

Lecture 2

Recall from last lecture...

Our Starting Point:

In an isolated system (fixed N, V, E), all microstates are equally probable.

Mathematically, at fixed N, V, E :

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

Distribution must be normalized.

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

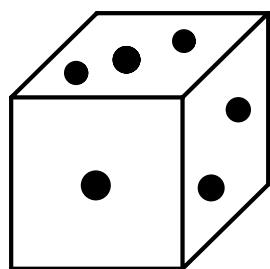
$$\Rightarrow \sum_{\substack{\nu \text{ with} \\ (N, V, E)}} (1) = \Omega(N, V, E)$$

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

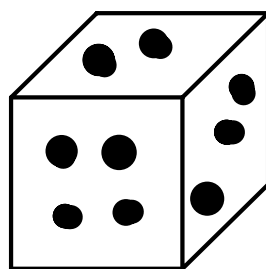
WARNING: I am not being careful to distinguish between discrete probability distributions and continuous probability densities. If ν were a continuous degree of freedom ... $\int d\nu \dots$

How big is Ω ?

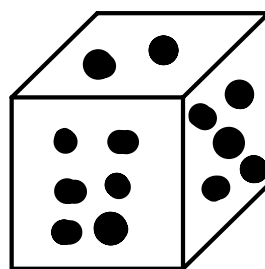
For idealized independent events...



$$\Omega = 6$$



$$\Omega = 6^2$$

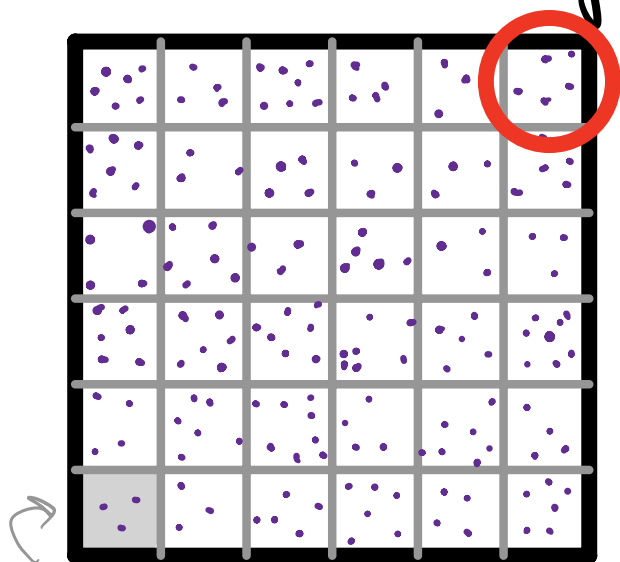


... n dice

$$\Omega = 6^n$$

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

For effectively independent subsystems...



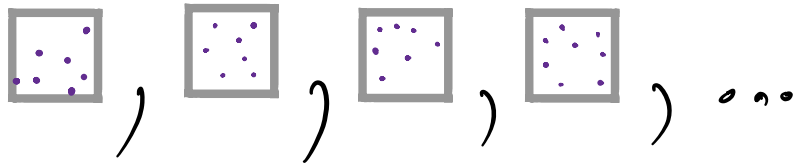
Volume v per cell

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

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

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

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,

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

Rename $\omega \equiv \tilde{\omega}^{\frac{1}{P_V}}$

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!

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

Intensive $\frac{v}{n}$

$\frac{N}{V}$

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 ...

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

Why the k_B ?

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

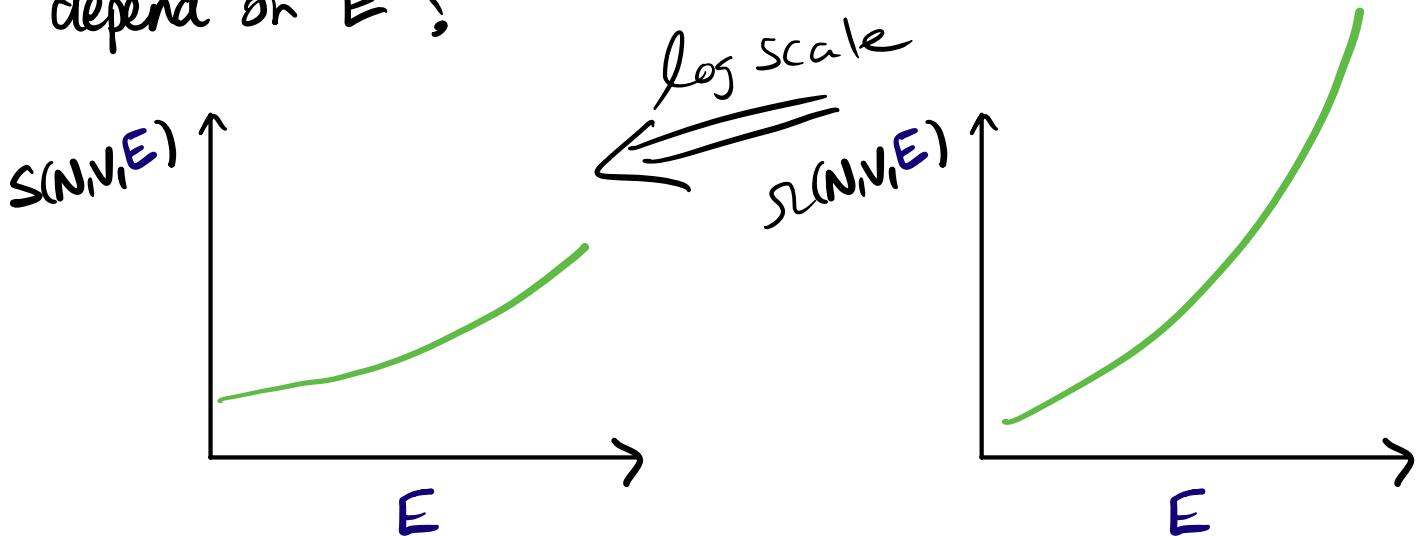
Units of thermodynamic entropy...? Not Unitless

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 ?



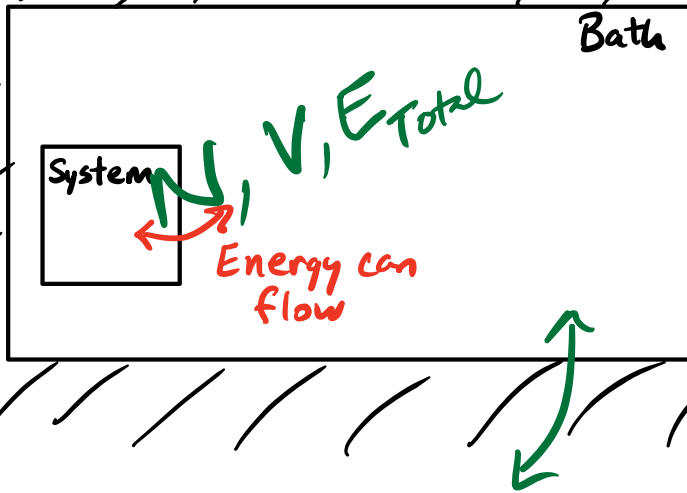
Holding N, V, E fixed made sense for a closed, isolated system. Often we are interested in things which are not closed and isolated.

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



N_B, V_B, E_B
 V_B

Variables with no flow:

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

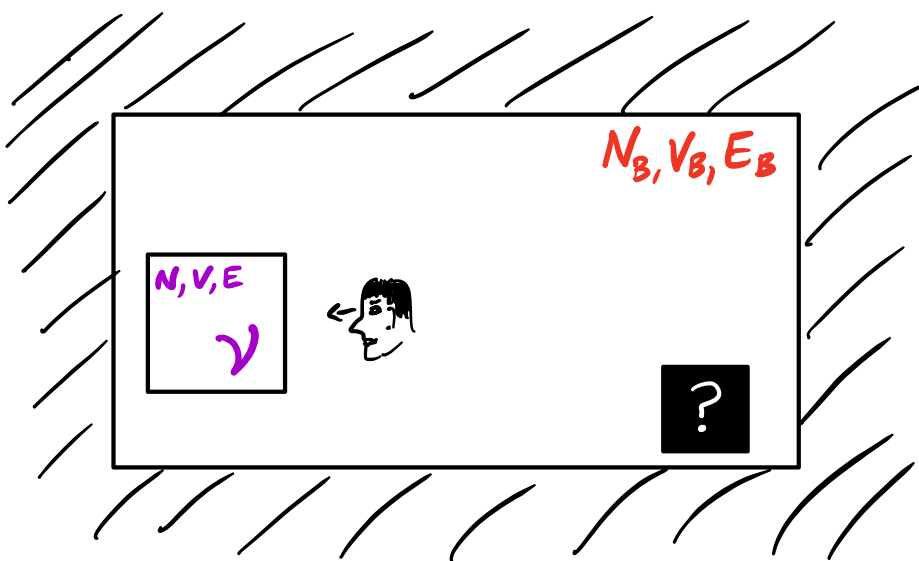
Variable with flow:

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

System microstate Bath microstate

Microstate of the full system + bath is defined by

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



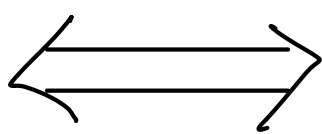
What if I cannot observe the state of the bath?

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:

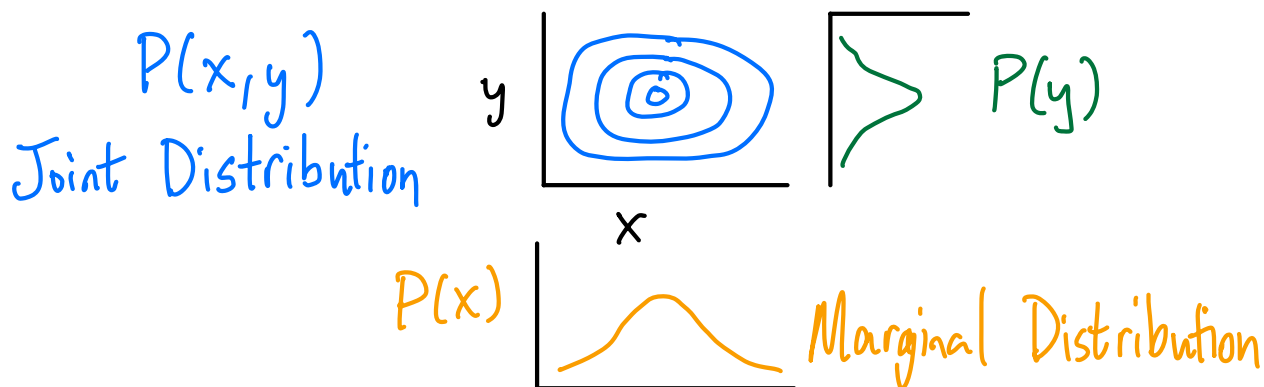
$$P(v) = \sum_{v_B} P(v, v_B)$$

↑ ↑

Marginal distribution

Joint distribution

Aside on Marginal Distributions



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

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

(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.

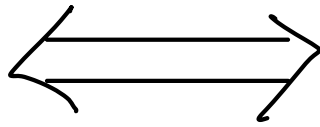
(2) Why is $\Omega(E_T)$ the right normalization?

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

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

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

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 ?