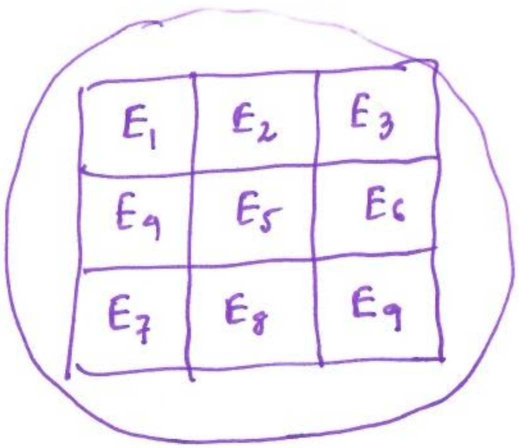
Lecture - 8

Canonical Ensembles

* You can see this as a collection of micro-canonical ensembles



E_i's are constant in each MCE but $\langle E \rangle$ for the whole exists and ~~were~~ well defined.

$\longrightarrow$ Canonical ensemble

* ~~E~~ N, V, T $\longrightarrow$ parameters

* $\overline{E}$ and T are connected through equipartition theorem.

* Phase-space density $= \rho_c(p, q)$

$$= A \cdot \exp(-\beta H)$$

* A can be obtained from normalization.

$$\iint_{\Phi_{6N}} A\, e^{-\beta H} \frac{d^{3N}p\, d^{3N}q}{h^{3N}} = 1$$

a $\quad A = \dfrac{1}{\displaystyle\iint_{6N} \frac{d^{3N}p\, d^{3N}q}{h^{3N}} \cdot e^{-\beta H}} = \dfrac{1}{Z}$

$$\rho_c(p,q) = \frac{e^{-\beta H}}{Z}$$

$$Z = \frac{1}{h^{3N}} \iint_{6N} d^{3N}p \, d^{3N}q \; e^{-\beta H}$$ = partion function

= Sum over states

= Zustand summe

* $S = \langle -k \ln \rho_c \rangle$

$$\langle f \rangle = \frac{1}{h^{3N}} \iint d^{3N}p \, d^{3N}q \; f(p,q) \, \rho(p,q)$$

$$\langle f \rangle_{MC} = \frac{1}{h^{3N}} \iint_{E < H < E+\Delta} d^{3N}p \, d^{3N}q \, . \; f(p,q) \, . \left(\frac{1}{\Omega} \right)$$

$$\cancel{S = k \, . \ln \Omega \Rightarrow = k \ln \left(-\frac{1}{\rho_{MC}} \right) = -k \ln \rho_{MC}}$$

$$\cancel{\langle f \rangle_{MC} = \frac{1}{h^{3N}} \iint d^{3N}p \, d^{3N}q \, . \; f(p,q) \, . \frac{1}{\Omega}}$$

$$S = k \ln \Omega = - \left[k \ln \left(\frac{1}{\rho_{MC}} \right) \right]_{E \leq H \leq E+\Delta}$$

$$S = \langle k \ln \Omega \rangle = \frac{1}{h^{3N}} \iint d^{3N}p \, d^{3N}q \; \rho_{MC} \left[-k \ln \rho_{MC} \right] \quad \text{--- (1)}$$

$$= \langle -k \ln \rho_{MC} \rangle$$

Equation ① is true for non-MCE as well.

$$S = \langle -k \ln \rho \rangle$$

In Canonical ensembles,

$$S = \langle -k \ln \rho_c \rangle = \frac{1}{h^{3N}} \iint \frac{d^{3N}p \, d^{3N}q}{h^{3N}} \cdot \rho_c(p,q) \left[-k \ln \rho_c \right]$$

But $\rho_c = \dfrac{e^{-\beta H}}{Z}$

So,

$$S = \frac{1}{\cancel{h}^{3N}} \iint \frac{d^{3N}p \, d^{3N}q}{h^{3N}} \cdot \left[\rho_c \right] \left[-k \left\{ -\beta H - \ln Z \right\} \right]$$

$$= \frac{1}{h^{3N}} \iint d^{3N}p \, d^{3N}q \; \rho_c \left[k\beta H + k \ln Z \right]$$

$$= \frac{1}{h^{3N}} \iint d^{3N}p \, d^{3N}q \; k\beta H + \frac{1}{h^{3N}} \iint d^{3N}p \, d^{3N}q \; \rho_c . \, k \ln Z$$

$$= k\beta . \langle H \rangle + k . \ln Z . \underbrace{\frac{1}{h^{3N}} \iint d^{3N}p \, d^{3N}q . \, \rho_c}_{= 1 \text{ for normalized } \rho_c}$$

$$= k\beta \langle H \rangle + k . \ln Z$$

$$= k\beta U + k \ln Z$$ [writing $\langle H \rangle = U =$ internal energy]

Now, $k \ln Z = S - k\beta U = -[k\beta U - S]$

a $-k \ln Z = k\beta U - S = k\beta \left[U - \frac{S}{k\beta} \right]$

a $-kT \ln Z = k . \beta . T \left[U - \frac{S}{k\beta} \right] = U - \frac{S}{k . \frac{1}{kT}} = U - TS$

a $U - TS = -kT \ln Z = F$

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$$F = -kT \ln Z$$

or

$$\ln Z = -\frac{F}{kT} \Rightarrow \boxed{Z = e^{-\frac{F}{kT}}}$$

<u>Canonical</u>:

$$-\frac{F}{\cancel{k}T} = k \ln Z_c$$

<u>Microcanonical</u>:

$$S = k \ln \Omega_{MCE}$$

Note: $-\frac{F}{T} = -\frac{W - TS}{T} = -\frac{W}{T} + S = S_0 + S$ [$S_0 = -\frac{W}{T}$ is constant if T a constant and is a constant]

Problem

Given $$H = \sum_{j=1}^{N} \hbar\omega \left(a_j^{+} a_j + \frac{1}{2} \right) \rightarrow$$ N identical harmoni[c] oscillators in Q.M.

Find $\Omega(E)$?

Answer:

$$\Omega(E) = \exp\left[N \left\{ x \ln x - y \ln y \right\} \right]$$

$$x = \frac{E/N + \frac{1}{2}\hbar\omega}{\hbar\omega} = \frac{E}{N\hbar\omega} + \frac{1}{2}$$

$$y = \frac{E/N - \frac{1}{2}\hbar\omega}{\hbar\omega} = \frac{E}{N\hbar\omega} - \frac{1}{2}$$

Hint :

* $$\Omega(E) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \delta\left(E - \hbar\omega \sum_{j=1}^{N} \left(n_j + \tfrac{1}{2}\right) \hbar\omega\right)$$

* $$\delta(x) = \int \frac{dk}{2\pi} \cdot e^{ikx}$$

* $$\delta\left(E - \hbar\omega \sum_{j=1}^{N} \left(n_j + \tfrac{1}{2}\right)\right) = \int \frac{dk}{2\pi}\, e^{ik\left[E - \sum_{j=1}^{N} \left(n_j + \frac{1}{2}\right)\hbar\omega\right]}$$

* $$\Omega(E) = \sum_{n_1=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \int \frac{dk}{2\pi}\, e^{ik\left[E - \sum_{j=1}^{N} \left(n_j + \frac{1}{2}\right)\hbar\omega\right]}$$