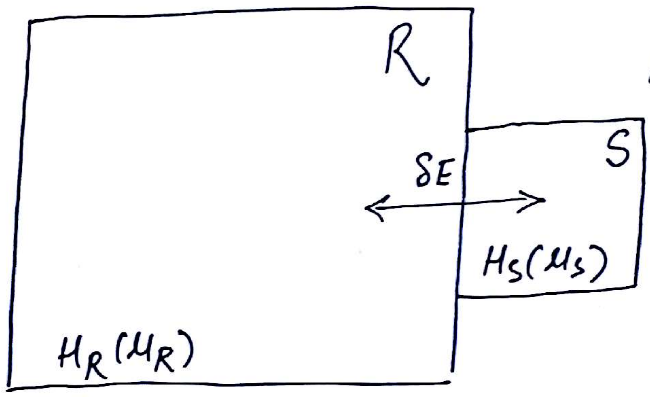
Canonical Ensemble: A system at constant $(N, \vec{X}, T)$

Consider a system S in contact with a reservoir R. The reservoir maintains the system at a constant temperature T. Naturally for this to happen there must be energy exchange between 'S' & 'R'. The total energy of S+R is fixed. Hence the joint system of R and S behaves as a micro-canonical ensemble.



$$E_{tot} = E_S + E_R \gg E_S$$

let μ_R & μ_S denote the microstates of R and S respectively. then the joint probability of microstates $(\mu_S \otimes \mu_R)$ is

$$p(\mu_S \otimes \mu_R) = \frac{1}{\Omega_{S \oplus R}(E_{Tot})}, \quad H_S(\mu_S) + H_R(\mu_R) = E_S + E_R = E_{tot}$$

$$= 0, \quad \text{otherwise} \qquad \text{—— (1)}$$

the unconditional probability for microstates of S is now obtained from

$$p(\mu_S) = \sum_{\{\mu_R\}} p(\mu_S \otimes \mu_R) \qquad \text{—— (2)}$$

the summation in eq^n (2) is a restricted sum in the sense that only those microstates of reservoir μ_R are considered such that $H_R(\mu_R) + H_S(\mu_S) = E_{tot}$

$$\therefore \; p(\mu_S) = \frac{\Omega_R\left(E_{tot} - H_S(\mu_S) \,/\, H_S(\mu_S)\right)}{\Omega_{S\oplus R}(E_{tot})}$$ Bayes theorem.

Since the denominator is constant (E_{tot} = const), we can write:

$$p(\mu_S) \propto e^{S_R(E_{tot} - H_S(\mu_S))/k_B} \qquad \left\{\because S_R(E_{tot} - H_S(\mu_S)) = k_B \ln \Omega_R\right\}$$

Since $H_S(\mu_S) \ll H_R(\mu_R)$, we write for $S_R(E_{tot} - H_S(\mu_S))$ as

$$S_R(E_{tot} - H_S(\mu_S)) = S_R(E_{tot}) - H_S(\mu_S)\frac{\partial S_R}{\partial E_R} + O(H_S(\mu_S)^2)$$

$$\simeq S_R(E_{tot}) - H_S(\mu_S)\frac{\partial S_R}{\partial E_R} = S_R(E_{tot}) - \frac{H_S(\mu_S)}{T}$$

$$\therefore \; p(\mu_S) \propto e^{S_R(E_{tot})/k_B} \cdot e^{-\beta H_S(\mu_S)}$$

After dropping the subscript 's' for convenience and normalizing $p(\mu_S)$, we write:

$$p_{T,\vec{x}}(\mu) = \frac{e^{-\beta H(\mu)}}{Z(T,\vec{x})} \qquad (3)$$

where $Z(T,\vec{x})$ is the partition function. $\beta = \frac{1}{k_B T}$

The probability distribution for energy is straightforwardly written as:

$$p(\epsilon) = \sum_{\{\mu\}} p(\mu)\,\delta(H(\mu)-\epsilon) = \frac{e^{-\beta\epsilon}}{Z} \sum_{\{\mu\}} \delta(H(\mu)-\epsilon)$$

The restricted sum simply picks up the number of microstates with energy ϵ.

$$\therefore \quad p(\epsilon) = \frac{\Omega(\epsilon)\, e^{-\beta\epsilon}}{Z} = \frac{e^{-\beta(\epsilon - TS(\epsilon))}}{Z}$$

$$\because \Omega(\epsilon) = e^{S/k_B}$$

Now since the free energy $F(\epsilon) = \epsilon - TS(\epsilon)$, we write

$$p(\epsilon) = \frac{e^{-\beta F(\epsilon)}}{Z} \quad \text{--- (4)}$$

"The probability $p(\epsilon)$ peaks sharply when $F(\epsilon)$ is minimized or when $S(\epsilon)$ is maximized."

We can write for Z as:

$$Z = \sum_{\mu} e^{-\beta H(\mu)} = \sum_{\epsilon} e^{-\beta F(\epsilon)} \approx e^{-\beta F(\epsilon^*)} \quad \text{--- (5)}$$

The last approximation is due to Saddle point approximation of the series sum by its largest value.

$$\langle H \rangle = \frac{\sum_{\mu} H(\mu)\, e^{-\beta H(\mu)}}{Z} = \frac{-1}{Z} \cdot \frac{\partial}{\partial \beta} \sum_{\mu} e^{-\beta H(\mu)} = \frac{-\partial}{\partial \beta}(\ln Z)$$

--- (6)

A similar expression for energy comes for thermodynamics

$$E = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{\vec{x}}$$

$\left\{ \because E = F + TS \right.$
$\therefore dE = dF + Tds + sdT$

or $Tds - Pdv + \mu dN = dF + Tds + sdT$

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

$$\therefore E = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right) = \frac{\partial}{\partial \beta}(\beta F) \qquad \because \frac{\partial}{\partial \beta} \equiv -K_B T^2 \frac{\partial}{\partial T} \quad \text{—— (7)}$$

Comparing (6) & (7), we get

$$F(T, \vec{x}) = -K_B T \ln Z(T, \vec{x}) \quad \text{—— (8)}$$

Ques: How closely are the average energy $\langle H(\mu)\rangle$ and the most probable energy E^* to each other?

Ans. For this we can calculate the variance of $H(\mu)$

i.e $\langle H^2(\mu)\rangle_c$.

We first note that

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

& $\langle H^2(\mu)\rangle = \dfrac{\sum_\mu H^2(\mu)\, e^{-\beta H(\mu)}}{Z}$

$$\therefore \langle H^2\rangle_c = \langle H^2\rangle - \langle H\rangle^2$$

$$= \frac{\sum_\mu H^2(\mu)\, e^{-\beta H(\mu)}}{Z} - \left(\frac{\sum_\mu H(\mu)\, e^{-\beta H(\mu)}}{Z}\right)^2 \quad \text{———} (9)$$

Now since $\sum_\mu H(\mu) e^{-\beta H(\mu)} = -\dfrac{\partial Z}{\partial \beta}$

& $\sum_\mu H^2(\mu) e^{-\beta H(\mu)} = \dfrac{\partial^2 Z}{\partial \beta^2}$

Eqⁿ (9) becomes

$$\langle H^2\rangle_c = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \frac{\partial^2}{\partial \beta^2}(\ln Z) \quad \text{———} (10)$$

In general, $\langle H^n\rangle_c = (-1)^n \dfrac{\partial^n}{\partial \beta^n}(\ln Z)$ ——— (11)

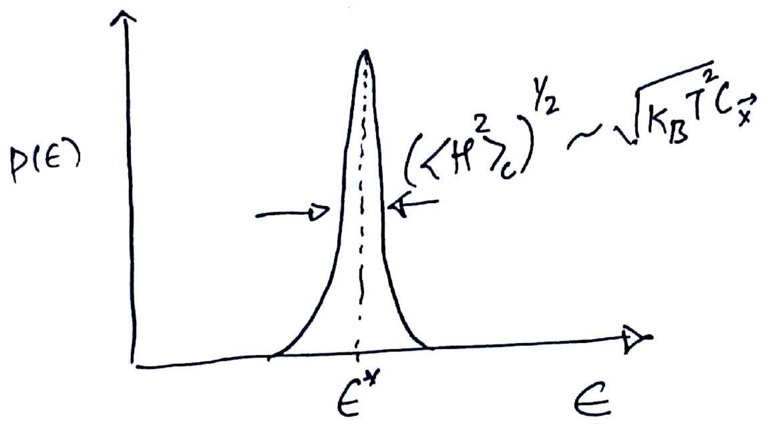
Also from eqⁿ (10) we can write,

$$\langle H^2\rangle_c = \frac{\partial}{\partial \beta}(\ln Z) = -\frac{\partial}{\partial \beta}\langle H\rangle = -\frac{\partial}{\partial\left(\frac{1}{K_B T}\right)}\langle H\rangle = K_B T^2 \frac{\partial}{\partial T}\langle H\rangle\Big|_{\vec{x}} = K_B T^2 C_{\vec{x}} \quad \text{———} (12)$$

$\therefore \langle H^2 \rangle_c \sim N \qquad \because C_x \sim N$

thus $\dfrac{(\langle H^2 \rangle_c)^{1/2}}{\langle H \rangle_c} \sim N^{-1/2} \longrightarrow 0$ as N goes to infinity

Hence energy fluctuations in a canonical ensemble goes to zero as the system goes to thermodynamic limit.



" The ratio of width to the mean energy goes to zero in the thermodynamic limit making canonical & micro-canonical ensembles identical in large N limit "

$$\therefore p(E) = \frac{e^{-\beta F(E)}}{Z} \xrightarrow[N \to \infty]{} \frac{e^{-(E - \langle H \rangle)^2 / 2\langle H^2 \rangle_c}}{(2\pi \langle H^2 \rangle_c)^{1/2}}$$

(Canonical ensemble) (Microcanonical Ensemble)