Lecture 2: Microcanonical ensemble

Where does this concept of entropy come from??

Easiest to start from a microscopic view IMHO

Quantum mechanical systems — energy is <u>discrete</u>
Comes in quanta

Imagine a two state system

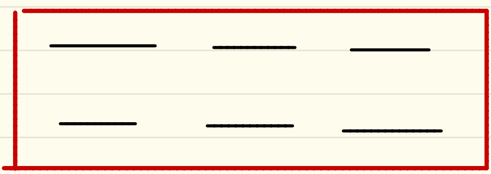
ε

0

$U = 0$ or $U = \varepsilon$

- magnet
- trans v. gauche

Now combine a few of these:



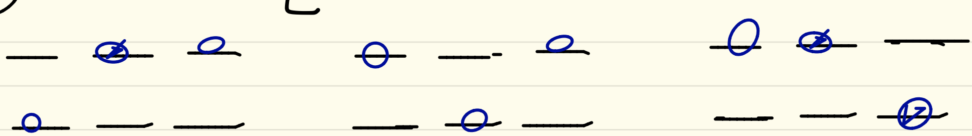
ε

0

suppose the system has $q < N$ quanta of energy
$U = Nq$

what microstates could it be in?

(1) $N = 3 \quad q = 2$



(0 1 1) (1 0 1) (1 1 0)

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, $N=4$, $q=2$

(0110) (1010) (1100) plus (0011) (1001) (0101)

Now 6 possibilities > 3

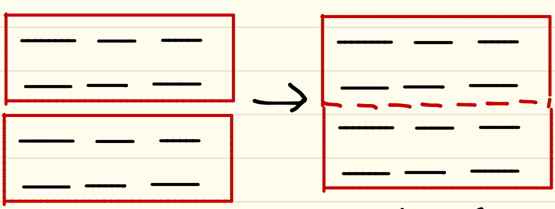
As system size grows, possibilities Ω grow. Sounding familiar?

How many in general? N systems, q quanta

$$\binom{N}{q} = \frac{N!}{q!\,(N-q)!}$$

unique combinations assuming quanta are indistinguishable

3 Allow two $N=3$, $q=2$ systems to interact



$$\Omega_1 = \Omega_2 = \binom{3}{2} = 3 \qquad \Omega_{12} = \binom{6}{4} = \frac{6!}{4!\,2!} = 15$$

Boltzmann had the key insight, and its on his tomb! $S \propto \ln \Omega$ or $\boxed{S = k \ln \Omega}$

$S_1 = S_2 = k \ln 3 \quad S_{12} = k \ln 15 > 2k \ln 3$

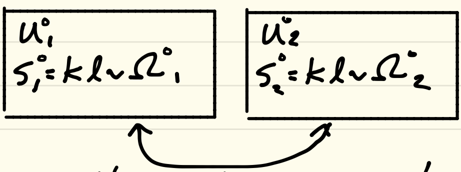
$S_1 + S_2 = 2k \ln 3$

Why ln? 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



$U = U_1 + U_2$

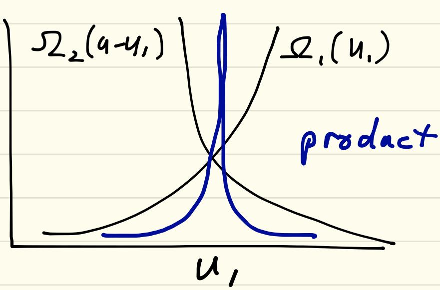
thermal contact (exchange quanta)

What's U_1 @ equilibrium?

Ω_1 increases very rapidly with U_1

Ω_2 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 Ω

$$\frac{d\Omega}{dU_1} = \Omega_2(U-U_1)\frac{d\Omega_1}{dU_1} + \Omega_1(U_1)\frac{d\Omega_2}{dU_1} = 0 \quad \Big| \; \frac{1}{\Omega_1\Omega_2}$$

$$\frac{1}{\Omega_1}\frac{d\Omega_1}{U_1} + \frac{1}{\Omega_2}\frac{d\Omega_2}{dU_2} = 0$$

$$\frac{1}{\Omega_1}\frac{d\Omega_1}{dU_1} = -\frac{1}{\Omega_2}\frac{d\Omega_2}{dU_1} \qquad \text{but } dU_2 = -dU_1$$

$$\boxed{\frac{d\ln\Omega_1}{dU_1} = \frac{d\ln\Omega_2}{dU_2}}$$ Condition for thermal equilibrium!!

Peak back at Boltzmann's tomb

$$\frac{dS_1}{dU_1} = \frac{dS_2}{dU_2} = \frac{1}{T} \quad !!$$ constant V, N here

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

$$dU = \left(\frac{\partial U}{\partial S}\right) dS + \dots \approx T\,dS = đq_{rev}$$ for a reversible process w/o work

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Now back to the 2 state example.

$$S = k\ln\Omega = k\left[\ln N! - \ln q! - \ln(N-q)!\right]$$

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

$$N! \approx N^N e^{-N}\sqrt{2\pi N} \qquad \underline{\ln N! \approx N\ln N - N}$$

$$S = k\left[N\ln N - \cancel{N} - (q\ln q - \cancel{q}) - \left((N-q)\ln(N-q) - \cancel{(N-q)}\right)\right]$$

$$= k\left[N\ln N - q\ln q - (N-q)\ln(N-q)\right]$$

Add and subtract $q\ln N$

$$= k\left[(N-q)\ln N + q\ln N - q\ln q - (N-q)\ln(N-q)\right]$$

$$\boxed{S = k\left[-q\ln\frac{q}{N} - (N-q)\ln\left(\frac{N-q}{N}\right)\right]}$$

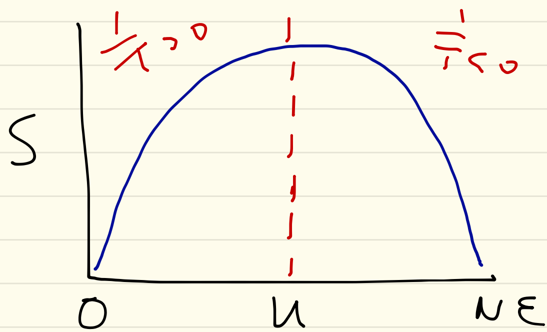
Let $U = q\varepsilon$

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

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

Plot S vs U

$\frac{1}{T} = \frac{dS}{dU}$



Note we only get physical temperatures when $U < \frac{N\varepsilon}{2}$

Classical stat mech only works when the number of states is >> the number of quanta. (Almost) always true.

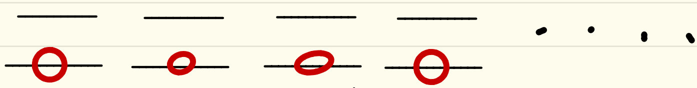
For our toy problem, $\Omega(U)$ decreases when $U > \frac{N}{2}\varepsilon$. Typically an unphysical situation, except for exotic matter.

Ok, let's evaluate $\left(\frac{\partial S}{\partial U}\right)_N = \frac{1}{T}$

$\Rightarrow \quad \frac{k_B}{\varepsilon} \ln\left[\frac{N\varepsilon}{U} - 1\right] = \frac{1}{T}$ "thermal equation of state"

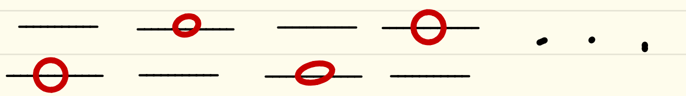
$\Rightarrow \quad \boxed{U(T) = \frac{N\varepsilon}{1 + e^{\varepsilon/k_B T}}}$

$\lim_{T\to 0} U(T) = 0$



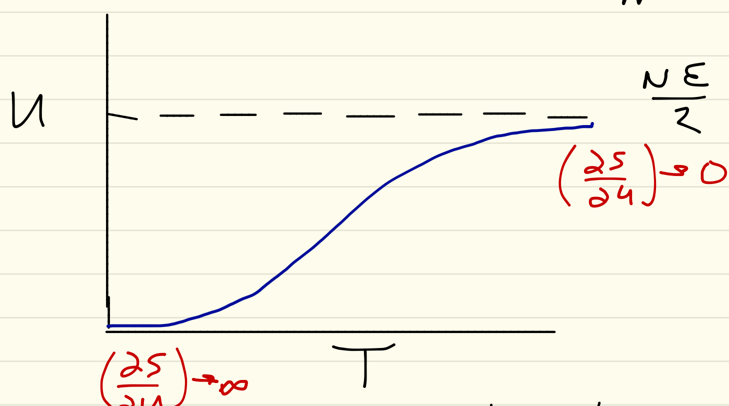
All in the ground state

$\lim_{T\to\infty} U(T) = \frac{N\varepsilon}{2}$



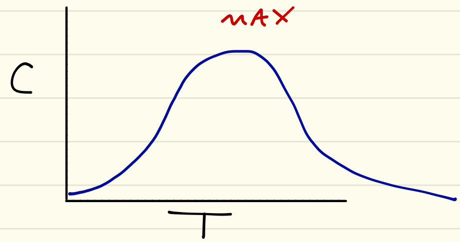
half in the ground state
random order

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



Thermally, can't access $U > \frac{N}{2}\varepsilon$!

Could intentionally construct a closed system w/ $U > \frac{N\varepsilon}{2}$ but given the chance it will spontaneously decay — laser heat capacity $C = \frac{dU}{dT}$ = a bit of a mess eqn



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.