Stochastic thermodynamics

1 Principles of stochastic thermodynamics

In stochastic thermodynamics, thermodynamic quantities are defined at the trajectory level and are time-dependent quantities. We illustrate these ideas on the classic example of a Langevin equation in 1D of the form :

$$\dot{x} = \mu F(x, \lambda) + \xi(t), \tag{1}$$

where $F(x, \lambda)$ is the force acting on the particle of position x, λ is a control parameter, μ is the mobility and $\xi(t)$ is a white noise satisfying $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = 2D\delta(t - t')$. The force F can be decomposed into a conservative force, deriving from the potential $V(x, \lambda)$ and a non-conservative force $f(x, \lambda)$. The Einstein relation is assumed $D = T\mu$.

▷ **1-1** Define the work and the heat at the trajectory level, and write the first law for this Langevin equation. Why is the assumption of the Einstein relation required ?

▷ **1-2** What is the form of the Fokker-Planck equation associated to this Langevin equation ? The solution of that equation will be written $p(x, t)$.

▷ **1-3** One introduces the stochastic entropy defined as $s = -\ln p(x(t), t)$, where $x(t)$ satisfies the Langevin equation above. In an evolution between time 0 and time τ, what is the change of stochastic entropy Δs ?

▷ **1-4** The change of entropy of the medium Δs_m is defined as the heat which is released into it. Show that the total entropy production can be splitted into Δs_m and Δs.

▷ **1-5** Calculate $\langle \Delta \dot{s}_{tot} \rangle$, $\langle \Delta \dot{s}_m \rangle$ as integrals over the variable x involving the current $j(x, t)$ associated with the Fokker-Planck equation. Verify that the second law holds with these expressions.

▷ **1-6** Show using a path integral representation of the Langevin equation that Δs_m can be expressed as the ratio of two distributions of trajectories associated with a forward and backward evolution.

▷ **1-7** Show that $\langle \exp(-\Delta s_{tot}) \rangle$=1, deduce from that the Jarzynski relation as a particular case.

2 Detailed Jarzynski equality for a logically irreversible procedure

We consider a system obeying a stochastic dynamics with a Hamiltonian $H(x, \lambda)$, where x is the fluctuating variable which is observed and λ is a variable which is controlled externally. The system is in contact with a heat bath at the temperature $T = 1/\beta$. In the absence of non-conservative forces, the expression of the work in a process that starts at x_0 at time 0 with a value of the control parameter fixed to λ_0 and ends at position $x(t) = x_t$ at time t with $\lambda(t) = \lambda_t$ is

$$W = \int_0^t dt' \dot{\lambda_t} \frac{\partial H(x_t, \lambda_t)}{\partial \lambda}. \tag{2}$$

We now assume that the system starts initially at $t = 0$ at equilibrium, characterized by a p.d.f. $\rho_{eq}(x, \lambda)$ and ends at time t in a non-equilibrium state characterized by a p.d.f. $\rho(x, t)$. It is possible to prove a variant of Jarzynski relation in the form

$$\langle \delta(x - x_t) e^{-\beta W} \rangle = \frac{e^{-\beta H(x, \lambda_t)}}{Z_0}, \tag{3}$$

where Z_0 represents the partition function at the initial state.

▷ **2-1** Derive from this equation the relation which is usually known as the Jarzynski relation.

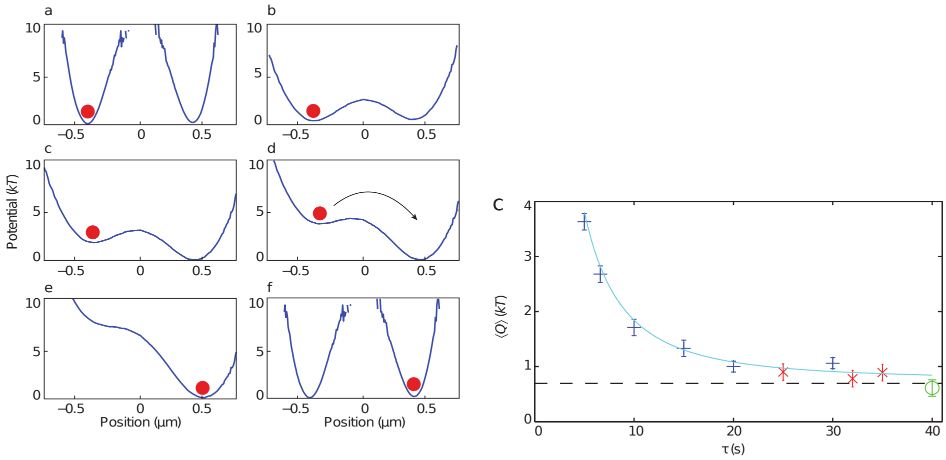

FIGURE 1 – Left : Evolution of the potential in chronological order from state a to state f when a time-dependent force is applied to a brownian particle represented here as the red circle. Right : Evolution of the average heat divided by $k_B T$ as a function of the duration of the cycle τ. The symbols represent experimental data points.

▷ **2-2** Show that Eq. 3 is equivalent to

$$\frac{\rho(x,t)}{\rho_{eq}(x,\lambda_t)}\langle e^{-\beta W}|x=x_t\rangle = e^{-\beta\Delta F(t)}, \tag{4}$$

where the notation $\langle ..|x=x_t\rangle$ means a conditional average for the variable x_t to have the value x at time t and $\Delta F(t)$ is a quantity which you will define.

We now want to apply these results to an experiment which consists in manipulating a brownian particle by applying a time-dependent force with a given protocol (see Fig.1). Initially, the particle is in a symmetric potential and it can be found in one of the two wells of the potential with equal probability (Fig 1a). Then the barrier of this potential is lowered (Fig 1b), it is tilted (Fig 1c,d) in such a way that the particle always ends up in the right minimum of the potential (Fig 1e). The force is then returned to its original value (Fig 1f).

▷ **2-3** What are the difference of free energy and internal energy during a complete cycle of such a process, why ?

▷ **2-4** Show that in these conditions,

$$\langle e^{-\beta W}\rangle_{\to 0} = \frac{1}{2}, \tag{5}$$

where the notation $\langle..\rangle_{\to 0}$ means an average over a process which will end with the particle in the right minimum of the potential as in figure 1f.

▷ **2-5** We now assume that the process is not perfect and that the particle ends up most of the time in the right minimum (with probability P_s), but occasionnaly may also end up in the left minimum (with probability $1-P_s$). Calculate the corresponding exponential average of the work for these two situations and show that together they are compatible with the Jarzynski relation.

From the results obtained above, derive a bound for the average work which depends only on P_s (irrespectively of the final state). Show that this bound can be interpreted as a change of entropy of the system.

▷ **2-6** Fig. 1 shows the average heat recorded in the experiment as function of the duration of the cycle. Explain how this experiment relates with the Landauer principle which states that in any irreversible logical operation, the minimum dissipation is $-k_B \ln(2)$ per bit involved in the logical operation.