

8.808/8.308 IAP 2026 Recitation 4: the Jarzynski equality

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These notes are adapted from Sunghan Ro's recitations from the 2024 iteration of this class.

1 the Jarzynski equality

In class, we learned the “fluctuation theorem” (FT)

$$\frac{P[\Gamma(t)]}{P[\Gamma^R(t)]} = \exp\left(\Sigma[\Gamma(t)]\right), \quad (1)$$

where $P[\Gamma(t)]$ is the probability of a trajectory $\Gamma(t)$, $\Gamma^R(t) = \Gamma(t_f - t)$ is the reverse of that trajectory, and $\Sigma[\Gamma(t)]$ is the change in entropy of the fluid along the trajectory. Here, $\Gamma(t)$ includes all the system's degrees of freedom including particle positions, momenta, etc. We will show that the fluctuation theorem can be used to measure things experimentally that are otherwise inaccessible.

1.1 Difficulty of measuring free energy

Typically in experiments, we measure the average of some observable \mathcal{O} by sampling it through repeated experimentation:

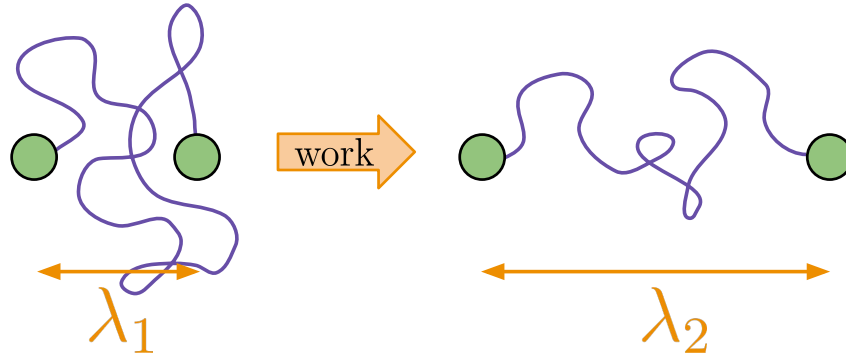
$$\langle \mathcal{O} \rangle = \frac{1}{N_{\text{sim.}}} \sum_{n=1}^{N_{\text{sim.}}} \mathcal{O}_n \xrightarrow{N_{\text{sim.}} \rightarrow \infty} \int d\Gamma \mathcal{O}(\Gamma) P(\Gamma). \quad (2)$$

However, we may be interested in the free energy of a system of interest. This can, for instance, help us understand the underlying Hamiltonian of a complicated experiment. But $F = -\frac{1}{\beta} \ln Z$ is difficult to measure using the above sampling method.

1.2 Parametrized Hamiltonian: stretching a polymer

Let's consider a Hamiltonian that is parametrized by some externally-imposed parameter $\lambda(t)$ that we vary in time. It is important to note that each value of λ specifies a different system with its own value of the free energy $F(\lambda)$. We will show that the fluctuation theorem allows us to measure the changes in free energy between different values of λ , i.e. measure $\Delta F = F(\lambda_2) - F(\lambda_1)$.

Let's consider an ideal polymer (similar to the one we studied in the previous recitation), where we control the end-to-end separation λ , visualized below:



Changing λ from a value λ_1 to λ_2 does work on the system, W . This experiment can be done (and has been done¹) using optical tweezers, which allows directly measuring the work done on the polymer by changing λ . The first law of thermodynamics (conservation of energy) tells us that

$$W = \Delta E_{\text{sys}} + \Delta E_{\text{bath}} = \Delta E_{\text{sys}} + Q_{s \rightarrow b} , \quad (3)$$

where E_{sys} is the energy of the system (the polymer) and $Q_{s \rightarrow b}$ is the heat that flows from the system to the bath. Thus, $Q_{s \rightarrow b} = W - \Delta E_{\text{sys}}$. We can then write the total change in entropy

$$\Delta S_{\text{tot}} = \Delta S_{\text{bath}} + \Delta S_{\text{sys}} \quad (4)$$

as

$$\Delta S_{\text{tot}} = \Delta S_{\text{bath}} + \Delta S_{\text{sys}} = \frac{Q_{s \rightarrow b}}{T} + \Delta S_{\text{sys}} = \frac{W - \Delta E_{\text{sys}}}{T} + \Delta S_{\text{sys}} = \frac{W - \Delta E_{\text{sys}} + T \Delta S_{\text{sys}}}{T} = \frac{W - \Delta F_{\text{sys}}}{T} . \quad (5)$$

But if we recall Lecture 7, the total change in entropy has an information-theoretic meaning:

$$\Delta S_{\text{tot}} = k_B \Sigma[\Gamma(t)] \stackrel{\text{FT}}{=} k_B \ln \left(\frac{P[\Gamma(t)]}{P[\Gamma^R(t)]} \right) . \quad (6)$$

We can then use the other relation from class (the proof of which I reproduce here):

$$\langle e^{-\Sigma[\Gamma(t)]} \rangle = \int D[\Gamma(t)] P[\Gamma(t)] e^{-\Sigma[\Gamma(t)]} = \int D[\Gamma(t)] P[\Gamma(t)] \frac{P[\Gamma^R(t)]}{P[\Gamma(t)]} = \int D[\Gamma(t)] P[\Gamma^R(t)] = 1 \quad (7)$$

to show that

$$\langle e^{(\Delta F_{\text{sys}} - W)/k_B T} \rangle = \langle e^{-\Delta S_{\text{tot}}/k_B} \rangle = \langle e^{-\Sigma[\Gamma(t)]} \rangle = 1 . \quad (8)$$

Then, because ΔF_{sys} is a constant property of the entire ensemble, the averaging doesn't affect it, and we can divide both sides by $e^{\Delta F_{\text{sys}}/k_B T}$ to find

$$\langle e^{-W/k_B T} \rangle = e^{-\Delta F_{\text{sys}}/k_B T} . \quad (9)$$

This is known as the **Jarzynski equality**.

2 Numerics

You will validate the Jarzynski equality on a numerical stretching experiment of an ideal polymer, using the code [Rec3_Polymer.jl](#) which uses [Rec3_module.jl](#) (both on the website).

¹Collin, D. et al. (2005). *Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies*. Nature, 437(7056), 231-234.