Unit 3-10: Pauli Paramagnetism of the Electron Gas

Pauli paramagnetism describes the magnetization of a degenerate ideal (non-interacting particles) Fermi gas of electrons with an external magnetic field.

An electron has a half integer spin $\mathbf{s} = \frac{1}{2}\hbar\boldsymbol{\sigma}$, with $\sigma_z = \pm 1$. The spin gives rise to an intrinsic magnetic moment $\boldsymbol{\mu} = -\mu_B \boldsymbol{\sigma}$, with $\mu_B = \dfrac{|e|\hbar}{2mc}$ the Bohr magneton.

In an external magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$, there is an interaction energy between the spin and the field, $-\boldsymbol{\mu}\cdot\mathbf{B} = \mu_B \sigma_z B$. Assuming a model of non-interacting electrons (neither Coulomb interaction between the electron charges, nor an interaction between their magnetic moments), the energy for an electron with a parallel ("up" with $\sigma_z = +1$) or anti-parallel ("down, with $\sigma_z = -1$) spin is,

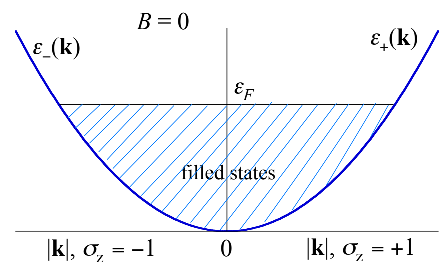
$$\epsilon_\pm(\mathbf{k}) = \epsilon(\mathbf{k}) \pm \mu_B B \qquad \text{where } \epsilon(\mathbf{k}) \text{ is the energy spectrum at } \mathbf{B} = 0 \tag{3.10.1}$$

Since spin-up and spin-down electrons now have different energy spectra, we should treat them as two different populations of particles, which can convert one into the other by flipping their spin. This implies that they will be in equilibrium with each other when their chemical potentials are equal, i.e. when $\mu_+ = \mu_-$.

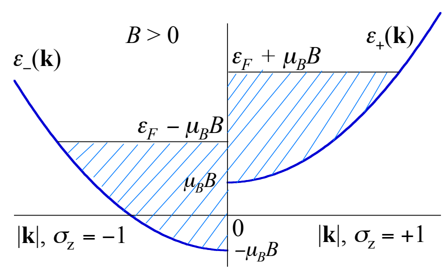
This will induce a net magnetization in the system, known as Pauli paramagnetism.

To see how this effect works, consider free electrons at $T = 0$.

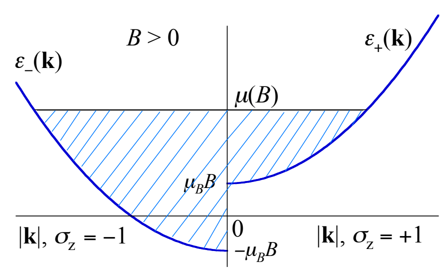
When $\mathbf{B} = 0$, then $\epsilon_+(\mathbf{k}) = \epsilon_-(\mathbf{k})$. In the sketch on the right, the right hand side shows the energy spectrum $\epsilon_+(\mathbf{k})$ of the spin-up electrons, while the left hand side shows the energy spectrum $\epsilon_-(\mathbf{k})$ of the spin-down electrons. Since these spectra are equal when $\mathbf{B} = 0$, the spin-up electrons fill up states to the same Fermi energy $\mu = \epsilon_F$ as do the spin-down electrons. The shaded area shows the states $\epsilon \le \epsilon_F$ that are occupied. We thus have equal numbers of spin-up and spin-down electrons, $n_+ = n_-$, and there is no net magnetization.



When $\mathbf{B}$ is turned on, if there were no redistribution of the electron spins, the situation wold look like in the sketch on the right. The spin-up electrons just shift up in energy, while the spin-down electrons shift down in energy. Clearly the system could then lower its total energy by flipping spin-up electrons into spin-down electrons.



When the system reaches its new equilibrium, the situation would look like in the sketch on the right. As we had when $\mathbf{B} = 0$, it must now also be the case that the spin-up and spin-down populations of electrons fill up to the same maximum energy $\mu(B)$. But to make that happen, there must now be more spin-down electrons than there are of spin-up electrons, $n_- > n_+$. This induces a net magnetization density,



$$\frac{M}{V} = -\mu_B(n_+ - n_-) > 0 \tag{3.10.2}$$

Because $M > 0$, then $\mathbf{M} = M\hat{\mathbf{z}}$ is parallel to the direction of $\mathbf{B}$, and this is a *paramagnetic* effect.

Now we will do the calculation to quantify this effect.

<u>The calculation</u>:

Let $g(\epsilon)$ be the density of states when $\mathbf{B} = B\hat{\mathbf{z}} = 0$. In this $B = 0$ case, the density of states for the spin-up electrons is just half the total, i.e. $g(\epsilon)/2$, while the density of states for the spin-down electrons is similarly $g(\epsilon)/2$. When $B > 0$, the energy of a spin-up electron shifts $\epsilon \to \epsilon + \mu_B B$, while the energy of a spin-down electron shifts to $\epsilon \to \epsilon - \mu_B B$.

The density of states for spin-up (+) and for spin-down (−) electrons therefore become,

$$g_+(\epsilon + \mu_B B) = \frac{1}{2} g(\epsilon) \quad \Rightarrow \quad g_+(\epsilon) = \frac{1}{2} g(\epsilon - \mu_B B) \tag{3.10.3}$$

$$g_-(\epsilon - \mu_B B) = \frac{1}{2} g(\epsilon) \quad \Rightarrow \quad g_-(\epsilon) = \frac{1}{2} g(\epsilon + \mu_B B) \tag{3.10.4}$$

The density of spin-up and spin-down electrons is then,

$$n_\pm = \int_{\epsilon_{\pm\,\mathrm{min}}}^{\infty} d\epsilon\, g_\pm(\epsilon)\, f(\epsilon, \mu(B)) \tag{3.10.5}$$

where $\epsilon_{\pm\,\mathrm{min}} = \pm\mu_B B$ is the lowest energy level of a spin-up (+) electron and a spin-down (−) electron, and where,

$$f(\epsilon, \mu(B)) \equiv \frac{1}{\mathrm{e}^{(\epsilon - \mu(B))/k_B T} + 1} \tag{3.10.6}$$

is the Fermi occupation function. Here $\mu(B)$ is the chemical potential, which might depend on the value of the external magnetic field B. This chemical potential is the same for spin-up and spin-down electrons, since the two populations are in equilibrium with one another. Please don't be confused by the notation – $\mu(B)$ is the chemical potential, while μ_B is the Bohr magneton!

We will consider only the case that the shift in energy due to the external magnetic field is small compared to ϵ_F,

$$\mu_B B \ll \mu(B) \approx \epsilon_F \tag{3.10.7}$$

First we will show that the shift in the chemical potential when one turns on the B is small, i.e.,

$$\mu(B) \approx \mu(B = 0)\Big[1 + O(\mu_B B/\epsilon_F)^2\Big] \tag{3.10.8}$$

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

Then we will calculate the induced magnetization due to the population imbalance $n_+ - n_-$ induced by turning on B.

1) <u>Shift in chemical potential with B</u>

Consider the total density of electrons,

$$n = n_+ + n_- = \int_{\mu_B B}^{\infty} d\epsilon\, g_+(\epsilon) f(\epsilon, \mu(B)) \; + \int_{-\mu_B B}^{\infty} d\epsilon\, g_-(\epsilon) f(\epsilon, \mu(B)) \tag{3.10.9}$$

$$= \frac{1}{2} \int_{\mu_B B}^{\infty} d\epsilon\, g(\epsilon - \mu_B B) f(\epsilon, \mu(B)) + \frac{1}{2} \int_{-\mu_B B}^{\infty} d\epsilon\, g(\epsilon + \mu_B B) f(\epsilon, \mu(B)) \tag{3.10.10}$$

In the first integral we will shift the integration variable to $\epsilon' = \epsilon - \mu_B B$; in the second integral we will shift the integration variable to $\epsilon' = \epsilon + \mu_B B$. Then, relabeling $\epsilon' \to \epsilon$, we get,

$$n = \frac{1}{2} \int_0^{\infty} d\epsilon\, g(\epsilon) \Big[f(\epsilon + \mu_B B, \mu(B)) + f(\epsilon - \mu_B B, \mu(B))\Big] \tag{3.10.11}$$

Next we use the fact that $f(\epsilon,\mu)$ depends only on $\epsilon-\mu$ to write,

$$n=\frac{1}{2}\int_0^\infty d\epsilon\, g(\epsilon)\,\Big[f(\epsilon,\mu(B)-\mu_B B)+f(\epsilon,\mu(B)+\mu_B B)\Big] \tag{3.10.12}$$

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

$$n=\frac{1}{2}\int_0^\infty g(\epsilon)\,\left[f(\epsilon,\mu(B))-\left(\frac{\partial f}{\partial\mu}\right)(\mu_B B)+\frac{1}{2}\left(\frac{\partial^2 f}{\partial\mu^2}\right)(\mu_B B)^2+\cdots\right. \tag{3.10.13}$$

$$\left.+f(\epsilon,\mu(B))+\left(\frac{\partial f}{\partial\mu}\right)(\mu_B B)+\frac{1}{2}\left(\frac{\partial^2 f}{\partial\mu^2}\right)(\mu_B B)^2+\cdots\right] \tag{3.10.14}$$

where the derivatives above are evaluated at $\mu=\mu(B)$. The terms linear in B cancel, and we are left with,

$$n=\int_0^\infty d\epsilon\, g(\epsilon)\left[f(\epsilon,\mu(B))+\frac{1}{2}\left(\frac{\partial^2 f}{\partial\mu^2}\right)(\mu_B B)^2+\cdots\right] \tag{3.10.15}$$

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

$$n=\int_0^\infty d\epsilon\, g(\epsilon) f(\epsilon,\mu(B)) \tag{3.10.16}$$

But this is just the same formula we use to compute n when $B=0$! The magnetic field B appears nowhere in the above expression, except via $\mu(B)$. Since the density of electrons n is fixed and cannot vary as B is turned on, we would conclude from the above that $\mu(B)=\mu(0)$ is independent of B.

But that conclusion depends on our having ignored the $(\mu_B B)^2$ term. Hence we expect that the shift in $\mu(B)$ should be proportional to this term, i.e.,

$$\mu(B)-\mu(0)\approx\frac{(\mu_B B)^2}{\epsilon_F} \tag{3.10.17}$$

where the factor $1/\epsilon_F$ appears on dimensional grounds.

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

$$n=\int_0^\infty d\epsilon\, g(\epsilon)\left[f(\epsilon,\mu(B))+\frac{1}{2}\left(\frac{\partial^2 f}{\partial\mu^2}\right)(\mu_B B)^2\right] \tag{3.10.18}$$

Since we believe the shift in $\mu(B)$ is small, let's write $\mu(B)=\mu(0)+\delta\mu$, and then expand the first term in $\delta\mu$,

$$n=\int_0^\infty d\epsilon\, g(\epsilon)\left[f(\epsilon,\mu(0)+\delta\mu)+\frac{1}{2}\left(\frac{\partial^2 f}{\partial\mu^2}\right)(\mu_B B)^2\right] \tag{3.10.19}$$

$$=\int_0^\infty d\epsilon\, g(\epsilon) f(\epsilon,\mu(0)) \;+\; \int_0^\infty d\epsilon\, g(\epsilon)\left(\frac{\partial f}{\partial\mu}\right)\bigg|_{\mu=\mu(0)}\delta\mu \;+\; \frac{1}{2}\int_0^\infty d\epsilon\, g(\epsilon)\left(\frac{\partial^2 f}{\partial\mu^2}\right)\bigg|_{\mu=\mu(B)}(\mu_B B)^2 \tag{3.10.20}$$

The first term is just the density n when $B=0$, and since this stays fixed we then have,

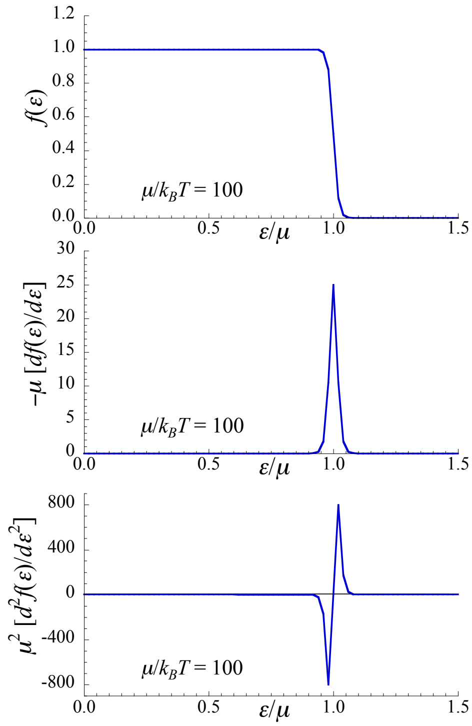
$$0=\int_0^\infty d\epsilon\, g(\epsilon)\left(\frac{\partial f}{\partial\mu}\right)\bigg|_{\mu=\mu(0)}\delta\mu \;+\; \frac{1}{2}\int_0^\infty d\epsilon\, g(\epsilon)\left(\frac{\partial^2 f}{\partial\mu^2}\right)\bigg|_{\mu=\mu(B)}(\mu_B B)^2 \tag{3.10.21}$$

So we then have,

$$\delta\mu=\frac{-\dfrac{1}{2}\displaystyle\int_0^\infty d\epsilon\, g(\epsilon)\left(\frac{\partial^2 f}{\partial\mu^2}\right)\bigg|_{\mu=\mu(B)}(\mu_B B)^2}{\displaystyle\int_0^\infty d\epsilon\, g(\epsilon)\left(\frac{\partial f}{\partial\mu}\right)\bigg|_{\mu=\mu(0)}} \tag{3.10.22}$$

To evaluate the above, first note that the numerator is already explicitly of $O(\mu_B B)^2$, so we can evaluate the derivative at $\mu=\mu(0)$ rather than $\mu=\mu(B)$ — using $\mu=\mu(B)$ would just introduce higher order terms in $\mu_B B$.

Now we consider the derivatives of $f(\epsilon, \mu)$ that appear in the integrands of the numerator and denominator.



On the left we plot $f(\epsilon, \mu)$, $-\mu[df/d\epsilon]$, and $\mu^2[d^2f/d\epsilon^2]$ vs ϵ/μ, for the case where $\mu/k_BT = 100$ (recall, for typical metals, $\mu/k_BT \approx 10^4$). As μ/k_BT increases, the features sharpen up.

In the $T \to 0$ limit, where $\mu/k_BT \to \infty$, the occupation function $f(\epsilon, \mu)$ becomes a sharp step function at $\epsilon = \mu$, and $\mu(0) = \epsilon_F$. Since $f(\epsilon, \mu)$ depends only on $\epsilon - \mu$, we have that $(\partial f/\partial \mu) = -(\partial f/\partial \epsilon)$. We therefore have as $T \to 0$,

$$\left(\frac{\partial f}{\partial \mu}\right) = -\left(\frac{\partial f}{\partial \epsilon}\right) = \delta(\epsilon - \mu) = \delta(\epsilon - \epsilon_F) \tag{3.10.23}$$

$$\left(\frac{\partial^2 f}{\partial \mu^2}\right) = \left(\frac{\partial^2 f}{\partial \epsilon^2}\right) = -\frac{\partial \delta(\epsilon - \mu)}{\partial \epsilon} = -\delta'(\epsilon - \mu) = -\delta'(\epsilon - \epsilon_F) \tag{3.10.24}$$

Therefore, as $T \to 0$, we have for the integrals that appear in the denominator and in the numerator of Eq. (3.10.22),

$$\int_0^\infty d\epsilon\, g(\epsilon) \left(\frac{\partial f}{\partial \mu}\right)\bigg|_{\mu=\mu(0)} = g(\epsilon_F) \tag{3.10.25}$$

$$\int_0^\infty d\epsilon\, g(\epsilon) \left(\frac{\partial^2 f}{\partial \mu^2}\right)\bigg|_{\mu=\mu(0)} = g'(\epsilon_F) \tag{3.10.26}$$

In the last equation we used the fact that $\int dx\, g(x)\delta'(x) = -\int dx\, g'(x)\delta(x)$, as obtained by an integration by parts.

Thus, as $T \to 0$, Eq. (3.10.22) gives,

$$\boxed{\delta\mu = \mu(B) - \mu(0) = -\frac{1}{2}\frac{g'(\epsilon_F)}{g(\epsilon_F)}(\mu_B B)^2} \tag{3.10.27}$$

For *free electrons* with $g(\epsilon) = C\sqrt{\epsilon}$, and $g'(\epsilon) = C/2\sqrt{\epsilon}$, we then get,

$$\mu(B) - \mu(0) = \mu(B) - \epsilon_F = -\frac{(\mu_B B)^2}{4\epsilon_F} \qquad \Rightarrow \qquad \boxed{\mu(B) = \epsilon_F\left[1 - \left(\frac{\mu_B B}{2\epsilon_F}\right)^2\right]} \tag{3.10.28}$$

2) Magnetization density

Now we compute the magnetization density induced by turning on the magnetic field B.

$$\frac{M}{V} = -\mu_B\Big[n_+ - n_-\Big] = \mu_B\Big[n_- - n_+\Big] = \mu_B \int d\epsilon\, f(\epsilon, \mu)\Big[g_-(\epsilon) - g_+(\epsilon)\Big] \tag{3.10.29}$$

$$= \mu_B \int d\epsilon\, f(\epsilon, \mu)\Big[\frac{1}{2}g(\epsilon + \mu_B B) - \frac{1}{2}g(\epsilon - \mu_B B)\Big] \tag{3.10.30}$$

$$= \frac{1}{2}\mu_B \int d\epsilon\, g(\epsilon)\Big[f(\epsilon, \mu + \mu_B B) - f(\epsilon, \mu - \mu_B B)\Big] \qquad \text{just as we did in our calculation for } \mu(B) \tag{3.10.31}$$

Now expand $f(\epsilon, \mu \pm \mu_B B) \approx f(\epsilon, \mu) \pm \left(\frac{\partial f}{\partial \mu}\right)(\mu_B B)$, and we get to lowest order,

$$\frac{M}{V} = \frac{1}{2}\mu_B \int d\epsilon\, g(\epsilon) \left[2\left(\frac{\partial f}{\partial \mu}\right)(\mu_B B)\right] = \mu_B^2 B \int d\epsilon\, g(\epsilon) \left(-\frac{\partial f}{\partial \epsilon}\right) \tag{3.10.32}$$

Here the leading terms in the expansion of $f(\epsilon, \mu \pm \mu_B B)$ cancel, and if we had kept the expansion to second order, those second order terms would also cancel. We also used $(\partial f/\partial \mu) = -(\partial f \partial \epsilon)$.

Now as $T \to 0$, we have as before that $-(\partial f/\partial \epsilon) \to \delta(\epsilon - \epsilon_F)$. So in the $T = 0$ limit we get,

$$\boxed{\frac{M}{V} = \mu_B^2 B\, g(\epsilon_F)} \tag{3.10.33}$$

If we wanted the magnetization at finite temperatures, we could use the Sommerfeld expansion to evaluate the integral in Eq. (3.10.32). We would find that the corrections to the $T = 0$ result are of order $O(k_B T/\epsilon_F)^2$.

The $T = 0$ *Pauli paramagnetic susceptibility* is then, $\chi_P = \lim\limits_{B\to 0} \dfrac{\partial(M/V)}{\partial B}$

$$\boxed{\chi_P = \mu_B^2\, g(\epsilon_F)} \qquad \text{since } \chi_P > 0\text{, this is a paramagnetic effect; } \mathbf{M} \text{ aligns in the same direction as } \mathbf{B} \tag{3.10.34}$$

For *free electrons*, we have $g(\epsilon_F) = \dfrac{3}{2}\dfrac{n}{\epsilon_F}$, and so,

$$\frac{M}{V} = \mu_B^2 B \frac{3}{2}\frac{n}{\epsilon_F}, \qquad \chi_P = \mu_B^2 \frac{3}{2}\frac{n}{\epsilon_F} \qquad \text{free electrons} \tag{3.10.35}$$

<u>Classical paramagnetic susceptibility for spin 1/2 electrons</u>

It is interesting to compare our result of χ_P for the degenerate Fermi gas with what we would get classically for spin 1/2 electrons. Since the single particle Hamiltonian is $\mathcal{H}^{(1)}(\sigma_z) = \mu_B B \sigma_z$, then in the classical limit, the probability that an electron spin would have $\sigma_z = \pm 1$ would be,

$$\mathcal{P}(\sigma_z) = \frac{\mathrm{e}^{-\beta\mu_B B \sigma_z}}{\mathrm{e}^{\beta\mu_B B} + \mathrm{e}^{-\beta\mu_B B}} \tag{3.10.36}$$

The average magnetization of a single electron would then be,

$$\frac{M}{N} = -\mu_B \langle \sigma_z \rangle = -\mu_B \Big[(1)\mathcal{P}(1) + (-1)\mathcal{P}(-1)\Big] = -\mu_B \left[\frac{(+1)\mathrm{e}^{-\beta\mu_B B} + (-1)\mathrm{e}^{\beta\mu_B B}}{\mathrm{e}^{\beta\mu_B B} + \mathrm{e}^{-\beta\mu_B B}}\right] \tag{3.10.37}$$

$$= \mu_B \tanh(\beta\mu_B B) \tag{3.10.38}$$

The magnetization density would then be,

$$\frac{M}{V} = \frac{N}{V}\frac{M}{N} = -n\mu_B\langle\sigma_z\rangle = n\mu_B \tanh(\beta\mu_B B) \qquad \text{where } n = N/V \text{ is the electron density} \tag{3.10.39}$$

Then the classical magnetic susceptibility is,

$$\chi = \frac{d(M/V)}{dB} \tag{3.10.40}$$

At low $T \to 0$ ($\beta \to \infty$), $\tanh(\beta\mu_B B) \to 1$, $M/V \to \mu_B n$, so all spins are aligned. Compare that to the quantum case where from Eq. (3.10.35) we get, $M/V = (3/2)(n/\epsilon_F)\mu_B^2 B$. The quantum result for M/V is smaller than the classical result by a factor,

$$\frac{3}{2}\frac{\mu_B B}{\epsilon_F} \ll 1 \tag{3.10.41}$$

At high T ($\beta \to 0$), $\tanh(\beta\mu_B B) \to \beta\mu_B B$, so,

$$\frac{M}{V} = \frac{\mu_B^2 B n}{k_B T} \qquad \Rightarrow \qquad \chi = \frac{\mu_B^2 n}{k_B T} \sim \frac{1}{T} \tag{3.10.42}$$

Compare that to the quantum case. At room temperature we still have $T \ll T_F$, and so the susceptibility is essentially the same at at $T = 0$. From Eq. (3.10.35) we have,

$$\chi_P = \frac{3\mu_B^2 n}{2\epsilon_F} \qquad \text{independent of } T \tag{3.10.43}$$

The quantum χ_P is then smaller than the classical χ by a factor,

$$\frac{3}{2}\left(\frac{k_B T}{\epsilon_F}\right) = \frac{3}{2}\left(\frac{T}{T_F}\right) \ll 1 \tag{3.10.44}$$

A General Observation

If you review our calculations of quantities for the degenerate Fermi gas, such as $\mu(T)$, c_V, and χ_P, you should notice that these all depend on the density of states at the Fermi energy, $g(\epsilon_F)$, and its derivatives at ϵ_F. Thus $g(\epsilon_F)$ is a key parameter that determines many features of the degenerate Fermi gas. You might wonder why?

The reason is that, for a degenerate Fermi gas, $k_B T \ll \epsilon_F$. And so at finite temperature, it is only the electrons within $k_B T$ of the Fermi energy that can do anything. Electron states at energies much below $\epsilon_F - k_B T$ are all occupied, and cannot become doubly occupied (Pauli exclusion principle), so an electron here would have to absorb an energy much larger than $k_B T$ to get excited to an unoccupied state above ϵ_F. That is not likely. So it is only the electrons within $k_B T$ of ϵ_F that can absorb thermal energy and get excited into the unoccupied states above ϵ_F. How many such electrons, per unit volume, are there? There are $g(\epsilon_F)k_B T$.