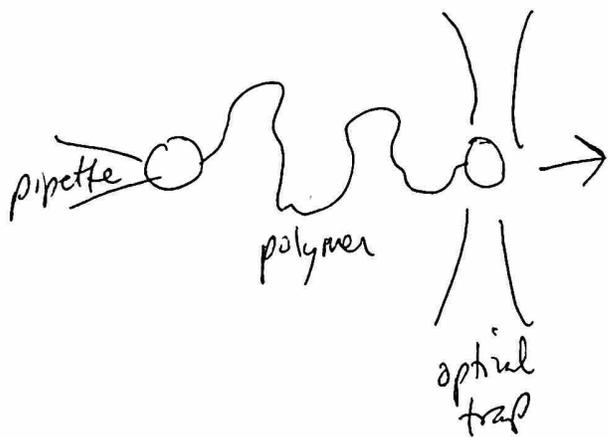


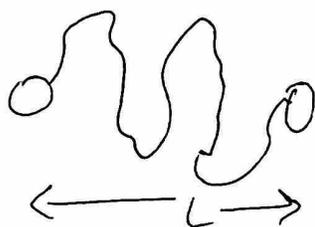
Recap:



pull slowly (reversibly)
and measure the work: $\int_{L_i}^{L_f} dL \cdot \text{force}$

$$W_{\text{rev}} = A(L_f) - A(L_i) = \Delta A$$

We saw that ΔA is related to the probability distribution for L when the polymer is free to fluctuate.



$$\frac{P(L_f)}{P(L_i)} = e^{-\beta \Delta A}$$

Reversible
Work
Thm.

Check signs: Assume $L_i < L_f$. $P(L_i) > P(L_f) \Rightarrow \Delta A$ is positive
I must do work on the polymer to stretch it from L_i to L_f .

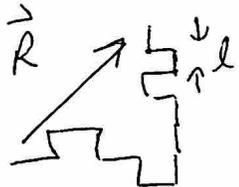
Remember $\ln Q = -\beta A$, so we could see the reversible work
through another way

$$\frac{P(L_f)}{P(L_i)} = \frac{Q(L_f)}{Q(L_i)} = \frac{e^{-\beta A(L_f)}}{e^{-\beta A(L_i)}} = e^{-\beta W_{\text{rev}}(L_i \rightarrow L_f)}$$

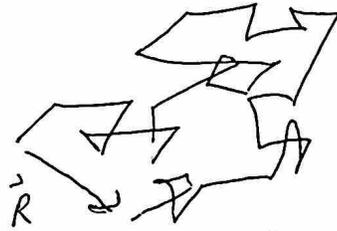
ratio of canonical
partition functions

What is the reversible work ~~to~~ needed to unfold a polymer? First, how about a model of a polymer.

We have already explored two simple models of a polymer.



lattice polymer



Gaussian polymer

In both cases, for a large # of segments/steps/bonds (N),

$$\langle \vec{R} \rangle = 0, \quad \langle \delta \vec{R}^2 \rangle = Nl^2$$

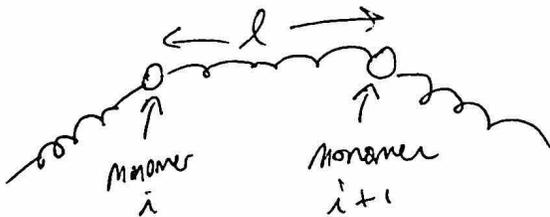
$$\langle \delta R_x^2 \rangle = \frac{Nl^2}{d} \leftarrow d \text{ dimensions}$$

↑
Along 1 dimension

$$P_N(\vec{R}) = \left(\frac{d}{2\pi Nl^2} \right)^{d/2} \exp \left[-\frac{dR^2}{2Nl^2} \right]$$

- Central limit theorem tells us it must be Gaussian

- Once you know $\mu + \sigma^2$, you can just plug it in.



How does l relate to energy & temperature?

Suppose our polymer consisted of harmonic springs

$$E_{\text{spring}} = \frac{k}{2} (\vec{R}_{i+1} - \vec{R}_i)^2$$

↑
Spring constant

The polymer in the thermal bath would sample the Boltzmann distribution:

$$P(\{\vec{R}_i\}) \propto \exp[-\beta E(\{\vec{R}_i\})] = \exp \left[-\frac{\beta k}{2} \sum_i (\vec{R}_{i+1} - \vec{R}_i)^2 \right]$$

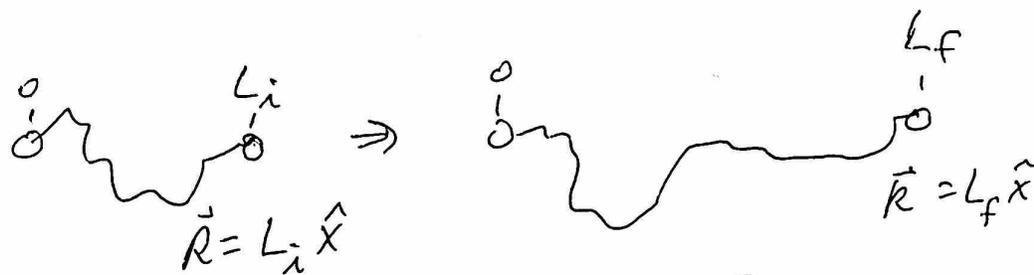
↑
positions for all beads

↑
energy of polymer

Exactly what you studied in your homework except $\beta k = \frac{d}{l^2}$

So the thermal polymer w/ N segments, spring constant k , and inverse temperature β will have an end-to-end vector \vec{R} that samples the Gaussian distribution

$$P_N(\vec{R}) = \left(\frac{\beta k}{2\pi N} \right)^{d/2} \exp \left[-\frac{\beta k R^2}{2N} \right]$$



$$\Rightarrow \frac{P(L_f)}{P(L_i)} = \frac{\left(\frac{\beta k}{2\pi N} \right)^{d/2} \exp \left[-\frac{\beta k L_f^2}{2N} \right]}{\left(\frac{\beta k}{2\pi N} \right)^{d/2} \exp \left[-\frac{\beta k L_i^2}{2N} \right]} = \exp \left[-\frac{\beta k}{2N} (L_f^2 - L_i^2) \right]$$

$$\Rightarrow A(L) = \frac{kL^2}{2N}$$

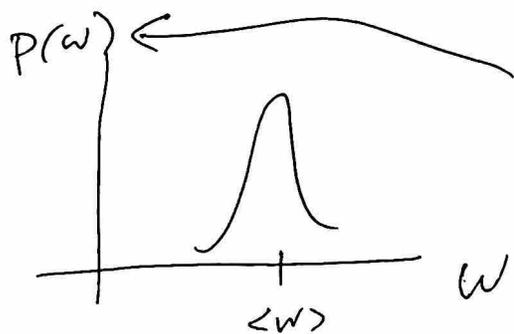
Or put another way, starting from $L_i = 0$, the reversible work to stretch the polymer to L is $W_{rev}(L) = \frac{kL^2}{2N}$!

Let's see it in simulation... <http://gingrich.chem.northwestern.edu/teaching/polymer>

If I pull quickly, how much work do I do?

$W < W_{rev}$ OR $W = W_{rev}$ OR $W > W_{rev}$?

It can depend on the trajectory! Discuss.



A distribution of work for different realizations of the experiment.

$$\langle W \rangle < W_{rev} \text{ OR } \langle W \rangle = W_{rev} \text{ OR } \boxed{\langle W \rangle > W_{rev}} ?$$

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

W_{diss}
↑
dissipated work

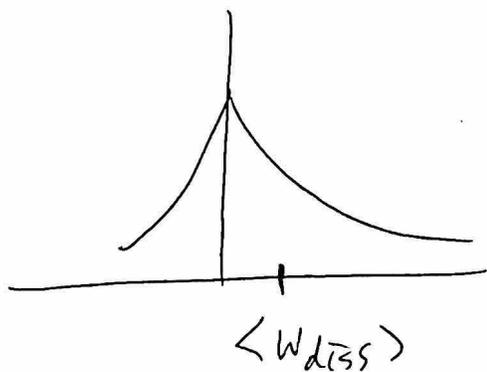
- How much of your work was wasted because you were impatient + wanted to move quickly?

One way to see that wasted work is to look at a cyclic process



Now $\Delta A = 0$ (We end up at the same state we started at)

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



How does $P(W_{diss})$ compare to $P(-W_{diss})$?

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

Crooks Fluctuation Theorem.

$$\frac{P(W_{\text{diss}})}{P(-W_{\text{diss}})} = e^{\beta W_{\text{diss}}} \quad (HW) \quad \Rightarrow \quad \langle e^{-\beta W_{\text{diss}}} \rangle = 1$$

⇓ Jensen's inequality

$$\langle W_{\text{diss}} \rangle \geq 0$$

No matter how we pull, our impatience will always require more work on average than if we 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.

Because the system returns to its original state, its entropy does not change. Hence the bath's increase in entropy means "the universe" has increased in entropy.

Equivalently, the Second Law.