For free electrons where $g(\epsilon) = C\sqrt{\epsilon}$

$$g'(\epsilon) = \tfrac{1}{2} C \frac{1}{\sqrt{\epsilon}}$$

$$\mu(T) \simeq \epsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{1}{2\epsilon_F} = \epsilon_F - \frac{\pi^2}{12}\frac{(k_B T)^2}{\epsilon_F}$$

$$\boxed{\mu(T) \simeq \epsilon_F\left(1 - \tfrac{1}{3}\left(\frac{\pi k_B T}{2\epsilon_F}\right)^2\right) = \epsilon_F\left(1 - \tfrac{1}{3}\left(\frac{\pi}{2}\frac{T}{T_F}\right)^2\right)}$$

Correction is small for metals at room temp as $T_F \sim 10{,}000\,^\circ K$

② energy $\frac{E}{V} = \int_0^\infty d\epsilon\, g(\epsilon)\,\epsilon\, n(\epsilon) \quad \Rightarrow \phi(\epsilon) = g(\epsilon)\,\epsilon$

$$u = \frac{E}{V} = \int_0^\mu d\epsilon\, g(\epsilon)\,\epsilon + \frac{\pi^2}{6}(k_B T)^2\left[g(\mu) + \mu g'(\mu)\right]$$

$$= \underbrace{\int_0^{\epsilon_F} d\epsilon\, g(\epsilon)\,\epsilon}_{= u(0)} + \underbrace{\int_{\epsilon_F}^{\mu} d\epsilon\, g(\epsilon)\,\epsilon}_{\simeq (\mu - \epsilon_F) g(\epsilon_F)\epsilon_F} + \frac{\pi^2}{6}(k_B T)^2\left[g(\mu) + \mu g'(\mu)\right]$$

$u(0)$: ground state energy density

$\simeq (\mu - \epsilon_F) g(\epsilon_F)\epsilon_F$: as before

replace $\mu \approx \epsilon_F$ as before

$$u(T) = u(0) + (\mu - \epsilon_F) g(\epsilon_F)\epsilon_F + \frac{\pi^2}{6}(k_B T)^2\left[g(\epsilon_F) + \epsilon_F g'(\epsilon_F)\right]$$

$$= u(0) + \left[-\frac{\pi^2}{6}(k_B T)^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)}\right] g(\epsilon_F)\epsilon_F + \frac{\pi^2}{6}(k_B T)^2\left[g(\epsilon_F) + \epsilon_F g'(\epsilon_F)\right]$$

$$\boxed{u(T) = u(0) + \frac{\pi^2}{6}(k_B T)^2 g(\epsilon_F)}$$

specific heat per volume

$$c_V \equiv \frac{C_V}{V} = \frac{1}{V}\left(\frac{dE}{dT}\right)_V = \left(\frac{du}{dT}\right)_V$$

$$\boxed{c_V = \frac{\pi^2}{3} k_B^2 T\, g(\epsilon_F)}$$

for free electrons we can write $g(\epsilon) = C\sqrt{\epsilon}$

$$n = \int_0^{\epsilon_F} d\epsilon\, g(\epsilon) = \frac{2}{3} C \epsilon^{3/2} \Rightarrow C = \frac{3}{2}\frac{n}{\epsilon^{3/2}}$$

$$\Rightarrow g(\epsilon_F) = \frac{3}{2}\frac{n}{\epsilon_F^{3/2}} \cdot \epsilon_F^{1/2} = \frac{3}{2}\frac{n}{\epsilon_F}$$

density of states at fermi energy

$$\boxed{c_V = \frac{\pi^2}{2}\left(\frac{k_B T}{\epsilon_F}\right) n k_B}$$

or total specific heat $C_V = V c_V$ $\qquad nV = N$

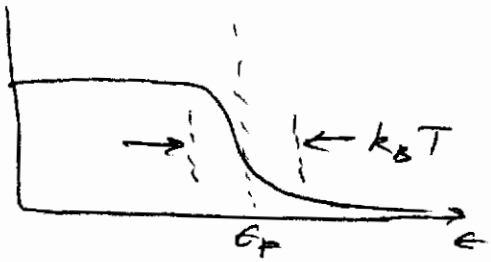
$$C_V = \frac{\pi^2}{2}\left(\frac{k_B T}{\epsilon_F}\right) N k_B$$

$\Rightarrow$ Specific heat due to fermi gas of electrons in a conductor is $C_V \sim T$ at low temperatures

We already saw that specific heat due to ionic vibrations (phonons) in a solid went like $C_V \sim T^3$ at low temperatures (Debye model)

$\Rightarrow$ electronic contribution to C_V dominates at sufficiently low T.

Simple estimate of C_V



When increase temperature to $k_B T$, the electrons near the fermi energy ϵ_F will increase their energy by an amount $\sim k_B T$. The number of such electrons ~~is roughly~~ per unit volume is roughly

$g(\epsilon_F)(k_B T)$

- $g(\epsilon_F)$: density of states at ϵ_F
- $k_B T$: energy interval about ϵ_F of states which ~~increase~~ get excited

$\Rightarrow$ increase in energy per unit volume is

$$\Delta u \sim \left(g(\epsilon_F)\, k_B T\right)(k_B T) \sim g(\epsilon_F)(k_B T)^2$$

- $g(\epsilon_F)\, k_B T$: # electrons excited
- $k_B T$: excitation energy per excited electron

$$\Rightarrow C_V = \frac{d\Delta u}{dT} \sim g(\epsilon_F) k_B^2 T = \frac{3}{2}\frac{n}{\epsilon_F} k_B^2 T = \frac{3}{2} n k_B \left(\frac{T}{T_F}\right)$$

for free electrons

The previous calculation gives the precise numerical coefficient

electronic specific heat per volume

$$C_V^{elec} = \frac{\pi^2}{2}\left(\frac{k_B T}{\epsilon_F}\right)\frac{N}{V}k_B \quad \left(1 + o\left(\frac{k_B T}{\epsilon_F}\right)^2\right)$$

compare to classical result $C_V^{classical} = \frac{N}{V}k_B$

The correct result for degenerate fermi gas is a factor $\frac{\pi^2}{2}\left(\frac{k_B T}{\epsilon_F}\right) = \frac{\pi^2}{2}\left(\frac{T}{T_F}\right)$ smaller than classical result by factor $\sim \frac{10^2}{10^4} = 10^{-2}$ at room temperature

also, classical C_V is indep of T, whereas fermi gas result is $\propto T$.

At low T, the ionic contribution to C_V is

$$C_V^{ion} = \frac{12\pi^4}{5}\left(\frac{T}{\theta_D}\right)^3 \frac{N}{V}k_B$$

$$\frac{C^{elec}}{C^{ion}} = \frac{\pi^2}{2}\left(\frac{k_B T}{\epsilon_F}\right)\frac{5}{12\pi^4}\left(\frac{\theta_D}{T}\right)^3 \simeq \frac{5}{24\pi^2}\left(\frac{\theta_D}{T_F}\right)\left(\frac{\theta_D}{T}\right)^2$$

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

for metals, $T_F \sim 10^4\,^\circ K$, $\theta_D \sim 10^2\,^\circ K$

$$T^* = 0.15\sqrt{10^{-2}}\,\theta_D \simeq 0.015\,\theta_D$$

So ionic contrib to C_V dominates over electronic contrib until $T \lesssim 0.01\,\theta_D$ ie at $O(1)\,^\circ K$. The electronic contrib dominates at lower temperatures.

Pauli paramagnetism of electron gas

($\vec{S} = \frac{1}{2}\hbar\vec{\sigma}$)

electron has intrinsic spin $\vec{\sigma}$ with intrinsic magnetic moment $\vec{\mu} = -\mu_B \vec{\sigma}$ $\quad \mu_B = \frac{|e|\hbar}{2mc}$ 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

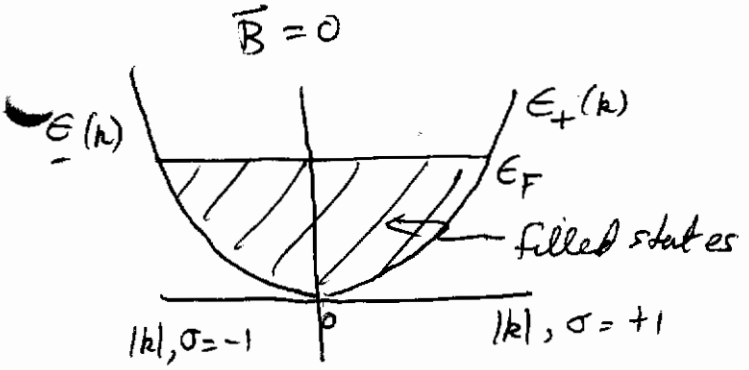
$$\epsilon_\pm(\vec{k}) = \epsilon(\vec{k}) \pm \mu_B B$$

where $\epsilon(\vec{k})$ is spectrum at $\vec{B} = 0$

Since ↑ and ↓ electrons now have different energy spectra, we should treat them as two different populations of particles ⇒ they will be in equilibrium when their chemical potentials are equal, i.e. $\mu_+ = \mu_-$

this will induce a net magnetization in the system.

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

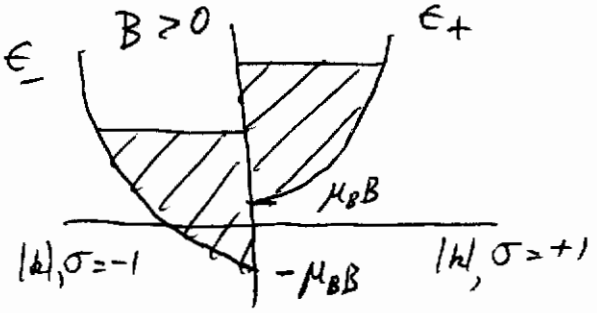


when $\vec{B} = 0$, $\epsilon_+(\vec{k}) = \epsilon_-(\vec{k})$

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

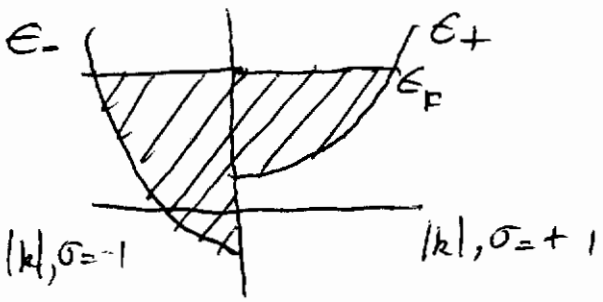
$n_+ = n_-$

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



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

At equilibrium the system will look like



again the two populations have the same max energy ϵ_F. But there are now more ↓ electrons than ↑ electrons

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

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

The calculation

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

When $B > 0$, the density of states for ↑ and ↓ electrons are

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

The density of ↑ and ↓ electrons is then

$$n_\pm = \int_{-\infty}^{\infty} d\epsilon \; g_\pm(\epsilon) \, f(\epsilon, \mu(B))$$

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
– it is same for ↑ and ↓

We will consider only the case that

$$\mu_B B \ll \mu(B) \approx \varepsilon_F$$

i.e. spin interaction is small compared to ε_F

First we will show that

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

since we will work in the $\mu_B B \ll \epsilon_F$ 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

$$n = n_+ + n_- = \int_{-\infty}^{\infty} d\epsilon\, f(\epsilon, \mu(B))\left[g_+(\epsilon) + g_-(\epsilon)\right]$$

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

shift integration variable $\epsilon - \mu_B B \to \epsilon$; shift integration variable $\epsilon + \mu_B B \to \epsilon$

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

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

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

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

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

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

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

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

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

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

But this is just the same ~~result~~ formula we use to compute n at $B=0$! The magetic 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

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

This conclusion 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...

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

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

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

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

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

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

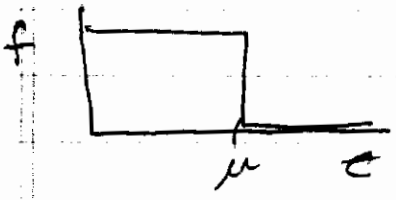
The first term is just the density when $B=0$, ie n. Hence we get

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

So the correction to μ due to finite B is

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

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



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

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

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

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

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

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

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

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

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

Now we compute

(2) Magnetization $\frac{M}{V} = -\mu_B (n_+ - n_-) = \mu_B (n_- - n_+)$

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

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

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

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

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

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

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

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

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

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

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

$\left(\epsilon_k = \hbar^2 k^2/2m\right)$

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

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

Compare this to classical result. Average magnetization of a single spin is

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

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

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

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

at low $T \to 0$, $\tanh(\beta\mu B) \to 1$, $\frac{M}{V} \to \mu_B n$ 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 $(\beta \to 0)$ $\tanh(\beta\mu_B B) \longrightarrow \beta\mu_B B$

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

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

$$\chi_p = \mu_B^2 \frac{3}{2}\frac{n}{\epsilon_F}$$ indep of T

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