Lecture 6

Recall from last lecture...

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

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

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

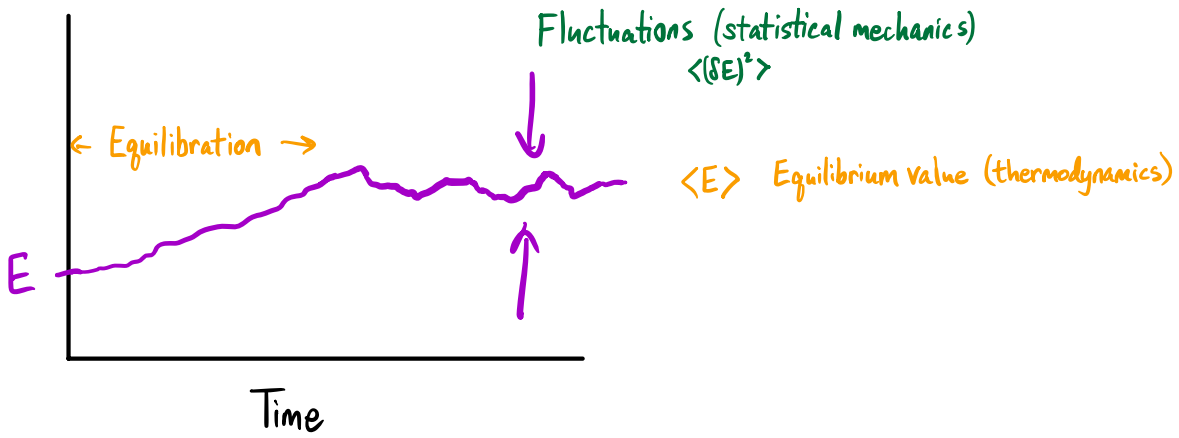
1st cumulant (mean)

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

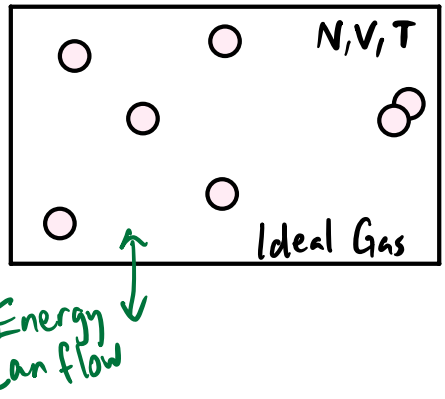
2nd cumulant (variance)

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

Fluctuations are linked to response.



This statistical approach goes beyond what we would have done in thermodynamics.



What is the energy of the (monatomic) gas?

Thermodynamics: $E = \frac{3}{2} N k_B T$

A single number, not a # from a fluctuating distribution

Statistical Mechanics:

$$\langle E \rangle = \frac{3}{2} N k_B T$$

In a really large system, $\frac{\langle E \rangle}{N} \to \frac{3}{2} k_B T$ and the distribution becomes **very sharply** peaked for large N.

(Remember coin flips and how $f = \frac{N_H}{N}$ became sharply peaked at $f = \frac{1}{2}$.

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 <u>not</u> 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)

(2) We can derive thermodynamic relationships that may have felt foreign. Things like $A = E - TS$.

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

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

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.

(If E fluctuations weren't important, this sum would have a single term. ... wait for it.)

How does S relate to Ω?

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

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

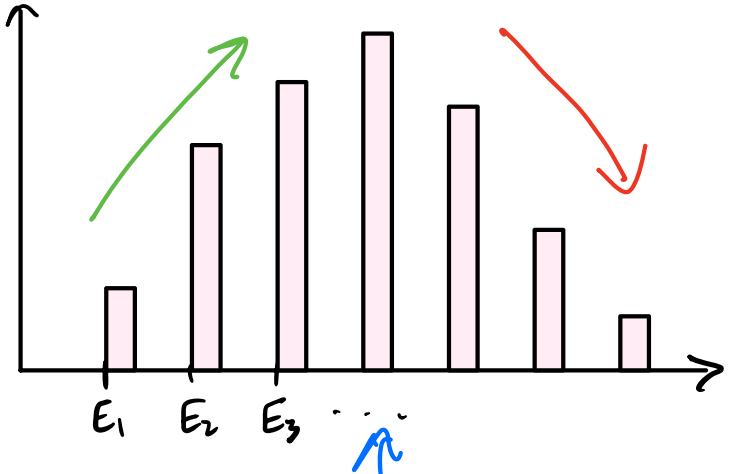
$$Q(N,V,T) = \sum_E e^{S(N,V,E)/k_B} e^{-\beta E}$$

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

Do I mean for $\sum_E$ to be a sum or an integral?

Remember, by $\sum_E$ I mean the idea of summing over all possible E, which is either a sum or an integral depending on if the energies are discrete or continuous.

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



More system states w/ more E

Fewer bath states as E increases

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

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

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

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

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

$E=E^*$ term of the sum

all of these will be negligible in the large system limit

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

thermodynamic limit (large system)

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

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

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

Legendre transform $= \min_E \left(E - TS(N,V,E) \right)$

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

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

$$= A(N,V,T)$$

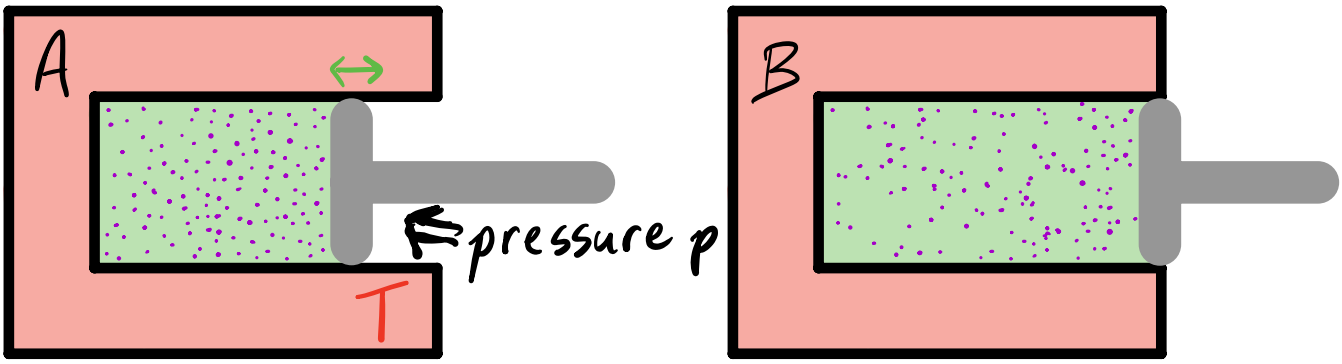
Free energy

Partition Function $\ln Q = -\beta A$ Free energy

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

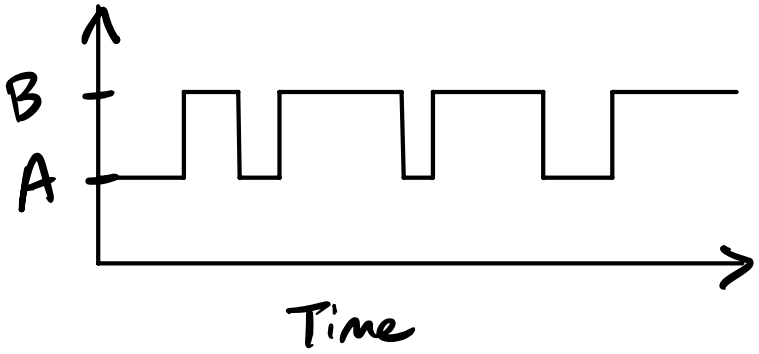
(II) What is free about free energy?

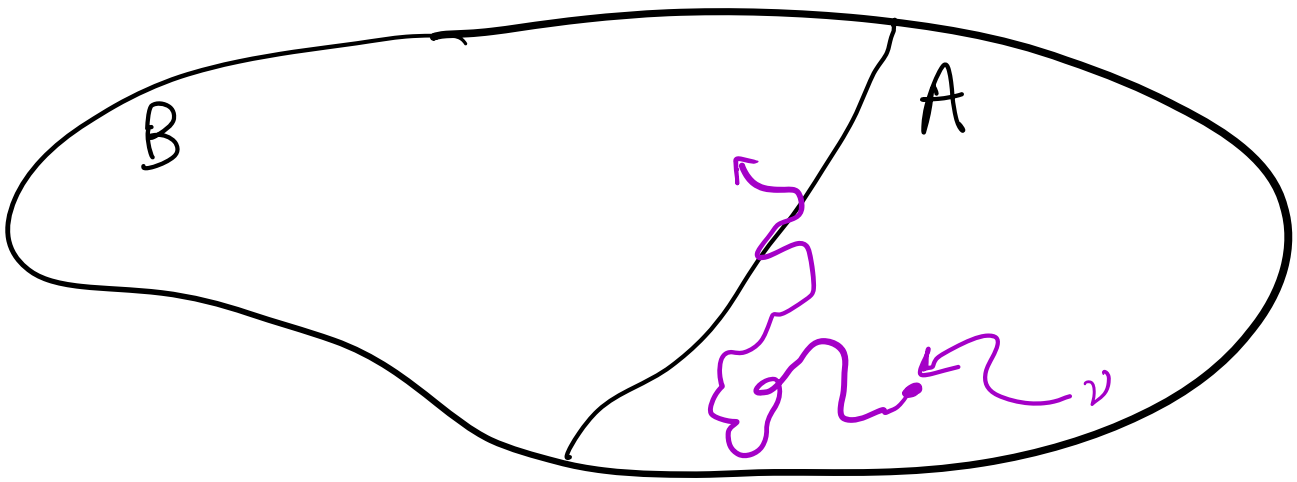
I.



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.

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

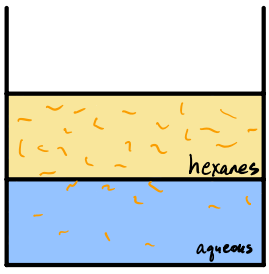
$$P(A) = \sum_{\nu \in A} P(\nu) = \sum_{\nu \in A} \frac{e^{-\beta E(\nu)}}{Q} = \frac{Q_A}{Q}$$

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

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

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.

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

(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? → S

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

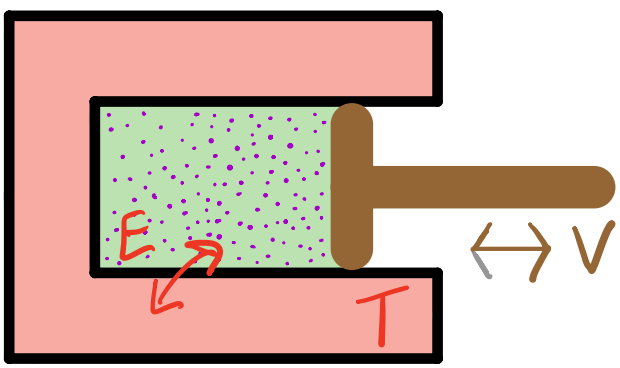
This A was a Legendre transform of $E(S,V,N)$, and the transform had the effect of switching between S dependence and T dependence.

$$A(T,V,N) = \min_E \left(E - TS(E,V,N) \right) = E - TS(E,V,N)$$

E: conjugate intensive variable

TS: 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!

(at least not directly in the sense that we are controlling V)

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.

We call that energy flow heat.

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

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 use this energy — work.

First Law: 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

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

$đW = f_{ext} \cdot dX$, e.g. $đW = -pd$

Heat: Everything else that you manipulate indirectly through baths. E.g., the energy exchanged with the temperature bath through the walls of the piston. $đQ = TdS$.