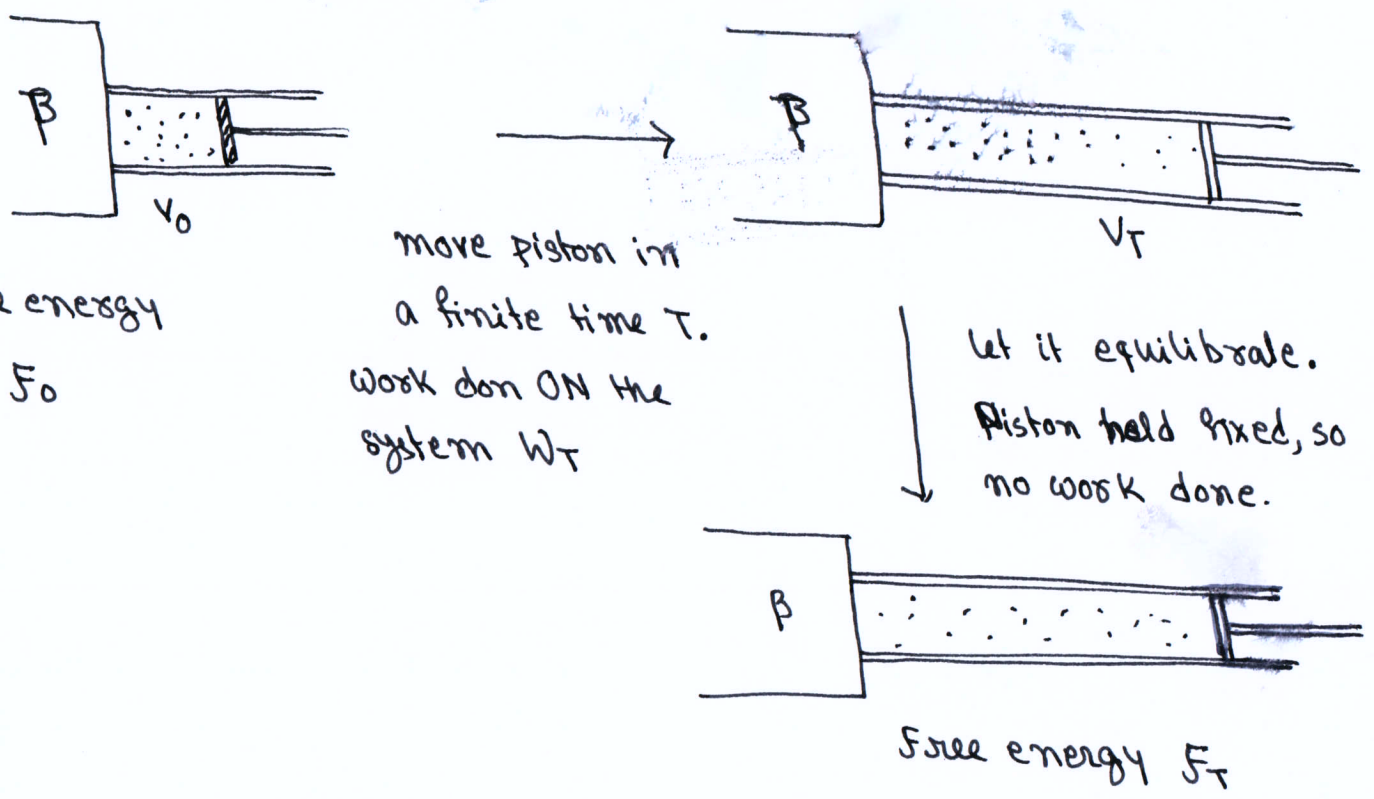


Jarzynski equality: The above relation, that we obtained for Langevin equation, holds ~~also~~ for more general system.



In 1997, Jarzynski showed that

$$\langle e^{-\beta W_T} \rangle = e^{-\beta(F_T - F_0)}$$

Team papers.

Ref: PRL, 78, 2690 (1997) An. rev. cond. matt. 2, 329 (2011)

Important points:

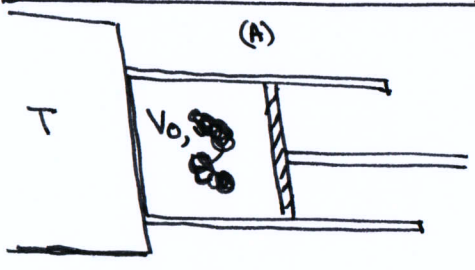
- ① The relation holds irrespective of how one moves the piston.
- ② Using Jensen inequality [for a convex function $f(x)$, $\langle f(x) \rangle \geq f(\langle x \rangle)$] we get

$$e^{-\beta(F_T - F_0)} = \langle e^{-\beta W_T} \rangle \geq e^{-\beta \langle W_T \rangle}$$

$$\Rightarrow \boxed{F_T - F_0 \leq \langle W_T \rangle}$$

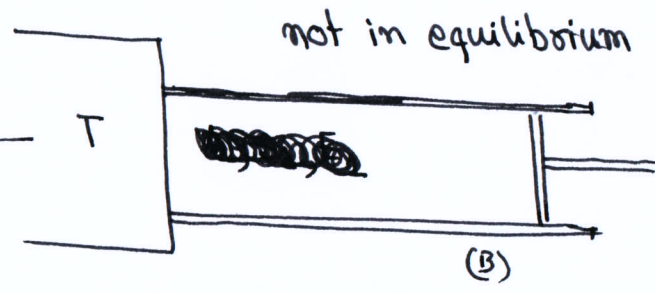
This is consistent with ^{the} second law of thermodynamics.

Brief review of thermodynamics:



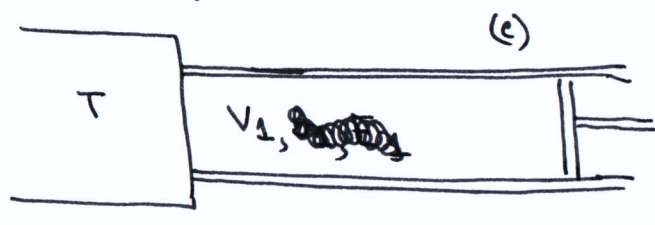
in equilibrium
Canonical, fixed volume ensemble

finite time



* T is temperature
"a change in notation" *

equilibrate



inequilibrium
canonical, fixed volume ensemble

The equilibrium state is characterized by Free energy

$$F_0 = F(T, V_0) = \langle E_0 \rangle - T \langle S_0 \rangle$$

and

$$F_1 = F(T, V_1) = \langle E_1 \rangle - T \langle S_1 \rangle$$

Free energy is a thermodynamic potential, as it gives an estimate (bound) on how much work can be extracted. This bound comes from second law of thermodynamics

$$\langle \Delta S_{universe} \rangle \geq 0.$$

If we ~~went~~ ^{went} from A \rightarrow C in a quasistatic process (reversible), then

$$-\frac{\langle \Delta Q \rangle_{quasi}}{T} \bullet \langle S_1 \rangle - \langle S_0 \rangle = \bullet \langle \Delta S_{universe} \rangle = 0$$

average heat
flowed from reservoir
into the system.

reversible
process.

Then

$$\langle S_2 \rangle - \langle S_0 \rangle = \frac{\langle \Delta Q \rangle_{\text{quasi}}}{T}$$

gives the difference in state variable $\langle S \rangle$ between the initial and final equilibrium states.

Non-quasi-static : When the process is done in a finite time t_f , the process is irreversible. Then, ~~some~~ ~~law~~

$$-\underbrace{\frac{\langle \Delta Q \rangle_{\text{irr}}}{T}}_{\langle \Delta S_{\text{env}} \rangle} + \underbrace{\langle S_1 \rangle - \langle S_0 \rangle}_{\langle \Delta S_{\text{sys}} \rangle} \geq 0$$

second law of thermodynamics.

\Rightarrow ~~some~~ Entropy change

$$\langle \Delta S_{\text{prod}} \rangle = \langle \Delta S_{\text{env}} \rangle + \langle \Delta S_{\text{sys}} \rangle \geq 0$$

\hookrightarrow This much entropy is produced by the irreversible change

Relation to work : using first law of thermodynamics

$$\langle \Delta Q \rangle + \langle W \rangle = \langle E_1 \rangle - \langle E_0 \rangle$$

We get

$$\langle \Delta S_{\text{prod}} \rangle = \langle S_1 \rangle - \langle S_0 \rangle - \frac{1}{T} \{ \langle E_1 \rangle - \langle E_0 \rangle - \langle W \rangle \}$$

For later use

$$\langle \Delta S_{\text{prod}} \rangle T = \langle W \rangle - \Delta F$$

$$\Rightarrow T \langle \Delta S_{\text{prod}} \rangle = [\langle E_0 \rangle - T \langle S_0 \rangle] - [\langle E_1 \rangle - T \langle S_1 \rangle] + \langle W \rangle = F_0 - F_1 + \langle W \rangle \geq 0$$

$$\Rightarrow \langle W \rangle \geq F_1 - F_0$$

work done on the system is bounded by the change in Free energy.

Some amount of work gets dissipated, ~~and there~~ as compared to a reversible process. That's why $\langle W \rangle - \Delta F = \langle W_{\text{diss}} \rangle$ is called dissipated work.

Remark : work done by the system (extracted work) ~~($\langle W_{\text{ex}} \rangle$)~~ $W_{\text{ex}} = -W$

and then

$$\langle W_{\text{ex}} \rangle \leq F_1 - F_0$$

Important : note that for each experiment there is a different W , ie the work done is a fluctuating quantity.

These are trajectories for which

$$W < F_1 - F_0 \quad (F \text{ does not depend on trajectory})$$

This is some times called transient violation second law. (discussed by Peresin)

Second law gives bound only for the average work $\langle W \rangle$.

Alternate versions of Jarzynski equality :

① We saw that ^{average} entropy production (in an irreversible process)

$$\langle S_{\text{production}} \rangle = (\langle W \rangle - \Delta F) \frac{1}{T}$$

~~Entropy is a state variable~~ In thermodynamics entropy always is an averaged quantity (it is a state variable)

We can be a bit ambitious and define entropy production

$$S_{\text{production}} = (W[x^{(t)}] - \Delta F) \frac{1}{T}$$

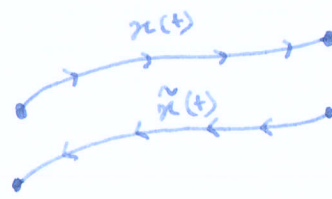
for each trajectory. This is then a fluctuating quantity.

Jarzynski relation then tells

$$\left\langle e^{-\frac{S_{\text{prod}}}{k_B}} \right\rangle = 1$$

non-equilibrium fluctuation relation.

(a) Crook's equality:



We have shown

$$\text{Prob}[\tilde{x}(t) | P_{eq}, U_T] = \text{Prob}[x(t) | P_{eq}, U_0] e^{\frac{\Delta F}{D} - \frac{W}{D}}$$

W is the work done for the forward process.

The backward protocol then has $-W$ amount of work done on the system

If we add all such paths for W amount of work, then we get

$$\text{Prob}_{\text{Back}}(-W) = \text{Prob}_{\text{For}}(W) \cdot e^{\frac{\Delta F - W}{D}}$$

This is Crook's work relation.

Considering ΔF is not a fluctuating quantity, we also get equivalently (using $T \cdot S_{\text{prod}} = W - \Delta F$)

$$\text{Prob}_{\text{Back}}(-S_{\text{prod}}) = \text{Prob}_{\text{For}}\left(S_{\text{prod}} + \frac{\Delta F}{T}\right) e^{-S_{\text{prod}}}$$

$$\Rightarrow \frac{\text{Prob}_{\text{Back}}(-S_{\text{prod}})}{\text{Prob}_{\text{For}}(S_{\text{prod}})} = e^{-S_{\text{prod}}}$$

[This is for a time varying potential.]

* If the ~~system~~ initial and final state are in same equilibrium, i.e., $\Delta F = 0$, the

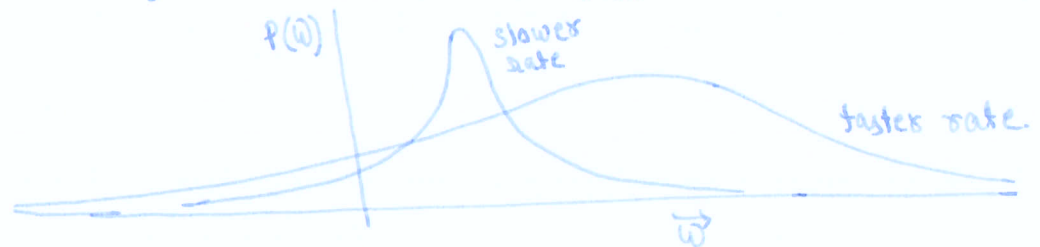
$$\frac{P(-S_{\text{prod}})}{P(S_{\text{prod}})} = e^{-S_{\text{prod}}}$$

Why are fluctuation theorems important?

① They are general exact results valid arbitrarily far from equilibrium (beyond linear response regime).

② ~~Second law of~~ Thermodynamics gives law for averages. Statistical mechanics (equilibrium) gives information of fluctuations, but primarily in ~~eq~~ and near equilibrium. ~~Fluctuation~~ Fluctuation theorems give quantitative results for fluctuations outside equilibrium.

For example, work done has distribute



Thermodynamics only give bound for $\langle w \rangle$.

~~These~~ For large systems ($N \sim 10^{23}$) such fluctuations are ~~are~~ extremely rare. They become important for small scale systems, like biomolecules, nano-scale systems. Fluctuation theorem quantifies how rare these fluctuations are.

③ ~~Using~~ Jarzynski equality, gives a method for estimating equilibrium free energy from ~~non-eq~~ experiments.

$$F_1 - F_0 = -k_B T \log \left\langle e^{-\frac{w}{k_B T}} \right\rangle$$

example: in biomolecules, F. Ritort, J. Phys, 18, R531 (2006).

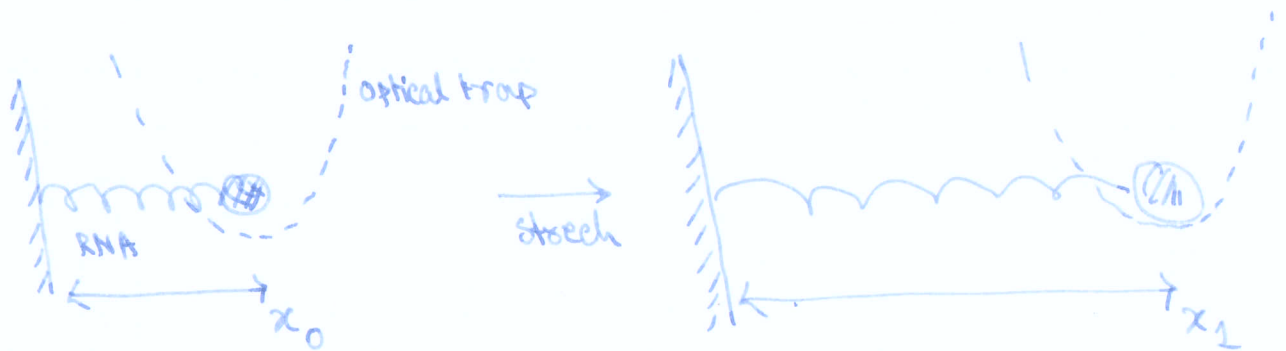
④ Liphardt et al, Science, 296, 1832 (2002).

③ Bustamante et al., Phys today, 43 (2005).

Remarks:

- ① There are several derivations of Jarzynski relation, in Hamiltonian systems [Jarzynski, PRL, 79, 2050 (1997)], stochastic dynamics ~~Master equations~~ [Jarzynski, PRE, 56, 5018 (1997), PRE, 73, 046105 (2006)], and in exactly solvable models [Jarzynski, Ann Rev Cond Mat 2, 329 (2011)] and in quantum systems [Kurchan, Tasaki,

- ② The relation has been verified in several experiments. of ~~one such experiment is by RNA stretching and~~ RNA-stretching, and ~~other~~ trapped colloidal particles, for example
 ↳ Ref: Collin et al, Nature, 437, 231 (2005)



Both at initial and final state the RNA is in equilibrium with surrounding fluid medium.

Detailed fluctuation theorem

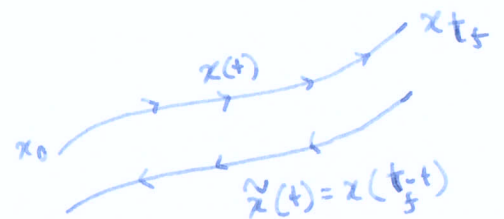
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Until now we discussed gradient force (conservative force) $F_t(x) = -U'_t(x)$, such that stationary state is in equilibrium. For more general scenario the system is out-of-equilibrium. This could be systems that is evolving towards equilibrium stationary state, or it could be the stationary state is out-of-equilibrium.

In this case, the dynamics is not time reversible. Can we quantify this?

[We shall learn : ① entropy production for trajectories, and
② Gallavotti-cohen fluctuation relation.]

Let's follow a similar analysis as earlier



$$\begin{aligned} P[\tilde{x}(t)] &= e^{-\frac{1}{4D} \int_0^{t_f} dt \left(\tilde{x}(t) - F_{t_f-t}(\tilde{x}(t)) \right)^2} \\ &\quad \times e^{-\frac{1}{2} \int_0^{t_f} dt F'_{t_f-t}(\tilde{x}(t))} \times P_{t_f}(x_{t_f}) \\ &= e^{-\frac{1}{4D} \int_0^{t_f} dt \left(x(t) - F_t(x(t)) \right)^2} - \frac{1}{2} \int_0^{t_f} dt \cdot F'_t(x(t)) \times P_0(x_0) \\ &\quad \times e^{-\frac{1}{D} \int_0^{t_f} dt \cdot \dot{x}(t) \cdot F_t(x(t))} \times \frac{P_{t_f}(x_{t_f})}{P_0(x_0)} \end{aligned}$$

$\tilde{x}(t) = x(t_f - t)$

This gives

$$P[\tilde{x}(t)] = P[x(t)] \times e^{-\frac{\Delta S_{\text{prod}}(t)}{k_B}}$$

where we define

$$\Delta S_{\text{prod}}(t_f) = + \frac{\int_0^{t_f} dt \cdot \dot{x} \cdot F_t(x(t))}{T} - k_B \log P_{t_f}(x(t_f)) + k_B \log P_0(x(0)).$$

(defining!)

(* used $D = k_B T$)

Recognising that ΔS_{prod} is the entropy production in each trajectory, the above relation is known as the Gallavotti-Cohen fluctuation relation. This is a topological relation, but we shall see that there are interesting consequences for observed quantities.

Why it is entropy production?

① By a similar argument as before, $-\int_0^{t_f} dt \cdot \dot{x} \cdot F_t(x(t)) = Q_{t_f}$ is the energy (heat) flow from bath to the particle. Therefore

$$\Delta S_{\text{env}} = - \frac{Q_{t_f}}{T}$$

② ~~Extending the idea of Shannon~~
Shannon entropy in equilibrium

$$\langle S_{\text{sys}} \rangle = - k_B \int dx P_{\text{eq}}(x) \log P_{\text{eq}}(x) = - \langle k_B \log P_{\text{eq}}(x) \rangle$$

One way to extend this idea for ~~some~~ ~~reversed~~ non-equilibrium is

$$\langle S_{sys}(t) \rangle = -k_B \int dx \cdot P_t(x) \log P_t(x) = - \langle k_B \log P_t(x) \rangle_t$$

This is consistent with Boltzmann's H-function.

Further extending this idea, we could assign entropy to each trajectory

$$S_{sys}(t) = -k_B \log P_t(x(t))$$

\downarrow
 This means, solve the $P_t(x)$ from FP equation for a given initial P_0 , then ~~get~~ for a trajectory $x(t)$, get

$$P_t(x(t)) = P_t(x) \Big|_{x=x(t)}$$

Following this definition

$$\Delta S_{sys}(t_f) = -k_B \log P_{t_f}(x(t_f)) + k_B \log P_0(x(0))$$

Further justification

① When in equilibrium: $\langle \Delta S_{env} \rangle = - \frac{\langle \Delta Q \rangle}{T} = 0$

$$\left[\Delta Q = \int_0^t dt \cdot \dot{x} \cdot F(x) = - \int_{x_0}^{x_t} dx \cdot U'(x) = U(x_0) - U(x_t) \right] \\
 \Rightarrow \langle \Delta Q \rangle = 0$$

and $\langle S_{sys} \rangle = -k_B \int dx P_{eq}(x) \log P_{eq}(x)$

$$= -k_B \int dx \frac{e^{-\beta U(x)}}{Z} \log \frac{e^{-\beta U}}{Z} = \frac{1}{T} \langle U \rangle$$

① In equilibrium :

$$\begin{aligned} S_{\text{sys}}(t) &= -k_B \log \frac{e^{-\beta U(x(t))}}{\mathcal{Z}_N} \\ &= \frac{1}{T} U(x(t)) - \underbrace{\left(-k_B \log \mathcal{Z}_N \right)}_F \end{aligned}$$

$$\Rightarrow \Delta S_{\text{sys}} = \frac{1}{T} \left(U(x(t_f)) - U(x(t_0)) \right)$$

Similarly

$$\Delta S_{\text{env}} = -\frac{\Delta Q}{T} = -\frac{1}{T} \int_0^{t_f} dt \cdot \dot{x}(t) \cdot U'(x(t)) = -\frac{1}{T} \left(U(x(t_f)) - U(x(t_0)) \right)$$

$\Rightarrow \Delta S_{\text{prod}} = 0$ for every evolution in equilibrium.

Also means $\langle \Delta S_{\text{prod}} \rangle = 0$ as demanded from thermodynamics.

Also see that, $T \langle S_{\text{sys}} \rangle = \langle U \rangle - F$ definition of free energy in stat mech and thermodynamics.

② ~~Our~~ Our definition ΔS_{prod} is consistent with

$\langle \Delta S_{\text{prod}}(t) \rangle$ is a monotonically increasing function as demanded by second law.

For proof see: eq (26) in lecture note of Seifert.

③ This choice leads to detailed fluctuation relations whose consequences have been tested in models and in experiments.

Entropy Production in Stochastic process:

For a continuous time Markov process, defined by

$$\frac{\partial P_t(c)}{\partial t} = \sum_{c'} \underbrace{[w(c, c') P_t(c') - w(c', c) P_t(c)]}_{J_t(c, c')}$$

~~$\Delta S_{sys}(t_f) = -k_B \log$~~ trajectories are made of jumps



For a trajectory, we define

$$\Delta S_{sys}(t) = -k_B \log P_t(c(t)) + k_B \log P_0(c(0))$$

$$\Delta S_{env}(t) = k_B \sum_i \log \frac{w_{ti}(c_i^+, c_i^-)}{w_{ti}(c_i^-, c_i^+)}$$

Reasons for this choice are similar as before

① In equilibrium: $\frac{w(c', c)}{w(c, c')} = \frac{P_{eq}(c')}{P_{eq}(c)} = e^{-\beta [E(c') - E(c)]}$

$\Rightarrow \Delta S_{env} = -\frac{1}{T} \sum_i E(c_i^+, c_i^-) = -\frac{1}{T} \Delta E$
 net energy (heat) flow from reservoir.

and $\Delta S_{sys} = \frac{1}{T} E(c(t)) - \frac{1}{T} E(c(0))$

$\Rightarrow \Delta S_{prod} = \Delta S_{env} + \Delta S_{sys} = 0.$

② It can be shown that for this choice

$\langle \dot{S}_{\text{prod}} \rangle$ is a monotonically increasing function, consistent with second law.

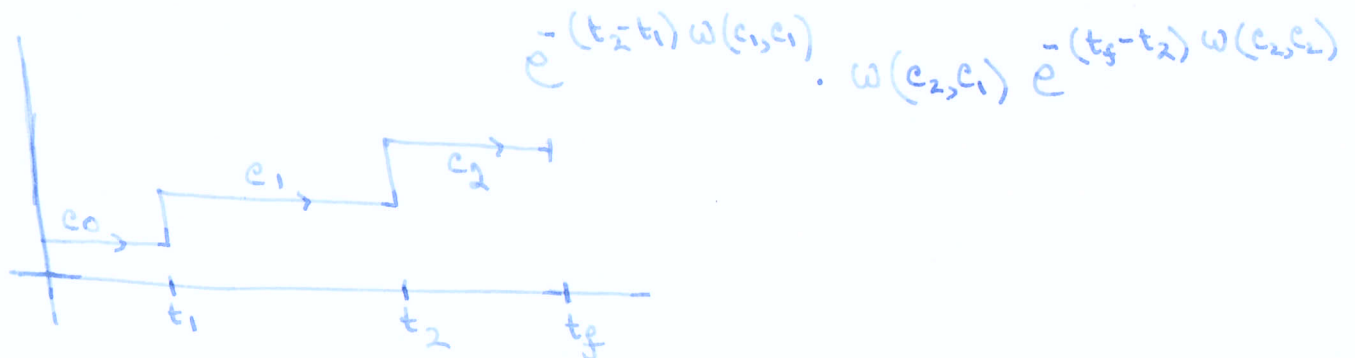
Moreover, using the Master equation, it can be shown [see article by Kishore Mallik, Thermodynamic and information theory, eq (48).] that

Entropy production rate

$$\langle \dot{S}_{\text{prod}} \rangle = \frac{1}{2} \sum_c \sum_{c'} \mathcal{J}_+(c, c') \log \frac{w(c, c') P_+(c')}{w(c', c) P_+(c)} \geq 0.$$

③ Quantifies breaking of time reversal symmetry.

$$P[c(t)] = P_0(c_0) e^{-t_1 \omega(c_0, c_0)} \cdot w(c_1, c_0)$$



$$P[\tilde{c}(t)] = P(c_2) e^{-(t_f - t_2) \omega(c_2, c_2)} w(c_1, c_2) e^{-(t_2 - t_1) \omega(c_1, c_1)} w(c_0, c_1) e^{-t_1 \omega(c_0, c_0)}$$

gives

$$\frac{P[\tilde{c}(t)]}{P[c(t)]} = \frac{w(c_1, c_2)}{w(c_2, c_1)} \times \frac{w(c_0, c_1)}{w(c_1, c_0)} \times \frac{P(c_2 = c_{t_f})}{P(c_0)}$$

$$\Rightarrow \boxed{\frac{P[\tilde{c}(t)]}{P[c(t)]} = e^{-\Delta S_{\text{prod}}/k_B}}$$

$$\text{with } \Delta S_{\text{prod}} = k_B \left[\log \frac{\omega(c_2, c_1)}{\omega(c_1, c_2)} + \log \frac{\omega(c_1, c_0)}{\omega(c_0, c_1)} \right] \\ - k_B \log P(c_t) + k_B \log P(c_0)$$

Remarks: ① Spont quantifies breaking of time reversal invariance.

In equilibrium, detailed balance makes $\Delta S_{\text{prod}} = 0$

$$\Rightarrow P[\tilde{c}(t)] = P[c(t)]$$

② Noting that, ~~if~~ in our definition, if ΔS_{prod} is the entropy produced in path $c(t)$, then in time reversed path $\tilde{c}(t)$ ~~entropy produced~~ entropy produced is $-\Delta S_{\text{prod}}$. Then, just as in Crook's rel,

$$\boxed{\frac{P(-S_{\text{prod}})}{P(S_{\text{prod}})} = e^{-S_{\text{prod}}}}$$

Gallavotti-Cohen fluctuation relation
[Detailed fluctuation relation].

③ In stationary state (non-equilibrium in particular),

S_{env} grows linearly with time, as the system ~~is~~ moves in its configuration space.

In comparison, S_{sys} has slower ~~depen~~ growth or does not grow.

This means, $\frac{S_{\text{prod}}}{t} \approx \frac{S_{\text{env}}}{t}$ for large t .

Here, σ is the entropy production rate.

This means

$$\frac{P\left(\frac{S_{\text{prod}}}{t} = -\sigma\right)}{P\left(\frac{S_{\text{prod}}}{t} = \sigma\right)} \approx e^{-t \frac{\sigma}{k_B}} \quad \text{for large } t$$

This is the precise statement of Gallavotti-Cohen relation, which considers $P(S_{\text{env}})$.

This relation, along with large deviation form $P\left(\frac{S_{\text{prod}}}{t} = \sigma\right) \sim e^{-t \phi(\sigma)}$

give

$$\phi(\sigma) = \phi(-\sigma) - \frac{\sigma}{k_B}$$

more commonly known form of GC-relation.

This relation has been proven rigorously in many different dynamics

- (1) Chaotic systems: Gallavotti & Cohen, J. Stat. Phys. 80, 931 (1995).
- (2) Langevin dynamics: Kurchan, J. Phys. A, 31, 3719 (1998).
- (3) Markov process: Lebowitz & Spohn, J. Stat. Phys. (1999).

Why is this useful? (1) Entropy production rate is a quantitative (macro) measure of how far a system is away from equilibrium.

Ref: Fodor et al, "How far from equilibrium is Active matter?" PRL, 117, 038103 (2016).

② Callavotti-cohen gives non-trivial symmetry relation for energy (heat) transport in systems arbitrarily far from Equilibrium.

considers a ~~common~~ typical ~~nonequi~~ transport system



let Q_t amount of heat transferred from T_1 to T_2 ($T_1 > T_2$), in long time t .

Then,

$$\Delta S_{env}(t) \approx -\frac{Q_t}{T_1} + \frac{Q_t}{T_2} \quad \left| \quad \begin{array}{l} \text{In large } t \\ \Delta S_{sys} \approx 0 \end{array} \right.$$

⇒ Entropy production rate

$$\sigma \approx \frac{\Delta S_{env}}{t} = j \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

① Second law of thermodynamics gives, $\langle j \rangle > 0$ (heat flows from hot to cold). Clausius version of second law: "no process is possible whose sole result is the transfer of heat from a cooler body to a hotter body". However, j is a fluctuating quantity. Callavotti-cohen relation tells how improbable it is to see a negative current

$$\frac{P(-j)}{P(j)} = e^{-t(\beta_2 - \beta_1) \cdot j}$$

longer you measure, harder it gets to see negative j .

$$\phi(j) - \phi(-j) = -j(\beta_2 - \beta_1)$$

* These symmetries are like underlined symmetries in free energy ($F(-m) = F(m)$ for Ising model). In building a statmech of non-equilibrium, ~~these are~~ where ϕ is like free energy, these non-trivial symmetries must be included.

In a very naive understanding, these symmetries are related to the assumption that our universe is heading to a final equilibrium state. Therefore, global dynamics (bath+system) satisfies detailed balance, and this makes only certain dynamics realistic. The fluctuation symmetries are consequence of such constraints.

* The Gallavotti-Cohen relation ~~also~~ also gives symmetry for cumulant generating func: $\mu(\lambda) = \mu(-\beta_2 + \beta_1 - \lambda)$.

This then relates cumulants of j to its higher cumulants.

For example: we can show

$$\langle j \rangle_{\Delta T} = \frac{\Delta T}{2k_B T^2} \int_0^{\infty} dt \langle j(t) j(0) \rangle_{\Delta T=0}$$

$$\begin{aligned} T_2 &= T \\ T_1 &= T + \Delta T \end{aligned}$$

A generalization of linear response for current.

(Green-Kubo relation for open transport systems)

* For more reading, connection to information theory, ~~Landauer principle~~ $\frac{[x]}{[y]}$ d
Landauer principle, see the article by Kirone Mallick on Courx site.