## Contents

1. Introduction
2. **Fluids**
3. Physics of Microfluidic Systems
4. Microfabrication Technologies
5. Flow Control
6. Micropumps
7. Sensors
8. Ink-Jet Technology
9. Liquid Handling
10. Microarrays
11. Microreactors
12. Analytical Chips
13. Particle-Laden Fluids
   a. Measurement Techniques
   b. Fundamentals of Biotechnology
   c. High-Throughput Screening
2. Fluids

2.1. General Characteristics
2.2. Dispersions
2.3. Thermodynamics
2.4. Transport Phenomena
2.5. Solutions
2.6. Surface Tension
2.7. Electrical Properties
2.8. Optical Properties
2.9. Biological Fluids
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 in 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

\[ \sigma = \frac{F_\sigma}{l} \]

*Fig. 0.1.* Surface tension \( \sigma \) can be measured by pulling a liquid membrane by a movable wire of edge length \( l \) with the force \( F \) which counteracts the overall forces due to surface tension \( F_\sigma = \sum F_s \).
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
- $F_\sigma$ cumulative sum of $F_s$

Fig. 0.1. Cross-section of surface tension forces in a liquid membrane. An overall contractive force $F_\sigma$ composed of individual intermolecular forces $F_s$ at the two surfaces of the membrane has to be neutralized by the external force $F$ in order to stabilize the wire.
2.6.1 Definition of Surface Tension

• Definition

\[ \sigma = \frac{F_{\sigma}}{l} \]

- 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) \( F_s / A \)
    - Perimeter of contact region \( l \)
2.6.1 Temperature Dependence

- Surface tension decreases with temperature
  - Empirical formula: $\sigma(T) = k(\tilde{T} - T)^n$
  - $n \sim 2$
  - 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. $T^* = 647.4$ K for $\text{H}_2\text{O}$
## 2.6. Surface Tension

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

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

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

- Thermodynamic Model
  - Thermal motion of molecules: $E_{\text{kin}} = 0.5 m v^2$

- 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 distribution
  - Statistical fraction 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

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

**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

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

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

➢ Intermolecular potential
➢ Parameters for spatial extension and potential energy \( a \) and \( b \), respectively

\[
\sigma = \frac{F_{\sigma}}{l} = \frac{F_{S}}{r_{s}} = \frac{1}{r_{s}} \left( \frac{dV_{\text{LJ}}}{dr} \right)_{r=r_{s}} = \frac{b}{r_{s}} \left[ -\frac{12a^{12}}{r^{13}} + \frac{6a^{6}}{r^{7}} \right]_{r=r_{s}}
\]

➢ Equilibrium distance \( r_{0} \)
➢ Mean intermolecular distance at surface \( r_{s} \)
➢ Lennard-Jones force \( F_{S} \)
➢ Setting \( a = r_{0} / 2^{1/6} \) and \( b = V_{\text{LJ}}(r_{0}) \)

Lennard-Jones Potential

Microfluidics - Jens Ducrée  Fluids: Surface Tension 13
2.6.2. Molecular Picture of Surface Tension

\[ \sigma = \frac{F_\sigma}{l} = -\frac{F_s}{r_s} = \frac{1}{r_s} \left( \frac{dV_{LJ}}{dr} \right) \bigg|_{r=r_s} = \frac{b}{r_s} \left[ -\frac{12a^{12}}{r^{13}} + \frac{6a^6}{r^7} \right] \bigg|_{r=r_s} \]

⇒ By assuming \( r_s = 1.1 \ r_0 \)

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

**Water:**
- \( b = 2 \times 10^{-21} \ \text{J} \)
- \( r_0 = 3 \times 10^{-10} \ \text{m} \)
⇒ \( \sigma_{\text{LJ}} = 13.5 \ \text{mN m}^{-1} \) same order
⇒ \( \sigma_{\text{exp}} = 72.5 \ \text{mN m}^{-1} \) of magnitude
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
2.6.3. Pressure Drop at Bent Surfaces

• Pressure drop at bent surfaces
  ➢ Definition
  \[ p_r = \frac{F_\perp}{A} \]

• 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

- 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
  - $\phi_i$ angle enclosed by lines
  $$ A = \delta l_1 \times \delta l_2 $$

- Shift $\Delta r \ll r_i$ 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

- Energy required for expansion

\[ \Delta E = \sigma \Delta A = F_\perp \Delta r \]

- Resulting bending pressure

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

\[ p_r = \frac{F_\perp}{A} = \frac{\Delta E}{A \Delta r} = \frac{\sigma \Delta A}{A \Delta r} \simeq \frac{\sigma (r_1 + r_2) \phi_1 \phi_1}{r_1 \phi_1 r_2 \phi_2} = \sigma \frac{r_1 + r_2}{r_1 r_2} \]
2.6.3. Pressure Drop at Bent Surfaces

- For **cylindrical** surface with cylinder radius $r_0$
  \[ p_r = \frac{\sigma}{r_0} \]

- For **sphere**
  \[ p_r = \frac{2\sigma}{r_0} \]

- $p_r$ can be large in microworld
  - Sphere of water with $r_0 = 10 \text{ µm}$ and $\sigma$ approx. $100 \text{ mN m}^{-1}$
  - $p_r = 96800 \text{ hPa} \sim 2 \text{ bar} !!!$

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

\[ p_{vap} = p_{vap,\infty} e^{\frac{2m\sigma}{k_B T \varphi r}} \]
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
2.6.4. Droplet Formation

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

![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.](image)
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
2.6.5. 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 $\text{H}_2\text{SO}_4$ increases with $c$ while the reverse trend is observed for homopolar ethanol $\text{C}_2\text{H}_5\text{OH}$.
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
2.6.6. Surfactants

- **Surfactants**
  - Also tensides
  - Surface-active agents
  - 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

Diagram: 0.2 nm²