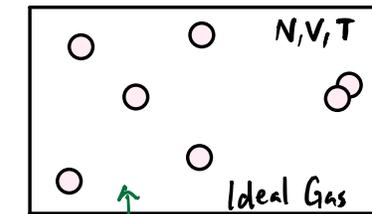


Lecture 10

Recall from last lecture...

Our study of statistical mechanics goes beyond what you discuss in thermodynamics.



What is the energy of the (monatomic) gas?

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

A single number, not discussed in terms of a distribution

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

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

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 $E = \langle E \rangle$.

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)

Partition Function: $Z(\beta) = \sum_v e^{-\beta E(v)}$

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

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

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

1st cumulant (mean)

2nd cumulant (variance)

② We can systematically derive (from a microscopic basis) thermodynamic relationships that may have felt ad hoc or foreign. Things like

$$A = E - TS$$

Helmholtz Free Energy

Actual Energy

Temperature

Entropy

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

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 accommodate.

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

How does S relate to Ω ?

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

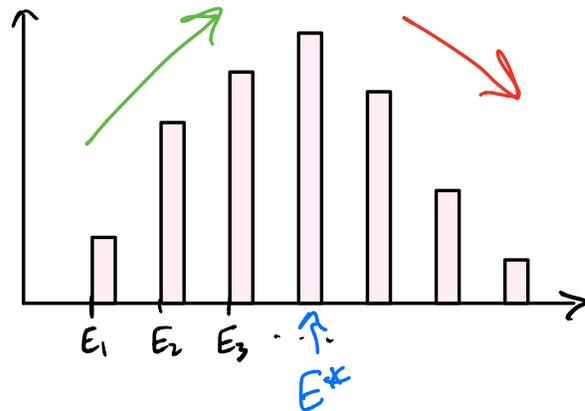
$$\Rightarrow \underbrace{\Omega(N, V, E)} = e^{S(N, V, E)/k_B}$$

$$\begin{aligned} Q(N, V, T) &= \sum_v e^{-\beta E(v)} = \sum_E e^{S(N, V, E)/k_B} e^{-\beta E} \\ &= \sum_E e^{\beta(TS(N, V, E) - E)} \end{aligned}$$

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.

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



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

More system states as E increases
Fewer bath states as E increases

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

extensive \swarrow extensive \searrow extensive
 extensive \swarrow extensive \searrow extensive
 intensive \downarrow extensive

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

[...] Positive or Negative?
Extensive or Intensive?

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

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

$\approx e^{\beta(TS(N,V,E^*) - E^*)}$
↑
thermodynamic limit
(large system)

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

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

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

$$= \min_E (E - TS(N,V,E))$$

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

$$E - TS = A(N,V,T) \quad \text{Helmholtz Free Energy}$$

Helmholtz Free energy

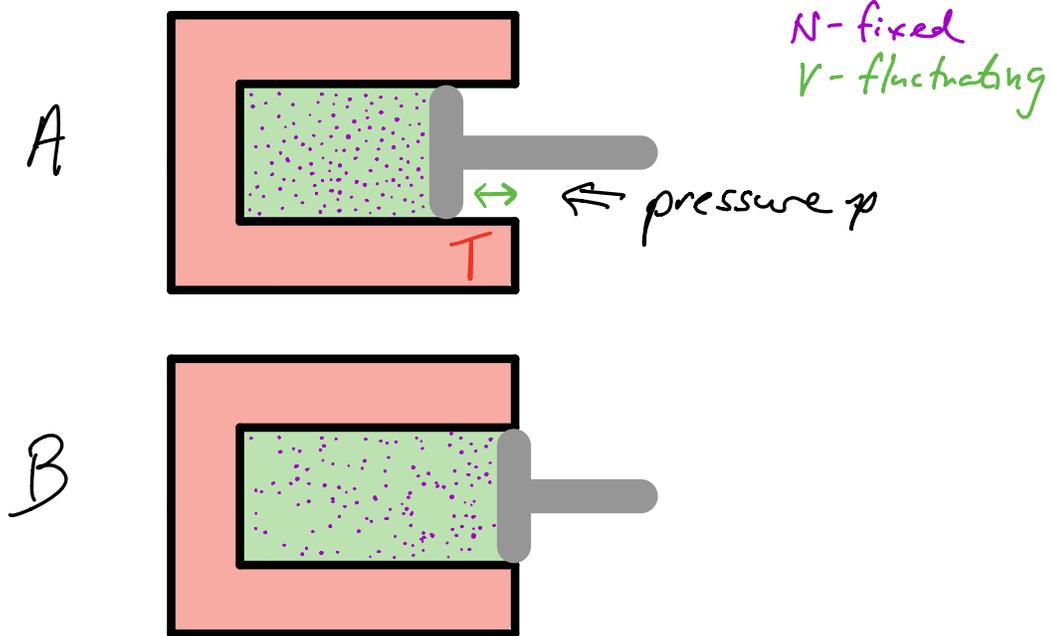
$$-\beta A = \ln Q$$

Canonical Partition Function

$\Omega(N, V, E)$: Normalization constant
for when V has a fixed
 N, V, E

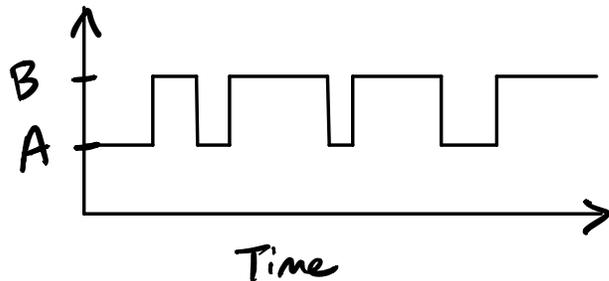
$$S(N, V, E) = k_B \ln \Omega(N, V, E)$$

① What is partition-y about a partition function?

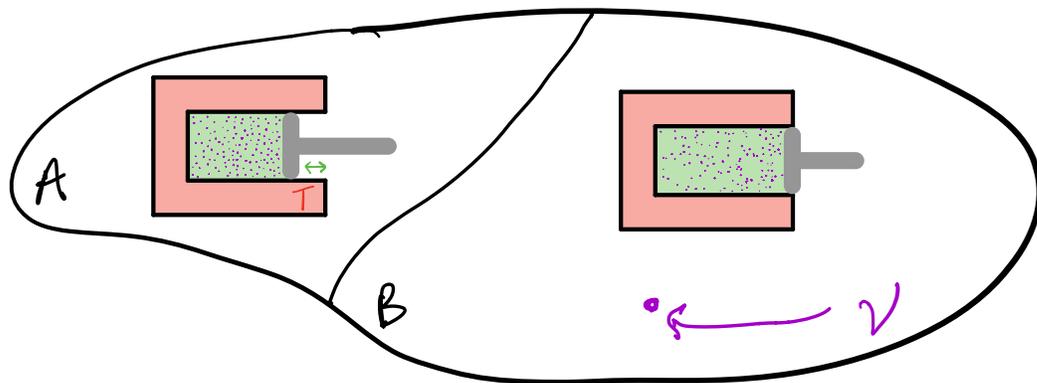


Imagine there were only
two possible volumes.

How do we partition probability across the two possibilities?



ν : all gas molecules locations & the location of the piston



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

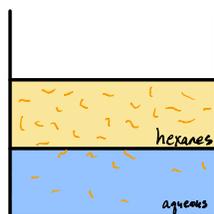
$$P(A) = \sum_{\nu \in A} P(\nu) = \sum_{\nu \in A} \frac{e^{-\beta E(\nu)}}{Q} = \frac{Q_A}{Q}$$

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

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

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.