Lecture 8

Recall from last lecture...

(I) What is partition-y about a partition function?

$$\frac{P(A)}{P(B)} = \frac{\frac{Q_A}{\cancel{Q}}}{\frac{Q_B}{\cancel{Q}}} = \frac{Q_A}{Q_B}$$

The ratio of partition functions tells how probability partitions between two options.

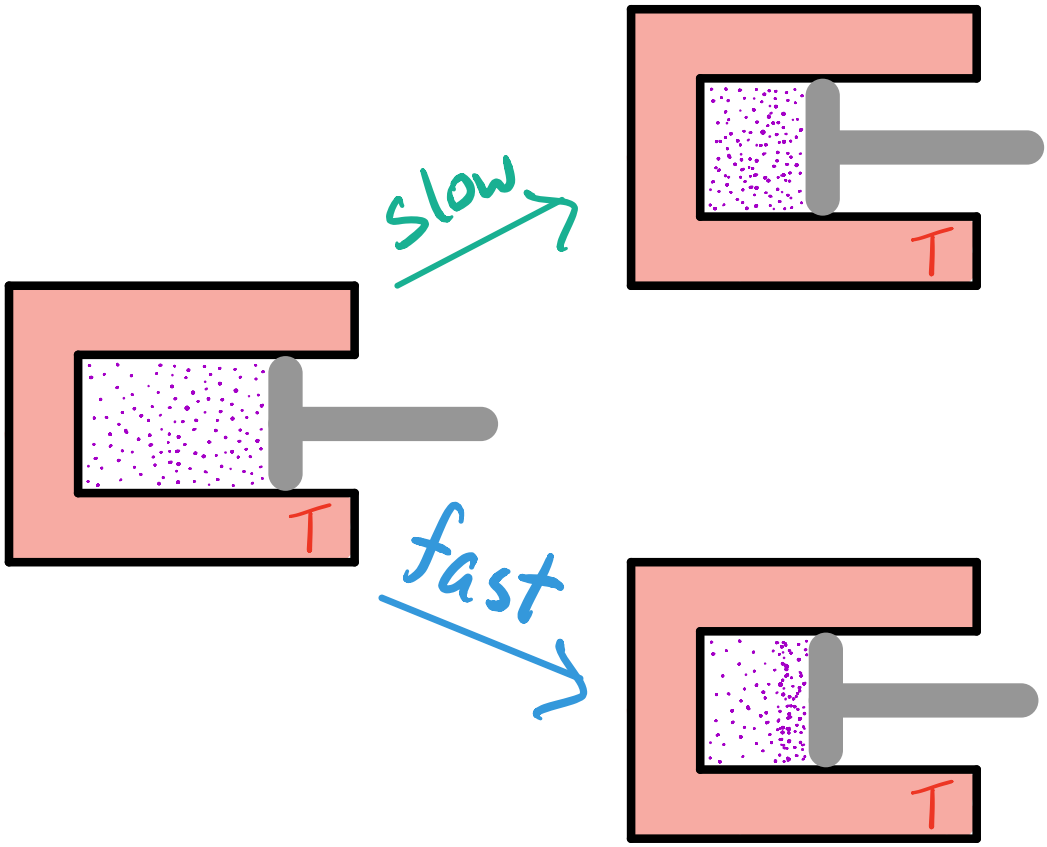
(II) What is free about a free energy?

$$dE = TdS - pdV + \mu dN$$

$\mu dN \to 0$

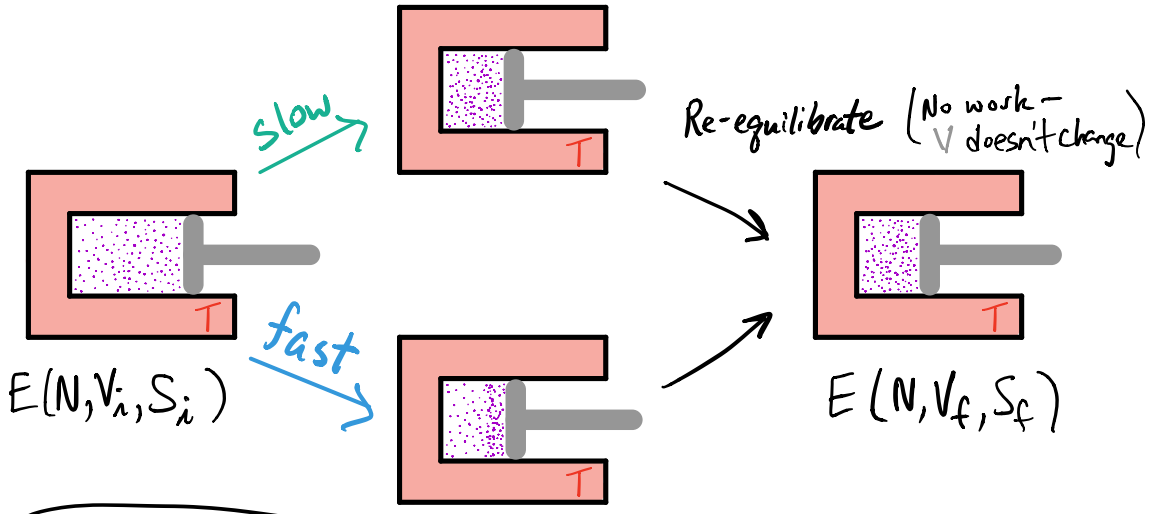
Work: Change in energy due to variables I manipulate

Heat: Change in energy due to flows into or out of the thermal bath. We don't get to use these — they're along for the ride.



In the slow process I have to do work to push particles out of the way but I go slowly enough that particles can diffuse out of the way on their own without my pushing.

In the fast process I'm too impatient to let them get out of the way on their own so I have to push harder than I would have in a reversible process.



$$\int_{\text{fast}} dt \, \frac{dE(t)}{dt} = E(N, V_f, T) - E(N, V_i, T)$$

$$\int_{\text{slow}} dt \, \frac{dE(t)}{dt} = E(N, V_f, T) - E(N, V_i, T)$$

shorthand

$$\Rightarrow \int_{\text{fast}} dE = \int_{\text{slow}} dE$$

$$\Rightarrow \int_{\text{fast}} (đQ + đW) = \int_{\text{slow}} (đQ + đW)$$

(Sign convention: Positive W is work done on the system
Positive Q is heat flow into the system)

The fast process effectively pushes against more molecules

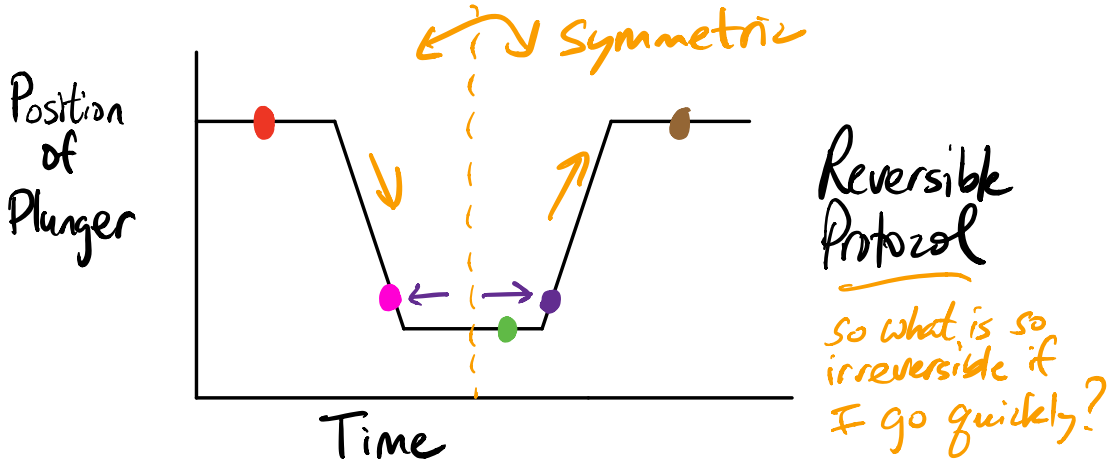
$$\Rightarrow \int_{\text{fast}} đW > \int_{\text{slow}} đW$$

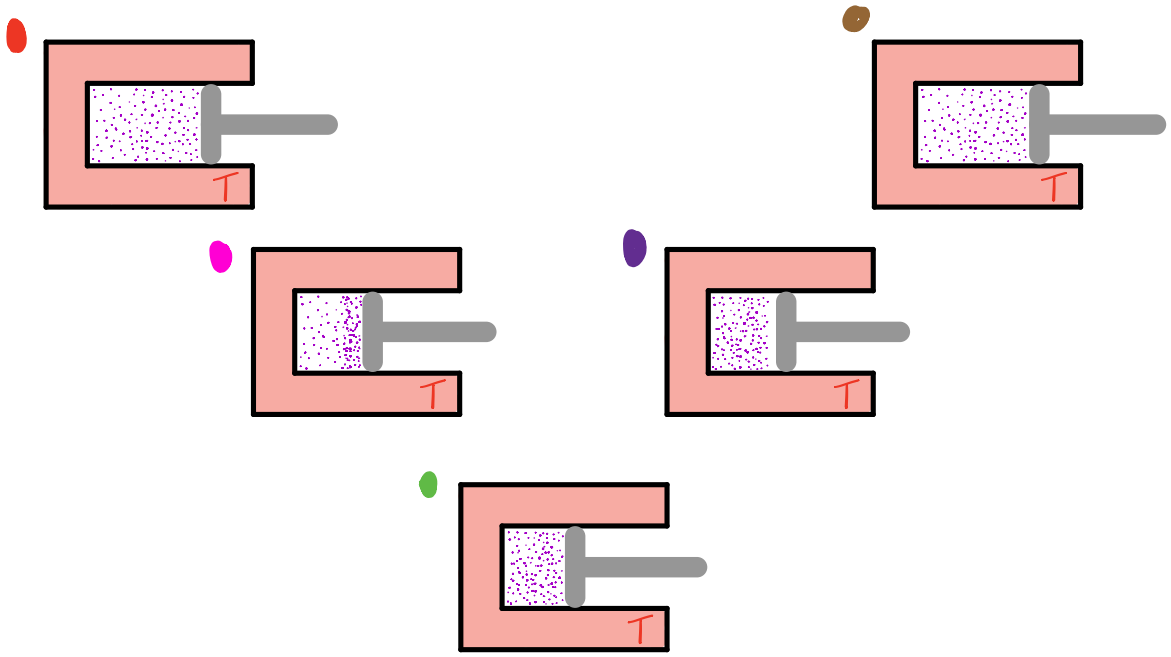
$$\text{Hence} \quad \int_{\text{fast}} đQ < \int_{\text{slow}} đQ \qquad (đQ \text{ is negative})$$

Fast process has MORE heat flow out of the system.

The best we'll ever do is to go slowly (reversibly) so that the gas gets to re-equilibrate before I push any more.

Reversible vs Irreversible...





Visit different microstates unless I go slowly enough to be visiting equilibrium microstates.

$$dW \geq dW_{rev}$$

A reversible transformation requires the least amount of work at fixed T.

If we go reversibly...

$$dW_{rev} = -pdV, \quad \text{so} \quad dE = TdS + dW_{rev}$$

$$\Rightarrow \quad đW_{rev} = dE - TdS$$

$$= d(E-TS)_T \quad \Longleftarrow \text{Fixed } T$$

$$= (dA)_T$$

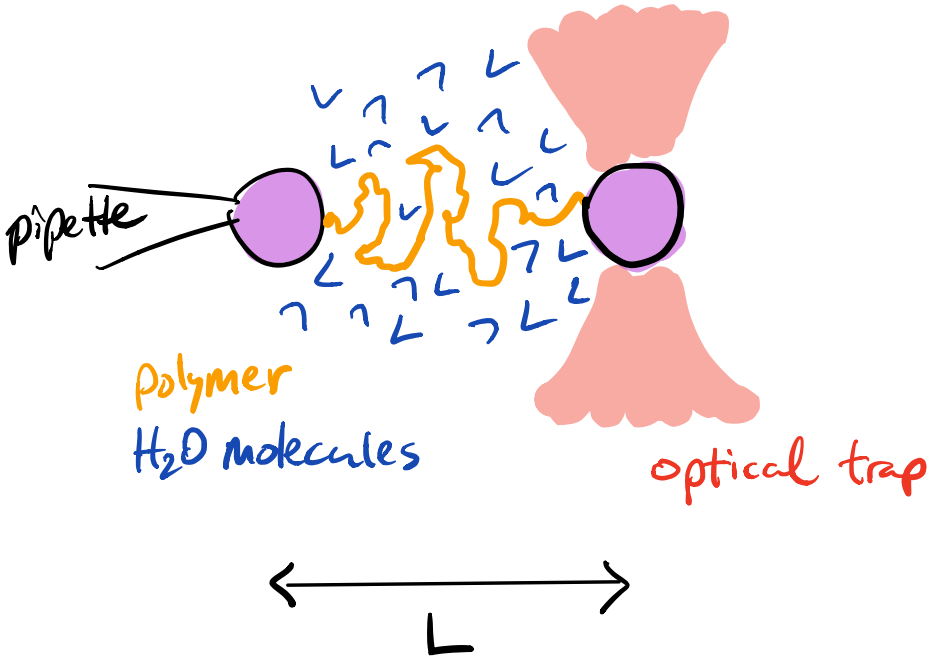
provided I am in contact w/ a fixed T heat bath.

$$\boxed{đW \geq (dA)_T}$$

The most work that can be extracted comes from a reversible transformation, in which case

$$W = \Delta A = A(N, V_f, T) - A(N, V_i, T).$$

These ideas extend beyond gases and pistons. They also apply to microscopic systems...



What am I going to measure? L

What am I not going to measure? ...

Interior monomers of the polymer

H_2O molecules (Both) ⇒ Contribute $\alpha\beta$

My microstates ν are given by the polymer configurations

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

L: end-to-end distance; $\{i\}$: 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)

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

$\{i\}$: Marginalize over degrees of freedom I'm not measuring provided the end-to-end distance is L.

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

Differentiate wrt L

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

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

Therefore

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

average over all possible $\{i\}$ for the fixed L

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

$$= -\beta \left(\begin{array}{c} \text{mean force applied to} \\ \text{system to fix } L \end{array} \right)$$

Integrate wrt L from some initial L_i to a final L_f ...

$$\ln P(L_f) - \ln P(L_i) = -\beta \int_{L_i}^{L_f} dL \left\langle -\frac{dE(L, \{z_i\})}{dL} \right\rangle_{\{z_i\}}$$

distance — mean force

$$= -\beta W_{rev}$$

Reversible Work Theorem:

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

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

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

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

$$Q(L_f) = \sum_{\{\xi_i\} \text{ w/ } L_f} e^{-\beta E(L_f, \{\xi_i\})}$$