

Molecular Biophysics

2013/2014, lecturer: Martin Zápotocký

4 lectures:

1. Molecular interactions, states of matter, Gibbs rule of phases, properties of ideal gas
2. Transport phenomena, fluid mechanics
3. Classification of dispersion systems, properties of solutions
4. Other analytical dispersions; properties of colloids

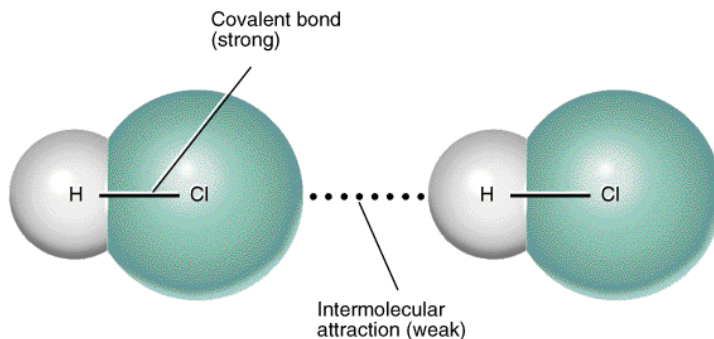
Warning: figures and equations
drawn on the blackboard are not
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Lecture 1

Molecular interactions

Intra-molecular and inter-molecular interactions

- Distinguish interactions **within molecules** (e.g. covalent or ionic bonds) vs. interactions **between molecules**

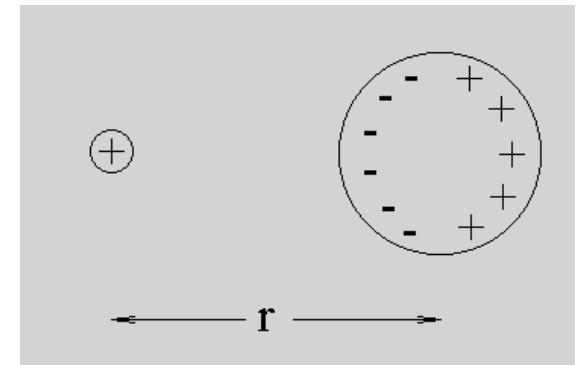
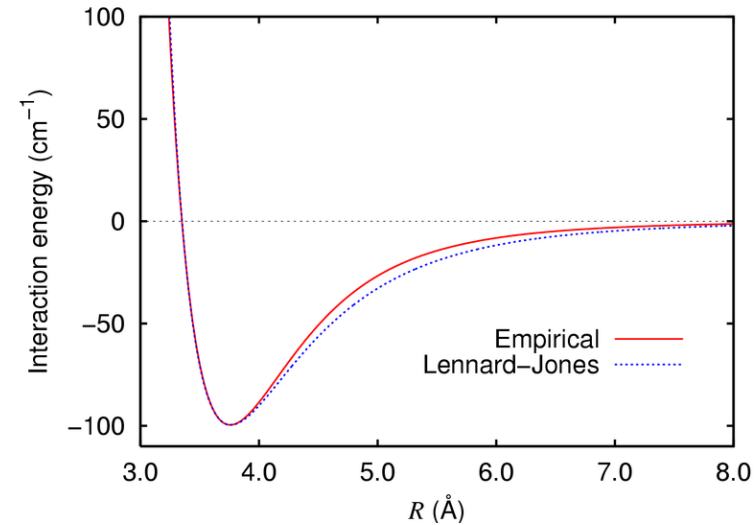


- Intra-molecular interactions determine the structure of molecules; **inter-molecular interactions determine the phase of matter** (gas, liquid, solid, ...)

- Inter-molecular interactions are weaker than intra-molecular
- Bond energy: energy required to move the constituents very far from each other
- **Intra-molecular bond energies** (for 1 mole of molecules): typically 100 – 400 kJ/mol
- Typical **inter-molecular interaction strength**: up to several kJ/mol
- **Hydrogen bonds**: 10 – 45 kJ/mol

Types of inter-molecular forces

- Short-range repulsion + long-range attraction
- The long-range part is non-covalent, and is due to electrostatic interactions. **Strongest between two ions** (force $F \sim r^{-2}$) or between ions and permanent dipole ($F \sim r^{-5}$, thermal averaging)
- **Van der Waals forces** are interactions involving **neutral** molecules, $F \sim r^{-7}$
 - **Keesom** force:
between two **permanent dipoles**
 - **inductive** force (Debye):
involves an **induced dipole**
 - **dispersion** force (London):
between **transitory dipoles** (fluctuations).
E.g. noble gases. Weakest force.



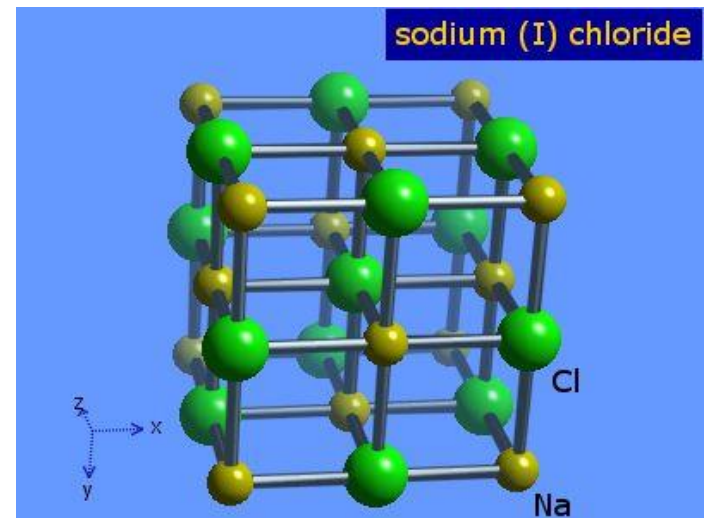
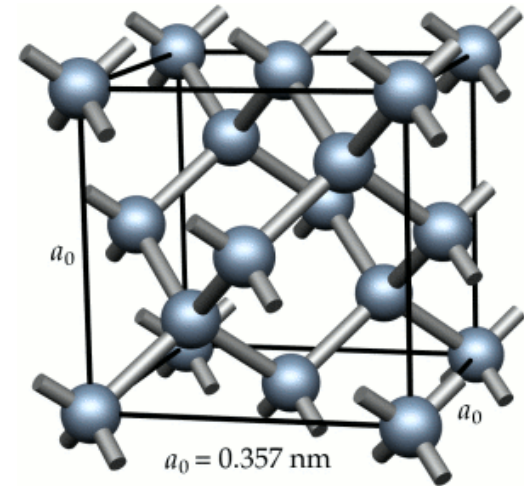
Phases of matter

Phases of matter

- A phase is a form of matter that is **homogeneous in chemical composition and physical state**
- The phase is characterized by **state variables**: pressure p , volume V , temperature T , composition, ...
- Examples of distinct phases: ice cubes in water; oil droplets in water
- All materials have the following 4 basic phases:
 - solid
 - liquid
 - gas
 - plasma
- In addition, some materials have **mesomorphic phases** (such as liquid crystals)
- The phase is determined by the **competition of the weak intermolecular forces with thermal (disordering) effects**

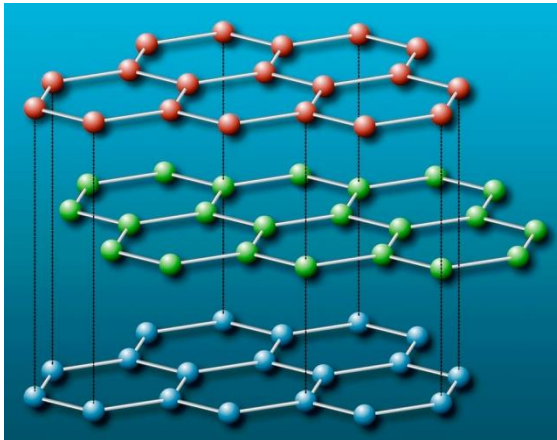
Crystalline solids

- In a crystal, inter-atomic forces arrange the atoms into a **spatial lattice**: the atoms have **fixed equilibrium positions**
- Covalent, metallic, ionic, molecular crystals
- The details of inter-atomic interactions determine the type of lattice (cubic, hexagonal, ...)
- How do we know this? **X-ray diffraction**: can probe structures of scale comparable to the wavelength of X-ray photons (Angstroms).



Crystalline solids

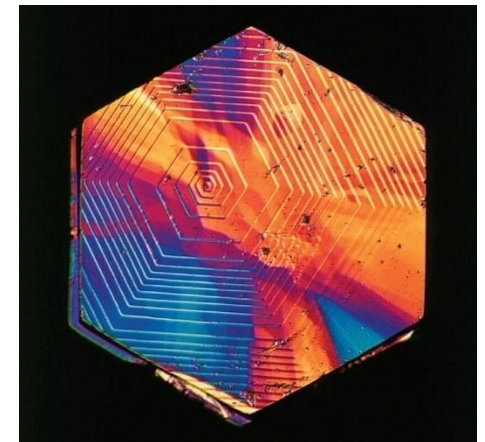
- The type of lattice (cubic, hexagonal, ...) determines the shape of grown crystals and their macroscopic properties
- Example: **graphite** (one of the phases of Carbon) – stack of planes with hexagonal order, can easily slide along the planes
- When temperature is increased, vibrations around equilibrium positions are more pronounced and the **crystal lattice can melt**
- **Lindemann criterion:** lattice will melt when **amplitude of vibrations reaches 10% of inter-molecular distance**



Within graphite layers:
covalent bonds

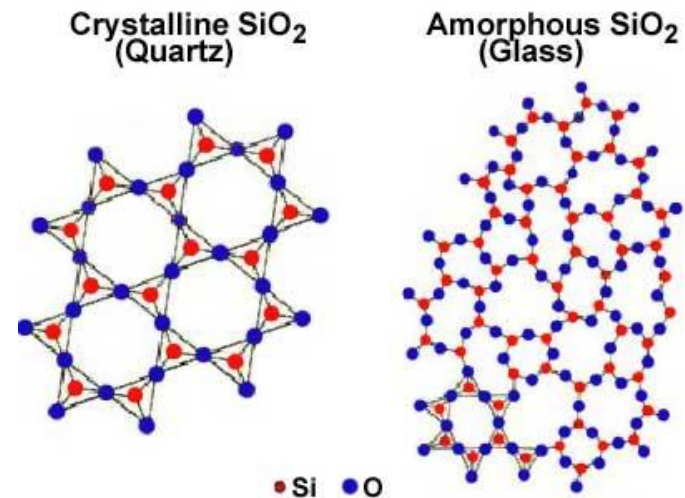
Between graphite layers:
Van der Waals interactions

Graphene: Nobel prize 2010



Amorphous solids

- Materials such as glass or rubber have the mechanical properties of solids, but there is **no crystalline lattice**
- Atoms are rigidly bound, but only short-range lattice ordering may be found
- Glass can be prepared by **quickly** cooling below the crystallization temperature
- Amorphous **solids** as they have rigidity against shear. Some literature views them as extremely viscous fluids.

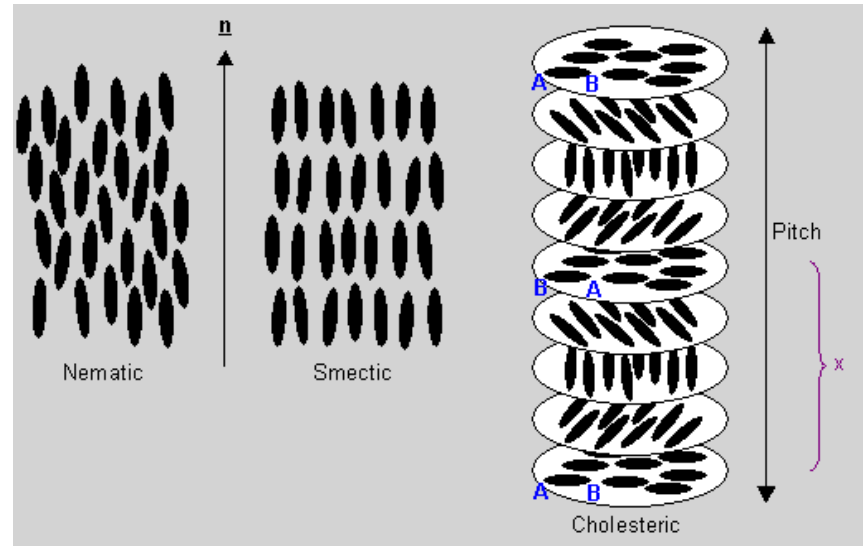


Liquids

- Unlike solids, liquids flow. Molecules do not have fixed equilibrium positions.
- Liquids have surface tension: will tend to minimize the area of the interface with another liquid or with gas. Due to van der Waals forces.
- Most liquids are isotropic (properties do not depend on direction)
- Anisotropic liquids: have anisotropic molecules which tend to order in a common direction (orientational order vs. positional order).
- However, most liquids with anisotropic molecules (such as H₂O) do not have orientational order, and are isotropic.

Types of liquid crystals

- Liquid crystals are **anisotropic liquids**
- **Nematic** LC: molecules have a common preferred direction
- **Smectic** LC: molecules have preferred direction and move within a preferred plane
- **Cholesteric** LC (chiral nematic): preferred direction rotates in a helix along the pitch axis
- Their anisotropic optical properties are used in LCDs (liquid crystal displays)

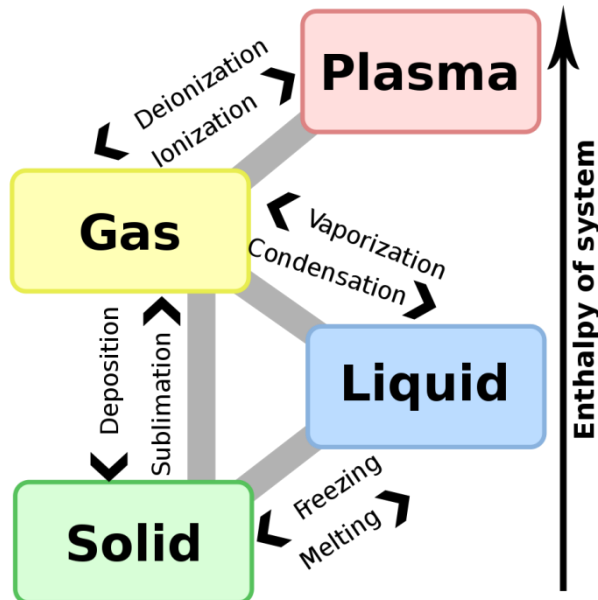


Plasma

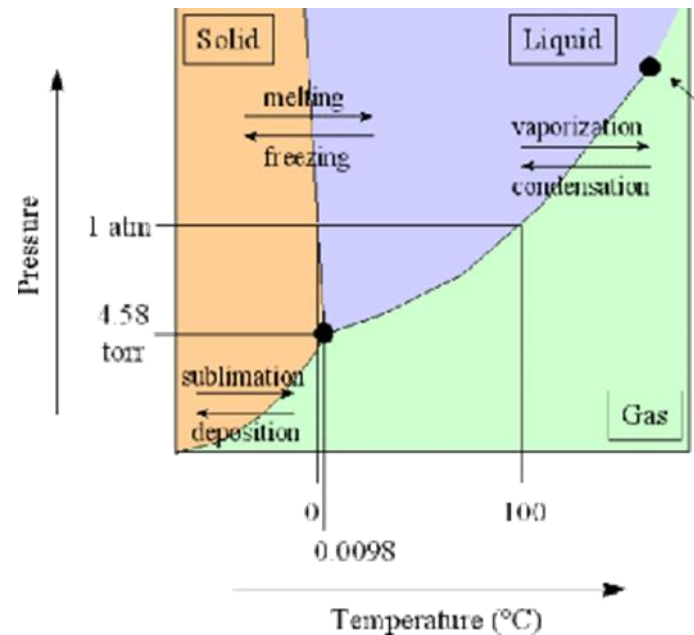
- At very high temperatures, gases **ionize** – the neutral molecules are split into **ions and free electrons**.
- Partial ionization above 1000 °C, full above 100 000 °C
- Plasma can also be generated non-thermally: by **ionizing radiation**, or by high-intensity electric fields. In this case it is **not** in thermal equilibrium.

Phase transitions

- A **phase transition** is a change in phase that occurs due to an external influence (heat, pressure, ...)



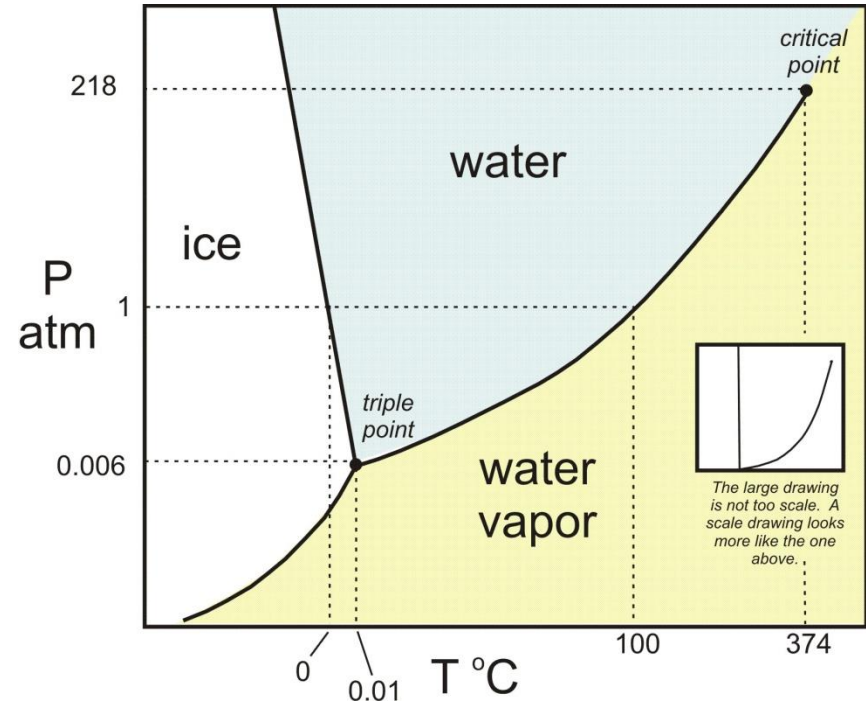
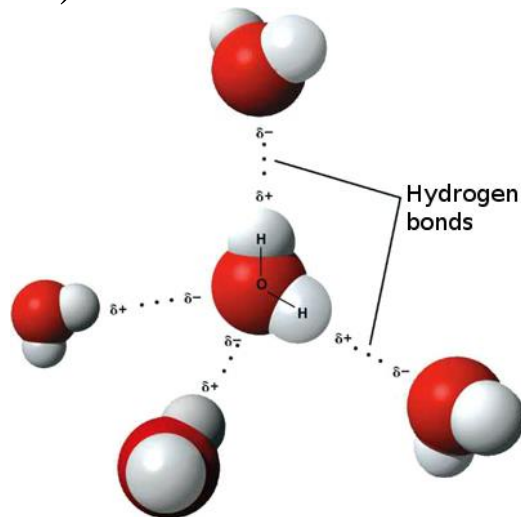
- Typical **phase diagram**:



- Example: boiling of water (liquid → gas) can occur due to increase in T or decrease in p

Phases of water

- **Hydrogen bond:** an H atom bridges two electronegative atoms (typically O, N, F)
- Up to 4 bonds per molecule
- Results in high boiling point, melting point, and viscosity (compared to fluids without H-bonds)



- **Triple point:** ice, water, and vapor are in thermal equilibrium
- **Critical point:** water and vapor become indistinguishable (one phase)

Gibbs rule of phases

- Applies to **systems at thermodynamic equilibrium** that contain multiple phases
- Follows from equality of chemical potentials (see lectures on thermodynamics)
- Gibbs rule:

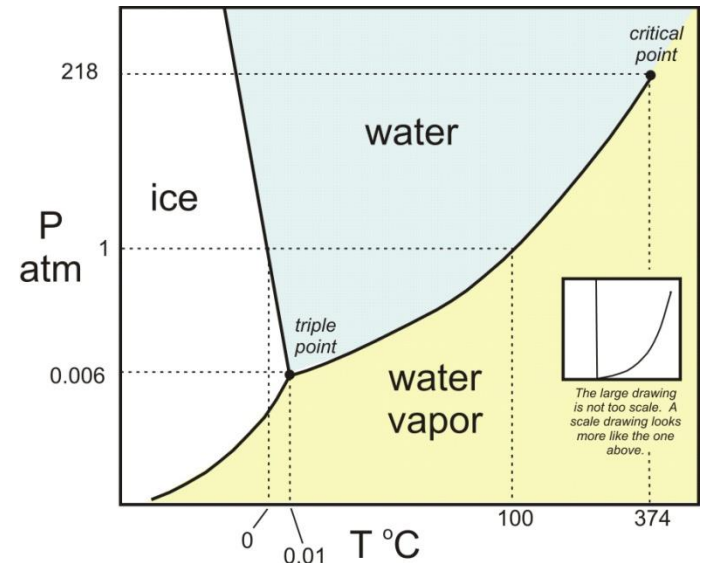
$$p + d = c + 2$$

p = number of phases

c = number of components

d = number of independent state variables (number of degrees of freedom)

- Examples:
 - water-ice coexistence: $p=2$, $c=1$, so $d=1$
 - water at triple point: $p=3$, $c=1$, so $d=0$
 - binary mixture: $c = 2$, $p \geq 1$, so $d = \text{up to } 3$ (relative concentration as additional degree of freedom)



Properties of gases

Gas phase

- A gas has **no surface tension**, and expands to fill the container
- There is no positional or orientational order of the molecules
- **Ideal gas**: is a theoretical construct, a gas of point-like molecules bouncing off each other elastically
- A gas is **approximately ideal** when:
 - there are no van der Waals interactions
 - average inter-molecular distance \gg molecular size
 - only translational degrees of freedom are active
- Satisfied well by the noble gases (Ar) in a wide range of p and T , and most other gases under typical conditions (but not close to condensation!)

Equation of state for ideal gas

- Equation of state relates the basic state variables (in thermal equilibrium):

$$pV = nRT$$

- $R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$ is the universal gas constant
- n is the number of moles of the gas; 1 mole contains $N_A = 6.02 \times 10^{23}$ molecules (Avogadro constant)

- Alternative form of equation of state:

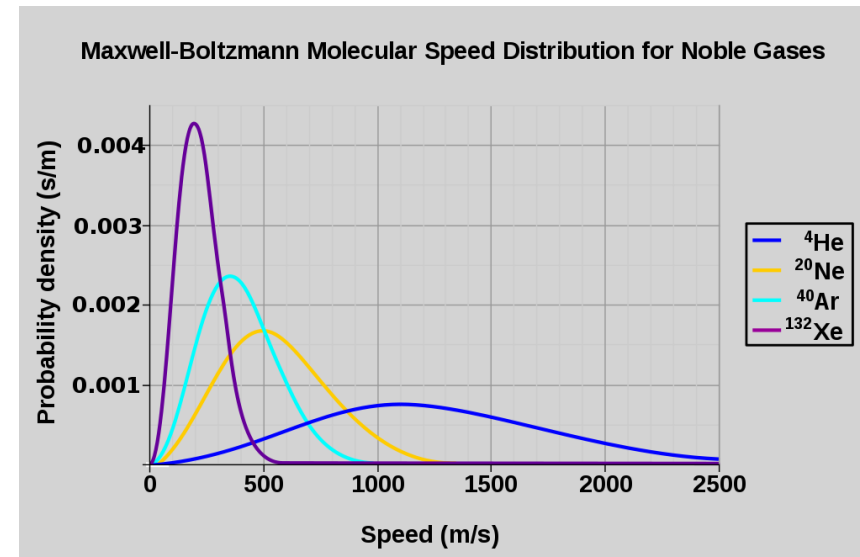
$$pV = NkT$$

- $N = nN_A$ is the total number of molecules
- $k = 1.38 \times 10^{-23} \text{ J/K}$ is the Boltzmann constant
- Isothermal process: change in state that occurs at fixed T
- Boyle's law: $pV = \text{const}$ during an isothermal process
- Isobaric process: fixed p , $V/T = \text{const}$
- Isochoric process: fixed V , $p/T = \text{const}$

Maxwell-Boltzmann distribution

- Valid for ideal gas at thermal equilibrium
- Gives the proportion of molecules which have a given velocity v
- The most probable velocity: peak of the distribution, occurs for $v_{mp} = \sqrt{2kT/m}$
- This is distinct from the mean (average) velocity,
$$v_{av} = \sqrt{8kT/\pi m}$$
- The root mean square velocity:
$$v_{rms} = \sqrt{3kT/m}$$

- Velocities increase with T , decrease with m



$$f(v) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^3 v^2 \exp\left(\frac{-mv^2}{2kT}\right)$$

Average energy per molecule

- Each molecule has kinetic energy $E = \frac{1}{2}mv^2$
- Average kinetic energy of 1 molecule of ideal gas:
$$E_{av} = \left\langle \frac{1}{2}mv^2 \right\rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}m v_{rms}^2 = \frac{3}{2}kT$$
- I.e., for each direction of motion (translational **degree of freedom**), the average energy is

$$\frac{1}{2}kT$$

- Translational vs rotational degrees of freedom:
 - monoatomic molecule: $3 + 0 = 3$
 - rigid diatomic molecule: $3 + 2 = 5$
 - rigid 3 (and more)-atomic: $3 + 3 = 6$
 - non-rigid: in addition vibrational degrees of freedom

Theorem of the equipartition of energy

- Maxwell's equipartition theorem: each degree of freedom has on average the energy

$$\frac{1}{2}kT$$

- Is valid not only for the ideal gas, but for **any system in thermodynamic equilibrium**
- Therefore, the total kinetic energy of 1 mole of diatomic gas is $\frac{5}{2}N_AkT = \frac{5}{2}RT$

- Note: memorize

$$\frac{1}{2}k_B T = 2.07 \times 10^{-21} \text{ J} = 0.013 \text{ eV}$$

(at room temperature 300 K)

- This typical thermal energy scale should be always compared to other microscopic energy scales (e.g. electrostatic interactions) in the system

Non-ideal gas

- **Real gases** have attractive inter-molecular forces and a finite molecular size
- Improvement on the ideal gas equation: **van der Waals equation of state** (for 1 mole)
- Note: an ideal gas would never liquify! Van der Waals interactions are needed for transition into liquid phase.

$$\left(p + \frac{a}{V^2}\right) (V - b) = RT$$

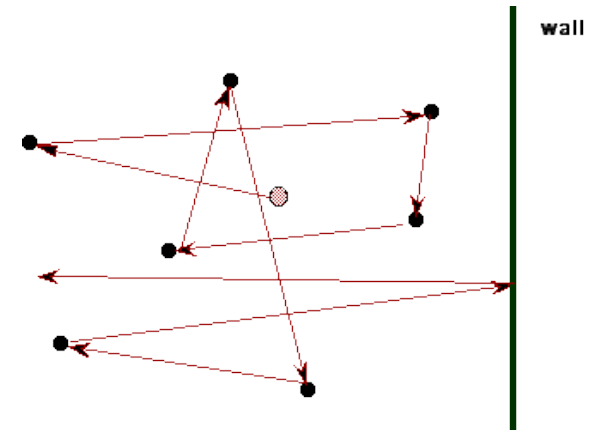
- Here **b** quantifies the volume of the molecules and **a** quantifies the van der Waals interactions

Lecture 2

Microscopic vs. continuum description of a fluid

(note: fluids = gases + liquids)

- **Mean free path** in a gas: average distance covered by a molecule between successive collisions
 - 7 μm for air at standard conditions
 - increases with temperature
 - decreases with pressure
- In a liquid, mean free path is comparable to distance between molecules (and almost no free path for liquids with hydrogen bonds)
- **Microscopic description of a fluid**: in terms of positions and velocities of molecules (e.g. the Maxwell-Boltzmann distribution)
- **Continuum description**: in terms of local density, local average velocity (averaged over a small volume)
 - can be used only if **dimensions of interest** \gg **mean free path**



Fluid statics

Pressure

- A fluid transmits a force uniformly in all directions
- Force acting on surface A in a fluid at rest:

$$F = pA$$

where p is the **pressure**; the force is normal to the surface

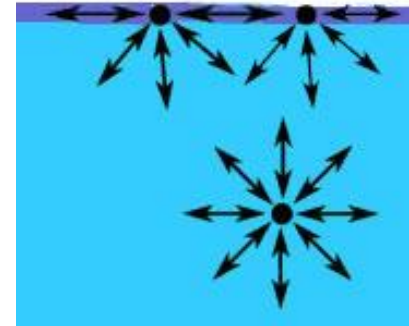
- Hydrostatic pressure is due to the weight of fluid:

$$p(h) = \rho gh + p_{atm}$$

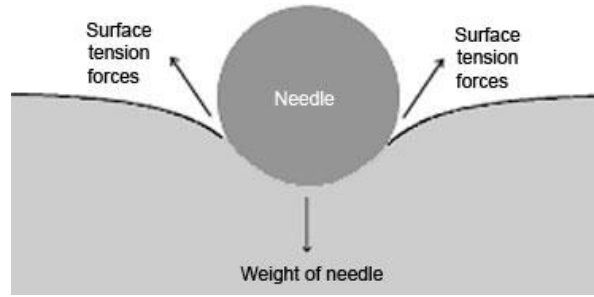
- Units:
 - in SI, 1 Pascal = 1 Newton / m²
 - 1 atm = 101 325 Pa = 760 mm Hg = 760 torr
 - 1 bar = 100 000 Pa
- **Incompressible liquid**: density does not change under applied force
- **Pascal's principle** for incompressible liquids: an increase in pressure is transmitted uniformly and isotropically to all parts of the liquid.
Used in **hydrostatic machines** to amplify applied force.

Surface tension

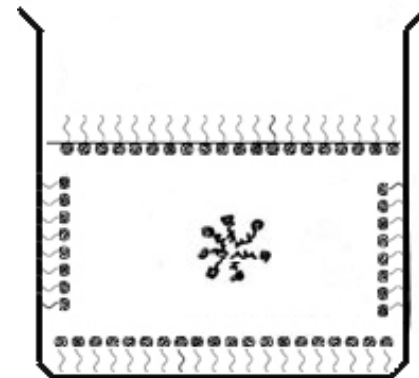
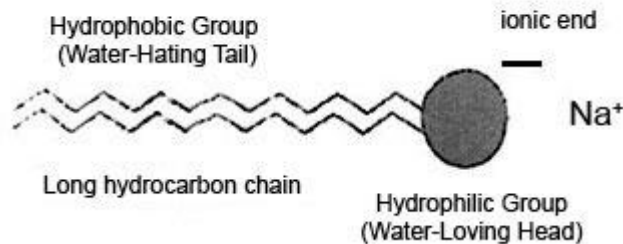
- Arises at the **surface of a liquid**. Molecules pulled inwards → higher cohesion at the surface.
- Force acting on a line segment L in the surface:
 - normal to the line, tangent to the surface
 - magnitude $F = \sigma L$, $\sigma =$ surface tension
 - for water at 20 deg C: $\sigma = 7.3 \cdot 10^{-2}$ N/m. Decreases with T.
- In terms of **energy**: molecules at surface have fewer neighbors → cannot lower their energy as much as in bulk. Therefore, **work is required to increase the surface of a liquid** (to increase by 1 m^2 , need energy = **capillary constant** = σ)
- Small droplets are spherical, as a sphere minimizes surface area for given volume
- Bigger droplets are deformed due to gravitation and other forces. Note: mercury has 7 x larger σ than water; glycerin slightly smaller σ .



Surface tension examples



- Weight of needle balanced by water surface tension
- Insects walking on water
- **Surfactants** (soaps, detergents): materials composed of **amphiphilic molecules**. These concentrate at the liquid boundary, weaken interactions among water molecules → dramatic **decrease in surface tension** upon addition of detergent



Laplace's law

- Relates the shape of a fluid boundary to the pressure difference Δp across the boundary:

$$\Delta p = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

where σ is the tension in the boundary,

R_1 and R_2 are the principal radii of curvature

- Reflects the balance of forces at the stationary boundary; p larger inside
- Example: a spherical water droplet of radius R has

$$R_1 = R_2 = R, \sigma = \text{the surface tension}, \Delta p = 2 \sigma / R$$

- Example: a cylindrical blood vessel of radius R has

$$R_1 = R, R_2 = \infty, \sigma = \text{elastic tension of vessel wall}, p = \sigma / R$$

- E.g. for aorta, $p=13$ kPa $\rightarrow \sigma=170$ N/m, for vein, $p=2$ kPa $\rightarrow \sigma=0.4$ N/m (see table in lecture notes)

Fluid dynamics

Equation of continuity

- Consider an incompressible fluid in a tube with cross-section A
- Flow rate Q: volume of fluid flowing through A per unit time,

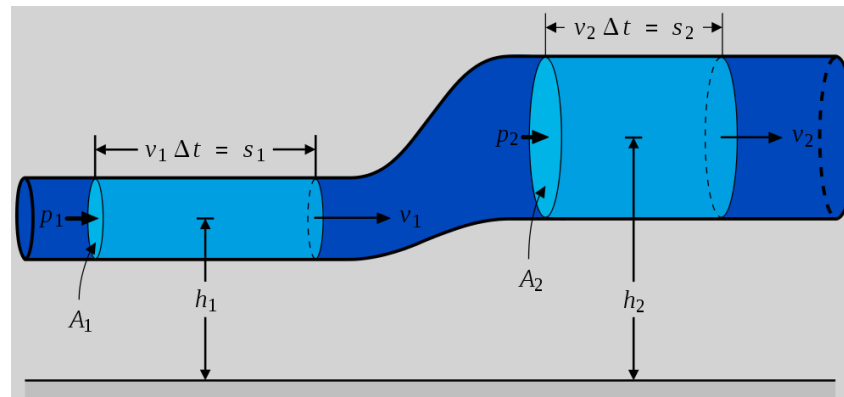
$$Q = \frac{\Delta V}{\Delta t} = \frac{A\Delta x}{\Delta t} = Av$$

where v is the velocity of the fluid

- Equation of continuity:

volume of fluid that enters = volume of fluid that leaves

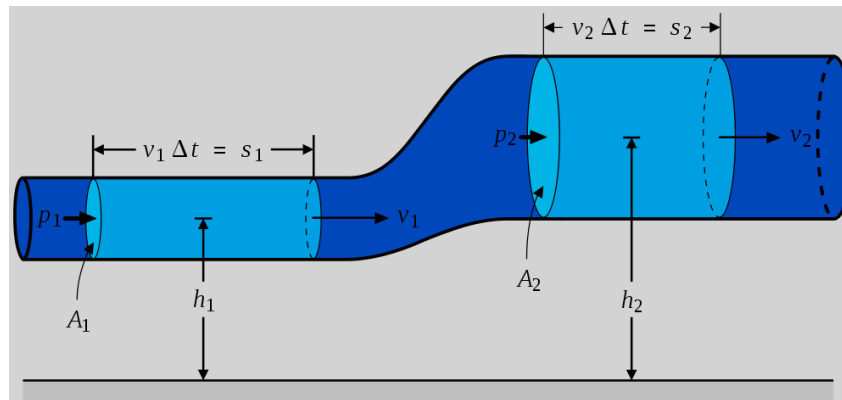
$$A_1 v_1 = A_2 v_2$$



Bernoulli's equation

- Equation of continuity gives the change in velocity. How to calculate the change in pressure?
- **Conservation of energy**: potential energy + kinetic energy = const.
- Bernoulli's equation:

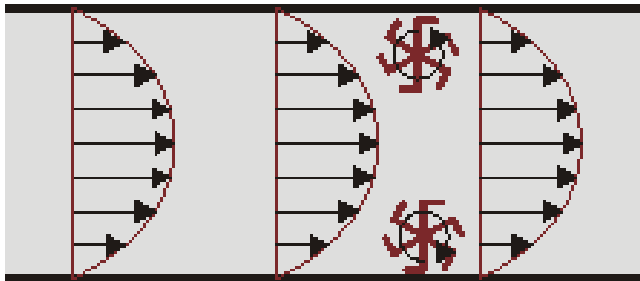
$$p_1 + \frac{1}{2} \rho v_1^2 + \rho g h_1 = p_2 + \frac{1}{2} \rho v_2^2 + \rho g h_2$$



- Bernoulli's equation is **valid only if there are no energy losses**, i.e. friction can be neglected (ideal fluid)
- If fluid is not moving, we recover the equation for hydrostatic pressure

Viscosity

- Real fluids have **internal friction** and **dissipate energy** (kinetic energy is transformed into heat)
- At contact of viscous fluid with a non-moving wall, velocity = 0
- Parabolic velocity profile for slowly moving fluid in a tube:



$$v = v_{max} \left(1 - \frac{r^2}{R^2}\right)$$

- The **velocity gradient** leads to friction between the moving layers, resulting in **tangential** tension (**shear stress**) Σ :

$$\Sigma = \eta \frac{\Delta v}{\Delta r}$$

- The constant η is the **dynamic viscosity**, units Pa sec
- **Kinematic viscosity**: $\eta_{kin} = \eta / \rho$, units m^2 / sec

Hagen-Poiseuille law

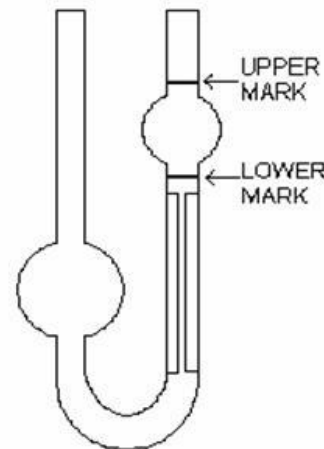
- **Ideal** fluid: no driving force needed to maintain motion
- But for a **viscous** fluid, **pressure decreases** in the direction of flow. For a **tube of length L and radius R**:

$$\Delta p = R_f Q$$

where Q is the volume rate of flow, and the **flow resistance R_f** is

$$R_f = \frac{8\eta L}{\pi R^4}$$

- Note that for given Δp , the rate of flow increases very strongly with R!
- **Ostwald viscometer**:
 - measurement of viscosity based on H-P law
 - Δp given by $\rho g L$, where L is the length of the capillary
 - measure time needed for flow of known volume $\rightarrow Q \rightarrow \eta$
 - in practice, compare to standard liquid, ratio of times of flow = ratio of kinematic viscosities



Stokes law, Reynolds number

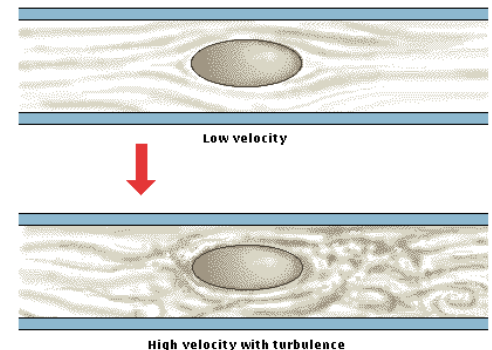
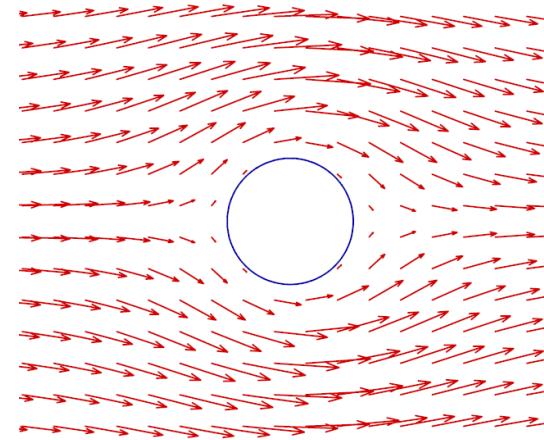
- Spherical object slowly moving relative to a fluid:
- Viscous forces result in **drag force** F on the object

$$F = 6\pi\eta r v \quad (\text{Stokes law})$$

where r is the radius and v the velocity of the object

- Falling object reaches **terminal velocity** when gravitational force = frictional force
- For low velocities, flow is **laminar** (sliding of layers)
- For high velocities, flow becomes **turbulent** (streamlines mix), Hagen-Poiseuille and Stokes laws no longer valid. Energy losses increase in turbulent flow. Heard as sound in stethoscope.

- **Reynolds number:** $Re = \frac{2\rho v R}{\eta}$ (dimensionless)
- If $Re < 2000$ laminar flow, if $Re > 3000$ turbulent



Typical viscosities and Reynolds numbers

- Air $\eta = 0.02$ mPa s (real gases are viscous!)
- Water 1 mPa s, blood 3 mPa s, glycerin 1 Pa s
- Viscosity increases with T in gases, decreases with T in liquids
- Typical boat: $Re = 10^8$, highly turbulent
- Blood flow in aorta: $Re = 1000 - 3000$, in vein 100, in capillary 0.002
- Turbulence produces sound heard in stethoscope
- Moving bacteria: $Re = 10^{-5}$, no inertia

Lecture 3

Classification of dispersion systems

- Dispersion system: particles of one **dispersive portion** are dispersed in a continuous **dispersive medium**
- Classification according to particle size:
 - up to 1 nm, **analytical dispersion** (homogeneous)
 - 1 nm to 1 μm , **colloidal dispersion**
 - above 1 μm , **coarse dispersion**
 - dispersion degree: $1/\text{size}$ (m^{-1})
- Classification according to phase of dispersive portion and medium
 - **see table in lecture notes**
 - liquid in gas: vapours; aerosols; rain, fog
 - gas in liquid: gas solution; foams; bubbles
- Common in living matter; pharmacy applications

Properties of solutions

Molecular diffusion

- Consider a particular molecule moving in a fluid
- It undergoes a **random walk** with
average step size = mean free path L
- Fundamental property of random walk:

rms displacement after N steps is proportional to \sqrt{N} (not to N !)

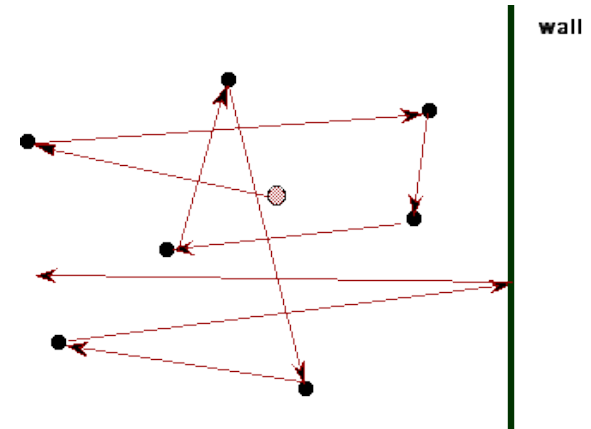
- Therefore **square of displacement** of molecule after time τ is

$$x_{rms}^2 = 2D\tau \quad (\text{in each direction})$$

- **Diffusion coefficient D** for spherical particle:

$$D = \frac{k_B T}{6\pi r \eta}$$

- Typical values: e.g. haemoglobin in water $7 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$
- Time required to diffuse (in water) over distance $10 \mu\text{m}$: 10 msec,
over distance 1 cm: 1 hour!



Transport by diffusion

- Diffusion tends to remove gradients in concentration
- **Diffusion flux J** : net number of moles crossing (in one direction) a unit area per unit time
- **Fick's law of diffusion**: diffusion flux is proportional to concentration gradient

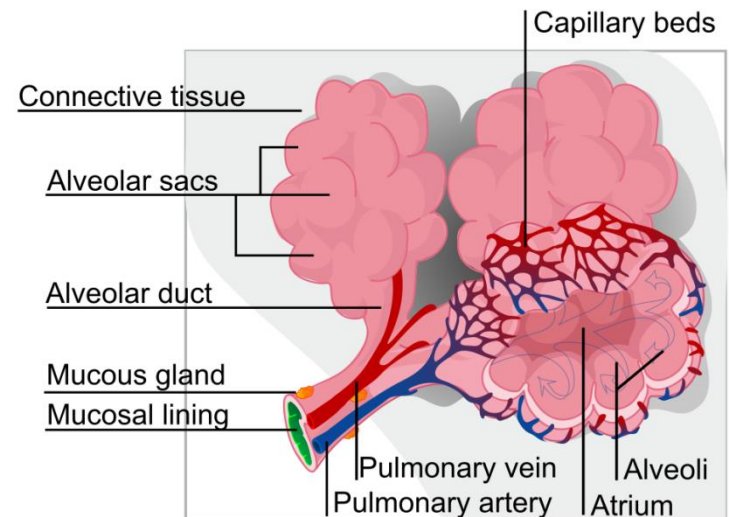
$$J = \frac{n}{A\tau} = -D \frac{\Delta c}{\Delta x}$$

(net transport of molecules in direction **opposite** to concentration gradient)

- **Transport by diffusion vs. transport by advection**: diffusion effective only for short distances

Transport of oxygen in breathing

- Human body (in rest) needs about 15 liters of O₂ per hour
- Diffusion through skin is insufficient (only about 2% in humans). Sufficient only for small animals (below 0.5 cm, insects).
- Transport of air **by convection** into lungs, terminating in **alveoli** (cavities of diameter 0.1 mm to 0.3 mm). **Diffusion of O₂** into blood across the walls of alveoli. Total surface area of alveoli 100 m².
- How much air pressure is required to inflate the alveoli? Wall is coated with fluid; Laplace's law $\Delta p = 2 \sigma / R$
- For $\sigma = 7.3 \cdot 10^{-2}$ N/m (water), Δp would be 3 atm! Fluid on alveoli contains **surfactants** (lipids + proteins), **reduces σ to 10^{-3} N/m**.
- Infant respiratory distress syndrome: treatment with artificial surfactants



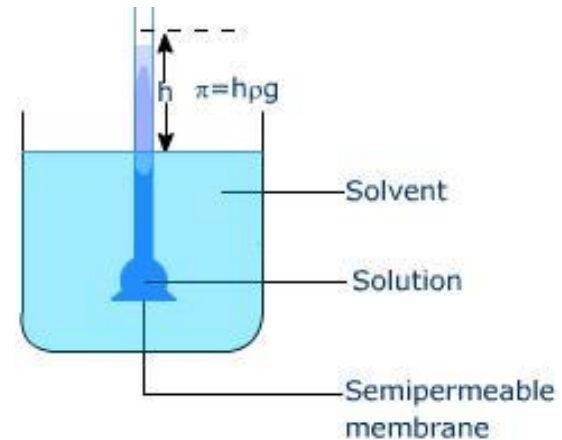
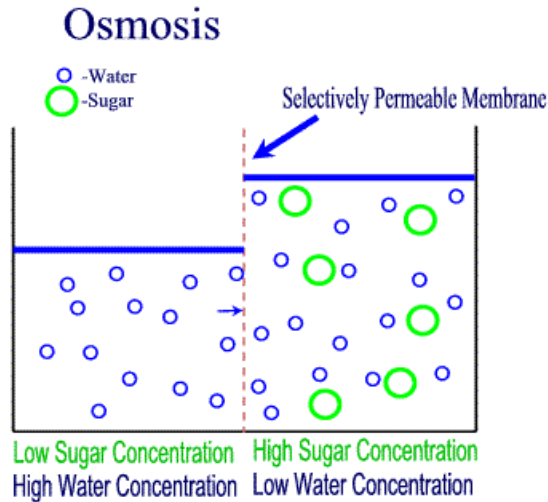
Colligative properties of solutions

- Colligative properties **depend only on the number (concentration) of solute particles**. Do not depend on size, shape, or chemical properties.
- Proportional to molar concentration $C_m = \frac{N/N_A}{V} = \frac{c}{N_A} = \frac{c_g}{M}$
(N = number of particles, c_g = mass concentration, M = molar mass)

Osmotic pressure

Raoult's laws

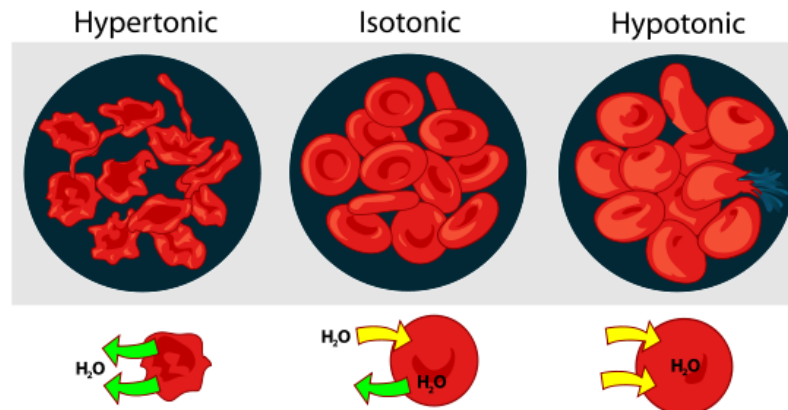
Osmotic pressure



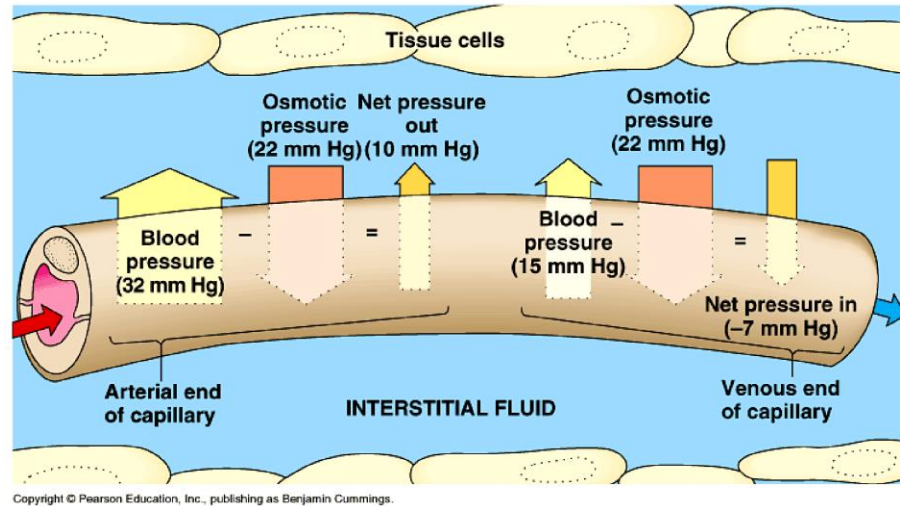
- **Osmosis**: diffusion of water across a **semi-permeable membrane** (molecules of solute cannot pass through)
- In solution, water concentration is lowered due to solute → concentration gradient → diffusion of water molecules into the solution → increase in pressure in solution until flow is stopped
- The extra pressure in solution is the **osmotic pressure**
- Van't Hoff laws: $P_{\text{osm}} = RTC_m$
 - osmotic pressure proportional to molar concentration
 - analytical solutions have higher osmotic pressure than colloids

Hypertonic, hypotonic solutions

- Measuring osmotic pressure: can use hydrostatic pressure
- Two solutions with equal osmotic pressure are **isotonic**
- **Hypertonic solution** has greater amount of impermeable solute than cytosol. Draws water out of cells. In **hypotonic solution**, cells swell.
- Osmotic pressure crucial in cell physiology. Plants keep erect thanks to osmotic pressure (turgor pressure acting on cell wall).
- Red blood cells in **pure water** rupture (haemolysis) before the equilibrium osmotic pressure 800 kPa is reached



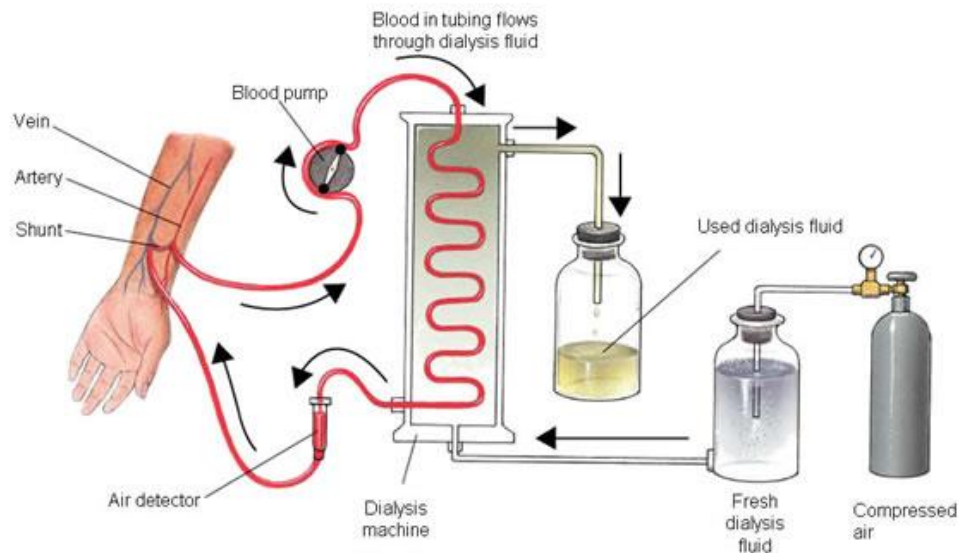
Osmosis and water transport in the body



- Arterial capillary: blood pressure $>$ osmotic pressure, net water transport out of the capillary
- Venous capillary: blood pressure $<$ osmotic pressure, net water intake
- Kidney: removal of waste products, regulation of water volume
- Regulation of osmotic pressure by excretion of urine (hypertonic compared to blood)

Hemodialysis

- **Dialysis**: replaces kidney function (except for hormone production)
- Blood and dialysis solution separated by membrane permeable to metabolites and ions, impermeable to proteins and blood cells.
- **Diffusion** of metabolites into dialysis solution
- **Ultrafiltration** (water removal / intake due to pressure difference)



Raoult's laws

- Boiling temperature (at given pressure) is **higher for solution** than for pure solvent and is proportional to the molar concentration C_m of solute

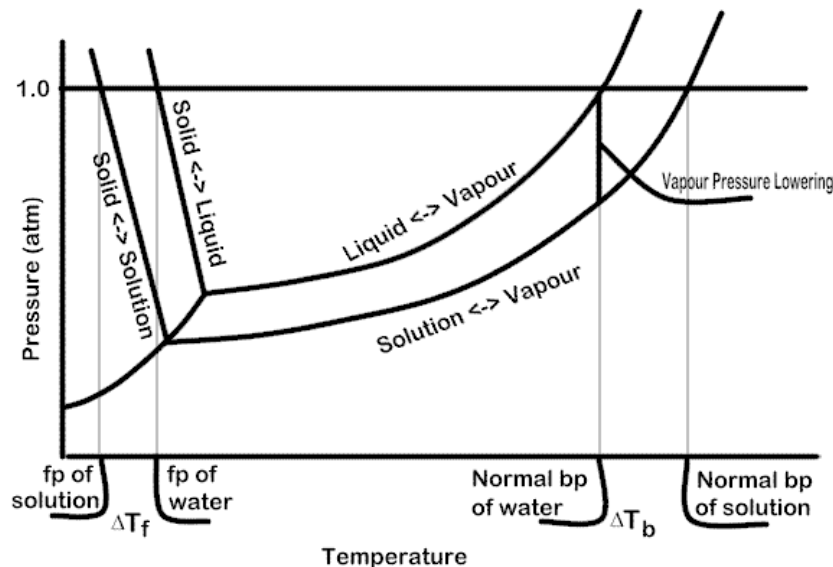
$$\Delta T_b = K_e C_m \quad (K_e = \text{ebullioscopic constant})$$

- Freezing temperature (at given pressure) is **lower for solution**:

$$\Delta T_b = -K_c C_m \quad (K_c = \text{cryoscopic constant})$$

- Pressure of vapors for a solution is lower than for pure solvent and is proportional to the number of particles dissolved:

$$\frac{\Delta p}{p_0} = \frac{n_2}{n_1 + n_2}$$



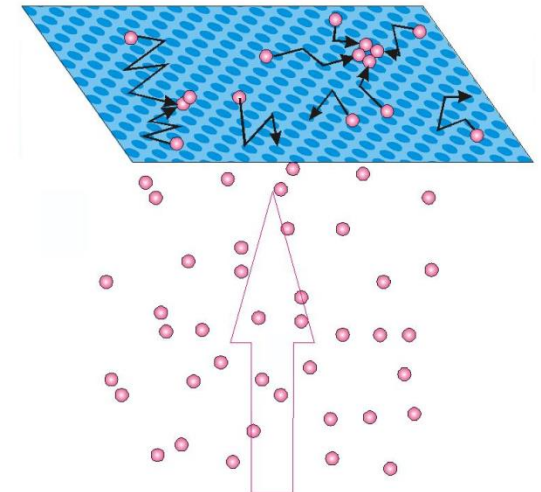
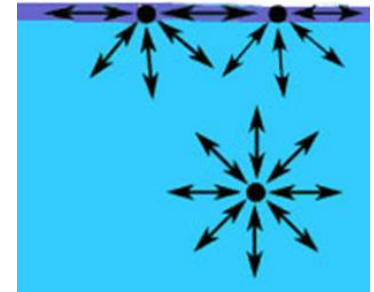
Adsorption at a boundary

- Adsorption is the adhesion of solute at the fluid boundary (moves within a thin layer)
- An increase in concentration (Δc) of surfactant decreases the surface tension ($\Delta \sigma$) of solution
- Tendency to decrease interfacial energy is balanced with diffusion, results in the **Gibb's adsorption equilibrium equation**:

$$\Gamma = - \frac{c}{RT} \frac{\Delta \sigma}{\Delta c}$$

where Γ is the **surface concentration** (in mol/m²)

- A **surfactant** solute has $\frac{\Delta \sigma}{\Delta c} < 0$, $\Gamma > 0$. The value $\frac{\Delta \sigma}{\Delta c}$ is different for different surfactants, i.e. Γ is **not** a colligative property



Lecture 4

Other analytical dispersions

Mixture of gases

- **Partial pressure** of a gas in a gas mixture (with given p , V , T) is the pressure the gas would have alone, if maintained at the **same V , T**
- **Partial volume** of a gas in a gas mixture is the volume it would have alone at the **same p , T**
- **Dalton's law**: the pressure of a gas mixture is the sum of partial pressures of its components (fully valid only for ideal gases)
- **Amagad's law**: the volume of a gas mixture is the sum of partial volumes of its components

Vapor

- **Vapor pressure** is the pressure at which vapor is in thermodynamic equilibrium with the liquid phase
- Vapor pressure increases with temperature. The liquid boils when its vapor pressure reaches the surrounding pressure
- **Saturated vapor**: any extra amount of vapor will condense
- **Absolute humidity**: mass of water vapor in unit volume of air
- **Maximum humidity**: mass of **saturated** vapor in unit volume.
E.g. at 1atm and 20 °C, $\phi = 17 \text{ g/m}^3$; at 30 °C, $\phi = 30 \text{ g/m}^3$
- **Relative air humidity**: absolute humidity / maximum humidity
- Air at at 20 °C, saturated with water vapor: has partial pressures 23 mbar of water vapor, 780 mbar of nitrogen, 210 mbar of oxygen and 9 mbar of argon.

Gas in liquid

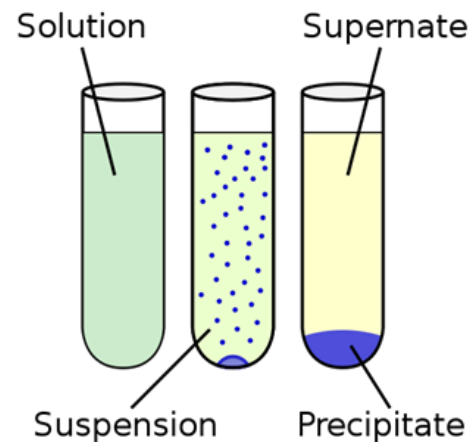
- Gas in contact with a liquid (**any** liquid with which it **does not react chemically**): dissolves in the liquid, dynamic equilibrium of gas \rightarrow liquid and liquid \rightarrow gas
- **Henry's law**: amount of gas dissolved in liquid is proportional to the partial pressure of the gas above liquid
- Molar concentration of gas in liquid:

$$c = \alpha_B p, \quad \alpha_B = \text{Bunsen's absorption coefficient}$$

- Solubility decreases with increasing T
- Water at 20 °C: for oxygen $\alpha_B=0.031$, for nitrogen $\alpha_B=0.016$. I.e. in water, higher amount of oxygen relative to nitrogen (compared to air)
- **Nitrogen embolism**: when air inhaled at high p \rightarrow high amount of nitrogen dissolved \rightarrow released when returned to atmospheric p \rightarrow nitrogen bubbles in capillaries, fatal if in brain. Need slow return to surface or decompression chamber.

Solid in liquid

- Compounds that dissolve easily in polar solvent (water is strongly polar, dielectric $\epsilon_r = 80$):
 - dissociable into ions (e.g. NaCl)
 - organic compounds with polar groups
- Solubility of solids increases with increasing T
- If solution is saturated, any additional solid will form **precipitate**
- Can precipitate by lowering temperature
- **Oversaturated solution** can be obtained when solidification centers (e.g. impurities) are absent from solution



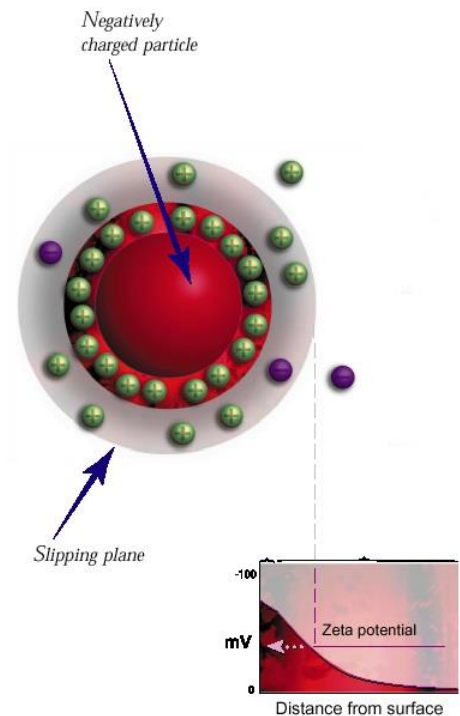
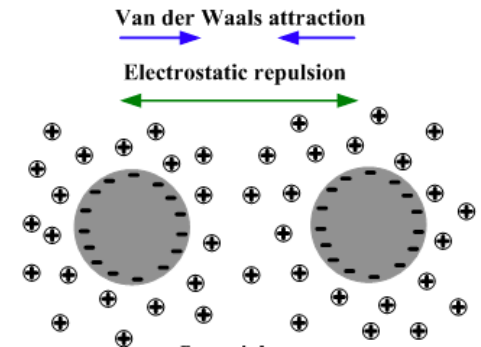
Properties of colloids

Colloidal dispersions

- Dispersive portion consists of particles of size 1 nm to 1 μm
- Solid in liquid: sol; liquid in liquid: colloidal emulsion
- Examples: ink; milk
- **Lyophilic colloids**: disperse spontaneously, colloid has lower energy (solvation decreases surface tension). E.g. starch, protein in water.
- **Lyophobic colloids** are unstable (hydrophobic molecules aggregate). E.g. emulsion of oil in water; metal compounds in water.
- **Tyndall effect**: intense light scattering from a colloid, with intensity proportional to concentration. Most intense scattering for shorter wavelengths \rightarrow blue color.

Electric double layer of colloidal particles

- Plays crucial role in **stabilization of colloids**
- Colloidal particles (macromolecules, micelles) have attractive Van der Waals interactions. If no repulsion, particles may **coagulate**.
- Repulsive Coulomb interaction due to **electric double layer**:
 - negatively charged ions from electrolyte dispersive medium are **adsorbed** on the surface of particles
 - these attract positively charged **counterions**
 - overall, the double layer is neutral
 - **slipping plane**: part of the double layer that moves with the particle
 - **zeta potential** ζ : value of electrostatic potential at the slipping plane. Good stability of colloid for $\zeta \geq 40\text{mV}$.



Electrophoresis

- In a uniform electric field E , the colloidal particles will move relative to the fluid dispersive medium, with velocity

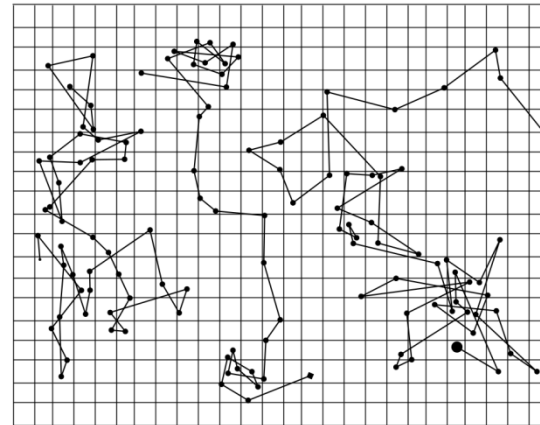
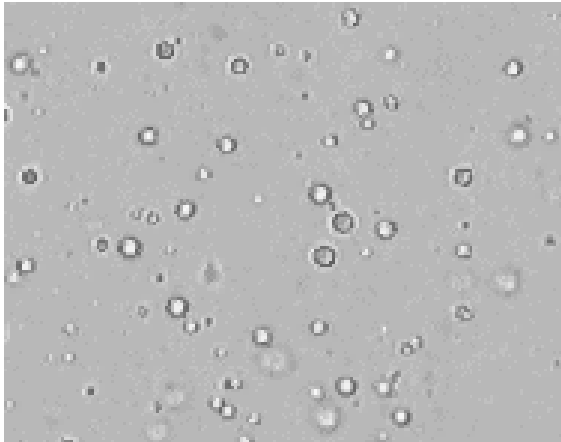
$$v = \mu_e E$$

where μ_e is the **electrophoretic mobility**

- **Smoluchowski equation:** $\mu_e = \epsilon_r \epsilon_0 \zeta / \eta$, where ϵ_r is the dielectric constant of fluid, η is the viscosity of fluid
- Zeta potential ζ also called **electrokinetic potential**
- Distinct colloidal particles have different μ_e , allows separation of particles (e.g. separation of albumin and globulin in blood serum)

Brownian motion

- Colloidal particles in a liquid or gas exhibit Brownian motion
- Due to imbalances of **impact forces of molecules on the particle**
- Understood before direct observation of molecules (Einstein, Smoluchowski)
- Kinetic energy of 1 collidal particle is of the order of $k_B T$



Sedimentation

- Due to gravity, particles of size r and density ρ_0 move through fluid with **terminal velocity** v
- For spherical particles: Stokes force $6\pi\eta r v$ balanced with buoyancy force $(4/3)\pi r^3(\rho - \rho_0)g$, which gives the **sedimentation velocity**

$$v = \frac{2(\rho - \rho_0)gr^2}{9\eta}$$

- In equilibrium, a **profile of colloid concentration** is established, balance of sedimentation and diffusion
- Time needed to sediment: fast for coarse solutions, effectively infinite for analytical solutions
- **Sedimentation rate test**: aggregates of erythrocytes are formed during inflammation and sediment faster (bigger r).
- **Centrifugation**: enhanced sedimentation due to increased g (inertial force). Used e.g. to efficiently separate blood components.