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# 3. Physics of Microfluidic Systems

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3.1. Navier-Stokes Equations

3.2. Laminar and Turbulent Flow

3.3. Fluid Dynamics

3.4. Fluidic Networks

3.5. Transport of Heat

**3.6. Interfacial Surface Tension**

3.7. Electrokinetics

## 3.6. Interfacial Surface Tension

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1. Contact Angle
2. Capillarity
3. Gas Bubbles and Priming Issues
4. Marangoni Effect
5. Thermocapillary Flow
6. Capillary Control by Surface-Active Agents
7. Lotus Effect

## 3.6. Interfacial Surface Tension

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1. **Contact Angle**
2. Capillarity
3. Gas Bubbles and Priming Issues
4. Marangoni Effect
5. Thermocapillary Flow
6. Capillary Control by Surface-Active Agents

## 3.6. Interfacial Surface Tension

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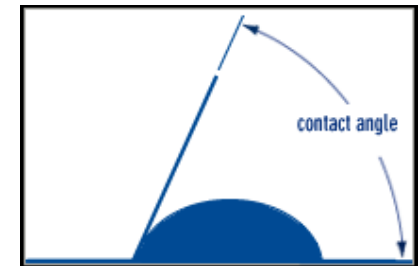
- Interfaces

- Solids
- Liquids
- Gases
  - Low density
  - Surface tension widely independent of gas type



- Effects

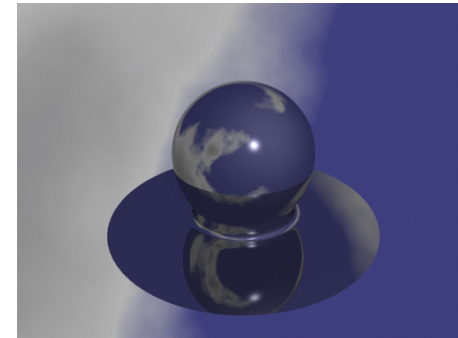
- Contact angle
- Wetting behavior
- Surface tension
  - Interfacial tension
    - Liquid
    - Own vapor



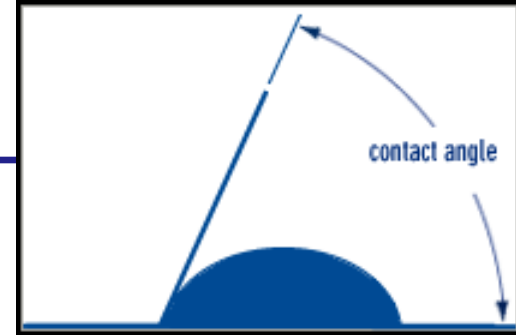
## 3.6. Interfacial Surface Tension

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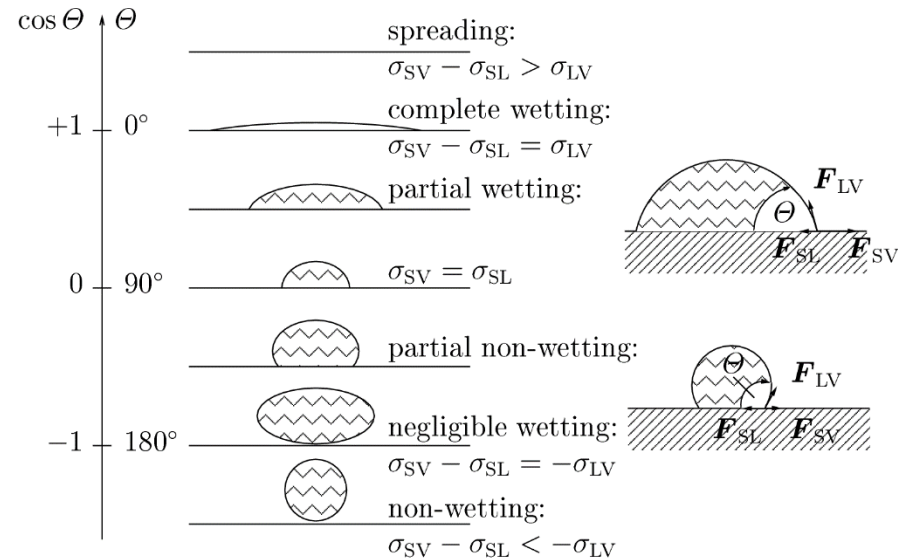
- Interfacial energies
  - Liquid-gas (vapor):  $\sigma_{LG}$
  - Liquid-solid:  $\sigma_{SL}$
  - Solid-gas (vapor):  $\sigma_{SG}$
  - Liquid-liquid (immiscible):  $\sigma_{LL}$
- Physics
  - Strongly dependent on type of media
- „Polarity“
  - Hydrophilicity
  - Hydrophobicity



# 3.6.1. Contact Angle



- Measure
  - Wetting of surfaces
  
- Angle
  - Three-phase contact point
  - Solid surface
  - Tangent of liquid-vapor boundary
  - Regimes
  
- Equilibrium of forces
  - **Tangential** to mutual interface



$$F_{SL} + F_{LV} \cos \theta + F_{SV} = 0$$

Young:

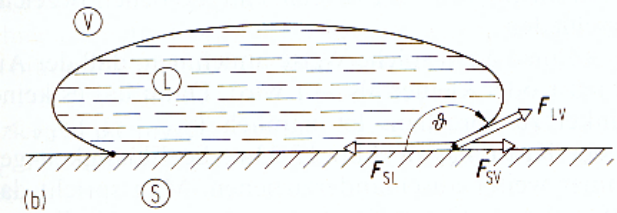
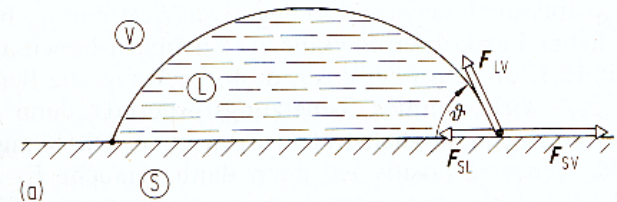
$$\sigma_{SG} - \sigma_{SL} = \sigma_{LG} \cos \theta$$

## 3.6.1. Contact Angle

solid	liquid	$\theta$
amalgam	water	$77^\circ$
acrylic	alcohol	$0^\circ$
	water	$75^\circ$
polystyrene	water	$86^\circ$
glass	water	$14^\circ$
silicone	water	$110^\circ$
wax, paraffin	water	$109^\circ$

**Table 3.5.** The angle of contact  $\theta$  for various liquid–solid pairs.  $\theta$  is a measure of the tendency for the liquid to wet a solid surface. The lower  $\theta$ , the greater the tendency of the liquid to spread, the liquid is increasingly repelled by the surface towards large  $\theta$

- Variations in tabulated data
  - Sensitivity
    - Air-liquid-solid contact conditions
    - Liquid meniscus geometry
    - Buoyancy
- Static hysteresis
  - Advanced / receded
- Dynamic hysteresis
  - Advancing / receding



## 3.6.1. Cohesion Energy

- Interpretation of interfacial energy
  - Energy  $W_{ij}$  released for wetting per length of wetted perimeter
  - Dupré relation

$$W_{ij} = \sigma_{i,G} + \sigma_{j,G} - \sigma_{ij}$$

- Interfacial tension at mutual interface  $\sigma_{ij}$

- Models to derive  $W_{ij}$ 
  - Splitting interfacial tension into components for each phase
    - Given phase  $i$

$$\sigma_i = \sigma_{\text{dis},i} + \sigma_{\text{pol},i}$$

- Dispersive component
- Polar component
- Tabulated values

### 3.6.1. Cohesion Energy

optional

- Owens and Wendt
  - Polymer surfaces

$$\sigma_i = \sigma_{\text{dis},i} + \sigma_{\text{pol},i}$$

$$\mathcal{W}_{ij} = 2 \left( \sqrt{\sigma_{\text{dis},i} \sigma_{\text{dis},j}} + \sqrt{\sigma_{\text{pol},i} \sigma_{\text{pol},j}} \right)$$

- Wu
  - At least one highly energetic phase

$$\mathcal{W}_{ij} = 4 \left( \frac{\sigma_{\text{dis},i} \sigma_{\text{dis},j}}{\sigma_{\text{dis},i} + \sigma_{\text{dis},j}} + \frac{\sigma_{\text{pol},i} \sigma_{\text{pol},j}}{\sigma_{\text{pol},i} + \sigma_{\text{pol},j}} \right)$$

- Contact angle
  - Cohesion energy
  - Surface tension

$$\mathcal{W}_{ij} = \sigma_{i,G} + \sigma_{j,G} - \sigma_{ij}$$
$$2\sigma_G - \sigma_{\Gamma G} = \sigma_{\Gamma G} \cos \Theta$$

$$\mathcal{W}_{ij}(\sigma, \Theta) = \sigma_{\text{LG}} (1 + \cos \Theta)$$

## 3.6.1. Goniometric Measurement of $\sigma$ and $\theta$

- Geometric fingerprints of droplets
- Applicable to wide range of situations
- Constituents
  - Source of light
  - Sample stage
  - Lens
  - Image capture
- Common Problems
  - Visual assignment of geometric parameters
    - E.g., shadow

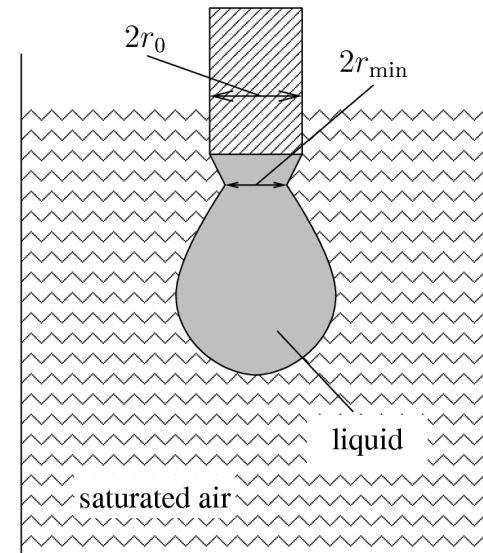


Fig. A.1. Droplet-volume method to determine interfacial surface tensions



## 3.6.1. Goniometric Measurement of $\sigma$

- Method
  - Orifice of small tube
  - Growing droplet
  - Detachment at

$$\rho V g = 2\pi r_{\min} \sigma$$

weight

force

- Sources of error
  - Minimum radius  $r_{\min}$
  - Droplet volume  $V$

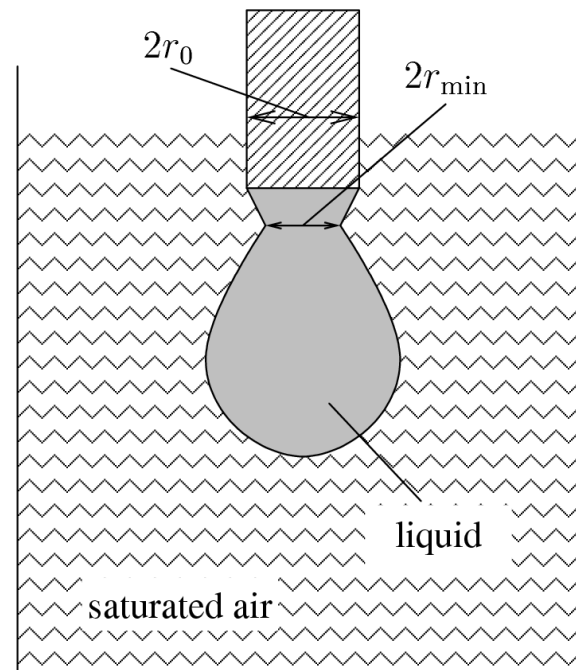
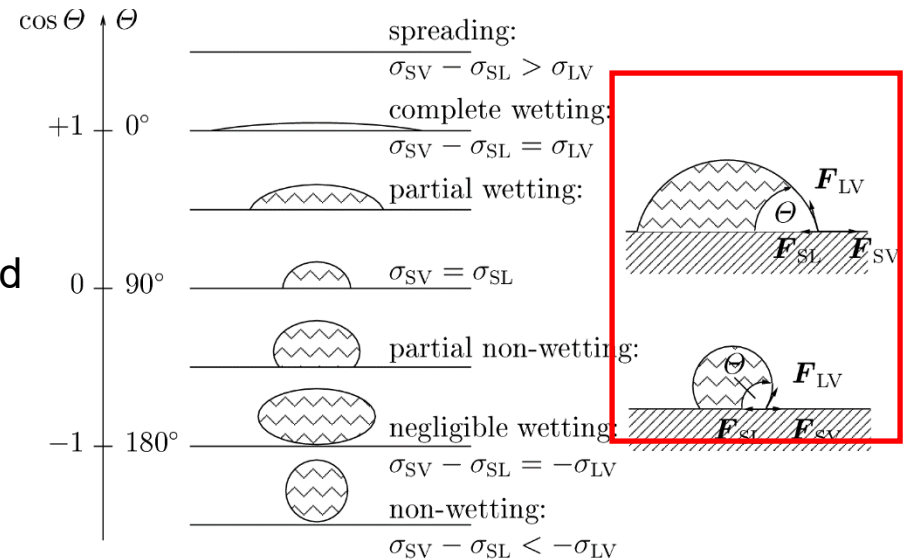


Fig. A.1. Droplet-volume method to determine interfacial surface tensions

## 3.6.1. Goniometric Measurement of $\theta$

- Tangent
  - Liquid-gas contact line
- Image processing software
- Static measurement
  - Receded angles
    - Evaporation / withdrawal of liquid
  - Advanced angle
    - Addition of liquid
- Dynamic measurement
  - Tilting of substrate
- Problems
  - [Parallax](#)
  - Small amount of probed surface area
  - Limited to flat surfaces
  - Dynamic measurement hardly reproducible



## 3.6.1. Tensiometry: Wilhelmy Principle

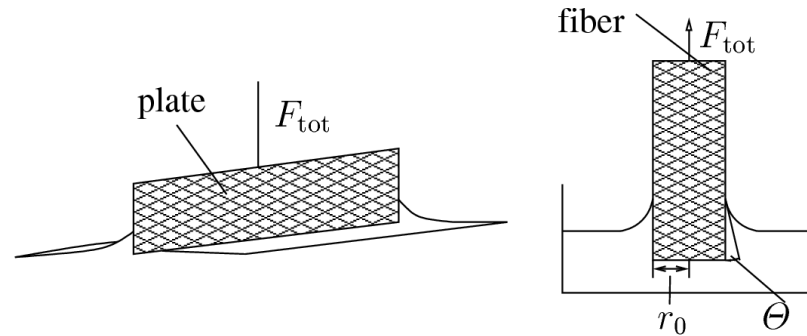


Fig. A.2. Wilhelmy setup for measuring the surface contact angle  $\theta$  on a plate and a fiber of radius  $r_0$

$$F_{\text{tot}} = m_{\text{setup}}g + F_{\Delta m} + F_{\eta}$$

- Straight-forward method by Wilhelmy (1863)
- Total force  $F_{\text{tot}}$  picked up by torsion balance
  - Weight of setup  $m_{\text{setup}}g$ 
    - Can, for instance, be eliminated by taring prior to measurement
  - Buoyancy  $F_{\Delta m}$ 
    - Displaced (buoyancy) / elevated liquid
  - Viscosity (dynamic measurement only)

## 3.6.1. Tensiometry: Wilhelmy Principle

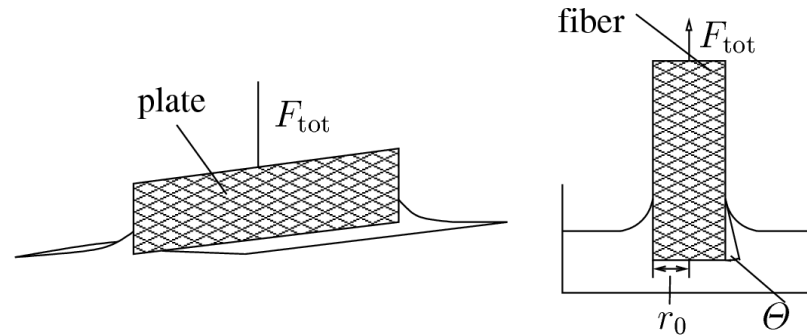


Fig. A.2. Wilhelmy setup for measuring the surface contact angle  $\theta$  on a plate and a fiber of radius  $r_0$

- Static
- Taring

$$F_{\text{tot}} = m_{\text{setup}}g + F_{\Delta m} + F_{\eta}$$

- Interfacial term

- Transmission of force to liquid
- Dubbed „Wilhelmy force“
  - Effective length of wetted perimeter  $l^*$

$$F_{\Theta} = l^* \sigma \cos \Theta$$

- Point of detachment

- Evaluation of  $\sigma$  and  $\theta$

$$l^* \sigma \cos \Theta = F_{\text{tot}}$$

## 3.6.1. Tensiometry: Wilhelmy Principle

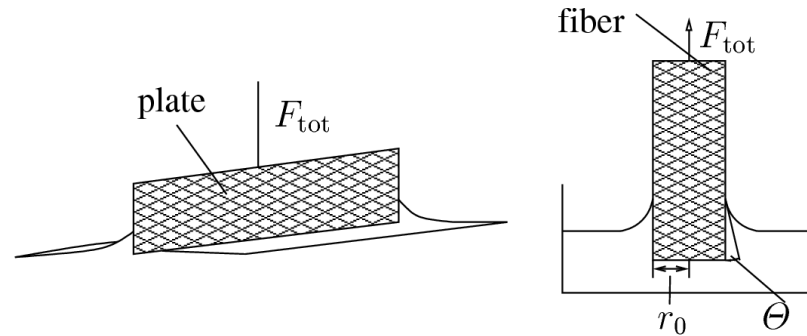


Fig. A.2. Wilhelmy setup for measuring the surface contact angle  $\theta$  on a plate and a fiber of radius  $r_0$

$$l^* \sigma \cos \theta = F_{\text{tot}}$$

- Elimination of  $\theta$ 
  - Induce perfect spreading  $\theta = 0$ 
    - $\cos \theta = 1$
    - E.g., platinum substrates, coatings

$$\sigma = \frac{F_{\text{tot}}}{l^*}$$

## 3.6.1. Tensiometry: du Noüy Ring

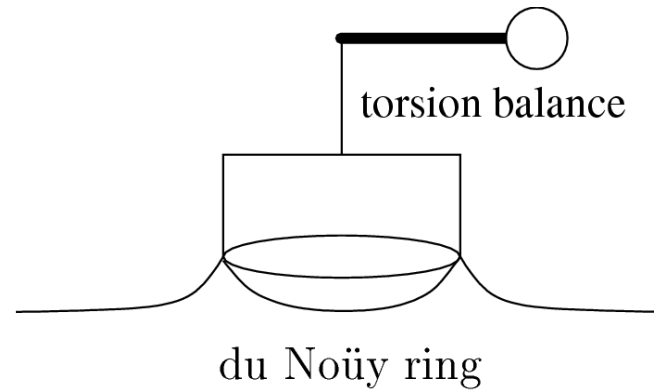


Fig. A.3. Du-Noüy-ring setup for measuring the surface tension  $\sigma$

$$F_{\text{tot}} = m_{\text{setup}}g + F_{\Delta m} + F_{\eta}$$

- Lecomte du Noüy (1919)

- Effective perimeter

- $l^* = f \cdot l$

- Inner and outer surface of ring:  $l = 2(2\pi r_0)$

- Correction factor  $f$

- Different components of Wilhelmy force for inner and outer surfaces

$$F_{\Theta} = l^* \sigma \cos \Theta$$

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## 3.6.2. Capillarity

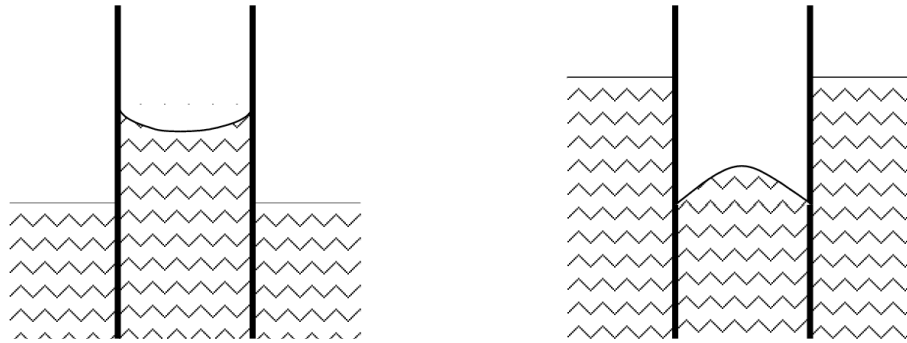


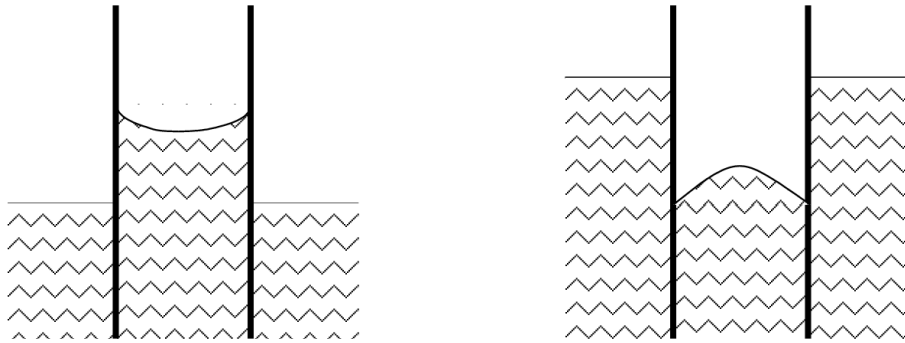
Fig. 3.36. Capillary pressure visualized in a tube whose inner surface is coated with a hydrophilic (left) and hydrophobic (right) layer



- Important driving force in life
  - Water climbs up trees
- Capillary pressure  $p_{\Theta}$ 
  - Surface tension  $\sigma$
  - Scaling with radius  $r$ 
    - Wetted perimeter  $2\pi r$
    - By surface area  $\pi r^2$
    - Pressure

$$p_{\Theta} = \frac{2\sigma}{r} \cos \Theta$$

## 3.6.2. Capillarity



**Fig. 3.36.** Capillary pressure visualized in a tube whose inner surface is coated with a hydrophilic (left) and hydrophobic (right) layer

### Example

- Water:  $\sigma = 72 \times 10^{-3} \text{ N m}^{-1}$
- Perfect wetting:  $\theta = 0$ 
  - $p_{\Theta} = 30 \text{ hPa}$  ( $d = 100 \text{ }\mu\text{m}$ )
  - $p_{\Theta} = 3 \text{ hPa}$  ( $d = 1000 \text{ }\mu\text{m}$ )
- Hydrophobic surface:  $\theta > 90^\circ$ 
  - $\cos \theta < 0 \Rightarrow p_{\Theta} < 0$
- Hydrophilic surface:  $\theta < 90^\circ$ 
  - $\cos \theta > 0 \Rightarrow p_{\Theta} > 0$

$$p_{\Theta} = \frac{2\sigma}{r} \cos \Theta$$

### 3.6.3. Progression of Meniscus

- Model



- Flow in  $z$ -direction

- 2-dimensional case (lateral coord.  $x$ )
- Channel height  $h$
- Quasi-stationary
- Laminar

$$-\frac{\partial p}{\partial z} = -\eta \frac{\partial^2 v}{\partial x^2}$$

- Fluid

- Newtonian, incompressible

- Equation of motion  $z = \int v dt$

$$t = \frac{2\eta l^2}{r_0 \sigma \cos \Theta}$$

- Analytical solution for Stokes equation

- Channel of radius  $r_0$

- Time needed for reaching depth  $l$

$$z(t) = \sqrt{\frac{(r_0 \sigma \cos \Theta) t}{2\eta}}$$

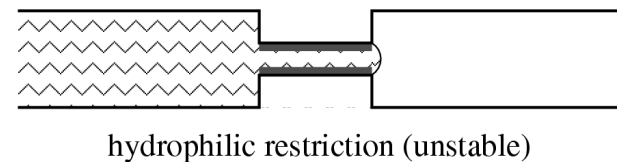
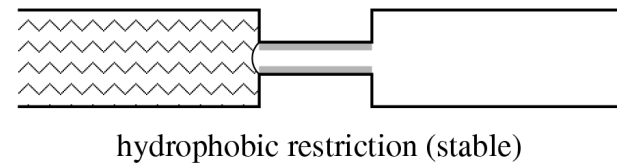
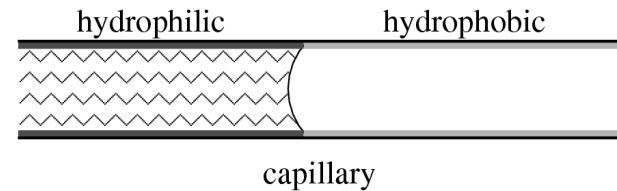
- Depth of penetration  $z$  in channel at time  $t$

- Velocity

$$v(t) = \frac{dz}{dt} = \sqrt{\frac{r_0 \sigma \cos \Theta}{8\eta t}}$$

## 3.6.2. Hydrophobic Barriers

- Capillary pressure
- Geometric constriction
  - Hydrophobic: stable
  - Hydrophilic: unstable
- Pressure barrier
  - Meniscus
- Net pressure by difference of  $p_{\Theta}$  and backward menisci 1 and 2



Round

$$\Delta p_{\Theta} = 2\sigma \cos \Theta \left[ \frac{1}{r_1} - \frac{1}{r_2} \right]$$

Rectangular (widths  $w_i$  and heights  $h_i$ )

$$\Delta p_{\Theta} = 2\sigma \cos \Theta \left[ \left( \frac{1}{w_1} + \frac{1}{h_1} \right) - \left( \frac{1}{w_2} + \frac{1}{h_2} \right) \right]$$

## 3.6.2. Scaling of Surface Tension Force

optional

- Bond number

- Buoyancy
- Surface tension

$$Bo = \frac{g(\rho_{\text{liquid}} - \rho_{\text{gas}})l^2}{\sigma}$$

- Weber number

- Inertia
- Surface tension

$$We = \frac{\rho v^2 l}{\sigma}$$

- Capillary number

- Viscous force
- Surface tension

$$Ca = \frac{We}{Re} = \frac{\eta v}{\sigma}$$

## 3.6. Interfacial Surface Tension

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- 3. Gas Bubbles and Priming Issues**
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## 3.6.3. Gas Bubbles and Priming Issues

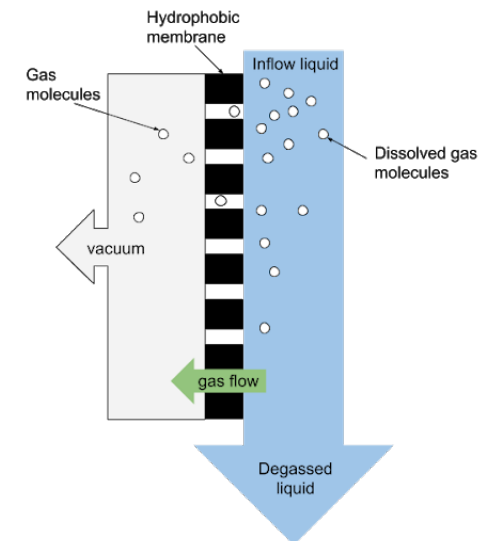
- Priming of microstructures
  - Initially filled with air
  - Filling with liquid by capillary action
- Gas bubbles
  - Cavitation
  - Evaporation
  - Hydrolysis
  - Pockets
  - Capillary pressure in uniform channel radius
    - Compression / expansion
    - No net motion
  - Motion
    - External pressure gradient
    - Frictional „pressure“
      - Frictional constant  $k_{\text{fric}}$



$$\Delta p_{\text{fric}} = \frac{2k_{\text{fric}}}{r_0}$$

## 3.6.3. Bubble-Free Priming

- Principle
  - Dissolution of gas bubbles
  - Solubility of gas in liquid
  - Underpressure
- Methods
  - Priming with ethanol
    - High solubility for gases
    - Gas pockets dissolve
    - Ethanol replaced by liquid of choice
  - Filling with CO<sub>2</sub>
    - Well-dissolvable in liquids
  - Degassing
    - Underpressure  $p$  at gas-permeable membrane in contact with liquid, e.g., PDMS
    - Liquid seeks to establish saturated vapor pressure  $p_{\text{vap}} > p$



## 3.6. Interfacial Surface Tension

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## 3.6.4. Marangoni Effect

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- Surface-tension related phenomenon
- Coupling
  - Fluid motion on surface
  - Internal flows
- Marangoni effect
  - Surface flow induced by gradients in surface tension
  - Mechanisms
    - Thermal gradients
    - Non-uniform evaporation patterns
    - Non-uniform solute concentrations



## 3.6.4. Marangoni Effect: Example

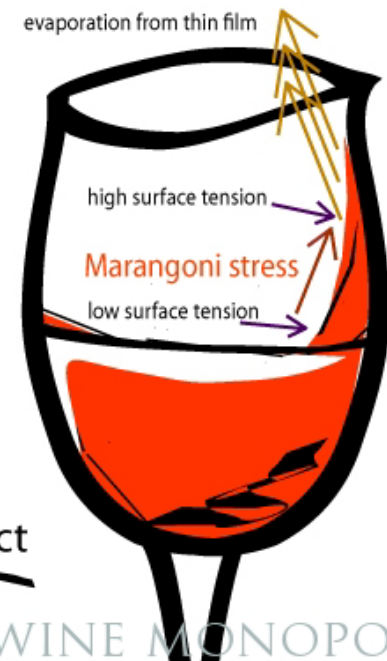
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- Experiment
  - Pour glass of port or spirit
  - Waiting
  - Do not drink so far!
  - Film climbs up wall
  
- Observation
  - Formation of „tears“
    - Swelling
    - “Drops” rolling down from top!



## 3.6.4. Marangoni Effect: Mechanism

- Surface tension decreases with solute (alcohol) concentration
- Volatile solute
  - Fast evaporation of alcohol in water
  - Fast evaporation at edge of in thin film
    - High surface-to-volume ratio
- Lowest solute concentration at upper edge
- Liquid seeks to minimize its surface
  - Droplets
- Tears nucleate on upper edge



The Marangoni Effect

WINE MONOPOLE

## 3.6. Interfacial Surface Tension

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### 3.6.5. Thermocapillary Flow



$$\sigma(T) = k(\tilde{T} - T)^n$$

- Temperature dependence of surface tension  $\sigma(T)$ 
  - Increasing towards colder regions
- Internal pressure
  - Surface tension  $\sigma(T)$
  - Environmental pressure  $p_0$
  - Capillary pressure  $p_\Theta$
  - Geometrical coefficient  $k_{\text{geom}}$

$$p_{\text{int}} = p_0 - \underbrace{\frac{k_{\text{geom}} \sigma}{d}}_{p_\Theta} \cos \Theta$$

- Velocity of flow
  - Poiseuille model

$$\bar{v}_{\text{TCF}} = \frac{dk_{\text{geom}} k'_\sigma \cos \Theta_{\text{rec}}^*}{lk_{\text{shape}} \eta} \cdot \left[ T_{\text{adv}} - T_{\text{rec}} - \left( \frac{k_\sigma}{k'_\sigma} - T_{\text{adv}} \right) \left( 1 - \frac{\cos \Theta_{\text{adv}}^*}{\cos \Theta_{\text{rec}}^*} \right) \right]$$

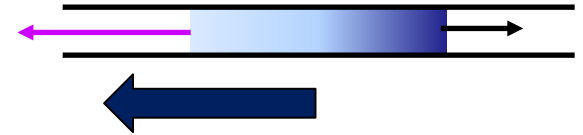
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## 3.6.6. Capillary Control by Surface-Active Agents

- Gradients in surface tension
- **Cohesion energy**



$$\mathcal{W}_{ij} = \sigma_{i,G} + \sigma_{j,G} - \sigma_{ij}$$

- Controlled by properties of **liquid**
- Passive control
  - Addition of fixed and uniform concentration of surfactant
- Active control
  - Spatial and temporal gradients of solute concentration
  - Example
    - Surfactants with redox-active groups
    - Electrochemistry at protruding electrodes
    - Conversion
      - Surface-active states
      - Surface-inactive states

## 3.6. Interfacial Surface Tension

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## 3.6.7. Lotus Effect

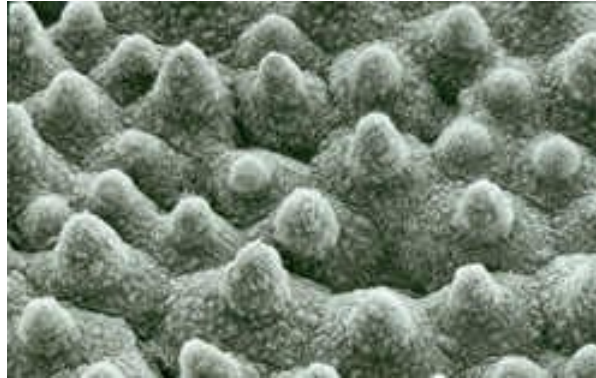
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- Queen of interfacial functionality
- Self-cleaning effect
  - Protection against various kinds of dirt
- Plants
  - Lotus
    - Symbol of purity
    - Holy flower in Asian cultures
  - Cabbage
  - Reed
  - Tulips
- Animals
  - Dragonflies (wings)
  - Butterflies (wings)



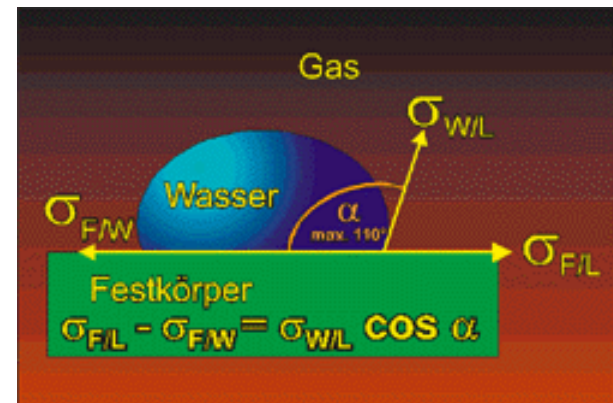
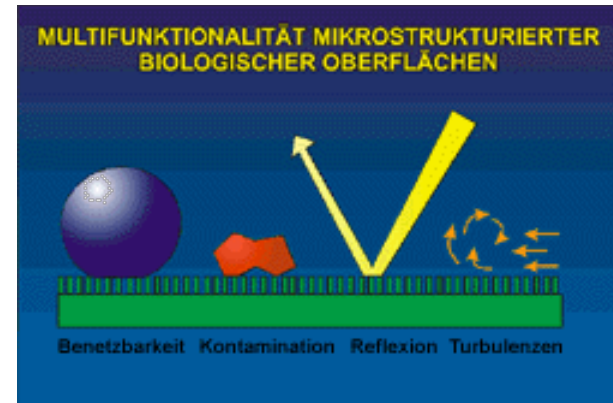
## 3.6.7. Lotus Effect

- Coating of leafs
  - Wax (lipids)
  - Self-regenerating
- Leafs
  - Hard to make wet
  - Repelling dirt, even
    - Soot
    - Honey
    - Glue
  - Interplay
    - Chemistry
    - Microtexture
    - Interfacial energy



## 3.6.7. Lotus Effect: Protective: Layer

- „Engineered“ by evolution
- Multifunctional
  - Wetting
  - Dirt
  - Reflection (optical / thermal)
  - Turbulences
- Protection against
  - Inorganic contaminants
    - Enhanced heat transfer
    - Acidity
    - Blocking pores
  - Biological enemies
    - Fungi
    - Bacteria
    - Algae
- Principles
  - Washing off during rain
  - Microorganism die by drying out



## 3.6.7. Superhydrophobicity

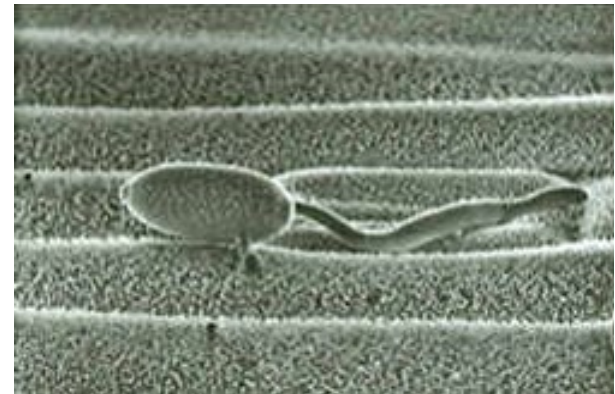
- High interfacial energy
  - Enhanced wetting
- Low interfacial energy
  - Reduced wetting
  - E.g., Teflon
- Interfacial energy
  - Product
    - Energy density
    - Surface area
  - Rough surface
    - Large effective contact area
- Rough hydrophilic surface
  - Enhanced wetting
- Very rough hydrophobic surface
  - Super-hydrophobicity



## 3.6.7. Dirt Removal

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- Hydrophilic dirt
  - Absorbed in rainwater
  - Carried away by „rolling“ droplet
- Hydrophobic dirt
  - Contact at very tips of wax crystals
  - Small overall contact area
  - Small overall interfacial energy
  - Attachment to surface of droplets
  - Homogeneous distribution



# Self-Cleaning Superhydrophobic Surface

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Courtesy of Dr. Charles Nwankire

## 3.6.7. Technical Implementation

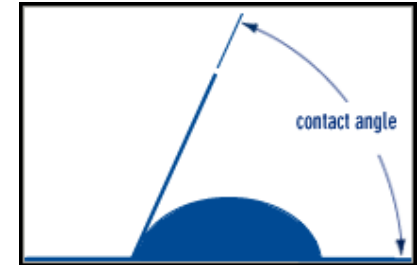
- Lotus effect
  - Mere physico-chemical mechanism
  - No traits specific to living organism
- Implementation
  - Materials available for some time
  - Potential „overlooked“
  - Bionics
  - Ultraphobic surfaces
    - Hydrophobic
    - Oleophobic (repelling oil)
  - Coatings
    - Roofs
    - Facades
    - Textiles
    - Paint industry



# Summary

Contact angle & wetting

$$F_{SL} + F_{LV} \cos \Theta + F_{SV} = 0$$



Capillary pressure

$$p_{\Theta} = \frac{2\sigma}{r} \cos \Theta$$

Capillary priming

$$t = \frac{2\eta l^2}{r_0 \sigma \cos \Theta}$$

$$z(t) = \sqrt{\frac{(r_0 \sigma \cos \Theta) t}{2\eta}}$$

$$v(t) = \frac{dz}{dt} = \sqrt{\frac{r_0 \sigma \cos \Theta}{8\eta t}}$$

