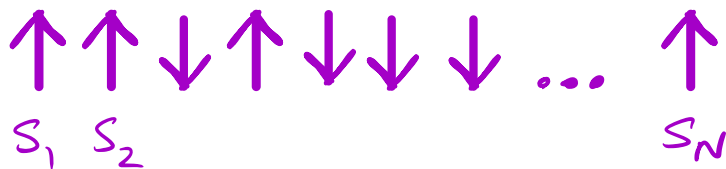


Lecture 10

Recall from last lecture...

Let's work through a calculation both ways.

Non-interacting spins in an external field.

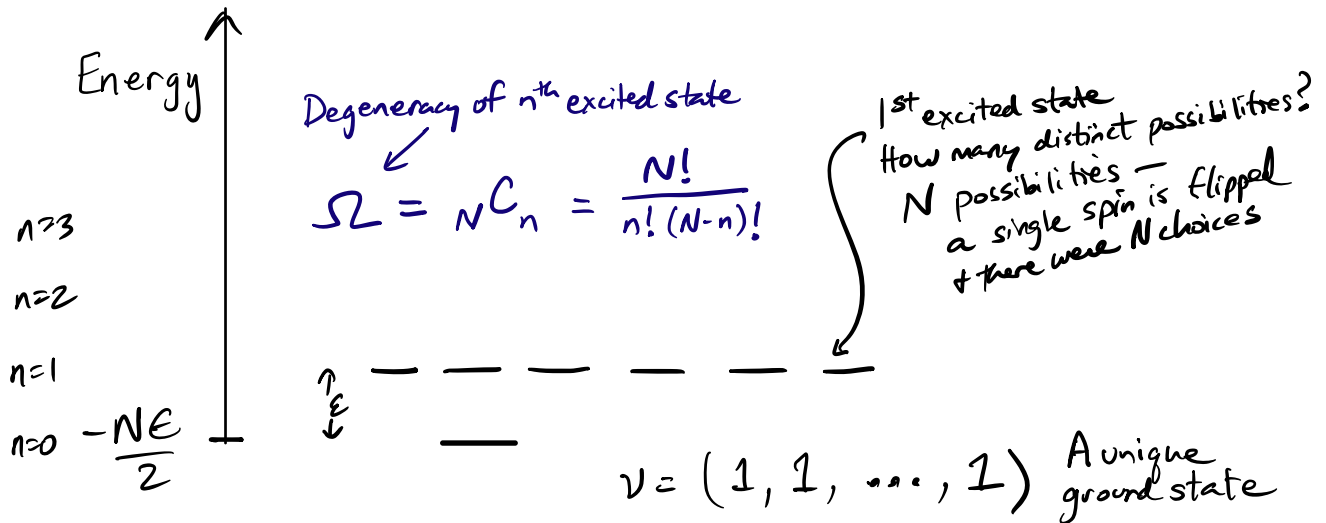


$$S_i = \begin{cases} +1, & \text{aligned with the field} \\ -1, & \text{anti-aligned} \end{cases}$$

$$\nu = \{S_1, S_2, \dots, S_N\} \quad E(\nu) = -\frac{\epsilon}{2} \sum_i S_i$$

We are after a relationship between T and the fraction of excited spins (an excited spin has $S_i = -1$).

Route 1: Microcanonical



$$S = -Nk_B [(1-f)\ln(1-f) + f\ln f]$$

↑
"Entropy of mixing"

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_N = \frac{k_B}{\epsilon} \ln \frac{1-f}{f}$$

⇒ Microcanonical calculation yields:

$$\boxed{\frac{\epsilon}{k_B T} = \ln \frac{1-f}{f}}$$

Route 2: Canonical

$$E(v) = -\frac{E}{2} \sum_i S_i$$

$$P(S_1, S_2, \dots, S_N) \propto e^{-\beta E(S_1, S_2, \dots, S_N)}$$

It factorizes! $\Rightarrow = e^{\beta \frac{E}{2} \sum_i S_i}$

$$= e^{\beta \frac{E}{2} S_1} e^{\beta \frac{E}{2} S_2} \dots e^{\beta \frac{E}{2} S_N}$$

$$= p(S_1) p(S_2) \dots p(S_N) \leftarrow \begin{array}{l} \text{Spins are} \\ \text{statistically} \\ \text{independent} \\ \text{(b/c they are} \\ \text{non-interacting)} \end{array}$$

$$p(s) \propto e^{-\beta E(s)}$$

$$p(s=1) \propto e^{+\beta E/2}$$

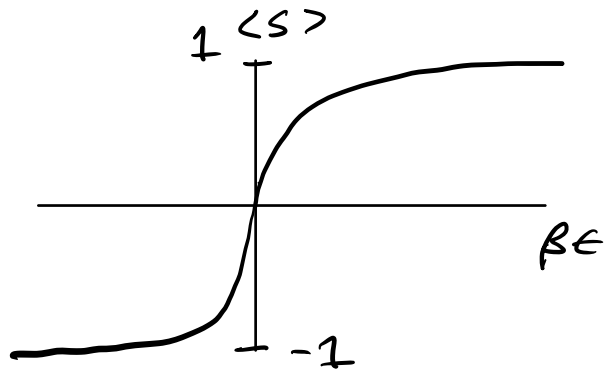
$$p(s=-1) \propto e^{-\beta E/2}$$

$$\Rightarrow p(s) = \frac{e^{\beta E s/2}}{e^{+\beta E/2} + e^{-\beta E/2}}$$

$$\therefore \langle s \rangle = p(s=1) * 1 + p(s=-1) * (-1)$$

$$= \frac{e^{\beta E/2} - e^{-\beta E/2}}{e^{\beta E/2} + e^{-\beta E/2}} = \tanh\left(\frac{\beta E}{2}\right)$$

$$\Rightarrow \langle s \rangle = \frac{e^{\beta E} - 1}{e^{\beta E} + 1} \quad (*)$$



To compare w/ the microcanonical result,

$$\langle s \rangle = \underset{\substack{\uparrow \\ \text{fraction of} \\ \text{excited spins}}}{f}(-1) + (1-f) \underset{\substack{\uparrow \\ \text{fraction of} \\ \text{unexcited spins}}}{(1)} = 1 - 2f$$

So (*) becomes $(1-2f)(e^{\beta E} + 1) = e^{\beta E} - 1$

$$\Rightarrow \cancel{e^{\beta E}} + 1 - 2f \cancel{e^{\beta E}} - 2f = \cancel{e^{\beta E}} - 1$$

$$\Rightarrow -2f e^{\beta E} = 2f - 2$$

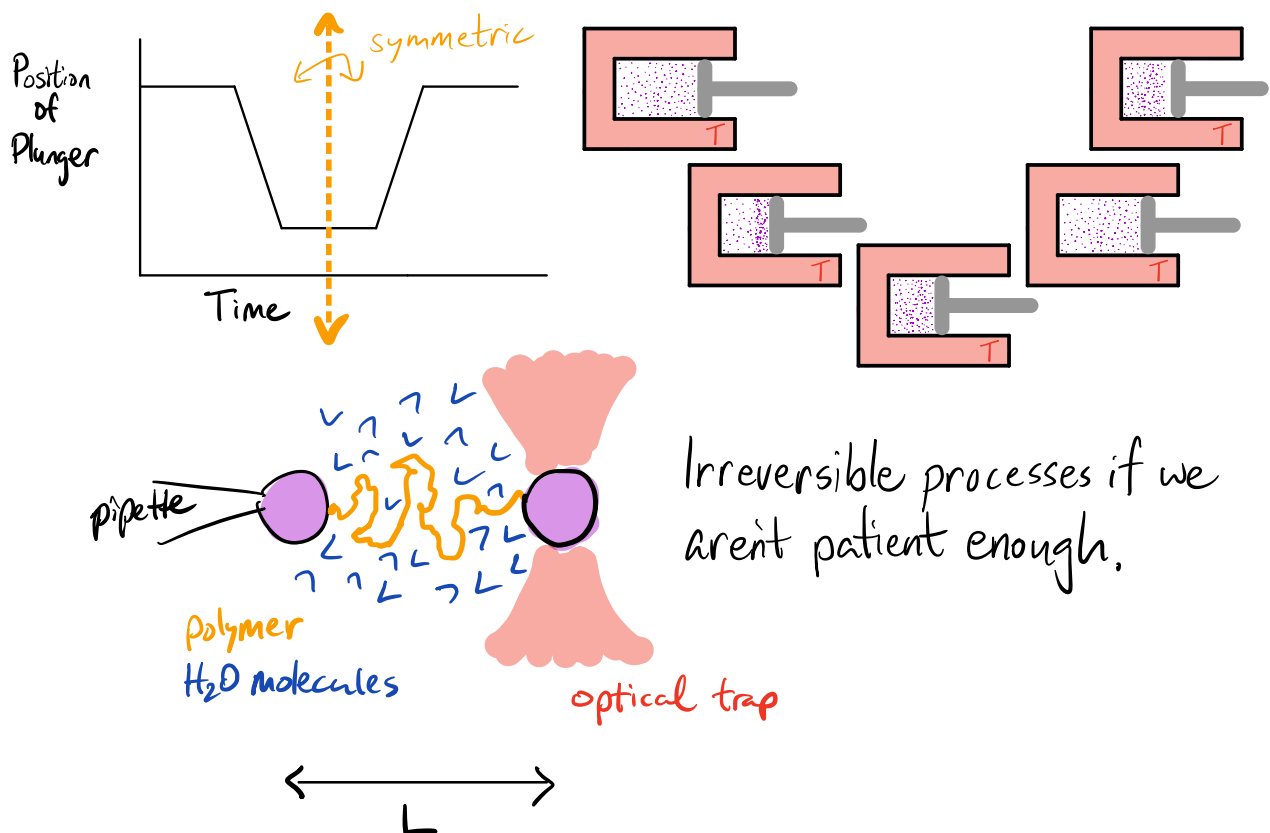
$$\Rightarrow e^{\beta E} = \frac{1-f}{f}$$

$$\Rightarrow \boxed{\frac{E}{k_B T} = \ln \frac{1-f}{f}}$$

Macroscopically, it doesn't matter if we constrain E or instead fix its average value $\langle E \rangle$ by choosing T .

We were after a relationship between T and the fraction of excited spins (an excited spin has $S_i = -1$). NVE and NVT give the same answer!

Up to this point we have been focused on equilibrium statistical mechanics with one exception:



What can I say about this sort of non-equilibrium process, both on macroscopic and microscopic scales?

The easiest thing to talk about is the equilibrium limit.

Pull slowly (reversibly) and measure the work:

$$W = \int_{L_i}^{L_f} dL \cdot F = \int dt F(t) \left(\frac{dL}{dt} \right)$$

pulling rate

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

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

Reversible Work Theorem:

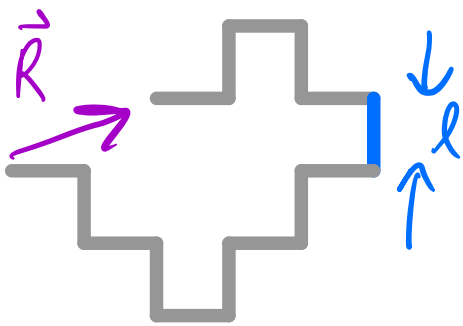
$$\frac{P(L_f)}{P(L_i)} = e^{-\beta W_{\text{rev}}(L_i \rightarrow L_f)} = e^{-\beta [A(L_f) - A(L_i)]}$$

Assume $L_i < L_f$.

$$P(L_f) < P(L_i) \Rightarrow \Delta A > 0.$$

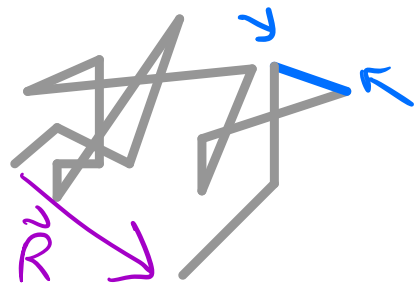
I must do work on the polymer to stretch it from L_i to L_f .

What is the reversible work to unfold a polymer?
model of



lattice
polymer

$$\sqrt{\langle (\vec{R}_i - \vec{R}_{i-1})^2 \rangle} = l$$



Gaussian
polymer

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

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

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

← dimensions

↑
Along 1
dimension

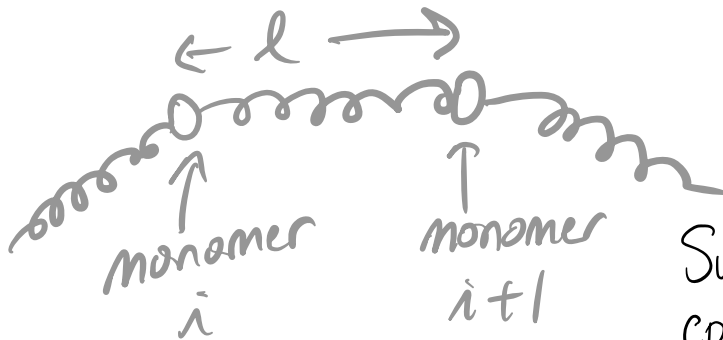
$$P_N(\vec{R}) = \left(\frac{d}{2\pi Nl^2} \right)^{d/2} \exp \left[\frac{-d \cdot R^2}{2Nl^2} \right]$$



That distribution must be Gaussian for large N .

Once you know μ and σ^2 , you can just plug in.

How does l relate to temperature?



Suppose the polymer consists of harmonic springs

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

Spring constant

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

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

$\{\vec{R}\} = (\vec{R}_0, \vec{R}_1, \dots, \vec{R}_N)$
positions of all beads

Energy of polymer

Exactly what you have studied on your homework except with $\beta k = \frac{d}{2l^2}$!

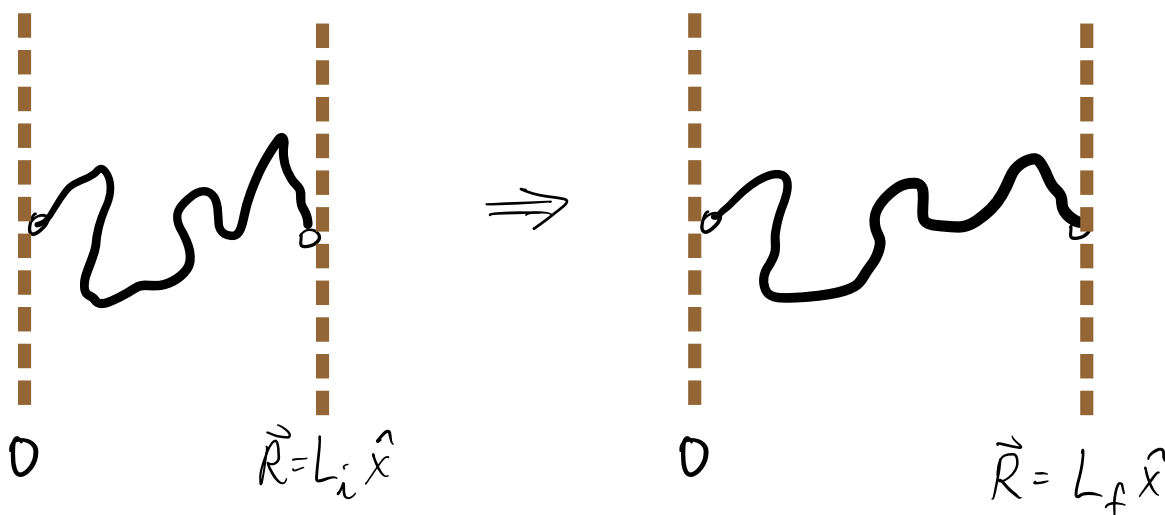
So the thermal polymer with N segments, spring constant k , and inverse temperature β will have an end-to-end vector which samples from the Gaussian distribution:

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

⇓

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

Plugging into the reversible work theorem...



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

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

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

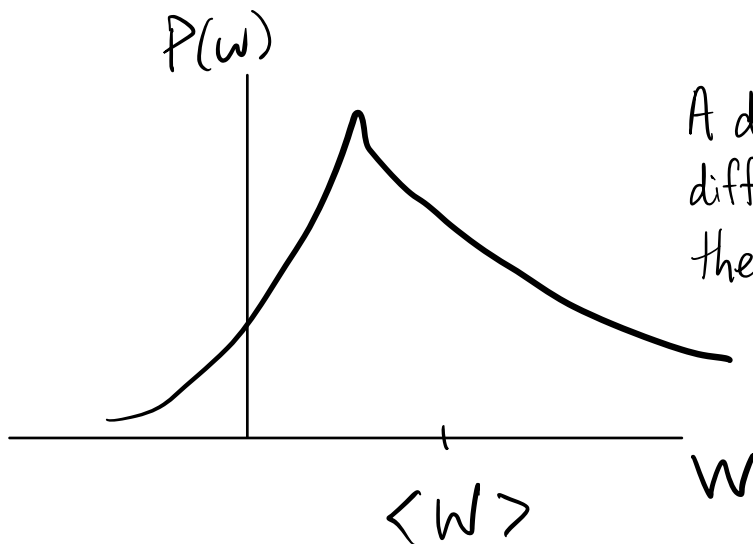
Or put another way, starting from $L_i = 0$, the reversible work to stretch the polymer L is:

$$W_{\text{rev}}(L) = \frac{kL^2}{2N}$$

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

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

TRICK QUESTION



A distribution of work for different realizations of the experiment.

Usually $W > W_{rev}$, but not *always* true. It depends on the trajectory's particular fluctuations,

on average \rightarrow

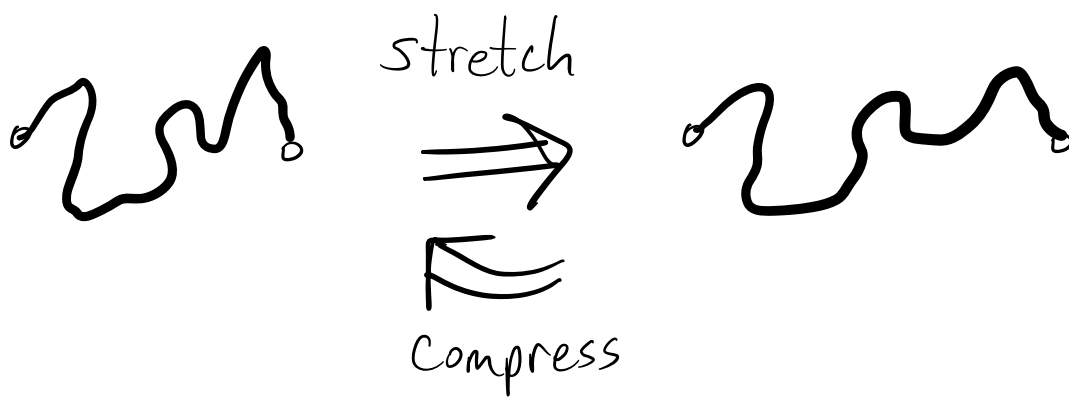
If I pull quickly, how much work do I do?

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

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

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.

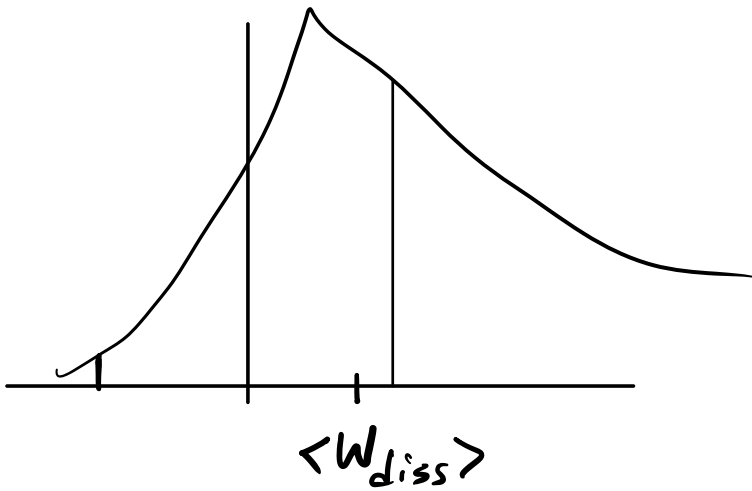


$$\text{Now } \Delta A = 0$$

$$\Rightarrow W_{\text{diss}} = 0$$

(We end up at the same
L we started at)

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



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

Crooks Fluctuation
Theorem