Assignment 4

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1 Kadar Ch. 4 Problem 8

Curie Susceptibility: Calculate the Gibbs partition function of N non-interacting quantized spins in a magnetic field $\vec{B} = B\hat{z}$ at T. The work done is NM_z with $M_z = \mu \sum_{i=1}^{N} m_i$. For each spin m_i takes $2s+1$ values $(-s, -s+1, \ldots, s-1, s)$.

1.1 Part a)

$$\mathcal{Z} = tr\left[\exp\left(\beta\vec{B}\cdot\vec{M} - \beta\mathcal{H}\right)\right]$$

When there are no interactions between spins $\mathcal{H} = 0$.

$$\begin{aligned}
\mathcal{Z} &= \sum_{\{\mu_s\}} e^{\beta\vec{B}\cdot\vec{M}} \\
&= \sum_{\{\mu_s\}} e^{\beta B M_z} \\
&= \sum_{\{\mu_s\}} e^{\beta B\mu \sum i=1^N m_i} \\
&= \left(\sum_{\{2s+1\}} e^{\beta B\mu m_1}\right)\left(\sum_{\{2s+1\}} e^{\beta B\mu m_2}\right)\cdots\left(\sum_{\{2s+1\}} e^{\beta B\mu m_N}\right) \\
&= \left(\sum_{\{2s+1\}} e^{\beta B\mu m}\right)^N \\
&= \left(e^{\beta B\mu(-s)} + e^{\beta B\mu(-s+1)} + \ldots + e^{\beta B\mu(s-1)} + e^{\beta B\mu s}\right)^N \\
&= e^{-\beta B\mu s}\left(e^{\beta B\mu\times 0} + e^{\beta B\mu(1)} + \ldots + e^{\beta B\mu(2s-1)} + e^{\beta B\mu(2s)}\right)^N \\
&= \left(e^{-\beta B\mu s}\sum_{i=0}^{2s+1} e^{\beta B\mu i}\right)^N
\end{aligned}$$

At this point we recognize a geometric series and say $\sum_{i=0}^{2s} ae^i = \frac{1-ae^{2s+1}}{1-ae}$ which leads us to

$$\begin{aligned}
\mathcal{Z} &= \left(e^{-\beta B\mu s}\frac{1-e^{\beta B\mu(2s+1)}}{1-e^{\beta B\mu}}\right)^N \\
&= \left(\frac{e^{-\beta B\mu s}-e^{\beta B\mu(s+1)}}{1-e^{\beta B\mu}}\right)^N \\
&= \left(\frac{e^{-\beta B\mu/2}}{e^{-\beta B\mu/2}}\frac{e^{-\beta B\mu s}-e^{\beta B\mu(s+1)}}{1-e^{\beta B\mu}}\right)^N \\
&= \left(\frac{e^{-\beta B\mu(s+1/2)}-e^{\beta B\mu(s+1/2)}}{e^{-\beta B\mu/2}-e^{\beta B\mu/26}}\right)^N \\
&= \left(\frac{-2\sinh\left(\beta B\mu\left[s+1/2\right]\right)}{-2\sinh\left(\beta B\mu/2\right)}\right)^N
\end{aligned}$$

$$\boxed{\mathcal{Z} = \left(\frac{\sinh\left(\beta B\mu\left[s+1/2\right]\right)}{\sinh\left(\beta B\mu/2\right)}\right)^N} \tag{1}$$

1.2 Part b)

The sinh is made up os exponents so we easily know the expansion is

$$\begin{aligned}
\sinh\theta &\approx \theta + \frac{\theta^3}{3!} + \dots \\
\ln(1+x) &= x - \frac{x^2}{2} + \frac{x^3}{3} - \dots
\end{aligned}$$

So the plan is to expand the hyperbolic sine and then expand the logarithm. Let's call $b \equiv \beta B\mu$ for a while.

$$\begin{aligned}
G &= -k_\mathrm{B}T\ln\mathcal{Z} \\
&= -k_\mathrm{B}T\ln\left[\left(\frac{\sinh\left(\beta B\mu\left[s+1/2\right]\right)}{\sinh\left(\beta B\mu/2\right)}\right)^N\right] \\
&= -Nk_\mathrm{B}T\left[\ln\sinh\left(b\left[s+1/2\right]\right) - \ln\sinh\left(b/2\right)\right] \\
&= -Nk_\mathrm{B}T\left[\ln\left\{b\left(s+\frac{1}{2}\right)+\frac{b^3}{6}\left(s+\frac{1}{2}\right)^3+\dots\right\} - \ln\left\{\frac{b}{2}+\frac{1}{6}\frac{b^3}{2^3}+\dots\right\}\right] \\
&= -Nk_\mathrm{B}T\left[\ln\left\{b\left(s+\frac{1}{2}\right)\left[1+\frac{b^2}{6}\left(s+\frac{1}{2}\right)^2+\dots\right]\right\} - \ln\left\{\frac{b}{2}\left[1+\frac{1}{6}\frac{b^2}{2^2}+\dots\right]\right\}\right] \\
&\approx -Nk_\mathrm{B}T\left[\ln\left\{b\left(s+\frac{1}{2}\right)\left[1+\frac{b^2}{6}\left(s+\frac{1}{2}\right)^2\right]\right\} - \ln\left\{\frac{b}{2}\left[1+\frac{1}{6}\frac{b^2}{2^2}\right]\right\}\right] \\
&= -Nk_\mathrm{B}T\left[\ln\left\{b\left(s+\frac{1}{2}\right)\right\} + \ln\left\{\left[1+\frac{b^2}{6}\left(s+\frac{1}{2}\right)^2\right]\right\} - \ln\left\{\frac{b}{2}\right\} - \ln\left\{\left[1+\frac{1}{6}\frac{b^2}{2^2}\right]\right\}\right] \\
&= -Nk_\mathrm{B}T\left[\ln\left\{b\left(s+1\right)\right\} + \ln\left\{\left[1+\frac{b^2}{6}\left(s+\frac{1}{2}\right)^2\right]\right\} - \ln\left\{\left[1+\frac{1}{6}\frac{b^2}{2^2}\right]\right\}\right].
\end{aligned}$$

Now the logarithms

$$
\begin{aligned}
G &= -Nk_{\mathrm{B}}T\left[\ln\left\{b\left(s+1\right)\right\} + \ln\left\{\left[1+\frac{b^2}{6}\left(s+\frac{1}{2}\right)^2\right]\right\} - \ln\left\{\left[1+\frac{1}{6}\frac{b^2}{2^2}\right]\right\}\right] \\
&= -Nk_{\mathrm{B}}T\left[\ln\left\{b\left(s+1\right)\right\} + \left\{\frac{b^2}{6}\left(s+\frac{1}{2}\right)^2 - \frac{b^4}{26^2}\left(s+\frac{1}{2}\right)^4 + \dots\right\} - \left\{\frac{1}{6}\frac{b^2}{2^2} - \frac{1}{6}\frac{b^4}{2\times 2^2} + \dots\right\}\right] \\
&\approx -Nk_{\mathrm{B}}T\left[\ln\left\{b\left(s+1\right)\right\} + \left\{\frac{b^2}{6}\left(s+\frac{1}{2}\right)^2\right\} - \left\{\frac{1}{6}\frac{b^2}{2^2}\right\}\right] \\
&= -Nk_{\mathrm{B}}T\left[\ln\left\{b\left(s+1\right)\right\} + \frac{b^2}{6}\left\{s^2+s+\frac{1}{4}-\frac{1}{4}\right\}\right] \\
&= -Nk_{\mathrm{B}}T\left[\ln\left\{b\left(s+1\right)\right\} + \frac{b^2}{6}s(s+1)\right] \\
&= -Nk_{\mathrm{B}}T\ln\left\{\beta B\mu\left(s+1\right)\right\} - Nk_{\mathrm{B}}T\frac{(\beta B\mu)^2}{6}s(s+1)
\end{aligned}
$$

$$
\boxed{G = G_0 - N\frac{B^2\mu^2}{6k_{\mathrm{B}}T}s(s+1)} \tag{2}
$$

1.3 Part c)

The average magnetization is

$$
\begin{aligned}
< M_z > &= -\frac{\partial G}{\partial B} \\
&= -\frac{\partial}{\partial B}\left(G(0) - \frac{N\mu^2 s(s+1)}{6k_{\mathrm{B}}T}B^2 + \mathcal{O}(B^4)\right) \\
&= 0 + \frac{2N\mu^2 s(s+1)}{6k_{\mathrm{B}}T}B + \mathcal{O}(B^3)
\end{aligned}
$$

So then the zero field susceptibility is

$$
\begin{aligned}
\chi &= \left.\frac{\partial M_z}{\partial B}\right|_{B=0} \\
&= \frac{\partial}{\partial B}\left[\frac{N\mu^2 s(s+1)}{3k_{\mathrm{B}}T}B + \mathcal{O}(B^3)\right]_{B=0} \\
&= \boxed{\frac{N\mu^2 s(s+1)}{3k_{\mathrm{B}}T} + \left.\mathcal{O}(B^2)\right|_{B=0}} \qquad (3) \\
&= c/T
\end{aligned}
$$

where $c = \frac{N\mu^2 s(s+1)}{3k_{\mathrm{B}}}$

1.4 Part d)

To find the heat capacity we think about the enthalpy in a different way:

$$
\begin{aligned}
H &=< \mathcal{H} - BM > \\
&= -BM
\end{aligned}
$$

Therefore,

$$\begin{aligned} C_B &= \left.\frac{\partial H}{\partial T}\right|_B \\ &= -B \left.\frac{\partial M}{\partial T}\right|_B \\ C_M &= \left.\frac{\partial H}{\partial T}\right|_M \\ &= -M \left.\frac{\partial B}{\partial T}\right|_M \end{aligned}$$

but B is an external field and doesn't have temperature dependence. Therefore,

$$\boxed{C_M = 0}. \tag{4}$$

and to find C_B we use the $< M >$ as found previously to give

$$\begin{aligned} C_B &= \left.\frac{\partial H}{\partial T}\right|_B \\ &= -B \left.\frac{\partial < M_z >}{\partial T}\right|_B \\ &\approx -B\frac{\partial}{\partial T}\frac{2N\mu^2 s(s+1)}{6k_{\mathrm{B}}T}B \\ &= -\frac{2N\mu^2 s(s+1)}{6k_{\mathrm{B}}T}B^2\frac{\partial}{\partial T}\frac{1}{T} \\ &= \frac{2N\mu^2 s(s+1)}{6k_{\mathrm{B}}T}\frac{B^2}{T^2} \end{aligned}$$

$$\boxed{C_B = c\frac{B^2}{T^2}} \tag{5}$$

2 Kadar Ch. 4 Problem 12

We have a Hamiltonian for the polar rods:

$$\mathcal{H}_{\mathrm{rot}} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) - \mu E\cos\theta \tag{6}$$

where I is the moment of inertia of the rod, μ is it's dipole moment, E is the external field and $\vec{p}$ is the momentum.

2.1 Part a)

For a single rod, we find the partition function by assuming that the rod does not translate ($\int dr = 1$ and $\int dp_r = 1$) and remember when we integrate $\vec{q}$ we are **not** integrating over volume space but rather we are integrating over

coordinate space. These are often the same but in this case they are not: There is no $\sin\theta$ term which is needed when we integrate over volume space.

$$
\begin{aligned}
Z_1 &= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\phi \exp\left[-\beta \mathcal{H}_{\mathrm{rot}}\right] \\
&= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\phi \exp\left[-\frac{\beta}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) + \beta\mu E\cos\theta\right] \\
&= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\phi \exp\left[-\frac{\beta p_\theta^2}{2I}\right] \exp\left[-\frac{\beta p_\phi^2}{2I\sin^2\theta}\right] \exp\left[\beta\mu E\cos\theta\right] \\
&= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \exp\left[\beta\mu E\cos\theta\right] \underbrace{\int_{-\infty}^{\infty} dp_\theta \exp\left[-\frac{\beta p_\theta^2}{2I}\right]}_{\text{Gaussian}} \underbrace{\int_{-\infty}^{\infty} dp_\phi \exp\left[-\frac{\beta p_\phi^2}{2I\sin^2\theta}\right]}_{\text{Gaussian}} \\
&= 2\pi \int_0^{\pi} d\theta \exp\left[\beta\mu E\cos\theta\right] \left(\sqrt{\frac{2\pi I}{\beta}}\right)\left(\sqrt{\frac{2\pi I\sin^2\theta}{\beta}}\right) \\
&= 2\pi \frac{2\pi I}{\beta} \int_0^{\pi} d\theta \exp\left(\beta\mu E\cos\theta\right)\sin\theta \\
&= 2\pi \frac{2\pi I}{\beta} \int_1^{-1} dx \exp\left(\beta\mu E x\right)(-1) \\
&= (2\pi)^2 \frac{I}{\beta} \int_{-1}^{1} dx \exp\left(\beta\mu E x\right) \\
&= \left(\frac{2\pi}{\beta}\right)^2 \frac{I}{\mu E}\left(e^{-\beta\mu E} - e^{\beta\mu E}\right) \\
&= 2\left(\frac{2\pi}{\beta}\right)^2 \frac{I}{\mu E}\sinh\left(\beta\mu E\right).
\end{aligned}
$$

So if that's the partition function for one polarizable rod, the partition function for N rods is

$$
\boxed{Z_N = \left(2\left(\frac{2\pi}{\beta}\right)^2 \frac{I}{\mu E}\sinh\left(\beta\mu E\right)\right)^N} \tag{7}
$$

2.2 Part b)

It is good to remember the general formula

$$
< x >= k_{\mathrm{B}} T \frac{\partial}{\partial J}\ln Z. \tag{8}
$$

For instance, if we want to find the mean polarization $< P >$ due to a field E

$$
\begin{aligned}
< P > &= k_{\mathrm{B}} T \frac{\partial}{\partial E} \ln Z \\
&= N k_{\mathrm{B}} T \frac{\partial}{\partial E} \ln \left(2 \left(\frac{2\pi}{\beta} \right)^2 \frac{I}{\mu E} \sinh (\beta \mu E) \right) \\
&= N k_{\mathrm{B}} T \frac{\partial}{\partial E} \left[\ln \left(2 \left(\frac{2\pi}{\beta} \right)^2 \right) + \ln \left(\frac{I}{\mu E} \right) + \ln (\sinh (\beta \mu E)) \right] \\
&= N k_{\mathrm{B}} T \frac{\partial}{\partial E} \left[- \ln \left(\frac{\mu E}{I} \right) + \ln (\sinh (\beta \mu E)) \right] \\
&= N k_{\mathrm{B}} T \left[- \frac{1}{E} + \frac{\partial}{\partial E} \ln \sinh (\beta \mu E) \right] \\
&= N k_{\mathrm{B}} T \left[- \frac{1}{E} + \frac{1}{\sinh (\beta \mu E)} \frac{\partial}{\partial E} \sinh (\beta \mu E) \right] \\
&= N k_{\mathrm{B}} T \left[- \frac{1}{E} + \frac{1}{\sinh (\beta \mu E)} \cosh (\beta \mu E) \, \beta \mu \right]
\end{aligned}
$$

$$
\boxed{< P >= N k_{\mathrm{B}} T \left[\beta \mu \coth (\beta \mu E) - \frac{1}{E} \right]} \tag{9}
$$

2.3 Part c)

If we want to look for an analytic solution

$$
\begin{aligned}
\chi_T &= \frac{\partial P}{\partial E} \\
&= N k_{\mathrm{B}} T \frac{\partial}{\partial E} \left[\beta \mu \coth (\beta \mu E) - \frac{1}{E} \right] \\
&= N k_{\mathrm{B}} T \frac{1}{E^2} + N \mu \frac{\partial}{\partial E} \coth (\beta \mu E) \\
&= N k_{\mathrm{B}} T \frac{1}{E^2} - N k_{\mathrm{B}} T \operatorname{csch}^2 (\beta \mu E) \\
&= N k_{\mathrm{B}} T \frac{1}{E^2} - \frac{N k_{\mathrm{B}} T}{\sinh^2 (\beta \mu E)}
\end{aligned}
$$

But since we are look for the *zero-field* limit, we can assume that E is small enough that expanding coth() is acceptable. So we find

$$\begin{aligned}
\chi_T &= \left.\frac{\partial P}{\partial E}\right|_{E=0} \\
&= Nk_{\mathrm{B}}T\frac{\partial}{\partial E}\left[\beta\mu\coth\left(\beta\mu E\right) - \frac{1}{E}\right]\Bigg|_{E=0} \\
&= Nk_{\mathrm{B}}T\left[\frac{1}{E^2} + \mu\beta\frac{\partial}{\partial E}\coth\left(\beta\mu E\right)\right]_{E=0} \\
&= Nk_{\mathrm{B}}T\left[\frac{1}{E^2} + \mu\beta\frac{\partial}{\partial E}\left(\frac{1}{\beta\mu E} + \frac{\beta\mu E}{3} - \frac{\left(\beta\mu E\right)^3}{45} + \dots\right)\right]_{E=0} \\
&= Nk_{\mathrm{B}}T\left[\frac{1}{E^2} + \mu\beta\left(-\frac{1}{\beta\mu E^2} + \frac{\beta\mu}{3} - \frac{\left(\beta\mu\right)^3 E^2}{15} + \dots\right)\right]_{E=0} \\
&= Nk_{\mathrm{B}}T\left[\frac{\left(\beta\mu\right)^2}{3} - \frac{\left(\beta\mu\right)^4}{15}E^2\right]_{E=0}
\end{aligned}$$

$$\boxed{\chi_T = N\beta\frac{\mu^2}{3}} \tag{10}$$

2.4 Part d)

The average energy is given by

$$\begin{aligned}
<\mathcal{H}> &= -\frac{\partial\ln Z}{\partial\beta} \\
&= -\frac{\partial}{\partial\beta}\left[\ln\left(-2\left(\frac{2\pi}{\beta}\right)^2\right) + \ln\left(\frac{I}{\mu E}\right) + \ln\left(\sinh\left(\beta\mu E\right)\right)\right] \\
&= -\frac{\partial}{\partial\beta}\left[\ln\left(\frac{2\pi}{\beta}\right)^2 + 0 + \ln\left(\sinh\left(\beta\mu E\right)\right)\right] \\
&= 2\frac{\partial}{\partial\beta}\ln\beta + \frac{\partial}{\partial\beta}\ln\left(\sinh\left(\beta\mu E\right)\right) \\
&= \frac{2}{\beta} + \frac{1}{\sinh\left(\beta\mu E\right)}\cosh\left(\beta\mu E\right)\mu E
\end{aligned}$$

$$\boxed{<\mathcal{H}>= \frac{2}{\beta} + \mu E\coth\left(\beta\mu E\right)} \tag{11}$$

2.5 Part e)

The heat capacity is just

$$
\begin{aligned}
C &= \frac{\partial < \mathcal{H} >}{\partial T} \\
&= \frac{\partial}{\partial T}\left(2k_{\mathrm{B}}T + \mu E \coth\left(\frac{\mu E}{k_{\mathrm{B}}T}\right)\right) \\
&= 2k_{\mathrm{B}} + \mu E\left(1 - \coth^2\left(\frac{\mu E}{k_{\mathrm{B}}T}\right)\right)\left(\frac{\mu E}{k_{\mathrm{B}}}\right)\left(-\frac{1}{T^2}\right) \\
&= 2k_{\mathrm{B}} - k_{\mathrm{B}}\left(\frac{\mu E}{k_{\mathrm{B}}T}\right)^2 \sinh^{-2}\left(\frac{\mu E}{k_{\mathrm{B}}T}\right)
\end{aligned}
$$

3 Harden Problem 3

Consider M binding sites each of which **may** trap up to one electron. The binding energy is $-\epsilon_0$ but in the presence of a magnetic field $\vec{B} = B\hat{z}$, the energy levels split to $\epsilon_\pm = -\epsilon_0 \mp \sigma B$.

I made an error when talking to you. I told you all that part a) was a three state problem because it says each site MAY trap up to one electron. But in part a), he wanted you to assume that all N electrons were trapped. This is the only way to get the energies to equal. Sorry for the confusion. I present both the solutions for if it were a three state and if it were a two state for part a) so that you can check your answer no matter how you interpreted the question.

3.1 Part a) Three states

Consider the canonical case: temperature fixed at T and the number of electrons availiable to be trapped is fixed at $N < M$.

3.1.1 Question i)

Calculate the partition function $Z_N(T, M)$.

The particle can either

1. not be trapped
2. be bound with ϵ_+
3. be bound with ϵ_-.

So then, the partition function for a single electron is

$$
\begin{aligned}
Z_1 &= \sum_{\{\mu_s\}} e^{-\beta\mathcal{H}} \\
&= e^0 + e^{-\beta\epsilon_+} + e^{-\beta\epsilon_-} \\
&= 1 + e^{\beta(\epsilon_0+\sigma B)} + e^{\beta(\epsilon_0-\sigma B)}
\end{aligned}
$$

Now we can find the partition function of the system **but** we need to consider one extra fact: if the electrons are not trapped they are indistinguishable. Therefore, we need to scale by the number of ways that we can place the N electrons into M sites.

$$\begin{aligned}
Z &= \begin{pmatrix} M \\ N \end{pmatrix} Z_1^N \\
&= \frac{M!}{N!(M-N)!}\left(1 + e^{\beta(\epsilon_0+\sigma B)} + e^{\beta(\epsilon_0-\sigma B)}\right)^N \\
&= \frac{M!}{N!(M-N)!}\left(1 + e^{\beta\epsilon_0}\left(e^{\sigma B\beta} + e^{-\sigma B\beta}\right)\right)^N
\end{aligned}$$

$$\boxed{Z = \frac{M!}{N!(M-N)!}\left(1 + 2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)^N} \tag{12}$$

3.1.2 Question ii)

Find the Helmholtz free energy.

From the partition function

$$\begin{aligned}
F(T,M) &= -k_{\mathrm{B}}T\ln Z \\
&= -k_{\mathrm{B}}T\ln\left(\frac{M!}{N!(M-N)!}\left(1 + 2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)^N\right)
\end{aligned}$$

$$\boxed{F(T,M) = -k_{\mathrm{B}}T\left(\ln M! - \ln N! - \ln(M-N)! + N\ln\left(1 + 2e^{\frac{\epsilon_0}{k_{\mathrm{B}}T}}\cosh\left(\frac{\sigma B}{k_{\mathrm{B}}T}\right)\right)\right)} \tag{13}$$

3.1.3 Question iii)

What is the internal energy of the system?

Just like in the last two questions, we can find the average energy by

$$\begin{aligned}
E &=< \mathcal{H} >= -\frac{\partial \ln Z}{\partial \beta} \\
&= -\frac{\partial}{\partial\beta}\left(\ln M! - \ln N! - \ln(M-N)! + N\ln\left(1 + 2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)\right) \\
&= 0 + 0 + 0 - N\frac{\partial}{\partial\beta}\ln\left(1 + 2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right) \\
&= -N\frac{1}{1 + 2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)}\left[2\epsilon_0 e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right) + 2\sigma B e^{\beta\epsilon_0}\sinh\left(\sigma B\beta\right)\right] \\
&= -2N\frac{\epsilon_0\cosh\left(\sigma B\beta\right) + \sigma B\sinh\left(\sigma B\beta\right)}{e^{-\beta\epsilon_0} + 2\cosh\left(\sigma B\beta\right)}
\end{aligned}$$

$$\boxed{E = -2N\frac{\epsilon_0 + \sigma B\tanh\left(\sigma B\beta\right)}{2 + e^{-\beta\epsilon_0}\mathrm{sech}\left(\sigma B\beta\right)}} \tag{14}$$

3.1.4 Question iv)

What's the chemical potential of the trapped electrons?

The chemical potential is the difference between being trapped and not being trapped and the free electrons don't have a chemical potential so the chemical potential of the trapped electrons is the chemical potential of the system. And we can find chemical potential by

$$
\begin{aligned}
\mu &= \left.\frac{\partial F}{\partial N}\right|_{T,B} \\
&= -k_{\mathrm{B}}T\frac{\partial}{\partial N}\ln\left(\frac{M!}{N!(M-N)!}\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)^N\right) \\
&= -k_{\mathrm{B}}T\frac{\partial}{\partial N}\left(\ln M! - \ln N! - \ln(M-N)! + \ln\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)^N\right) \\
&= -k_{\mathrm{B}}T\left(-\frac{\partial}{\partial N}\ln N! - \frac{\partial}{\partial N}\ln(M-N)! + \frac{\partial}{\partial N}N\ln\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)\right) \\
&= -k_{\mathrm{B}}T\left(-\frac{\partial}{\partial N}N\ln N + 1 - \frac{\partial}{\partial N}(M-N)\ln(M-N) - 1 + \ln\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)\right) \\
&= -k_{\mathrm{B}}T\left(-\ln N - \frac{N}{N} + \ln(M-N) + \frac{M-N}{M-N} + \ln\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)\right) \\
&= -k_{\mathrm{B}}T\left(\ln\left(\frac{M-N}{N}\right) + \ln\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)\right)
\end{aligned}
$$

$$
\boxed{\mu = -k_{\mathrm{B}}T\ln\left(\frac{M-N}{N}\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)\right)} \tag{15}
$$

3.1.5 Question v)

The very definition of the partition function is

$$
p_\mu = \frac{e^{-\beta\mathcal{H}_\mu}}{Z} \tag{16}
$$

$$
Z(T,\vec{x}) = \sum_{\{\mu\}} e^{-\beta\mathcal{H}_\mu} \tag{17}
$$

So then the probability of being in the either the $\pm$-states is

$$
\begin{aligned}
p_\pm &= \frac{e^{-\beta\mathcal{H}}}{Z} \\
&= \frac{e^{-\beta\epsilon_\pm}}{Z} \\
&= \frac{e^{-\beta\epsilon_\pm}}{\frac{M!}{N!(M-N)!}\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)^N} \\
&= \frac{N!(M-N)!}{M!}\frac{e^{-\beta\epsilon_\pm}}{\left(1+2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)^N}
\end{aligned}
$$

And the average number of particles in each state is

$$
\begin{aligned}
< N_{\pm} > &= N p_{\pm} \\
&= N \frac{N!(M-N)!}{M!} \frac{e^{-\beta \epsilon_{\pm}}}{\left(1 + 2e^{\beta \epsilon_0} \cosh\left(\sigma B \beta\right)\right)^N}
\end{aligned}
$$

$$
\boxed{< N_{\pm} >= \frac{(N+1)!(M-N)!}{M!} \frac{e^{-\beta \epsilon_{\pm}}}{\left(1 + 2e^{\beta \epsilon_0} \cosh\left(\sigma B \beta\right)\right)^N}} \tag{18}
$$

3.2 Part a) Two states

Consider the canonical case: temperature fixed at T and the number of electrons trapped is fixed at $N < M$.

3.2.1 Question i)

Calculate the partition function $Z_N(T, M)$.

The particle can either

1. be bound with ϵ_+
2. be bound with ϵ_-.

So then, the partition function for a single electron is

$$
\begin{aligned}
Z_1 &= \sum_{\{\mu_s\}} e^{-\beta \mathcal{H}} \\
&= e^{-\beta \epsilon_+} + e^{-\beta \epsilon_-} \\
&= e^{\beta(\epsilon_0 + \sigma B)} + e^{\beta(\epsilon_0 - \sigma B)}
\end{aligned}
$$

Now we can find the partition function of the system but we still need to consider we need to scale by the number of ways that we can place the N electrons into M sites.

$$
\begin{aligned}
Z &= \begin{pmatrix} M \\ N \end{pmatrix} Z_1^N \\
&= \frac{M!}{N!(M-N)!} \left(e^{\beta(\epsilon_0 + \sigma B)} + e^{\beta(\epsilon_0 - \sigma B)}\right)^N \\
&= \frac{M!}{N!(M-N)!} \left(e^{\beta \epsilon_0} \left(e^{\sigma B \beta} + e^{-\sigma B \beta}\right)\right)^N
\end{aligned}
$$

$$
\boxed{Z = \frac{M!}{N!(M-N)!} 2^N e^{\beta N \epsilon_0} \cosh^N\left(\sigma B \beta\right)} \tag{19}
$$

3.2.2 Question ii)

Find the Helmholtz free energy.

From the partition function

$$F(T,M) = -k_\mathrm{B} T \ln Z$$
$$= -k_\mathrm{B} T \ln \left(\frac{M!}{N!(M-N)!} \left(2e^{\beta\epsilon_0} \cosh(\sigma B \beta)\right)^N \right)$$

$$\boxed{F(T,M) = -k_\mathrm{B} T \left[\ln M! - \ln N! - \ln(M-N)! + N \ln\left(2e^{\frac{\epsilon_0}{k_\mathrm{B} T}} \cosh\left(\frac{\sigma B}{k_\mathrm{B} T}\right)\right)\right]} \tag{20}$$

3.2.3 Question iii)

What is the internal energy of the system?

Just like in the last two questions, we can find the average energy by

$$E = <\mathcal{H}> = -\frac{\partial \ln Z}{\partial \beta}$$
$$= -\frac{\partial}{\partial \beta}\left(\ln M! - \ln N! - \ln(M-N)! + N \ln\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)\right)$$
$$= 0 + 0 + 0 - N \frac{\partial}{\partial \beta} \ln\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)$$
$$= -N \frac{1}{2e^{\beta\epsilon_0}\cosh(\sigma B\beta)}\left[2\epsilon_0 e^{\beta\epsilon_0}\cosh(\sigma B\beta) + 2\sigma B e^{\beta\epsilon_0}\sinh(\sigma B\beta)\right]$$
$$= -N \frac{1}{\cosh(\sigma B\beta)}\left[\epsilon_0 \cosh(\sigma B\beta) + \sigma B \sinh(\sigma B\beta)\right]$$

$$\boxed{E = -N\left[\epsilon_0 + \sigma B \tanh(\sigma B\beta)\right]} \tag{21}$$

3.2.4 Question iv)

What's the chemical potential of the trapped electrons?

The chemical potential is the difference between being trapped and not being trapped and the free electrons don't have a chemical potential so the chemical potential of the trapped electrons is the chemical potential of the system. And we can find chemical potential by

$$\begin{aligned}
\mu &= \left.\frac{\partial F}{\partial N}\right|_{T,B} \\
&= -k_{\mathrm{B}} T \frac{\partial}{\partial N} \ln\left(\frac{M!}{N!(M-N)!}\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)^N\right) \\
&= -k_{\mathrm{B}} T \frac{\partial}{\partial N}\left(\ln M! - \ln N! - \ln(M-N)! + \ln\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)^N\right) \\
&= -k_{\mathrm{B}} T\left(-\frac{\partial}{\partial N}\ln N! - \frac{\partial}{\partial N}\ln(M-N)! + \frac{\partial}{\partial N} N\ln\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)\right) \\
&= -k_{\mathrm{B}} T\left(-\frac{\partial}{\partial N} N\ln N + 1 - \frac{\partial}{\partial N}(M-N)\ln(M-N) - 1 + \ln\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)\right) \\
&= -k_{\mathrm{B}} T\left(-\ln N - \frac{N}{N} + \ln(M-N) + \frac{M-N}{M-N} + \ln\left(1 + 2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)\right) \\
&= -k_{\mathrm{B}} T\left(\ln\left(\frac{M-N}{N}\right) + \ln\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)\right)
\end{aligned}$$

$$\boxed{\mu = -k_{\mathrm{B}} T \ln\left(\frac{M-N}{N}\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)\right)} \tag{22}$$

3.2.5 Question v)

The very definition of the partition function is

$$p_\mu = \frac{e^{-\beta\mathcal{H}_\mu}}{Z} \tag{23}$$

$$Z(T,\vec{x}) = \sum_{\{\mu\}} e^{-\beta\mathcal{H}_\mu} \tag{24}$$

So then the probability of being in the either the $\pm$-states is

$$\begin{aligned}
p_\pm &= \frac{e^{-\beta\mathcal{H}}}{Z} \\
&= \frac{e^{-\beta\epsilon_\pm}}{Z} \\
&= \frac{e^{-\beta\epsilon_\pm}}{\frac{M!}{N!(M-N)!}\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)^N} \\
&= \frac{N!(M-N)!}{M!}\frac{e^{-\beta\epsilon_\pm}}{\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)^N}
\end{aligned}$$

And the average number of particles in each state is

$$\begin{aligned}
< N_\pm > &= N p_\pm \\
&= N\frac{N!(M-N)!}{M!}\frac{e^{-\beta\epsilon_\pm}}{\left(2e^{\beta\epsilon_0}\cosh(\sigma B\beta)\right)^N}
\end{aligned}$$

$$\boxed{< N_\pm >= \frac{(N+1)!(M-N)!}{M!} \frac{e^{-\beta\epsilon_\pm}}{\left(2e^{\beta\epsilon_0}\cosh\left(\sigma B\beta\right)\right)^N}} \tag{25}$$

3.3 Part b)

Next consider the grand canonical case where the temperature is fixed but the number of electrons are in equalibrium with a reservior.

3.3.1 Question i)

Calculate the grand partition function.

The grand canonical ensemble is a two level system: there is a reservior of as many particles that we need (no longer limited to N but there's still only M sites) and the particles in the system are in one of two states.

$$\begin{aligned}
\mathcal{Q} &= \sum_{\mu_s} e^{\beta\mu N - \beta\mathcal{H}} \\
&= \sum_{N=0}^{M} e^{\beta\mu N} \sum_{\mu_S|N} e^{-\beta\mathcal{H}} \\
&= \sum_{N=0}^{M} e^{\beta\mu N} \left(e^{-\beta\epsilon_+} + e^{-\beta\epsilon_-}\right)^N \\
&= \sum_{N=0}^{M} e^{\beta\mu N} \left(e^{-\beta\epsilon_0 + \sigma B\beta} + e^{-\beta\epsilon_0 - \sigma B\beta}\right)^N \\
&= \sum_{N=0}^{M} e^{\beta\mu N} e^{-\beta\epsilon_0 N} \left(e^{\sigma B\beta} + e^{-\sigma B\beta}\right)^N \\
&= \sum_{N=0}^{M} e^{\beta N(\mu-\epsilon_0)} \left(2\cosh\left(\sigma B\beta\right)\right)^N \\
&= \sum_{N=0}^{M} \left(2e^{\beta(\mu-\epsilon_0)}\cosh\left(\sigma B\beta\right)\right)^N
\end{aligned}$$

$$\boxed{\mathcal{Q} = \left(1 + 2e^{\beta(\mu-\epsilon_0)}\cosh\left(\sigma B\beta\right)\right)^M} \tag{26}$$

3.3.2 Question ii)

Find the grand potential.

The grand potential is just the "free energy" associated with the grand canonical ensemble so

$$\begin{aligned}
\mathcal{G} &= -k_{\mathrm{B}}T\ln\mathcal{Q} \\
&= -Mk_{\mathrm{B}}T\ln\left(1 + 2e^{\beta(\mu-\epsilon_0)}\cosh\left(\sigma B\beta\right)\right)
\end{aligned}$$

which is just waiting to be expanded.

3.3.3 Question iii)

What is the internal energy of the system?

Just as in the canonical ensemble, we use

$$\begin{aligned}
E =< \mathcal{H} > &= -\frac{\partial \ln \mathcal{Q}}{\partial \beta} \\
&= -M\frac{\partial}{\partial \beta} \ln\left(1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)\right) \\
&= -M\frac{1}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)} \frac{\partial}{\partial \beta}\left(1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)\right) \\
&= -2M\frac{1}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)} \frac{\partial}{\partial \beta}\left(e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)\right) \\
&= -\frac{2M}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)}\left((\mu-\epsilon_0)e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta) + e^{\beta(\mu-\epsilon_0)} \sinh(\sigma B\beta)\,\sigma B\right) \\
&= -M\frac{2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)}\left((\mu-\epsilon_0) + \tanh(\sigma B\beta)\,\sigma B\right)
\end{aligned}$$

$$\boxed{E = -M\frac{2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)}\left(\mu-\epsilon_0 + \sigma B \tanh(\sigma B\beta)\right)} \tag{27}$$

We'll answer whether this is the same as Part a) from the two level system as soon as we know the average number of trapped electrons $< N >$.

3.3.4 Question iv)

What is the average number of trapped electrons?

We use

$$\begin{aligned}
< N > &= -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{T,B} \\
&= \frac{\partial}{\partial \mu} M k_{\mathrm{B}} T \ln\left(1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)\right) \\
&= M k_{\mathrm{B}} T \frac{1}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)} \frac{\partial}{\partial \mu}\left(1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)\right) \\
&= M k_{\mathrm{B}} T \frac{2\cosh(\sigma B\beta)}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)} \frac{\partial}{\partial \mu} e^{\beta\mu} e^{-\beta\epsilon_0} \\
&= M k_{\mathrm{B}} T \frac{2\cosh(\sigma B\beta)}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)} \beta e^{\beta\mu} e^{-\beta\epsilon_0} \\
&= M\frac{2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)}{1 + 2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B\beta)}
\end{aligned}$$

$$\boxed{< N > = \frac{2M}{2 + e^{\beta(\epsilon_0-\mu)} \mathrm{sech}(\sigma B\beta)}} \tag{28}$$

Now we can answer whether or not the energy from Part a) is equal to the energy in Part b) when $N =< N >$. We notice in the equation for E the average number of electrons is just sitting there:

$$
\begin{aligned}
E &= -M \frac{2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B \beta)}{1+2e^{\beta(\mu-\epsilon_0)} \cosh(\sigma B \beta)} \left((\mu-\epsilon_0)+\tanh(\sigma B \beta)\, \sigma B\right) \\
&= -<N> (\mu-\epsilon_0+\sigma B \tanh(\sigma B \beta))
\end{aligned} \tag{29}
$$

So the energies are the same when the number of electrons is the average and the binding energy is replaced by $\mu - \epsilon_0$.

3.3.5 Question v)

Now we are asked to find the average number of electrons in each energy level. Again, we find the probability in the exact same way and then state

$$
<N_{\pm}> = M p_{\pm}. \tag{30}
$$

So once the probability is found the difference is that we use M not N.