Contribution to specific heat of a metal due to
the electrons is

$$C_V^{elec} = \frac{\pi^2}{2}\left(\frac{T}{T_F}\right) n k_B \left(1 + 0\left(\frac{T}{T_F}\right)^2\right)$$

Classical result would be $C_V^{elec} = \frac{3}{2} n k_B$

So quantum result is smaller by a factor
$$\frac{\pi^2}{2}\left(\frac{T}{T_F}\right) \sim \frac{10^2}{10^4} \sim 10^{-2}$$

classical C_V^{elec} is independent of T
quantum result is $\propto T$

We also had that the contribution to the specific heat
due to ionic vibrations (quantized sound modes = phonons)
at low temperatures is

$$C_V^{ion} = \frac{12\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3 n k_B \qquad \sim T^3$$

at room temperature $C_V^{ion} \gg C_V^{elec}$. But at sufficiently
low T, since $C_V^{ion} \sim T^3$ while $C_V^{elec} \sim T$, eventually
C_V^{elec} becomes the dominant contribution. This
happens at a T^* such that

$$1 = \frac{C_V^{elec}}{C_V^{ion}} = \frac{\pi^2}{2}\left(\frac{T^*}{T_F}\right)\frac{5}{12\pi^4}\left(\frac{\Theta_D}{T^*}\right)^3 = \frac{5}{24\pi^2}\left(\frac{\Theta_D}{T_F}\right)\left(\frac{\Theta_D}{T^*}\right)^2$$

$$T^* = \sqrt{\frac{5}{24\pi^2}\left(\frac{\Theta_D}{T_F}\right)}\,\Theta_D \simeq 0.15\left(\frac{\Theta_D}{T_F}\right)^{1/2}\Theta_D$$

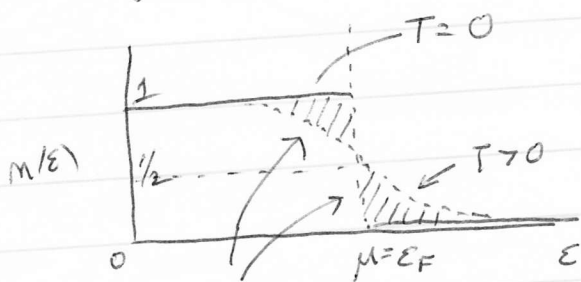$T_F \sim 10^4 K$, $\Theta_D \sim 10^2 K$, $\Rightarrow T^* \simeq 0.05\,\Theta_D \sim O(1) K$

At $T=0$, $\mu = \varepsilon_F$. As T increases, does μ increase, decrease, or stay the same?

Note: μ must vary with temperature so that the density

$$n = \int_0^\infty d\varepsilon \; n(\varepsilon) g(\varepsilon) \qquad n(\varepsilon) = \frac{1}{z^{-1} e^{\beta \varepsilon} + 1}$$

stays constant.

Suppose μ stayed constant, $\mu = \varepsilon_F$, as T increased

because $\frac{\partial n}{\partial \varepsilon}$ is symmetric about μ, these two areas are equal.

The number of electrons that get removed from below ε_F is then $\sim g(\mu - \frac{k_B T}{2}) k_B T$, while the number of electrons added above ε_F is $g(\mu + \frac{k_B T}{2}) k_B T$. These two should be equal.

But since $g(\varepsilon) \sim \sqrt{\varepsilon}$ is an <u>increasing</u> function of ε there are more energy states within $k_B T$ above ε_F than there are energy states within $k_B T$ below ε_F, ie $g(\mu + \frac{k_B T}{2}) k_B T > g(\mu - \frac{k_B T}{2}) k_B T$

The only way we can keep n constant is for μ to <u>decrease</u> as T increases. From Sommerfeld expansion:

$$\mu(T) = \varepsilon_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} + \cdots$$

Pauli paramagnetism of electron gas

$$\underbrace{\vec{s} = \tfrac{1}{2}\hbar\vec{\sigma}}$$

electron has intrinsic spin $\vec{\sigma}$ with intrinsic magnetic moment $\vec{\mu} = -\mu_B \vec{\sigma}$ $\mu_B = \dfrac{|e|\hbar}{2mc}$ is Bohr magneton

In an external magnetic field $\vec{B}$, there is an interaction energy $-\vec{\mu}\cdot\vec{B} = \mu_B \sigma B$ where $\sigma = \pm 1$ for spins parallel and antiparallel to $\vec{B}$. The energy spectra for up and down electron spins becomes

$$\epsilon_{\pm}(\vec{k}) = \epsilon(\vec{k}) \pm \mu_B B \qquad \text{where } \epsilon(\vec{k}) \text{ is spectrum at } \vec{B} = 0$$

Since $\uparrow$ and $\downarrow$ electrons now have different energy spectra, we should treat them as two different populations of particles $\Rightarrow$ ~~they~~ they will be in equilibrium when their chemical potentials are equal, ie $\mu_+ = \mu_-$

this will induce a net magnetization in the system.

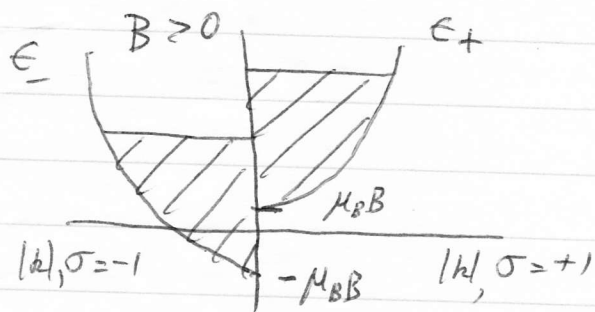To see this, consider free electrons at $T=0$

$$\vec{B} = 0$$

$\mathcal{E}(k)$ $\mathcal{E}_+(k)$

$\mathcal{E}_F$

filled states

$|k|, \sigma = -1$ 0 $|k|, \sigma = +1$
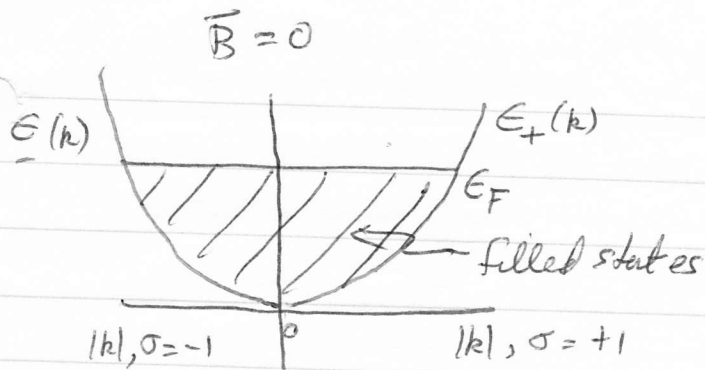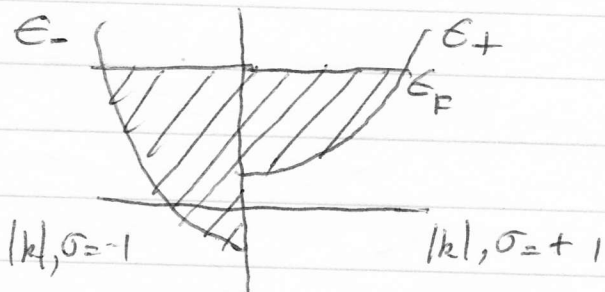
When $\vec{B} = 0$, $\mathcal{E}_+(\vec{k}) = \mathcal{E}_-(\vec{k})$

ground state occupations look as shown on the left. Equal numbers of ↑ and ↓ electrons

$$n_+ = n_-$$

When $\vec{B}$ is turned on, if there were no redistribution of electron spins, the situation would look like

$\mathcal{E}_-$ $B > 0$ $\mathcal{E}_+$

$\mu_B B$

$|k|, \sigma = -1$ $-\mu_B B$ $|k|, \sigma = +1$

Clearly the system can lower its energy by transferring ↑ electrons to ↓ electrons.

At equilibrium the system will look like

$\mathcal{E}_-$ $\mathcal{E}_+$

$\mathcal{E}_F$

$|k|, \sigma = -1$ $|k|, \sigma = +1$

again the two populations have the same max energy $\mathcal{E}_F$. But there are now more ↓ electrons than ↑ electrons

magnetization $\dfrac{M}{V} = -\mu_B (n_+ - n_-) > 0$

$\dfrac{\vec{M}}{V}$ is parallel to $\vec{B}$ $\Rightarrow$ <u>paramagnetic</u> <u>effect</u>

the calculation

Let $g(\epsilon)$ be the density of states when $B = 0$

when $B > 0$, the density of states for $\uparrow$ and $\downarrow$ electrons are

$$g_+(\epsilon + \mu_B B) = \tfrac{1}{2} g(\epsilon) \quad \Rightarrow \quad g_+(\epsilon) = \tfrac{1}{2} g(\epsilon - \mu_B B)$$
$$g_-(\epsilon - \mu_B B) = \tfrac{1}{2} g(\epsilon) \qquad\qquad g_-(\epsilon) = \tfrac{1}{2} g(\epsilon + \mu_B B)$$

The density of $\uparrow$ and $\downarrow$ electrons is then

$$m_\pm = \int_{\epsilon_{\pm min}}^{\infty} d\epsilon \; g_\pm(\epsilon) \, f(\epsilon, \mu(B)) \qquad\qquad \epsilon_{\pm min} = \pm \mu_B B$$

where
$$f(\epsilon, \mu(B)) = \frac{1}{e^{(\epsilon - \mu(B))/k_B T} + 1}$$

$\mu(B)$ is the chemical potential — it might depend on B
$\qquad\qquad$ — it is same for $\uparrow$ and $\downarrow$

we will consider only the case that
$$\mu_B B \ll \mu(B) \approx \epsilon_F$$
ie spin interaction is small compared to ϵ_F

First we will show that

① $\quad \mu(B) \approx \mu(B=0) \left[1 + O\left(\frac{\mu_B B}{\varepsilon_F} \right)^2 \right]$

Since we will work in the $\mu_B B \ll \varepsilon_F$ limit, we will then be able to ignore changes in μ due to the finite B and just use $\mu(B=0)$

proof: Consider the total density of electrons

$$M = M_+ + M_- = \int_{\mu_B B}^{\infty} d\varepsilon \, f(\varepsilon, \mu(B)) \, g_+(\varepsilon) + \int_{-\mu_B B}^{\infty} d\varepsilon \, f(\varepsilon, \mu(B)) \, g_-(\varepsilon)$$

$$= \frac{1}{2} \int_{\mu_B B}^{\infty} d\varepsilon \, f(\varepsilon, \mu(B)) \, g(\varepsilon - \mu_B B) + \frac{1}{2} \int_{-\mu_B B}^{\infty} d\varepsilon \, f(\varepsilon, \mu(B)) \, g(\varepsilon + \mu_B B)$$

$\underset{\text{shift integration variable } \varepsilon - \mu_B B \to \varepsilon}{\uparrow} \qquad\qquad \underset{\text{shift integration variable } \varepsilon + \mu_B B \to \varepsilon}{\uparrow}$

$$= \frac{1}{2} \int_0^{\infty} d\varepsilon \, g(\varepsilon) \left[f(\varepsilon + \mu_B B, \mu(B)) + f(\varepsilon - \mu_B B, \mu(B)) \right]$$

use the fact that $f(\varepsilon, \mu)$ depends only on $\varepsilon - \mu$

$$\mu = \frac{1}{2} \int_0^{\infty} d\varepsilon \, g(\varepsilon) \left[f(\varepsilon, \mu(B) - \mu_B B) + f(\varepsilon, \mu(B) + \mu_B B) \right]$$

expand f about $\mu(B)$ for small $\mu_B B$

$$m \simeq \frac{1}{2} \int d\epsilon \, g(\epsilon) \left[f(\epsilon, \mu(B)) - \frac{df}{d\mu} \mu_B B + \frac{1}{2} \frac{d^2 f}{d\mu^2} (\mu_B B)^2 + \cdots \right.$$

$$\left. + f(\epsilon, \mu(B)) + \frac{df}{d\mu} \mu_B B + \frac{1}{2} \frac{d^2 f}{d\mu^2} (\mu_B B)^2 + \cdots \right]$$

where derivatives above are evaluated at $\mu = \mu(B)$. the terms linear in B cancell!

$$m \simeq \int d\epsilon \, g(\epsilon) \left[f(\epsilon, \mu(B)) + \frac{1}{2} \frac{d^2 f}{d\mu^2} (\mu_B B)^2 + \cdots \right]$$

If we ignored the $(\mu_B B)^2$ term the above would be

$$m = \int d\epsilon \, g(\epsilon) \, f(\epsilon, \mu(B))$$

But this is just the same formula we use to compute n at $B = 0$! The magnetic field B appears nowhere in the above, except via $\mu(B)$. Since the density is physically fixed by the sample and cannot change as one varies B, we would conclude that

$$\mu(B) = \mu(0) \text{ is independent of } B!$$

conclusion
This depends on our having ignored the $\mu_B B^2$ term, so we can expect

$$\mu(B) \simeq \mu(0) + \frac{(\mu_B B)^2}{\epsilon_F}$$

where $\frac{1}{\epsilon_F}$ appears on dimensional grounds.

To see this is so more explicitly, lets include the $(\mu_B B)^2$ term and continue to calculate ...

$$m = \int d\epsilon \, g(\epsilon) \left[f(\epsilon, \mu(B)) + \frac{1}{2} \frac{d^2 f}{d\mu^2} (\mu_B B)^2 \right]$$

write $\mu(B) = \mu(B=0) + \delta\mu$ and expand in first term

$$m = \int d\epsilon \, g(\epsilon) \left[f(\epsilon, \mu(B=0) + \delta\mu) + \frac{1}{2} \frac{d^2 f}{d\mu^2} (\mu_B B)^2 \right]$$

$$= \int d\epsilon \, g(\epsilon) \, f(\epsilon, \mu(B=0))$$

$$+ \int d\epsilon \, g(\epsilon) \left. \frac{df}{d\mu} \right|_{\mu=\mu(B=0)} \delta\mu$$

$$+ \frac{1}{2} \int d\epsilon \, g(\epsilon) \left. \frac{d^2 f}{d\mu^2} \right|_{\mu=\mu(B)} (\mu_B B)^2$$

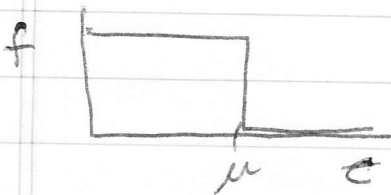The first term is just the density when $B = 0$, ie m. Hence we get

$$0 = \int d\epsilon \, g(\epsilon) \left. \frac{df}{d\mu} \right|_{\mu=\mu(B=0)} \delta\mu + \frac{1}{2} \int d\epsilon \, g(\epsilon) \left. \frac{d^2 f}{d\mu^2} \right|_{\mu=\mu(B)} (\mu_B B)^2$$

So the correction to μ due to finite B is

$$\delta\mu = \frac{-\frac{1}{2} \int d\epsilon \, g(\epsilon) \left. \frac{d^2 f}{d\mu^2} \right|_{\mu=\mu(B)} (\mu_B B)^2}{\int d\epsilon \, g(\epsilon) \left. \frac{df}{d\mu} \right|_{\mu=\mu(B=0)}} \approx - \frac{g'(\epsilon_F)}{2 g(\epsilon_F)} (\mu_B B)^2$$

To see how big this is, consider the limit $T \to 0$ where $\mu(B=0) = \epsilon_F$, and f is a step function

$$\frac{df}{d\mu} = -\frac{df}{d\epsilon} = \delta(\epsilon - \mu)$$

$$\frac{d^2 f}{d\mu^2} = \frac{d^2 f}{d\epsilon^2} = -\frac{d\,\delta(\epsilon - \mu)}{d\epsilon}$$

so $\displaystyle \int d\epsilon\, g(\epsilon) \frac{df}{d\mu}\bigg|_{\mu = \mu(B=0)} = g(\mu(B=0)) = g(\epsilon_F)$

$$\int d\epsilon\, g(\epsilon) \frac{d^2 f}{d\mu^2}\bigg|_{\mu = \mu(B)} (\mu_B B)^2 \simeq g'(\mu(B)) (\mu_B B)^2$$

$$\delta\mu = -\frac{1}{2}\, \frac{g'(\mu(B)) (\mu_B B)^2}{g(\epsilon_F)}$$

to lowest order, evaluate $g'(\mu(B))$ as $g'(\epsilon_F)$
The difference will only give higher order corrections of $O(\mu_B B)^4$

$$\delta\mu = -\frac{g'(\epsilon_F)(\mu_B B)^2}{2 g(\epsilon_F)}$$

for free electrons with $g(\epsilon) = c\sqrt{\epsilon}$ so
$g'(\epsilon) = \frac{1}{2}\frac{c}{\sqrt{\epsilon}}$ we get

$$\boxed{\delta\mu = -\frac{(\mu_B B)^2}{4\epsilon_F}}$$ so $\boxed{\mu(B) = \epsilon_F\left(1 - \left(\frac{\mu_B B}{2\epsilon_F}\right)^2\right)}$

Now we compute

② <u>Magnetization</u> $\dfrac{M}{V} = -\mu_B (m_+ - m_-) = \mu_B (m_- - m_+)$

$$\frac{M}{V} = \mu_B \int d\epsilon \; f(\epsilon, \mu) \left[g_-(\epsilon) - g_+(\epsilon) \right]$$

$$= \mu_B \int d\epsilon \; f(\epsilon, \mu) \left[\tfrac{1}{2} g(\epsilon + \mu_B B) - \tfrac{1}{2} g(\epsilon - \mu_B B) \right]$$

$$= \tfrac{1}{2} \mu_B \int d\epsilon \; g(\epsilon) \left[f(\epsilon, \mu + \mu_B B) - f(\epsilon, \mu - \mu_B B) \right] \qquad \text{as before}$$

expand $f(\epsilon, \mu \pm \mu_B B) = f(\epsilon, \mu) \pm \dfrac{df}{d\mu} \mu_B B$

$$\frac{M}{V} = \tfrac{1}{2} \mu_B \int d\epsilon \; g(\epsilon) \left[2 \frac{df}{d\mu} \mu_B B \right]$$

$$= \mu_B^2 B \int_{-\infty}^{\infty} d\epsilon \; g(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right) \qquad \text{since } \frac{\partial f}{\partial \mu} = -\frac{\partial f}{\partial \epsilon}$$

To lowest order in temperature $-\dfrac{\partial f}{\partial \epsilon} \approx \delta(\epsilon - \mu)$ with $\mu = \epsilon_F$

$$\boxed{\frac{M}{V} = \mu_B^2 B \, g(\epsilon_F)}$$

could use Sommerfeld expansion
to get corrections of order $\left(\dfrac{k_B T}{\epsilon_F} \right)^2$

magnetic susceptibility $\chi = \dfrac{\partial (M/V)}{\partial B}$

Pauli susceptibility $\boxed{\chi_p = \mu_B^2 g(\epsilon_F)}$ $\sim$ density of states at ϵ_F

$\boxed{\epsilon_k = \hbar^2 k^2 / 2m}$

For free electron gas we earlier had $g(\epsilon_F) = \dfrac{3}{2} \dfrac{m}{\epsilon_F}$

$$\Rightarrow \boxed{\chi_p = \mu_B^2 \frac{3}{2} \frac{m}{\epsilon_F}}$$ $\chi_p > 0 \Rightarrow$ paramagnetic

Compare this to __classical result__. Average magnetization of a single spin is

$$\langle m \rangle \underset{(-\mu_B)}{=} \left[\frac{e^{-\beta \mu_B B}(+1) + e^{+\beta \mu_B B}(-1)}{e^{\beta \mu_B B} + e^{-\beta \mu_B B}} \right]$$

$$\langle m \rangle = \mu_B \tanh(\beta \mu_B B)$$

$$\frac{M}{V} = \langle m \rangle \frac{N}{V} = \mu_B \, n \tanh(\beta \mu_B B)$$

$$\chi = \frac{d(M/V)}{dB}$$

at low $T \to 0$, $\tanh(\beta \mu B) \to 1$, $\quad \frac{M}{V} \Rightarrow \mu_B \, n$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ all spins aligned!

Compare to quantum case:

$$\frac{M}{V} = \frac{3}{2} \frac{n}{\epsilon_F} \mu_B^2 B$$

smaller than classical result by factor $\frac{3}{2} \frac{\mu_B B}{\epsilon_F} \ll 1$

at high T $(\beta \to 0)$ $\tanh(\beta \mu_B B) \to \beta \mu_B B$

$$\frac{M}{V} = \frac{\mu_B^2 B \, n}{k_B T}, \qquad \chi = \frac{\mu_B^2 n}{k_B T} \sim \frac{1}{T}$$

Compare to quantum case — at room temp finite T corrections remain negligible and still

$$\chi_P = \mu_B^2 \frac{3}{2} \frac{n}{\epsilon_F} \qquad \text{indep of } T$$

smaller than classical by factor $\frac{3}{2}\left(\frac{k_B T}{\epsilon_F}\right) \ll 1$