

Lecture 11

Recall from last lecture...

The thermodynamic limit

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 $E \equiv \langle E \rangle$. (Orange is thermo/Green is stat mech)

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

① We related thermodynamic quantities like C_V (response coefficients) to things like $\langle \delta E^2 \rangle$ (fluctuations)
[Lecture 8/9]

② We can derive thermodynamic relationships that may have felt foreign.

$$-\frac{1}{k_B T} \ln Q(N, V, T) \approx \min_E (E - TS(N, V, E))$$

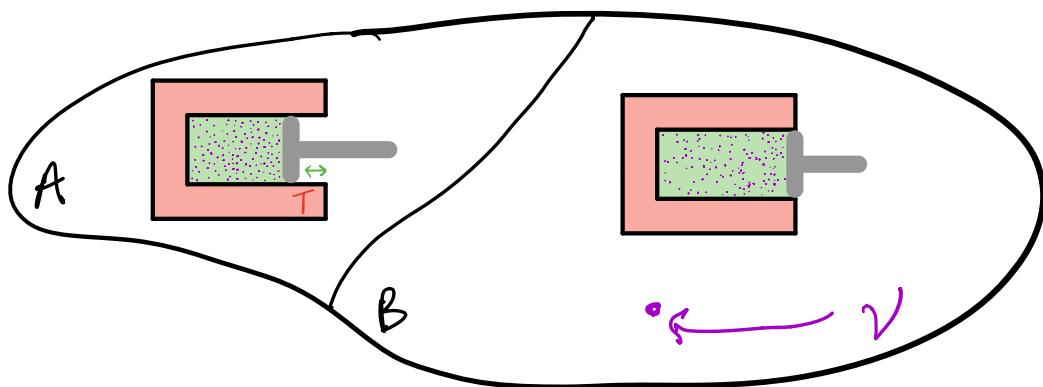
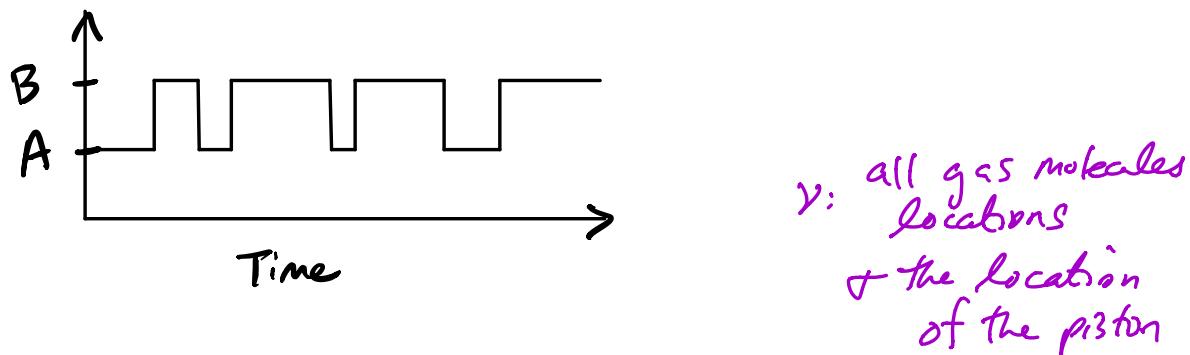
$= E - TS$ ← This is really shorthand for that

$= A(N, V, T)$ ← Free energy

① What is partition-y about a partition function?

② What is free about a free energy?

How do we partition probability across the two possibilities?



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

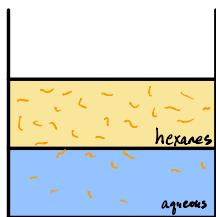
$$P(A) = \sum_{v \in A} p(v) = \sum_{v \in A} \frac{e^{-\beta E(v)}}{Q} = \frac{Q_A}{Q}$$

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

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

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

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.

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

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

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.

② What is free about a free energy?

"Energy which is free (available) to extract"

Let's start with a little thermo recap...

$S(E, V, N)$ - All extensive!

$$dS = \underbrace{\frac{1}{T} dE}_{\uparrow} + \underbrace{\frac{P}{T} dV}_{\text{By how much would the number of states increase (log scale) if we increased energy.}} - \underbrace{\frac{\mu}{T} dN}_{\text{}}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \quad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}$$

Rearranging...

$$dE = TdS - PdV + \mu dN$$

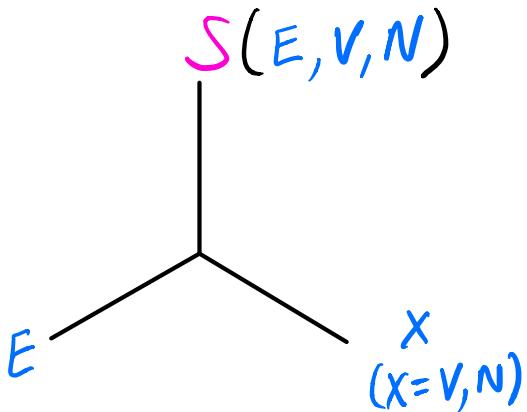
Now we're thinking of E as a function of $S, V, + N$

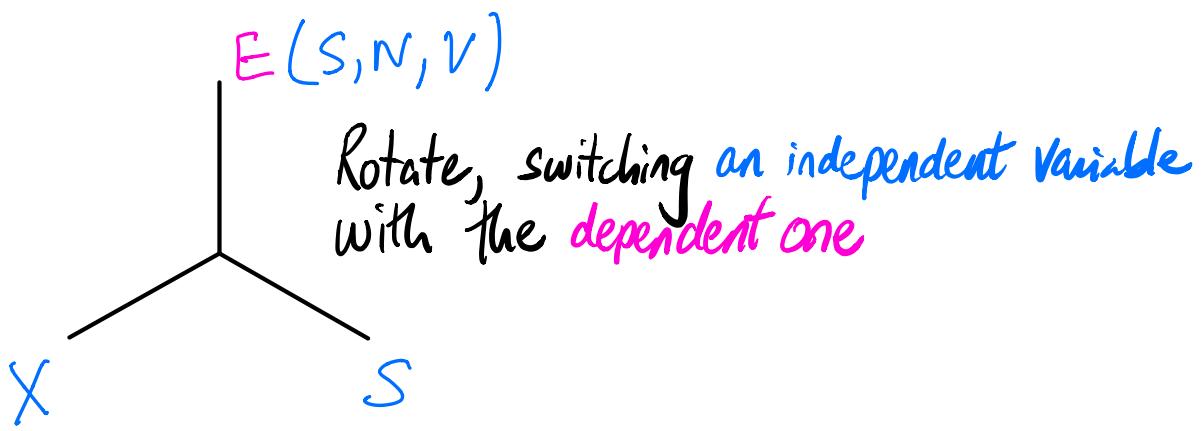
$$E(S, V, N)$$

How can we do this?

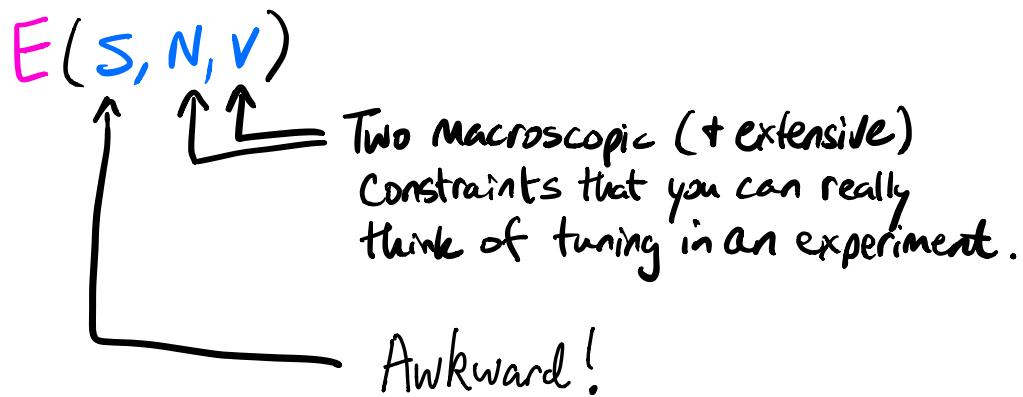
Dependent Variable

Independent Variables





We are inverting the function, like $y(x)$ vs. $x(y)$



How do you tune the entropy knob in an experiment?

What we can actually tune are V , N , + T !

So we defined the Helmholtz free energy.

$$A = E - TS$$

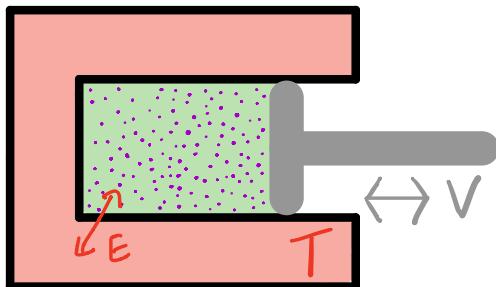
↑ extensive variable
 ↓ conjugate intensive variable

Why did we introduce such a function?

$$\begin{aligned} dA &= d(E - TS) \\ &= dE - d(TS) \\ &= dE - TdS - SdT \\ &= \cancel{dS} - pdV + \mu dN - \cancel{TdS} - SdT \\ &= -SdT - pdV + \mu dN \end{aligned}$$

$$\Rightarrow A(T, V, N)$$

Now we are thinking about a temperature knob.



Fixed # of particles
 $\Rightarrow dN = 0$

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

We tune V

\Rightarrow The # of gas configurations changes

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

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

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

\Rightarrow Some E flow with the bath to re-equilibrate.

$$dE = T dS - p dV$$

Change in energy of the system

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

The change in energy due to the degree of freedom I control, V . I can hook something up to the piston to use this energy-work.

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

$$dE = dQ + dW$$

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

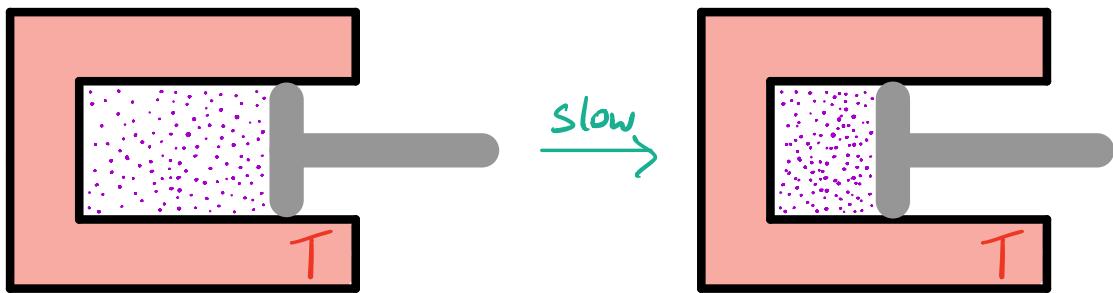
$$X = \{V, N, \dots\}$$

$$dW = f_{ext} \cdot dX, \quad \text{e.g. } dW = -pdV$$

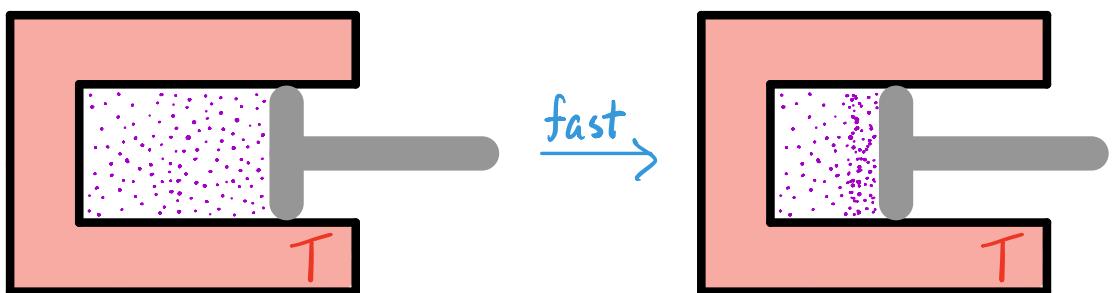
Heat: Everything else that you manipulate indirectly through baths. E.g., the energy exchanged w/ the temperature bath through the walls of the piston

$$dQ = TdS$$

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
 $N, V - \Delta V, T$

Reversible vs Irreversible...

- ⇒ The effective pressure pushing up against the plunger is not the equilibrium value for that volume $V - \Delta V$.
 - ⇒ I actually push harder than equilibrium would predict. (A cost for impatience)
- The least work is when I push reversibly + let $\textcolor{violet}{v}$ re-equilibrate before further adjusting V . Then $dW_{\text{rev}} = -pdV$