Statistical Physics IV: Non-equilibrium statistical physics
ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE (EPFL)

Exercise No.8

8.1 Crooks fluctuation theorem and Jarzynski equality

The Crooks fluctuation theorem gives a relation between probabilities P_F and P_R to produce work W in the process of forward and reversed (in time) changes of a system under the influence of an external perturbation:

$$\frac{P_F(W)}{P_R(-W)} = \exp\left(\frac{W - \Delta G}{k_B T}\right),$$

whereby the initial and final (equilibrium) states of the system are thermal states at temperature T separated by a free energy ΔG. Note that from the Crooks theorem the **Jarzynksi equality** follows as well,

$$\exp\left(-\frac{\Delta G}{k_B T}\right) = \left\langle \exp\left(-\frac{W}{k_B T}\right)\right\rangle.$$

where the average is taken over a large set of repeated measurements.

1. The Crooks fluctuation theorem was experimentally verified by Collin et al. in Nature 437, 231 (2005) "Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies". Explain how the Crooks fluctuation theorem is applied to the probability distribution of the forward and backward work (cf. Figure 2 and 3 of the reference).

2. Within the context of the experimental determination of folding energies (i.e. free energy differences), explain the experimental advantages of demonstrating the Crooks fluctuation theorem over the Jarzynski equality.

8.2 Validation of Crooks equality with Metropolis Monte Carlo simulation*

This exercise is an investigation of the Crooks' equality based on the PRE article: G. Crooks, Phys. Rev. E **60**, 2721 (1999). The aim is to reproduce the numerical simulations presented in figures 1 and 2 of the aforementioned paper by using the mesoscopic master equation in combination with the metropolis algorithm along with the definition of entropy.
We ask you to provide all your code for the exercise. All the numerical simulations should be implemented yourself with only minimal use of pre-packaged solvers such as those found in Matlab or Scipy. You may use the programming language of your choice, though we recommend using Python, C++ or Matlab.

1. Simulate using the Metropolis Monte Carlo algorithm the probability distribution $P_n(t)$ in equilibrium without movement of the energy landscape (c.f. Fig 1).

2. Next, assuming that the potential moves to the right every 8th time step (i.e. taking the system far out of equilibrium as described in the article), re-simulate the resulting probability distribution for various speeds (e.g. 2 times faster or slower and original case). Remove the time dependence of the probability distribution by switching to a frame moving with the energy landscape.

3. Starting from the equilibirum non-moving energy landscape, and using the results form the previous simulations, construct the work probability distribution for a different number of cycles (i.e. reproduce Fig. 2).

8.3 Quantization and coherent states [1]

Electromagnetic modes, vibrational or magnetic excitations in solids are all examples of harmonic oscillators. The quantization of the underlying canonical variables (e.g. position and momentum, quadratures of the electric and magnetic field, etc. . .) leads to a quantum mechanical harmonic oscillator. We consider here the quantum mechanical excitations that are closest to classical states: coherent states

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \alpha^n \frac{|n\rangle}{\sqrt{n!}},$$

where α is a complex parameter and $|n\rangle$ are states of the oscillator with occupation equal to n.

(a) Show that the average occupation $\langle \hat{n} \rangle = \langle \hat{a}^\dagger \hat{a} \rangle$ of the coherent state obeys $\langle \hat{n} \rangle = |\alpha|^2$. Calculate the variance in the number of quanta $\langle \hat{n}^2 \rangle - \langle \hat{n} \rangle^2$.

(b) Show that the unnormalized coherent states (or "Bargmann states") $|\alpha\rangle = \sum \frac{\alpha^n}{\sqrt{n!}} |n\rangle$ obey $\hat{a}^\dagger |\alpha\rangle = \frac{\partial}{\partial \alpha} |\alpha\rangle$

[1] See e.g. "Stochastic Methods", C. Gardiner, Chapter 10