

Lecture 4

Recall from last lecture...

System + (Thermal) Bath

N_T, V_T, E_T

Variables with no flow:

$$N_T = N + N_B$$

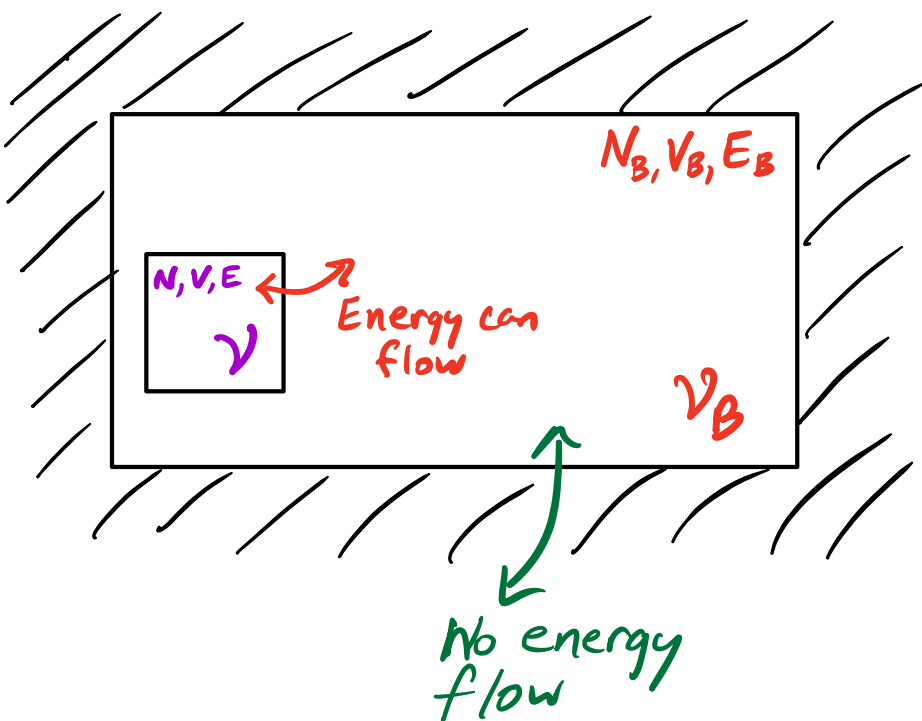
$$V_T = V + V_B$$

Variable with flow:

$$E_T = E(v) + E_B(v_B)$$

System
microstate

Bath
microstate



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

Boltzmann
Distribution!

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

β : Boltzmann B : Bath

is an intensive
property of a
very large bath.

$$\langle E \rangle = \sum_{\nu} E(\nu) P(\nu)$$

$$= \frac{1}{Q} \sum_E \Omega(E) E e^{-\beta E}$$

$$= \sum_E P(E) E, \text{ where } P(E) \propto \Omega(E) e^{-\beta E}$$

(see last lecture)



When more ν 's have energy E , you're more likely to measure that E

Impact of fewer bath microstates when the system hogs more energy

(A) There are more ways to configure a system as more energy is added, increasing the system multiplicity $\Omega(E)$.

(B) As you put more energy in the system, you're requiring the bath to supply more, thereby lowering the bath multiplicity $\Omega_B(E_T - E)$.

(c) Within any one bar of fixed E , all microstates are equally likely.

(That uniform distribution over microstates) is called "microcanonical".

Now Recall:

Let's actually Taylor expand $\ln \Omega_B(E_T - E)$ not $\Omega_B(E_T - E)$

Q: Why did we make this choice?

A: We sought an intensive property of the bath.

"Put your sample in a 25 C water bath"

VS.

"Put your sample in a 2L water bath with total energy x ."

From the first homework you should see that intensive quantities (like $f = N_H/N$) behave very deterministically when you average over a large system (many coin flips), so it will make sense to characterize our bath based on those intensive quantities.

Two options:

$$\Omega_B(E_T - E) \approx \Omega_B(E_T) - E \left(\frac{\partial \Omega_B}{\partial E_B} \right) + \dots$$

$$\ln \Omega_B(E_T - E) \approx \ln \Omega_B(E_T) - E \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right) + \dots$$

Is $\left(\frac{\partial \Omega_B}{\partial E_B} \right)$ intensive? (And why?)

No! $\Omega_B \sim e^N$
 $E_B \sim N$ $\left(\frac{\partial \Omega_B}{\partial E_B} \right) \sim \frac{e^N}{N}$

What about $\left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)$?

Yes! $\ln \Omega_B \sim N$
 $E_B \sim N$ $\left(\frac{\partial \ln \Omega_B}{\partial E_B} \right) \sim 1$

On HW 2, you get to explore this idea from a complementary perspective.

So

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

k_B : Boltzmann

B : Bath

is an intensive property of a very large 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

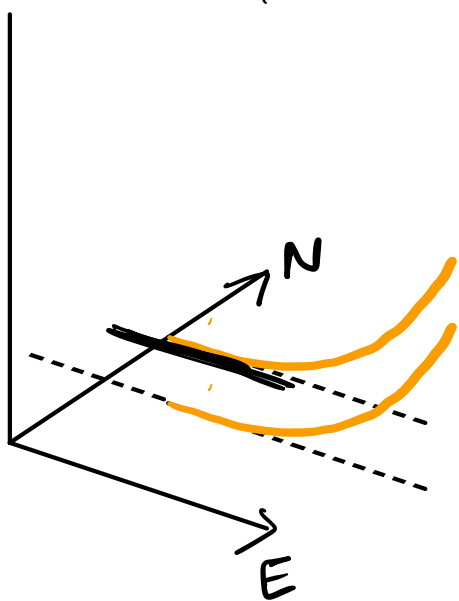
Baths which are desperate to suck energy away:

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:

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

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

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

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...

$$\beta = 1/k_B T$$

Aside:

What are the units of β ? $1/\text{Energy}$

$$e^{-\beta E}$$

This had better be
unitless

If we would have tried $S = \ln \Omega$ all the way back, we would have just deduced $\beta = 1/T$. 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**? $\frac{1}{k_B} \left(\frac{\partial S}{\partial E} \right)_{N,V}$

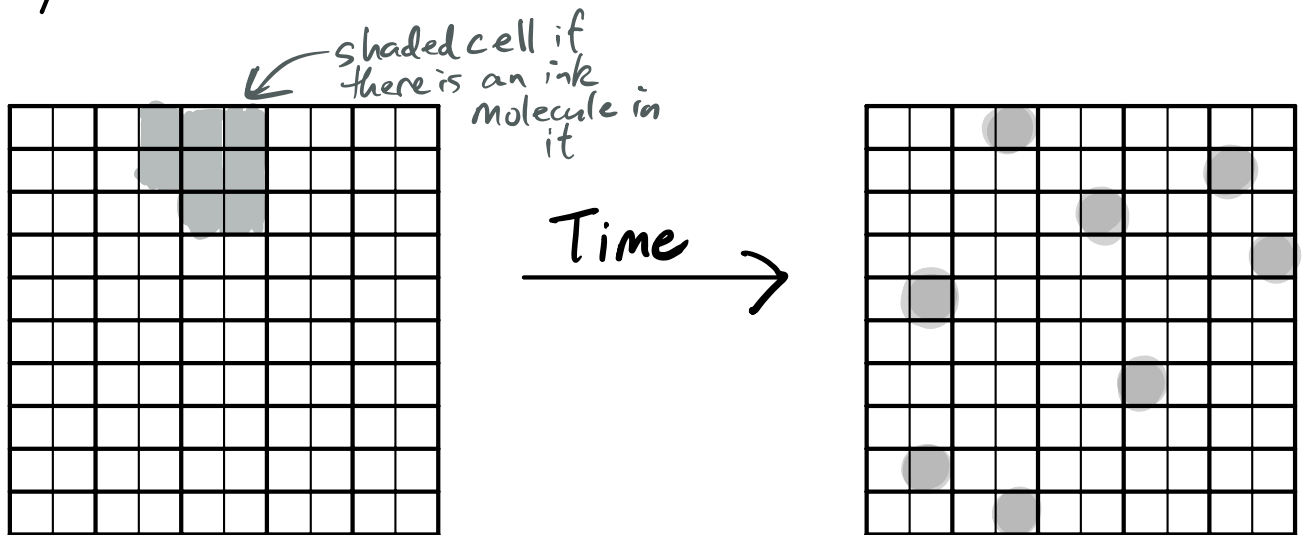
Temperature of the **bath**? $\frac{1}{k_B} \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B, V_B}$

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)



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 equilibrated"

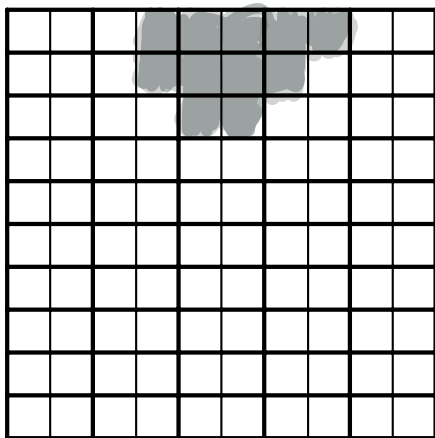
Memory of the initial condition is completely lost, so the probability of observing a particular equilibrium configuration is just a function of the extensive constraints:

$$N, V, E$$

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

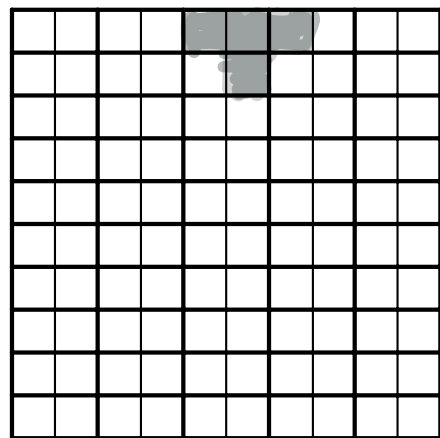
1. Why do they change at all?

N_1 concentrated

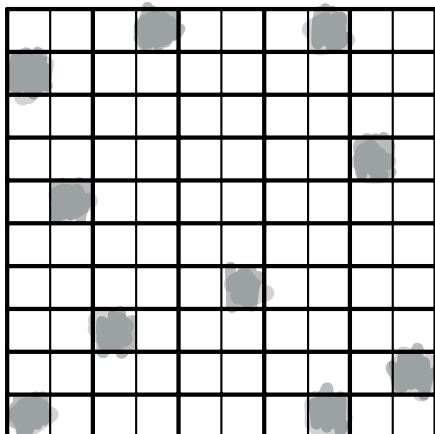


Not
Equilibrated

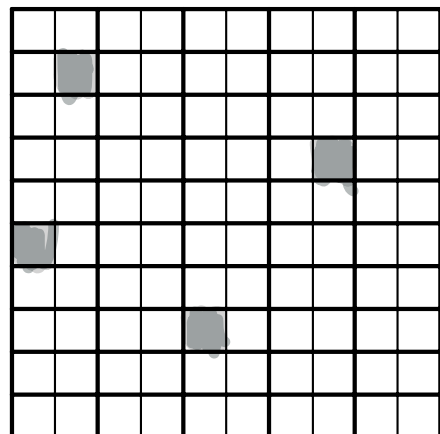
N_2 dilute



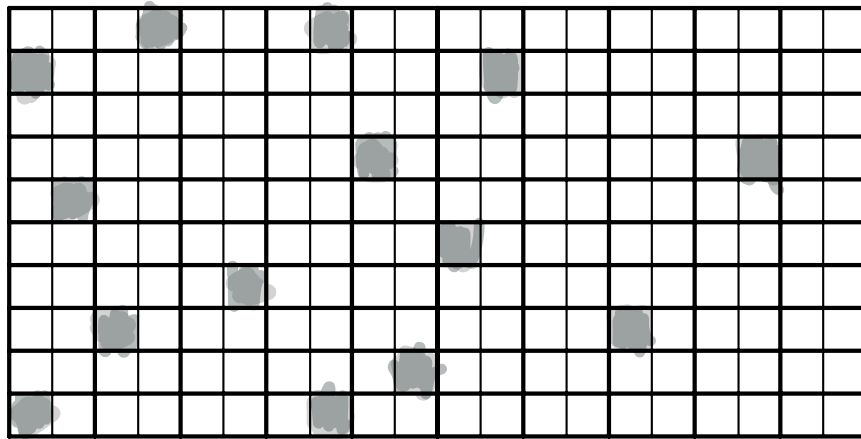
Time
↓



Time
↓

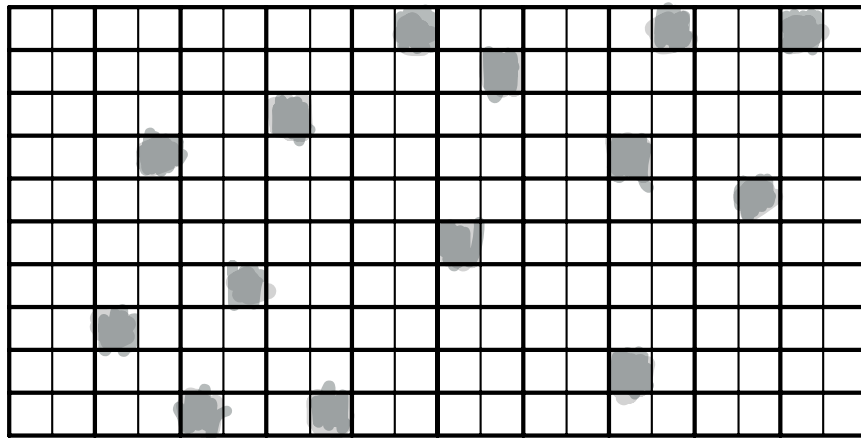


Combine the two *equilibrated* systems



Time
↓

$N_1 + N_2$



We have relaxed one constraint!

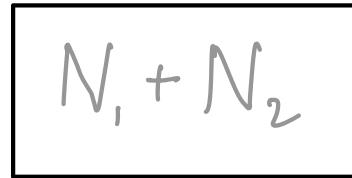
Before, we required exactly N_1 on the left and N_2 on the right. After combining, the number of particles on the left and right can fluctuate.

How many microstates for the combined system?

Before combining

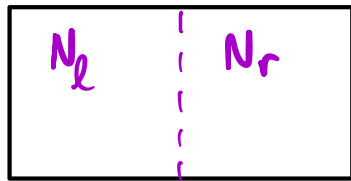


After combining



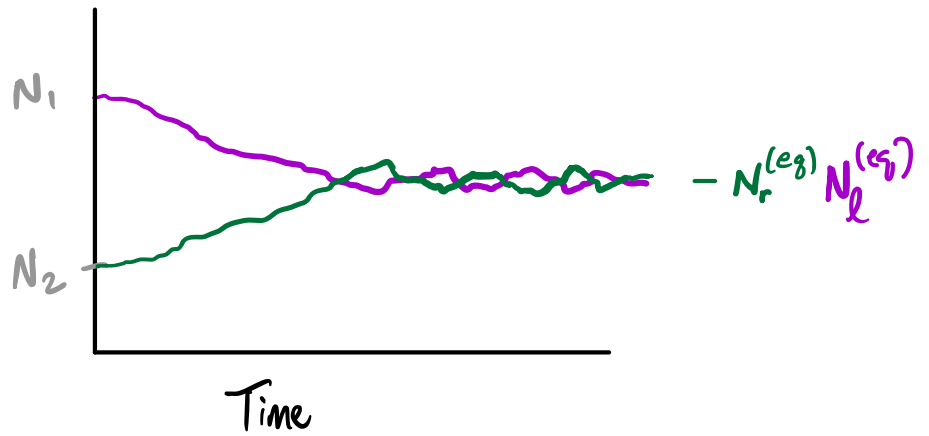
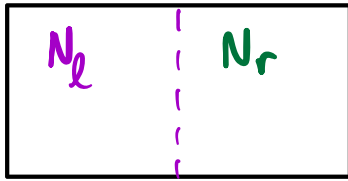
Only count microstates
meeting both constraints

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 $N_l \neq N_1$ 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 $N_l \approx N_r$



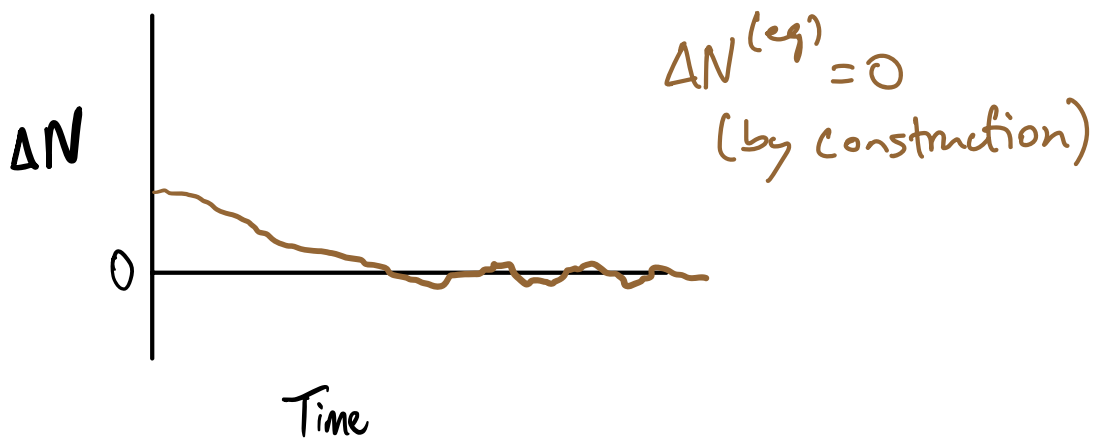
1. Why do they change at all?

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

$$\begin{aligned}
 N_l &= N_l^{(eq)} + \Delta N \\
 N_r &= N_r^{(eq)} - \Delta N
 \end{aligned}
 \quad \Delta N \text{ is defined to be the amount by which } N_l \text{ exceeds } N_l^{(eq)}$$



of microstates of left system: $\Omega_L(N_L)$
 # of microstates of right system: $\Omega_R(N_R)$
 # of microstates of joint system: $\Omega_L(N_L) \Omega_R(N_R)$

Entropy of left system: $S_L(N_L) = k_B \ln \Omega_L(N_L)$

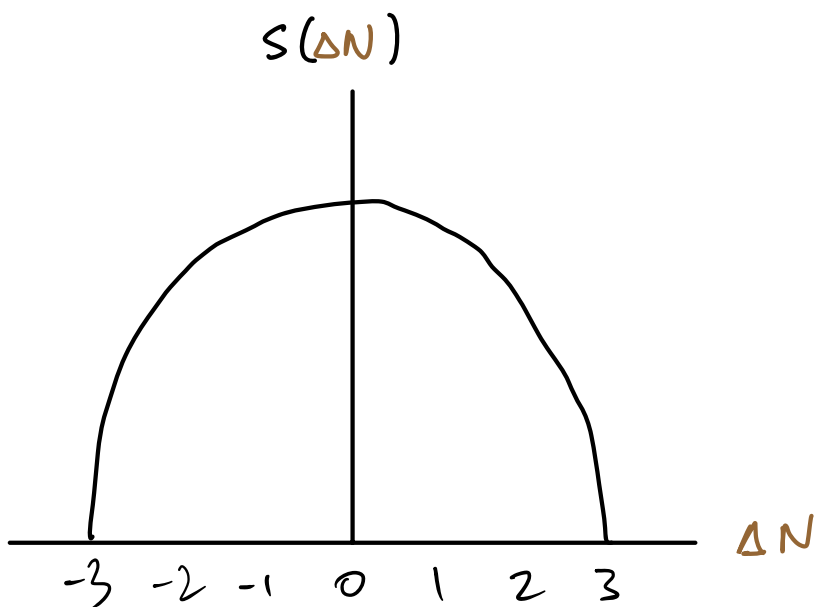
Entropy of right system: $S_R(N_R) = k_B \ln \Omega_R(N_R)$

Entropy of joint system: $S_L(N_L) + S_R(N_R)$

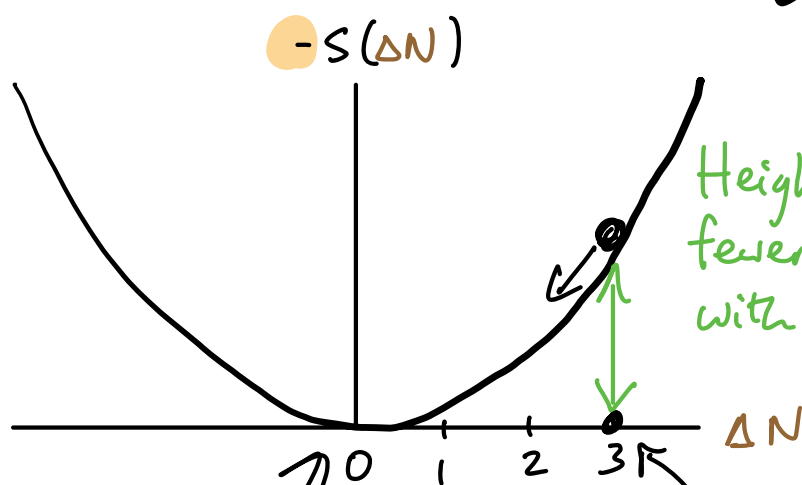
$$S(\Delta N) = S_L(N_L^{(eq)} + \Delta N) + S_R(N_R^{(eq)} - \Delta N)$$



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



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



Height indicates how many fewer microstates are available with that partitioning

Specifies a partitioning with 3 extra particles on one side

There are the most microstates of the joint system with:

$$N_l = N_l^{(eq)} \text{ and } N_r = N_r^{(eq)}$$

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 $-S(\Delta N)$]

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

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

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

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

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

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

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