

03/02/25

Lecture 9

Variational Principle in Stat. Mech

Consider a System with true hamiltonian H . If it is not possible to get the Solutions (eigen functions or partition function or eqⁿ of state) exactly or if it very tough to find them, then we can use variational principle to get approximate solution.

We consider a trial hamiltonian H_0 whose Solutions are known & which mimic's the original hamiltonian as much as possible which also contains atleast one adjustable parameter.

By Bogoliubov's inequality we get,

$$F \leq F_0 + \langle H - H_0 \rangle$$

$$F_0 = -k_B T \ln(Z_0) \text{ where } Z_0 = \text{Trace} \left[e^{-\beta H_0} \right]$$

↳ free energy. for approx. Hamiltonian.

F_0 is the free energy by trial Hamiltonian & $\langle H - H_0 \rangle_0$ is average of the difference b/w true & trial hamiltonians taken w.r.t the eigen states of H_0 .

$$\langle H - H_0 \rangle_0 = \frac{\sum_{\nu} \langle \nu | (H - H_0) | \nu \rangle e^{-\beta \langle \nu | H_0 | \nu \rangle}}{Z_0}$$

($|\nu\rangle \Rightarrow$ eigen states of H_0). The approx. free energy will always be greater than or equal to the true free energy.

Then we extremize the function $\Phi = F_0 + \langle H - H_0 \rangle_0$ w.r.t. all the adjustable parameters.

This puts an upper bound on the true free energy as shown by the Bogoliubov inequality.

Justifying mean field theory for Ising Model through Variational Principle

Consider a d -dimensional Ising model Hamiltonian with external field,

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} J_{ij} S_i S_j - h \sum_i S_i$$

$\hookrightarrow$ (to remove double counting)

choose the trial hamiltonian as

$$\mathcal{H}_0 = -H \sum_i S_i, \text{ as found before}$$

we get $Z_0 = [2 \cosh(BH)]^N$

$$F_0 = -\frac{1}{B} \ln [\text{Trace}(Z_0)] = -\frac{1}{B} \ln(Z_0)$$

$$F_0 = -\frac{N}{B} \ln [2 \cosh(BH)]$$

we should now find $\langle \mathcal{H} - \mathcal{H}_0 \rangle$.

$$\langle \mathcal{H} - \mathcal{H}_0 \rangle = \langle \mathcal{H} \rangle_0 - \langle \mathcal{H}_0 \rangle_0$$

$$\langle \mathcal{H}_0 \rangle = H \sum_i \langle S_i \rangle$$

$$\& \langle \mathcal{H} \rangle = \left\langle \left(-\frac{1}{2} \sum_{ij} J_{ij} S_i S_j - h \sum_i S_i \right) \right\rangle$$

$$= -\frac{1}{2} \sum_{ij} J_{ij} \langle S_i S_j \rangle - h \sum_i \langle S_i \rangle$$

$$\Rightarrow \langle \mathcal{H} \rangle = -\frac{1}{2} \sum_{ij} J_{ij} \langle S_i S_j \rangle - h \sum_i \langle S_i \rangle$$

now $\langle S_i S_j \rangle = \frac{\sum_{\{S_i\}} S_i S_j e^{-\beta \mathcal{H}_0}}{Z_0}$

$$\langle S_i S_j \rangle = \frac{\sum_{\{S_i\}} S_i S_j e^{\beta H \sum_k S_k}}{Z_0}$$

$$= \frac{1}{Z_0} \sum_{\{S_1, S_2, \dots, S_N\}} e^{\beta H S_1} e^{\beta H S_2} \dots (S_i e^{\beta H S_i}) \dots$$

$$\dots (S_j e^{\beta H S_j}) \dots e^{\beta H S_N}$$

But $Z_0 = \sum_{\{S_i\}} e^{\beta H \sum_i S_i}$

$$= \sum_{S_1} e^{\beta H S_1} \sum_{S_2} e^{\beta H S_2} \dots \sum_{S_i} e^{\beta H S_i} \dots \sum_{S_N} e^{\beta H S_N}$$

$$\langle S_i S_j \rangle_0 = \sum_{S_1} e^{\beta H S_1} \sum_{S_2} e^{\beta H S_2} \dots \left(\sum_{S_i} S_i e^{\beta H S_i} \right) \\ \times \dots \left(\sum_{S_j} S_j e^{\beta H S_j} \right) \times \dots \sum_{S_N} e^{\beta H S_N}$$

$$\sum_{S_1} e^{\beta H S_1} \sum_{S_2} e^{\beta H S_2} \dots \sum_{S_i} e^{\beta H S_i} \dots \sum_{S_j} e^{\beta H S_j} \dots \sum_{S_N} e^{\beta H S_N}$$

$$\Rightarrow \langle S_i S_j \rangle_0 = \frac{\sum_{S_i = \{\pm 1\}} S_i e^{\beta H S_i} \sum_{S_j = \{\pm 1\}} S_j e^{\beta H S_j}}{\sum_{S_i} e^{\beta H S_i} \sum_{S_j} e^{\beta H S_j}}$$

multiply & divide by Z_0^2 ,

$$\langle S_i S_j \rangle_0 = \left[\frac{Z_0 \sum_{S_i = \{\pm 1\}} S_i e^{\beta H S_i}}{Z_0 \sum_{S_i} e^{\beta H S_i}} \right] \left[\frac{Z_0 \sum_{S_j = \{\pm 1\}} S_j e^{\beta H S_j}}{Z_0 \sum_{S_j} e^{\beta H S_j}} \right]$$

$I_1 \qquad I_2$

$$I_1 = \frac{\sum_{\{S_i\}} e^{-\beta H \sum_i S_i} \sum_{S_i = \{\pm 1\}} S_i e^{\beta H S_i}}{\sum_{S_i} e^{\beta H S_i} Z_0}$$

$$I_1 = \frac{\left(\sum_{S_1} e^{\beta H S_1} \sum_{S_2} e^{\beta H S_2} \dots \sum_{S_i} e^{\beta H S_i} \dots \sum_{S_N} e^{\beta H S_N} \right) \times \left[\sum_{S_i = \pm 1} S_i e^{\beta H S_i} \right]}{\sum_{S_i} e^{\beta H S_i} Z_0}$$

$$= \frac{\sum_{S_1} e^{\beta H S_1} \sum_{S_2} e^{\beta H S_2} \dots \sum_{S_i = \pm 1} S_i e^{\beta H S_i} \dots \sum_{S_N} e^{\beta H S_N}}{Z_0}$$

$$I_1 = \sum_{\{S_i\}} \frac{S_i e^{-\beta \sum_k S_k}}{Z_0} = \langle S_i \rangle$$

Similarly $\underline{I_2 = \langle S_j \rangle}$

$$\Rightarrow \underline{\langle S_i S_j \rangle_0 = \langle S_i \rangle_0 \langle S_j \rangle_0}$$

Thus $G^{(0)}(x) = \langle S_i S_{i+x} \rangle_0 - \langle S_i \rangle_0 \langle S_{i+x} \rangle_0 = 0 //$

↓
(Correlation function
in mean field
approx.)

$G(x) = 0$ in
Mean field theory of
ising Model

$$\Rightarrow \langle \mathcal{H} \rangle_0 = -\frac{1}{2} \sum_{i,j} J_{ij} \langle S_i \rangle_0 \langle S_j \rangle_0 - h \sum_i \langle S_i \rangle$$

$$\langle S_i \rangle_0 = \frac{\sum_{S_i = \pm 1} S_i e^{BHS_i}}{\sum_{S_i} e^{BHS_i}}$$

$$\langle S_i \rangle_0 = \frac{e^{BH} - e^{-BH}}{e^{BH} + e^{-BH}} = \tanh(BH)$$

$\langle S_i \rangle_0 = \tanh(BH) \Rightarrow$ It is independent of 'i' (lattice position)

defining $m_0 = \langle S_i \rangle_0 = \tanh(BH)$ we get

$$\langle \mathcal{H} \rangle_0 = -\frac{1}{2} \sum_{i,j} J_{ij} m_0^2 - h \sum_i m_0$$

$$= -\frac{1}{2} m_0^2 \left[\sum_{i,j} J_{ij} \right] - h m_0 N$$

$$\text{Now } \sum_{i,j} J_{ij} = \sum_i \sum_j J_{ij}$$

$$= \sum_i \left[\sum_j J_{ij} \right] = \sum_i g_i = g \sum_i \underbrace{1}_N$$

$$(g_i = g, \text{ due to lattice translation symmetry}) \Rightarrow \sum_{i,j} J_{ij} = Ng$$

$$\Rightarrow \langle \mathcal{H} \rangle_0 = \frac{-g N m_0^2 - h m_0 N}{2}$$

$$\& \langle \mathcal{H}_0 \rangle_0 = -H \sum_i \langle S_i \rangle_0 = -H m_0 \sum_{\substack{i \\ N}} 1 = -H m_0 N$$

$$\Rightarrow \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 = \frac{-g N m_0^2 - h m_0 N}{2} + H m_0 N$$

$$\Rightarrow \underbrace{\Phi = F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0}_{\substack{\text{Should extremize} \\ \text{w.r.t 'H'}}} = \frac{-N}{\beta} \ln[2 \cosh(\beta H)] - \frac{g N m_0^2 - h m_0 N + H m_0 N}{2}$$

$$\Rightarrow \underbrace{-\frac{N}{\beta} \left[\frac{2\beta \sinh(\beta H)}{2 \cosh(\beta H)} \right]}_{\substack{\text{diff} \\ \text{w.r.t } H}} - g N m_0 \frac{\partial m_0}{\partial H} - h N \frac{\partial m_0}{\partial H} + \cancel{N m_0} + H N \frac{\partial m_0}{\partial H} = 0$$

$$\Rightarrow \left[-g m_0 - h + H \right] \frac{\partial m_0}{\partial H} = 0$$

$$\Rightarrow \boxed{H = g m_0 + h} \Rightarrow \text{Mean-field 'H' recovered.}$$

Thus we get the Mean-field approx. to minimize the free energy.

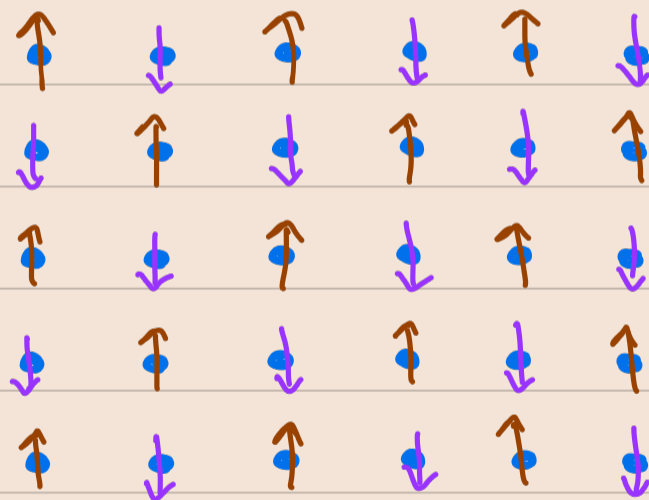
Anti - Ferro Magnet

The intrinsic hamiltonian for the anti-ferromagnet interaction is,

$$H = J \sum_{\langle i j \rangle} S_i S_j \quad (J > 0)$$

Thus to minimize the energy the nearby spins has to be oriented in opposite direction.

The ground state is given by,



} Called as
Neel
Order
or
anti-ferro
magnetic
order

For a bipartite lattice whose sites can be divided to two sub lattice such that a lattice point on one site can interact only with a site from the other lattice we can divide the original lattice to two sub-lattices 'A' & 'B'.

'A' $\Rightarrow$ which has all up spins &
'B' $\Rightarrow$ which has all down spin.

If $i \in A \Rightarrow$ its neighbours
are all in 'B' lattice & vice versa.

The order parameter here is
given by $\frac{m_A - m_B}{2}$

$$m_A = \langle S_i \rangle_{i \in A} \quad \& \quad m_B = \langle S_i \rangle_{i \in B}$$

But $m_B = -m_A$ since they
are opposite oriented.

$$\Rightarrow \text{order parameter} = \frac{m_A - m_B}{2} = m_A = -m_B$$

$$M_{\text{net}} = \sum_i \underbrace{\langle S_i \rangle}_{\text{for both sub lattice}}$$

$$= \sum_{i \in A} \langle S_i \rangle + \sum_{i \in B} \langle S_i \rangle$$

$$\begin{array}{l} M_{\text{net}} = \text{sum of all} + \text{sum of all} \\ \quad \downarrow \quad \quad \quad \text{avg. up spin} \quad \quad \quad \text{avg. down spin} \\ \text{(not order Parameter)} \end{array}$$

If neel order is not present then
 $m = \frac{M_{\text{net}}}{N} = \text{Zero}$ (Random fluctuation)

But even at Neel order $m = \frac{M_{\text{net}}}{N} = 0$

as equal amount of up & down spins are present at Neel order.

Thus $m = \frac{M_{\text{net}}}{N}$ is not the order parameter.

$$\text{But } m_s = \frac{\sum_{i \in A} \langle s_i \rangle - \sum_{i \in B} \langle s_i \rangle}{N}$$

is the order parameter. Since it is this parameter which can tell if the Neel order is achieved or not.

$$m_s = \frac{m_A - m_B}{2} = \begin{cases} 1, & \text{Neel order} \\ 0, & \text{no Neel order} \end{cases}$$

We also have a critical temperature in anti-ferromagnets & is called as the Neel Temperature.

We can use mean field theory to describe anti-ferromagnetism. Consider a external field 'h' applied on the system. Then the net hamiltonian becomes,

$$\mathcal{H} = \frac{J}{2} \sum_{\langle ij \rangle} S_i S_j + h \sum_i S_i \quad (J > 0)$$

$$S_i S_j \rightarrow \langle S_i \rangle S_j + \langle S_j \rangle S_i - \underbrace{\langle S_i \rangle \langle S_j \rangle}_{(\text{ignore})}$$

$$\mathcal{H} = J \sum_{\langle ij \rangle} \langle S_i \rangle S_j + h \sum_i S_i$$

Now we consider two sub lattices.

$$\mathcal{H} = J \left[\sum_{i \in A} \sum_{j \in n(i) \in B} \langle S_j \rangle_B S_i + \sum_{i \in B} \sum_{j \in n(i) \in A} \langle S_j \rangle_A S_i \right] - h \sum_{i \in A} S_i - h \sum_{i \in B} S_i$$

$n(i) \Rightarrow$ nearest neighbour of 'i'

$\langle S_j \rangle_B \Rightarrow$ avg. mag. field around ' S_i ' ($i \in A$)
& $j \in n(i)$

$\langle S_j \rangle_A \Rightarrow$ avg. mag. field around ' S_i ' ($i \in B$)
& $j \in n(i)$

$$\langle S_j \rangle_B = m_B \quad \& \quad \langle S_j \rangle_A = m_A$$

$$\mathcal{H} = \sum_{i \in A} S_i \left\{ \left[m_B J \underbrace{\sum_{j \in n(i)} 1}_Z \right] - h \right\} \\ + \sum_{i \in B} S_i \left\{ \left[m_A J \underbrace{\sum_{j \in n(i)} 1}_Z \right] - h \right\}$$

$Z \Rightarrow$ coordination number of original lattice

$$\Rightarrow \mathcal{H} = \sum_{MF} \sum_{i \in A} S_i [m_B J Z - h] \\ + \sum_{i \in B} S_i [m_A J Z - h]$$

use $JZ = g$

$$\mathcal{H}_{M.F} = - \sum_{i \in A} S_i (h - m_B g) - \sum_{i \in B} S_i (h - m_A g)$$

$$\& \quad \underline{H_A = h - m_A g} \quad \& \quad \underline{H_B = h - m_B g}$$

$$\Rightarrow \mathcal{H}_{M.F} = - \sum_{i \in A} H_B S_i - \sum_{i \in B} H_A S_i$$

$$\Rightarrow \mathcal{Z} = \left[\overset{\rightarrow \text{for } i \in A}{2 \cosh(\beta H_B)} \right]^{\frac{N}{2}} \left[\overset{\rightarrow \text{for } i \in B}{2 \cosh(\beta H_A)} \right]^{\frac{N}{2}}$$

$$M_{\text{net}} = \frac{\partial \ln(\mathcal{Z})}{\partial h} = \frac{\partial}{\partial h} \ln \left[2^N \cosh(\beta H_B)^{\frac{N}{2}} \times \cosh(\beta H_A)^{\frac{N}{2}} \right]$$

$$\frac{M_{\text{net}}}{N} = \frac{\partial}{\partial h} \left[\frac{1}{2} \left(\ln [\cosh(\beta H_B)] + \ln [\cosh(\beta H_A)] \right) \right]$$

$$m = \frac{1}{2} \left[\tanh(\beta H_B) + \tanh(\beta H_A) \right]$$

$$m = m_B + m_A$$

we can similarly show that

$$\boxed{\begin{aligned} m_A &= \frac{1}{2} \tanh[\beta (h - m_B g)] \\ m_B &= \frac{1}{2} \tanh[\beta (h - m_A g)] \end{aligned}}$$

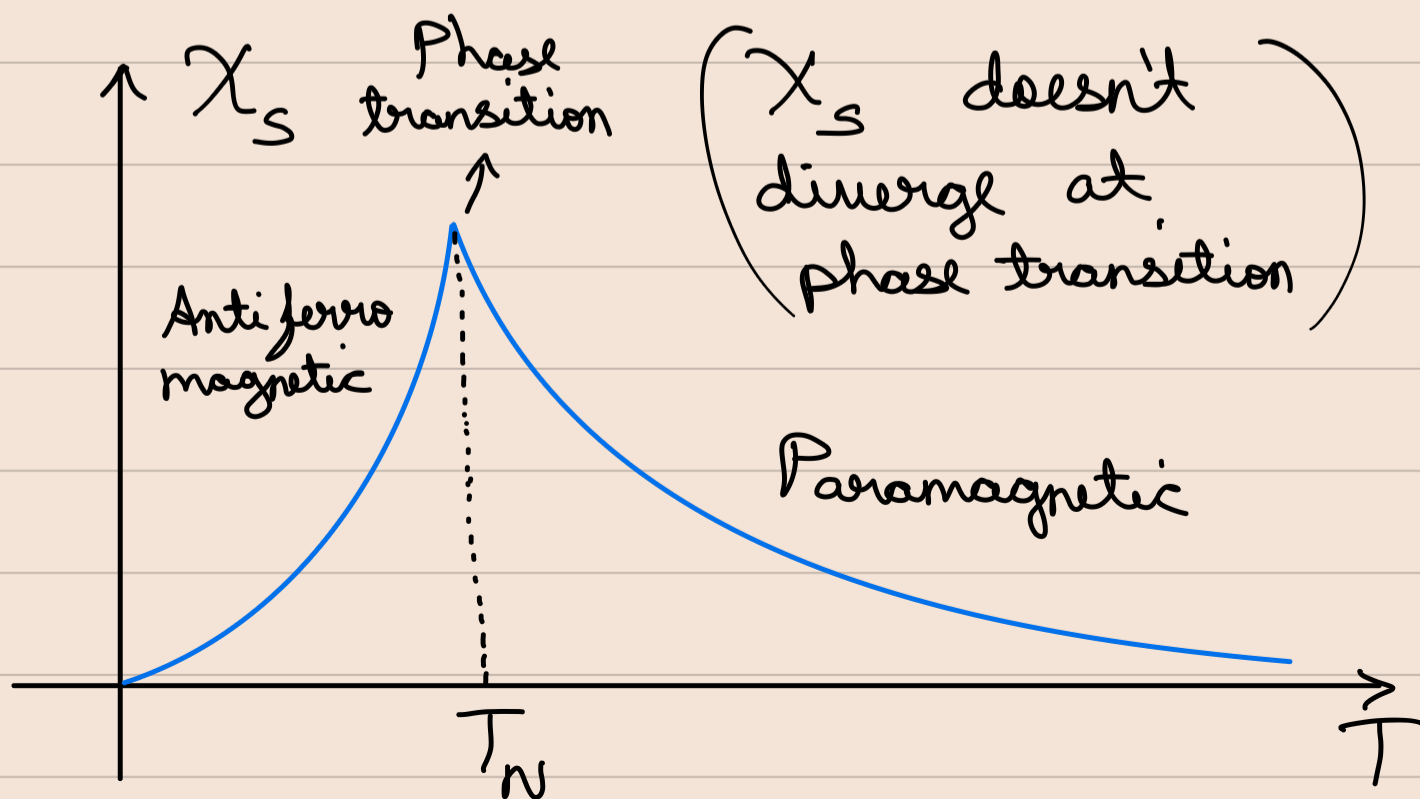
We get two self consistent eqⁿ.

$$m = \frac{1}{2} \left(\tanh[\beta(h - m_B g)] + \tanh[\beta(h - m_A g)] \right)$$

$$\chi_s = \frac{\partial m}{\partial h} = \frac{1}{2} \left[\operatorname{sech}^2[\beta(h - m_B g)] \left[\beta \left[1 - g \frac{\partial m_B}{\partial h} \right] \right] + \operatorname{sech}^2[\beta(h - m_A g)] \left[\beta \left[1 - g \frac{\partial m_A}{\partial h} \right] \right] \right]$$

$$\chi_s = \frac{\beta}{2} \left[(1 - m_A^2) \left[1 - g \frac{\partial m_B}{\partial h} \right] + (1 - m_B^2) \left[1 - g \frac{\partial m_A}{\partial h} \right] \right]$$

When it is solved self-consistently at $h=0$ we get χ_s vs T as



The Susceptibility doesn't diverge at the Critical point since the external field doesn't couple to the order parameter. The external field favours one sub lattice over the other, thus no divergence.

Consider a Staggered ext. field with the interaction energy as shown below.

$$e = -\hbar \sum_{i \in A} S_i + \hbar \sum_{i \in B} S_i$$

$\downarrow$ up-direction $\rightarrow$ up spin lattice $\rightarrow$ down direction $\rightarrow$ down spin lattice

This staggered ext. field exactly can couple with the order parameter $\frac{M_A - M_B}{2}$, thus can show divergence in χ_s at phase transition.

Density Matrix

Consider an ensemble of systems which are characterized by their quantum states represented by $|\alpha_i\rangle$. ($\{|\alpha_i\rangle\}$ need not be O.N. but have to be linearly independent) In those collection of systems let ' w_i ' fraction of systems be in the state $|\alpha_i\rangle$. Such that $\sum_i w_i = 1$. ' w_i ' is the classical probability of a system in the ensemble to be in the state $|\alpha_i\rangle$. ($i=1,2,\dots$) which represents the no. of states in the ensemble.

Suppose we need to find the ensemble average expectation value of an observable $\hat{A}$, then the ensemble average is given by,

$$\langle A \rangle = \sum_i w_i \langle \alpha_i | \hat{A} | \alpha_i \rangle$$

$\langle \alpha_i | \hat{A} | \alpha_i \rangle$ is the usual quantum mechanical expectation value of observable $\hat{A}$ in the state $|\alpha_i\rangle$. Where as $w_i \Rightarrow$ classical probability.

We can expand $|\alpha_i\rangle$ in a general O.N. complete basis $\{|n\rangle\}$ as,

$$|\alpha_i\rangle = \sum_n \langle n|\alpha_i\rangle |n\rangle$$

Note: The length of $\{|n\rangle\}$ basis is equal to the dimension of the Hilbert space that $|\alpha_i\rangle$ lives.

Substituting this in $\langle \hat{A} \rangle$ we get

$$\langle \hat{A} \rangle = \sum_i w_i \sum_{m,n} \langle m|\alpha_i\rangle^* \langle m|\hat{A}|n\rangle \langle n|\alpha_i\rangle$$

$$= \sum_i w_i \sum_{m,n} \langle n|\alpha_i\rangle \langle \alpha_i|m\rangle \langle m|\hat{A}|n\rangle$$

$$= \sum_{m,n} \langle n| \left[\sum_i w_i |\alpha_i\rangle \langle \alpha_i| \right] |m\rangle \underbrace{\langle m|\hat{A}|n\rangle}_{\hat{A}}$$

$$= \sum_n \langle n| \left[\sum_i w_i |\alpha_i\rangle \langle \alpha_i| \right] \hat{A} |n\rangle$$

defining $\hat{\rho} = \sum_i w_i |\alpha_i\rangle \langle \alpha_i|$ we

get $\langle \hat{A} \rangle = \sum_n \langle n| \hat{\rho} \hat{A} |n\rangle$

$$\Rightarrow \boxed{\langle \hat{A} \rangle = \text{Trace}(\hat{\rho} \hat{A})}$$

The operator $\hat{\rho}$ is defined as the density operator / density Matrix.

The density operator contains every possible information of the ensemble. Also since the trace is independent of basis. $\langle \hat{A} \rangle = \text{Trace}(\hat{\rho} \hat{A})$ can be evaluated in any convenient basis.

Note: $\text{Trace}(\hat{\rho}) = 1$

proof $\hat{\rho} = \sum_i w_i |\alpha_i\rangle \langle \alpha_i|$

$$\text{trace}(\hat{\rho}) = \sum_n \langle n | \hat{\rho} | n \rangle$$

$$= \sum_i \sum_n w_i \langle n | \alpha_i \rangle \langle \alpha_i | n \rangle$$

$$= \sum_i w_i \sum_n \underbrace{|\langle n | \alpha_i \rangle|^2}_1 \quad \left(\text{as } |\alpha_i\rangle \text{ is normalized} \right)$$

$$\Rightarrow \underline{\text{trace}(\hat{\rho}) = \sum_i w_i = 1}$$

Density operator in continuum basis

The elements of density matrix in position space is given by

$$\begin{aligned}\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle &= \langle \vec{r}' | \left[\sum_i w_i |\alpha_i\rangle \langle \alpha_i| \right] | \vec{r} \rangle \\ &= \sum_i w_i \underbrace{\langle \vec{r}' | \alpha_i \rangle}_{\psi_{\alpha_i}^*(\vec{r}')} \underbrace{\langle \alpha_i | \vec{r} \rangle}_{\psi_{\alpha_i}(\vec{r})}\end{aligned}$$

$$\Rightarrow \boxed{\langle \vec{r}' | \hat{\rho} | \vec{r} \rangle = \sum_i w_i \psi_{\alpha_i}^*(\vec{r}') \psi_{\alpha_i}(\vec{r})}$$

The diagonal elements of density operator in position basis are

$$\langle \vec{r} | \hat{\rho} | \vec{r} \rangle = \sum_i w_i |\psi_{\alpha_i}(\vec{r})|^2$$

Thus the diagonal terms are the weighted sum of probability densities.

Relation between density matrix & Statistical Mechanics

For states in thermal equilibrium with the surrounding at temperature 'T' we can write the density matrix in two equivalent ways. One being the usual definition as stated previously, which is a general definition.

But for systems in thermal equilibrium we get the ensemble average of energy to be,

$$\langle \hat{H} \rangle = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \quad \left(\beta = \frac{1}{k_B T} \right)$$

where E_n are the eigen values of the hamiltonian ($\hat{H}$) operator.

$$\Rightarrow E_n = \langle n | \hat{H} | n \rangle$$

$$\& E_n e^{-\beta E_n} = \langle n | \hat{H} e^{-\beta \hat{H}} | n \rangle \quad \left(|n\rangle \Rightarrow \text{eigen kets of } \hat{H} \right)$$

$$\Rightarrow \langle \hat{H} \rangle = \frac{\text{Trace}(\hat{H} e^{-\beta \hat{H}})}{\text{Trace}(e^{-\beta \hat{H}})}$$

Since $Z = \text{Trace}(e^{-\beta \hat{H}})$

$$\Rightarrow \langle \hat{H} \rangle = \text{Trace} \left[\frac{e^{-\beta \hat{H}}}{Z} \hat{H} \right]$$

But in terms of density matrix

$$\underline{\langle \hat{H} \rangle = \text{Trace}(\hat{\rho} \hat{H})}$$

Similarly the ensemble average of any observable is given in two ways

$$\langle \hat{A} \rangle = \text{Trace} \left(\frac{e^{-\beta \hat{H}}}{Z} \hat{A} \right) \Rightarrow \text{In stat. mech.}$$

$$\& \langle \hat{A} \rangle = \text{Trace}(\hat{\rho} \hat{A}) \Rightarrow \text{According to density matrix.}$$

Thus for an ensemble in thermal eq. br.

$$\boxed{\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Trace}[e^{-\beta \hat{H}}]} = \frac{e^{-\beta \hat{H}}}{Z}}$$

Entropy in terms of Density Matrix

In terms of free energy entropy is defined as,

$$\begin{aligned} S &= \frac{E - F}{T} = k_B \beta \langle \hat{H} \rangle + k_B \ln(Z) \\ &= k_B [\beta \text{Trace}(\rho \hat{H}) + \ln(Z)] \\ &= k_B \left[\frac{\beta \text{Trace}(e^{-\beta \hat{H}} \hat{H})}{Z} + \ln(Z) \right] \\ &= k_B \left[\frac{\beta \text{Trace}(e^{-\beta \hat{H}} \hat{H}) + \text{Trace}(e^{-\beta \hat{H}}) \ln(Z)}{Z} \right] \\ &= k_B \text{Trace} \left[\frac{\beta \hat{H} e^{-\beta \hat{H}} + e^{-\beta \hat{H}} \ln(Z)}{Z} \right] \\ &= k_B \text{Trace} \left[\frac{e^{-\beta \hat{H}}}{Z} (\beta \hat{H} + \ln(Z)) \right] \\ &= k_B \text{Trace} \left[\frac{e^{-\beta \hat{H}}}{Z} [-\ln(e^{-\beta \hat{H}}) + \ln(Z)] \right] \end{aligned}$$

$$\Rightarrow S = -k_B \text{Trace} \left[\frac{e^{-\beta \hat{H}}}{Z} \ln \left(\frac{e^{-\beta \hat{H}}}{Z} \right) \right]$$

$$= -k_B \text{Trace} [\hat{\rho} \ln(\hat{\rho})]$$

$$\Rightarrow \boxed{S = -k_B \text{Trace} [\hat{\rho} \ln(\hat{\rho})]}$$

$$S = \text{Trace} \{ \hat{\rho} [-k_B \ln(\hat{\rho})] \}$$

$$\hat{S} = -k_B \ln(\hat{\rho}) \quad \longrightarrow \quad \left(\text{Can be thought as entropy operator that measures disorderness} \right)$$

Free energy in terms of density matrix

$$F = E - TS = \langle \hat{H} \rangle - TS$$

$$\boxed{F = \text{Trace} (\hat{\rho} \hat{H}) + \frac{1}{\beta} \text{Trace} [\hat{\rho} \ln(\hat{\rho})]}$$

$$\Rightarrow F = \text{Trace} \left[\hat{\rho} \left(\hat{H} + \frac{\ln(\hat{\rho})}{\beta} \right) \right]$$

$$\boxed{\hat{F} = \hat{H} + \frac{\ln(\hat{\rho})}{\beta}}$$

$\hat{F}$ (Can be thought as free energy operator)

Density matrix for Spin System

A Spin state can be represented as a 2-spinor as $|\alpha\rangle = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$

in the basis of either $\hat{S}_x$ or $\hat{S}_y$ or $\hat{S}_z$. Conventionally we choose to work in $\hat{S}_z$ basis.

Let $|S_z, +\rangle \equiv |1\rangle$ & $|S_z, -\rangle \equiv |-1\rangle$ be the basis. Then any general state can be written as

$$|\alpha\rangle = c_1 |1\rangle + c_2 |-1\rangle$$

where $|c_1|^2 + |c_2|^2 = 1$.

$$\Rightarrow |\alpha\rangle\langle\alpha| = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \begin{bmatrix} c_1^* & c_2^* \end{bmatrix}$$

$$|\alpha\rangle\langle\alpha| = \begin{bmatrix} |c_1|^2 & c_1 c_2^* \\ c_1^* c_2 & |c_2|^2 \end{bmatrix} \Rightarrow \text{This is the density matrix for a single spin.}$$

$$\hat{\rho}_{(\text{single spin})} = \begin{bmatrix} |c_1|^2 & c_1 c_2^* \\ c_1^* c_2 & |c_2|^2 \end{bmatrix}$$

Any 2×2 hermitian matrix is expandable in $\{\hat{I}, \hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z\}$ basis where

$$\begin{bmatrix} a & b^* \\ b & c \end{bmatrix} = \frac{(a+c)}{2} \hat{I} + \frac{(b+b^*)}{2} \hat{\sigma}_x + \frac{(b-b^*)}{2i} \hat{\sigma}_y + \left(\frac{a-c}{2}\right) \hat{\sigma}_z$$

($a, c \Rightarrow \text{real}$)

$$\Rightarrow \hat{\rho} = \left(\frac{|c_1|^2 + |c_2|^2}{2}\right) \hat{I} + \frac{(c_1^* c_2 + c_1 c_2^*)}{2} \hat{\sigma}_x + \frac{(c_1^* c_2 - c_1 c_2^*)}{2i} \hat{\sigma}_y + \frac{(|c_1|^2 - |c_2|^2)}{2} \hat{\sigma}_z$$

$$\Rightarrow \hat{\rho} = \frac{\hat{I}}{2} + \text{Re}(c_1^* c_2) \hat{\sigma}_x + \text{Im}(c_1^* c_2) \hat{\sigma}_y + \left[\frac{|c_1|^2 - |c_2|^2}{2}\right] \hat{\sigma}_z$$

Now we can also find average magnetization using density matrix as

$$\begin{aligned} \langle m^z \rangle &= \langle \hat{\sigma}_z \rangle = \text{trace}(\hat{\rho} \hat{\sigma}_z) \\ \text{(average } z \text{ magnetization)} &= \text{trace} \left[\frac{(|c_1|^2 - |c_2|^2) \hat{I}}{2} \right] \\ &\quad \text{(other terms cancel out)} \end{aligned}$$

$$\langle m^z \rangle = |c_1|^2 - |c_2|^2$$

$$\& \langle m^x \rangle = \langle \hat{\sigma}_x \rangle = \text{trace}(\hat{\rho} \hat{\sigma}_x)$$

$$\Rightarrow \langle m^x \rangle = 2 \text{Re}(c_1^* c_2)$$

$$\& \langle m^y \rangle = \langle \hat{\sigma}_y \rangle = \text{trace}(\hat{\rho} \hat{\sigma}_y) = 2 \text{Im}(c_1^* c_2)$$

Thus for a general spin state we get

$$\hat{\rho} = \frac{\hat{I} + \langle m^x \rangle \hat{\sigma}_x + \langle m^y \rangle \hat{\sigma}_y + \langle m^z \rangle \hat{\sigma}_z}{2}$$

For a Spin oriented along $\hat{z}$
i.e. if it is some eigen state
of $\hat{S}_z$ then $|\alpha\rangle = \pm |\pm 1\rangle$

$$\& \langle m_x \rangle = \langle m_y \rangle = 0$$

$$\Rightarrow \hat{\rho} = \frac{\hat{I} + \langle m_z \rangle \hat{\sigma}_z}{2}$$

$$\text{Let } \langle m_z \rangle = m \Rightarrow \hat{\rho} = \frac{\hat{I} + m \hat{\sigma}_z}{2}$$

$$\Rightarrow \hat{\rho} = \begin{bmatrix} \frac{1+m}{2} & 0 \\ 0 & \frac{1-m}{2} \end{bmatrix}$$

$\hookrightarrow$ For a Spin which
is oriented along z -axis. &
when the basis is along $\hat{\sigma}_z$.

Density Matrix for Ising Model

The Hamiltonian operator for Ising model is given as,

$$\hat{H} = -\frac{1}{2} \sum_{ij} J_{ij} \hat{\sigma}_i^z \hat{\sigma}_j^z - h \sum_i \hat{\sigma}_i^z$$

Note: Before we used to work with $H = -\frac{1}{2} \sum_{ij} J_{ij} S_i S_j - h \sum_i S_i$ where ' S_i ' are possible eigen values of $\hat{\sigma}_i^z$ ($S_i = \pm 1, -1$).

The Hilbert Space for the total Hamiltonian is now the tensor product of the Spin Space of each individual Spins at each lattice points.

$$\Rightarrow H = H_1 \otimes H_2 \otimes H_3 \dots \otimes H_i \dots \otimes H_n$$

Where H_i is the Spin Space of spin at i^{th} site. The Spin state of i^{th} spin is $|S_i\rangle = \{|1\rangle \text{ or } |-1\rangle\}$

Then the state of the entire system is given by $|S_1, S_2, S_3, \dots, S_i, \dots, S_n\rangle$ which lives in the bigger Hilbert space 'H'.

For such a complicated H which has inter spin interactions it is not possible to write the general state $|S_1, S_2, S_3, \dots, S_i, \dots, S_n\rangle$ as the product of individual spin states $|S_i\rangle$ due to inter spin interactions. Thus the density matrix is just,

$$\hat{\rho}_{\text{Ising}} = \frac{\sum_{\{S_i\}} e^{-\beta H(\{S_i\})} |S_1, S_2, \dots, S_i, \dots, S_n\rangle \langle S_1, S_2, \dots, S_i, \dots, S_n|}{\sum_{\{S_i\}} e^{-\beta H(\{S_i\})}}$$

$H(\{S_i\})$ = Energy in the Configuration $\{S_i\}$

$$\text{Here } \frac{e^{-\beta H(\{S_i\})}}{\sum_{\{S_i\}} e^{-\beta H(\{S_i\})}} = W_{\{S_i\}} \Rightarrow \text{Probability of System being in the Configuration } \{S_i\}$$

Density Matrix for Mean field theory of Ising Model

$$\hat{H}_{\text{Ising}} = -\frac{1}{2} \sum_{ij} J_{ij} \hat{\sigma}_i^z \hat{\sigma}_j^z - h \sum_i \hat{\sigma}_i^z$$

But under Mean field approximation we remove the interaction term by replacing,

$$\hat{\sigma}_i^z \hat{\sigma}_j^z \rightarrow \hat{\sigma}_i^z \langle \hat{\sigma}_j^z \rangle + \langle \hat{\sigma}_i^z \rangle \hat{\sigma}_j^z - \langle \hat{\sigma}_i^z \rangle \langle \hat{\sigma}_j^z \rangle$$

This gives the mean field Hamiltonian as,

$$\underline{\hat{H}_0 = -H \sum_{i=1}^N S_i}$$

$$H = Jm + h$$

$$J_i = \sum_j J_{ij} = J$$

Due to the absence of interaction between the spins, the state of entire system under mean field approx. can be decomposed as tensor product.

$$\Rightarrow |S_1, S_2, \dots, S_i, \dots, S_N\rangle_0 = |S_1\rangle_0 \otimes |S_2\rangle_0 \dots \otimes |S_i\rangle_0 \dots \otimes |S_N\rangle_0$$

eigen state of $\hat{H}_0$

Then the mean field density matrix for the entire system is given by,

$$\hat{\rho}_0 = \frac{\sum_{\{S_i\}} e^{-\beta \mathcal{H}_0(\{S_i\})} |S_1, S_2, \dots, S_i, \dots, S_N\rangle \langle S_1, S_2, \dots, S_i, \dots, S_N|_0}{\sum_{\{S_i\}} e^{-\beta \mathcal{H}_0(\{S_i\})}}$$

Here $\frac{e^{-\beta \mathcal{H}_0(\{S_i\})}}{\sum_{\{S_i\}} e^{-\beta \mathcal{H}_0(\{S_i\})}} = W_0(\{S_i\}) \Rightarrow$ Probability factor given by trial Hamiltonian

Since $\mathcal{H}_0 = -H \sum_i S_i$

$$e^{-\beta \mathcal{H}_0(\{S_i\})} = e^{\beta H \sum_i S_i} = e^{\beta H S_1} e^{\beta H S_2} \dots e^{\beta H S_N}$$

$$\Rightarrow \sum_{\{S_i\}} e^{-\beta \mathcal{H}_0(\{S_i\})} = \sum_{S_1} e^{\beta H S_1} \sum_{S_2} e^{\beta H S_2} \dots \sum_{S_N} e^{\beta H S_N}$$

Substituting these in $\hat{\rho}_0$ defⁿ we get,

$$\hat{\rho}_0 = \frac{\sum_{\{S_i\}} e^{\beta H S_1} e^{\beta H S_2} \dots e^{\beta H S_N} |S_1, S_2, \dots, S_N\rangle_0 \langle S_1, S_2, \dots, S_N|_0}{\sum_{S_1} e^{\beta H S_1} \sum_{S_2} e^{\beta H S_2} \dots \sum_{S_N} e^{\beta H S_N}}$$

Using,

$$|S_1, S_2, \dots, S_N\rangle_0 \langle S_1, S_2, \dots, S_N|_0 = (|S_1\rangle_0 \otimes |S_2\rangle_0 \dots \otimes |S_N\rangle_0) (\langle S_1|_0 \otimes \langle S_2|_0 \dots \otimes \langle S_N|_0)$$

$$\hat{\rho}_0 = \left[\frac{\sum_{S_1} e^{\beta H S_1} |S_1\rangle \langle S_1|}{\sum_{S_1} e^{\beta H S_1}} \right] \otimes \left[\frac{\sum_{S_2} e^{\beta H S_2} |S_2\rangle \langle S_2|}{\sum_{S_2} e^{\beta H S_2}} \right] \otimes \dots \otimes \left[\frac{\sum_{S_N} e^{\beta H S_N} |S_N\rangle \langle S_N|}{\sum_{S_N} e^{\beta H S_N}} \right]$$

For spin ' S_i ' its own density

matrix is

$$\rho_{0_i} = \frac{\sum_{S_i} e^{\beta H S_i} |S_i\rangle \langle S_i|}{\sum_{S_i} e^{\beta H S_i}}$$

$$\frac{e^{\beta H S_i}}{\sum_i e^{\beta H S_i}} \Rightarrow \text{Prob. of } i^{\text{th}} \text{ site to have spin to be } S_i.$$

$$\Rightarrow \hat{\rho}_0 = \hat{\rho}_{o_1} \otimes \hat{\rho}_{o_2} \otimes \dots \otimes \hat{\rho}_{o_N}$$

$$\Rightarrow \hat{\rho}_0 = \prod_{i=1}^N \hat{\rho}_{o_i}$$

$\searrow$ tensor product

Since each Spin is oriented along z -axis (either up or down) then as seen before the density matrix for a particular Spin site is,

$$\hat{\rho}_{o_i} = \begin{bmatrix} \frac{1+m_i}{2} & 0 \\ 0 & \frac{1-m_i}{2} \end{bmatrix} \quad \underline{m_i = \langle \sigma_i^z \rangle}$$

Variational Principle in Statistical mechanics using density matrix

We previously saw the variational principle in terms of the eigen states of the trial Hamiltonian.

But now we can create a trial density matrix $\hat{\rho}_0$ of the system & then easily find the function $\Phi = F_0 + \langle \hat{H} - \hat{H}_0 \rangle_0$

$$F_0 = -k_B T \ln(Z_0) \text{ where } Z_0 = \text{Trace}(e^{-\beta \hat{H}_0})$$

But in terms of density matrix,

$$F_0 = \langle \hat{H}_0 \rangle - TS_0 \text{ where,}$$

$$\langle \hat{H}_0 \rangle = \text{Trace}(\hat{\rho}_0 \hat{H}_0), S_0 = -k_B \text{Trace}[\hat{\rho}_0 \ln(\hat{\rho}_0)]$$

$$\Rightarrow F_0 = \text{Trace}(\hat{\rho}_0 \hat{H}_0) + \frac{1}{\beta} \text{Trace}(\hat{\rho}_0 \ln(\hat{\rho}_0))$$

$$\& \quad \langle \hat{H} - \hat{H}_0 \rangle_0 = \text{Trace}[\hat{\rho}_0 (\hat{H} - \hat{H}_0)]$$

$$\Rightarrow \Phi = F_0 + \langle \hat{H} - \hat{H}_0 \rangle$$

$$= \text{Trace}(\cancel{\hat{P}_0} \hat{H}_0) + \frac{1}{\beta} \text{Trace}[\hat{P}_0 \ln(\hat{P}_0)] \\ + \text{Trace}(\hat{P}_0 \hat{H} - \cancel{\hat{P}_0} \hat{H}_0)$$

$$\Rightarrow \boxed{\Phi = \text{Trace}(\hat{P}_0 \hat{H}) + \frac{1}{\beta} \text{Trace}[\hat{P}_0 \ln(\hat{P}_0)]}$$

$\Phi \Rightarrow$ Approx. Free energy of actual Hamiltonian taken with respect to the trial density matrix ($\hat{P}_0$) that corresponds to the trial Hamiltonian ($\hat{H}_0$).

It is this free energy Φ which has to be extremized to get the upper bound of the true free energy of actual Hamiltonian $\hat{H}$.

Onstein Zernike Theory for Ising Model Mean field Theory

Here we aim to find the correlation function b/w two spin sites of the Ising model in terms of the response function.

We define χ_{ij} as the susceptibility at j^{th} site due to the small magnetic field present at the i^{th} site.

$$\Rightarrow \chi_{ij} = \frac{\partial m_j}{\partial h_i} \quad \left(\text{local response function} \right)$$

The Hamiltonian operator for Ising model is given as,

$$\hat{H} = -\frac{1}{2} \sum_{ij} J_{ij} \hat{\sigma}_i^z \hat{\sigma}_j^z \quad \left(\begin{array}{l} \text{external} \\ h=0 \end{array} \right)$$

For this hamiltonian we can show,

$$\chi_{ij} = \beta \left[\langle \hat{\sigma}_i^z \hat{\sigma}_j^z \rangle - \langle \hat{\sigma}_i^z \rangle \langle \hat{\sigma}_j^z \rangle \right]$$

Thus knowing X_{ij} we can find the correlation function b/w spins at $i^{\text{th}} \neq j^{\text{th}}$ site.

Let us add magnetic field ' h_i ' at i^{th} lattice site, then,

$$\hat{H} = - \sum_{i,j} J_{ij} \hat{\sigma}_i^z \hat{\sigma}_j^z - \sum_i h_i \hat{\sigma}_i^z$$

Because of this small perturbation we can assume that the average magnetization at j^{th} site changes by a small amount δm_j .

$$\text{i.e. } m_j = m + \delta m_j$$

where ' m ' was average magnetization before perturbation. It was same for all sites before perturbation due to the lattice translational symmetry. But the presence of ' h_i ' at site ' i ', breaks the lattice translational symmetry, due to non-zero ' δm_j '.

Now we wish to calculate the free energy (Φ) of the perturbed Ising hamiltonian with respect to the eigen states of trial mean field $\hat{H}_0$.

$$\Rightarrow \Phi = \underbrace{\text{Trace}(\hat{P}_0 \hat{H})}_{\text{Avg. energy term}} + \frac{1}{\beta} \underbrace{\text{Trace}[\hat{P}_0 \ln(\hat{P}_0)]}_{\text{entropy term}}$$

$\hat{P}_0$ is the mean field density matrix.

$$\begin{aligned} \text{Trace}(\hat{P}_0 \hat{H}) &= \text{Trace}\left(\hat{P}_0 \left[-\sum_{i,j} J_{ij} \frac{\hat{\sigma}_i^z \hat{\sigma}_j^z}{2} - \sum_i h_i \hat{\sigma}_i^z \right]\right) \\ &= -\text{Trace}\left[\sum_{i,j} \frac{1}{2} J_{ij} (\hat{P}_0 \hat{\sigma}_i^z \hat{\sigma}_j^z)\right] - \text{Trace}\left[\sum_i h_i \hat{P}_0 \hat{\sigma}_i^z\right] \end{aligned}$$

$$\Rightarrow \underbrace{\langle H \rangle_0 = -\sum_{i,j} \frac{1}{2} J_{ij} \text{Trace}(\hat{P}_0 \hat{\sigma}_i^z \hat{\sigma}_j^z) - \sum_i h_i \text{Trace}(\hat{P}_0 \hat{\sigma}_i^z)}$$

Here the multiplication of $\hat{P}_0$ on the pauli matrices $\hat{\sigma}_i^z \hat{\sigma}_j^z$ should be thought as

$$\hat{P}_0 \hat{\sigma}_i^z \hat{\sigma}_j^z = \hat{P}_{0_1} \otimes \hat{P}_{0_2} \otimes \dots \otimes \hat{P}_{0_i} \hat{\sigma}_i^z \dots \hat{P}_{0_j} \hat{\sigma}_j^z \dots \otimes \hat{P}_{0_N}$$

$$\Rightarrow \text{Trace}(\hat{P}_0 \hat{\sigma}_i^z) = \sum_{\{S_i\}} \langle S_1, S_2, \dots, S_N | \hat{P}_0 \hat{\sigma}_i^z | S_1, S_2, \dots, S_N \rangle$$

$$(\text{since } |S_1, S_2, \dots, S_N\rangle_0 = |S_1\rangle_0 \otimes |S_2\rangle_0 \dots |S_N\rangle_0)$$

$$= \sum_{\{S_i\}} \langle S_1 |_0 \otimes \langle S_2 |_0 \dots \langle S_N |_0 (\hat{P}_{0_1} \hat{P}_{0_2} \dots (\hat{P}_{0_i} \hat{\sigma}_i^z) \dots \hat{P}_{0_N})$$

$$\times |S_1\rangle_0 \otimes |S_2\rangle_0 \dots \otimes |S_N\rangle_0$$

$$= \sum_{S_1} \langle S_1 |_0 \hat{P}_{0_1} |S_1\rangle_0 \sum_{S_2} \langle S_2 |_0 \hat{P}_{0_2} |S_2\rangle_0 \times \dots$$

$$\times \dots \sum_{S_i} \langle S_i |_0 \hat{P}_{0_i} \hat{\sigma}_i^z |S_i\rangle_0 \times \dots$$

$$\dots \times \dots \sum_N \langle S_N |_0 \hat{P}_{0_N} |S_N\rangle_0$$

$$= \text{tr}_1(\hat{P}_{0_1}) \text{tr}_2(\hat{P}_{0_2}) \times \dots \text{tr}_i(\hat{P}_{0_i} \sigma_i^z) \times \dots \text{tr}_N(\hat{P}_{0_N})$$

$$= 1 \times 1 \times \dots \times m_i \times \dots \times 1 = m_i$$

$$\Rightarrow \underline{\text{Trace}(\hat{P}_0 \hat{\sigma}_i^z) = m_i}$$

$$\text{Similarly } \underline{\text{Trace}(\hat{P}_0 \hat{\sigma}_i^z \hat{\sigma}_j^z) = m_i m_j}$$

Note: Here 'Trace' is trace w.r.t complete state $|S_1, S_2, \dots, S_N\rangle_0$. &
' tr_i ' is trace w.r.t the state $|S_i\rangle_0$

$$\Rightarrow \langle \mathcal{H}_0 \rangle = \left[\frac{-1}{2} \sum_{i,j} J_{ij} m_i m_j \right] - \sum_i h_i m_i$$

Then the entropy term $\text{Trace}[\hat{\rho}_0 \ln(\hat{\rho}_0)]$ should be calculated.

$$\hat{\rho}_0 = \hat{\rho}_{o_1} \otimes \hat{\rho}_{o_2} \otimes \dots \otimes \hat{\rho}_{o_N}$$

$$\ln(\hat{\rho}_0) = \ln[\hat{\rho}_{o_1} \otimes \hat{\rho}_{o_2} \otimes \dots \otimes \hat{\rho}_{o_N}]$$

$$= \ln(\hat{\rho}_{o_1}) \otimes \hat{I} \otimes \hat{I} \dots \otimes \hat{I} \\ + \hat{I} \otimes \ln(\hat{\rho}_{o_2}) \otimes \hat{I} \otimes \dots \otimes \hat{I} \\ \dots + \hat{I} \otimes \hat{I} \otimes \dots \otimes \ln(\hat{\rho}_{o_N})$$

$$\Rightarrow \hat{\rho}_0 \ln(\hat{\rho}_0) = [\hat{\rho}_{o_1} \otimes \hat{\rho}_{o_2} \otimes \dots \otimes \hat{\rho}_{o_N}] \times \\ \left[\begin{aligned} &\ln(\hat{\rho}_{o_1}) \otimes \hat{I} \otimes \hat{I} \dots \otimes \hat{I} \\ &+ \hat{I} \otimes \ln(\hat{\rho}_{o_2}) \otimes \hat{I} \otimes \dots \otimes \hat{I} \\ &\dots + \hat{I} \otimes \hat{I} \otimes \dots \otimes \ln(\hat{\rho}_{o_N}) \end{aligned} \right]$$

$$= [\hat{\rho}_{o_1} \ln(\hat{\rho}_{o_1}) \otimes \hat{\rho}_{o_2} \otimes \dots \otimes \hat{\rho}_{o_N}] + [\hat{\rho}_{o_1} \ln(\hat{\rho}_{o_1}) \otimes \hat{\rho}_{o_2} \dots \otimes \hat{\rho}_{o_N}] + \\ \dots + [\hat{\rho}_{o_1} \otimes \hat{\rho}_{o_2} \otimes \dots \otimes \hat{\rho}_{o_N} \ln(\hat{\rho}_{o_N})]$$

$$\begin{aligned}
 \text{Trace} [\hat{\rho}_0 \ln(\hat{\rho}_0)] &= \text{tr}_1 [\hat{\rho}_{01} \ln(\hat{\rho}_{01})] \text{tr}_2(\hat{\rho}_{02}) \dots \text{tr}_n(\hat{\rho}_{0n}) \\
 &\quad + \text{tr}_1(\hat{\rho}_{01}) \text{tr}_2 [\hat{\rho}_{02} \ln(\hat{\rho}_{02})] \dots \text{tr}_n(\hat{\rho}_{0n}) \\
 &\quad + \dots + \text{tr}_1(\hat{\rho}_{01}) \text{tr}_2(\hat{\rho}_{02}) \dots \text{tr}_n [\hat{\rho}_{0n} \ln(\hat{\rho}_{0n})] \\
 &= \text{tr}_1 [\hat{\rho}_{01} \ln(\hat{\rho}_{01})] + \text{tr}_2 [\hat{\rho}_{02} \ln(\hat{\rho}_{02})] + \dots \\
 &\quad \dots + \text{tr}_n [\hat{\rho}_{0n} \ln(\hat{\rho}_{0n})]
 \end{aligned}$$

Trace of a matrix is sum of its eigen values which is independent of the basis. Thus we can calculate the trace of $\hat{\rho}_{0j} \ln(\hat{\rho}_{0j})$ by finding its eigen values.

$$\hat{\rho}_{0j} = \begin{bmatrix} \frac{(1+m_j)}{2} & 0 \\ 0 & \frac{(1-m_j)}{2} \end{bmatrix} \quad \left(\begin{array}{l} \text{as found} \\ \text{before} \end{array} \right)$$

$$\Rightarrow \hat{\rho}_{0j} \ln(\hat{\rho}_{0j}) = \begin{bmatrix} \left(\frac{1+m_j}{2} \right) \ln \left(\frac{1+m_j}{2} \right) & 0 \\ 0 & \left(\frac{1-m_j}{2} \right) \ln \left(\frac{1-m_j}{2} \right) \end{bmatrix}$$

$\Rightarrow \text{trace} [\hat{P}_{0j} \ln(\hat{P}_{0j})]$ is given by

$$\left(\frac{1+m_j}{2}\right) \ln\left(\frac{1+m_j}{2}\right) + \left(\frac{1-m_j}{2}\right) \ln\left(\frac{1-m_j}{2}\right)$$

$$\begin{aligned} \Rightarrow \text{Trace} [\hat{P}_0 \ln(\hat{P}_0)] &= \sum_j \text{trace} [\hat{P}_{0j} \ln(\hat{P}_{0j})] \\ &= \sum_i \left[\left(\frac{1+m_i}{2}\right) \ln\left(\frac{1+m_i}{2}\right) + \left(\frac{1-m_i}{2}\right) \ln\left(\frac{1-m_i}{2}\right) \right] \end{aligned}$$

$$\Rightarrow \Phi = \text{Trace}(\hat{P}_0 \mathcal{H}) + \frac{1}{\beta} \text{Trace} [\hat{P}_0 \ln(\hat{P}_0)]$$

$$\Rightarrow \Phi = \left[-\frac{1}{2} \sum_{i,j} J_{ij} m_i m_j \right] - \sum_i h_i m_i + \frac{1}{\beta} \sum_j \left[\left(\frac{1+m_j}{2}\right) \ln\left(\frac{1+m_j}{2}\right) + \left(\frac{1-m_j}{2}\right) \ln\left(\frac{1-m_j}{2}\right) \right]$$

This free energy function has to be extremized w.r.t the variational parameters $\{m_j\}$ where $m_j = m + \delta m_j$.

$\Rightarrow$ We need those m_j where $\frac{\partial \Phi}{\partial m_j} = 0$

$$\frac{\partial \Phi}{\partial m_n} = \sum_{i,j} \left(\frac{-1}{2} \right) J_{ij} \left[(m_i \delta_{jn}) + (\delta_{in} m_j) \right] - \sum_i h_i \delta_{in} \\ + \frac{1}{\beta} \sum_j \left[\frac{\left(\frac{1+m_j}{2} \right) \left(\frac{\delta_{jn}}{2} \right) + \left(\frac{\delta_{jn}}{2} \right) \ln \left(\frac{1+m_j}{2} \right)}{\left(\frac{1+m_j}{2} \right)} \right. \\ \left. + \frac{\left(\frac{1-m_j}{2} \right) \left(-\frac{\delta_{jn}}{2} \right) + \left(-\frac{\delta_{jn}}{2} \right) \ln \left[\frac{1-m_j}{2} \right]}{\left(\frac{1-m_j}{2} \right)} \right]$$

$$= -\frac{1}{2} \left[\sum_{i,j} J_{ij} m_i \delta_{jn} + \sum_{i,j} J_{ij} m_j \delta_{in} \right] - \sum_i h_i \delta_{in} \\ + \frac{1}{\beta} \sum_j \frac{\delta_{jn}}{2} \left[\ln(1+m_j) - \ln(1-m_j) \right]$$

$$= -\frac{1}{2} \left[\sum_i J_{in} m_i + \sum_j J_{nj} m_j \right] - \sum_i h_i \delta_{in} \\ + \frac{1}{2\beta} \ln \left[\frac{1+m_j}{1-m_j} \right]$$

Since 'J' matrix is symmetric we get

$$\frac{\partial \Phi}{\partial m_n} = - \sum_j \left[J_{nj} m_j - h_j \delta_{jn} \right] + \frac{1}{2\beta} \ln \left[\frac{1+m_j}{1-m_j} \right]$$

But we need to extremize Φ w.r.t 'm'. Thus we need those m_n values for which $\frac{\partial \Phi}{\partial m_n} = 0$

$$\Rightarrow - \sum_j \left[J_{nj} m_j - h_j \delta_{jn} \right] + \frac{1}{2\beta} \ln \left[\frac{1+m_n}{1-m_n} \right] = 0$$

Thus we have 'N' coupled eqⁿ to solve for 'N' unknowns $\{m_1, m_2, \dots, m_N\}$.

We assume the effect of the magnetic field at i^{th} cell is to make the magnetization of every site to change by a small value compared to the unperturbed uniform magnetization. $\Rightarrow m_n = m + \delta m_n$

& δm_n is very small that $(\delta m_n)^2$ & higher order terms vanish.

$$\Rightarrow - \sum_j J_{nj} m - \sum_j J_{nj} \delta m_j - \sum_j h_j \delta_{jn} + \frac{1}{2\beta} \left[\ln(1+m+\delta m_n) - \ln(1-m-\delta m_n) \right] = 0$$

$$\text{Now, } \ln(1+m+\delta m_n) = \ln(1+m) + \frac{1}{(1+m)} \delta m_n$$

$$\& \ln(1-m-\delta m_n) = \ln(1-m) + \frac{1}{1-m} (-\delta m_n)$$

$$\begin{aligned} \Rightarrow \ln \left(\frac{1+m+\delta m_n}{1-m-\delta m_n} \right) &= \ln(1+m) - \ln(1-m) + \delta m_n \left[\frac{2}{1-m^2} \right] \\ &= \ln \left[\frac{1+m}{1-m} \right] + \left(\frac{2}{1-m^2} \right) \delta m_n \end{aligned}$$

$$\begin{aligned} \Rightarrow - \sum_j J_{nj} m - \sum_j J_{nj} (\delta m_j) - \sum_j h_j \delta_{jn} \\ + \frac{1}{2\beta} \ln \left[\frac{1+m}{1-m} \right] + \frac{1}{\beta} \left(\frac{1}{1-m^2} \right) \delta m_n = 0 \end{aligned}$$

Now if we add ' h_j ' to j^{th} site perturbatively, i.e. if

$$h_j = h + \delta h_j \quad (\forall j)$$

$$\begin{aligned} \Rightarrow - \sum_j J_{nj} m - \sum_j J_{nj} (\delta m_j) - \sum_j h \delta_{jn} \\ - \sum_j \delta h_j \delta_{jn} + \frac{1}{2\beta} \ln \left[\frac{1+m}{1-m} \right] + \frac{1}{\beta} \left(\frac{1}{1-m^2} \right) \delta m_n = 0 \end{aligned}$$

0th order in ' δm_n '

$$-\sum_j J_{nj} m + \frac{1}{2\beta} \ln\left(\frac{1+m}{1-m}\right) - \sum_j h \delta_{jn} = 0$$

$$\Rightarrow -m \sum_j J_{jn} + \frac{1}{2\beta} \ln\left(\frac{1+m}{1-m}\right) = h$$

$$\Rightarrow \frac{1}{2\beta} \ln\left(\frac{1+m}{1-m}\right) = m \underbrace{\sum_j J_{nj}}_{g_n = g \left\{ \begin{array}{l} \text{for 0th order} \\ \text{(uniform m)} \end{array} \right\}} + h$$

$$\Rightarrow \ln\left(\frac{1+m}{1-m}\right) = 2\beta [gm + h]$$

$$\text{Let } H = gm + h \Rightarrow (\text{Effective field})$$

$$\Rightarrow \frac{1-m}{1+m} = e^{2\beta H}$$

$$\Rightarrow 1-m = e^{2\beta H} + m e^{2\beta H}$$

$$\Rightarrow m(e^{2\beta H} + 1) = (e^{2\beta H} - 1)$$

$$\Rightarrow m = \frac{e^{2\beta H} - 1}{e^{2\beta H} + 1}$$

$$\Rightarrow m = \frac{e^{\beta H} - e^{-\beta H}}{e^{\beta H} + e^{-\beta H}}$$

$$\Rightarrow m = \tanh(\beta H)$$

$$(H = g m + h)$$

$$\Rightarrow \boxed{m = \tanh(\beta g m + \beta h)} \quad \left(\begin{array}{l} \text{Uniform} \\ \text{magnetization} \\ \text{in absence of} \\ \text{Perturbation} \end{array} \right)$$

Thus we could recover the usual mean field Magnetization in the 0th order term (if perturbation = 0)

1st order in δm_n & δh_j

$$-\sum_j J_{nj} \delta m_j + \frac{\delta m_n}{B(1-m^2)} - \sum_j \delta h_j \delta_{jn} = 0$$

$$\Rightarrow \sum_j \left[J_{nj} \delta m_j + \delta h_j \delta_{jn} \right] = \frac{\delta m_n}{B(1-m^2)}$$

going to fourier space by the discrete fourier transformation,

$$\mathcal{Z}_{\vec{m}_{\vec{q}}} = \sum_{\vec{r}_j} e^{i\vec{q} \cdot \vec{r}_j} \mathcal{Z}_{m_{\vec{r}_j}}$$

where $\vec{r}_j \Rightarrow$ position vector of j^{th} lattice site.

Then the inverse fourier transform is given by,

$$\mathcal{Z}_{m_{\vec{r}_n}} = \frac{1}{N} \sum_{\vec{q}} \mathcal{Z}_{\vec{m}_{\vec{q}}} e^{-i\vec{q} \cdot \vec{r}_n}$$

The kronekar delta is given by

$$\mathcal{Z}_{in} = \frac{1}{N} \sum_{\vec{q}} e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_n)}$$

$$J_{nj} = \frac{1}{N} \sum_{\vec{q}} e^{-i\vec{q} \cdot (\vec{r}_n - \vec{r}_j)} g(\vec{q})$$

$g(\vec{q}) \Rightarrow$ fourier transform of Interaction matrix

The below eqⁿ in fourier space is,

$$\sum_j \left[J_{nj} \delta m_j + \delta h_i \delta i_n \right] = \frac{\delta m_n}{B(1-m^2)}$$

$$\Rightarrow \sum_j \left(\frac{1}{N} \sum_{\vec{q}} e^{-i\vec{q} \cdot (\vec{r}_n - \vec{r}_j)} f(\vec{q}) \right) \frac{1}{N} \sum_{\vec{q}'} \delta \tilde{m}_{\vec{q}'} e^{-i\vec{q}' \cdot \vec{r}_j} \\ + \sum_j \frac{\delta h_j}{N} \sum_{\vec{q}} e^{i\vec{q} \cdot (\vec{r}_j - \vec{r}_n)} = \frac{1}{N} \sum_{\vec{q}} \delta \tilde{m}_{\vec{q}} \frac{e^{-i\vec{q} \cdot \vec{r}_n}}{B(1-m^2)}$$

$$\Rightarrow \sum_{\vec{q}, \vec{q}'} \frac{e^{-i\vec{q} \cdot \vec{r}_n}}{N} f(\vec{q}) \delta \tilde{m}_{\vec{q}'} \sum_j \frac{e^{i(\vec{q} - \vec{q}') \cdot \vec{r}_j}}{N} \\ + \sum_j \frac{\delta h_j}{N} \sum_{\vec{q}} e^{i\vec{q} \cdot (\vec{r}_j - \vec{r}_n)} = \frac{1}{N} \sum_{\vec{q}} \delta \tilde{m}_{\vec{q}} \frac{e^{-i\vec{q} \cdot \vec{r}_n}}{B(1-m^2)}$$

$$\left(\text{using } \frac{1}{N} \sum_j e^{i(\vec{q} - \vec{q}') \cdot \vec{r}_j} = \delta_{\vec{q}, \vec{q}'} \right)$$

$$\begin{aligned}
&\Rightarrow \frac{1}{N} \sum_{\vec{q}} g(\vec{q}) \delta \vec{m}_{\vec{q}} e^{-i\vec{q} \cdot \vec{r}_n} \\
&+ \frac{1}{N} \sum_{\vec{q}} \left[\sum_j \delta h_j e^{i\vec{q} \cdot \vec{r}_j} \right] e^{-i\vec{q} \cdot \vec{r}_n} \\
&= \frac{1}{N} \sum_{\vec{q}} \left[\frac{\delta \vec{m}_{\vec{q}}}{B(1-m^2)} \right] e^{-i\vec{q} \cdot \vec{r}_n}
\end{aligned}$$

Using $\tilde{\delta h}(\vec{q}) = \sum_j \delta h_j e^{i\vec{q} \cdot \vec{r}_j}$ &

Comparing the above eqⁿ we get

$$g(\vec{q}) \delta \vec{m}_{\vec{q}} + \tilde{\delta h}(\vec{q}) = \frac{\delta \vec{m}_{\vec{q}}}{B(1-m^2)}$$

$$\tilde{\delta h}(\vec{q}) = \left[\frac{1}{B(1-m^2)} - g(\vec{q}) \right] \delta \vec{m}_{\vec{q}}$$

$$\Rightarrow \tilde{\delta h}(\vec{q}) = \left[\frac{1 - g(\vec{q}) B(1-m^2)}{B(1-m^2)} \right] \delta \vec{m}_{\vec{q}}$$

$$\Rightarrow \frac{\partial \tilde{m}_{\vec{q}}}{\partial \tilde{h}(\vec{q})} = \frac{\beta(1-m^2)}{[1 - g(\vec{q}) \beta(1-m^2)]}$$

define $\Gamma(\vec{q}) = \frac{\partial \tilde{m}_{\vec{q}}}{\partial \tilde{h}(\vec{q})} \sim$ Susceptibility in fourier space

$$\Rightarrow \Gamma(\vec{q}) = \frac{\beta(1-m^2)}{1 - g(\vec{q}) \beta(1-m^2)}$$

$\Gamma(\vec{q})$ is fourier transform of the correlation function $G(\vec{r})$.

$$\Rightarrow \Gamma(\vec{q}) = \sum_{\vec{r}} e^{i\vec{q} \cdot \vec{r}} G(\vec{r})$$

since we know $\Gamma(\vec{q})$ we just need to find its inverse fourier transform to get $G(\vec{r})$.

$$\text{where } G(\vec{r}) = \frac{1}{N} \sum_{\vec{q}} e^{-i\vec{q} \cdot \vec{r}} \Gamma(\vec{q})$$
