Statistical mechanics

QM — tiny things, many states, uncertainty

$\Big\downarrow$ stat mech

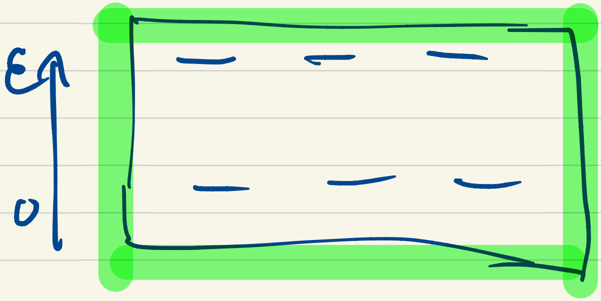
Macro — big things, state fns, deterministic

$H, S, G, K_{eq}, k, \ldots$

Example: 2 state system

either 0 or ε of energy

Maybe an e^- in a magnetic field.



$N = 3$

$U = 2\varepsilon$

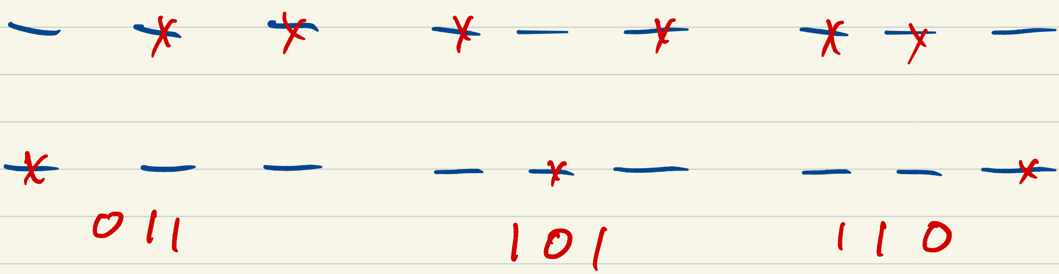
Closed system, some number N of 2 state systems, able to xc energy

$$U = q \cdot \varepsilon$$

q = # of elements with energy ε

How many ways?

$N = 3 \quad q = 2 \quad U = 2\varepsilon$



Three different μstates corresponding to the same N, U

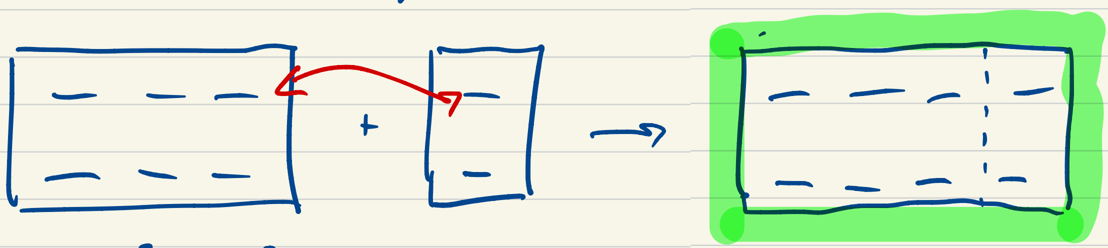
$$\Omega = 3$$

a priori, no reason to favor one μstate over another.

postulate of equal a priori probabilities

All μstates consistent with given constraints are equally likely

Combine 2 systems



$N=3 \quad q=2$
$\Omega = 3$

$N=1 \quad q=0$
$\Omega = 1$

$N=4 \quad q=2$

$$\Omega = \frac{4 \cdot 3}{2} = 6$$

What happens to U from beginning to end? Conserved!!

What happens to Ω? Goes up!!
Will always do so... whenever a

constraint is relaxed, $\Omega \uparrow$

What is Ω ?!?   <u>Entropy</u>

Measure of # ways a system can exist.

Always increases in closed systems when constraint relaxed

Would like it to be additive.
" " entropy of two identical, independent boxes to be twice that of a single box

$n=3 \quad q=2$
$\Omega=3$

ditto

composite
$\Omega = 3\times 3 = 9$
$\neq 2\cdot\Omega$

$S = k\ln 3$ $S = k\ln 3$ $S = k\ln 9 = 2k\ln 3$

<u>Boltzmann</u> realized these ideas and said

$$\underline{S = k\ln\Omega}$$

on his grave

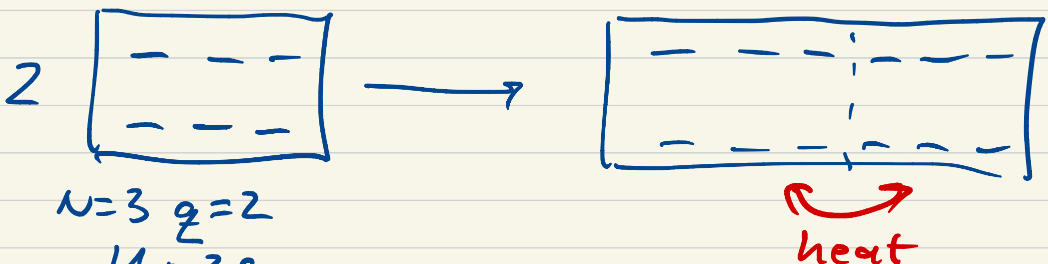
additive over independent systems.

What is k? In principle, could be anything or nothing. But due to the course of development of the ideas, $k = k_B$ Boltzmann's constant

Gives your familiar units of entropy, E/T

For 2 state system, can see

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



$N=3$ $q=2$

$U = 2\varepsilon$

$\Omega = 3$

$S = k \ln 3$

$N=6$ $q=4$ $U = 4\varepsilon$

$\Omega = \binom{6}{4} = 15$

$S = k \ln 15$

$$\Delta S = k \ln 15 - 2k \ln 3$$
$$= k \ln 5/3 > 0$$

Die Energie der Welt ist konstant.
Die Entropy der Welt strebt
einem Maximum zu.

– Clausius

If we look at the combined system, we will find it in some μstate, some amt of energy on each side. Not consistent w/ observation. We <u>know</u> if we allow 2 identical boxes to xc heat, the energy will be equally divided.

Big N.

U_1	U_2
$S_1 = k \ln \Omega_1$	$S_2 = k \ln \Omega_2$

heat

$$U = U_1 + U_2$$

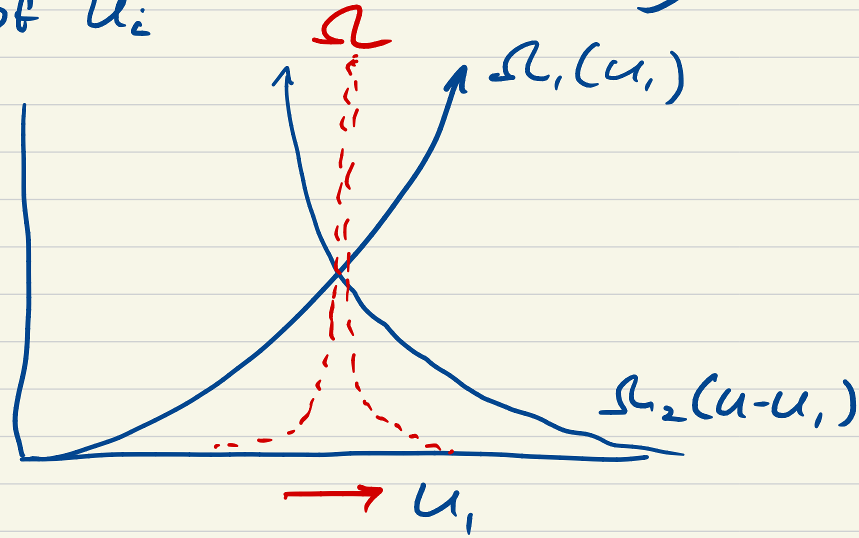
$$\Omega = \sum_{U_1=0}^{U} \Omega_1(U_1)\,\Omega_2(U-U_1)$$

add up all μstates from putting any amt of energy on either side.

What is largest term in this sum? What U_1 contributes most to Ω?

If $N \gg q$ (more states than energy to put them)

$\Omega_i(U_i)$ will be an increasing ftn of U_i



$$\frac{d\,\Omega_1\Omega_2}{dU_1} = 0 \ ?$$

$$\Omega_2 \frac{d\Omega_1}{dU_1} + \Omega_1 \frac{d\Omega_2}{dU_1} = 0$$

$$U = U_1 + U_2$$

$$dU = 0 \Rightarrow dU_1 = -dU_2$$

divide by $\Omega_1 \Omega_2$

$$\frac{1}{\Omega_1} \frac{d\Omega_1}{dU_1} = \frac{1}{\Omega_2} \frac{d\Omega_2}{dU_2}$$

$$\frac{d \ln \Omega_1}{dU_1} = \frac{d \ln \Omega_2}{dU_2}$$

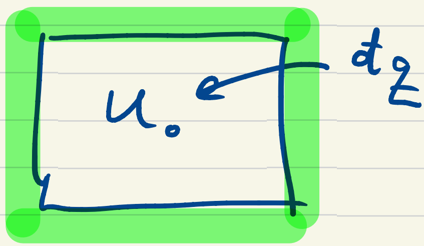
$$\boxed{\frac{dS_1}{dU_1} = \frac{dS_2}{dU_2}}$$

Most likely/most important contribution to Ω is when condition holds.

As $N \to$ big, only contribution that matters.

$$\frac{dS}{dU} = ?? \quad \frac{1}{\text{temperature}}!!$$

Condition of thermal equilibrium is that $\frac{dS_i}{dU_i}$ for each subsystem is the same. Maximizes (most probable contribution) to Ω.



$$U = U_0 + đq$$
$$= U_0 + \left(\frac{dU}{dS}\right)_{V,N} dS$$

$$đq = \frac{dU}{dS} dS = T\, dS$$

<u>2nd law of thermo</u>

Example: 2 state system

$$N \quad , \quad U = q\varepsilon \quad , \quad \Omega = \binom{N}{q} = \frac{N!}{q!(N-q)!}$$

$S = k \ln \Omega =$

$$k\left(\ln N! - \ln q! - \ln (N-q)!\right)$$

If N, q are large ($\gtrsim 100$), use Stirling's approximation

$$\ln N! \approx N \ln N - N$$

. . .

$$S = -k_B \left\{ q \ln\left(q/N\right) + (N-q) \ln\left(\frac{N-q}{N}\right) \right\}$$

$$= -k_B \left\{ \frac{U}{\varepsilon} \ln\left(U/N\varepsilon\right) + \left(N - \frac{U}{\varepsilon}\right) \ln\left(1 - U/N\varepsilon\right) \right\}$$

$S(U)$ fundamental eq

Most important thermodynamic relationship

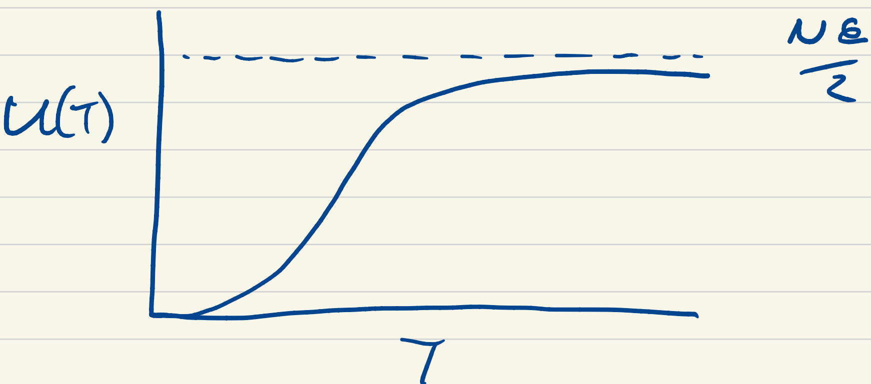
$$\frac{1}{T} = \left(\frac{dS}{dU}\right)_N = \frac{k_B}{\varepsilon} \ln\left(\frac{N\varepsilon}{U} - 1\right)$$

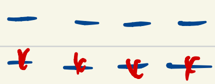
$$\Rightarrow \quad U(T) = \frac{N\varepsilon}{1 + e^{\varepsilon/kT}}$$

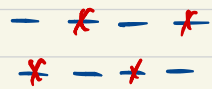
thermodynamic equation of state

$$\lim_{T \to 0} U(T) = \frac{N\varepsilon}{1+\infty} = 0 \;!!$$

$$\lim_{T \to \infty} U(T) = \frac{N\varepsilon}{1+1} = \frac{N}{2}\varepsilon \;!!$$







minimum degeneracy

maximum degeneracy

heat capacity

$$\frac{dU}{dT} = \frac{N\varepsilon^2}{k_B T^2} \frac{e^{\varepsilon/k_BT}}{(1+e^{\varepsilon/k_BT})^2} = C_v$$

$\lim_{T\to 0} C_v = 0$ denominator blows up

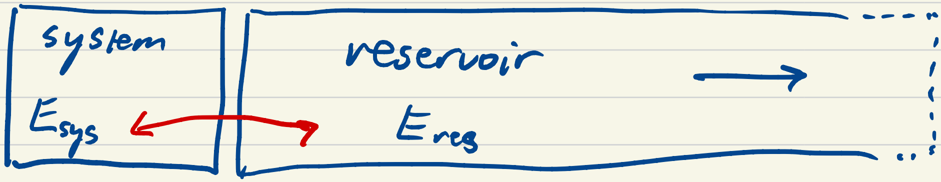
$\lim_{T\to\infty} C_v = 0$ prefactor vanishes

This approach of finding $S(U,V,N)$ is called the μcanonical ensemble. Illuminating, but not generally applicable.

Canonical ensemble

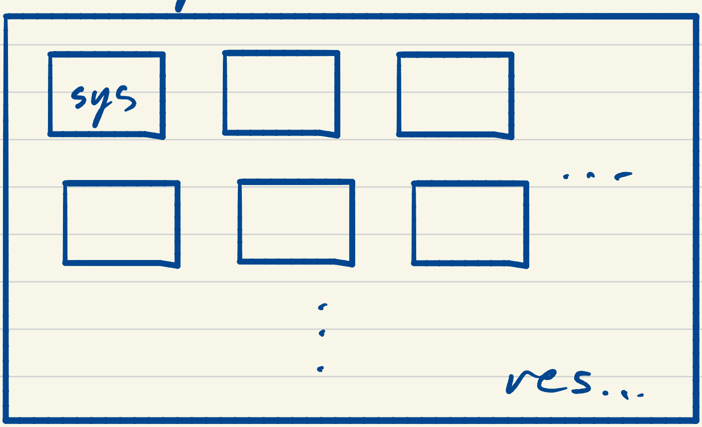
T is easier to measure/control than U.

Imagine a system in thermal contact with a much larger reservoir.



system - many elements. Maybe huge bunch of 2 state systems. Could be in any number of E_j

reservoir - even BIGGER thing, many many many possible energy states



Total
E fixed but can be divided btw the two

$$E = E_{sys} + E_{res}$$

What is probability that system has some amt of energy E_j ??

large N statistics
multinomial dist
equal a priori probability

$\downarrow$

$$\boxed{p_j \propto e^{-E_j \beta} = e^{-E_j / k_B T}}$$

where $T = dU^{res} / dS^{res}$
$= \text{constant !!}$

$\beta = 1/k_B T$ convenient

Origins of Boltzmann dist.

* What we observe is weighted average of all E_j.
ergodicity

If P_j is a probability, can normalize

$$\sum_j P_j = \sum_j e^{-E_j/kT} = Q(T)$$

Called a "partition function"

If we know E_j can construct this sum for any T.

Most commonly "system" is composed of elements, so that total energy $E_j = \sum_{\text{elements}} \varepsilon_i$

If elements are identical and distinguishable

$$Q(T) = q(T)^N \qquad N \text{ elements}$$

$$q(T) = \sum_i e^{-\varepsilon_i/kT}$$

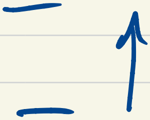
element partition fn.

If indistinguishable (messier)

$$Q(T) = q(T)^N / N!$$

Example: N distinguishable Two-state systems. in thermal equilibrium

one element, $\varepsilon_i = 0, \varepsilon$

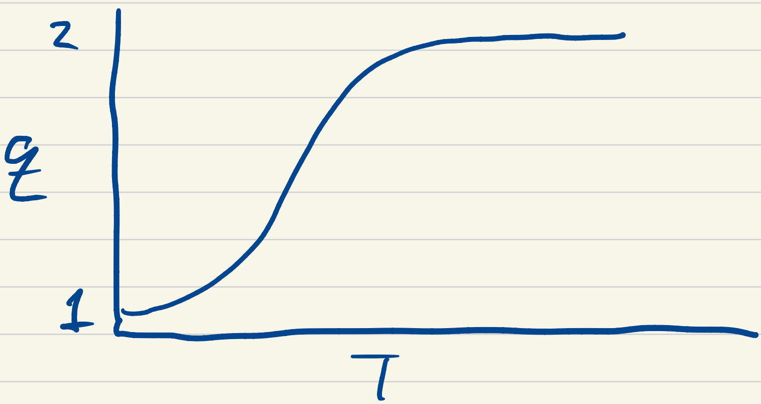


• partition fn $\quad q = \sum_i e^{-\varepsilon_i \beta} = 1 + e^{-\varepsilon\beta}$

$$= 1 + e^{-\varepsilon / k_B T}$$

$T \to 0 \quad \beta \to \infty \quad q \to 1$

$T \to \infty \quad \beta \to 0 \quad q \to 2$



# of accessible states vs T

$Q = q^N$ runs from 1 to 2^N

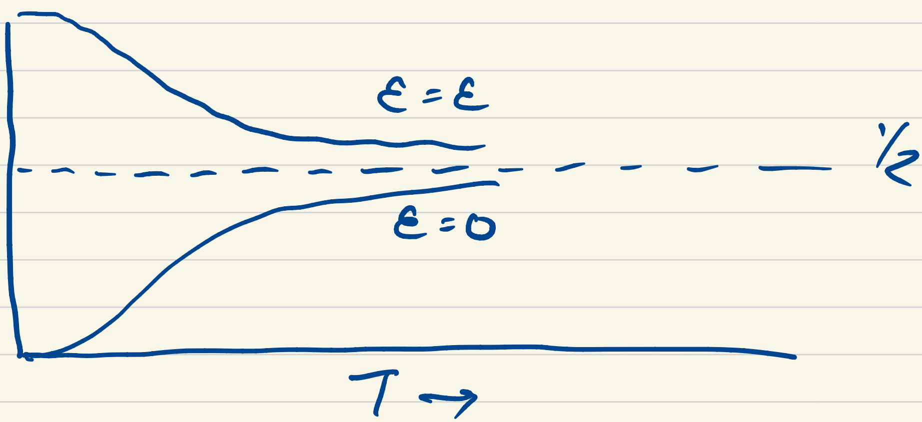
- probability of one of the elements to have an energy?

$$P(\varepsilon=0) = \frac{e^{-0\beta}}{1+e^{-\varepsilon\beta}} = \frac{1}{1+e^{-\varepsilon\beta}}$$

$$\lim_{\beta\to\infty} = 1 \qquad \lim_{\beta\to 0} = 1/2$$

$$P(\varepsilon=\varepsilon) = \frac{e^{-\varepsilon\beta}}{1+e^{-\varepsilon\beta}}$$

$$\lim_{\beta\to\infty} = 0 \qquad \lim_{\beta\to 0} = 1/2$$



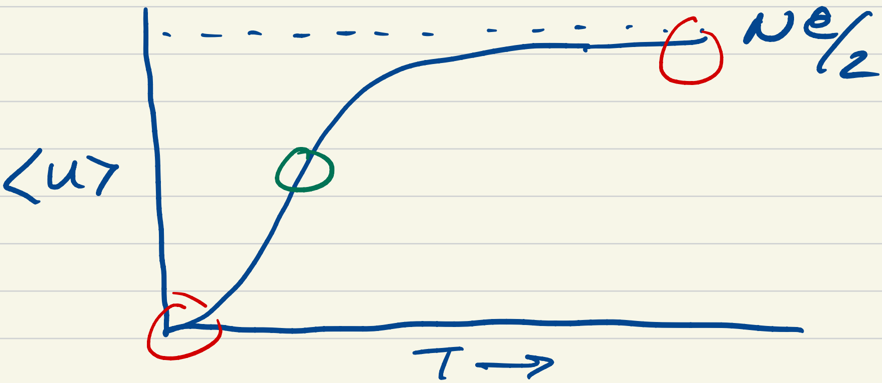
Remember: this is probability of big ensemble. Any element is 0 or ε!!

$$U = N\langle \varepsilon \rangle$$

$$= N\left\{ 0 \cdot P(\varepsilon = 0) + \varepsilon \cdot P(\varepsilon = \varepsilon) \right\}$$

$$= \frac{N\varepsilon e^{-\varepsilon\beta}}{1+e^{-\varepsilon\beta}} = \frac{N\varepsilon}{1+e^{\varepsilon\beta}}$$

$$\lim_{\beta \to \infty} = 0 \qquad \lim_{\beta \to 0} = N\frac{\varepsilon}{2}$$



Exactly as we had above.

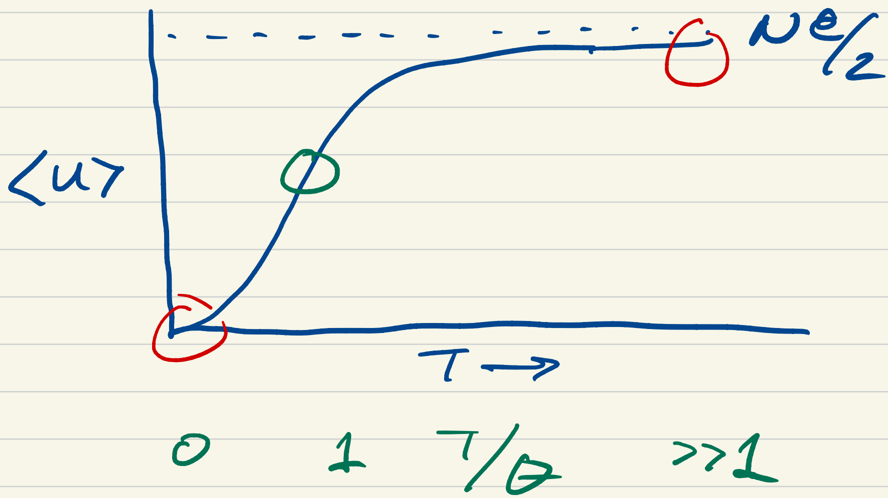
- little bit of energy changes T a lot

- energy (occupancies) change little w/T

Will depend on characteristic temperature, $\Theta_{2state} = \varepsilon / k_B$

Could rewrite

$$U = N \frac{\Theta k_B}{1 + e^{\Theta/T}}$$



Heat capacity

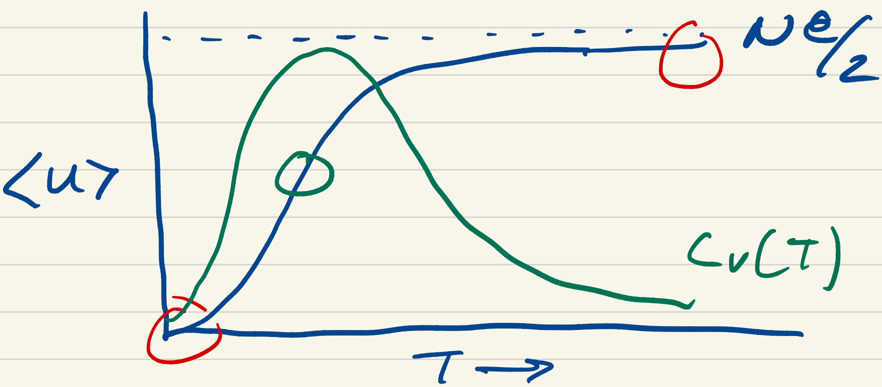
$$C_v = \left(\frac{\partial U}{\partial T}\right)_{V,N} = -k_B \beta^2 \left(\frac{\partial U}{\partial \beta}\right)_{V,N}$$

$$U = \frac{N\varepsilon}{1+e^{\varepsilon\beta}}$$

$$\frac{dU}{d\beta} = -\frac{N\varepsilon^2 e^{\varepsilon\beta}}{(1+e^{\varepsilon\beta})^2}$$

$$C_v = Nk_B\beta^2\varepsilon^2 \frac{e^{\varepsilon\beta}}{(1+e^{\varepsilon\beta})^2}$$

$$\lim_{\beta\to\infty} = 0 \qquad \lim_{\beta\to 0} = 0$$



Maximum @ inflection point.

$$\frac{\partial C_v}{\partial T} = 0 \Rightarrow T = ?$$

Compare:

$$-\left(\frac{\partial \ln Q}{\partial \beta}\right) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)$$

$$= -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right) \qquad \left(\frac{\partial q}{\partial \beta}\right) = -\varepsilon e^{-\varepsilon\beta}$$

$$= \frac{N\varepsilon e^{-\varepsilon\beta}}{1+e^{-\varepsilon\beta}}$$

$$= U \; !!$$

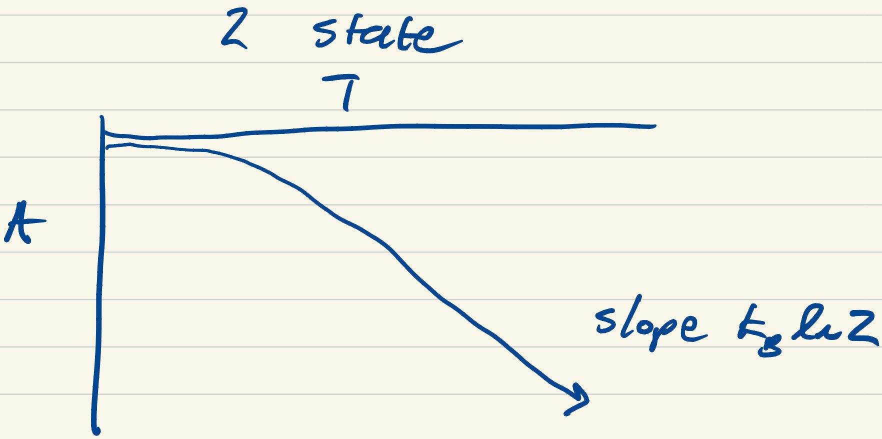
thermo fcns can always be written in terms of Q!!

Helmholtz energy

"Natural" ftn of NVT.

ΔA = maximum work @ const NVT.

$$A = -k_B T \ln Q = -N k_B T \ln q$$



entropy

$$A = U - TS$$

$$\Rightarrow S = \frac{U - A}{T}$$

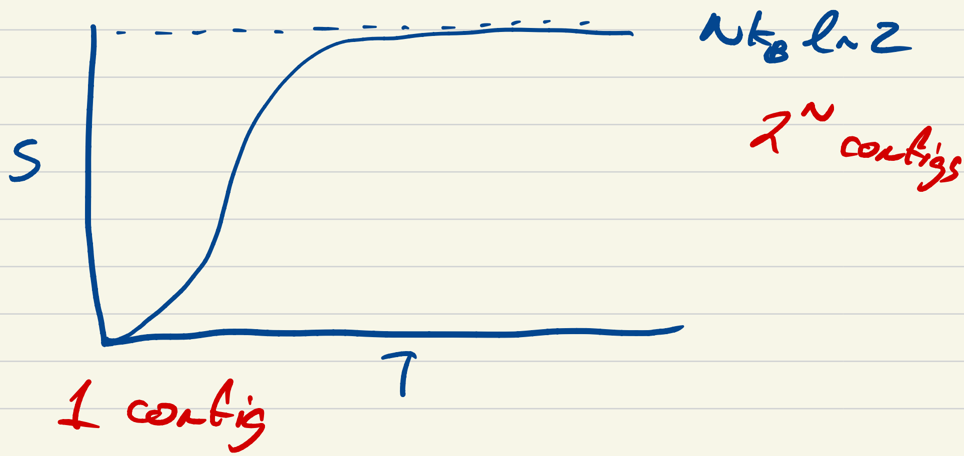
$$= k_B(\beta U + \ln Q)$$

2 state

$$\Rightarrow S = Nk_B\left(\frac{\beta\varepsilon}{1+e^{\varepsilon\beta}} + \ln\left(1+e^{-\varepsilon\beta}\right)\right)$$

$$\lim_{\beta\to\infty} = 0$$ Third Law!!

$$\lim_{\beta\to 0} = Nk_B \ln 2$$



Pretty cool!

With this tool set, can find thermo functions for any type of system!!