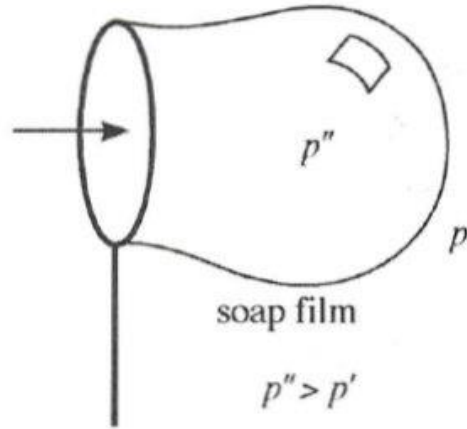# Physical Chemistry of Colloids
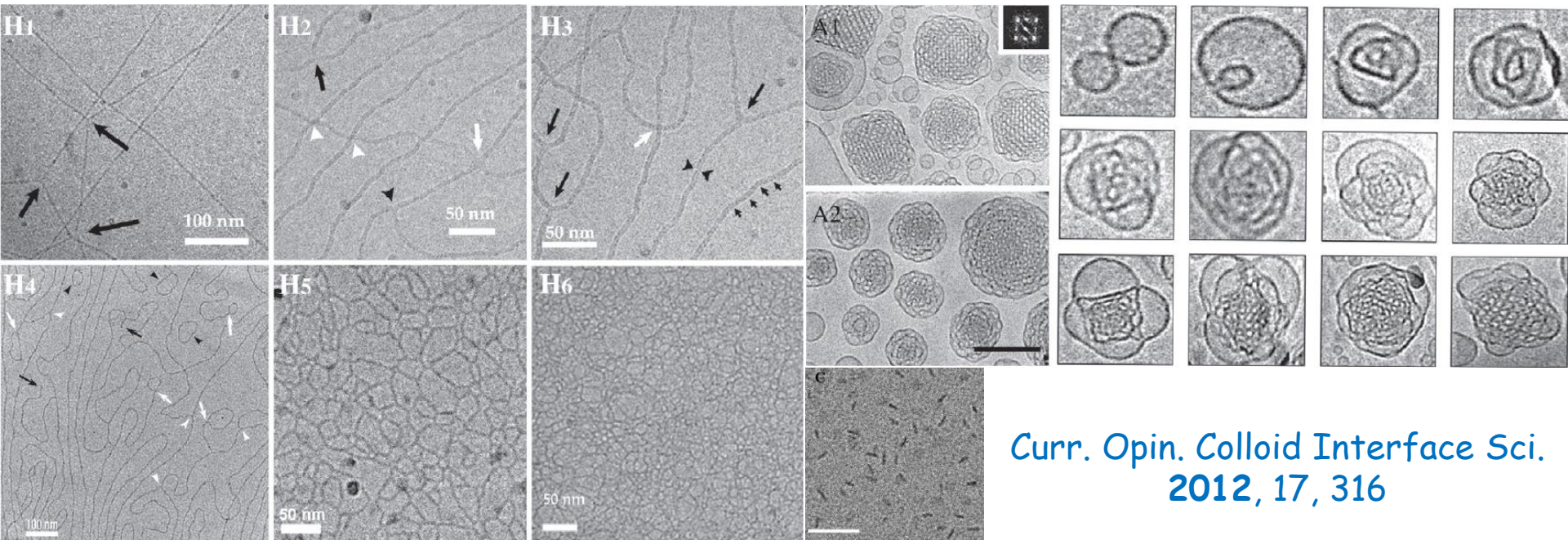
Lecture 4, *March 13, 2019*

Manos Anyfantakis
Physics & Materials Science Research Unit

Previously in ColloidsPhysChem...(I)
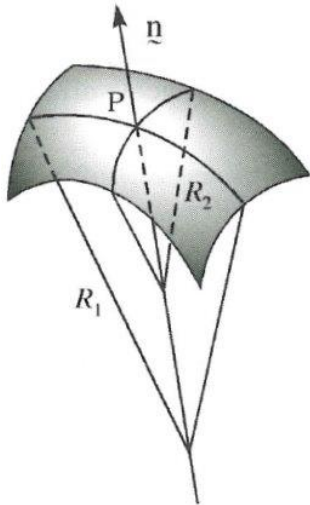
Pierre-Simon Laplace   **Thomas Young**

$$\Delta p = p'' - p' = \sigma \kappa$$

p''

p'

soap film

$p'' > p'$

Δp: pressure jump across a curved fluid interface

σ: interfacial tension

κ: local curvature

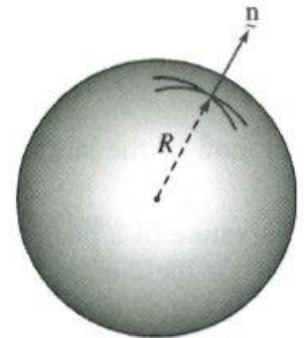## Curvature of a surface

two orthogonal planes passing through normal

planes cut surface in two plane curves

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

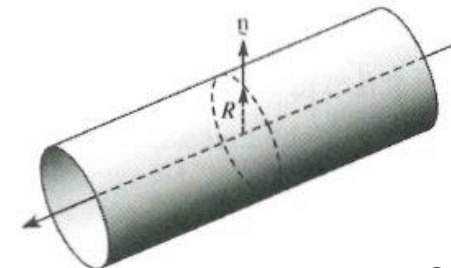R_1, R_2: principal radii of curvature

Spheres/spherical caps

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

Cylindrical surfaces

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

Previously in ColloidsPhysChem…(II)

Basis of methods to measure σ: solutions to the Young-Laplace (Y-L)

Geometric methods: direct determination of interface shape or position

Force methods: measurement of a force (or mass, volume, pressure) & its comparison with the value computed from the Y-L eq.

Pendant drop method

Drop shape: interfacial tension – gravity competition

$$\Delta P = (P_{\text{int}} - P_{\text{ext}}) = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \qquad \Delta P(z) = \Delta P_0 \pm \Delta \rho g z$$
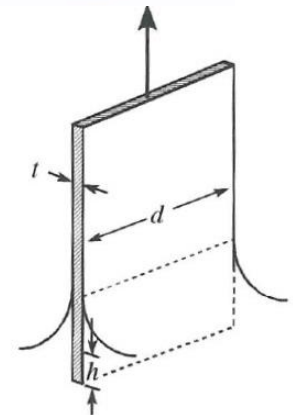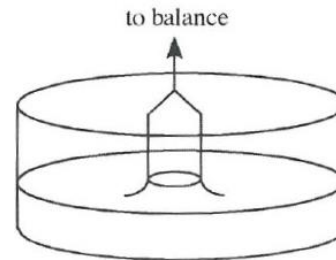
wikipedia

du Noüy ring & Wilhelmy plate methods

measurement of downward force on an partially immersed object

maximum in measured force against height of ring above undisturbed surface

to balance

max. downward force $F \downarrow = \dfrac{4\pi r \sigma}{F_c}$

r: ring radius F_c: correction factor

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

3

Hydrophobic effect

Tendency of hydrocarbons (or of lipophilic groups in solutes) to form intermolecular aggregates in an aqueous medium

Name arises from the attribution of the phenomenon to the apparent repulsion between water & hydrocarbons. However, the phenomenon must be attributed to the effect of the hydrocarbon-like groups on water-water interaction.

chem.libretexts.org

Hydrophobic Region

Hydrophilic Region

Isolated Protein
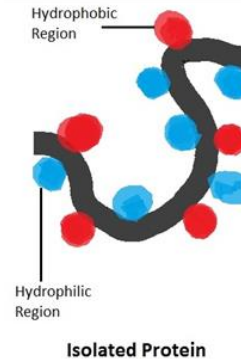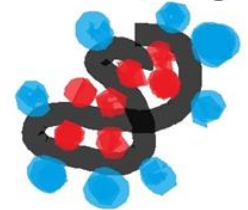
Protein in aqueous solution

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

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**

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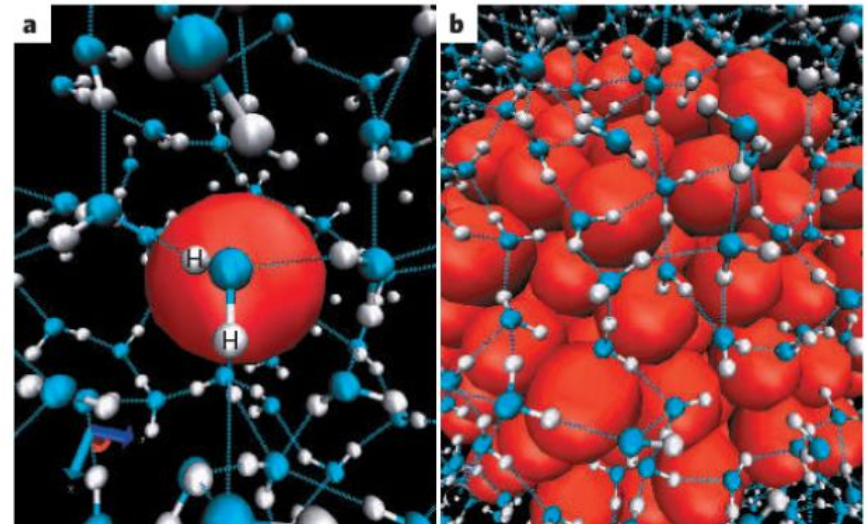- replacement of H-bond with vdW interaction (lower inter. energy)

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

Previously in ColloidsPhysChem...(IV)

surfactant: short for **surf**ace **act**ive **agent** (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")

key feature of surfactants: segregation of hydrophilic & hydrophobic moieties

hydrophobic   hydrophilic

dataphysics-instruments.com
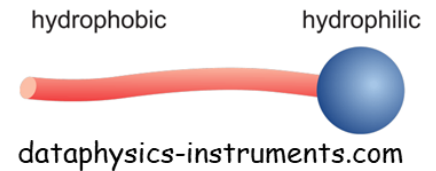
hydrophilic head
can form H-bonds with water
→ "immerses" in aqueous phases
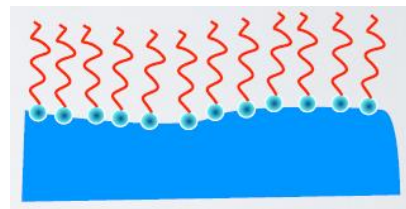
hydrophobic tail
cannot form H-bonds with water
→ "immerses" in oil phases or
   "sticks" to hydrophobic solids

Anionic   Cationic   Non-ionic   Zwitterionic

SDS   CTAB   Brij   DMPC

Na$^+$ Br$^-$ HO   n~4

O=S=O

5
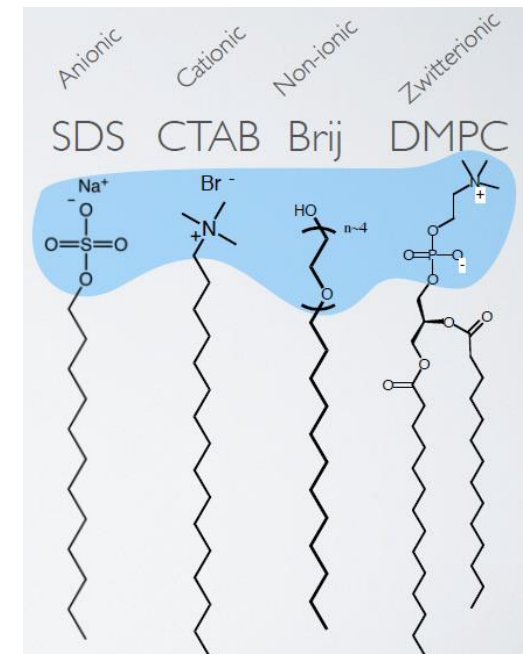
Surfactant adsorption at interfaces

Surfactants seek interfaces because only there thy can orient themselves to satisfy the solubility characteristics of both parts of their structure

surfactants in solution
the hydrophobic tail is surrounded
by an 'iceberg' of structured water

adsoprtion to (LG or LS) interface

$$\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad}$$

- 'iceberg' water molecules released into the solution → large ΔS increase

- ΔH_{ad}: often small; either negative (e.g. tail-tail vdW attractions) or positive (electrostatic repulsion between heads)

ΔG_{ad} large & negative → adsorption favorable

apparent attraction of hydrophobic moieties in water for air or solid surface
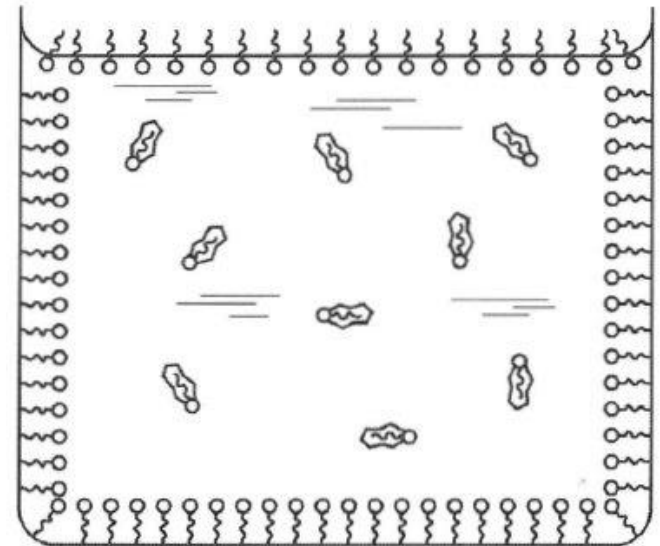→ hydrophobic effect

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.

Application to colloidal dispersions

Numerous nanoparticle (NP) types are hydrophobic (e.g. carbon nanotubes)

Aqueous dispersions of hydrophobic NPs particles aggregate if not stabilized (hydrophobic effect)

common solution: addition of surfactant
→ surfactants adsorb on NP surface
→ hydrophilic coating around the NPs
→ addition of repulsive forces between NPs that prevent aggregation

Mater. Lett. **2016**, *178*, 128
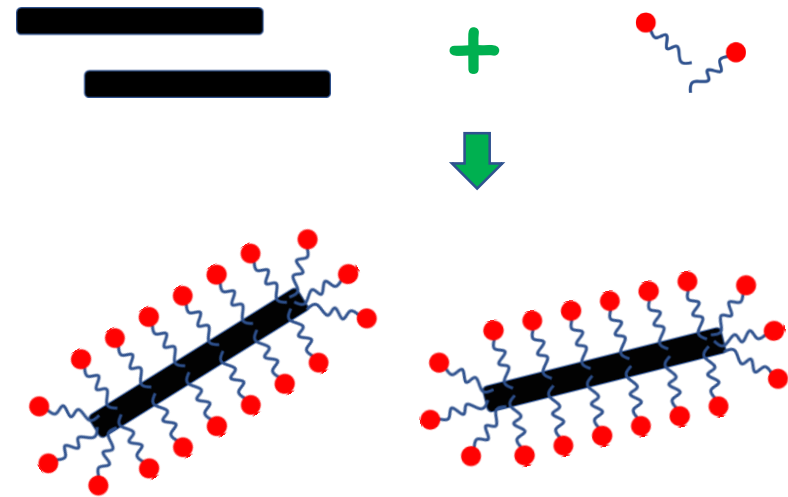
Repulsive interparticle forces

eletrostatic (ionic surfactants)

steric (neutral surfactants, polymers)
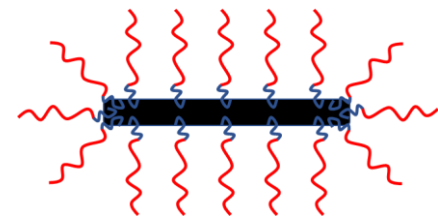
Surfactant-induced surface tension decrease

surfactants migrate to the interface with their
tails sticking out → creation of a new interface

low [surfactant]: *some* water molecules replaced
by surfactants (incomplete monolayer)

hydrocarbon tails interact through London
forces (weaker than H-bonding) → σ is reduced

σ decrease becomes stronger the more
surfactants are adsorbed at the interface

interface saturation: addition of more surfactant
does not decrease σ further

SDS in phosphate buffer

solvent

CMC
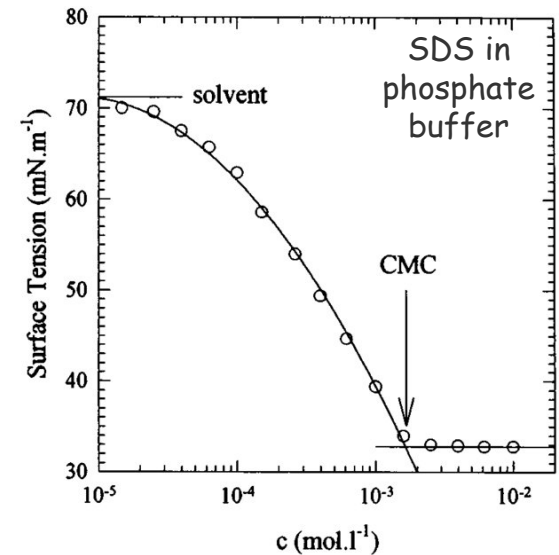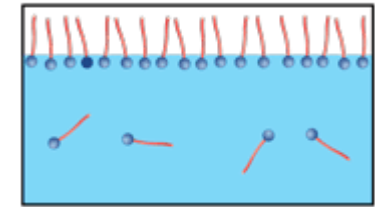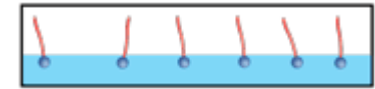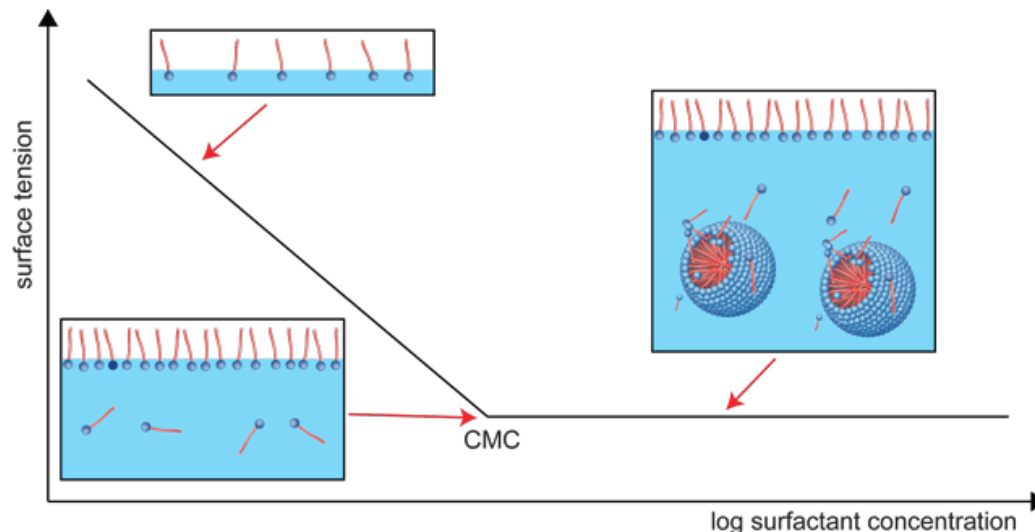
micelle self-assembly
spontaneous formation of
aggregates to minimize
contact of apolar chains
with the polar solvent

Characteristics of surfactant micelles

tendency to form micelles (as for adsorption):
hydrophobic effect

CMC: critical micelle concentration
≈ 1-10 mM (0.01-0.1 wt%)

equilibrium between monomers, micelles & adsorbed
(mono) layers (typical lifetimes ~ s-min)
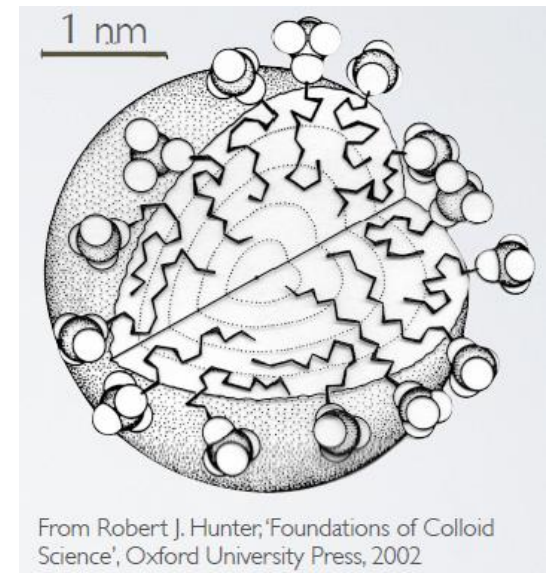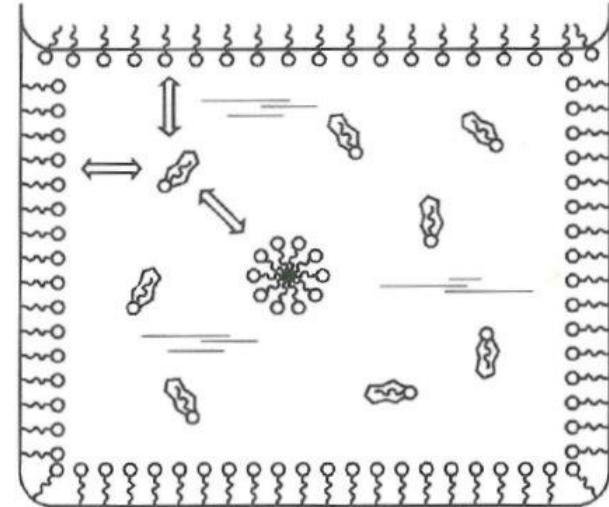
micellar size & shape varies; often they are spherical
  - micelle radius ≈ length of hydrophobic tail
  - limited number of 'monomers' (aggregation number)
  -spherical micelles: few tens - hundreds surfactants

although an apparent ordering of the surfactants
takes place, S_{tot} increases → G decreases

alkyl chains in the micelle core are disordered

H-bonds & dipole interactions very important:
  - weaker micellization tendency in non-aqueous solvents
  - amphiphiles with small non-ionic heads (e.g. alcohols)
     → no micelles

1 nm

From Robert J. Hunter, 'Foundations of Colloid
Science', Oxford University Press, 2002

Effect of CMC on solution properties

many of the solution properties show dramatic slope changes near the CMC

→ can be explained by micelle formation

→ serve as methods for measuring CMC

interfacial tension
its decrease stops with [surf.] as more surfactants do not increase interfacial packing, but contribute to micelle formation

molar electrical conductivity
(for ionic surfactants) decreases sharply with micellization due counterion binding to the micelle interface
→ neutralization of portion of electrolyte

Fig. 3-20: Schematic diagram of physical property changes of aqueous solutions of sodium dodecyl sulfate at 25°C as a function of concentration.

turbidity
sharp increase beyond CMC; micelles scatter light more strongly than isolated surfactants

osmotic pressure
depends on the number of particles in a unit volume of solution
increases more slowly with [surf.] when additional surfactants aggregate into micelles
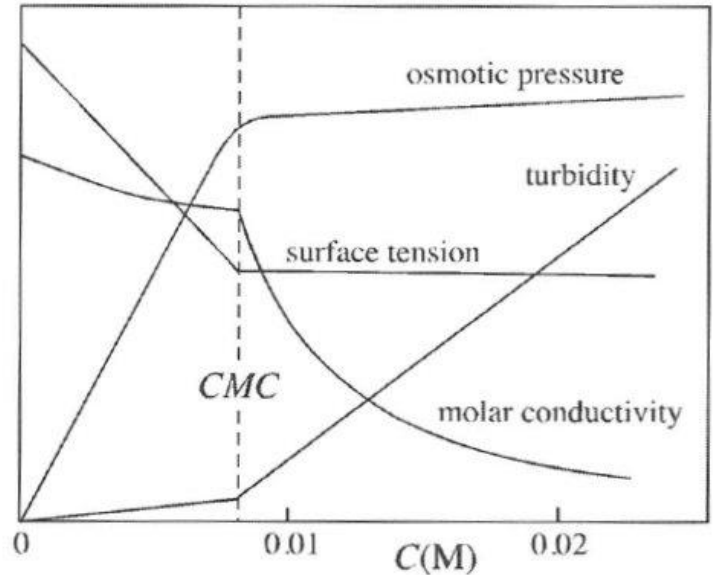→ can be used to determine aggregation number too

Parameters affecting the CMC

large database of CMCs for numerous surfactants → trends with various factors

increase of hydrophobic chain length
CMC decreased regularly
ionic surfactants: addition of a –CH$_2$- → ~ CMC/2
non-ionic (PEO type): –CH$_2$- addition → ~ CMC/3

13.4 mM
$CH_3(CH_2)_{10}CH_2-N^+-CH_3$ with CH_3, CH_3, Br^-

0.92 mM
$H_3C(H_2C)_{15}-N^+-CH_3$ with CH_3, CH_3, Br^-

**non-ionic surfactants (PEO type) lower CMCs than ionic ones (same tail, T)**
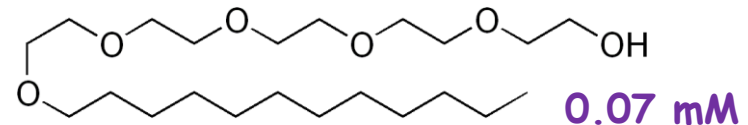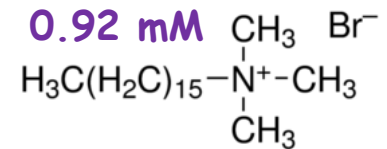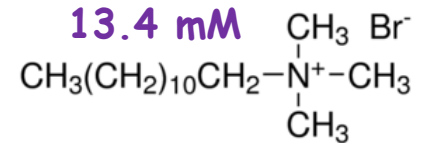no repulsion between head groups in the former
same tail: CMCs differ by an order of magnitude

0.07 mM

anything reducing repulsion between head groups decreases CMC of ionic surfactants
addition of salt → screening effect
given compound: CMC directly depends on [counterion]

$C_{14}TAB$

■ without NaCl
□ 1.0 M NaCl

σ / mN m^{-1}

c / M

11
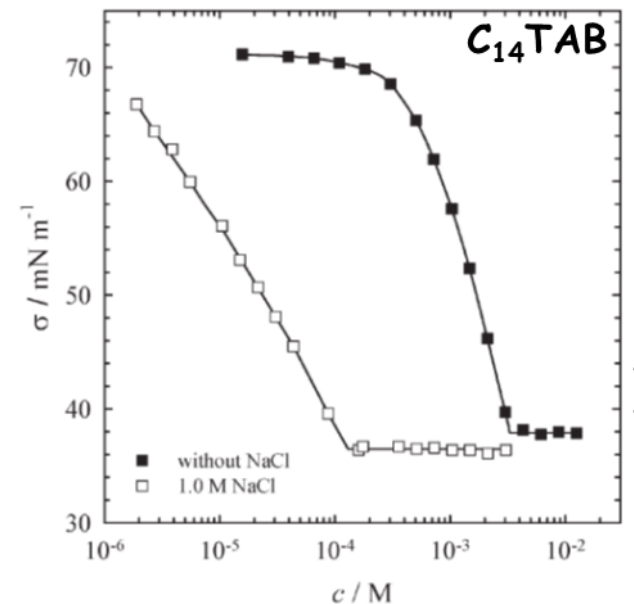
Parameters affecting the CMC (II)

T effects on CMC can be complex
ionic micelles: weak effect over significant T ranges
neutral micelles: T increase → sharp CMC decrease

Krafft point: minimum T to form micelles (ionic surfactants)
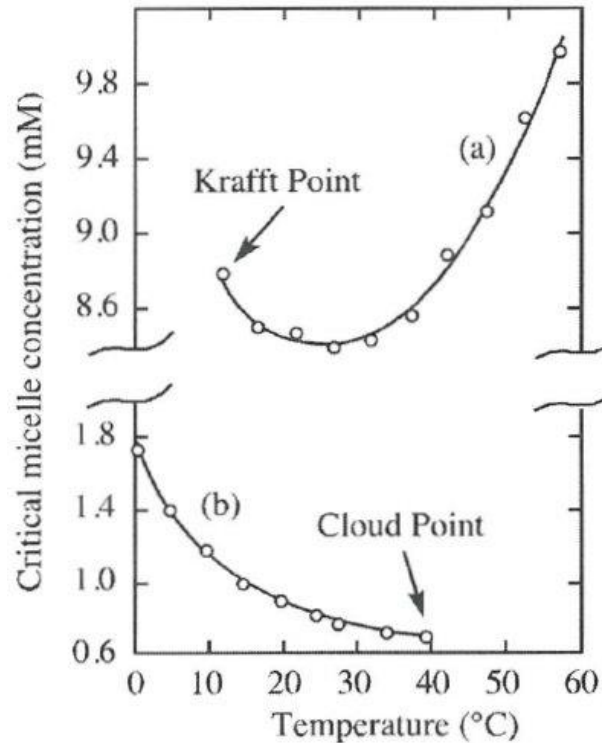**Cloud point:** large aggregates, turbidity (non-ionic surfactants)

Fig. 3-23: Variation of *CMC* with temperature for:
(a) sodium dodecyl sulfate;
(b) $CH_3(CH_2)_9(C_2H_4O_5)OH$
After [Elworthy, P. H., Florence, A. T., and Macfarlane, C. B., **Solubilization by Surface Active Agents**, Chapman and Hall, London, 1968.]

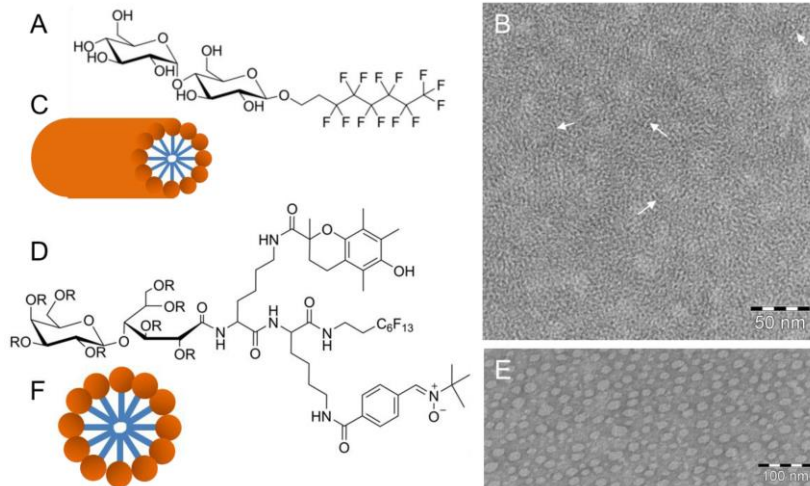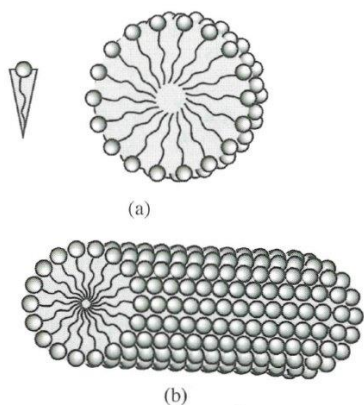**Factors that decrease CMC increase micelle size**
aggregation number: 30-300 (ionic); 200-20,000 (PEO)

Coffee break

chem.libretexts.org

Why Mario must add *detergent* in the washing machine in order to get clean clothes?

Micelles are not always spherical

(a)

(b)

A

C

D

F

B

50 nm

E

100 nm

Polymers **2017**, *9*(10), 521

(A) The nonionic fluorinated octyl maltoside derivative (F6OM). (B) TEM image of a negatively stained sample showing a dense ==fiber network==. (C) Schematic model of a rod-shaped micelle. (D) Chemical structure of FATxPBN with R = H. (E) TEM image of a negatively stained sample showing large ==globular micelles==. (F) Schematic model of a spherical micelle.
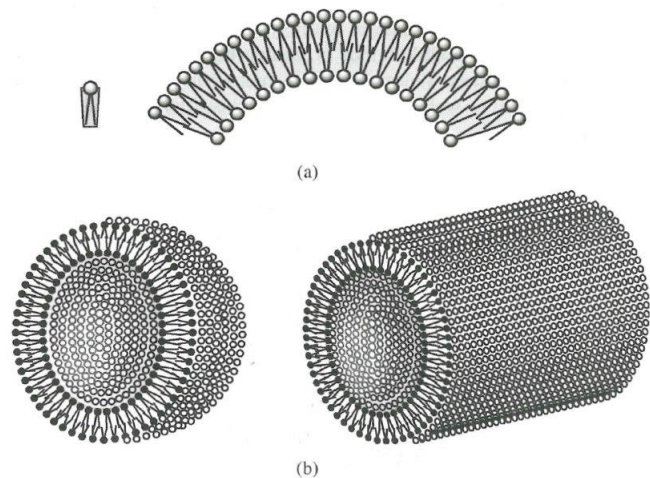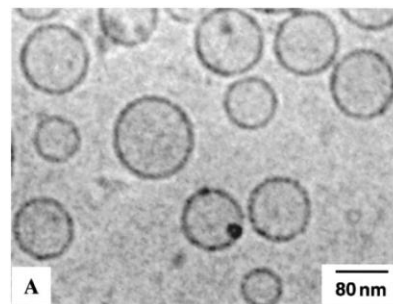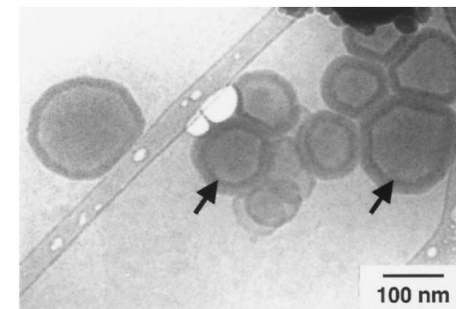
Proc Natl Acad Sci. **2001**, *98*, 1353

(a)

(b)

Fig. 3-33: (a) Curved bilayers structures: ½ < *CPP* < 1; (b) Unilamellar vesicle and tubule.

A

80 nm

(A) Cryo-TEM image of CTAB/SOS/water (2 wt % total surfactant, CTAB/SOS ratio of 3:7 by weight) system showing ==unilamellar vesicles==.

100 nm

Cryo-TEM of CTAByFC7 (2 wt% total surfactant, CTAByFC7 ratio of 2:8 by weight) in 1 wt % NaBr. ==Two-layer vesicles== are distinguished from one-layer vesicles by the darker rim on the inside edge of the vesicle membrane (arrows)

14

What determines the micelle shape?

surfactants to form a space-filling sphere
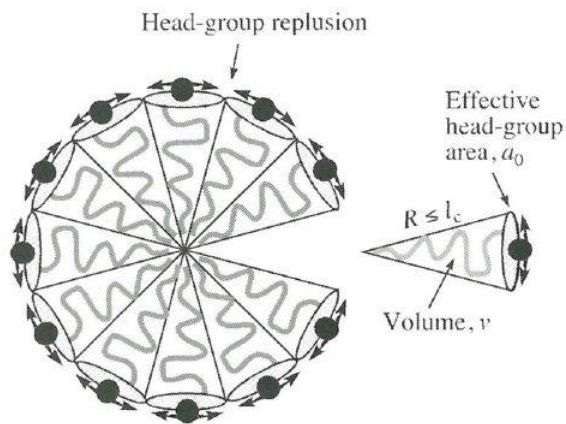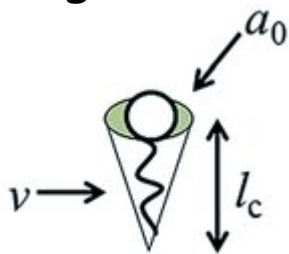→ geometric constraints on heads & tails

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

Critical Packing Parameter
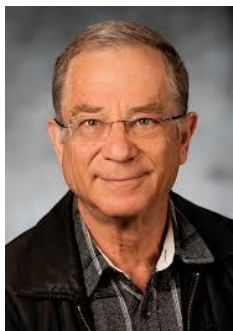
$$p = \frac{v}{a_0 l_c}$$

Jacob Israelachvili

v: volume of apolar tail

a_0: area of polar head interfcace

l_c: max. length of apolar tail

| Critical Packing Parameter $(v/a_0 l_c)$	Critical Packing Shape	Structures Formed
< 1/3	Cone	Spherical micelles
1/3 – 1/2	Truncated cone	Cylindrical micelles
1/2 -1	Truncated cone	Flexible bilayers, vesicles
~1	Cylinder	Planar bilayers
>1	Inverted truncated cone or wedge	Inverted micelles

Examples using the Packing Parameter
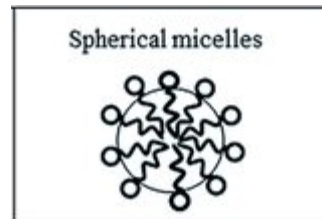
apolar aliphatic chains

- $v_{CH2} \approx 26.9 \times 10^{-3}$ nm^3
- $v_{CH3} \approx 27.4 \times 10^{-3}$ nm^3

- $l_{c,CH2} \approx 0.127$ nm
- $l_{c,CH3} \approx 0.154$ nm

$$p = \frac{v}{a_0 l_c}$$

example I: SDS

O–S–O$^-$ Na$^+$

Spherical micelles
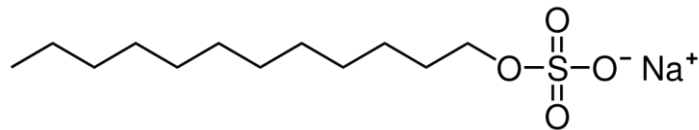
- sulphate head area $a_0 \approx 0.127$ nm^2
- **p ≈ 0.37**

example II: DPPC

Flexible bilayers, vesicles
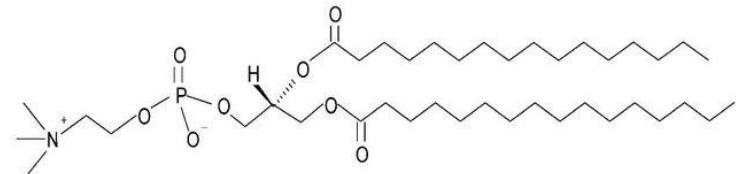
- phosphatidyl choline $a_0 \approx 0.72$ nm
- **p ≈ 0.58**
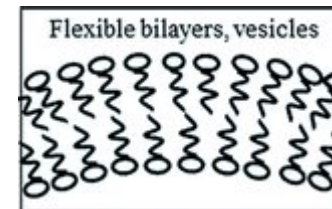
spherical micelles: common single-tail surfactants @ low [salt]

cylindrical micelles: common single-tail surfactants @ high [salt], single-tail nonionics with small head groups

*flexible bilayers/vesicles:* double-chain surfactant with large heads

Lyotropic liquid crystals from surfactants

surfactants in aqueous solutions form *lyotropic* liquid crystals

liquid crystals (LC)

- matter state with properties between liquids (e.g. flow) & solid crystals (long-range order)

- made from molecules, aggregates or nanoparticles that are anisometric (e.g. rod-like (calamitics) or disc-like (discotics))
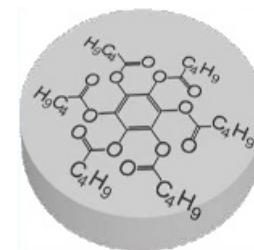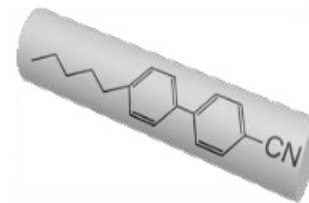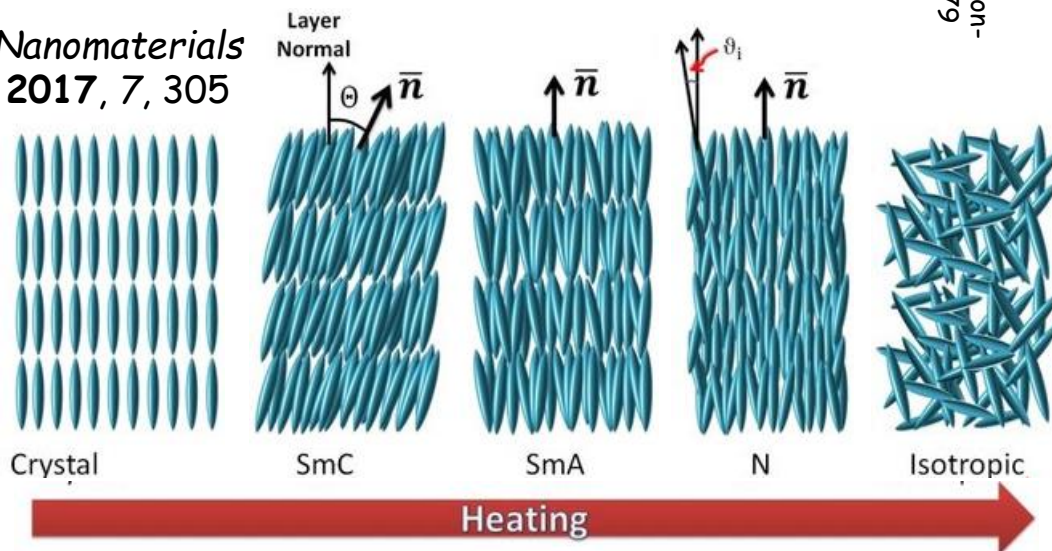
thermotropic LCs

- typical constituents: small, anisometric organic molecules

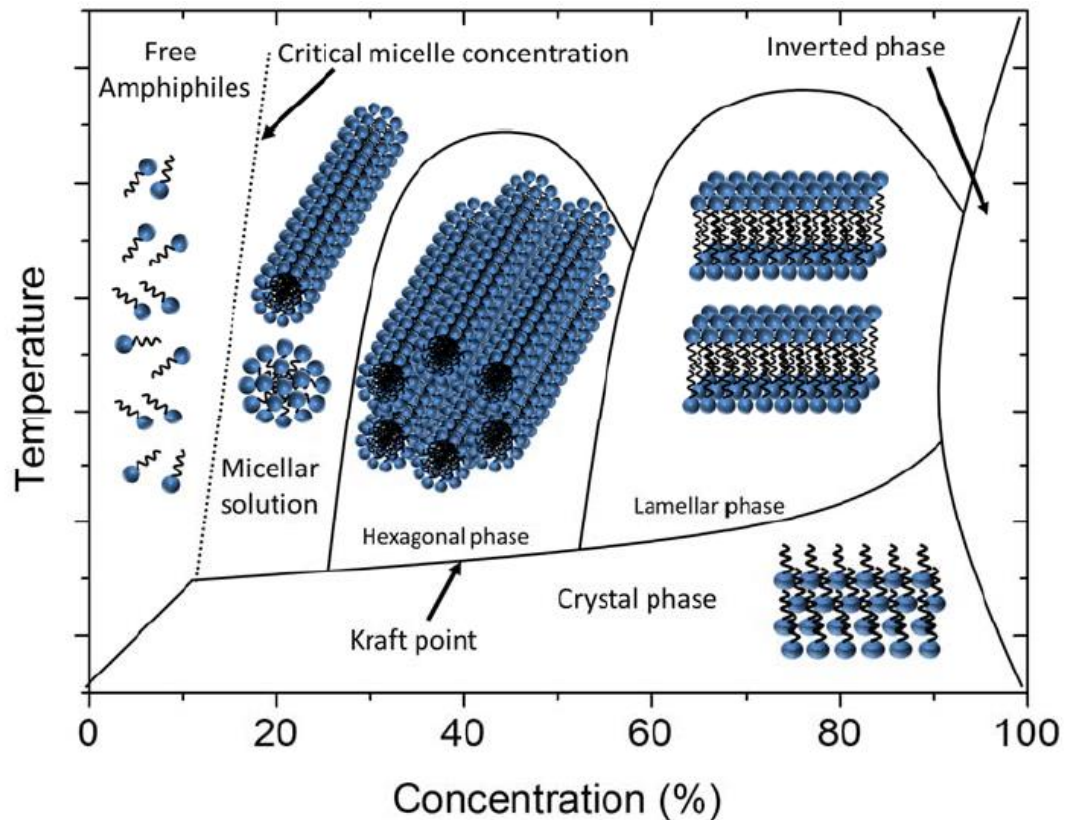- phase transitions occur with changes in temperature

lyotropic LCs

- molecule aggregates or particles in a solvent

- phase transitions occur with changes in T & concentration

Nanomaterials **2017**, *7*, 305

Figure 3. Schematic illustration of the phase diagram of an amphiphilic surfactant in an isotropic solvent, forming lyotropic phases. Crossing the critical micelle concentration, cmc, spherical or cylindrical micelles are formed. At higher surfactant concentrations, these can aggregate to liquid crystalline phases, namely the hexagonal and the lamellar phase, for increasing concentration. Cubic phases, which are not shown in this figure, can occur at different regimes of the phase diagram.

Nanomaterials **2017**, *7*, 305

Wetting: interaction between a liquid & a solid

wetting

the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together

wettability

the degree of wetting; determined by the balance between adhesive (forces between molecules in the liquid & the solid) & cohesive forces (forces between molecules in the liquid, holding them together)

youtube.com/watch?
v=_StEfIF9qU4

youtube.com/watch?
v=C7ZiLbTul9U

Table 4-1: Importance of wetting behavior in various applications.		
Situations where good wetting is desired	Situations where non-wetting is desired	Situations requiring patterned wetting or wetting differences
• Coating • Washing • Adhesion • Absorbency (wicking)	• Water-proofing • Anti-stick surfaces • Anti-soil surfaces • Release coatings	• Printing plates • Ore flotation

Contact angle & Young's equation

three-phase contact line
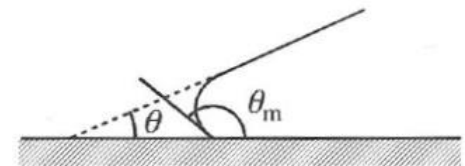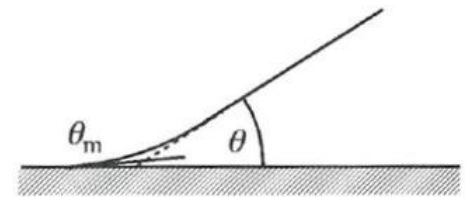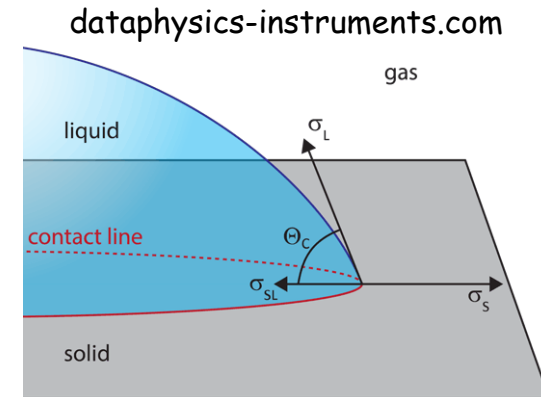line where the solid (S), liquid (L) & gas (G) phases meet

contact angle (θ)

the angle that is formed between the tangent to the LG interface @ the contact line & the LS interface horizontal

- measured by convention @ the liquid side
- a quantitative measure of the liquid-solid interaction
- macroscopic quantity → integral result of long-range intermolecular forces in the three phases
- *microscopic contact angle ($θ_m$) might differ (generally no effect in macroscopic wetting)*

Young's equation

- force equilibrium @ contact line
- three interfaces → three σ, each normal to the contact line, directed as to minimize area

- assumes perfectly flat and rigid surface ***(ideal surface)***
- usually surfaces are non-ideal
- *rough surfaces*, smooth surfaces that are *finitely rigid*

dataphysics-instruments.com

$$\sigma_{SG} = \sigma_{SL} + \sigma_{LG}\cos\vartheta$$