a) Gallavotti - Cohen theorem

- Based on computer simulations of Evans et al. (1993), Gallavotti & Cohen (1995) show that the probability distribution $P(\bar{\sigma}_t)$ of the time averaged entropy production

$$\bar{\sigma}_t = \frac{1}{t}\int_0^t ds\, \sigma(s) \quad , \quad \sigma(s): \text{ entropy production in a NESS}$$

satisfies the symmetry relation

$$\lim_{t\to\infty} \frac{k_B}{t} \ln \frac{P(\bar{\sigma}_t)}{P(-\bar{\sigma}_t)} = \bar{\sigma}_t \qquad \text{(GC)}$$

that is, for long enough times

$$\frac{P(-\bar{\sigma}_t)}{P(\bar{\sigma}_t)} \simeq e^{-t\bar{\sigma}_t/k_B}$$

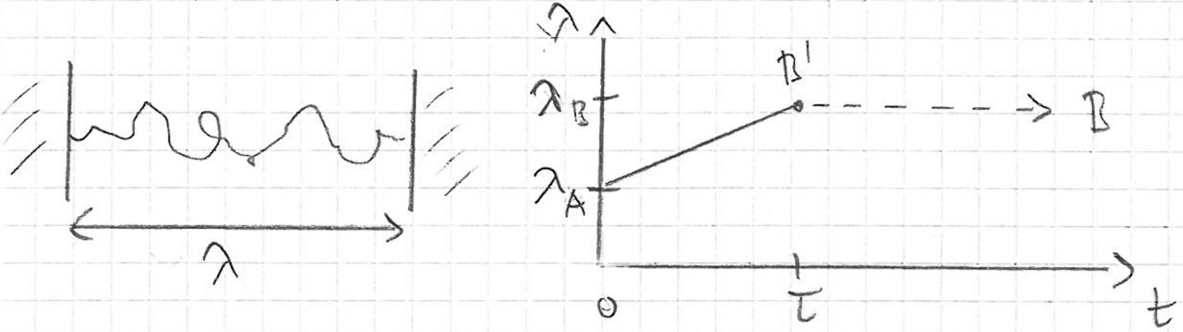
- This implies that trajectories with $\bar{\sigma}_t < 0$ (which violate the 2nd law of thermodynamics) are exponentially unlikely but occur with finite probability.

- The Onsager relations can be derived from (GC) (Gallavotti, 1996)

b) Work theorems

Consider a small system in contact with a heat bath at temperature T. By changing a control parameter λ, the system is taken from an equilibrium state A to some other (generally non equilibrium) state B', which eventually relaxes to an equilibrium state B.

Example: Stretching of a polymer



Let W denote the work required to stretch the system, and $F_{A,B}$ the free energies of the equilibrium state A and B. Then we have

$$\Delta F = F_B - F_A = \underbrace{E_B - E_A}_{W} - T(\underbrace{S_B - S_A}_{\Delta S})$$

with $\langle \Delta S \rangle = 0$ reversible process $(\tau \to \infty)$

$\langle \Delta S \rangle > 0$ irreversible process

$\Rightarrow$ generally $\langle W \rangle \geq \Delta F$.

For small systems W is a fluctuating quantity and

$$\langle e^{-W/k_BT} \rangle = e^{-\Delta F/k_BT} \qquad (J)$$

(Jarzynski, 1997)

Using Jensens inequality

$$\langle f(x) \rangle \geq f(\langle x \rangle) \quad \text{for convex functions}$$

it follows that

$$1 = \langle e^{-\frac{W-\Delta F}{k_BT}} \rangle \geq e^{-\frac{\langle W - \Delta F \rangle}{k_BT}}$$

$$\Rightarrow \underline{\langle W \rangle \geq \Delta F}$$

(J) can be derived from the more general Crooks fluctuation theorem (1999)

$$\frac{P_F(W)}{P_R(-W)} = \exp\left(\frac{W - \Delta F}{k_BT}\right) \qquad (C)$$

which compares the work distribution for forward (P_F) and time-reversed (P_R) processes.

<u>Derivation of (J) from (C):</u>

$$P_F(W)\, e^{-W/k_BT} = P_R(-W)\, e^{-\Delta F/k_BT}$$

$$\Rightarrow \langle e^{-W/k_BT} \rangle = e^{-\Delta F/k_BT}$$

by integration.

Application: In the form

$$\Delta F = -k_B T \ln \langle e^{-W/k_B T} \rangle$$

(?) can be used to estimate free energy differences from irreversible trajectories. In particular, if the distribution of W is Gaussian, then

$$\langle e^{-W/k_B T} \rangle = e^{-\beta \langle W \rangle} \, e^{\frac{1}{2}\beta^2 (\langle W^2 \rangle - \langle W \rangle^2)}$$

$$\beta = 1/k_B T$$

$$\Rightarrow \quad \left. \begin{array}{l} \Delta F = \langle W \rangle - \frac{1}{2} \beta \sigma_W^2 \\ \sigma_W^2 : \text{variance of } W \end{array} \right\}$$

In general, ΔF is given in terms of the cumulants of W.

c) A simple proof of the Jarzynski relation

Fluctuation theorems and work relations have been established in a variety of settings (classical mechanics, stochastic dynamics, quantum). Here we sketch the original derivation of Jarzynski for a simple case.

Consider a Hamiltonian system with phase space variables

$$(q, p) = (q_1, \dots, q_n, p_1, \dots, p_n) =: x$$

The system evolves under a Hamiltonian $H_\lambda(x)$ depending on a time-dependent parameter λ:

$$\lambda(t): \quad \lambda(0) = 0, \quad \lambda(\tau) = 1 \qquad \tau: \text{final time}$$

Example:
- Distance between beads in a polymer stretching experiment.
- Particle & piston ⊛

Protocol:

- System starts at $t=0$ in equilibrium state at temperature T

  $\Rightarrow$ initial point $x(0)$ is drawn from the canonical phase space density

$$f(x,0) = \frac{1}{Z_0} e^{-\beta H_0(x)}$$

- System evolves without contact to the heat bath up to time t_1, while $\lambda(t)$ changes from 0 to 1, and H_λ from H_0 to H_1.

- The work performed along a given trajectory ending at x is then

$$W(x) = H_1(x) - H_0(x_0(x))$$

where $x_0(x)$ is the unique initial point of this trajectory.

$$\Rightarrow \langle e^{-\beta W} \rangle = \int dx\, f(x,\tau)\, e^{-\beta (H_1(x) - H_0(x_0(x)))}$$

Now we use the fact that, according to Liouville's theorem, the phase space density is constant along trajectories

$$\Rightarrow \quad f(x,\tau) = f(x_0(x), 0) = \frac{1}{Z_0} e^{-\beta H_0(x_0(x))}$$

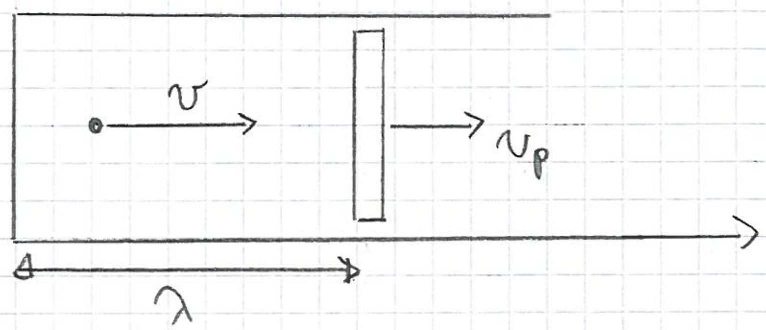
$$\Rightarrow \underline{\langle e^{-\beta W} \rangle} = \int dx \frac{1}{Z_0} e^{-\beta H_1(x)} =$$

$$= \frac{Z_1}{Z_0} = e^{-\beta (F_1 - F_0)} = \underline{e^{-\beta \Delta F}}$$

$\square$

More work is required to show that the result remains true when the system is (weakly) coupled to the temperature reservoir during the process.

⊛ Lua & Grosberg, J. Phys. Chem. B 109 (2005) 6805

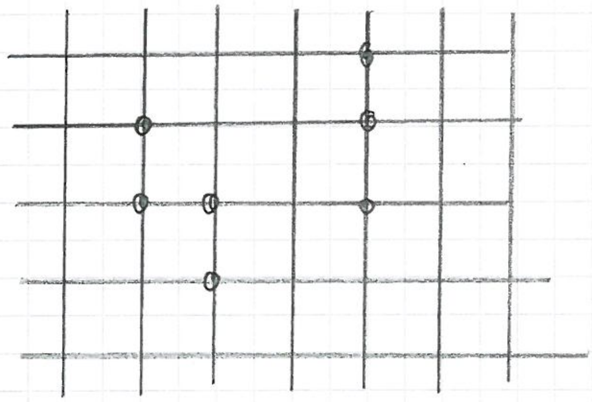


II. Statistical physics of driven diffusive systems

Motivation:

(i) Discrete state space easier to handle than continuous phase space (cf. Ising model)

Here we consider lattice gas models:



- particles occupy sites of (finite) d-dim lattice $\Omega \subset \mathbb{Z}^d$
- Configuration $\eta = \{\eta_x\}_{x \in \Omega}$

$$\eta_x = \begin{rcases} 0 & x \text{ is vacant} \\ 1 & x \text{ is occupied} \end{rcases}$$

- indistinguishable particles with exclusion interaction (at most one particle per site)

(ii) Stochastic microscopic dynamics to avoid problems associated with ergodicity, chaos and dissipation in deterministic Hamiltonian dynamics.

Driven diffusive systems: (v. Beijeren, Kutner, Spohn 1985)

Stochastic lattice gas with single conserved density ($\rightarrow$ "diffusive") in NESS ($\rightarrow$ "driven").

In mathematics these are known as exclusion processes

1° Introduction to exclusion processes

(F. Spitzer, 1970)

- Lattice gas configuration $\eta = \{\eta_x\}_{x \in \Omega}$, $\Omega \subset \mathbb{Z}^d$
- Dynamics (continuous time Markov process):

(i) each particle carries "clock" that rings according to Poisson process of unit rate (= exponentially distributed waiting times)

(ii) when clock rings, particle at site x selects target site y with probability

$$q_{xy}(\eta), \quad \sum_y q_{xy}(\eta) = 1$$

(iii) particle jumps to y if $\eta_y = 0$, else the move is discarded (= exclusion interaction)

Simplest case: One-dimensional lattice with

- nearest neighbor hopping
- translation invariance
- only exclusion interaction

$$\Rightarrow \quad q_{xy}(\eta) = q\, \delta_{y,x+1} + (1-q)\, \delta_{y,x-1}$$

Special cases:

(i) $q = \frac{1}{2}$ $\Rightarrow$ symmetric simple exclusion process (SSEP)

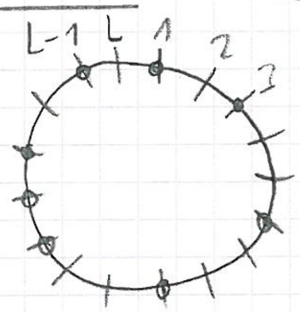
(ii) $q \neq \frac{1}{2}$ $\Rightarrow$ asymmetric simple exclusion process (ASEP)

(iii) $q = 1$ (or 0) $\Rightarrow$ totally asymmetric simple exclusion process (TASEP)

(iv) $q = \frac{1}{2} + \varepsilon$: WASEP

Boundary conditions:

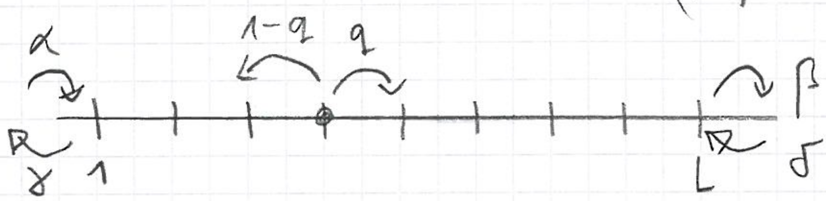
(i) periodic:



- identify sites $L+1$ and 1
- steady particle current for $q \neq 1/2$

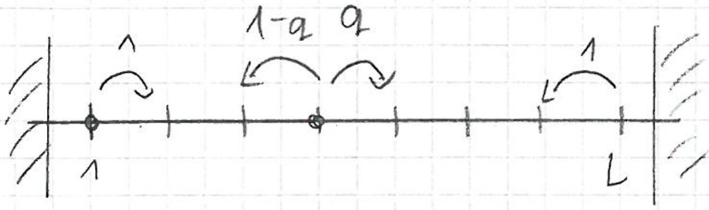
- particle number N fixed $\Rightarrow$ $\binom{L}{N}$ configurations

(ii) open:



- boundary rates $\alpha, \beta, \gamma, \delta$
- boundary-induced NESS for $q = \frac{1}{2}$
- particle number not fixed $\Rightarrow$ 2^L configurations

(iii) closed:

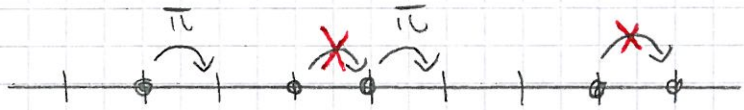


- particle number fixed
- inhomogeneous equilibrium state for $q \neq \frac{1}{2}$, but no NESS

$\Rightarrow$ boundary conditions are very important!

Variants of the basic model

- TASEP with discrete time dynamics (dTASEP)[1]:



$t \rightarrow t+1$

All eligible particles jump simultaneously with probability π, $\pi \in (0, 1]$.

$\pi \rightarrow 0$: continuous time TASEP in time πt

$\pi = 1$: deterministic cellular automaton (Wolfram's CA 184)

- Jump probability q_{xy} can depend on position (spatial disorder) or on the particle label (particlewise disorder)

[1] Yaguchi 1986; Schadschneider & Schreckenberg 1993