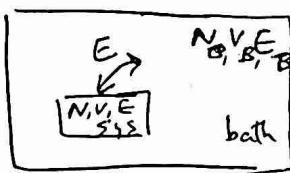


Lecture 3

Recap:



$$E_T = E_B + E$$

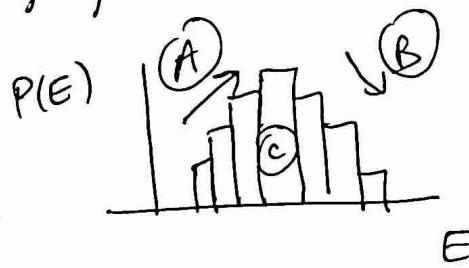
$$P(v) \propto e^{-\beta E(v)}$$

↑
Microstate
of system

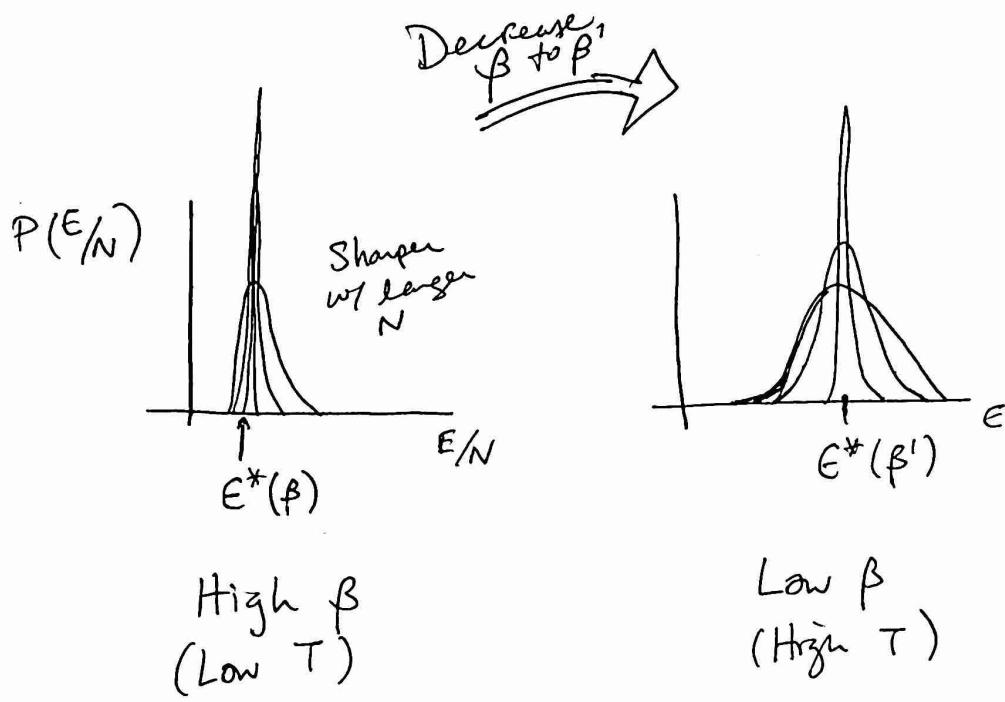
$\left\{ \begin{array}{l} \beta = \frac{1}{k_B T}, \text{ but we haven't} \\ \text{really seen that yet.} \\ \text{We just defined } \beta = \left(\frac{\partial \ln S_B}{\partial E_B} \right)_{N_B, V_B} \end{array} \right.$

Given this dist. over microstates, we consider the resulting dist. over $E \leftarrow$ a macrostate (why do I call it that?)

Roughly



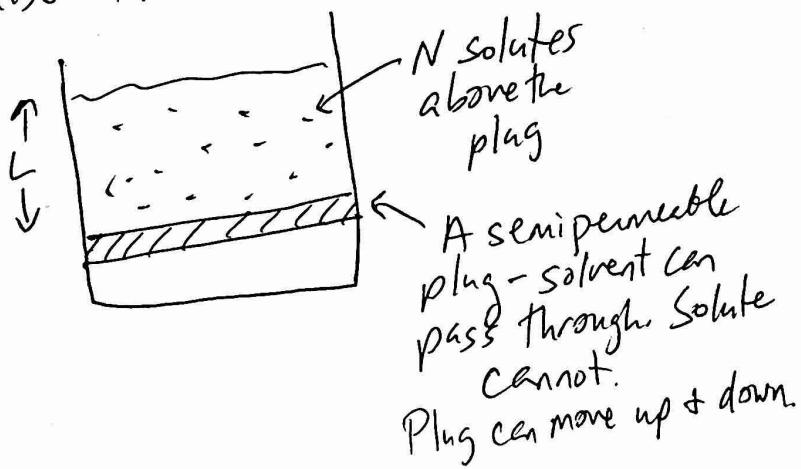
- (A) There are more and more ways to configure a system as more energy is added, increasing the (system) multiplicity $S(E)$.
- (B) As you put more energy into the system, you're requiring the bath to supply more, thereby lowering the bath multiplicity $S_B(E_T - E)$.
- (C) Within any one bar of fixed E , all microstates are equally likely, effectively a different microcanonical ensemble for each bar.



Distribution for an intensive variable becomes sharp in the "thermodynamic limit". The value E^* that dominates depends on parameters of the large bath (β).
~~The system no longer looks stochastic/random, but~~
~~returning to~~

In large systems, the distributions get so sharp that we focus only on the E^* that maximizes the probability.

We were considering a prob. dist over E because energy was allowed to fluctuate between system and bath, but it is possible for V to also fluctuate!

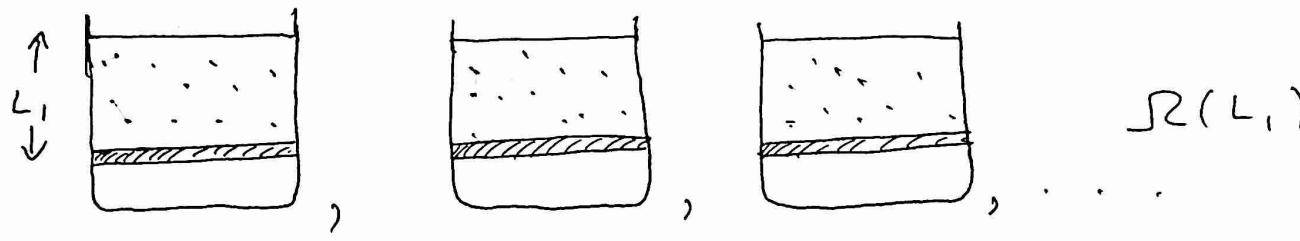


What is system?
What is bath?
Why can Volume fluctuate?

Where is the plug most likely to be positioned?

To find out, we count solute microstates

Each plug position is consistent with many different solute configurations



If $L_2 > L_1$, $S_2(L_2) > S_2(L_1)$

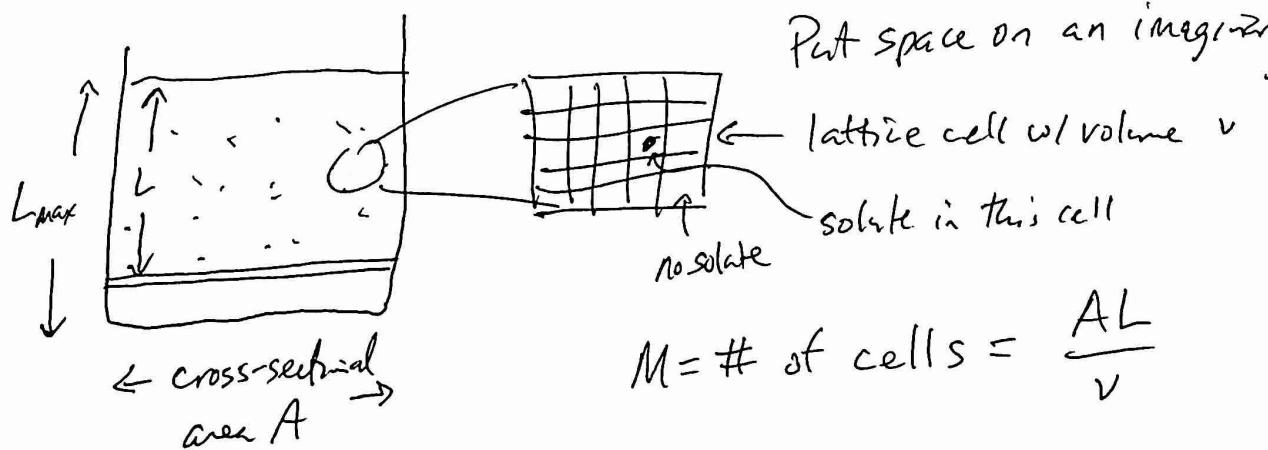
But we don't only compare two particular choices for L ($L_1 + L_2$),

we consider $P(L) \propto S_2(L)$

The most probable plug position is that ~~which maximizes~~ with the greatest number of microstates (maximize $S_2(L)$)

How can we count the number of solute microstates?! It's huge.

It would be easier if the solute positions were discrete rather than continuous. (We can come back to why this is reasonable if people want to.)



How many ways could I put N solutes in M cells?

If solutes cannot occupy the same cell...

$M^C_N \approx$ "M cells, choose N to be occupied"

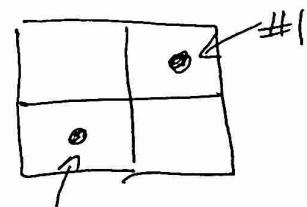
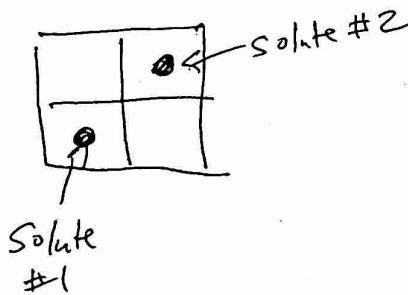
$$\left(= \frac{M!}{N!(M-N)!} \right)$$

These solutes are interacting!

If solutes can occupy the same cell...

$$\frac{M \text{ possible cells}}{\text{Solute } \#1} \times \frac{M \text{ possible}}{\text{Solute } \#2} \times \dots \times \frac{M}{\text{Solute } \#N} = M^N$$

But



These solutes are not interacting!

which reduces the number of configurations by a factor of $N!$

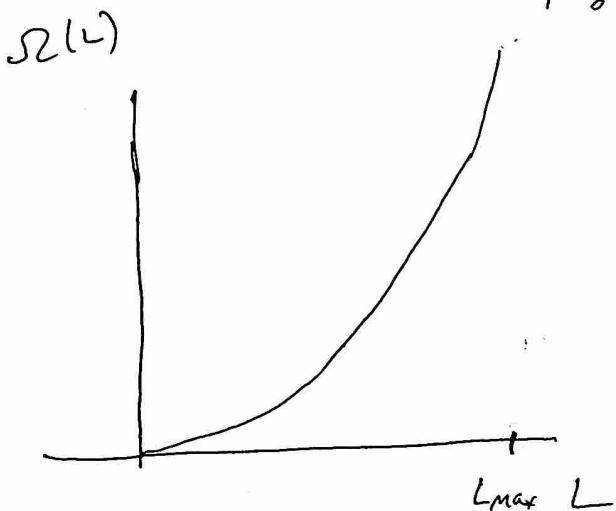
$$S(L) = \begin{cases} \frac{\left(\frac{AL}{v}\right)!}{N! \left(\frac{AL}{v} - N\right)!} & \text{if solutes are "volume excluding"} \\ \frac{\left(\frac{AL}{v}\right)^N}{N!} & \text{if solutes are "ideal"} \end{cases}$$

Let's assume the solution is dilute $\Rightarrow N \ll M$ (most cells are unoccupied)

then

$$\frac{\left(\frac{AL}{v}\right)!}{N! \left(\frac{AL}{v} - N\right)!} = \frac{\frac{AL}{v} \times \left(\frac{AL}{v} - 1\right) \times \dots \times \left(\frac{AL}{v} - N + 1\right)}{N!}$$

$$\approx \frac{\left(\frac{AL}{v}\right)^N}{N!} \quad (\text{the ideal form})$$



$S(L) \propto L^N$, which is maximized by the largest possible value of L , L_{\max} .

In a macroscopic system, with overwhelming probability, the plug settles in the bottom & it is very unlikely (but not impossible) to see it "randomly" fluctuate upward.

What if we push it up?



$$L_{\max} = L + L_s \quad \text{fixed}$$

$$E_T = E + E_{st} + E_B$$

↑ ↑ ↑
energy of energy of energy of
Solvent + the Solvent bath
solute spring + outside
above the plug air

When the plug moves up, there is less volume for the solute to explore but also ~~less~~ energy in the spring

$$P(L) \propto \underbrace{\mathcal{S}(L)}_{\# \text{ of solute states}} \underbrace{e^{-\beta(E + E_s)}}_{\substack{\text{Boltzmann} \\ \text{factor that} \\ \text{prefers lower} \\ \text{energy in the} \\ \text{beaker}}} \propto \mathcal{S}(L) e^{-\beta E_s(L)}$$

The energy in the spring is a function of L.

What is the most likely value of L?

The value of L that maximizes P(L).

$\Rightarrow \frac{dP(L)}{dL} \Big|_{L=L^*} = 0$ solve for L^* , but this is more complicated than it needs to be

$\log(x)$ is monotonic, so $P(L)$ is maximized at the same L^* that maximizes $\ln P(L)$.

$\frac{d \ln P(L)}{dL} \Big|_{L=L^*} = 0$ solve for L^*

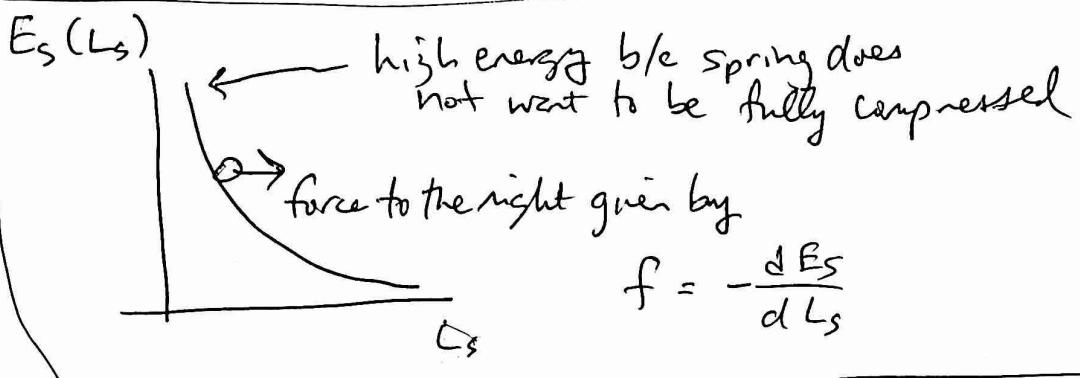
$$\frac{d \ln P(L)}{dL} \Big|_{L=L^*} = \text{a constant}$$

$$\begin{aligned} \frac{d \ln P(L)}{dL} &= \frac{d}{dL} (\ln \mathcal{S}(L) - \beta E_s(L) + C) \\ &= \frac{d}{dL} \left(N \ln L - \beta E_s(L) + C' \right) \end{aligned}$$

a different constant

$$= \frac{N}{L} - \beta \frac{dE_s(L)}{dL}$$

$$= \frac{N}{L} - \beta \frac{dE_s}{dL_s} \frac{dL_s}{dL} = \frac{N}{L} + \beta \left(\frac{dE_s}{dL_s} \right)$$



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

$$\text{So } \left. \frac{d \ln P(L)}{dL} \right|_{L=L^*} = \frac{N}{L^*} + \beta (-f)$$

↑
 force exerted
 by the spring

$$\Rightarrow \frac{N}{L^*} = \beta f, \text{ where } L^* \text{ again is the most likely value of } L.$$

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

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

$$\Rightarrow \frac{N}{LA} = \beta \frac{f}{A} \quad \text{like pressure, call it osmotic pressure } \pi$$

density ρ

$$\Rightarrow \boxed{\rho = \beta \pi} \quad \text{This is an ideal law.}$$

If our particles were molecules in free space rather than solutes in solution, the same counting would have given $\pi \rightarrow p$ (pressure) with

$$\boxed{p = \beta \rho} \quad \text{ideal gas law.}$$

If there were no solvent, this would have been an ideal gas

~~$\pi \rightarrow p$~~

\Rightarrow ~~$\beta p = p$~~ The ideal gas law.

Don't recognize it in this form?

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

this must be RT

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K} \quad \text{Boltzmann's const.}$$

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

Ideal gas law is a consequence of uncorrelated density fluctuations