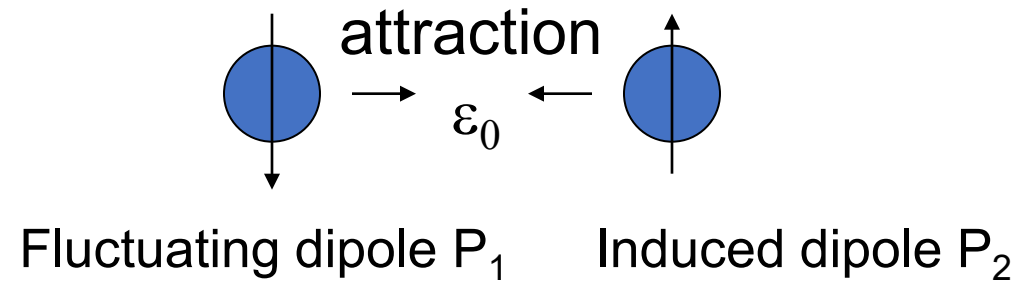


3. Some relevant energy scales:

- Thermal energy: $kT = 1/40 \text{ eV @ } 300\text{K}$
- Quantum mechanics: $\hbar c = 197 \text{ eV nm}$
- Electrostatics: $\alpha \hbar c = 1.4 \text{ eV nm}$
- Macroscopic measure: $1\text{kJ/mole} = 10 \text{ meV}$
- Absorption of radiation: $1\text{eV} = 8000 \text{ cm}^{-1}$
- Wavelength: $1 \text{ eV} = 1240 \text{ nm}$
- ATP phosphate group: 300 meV

3.1 Van der Waals interaction:

$E \sim 20 \text{ meV}$

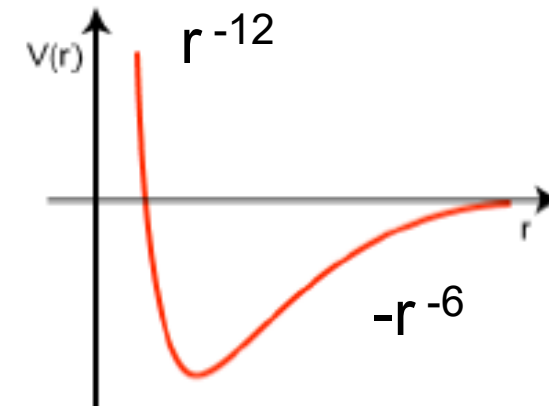


$$E_1 = \frac{P_1}{4\pi\epsilon_0 r^3}$$

$$P_2 = \alpha_2 E_1 = \frac{\alpha_2 P_1}{4\pi\epsilon_0 r^3}$$

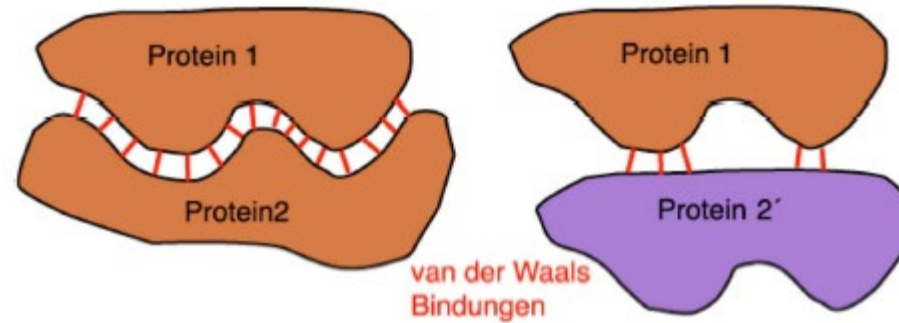
This dipole P_2 is attracted by the field gradient of E_1 resulting in an attractive interaction potential

$$V_{vdw}(r) = -P_2 E_1 = -\frac{\alpha_2 P_1^2}{4\pi^2 \epsilon_0^2 r^6}$$



This attraction is counterbalanced by “steric” repulsion at short distances

N.B: For large contact areas the vdW interaction may become significant

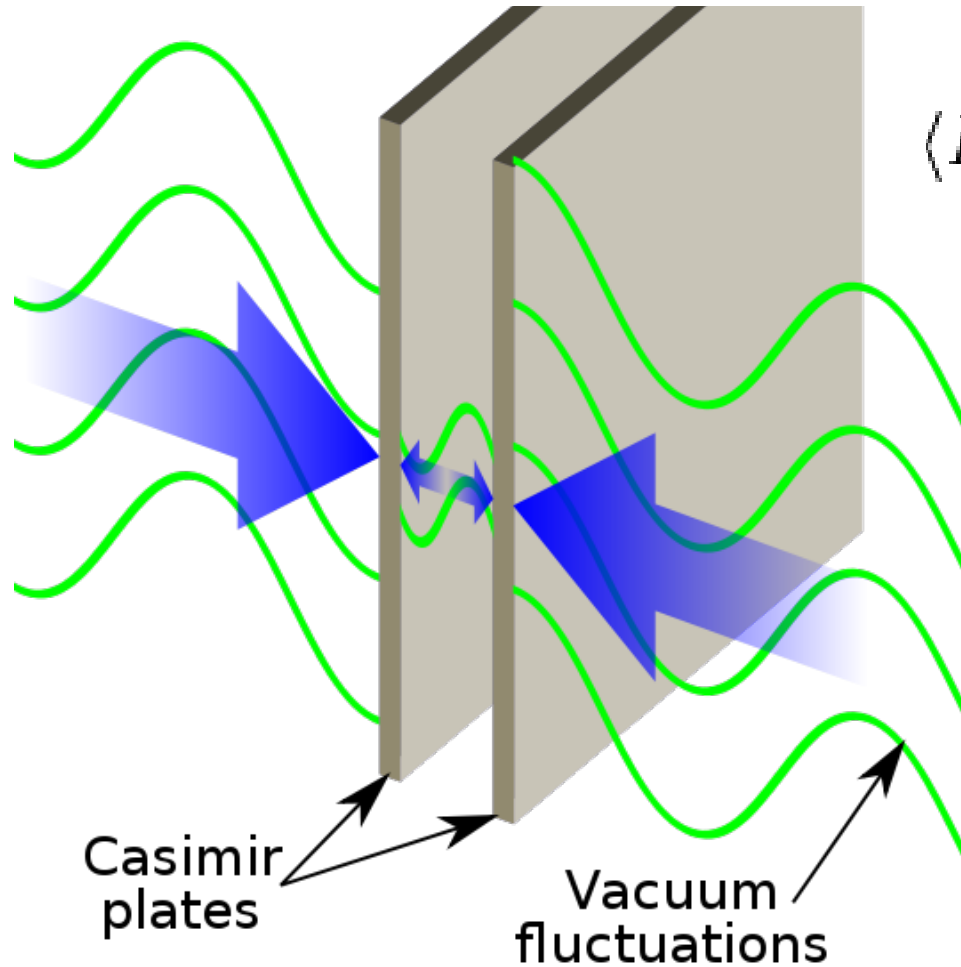


Quick aside: Repulsion due to the Pauli principle does not give a r^{-12} term as in the Lennard-Jones potential. This repulsion is due to overlap of wavefunctions, which for closed shells are exponential. I.e. the short term repulsion is given by the Born-Mayer potential:

$$V_{BM} = E_B \exp(-r/a_0)$$

At distances where this is significant, the r^{-6} in vdW is no longer correct...

Casimir-force:

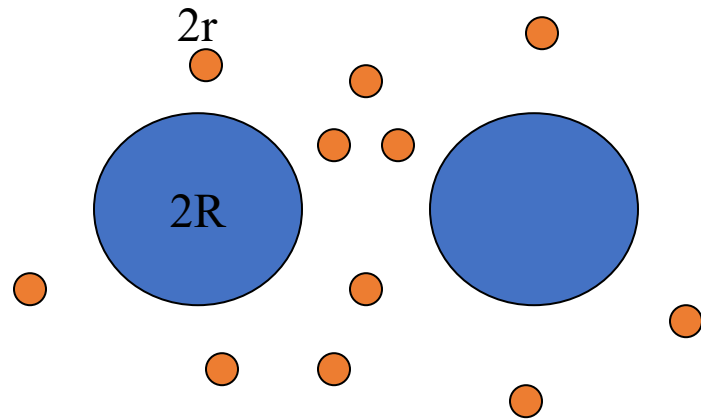


$$\langle E \rangle = \frac{\hbar}{2} \cdot 2 \int \frac{A dk_x dk_y}{(2\pi)^2} \sum_{n=1}^{\infty} \omega_n$$

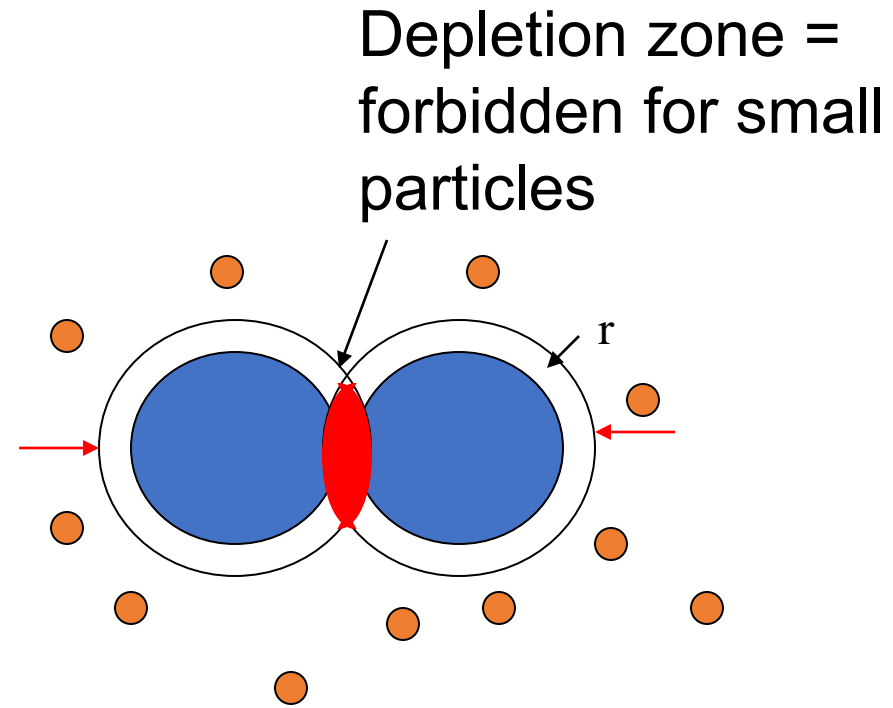
$$\frac{\langle E \rangle}{A} = \frac{-\hbar c \pi^2}{3 \cdot 240 a^3}$$

$$\frac{F_c}{A} = -\frac{d \langle E \rangle}{da A} = -\frac{\hbar c \pi^2}{240 a^4}$$

3.2 Entropic interactions:



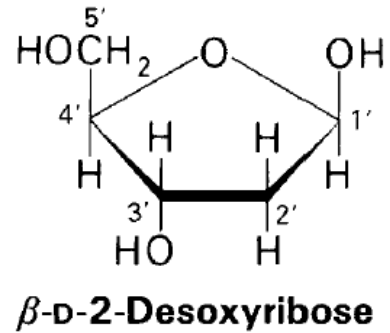
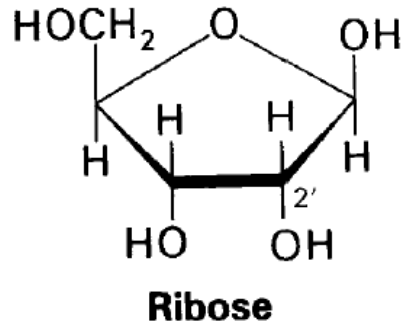
Mixture of big and small particles



Depletion interaction = attraction between big particles

3.3 Covalent bonds – driven by quantum mechanics

Example: nucleic acid phosphate backbone



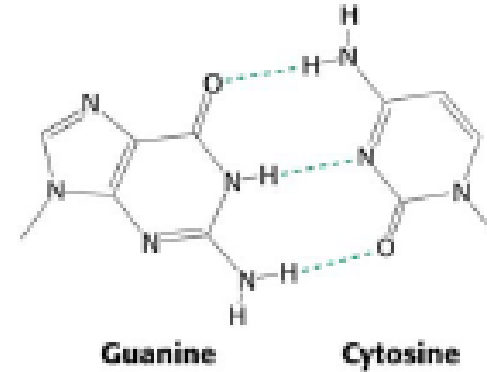
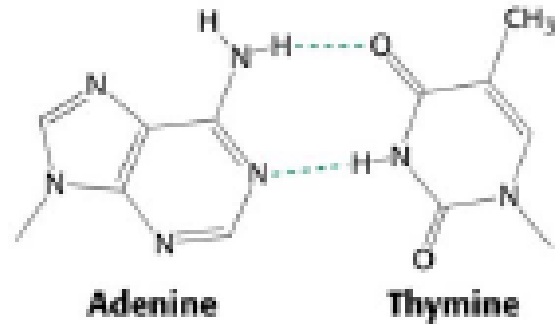
very strong: e.g. C - C bond with energy $E \sim 3.5 \text{ eV}$
C = C bond $E \sim 7.3 \text{ eV}$

stable: “irreversible”, cannot be broken by thermal energy
 $k_B T \sim 2.5 \text{ kJ/mole} \sim 200 \text{ cm}^{-1} \sim 25 \text{ meV}$

directional (orbitals), with short distance ($\sim 0.1\text{-}0.2 \text{ nm}$)

3.4 Hydrogen bonds:

Example: specific binding of nucleic acid bases



E ~ 80 meV

electro-negative hydrogen bond acceptor (attracting electrons) and electro-positive hydrogen bond donor (pushing electrons away).

The partial charges δ^+ and δ^- result in electrostatic forces - think of it as a delocalized proton.

→ Directed attractive force, opposed by “steric” repulsion, Equilibrium distance 0.15 – 0.25 nm

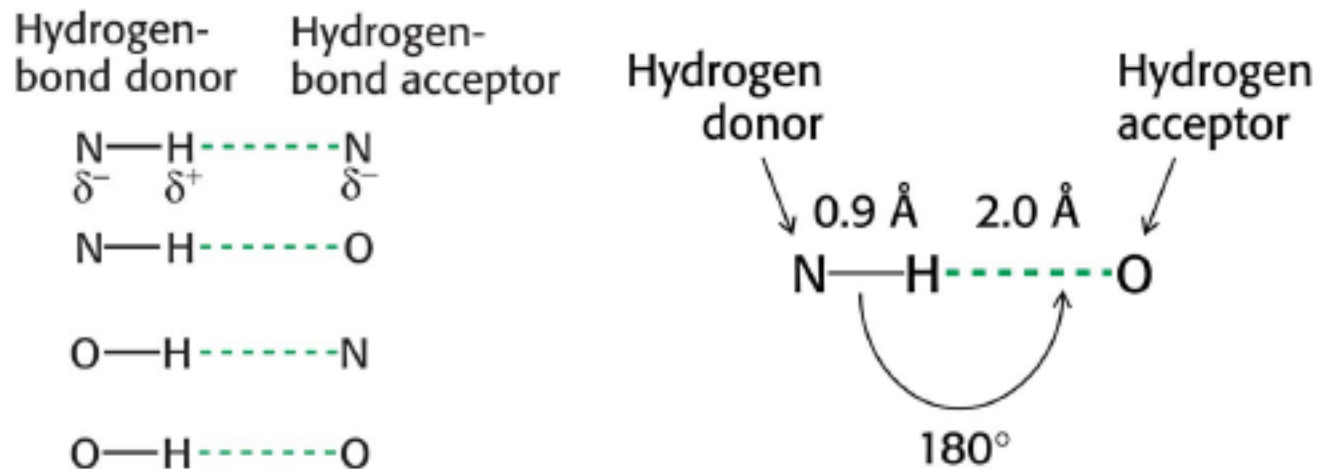
Quick estimate of the Energy:

Heisenberg uncertainty of the proton: $p \times x \sim h$

x here is roughly the bond length, i.e. a few times the Bohr radius, which gives an energy of:

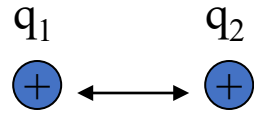
$$E = p^2/2m_p = h^2/(8a_0^2m_p)$$

Different types of Hydrogen bonds with O and N



3.5 Electrostatic interactions in solution:

Coulomb interaction



$$E = \frac{1}{4\pi\epsilon_0\epsilon} \frac{q_1 q_2}{r}$$

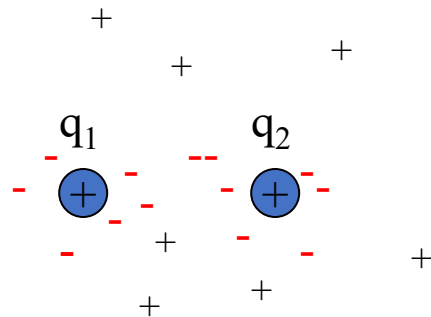
e.g. simple ions
@ 0.3nm distance
in water have

E ~ 60 meV

$\epsilon \sim 2$ (oil) $\epsilon \sim 80$ (water)

Screened Coulomb interaction:

$$E = \frac{1}{4\pi\epsilon_0\epsilon} \frac{q_1 q_2}{r} \exp(-\kappa r)$$



$\kappa = 1/\lambda$ Debye screening parameter

e.g. **$\lambda \sim 1$ nm** @ 0.15 molar
concentration of monovalent
ions in water

4. Reminder Thermodynamics and statistical mechanics

In condensed matter, we are always dealing with a collection of extremely many particles, so the concepts of thermodynamics and statistical mechanics are of utmost importance.

Therefore let us quickly remind the basics and how the two are coupled. Note that the macroscopic thermodynamics can be derived without knowing the microscopic mechanism of statistical mechanics.

4.1 Entropy and the second Law

Not only energy scales (U) are important – what is actually minimised is the free energy

$$F = U - TS$$

What is entropy?

- Number of microscopic states possible to make up a macroscopic state.
- Symmetry
- Disorder
- Information

Colloidal crystals/ Entropy is not disorder



Let's make this quantitative:



W is the number of different possible microstates for a given macrostate, i.e. the probability of finding one specific, microscopic realization of a macroscopic state

Statistical description: The Boltzmann factor

Expand the Entropy of a state in terms of its energy:

$$S(E_0 - \Delta E) = S(E_0) - dS/dE \Delta E$$

Remember the free energy $F = E - TS$ so $dS/dE = 1/T$

With Boltzmann's entropy, this directly gives the probability distribution:

$$p(E) = \text{const} \exp(-\Delta E/k_B T)$$

4.2 free energy and thermodynamic potentials

$$dU = TdS - PdV \quad U(S, V)$$

$$dH = TdS + VdP \quad H(S, P)$$

$$dF = -PdV - SdT \quad F(V, T)$$

$$dG = -SdT + VdP \quad G(T, P)$$

$$d\Phi = \sum_i x_i dy_i \quad x_j = \left(\frac{\partial \Phi}{\partial y_j} \right)_{\{y_{i \neq j}\}}$$

Legendre transformation imply the equations of state

$$\begin{aligned} -p &= \left(\frac{\partial U}{\partial V} \right)_{S, \{N_i\}} = \left(\frac{\partial F}{\partial V} \right)_{T, \{N_i\}} \\ +V &= \left(\frac{\partial H}{\partial p} \right)_{S, \{N_i\}} = \left(\frac{\partial G}{\partial p} \right)_{T, \{N_i\}} \\ +T &= \left(\frac{\partial U}{\partial S} \right)_{V, \{N_i\}} = \left(\frac{\partial H}{\partial S} \right)_{p, \{N_i\}} \\ -S &= \left(\frac{\partial G}{\partial T} \right)_{p, \{N_i\}} = \left(\frac{\partial F}{\partial T} \right)_{V, \{N_i\}} \end{aligned}$$

Legendre transformation and second law imply the “Maxwell relations”

$$\left(\frac{\partial}{\partial y_j} \left(\frac{\partial \Phi}{\partial y_k} \right)_{\{y_i \neq k\}} \right)_{\{y_i \neq j\}} = \left(\frac{\partial}{\partial y_k} \left(\frac{\partial \Phi}{\partial y_j} \right)_{\{y_i \neq j\}} \right)_{\{y_i \neq k\}}$$

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad - \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

4.3 Partition function

$$P_s = \frac{1}{Z} e^{-\beta E_s} \quad \beta \equiv \frac{1}{k_B T}$$

$$Z = \sum_s e^{-\beta E_s} \quad Z = \text{tr}(e^{-\beta \hat{H}})$$

$$\langle E \rangle = \sum_s E_s P_s = \frac{1}{Z} \sum_s E_s e^{-\beta E_s} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z(\beta, E_1, E_2, \dots) = -\frac{\partial \ln Z}{\partial \beta}$$

$$S \equiv -k_B \sum_s P_s \ln P_s = k_B (\ln Z + \beta \langle E \rangle) = \frac{\partial}{\partial T} (k_B T \ln Z) = -\frac{\partial A}{\partial T}$$

$$A = \langle E \rangle - TS = -k_B T \ln Z.$$

5.1 Linear non-equilibrium and stationary states (Onsager)

Generalized entropic forces:

$$dS = \sum I_i dE_i \quad I_i := \frac{\partial S}{\partial E_i}$$

$$\mathbf{F}_i = -\nabla I_i$$

I and E are
thermodynamically
conjugate variables

These lead to a current density:

$$\mathbf{J}_i = \sum_j L_{ij} \mathbf{F}_j$$

And with this an equation of continuity:

$$\partial_t E_i = \nabla \cdot \sum_j L_{ij} \nabla I_j$$



$$dU = T dS - P dV + \mu dM$$

$$du = T ds + \mu d\rho$$

$$ds = (1/T) du + (-\mu/T) d\rho$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{J}_\rho = 0$$

$$\frac{\partial u}{\partial t} + \nabla \cdot \mathbf{J}_u = 0$$

$$\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_s = \frac{\partial s_c}{\partial t}$$

$$\mathbf{J}_u = -k \nabla T \qquad \mathbf{J}_\rho = -D \nabla \rho$$

$$\mathbf{J}_u = kT^2 \nabla(1/T) \qquad \mathbf{J}_\rho = D' \nabla(-\mu/T)$$

$$\mathbf{J}_u = L_{uu} \nabla(1/T) + L_{u\rho} \nabla(-\mu/T) \qquad \mathbf{J}_\rho = L_{\rho u} \nabla(1/T) + L_{\rho\rho} \nabla(-\mu/T)$$

$$\mathbf{J}_\alpha = \sum_{\beta} L_{\alpha\beta} \nabla f_\beta$$

$$\frac{\partial s}{\partial t} = (1/T) \frac{\partial u}{\partial t} + (-\mu/T) \frac{\partial \rho}{\partial t} \qquad \mathbf{J}_s = (1/T) \mathbf{J}_u + (-\mu/T) \mathbf{J}_\rho = \sum_{\beta} \mathbf{J}_\alpha f_\alpha$$

$$\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_s = \frac{\partial s_c}{\partial t}$$

$$\frac{\partial s_c}{\partial t} = \mathbf{J}_u \cdot \nabla (1/T) + \mathbf{J}_\rho \cdot \nabla (-\mu/T) = \sum_{\alpha} \mathbf{J}_{\alpha} \cdot \nabla f_{\alpha}$$

$$\frac{\partial s_c}{\partial t} = \sum_{\alpha} \sum_{\beta} L_{\alpha\beta} (\nabla f_{\alpha}) \cdot (\nabla f_{\beta})$$

Stationary state in an open system:

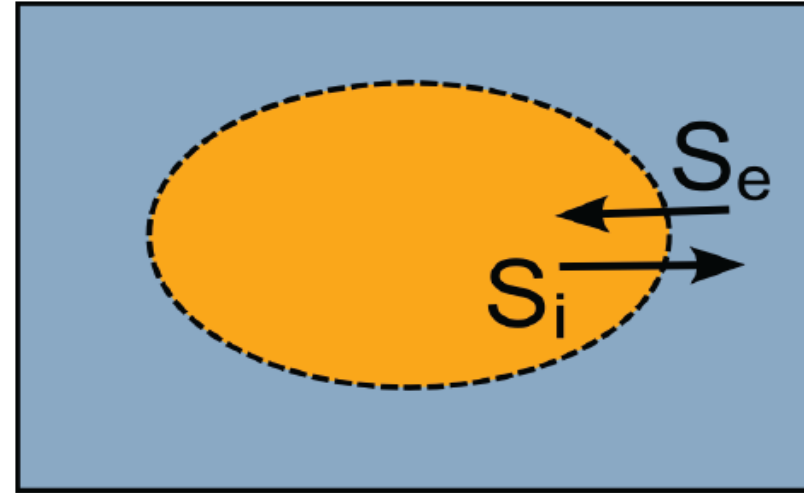
$$dS = 0$$

Stationary state in an open system:

For the total we have:

$$dS = 0$$

$$dS_e + dS_i = 0$$



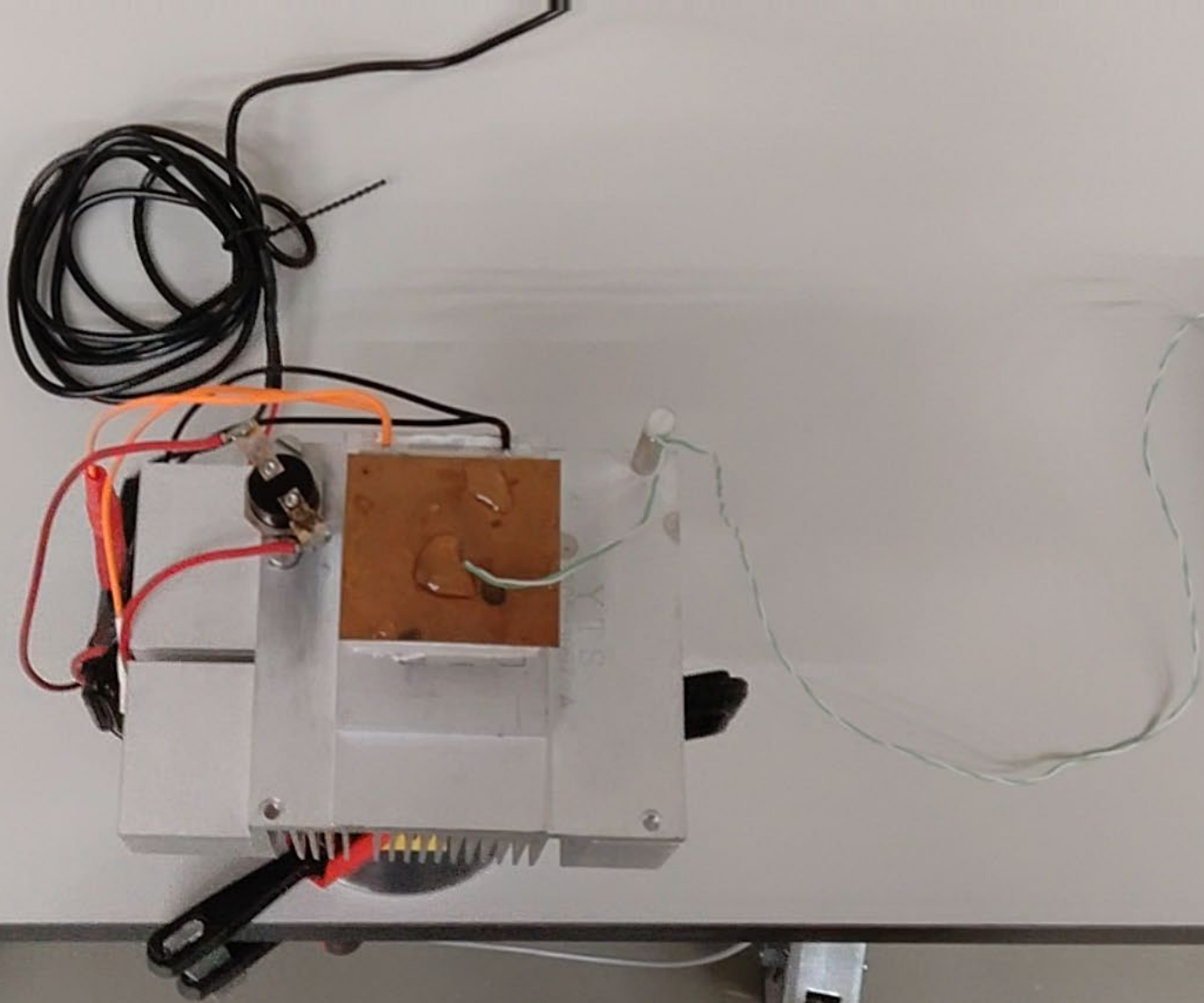
We are looking for the entropy production in the interior:

$$P = \frac{dS_i}{dt}$$

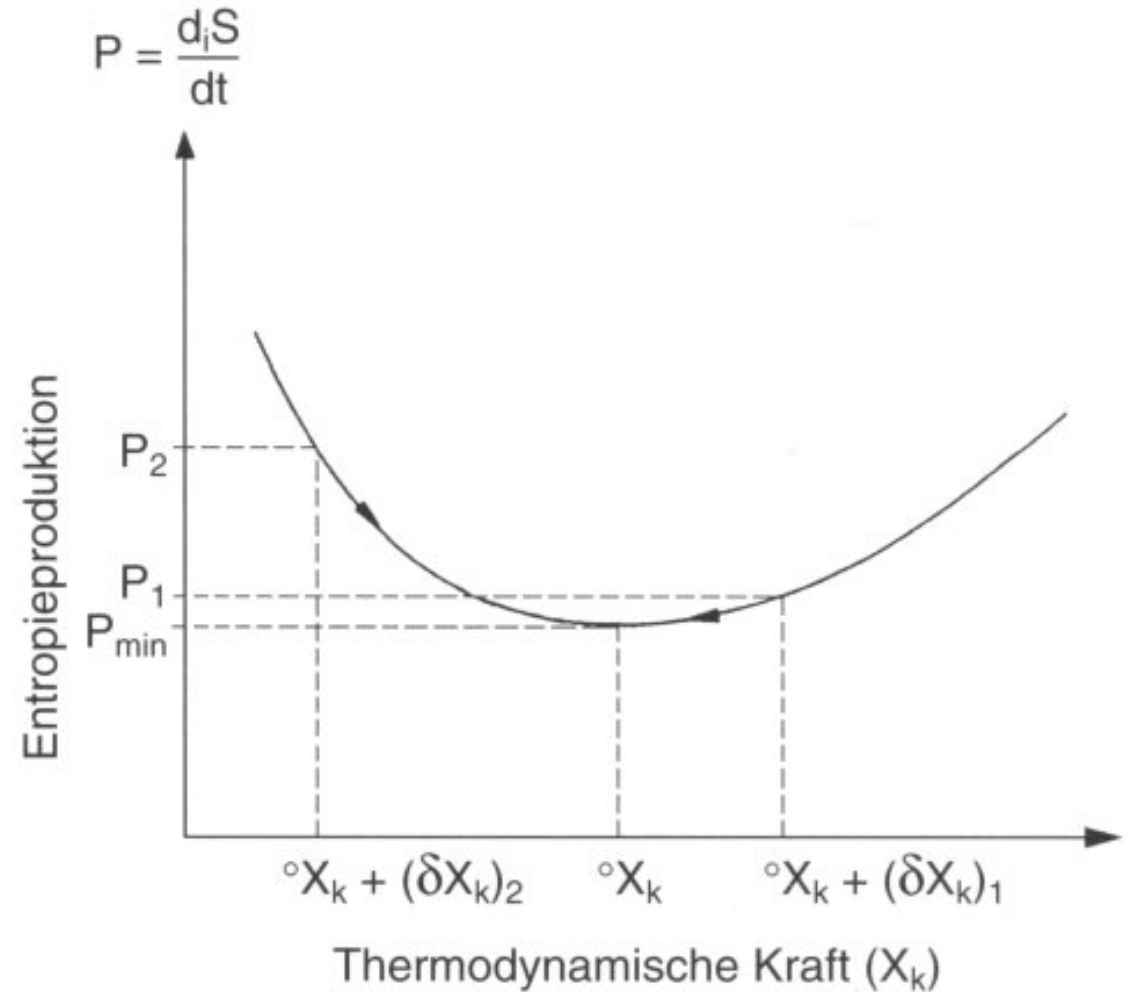
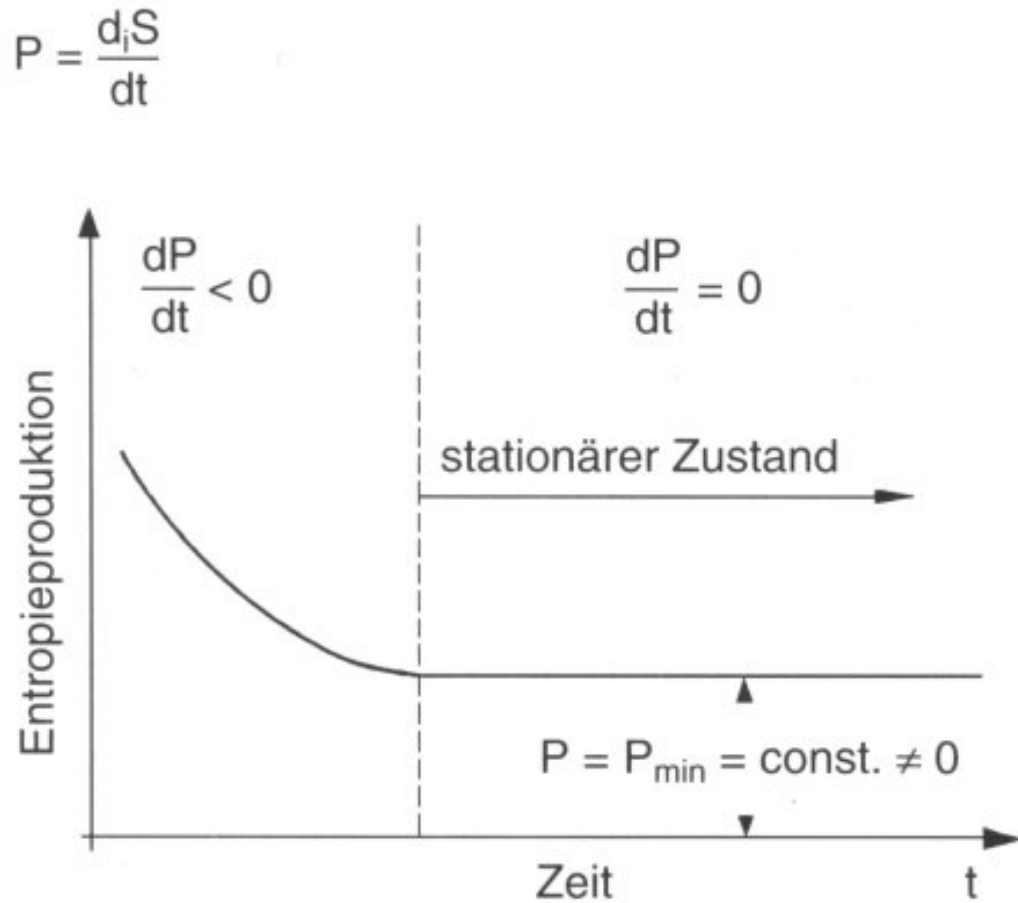
This can be obtained from the generalized forces and currents:

$$\delta P = \delta J_k \delta F_k$$

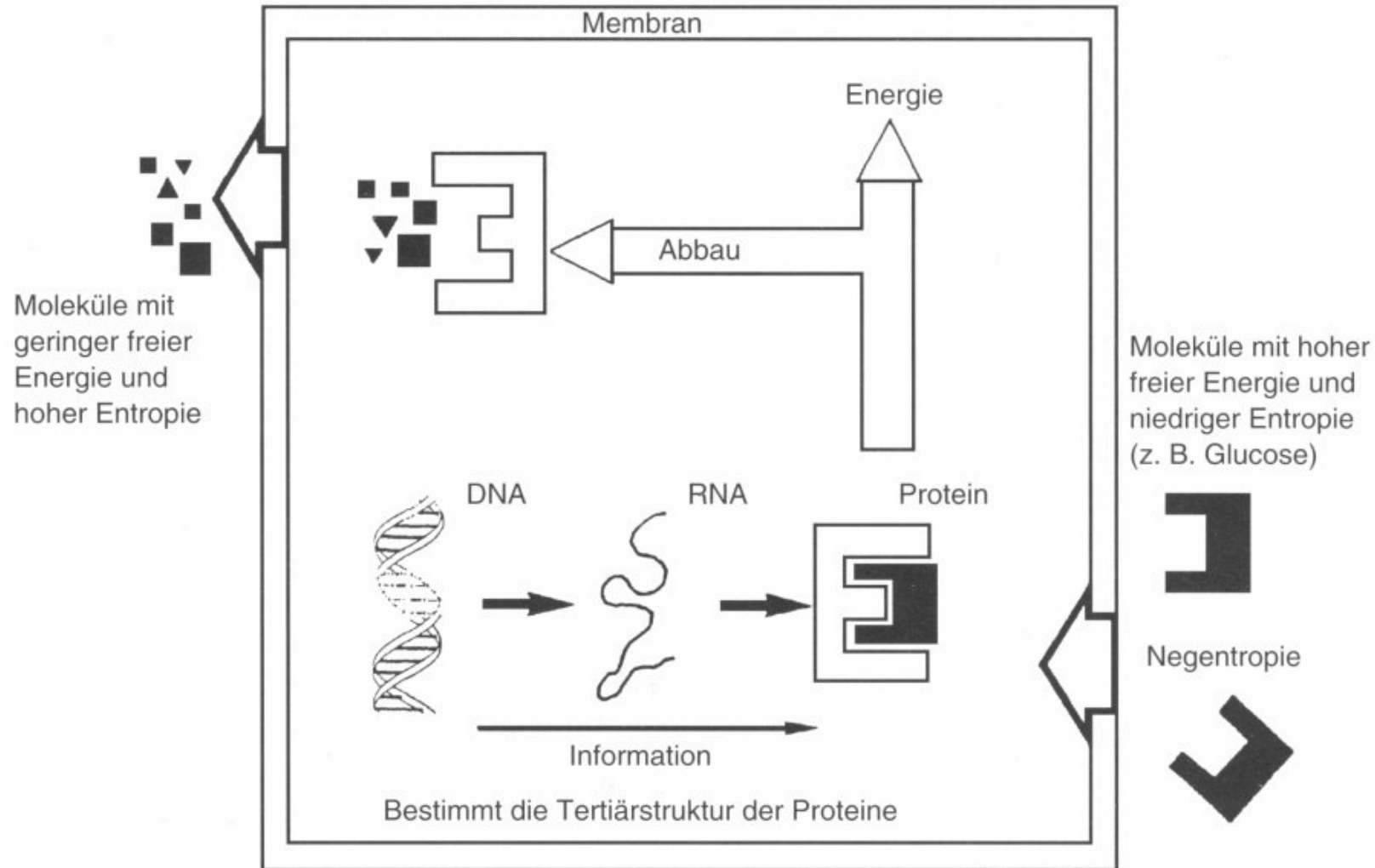
$$\delta J_k = L_{kk} \delta F_k$$



Therefore δP is negative and eventually, a state of minimal Entropy production is reached:



Schematically, this is what happens in a cell (and in all of life) as well:



If you relax the condition $dS = 0$ (i.e. go to non-equilibrium), fluctuations in entropy production are enhanced:

