Recap of L8

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

assumed very large

* 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

$$\langle O \rangle = \sum_i P_i \, O(i)$$

$O(i)$ = value of O in microstate i

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

$$\boxed{\begin{aligned} P_i &= \frac{1}{\Omega(E,V,N)} \quad \text{(if microstate } i \text{ has } E_i = E,\ N_i = N,\ V_i = V\text{)} \\ &= 0 \quad \text{(else)} \end{aligned}}$$

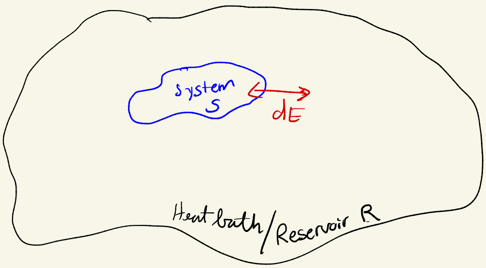
$$\Rightarrow \quad \langle O \rangle = \frac{1}{\Omega} \sum_{i=1}^{\Omega} O(i)$$

* Simple conceptually, but often hard to do practical calculations

* also, fixed E often at odds w/ what we have in the lab

(2) Canonical Ensemble (every copy has fixed T,V,N)

* Here I give a slightly expanded derivation of $p(i)$ from last time based on some of your questions



* R is much bigger than S so temperature stays fixed

* S can exchange energy w/R, so its energy not fixed

* Usually, S is macroscopic too. But it's not required to be.

* Treat (R+S) as closed system with fixed

$$E = E_R + E_S \quad (E_R \gg E_S)$$

* Treat (R+S) in microcanonical ensemble

let α = microstate of R
i = microstate of S

$$p(\alpha, i) = \frac{1}{\Omega_{TOT}(E)} \quad \text{for } E_\alpha + E_i = E$$

$$= 0 \quad \text{else}$$

$$= \frac{1}{\Omega_{TOT}(E)} \delta_{E_\alpha + E_i, E}$$

* Now, $p(\alpha, i)$ is a <u>joint</u> probability for R to be in microstate α <u>and</u> S to be in microstate i.

* If I want the <u>unconditional</u> probability for S to be in microstate i, the rules of probability tell me

$$p(i) = \sum_{\alpha} p(\alpha, i)$$

$$= \frac{1}{\Omega_{TOT}(E)} \sum_{\alpha} \delta_{E_\alpha + E_i, E}$$

just counts the # of microstates of R with energy $E - E_i$

$$\parallel$$

$$\Omega_R(E - E_i)$$

$$\boxed{\therefore \; p(i) = \frac{\Omega_R(E - E_i)}{\Omega_{TOT}(E)}}$$

* as we did previously, we use $E_i \ll E$ + taylor expand

$$\log\left(\Omega_R(E-E_i)\right) \simeq \log \Omega_R(E) - E_i \frac{\partial}{\partial E}\log\Omega_R(E) + \underbrace{\cdots}_{\text{Negligible Since R so huge}}$$

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

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

$$\boxed{\Rightarrow p(i) \propto e^{-\beta E_i}}$$

* Finally, demanding $\sum_i p(i) = 1$ gives us the overall normalization

$$p(i) = \frac{1}{Z} e^{-\beta E_i}$$

$$Z = \sum_j e^{-\beta E_j} \quad \text{"partition function"}$$

$$\Rightarrow \langle O \rangle = \frac{1}{Z}\sum_i O_i\, e^{-\beta E_i}$$

O_i = value of O in microstate i

Example: Spin 1/2 Paramagnet

$$E = -B\sum_{j=1}^{N}\sigma_j \qquad \sigma_j = \pm 1$$

$$Z = \sum_{\sigma_1=\pm1}\sum_{\sigma_2=\pm1}\cdots\sum_{\sigma_N=\pm1} e^{\beta B\sum_i \sigma_i}$$

$$= \sum_{\sigma_1=\pm1} e^{\beta B\sigma_1}\sum_{\sigma_2=\pm1} e^{\beta B\sigma_2}\cdots\sum_{\sigma_N=\pm1} e^{\beta B\sigma_N}$$

$$= \prod_{i=1}^{N}\sum_{\sigma_i=\pm1} e^{\beta B\sigma_i}$$

$$= \prod_{i=1}^{N}\left(e^{\beta B}+e^{-\beta B}\right) = \prod_{i=1}^{N} 2\cosh(\beta B)$$

$$\Rightarrow \boxed{Z = \left[2\cosh\beta B\right]^N}$$

$$\langle\sigma_K\rangle = \frac{1}{Z}\sum_{\{\sigma_1\sigma_2\cdots\sigma_N\}}\sigma_K\, e^{\beta B\sum_i\sigma_i}$$

$$= \frac{\cancel{\prod_{i\neq K}\sum_{\sigma_i=\pm} e^{\beta B\sigma_i}} \times \sum_{\sigma_K=\pm1}\sigma_K e^{\beta B\sigma_K}}{\cancel{\prod_{i\neq K}\sum_{\sigma_i} e^{\beta B\sigma_i}} \times \sum_{\sigma_K} e^{\beta B\sigma_K}}$$

$$\therefore \langle \sigma_k \rangle = \frac{\sum_{\sigma_k} \sigma_k e^{\beta B \sigma_k}}{\sum_{\sigma_k} e^{\beta B \sigma_k}} = \frac{e^{\beta B} - e^{-\beta B}}{e^{\beta B} + e^{\beta B}} = \tanh \beta B$$

<u>Note</u> ① $\langle \sigma_1 \rangle = \langle \sigma_2 \rangle = \cdots = \langle \sigma_N \rangle$ by translational symmetry

② $N_\uparrow - N_\downarrow = N \langle \sigma_k \rangle = N x$ $\quad$ ($x = \frac{2s}{N}$ from last class)

* What if we use the <u>microcanonical</u> ensemble?

<u>entropy</u> $S = k_B \log \Omega(N, x)$

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

(recall, $E = -2Bs = -2BNx$)

$$\Downarrow$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = -\frac{1}{2BN} \left.\frac{\partial S}{\partial x}\right|_{V,N}$$

plugging in S + letting Mathematica do the dirty work...

$$\Rightarrow x = \tanh \frac{B}{k_B T} = \tanh \beta B$$ <u>as before</u>!

[This is a general result. In the $N \gg 1$ limit, all the ensembles give the same predictions]

Connecting to Thermodynamics

* We've alluded to the fact that various TD quantities (internal energy, Free energy, etc.) are related to average values in SM. Let's develop this further....

Internal Energy

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

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

* but $\beta = \frac{1}{k_B T}$ (or $\beta = \frac{1}{T}$ in units where $k_B = 1$)

* NOTE: I will more often than not use $k_B = 1$ units

$$\therefore \quad \frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T} = -\frac{1}{\beta^2} \frac{\partial}{\partial T} = -T^2 \frac{\partial}{\partial T}$$

$$\boxed{\Rightarrow \langle E \rangle = T^2 \frac{\partial}{\partial T} \log Z}$$

We tentatively identify $\langle E \rangle$ with the TD state function E (internal energy)

* 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,

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

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

but $T\frac{\partial}{\partial T} = -\beta\frac{\partial}{\partial \beta} \longrightarrow$

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

$$\Rightarrow \langle E \rangle = -\frac{\partial}{\partial \beta}\log Z = \frac{\partial}{\partial \beta}(\beta F)_{V,N}$$

$$\Downarrow$$

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

* Having identified $F = -\frac{1}{\beta}\log Z$, let's see what other insights SM provides.

* Consider $C_v = \left.\frac{đQ}{dT}\right|_{V,N} = \left.\frac{dE - đW}{dT}\right|_{V,N} = \left.\frac{dE + P\cancelto{0}{dV}}{dT}\right|_{V,N}$

$$\therefore C_v = \left.\frac{\partial E}{\partial T}\right|_{V,N} = \left.\frac{\partial}{\partial T}\left(-\frac{\partial}{\partial \beta}\log Z\right)\right|_{V,N}$$

algebra

$$= -\beta^2 \frac{\partial^2}{\partial \beta^2}(\beta F)\Big|_{V,N}$$

* but since $\beta F = -\log Z$, after a little algebra you get

$$-\frac{\partial^2}{\partial \beta^2}(\beta F) = \frac{1}{Z}\sum_i E_i^2 e^{-\beta E_i} - \left(\frac{\sum_i E_i e^{-\beta E_i}}{Z}\right)^2$$

$$= \langle E^2 \rangle - \langle E \rangle^2$$

$$= \langle (E - \langle E \rangle)^2 \rangle$$

$\Rightarrow$ C_v gives a measure of fluctuations in energy for canonical dist. //

* We will discuss general fluctuations (+ their PDFs) in a couple of lectures from now....

* Continuing our discussion revisiting various TD quantities in the language of Stat. Mech., let's now look at pressure + entropy in the canonical ensemble.

$$dF = -S\,dT - P\,dV \quad \text{from TD.}$$

∴ It better be true for $F = -\frac{1}{\beta}\log Z$

$$-\left(\frac{\partial F}{\partial V}\right)_T = P = -\frac{\partial}{\partial V}\left(-\frac{1}{\beta}\log Z\right)_T$$

$$= \frac{1}{\beta}\frac{\frac{\partial Z}{\partial V}}{Z} = \frac{1}{\beta Z}\frac{\partial}{\partial V}\sum_i e^{-\beta E_i}$$

$$= \frac{1}{\beta Z}\sum_i (-\beta)\frac{\partial E_i}{\partial V} e^{-\beta E_i}$$

$$= \frac{1}{Z}\sum_i \left(-\frac{\partial E_i}{\partial V}\right)_T e^{-\beta E_i}$$

$$= \frac{1}{Z}\sum_i P_i\, e^{-\beta E_i}$$

pressure for i^{th} state $P_i = -\frac{\partial E_i}{\partial V}\Big|_T$

∴ It makes sense that TD P is the canonical ensemble average $P = \sum_i p_i P_i$

Entropy: $S = -\left.\frac{\partial F}{\partial T}\right|_V$ $\qquad \beta = \frac{1}{k_B T}$

$\therefore \frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta} = -k_B \beta^2 \frac{\partial}{\partial \beta}$

$$= k_B \beta^2 \left.\frac{\partial F}{\partial \beta}\right|_V$$

$$= k_B \beta^2 \frac{\partial}{\partial \beta}\left(-\frac{1}{\beta}\log Z\right)$$

$$= k_B \beta^2 \left\{\frac{1}{\beta^2}\log Z - \frac{1}{\beta}\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right\}$$

$$= k_B \log Z - k_B \beta \frac{1}{Z}\sum_i -E_i e^{-\beta E_i}$$

$$= k_B \frac{\sum_i e^{-\beta E_i}}{Z}\log Z + k_B \beta \frac{\sum_i E_i e^{-\beta E_i}}{Z}$$

$$= k_B \sum_i \frac{e^{-\beta E_i}}{Z}\left(\log Z + \beta E_i\right)$$

* but $p_i = \frac{e^{-\beta E_i}}{Z}$ $\Rightarrow$ $\boxed{S = -k_B \sum_i p_i \log p_i}$ ⊗

How to interpret this? If all the i states have same $E_i = E^*$, then $p_i = 1/\Omega(E^*)$ for all i

$S = -k_B \sum_i \frac{1}{\Omega(E^*)}\log\frac{1}{\Omega(E^*)} = k_B \log \Omega(E^*)$ as before

i.e. ⊗ is a generalization from a system of fixed E to one where can sample all E. Say more next time...