3. Diamagnetism

Diamagnetism is defined by $\chi^{\mathrm{dia}} < 0$ where $\chi^{\mathrm{dia}} = $ constant. The simple explanation is that this is an induction effect: The external field induces magnetic dipoles which, according to Lenz's law, are oriented antiparallel to the field and therefore χ is negative. We will see in a moment that strictly speaking, this easily understandable picture is not quite true, as without quantum mechanical effects, there is not even diamagnetism.

Empirically, the effect of diamagnetism is displayed by all materials; however, they are only called diamagnets if no other, stronger type of magnetism like paramagnetism or collective magnetism is present. Examples for diamagnets are almost all organic substances, metals like Bi, Zn and Hg, nonmetals like S, I and Si, and superconductors for $T < T_c$; in fact they are perfect diamagnets: $\chi^{\mathrm{dia}} = -1$ which is called the Meissner-Ochsenfeld effect.

3.1 Bohr-van-Leeuwen theorem

The Bohr-van Leeuwen theorem states: Magnetism is a quantum mechanical effect. Strictly classically, there cannot be either dia-, para- or collective magnetism.

Proof: We assume a solid of identical ions with translational symmetry. Then the magnetization is

$$\vec{M} = \frac{N}{V} \langle \vec{m} \rangle \,,$$

where $\vec{m}$ is the magnetic moment of the individual ion, and N is the number of ions in volume V. The magnetic moment can be related to the energy W of the magnetic system and to the Hamiltonian H:

$$\vec{m} = -\frac{\partial W}{\partial \vec{B}_0} = -\frac{\partial H}{\partial \vec{B}_0} \,, \tag{3.1}$$

where H is the classical Hamiltonian function of a single ion. The classical average can be calculated by

$$\langle \vec{m} \rangle = \frac{1}{Z^*} \int \cdots \int dx_1 \ldots dx_{3N_e} \int dp_1 \ldots dp_{3N_e} \vec{m} e^{-\beta H} \tag{3.2}$$

with the number of electrons N_e and with the classical partition function

$$Z = \frac{Z^*}{N_e! h^{3N_e}}$$

given by

$$Z^* = \int \cdots \int dx_1 \ldots dx_{3N_e} \int dp_1 \ldots dp_{3N_e} e^{-\beta H} \tag{3.3}$$

with the inverse temperature $\beta = \frac{1}{k_B T}$. Then

$$\begin{aligned} \frac{1}{\beta Z} \frac{\partial Z}{\partial \vec{B}_0} &= \frac{1}{\beta Z^*} \frac{\partial Z^*}{\partial \vec{B}_0} \\ &= \frac{1}{\beta Z^*} \int \cdots \int dx_1 \ldots dx_{3N_e} \int dp_1 \ldots dp_{3N_e} e^{-\beta H} \Big(- \beta \frac{\partial H}{\partial \vec{B}_0} \Big) \\ &= \frac{1}{Z^*} \int \cdots \int dx_1 \ldots dx_{3N_e} \int dp_1 \ldots dp_{3N_e} e^{-\beta H} \vec{m} = \langle \vec{m} \rangle \end{aligned} \tag{3.4}$$

Thus,

$$\langle \vec{m} \rangle = \frac{1}{\beta Z} \frac{\partial Z}{\partial \vec{B}_0} . \tag{3.5}$$

If we can show that Z doesn't change when an external field $\vec{B}_0$ is switched on, the theorem is proven. The general form of H in the presence of a magnetic field $\vec{B}_0 = \nabla \times \vec{A}$ is

$$H = \frac{1}{2m} \sum_{i=1}^{N_e} (\vec{p}_i + e\vec{A}_i)^2 + H_1(x_1, \ldots, x_{3N_e}) \tag{3.6}$$

where H_1 represents the electron-electron interactions. Then we can write for the partition function

$$\begin{aligned} Z^* = \int \ldots \int dx_1 \ldots dx_{3N_e} e^{-\beta H_1(x_1, \ldots, x_{3N_e})} \times \\ \times \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dp_1 \ldots dp_{3N_e} e^{-\frac{\beta}{2m} \sum_{i=1}^{N_e} (\vec{p}_i + e\vec{A}_i)^2} \end{aligned} \tag{3.7}$$

As the momentum integration runs from $-\infty$ to ∞, we can substitute $\vec{u}_i = \vec{p}_i + e\vec{A}_i$ without changing the limits of integration:

$$Z^* = \int \ldots \int dx_1 \ldots dx_{3N_e} e^{-\beta H_1(x_1, \ldots, x_{3N_e})} \times \\ \times \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dp_1 \ldots dp_{3N_e} e^{-\frac{\beta}{2m} \sum_{i=1}^{N_e} \vec{u}_i^2} \tag{3.8}$$

which obviously is independent of the magnetic field, $Z \neq Z(B_0)$. Thus, the average magnetic moment vanishes in all cases:

$$\langle \vec{m} \rangle \equiv 0 \, .$$

Rigorously, classically, there is no magnetism, and it is best to always argue quantum mechanically.

In matter, we have charged particles in motion which respond to an external magnetic field $\vec{B}_0$. Either the system contains permanent magnetic moments. Then they will order in a field and give rise to collective phenomena like paramagnetism, ferromagnetism, antiferromagnetism or ferrimagnetism. Or, the field itself induces the magnetic moments. This is called diamagnetism and is only observable if no permanent moments are present. We can distinguish between the diamagnetism of insulators which is called Larmor diamagnetism and diamagnetism of itinerant electrons in metals which is called Landau diamagnetism.

3.2 Larmor diamagnetism

As diamagnetism is only observable in a system without other kinds of magnetism, we consider a solid made up out of ions with completely filled shells. For the ground state, we have

$$\vec{J}|0\rangle = \vec{L}|0\rangle = \vec{S}|0\rangle = 0 \tag{3.9}$$

We switch on an external magnetic field given by

$$\vec{B}_0 = \mu_0 \vec{H} = (0, 0, B_0)$$

and look for the response of the system, *i.e.* the field induced magnetic moment, the magnetization. We consider an insulator where all electrons are strictly localized. Then

$$\vec{M}(B_0) = \frac{N}{V} \langle 0|\vec{m}|0\rangle \tag{3.10}$$

for N ions in volume V. We already know that magnetic energies $\approx \mu_{\mathrm{B}} B_0$ are usually so small that the system remains in the ground state $|0\rangle$ in the average. We now need the Hamiltonian in a homogeneous magnetic field from which we obtain the magnetization as $\vec{m} = -\frac{\partial H}{\partial \vec{B}_0}$. We consider only the electrons and ignore the interactions between them and with the nucleus for the time being. We choose the vector potential in the Coulomb gauge so that

$$\vec{B}_0 = \nabla \times \vec{A} \quad \text{with } \nabla \cdot \vec{A} = 0\,. \tag{3.11}$$

This can be achieved by

$$\vec{A} = \frac{1}{2}\vec{B}_0 \times \vec{r}\,.$$

The kinetic energy without field is

$$T_0 = \sum_{i=1}^{n} \frac{p_i^2}{2}$$

for n electrons with charge $-e$ so that $e > 0$. In the field, the canonical momentum $\vec{p}_i$ is different from the mechanical momentum $m\vec{v}_i$:

$$\vec{p}_i = m\vec{v}_i - e\vec{A}(\vec{r}_i)\,. \tag{3.12}$$

Then we have for the kinetic energy

$$T = \frac{1}{2m}\sum_{i=1}^{n} \left(\vec{p}_i + e\vec{A}(\vec{r}_i)\right)^2 = \frac{1}{2m}\sum_{i=1}^{n} \left[\vec{p}_i^2 + e\left(\vec{p}_i\cdot\vec{A}(\vec{r}_i) + \vec{A}(\vec{r}_i)\cdot\vec{p}_i\right) + e^2\vec{A}^2(\vec{r}_i)\right] \tag{3.13}$$

In general, operators $\vec{p}_i$ and $\vec{A}(\vec{r}_i)$ do not commute, but in Coulomb gauge they do:

$$\vec{p}_i \cdot \vec{A}(\vec{r}_i) = \frac{\hbar}{i}\big(\underbrace{\nabla_i \cdot \vec{A}}_{=0} + \vec{A} \cdot \nabla_i\big) = \vec{A}(\vec{r}_i) \cdot \vec{p}_i\,.$$

Therefore, the kinetic energy becomes

$$T = T_0 + \frac{e}{m}\sum_{i=1}^{n} \vec{A}(\vec{r}_i) \cdot \vec{p}_i + \frac{e^2}{2m}\sum_{i=1}^{n} \vec{A}^2(\vec{r}_i) \tag{3.14}$$

With the field $\vec{B}_0$ in z direction $\vec{B}_0 = (0, 0, B_0)$, the vector potential is

$$\vec{A} = \frac{1}{2}\vec{B}_0 \times \vec{r} = \frac{B_0}{2}(-y, x, 0)\,. \tag{3.15}$$

The scalar product $\vec{A}(\vec{r}_i) \cdot \vec{p}_i$ can be expressed by the orbital angular momentum $\vec{l}_i$ of electron i:

$$\vec{A}(\vec{r}_i) \cdot \vec{p}_i = \frac{B_0}{2}(-y_i p_{ix} + x_i p_{iy}) = \frac{1}{2} B_0 l_{iz} = \frac{1}{2} \vec{B}_0 \cdot \vec{l}_i \, .$$

Then using the total orbital angular momentum $\vec{L} = \sum_{i=1}^{n} \vec{l}_i$, we have

$$T = T_0 + \frac{\mu_B}{\hbar} \vec{L} \cdot \vec{B}_0 + \frac{e^2 B_0^2}{8m} \sum_{i=1}^{n} \left(x_i^2 + y_i^2 \right) . \tag{3.16}$$

In this derivation we have neglected the spin $\vec{S}$ of the electrons; we already know that the field couples not only to $\vec{L}$ but actually to $\vec{J} = \vec{L} + 2\vec{S}$. Thus, two terms in the Hamiltonian contain the magnetic field,

$$H_Z = -\frac{\mu_B}{\hbar}(L_z + 2S_z) B_0 \text{ and } H_{\text{dia}} = \frac{e^2 B_0^2}{8m} \sum_{i=1}^{n} \left(x_i^2 + y_i^2 \right) \tag{3.17}$$

Performing the average for the first term (considering completely filled shells, Equation 3.9) gives

$$\left\langle 0 \middle| \frac{\partial H_Z}{\partial \vec{B}_0} \middle| 0 \right\rangle = 0 \, .$$

We are left with

$$\vec{M}(B_0) = -\frac{N}{V} \left\langle 0 \middle| \frac{\partial H_{\text{dia}}}{\partial \vec{B}_0} \middle| 0 \right\rangle \tag{3.18}$$

Due to the spherical symmetry of the ion (noble gas configuration), we have

$$\sum_{i=1}^{n} \langle 0 | x_i^2 | 0 \rangle = \sum_{i=1}^{n} \langle 0 | y_i^2 | 0 \rangle = \sum_{i=1}^{n} \langle 0 | z_i^2 | 0 \rangle = \frac{1}{3} \sum_{i=1}^{n} \langle 0 | \vec{r}_i^{\,2} | 0 \rangle \, .$$

As x and y components of the magnetization vanish, we find for the z component

$$M(B_0) = -\frac{N e^2}{6mV} B_0 \sum_{i=1}^{n} \langle \vec{r}_i^{\,2} \rangle \, . \tag{3.19}$$

The diamagnetic susceptibility is obtained by differentiating again with respect to B_0:

$$\chi^{\text{dia}} = \mu_0 \left(\frac{\partial M}{\partial \vec{B}_0} \right)_T = -\frac{Ne^2}{6mV} \sum_{i=1}^{n} \langle 0 | \vec{r}_i^{\,2} | 0 \rangle \,, \tag{3.20}$$

where the negative sign indicates diamagnetism. The external field induces a moment whose field is directed opposite to the applied field.
To estimate the order of magnitude of χ^{dia}, we first note that in the literature, usually the molar susceptibility is given:

$$\chi_m^{\text{dia}} = \frac{N_A V}{N} \chi^{\text{dia}} \quad \left[\frac{\text{cm}^3}{\text{mol}} \right] \tag{3.21}$$

with Avogadro number $N_A = 6.022 \cdot 10^{23}\,\text{mol}^{-1}$. The average ion radius

$$\langle r^2 \rangle = \frac{1}{n} \sum_{i=1}^{n} \langle 0 | r_i^2 | 0 \rangle$$

can be expressed in units of the Bohr radius

$$a_B = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529\,\text{Å}\,.$$

Then the molar susceptibility is

$$\chi_m^{\text{dia}} = -0.995 \cdot 10^{-5} n \left\langle \frac{r^2}{a_B^2} \right\rangle \quad \left[\frac{\text{cm}^3}{\text{mol}} \right], \tag{3.22}$$

where $\left\langle \frac{r^2}{a_B^2} \right\rangle$ is of the order of 1. Thus, χ_m^{dia} is very small and diamagnetism is only observable when it is not shadowed by paramagnetism or collective magnetism.

Table 3.1: Examples of diamagnetic molar susceptibilities χ_m^{dia} in $10^{-6}\text{cm}^3/\text{mol}$.

		He	-1.9	Li^+	-0.7
F^-	-9.4	Ne	-7.2	Na^+	-6.1
Cl^-	-24.2	Ar	-19.4	K^+	-14.6
Br^-	-34.5	Kr	-28.0	Rb^+	-22.0
I^-	-50.6	Xe	-43.0	Cs^+	-35.1

Examples are noble gases and simple ionic crystals like alkali metal halides for which contributions of cations and anions add up.
In Table3.1, the electron number increases within each column, and so does $|\chi_m^{\text{dia}}|$ (see Eq. 3.22). In each row, electron number is the same but the nuclear charge Z increases, increasing the attractive force on the electron shells and thus shrinking the size of the ion $\langle r^2 \rangle$ from left to right; thus, $|\chi_m^{\text{dia}}|$ decreases.

3.3 Landau diamagnetism

There is also a diamagnetic contribution to the susceptibility due to (nearly) free electrons in metals; free electrons in an electron gas lead to charge currents in a magnetic field which generate magnetic moments. This would still be true if the electrons had no spin (no spin magnetic moment). This diamagnetic response, due to the Bohr-van Leeuwen theorem, has to be a quantum-mechanical phenomenon.

3.3.1 Two-dimensional electron gas

As a first step, we consider a two-dimensional electron gas in a uniform magnetic field based on the single-electron Hamiltonian

$$H = \frac{1}{2m}\left[\vec{p} + e\vec{A}(\vec{r})\right]^2 \tag{3.23}$$

with charge $-e$. The Zeeman term which would lead to paramagnetism is neglected here. Without loss of generality, we assume he uniform field to point in z direction, $\vec{B}_0 = (0, 0, B_0)$. We choose the so-called Landau gauge

$$\vec{A}(\vec{r}) = (-B_0 y, 0, 0)$$

which gives

$$\vec{B}_0 = \nabla \times \vec{A} = \begin{pmatrix} \partial_y 0 - \partial_z 0 \\ -\partial_z B_0 y - \partial_x 0 \\ \partial_x 0 + \partial_y B_0 y \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}. \tag{3.24}$$

Thus

$$H = \frac{1}{2m}(p_x - eB_0 y)^2 + \frac{1}{2m}p_y^2 \tag{3.25}$$

we have $[H, p_x] = 0$ as H doesn't contain x; p_x is a constant of motion, and we can replace it by its eigenvalue $\hbar k_x$. If we define $y_0 := \frac{\hbar}{eB_0}k_x$ and

$\omega_c := \frac{eB_0}{m}$ with cyclotron frequency ω_c, we obtain

$$H = \frac{1}{2m}p_y^2 + \frac{m}{2}\omega_c^2(y - y_0)^2 . \tag{3.26}$$

This Hamiltonian describes a harmonic oscillator with potential minimum shifted to y_0. It has the eigenvalues

$$E_{n,k_x} = \hbar\omega_c\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \dots \tag{3.27}$$

This is a huge degeneracy because the energies do not depend on k_x. The apparent asymmetry between x and y direction in H is gauge dependent and therefore without physical consequence. We could have chosen the vector potential to point in any direction within the xy plane. The isotropy of the two-dimensional space is not broken by the choices of a special gauge. The magnetic field transforms the spectrum of the two-dimensional electron gas

$$E_{\vec{k}} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2)$$

into a discrete spectrum of Landau levels enumerated by n. For $B_0 = 0$, the density of states is

$$\begin{aligned} D(\varepsilon) &= \int \frac{d^2k}{(2\pi)^2}\delta\left(\varepsilon - \frac{\hbar^2k^2}{2m}\right) = \frac{1}{2\pi}\int_0^\infty dk\, k\delta\left(\varepsilon - \frac{\hbar^2k^2}{2m}\right) \\ &\underbrace{=}_{u=k^2,\, du=2k\,dk} \frac{1}{4\pi}\int_0^\infty du\delta\left(\varepsilon - \frac{\hbar^2u}{2m}\right) = \frac{1}{4\pi}\int_0^\infty dE\frac{2m}{\hbar^2}\delta(\varepsilon - E) \\ &= \frac{m}{2\pi\hbar^2} \quad \text{for } \varepsilon \geqslant 0 \end{aligned} \tag{3.28}$$

Thus, the density of states is constant. For $B_0 > 0$, it is replaced by δ function peaks (Figure 3.1).

We can now determine the degeneracy of the Landau levels. Since the total number of states does not change, the Landau levels must accommodate these states; thus, the degeneracy of the first one, and all others, is (for an electron gas enclosed in a sample with area L^2)

$$N_L = L^2\int_0^{\hbar\omega_c} d\varepsilon\, D(\varepsilon) = \frac{m}{2\pi\hbar^2}\hbar\omega_c L^2 = \frac{m}{2\pi\hbar}\frac{eB_0}{m}L^2 = \frac{eB_0}{h}L^2 \tag{3.29}$$

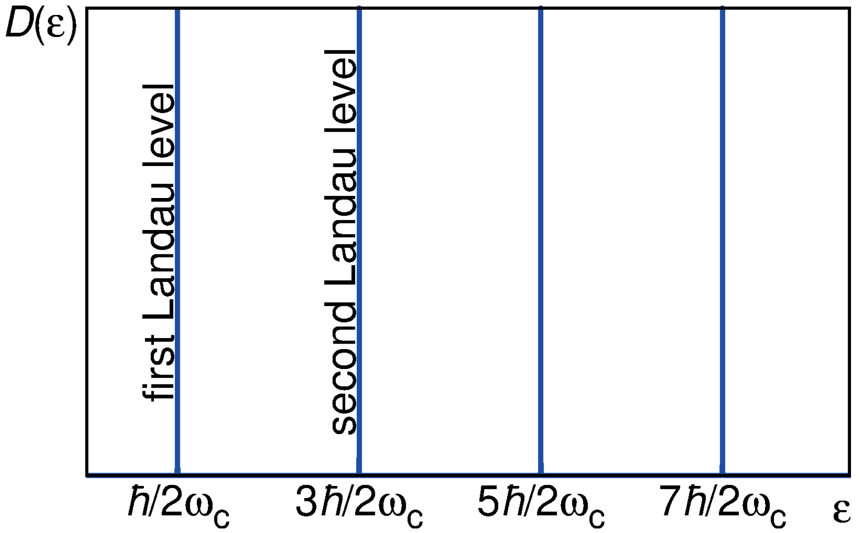

Figure 3.1: Density of states of two-dimensional electron gas at finite magnetic field $B_0 > 0$.

At low temperature, the low energy states are filled successively until all N electrons are accommodated. If

$$N = 2nN_L \quad \text{with } n = 1, 2, \dots$$

the n lowest Landau levels are completely filled and the others are empty. The factor 2 is due to the two spin directions. In case that $\frac{N}{2N_L}$ is not an integer, the highest Landau level is partially filled. Landau level quantization is one of the key ingredients of the integer quantum Hall effect. For calculating the total energy of N electrons, we define $\lfloor x \rfloor$ as the largest integer smaller or equal to x, and $\underline{n} = \left\lfloor \frac{N}{2N_L} \right\rfloor$; then

$$E = \sum_{n=0}^{\underline{n}-1} 2N_L \hbar\omega_c \Big(n + \frac{1}{2}\Big) + (N - \underline{n}2N_L)\hbar\omega_c \Big(\underline{n} + \frac{1}{2}\Big) . \tag{3.30}$$

The first term describes the filled Landau levels, and the second the partially filled one. With the filling factor $\nu := \frac{N}{2N_L}$, the energy per electron is

$$\frac{E}{N} = \sum_{n=0}^{\underline{n}-1} \frac{2}{\nu} \hbar\omega_c \Big(n + \frac{1}{2}\Big) + \Big(1 - \frac{2\underline{n}}{\nu}\Big) \hbar\omega_c \Big(\underline{n} + \frac{1}{2}\Big) . \tag{3.31}$$

with $\underline{n} = \left\lfloor \frac{\nu}{2} \right\rfloor$. This function is continuous but not everywhere differentiable (see Figure 3.2). B_t is the field for which $\nu = 2$, *i.e.* for which the lowest Landau level is completely filled:

$$\frac{N}{N_L} = \frac{Nh}{eB_tL^2} \overset{!}{=} 2 \curvearrowright B_t = \frac{hN}{2eL^2}$$

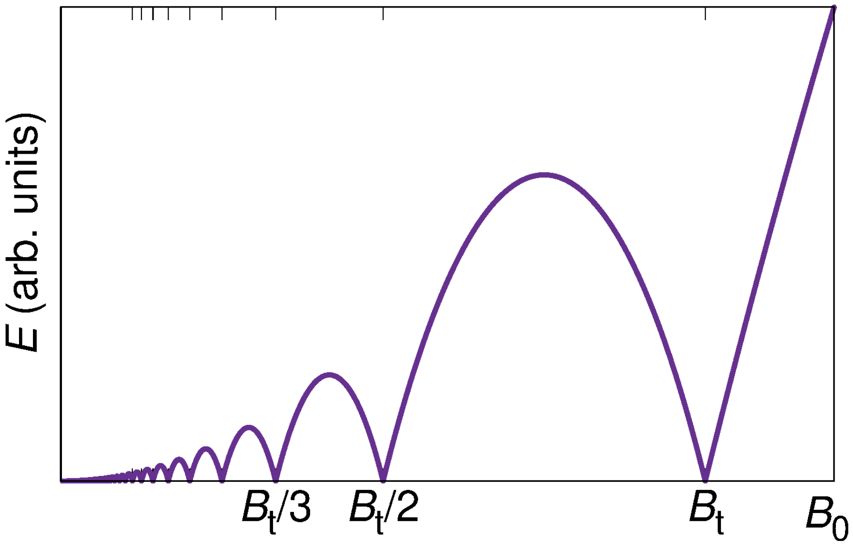

Figure 3.2: Energy of the two-dimensional electron gas as function of magnetic field B_0.

The areal magnetization

$$M = -\frac{1}{L^2}\frac{\partial E}{\partial B_0}$$

shows oscillations that are periodic in $\frac{1}{B_0}$. These are the de Haas-van Alphen oscillations (see Figure 3.3).

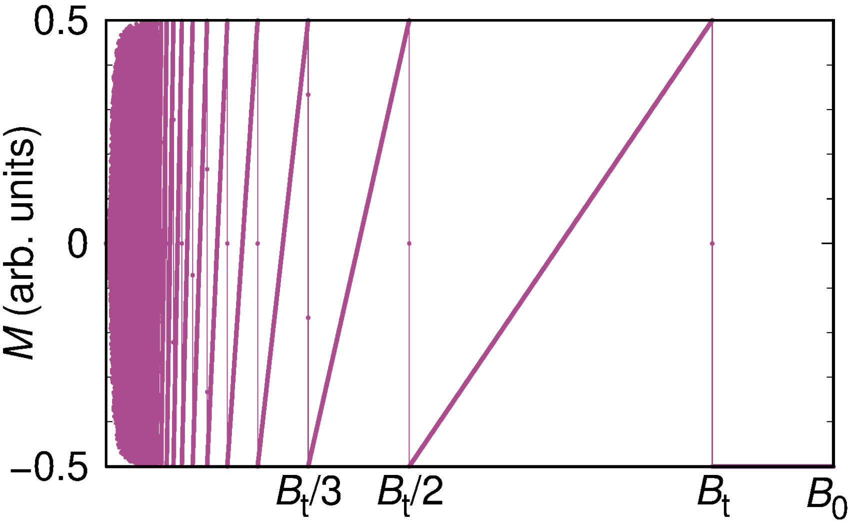

Figure 3.3: Magnetization of the two-dimensional electron gas as function of magnetic field B_0.

The limit $\lim_{B_0 \to 0} M$ does not exist; neither does the limit $\lim_{B_0 \to 0} \chi$ for the susceptibility $\chi = \frac{\partial M}{\partial B_0}$. This unphysical result is due to the assumption of zero temperature $T = 0$. At any $T > 0$, the thermal energy $k_B T$ will be large compared to the energy spacing $\hbar\omega_c$ between the Landau levels for sufficiently small B_0. In this regime, the discreteness of the Landau levels can be neglected, and the energy becomes

$$
\begin{aligned}
E &\overset{N\gg 2N_L}{\cong} \int_0^{\frac{N}{2N_L}} dn\, 2N_L\hbar\omega_c n = \frac{2eB_0}{h}L^2\frac{\hbar eB_0}{m}\left[\frac{n^2}{2}\right]_0^{\frac{Nh}{2eB_0L^2}} \\
&= \frac{e^2B_0^2}{\pi m}L^2\frac{1}{2}\frac{N^2h^2}{4e^2B_0^2L^4} = \frac{N^2h^2}{8\pi m}\frac{1}{L^2}\,. \qquad (3.32)
\end{aligned}
$$

Thus, the areal magnetization vanishes:

$$M = -\frac{1}{L^2}\frac{\partial E}{\partial B_0} = 0$$

We could have guessed this result: Smearing out the rapid oscillations at small B_0 would lead to $M = 0$. Thus, $\chi = \frac{\partial M}{\partial B_0} = 0$ in this limit; the diamagnetic susceptibility of the two-dimensional electron gas vanishes.

3.3.2 The three-dimensional electron gas

The Hamiltonian of free electrons in three dimensions in the presence of a uniform magnetic field $\vec{B}_0 = B_0\vec{e}_z$ is

$$H = \frac{1}{2m}\left[\vec{p} + e\vec{A}(\vec{r})\right]^2 = \frac{1}{2m}p_y^2 + \frac{m}{2}\omega_c^2(y-y_0)^2 + \frac{1}{2m}p_z^2\,, \qquad (3.33)$$

using again the Landau gauge $A = (-B_0y, 0, 0)$. Now we obtain free motion in z direction in addition to shifted harmonic oscillators in the xy plane. The eigenenergies are

$$E_{n,\vec{k}} = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{\hbar^2k_z^2}{2m}, \quad n = 0, 1, 2, \dots \qquad (3.34)$$

The density of states is thus a sum of the densities of states of the one-dimensional electron gas, shifted to the minimum energies $\hbar\omega_c\left(n + \frac{1}{2}\right)$, $n = 0, 1, 2, \dots$. The resulting density of states is for one spin direction

$$
\begin{aligned}
D(\varepsilon) &= \frac{N_L}{L^2}\sum_{n=0}^{\infty}\frac{1}{\pi\hbar}\sqrt{\frac{m}{2\left(\varepsilon - \hbar\omega_c\left(n+\frac{1}{2}\right)\right)}}\,\Theta\left(\varepsilon - \hbar\omega_c\left(n + \frac{1}{2}\right)\right) \\
&= \frac{1}{\pi\hbar}\sqrt{\frac{m}{2}}\frac{N_L}{L^2}\sum_{n=0}^{\infty}\frac{\Theta\left(\varepsilon - \hbar\omega_c\left(n+\frac{1}{2}\right)\right)}{\sqrt{\varepsilon - \hbar\omega_c\left(n+\frac{1}{2}\right)}}
\end{aligned}
$$

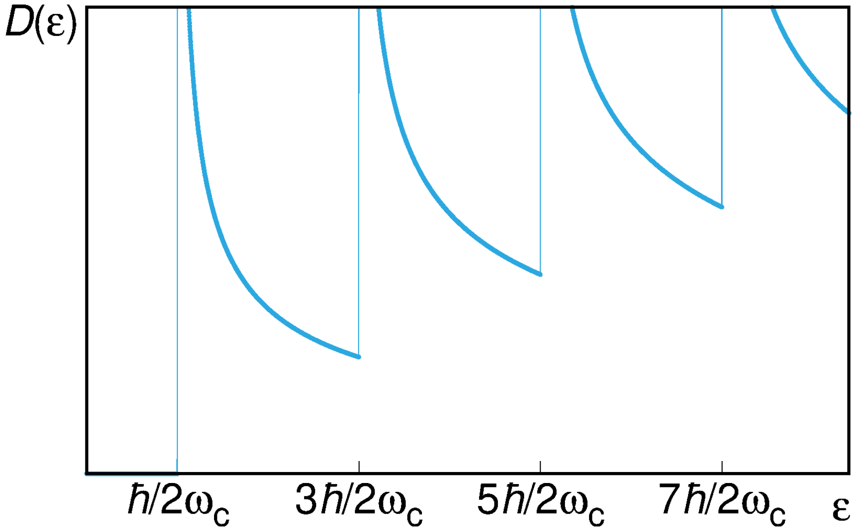

Figure 3.4: Density of states of three-dimensional electron gas at finite magnetic field $B_0 > 0$.

(3.35)

For $k_B T \ll \hbar\omega_c$, the low-energy states are filled up until all electrons are accommodated, as in the case of the two-dimensional electron gas. As before, we expect special features whenever the chemical potential μ reaches $\hbar\omega_c\big(1+\frac{1}{2}\big)$ with $n = 1, 2, \ldots$. Since μ is roughly constant in three dimensions (it has a sawtooth behaviour in two dimensions, with discontinuities at $B_t, B_t/2, B_t/3, \ldots$) while $\hbar\omega_c \propto B_0$, the total energy $E(B_0)$ and therefore the magnetization $M = -\frac{1}{V}\frac{\partial E}{\partial B_0}$ (with volume V) will have features which are periodic in $\frac{1}{B_0}$; these are again de Haas-van Alphen oscillations. They become visible in large magnetic fields.

In the context of conduction electron diamagnetism, we are interested in the susceptibility for small fields. We have $\hbar\omega_c \ll k_B T$, and for a typical metal, we assume $k_B T \ll \mu$. It is useful to define the iterated integrals of the density of states

$$\begin{aligned} P_1(x) &:= \int_0^x d\varepsilon\, D(\varepsilon)\,, \\ P_2(x) &:= \int_0^x d\varepsilon\, P_1(\varepsilon)\,, \end{aligned} \tag{3.36}$$

The total number of electrons is

$$N = 2VP_1(\mu)$$

where the factor 2 accounts for two spin directions. The total energy is

$$E = 2V \int_0^{\mu} d\varepsilon\, \varepsilon D(\varepsilon)\,.$$

Partial integration gives

$$E = 2V\left[\mu P_1(\mu) - \int_0^\mu d\varepsilon\, P_1(\varepsilon)\right] = \mu N - 2VP_2(\mu)\,. \tag{3.37}$$

The explicit expression for $P_2(\mu)$ is

$$P_2(\mu) = \frac{1}{\pi\hbar}\sqrt{\frac{m}{2}}\frac{N_L}{L^2}\sum_{n=0}^{\infty}\frac{4}{3}\left(\mu - \hbar\omega_c\left(n+\frac{1}{2}\right)\right)^{\frac{3}{2}}\Theta\left(\mu - \hbar\omega_c\left(n+\frac{1}{2}\right)\right). \tag{3.38}$$

Since $\hbar\omega_c \ll \mu$, we can replace the sum over n by a integral. The Poisson summation formula provides the correct expression for this:

$$\sum_{n=0}^{\infty} f\left(n+\frac{1}{2}\right) = \int_0^\infty dx\, f(x) + 2\sum_{s=0}^{\infty}(-1)^s\int_0^\infty dx\, f(x)\cos(2\pi s x) \tag{3.39}$$

We find

$$\begin{aligned} P_2(\mu) = \frac{1}{\pi\hbar}\sqrt{\frac{m}{2}}\frac{N_L}{L^2}\frac{4}{3}\Bigg\{ & \int_0^{\frac{\mu}{\hbar\omega_c}-\frac{1}{2}} dx\,(\mu - x\hbar\omega_c)^{\frac{3}{2}} \\ & + 2\sum_{s=1}^{\infty}(-1)^s\int_0^{\frac{\mu}{\hbar\omega_c}-\frac{1}{2}} dx\,(\mu - x\hbar\omega_c)^{\frac{3}{2}}\cos(2\pi s x)\Bigg\} \\ = \frac{1}{\pi\hbar}\sqrt{\frac{m}{2}}\frac{N_L}{L^2}\frac{4}{3}\Bigg\{ & \frac{2}{5}\frac{\mu^{\frac{5}{2}}}{\hbar\omega_c} - \frac{1}{10\sqrt{2}}(\hbar\omega_c)^{\frac{3}{2}} + 2\sum_{s=1}^{\infty}(-1)^s\frac{3}{8\pi^2}\frac{\hbar\omega_c\sqrt{\mu}}{s^2} \\ & + \text{oscillating terms}\Bigg\} \end{aligned} \tag{3.40}$$

The oscillating terms contain $\cos\left(\frac{2\pi s\mu}{\hbar\omega_c}\right)$ or $\sin\left(\frac{2\pi s\mu}{\hbar\omega_c}\right)$, become rapidly oscillating in the limit $\frac{\mu}{\hbar} \to \infty$ (i.e. $B \to 0$) and are neglected. Then using

$$\sum_{s=0}^{\infty}\frac{(-1)^s}{s^2} = -\frac{\pi^2}{12}$$

we get

$$P_2(\mu) \cong \frac{1}{\pi\hbar}\sqrt{\frac{m}{2}}\frac{N_L}{L^2}\frac{4}{3}\left\{\frac{2}{5}\frac{\mu^{\frac{5}{2}}}{\hbar\omega_c} - \frac{1}{10\sqrt{2}}(\hbar\omega_c)^{\frac{3}{2}} - \frac{1}{16}\hbar\omega_c\sqrt{\mu}\right\}. \tag{3.41}$$

Since $N_L \propto B_0$ and $\hbar\omega_c \propto B_0$, the second term is of order $B_0^{\frac{5}{2}}$ and is not important for the susceptibility in the limit $B_0 \to 0$. The first term is of order B_0^0 and determines the energy in the absence of a magnetic field. Thus

$$E = E(B_0 = 0) + 2V\frac{1}{\pi\hbar}\sqrt{\frac{m}{2}}\frac{N_L}{L^2}\frac{4}{3}\frac{1}{16}\hbar\omega_c\sqrt{\mu} = E(B_0 = 0) + \frac{1}{12\pi^2}V\frac{e^2\sqrt{\mu}}{\sqrt{2m}\hbar}B_0^2 \tag{3.42}$$

and the derivatives are

$$\begin{aligned} M &= -\frac{1}{V}\frac{\partial E}{\partial B_0} = -\frac{1}{6\pi^2}\frac{e^2\sqrt{\mu}}{\sqrt{2m}\hbar}B_0\,, \\ \chi &= \frac{\partial M}{\partial B_0} = -\frac{1}{6\pi^2}\frac{e^2\sqrt{\mu}}{\sqrt{2m}\hbar}\,. \end{aligned} \tag{3.43}$$

Using the zero field density of states at the chemical potential $D(\mu) = \frac{m}{2\pi^2\hbar^3\sqrt{2m\mu}}$ we get (with $g = 2$)

$$\chi = -\frac{e^2\hbar^2}{6m^2}D(\mu) = -\frac{g^2\mu_B^2}{6}D(\mu)\,. \tag{3.44}$$

We will see later that this value is minus one third the value of the Pauli susceptibility, the paramagnetic response of the free electrons.