

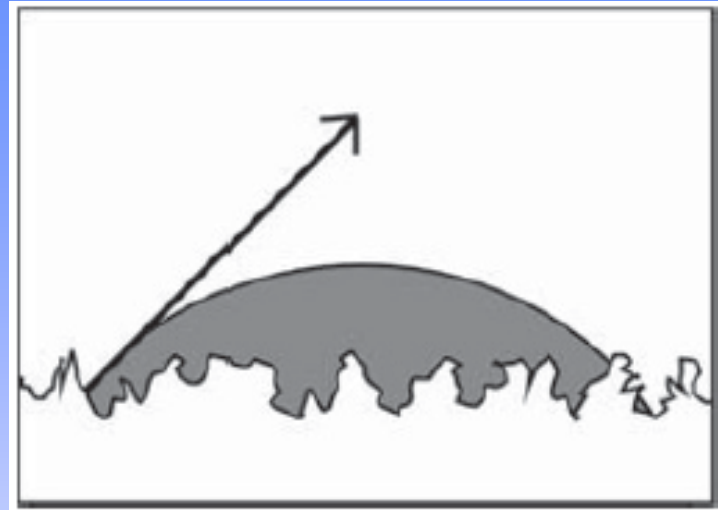
Fundamental Equations of Colloid and Interface Science

Contact Angle: The Young Equation

Thomas Young (1773–1829)



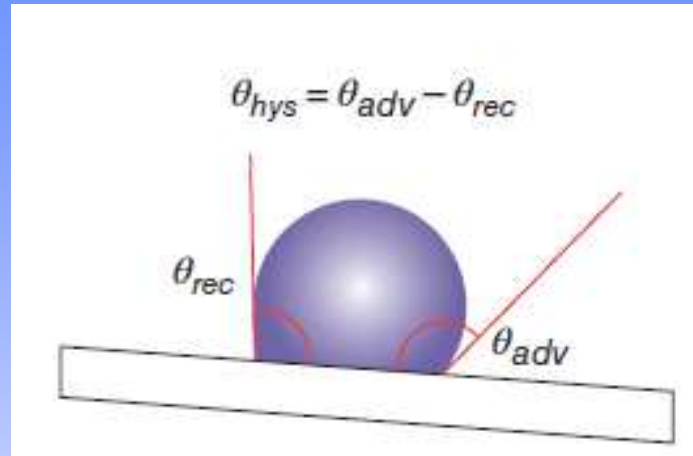
Reproduced from [http://commons.wikimedia.org/wiki/File:Thomas_Young_\(scientist\).jpg](http://commons.wikimedia.org/wiki/File:Thomas_Young_(scientist).jpg)



$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta$$

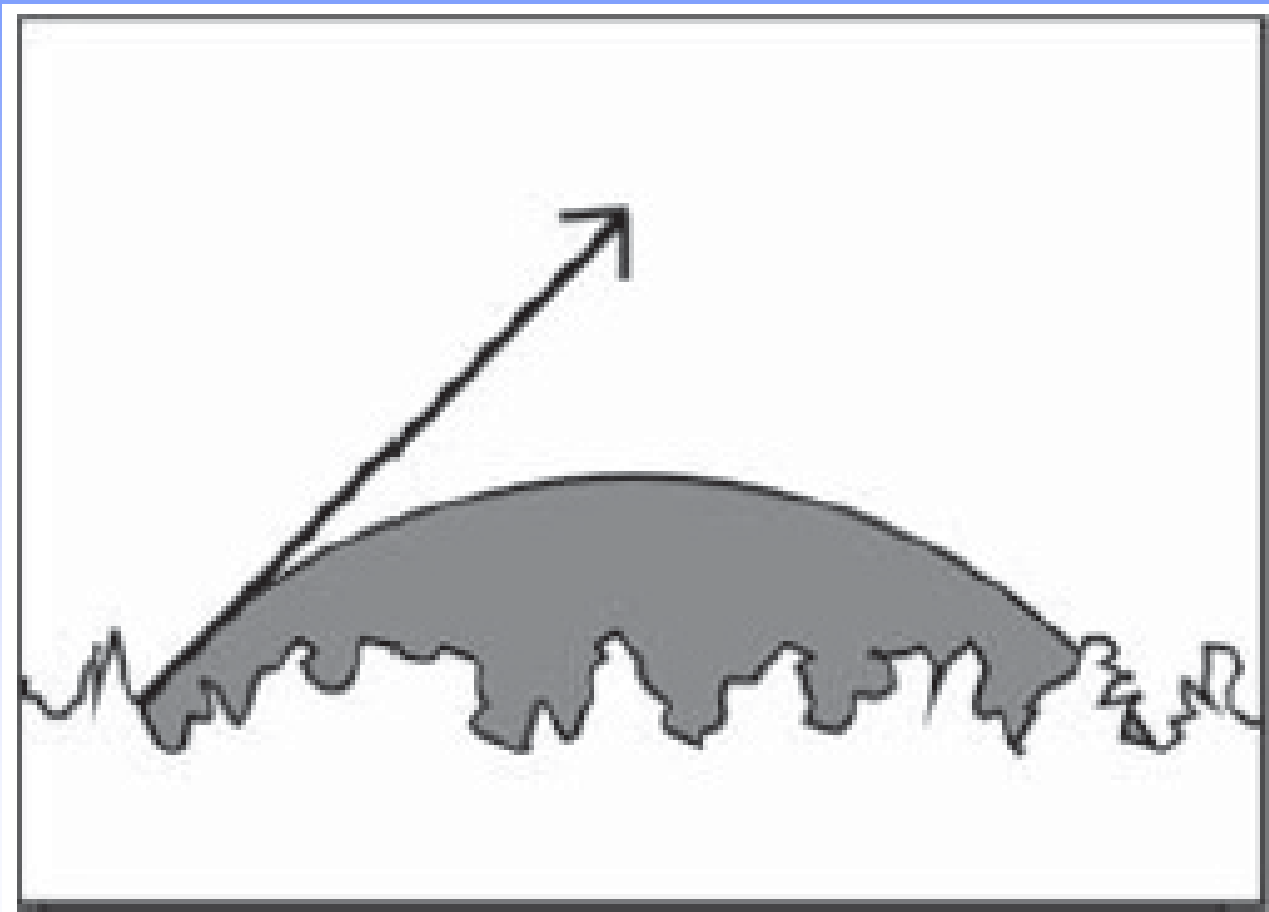
$$\cos \theta = (\gamma_S - \gamma_{SL}) / \gamma_L$$

Causes of contact angle hysteresis:



- surfaces are not (almost never) absolutely smooth, i.e., they have some roughness (*perhaps the most important reason*);
- equilibrium is not reached;
- surfaces can be contaminated (adsorbed liquids or even solid particles, e.g., dust);
- surfaces may undergo some changes during contact with the test liquid;
- the spreading pressure may be significant for low values of contact angle.

The Effect of Surface Roughness



The Wenzel Roughness Factor, R_f :

$$\cos \theta_{\text{smooth}} = (\gamma_S - \gamma_{SL})/\gamma_L \quad (\text{Young Eq.})$$

Takes into account the effect of roughness on contact angle.

$$\cos \theta_{\text{rough}} = R_f (\gamma_S - \gamma_{SL})/\gamma_L \quad (\text{Wenzel})$$

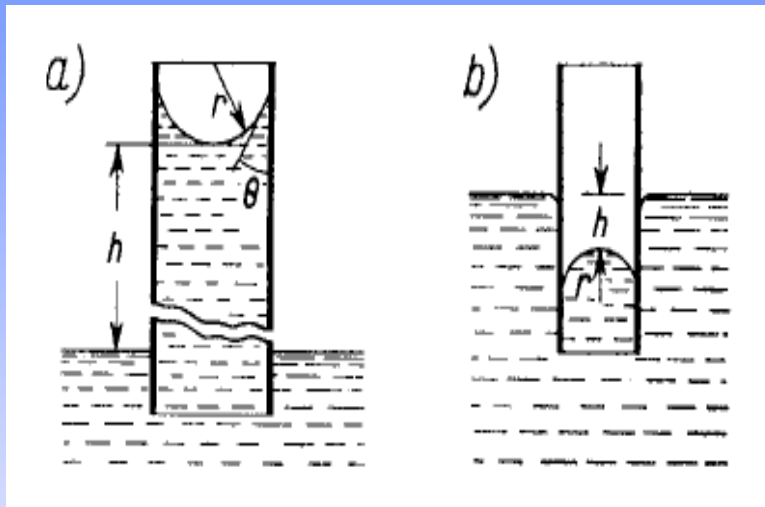
$$\text{where } R_f = A_{\text{real}}/A_{\text{geom}} = \cos \theta_{\text{rough}}/\cos \theta_{\text{smooth}} \geq 1$$

If $\theta_{\text{smooth}} < 90^\circ$ (partial wetting) then $\theta_{\text{rough}} < \theta_{\text{smooth}}$ (better wetting)

If $\theta_{\text{smooth}} > 90^\circ$ (partial non-wetting) then $\theta_{\text{rough}} > \theta_{\text{smooth}}$ (poorer wetting)

<http://www.lehigh.edu/~mkc4/our papers/surface roughness and contact angle.pdf>

Capillary Rise



$$f_1 = 2\pi r \gamma \cos \theta$$

$$f_2 = \pi r^2 h \rho g$$

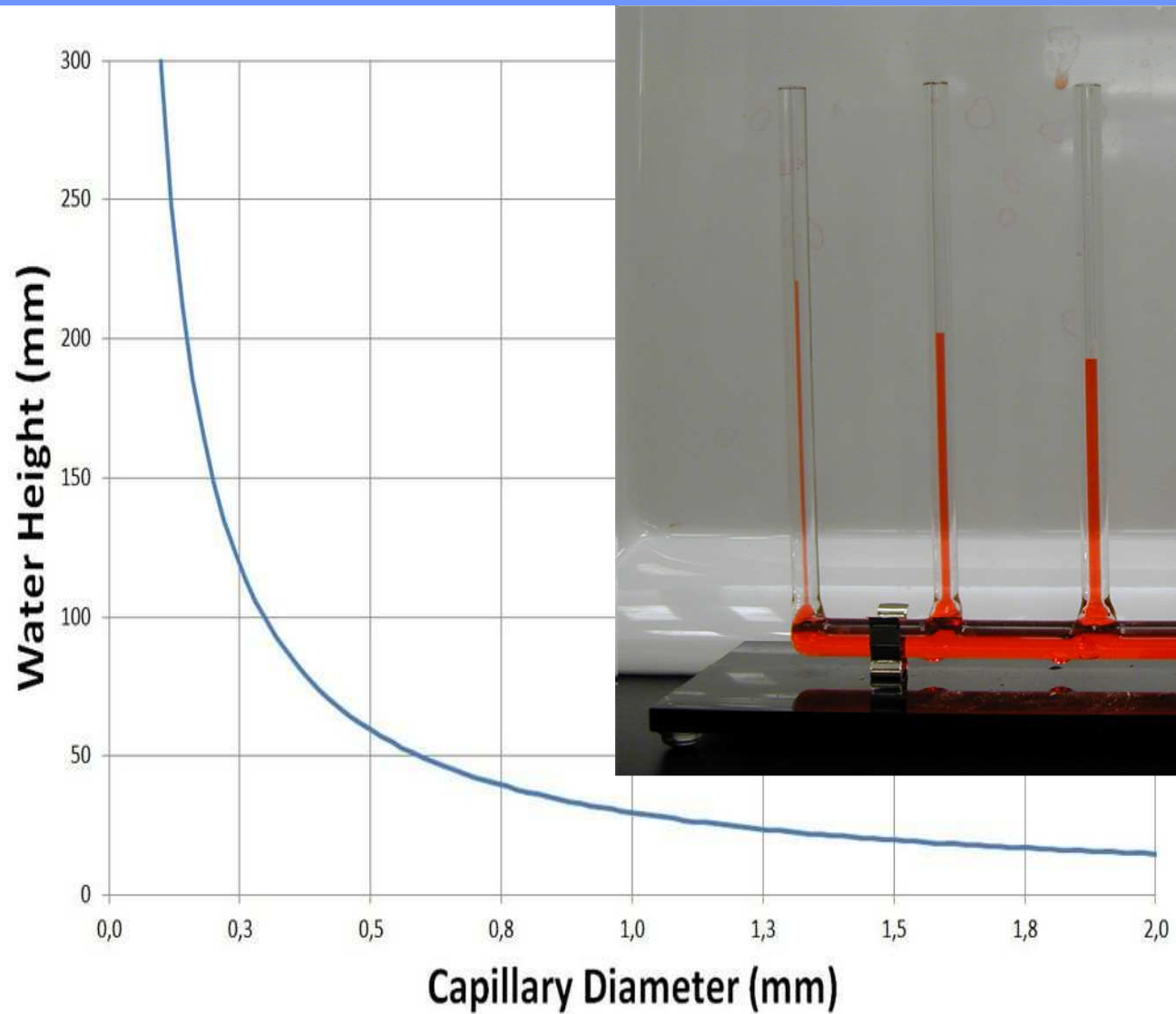
$$2\pi r \gamma \cos \theta = \pi r^2 h \rho g$$

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

For Water ($\theta = 0$): $h = 14.8/r$ (in mm)

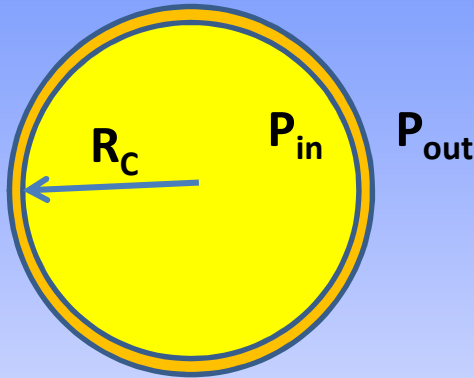
Diam.	r	h
1000 mm	500 mm	0.03 mm
40 mm	20 mm	0.74 mm
1 mm	0.5 mm	29 mm
0.4 mm	0.2 mm	74 mm
0.1 mm	0.05 mm	296 mm

Capillary Rise of Water as a Function of Capillary Diameter



The Young–Laplace equation:

gives the pressure difference (inside–outside) across a curved surface.



$$\Delta P = P_{in} - P_{out} = G \gamma / R_c$$

The geometrical factor **G** is:

2 for a spherical liquid drop,

4 for a soap bubble with a two-sided film
(because it has 2 radii of curvature).

1 for a cylinder.

The Young–Laplace equation:

How big can the pressure difference be?

Water droplets:

R_c	ΔP
10 μm	0.15 bar
100 nm	15 bar
1 nm	1500 bar

The Young–Laplace equation:

Derivation

$$dA \text{ (Helmholz free energy)} = -P dV - S dT + \gamma d\text{Area}$$

At isothermal equilibrium:

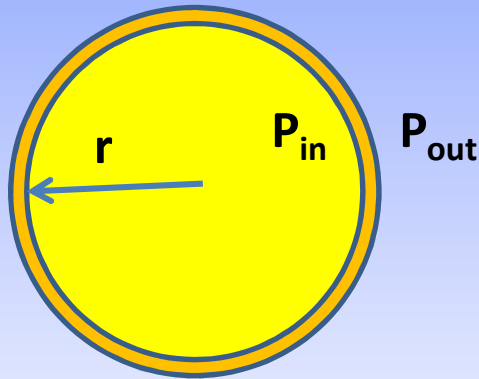
$$0 = -P dV + \gamma d\text{Area}$$

$$\text{Since } P = \Delta P = P_{\text{inside}} - P_{\text{outside}}$$

$$\Delta P = \gamma d\text{Area}/dV$$

The Young–Laplace equation:

Spherical Drop



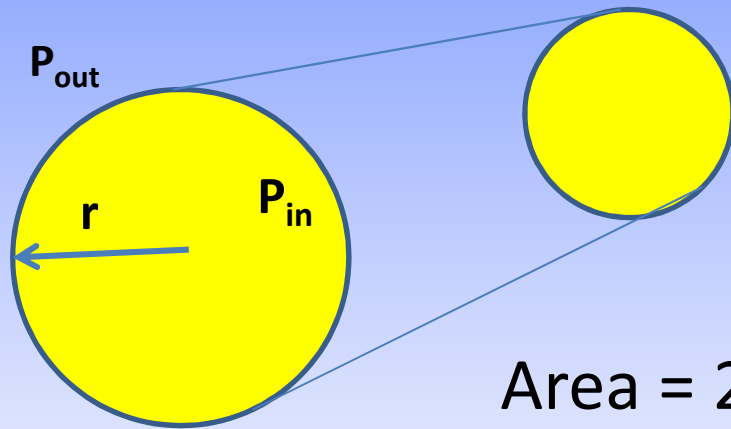
$$\Delta P dV = \gamma d\text{Area}$$

$$\begin{aligned} \text{Area} &= 4\pi r^2 & d\text{Area} &= 8\pi r dr \\ \text{Volume} &= (4/3)\pi r^3 & dV &= 4\pi r^2 dr \end{aligned}$$

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

The Young–Laplace equation:

Infinite Cylinder



$$\Delta P = \gamma \, d\text{Area}/dV$$

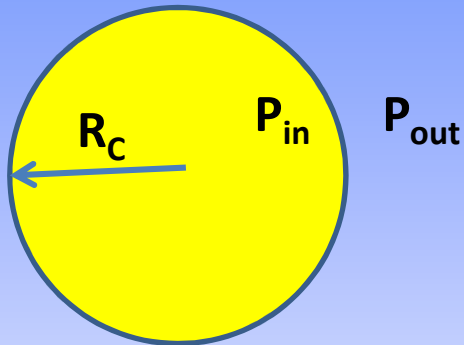
$$\begin{aligned}\text{Area} &= 2\pi rL \\ \text{Volume} &= \pi r^2L\end{aligned}$$

$$\begin{aligned}d\text{Area} &= 2\pi L \, dr \\ dV &= 2\pi rL \, dr\end{aligned}$$

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

The Young–Laplace equation:

gives the pressure difference (inside–outside) across a curved surface.



$$\Delta P = P_{in} - P_{out} = \gamma (1/R_C + 1/R_{C'})$$

The geometrical factor **G** is:

2 for a spherical liquid drop,

4 for a soap bubble with a two-sided film
(because it has 2 radii of curvature).

1 for a cylinder.

The Young–Laplace equation:

How big can the pressure difference be?

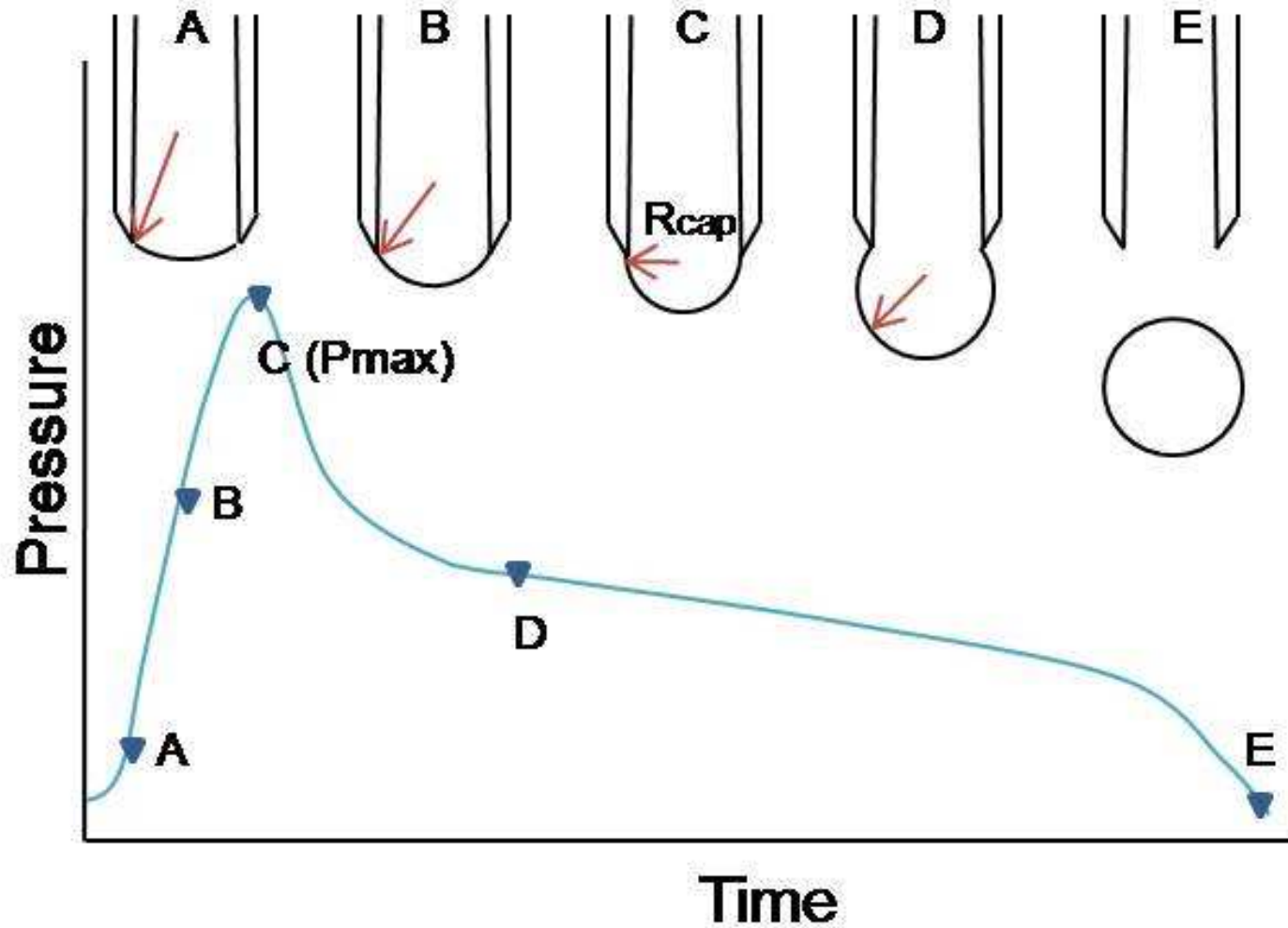
Water droplets:

R_c	ΔP
10 μm	0.15 bar
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The Young–Laplace equation:

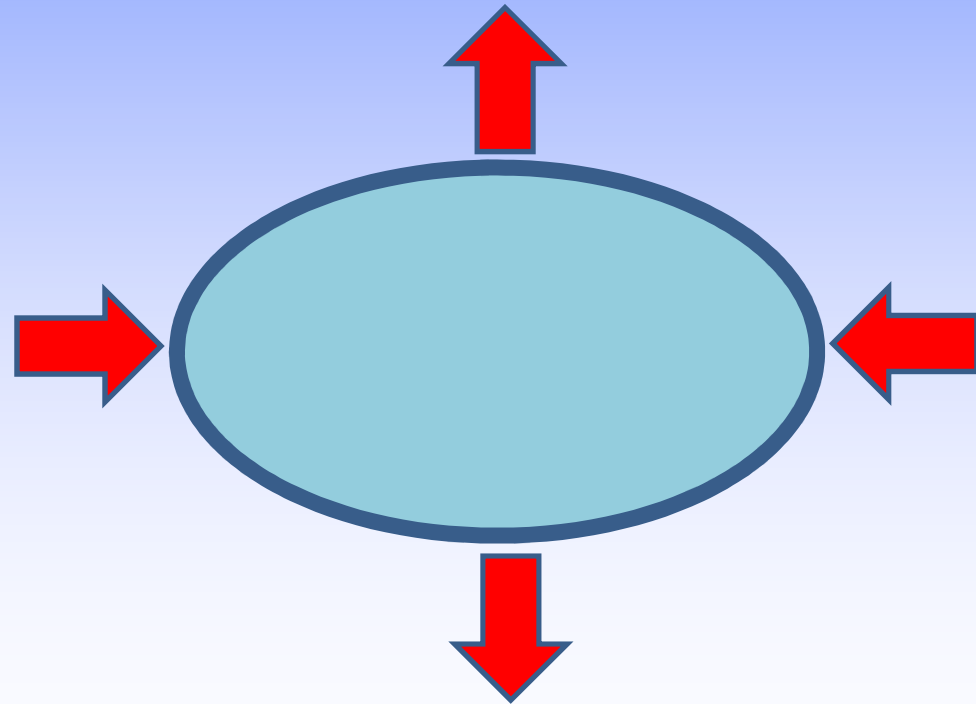
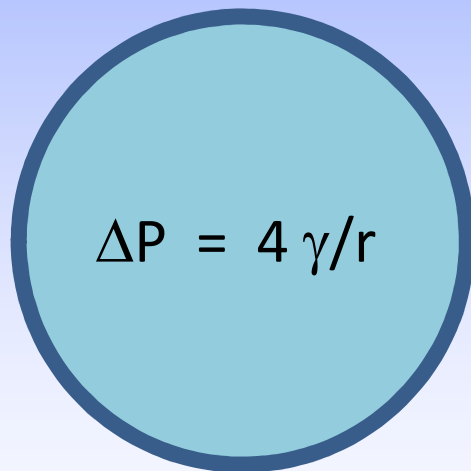
Maximum Bubble **Pressure**

$$\Delta P = 2 \gamma / r \quad \gamma = R_{\text{cap}} \Delta P / 2$$



The Young–Laplace equation:

$$\Delta P = P_{\text{in}} - P_{\text{out}} = \gamma \Sigma (1/R_C + 1/R_C')$$



The Kelvin Equation:

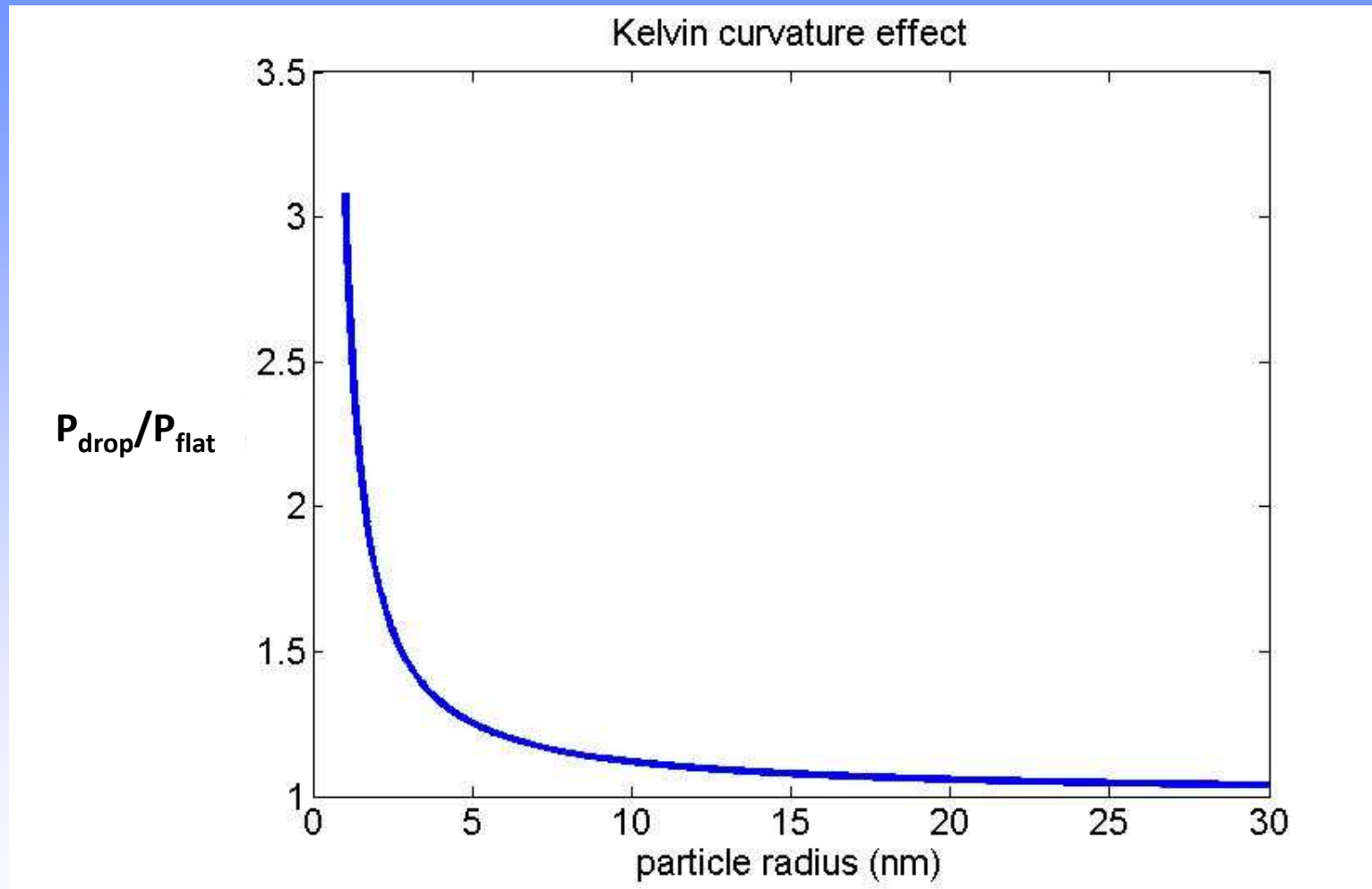
$$\ln (P_{\text{drop}}/P_{\text{flat}}) = (V_m^{\text{liq}}/RT)(2\gamma/R_C)$$

For the vapor pressure of a liquid drop relative to a flat surface.

The fundamental difficulty of nucleation!

R_C:	1 mm	100 nm	10 nm	1 nm
P_{drop}/P_{flat} :	1.001	1.011	1.11₄	2.95

[Valid down to at least 2.5 nm for organic liquids and 1.5 nm for water]

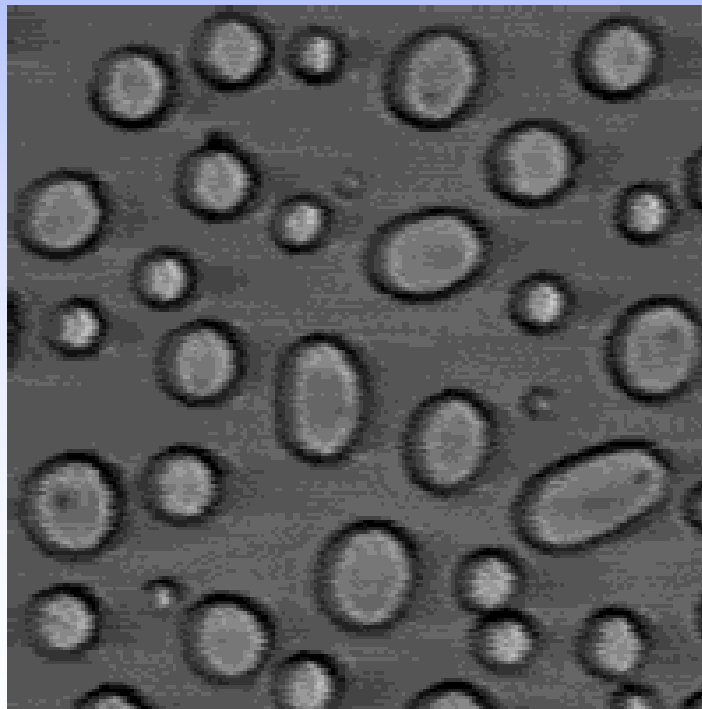


Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

Ostwald Ripening:

$$\ln [S(R_C)/S(R_C \rightarrow \infty)] = (V_m^{\text{liq}}/RT)(2\gamma_{\text{SL}}/R_C)$$

Small crystals or drops are more soluble than large ones.



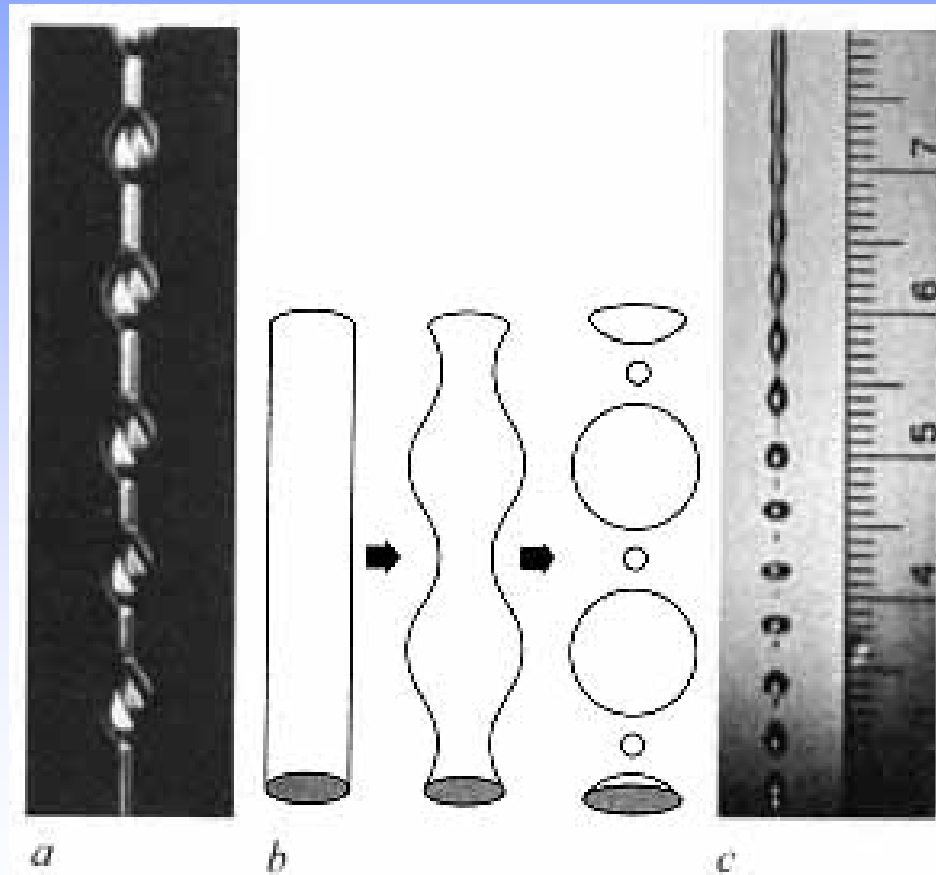
<http://www.weizmann.ac.il/complex/stavans/ostwald-ripening-nonequilibrium-liquid-solid-thin-layers>

Condensation



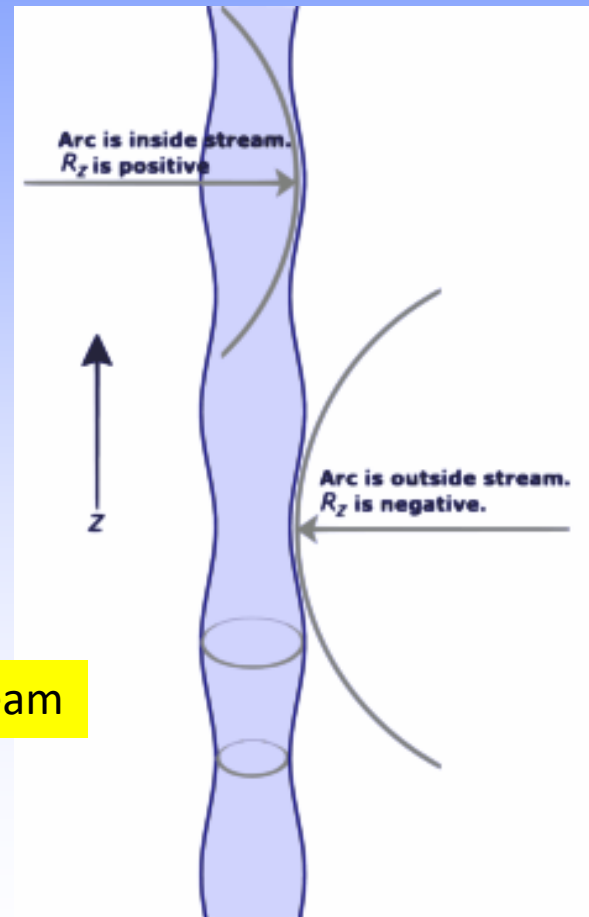
Nucleation increases the radius of curvature and hence diminishes the Kelvin effect on condensation.

Plateau-Rayleigh Instability of a liquid stream



Plateau-Rayleigh Instability of a liquid stream

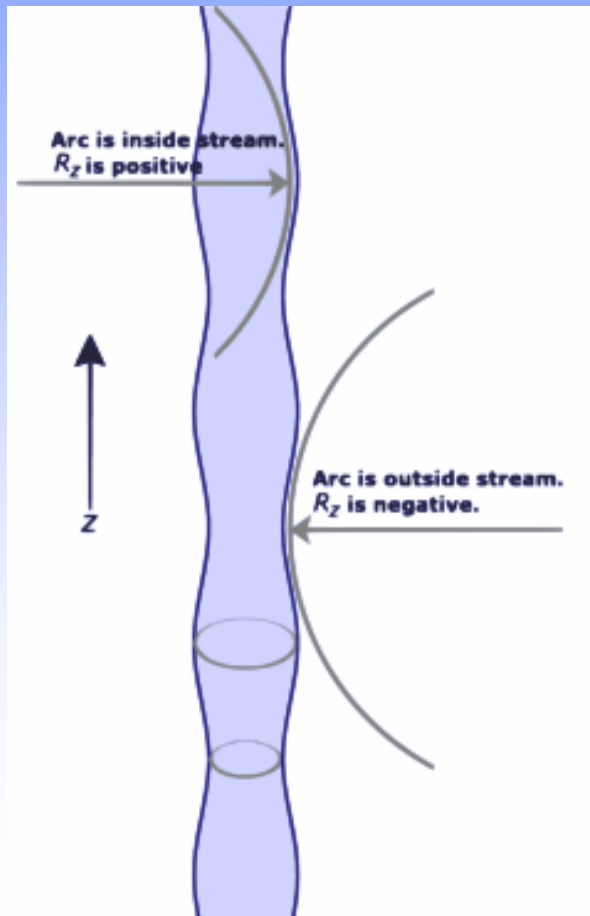
$$\Delta P = P_{in} - P_{out} = \gamma \Sigma (1/R_C + 1/R_C')$$



Radii of the Stream

Radii of curvature
of the instabilities

Plateau-Rayleigh Instability of a liquid stream



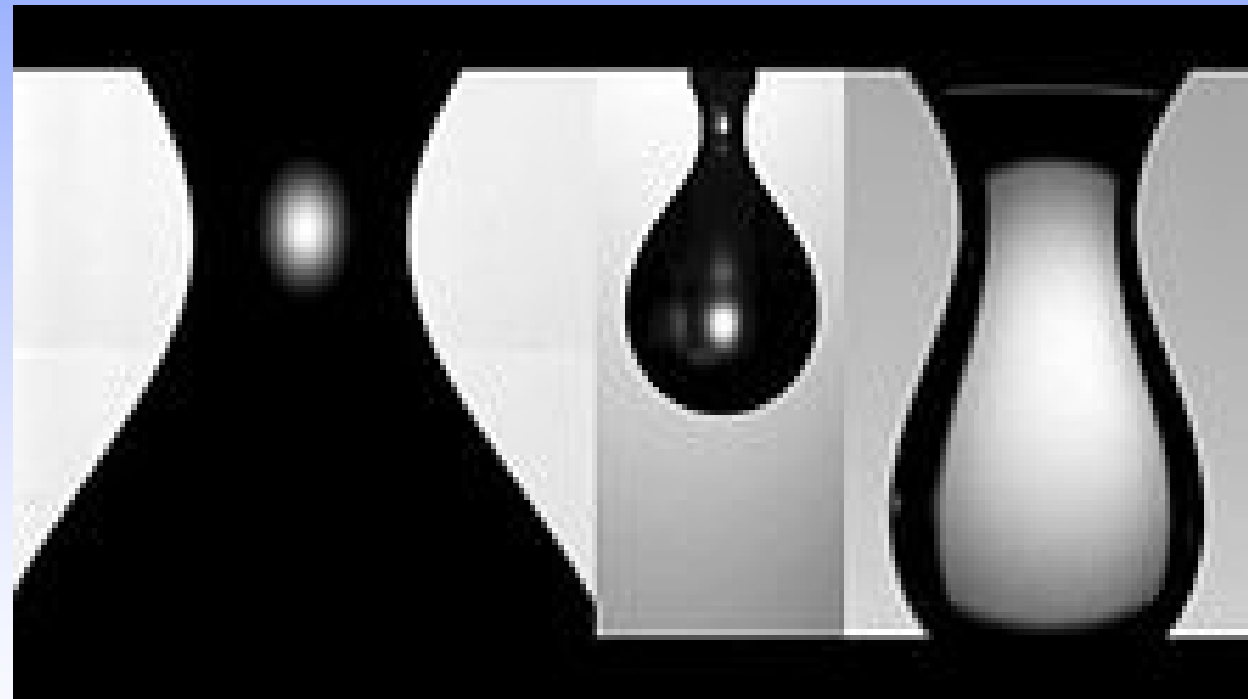
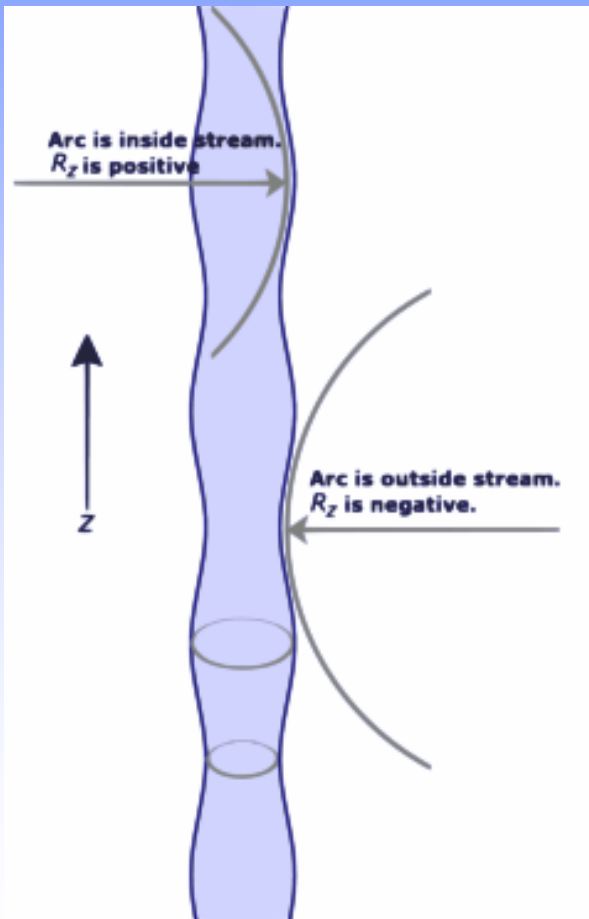
The two effects, in general, do not exactly cancel. One of them will have greater magnitude than the other, depending upon wave number and the initial radius of the stream. When the wave number is such that the radius of curvature of the wave dominates that of the radius of the stream, such components will decay over time. When the effect of the radius of the stream dominates that of the curvature of the wave, such components grow exponentially with time.

The unstable components (that grow over time) are only those where the product of the wave number with the initial radius is less than unity ($kR_0 < 1$). The component that grows the fastest is the one whose wave number satisfies the equation:

$$kR_0 < 0.697$$

(Wikipedia)

Plateau-Rayleigh Equilibrium in the pendant drop

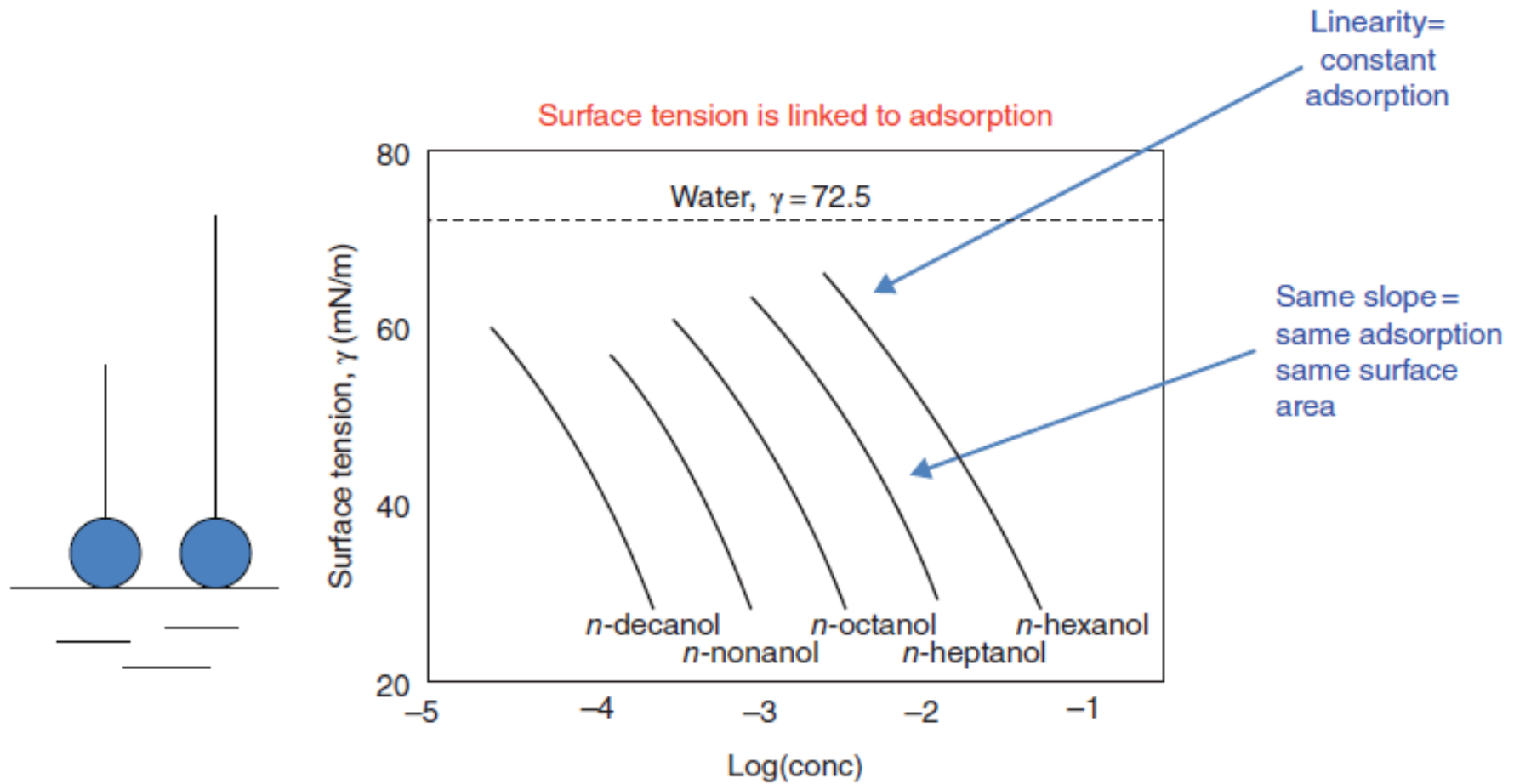


Water+PEG

Water

Glycerol

The Gibbs Adsorption Equation:



Deriving the Gibbs Adsorption Equation:

BULK Phase:

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

SURFACE Phase:

$$dG^\sigma = V^\sigma dP - S^\sigma dT + \gamma dA + \sum_i \mu_i^\sigma dn_i^\sigma$$

(Constant T and P):

$$dG^\sigma = \gamma dA + \sum_i \mu_i^\sigma dn_i^\sigma$$

(Euler Theorem):

$$G^\sigma = \gamma A + \sum_i \mu_i^\sigma n_i^\sigma$$

$$dG^\sigma = \gamma dA + A d\gamma + \sum_i \mu_i^\sigma dn_i^\sigma + \sum_i n_i^\sigma d\mu_i$$

$$\sum_i n_i^\sigma d\mu_i + A d\gamma = 0$$

Deriving the Gibbs Adsorption Equation:

$$\sum_i n_i^\sigma d\mu_i + Ad\gamma = 0$$

The Surface Excess:

$$\Gamma_i = \frac{n_i^\sigma}{A} = - \left(\frac{\partial \gamma}{\partial \mu_i} \right)_{T, P, \mu_j \neq i}$$

$$-d\gamma = \sum_i \Gamma_i d\mu_i = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2$$

For a Binary System with Solvent (Component 1) and Solute (Component 2).

Deriving the Gibbs Adsorption Equation:

$$\sum_i n_i^\sigma d\mu_i + Ad\gamma = 0$$

The Surface Excess:

$$\Gamma_i = \frac{n_i^\sigma}{A} = - \left(\frac{\partial \gamma}{\partial \mu_i} \right)_{T, P, \mu_j \neq i}$$

$$-d\gamma = \sum_i \Gamma_i d\mu_i = \cancel{\Gamma_1 d\mu_1} + \Gamma_2 d\mu_2$$

For a Binary System with Solvent (Component 1) and Solute (Component 2).

Choose an imaginary dividing surface where there is no surface excess of the solvent ($\Gamma_1=0$).

The Gibbs Excess and the localization of the Interface

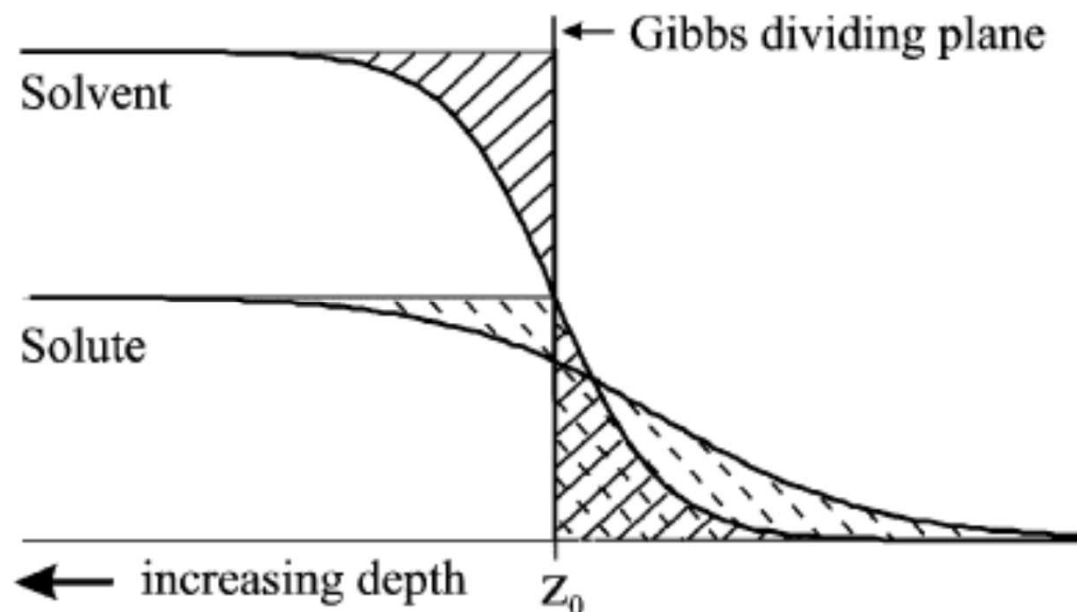
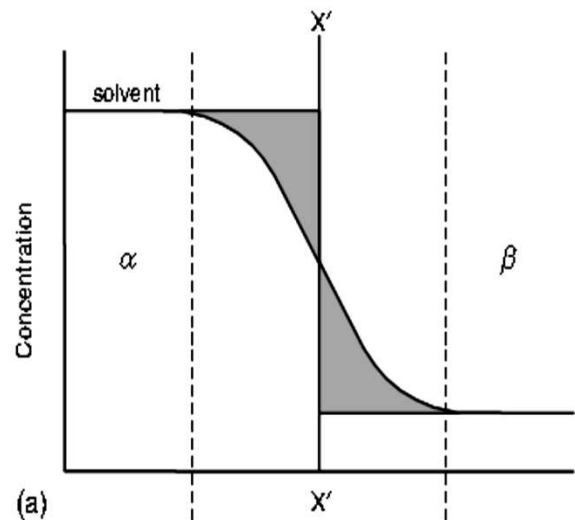


Fig. 1 Schematic illustration of the concept of the Gibbs dividing plane according to Adamson.¹⁶ The position of the Gibbs dividing plane is chosen in a way that $\Gamma_{\text{solvent}}^{\text{excess}}$ is equal to zero, *i.e.* the areas left and right of the Gibbs dividing plane marked with solid lines are equal.

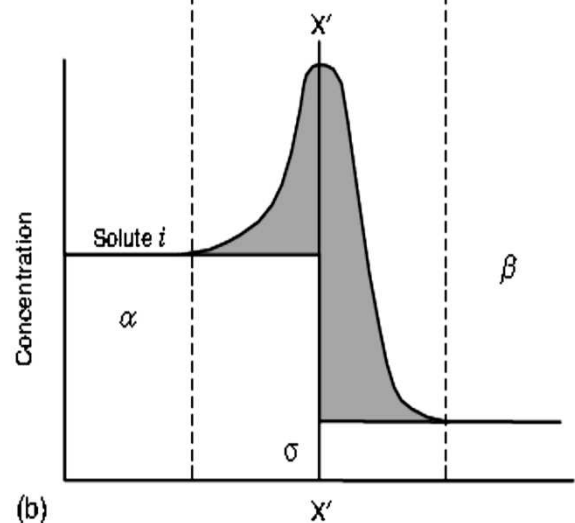
$\Gamma_{\text{solute}}^{\text{excess}}$ is the difference between the areas marked by dashed lines right and left of the Gibbs dividing plane.

The Gibbs Excess and the localization of the Interface



(a)

τ



(b)

Distance to interface

In the Gibbs approach to define the surface excess concentration Γ , the Gibbs dividing surface X' is defined as the plane in which the solvent excess concentration becomes zero (the shaded area of is equal on each side of the plane) as in (a). The (probably unknown) thickness of the interfacial region is then τ .

The surface excess of component i will then be the difference in the concentrations of that component on either side of the plane within the interfacial region (the shaded area) in (b).

The Gibbs Excess and the localization of the Interface

Tetrabutylphosphonium Bromide in Formamide

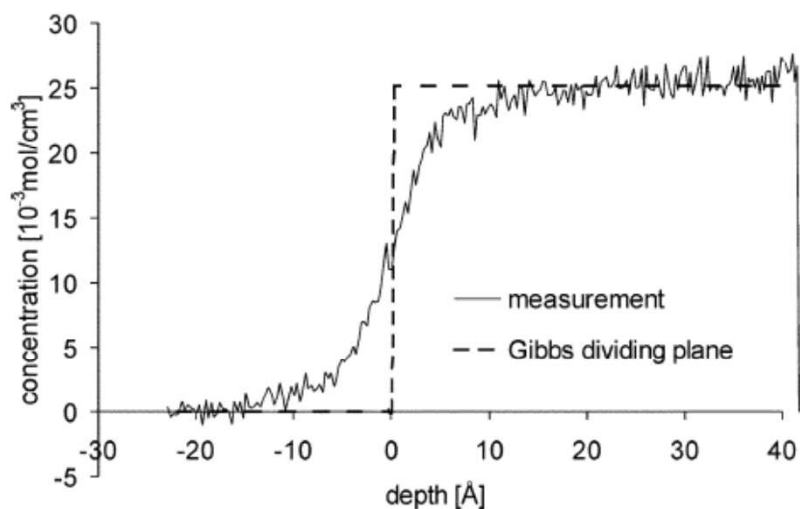


Fig. 5 Concentration depth profile of formamide (represented by oxygen) of the pure solvent and the Gibbs dividing plane. The depth profile of the oxygen is broadened due to the NICISS method and the reasons are known quantitatively.¹⁷ The depth profiles could be deconvoluted. Since in this case we would not gain additional information the deconvolution is not carried out.

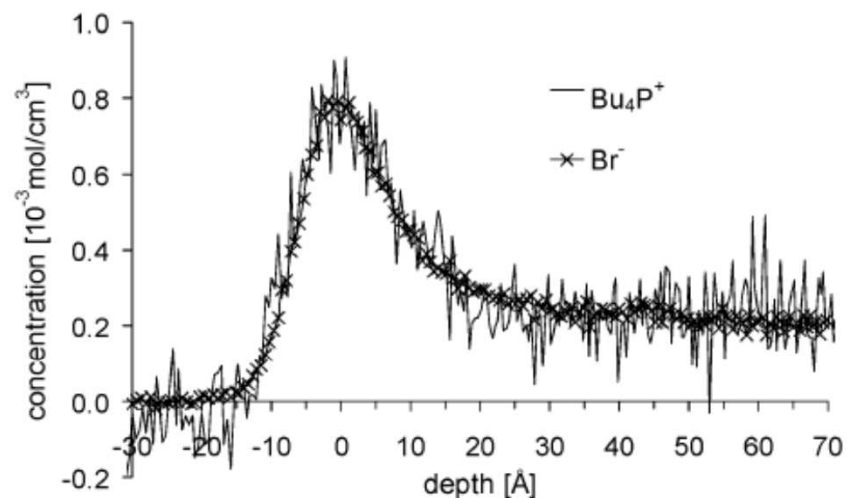


Fig. 6 Depth profiles of the cation Bu_4P^+ and the anion Br^- . The depth profiles overlap within the statistics of the measurements. Thus the amount of adsorbed cation and anion is the same.

The Gibbs Excess and the localization of the Interface

Tetrabutylphosphonium Bromide in Formamide

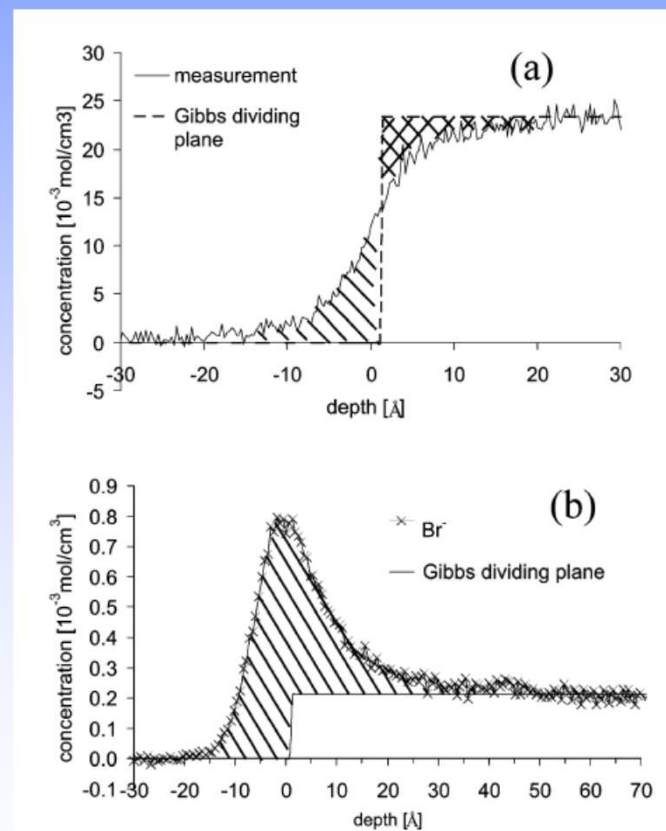
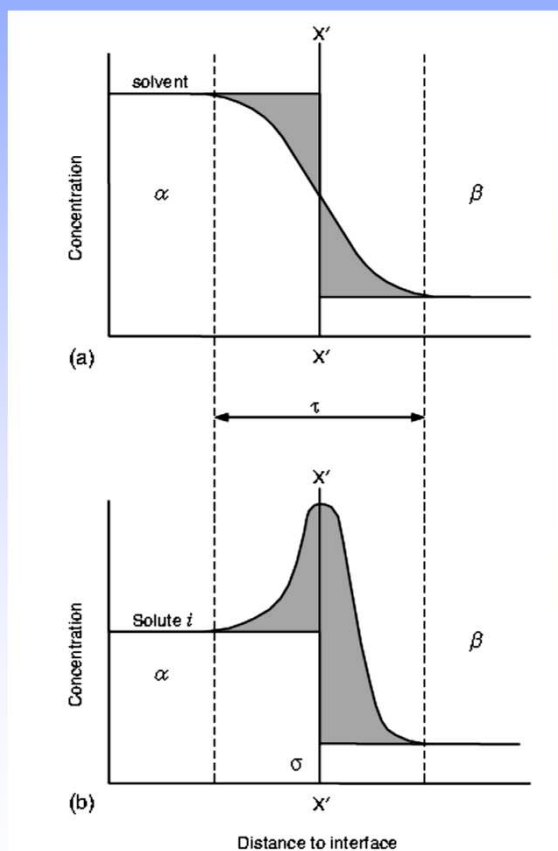


Fig. 7 Depth profile of the solvent (a) and solute (b) with the Gibbs dividing plane of the 0.2 molal solution.

The Gibbs Excess and the localization of the Interface

SDS & CsDS in Formamide

Difference between the Surface Excess and the Surface Concentration

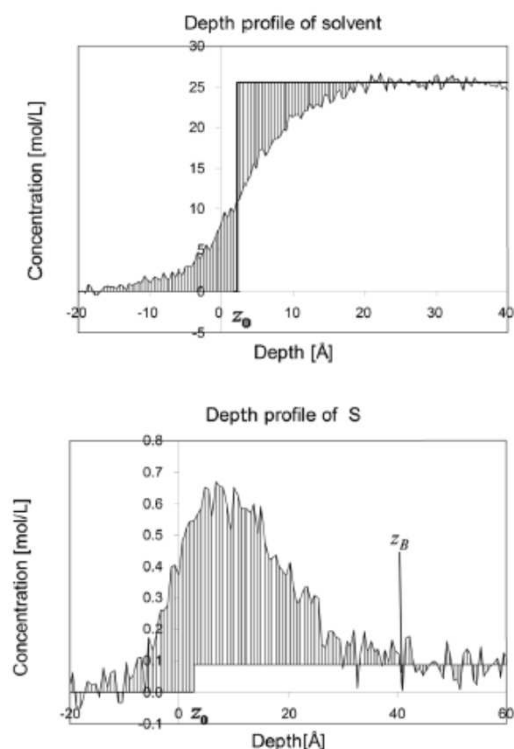


Fig. 2 Illustration of the determination of the Gibbs dividing plane, surface excess and surface concentration. The upper panel shows the definition of the Gibbs plane, z_0 , making the excess of solvent zero, and the lower one illustrates the determination of surface excess and surface concentration of surfactant. z_B is defined as the surface-bulk phase boundary. The surface concentration is calculated by integrating the concentration profile along the depth axis up to z_B .

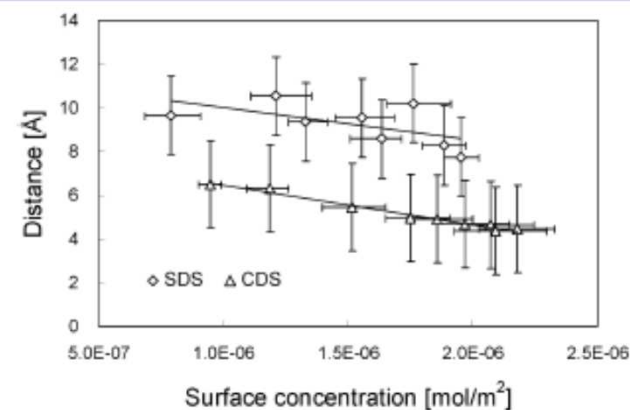


Fig. 7 The distance between the density maxima of cation and of anion as a function of surface concentration. The straight lines are added to guide the sight.

Deriving the Gibbs Adsorption Equation:

$$\sum_i n_i^\sigma d\mu_i + A d\gamma = 0$$

The Surface Excess:

$$\Gamma_i = \frac{n_i^\sigma}{A} = - \left(\frac{\partial \gamma}{\partial \mu_i} \right)_{T, P, \mu_j \neq i}$$

$$-d\gamma = \sum_i \Gamma_i d\mu_i = \cancel{\Gamma_1 d\mu_1} + \Gamma_2 d\mu_2$$

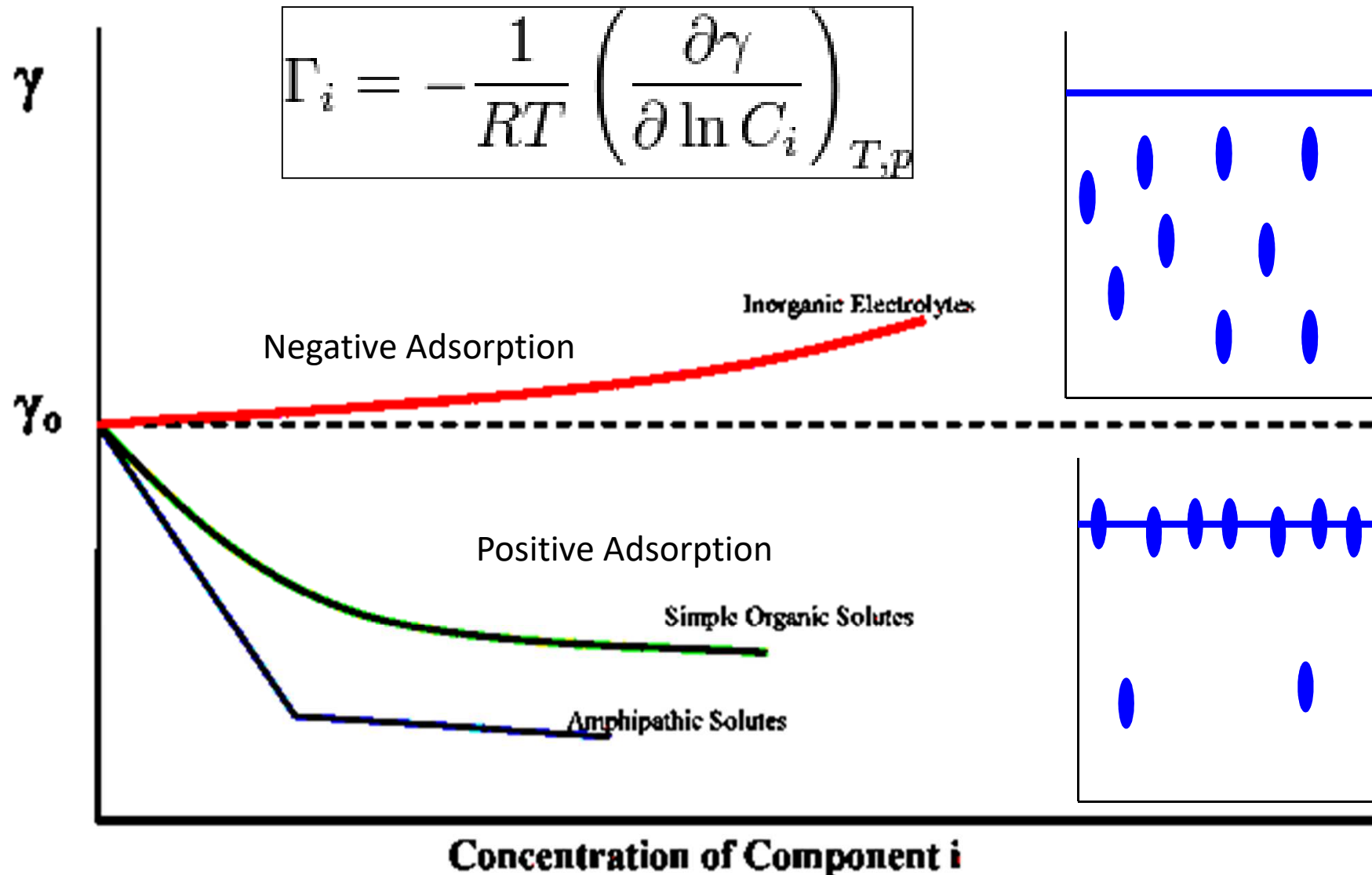
For a Binary System with Solvent (Component 1) and Solute (Component 2).

Choose an imaginary dividing surface where there is no surface excess of the solvent ($\Gamma_1=0$).

Then:

$$\Gamma_2 = - \frac{d\gamma}{d\mu_2} = - \frac{1}{R T} \frac{d\gamma}{d \ln C_2} = - \frac{C_2}{R T} \frac{d\gamma}{dC_2}$$

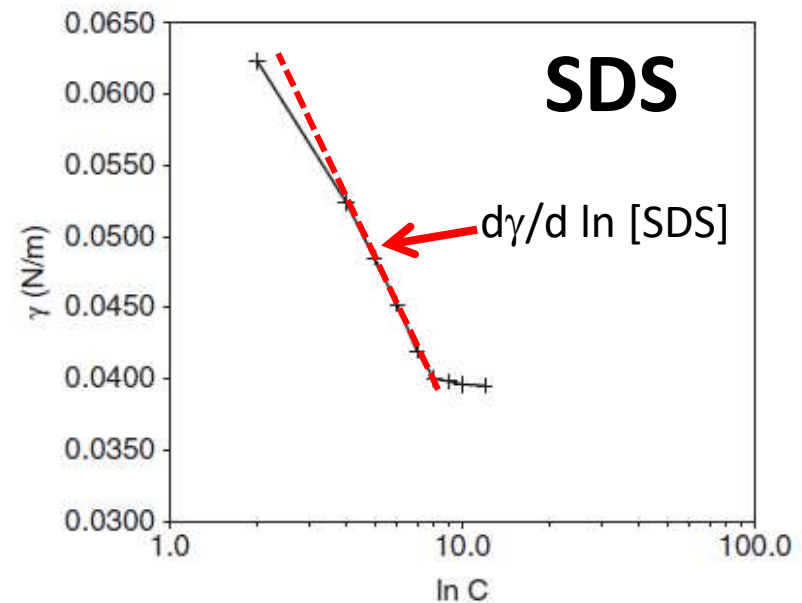
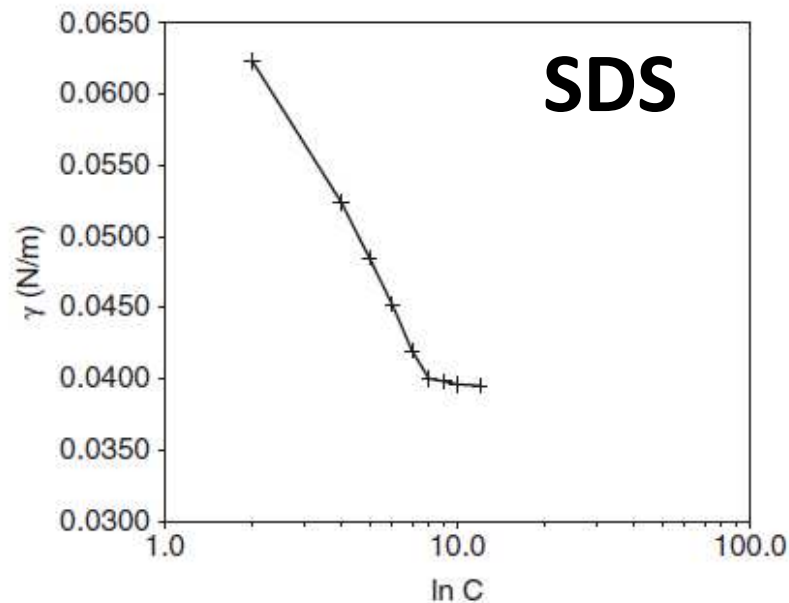
Surface Tension and the Gibbs Adsorption Isotherm



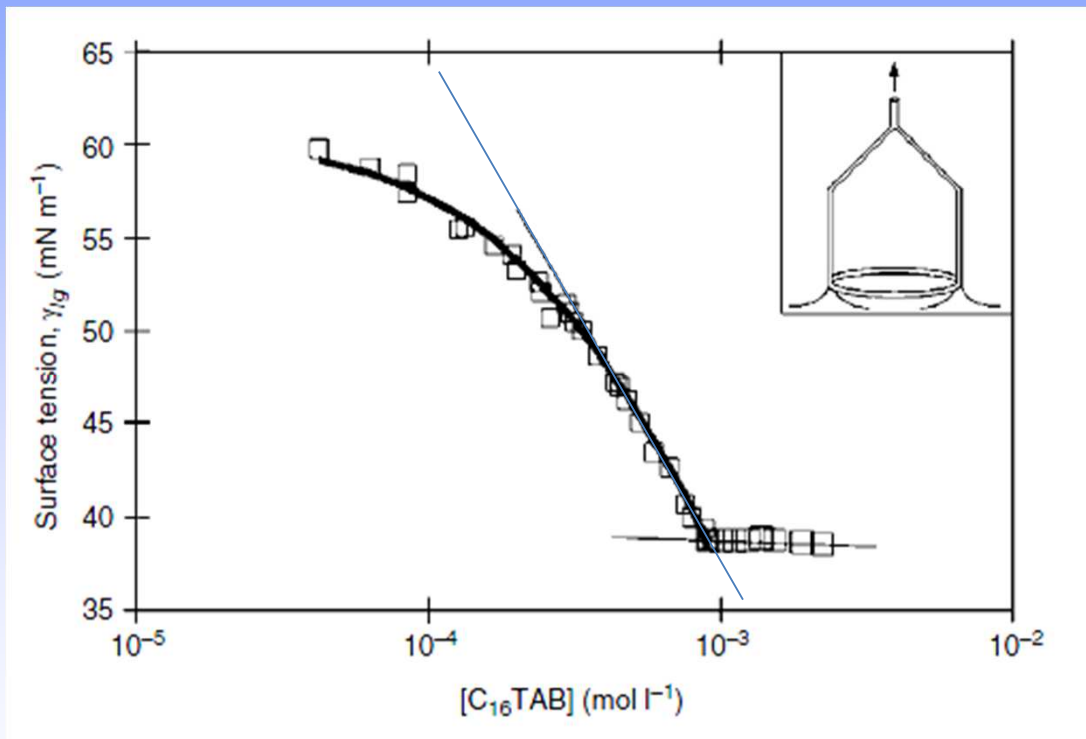
The Gibbs Adsorption Equation:

For a Binary System with Solvent (Component 1) and Solute (Component 2),
Choose an imaginary dividing surface where there is no surface excess of the solvent ($\Gamma_1=0$).
Then:

$$\Gamma_2 = -\frac{d\gamma}{d\mu_2} = -\frac{1}{R T} \frac{d\gamma}{d \ln C_2} = -\frac{C_2}{R T} \frac{d\gamma}{dC_2}$$



Gibbs Excess and the Area per Molecule at the Surface



Surface coverage in mol/m²:

$$\Gamma = \frac{n_i^\sigma}{A} = - \frac{1}{R_{ig} T} \frac{d\gamma_i}{d \ln C_i}$$

Area per Surfactant, m²/molecule:

$$A = \frac{10^{18}}{N_A \Gamma}$$

Surface pressure at the CMC, mN/m:

$$\pi = \gamma_0 - \gamma$$

Ideal Gas Area, m²/molecule:

$$A = \frac{k_B T}{\pi}$$

The Harkins Spreading Coefficient, S :

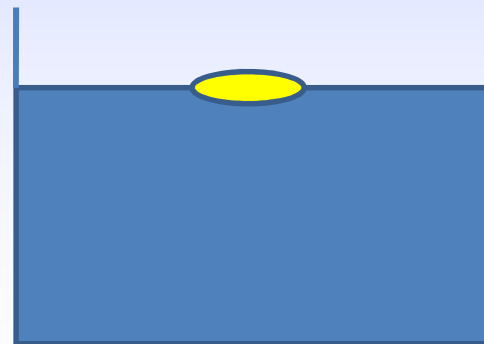
$$S = \gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = W_{adh, OW} - W_{coh, O}$$

↑ ↑ ↑
Water/Air Oil/Air Oil/Water

$S > 0$ Spreading



$S < 0$ Non-Spreading



The Harkins Spreading Coefficient, S:

$$S = \gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = W_{adh,OW} - W_{coh,O}$$

Spreading

$$\text{Butanol: } S = \gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = 72.8 - (24.6 + 1.8) = 46.4$$

$$\text{Aniline: } S = \gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = 72.8 - (42.9 + 5.8) = 24.1$$

Non-Spreading

$$\text{Bromoform: } S = \gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = 72.8 - (41.5 + 40.8) = -9.5$$

Surface Tensions of a Liquid Lens on the Surface of an Immiscible Liquid

$$S = \gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = W_{adh, OW} - W_{coh, O}$$

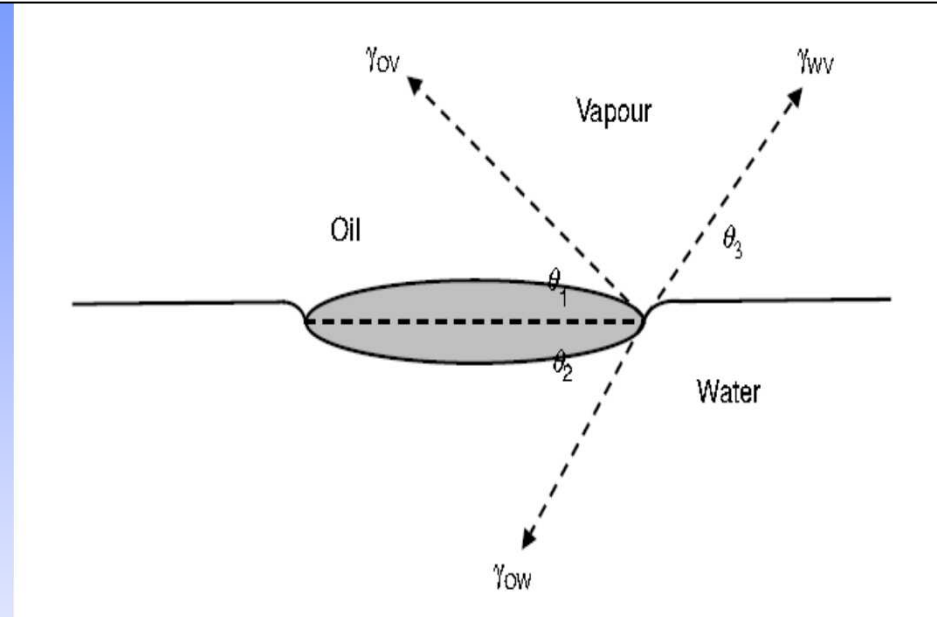


Table 10.4 Spreading of benzene on water

	γ_{water} (mN m^{-1})	γ_{benzene} (mN m^{-1})	S (mN m^{-1})
Initial	72.8	28.9	8.9
	72.8	28.8	9
Final $\gamma_{WB} = 35 \text{ mN m}^{-1}$	62.2	28.8	-1.6

Review of the Fundamental Equations

Theory	Equation	Comments
Young–Laplace equation (pressure difference across a curved surface)	$\Delta P = \frac{2\gamma}{R}$	Applied in the derivation of the Kelvin equation
Kelvin equation for vapour pressure of a droplet (curved surface)	$\ln\left(\frac{P}{p_{sat}}\right) = \frac{V^l}{R_{ig}T} \frac{2\gamma}{R}$	Explains the Ostwald ripening destabilization mechanisms in colloids
Young equation for the contact angle	$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_l}$ or $\cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l}$ provided that the spreading pressure is zero (almost always true for low surface energy surfaces like polymers)	Two properties are readily measurable, two are not. Mostly used together with theories for the solid–liquid interfacial tension. Very important in wetting and adhesion studies (Chapter 6)
Harkins spreading coefficient (for an oil (O) in water (W))	$S = \gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = W_{adh, OW} - W_{coh, O}$	Can be applied both to liquid–liquid and liquid–solid interfaces (see also Chapter 6)
Work of adhesion	$W_{adh} = \gamma_A + \gamma_B - \gamma_{AB}$ Between solid/liquid (spreading pressure ignored): $W_{adh} = W_{sl} = \gamma_s + \gamma_l - \gamma_{sl} = \gamma_l(1 + \cos\theta)$	The first form is called Dupre and the second one, valid for solid–liquid interfaces, is the Young–Dupre equation
Gibbs adsorption equation – relationship between adsorption and change of surface tension with concentration	$\Gamma_i = \frac{n_i^{\sigma}}{A} = -\frac{C_i}{R_{ig}T} \frac{d\gamma}{dC_i} = -\frac{1}{R_{ig}T} \frac{d\gamma}{d \ln C_i}$	Possibly the most important of these general equations. Numerous applications related to adsorption in general, e.g. surfactants and polymers. Often used in the simple form shown here based on the concentrations. For ionic surfactants, we should use “ $2R_{ig}T$ ” instead in the denominator