Syllabus

1. Introduction

2. Fluids

1. General Characteristics
2. Dispersions
3. Thermodynamics
4. Transport Phenomena
5. Solutions
6. **Surface Tension**
7. Electrical Properties
8. Optical Properties
9. Biological Fluids

Physics of Microfluidic Systems

1. Navier-Stokes Equation
2. Laminar and Turbulent Flow
3. Fluid Dynamics
4. Fluid Networks
5. Transport of Heat
6. Interfacial Surface Tension
7. Electrokinetics

2.6. Surface Tension

- One of most important phenomena in nature
  - Especially in nature & biology
    - Water climbing up trees
    - Shape of raindrops
  - Phenomenon microscopically relates to
    - Energy required to **transport molecule** from **bulk** to **surface** region
- Important effect for liquids, especially towards **microworld**
  - Volumes decrease
  - Surface-to-volume ratios grow
  - Surface forces prevail over volume forces
  - Decisive influence on shape of liquid volumes
- Surface tension also present in solids and gases
  - Surface tension forces negligible compared to strong bulk forces
  - Gas volumes always adapt surface to shape of container wall

2.6. Surface Tension

2.6.1. Basic Experiments

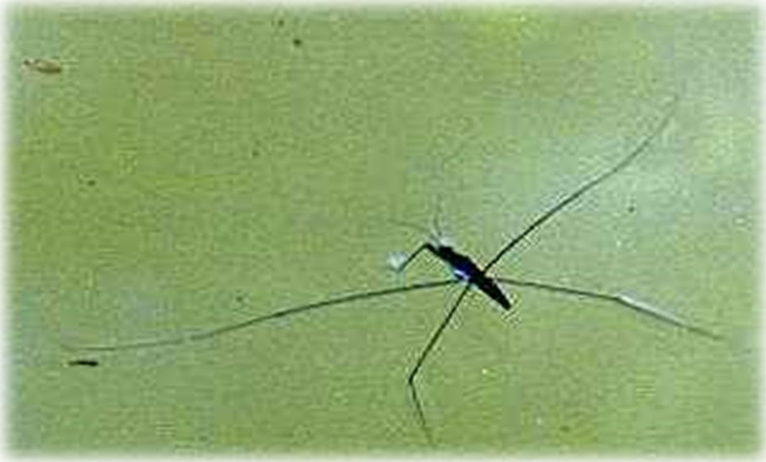
2.6.2. Molecular Picture of Surface Tension

2.6.3. Pressure Drop at Bent Surfaces

2.6.4. Droplet Formation

2.6.5. Solute Concentration

2.6.6. Surfactants



2.6.1. Basic Experiments

- Measurement
  - Liquid membrane enclosed in rectangular frame of wire
  - Movable wire on one side

$$\boxed{\sigma = \frac{\boxed{F_\sigma}}{\boxed{l}}}$$

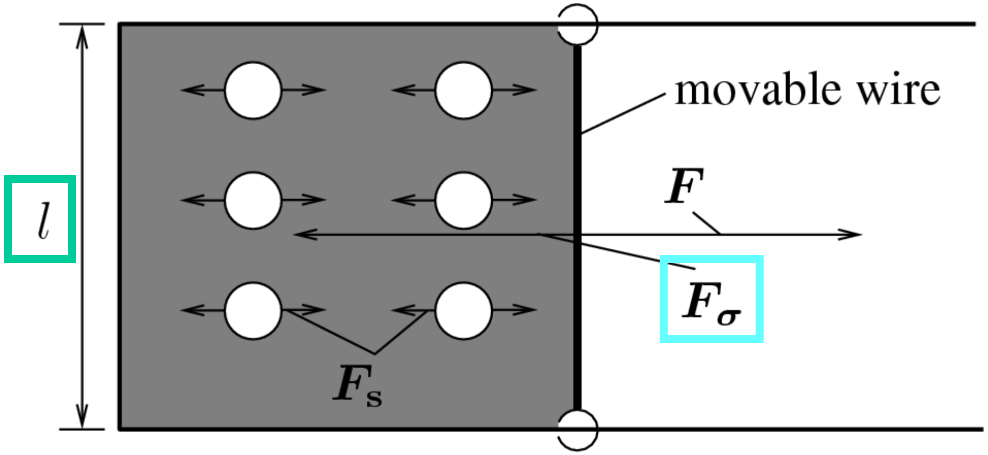


Fig. 0.1. Surface tension σ can be measured by pulling a liquid membrane by a movable wire of edge length l with the force $\boldsymbol{F}$ which counteracts the overall forces due to surface tension $\boldsymbol{F_\sigma} = \sum \boldsymbol{F_\mathrm{s}}$.

2.6.1. Basic experiments

- Force F applied to wire of length l
- Intermolecular forces F_s
  - Directed tangentially to surface, i.e., in plane of membrane
- F_σ cumulative sum of F_s

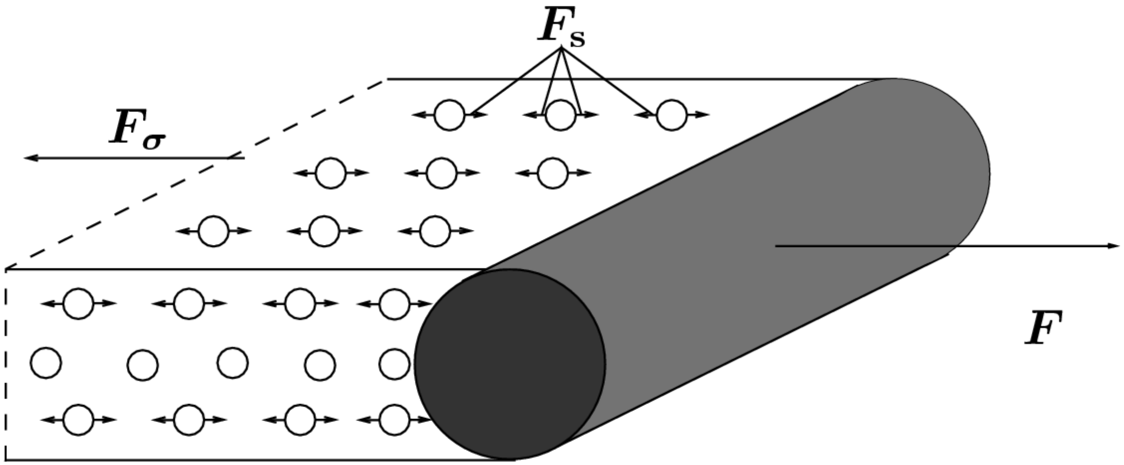
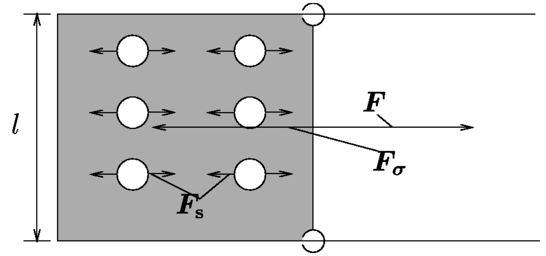


Fig. 0.1. Cross-section of surface tension forces in a liquid membrane. An overall contractive force $\boldsymbol{F_\sigma}$ composed of individual intermolecular forces $\boldsymbol{F_\mathrm{s}}$ at the two surfaces of the membrane has to be neutralized by the external force $\boldsymbol{F}$ in order to stabilize the wire.

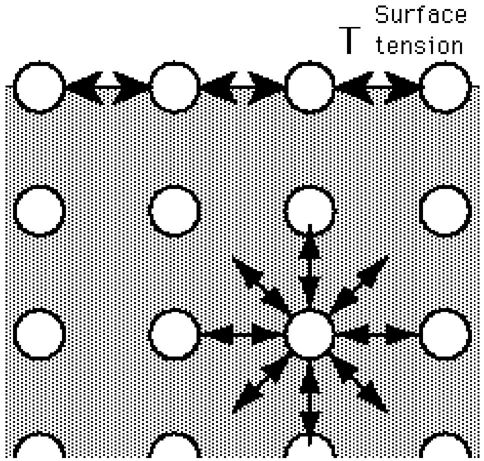
2.6.1 Definition of Surface Tension

- Definition

$$\boxed{\sigma = \frac{F_\sigma}{l}}$$



  - ➢ Quotient of **force** over **length**



- Term „tension“ bad choice
  - ➢ Commonly referred to as force per **area**
- More physical definition of surface tension
  - ➢ Product of **tension times length**
  - ➢ Scaling with
    - Surface density of (surface) force (tension) $\boldsymbol{F_s}/A$
    - Perimeter of contact region l

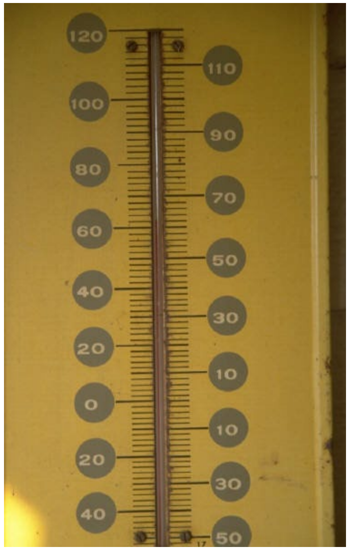
2.6.1 Temperature Dependence

optional

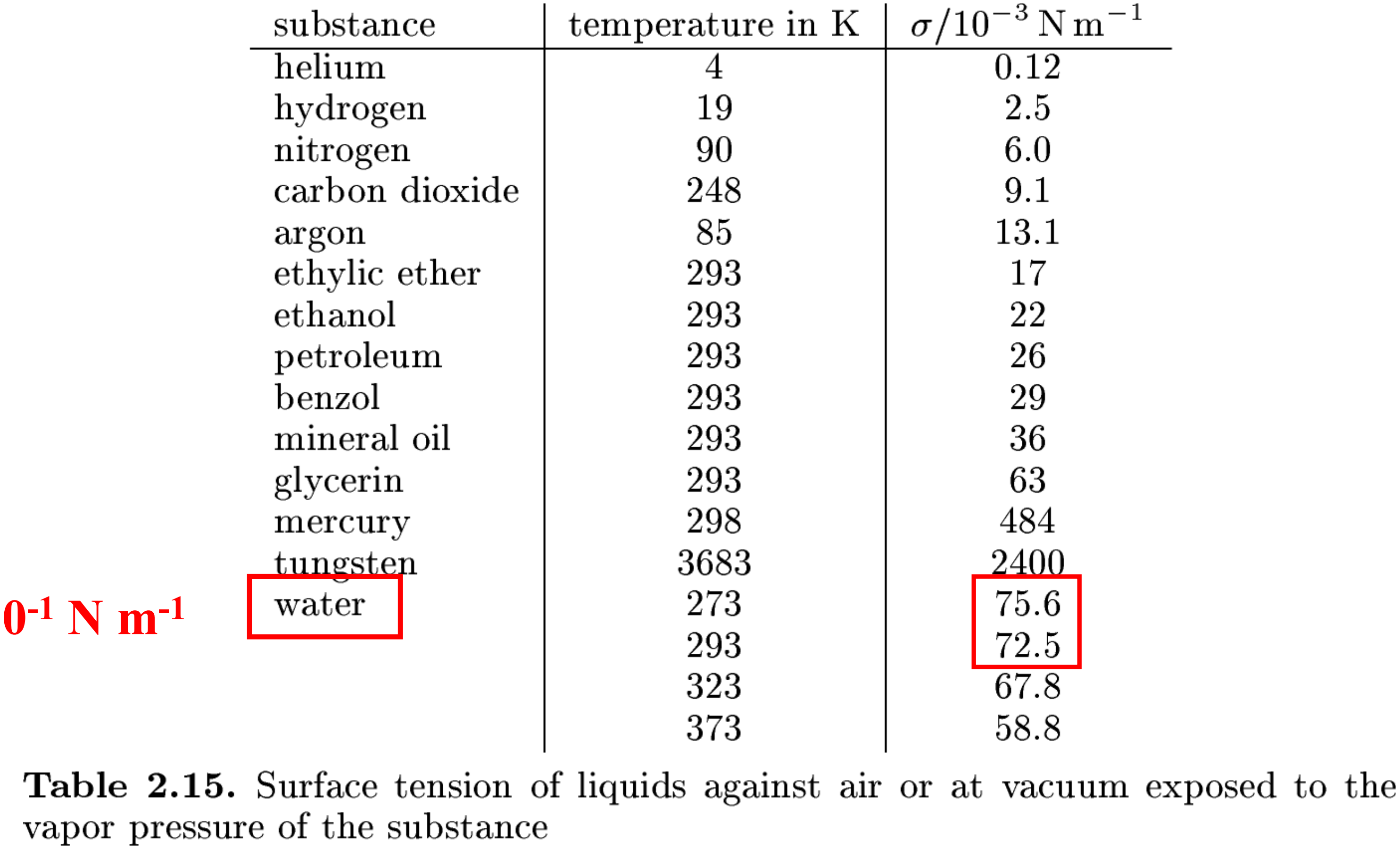
- Surface tension decreases with temperature
  - Empirical formula

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

  - $n \sim 2$
  - Surface tension strongly decreases with T
    - Phenomenon related to coexistence of two phases
    - Two phases „merge“ towards increasing T
  - $\tilde{T}$ lies about 6 K below critical temperature T^*
    - e.g., $T^* = 647.4\ \mathrm{K}$ for H_2O



2.6. Surface Tension



substance	temperature in K	$\sigma/10^{-3}\,\mathrm{N\,m^{-1}}$
helium	4	0.12
hydrogen	19	2.5
nitrogen	90	6.0
carbon dioxide	248	9.1
argon	85	13.1
ethylic ether	293	17
ethanol	293	22
petroleum	293	26
benzol	293	29
mineral oil	293	36
glycerin	293	63
mercury	298	484
tungsten	3683	2400
water	273	75.6
	293	72.5
	323	67.8
	373	58.8

Table 2.15. Surface tension of liquids against air or at vacuum exposed to the vapor pressure of the substance

$\sim 10^{-1}\,\mathrm{N\,m^{-1}}$

2.6. Surface Tension

2.6.1. Basic Experiments

2.6.2. Molecular Picture of Surface Tension

2.6.3. Pressure Drop at Bent Surfaces

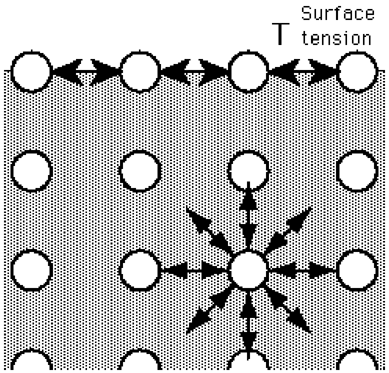
2.6.4. Droplet Formation

2.6.5. Solute Concentration

2.6.6. Surfactants

2.6.2. Molecular Picture of Surface Tension

optional



- Thermodynamic Model
  - Thermal motion of molecules: $E_{\mathrm{kin}} = 0.5\, m\, v^2$
- Dynamic exchange
  - Energetic particles leave surface layers
  - Molecules from gaseous phase rejoin liquid
  - Traversing potential resulting from attractive intermolecular forces
  - Potential tries to keep molecules from leaving liquid phase
  - Equilibrium
    - Saturated (partial) vapor pressure reached
- Maxwell-Boltzmann distributions
  - Statistical fraction (“high-end tail”) of molecules escaping liquid phase

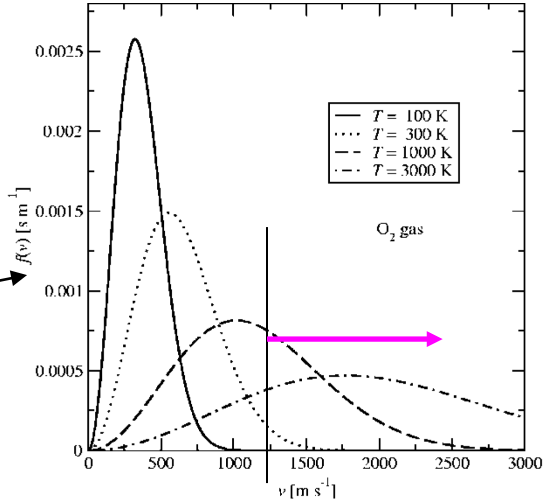
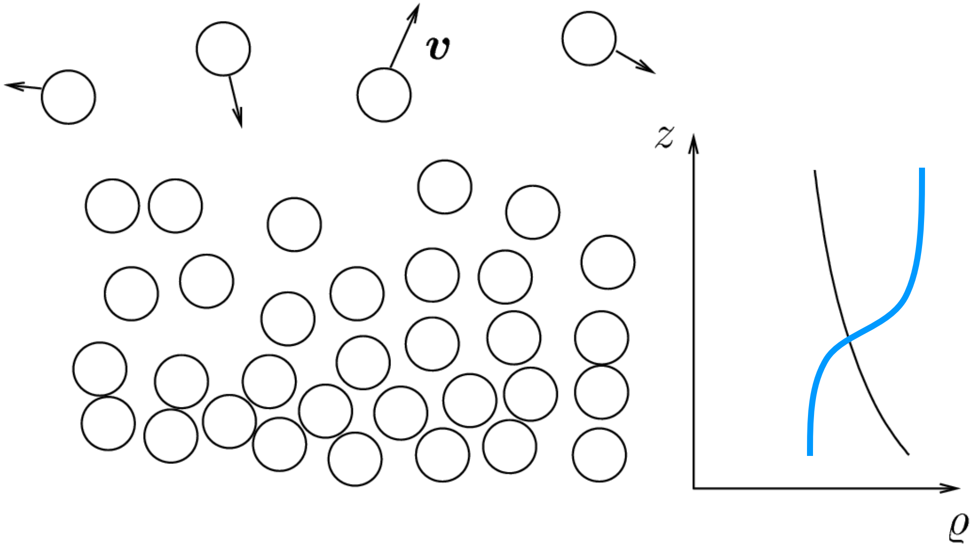


Fig. 2.12. Maxwellian function $f(v)$ for O_2 gas at different temperatures

2.6.2. Molecular Picture of Surface Tension

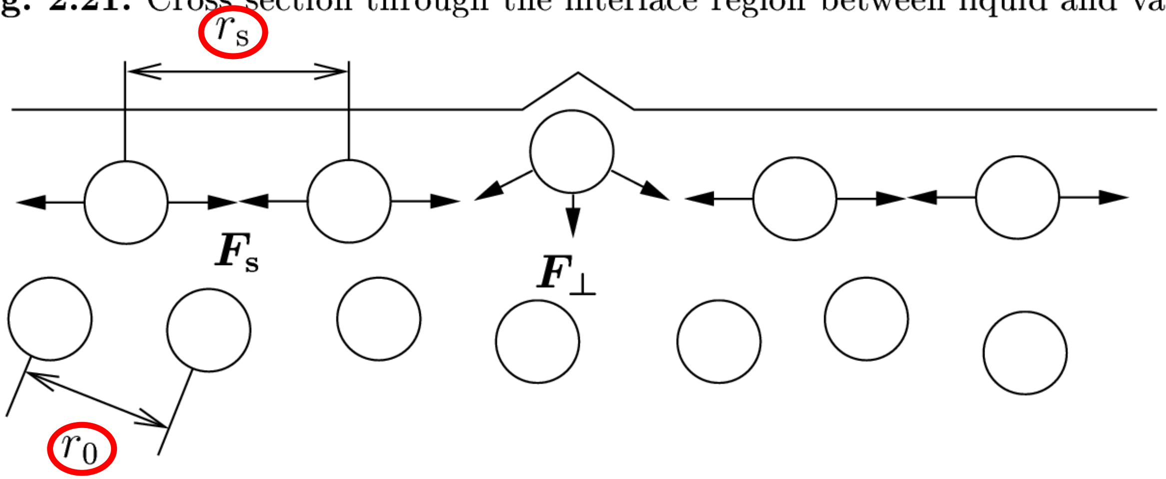
optional



Density distribution

Surface Potential

Fig. 2.21. Cross section through the interface region between liquid and vapor



Surface forces

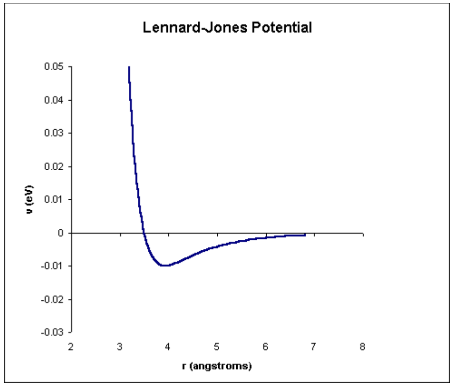
Fig. 2.22. Force $F_\perp$ on molecule moved perpendicular to surface plane results from perpendicular components $F_\perp$ of forces F_s acting in surface plane

2.6.2. Molecular Picture of Surface Tension

optional

- Lennard-Jones Model
  - ➢ Experimental values well approximated starting out with LJ Ansatz

$$V_{\mathrm{LJ}} = b\left[\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r}\right)^{6}\right]$$



  - ➢ Intermolecular potential
  - ➢ Parameters for spatial extension and potential energy a and b, respectively

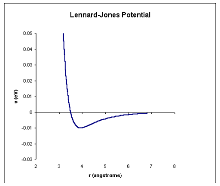
$$\boxed{\sigma = \frac{F_\sigma}{l} =- \frac{F_\mathrm{s}}{r_\mathrm{s}} = \frac{1}{r_\mathrm{s}}\left(\frac{\mathrm{d}V_{\mathrm{LJ}}}{\mathrm{d}r}\right)_{r=r_\mathrm{s}} = \frac{b}{r_\mathrm{s}}\left[-\frac{12a^{12}}{r^{13}} + \frac{6a^{6}}{r^{7}}\right]_{r=r_\mathrm{s}}}$$

  - ➢ Equilibrium distance r_0
  - ➢ Mean intermolecular distance at surface r_s
  - ➢ Lennard-Jones force F_S
  - ➢ Setting $a = r_0 / 2^{1/6}$ and $b = V_{\mathrm{LJ}}(r_0)$

2.6.2. Molecular Picture of Surface Tension

Lennard-Jones potential

$$\sigma = \frac{F_\sigma}{l} =- \frac{F_s}{r_s} = \frac{1}{r_s}\left(\frac{\mathrm{d}V_{\mathrm{LJ}}}{\mathrm{d}r}\right)_{r=r_s} = \frac{b}{r_s}\left[-\frac{12a^{12}}{r^{13}} + \frac{6a^6}{r^7}\right]_{r=r_s}$$



- By assuming $r_s = 1.1\, r_0$

$$\sigma = \frac{b}{1.1 r_0^2}\left[-\frac{12}{4 \cdot 1.1^{13}} + \frac{6}{2 \cdot 1.1^7}\right] = 0.67\,\frac{\boxed{b}}{1.1\boxed{r_0^2}}$$

Water:

- $b = 2 \times 10^{-21}$ J
- $r_0 = 3 \times 10^{-10}$ m

⇒ $\sigma_{\mathrm{LJ}} = \mathbf{13.5\ mN\ m^{-1}}$

⇒ $\sigma_{\exp} = \mathbf{72.5\ mN\ m^{-1}}$

same order of magnitude

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2.6.3. Pressure Drop at Bent Surfaces

2.6.4. Droplet Formation

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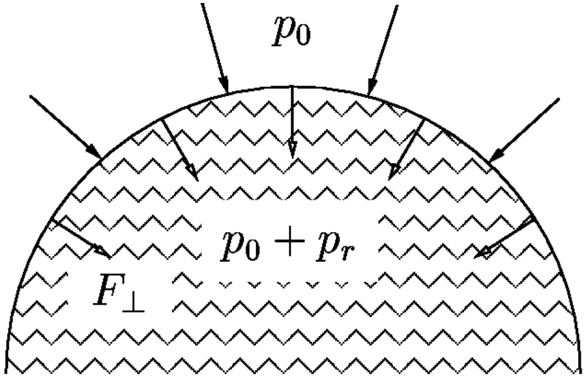
2.6.6. Surfactants

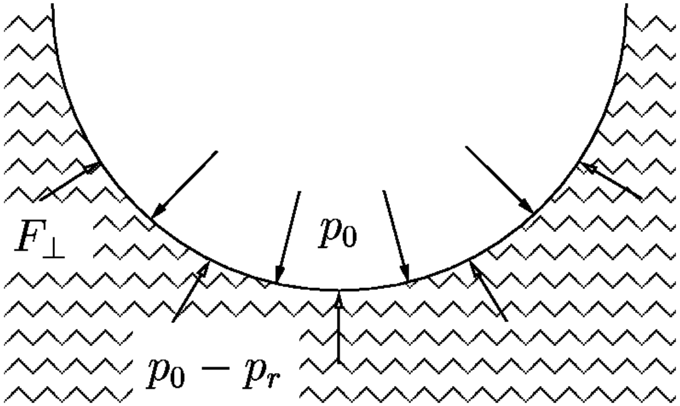
2.6.3. Pressure Drop at Bent Surfaces

- Definition

$$\boxed{p_r = \frac{F_\perp}{A}}$$



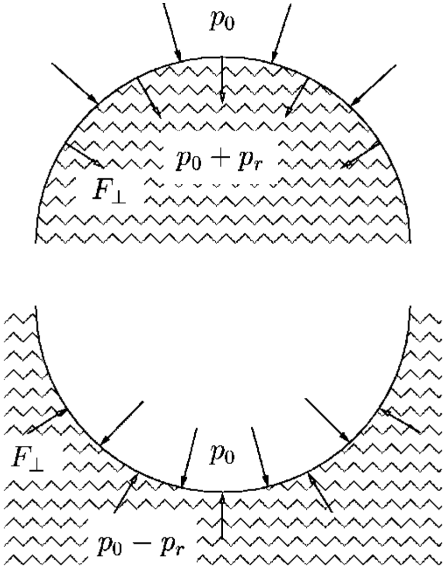
- Convex surface
  - $F_\perp$ points towards center
  - Adds to internal pressure



- Concave surface
  - $F_\perp$ pointing away from center
  - Reduced internal pressure

2.6.3. Pressure Drop at Bent Surfaces

optional



- Energy to „build“ surface
  - Surface element *A* spanned by two perpendicular lines of lengths $\delta l_i = r_i \phi_i$
  - r_i bending radius
  - ϕ_i angle enclosed by lines

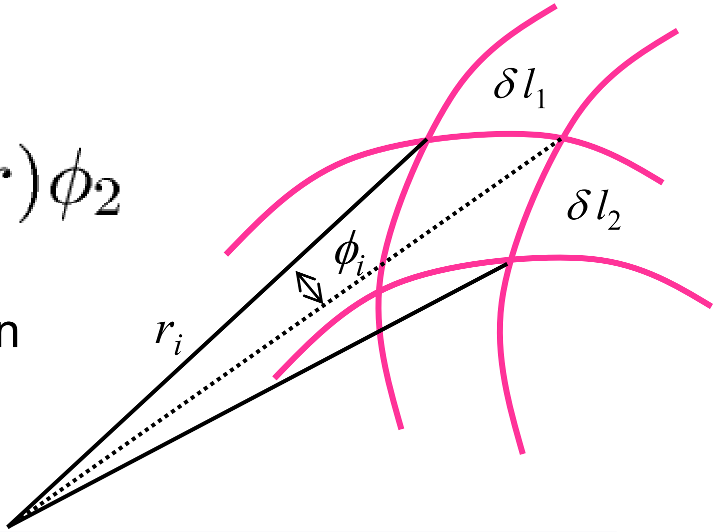
$$A = \delta l_1 \times \delta l_2$$

  - Shift $\Delta r << r_i$ enforced by $F_\perp$

$$A + \Delta A = (r_1 + \Delta r)\phi_1 (r_2 + \Delta r)\phi_2$$

  - **Overall expansion** in linear approximation

$$\Delta A \simeq (r_1 + r_2)\phi_1 \phi_2 \Delta r$$



2.6.3. Pressure Drop at Bent Surfaces

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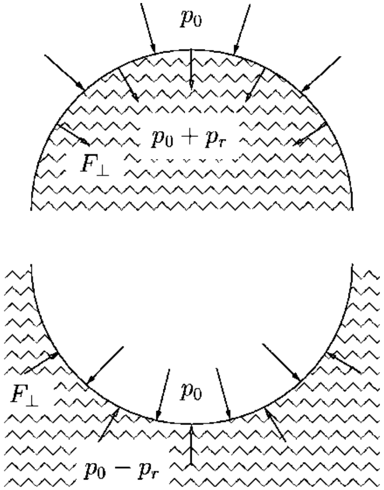

- Energy required for expansion

$$\Delta E = \sigma \Delta A = F_\perp \Delta r$$

  - Resulting **bending pressure**

$$\Delta A \simeq (r_1 + r_2)\phi_1\phi_2\Delta r$$

$$p_r = \frac{F_\perp}{A} = \frac{\Delta E}{A\Delta r} = \frac{\sigma\Delta A}{A\Delta r} \simeq \frac{\sigma(r_1 + r_2)\phi_1\phi_1}{r_1\phi_1 r_2\phi_2} = \sigma\frac{r_1 + r_2}{r_1 r_2}$$

$$\boxed{p_r = \boxed{\sigma}\left(\boxed{\frac{1}{r_1} + \frac{1}{r_2}}\right)}$$

2.6.3. Pressure Drop at Bent Surfaces

- For **cylindrical** surface with cylinder radius r_0

$$p_r = \frac{\sigma}{r_0}$$

- For **sphere**

$$p_r = \frac{2\boxed{\sigma}}{\boxed{r_0}}$$

  - p_r may be large in microworld
    - Sphere of water with $r_0 = \mathbf{10\ \mu m}$ and σ approx. $100\ \mathrm{mN\ m^{-1}}$

    $\Rightarrow p_r = 96800\ \mathrm{hPa} \sim$ **100 bar** !!!

- **Elevated vapor pressure** at convex surface with radius r
  - Consequence of bending pressure

$$\boxed{p_{\mathrm{vap}} = p_{\mathrm{vap},\infty} \mathrm{e}^{\frac{2m\sigma}{k_\mathrm{B} T \varrho r}}}$$

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2.6.4. Droplet Formation

- Surface tension from **energetic** point of view
- Liquid **spends energy** to move **bulk** molecule to **surface**
  - Analogy to rubber balloon
  - Enlarging surface of liquid volume affords energy
  - Energy released by shrinking of surface

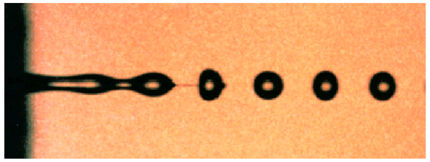

Fig. 8.1. Rayleigh instability in a liquid jet issued by a continuous inkjet printer at 10 kHz. The orifice diameter and the initial jet measures 50 µm, after the break off the droplets possess about twice the diameter of the orifice

- Formation of droplets from liquid jet
  - 19th century: Lord Rayleigh
  - Cylinder-like jet shape not stable
  - Liquid volumes ("droplet") tend to assume spherical shape
- Size of droplets
  - Dimensions and geometry of orifice
  - Perturbations
- Continuous ink-jet technology
  - Controlled external perturbations adapted to nozzle geometry

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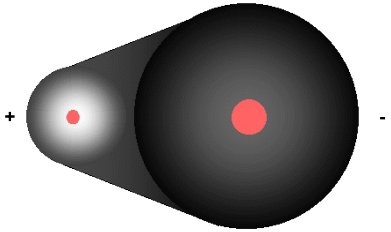
2.6.5. Solute Concentration

- Strongly **heteropolar** molecules in **polar solvents** like water
  - Dissociation into H^+ ions and negatively charged ions
    - E.g., Cl^-, SO_4^{2-} and CO_3^{2-}
  - Tend to **stay** within liquid **bulk** away from surface
  - **Surface tension increases**
    - Additional attraction of water molecules on surface



- **Homopolar** substances like ethanol or stearic acid
  - Hydrophobic nature
  - Dissolving in nonpolar solvents
  - **Escaping** to **surface** in aqueous solutions
  - **Decrease** in **surface tension**

2.6.5. Solute Concentration

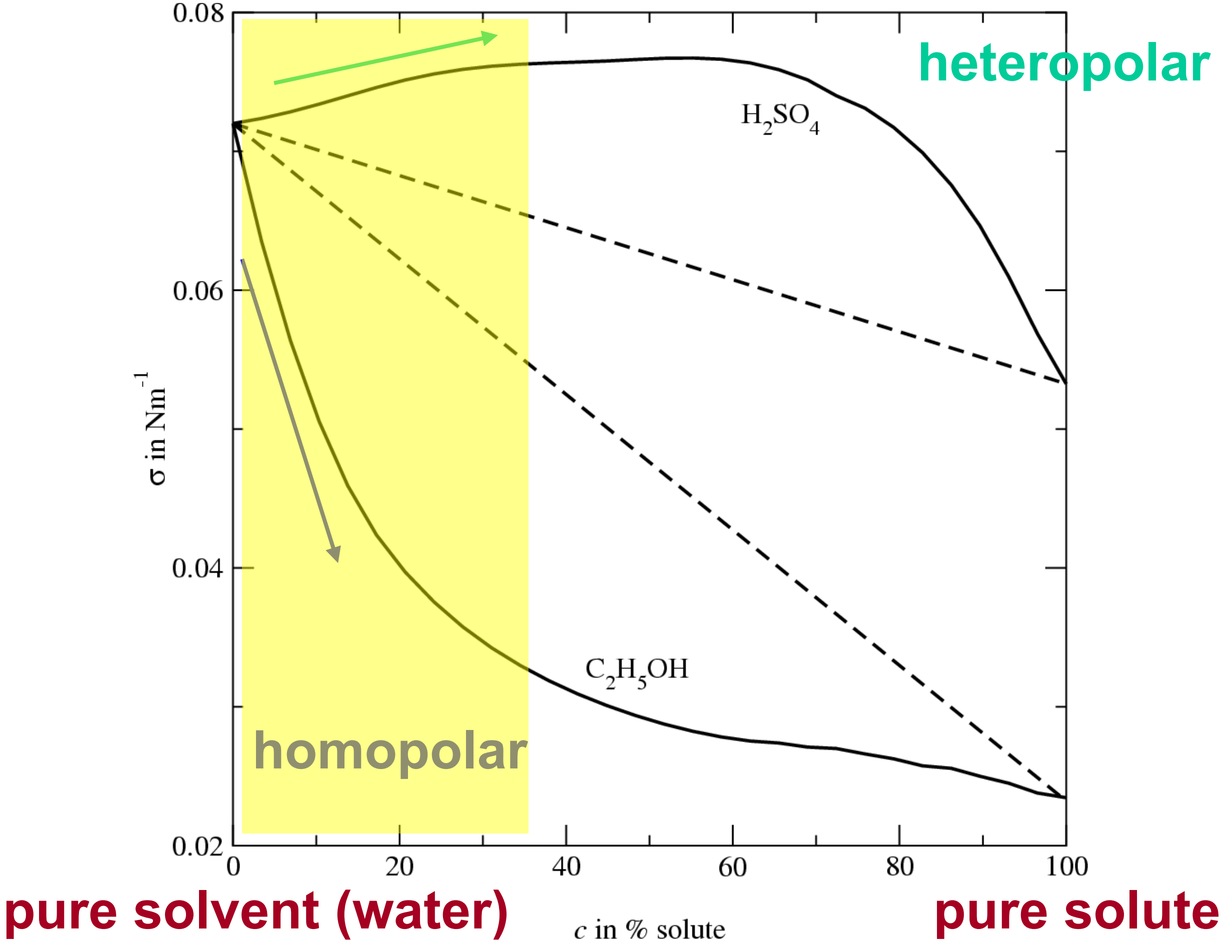


Fig. 2.24. Surface tension of water as a nonlinear function of solute concentration . In the region of low (relative) solvent concentration c, the surface tension of heteropolar sulphuric acid H_2SO_4 increases with c while the reverse trend is observed for homopolar ethanol C_2H_5OH

2.6. Surface Tension

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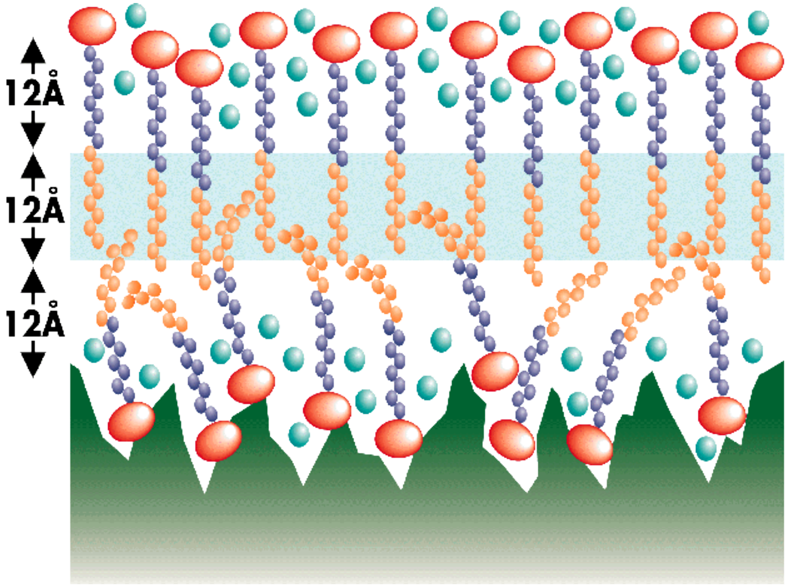


2.6.6. Surfactants

- Surface-active agents (also: tensides)
- Surfactant **lowers surface tension** of liquid
- Promoting **wetting**
- Small concentrations of surfactants
  - May alter surface tension dramatically
  - By typical factor 3!
- Classes of surface-active agents
- Soaps
  - Water-dispersible salts of fatty acid
  - At least eight carbon atoms
  - Commonly used for cleaning
- Detergents
  - Cleaning properties in dilute solutions
  - Commercial detergents
    - Formulations containing number of chemical components besides surfactants
  - Synthetic substance

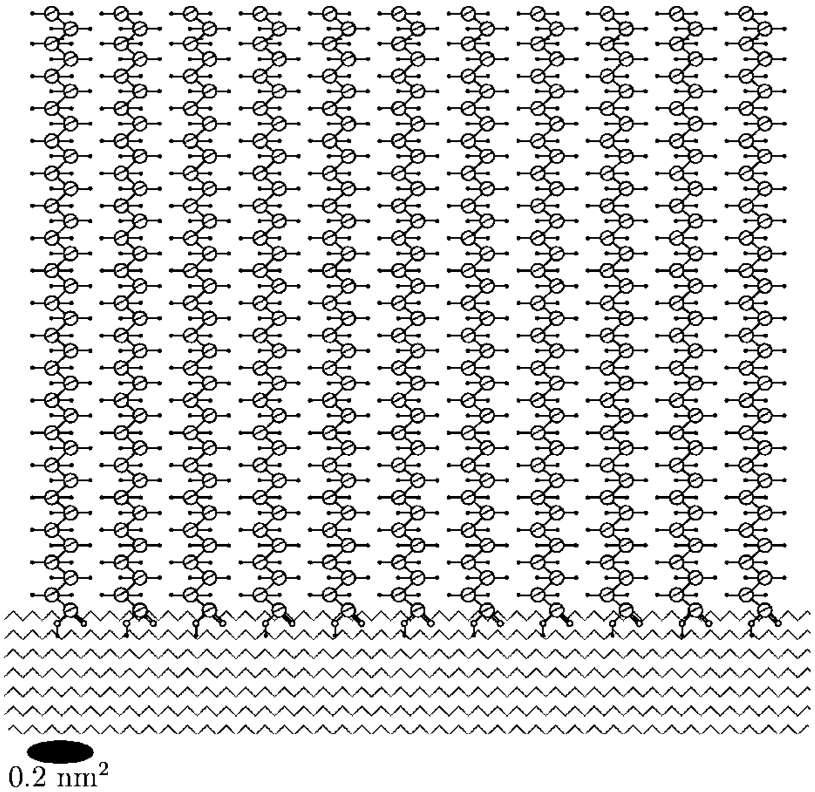
2.6.6. Surfactants

- Micelles
  - Aggregates of surfactant molecules
  - Forming spontaneously at or above surfactant concentration called **critical micelle concentration**

- Surface tension
  - Varies with surfactant **concentration** in **nonlinear** fashion
  - Binding energy regulates mixing or separation

- Segregation of solute at surface may be influenced by
  - **Space requirement** of solute molecules and hydrophilic (polar) or hydrophobic (non-polar) nature of molecular ends
  - Amphiphilic monolayers

2.6.6 Amphiphilic Monolayers



- Alignment of amphiphilic monolayer on water surface
  - Sufficient concentration
  - n-hexatriacontan acid orients its hydrophobic carbohydrate chains away from surface
  - Configuration stabilized by hydrogen bonding between adjacent C-H chains
  - Hydrophilic polar end penetrates into water
  - Surface area covered by one molecule about 0.2 nm²

Summary

Surface tension:

$$\boxed{\sigma = \frac{F_\sigma}{l}}$$

Bending pressure:

$$\boxed{p_r = \frac{F_\perp}{A}}$$

For sphere:

$$p_r = \frac{2\boxed{\sigma}}{\boxed{r_0}}$$