

# 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 ( $p$ )	$J_V = -\frac{R^2 \Delta p}{8\eta \Delta x}$	Hagen-Poiseuille
Electric current	Electric potential ( $\phi$ )	$J_Q = -\frac{1}{\rho} \frac{\Delta \phi}{\Delta x}$	Ohm
Material transport (diffusion)	Chemical potential ( $\mu$ )	$J_n = -D \frac{\Delta c}{\Delta x}$	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).

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

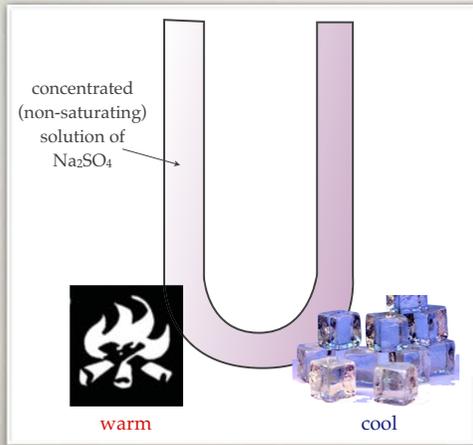
$$J_2 = L_{21}X_1 + L_{22}X_2$$

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

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

# THERMODIFFUSION

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



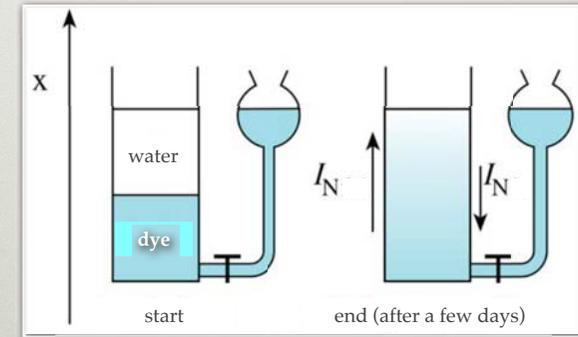
Two types of currents:

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

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

# DIFFUSION

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



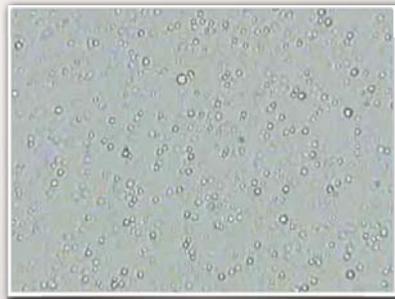
$$x^2 = 2Dt$$

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

# Microscopic manifestation of diffusion: Brownian movement

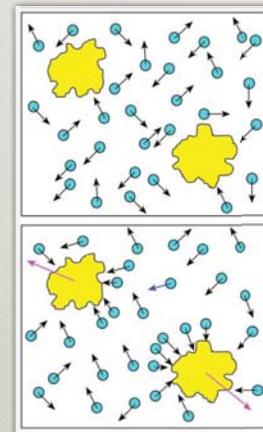


Robert Brown  
(1773-1858)

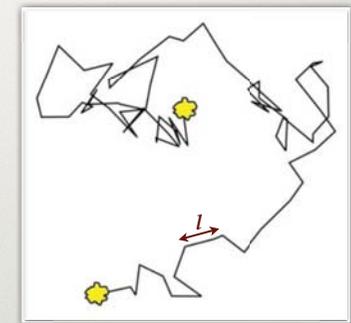


Fat droplets suspended in milk (droplet sizes 0.5 - 3 μm)

# 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  
 $\eta$  = viscosity  
 $r$  = radius of particle

# DIFFUSION

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

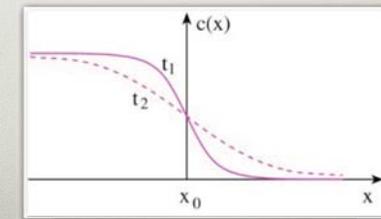
Material flow intensity:  $-\frac{\Delta J_n}{\Delta x} = \frac{\Delta c}{\Delta t}$

$J_n$  = Flow intensity  
 $x$  = distance  
 $t$  = time

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

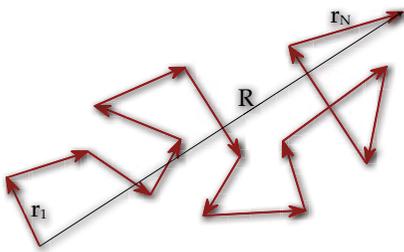
$D$  = diffusion coefficient

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:  $v = \frac{l}{\tau}$

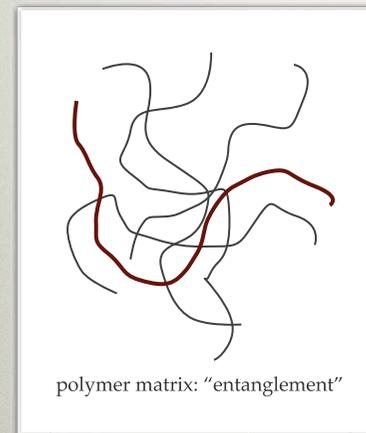
Full walk time:  $t = N\tau$

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

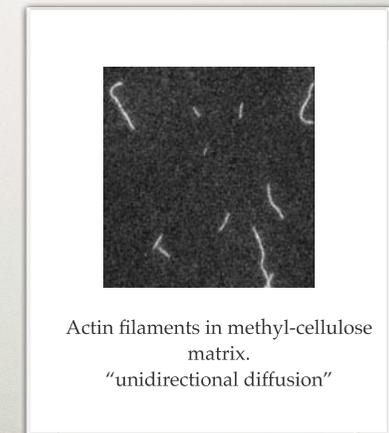
$$\langle R \rangle = \sqrt{N l^2} = \sqrt{\frac{t}{\tau} l^2} = \sqrt{t v l} = \sqrt{3 D t}$$

## 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

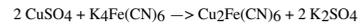
**History:** -Nollet (1748): pig bladder containing alcohol swells in water  
 -Dutrochet (1830): first osmometer  
 -van't Hoff: gas-law mechanism of osmosis  
 -Arrhenius and Findlay: vapor-pressure mechanism of osmosis

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

**Osmotic pressure ( $\pi$ )** = equilibrium hydrostatic pressure between each side of the semipermeable membrane ( $dP$ ).

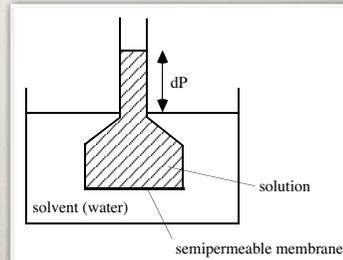
Semipermeable membranes:

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



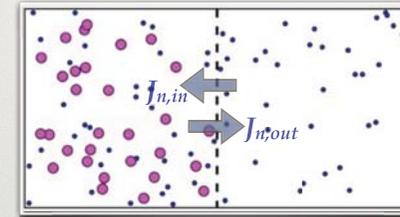
-cellulose membrane, dialysis bag

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/dm<sup>3</sup>) 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:  $\mu_s = \mu_s^0 + RT \ln \chi_s$

$\mu_s^0$  = standard chemical potential of solvent  
 $\chi_s$  = 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 (cm<sup>3</sup>/mol; for water: 18)

# IMPORTANCE OF OSMOSIS

Properties of the semipermeable membrane: *reflexion coefficient* ( $\sigma$ )

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)

$\pi_1$  = initial osmotic pressure

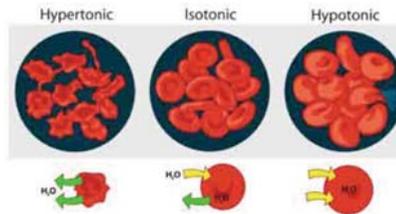
$\pi_2$  = final osmotic pressure (after equilibration)

**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.



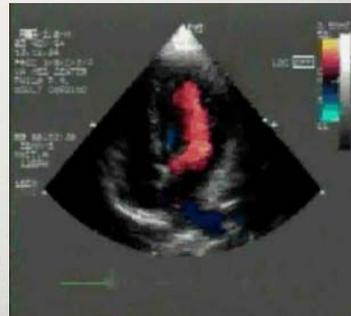
# BIOPHYSICS OF FLUIDS

## Importance of the physics of fluids



### I. Hemodynamics

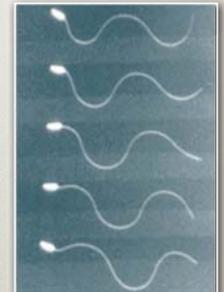
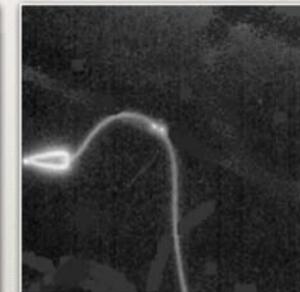
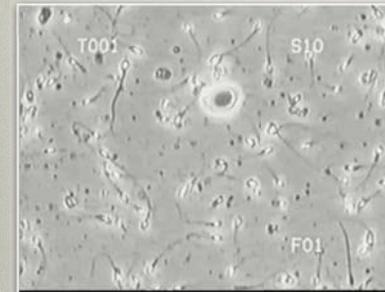
Characteristics of blood flow along the circulatory system.



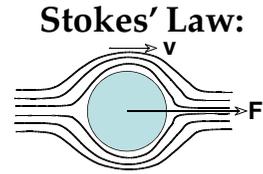
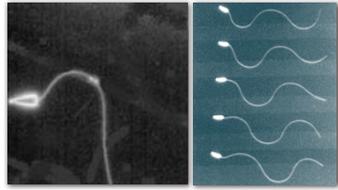
## Significance of the physics of fluids

### II. Motion in fluids

Force exerted by a single spermatoocyte during its motion.



# Drag coefficient of the spermatoocyte



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

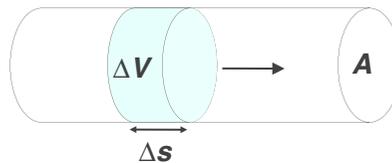
$$F = \gamma v = 3 \times 10^{-8} Ns/m \cdot 5 \times 10^{-5} m/s = 1.5 \times 10^{-12} N = 1.5 pN$$

# Biophysics of fluids

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

# Basic principles I.

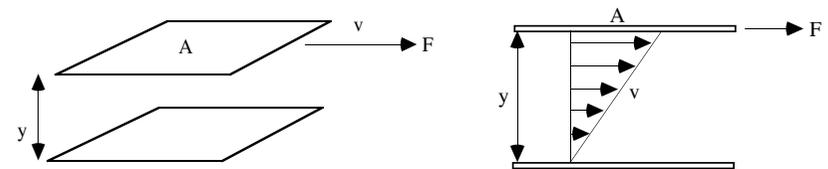
Volumetric flow rate (Q):



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

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

# Basic principles II. Viscosity (internal friction)



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

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

F/A = shear stress ( $\tau$ )  
 $\Delta v / \Delta y$  = 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  
 $\rho = \text{constant}, \eta = 0$

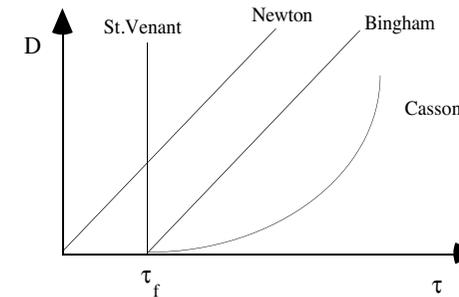
## 2. Non-ideal (real)

a. *Newtonian (viscous)*  
 $\eta$  independent of shear stress

b. *Non-newtonian (anomalous)*  
 $\eta$  varies with shear stress

# Types of fluids II.

Relationship between velocity gradient and shear stress in real fluids



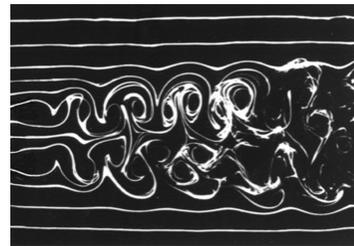
$\tau_f$  = flow threshold

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

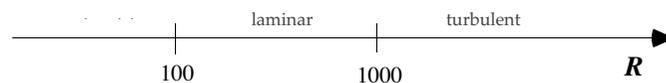
- Stationary**  
Flow intensity stays constant.
- Laminar**  
Fluid layers do not mix.
- Turbulent**  
Fluid layers mix.



Reynolds number:

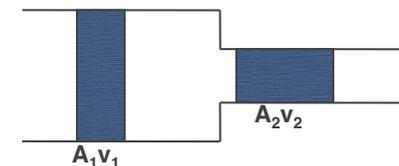
$$R = \frac{vr\rho}{\eta}$$

$v$  = flow rate (m/s)  
 $r$  = tube radius (m)  
 $\rho$  = density of fluid (kg/m<sup>3</sup>)  
 $\eta$  = viscosity (Ns/m<sup>2</sup>)



# Laws of flow in ideal fluids I.

## Continuity equation



$$A_1 v_1 = A_2 v_2 = \text{konst}$$

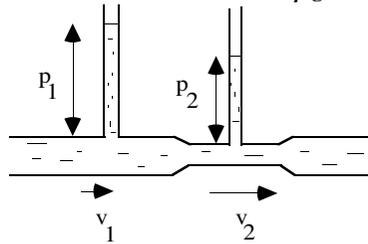
$A$  = cross-sectional area  
 $v$  = flow rate

# Laws of flow in ideal fluids II.

## Bernoulli's law

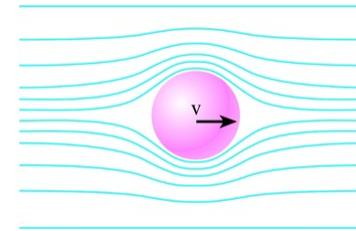
$$p + \frac{1}{2} \rho v^2 + \rho gh = konst$$

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



# Laws of flow in viscous fluids I.

## Stokes' law

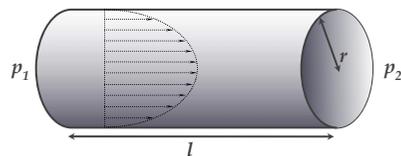


$$F = \gamma = 6r\pi\eta v$$

- F = force
- $\gamma$  = drag coefficient (shape factor)
- v = flow rate
- r = radius of sphere
- $\eta$  = viscosity

# Laws of flow in viscous fluids II.

## Hagen-Poiseuille's law

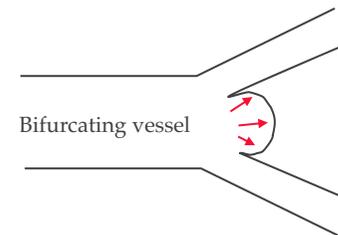


$$\frac{V}{t} = \frac{\pi r^4}{8\eta} \frac{dp}{dl}$$

- V = volume
- t = time
- (V/t = Q = flow intensity)
- r = tube radius
- $\eta$  = viscosity
- p = pressure
- l = length of tube
- (dp/dl = 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)