12. (Statistical Mechanics)

Consider a volume V containing N electrons of mass m which have no mutual interactions, other than those associated with the Pauli exclusion principle. The spectrum of states available to each electron contains a continuous part with energy $E = \mathbf{p}^2/2m$ for $E > 0$, and a bound state part with energy $E = -\varepsilon$ and $\varepsilon > 0$. The total number of bound states $\mathcal{M}$ available to the N electrons is assumed to be larger than N. The parameters m, ε, $\mathcal{M}$ are considered fixed throughout.

(a) Give the expressions for the number N_b of electrons in the bound states, and the number N_c of electrons in the continuum, as a function of T, V and the chemical potential μ. Justify your answer.

(b) Obtain the relation between N and μ for given T, V.

(c) At low temperature $k_B T \ll \varepsilon$, most of the electrons occupy the bound states, and therefore few occupy the continuum state. Using the approximation of the classical distribution for the occupation number of states in the continuum spectrum, and in the limit $k_b T \ll \varepsilon$, evaluate N_c and μ as a function of T, V.

(d) * The system is placed in a uniform external magnetic field B that splits each energy level into two levels whose energies are shifted by $+\kappa B$ and $-\kappa B$ respectively, where κ is the magnetic moment of the electron. Work with the thermodynamic potential suitable for the independent variables T, V, μ, B. Define the magnetic susceptibility as the induced magnetic dipole moment per unit volume per unit applied magnetic field B. Expressing the magnetic susceptibility at $B = 0$ in terms of the thermodynamic potential in the absence of a magnetic field, obtain the magnetic susceptibility as a function of T, V, N, using the results obtained in part (c).

*Note that part (d) is more difficult than the first three parts of this problem.

Solution: *Solution by Jonah Hyman (jthyman@g.ucla.edu)*

For this stat mech problem, we need to know about the occupation number formalism—

> **Occupation numbers:**
> When a statistical mechanics problem describes a system of bosons or fermions, you should consider using occupation numbers.
> Occupation numbers describe the average number of particles in each state.
>
> $$\text{For fermions (Fermi-Dirac statistics):} \quad n^{FD}(\epsilon_k, \mu) = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} \quad (210)$$
>
> $$\text{For bosons (Bose-Einstein statistics):} \quad n^{BE}(\epsilon_k, \mu) = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} \quad (211)$$
>
> $$\text{For classical particles (Maxwell-Boltzmann statistics):} \quad n^{MB}(\epsilon_k, \mu) = e^{-\beta(\epsilon_k - \mu)} \quad (212)$$
>
> Here, ϵ_k is the energy of the state k, μ is the chemical potential, and $\beta = 1/(kT)$.

—as well as the density of states in phase space:

> **Phase space:**
> Consider a particle in d-dimensional space. The particle's state can be defined by its position $\mathbf{x} = (x_1, \ldots, x_d)$, its momentum $\mathbf{p} = (p_1, \ldots, p_d)$, and any internal degrees of freedom (e.g. spin). Assume that there are g possible internal states for the particle.
> The position and momentum of the particle constitute a point in $2d$-dimensional phase space: $(x_1, \ldots, x_d, p_1, \ldots, p_d)$.
> To solve problems, discretize phase space by dividing it into $2d$-dimensional boxes. The volume of each box is h^d, where h is Planck's constant (which has units of position times momentum). The number of boxes in a phase-space volume $d^d p \, d^d x$ is the total volume divided by the volume of each box, or $\frac{d^d p \, d^d x}{h^d}$. Each box has g possible states, corresponding to the internal degrees of freedom of the particle. Therefore, the number of possible states in a phase-space volume $d^d p \, d^d x$ is
>
> $$\text{Number of possible states in a phase-space volume } d^d p \, d^d x = g \frac{d^d p \, d^d x}{h^d} \quad (213)$$

(a) Consider the kth bound state. When occupied, the energy of that state is $\epsilon_k = -\varepsilon$. Therefore, the average number of electrons in the kth bound state is given by the occupation number

$$n_b^{FD}(\epsilon_k, \mu) = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} = \frac{1}{e^{\beta(-\varepsilon - \mu)} + 1} \quad (214)$$

There are $\mathcal{M}$ independent bound states, so the average number of electrons in all the bound states is $\mathcal{M}$ times the average number electrons in one bound state:

$$N_b = \mathcal{M} \, n_b^{FD}(\epsilon_k, \mu) = \frac{\mathcal{M}}{e^{\beta(-\varepsilon - \mu)} + 1} \quad (215)$$

Now consider the continuum state with position $\mathbf{x}$ and momentum $\mathbf{p}$. When occupied, the energy of that state is $\epsilon_k = \frac{p^2}{2m}$. Therefore, the average number of electrons in this continuum state is given by the occupation number

$$n_c^{FD}(\epsilon_k, \mu) = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} = \frac{1}{e^{\beta(p^2/(2m) - \mu)} + 1} \quad (216)$$

To connect the occupation number to the total number of particles, use the following relation:

Number of particles in a phase-space volume $d^3 p \, d^3 x$

$\quad = \big(\text{Number of states in the phase-space volume } d^3 p \, d^3 x\big) \cdot \big(\text{Average number of particles per state}\big)$

(213) tells us that the number of states in the phase-space volume $d^3p\,d^3x$ is $g\frac{d^3p\,d^3x}{h^d}$. Here, g is the number of internal states for each electron. Since the electron is a spin-1/2 particle, there are two internal states and so $g = 2$. The average number of particles per state is just the occupation number $n_c^{FD}(\epsilon_k, \mu)$ found in (216). With that in mind, we get

$$\text{Number of electrons in a phase-space volume } d^3p\,d^3x = 2\frac{d^3p\,d^3x}{h^3}\frac{1}{e^{\beta(p^2/(2m)-\mu)}+1} \quad (217)$$

To find the total number of electrons in the continuum, integrate over phase space:

$$N_c = 2\int \frac{d^3p\,d^3x}{h^3}\frac{1}{e^{\beta(p^2/(2m)-\mu)}+1}$$

The integral over d^3x yields the volume of space:

$$N_c = 2V\int\frac{d^3p}{h^3}\frac{1}{e^{\beta(p^2/(2m)-\mu)}+1} \quad (218)$$

Summarizing our results, we have that the number of electrons in the bound states and in the continuum are

$$\boxed{N_b = \frac{\mathcal{M}}{e^{\beta(-\varepsilon-\mu)}+1} \quad \text{and} \quad N_c = \frac{2V}{h^3}\int d^3p\,\frac{1}{e^{\beta(p^2/(2m)-\mu)}+1} \quad \text{where } \beta = \frac{1}{kT}} \quad (219)$$

(b) The total number of electrons is equal to the number of electrons in the bound states, plus the number of electrons in the continuum states:

$$N = N_b + N_c \quad (220)$$

Plugging in our answers from part (a), we get

$$\boxed{N = \frac{\mathcal{M}}{e^{\beta(-\varepsilon-\mu)}+1} + \frac{2V}{h^3}\int d^3p\,\frac{1}{e^{\beta(p^2/(2m)-\mu)}+1} \quad \text{where } \beta = \frac{1}{kT}} \quad (221)$$

(c) The problem hints that we should use the classical distribution for the occupation number of states in the continuum spectrum. This means that we need to do the following:

$$\text{Replace } n_c^{FD}(\epsilon_k, \mu) = \frac{1}{e^{\beta(p^2/(2m)-\mu)}+1} \text{ with } n_c^{MB}(\epsilon_k, \mu) = e^{-\beta(\epsilon_k-\mu)} = e^{-\beta(p^2/(2m)-\mu)}$$

Once we make this approximation, we can simplify the integral for N_c in our part (b) answer:

$$N_c \approx \frac{2V}{h^3}\int d^3p\,e^{-\beta(p^2/(2m)-\mu)}$$
$$= \frac{2V}{h^3}\int_0^\infty (dp\cdot 4\pi p^2)\,e^{-\beta(p^2/(2m)-\mu)} \quad \text{converting to spherical coordinates}$$
$$= \frac{8\pi V}{h^3}e^{\beta\mu}\int_0^\infty dp\,p^2 e^{-\beta p^2/(2m)} \quad (222)$$

This is a Gaussian integral, which we can solve by hand. Define $A \equiv \beta/(2m)$. Then

$$\int_0^\infty dp\,p^2 e^{-\beta p^2/(2m)} = \int_0^\infty dp\,p^2 e^{-Ap^2} = \frac{1}{2}\int_{-\infty}^\infty dp\,p^2 e^{-Ap^2}$$

In the last step, we have used the fact that the integrand is even to change the lower limit to $-\infty$. The trick now is to simplify this integral into the standard Gaussian integral by means of a derivative in A:

$$\int_0^\infty dp\, p^2 e^{-\beta p^2/(2m)} = \frac{1}{2}\int_{-\infty}^\infty dp\, p^2 e^{-Ap^2} = -\frac{1}{2}\frac{d}{dA}\left[\int_{-\infty}^\infty dp\, e^{-Ap^2}\right]$$

The standard Gaussian integral is solvable using a change of variables $x \equiv \sqrt{A}\,p$ and the result $\int_{-\infty}^\infty dx\, e^{-x^2} = \sqrt{\pi}$:

$$\int_{-\infty}^\infty dp\, e^{-Ap^2} = \frac{1}{(A)^{1/2}}\int_{-\infty}^\infty dx\, e^{-x^2} = \left(\frac{\pi}{A}\right)^{1/2}$$

Taking the derivative of this with respect to A, we get

$$\int_0^\infty dp\, p^2 e^{-\beta p^2/(2m)} = -\frac{1}{2}\frac{d}{dA}\left[\int_{-\infty}^\infty dp\, e^{-Ap^2}\right] = \frac{1}{4}\frac{\pi^{1/2}}{A^{3/2}}$$

Plugging in the definition of A, $A \equiv \beta/(2m) = 1/(2mkT)$, we get

$$\int_0^\infty dp\, p^2 e^{-\beta p^2/(2m)} = \frac{\pi^{1/2}}{4}(2mkT)^{3/2}$$

Plugging this into (222), we get

$$N_c \approx \frac{8\pi V}{h^3}e^{\beta\mu}\left[\frac{\pi^{1/2}}{4}(2mkT)^{3/2}\right] = 2Ve^{\beta\mu}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{223}$$

This isn't quite what we're looking for, since it depends on the chemical potential μ. We want our answer as a function of T and V. Even though the problem doesn't explicitly state this, we should also expect our answer to be in terms of N (part (b), in which we got N in terms of μ, slightly hints at this). Therefore, we should consider our part (b) answer for N in terms of N_b and N_c:

$N = N_b + N_c$

$$N \approx \frac{\mathcal{M}}{e^{\beta(-\varepsilon-\mu)}+1} + 2Ve^{\beta\mu}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \quad \text{(classical distribution for continuum)} \tag{224}$$

We have not yet used two of the approximations in the problem: "few electrons occupy the continuum state" (which means $N_c \ll N_b$), and $kT \ll \varepsilon$ (which means $\beta\varepsilon \gg 1$). Since $N_c \propto (kT)^{3/2}$, the second approximation implies the first. To use the approximation $N_c \ll N_b$, we can simply drop the N_c term in the equation $N = N_b + N_c$:

$$N \approx N_b = \frac{\mathcal{M}}{e^{\beta(-\varepsilon-\mu)}+1} \tag{225}$$

We can solve this equation for μ in terms of T and N:

$$N\left(e^{\beta(-\varepsilon-\mu)}+1\right) \approx \mathcal{M}$$

$$e^{\beta(-\varepsilon-\mu)} \approx \frac{\mathcal{M}-N}{N}$$

$$\beta\left(-\varepsilon-\mu\right) \approx \ln\left(\frac{\mathcal{M}-N}{N}\right)$$

$$\mu \approx -\varepsilon - \frac{1}{\beta}\ln\left(\frac{\mathcal{M}-N}{N}\right)$$

Since $\beta \equiv 1/(kT)$, the chemical potential can be approximated by

$$\boxed{\mu \approx -\varepsilon - kT \ln\left(\frac{\mathcal{M} - N}{N}\right)} \tag{226}$$

We can now plug this result back into our earlier equation for N_c in terms of T, V, and μ. We have

$$e^{\beta\mu} \approx e^{-\beta\varepsilon} \cdot \frac{N}{\mathcal{M} - N} \tag{227}$$

so by (222)

$$\boxed{N_c \approx 2Ve^{\beta\mu}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \approx 2V\, e^{-\beta\varepsilon} \cdot \frac{N}{\mathcal{M} - N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} \tag{228}$$

This part has illustrated an important fact about solving stat mech problems with chemical potentials:

> In problems with Fermi-Dirac or Bose-Einstein statistics, to find the chemical potential μ, first write the number of particles N in terms of μ and then solve for μ.

(d) This part deals with a phenomenon called "Pauli paramagnetism." Broadly speaking, the only way to know how to solve this problem is to have seen it before. However, the problem does give a few hints. First among them is to "work with the thermodynamic potential suitable for the independent variables T, V, μ, B."

Ignoring the magnetic field for a moment, you are probably most used to thermodynamic potentials that are in terms of N, not V. For example, the energy is written in terms of S, V, and N, as we can see from its differential:

$$dE = T\, dS - P\, dV + \mu\, dN \tag{229}$$

Recall that the free energy F swaps S for T by means of a Legendre transform ($F \equiv E - TS$), so F is written in terms of T, V, and N:

$$F \equiv E - TS \quad \text{and} \quad dF = -S\, dT - P\, dV + \mu\, dN \tag{230}$$

To get a thermodynamic potential in terms of T, V, and μ, we should do another Legendre transform to get a new potential Ω, which is called the "grand potential."

$$\Omega \equiv F - \mu N \quad \text{and} \quad d\Omega = -S\, dT - P\, dV - N\, d\mu \tag{231}$$

Given a system in the canonical ensemble, we can find its free energy using the partition function Z:

$$Z(\beta) \equiv \sum_{\text{microstates } r} e^{-\beta E_r} \quad \text{and} \quad F = -kT \ln Z \tag{232}$$

Analogously, for a system in the *grand* canonical ensemble, we can find the grand potential using the grand partition function $\mathcal{Z}$:

$$\mathcal{Z}(T, \mu) \equiv \sum_{\text{microstates } r} e^{-\beta(E_r - \mu N_r)} \quad \text{and} \quad \Omega = -kT \ln \mathcal{Z} \tag{233}$$

The second hint the problem gives us is to "define the magnetic susceptibility as the induced magnetic dipole moment per unit volume per unit applied magnetic field B." Suppose we have a system where each microstate is identified by a magnetic moment m and a set of other

independent quantum numbers r. Then, we introduce a magnetic field B, as stated in the problem, taking $E_r \to E_r - mB$. (The minus sign in the energy comes from the fact that it is energetically favorable for a magnetic dipole to align with an external magnetic field, so the energy is lower when m and B have the same sign.) Then, by definition, the grand partition function for this system will be

$$\mathcal{Z}(T, \mu, B) = \sum_{m,r} e^{-\beta(E_r - mB - \mu N_r)} \tag{234}$$

The average magnetic dipole moment of the system is then equal to the expectation value of the magnetic dipole moment m in the grand canonical ensemble, or

$$\begin{aligned}
\langle m \rangle &= \frac{1}{\mathcal{Z}} \sum_{m,r} m e^{-\beta(E_r - mB - \mu N_r)} \\
&= \frac{1}{\mathcal{Z}} \left[\frac{1}{\beta} \frac{\partial}{\partial B} \left(\sum_{m,r} e^{-\beta(E_r - mB - \mu N_r)} \right) \right] \\
&= \frac{1}{\beta} \cdot \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial B} \\
&= kT \frac{\partial (\ln \mathcal{Z})}{\partial B} \\
&= -\frac{\partial \Omega}{\partial B} \tag{235}
\end{aligned}$$

To get the magnetic susceptibility, divide the average magnetic dipole moment by the volume and take another derivative in the applied magnetic field B, as suggested by the problem statement:

$$\chi_m = \frac{1}{V} \frac{\partial \langle m \rangle}{\partial B} = -\frac{1}{V} \frac{\partial^2 \Omega}{\partial B^2} \tag{236}$$

Hint number three is to "express the magnetic susceptibility at $B = 0$ in terms of the thermodynamic potential in the absence of a magnetic field." Here, the thermodynamic potential we're working with is the grand potential, and we need to differentiate the grand potential twice to get the magnetic susceptibility. Therefore, to follow the hint, we should write the grand potential for $B \neq 0$ in terms of the grand potential for $B = 0$. Since the grand potential comes from the grand partition function, we should start by writing the grand partition function for $B \neq 0$ in terms of the grand partition function for $B = 0$.

Since we are working with fermions, the only way to incorporate the Fermi-Dirac statistics is by considering single-particle states. Usually, we don't worry too much about spin when talking about single-particle states. But for this part of the problem, the spin of the particle changes the energy level, so we must pay close attention.

Let's start by talking about what how we would calculate the grand partition function in parts (a)-(c) of this problem. Consider a single-particle state for an electron. Whether it is a bound state or a continuum state, this state is identified by two quantum numbers:

- the spin of the electron s, where we can take $s = +1$ for spin up and $s = -1$ for spin down, and

- all other quantum numbers, which we will call r.

By the Pauli exclusion principle, there can be at most one electron in this state. Assuming $B = 0$, the energy of filling this state with a single electron ϵ_r depends only on r, not on the

electron spin s. By definition of the grand partition function, the grand partition function for this single-particle state with $B = 0$ is

$$\mathcal{Z}_{0,r}(T, \mu) = 1 + e^{-\beta(\epsilon_r - \mu)} \quad \text{for } B = 0 \tag{237}$$

The "1" term corresponds to the state being empty, while the $e^{-\beta(\epsilon_r - \mu)}$ term corresponds to the state being filled with one electron. Note that the two-argument form of $\mathcal{Z}_0(T, \mu)$ will be used to indicate the grand partition function with $B = 0$.

We can get the grand potential from this grand partition function. Since the single-particle states are independent in the grand canonical ensemble, the grand partition function of the entire system is the product of the grand partition functions of each single-particle state:

$$\mathcal{Z}_0(T, \mu) = \prod_{r,s} \mathcal{Z}_{0,r}(T, \mu) \quad \text{for } B = 0 \tag{238}$$

To get the grand potential of the system with no magnetic field, take the logarithm:

$$\begin{aligned}
\Omega_0(T, \mu) &= -kT \ln \mathcal{Z}_0(T, \mu) \\
&= -kT \ln \left[\prod_{r,s} \mathcal{Z}_{0,r}(T, \mu) \right] \\
&= -kT \sum_{r,s} \ln \left[\mathcal{Z}_{0,r}(T, \mu) \right] \quad \text{by log rules} \\
&= -kT \sum_r \left(\ln \left[\mathcal{Z}_{0,r}(T, \mu) \right] + \ln \left[\mathcal{Z}_{0,r}(T, \mu) \right] \right) \quad \text{since } s = \pm 1 \\
\implies \Omega_0(T, \mu) &= -2kT \sum_r \ln \left[\mathcal{Z}_{0,r}(T, \mu) \right] \quad \text{for } B = 0 \tag{239}
\end{aligned}$$

Notice that the spin degeneracy prefactor of 2 has entered the grand potential.

Now suppose we add in the contribution of the magnetic field. The grand partition function for this single-particle state now depends on the spin $s = \pm 1$. The magnetic moment of the electron is $m = s\kappa$, so if the state is filled, the energy is now $\epsilon_r - mB = \epsilon_r - s\kappa B$. The grand partition function for this state is now

$$\mathcal{Z}_{r,s}(T, \mu, B) = 1 + e^{-\beta(\epsilon_r - s\kappa B - \mu)} \tag{240}$$

Now for the key trick: writing the grand partition function for $B \neq 0$ in terms of the grand partition function for $B = 0$, i.e., writing (240) in terms of (237). By inspection, we can fold the energy shift $-s\kappa B$ into a change in the chemical potential:

$$\mathcal{Z}_{r,s}(T, \mu, B) = \mathcal{Z}_{0,r}(T, \mu + s\kappa B) \tag{241}$$

We are ready to carry this relation between partition functions through to a relation between grand potentials. Since the single-particle states are independent in the grand canonical ensemble, the grand partition function of the entire system is the product of the grand partition functions of each single-particle state:

$$\mathcal{Z}(T, \mu, B) = \prod_{r,s} \mathcal{Z}_{r,s}(T, \mu, B) \tag{242}$$

Applying (241), this gives us

$$\mathcal{Z}(T, \mu, B) = \prod_{r,s} \mathcal{Z}_{0,r}(T, \mu + s\kappa B) \tag{243}$$

We can take the logarithm of this relation to derive a relation between grand potentials:

$$\Omega(T, \mu, B) = -kT \ln \mathcal{Z}(T, \mu, B)$$

$$= -kT \ln \left[\prod_{r,s} \mathcal{Z}_{0,r}(T, \mu + s\kappa B) \right]$$

$$= -kT \sum_{r,s} \ln \left[\mathcal{Z}_{0,r}(T, \mu + s\kappa B) \right]$$

$$= -kT \ln \left[\mathcal{Z}_{0,r}(T, \mu + \kappa B) \right] - kT \ln \left[\mathcal{Z}_{0,r}(T, \mu - \kappa B) \right] \quad \text{since } s = \pm 1$$

$$\Omega(T, \mu, B) = \frac{1}{2} \left[\Omega_0(T, \mu + \kappa B) + \Omega_0(T, \mu - \kappa B) \right] \quad \text{comparing with (239)} \tag{244}$$

The factor of $1/2$ is needed to make this equation self-consistent when $B = 0$.

We can plug this equation into (236) to get an expression for the magnetic susceptibility in terms of the grand potential for $B = 0$:

$$\chi_m = -\frac{1}{V} \frac{\partial^2 \Omega}{\partial B^2}$$

$$= -\frac{1}{2V} \left[\kappa^2 \frac{\partial^2 \Omega_0}{\partial \mu^2} + (-\kappa)^2 \frac{\partial^2 \Omega_0}{\partial \mu^2} \right] \quad \text{using the chain rule on (244)}$$

$$\chi_m = -\frac{\kappa^2}{V} \frac{\partial^2 \Omega_0}{\partial \mu^2} \tag{245}$$

Finally, hint number 4 is to "use the results obtained in part (c)." We did not calculate the grand potential in part (c). However, we did find an closed-form expression for the number of particles in the continuum N_c in terms of T, V, and μ, assuming $B = 0$. We already had an expression for the number of particles in the bound states N_b in terms of T, V, and μ, assuming $B = 0$. So we have a closed-form expression for the total number of particles in the system N.

Noticing that the grand potential Ω_0 is also in terms of T, V, and μ, we might try to relate Ω_0 to N. For a general system (with or without spin), the average number of particles in that system is the expectation value of N:

$$\langle N \rangle = \frac{1}{\mathcal{Z}} \sum_r N_r e^{-\beta(E_r - \mu N_r)} \tag{246}$$

$$= \frac{1}{\mathcal{Z}} \left[-\frac{1}{\beta} \frac{\partial}{\partial \mu} \left(\sum_r e^{-\beta(E_r - \mu N_r)} \right) \right]$$

$$= \frac{1}{\mathcal{Z}} \left[\frac{1}{\beta} \frac{\partial \mathcal{Z}}{\partial \mu} \right]$$

$$= \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

$$= -\frac{\partial(-kT \ln \mathcal{Z})}{\partial \mu}$$

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} \tag{247}$$

Substituting this in (245), we get an expression for the magnetic susceptibility in terms of the number of electrons in the system when $B = 0$, which we calculated in part (c):

$$\chi_m = \frac{\kappa^2}{V} \frac{\partial N}{\partial \mu} \tag{248}$$

From part (c) (see (223)), we have an approximation for the number of electrons in the system, in terms of T, V, and μ:

$$N_0 = N_b + N_c \approx \frac{\mathcal{M}}{e^{\beta(-\varepsilon-\mu)} + 1} + 2Ve^{\beta\mu}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \tag{249}$$

Taking the derivative with respect to μ, we get

$$\frac{\partial N}{\partial \mu} \approx \frac{\mathcal{M}\beta e^{\beta(-\varepsilon-\mu)}}{\left(e^{\beta(-\varepsilon-\mu)} + 1\right)^2} + 2\beta Ve^{\beta\mu}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

By (227),

$$e^{\beta\mu} \approx e^{-\beta\varepsilon} \cdot \frac{N}{\mathcal{M} - N}$$

Plugging this in, we get

$$\frac{\partial N}{\partial \mu} \approx \frac{\mathcal{M}\beta\left(\frac{\mathcal{M}-N}{N}\right)}{\left(\left(\frac{\mathcal{M}-N}{N}\right) + 1\right)^2} + 2\beta Ve^{-\beta\varepsilon} \cdot \frac{N}{\mathcal{M} - N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

The first term can be simplified:

$$\frac{\mathcal{M}\beta\left(\frac{\mathcal{M}-N}{N}\right)}{\left(\left(\frac{\mathcal{M}-N}{N}\right) + 1\right)^2} = \frac{\mathcal{M}}{kT}\frac{\frac{\mathcal{M}-N}{N}}{\left(\left(\frac{\mathcal{M}-N}{N}\right) + 1\right)^2}$$

$$= \frac{\mathcal{M}}{kT}\frac{\frac{\mathcal{M}-N}{N}}{\frac{\mathcal{M}^2}{N^2}}$$

$$= \frac{N}{kT}\frac{\mathcal{M}-N}{\mathcal{M}}$$

This gets us

$$\frac{\partial N}{\partial \mu} \approx \frac{N}{kT}\left(\frac{\mathcal{M}-N}{\mathcal{M}}\right) + \frac{N}{kT}\left(2Ve^{-\beta\varepsilon}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{1}{\mathcal{M}-N}\right) \tag{250}$$

Plugging this into (248), we get a result for the magnetic susceptibility

$$\boxed{\chi_m \approx \frac{N\kappa^2}{VkT}\left(\frac{\mathcal{M}-N}{\mathcal{M}} + \frac{2V}{\mathcal{M}-N}e^{-\beta\varepsilon}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) \quad \text{where } \beta = 1/(kT)} \tag{251}$$

Since we are assuming low temperature, $\beta\varepsilon \gg 1$ and so the second term is subleading compared to the first. In fact, we could have ignored the second term altogether in this part, on the grounds that $N_c \ll N_b$ at low temperature.