Entropy Revisited

a) This is the combinatorics of choosing

$$\Omega = \frac{N!}{N_0!\,N_1!}$$

These cancel $N = \sum_s N_s$

b) $$\ln \Omega = N \ln N - \cancel{N} - \sum_{s=0}^{1} N_s \ln N_s - \cancel{N_s}$$

Now $N = N_0 + N_1 = \sum_s N_s$, so we have:

$$\ln \Omega = \sum_s N_s (\ln N - \ln N_s)$$

$$\ln \Omega = -\sum_s N_s \ln\left(\frac{N_s}{N}\right)$$

But $N_s/N = P_s$ or the probability to be in state s.
So we find

$$\ln \Omega = N\left(-\sum_s P_s \ln P_s\right)$$

c) For three states

$$\Omega = \frac{N!}{N_A!\,N_B!\,N_C!} \quad \text{with} \quad N = N_A + N_B + N_C$$

The rest is unchanged

$$\ln \Omega = N \sum_{s=A,B,C} -P_s \ln P_s$$

Entropy of Mixing From Gibbs Formula

a) This was derived in lecture

$$\Delta S_1 = \frac{1}{T} dE_1 + \frac{P}{T} dV_1$$

- But the temperature is unchanged, so $dE = 0$ (for an ideal gas!), and $P/T = \frac{Nk}{V}$

$$dS = Nk \frac{dV}{V}$$

So

(1) $$\Delta S_1 = \int N_1 k \frac{dV}{V} = N_1 \ln \frac{V}{xV} = -N_1 \ln x$$

(2) $$\Delta S_2 = N_2 \ln \frac{V}{(1-x)V} = -N_2 \ln (1-x)$$

Now $P_1/T_1 = P_2/T_2 = P/T$ ← final temperature and volume

So

$$\frac{N_1 k}{V_1} = \frac{N_1}{xV} = \frac{N_2 k}{(1-x)V} = \frac{Nk}{V}, \text{ implying}$$

i.e. $N_1 = Nx$ and $N_2 = N(1-x)$.

So

$$\boxed{\Delta S = N\left[-x\ln x - (1-x)\ln(1-x)\right]}$$

(b) We can use the gibbs formula.
Let's define P_L and P_R as the probability to be in the left and right halves of the container (see below)

Before the value is openned:

$$\left.\begin{array}{l} P_L^{(1)} = 1 \\ P_R^{(1)} = 0 \end{array}\right\} \text{Gas System 1} \qquad \left.\begin{array}{l} P_L^{(2)} = 0 \\ P_R^{(2)} = 1 \end{array}\right\} \text{Gas system 2}$$

After the value is oppened then the molecules of gas 1 are equally likely to be anywhere in the volume. Since the volume of the left side of the container is a fraction x of the full volume $P_L^{(1)} = x$.

$$\left.\begin{array}{l} P_L^{(1)} = x \\ P_R^{(1)} = (1-x) \end{array}\right\} \text{Gas system 1} \qquad \left.\begin{array}{l} P_L^{(2)} = x \\ P_R^{(2)} = (1-x) \end{array}\right\} \text{Gas System 2}$$

So

$$S_1^{\text{before}}/k = N_1 \sum_{L,R} -P_s^{(1)} \ln P_s^{(1)} = N_1\left[-1\ln 1 - 0\ln 0\right] = 0$$

entropy of system 1

entropy of system 1 after the value is openned

$$\frac{S_1^{after}}{k} = N_1 \left[-\sum_{L,R} p_s^{(1)} \ln p_s^{(1)} \right]$$

$$= N_1 \left[-x \ln x - (1-x) \ln (1-x) \right]$$

System 2, works similary

$$S_2^{before}/k = 0$$

$$\frac{S_2^{after}}{k} = N_2 \left[-x \ln x - (1-x) \ln (1-x) \right]$$

The total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$\boxed{\frac{\Delta S}{k} = (N_1 + N_2) \left[-x \ln x - (1-x) \ln (1-x) \right]}$$

Paramagnets

a) Then

$$Z = Z_1^N \qquad Z_1 = \sum_s e^{-\beta \varepsilon_s}$$

So

$$= e^{\beta \mu_B B} + e^{-\beta \mu_B B}$$

$$F = -k_B T \ln Z \qquad = 2\cosh(\beta \mu_B B)$$

$$= -kTN \ln Z_1$$

$$\boxed{F = -kTN \ln(2\cosh(\beta \mu_B B))}$$

So

$$S = -\left(\frac{\partial F}{\partial T}\right)_B = Nk \ln(2\cosh(\mu_B B \beta))$$

$$+ kTN \frac{2\sinh(\beta \mu_B B)}{2\cosh(\beta \mu_B B)} \left(\frac{-1}{kT^2} \mu_B B\right)$$

So

$$\boxed{S = Nk \left[\ln(2\cos(\mu_B B \beta)) - \tanh(\beta \mu_B B)\, \beta \mu_B B \right]}$$

Then $F = U - TS$ or $U = F + TS$ or

$$U = -NkT \cdot \tanh(\beta \mu_B B)\, \beta \mu_B B = \boxed{-N \mu_B B \tanh(\beta \mu_B B)}$$

So

$$C = \left(\frac{\partial U}{\partial T}\right)_B = -N\mu_B B \frac{\partial}{\partial T} \tanh(\beta\mu_B B)$$

$$\frac{d}{dx}\frac{\sinh x}{\cosh x} = \frac{\cosh x}{\cosh x} - \frac{\sinh^2 x}{\cosh^2 x} = 1 - \tanh^2 x = \operatorname{sech}^2 x$$

So

$$C = -N\mu_B B \operatorname{sech}^2(\beta\mu_B B)(-\beta^2 k_B \mu_B B)$$

$$\boxed{C = Nk_B (\beta\mu_B B)^2 \operatorname{sech}^2(\beta\mu_B B)}$$

$\boxed{b)}$ Then

$$n = \frac{N\downarrow}{N} = \frac{e^{\beta\mu_B B}}{Z_1} =$$ this is the probability of being spin $\downarrow$

$$n = \frac{e^{\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = \boxed{\frac{1}{1+e^{-\beta\Delta}} = n}$$

with $\Delta = 2\mu_B B$

$$\frac{1}{n} = 1 + e^{-\beta\Delta} \quad \text{and} \quad e^{-\beta\Delta} = 1 - \frac{1}{\bar{n}}$$

and so $\boxed{\beta\Delta = \ln((1-\bar{n})/\bar{n})}$

Then

$$M = \langle N_\uparrow - N_\downarrow \rangle \mu_B$$

$$= N\left(1 - 2\frac{N_\downarrow}{N}\right)\mu_B$$

$$= N\left(1 - 2\frac{1}{1+e^{-\beta\Delta}}\right)\mu_B$$

$$= N\left(\frac{1 - e^{-\beta\Delta}}{1+e^{-\beta\Delta}}\right)\mu_B$$

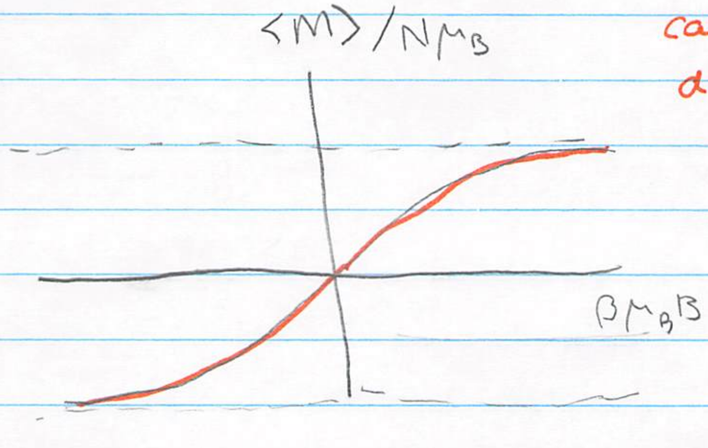
$$\boxed{M = N \tanh(\beta \mu_B B)\,\mu_B}$$

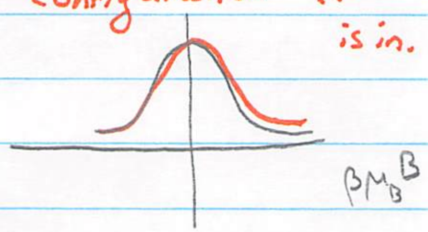
Finally

$$\chi = \frac{\partial \langle M \rangle}{\partial H} \simeq \frac{\partial \langle M \rangle}{\partial B} = N \operatorname{sech}^2(\beta \mu_B B)\,\mu_B^2\,\beta$$

$$\boxed{\chi = \frac{N\mu_B^2}{kT}\operatorname{sech}^2(\beta\mu_B B)}$$

this describes the fluctuations in $\langle M \rangle$. Qualitatively it is maxmal when $B=0$, and the system can't decide what configuration it is in.





e) The variance in the magnetization follows similarly. Let σ_1 be the spin of the first atom $+1$ if it's spin up, and -1 if it's spin down

$$\langle \sigma_1 \rangle = (+1) P_\uparrow + (-1) P_\downarrow$$

$$= \frac{e^{\beta \mu_B B}}{2 \cosh(\mu_B B \beta)} - \frac{e^{-\beta \mu_B B}}{2 \cosh(\mu_B B \beta)}$$

$$= \tanh(\mu_B B \beta)$$

- Now

$$\langle \sigma_1^2 \rangle = (+1)^2 P_\uparrow + (-1)^2 P_\downarrow = P_\uparrow + P_\downarrow = 1$$

So

$$\langle \delta \sigma_1^2 \rangle = \langle \sigma_1^2 \rangle - \langle \sigma_1 \rangle^2 = 1 - \tanh^2(\beta \mu_B B) = \operatorname{sech}^2(\beta \mu_B B)$$

- We could do the same calculation for any site. Now

$$N_\Delta \doteq N_\uparrow - N_\downarrow = \sigma_1 + \sigma_2 + \ldots + \sigma_N$$

- So, recalling that the variance of a sum of independent random variables is the sum of the variances:

$$\langle \delta N_\Delta^2 \rangle = \langle \delta \sigma_1^2 \rangle + \langle \delta \sigma_2^2 \rangle + \ldots \langle \delta \sigma_N^2 \rangle$$

we find;

$$\boxed{\langle \delta N_\Delta^2 \rangle = N \langle \delta \sigma_1^2 \rangle = N \operatorname{sech}^2(\beta \mu_B B)}$$

Paramagnets From The Microcanonical Ensemble

a) The ground state is all up.
If $N_\downarrow$ are flipped from up to down
the change in energy is

#flipped

$$\mathcal{E} = 2\mu_B B N_\downarrow = \Delta N_\downarrow$$

energy cost per flip

So

$$\boxed{\frac{\mathcal{E}}{N} = n\,\Delta} \qquad \text{where} \quad n = N_\downarrow / N$$

b) If we have $N_\downarrow$ down and $N_\uparrow$ up
then the # of configs with this energy is

$$\Omega = \frac{N!}{N_\downarrow!\,N_\uparrow!}$$

From problem, the Entropy Revisted Problem

$$\ln \Omega = -N_\downarrow \ln \frac{N_\downarrow}{N} - N_\uparrow \ln \frac{N_\uparrow}{N}$$

use $N_\downarrow / N = n$

$$\frac{S}{N k} = \frac{\ln \Omega}{N} = -n \ln n - (1-n)\ln(1-n) \qquad (\star)$$

from $\partial n / \partial \mathcal{E}$

c) $$\frac{1}{T} = \frac{\partial S}{\partial \mathcal{E}} = \frac{\partial S}{\partial n}\left(\frac{\partial n}{\partial \mathcal{E}}\right) = Nk\left(\frac{\partial S/Nk}{\partial n}\right)\cdot\left(\frac{1}{N\Delta}\right) = \frac{k}{\Delta}\frac{\partial(S/Nk)}{\partial n}$$

So we have to compute the derivative of ☆

$$\frac{1}{NK}\frac{\partial S}{\partial n} = \frac{\partial}{\partial n}\left(-n\ln n - (1-n)\ln(1-n)\right)$$

$$= -\ln n - 1 + \ln(1-n) + 1$$

$$\frac{\partial(S/NK)}{\partial n} = \ln\frac{(1-n)}{n}$$

So

$$\boxed{\frac{1}{T} = \frac{k}{\Delta}\ln\frac{(1-n)}{n}}$$ ✓