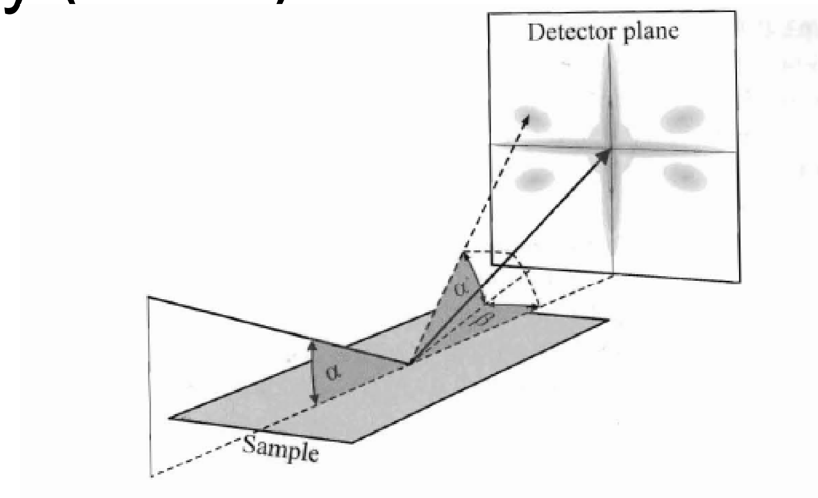
AFM microscopy

Study of film structure

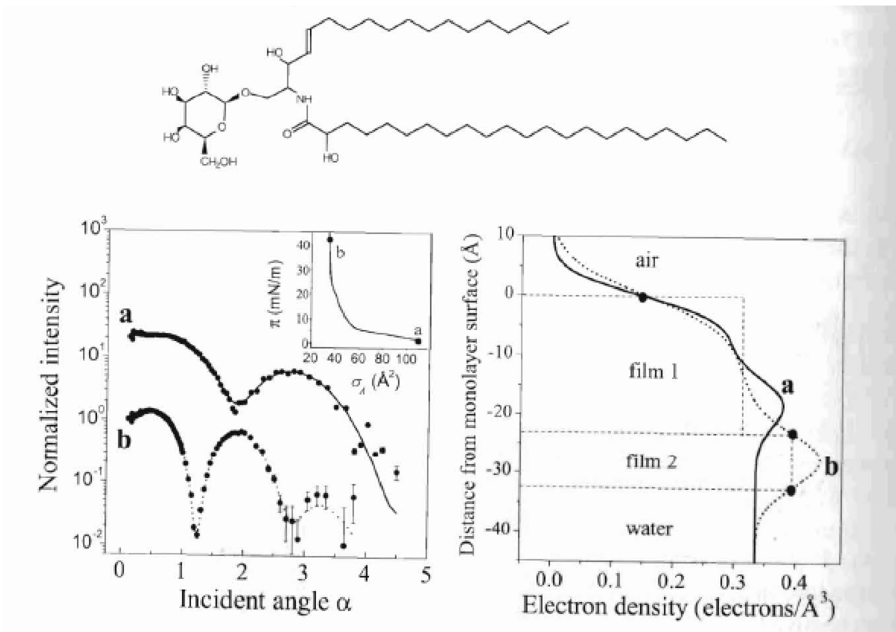
- grazing incidence X-ray (GIXD)

$$d_{hk} = n\lambda / 2\sin\theta$$



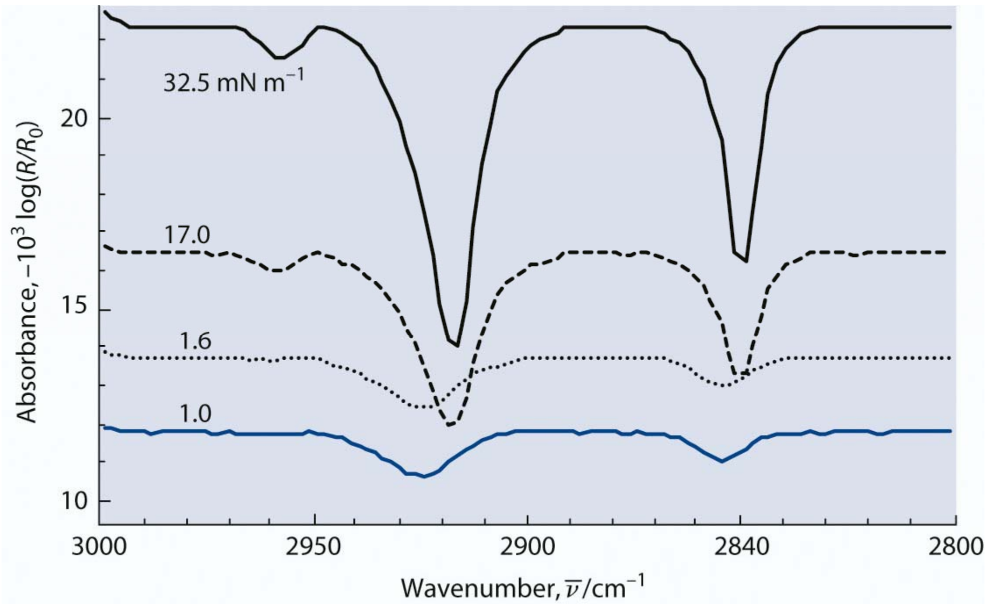


- low penetration depth can be achieved (5nm at 0.1^0)
- typically 0-5^0 angles
- sensitive to the electron density in the layer

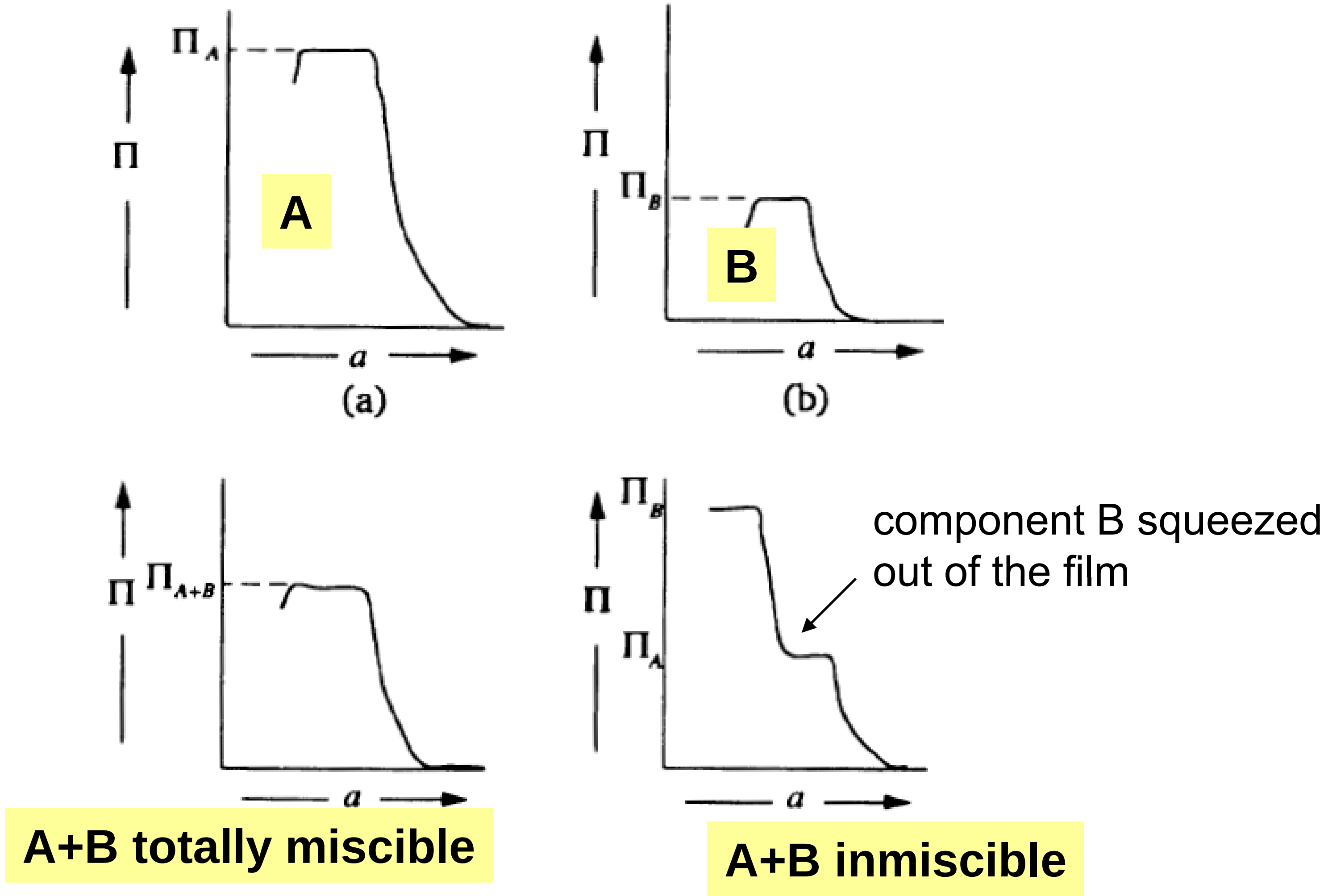


Study of film structure

- neutron scattering
- UV-VIS spectroscopy
- Fourier transform infrared spectroscopy as reflection adsorption (FTIR-RAS)



Mixed monolayers



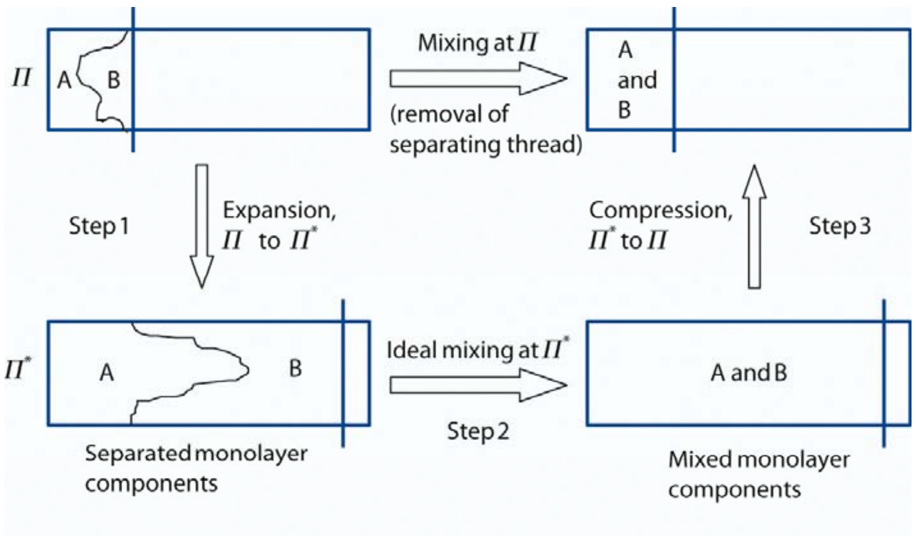
- effect of miscibility on pressure/area isotherms

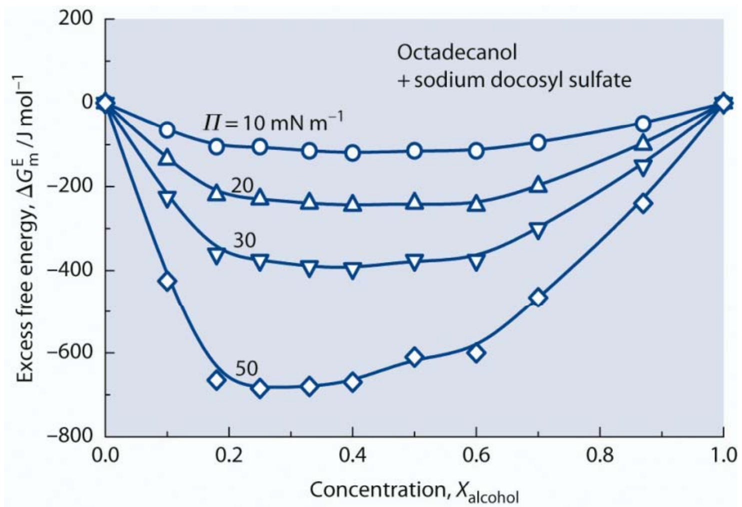
Interactions in a monolayer

- two water-insoluble components

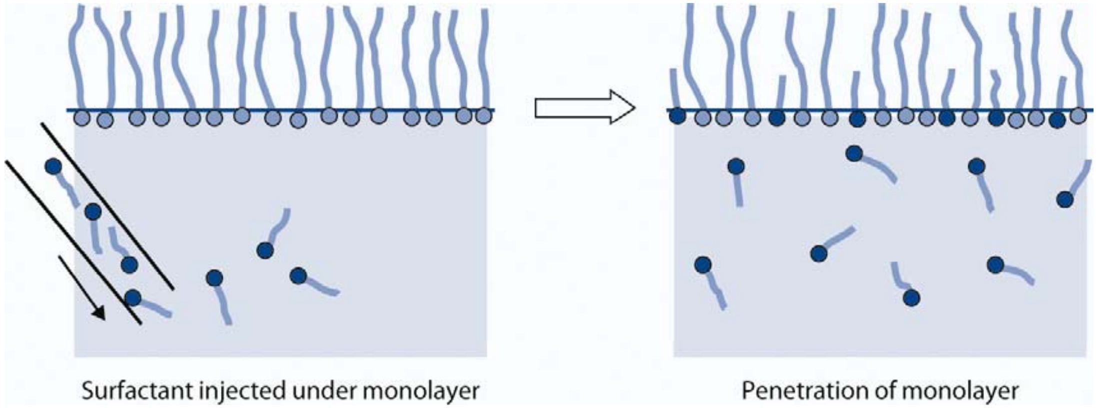
$$A_{AB} = x_A A_A + x_B A_B$$

mixing free energy (excess) $$\Delta G^E = \int_{\Pi^*}^{\Pi} A_{AB} d\Pi - x_A \int_{\Pi^*}^{\Pi} A_A d\Pi - x_B \int_{\Pi^*}^{\Pi} A_B d\Pi$$

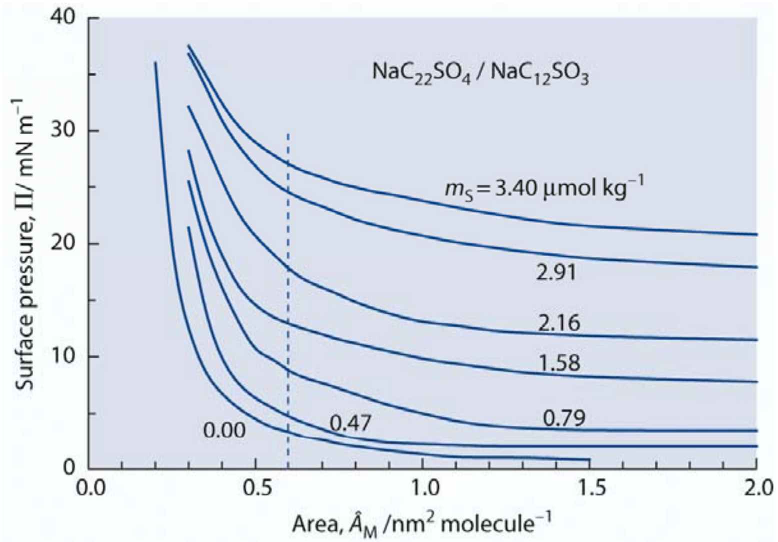




Penetration of monolayers by soluble surfactants



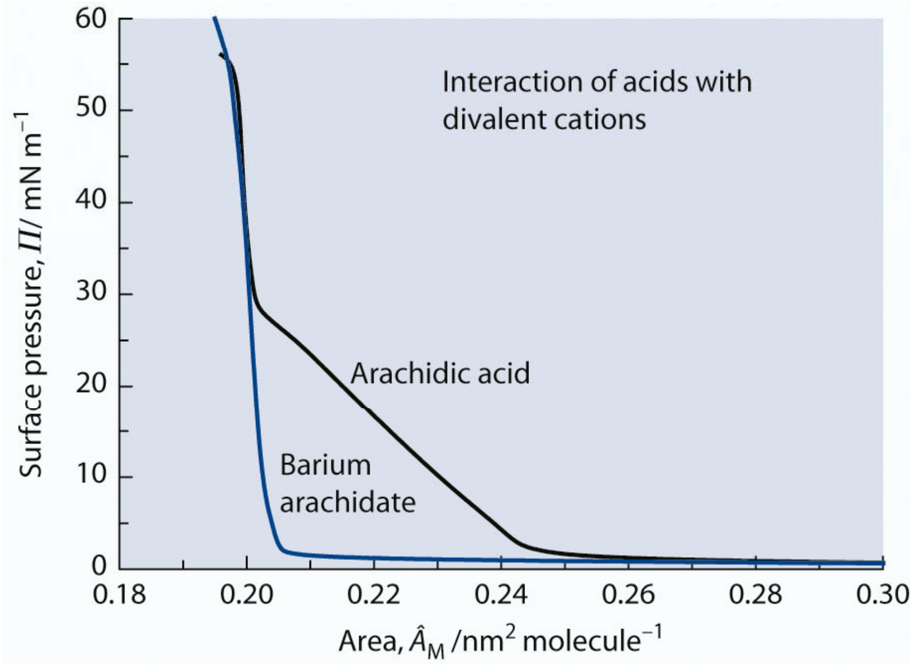
- penetration of surfactant increases the surface pressure per monolayer molecule, although the amount of surfactant is difficult to determine



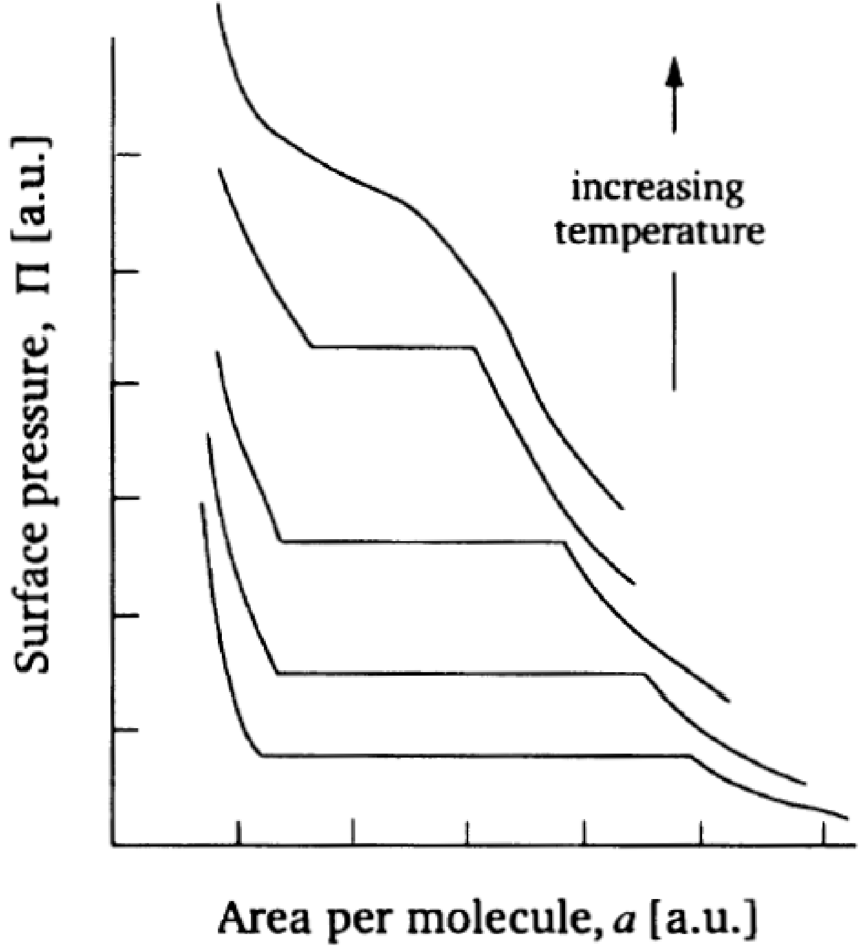
injection of dodecylsulfonate

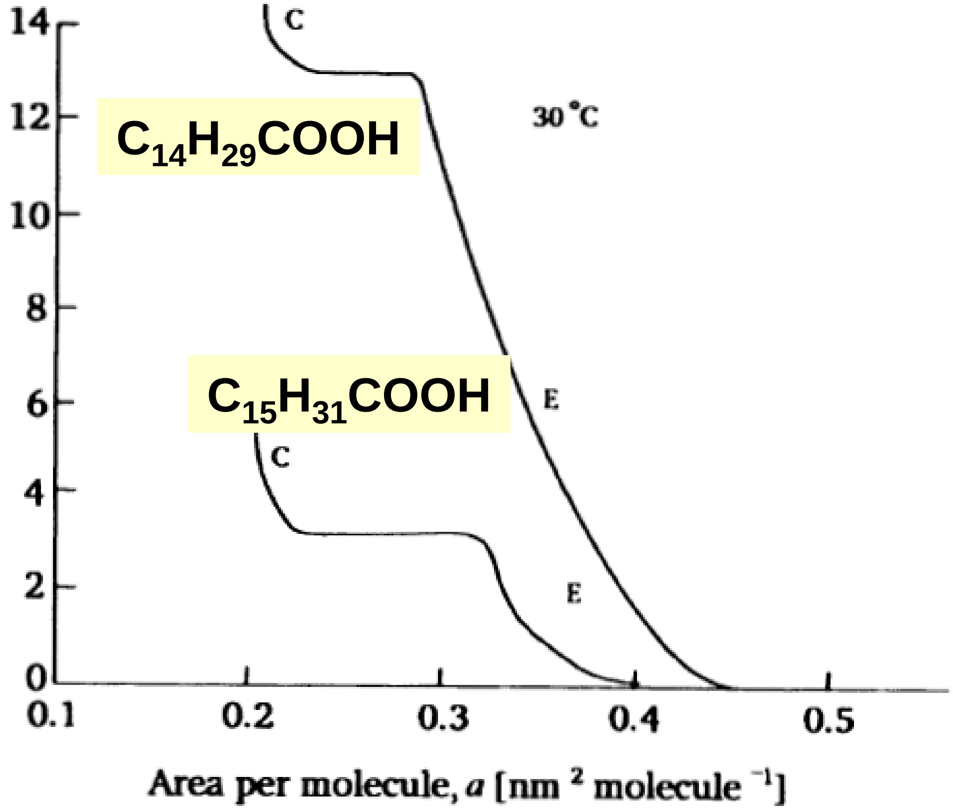
Reaction in monolayers

- arachidic acid on acidic and alkaline subphases



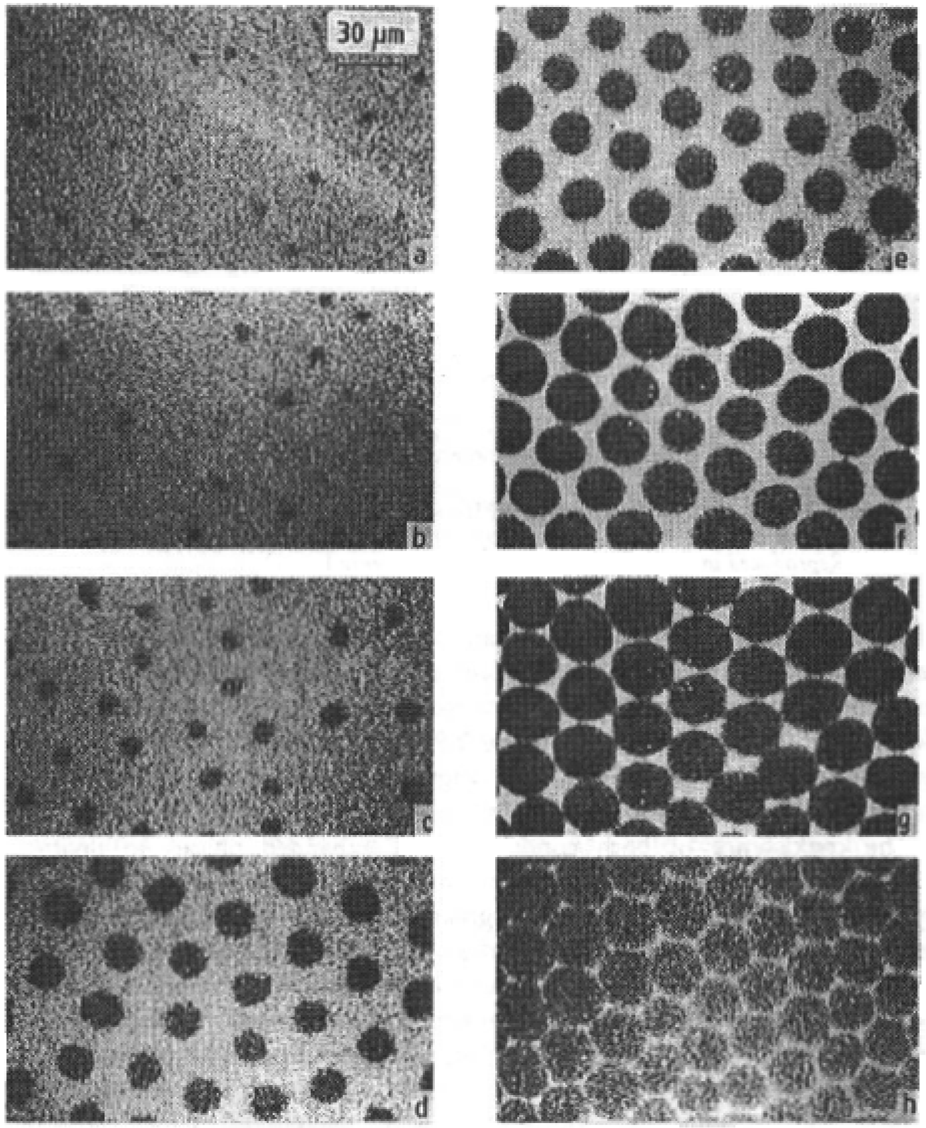
Temperature dependence

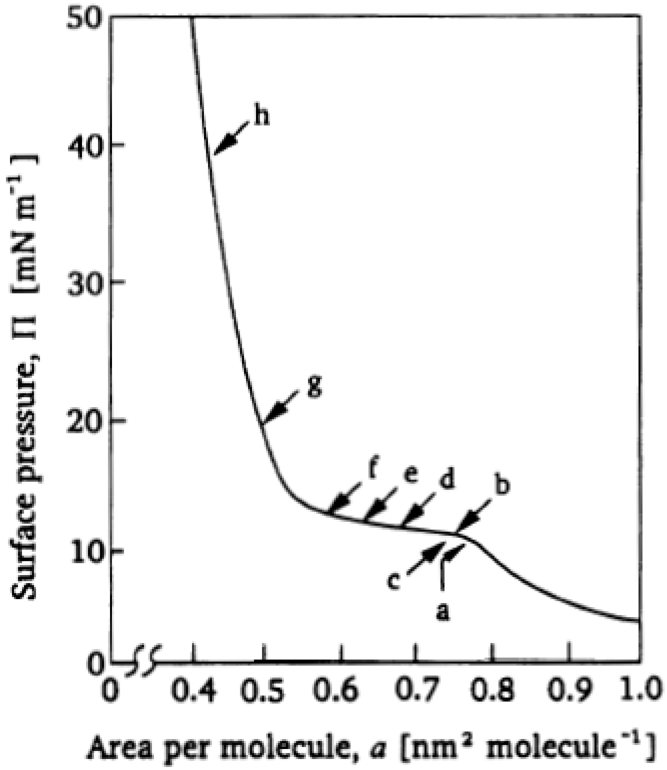




- Effect of temperature and chain length on the pressure/area isotherms

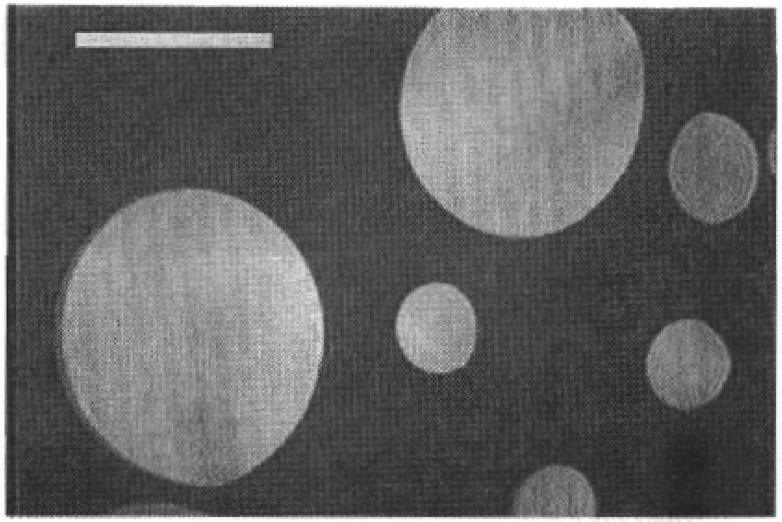
Fluorescent microscopy of LB

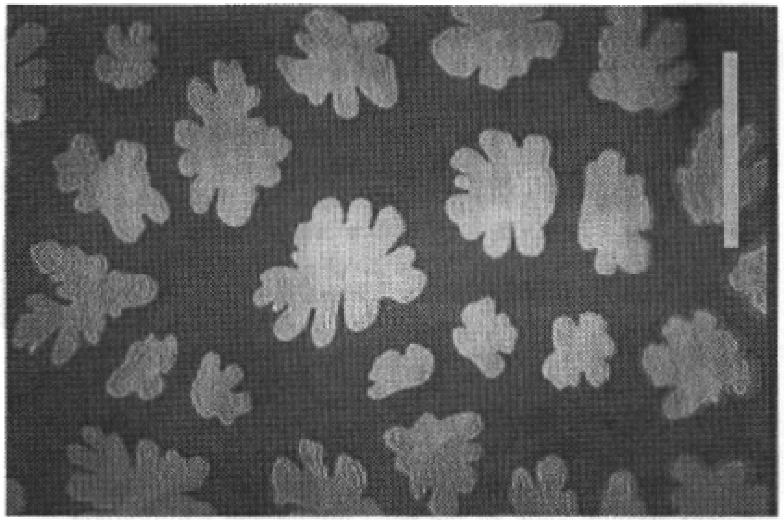


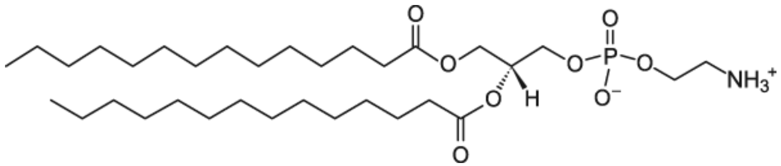


- incorporating a small fluorescent dye probe in the phospholipid monolayer

Brewster angle microscopy







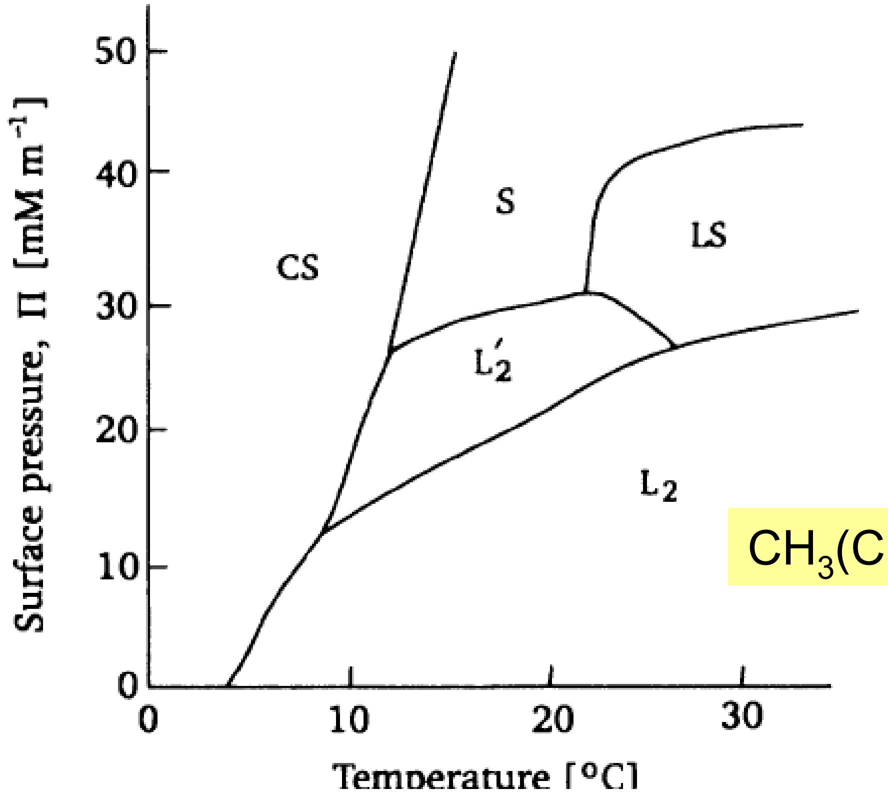
- Typical structures of phospholipid and pentadecanoic acid

Phase diagram for LB monolayers

- Gibbs phase rule for LB

$$F = (C^b + C^S) - (P^b + P^S) + 3$$

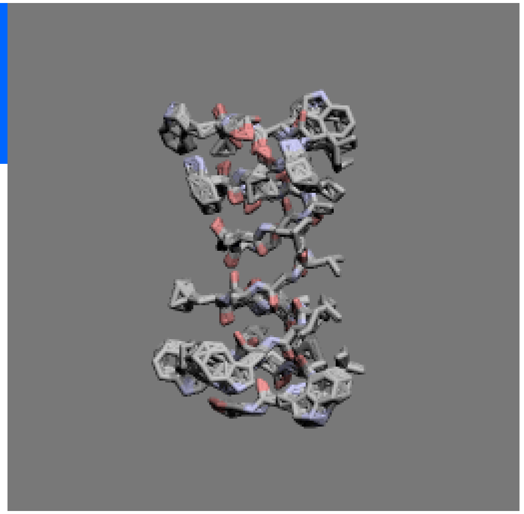
  - For 1 surface phase: F=3 (Π and a, @ T=const)
  - For 2 surface phases F=2 ((Π =f(a), @ T=const)

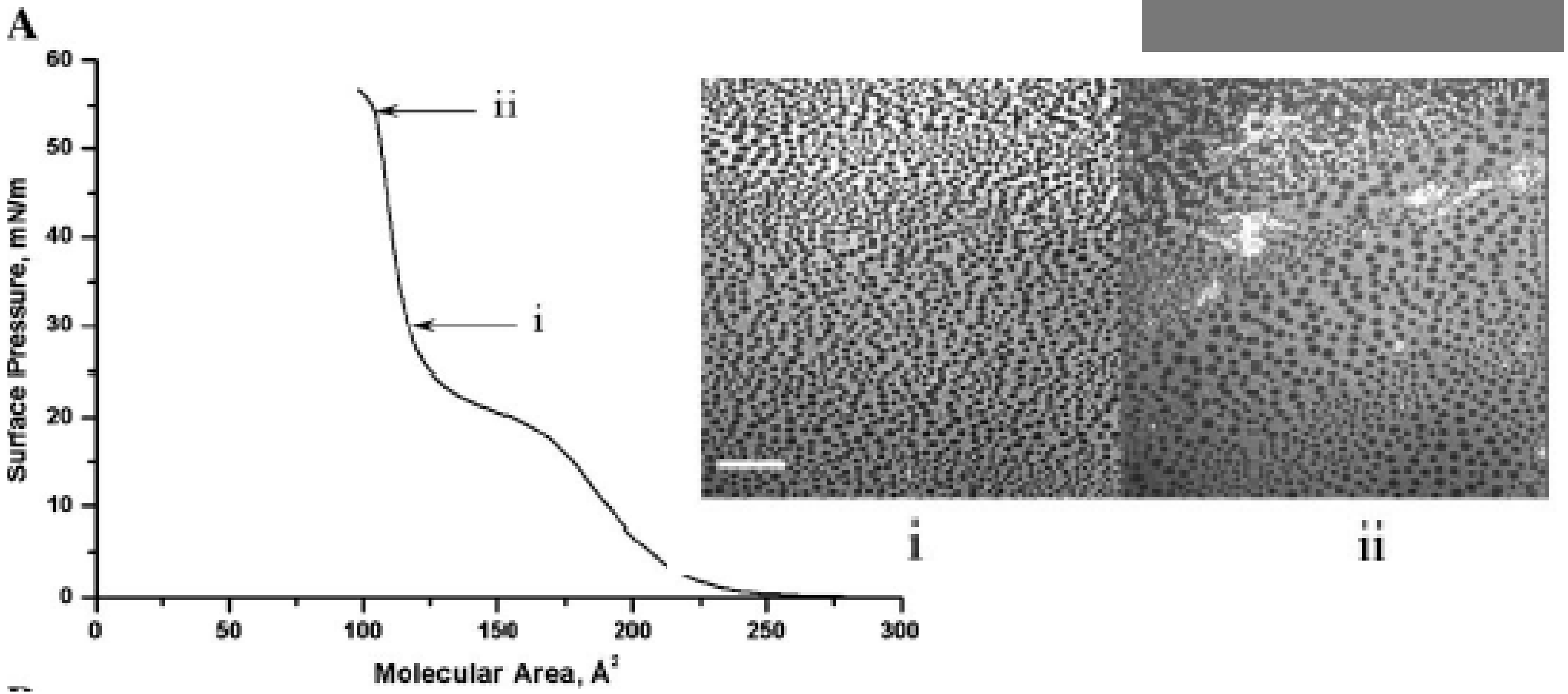


$CH_3(CH_2)_{20}COOH$

- Phase diagram for n-docosanoic acid

Brewster angle microscopy

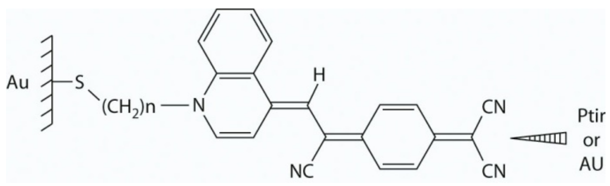




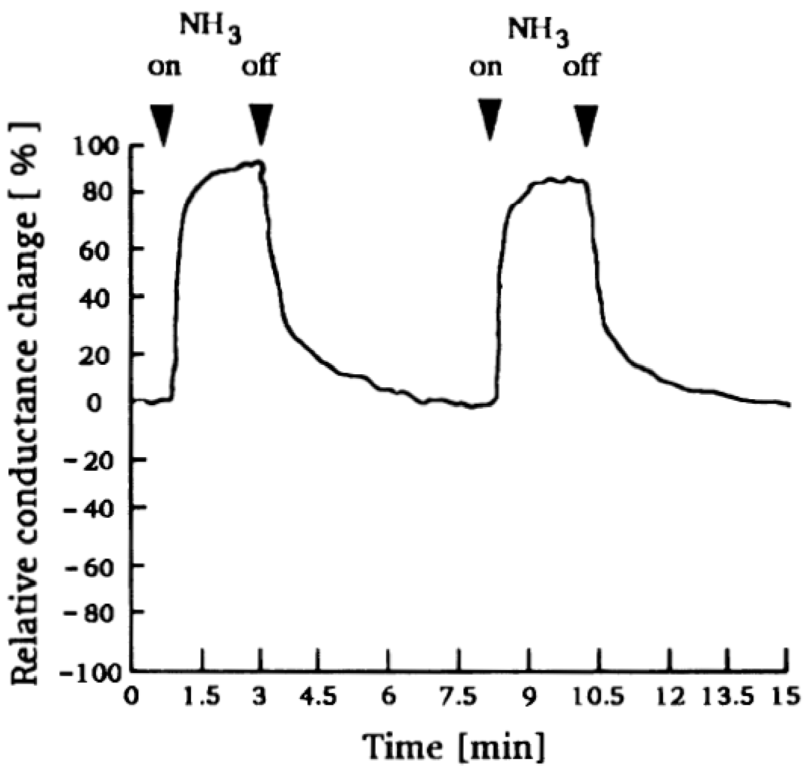
- Interaction of gramicidin with phospholipid LB

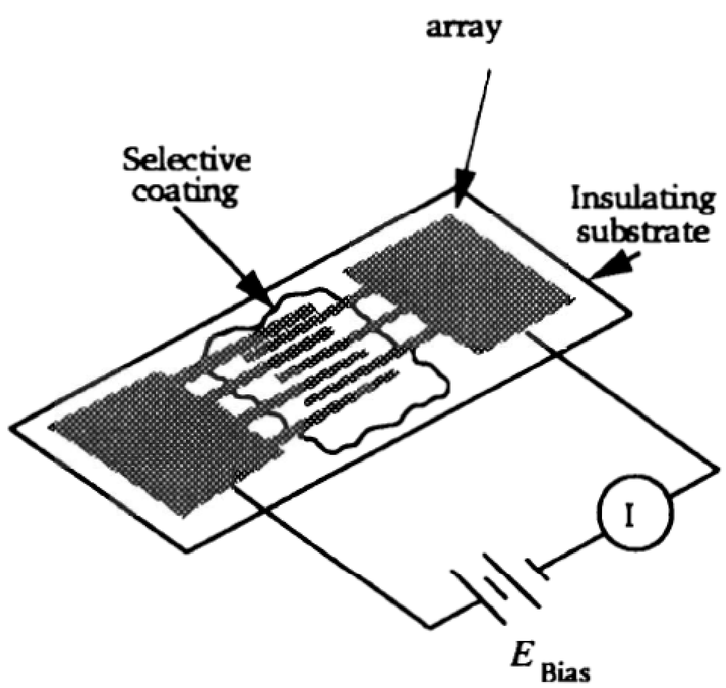
Applications of LB films

- molecular size, shape and packing can be determined
- membrane modeling
- lung surfactant
- water conservation
- Molecular electronics
- Second harmonic generation
- Chemical and biological sensors



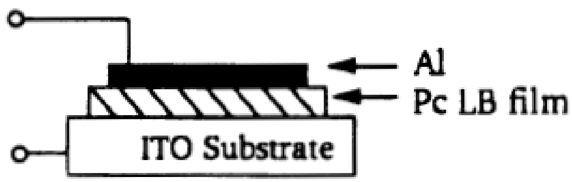
LB applications: Gas sensor

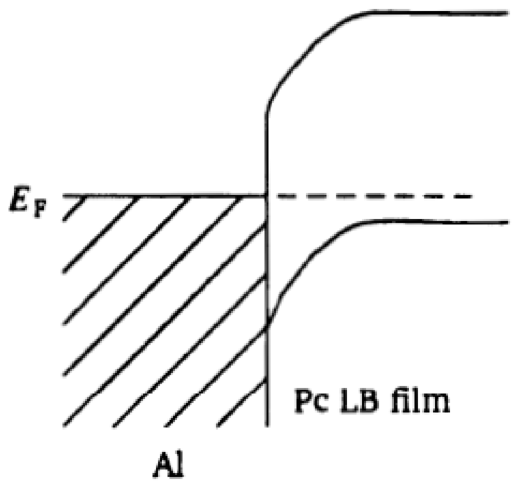


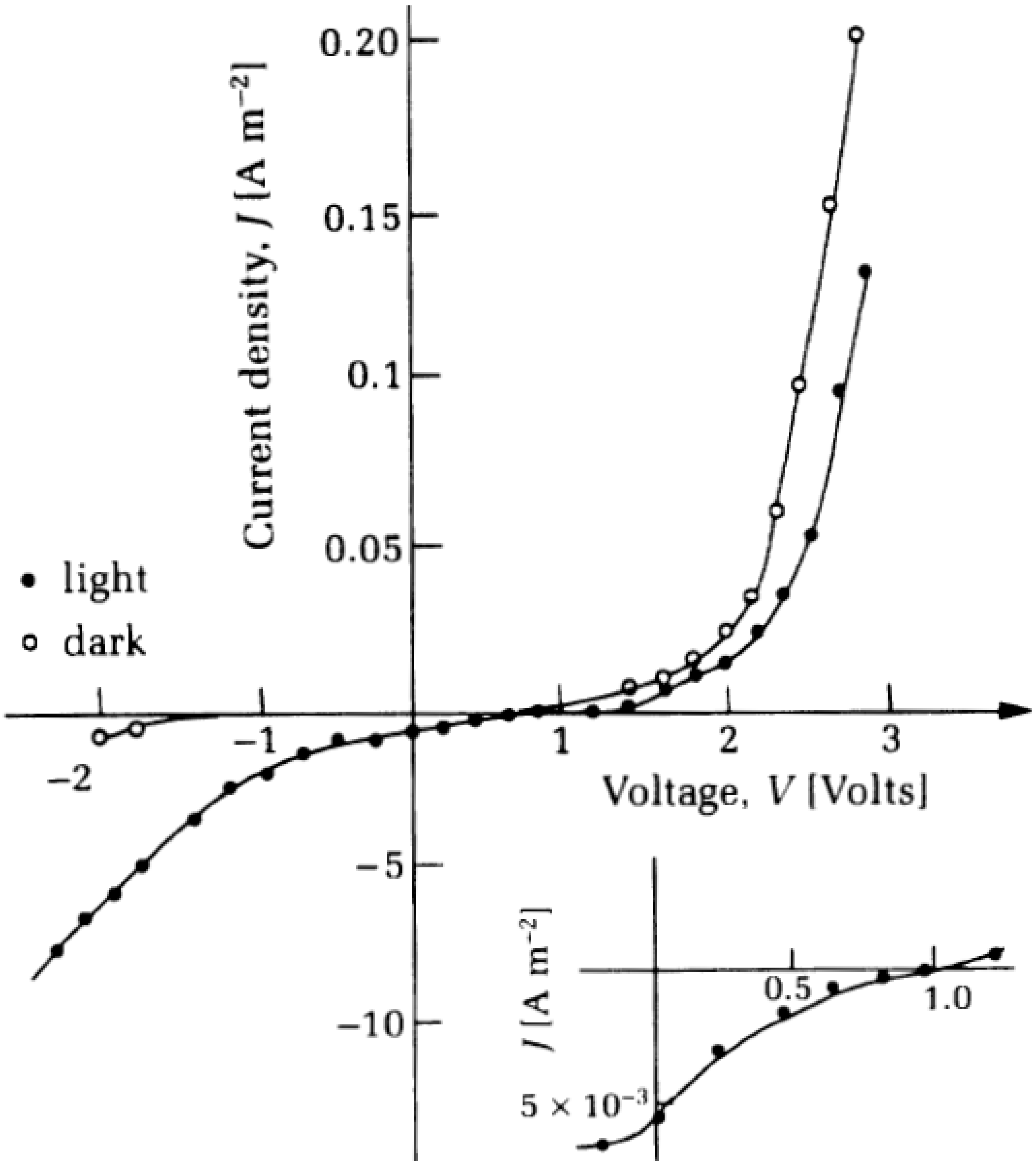


- response of a 45 layer copper-phtalocyanine LB film to 2 ppm of NH_3.

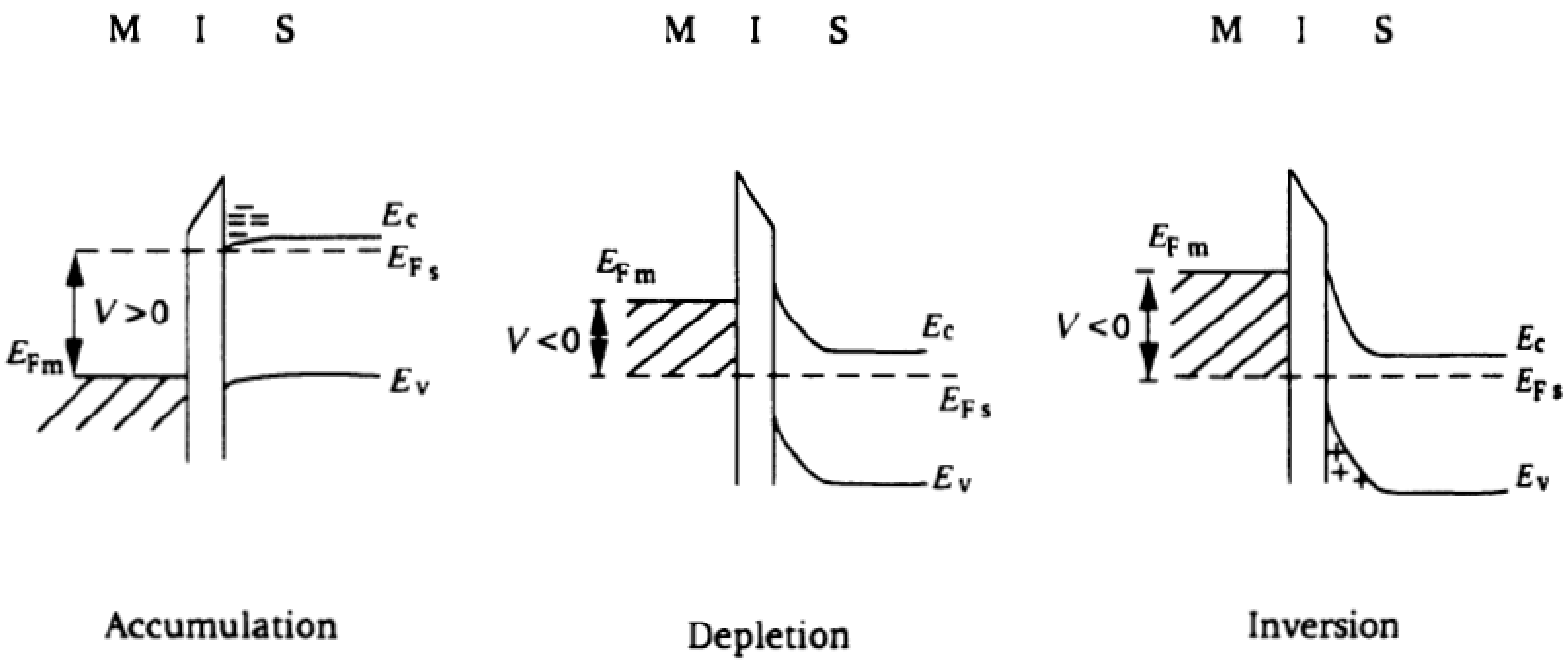
LB applications: Diode







LB applications: Insulator

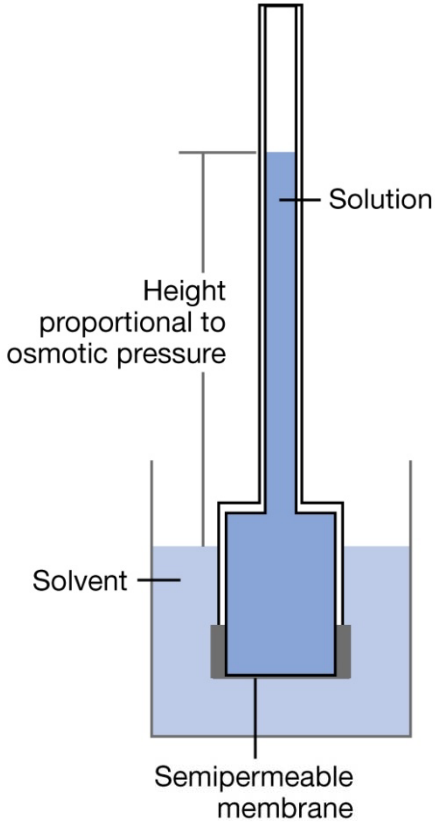


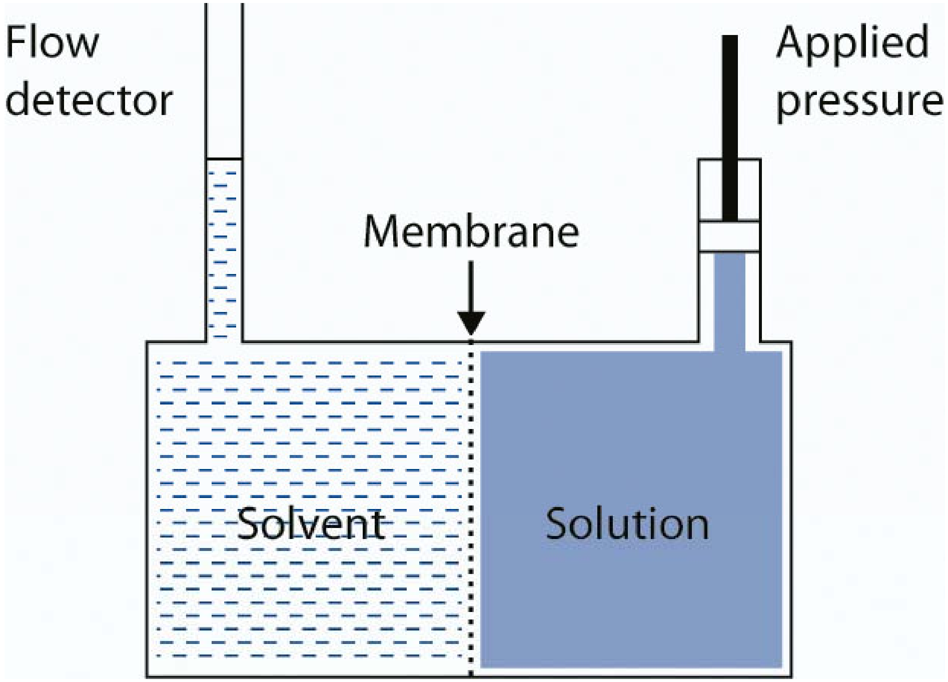
- Energy band diagram for MIS structure

Osmosis and Donnan potential

Colligative properties

- **Osmosis – spontaneous passage of pure solvent into solution separated by semipermeable membrane**





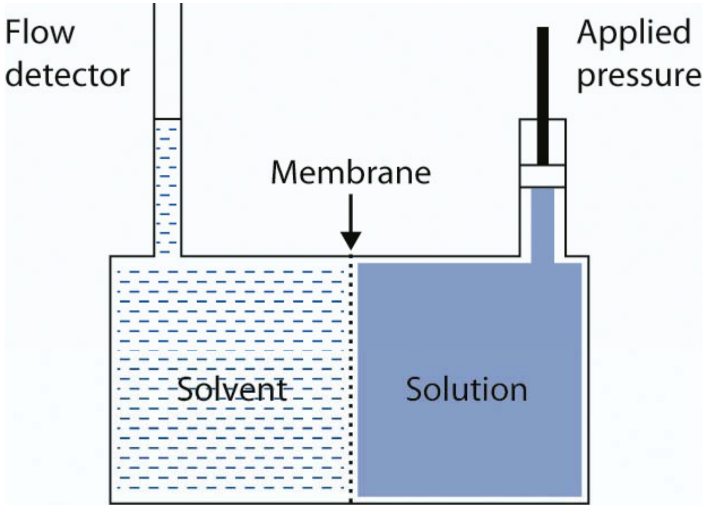
Van't Hoff equation: $\Pi = [B]RT, \quad [B] = n_B / V$

Colligative properties

Van't Hoff equation: $\Pi = [B]RT, \quad [B] = n_B / V$

$$\mu_A^*(p) = \mu_A^*(p+\Pi) + RT\ln x_A$$

$$\mu_A^*(p+\Pi) = \mu_A^*(p) + \int_p^{p+\Pi} V_m dp$$



For dilute solution: $RTx_\mathbf{B} = \Pi V_m$

$\boxed{V / n_A}$

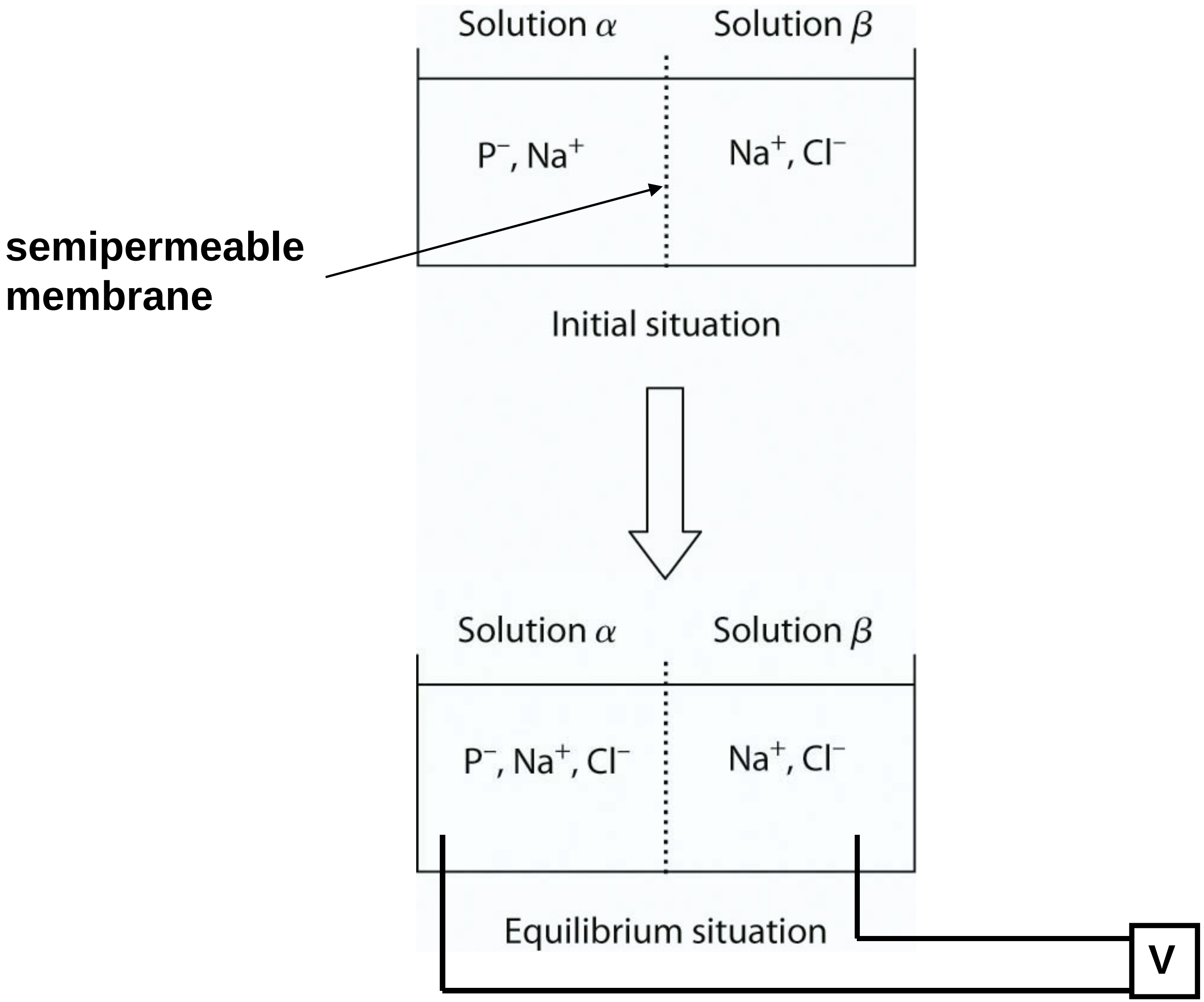
$\boxed{n_B / n_A}$

- van't Hoff factor for ionic solution was a proof for Arrhenius theory

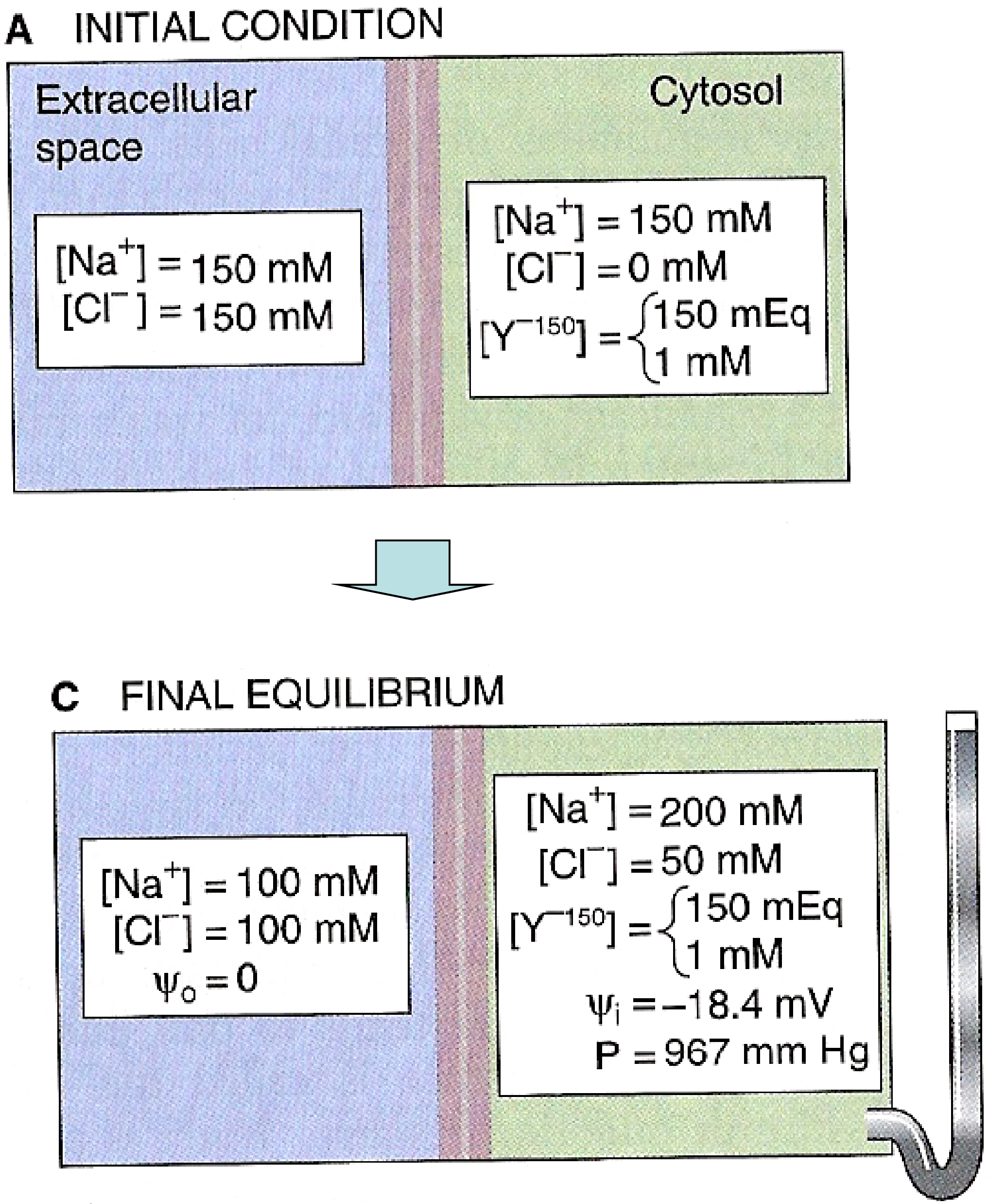
More generally: $\Pi = [B]RT(1 + b[B] + \ldots)$

Osmotic virial coefficients

Donnan membrane equilibrium



Donnan potential



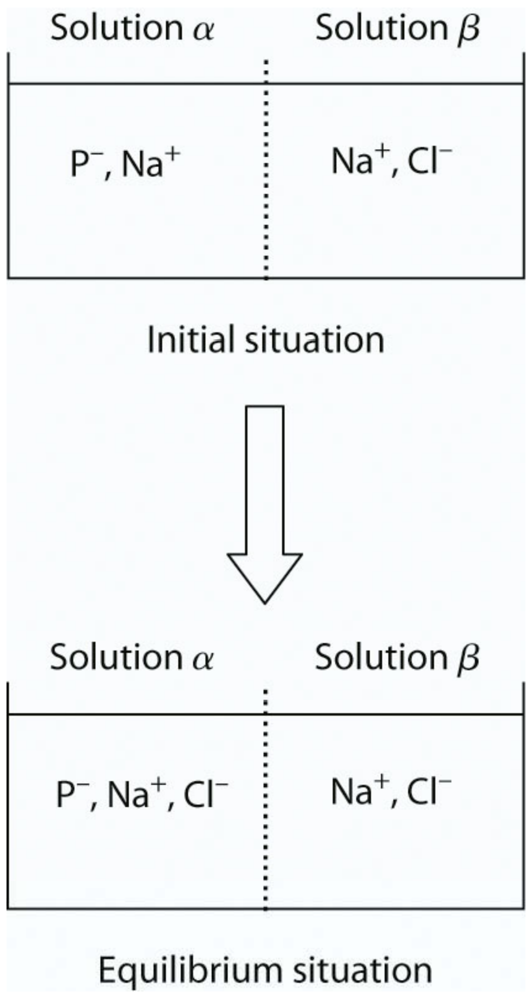
Donnan membrane equilibrium

$$\bar{\mu}_i = \mu_i + z_i F \Phi$$

$$\bar{\mu}^{\beta}_{Na^+} - \bar{\mu}^{\alpha}_{Na^+} = 0 = \bar{\mu}^{\beta}_{Cl^-} - \bar{\mu}^{\alpha}_{Cl^-}$$

$$\Phi^{\beta} - \Phi^{\alpha} = -\frac{RT}{F} \ln \frac{c^{\beta}_{Na^+}}{c^{\alpha}_{Na^+}} = -\frac{RT}{F} \ln \frac{c^{\beta}_{Cl^-}}{c^{\alpha}_{Cl^-}}$$

$$\frac{c^{\beta}_{Na^+}}{c^{\alpha}_{Na^+}} = 1 - \frac{z_{P^-} c_{P^-}^{\alpha}}{2 c^{\beta}_{Na^+}}$$



Probelms

- **5.3:** A cholesterol monolayer has an area of 0.405 and 0.40 nm^2 $molecule^{-1}$ at 5 and 20 mN m^{-1} respectively and a monolayer of dipalmitoyl phosphatidylcholine (DPPC) has areas of 0.68 and 0.43 nm^2 $molecule^{-1}$ at these surface pressures. The corresponding areas for a mixed monolayer consisting of 1:3.4 cholesterol:DPPC are 0.38 and 0.40 nm^2 $molecule^{-1}$. Calculate the excess areas of mixing at these two surface pressures.

- **6.4** After equilibration the Donnan potential across a membrane separating a solution of a negatively charged polyelectrolyte and a solution of sodium chloride is found to be 45 mV (with the polyelectrolyte solution at the lower potential). Calculate the ratio of sodium ion concentrations in the two solutions. (Ignore any osmotic movement).

- **5.2**: Calculate the average molar mass and molecular area of egg albumin from the data in the table. The data refer to a monolayer of egg albumin spread on water in a film balance at 25ºC.

Surface Pressure, Π / mN m^{-1}	**Area, A / m^2 mg^{-1}**
0.07	2.00
0.11	1.64
0.18	1.50
0.20	1.45
0.26	1.38
0.33	1.36
0.38	1.32

- **Ch. 13 Problem 3.**