

Lecture 2

Recall from last lecture...

$$P(\nu) = \begin{cases} \frac{1}{\Omega(N, V, E)}, & \text{if } N_\nu = N, V_\nu = V, E_\nu = E \\ 0, & \text{otherwise} \end{cases}$$

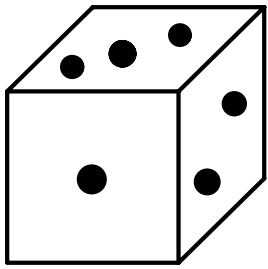
where $\sum_{\nu \text{ with } (N, V, E)} (1) = \Omega(N, V, E)$

Number of possible microstates
satisfying the constraints
 (N, V, E)

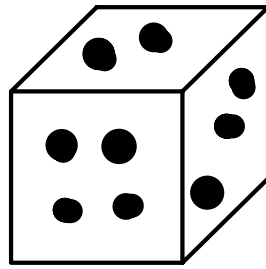
WARNING: I am not being careful to distinguish between discrete probability distributions and continuous probability densities. If ν were a continuous degree of freedom ...
 $\int d\nu \dots$

How big is Ω ?

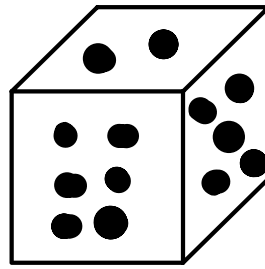
For idealized independent events...



$$\Omega = 6$$



$$\Omega = 6^2$$

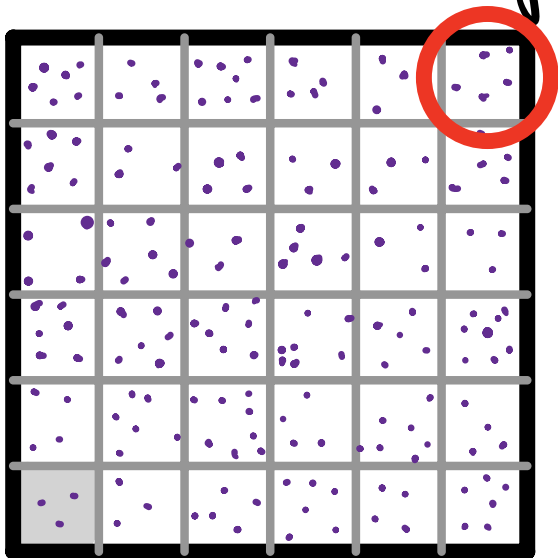


$$\Omega = 6^n$$

... dice

$$\Rightarrow \Omega = e^{n \ln 6} \quad (\text{exponential growth})$$

For effectively independent subsystems...



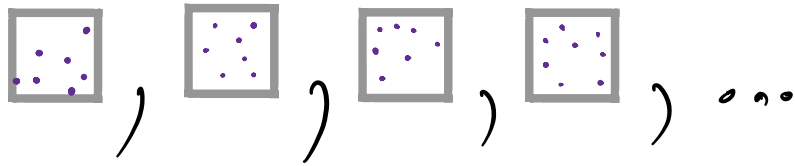
Each cell is big enough that it is uncorrelated from the others.

$$\text{Density } \rho = \frac{N}{V} \quad \begin{array}{l} \leftarrow \# \text{ of particles} \\ \leftarrow \text{Total volume} \end{array}$$

Volume v per cell

$$\# \text{ of independent cells } M = \frac{(N/\rho)}{v}$$

Each cell (subsystem) has some huge # of possible microstates



Let's call that number $\tilde{\omega}$. (It is the same # for each identical, independent cell in the gas.)

Because the cells are independent,

$$\Omega = \tilde{\omega}^M = \left(\tilde{\omega} \frac{1}{\rho V} \right)^N = \omega^N$$

Rename $\omega \equiv \tilde{\omega} \frac{1}{\rho V}$

Therefore $\Omega(N, V, E) = e^{N \ln \omega}$ (Large Deviation Form)

(Ω grows exponentially with system size)

What does w depend on? on N ? No
 Intensive stuff!

$$w = \tilde{w} \frac{1}{\rho v}$$

Intensive $\frac{v}{m}$

$\frac{N}{V}$

M, V, N all growing proportionally to each other

volume per cell
 # of particles per cell
 (Also energy per cell $\epsilon = E/V$)
 (would impact \tilde{w})

Why is \tilde{w} intensive?

The # of microstates per cell does not care how many cells we stack together when the cells are independent

$$\ln \Omega = \underbrace{N}_{\uparrow} \ln \underbrace{w(v, \rho, \epsilon)}_{\uparrow}$$

Extensive Intensive (entropy per particle)

It turns out to be useful to focus on $\ln \Omega$ as an object in its own right. We call it S ...

$$S(N, V, E) = \underbrace{k_B}_{\substack{\uparrow \\ \text{Boltzmann's Constant}}} \ln \Omega(N, V, E)$$

Why the k_B ?

Units of $\ln \Omega$...? Unitless

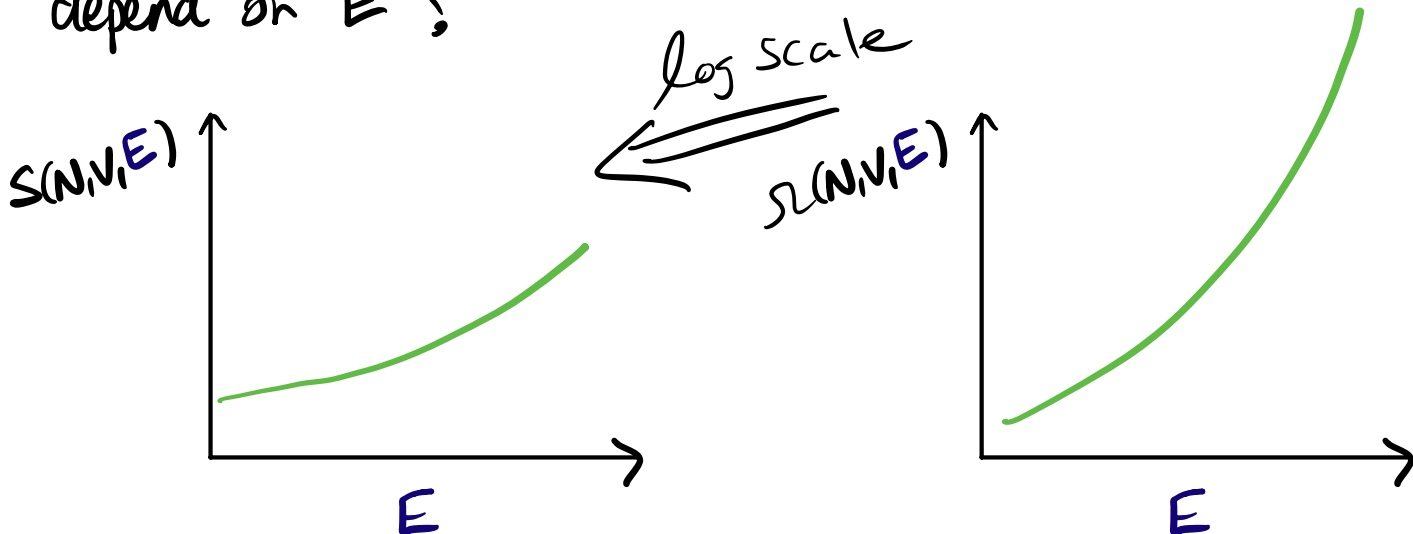
Units of thermodynamic entropy...? Not Unitless

We will be seeing more about why S , defined this way, agrees with the things you got used to in a thermodynamic entropy function.

IMPORTANT NOTE:

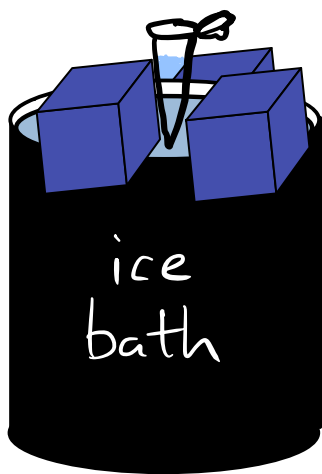
$S(N, V, E)$ takes 3 arguments and returns a number. That number for any fixed N, V, E is far less interesting than the FUNCTION S , which tells how the number of states would change if you were to relax/change the constraints.

Hold N and V fixed. How does $S(N, V, E)$ depend on E ?



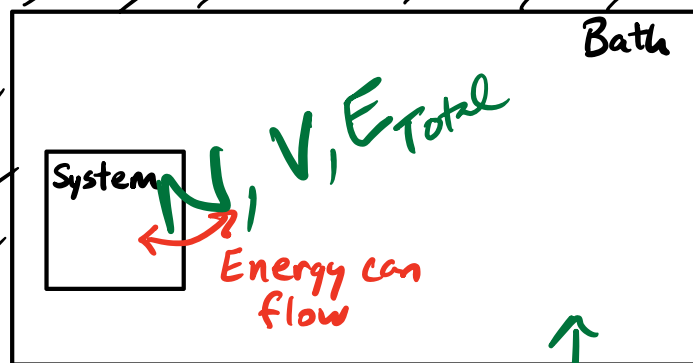
Holding N, V, E fixed made sense for a closed, isolated system. Often we are interested in things which are not closed and isolated.

Ex:



If energy can be exchanged with a "bath", then what should we do?

System + (Thermal) Bath



Although energy can flow between system and bath, they are isolated from the outside

No energy flow

(We might also call the bath the environment, the reservoir, the surroundings, ...)

When the bath is much bigger than the system, we can make useful approximations

The Big Idea...



System + Bath is isolated

Variables with no flow:

$$N_T = N + N_B$$
$$V_T = V + V_B$$

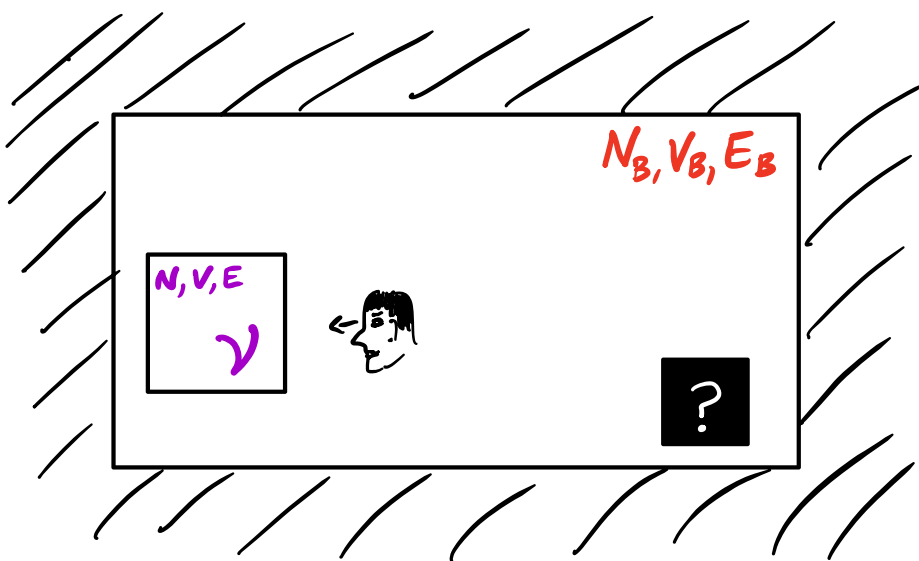
Variable with flow:

$$E_T = E(\nu) + E_B(\nu_B)$$

System microstate Bath microstate

Microstate of the full system + bath is defined by

$$\nu_T = \{ \nu, \nu_B \}$$



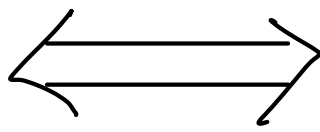
What if I cannot observe the state of the bath?

From the conservation of energy we still know something about the bath state merely by measuring ν

If the system is in state ν , then the bath could be in any state ν_B for which:

$$E_B(\nu_B) = E_T - E(\nu)$$

Probability of
system microstate
 ν



How many bath
microstates have
energy

$$E_T - E(\nu)$$

This is the distribution
for the thing we observe.
It's what we're after.

We could get to it
if we knew how to
count this.

How do we connect the left and right sides?

RHS:

$$\Omega_B(E_B) = \# \text{ of Bath microstates w/ energy } E_B$$

LHS:

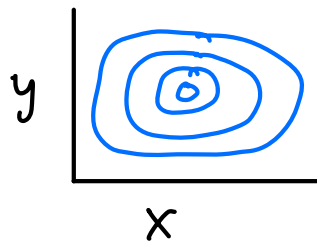
$$P(v) = \sum_{v_B} P(v, v_B)$$

Marginal distribution

Joint distribution

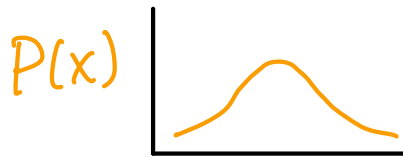
Aside on Marginal Distributions

$P(x, y)$
Joint Distribution



$P(y)$

Marginal Distribution



$$\int dx \int dy P(x, y) = 1 \quad (\text{Normalization of joint})$$

$P(x)$ Marginal Distribution

$$P(v) = \sum_{v_B} P(v, v_B) = \frac{1}{\Omega(E_T)} \Omega_B(E_T - E(v))$$

(1) What is $\Omega(E_T)$? Why not write $\Omega(N_T, V_T, E_T)$?

Lazy shorthand for $\Omega(N_T, V_T, E_T)$. Because we are not changing volumes or #'s of particles at the moment, we are focused only on the energy-dependence.

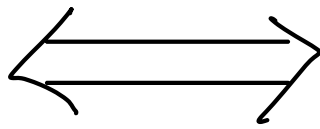
(2) Why is $\Omega(E_T)$ the right normalization?

$$P(\nu, \nu_B) = P(\nu_T) = \begin{cases} \frac{1}{\Omega(E_T)} & \nu + \nu_B \text{ s.t.} \\ & E(\nu) + E(\nu_B) = E_T \\ 0, & \text{otherwise} \end{cases}$$

(3) Where does the $\Omega_B(E_T - E(\nu))$ come from?

$$\sum_{\nu_B} P(\nu, \nu_B) = \frac{1}{\Omega(E_T)} \times \underbrace{\left(\text{How many } \nu_B \text{ s.t.} \right.}_{\Omega_B(E_T - E(\nu))} \\ \left. E(\nu) + E(\nu_B) = E_T \right)$$

Probability of
System microstate
 ν



How many bath
microstates have
energy $E_T - E(\nu)$

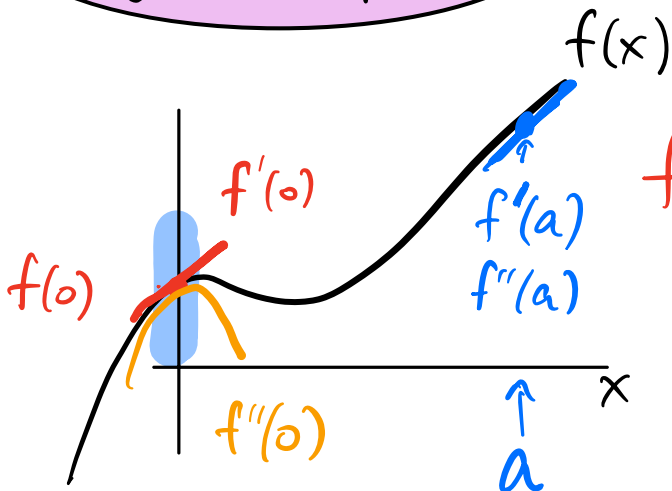
$$P(\nu) \propto \Omega_B(E_T - E(\nu))$$

Now we employ a (reasonable) approximation.
When the bath is HUGE,

$$E(\nu) \ll E_T \dots$$

What is $\Omega_B(E_T - E)$ in the limit of small E ?

Taylor Expand!



$$f(x) \approx f(0) + x f'(0) + x^2 \frac{f''(0)}{2!}$$

$$f(x-a) = f(a) + (x-a) f'(a) + (x-a)^2 \frac{f''(a)}{2!}$$

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

Zeroth Order: $\ln \Omega_B(E_T - E)|_{E=0} = \ln \Omega_B(E_T)$

First Order: $E \left(\frac{\partial \ln \Omega_B}{\partial E} \right) \Big|_{E=0}$

$$\ln \Omega_B(E_T - E) \approx \ln \Omega_B(E_T) + E \left(\frac{\partial \ln \Omega_B}{\partial E} \right) \Big|_{E=0}$$

How do the # of bath microstates change with a change in system energy E ?

Notice that

$$E_T - E = E_B \Rightarrow$$

$$\left. \left(\frac{\partial \ln \Omega_B}{\partial E} \right) \right|_{E=0} = \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right) \left(\frac{\partial E_B}{\partial E} \right)^{-1}$$

$$= - \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)$$

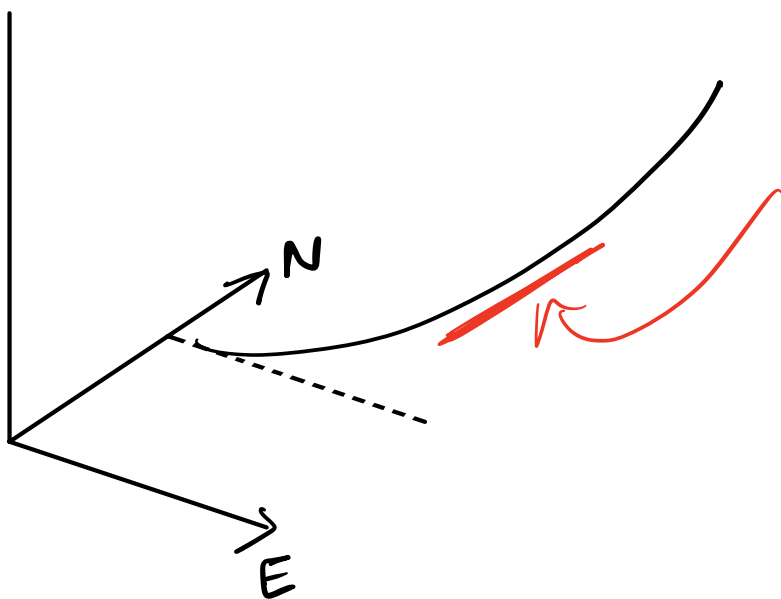
N_B, V_B

Say what?

Well really we should have been writing

$$\Omega_B(N_B, V_B, E_B) \quad (\text{Not only a function of } E_B)$$

$$S_B(N, V, E)$$



Slope of S_B
along a slice
with $N_B + V_B$
fixed

The BIG INSIGHT...

$\left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)_{N_B, V_B}$ has nothing to do with the system.
It is a property of the bath!

Let's just define (for now) that bath property as

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

The Taylor expansion becomes

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

?

Exponentiating both sides yields

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

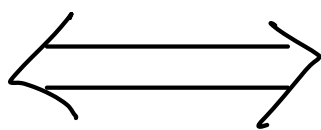
Q: Why am I discarding $\Omega_B(E_T)$?

A: It doesn't have to do with the system energy E , so it is just a constant that won't vary from one system microstate to the next.

By contrast, E is a function of ν .

Let's combine things...

Probability of
system microstate
 ν



How many bath
microstates have
energy $E_T - E(\nu)$

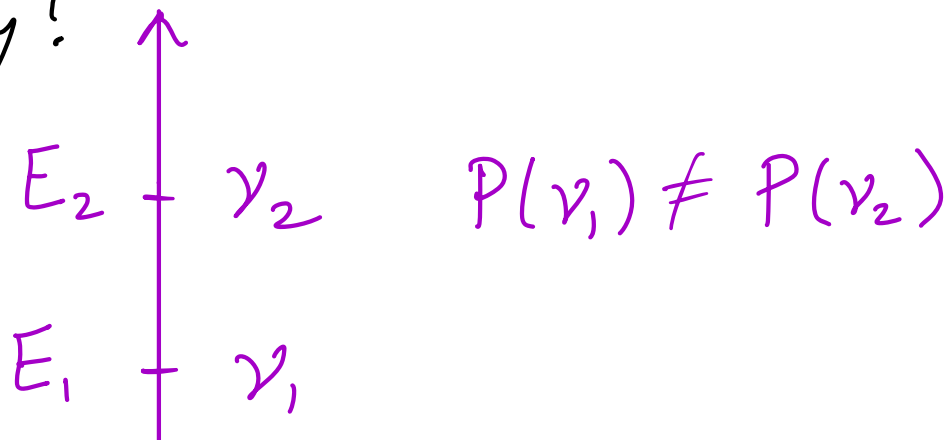
$$P(\nu) \propto \Omega_B(E_T - E(\nu))$$

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

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

E is no longer fixed. It fluctuates!

Are the system microstates ν equally likely?



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 ."