# Fluctuation theorems

Proseminar in theoretical physics

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# Equilibrium systems

- A thermodynamic system is said to be in **thermodynamic equilibrium** if

$$\frac{\partial \rho(x,t)}{\partial t} = 0 \qquad\qquad \forall x, t$$

where $\rho(x,t)$ denotes the phase-space distribution at position $x$ and time $t$.

- A thermodynamic system is in **thermodynamic quasi-equilibrium** if $\rho(x,t)$ varies very slowly in time.
- Equilibrium systems obey classical thermodynamics.

# Theoretical background

- $1^{st}$ law of thermodynamics:

$$dU = \delta Q + \delta W$$

where

  - $Q$ is the heat transferred to the system.
  - $W$ is the work performed upon it.

- $2^{nd}$ law of thermodynamics:

  The entropy of a thermally isolated system that is not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium.

or:

$$dS = \frac{\delta Q_{rev}}{T} \geq 0$$

# Theoretical background (2)

- Consider a system coupled to a heat bath at **constant temperature**.
- If we perform some work $W$ upon the system, the total entropy change of the universe between its initial and final configurations is

$$\Delta S_{tot} = \frac{W - \Delta F_{sys}}{T} \geq 0$$

where

- $\Delta F_{sys}$ is the free energy difference of the system.
- $T$ is the temperature of the heat bath.

# Non-equilibrium systems

- A thermodynamic system is said to be in **thermodynamic non-equilibrium** if

$$\frac{\partial \rho\left(x,t\right)}{\partial t} \neq 0$$

  where $\rho\left(x,t\right)$ denotes the phase-space distribution at position $x$ and time $t$.
- Systems that share energy with other systems are not in equilibrium.
- Most systems found in nature are not in equilibrium.
- Classical thermodynamics does not apply to these systems.

# Fluctuations and small systems

- Consider an ideal gas containing $N$ particles.
- The kinetic energy distribution of the particles is described by the Maxwell-Boltzmann distribution.
- Then

$$\left\langle E_{kin}^{tot} \right\rangle = \frac{3}{2} N k_B T$$

and

$$Var\left(E_{kin}^{tot}\right) = \frac{3}{2} N \left(k_B T\right)^2$$

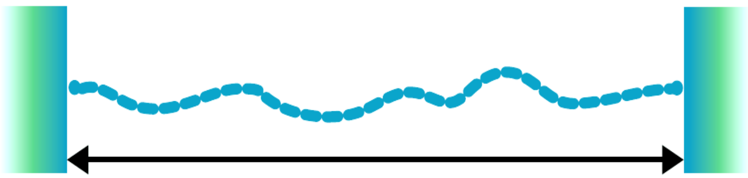
- The fluctuations are of order $1/\sqrt{N}$ .

# Fluctuation theorems

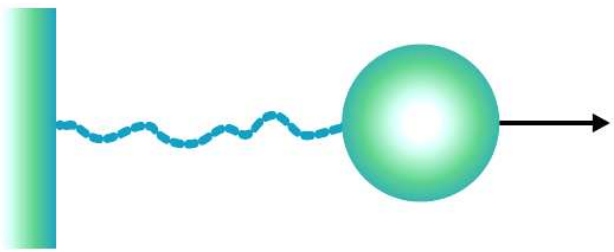
- Only a small number of variables are needed to describe an equilibrium system.
- Non-equilibrium systems cannot be described in that way.
- The **control parameter** is the variable that must be specified to unambiguously define the system's state, while other variables are allowed to fluctuate.

  e.g. string of monomers in water at constant temperature

Control parameter: length



Control parameter: force



# Crooks’ fluctuation theorem (CFT)

G. E. Crooks, Phys. Rev. E 60, 2721 (1999)

- Consider some **finite classical system** coupled to a **constant temperature** heat bath.

- It is then driven out of equilibrium by some time-dependent work process described by a control parameter $\lambda(t)$ .

- The dynamics of the system are required to be:
  - stochastic
  - Markovian
  - microscopically reversible

# Crooks' fluctuation theorem (2)

- Then **Crooks' fluctuation theorem** asserts

$$\frac{P_F\left(s\right)}{P_R\left(-s\right)} = e^{\frac{s}{k_B}}$$

where

- $s$ is the entropy production of the system and the heat bath over some time interval.
- $P_{F/R}\left(s\right)$ the probability of a given entropy production along the forward / reverse path.

- CFT generalizes to systems coupled to a set of baths, each being characterized by a constant intensive parameter.

# CFT: consequences

- Thus we have

$$\frac{P_F(s)}{P_R(-s)} = e^{\frac{s}{k_B}}$$

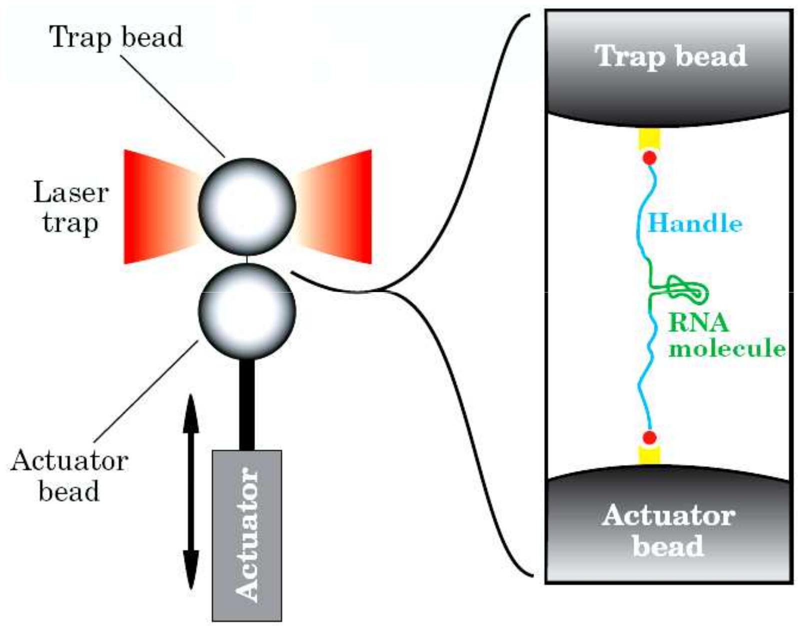
and we know that the entropy – hence the entropy production – is an extensive quantity, i.e. increases with increasing volume of the system.

- This statement solves **Loschmidt's paradox**:

  "Since the microscopic laws of mechanics are invariant under time reversal, there must also exist entropy-decreasing evolutions, in apparent violation of the 2$^{nd}$ law."

# Testing Crooks' fluctuation theorem

D. Collin et al. , *Nature* **437**, 231-234 (2005)




Difference in positions of the bottom and top beads as control parameter.

Work needed to stretch the RNA molecule fluctuates.

# Testing CFT (2)

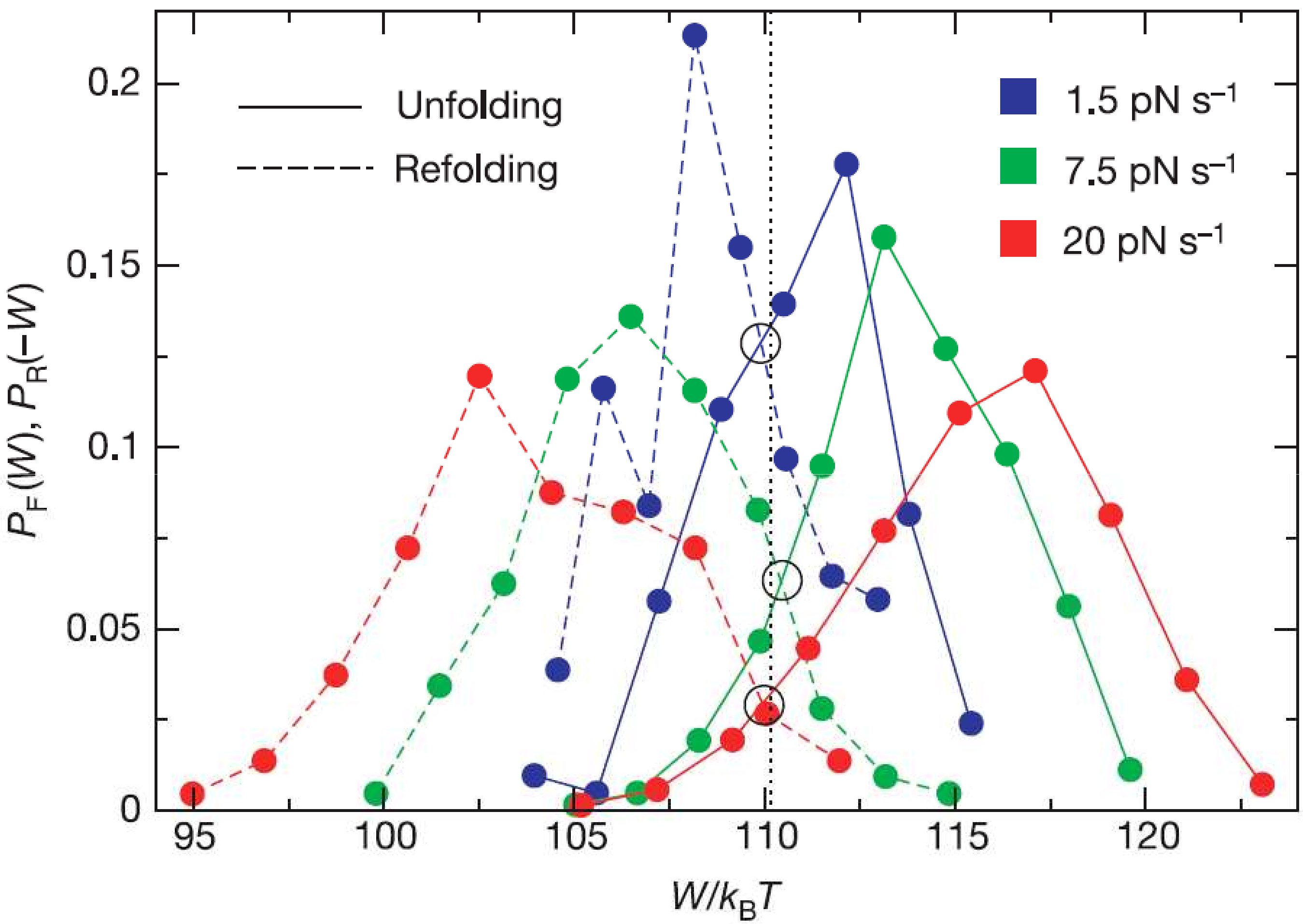
- The unfolding and refolding processes need to be related by time-reversal symmetry.
- If the molecular transition starts in an equilibrium state and reach a well-defined final state. The CFT predicts:

$$\frac{P_F(W)}{P_R(-W)} = e^{\frac{W-\Delta F_{sys}}{k_B T}}$$

Since $s = \Delta S_{tot} = (W - \Delta F_{sys})/T$.

- The CFT does not require that the system studied reaches its final equilibrium state immediately after the unfolding and refolding processes have been completed.

Fluctuation theorems: Testing CFT




$$P_F(W) = P_R(-W) \Leftrightarrow W = \Delta F_{sys}$$

# Proof of CFT

- Consider a finite classical system coupled to a heat bath at constant temperature.
- State of the system specified by $x$ and $\lambda$ .
- Particular path denoted by: $(x(t), \lambda(t))$,

  the corresponding reversed path by: $\big(\bar{x}(-t), \bar{\lambda}(-t)\big)$

  where we shifted origin such that: $t \in [-\tau, \tau]$

# Proof of CFT (2)

- Dynamics are stochastic, Markovian and satisfy the following microscopically reversible condition:

$$\frac{P\left[x(t) \mid \lambda(t)\right]}{P\left[\bar{x}(-t) \mid \bar{\lambda}(-t)\right]} = e^{-\frac{Q[x(t),\lambda(t)]}{k_B T}}$$

  where $Q\left[x(t),\lambda(t)\right] = -Q\left[\bar{x}(-t),\bar{\lambda}(-t)\right]$ is the heat or amount of energy transferred to the system from the bath along the path.
- Let $\rho\left(x,t\right)$ denote the phase-space distribution at time $t$ and position $x$ .
- To be continued on the white board.

# CFT: particular cases
# Jarzynski's equality

C. Jarzynski, Phys. Rev. Lett. 78, 2690 (1997)

- It follows from CFT that for systems starting and ending in equilibrium

$$P_F\left(W\right)e^{-\frac{W-\Delta F_{sys}}{k_BT}} = P_R\left(-W\right)$$

- Then integrating over $W$ yields **Jarzynski's equality**

$$\left\langle e^{-\frac{W-\Delta F_{sys}}{k_BT}} \right\rangle = 1 \Leftrightarrow e^{-\frac{\Delta F_{sys}}{k_BT}} = \left\langle e^{-\frac{W}{k_BT}} \right\rangle$$

where the angle brackets denote an average over a large number of non-equilibrium processes between the two equilibrium states.

# Jarzynski’s equality (2)

- Jarzynski’s equality holds for systems driven arbitrarily far from equilibrium.
- Using Jensen’s inequality for convex functions

$$\langle f(x) \rangle > f(\langle x \rangle)$$

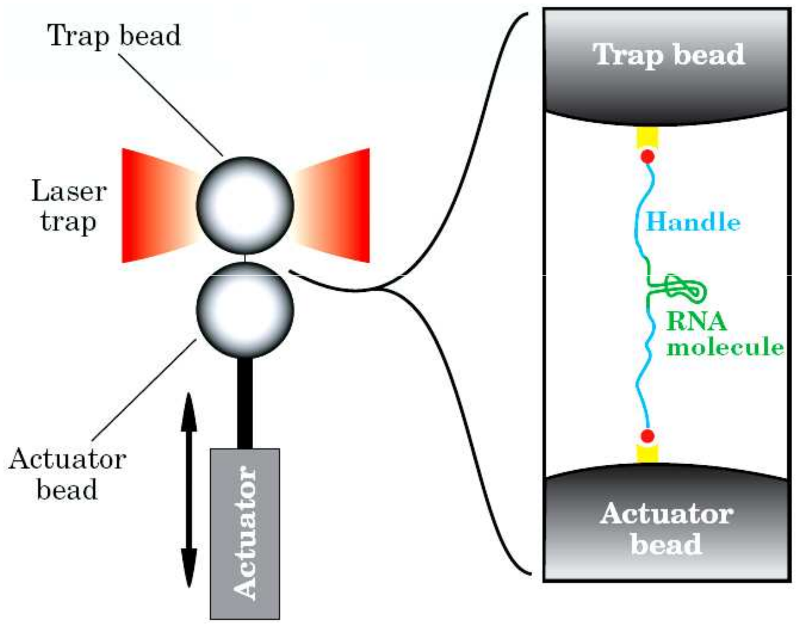
one can readily show that Jarzynski’s equality implies the 2nd law of thermodynamics

$$\langle W \rangle > \Delta F_{sys}$$

- Jarzynski’s equality was successfully tested in 2002 by stretching a polymer between its folded and unfolded configuration, both reversibly and irreversibly.

# Testing Jarzynski's equality

J. Liphardt et al. , *Science* **296**, 1832 (2002)



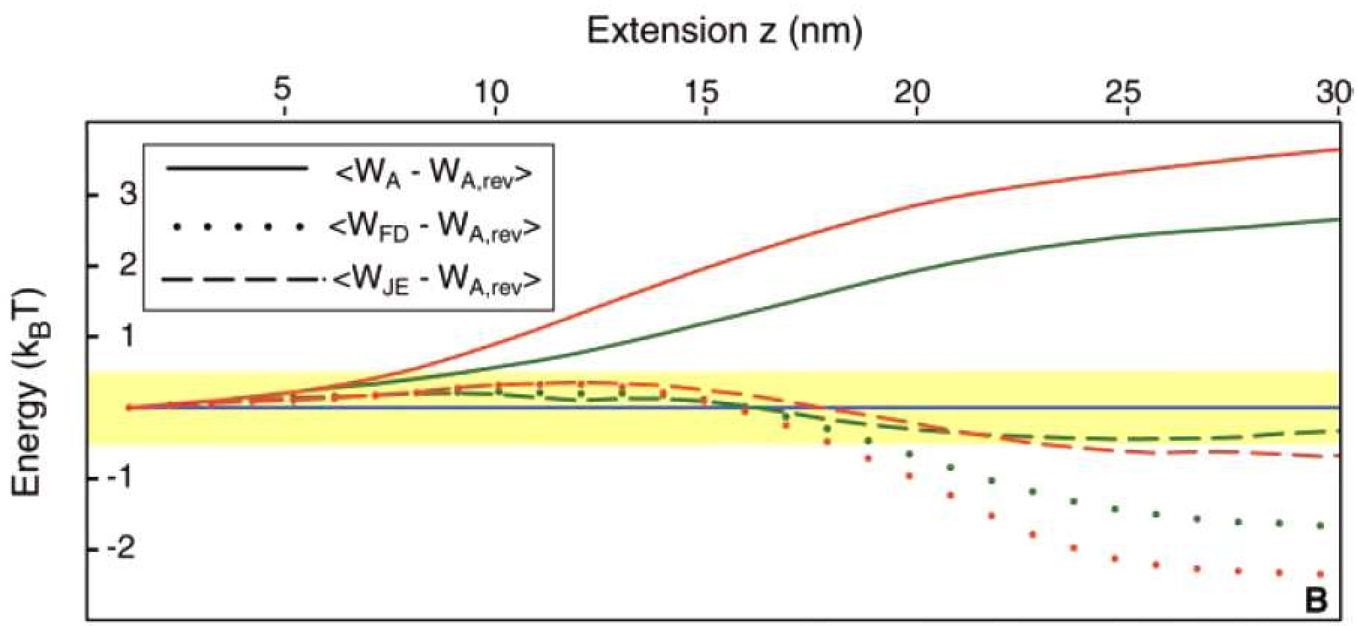

Difference in positions of the bottom and top beads as control parameter.

Work needed to stretch the RNA molecule fluctuates.

Compare three different estimates for $\Delta F_{sys}$ :

- the average work: $W_A = \langle W \rangle$
- the fluctuation dissipation estimate: $W_{FD} = \langle W \rangle - \frac{1}{2}\beta\sigma^2$
- the estimate from Jarzynski's equality:

$$W_{JE} = -(k_B T)^{-1} \log\left(\left\langle e^{-\frac{W}{k_B T}} \right\rangle\right)$$



# CFT: particular cases (2) Gallavotti-Cohen's fluctuation theorem

G. Gallavotti, E. Cohen, *Phys. Rev. Lett.* **74**, 2694 (1995)

- A system driven by a time symmetric periodic process will settle into a **non-equilibrium steady state**.
- If we begin where the control parameter is also time symmetric, CFT is valid for any integer number of cycles and reads

$$\frac{P(s)}{P(-s)} = e^{\frac{s}{k_B}}$$

where

- $s$ is the entropy production of the system and the heat bath over some time interval.
- $P(s)$ the probability of a given entropy production along the path.

# GC fluctuation theorem (2)

- Since the system begins and ends in the same probability distribution, the average entropy production depends only on the average amount of heat transferred to the system.
- Approximation

$$s \approx -Q/T$$

where $Q$ is the heat transferred from the bath to the system during the time $t$.

- In the long-time limit we obtain **Gallavotti-Cohen's fluctuation theorem**:

$$\lim_{t \to \infty} \frac{P(Q)}{P(-Q)} = e^{\frac{Q}{k_B T}}$$

# GC fluctuation theorem (2)

- Gallavotti-Cohen’s fluctuation theorem simply ignores the relatively small and difficult to measure microscopic entropy of the system.
- It is only asymptotically true, whereas Crooks’ fluctuation theorem is valid at any time.
- It was successfully tested in 2005, collecting the probability distributions of power injected and dissipated by a small electrical dipole that was maintained in a non-equilibrium steady state by injection of a constant current.

  (N. Garnier and S. Ciliberto, *Phys. Rev. Lett.* **71**, 060101(2005))

# Summary

- Fluctuations cannot be neglected for small systems.
- There are only few analytic relations in the non-equilibrium thermodynamics of small systems: these are the so-called fluctuation theorems.
- Paths with negative entropy production are possible, but become exponentially unlikely for macroscopic systems ($2^{nd}$ law of thermodynamics is not violated).
- Fluctuation theorems allow for a measurement of the free energy difference between two equilibrium states using non-equilibrium processes (CFT and Jarzynski equality).