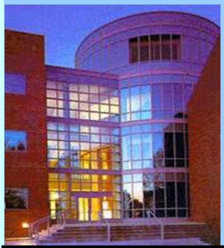
Introduction to:



Surface Science in Paper Recycling

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Papermaking: A "Colloidal" Soup

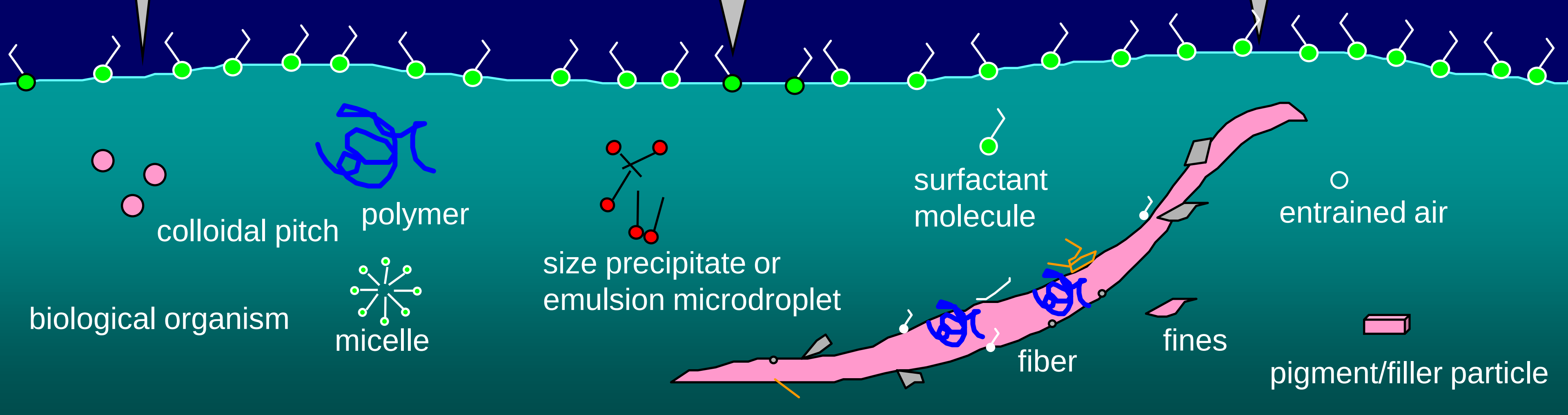
Pulping & Bleaching

Chemical Additives

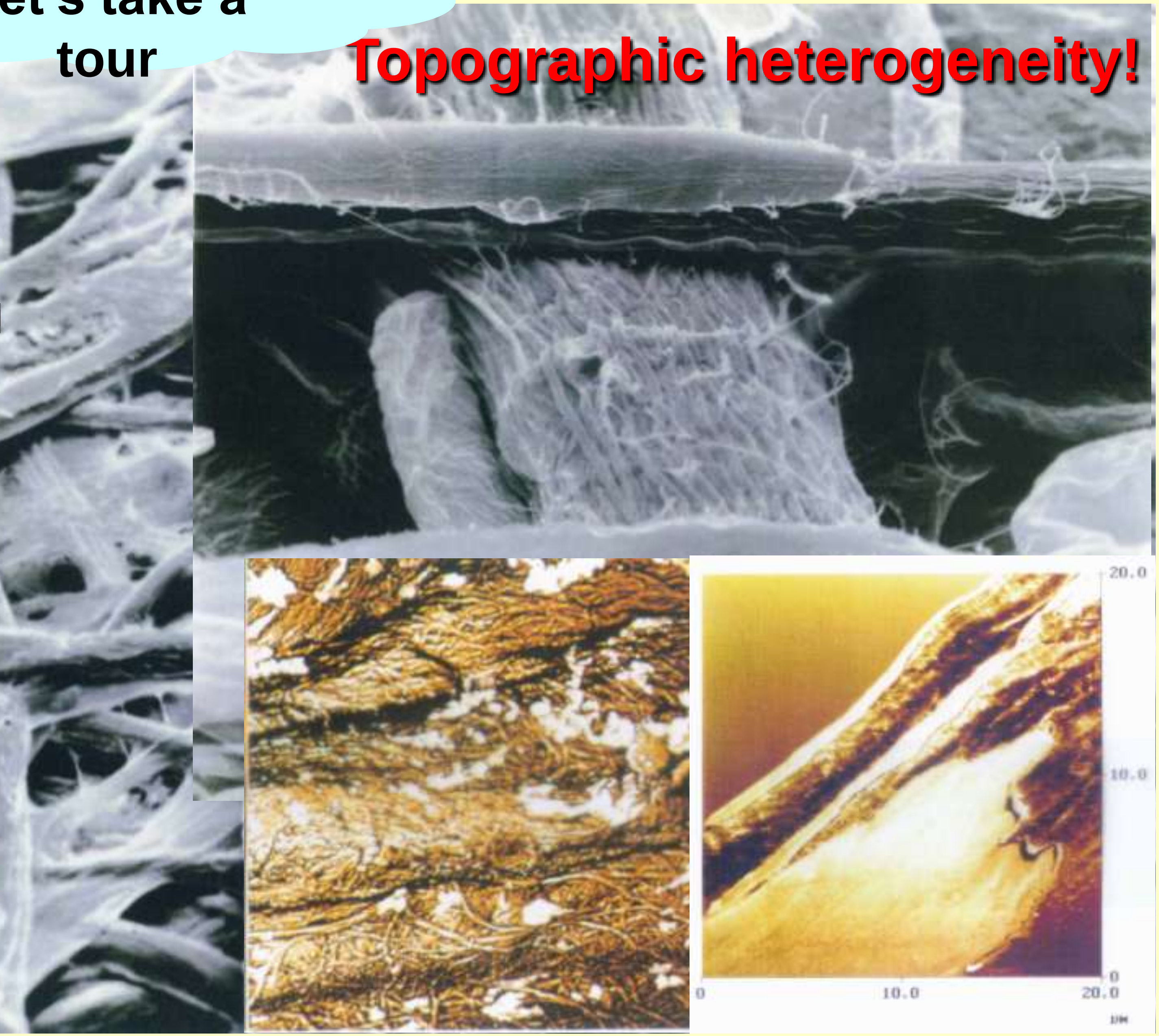
- dry strength resins
- wet strength resins
- release emulsions
- surfactants
- retention aids
- pitch control aids
- promoters
- dyes
- defoamers
- slimicides
- glue

Recycling & other process streams

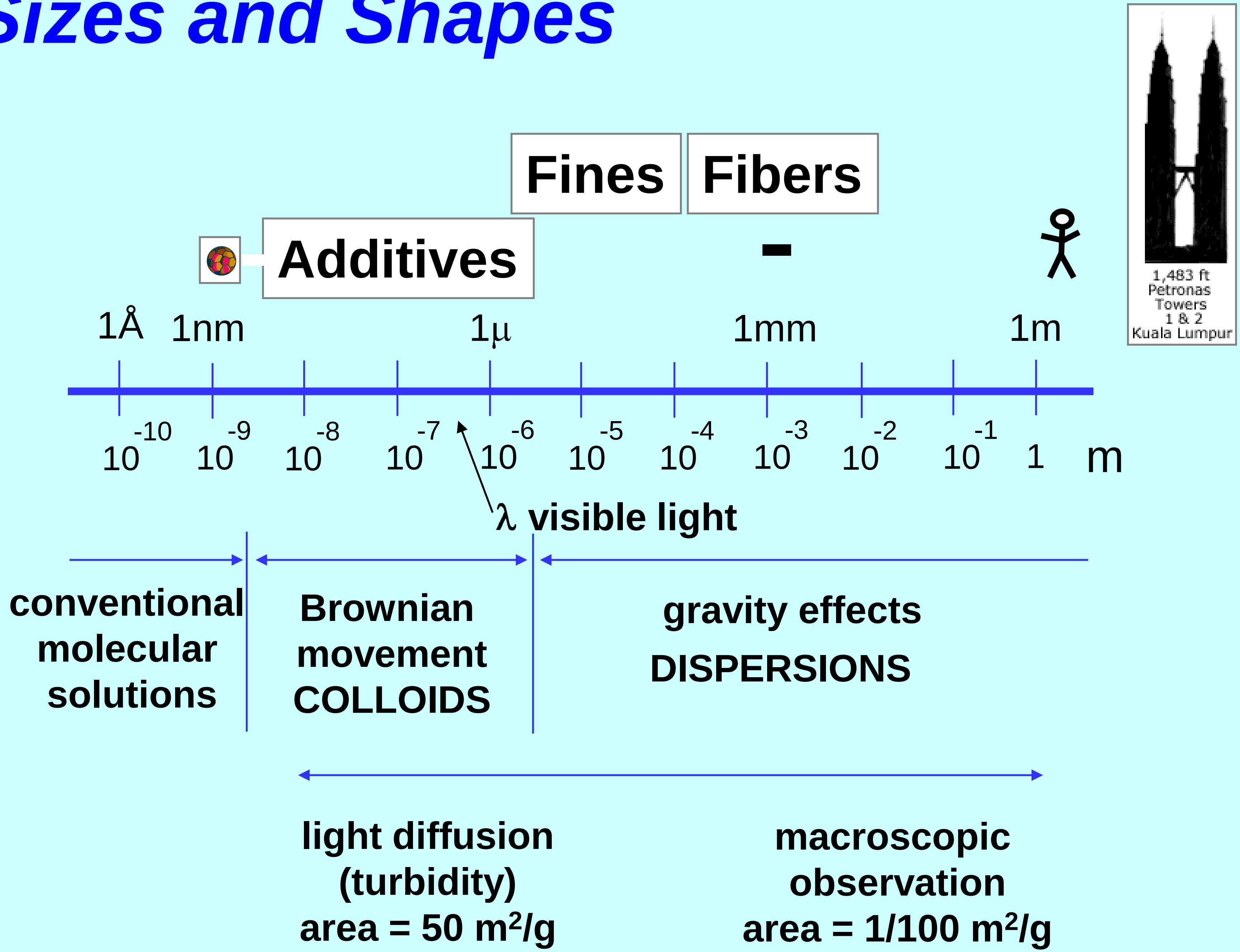
- salts
- dissolved & organic compd's
- suspended solids
- carry-over chemicals



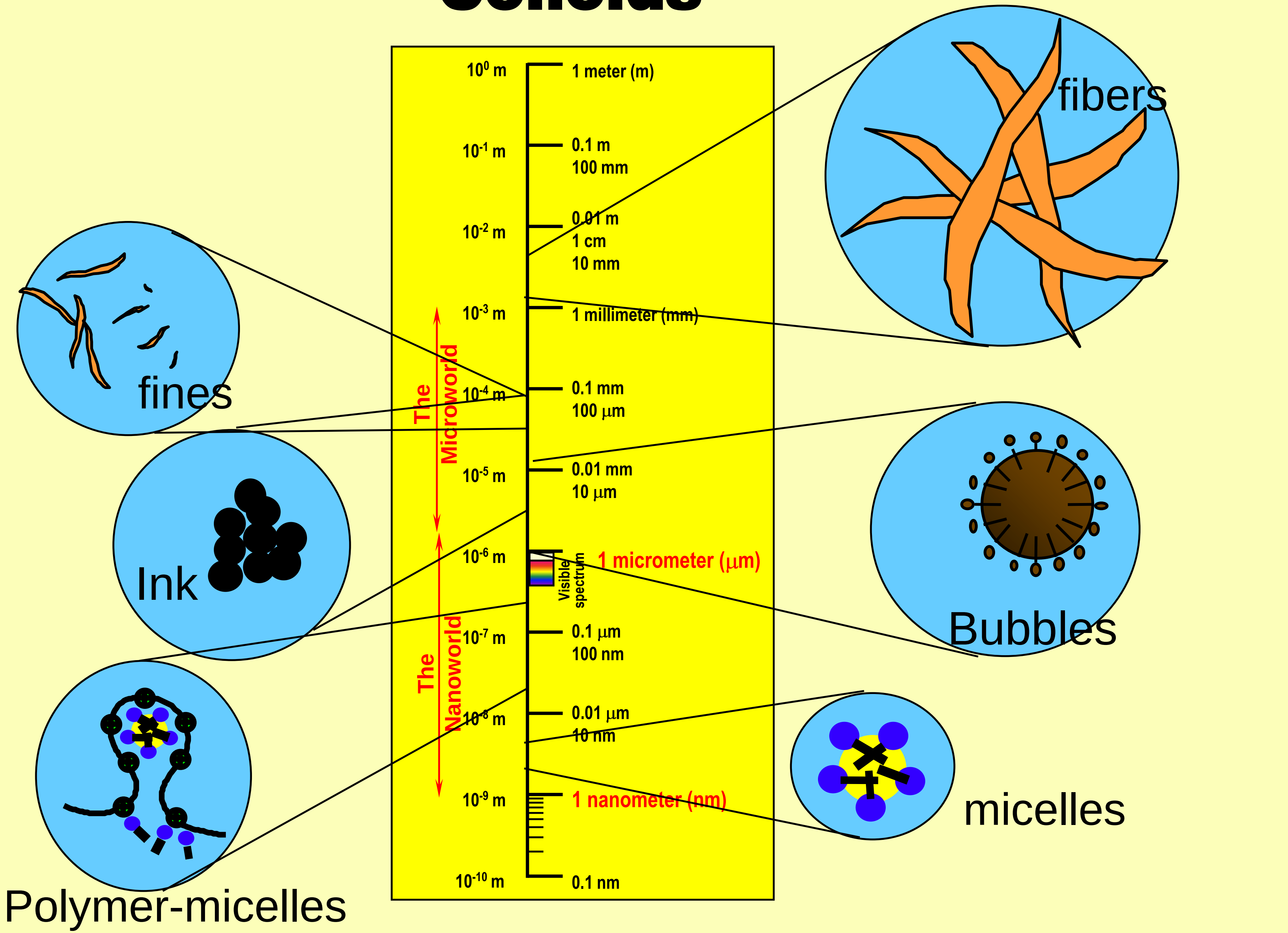
Papermaking Fibers



Sizes and Shapes



Colloids



10^0 m
1 meter (m)
10^{-1} m
0.1 m
100 mm
10^{-2} m
0.01 m
1 cm
10 mm
10^{-3} m
1 millimeter (mm)
10^{-4} m
0.1 mm
100 µm
10^{-5} m
0.01 mm
10 µm
10^{-6} m
1 micrometer (µm)
Visible spectrum
10^{-7} m
0.1 µm
100 nm
10^{-8} m
0.01 µm
10 nm
10^{-9} m
1 nanometer (nm)
10^{-10} m
0.1 nm
The Microworld
The Nanoworld
fibers
fines
Ink
Bubbles
micelles
Polymer-micelles

Deinking Chemicals

Sodium Hydroxide	Pulper – Bleaching
Sodium Silicate	Pulper – Bleaching
Chelating Agents	Pulper – Bleaching
Hydrogen Peroxide	Pulper – Bleaching
Surfactants	**Pulper – Flotation - Washing**
Collector Chemicals	Pulper – Flotation
Agglomeration Chemicals	Pulper – Cleaners
Calcium chloride	Flotation
Dispersants	Washing – Stock prep

Inks = complex formulations

Component	Function	Concentration, %
Deionized water	Aqueous carrier medium	60 - 90
Water soluble solvent	Humectant, viscosity control	5 - 30
Dye/pigment	Provides color	1 - 10
Surfactant	Wetting, penetrating	0.1 - 10
Biocide	Prevents biological growth	0.05 - 1
Buffer	Controls the pH of ink	0.1 - 0.5
Other additives	Chelating agent, defoamer, solublizer, etc.	> 1

Here we will talk about...

Surfaces

Surfactants

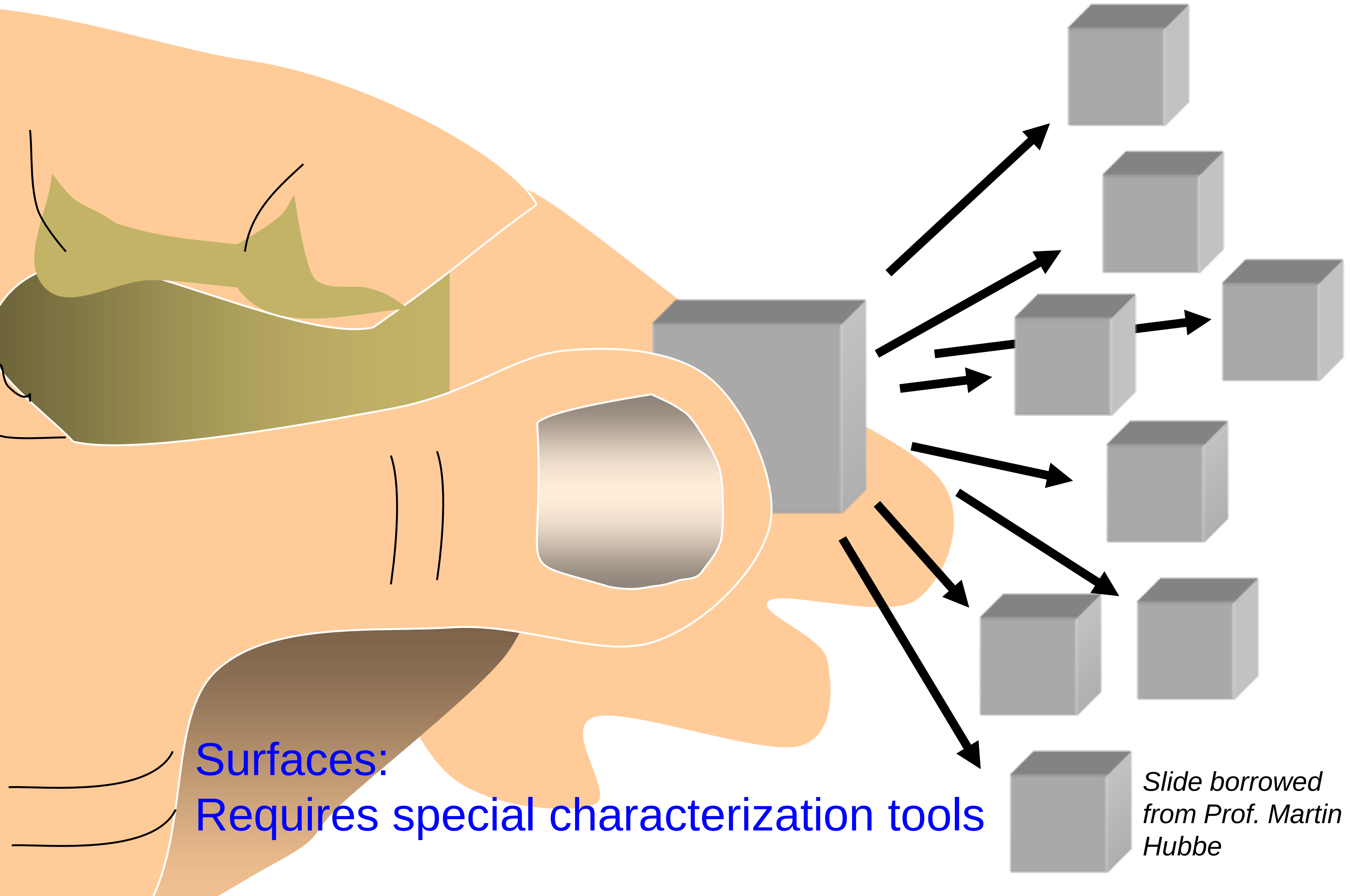
Surface energies

Contact angles

Water penetration

paper recycling, deinking, deposits, stickies, etc.

Surface area and particle size



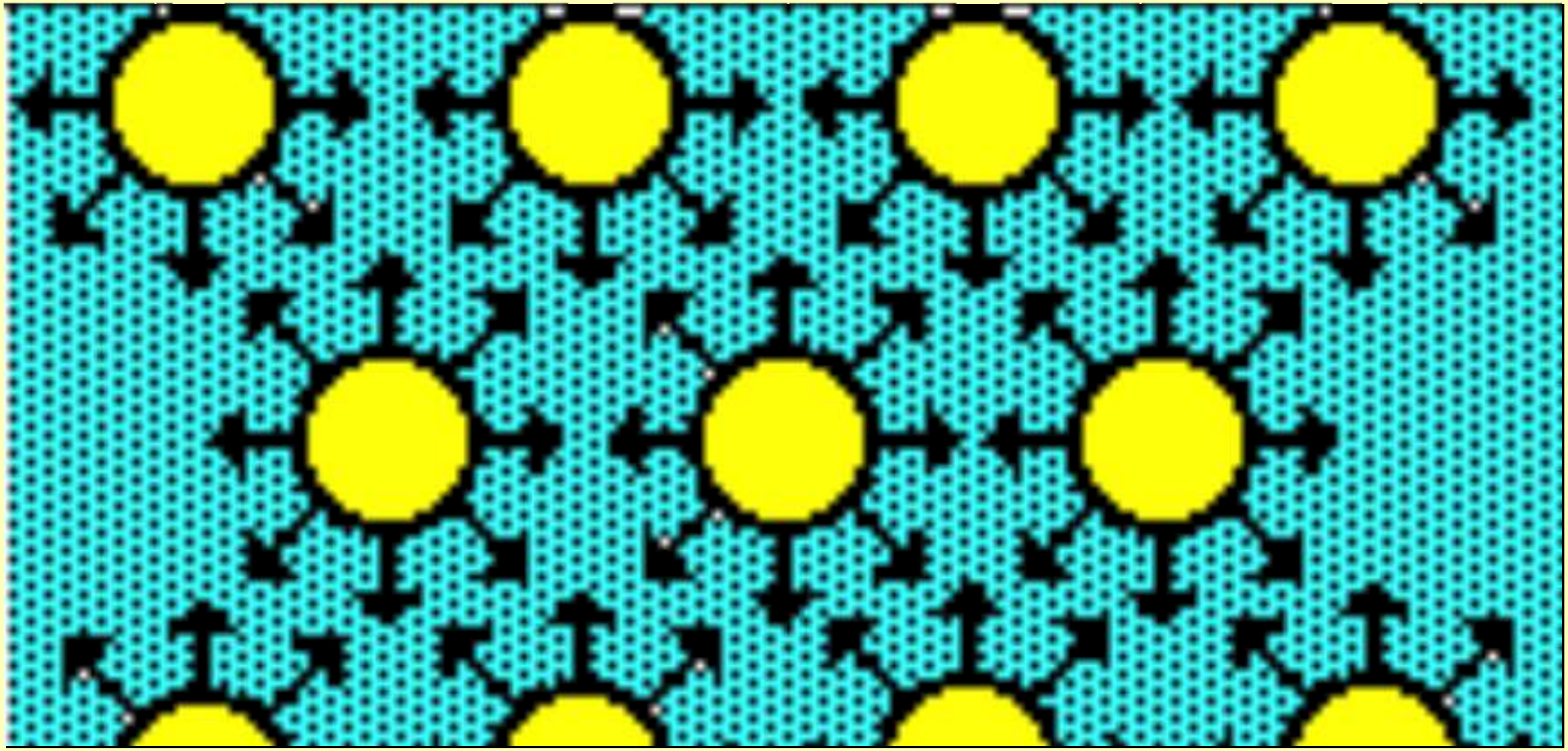
Surfaces:
Requires special characterization tools

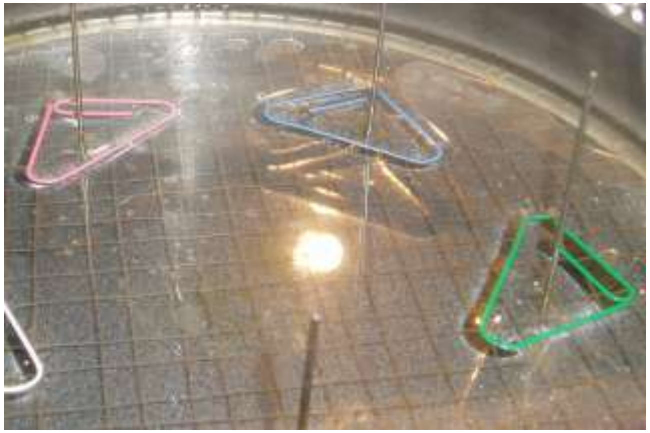
Slide borrowed from Prof. Martin Hubbe

Surface and Interfacial Tension

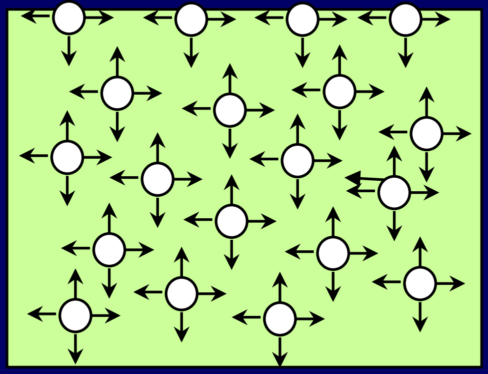
Surface Tension

- **Surface net inward force**



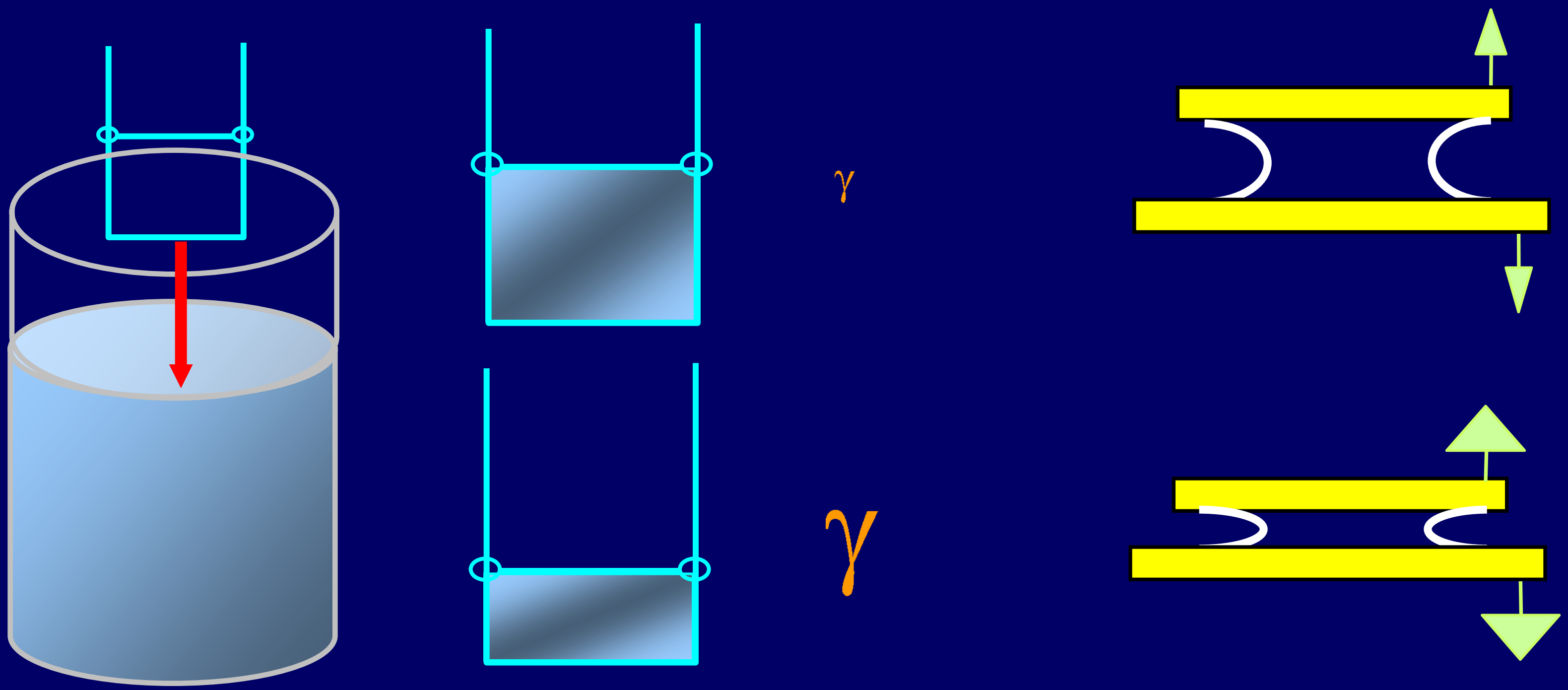
Surface Energy and Surface Tension (γ)



Unbalance of intermolecular forces exists at the liquid-air interface

At surface: net "inward" force

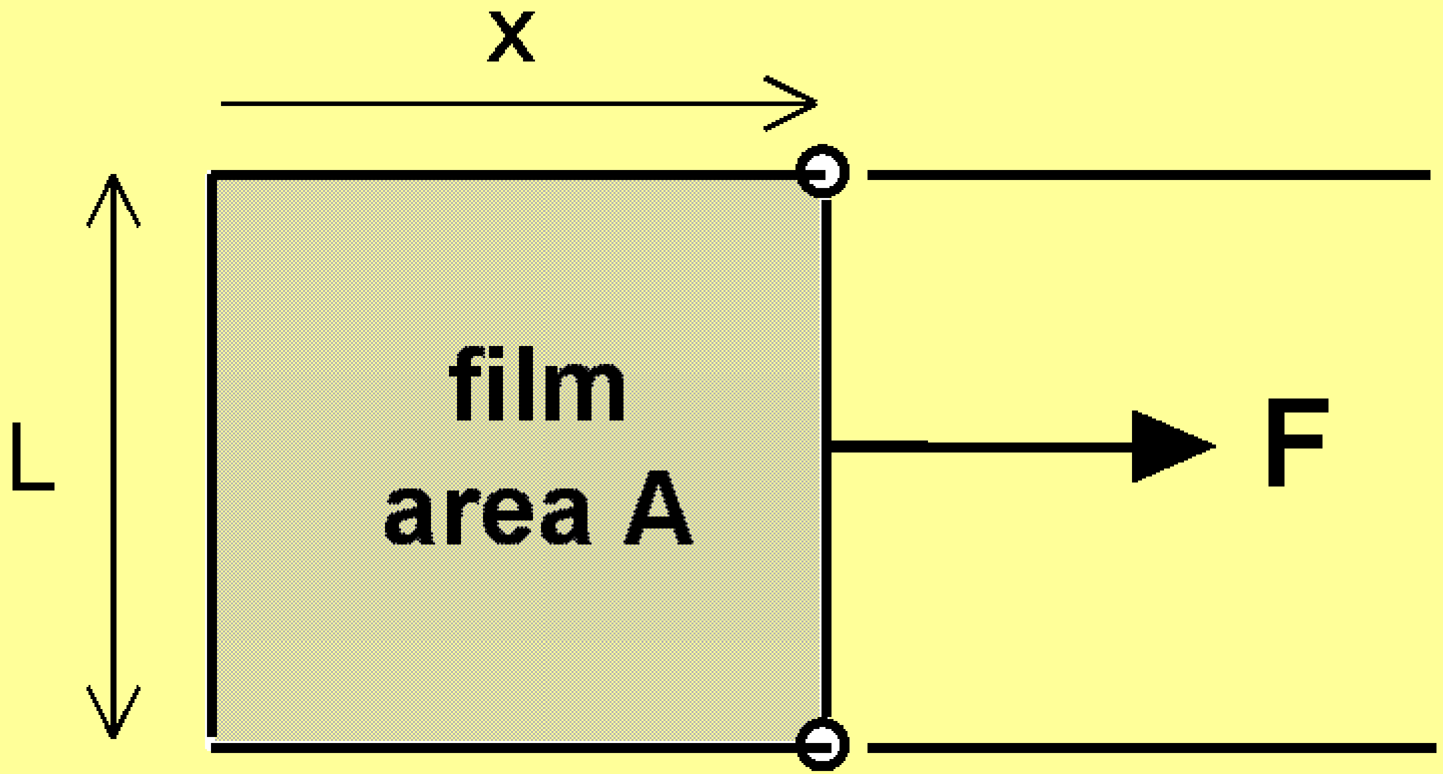
Surface energy of a fluid... It is translated as the resistant to the creation of new surface area.



Surface Energy

In nature every system tries to minimize its surface energy.

For example a drop of water in air will be spherical, not extended like a cylinder….



dx → dW = F dx

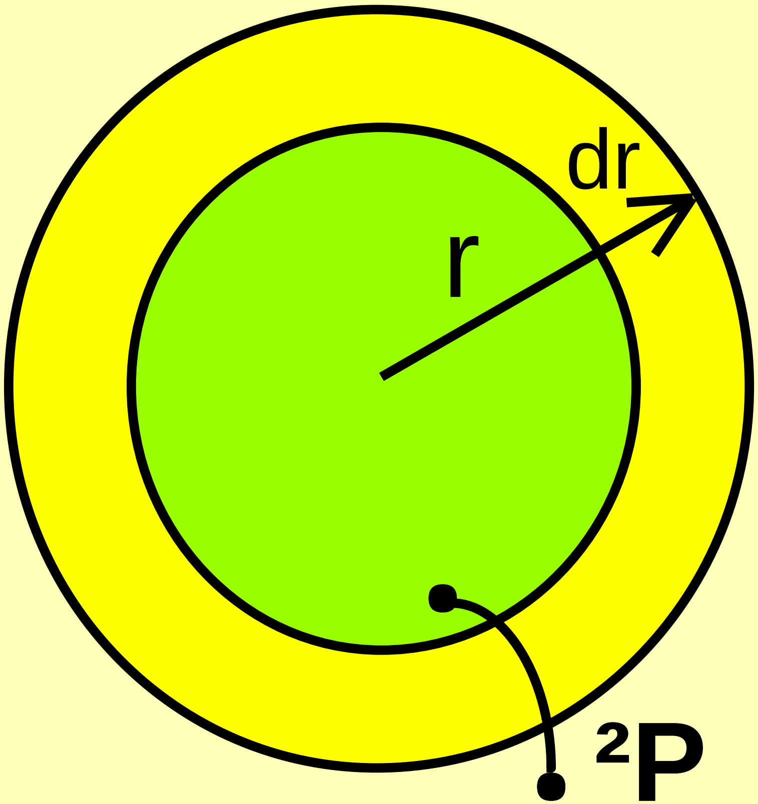
Force on the wire: $F = 2\,\gamma\,L$ (2 sides)

$dW = 2\,\gamma\,L\,dx = \gamma\,dA$

Mechanical Definition

area $A = 4 \Pi r^2$

$dA = 8 \Pi r\, dr$



Work against surface tension

$dW = \gamma\, dA = 8 \Pi \gamma\, r\, dr$

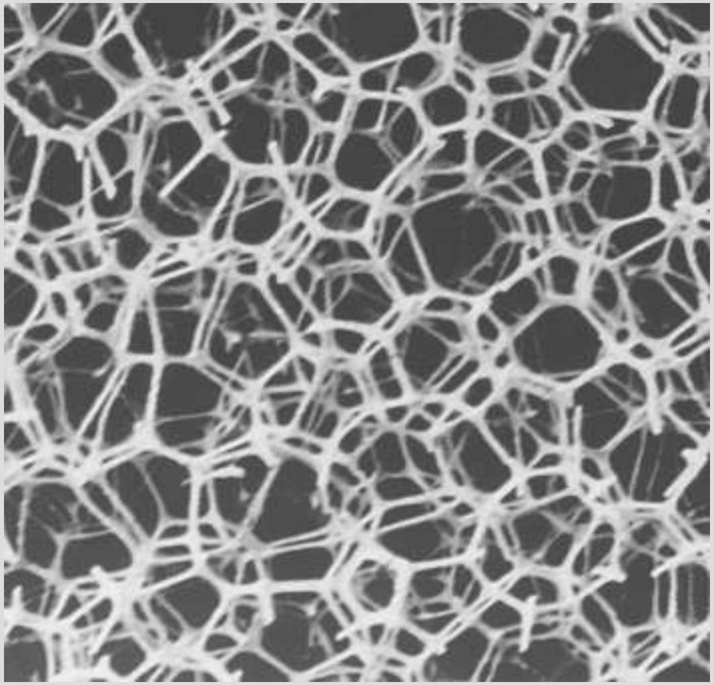
Work against Pressure

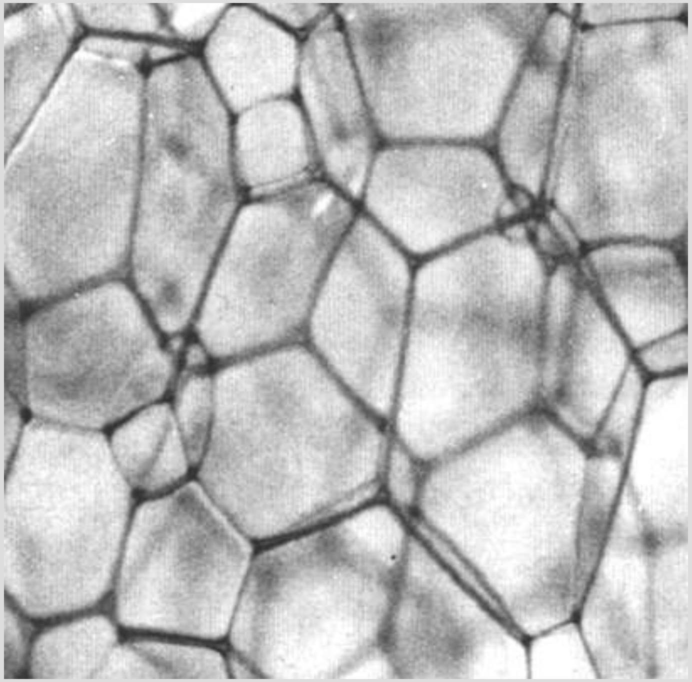
$dW = \Delta P\, dV = \Delta P\, A\, dr$

$= \Delta P\, 4 \Pi r^2\, dr$

Equating both expression for dW
Young-Laplace Eq. is obtained

$$\Delta P = 2\gamma / r$$



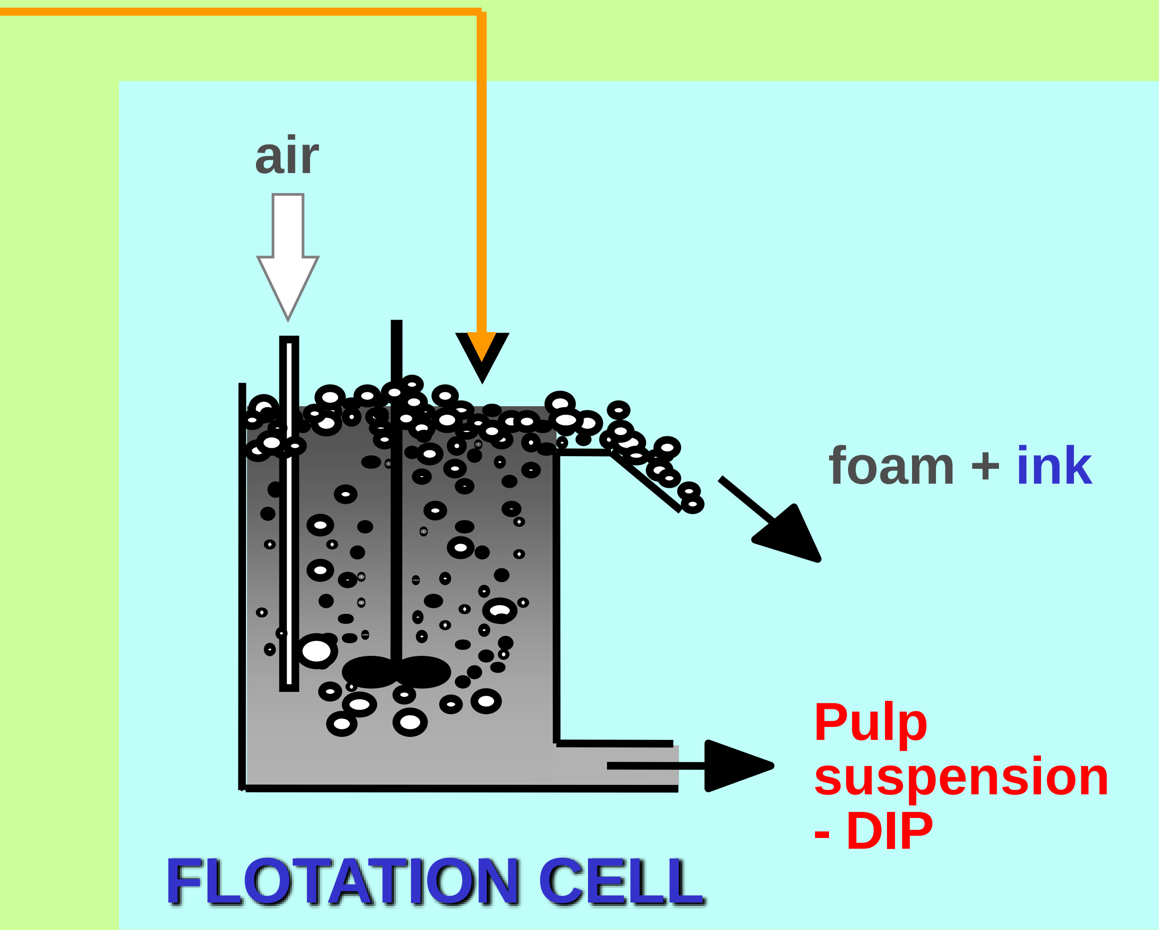


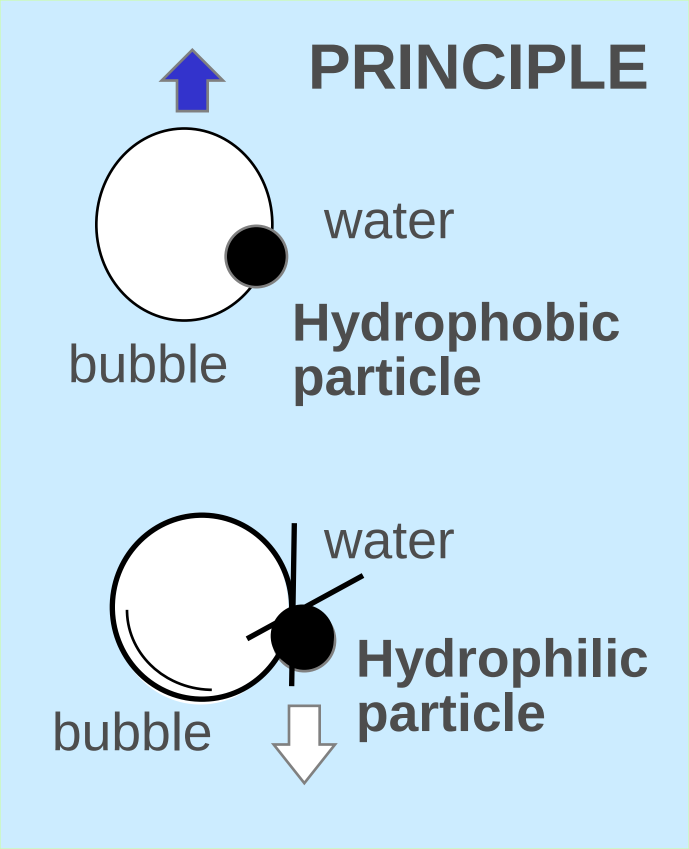
solid and liquid foams: can be formed from low Surface tension media

Flotation

Hydrophobic particles (pigments)

...





Surface Tensions of Some Pure Liquids at 293 K

Substance	γ *(mN/m)*
Acetone	23.7
Benzene	28.8
Carbon Tetrachloride	27.0
Methylene Iodide	50.8
Water	72.8
Methanol	22.6
n-Hexane	18.4

Organic molecules with polar groups such as iodide and hydroxyl have a slightly lower surface energy than water.

Pure hydrocarbons are even lower, while fluorinated compounds are very low because the fluorine atom won't share electrons very well so only dispersion interactions occur.

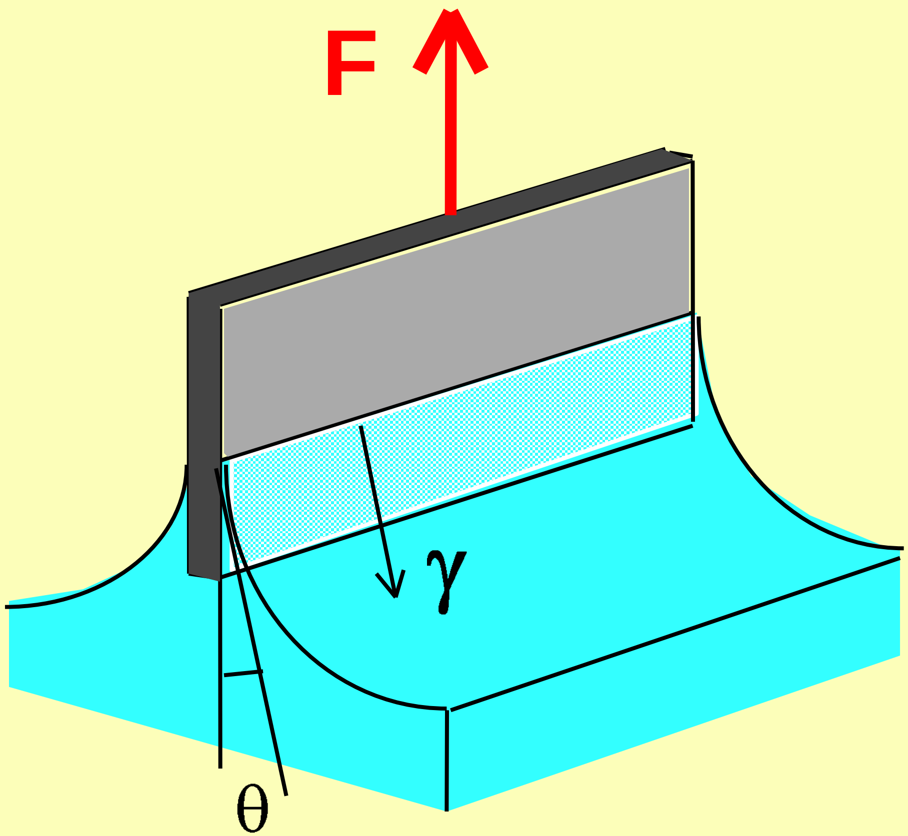
Surface Tension Measurement

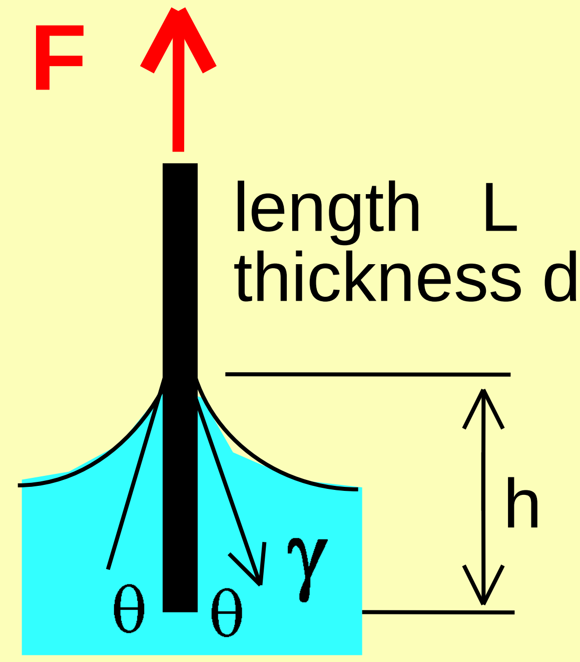
Surface Tension Measurement

3 methods

- Force measurement
- Pressure measurement
- Deformation measurement

Wilhelmy Plate



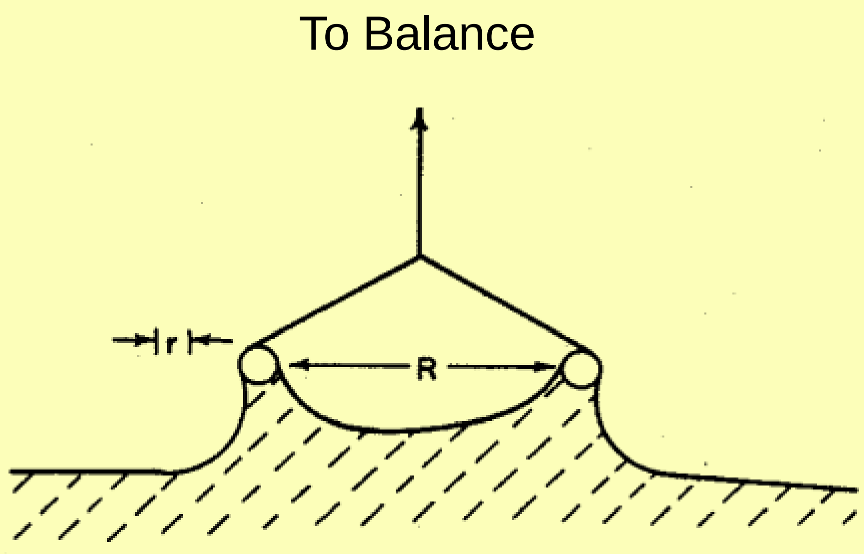


$$F = 2\,(L + d)\,\gamma\,\cos\theta$$

↑

2 sides

du Noüy Ring Method



Adamson & Gast (1997)

Detachment Method

$$W_{total} = W_{ring} + 4\pi R\gamma_{obs}$$

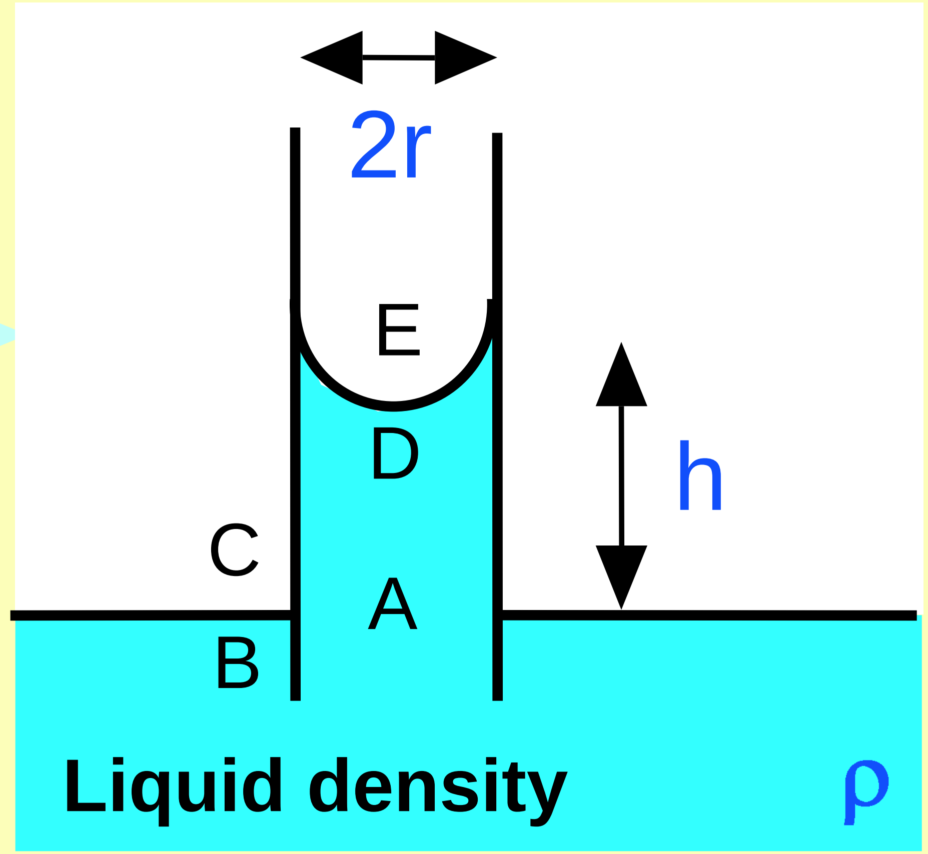
Correction due to width of ring material

$$\gamma_{true} = f \cdot \gamma_{obs}$$

where $f = f\,(R^3/V,\ R/r)$ [V =meniscus volume]

Capillary Rise

$$\rho g h = \frac{2\gamma}{r}$$



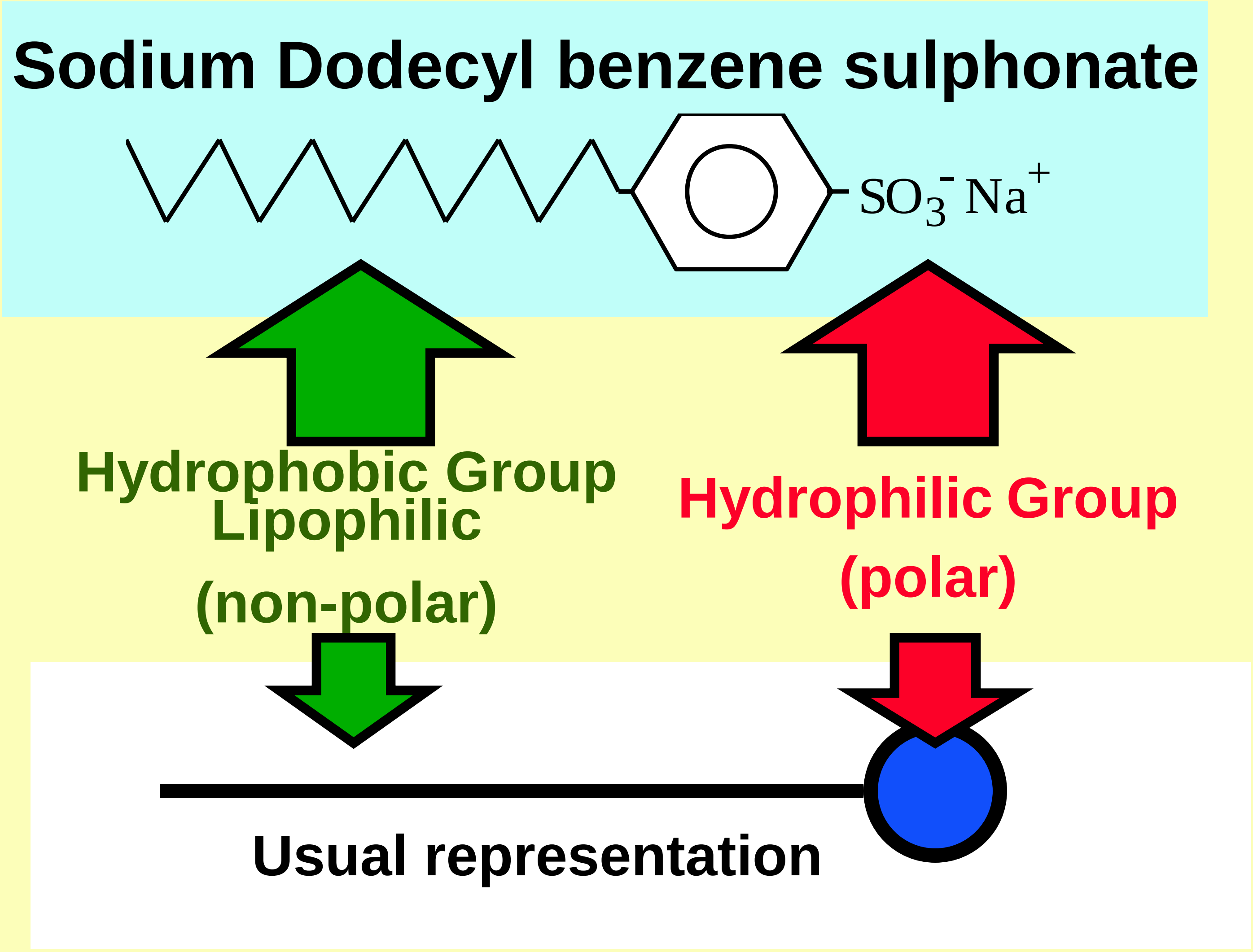
Methods for Measuring γ

Method	Pure Liquids	Solutions
✓ Capillary Rise	Good when liquid wets reproducibly	Difficult
Sessile Drop	Good	Good for aging effects
Pendant Drop	Satisfactory, but has expt'l difficulties	Good for studying aging effects
✓ Wilhelmy Plate	Accurate, convenient with good set-up	Good, including aging effects
Maximum pull on cylinder	Good, easy to operate and simple apparatus	Satisfactory if used with care
✓ du Noüy Ring	Satisfactory	Unsatisfactory
✓ Drop Weight	Good	Poor if aging effects expected
Max. Bubble Pressure	Satisfactory when others impractical	Poor if aging effects expected

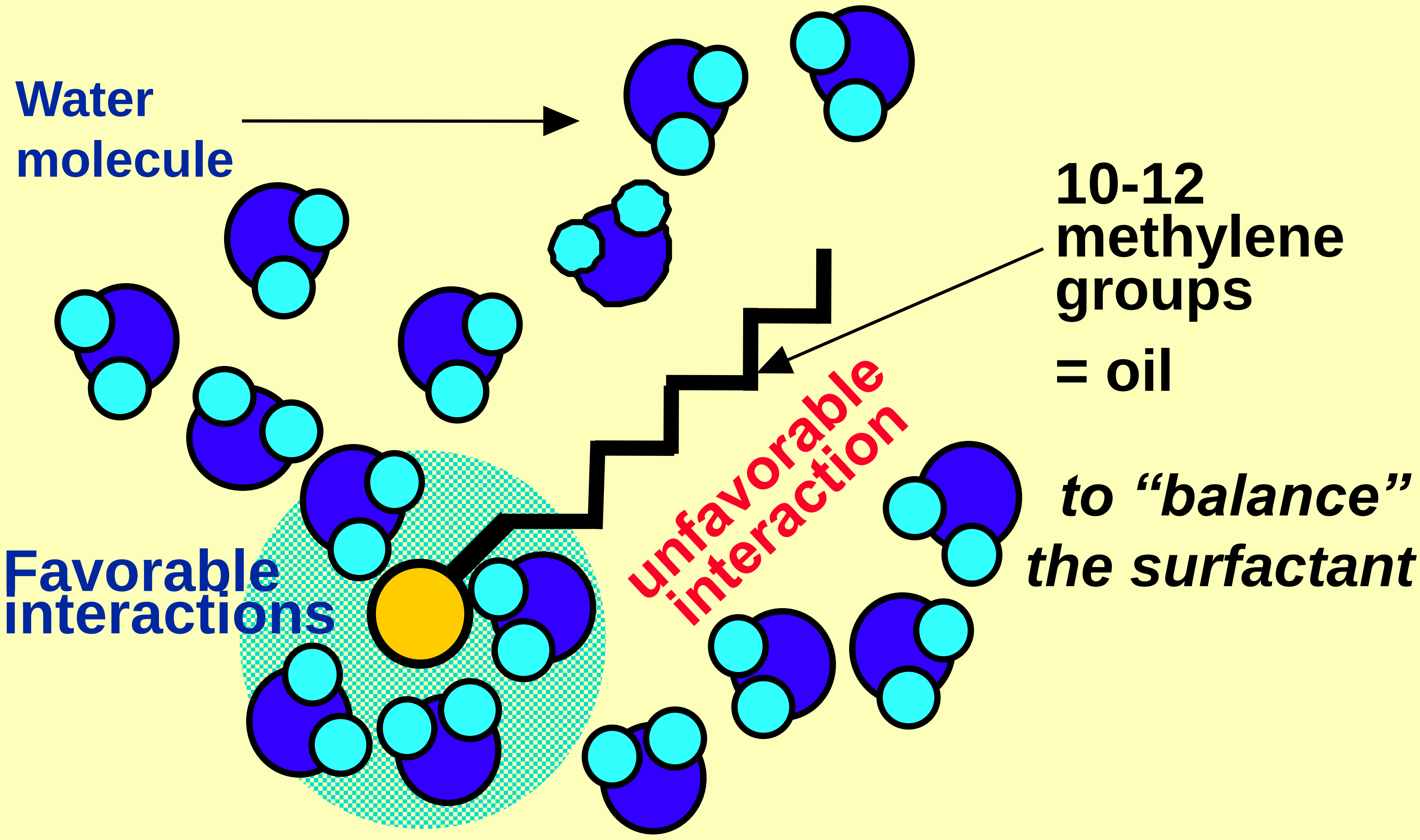
Jaycock and Parfitt (1986)

Surfactants

Surfactant = Amphiphile

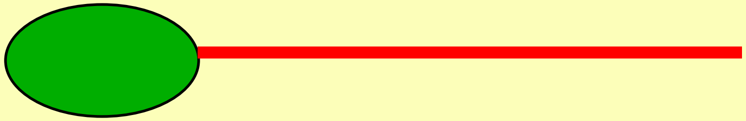


In aqueous solution
Favorable & unfavorable Interactions



Surfactants

Amphiphilic nature



hydrophilic **hydrophobic**

(lipophobic) **(lipophilic)**

Classification according to head-group:

- Anionic
- Cationic
- Nonionic
- Zwitterionic

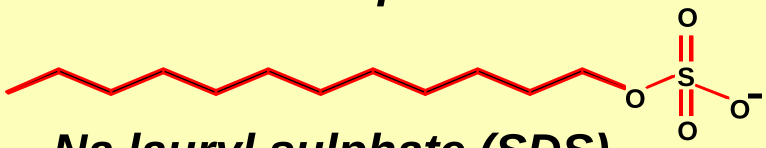
*****(See hand out)***

Anionic surfactants

- **Largest group of surfactants** *(~65% world market)*
- **Sensitive to electrolytes (salt and Ca^{2+})**
- **Sulphates hydrolyse at low pH, otherwise chemically stable**
- **Soaps still important (foam and washing)**
- **Alkylether sulphates, lower cmc, compatible low pH and high hardness.**
- **Phosphate esters; good wetting agents, corrosion inhibitors, antistatic properties**

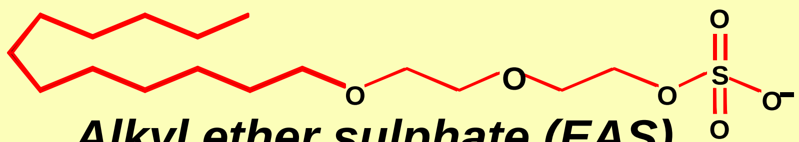
Biodegradable under aerobic conditions
Shampoos, handsoaps, laundry detergents

soap



Na lauryl sulphate (SDS)

Linear alkyl benzene sulphonate (LABS)



Alkyl ether sulphate (EAS)

Phosphate ester

$$\begin{array}{l} R_1CO_2CH_2 \\ \quad\quad\;\; | \\ R_2CO_2CH \\ \quad\quad\;\; | \\ R_3CO_2CH_2 \end{array} \xrightarrow[H_2O]{NaOH} R_1CO_2Na + R_2CO_2Na + R_3CO_2Na + \begin{array}{l} HOCH_2 \\ \quad\;\; | \\ HOCH \\ \quad\;\; | \\ HOCH_2 \end{array}$$

three carboxylate salts

C12-C20 saturated acids

$CH_3(CH_2)_{10}CO_2H$	lauric acid
$CH_3(CH_2)_{12}CO_2H$	myristic acid
$CH_3(CH_2)_{14}CO_2H$	palmitic acid
$CH_3(CH_2)_{16}CO_2H$	stearic acid
$CH_3(CH_2)_{18}CO_2H$	arachidic acid

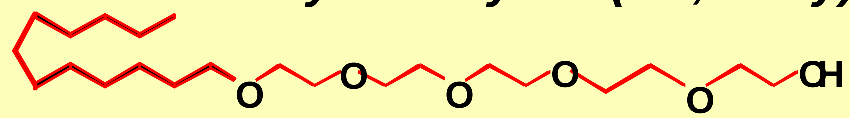
C18 unsaturated acids:

$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	oleic acid
$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6CO_2H$	linoleic acid
$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6CO_2H$	linolenic acid

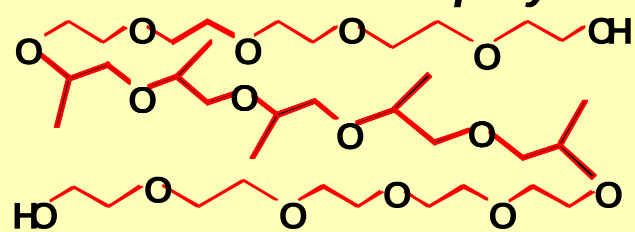
Non-ionic surfactants

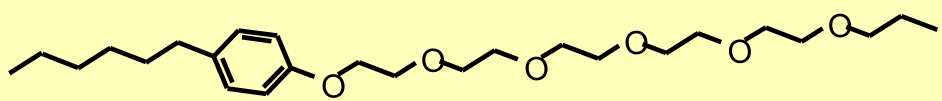
- **Second largest group of surfactants** (~25% world market)
- **Dominated by polyoxyethylene products**
- **Not sensitive to salts (e.g. Ca^{2+})**
- **Temperature sensitive: water solubility reduced at higher T**
- **Much lower cmc than nonionic surfactants; efficient at low concentrations**

Alkyl ethoxylate (AE, CxEy)



EO-PO blockpolymer





(Joy dish soap)

Spans (Sorbitan Esters)
Tweens (Polyoxyethylene Sorbitan Esters)

Smooth rinsing (no water spots)
Dish soaps, window washers, insecticides

Cationic surfactants

(~10% world market)

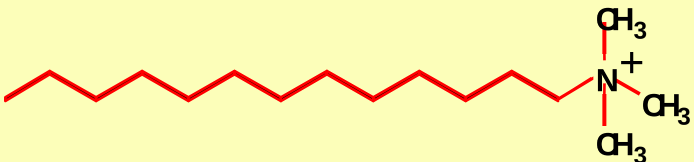
- **Composed of a quaternary amino group as cationic head**
- **Not compatible with anionic surfactants**
- **Adsorbs strongly to many surfaces**
- **Used to modify a surface properties:**

  Textile softener
  Adhesion promoter
  Corrosion inhibitor
  Anticaking agent
  Mineral flotation

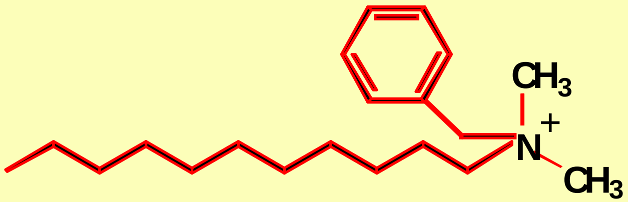
- **Counter ions: halides (Cl^-, Br^-) or organic ($MeSO_4^-$)**

Alkyl amine salt

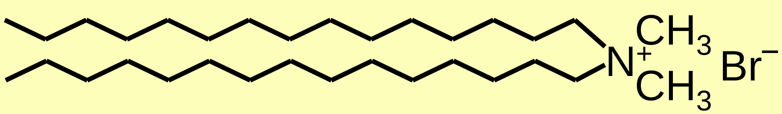
Alkyl diamine salt



Alkyl trimethyl ammonium salt (Quat)

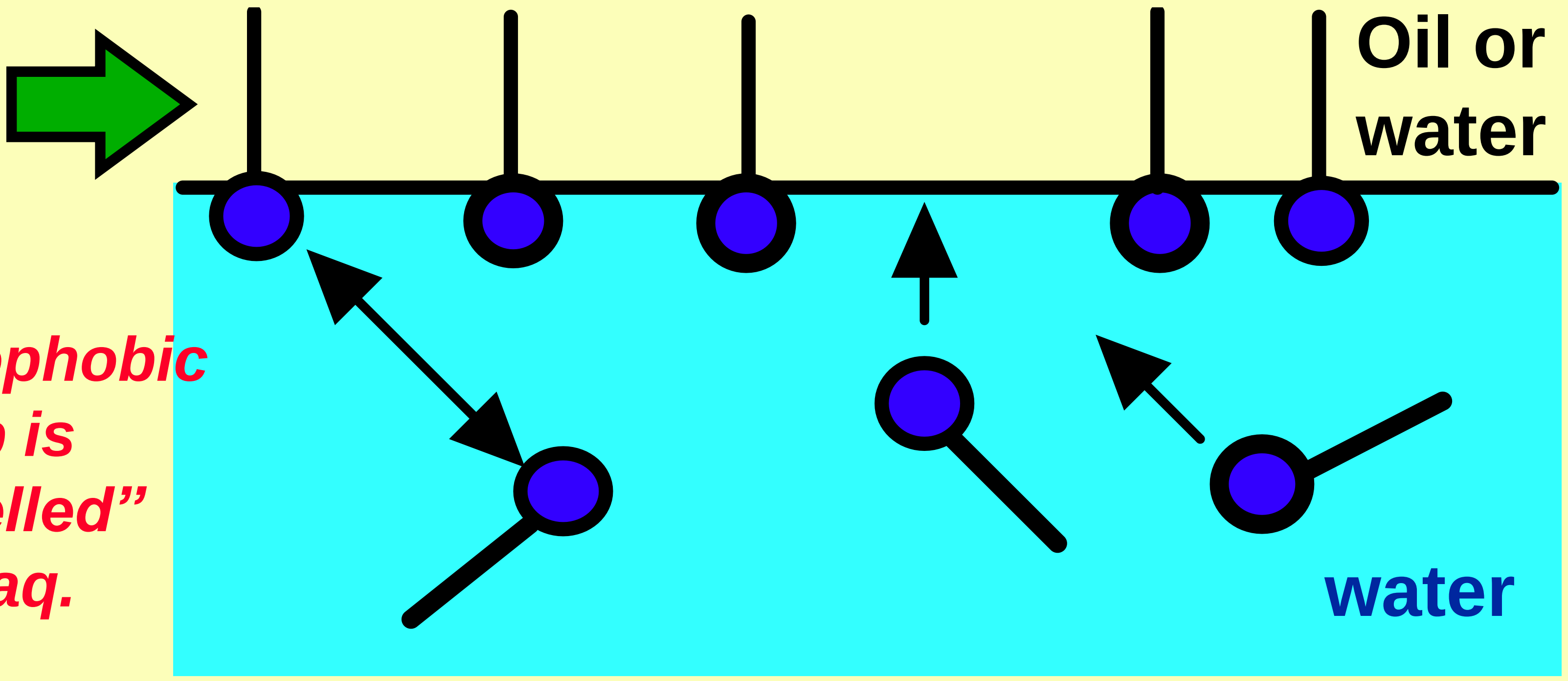


Benzalkonium salt



(Downey fabric softener)

Surface or Interfacial Adsorption



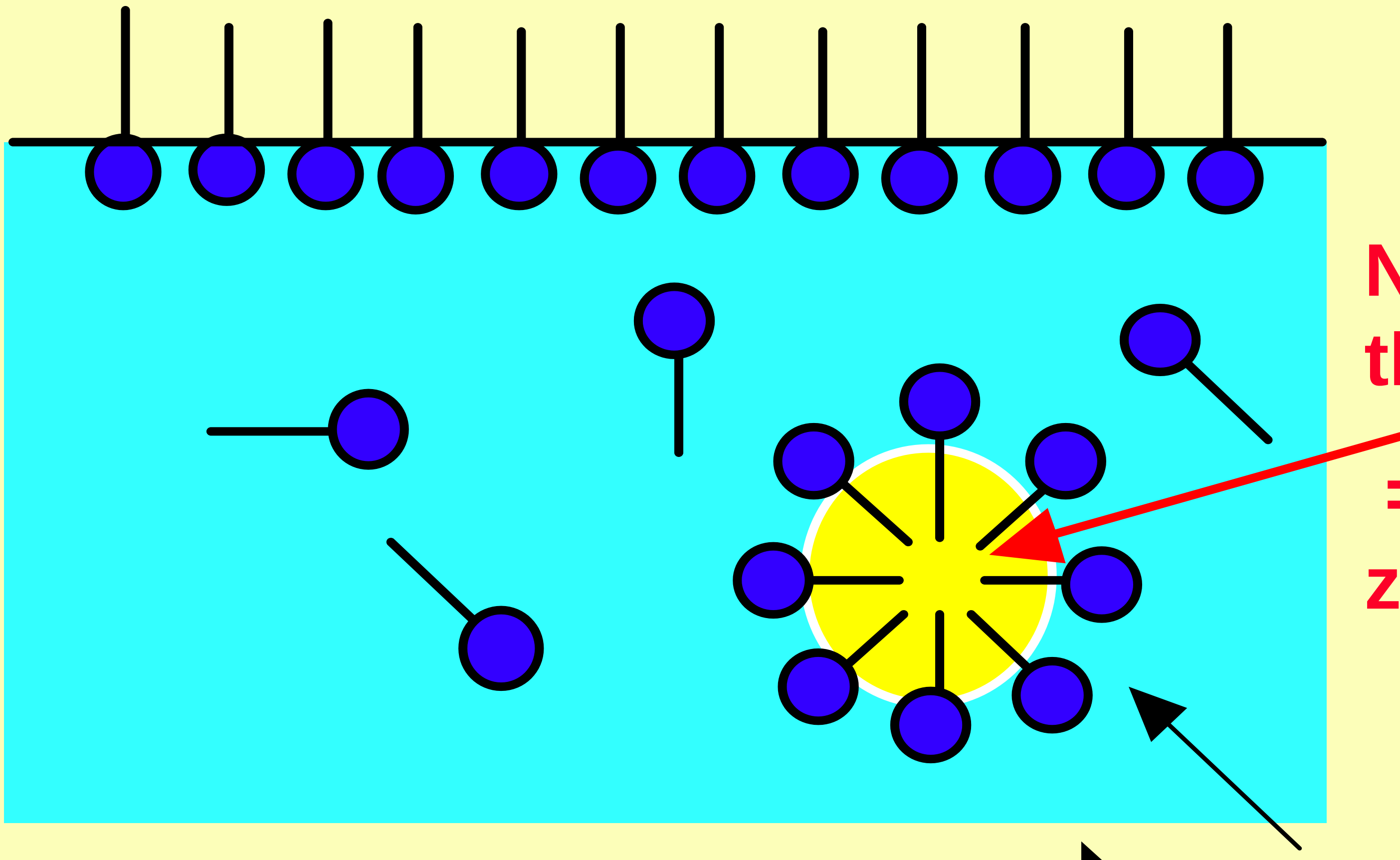
The hydrophobic group is "expelled" from aq. soltn.

First added molecules ...

... In aqueous solution

are adsorbed at the surface or interface

When the surface is saturated...



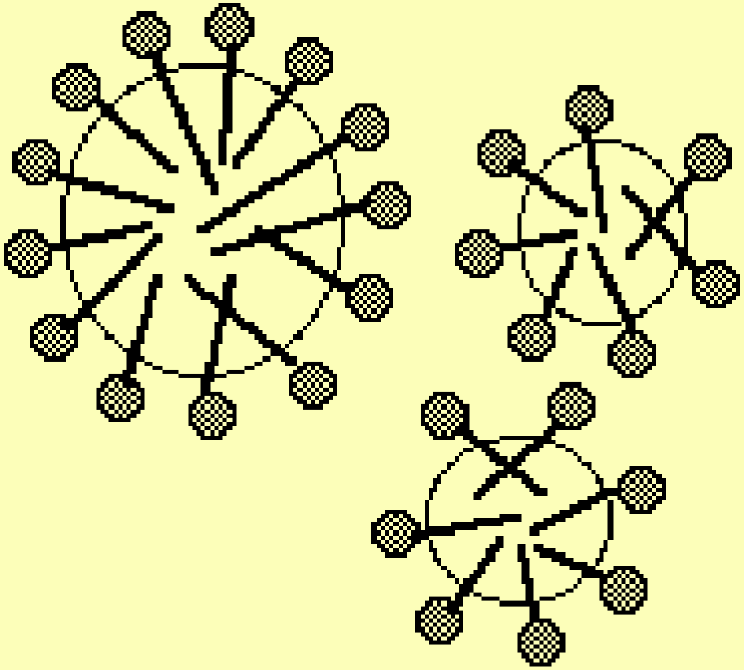
No water in the core

= exclusion zone

Association occurs ⇨ **MICELLES**

MUKERJEE P. [1977[a,b

MICELLE =
aggregation colloid

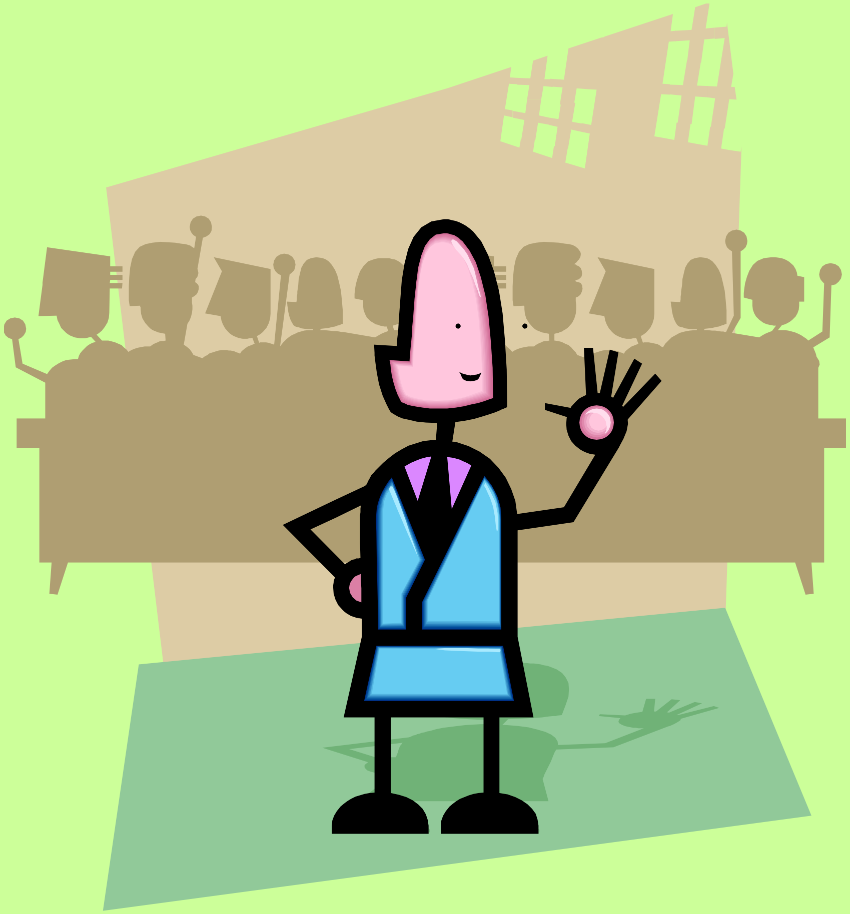


- size ± 20 - 50 Å depending on surfactant
- Aggregation number 50-100 molecules

- Spherical form ± depending on medium
- cylindrical, elongated, spaghetti ...

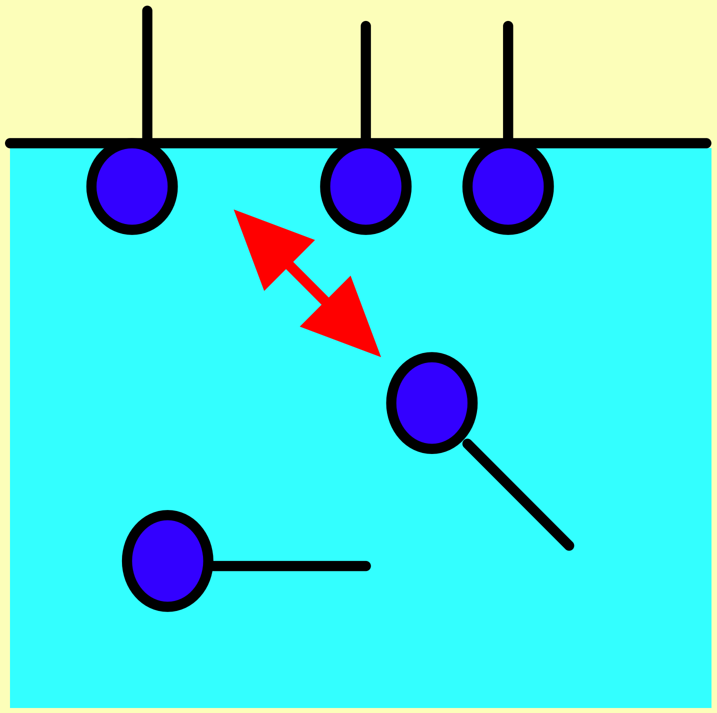
Aniansson et al,. 1976;; Elworthy & Mysels, 1966; Murray & Hartley, 1935; Mysels et al. 1963; Shinoda & Hutchinson, 1962; Tondre et al., 1975

Surface Activity



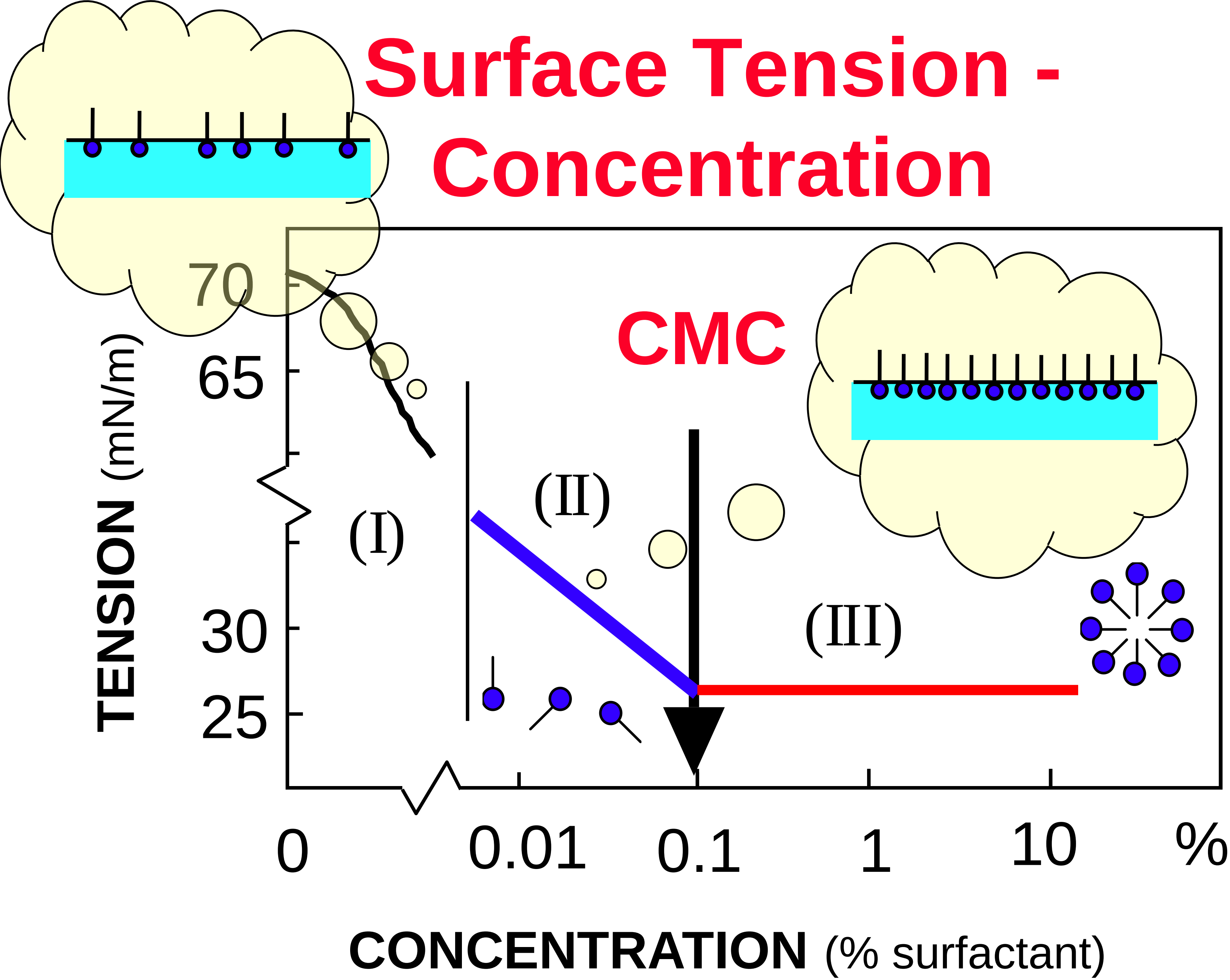
Surface Activity

Tension (= free energy per unit area) is linked to ...



- **Surface adsorption**
- **surface concentration**

Surface Tension - Concentration



Surfactants

- Because they have both Hydrophillic and lipophillic parts they are compatible at surfaces
- This lowers surface energy of the system
- Enables foaming!!
- But be careful, surfactant will also attach to hydrophobic contaminants making them more stable in water
  - Bad for flotation
  - Good for anti-deposition
  - Good for washing

Simple Surfactant Characterization Parameter: HLB

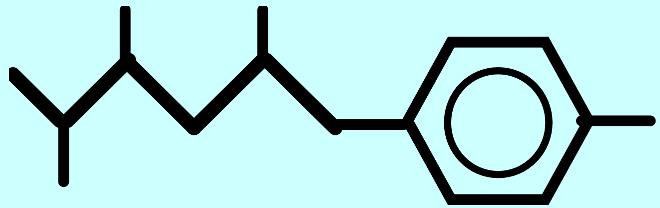
- Hydrophillic to lipophillic balance

HLB calculated from empirical formula

- *for instance* - ethoxylated nonionics

HLB = 1/5 of polyether wt. %

nonylphenol + 5 OE



$O-[CH_2-CH_2-O]_5-H$

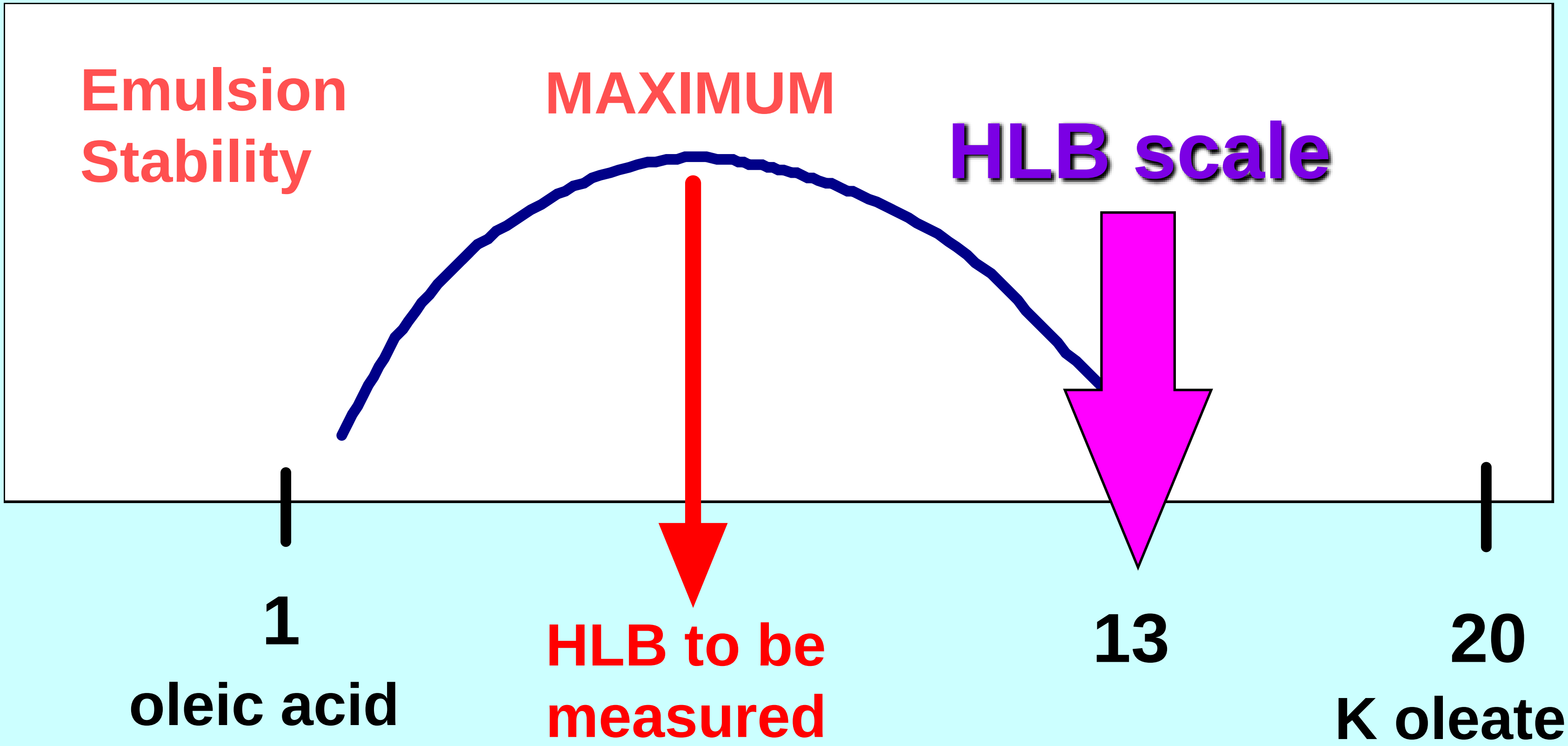
$$\mathbf{HLB} = \frac{1}{5}\ \frac{44 \times 5}{220 + 44 \times 5} \times 100 = \mathbf{10}$$

Griffin W., Calculation of HLB of nonionic surfactants. *J. Soc. Cosm. Chem*. **5**: 249 (195

HLB

Griffin 1949

- **original method based on the**
- **stability of O/W emulsions**
- **tedious and inaccurate**



Griffin W., Classification of surface active agents by HLB. *J. Soc. Cosm. Chem.* **1**: 311 (1

HLB can be related to structure

- Davies' relationship (1957)

$$HLB = 7 + \sum \text{contributions of hydrophilic groups} - \sum \text{contributions of lipophilic groups}$$

Contribution values

$-SO_4Na$	+ 39	-COOH	+ 2,1	>CH-	- 0,5
-COOK	+ 21	-OH	+ 2,0	$-CH_2-$	- 0,5
-COONa	+ 19	- O -	+ 1,3	$-CH_3$	- 0,5

Davies J. T., A quantitative kinetic theory of emulsion type. I. Physical chemistry of the emulsifying agent, *Gas/Liquid and Liquid/Liquid Interfaces. Proceedings 2nd Intern. Congress Surface Activity*, volume I, pag 426-438, Butterworths, London (1957)

HLB

main advantage is ➡ its simplicity

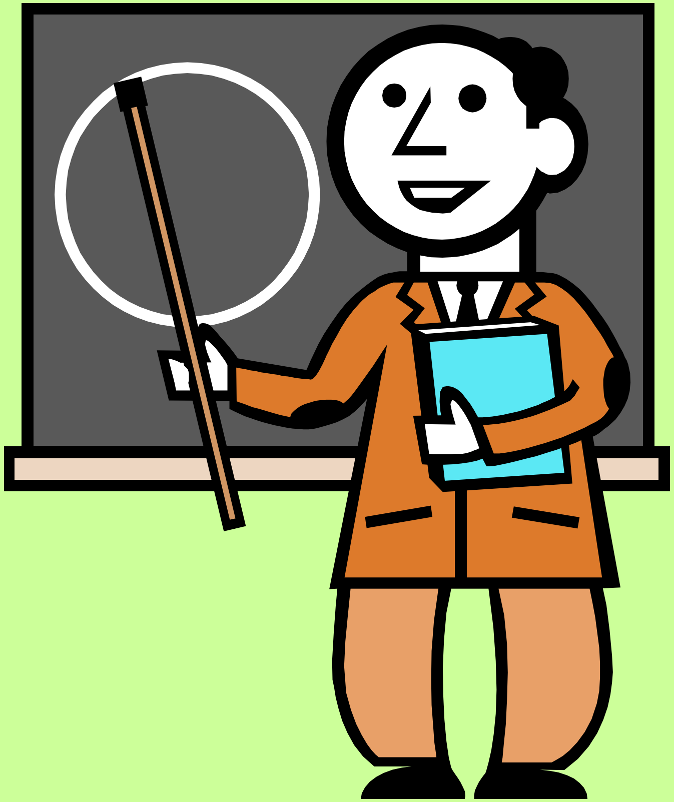
but ...

- to be used with caution (± 2 units)
- as a property of the surfactant only
- varies with temperature and other factors

useful to compare surfactants in a same physico-chemical environment !!!

Critical Micelle Concentration

CMC



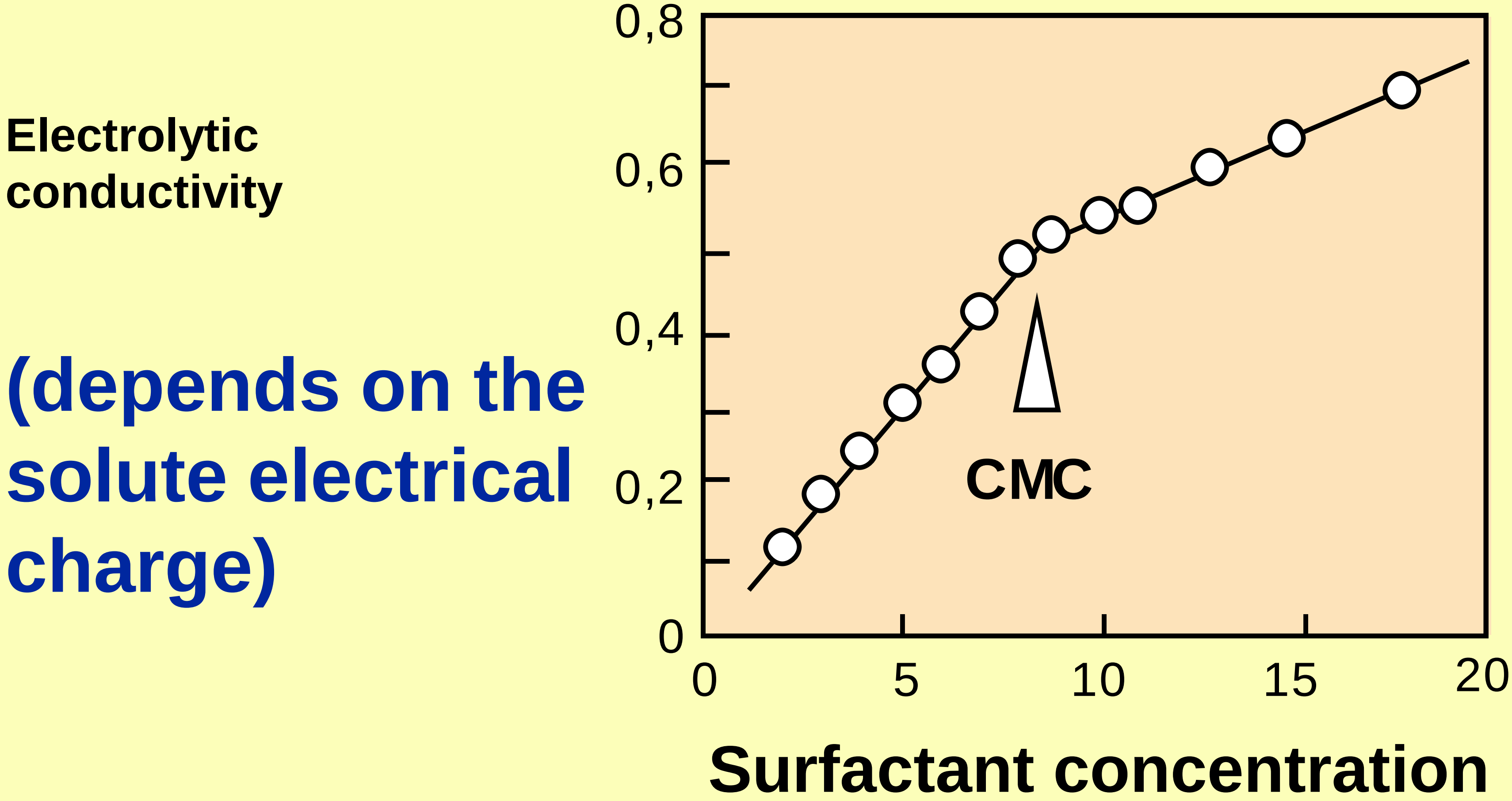
how to measure it and
how it can be affected

CMC micelle critical concentration can be detected in many ways

- **Surface/interface tension**
- **Electrolytic conductivity (ions)**
- **Osmotic pressure, Cryoscopy**
- **Dye solubilization**
- **Laser scattering (laser) and light diffraction (X-rays (SAXS), neutrons (SANS))**
- **Solubility of an apolar probe, NMR, UV/Vis**

CMC

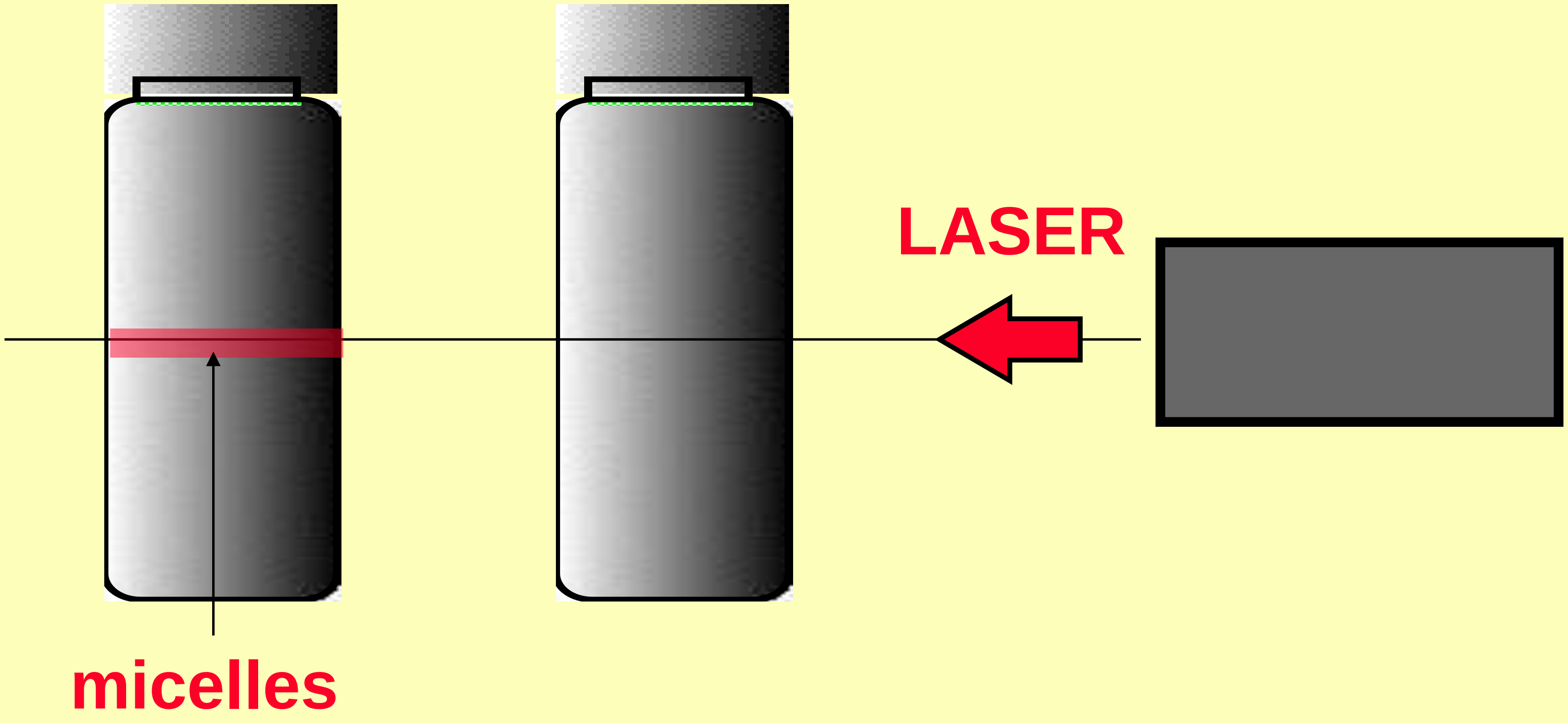
- **Electrolytic conductivity (ionic surfactants)**



(depends on the solute electrical charge)

CMC

- **Laser scattering (laser)**



‘Critical” in CMC means a phase transition, a micro-precipitation

When C > CMC

- Any additional molecule goes to the micelles
- Concentration around micelles ...

... Remains constant

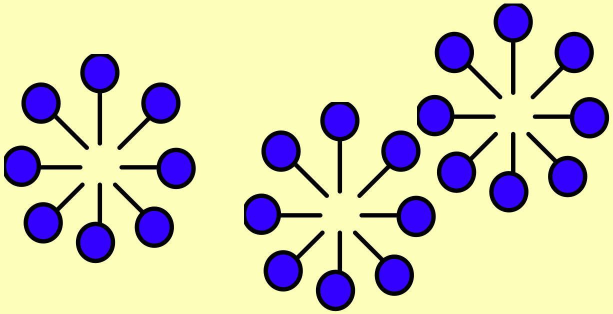
- There are more micelles

…anything that depends on it remains constant

Factors that lower CMC
(favor micelle formation)

Anything that turns the surfactant more hydrophobic

- **Larger non-polar group -> larger hydrophobic effect**



or promotes aggregation

- **Larger ionic strength**

  -> lower repulsion between polar heads
- **Less interaction with water (less solvency)**
- **Presence of an alcohol or any non-ionic additive**

CMC for some non-ionic surfactants

→ µ mol / L

Octyl phenol + 1 EO	45
Octyl phenol + 2 EO	70
Octyl phenol + 3 EO	105
Octyl phenol + 4 EO	135
Octyl phenol + 5 EO	180
Octyl phenol + 7 EO	290
Octyl phenol + 9 EO	325

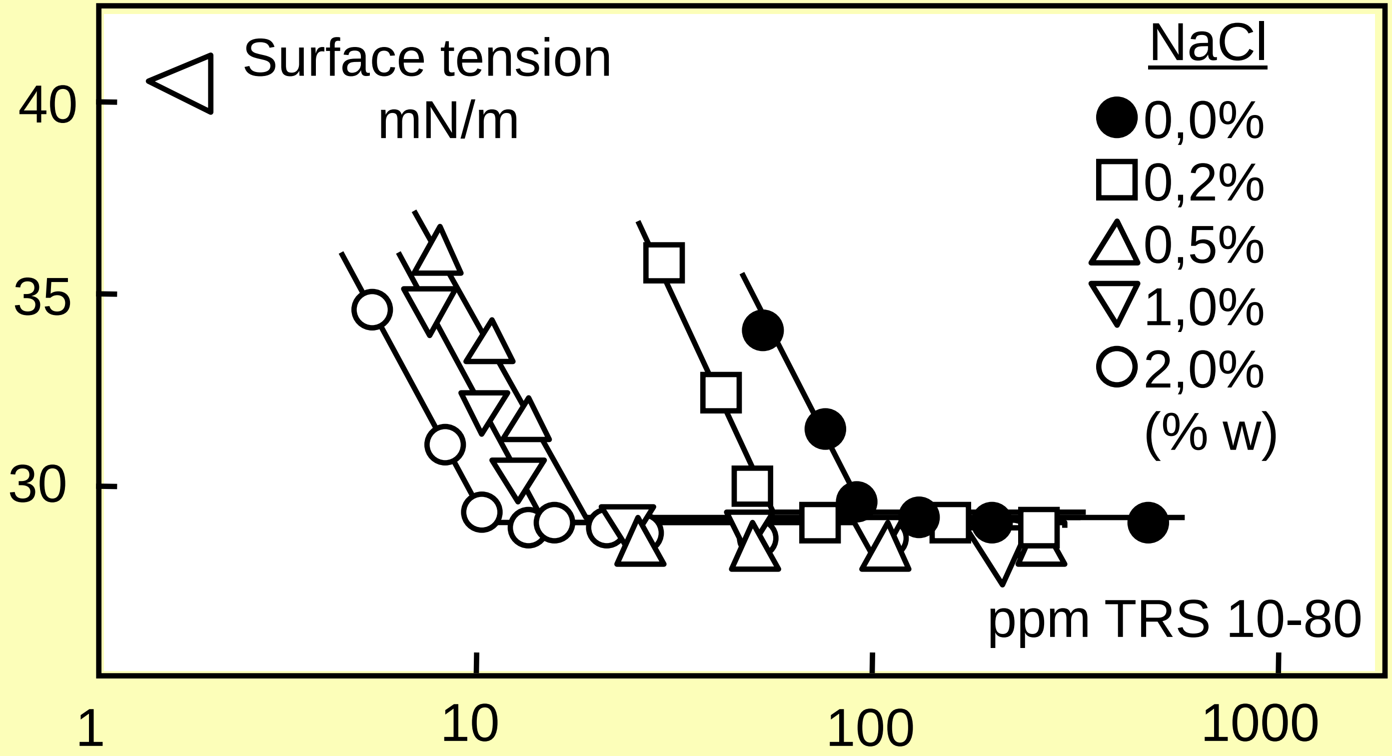
Effect of length of tail chain

CMC for some surfactants

	mmol/L
Na Octyl sulfate	120
Na Decyl sulfate	30
Na Dodecyl sulfate	8
Na Tetradecyl sulfate	2
Na Hexadecyl sulfate	0.6
Na Octadecyl sulfate	0.2

Log CMC = A - 0.30 N (carbons)

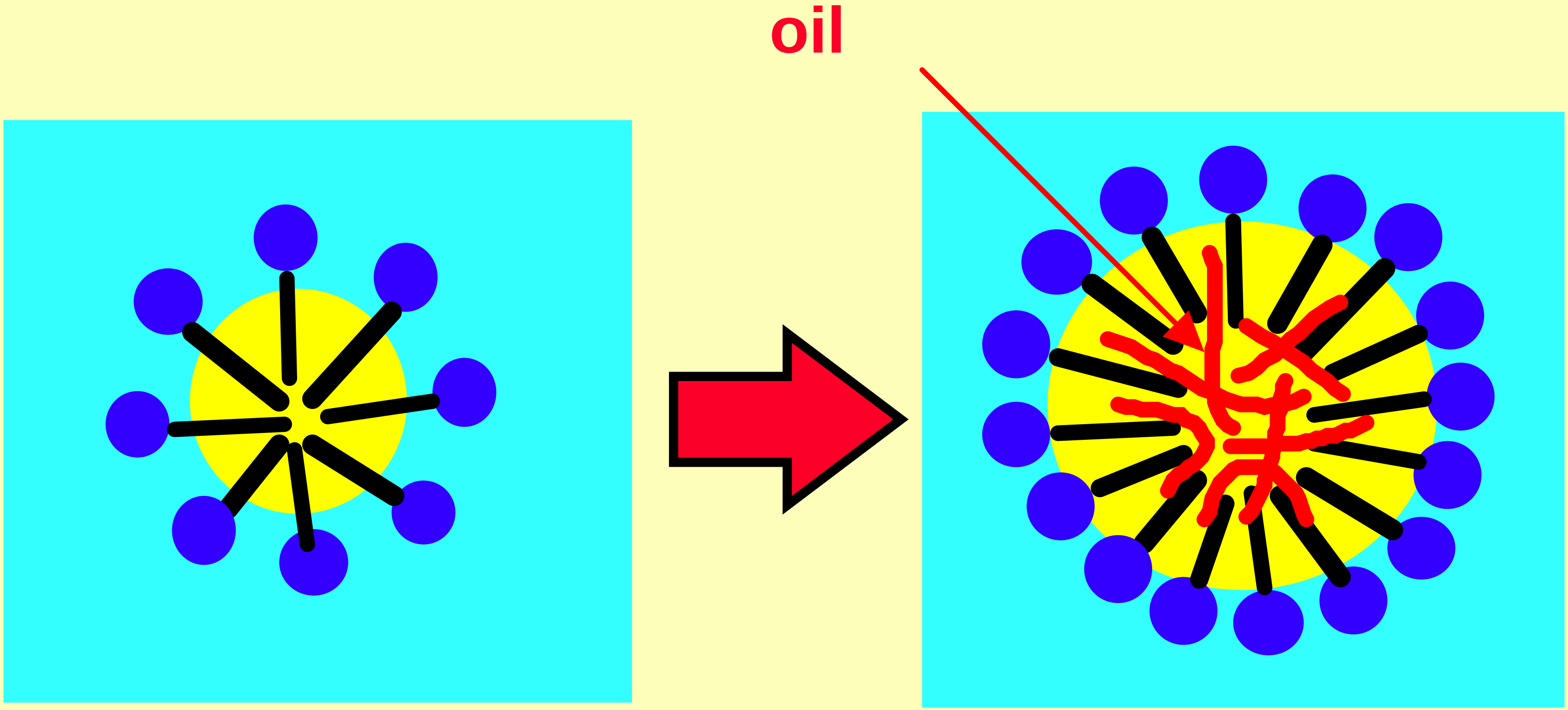
CMC as a function of salinity



log CMC = A - B log S

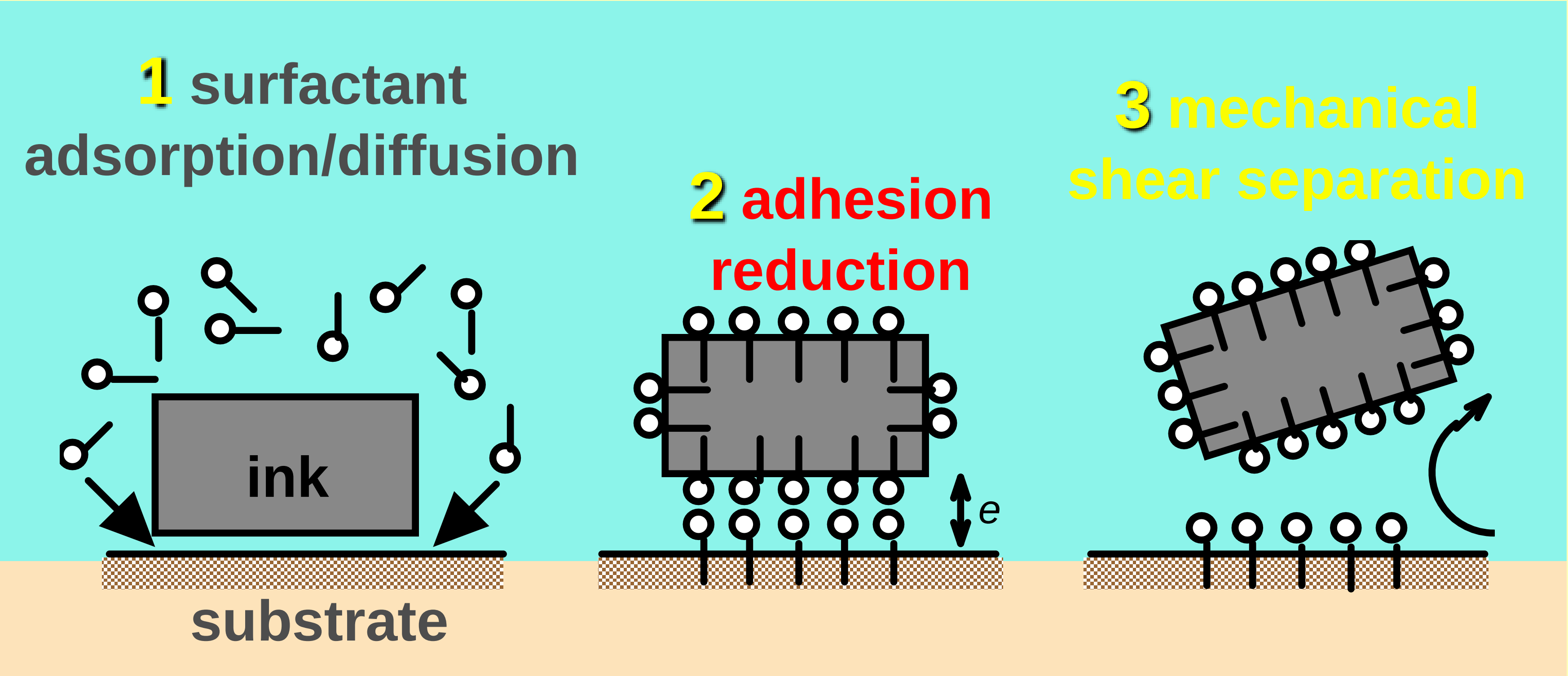
Micellar Solubilization

oil in the core of the micelle



Micellization related to Detergency

“separation” of solid (ink/stickies) particle from solid and stabilized in water



Claesson, P.M.; Dedinaite, A.; Rojas, O.J.
Advances in Colloid and Interface Science
104: 53-74 (2003)

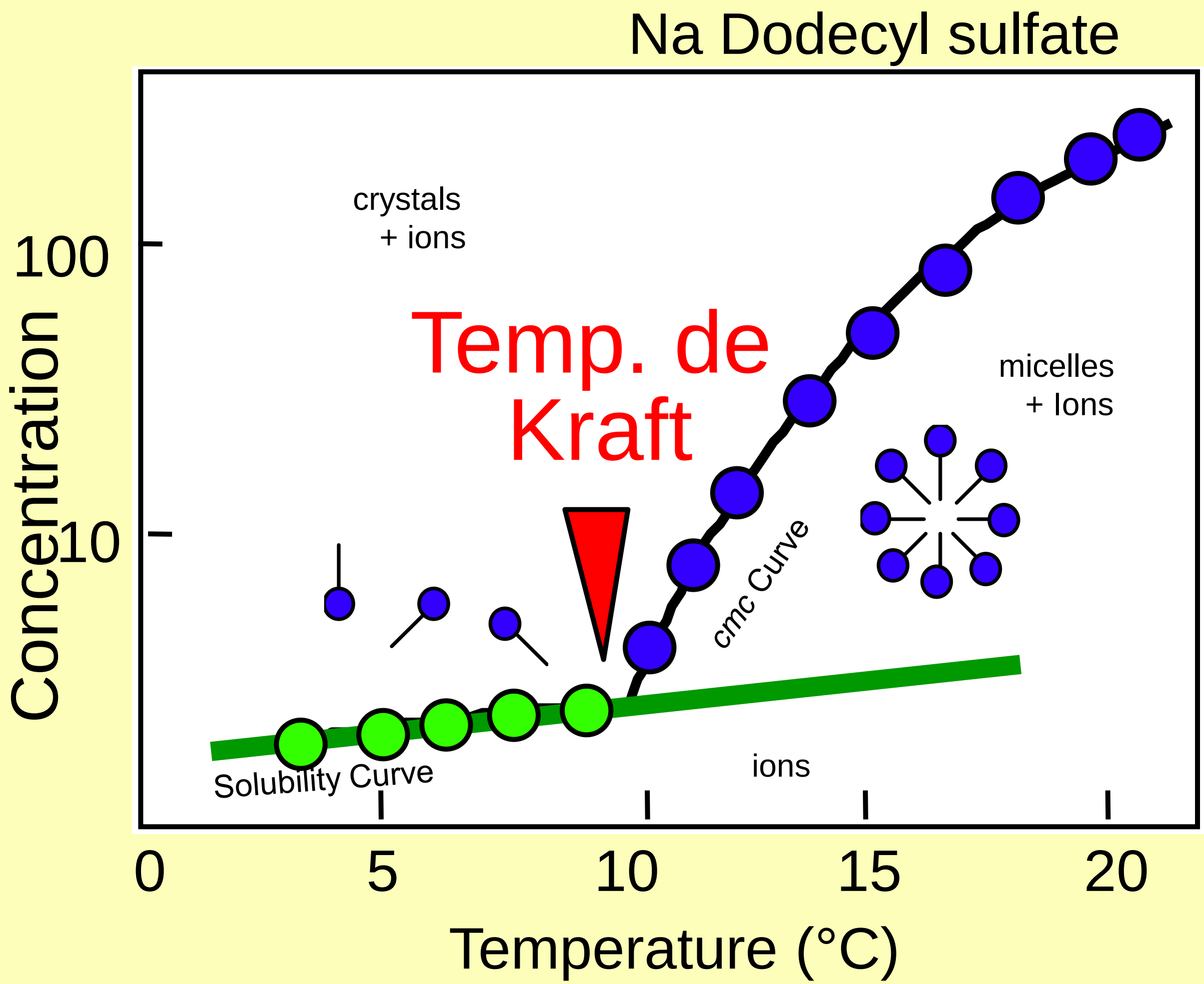
Solubility

(different than solubilization)

- *Kraft Temperature*
- *Cloud Point*

Kraft Temperature (ionics)

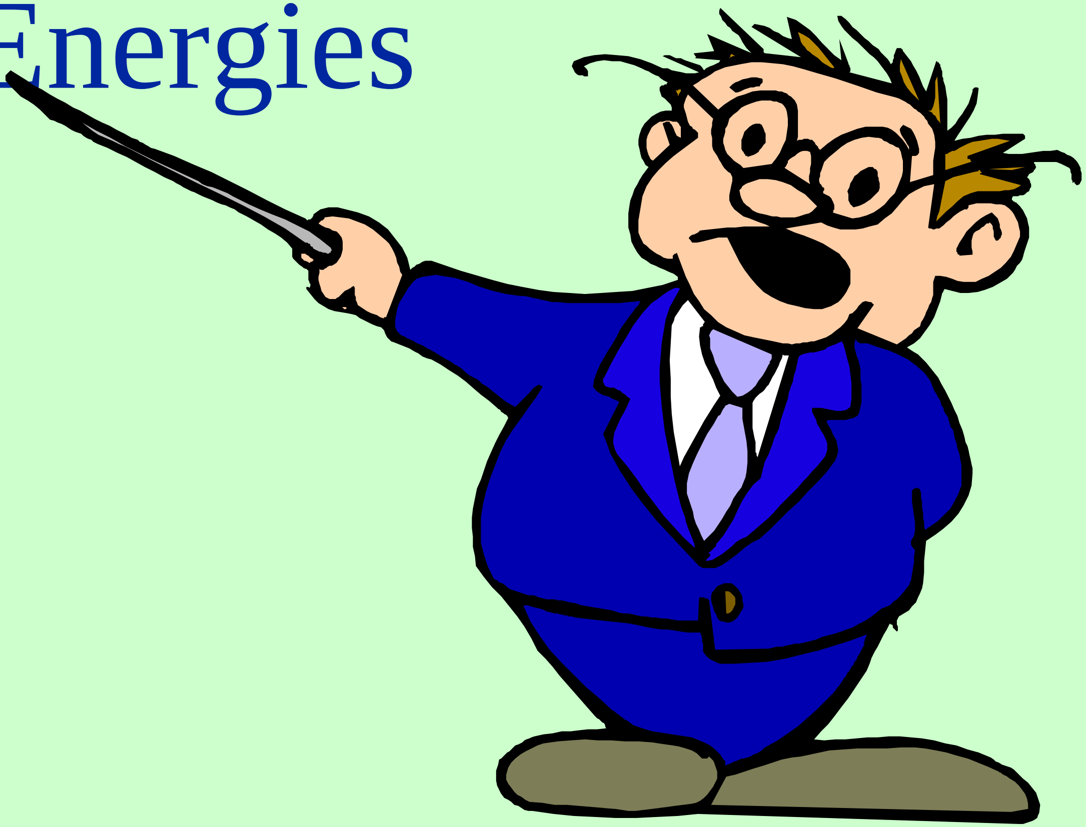
The temperature below which micelles do not form. Apparent solubility increases greatly above T_K.



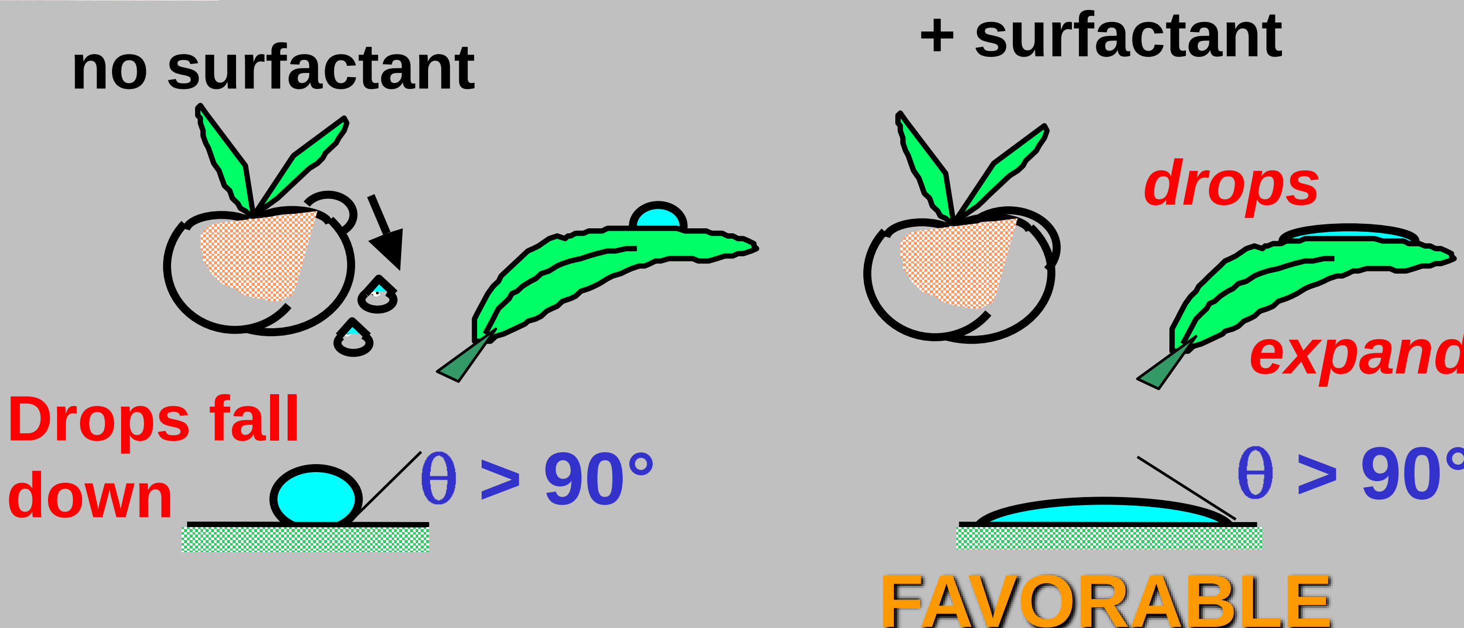
Cloud Point (non-ionics)

- **T at which the surfactant solution becomes cloudy**
- **This is due to de-solvation of poly-EO chain due to thermal energy/motion**
- **A Surfactant phase separates in the form of little drops TURBIDITY**

Solid Surfaces and Surface Energies

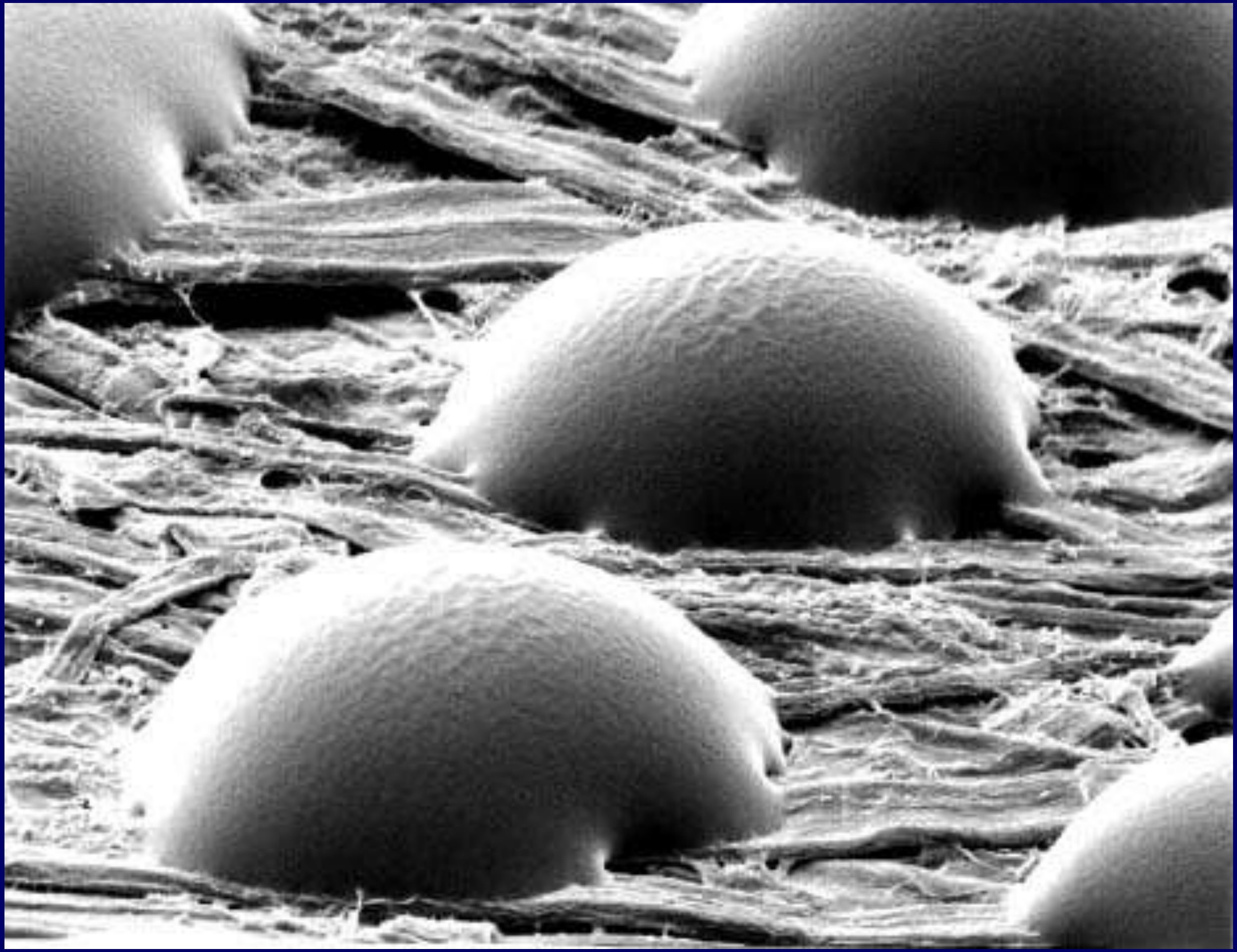


Surface modification



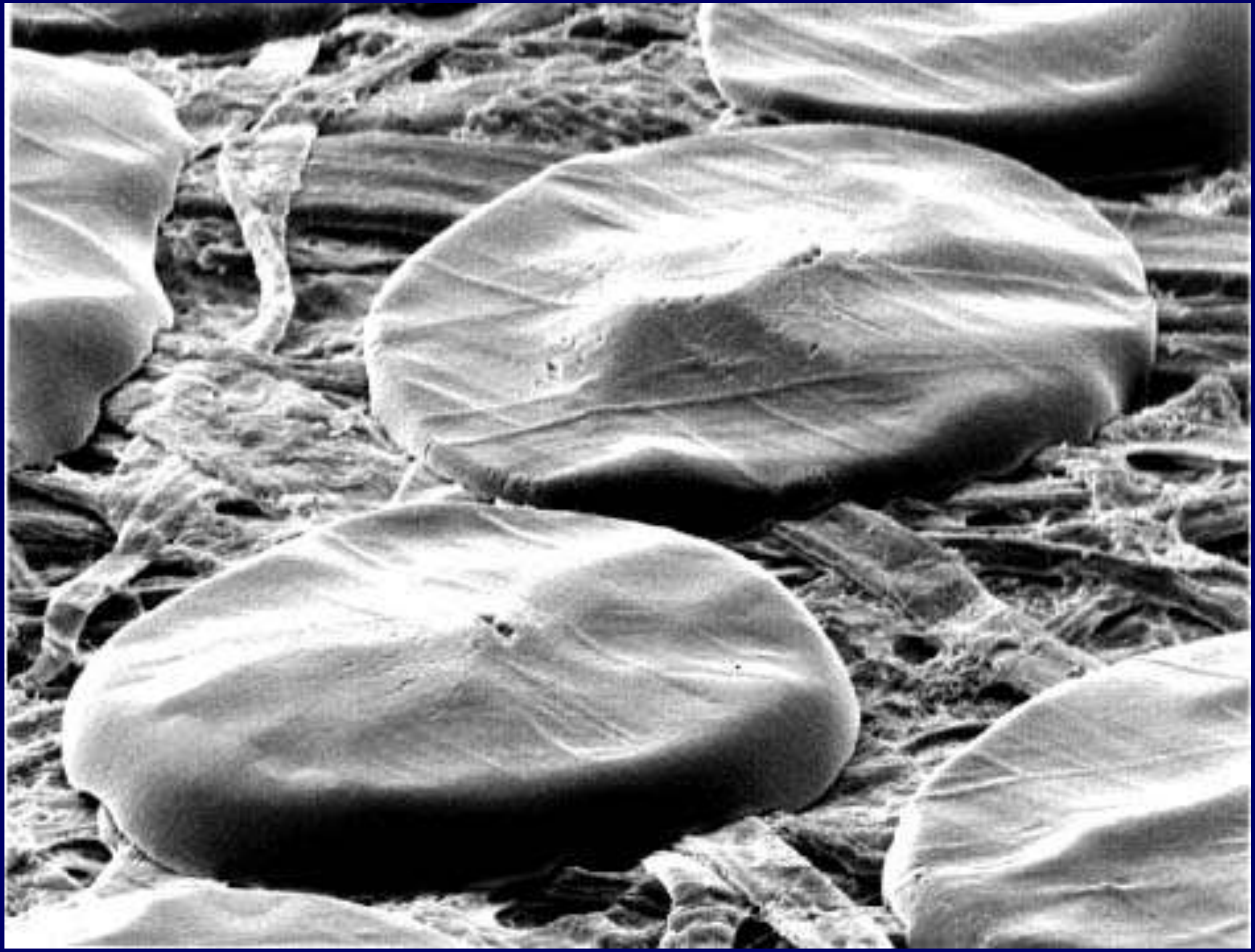
others...

A SEM photograph of phase-change ink drops on the surface of a bond paper



Hue P. Le Progress and Trends in Ink-jet Printing Technology, Part 4
Journal of Imaging Science and Technology · 42(1), 1998

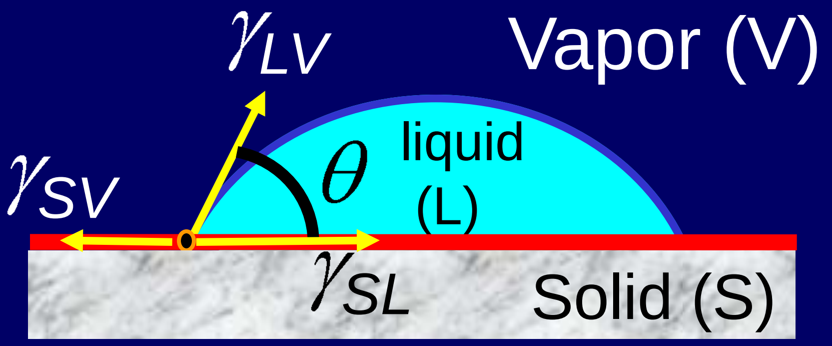
A SEM photograph of phase-change ink drops after fuse by cold pressure rollers



Hue P. Le Progress and Trends in Ink-jet Printing Technology, Part 4
Journal of Imaging Science and Technology · 42(1), 1998

Contact Angle

The concept of contact angle is rooted in the *surface energy*.



γ = interfacial tension or surface free energy

When a liquid droplet interacts with a solid surface, the droplet attains an equilibrium shape. The droplet can be characterized by the angle formed at its edge where the liquid contacts the solid surface . This angle is called the contact angle.

Contact Angles

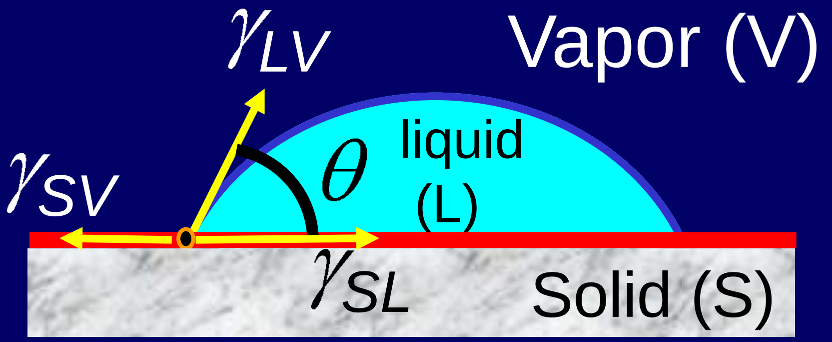
Solid	Liquid	θ
α-cellulose	water oil	0 0
TiO_2	water	0
Talc	water	88
Paraffin	water	110
Polyethylene	water	95
Teflon	water mercury	112 150
AKD Film	water	135-140

Contact Angles for various cellulose fibers:

Pulp Type	Contact Angle
Disolved pulp; cotton	0°
Bleached softwood	20-30°
TMP (sof/hardwood)	40-50°
Unbleached softwood	50-65°
Softwood / ASA	65-90°
Softwood / AKD	60-140°
Douglas fir “self sized”	65-70°

Contact angle can be used quantitatively to measure the interaction between any liquid and solid surface. The surface free energy components of the liquid and solid can be modeled as vectors:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$$



γ_{lv} = surface free energy of the liquid

γ_{sl} = interfacial free energy between the solid and liquid

γ_{sv} = surface free energy of the solid

This equation is derived simply from an energy balance in the horizontal direction.

Wetting can be defined based on the contact angle:

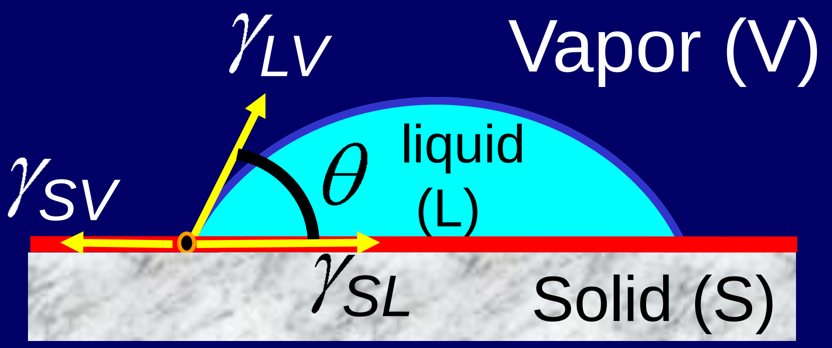
$\theta = 0°$ for spreading
$0° < \theta < 90°$ for wetting
$90° < \theta < 180°$ for non-wetting

It is possible to have a greater thermodynamic driving force even though it is not possible to measure an angle less than zero. This greater force can be characterized by the *spreading coefficient*.

Contact angle and Interfacial Tensions

Young Eq.:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$$



γ_{lv} = surface free energy of the liquid

γ_{sl} = interfacial free energy between the solid and liquid

γ_{sv} = surface free energy of the solid

Let's talk about surface tension...

Solids Critical Surface Tension

Young Eq.:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

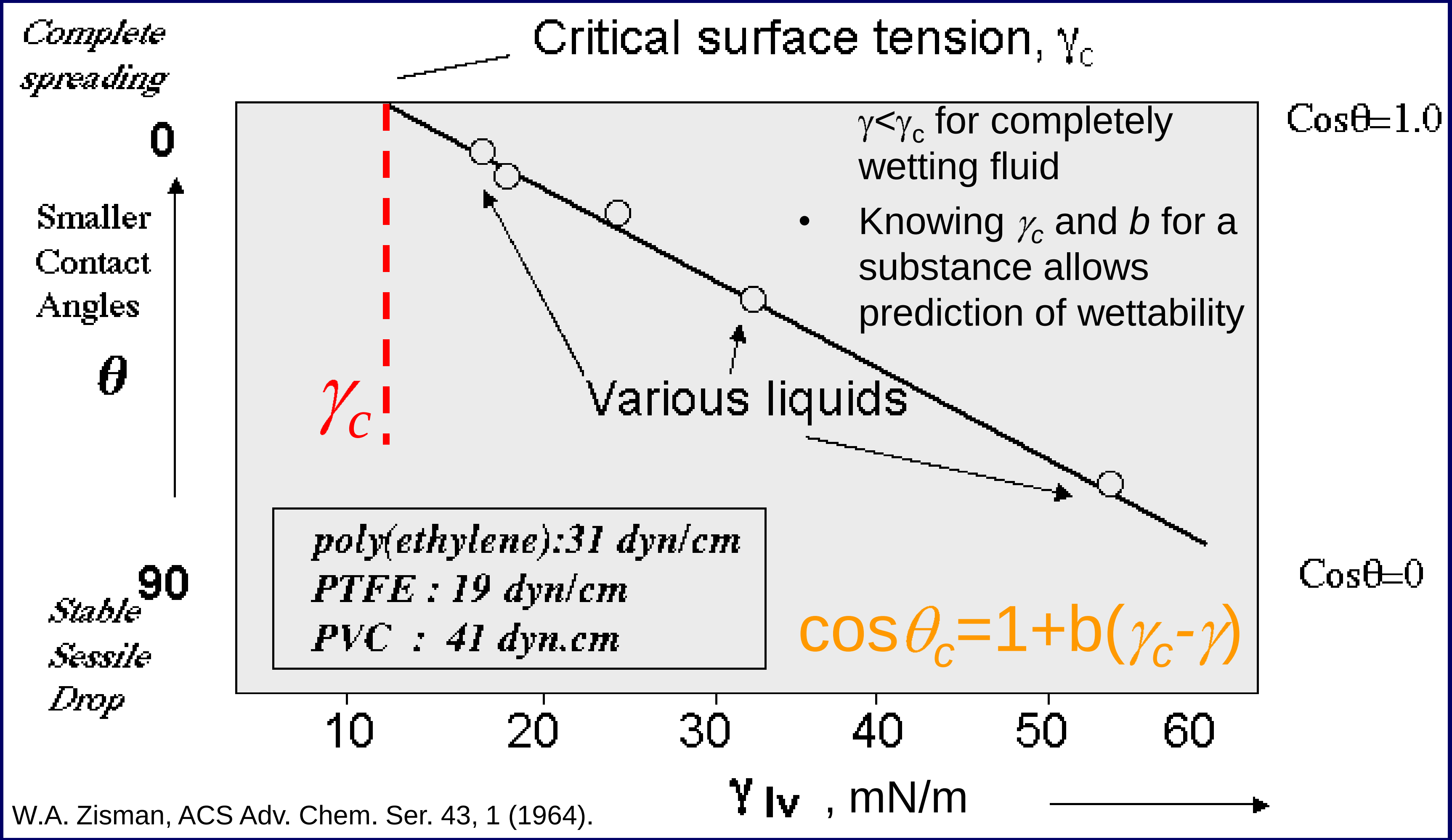
?

Surface free energy is time consuming to measure. It would be helpful if structure could be correlated with surface free energy to enable prediction of the surface energy: Zisman plot.

Zisman Plots and Critical Surface Energy

Cosine of the contact angle versus the surface free energy of various wetting liquids on a given solid. The resulting plot is a straight line. Thus, there exists some unique value for each polymeric solid where the cosine of the contact angle is unity. This value is termed the critical surface free energy. A liquid with surface free energy below the critical value will wet and spread over the solid surface, whereas a liquid with surface energy above the critical value might wet but won't spread.

Zisman Method
Critical Surface Tension



Zisman's empirical prediction fails for liquids that form hydrogen bonds or acid-base interactions with the substrate. These liquids would spread spontaneously on the substrate

Critical Surface Tension (γ_C):

Solid	γ_C (mN/m)
Teflon	18.5
Polyethylene	31
Paraffin wax	30
Starch	39
Regenerated cellulose	44
Bleached kraft pulp	34
CTMP pulp	36
AKD Film	20

Critical surface tensions

Surface groups

Surface constitution	γ_c (mN/m)
Fluorocarbon	6-25
Hydrocarbon	22-35
Chlorocarbon	≈40
Nitrated HC	40-45

Polymers

Polymer	γ_c (mN/m)
Teflon	≈18
Silicone (PDMS)	24
Polyethylene	31
PMMA, PVC	39
PET, Nylon	43

Control wetting by surface modification;
e.g. adsorption of surfactants!!!!!

Surface Energies[*]

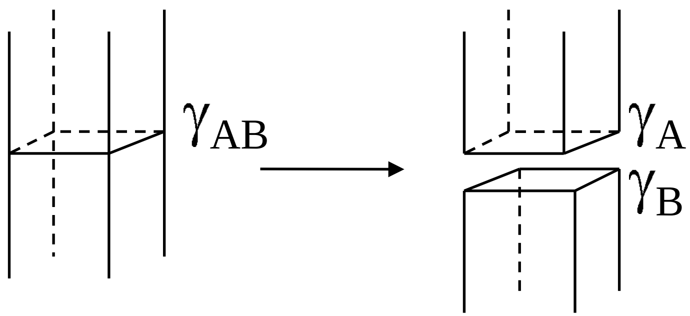
Substrate Type	Surface energy (mNm^{-1})	Description
Quartz (SiO_2)* [a][e]	25-40	Hydrophilic, acidic oxide
Poly-tetrafluoroethylene* [b]	18.5	Highly hydrophobic plastic (*e.g.* Teflon®)
316L stainless steel [c]	52-53	Hydrophilic, high surface energy oxide
Polyethyleneterephthalate [d]	39-61	Hydrophobic plastic (polyester)
Borosilicate glass [e]	25-40	Hydrophilic (for comparison with quartz)
Cellulose (LB-monolayer) [f]	33-36	Hydrophilic, low-charge
Wood resin[g]	25-28	Hydrophobic, extracted from wood
Gold[h]	40-45	QCM-D typical electrode, contaminant-free
Talc[i]	30-32	Hydrophobic

The critical surface tension for wetting (γ_c) is a useful interfacial parameter for comparison, though it is worth noting that γ_c is not a fundamental property of the solid and depends upon the specific (probe) liquid system [Good, W. R., “A Comparison of Contact Angle Interpretations,“ *J. Colloid Interface Sci. 44* (1): 63-71 (1973)]

Surface Energies of Solids

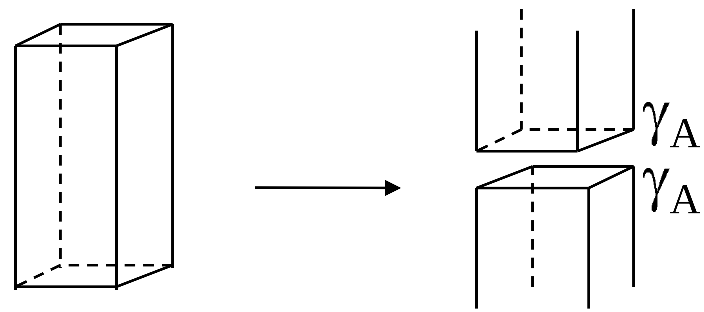
Work of Adhesion & Cohesion

Adhesion



$$W_{adh} = W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}$$

Cohesion



Here, $\gamma_A = \gamma_B$ and $\gamma_{AB} = 0$, so

$$W_{coh} = W_{AA} = 2\gamma_A$$

Adhesion – state in which 2 dissimilar bodies are held together in intimate contact such that a force can be transferred across the interface.

Thermodynamic adhesion is driven by interfacial forces associated with reversible procesess.

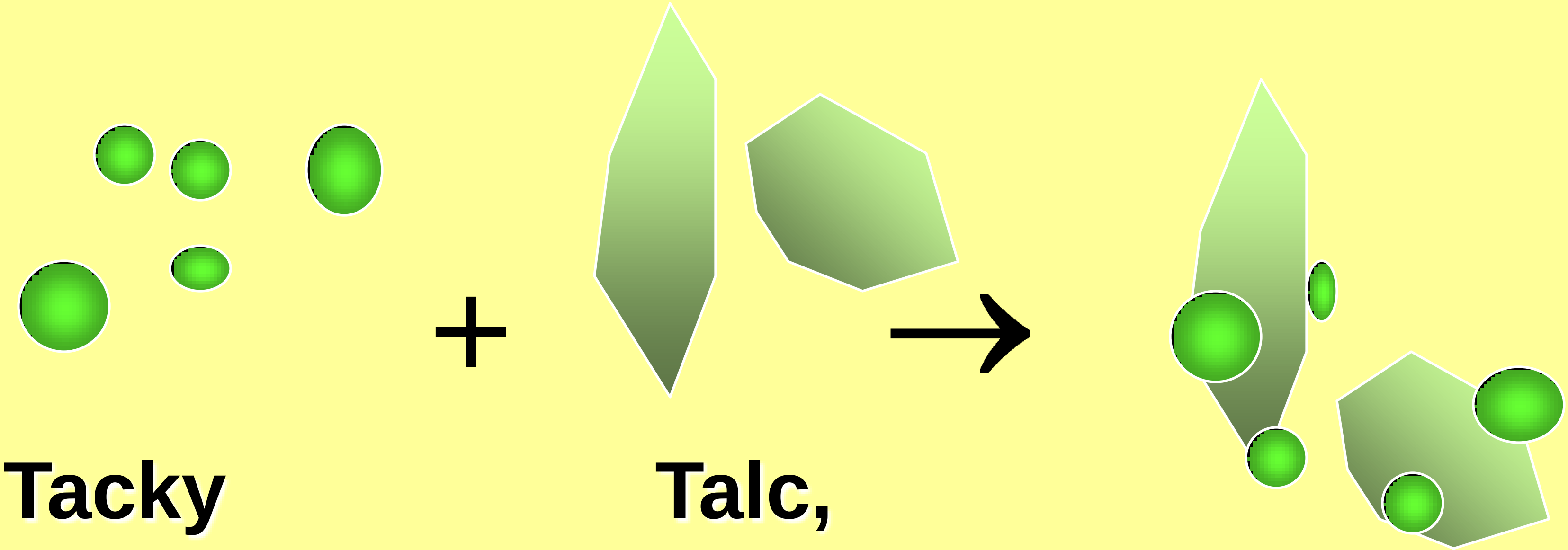
Surface Energy

In nature every system tries to minimize its surface energy.

Example: like dissolves like.

Example: hydrophobic will try to be surrounded by hydrophobic.

Deposits



Tacky substances

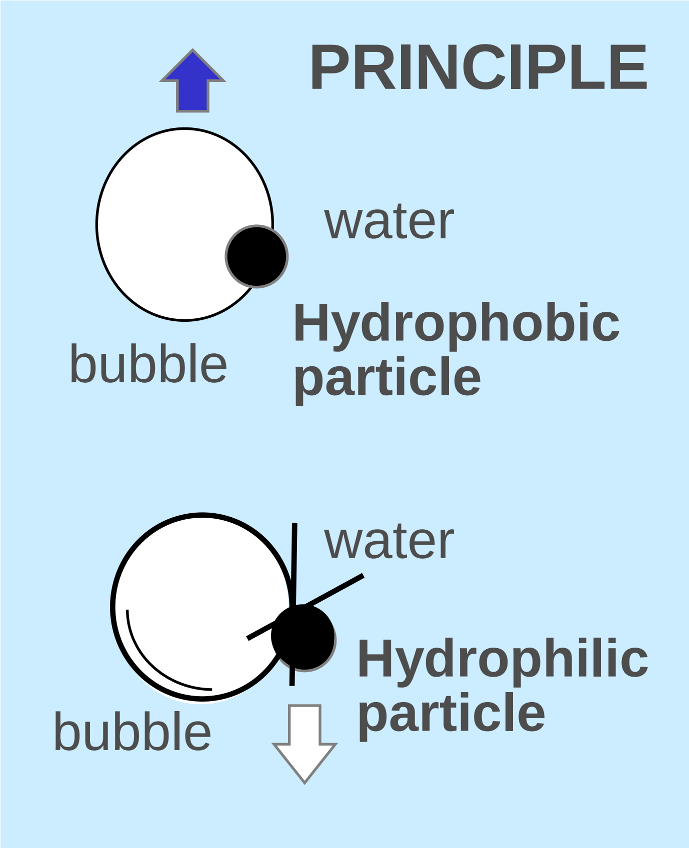
Talc, *etc.*

Less tacky
Better retained

From Hubbe

Flotation

Hydrophobic particles attach to hydrophobic air



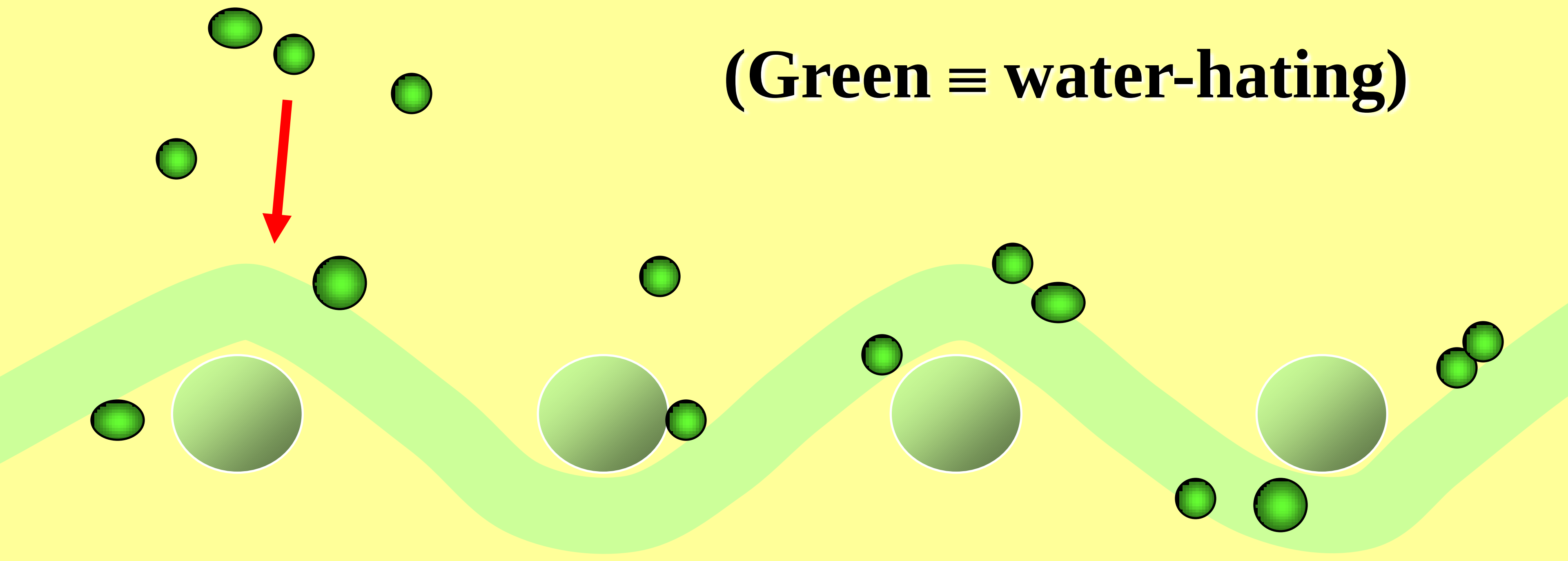
Note: the higher the contact angle between water and particle: the deeper the particle will "penetrate" the air bubble.

Surfactants work against this, actually trying to wet surface.

Stickies and deposit control

Stickies on fabrics

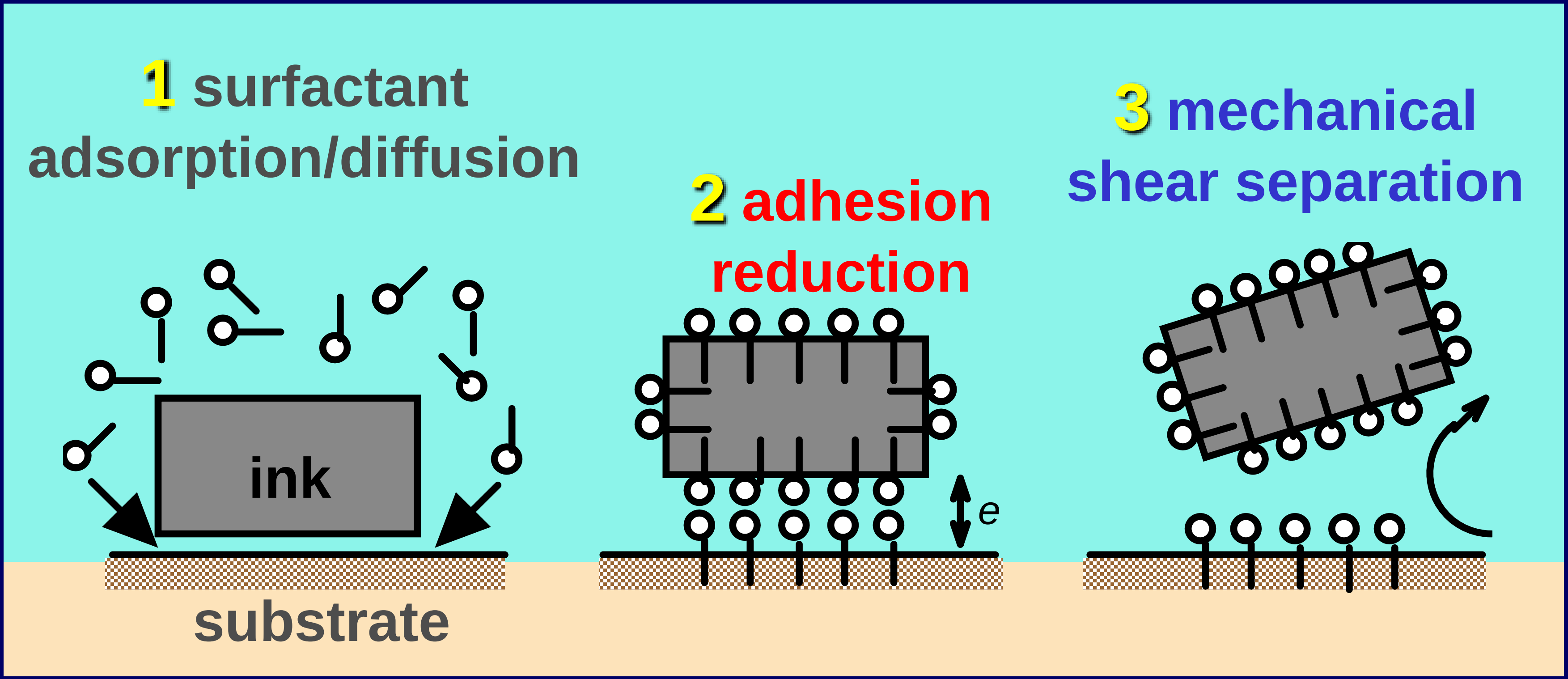
(Green ≡ water-hating)



From Hubbe

Detergency

"separation" of solid (ink/stickies) particle



Claesson, P.M.; Dedinaite, A.; Rojas, O.J.
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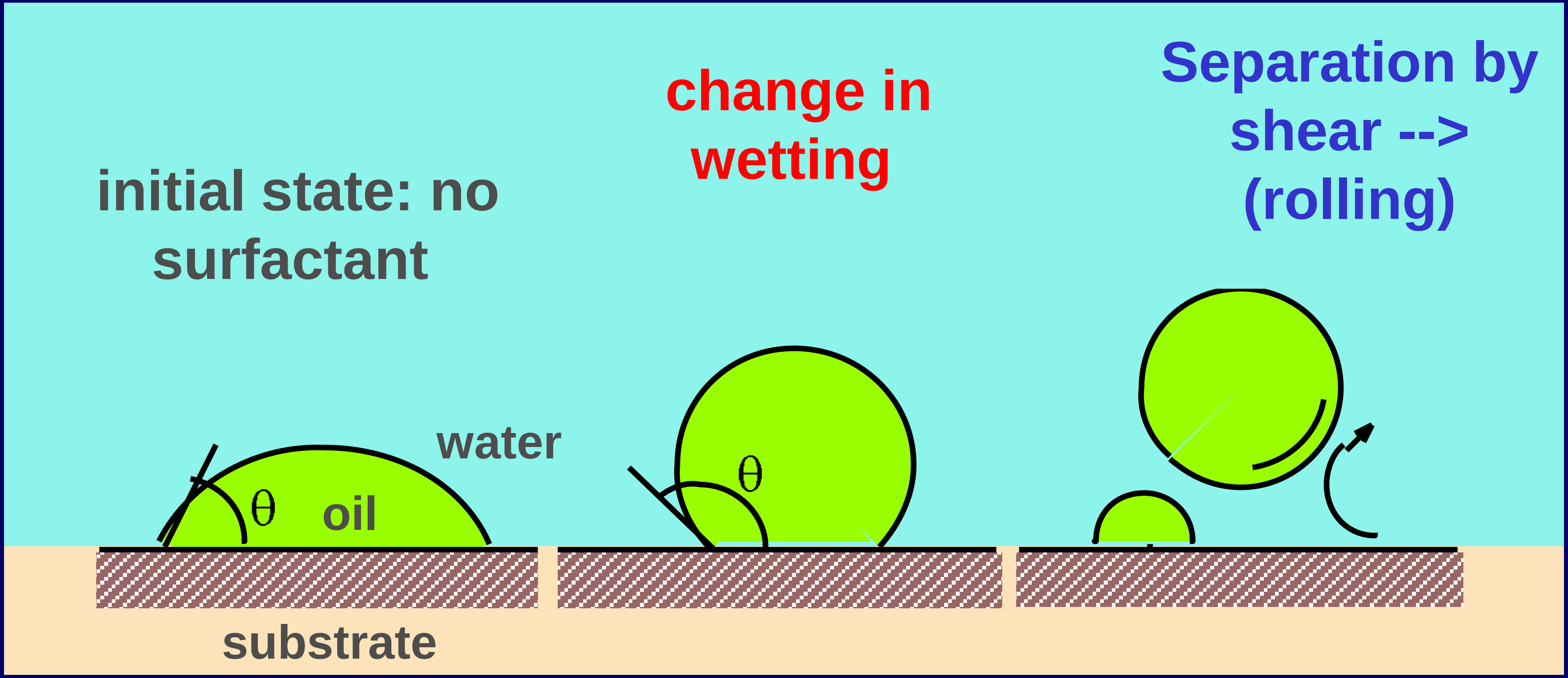
Detergency

Separation of ink drop

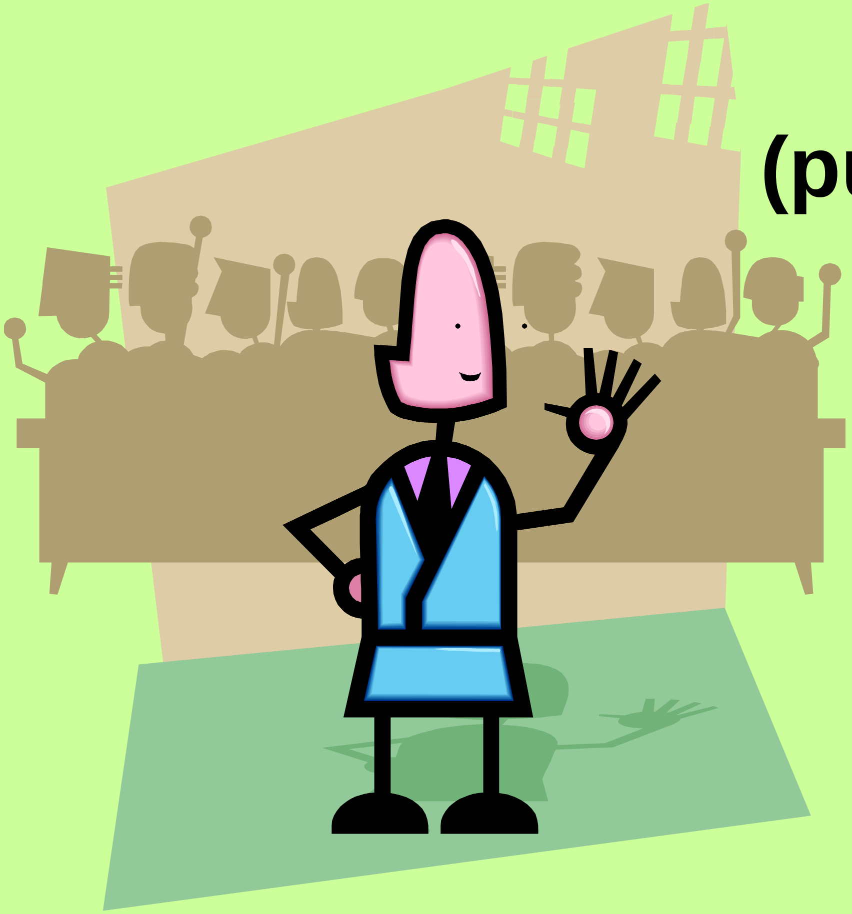


Summary

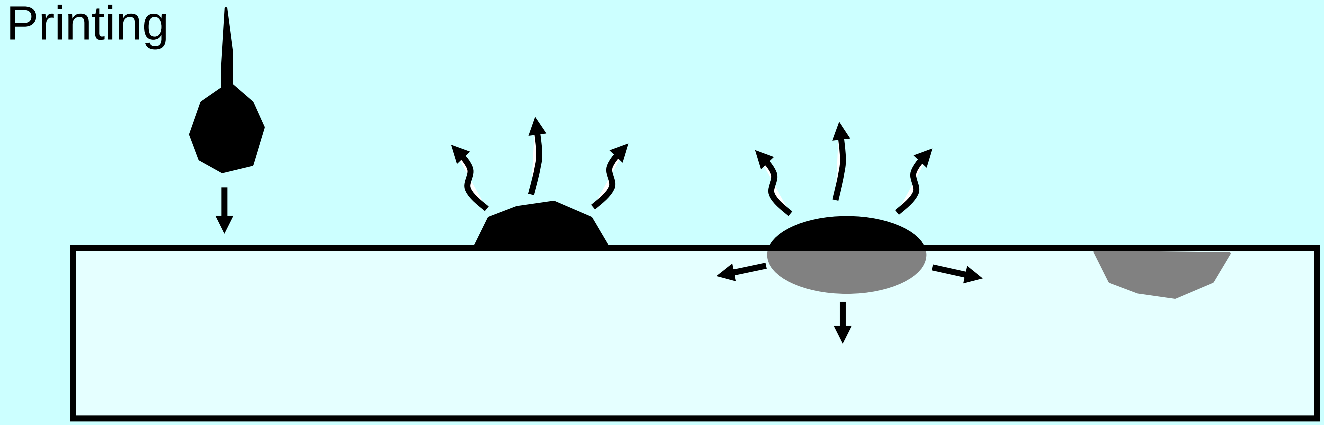
- In nature every system tries to minimize its surface energy.
- Like dissolves like.
- Surfactants have hydrophillic and hydrophobic parts
- Surfactants lower surface tension of liquids
- Surfactants will preferentially exist at surfaces, changing the surface energy of the system, affecting:
  - Foaming
  - Liquid Penetration
  - Stabilization of hydrophobic particles and liquids in water (micellization)

Liquid Penetration

(pulping, deinking, bleaching!)



Printing = different mechanisms



Wetting Delay & Evaporation

Wetting Penetration & Evaporation

Drying

Drying mechanisms of a water-based ink-jet drop on a plain paper

Liquid Penetration

Mechanism of liquid penetration on a paper sheet:

- capillary penetration
- liquid diffusion in porous media
- diffusion throughout the fiber solid fraction

Capillary flow in paper depends on:

- Surface chemistry (wettability)
- Paper structure

Liquid Penetration

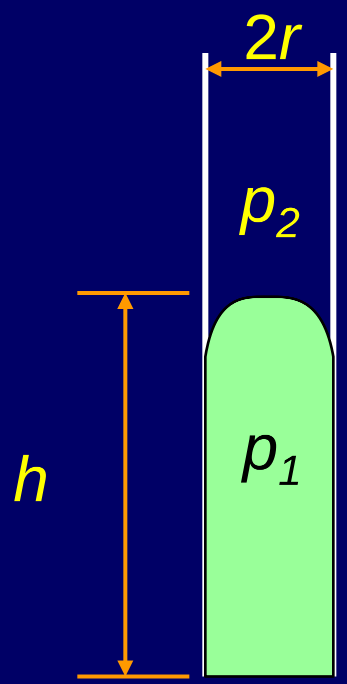
Why is it important in pulping:

- **Water must penetrate inter fiber spaces as a prerequisite to separation of fibers**

- **Swelling of fibers (with accompanying fiber dimension changes) helps to separate ink from fiber surface**

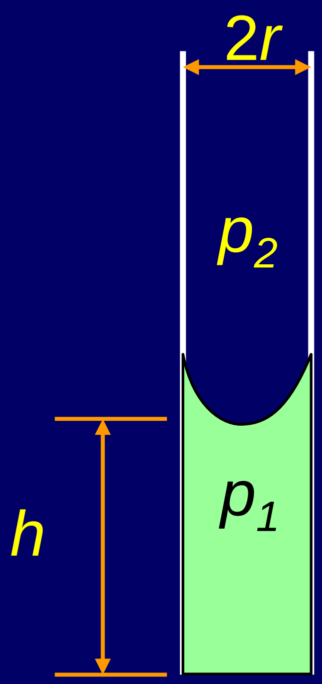
Capillary Wetting

Non-Wetting Condition



$$\theta > 90^o$$

Wetting Condition



$$\theta < 90^o$$

$$\Delta p = p_1 - p_2$$

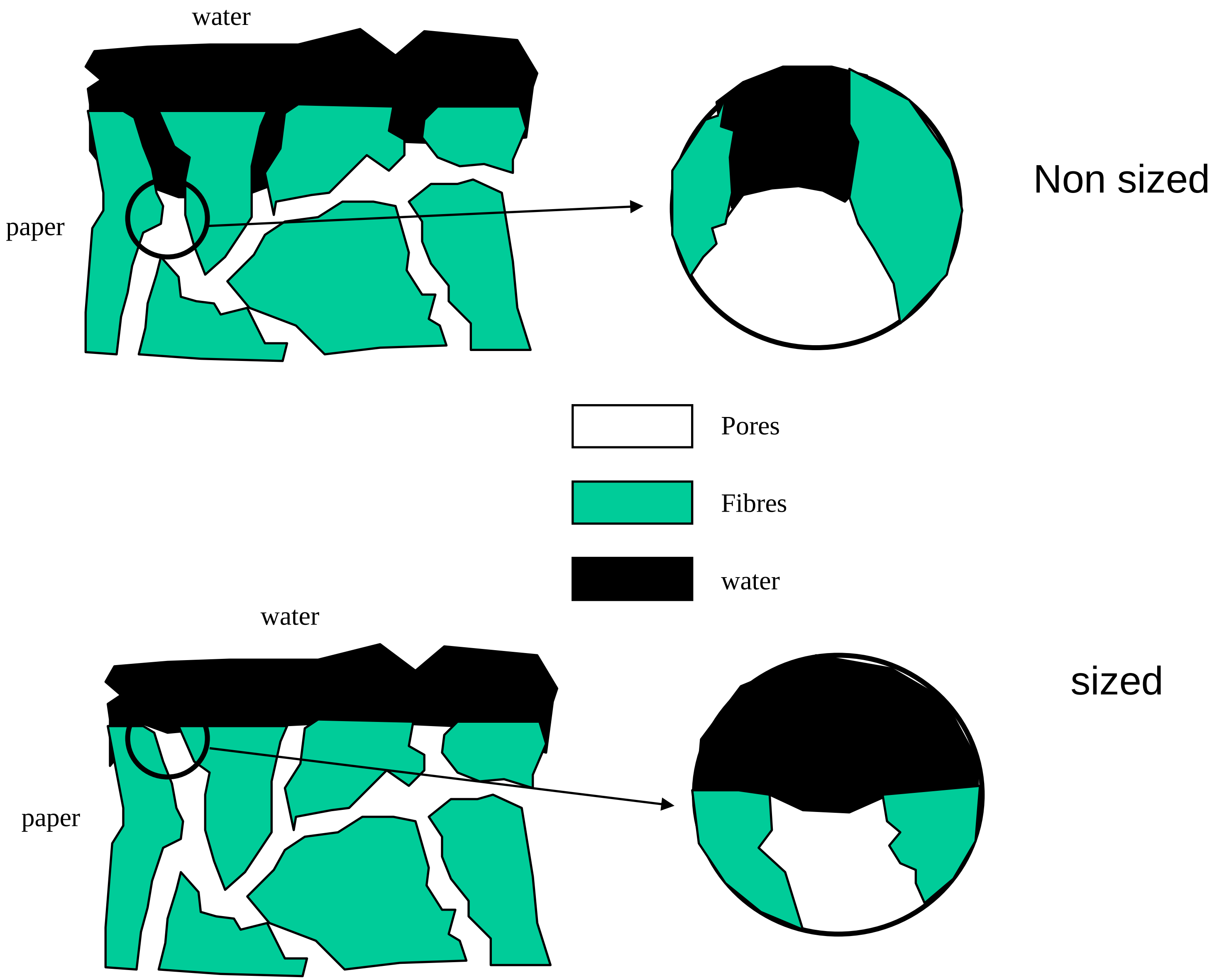
- Liquid enters the paper by capillary imbibition and enters the space between the fibers.

- If the liquid can cause swelling, it will also then enter the fiber walls.

- Any expansion in paper is due to water inside fiber walls and not between the fibers.

- Swelling is often just used as an expression for water absorption by the fibers, because of the resulting dimensional changes.

- This is no longer really a capillary effect although it can appear to obey the same laws.


water
paper
Non sized
Pores
Fibres
water
water
paper
sized

Interaction of Water with Paper

Capillary sorption is described by the Hagen-Poiseuille equation but this must be used carefully where swelling occurs. For a single capillary:

$$\frac{dh}{dt} = \frac{r^2 \Delta P}{8\eta h}$$

Assume paper is a set of capillaries of radius r perpendicular to the surface. The pressure caused by the meniscus of a liquid in one of these capillaries is

$$\Delta P = \frac{2\gamma \cos\theta}{r}$$

Lucas-Washburn Equation

Combining the last two equations:

$$\frac{dh}{dt} = \frac{r\gamma\cos(\theta)}{4\eta h}$$

(differential form)

h = height of penetration up a capillary

r = radius of the capillary

t = time

γ = surface tension

η = viscosity of the liquid

θ = contact angle of the liquid and capillary wall

$$h^2 = \frac{r\gamma\cos\theta}{2\eta}t$$

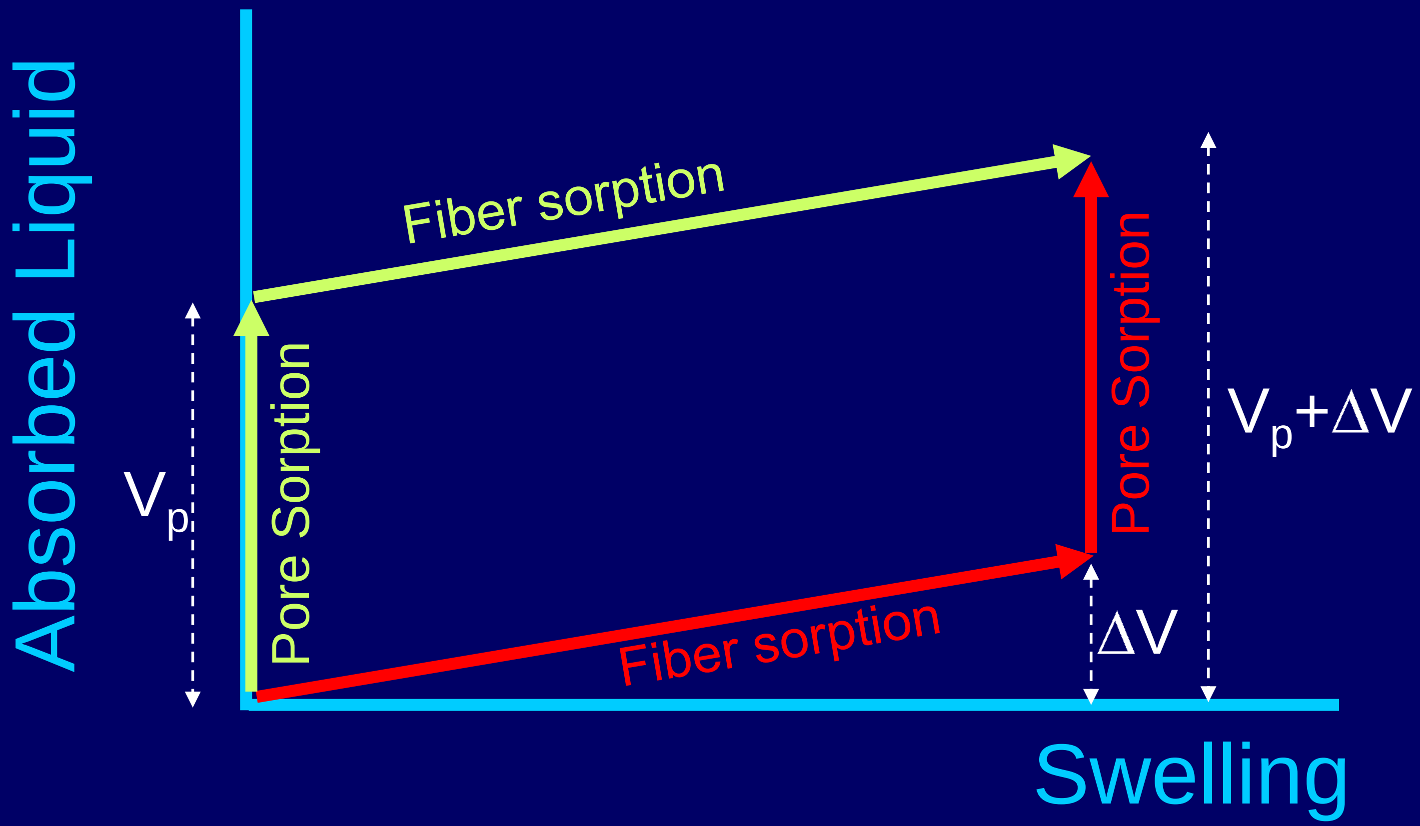
Internal sizing
Refining/surface sizing

This tells us that the flow of water into the pores of the structure due to capillary action should be proportional to the square root of time (which is more or less a general law for porous materials).

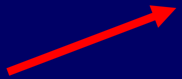
Sorption into fibers involves capillary action but also involves surface diffusion and diffusion through cellulose. It does, however, still follow a square root law (dist penetrated to sqrt time).

The degree of intra-fiber sorption can be determined by measuring z-direction swelling and the total sorption can be determined gravimetrically, so it is possible to separate the two and express the combined system as a parallelogram model.

Sorption of water into paper



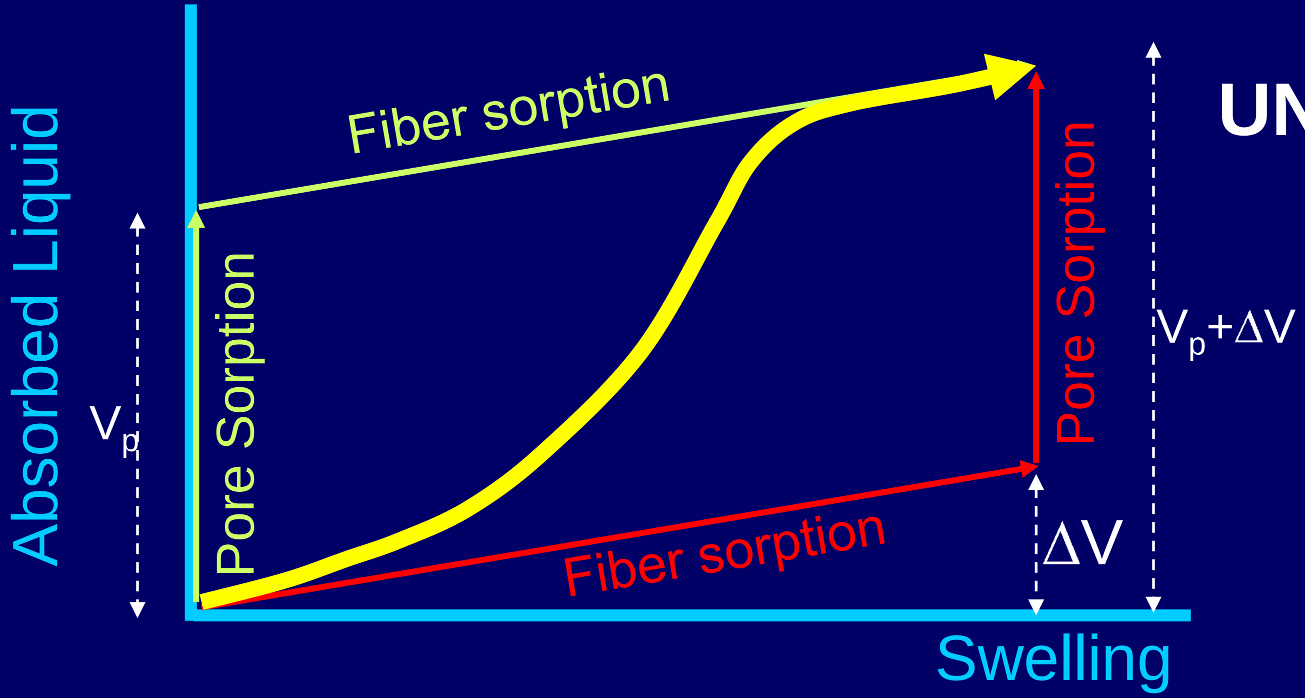

macropores are filled first followed by slower fiber swelling


fibers absorb water first followed by macropores (e.g. vapor exposure).

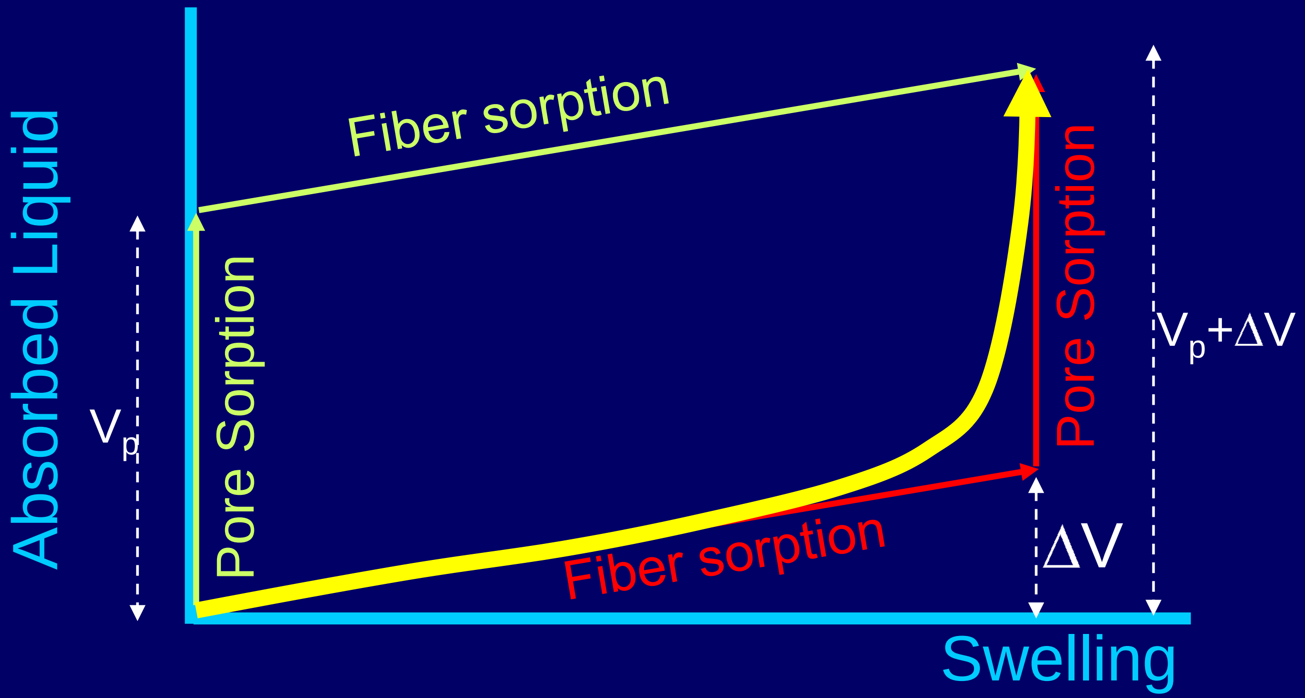
Pore sorption: absorption by capillary action into the gaps between fibers

Fiber sorption: absorption into the fibers themselves, which causes swelling.

UNSIZED PAPER



SIZED PAPER



Sorption into the gaps between fibers is prevented. The inside of the fibers can still be filled by vapor diffusion

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