Lecture 4
Recall from last lecture...

System + (Thermal) Bath

N_T, V_T, E_T

N,V,E
ν

Energy can flow

No energy flow

N_B, V_B, E_B

ν_B

Variables with no flow:

$$N_T = N + N_B$$
$$V_T = V + V_B$$

Variable with flow:

$$E_T = E(\nu) + E_B(\nu_B)$$

System microstate

Bath Microstate

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

Boltzmann Distribution!

$$\beta = \left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)_{N_B, V_B} = \frac{1}{k_B}\left(\frac{\partial S_B}{\partial E_B}\right)_{N_B, V_B}$$

is an intensive property of a very large bath.

B : Boltzmann B : Bath

It measures how quickly the number of bath microstates increases when you put a little more energy in the bath.

β regulates (or perhaps characterizes) the propensity for a bath to donate or withdraw energy from the system.

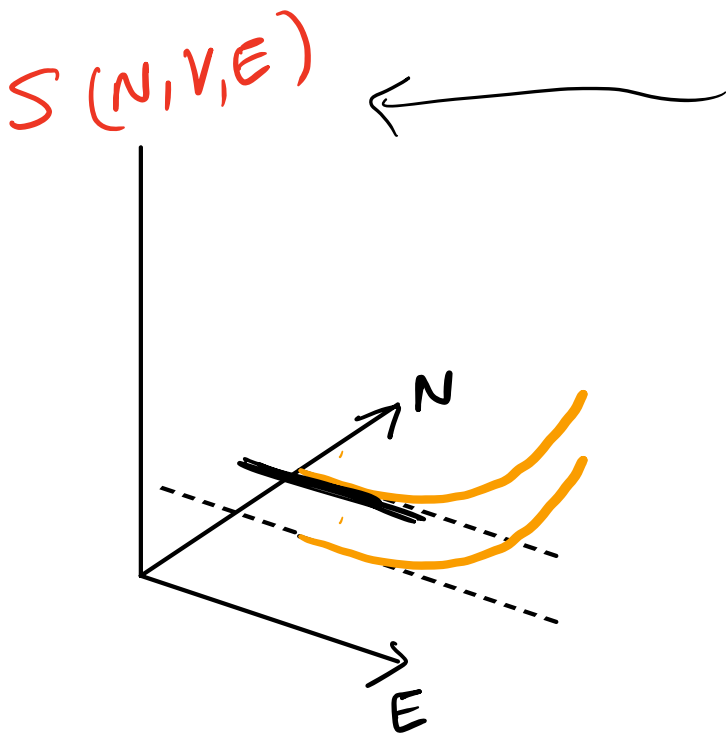Baths which are happy to donate energy:

High Temperature

Baths which are desperate to suck energy away:

Low Temperature

Why are we sure we should be talking about temperature?

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

$S(N, V, E)$

A function of multiple variables (each of the physical constraints we can think about macroscopically adjusting.)

Multivariable chain rule...

$$dS = \left(\frac{\partial S}{\partial N}\right)_{V,E} dN + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial E}\right)_{N,V} dE$$

Let's remember our thermodynamics:

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

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

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

From above...

$$\frac{1}{k_B}\left(\frac{\partial S_B}{\partial E_B}\right)_{N_B, V_B} = \beta$$

To be consistent with our notion of temperature in classical thermodynamics, it must be that...

$$\boxed{\beta = 1/k_B T}$$

What are the units of β? $1/$Energy

$e^{-\beta E}$ This had better be unitless

If we would have tried $S = \ln \Omega$ all the way back, we would have just deduced $\beta = \frac{1}{T}$. By looking at $e^{-\beta E}$, we would have seen that T would have needed units of energy.

I have thrown the word "temperature" around a lot today. Am I talking about...

Temperature of the system? $\frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)_{N,V}$

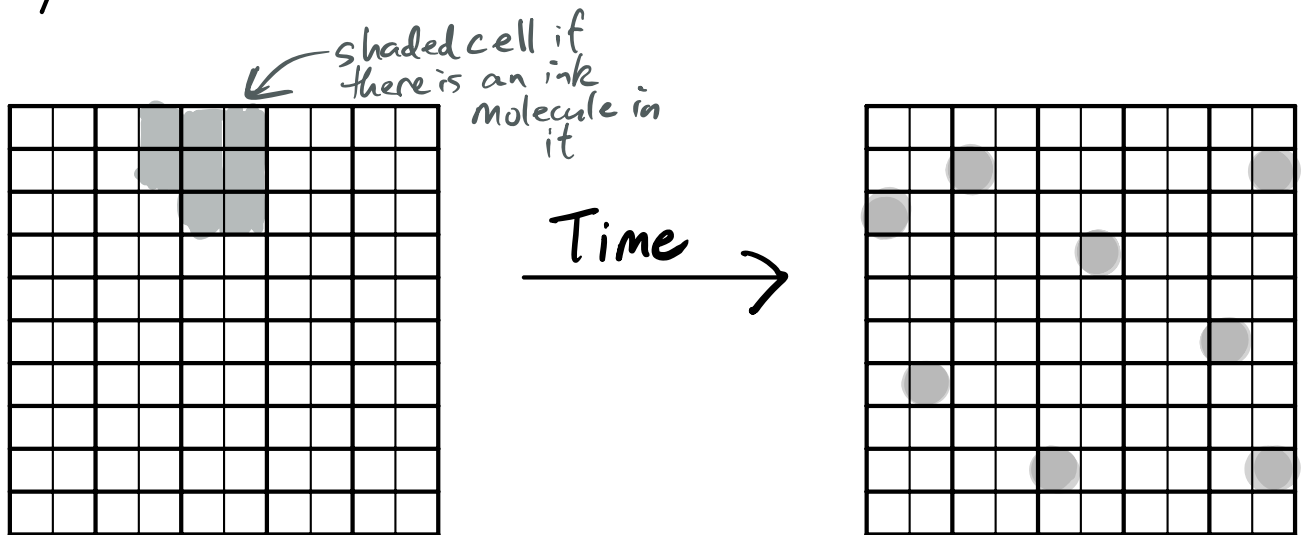Temperature of the bath? $\frac{1}{k_B}\left(\frac{\partial S_B}{\partial E_B}\right)_{N_B, V_B}$

When the system is in equilibrium with the bath, the temperatures are the same.

Let's dig into "equilibration"

System with fixed E, N, V (Think of an ink drop)

shaded cell if there is an ink molecule in it

Time →

Regardless of the initial condition, after enough time, the system explores the possible microstates and ends up in one of the most likely macrostates.

(dilute and dispersed macrostate)

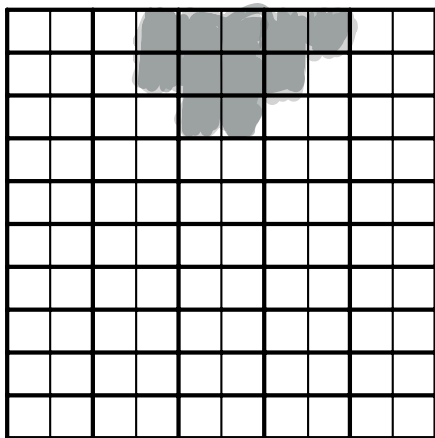Then "the system has equillibrated"

Memory of the initial condition is completely lost, so the probability of observing a particular equilibrium configuration is just a function of the extensive constraints:

$$N, V, E$$

How do these equilibrated systems change when they are put in contact with other equilibrated systems?
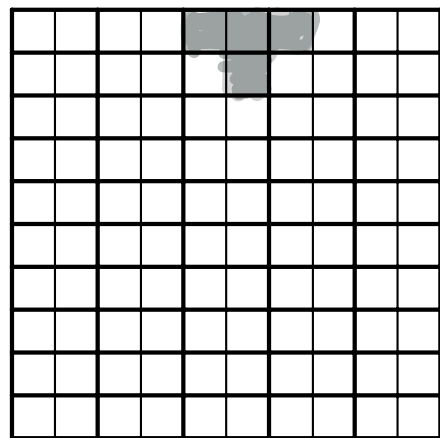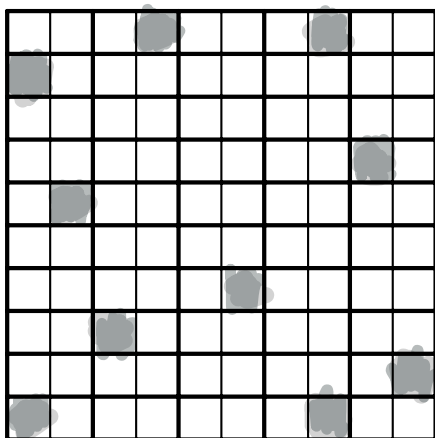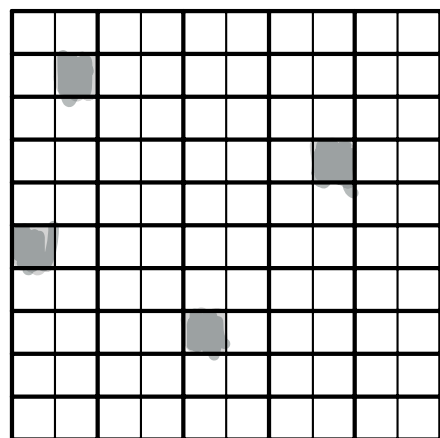
1. Why do they change at all?

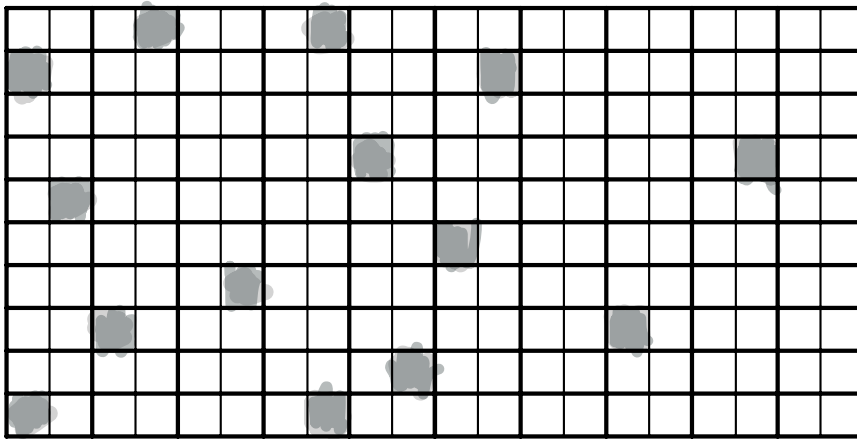N$_1$ concentrated

N$_2$ dilute
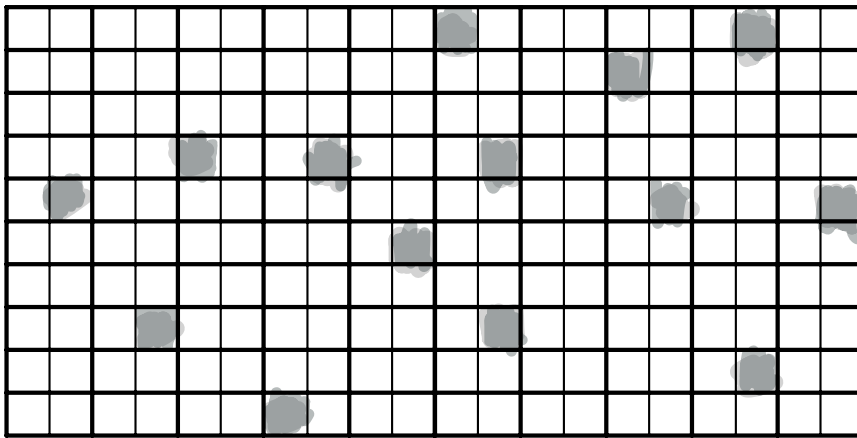

Not Equilibrated

Time

Time

Combine the two *equilibrated* systems
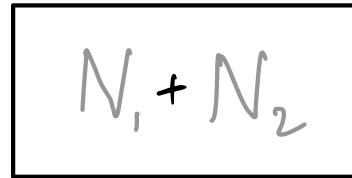

$N_1 + N_2$

Time

We have relaxed one constraint!

Before, we required __exactly__ N_1 on the left
and N_2 on the right. After combining, the
number of particles on the left and right can fluctuate.
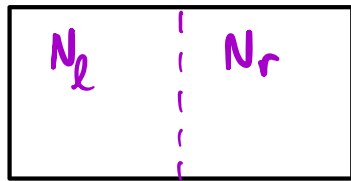
How many microstates for the combined system?

Before combining

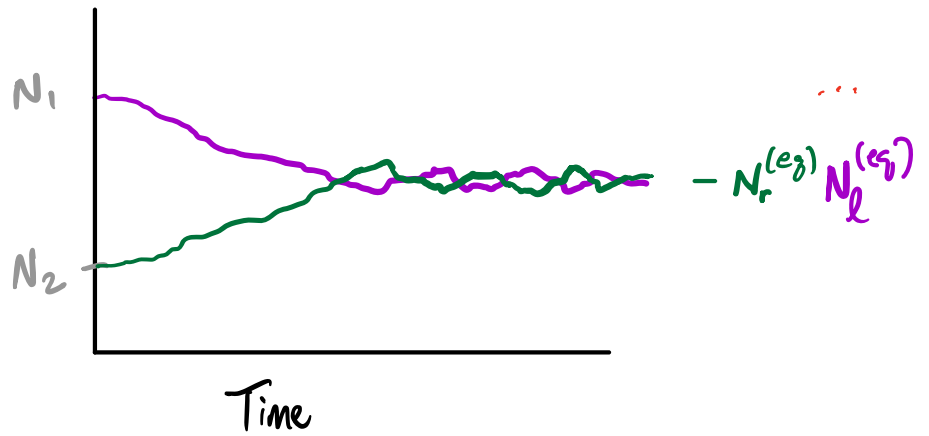$$N_1 \qquad N_2$$

Only count microstates
meeting both constraints

After combining

$$N_1 + N_2$$

We can still imagine splitting the box in
two and count how many ink molecules
are on each side

$$N_\ell \quad \vdots \quad N_r$$

There are lots of extra microstates which
can be explored for which $N_\ell \neq N_1$ and $N_r \neq N_2$.

Assume the left and right volumes are equal. It is
not hard to imagine that there will be the most microstates
when $N_\ell \approx N_r$

N_ℓ N_r

N_1

N_2

Time

$- N_r^{(eq)} \, N_\ell^{(eq)}$

1. Why do they change at all?

By counting microstates we expect ink to flow
from the concentrated to dilute side
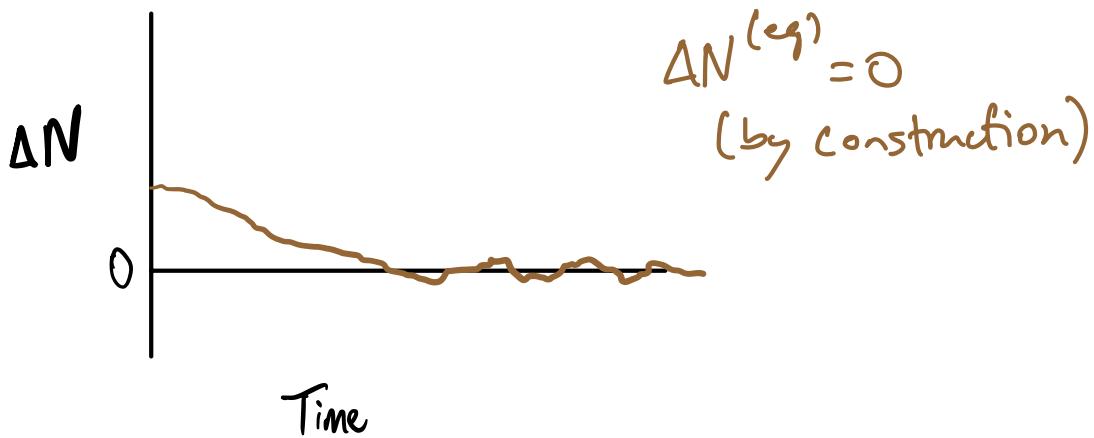until the concentrations are equal
(w/ fluctuations on top)

2. When does the transport between subsystems stop?

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

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

ΔN is defined to be the amount by
which N_ℓ exceeds $N_\ell^{(eq)}$
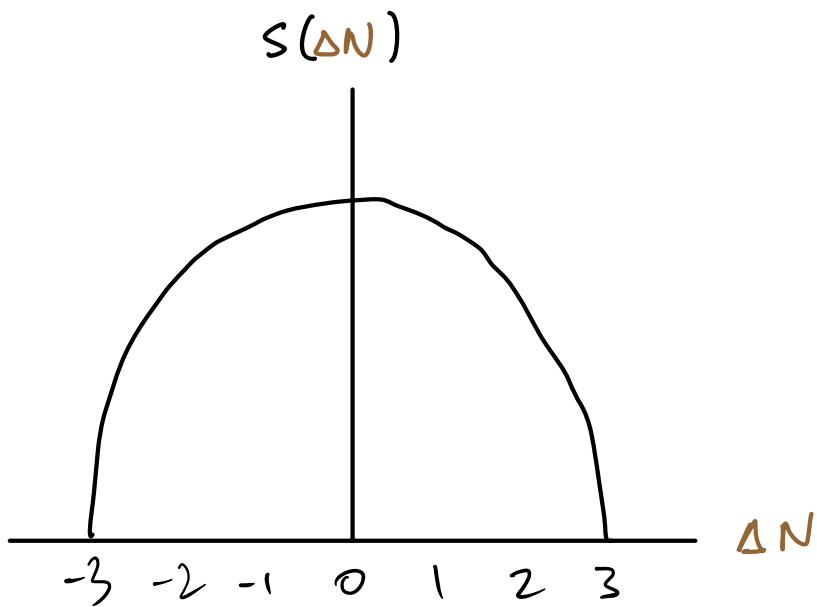
$\Delta N^{(eq)} = 0$
(by construction)

# of microstates of left system: $\Omega_\ell(N_\ell)$
# of microstates of right system: $\Omega_r(N_r)$
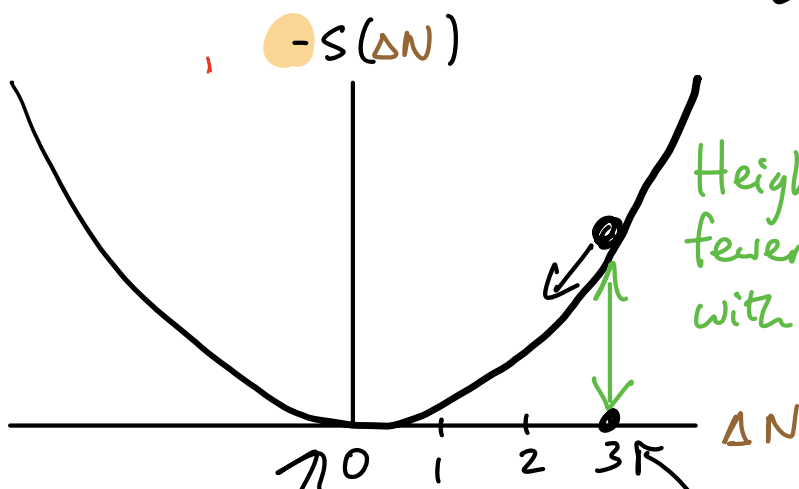# of microstates of joint system: $\Omega_\ell(N_\ell)\,\Omega_r(N_r)$

Entropy of left system: $S_\ell(N_\ell) = k_B \ln \Omega_\ell(N_\ell)$
Entropy of right system: $S_r(N_r) = k_B \ln \Omega_r(N_r)$
Entropy of joint system: $S_\ell(N_\ell) + S_r(N_r)$

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

Log of the # of microstates given a partitioning w/ ΔN particles shifted away from the equilibrium value toward the left side.

$S(\Delta N)$

ΔN

$-3 \ -2 \ -1 \ \ 0 \ \ 1 \ \ 2 \ \ 3$

Flip because we want to
visualize the dynamics like
a ball on a hill.

$-S(\Delta N)$

Height indicates how many
fewer microstates are available
with that partitioning

ΔN

$0 \ \ 1 \ \ 2 \ \ 3$

Specifies a partitioning with
3 extra particles on one side

There are the most
microstates of the joint
system with:
$N_\ell = N_\ell^{(eq)}$ and $N_r = N_r^{(eq)}$

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

$$= \left.\left(\frac{\partial S}{\partial N}\right)_{E,V}\right|_{N_\ell = N_\ell^{(eq)}} - \left.\left(\frac{\partial S}{\partial N}\right)_{E,V}\right|_{N_r = N_r^{(eq)}}$$
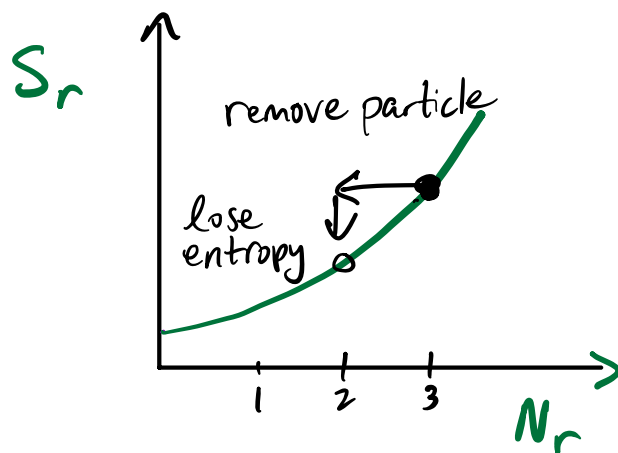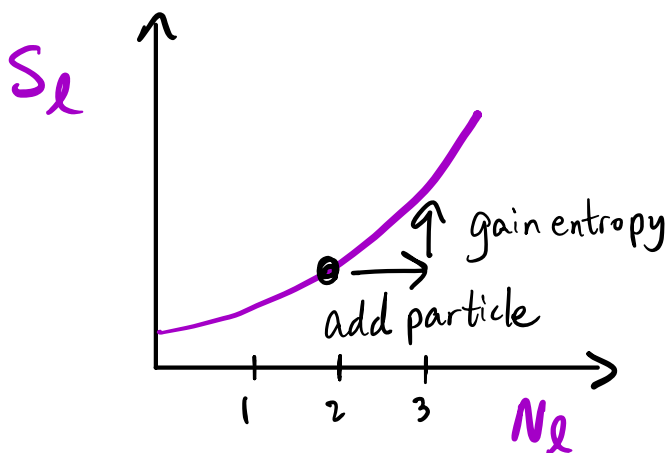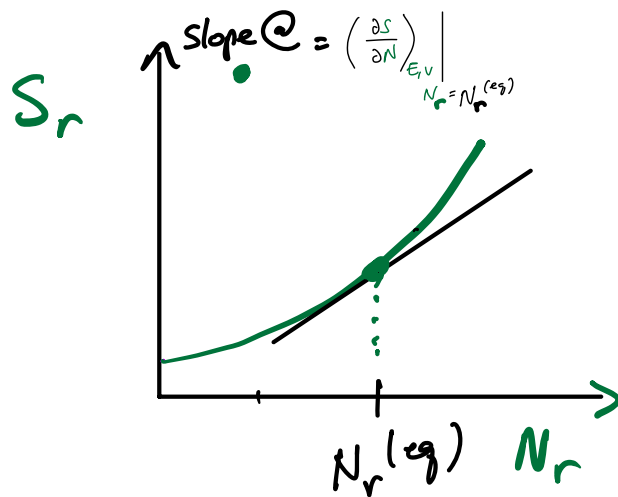
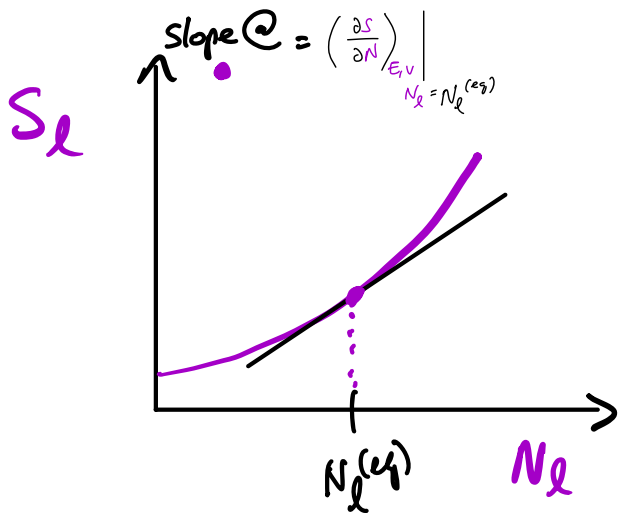So at equilibrium it must be the case that...

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

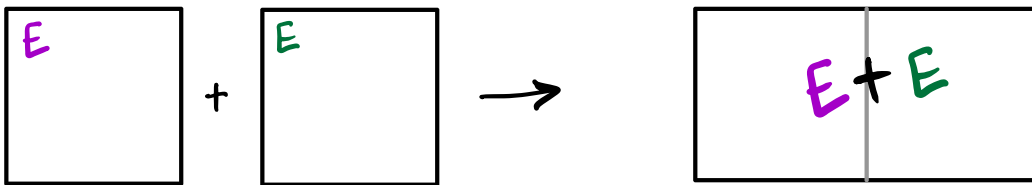Particles repartion until the slopes of entropy with respect to changing particle number are equal.

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.

S_ℓ

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

$N_\ell^{(eq)}$ N_ℓ

S_r

slope @ $= \left(\dfrac{\partial S}{\partial N}\right)_{E,V}\Bigg|_{N_r = N_r^{(eq)}}$

$N_r^{(eq)}$ N_r

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

E $+$ E $\longrightarrow$ E $+$ E

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

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

Energy flows until $T = T$

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

E

$\left(\frac{\partial S}{\partial E}\right)_{N,V} = 5$

Flow of energy

E

$\left(\frac{\partial S}{\partial E}\right)_{N,V} = 3$

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

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