Non-equilibrium work relations

Références

[1] Equalities and inequalities : irreversibility and the second law of thermodynamics at the nanoscale, C. Jarzynski, Annu. Rev. Condens. Matter Phys., 2 :329-51 (2011).

1 Jarzynski and Crooks fluctuation relations

One considers a classic hamiltonian system, initially at thermal equilibrium at temperature T, which is then driven out of equilibrium by the application of a time-dependent driving $\lambda(t)$. Remarkably, non-equilibrium work relations provide a way to relate for arbitrary non-equilibrium process, thermodynamic quantities (like free energy difference) to specific non-equilibrium averages. These averages are done over many realizations of the non-equilibrium process with the same imposed driving $\lambda(t)$, which varies in a controlled way between λ_A and λ_B corresponding to an initial state A (at time 0) and a final state B (reached at time τ). The work received by the system in the operation is

$$W = H(x_\tau, \lambda_B) - H(x_0, \lambda_A), \tag{1}$$

where x_τ denotes a phase point at the final time τ and $H(x, \lambda)$ is the hamiltonian at phase point x with the value of the control parameter λ.

▷ **1-1** Derive from these definitions, the Jarzynski relation, namely :

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}, \tag{2}$$

where ΔF represents the free energy difference between A and B.

Now, one considers two processes a forward one which starts at equilibrium and proceeds until time τ according to the protocol $\lambda(t)$ as before, and a reversed one which also starts at equilibrium but at time τ and then proceeds backwards with the time-reversed driving $\lambda(\tau - t)$.

▷ **1-2** Show that the ratio of the probabilities of the phase space densities for the forward and for the reversed process is $\exp(\beta(W - \Delta F))$ in the hamiltonian case. Deduce from this, the Crooks work relation :

$$P_F(W) = P_R(-W) e^{-\beta(W - \Delta F)}, \tag{3}$$

relating the probabilities to observe a work W in the forward process, $P_F(W)$ or a work $-W$ in the reversed process, $P_R(-W)$.

▷ **1-3** Extend the result above to the dynamics of a system in contact with a reservoir at temperature T.

2 Heat and work exchanges during an ensemble switch

Consider an overdamped brownian particle in a time-dependent harmonic potential.

$$U(x,t) = \frac{\kappa(t)}{2} x^2, \qquad \text{with} \qquad \kappa(t) = \begin{cases} \kappa_1 & \text{if } 0 < t < t_s \\ \kappa_2 & \text{if } t_s < t < t' \end{cases}$$

arising from a switching protocol running from time $t = 0$ to $t = t'$.

▷ **2-1** Write down the work done by the switch as a functional of the particle trajectory $x(t)$, likewise the change in internal energy and hence the heat surrendered to the bath.

▷ **2-2** Write down conditions under which the entropy of the bath decreases as a consequence of the switch.

▷ **2-3** Assume that the particle is at equilibrium with the bath at time $t = 0$ and take $t' \to \infty$ so that it ultimately equilibrates with the new potential. Show that $\langle \Delta U \rangle = 0$. Further show that

$$\langle \Delta W \rangle = \langle \Delta Q \rangle = \frac{kT}{2} \left(\frac{\kappa_2}{\kappa_1} - 1 \right). \tag{4}$$

▷ **2-4** Show that

$$\Delta F = \frac{kT}{2} \ln \frac{\kappa_2}{\kappa_1}, \tag{5}$$

and hence that the minimum work principle is satisfied.

▷ **2-5** Explicitly verify the Jarzynski equality $\langle e^{-\Delta W/kT} \rangle = e^{-\Delta F/kT}$ for this switching protocol.