

# 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:

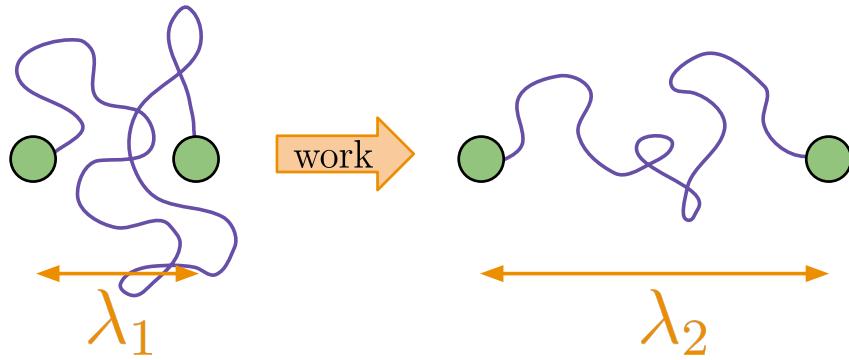
$$\langle \mathcal{O} \rangle = \frac{1}{N_{\text{sim.}}} \sum_{n=1}^{N_{\text{sim.}}} \mathcal{O}_n \xrightarrow{N_{\text{sim.}} \rightarrow \infty} \int d\Gamma \mathcal{O}(\Gamma) P(\Gamma). \quad (2)$$

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  $\lambda$  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  $\lambda$ , 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  $\lambda$ , visualized below:



Changing  $\lambda$  from a value  $\lambda_1$  to  $\lambda_2$  does work on the system,  $W$ . This experiment can be done (and has been done<sup>1</sup>) using optical tweezers, which allows directly measuring the work done on the polymer by changing  $\lambda$ . 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  $E_{\text{sys}}$  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  $\Delta F_{\text{sys}}$  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).

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