Imagine a two state system

$E$ $U=0$ or $U=E$

Quantum mechanical systems — energy is discrete

Imagine a two state system

Now combine a few of these:

$s$ $U=Nq$

What microstates could it be in?

1. $N=3$ $q=2$

$|000\rangle$ $|001\rangle$ $|010\rangle$ $|011\rangle$ $|100\rangle$ $|101\rangle$ $|110\rangle$
3 possibilities. Any reason to favor one over the others?

Postulate of equal a priori probabilities

In the absence of any further information, all are equally likely!!

2 Add another state, \( N = 4, \varphi = 2 \)

\[
\begin{align*}
(0110) & \quad (1010) & \quad (1100) \\
\text{plus} & \quad (0011) & \quad (1001) \quad (0101)
\end{align*}
\]

Now 6 possibilities > 3

As system size grows, possibilities \( \Omega \) grow.

Sounding familiar?

How many in general? \( N \) systems, \( \varphi \) quanta

\[
\Omega = \frac{N!}{\varphi! (N-\varphi)!}
\]

unique combinations assuming quanta are indistinguishable

3 Allow two \( N = 3, \varphi = 2 \) systems to interact

\[
\begin{array}{ccc}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{array}
\rightarrow
\begin{array}{ccc}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{array}
\]

\( \Omega_1 = \Omega_2 = \binom{3}{2} = 3 \quad \Omega_{12} = \binom{6}{4} = \frac{6!}{4!2!} = 15 \)

Boltzmann had the key insight, and it's on his tomb!

\[
S = k \ln \Omega \quad \text{or} \quad S = k \ln \Omega
\]
\[ S_1 = S_2 = k \ln 3 \quad S_{12} = k \ln 15 > 2k \ln 3 \]
\[ S_1 + S_2 = 2k \ln 3 \]

Why \( k \)? Only way to get the extensivity property we want.

**Amazing it was figured out!!**

In our small example here \( S \) is not continuous.

Consider 2 big systems

\[
\begin{align*}
U_1 & \quad S_i = k \ln \Omega_1 \\
U_2 & \quad S_i = k \ln \Omega_2
\end{align*}
\]

**thermal contact (exchange quanta)**

What's \( U \), @ equilibrium?

\[ \Omega_1 \text{ increases very rapidly with } U_1, \quad \Omega_2 \text{ decreases } \]

\[ \Omega = \Omega_1(U_1) \Omega_2(U - U_1) \]

Any value of \( U_1 \) is possible, but one value is overwhelmingly more likely than all others.

Flip enough fair coins and you'll get 50:50 to arbitrary accuracy (HW)
Maximize $\Omega$

\[
\frac{d\Omega}{du_1} = \Omega_2 (u-u_1) \frac{d\Omega_1}{du_1} + \Omega_1 (u) \frac{d\Omega_2}{du_1} = 0 \quad \frac{1}{\Omega_1, \Omega_2}
\]

\[
\frac{1}{\Omega_1} \frac{d\Omega_1}{du_1} + \frac{1}{\Omega_2} \frac{d\Omega_2}{du_2} = 0
\]

\[
\frac{1}{\Omega_1} \frac{d\Omega_1}{du_1} = -\frac{1}{\Omega_2} \frac{d\Omega_2}{du_2} \quad \text{but} \quad du_2 = -du_1
\]

\[
\frac{d\ln\Omega_1}{du_1} = \frac{d\ln\Omega_2}{du_2} \rightarrow \text{condition for thermal equilibrium!!}
\]

Peak back at Boltzmann's tomb

\[
\frac{dS_1}{du_1} = \frac{dS_2}{du_2} = \frac{1}{T} \quad \text{!! constant} \quad V, N \text{ here}
\]

Temperature emerges as simply the way to ensure the most likely distribution of quanta!!

\[
dl = \left(\frac{du}{dS}\right) ds + \ldots \sim T ds = d\xi \text{rew for a reversible process w/o work}
\]

Now back to the 2 state example.

\[
S = k \ln N = k [\ln N! - \ln e! - \ln(N - e)!]
\]

If $N$ is any bigger than 100, Stirling's approximation is nearly exact:

\[
N! \sim N^N e^{-N} \sqrt{2\pi N} \quad \ln N! \sim N \ln N - N
\]
\[ S = k \left[ N \ln N - \frac{N}{2} \ln \frac{2}{N} - \left( 1 - \frac{N}{2} \right) \ln \left( 1 - \frac{N}{2} \right) \right] \]

Add and subtract \( \frac{N}{2} \ln N \)

\[ S = k \left[ (N-\frac{N}{2}) \ln N + \frac{N}{2} \ln N - \frac{N}{2} \ln \left( 1 - \frac{N}{2} \right) \right] \]

\[ S = k \left[ \frac{N}{2} \ln \frac{N}{2} - (N-\frac{N}{2}) \ln \left( 1 - \frac{N}{2} \right) \right] \]

Let \( U = \frac{N}{2} \)

\[ S = k \left[ -\left( \frac{U}{e} \right) \ln \left( \frac{U}{Ne} \right) - (N-\frac{U}{e}) \ln \left( 1 - \frac{N}{e} \right) \right] \]

Entropy in terms of energy. The fundamental equation of this system.

Plot \( S \) vs \( U \)

\[ \frac{1}{T} = \frac{dS}{dU} \]

Classical stat mech only works when the number of states is \( \gg \) the number of quanta. (Almost) Always true.

For our toy problem, \( \Omega(U) \) decreases when \( U > \frac{N}{2} e \). Typically an unphysical situation, except for exotic matter.
Ok, let's evaluate \( \frac{\partial S}{\partial U} \bigg|_N = \frac{1}{T} \)

\[
Z \to \quad \frac{k_B}{e} \ln \left[ \frac{N e}{u} - 1 \right] = \frac{1}{T} \quad \text{"thermal equation of state"}
\]

\[
Z \to \quad U(T) = \frac{N e}{1 + e^{E/k_B T}}
\]

\[
\lim_{T \to 0} U(T) = 0 \quad \ldots \ldots \quad \text{all in the ground state}
\]

\[
\lim_{T \to \infty} U(T) = \frac{N e}{2} \quad \ldots \ldots \quad \text{half in the ground state}
\]

Random order

Can show \( S \left( \frac{N e}{2} \right) = k \ln 2 \), maximum possible entropy in 2-state system

\[
\begin{array}{c}
U \\
\hline
\text{\( \frac{N e}{2} \)} \\
(\frac{\partial S}{\partial U}) \to 0 \\
(\frac{\partial S}{\partial U}) \to \infty \\
T
\end{array}
\]

(\text{Thermally, can't access } U > \frac{N e}{2} !)

(\text{Could intentionally construct a closed system with } U > \frac{N e}{2} \text{ but given the chance it will spontaneously decay - laser})
Heat capacity \[ C = \frac{dU}{dT} \] is a bit of a mess even definitely non-linear.

This is an example of a microcanonical treatment, often called "NVE".

Can only be solved analytically for a few simple systems:
- 2 state
- harmonic oscillator: infinite ladder of states
- polymer chain: fancy 2 state

Statistical mechanics uses other approaches to solve this problem. For now we'll return to the classical approach.