L7 Recap

* Want to understand macro ($N \gg 1$) systems from microscopic DOF + dynamics (i.e., derive/explain Thermodynamics)

* Impractical to solve Schrödinger/Hamilton's eqns. AND know all initial conditions for (say) 10^{23} particles

* Many-to-1 relationship of micro- + macrostates

  e.g., Huge # micro $(\vec{q}_1, \ldots \vec{q}_N, \vec{p}_1, \ldots \vec{p}_N)$ configs consistent with a given macro (E, V, N).

* Since our measurement/knowledge of the macrostate cannot distinguish between the huge # of microstates that are consistent with (E,V,N), the simplest and most unbiased assumption is that all such microstates are equally probable

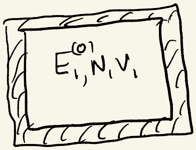
* Multiplicity function $\Omega(E,V,N)$ = # of microstates that give E, V, N

"Equal a priori probability postulate"

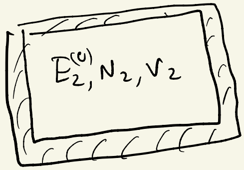
$$P(i) = \frac{1}{\Omega(E,V,N)} \quad \text{for } i = \text{one of the } \Omega\text{-microstates}$$

$$= 0 \quad \text{for } i \neq \text{" \quad "}$$

Relation to Entropy



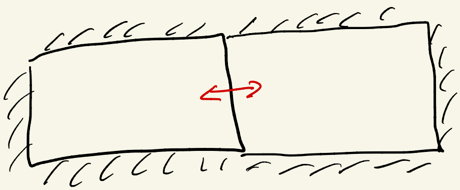
$\Omega_1(E_1^{(0)}, N_1, V_1)$



$\Omega_2(E_2^{(0)}, N_2, V_2)$

$\Downarrow$

put in thermal contact
so can exchange heat w/ each other



E_1 + E_2 will change, but such that

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

$\Omega_{TOT}(E)$ = total # microstates for combined system with E, N, V

$$= \sum_{E_1} \Omega_1(E_1)\,\Omega_2(E - E_1)$$

*From experience we know if we wait long enough, E_1 + E_2 settle down to E_1^*, E_2^*

⇒ For large systems, find one particular term $E_1 = E_1^*$ dominates by a lot

$$\simeq \Omega_1(E_1^*)\,\Omega_2(E - E_1^*)$$

E_1^* (+ hence $E_2^* = E - E_1^*$) determined by maximizing

$$\frac{d}{dE_1}\Big[\Omega_1(E_1)\,\Omega_2(E - E_1)\Big]_{N,V} = 0$$

* algebra... (see last class)

$$\Rightarrow \boxed{\left.\frac{d}{dE_1}(\ln\Omega_1)\right|_{N_1,V_1,E_1=E_1^*} = \left.\frac{d}{dE_2}\ln\Omega_2\right|_{N_2,V_2,E_2=E_2^*} \equiv \beta}$$

* So if 2 isolated systems are put into thermal contact so they can exchange energy (heat), they eventually settle down so that $\beta_1 = \beta_2 = \beta$

* This tells us β has something to do w/ temperature, and since TD tells us $\left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{1}{T}$, we expect S + $\ln\Omega$ are equal up to a universal constant (which we know from experiment is k_B)

$$\Rightarrow \boxed{S(E,N,V) = k_B \log \Omega(E,N,V)} \quad **$$

Side note: I find it very bizarre + interesting that we've related S, a quantity that was invented thinking about heat engines, to the # of microscopic (+ ultimately QM) states!

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

*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)

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

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

$N+1$ 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 <u>order</u> 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:

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

Simple proof for leading piece

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

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

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

$\ln n + n$

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

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

$$\simeq N \ln N - N$$

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

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

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

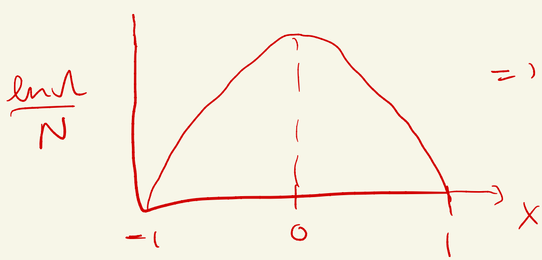
$$\overset{N \gg 1}{\simeq} N\ln N - \cancel{N} - \left(\frac{N}{2}+S\right)\ln\left(\frac{N}{2}+S\right) + \left(\cancel{\frac{N}{2}+S}\right)$$
$$- \left(\frac{N}{2}-S\right)\ln\left(\frac{N}{2}-S\right) + \left(\cancel{\frac{N}{2}-S}\right)$$

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

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

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

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



$\Rightarrow$ $\ln \Omega$ 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 $|x| = \left|\frac{2s}{N}\right| \ll 1$

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

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

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

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

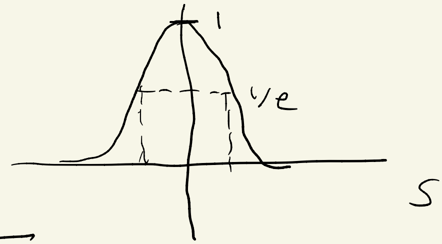
$$\Rightarrow \boxed{\begin{aligned}\Omega(N,x) &\simeq e^{\ln 2^N} \times e^{-\frac{Nx^2}{2}} \\ &= \Omega(N,0)\, e^{-\frac{Nx^2}{2}}\end{aligned}}$$

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 $$P(s) = \frac{\Omega(N,s)}{\Omega_{TOT}} = \frac{\Omega(N,s)}{2^N}$$

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

Ensemble Theory

assumed very large

ensemble ≡ imaginary set of copies of our original system that can be in any macroscopically allowed microstate

* Task of SM is to find probability P_i that a randomly drawn copy from the ensemble is in microstate i

* Knowing this, we can then calculate average quantities

$$\langle O \rangle = \sum_i P_i O(i) \qquad O(i) = \text{value of } O \text{ in microstate } i$$

*Later, when we discuss Ergodic systems, we'll see

$$\langle O \rangle = \sum_i P_i O(i) = \overline{O} = \frac{1}{T}\int_0^T dt\, O(t)$$

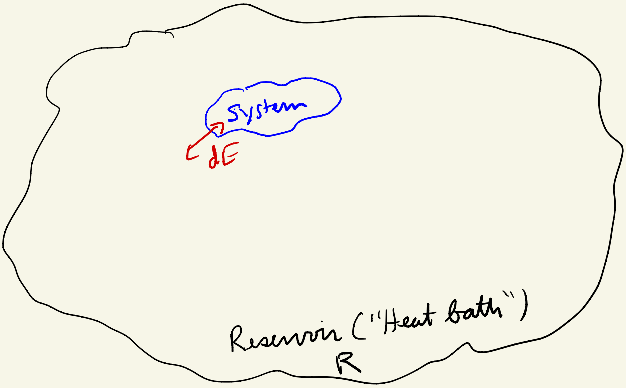
① Microcanonical Ensemble (every copy has fixed (E, V, N))

$$P_i = \frac{1}{\Omega(E,N,V)} \quad \text{for } i \text{ giving fixed } (E,V,N)$$

$$\langle O \rangle = \sum_i P_i O(i) = \frac{1}{\Omega} \sum_i O(i)$$

Sum only over microstates w/ fixed (E, V, N)

Canonical Ensemble (members at fixed T, V, N but E can fluctuate)



* R is much bigger than System, though the latter is still macroscopic

* Since R is so huge, can view it as holding S at fixed T.

$$E_s + E_R = E = \text{fixed} \quad (\text{together } S+R = \text{closed system})$$

* What is $p(i)$ = prob. of system to be in i^{th} microstate ?

$$\Downarrow$$

* To answer this, treat $(S+R)$ in microcanonical ensemble & consider 2 cases:

① S is in the particular microstate i

$$\Omega_R(E_R)\,\Omega_S(E_s=E_i) = \Omega_R(E-E_i)\,\cancelto{1}{\Omega_S}(E_i) = \text{\# of ways sys can be in microstate } i$$

② S is in the particular microstate j

$$\Omega_R(E_R)\,\Omega_S(E_s=E_j) = \Omega_R(E-E_j)\,\cancelto{1}{\Omega_S}(E_j) = \text{\# of ways Sys can be in microstate } j$$

* Since the combined S+R is closed & treated in the microcanonical ensemble, all microstates equally likely

$$\therefore \quad \frac{p(i)}{p(j)} = \frac{\text{\# of ways sys can be in } i}{\text{\# of ways sys can be in } j} = \frac{\Omega_R(E-E_i)}{\Omega_R(E-E_j)}$$

* Since $|E_i| << E$ by assumption that $R >> S$

$$\log\left[\Omega_R(E-E_i)\right] \approx \log \Omega_R(E) - E_i \frac{\partial}{\partial E}\log \Omega_R + \cdots\cdots$$

ignore (why?) Think physically!

$$= \log \Omega_R(E) - E_i \beta$$

$$\Rightarrow \quad \Omega_R(E-E_i) \approx e^{\log \Omega_R(E) - E_i\beta}$$

$$= \Omega_R(E)\, e^{-\beta E_i}$$

$$\Rightarrow \quad \boxed{\frac{p(i)}{p(j)} = \frac{e^{-\beta E_i}}{e^{-\beta E_j}}}$$

$\therefore\ p(i) = c\, e^{-\beta E_i}$ "Boltzmann Weight"

Requiring $\sum_i p(i) = 1 \Rightarrow c = \dfrac{1}{\sum_j e^{-\beta E_j}}$

$$\Rightarrow \boxed{p(i) = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}\ ; \quad \sum_j e^{-\beta E_j} \equiv Z \quad \text{"partition function"}}$$

Note: We'll re-derive $p(i)$ & Z from a more ensemble based argument in a couple of lectures

Ensemble averages (canonical)

$$\boxed{\langle O \rangle = \sum_i p(i) O(i) = \frac{1}{Z} \sum_j O_j e^{-\beta E_j}}$$

ex: $\langle E \rangle = \dfrac{1}{Z} \sum_j E_j e^{-\beta E_j}$

$$= \frac{1}{Z} \frac{-\partial}{\partial \beta} \sum_j e^{-\beta E_j} = -\frac{1}{Z}\frac{\partial}{\partial \beta} Z = -\frac{\partial}{\partial \beta} \log Z$$

$$= T^2 \frac{\partial}{\partial T} \log Z$$

*Note: $\langle E^2 \rangle - \langle E \rangle^2 \neq 0$

(fluctuations), but we'll show shortly that they vanish in TD Limit.

* Connecting further to Thermodynamics, recall that canonical ensemble $\Rightarrow$ systems w/ fixed $\underline{\underline{V, T, N}}$

* Suggests looking at Helmholtz F

$$F = E - TS$$

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \; ; \quad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -P \; ; \quad \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$$

* From prior example,

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z \Big|_{N,V} = F + TS$$

$$= F - T\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$\doteq F + \left(\frac{\partial F}{\partial \log \beta}\right)_{N,V}$$

$$= F + \left(\frac{\partial (\beta F)}{\partial \beta}\right)_{N,V}$$

$$\therefore \; F = -\frac{\partial}{\partial \beta} \log Z - \frac{\partial}{\partial \beta}(\beta F)_{N,V}$$

$$** \quad \boxed{\Rightarrow \; F = -\frac{1}{\beta} \log Z} \quad **$$