Foundations of Stat. Mech.

* Now we turn to one of our main goals. How can we understand/derive TD from 1st principles (i.e, from knowledge of microscopic dof + dynamics)

* Let's first think classically. Say we have a gas of N particles ($N \sim 10^{23}$). If we work in the framework of Hamiltonian mechanics, our state is specified by

$$\left(\vec{q}_1 \vec{q}_2 \cdots \vec{q}_N\ \vec{p}_1 \vec{p}_2 \cdots \vec{p}_N\right) = \text{point in 6N-dim phase space}$$

* as time evolves, the initial point in PS traces out a trajectory via Hamilton's eqns:

EOM:
$$\frac{d\vec{q}_i}{dt} = \frac{\partial \mathcal{H}(\vec{q},\vec{p})}{\partial \vec{p}_i}$$

$$\frac{d\vec{p}_i}{dt} = -\frac{\partial \mathcal{H}(\vec{q},\vec{p})}{\partial \vec{q}_i}$$

* what we measure in a macroscopic system is really not an instantaneous value of some quantity, but a time average over some time $T \gg t_{\text{microscopic}}$

e.g., $$\overline{\mathcal{O}(\vec{q},\vec{p})} = \frac{1}{T}\int_0^T dt\, \mathcal{O}(\vec{q}(t),\vec{p}(t))$$

$\mathcal{O}$ = some observable

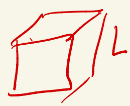
* This is a hopeless task trying to tackle it head-on (i.e., solving Hamilton's equations, which would be $\mathcal{O}(10^{23})$ coupled ODE's, & then performing the time-average)

* Moreover, even if you could integrate 10^{23} coupled ODE's, you would still have to plug in 10^{23} initial conditions to the general solutions (i.e., you would have to know the initial values of $(\vec{p}, \vec{q})$ for 10^{23} particles... absurd!)

* How to proceed? Use probability arguments!

* whether we're using CM or QM, the fact is there is a many-to-1 mapping of microscopic states to an observed macroscopic state

e.g.: N non-interacting particles in a box



$V = L^3$

$$E = \sum_i n_i \varepsilon_i$$

$$N = \sum_i n_i$$

$$-\frac{\hbar^2}{2m}\nabla^2 \psi_i = \varepsilon_i \psi_i$$

$$\psi_i(\text{walls}) = 0$$

$$\Downarrow$$

$$\varepsilon_i = \frac{\hbar^2 i^2}{2mL^2} \qquad i = 0, \pm 1, \ldots$$

Macro state: (E, N, V)

Micro state: $\{n_i, \varepsilon_i\}$ (Many possible configs that sum up to give E, N)

(☆) Let $\Omega(N,V,E)$ = # of micro configs that give the macro state N,V,E.

* $\Omega(N,V,E)$ is basically a measure of our ignorance or uncertainty about the system, since our macro measurements of E,N,V can't differentiate between the Ω - microstates.

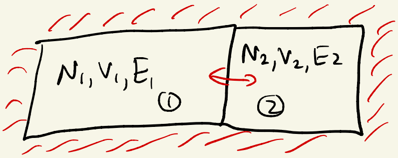
$\Downarrow$

* Therefore, the most unbiased/reasonable thing we can do is to assume the system is in any of the $\Omega(E,N,V)$ microstates with equal probability

$$\boxed{\text{This "assumption of equal a-priori probabilities" is THE foundation of the entire field of Stat. Mech!}}$$

* Before calculating Ω for a few simple models, let's see the implications + make our 1st connection to TD.

Boltzmann Entropy + TD entropy



* total system adiabatic
* but 1 + 2 can exchange energy w/ each other

$$E^{(0)} = E_1 + E_2 = \text{const.}$$

total # of micro states $= \Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E^{(0)} - E_1)$

$$= \Omega^{(0)}(E^{(0)}, E_1)$$

* What value will E_1 relax to over a long time?

* applying our equal probability assumption for the microstates, the equilibrium E_1 will maximize $\Omega^{(0)}$:

$$\Rightarrow \frac{d\Omega^{(0)}}{dE_1} = \Omega_2 \frac{d\Omega_1}{dE_1} + \Omega_1 \frac{d(E^0 - E_1)}{dE_1} \cdot \frac{d\Omega_2}{d(E^0 - E_1)}$$

$$= \Omega_2 \frac{d\Omega_1}{dE_1} - \Omega_1 \frac{d\Omega_2}{dE_2} = 0$$

$$\Rightarrow \boxed{\frac{d}{dE_1}\ln\Omega_1 = \frac{d}{dE_2}\ln\Omega_2}$$

$\Rightarrow$ new eq. $\bar{E}_1$ + $\bar{E}_2$ maximize $\Omega_1(\bar{E}_1) + \Omega_2(\bar{E}_2)$

* let $\beta \equiv \left(\frac{\partial}{\partial E} \ln \Omega\right)_{N,V}$

$\Rightarrow \beta_1 = \beta_2$ in equilibrium

* But we already learned (0^{th} Law) about a quantity that is equal between 2 systems in equilibrium – the temperature!

$\therefore$ suspect β is closely related to T.

* Recall from TD:

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{V_1 N_1} = \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2 N_2} = \frac{1}{T}$$

$$\left(\frac{\partial \ln \Omega_1}{\partial E_1}\right)_{V_1 N_1} = \left(\frac{\partial \ln \Omega_2}{\partial E_2}\right)_{V_2 N_2} = \beta$$

$$\Downarrow$$

$$\frac{\Delta S}{\Delta \ln \Omega} = \frac{1}{\beta T} = \text{constant}$$

* Since this is general & makes no reference to a particular system, expect this constant is universal, call it k_B

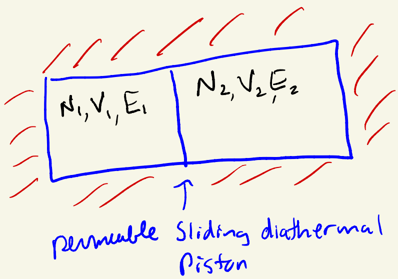
$\therefore$ Having seen the similarity between $\ln \Omega$ + S_{thermo}, let's define the Boltzmann entropy

$$\boxed{S \equiv k_B \ln \Omega(E,N,V)}$$

and assume it's equivalent to the TD Entropy of Clausius, Nernst, et al.

Note: The Boltzmann defintion removes the "mystery" why S always increases. It is merely a statement that a system wants to go to a macrostate with the highest multiplicity (probability)

* You can consider more elaborate cases where the 2 systems can exchange energy, volume, particles



energy: $$\left(\frac{\partial}{\partial E_1}\ln \Omega_1\right)_{E_1=\bar{E}_1, N_1, V_1} = \left(\frac{\partial}{\partial E_2}\ln \Omega_2\right)_{E_2=\bar{E}_2, N_2, V_2} = \beta$$

Volume: $$\left(\frac{\partial}{\partial V_1}\ln \Omega_1\right)_{E_1, N_1, V_1=\bar{V}_1} = \frac{\partial}{\partial V_2}\left(\ln \Omega_2\right)_{E_2, N_2, V_2=\bar{V}_2} = \eta$$

particle #: $$\left(\frac{\partial}{\partial N_1}\ln \Omega_1\right)_{E_1, N_1=\bar{N}_1, V_1} = \left(\frac{\partial}{\partial N_2}\ln \Omega_2\right)_{E_2, N_2=\bar{N}_2, V_2} = \xi$$

$$\Rightarrow \boxed{\beta = \frac{1}{k_B T}\ ;\ \eta = \frac{P}{T},\ \xi = -\frac{\mu}{T}}$$

*Example: N Spin 1/2 particles in external B-field (take $B \parallel \hat{z}$)

$$E = -B\sum_{j=1}^{N} \sigma_{z,j}$$

(absorbed $g=2$ & μ_B Bohr Magneton into def. of B)

$$= -2BS_z^{tot} \qquad S_z^{tot} = \sum_{i=1}^{N} S_z(i)$$

$$\Rightarrow E = \{-NB, -(N-2)B, -(N-4)B, \ldots, (N-2)B, NB\}$$

$N+1$ total energy values (macrostates)

2^N total microstates

Note: Macrostate can be equivalently labelled by E or $S_z^{tot} \equiv S$ value (Bad notation alert! Don't confuse this w/ Entropy)

Find $\Omega(S)$: Note that $S = \frac{1}{2}\sum_{j=1}^{N} \sigma_{z,j}$

$$= \frac{N_\uparrow - N_\downarrow}{2}$$

$$= N_\uparrow - \frac{N}{2}$$

$\therefore$ Finding $\Omega(S) \Rightarrow$ count the number of ways of choosing $N_\uparrow$ out of N to have spin $\uparrow$.

* imagine randomly picking particles + placing them in a row with 1st $N_\uparrow$ in $\uparrow$-state + rest $N_\downarrow$ in down state

$$|\underbrace{\circ\ \circ\ \circ\ \circ\ \circ \cdots \bullet}_{N_\uparrow}|\underbrace{\circ\ \circ\ \circ \cdots \circ}_{N_\downarrow}| \qquad N = N_\uparrow + N_\downarrow$$

* $N!$ ways to arrange particles in row
* But a state w/ the same $N_\uparrow$ particles in the 1st bin is the same state no matter which order the particles are in

$\therefore$ "Overcount" by $N_\uparrow!\, N_\downarrow!$

$$\Rightarrow \Omega(N_\uparrow, N_\downarrow) = \frac{N!}{N_\uparrow!\, N_\downarrow!} = \frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}$$

but recall $S = N_\uparrow - \frac{N}{2} \Rightarrow N_\uparrow = S + \frac{N}{2}$

$$\boxed{\begin{gathered} \therefore\ \Omega(S,N) = \frac{N!}{\left(\frac{N}{2}+S\right)!\left(\frac{N}{2}-S\right)!} \\ \text{or, since } E = -2BS \\ \Omega(E,N) = \frac{N!}{\left(\frac{N}{2}+\frac{E}{2B}\right)!\left(\frac{N}{2}-\frac{E}{2B}\right)!} \end{gathered}}$$

* Keeping in mind that we are interested in macroscopic systems w/ $N \sim 10^{23}$, it's useful to have an analytic approx for $N!$ @ large $N \gg 1$.

Stirling's approximation:

$$\ln N! \sim \underbrace{N\ln N - N}_{\text{Leading piece}} + \underbrace{\tfrac{1}{2}\ln(2\pi N)}_{\text{Sub-leading often dropped}} + \underbrace{\frac{1}{12N} + \mathcal{O}\left(\frac{1}{N^2}\right)}_{\text{Can always ignore for } N\sim 10^{23}} \cdots$$

Simple proof for leading piece

$$\ln N! = \ln[N\cdot(N-1)\cdot(N-2)\cdots 1]$$

$$= \ln N + \ln(N-1) + \ln(N-2) \cdots + \ln 1$$

$$= \sum_{n=1}^{N} \ln n \approx \int_1^N \ln n \, dn$$

$\ln n + n$

$$= (n\ln n - n)\Big|_1^N$$

$$= N\ln N - N + 1$$

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

* See Pathria & Beale appendix (or maybe HW #2?) for a more sophisticated derivation including subleading terms via Steepest Descents method.

$$\therefore \Omega(S,N) = \frac{N!}{\left(\frac{N}{2}+S\right)!\left(\frac{N}{2}-S\right)!}$$

$$\Rightarrow \ln \Omega(S,N) = \ln N! - \ln\left[\left(\frac{N}{2}+S\right)!\right] - \ln\left[\left(\frac{N}{2}-S\right)!\right]$$

$$\overset{N \gg 1}{\simeq} N\ln N - \cancel{N} - \left(\frac{N}{2}+S\right)\ln\left(\frac{N}{2}+S\right) + \left(\cancel{\frac{N}{2}}+\cancel{S}\right)$$

$$- \left(\frac{N}{2}-S\right)\ln\left(\frac{N}{2}-S\right) + \left(\cancel{\frac{N}{2}}-\cancel{S}\right)$$

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

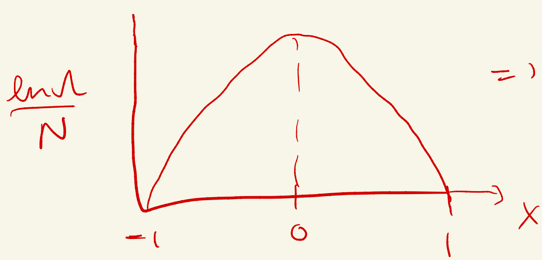
$$- \left(\frac{N}{2}-S\right)\ln\left[\frac{N}{2}\left(1-\frac{2S}{N}\right)\right]$$

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

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

let $x = \frac{2S}{N}$ $\quad (x \in [-1, 1])$

$$\boxed{\ln \Omega \simeq -N\left[\left(\frac{1+x}{2}\right)\ln\left(\frac{1+x}{2}\right) + \left(\frac{1-x}{2}\right)\ln\left(\frac{1-x}{2}\right)\right]}$$



$\Rightarrow$ $\ln \Omega$ will be sharply peaked @ $x \sim 0$

*Note: $\ln \Omega(x=0) = N \ln 2 \Rightarrow \Omega(x=0) = 2^N$

which is a bit strange since 2^N is the total # of microstates possible.

* This is an artifact of the leading Stirling approx., but it also makes the point that the probabilities are dominated by a single term when $N \to \infty$.

* If we kept the subleading term

$$\ln N! \simeq N \ln N - N + \underline{\underline{\tfrac{1}{2}\ln(2\pi N)}},$$

would find $\Omega(x=0) \simeq \left(\frac{2}{\pi N}\right)^{1/2} 2^N$

Shapness of Ω

* Even though probabilistic arguments underly Stat. Mech., we know for macroscopic ($N \sim 10^{23}$) systems, SM makes essentially exact statements (i.e., fluctuations of macro state variables are negligible)

* We'll see this is a consequence of how sharply peaked Ω becomes for large N.

* Start from:

$$\ln \Omega \simeq -N\left[\left(\frac{1+x}{2}\right)\ln\left(\frac{1+x}{2}\right)+\left(\frac{1-x}{2}\right)\ln\left(\frac{1-x}{2}\right)\right]$$

* analyze this in the limit $N \gg 1$ and $|x| = \left|\frac{2s}{N}\right| \ll 1$

$$\Rightarrow \ln\left(\frac{1+x}{2}\right) \simeq -\ln 2 + x - \frac{x^2}{2} + O(x^3)$$

$$\ln\left(\frac{1-x}{2}\right) \simeq -\ln 2 - x - \frac{x^2}{2} + O(x^3)$$

$$\Rightarrow \ln \Omega \simeq -N\left[\left(\frac{1+x}{2}\right)(-\ln 2 + x + \cdots) + \left(\frac{1-x}{2}\right)(-\ln 2 - x + \cdots)\right]$$

$$= -N\left[-\ln 2 + \frac{x^2}{2} + O(x^4)\right] = \ln 2^N - \frac{Nx^2}{2}$$

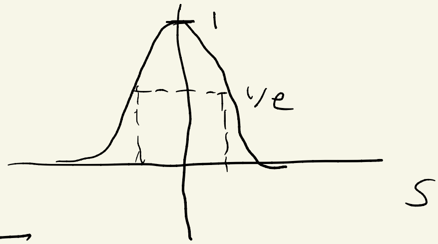
$$\Rightarrow \boxed{\begin{aligned}\Omega(N,x) &\simeq e^{\ln 2^N} \times e^{-\frac{Nx^2}{2}} \\ &= \Omega(N,0)\, e^{-\frac{Nx^2}{2}}\end{aligned}}$$

or in terms of $s = \frac{Nx}{2}$

$$\Rightarrow \boxed{\Omega(N,s) = \Omega(N,0)\, e^{-2s^2/N}}$$

$\therefore$ Fractional width (i.e., when $\Omega(N,S)$ drops by $1/e$ compared to $\Omega(N,0)$)

$$\frac{S}{N} = \sqrt{\frac{1}{2N}}$$



e.g.: $N = 10^{22} \Rightarrow \sqrt{\frac{1}{2N}} \sim 10^{-11}$

$\therefore$ The peak is very sharp for large N

i.e., if $P(S) = \dfrac{\Omega(N,S)}{\Omega_{TOT}} = \dfrac{\Omega(N,S)}{2^N}$

then this is essentially a δ-function as $N \to \infty$.