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Chapter 5

Metals

5.1 Introduction

Metals are characterized by a finite electronic density of states $f(\varepsilon_{\mathrm{F}})$ at the Fermi level at zero temperature. This entails a number of salient features, such as thermodynamic, electrodynamic, and transport properties.

5.2 $T = 0$ and the Fermi Surface

5.2.1 Definition of the Fermi surface

The Pauli principle says that each fermionic energy state can accommodate either zero or one electrons[1]. At zero temperature, the ground state of a noninteracting Fermi gas is obtained by filling up all the distinct eigenstates in order of energy, starting from the bottom of the spectrum, until all the fermions are used up. The energy of the last level to be filled is called the *Fermi energy*, and is written ε_{F}. The energy distribution function at $T = 0$ is thus $n(\varepsilon) = \Theta(\varepsilon_{\mathrm{F}} - \varepsilon)$, which says that all single particle energy states up to $\varepsilon = \mu$ are filled, and all energy states above $\varepsilon = \mu$ are empty. As we shall see in the next section, the Fermi energy is the zero temperature value of the chemical potential: $\varepsilon_{\mathrm{F}} = \mu(T = 0)$. If the single particle dispersion $\varepsilon(\boldsymbol{k})$ depends only on the wavevector $\boldsymbol{k}$, then the locus of points in $\boldsymbol{k}$-space for which $\varepsilon(\boldsymbol{k}) = \varepsilon_{\mathrm{F}}$ is called the *Fermi surface*. For isotropic systems, $\varepsilon(\boldsymbol{k}) = \varepsilon(k)$ is a function only of the magnitude $k = |\boldsymbol{k}|$, and the Fermi surface is a sphere in $d = 3$ or a circle in $d = 2$. The radius of this circle is the *Fermi wavevector*, k_{F}. When there is internal (*e.g.* spin) degree of freedom, there is a Fermi

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[1] We consider two degenerate energy states with different spin polarizations ↑ and ↓ to be distinct quantum states.

surface and Fermi wavevector (for isotropic systems) for each polarization state of the internal degree of freedom.

Let's compute the Fermi wavevector k_{F} and Fermi energy ε_{F} for the IFG with a ballistic dispersion $\varepsilon(\boldsymbol{k}) = \hbar^2 \boldsymbol{k}^2/2m$. We allow for a common degeneracy g for each of the $\boldsymbol{k}$ states, *e.g.*, due to spin, for which $\mathsf{g} = 2S+1$, with $S = \frac{1}{2}$ for electrons. The number density is

$$n = \mathsf{g} \int d^d\!k \, \Theta(k_{\mathrm{F}} - k) = \frac{\mathsf{g}\,\Omega_d}{(2\pi)^d} \cdot \frac{k_{\mathrm{F}}^d}{d} = \begin{cases} \mathsf{g}\, k_{\mathrm{F}}/\pi & (d=1) \\[2mm] \mathsf{g}\, k_{\mathrm{F}}^2/4\pi & (d=2) \\[2mm] \mathsf{g}\, k_{\mathrm{F}}^3/6\pi^2 & (d=3) \end{cases}, \tag{5.1}$$

where $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the area of the unit sphere in d space dimensions ($\Omega_1 = 2$, $\Omega_2 = 2\pi$, $\Omega_3 = 4\pi$, *etc.*). Note that the form of $n(k_{\mathrm{F}})$ is independent of the dispersion relation, so long as it remains isotropic. Inverting the above expressions, we obtain $k_{\mathrm{F}}(n)$:

$$k_{\mathrm{F}} = 2\pi \left(\frac{d\,n}{\mathsf{g}\,\Omega_d} \right)^{1/d} = \begin{cases} \pi n/\mathsf{g} & (d=1) \\[2mm] (4\pi n/\mathsf{g})^{1/2} & (d=2) \\[2mm] (6\pi^2 n/\mathsf{g})^{1/3} & (d=3) \end{cases}. \tag{5.2}$$

The Fermi energy in each case, for ballistic dispersion, is therefore

$$\varepsilon_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m} = \frac{2\pi^2\hbar^2}{m} \left(\frac{d\,n}{\mathsf{g}\,\Omega_d} \right)^{2/d} = \begin{cases} \frac{\pi^2\hbar^2 n^2}{2\mathsf{g}^2 m} & (d=1) \\[2mm] \frac{2\pi\hbar^2\, n}{\mathsf{g}\, m} & (d=2) \\[2mm] \frac{\hbar^2}{2m} \left(\frac{6\pi^2 n}{\mathsf{g}} \right)^{2/3} & (d=3) \end{cases}. \tag{5.3}$$

Another useful result for the ballistic dispersion, which follows from the above, is that the density of states at the Fermi level is given by

$$g(\varepsilon_{\mathrm{F}}) = \frac{\mathsf{g}\,\Omega_d}{(2\pi)^d} \cdot \frac{m k_{\mathrm{F}}^{d-2}}{\hbar^2} = \frac{d}{2} \cdot \frac{n}{\varepsilon_{\mathrm{F}}}. \tag{5.4}$$

For the electron gas, we have $\mathsf{g} = 2$. In a metal, one typically has $k_{\mathrm{F}} \sim 0.5\,\text{Å}^{-1}$ to $2\,\text{Å}^{-1}$, and $\varepsilon_{\mathrm{F}} \sim 1\,\text{eV} - 10\,\text{eV}$. Due to the effects of the crystalline lattice, electrons in a solid behave as if they had an *effective mass* m^* which is typically on the order of the electron mass but very often about an order of magnitude smaller, particularly in semiconductors.
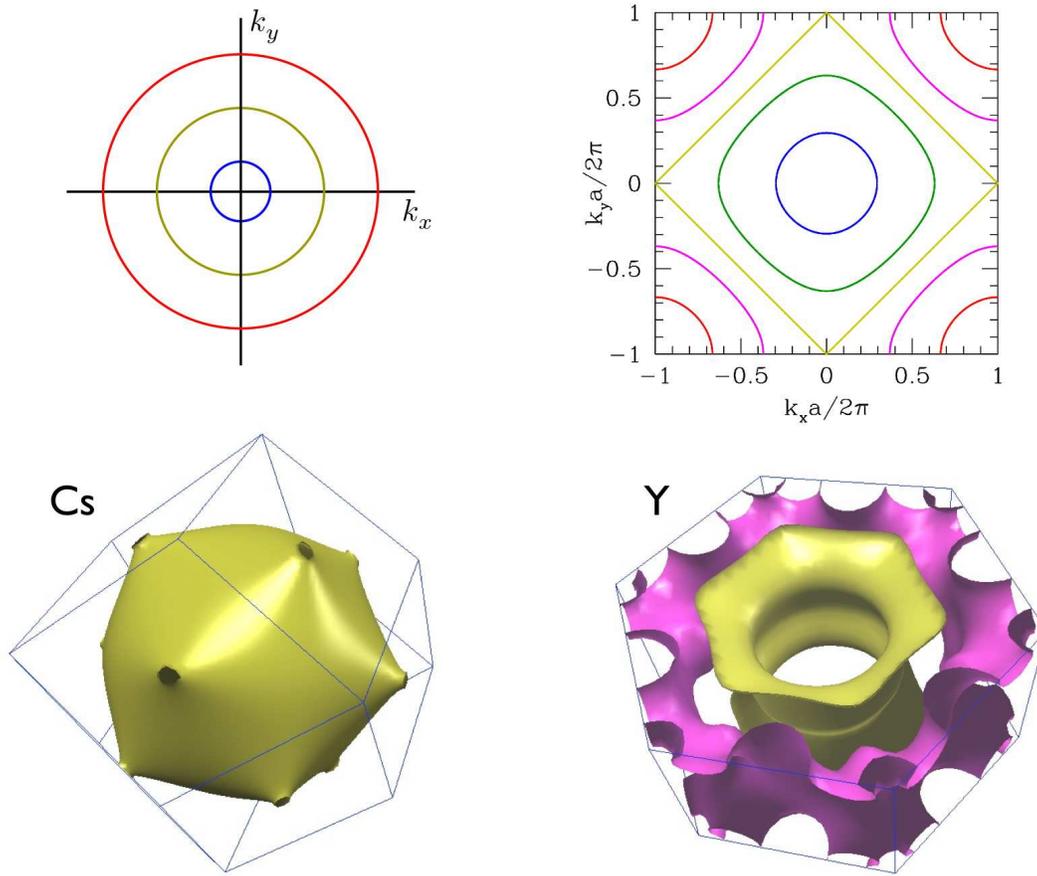
Figure 5.1: Fermi surfaces for two and three-dimensional structures. Upper left: free particles in two dimensions. Upper right: 'tight binding' electrons on a square lattice. Lower left: Fermi surface for cesium, which is predominantly composed of electrons in the $6s$ orbital shell. Lower right: the Fermi surface of yttrium has two parts. One part (yellow) is predominantly due to $5s$ electrons, while the other (pink) is due to $4d$ electrons. (Source: www.phys.ufl.edu/fermisurface/)

In solids, the dispersions $\varepsilon(\boldsymbol{k})$ are in general anisotropic, and give rise to non-spherical Fermi surfaces. The simplest example is that of a two-dimensional tight-binding model of electrons hopping on a square lattice, as may be appropriate in certain layered materials. The dispersion relation is then

$$\varepsilon(k_x, k_y) = -2t \, \cos(k_x a) - 2t \, \cos(k_y a) \quad , \tag{5.5}$$

where k_x and k_y are confined to the interval $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$. The quantity t has dimensions of energy and is known as the *hopping integral*. The Fermi surface is the set of points (k_x, k_y) which satisfies $\varepsilon(k_x, k_y) = \varepsilon_{\mathrm{F}}$. When ε_{F} achieves its minimum value of $\varepsilon_{\mathrm{F}}^{\min} = -4t$, the Fermi surface collapses to a point at $(k_x, k_y) = (0, 0)$. For energies just above this minimum value, we can

expand the dispersion in a power series, writing

$$\varepsilon(k_x, k_y) = -4t + ta^2 \left(k_x^2 + k_y^2\right) - \tfrac{1}{12}\, ta^4 \left(k_x^4 + k_y^4\right) + \ldots \quad . \tag{5.6}$$

If we only work to quadratic order in k_x and k_y, the dispersion is isotropic, and the Fermi surface is a circle, with $k_F^2 = (\varepsilon_F + 4t)/ta^2$. As the energy increases further, the continuous $O(2)$ rotational invariance is broken down to the discrete group of rotations of the square, C_{4v}. The Fermi surfaces distort and eventually, at $\varepsilon_F = 0$, the Fermi surface is itself a square. As ε_F increases further, the square turns back into a circle, but centered about the point $\left(\frac{\pi}{a}, \frac{\pi}{a}\right)$. Note that everything is periodic in k_x and k_y modulo $\frac{2\pi}{a}$. The Fermi surfaces for this model are depicted in the upper right panel of Fig. 5.1.

Fermi surfaces in three dimensions can be very interesting indeed, and of great importance in understanding the electronic properties of solids. Two examples are shown in the bottom panels of Fig. 5.1. The electronic configuration of cesium (Cs) is $[\mathrm{Xe}]\, 6s^1$. The $6s$ electrons 'hop' from site to site on a body centered cubic (BCC) lattice, a generalization of the simple two-dimensional square lattice hopping model discussed above. The elementary unit cell in $\boldsymbol{k}$ space, known as the *first Brillouin zone*, turns out to be a dodecahedron. In yttrium, the electronic structure is $[\mathrm{Kr}]\, 5s^2\, 4d^1$, and there are two electronic energy bands at the Fermi level, meaning two Fermi surfaces. Yttrium forms a hexagonal close packed (HCP) crystal structure, and its first Brillouin zone is shaped like a hexagonal pillbox.

5.2.2   Fermi surface vs. Brillouin zone

The construction of the first Brillouin zone proceeds as follows. Draw the bisecting planes $(d = 3)$ or lines $(d = 2)$ for each of the reciprocal lattice vectors $\boldsymbol{G} = \sum_{\mu=1}^d n_\mu\, \boldsymbol{b}_\mu$. The region bounded by these bisectors which contains the origin is the first Brillouin zone. The regions for which a minimum of one bisector is crossed in order to get to the first zone defines the second zone. Points for which a minimum of $(j-1)$ bisectors must be crossed to arrive in the first zone comprise the jth zone. For the square lattice, this scheme is depicted in Fig. 5.2. By shifting all the various fragments of the jth zone by reciprocal lattice vectors, one can completely cover the first zone, with no overlapping areas. Thus, the volume of each of the zones is always $\hat{v}_0$.

Suppose there are Z electrons per unit cell. The Fermi wavevector k_F is determined by $k_F = (2\pi n)^{1/2}$ with $na^2 = Z$. The side length of the Brillouin zone is $b = 2\pi/a$. Thus, the ratio of the diameter of the free electron Fermi circle to the elementary RLV is

$$r \equiv \frac{2k_F}{b} = \sqrt{\frac{2Z}{\pi}} \quad . \tag{5.7}$$

If $r < 1$, the Fermi circle lies entirely within the first Brillouin zone $\widehat{\Omega}$. This is the case for $Z = 1$, when $r = 0.798$, but for $Z = 2$ the area of the Fermi circle is precisely the Brillouin zone area,

Figure 5.2: Extended zones and their folding for the square lattice. Reciprocal lattice points are shown as yellow dots. The central square, defined by the thick black line, is the first Brillouin zone. The colored lines denote bisectors of reciprocal lattice vectors $\boldsymbol{G} = n_1 \boldsymbol{b}_1 + n_2 \boldsymbol{b}_2$ and are labeled by n_1 and n_2. In general, a minimum of $j - 1$ such bisectors must be crossed in going from the jth Brillouin zone to the first Brillouin zone., with j labeled in black. (Not all of the fourth zone is labeled.)

and $r = (4/\pi)^{1/2} = 1.128$, so the Fermi circle spills over into the second zone. The situation is depicted in the left panel of Fig. 5.3. Since $r < \sqrt{2}$, it does not cross any of the red lines in the left panel, *i.e.* the Fermi circle is confined to the first and second zones. The effect of a weak crystalline potential, as we have seen, is to introduce energy gaps along the Brillouin zone boundaries. If the crystalline potential is strong enough, it can pull all of the states from the second zone into the first zone, completely filling it , thereby resulting in a band insulator.

When $Z = 3$, find $r = 1.382 < \sqrt{2}$, so again the Fermi surface lies only within the first and second zones. For $Z = 4$, $r = 1.596 > \sqrt{2}$, and as we see in the right panel of the figure, the Fermi sea completely encloses the first zone, and spills over into zones two, three, and four.

What happens in $d = 3$ dimensions? Fig. 5.4 shows some examples. Sodium (Na) is mono-valent, and the volume of its free electron Fermi sphere is half that of the Brillouin zone and fits entirely within $\widehat{\Omega}$. The crystal structure is bcc and the first Brillouin zone has the shape of a rhombic dodecahedron. Copper (Cu) is also monovalent, but the crystalline potential is stronger and leads to the eight Fermi surface 'necks' shown in the figure. The crystal structure is fcc, and the Brillouin zone has the shape of a truncated octahedron. The necks straddle the eight hexagonal faces of the first zone. Calcium (Ca) is divalent, hence the free electron Fermi

Figure 5.3: Brillouin zones and free electron Fermi seas (in blue) for the square lattice. Left: $Z = 2$ electrons per cell. The Fermi surface has area $\hat{v}_0$, and the free electron Fermi sea extends into the second zone. Right: $Z = 4$ electrons per cell. The Fermi surface has area $2\hat{v}_0$. and the free electron Fermi sea completely covers the first zone, and extends into portions of the second, third, and fourth zones.

sphere has exactly the same volume as that of the first Brillouin zone. Thus, this sphere must cut across the Brillouin zone boundaries, resulting in two bands, the Fermi surface in the first of which is depicted in the figure. The lattice potential pulls most but not all of the states in the second zone into the first zone.

5.2.3 Spin-split Fermi surfaces

Consider an electron gas in an external magnetic field H. The single particle Hamiltonian is then

$$\hat{H} = \frac{\boldsymbol{p}^2}{2m} + \mu_{\mathrm{B}} H \sigma \quad , \tag{5.8}$$

where μ_{B} is the *Bohr magneton*,

$$\mu_{\mathrm{B}} = \frac{e\hbar}{2mc} = 5.788 \times 10^{-9} \, \mathrm{eV/G}$$

$$\mu_{\mathrm{B}}/k_{\mathrm{B}} = 6.717 \times 10^{-5} \, \mathrm{K/G} \quad , \tag{5.9}$$

where m is the electron mass. What happens at $T = 0$ to a noninteracting electron gas in a magnetic field?
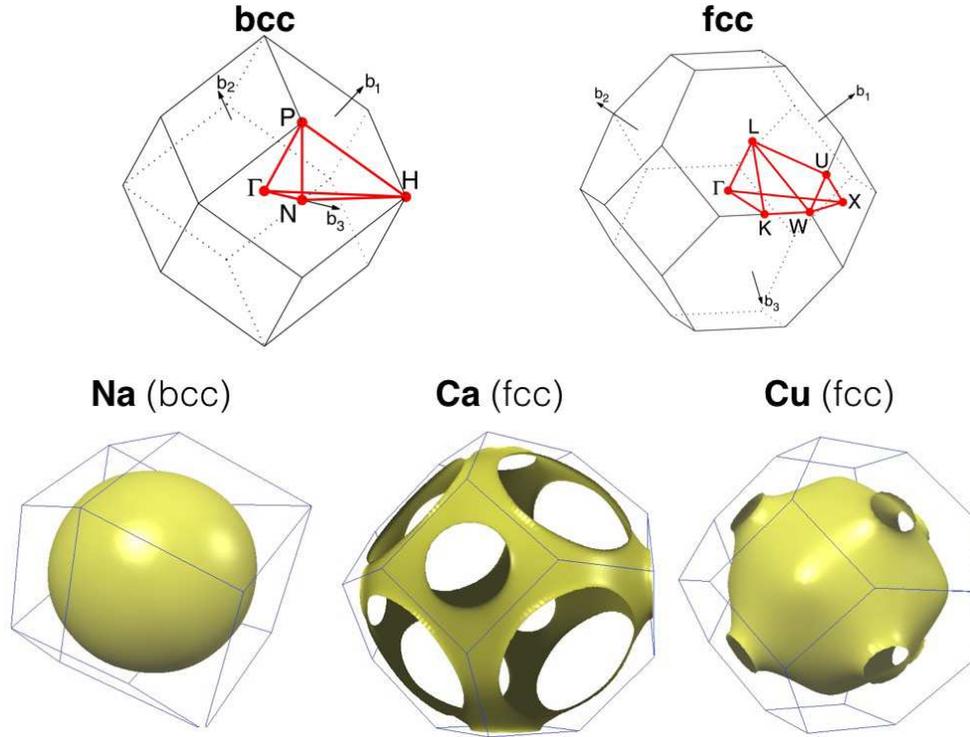
Figure 5.4: Top: First Brillouin zones for bcc (left) and fcc (right) lattice solids. Bottom: Fermi surfaces for Na (left), Ca (center), and Cu (right). (Source: www.phys.ufl.edu/fermisurface/)

Electrons of each spin polarization form their own Fermi surfaces. That is, there is an up spin Fermi surface, with Fermi wavevector $k_{F\uparrow}$, and a down spin Fermi surface, with Fermi wavevector $k_{F\downarrow}$. The individual Fermi energies, on the other hand, must be equal, hence

$$\frac{\hbar^2 k_{F\uparrow}^2}{2m} + \mu_B H = \frac{\hbar^2 k_{F\downarrow}^2}{2m} - \mu_B H \quad , \tag{5.10}$$

which says

$$k_{F\downarrow}^2 - k_{F\uparrow}^2 = \frac{2eH}{\hbar c} \quad . \tag{5.11}$$

The total density is

$$n = \frac{k_{F\uparrow}^3}{6\pi^2} + \frac{k_{F\downarrow}^3}{6\pi^2} \qquad \Longrightarrow \qquad k_{F\uparrow}^3 + k_{F\downarrow}^3 = 6\pi^2 n \quad . \tag{5.12}$$

Clearly the down spin Fermi surface grows and the up spin Fermi surface shrinks with increasing H. Eventually, the minority spin Fermi surface vanishes altogether. This happens for the up spins when $k_{F\uparrow} = 0$. Solving for the critical field, we obtain

$$H_c = \frac{\hbar c}{2e} \cdot \left(6\pi^2 n\right)^{1/3} \quad . \tag{5.13}$$

In real magnetic solids, like cobalt and nickel, the spin-split Fermi surfaces are not spheres, just like the case of the (spin degenerate) Fermi surfaces for Cs and Y shown in Fig. 5.1.

5.3   Quantum Thermodynamics of the Electron Gas

Electrons are fermions, and from this flows some universal features of their thermodynamic properties. We shall assume for the moment that the electrons are noninteracting, or that their mutual interactions can be treated within a "mean field" scheme. In this case, the grand potential of the electron gas is given by

$$
\begin{aligned}
\Omega(T, V, \mu) &= -V k_{\mathrm{B}} T \sum_{\alpha} \ln\left(1 + e^{\mu/k_{\mathrm{B}}T}\, e^{-\varepsilon_\alpha/k_{\mathrm{B}}T}\right) \\
&= -V k_{\mathrm{B}} T \int\limits_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, \ln\left(1 + e^{(\mu-\varepsilon)/k_{\mathrm{B}}T}\right) \quad .
\end{aligned}
\tag{5.14}
$$

The average number of particles in a state with energy ε is

$$
n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_{\mathrm{B}}T} + 1} \quad ,
\tag{5.15}
$$

hence the total number of particles is

$$
N = V \int\limits_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, \frac{1}{e^{(\varepsilon-\mu)/k_{\mathrm{B}}T} + 1} \quad .
\tag{5.16}
$$

5.3.1   Fermi distribution

We define the function $f(x) = 1/(e^{\beta x} + 1)$, known as the *Fermi distribution*. In the $T \to \infty$ limit, $f(\epsilon) \to \frac{1}{2}$ for all finite values of ε. As $T \to 0$, $f(\epsilon)$ approaches a step function $\Theta(-\epsilon)$. The average number of particles in a state of energy ε in a system at temperature T and chemical potential μ is $n(\varepsilon) = f(\varepsilon - \mu)$. In Fig. 5.5 we plot $f(\varepsilon - \mu)$ *versus* ε for three representative temperatures.

5.3.2   Sommerfeld expansion

In dealing with the ideal Fermi gas, we will repeatedly encounter integrals of the form

$$
\mathcal{I}(T, \mu) \equiv \int\limits_{-\infty}^{\infty} d\varepsilon\, f(\varepsilon - \mu)\, \phi(\varepsilon) \quad .
\tag{5.17}
$$
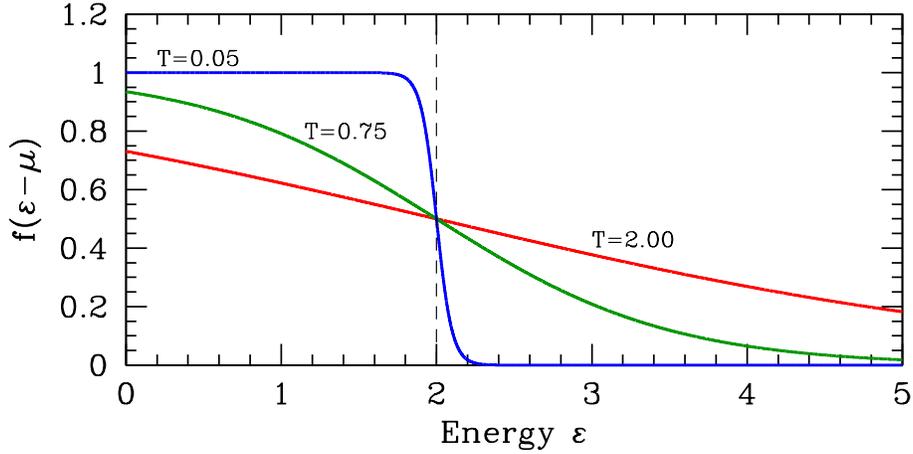
Figure 5.5: The Fermi distribution, $f(\varepsilon - \mu) = \left[\exp\left((\varepsilon - \mu)/k_{\mathrm{B}}T \right) + 1 \right]^{-1}$. Here we have set $k_{\mathrm{B}} = 1$ and taken $\mu = 2$, with $T = \frac{1}{20}$ (blue), $T = \frac{3}{4}$ (green), and $T = 2$ (red). In the $T \to 0$ limit, $f(\varepsilon - \mu)$ approaches a step function $\Theta(\mu - \varepsilon)$.

The Sommerfeld expansion provides a systematic way of expanding these expressions in powers of T and is an important analytical tool in analyzing the low temperature properties of the ideal Fermi gas (IFG). We start by defining

$$\Phi(\varepsilon) \equiv \int\limits_{-\infty}^{\varepsilon} d\varepsilon' \, \phi(\varepsilon') \tag{5.18}$$

so that $\phi(\varepsilon) = \Phi'(\varepsilon)$. We then have

$$\mathcal{I} = \int\limits_{-\infty}^{\infty} d\varepsilon \, f(\varepsilon - \mu) \, \frac{d\Phi}{d\varepsilon} = -\int\limits_{-\infty}^{\infty} d\varepsilon \, f'(\varepsilon) \, \Phi(\mu + \varepsilon) \quad , \tag{5.19}$$

where we assume $\Phi(-\infty) = 0$. Next, we invoke Taylor's theorem, to write

$$\Phi(\mu + \varepsilon) = \sum_{n=0}^{\infty} \frac{\varepsilon^n}{n!} \frac{d^n \Phi}{d\mu^n} = \exp\left(\varepsilon \, \frac{d}{d\mu} \right) \Phi(\mu) \quad . \tag{5.20}$$

This last expression involving the exponential of a differential operator may appear overly formal but it proves extremely useful. Since

$$f'(\varepsilon) = -\frac{1}{k_{\mathrm{B}}T} \frac{e^{\varepsilon/k_{\mathrm{B}}T}}{\left(e^{\varepsilon/k_{\mathrm{B}}T} + 1 \right)^2} \quad , \tag{5.21}$$

we can write

$$\mathcal{I} = \int\limits_{-\infty}^{\infty} dv \, \frac{e^{vD}}{(e^v + 1)(e^{-v} + 1)} \, \Phi(\mu) \quad , \tag{5.22}$$
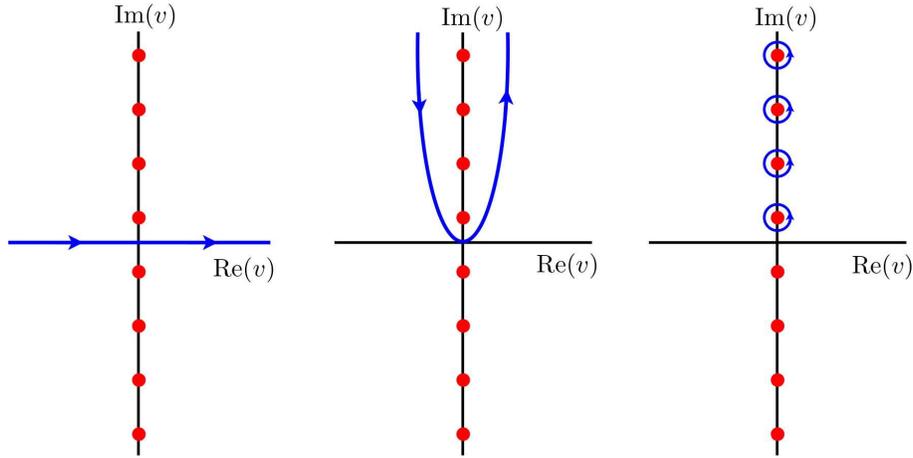
Figure 5.6: Deformation of the complex integration contour in Eqn. 5.23.

with $v = \varepsilon/k_{\mathrm{B}}T$, where $D = k_{\mathrm{B}}T\frac{d}{d\mu}$ is a dimensionless differential operator. The integral can now be done using the methods of complex integration:[2]

$$\int_{-\infty}^{\infty} dv\, \frac{e^{vD}}{(e^v + 1)(e^{-v} + 1)} = 2\pi i \sum_{n=1}^{\infty} \mathrm{Res}\left[\frac{e^{vD}}{(e^v + 1)(e^{-v} + 1)}\right]_{v=(2n+1)i\pi}$$

$$= -2\pi i \sum_{n=0}^{\infty} D\, e^{(2n+1)i\pi D} = -\frac{2\pi i D\, e^{i\pi D}}{1 - e^{2\pi i D}} = \pi D\, \csc \pi D \quad . \tag{5.23}$$

Thus,

$$\mathcal{I}(T, \mu) = \pi D\, \csc(\pi D)\, \Phi(\mu) \quad , \tag{5.24}$$

which is to be understood as the differential operator $\pi D \csc(\pi D) = \pi D/\sin(\pi D)$ acting on the function $\Phi(\mu)$. Appealing once more to Taylor's theorem, we have

$$\pi D \csc(\pi D) = 1 + \frac{\pi^2}{6}\,(k_{\mathrm{B}}T)^2\,\frac{d^2}{d\mu^2} + \frac{7\pi^4}{360}\,(k_{\mathrm{B}}T)^4\,\frac{d^4}{d\mu^4} + \ldots \quad . \tag{5.25}$$

Thus,

$$\mathcal{I}(T, \mu) = \int_{-\infty}^{\infty} d\varepsilon\, f(\varepsilon - \mu)\, \phi(\varepsilon) = \int_{-\infty}^{\mu} d\varepsilon\, \phi(\varepsilon) + \frac{\pi^2}{6}\,(k_{\mathrm{B}}T)^2\,\phi'(\mu) + \frac{7\pi^4}{360}\,(k_{\mathrm{B}}T)^4\,\phi'''(\mu) + \ldots \quad . \tag{5.26}$$

If $\phi(\varepsilon)$ is a polynomial function of its argument, then each derivative effectively reduces the order of the polynomial by one degree, and the dimensionless parameter of the expansion is $(T/\mu)^2$. This procedure is known as the *Sommerfeld expansion*.

---

[2]Note that writing $v = (2n + 1)\,i\pi + \epsilon$ we have $e^{\pm v} = -1 \mp \epsilon - \frac{1}{2}\epsilon^2 + \ldots$, so $(e^v + 1)(e^{-v} + 1) = -\epsilon^2 + \ldots$ We then expand $e^{vD} = e^{(2n+1)i\pi D}\left(1 + \epsilon D + \ldots\right)$ to find the residue: $\mathrm{Res} = -D\,e^{(2n+1)i\pi D}$.

5.3.3 Chemical potential shift

As our first application of the Sommerfeld expansion formalism, let us compute $\mu(n, T)$ for the ideal Fermi gas. The number density $n(T, \mu)$ is

$$n = \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) \, f(\varepsilon - \mu) = \int_{-\infty}^{\mu} d\varepsilon \, g(\varepsilon) + \frac{\pi^2}{6} \, (k_{\mathrm{B}}T)^2 \, g'(\mu) + \ldots \quad . \tag{5.27}$$

Let us write $\mu = \varepsilon_{\mathrm{F}} + \delta\mu$, where $\varepsilon_{\mathrm{F}} = \mu(T = 0, n)$ is the Fermi energy, which is the chemical potential at $T = 0$. We then have

$$
\begin{aligned}
n &= \int_{-\infty}^{\varepsilon_{\mathrm{F}}+\delta\mu} d\varepsilon \, g(\varepsilon) + \frac{\pi^2}{6} \, (k_{\mathrm{B}}T)^2 \, g'(\varepsilon_{\mathrm{F}} + \delta\mu) + \ldots \\
&= \int_{-\infty}^{\varepsilon_{\mathrm{F}}} d\varepsilon \, g(\varepsilon) + g(\varepsilon_{\mathrm{F}}) \, \delta\mu + \frac{\pi^2}{6} \, (k_{\mathrm{B}}T)^2 \, g'(\varepsilon_{\mathrm{F}}) + \ldots \quad ,
\end{aligned}
\tag{5.28}
$$

from which we derive

$$\delta\mu = -\frac{\pi^2}{6} \, (k_{\mathrm{B}}T)^2 \, \frac{g'(\varepsilon_{\mathrm{F}})}{g(\varepsilon_{\mathrm{F}})} + \mathcal{O}(T^4) \quad . \tag{5.29}$$

Note that $g'/g = (\ln g)'$. For a ballistic dispersion, assuming $\mathsf{g} = 2$,

$$g(\varepsilon) = 2 \int \frac{d^3k}{(2\pi)^3} \, \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) = \frac{m \, k(\varepsilon)}{\pi^2 \hbar^2}\bigg|_{k(\varepsilon)=\frac{1}{\hbar}\sqrt{2m\varepsilon}} \tag{5.30}$$

Thus, $g(\varepsilon) \propto \varepsilon^{1/2}$ and $(\ln g)' = \frac{1}{2} \varepsilon^{-1}$, so

$$\mu(n, T) = \varepsilon_{\mathrm{F}} - \frac{\pi^2}{12} \frac{(k_{\mathrm{B}}T)^2}{\varepsilon_{\mathrm{F}}} + \ldots \quad , \tag{5.31}$$

where $\varepsilon_{\mathrm{F}}(n) = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$.

5.3.4   Specific heat

The energy of the electron gas is

$$
\begin{aligned}
\frac{E}{V} &= \int\limits_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon)\, \varepsilon \, f(\varepsilon - \mu) = \int\limits_{-\infty}^{\mu} d\varepsilon \, g(\varepsilon)\, \varepsilon + \frac{\pi^2}{6}\, (k_{\mathrm{B}}T)^2\, \frac{d}{d\mu}\Big(\mu\, g(\mu)\Big) + \ldots \\[2mm]
&= \int\limits_{-\infty}^{\varepsilon_{\mathrm{F}}} d\varepsilon \, g(\varepsilon)\, \varepsilon + g(\varepsilon_{\mathrm{F}})\, \varepsilon_{\mathrm{F}}\, \delta\mu + \frac{\pi^2}{6}\, (k_{\mathrm{B}}T)^2\, \varepsilon_{\mathrm{F}}\, g'(\varepsilon_{\mathrm{F}}) + \frac{\pi^2}{6}\, (k_{\mathrm{B}}T)^2\, g(\varepsilon_{\mathrm{F}}) + \ldots \\[2mm]
&= \mathrm{e}_0 + \frac{\pi^2}{6}\, (k_{\mathrm{B}}T)^2\, g(\varepsilon_{\mathrm{F}}) + \ldots \quad ,
\end{aligned}
\tag{5.32}
$$

where $\mathrm{e}_0 = \int\limits_{-\infty}^{\varepsilon_{\mathrm{F}}} d\varepsilon \, g(\varepsilon)\, \varepsilon$ is the ground state energy density (*i.e.* ground state energy per unit volume). Thus,

$$
C_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{\pi^2}{3}\, V k_{\mathrm{B}}^2\, T\, g(\varepsilon_{\mathrm{F}}) \equiv V\gamma T \quad ,
\tag{5.33}
$$

where

$$
\gamma = \frac{\pi^2}{3}\, k_{\mathrm{B}}^2\, g(\varepsilon_{\mathrm{F}}) \quad .
\tag{5.34}
$$

Note that the molar heat capacity is

$$
c_V = \frac{N_{\mathrm{A}}}{N} \cdot C_V = \frac{\pi^2}{3} R \cdot \frac{k_{\mathrm{B}}T\, g(\varepsilon_{\mathrm{F}})}{n} = \frac{\pi^2}{2}\left(\frac{k_{\mathrm{B}}T}{\varepsilon_{\mathrm{F}}}\right) R \quad ,
\tag{5.35}
$$

where in the last expression on the RHS we have assumed a ballistic dispersion, for which

$$
\frac{g(\varepsilon_{\mathrm{F}})}{n} = \frac{\mathsf{g}\, m k_{\mathrm{F}}}{2\pi^2 \hbar^2} \cdot \frac{6\pi^2}{\mathsf{g}\, k_{\mathrm{F}}^3} = \frac{3}{2\, \varepsilon_{\mathrm{F}}} \quad .
\tag{5.36}
$$

The molar heat capacity in Eqn. 5.35 is to be compared with the classical ideal gas value of $\frac{3}{2}R$. Relative to the classical ideal gas, the IFG value is reduced by a fraction of $(\pi^2/3) \times (k_{\mathrm{B}}T/\varepsilon_{\mathrm{F}})$, which in most metals is very small and even at room temperature is only on the order of 10^{-2}. Most of the heat capacity of metals at room temperature is due to the energy stored in lattice vibrations.

5.4 Effects of External Magnetic Fields

5.4.1 Magnetic susceptibility and Pauli paramagnetism

Magnetism has two origins: (i) orbital currents of charged particles, and (ii) intrinsic magnetic moment. The intrinsic magnetic moment $\boldsymbol{m}$ of a particle is related to its quantum mechanical *spin* via

$$\boldsymbol{m} = \overline{g}\mu_0 \boldsymbol{S}/\hbar \quad , \quad \mu_0 = \frac{q\hbar}{2mc} = \text{magneton} \quad , \tag{5.37}$$

where $\overline{g}$ is the particle's g-factor[3], μ_0 its magnetic moment, and $\boldsymbol{S}$ is the vector of quantum mechanical spin operators satisfying $\left[S^\alpha, S^\beta \right] = i\hbar\epsilon_{\alpha\beta\gamma} S^\gamma$, *i.e.* SU(2) commutation relations. The Hamiltonian for a single particle is then

$$\hat{H} = \frac{1}{2m^*}\left(\boldsymbol{p} - \frac{q}{c}\boldsymbol{A}\right)^2 - \boldsymbol{H} \cdot \boldsymbol{m} = \frac{1}{2m^*}\left(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A}\right)^2 + \tfrac{1}{2}\overline{g}\,\mu_{\text{B}} H\,\sigma \quad , \tag{5.38}$$

where in the last line we've restricted our attention to the electron, for which $q = -e$. The g-factor for an electron is $\overline{g} = 2$ at tree level, and when radiative corrections are accounted for using quantum electrodynamics (QED) one finds $\overline{g} = 2.0023193043617(15)$. For our purposes we can take $\overline{g} = 2$, although we can always absorb the small difference into the definition of μ_{B}, writing $\mu_{\text{B}} \to \tilde{\mu}_{\text{B}} = \overline{g}e\hbar/4mc$. We've chosen the $\hat{\boldsymbol{z}}$-axis in spin space to point in the direction of the magnetic field, and we wrote the eigenvalues of S^z as $\tfrac{1}{2}\hbar\sigma$, where $\sigma = \pm 1$. The quantity m^* is the *effective mass* of the electron, here assumed to be isotropic in the vicinity of a band edge. An important distinction is that it is m^* which enters into the kinetic energy term $\boldsymbol{p}^2/2m^*$, but it is the electron mass m itself ($m = 511\,\text{keV}$) which enters into the definition of the Bohr magneton. We shall discuss the consequences of this further below.

In a crystalline semiconductor, the spin-orbit interaction,

$$V_{\text{so}} = \frac{\hbar}{4m^2c^2}\,\boldsymbol{p} \cdot \boldsymbol{\sigma} \times \boldsymbol{\nabla} V \quad , \tag{5.39}$$

leads to an effective $\overline{g}$ which is often very far from the free electron value. For cubic systems with a direct band gap, the g-factor in band n is given by[4]

$$\frac{\overline{g}}{2} = 1 + \frac{2}{m}\,\text{Im}\,\sum_{n'}{}' \frac{\langle\,n\,\Gamma\,|\,p_x\,|\,n'\,\Gamma\,\rangle\langle\,n'\,\Gamma\,|\,p_y\,|\,n\,\Gamma\,\rangle}{E_n(\Gamma) - E_{n'}(\Gamma)} + \dots \quad , \tag{5.40}$$

where the wavefunctions and the energies are all taken at the zone center Γ. InSb, for example, has $\overline{g} \simeq -44$, while in GaAs $\overline{g} \simeq 0.4$.

---

[3]We denote the g-factor by $\overline{g}$ in order to obviate confusion with the density of states function $g(\varepsilon)$.
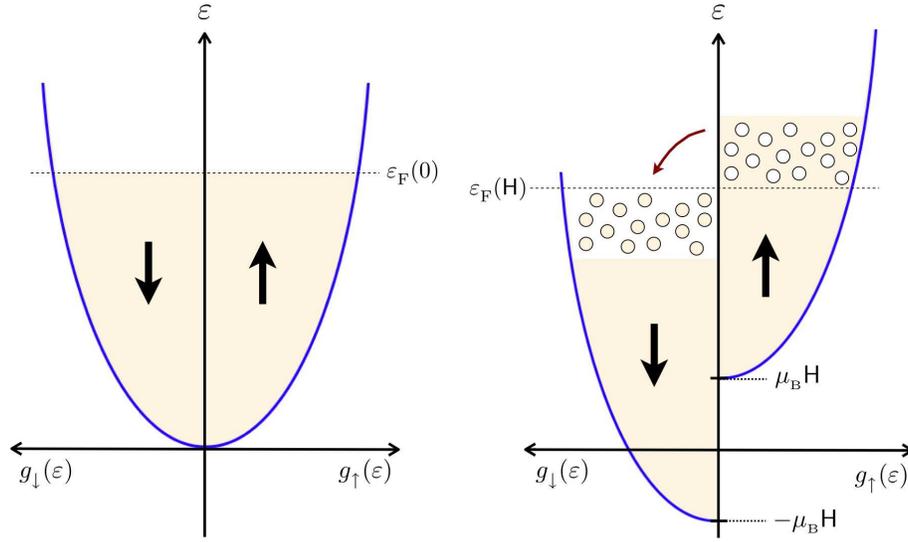[4]See, *e.g.*, ch. 14 of C. Kittel, *Quantum Theory of Solids.*

Figure 5.7: Fermi distributions in the presence of an external Zeeman-coupled magnetic field.

In the absence of orbital magnetic coupling, the single particle dispersion is

$$\varepsilon_\sigma(\boldsymbol{k}) = \frac{\hbar^2 \boldsymbol{k}^2}{2m^*} + \tilde{\mu}_{\mathrm{B}} H\, \sigma \quad . \tag{5.41}$$

At $T = 0$, we have the results of §5.2.3. At finite T, we once again use the Sommerfeld expansion. We then have

$$
\begin{aligned}
n &= \int\limits_{-\infty}^{\infty} d\varepsilon\, g_\uparrow(\varepsilon)\, f(\varepsilon - \mu) \;+\; \int\limits_{-\infty}^{\infty} d\varepsilon\, g_\downarrow(\varepsilon)\, f(\varepsilon - \mu) \\[4pt]
&= \tfrac{1}{2}\int\limits_{-\infty}^{\infty} d\varepsilon \left\{ g(\varepsilon - \tilde{\mu}_{\mathrm{B}} H) + g(\varepsilon + \tilde{\mu}_{\mathrm{B}} H) \right\} f(\varepsilon - \mu) \\[4pt]
&= \int\limits_{-\infty}^{\infty} d\varepsilon \left\{ g(\varepsilon) + (\tilde{\mu}_{\mathrm{B}} H)^2\, g''(\varepsilon) + \dots \right\} f(\varepsilon - \mu) \quad .
\end{aligned}
\tag{5.42}
$$

We now invoke the Sommerfeld expension to find the temperature dependence:

$$
\begin{aligned}
n &= \int\limits_{-\infty}^{\mu} d\varepsilon\, g(\varepsilon) + \frac{\pi^2}{6}\,(k_{\mathrm{B}} T)^2\, g'(\mu) + (\tilde{\mu}_{\mathrm{B}} H)^2\, g'(\mu) + \dots \\[4pt]
&= \int\limits_{-\infty}^{\varepsilon_{\mathrm{F}}} d\varepsilon\, g(\varepsilon) + g(\varepsilon_{\mathrm{F}})\, \delta\mu + \frac{\pi^2}{6}\,(k_{\mathrm{B}} T)^2\, g'(\varepsilon_{\mathrm{F}}) + (\tilde{\mu}_{\mathrm{B}} H)^2\, g'(\varepsilon_{\mathrm{F}}) + \dots \quad .
\end{aligned}
\tag{5.43}
$$

Note that the density of states for spin species σ is

$$g_\sigma(\varepsilon) = \tfrac{1}{2}\, g(\varepsilon - \tilde{\mu}_{\mathrm{B}} H \sigma) \quad , \tag{5.44}$$

where $g(\varepsilon)$ is the total density of states per unit volume, for both spin species, in the absence of a magnetic field. We conclude that the chemical potential shift in an external field is

$$\delta\mu(T, n, H) = -\left\{ \frac{\pi^2}{6}\, (k_{\mathrm{B}} T)^2 + (\tilde{\mu}_{\mathrm{B}} H)^2 \right\} \frac{g'(\varepsilon_{\mathrm{F}})}{g(\varepsilon_{\mathrm{F}})} + \dots \quad . \tag{5.45}$$

We next compute the difference $n_\uparrow - n_\downarrow$ in the densities of up and down spin electrons:

$$
\begin{aligned}
n_\uparrow - n_\downarrow &= \int\limits_{-\infty}^{\infty} d\varepsilon\, \left\{ g_\uparrow(\varepsilon) - g_\downarrow(\varepsilon) \right\} f(\varepsilon - \mu) \\[4pt]
&= \tfrac{1}{2} \int\limits_{-\infty}^{\infty} d\varepsilon\, \left\{ g(\varepsilon - \tilde{\mu}_{\mathrm{B}} H) - g(\varepsilon + \tilde{\mu}_{\mathrm{B}} H) \right\} f(\varepsilon - \mu) \\[4pt]
&= -\tilde{\mu}_{\mathrm{B}} H \cdot \pi D \csc(\pi D)\, g(\mu) + \mathcal{O}(H^3) \quad .
\end{aligned}
\tag{5.46}
$$

We needn't go beyond the trivial lowest order term in the Sommerfeld expansion, because H is already assumed to be small. Thus, the magnetization density is

$$M = -\tilde{\mu}_{\mathrm{B}}(n_\uparrow - n_\downarrow) = \tilde{\mu}_{\mathrm{B}}^2\, g(\varepsilon_{\mathrm{F}})\, H \quad . \tag{5.47}$$

in which the magnetic susceptibility is

$$\chi = \left(\frac{\partial M}{\partial H} \right)_{T,N} = \tilde{\mu}_{\mathrm{B}}^2\, g(\varepsilon_{\mathrm{F}}) \quad . \tag{5.48}$$

This is called the *Pauli paramagnetic susceptibility*.

5.4.2   Landau diamagnetism

When orbital effects are included, the single particle energy levels are given by

$$\varepsilon(n, k_z, \sigma) = (n + \tfrac{1}{2})\hbar\omega_{\mathrm{c}} + \frac{\hbar^2 k_z^2}{2m^*} + \tilde{\mu}_{\mathrm{B}} H\, \sigma \quad . \tag{5.49}$$

Here n is a Landau level index, and $\omega_{\mathrm{c}} = eH/m^*c$ is the *cyclotron frequency*. Note that

$$\frac{\tilde{\mu}_{\mathrm{B}} H}{\hbar\omega_{\mathrm{c}}} = \frac{ge\hbar H}{4mc} \cdot \frac{m^*c}{\hbar e H} = \frac{\bar{g}}{4} \cdot \frac{m^*}{m} \quad . \tag{5.50}$$
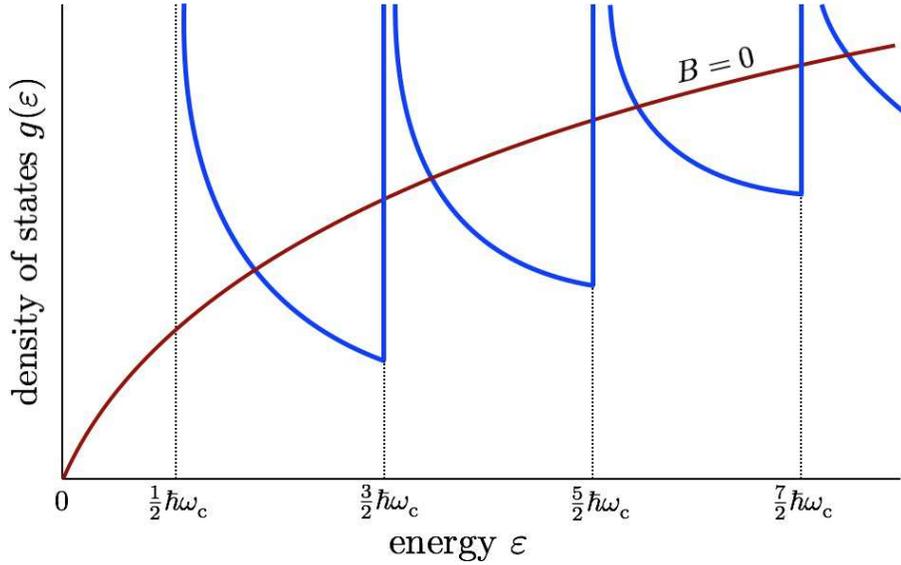
Figure 5.8: Density of states for a three-dimensional free electron gas with $\overline{g} = 0$ in the presence of an external magnetic field (blue), compared with $B = 0$ result (dark red).

Accordingly, we define the ratio $r \equiv (\overline{g}/2) \times (m^*/m)$. We can then write

$$\varepsilon(n, k_z, \sigma) = \left(n + \tfrac{1}{2} + \tfrac{1}{2}r\sigma\right)\hbar\omega_{\rm c} + \frac{\hbar^2 k_z^2}{2m^*} \quad . \tag{5.51}$$

The density of states per unit volume is then

$$g(\varepsilon) = \frac{1}{2\pi\ell^2} \sum_{n,\sigma} \int\limits_{-\infty}^{\infty} \frac{dk_z}{2\pi}\, \delta\big(\varepsilon - \varepsilon(n, k_z, \sigma)\big) \quad , \tag{5.52}$$

where $\ell = (\hbar c/eH)^{1/2}$ is the *magnetic length*. The significance of ℓ is that the area per Dirac fluxoid $\phi_0 = hc/e$ is $2\pi\ell^2$.

The grand potential is then given by

$$\Omega = -\frac{HA}{\phi_0} \cdot L_z \cdot k_{\rm B}T \int\limits_{-\infty}^{\infty} \frac{dk_z}{2\pi} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} \ln\left[1 + e^{\mu/k_{\rm B}T}\, e^{-(n+\frac{1}{2}+\frac{1}{2}r\sigma)\,\hbar\omega_{\rm c}/k_{\rm B}T}\, e^{-\hbar^2 k_z^2/2m^* k_{\rm B}T}\right] \quad . \tag{5.53}$$

A few words are in order here regarding the prefactor. In the presence of a uniform magnetic field, the energy levels of a two-dimensional ballistic charged particle collapse into Landau levels. The number of states per Landau level scales with the area of the system, and is equal to the number of flux quanta through the system: $N_\phi = HA/\phi_0$, where $\phi_0 = hc/e$ is the Dirac flux quantum. Note that

$$\frac{HA}{\phi_0} \cdot L_z \cdot k_{\rm B}T = \hbar\omega_{\rm c} \cdot \frac{V}{\lambda_T^3} \quad , \tag{5.54}$$

hence we can write

$$\Omega(T, V, \mu, H) = \hbar\omega_{\mathrm{c}} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} Q\big((n + \tfrac{1}{2} + \tfrac{1}{2}r\sigma)\,\hbar\omega_{\mathrm{c}} - \mu\big) \quad , \tag{5.55}$$

where we have defined the dimensionless function

$$Q(\varepsilon) = -\frac{V}{\lambda_T^2} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi}\, \ln\Big[1 + e^{-\varepsilon/k_{\mathrm{B}}T}\,e^{-\hbar^2 k_z^2/2m^* k_{\mathrm{B}}T}\Big] \quad . \tag{5.56}$$

We now invoke the Euler-MacLaurin formula,

$$\sum_{n=0}^{\infty} F(n) = \int_0^{\infty} dx\, F(x) + \tfrac{1}{2}\,F(0) - \tfrac{1}{12}\,F'(0) + \dots \quad , \tag{5.57}$$

resulting in

$$\Omega(T, V, \mu, H) = \sum_{\sigma=\pm 1} \Bigg\{ \int_{\frac{1}{2}(1+r\sigma)\hbar\omega_{\mathrm{c}}}^{\infty} d\varepsilon\, Q(\varepsilon - \mu) + \tfrac{1}{2}\,\hbar\omega_{\mathrm{c}}\, Q\big(\tfrac{1}{2}(1+r\sigma)\,\hbar\omega_{\mathrm{c}} - \mu\big)$$
$$- \tfrac{1}{12}\,(\hbar\omega_{\mathrm{c}})^2\, Q'\big(\tfrac{1}{2}(1+r\sigma)\,\hbar\omega_{\mathrm{c}} - \mu\big) + \dots \Bigg\} \quad . \tag{5.58}$$

We next expand in powers of the magnetic field H to obtain

$$\Omega(T, V, \mu, H) = 2 \int_0^{\infty} d\varepsilon\, Q(\varepsilon - \mu) + \tfrac{1}{4}\big(r^2 - \tfrac{1}{3}\big)\,(\hbar\omega_{\mathrm{c}})^2\, Q'(-\mu) + \dots \quad . \tag{5.59}$$

Thus, the magnetic susceptibility is

$$\chi = -\frac{1}{V}\frac{\partial^2 \Omega}{\partial H^2} = \big(r^2 - \tfrac{1}{3}\big) \cdot \tilde{\mu}_{\mathrm{B}}^2 \cdot (m/m^*)^2 \cdot \Big(-\frac{2}{V}\,Q'(-\mu)\Big)$$
$$= \Big(\frac{\overline{g}^2}{4} - \frac{m^2}{3m^{*2}}\Big) \cdot \tilde{\mu}_{\mathrm{B}}^2 \cdot n^2 \kappa_T \quad , \tag{5.60}$$

where κ_T is the isothermal compressibility[5], which at $T = 0$ is related to the density of states by $\kappa_T(T = 0, n) = n^{-2} g(\varepsilon_{\mathrm{F}})$. In most metals we have $m^* \approx m$ and the term in brackets is positive

---

[5]We've used $-\frac{2}{V}\,Q'(\mu) = -\frac{1}{V}\frac{\partial^2 \Omega}{\partial \mu^2} = n^2 \kappa_T$.

(recall $\overline{g} \approx 2$). In semiconductors, however, we can have $m^* \ll m$; for example in GaAs we have $m^* = 0.067\,m$ and $\overline{g} = 0.4$. Thus, semiconductors can have a *diamagnetic* response. If we take $\overline{g} = 2$ and $m^* = m$, we see that the orbital currents give rise to a diamagnetic contribution to the magnetic susceptibility which is exactly $-\frac{1}{3}$ times as large as the contribution arising from Zeeman coupling. The net result is then paramagnetic ($\chi > 0$) and $\frac{2}{3}$ as large as the Pauli susceptibility. The orbital currents can be understood within the context of *Lenz's law*.

5.4.3   de Haas-van Alphen oscillations

The Landau level structure in the density of states (see Fig. 5.8) is responsible for striking behavior in metals when subjected to an external magnetic field. For weak fields, the magnetization density is $m = \chi H$, but at stronger fields we have

$$
m(T, H, \mu) = -\frac{1}{V}\frac{\partial \Omega}{\partial H} = \left(\frac{e^2}{4\pi^2 \hbar}\right)\left(\frac{2\mu}{m^*}\right)^{1/2} H \cdot \left\{ \left(r^2 - \tfrac{1}{3}\right) + \right.
$$
$$
\left. + \left(\frac{2\pi k_{\mathrm{B}} T}{\hbar \omega_{\mathrm{c}}}\right)\left(\frac{2\mu}{\hbar \omega_{\mathrm{c}}}\right)^{1/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{\sqrt{l}} \frac{\sin\left(\frac{2\pi l \mu}{\hbar \omega_{\mathrm{c}}} - \frac{\pi}{4}\right)\cos\left(l\pi r\right)}{\sinh\left(2\pi^2 l k_{\mathrm{B}} T / \hbar \omega_{\mathrm{c}}\right)} \right\} \quad .
$$
$$(5.61)$$

The electron number density is given by

$$
n(T, H, \mu) = -\frac{1}{V}\frac{\partial \Omega}{\partial \mu} = \frac{1}{3\pi^2}\left(\frac{2m^* \mu}{\hbar^2}\right)^{1/2} \cdot \left\{ 1 + \frac{3}{32}\left(\frac{\hbar \omega_{\mathrm{c}}}{\mu}\right)\left(r^2 - \tfrac{1}{3}\right) + \right.
$$
$$
\left. + \left(\frac{3\pi k_{\mathrm{B}} T}{\hbar \omega_{\mathrm{c}}}\right)\left(\frac{\hbar \omega_{\mathrm{c}}}{2\mu}\right)^{3/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{\sqrt{l}} \frac{\sin\left(\frac{2\pi l \mu}{\hbar \omega_{\mathrm{c}}} - \frac{\pi}{4}\right)\cos\left(l\pi r\right)}{\sinh\left(2\pi^2 l k_{\mathrm{B}} T / \hbar \omega_{\mathrm{c}}\right)} \right\} \quad .
$$
$$(5.62)$$

These expressions are valid in the limit $\mu \gg \hbar \omega_{\mathrm{c}}$ and $\mu \gg k_{\mathrm{B}} T$. Under experimental conditions, it is the electron number density n which is held constant, and not the chemical potential μ. Thus, one must invert to obtain $\mu(n, T, H)$ and substitute this in the expression for $m(T, H, \mu)$ to obtain $m(n, T, H)$.

To derive the above results, we integrate Eqn. 5.14 twice by parts to obtain

$$
\Omega = -V \int_{-\infty}^{\infty} d\varepsilon\, R(\varepsilon) \left(-\frac{\partial f}{\partial \varepsilon}\right) \quad ,
$$
$$(5.63)$$

where $R(\varepsilon)$ is given by

$$
R(\varepsilon) = \int_{-\infty}^{\varepsilon} d\varepsilon' \int_{-\infty}^{\varepsilon'} d\varepsilon''\, g(\varepsilon'') \quad ,
$$
$$(5.64)$$

i.e. $g(\varepsilon) = R''(\varepsilon)$. In the presence of a uniform magnetic field, the density of states for a ballistic particle with dispersion $\varepsilon(\boldsymbol{k}) = \hbar^2 \boldsymbol{k}^2 / 2m^*$ is

$$g(\varepsilon) = \frac{1}{2\pi\ell^2} \frac{\sqrt{m^*}}{\sqrt{2}\,\pi\hbar} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} \left[\varepsilon - \left(n + \tfrac{1}{2} + \tfrac{1}{2}\sigma r \right) \hbar\omega_{\mathrm{c}} \right]_+^{-1/2} \quad , \tag{5.65}$$

where $r = \bar{g}\,m^*/2m$ as before, and $[x]_+ \equiv x\,\Theta(x)$. Thus,

$$R(\varepsilon) = \frac{\sqrt{2}}{3\pi^2} \left(\frac{m^*}{\hbar^2} \right)^{3/2} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} \left[\varepsilon - \left(n + \tfrac{1}{2} + \tfrac{1}{2}\sigma r \right) \hbar\omega_{\mathrm{c}} \right]_+^{3/2} \quad , \tag{5.66}$$

We now invoke the result

$$\sum_{n=0}^{\infty} \phi(n + \tfrac{1}{2}) = \int_0^{\infty} du\, \phi(u) + \tfrac{1}{24}\phi'(0) - \sum_{n=1}^{\infty} \frac{(-1)^l}{2\pi^2 l^2} \int_0^{\infty} du\, \phi''(u) \cos(2\pi l u) \quad , \tag{5.67}$$

which is valid provided $\phi(\infty) = \phi'(\infty) = 0$. This follows from applying the Poisson summation formula[6],

$$\sum_{n=-\infty}^{\infty} \delta(x - n) = \sum_{l=-\infty}^{\infty} e^{2\pi i l x} \quad , \tag{5.68}$$

integrating by parts twice, and using $\sum_{l=1}^{\infty} (-1)^{l+1}/l^2 = \frac{\pi^2}{12}$.

$$R(\varepsilon) = \frac{2\sqrt{2}}{15\pi^2} \left(\frac{m^*}{\hbar^2} \right)^{3/2} \frac{\left[\varepsilon - \tfrac{1}{2} r\hbar\omega_{\mathrm{c}} \right]_+^{5/2}}{\hbar\omega_{\mathrm{c}}} - \frac{\sqrt{2}}{48\pi^2} \left(\frac{m^*}{\hbar^2} \right)^{3/2} \hbar\omega_{\mathrm{c}} \left[\varepsilon - \tfrac{1}{2} r\hbar\omega_{\mathrm{c}} \right]_+^{3/2} +$$

$$- \frac{1}{8\pi^4} \left(\frac{m^*}{\hbar^2} \right)^{3/2} (\hbar\omega_{\mathrm{c}})^{3/2} \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{5/2}} \cos\left(\frac{2\pi l \varepsilon}{\hbar\omega_{\mathrm{c}}} - \pi l r \sigma - \frac{\pi}{4} \right) \quad . \tag{5.69}$$

We next integrate over ε, using the Sommerfeld expansion and the result

$$\int_{-\infty}^{\infty} d\varepsilon\, e^{is\varepsilon} \left(-\frac{\partial f}{\partial \varepsilon} \right) = \frac{\pi s\, k_{\mathrm{B}} T}{\sinh(\pi s\, k_{\mathrm{B}} T)} \quad . \tag{5.70}$$

The final result for $\Omega(T, V, \mu, H)$, valid for $\hbar\omega_{\mathrm{c}} \ll \mu$ and $k_{\mathrm{B}} T \ll \mu$, is

$$\Omega(T, V, \mu, H) = -V \cdot \frac{\sqrt{2}}{\pi} \left(\frac{m^*}{\hbar^2} \right)^{3/2} \left\{ \tfrac{4}{15} \left\langle \varepsilon^{5/2} \right\rangle + \tfrac{1}{8} (\hbar\omega_{\mathrm{c}})^2 \left(r^2 - \tfrac{1}{3} \right) \left\langle \varepsilon^{1/2} \right\rangle + \right.$$

$$\left. + \tfrac{1}{2\sqrt{2}} (\hbar\omega_{\mathrm{c}})^{3/2} k_{\mathrm{B}} T \sum_{l=1}^{\infty} \frac{(-1)^l}{l^{3/2}} \frac{\cos\left(\frac{2\pi l \mu}{\hbar\omega_{\mathrm{c}}} - \frac{\pi}{4} \right) \cos(l\pi r)}{\sinh\left(2\pi^2 l k_{\mathrm{B}} T / \hbar\omega_{\mathrm{c}} \right)} \right\} \quad . \tag{5.71}$$

---

[6]One first extends the function $\phi(u)$ to the entire real line, symmetrically, so $\phi(-u) = \phi(u)$.
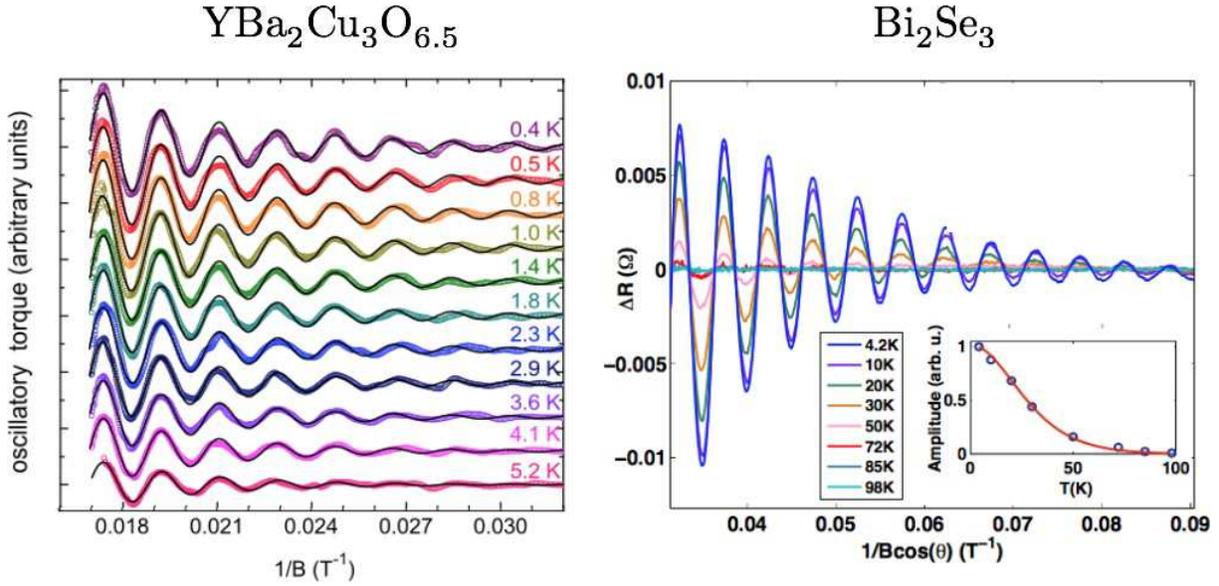
Figure 5.9: Left: de Haas-van Alphen oscillations in the underdoped high temperature superconductor $YBa_2Cu_3O_{6.5}$, measured by C. Jaudet *et al* in *Phys. Rev. Lett.* **100**, 187005 (2008). Right: Schubnikov-de Haas oscillations and their temperature dependence in the three-dimensional topological insulator Bi_2Se_3, indicating the presence of metallic surface states. A smooth polynomial background has been subtracted. Measurements by M. Petrushevsky *et al.* in *Phys. Rev. B* **86**, 045131 (2013).

Here, we have used the notation

$$\langle \psi(\varepsilon) \rangle \equiv \int_{-\infty}^{\infty} d\varepsilon \, \psi(\varepsilon) \left(-\frac{\partial f}{\partial \varepsilon} \right) \quad . \tag{5.72}$$

For homogeneous functions,

$$\left\langle \varepsilon^p \right\rangle = \mu^p + \frac{\pi^2}{6} \, p(p-1) \, (k_{\rm B}T)^2 \, \mu^{p-2} + \mathcal{O}(T^4) \quad . \tag{5.73}$$

Differentiation of $\Omega(T, V, H)$ with respect to H and μ yields[7], respectively, the results in Eqns. 5.61 and 5.62. From Eqn. 5.71, we see that the oscillating factors are periodic in $1/H$ with periods $\Delta(1/H) = \hbar e/2\pi l\mu m^* c$. In experiments, the magnetization M is typically measured with a torque-magnetometer. The oscillatory nature of $M(H)$ is called the de Haas-van Alphen effect. A related periodicity occurs in the magnetoresistance $R(H)$, where it is called the Schubnikov-de Haas effect. Experimental data for both effects is shown in Fig. 5.9.

---

[7]The cyclotron energy $\hbar\omega_{\rm c} = \hbar eH/m^*c$ is linear in the magnetic field H. For $\mu \gg \hbar\omega_{\rm c} \gg k_{\rm B}T$, the dominant contribution to the magnetization comes from differentiating the cosine factor.
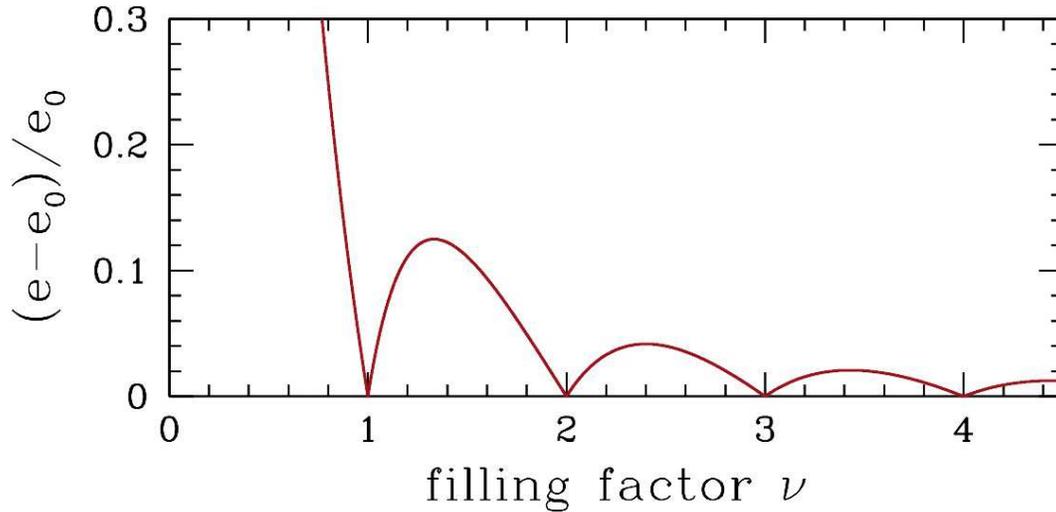
Figure 5.10: Two dimensional oscillations in the energy per unit area $e = E/A$ for a spinless electron gas in a uniform magnetic field $\boldsymbol{H} = H\hat{\boldsymbol{z}}$.

Oscillations at $T = 0$: spinless fermions in $d = 2$ dimensions

Apparently the oscillations do not vanish, even at $T = 0$. The prefactor of T which multiplies the oscillating sum in Eqn. 5.61 cancels with the $\sinh(2\pi^2 l k_{\mathrm{B}} T / \hbar\omega_{\mathrm{c}})$ denominator in the $T \to 0$ limit. Consider the simple case of ballistic spinless electrons in $d = 2$ dimensions. We know that each Landau level can accommodate $N_{\mathrm{L}} = HA/\phi_0$ electrons, where $\phi_0 = hc/e$ is the Dirac flux quantum. It is convenient to define the *filling fraction* ν, as

$$\nu = \frac{N}{N_{\mathrm{L}}} = 2\pi\ell^2 n = \frac{2\pi\hbar c}{eH}\, n \quad , \tag{5.74}$$

where $\ell = \sqrt{\hbar c/eH}$ is the magnetic length. The cyclotron energy is

$$\hbar\omega_{\mathrm{c}} = \frac{\hbar e H}{m^* c} = \frac{2\pi\hbar^2}{m^*}\frac{n}{\nu} \quad . \tag{5.75}$$

We now evaluate the energy per unit area, $e = E/A$, as a function of n and ν. With the electron number density n fixed, the magnetization per unit area is given by

$$m = \frac{\partial e}{\partial H} = \frac{\partial\nu}{\partial H}\frac{\partial e}{\partial\nu} = -\frac{\nu}{H}\frac{\partial e}{\partial\nu} \quad . \tag{5.76}$$

Now if $\nu \in [j, j+1]$, the total energy is

$$E = N_{\mathrm{L}} \cdot \tfrac{1}{2}\hbar\omega_{\mathrm{c}} \cdot \left(1 + 3 + 5 + \ldots + (2j - 1)\right) + (N - jN_{\mathrm{L}}) \cdot (j + \tfrac{1}{2})\,\hbar\omega_{\mathrm{c}}$$
$$= N_{\mathrm{L}} \cdot \tfrac{1}{2}\hbar\omega_{\mathrm{c}} \cdot \left(j^2 + (\nu - j)(2j + 1)\right) \quad . \tag{5.77}$$

Thus,

$$e(n, \nu) = \frac{E}{A} = \frac{\pi \hbar^2 n^2}{m^*} \cdot \left\{ \frac{(2j+1)\nu - j(j+1)}{\nu^2} \right\} \quad . \tag{5.78}$$

Defining, $e_0(n) = \pi \hbar^2 n^2 / m^*$, we have that $e(n, j) = e(n, j+1) = e_0(n)$. Furthermore, since

$$\left. \frac{\partial e}{\partial \nu} \right|_{\nu=j} = \frac{e_0(n)}{j^2} > 0 \qquad \text{and} \qquad \left. \frac{\partial e}{\partial \nu} \right|_{\nu=j+1} = -\frac{e_0(n)}{j^2} > 0 \quad , \tag{5.79}$$

we see that $e(n, \nu)$ has a cusp at every integer value of ν. This behavior is depicted in Fig. 5.10. The magnetization density $m(n, \nu)$ therefore *discontinuously changes sign* (from negative to positive) across all integer values of the filling fraction![8] Note also that the periodicity is $\Delta \nu = 1$, hence

$$\Delta \left(\frac{1}{H} \right) = \frac{e}{hcn} = \frac{1}{2\pi n \phi_0} \quad . \tag{5.80}$$

5.4.4 de Haas-von Alphen effect for anisotropic Fermi surfaces

We consider a nontopological band structure, for which the semiclassical equations of motion in the presence of a uniform magnetic field are

$$\frac{d\boldsymbol{r}}{dt} = \boldsymbol{v}_n(\boldsymbol{k}) \qquad , \qquad \frac{d\boldsymbol{k}}{dt} = -\frac{e}{\hbar c} \, \boldsymbol{v}_n(\boldsymbol{k}) \times \boldsymbol{B} \quad . \tag{5.81}$$

These equations entail the conservation of the band energy $E_n(\boldsymbol{k})$:

$$\frac{dE_n(\boldsymbol{k})}{dt} = \frac{\partial E_n(\boldsymbol{k})}{\partial \boldsymbol{k}} \cdot \frac{d\boldsymbol{k}}{dt} = \hbar \boldsymbol{v}_n(\boldsymbol{k}) \cdot \left(-\frac{e}{\hbar c} \, \boldsymbol{v}_n(\boldsymbol{k}) \times \boldsymbol{B} \right) = 0 \quad . \tag{5.82}$$

Define $\boldsymbol{k}_\perp = \boldsymbol{k} - \widehat{\boldsymbol{B}}(\widehat{\boldsymbol{B}} \cdot \boldsymbol{k})$, the component of $\boldsymbol{k}$ along the direction $\widehat{\boldsymbol{B}}$. We then have $\dot{\boldsymbol{k}}_\perp = -\frac{e}{\hbar c} \, \boldsymbol{v}_n(\boldsymbol{k}) \times \boldsymbol{B}$ and $\frac{d}{dt}(\boldsymbol{k} \cdot \widehat{\boldsymbol{B}}) = 0$. Thus, the orbits $\boldsymbol{k}(t)$ lie in planes perpendicular to $\widehat{\boldsymbol{B}}$ (see the sketch in Fig. 5.11).

Consider now the differential $\boldsymbol{k}$-space area element $d^2 k_\perp$ between transverse (to $\widehat{\boldsymbol{B}}$) slices of isoenergy surfaces at energies ε and $\varepsilon + d\varepsilon$. Clearly

$$d^2 k_\perp = \frac{d\varepsilon \, d\ell(\varepsilon)}{|\partial \varepsilon / \partial \boldsymbol{k}_\perp|} \tag{5.83}$$

where $d\ell(\varepsilon)$ is the differential path length in the transverse plane along the surface of energy ε. Note that

$$\left| \frac{\partial \varepsilon}{\partial \boldsymbol{k}_\perp} \right| = \left| \hbar \boldsymbol{v}_\perp \right| = \hbar \left| \boldsymbol{v}_\perp \times \widehat{\boldsymbol{B}} \right| = \frac{\hbar^2 c}{eB} \left| \dot{\boldsymbol{k}}_\perp \right| \quad . \tag{5.84}$$

---

[8] In the three-dimensional case, m oscillates but usually does not change sign.
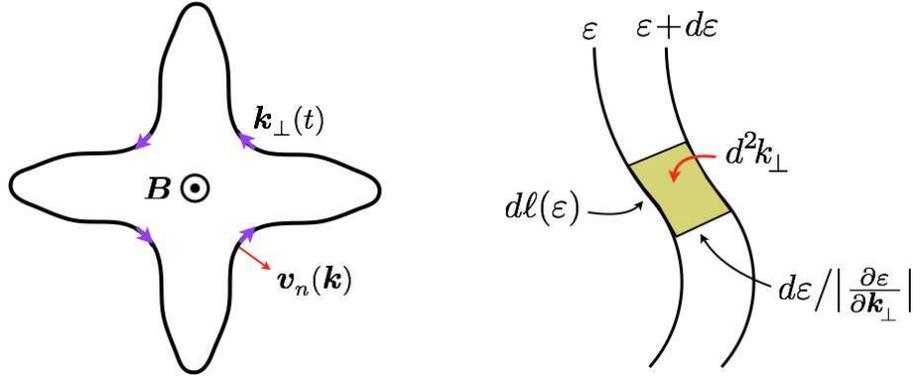
Figure 5.11: Left: Orbit of $\boldsymbol{k}(t)$ in the plane perpendicular to the field $\boldsymbol{B}$. Right: Geometry of Fermi surface orbits in the calculation of the de Haas-van Alphen effect.

Thus, the area enclosed by an orbit of energy ε and parallel wavevector component $k_\parallel = \boldsymbol{k} \cdot \widehat{\boldsymbol{B}}$ is

$$
A(\varepsilon, k_\parallel) = \int d^2k_\perp \, \Theta\big(\varepsilon - \varepsilon(\boldsymbol{k}_\perp, k_\parallel)\big) = \int\limits_{-\infty}^{\infty} d\varepsilon' \, \Theta(\varepsilon - \varepsilon') \oint \frac{d\ell(\varepsilon')}{\big|\partial\varepsilon'/\partial\boldsymbol{k}_\perp\big|}
$$

$$
= \frac{eB}{\hbar^2 c} \int\limits_{-\infty}^{\infty} d\varepsilon' \, \Theta(\varepsilon - \varepsilon') \oint \frac{d\ell(\varepsilon')}{\big|\dot{\boldsymbol{k}}_\perp\big|} = \frac{eB}{\hbar^2 c} \int\limits_{-\infty}^{\varepsilon} d\varepsilon' \, T(\varepsilon', k_\parallel) \quad ,
$$

(5.85)

where $T(\varepsilon, k_\parallel)$ is the period of the orbit. Note that we have assumed that the surface $\mathcal{S}_\varepsilon$ is closed, *i.e.* that there are no "open orbits" which run periodically across the Brillouin zone. We now have the result

$$
\frac{\partial A(\varepsilon, k_\parallel)}{\partial \varepsilon} = \frac{eB}{\hbar^2 c} T(\varepsilon, k_\parallel) \quad .
$$

(5.86)

For a free electron in a magnetic field, the orbital period is $2\pi/\omega_{\rm c}$. We accordingly define the *cyclotron mass* by the relation

$$
T(\varepsilon, k_\parallel) = \frac{\hbar^2 c}{eB} \frac{\partial A(\varepsilon, k_\parallel)}{\partial \varepsilon} \equiv \frac{2\pi m_{\rm cyc} c}{eB} \qquad \Longrightarrow \qquad m_{\rm cyc} = \frac{\hbar^2}{2\pi} \frac{\partial A(\varepsilon, k_\parallel)}{\partial \varepsilon} \quad .
$$

(5.87)

Semiclassical quantization then yields the following relation for the energy level spacing:

$$
\varepsilon_{n+1}(k_\parallel) - \varepsilon_n(k_\parallel) = \frac{2\pi\hbar}{T\big(\varepsilon_n(k_\parallel), k_\parallel\big)} = \frac{2\pi eB}{\hbar c} \bigg/ \frac{\partial A(\varepsilon, k_\parallel)}{\partial \varepsilon}\bigg|_{\varepsilon = \varepsilon_n(k_\parallel)} \quad .
$$

(5.88)

Note that for free electrons,

$$
A(\varepsilon, k_\parallel) = \pi\big(\boldsymbol{k}^2 - k_\parallel^2\big) = \frac{2\pi m\varepsilon}{\hbar^2} - \pi k_\parallel^2 \quad ,
$$

(5.89)

and so

$$\frac{\partial A(\varepsilon, k_\parallel)}{\partial \varepsilon} = \frac{2\pi m}{\hbar^2} \qquad \Longrightarrow \qquad \varepsilon_{n+1}(k_\parallel) - \varepsilon_n(k_\parallel) = \frac{\hbar e B}{mc} = \hbar \omega_c \quad . \tag{5.90}$$

If the semiclassical orbit index n is large, we may approximate $\partial A / \partial \varepsilon$ by a ratio of differences, *viz.*

$$\frac{\partial A(\varepsilon, k_\parallel)}{\partial \varepsilon} \bigg|_{\varepsilon = \varepsilon_n(k_\parallel)} \simeq \frac{A\big(\varepsilon_{n+1}(k_\parallel), k_\parallel\big) - A\big(\varepsilon_n(k_\parallel), k_\parallel\big)}{\varepsilon_{n+1}(k_\parallel) - \varepsilon_n(k_\parallel)} \quad , \tag{5.91}$$

and invoking Eqn. 5.88 then gives

$$A\big(\varepsilon_{n+1}(k_\parallel), k_\parallel\big) - A\big(\varepsilon_n(k_\parallel), k_\parallel\big) = \frac{2\pi e B}{\hbar c} \quad . \tag{5.92}$$

We then conclude that the areas of the orbits in the plane transverse to $\widehat{B}$ are quantized according to

$$A\big(\varepsilon_n(k_\parallel), k_\parallel\big) = (n + \alpha) \frac{2\pi e B}{\hbar c} \quad , \tag{5.93}$$

where α is a constant, a result first derived by Lars Onsager in 1952.

In the free particle model, the each dH-vA oscillation is associated with a Fermi level crossing by one of the Landau levels. Neglecting Zeeman splitting, the semiclassical density of states per unit volume is

$$\begin{aligned}
g(\varepsilon) &= \frac{1}{2\pi \ell^2} \sum_n \int_{-\infty}^{\infty} \frac{dk_\parallel}{2\pi} \, \delta\big(\varepsilon - \varepsilon_n(k_\parallel)\big) \\
&= \frac{1}{2\pi \ell^2} \sum_n \int_{-\infty}^{\infty} \frac{dk_\parallel}{2\pi} \frac{\delta\big(k_\parallel - \varepsilon_n^{-1}(\varepsilon)\big)}{\big|\partial \varepsilon_n / \partial k_\parallel\big|} \quad ,
\end{aligned} \tag{5.94}$$

where $\varepsilon_n^{-1}(\varepsilon) = k_\parallel$ when $\varepsilon_n(k_\parallel) = \varepsilon$, *i.e.* it is the inverse function. The DOS is peaked when the denominator vanishes, *i.e.* when $\partial \varepsilon_n / \partial k_\parallel = 0$. This entails that the cross sectional Fermi surface area is at a maximum:

$$\frac{\partial}{\partial k_\parallel} A\big(\varepsilon_n(k_\parallel), k_\parallel\big) = \overbrace{\frac{\partial \varepsilon_n(k_\parallel)}{\partial k_\parallel}}^{= 0} \cdot \frac{\partial A(\varepsilon, k_\parallel)}{\partial \varepsilon} \bigg|_{\varepsilon = \varepsilon_n(k_\parallel)} + \frac{\partial A(\varepsilon, k_\parallel)}{\partial k_\parallel} \bigg|_{\varepsilon = \varepsilon_n(k_\parallel)} \quad . \tag{5.95}$$

Thus, the DOS peaks when the Fermi energy lies on an *extremal orbit*, *i.e.* one which extremizes the cross-sectional Fermi surface area:

$$(n + \alpha) \frac{2\pi e B}{\hbar c} = S^*(\varepsilon_{\mathrm{F}}) \qquad \Longrightarrow \qquad \Delta\left(\frac{1}{B}\right) = \frac{2\pi e}{\hbar c} \frac{1}{S^*(\varepsilon_{\mathrm{F}})} \quad , \tag{5.96}$$

where $S^*(\varepsilon)$ is a (possibly multi-valued) function giving the area(s) of the extremal orbits. Since

$$\frac{\hbar\omega_{\mathrm{c}}}{k_{\mathrm{B}}T} = 1.34 \times 10^{-4} \cdot \frac{B[\mathrm{T}]}{T[\mathrm{K}]} \quad , \tag{5.97}$$

(assuming $m = m_{\mathrm{e}}$), one needs high fields or low temperatures in order that the oscillations not be washed out by thermal fluctuations.

5.5 Simple Theory of Electron Transport in Metals

5.5.1 Drude model

Consider a particle of mass m^* and charge $(-e)$ moving in the presence of an electric field $\boldsymbol{E}$ and magnetic field $\boldsymbol{B}$. Newton's second law says that

$$\frac{d\boldsymbol{p}}{dt} = -e\boldsymbol{E} - \frac{e}{m^*c}\,\boldsymbol{p} \times \boldsymbol{B} - \frac{\boldsymbol{p}}{\tau} \quad , \tag{5.98}$$

where the last term on the RHS is a phenomenological dissipative (*i.e.* frictional) force. The constant τ, which has dimensions of time, is interpreted as the *momentum relaxation time* due to scattering off impurities, lattice excitations (*i.e.* phonons), or sample boundaries. Clearly when $\boldsymbol{E} = \boldsymbol{B} = 0$ we have $\boldsymbol{p}(t) = \boldsymbol{p}(0)\exp(-t/\tau)$, which says that $\boldsymbol{p}$ relaxes on a time scale τ.

When $\boldsymbol{E} \neq 0$ but $\boldsymbol{B} = 0$, we have $\dot{\boldsymbol{p}} = -e\boldsymbol{E} - \tau^{-1}\boldsymbol{p}$, and for time-independent $\boldsymbol{E}$ the steady state solution, valid at long times, is $\boldsymbol{p} = -e\tau\boldsymbol{E}$. is then

$$\boldsymbol{j} = -ne\boldsymbol{v} = -ne\,\frac{\boldsymbol{p}}{m^*} = \frac{ne^2\tau}{m^*}\,\boldsymbol{E} \quad . \tag{5.99}$$

Thus there is a linear relationship between the current density $\boldsymbol{j}$ and the applied field $\boldsymbol{E}$. One writes $\boldsymbol{j} = \sigma\boldsymbol{E}$, where σ is the *electrical conductivity*. The above theory says that $\sigma = ne^2\tau/m^*$, where n is the particle density.

We can extend our analysis to include time-dependent fields of the form $\boldsymbol{E}(t) = \mathsf{Re}\left[\widehat{\boldsymbol{E}}(\omega)\,e^{-i\omega t}\right]$. In steady state, $\boldsymbol{p}$ oscillates with the same frequency, and writing $\boldsymbol{p}(t) = \mathsf{Re}\left[\widehat{\boldsymbol{p}}(\omega)\,e^{-i\omega t}\right]$, we obtain the relation $(\tau^{-1} - i\omega)\,\widehat{\boldsymbol{p}}(\omega) = -e\widehat{\boldsymbol{E}}(\omega)$, and thus $\boldsymbol{j}(t) = \mathsf{Re}\left[\sigma(\omega)\,\widehat{\boldsymbol{E}}(\omega)\,e^{-i\omega t}\right]$, with

$$\sigma(\omega) = \frac{ne^2\tau}{m^*} \cdot \frac{1}{1 - i\omega\tau} \quad . \tag{5.100}$$

The power density $\boldsymbol{j}(t) \cdot \boldsymbol{E}(t)$ then has terms which are constant, as well as terms oscillating with frequency 2ω. The average power dissipated is obtained by integrating over a period $\Delta t = 2\pi/\omega$, which eliminates the $e^{\pm 2i\omega t}$ terms, resulting in

$$\overline{\boldsymbol{j}(t) \cdot \boldsymbol{E}(t)} = \mathsf{Re}\,\sigma(\omega)\left|\widehat{\boldsymbol{E}}(\omega)\right|^2 \quad , \tag{5.101}$$
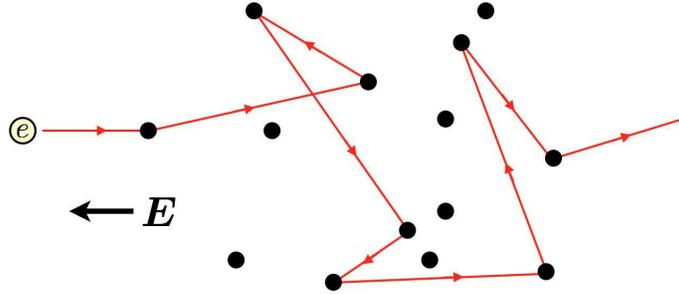
Figure 5.12: Scattering of an electron by impurities in the presence of a uniform electric field $\boldsymbol{E}$ is an example of a biased random walk.

where the bar denotes time averaging over the period $\Delta t = \pi/\omega$. So it is the real part of the conductivity which is responsible for power dissipation.

Another way to see it: write $\hat{\boldsymbol{\jmath}}(\omega) = \sigma(\omega)\,\widehat{\boldsymbol{E}}(\omega)$, which is a complex vector quantity. If we separate the frequency-dependent conductivity $\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega)$ into its real and imaginary parts, we see that the $\sigma'(\omega)$ term leads to a current component which is in phase with the drive $\boldsymbol{E}(t)$, while the $\sigma''(\omega)$ term leads to a current component which is $90°$ out of phase with the drive $\boldsymbol{E}(t)$. The latter current leads to periodic fluctuations in the local energy density, but no net dissipation. The real and imaginary parts of $\sigma(\omega)$ are given by

$$\sigma'(\omega) = \frac{ne^2\tau}{m^*} \cdot \frac{1}{1+\omega^2\tau^2} \qquad , \qquad \sigma''(\omega) = \frac{ne^2\tau}{m^*} \cdot \frac{\omega\tau}{1+\omega^2\tau^2} \quad . \tag{5.102}$$

When we try to apply the above physics to electrons in solids, we are confronted with several issues. One obvious question is: what do we mean by n? Filled bands carry no current, because the current density of the nth filled band (accounting for spin),

$$j_n = -2e \int_{\widehat{\Omega}} \frac{d^3k}{(2\pi)^3} \; \overbrace{\frac{1}{\hbar} \frac{\partial E_n(\boldsymbol{k})}{\partial k^\alpha}}^{v_n(\boldsymbol{k})} = 0 \quad , \tag{5.103}$$

vanishes because $E_n(\boldsymbol{k})$ is periodic in the Brillouin zone, and the integral of the derivative of a periodic function over its period is zero. So the density n must only include contributions from partially filled bands. In fact, the situation is even more complicated because the scattering time can vary from band to band, may be energy-dependent, and there can even be *interband scattering* of electrons. Another question is how we account for scattering within the semiclassical model. We can't just add a term $-\boldsymbol{p}/\tau$ to the right hand side of the equation for $\hbar\dot{\boldsymbol{k}}$, because $\boldsymbol{p} = \hbar\boldsymbol{k}$ is not well-defined in a crystal. A more rigorous approach to transport is based on the Boltzmann equation, which describes how the distribution $f(\boldsymbol{r}, \boldsymbol{k}, t)$ of electron wave packets evolves and takes a steady state form.

The DC conductivity $\sigma = ne^2\tau/m^*$ is proportional to the number of carriers n. Another figure of merit is the *mobility* $\mu = e\tau/m^*$, which is independent of n. Note that the mobility is the ratio of the speed of the electron to the magnitude of the applied field: $\mu = v/E$. The conventional units of mobility are $[\mu] = \mathrm{cm}^2/\mathrm{V\cdot s}$. Mobility tells us mostly about the scattering time τ. For highly disordered systems, the scattering time τ is short and consequently μ is small. The electrons then move slowly as they execute a biased random walk scattering off impurities in the presence of an electric field (see Fig. 5.12. However, even low mobility systems may have high conductivity, owing to a large density n of conduction electrons. The highest purity semiconductors have mobilities on the order of $10^7 \mathrm{\ cm}^2/\mathrm{V\cdot s}$.

5.5.2 Magnetoresistance and magnetoconductance

Now let's introduce a uniform magnetic field $\boldsymbol{B}$. In component notation, Newton's second law gives

$$\left(\frac{1}{\tau} \delta_{\alpha\beta} + \frac{e}{m^*c} \varepsilon_{\alpha\beta\gamma} B^\gamma \right) p^\beta = -eE^\alpha \quad . \tag{5.104}$$

The current density is $\boldsymbol{j} = -ne\boldsymbol{v} = -ne\boldsymbol{p}/m^*$, hence $\boldsymbol{p} = -m^*\boldsymbol{j}/ne$, and we thus have

$$E^\alpha = \overbrace{\frac{1}{ne^2}\left(\frac{m^*}{\tau} \delta_{\alpha\beta} + \frac{e}{c} \varepsilon_{\alpha\beta\gamma} B^\gamma \right)}^{\rho_{\alpha\beta}} j^\beta \quad . \tag{5.105}$$

The *resistivity matrix* $\rho_{\alpha\beta}(B)$ defines the linear relationship between the electric field $\boldsymbol{E}$ and the current density $\boldsymbol{j}$. At finite frequency, it is easy to see that τ^{-1} must be replaced by $\tau^{-1} - i\omega$, hence, taking $\boldsymbol{B} = B\hat{z}$, the $T = 0$ resistivity tensor is

$$\rho_{\alpha\beta}(\omega, B) = \frac{m^*}{ne^2\tau} \begin{pmatrix} 1 - i\omega\tau & \omega_c\tau & 0 \\ -\omega_c\tau & 1 - i\omega\tau & 0 \\ 0 & 0 & 1 - i\omega\tau \end{pmatrix} \quad , \tag{5.106}$$

with $\omega_c = eB/m^*c$ the cyclotron frequency, as before. Note that the diagonal elements are independent of B, which says that the *magnetoresistance*

$$\Delta\rho_{xx}(B) = \rho_{xx}(B) - \rho_{xx}(0) \tag{5.107}$$

vanishes: $\Delta\rho_{xx}(B) = 0$.

The magnetoconductance, however, does not vanish! Recall that

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{ad - bc} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix} \quad , \tag{5.108}$$

from which we have

$$\sigma_{\alpha\beta} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{yx} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} \quad , \tag{5.109}$$

with

$$\sigma_{xx}(\omega, B) = \sigma_{yy}(\omega, B) = \frac{ne^2\tau}{m^*} \cdot \frac{1 - i\omega\tau}{(1 - i\omega\tau)^2 + (\omega_{\rm c}\tau)^2}$$

$$\sigma_{yx}(\omega, B) = -\sigma_{xy}(\omega, B) = \frac{ne^2\tau}{m^*} \cdot \frac{\omega_{\rm c}\tau}{(1 - i\omega\tau)^2 + (\omega_{\rm c}\tau)^2} \tag{5.110}$$

$$\sigma_{zz}(\omega, B) = \frac{ne^2\tau}{m^*} \cdot \frac{1}{1 - i\omega\tau} \quad .$$

Note that σ_{xx} is field-dependent, unlike ρ_{xx}.

Thus far we have assumed that the effective mass tensor $m^*_{\alpha\beta}$ is isotropic. In the general anisotropic case, $m^*_{\alpha\beta}$, which is a symmetric matrix, will have three orthogonal principal axes, which we denote as $\hat{x}$, $\hat{y}$, and $\hat{z}$. In this case, the resistivity tensor assumes the more general form

$$\rho_{\alpha\beta}(\omega, B) = \frac{1}{ne^2} \begin{pmatrix} (\tau^{-1} - i\omega)\, m^*_x & \pm eB_z/c & \mp eB_y/c \\ \mp eB_z/c & (\tau^{-1} - i\omega)\, m^*_y & \pm eB_x/c \\ \pm eB_y/c & \mp eB_x/c & (\tau^{-1} - i\omega)\, m^*_z \end{pmatrix} \quad , \tag{5.111}$$

where (m^*_x, m^*_y, m^*_z) are the three eigenvalues of $m^*_{\alpha\beta}$. The $\pm$ sign in the off-diagonal term distinguishes the case where the Fermi level is just above a quadratic minimum ($+$ sign), versus where it is just below quadratic maximum ($-$ sign). The latter case is described in terms of *holes* in a filled band, as opposed to *electrons* in an empty band. The effective mass tensors are then defined as

$$\left(m^*\right)^{-1}_{\alpha\beta} = \pm \frac{1}{\hbar^2} \frac{\partial^2 E_n(\boldsymbol{k})}{\partial k^\alpha\, \partial k^\beta} \quad , \tag{5.112}$$

where the top sign corresponds to electrons and the bottom sign to holes.

Note that the diagonal elements in Eqn. 5.111 are still independent of B and there is no magnetoresistance. Taking $\boldsymbol{B}$ along $\hat{z}$, the corresponding elements of $\sigma_{\alpha\beta}$ are

$$\sigma_{xx}(\omega, B) = \frac{ne^2\tau}{m^*_x} \cdot \frac{1 - i\omega\tau}{(1 - i\omega\tau)^2 + (\omega_{\rm c}\tau)^2}$$

$$\sigma_{yy}(\omega, B) = \frac{ne^2\tau}{m^*_y} \cdot \frac{1 - i\omega\tau}{(1 - i\omega\tau)^2 + (\omega_{\rm c}\tau)^2}$$

$$\sigma_{yx}(\omega, B) = \pm \frac{ne^2\tau}{m^*_\perp} \cdot \frac{\omega_{\rm c}\tau}{(1 - i\omega\tau)^2 + (\omega_{\rm c}\tau)^2} \tag{5.113}$$

$$\sigma_{zz}(\omega, B) = \frac{ne^2\tau}{m^*_z} \cdot \frac{1}{1 - i\omega\tau} \quad ,$$

where $\omega_{\rm c} = eB/m^*_\perp c$ and $m^*_\perp = \sqrt{m^*_x m^*_y}$.

5.5.3 Hall effect in high fields

In the high field limit, we have that the resistivity and conductivity tensors are purely off-diagonal, with

$$\rho_{xy}(B) = \pm\frac{B}{nec} \quad , \quad \sigma_{xy}(B) = \mp\frac{nec}{B} \tag{5.114}$$

where the upper sign is again for conduction electrons, and the bottom sign for valence holes. Thus, the high field Hall effect may be used to determine the carrier concentration:

$$n = \pm \lim_{B\to\infty} \frac{B}{ec\rho_{xy}(B)} \quad . \tag{5.115}$$

5.5.4 Cyclotron resonance in semiconductors

A typical value for the effective mass in semiconductors is $m^* \sim 0.1\,m_{\rm e}$. From

$$\frac{e}{m_{\rm e}\,c} = 1.75 \times 10^7\,{\rm Hz/G} \quad , \tag{5.116}$$

we find that $eB/m^*c = 1.75 \times 10^{11}\,{\rm Hz}$ in a field of $B = 1\,{\rm kG}$. In metals, the disorder is such that even at low temperatures $\omega_c\tau$ typically is small. In semiconductors, however, the smallness of m^* and the relatively high purity (sometimes spectacularly so) mean that $\omega_c\tau$ can get as large as 10^3 at modest fields. This allows for a measurement of the effective mass tensor using the technique of *cyclotron resonance*.

The absorption of electromagnetic radiation is proportional to the dissipative (*i.e.* real) part of the diagonal elements of $\sigma_{\alpha\beta}(\omega, B)$, which, again taking $\boldsymbol{B}$ along $\hat{z}$, is given by

$$\sigma'_{xx}(\omega, B) = \frac{ne^2\tau}{m_x^*}\,\frac{1 + (\lambda^2 + 1)s^2}{1 + 2(\lambda^2 + 1)s^2 + (\lambda^2 - 1)^2 s^4} \quad , \tag{5.117}$$

where $\lambda = B/B_\omega$, with $B_\omega = m_\perp^* c\omega/e$, and $s = \omega\tau$. For fixed ω, the conductivity $\sigma'_{xx}(B)$ is then peaked at $B = B^*$. When $\omega\tau \gg 1$ and $\omega_c\tau \gg 1$, B^* approaches B_ω, where $\sigma'_{xx}(\omega, B_\omega) = ne^2\tau/2m_x^*$. By measuring B_ω one can extract the quantity $m_\perp^* = eB_\omega/\omega c$. Varying the direction of the magnetic field, the entire effective mass tensor may be determined.

For finite $\omega\tau$, we can differentiate the above expression to obtain the location of the cyclotron resonance peak. One finds $B = (1 + \alpha)^{1/2}\,B_\omega$, with

$$\alpha = \frac{-(2s^2 + 1) + \sqrt{(2s^2 + 1)^2 - 1}}{s^2}$$

$$= -\frac{1}{4s^4} + \frac{1}{8s^6} + \mathcal{O}(s^{-8}) \quad .$$

As depicted in Fig. 5.13, the resonance peak shifts to the left of B_ω for finite values of $\omega\tau$. The peak collapses to $B = 0$ when $\omega\tau \leqslant 1/\sqrt{3} = 0.577$.
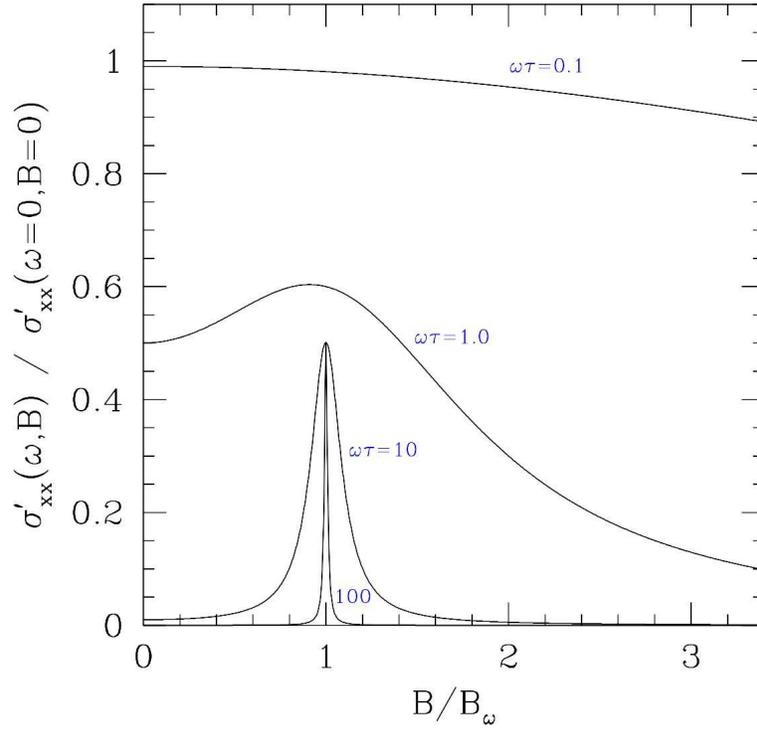
Figure 5.13: Theoretical cyclotron resonance peaks as a function of B/B_ω for different values of $\omega\tau$.

5.5.5   Magnetoresistance in a two band model

For a semiconductor with both electrons and holes present – a situation not uncommon to metals either (*e.g.* Aluminum) – each band contributes to the conductivity. The individual band conductivities are *additive* because the electron and hole conduction processes occur *in parallel*, *i.e.*

$$\sigma_{\alpha\beta}(\omega) = \sum_n \sigma^{(n)}_{\alpha\beta}(\omega) \quad , \tag{5.118}$$

where $\sigma^{(n)}_{\alpha\beta}$ is the conductivity tensor for band n, which may be computed in either the electron or hole picture (whichever is more convenient). We assume here that the two bands c and v may be treated independently, *i.e.* there is no interband scattering to account for.

The resistivity tensor of each band, $\rho^{(n)}_{\alpha\beta}$ exhibits no magnetoresistance, as we have found. However, if two bands are present, the total resistivity tensor ρ is obtained from $\rho^{-1} = \rho_c^{-1} + \rho_v^{-1}$, and

$$\rho = \left(\rho_c^{-1} + \rho_v^{-1}\right)^{-1} \tag{5.119}$$

will in general exhibit the phenomenon of magnetoresistance.

Explicitly, then, let us consider a model with isotropic and nondegenerate conduction band

minimum and valence band maximum. Taking $\boldsymbol{B} = B\hat{z}$, we have

$$\rho_{\mathrm{c}} = \frac{(1 - i\omega\tau_{\mathrm{c}})m_{\mathrm{c}}}{n_{\mathrm{c}}e^2\tau_{\mathrm{c}}}\, \mathbb{I} + \frac{B}{n_{\mathrm{c}}ec}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \alpha_{\mathrm{c}} & \beta_{\mathrm{c}} & 0 \\ -\beta_{\mathrm{c}} & \alpha_{\mathrm{c}} & 0 \\ 0 & 0 & \alpha_{\mathrm{c}} \end{pmatrix}$$

(5.120)

$$\rho_{\mathrm{v}} = \frac{(1 - i\omega\tau_{\mathrm{v}})m_{\mathrm{v}}}{n_{\mathrm{v}}e^2\tau_{\mathrm{v}}}\, \mathbb{I} - \frac{B}{n_{\mathrm{v}}ec}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \alpha_{\mathrm{v}} & -\beta_{\mathrm{v}} & 0 \\ \beta_{\mathrm{v}} & \alpha_{\mathrm{v}} & 0 \\ 0 & 0 & \alpha_{\mathrm{v}} \end{pmatrix} \quad,$$

where

$$\alpha_{\mathrm{c}} = \frac{(1 - i\omega\tau_{\mathrm{c}})m_{\mathrm{c}}}{n_{\mathrm{c}}e^2\tau_{\mathrm{c}}} \qquad\qquad \beta_{\mathrm{c}} = \frac{B}{n_{\mathrm{c}}ec}$$

(5.121)

$$\alpha_{\mathrm{v}} = \frac{(1 - i\omega\tau_{\mathrm{v}})m_{\mathrm{v}}}{n_{\mathrm{v}}e^2\tau_{\mathrm{v}}} \qquad\qquad \beta_{\mathrm{v}} = \frac{B}{n_{\mathrm{v}}ec} \quad,$$

we obtain for the upper left 2×2 block of ρ:

$$\rho_{\perp} = \left[\left(\frac{\alpha_{\mathrm{v}}}{\alpha_{\mathrm{v}}^2 + \beta_{\mathrm{v}}^2} + \frac{\alpha_{\mathrm{c}}}{\alpha_{\mathrm{c}}^2 + \beta_{\mathrm{c}}^2}\right)^2 + \left(\frac{\beta_{\mathrm{v}}}{\alpha_{\mathrm{v}}^2 + \beta_{\mathrm{v}}^2} + \frac{\beta_{\mathrm{c}}}{\alpha_{\mathrm{c}}^2 + \beta_{\mathrm{c}}^2}\right)^2\right]^{-1}$$
$$\times \begin{pmatrix} \frac{\alpha_{\mathrm{v}}}{\alpha_{\mathrm{v}}^2 + \beta_{\mathrm{v}}^2} + \frac{\alpha_{\mathrm{c}}}{\alpha_{\mathrm{c}}^2 + \beta_{\mathrm{c}}^2} & \frac{\beta_{\mathrm{v}}}{\alpha_{\mathrm{v}}^2 + \beta_{\mathrm{v}}^2} + \frac{\beta_{\mathrm{c}}}{\alpha_{\mathrm{c}}^2 + \beta_{\mathrm{c}}^2} \\ -\frac{\beta_{\mathrm{v}}}{\alpha_{\mathrm{v}}^2 + \beta_{\mathrm{v}}^2} - \frac{\beta_{\mathrm{c}}}{\alpha_{\mathrm{c}}^2 + \beta_{\mathrm{c}}^2} & \frac{\alpha_{\mathrm{v}}}{\alpha_{\mathrm{v}}^2 + \beta_{\mathrm{v}}^2} + \frac{\alpha_{\mathrm{c}}}{\alpha_{\mathrm{c}}^2 + \beta_{\mathrm{c}}^2} \end{pmatrix} \quad,$$

(5.122)

from which we compute the magnetoresistance,

$$\frac{\rho_{xx}(B) - \rho_{xx}(0)}{\rho_{xx}(0)} = \frac{\gamma_{\mathrm{c}}\,\gamma_{\mathrm{v}}\left(\frac{\gamma_{\mathrm{c}}}{n_{\mathrm{c}}ec} - \frac{\gamma_{\mathrm{v}}}{n_{\mathrm{v}}ec}\right)^2 B^2}{(\gamma_{\mathrm{c}} + \gamma_{\mathrm{v}})^2 + (\gamma_{\mathrm{c}}\,\gamma_{\mathrm{v}})^2\left(\frac{1}{n_{\mathrm{c}}ec} + \frac{1}{n_{\mathrm{v}}ec}\right)^2 B^2} \quad,$$

(5.123)

where

$$\gamma_{\mathrm{c}} \equiv \alpha_{\mathrm{c}}^{-1} = \frac{n_{\mathrm{c}}e^2\tau_{\mathrm{c}}}{m_{\mathrm{c}}} \cdot \frac{1}{1 - i\omega\tau_{\mathrm{c}}}$$

$$\gamma_{\mathrm{v}} \equiv \alpha_{\mathrm{v}}^{-1} = \frac{n_{\mathrm{v}}e^2\tau_{\mathrm{v}}}{m_{\mathrm{v}}} \cdot \frac{1}{1 - i\omega\tau_{\mathrm{v}}} \quad.$$

Note that the magnetoresistance is *positive* within the two band model, and that it *saturates* in the high field limit:

$$\frac{\rho_{xx}(B \to \infty) - \rho_{xx}(0)}{\rho_{xx}(0)} = \frac{\gamma_{\mathrm{c}}\,\gamma_{\mathrm{v}}\left(\frac{\gamma_{\mathrm{c}}}{n_{\mathrm{c}}ec} - \frac{\gamma_{\mathrm{v}}}{n_{\mathrm{v}}ec}\right)^2}{(\gamma_{\mathrm{c}}\,\gamma_{\mathrm{v}})^2\left(\frac{1}{n_{\mathrm{c}}ec} + \frac{1}{n_{\mathrm{v}}ec}\right)^2} \quad.$$

(5.124)

The longitudinal resistivity is found to be

$$\rho_{zz} = (\gamma_{\mathrm{c}} + \gamma_{\mathrm{v}})^{-1} \quad , \tag{5.125}$$

and is independent of B.

In an intrinsic semiconductor, $n_{\mathrm{c}} = n_{\mathrm{v}} \propto \exp(-E_{\mathrm{g}}/2k_{\mathrm{B}}T)$, and $\Delta\rho_{xx}(B)/\rho_{xx}(0)$ is finite even as $T \to 0$. In the extrinsic (*i.e.* doped) case, one of the densities (say, n_{c} in a p-type material) vanishes much more rapidly than the other, and the magnetoresistance vanishes with the ratio $n_{\mathrm{c}}/n_{\mathrm{v}}$.

5.5.6   Optical reflectivity of metals and semiconductors

What happens when an electromagnetic wave is incident on a metal? Inside the metal we have Maxwell's equations:

$$\boldsymbol{\nabla} \times \boldsymbol{H} = \frac{4\pi}{c}\,\boldsymbol{j} + \frac{1}{c}\frac{\partial \boldsymbol{D}}{\partial t} \qquad \Longrightarrow \qquad i\boldsymbol{k} \times \boldsymbol{B} = \left(\frac{4\pi\sigma}{c} - \frac{i\omega}{c}\right)\boldsymbol{E} \tag{5.126}$$

and

$$\boldsymbol{\nabla} \times \boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} \qquad \Longrightarrow \qquad i\boldsymbol{k} \times \boldsymbol{E} = \frac{i\omega}{c}\boldsymbol{B} \tag{5.127}$$

and

$$\boldsymbol{\nabla} \cdot \boldsymbol{E} = \boldsymbol{\nabla} \cdot \boldsymbol{B} = 0 \qquad \Longrightarrow \qquad i\boldsymbol{k} \cdot \boldsymbol{E} = i\boldsymbol{k} \cdot \boldsymbol{B} = 0 \quad , \tag{5.128}$$

where we've assumed $\mu = \epsilon = 1$ inside the metal, ignoring polarization due to virtual interband transitions (*i.e.* from core electrons). Hence,

$$\begin{aligned} \boldsymbol{k}^2 &= \frac{\omega^2}{c^2} + \frac{4\pi i\omega}{c^2}\,\sigma(\omega) \\ &= \frac{\omega^2}{c^2} + \frac{\omega_{\mathrm{p}}^2}{c^2}\frac{i\omega\tau}{1 - i\omega\tau} \equiv \epsilon(\omega)\,\frac{\omega^2}{c^2} \quad , \end{aligned} \tag{5.129}$$

where $\omega_{\mathrm{p}} = \sqrt{4\pi ne^2/m^*}$ is the *plasma frequency* for the conduction band. The dielectric function,

$$\epsilon(\omega) = 1 + \frac{4\pi i\sigma(\omega)}{\omega} = 1 + \frac{\omega_{\mathrm{p}}^2}{\omega^2}\frac{i\omega\tau}{1 - i\omega\tau} \tag{5.130}$$

determines the complex refractive index, $N(\omega) = \sqrt{\epsilon(\omega)}$, leading to the electromagnetic dispersion relation $k = N(\omega)\,\omega/c$.

Consider a wave normally incident upon a metallic surface normal to $\hat{\boldsymbol{z}}$. In the vacuum ($z < 0$), we write

$$\begin{aligned} \boldsymbol{E}(\boldsymbol{r}, t) &= E_1\,\hat{\boldsymbol{x}}\,e^{i\omega z/c}e^{-i\omega t} + E_2\,\hat{\boldsymbol{x}}\,e^{-i\omega z/c}e^{-i\omega t} \\ \boldsymbol{B}(\boldsymbol{r}, t) &= \frac{c}{i\omega}\,\boldsymbol{\nabla} \times \boldsymbol{E} = E_1\,\hat{\boldsymbol{y}}\,e^{i\omega z/c}e^{-i\omega t} - E_2\,\hat{\boldsymbol{y}}\,e^{-i\omega z/c}e^{-i\omega t} \end{aligned} \tag{5.131}$$

while in the metal ($z > 0$),

$$\boldsymbol{E}(\boldsymbol{r}, t) = E_3\,\hat{\boldsymbol{x}}\,e^{iN\omega z/c}e^{-i\omega t}$$
$$\boldsymbol{B}(\boldsymbol{r}, t) = \frac{c}{i\omega}\,\boldsymbol{\nabla} \times \boldsymbol{E} = NE_3\,\hat{\boldsymbol{y}}\,e^{iN\omega z/c}e^{-i\omega t} \quad .$$

(5.132)

Continuity of $\boldsymbol{E} \times \hat{\boldsymbol{n}}$ gives $E_1 + E_2 = E_3$. Continuity of $\boldsymbol{H} \times \hat{\boldsymbol{n}}$ gives $E_1 - E_2 = NE_3$. Thus,

$$\frac{E_2}{E_1} = \frac{1-N}{1+N} \qquad , \qquad \frac{E_3}{E_1} = \frac{2}{1+N}$$

(5.133)

and the reflection and transmission coefficients are

$$R(\omega) = \left|\frac{E_2}{E_1}\right|^2 = \left|\frac{1 - N(\omega)}{1 + N(\omega)}\right|^2$$
$$T(\omega) = \left|\frac{E_3}{E_1}\right|^2 = \frac{4}{\left|1 + N(\omega)\right|^2} \quad .$$

(5.134)

We've now solved the electromagnetic boundary value problem.

Typical values – For a metal with $n = 10^{22}\,\text{cm}^3$ and $m^* = m_\text{e}$, the plasma frequency is $\omega_\text{p} = 5.7 \times 10^{15}\,\text{s}^{-1}$. The scattering time varies considerably as a function of temperature. In high purity copper at $T = 4\,\text{K}$, $\tau \approx 2 \times 10^{-9}\,\text{s}$ and $\omega_\text{p}\tau \approx 10^7$. At $T = 300\,\text{K}$, $\tau \approx 2 \times 10^{-14}\,\text{s}$ and $\omega_\text{p}\tau \approx 100$. In either case, $\omega_\text{p}\tau \gg 1$. There are then three regimes to consider:

Low frequencies : $\omega\tau \ll 1 \ll \omega_\text{p}\tau$

We may approximate $1 - i\omega\tau \approx 1$, hence

$$N^2(\omega) = 1 + \frac{i\,\omega_\text{p}^2\tau}{\omega(1 - i\omega\tau)} \approx \frac{i\,\omega_\text{p}^2\tau}{\omega}$$
$$N(\omega) \approx \frac{1+i}{\sqrt{2}}\left(\frac{\omega_\text{p}^2\tau}{\omega}\right)^{1/2} \implies R \approx 1 - \frac{2\sqrt{2\omega\tau}}{\omega_\text{p}\tau} \quad .$$

(5.135)

Hence $R \approx 1$ and the metal reflects.

Intermediate frequencies : $1 \ll \omega\tau \ll \omega_\text{p}\tau$

In this regime,

$$N^2(\omega) \approx 1 - \frac{\omega_\text{p}^2}{\omega^2} + \frac{i\,\omega_\text{p}^2}{\omega^3\tau}$$

(5.136)

which is almost purely real and negative. Hence N is almost purely imaginary and $R \approx 1$. (To lowest nontrivial order, $R = 1 - 2/\omega_\text{p}\tau$.) Still high reflectivity.

High frequencies : $1 \ll \omega_{\mathrm{p}} \tau \ll \omega \tau$

Here we have

$$N^2(\omega) \approx 1 - \frac{\omega_{\mathrm{p}}^2}{\omega^2} \quad \Longrightarrow \quad R = \frac{\omega_{\mathrm{p}}}{2\omega} \tag{5.137}$$

and $R \ll 1$ – the metal is transparent at frequencies large compared to ω_{p}.

Optical reflectivity of semiconductors

In our analysis of the electrodynamics of metals, we assumed that the dielectric constant due to all the filled bands was simply $\epsilon = 1$. This is not quite right. We should instead have written

$$\mathbf{k}^2 = \epsilon_\infty \frac{\omega^2}{c^2} + \frac{4\pi i \omega \sigma(\omega)}{c^2}$$

$$\tag{5.138}$$

$$\epsilon(\omega) = \epsilon_\infty \left\{ 1 + \frac{\omega_{\mathrm{p}}^2}{\omega^2} \frac{i\omega\tau}{1 - i\omega\tau} \right\} \quad ,$$

where ϵ_∞ is the dielectric constant due to virtual transitions to fully occupied (*i.e.* core) and fully unoccupied bands, at a frequency small compared to the interband frequency. The plasma frequency is now defined as

$$\omega_{\mathrm{p}} = \left(\frac{4\pi n e^2}{m^* \epsilon_\infty} \right)^{1/2} \tag{5.139}$$

where n is the conduction electron density. Note that $\epsilon(\omega \to \infty) = \epsilon_\infty$, although again this is only true for ω smaller than the gap to neighboring bands. It turns out that for insulators one can write

$$\epsilon_\infty \simeq 1 + \frac{\omega_{\mathrm{pv}}^2}{\omega_{\mathrm{g}}^2} \tag{5.140}$$

where $\omega_{\mathrm{pv}} = \sqrt{4\pi n_{\mathrm{v}} e^2 / m_{\mathrm{e}}}$, with n_{v} the number density of valence electrons, and ω_{g} is the energy gap between valence and conduction bands. In semiconductors such as Si and Ge, $\omega_{\mathrm{g}} \sim 4\,\mathrm{eV}$, while $\omega_{\mathrm{pv}} \sim 16\,\mathrm{eV}$, hence $\epsilon_\infty \sim 17$, which is in rough agreement with the experimental values of ~ 12 for Si and ~ 16 for Ge. In metals, the band gaps generally are considerably larger.

There are some important differences to consider in comparing semiconductors and metals:

- The carrier density n typically is much smaller in semiconductors than in metals, ranging from $n \sim 10^{16}\,\mathrm{cm}^{-3}$ in intrinsic (*i.e.* undoped, thermally excited at room temperature) materials to $n \sim 10^{19}\,\mathrm{cm}^{-3}$ in doped materials.

- $\epsilon_\infty \approx 10 - 20$ and $m^*/m_{\mathrm{e}} \approx 0.1$. The product $\epsilon_\infty m^*$ thus differs only slightly from its free electron value.

Since $n_{\text{semi}} \lesssim 10^{-4} \, n_{\text{metal}}$, one has

$$\omega_{\text{p}}^{\text{semi}} \approx 10^{-2} \, \omega_{\text{p}}^{\text{metal}} \approx 10^{-14} \, \text{s} \quad . \tag{5.141}$$

In high purity semiconductors the mobility $\mu = e\tau/m^* \gtrsim 10^5 \, \text{cm}^2/\text{vs}$ the low temperature scattering time is typically $\tau \approx 10^{-11} \, \text{s}$. Thus, for $\omega \gtrsim 3 \times 10^{15} \, \text{s}^{-1}$ in the optical range, we have $\omega\tau \gg \omega_{\text{p}}\tau \gg 1$, in which case $N(\omega) \approx \sqrt{\epsilon_\infty}$ and the reflectivity is

$$R = \left| \frac{1 - \sqrt{\epsilon_\infty}}{1 + \sqrt{\epsilon_\infty}} \right|^2 \quad . \tag{5.142}$$

Taking $\epsilon_\infty = 10$, one obtains $R = 0.27$, which is high enough so that polished Si wafers appear shiny.

5.5.7 Theory for Bloch wavepackets

But then how do we implement the semiclassical equations of motion for Bloch wavepackets,

$$\begin{aligned}
\frac{d\boldsymbol{r}}{dt} &= \boldsymbol{v}_n(\boldsymbol{k}) - \frac{d\boldsymbol{k}}{dt} \times \boldsymbol{\Omega}_n(\boldsymbol{k}) \\
\hbar \frac{d\boldsymbol{k}}{dt} &= -e\boldsymbol{E}(\boldsymbol{r}, t) - \frac{e}{c} \frac{d\boldsymbol{r}}{dt} \times \boldsymbol{B}(\boldsymbol{r}, t) \quad ?
\end{aligned} \tag{5.143}$$

In particular, how do we account for scattering within the semiclassical model? In what follows, we shall assume that the topological density $\boldsymbol{\Omega}_n(\boldsymbol{k}) = 0$.

A more rigorous approach to this issue is based on the Boltzmann equation, which describes how the distribution $f(\boldsymbol{r}, \boldsymbol{k}, t)$ of electron wave packets evolves and takes a steady state form. Here we will opt for a more callow treatment which yields equivalent results. The most naïve generalization of the semiclassical equations would involve adding the 'scattering' term $-\boldsymbol{p}/\tau$ to the right hand side of the equation for $\dot{\boldsymbol{p}} = \hbar\dot{\boldsymbol{k}}$, i.e.

$$M(\boldsymbol{k}) \frac{d\boldsymbol{v}(\boldsymbol{k})}{dt} = -e\boldsymbol{E}(\boldsymbol{r}, t) - \frac{e}{c} \frac{d\boldsymbol{r}}{dt} \times \boldsymbol{B}(\boldsymbol{r}, t) - \frac{1}{\tau} M(\boldsymbol{k}) \, \boldsymbol{v}(\boldsymbol{k}) \quad , \tag{5.144}$$

where

$$M_{\alpha\beta}(\boldsymbol{k}) = \hbar \frac{\partial k^\alpha}{\partial v^\beta} \qquad \Longleftrightarrow \qquad M_{\alpha\beta}^{-1}(\boldsymbol{k}) = \frac{1}{\hbar^2} \frac{\partial^2 E(\boldsymbol{k})}{\partial k^\alpha \, \partial k^\beta} \quad . \tag{5.145}$$

However, while $\dot{\boldsymbol{k}}$ is well-defined, $\boldsymbol{k}$ itself, and hence $\boldsymbol{p} = \hbar\boldsymbol{k}$, is not, because it is defined only modulo a reciprocal lattice vector.

5.6   Boltzmann Equation in Solids

5.6.1   Semiclassical dynamics and distribution functions

The semiclassical dynamics of a wavepacket in a solid are described by the equations[9]

$$
\frac{d\boldsymbol{r}}{dt} = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\boldsymbol{k})}{\partial \boldsymbol{k}} - \frac{d\boldsymbol{k}}{dt} \times \boldsymbol{\Omega}_n(\boldsymbol{k})
\tag{5.146}
$$

$$
\frac{d\boldsymbol{k}}{dt} = -\frac{e}{\hbar}\boldsymbol{E}(\boldsymbol{r},t) - \frac{e}{\hbar c}\frac{d\boldsymbol{r}}{dt} \times \boldsymbol{B}(\boldsymbol{r},t) - \frac{e}{2\hbar mc}\boldsymbol{\nabla}(\boldsymbol{\sigma}\cdot\boldsymbol{B}) \quad . \quad .
\tag{5.147}
$$

Here n is the band index and $\varepsilon_n(\boldsymbol{k})$ is the dispersion relation for band n. The Zeeman contribution to the Hamiltonian is $H_Z = (e\hbar/2mc)\boldsymbol{\sigma}\cdot\boldsymbol{B}$, and we will typically choose the internal $\hat{z}$ axis as the spin quantization axis, in which case $H_Z = (e\hbar/2mc)\sigma B^z$. The wavevector is $\boldsymbol{k}$ ($\hbar\boldsymbol{k}$ is the 'crystal momentum'), and $\varepsilon_n(\boldsymbol{k})$ is periodic under $\boldsymbol{k} \to \boldsymbol{k} + \boldsymbol{G}$, where $\boldsymbol{G}$ is any reciprocal lattice vector. The second term on the RHS of Eqn. 5.146 is the so-called Karplus-Luttinger term, defined by

$$
\mathcal{A}_n^\mu(\boldsymbol{k}) = i\left\langle u_n(\boldsymbol{k}) \Big| \frac{\partial}{\partial k^\mu} \Big| u_n(\boldsymbol{k}) \right\rangle
\tag{5.148}
$$

$$
\Omega_n^\mu(\boldsymbol{k}) = \epsilon^{\mu\nu\lambda}\frac{\partial \mathcal{A}_n^\lambda(\boldsymbol{k})}{\partial k^\nu} \quad ,
\tag{5.149}
$$

arising from the Berry phases generated by the one-particle Bloch cell functions $|u_n(\boldsymbol{k})\rangle$. These formulae are valid only at sufficiently weak fields. They neglect, for example, Zener tunneling processes in which an electron may change its band index as it traverses the Brillouin zone. We assume $\boldsymbol{\Omega}_n(\boldsymbol{k}) = 0$ in our discussion, *i.e.* we assume the Bloch bands are non topological. Finally, we neglect the orbital magnetization of the Bloch wavepacket and contributions from the spin-orbit interaction. When the orbital moment of the Bloch electrons is included, we must substitute

$$
\varepsilon_n(\boldsymbol{k}) \to \varepsilon_n(\boldsymbol{k}) - \boldsymbol{M}_n(\boldsymbol{k})\cdot\boldsymbol{B}(\boldsymbol{r},t)
\tag{5.150}
$$

where

$$
M_n^\mu(\boldsymbol{k}) = e\,\epsilon^{\mu\nu\lambda}\,\mathsf{Im}\left\langle \frac{\partial u_n}{\partial k^\nu} \Big| \varepsilon_n(\boldsymbol{k}) - H_0(\boldsymbol{k}) \Big| \frac{\partial u_n}{\partial k^\lambda} \right\rangle \quad ,
\tag{5.151}
$$

where $\hat{H}_0(\boldsymbol{k}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\,\hat{H}_0\,e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}$ and $\hat{H}_0 = \frac{p^2}{2m} + V(\boldsymbol{r})$ is the one-electron Hamiltonian in the crystalline potential $V(\boldsymbol{r}) = V(\boldsymbol{r}+\boldsymbol{R})$, where $\boldsymbol{R}$ is any direct lattice vector. Note $\hat{H}_0(\boldsymbol{k})\,|u_n(\boldsymbol{k})\rangle = \varepsilon_n(\boldsymbol{k})\,|u_n(\boldsymbol{k})\rangle$ and that $u_n(\boldsymbol{k},\boldsymbol{r}+\boldsymbol{R}) = u_n(\boldsymbol{k},\boldsymbol{r})$ is periodic in the direct lattice.

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[9]See G. Sundaram and Q. Niu, *Phys. Rev. B* **59**, 14915 (1999).

We are of course interested in more than just a single electron, hence to that end let us consider the distribution function $f_n(\boldsymbol{r}, \boldsymbol{k}, t)$, defined such that[10]

$$f_{n\sigma}(\boldsymbol{r}, \boldsymbol{k}, t) \frac{d^3r \, d^3k}{(2\pi)^3} \equiv \begin{array}{l} \text{\# of electrons of spin } \sigma \text{ in band } n \text{ with positions within} \\ d^3r \text{ of } \boldsymbol{r} \text{ and wavevectors within } d^3k \text{ of } \boldsymbol{k} \text{ at time } t. \end{array} \tag{5.152}$$

Note that the distribution function is dimensionless. By performing integrals over the distribution function, we can obtain various physical quantities. For example, the current density at $\boldsymbol{r}$ is given by

$$\boldsymbol{j}(\boldsymbol{r}, t) = -e \sum_{n,\sigma} \int\limits_{\widehat{\Omega}} \frac{d^3k}{(2\pi)^3} \, f_{n\sigma}(\boldsymbol{r}, \boldsymbol{k}, t) \, \boldsymbol{v}_n(\boldsymbol{k}) \quad . \tag{5.153}$$

The symbol $\widehat{\Omega}$ in the above formula is to remind us that the wavevector integral is performed only over the first Brillouin zone.

We now ask how the distribution functions $f_{n\sigma}(\boldsymbol{r}, \boldsymbol{k}, t)$ evolve in time. To simplify matters, we will consider a single band and drop the indices n and σ. It is clear that in the absence of collisions, the distribution function must satisfy the continuity equation,

$$\frac{\partial f}{\partial t} + \boldsymbol{\nabla} \cdot (\boldsymbol{u} f) = 0 \quad . \tag{5.154}$$

This is just the condition of number conservation for electrons. Take care to note that $\boldsymbol{\nabla}$ and $\boldsymbol{u}$ are *six*-dimensional *phase space* vectors:

$$\boldsymbol{u} = (\, \dot{x} \,,\, \dot{y} \,,\, \dot{z} \,,\, \dot{k}_x \,,\, \dot{k}_y \,,\, \dot{k}_z \,)$$

$$\boldsymbol{\nabla} = \left(\frac{\partial}{\partial x} \,, \frac{\partial}{\partial y} \,, \frac{\partial}{\partial z} \,, \frac{\partial}{\partial k_x} \,, \frac{\partial}{\partial k_y} \,, \frac{\partial}{\partial k_z} \right) \quad . \tag{5.155}$$

Now note that as a consequence of the dynamics (5.146,5.147) that, provided $\boldsymbol{\Omega}_n(\boldsymbol{k}) = 0$, we have $\boldsymbol{\nabla} \cdot \boldsymbol{u} = 0$, *i.e.* phase space flow is *incompressible*, provided that $\varepsilon(\boldsymbol{k})$ is a function of $\boldsymbol{k}$ alone, and not of $\boldsymbol{r}$. Thus, in the absence of collisions, we have

$$\frac{\partial f}{\partial t} + \boldsymbol{u} \cdot \boldsymbol{\nabla} f = 0 \quad . \tag{5.156}$$

The differential operator $D_t \equiv \partial_t + \boldsymbol{u} \cdot \boldsymbol{\nabla}$ is sometimes called the 'convective derivative'.

When $\boldsymbol{\Omega}_n(\boldsymbol{k}) \neq 0$, we found in §4.5.2 that $\boldsymbol{\nabla} \cdot \boldsymbol{u} = -d \ln D_n/dt$, with

$$D_n(\boldsymbol{r}, \boldsymbol{k}, t) = 1 + \frac{e}{\hbar c} \, \boldsymbol{B}(\boldsymbol{r}, t) \cdot \boldsymbol{\Omega}(\boldsymbol{k}) \quad . \tag{5.157}$$

---

[10]We will assume three space dimensions. The discussion may be generalized to quasi-two dimensional and quasi-one dimensional systems as well.

In this case, we must redefine the phase space measure as

$$d\mu = \frac{d^3r\, d^3k}{(2\pi)^3} \quad \longrightarrow \quad d\tilde{\mu} \equiv D_n(r, k, t)\, \frac{d^3r\, d^3k}{(2\pi)^3} \quad . \tag{5.158}$$

This means that the expectation of any local observable $\mathcal{O}$ is given by

$$\begin{aligned}
\langle \mathcal{O} \rangle (r', t) &= \sum_n \int_{\widehat{\Omega}} d\tilde{\mu}\, f_n(r, k, t)\, \langle u_{nk} | \mathcal{O} | u_{nk} \rangle\, \delta(r - r') \\
&= \sum_n \int_{\widehat{\Omega}} \frac{d^3k}{(2\pi)^3}\, D_n(r',\, k, t)\, f_n(r', k, t)\, \langle u_{nk} | \mathcal{O} | u_{nk} \rangle \quad ,
\end{aligned} \tag{5.159}$$

Thus, for example

$$\begin{aligned}
j(r, t) &= \sum_n \int_{\widehat{\Omega}} \frac{d^3k}{(2\pi)^3}\, D_n(r, k, t)\, f_n(r, k, t)\, (-e\dot{r}) \\
&= -e \int_{\widehat{\Omega}} \frac{d^3k}{(2\pi)^3} \left\{ v_n + \frac{e}{\hbar c}\, (v_n \cdot \Omega_n)\, B + \frac{e}{\hbar}\, E \times \Omega_n \right\} f_n(r, k, t) \quad .
\end{aligned} \tag{5.160}$$

Throughout the rest of this chapter, we will assume $\Omega_n(k) = 0$. Here we have absorbed the spin polarization index σ into the band index, so there are twice as many n values as before. This notation is more appropriate when spin-orbit interaction terms are present, which can lead to cell functions $|u_{nk}\rangle$ which have internal spin space structure.

Next we must consider the effect of *collisions*, which are not accounted for by the semiclassical dynamics. In a collision process, an electron with wavevector k and one with wavevector k' can instantaneously convert into a pair with wavevectors $k + q$ and $k' - q$ (modulo a reciprocal lattice vector G), where q is the wavevector transfer. Note that the total wavevector is preserved (mod G). This means that $D_t f \neq 0$. Rather, we should write

$$\frac{\partial f}{\partial t} + \dot{r} \cdot \frac{\partial f}{\partial r} + \dot{k} \cdot \frac{\partial f}{\partial k} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \equiv \mathcal{I}_k[f] \tag{5.161}$$

where the right side is known as the *collision integral*. The collision integral is in general a *function* of r, k, and t and a *functional* of the distribution f. As the k-dependence is the most important for our concerns, we will write $\mathcal{I}_k$ in order to make this dependence explicit. Some examples should help clarify the situation.

First, let's consider a very simple model of the collision integral,

$$\mathcal{I}_k[f] = -\frac{f(r, k, t) - f^0(r, k)}{\tau(\varepsilon(k))} \quad . \tag{5.162}$$

This model is known as the *relaxation time approximation*. Here, $f^0(r, k)$ is a static distribution function which describes a *local equilibrium* at r. The quantity $\tau(\varepsilon(k))$ is the *relaxation time*, which may be energy-dependent. Note that the collision integral indeed depends on the variables (r, k, t), and has a particularly simple functional dependence on the distribution f.

A more sophisticated model might invoke Fermi's golden rule, Consider elastic scattering from a static potential $\mathcal{U}(r)$ which induces transitions between different momentum states. We can then write

$$
\begin{aligned}
\mathcal{I}_k[f] &= \frac{2\pi}{\hbar} \sum_{k' \in \widehat{\Omega}} |\langle\, k' \,|\, \mathcal{U} \,|\, k \,\rangle|^2 \, (f_{k'} - f_k) \, \delta(\varepsilon_k - \varepsilon_{k'}) \\
&= \frac{2\pi}{\hbar V} \int_{\widehat{\Omega}} \frac{d^3 k'}{(2\pi)^3} \, |\hat{\mathcal{U}}(k - k')|^2 \, (f_{k'} - f_k) \, \delta(\varepsilon_k - \varepsilon_{k'}) \quad,
\end{aligned}
\tag{5.163}
$$

where we abbreviate $f_k \equiv f(r, k, t)$. In deriving the last line we've used plane wave wavefunctions[11] $\psi_k(r) = \exp(ik \cdot r)/\sqrt{V}$, as well as the result

$$
\sum_{k \in \widehat{\Omega}} A(k) = V \int_{\widehat{\Omega}} \frac{d^3 k}{(2\pi)^3} \, A(k)
\tag{5.164}
$$

for smooth functions $A(k)$. Note the factor of V^{-1} in front of the integral in Eqn. 5.163. What this tells us is that for a bounded localized potential $\mathcal{U}(r)$, the contribution to the collision integral is inversely proportional to the size of the system. This makes sense because the number of electrons scales as V but the potential is only appreciable over a region of volume $\propto V^0$. Later on, we shall consider a finite density of scatterers, writing $\mathcal{U}(r) = \sum_{i=1}^{N_{\mathrm{imp}}} U(r - R_i)$, where the impurity density $n_{\mathrm{imp}} = N_{\mathrm{imp}}/V$ is finite, scaling as V^0. In this case $\hat{\mathcal{U}}(k - k')$ apparently scales as V, which would mean $\mathcal{I}_k\{f\}$ scales as V, which is unphysical. As we shall see, the random positioning of the impurities means that the $\mathcal{O}(V^2)$ contribution to $|\hat{\mathcal{U}}(k - k')|^2$ is *incoherent* and averages out to zero. The coherent piece scales as V, canceling the V in the denominator of Eqn. 5.163, resulting in a finite value for the collision integral in the thermodynamic limit (*i.e.* neither infinite nor infinitesimal).

Later on we will discuss electron-phonon scattering, which is *inelastic*. An electron with wavevector k' can scatter into a state with wavevector $k = k' - q \mod G$ by absorption of a phonon of wavevector q or emission of a phonon of wavevector $-q$. Similarly, an electron of wavevector k can scatter into the state k' by emission of a phonon of wavevector $-q$ or absorption of a phonon of wavevector q. The matrix element for these processes depends on k, k', and the polarization index of the phonon. Overall, energy is conserved. These considerations lead us

---

[11] Rather than plane waves, we should use Bloch waves $\psi_{nk}(r) = \exp(ik \cdot r) \, u_{nk}(r)$, where cell function $u_{nk}(r)$ satisfies $u_{nk}(r + R) = u_{nk}(r)$, where R is any direct lattice vector. Plane waves do not contain the cell functions, although they do exhibit Bloch periodicity $\psi_{nk}(r + R) = \exp(ik \cdot R) \, \psi_{nk}(r)$.

(a) k'→k via emission of q   (b) k'→k via absorption of −q

(c) k→k' via emission of −q   (d) k→k' via absorption of q
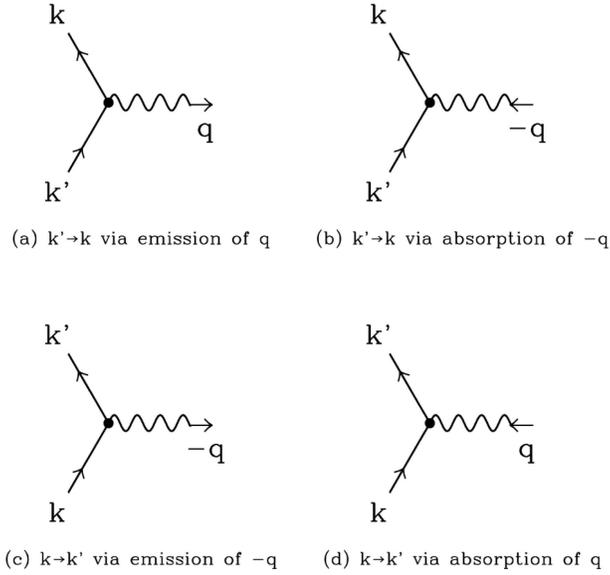
Figure 5.14: Electron-phonon vertices.

to the following collision integral:

$$\mathcal{I}_{\boldsymbol{k}}[f, n] = \frac{2\pi}{\hbar V} \sum_{\boldsymbol{k}', \lambda} |g_\lambda(\boldsymbol{k}, \boldsymbol{k}')|^2 \Big\{ (1 - f_{\boldsymbol{k}})\, f_{\boldsymbol{k}'}\, (1 + n_{\boldsymbol{q}, \lambda})\, \delta(\varepsilon_{\boldsymbol{k}} + \hbar\omega_{\boldsymbol{q}\lambda} - \varepsilon_{\boldsymbol{k}'}) \tag{5.165}$$

$$+ (1 - f_{\boldsymbol{k}})\, f_{\boldsymbol{k}'}\, n_{-\boldsymbol{q}\lambda}\, \delta(\varepsilon_{\boldsymbol{k}} - \hbar\omega_{-\boldsymbol{q}\lambda} - \varepsilon_{\boldsymbol{k}'}) - f_{\boldsymbol{k}}\, (1 - f_{\boldsymbol{k}'})\, (1 + n_{-\boldsymbol{q}\lambda})\, \delta(\varepsilon_{\boldsymbol{k}} - \hbar\omega_{-\boldsymbol{q}\lambda} - \varepsilon_{\boldsymbol{k}'})$$

$$- f_{\boldsymbol{k}}\, (1 - f_{\boldsymbol{k}'})\, n_{\boldsymbol{q}\lambda}\, \delta(\varepsilon_{\boldsymbol{k}} + \hbar\omega_{\boldsymbol{q}\lambda} - \varepsilon_{\boldsymbol{k}'}) \Big\}\, \delta_{\boldsymbol{q}, \boldsymbol{k}' - \boldsymbol{k} \bmod \boldsymbol{G}} \quad ,$$

which is a functional of both the electron distribution $f_{\boldsymbol{k}}$ as well as the phonon distribution $n_{\boldsymbol{q}\lambda}$. The four terms inside the curly brackets correspond, respectively, to cases (a) through (d) in Fig. 5.14.

Collisional invariants

While collisions will violate crystal momentum conservation, they do not violate conservation of particle number. Hence we should have[12]

$$\int d^3r \int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\, \mathcal{I}_{\boldsymbol{k}}[f] = 0 \quad . \tag{5.166}$$

---

[12]If collisions are purely local, then $\int_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\, \mathcal{I}_{\boldsymbol{k}}[f] = 0$ at every point $\boldsymbol{r}$ in space.

The total particle number,

$$N = \int d^3r \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \; f(\boldsymbol{r}, \boldsymbol{k}, t) \tag{5.167}$$

is a *collisional invariant* - a quantity which is preserved in the collision process. Other collisional invariants include energy (when all sources are accounted for), spin (total spin), and crystal momentum (if there is no breaking of lattice translation symmetry)[13]. Consider a function $F(\boldsymbol{r}, \boldsymbol{k})$ of position and wavevector. Its average value is

$$\bar{F}(t) = \int d^3r \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \; F(\boldsymbol{r}, \boldsymbol{k}) \, f(\boldsymbol{r}, \boldsymbol{k}, t) \quad . \tag{5.168}$$

Taking the time derivative,

$$
\begin{aligned}
\frac{d\bar{F}}{dt} = \frac{\partial \bar{F}}{\partial t} &= \int d^3r \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \, F(\boldsymbol{r}, \boldsymbol{k}) \left\{ -\frac{\partial}{\partial \boldsymbol{r}} \cdot (\dot{\boldsymbol{r}} f) - \frac{\partial}{\partial \boldsymbol{k}} \cdot (\dot{\boldsymbol{k}} f) + \mathcal{I}_{\boldsymbol{k}}[f] \right\} \\
&= \int d^3r \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \left\{ \left[\frac{\partial F}{\partial \boldsymbol{r}} \cdot \frac{d\boldsymbol{r}}{dt} + \frac{\partial F}{\partial \boldsymbol{k}} \cdot \frac{d\boldsymbol{k}}{dt} \right] f + F \, \mathcal{I}_{\boldsymbol{k}}[f] \right\} \quad .
\end{aligned}
\tag{5.169}
$$

Hence, if F is preserved by the dynamics between collisions, then

$$\frac{d\bar{F}}{dt} = \int d^3r \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \, F \, \mathcal{I}_{\boldsymbol{k}}[f] \quad , \tag{5.170}$$

which says that $\bar{F}(t)$ changes only as a result of collisions. If F is a collisional invariant, then $\dot{\bar{F}} = 0$. This is the case when $F = 1$, in which case $\bar{F}$ is the total number of particles, or when $F = \varepsilon(\boldsymbol{k})$, in which case $\bar{F}$ is the total energy.

5.6.2 Local equilibrium

The equilibrium Fermi distribution,

$$f^0(\boldsymbol{k}) = \left\{ \exp\left(\frac{\varepsilon(\boldsymbol{k}) - \mu}{k_{\mathrm{B}} T} \right) + 1 \right\}^{-1} \tag{5.171}$$

is a space-independent and time-independent solution to the Boltzmann equation. Since collisions act *locally* in space, they act on short time scales to establish a *local equilibrium* described

---

[13]Note that the relaxation time approximation violates all such conservation laws. Within the relaxation time approximation, there are no collisional invariants.

by a distribution function

$$f^0(\boldsymbol{r}, \boldsymbol{k}, t) = \left\{ \exp\left(\frac{\varepsilon(\boldsymbol{k}) - \mu(\boldsymbol{r}, t)}{k_{\mathrm{B}} T(\boldsymbol{r}, t)} \right) + 1 \right\}^{-1} \quad . \tag{5.172}$$

This is, however, not a solution to the full Boltzmann equation due to the 'streaming terms' $\dot{\boldsymbol{r}} \cdot \partial_{\boldsymbol{r}} + \dot{\boldsymbol{k}} \cdot \partial_{\boldsymbol{k}}$ in the convective derivative. These, though, act on longer time scales than those responsible for the establishment of local equilibrium. To obtain a solution, we write

$$f(\boldsymbol{r}, \boldsymbol{k}, t) = f^0(\boldsymbol{r}, \boldsymbol{k}, t) + \delta f(\boldsymbol{r}, \boldsymbol{k}, t) \tag{5.173}$$

and solve for the deviation $\delta f(\boldsymbol{r}, \boldsymbol{k}, t)$. We will assume $\mu = \mu(\boldsymbol{r})$ and $T = T(\boldsymbol{r})$ are time-independent. We first compute the differential of f^0,

$$\begin{aligned} df^0 &= k_{\mathrm{B}} T \frac{\partial f^0}{\partial \varepsilon} \, d\left(\frac{\varepsilon - \mu}{k_{\mathrm{B}} T} \right) \\ &= k_{\mathrm{B}} T \frac{\partial f^0}{\partial \varepsilon} \left\{ -\frac{d\mu}{k_{\mathrm{B}} T} - \frac{(\varepsilon - \mu)\, dT}{k_{\mathrm{B}} T^2} + \frac{d\varepsilon}{k_{\mathrm{B}} T} \right\} \\ &= -\frac{\partial f^0}{\partial \varepsilon} \left\{ \frac{\partial \mu}{\partial \boldsymbol{r}} \cdot d\boldsymbol{r} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial \boldsymbol{r}} \cdot d\boldsymbol{r} - \frac{\partial \varepsilon}{\partial \boldsymbol{k}} \cdot d\boldsymbol{k} \right\} \quad , \end{aligned} \tag{5.174}$$

from which we read off

$$\begin{aligned} \frac{\partial f^0}{\partial \boldsymbol{r}} &= \left\{ \frac{\partial \mu}{\partial \boldsymbol{r}} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial \boldsymbol{r}} \right\} \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \\ \frac{\partial f^0}{\partial \boldsymbol{k}} &= \hbar \boldsymbol{v} \frac{\partial f^0}{\partial \varepsilon} \quad . \end{aligned} \tag{5.175}$$

We thereby obtain

$$\frac{\partial \delta f}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} \, \delta f - \frac{e}{\hbar} \left[\boldsymbol{E} + \frac{1}{c} \boldsymbol{v} \times \boldsymbol{B} \right] \cdot \frac{\partial \, \delta f}{\partial \boldsymbol{k}} + \boldsymbol{v} \cdot \left[e \, \boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T} \boldsymbol{\nabla} T \right] \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \mathcal{I}_{\boldsymbol{k}} \big[f^0 + \delta f \big] \quad , \tag{5.176}$$

where $\boldsymbol{\mathcal{E}} = -\boldsymbol{\nabla}(\phi - \mu/e)$ is the gradient of the 'electrochemical potential'; we'll henceforth refer to $\boldsymbol{\mathcal{E}}$ as the electric field. Eqn (5.176) is a nonlinear integrodifferential equation in δf, with the nonlinearity coming from the collision integral. (In some cases, such as impurity scattering, the collision integral may be a linear functional.) We will solve a *linearized* version of this equation, assuming the system is always close to a state of local equilibrium.

Note that the inhomogeneous term in (5.176) involves the electric field and the temperature gradient $\boldsymbol{\nabla} T$. This means that δf is proportional to these quantities, and if they are small then δf is small. The gradient of δf is then of second order in smallness, since the external fields

$\phi - \mu/e$ and T are assumed to be slowly varying in space. To lowest order in smallness, then, we obtain the following *linearized Boltzmann equation*:

$$\frac{\partial \delta f}{\partial t} - \frac{e}{\hbar c} \boldsymbol{v} \times \boldsymbol{B} \cdot \frac{\partial \, \delta f}{\partial \boldsymbol{k}} + \boldsymbol{v} \cdot \left[e\boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T} \boldsymbol{\nabla} T \right] \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \mathcal{L} \, \delta f \quad , \tag{5.177}$$

where $\mathcal{L} \, \delta f$ is the *linearized collision integral*; $\mathcal{L}$ is a linear operator acting on δf (we suppress denoting the $\boldsymbol{k}$ dependence of $\mathcal{L}$). Note that we have not assumed that $\boldsymbol{B}$ is small. Indeed later on we will derive expressions for high B transport coefficients.

Note also that we also have dropped the term

$$\frac{\partial f^0}{\partial t} = -\frac{\partial f^0}{\partial \varepsilon} \left\{ \frac{\partial \mu}{\partial t} + \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial t} \right\} \tag{5.178}$$

from the LHS of the linearized Boltzmann equation. This is because we assume that the spatially uniform components of $\mu(\boldsymbol{r}, t)$ and $T(\boldsymbol{r}, t)$ are time-independent, which means that the nonzero contributions to $\partial \mu / \partial t$ and $\partial T / \partial t$ involve at least one space derivative as well as one time derivative, and are thus doubly small and therefore negligible.

5.7 Conductivity of Normal Metals

5.7.1 Relaxation time approximation

Consider a normal metal in the presence of an electric field $\boldsymbol{\mathcal{E}}$. We'll assume $\boldsymbol{B} = 0$, $\boldsymbol{\nabla} T = 0$, and also that $\boldsymbol{\mathcal{E}}$ is spatially uniform as well. This in turn guarantees that δf itself is spatially uniform. The Boltzmann equation then reduces to

$$\frac{\partial \, \delta f}{\partial t} - \frac{\partial f^0}{\partial \varepsilon} \, e\boldsymbol{v} \cdot \boldsymbol{\mathcal{E}} = \mathcal{I}_{\boldsymbol{k}} \big[f^0 + \delta f \big] \quad . \tag{5.179}$$

We'll solve this by adopting the relaxation time approximation for $\mathcal{I}_{\boldsymbol{k}}[f]$:

$$\mathcal{I}_{\boldsymbol{k}}[f] = -\frac{f - f^0}{\tau} = -\frac{\delta f}{\tau} \quad , \tag{5.180}$$

where τ, which may be $\boldsymbol{k}$-dependent, is the *relaxation time*. In the absence of any fields or temperature and electrochemical potential gradients, the Boltzmann equation becomes $\dot{\delta f} = -\delta f / \tau$, with the solution $\delta f(t) = \delta f(0) \exp(-t/\tau)$. The distribution thereby relaxes to the equilibrium one on the scale of τ. In fact, this result is *wrong*, because the total particle number is a collisional invariant. Electrons can's simply disappear! Rather, the local number density must relax to the equilibrium value via the slower mechanism of *diffusion*. While the fact that collisional invariants are not respected is a defect of the relaxation time approximation, this won't

much affect the validity of our conclusions regarding various transport coefficients, such as the electrical conductivity.

Writing $\boldsymbol{\mathcal{E}}(t) = \boldsymbol{\mathcal{E}}\, e^{-i\omega t}$, we solve

$$\frac{\partial\, \delta f(\boldsymbol{k}, t)}{\partial t} - e\, \boldsymbol{v}(\boldsymbol{k}) \cdot \boldsymbol{\mathcal{E}}\, e^{-i\omega t}\, \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f(\boldsymbol{k}, t)}{\tau(\varepsilon(\boldsymbol{k}))} \tag{5.181}$$

and obtain

$$\delta f(\boldsymbol{k}, t) = \frac{e\, \boldsymbol{\mathcal{E}} \cdot \boldsymbol{v}(\boldsymbol{k})\, \tau(\varepsilon(\boldsymbol{k}))}{1 - i\omega\tau(\varepsilon(\boldsymbol{k}))}\, \frac{\partial f^0}{\partial \varepsilon}\, e^{-i\omega t} \qquad . \tag{5.182}$$

The equilibrium distribution $f^0(\boldsymbol{k})$ results in zero current, since $f^0(-\boldsymbol{k}) = f^0(\boldsymbol{k})$. Thus, the current density is given by the expression

$$\begin{aligned}
j^\alpha(\boldsymbol{r}, t) &= -2e \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\, \delta f\, v^\alpha \\
&= 2e^2\, \mathcal{E}^\beta\, e^{-i\omega t} \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\, \frac{\tau(\varepsilon(\boldsymbol{k}))\, v^\alpha(\boldsymbol{k})\, v^\beta(\boldsymbol{k})}{1 - i\omega\tau(\varepsilon(\boldsymbol{k}))}\, \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \qquad .
\end{aligned} \tag{5.183}$$

In the above calculation, the factor of two arises from summing over spin polarizations. The conductivity tensor is defined by the linear relation $j^\alpha(\omega) = \sigma_{\alpha\beta}(\omega)\, \mathcal{E}^\beta(\omega)$. We have thus derived an expression for the conductivity tensor,

$$\sigma_{\alpha\beta}(\omega) = 2e^2 \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\, \frac{\tau(\varepsilon(\boldsymbol{k}))\, v^\alpha(\boldsymbol{k})\, v^\beta(\boldsymbol{k})}{1 - i\omega\tau(\varepsilon(\boldsymbol{k}))}\, \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \qquad . \tag{5.184}$$

Note that the conductivity is a property of the *Fermi surface*. For $k_{\mathrm{B}}T \ll \varepsilon_{\mathrm{F}}$, we have $-\partial f^0/\partial\varepsilon \approx \delta(\varepsilon_{\mathrm{F}} - \varepsilon(\boldsymbol{k}))$ and the above integral is over the Fermi surface alone. Explicitly, we change variables to energy ε and coordinates along a constant energy surface, writing

$$d^3k = \frac{d\varepsilon\, dS_\varepsilon}{|\partial\varepsilon/\partial\boldsymbol{k}|} = \frac{d\varepsilon\, dS_\varepsilon}{\hbar|\boldsymbol{v}|} \qquad , \tag{5.185}$$

where dS_ε is the differential area on the constant energy surface $\varepsilon(\boldsymbol{k}) = \varepsilon$, and $\boldsymbol{v}(\boldsymbol{k}) = \hbar^{-1}\boldsymbol{\nabla}_{\!\boldsymbol{k}}\, \varepsilon(\boldsymbol{k})$ is the velocity. For $T \ll T_{\mathrm{F}}$, then,

$$\sigma_{\alpha\beta}(\omega) = \frac{e^2}{4\pi^3\hbar}\, \frac{\tau(\varepsilon_{\mathrm{F}})}{1 - i\omega\tau(\varepsilon_{\mathrm{F}})} \int dS_{\mathrm{F}}\, \frac{v^\alpha(\boldsymbol{k})\, v^\beta(\boldsymbol{k})}{|\boldsymbol{v}(\boldsymbol{k})|} \qquad . \tag{5.186}$$

For free electrons in a parabolic band, we write $\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m^*$, so $v^\alpha(\boldsymbol{k}) = \hbar k^\alpha/m^*$. To further simplify matters, let us assume that τ is constant, or at least very slowly varying in the vicinity

of the Fermi surface. We find

$$\sigma_{\alpha\beta}(\omega) = \delta_{\alpha\beta} \frac{2}{3m^*} \frac{e^2\tau}{1 - i\omega\tau} \int\limits_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, \varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \quad , \tag{5.187}$$

where $g(\varepsilon)$ is the *density of states*,

$$g(\varepsilon) = 2 \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\, \delta\left(\varepsilon - \varepsilon(\boldsymbol{k}) \right) \quad . \tag{5.188}$$

The (three-dimensional) parabolic band density of states is found to be

$$g(\varepsilon) = \frac{(2m^*)^{3/2}}{2\pi^2\hbar^3} \sqrt{\varepsilon}\, \Theta(\varepsilon) \quad , \tag{5.189}$$

where $\Theta(x)$ is the step function. In fact, integrating (5.187) by parts, we only need to know about the $\sqrt{\varepsilon}$ dependence in $g(\varepsilon)$, and not the details of its prefactor:

$$\int d\varepsilon\, \varepsilon\, g(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \int d\varepsilon\, f^0(\varepsilon) \frac{\partial}{\partial \varepsilon} \left(\varepsilon\, g(\varepsilon) \right) = \tfrac{3}{2} \int d\varepsilon\, g(\varepsilon)\, f^0(\varepsilon) = \tfrac{3}{2} n \quad , \tag{5.190}$$

where $n = N/V$ is the electron number density for the conduction band. The final result for the conductivity tensor is

$$\sigma_{\alpha\beta}(\omega) = \frac{ne^2\tau}{m^*} \frac{\delta_{\alpha\beta}}{1 - i\omega\tau} \quad . \tag{5.191}$$

We have recovered the the Drude theory of electrical conduction in metals.

5.7.2 Optical conductivity and the Fermi surface

At high frequencies, when $\omega\tau \gg 1$, our expression for the conductivity, Eqn. (5.184), yields

$$\sigma(\omega) = \frac{ie^2}{12\pi^3\hbar\omega} \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon\, |\boldsymbol{v}(\boldsymbol{k})| \quad , \tag{5.192}$$

where we have presumed sufficient crystalline symmetry to guarantee that $\sigma_{\alpha\beta} = \sigma\,\delta_{\alpha\beta}$ is diagonal. In the isotropic case, and at temperatures low compared with $T_{\rm F}$, the integral over the Fermi surface gives $4\pi k_{\rm F}^2\, v_{\rm F} = 12\pi^3\hbar n/m^*$, whence $\sigma = ine^2/m^*\omega$, which is the large frequency limit of our previous result. For a general Fermi surface, we can define

$$\sigma(\omega \gg \tau^{-1}) \equiv \frac{ine^2}{m_{\rm opt}\omega} \tag{5.193}$$
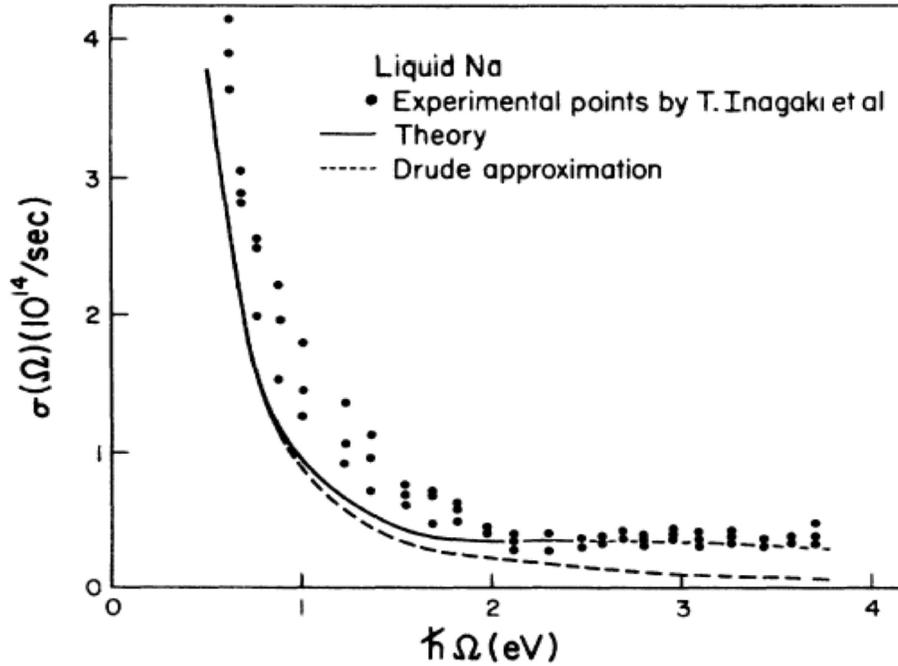
Figure 5.15: Frequency-dependent conductivity of liquid sodium by T. Inagaki *et al*, *Phys. Rev. B* **13**, 5610 (1976).

where the *optical mass* m_{opt} is given by

$$\frac{1}{m_{\text{opt}}} = \frac{1}{12\pi^3\hbar n} \int d\varepsilon \left(-\frac{\partial f^0}{\partial \varepsilon}\right) \int dS_\varepsilon \left|\boldsymbol{v}(\boldsymbol{k})\right| \quad . \tag{5.194}$$

Note that at high frequencies $\sigma(\omega)$ is purely imaginary. What does this mean? If

$$\boldsymbol{\mathcal{E}}(t) = \boldsymbol{\mathcal{E}} \cos(\omega t) = \tfrac{1}{2}\boldsymbol{\mathcal{E}} \left(e^{-i\omega t} + e^{+i\omega t}\right) \tag{5.195}$$

then

$$\boldsymbol{j}(t) = \tfrac{1}{2}\boldsymbol{\mathcal{E}} \left\{\sigma(\omega)\, e^{-i\omega t} + \sigma(-\omega)\, e^{+i\omega t}\right\} = \frac{ne^2}{m_{\text{opt}}\omega}\boldsymbol{\mathcal{E}} \sin(\omega t) \quad , \tag{5.196}$$

where we have invoked $\sigma(-\omega) = \sigma^*(\omega)$. The current is therefore $90°$ out of phase with the voltage, and the average over a cycle $\langle \boldsymbol{j}(t) \cdot \boldsymbol{\mathcal{E}}(t)\rangle = 0$. Recall that we found metals to be transparent for $\omega \gg \omega_{\text{p}} \gg \tau^{-1}$.

At zero temperature, the optical mass is given by

$$\frac{1}{m_{\text{opt}}} = \frac{1}{12\pi^3\hbar n} \int dS_{\text{F}} \left|\boldsymbol{v}(\boldsymbol{k})\right| \quad . \tag{5.197}$$

Metal	$m^*_{\mathrm{opt}}/m_{\mathrm{e}}$		$m^*_{\mathrm{th}}/m_{\mathrm{e}}$	
	thy	expt	thy	expt
Li	1.45	1.57	1.64	2.23
Na	1.00	1.13	1.00	1.27
K	1.02	1.16	1.07	1.26
Rb	1.08	1.16	1.18	1.36
Cs	1.29	1.19	1.75	1.79
Cu	-	-	1.46	1.38
Ag	-	-	1.00	1.00
Au	-	-	1.09	1.08

Table 5.1: Optical and thermodynamic effective masses of monovalent metals. (Taken from Smith and Jensen).

The density of states, $g(\varepsilon_{\mathrm{F}})$, is

$$g(\varepsilon_{\mathrm{F}}) = \frac{1}{4\pi^3\hbar} \int dS_{\mathrm{F}} \left|\boldsymbol{v}(\boldsymbol{k})\right|^{-1} \quad , \tag{5.198}$$

from which one can define the thermodynamic effective mass m^*_{th}, appealing to the low temperature form of the specific heat,

$$c_V = \frac{\pi^2}{3} k_{\mathrm{B}}^2 T g(\varepsilon_{\mathrm{F}}) \equiv \frac{m^*_{\mathrm{th}}}{m_{\mathrm{e}}} c_V^0 \quad , \tag{5.199}$$

where

$$c_V^0 \equiv \frac{m_{\mathrm{e}} k_{\mathrm{B}}^2 T}{3\hbar^2} \left(3\pi^2 n\right)^{1/3} \tag{5.200}$$

is the specific heat for a free electron gas of density n. Thus,

$$m^*_{\mathrm{th}} = \frac{\hbar}{4\pi(3\pi^2 n)^{1/3}} \int dS_{\mathrm{F}} \left|\boldsymbol{v}(\boldsymbol{k})\right|^{-1} \tag{5.201}$$

5.8 Calculation of the Scattering Time

5.8.1 Potential scattering and Fermi's golden rule

Let us go beyond the relaxation time approximation and calculate the scattering time τ from first principles. We will concern ourselves with scattering of electrons from crystalline impuri-

ties. We begin with Fermi's Golden Rule[14],

$$\mathcal{I}_{\boldsymbol{k}}[f] = \frac{2\pi}{\hbar} \sum_{\boldsymbol{k}'} \left| \langle \boldsymbol{k}' \, | \, \mathcal{U} \, | \, \boldsymbol{k} \, \rangle \right|^2 (f_{\boldsymbol{k}'} - f_{\boldsymbol{k}}) \, \delta(\varepsilon(\boldsymbol{k}) - \varepsilon(\boldsymbol{k}')) \quad , \tag{5.202}$$

where $\mathcal{U}(\boldsymbol{r})$ is a sum over individual impurity ion potentials, $\mathcal{U}(\boldsymbol{r}) = \sum_{j=1}^{N_{\text{imp}}} U(\boldsymbol{r} - \boldsymbol{R}_j)$. Thus,

$$\left| \langle \boldsymbol{k}' \, | \, \mathcal{U} \, | \, \boldsymbol{k} \, \rangle \right|^2 = V^{-2} \, |\hat{U}(\boldsymbol{k} - \boldsymbol{k}')|^2 \cdot \left| \sum_{j=1}^{N_{\text{imp}}} e^{i(\boldsymbol{k} - \boldsymbol{k}') \cdot \boldsymbol{R}_j} \right|^2 \quad , \tag{5.203}$$

where V is the volume of the solid and

$$\hat{U}(\boldsymbol{q}) = \int d^3r \, U(\boldsymbol{r}) \, e^{-i\boldsymbol{q} \cdot \boldsymbol{r}} \tag{5.204}$$

is the Fourier transform of the impurity potential. Note that we are assuming a single species of impurities; the method can be generalized to account for different impurity species.

To make progress, we assume the impurity positions are random and uncorrelated, and we average over them. Using

$$\overline{\left| \sum_{j=1}^{N_{\text{imp}}} e^{i\boldsymbol{q} \cdot \boldsymbol{R}_j} \right|^2} = N_{\text{imp}} + N_{\text{imp}}(N_{\text{imp}} - 1) \, \delta_{\boldsymbol{q},0} \quad , \tag{5.205}$$

we obtain

$$\overline{\left| \langle \boldsymbol{k}' \, | \, \mathcal{U} \, | \, \boldsymbol{k} \, \rangle \right|^2} = \frac{N_{\text{imp}}}{V^2} \, |\hat{U}(\boldsymbol{k} - \boldsymbol{k}')|^2 + \frac{N_{\text{imp}}(N_{\text{imp}} - 1)}{V^2} \, |\hat{U}(0)|^2 \, \delta_{\boldsymbol{k}\boldsymbol{k}'} \quad . \tag{5.206}$$

EXERCISE: Verify Eqn. (5.205).

We will neglect the second term in Eqn. 5.206 arising from the spatial average ($\boldsymbol{q} = 0$ Fourier component) of the potential. As we will see, in the end it will cancel out. Writing $f = f^0 + \delta f$, we have

$$\mathcal{I}_{\boldsymbol{k}}[f] = \frac{2\pi n_{\text{imp}}}{\hbar} \int\limits_{\hat{\Omega}} \frac{d^3k'}{(2\pi)^3} \, |\hat{U}(\boldsymbol{k} - \boldsymbol{k}')|^2 \, \delta\left(\frac{\hbar^2 \boldsymbol{k}^2}{2m^*} - \frac{\hbar^2 \boldsymbol{k}'^2}{2m^*} \right) (\delta f_{\boldsymbol{k}'} - \delta f_{\boldsymbol{k}}) \quad , \tag{5.207}$$

where $n_{\text{imp}} = N_{\text{imp}}/V$ is the number density of impurities. Note that we are assuming a parabolic band. We next make the *Ansatz*

$$\delta f_{\boldsymbol{k}} = \tau(\varepsilon(\boldsymbol{k})) \, e \, \boldsymbol{\mathcal{E}} \cdot \boldsymbol{v}(\boldsymbol{k}) \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon(\boldsymbol{k})} \tag{5.208}$$

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[14]We'll treat the scattering of each spin species separately. We assume no spin-flip scattering takes place.

and solve for $\tau(\varepsilon(\boldsymbol{k}))$. The (time-independent) Boltzmann equation is

$$-e\,\boldsymbol{\mathcal{E}} \cdot \boldsymbol{v}(\boldsymbol{k})\,\frac{\partial f^0}{\partial \varepsilon} = \frac{2\pi}{\hbar}\,n_{\text{imp}}\,e\,\boldsymbol{\mathcal{E}} \cdot \int\limits_{\hat{\Omega}} \frac{d^3k'}{(2\pi)^3}\,|\hat{U}(\boldsymbol{k} - \boldsymbol{k}')|^2\,\delta\!\left(\frac{\hbar^2\boldsymbol{k}^2}{2m^*} - \frac{\hbar^2\boldsymbol{k}'^2}{2m^*}\right)$$

$$\times \left(\tau(\varepsilon(\boldsymbol{k}'))\,\boldsymbol{v}(\boldsymbol{k}')\,\frac{\partial f^0}{\partial \varepsilon}\bigg|_{\varepsilon(\boldsymbol{k}')} - \tau(\varepsilon(\boldsymbol{k}))\,\boldsymbol{v}(\boldsymbol{k})\,\frac{\partial f^0}{\partial \varepsilon}\bigg|_{\varepsilon(\boldsymbol{k})}\right) \quad . \tag{5.209}$$

Due to the isotropy of the problem, we must have $\tau(\varepsilon(\boldsymbol{k}))$ is a function only of the magnitude of $\boldsymbol{k}$. We then obtain[15]

$$\frac{\hbar\boldsymbol{k}}{m^*} = \frac{n_{\text{imp}}}{4\pi^2\hbar}\,\tau(\varepsilon(\boldsymbol{k}))\int\limits_0^\infty \! dk'\,k'^2 \int \! d\hat{\boldsymbol{k}}'\,|\hat{U}(\boldsymbol{k} - \boldsymbol{k}')|^2\,\frac{\delta(k - k')}{\hbar^2 k/m^*}\,\frac{\hbar}{m^*}(\boldsymbol{k} - \boldsymbol{k}') \quad , \tag{5.210}$$

whence

$$\frac{1}{\tau(\varepsilon_{\text{F}})} = \frac{m^*\,k_{\text{F}}\,n_{\text{imp}}}{4\pi^2\hbar^3}\int d\hat{\boldsymbol{k}}'\,|U(k_{\text{F}}\hat{\boldsymbol{k}} - k_{\text{F}}\hat{\boldsymbol{k}}')|^2\,(1 - \hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{k}}') \quad . \tag{5.211}$$

If the impurity potential $U(\boldsymbol{r})$ itself is isotropic, then its Fourier transform $\hat{U}(\boldsymbol{q})$ is a function of $q^2 = 4k_{\text{F}}^2 \sin^2 \frac{1}{2}\vartheta$ where $\cos \vartheta = \hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{k}}'$ and $\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k}$ is the transfer wavevector. Recalling the Born approximation for differential scattering cross section,

$$\sigma(\vartheta) = \left(\frac{m^*}{2\pi\hbar^2}\right)^2 |\hat{U}(\boldsymbol{k} - \boldsymbol{k}')|^2 \quad , \tag{5.212}$$

we may finally write

$$\frac{1}{\tau(\varepsilon_{\text{F}})} = 2\pi n_{\text{imp}} v_{\text{F}} \int\limits_0^\pi d\vartheta\,\sigma_{\text{F}}(\vartheta)\,(1 - \cos\vartheta)\,\sin\vartheta \quad , \tag{5.213}$$

where $v_{\text{F}} = \hbar k_{\text{F}}/m^*$ is the Fermi velocity[16]. The *mean free path* is defined by $\ell = v_{\text{F}}\tau$.

Notice the factor $(1 - \cos\vartheta)$ in the integrand of (5.213). This tells us that forward scattering ($\vartheta = 0$) doesn't contribute to the scattering rate, which justifies our neglect of the second term in Eqn. (5.206). Why should τ be utterly insensitive to forward scattering? Because $\tau(\varepsilon_{\text{F}})$ is the *transport lifetime*, and forward scattering does not degrade the current. Therefore, $\sigma(\vartheta = 0)$ does not contribute to the 'transport scattering rate' $\tau^{-1}(\varepsilon_{\text{F}})$. Oftentimes one sees reference in the literature to a 'single particle lifetime' as well, which is given by the same expression but without this factor:

$$\left\{\begin{array}{c}\tau_{\text{sp}}^{-1}\\\tau_{\text{tr}}^{-1}\end{array}\right\} = 2\pi n_{\text{imp}} v_{\text{F}} \int\limits_0^\pi d\vartheta\,\sigma_{\text{F}}(\vartheta)\left\{\begin{array}{c}1\\(1 - \cos\vartheta)\end{array}\right\}\sin\vartheta \quad . \tag{5.214}$$

---

[15]We assume that the Fermi surface is contained within the first Brillouin zone.

[16]The subscript on $\sigma_{\text{F}}(\vartheta)$ is to remind us that the cross section depends on k_{F} as well as ϑ.

Note that $\tau_{\mathrm{sp}} = (n_{\mathrm{imp}}\, v_{\mathrm{F}}\, \sigma_{\mathrm{F,tot}})^{-1}$, where $\sigma_{\mathrm{F,tot}}$ is the total scattering cross section at energy ε_{F}, a formula familiar from elementary kinetic theory.

The Boltzmann equation defines an infinite hierarchy of lifetimes classified by the angular momentum scattering channel. To derive this hierarchy, one can examine the linearized time-*dependent* Boltzmann equation with $\boldsymbol{\mathcal{E}} = 0$,

$$\frac{\partial\, \delta f_{\boldsymbol{k}}}{\partial t} = n_{\mathrm{imp}}\, v_{\mathrm{F}} \int d\hat{\boldsymbol{k}}'\, \sigma(\vartheta_{\boldsymbol{k}\boldsymbol{k}'})\, (\delta f_{\boldsymbol{k}'} - \delta f_{\boldsymbol{k}}) \quad , \tag{5.215}$$

where $v = \hbar k/m^*$ is the velocity, and where the kernel is $\vartheta_{\boldsymbol{k}\boldsymbol{k}'} = \cos^{-1}(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{k}}')$. We now expand in spherical harmonics, writing

$$\sigma(\vartheta_{\boldsymbol{k}\boldsymbol{k}'}) \equiv \sigma_{\mathrm{tot}} \sum_{L,M} \nu_L\, Y_{LM}(\hat{\boldsymbol{k}})\, Y_{LM}^*(\hat{\boldsymbol{k}}') \quad , \tag{5.216}$$

where as before

$$\sigma_{\mathrm{tot}} = 2\pi \int\limits_0^\pi d\vartheta\, \sin\vartheta\, \sigma(\vartheta) \quad , \tag{5.217}$$

which fixes $\nu_{L=0} = 1$. Expanding

$$\delta f_{\boldsymbol{k}}(t) = \sum_{L,M} A_{LM}(t)\, Y_{LM}(\hat{\boldsymbol{k}}) \quad , \tag{5.218}$$

the linearized Boltzmann equation simplifies to

$$\frac{\partial A_{LM}}{\partial t} + (1 - \nu_L)\, n_{\mathrm{imp}} v_{\mathrm{F}}\, \sigma_{\mathrm{tot}}\, A_{LM} = 0 \quad , \tag{5.219}$$

whence one obtains a hierarchy of relaxation rates,

$$\tau_L^{-1} = (1 - \nu_L)\, n_{\mathrm{imp}} v_{\mathrm{F}}\, \sigma_{\mathrm{tot}} \quad , \tag{5.220}$$

which depend only on the total angular momentum quantum number L. These rates describe the relaxation of nonuniform distributions when $\delta f_{\boldsymbol{k}}(t = 0)$ is proportional to some spherical harmonic $Y_{LM}(\boldsymbol{k})$. Note that $\tau_{L=0}^{-1} = 0$, which reflects the fact that the total particle number is a collisional invariant. The single particle lifetime is identified as

$$\tau_{\mathrm{sp}} \equiv \tau_{L\to\infty} = \left(n_{\mathrm{imp}} v_{\mathrm{F}}\, \sigma_{\mathrm{tot}}\right)^{-1} \quad , \tag{5.221}$$

corresponding to a point distortion of the uniform distribution. The transport lifetime is then $\tau_{\mathrm{tr}} = \tau_{L=1}$.

5.8.2 Screening and the transport lifetime

For a Coulomb impurity, with $U(r) = -Ze^2/r$ we have $\hat{U}(q) = -4\pi Ze^2/q^2$. Consequently,

$$\sigma_{\mathrm{F}}(\vartheta) = \left(\frac{Ze^2}{4\varepsilon_{\mathrm{F}} \sin^2 \frac{1}{2}\vartheta} \right)^2 \quad , \tag{5.222}$$

and there is a strong divergence as $\vartheta \to 0$, with $\sigma_{\mathrm{F}}(\vartheta) \propto \vartheta^{-4}$. The transport lifetime diverges logarithmically! What went wrong?

What went wrong is that we have failed to account for *screening*. Free charges will rearrange themselves so as to screen an impurity potential. At long range, the effective (screened) potential decays exponentially, rather than as $1/r$. The screened potential is of the Yukawa form, and its increase at low q is cut off on the scale of the inverse screening length λ^{-1}. There are two types of screening to consider:

- Thomas-Fermi Screening : This is the typical screening mechanism in metals. A weak local electrostatic potential $\phi(r)$ will induce a change in the local electronic density according to $\delta n(r) = e\phi(r) \, g(\varepsilon_{\mathrm{F}})$, where $g(\varepsilon_{\mathrm{F}})$ is the density of states at the Fermi level. This charge imbalance is again related to $\phi(r)$ through the Poisson equation. The result is a self-consistent equation for $\phi(r)$,

$$\begin{aligned} \nabla^2 \phi &= 4\pi e \, \delta n \\ &= 4\pi e^2 g(\varepsilon_{\mathrm{F}}) \, \phi \equiv \lambda_{\mathrm{TF}}^{-2} \, \phi \quad . \end{aligned} \tag{5.223}$$

  The Thomas-Fermi screening length is $\lambda_{\mathrm{TF}} = \left(4\pi e^2 g(\varepsilon_{\mathrm{F}}) \right)^{-1/2}$.

- Debye-Hückel Screening : This mechanism is typical of ionic solutions, although it may also be of relevance in solids with ultra-low Fermi energies. From classical statistical mechanics, the local variation in electron number density induced by a potential $\phi(r)$ is

$$\delta n(r) = n \, e^{e\phi(r)/k_{\mathrm{B}}T} - n \approx \frac{ne\phi(r)}{k_{\mathrm{B}}T} \quad , \tag{5.224}$$

  where we assume the potential is weak on the scale of $k_{\mathrm{B}}T/e$. Poisson's equation now gives us

$$\nabla^2 \phi = 4\pi e \, \delta n = \frac{4\pi n e^2}{k_{\mathrm{B}}T} \phi \equiv \lambda_{\mathrm{DH}}^{-2} \, \phi \quad . \tag{5.225}$$

A screened test charge Ze at the origin obeys

$$\nabla^2 \phi = \lambda^{-2} \, \phi - 4\pi Ze \, \delta(r) \quad , \tag{5.226}$$

the solution of which is

$$U(\boldsymbol{r}) = -e\phi(\boldsymbol{r}) = -\frac{Ze^2}{r}e^{-r/\lambda} \quad \Longrightarrow \quad \hat{U}(\boldsymbol{q}) = -\frac{4\pi Ze^2}{q^2 + \lambda^{-2}} \quad . \tag{5.227}$$

The differential scattering cross section is now

$$\sigma_{\mathrm{F}}(\vartheta) = \left(\frac{Ze^2}{4\varepsilon_{\mathrm{F}}} \cdot \frac{1}{\sin^2\frac{1}{2}\vartheta + (2k_{\mathrm{F}}\lambda)^{-2}}\right)^2 \tag{5.228}$$

and the divergence at small angle is cut off. The transport lifetime for screened Coulomb scattering is therefore given by

$$\frac{1}{\tau(\varepsilon_{\mathrm{F}})} = 2\pi n_{\mathrm{imp}} v_{\mathrm{F}} \left(\frac{Ze^2}{4\varepsilon_{\mathrm{F}}}\right)^2 \int_0^\pi d\vartheta \, \sin\vartheta \, (1 - \cos\vartheta) \left(\frac{1}{\sin^2\frac{1}{2}\vartheta + (2k_{\mathrm{F}}\lambda)^{-2}}\right)^2$$

$$= 2\pi n_{\mathrm{imp}} v_{\mathrm{F}} \left(\frac{Ze^2}{2\varepsilon_{\mathrm{F}}}\right)^2 \left\{\ln(1+\pi\zeta) - \frac{\pi\zeta}{1+\pi\zeta}\right\} \quad , \tag{5.229}$$

with $\zeta = \frac{4}{\pi}k_{\mathrm{F}}^2\lambda^2$, In the case of Thomas-Fermi screening, from $g(\varepsilon_{\mathrm{F}}) = m^*k_{\mathrm{F}}/\pi^2\hbar^2$, and we have

$$\zeta = \frac{4}{\pi}k_{\mathrm{F}}^2\lambda^2 = \frac{\hbar^2 k_{\mathrm{F}}}{m^*e^2} = k_{\mathrm{F}}a_{\mathrm{B}}^* \quad . \tag{5.230}$$

Here $a_{\mathrm{B}}^* = \epsilon_\infty \hbar^2/m^*e^2$ is the effective Bohr radius (restoring the ϵ_∞ factor). The resistivity is therefore given by

$$\rho = \frac{m^*}{ne^2\tau} = \frac{h}{e^2} Z^2 a_{\mathrm{B}}^* (n_{\mathrm{imp}}/n) F(k_{\mathrm{F}} a_{\mathrm{B}}^*) \quad , \tag{5.231}$$

where

$$F(\zeta) = \frac{1}{\zeta^3}\left\{\ln(1+\pi\zeta) - \frac{\pi\zeta}{1+\pi\zeta}\right\} \quad . \tag{5.232}$$

With $h/e^2 = 25,813\,\Omega$ and $a_{\mathrm{B}}^* \approx a_{\mathrm{B}} = 0.529\,\text{Å}$, we have

$$\rho = 1.37 \times 10^{-4}\,\Omega \cdot \text{cm} \times Z^2 (n_{\mathrm{imp}}/n) F(k_{\mathrm{F}}a_{\mathrm{B}}) \quad . \tag{5.233}$$

In Tab. 5.2, we show the observed residual resistivity per percent impurity for various ions in copper at low temperatures.

5.9   Dynamics of Holes

5.9.1   Properties of holes

Since filled bands carry no current, we have that the current density from band n is

$$\boldsymbol{j}_n(\boldsymbol{r},t) = -2e\int_{\hat{\Omega}}\frac{d^3k}{(2\pi)^3} f_n(\boldsymbol{r},\boldsymbol{k},t)\,\boldsymbol{v}_n(\boldsymbol{k}) = +2e\int_{\hat{\Omega}}\frac{d^3k}{(2\pi)^3} \bar{f}_n(\boldsymbol{r},\boldsymbol{k},t)\,\boldsymbol{v}_n(\boldsymbol{k}) \quad , \tag{5.234}$$
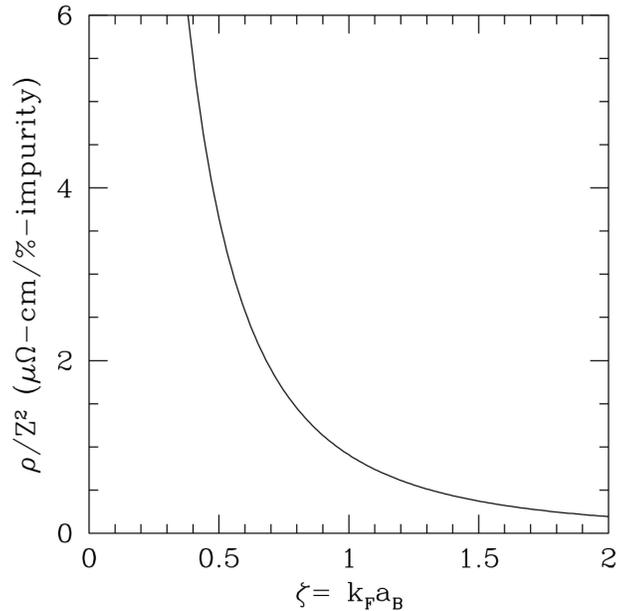
Figure 5.16: Residual resistivity per percent impurity.

where $\bar{f} \equiv 1 - f$. Thus, we can regard the current to be carried by fictitious particles of charge $+e$ with a distribution $\bar{f}(\boldsymbol{r}, \boldsymbol{k}, t)$. These fictitious particles are called *holes*.

The Four Laws of Holes

1. Under the influence of an applied electromagnetic field, the unoccupied levels of a band evolve as if they were occupied by real electrons of charge $-e$. That is, whether or not a state is occupied is irrelevant to the time evolution of that state, which is described by the semiclassical dynamics of eqs. (5.146, 5.147).

2. The current density due to a hole of wavevector $\boldsymbol{k}$ is $+e\, \boldsymbol{v}_n(\boldsymbol{k})/V$.

3. The crystal momentum of a hole of wavevector $\boldsymbol{k}$ is $\boldsymbol{P} = -\hbar\boldsymbol{k}$.

4. Any band can be described in terms of electrons or in terms of holes, but not both simultaneously. A "mixed" description is redundant at best, wrong at worst, and confusing always. However, it is often convenient to treat some bands within the electron picture and others within the hole picture.

It is instructive to consider the exercise of Fig. 5.17. The two states to be analyzed are

$$
\begin{aligned}
\big|\,\Psi_{\mathrm{A}}\,\big\rangle &= \psi^{\dagger}_{\mathrm{c},k}\,\psi_{\mathrm{v},k}\big|\,\Psi_0\,\big\rangle = e^{\dagger}_k\, h^{\dagger}_k\big|\,0\,\big\rangle \\
\big|\,\Psi_{\mathrm{B}}\,\big\rangle &= \psi^{\dagger}_{\mathrm{c},k}\,\psi_{\mathrm{v},-k}\big|\,\Psi_0\,\big\rangle = e^{\dagger}_k\, h^{\dagger}_{-k}\big|\,0\,\big\rangle \quad,
\end{aligned}
\tag{5.235}
$$

Impurity Ion	$\Delta\rho$ per % ($\mu\Omega$-cm)	Impurity Ion	$\Delta\rho$ per % ($\mu\Omega$-cm)
Be	0.64	Si	3.2
Mg	0.60	Ge	3.7
B	1.4	Sn	2.8
Al	1.2	As	6.5
In	1.2	Sb	5.4

Table 5.2: Observed residual resistivity of copper per percent impurity. (From Smith and Jensen.)

$$\left|\Psi_A\right\rangle \qquad\qquad\qquad \left|\Psi_B\right\rangle$$
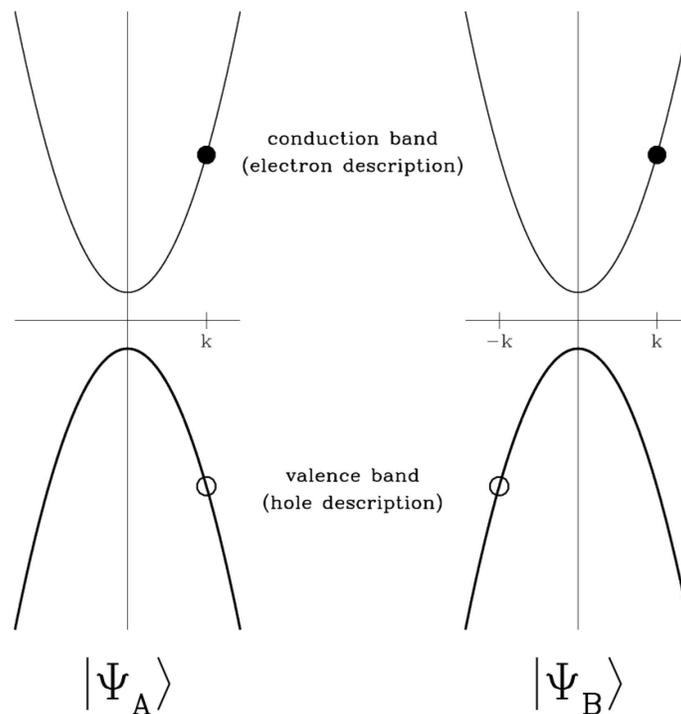
Figure 5.17: Two states: $\left|\Psi_A\right\rangle = e_k^\dagger h_k^\dagger \left|0\right\rangle$ and $\left|\Psi_B\right\rangle = e_k^\dagger h_{-k}^\dagger \left|0\right\rangle$. Which state carries more current? What is the crystal momentum of each state?

where $e_k^\dagger \equiv \psi_{c,k}^\dagger$ is the creation operator for electrons in the conduction band, and $h_k^\dagger \equiv \psi_{v,k}$ is the creation operator for holes (and hence the destruction operator for electrons) in the valence band. The state $\left|\Psi_0\right\rangle$ has all states below the top of the valence band filled, and all states above the bottom of the conduction band empty. The state $\left|0\right\rangle$ is the same state, but represented now as a *vacuum* for conduction electrons and valence *holes*. The current density in each state is given by $j = e(v_h - v_e)/V$, where V is the volume (*i.e.* length) of the system. The dispersions are taken to be $\varepsilon_{c,v}(k) = \pm\frac{1}{2}E_g \pm \hbar^2 k^2/2m^*$, where E_g is the energy gap.

- State $\big| \Psi_A \big\rangle$:
  The electron velocity is $v_e = \hbar k/m^*$; the hole velocity is $v_h = -\hbar k/m^*$. The total current density is $j = x - 2e\hbar k/m^* V$ and the total crystal momentum is $P = p_e + p_h = \hbar k - \hbar k = 0$.

- State $\big| \Psi_B \big\rangle$:
  The electron velocity is $v_e = \hbar k/m^*$; the hole velocity is $v_h = -\hbar(-k)/m^*$. The total current density is $j = 0$, and the total crystal momentum is $P = p_e + p_h = \hbar k - \hbar(-k) = 2\hbar k$.

Consider next the dynamics of electrons near the bottom of the conduction band and holes near the top of the valence band. (We'll assume a 'direct gap', *i.e.* the conduction band minimum is located directly above the valence band maximum, which we take to be at the Brillouin zone center $k = 0$, otherwise known as the Γ point.) Expanding the dispersions about their extrema to second order,

$$
\begin{aligned}
\varepsilon_v(\boldsymbol{k}) &= \varepsilon_0^v - \tfrac{1}{2}\hbar^2 (m^v)_{\alpha\beta}^{-1} \, k^\alpha \, k^\beta \\
\varepsilon_c(\boldsymbol{k}) &= \varepsilon_0^c + \tfrac{1}{2}\hbar^2 (m^c)_{\alpha\beta}^{-1} \, k^\alpha \, k^\beta \quad .
\end{aligned}
\tag{5.236}
$$

The velocity is

$$
v^\alpha(\boldsymbol{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k^\alpha} = \pm\hbar \, m_{\alpha\beta}^{-1} \, k^\beta \quad ,
\tag{5.237}
$$

where the $+$ sign is used in conjunction with m^c and the $-$ sign with m^v. We compute the acceleration $a = \ddot{r}$ via the chain rule,

$$
\begin{aligned}
a^\alpha &= \frac{\partial v^\alpha}{\partial k^\beta} \cdot \frac{dk^\beta}{dt} \\
&= \mp e \, m_{\alpha\beta}^{-1} \left[E^\beta + \frac{1}{c}\,(\boldsymbol{v} \times \boldsymbol{B})^\beta \right] \\
F^\alpha &= m_{\alpha\beta}\, a^\beta = \mp e\left[E^\beta + \frac{1}{c}\,(\boldsymbol{v} \times \boldsymbol{B})^\beta \right] \quad .
\end{aligned}
\tag{5.238}
$$

Thus, the hole wavepacket accelerates as if it has charge $+e$ but a *positive* effective mass. Note that we have above presumed a *direct band gap*, *i.e.* that the conduction band minimum lies directly above the valence band maximum, at the same value of k (typically the Γ point in the Brillouin zone). However, many materials have an *indirect band gap* in which case

$$
\begin{aligned}
\varepsilon_v(\boldsymbol{k}) &= \varepsilon_0^v - \tfrac{1}{2}\hbar^2 (m^v)_{\alpha\beta}^{-1} \, (k^\alpha - K_v^\alpha)\,(k^\beta - K_v^\beta) \\
v_v^\alpha(\boldsymbol{k}) &= -(m^v)_{\alpha\beta}^{-1}\,(k^\beta - K_v^\beta)
\end{aligned}
\tag{5.239}
$$

and

$$
\begin{aligned}
\varepsilon_c(\boldsymbol{k}) &= \varepsilon_0^c + \tfrac{1}{2}\hbar^2 (m^c)_{\alpha\beta}^{-1} \, (k^\alpha - K_c^\alpha)\,(k^\beta - K_c^\beta) \\
v_c^\alpha(\boldsymbol{k}) &= +(m^c)_{\alpha\beta}^{-1}\,(k^\beta - K_c^\beta) \quad .
\end{aligned}
\tag{5.240}
$$

5.9.2 Boltzmann equation for holes

Finally, what form does the Boltzmann equation take for holes? Starting with the Boltzmann equation for electrons,

$$\frac{\partial f}{\partial t} + \dot{\boldsymbol{r}} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \dot{\boldsymbol{k}} \cdot \frac{\partial f}{\partial \boldsymbol{k}} = \mathcal{I}_{\boldsymbol{k}}[f] \quad , \tag{5.241}$$

we recast this in terms of the hole distribution $\bar{f} = 1 - f$, and obtain

$$\frac{\partial \bar{f}}{\partial t} + \dot{\boldsymbol{r}} \cdot \frac{\partial \bar{f}}{\partial \boldsymbol{r}} + \dot{\boldsymbol{k}} \cdot \frac{\partial \bar{f}}{\partial \boldsymbol{k}} = -\mathcal{I}_{\boldsymbol{k}}\big[1 - \bar{f}\big] \quad . \tag{5.242}$$

This then is the Boltzmann equation for the hole distribution $\bar{f}$. Recall that we can expand the collision integral functional as

$$\mathcal{I}_{\boldsymbol{k}}\big[f^0 + \delta f\big] = \mathcal{L}\, \delta f + \dots \tag{5.243}$$

where $\mathcal{L}$ is a linear operator, and the higher order terms are formally of order $(\delta f)^2$. Note that the zeroth order term $\mathcal{I}_{\boldsymbol{k}}\big[f^0\big]$ vanishes due to the fact that f^0 represents a local equilibrium. Thus, after writing $\bar{f} = \bar{f}^0 + \delta\bar{f}$

$$-\mathcal{I}_{\boldsymbol{k}}\big[1 - \bar{f}\big] = -\mathcal{I}_{\boldsymbol{k}}\big[1 - \bar{f}^0 - \delta\bar{f}\big] = \mathcal{L}\, \delta\bar{f} + \dots \tag{5.244}$$

and the linearized collisionless Boltzmann equation for holes is

$$\frac{\partial \delta\bar{f}}{\partial t} - \frac{e}{\hbar c}\, \boldsymbol{v} \times \boldsymbol{B} \cdot \frac{\partial \delta\bar{f}}{\partial \boldsymbol{k}} - \boldsymbol{v} \cdot \left[e\boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T}\boldsymbol{\nabla}T\right]\frac{\partial \bar{f}^0}{\partial \varepsilon} = \mathcal{L}\, \delta\bar{f} \quad , \tag{5.245}$$

which is of precisely the same form as the electron case in Eqn. (5.177). Note that the local equilibrium distribution for holes is given by

$$\bar{f}^0(\boldsymbol{r}, \boldsymbol{k}, t) = \left\{\exp\left(\frac{\mu(\boldsymbol{r}, t) - \varepsilon(\boldsymbol{k})}{k_{\mathrm{B}}T(\boldsymbol{r}, t)}\right) + 1\right\}^{-1} \quad . \tag{5.246}$$

5.10 Magnetoresistance and Hall Effect

5.10.1 Boltzmann theory for $\rho_{\alpha\beta}(\omega, \boldsymbol{B})$

In the presence of an external magnetic field $\boldsymbol{B}$, the linearized Boltzmann equation takes the form[17]

$$\frac{\partial \delta f}{\partial t} - e\, \boldsymbol{v} \cdot \boldsymbol{\mathcal{E}}\, \frac{\partial f^0}{\partial \varepsilon} - \frac{e}{\hbar c}\, \boldsymbol{v} \times \boldsymbol{B} \cdot \frac{\partial \delta f}{\partial \boldsymbol{k}} = \mathcal{L}\, \delta f \quad . \tag{5.247}$$

---

[17]For holes, we replace $f^0 \to \bar{f}^0$ and $\delta f \to \delta\bar{f}$.

We will obtain an explicit solution within the relaxation time approximation $\mathcal{L}\,\delta f = -\delta f/\tau$ and the effective mass approximation,

$$\varepsilon(\boldsymbol{k}) = \pm\tfrac{1}{2}\,\hbar^2\,m_{\alpha\beta}^{-1}\,k^\alpha\,k^\beta \quad \Longrightarrow \quad v^\alpha = \pm\,\hbar\,m_{\alpha\beta}^{-1}\,k^\beta \quad, \tag{5.248}$$

where the top sign applies for electrons and the bottom sign for holes. With $\boldsymbol{\mathcal{E}}(t) = \boldsymbol{\mathcal{E}}\,e^{-i\omega t}$, we try a solution of the form

$$\delta f(\boldsymbol{k}, t) = \boldsymbol{k}\cdot\boldsymbol{A}(\varepsilon)\,e^{-i\omega t} \equiv \delta f(\boldsymbol{k})\,e^{-i\omega t} \tag{5.249}$$

where $\boldsymbol{A}(\varepsilon)$ is a vector function of ε to be determined. Each component A_α is a function of $\boldsymbol{k}$ through its dependence on $\varepsilon = \varepsilon(\boldsymbol{k})$. We now have

$$(\tau^{-1} - i\omega)\,k^\mu A^\mu - \frac{e}{\hbar c}\,\epsilon_{\alpha\beta\gamma}\,v^\alpha\,B^\beta\,\frac{\partial}{\partial k^\gamma}\,(k^\mu A^\mu) = e\,\boldsymbol{v}\cdot\boldsymbol{\mathcal{E}}\,\frac{\partial f^0}{\partial\varepsilon} \quad, \tag{5.250}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor. Note that

$$\begin{aligned}
\epsilon_{\alpha\beta\gamma}\,v^\alpha B^\beta\,\frac{\partial}{\partial k^\gamma}\,(k^\mu A^\mu) &= \epsilon_{\alpha\beta\gamma}\,v^\alpha B^\beta\left(A^\gamma + k^\mu\,\frac{\partial A^\mu}{\partial k^\gamma}\right) \\
&= \epsilon_{\alpha\beta\gamma}\,v^\alpha B^\beta\left(A^\gamma + \hbar\,k^\mu\,v^\gamma\,\frac{\partial A^\mu}{\partial\varepsilon}\right) = \epsilon_{\alpha\beta\gamma}\,v^\alpha B^\beta A^\gamma \quad,
\end{aligned} \tag{5.251}$$

owing to the asymmetry of the Levi-Civita tensor: $\epsilon_{\alpha\beta\gamma}\,v^\alpha\,v^\gamma = 0$. We now invoke the identity $\hbar\,k^\alpha = \pm m_{\alpha\beta}\,v^\beta$ and match the coefficients of v^α in each term of the Boltzmann equation. This yields,

$$\left[(\tau^{-1} - i\omega)\,m_{\alpha\beta} \pm \frac{e}{c}\,\epsilon_{\alpha\beta\gamma}\,B^\gamma\right]A^\beta = \pm\,\hbar\,e\,\frac{\partial f^0}{\partial\varepsilon}\,\mathcal{E}^\alpha \quad. \tag{5.252}$$

Defining

$$\Gamma_{\alpha\beta} \equiv (\tau^{-1} - i\omega)\,m_{\alpha\beta} \pm \frac{e}{c}\,\epsilon_{\alpha\beta\gamma}\,B^\gamma \quad, \tag{5.253}$$

we obtain the solution

$$\delta f = \pm e\,v^\alpha\,m_{\alpha\beta}\,\Gamma_{\beta\gamma}^{-1}\,\mathcal{E}^\gamma\,\frac{\partial f^0}{\partial\varepsilon} \quad. \tag{5.254}$$

From this, we can compute the current density and the conductivity tensor. The electrical current density is

$$j^\alpha = \mp 2e\int_{\hat{\Omega}}\frac{d^3k}{(2\pi)^3}\,v^\alpha\,\delta f = +2e^2\,\mathcal{E}^\gamma\int_{\hat{\Omega}}\frac{d^3k}{(2\pi)^3}\,v^\alpha\,v^\nu\,m_{\nu\beta}\,\Gamma_{\beta\gamma}^{-1}(\varepsilon)\left(-\frac{\partial f^0}{\partial\varepsilon}\right) \quad, \tag{5.255}$$

where we allow for an energy-dependent relaxation time $\tau(\varepsilon)$. Note that $\Gamma_{\alpha\beta}(\varepsilon)$ is energy-dependent due to its dependence on τ. The conductivity is then

$$
\sigma_{\alpha\beta}(\omega, \boldsymbol{B}) = 2\hbar^2 e^2\, m_{\alpha\mu}^{-1} \left\{ \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\; k^\mu\, k^\nu \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \Gamma_{\nu\beta}^{-1}(\varepsilon) \right\}
$$

$$
= \tfrac{2}{3}\, e^2 \int\limits_{-\infty}^{\infty} d\varepsilon\; \varepsilon\; g(\varepsilon)\; \Gamma_{\alpha\beta}^{-1}(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \quad ,
$$

(5.256)

where the chemical potential is measured with respect to the band edge. Thus,

$$
\sigma_{\alpha\beta}(\omega, \boldsymbol{B}) = n e^2\, \langle \Gamma_{\alpha\beta}^{-1} \rangle \quad ,
$$

(5.257)

where averages denoted by angular brackets are defined by

$$
\langle \Gamma_{\alpha\beta}^{-1} \rangle \equiv \frac{\displaystyle\int\limits_{-\infty}^{\infty} d\varepsilon\; \varepsilon\; g(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \Gamma_{\alpha\beta}^{-1}(\varepsilon)}{\displaystyle\int\limits_{-\infty}^{\infty} d\varepsilon\; \varepsilon\; g(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right)} \quad .
$$

(5.258)

The quantity n is the carrier density,

$$
n = \int\limits_{-\infty}^{\infty} d\varepsilon\; g(\varepsilon) \times
\begin{cases}
f^0(\varepsilon) & \text{(electrons)} \\
\left[1 - f^0(\varepsilon) \right] & \text{(holes)}
\end{cases}
$$

(5.259)

EXERCISE: Verify Eqn. (5.256).

For the sake of simplicity, let us assume an energy-independent scattering time, or that the temperature is sufficiently low that only $\tau(\varepsilon_{\mathrm{F}})$ matters, and we denote this scattering time simply by τ. Putting this all together, then, we obtain

$$
\sigma_{\alpha\beta} = n e^2\, \Gamma_{\alpha\beta}^{-1}
$$

$$
\rho_{\alpha\beta} = \frac{1}{n e^2} \Gamma_{\alpha\beta} = \frac{1}{n e^2} \left[(\tau^{-1} - i\omega) m_{\alpha\beta} \pm \frac{e}{c}\, \epsilon_{\alpha\beta\gamma}\, B^\gamma \right] \quad .
$$

(5.260)

We thereby recover the results of §5.5.2.

5.10.2 Hall effect in high fields

In the high field limit, one may neglect the collision integral entirely, and write (at $\omega = 0$)

$$
-e\, \boldsymbol{v} \cdot \boldsymbol{\mathcal{E}}\, \frac{\partial f^0}{\partial \varepsilon} - \frac{e}{\hbar c}\, \boldsymbol{v} \times \boldsymbol{B} \cdot \frac{\partial \delta f}{d\boldsymbol{k}} = 0 \quad .
$$

(5.261)

Figure 5.18: Energy bands in aluminum.

We'll consider the case of electrons, and take $\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{y}$ and $\boldsymbol{B} = B\hat{z}$, in which case the solution is

$$\delta f = \frac{\hbar c \mathcal{E}}{B} k_x \frac{\partial f^0}{\partial \varepsilon} \quad . \tag{5.262}$$

Note that k_x is not a smooth single-valued function over the Brillouin-zone due to Bloch periodicity. This treatment, then, will make sense only if the derivative $\partial f^0 / \partial \varepsilon$ confines $\boldsymbol{k}$ to a closed orbit within the first Brillouin zone. In this case, we have

$$j_x = 2ec \frac{\mathcal{E}}{B} \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial \varepsilon}{\partial k_x} \frac{\partial f^0}{\partial \varepsilon} = 2ec \frac{\mathcal{E}}{B} \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial f^0}{\partial k_x} \quad . \tag{5.263}$$

Now we may integrate by parts, if we assume that f^0 vanishes on the boundary of the Brillouin zone. We obtain

$$j_x = -\frac{2ec\mathcal{E}}{B} \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} f^0 = -\frac{nec}{B} \mathcal{E} \quad . \tag{5.264}$$

We conclude that

$$\sigma_{xy} = -\sigma_{yx} = -\frac{nec}{B} \quad , \tag{5.265}$$

independent of the details of the band structure. "Open orbits" – trajectories along Fermi surfaces which cross Brillouin zone boundaries and return in another zone – pose a subtler problem, and generally lead to a finite, *non-saturating* magnetoresistance. For holes, we have $\bar{f}^0 = 1 - f^0$ and

$$j_x = -\frac{2ec\mathcal{E}}{B} \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} k_x \frac{\partial \bar{f}^0}{\partial k_x} = +\frac{nec}{B} \mathcal{E} \tag{5.266}$$
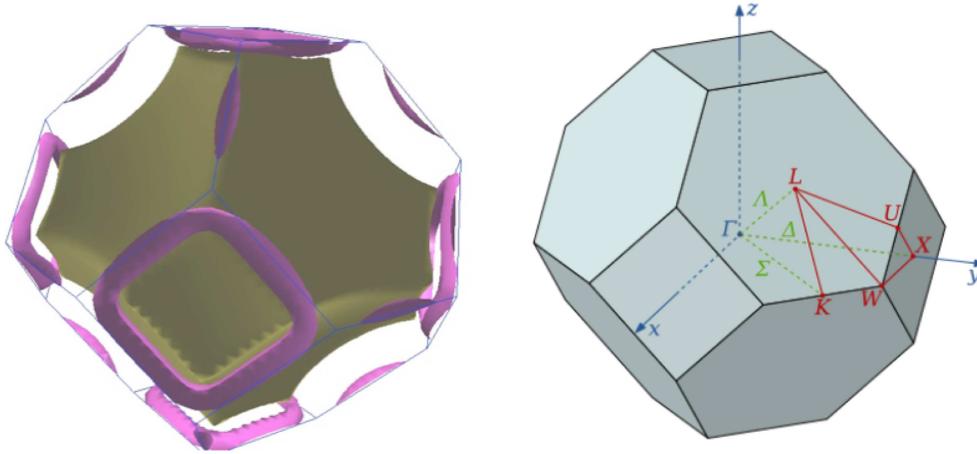
Figure 5.19: Fermi surfaces for electron (pink) and hole (gold) bands in Aluminum.

and $\sigma_{xy} = +nec/B$, where n is the hole density.

We define the *Hall coefficient* $R_{\mathrm{H}} = -\rho_{xy}/B$ and the *Hall number*

$$z_{\mathrm{H}} \equiv -\frac{1}{n_{\mathrm{ion}} ec R_{\mathrm{H}}} \quad , \tag{5.267}$$

where n_{ion} is the ion density. For high fields, the off-diagonal elements of both $\rho_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are negligible, and $\rho_{xy} \approx -1/\sigma_{xy}$. Hence $R_{\mathrm{H}} \approx \mp 1/nec$, and $z_{\mathrm{H}} \approx \pm n/n_{\mathrm{ion}}$. The high field Hall coefficient is used to determine both the carrier density as well as the sign of the charge carriers; z_{H} is a measure of valency.

In Al, the high field Hall coefficient saturates at $z_{\mathrm{H}} = -1$. Why is z_{H} negative? As it turns out, aluminum has both electron and hole bands. Its valence is 3; two electrons go into a filled band, leaving one valence electron to split between the electron and hole bands. Thus $n = 3n_{\mathrm{ion}}$ The Hall conductivity is $\sigma_{xy} = (n_{\mathrm{h}} - n_{\mathrm{e}})\, ec/B$. The difference $n_{\mathrm{h}} - n_{\mathrm{e}}$ is determined by the following argument. The *electron* density in the hole band is $n'_{\mathrm{e}} = 2n_{ion} - n_{\mathrm{h}}$, *i.e.* the total density of levels in the band (two states per unit cell) minus the number of empty levels in which there are holes. Thus, $n_{\mathrm{h}} - n_{\mathrm{e}} = 2n_{\mathrm{ion}} - (n_{\mathrm{e}} + n'_{\mathrm{e}}) = n_{\mathrm{ion}}$, where we've invoked $n_{\mathrm{e}} + n'_{\mathrm{e}} = n_{\mathrm{ion}}$, since precisely one electron from each ion is shared between the two partially filled bands. Thus, $\sigma_{xy} = n_{\mathrm{ion}} ec/B = nec/3B$ and $z_{\mathrm{H}} = -1$. At lower fields, $z_{\mathrm{H}} = +3$ is observed, which is what one would expect from the free electron model. Interband scattering, which is suppressed at high fields, leads to this result.

5.11 Thermal Transport

5.11.1 Boltzmann theory

Consider a small region of solid with a fixed volume ΔV. The first law of thermodynamics applied to this region gives $T\Delta S = \Delta E - \mu \Delta N$. Dividing by ΔV gives

$$dq \equiv T\,ds = d\varepsilon - \mu\,dn \quad, \tag{5.268}$$

where s is the entropy density, ε is energy density, and n the number density. This can be directly recast as the following relation among current densities:

$$\boldsymbol{j}_q = T\boldsymbol{j}_s = \boldsymbol{j}_\varepsilon - \mu\,\boldsymbol{j}_n \quad, \tag{5.269}$$

where $\boldsymbol{j}_n = \boldsymbol{j}/(-e)$ is the number current density, $\boldsymbol{j}_\varepsilon$ is the energy current density,

$$\boldsymbol{j}_\varepsilon = 2\int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\ \varepsilon\,\boldsymbol{v}\,\delta f \quad, \tag{5.270}$$

and $\boldsymbol{j}_s$ is the entropy current density. Accordingly, the thermal (heat) current density $\boldsymbol{j}_q$ is defined as

$$\boldsymbol{j}_q \equiv T\boldsymbol{j}_s = \boldsymbol{j}_\varepsilon + \frac{\mu}{e}\,\boldsymbol{j} = 2\int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\ (\varepsilon - \mu)\,\boldsymbol{v}\,\delta f \quad. \tag{5.271}$$

In the presence of a time-independent temperature gradient and electric field, linearized Boltzmann equation in the relaxation time approximation has the solution

$$\delta f = -\tau(\varepsilon)\,\boldsymbol{v}\cdot\left(e\boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T}\,\boldsymbol{\nabla}T\right)\left(-\frac{\partial f^0}{\partial\varepsilon}\right) \quad. \tag{5.272}$$

We now consider both the electrical current $\boldsymbol{j}$ as well as the thermal current density $\boldsymbol{j}_q$. One readily obtains

$$\boldsymbol{j} = -2e\int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\ \boldsymbol{v}\,\delta f \equiv L_{11}\,\boldsymbol{\mathcal{E}} - L_{12}\,\boldsymbol{\nabla}T$$

$$\boldsymbol{j}_q = 2\int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\ (\varepsilon - \mu)\,\boldsymbol{v}\,\delta f \equiv L_{21}\,\boldsymbol{\mathcal{E}} - L_{22}\,\boldsymbol{\nabla}T \tag{5.273}$$

where the *transport coefficients* L^{11} *etc.* are matrices:

$$L_{11}^{\alpha\beta} = \frac{e^2}{4\pi^3\hbar} \int\limits_{-\infty}^{\infty} d\varepsilon\, \tau(\varepsilon) \left(-\frac{\partial f^0}{\partial\varepsilon}\right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|v|}$$

$$L_{21}^{\alpha\beta} = T L_{12}^{\alpha\beta} = -\frac{e}{4\pi^3\hbar} \int\limits_{-\infty}^{\infty} d\varepsilon\, \tau(\varepsilon)\,(\varepsilon-\mu) \left(-\frac{\partial f^0}{\partial\varepsilon}\right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|v|} \qquad (5.274)$$

$$L_{22}^{\alpha\beta} = \frac{1}{4\pi^3\hbar\, T} \int\limits_{-\infty}^{\infty} d\varepsilon\, \tau(\varepsilon)\,(\varepsilon-\mu)^2 \left(-\frac{\partial f^0}{\partial\varepsilon}\right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|v|} \quad .$$

If we define the hierarchy of integral expressions

$$\mathcal{J}_n^{\alpha\beta} \equiv \frac{1}{4\pi^3\hbar} \int\limits_{-\infty}^{\infty} d\varepsilon\, \tau(\varepsilon)\,(\varepsilon-\mu)^n \left(-\frac{\partial f^0}{\partial\varepsilon}\right) \int dS_\varepsilon \frac{v^\alpha v^\beta}{|v|} \qquad (5.275)$$

then we may write

$$L_{11}^{\alpha\beta} = e^2\, \mathcal{J}_0^{\alpha\beta} \qquad\qquad L_{21}^{\alpha\beta} = T L_{12}^{\alpha\beta} = -e\, \mathcal{J}_1^{\alpha\beta} \qquad\qquad L_{22}^{\alpha\beta} = \frac{1}{T}\, \mathcal{J}_2^{\alpha\beta} \quad . \qquad (5.276)$$

The linear relations in Eqn. (5.273) may be recast in the following form:

$$\boldsymbol{\mathcal{E}} = \rho\, \boldsymbol{j} + Q\, \boldsymbol{\nabla} T$$
$$\boldsymbol{j}_q = \Pi\, \boldsymbol{j} - \kappa\, \boldsymbol{\nabla} T \quad , \qquad\qquad (5.277)$$

where the matrices ρ, Q, Π, and κ are given by

$$\rho = L_{11}^{-1} \qquad\qquad\qquad\qquad Q = L_{11}^{-1}\, L_{12} \qquad\qquad (5.278)$$
$$\Pi = L_{21}\, L_{11}^{-1} \qquad\qquad\qquad \kappa = L_{22} - L_{21}\, L_{11}^{-1}\, L_{12} \quad ,$$

or, in terms of the $\mathcal{J}_n$,

$$\rho = \frac{1}{e^2}\, \mathcal{J}_0^{-1} \qquad\qquad\qquad Q = -\frac{1}{e\, T}\, \mathcal{J}_0^{-1}\, \mathcal{J}_1 \qquad\qquad (5.279)$$
$$\Pi = -\frac{1}{e}\, \mathcal{J}_1\, \mathcal{J}_0^{-1} \qquad\qquad \kappa = \frac{1}{T} \left(\mathcal{J}_2 - \mathcal{J}_1\, \mathcal{J}_0^{-1}\, \mathcal{J}_1 \right) \quad ,$$

The names and physical interpretation of these four transport coefficients is as follows:

- ρ is the *resistivity*: $\boldsymbol{\mathcal{E}} = \rho\boldsymbol{j}$ under the condition of zero thermal gradient (*i.e.* $\boldsymbol{\nabla} T = 0$).
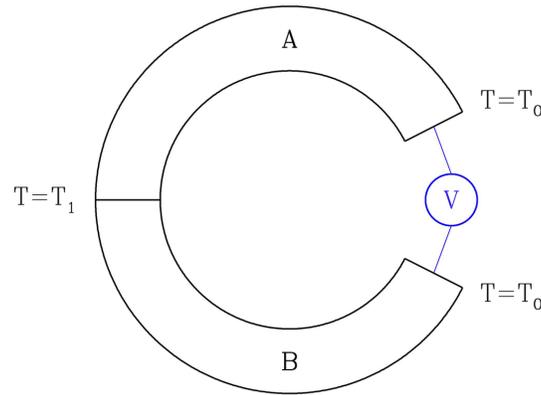
$$V = (Q_B - Q_A)(T_1 - T_0)$$

Figure 5.20: A thermocouple is a junction formed of two dissimilar metals. With no electrical current passing, an electric field is generated in the presence of a temperature gradient, resulting in a voltage $V = V_A - V_B$.

- Q is the *thermopower*: $\boldsymbol{\mathcal{E}} = Q\,\boldsymbol{\nabla}T$ under the condition of zero electrical current (*i.e. $\boldsymbol{j} = 0$*). Q is also called the *Seebeck coefficient*.

- $\sqcap$ is the *Peltier coefficient*: $\boldsymbol{j}_q = \sqcap\boldsymbol{j}$ when $\boldsymbol{\nabla}T = 0$.

- κ is the *thermal conductivity*: $\boldsymbol{j}_q = -\kappa\,\boldsymbol{\nabla}T$ when $\boldsymbol{j} = 0$.

One practical way to measure the thermopower is to form a junction between two dissimilar metals, A and B. The junction is held at temperature T_1 and the other ends of the metals are held at temperature T_0. One then measures a voltage difference between the free ends of the metals – this is known as the Seebeck effect. Integrating the electric field from the free end of A to the free end of B gives

$$V_A - V_B = -\int_A^B \boldsymbol{\mathcal{E}} \cdot d\boldsymbol{l} = (Q_B - Q_A)(T_1 - T_0) \quad . \tag{5.280}$$

What one measures here is really the difference in thermopowers of the two metals. For an absolute measurement of Q_A, replace B by a superconductor ($Q = 0$ for a superconductor). A device which converts a temperature gradient into an emf is known as a *thermocouple*.

The Peltier effect has practical applications in refrigeration technology. Suppose an electrical current I is passed through a junction between two dissimilar metals, A and B. Due to the difference in Peltier coefficients, there will be a net heat current into the junction of $W = (\sqcap_A - \sqcap_B)\,I$. Note that this is proportional to I, rather than the familiar I^2 result from Joule heating.
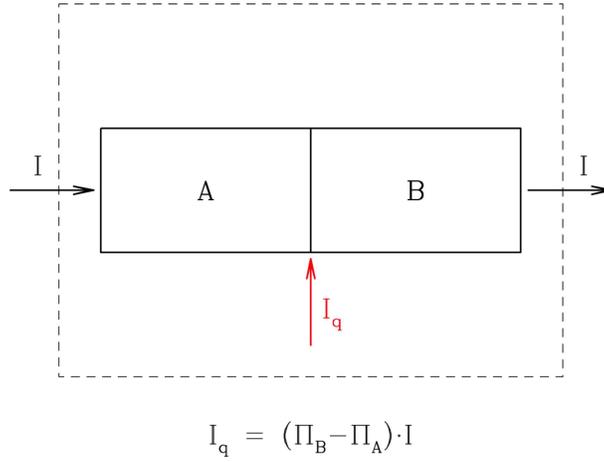
$$I_q \;=\; (\Pi_B - \Pi_A) \cdot I$$

Figure 5.21: A sketch of a Peltier effect refrigerator. An electrical current I is passed through a junction between two dissimilar metals. If the dotted line represents the boundary of a thermally well-insulated body, then the body cools when $\Pi_B > \Pi_A$, in order to maintain a heat current balance at the junction.

The sign of W depends on the direction of the current. If a second junction is added, to make an ABA configuration, then heat absorbed at the first junction will be liberated at the second[18].

5.11.2   The heat equation

We begin with the continuity equations for charge density ρ and energy density ε:

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j} = 0 \qquad , \qquad \frac{\partial \varepsilon}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_\varepsilon = \boldsymbol{j} \cdot \boldsymbol{E} \quad , \tag{5.281}$$

where $\boldsymbol{E}$ is the electric field[19]. Now we invoke local thermodynamic equilibrium and write

$$\frac{\partial \varepsilon}{\partial t} = \frac{\partial \varepsilon}{\partial n}\frac{\partial n}{\partial t} + \frac{\partial \varepsilon}{\partial T}\frac{\partial T}{\partial t} = -\frac{\mu}{e}\frac{\partial \rho}{\partial t} + c_V\,\frac{\partial T}{\partial t} \quad , \tag{5.282}$$

where n is the electron *number density* ($n = -\rho/e$) and c_V is the specific heat. We may now write

$$
\begin{aligned}
c_V\,\frac{\partial T}{\partial t} &= \frac{\partial \varepsilon}{\partial t} + \frac{\mu}{e}\frac{\partial \rho}{\partial t} \\
&= \boldsymbol{j} \cdot \boldsymbol{E} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_\varepsilon - \frac{\mu}{e}\boldsymbol{\nabla} \cdot \boldsymbol{j} = \boldsymbol{j} \cdot \boldsymbol{\mathcal{E}} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_q \quad .
\end{aligned}
\tag{5.283}
$$

---

[18] To create a refrigerator, stick the cold junction inside a thermally insulated box and the hot junction outside the box.

[19] Note that it is $\boldsymbol{E} \cdot \boldsymbol{j}$ and *not* $\boldsymbol{\mathcal{E}} \cdot \boldsymbol{j}$ which is the source term in the energy continuity equation.

Invoking $j_q = \sqcap j - \kappa \, \nabla T$, we see that if there is no electrical current ($j = 0$), we obtain the *heat equation*

$$c_V \frac{\partial T}{\partial t} = \kappa_{\alpha\beta} \frac{\partial^2 T}{\partial x^\alpha \, \partial x^\beta} \quad . \tag{5.284}$$

This results in a time scale τ_T for temperature diffusion $\tau_T = \mathcal{C} L^2 c_V / \kappa$, where L is a typical length scale and $\mathcal{C}$ is a numerical constant. For a cube of size L subjected to a sudden external temperature change, L is the side length and $\mathcal{C} = 1/3\pi^2$ (solve by separation of variables).

5.11.3 Calculation of transport coefficients

We will henceforth assume that sufficient crystalline symmetry exists (*e.g.* cubic symmetry) to render all the transport coefficients multiples of the identity matrix. Under such conditions, we may write $\mathcal{J}_n^{\alpha\beta} = \mathcal{J}_n \, \delta_{\alpha\beta}$ with

$$\mathcal{J}_n = \frac{1}{12\pi^3\hbar} \int\limits_{-\infty}^{\infty} d\varepsilon \, \tau(\varepsilon) \, (\varepsilon - \mu)^n \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \int dS_\varepsilon \, |v| \quad . \tag{5.285}$$

The low-temperature behavior is extracted using the Sommerfeld expansion (see §5.3.2),

$$\mathcal{I} \equiv \int\limits_{-\infty}^{\infty} d\varepsilon \, H(\varepsilon) \left(-\frac{\partial f^0}{\partial \varepsilon} \right) = \pi\mathcal{D} \csc(\pi\mathcal{D}) \, H(\varepsilon) \Big|_{\varepsilon=\mu} = H(\mu) + \frac{\pi^2}{6} (k_{\mathrm{B}}T)^2 \, H''(\mu) + \dots \tag{5.286}$$

where $\mathcal{D} \equiv k_{\mathrm{B}} T \frac{\partial}{\partial \varepsilon}$ is a dimensionless differential operator.[20]

Let us now perform some explicit calculations in the case of a parabolic band with an energy-independent scattering time τ. In this case, one readily finds

$$\mathcal{J}_n = \frac{\sigma_0}{e^2} \, \varepsilon_{\mathrm{F}}^{-3/2} \, \pi\mathcal{D} \csc \pi\mathcal{D} \, \varepsilon^{3/2} \, (\varepsilon - \mu)^n \Big|_{\varepsilon=\mu} \quad , \tag{5.287}$$

where $\sigma_0 = ne^2\tau/m^*$. Note that

$$n = \frac{1}{3\pi^2} \left(\frac{2m^*\varepsilon_{\mathrm{F}}}{\hbar^2} \right)^{3/2} \tag{5.288}$$

and that ε_{F} and μ are related by

$$\varepsilon_{\mathrm{F}}^{3/2} = \pi\mathcal{D} \csc \pi\mathcal{D} \, \varepsilon^{3/2} \Big|_{\varepsilon=\mu} \quad . \tag{5.289}$$

---

[20]Remember that physically the fixed quantities are temperature and total carrier number density (or charge density, in the case of electron and hole bands), and *not* temperature and chemical potential. An equation of state relating n, μ, and T is then inverted to obtain $\mu(n, T)$, so that all results ultimately may be expressed in terms of n and T.
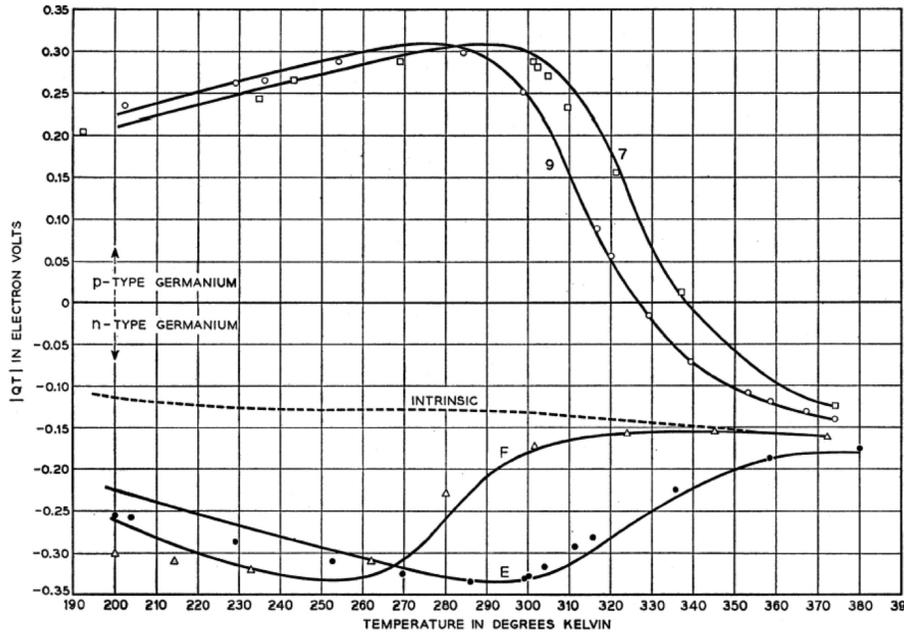
Figure 5.22: QT product for p-type and n-type Ge, from T. H. Geballe and J. W. Hull, *Phys. Rev.* **94**, 1134 (1954). Samples 7, 9, E, and F are distinguished by different doping properties, or by their resistivities at $T = 300\,\mathrm{K}$: $21.5\,\Omega$-cm (7), $34.5\,\Omega$-cm (9), $18.5\,\Omega$-cm (E), and $46.0\,\Omega$-cm (F).

Thus,

$$\mathcal{J}_0 = \frac{\sigma_0}{e^2} \qquad , \qquad \mathcal{J}_1 = \frac{\sigma_0}{e^2}\frac{\pi^2}{2}\frac{(k_{\mathrm{B}}T)^2}{\varepsilon_{\mathrm{F}}} + \dots \qquad , \qquad \mathcal{J}_2 = \frac{\sigma_0}{e^2}\frac{\pi^2}{3}(k_{\mathrm{B}}T)^2 + \dots \quad , \qquad (5.290)$$

from which we obtain the low-T results $\rho = \sigma_0^{-1}$,

$$Q = -\frac{\pi^2}{2}\frac{k_{\mathrm{B}}^2 T}{e\,\varepsilon_{\mathrm{F}}} \qquad , \qquad \kappa = \frac{\pi^2}{3}\frac{n\tau}{m^*}k_{\mathrm{B}}^2 T \quad , \qquad (5.291)$$

and of course $\sqcap = TQ$. The predicted universal ratio

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}(k_{\mathrm{B}}/e)^2 = 2.45 \times 10^{-8}\,\mathrm{V}^2\,\mathrm{K}^{-2} \quad , \qquad (5.292)$$

is known as the *Wiedemann-Franz law*. Note also that our result for the thermopower is unambiguously negative. In actuality, several nearly free electron metals have positive low-temperature thermopowers (Cs and Li, for example). What went wrong? We have neglected electron-phonon scattering!

5.11.4 Onsager relations

Transport phenomena are described in general by a set of linear relations,

$$J_i = L_{ik} F_k \quad , \tag{5.293}$$

where the $\{F_k\}$ are *generalized forces* and the $\{J_i\}$ are *generalized currents*. Moreover, to each force F_i corresponds a unique conjugate current J_i, such that the rate of internal entropy production is

$$\dot{S} = \sum_i F_i J_i \quad \Longrightarrow \quad F_i = \frac{\partial \dot{S}}{\partial J_i} \quad . \tag{5.294}$$

The Onsager relations (also known as *Onsager reciprocity*) states that

$$L_{ik}(\boldsymbol{B}) = \eta_i \, \eta_k \, L_{ki}(-\boldsymbol{B}) \quad , \tag{5.295}$$

where η_i describes the parity of J_i under time reversal:

$$\mathcal{T} J_i = \eta_i \, J_i \quad . \tag{5.296}$$

We shall not prove the Onsager relations.

The Onsager relations have some remarkable consequences. For example, they require, for $\boldsymbol{B} = 0$, that the thermal conductivity tensor κ_{ij} of any crystal must be symmetric, independent of the crystal structure. In general,this result does not follow from considerations of crystalline symmetry. It also requires that for every 'off-diagonal' transport phenomenon, *e.g.* the Seebeck effect, there exists a distinct corresponding phenomenon, *e.g.* the Peltier effect.

For the transport coefficients studied, Onsager reciprocity means that in the presence of an external magnetic field,

$$\begin{aligned}
\rho_{\alpha\beta}(\boldsymbol{B}) &= \rho_{\beta\alpha}(-\boldsymbol{B}) \\
\kappa_{\alpha\beta}(\boldsymbol{B}) &= \kappa_{\beta\alpha}(-\boldsymbol{B}) \\
\Pi_{\alpha\beta}(\boldsymbol{B}) &= T \, Q_{\beta\alpha}(-\boldsymbol{B}) \quad .
\end{aligned} \tag{5.297}$$

Let's consider an isotropic system in a weak magnetic field, and expand the transport coefficients to first order in $\boldsymbol{B}$:

$$\begin{aligned}
\rho_{\alpha\beta}(\boldsymbol{B}) &= \rho \, \delta_{\alpha\beta} + \nu \, \epsilon_{\alpha\beta\gamma} \, B^\gamma \\
\kappa_{\alpha\beta}(\boldsymbol{B}) &= \kappa \, \delta_{\alpha\beta} + \varpi \, \epsilon_{\alpha\beta\gamma} \, B^\gamma \\
Q_{\alpha\beta}(\boldsymbol{B}) &= Q \, \delta_{\alpha\beta} + \zeta \, \epsilon_{\alpha\beta\gamma} \, B^\gamma \\
\Pi_{\alpha\beta}(\boldsymbol{B}) &= \Pi \, \delta_{\alpha\beta} + \theta \, \epsilon_{\alpha\beta\gamma} \, B^\gamma \quad .
\end{aligned} \tag{5.298}$$

Onsager reciprocity requires $\sqcap = T\,Q$ and $\theta = T\,\zeta$. We can now write

$$\boldsymbol{\mathcal{E}} = \rho\,\boldsymbol{j} + \nu\,\boldsymbol{j} \times \boldsymbol{B} + Q\,\boldsymbol{\nabla}T + \zeta\,\boldsymbol{\nabla}T \times \boldsymbol{B}$$
$$\boldsymbol{j}_q = \sqcap\,\boldsymbol{j} + \theta\,\boldsymbol{j} \times \boldsymbol{B} - \kappa\,\boldsymbol{\nabla}T - \varpi\,\boldsymbol{\nabla}T \times \boldsymbol{B} \quad . \tag{5.299}$$

There are several new phenomena lurking!

- **Hall Effect** ($\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = j_y = 0$)
  An electrical current $\boldsymbol{j} = j_x\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an electric field $\boldsymbol{\mathcal{E}}$. The Hall coefficient is $R_{\mathrm{H}} = \mathcal{E}_y/j_x\,B_z = -\nu$.

- **Ettingshausen Effect** ($\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$)
  An electrical current $\boldsymbol{j} = j_x\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield a temperature gradient $\frac{\partial T}{\partial y}$. The Ettingshausen coefficient is $P = \frac{\partial T}{\partial y}\big/j_x\,B_z = -\theta/\kappa$.

- **Nernst Effect** ($j_x = j_y = \frac{\partial T}{\partial y} = 0$)
  A temperature gradient $\boldsymbol{\nabla}T = \frac{\partial T}{\partial x}\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an electric field $\boldsymbol{\mathcal{E}}$. The Nernst coefficient is $\Lambda = \mathcal{E}_y\big/\frac{\partial T}{\partial x}\,B_z = -\zeta$.

- **Righi-Leduc Effect** ($j_x = j_y = \mathcal{E}_y = 0$)
  A temperature gradient $\boldsymbol{\nabla}T = \frac{\partial T}{\partial x}\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an orthogonal temperature gradient $\frac{\partial T}{\partial y}$. The Righi-Leduc coefficient is $\mathcal{L} = \frac{\partial T}{\partial y}\big/\frac{\partial T}{\partial x}\,B_z = \zeta/Q$.

5.12 Electron-Phonon Scattering

5.12.1 Introductory remarks

We begin our discussion by recalling some elementary facts about phonons in solids:

- In a crystal with r atoms per unit cell, there are $3(r-1)$ optical modes and 3 acoustic modes, the latter guaranteed by the breaking of the three generators of space translations. We write the phonon dispersion as $\omega = \omega_\lambda(\boldsymbol{q})$, where $\lambda \in \{1, \ldots, 3r\}$ labels the phonon branch, and $\boldsymbol{q} \in \widehat{\Omega}$. If j labels an acoustic mode, $\omega_j(\boldsymbol{q}) = c_j(\hat{\boldsymbol{q}})\,q$ as $\boldsymbol{q} \to 0$.

- Phonons are bosonic particles with zero chemical potential. The equilibrium phonon distribution is

$$n_{\boldsymbol{q}\lambda}^0 = \frac{1}{\exp(\hbar\omega_\lambda(\boldsymbol{q})/k_{\mathrm{B}}T) - 1} \quad . \tag{5.300}$$

- The maximum phonon frequency is roughly given by the Debye frequency ω_{D}. The Debye temperature $\Theta_{\mathrm{D}} = \hbar\omega_{\mathrm{D}} \sim 100\,\mathrm{K} - 1000\,\mathrm{K}$ in most solids.

At high temperatures, equipartition gives $\langle (\delta \boldsymbol{R}_i)^2 \rangle \propto k_{\text{B}} T$, hence the effective scattering cross-section σ_{tot} increases as T, and $\tau \gtrsim 1/n_{\text{ion}} v_{\text{F}} \sigma_{\text{tot}} \propto T^{-1}$. From $\rho = m^* / n e^2 \tau$, then, we deduce that the high temperature resistivity should be linear in temperature due to phonon scattering: $\rho(T) \propto T$. Of course, when the mean free path $\ell = v_{\text{F}} \tau$ becomes as small as the Fermi wavelength λ_{F}, the entire notion of coherent quasiparticle transport becomes problematic, and rather than continuing to grow we expect that the resistivity should saturate: $\rho(T \to \infty) \approx h/k_{\text{F}} e^2$, known as the *Ioffe-Regel limit*. For $k_{\text{F}} = 10^8 \, \text{cm}^{-1}$, this takes the value $260 \, \mu\Omega \, \text{cm}$.

5.12.2 Electron-phonon interaction

Let $\boldsymbol{R}_i = \boldsymbol{R}_i^0 + \delta \boldsymbol{R}_i$ denote the position of the ith ion, and let $U(\boldsymbol{r}) = -Z e^2 \exp(-r/\lambda_{\text{TF}})/r$ be the electron-ion interaction. Expanding in terms of the ionic displacements $\delta \boldsymbol{R}_i$,

$$\mathcal{H}_{\text{el-ion}} = \sum_i U(\boldsymbol{r} - \boldsymbol{R}_i^0) - \sum_i \delta \boldsymbol{R}_i \cdot \boldsymbol{\nabla} \, U(\boldsymbol{r} - \boldsymbol{R}_i^0) \quad , \tag{5.301}$$

where i runs from 1 to N_{ion}[21]. The deviation $\delta \boldsymbol{R}_i$ may be expanded in terms of the vibrational normal modes of the lattice, *i.e.* the phonons, as

$$\delta R_i^\alpha = \frac{1}{\sqrt{N_{\text{ion}}}} \sum_{q\lambda} \left(\frac{\hbar}{2 \, \omega_\lambda(\boldsymbol{q})} \right)^{1/2} \hat{\text{e}}_\lambda^\alpha(\boldsymbol{q}) \, e^{i \boldsymbol{q} \cdot \boldsymbol{R}_i^0} \, (a_{\boldsymbol{q}\lambda} + a_{-\boldsymbol{q}\lambda}^\dagger) \quad . \tag{5.302}$$

The phonon polarization vectors satisfy $\hat{e}_\lambda(\boldsymbol{q}) = \hat{e}_\lambda^*(-\boldsymbol{q})$ as well as the generalized orthonormality relations

$$\sum_\alpha \hat{\text{e}}_\lambda^\alpha(\boldsymbol{q}) \, \hat{\text{e}}_{\lambda'}^\alpha(-\boldsymbol{q}) = M^{-1} \delta_{\lambda\lambda'}$$

$$\sum_\lambda \hat{e}_\lambda^\alpha(\boldsymbol{q}) \, \hat{e}_\lambda^\beta(-\boldsymbol{q}) = M^{-1} \delta_{\alpha\beta} \quad , \tag{5.303}$$

where M is the ionic mass. The number of unit cells in the crystal is $N_{\text{ion}} = V/\Omega$, where Ω is the Wigner-Seitz cell volume. Again, we approximate Bloch states by plane waves $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \exp(i \boldsymbol{k} \cdot \boldsymbol{r})/\sqrt{V}$, in which case

$$\left\langle \boldsymbol{k}' \, \middle| \, \boldsymbol{\nabla} \, U(\boldsymbol{r} - \boldsymbol{R}_i^0) \, \middle| \, \boldsymbol{k} \right\rangle = -\frac{i}{V} \, e^{i(\boldsymbol{k}-\boldsymbol{k}') \cdot \boldsymbol{R}_i^0} \, \frac{4\pi Z e^2 \, (\boldsymbol{k} - \boldsymbol{k}')}{(\boldsymbol{k} - \boldsymbol{k}')^2 + \lambda_{\text{TF}}^{-2}} \quad . \tag{5.304}$$

The sum over lattice sites gives

$$\sum_{i=1}^{N_{\text{ion}}} e^{i(\boldsymbol{k}-\boldsymbol{k}'+\boldsymbol{q}) \cdot \boldsymbol{R}_i^0} = N_{\text{ion}} \, \delta_{\boldsymbol{k}', \boldsymbol{k}+\boldsymbol{q} \bmod \boldsymbol{G}} \quad , \tag{5.305}$$

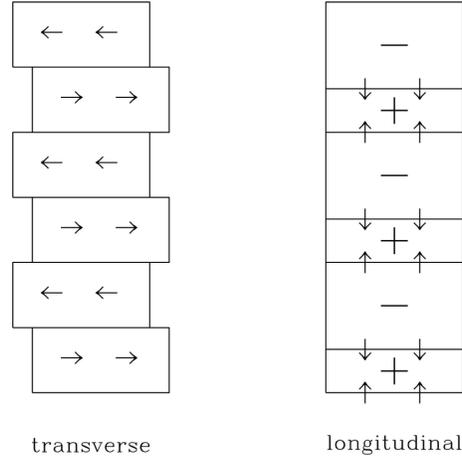[21]We assume a Bravais lattice, for simplicity.

Figure 5.23: Transverse and longitudinal phonon polarizations. Transverse phonons do not result in charge accumulation. Longitudinal phonons create local charge buildup and therefore couple to electronic excitations via the Coulomb interaction.

so that

$$\mathcal{H}_{\text{el}-\text{ph}} = \frac{1}{\sqrt{V}} \sum_{\substack{kk'\sigma \\ q\lambda G}} g_\lambda(k, k') \, (a^\dagger_{q\lambda} + a_{-q\lambda}) \, \psi^\dagger_{k\sigma} \, \psi_{k'\sigma} \, \delta_{k',k+q+G} \quad , \tag{5.306}$$

with

$$g_\lambda(k, k+q+G) = -i \left(\frac{\hbar}{2\,\Omega\,\omega_\lambda(q)} \right)^{1/2} \frac{4\pi Z e^2}{(q+G)^2 + \lambda_{\text{TF}}^{-2}} \, (q+G) \cdot \hat{e}^*_\lambda(q) \quad . \tag{5.307}$$

In an isotropic solid[22] ('jellium'), the phonon polarization at wavevector q either is parallel to q (longitudinal waves), or perpendicular to q (transverse waves). We see that only longitudinal waves couple to the electrons. This is because transverse waves do not result in any local accumulation of charge density, and it is to the charge density that electrons couple, via the Coulomb interaction.

Restricting our attention to the longitudinal phonon, we have $\hat{e}_{\text{L}}(q) = \hat{q}/\sqrt{M}$ and hence, for small $q = k' - k$,

$$g_{\text{L}}(k, k+q) = -i \left(\frac{\hbar}{2M\Omega} \right)^{1/2} \frac{4\pi Z e^2}{q^2 + \lambda_{\text{TF}}^{-2}} \, c_{\text{L}}^{-1/2} \, q^{1/2} \quad , \tag{5.308}$$

where c_{L} is the longitudinal phonon velocity. Thus, for small q we that the electron-longitudinal phonon coupling $g_{\text{L}}(k, k+q) \equiv g_q$ satisfies

$$|g_q|^2 = \lambda_{\text{el}-\text{ph}} \cdot \frac{\hbar c_{\text{L}} q}{g(\varepsilon_{\text{F}})} \quad , \tag{5.309}$$

---

[22]The jellium model ignores $G \neq 0$ *Umklapp* processes.

Metal	Θ_{s}	Θ_{D}	$\lambda_{\mathrm{el-ph}}$	Metal	Θ_{s}	Θ_{D}	$\lambda_{\mathrm{el-ph}}$
Na	220	150	0.47	Au	310	170	0.08
K	150	100	0.25	Be	1940	1000	0.59
Cu	490	315	0.16	Al	910	394	0.90
Ag	340	215	0.12	In	300	129	1.05

Table 5.3: Electron-phonon interaction parameters for some metals. Temperatures are in Kelvins.

where $g(\varepsilon_{\mathrm{F}})$ is the electronic density of states, and where the dimensionless *electron-phonon coupling constant* is

$$\lambda_{\mathrm{el-ph}} = \frac{Z^2}{2Mc_{\mathrm{L}}^2\,\Omega g(\varepsilon_{\mathrm{F}})} = \frac{2Z}{3}\frac{m^*}{M}\left(\frac{\varepsilon_{\mathrm{F}}}{k_{\mathrm{B}}\Theta_{\mathrm{s}}}\right)^2 \quad, \tag{5.310}$$

with $\Theta_{\mathrm{s}} \equiv \hbar c_{\mathrm{L}} k_{\mathrm{F}}/k_{\mathrm{B}}$. Table 5.3 lists Θ_{s}, the Debye temperature Θ_{D}, and the electron-phonon coupling $\lambda_{\mathrm{el-ph}}$ for various metals.

EXERCISE: Derive Eqn. (5.310).

5.12.3   Boltzmann equation for electron-phonon scattering

Earlier we had quoted the result for the electron-phonon collision integral,

$$\mathcal{I}_{\boldsymbol{k}}[f,n] = \frac{2\pi}{\hbar V}\sum_{\boldsymbol{k}',\lambda}|g_\lambda(\boldsymbol{k},\boldsymbol{k}')|^2\Big\{(1-f_{\boldsymbol{k}})\,f_{\boldsymbol{k}'}\,(1+n_{\boldsymbol{q},\lambda})\,\delta(\varepsilon_{\boldsymbol{k}}+\hbar\omega_{\boldsymbol{q}\lambda}-\varepsilon_{\boldsymbol{k}'}) \tag{5.311}$$

$$+ (1-f_{\boldsymbol{k}})\,f_{\boldsymbol{k}'}\,n_{-\boldsymbol{q}\lambda}\,\delta(\varepsilon_{\boldsymbol{k}}-\hbar\omega_{-\boldsymbol{q}\lambda}-\varepsilon_{\boldsymbol{k}'}) - f_{\boldsymbol{k}}\,(1-f_{\boldsymbol{k}'})\,(1+n_{-\boldsymbol{q}\lambda})\,\delta(\varepsilon_{\boldsymbol{k}}-\hbar\omega_{-\boldsymbol{q}\lambda}-\varepsilon_{\boldsymbol{k}'})$$

$$- f_{\boldsymbol{k}}\,(1-f_{\boldsymbol{k}'})\,n_{\boldsymbol{q}\lambda}\,\delta(\varepsilon_{\boldsymbol{k}}+\hbar\omega_{\boldsymbol{q}\lambda}-\varepsilon_{\boldsymbol{k}'})\Big\}\,\delta_{\boldsymbol{q},\boldsymbol{k}'-\boldsymbol{k}\bmod\boldsymbol{G}}\quad.$$

The four terms inside the curly brackets correspond, respectively, to cases (a) through (d) in Fig. 5.14. The $(1+n)$ factors in the phonon emission terms arise from both spontaneous as well as stimulated emission processes. There is no spontaneous absorption.

EXERCISE: Verify that in equilibrium $\mathcal{I}_{\boldsymbol{k}}\{f^0, n^0\} = 0$.

In principle we should also write down a Boltzmann equation for the phonon distribution $n_{\boldsymbol{q}\lambda}$ and solve the two coupled sets of equations. The electronic contribution to the phonon collision

integral is written as $\mathcal{J}_{q\lambda}[f, n]$, with

$$
\begin{aligned}
\mathcal{J}_{q\lambda}[f, n] \equiv \left(\frac{\partial n_{q\lambda}}{\partial t}\right)_{\text{coll}} = \frac{4\pi}{\hbar V} \left|g_{q\lambda}\right|^2 \sum_{k \in \widehat{\Omega}} \Big\{ & (1 + n_{q\lambda}) \, f_{k+q} \, (1 - f_k) \\
& - n_{q\lambda} \, f_k \, (1 - f_{k+q}) \Big\} \times \delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_{q\lambda}) \quad .
\end{aligned}
$$

(5.312)

Phonon equilibrium can be achieved via a number of mechanisms we have not considered here, such as impurity or lattice defect scattering, anharmonic effects (*i.e.* phonon-phonon scattering), or grain boundary scattering. At low temperatures,

$$
\frac{1}{\tau(\omega)} = \begin{cases} A\,\omega^2 & \text{impurity scattering} \\ B\,\omega^2\,T^3 & \text{anharmonic phonon scattering} \\ C/L & \text{boundary scattering } (L = \text{grain size}) \end{cases}
$$

(5.313)

where A, B, and C are constants.

Of course phonons and electrons scatter from each other – this is the process we are studying – and in principle we should write $f_k = f_k^0 + \delta f_k$ and $n_{q\lambda} = n_{q\lambda}^0 + \delta n_{q\lambda}$, and linearize the two Boltzmann equations for the electron and phonon distributions in order to study how each species comes to equilibrium. To compute the phonon lifetime due to electron-phonon scattering, we adopt the simplifying assumption that the electrons are in equilibrium at $T = 0$ and linearize in $\delta n_{q\lambda}$. This gives a phonon scattering rate of

$$
\begin{aligned}
\frac{1}{\tau_{q\lambda}} &= \frac{4\pi}{\hbar} \left|g_{q\lambda}\right|^2 \cdot \frac{1}{V} \sum_{k \in \widehat{\Omega}} \left(f_{k+q}^0 - f_k^0\right) \delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_{q\lambda}) \\
&= \frac{4\pi}{\hbar^2} \left|g_{q\lambda}\right|^2 \int_{\widehat{\Omega}} \frac{d^3k}{(2\pi)^3} \left[\Theta\left(k_{\text{F}} - |k + q|\right) - \Theta\left(k - k_{\text{F}}\right)\right] \delta\left(\omega_{q\lambda} - \frac{\hbar q^2}{2m^*} - \frac{\hbar k \cdot q}{m^*}\right) \\
&= \frac{4\pi}{\hbar^2} \left|g_{q\lambda}\right|^2 S\left(q, \omega_{q\lambda}\right) \quad ,
\end{aligned}
$$

(5.314)

where we assume a spherical Fermi surface and isotropic effective mass m^*. Here, $S(q, \omega)$ is the *dynamic structure factor* (dsf) of the filled Fermi sphere – we will compute this in detail in chapter three. For now, all we need to know is that

$$
S(q, \omega) = g(\varepsilon_{\text{F}}) \frac{\pi\omega}{2v_{\text{F}}q} \quad \text{for} \quad \omega < v_{\text{F}}q\left(1 - \frac{q}{2k_{\text{F}}}\right) \quad .
$$

(5.315)

We then obtain, for longitudinal acoustic phonons,

$$
\frac{1}{\tau_{\text{L},q}} = 2\pi^2 \lambda_{\text{el-ph}} \frac{c_{\text{L}}^2}{v_{\text{F}}} q \quad ,
$$

(5.316)

where $c_{\rm L}$ is the acoustic phonon velocity. Thus, $\tau_{\rm L}^{-1}(\omega) = 2\pi^2 \lambda_{\rm el-ph} \left(c_{\rm L}/v_{\rm F} \right) \omega$.

To compute the electron lifetime due to electron-phonon scattering, we first make the simplifying assumption that the phonons are in equilibrium, *i.e.* $n_{q\lambda} = n_{q\lambda}^0$. We then write $f_{\bm{k}} = f_{\bm{k}}^0 + \delta f_{\bm{k}}$ and linearize $\mathcal{I}_{\bm{k}}[f]$, to obtain

$$\mathcal{L}\,\delta f = \frac{2\pi}{\hbar V} \sum_{q\lambda} |g_{q\lambda}|^2 \bigg\{ \Big[(1 - f_{\bm{k}}^0 + n_{q\lambda}^0) \delta f_{\bm{k}+\bm{q}} - (f_{\bm{k}+\bm{q}}^0 + n_{q\lambda}^0) \delta f_{\bm{k}} \Big] \delta(\varepsilon_{\bm{k}+\bm{q}} - \varepsilon_{\bm{k}} - \hbar\omega_{q\lambda})$$
$$- \Big[(1 - f_{\bm{k}+\bm{q}}^0 + n_{-q\lambda}^0) \delta f_{\bm{k}} - (f_{\bm{k}}^0 + n_{-q\lambda}^0) \delta f_{\bm{k}+\bm{q}} \Big] \delta(\varepsilon_{\bm{k}+\bm{q}} - \varepsilon_{\bm{k}} + \hbar\omega_{-q\lambda}) \bigg\} \quad . \tag{5.317}$$

This integral operator must be inverted in order to solve for $\delta f_{\bm{k}}$ in

$$\mathcal{L}\,\delta f = e\,\bm{v}\cdot\bm{\mathcal{E}} \left(-\frac{\partial f^0}{\partial \varepsilon} \right) \quad . \tag{5.318}$$

Unfortunately, the inversion is analytically intractable – there is no simple solution of the form $\delta f_{\bm{k}} = e\tau_{\bm{k}} \bm{v}_{\bm{k}} \cdot \bm{\mathcal{E}}\,(\partial f^0/\partial\varepsilon)$ as there was in the case of isotropic impurity scattering. However, we can still identify the coefficient of $-\delta f_{\bm{k}}$ in $\mathcal{L}\,\delta f$ as the scattering rate $\tau_{\bm{k}}^{-1}$. As before, $\tau_{\bm{k}}$ in fact is a function of the energy $\varepsilon(\bm{k})$:

$$\frac{1}{\tau(\varepsilon)} = \frac{1}{4\pi^2\hbar^2} \int d\varepsilon' \int dS_{\varepsilon'} \frac{|g_{\bm{k}'-\bm{k}}|^2}{|v_{\bm{k}'}|} \bigg\{ \big[f^0(\varepsilon') + n_{\bm{k}'-\bm{k}}^0 \big]\, \delta(\varepsilon' - \varepsilon - \hbar\omega_{\bm{k}'-\bm{k}})$$
$$+ \big[1 + f^0(\varepsilon') + n_{\bm{k}-\bm{k}'}^0 \big]\, \delta(\varepsilon' - \varepsilon + \hbar\omega_{\bm{k}-\bm{k}'}) \bigg\} \tag{5.319}$$

In an isotropic system, $\tau(\varepsilon(\bm{k}))$ is independent of $\hat{\bm{k}}$. This means we can take $\bm{k} = \sqrt{2m^*\varepsilon/\hbar^2}\,\hat{\bm{z}}$ in performing the above integral.

It is convenient to define the dimensionless function

$$\alpha^2 F(\omega) \equiv \frac{1}{8\pi^3\hbar^2} \int dS_{\varepsilon'}\, \frac{|g_{\bm{k}'-\bm{k}}|^2}{|v_{\bm{k}'}|}\, \delta(\omega - \omega_{\bm{k}'-\bm{k}}) \quad . \tag{5.320}$$

For parabolic bands, one obtains

$$\alpha^2 F(\omega) = \frac{1}{8\pi^3\hbar^2} \frac{\lambda_{\rm el-ph}\,\hbar\omega}{m^* k_{\rm F}/\pi^2\hbar^2} \frac{m^*}{\hbar k_{\rm F}}\, k_{\rm F}^2 \int d\hat{\bm{k}}'\, \delta\big(\omega - c_{\rm L} k_{\rm F} |\hat{\bm{k}}' - \hat{\bm{z}}|\big)$$
$$= \lambda_{\rm el-ph} \left(\frac{\hbar\omega}{k_{\rm B}\Theta_{\rm s}} \right)^2 \Theta(2k_{\rm B}\Theta_{\rm s} - \hbar\omega) \quad . \tag{5.321}$$

The scattering rate is given in terms of $\alpha^2 F(\omega)$ as

$$\frac{1}{\tau(\varepsilon)} = 2\pi \int\limits_0^\infty d\omega\, \alpha^2 F(\omega) \left\{ f^0(\varepsilon + \hbar\omega) - f^0(\varepsilon - \hbar\omega) + 2n^0(\omega) + 1 \right\} \quad . \tag{5.322}$$

At $T = 0$ we have $f^0(\varepsilon) = \Theta(\varepsilon_{\mathrm{F}} - \varepsilon)$ and $n^0(\omega) = 0$, whence

$$
\frac{1}{\tau(\varepsilon)} = 2\pi \int_0^\infty d\omega\, \alpha^2 F(\omega)\, \left\{ \Theta(\varepsilon_{\mathrm{F}} - \varepsilon - \hbar\omega) - \Theta(\varepsilon_{\mathrm{F}} - \varepsilon + \hbar\omega) + 1 \right\}
$$

$$
= \begin{cases} \dfrac{\lambda_{\mathrm{el-ph}}}{12} \dfrac{2\pi}{\hbar} \cdot \dfrac{|\varepsilon - \varepsilon_{\mathrm{F}}|^3}{(k_{\mathrm{B}}\Theta_{\mathrm{s}})^2} & \text{if } |\varepsilon - \varepsilon_{\mathrm{F}}| < 2k_{\mathrm{B}}\Theta_{\mathrm{s}} \\[4mm] \dfrac{2\lambda_{\mathrm{el-ph}}}{3} \dfrac{2\pi}{\hbar} \cdot (k_{\mathrm{B}}\Theta_{\mathrm{s}}) & \text{it } |\varepsilon - \varepsilon_{\mathrm{F}}| > 2k_{\mathrm{B}}\Theta_{\mathrm{s}} \end{cases} .
$$

(5.323)

Note that $\tau(\varepsilon_{\mathrm{F}}) = \infty$, unlike the case of impurity scattering. This is because at $T = 0$ there are no phonons! For $T \neq 0$, the divergence is cut off, and one obtains

$$
\frac{1}{\tau(\mu)} = \frac{2\pi \lambda_{\mathrm{el-ph}}}{\hbar} \frac{k_{\mathrm{B}} T^3}{\Theta_{\mathrm{s}}^2} G\!\left(\frac{2\Theta_{\mathrm{s}}}{T} \right)
$$

(5.324)

with

$$
G(y) = \int_0^y dx\, \frac{x^2}{2\sinh x} = \begin{cases} \frac{7}{4}\zeta(3) & \text{if } y = \infty \\[4mm] \frac{1}{4} y & \text{if } y \ll 1 \end{cases} .
$$

(5.325)

Thus,

$$
\frac{1}{\tau(\mu)} = \begin{cases} \dfrac{7\pi\zeta(3)}{2\hbar} \dfrac{k_{\mathrm{B}} T^3}{\Theta_{\mathrm{s}}^2} \lambda_{\mathrm{el-ph}} & \text{if } T \ll \Theta_{\mathrm{s}} \\[4mm] \dfrac{2\pi}{\hbar} k_{\mathrm{B}} T\, \lambda_{\mathrm{el-ph}} & \text{if } T \gg \Theta_{\mathrm{s}} \end{cases} .
$$

(5.326)

This calculation predicts that $\tau \propto T^{-3}$ at low temperatures. This is correct if τ is the *thermal lifetime*. However, a more sophisticated calculation shows that the *transport lifetime* behaves as $\tau_{\mathrm{tr}} \propto T^{-5}$ at low T. The origin of the discrepancy is our neglect of the $(1 - \cos\vartheta)$ factor present in the average of the momentum relaxation time. At low T, there is only small angle scattering from the phonons, and $\langle \vartheta^2 \rangle \propto \langle q^2/k_{\mathrm{F}}^2 \rangle \propto T^2$. The Wiedemann-Franz law, $\tau_\sigma = \tau_\kappa$, is valid for $k_{\mathrm{B}} T \gtrsim \hbar c_{\mathrm{L}} k_{\mathrm{F}}$, as well as at low T in isotropic systems, where impurity scattering is the dominant mechanism. It fails at intermediate temperatures.