PHY 460 — Thermodynamics and Statistical Physics

Name: Khalifa Salem Almatrooshi
Student Number: @00090847

Due Date: 7 May 2024
Assignment: 3

Statement of the Problem

Consider a system of non-interacting electrons, each with a Hamiltonian $\mathcal{H}_1 = \dfrac{\hbar^2 \boldsymbol{k}^2}{2m} - \mu_0\, \boldsymbol{\sigma} \cdot \boldsymbol{B}$, where $\mu_0 = \dfrac{e\hbar}{2mc}$ and the eignevalues of $\boldsymbol{\sigma} \cdot \boldsymbol{B}$ are $\pm B$. ($\boldsymbol{B}$ is an external magnetic field) The energy of the electron system can be written as

$$E = \sum_{\vec{k}} \left(\frac{\hbar^2 \boldsymbol{k}^2}{2m} - \mu_0 B \right) n_k^+ + \left(\frac{\hbar^2 \boldsymbol{k}^2}{2m} + \mu_0 B \right) n_k^- \tag{1}$$

(a) Compute the grand potential $\mathcal{G} = -k_{\mathrm{B}} T \ln \mathcal{Z}$ where $\mathcal{Z}$ is the grand partition function of the system at a chemical potential μ. (Do not confuse μ with μ_0)

Solution In lecture we have derived the grand partition function $\mathcal{Z}$ for a system of non-interacting bodies in finding the trace of $\mathcal{Z}$, $\operatorname{tr}\left(\exp\left(-\beta \hat{H} + \beta \hat{N}\right)\right)$, by working with the Fock basis. I will use those steps to find $\mathcal{Z}$ of this system.

$$\mathcal{Z} = \sum_{n_q} \exp\left\{ -\beta \sum_q \varepsilon_q \hat{n}_q + \beta\mu \sum_q \hat{n}_q \right\} = \cdots = \prod_q \sum_{n_q} \exp\left\{ (-\beta\varepsilon_q + \beta\mu) n_q \right\} \tag{2}$$

For n_q, we only iterate over n_k^+ and n_k^-. Let $\varepsilon_k^{\pm} = \frac{\hbar^2 \boldsymbol{k}^2}{2m} \mp \mu_0 B$

$$\mathcal{Z} = \sum_{n_k^+} \sum_{n_k^-} \exp\left\{ -\beta \sum_k \left[\varepsilon_k^+ n_k^+ + \varepsilon_k^- n_k^- \right] + \beta\mu \sum_k (n_k^+ + n_k^-) \right\} \tag{3}$$

Combing all n_k terms.

$$\mathcal{Z} = \sum_{n_k^+} \sum_{n_k^-} \exp\left\{ \beta \sum_k \left[\left(\mu - \varepsilon_k^+\right) n_k^+ + \left(\mu - \varepsilon_k^-\right) n_k^- \right] \right\} \tag{4}$$

The sum of the exponents in an exponential is equivalent to the product of exponentials.

$$\mathcal{Z} = \prod_k \sum_{n_k^+} \sum_{n_k^-} \exp\left\{ \beta \left(\mu - \varepsilon_k^+\right) n_k^+ + \beta \left(\mu - \varepsilon_k -\right) n_k^- \right\} \tag{5}$$

For fermions the occupation number n_k can only take the values 0 or 1 due to the Pauli exclusion principle.

$$\mathcal{Z} = \prod_k \left(1 + \exp\left\{ -\beta \left(\varepsilon_k^+ - \mu\right) \right\}\right) \left(1 + \exp\left\{ -\beta \left(\varepsilon_k^- - \mu\right) \right\}\right) \tag{6}$$

$$\mathcal{Z} = \prod_k \left[Z_k^+ \cdot Z_k^- \right] \tag{7}$$

$$\ln(\mathcal{Z}) = \sum_k \left[\ln\left(Z_k^+\right) + \ln\left(Z_k^-\right) \right] \tag{8}$$

Now we have the final expression for the grand potential G. $\beta = \frac{1}{\tau} = \frac{1}{k_{\mathrm{B}} T}$

$$G = -\frac{1}{\beta} \sum_k \left[\ln\left(Z_k^+\right) + \ln\left(Z_k^-\right) \right] \tag{9}$$

$$G = G_+ + G_- \tag{10}$$

At this point we convert the summation to an integral by taking the first term in the Euler–Maclaurin approximation.

$$\sum_{i=m}^{n} f(i) = \int_m^n f(x)\, dx + \frac{f(n) + f(m)}{2} + \cdots + R_p \tag{11}$$

This introduces the density of states $g(k)$ and the spin degeneracy $2S + 1$ (inside $g(k)$).

$$G = -\frac{1}{\beta} \int_k g(k) \left[G_+ + G_- \right]\, dk \tag{12}$$

The density of states $g(k)$ can found by considering a quantum gas in a box with length L and corner at the origin.

$$g(k)\ dk = \frac{\text{Volume in k-space of one octant of a spherical shell}}{\text{Volume of k-space occupied per allowed state}} \tag{13}$$

$$= \frac{\frac{1}{8}\cdot 4\pi k^2\ dk}{(\pi/L)^3} = \frac{Vk^2\ dk}{2\pi^2} \tag{14}$$

We add the spin degeneracy $2S+1$, but in a magnetic field the spin degeneracy is lifted because of the Zeeman effect, where the energy levels of the spin states split.

$$g(k)\ dk = \frac{Vk^2\ dk}{2\pi^2} \tag{15}$$

$$G = -\frac{V}{2\beta\pi^2}\left[\int_0^\infty k^2 \ln\left(1+\exp\left\{-\beta\left(\varepsilon_k^+ - \mu\right)\right\}\right)\ dk + \int_0^\infty k^2 \ln\left(1+\exp\left\{-\beta\left(\varepsilon_k^- - \mu\right)\right\}\right)\ dk\right] \tag{16}$$

We can define the fugacity $\lambda \equiv \exp(\beta\mu)$. Also I will merge the integrals together to simplify computation.

$$G = -\frac{V}{2\beta\pi^2}\int_0^\infty k^2 \ln\left(1+\lambda\exp\left\{-\beta\left(\frac{\hbar^2\boldsymbol{k}^2}{2m} \mp \mu_0 B\right)\right\}\right)\ dk \tag{17}$$

$$G = -\frac{V}{2\beta\pi^2}\int_0^\infty k^2 \ln\left(1+\lambda e^{\pm\beta\mu_0 B}\exp\left\{-\beta\frac{\hbar^2\boldsymbol{k}^2}{2m}\right\}\right)\ dk \tag{18}$$

A change of variables, $x = \beta\frac{\hbar^2 k^2}{2m}$.

$$G = -\frac{V}{2\beta\pi^2}\int_0^\infty k^2 \ln\left(1+\lambda e^{\pm\beta\mu_0 B}e^{-x}\right)\frac{m}{\beta\hbar^2 k}\ dx \tag{19}$$

$$G = -\frac{V}{2\beta\pi^2}\frac{m}{\beta\hbar^2}\sqrt{\frac{2m}{\beta\hbar^2}}\int_0^\infty \sqrt{x}\ln\left(1+\lambda e^{\pm\beta\mu_0 B}e^{-x}\right)\ dx \tag{20}$$

$$G = -\frac{V\sqrt{2}}{2\beta\pi^2}\left(\frac{m}{\beta\hbar^2}\right)^{3/2}\int_0^\infty \sqrt{x}\ln\left(1+\lambda e^{\pm\beta\mu_0 B}e^{-x}\right)\ dx \tag{21}$$

We can rearrange to find $\lambda_{th} = \sqrt{\frac{h^2}{2\pi m k_{\mathrm{B}}T}} = \sqrt{\frac{2\pi\hbar^2\beta}{m}}$.

$$G = -\frac{V2^{1/2}2^{3/2}\sqrt{\pi}}{2\beta\pi^2}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}\int_0^\infty \sqrt{x}\ln\left(1+\lambda e^{\pm\beta\mu_0 B}e^{-x}\right)\ dx \tag{22}$$

$$G = -\frac{V}{\beta\lambda_{th}^3}\frac{2}{\sqrt{\pi}}\int_0^\infty \sqrt{x}\ln\left(1+\lambda e^{\pm\beta\mu_0 B}e^{-x}\right)\ dx \tag{23}$$

Integrating by parts, $u = \ln\left(1+\lambda e^{\pm\beta\mu_0 B}e^{-x}\right)$, $dv = \sqrt{x}$.

$$G = -\frac{V}{\beta\lambda_{th}^3}\frac{2}{\sqrt{\pi}}\left[\ln\left(1+\lambda e^{\pm\beta\mu_0 B}e^{-x}\right)\frac{2}{3}x^{3/2}\Big|_0^\infty - \int_0^\infty \frac{2}{3}x^{3/2}\frac{-\lambda e^{\pm\beta\mu_0 B}e^{-x}}{1+\lambda e^{\pm\beta\mu_0 B}e^{-x}}\ dx\right] \tag{24}$$

$$G = -\frac{V}{\beta\lambda_{th}^3}\frac{4}{3\sqrt{\pi}}\left[\int_0^\infty \frac{x^{3/2}}{(\lambda e^{\pm\beta\mu_0 B})^{-1}e^x+1}\ dx\right] \tag{25}$$

$$G = -\frac{V}{\beta\lambda_{th}^3}\frac{4}{3\sqrt{\pi}}\left[\int_0^\infty \frac{x^{3/2}}{(\lambda e^{\beta\mu_0 B})^{-1}e^x+1}\ dx + \int_0^\infty \frac{x^{3/2}}{(\lambda e^{-\beta\mu_0 B})^{-1}e^x+1}\ dx\right] \tag{26}$$

From appendix C in Concepts in Thermal Physics by Katherine Blundell and Stephen Blundell. The integrals can be written in terms of the polylogarithm function $\mathrm{Li}_n(z)$.

$$\int_0^\infty \frac{x^{n-1}\ dx}{z^{-1}e^x \pm 1} = \mp\Gamma(n)\mathrm{Li}_n(\mp z) \tag{27}$$

$$G = \frac{V}{\beta\lambda_{th}^3}\frac{4}{3\sqrt{\pi}}\Gamma(\tfrac{5}{2})\left[\mathrm{Li}_{\frac{5}{2}}(-\lambda e^{\beta\mu_0 B}) + \mathrm{Li}_{\frac{5}{2}}(-\lambda e^{-\beta\mu_0 B})\right] \tag{28}$$

We can further simplify by $\lambda^{\pm} = \lambda e^{\pm\beta\mu_0 B}$ and $\Gamma(\frac{5}{2}) = 3\sqrt{\pi}/4$.

$$\boxed{G = \frac{V}{\beta\lambda_{th}^3}\left[\mathrm{Li}_{\frac{5}{2}}(-\lambda^+) + \mathrm{Li}_{\frac{5}{2}}(-\lambda^-)\right]} \tag{29}$$

(b) Calculate the densities $n^+ = \frac{N^+}{V}$ and $n^+ = \frac{N^+}{V}$ of electrons pointing parallel and anti-parallel to the field.

Solution The average number of particles is found by

$$\left\langle \hat{N} \right\rangle = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln(\mathcal{Z}) = -\frac{\partial}{\partial \mu}G \tag{30}$$

Working from equation 21 as working with a logarithm is easier.

$$-\frac{\partial}{\partial \mu}G = \frac{V}{\beta\lambda_{th}^3}\frac{4}{3\sqrt{\pi}}\int_0^\infty \sqrt{x}\frac{\partial}{\partial \mu}\left(\ln\left(1+e^{\mu\beta}e^{\pm\beta\mu_0 B}e^{-x}\right)\right)\,dx \tag{31}$$

$$= \frac{V}{\beta\lambda_{th}^3}\frac{4}{3\sqrt{\pi}}\int_0^\infty \sqrt{x}\frac{\beta e^{\mu\beta}e^{\pm\beta\mu_0 B}e^{-x}}{1+e^{\mu\beta}e^{\pm\beta\mu_0 B}e^{-x}}\,dx \tag{32}$$

$$N^\pm = \frac{V}{\lambda_{th}^3}\frac{4}{3\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}}{(\lambda e^{\pm\beta\mu_0 B})^{-1}e^x+1}\,dx \tag{33}$$

$$n^\pm = \frac{1}{\lambda_{th}^3}\frac{4}{3\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}}{(\lambda e^{\pm\beta\mu_0 B})^{-1}e^x+1}\,dx \tag{34}$$

Converting to polylogarithm and $\lambda^\pm$.

$$\boxed{n^\pm = \frac{1}{\lambda_{th}^3}\mathrm{Li}_{\frac{3}{2}}(-\lambda^\pm)} \tag{35}$$

$$N = N^+ + N^- = \frac{V}{\lambda_{th}^3}\left[\mathrm{Li}_{\frac{3}{2}}(-\lambda^+) + \mathrm{Li}_{\frac{3}{2}}(-\lambda^-)\right] \tag{36}$$

(c) Determine an expression of the magnetization $M = \mu_0(N_+ - N_-)$ and expand the result for small magnetic field B.

Solution

$$M = \frac{V\mu_0}{\lambda_{th}^3}\left[\mathrm{Li}_{\frac{3}{2}}(-\lambda^+) - \mathrm{Li}_{\frac{3}{2}}(-\lambda^-)\right] \tag{37}$$

$$M = \frac{V\mu_0}{\lambda_{th}^3}\left[\mathrm{Li}_{\frac{3}{2}}(-\lambda e^{\beta\mu_0 B}) - \mathrm{Li}_{\frac{3}{2}}(-\lambda e^{-\beta\mu_0 B})\right] \tag{38}$$

The only term affected by the magnetic field B is the exponential. At small magnetic field B, the exponential can be approximated by the first few terms of its taylor series, $e^x = \sum \frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \cdots$. For simplicity we take the first two terms.

$$M = \frac{V\mu_0}{\lambda_{th}^3}\left[\mathrm{Li}_{\frac{3}{2}}(-\lambda(1+\beta\mu_0 B)) - \mathrm{Li}_{\frac{3}{2}}(-\lambda(1-\beta\mu_0 B))\right] \tag{39}$$

$$M = \frac{V\mu_0}{\lambda_{th}^3}\left[\mathrm{Li}_{\frac{3}{2}}(-\lambda-\lambda\beta\mu_0 B) - \mathrm{Li}_{\frac{3}{2}}(-\lambda+\lambda\beta\mu_0 B)\right] \tag{40}$$

The polylogarithm function can also be expanded for small B by approximating with the first order taylor expansion, $f(x \pm \Delta x) \approx f(x) \pm \Delta x f'(x)$.

$$M = \frac{V\mu_0}{\lambda_{th}^3}\left[\mathrm{Li}_{\frac{3}{2}}(-\lambda) + \lambda\beta\mu_0 B\frac{\partial}{\partial\lambda}\mathrm{Li}_{\frac{3}{2}}(-\lambda) - \left(\mathrm{Li}_{\frac{3}{2}}(-\lambda) - \lambda\beta\mu_0 B\frac{\partial}{\partial\lambda}\mathrm{Li}_{\frac{3}{2}}(-\lambda)\right)\right] \tag{41}$$

$$M = \frac{V\mu_0}{\lambda_{th}^3}\left[2\lambda\beta\mu_0 B\frac{\partial}{\partial\lambda}\mathrm{Li}_{\frac{3}{2}}(-\lambda)\right] \tag{42}$$

From https://mathworld.wolfram.com/Polylogarithm.html, we can easily find the derivative of the polylogarithm function where $x\partial_x \mathrm{Li}_n(x) = \mathrm{Li}_{n-1}(x)$.

$$\boxed{M = \frac{2V\mu_0^2\beta B}{\lambda_{th}^3}\mathrm{Li}_{\frac{1}{2}}(-\lambda)} \tag{43}$$

(d) Determine the zero-field susceptibility $\mathcal{X}(T) = \left.\frac{\partial M}{\partial B}\right|_{B=0}$ and give its behavior at low and at high temperatures.

Solution

$$\left.\frac{\partial M}{\partial B}\right|_{B=0} = \frac{2V\mu_0^2\beta}{\lambda_{th}^3}\mathrm{Li}_{\frac{1}{2}}(-\lambda) \tag{44}$$

We also know that N depends on B, so from equation 36, it reduces to

$$N = N^+ + N^- = \frac{2V}{\lambda_{th}^3}\mathrm{Li}_{\frac{3}{2}}(-\lambda) \tag{45}$$

Starting with the high temperature limit, since $\lambda \equiv e^{\beta\mu}$, as $k_\mathrm{B}T \to \infty$ then $\beta \to 0$. We can drop the +1 in $\mathrm{Li}_n(-\lambda)$ as it is negligible at this limit.

$$\mathrm{Li}_n(-\lambda) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}\,dx}{\lambda^{-1}e^x+1} \approx \frac{\lambda}{\Gamma(n)}\int_0^\infty x^{n-1}e^{-x}\,dx = \lambda \tag{46}$$

$$\mathcal{X}(T\to\infty) = \frac{2V\mu_0^2}{k_\mathrm{B}T\lambda_{th}^3}\lambda \tag{47}$$

We can define λ in terms of N.

$$N = \frac{2V}{\lambda_{th}^3}\lambda \tag{48}$$

$$\lambda = \frac{N\lambda_{th}^3}{2V} \tag{49}$$

$$\mathcal{X}(T\to\infty) = \frac{N\mu_0^2}{k_\mathrm{B}T} \tag{50}$$

$$\boxed{\left.\frac{\mathcal{X}}{N}\right|_{T\to\infty} = \frac{\mu_0^2}{k_\mathrm{B}T}} \tag{51}$$

Now the low temperature limit, since $\lambda \equiv e^{\beta\mu}$, as $k_\mathrm{B}T \to 0$ then $\beta \to \infty$.

$$\begin{aligned}\mathrm{Li}_n(-\lambda) &= \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}\,dx}{e^{x-\beta\mu}+1} && (52)\\ &= \frac{1}{\Gamma(n)}\left[\left(e^{x-\beta\mu}+1\right)^{-1}\left.\frac{x^n}{n}\right|_0^\infty - \int_0^\infty \frac{x^n}{n}\frac{e^{x-\beta\mu}\,dx}{\left(e^{x-\beta\mu}+1\right)^2}\right] && (53)\\ &= \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^n}{n}\frac{e^{x-\beta\mu}\,dx}{\left(e^{x-\beta\mu}+1\right)^2} && (54)\end{aligned}$$

As T decreases, μ approaches the Fermi energy ϵ_F, so we can redefine x as $x_\mathrm{F} = \beta\frac{\hbar^2k_\mathrm{F}^2}{2m} = \beta\epsilon_\mathrm{F} = \beta k_\mathrm{B}T_\mathrm{F}$

$$\mathrm{Li}_n(-\lambda) = \frac{x_\mathrm{F}^n}{n\Gamma(n)}\int_0^{x_\mathrm{F}} \frac{e^{x-\beta\mu}\,dx}{\left(e^{x-\beta\mu}+1\right)^2} \tag{55}$$

$$\left.\frac{\mathcal{X}}{N}\right|_{T\to 0} = \frac{\mu_0^2}{k_\mathrm{B}T}\frac{\mathrm{Li}_{1/2}(-\lambda)}{\mathrm{Li}_{3/2}(-\lambda)} \tag{56}$$

Since the integral in the expression is the same for both polylogarithms, they cancel out.

$$\begin{aligned}&= \frac{\mu_0^2}{k_\mathrm{B}T}\frac{x_\mathrm{F}^{1/2}}{\frac{1}{2}\Gamma(\frac{1}{2})}\frac{\frac{3}{2}\Gamma(\frac{3}{2})}{x_\mathrm{F}^{3/2}} && (57)\\ &= \frac{3\mu_0^2}{k_\mathrm{B}T}\frac{1}{\sqrt{\pi}}\frac{\frac{\sqrt{\pi}}{2}}{x_\mathrm{F}} && (58)\\ &= \frac{3\mu_0^2}{2k_\mathrm{B}T}\frac{1}{\beta\epsilon_\mathrm{F}} && (59)\end{aligned}$$

$$\boxed{\left.\frac{\mathcal{X}}{N}\right|_{T\to 0} = \frac{3\mu_0^2}{2k_\mathrm{B}T_\mathrm{F}}} \tag{60}$$

(e) Graph $\dfrac{\mathcal{X}}{N\mu_0^2}$ versus T, here $N = N^+ + N^-$ is the total number of electrons.

Solution The two limits form asymptotes for the zero-field susceptibility. The limit to infinity depends on T, while the limit to zero does not depend on T (straight line).