N - non interacting spins in const. field $\vec{B} = B_0 \hat{z}$

$\uparrow \downarrow \uparrow \downarrow \downarrow \cdots$ N - spins

$\vec{B} \uparrow$

M_ν : Magnetization of microstate ν $= \sum_{i=1}^{N} \mu m_i$

$m_i \in [-s, -s+1, \ldots -2, -1, 0, 1, 2, \ldots s-1, s]$: $2s+1$ values

$\nu : \{m_i\}$

For eg. $\nu_1 = \{m_1 = 4,\ m_2 = 3, \ldots\ m_N = -2\}$

$\nu_2 = \{m_1 = 2,\ m_2 = -2, \ldots\ m_N = 0\}$

$\vdots$

Identify energy scale : $\mathcal{H}_\nu = -B M_\nu$ "Magnetic enthalpy"

$$\mathcal{H}_{\{m_i\}} = -B M_{\{m_i\}} = -B\mu \sum_{i=1}^{N} m_i$$

1. Partition function $Z(T, B, N)$
2. Gibbs free energy $G(B, T)$
3. Magnetic susceptibility $\chi = \left.\frac{\partial M}{\partial B}\right|_{B=0}$
4. Heat capacity at const B, M : C_B & C_M.

(a) Partition function

$$Z(N, B, T) = \sum_{\{m_i\}} e^{-\beta \mathcal{H}(\{m_i\})}$$

$$= \sum_{\{m_i\}} e^{\beta B \mu \sum_{i=1}^{N} m_i} = \sum_{\{m_i\}} e^{\beta B M_{\{m_i\}}}$$

//

$$\because \quad M_{\{m_i\}} = \sum_{i=1}^{N} \mu m_i$$

Average magnetization: $\langle M \rangle = M = \dfrac{\sum_{\{m_i\}} M_{\{m_i\}} e^{\beta B M_{\{m_i\}}}}{\underbrace{\sum_{\{m_i\}} e^{\beta B M_{\{m_i\}}}}_{Z(N,B,T)}}$

$$\langle M \rangle = \frac{1}{Z} \frac{\partial}{\partial(\beta B)} Z = \frac{\partial}{\partial(\beta B)} \ln Z \qquad \text{—— } 1$$

$$Z(N,B,T) = \sum_{\{m_i\}} e^{\beta B \mu \sum_{i=1}^{N} m_i}$$

$$= \prod_{i=1}^{N} \sum_{m_i=-s}^{+s} e^{\beta B \mu m_i}$$

Recall $m_i \in [-s, -s+1, \dots 0, \dots s-1, s]$ $2s+1$ values.

$$Z(N,B,T) = \left(\sum_{m=-s}^{+s} e^{\beta B \mu m} \right)^N = \left(\sum_{m=-s}^{+s} e^{gm} \right)^N$$

For convenience $\beta B \mu = g$ ...

$$Z(N,B,T) = \left(e^{gs} + e^{g(s-1)} + \dots e^{g} + 1 + e^{-g} + \dots e^{-g(s-1)} + e^{-gs} \right)^N$$

$$= \left[1 + (e^{g} + e^{-g}) + (e^{2g} + e^{-2g}) + \dots (e^{sg} + e^{-sg}) \right]^N$$

$$= \left[1 + 2\cosh g + 2\cosh 2g + \dots\dots 2\cosh sg \right]^N$$

$$Z(N,B,T) = 2^N\left[\frac{1}{2} + \sum_{i=1}^{S} \cosh gi\right]^N$$ .... For any B

$$= 2^N\left[\frac{1}{2} + \sum_{i=1}^{S} \frac{(e^{gi} + e^{-gi})}{2}\right]^N$$

$$= 2^N\left[\frac{1}{2} + \sum_{i=1}^{S} \frac{1}{2}\left(1 + gi + \frac{(gi)^2}{2!} + \dots \quad 1 - gi + \frac{(gi)^2}{2!} \dots\right)\right]^N$$

$$= 2^N\left[\frac{1}{2} + \sum_{i=1}^{S} \frac{1}{2}\left(2 + g^2 i^2 + \underbrace{O(g^4)}_{0}\right)\right]^N$$

$g = \mu B \beta$

for small B, dropping $O(g^4)$ and above!

$$= 2^N\left[\frac{1}{2} + S + \frac{g^2}{2}\sum_{i=1}^{S} i^2\right]^N$$

Substituting $\sum_{i=1}^{S} i^2 = \frac{S(S+1)(2S+1)}{6}$

$S = 3$

$1 + 4 + 9 = 14$

$\frac{3(4)7}{6} = 14$

$$Z(N,B,T) = 2^N\left[\frac{1}{2} + S + \frac{g^2}{12} S(S+1)(2S+1)\right]^N$$ .... B small

(b) Gibbs free energy: $G(B) = -k_B T \ln Z$

$$= -k_B T \ln\left[2^N\left[\frac{1}{2} + \sum_{i=1}^{S} \cosh gi\right]^N\right]$$

$$= -k_B T\left[N \ln 2 + N \ln\left[\frac{1}{2} + \sum_{i=1}^{S} \cosh gi\right]\right]$$ ... $\ln(A.B) = \ln A + \ln B$

.... Any B.

However for small B !

$$G = -k_B T \ln\left[2^N\left[\frac{1}{2} + s + \frac{g^2}{12} s(s+1)(2s+1)\right]^N\right]$$

$$= -k_B T N\left[\ln 2 + \ln\left(\frac{1}{2} + s + \frac{g^2 s(s+1)(2s+1)}{12}\right)\right]$$

$$= -k_B T N\left[\ln\left(2s+1 + \frac{g^2 s(s+1)(2s+1)}{6}\right)\right]$$

$$G(B) = -k_B T N\left[\ln(2s+1) + \ln\left(\frac{g^2 s(s+1)}{6} + 1\right)\right]$$

$$= G(0) - N k_B T \ln\left(1 + \frac{g^2 s(s+1)}{6}\right) \quad \text{———} \; \mathrm{I}$$

$$\ldots G(0) = -N k_B T \ln(2s+1) \ldots$$

For small x : $x \ll 1$

$$\boxed{\ln(1+x) \approx x}$$

$$\rightarrow 0 + x\left(\frac{1}{x}\right)_{x=1} + \frac{x^2}{2!}\cdot\left(\frac{-1}{x^2}\right)_{x=1} + \ldots$$

$$x - \cancel{\frac{x^2}{2}}_{0} + \ldots$$

Rewriting I with approximation that $g^2 s(s+1)/6 \ll 1$ $\qquad g^2 = (\mu B \beta)^2 \ll 1$

$$\boxed{G(B) = G(0) - \frac{N k_B T \cdot g^2 s(s+1)}{6}} + \cancel{O(\beta^4)}_{0}$$

$\rightarrow$ II

(c) M = Thermodynamic magnetization

$$= \frac{\partial}{\partial(\beta B)} \ln Z$$

$$= \frac{\partial}{\partial(\beta B)} (-\beta G) \qquad \text{..... Since } G = \frac{-1}{\beta} \ln Z$$

$$= -\frac{\partial G}{\partial B}$$

$$= \frac{-\partial}{\partial B}\left[- \frac{N k_B T \cdot g^2 s(s+1)}{6} \right] \qquad \text{..... for small } B.$$

$$M = \frac{N k_B T\, s(s+1)}{3} \cdot \mu^2 \beta^2 B \qquad g = \mu B \beta$$

$=$

(c) Magnetic susceptibility: $\chi = \left.\frac{\partial M}{\partial B}\right|_{B=0}$

$$= -\frac{\partial}{\partial B} \cdot \left.\frac{\partial G}{\partial B}\right|_{B=0} = \left.\frac{-\partial^2 G}{\partial B^2}\right|_{B=0}$$

$$= \frac{N k_B T\, s(s+1)}{3} \mu^2 \beta^2$$

(d) Heat capacity at const B & M:

$$C_B = \left.\frac{\partial}{\partial T}(-BM)\right|_B = \left. -B \frac{\partial M}{\partial T}\right|_B$$

$$= -B \frac{\partial}{\partial T}\left[\frac{N k_B T\, s(s+1)}{3} \cdot \mu^2 \beta^2 B \right]$$

$$= \frac{-B^2 \cdot N s(s+1)\mu^2}{3} \cdot \frac{\partial}{\partial T}\left(\frac{1}{k_B T}\right)$$

$$= \frac{B^2 \, N s(s+1)\mu^2}{3 k_B T^2} \longrightarrow \text{const.}$$

$$C_B = \text{Const.}(N) \cdot \frac{B^2}{T^2} \qquad \propto \; B^2/T^2$$

$$C_M = \frac{\partial(-BM)}{\partial T}\bigg|_M = -B \underbrace{\cancel{\frac{\partial M}{\partial T}}}_{\substack{0 \\ M \text{ const.}}} + M \underbrace{\cancel{\frac{\partial(-B)}{\partial T}}}_{\substack{0 \\ B \text{ const.}}} = 0$$

$$C_B - C_M = \text{Const}(N) \, \frac{B^2}{T^2}$$