ICFP M2 - Statistical physics: Advanced and New Applications
TD3: Stochastic Thermodynamics

Giulio Biroli and Gregory Schehr

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The field of stochastic thermodynamics began at the end of the 90s and has been a very active research area since then. As we will see, it is both important from a fundamental point of view and for experiments and applications on nano- and micro-objects.

The results we are going to derive hold in very general settings, but to be concrete we focus on a simple case: we consider a non-equilibrium process in which a one dimensional particle verifies the Langevin equation:

$$\frac{dx}{dt} = -\frac{\partial}{\partial x} V(x(t), \lambda(t)) + \xi(t)$$

where the potential $V(x(t), \lambda(t))$ depends on an external parameter that varies with time from $t = 0$ to $t = \tau$. At time $t = 0$ the system is at equilibrium and it is brought out of equilibrium at subsequent times because $\lambda(t)$ is changing. As discussed during the lecture, we are also going to consider the time-reversed stochastic process in which the coupling varies as $\lambda_R(t) = \lambda(\tau - t)$. In the time-reversed process the system also starts from equilibrium but with the potential $V(x, \lambda(\tau))$. The time-reversed counterpart of a given path $x(t)$ is defined as $x_R(t) = x(\tau - t)$. We also recall the general identity on paths probability densities obtained during the lecture:

$$P[x_R(t)|x_R(0) = x_f] = P[x(t)|x(0) = x_0] e^{-\frac{1}{T}\int_0^\tau dt \frac{dx}{dt} F}$$

where $F = -\frac{\partial}{\partial x} V(x(t), \lambda(t))$.

1 Jarzynski identity

By definition the mechanical work done on the system during a given path is

$$W = \int_0^\tau dt \frac{\partial V}{\partial \lambda} \frac{d\lambda}{dt}$$

1. Show that

$$P[x_R(t)|x_R(0) = x_f] = P[x(t)|x(0) = x_0] e^{\frac{V(x_f,\lambda(\tau)) - V(x_0,\lambda(0))}{T} - \frac{W}{T}}$$

2. Using that the initial condition is at equilibrium show that

$$P[x_R(t)] = P[x(t)] e^{\frac{-W + \Delta F}{T}} \tag{1}$$

   where $\Delta F = F_f - F_i$ is the difference between the free-energy of an equilibrium system with $\lambda = \lambda(\tau)$ and the one of an equilibrium system with $\lambda = \lambda(0)$.

3. Using the previous result show that

$$\langle e^{-\frac{W}{T}} \rangle = e^{-\frac{\Delta F}{T}}$$

   where the average is over the stochastic process (note that the work is a stochastic quantity). This is the famous Jarzynski relation.

4. Starting from the Jarzynski relation show the general thermodynamic (Clausius) inequality:

$$\langle W \rangle - \Delta F \geq 0$$

   The quantity $\langle W \rangle - \Delta F$ is the dissipated part of the work.

2 Crooks identity

We now study relationships between the forward process and its time-reversed counterpart. Since the system is out of equilibrium the two processes are not equivalent but one can obtain general relationships among them.

1. Obtain that the work done during the time-reversed process is $W_R = -W$.

2. By using the identity (1) show that

$$P_R(-W) = P(W)e^{\frac{-W+\Delta F}{T}}$$

   where $P(W)$ is the probability density to observe the work W during the out of equilibrium process and $P_R(W)$ the probability density to observe the work W during the time-reversed process. This is the Crooks identity.

3. A measure of the distance between two probability distribution R and Q is given by the Kullback Leibler divergence

$$D_{KL}(R(x)||Q(x)) = \int dx R(x) \log \frac{R(x)}{Q(x)}$$

   Show that

$$\langle W \rangle - \Delta F = T D_{KL}(P(W)||P_R(-W))$$

   This equality is a way to related the dissipated part of the work to the difference between the forward process probability density of the work and its time reversed counterpart.

4. Consider a cyclic process in which in an interval of time τ, $\lambda(t)$ is brought from λ_0 to λ_1 by a given protocol and then back to λ_0 following the time-reversed protocol. In the adiabatic limit one expects $\langle W \rangle = 0$. When the coupling λ instead is changed rapidly one expects $\langle W \rangle > 0$. Show that the Crooks identity implies that during the cycle the probability of negative work is non-zero.

5. Why is negative work never observed for macroscopic objects? Note that negative work in a cyclic process violates the second law of thermodynamics.
   For which system do you expect that this "violation of the second law" can be observed?

3 Crooks identity for isolated quantum systems

The out of equilibrium protocol is the same one discussed above: the system has a Hamiltonian in which a coupling $\lambda(t)$ is varied; at time $t = 0$ the system is at equilibrium, hence characterized by a Boltzmann density matrix, and it is brought out of equilibrium at subsequent times because $\lambda(t)$ is changing. We are also going to consider the time-reversed process in which the coupling varies as $\lambda_R(t) = \lambda(\tau - t)$. In the time-reversed process the system also starts from equilibrium but with the Hamiltonian correspondent to $\lambda(\tau)$.
The study of the quantum version of the Jarzynski and Crooks identities lead to debates in the literature on the notion of "work" in quantum mechanics.
In the following we shall define the work following a thought experiment: at time $t = 0$ one does a single measurement of the energy of the system, and gets E_i, at the final time $t = \tau$ one does another single measurement of the energy of the system, and gets E_f. The work done on the system is defined as $W = E_f - E_i$ (there is no heat exchange since the system is isolated).

1. Write down the general expression of the probability $P(E_f, E_i)$ to observe the energy E_i at time $t = 0$ and the energy E_f at time t_f in terms of the evolution operator and the eigenstates of the initial and final Hamiltonian.

2. Write the probability $P(W)$ of observing the work W in terms of $P(E_f, E_i)$.

3. Repeat the analysis for the time-reversed process and obtain the expression of $P_R(-W)$.

4. Obtain the Crooks identity for this out-of equilibrium protocol:

$$P_R(-W) = P(W)e^{\frac{-W+\Delta F}{T}}$$

4 Small challenge-exercise (for later): Jarzynski identity for isolated classical systems

We now consider a classical isolated system and, again, the same protocol defined above. The mechanical work done on the system is

$$W = \int_0^\tau dt \frac{\partial H}{\partial \lambda}\frac{d\lambda}{dt}$$

where H is the Hamiltonian (there is no heat exchange since the system is isolated).
Show that the Jarzynski identity

$$\langle e^{-\frac{W}{T}} \rangle = e^{-\frac{\Delta F}{T}}$$

holds (hint: you will have to use Liouville theorem).

Suggested readings to know more on Stochastic Thermodynamics are: U. Seifert "Lecture Notes: Soft Matter. From Synthetic to Biological Materials" (available on the internet); "Stochastic thermodynamics, fluctuation theorems and molecular machines", Rep. Prog. Phys. 75 (2012) 126001.