

DIFFUSION AND OSMOSIS

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OUTLINE

- Thermodynamic system.
- Characterization of the system. Thermodynamic variables.
- Microscopic structure of the system - internal energy.
- Equilibrium, reversibility.
- Zeroth Law of thermodynamics.
- Change, reversible change, thermodynamic processes.
- First Law of thermodynamics. Change in internal energy. Energy is conserved!
- Enthalpy.
- Second Law of thermodynamics.
- Direction of spontaneous processes. Entropy. Statistical interpretation. Thermodynamic probability. Phenomenological interpretation of entropy.
- Third Law of thermodynamics.
- Helmholtz- and Gibbs-free energy. Significance of free energy and entropy.
- Chemical potential.
- Irreversible thermodynamics, transport phenomena.
- **Diffusion, Brown-movement.**
- **Osmosis.**

THERMODYNAMIC CURRENTS

- Natural processes are rarely reversible.
- If there are inequalities in the intensive variables at different locations within the system, thermodynamic currents arise.
- Thermodynamic currents aim at the restoration of equilibrium.

Thermodynamic current	Relevant intensive variable (its difference maintains current)	Current density	Physical law
Heat flow	Temperature (T)	$J_E = -\lambda \frac{\Delta T}{\Delta x}$	Fourier
Volumetric flow	Pressure (p)	$J_v = -\frac{R^2}{8\eta} \frac{\Delta p}{\Delta x}$	Hagen-Poiseuille
Electric current	Electric potential (ϕ)	$J_Q = -\frac{1}{\rho} \frac{\Delta \phi}{\Delta x}$	Ohm
Material transport (diffusion)	Chemical potential (μ)	$J_n = -D \frac{\Delta c}{\Delta x}$	Fick

ONSAGER'S LINEAR FUNCTION

- Lars Onsager (1903-1976), Nobel prize (1968)
- General relationship between transport processes.

$$J = LX$$

Flow intensity of transported extensive variable (thermodynamic current, J)
 $J = \frac{\Delta x_{ext}}{\Delta t}$

=

Coefficient of conductance (thermodynamic coefficient, L)

x

Change in intensive variable ("gradient", thermodynamic force, X)
 $X = -\frac{\Delta y_{int}}{\Delta x}$

A thermodynamic current may be evoked by several different intensive variables.
E.g., thermodiffusion (material transport evoked by temperature gradient).

$$J_1 = L_{11}X_1 + L_{12}X_2$$

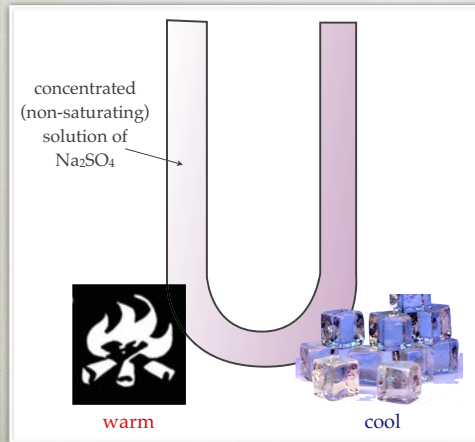
$$J_2 = L_{21}X_1 + L_{22}X_2$$

L_{11}, L_{22} = "linear" coefficients of conductance

L_{12}, L_{21} = "cross" coefficients of conductance

THERMODIFFUSION

- Ludwig-Soret effect
- Carl Friedrich Wilhelm Ludwig (1856)
- Charles Soret (1879)



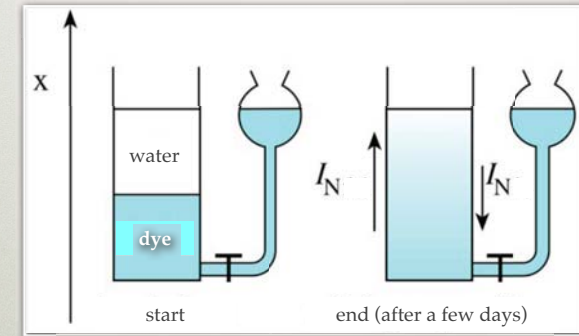
Two types of currents:

material flow $J_V = -L_T \frac{\Delta T}{\Delta x}$

heat flow flow $J_E = -\lambda \frac{\Delta T}{\Delta x}$

DIFFUSION

- Spontaneous mixing, distribution, concentration-equilibration driven by the thermal motion of particles.



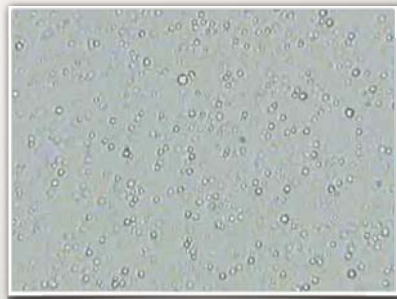
$$x^2 = 2Dt$$

x = displacement of boundary
 t = time
 D = constant ("diffusion coefficient")

Microscopic manifestation of diffusion: Brownian movement

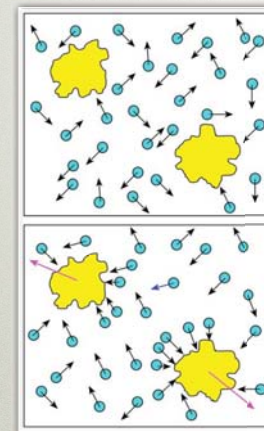


Robert Brown
(1773-1858)

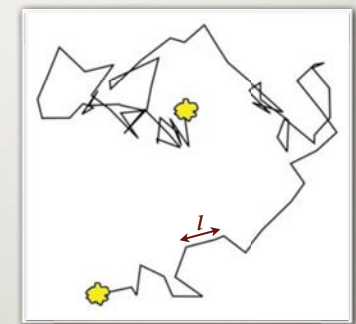


Fat droplets suspended in milk (droplet sizes 0.5 - 3 μm)

Brownian movement



Movement of microscopic particle is the result of random collisions with molecules.



l = mean free path (average distance between consecutive collisions)
 v = average velocity of thermally propelled particle

DIFFUSION

- *Fick's First law*: material flow density is the product of the evoking concentration gradient and the diffusion coefficient

Material transport: $J_n = -D \frac{\Delta c}{\Delta x}$

J_n = material flow
 $\Delta c / \Delta x$ = drop in concentration ("gradient")
 D = constant ("diffusion coefficient")

Diffusion coefficient: $D = \frac{1}{3} v l$

v = average velocity of thermally propelled particle
 l = mean free path (average distance between consecutive collisions)
 D = amount of material transported through unit area per unit time (m^2/s) (at unitary concentration drop).



Brown-movement

Diffusion coefficient for spherical particle: $D = \frac{k_B T}{6 \pi \eta r}$

Einstein-Stokes formula:
 k_B = Boltzmann's constant
 T = absolute temperature
 η = viscosity
 r = radius of particle

DIFFUSION

- *Fick's Second Law*: instantaneous material flow density depends on the temporal change in evoking concentration gradient.

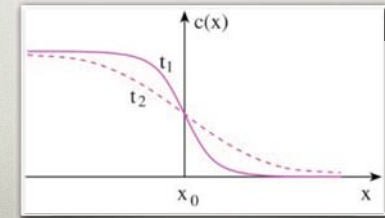
Material flow intensity: $-\frac{\Delta J_n}{\Delta x} = \frac{\Delta c}{\Delta t}$

J_n = Flow intensity
 x = distance
 t = time

Diffusion coefficient: $D \frac{\Delta \left(\frac{\Delta c}{\Delta x} \right)}{\Delta x} = \frac{\Delta c}{\Delta t}$

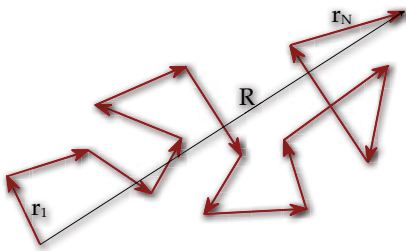
D = diffusion coefficient

Concentration gradient decreases with time (boundary becomes "smeared")



RELATIONSHIP BETWEEN RANDOM WALK AND DIFFUSION

Brown-movement - "random walk"



"Square-root law":

$$\langle R^2 \rangle = N l^2 = L l$$

R = displacement
 N = number of unit vectors (steps)
 $l = |r_i|$ = mean free path
 r_i = unit step
 $Nl = L$ = total distance

Mean particle velocity: $v = \frac{l}{\tau}$

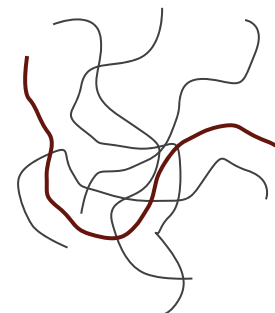
Full walk time: $t = N \tau$

Diffusion coefficient: $D = \frac{1}{3} v l$

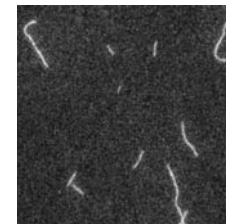
$$\langle R \rangle = \sqrt{N l^2} = \sqrt{\frac{t}{\tau} l^2} = \sqrt{t v l} = \sqrt{3 D t}$$

A SPECIAL CASE OF DIFFUSION: REPTATION

- *Reptation*: "snake-like" diffusion within polymer network (*Reptilia*)



polymer matrix: "entanglement"



Actin filaments in methyl-cellulose matrix.

"unidirectional diffusion"

A SPECIAL CASE OF DIFFUSION: OSMOSIS

Osmosis ~ osmos (Gr) thrust, push

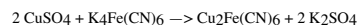
History: -Nollet (1748): pig bladder containing alcohol swells in water
-Dutrochet (1830): first osmometer
-van't Hoff: gas-law mechanism of osmosis
-Arrhenius and Findlay: vapor-pressure mechanism of osmosis

Osmosis: diffusion-driven process between two compartments separated by semipermeable membrane (solvent diffusion).

Osmotic pressure (π) = equilibrium hydrostatic pressure between each side of the semipermeable membrane (dP).

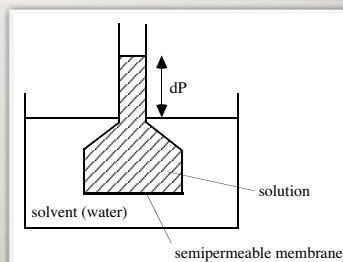
Semipermeable membranes:

-frog membrane
-copper-ferrocyanide gel (precipitated on the pores of clay cylinder):



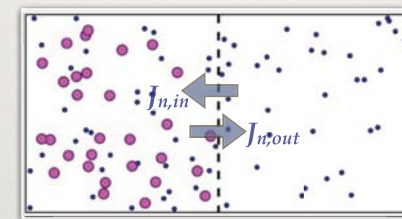
-cellulose membrane, dialysis bag

Biomedical importance: biological membranes, compartment surfaces.



A SPECIAL CASE OF DIFFUSION: OSMOSIS

- **Osmosis:** one-directional solvent transport by diffusion.



$J_{n,in}$ driving force: solvent concentration difference

$J_{n,out}$ driving force: pressure difference

Osmotic equilibrium: $J_{n,in} = J_{n,out}$

MECHANISMS OF OSMOSIS I.

van't Hoff's gas-law mechanism

Universal gas law: $pV = RT$

$$p = \frac{1}{V}RT$$

Osmotic pressure: $p_{osm} = \pi = cRT$

p = pressure
 V = volume
 R = gas constant (8,3 J/mol.K)
 T = absolute temperature
 c = molar concentration of solute

Problem:

What is the osmotic pressure of a 0.1 M (0.1 mol/dm³) sucrose solution?

$$\pi = 8.3 \text{ (J/mol.K)} \times 293 \text{ (K)} \times 0.1 \text{ (mol/dm}^3\text{)} = 243 \text{ kPa} \sim 2.4 \text{ atm.}$$

Note: the formula applies to dilute solutions.

MECHANISMS OF OSMOSIS II.

Corrected van't Hoff's law

$$\pi = fnRTc$$

n = number of ions produced during complete dissociation

f = osmotic coefficient:

$$f = \frac{\pi_{measured}}{\pi_{calculated}} = \frac{\pi_{measured}}{nRTc}$$

Arrhenius-Findlay's vapor pressure mechanism

Changes in the chemical potential of the solvent due to the solute (chemical activity of the solvent becomes reduced upon the addition of the solute).

Chemical potential of solvent: $\mu_s = \mu_s^0 + RT \ln \chi_s$

μ_s^0 = standard chemical potential of solvent
 χ_s = mole fraction of solvent

Mole fraction of solvent: $\frac{n_0}{n_0 + n_1}$

n_0 = number of moles of solvent
 n_1 = number of moles of solute

Raoult's law: $\frac{p_1}{p_0} = \frac{n_0}{n_0 + n_1}$

p_0 = vapor pressure of pure water
 p_1 = vapor pressure of solution water

Arrhenius-Findlay law: $\pi = \frac{RT}{v} \ln \frac{p_0}{p_1}$

v = molar volume of solvent (cm³/mol; for water: 18)

IMPORTANCE OF OSMOSIS

Properties of the semipermeable membrane: *reflexion coefficient* (σ)

For a perfect semipermeable membrane:

$$\Delta P = \Delta \pi \quad \text{and} \quad \sigma = \frac{\Delta P}{\Delta \pi} = 1$$

In reality:

$$\Delta P < \Delta \pi \quad \text{and} \quad \sigma = \frac{\Delta P}{\Delta \pi} < 1$$

$$0 < \sigma < 1$$

Osmotic work:

$$-L = nRT \ln \frac{c_1}{c_2} = nRT \ln \frac{\pi_1}{\pi_2}$$

R = gas constant

n = total number of moles of solute

c_1 = initial molarity of solution

c_2 = final molarity of solution (after equilibration)

π_1 = initial osmotic pressure

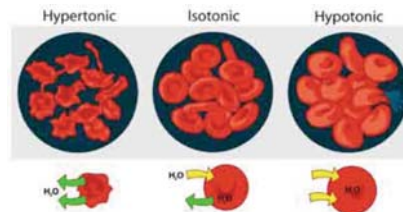
π_2 = final osmotic pressure (after equilibration)

Equivalent osmotic pressure (osmotic concentration):
concentration of non-electrolyte solution in
equilibrium with a heterogenous solution system.

Units: mmol/kg = mOsmol/kg = mOsm

Osmolarity of blood plasma ~ 300 mOsm.

Oncotic pressure: colloid osmotic pressure. Osmotic
pressure of a solution of colloidal macromolecules.



BIOPHYSICS OF FLUIDS

Importance of the physics of fluids

I. Hemodynamics

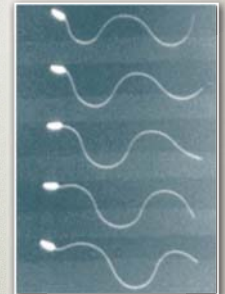
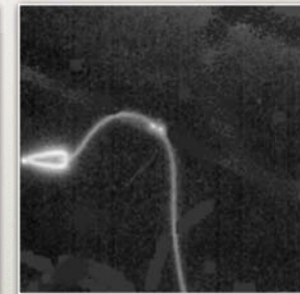
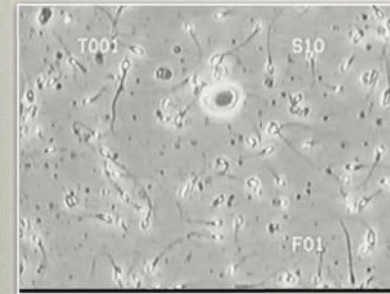
Characteristics of blood flow along the circulatory system.



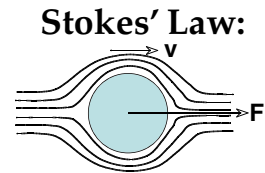
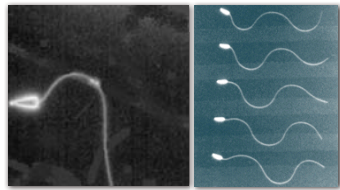
Significance of the physics of fluids

II. Motion in fluids

Force exerted by a single spermatoocyte during its motion.



Drag coefficient of the spermatoocyte



Stokes' Law:

$$\gamma = 6r\pi\eta = 6 \cdot 1.6 \times 10^{-6} (m) \cdot \pi \cdot 10^{-3} (Pas) = 3 \times 10^{-8} Ns/m$$

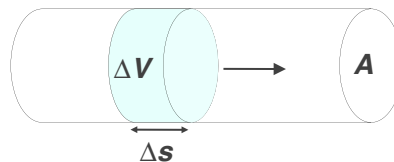
$$F = \gamma v = 3 \times 10^{-8} Ns/m \cdot 5 \times 10^{-5} m/s = 1.5 \times 10^{-12} N = 1.5 pN$$

Biophysics of fluids

- Basic principles
- Types of fluids
- Types of fluid flow
- Laws of fluid flow
- Biomedical importance

Basic principles I.

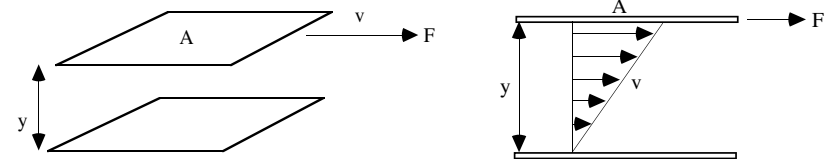
Volumetric flow rate (Q):



$$Q = \frac{\Delta V}{\Delta t} = A \frac{\Delta s}{\Delta t} = A \bar{v}$$

Average velocity: $\bar{v} = \frac{Q}{A}$

Basic principles II. Viscosity (internal friction)



F = shear force
A = area of fluid layer
 η = viscosity
v = flow velocity
y = distance between fluid layers

$$\frac{F}{A} = \eta \frac{\Delta v}{\Delta y}$$

F/A = shear stress (τ)
 $\Delta v / \Delta y$ = velocity gradient (D)

$$\eta = \frac{\tau}{D}$$

Units of viscosity: $1 Pas = 1 \frac{Ns}{m^2} = 10P (poise)$

Types of fluids I.

1. Ideal

frictionless, incompressible
 $\rho = \text{constant}$, $\eta = 0$

2. Non-ideal (real)

a. *Newtonian (viscous)*

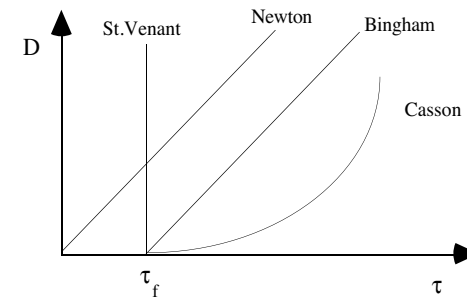
η independent of shear stress

b. *Non-newtonian (anomalous)*

η varies with shear stress

Types of fluids II.

Relationship between velocity gradient and shear stress in real fluids



τ_f = flow threshold

Viscoelastic materials: combination of elastic and viscous properties (e.g., polymer solutions)

Stress-relaxation: decay of shear stress in viscoelastic material following sudden stretch.

NB: Blood is non-newtonian fluid!

Types of fluid flow

1. Stationary

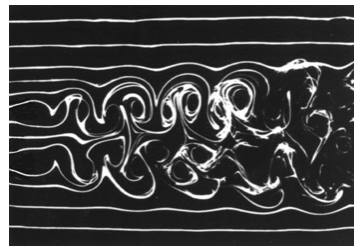
Flow intensity stays constant.

2. Laminar

Fluid layers do not mix.

3. Turbulent

Fluid layers mix.



Reynolds number:

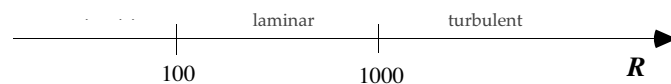
$$R = \frac{vr\rho}{\eta}$$

v = flow rate (m/s)

r = tube radius (m)

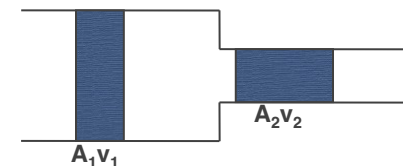
ρ = density of fluid (kg/m³)

η = viscosity (Ns/m²)



Laws of flow in ideal fluids I.

Continuity equation



$$A_1v_1 = A_2v_2 = \text{konst}$$

A = cross-sectional area

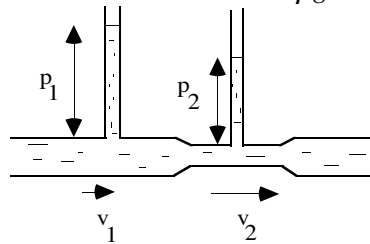
v = flow rate

Laws of flow in ideal fluids II.

Bernoulli's law

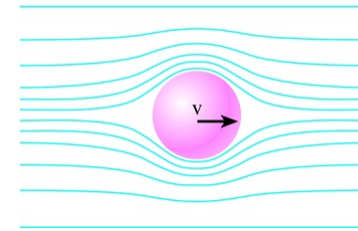
$$p + \frac{1}{2}\rho v^2 + \rho gh = \text{konst}$$

p = static pressure
 $\frac{1}{2}\rho v^2$ = dynamic pressure
 ρgh = hydrostatic pressure



Laws of flow in viscous fluids I.

Stokes' law

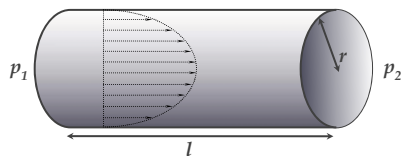


$$F = \gamma = 6r\pi\eta v$$

F = force
 γ = drag coefficient (shape factor)
 v = flow rate
 r = radius of sphere
 η = viscosity

Laws of flow in viscous fluids II.

Hagen-Poiseuille's law

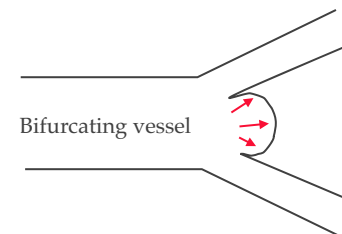


$$\frac{V}{t} = \frac{\pi r^4}{8\eta} \frac{dp}{dl}$$

V = volume
 t = time
 $(V/t = Q = \text{flow intensity})$
 r = tube radius
 η = viscosity
 p = pressure
 l = length of tube
 $(dp/dl = \text{pressure gradient, maintained by } p_1 - p_2)$

Biomedical significance

Bernoulli's law:



aneurysm:
 ➔ flow rate decreases (according to continuity equation)
 ➔ pressure increases
 ➔ aneurysm increases

Hagen-Poiseuille's law:

$$\frac{V}{t} = \frac{\pi r^4}{8\eta} \frac{dp}{dl}$$

Flow intensity may be **drastically reduced** in certain pathological conditions:

- constriction of blood vessels (e.g., diabetes, Bürger's disease)
- change in blood viscosity (e.g., fever, anaemia)