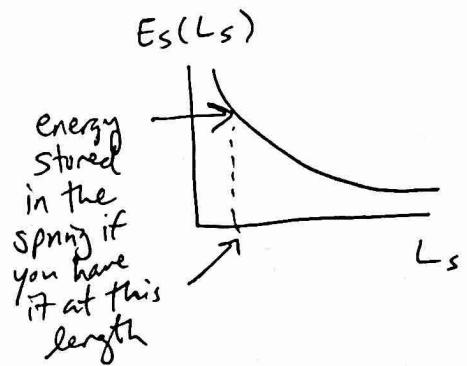
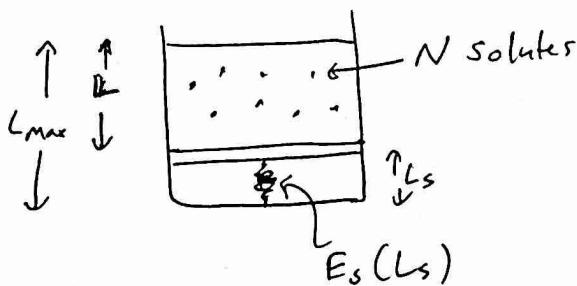


Lecture 4

Recap:



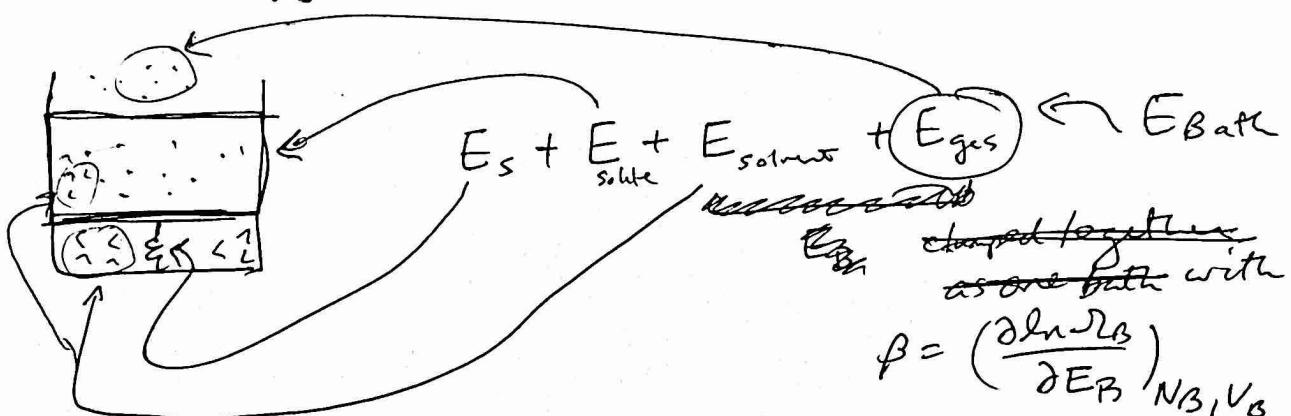
$$f = -\frac{dE_s}{dL_s}$$

↑ Force exerted by the spring

Note the minus sign

$$L + L_s = L_{\max}$$

What about energy?



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

How likely is it to find the plug at length L ?

$$P(L) \propto \underbrace{\Omega(L)}_{\substack{\# \text{ of ways} \\ \text{to arrange} \\ \text{solute w/ length}}} e^{-\beta(E_s + E)}$$

β is the bath's β

system's energy = $E_{\text{solute}} + E_{\text{solvent}}$
spring's energy

$$\propto \frac{L^N}{N!} e^{-\beta E_s(L)}$$

$$\Rightarrow \ln P(L) = N \ln L - \beta E_s(L) + C \quad \text{a constant}$$

The most likely L maximizes $P(L)$ (equivalently maximizes $\ln P(L)$)

$$\Rightarrow 0 = \left. \frac{d \ln P(L)}{d L} \right|_{L=L^*} = \frac{N}{L^*} - \beta \frac{d E_s(L)}{d L}$$

$$= \frac{N}{L^*} - \beta \frac{d E_s}{d L_s} \frac{d L_s}{d L}$$

$$= \frac{N}{L^*} + \beta \left(\frac{d E_s}{d L_s} \right)$$

$$= \frac{N}{L^*} - \beta f$$

L^* is the most likely value of L . When the system is big, we expect fluctuations to be so negligible that we just call this most likely value *the* value of L .

$$\Rightarrow \frac{N}{L} = \beta f \quad \text{After dividing through by the cross-sectional area } A,$$

$$\frac{N}{LA} = \beta \frac{f}{A}$$

$$\rho = \beta \pi \leftarrow \text{An ideal law like } \rho = \beta p$$

$$\frac{N}{V} = \beta p \Rightarrow pV = \beta^{-1} N = (N_A \beta^{-1}) \underbrace{\frac{N}{N_A}}_{\# \text{ of mols}}$$

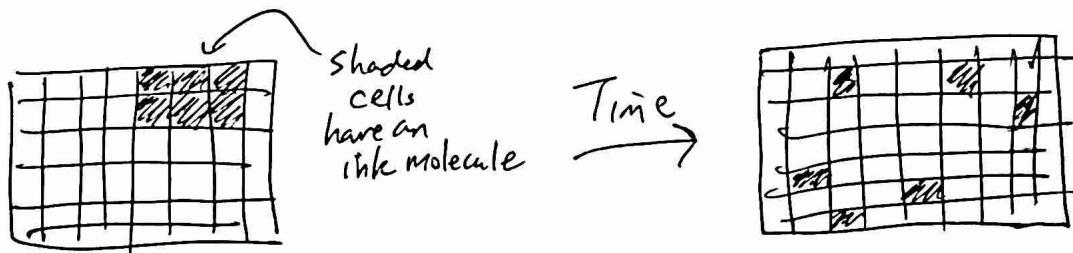
$$N_A \beta^{-1} = RT \Rightarrow \frac{N_A}{RT} = \beta$$

$$\text{and } \frac{R}{N_A} = k_B \Rightarrow \beta = \frac{1}{k_B T} = \left(\frac{\partial \ln \mathcal{Z}}{\partial E} \right)_{V,N}$$

Is β the "inverse temperature" of the system or the bath?
or BOTH?!

When the system is equilibrated with the bath, the temperatures are the same. Let's dig into that equilibration a little more.

Set up a system w/ fixed N, E, V (Think of an ink drop)

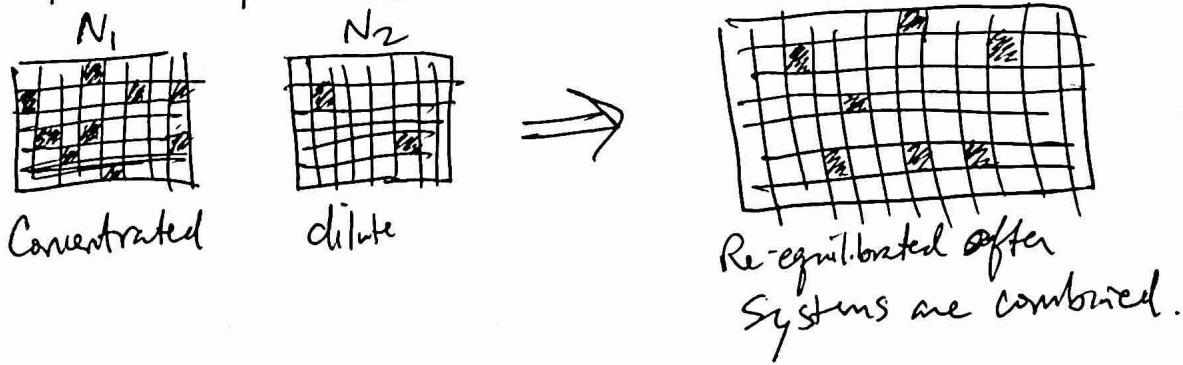


Regardless of initial condition, after enough time the system explores the possible microstates and ends up in one of the most likely states (ok, all microstates are equally likely, but it will tend to one of the more likely macrostates — dispersed ink state here).

Then we would say "the system has equilibrated"

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

1. Why do they change at all?

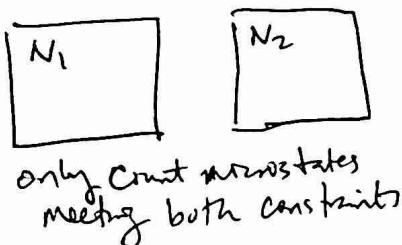


In combining the systems we have relaxed a constraint!

Before combining, the only possible configurations had exactly N_1 on the left and N_2 on the right. After combining, each of those configurations are still possible but we have gained lots of new possibilities.

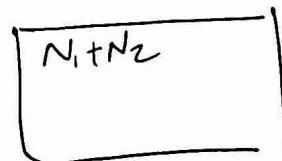
Pictorially:-

Before:



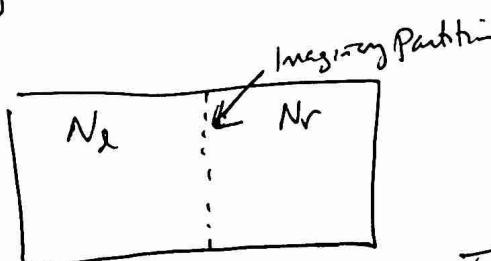
only Count microstates
meeting both constraints

After:



the only constraint
is that the total
is $N_1 + N_2$

Imagine splitting the combined box in two with an imaginary partition and counting the number of particles on the left: N_l and the number of particles on the right: N_r .



There are lots of extra microstates for which $N_l \neq N_1$ & $N_r \neq N_2$.

Assume $V_1 = V_2$. It should seem intuitive that $N_l \approx N_r$ after equilibration. So if we start with $N_1 > N_2$

$$N_1 \rightarrow \frac{N_1 + N_2}{2} \text{ decreases}$$

$$N_2 \rightarrow \frac{N_1 + N_2}{2} \text{ increases}$$

upon equilibration (w/ fluctuations)
on top.

2. When does the transport between subsystems stop?

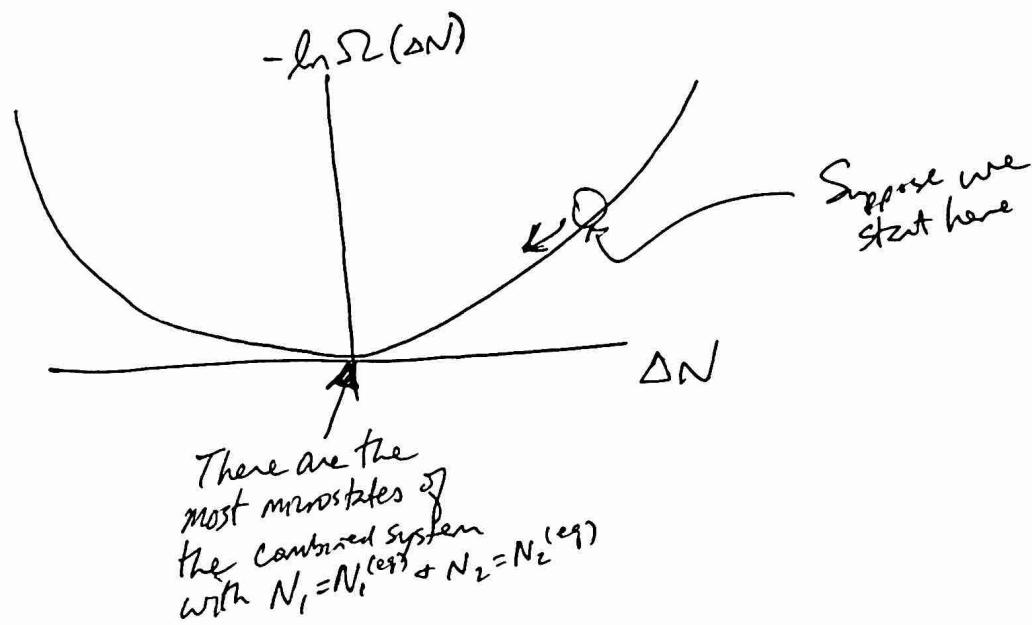
Equilibrium will induce changes (repartitionings) until the new combined system is in its most likely partitioning.

$$N_1 = N_1^{(eq)} + \Delta N$$

$$N_2 = N_2^{(eq)} - \Delta N$$

of microstates w/ (N_1, N_2) is
 $\Omega(\Delta N)$

Let's plot $-\ln \Omega(\Delta N)$ as a function of the deviation from equilibrium.



What is so special about $\ln \Omega(\Delta N)$ as compared to $\Omega(\Delta N)$?

Remember that $\Omega \propto e^{-N \ln \omega}$ grows exponentially w/ N

$\Rightarrow \ln \Omega$ is extensive.

A	B
w/ Ω_A	w/ Ω_B

Total # of states: $\Omega_A * \Omega_B$

$\Rightarrow \ln(\text{Total # of states}) = \ln \Omega_A + \ln \Omega_B$

or for our problem

$$\ln \Omega(\Delta N) = \ln \Omega_{(N_1^{(eq)} + \Delta N)} + \ln \Omega_{(N_2^{(eq)} - \Delta N)}$$

The condition for equilibrium is that the "ball" ends up at the bottom $\Rightarrow \frac{d \ln \Omega(\Delta N)}{d \Delta N} = 0$

$$\Rightarrow \frac{d \ln \Omega_1(N_1^{(eq)} + \Delta N)}{d \Delta N} + \frac{d \ln \Omega_2(N_2^{(eq)} - \Delta N)}{d \Delta N} = 0$$

This - sign yields this one

$$\Rightarrow \left(\frac{\partial \ln \Omega_1}{\partial N} \right)_{E_1, V_1} - \left(\frac{\partial \ln \Omega_2}{\partial N} \right)_{E_2, V_2} = 0$$

$$\Rightarrow \boxed{\left(\frac{\partial \ln \Omega_1}{\partial N} \right)_{E_1, V_1} = \left(\frac{\partial \ln \Omega_2}{\partial N} \right)_{E_2, V_2} \text{ at equilibrium}}$$

If these derivatives were not equal more particles would flow from one side to the other until the partials were equal.

The exact same re-partitioning game can be played w/ energy rather than N .

$$E_1 \quad E_2 \rightarrow E_1 + E_2$$

Energy won't stop flowing until

$$\left(\frac{\partial \ln \Omega_1}{\partial E} \right)_{N_1, V_1} = \left(\frac{\partial \ln \Omega_2}{\partial E} \right)_{N_2, V_2}$$

This is exactly what we expect of an everyday notion of temperature!
Energy will flow until the temperatures are equal.

Now we have a choice. Do we want energy to flow from high T to low T or low T to high T ? To go from high to low, we identify

$$\left(\frac{\partial \ln \mathcal{R}_1}{\partial E} \right)_{N,V} \propto \frac{1}{T_1} \leftarrow \text{Temperature of system 1}$$

$$\left(\frac{\partial \ln \mathcal{R}_2}{\partial E} \right)_{N,V} \propto \frac{1}{T_2} \leftarrow \text{Temperature of system 2}$$

What are the units of that proportionality constant?

$$\left(\frac{\partial \ln \mathcal{R}_1}{\partial E} \right) \leftarrow \text{unitless} = \frac{1}{k_B T} \leftarrow \begin{array}{l} \text{unitless} \\ \text{Kelvin degrees} \end{array}$$

\uparrow
 $\frac{\text{energy}}{\text{degree}}$

k_B is essentially a unit constant.

Now you probably know that classical thermodynamics had a quantity S called entropy long before entropy was understood statistically. From thermodynamics

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

$$\Rightarrow \cancel{dS} dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

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

Boltzmann's statistical form
of entropy.