Introduction to Nonequilibrium Thermodynamics: From Onsager to Micromotors

Based on the lecture "Nonequilibrium phenomena in micro and nanosystems" taught by Dr. Eric Lutz, Freie Universität Berlin

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Minisymposium on fundamental aspects behind cell systems biology, Nové Hrady

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History & Motivation

- Theory of nonequilibrium thermodynamics originates from the first half of 20. century
- It was mainly developed by Onsager, Rayleigh...
- Aim: to extend a formalism of equilibrium processes to dissipative or fast processes
- Many processes observed in real system exhibit behavior of irreversible processes
- Applications: biophysics, nanosystems,...

Equilibrium thermodynamics

Basic notes

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- Small fluctuations can be neglected

$$\frac{\Delta E}{< E >} \simeq \frac{\sqrt{N}}{N} \simeq \frac{1}{\sqrt{N}} \tag{1}$$

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- Equilibrium: state of a system, where we cannot observe any change of measurable quantities
- Structure of Thermodynamics:
  - General laws
  - System-specific response coefficients: $c_p, c_v, \beta_T, \ldots$

Equilibrium thermodynamics

Laws of thermodynamics

- First law (Claussius 1850, Helmholtz 1847): Energy is conserved.

$$\mathrm{d}U = \delta Q - \delta W \tag{2}$$

- Second law (Carnot 1824, Claussius 1854, Kelvin): Heat cannot be fully transformed into work.

$$\mathrm{d}S \geq \frac{\delta Q}{T} \tag{3}$$

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$$\mathrm{d}S_R = \frac{\mathrm{d}U}{T} + \sum_i Y_i \mathrm{d}X_i \qquad \left(Y_i = \frac{\partial S_R}{\partial X_i}\right) \tag{4}$$

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- aim of Nonequilibrium TD: to compute entropy production rate

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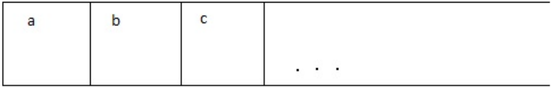

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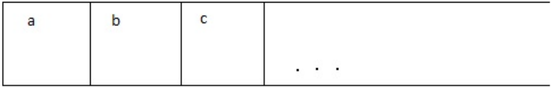

- Total entropy is: $S = S^a(X_i^a) + S^b(X_i^b) + \dots$
- Entropy production rate for a subsystem **a**:

$$\sigma^a = \frac{\mathrm{d}S^a}{\mathrm{d}t} = \sum_i Y_i^a \dot{X}_i^a = \sum_i Y_i^a J_i^a \tag{6}$$

Nonequilibrium thermodynamics

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- L_{ij} nonequilibrium response coefficients
- Generally are L_{ij} functions of Γ's, but near equilibrium are assumed to be constants - J_i's are linear functions of Γ's

Nonequilibrium thermodynamics

Onsager relations

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- For two currents: $L_{12}^2 \leq L_{11} L_{22}$
- It says more than second law of TD: if $L = L^S + L^A$, then

$$\sigma = \sum_{ij} L_{ij} \Gamma_i \Gamma_j = \sum_{ij} \left(L_{ij}^S + L_{ij}^A \right) \Gamma_i \Gamma_j = \sum_{ij} L_{ij}^S \Gamma_i \Gamma_j \geq 0. \tag{9}$$

Application: Brownian motors

Microsystems

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  - Volume scales as L^3 - inertial forces, weight,...
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Microsystems

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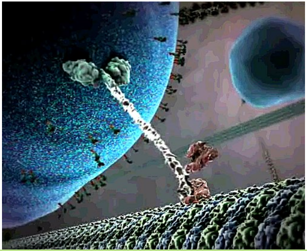
  - Volume scales as L^3 - inertial forces, weight,...
  - Surface scales as L^2 - friction, heat transfer,...
  - $\frac{\text{friction}}{\text{inertia}} \sim \frac{1}{L}$ - for small systems become friction forces important
  - For microsystems is the thermalization time very small - instant thermalization
- Macromotor: based on inertia and temperature difference
- Micromotor: based on random fluctuations

Brownian motors

Transport in living cells

- In living cells we can observe a few types of transport mechanisms
- One is transport of kinesin protein with cargo on the actin filament
- We can see a directed “walking” of kinesin on the filament
- The mechanism is based on nonequilibrium fluctuations - Brownian motors



Brownian motors

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Types of ratchets

- Flashing (on-off) ratchet
- Rocking ratchet
- Correlation ratchet (based on the disruption of fluctuation-dissipation theorem)
- Chemical ratchet

Brownian motors

Flashing ratchet

Brownian motors

Flashing ratchet

- The transport is based on switching on and off of an periodic, asymmetric potential
- Examples of potentials: asymmetric sawtooth, $V(x) = \sin(x) + \frac{1}{4}\sin\left(2x + \frac{\pi}{4}\right)$

Brownian motors

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- When the potential is off - diffusion: $p(x,t) \simeq \exp\left(\frac{-x^2}{2Dt}\right)$
- When the potential is on - particles tend to get to minimums - localization: $p(x) \simeq \exp(-\beta V(x))$

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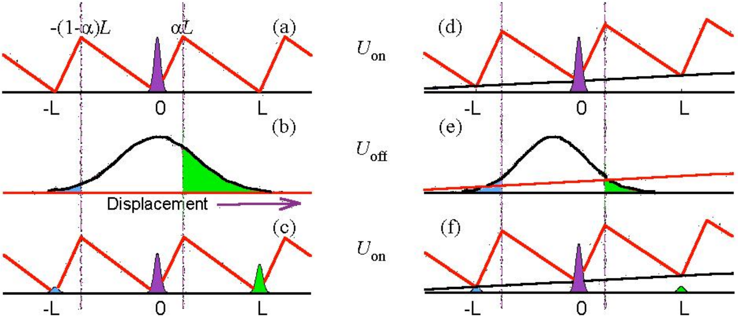
- When the potential is on - particles tend to get to minimums - localization: $p(x) \simeq \exp(-\beta V(x))$
- Because the potential is periodic, no force is present on average
- We can observe a particle flow

Brownian motors

Flashing ratchet



Brownian motors

Rocking ratchet

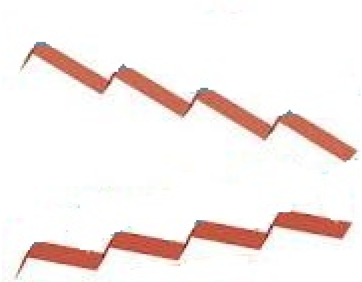
Brownian motors

Rocking ratchet

- We use again the asymmetric potential, but instead of switching on and off, we tilt the potential a little bit:

$$V(x, t) = V_0(x) + c_1 x \sin(c_2 t) \tag{10}$$

- Again, due to asymmetry of the potential is the current produced with zero average force.



Brownian motors

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- Chemical ratchet is kind of flashing ratchet, where the energy to switch of the potential is from the reaction of ATP

Brownian motors

Efficiency of a Chemical ratchet

Brownian motors

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- Efficiency is defined as a ratio between the performed work and consumed energy

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Brownian motors

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- We define the chemical force, which is nothing else than difference between chemical potentials, $\Delta\mu = \mu_L - \mu_R$. The consumed energy per unit time is $\dot{Q} = r\Delta\mu$, where r is chemical reaction rate.

Brownian motors

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- We define the chemical force, which is nothing else than difference between chemical potentials, $\Delta\mu = \mu_L - \mu_R$. The consumed energy per unit time is $\dot{Q} = r\Delta\mu$, where r is chemical reaction rate.
- Similarly we obtain the performed work per unit time, which is $\dot{W} = f_{ext} v$, where f_{ext} is a external force and v is the velocity of particles. The efficiency is then

$$\eta = -\frac{f_{ext} v}{r\Delta\mu} \tag{13}$$

Brownian motors

Efficiency of a Chemical ratchet

- Near to equilibrium we can consider a linear thermodynamics, which means that currents are linear functions of forces

$$
\begin{aligned}
v &= L_{11} f_{ext} + L_{12} \Delta\mu \\
r &= L_{21} f_{ext} + L_{22} \Delta\mu
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Brownian motors

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- The efficiency for linear regime has the form

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where $a = f_{ext}/\Delta\mu$.

Brownian motors

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  where $a = f_{ext}/\Delta\mu$.

- The maximal efficiency is given by the relation $\frac{\partial \eta}{\partial a} = 0$ and the maximal value is in terms of $\Lambda = \frac{L_{12}^2}{L_{11} L_{22}}$:

$$\eta_{\max} = \frac{1 - \sqrt{1 - \Lambda^2}}{\Lambda} \tag{15}$$

Brownian motors

Efficiency of a Chemical ratchet

- The maximal efficiency we get for $L_{12}^2 = L_{11}L_{22}$ which means maximal permissible coupling of currents from second law of thermodynamics, the efficiency is therefore $\eta = 1$!
- In comparison to macromotors, where the efficiency is limited by $\eta \leq 1 - \frac{T_c}{T_h}$, here is no restriction to maximal efficiency and micromotors have usually much higher efficiency than macromotors.

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Thank you for attention!