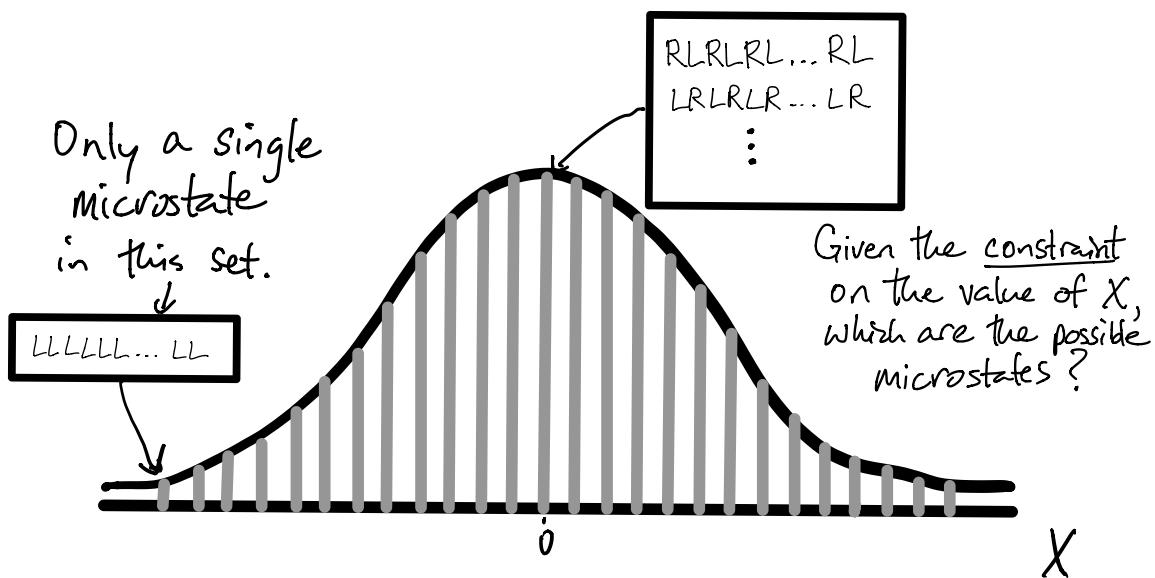


## Lecture 4

Recall from last lecture...

After a LONG time...



$$P_T(X) = \frac{T C_{\frac{X+T}{2}}}{2^T}$$

← Combinatorial Factor:  
How many microstates satisfy the constraints

Fraction of microstates which satisfy the constraint  $X$  at time  $T$

Number of possible microstates

I think you probably know that the number of microstates is connected to entropy but let's build that up.

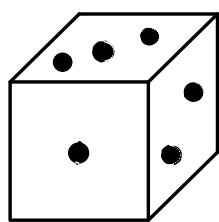
$$P(v) = \begin{cases} \frac{1}{\Omega(N, V, E)}, & \text{if } N=N_v, V=V_v, E=E_v \\ 0, & \text{otherwise} \end{cases}$$

$\Omega(N, V, E)$  was the # of allowed microstates

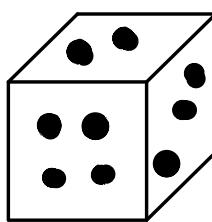
Meaning the # of microstates that satisfied our constraints.

How does  $\Omega$  grow with system size?

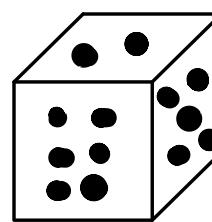
For idealized independent events...



$$\Omega = 6$$



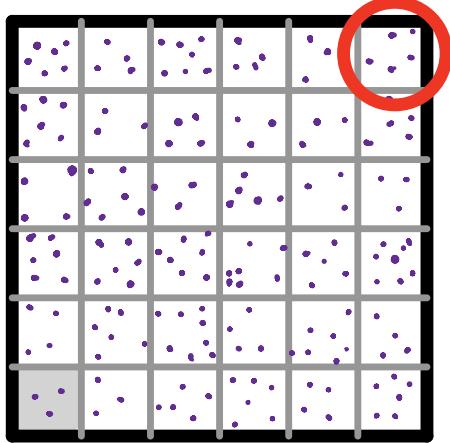
$$\Omega = 6^2$$



$$\Omega = 6^n$$

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

# Now a dilute gas...



Volume of a cell  $V$

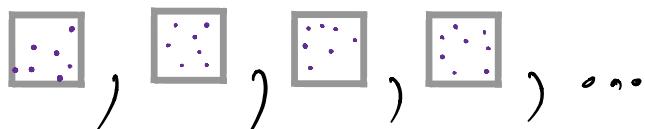
Each cell is big enough  
that it is uncorrelated from  
the others.

⇒ The cells are  
effectively  
independent.

$$\text{Density } \rho = \frac{N}{V} \quad \begin{matrix} \text{\# of particles} \\ \text{Total Volume} \end{matrix}$$

$$M = \# \text{ of independent cells} = \frac{\text{Total Volume } V}{\text{Volume of a cell } V} \\ = \frac{N/\rho}{V}$$

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



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

Because the cells are independent,

$$\Omega = \tilde{\omega}^M \quad M = \frac{N/p}{V}$$

$$= \tilde{\omega}^{\frac{N/p}{V}} = \underbrace{\left( \tilde{\omega}^{\frac{1}{pV}} \right) N}_{\downarrow} = \omega^N$$

Redefine as  $\omega$

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

( $\Omega$  grows exponentially with system size)

What does  $\omega$  depend on? On  $N$ ? Not on  $N$ .

Intensive stuff!

$$\omega = \tilde{\omega}^{\frac{1}{pV}}$$

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

Why is  $\tilde{\omega}$  intensive?

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

$$\ln \Omega = \underbrace{N}_{\text{Extensive}} \underbrace{\ln \omega(v, p, e)}_{\text{Intensive (entropy per particle)}}$$

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  $\ln S \dots ?$  Unitless

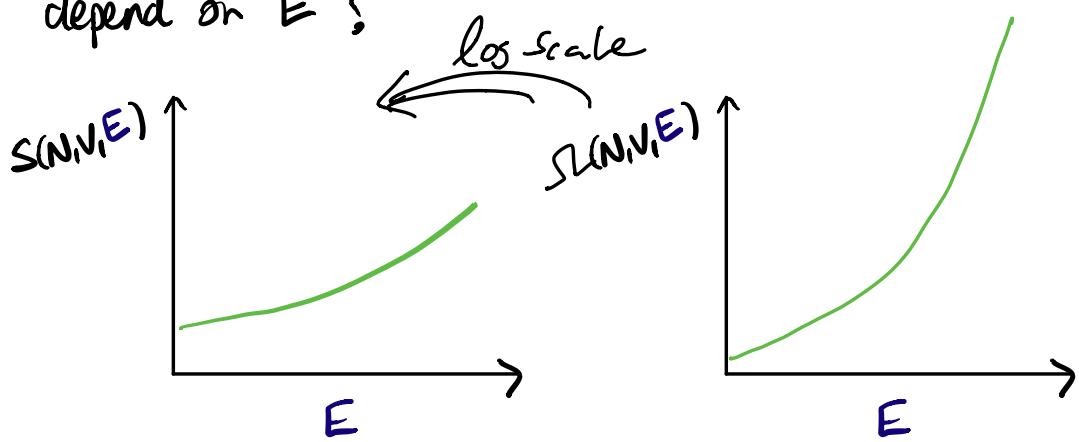
Units of thermodynamic entropy...? Not unitless

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:

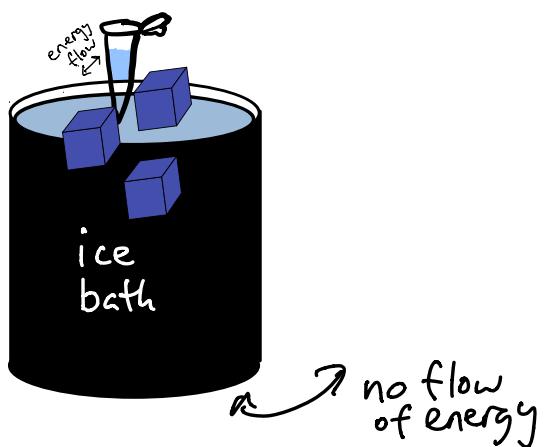
$S(N, V, E)$  takes 3 arguments and returns a number. That number for any fixed  $N, V, E$  is far less interesting than the FUNCTION  $S$  which tells how the number of states would change if you were to relax/change the constraints.

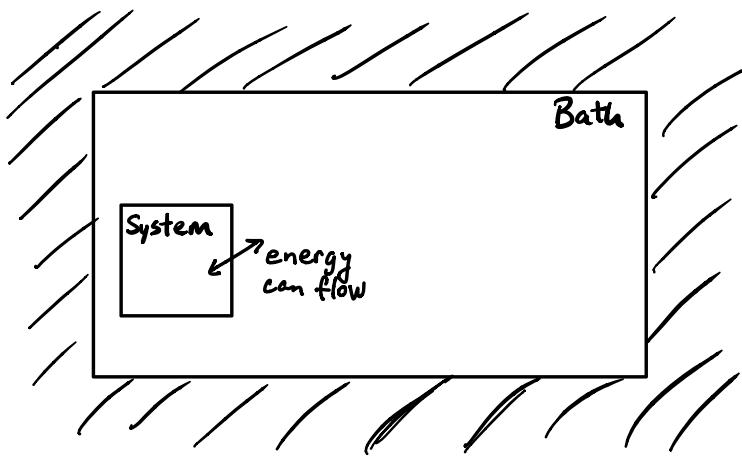
Hold  $N$  and  $V$  fixed. How does  $S(N, V, E)$  depend on  $E$ ?



It made sense to have fixed  $N, V, E$  for a closed, isolated system. Often things are not closed and isolated.

Ex.



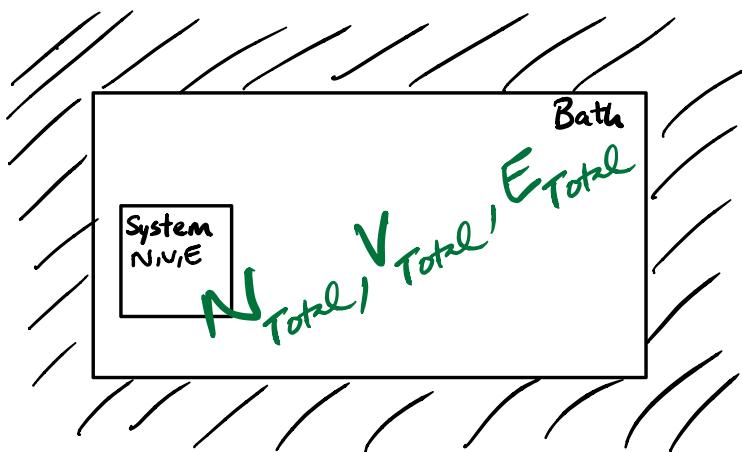


If energy can be exchanged with a "bath", then what should we do?

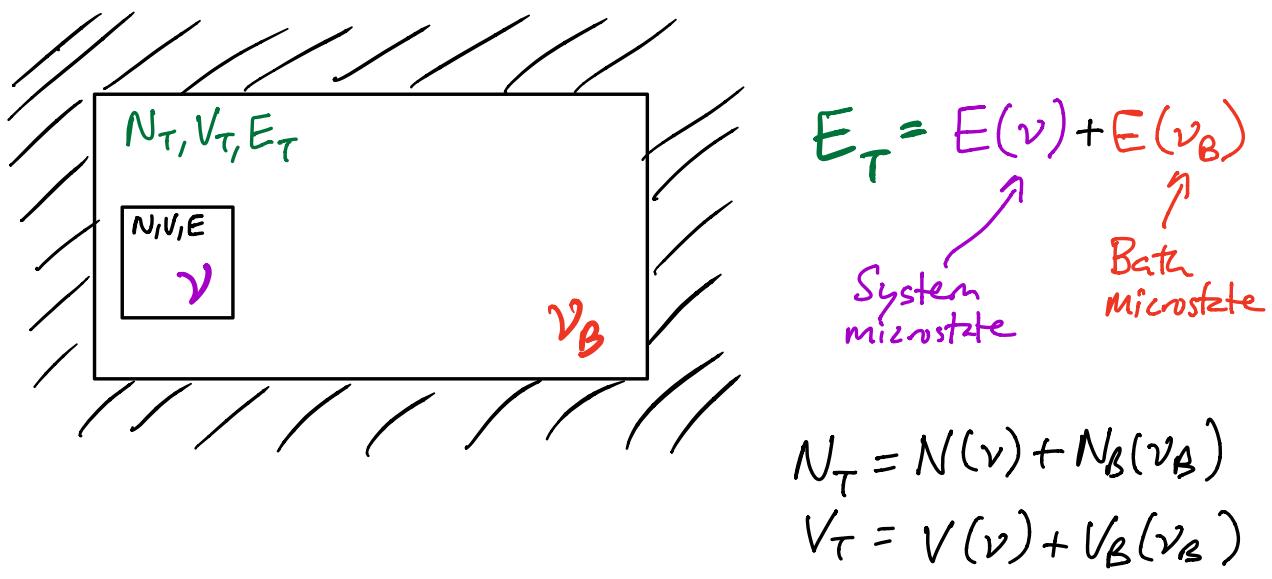
(Bath might also be called environment, reservoir, surroundings...)

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

The Big Idea...



System + Bath  
is isolated



Microstate of the full system + bath is defined by

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

If the system is in state  $\nu$ , then the bath could be in any state  $\nu_B$  for which:

