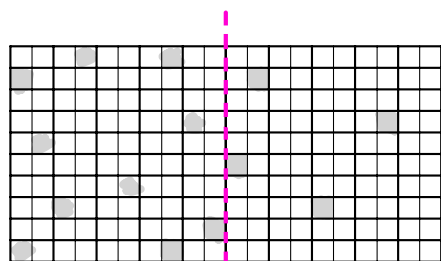
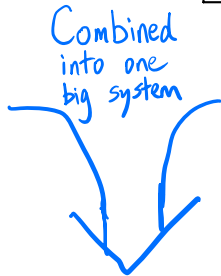
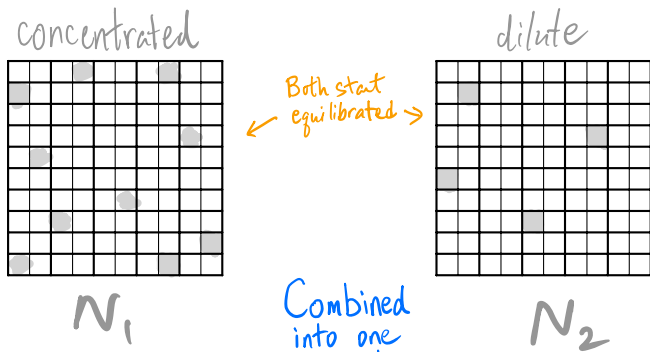


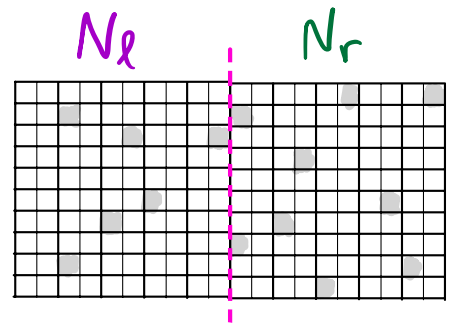
# Lecture 5

Recall from last lecture...

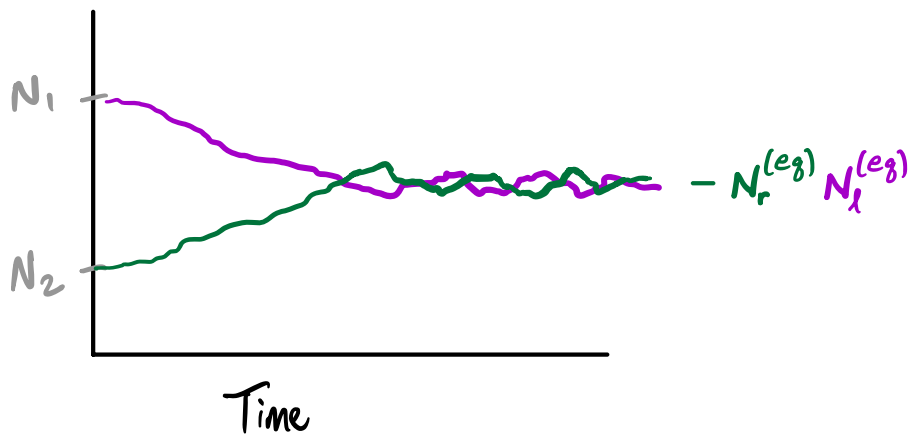


Ink molecules can now cross the imaginary partition

Time  
(Re-equilibrate)



Equilibration Time



1. Why do particles re-partition?

2. What is the condition that determines the equilibrium partitioning?

Equilibration will induce changes (repartitionings) until the new combined system is in its most likely partitioning - the partitioning with the most microstates

The most likely partitioning will maximize ...

$$S(\Delta N) = S_l(N_l^{(eq)} + \Delta N) + S_r(N_r^{(eq)} - \Delta N)$$

[or equivalently minimizing  $-S(\Delta N)$ ]

$$\begin{aligned} \Rightarrow 0 &= \left. \frac{dS(\Delta N)}{d\Delta N} \right|_{\Delta N = \Delta N^{(eq)}} \\ &= \left( \frac{\partial S}{\partial N} \right)_{E, V} \Big|_{\Delta N = \Delta N^{(eq)}} - \left( \frac{\partial S}{\partial N} \right)_{E, V} \Big|_{\Delta N = \Delta N^{(eq)}} \end{aligned}$$

Remember  $N_l = N_l^{(eq)} + \Delta N$   
 $N_r = N_r^{(eq)} - \Delta N$  and  $\Delta N^{(eq)} = 0$

$$= \left( \frac{\partial S}{\partial N} \right)_{E, V} \Big|_{N_l = N_l^{(eq)}} - \left( \frac{\partial S}{\partial N} \right)_{E, V} \Big|_{N_r = N_r^{(eq)}}$$

So at equilibrium it must be the case that...

$$\left( \frac{\partial S}{\partial N} \right)_{E, V} \bigg|_{N_l = N_l^{(eq)}} = \left( \frac{\partial S}{\partial N} \right)_{E, V} \bigg|_{N_r = N_r^{(eq)}}$$

Particles repartition until the slopes of entropy with respect to changing particle number are equal.

The exact same repartitioning game can be played with energy (rather than particles) flowing between two systems.

⇒ Energy repartitions until  $\underbrace{\left( \frac{\partial S}{\partial E} \right)_{N, V}}_{\frac{1}{T}} = \underbrace{\left( \frac{\partial S}{\partial E} \right)_{N, V}}_{\frac{1}{T}}$

$$\boxed{\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N, V}}$$

← consistent

$$dE = T dS - p dV + \mu dN$$

Let's view our thermodynamic expression

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

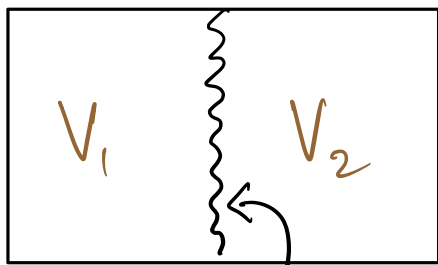
in terms of statistical mechanics (counting that is)

We are thinking of  $S(E, V, N)$  which counts the # of microstates (log scale) as a function of the three constraints:

$E, V, N$

But some day we may choose to change/relax one of the constraints. By how much would  $S$  change in response?

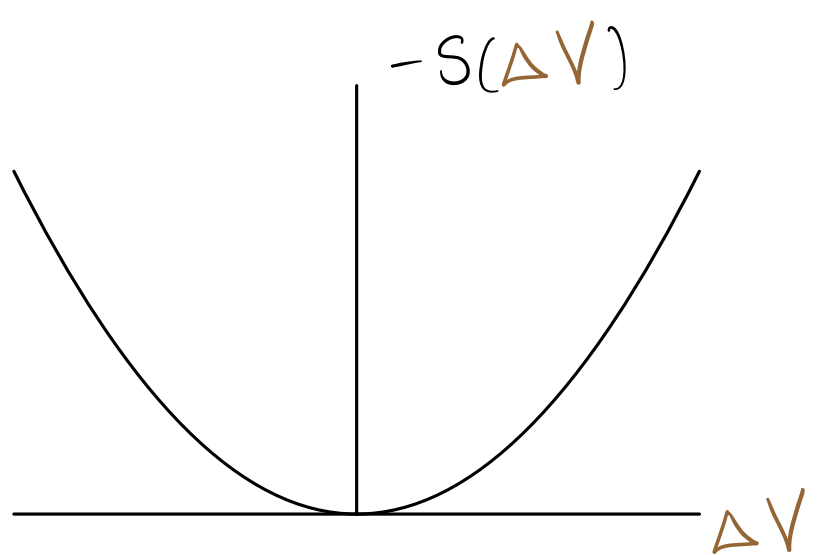
$$dS = \underbrace{\left( \frac{\partial S}{\partial E} \right)_{V, N}}_{\frac{1}{T}} dE + \underbrace{\left( \frac{\partial S}{\partial V} \right)_{E, N}}_{\text{something to do with pressure}} dV + \underbrace{\left( \frac{\partial S}{\partial N} \right)_{E, V}}_{\text{something to do with chemical potential}} dN$$



deformable,  
impermeable  
membrane

$$V_1 = V_1^{(eq)} + \Delta V$$

$$V_2 = V_2^{(eq)} - \Delta V$$



$$\frac{dS}{d\Delta V} = 0 \text{ at equilibrium.}$$

$$\Rightarrow \left( \frac{\partial S_1}{\partial V} \right)_{N_1, E_1} = \left( \frac{\partial S_2}{\partial V} \right)_{N_2, E_2} \text{ at equilibrium.}$$

After volumes have equilibrated, what do you expect to equal on both sides of the membrane?

Pressure!

$$So \left( \frac{\partial S}{\partial V} \right)_{E, N} = P ? \quad \text{Not quite}$$

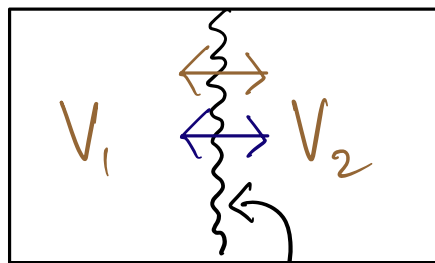
Units

$$S = k_B \ln \Omega \quad \frac{\text{Energy}}{\text{Temp.}}$$

$$\left( \frac{\partial S}{\partial V} \right)_{E, N} \quad \frac{\text{Energy}}{\text{Volume} \times T}$$

$$P \quad \frac{\text{Energy}}{\text{Volume}}$$

$$\Rightarrow \left( \frac{\partial S}{\partial V} \right)_{E, N} = \frac{P}{T}$$



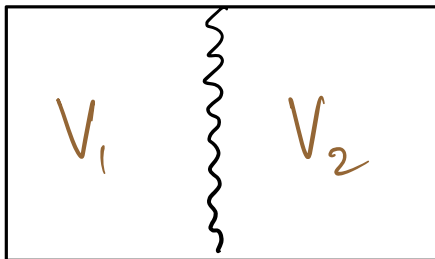
deformable,  
impermeable  
membrane

Similarly, when particles are exchanged

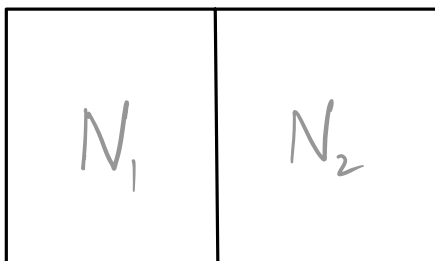
$$\left( \frac{\partial S}{\partial N} \right)_{E, V} = - \frac{\mu}{T}$$

Why the minus sign?

Particles flow from high  $\mu$  to low  $\mu$ .



Suppose  $p_1 > p_2 \Rightarrow V_1$  grows



Suppose  $\mu_1 > \mu_2 \Rightarrow N_1$  shrinks

They are opposite (just a convention)

$$dS = \underbrace{\left(\frac{\partial S}{\partial E}\right)_{V,N}}_{\frac{1}{T}} dE + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{E,N}}_{\frac{p}{T}} dV + \underbrace{\left(\frac{\partial S}{\partial N}\right)_{E,V}}_{-\frac{\mu}{T}} dN$$

Here we are thinking of  $S(E, V, N)$

Count states  $\rightarrow$  as a function of constraints

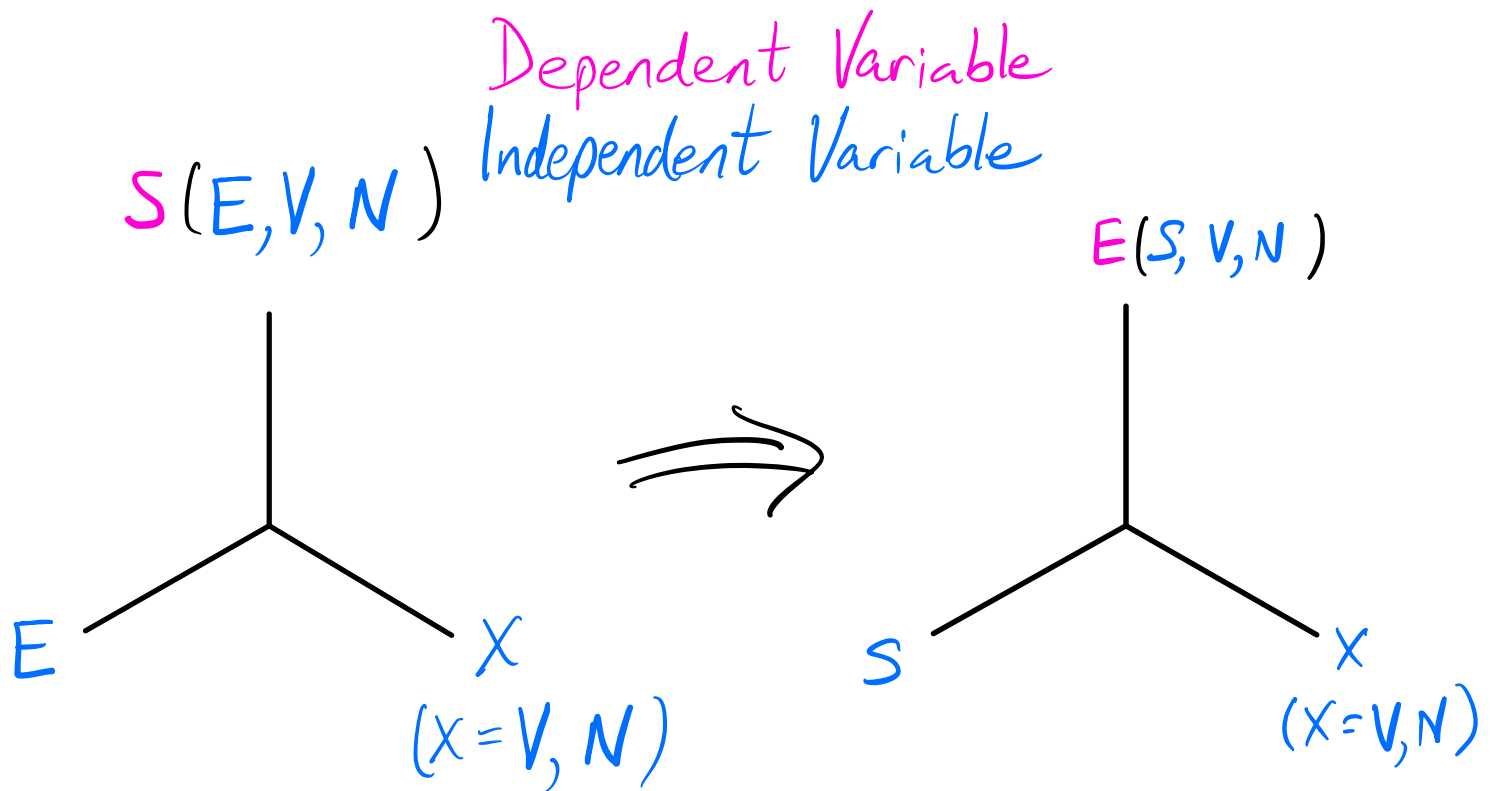
Rearranging gives

$$dE = T dS - p dV + \mu dN$$

Here we are thinking of  $E(\underline{S}, V, N)$

$\uparrow$  Tuning entropy rather than a physical constraint?





Rotate, switching an independent variable with the dependent one.

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

$E(S, N, V)$

↑

↑

Two macroscopic (+ extensive) constraints that you can really think of tuning in an experiment

↗

↘

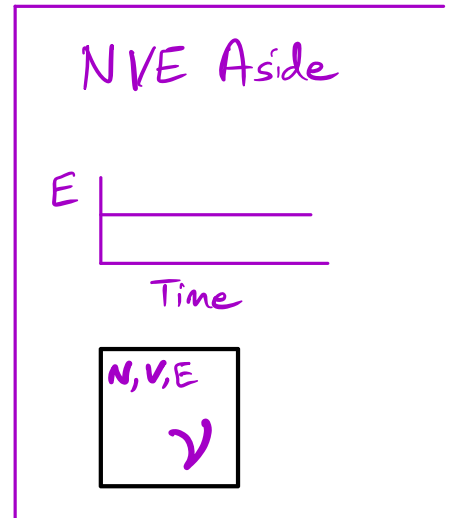
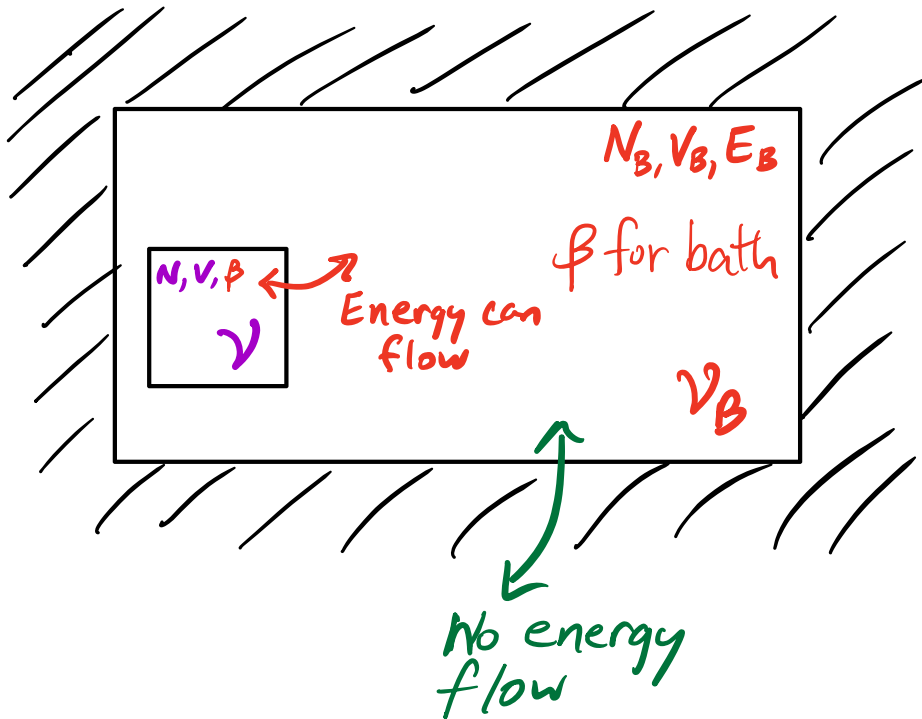
Awkward

How can we tune an entropy knob?!

If we are not directly controlling  $E$ , what could we control?

$NVT$

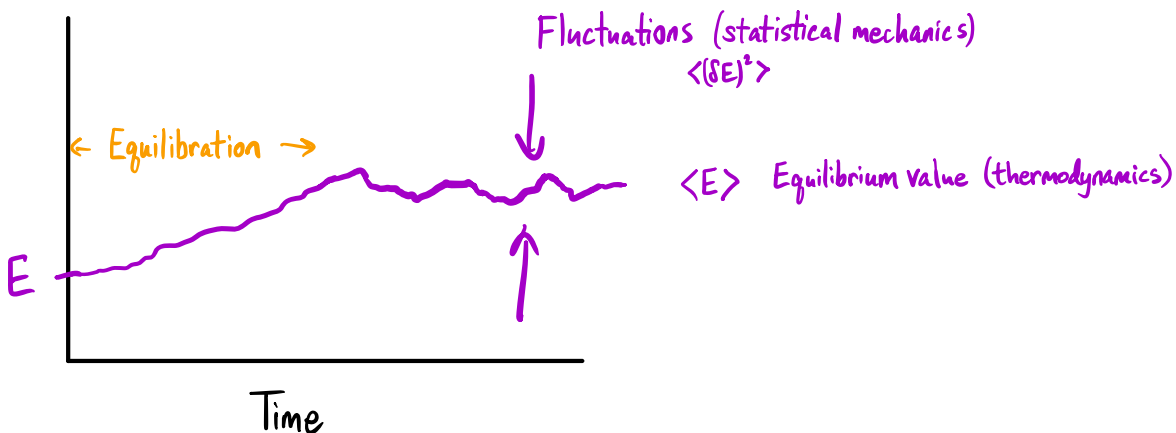
How do we relax the constant energy constraint?



Now we have a fluctuating  $E$  but a fixed  $\beta$ .

Why a fixed value of  $\beta$ ?

$$[\beta = \frac{1}{k_B T} = \left( \frac{\partial S}{\partial E} \right)_{N, V} \text{ set by the bath}]$$



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

$$\langle (\delta E)^2 \rangle : \text{Variance}$$

Some questions:

1. What is the expected equilibrium energy and how does it depend on the bath temperature?
2. What sets the scale of the fluctuations?

We have already seen that

$$\boxed{\begin{array}{l} N, V, \beta \\ \nu \end{array}}$$

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

- Why is this merely proportional and not equal?  
We need to normalize the distribution.

- How do I normalize?

$$1 = \sum_{\nu} P(\nu) \quad \text{and} \quad P(\nu) = \frac{e^{-\beta E(\nu)}}{\sum_{\nu} e^{-\beta E(\nu)}}$$

Normalization Constant

"Canonical Distribution"

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

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

Let's look back at our normalization constant  $Q$ .

We can view it as a function of  $\beta$ !

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

Notice...

$$\begin{aligned} \frac{\partial Q}{\partial \beta} &= \sum_{\nu} -E(\nu) \underbrace{e^{-\beta E(\nu)}}_{\text{Boltzmann factor}} \\ &= - \sum_{\nu} E(\nu) P(\nu) Q(\beta) \\ &= -Q(\beta) \sum_{\nu} E(\nu) P(\nu) \\ &= -Q(\beta) \langle E \rangle \end{aligned}$$

[  $Q(\beta)$  does not depend on  $\nu$  ]

$$\Rightarrow \frac{1}{Q(\beta)} \frac{\partial Q}{\partial \beta} = -\langle E \rangle$$

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

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

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

Generating functions generate expectation values by taking derivatives.

So let's take a second derivative...

$$\begin{aligned} \frac{\partial^2 \ln Q(\beta)}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \left( \frac{\partial \ln Q(\beta)}{\partial \beta} \right) \\ &= \frac{\partial}{\partial \beta} (-\langle E \rangle) \end{aligned}$$

Aside:

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

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

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

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

$$= \frac{C_V}{k_B \beta^2} \quad C_V \text{ is the heat capacity (at constant volume)}$$

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

But wait, there's more!

(There is another way to think about the 2<sup>nd</sup> derivative of  $\ln Q(\beta)$  wrt  $\beta$ )

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

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

Take another derivative wrt  $\beta$  here  $\downarrow$

"Quotient Rule"

Take one more derivative

$$k_B T^2 C_V$$

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

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

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

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

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

Wow!

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

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

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

1<sup>st</sup> cumulant  
(mean)

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

2<sup>nd</sup> cumulant  
(variance)

What's so Wow about  $\langle (\delta E)^2 \rangle = k_B T^2 C_V$  ?

LHS is all about fluctuations

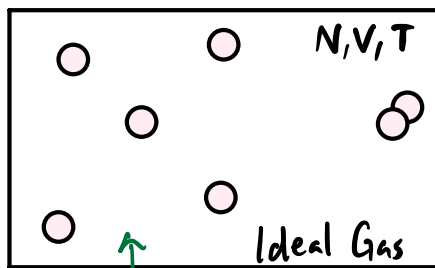
RHS is straight from classical thermodynamics -  
huge systems, no fluctuations

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

An example of a "fluctuation-response relation"



This statistical approach goes 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,  $\frac{\langle E \rangle}{N} \rightarrow \frac{3}{2} k_B T$  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:

$$Q(N, V, T) = \sum_V e^{-\beta E(V)} = \sum_E \underbrace{\Omega(N, V, E)}_{\text{Number of ways the system could have that energy (degeneracy) given the fixed } N+V.} e^{-\beta E}$$

$\uparrow$  Number of ways the bath can accommodate.

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  $\Omega$ ?

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

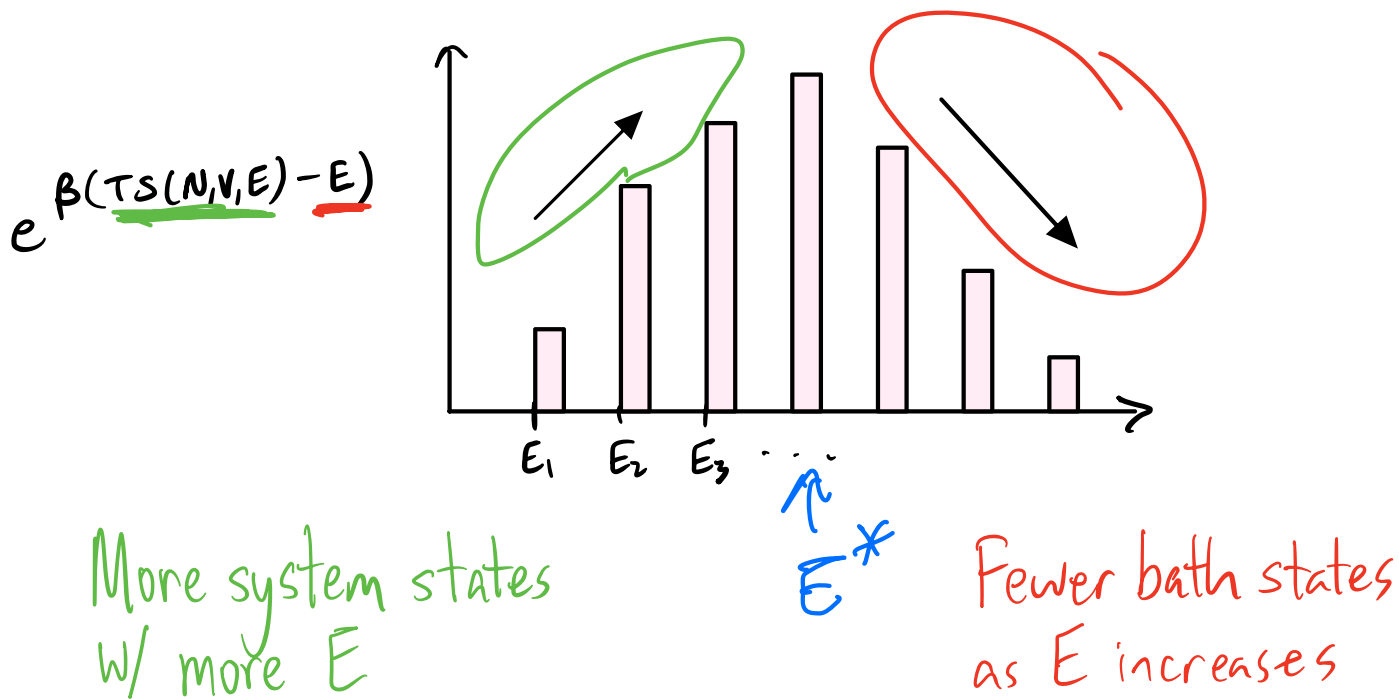
$$\Rightarrow \Omega(N, V, E) = e^{S(N, V, E)/k_B}$$

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

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

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.



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

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

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

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

More to come ...