Capillarity: Static Considerations

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  - Relation to Molecular Structure
  - Temperature Dependence
- **Capillary Shapes**
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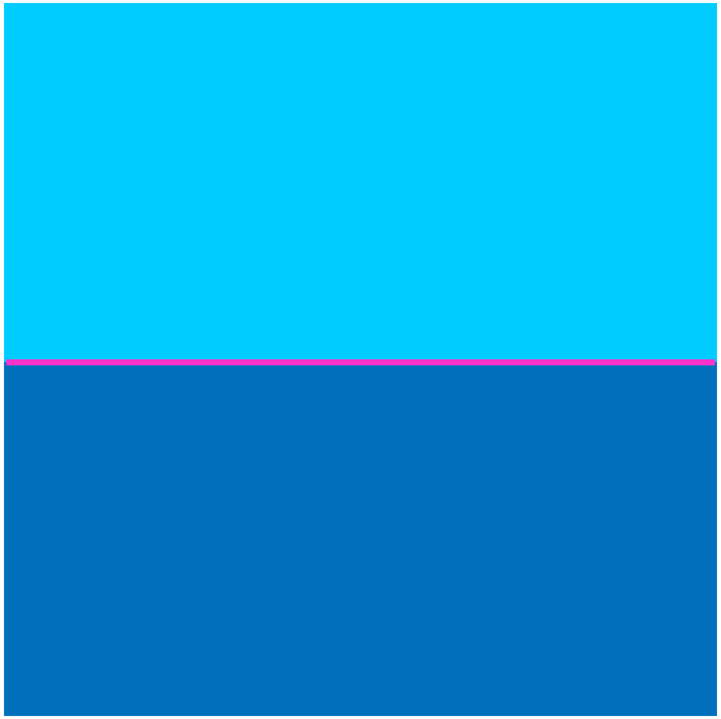
1. Surface Tension

- Macroscopic Approach
- Microscopic Approach
- Relation to Molecular Structure
- Temperature Dependence

Macroscopic Approach

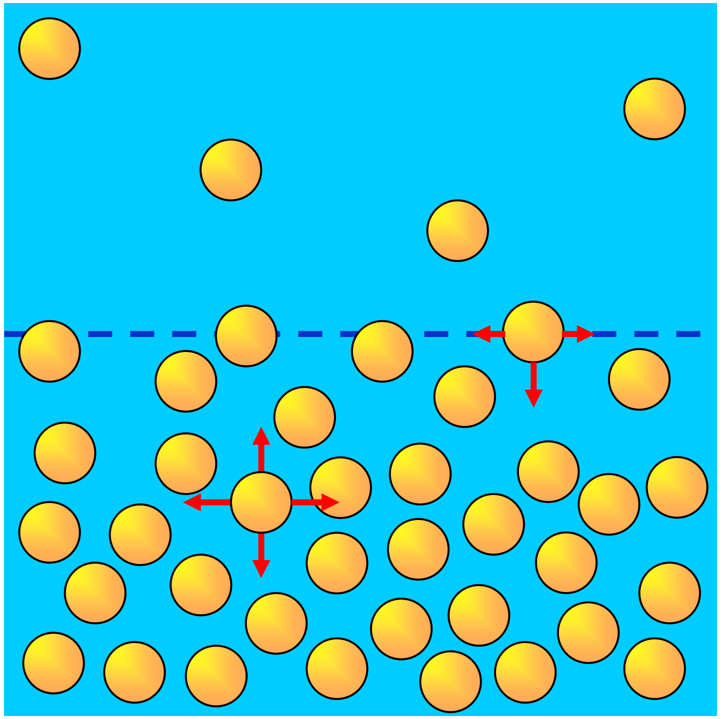


- Matter is continuous;
- The surface is sharp;
- The surface of the liquid behaves like an elastic skin (tends to shrink);
- Surface tension arises from the free energy excess at the surface.

$$\gamma = \frac{F}{A}$$

F – Helmholtz free energy, J
A – surface area, m²

Microscopic Approach



- Matter is grainy (discontinuous);
- Density changes gradually across the surface;
- Molecules try to avoid the surface;
- Surface tension arises from the different balance of forces acting on molecules located at the interface.

$$\gamma = \frac{\alpha N_C \varepsilon}{A}$$

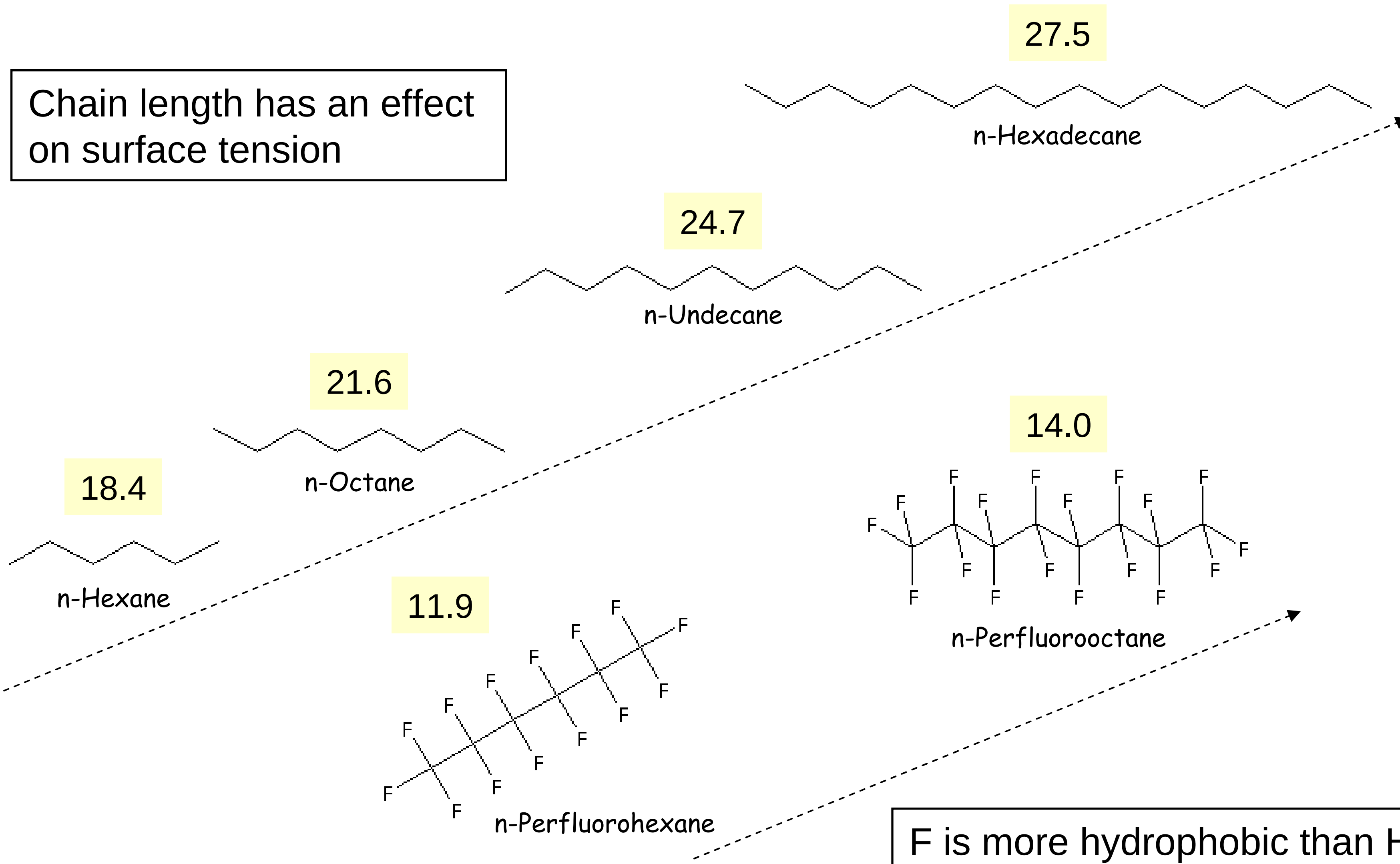
α – fraction of missing bonds
N_C – coordination number
ε – energy per bond, J
A – area per molecule, m²

Surface Tension: Some Values

Liquid	γ [mJ/m²]
Helium (-271 °C)	0.35
Perfluorohexane	11.9
Octane	21.6
Tetradecane	26.6
Benzene	28.9
Diiodomethane	50.8
Glycerol	64.0
Water	72.8
NaCl (801 °C)	116
Mercury (25 °C)	484
Gold (1064 °C)	1,138
Tungsten (3410 °C)	2,310

ST: Chemical Composition

Chain length has an effect on surface tension



F is more hydrophobic than H

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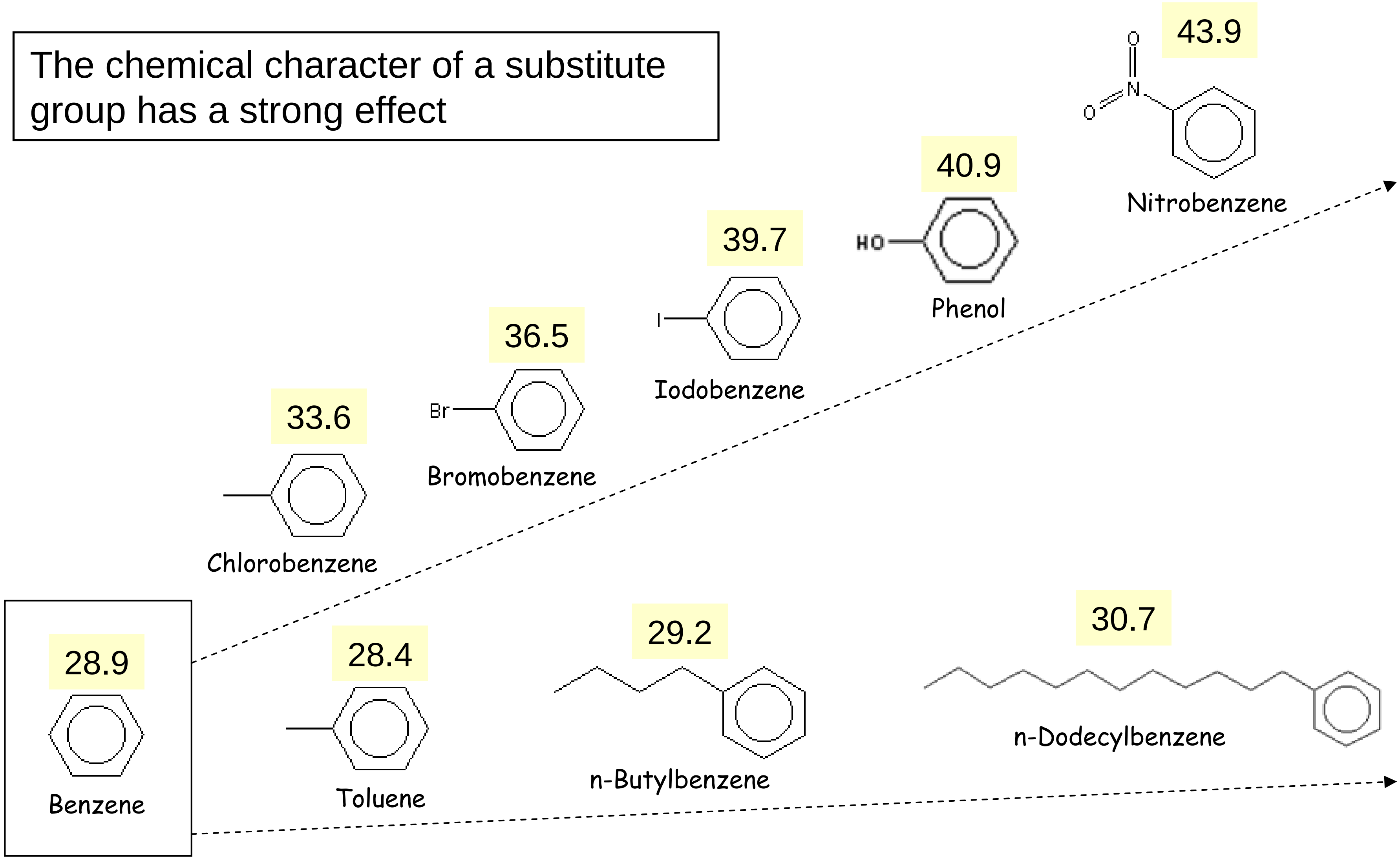
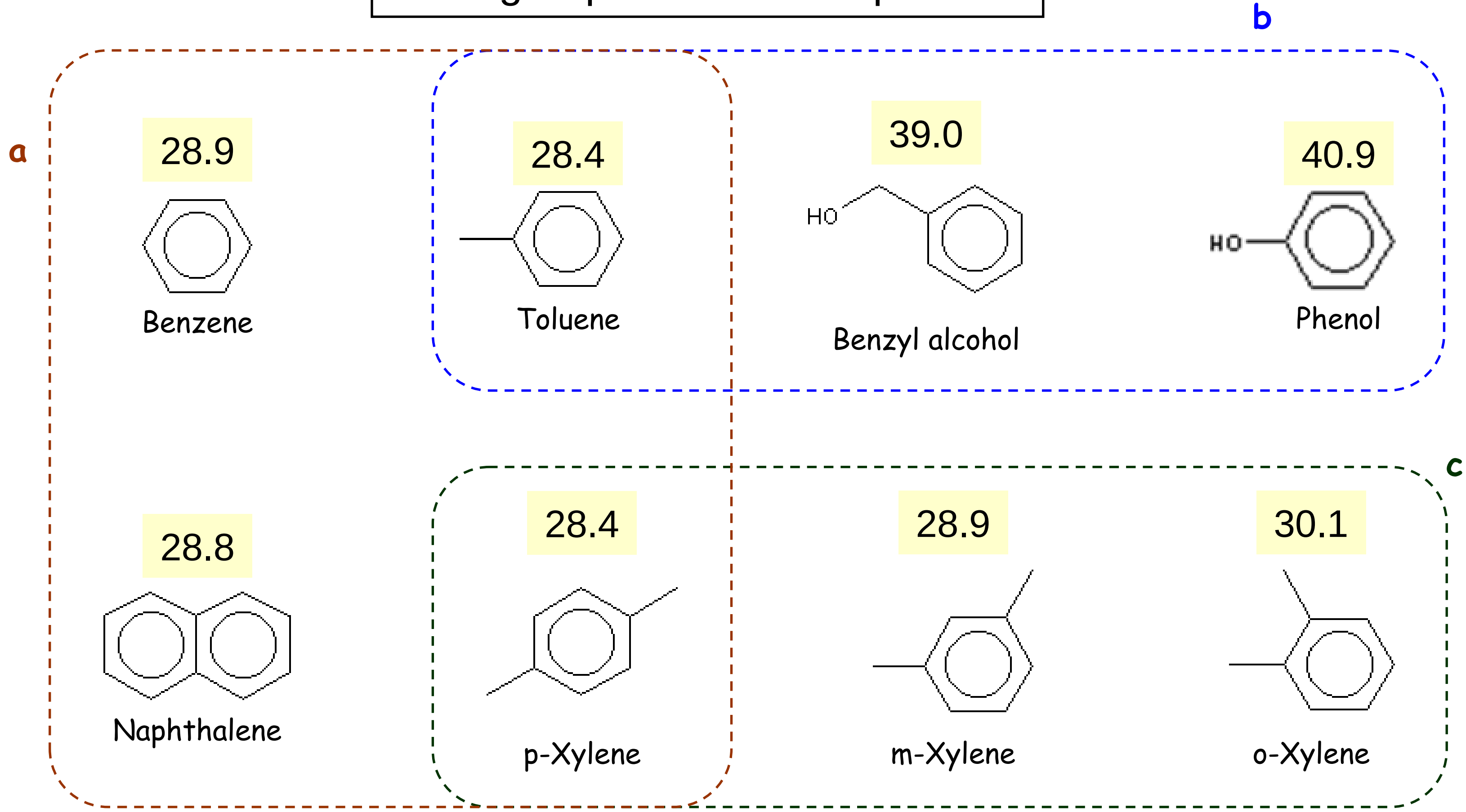
ST: Substitute Group

The chemical character of a substitute group has a strong effect



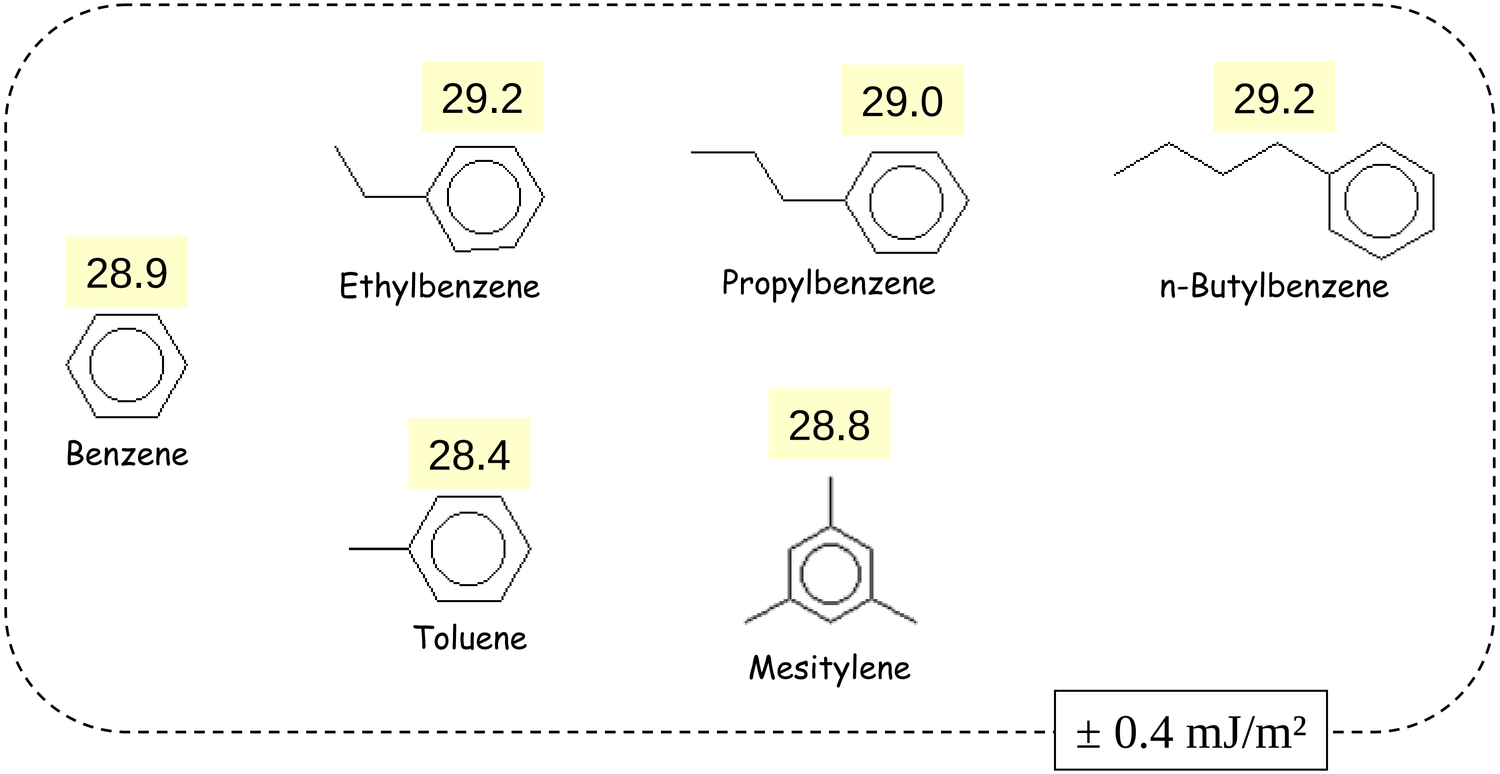
ST: Surface Orientation

End-groups are more important



Surface orientation is a key factor

ST: Chemical Character



Chemical structure strongly affects surface tension but in a non-specific fashion

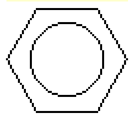
ST: Empirical Equivalence

28.9

Eicosane

⇔

28.9



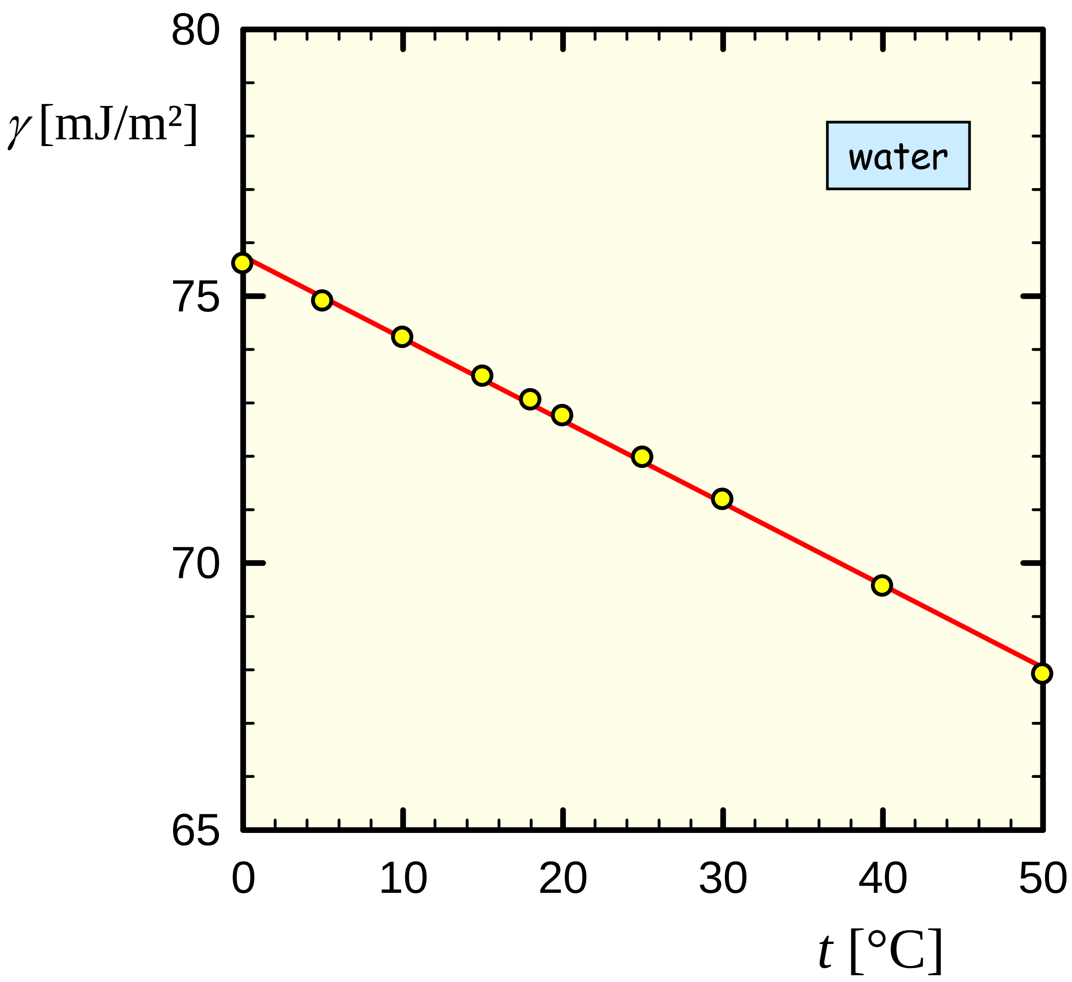
Benzene

If the two substances are taken to be equivalent (i.e. have equal surface tension) then 6 benzene carbons are equivalent to 20 alkane carbons:

$$1C(sp^2) \approx 3.3C(sp^3)$$

A rather basic yet useful rule.

Temperature Dependence



$$\gamma = a - bt$$

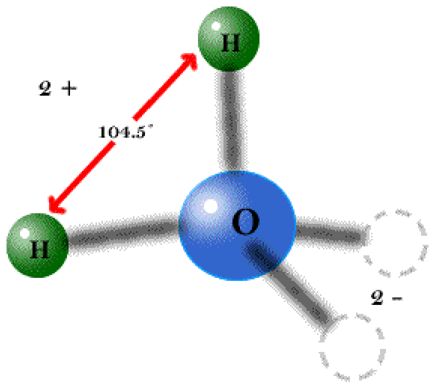
$b = 0.15$ mJ/(m²K)

$$\frac{S}{A} = -\frac{\partial \gamma}{\partial T} = b$$

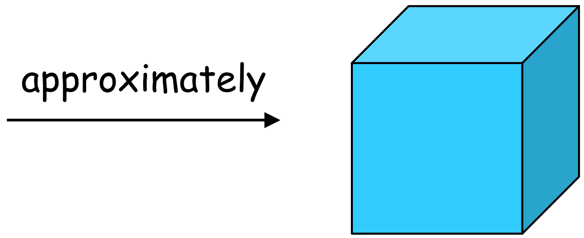
Higher disorder in the surface region.

Sharpness of a Liquid Surface

An estimate of the size of the water molecule:



Ball and stick model of water.

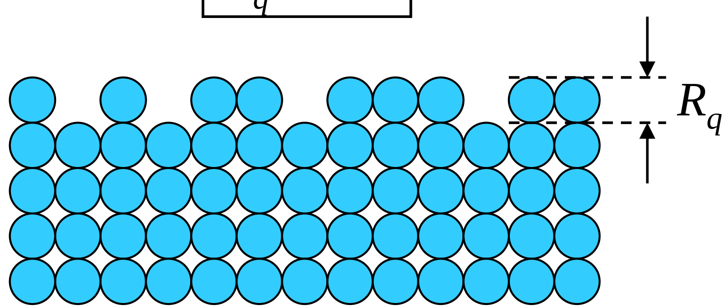


$$V_M = \frac{M}{\rho N_A} \approx 30 \text{ Å}^3$$

$$2r \cong V_M^{1/3} \approx 3.1 \text{ Å}$$

An experimental value (X-ray and neutron scattering) of the roughness of a water surface:

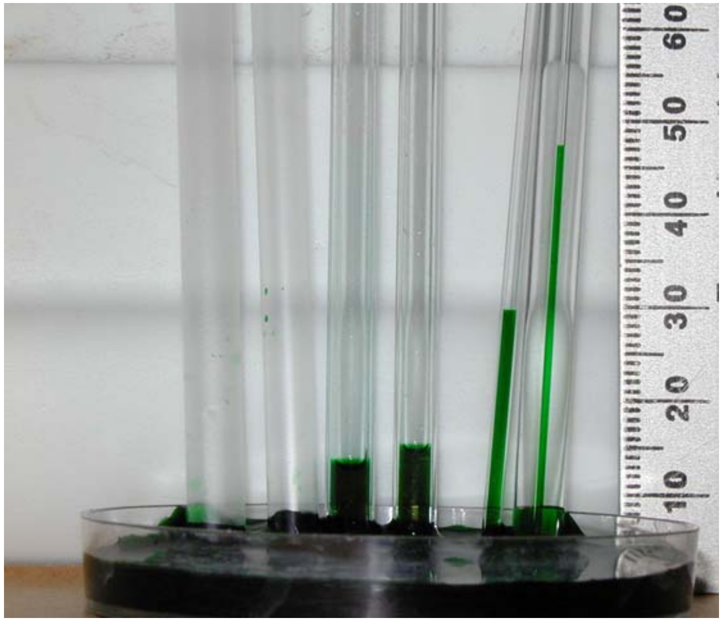
$$\boxed{R_q \approx 3 \text{ Å}}$$



2. Capillary Shapes

- Capillary Pressure
- Hydrostatic Pressure
- Examples
- Capillary Hysteresis

Capillarity – The Science of Liquid Shapes

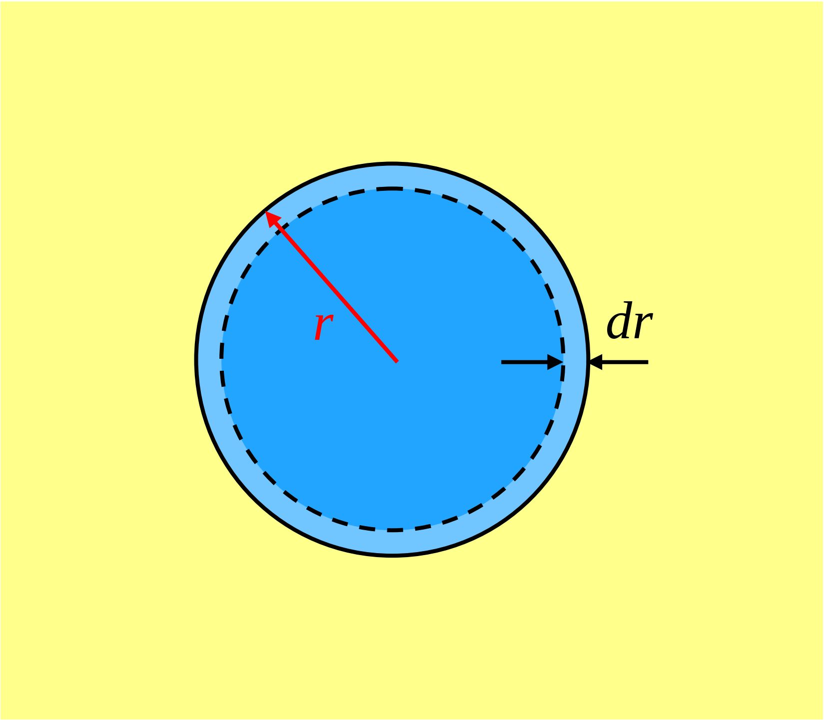


Laplace Equation

$$P_C = \frac{2\gamma}{R}$$

Capillary Pressure

A liquid droplet in saturated vapours
(no gravity)



$$\boxed{W_{\text{surf}} = W_{\text{bulk}}}$$

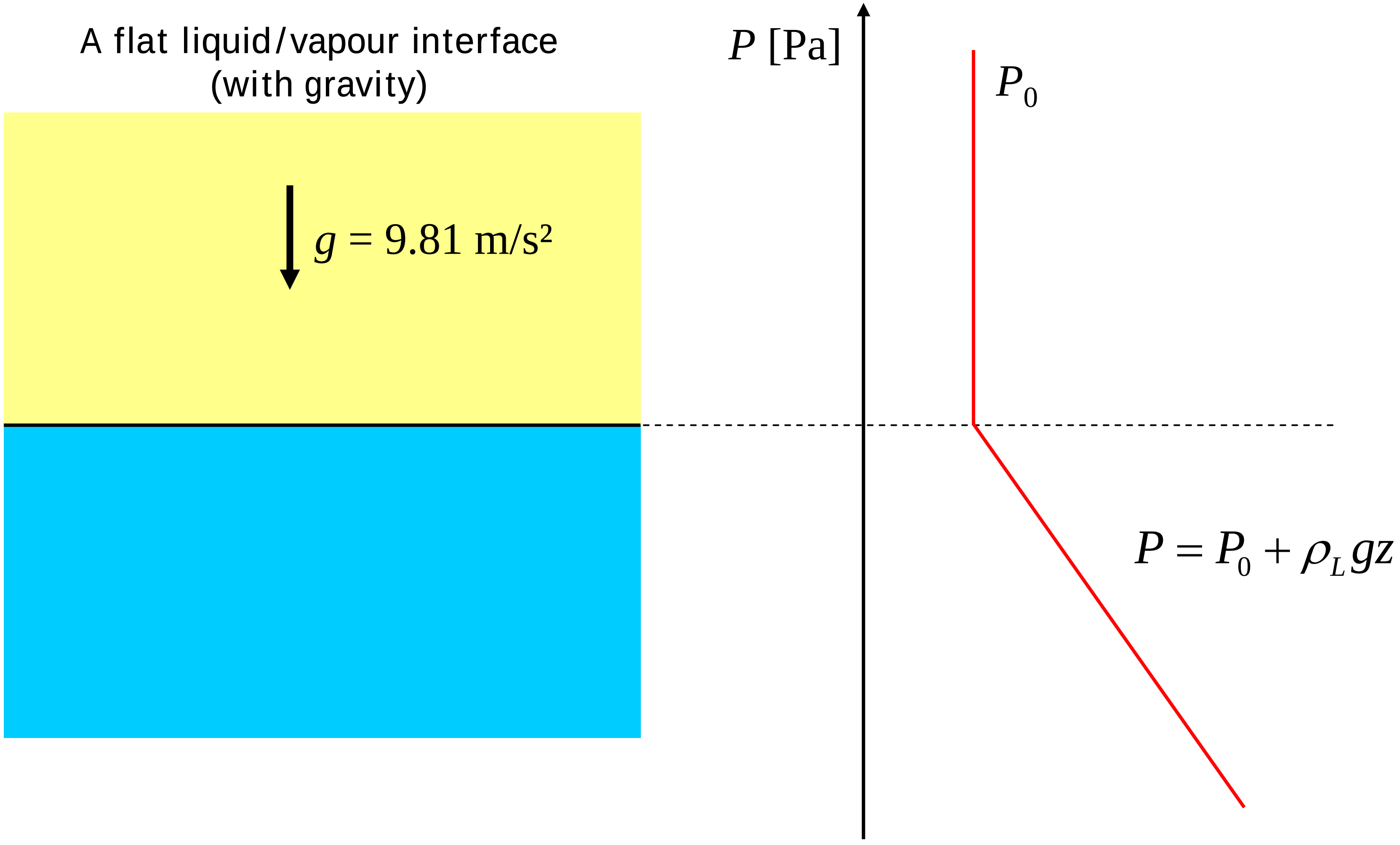
$$\gamma dA = P_C dV$$

$$dA = d\left(4\pi r^2\right) = 8\pi r dr$$

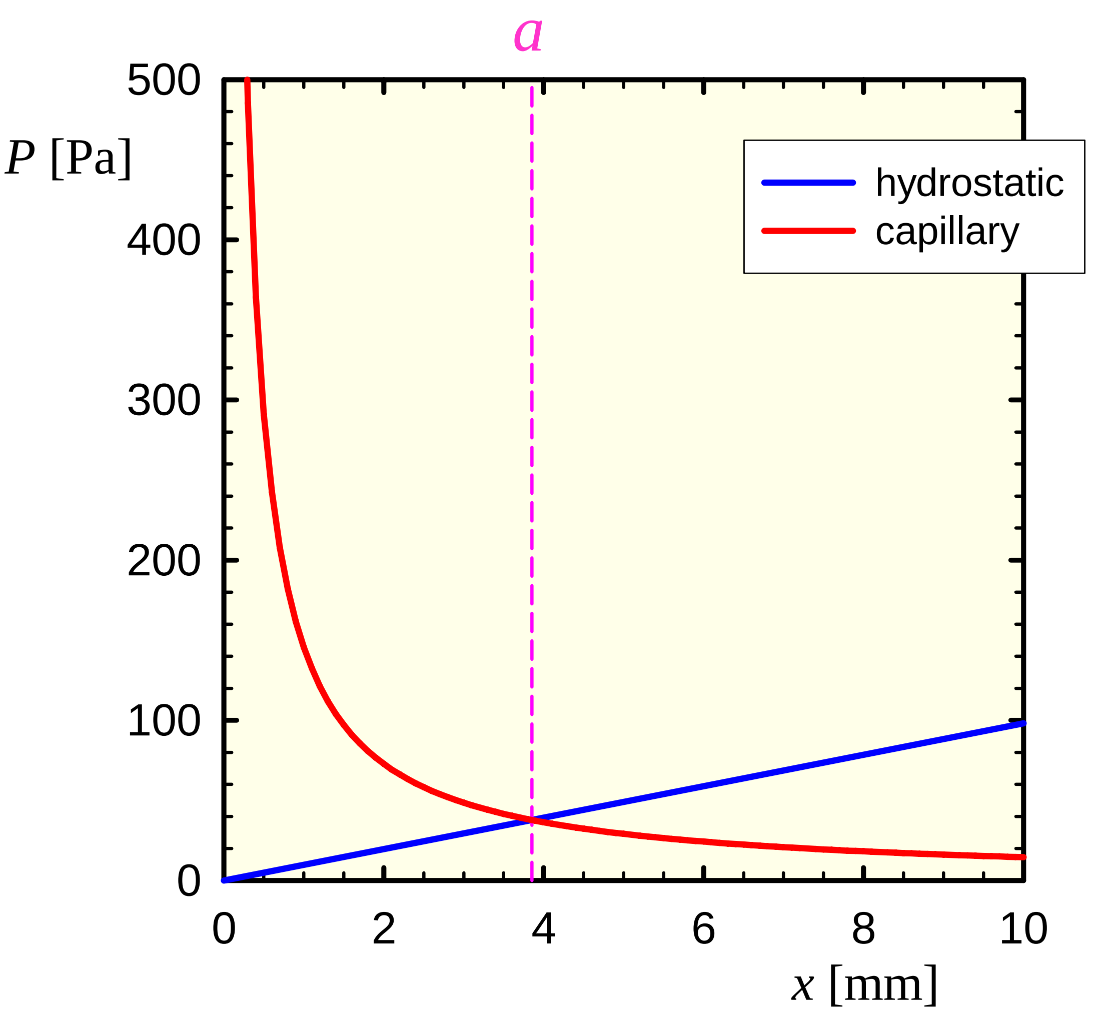
$$dV = d\left(\frac{4}{3}\pi r^3\right) = 4\pi r^2 dr$$

$$\boxed{P_C = \frac{2\gamma}{r}}$$

Hydrostatic Pressure



Capillary Constant, *a*



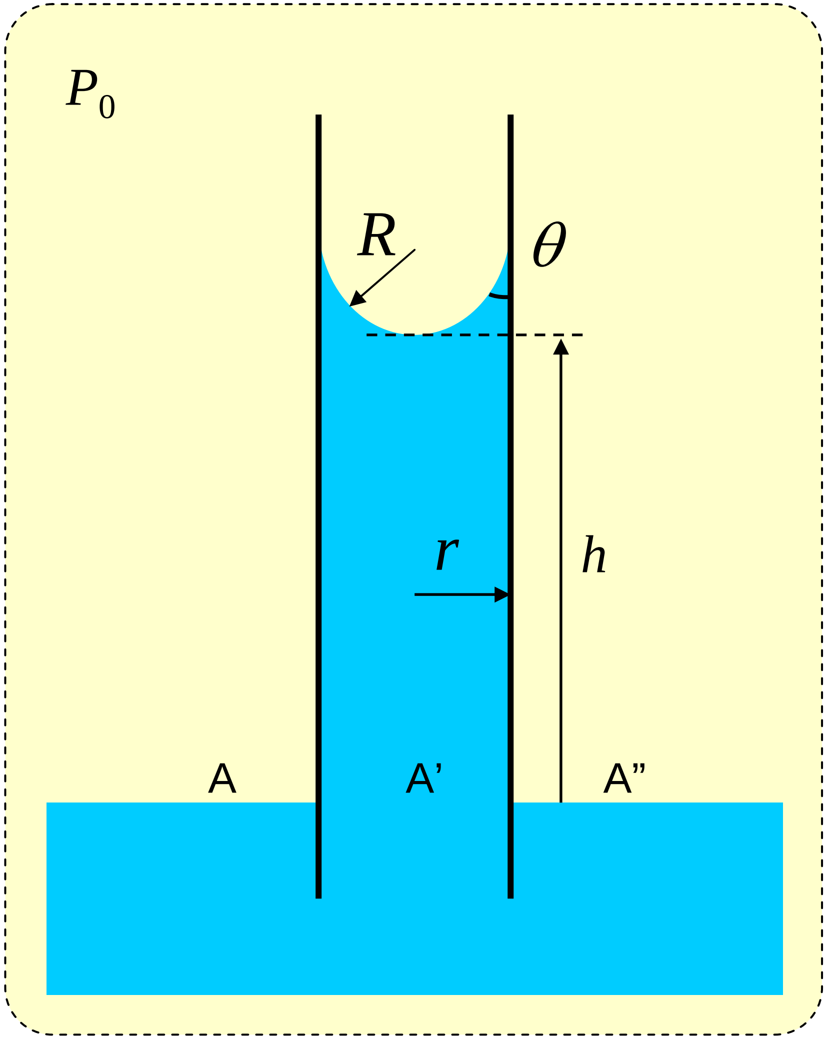
The point of equal importance:

$$\boxed{P_C = P_H}$$

$$\frac{2\gamma}{a} = \rho g a$$

$$\boxed{a = \sqrt{\frac{2\gamma}{\rho g}}}$$

Circular Capillary



$$\boxed{P_C = P_H}$$

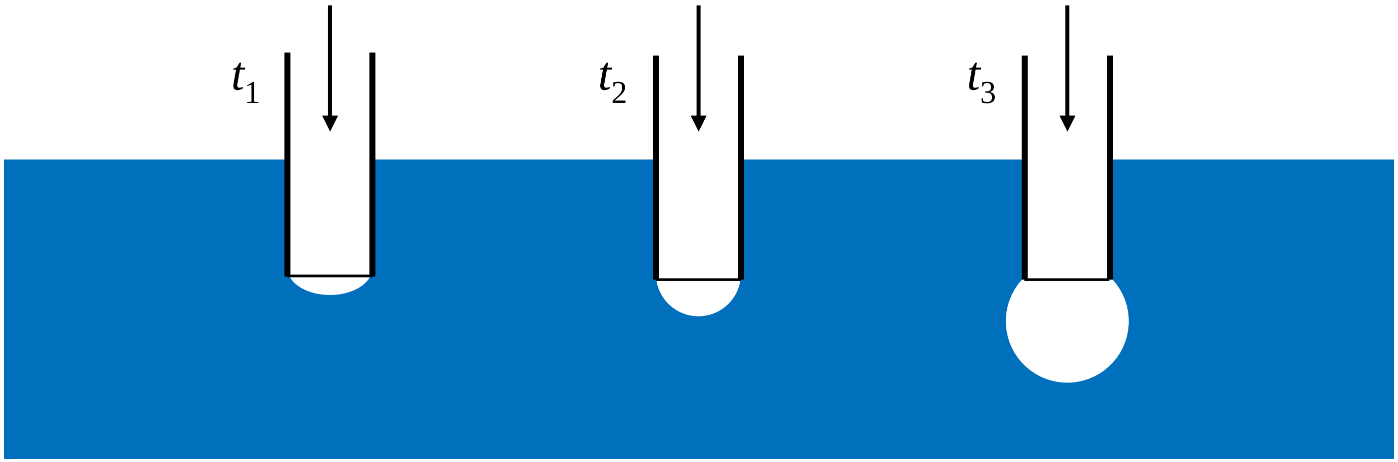
$$\frac{2\gamma}{R} = \frac{2\gamma}{r}\cos\theta = \rho g h$$

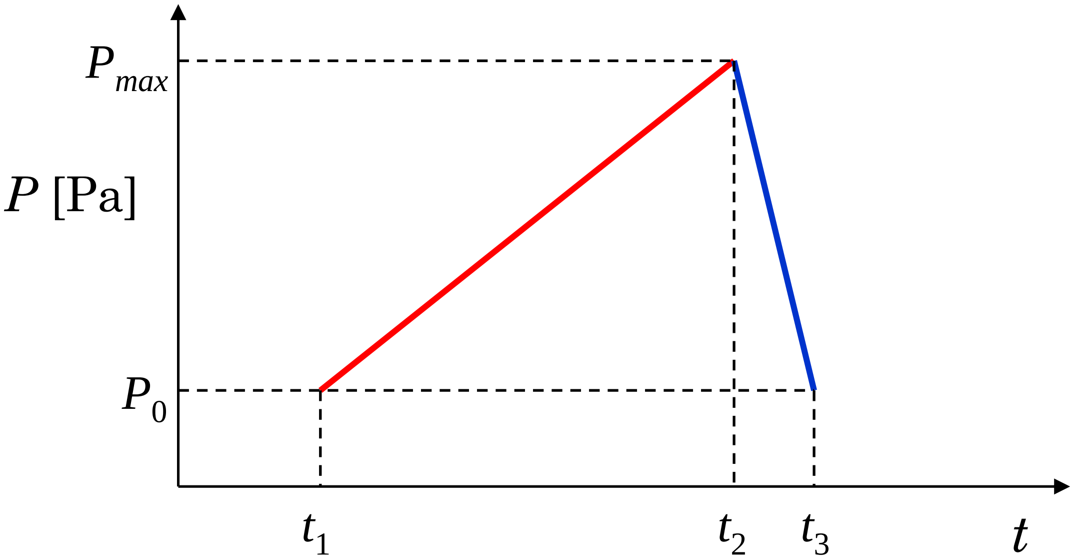
$$\boxed{rh = \frac{2\gamma}{\rho g}\cos\theta = a^2\cos\theta}$$

If $\theta = 0$ then:

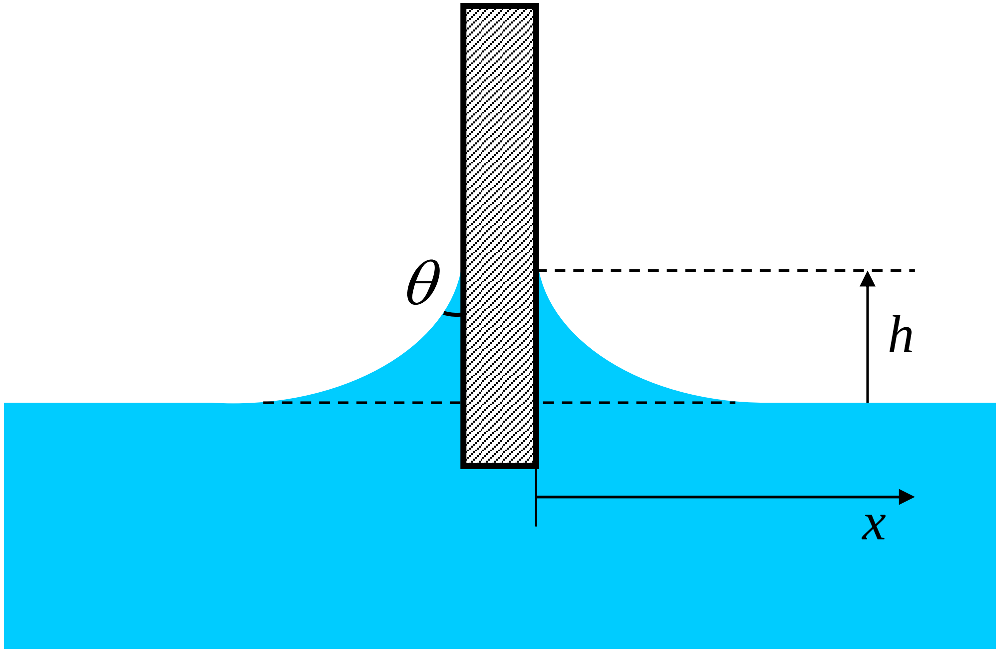
$$\boxed{rh = a^2}$$

Bubbles





Meniscus at a Vertical Plate



$$P_C = P_H$$

$$\frac{\gamma}{R(x)} = \rho g h(x)$$

$$h(x=0) = a\sqrt{1-\sin\theta}$$

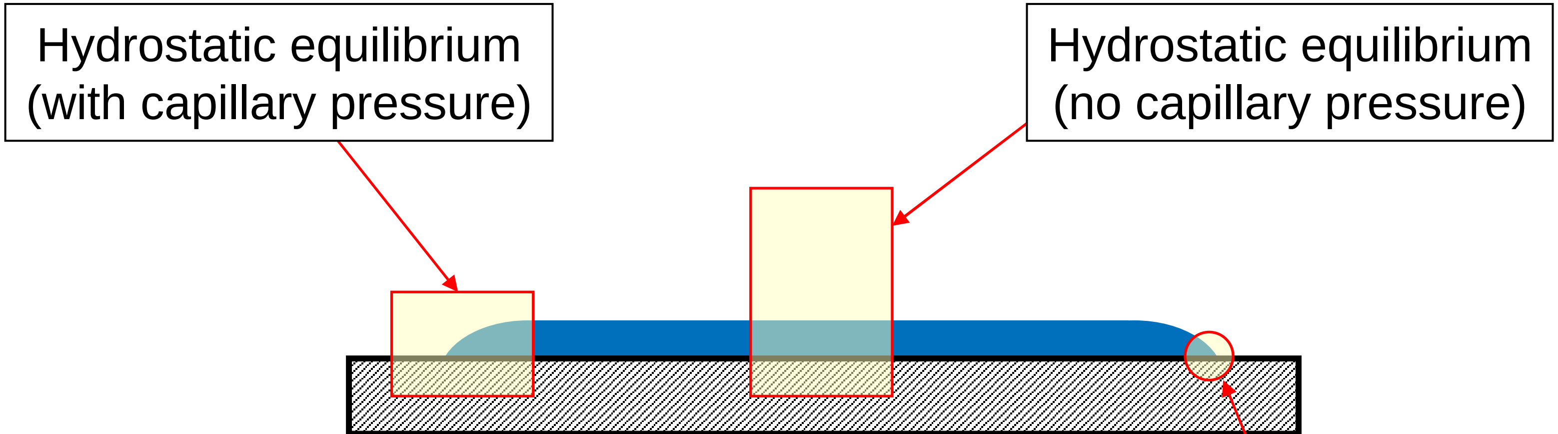
Weight of the whole liquid meniscus (*p* is the wetted perimeter of the plate):

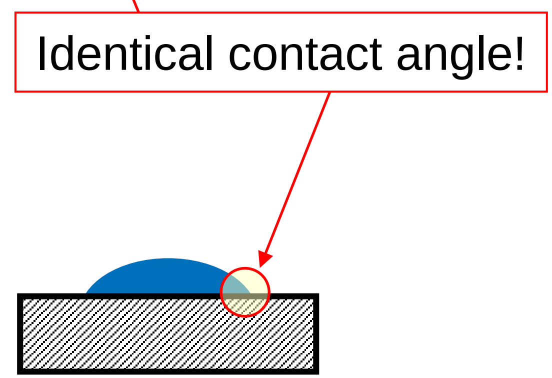
$$W = \rho V = \rho \int_0^\infty h dx = p\gamma\cos\theta$$

If $\theta = 0$ then:

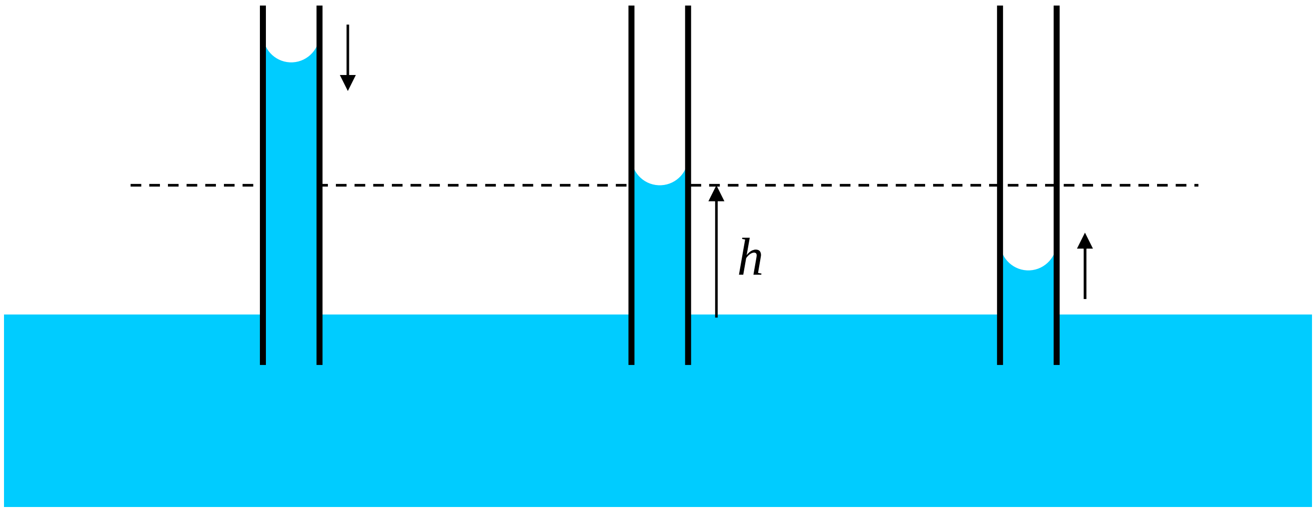
$$h(x=0) = a$$

Large Sessile Drop (Puddle)





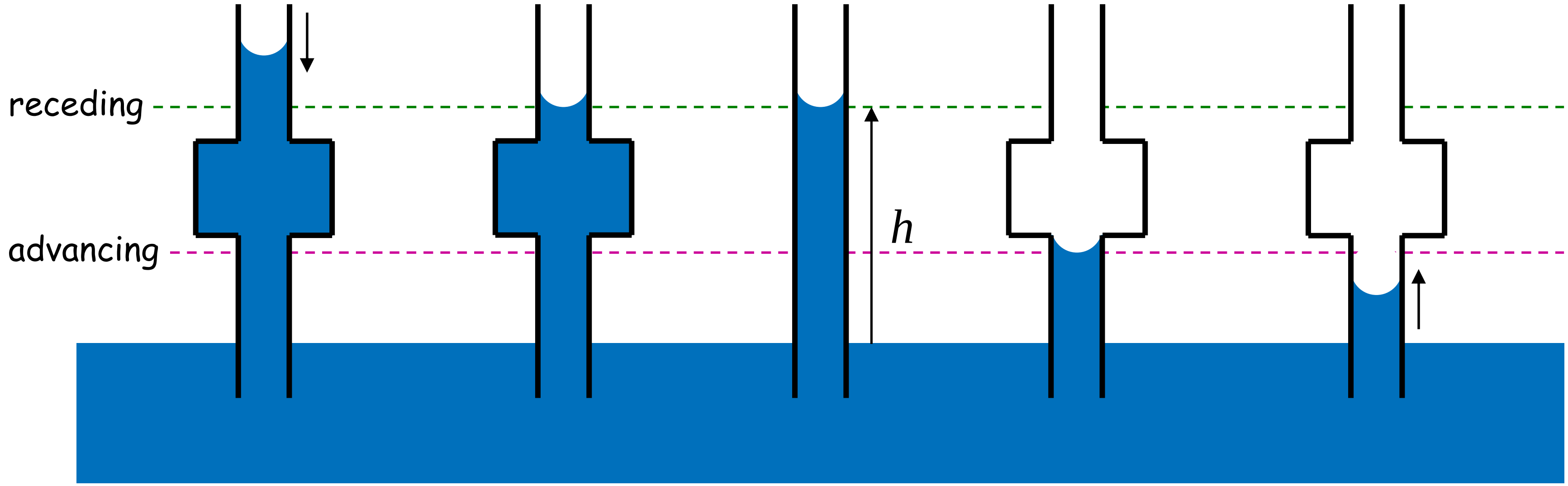
Equilibrium Capillary Rise



If the water level inside the capillary is not at its equilibrium value, *h*, a net force will act on the meniscus and move it (down or up).
Given enough time the equilibrium capillary height will be achieved:

$$h = \frac{a^2}{r}\cos\theta$$

Capillary Hysteresis

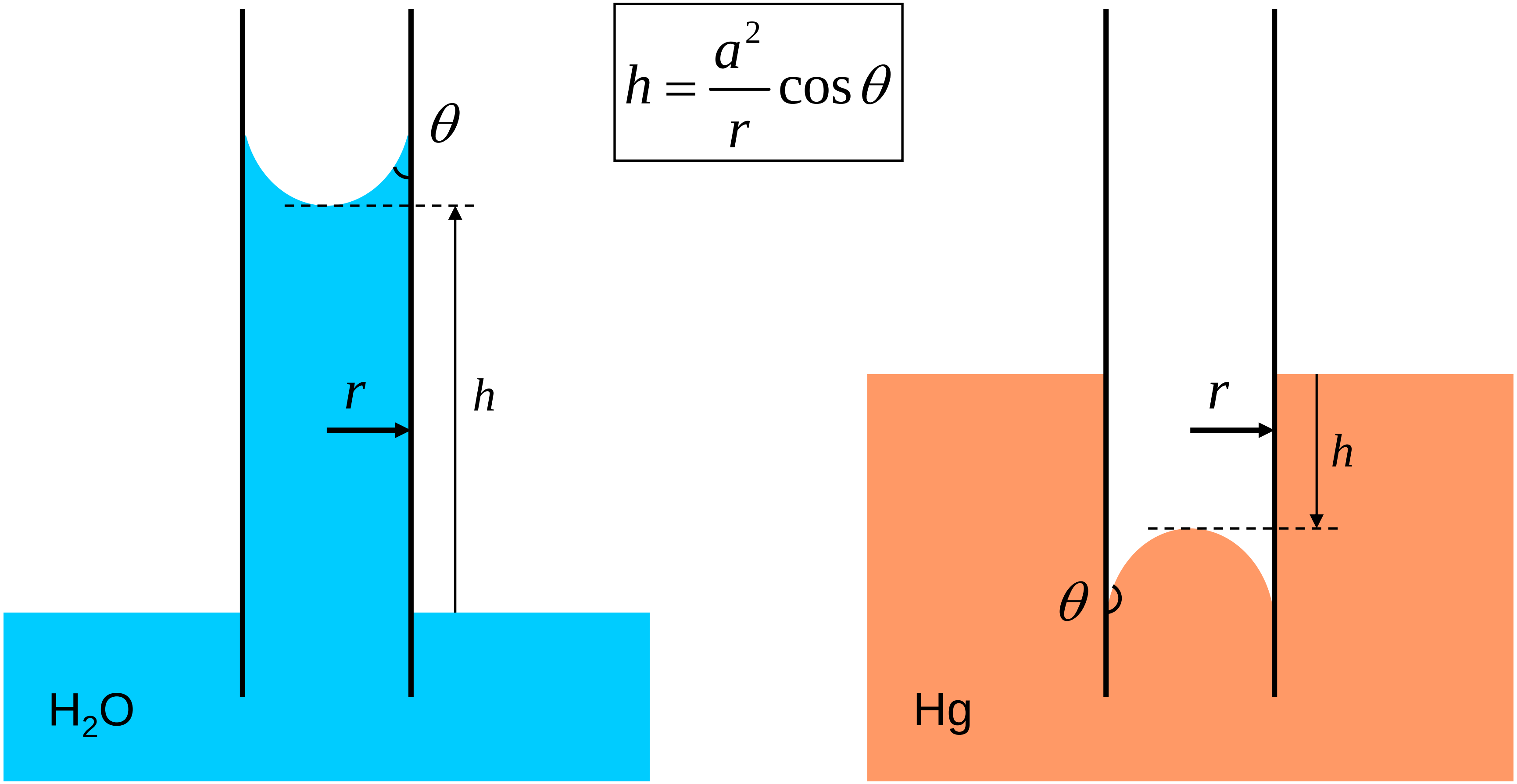


The water level inside the capillary will have a different value depending on the direction of liquid movement. This capillary hysteresis is entirely due to the non-uniform shape of the capillary tube (the contact angle is the same).

Rise or Depression?

The contact angle decides!

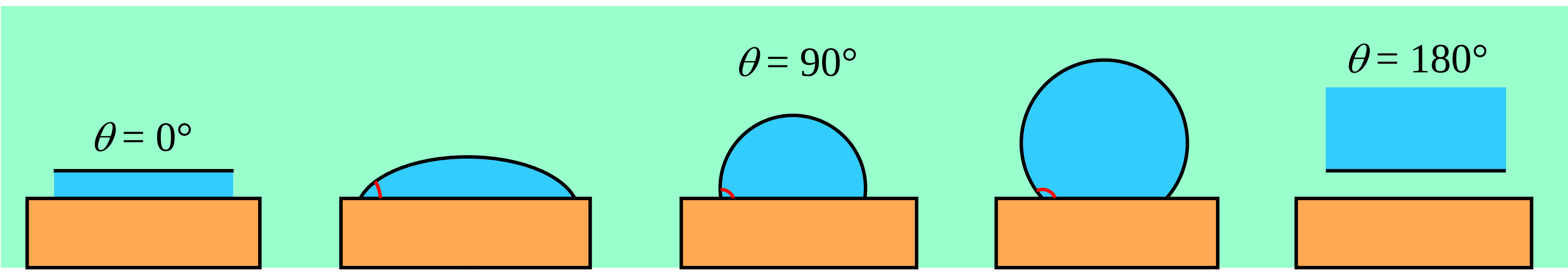
$$h = \frac{a^2}{r}\cos\theta$$



3. Wetting

- Contact Angle
- Critical Surface Tension
- Relation to Surface Constitution
- Heterogeneous & Rough Surfaces
- Contact Angle Hysteresis

Contact Angle – A Measure of Wettability



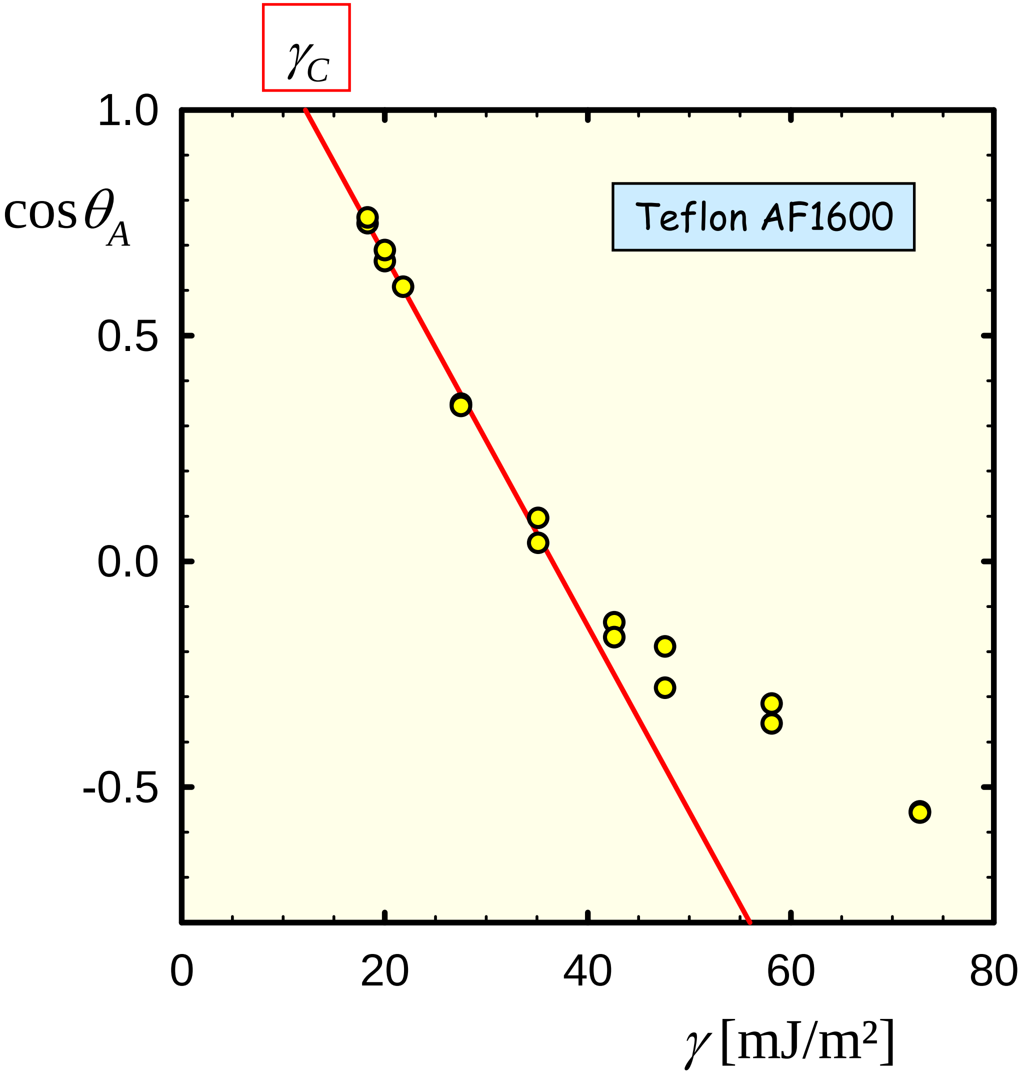
Hydrophobicity of the Solid Surface →

← Hydrophilicity of the Solid Surface

Contact Angle: Some Values

Liquid	Solid	θ [deg]
Water	PTFE	112
Water	Paraffin Wax	110
Water	Polyethylene	103
Water	Kapton	72
Water	Glass	0
Mercury	PTFE	150
Water	PTFE	112
Diiodomethane	PTFE	85
Benzene	PTFE	46
n-Decane	PTFE	40
n-Octane	PTFE	30

Critical Surface Tension of Wetting, γ_C



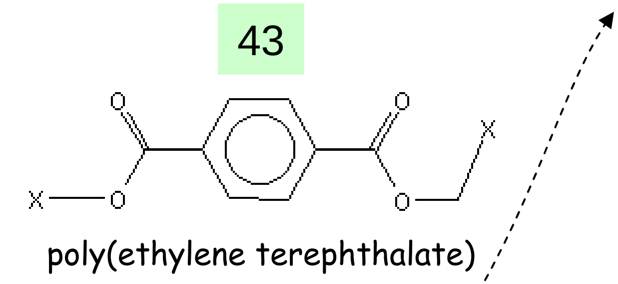
$$\cos\theta = 1 - a(\gamma - \gamma_C)$$

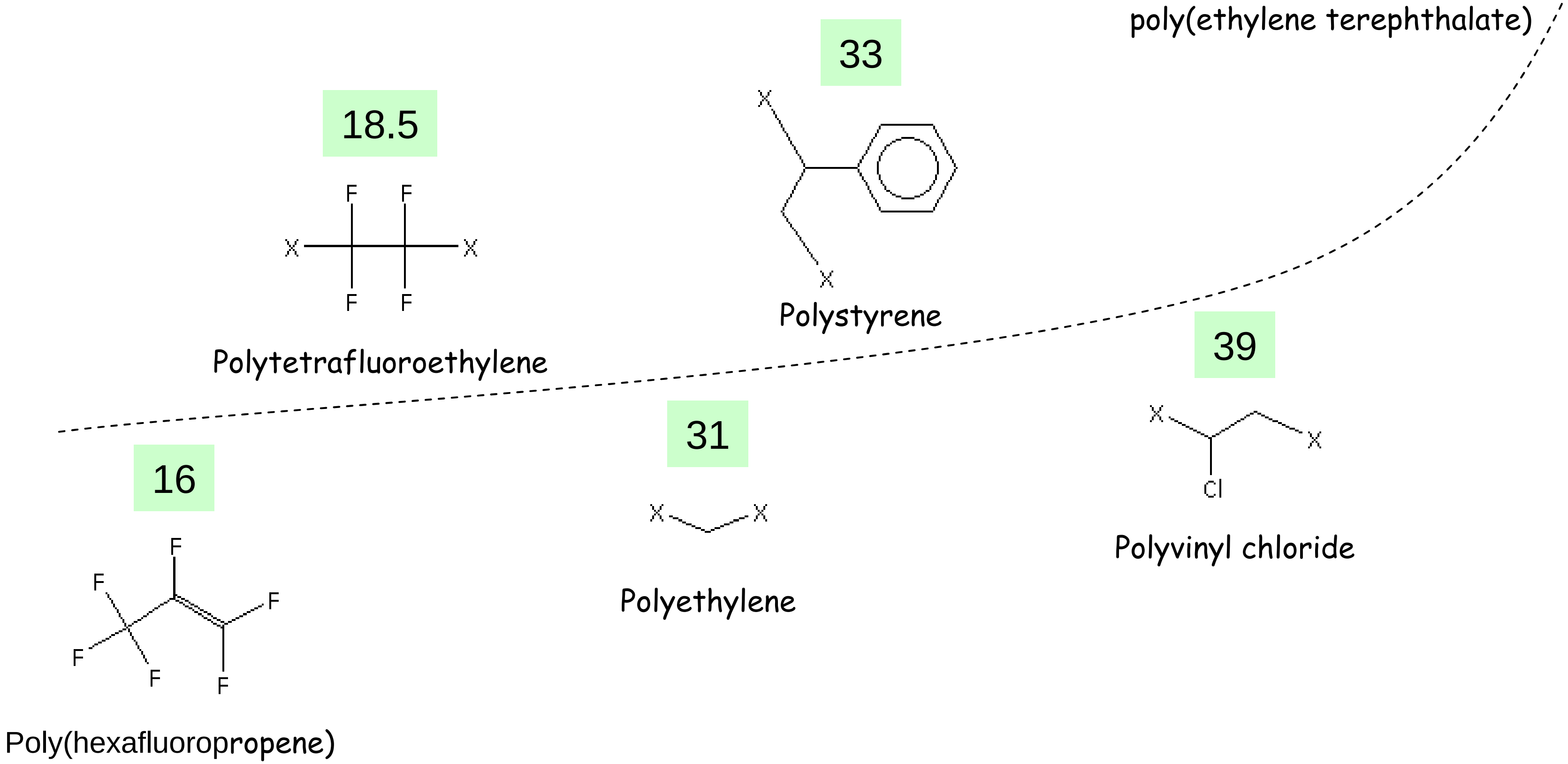
$\gamma_C = 12.8$ mJ/m²

The critical surface tension (CST) is a characteristics of the solid surface.

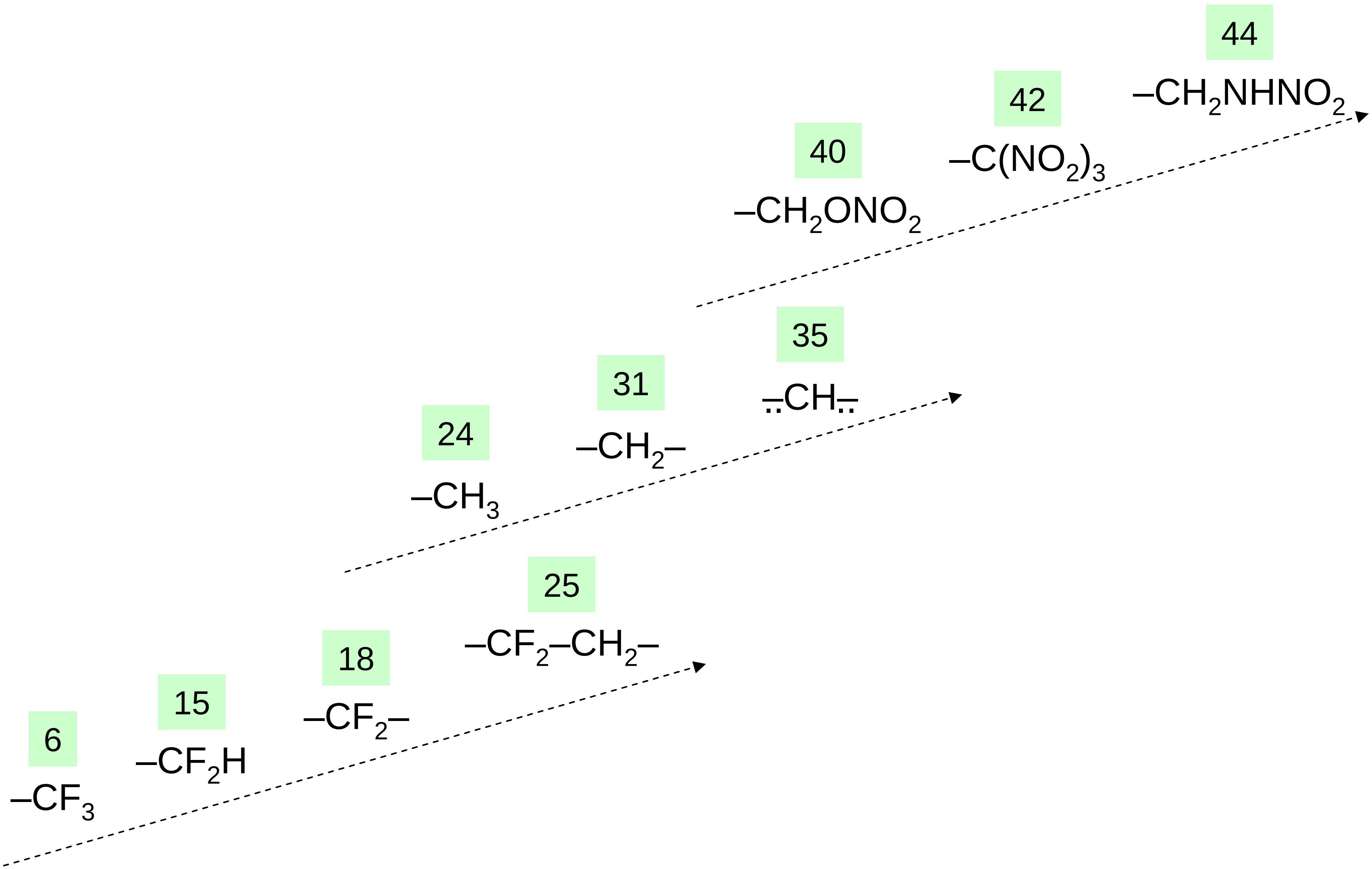
CST: Polymers

- Chemical character of the monomers;
- End groups;
- Surface orientation.

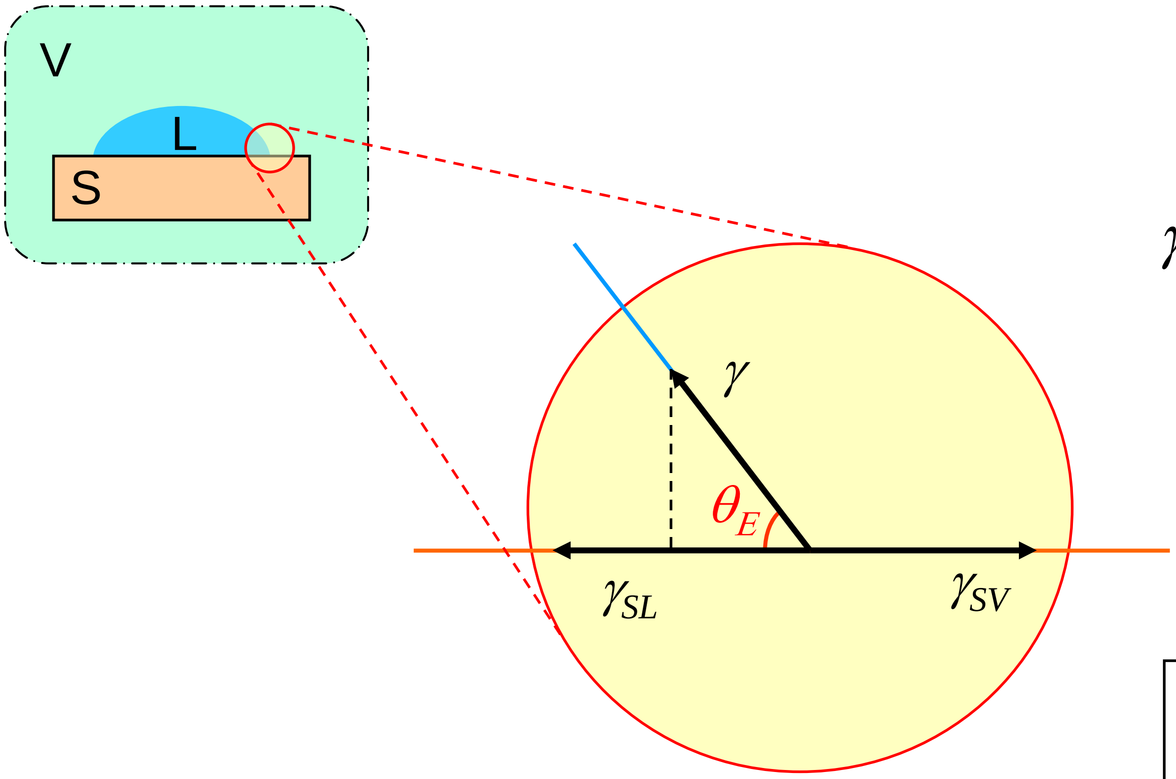




CST: Surface Groups



Young Equation: Force Balance



Static condition:

$$f_{\leftarrow} = f_{\rightarrow}$$

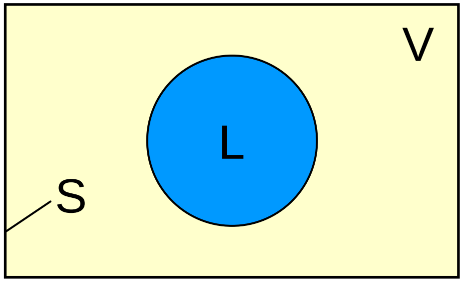
$$\gamma_{SL} + \gamma \cos\theta_E = \gamma_{SV}$$

$$\cos\theta_E = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma}$$

Free Energy Calculation

Free Drop

$F = F_0$

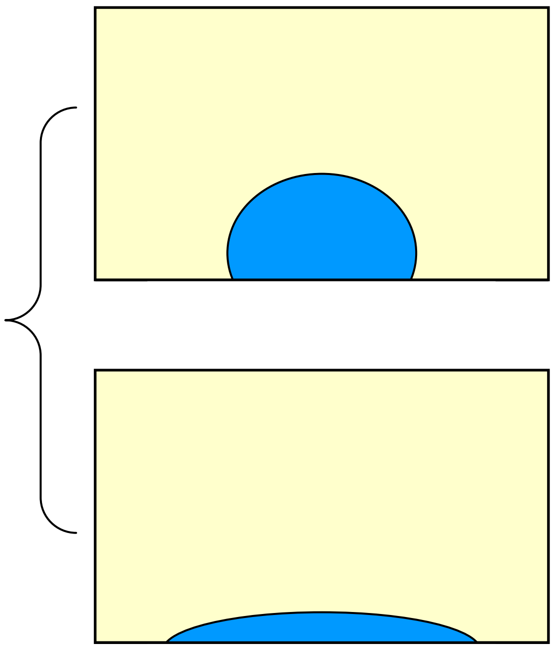


Interfacial Free Energy

$$F_{\text{int}} = \gamma_{SV} A_{SV} + \gamma_{SL} A_{SL} + \gamma A_{LV}$$

Sessile Drop

$F = f(\theta)$



Constant

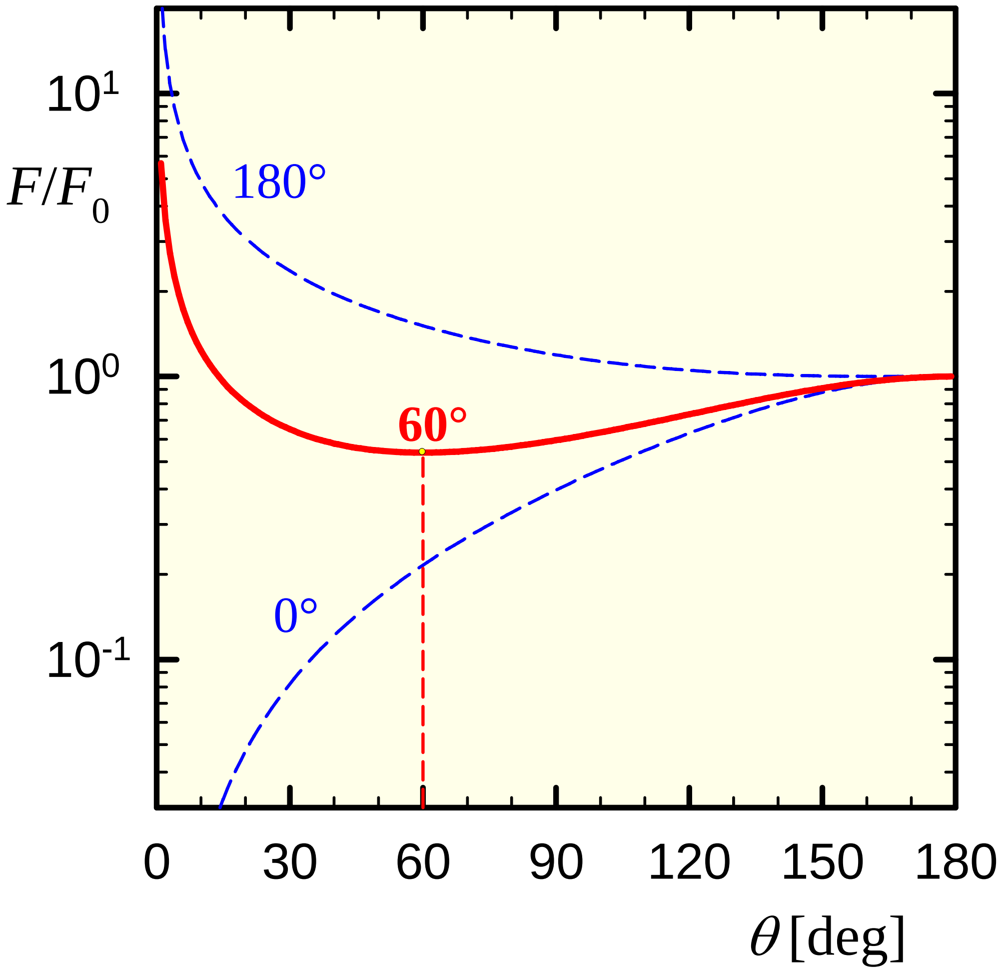
$$F = F_{\text{int}} - \gamma_{SV}\left(A_{SV} + A_{SL}\right) =$$

$$= \left(\gamma_{SL} - \gamma_{SV}\right) A_{SL} + \gamma A_{LV}$$

$$\frac{F}{F_0} = \frac{F}{4\pi R^2 \gamma}$$

Reference

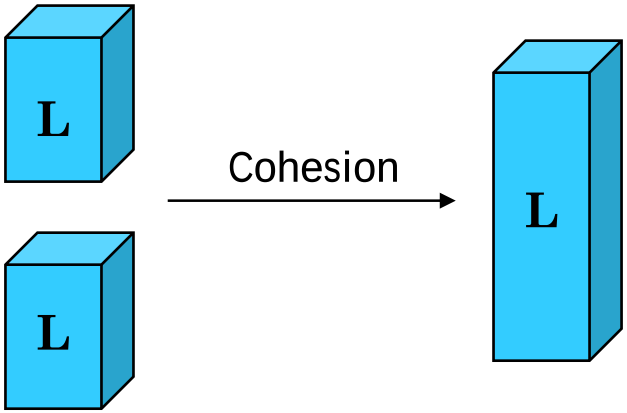
Young Equation: Free Energy Minimum



Equilibrium is reached at the minimum of the free energy curve, i.e. at an equilibrium contact angle, θ_E, given by:

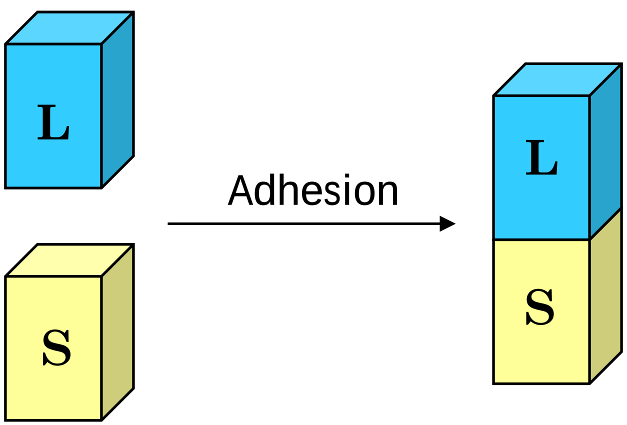
$$\cos\theta_E = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma}$$

Cohesion & Adhesion



Work of Cohesion

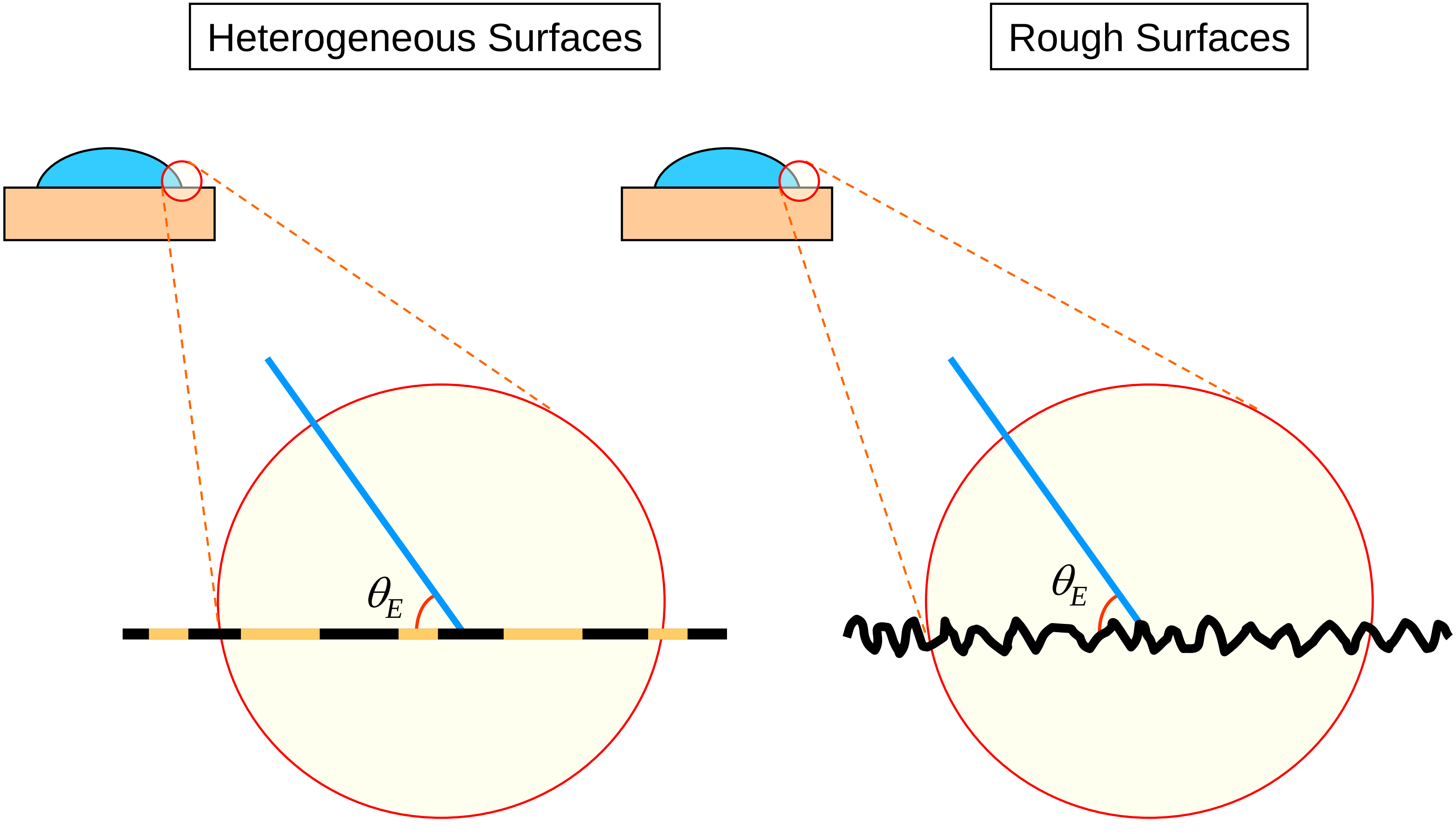
$$
\begin{aligned}
W_C &= F_1 - F_2 = \\
&= 2\gamma - 0 = \\
&= 2\gamma
\end{aligned}
$$



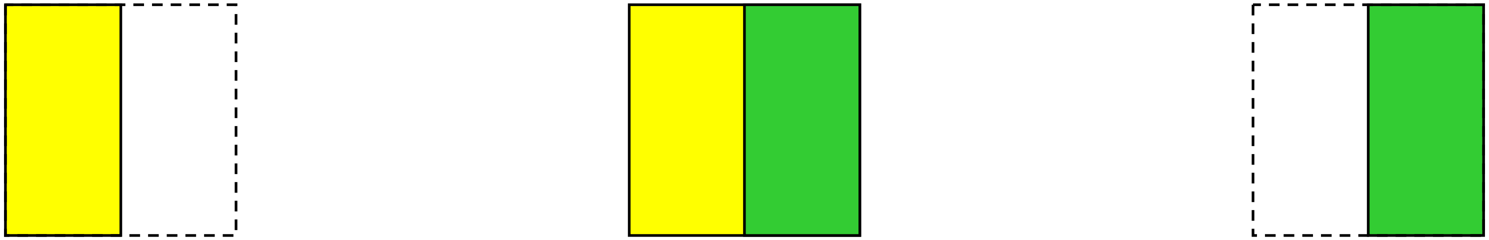
Work of Adhesion

$$
\begin{aligned}
W_A &= F_1 - F_2 = \\
&= \gamma + \gamma_{SV} - \gamma_{SL} = \\
&= \gamma\left(1 + \cos\theta_E\right)
\end{aligned}
$$

Non-Ideal Surfaces



Cassie Equation (Heterogeneity)

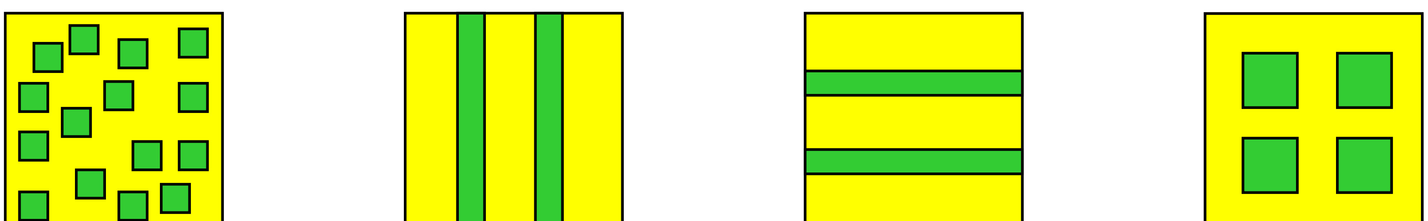


$W_{A1} A_1$ $\quad$ $W_A (A_1 + A_2)$ $\quad$ $W_{A2} A_2$

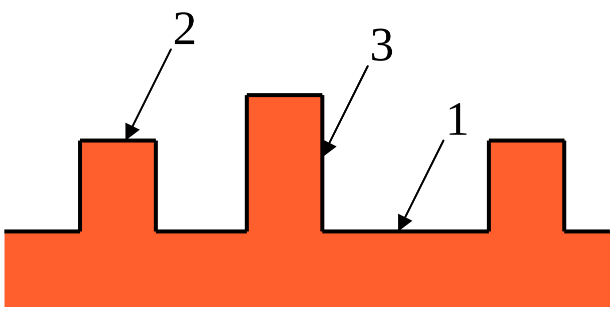
$$\boxed{\cos\theta_E = \phi_1 \cos\theta_1 + \phi_2 \cos\theta_2}$$ Cassie Equation

Area fractions: $\phi_{1,2} = \dfrac{A_{1,2}}{A_1 + A_2}$

The average equilibrium wettability of all these surfaces is the same (identical area fractions):



Wenzel Equation (Roughness)



Using Cassie equation we have:

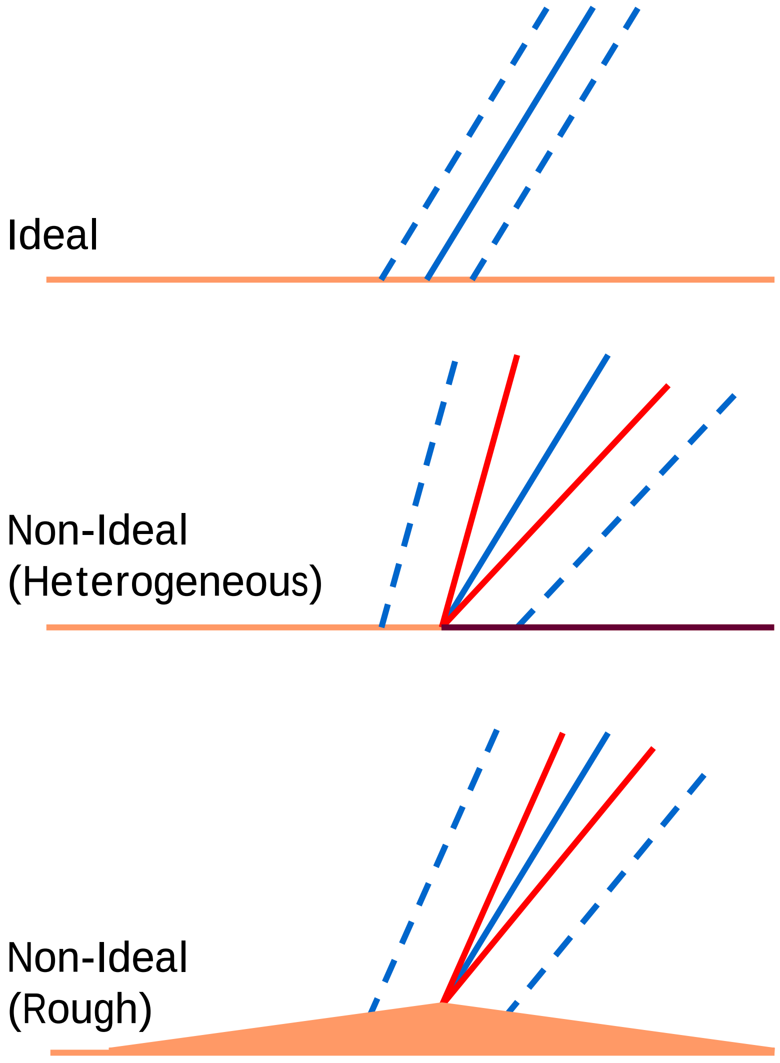
$$\cos\theta_E = \phi_1\cos\theta_1 + \phi_2\cos\theta_2 + \phi_3\cos\theta_3 =$$
$$= \phi_1\cos\theta + \phi_2\cos\theta + \phi_3\cos\theta$$

$$\boxed{\cos\theta_E = r\cos\theta}$$ Wenzel Equation

Wenzel ratio: $r = \dfrac{A_1 + A_2 + A_3}{A_1 + A_2} \geq 1$

Surface roughness increases the wettability of hydrophilic surfaces ($\theta < 90°$) and decreases the wettability of hydrophobic surfaces ($\theta > 90°$).

Pinning of the Contact Line

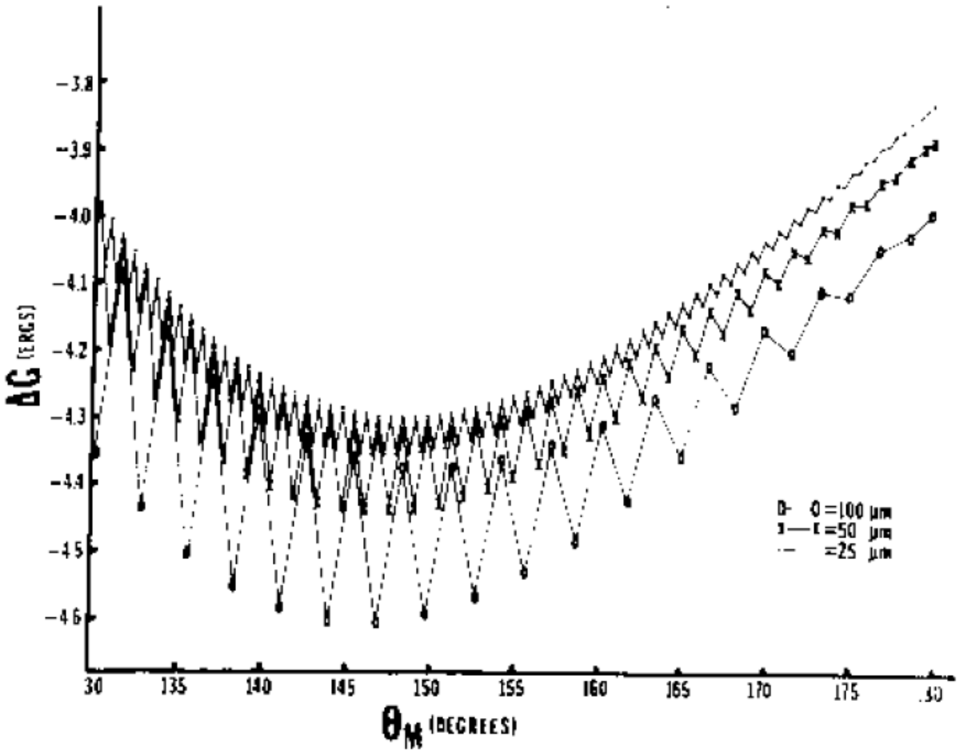


<u>Ideal Surface</u>:
Unrestricted liquid movement – and therefore achievement of the equilibrium configuration is possible.

<u>Non-Ideal Surface</u>:
Any chemical heterogeneity or roughness not only affects the equilibrium contact angle (Cassie, Wenzel) but also prevent the system from attaining it (contact angle hysteresis).

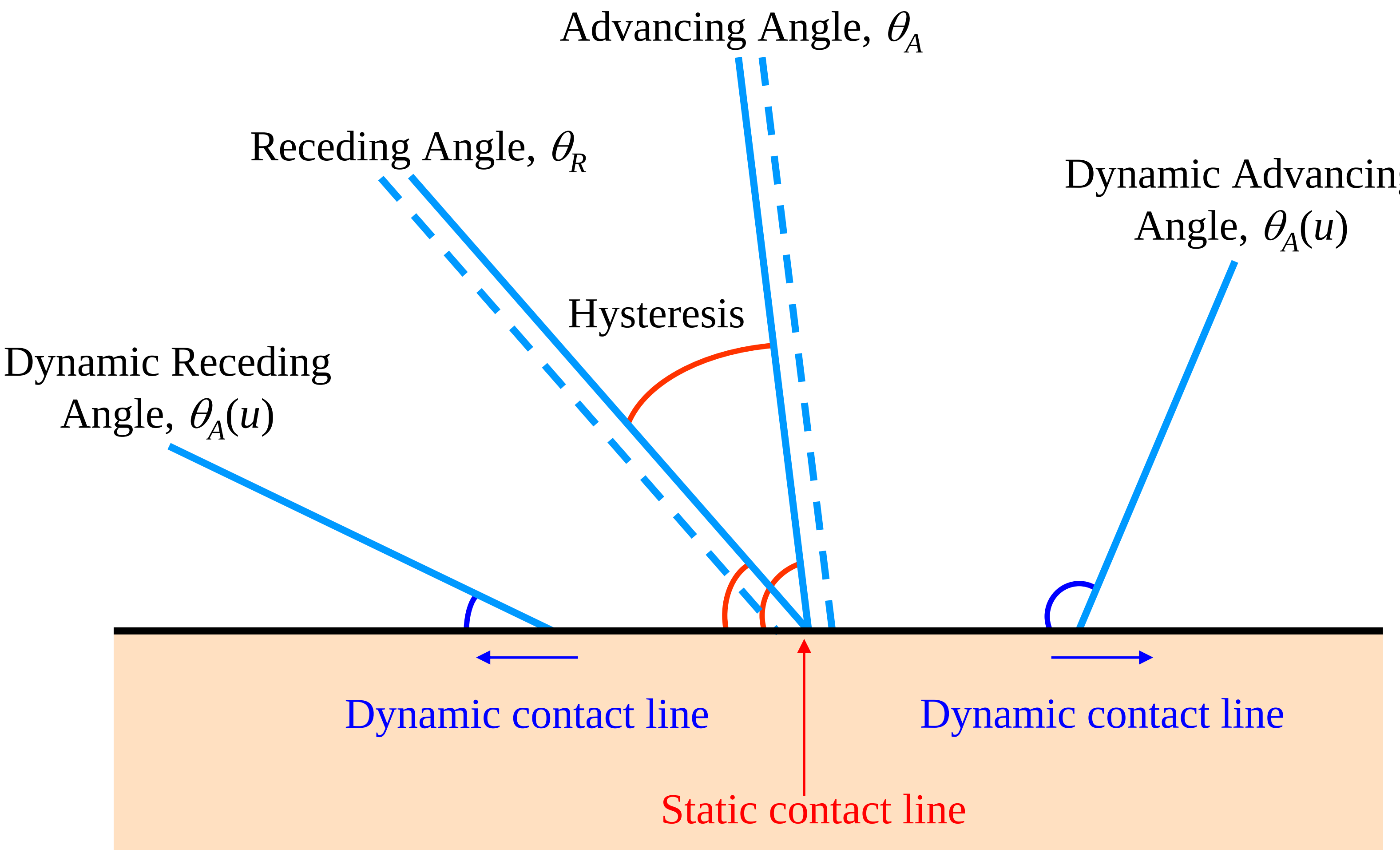
Contact Angle Hysteresis

Hysteresis is a non-equilibrium phenomenon. Energy barriers prevent the free energy of the system from attaining the absolute minimum, i.e., the Cassie or Wenzel angle.



*Eick, Good & Neumann (1975)

Contact Angles on a Real Surface



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