Building connection with thermodynamics (N,V,T)

Canonical Partition function: $\mathcal{Z}(N,V,T) = \sum_{\mu} e^{-\beta H(\mu)}$

$$= \sum_{\epsilon} e^{-\beta F(\epsilon)}$$

$$\simeq e^{-\beta F(\epsilon^*)}$$ "Saddle point approximation"

ϵ^* maximizes the $e^{-\beta F(\epsilon)}$

ϵ^* minimizes $F(\epsilon)$

Average energy: $E = \langle H \rangle = \sum_{\mu} H(\mu)\, p(\mu) = \sum_{\mu} H(\mu) \dfrac{e^{-\beta H(\mu)}}{\mathcal{Z}(N,V,T)}$

$$= \frac{-\frac{\partial}{\partial \beta} \sum_{\mu} e^{-\beta H(\mu)}}{\mathcal{Z}}$$

$$= -\frac{1}{\mathcal{Z}} \cdot \frac{\partial \mathcal{Z}}{\partial \beta}$$

$$\boxed{E = \langle H \rangle = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}} \quad \text{—— (1)}$$

"Macroscopic" "Microscopic"

From thermodynamics, $E = F + TS$ $\because F = E - TS$

$$dE = dF + TdS + SdT$$

$$\cancel{dE} = dF + PdV - \mu dN + \cancel{dE} + SdT$$

$$dF = -PdV + \mu dN - SdT$$

$$S = -\frac{\partial F}{\partial T}\Big|_{N,V}$$

$$E = F - \frac{\partial F}{\partial T}\Big|_{N,V} T$$

$$= -T^2 \frac{\partial}{\partial T}(F/T) = -T^2\left[\frac{-F}{T^2} + \frac{1}{T}\frac{\partial F}{\partial T}\right]$$

$$E = -k_B T^2 \frac{\partial}{\partial T}\left(\frac{F}{k_B T}\right)$$

Noticing $\frac{\partial}{\partial \beta} \equiv \frac{\partial}{\partial(1/k_B T)} \equiv -k_B T^2 \frac{\partial}{\partial T}$ ..... $\beta = \frac{1}{k_B T}$

$$\boxed{E = \frac{\partial}{\partial \beta}(\beta F)} \quad \text{—— (2)}$$

Comparing (2) with (1),

$$\boxed{F = -\frac{1}{\beta} \cdot \ln Z} \quad \text{—— (3)}$$

Q. What is the relationship between ϵ^* & $E = \langle H \rangle$?

ϵ^* → most probable

$E = \langle H \rangle$ → Thermodynamic

Ensemble equivalence : As $N \to \infty$ (thermodynamic limit)

Canonical Ensemble (N, V, T) ⟶ Micro-Canonical Ensemble. (N, V, E)

$$E = \langle H \rangle = -\frac{\partial}{\partial \beta}(\ln Z)$$

Variance of E: $\langle H^2 \rangle_c = \langle H^2 \rangle - \langle H \rangle^2$

$$= \sum_{\mu} H^2(\mu) \frac{e^{-\beta H(\mu)}}{Z} - \left(\sum_{\mu} H(\mu) \frac{e^{-\beta H(\mu)}}{Z}\right)^2$$

$$= \frac{1}{Z}\frac{\partial^2}{\partial\beta^2}\sum_\mu e^{-\beta H(\mu)} - \left(\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_\mu e^{-\beta H(\mu)}\right)^2$$

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

$$= \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\cdot\frac{\partial Z}{\partial\beta}\right)$$

$$= \frac{\partial}{\partial\beta}\left(\widetilde{\frac{\partial}{\partial\beta}\cdot\ln Z}\right)$$

$$\langle H^2\rangle_c = \frac{\partial^2}{\partial\beta^2}\ln Z = -\frac{\partial E}{\partial\beta} = k_B T^2\frac{\partial}{\partial T}\cdot E = k_B T^2 C_v$$

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

$\langle H^2\rangle_c = k_B T^2 C_v$ "Fluctuations in energy is related to Heat capacity"

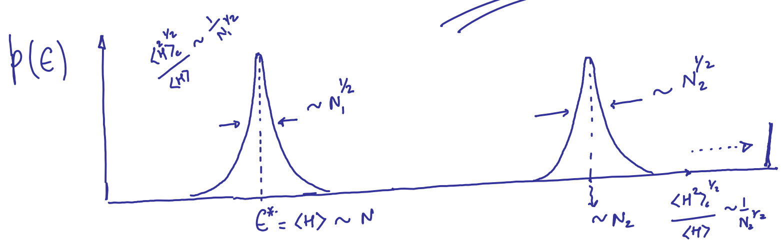
$\langle H^2\rangle_c \sim N$ "Scales with system size"

Width or Standard deviation: $\langle H_c^2\rangle^{1/2} \sim N^{1/2}$

Compute width/Mean $= N^{1/2}/N \sim 1/N^{1/2} \xrightarrow[N\to\infty]{} 0$

$$p(\epsilon) = \frac{e^{-\beta F(\epsilon)}}{Z(N,V,T)} \xrightarrow{N\to\infty} \frac{e^{-(\epsilon-\underbrace{\langle H\rangle}_{\epsilon^*})^2/2\langle H^2\rangle_c}}{(2\pi\langle H^2\rangle_c)^{1/2}}$$

Canonical Ensemble. Microcanonical ensemble



As $N \to \infty$, the distribution has negligible $\text{width}/\text{mean} \sim 1/N^{1/2} \longrightarrow 0$

Example: Two-level system (N, V, T)

$$\left.\begin{array}{l} \circ\circ\circ \text{———} \; \epsilon \\ \circ\circ\circ\circ\circ \text{———} \; 0 \end{array}\right\} \text{Two levels}$$

n_i represents excitation

$\hookrightarrow$ 0 (Ground)

1 (Excited)

$$H(\mu) = E = \sum_{i=1}^{N} n_i \epsilon$$

Canonical Partition Function:

$$Z(N,V,T) = \sum_{\mu} e^{-\beta H(\mu)}$$

$\mu_1 : \{n_1 = 1, n_2 = 1, n_3 = 0 \ldots n_N = 1\}$

$\mu_2 : \{n_1 = 0, n_2 = 0, n_3 = 1 \ldots n_N = 1\}$

$\vdots$

$\mu_N : \{n_1 = 1, n_2 = 1 \ldots n_N = 0\}$

$$= \sum_{\{n_i\}} e^{-\beta H(\{n_i\})}$$

$$= \sum_{\{n_1, n_2 \ldots n_N\}} e^{-\beta \sum_{i=1}^{N} n_i \epsilon}$$

$$= \sum_{\{n_1, n_2 \ldots n_N\}} e^{-\beta \epsilon n_1} \cdot e^{-\beta \epsilon n_2} \cdots e^{-\beta \epsilon n_N}$$

$$= \sum_{n_1 = 0,1} e^{-\beta \epsilon n_1} \sum_{n_2 = 0,1} e^{-\beta \epsilon n_2} \cdots \sum_{n_N = 0,1} e^{-\beta \epsilon n_N}$$

$$Z = \left(\sum_{n_1 = 0,1} e^{-\beta \epsilon n_1} \right)^N = \underline{\underline{\left(1 + e^{-\beta \epsilon}\right)^N}}$$

Build connection with thermodynamics

$$E = \frac{-\partial}{\partial\beta}(\ln Z) = \frac{-\partial}{\partial\beta} N \ln(1+e^{-\beta\epsilon})$$

$$= -N \cdot \frac{1}{(1+e^{-\beta\epsilon})} \cdot (-\epsilon)\, e^{-\beta\epsilon} = \frac{N\epsilon}{1+e^{\beta\epsilon}}$$

$$E = \frac{N\epsilon}{1+e^{\beta\epsilon}}$$

To reach $E = N/_2\,\epsilon$. $\Rightarrow$ $e^{\beta\epsilon} \longrightarrow 1$

$\beta \longrightarrow 0 \qquad T \longrightarrow \infty$

" Maximum energy corresponds to half filled excited state "

Free energy: $F = \frac{-1}{\beta} \cdot \ln Z$

$$= \frac{-1}{\beta} \cdot N \ln(1+e^{-\beta\epsilon}) \qquad \sim N$$

Entropy: $S = (E-F)/T$ ..... $E - TS = F$

$$= \left[\frac{N\epsilon}{1+e^{\beta\epsilon}} + Nk_BT \ln(1+e^{-\beta\epsilon})\right] / T$$

$$= \frac{Nk_B\beta\epsilon}{1+e^{\beta\epsilon}} + Nk_B \ln(1+e^{-\beta\epsilon})$$

$$S = Nk_B\left[\frac{\beta\epsilon}{1+e^{\beta\epsilon}} + \ln(1+e^{-\beta\epsilon})\right]$$