Lecture 11

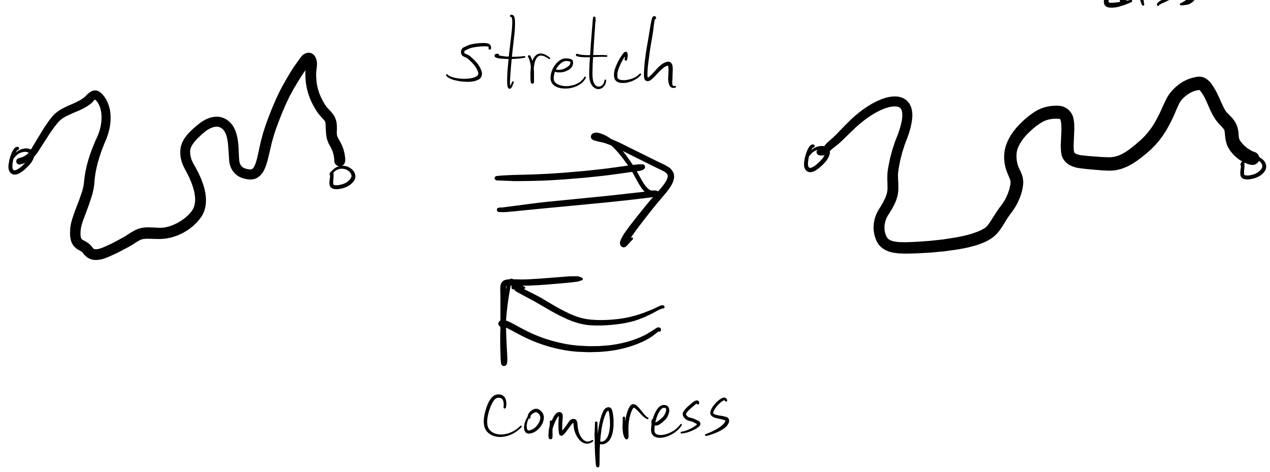
Recall from last lecture...

$$W_{diss} = W - W_{rev} = W - \Delta A$$

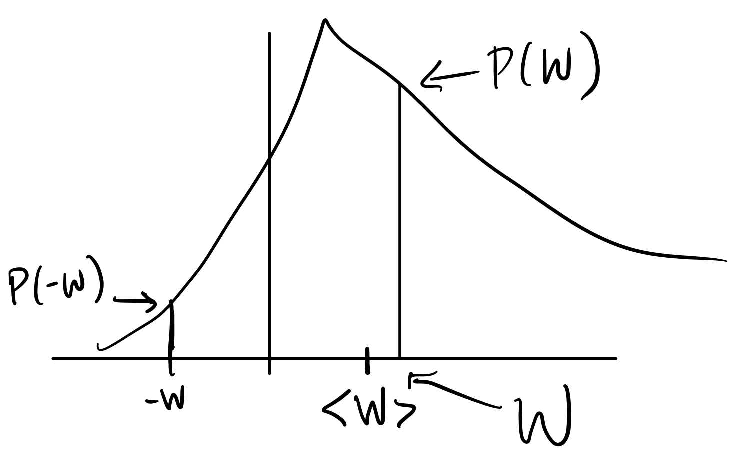
Dissipated Work: How much work was wasted because you were impatient and wanted to move quickly

One way to see the wasted work is to look at a cyclic process. Now $\Delta A = 0$

$$\Rightarrow W_{diss} = W$$



How does $P(W)$ compare to $P(-W)$?



$$\boxed{\frac{P(W)}{P(-W)} = e^{\beta W}}$$

(for the $\Delta A = W_{rev} = 0$ cyclic process)

When W_{rev} is not necessarily 0,

$$\boxed{\frac{P(W_{diss})}{P(-W_{diss})} = e^{\beta W_{diss}}}$$ Crooks Fluctuation Theorem

$\Downarrow$ (HW)

$\langle e^{-\beta W_{diss}} \rangle = 1.$
(Jarzynski Equality) $\xRightarrow{\text{Jensen's Inequality}}$ $\langle W_{diss} \rangle \geq 0.$

No matter how you pull, your impatience will always require more work on average than if you went infinitesimally slowly and stayed in equilibrium.

Equivalently, energy will be lost into the bath on average

Equivalently, the entropy of the bath will increase (on average)

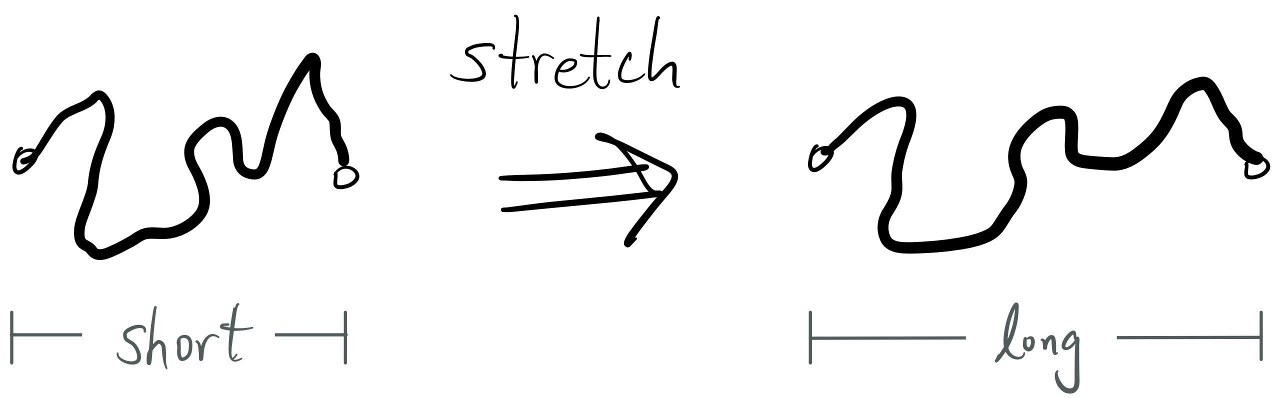
(Cyclic) Because the system returns to its original state (L_i), its <u>entropy</u> did not change. Hence the bath's increase in entropy means "<u>the universe</u>" has increased in <u>entropy</u>.

Equivalently, the second law holds <u>on average</u>.

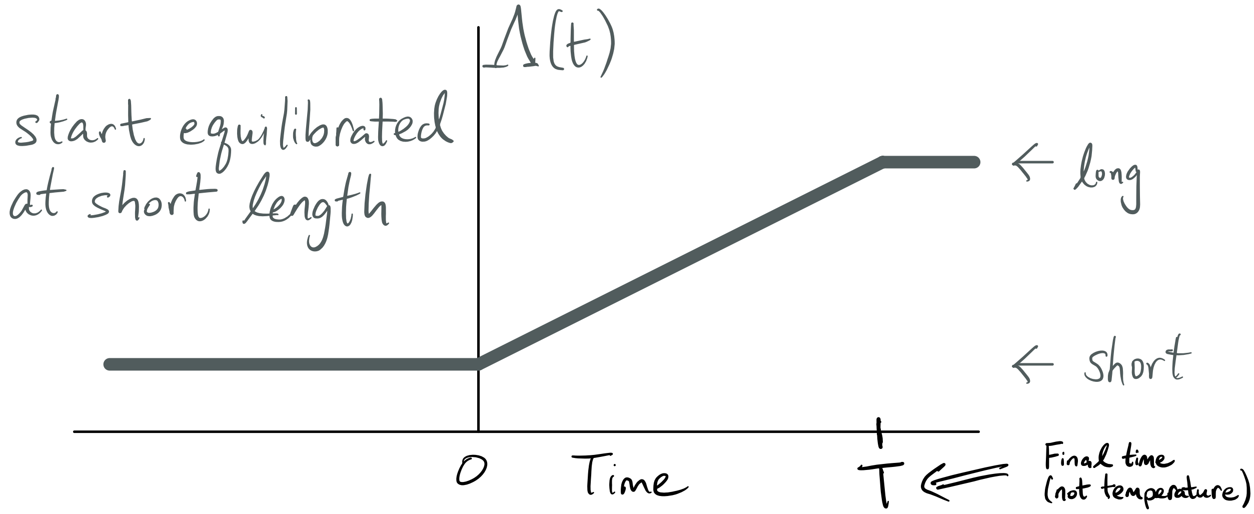
Where does the Crooks Fluctuation Theorem come from?

A Symmetry. Let's see...

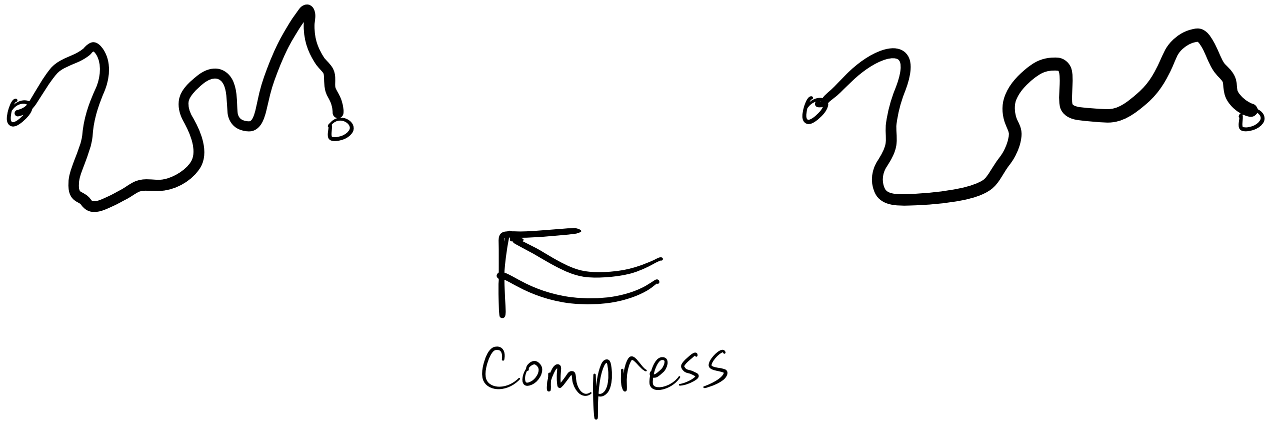
An experiment



$\Lambda(t)$: A time-dependent protocol, here specifying the length as a function of time:

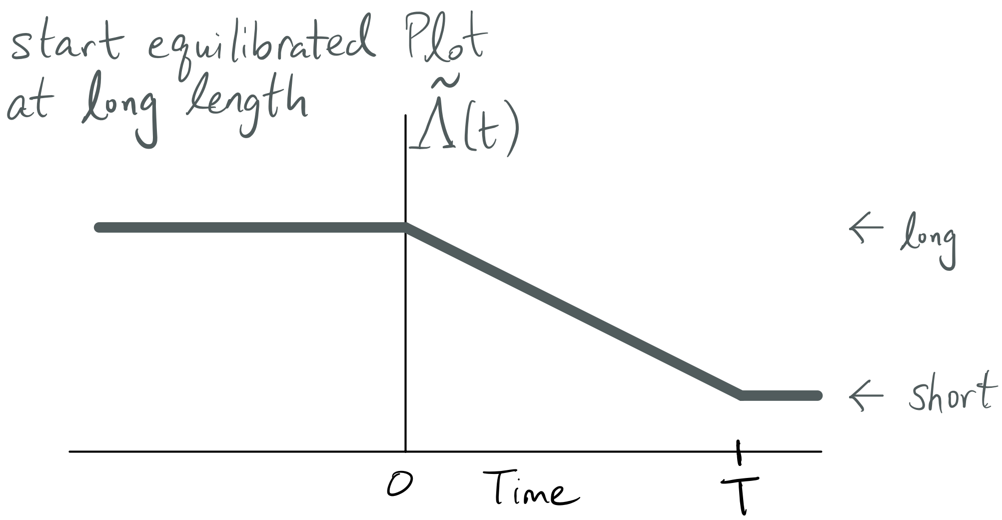


A time-reversed experiment



Time-reversal $\rightarrow$ $\tilde{\Lambda}(t)$

$$\Lambda(0) = \tilde{\Lambda}(T) \qquad \Lambda(T) = \tilde{\Lambda}(0)$$



These plots only show the time dependence of the controled degree of freedom (Λ), but there is also a high-dimensional trajectory $\vec{x}(t)$ telling the polymer configuration as a function of time.

How probable are the various trajectories $\vec{x}(t)$?
(movies)

The answer depends on the nature of the dynamics, i.e., are the beads of the polymer moving according to:

- Newton's laws? (MD)
- Langevin dynamics? (dynamics that mimics the effect of solvent through random kicks)

For the simplest illustration of the Crooks result, we assume Newton's laws (Hamiltonian dynamics)

Key Idea:

Let's think not only of protocol time reversal

$$\Lambda(t) \xleftrightarrow[\text{Time Reversal}]{} \tilde{\Lambda}(t)$$

but also of trajectory time reversal
(remember, high dimensions)

$$\underset{\text{(movie)}}{\vec{x}(t)} \xleftrightarrow[\text{Time Reversal}]{} \underset{\text{(movie)}}{\tilde{\vec{x}}(t)}$$

Both pass through the exact same sequence of polymer configurations but in reversed order.

$$P(\vec{x}(t) \mid \Lambda(t)) \equiv P_F(\vec{x}(t))$$ "Probability of a movie given a forward protocol"

$$P(\tilde{\vec{x}}(t) \mid \tilde{\Lambda}(t)) \equiv P_R(\tilde{\vec{x}}(t))$$ "Probability of a reversed movie given a reversed protocol"

What is the relative probability of these two?

$$\frac{P_F(\vec{x}(t))}{P_R(\tilde{\vec{x}}(t))}$$

$$P_F(\vec{x}(t)) = \text{Probability of the initial condition } \vec{x}(0) \times \text{Probability that a trajectory, initialized at } \vec{x}(0) \text{ and subject to } \Lambda(t) \text{, will yield } \vec{x}(t)$$

A conditional probability.

$$= \frac{e^{-\beta E(\vec{x}(0))}}{Q(\Lambda(0))} \times P(\vec{x}(t) \mid \vec{x}(0), \Lambda(t))$$

For Hamiltonian dynamics, this is like a δ-function — either 0 or 1.

$$P_R(\tilde{\vec{x}}(t)) = \frac{e^{-\beta E(\tilde{\vec{x}}(0))}}{Q(\tilde{\Lambda}(0))} \times P(\tilde{\vec{x}}(t) \mid \tilde{\vec{x}}(0), \tilde{\Lambda}(t))$$

$Q(\Lambda(0))$ and $Q(\tilde{\Lambda}(0))$ are different!

$Q(\Lambda(0))$: Normalization constant for all polymer configurations with Λ = short distance.

$Q(\tilde{\Lambda}(0))$: Normalization constant for all polymer configurations with Λ = long distance.

$$\Rightarrow \frac{P_F(\vec{x}(t))}{P_R(\tilde{\vec{x}}(t))} = \frac{e^{-\beta E(\vec{x}(0))} / Q_{short}}{e^{-\beta E(\tilde{\vec{x}}(0))} / Q_{long}}$$

$$= \frac{e^{-\beta E(\vec{x}(0))} / Q_{short}}{e^{-\beta E(\vec{x}(T))} / Q_{long}}$$

Is $E(\vec{x}(0))$ the same as $E(\vec{x}(t))$?
(Hamiltonian dynamics)

Careful!

Because we control $\Lambda(t)$, we can do work on the system, adding or removing energy.

$$E(\vec{x}(T)) - E(\vec{x}(0)) = W$$ done on the system over time T

$$\frac{P_F(\vec{x}(t))}{P_R(\tilde{\vec{x}}(t))} = \frac{e^{-\beta E(\vec{x}(0))} / Q_{short}}{e^{-\beta E(\vec{x}(T))} / Q_{long}} = e^{\beta W[\vec{x}(t)]} e^{-\beta \Delta A},$$

where $$e^{-\beta \Delta A} = \frac{Q_{long}}{Q_{short}}$$

$$\Delta A = A(long) - A(short) = W_{rev}(short \to long)$$

$$= -k_B T \ln \frac{P(long)}{P(short)}$$

ΔA is the reversible work, but $W[\vec{x}(t)]$ is the work measured in trajectory $\vec{x}(t)$, which was driven irreversibly by $\Lambda(t)$!

We now have $$\frac{P_F(\vec{x}(t))}{P_R(\tilde{\vec{x}}(t))} = e^{\beta W_{diss}[\vec{x}(t)]}$$

How does this differ from...

$$\boxed{\frac{P(W_{diss})}{P(-W_{diss})} = e^{\beta W_{diss}}}$$

We would like to re-express the LHS in terms of work rather than the full movie $\vec{x}(t)$.

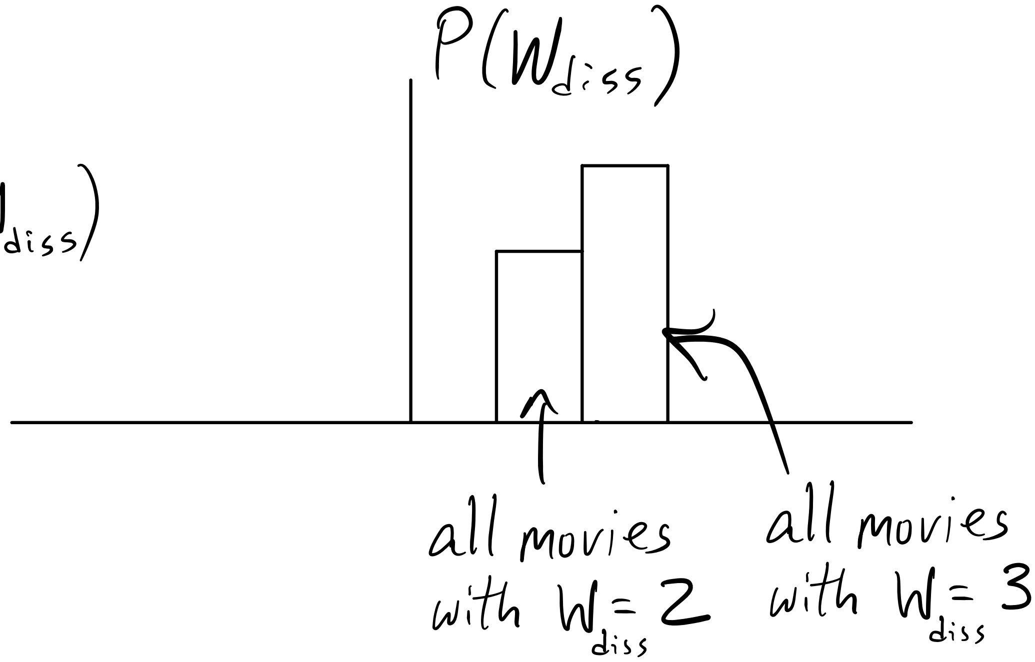
$P_F(\vec{x}(t))$ is super high dimensional!

specifies locations of every monomer at every frame of the movie.

I can always marginalize to get a low-dimensional (1d) distribution

$$P_F(W_{diss}) = \underbrace{\int d\vec{x}(t)\, P_F(\vec{x}(t))\, \delta(W_{diss} - W_{diss}[\vec{x}(t)])}_{\text{Add up the probability of every movie that yields work value } W.}$$

A function of one variable (W_{diss})



$$= \int d\tilde{\vec{x}}(t)\; P_R(\tilde{\vec{x}}(t))\; e^{\beta W_{diss}[\vec{x}(t)]}\; \delta\left(W_{diss} - W_{diss}[\vec{x}(t)]\right)$$

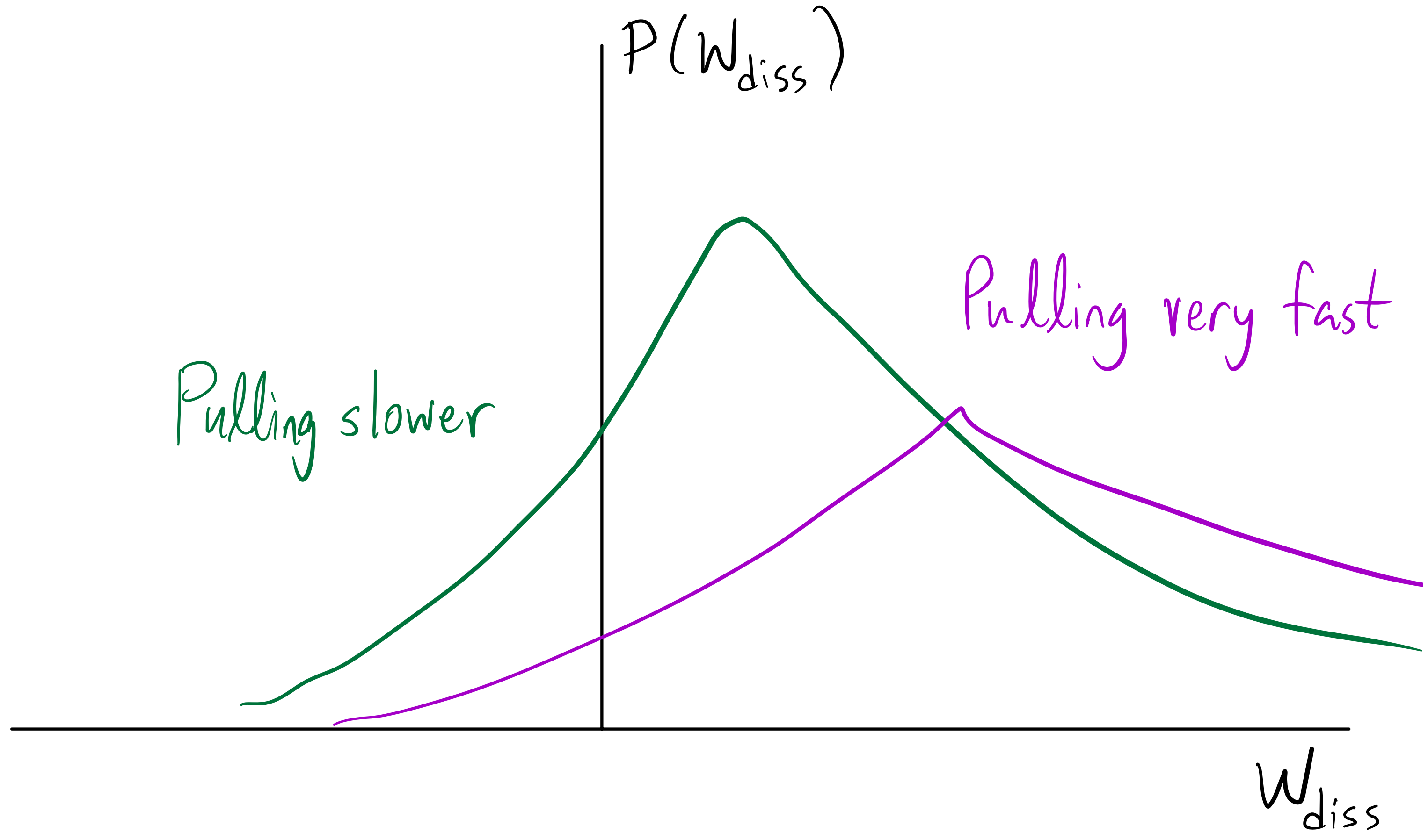
$$= e^{\beta W_{diss}} \int d\tilde{\vec{x}}(t)\; P_R(\tilde{\vec{x}}(t))\; \delta\left(W_{diss} - W_{diss}[\vec{x}(t)]\right)$$

$\downarrow$ Instead of summing over forward movies, sum over reversed ($\tilde{\vec{x}}$)

$$= e^{\beta W_{diss}} \int d\tilde{\vec{x}}(t)\; P_R(\tilde{\vec{x}}(t))\; \delta\left(W_{diss} + W_{diss}[\tilde{\vec{x}}(t)]\right)$$

$$= e^{\beta W_{diss}}\; P_R(-W_{diss})$$

$$\Longrightarrow \boxed{\frac{P(W_{diss})}{P(-W_{diss})} = e^{\beta W_{diss}}}$$



$P(W_{diss})$
Pulling very fast
Pulling slower
W_{diss}