Lecture 12

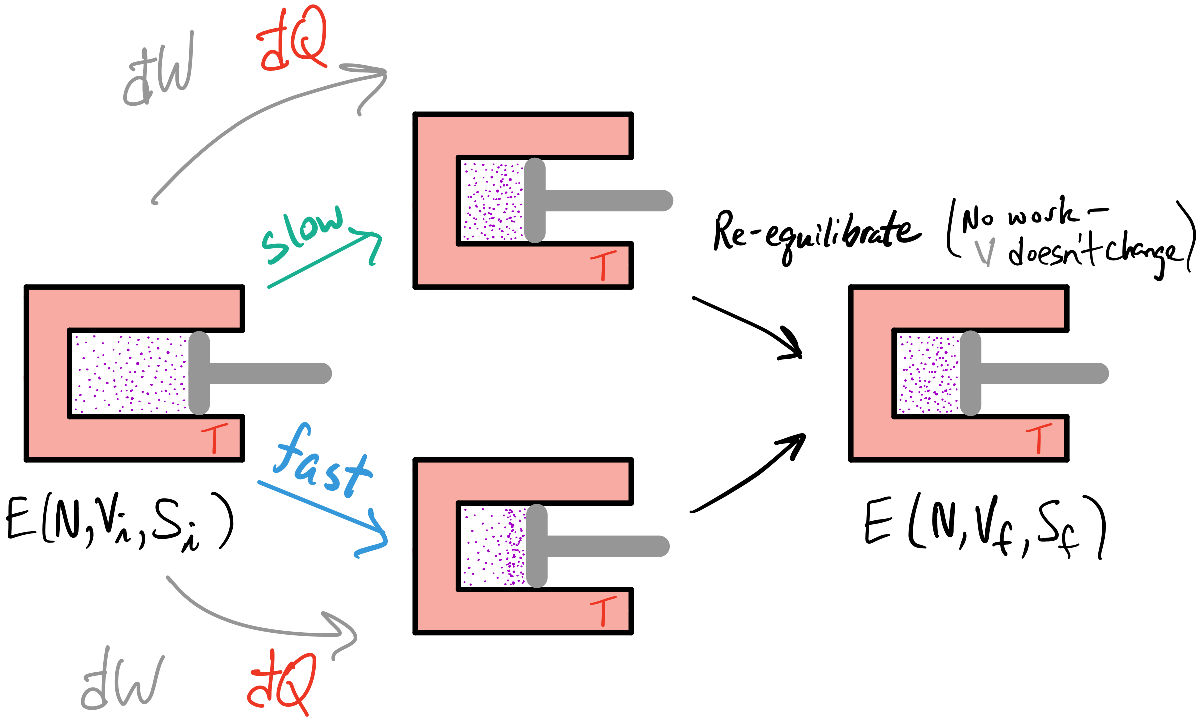
Recall from last lecture...

(II) What is free about a free energy?

$$dE = \underline{T\,dS} - \underline{p\,dV} + \overset{\nearrow 0}{\boxed{\mu\,dN}}$$

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.



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

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

shorthand

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

$$\Rightarrow \quad \int_{\text{fast}} (\text{đ}Q + \text{đ}W) = \int_{\text{slow}} (\text{đ}Q + \text{đ}W)$$

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

The fast process effectively pushes against more molecules

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

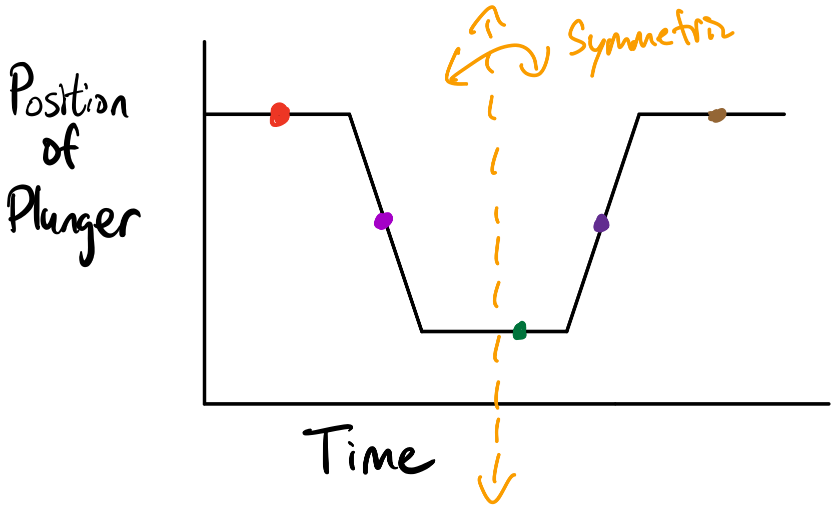
Hence $$\int_{\text{fast}} đQ < \int_{\text{slow}} đQ$$

(đQ is negative)

Fast process has MORE heat flow out of the system.

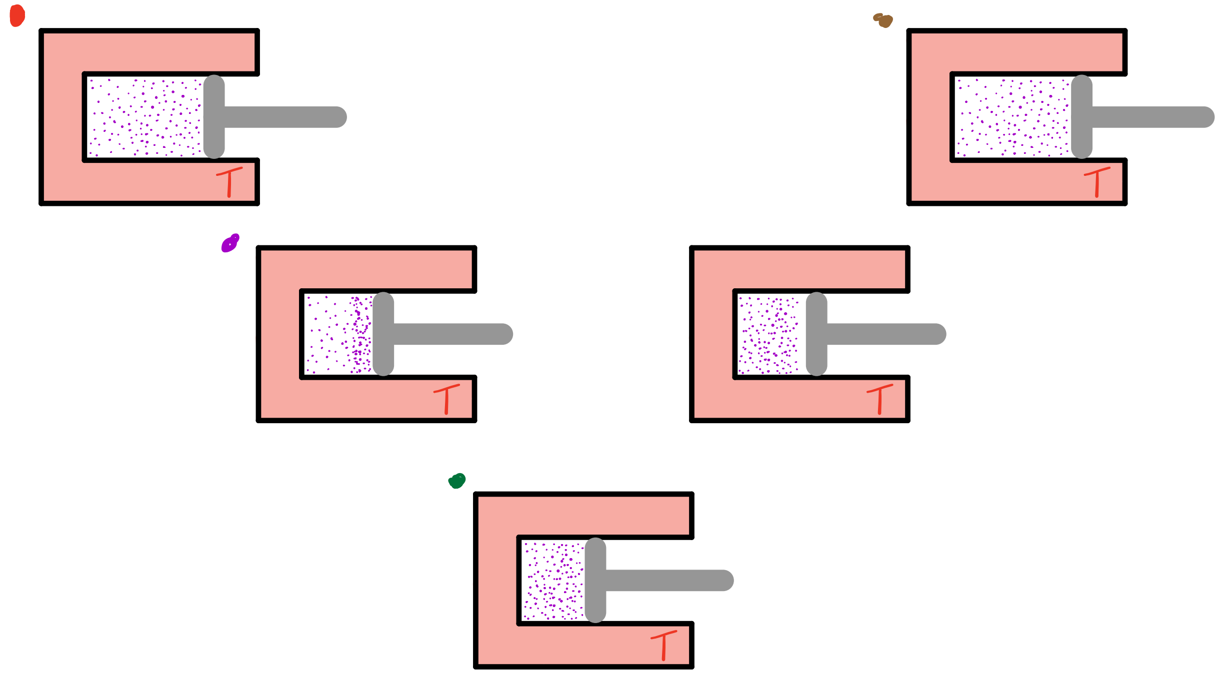
The best we'll ever do is to go slowly (reversibly) so that the gas gets to re-equilibrate before I push any more.

Reversible vs Irreversible...



Reversible Protocol

So what is irreversible if I go quickly?



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

$$\boxed{đW \geq đW_{rev}}$$

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

If we go reversibly...

$đW_{rev} = -p\,dV$, so $dE = T\,dS + đW_{rev}$

$$\Rightarrow \quad đW_{rev} = dE - T\,dS$$

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

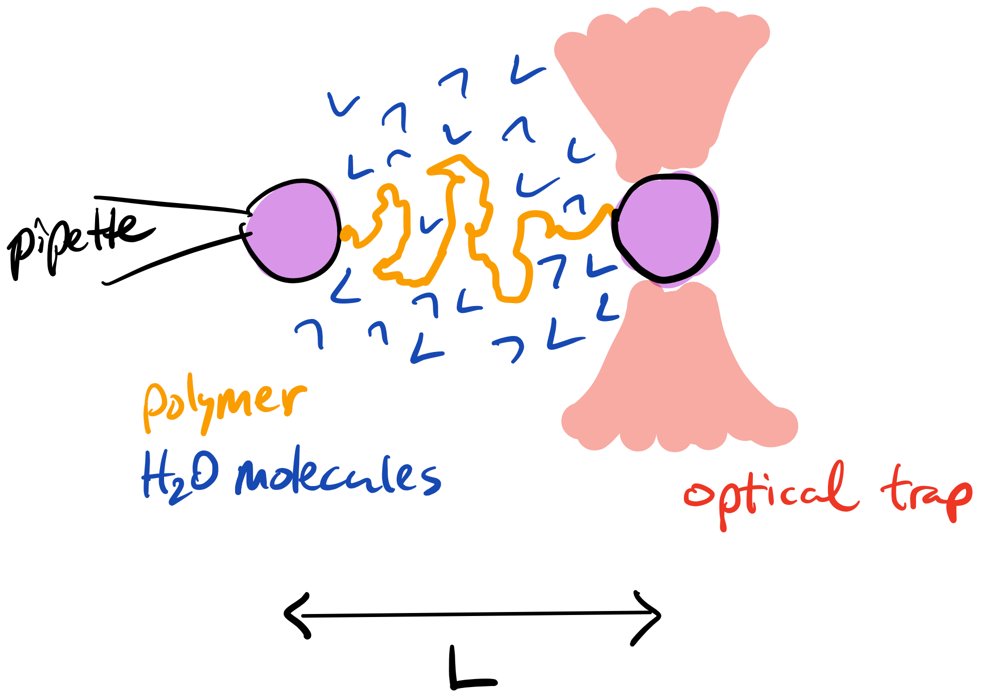
$$= (dA)_T \Longleftarrow \text{provided I am in contact w/ a fixed } T \text{ temp. bath}$$

$$\boxed{đW \geq (dA)_T}$$

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 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

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

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)

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

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

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

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

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

$$P(\{i\} \mid \text{fixed } L) = \frac{e^{-\beta E(L,\{i\})}}{\sum_{\{i\}} e^{-\beta E(L,\{i\})}}$$

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

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

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

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

$$\Rightarrow \quad \ln P(L_f) - \ln P(L_i) = -\beta W_{rev}$$

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

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