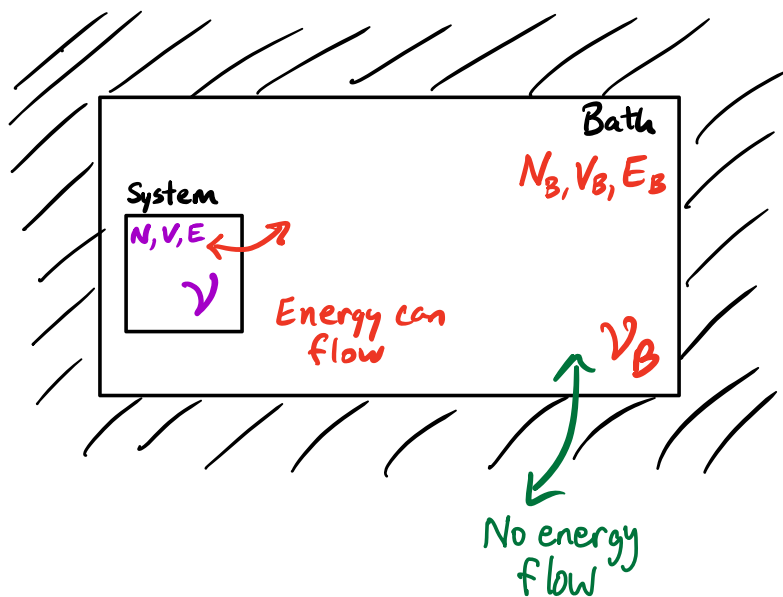


Lecture 6

Recall from last lecture...

System + (Thermal) Bath



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 ν Bath microstate ν_B

Averaging (marginalizing) over the bath gave...

$$P(\nu) \propto \Omega_B(E_T - E(\nu))$$

Probability of system microstate ν How many bath microstates have energy $E_T - E(\nu)$

When the bath is much larger than the system, we Taylor expanded

$$\ln \Omega_B(E_T - E) \approx \ln \Omega_B(E_T) - \beta E + \dots$$

Yielding

$$\Omega_B(E_T - E) \approx \Omega_B(E_T) e^{-\beta E} \propto e^{-\beta E}$$

in terms of the bath property $\beta \equiv \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)_{N_B, V_B}$

Combining gave...

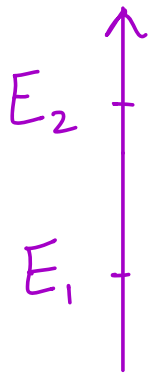
$$P(\nu) \propto e^{-\beta E(\nu)}$$

Boltzmann Distribution!

E is no longer fixed. It fluctuates!

Are the system microstates ν equally likely?

ν_1 vs. ν_2



X A	$P(\nu_1) = P(\nu_2)$
B	$P(\nu_1) > P(\nu_2)$
X C	$P(\nu_1) < P(\nu_2)$

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.

What's so great about an intensive property of a 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?)

$$\Omega_B \sim e^{N_B \cdot \#}$$

$$E_B \sim N_B$$

$\frac{e^{N_B}}{N_B}$ grows w/ N_B
 \Rightarrow Not intensive

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

$$\begin{array}{l} \ln \Omega_B \sim N_B \\ E_B \sim N_B \end{array} \Rightarrow \frac{\ln \Omega_B}{E_B} \sim \mathcal{O}(1)$$

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

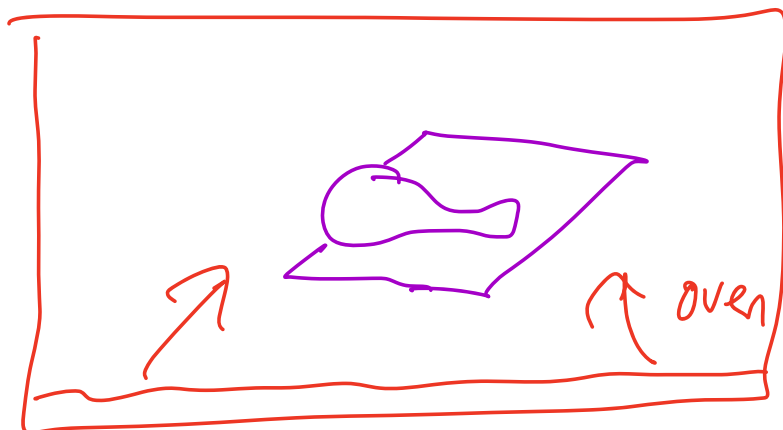
B : Bath

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.

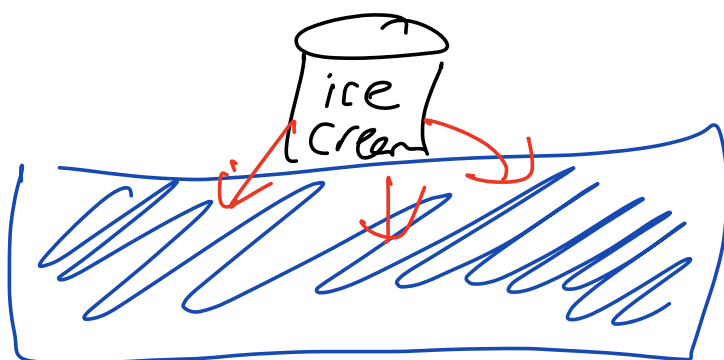
β regulates (or perhaps characterizes) the propensity for a bath to donate or take away energy from the system.

Baths which are happy to donate energy:



High
Temperature

Baths which are desperate to suck energy away:



Low
Temperature

Why are we sure that temperature is really the right word for this concept?

Let's remember our thermodynamics:

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

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

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

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 ?

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

This must be
unitless

$\Rightarrow \beta$ has units of $1/\text{Energy}$

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

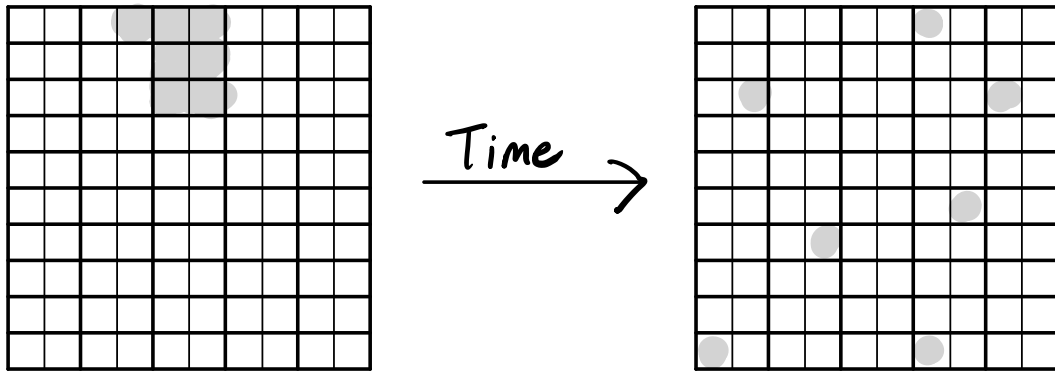
I have thrown the word "temperature" around a lot today. Am I talking about...

Temperature of the **system**?

Temperature of the **bath**?

When the **system** is equilibrated with the **bath**, the temperatures are the same.

Let's dig into "equilibration"...



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 & dispersed macrostate)

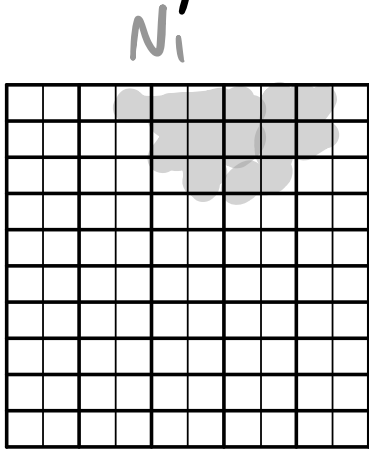
Then "the system has equilibrated"

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:

$$N, V, E$$

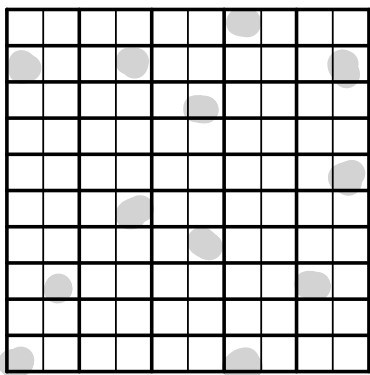
How do these equilibrated systems change when they are put in contact with other equilibrated systems?

1. Why do they change at all?

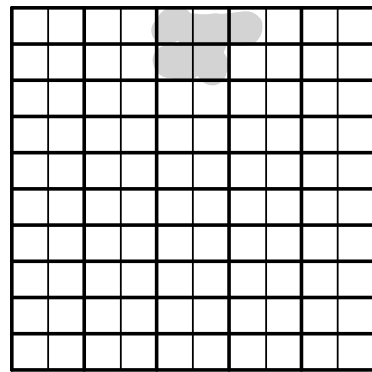


concentrated

↓ Time

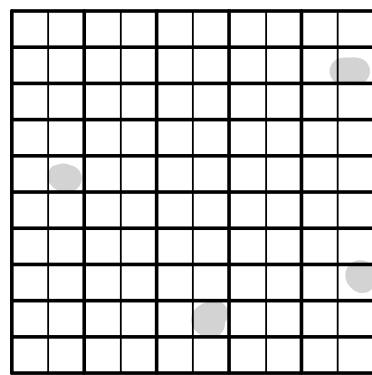


Not equilibrated



dilute

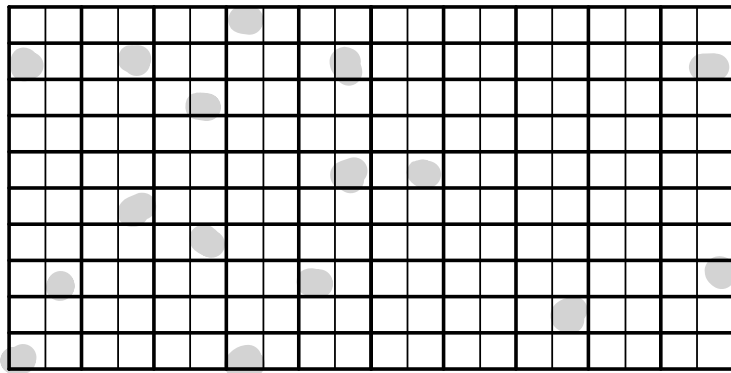
↓ Time



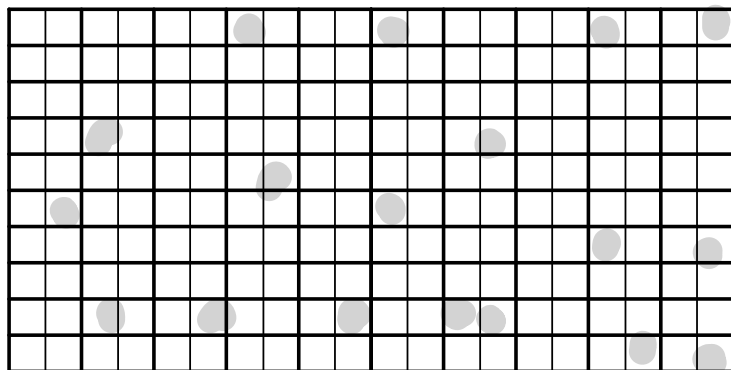
Equilibrated

Combine the two **equilibrated** systems

↔ ink molecules can go back & forth



↓ 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.