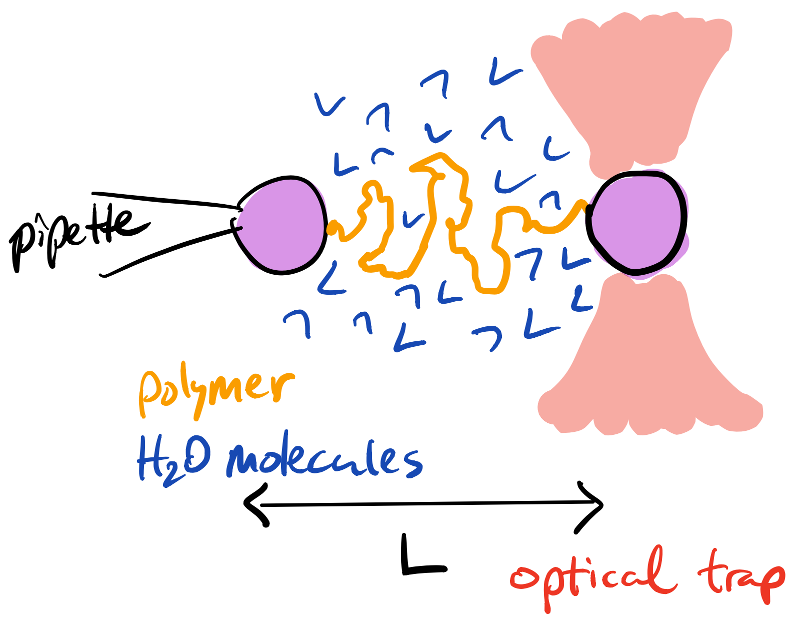
Lecture 13

Recall from last lecture/homework...



My microstates ν are given by the polymer configurations

$$\nu = (L, \{i\})$$

end-to-end distance — everything else

$$P(\nu) = \frac{e^{-\beta E(\nu)}}{Q}$$

(β from H_2O molecules)

What is $P(L)$? (Free polymer at this point — free to fluctuate that is)

We started a calculation to show that

$$P(L) \propto e^{-\beta A(L)}$$

Let's (re)start with $P(L)$ as a marginal over microstates...

$$P(L) \propto \sum_{\{i\}} e^{-\beta E(L,\{i\})}$$

Marginalize (average) over degrees of freedom I'm not measuring

$$\Rightarrow \ln P(L) = \ln(\text{const.}) + \ln\left(\sum_{\{i\}} e^{-\beta E(L,\{i\})}\right)$$

$$\Rightarrow \frac{\partial \ln P(L)}{\partial L} = \frac{\beta \sum_{\{i\}} \left(-\frac{dE(L,\{i\})}{dL}\right) e^{-\beta E(L,\{i\})}}{\sum_{\{i\}} e^{-\beta E(L,\{i\})}}$$

The statistical weight for microstate $\{i\}$ when L is fixed

Therefore

$$\frac{d\ln P(L)}{dL} = \beta \left\langle \frac{-dE(L,\{i\})}{dL} \right\rangle_{\{i\}}$$

Averaging over all possible polymers with length L

$$= \beta \left(\begin{matrix} \text{mean force } \underline{\text{by polymer}} \\ \text{on coordinate } L \end{matrix} \right)$$

$$= -\beta \left(\begin{matrix} \text{mean force applied to} \\ \text{the polymer to fix } L \end{matrix} \right)$$

$$\int_{L_i}^{L_f} dL \, \frac{d \ln P(L)}{dL} = -\beta \int_{L_i}^{L_f} dL \left(\begin{matrix} \text{mean force applied to} \\ \text{the polymer to fix } L \end{matrix} \right)$$

$$\ln P(L_f) - \ln P(L_i) = \beta \int_{L_i}^{L_f} \underbrace{dL}_{\text{distance}} \underbrace{\left\langle - \frac{dE(L, \{i\})}{dL} \right\rangle_{\{i\}}}_{\text{mean force}}$$

$$= -\beta W_{rev}(L_i \to L_f)$$

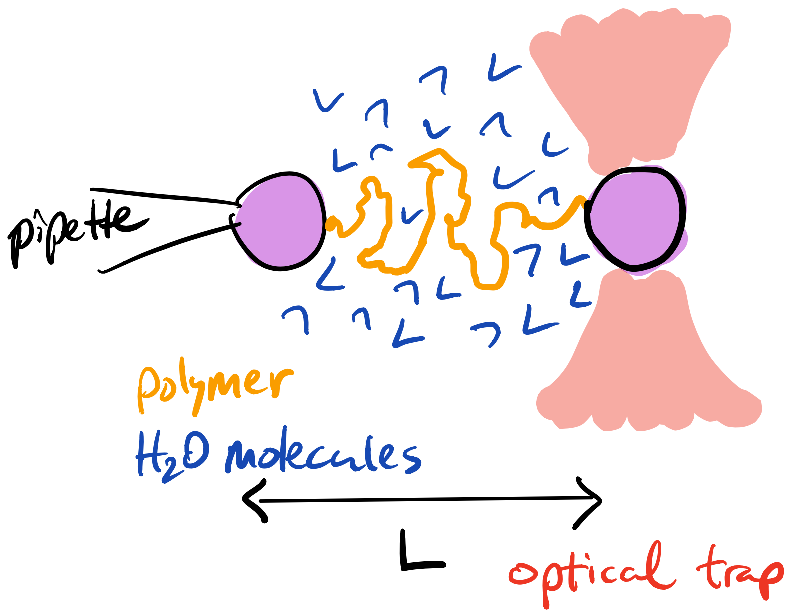
Reversible Work Theorem:

$$\frac{P(L_f)}{P(L_i)} = e^{-\beta W_{rev}(L_i \to L_f)}$$

$$= e^{-\beta [A(L_f) - A(L_i)]}$$

Remember $\ln Q = -\beta A$, so we could also have seen this as

$$\frac{P(L_f)}{P(L_i)} = \underbrace{\frac{Q(L_f)}{Q(L_i)}}_{\substack{\text{ratio of} \\ \text{partition functions}}} = \frac{e^{-\beta A(L_f)}}{e^{-\beta A(L_i)}} = e^{-\beta W_{rev}(L_i \to L_f)}$$



Springs - Hookean connecting beads of a polymer

$$\int dt\, F(t) \underbrace{\left(\frac{dL}{dt}\right)}_{\text{pulling rate}} = \text{Work}$$

What is $W_{rev}(0 \to L)$?

Prob. dist. for free polymer

$$W_{rev}(L_i \to L_f) = k_B T \ln \frac{P(L_i)}{P(L_f)}$$

When the springs connecting beads of the polymer are linear (Hooke's Law), the energy is quadratic, so $e^{-\beta E}$ is a (high-dimensional) Gaussian

$$P(\vec{R}_0, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N) \propto e^{-\frac{\beta k}{2} \sum_{i=1}^{N} |\vec{R}_i - \vec{R}_{i-1}|^2}$$

free polymer prob. dist.

"Integrate out" coordinates we won't measure

$$P(\vec{R}_N - \vec{R}_0)$$

This gave us this

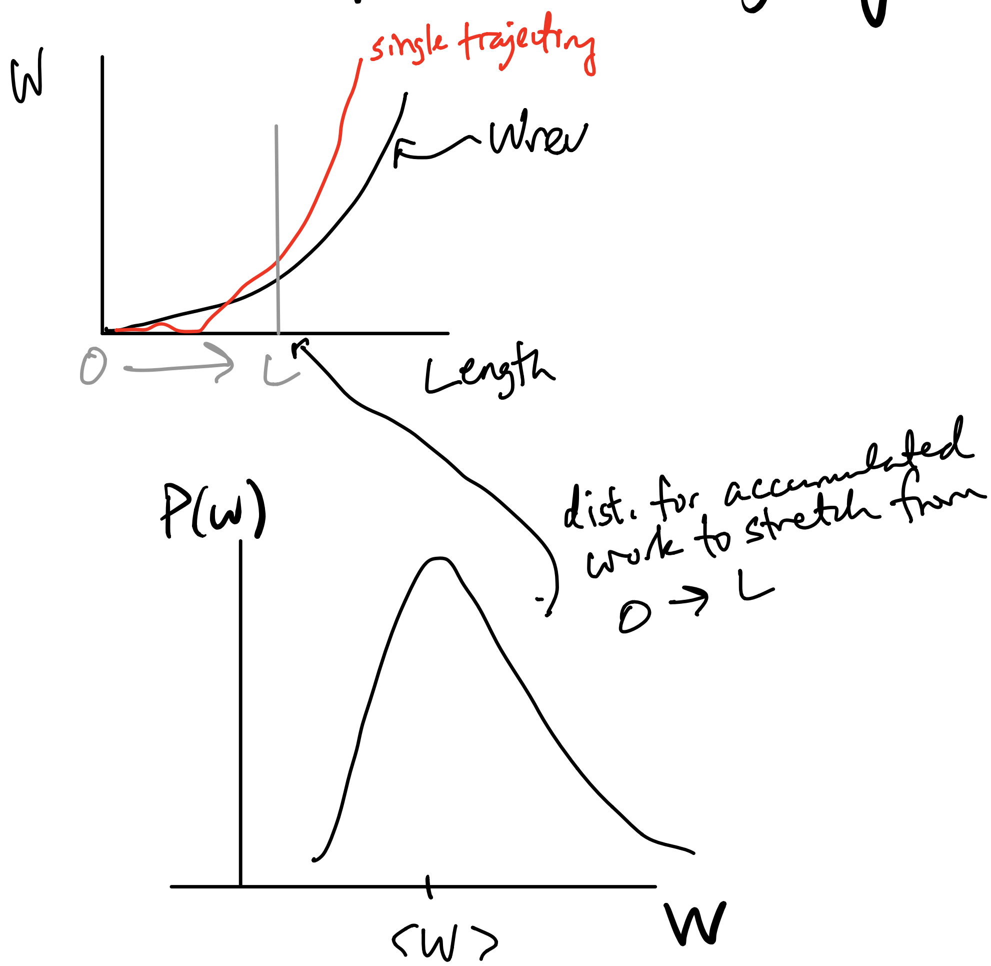
So we could explicitly find

$$W_{rev}(L_i \to L_f) = k_B T \ln \frac{P(L_i)}{P(L_f)}$$

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

Usually $W > W_{rev}$, but not *always* true.

It can depend on the trajectory!



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

$\langle W \rangle > W_{rev}$

The 2nd law holds on average!