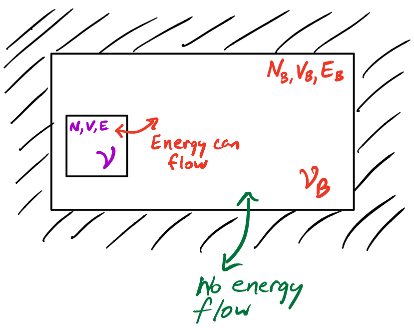
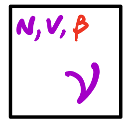
Lecture 9

Recall from last lecture...



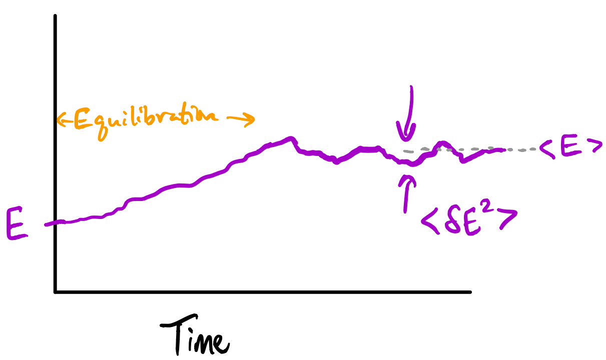


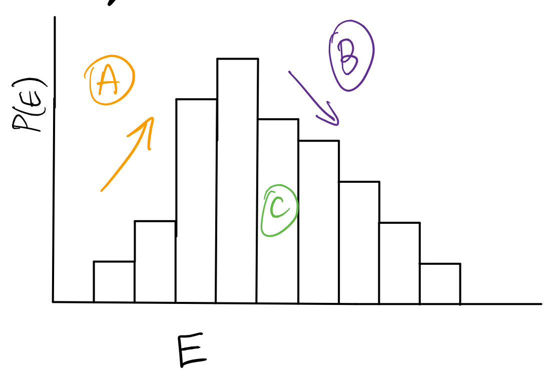
$$\boxed{P(\nu)=\frac{e^{-\beta E(\nu)}}{Z}}$$

"Canonical Distribution"

Go beyond the typical value $\langle E \rangle$.
Consider the whole distribution

$$P(E) \propto \Omega(E)\, e^{-\beta E}$$





Let's look back at our normalization constant Z.

We can view it as a *function* of β!

$$Z(\beta) = \sum_{\nu} e^{-\beta E(\nu)}$$

Notice...

$$\frac{\partial Z}{\partial \beta} = \sum_{\nu} -E(\nu)\, e^{-\beta E(\nu)}$$

$$\boxed{P(\nu) = \frac{e^{-\beta E(\nu)}}{Z}}$$

$$= -\sum_{\nu} E(\nu)\, Z(\beta)\, P(\nu)$$

$$= -Z(\beta) \sum_{\nu} E(\nu) P(\nu)$$

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

$Z(\beta)$ is called a partition function - we will see why later.

$\ln Z(\beta)$ is an example of a generating function.

Generating functions generate expectation values by taking derivatives.

So let's take a second derivative...

$$\frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left(\frac{\partial \ln Z(\beta)}{\partial \beta} \right)$$

$$= \frac{\partial}{\partial \beta}\left(- \langle E \rangle \right)$$

$$= - \underbrace{\frac{\partial \langle E \rangle}{\partial T}} \left(\frac{\partial T}{\partial \beta} \right) \quad \text{chain rule}$$

$$= + C_V / k_B \beta^2$$

C_V is the heat capacity (at constant volume)

Aside:

$$\beta = \frac{1}{k_B T}$$

$$\Rightarrow T = \frac{1}{k_B \beta}$$

$$\Rightarrow \frac{\partial T}{\partial \beta} = -\frac{1}{k_B \beta^2}$$

$$\Rightarrow \boxed{\frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} = k_B T^2 C_V}$$

But wait, there's more!

(There is another way to think about the 2nd derivative of $\ln Z(\beta)$ wrt β)

$$Z(\beta) = \sum_\nu e^{-\beta E(\nu)}$$

$$\Rightarrow \quad \frac{\partial \ln Z(\beta)}{\partial \beta} = \frac{-\sum_\nu E(\nu) e^{-\beta E(\nu)}}{Z(\beta)} = -\langle E \rangle$$

Take another derivative wrt β here

Take one more derivative

"Quotient Rule"

$k_B T^2 C_V$

$$\frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} = \frac{\frac{\partial}{\partial \beta}\left(-\sum_\nu E(\nu) e^{-\beta E(\nu)}\right) Z(\beta) - \frac{\partial}{\partial \beta}\left(Z(\beta)\right)\left[-\sum_\nu E(\nu) e^{-\beta E(\nu)}\right]}{Z(\beta)^2}$$

$$= \frac{\left(\sum_\nu E(\nu)^2 e^{-\beta E(\nu)}\right) Z(\beta) - \left[-\sum_\nu E(\nu) e^{-\beta E(\nu)}\right]^2}{Z(\beta)^2}$$

$$= \sum_\nu E(\nu)^2 \underbrace{\frac{e^{-\beta E(\nu)}}{Z(\beta)}}_{P(\nu)} - \left[\sum_\nu E(\nu) \underbrace{\frac{e^{-\beta E(\nu)}}{Z(\beta)}}_{P(\nu)}\right]^2$$

$$= \langle E^2 \rangle - \langle E \rangle^2 = \langle \delta E^2 \rangle$$

$$\therefore \quad \boxed{\langle \delta E^2 \rangle = k_B T^2 C_V}$$

WOW!

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

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

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

1st cumulant (mean)

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

2nd cumulant (variance)

What's so wow about $\boxed{\langle \delta E^2 \rangle = k_B T^2 C_v}$?

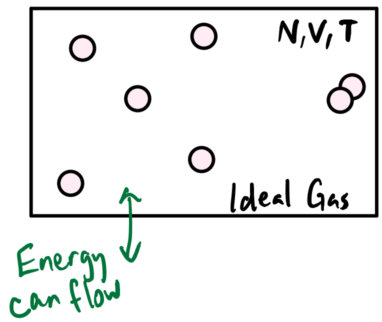
LHS is all about fluctuations.

RHS is straight from classical thermodynamics - huge systems, no fluctuations

Response Function: How does $\langle E \rangle$ respond to a change in T?

An example of a "fluctuation-response relation"

This statistical approach goes <u>beyond</u> 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 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)

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:

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

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?

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

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

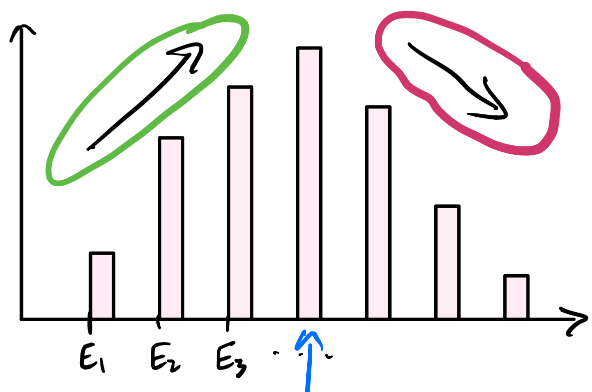
$$Q(N,V,T) = \sum_{\nu} e^{-\beta E(\nu)} = \sum_{E} e^{S(N,V,E)/k_B}\, e^{-\beta E}$$

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

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 <u>either</u> a sum or an integral depending on if the energies are discrete or continuous.

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



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

More system states as E increases

E^*

Fewer bath states as E increases

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

intensive, extensive, extensive, extensive, 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?

$$= e^{\beta(TS(N,V,E^*)-E^*)} \Big(\underset{\uparrow\, E=E^* \text{ term of the sum}}{1} + \underbrace{e^{-\beta(\text{Big}\,\#)} + e^{-\beta(\text{Different Big}\,\#)} + \dots}_{\text{all of these will be negligible in the large system limit}} \Big]$$

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

thermodynamic limit (large system)

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

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

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

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

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

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

Next time...

1. What is partition-y about a partition function?
2. What is free about a free energy?