PHYS 414 Problem Set 4: Unzipping and decohering

Problem 1

The goal of this problem is to directly verify two nonequilibrium fluctuation theorems (integral and Jarzynski) through a computational experiment: simulating an AFM apparatus where the extension of a biomolecular construct is varied in time, driving the system between different possible states. This is the numerical analogue of the RNA hairpin unzipping experiments where these fluctuation theorems were first confirmed over a decade ago (see references on the course website). The model consists of a protein molecule in solution attached to the AFM tip and a fixed surface by polymer handles (Fig. 2). The entire protein-handle system can be roughly approximated as an elastic spring of total extension x with spring constant k_1 (in the case where the protein is folded) or k_2 (if the protein is unfolded). Since the folded structure is more rigid than the unfolded one, $k_1 > k_2$. There is one additional energy contribution besides the spring potential: folding lowers the protein energy by an amount $\epsilon > 0$, which makes the folded state more favorable at small extensions. The resulting energies of state 1 (folded) and state 2 (unfolded) are:

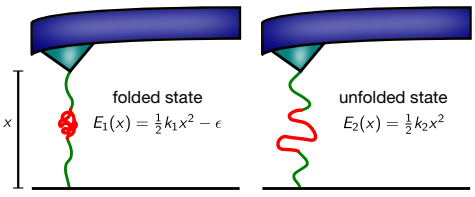

Figure 1: Two possible states of a biomolecular system in an AFM apparatus with a given extension x, and the corresponding state energies $E_n(x)$.

$$E_1(x) = \frac{1}{2}k_1x^2 - \epsilon, \qquad E_2(x) = \frac{1}{2}k_2x^2. \tag{1}$$

The transition rates between the two states, $W_{12}(x)$ and $W_{21}(x)$, satisfy detailed balance, $W_{12}(x)/W_{21}(x) = e^{-\beta(E_1(x)-E_2(x))}$, where $\beta = 1/k_BT$. Hence we will write them in the form:

$$W_{12}(x) = \omega e^{\beta E_2(x)}, \qquad W_{21}(x) = \omega e^{\beta E_1(x)}, \tag{2}$$

with a prefactor ω.

A single experimental run consists of starting the system with an extension $x = x_0$, and keeping it there for a long time until equilibrium is achieved. Then the experimentalist increases the extension x from x_0 to x_M over a time τ. Let us define an average pulling velocity $v = (x_M - x_0)/\tau$. For ease of computation, we will approximate pulling at constant velocity by a uniform series of small discrete jumps: divide the time interval τ into M parts of length $\Delta t = \tau/M$. At the beginning of each Δt interval (at time $t_i = i\Delta t$ for $i = 0, \ldots, M-1$), the extension x is suddenly increased by an amount $\Delta x = v\Delta t$. Assuming the system was in state n_i at time t_i, with initial extension $x_i = x_0 + i\Delta x$ (and remains in state n_i through the instantaneous increase in x), then the work done on the system in this jump is $E_{n_i}(x_{i+1}) - E_{n_i}(x_i)$. After each jump, the extension is kept constant through the following Δt interval, and the system can fluctuate between states, eventually arriving at state n_{i+1} at time t_{i+1}. Then the jump process repeats. The total work done *by* the system during the entire trajectory $\nu = (n_0, n_1, \ldots, n_M)$ is just minus the total work done on the system: $\Delta W(\nu) = -\sum_{i=0}^{M-1}\left[E_{n_i}(x_{i+1}) - E_{n_i}(x_i)\right]$. The jump at time t_{M-1} is the last one, and afterwards the system is kept at extension x_M until it equilibrates again.

Part A: Setting up the experiment

We will be designing a numerical algorithm to simulate trajectories ν and collect statistics on the work $\Delta W(\nu)$. There are several analytical calculations that we need to carry out before we can put together the algorithm:

a) The first step in any trajectory is choosing an initial state n_0 at time t_0 from the equilibrium distribution $p^s_{n_0}(x_0)$. Find analytical expressions for the partition function $Z(T, x_0)$ of the system and the corresponding equilibrium probabilities $p^s_{n_0}(x_0)$ for $n_0 = 1$ and $n_0 = 2$.

b) During the interval between t_i and t_{i+1} where we keep the system at fixed extension x_{i+1}, the system can make transitions between states, or stay in the same state. Let us now figure out the probability of whether a transition occurs or not during this interval. The transition matrix elements $W_{mn}(x_{i+1})$ are constant for times t between t_i and t_{i+1}. Hence write down the master equation for $p_1(t)$ and $p_2(t)$, where $t_{i+1} \geq t \geq t_i$, and solve it for arbitrary initial conditions $p_1(t_i)$ and $p_2(t_i)$. (*Hint:* plugging in $p_2(t) = 1 - p_1(t)$ into the equation for $\dot{p}_1(t)$ allows you to change a coupled set of differential equations into an equation for a single function. Once you solve for $p_1(t)$, you automatically know $p_2(t)$.) If you now substitute $p_1(t_i) = 1$, $p_2(t_i) = 0$ as initial conditions, you should find that the expression for $p_1(t_{i+1})$ takes the form:

$$\frac{W_{12}(x_{i+1}) + W_{21}(x_{i+1})e^{-\Delta t(W_{12}(x_{i+1})+W_{21}(x_{i+1}))}}{W_{12}(x_{i+1}) + W_{21}(x_{i+1})} \equiv p_{11}(x_{i+1})$$

Here we will use p_{11} as shorthand to denote the probability that the system is in state 1 at t_{i+1} if it was in state 1 at time t_i. Similarly if you substitute $p_1(t_i) = 0$, $p_2(t_i) = 1$ into your solution, you should find that $p_2(t_{i+1})$ looks like:

$$\frac{W_{21}(x_{i+1}) + W_{12}(x_{i+1})e^{-\Delta t(W_{12}(x_{i+1})+W_{21}(x_{i+1}))}}{W_{12}(x_{i+1}) + W_{21}(x_{i+1})} \equiv p_{22}(x_{i+1})$$

Here p_{22} denotes the probability that the system is in state 2 at t_{i+1} if it was in state 2 at time t_i. The probabilities of switching are related by normalization: $p_{21} = 1 - p_{11}$ (the probability to switch from 1 to 2), and $p_{12} = 1 - p_{22}$ (the probability to switch from 2 to 1).

We are now ready to construct the numerical algorithm. The parameters of each experimental run are as follows:

$$\begin{aligned} &k_1 = 0.05\ k_BT/\text{nm}^2, \quad k_2 = 0.01\ k_BT/\text{nm}^2, \quad \epsilon = 80\ k_BT, \quad \omega = 5 \times 10^{-9}\ \text{s}^{-1} \\ &M = 100, \quad x_0 = 62.5\ \text{nm}, \quad x_M = 64\ \text{nm} \end{aligned} \tag{3}$$

We will be considering different velocities v across the range $10^{-2} - 10^2$ nm/s.

c) Design a program that numerically outputs a trajectory ν and the work $\Delta W(\nu)$ done by the system during that trajectory. *Hint:* To choose an initial state n_0, get a random number r between 0 and 1. If $r \leq p^s_1(x_0)$, let $n_0 = 1$; otherwise let $n_0 = 2$. This ensures that n_0 is distributed according to the equilibrum stationary probability. You can use similar tricks to get subsequent states n_i in ν. For example, if $n_i = 1$, choose a random number r' between 0 and 1. If $r' \leq p_{11}$, then let $n_{i+1} = 1$; otherwise let $n_{i+1} = 2$. This works analogously for $n_i = 2$, but using p_{22}.

d) To check your program, choose a very slow pulling velocity, $v = 10^{-2}$ nm/s or lower. Since this approximately corresponds to a reversible process, $\Delta S^{\text{int}}(\nu) = -T^{-1}(\Delta W(\nu) + \Delta F) \approx 0$, the work done by the system in a single trajectory $\Delta W(\nu)$ should be roughly equal to $-\Delta F$. Remember that $\Delta F = F^s(T, x_M) - F^s(T, x_0)$, and can be calculated exactly using the partition function from part a, since $F^s(T, x) = -k_B T \ln Z(T, x)$. If your $\Delta W(\nu)$ does not equal $-\Delta F$ within a small discrepancy (a fraction of a $k_B T$), then you have a problem with your code or your analytical derivation. Fix it before proceeding to the next part!

Part B: Data collection and analysis

e) First we pay due to the laws of nature: collect a large number of trajectories (on the order of one thousand) and verify the integral fluctuation theorem (IFT), $\langle e^{-\Delta S^{\text{int}}(\nu)/k_B} \rangle = 1$. This involves calculating $e^{-\Delta S^{\text{int}}(\nu)/k_B}$ for each trajectory ν, and then averaging this quantity over all the trajectories you collected. Remember that $\Delta W(\nu) = -\Delta F - T\Delta S^{\text{int}}(\nu)$, so knowing ΔF beforehand and finding $\Delta W(\nu)$ from the simulation allows you to calculate a value for $\Delta S^{\text{in}}(\nu)$. The computed average $\langle e^{-\Delta S^{\text{int}}(\nu)/k_B} \rangle$ will differ slightly from 1 due to having a finite number of trajectories. Do this for $v = 10^{-2}, 10^{-1}, 10^{0}, 10^{1}$, and 10^{2} nm/s, and note that the IFT works regardless of how fast or slow you pull. Plot histograms of $\Delta S^{\text{int}}(\nu)$ for each of these pulling speeds, and note how the distribution changes qualitatively with v. What is the fraction of entropy-destroying trajectories in each case? Regardless of these qualitative changes in distribution shape, the quantity $\langle e^{-\Delta S^{\text{int}}(\nu)/k_B} \rangle = 1$ stays fixed, which is quite remarkable.

f) In collecting the trajectories, you obtained more than just information about the total $\Delta S^{\text{int}}(\nu)$ and $\Delta W(\nu)$ in each trajectory. Define partial sums of the work done along the trajectories,

$$\Delta W_\mu(\nu) = -\sum_{i=0}^{\mu-1} \left[E_{n_i}(x_{i+1}) - E_{n_i}(x_i) \right], \tag{4}$$

where $\Delta W_M(\nu) = \Delta W(\nu)$. Note that $\Delta W_\mu(\nu)$ for $\mu < M$ corresponds to the work done in an experiment where x was stopped at x_μ instead of x_M. We can now use this information, together with the Jarzynski equality, to calculate equilibrium free energy differences $F^s(T, x_\mu) - F^s(T, x_0)$ for $\mu = 1, \ldots, M$. The Jarzynski equality states that:

$$\langle e^{\beta W_\mu(\nu)} \rangle = e^{-\beta(F^s(T,x_\mu) - F^s(T,x_0))} \tag{5}$$

Use this equation to obtain a plot of $F^s(T, x_\mu) - F^s(T, x_0)$ versus x_μ. Check that you get roughly the same answer regardless of the pulling speed v, and that all your estimates agree with the analytically predicted free energy difference obtained from the partition function in the previous part. Graphically, this means that all your numerical results at different v and the analytical curve should overlap. This procedure is one example of *free energy reconstruction* using the Jarzynski equality, a method that is useful in both experimental and numerical contexts.

Problem 2: Decoherence at work

In class we discussed how a quantum measurement on a system can be seen as one specific example of an interaction of a system with some external environment. Here we will generalize that idea to "imperfect" measurements, where we imagine that our environment acts like an error-prone measurement apparatus.

a) Let us imagine that at time t we have a qubit ensemble with some arbitrary density matrix $\hat{\rho}(t)$. The matrix elements of this operator in the basis $\{|0\rangle, |1\rangle\}$ are denoted as $\rho_{ij}(t) = \langle i|\hat{\rho}(t)|j\rangle$. Between time t and $t + \delta t$, the environment (apparatus) does a measurement projecting the system on the $\{|0\rangle, |1\rangle\}$ basis. Imagine the measurement was a traditional, perfect quantum measurement: if your apparatus output 0, the system state post-measurement would be $|0\rangle$, and if it output 1, the system state post-measurement would be $|1\rangle$. For a perfect apparatus, what is the probability of measuring 0, and what is the probability of measuring 1, in terms of $\rho_{ij}(t)$?

b) An imperfect apparatus is defined as follows. For an initial density matrix $\hat{\rho}(t)$ it measures 0 with the same probability derived above, but it occasionally messes up the wavefunction collapse: the system will be in the wrong state $|1\rangle$ post-measurement of 0 with small probability ϵ_{10}, and the correct state $|0\rangle$ with probability $1 - \epsilon_{10}$. Analogously the apparatus measures 1 with the same probability derived in part a, but results in the wrong system state $|0\rangle$ with probability ϵ_{01}, and the right state $|1\rangle$ with probability $1 - \epsilon_{01}$. Write down the density matrix $\hat{\rho}(t + \delta t)$ post-measurement. *Hint:* Remember post-measurement you are either in state $|0\rangle$ or $|1\rangle$. To find the corresponding density matrix $\hat{\rho}(t + \delta t)$, you need to know what fraction of your ensemble is in either state, given that you started pre-measurement with $\hat{\rho}(t)$.

c) Show that you can express your answer from part b in the form of a Kraus representation:

$$\hat{\rho}(t + \delta t) = \sum_{k=1}^{4} \hat{M}_k \hat{\rho}(t) \hat{M}_k^\dagger$$

Find the four Kraus operators $\hat{M}_k$, and verify that $\sum_k \hat{M}_k^\dagger \hat{M}_k = \hat{I}$, where $\hat{I}$ is the identity.

d) By writing the equation for $\hat{\rho}(t + \delta t)$ explicitly in terms of matrix elements in the $\{|0\rangle, |1\rangle\}$ basis, and dividing by δt, show that you can rearrange the results to look like a classical master equation for the diagonal elements:

$$\frac{d\rho_{00}(t)}{dt} = W_{01}\rho_{11}(tt) - W_{10}\rho_{00}(t)$$
$$\frac{d\rho_{11}(t)}{dt} = W_{10}\rho_{00}(tt) - W_{01}\rho_{11}(t)$$

where $d\rho_{ii}(t)/dt = (\rho_{ii}(t + \delta t) - \rho_{ii}(t))/\delta t$. Find expressions for the transition rates W_{ij}. Also show that $\rho_{01}(t + \delta t) = \rho_{10}(t + \delta t) = 0$, and hence the off-diagonal elements of $\hat{\rho}(t)$ are sent to zero after the imperfect measurement: a simple example of decoherence in action.