

Pauli paramagnetism of electron gas

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

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

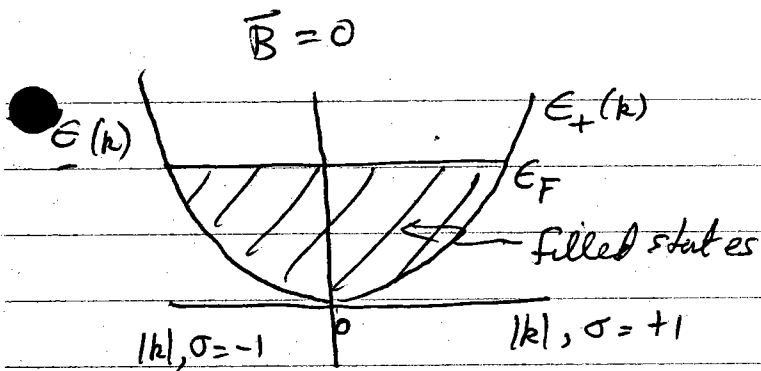
In an external magnetic field \vec{B} , there is an interaction energy $-\vec{\mu} \cdot \vec{B} = \mu_B \sigma B$ where $\sigma = \pm 1$ for spins parallel and antiparallel to \vec{B} . The energy spectra for up and down electron spins becomes

$$E_{\pm}(\vec{k}) = E(\vec{k}) \pm \mu_B B \quad \text{where } E(\vec{k}) \text{ is spectrum at } \vec{B} = 0$$

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

this will induce a net magnetization in the system.

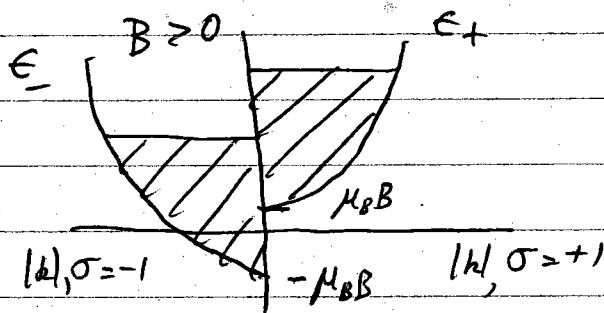
To see this, consider free electrons at $T=0$



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

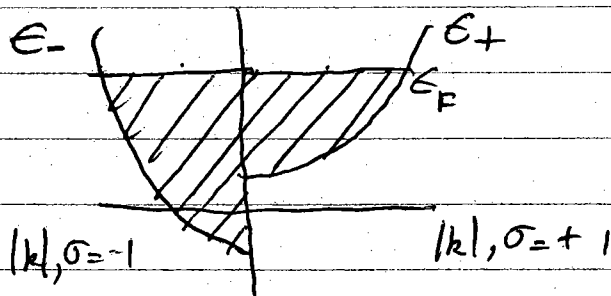
ground state occupations look as shown on the left. Equal numbers of \uparrow and \downarrow electrons
 $m_+ = m_-$

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 \uparrow electrons to \downarrow electrons.

At equilibrium the system will look like



again the two populations have the same max energy E_F .

But there are now more \downarrow electrons than \uparrow electrons

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

$\frac{\vec{M}}{V}$ is parallel to $\vec{B} \Rightarrow$ paramagnetic effect

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

$$\begin{aligned}g_+(\epsilon + \mu_B B) &= \frac{1}{2} g(\epsilon) \Rightarrow g_+(\epsilon) = \frac{1}{2} g(\epsilon - \mu_B B) \\g_-(\epsilon - \mu_B B) &= \frac{1}{2} g(\epsilon) \Rightarrow g_-(\epsilon) = \frac{1}{2} g(\epsilon + \mu_B B)\end{aligned}$$

The density of \uparrow and \downarrow electrons is then

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

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

$\mu(B)$ is the chemical potential - it might depend on B

- it is same for \uparrow and \downarrow

We will consider only the case that

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

i.e. spin interaction is small compared to ϵ_F

First we will show that

$$\textcircled{1} \mu(B) \approx \mu(B=0) \left[1 + O\left(\frac{\mu_{BB}}{E_F}\right)^2 \right]$$

Since we will work in the $\mu_{BB} \ll E_F$ 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

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

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

↑
shift integration
variable $\epsilon - \mu_{BB} \rightarrow \epsilon$

↑
shift integration
variable $\epsilon + \mu_{BB} \rightarrow \epsilon$

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

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

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

expand f about $\mu(B)$ for small μ_{BB}

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

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

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

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 ^{formula} ~~result~~ 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

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

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

To see this is so more explicitly, let's 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

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

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

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

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

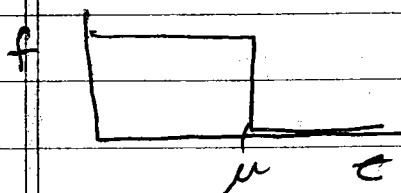
The first term is just the density when $B=0$, i.e. m . Hence we get

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

So the correction to μ due to finite B is

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

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



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

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

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

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

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

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

$$g'(\epsilon) = \frac{1}{2} \frac{c}{\sqrt{\epsilon}} \text{ we get}$$

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

Now we compute

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

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

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

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

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

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

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

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

$$\epsilon_F = \frac{\hbar^2 k^2}{2m}$$

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

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

$\chi_p > 0 \Rightarrow$ paramagnetic

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

$$\langle m \rangle = \frac{1}{2} \left[\frac{e^{-\beta \mu_B B} (+1) + e^{+\beta \mu_B B} (-1)}{e^{\beta \mu_B B} + e^{-\beta \mu_B B}} \right]$$

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

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

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

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

$$\frac{M}{V} = \frac{\mu_B^2 B n}{k_B T}$$

$$\chi = \frac{\mu_B^2 n}{k_B T} \sim \frac{1}{T}$$

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

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

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