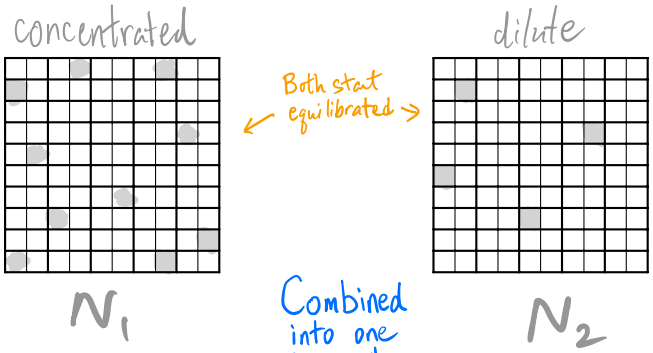
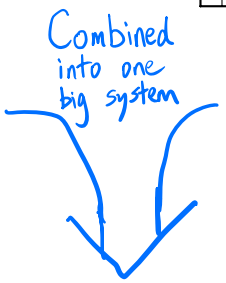
Lecture 5

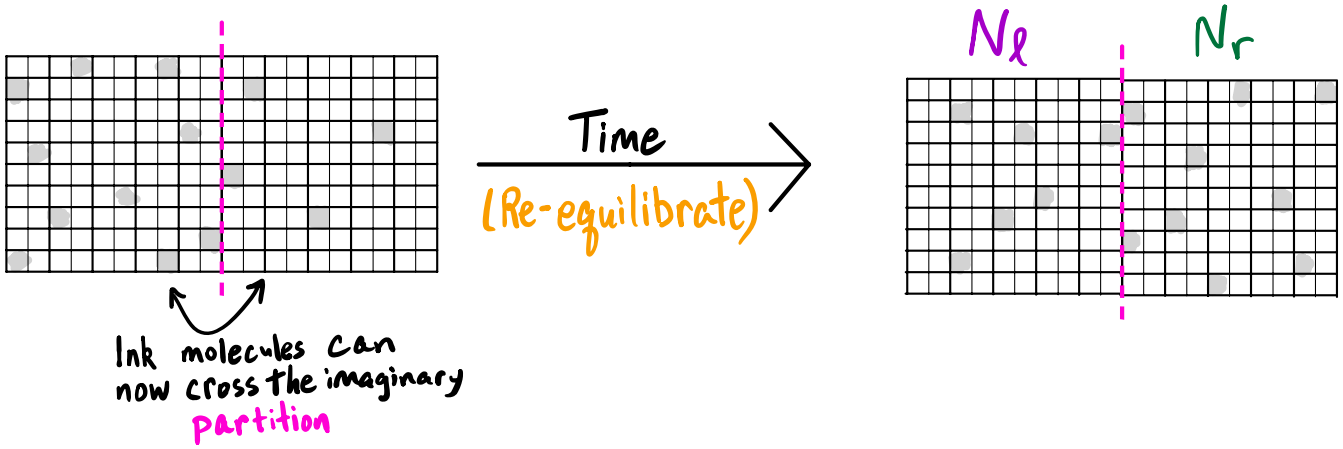
Recall from last lecture...

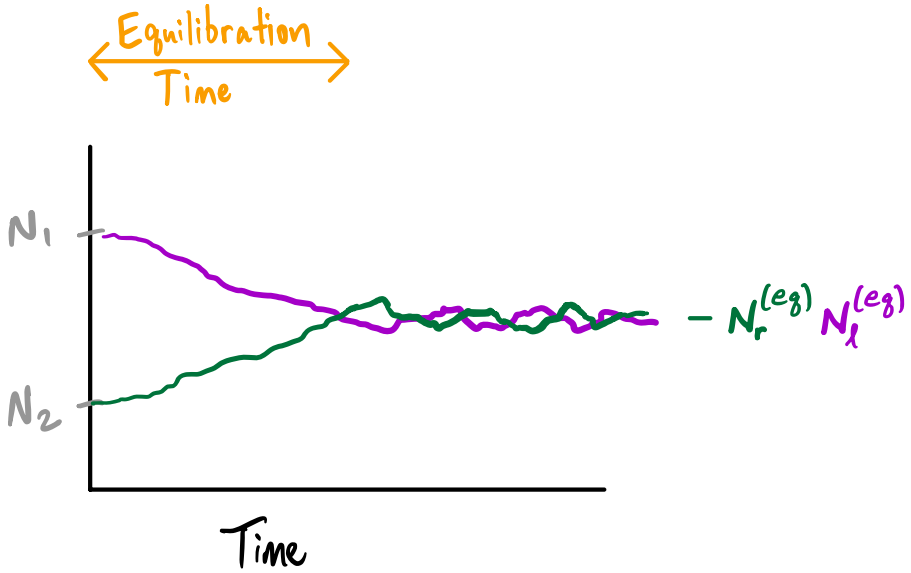


1. Why do particles repartition?



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...

$$S(\Delta N) = S_\ell(N_\ell^{(eq)} + \Delta N) + S_r(N_r^{(eq)} - \Delta N)$$

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

$$\Rightarrow \quad 0 = \left.\frac{dS(\Delta N)}{d\Delta N}\right|_{\Delta N = \Delta N^{(eq)}}$$

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

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

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

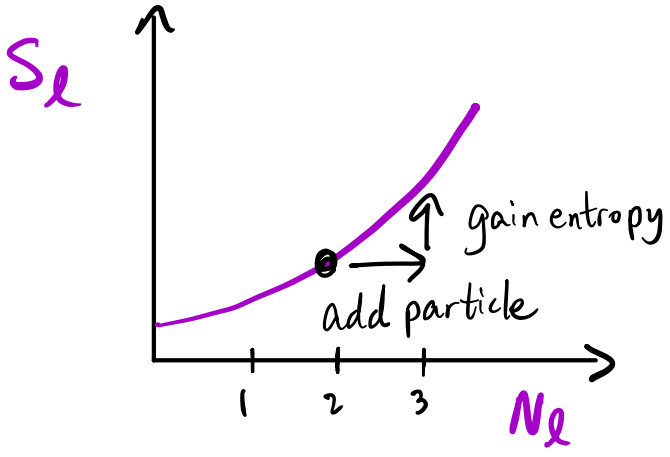
So at equilibrium it must be the case that...

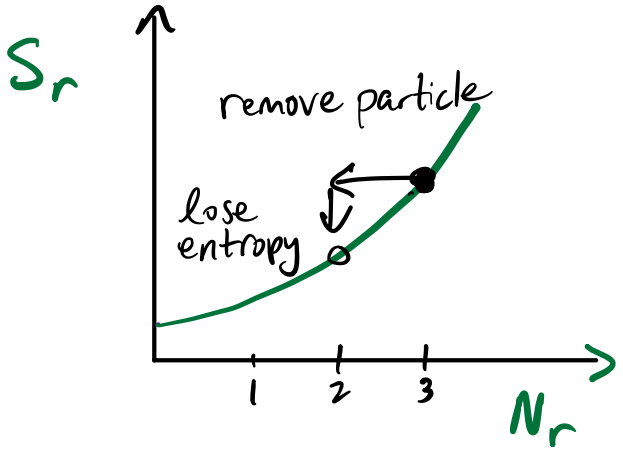
$$\left(\frac{\partial S}{\partial N}\right)_{E,V}\Bigg|_{N_\ell = N_\ell^{(eq)}} = \left(\frac{\partial S}{\partial N}\right)_{E,V}\Bigg|_{N_r = N_r^{(eq)}}$$

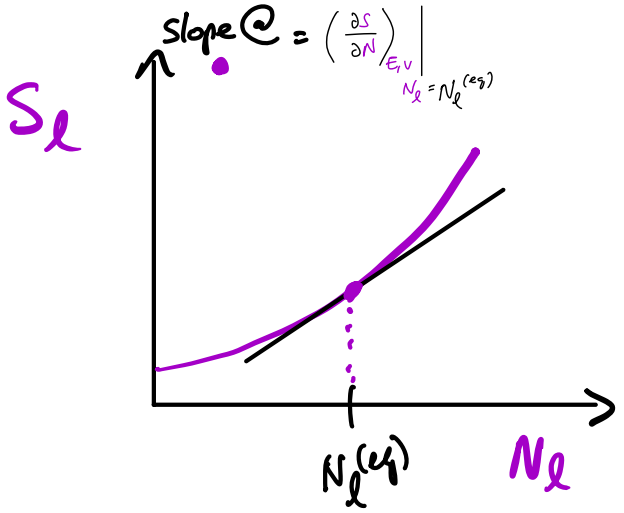
Particles reparition until the slopes of entropy with respect to changing particle number are equal.

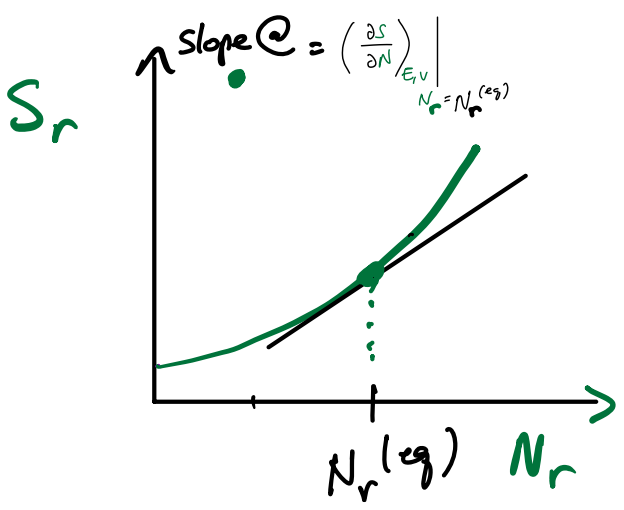
An illustration...

Each system has its own function $S(N)$ that tells how many more/fewer states are possible as the constraint N is altered.

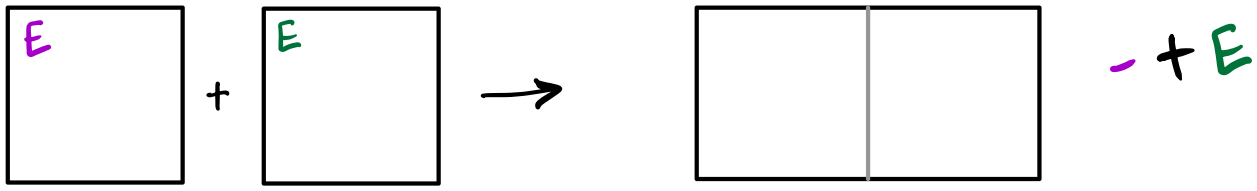








The exact same repartitioning game can be played with energy (rather than particles) flowing between two systems.

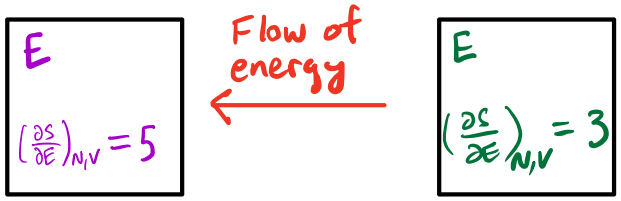


Energy repartitions until $\left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$

Let's think about our colloquial meaning of "temperature"

Energy flows until $T = T$

So... $T = \left(\frac{\partial S}{\partial E}\right)_{N,V}$?



Flow of energy goes from low $\left(\frac{\partial S}{\partial E}\right)_{N,V}$ to high $\left(\frac{\partial S}{\partial E}\right)_{N,V}$.

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

$$dS = \frac{dE}{T} + \frac{p\,dV}{T} - \frac{\mu\,dN}{T}$$

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

consistent

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

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

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

Let's view our thermodynamic expression

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

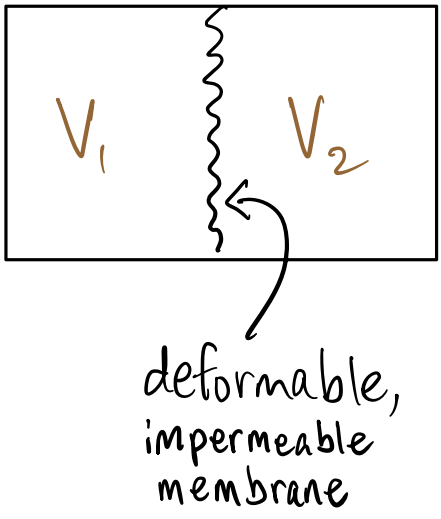
in terms of statistical mechanics (counting that is)

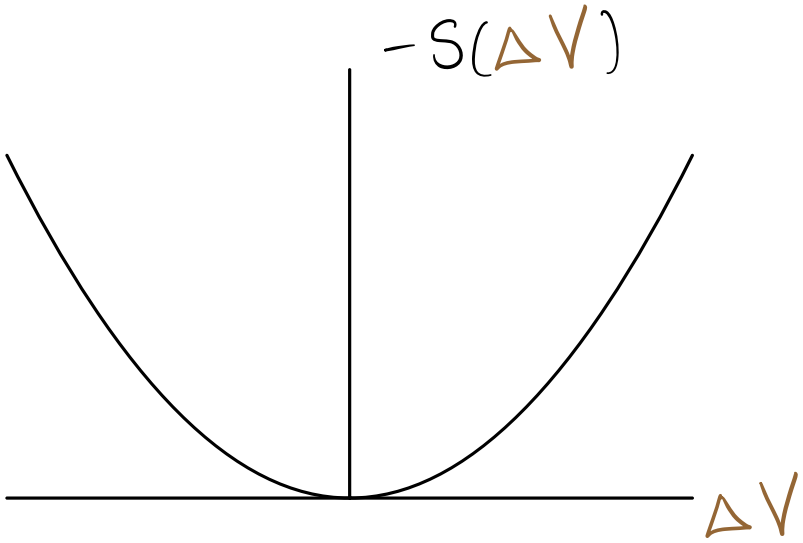
We are thinking of $S(E,V,N)$ which counts the # of microstates (log scale) as a function of the three constraints:

$$E, V, N$$

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

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





$$V_1 = V_1^{(eq)} + \Delta V$$
$$V_2 = V_2^{(eq)} - \Delta V$$

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

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

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

Pressure!

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

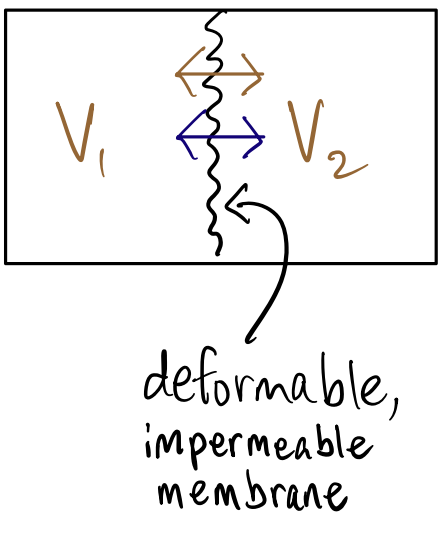
Units

$S = k_B \ln \Omega$ Energy / Temp.

$\left(\frac{\partial S}{\partial V}\right)_{E,N}$ Energy / Volume × T

p Energy / Volume

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

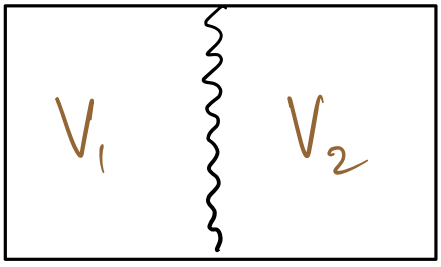


Similarly, when particles are exchanged

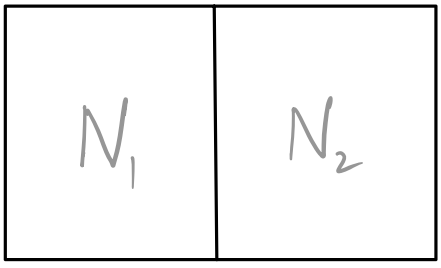
$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$

Why the minus sign?

Particles flow from high μ to low μ.



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 ↗ as a function of constraints

Rearranging gives

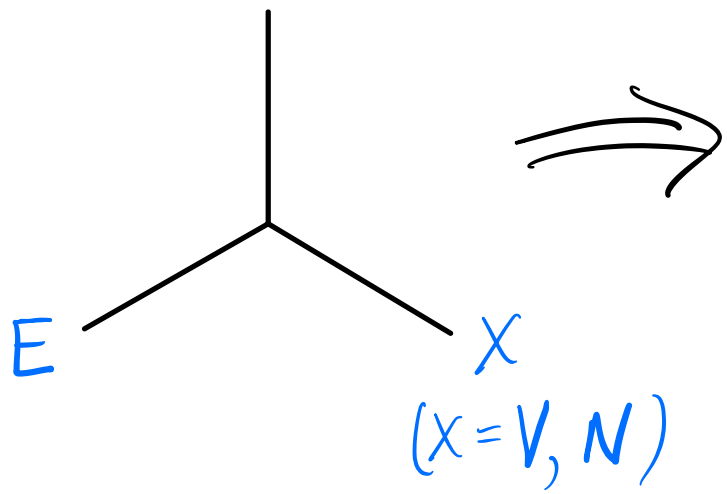
$$dE = TdS - pdV + \mu dN$$

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

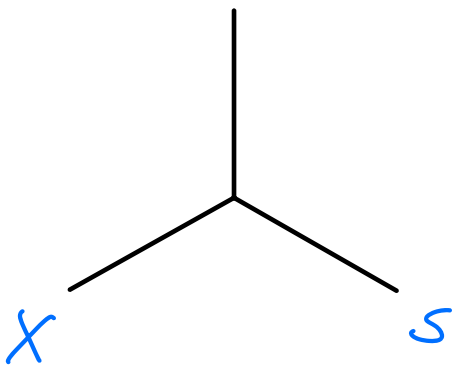
↑ Tuning entropy rather than a physical constraint?

Dependent Variable
Independent Variable

$S(E, V, N)$



$E(S, V, N)$



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

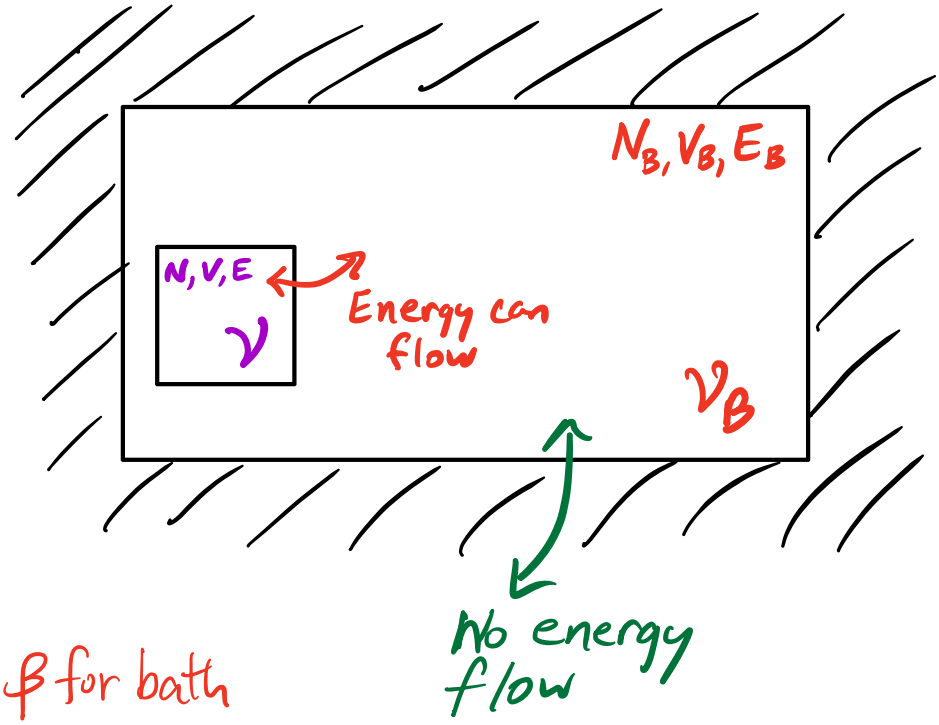
Awkward

How can we tune an entropy knob?!

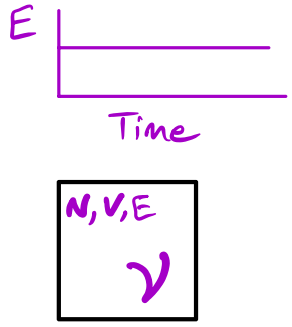
If we are not directly controlling E, what could we control?

N V T

How do we relax the constant energy constraint?



NVE Aside

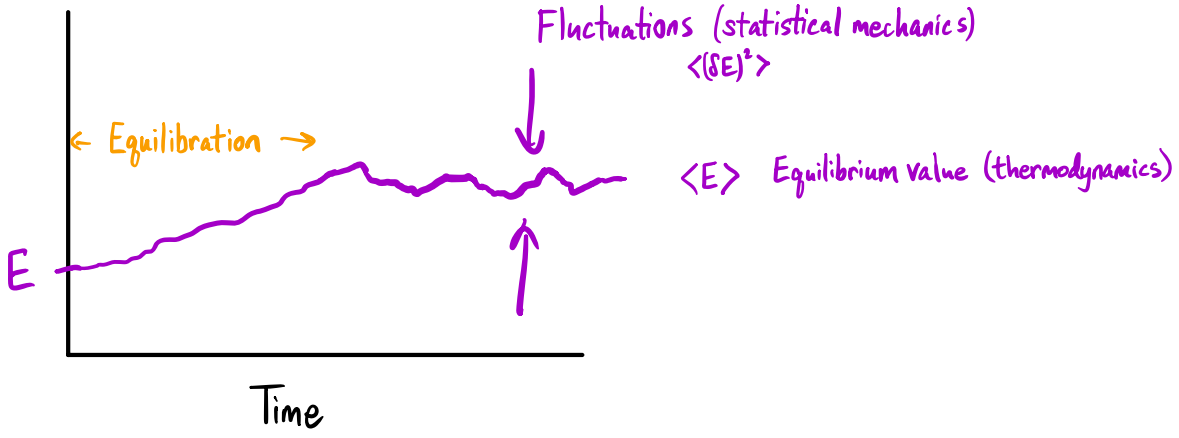


β for bath

Now we have a fluctuating E but a fixed β.

Why a fixed value of β?

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



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

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

- 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 β!

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

Notice...

$e^{-\beta E(\nu)}$ ← Boltzmann factor

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

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

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

[$Q(\beta)$ does not depend on ν]

$$= -Q(\beta) \langle E \rangle$$

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

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

$Q(\beta)$ 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...

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

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

Aside:

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

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

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

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

$$= \frac{C_V}{k_B \beta^2}$$

C_V 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 2nd derivative of $\ln Q(\beta)$ wrt β)

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

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

Take another derivative wrt β here ↓

"Quotient Rule"

Take one more derivative

$k_B T^2 C_V$

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

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

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

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

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

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

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

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

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)

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"