

$$\beta \underline{A} = -\ln \underline{Q}$$

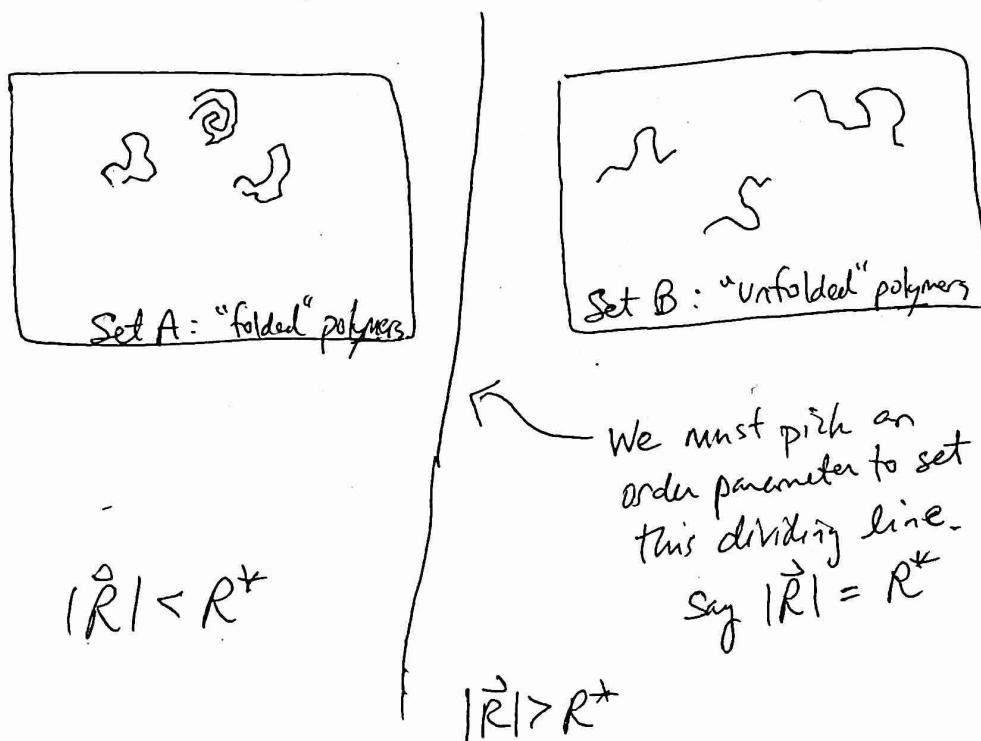
Helmholtz
Free Energy

Canonical
Partition Function

- What is free about free energy?
- What is partition-y about partition functions?

Partition functions first

How does probability partition between two (or more) possibilities.



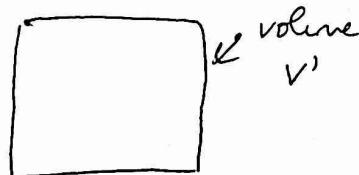
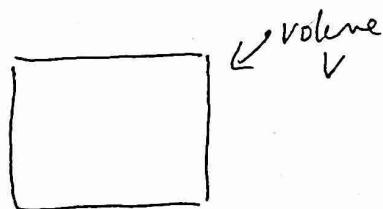
We seek $\frac{P(A)}{P(B)}$, the relative probability of finding a folded vs. unfolded polymer.

$$P(A) = \sum_{v \in A} P(v) = \sum_{v \in A} \frac{e^{-\beta E(v)}}{Q} = \frac{1}{Q} \left(\sum_{v \in A} e^{-\beta E(v)} \right) \quad \text{call this } Q_A = \frac{Q_A}{Q}$$

$$P(B) = \sum_{v \in B} P(v) = \sum_{v \in B} \frac{e^{-\beta E(v)}}{Q} = \frac{1}{Q} \sum_{v \in B} e^{-\beta E(v)} = \frac{Q_B}{Q}$$

$$\frac{P(A)}{P(B)} = \frac{Q_A/Q}{Q_B/Q} = \frac{Q_A}{Q_B} \leftarrow \text{The ratio of partition functions tells us how probability partitions between two options}$$

But we said $Q(N, V, T)$ is the partition function. Not something with a R^* .

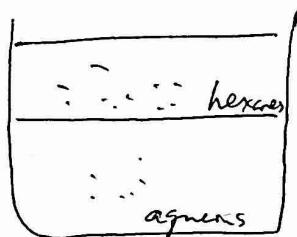


$$Q(N, V, T) = \sum_{\substack{\text{ways} \\ \text{volume } V}} P(v)$$

$$Q(N, V', T) = \sum_{\substack{\text{ways} \\ V'}} P(v')$$

It's the same idea. We're summing over collections of microstates.

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



Molecules partition into different phases and the split between the two must have to do with some partition functions.

Talk about final projects.

$$\frac{Q_A}{Q_B} = e^{-\beta \Delta A} = e^{-\beta (A(N, V, T) - A(N, V', T))}$$

↑
change in free energy when I change the ~~size~~ value of a piston.

relative probabilities assuming a piston fluidity

~~What's free about free energy next time.~~

What's free about free energy?

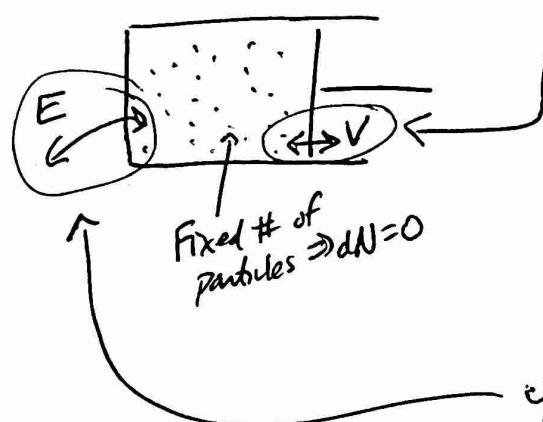
- This is the most work that can be extracted out of a transformation from microstates in set A to microstates in set B at fixed temperature T and fixed number of particles N .
- "Energy which is free (available) to extract."

Remember $E(S, V, N)$ with $dE = TdS - pdV + \mu dN$

Annoying!

These were ordinary knobs we could think about adjusting in an experiment.

Piston w/ gas:



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 whatever V we want.

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

What determines the flow? Remember $(\frac{\partial S}{\partial E})_{N,V} = \frac{1}{T}$.

As we tune V , the # of gas configurations changes

$\Rightarrow S$ changes $\Rightarrow S(N, V, E)$ changes \Rightarrow the amount

of E in the gas is no longer the right amount

so that $(\frac{\partial S}{\partial E})_{N,V} = \frac{1}{T} \leftarrow$ (fixed), so some

E must flow until that re-equilibrates.

$$\underline{dE} = \underline{TdS} - \underline{pdV}$$

charge in energy of 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 cannot be created or destroyed, only exchanged in the forms of heat and work.

Work: Energy change in the system due to manipulated variables

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

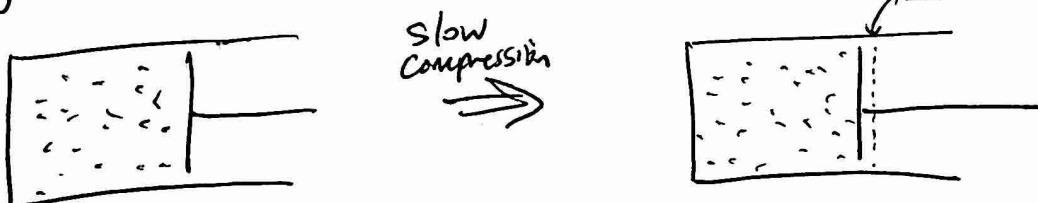
$$dW = f_{ext} \cdot dX, \text{ e.g. } dW = -pdV = -p_{ext} dV$$

↑ At equilibrium, external forces must exactly balance internal forces.

Heat: Everything else, e.g., the energy exchanged with the temperature bath through the walls of the piston. $dQ = TdS$

$$dE = dQ + dW$$

We can talk about heat + 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 rediscover the most likely microstates for N , $V-\Delta V$, & T .

Contrast with...



Now the effective pressure pushing up against the plunger is not the equilibrium value for that volume $V-\Delta V$.