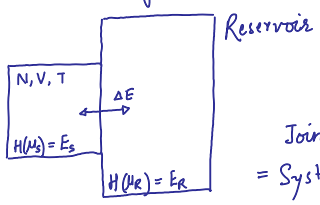
Canonical Ensemble (N, V, T)

$\downarrow$ allowing fluctions in E



Joint system $=$ System $+$ Reservoir is in Micro-canonical Ensemble.

$H(\mu_s) + H(\mu_R) = E_{total} = E_s + E_R$

Joint System is in (μ_s, μ_R)

$$p_{S+R}(\mu_s, \mu_R) = \frac{1}{\Omega_{S+R}(E_{total})}$$

What is the probability of obtaining

$$p_s(\mu_s) = \text{Unconditional probability}$$

$$= \frac{p_{S+R}(\mu_s, \mu_R)}{p(\mu_R \mid \mu_s)}$$

$p(\mu_R \mid \mu_s) \rightsquigarrow$ Conditional probability of Reservoir in μ_R provided System is in μ_s

$$p_s(\mu_s) = \frac{1}{\Omega_{S+R}(E_{total})} \cdot \Omega_R\left(E_{total} - E_s \mid H_s(\mu_s) = E_s\right)$$

By Boltzmann's Entropy : $S = k_B \ln \Omega$

$$\Omega = e^{S/k_B}$$

$$p_s(\mu_s) \propto e^{S_R(E_{total} - E_s)/k_B} \quad \ldots\ldots \quad \Omega_{S+R}(E_{total}) = \text{Const.}$$

$$p_s(\mu_s) \propto e^{\frac{1}{k_B} \cdot \left[S_R(E_R)\big|_{E_R = E_{total}} + (-H(\mu_s)) \frac{\partial S_R}{\partial E_R}\Big|_{E_R = E_{total}} + \cancelto{0}{O(H(\mu_s)^2)} \right]}$$

$$p_s(\mu_s) \propto e^{S_R(E_{total})/k_B} \cdot e^{-H(\mu_s)/T k_B} \quad \ldots\ldots \quad \because \frac{\partial S_R}{\partial E_R} = \frac{1}{T}$$

$$p_s(\mu_s) \propto \text{Const.}\ e^{-\beta H(\mu_s)} \quad \ldots\ldots \quad \beta = 1/k_B T$$

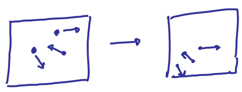
$$p_s(\mu_s) = \frac{e^{-\beta H(\mu_s)}}{\sum_{\mu_s} e^{-\beta H(\mu_s)}} \quad \ldots\ldots \text{ After Normalizing } p_s(\mu_s)$$

$$p(\mu) = \frac{e^{-\beta H(\mu)}}{Z(N,V,T)}$$ .... drop subscript s for convenience —— (1)

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

Transform $p(\mu) \longrightarrow p(E)$ "More useful"

Large no. of μ_s are degenerate.



$$p(E) = \sum_{\mu} p(\mu)\, \delta(H(\mu), E)$$

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

$$= \frac{\Omega(E)}{Z(N,V,T)} \cdot e^{-\beta E}$$ ... $\Omega(E)$ = No. of microstates with $H(\mu) = E$

By Boltzmann's entropy .. $\Omega(E) = e^{S/k_B}$

$$p(E) = \frac{e^{-\beta(E-TS)}}{Z(N,V,T)} = \frac{e^{-\beta F}}{Z(N,V,T)}$$ .... Free energy $F = E - TS$

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

Normalization required

$\because \sum_{E} p(E) = 1 = \sum_{\mu} p(\mu)$

Building connection with thermodynamics.

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

$$= \frac{-\frac{\partial}{\partial\beta} \sum_{\mu} e^{-\beta H(\mu)}}{Z(N,V,T)} = \frac{-1}{Z} \cdot \frac{\partial Z}{\partial\beta}$$

$$\Rightarrow \langle E \rangle = -\frac{\partial}{\partial\beta}(\ln Z)$$ —— (2)

Macroscopic World

Microscopic world.

Recall that: $Z = \sum_{\mu} e^{-\beta H(\mu)} = \sum_{E} e^{-\beta F(E)} \approx e^{-\beta F(E^*)}$

"Saddle point approximat."

→ Replaced the sum by the max. of summand ←

E^* maximizes $e^{-\beta F(E^*)}$

E^* minimizes $F(E)$

$Z \approx e^{-\beta F(E^*)}$ $\qquad E^*$ to be seen as thermodynamic in nature.

$\Rightarrow \ln Z \simeq -\beta F(E^*)$

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

Thermodynamic "Macroscopic"

"Microscopic"

$\langle E \rangle = \frac{-\partial}{\partial \beta}(-\beta F) = \frac{\partial}{\partial \beta}(\beta F)$