

Lecture 12

Recall from last lecture...

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

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

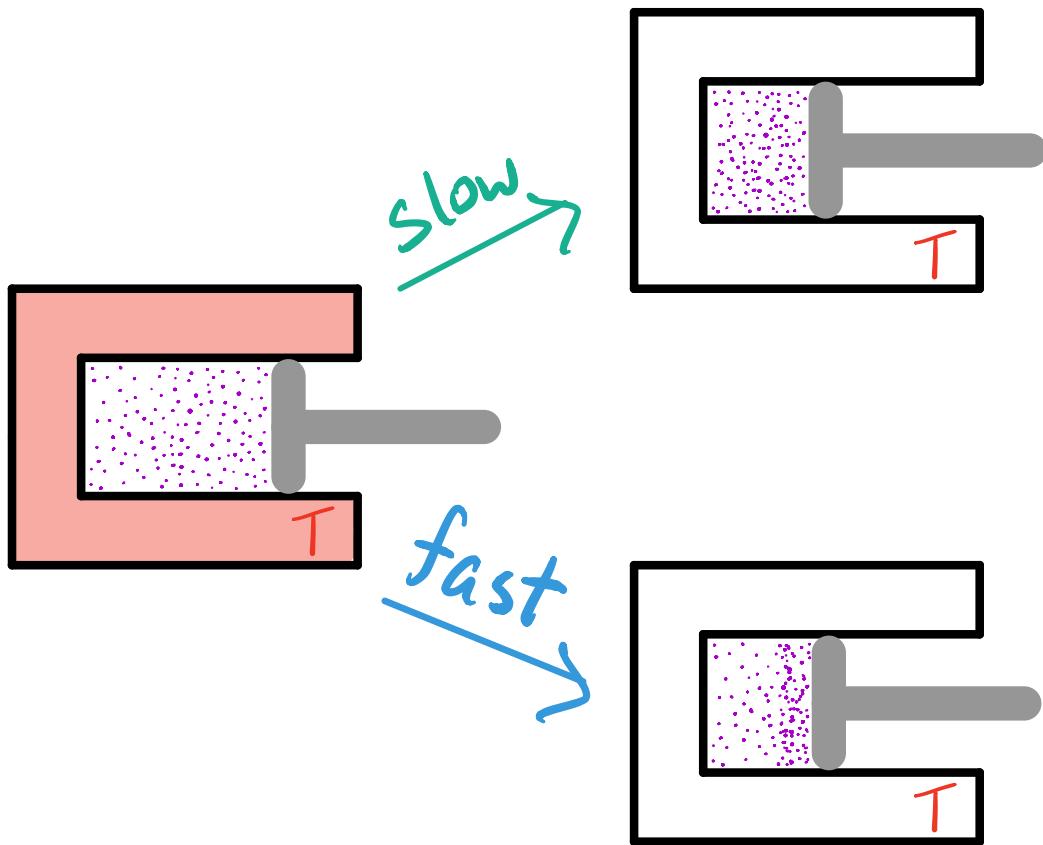
The ratio of partition functions tells how probability partitions between two options.

II) What is free about a free energy?

$$dE = \underbrace{T dS - p dV}_{\text{Work}} + \underbrace{\mu dN}_{\text{Heat}} \rightarrow 0$$

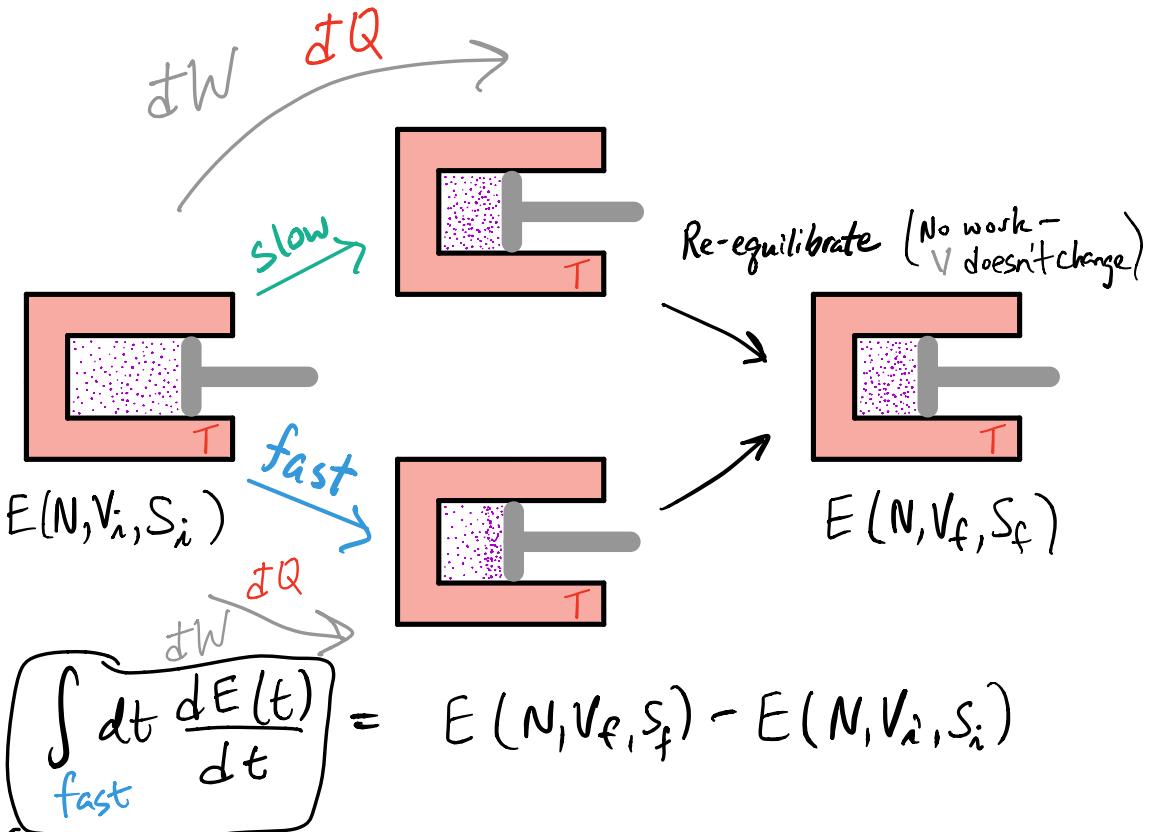
Work: Change in energy due to variables I manipulate

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.



$$\begin{aligned}
& \int_{\text{slow}} dt \frac{dE(t)}{dt} = E(N, V_f, S_f) - E(N, V_i, S_i) \\
& \int_{\text{slow}} dt \frac{dE(t)}{dt} = E(N, V_f, S_f) - E(N, V_i, S_i) \\
& \xrightarrow{\text{Shorthand}} \int_{\text{fast}} dE = \int_{\text{slow}} dE \\
& \Rightarrow \int_{\text{fast}} (\delta Q + \delta W) = \int_{\text{slow}} (\delta Q + \delta W)
\end{aligned}$$

(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

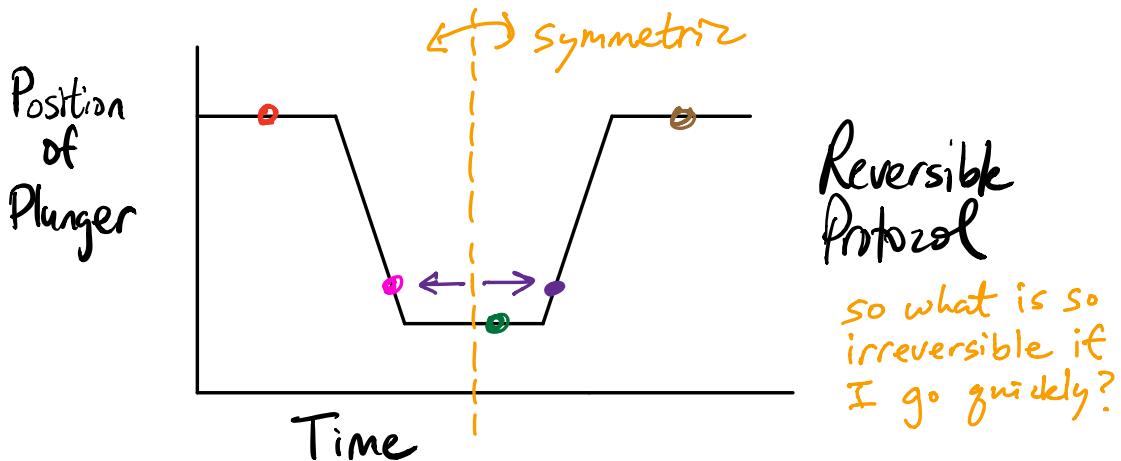
$$\Rightarrow \int_{\text{fast}} \delta W > \int_{\text{slow}} \delta W$$

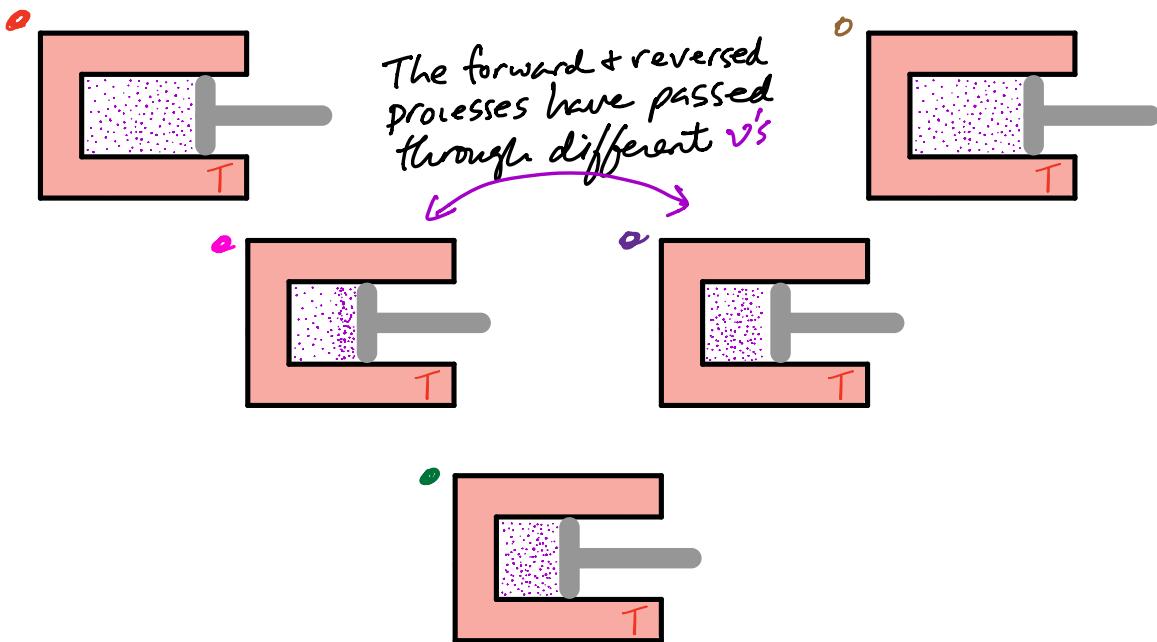
Hence $\int_{\text{fast}} \delta Q < \int_{\text{slow}} \delta Q$
(δQ is negative)

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...





I visit different microstates unless I go slowly enough to visit equilibrium microstates in each direction

$$\delta W \geq \delta W_{rev}$$

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

If we go reversibly...

$$\delta W_{rev} = -pdV, \text{ so } dE = TdS + \delta W_{rev}$$

$$\Rightarrow dW_{rev} = dE - TdS$$

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

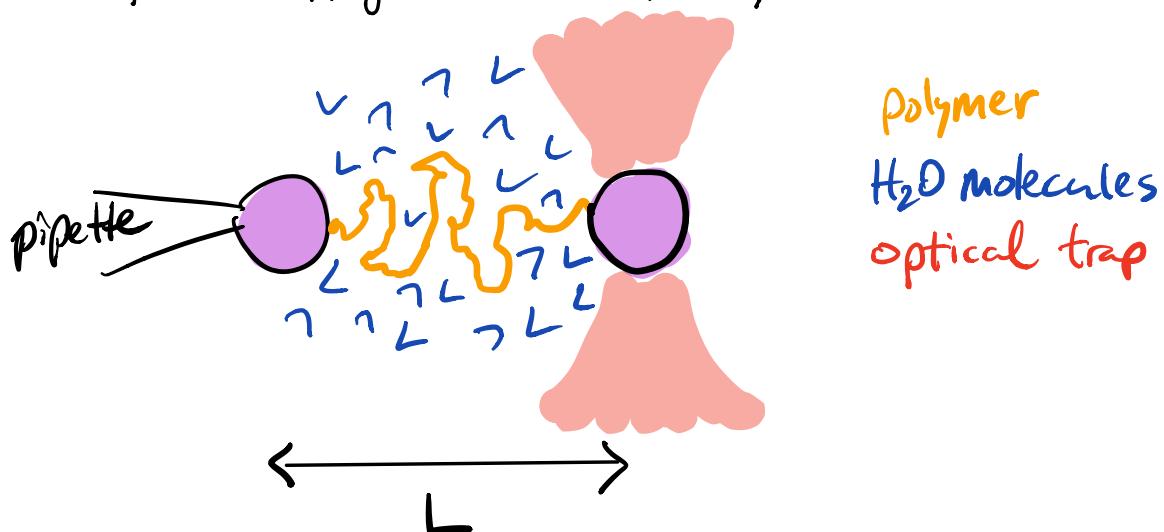
$$= (dA) \Big|_T \quad \begin{matrix} \text{provided I am in} \\ \text{contact w/ a fixed } T \\ \text{heat bath} \end{matrix}$$

$$dW \geq (dA) \Big|_T$$

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 gasses and pistons.
They also apply to microscopic systems...



What am I going to measure? L

What am I not going to measure?

H_2O molecules (Bath) Interior monomers of the polymer

My microstates ν are given by the polymer configurations

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

\uparrow \curvearrowright
end-to-end distance everything else

$$P(\nu) = \frac{e^{-\beta E(\nu)}}{Q} \quad (\beta \text{ from } H_2O \text{ molecules})$$

What is $P(L)$? $\left(\begin{array}{l} \text{Free polymer at this point -} \\ \text{free to fluctuate that is} \end{array} \right)$

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

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

$$\Rightarrow \ln P(L) = \ln(\text{const.}) + \ln \left(\sum_i e^{-\beta E(L, \xi_i^3)} \right)$$

Differentiate wrt L

$$\frac{d \ln P(L)}{dL} = \frac{\beta \sum_i \left(-\frac{dE(L, \xi_i^3)}{dL} \right) e^{-\beta E(L, \xi_i^3)}}{\sum_i e^{-\beta E(L, \xi_i^3)}}$$

The statistical weight for microstate ξ_i^3
when L is fixed.

Therefore

$$\frac{d \ln P(L)}{dL} = \beta \left\langle -\frac{dE(L, \xi_i^3)}{dL} \right\rangle_{\xi_i^3}$$

average over
all possible
 ξ_i^3

$$= \beta \left(\begin{array}{l} \text{mean force by polymer} \\ \text{on coordinate } L \end{array} \right) = -\beta \left(\begin{array}{l} \text{mean force applied to} \\ \text{system to fix } L \end{array} \right)$$