Lecture 7
Recall from last lecture...

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

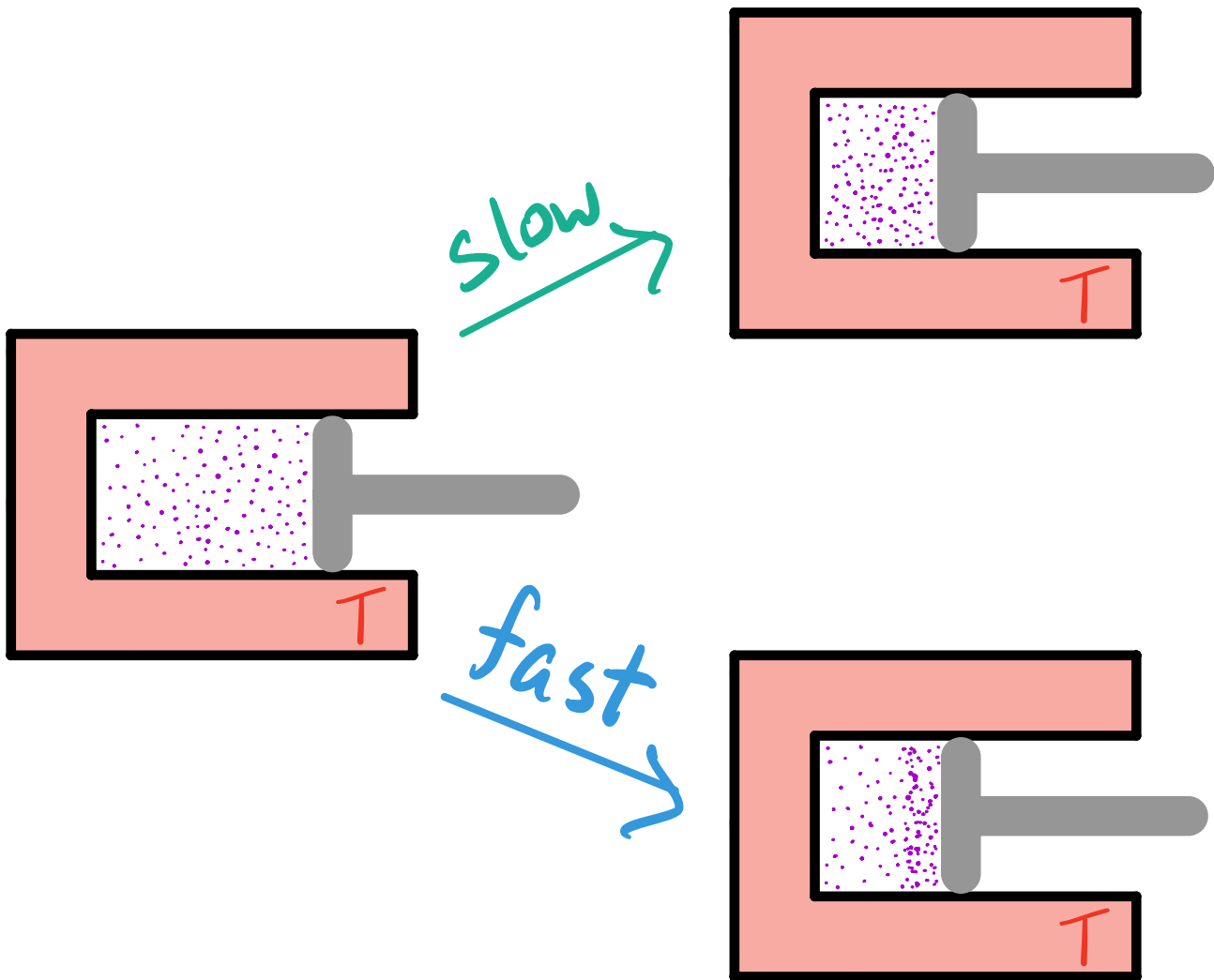$$\frac{P(A)}{P(B)} = \frac{\dfrac{Q_A}{Q}}{\dfrac{Q_B}{Q}} = \frac{Q_A}{Q_B}$$

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

(II) What is free about free energy?
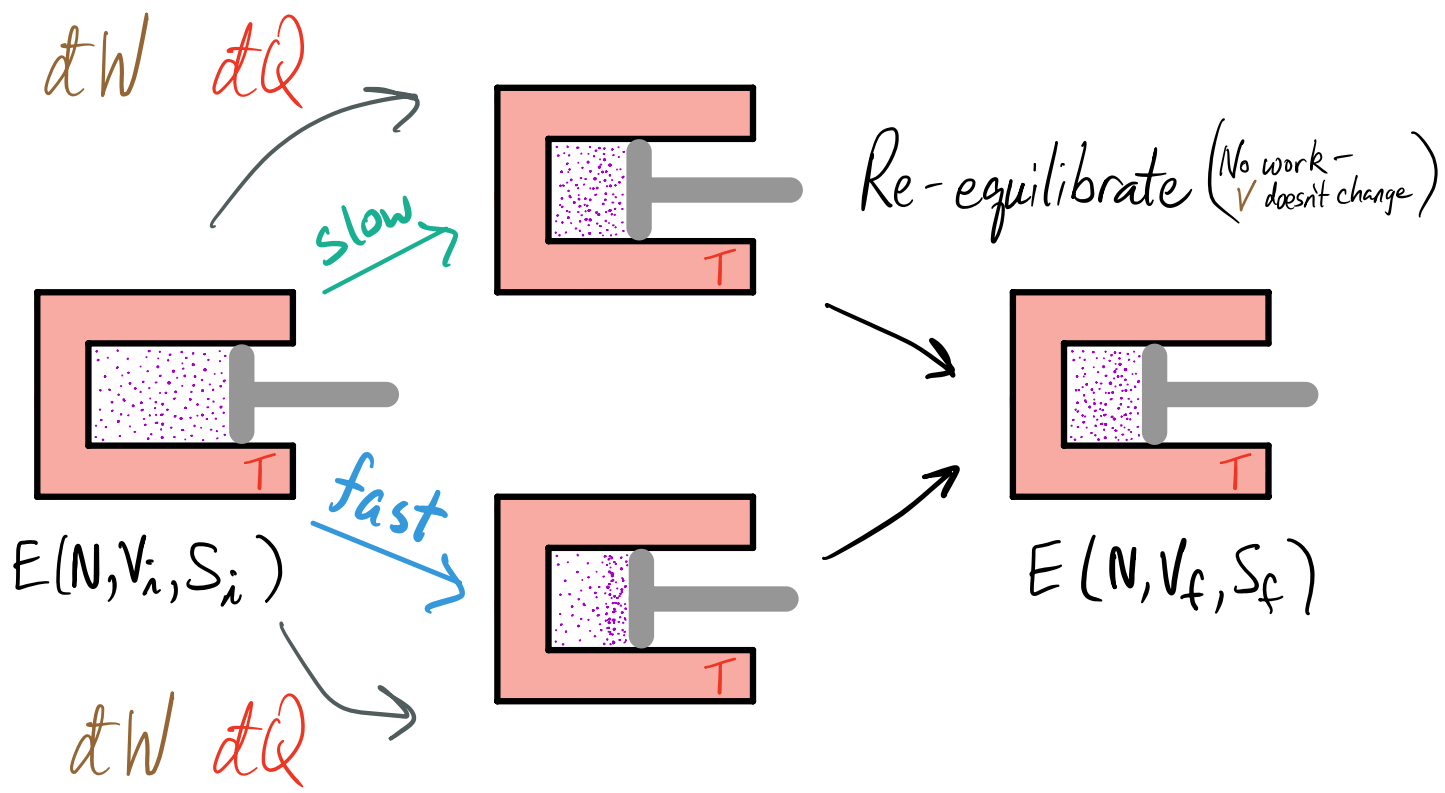
$$dE = TdS - pdV + \mu dN^{\nearrow 0}$$

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 flows — 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.

$$\text{đW} \quad \text{đQ}$$

slow

Re-equilibrate $\left(\begin{smallmatrix} \text{No work} - \\ \text{V doesn't change} \end{smallmatrix}\right)$

fast

$$E(N, V_i, S_i)$$

$$\text{đW} \quad \text{đQ}$$

$$E(N, V_f, S_f)$$

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

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

shorthand

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

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

$\left(\begin{smallmatrix} \text{Sign convention: Positive W is work done } \underline{on} \text{ the system} \\ \text{Positive Q is heat flow into the system} \end{smallmatrix}\right)$

The fast process effectively pushes against more molecules.

$$\Rightarrow \int_{fast} \bar{d}W \; > \; \int_{slow} \bar{d}W$$

Hence $$\int_{fast} \bar{d}Q \; < \; \int_{slow} \bar{d}Q$$

The 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...

symmetric

Position of Plunger

Time

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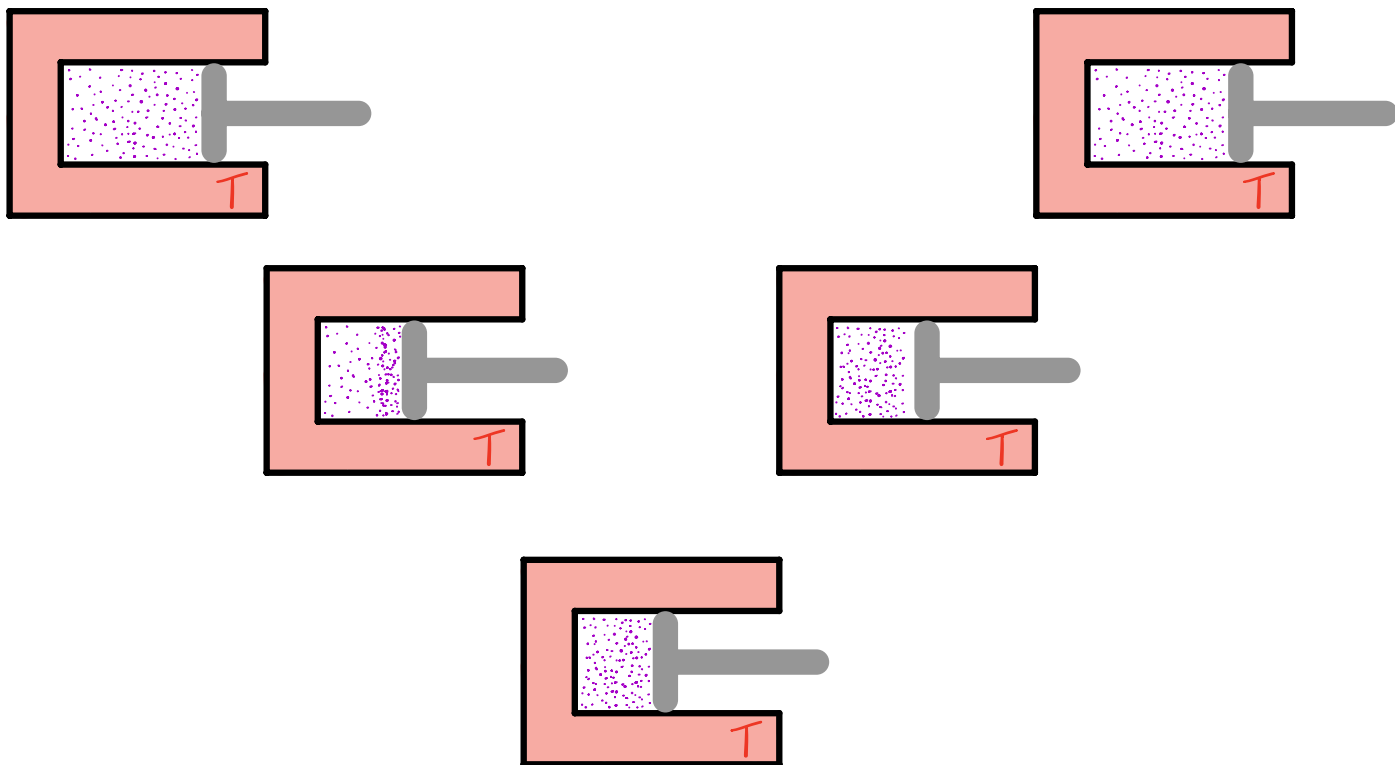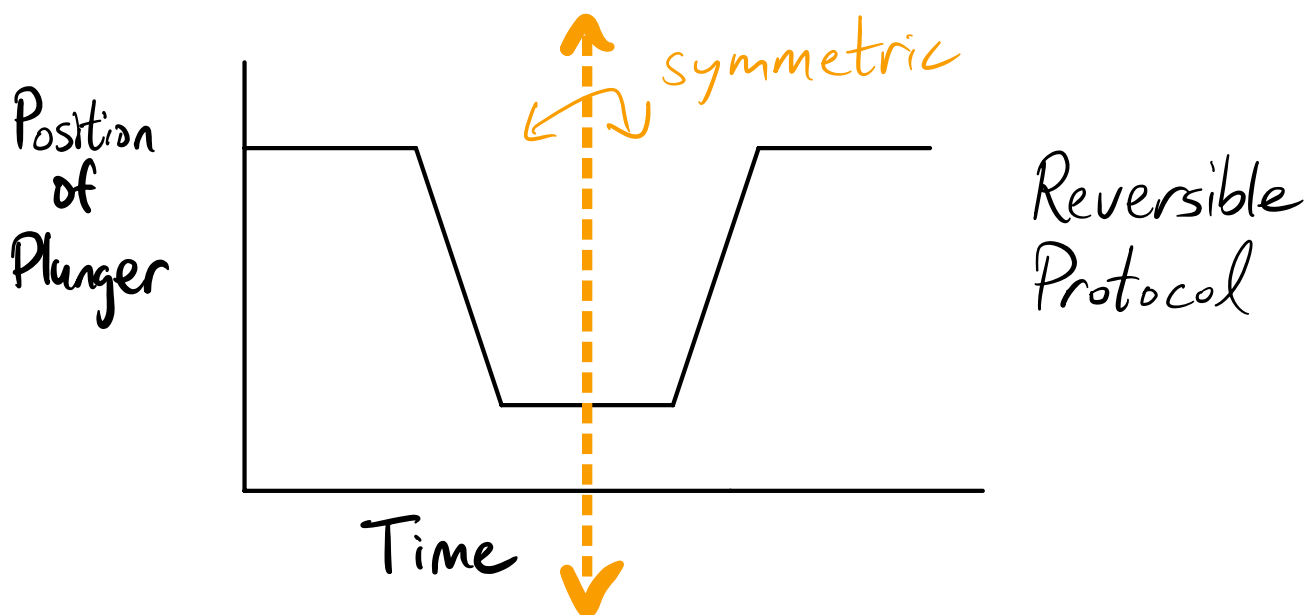
I visit different microstates unless I go slowly enough to visit equilibrium microstates in each direction

$$\boxed{dW \geq dW_{rev}}$$

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

In that reversible case...

$$dW_{rev} = -p\,dV, \quad \text{so}$$

$$dE = T\,dS - p\,dV$$

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

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

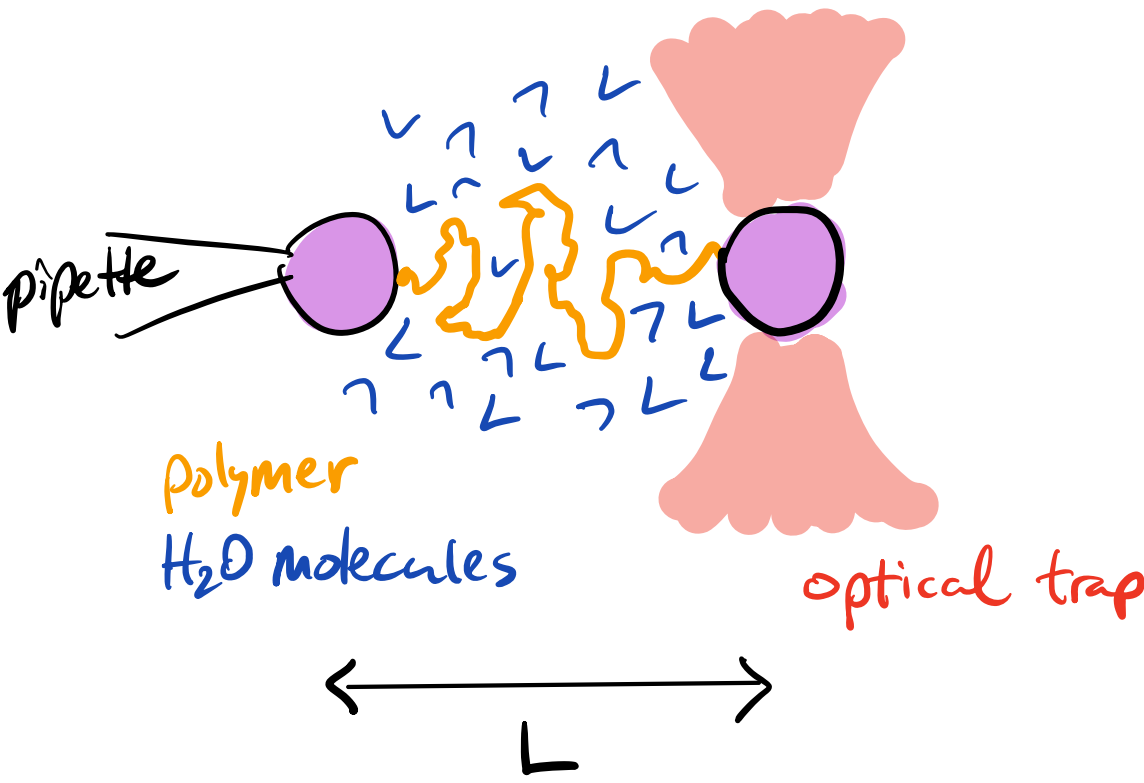$$= (dA)_T \quad \longleftarrow \text{Provided I am in contact w/ a fixed T temperature bath.}$$

$$\bar{d}W \geq (dA)_T$$

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 are now the knobs I'm actually directly controlling.

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

pipette

Polymer

H_2O molecules

optical trap

L

What am I going to measure? L

What am I not going to measure? H$_2$O molecules

interior monomers

My microstates ν are given by the polymer configurations

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

end-to-end distance ↑

everything else describing the polymer

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

(β from H$_2$O 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

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

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

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

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

Therefore

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

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

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

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

$$\ln P(L_f) - \ln P(L_i)$$

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

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

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

Spontaneous fluctuations
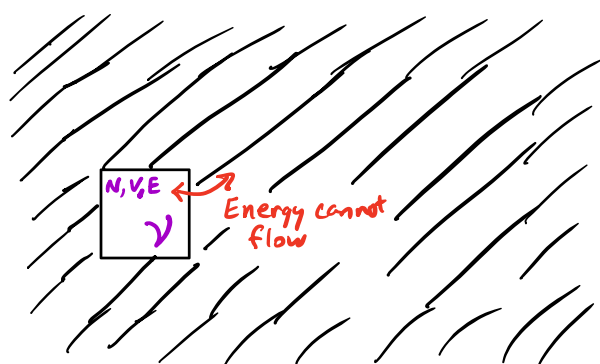
Doing work to stretch the polymer

How would I actually compute a change in entropy?
Will I really count the number of microstates?

$$S_f - S_i = - \frac{A_f - A_i - \langle E \rangle_f + \langle E \rangle_i}{T}$$

$$= \frac{-k_B T \ln \frac{P(L_f)}{P(L_i)} - \langle E \rangle_f + \langle E \rangle_i}{T}$$
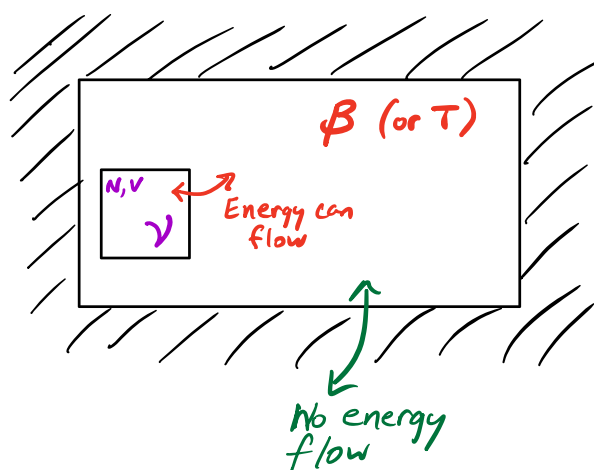
Ensembles or how do I replace a rigid constraint by a "softened" exponential bias?

Prob. distr. for ν

Microcanonical	Canonical

Microcanonical: box labeled N,V,E with ν, "Energy cannot flow"

Canonical: box labeled N,V with ν, "Energy can flow", β (or T), "No energy flow"

What is held fixed?

N, V, E $\qquad$ N, V, T

$P(\nu)$?

$$P(\nu) \propto \begin{cases} 1, & \text{Rigid constraints are met} \\ 0, & \text{Otherwise} \end{cases}$$

$$P(\nu) \propto \begin{cases} e^{-\beta E(\nu)}, & \text{Rigid constraints are met} \\ 0, & \text{Otherwise} \end{cases}$$

Partition Function? (Normalization)

$$\Omega(N,V,E) = \sum_{\substack{\nu \text{ meeting} \\ \text{rigid constraints}}} 1 \qquad Q(N,V,T) = \sum_{\substack{\nu \text{ meeting} \\ \text{rigid constraints}}} e^{-\beta E(\nu)}$$
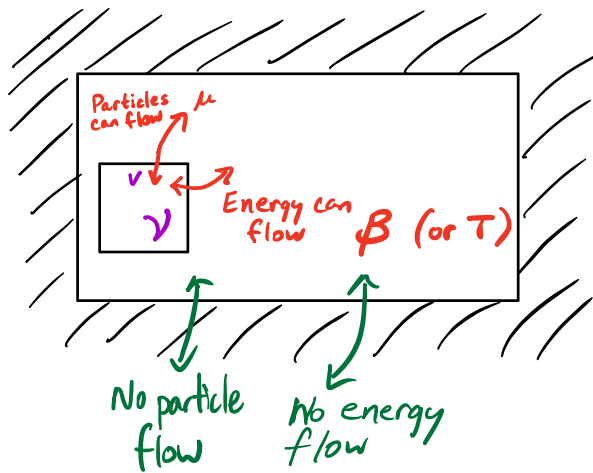
Thermodynamic Potential? (Effective Energy)

$$S(N,V,E) = k_B \ln \Omega(N,V,E) \qquad A(N,V,T) = -k_B T \ln Q(N,V,T)$$

$$Q(N,V,T) \approx e^{-\beta(E^* - TS(N,V,E^*))} = e^{-\beta A(N,V,T)}$$

↑
thermodynamic limit
(large system)

What if particles can fluctuate too?

Grand Canonical Ensemble

What exactly is μ? μ is like β, a bath property

$$-\beta\mu = \left(\frac{\partial \ln \Omega_B}{\partial N_B} \right) \qquad \beta = \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)$$

What is held fixed? $\qquad \mu, V, T$

$P(\nu)$? $\qquad P(\nu) \propto \begin{cases} e^{+\beta\mu N(\nu) - \beta E(\nu)}, & \text{Rigid constraint (only } V!\text{) met} \\ 0, & \text{Otherwise} \end{cases}$

Partition Function?
(Normalization)

$$Z(\mu, V, T) = \sum_{\substack{\nu \text{ meeting} \\ \text{rigid constraints}}} e^{+\beta\mu N(\nu) - \beta E(\nu)}$$

Thermodynamic
Potential?
(Effective Energy)

Grand potential

$$\Phi(\mu, V, T) = -k_B T \ln Z(\mu, V, T)$$

$$Z(\mu, V, T) \approx e^{-\beta \left(\underbrace{E^* - T S(N^*, V, E^*) - \mu N^*}_{\Phi = E - TS - \mu N} \right)}$$

like how we would write $A = E - TS$ in a thermo class.