Physical Chemistry of Colloids

joogleberry.com/acts/bubbleman/

Lecture 3, *March 6, 2019*

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Previously in ColloidsPhysChem…(I)

a fluid interface contracts → **minimum area**

zero-thickness membrane model to quantify **"contractile tendency"** of fluid interfaces
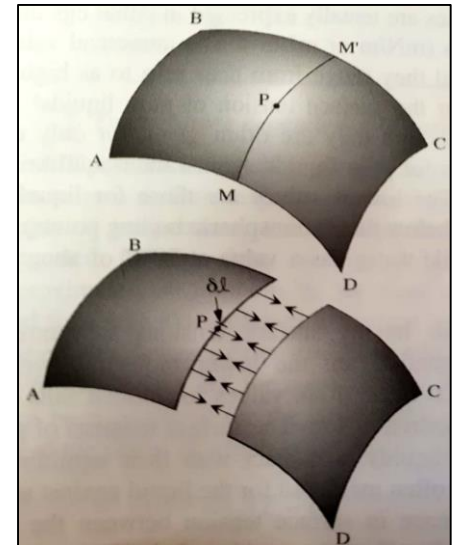
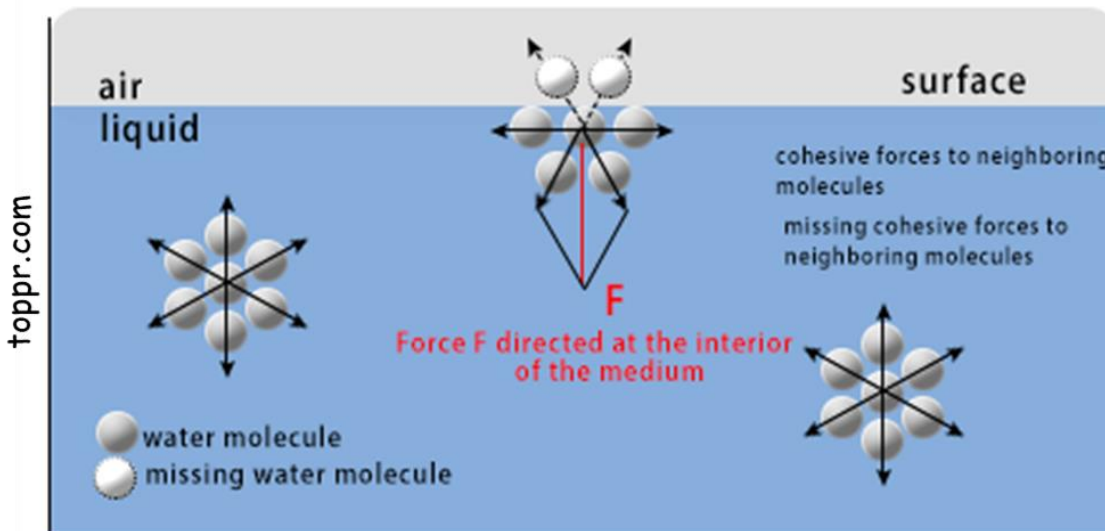**interfacial tension**
force/length along the dividing line @ P

$$\sigma = \frac{d|F|}{dl}$$

$$\delta W = \sigma dA$$

unit (SI): N/m or J/m²
more common: mN/m

Interfacial tension may be interpreted in terms of unbalanced intermolecular forces

air
surface
liquid

cohesive forces to neighboring molecules

missing cohesive forces to neighboring molecules

F

Force F directed at the interior of the medium

water molecule
missing water molecule

toppr.com

→ net inward attraction pulls surface molecules toward the interior; surface tries to minimize its area

Previously in ColloidsPhysChem...(II)

Attractive vdW interactions

δ⁺ *permanent* δ⁻   δ⁺ *permanent* δ⁻

$$V_{Keesom} = -\frac{B_{polar}}{r^6}$$

~ 5-25 kJ/mol

δ⁺ *permanent* δ⁻   δ⁺ *induced* δ⁻

$$V_{Debye} = -\frac{B_{induced}}{r^6}$$

~ 2-10 kJ/mol

δ⁺ *induced* δ⁻   δ⁺ *induced* δ⁻

$$V_{London} = -\frac{B_{disp}}{r^6}$$

~ 0.05-40 kJ/mol

(k_BT @ 25 ºC = 2.47 kJ/mol)

All attractive vdW interactions vary as 1/r⁶

$$V_{attractive} = -\frac{B_{attractive}}{r^6}$$

Repulsive vdW interactions

- strong repulsion when electron clouds overlap (hard-core repulsion)
- manifestation of Pauli's exclusion principle

$$V_{repulsive} = \frac{B_{repulsive}}{r^{12}}$$

Total interaction between two molecules: $V_{attractive} + V_{repulsive}$

$$V_{tot} = 4\varepsilon\left[\left(\frac{\delta}{r}\right)^{12} - \left(\frac{\delta}{r}\right)^{6}\right]$$

δ: r for which V_{tot} = 0
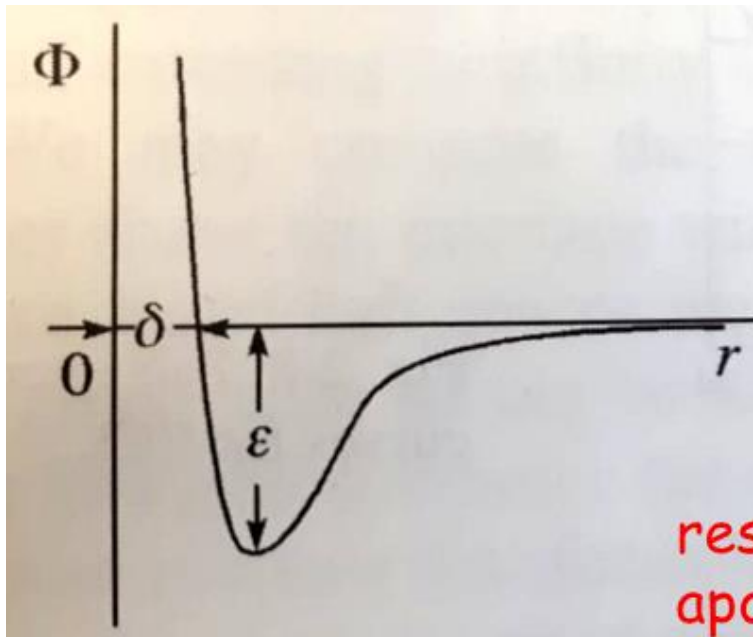   (molecular diemeter)

ε: depth of potential well

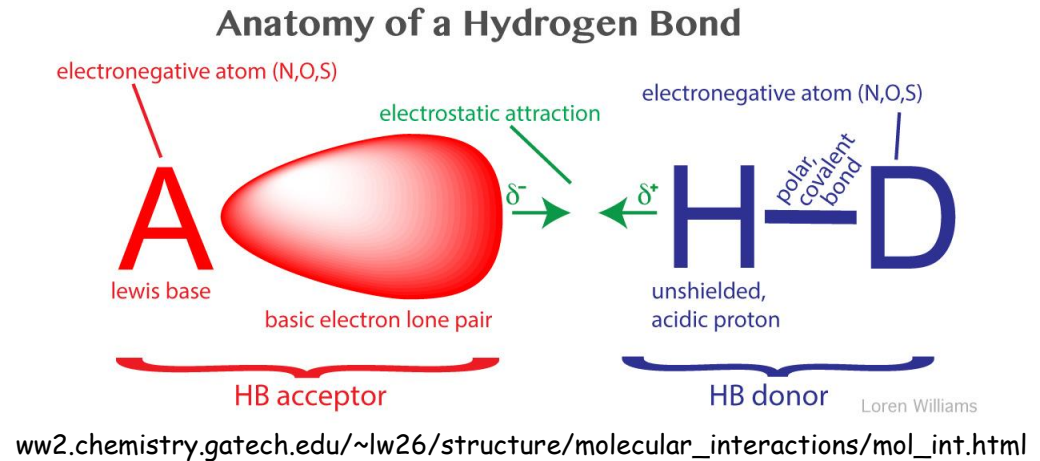Fig. 2-7: Schematic of Lennard-Jones potential function.

restricted to approx. spherical, apolar or weakly polar molecules

Previously in ColloidsPhysChem...(IV)

typically written: **D-H···A**

D: H-bond donor (N, O, F, S)

A: H-bond acceptor (N, O, F, S)
possesses a lone pair of e^-

Anatomy of a Hydrogen Bond

ww2.chemistry.gatech.edu/~lw26/structure/molecular_interactions/mol_int.html

water: the perfect example of H-bonding

- each water molecule can form 4 H-bonds
  with surrounding water molecules

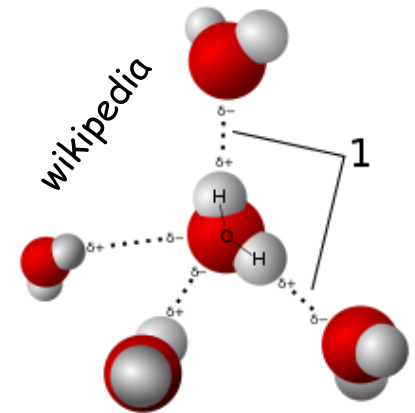- 2 lone e^- pairs + 2 δ^+ H

- reason for very high T_{boil}

- directional & with limited number of interaction partners

- strong; typical energies ~ 5-30 kJ/mol ($k_B T$ @ 25 ^{o}C = 2.47 kJ/mol)
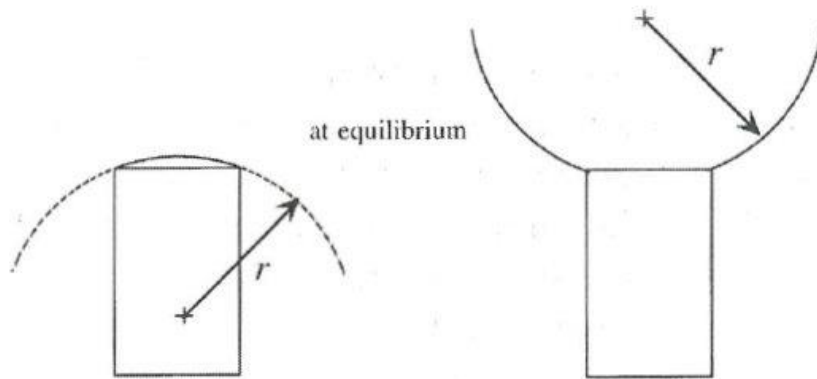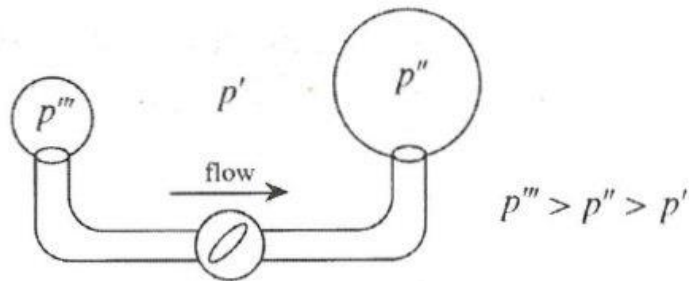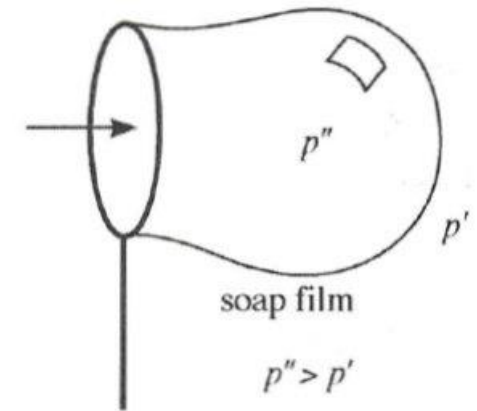
→ dynamically formed & broken

Pressure difference across curved interfaces

Defining the *shape & location* of fluid interfaces

-fundamental problem of capillary hydrostatics

- basis for most methods for measuring σ

- affects motion of liquids in porous media, thermodyn. properties of bubbles & drops

$p'' > p'$

$p''' > p'' > p'$

Deformation of an elastic membrane

- p" (concave side) > p' (convex side)

- Δp proportional to the curvature

- larger bubble grows @ the expense of the smaller one

- flow continues until curvatures are equal

Fig. 2-15: Spontaneous flow occurs from the smaller bubble (higher curvature) to the larger bubble until the spherical cap at the location where the smaller bubble started has the same radius of curvature as the final larger bubble.

Young-Laplace equation

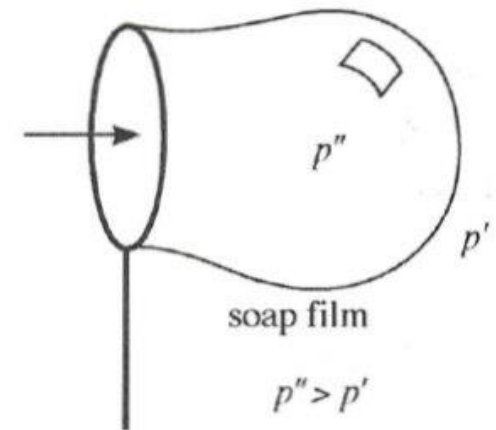**Pierre-Simon Laplace**
(1749-1827)

Thomas Young
(1773 – 1829)

wikipedia

$$\Delta p = p'' - p' = \sigma\kappa$$
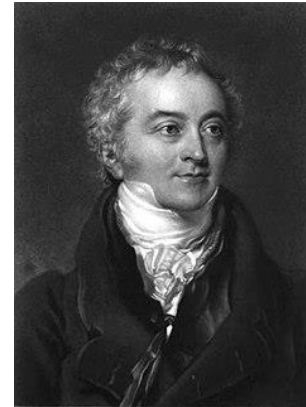
Δp: pressure jump across
a curved fluid interface

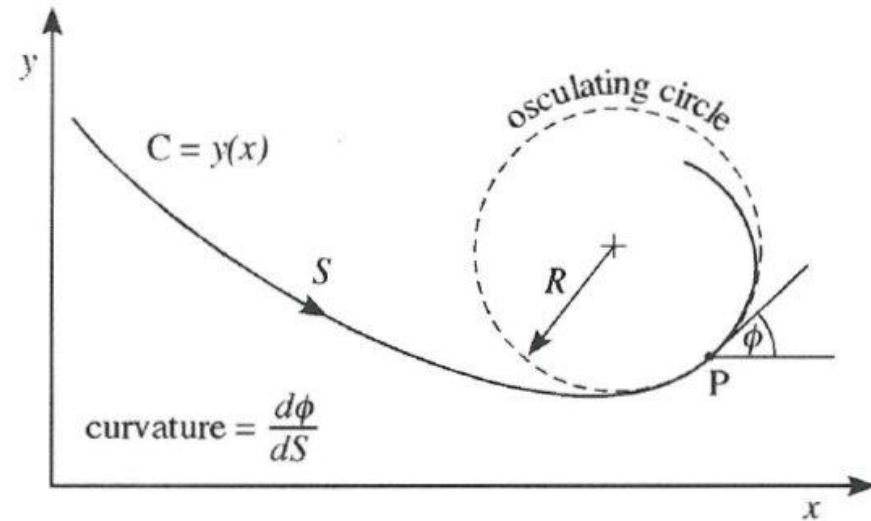σ: interfacial tension

κ: local curvature of the interface

p''

p'

soap film

$p'' > p'$

The curvature of a surface

Curvature of a plane curve y(x) @ P
rate of change of direction (φ) with arc length (S)

$$\kappa = \frac{d\varphi}{dS} = \pm\frac{d^2y}{dx^2}\left[1+\left(\frac{dy}{dx}\right)^2\right]^{-\frac{3}{2}}$$

for a circle (Ø 2R): $\kappa = \pm\dfrac{1}{R}$

radius of circle of curvature @ P: radius of curvature of y(x) @ P

$C = y(x)$

osculating circle

S

R

P

$$\text{curvature} = \frac{d\phi}{dS}$$

Curvature of a surface

two orthogonal planes passing through normal @ POI
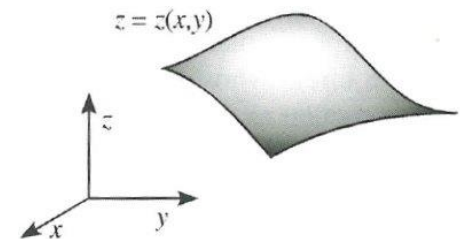
planes cut surface in two plane curves

$$\kappa = \pm\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$$

R_1, R_2: principal radii of curvature

General expression

$$\kappa = \pm\frac{\left(\frac{\partial^2 z}{\partial x^2}\right)\left[1+\left(\frac{\partial z}{\partial y}\right)^2\right]-2\left(\frac{\partial z}{\partial x}\right)\left(\frac{\partial z}{\partial y}\right)\left(\frac{\partial^2 z}{\partial x\partial y}\right)+\left(\frac{\partial^2 z}{\partial y^2}\right)\left[1+\left(\frac{\partial z}{\partial x}\right)^2\right]}{\left[1+\left(\frac{\partial z}{\partial x}\right)^2+\left(\frac{\partial z}{\partial y}\right)^2\right]^{3/2}}$$
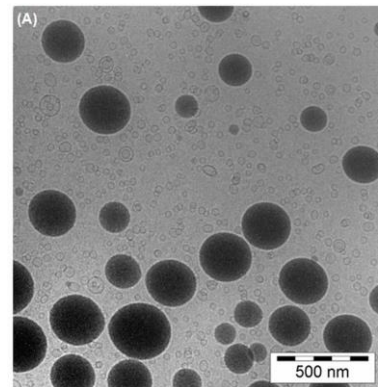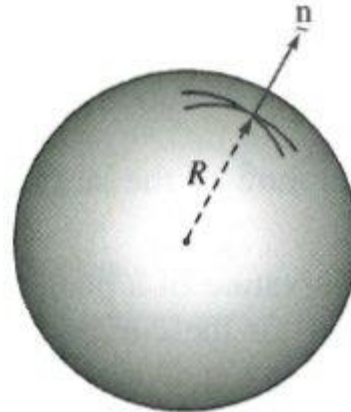
$z = z(x,y)$

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Curvatures of geometries of special interest

many surfaces of interest possess certain symmetries
→ simplified expressions for κ

Spheres or sperical caps
any normal to the surface
passes through center

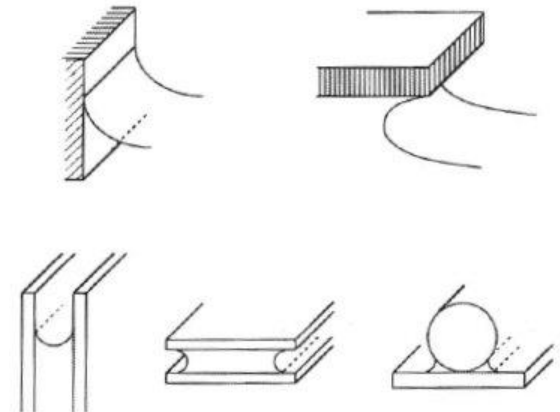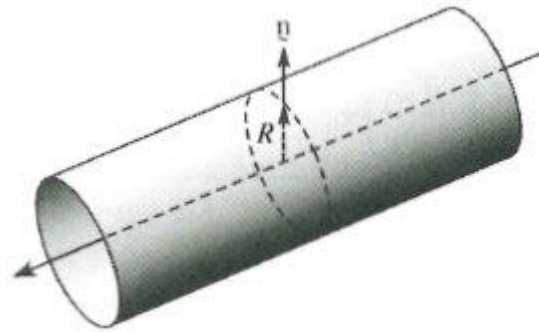$$\kappa = \pm\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{2}{R}$$

Cylindrical surfaces
any normal to the surface
passes through & is normal
to the axis of the cylinder

1st plane: circle with R
2nd plane: rectangle

$$\kappa = \pm\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{1}{R}$$

wikipedia

500 nm

Derivation of Young-Laplace equation

small patch (ADBC) of surface centered @ P
& enclosed by a curve @ a distance **ρ** from P

ρ is measured along the surface & is taken to
be very small

phase ('') is on the lower (concave) side of the
patch; phase (') is on the upper (convex) side

orthogonal lines AB and CD made by a pair of
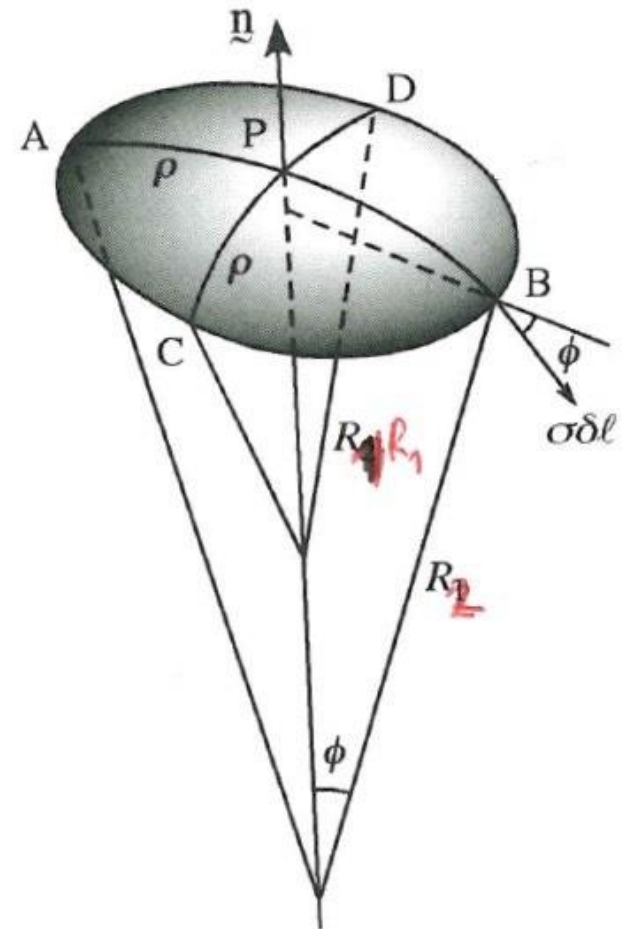orthogonal planes passing through $\hat{n}$

net upward (+$\hat{n}$ direction) force on the patch

$$F \uparrow = (p'' - p')\pi\rho^2$$

net downward (-$\hat{n}$ direction) force on the patch

$$F \downarrow = -\sigma\pi\rho^2\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

$$F \downarrow = F \uparrow \quad \Longrightarrow \quad \Delta p = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Methods for measuring surface tension

Basis: solutions to the Young-Laplace (Y-L)

Geometric methods
- based on direct determination of interface shape or position
- finding a σ value that produces the best match between a measured interfacial profile & a solution of the Y-L eq.

Force methods
- based on the measurement of a force (or mass, volume, pressure) & its comparison with the value computed from the Y-L eq.
- usually solid object is suspended in or detached from a fluid interface or drop/bubble detached from an orifice
- interfaces of high degree of symmetry used (axisymmetric/cylindrical)

Geometric methods
- capillary rise
- sessile drop (captive bubble)
- pendant drop (pendant bubble)
- spinning drop
- oscillating jet
- contracting circular jet

Force methods
- du Noüy ring detachment
- Wilhelmy plate (or rod)
- Langmuir barrier
- drop weight (volume)
- maximum bubble pressure

Coffee break

Why Mario must add *soap* to water to make bubbles? How *large* can the bubbles be?

Capillary rise

determination of meniscus position of a liquid in a tube (Ø r)

θ < 90°
→ concave meniscus
→ p_{up} > p_{down}

equilibrium
→ meniscus rises until p_{down}
   can support the
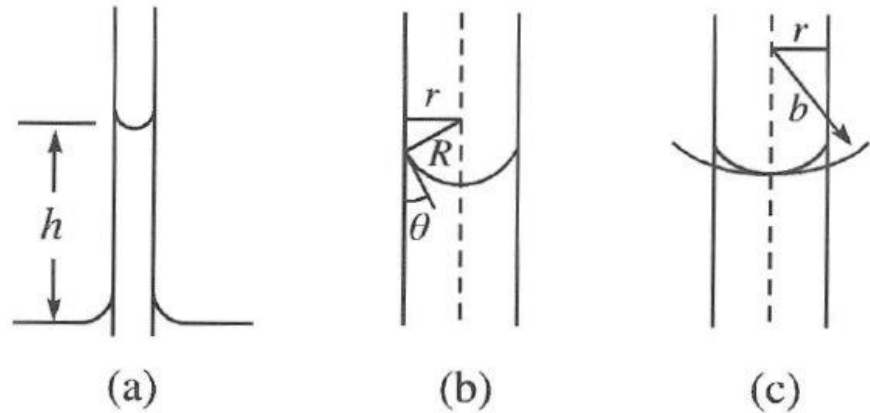   meniscus curvature

(a)   (b)   (c)

Fig. 2-38: The capillary rise method for measuring surface tension. (a) h is the equilibrium rise height, (b) If the meniscus is spherical, but the contact angle is > 0°, the radius of the meniscus is $R = r/\cos\theta$, where r is the radius of the capillary, and θ is the contact angle, (c) if the meniscus is flattened by gravity, the radius of the curvature at its apex is $b > r$.

for small r & θ = 0° gravity does not deform the meniscus

$$\Delta p = p_{up} - p_{down} = p_o - (p_0 - \rho gh) = \rho gh$$

$$\Delta p = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{2\sigma}{r}$$
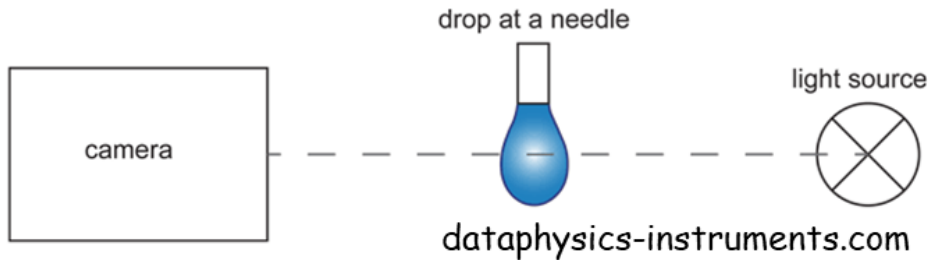
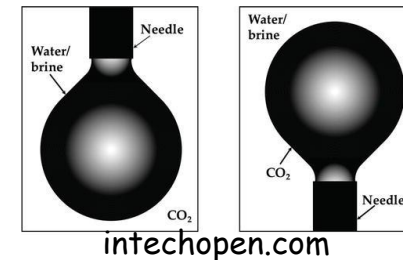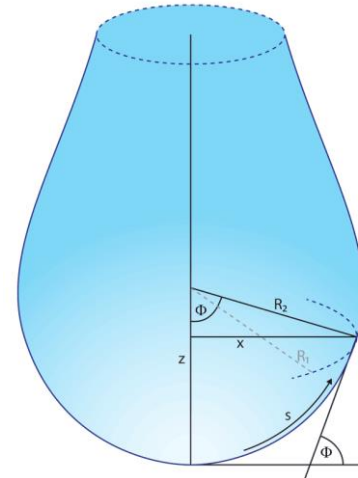$$\sigma = \frac{\rho grh}{2}$$

h: eq. rise height

ρ: liquid density

g: grav. acceleration

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Pendant drops & captive bubbles

Pendant drop (captive bubble): a drop (bubble) suspended from a needle (Ø 2r) in a bulk fluid phase

drop at a needle

camera

light source

dataphysics-instruments.com

optical system used to take an image of the drop
software performs drop shape analysis

intechopen.com

Drop shape: betermined by interfacial tension – gravity competition

$$\Delta P(z) = \Delta P_0 \pm \Delta \rho g z$$

$$\Delta P = (P_{\text{int}} - P_{\text{ext}}) = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

$$\frac{1}{R_1} + \frac{\sin \Phi}{x} = \frac{2}{R} \pm \frac{\Delta \rho g z}{\sigma}$$

$$\frac{d\Phi}{ds} = -\frac{\sin \Phi}{x} + \frac{2}{R} \pm \frac{\Delta \rho g z}{\sigma}$$

$$\frac{dx}{ds} = \cos \Phi$$

$$\frac{dz}{ds} = \sin \Phi$$

$$0 = x(s = 0) = z(s = 0) = \Phi(s = 0)$$

numerical fit of theor. drop shape to exp. shape → σ

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du Noüy ring & Wilhelmy plate

measurement of force required to detach a (Pt) ring (Ø 2r) from a liquid surface

maximum in measured force against height of ring above undisturbed surface

beyond max. force
→ meniscus contracts before final detachment

max. downward force $\quad F\downarrow = \dfrac{4\pi r\sigma}{F_c}$
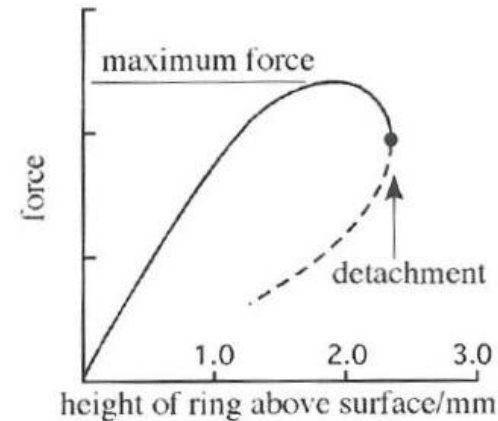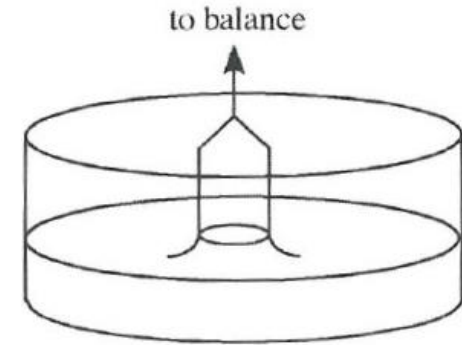
r: ring radius $\qquad F_c$: correction factor

to balance

maximum force

detachment

force

height of ring above surface/mm

1.0   2.0   3.0
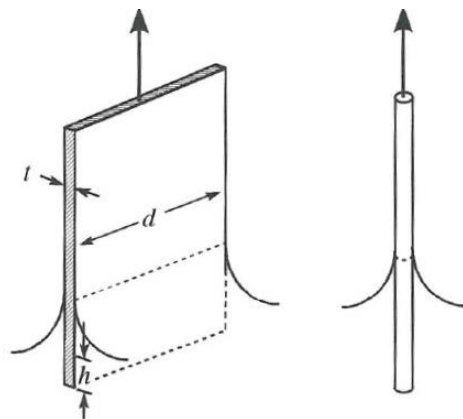

Fig. 2-41: Wilhelmy slide (or rod).

measurement of downward force on an partially immersed object

$$F_{net} = \sigma(2d + 2t) - (\rho g h t d)$$

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Maximum bubble pressure

formation of a bubble from a nozzle tip (Ø 2r)
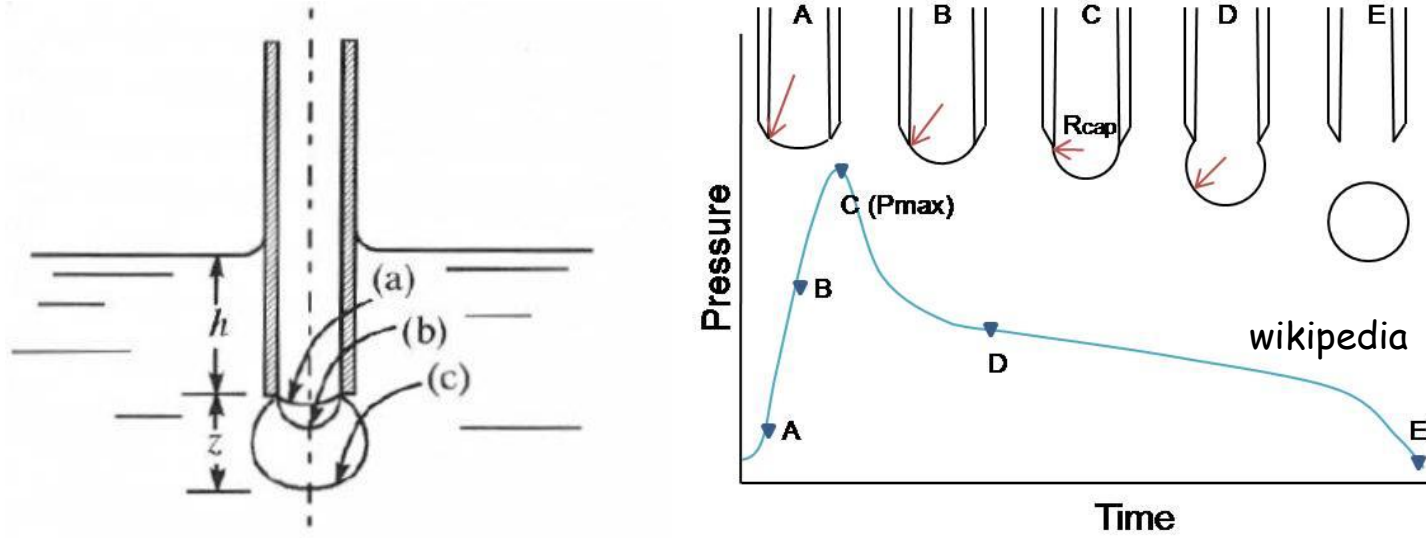
Fig. 2-46: Maximum bubble pressure method.

p_{max} required when radius of curvature of the bubble is minimum

hemispherical surface → $\quad p_{max} - p_{liq} = \dfrac{2\sigma}{r}$

advantages
- very rapid method (*ms* or less); can measure *dynamic σ*
- formed surface is fresh

The hydrophobic effect (I)

Hydrophobic interaction (IUPAC)

Tendency of hydrocarbons (or of lipophilic hydrocarbon-like groups in solutes) to form intermolecular aggregates in an aqueous medium, & analogous intramolecular interactions.
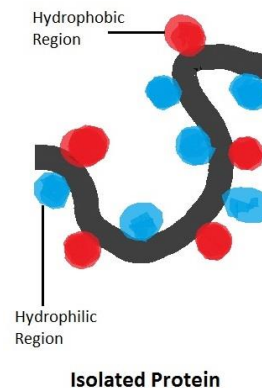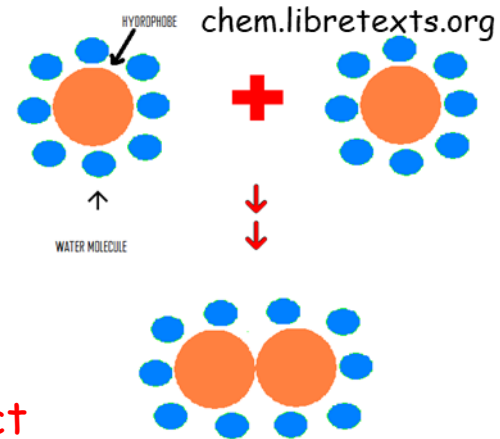
The name arises from the attribution of the phenomenon to the apparent repulsion between water & hydrocarbons. However, the phenomenon ought to be attributed to the effect of the hydrocarbon-like groups on the water-water interaction.

responsible for:

- the separation of oil-water mixtures into the two components

- biological effects: cell membrane & vesicle formation, protein folding, insertion of membrane proteins into the nonpolar lipid environment & protein-small molecule associations

hydrophobes: substances for which the hydrophobic eff. is observed

chem.libretexts.org

HYDROPHOBE
WATER MOLECULE

Hydrophobic Region

Hydrophilic Region

chem.libretexts.org

Isolated Protein
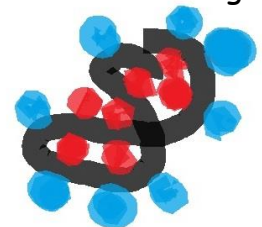
Protein in aqueous solution

The hydrophobic effect (II)

thermodynamic factors giving rise to the hydrophobic effect: complex & still not completely understood

$$\Delta G = \Delta H - T \Delta S$$

Small hydrophobic inclusions
- number of H-bonds retained but degree of freedom in how to form them reduces
- "structuring" of water molecules around the inclusion
  → **S is reduced, ΔG > 0**

Nature **2005**, *437, 640*

Figure 1 | Configurations of liquid water molecules near hydrophobic cavities in molecular-dynamics simulations.

Large (>1 nm) hydrophobic inclusions
- on average: one H-bond (~ 10 $k_B T$) per water molecule broken
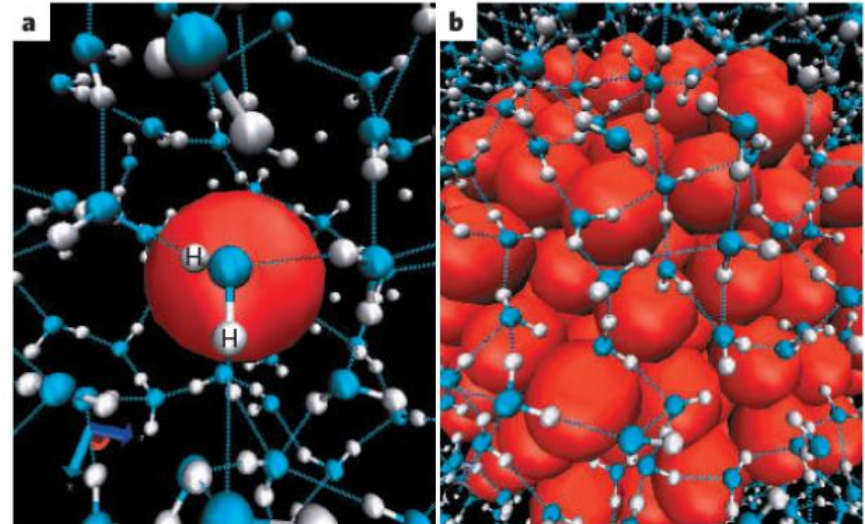- replacement of H-bond with vdW interaction (lower inter. energy)

High hydrophobe concentration
- segregation of water & hydrophobic species (phase separation)

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Surfactants or amphiphiles (I)

surfactant: short for **surf**ace **act**ive **ag**ent (Langmuir); a substance that is surface-active: adsorbs at an interface & reduces σ

amphiphile: a substance that has at least two portions segregated from one another, one being hydrophilic (head) & the other hydrophobic (tail)

(αμφί: "from both sides"; φίλος: "friend")

lipid: long chain aliphatic hydrocarbons (fats) & derivatives originating in living cells; ***only some***, such as fatty acids, are also surfactants

detergent: generally refers to synthetic surfactants used in cleaning agents

often classified according to head group

ionic

non-ionic
(C chain in head group interrupted by O atoms → polarity

zwitterionic
low pH: cationic
high pH: anionic

	Anionic	Cationic	Non-ionic	Zwitterionic
	SDS	CTAB	Brij	DMPC

Table 3-3: Some typical surfactant head groups

-OH	Hydroxyl
-COOH (low pH)	Carboxyl
-COO⁻ (high pH)	Carboxylate
-SO_4^-	Sulfate
-SO_3^-	Sulfonate
-$H_2PO_4^-$ (mod. pH)	Phosphate
-NH_2 (high pH)	Amino
-NH_3^+ (low pH)	Ammonium
-$N(CH_3)_3^+$	Trimethylammonium, or Quaternary ammonium
-$(OCH_2CH_2)OH$	Polyoxyethylene, or polyethylene oxide

Surfactants (II)

key feature of surfactants: segregation of hydrophilic & hydrophobic moieties

hydrophobic   hydrophilic

dataphysics-instruments.com
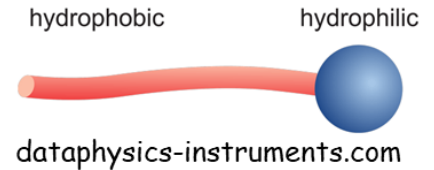
hydrophilic head
can form H-bonds with water
→ "immerses" in aqueous phases

hydrophobic tail
cannot form H-bonds with water
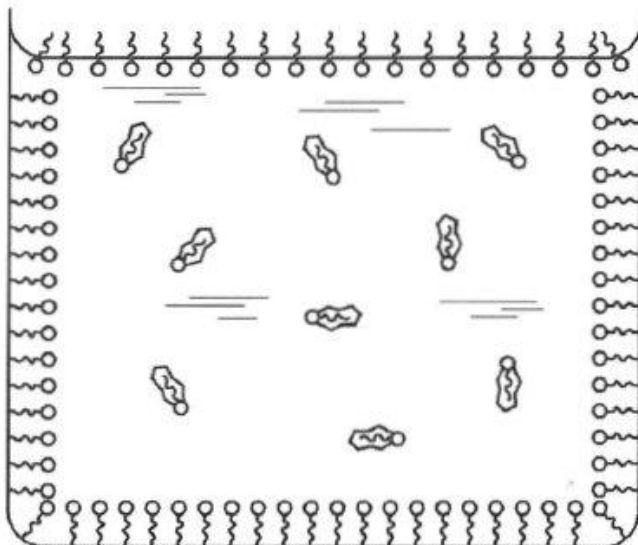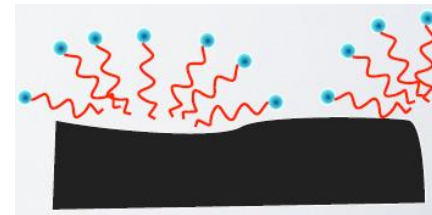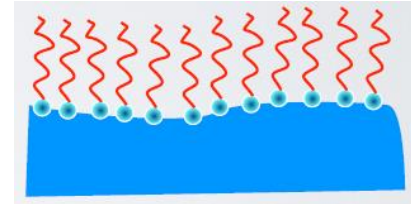→ "immerses" in oil phases or
   "sticks" to hydrophobic solids

Fig. 3-16: Schematic of surfactant adsorption from aqueous solution, both to the air-water surface and the water-solid interface of the container wall. The "iceberg" of structure water surrounding the hydrophobic tails in solution is depicted.

glucose not a surfactant because hydrophilic hydroxyl groups are not segregated from the hydrocarbon structure

CH$_2$OH

20
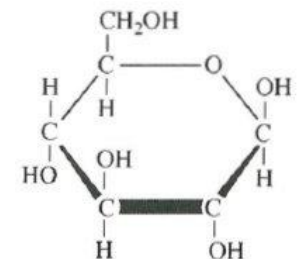
Surfactants (III)

surfactants strongly decrease σ, even @ low concentrations

σ (c_{surf}) curves remarkably similar for different surfactants

above a critical c_{surf}, σ remains constant
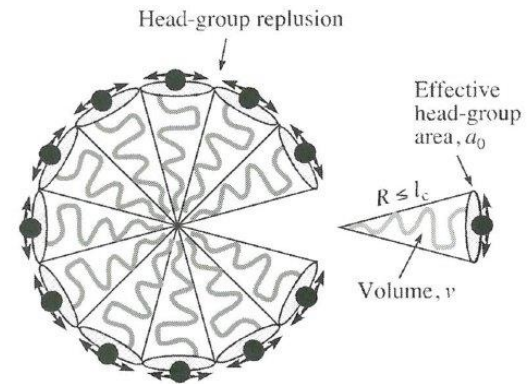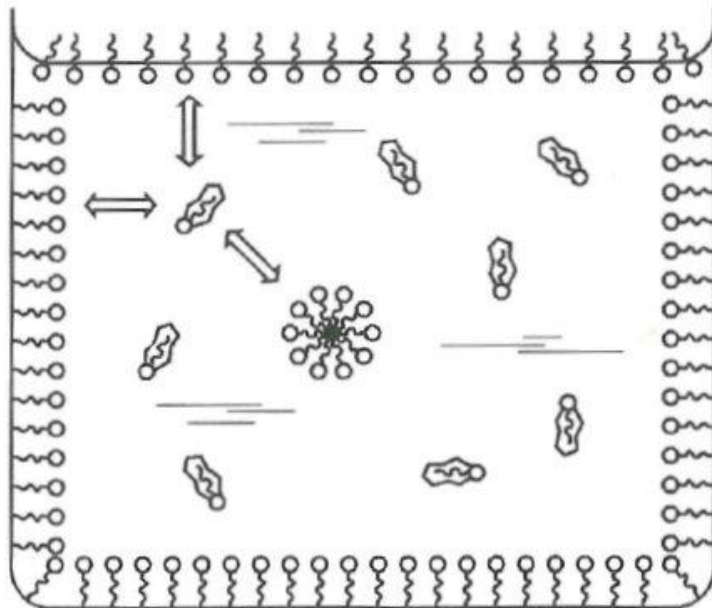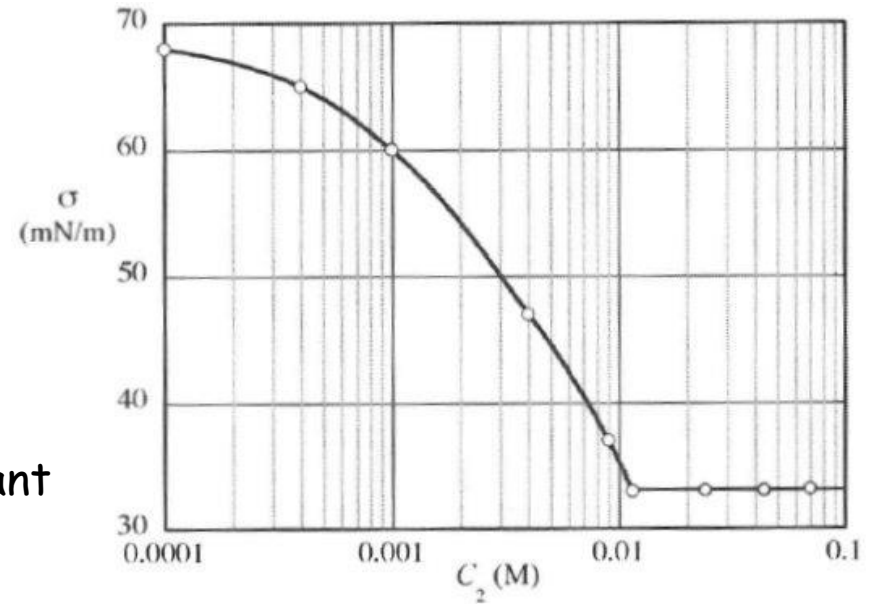→ *critical micellar concentration*

Fig. 3-31: Micelles as shape-filling structures, depend upon the size and shape characteristics of the monomer.