# VIII Introduction to stochastic thermodynamics

## 1° Historical perspective and context

1824 : birth of thermodynamics as a scientific field, with "Réflexions sur la puissance motrice du feu" (Reflections on the motive power of fire), by Sadi Carnot.
At the end of XIX th century, all concepts are in place (heat, work, thermodynamic potentials, entropy, first law, 2nd law...) Nowadays, thermo is certainly a useful tool ... but is there anything left to discover?

Thermo viewed as inherently applying to macroscopic systems. Statistical physics explains how the laws of thermo arise from microscopic interactions.

→ these 2 conceptions have been challenged since ~ 2000. The impetus comes from miniaturization of mechanical / electrical systems or devices, the rise of optical trapping/ manipulation techniques, and from biology. Biomolecules like kinesin, myosin etc. are often described as molecular motors or machines since they operate through cycles, reminiscent of those of macroscopic thermodynamics

→ necessity to reanalyze all concepts of " for small systems,

→ recent discovery of far from equilibrium fluctuation relations, beyond linear response, revealing unexpected features and symmetries : active field of research in φ, χ, bio, math.

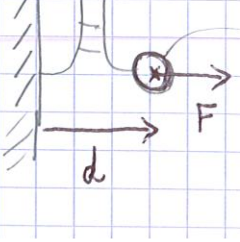
kT relevant energy fund

Def : Stochastic thermo is the thermo theory for mesoscopic, non equilibrium physical systems interacting with equilibrium heat reservoirs.

It thus relies on an assumption of time scale separation, were the reservoirs relax fast to equilibrium compared to mesoscopic degrees of freedom (such as colloids → same hypotheses for Langevin equation description)

$\tau_c \ll \gamma^{-1}$

### The hairpin as a paradigm




→ RNA hairpin, stabilized by hydrogen bonds (in water solvant)

→ colloidal bead (not to scale), of dielectric material, manipulated by optical tweezers : force F applied, d ↗

The hairpin unfolds / unties, by pulling on the bead. The external operator performs work $W$ on the system. If the experiment is repeated, $W$ will fluctuate, all the more as the pulling is fast. On the other hand, for a macroscopic system, we would have the second law, stating $W \geqslant \Delta F$ ($\Leftrightarrow \Delta S_{syst+reservoir} \geqslant 0$) In the present, mesoscopic case where $W$ fluctuates, situation more complex but on average over all possible repetitions of the experiment: $\langle W \rangle \geqslant \Delta F$

↳ what is the statistics of $W$? Can we have some realizations where $W \leqslant \Delta F$? where $W$ is measured on a single experiment?

## 2°) The first law of stochastic thermodynamics

The colloidal bead attached to the hairpin is manipulated by an external operator, that controls the time dependence of the force applied through a parameter (or collection of parameters) $\lambda(t)$. Experiments with optical tweezers provide typical examples: a laser creates an external potential that traps the bead / macromolecule. The operator chooses the stiffness and/or the position of the optical trap: $U_{operator}(x, \vec{\lambda}(t)) = \frac{1}{2} K(t) [x - x_0(t)]^2$ ; $\vec{\lambda}(t) = \begin{vmatrix} K(t) \\ x_0(t) \end{vmatrix}$

The operator can also apply a non-conservative force, see below, but this does not change much. We start by the conservative applied force situation.

The bead attached to the hairpin is subject to total potential

$$U(x, \lambda(t)) = U_{hairpin \to bead}(x) + U_{operator}(x, \lambda(t))$$

where $x$ is thus the bead position.

In some experiments, there is no hairpin ... just a colloidal bead (ie no internal relevant degrees of freedom)...

Langevin equation for the bead:

$$m \dot{v} = -\partial_x U \underbrace{- m\gamma v + R(t)}_{\text{force due to the bath / water}}$$

We define the heat exchanged with the bath, received by the system (bead) as the work of this force: $\delta Q = (-m\gamma v + R(t)) \circ dx$

$= (m\dot{v} + \partial_x U) \circ dx$ ↳ Stratonovich product

We can always consider the Langevin force as correlated over some small $\tau_c$, rather than $\tau_c = 0$, in which case Stratonovich is the natural framework. Those preferring Itō-Doblin calculus know how to work out the mapping to Strato.

For simplicity, we assume overdamped dynamics (very accurate for colloids), which amounts to setting $\dot{v} = 0$ above:

$$\delta Q = \partial_x U \circ dx$$

Besides, energy exchanges take the form of heat, or of work, and we impose a conservation relation, defining $\delta W$, as

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

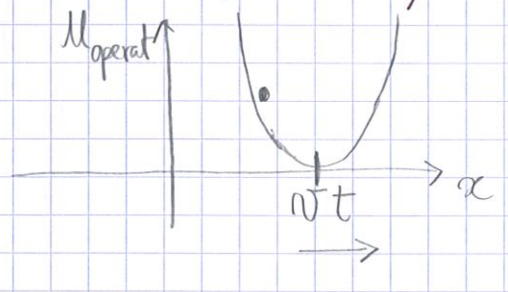
regular product

$$\Rightarrow \partial_\lambda U \, d\lambda + \partial_x U \circ dx = \delta W + \overbrace{\delta Q}^{\partial_x U \circ dx} \Rightarrow \left[ \begin{array}{l} dU = \delta W + \delta Q \\ \delta W = \partial_\lambda U . d\lambda \\ \delta Q = \partial_x U \circ dx \end{array} \right.$$

We have our first law of stochastic thermodynamics, were heat and work received by the system are defined for any trajectory (any realization) ie for any one single pulling experiment → Stochastic work / stochastic heat.

Illustration (see eg Ciliberto PRX 2017 for experimental review). If we pull at constant speed $v$: $U_{operator}(x, \lambda(t)) = \frac{1}{2} \kappa [x - vt]^2$ ; $\lambda(t) = vt$

$$\delta W = -\kappa(x - vt)$$




If $x(t) < vt$ (quite likely, since the bead is being pulled to the right, $v > 0$) then $\delta W > 0$ and the operator provides work; $W = -\int_{t_1}^{t_2} \kappa [x(\tau) - v\tau] \, d\tau$, work received between $t_1$ and $t_2$ → one trajectory

The expression of $\boxed{\delta W = \partial_\lambda U \, d\lambda}$ makes sense: the work performed by the operator is defined through the parameter(s) that the operator controls → $\lambda(t)$, that needs to change, otherwise no work is performed at all. Hence (and this is rather tautological), the operator can choose to have $\delta W = 0$, but cannot control $\delta Q$, in general $\neq 0$ even in equilibrium, stemming from the interactions with the bath (supposed to be at a well defined temperature $T$).

Note that
$$\left. \begin{array}{l} W = \int_{t_1}^{t_2} \partial_\lambda U(x(t), \lambda(t)) \, \dot{\lambda}(t) \, dt \\ Q = \int_{t_1}^{t_2} \partial_x U(x(t), \lambda(t)) \circ \dot{x}(t) \, dt \end{array} \right\}$$
depend on the trajectory, while $\underbrace{W + Q}_{\Delta U}$ does not (state function)

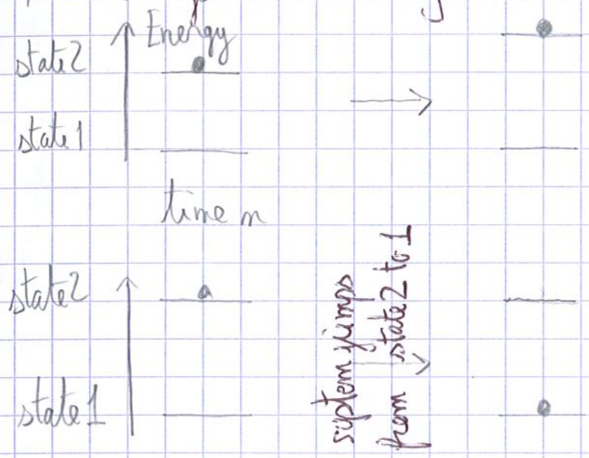
## What about discrete dynamics (such as with Markov chains)?

$x(t)$ is here discrete (mesoscopic states // position of a random walker), and time discrete.
The transition matrix encoding all transition probabilities between all pairs of states, depends on time through $\lambda(t)$, controlled externally

$$\underset{\text{state}}{P_i}\,(\underset{\text{time}}{t+1}) = \sum_j M_{ij}(\lambda(t))\, P_j(t)$$

↳ transition proba from $j$ to state $i$ in unit time step

For illustration, take a system with only two states (like a random walk with only 2 sites):




This is work: energy levels change because $\lambda(t)$ changes, the system remains in the same state

This is heat: jump between 2 energy levels, due to interactions with bath, energy levels unchanged

Because both the state $x$ of the system, and the externally controlled parameter $\lambda(t)$ change in time, we decompose each time step in two:

(i) stochastic step : $x_n$ at time $t_n \longrightarrow x_{n+1}$ with proba $M_{x_n, x_{n+1}}(\lambda_n)$

$$\delta Q_{n\to n+1} = U(x_{n+1}, \lambda_n) - U(x_n, \lambda_n)$$

(ii) update step : $\lambda_n$ is changed to $\lambda_{n+1}$, keeping $x_{n+1}$ fixed

$$\delta W_{n\to n+1} = U(x_{n+1}, \lambda_{n+1}) - U(x_{n+1}, \lambda_n)$$

Again, a first principle relation holds for $U[x(t), \lambda(t)]$

$$\delta W_{n\to n+1} + \delta Q_{n\to n+1} = U(x_{n+1}, \lambda_{n+1}) - U(x_n, \lambda_n) = dU$$

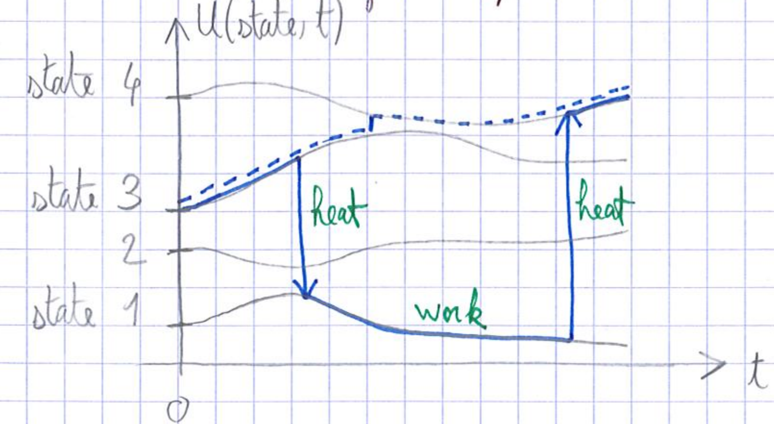
Summing over each elementary time step, we get $W$ and $Q$ over a trajectory, i.e. a path $x(t)$ for a chosen $\lambda(t)$; they depend on the trajectory, but $W+Q$ does not.

## What about driving with conservative and non conservative forces?

Here : $$m\dot{v} = \underbrace{\underbrace{-\partial_x U(x, \lambda(t))}_{\text{conservative}} + \underbrace{f(x,t)}_{\text{non-conservative}}}_{\text{from manipulation}} \underbrace{- \gamma m v + R(t)}_{\text{from bath}}$$

As before: $\delta Q = [-\gamma m v + R(t)] \circ dx \underset{\uparrow\,\text{overdamped}}{=} (\partial_x U - f) \circ dx$

With continuous time dynamics / discrete states :




—— trajectory 1 } of a manipulated

– – – trajectory 2 } system

The energy levels of the different states depend on time as a consequence of manipul. by the operator

the two trajectories start and end at the same points, but do not have the same $W$ or $Q$, yet they share the same $W + Q = U(\text{final state, final time}) - U(\text{initial state, initial time})$

and $\delta W = \partial_\lambda \mathcal{U}\, d\lambda + f_0\, dx$ , work of the conservative force,

so that $d\mathcal{U} = \delta W + \delta Q$

$$= \partial_\lambda \mathcal{U}\, d\lambda + \cancel{f_0 dx} + \partial_x \mathcal{U}\, dx - \cancel{f_0 dx}$$

## 3) From Feynman-Kac to Jarzynski: the work fluctuation relation

When an operator acts onto a Brownian-like system through an external parameter $\lambda(t)$ entering the energy $\mathcal{U}(x, \lambda(t))$, we have defined the stochastic work on a given trajectory by:

$$W = \int_0^t \partial_\lambda \mathcal{U}(x(t'), t')\, \dot{\lambda}(t')\, dt' \rightarrow \left\{ \begin{array}{l} \text{this is a functional of the trajectory,} \\ \text{that can be treated at Feynman-Kac level} \end{array} \right.$$

We use the forward Feynman-Kac formulation:

$$Q(x,t) = \left\langle e^{-\beta W} \delta\left(x - x(t)\right) \right\rangle ,$$

averaging over all trajectories, and with initial condition corresponding to equilibrium at time $t=0$, ie with $\lambda(0) = \lambda_0$

$$Q(x, t=0) = \left\langle \delta\left(x - x(0)\right) \right\rangle = p_{eq}(x, \lambda(0)) = \frac{1}{Z_0} e^{-\beta \mathcal{U}(x, \lambda(0))}$$

Feynman & Kac tell us that:

$$\partial_t Q = -\beta \partial_\lambda \mathcal{U}(x, \lambda(t))\, \dot{\lambda}\, Q + \mu\, \partial_x\left[Q\, \partial_x \mathcal{U}\right] + D\, \partial_x^2 Q$$

Remarkably, the solution corresponding to our initial conditions can be found:

$$Q(x,t) = \frac{1}{Z_0} e^{-\beta \mathcal{U}(x, \lambda(t))} \quad \text{since} \left\{ \begin{array}{l} \partial_t Q = -\beta \dot{\lambda}\, \partial_\lambda \mathcal{U}\, Q \\ \mu\, Q\, \partial_x \mathcal{U} + D \partial_x Q = 0 \ ; \text{ since } D = \mu k T \end{array} \right.$$

Thus:

$$\left\langle e^{-\beta W} \delta\left(x - x(t)\right) \right\rangle = \frac{1}{Z_0} e^{-\beta \mathcal{U}(x, \lambda(t))}$$

Next: integrate over $x$:

$$\left\langle e^{-\beta W} \right\rangle = \frac{1}{Z_0} \int dx\, e^{-\beta \mathcal{U}(x, \lambda(t))} = \frac{Z(\lambda(t))}{Z(\lambda(0))} = e^{-\beta\left[F(\lambda(t)) - F(\lambda(0))\right]}$$

In short:

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F} \quad ; \text{ Jarzynski relation (1997)}$$

Simple & remarkable: opened whole field research. (Fluctuation Relation)

$\boxed{\text{Validity}}$: way beyond Langevin / Fokker-Planck framework. A system at equilibrium at $t=0$ is driven away from equilibrium by an external operator, changing $\lambda(t)$. There is no assumption on the speed of the transformation, the system can be far from equilibrium, at $t > 0$. Thus, the stochastic work $W$ can be very much "non equilibrium". Yet, averaging over many repetitions of the experiment, ie starting from $\lambda(0)$, following the same protocol $\lambda(t)$, ending at the same $t_{final}$, we can compute the mean value $\langle e^{-\beta W}\rangle$ : it only depends on an equilibrium difference, $\Delta F$ → SURPRISING since the state reached at $t_{final}$ can be far from equilibrium (if $\lambda$ changes fast).

$$\langle e^{-\beta W}\rangle = \int dW\, e^{-\beta W} \underbrace{p(W,t)}_{\text{complicated, non equilibrium}} = \underbrace{e^{-\beta \Delta F}}_{\text{simple, equilibrium}}, \quad \Delta F = F(\lambda(t)) - F(\lambda(0))$$

The inverse temperature $\beta$ here is a trace of the initial condition; since the system is out of equilibrium for $t > 0$, it has then no temp at all!

## DISCUSSION

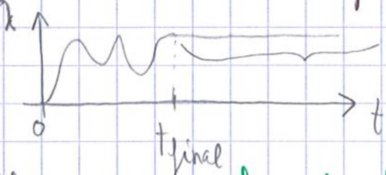
→ Jensen inequality : $\langle e^{A}\rangle \geq e^{\langle A\rangle}$ from convexity of $x \mapsto e^{x}$

$\langle e^{-\beta W}\rangle \geq e^{-\beta\langle W\rangle}$ ie $-\beta\Delta F \geq -\beta\langle W\rangle$

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

This is a generalization of the second principle (the final can be here out of equilibrium)

We recover the 2nd principle when we leave the system time to relax to equilibrium, from a given $\lambda(t_{final})$




no work performed for $t > t_{final}$ since $\lambda$ is frozen there.

What we are saying is that Jarzynski not only generalizes the second principle (an inequality), but also transforms it into AN EQUALITY

$$\langle W\rangle \geq \Delta F \Longleftarrow \langle e^{-\beta W}\rangle = e^{-\beta\Delta F}$$

→ On average, $W$ exceeds $\Delta F$ ; yet, nothing forbids to have $W \leq \Delta F$, for a given trajectory. How probable (or improbable) is that?

$$\Pr[W \leq \Delta F - \zeta] = \int_{-\infty}^{\Delta F-\zeta} p(W)\, dW$$

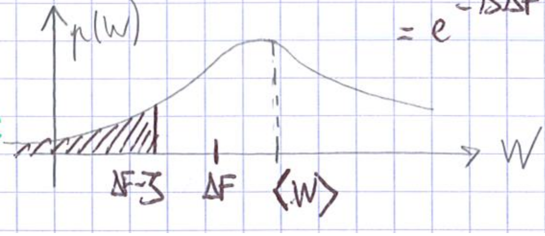
$$\leq \int_{-\infty}^{\Delta F-\zeta} \underbrace{e^{-\beta(\overbrace{W-\Delta F+\zeta}^{\leq 0})}}_{\geq 1} p(W)\, dW$$

$$\leq e^{\beta\Delta F} e^{-\beta\zeta} \underbrace{\int_{-\infty}^{\Delta F-\zeta} e^{-\beta W} p(W)\, dW}$$

$$\leq \int_{-\infty}^{+\infty} e^{-\beta W} p\, dW = \langle e^{-\beta W}\rangle$$

$$= e^{-\beta\Delta F}$$

$$\boxed{\Pr[W \leq \Delta F - \zeta] \leq e^{-\beta\zeta}}$$




Decreases as $\zeta \nearrow$ : tail is suppressed more than exponentially fast.

→ Noting that $\Delta S_{tot} = \frac{1}{T}(W - \Delta F)$ is the entropy creation (that we could just denote $S_{tot}$, Jarzynski relation states:

$$\langle e^{-S_{tot}/k} \rangle = 1 \quad (*)$$

Once more quite surprising because it holds at all times along the transformation. But on average, $\langle S_{tot} \rangle \nearrow$ with time. This means that $e^{-S_{tot}/k}$ is a martingale, an object of particular interest. In spite of the growth of $S_{tot}$ with time, $(*)$ remains true. Naively, one presumably expects that $\langle e^{-S_{tot}/k} \rangle$ decreases with time: fluctuations with a negative enough entropy creation prevent this from happening.

## 4) Crooks relation

For completeness, we switch to the Markov chain framework to obtain insightful and more general results (from which Jarzynski fluctuation relation can be derived/recovered). Discrete time / discrete states; the transition matrix depends on $\lambda(t)$: $M_{j\to i}(\lambda(t)) = M_{j\to i}(\lambda)$ from state $j$ to state $i$. We assume that this dynamics admits an equilibrium distribution $\propto e^{-\beta U(x,\lambda)}$ for a given (fixed) $\lambda$. Thus, we have detailed balance

$$\frac{M_{i\to j}(\lambda)}{M_{j\to i}(\lambda)} = e^{-\beta[U(x_j,\lambda) - U(x_i,\lambda)]}$$

The key idea here is to compare a (forward) trajectory $x_0 \xrightarrow{\lambda_0} x_1 \xrightarrow{\lambda_1} x_2 \cdots \xrightarrow{\lambda_{m-1}} x_m$ that we denote $\gamma$, to its backward (reversed) trajectory, denoted $\check{\gamma}$ and defined as:

final time

$$x_m \xrightarrow{\lambda_{m-1}} x_{m-1} \longrightarrow \cdots \longrightarrow x_2 \xrightarrow{\lambda_1} x_1 \xrightarrow{\lambda_0} x_0 \quad : \quad \check{\gamma}$$

and thus for the reversed, the update step (change of $\lambda$, is performed before the stochastic jump)

At $t=0$, the system is at equilibrium, with distribution $p_{eq}(x,\lambda_0) = \frac{1}{Z_0} e^{-\beta U(x,\lambda_0)}$

Thus, the probability of the forward trajectory is, making use of Markov property:

$$\Pr(\gamma) = \frac{1}{Z_0} e^{-\beta U(x_0,\lambda_0)} M_{x_0\to x_1}(\lambda_0)\, M_{x_1\to x_2}(\lambda_2) \cdots M_{x_{n-1}\to x_n}(\lambda_{m-1})$$

The protocol is reversed (meaning $\lambda_{reversed}(t) = \lambda_{forward}(t_{final} - t)$), and we start the reverse trajectory from equilibrium at $\lambda_m$: $p_{eq}(x,\lambda_m) = \frac{1}{Z_m} e^{-\beta U(x,\lambda_m)}$

$$P_r(\check{\gamma}) = \frac{1}{Z_n} e^{-\beta U(x_n,\lambda_n)} M_{x_n\to x_{n-1}}(\lambda_{n-1}) \cdots M_{x_2\to x_1}(\lambda_1) M_{x_1\to x_0}(\lambda_0)$$ 98

Taking detailed balance into account:

$$\frac{P_r(\gamma)}{P_r(\check{\gamma})} = \frac{1}{Z_0} \cancel{e^{-\beta U(x_0,\lambda_0)}} e^{-\beta[U(x_1,\lambda_0)-\cancel{U(x_0,\lambda_0)}]} e^{-\beta[U(x_2,\lambda_1)-U(x_1,\lambda_1)]} \cdots$$
$$e^{-\beta[U(x_3,\lambda_2)-U(x_2,\lambda_2)]} \cdots e^{-\beta[U(x_n,\lambda_{n-1})-U(x_{n-1},\lambda_{n-1})]} \times \left[\frac{1}{Z_n}\exp(-\beta U(x_n,\lambda_n))\right]^{-1}$$

$$= \frac{Z_n}{Z_0} e^{\beta W_{0\to 1}+\beta W_{1\to 2}+\cdots \beta W_{n-1\to n}}$$

$U(x_1,\lambda_1)-U(x_1,\lambda_0)$

$$= e^{\beta W(\gamma)} e^{-\beta\Delta F} \qquad e^{-\beta\Delta F} \equiv \frac{Z_n}{Z_0}$$

The work along the forward trajectory / backward trajectory is

$$W(\gamma) = U(x_1,\lambda_1)-U(x_1,\lambda_0)+U(x_2,\lambda_2)-U(x_2,\lambda_1)+\cdots+U(x_n,\lambda_n)-U(x_n,\lambda_{n-1})$$
$$W(\check{\gamma}) = U(x_n,\lambda_{n-1})-U(x_n,\lambda_n)+\cdots+U(x_1,\lambda_0)-U(x_1,\lambda_1)$$

$$\Rightarrow \mathbf{W(\check{\gamma}) = -W(\gamma)}$$

In other words, if a work 5 kT is required to unfold a hairpin following a specific path $\lambda(t)$ and sequence of steps, then a work 5 kT will be released into the bath, with the reversed protocol $(\lambda(t_{final}-t))$, for the trajectory that visits the same sequence of states, in reverse order. This assumes that both forward and reverse protocols start from equilibrium. Of course, since the $\lambda(t)$ driving can be fast, the system is not at equilibrium in the final state, at the end of the protocol.

$$e^{-\beta W(\gamma)} P_r(\gamma) = e^{-\beta\Delta F} P_r(\check{\gamma})$$

$$\sum_{\gamma/W(\gamma)=W} e^{-\beta W(\gamma)} P_r(\gamma) = e^{-\beta\Delta F} \sum_{\gamma/W(\gamma)=W} P_r(\check{\gamma})$$

$$e^{-\beta W} \underbrace{\sum_{\gamma/W(\gamma)=W} P_r(\gamma)}_{\substack{p_{Forward}(W) \\ \text{distribution of work in} \\ \text{Forward process}}} = e^{-\beta\Delta F} \underbrace{\sum_{\substack{\check{\gamma}/W(\gamma)=W \\ W(\check{\gamma})=-W}} P_r(\check{\gamma})}_{p_{Backward}(-W)}$$

since for each traj $\gamma$, there is a $\check{\gamma}$

$\sum_{\gamma} \Leftrightarrow \sum_{\check{\gamma}}$

$$\Rightarrow \boxed{e^{-\beta W} p_{Forward}(W) = e^{-\beta\Delta F} p_{Backward}(-W)}$$

CROOKS RELATION

Note that Crooks $\Rightarrow$ Jarzynski:

$$\langle e^{-\beta W}\rangle = \int dW\, e^{-\beta W} p_{Forward}(W) = e^{-\beta\Delta F} \underbrace{\int_{-\infty}^{+\infty} dW\, p_{Backward}(-W)}_{\int_{-\infty}^{+\infty} dW'\, p_{Backward}(W') = 1}, \quad W' = -W$$

$$= e^{-\beta\Delta F}$$

Note also that we have obtained something more general

$$\boxed{\frac{P_r(\gamma)}{P_r(\check{\gamma})} = e^{\beta(W-\Delta F)} = e^{S_{tot}/k}}$$

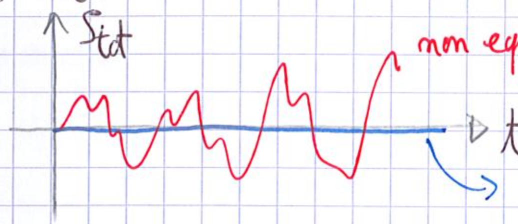
where it is understood that $W = W(\gamma)$

↳ central result in stochastic thermodynamics, connects entropy production ⟺ irreversibility

which implies in particular

$$\langle e^{-S_{tot}/k} \rangle = \sum_{\text{all } \gamma} P_r(\gamma)\, e^{-S_{tot}/k} = \sum_{\text{all } \gamma} P_r(\gamma) \frac{P_r(\check{\gamma})}{P_r(\gamma)} = 1$$

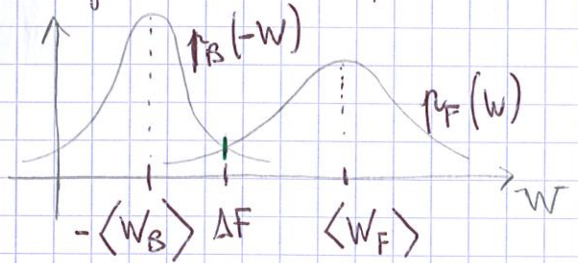
At equilibrium, there is no entropy creation, and it is equally probable to observe a trajectory, or its time-reversed




non equilibrium, $\langle S_{tot} \rangle \nearrow$ but $\langle e^{-S_{tot}/k} \rangle = 1$

equilibrium: $S_{tot} = 0$

In terms of work distribution, we have the following typical situation:




Indeed, from Crooks: search for curve crossing

$p_F(W) = p_B(-W) \Rightarrow W = \Delta F$

Besides $\langle W_F \rangle \geqslant \Delta F$

but we can apply similar consideration to the reverse (B) protocol: the free energy difference, for Backwards is $-\Delta F$ and

$$\langle W_B \rangle \geqslant -\Delta F \quad , \text{ as for all transformations ("2}^{\text{nd}}\text{ principle")}$$

$$\Rightarrow -\langle W_B \rangle \leqslant \Delta F \quad \text{and thus:} \quad -\langle W_B \rangle \leqslant \Delta F \leqslant \langle W_F \rangle$$

The fact that the forward protocol with distrib of work $p_F(W)$, and the backward are such that $p_F(W) \neq p_B(-W)$ means that the dynamics is irreversible

Let us indeed compute their Kullback-Leibler "distance"

$$D\left[\, p_F(W) \,\|\, p_B(-W) \right] = \int dW\, p_F(W) \log\left[\frac{p_F(W)}{p_B(-W)}\right] = \beta \int dW\, p_F(W) \left[W - \Delta F\right]$$

$$= \beta\left(\langle W \rangle - \Delta F\right)$$

$$\geqslant 0$$

We are here quantifying the "length of time's arrow", by looking at how distinct are forward trajectories from their time reversed.

# 5°) The stochastic entropy

Above, we could assign an entropy creation to each trajectory : $S_{tot} = \frac{1}{T}(W - \Delta F)$, which pertains to the system + reservoir. We did not assign an entropy to the system, that can fluctuate from a realization to the next. Let us do it : for a given stochastic process $x(t)$, we assume we know $p(x,t)$. At a given time, the Shannon entropy reads $-k_B \int p(x,t) \log p(x,t)\, dx$ and we define

$$S_{syst}(t) = -k_B \log p(x(t),t)$$

Note that although $S_{syst}(t)$ provides at each time the system's entropy for a given trajectory $x(t)$, it requires the knowledge of the whole statistics over all trajectories (ie $p(x,t)$) $\to$ not sthg convenient for experimental measures (at variance with heat / work).

For an overdamped dynamics as $\boxed{\dot{x} = \mu \overbrace{F(x,t)}^{-\partial_x U} + \sqrt{2D}\, \xi(t)}$, let us check that this definition is consistent, and yields a positive entropy creation, for {system + thermostat}.

$$S_{tot} = S_{syst} + S_{therm} \quad ; \quad \delta S_{therm} = -\frac{\delta Q}{T} = -\frac{1}{T} \partial_x U \circ dx$$

$$\frac{1}{k_B}\frac{d}{dt} S_{tot} = \frac{d}{dt} S_{syst}/k_B - \beta\, \partial_x U \circ \dot{x} \qquad \text{Stratonovich product}$$

$$= -\frac{1}{p(x(t),t)} (\partial_x p) \dot{x} - \frac{1}{p(x(t),t)} \partial_t p - \beta (\partial_x U) \circ \dot{x}$$

We also define the current $j(x,t) = \mu F(x,t)\, p(x,t) - D\, \partial_x p(x,t)$ s.t.

$$\partial_t p(x,t) = -\partial_x j \qquad \frac{\mu}{D} = \beta$$

$$\frac{1}{k_B} \dot{S}_{tot} = \frac{1}{p(x,t)} \underbrace{\left[ -\partial_x p + p \beta F \right]}_{j(x,t)/D} \circ \dot{x} - \frac{1}{p(x,t)} \partial_t p \quad ; \text{ here } x \text{ is } x(t)$$

$S_{tot}(x(t),t)$

$$\Rightarrow \frac{1}{k_B} \langle \dot{S}_{tot} \rangle = \frac{1}{k_B} \int \dot{S}_{tot}(x,t)\, p(x,t)\, dx$$

$$= \frac{1}{D} \left\langle \frac{j(x,t) \circ \dot{x}}{p(x,t)} \right\rangle - \underbrace{\int \frac{p(x,t)}{p(x,t)} \partial_t p\, dx}_{\partial_t \int p = \partial_t(1) = 0}$$

$$= \frac{1}{D} \left\langle \frac{j \mu F}{p} \right\rangle + \frac{1}{D} \underbrace{\left\langle \frac{j(x,t)}{p(x,t)} \circ \sqrt{2D}\, \xi(t) \right\rangle}_{= D \left\langle \partial_x \left( \frac{j}{p} \right) \right\rangle} \quad \text{at Stratonovich level}$$

$$\left\langle \mathring{S}_{tot}/k_B \right\rangle = \frac{1}{D} \left\langle \frac{j\mu F}{\rho} \right\rangle + \underbrace{\left\langle \frac{1}{\rho} \partial_x j \right\rangle}_{\int \frac{1}{\rho} \rho \, \partial_x j \, dx = \int \partial_x j \, dx = 0} - \left\langle j \frac{\partial_x \rho}{\rho^2} \right\rangle$$

$$= \frac{1}{D} \left\langle \frac{j}{\rho^2} \underbrace{\left( \mu F \rho - D \partial_x \rho \right)}_{j(x,t)} \right\rangle$$

$$= \frac{1}{D} \left\langle \frac{j^2}{\rho^2} \right\rangle$$

$$= \frac{1}{D} \int dx \, \frac{j^2(x,t)}{\rho(x,t)} \geqslant 0 \text{ , as it should } (2^{nd} \text{ principle})$$

↳ total entropy creation

Hence the connexion between current and entropy production.

Besides, while $\langle \mathring{S}_{tot} \rangle \geqslant 0$, and thus $\left\langle \int_0^t \mathring{S}_{tot}(s) \, ds \right\rangle \geqslant 0$, $\int_0^t \mathring{S}_{tot}(s) \, ds$ can be either positive or negative