Lecture 7

Recall from last lecture...

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

Boltzmann Distribution

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

B : Boltzmann
B : Bath

is an intensive property of a very large bath

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

$$\beta = 1/(k_B T)$$

Temperature of the system

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

Temperature of the bath

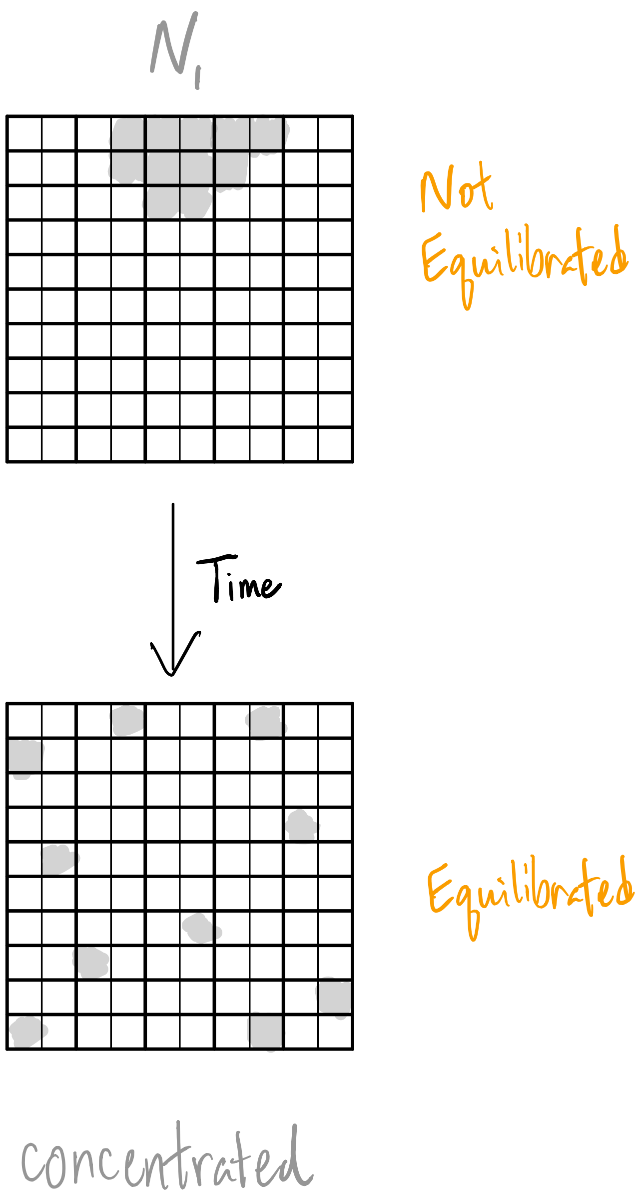
$$\frac{1}{k_B}\left(\frac{\partial S_B}{\partial E_B}\right)_{N_B, V_B}$$

When the system is <u>equilibrated</u> with the bath, the temperatures are the same.

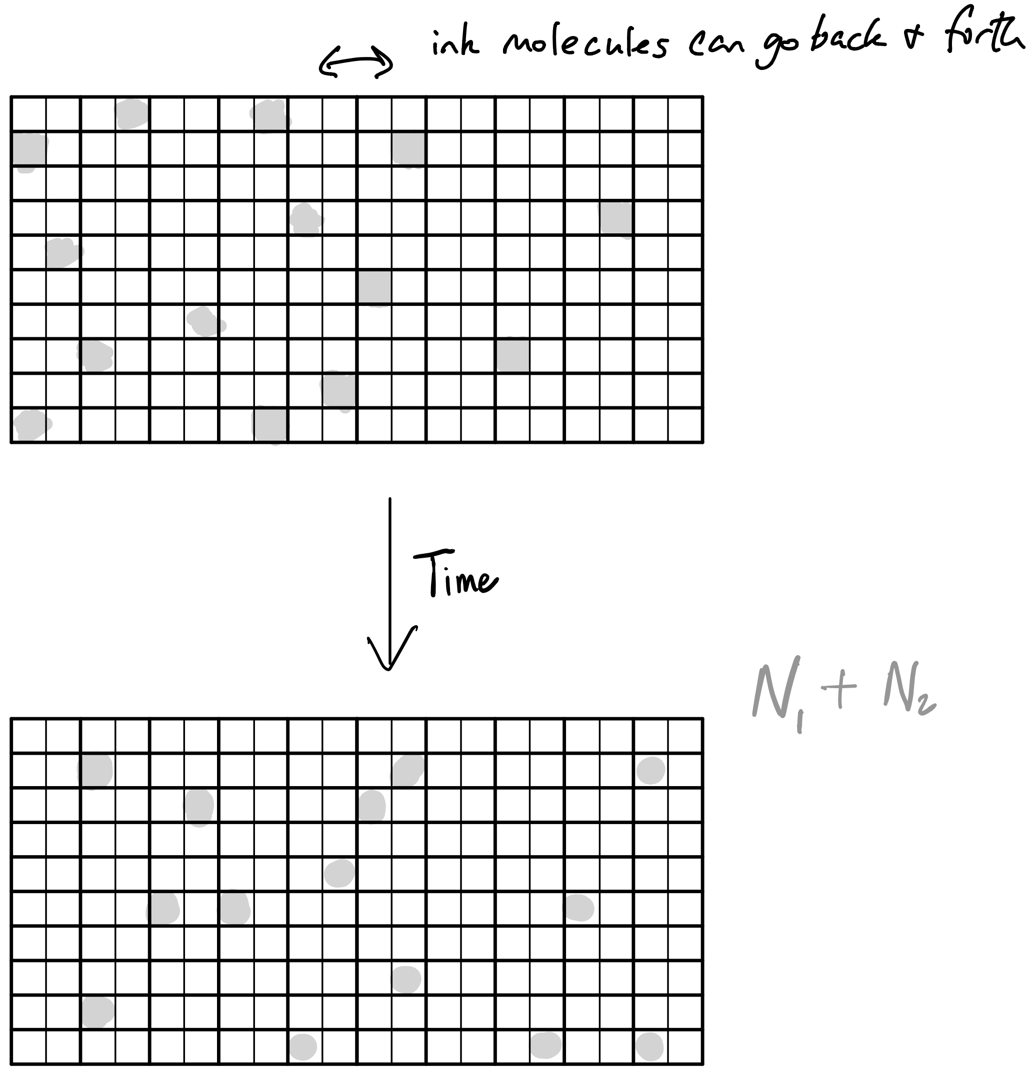
How do these equilibrated systems change when they are put in contact with other equilibrated systems?

1. Why do they change at all?

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



Combine the two equilibrated systems



We have relaxed one constraint!

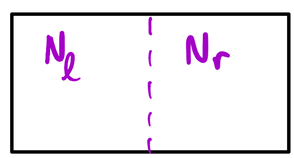
Before, we required exactly N_1 on the left and N_2 on the right. After combining, the number of particles on the left and right can fluctuate.

How many microstates for the combined system?

Before combining　　　　After combining

Only count microstates meeting both constraints

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



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

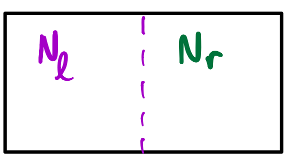
Assume the left and right volumes are equal. It is not hard to imagine that there will be the most microstates when $N_\ell \approx N_r$.

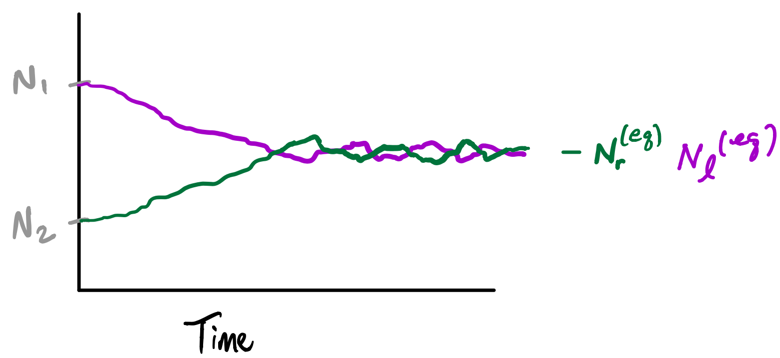
1. Why do they change at all?

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 $N_\ell^{(eq)}$

\# of microstates of left system: $\Omega_\ell(N_\ell)$

\# of microstates of right system: $\Omega_r(N_r)$

\# of microstates of joint system:

$$\Omega_\ell(N_\ell) \times \Omega_r(N_r)$$

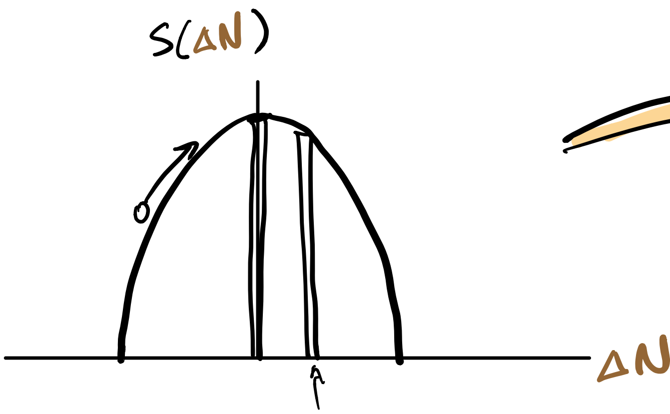
Entropy of left system: $S_\ell(N_\ell) = k_B \ln \Omega_\ell(N_\ell)$

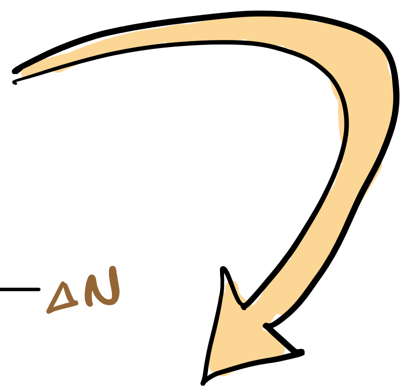
Entropy of right system: $S_r(N_r) = k_B \ln \Omega_r(N_r)$

Entropy of joint system: $S_\ell(N_\ell) + S_r(N_r)$

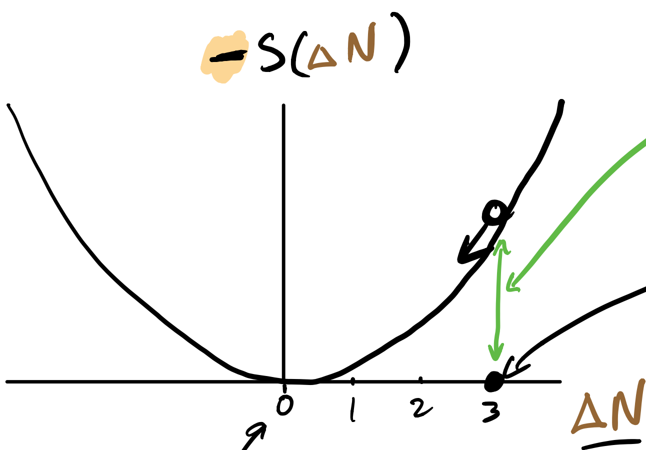
$$S(\Delta N) = S_\ell + S_r = S_\ell(N_\ell^{(eq)} + \Delta N) + S_r(N_r^{(eq)} - \Delta N)$$

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





Flip b/c we want to visualize the dynamics like a ball rolling downhill



Height indicates how many fewer microstates are available w/ that partitioning.

Specifies a partioning with 3 extra particles on one side.

There are the most microstates of the joint system with:

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

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 $-S(\Delta N)$]

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

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

$$\boxed{\text{Remember} \quad \begin{array}{l} N_\ell = N_\ell^{(eq)} + \Delta N \\ N_r = N_r^{(eq)} - \Delta N \end{array} \quad \text{and } \Delta N^{(eq)} = 0}$$

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

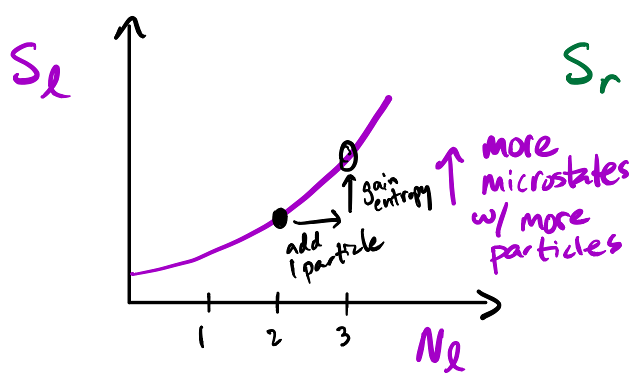
So at equilibrium it must be the case that

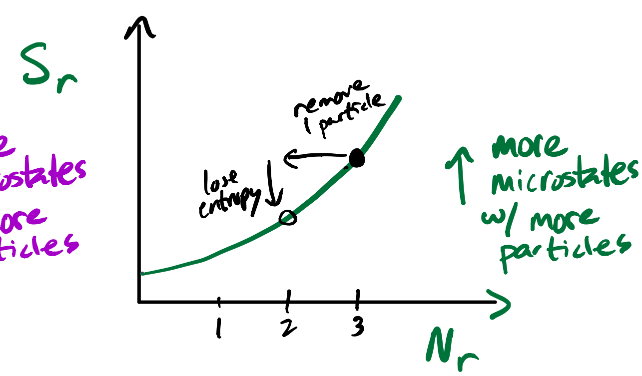
$$\left.\left(\frac{\partial S}{\partial N}\right)_{E,V}\right|_{N_\ell = N_\ell^{(eq)}} = \left.\left(\frac{\partial S}{\partial N}\right)_{E,V}\right|_{N_r = N_r^{(eq)}}$$

Particles repartition 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.





If both N_ℓ and N_r could be simultaneously increased, clearly $S = S_\ell + S_r$ would go up, but every time N_ℓ goes up, N_r must go down by the same amount, setting up a conflict...

Is the entropy gained from

$$N_\ell \rightarrow N_\ell + 1 \equiv N_\ell'$$

more than the entropy lost from

$$N_r \rightarrow N_r - 1 \equiv N_r' \qquad ?$$

If so, there will be more microstates with partitioning N_ℓ', N_r' than with N_ℓ, N_r

Of course the # of particles is discrete, but in a large system N could be so big that we can think of $N \rightarrow N+1$ as being a tiny change $\Rightarrow$ calculus is appropriate

Then the entropy gained from

$$N_\ell \to N_\ell + \delta \quad \text{is} \quad \left(\frac{\partial S}{\partial N_\ell}\right)\delta$$

and the entropy lost from

$$N_r \to N_r - \delta \quad \text{is} \quad \left(\frac{\partial S}{\partial N_r}\right)\delta$$

The particles stop flowing when even a small change in N_ℓ (by an amount δ) cannot increase the net entropy. That happens when

$$\left(\frac{\partial S}{\partial N_\ell}\right)\delta - \left(\frac{\partial S}{\partial N_r}\right)\delta = 0$$

Which is the same condition for equilibrium we wrote down above:

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