

Lecture 7

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 free energy?

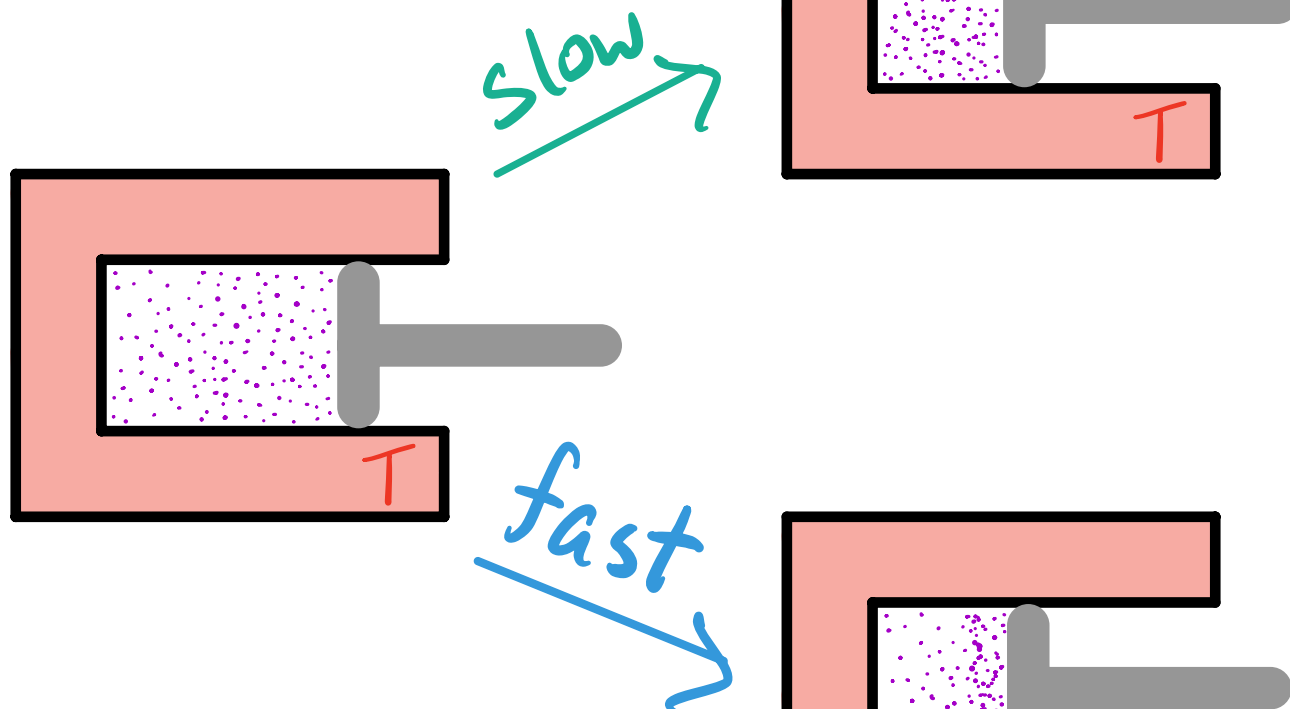
$$dE = TdS - p dV + \mu dN$$

Work: Change in energy due to variables I manipulate

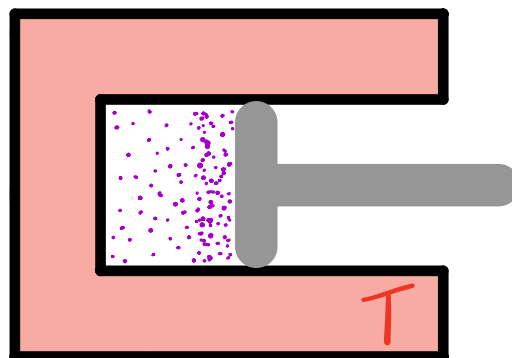
Heat: Change in energy due to flows into or out of the thermal bath. We don't get to use these flows - they're along for the ride.

We can talk about heat and work even if we do not perform a process slowly enough for the system to equilibrate.

For every ΔV , we give the gas time to relax and re-discover the most likely microstates for $N, V-\Delta V, T$

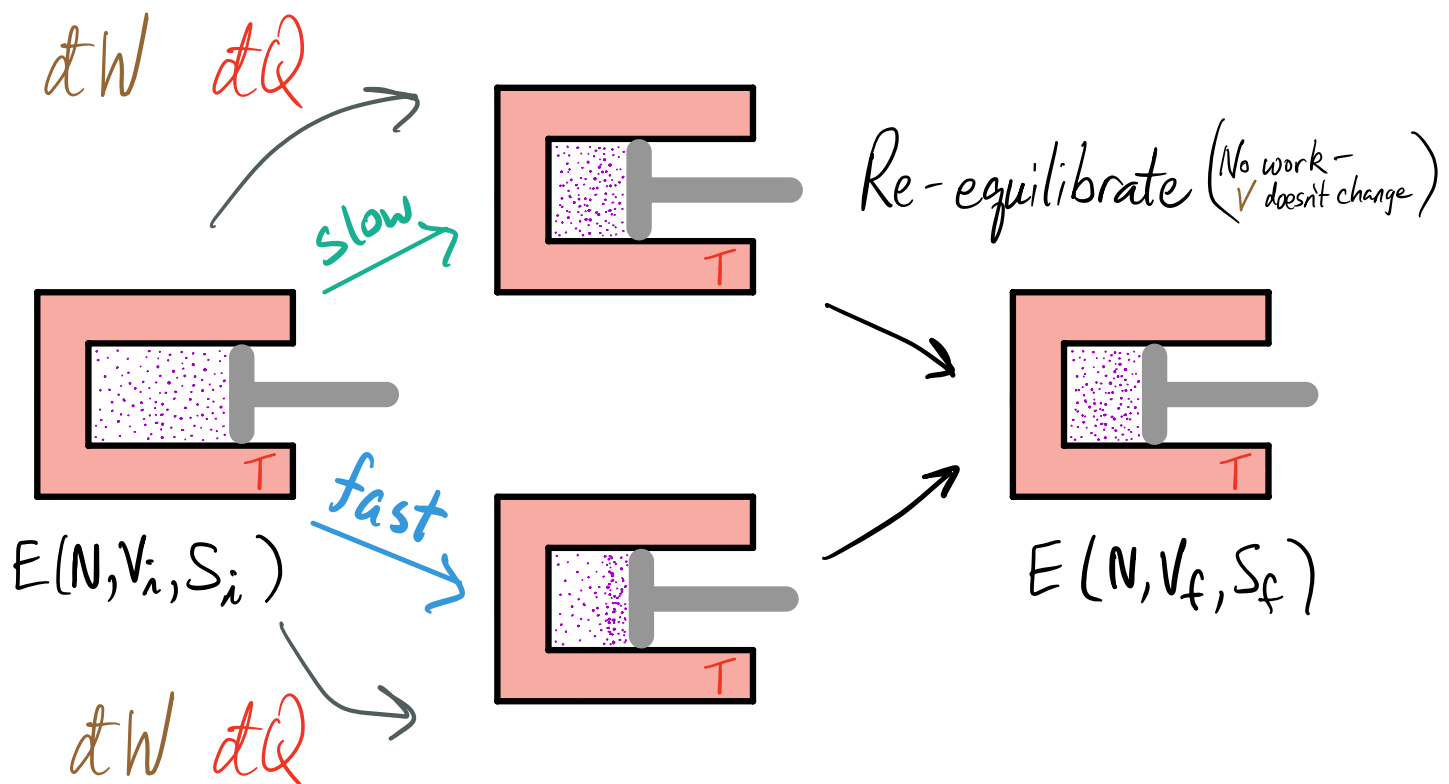


The fast compression forces the system to sample gas configurations that do not look like typical equilibrium microstates for $N, V-\Delta V, T$



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

$$\Rightarrow \int_{\text{fast}} (dQ + dW) = \int_{\text{slow}} (dQ + dW)$$

(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.

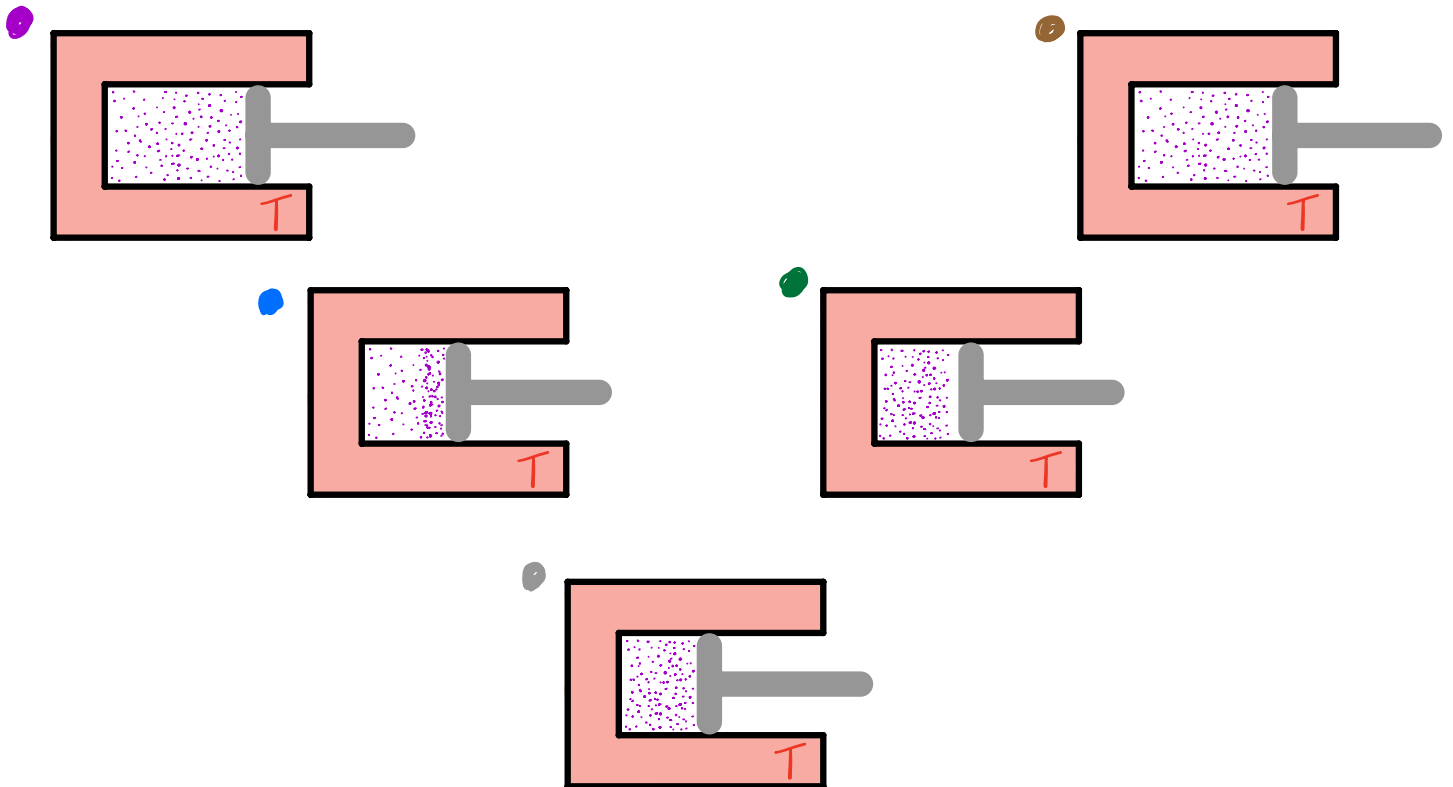
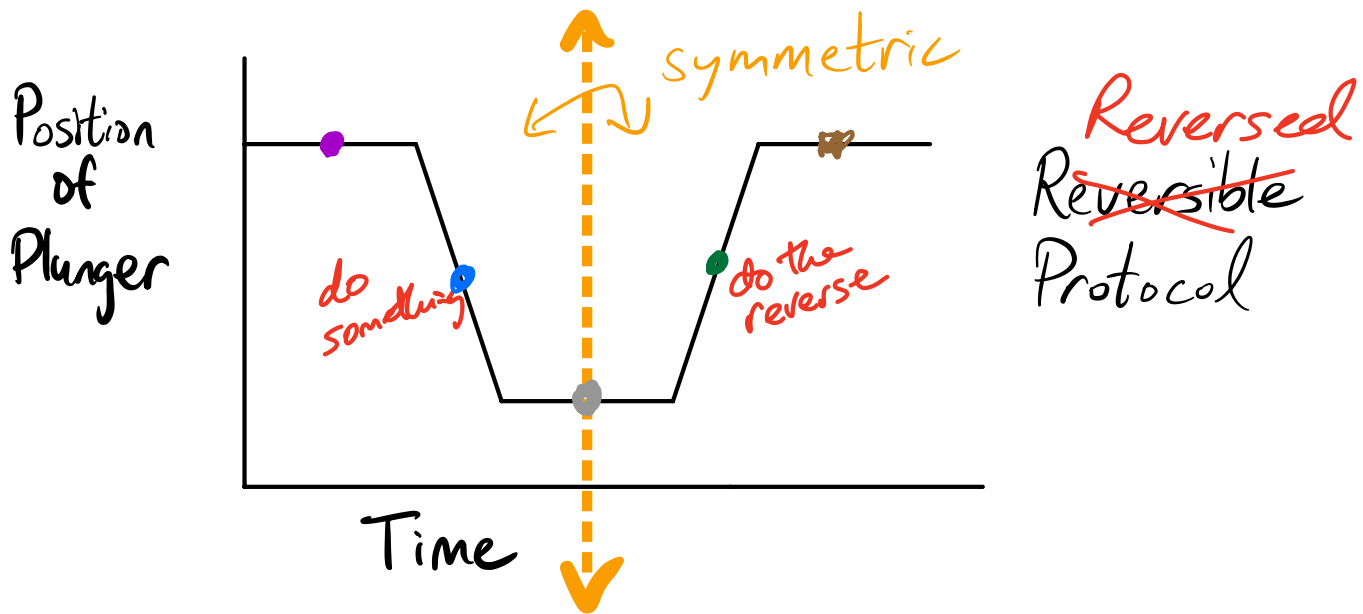
$$\Rightarrow \int_{\text{fast}} \delta W > \int_{\text{slow}} \delta W$$

Hence $\int_{\text{fast}} \delta Q < \int_{\text{slow}} \delta Q$

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...



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

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

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

In that reversible case...

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

$$dE = T dS - p dV$$

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

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

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

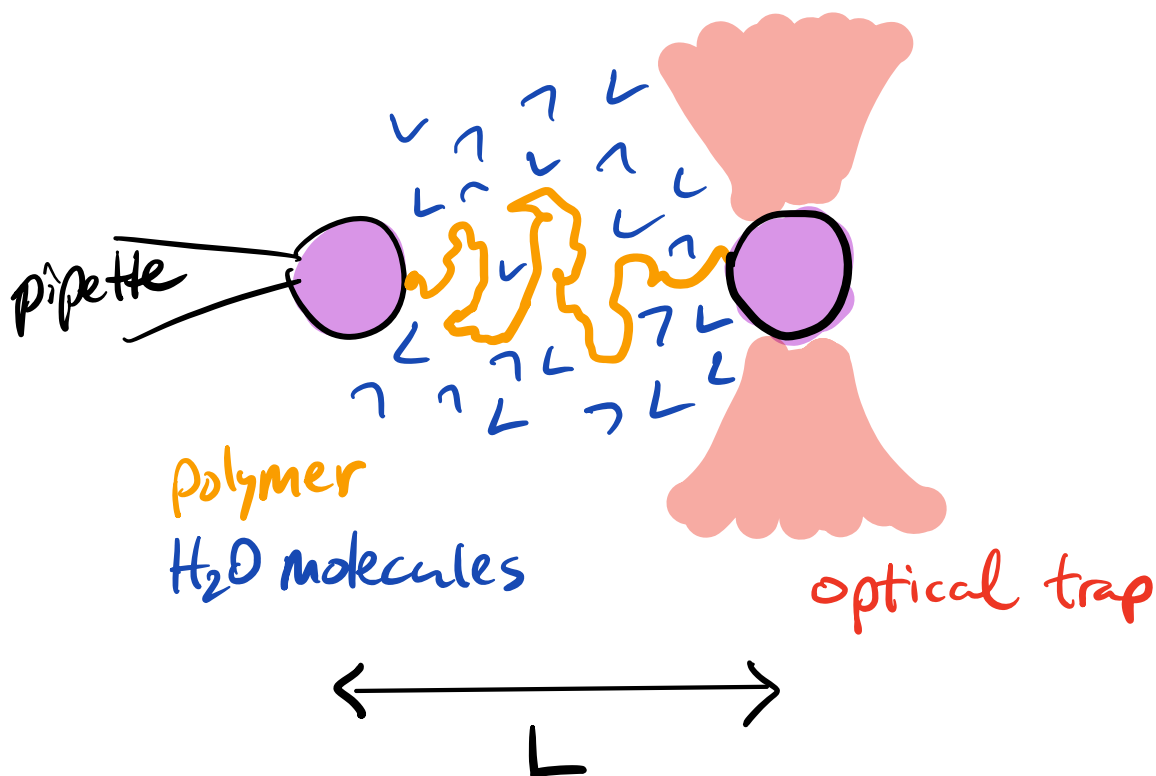
$$dW \geq (dA)_T$$

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...



What am I going to measure? L

What am I not going to measure? H_2O molecules
interior monomers

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

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

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

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

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

Averaging
over all possible
polymers with
length L

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

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

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

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

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

$$\ln \frac{P(L_f)}{P(L_i)}$$

Reversible Work Theorem:

$$\frac{P(L_f)}{P(L_i)} = e^{-\beta W_{\text{rev}}(L_i \rightarrow L_f)}$$
$$= e^{-\beta [A(L_f) - A(L_i)]}$$

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

$$\frac{P(L_f)}{P(L_i)} = \frac{Q(L_f)}{Q(L_i)} = \frac{e^{-\beta A(L_f)}}{e^{-\beta A(L_i)}} = e^{-\beta W_{\text{rev}}(L_i \rightarrow L_f)}$$

ratio of
partition functions

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?

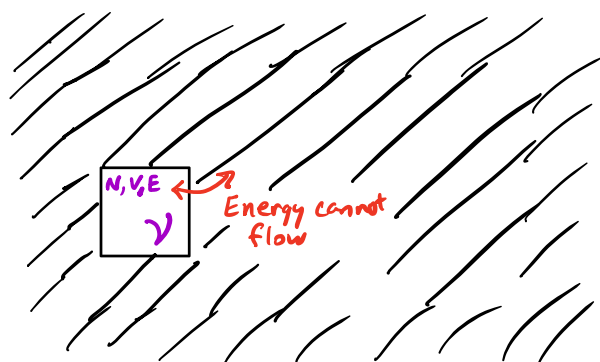
$$\underline{\underline{S_f - S_i}} = - \frac{A_f - A_i - \langle E \rangle_f + \langle E \rangle_i}{T}$$

$$= \frac{-k_B T \ln \frac{P(L_f)}{P(L_i)} - \langle E \rangle_f + \langle E \rangle_i}{T}$$

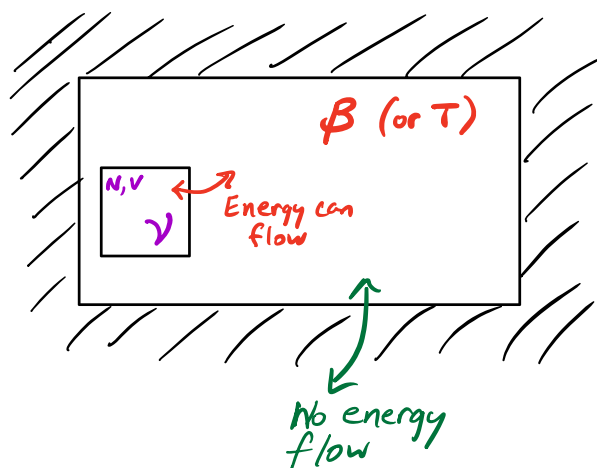
Ensembles or how do I replace a rigid constraint
 by a "softened" exponential bias?

Prob. dist. for ν

Microcanonical



Canonical



What is held fixed? N, V, E

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)

$$\Omega(N, V, E) = \sum_{\nu \text{ meeting rigid constraints}} 1$$

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

Thermodynamic
 Potential?
 (Effective Energy)

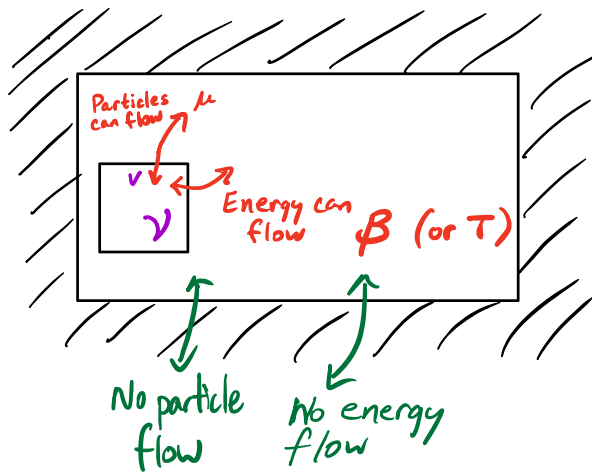
$$S(N, V, E) = k_B \ln \Omega(N, V, E)$$

$$A(N, V, T) = -k_B T \ln Q(N, V, T)$$

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


 thermodynamic limit
 (large system)

What if particles can fluctuate too?



Grand Canonical Ensemble

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

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

What is held fixed?

$$\mu, V, T$$

$P(v)$?

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

Partition Function?
(Normalization)

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

Thermodynamic
Potential?
(Effective Energy)

Grand potential

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

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

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