

08/01/25

Lecture 2

Heisenberg Model of Magnet

$$H = \sum_{\langle i, j \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

Here Spins are 3D vector operators.

Ising Model of Magnet

(Short range)

$$H = -J \sum_{\langle i, j \rangle} S_i^{(z)} S_j^{(z)} - h \sum_i S_i^{(z)}$$

$J \Rightarrow$ Interaction term

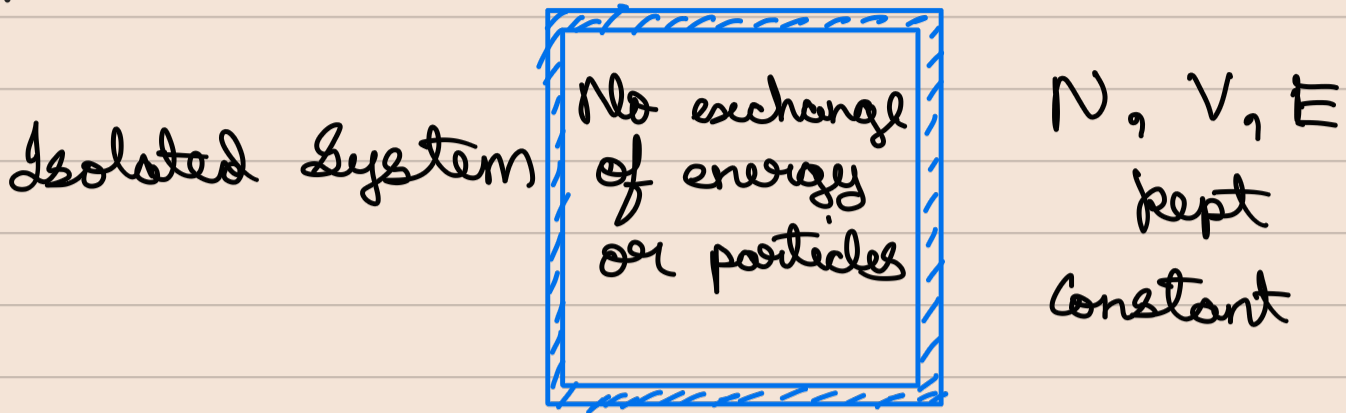
$S_i^z \Rightarrow z$ -Component of Spin
at i^{th} lattice

$\langle i, j \rangle \Rightarrow$ Summation over
nearest neighbours only

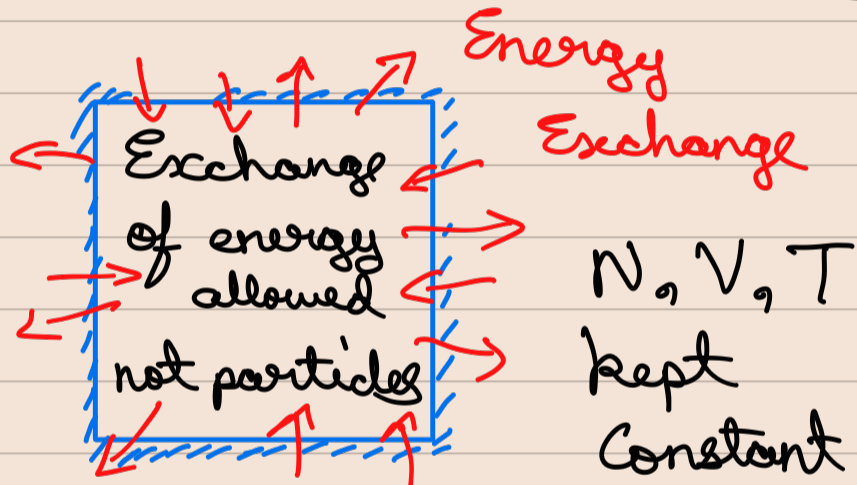
$h \Rightarrow$ External magnetic field

Ensembles

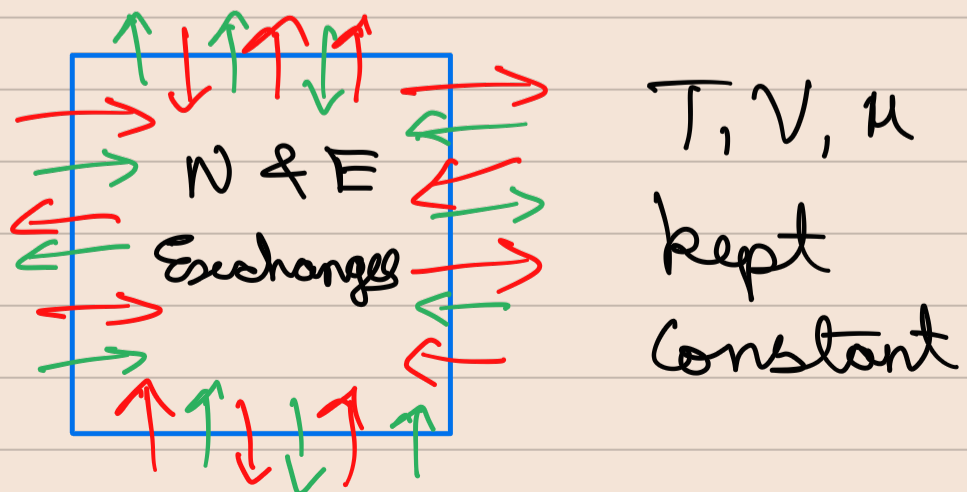
A System in Microcanonical Ensemble



A System in Canonical Ensemble



A System in Grand canonical Ensemble



Energy & Particles will be exchanged.

Generalized Forces & displacements

(Total work) $\delta W = \sum_i \vec{J}_i d\vec{x}_i = \vec{J} \cdot d\vec{x}$

$$\vec{J} = (J_1, J_2, \dots), \quad \vec{x} = (x_1, x_2, \dots)$$

<u>System</u>	<u>Generalized force</u>	<u>Generalized displacement</u>
Fluid	Pressure $(-P)$	Volume (V)
Magnet	Magnetic field (H)	magnetization (M)
Dielectric	Electric field (E)	Polarization (P)
Wire	Tension (F)	length (L)
	<u>Intensive quantities</u>	<u>Extensive quantities</u>

Response Functions

They help in characterizing the macroscopic behaviour of system.

Eg: $C_v, C_p, k_T, B_v, \chi_m, \chi_e$, etc.

Heat capacities

→ For fluids

$$C_v = \left(\frac{dQ}{dT} \right)_v = \left(\frac{\partial E}{\partial T} \right)_v$$

$$C_p = \left(\frac{dQ}{dT} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$E \Rightarrow$ total internal energy

$H \Rightarrow$ Enthalpy, $H = U + PV$

Force constants (Generalized Spring constants)

They are ratios of displacement to force & are generalized Spring const.

Eg:- $K_T = \frac{1}{V} \left(-\frac{\partial V}{\partial P} \right)_T$ (Isothermal Compressibility)

$$\chi_m = \left(\frac{\partial M}{\partial H} \right)_T \quad \left(\begin{array}{l} \text{Isothermal} \\ \text{Magnetic} \\ \text{Susceptibility} \end{array} \right)$$

Thermal responses

Eg: Coefficient of expansion for fluid is

$$\alpha = \left(\frac{\partial V}{\partial T} \right)_p$$

Hydrodynamic System

$$\varepsilon = \frac{E}{V}$$

$$\rho = \frac{N}{V}$$

$$\mathcal{S} = \frac{S}{V}$$

First law of Thermodynamics

$$dE = TdS - PdV + \mu dN$$

$$dS = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu dN}{T}$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \Rightarrow \frac{1}{V} \left[\frac{\partial S}{\partial (E/V)} \right]_{V,N} = \frac{1}{T}$$

$$\frac{1}{V} \left(\frac{\partial S}{\partial \varepsilon} \right)_\rho = \frac{1}{T} \quad \text{or} \quad \boxed{\left(\frac{\partial \mathcal{S}}{\partial \varepsilon} \right)_\rho = \frac{1}{T}}$$

$$\frac{-\mu}{T} = \left(\frac{\partial S}{\partial N} \right)_{E,V} = \left[\frac{\partial (S/V)}{\partial (N/V)} \right]_{E,V} = \left(\frac{\partial \mathcal{S}}{\partial \rho} \right)_\varepsilon$$

$$\Rightarrow \boxed{\frac{-\mu}{T} = \left(\frac{\partial \mathcal{S}}{\partial \rho} \right)_\varepsilon}$$

Helmholtz free energy

$$a = \frac{A}{V}$$

$$A = E - TS$$

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

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} \Rightarrow \frac{S}{V} = -\left[\frac{\partial (A/V)}{\partial T}\right]_{V,N}$$

$$\Rightarrow \boxed{S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}} \quad \& \quad \boxed{\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}}$$

Grand Potential (Λ)

$$\Lambda = E - TS - \mu N$$

$$d\Lambda = -SdT - PdV - N d\mu$$

$$\boxed{-S = \left(\frac{\partial \Lambda}{\partial T}\right)_{V,\mu}}$$

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

$$\text{But } G = \mu N = E + PV - TS$$

$$\Rightarrow \Lambda = E - TS - E - PV + TS$$

$$\Rightarrow \Lambda = -PV$$

$$d\Lambda = -PdV - VdP = -SdT - PdV - Nd\mu$$

$$\Rightarrow \underbrace{SdT - VdP + Nd\mu = 0}$$

This is Gibbs's duhem relation.

$$\Rightarrow dP = SdT + Pd\mu$$

$$\underbrace{S = \left(\frac{\partial P}{\partial T} \right)_{\mu}} \quad \underbrace{P = \left(\frac{\partial P}{\partial \mu} \right)_T}$$

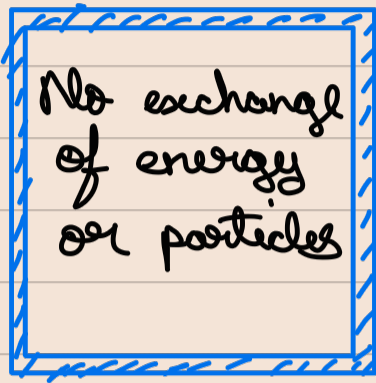
Also when PV is written as a function of (T, V, μ) & since $\Lambda = -PV$

$$\text{we get } S = \left(\frac{\partial(PV)}{\partial T} \right)_{V, \mu}$$

$$\& N = \left(\frac{\partial(PV)}{\partial \mu} \right)_{T, V}$$

Comparison of various ensembles of a hydrodynamic system

Microcanonical



$\Omega(E, p)$ is

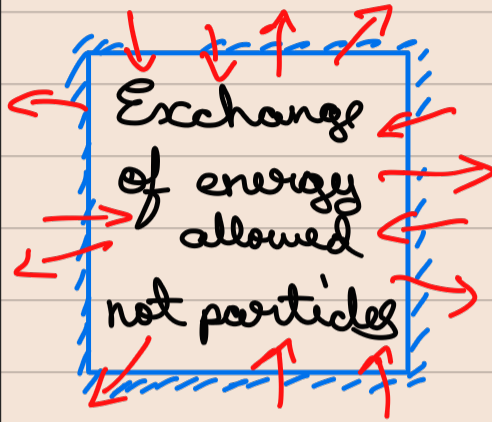
$$\frac{\int d^3q d^3p \delta(E_c - E) \times \delta(N_c - N)}{h^{3N} N!}$$

$$S = k_B \ln(\Omega)$$

$$\frac{1}{T} = \frac{1}{V} \left(\frac{\partial S}{\partial E} \right)_p$$

$$\frac{-\mu}{T} = \frac{1}{V} \left(\frac{\partial S}{\partial p} \right)_E$$

Canonical



$Q(\beta, p)$ is

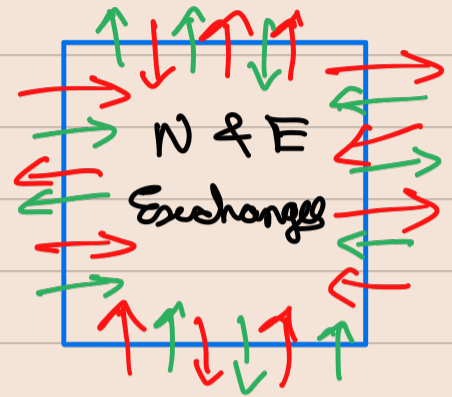
$$\int d^3q d^3p e^{-\beta H(\vec{q}, \vec{p})} \times \delta(N_c - N)$$

$$A = -k_B T \ln(Q)$$

$$\beta = -\frac{1}{V} \left(\frac{\partial A}{\partial T} \right)_V$$

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

Grand Canonical



$Z(\beta, \mu)$ is

$$\sum_N e^{\beta \mu N} Q(\beta, p)$$

$$\Delta = -PV$$

$$\Delta = -k_B T \ln(Z)$$

$$\beta = \frac{1}{V} \left(\frac{\partial (PV)}{\partial T} \right)_{V, \mu}$$

$$p = \frac{1}{V} \left(\frac{\partial (PV)}{\partial \mu} \right)_{V, T}$$

Relation b/w partition functions for hydrodynamic systems

$$Q(\beta, P) = \int dE \exp(-\beta V E) \Omega(E, P)$$

(canonical) (microcanonical)

$$Z(\beta, \mu) = \int dP \exp(\beta V P \mu) Q(\beta, P)$$

(grand canonical) (canonical)

Magnetic systems

Magnetic work, $dW = \vec{H} \cdot d\vec{M}$

Internal energy, $dE = T dS + \vec{H} \cdot d\vec{M}$

$A = E - TS$, $dA = -S dT + \vec{H} \cdot d\vec{M}$

$H_{en} = E - \vec{H} \cdot \vec{M}$
 $\rightarrow$ (enthalpy), $dH_{en} = T dS - \vec{M} \cdot d\vec{H}$

$G = E - TS - \vec{H} \cdot \vec{M}$, $dG = -S dT - \vec{M} \cdot d\vec{H}$

For a system with N_s number of spins, we define specific quantities

h = External magnetic field

$\&$ M = Magnetization of system

$$\varepsilon = \frac{E}{N_s}$$

$$m = \frac{M}{N_s}$$

$$s = \frac{S}{N_s}$$

First law of thermodynamics

$$dE = TdS + hdm$$

$$\Rightarrow dS = \frac{dE}{T} - \frac{h}{T} dm$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_m \quad \left(\frac{\partial S}{\partial m} \right)_E = -\frac{h}{T}$$

$$\text{or } \boxed{\frac{N_s}{T} = \left(\frac{\partial S}{\partial E} \right)_m} \quad \& \quad \boxed{-\frac{h}{T} = \frac{1}{N_s} \left(\frac{\partial S}{\partial m} \right)_E}$$

Helmholtz free energy is defined

$$\text{as, } A = E - TS$$

$$\Rightarrow dA = -SdT + hdm$$

$$\text{where } -S = \left(\frac{\partial A}{\partial T} \right)_m \quad \& \quad h = \left(\frac{\partial A}{\partial m} \right)_T$$

$$\text{or } \boxed{S = -\frac{1}{N_s} \left(\frac{\partial A}{\partial T} \right)_m} \quad \& \quad \boxed{h = \frac{1}{N_s} \left(\frac{\partial A}{\partial m} \right)_T}$$

Gibb's Free energy or Gibb's Potential or Free Energy

$$F = E - TS - hM = A - hM$$

$$dF = -SdT - Mdh$$

$$M = -\left(\frac{\partial F}{\partial h}\right)_T$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_h$$

$$\Rightarrow m = \frac{-1}{N_s} \left(\frac{\partial F}{\partial h}\right)_T$$

$$s = \frac{-1}{N_s} \left(\frac{\partial F}{\partial T}\right)_h$$

Gibb's Canonical Ensemble

Consider a system whose net work is of the form

$$\delta W_{\text{net}} = \vec{J} \cdot d\vec{x}$$

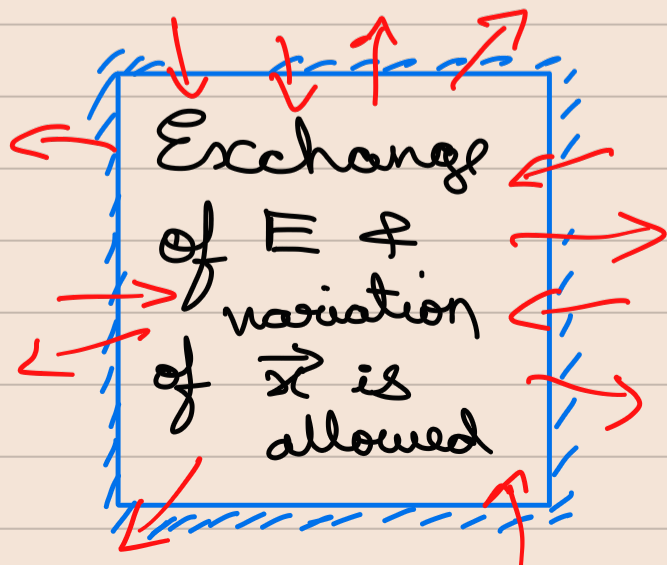
$\vec{J} \Rightarrow$ generalized force ($-P, h, \text{tension, etc}$)

$\vec{x} \Rightarrow$ generalized displacement ($V, M, \text{length, etc}$)

Gibbs canonical ensemble is a large collection of identical systems with same number of particles (N) same temperature (T), under same generalized force ($\vec{J}$) which allows exchange of heat & also variation in generalized displacement.

In these systems we allow energy (E) & generalized displacements ($\vec{x}$) to fluctuate.

A System
in Gibbs
Canonical
Ensemble



Gibbs's partition Function (Z)

$$Z \rightarrow Z(N, T, \vec{J}) = \sum_{\{c, \vec{x}\}} e^{-\beta(H_c - \vec{x} \cdot \vec{J})}$$

($H \Rightarrow$ Hamiltonian)

Probability of a particular configuration ' c ' with the generalized displacement ' $\vec{x}$ ' is

$$\text{Prob}(c, \vec{x}) = \frac{e^{-\beta(H_c - \vec{x} \cdot \vec{J})}}{Z}$$

$$\langle \vec{x} \rangle = \sum_{\{c, \vec{x}\}} \vec{x} \text{Prob}(c, \vec{x}) = \sum_{\{c, \vec{x}\}} \vec{x} \frac{e^{-\beta(H_c - \vec{x} \cdot \vec{J})}}{Z}$$

It is given by,

$$\langle \vec{x} \rangle = \frac{\left[\vec{\nabla}_{\vec{J}} (Z) \right]_{\beta, N}}{\beta Z}$$

$$\frac{\partial}{\partial \vec{J}} = \vec{\nabla}_{\vec{J}} = \left(\frac{\partial}{\partial J_1}, \frac{\partial}{\partial J_2}, \dots \right)$$

$J_i \Rightarrow$ Some generalized forces

$$\Rightarrow \langle \vec{x} \rangle = k_B T \left[\vec{\nabla}_{\vec{J}} \ln(Z) \right]_{\beta, N}$$

But Gibbs free energy / Potential is given by,

$$F = E - TS - \vec{x} \cdot \vec{J}$$

$$\Rightarrow dF = -SdT - \vec{x} \cdot d\vec{J}$$

$$\Rightarrow \vec{x} = - \left(\frac{\partial F}{\partial \vec{J}} \right)_T = - \left(\vec{\nabla}_{\vec{J}} F \right)_T$$

Thus on comparison we can relate the Gibbs partition function with the free energy as,

$$F = -k_B T \ln(Z)$$

Enthalpy is given by

$$H_{en.} = E - \vec{x} \cdot \vec{J}$$

$$\Rightarrow \langle H_{en} \rangle = \langle H_c - \vec{x} \cdot \vec{J} \rangle$$

$$\langle H_{en} \rangle = \frac{\sum_{\{c, \vec{x}\}} (H_c - \vec{x} \cdot \vec{J}) e^{-\beta (H_c - \vec{x} \cdot \vec{J})}}{Z}$$

$$= \frac{1}{Z} \left[-\frac{\partial}{\partial \beta} (Z) \right]_{N, \vec{J}}$$

$$\langle H_{en} \rangle = - \left[\frac{\partial \ln(Z)}{\partial \beta} \right]_{N, \vec{J}} \Rightarrow \text{Average enthalpy}$$

Heat Capacity at Constant generalized force, (analogous to C_p) is ' $C_{\vec{J}}$ ', given as

$$C_{\vec{J}} = \left[\frac{\partial \langle H_{en} \rangle}{\partial T} \right]_{\vec{J}, N} = \frac{\partial \beta}{\partial T} \left(\frac{\partial \langle H_{en} \rangle}{\partial \beta} \right)_{\vec{J}, N}$$

$$= \frac{1}{k_B} \left(\frac{-1}{T^2} \right) \left[\frac{\partial^2 \ln(Z)}{\partial \beta^2} \right]_{\vec{J}, N}$$

$$\Rightarrow \boxed{C_{\vec{J}} = \frac{1}{k_B T^2} \left(\frac{\partial^2 \ln(Z)}{\partial \beta^2} \right)_{\vec{J}, N}}$$

Since, $dF = -SdT - \vec{x} \cdot d\vec{J}$

$$\Rightarrow \vec{x} = - \left(\frac{\partial F}{\partial \vec{J}} \right)_{T, N} = - \left(\vec{\nabla}_{\vec{J}} F \right)_{T, N}$$

$$\& \quad S = - \left(\frac{\partial F}{\partial T} \right)_{\vec{J}, N}$$

For magnetic system we have

$$\vec{J} = h \quad (\text{external magnetic field})$$

$$\& \quad \vec{x} = M \quad (\text{magnetization})$$

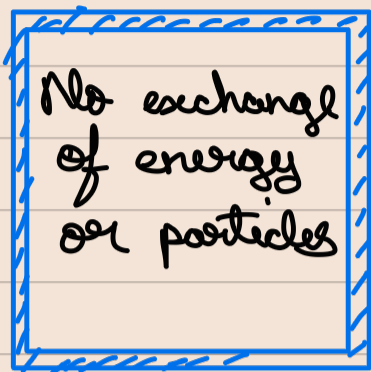
$$\Rightarrow M = - \left(\frac{\partial F}{\partial h} \right)_{T, N}$$

$$\Rightarrow \boxed{m = - \frac{1}{N_S} \left(\frac{\partial F}{\partial h} \right)_{T, N_S}}$$

$$\& \quad \boxed{s = - \frac{1}{N_S} \left(\frac{\partial F}{\partial T} \right)_{h, N_S}}$$

Various ensembles for magnetic spin systems

Microcanonical



Thermodynamic prob.
 $\Omega(E, m)$ is

$$\sum_c \delta(E_c - EN_s) \times \delta(M_c - mN_s)$$

$$S = k_B \ln(\Omega)$$

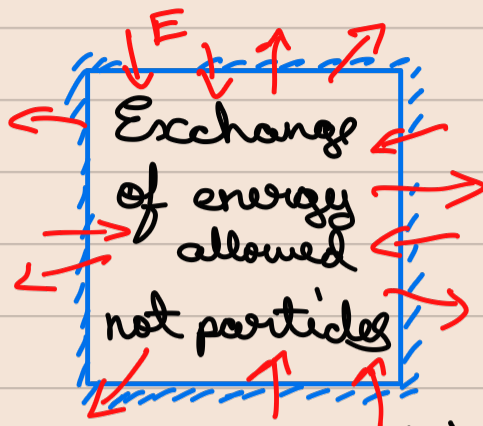
(Entropy)

$$\frac{1}{T} = \frac{1}{N_s} \left(\frac{\partial S}{\partial E} \right)_m$$

$$-\frac{h}{T} = \frac{1}{N_s} \left(\frac{\partial S}{\partial m} \right)_E$$

$h \Rightarrow$ Ext. field needed to achieve the existing m

Canonical



$\rightarrow$ Canonical partition
 $Q(\beta, m)$ is

$$\sum_c e^{-\beta E_c} \cdot \delta(M_c - mN_s)$$

$$A = -k_B T \ln(Q)$$

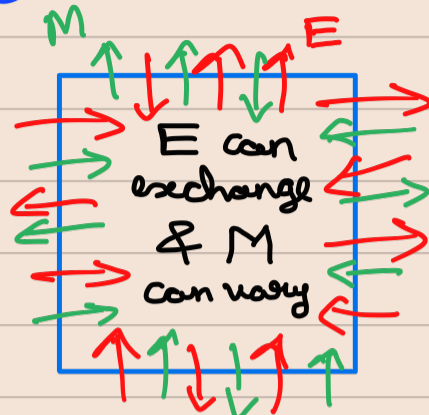
helmholtz free energy

$$\beta = \frac{1}{N_s} \left(\frac{\partial A}{\partial T} \right)_m$$

$$h = \frac{1}{N_s} \left(\frac{\partial A}{\partial m} \right)_T$$

$\beta =$ Specific Entropy

Gibbs Canonical



Gibbs partition
 $Z(\beta, h)$ is

$$\sum_c e^{-\beta(E_c - hM_c)}$$

$$F = -k_B T \ln(Z)$$

$\rightarrow$ Gibbs potential

$$\beta = \frac{1}{N_s} \left(\frac{\partial F}{\partial T} \right)_h$$

$$m = \frac{1}{N_s} \left(\frac{\partial F}{\partial h} \right)_T$$

Relation b/w partition functions for Spin Systems

$$Q(\beta, m) = \int d\varepsilon \exp(-\beta N_S \varepsilon) \Omega(\varepsilon, m)$$

(canonical) (micro canonical)

$$Z(\beta, h) = \int dm \exp(\beta N_S m h) Q(\beta, m)$$

(gibbs canonical) (canonical)

Equivalence of Ensembles (For Hydrodynamic System)

Relating Microcanonical with canonical

$$Q_{\text{can.}} = e^{-\beta A_{\text{can.}}} = \sum_c e^{-\beta E_c} = \sum_E \Omega(E) e^{-\beta E}$$

$$S = k_B \ln(\Omega) \Rightarrow \Omega = e^{S/k_B}$$

$$\Rightarrow Q = \sum_E e^{(S/k_B - \beta E)}$$

$$Q = \sum_E e^{[V(S/k_B - \beta E)]}$$

In thermodynamic limit

$V \rightarrow \infty$, $N \rightarrow \infty$. But $\frac{N}{V} \rightarrow \text{finite}$

So summation is dominated by that $\mathcal{E} = \bar{\mathcal{E}}$ which maximizes $\left(\frac{\mathcal{S}}{k_B} - \beta \mathcal{E} \right)$

$$\Rightarrow \left. \frac{\partial \left(\frac{\mathcal{S}}{k_B} - \beta \mathcal{E} \right)}{\partial \mathcal{E}} \right|_{\mathcal{E} = \bar{\mathcal{E}}} = 0$$

$$\Rightarrow \left. \frac{\partial \mathcal{S}}{\partial \mathcal{E}} \right|_{\mathcal{E} = \bar{\mathcal{E}}} = \frac{1}{T}$$

$$\Rightarrow Q = \exp \left[V \left(\frac{\mathcal{S}(\bar{\mathcal{E}})}{k_B} - \beta \bar{\mathcal{E}} \right) \right]$$

Now $V \left[\frac{\bar{\mathcal{S}}}{k_B} - \frac{\bar{\mathcal{E}}}{k_B T} \right] = \frac{1}{k_B} \left[\bar{\mathcal{S}} - \frac{\bar{\mathcal{E}}}{T} \right] = -\beta \bar{A}$

$\downarrow$
Microcanonical
Helmholtz free energy

$$\Rightarrow e^{-\beta A_{\text{can.}}} = e^{-\beta A_{\text{mic. can.}}}$$

$\rightarrow$ only at Thermodynamic limit.