SEMMELWEIS UNIVERSITY

Dept. of Biophysics and Radiation Biology,
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TRANSPORT PHENOMENA

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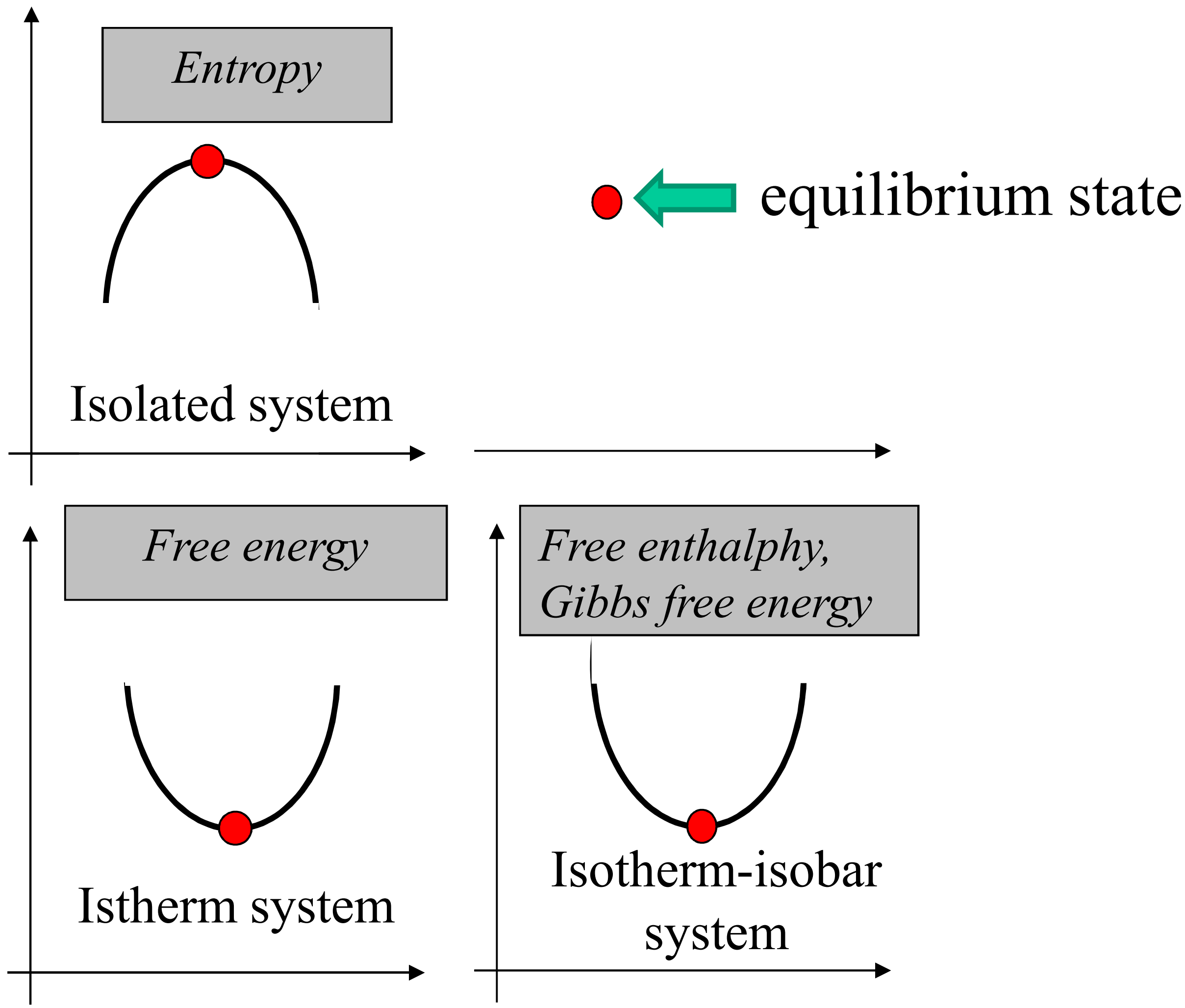
From non-equilibrium state to equilibrium state



Thermodynamic system

- time independent
  - equilibrium
  - steady state
- time dependent
  - non-equilibrium
  - reactive

steady state, non-equilibrium → *Transport processes*

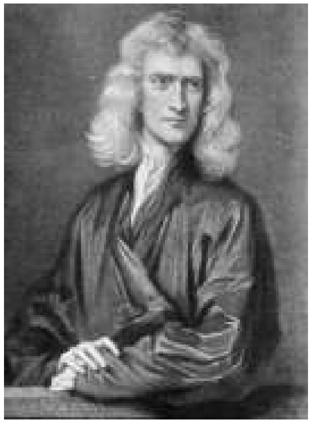
reactive → ***Reaction kinetics***

Driving force: **moving to equilibrium**

During spontaneous process $\Delta S > 0$ $\Delta F < 0$ $\Delta G < 0$

$F=U-TS$ $G=H-TS$

PIONEERS OF TRANSPORT PROCESSES



Sir Isac Newton
(1642-1727)

Jean-Babtiste-JosephFourier
(1768-1830)

Adolf Eugen Fick
(1829-1901)

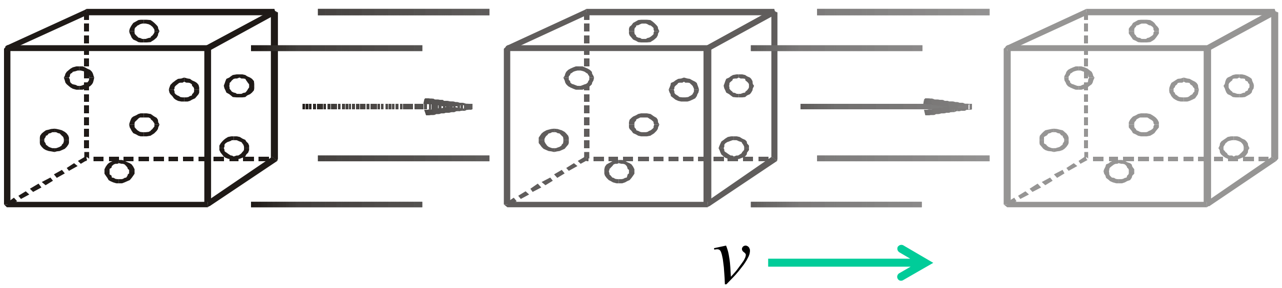
Lars Onsager)
(1903-1976)

transport phenomena concerns the exchange of **mass**, **energy**, and **momentum** between systems

CARRIER:

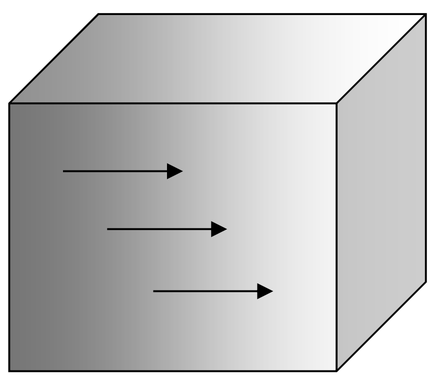
- **particles** (atoms, molecules and ions), *(matter, energy, momentum)*
- **electrons**,(*energy, momentum)*
- **fotons**,. *(energy)*

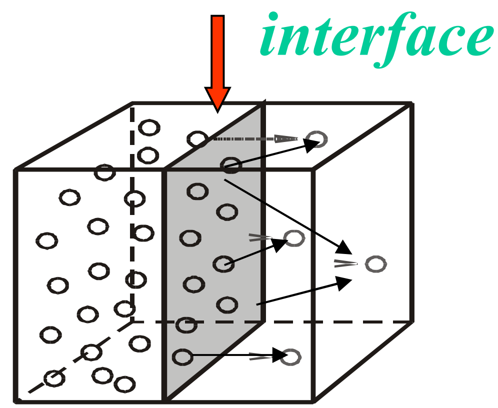
Convective transfer:



$$\frac{\Delta m}{\Delta t} = A_s \cdot \rho \cdot v$$

Conductive transfer:



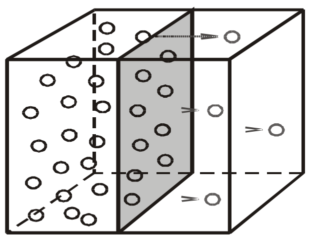


Transmitting transport

Basic quantities:

→ **flux** of extensive quantities

→ **Driving force** (intensive quantities

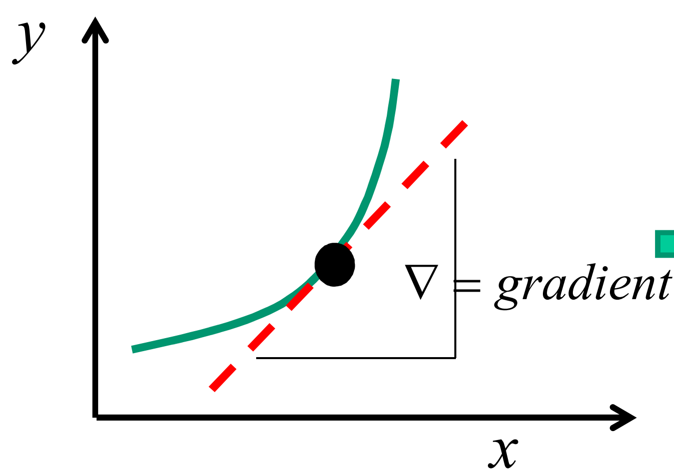


Flux is the trnsfer rate per unit area perpendicular to the direction of transfer

	Flux	**Driving force**
component:	$j_n \left[\mathrm{mol\, m^{-2} s^{-1}} \right]$	∇c
energy:	$j_U \left[\mathrm{J}\; m^{-2} s^{-1} \right]$	∇T
momentum:	$j_i \left[\mathrm{kg}\; m^{-1} s^{-2} \right]$	∇v

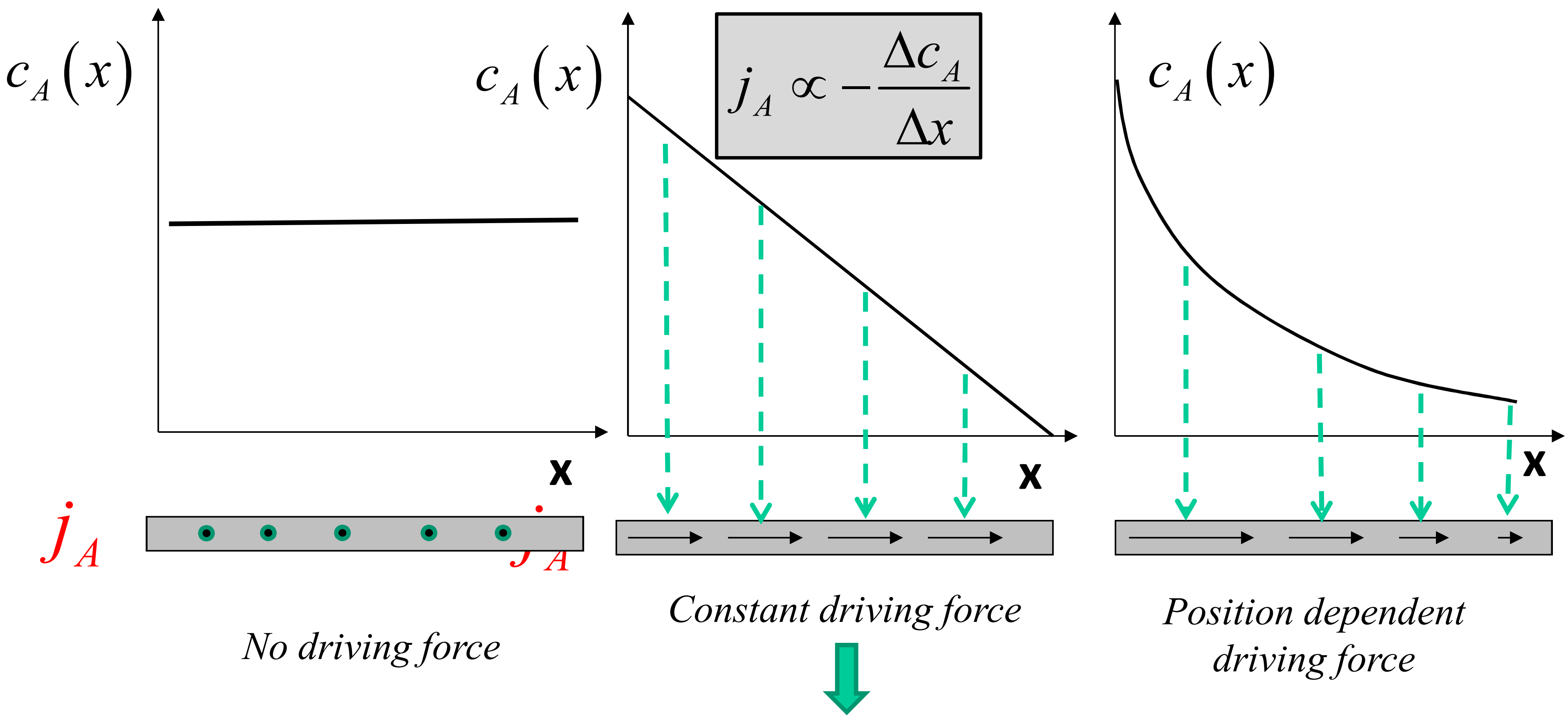
∇ = *gradient*

diffusion,
Heat conduction,
rheology,



gradient of intensive quantities.

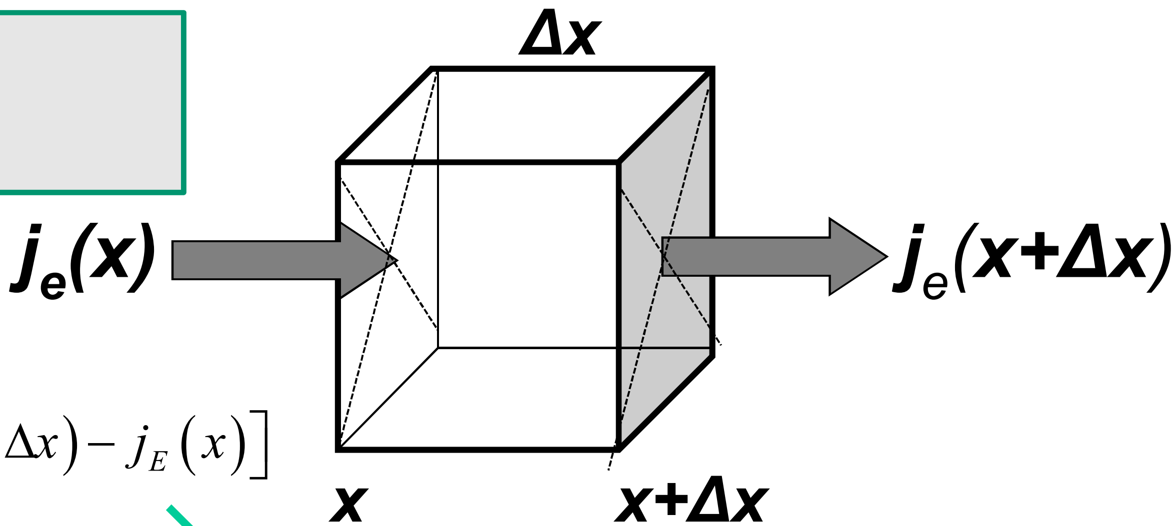
Flux is proportional to the gradient of intensive quantity



Steady state

Balance equation

$$\boxed{\frac{\Delta E}{\Delta t} = I_{in} + I_{out} = I}$$



$$I = \left.\frac{\Delta E}{\Delta t}\right|_{(\Delta x)^3} = -(\Delta x)^2\left[j_E(x+\Delta x) - j_E(x)\right]$$

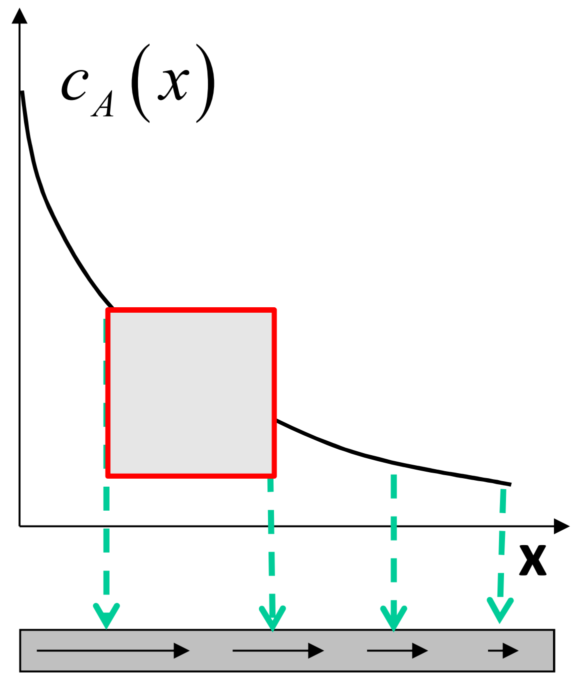
$$\frac{\Delta \rho_E}{\Delta t} = \frac{1}{V}\frac{\Delta E}{\Delta t} = \frac{1}{(\Delta x)^3}\cdot\frac{\Delta E}{\Delta t}$$

$$\frac{\Delta \rho_E}{\Delta t} = -\frac{j_E(x+\Delta x) - j_E(x)}{\Delta x}$$

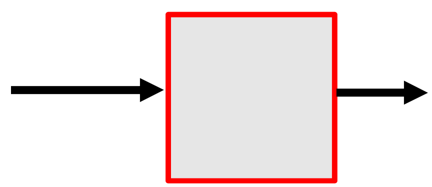
Continuity equation:

$$\boxed{\frac{\Delta \rho_E}{\Delta t} = -\nabla j_E}$$

$$\nabla j_E \equiv \frac{\Delta j_E}{\Delta x}$$



$$\frac{\Delta\rho_E}{\Delta t} = -\nabla j_E$$



$$\nabla j_E < 0 \qquad \frac{\Delta\rho_E}{\Delta t} > 0$$

Gradient of driving force

$$\nabla j_E > 0 \qquad \frac{\Delta\rho_E}{\Delta t} < 0$$

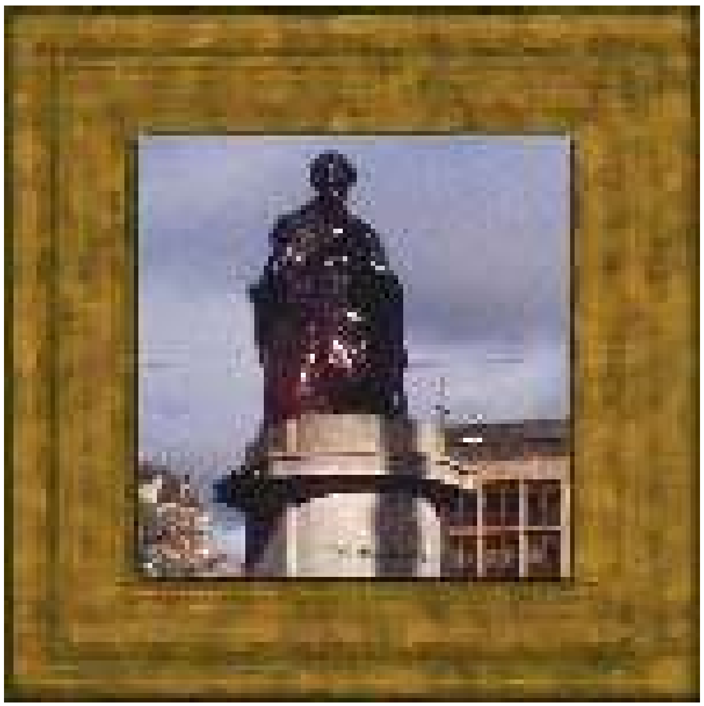
Crystals : fast diffusion

Graham's idea

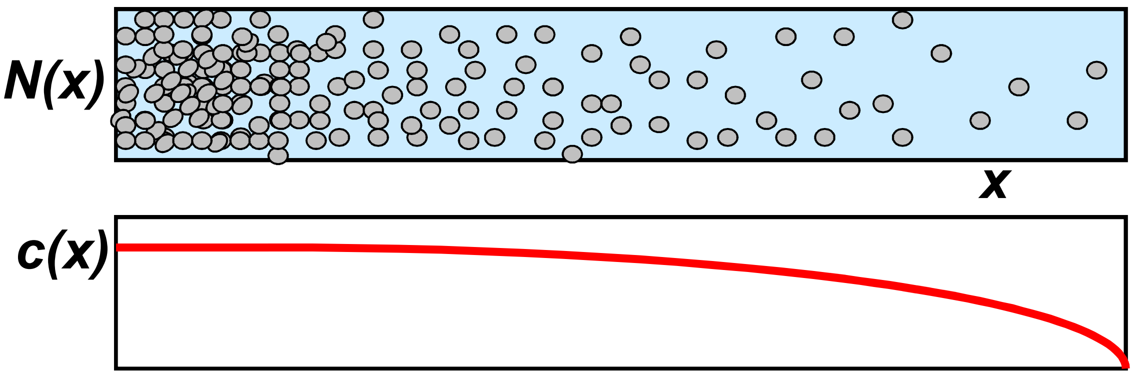
based on diffusion

Non-crystallyte **colloid** materials

slow diffusion



Diffusion: Fick laws



solution:

$$c(x,t)$$
$$c(\mathbf{r},t)$$

Fick I. law:

$$\mathbf{j}_A = -D \cdot \nabla c_A \quad \xrightarrow{1D} \quad j_A = -D \cdot \frac{\Delta c_A}{\Delta x}$$

-diffusional flux is proportioal to the gradient of concentration,

- flux is from higher concentration to lower concentration,

- $D > 0$

∇c is not the real driving force!

Fick's 2nd law

$$\frac{\Delta c_A(\mathbf{r},t)}{\Delta t} = -\nabla j_n$$

$$j_A = -D\nabla c_A$$

Fick I

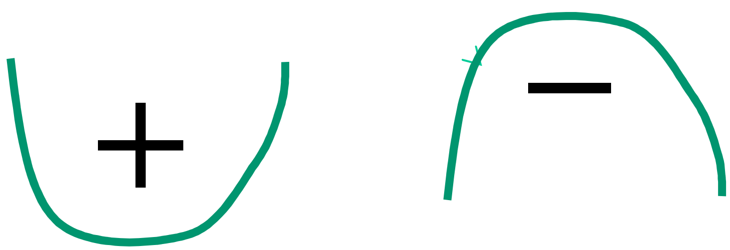
$$\frac{\Delta c_A}{\Delta t} = -\nabla\left(-D\nabla c_A\right)$$

$$\boxed{\frac{\Delta c_A}{\Delta t} = D\nabla^2 c_A}$$

Fick II

$\nabla^2 c$

curvature



convex

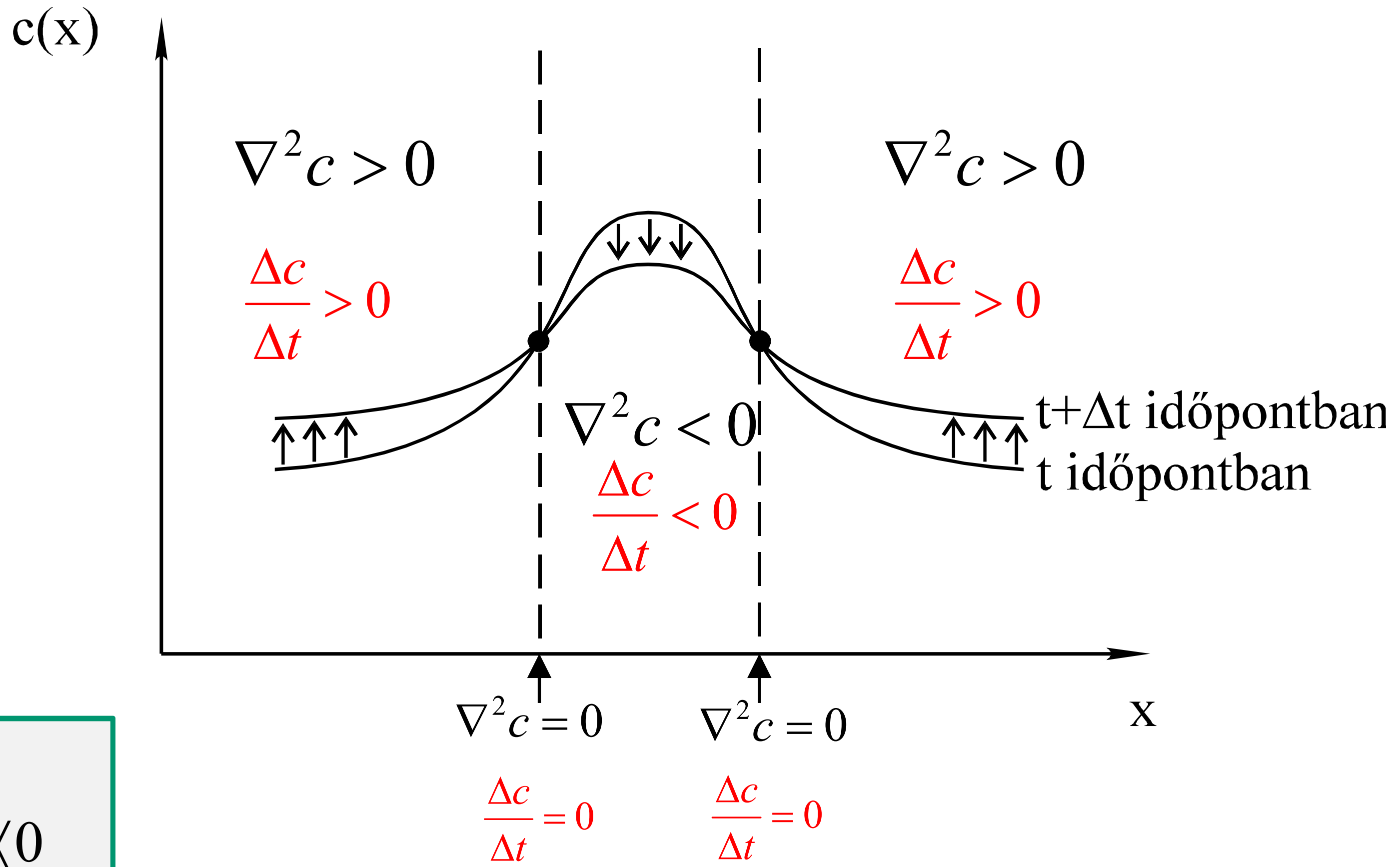
concave

$$j_A = -D \cdot \frac{\Delta c_A}{\Delta x}$$

Fick I. law

$$\left(\frac{\Delta c_A}{\Delta t}\right)_x = D\nabla^2 c_A$$

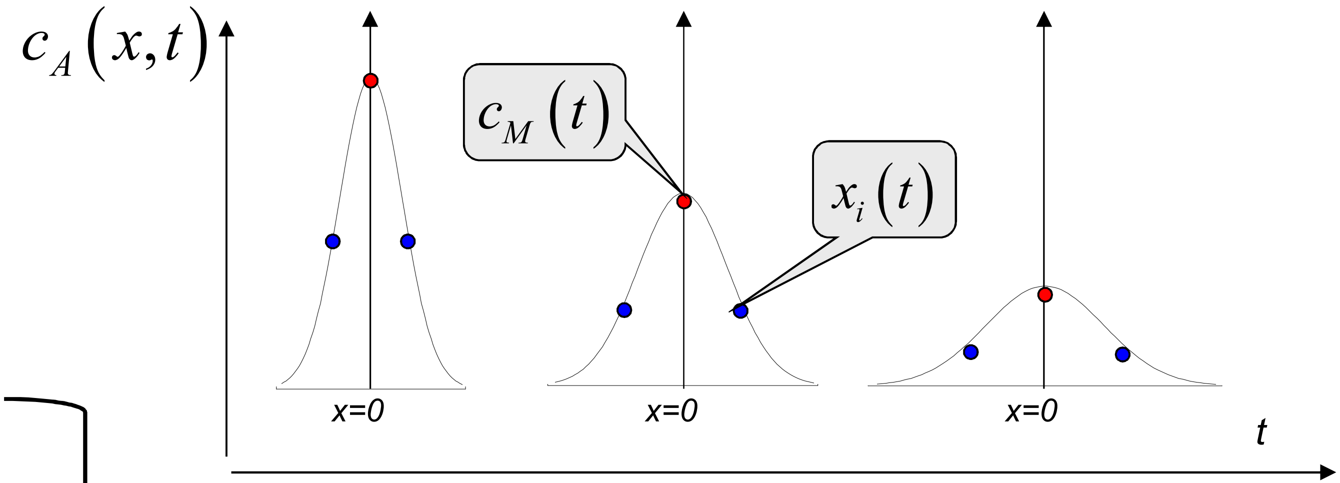
Fick II. law



$$\frac{\Delta}{\Delta t} \cdot \left|\nabla^2 c_A\right| \langle 0$$

„osculation law”

Free diffussion



$$c_M(t) = \frac{c_o \delta_x}{(4\pi D)^{1/2}} \cdot t^{-1/2}$$

$$x_i(t) = \sqrt{2D} \cdot t^{1/2}$$

$$c_i(t) = c_M(t) \cdot \frac{1}{\sqrt{e}}$$

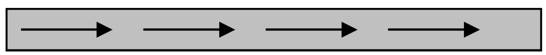
Characteristic distances scales with the square root of time!

Diffundáló anyag	Közeg	D, m^2/s
I_2	hexán (L)	$4{,}05 \cdot 10^{-9}$
I_2	benzol (L)	$2{,}13 \cdot 10^{-9}$
H_2O (L)	H_2O (L)	$2{,}25 \cdot 10^{-9}$
H_2O (V)	H_2O (V)	$2{,}80 \cdot 10^{-5}$
NH_3 (L)	H_2O (L)	$1{,}49 \cdot 10^{-9}$
NH_3 (V)	H_2O (V)	$1{,}98 \cdot 10^{-5}$
H^+	H_2O (L)	$9{,}30 \cdot 10^{-9}$
OH^-	H_2O (L)	$5{,}30 \cdot 10^{-9}$
H_2 (V)	Fe (S)	$1{,}10 \cdot 10^{-13}$
Al (S)	Cu (S)	$1{,}30 \cdot 10^{-34}$

12.2.1. TÁBLÁZAT ■ Néhány anyag diffúziós együtthatója 20 °C-on

Concentration profile at steady state diffusion

j_A *Steady state*

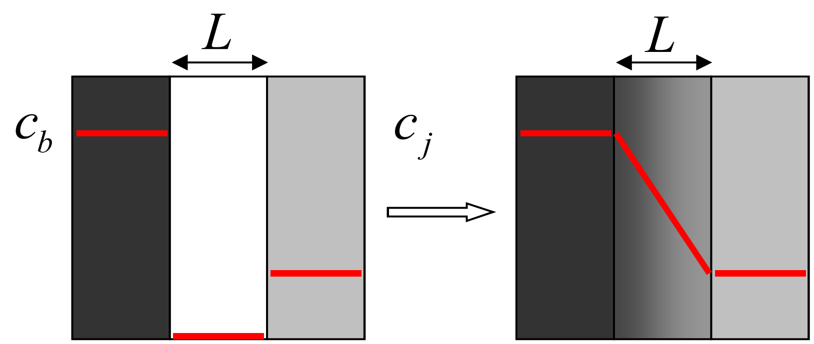


$$\frac{\Delta c_A}{\Delta t} = -\nabla j_n \Leftarrow \left(\frac{\Delta c_A}{\Delta t}\right)_x = D\nabla^2 c_A$$

$$\nabla j_n = 0 \qquad \frac{\Delta c_A}{\Delta t} = 0$$

$$\nabla^2 c_A = 0$$

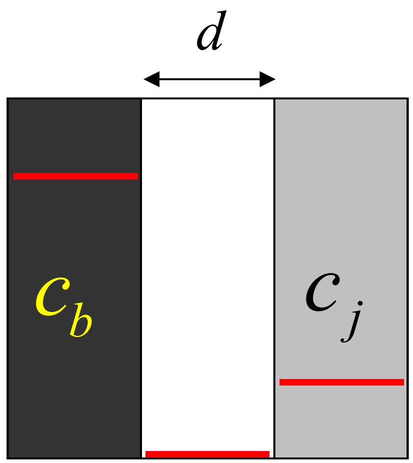
$$\nabla c_A = const.$$



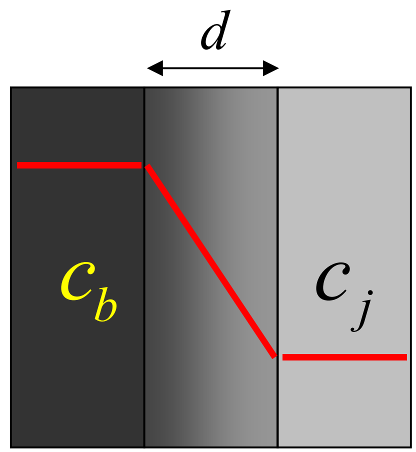
$$c(x) = -\frac{c_b - c_j}{L} x + c_b$$

Linear concentration - position dependence!

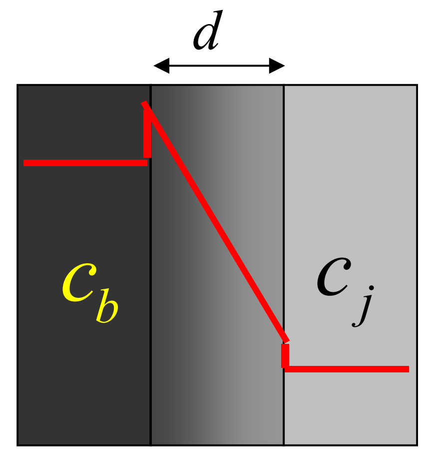
Concentration profile across a membrane at steady state



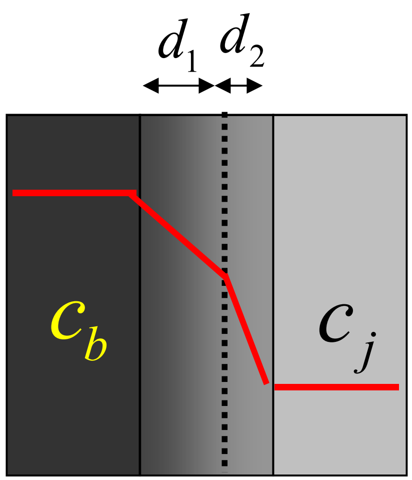
$K_m = 0$



$K_m = 1$



$K_m > 1$



$D_1 > D_2$

$K_m = 1$

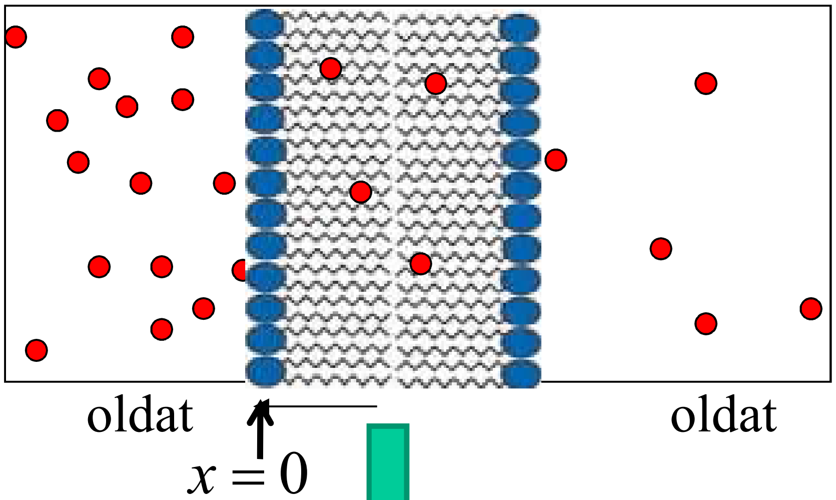
$$K_m = \frac{c_{b,mebrane}}{c_b}$$ Partition coefficient

$$j_{\mathbf{n,1}} = j_{\mathbf{n,2}}$$

$$-D_1 \left(\nabla c\right)_1 = -D_2 \left(\nabla c\right)_2$$

Composite membrane

Partition between membrane and solution

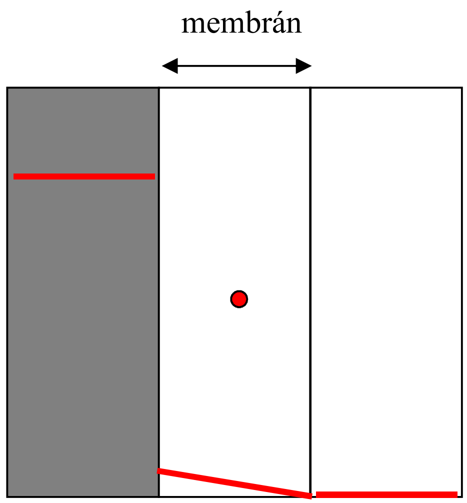


$$K_m = \frac{c_{b,mebrane}}{c_b}$$ Partition coefficient

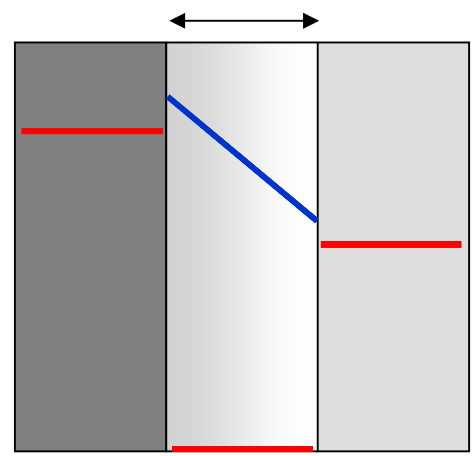
$$c_m\left(x=0\right) = K_m \cdot c_o\left(x=0\right)\cdot$$

Different solubility K_m

$$\boxed{c\left(x\right) = -K_m \frac{c_b - c_j}{d} x + K_m \cdot c_b}$$



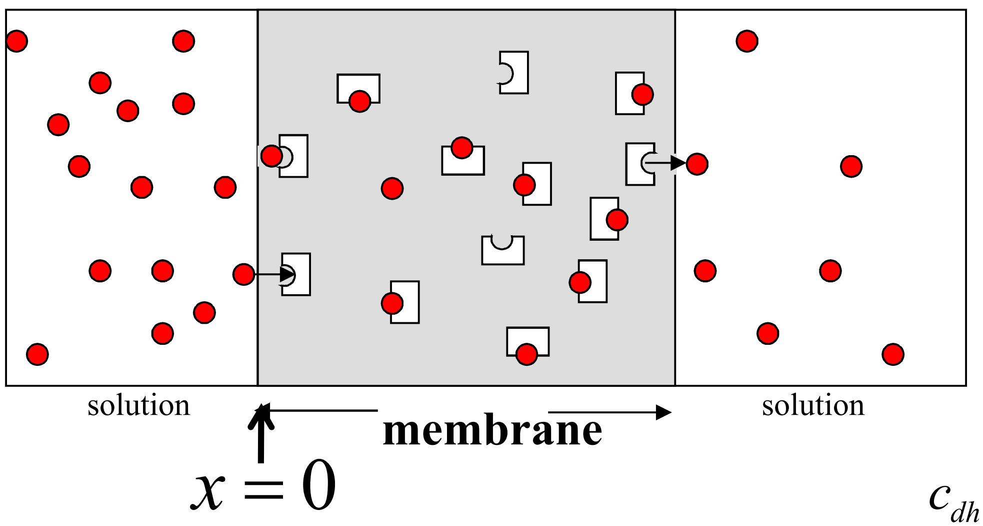
$K_m << 1$



$K_m > 1$

Facilitated diffusion

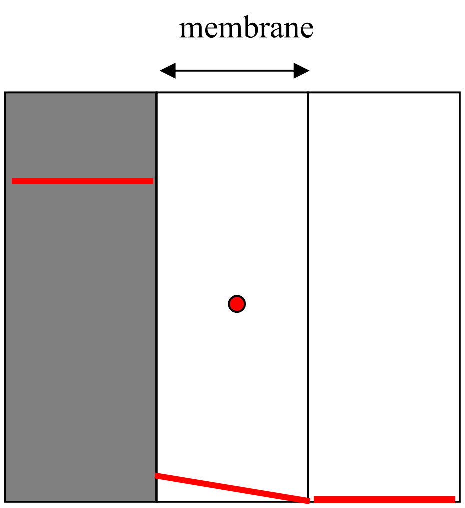
molecule c_d — complexing agant c_h — molecule-complex c_{dh}

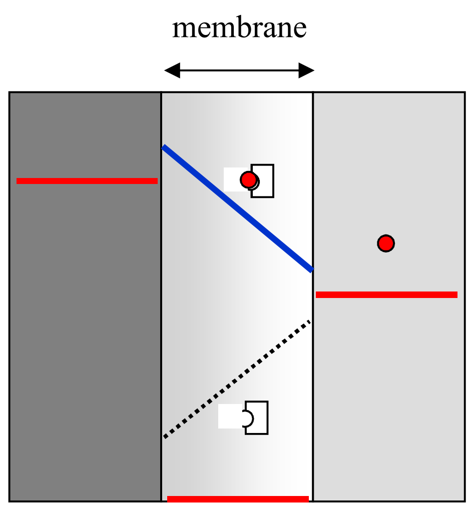


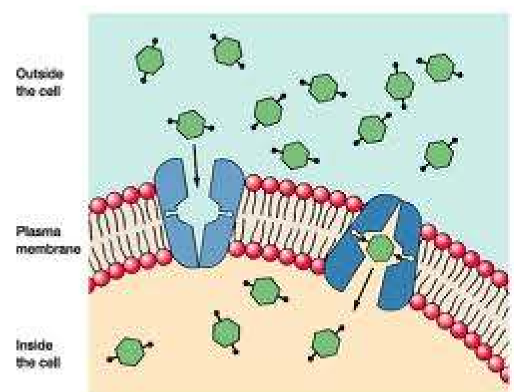
$$D + H = DH$$

$$K_k = \frac{[DH]}{[D][H]}$$

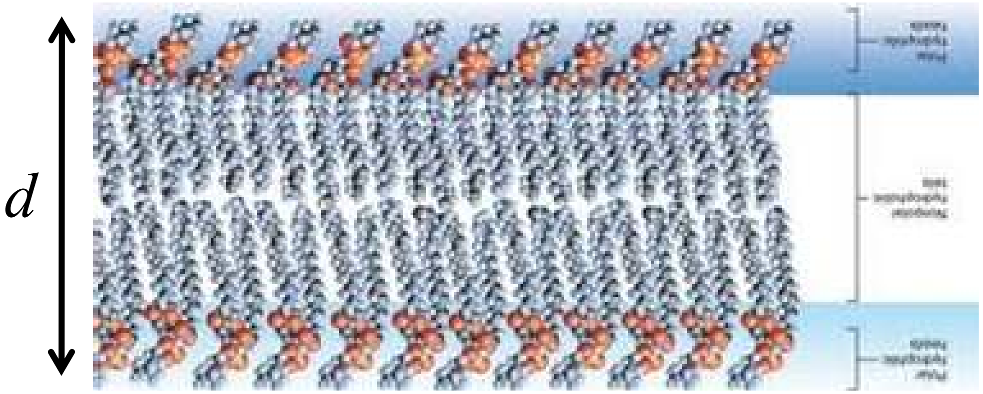
$$c_{dh}(x=0) = K_k \cdot c_d(x=0) \cdot c_h(x=0)$$







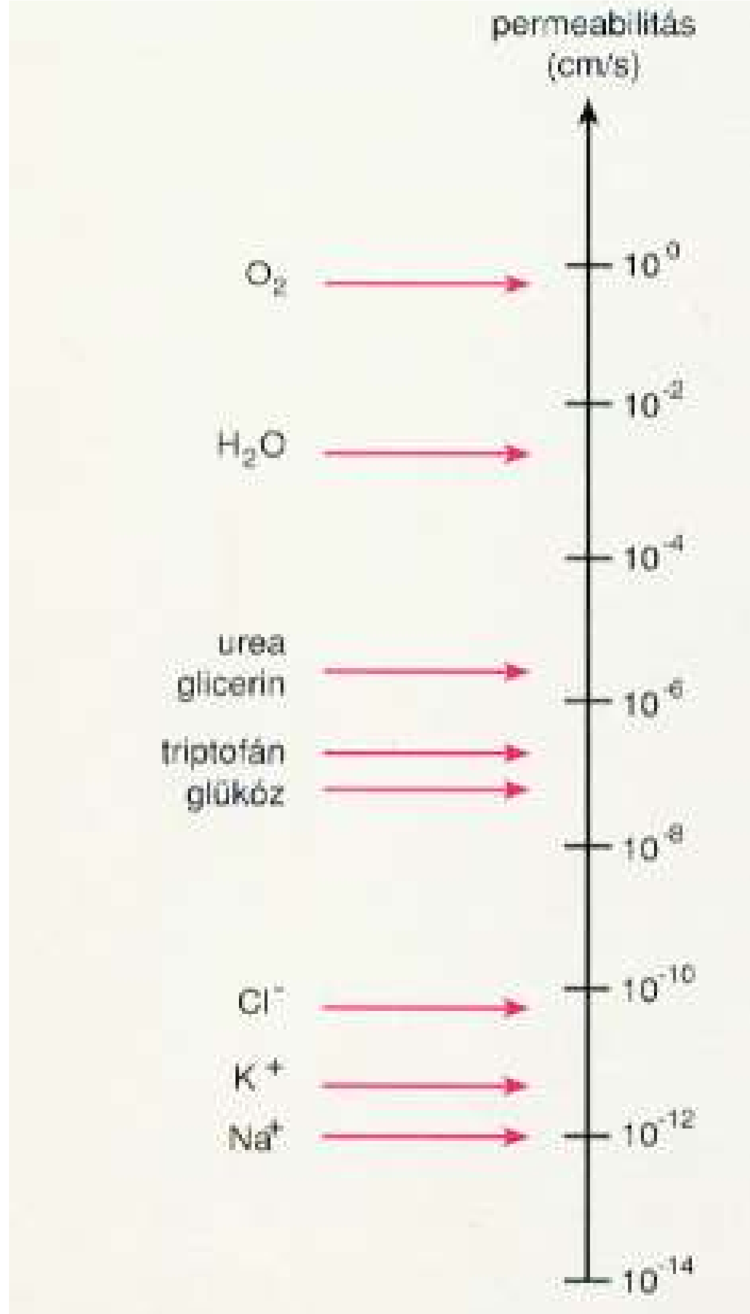
Membrane permeability: P_{erm}



$$j_n = -D\nabla c \qquad \nabla c = \frac{K_m\left(c_j - c_b\right)}{d} = -\frac{K_m \Delta c}{d}$$

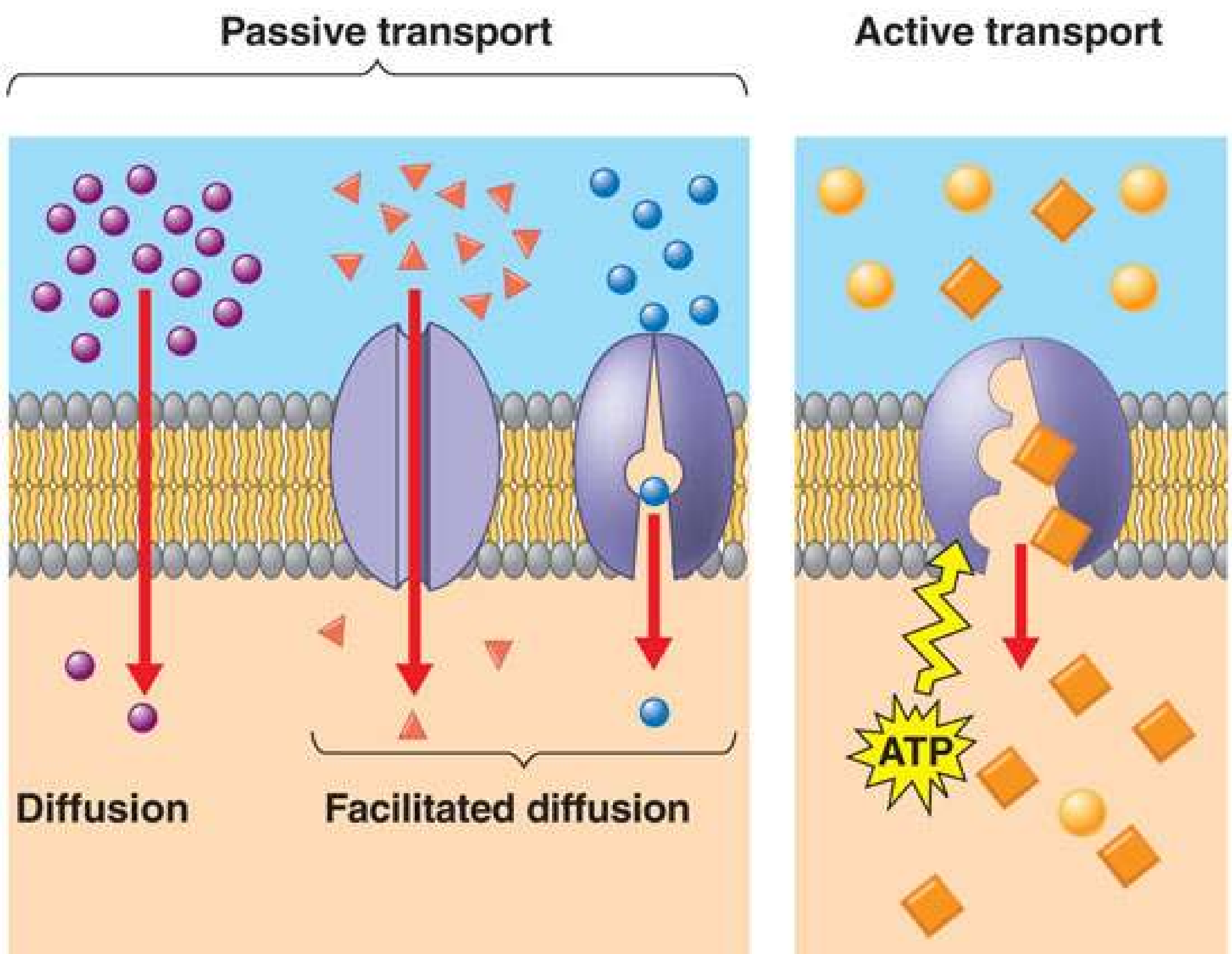
$$\boxed{P_{erm} = \frac{j_n}{\Delta c} = \frac{K_m D}{d}}$$

K_m*: partition coefficient*



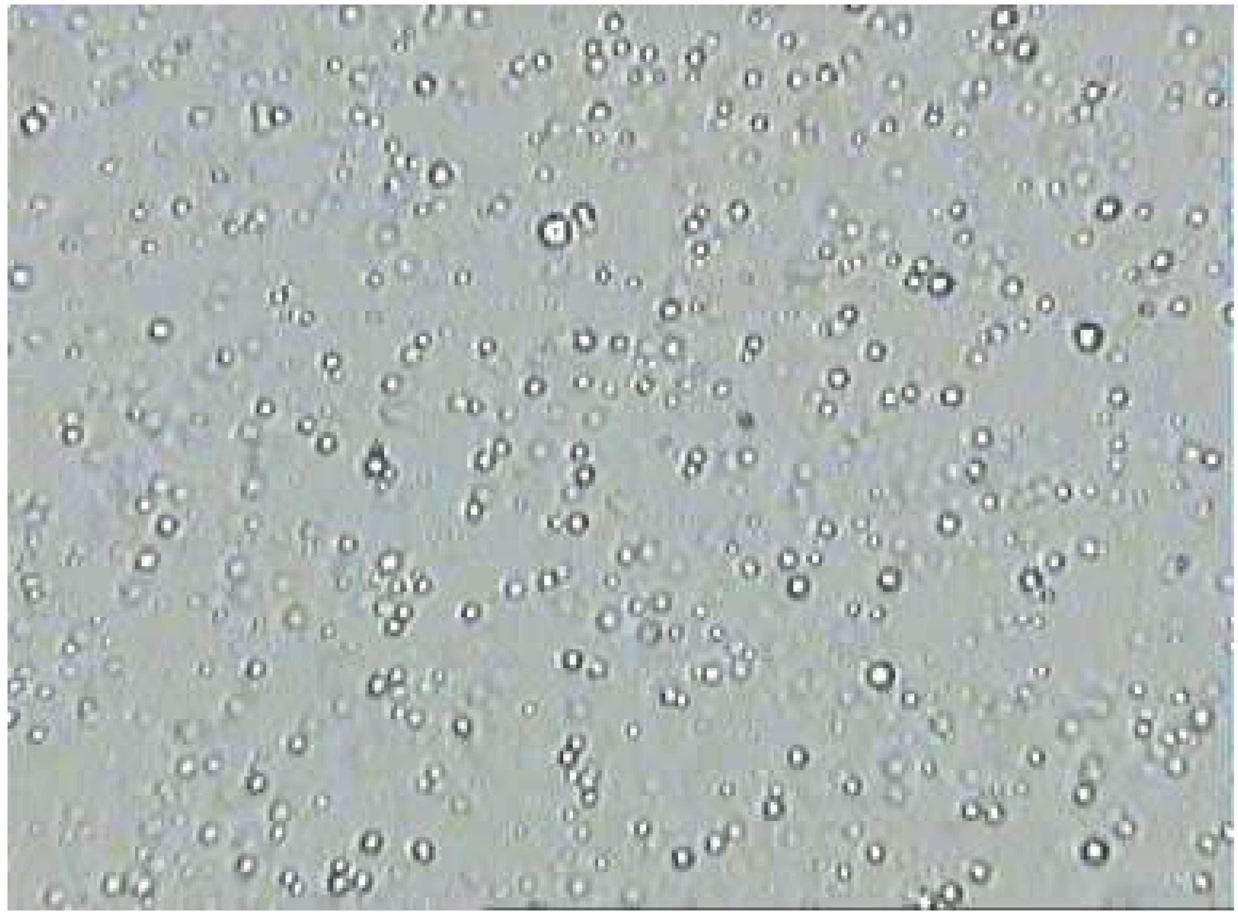
III.25. ábra. Mesterséges membránok kis molekulákra vonatkozó permeabilitási állandói

Active and passive transport



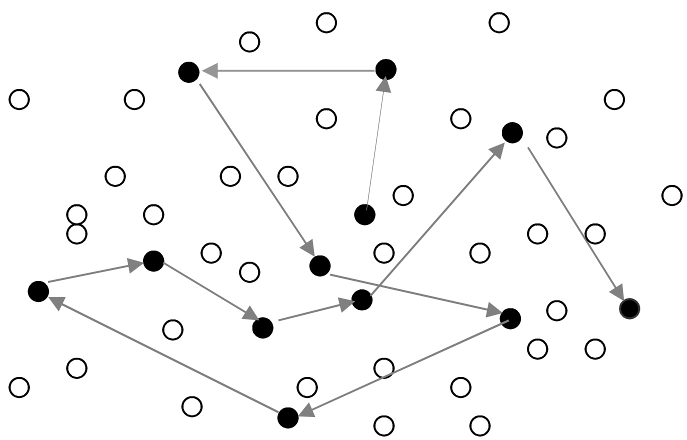
Molecular theory of diffusion: Brownian motion

Robert Brown
(1773-1858)



Fett droplett in milk. Dro size: 0.5 - 3 µm

Brownian motion

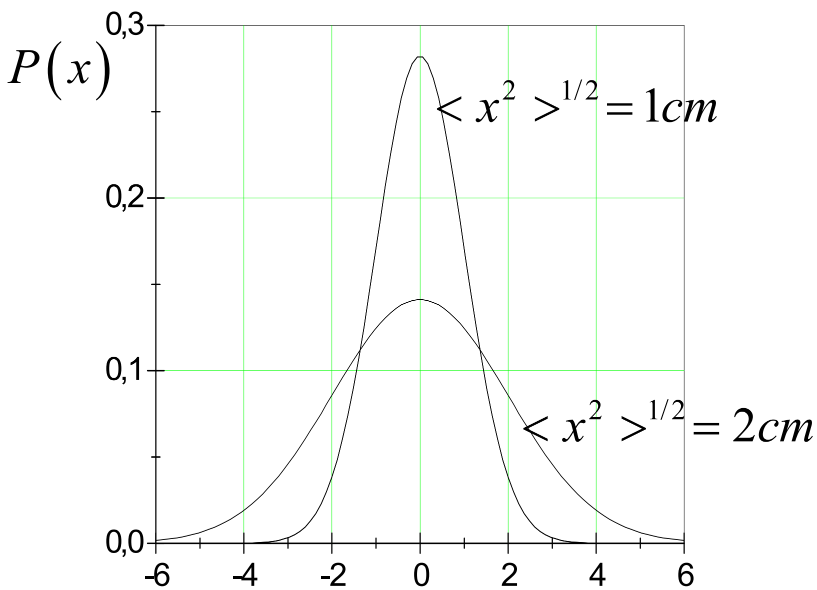


Due to collisions

1D	$< x^2 >= 2Dt$
2D	$< \sigma^2 >= 4Dt$
3D	$< r^2 >= 6Dt$

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

Stokes-Einstein law



Transport of internal energy

radiation

Heat conduction

Heat convetion

Loss of metabolic heat?

$$Q_{lost} = Q_{radiation} + \underbrace{Q_{convective} + Q_{conductive}}_{25\ \%} + Q_{evaporation} + Q_{breathing}$$

54-60 %

7 %

14 %

For unit area

radiation

Wien law: $R = \varepsilon\sigma T^4$ ε : emission

Stefan-Boltzmann const.: $\sigma = 5.67 \cdot 10^{-8}\ W/m^2K^4$

$$-\frac{\Delta Q_{sugárzó}}{\Delta t} = R \cdot A_s = \varepsilon\sigma T^4 \cdot A_s$$

$A_s = 1.85\ m^2$ *Average surface area of human*

$\varepsilon \cong 1$ Human skin

$$\frac{\Delta Q_{sugárzó}}{\Delta t} = \left.\frac{\Delta Q}{\Delta t}\right|_{nyereség} - \left.\frac{\Delta Q}{\Delta t}\right|_{veszteség}$$

$$\boxed{R = \varepsilon\sigma\left(T_{test}^4 - T_{környezet}^4\right)}$$

$\varepsilon_1 = \varepsilon_2 = \varepsilon$

material	emission
Human skin	0.95 – 0.99
wood	0.99
concrete	0.95
brick	0.92

Heat conduction: Fourier laws

$$j_Q = -k_T \frac{\Delta T}{\Delta x}$$

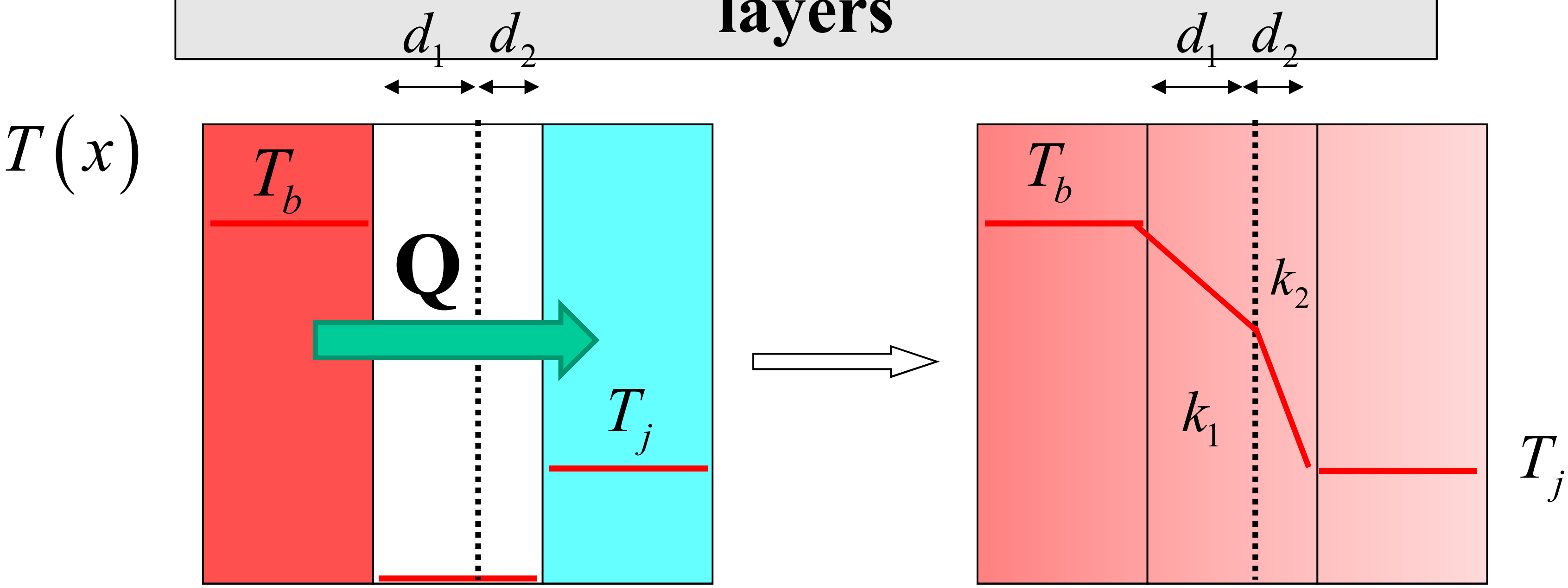
$$\boxed{\frac{\Delta Q}{\Delta t} = -k_T \cdot A_s \cdot \frac{\Delta T}{\Delta x}}$$

$$\frac{\Delta T}{\Delta t} = \alpha \nabla^2 T$$

thermal conductivity

material	T/K	$k_T \, / \, Wm^{-1}K^{-1}$
air	300	0.025
water	300	0.609
fett	298	0.21
blood	298	0.642
skin	310	0.442

Staady state heat consuction between layers



$$j_U = -k_1 \frac{\Delta T}{d_1} = -k_2 \frac{\Delta T}{d_2} = const. \Rightarrow \boxed{k_1 > k_2}$$

Convective heat exchange (1)

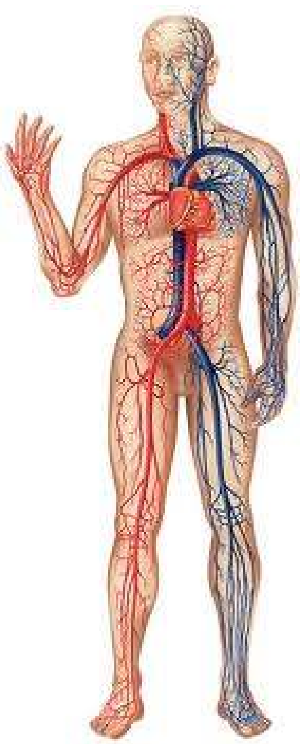
$$-\frac{1}{A_s}\frac{\Delta Q_{convective}}{\Delta t} = h_c \cdot \left(T_{skin} - T_{air}\right)$$

h_c : for unit surface

W/m^2C^o

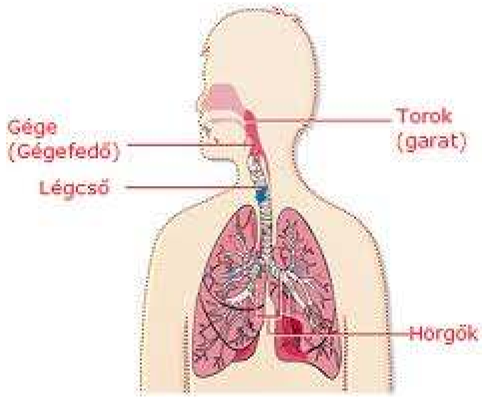
Speed of wind [m/s]	$h_c\left[W/m^2C^o\right]$
0,1	2,6
0,6	6,4
2,0	11,7
4,0	16,6

In wind: $h_c = 10{,}45 - v + 10v^{1/2}$ v Speed od wind in: *m/sec*



Heat exchange in the body (2)

$$-\frac{1}{A_s}\frac{\Delta Q_{bloodflow}}{\Delta t} = h_c \cdot \left(T_{blood} - T_{body}\right)$$



Heat lost by respiration (1)

volume: 500 ml
frequency: 12 – 14 / min

$$I_{air} = \frac{\Delta V_l}{\Delta t} \approx 0{,}1 \quad l \cdot s^{-1}$$

$$\boxed{-\frac{\Delta Q}{\Delta t} = \rho_l c_{p,l} \left(T_{ext} - T_{\text{int}} \right) \frac{\Delta V_l}{\Delta t}}$$

V_{sweat}

Heat lost by sweating (2)

Evaporation heat of water: $\Delta h_{evap.} = 2,25 \quad kJ / g$

$$-\frac{\Delta Q}{\Delta t} = \Delta h_{evap.} \cdot \left(\rho_{air}^{out} - \rho_{air}^{in}\right)\frac{\Delta V_{sweet}}{\Delta t}$$

(Rheos logos = rheology)

ΕΛΛΗΝΙΚΟΣ ΣΥΛΛΟΓΟΣ ΡΕΟΛΟΓΙΑΣ

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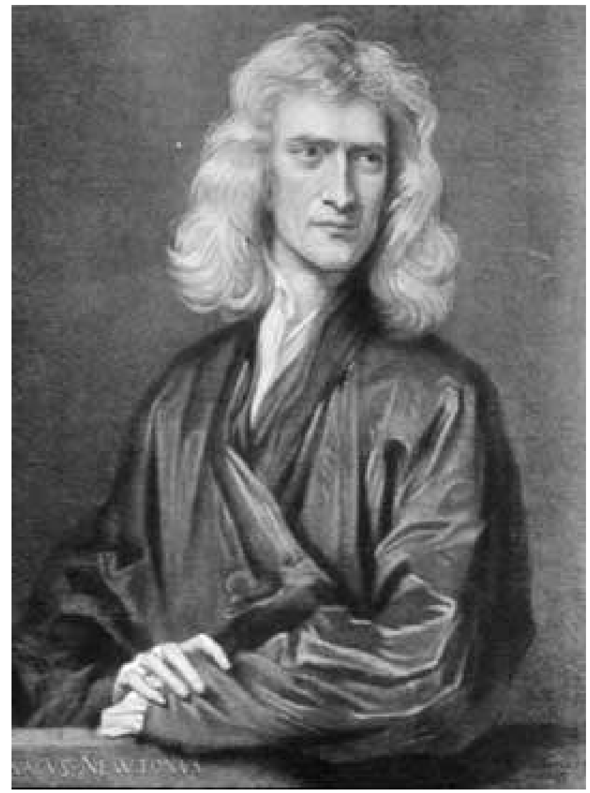
Τά πάντα ῥεῖ

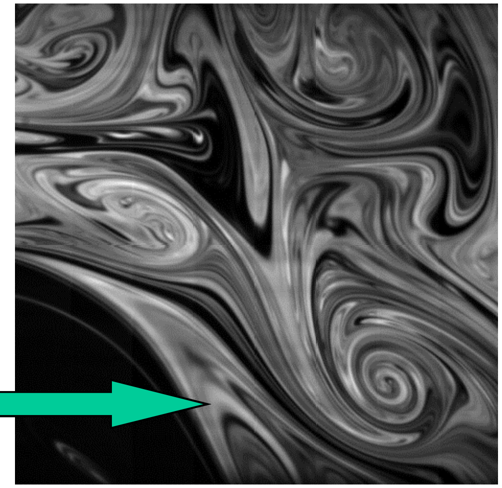
6ος π.Χ.

HELLENIC SOCIETY OF RHEOLOGY



Sir Isac Newton (1642-1727)

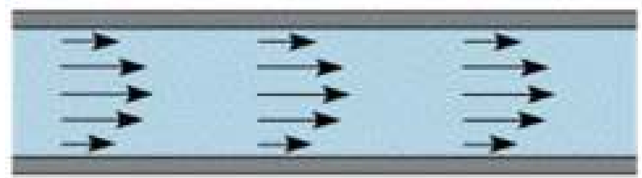
Two types of flow



Turbulent flow

$$R_e = \frac{v d \rho}{\eta}$$

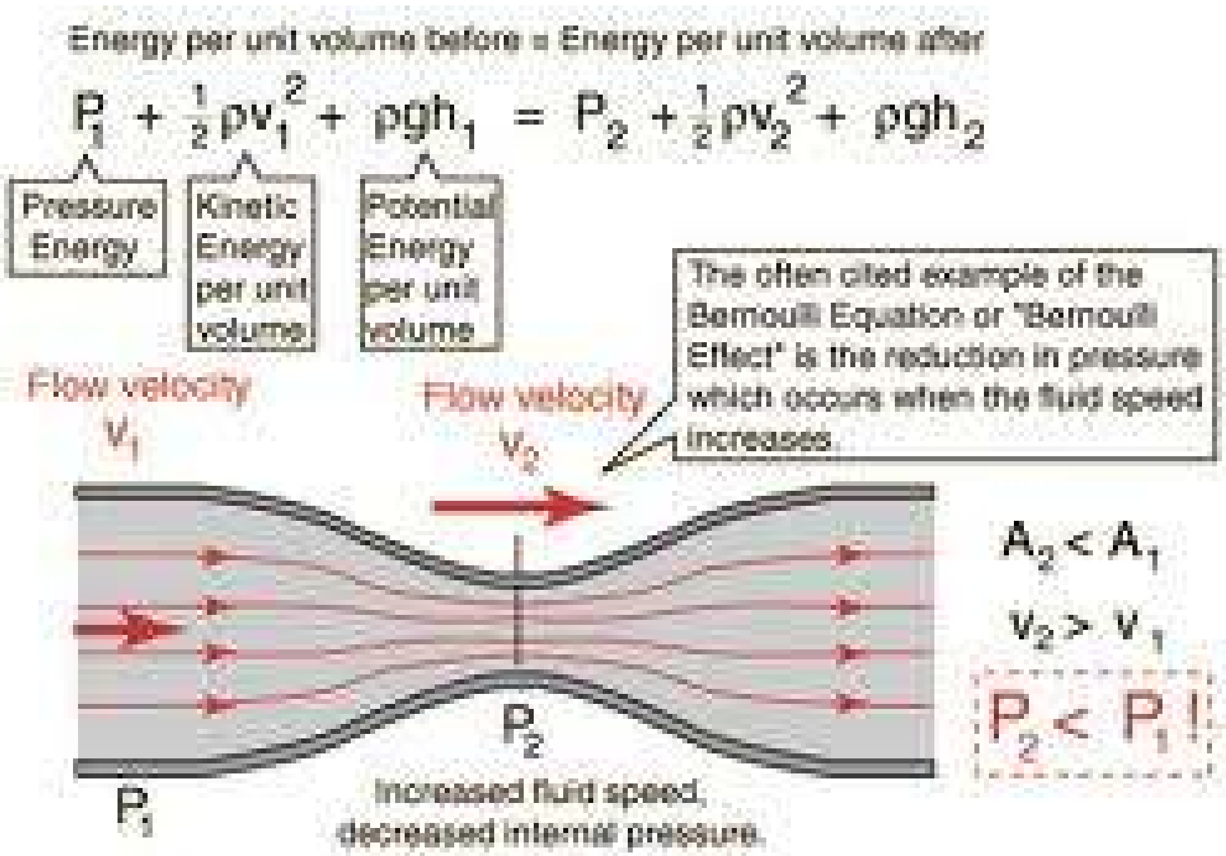
$$v_{kr} = R_e \cdot \frac{\eta}{\rho \cdot d}$$



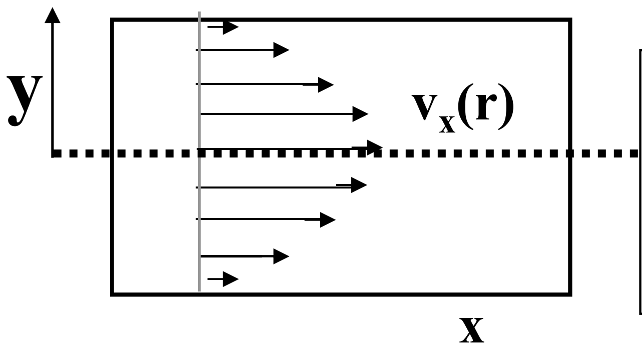
Laminar flow

$$R_e < 2100(?)$$

Bernoulli


Energy per unit volume before = Energy per unit volume after
$P_1 + \frac{1}{2}\rho v_1^2 + \rho g h_1 = P_2 + \frac{1}{2}\rho v_2^2 + \rho g h_2$
Pressure Energy
Kinetic Energy per unit volume
Potential Energy per unit volume
The often cited example of the Bernoulli Equation or "Bernoulli Effect" is the reduction in pressure which occurs when the fluid speed increases.
Flow velocity v_1
Flow velocity v_2
$A_2 < A_1$
$v_2 > v_1$
$P_2 < P_1$!
P_2
P_1
Increased fluid speed, decreased internal pressure.

RHEOLOGY



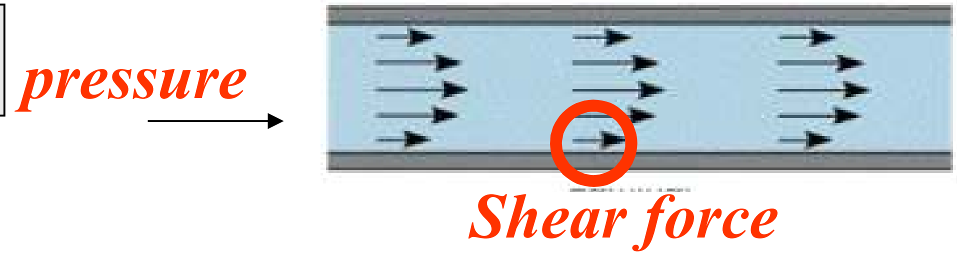
$$j_{mom} = -\eta \frac{\Delta v_x}{\Delta y}$$

$$\tau = \eta \frac{\Delta v_x}{\Delta y}$$

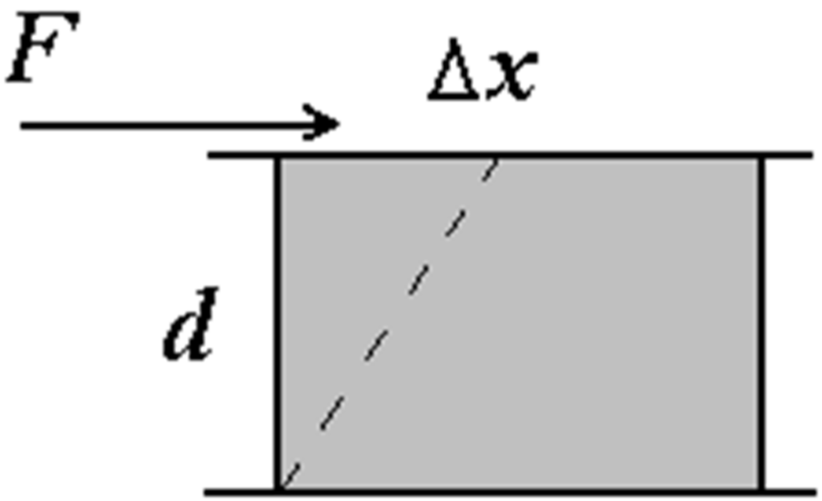
$$\tau = \eta \frac{\Delta v_x}{\Delta y}$$

$$[Pa] \qquad [Pa \cdot s] \qquad [s^{-1}]$$

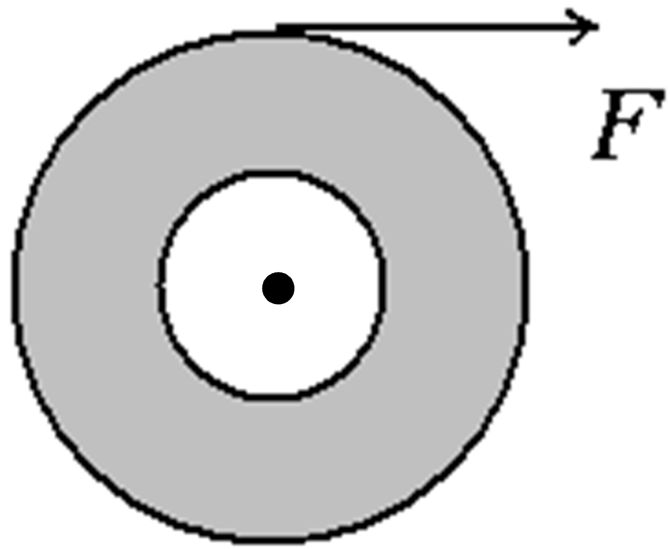
Fundamental quantities



shear: force acting on tangential direction and results in deformation



pure shear

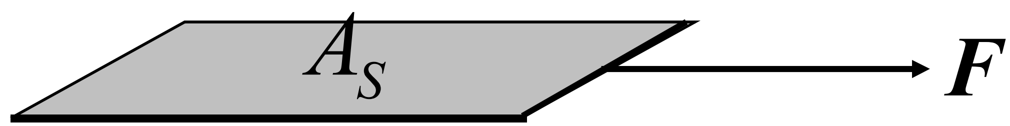


shear during rotation

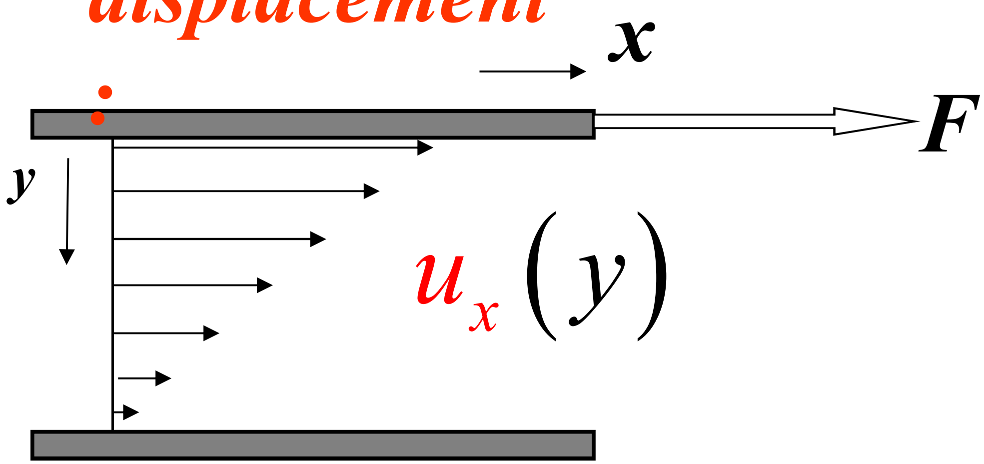
Fundamental quantities

Shear stress:

$$\tau = \frac{F}{A_S}$$



displacement

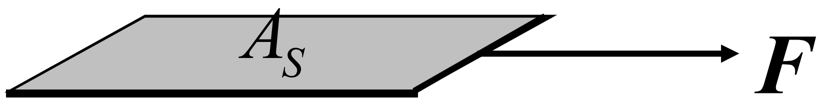


$$u_x(y)$$

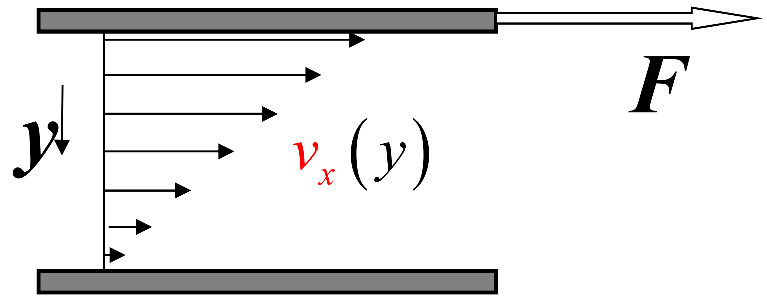
Deformation:

$$\gamma = \frac{du_x(y)}{dy}$$

shear stress:



velocity gradient:



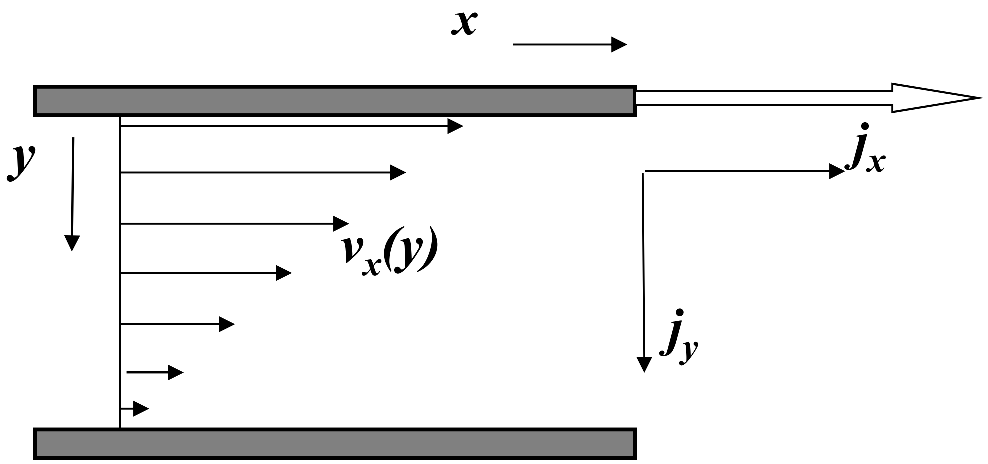
$$\tau = \frac{F}{A_S}$$

$$\frac{\Delta v_x}{\Delta y}$$

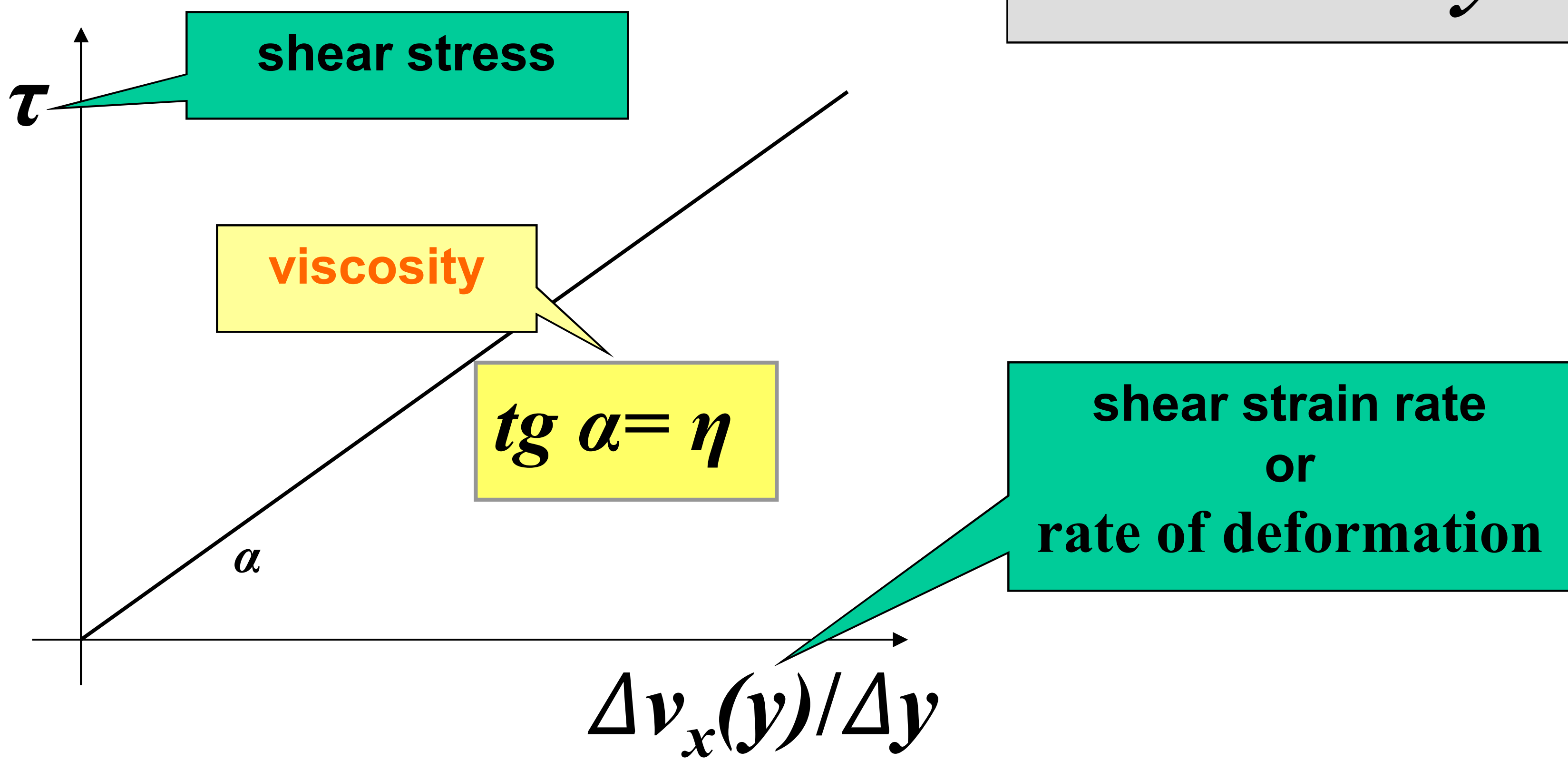
$$\tau = \eta \frac{\Delta v_x}{\Delta y}$$

Newton equation

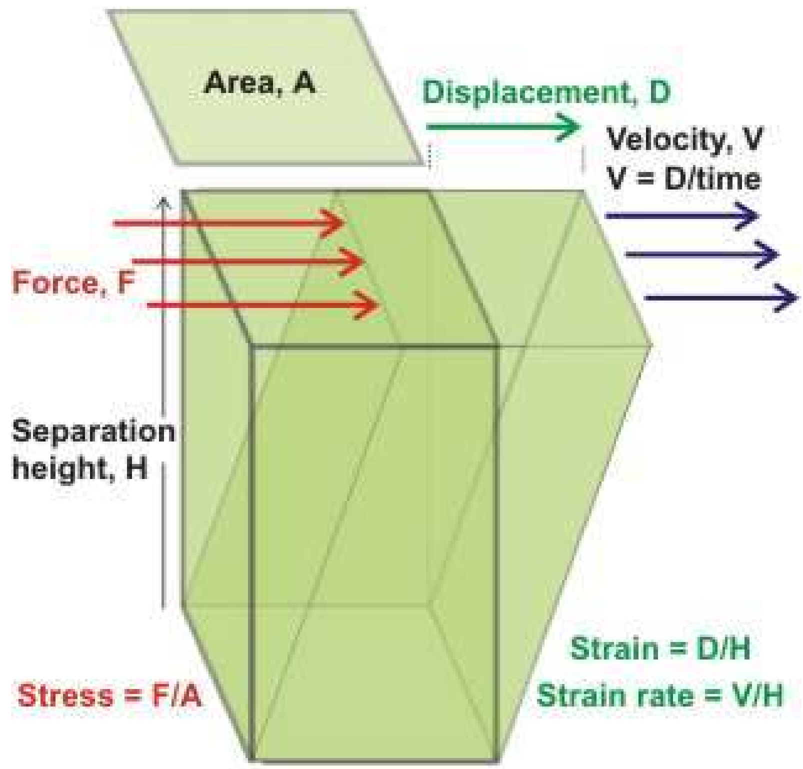
viscosity



$$\tau = \eta \frac{\Delta v_x}{\Delta y}$$



When a force is applied to a volume of material then a displacement (deformation) occurs. If two plates (area, A), separated by fluid distance (separation height, H) apart, are moved (at velocity V by a force, F) relative to each other, Newton's law states that the **shear stress** (the force divided by area parallel to the force, F/A) is proportional to the **shear strain rate** (V/H). The proportionality constant is known as the (dynamic) **viscosity** (η).



Viscosity is a property of matters describing their internal resistance to flow and may be thought of as a measure of molecular friction.

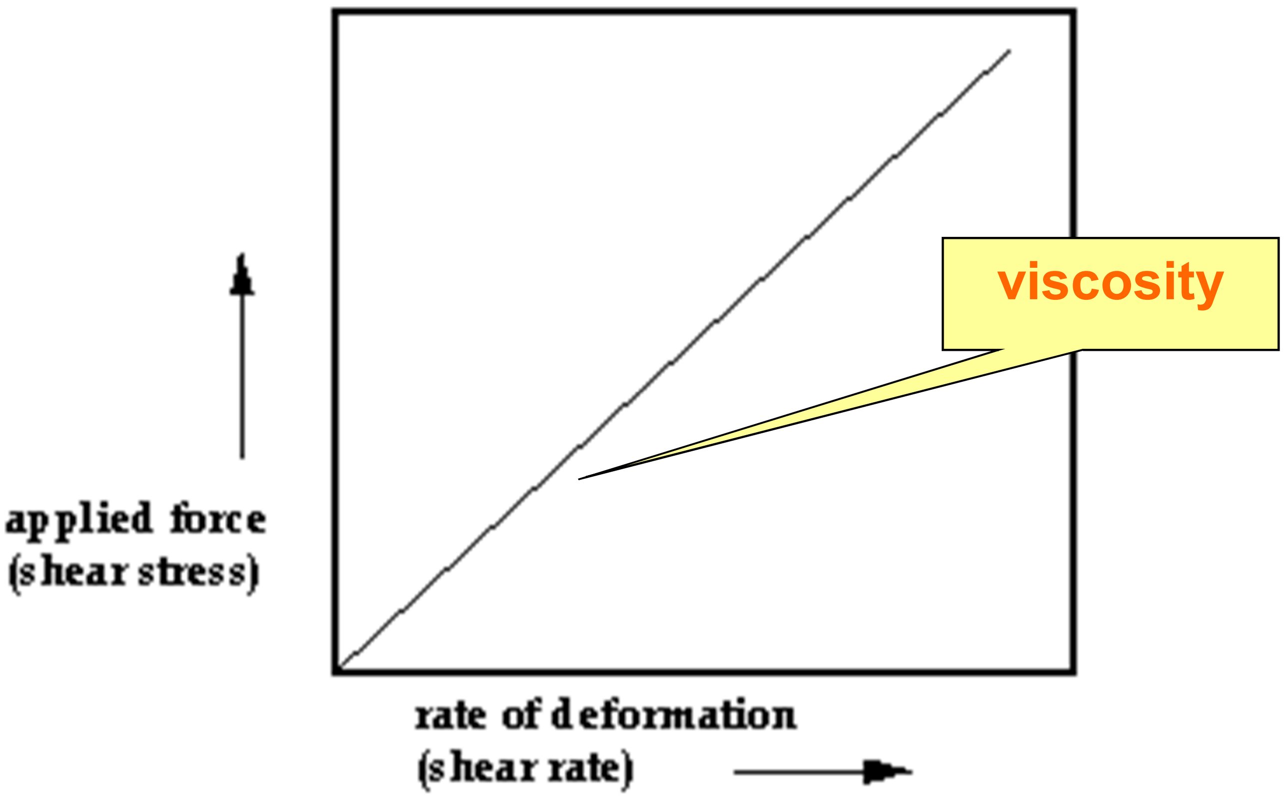
If the viscosity of a fluid is constant (neglecting temperature and pressure effects) it is said to be a Newtonian fluid.

Non-Newtonian fluids exhibit a variation of viscosity depending on gradients within the flow field, the history that a fluid 'particle' experiences on its flow path, etc.

Newtonian behaviour.

For ideal viscous materials, the rate of deformation is in proportion to the force applied. Deformation ceases when the applied force is removed. The apparent viscosity is constant with changing shear rates. This behaviour is typical of simple liquids such as water.

Flow curve

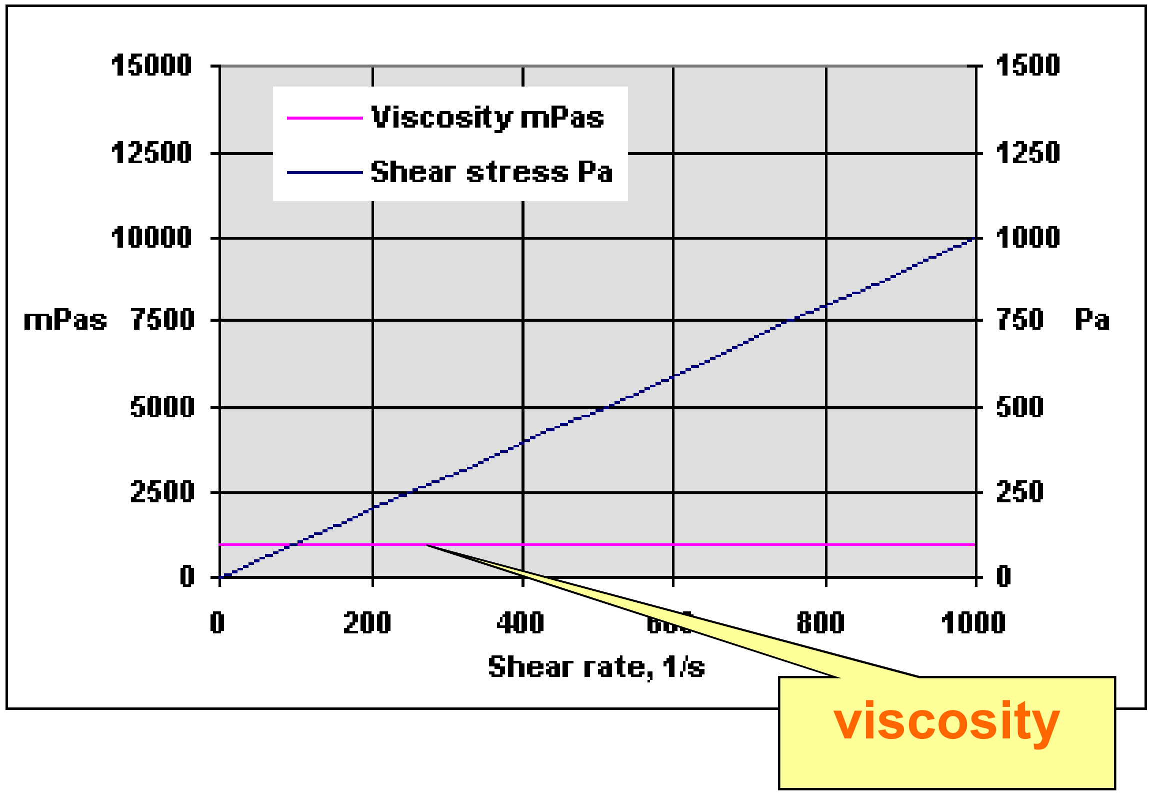


Newtonian fluids

The viscosity of a Newtonian fluid is dependent only on temperature but not on shear rate and time.

Examples:

- water
- milk
- sugar solution
- mineral oil



Dynamic viscosity is the commonly used form of viscosity, often abbreviated to just **viscosity**.
The units are either the *SI units of pascal seconds (Pa s)*

The old smaller cgs physical unit for dynamic viscosity is *poise* after Jean Louis Marie Poiseuille (1797-1869): 1 poise = 100 centipoise = 1 g/cms = 0.1 Pa·s.

Fluidity is the reciprocal of the viscosity (= $1/\eta$).

Kinematic viscosity is the dynamic viscosity divided by the density of the liquid (= η/ρ). The units are either the *SI units of meter squared per second ($m^2\ s^{-1}$) or the stoke (St).*

Gases (at 0 °C):

hydrogen 8.4×10^{-6} Pa·s

air 17.4×10^{-6} Pa·s

xenon 21.2×10^{-6} Pa·s

Liquids (at 20 °C):

ethyl alcohol 0.248×10^{-3} Pa·s

acetone 0.326×10^{-3} Pa·s

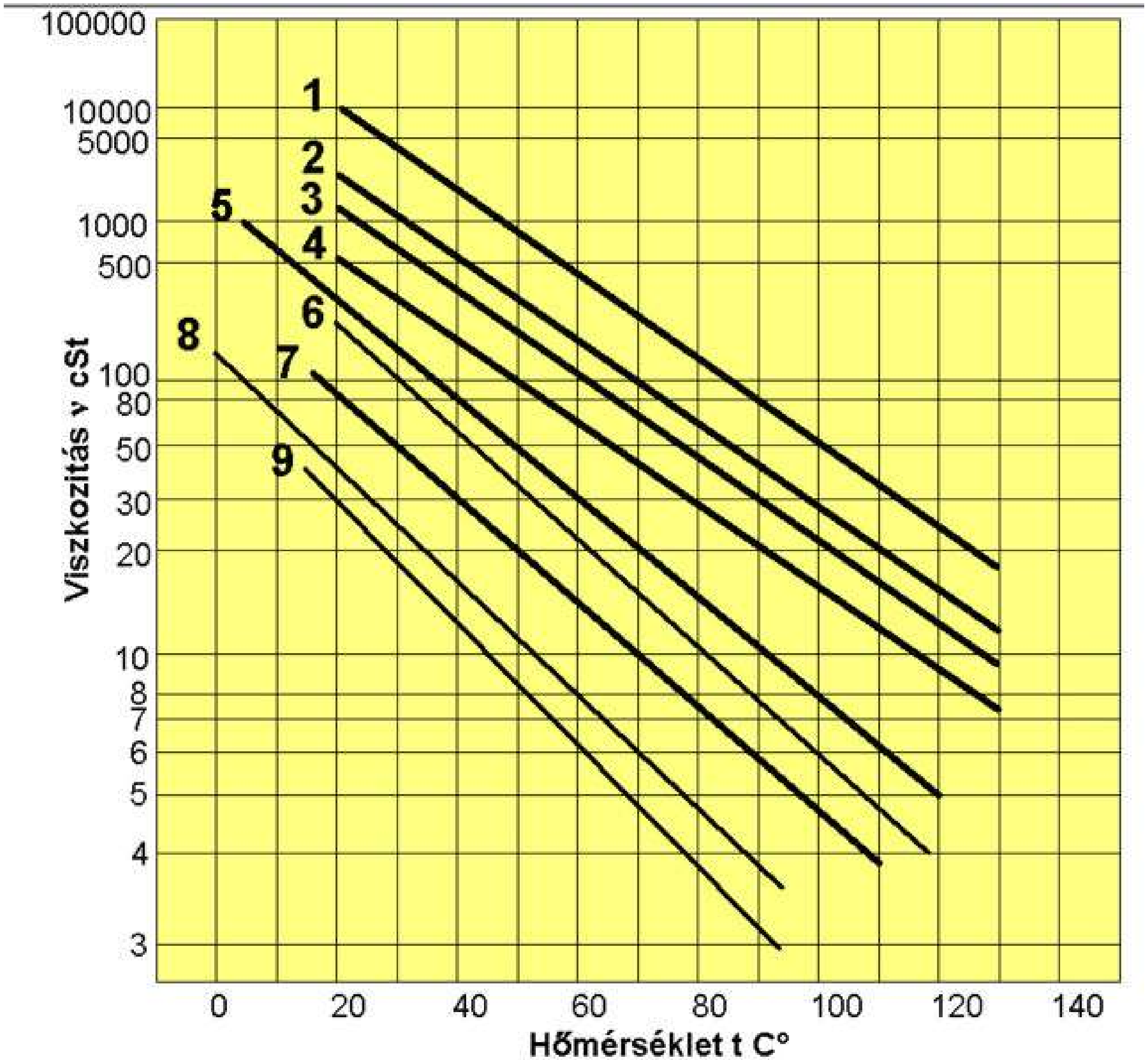
methanol 0.59×10^{-3} Pa·s

benzene 0.64×10^{-3} Pa·s

water1.025×10^{-3} Pa·s

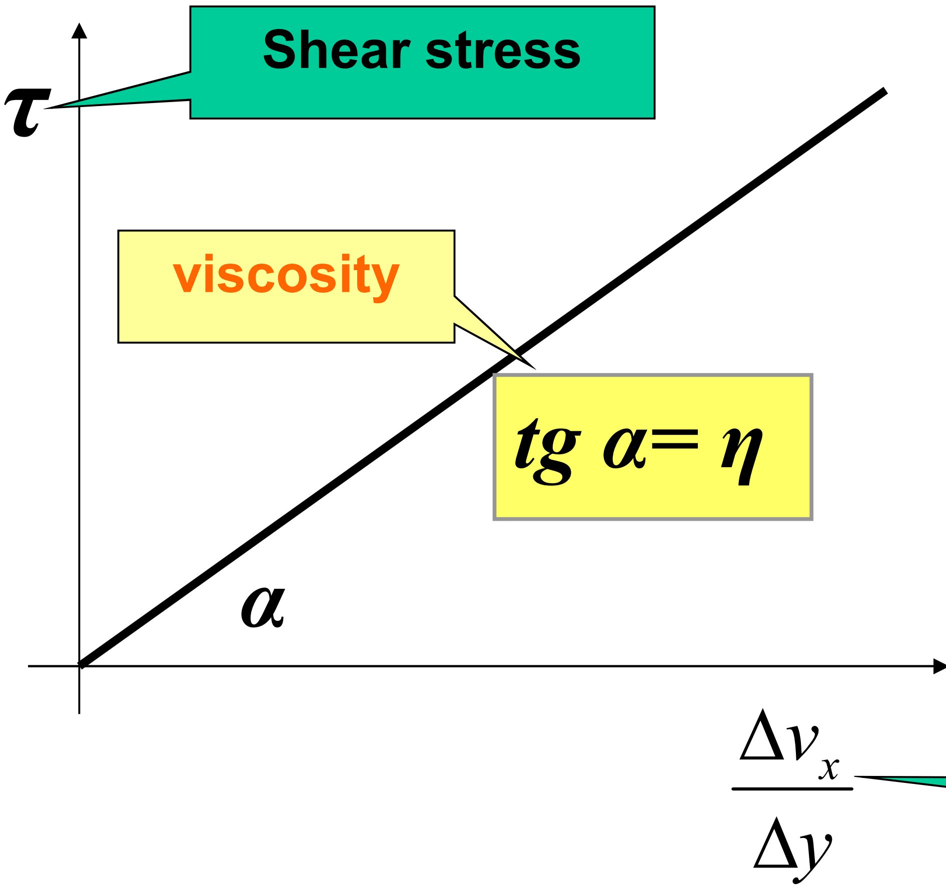
biofluid	**T/ °C**	**viscosity** $/ mPa \cdot s$
blood	37	4 (non Newtonian)
plasma	37	1,5
tear	37	0,73 – 0,97
air	20	$1,8 \cdot 10^{-2}$
sinovial fluid	20	$> 3 \cdot 10^{2}$ (non Newtonian)
liquor	20	1,02

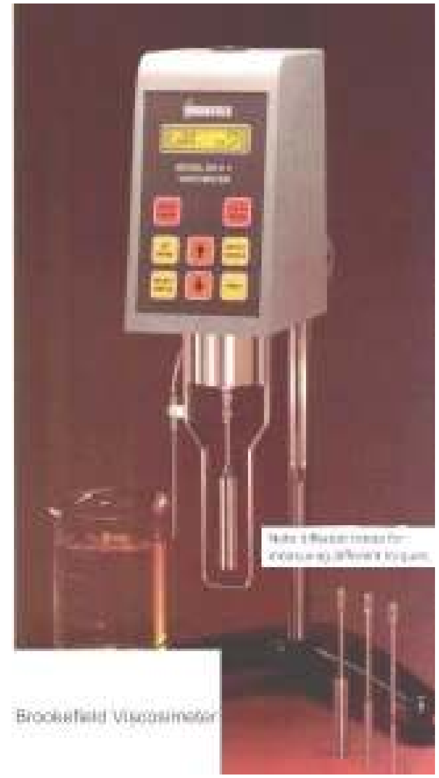
Dependence of viscosity on the temperature:



$$\eta\left(T\right)=\eta_o \exp\left(\frac{E_a}{RT}\right)$$

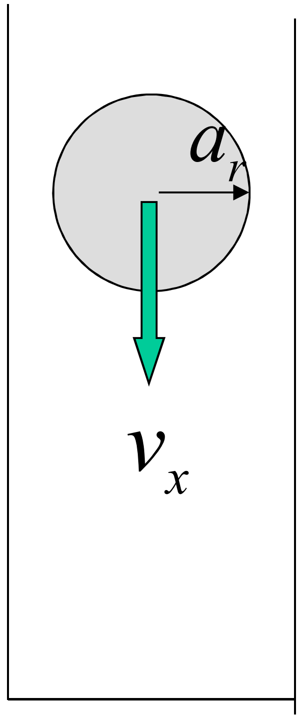
Flow curve of Newtonian liquid

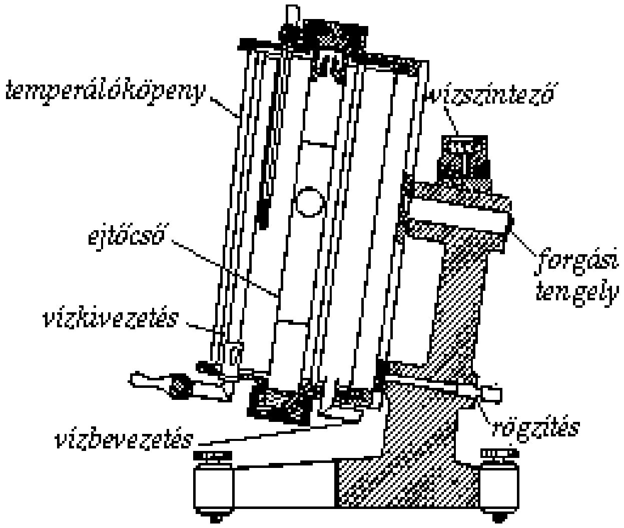


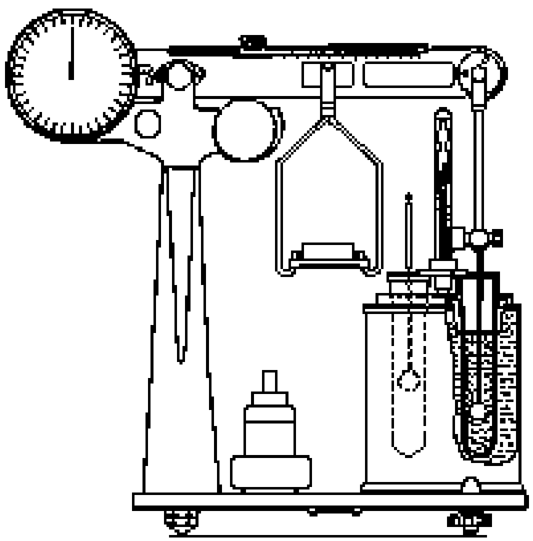


Stokes law:

$$f_\eta = 6\pi\eta a_r v_x$$

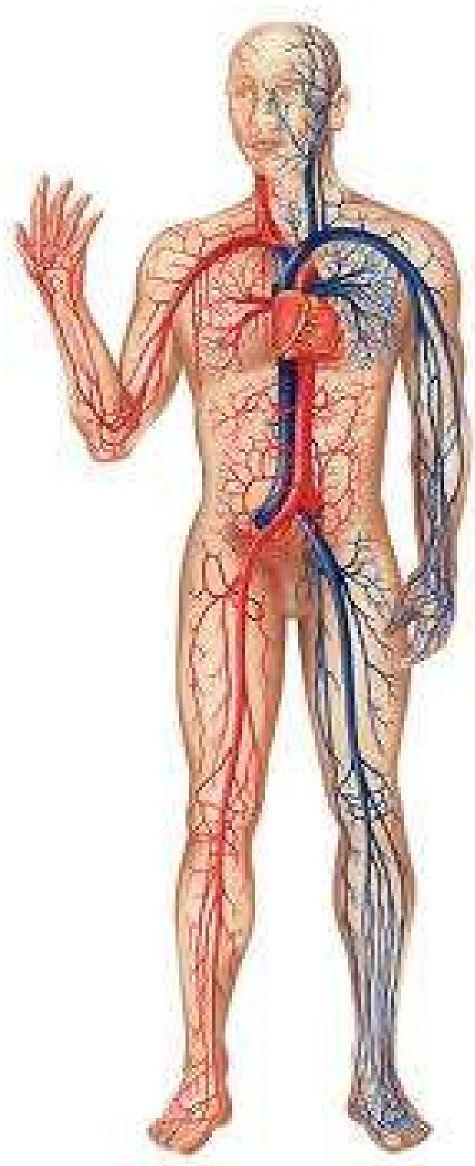


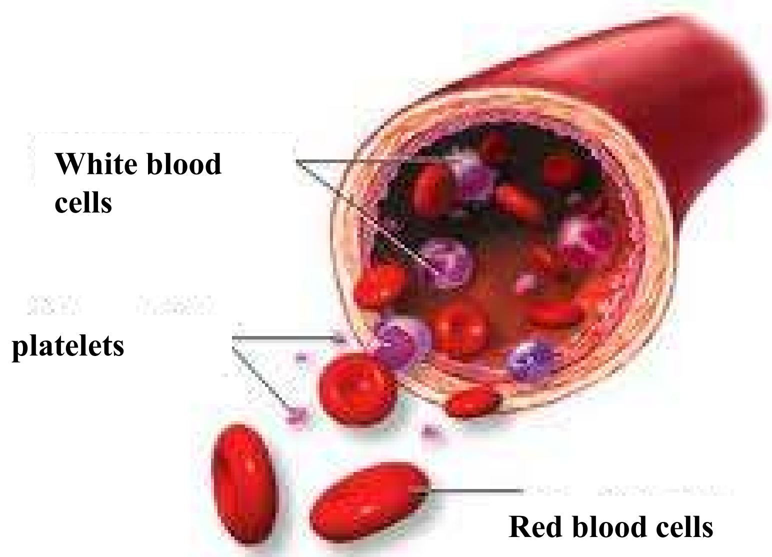




Höppler type viscometer

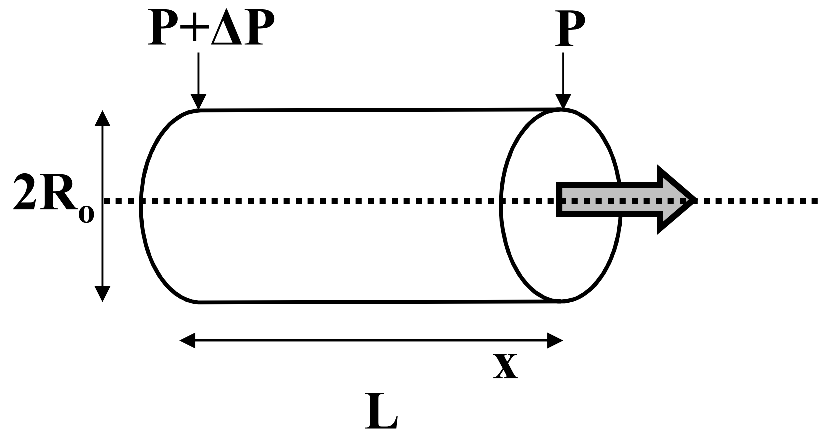
Hemorheology



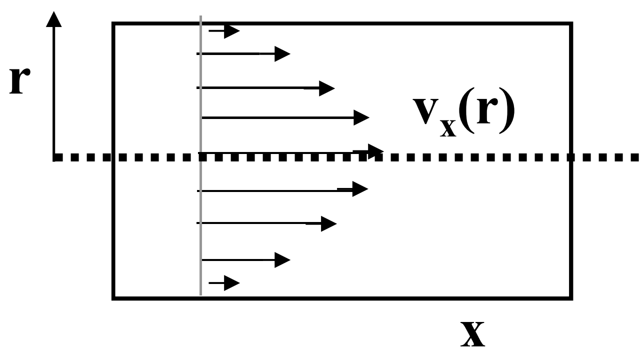


Laminar flow of Newtonian fluid

$$j_i = -\eta \frac{\Delta v_y}{\Delta x} \Rightarrow \boxed{\tau = \eta \frac{\Delta v_y}{\Delta x}}$$



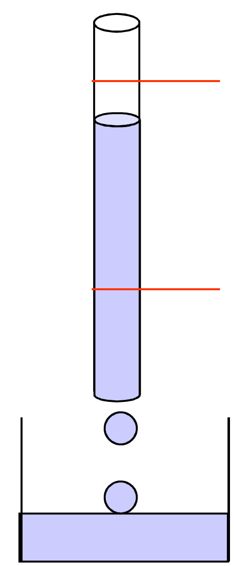
Parabolic velocity profile

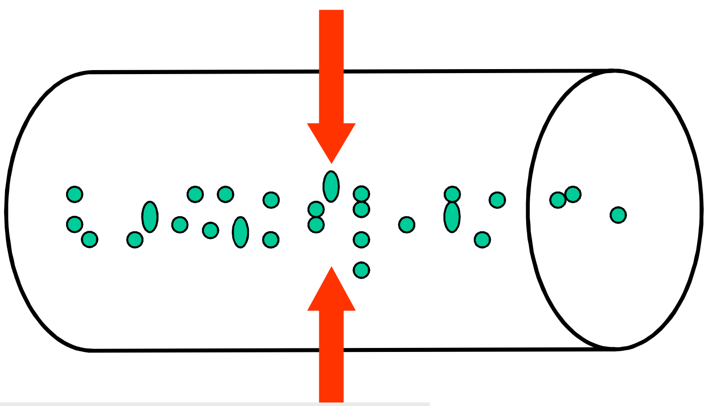


$$v_z(r) = \frac{\Delta P R_0^{\,2}}{4L\eta} \cdot \left(1 - \frac{r^2}{R_0^{\,2}}\right)$$

Hagen-Poiseuille law

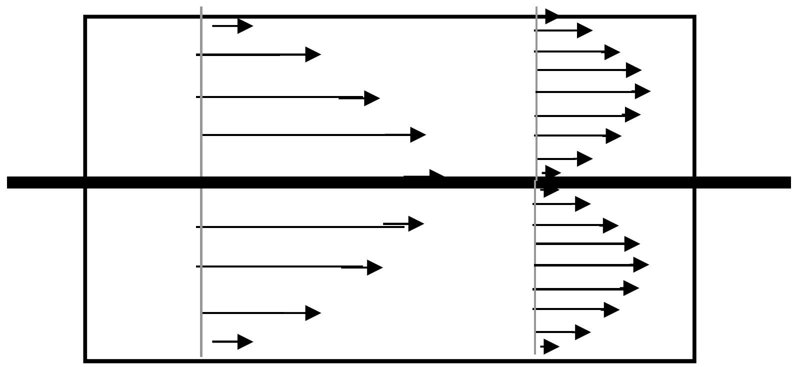
$$I_V = \frac{\pi \cdot R_o^{\,4}}{8\eta} \cdot \frac{\Delta P}{L}$$



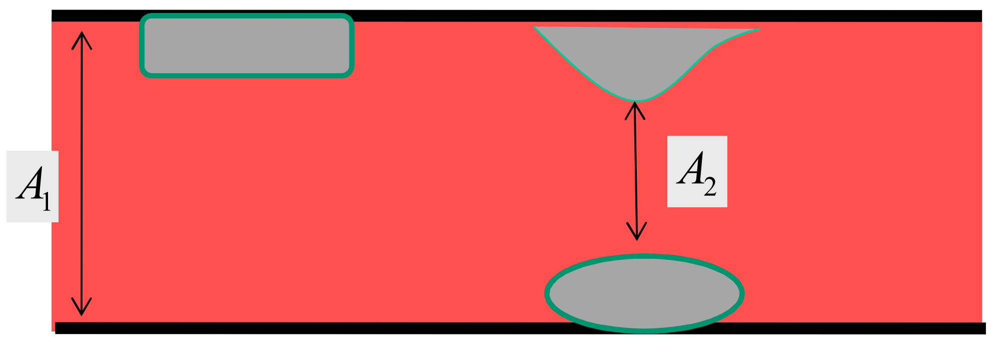


$$p + \frac{1}{2}\rho v_x^2 + \rho g h = const$$ Bernoulli law

Modification of parabolic velocity profile in the presence of catheter

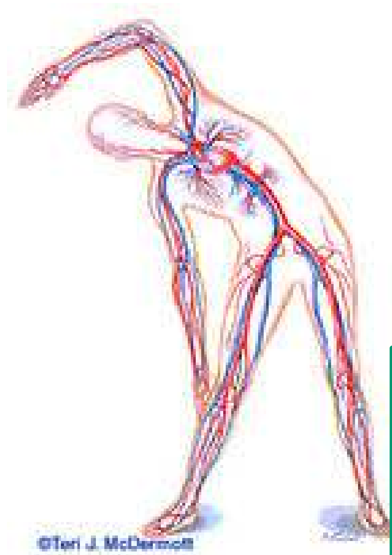


catheter



Turbulency occurs
at high speed

Blood flow



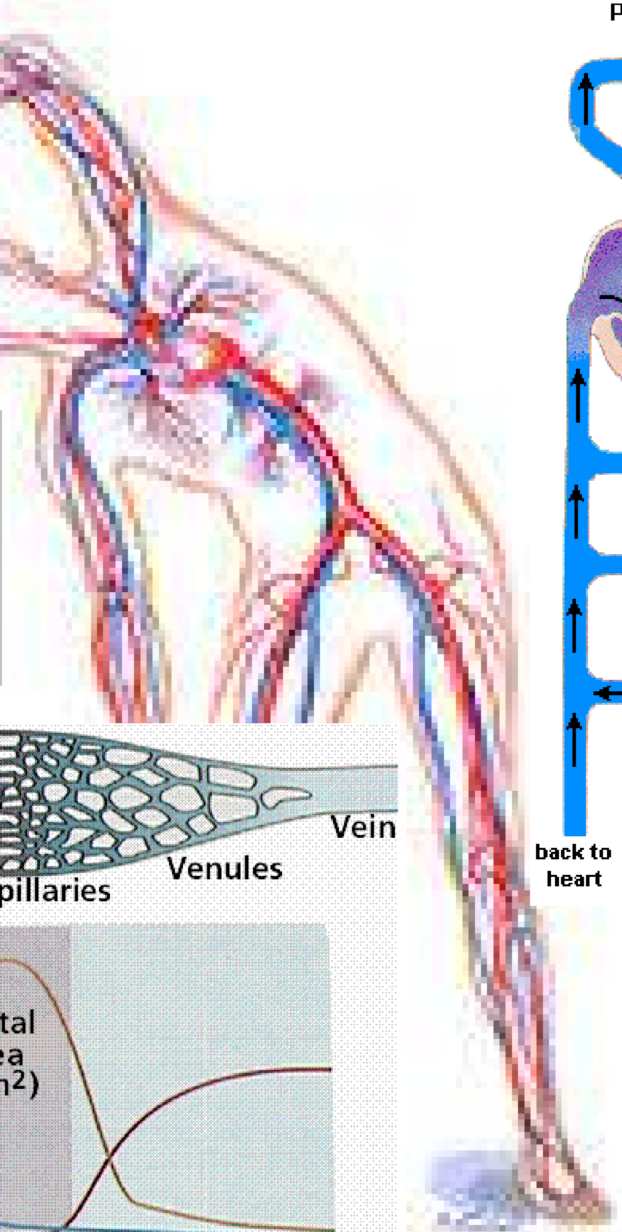
$$I_V = \frac{\pi \cdot R_o{}^4}{8\eta L} \cdot \Delta P = \frac{1}{R_{res}} \cdot \Delta P$$

$$R_{res}(consecutive) = \sum_i R_{res,i}$$

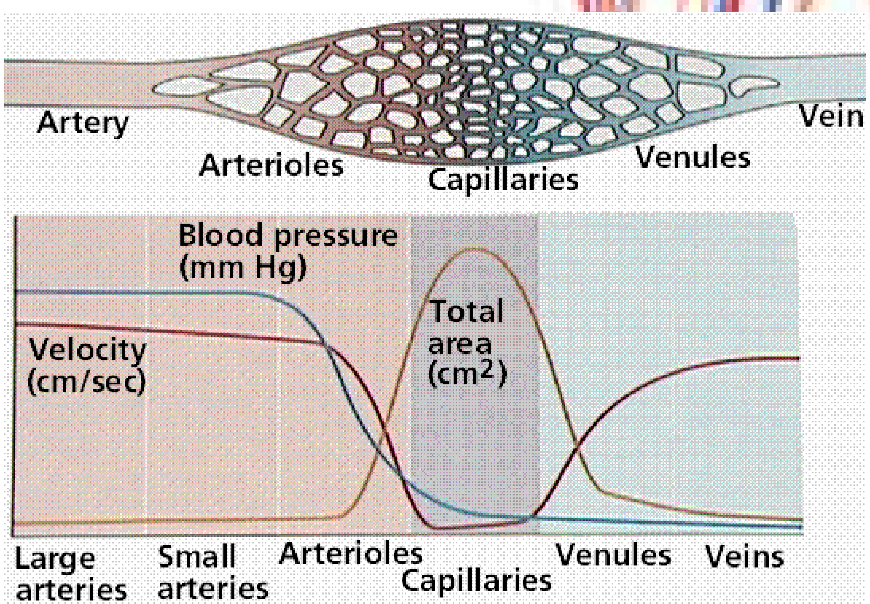
$$R_{res}(parallel) = \sum_i \frac{1}{R_{res,i}}$$

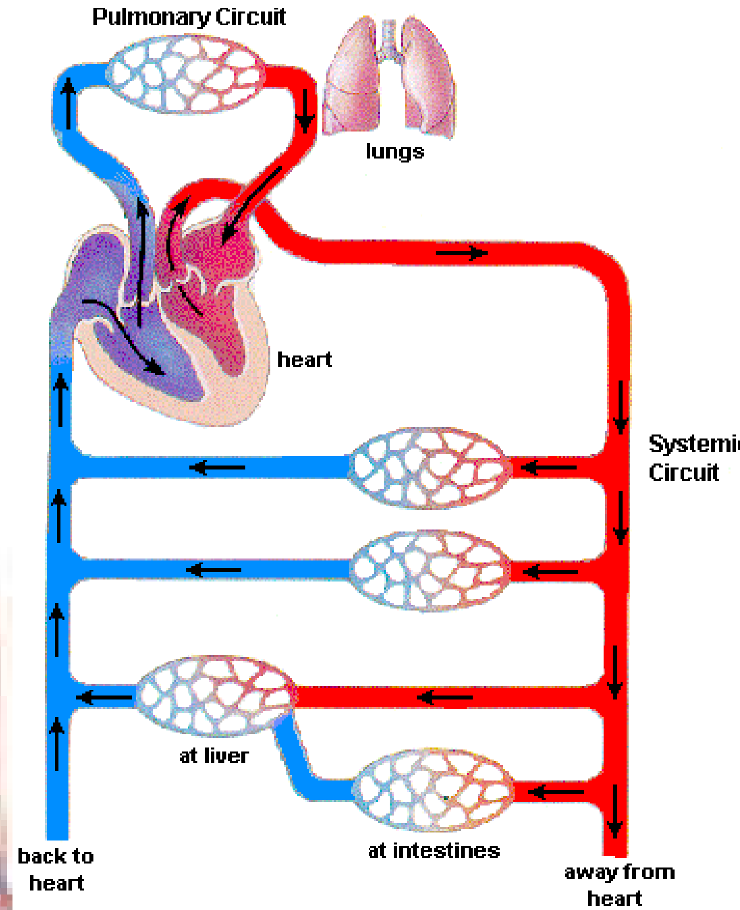
vessels	**diameter cm**	**length cm**	**number of branches**	**velocity. cm/s**
aorta	2.4	40	1	23
arteries	0.4	15	160	5
capillaries	0.0007	0,07	$1,2 \cdot 10^{10}$	0,022
veins	0.5	15	200	2,5

Nature Uses Microfluidics!



Pump, valves, manifold, functional “chips”, reagents





SUMMARY

	diffusion	heatconduction	rheology
TRANSFER:	component	energy	momentum
DRIVING FORCE:	∇c	∇T	∇v
FLUX:	$j_n = -D\nabla c$	$j_Q = -k\nabla T$	$j_i = -\eta\nabla v$
TIME DEPENDENCE:	$\frac{\Delta c}{\Delta t} = D\nabla^2 c$	$\frac{\Delta T}{\Delta t} = \alpha\nabla^2 T$	
	Fick	**Fourier**	**Newton**