Lecture 6

Recall from last lecture...

Canonical Partition Function: $Q(\beta) = \sum_{\nu} e^{-\beta E(\nu)}$

"Cumulant Generating Function": $\ln Q(\beta)$

$$\frac{\partial \ln Q(\beta)}{\partial \beta} = -\langle E \rangle$$

1st cumulant
(mean)

$$\frac{\partial^2 \ln Q(\beta)}{\partial \beta^2} = \langle \delta E^2 \rangle = k_B T^2 C_V$$

2nd cumulant
(variance)

$$\langle (\delta E)^2 \rangle = k_B T^2 C_V$$

Fluctuations are linked to response.

The limit of a large system is called the **thermodynamic limit**, and in some respects it is wasteful to carry along the whole distribution $P(E)$ when it is completely dominated by $\langle E \rangle$. We might as well replace the distribution by a single $E \equiv \langle E \rangle$.

In other (important) respects it is **not** wasteful to remember the probabilistic nature of $P(E)$.

Let's start where the statistical nature of E seems essential, with the canonical partition function:

$$Q(N, V, T) = \sum_{\nu} e^{-\beta E(\nu)} = \sum_{E} \underline{\Omega(N,V,E)}\, e^{-\beta E}$$

Sum over all possible energy fluctuations

Number of ways the system could have that energy (degeneracy) given the fixed $N + V$.

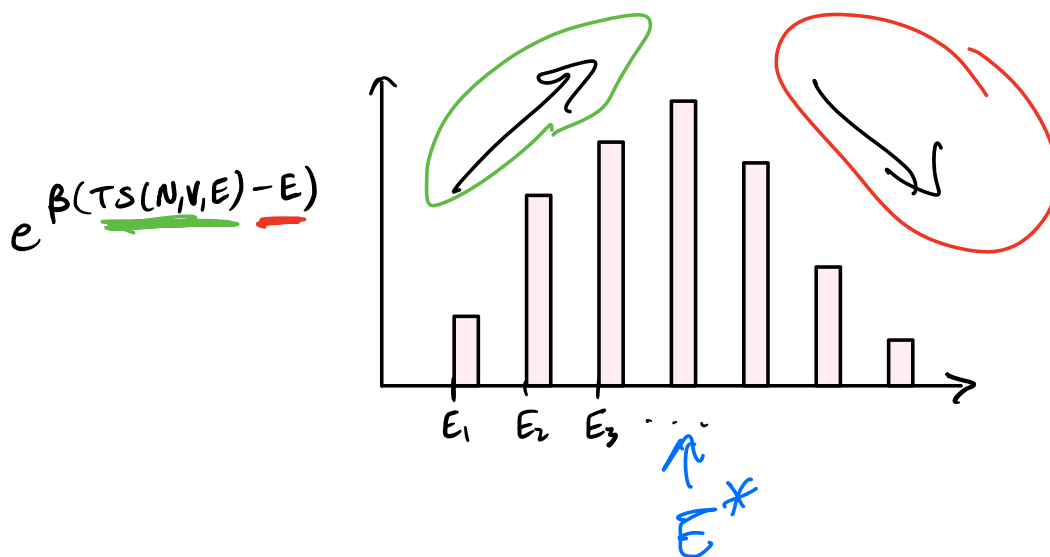Number of ways the bath can accomodate.

$\left(\begin{array}{c}\text{If } E \text{ fluctuations weren't important, this} \\ \text{sum would have a single term.} \quad \text{... wait for it.}\end{array}\right)$

How does S relate to Ω?

$$S(N, V, E) = k_B \ln \Omega(N, V, E)$$
$$\Rightarrow \Omega(N, V, E) = e^{S(N,V,E)/k_B}$$

$$Q(N, V, T) = \sum_{E} e^{S(N,V,E)/k_B}\, e^{-\beta E}$$

$$= \sum_{E} e^{\beta\, [\, TS(N,V,E)\, -\, E\,]}$$

$$e^{\beta(TS(N,V,E) - E)}$$

$E_1 \quad E_2 \quad E_3 \quad \cdots$

E^*

More system states
w/ more E

Fewer bath states
as E increases

E^*: the value of E that
has the biggest peak

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

intensive $\qquad$ extensive

$$= e^{\beta(TS(N,V,E^*) - E^*)} \sum_E e^{\beta[(TS(N,V,E) - E) - (TS(N,V,E^*) - E^*)]}$$

$[\cdots]$ Positive or Negative?
Extensive or Intensive?

$$= e^{\beta(TS(N,V,E^*) - E^*)} \left[1 + e^{-\beta(\text{Big} \#)} + e^{-\beta(\text{Big} \#)^{\text{Different}}} + \ldots \right]$$

$\uparrow$ $E = E^*$ term of the sum

all of these will be negligible in the large system limit

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

$\uparrow$ thermodynamic limit (large system)

Saddle Point Approximation
Laplace's Method
Stationary Phase Method
WKB Theory

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

$$\Rightarrow \quad -k_B T \ln Q(N,V,T) \approx E^* - TS(N,V,E^*)$$

Legendre transform $\qquad = \min_{E} \left(E - TS(N,V,E) \right)$

Notice that E^* is the energy with the biggest $P(E)$ term, so in the thermodynamic limit, $\langle E \rangle = E^* \equiv E$, which is why we often write

$$E - TS = A(N,V,T)$$

Helmholtz. Free energy

Repeating w/ different colors...

$$-k_B T \ln Q(N,V,T) \approx \min_E \left(E - TS(N,V,E) \right)$$

Partition Function

$$= E - TS \quad \leftarrow \text{This is really shorthand for that}$$

$$= A(N,V,T) \quad \leftarrow \quad \text{Free energy}$$
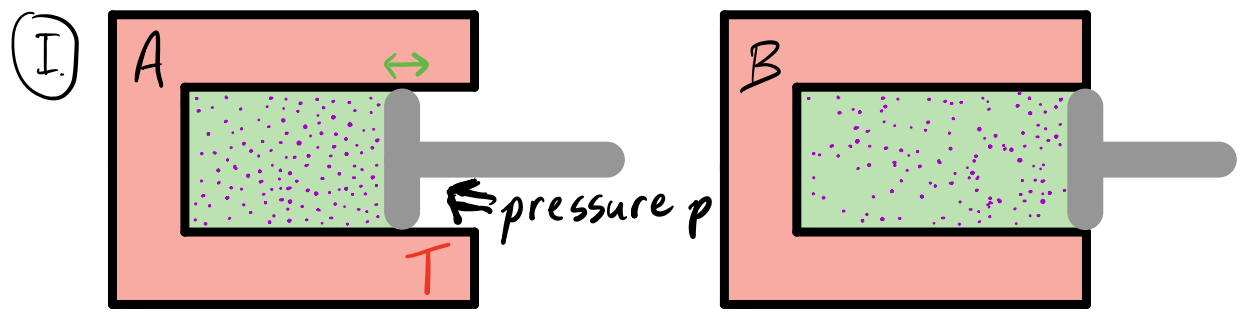
Free energy

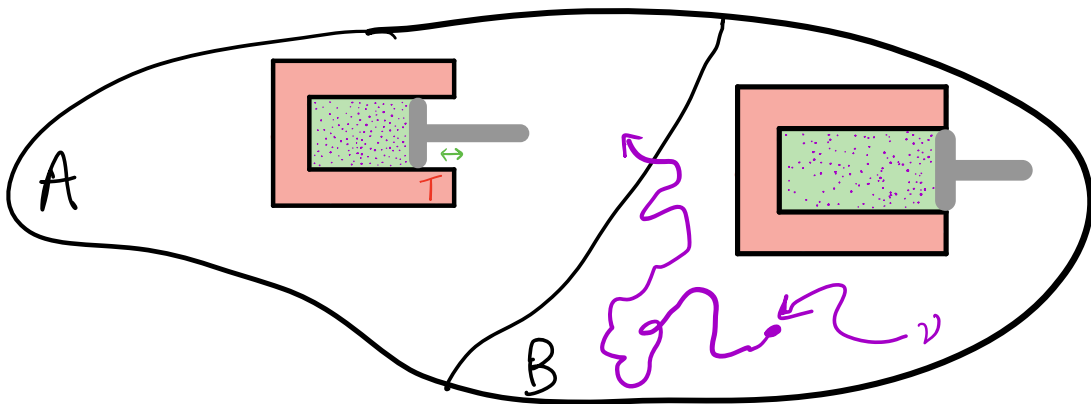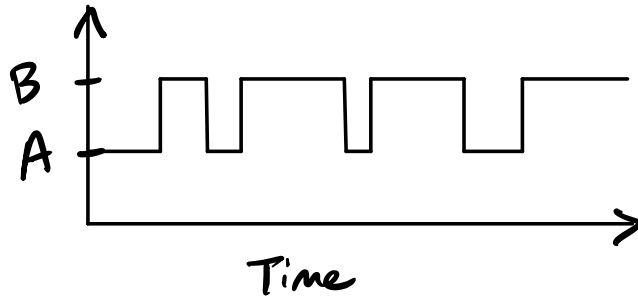$$-\beta A = \ln Q \quad \leftarrow \quad \text{Partition Function}$$

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

(II) What is free about free energy?

(I.)

Imagine there were only two possible volumes.

How do we partition probability across the two possibilities?

ν: microstate specifying all gas molecule locations and the location of the piston.

$$P(\nu) = \frac{e^{-\beta E(\nu)}}{Q} \quad \text{for any } \nu \text{ with } Q = \sum_{\nu} e^{-\beta E(\nu)}$$
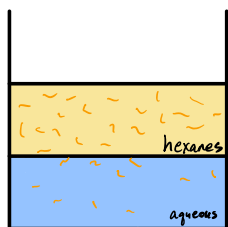
$$P(A) = \sum_{\nu \in A} P(\nu) = \sum_{\nu \in A} \frac{e^{-\beta E(\nu)}}{Q} = \frac{Q_A}{Q}$$

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

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

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

The name "partitioning" really makes a lot more sense if you think about your organic chemistry experiments...

Molecules partition into different phases and the split between the two is like the fraction of time any given molecule will be in hexanes (A) versus water (B). Hence partition function.

$$-k_B T \ln Q(N, V, T) = A(N, V, T), \quad \text{so...}$$

$$\frac{P_A}{P_B} = \frac{Q_A}{Q_B} = e^{-\beta \left[A(N, V_A, T) - A(N, V_B, T) \right]}$$

Relative probability of piston configuration A to piston configuration B, assuming the piston is free to fluctuate

Change in free energy when I change the volume of the piston by moving from A to B.

Ⅱ What is free about a free energy?

"Energy which is free (available) to extract"

Let's remember how (why) we got to talking about A...
↑
Helmholtz

We started by studying $S(E, V, N)$

Count states ⟶ as a function of constraints

and we inverted to get $E(S, V, N)$

Tuning entropy rather than a physical constraint?

Awkward

Two macroscopic (& extensive) constraints that you can really think of tuning in an experiment

We could not directly control S. What we could control was T, which would change $\langle E \rangle$.

We saw that the T control had to do with $Q(T, V, N)$, which we related to $A(T, V, N)$
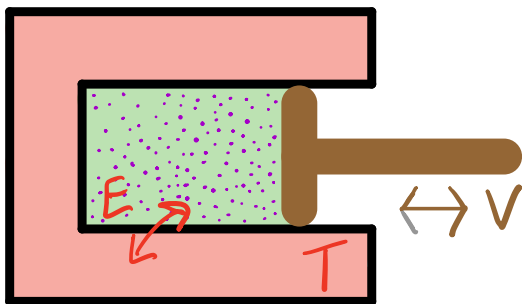
Same arguments

This A was a Legendre transform of $E(S, V, N)$, and the transform had the effect of switching between S dependence and T dependence.

$$A(T, V, N) = \min_{E} \left(E - TS(E, V, N) \right) = E - TS(E, V, N)$$

conjugate intensive variable

extensive variable

Now we are thinking of a temperature knob.

We will control T, V, N but will let E fluctuate between system and bath.

Let's hold N fixed while adjusting V

$$\Rightarrow dN = 0$$

By moving a plunger, we can exchange volume with the outside world. We imagine being able to move this at will, so we can pick any V.

If the system is in contact with a heat bath at temperature T, energy can be exchanged with that bath. **We are not controlling that energy flow!**

What does control the flow?

Remember $\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$ at equilibrium.

We tune V

$\Rightarrow$ The # of gas configurations changes

$\Rightarrow$ New $\Omega(E, V, N)$

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

But now $\left(\frac{\partial S}{\partial E}\right)_{N,V} \neq \frac{1}{T}$

$\Rightarrow$ Some E flows into/out of the bath to re-equilibrate.

$$dE = TdS - pdV + \mu dN \nearrow^0$$

Change in energy of the system

Amount of energy that had to flow in from the
temperature bath. *heat*

The change in energy due to the degree of freedom
I control, V. I can hook something up to the
piston to <u>use</u> this energy — WORK.

<u>First Law</u>: Energy is neither created nor destroyed, only
exchanged in the forms of heat and work.

$$dE = đQ + đW$$

Work: Energy change in the system due to the
manipulated variables

$$X = \{V, N, \ldots\}$$

$$\dbar W = f_{ext} \cdot dX, \quad e.g. \ \dbar W = -p dV$$

Heat: Everything else that you manipulate indirectly through baths. E.g., the energy exchanged with the temperature bath through the walls of the piston. $\dbar Q = T dS.$
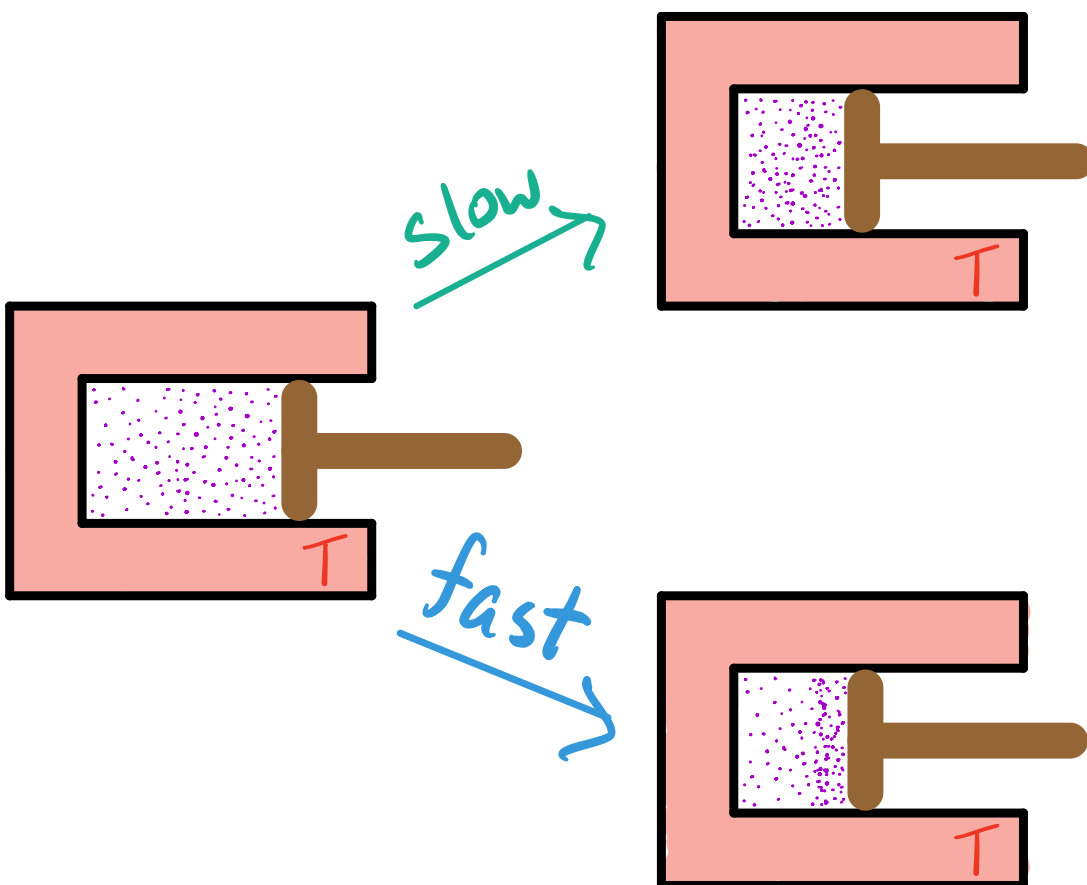
We can talk about heat and work even if we do not perform a process slowly enough for the system to equilibrate.
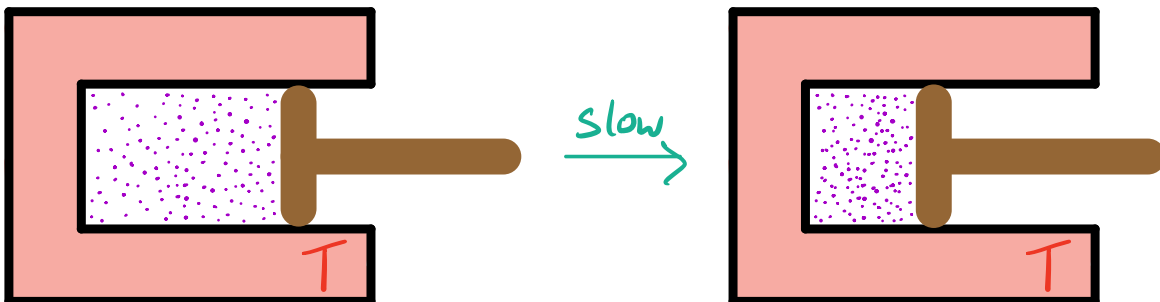
For every ΔV, we give the gas time to relax and re-discover the most likely microstates for $N, V - \Delta V, T$
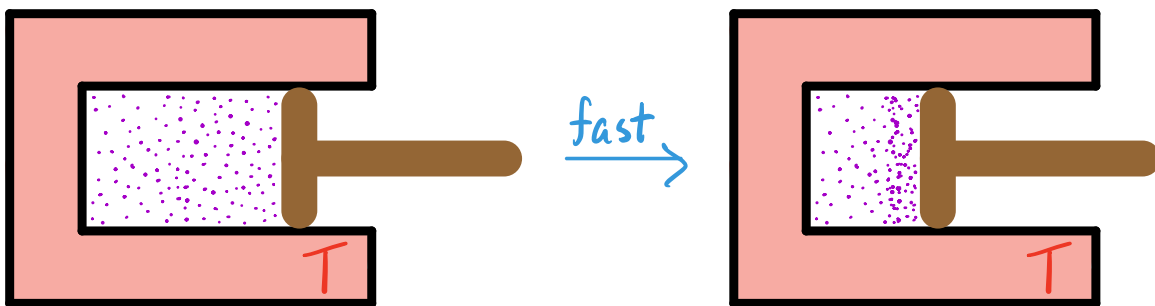
The fast compression forces the system to sample gas configurations that <u>do not</u> look like typical equilibrium microstates for N, $V - \Delta V$, T

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.

Reversible vs Irreversible...

Position of Plunger

Symmetric

Reversible Protocol

So what is irreversible if I go quickly?

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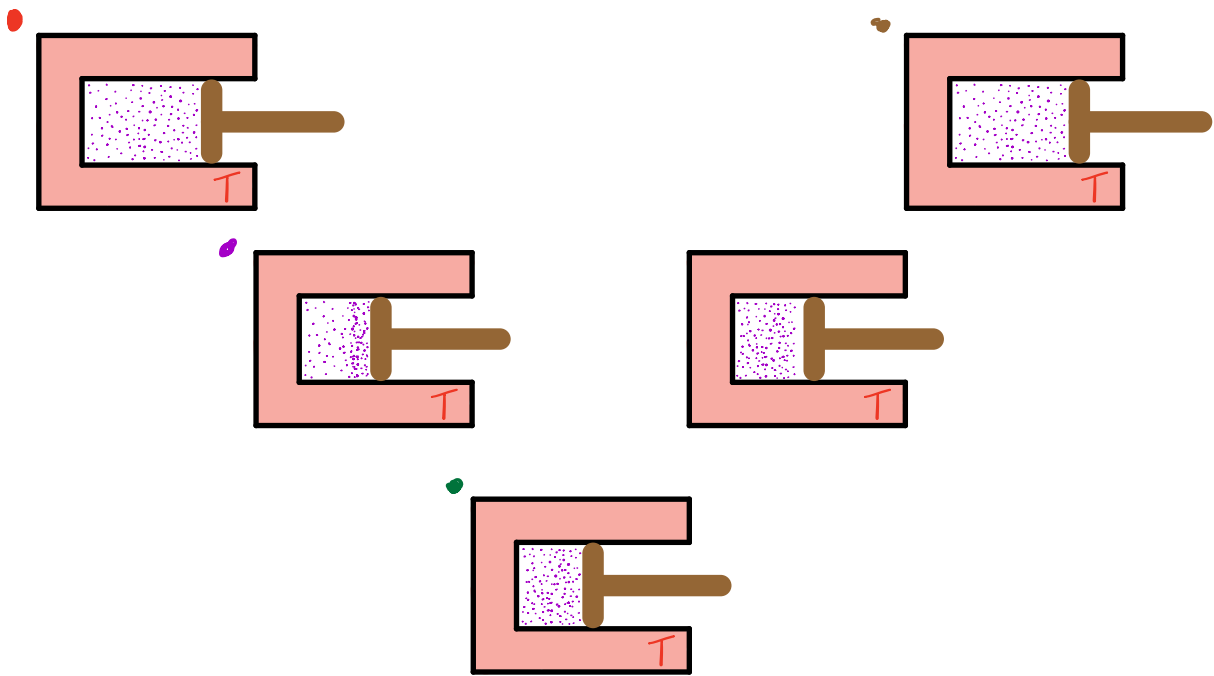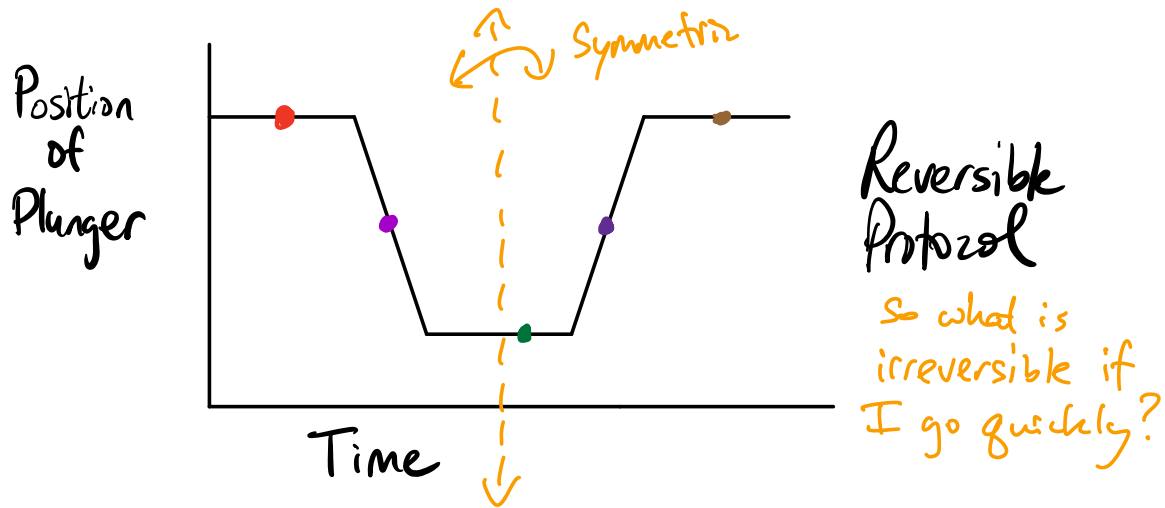
I visit different microstates unless I go slowly enough to visit equilibrium microstates in each direction