

Introduction to Solid State Physics

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1 The Drude theory of metals

1.1 Basic assumptions

In this script we follow closely the excellent textbook “Solid State Physics” by Neil W. Ashcroft and N. David Mermin. The current script will give you all the information you need for following this introductory course. Please consult the book if you want to delve deeper into the subject.

Paul Drude constructed in 1900 a theory to explain the electrical and thermal conductivity of metals. Just 3 years after the discovery of the electron by Sir Joseph John “J. J.” Thompson he attributed these properties to a gas of electrons. In more modern terms the idea is that when atoms of a metallic element (with an electron shell composed of core electrons and more loosely bound valence electrons, see Figure 1) come together to form a metal, the valence electrons become detached and can wander freely through the metal, forming so-called *conduction electrons*.

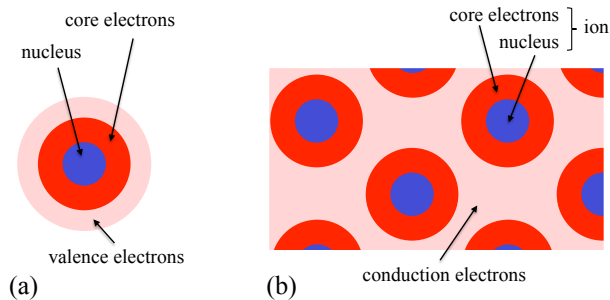


Figure 1: (a) Single atom with electron shell. The more loosely bound electrons typically determine the chemical properties of an atom. (b) When atoms of a metallic element come together only the core electrons stay unaffected whereas the valence electrons form an electron gas.

The density of the conduction electrons (number of electrons per volume, $n = N/V$) is given by

$$n = N_A \frac{Z \rho_m}{A} \quad (1)$$

with $N_A = 6 \times 10^{23}$, the Avogadro number, Z the number of conduction electrons per atom, ρ_m the mass density in gram per cm^3 and A the atomic mass of the

element. Therefore ρ_m/A is the number of moles per cm^3 . Typical densities are 10^{22} electrons per cm^3 .

Note that these densities are about 1000 times larger than the ones of a typical gas under normal temperature and pressure. Despite this and despite the huge electrostatic interactions between the conduction electrons and between conduction electrons and ions, Drude assumed that he could describe the electrons as a classical gas of particles. He made the following four assumptions that he borrowed from the kinetic theory of gases:

1. Between collisions the interaction of a given electron, both with the others and with the ions is neglected. Thus in the absence of an external electromagnetic field the electrons move in straight lines.
2. Collisions are instantaneous events abruptly changing the velocity of an electron.
3. Electrons experience collisions with probability $1/\tau$ per unit time.
4. Electrons emerge from a collision with a velocity distribution reflecting the temperature at the place where the collision occurred.

Some remarks: The neglect of electron-electron interactions in assumption 1 is called *independent electron approximation*, that of the neglect of ion-electron interactions is called the *free electron approximation*. The collisions in assumption 2 are thought to result through the scattering from ions, see Figure 2 but do not take this picture too seriously. The quantity τ in assumption 3 carries various names: *relaxation time*, *collision time* or *mean free time*. Here we assume it to be independent of the electron's position or velocity.

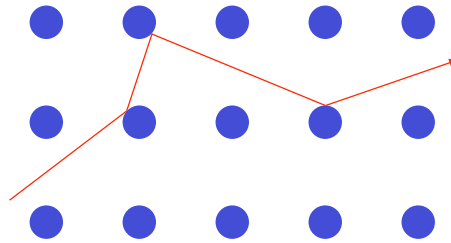


Figure 2: Trajectory of an conduction electron. In the Drude picture the electron is scattered at metal ions.

1.2 Electrical conductivity of a metal

According to *Ohm's law* the electric current I flowing through a wire is given by $V = IR$ with V denoting the potential drop and R the resistance of the wire. Instead of R which depends on the shape of the wire, we use a material property. The *resistivity* ρ relates the electrical field \mathbf{E} in a metal to the current density \mathbf{j} that the field induces

$$\mathbf{E} = \rho \mathbf{j}. \quad (2)$$

The current density is a vector whose magnitude is the amount of charge per unit time that crosses a unit area perpendicular to the flow. For instance, consider a uniform current I that flows through a wire of length L and cross-sectional area A . The current density is then $j = I/A$ and the potential drop $V = EL$. From Eq. 2 one finds $V = I\rho L/A$ and thus $R = \rho L/A$. In general, if n electrons per unit volume move with velocity \mathbf{v} , then the number of electrons passing the area A in the time dt is $n(vdt)A$. This leads to the current density

$$\mathbf{j} = -nev\mathbf{v}. \quad (3)$$

The minus sign reflects the fact that the electrons carry negative charges. Note that in Drude's electron gas picture the electrons move in various directions and \mathbf{v} has to be taken to be the average velocity. In the absence of a field, \mathbf{v} averages out to zero and there is no current.

We calculate now the current in the presence of a field \mathbf{E} . Consider an electron a time t after its last collision. Its velocity is the sum of the velocity \mathbf{v}_0 directly after the last collision plus the additional velocity $-e\mathbf{E}t/m$ (m : electron mass) that it has subsequently acquired. We now take the average over many collisions. Since the electron emerges from collisions in a random directions, \mathbf{v}_0 does not contribute to the average velocity. That average is entirely given by the average of $-e\mathbf{E}t/m$. Since the average of t is the relaxation time τ we find for the average velocity and the current density:

$$\mathbf{v}_{\text{avg}} = -\frac{e\mathbf{E}\tau}{m}; \quad \mathbf{j} = -nev_{\text{avg}} = \frac{ne^2\tau}{m}\mathbf{E}. \quad (4)$$

This result can be stated in terms of the conductivity $\sigma = 1/\rho$:

$$\mathbf{j} = \sigma\mathbf{E}; \quad \sigma = \frac{ne^2\tau}{m}. \quad (5)$$

Unfortunately we do not know τ and so we cannot predict σ . However, we can use this relation to estimate the value of τ since we can measure σ or ρ . One finds

$$\tau = \frac{m}{\rho ne^2}. \quad (6)$$

Room temperature resistivities are typically of the order of microhm centimeters leading to relaxation times on the order of 10^{-14} to 10^{-15} sec. Is this a reasonable number? A more useful quantity to look at is the *mean free path* $l = v_0\tau$ where v_0 denotes the average electronic speed. l is the distance travelled between collisions. The average speed of our electrons can be found from a well-known relation in thermodynamics, the equipartition theorem, $mv_0^2/2 = (3/2)k_B T$. It follows $v_0 \approx 10^7$ cm/s and thus a mean free path of 0.1 to 1 nm which corresponds indeed to typical interatomic distances. This would suggest that Figure 2 is appropriate.

However, the classical theory has its problems. As we shall discuss in the next chapter, the real v_0 is about 100 times larger due to the fermionic nature of the electrons. Also it is noteworthy that at sufficiently low temperatures the mean free path can be on the order of centimeters.

1.3 Thermal conductivity of a metal

Since we do not understand the cause for collisions in the Drude model, it is wise to look at quantities that do not depend on τ . Such quantities exist. One example, the Hall effect, will be studied in the exercise class. Here we discuss another example, the thermal conductivity of a metal. Its explanation was considered to be the most successful prediction of the Drude model at its time. Even though the thermal conductivity depends on τ according to the Drude model, the ratio κ/σ of the thermal to the electrical conductivity does not depend on it. More precisely the model seemed to explain the *Wiedemann-Franz law* (1853) which states that the ratio κ/σ for a large number of metals is directly proportional to the temperature T with a proportionality constant that is fairly independent of the metal. The ratio $\kappa/(\sigma T)$ is called the *Lorenz number* and its value is typically between 2.2 to 2.7×10^{-8} watt ohm/K².

Drude assumed that the bulk of the thermal current is carried by the free electrons and not by the ions. Analogous to Ohm's law for electrical currents the thermal current follows from *Fourier's law*:

$$\mathbf{j}^q = -\kappa \nabla T. \quad (7)$$

Here j^q gives the thermal flow per unit time crossing a unit area perpendicular to the flow, and κ is the *thermal conductivity*.

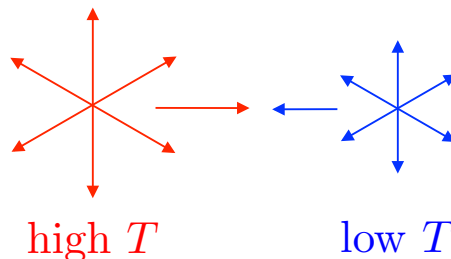


Figure 3: Schematic view of the origin of the thermal current. Electrons to the left emerge from their collision with a higher energy, then electrons to the right.

Let us calculate κ in the framework of the Drude model. Assume that the temperature drop is uniform in the positive x-direction, leading to $j^q = -\kappa dT/dx$. We use now assumption 4 of the Drude model, namely that electrons emerge from collisions with velocity distributions that reflect the temperature at the place of the collision, Figure 3. For simplicity we consider a one-dimensional model first where electrons can only move along the x-direction. Call $\mathcal{E}(T)$ the thermal energy per electron in a metal in equilibrium at temperature T . Electrons arriving at x from the high temperature side will, on average, have had their last collision at $x - v\tau$ and thus carry a thermal energy $\mathcal{E}(T(x - v\tau))$. Their contribution to the thermal current will be the number of such electrons per unit volume, $n/2$, times their velocity, v , times this energy,

i.e. $(n/2)v\mathcal{E}(T(x-v\tau))$. The electrons from the colder side will contribute $(n/2)(-v)\mathcal{E}(T(x+v\tau))$. Altogether this amounts to

$$j^q = \frac{1}{2}nv[\mathcal{E}(T(x-v\tau)) - \mathcal{E}(T(x+v\tau))] \quad (8)$$

If T does not vary much over the mean free path $l = v\tau$ we can expand around x leading to

$$j^q = nv^2\tau \frac{d\mathcal{E}}{dT} \left(-\frac{dT}{dx} \right). \quad (9)$$

To go the full 3D case we need to replace v by v_x using $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = v^2/3$. Furthermore we use $nd\mathcal{E}/dT = (N/V)d\mathcal{E}/dT = (dE/dT)/V = c_v$ (the electronic specific heat). Hence

$$\mathbf{j}^q = \frac{1}{3}v^2\tau c_v (-\nabla T) \quad (10)$$

or

$$\kappa = \frac{1}{3}v^2\tau c_v = \frac{1}{3}lv c_v. \quad (11)$$

To get rid of the mysterious τ we look at the ratio

$$\frac{\kappa}{\sigma} = \frac{\frac{1}{3}c_v m v^2}{n e^2} \quad (12)$$

where we used Eq. 5. To obtain c_v and v^2 Drude assumed the electrons to form an ideal gas, i.e. $c_v = (3/2)nk_B$ and $(1/2)mv^2 = (3/2)k_B T$ with $k_B = 1.38 \times 10^{-23}$ J/K, the Boltzmann constant. This leads to

$$\frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T. \quad (13)$$

The right side is proportional to T and the proportionality constant depends only on universal constants, in agreement with the Wiedemann-Franz law. The Lorenz number is predicted to be

$$\frac{\kappa}{\sigma T} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 = 1.11 \times 10^{-8} \text{ watt ohm/K}^2$$

which is about half the experimental value. Drude made a mistake in his calculation which gave him a factor 2 in his final result, suggesting extraordinary agreement with experiment. Beside this the good agreement turns out to be accidental since we will learn in the next chapter that the classical ideal gas laws cannot be applied to electrons in a metal. In fact two huge errors cancelled in Drude's calculation: at room temperature the electronic contribution to the specific heat is about 100 times smaller and the mean square electronic speed is about 100 times larger.

2 The Sommerfeld theory of metals

Drude's theory treated the electrons as an ordinary classical gas. Despite the success with respect to the Wiedemann-Franz law, the contribution to the specific heat $(3/2)k_B$ per electron was not observed. This paradox was only removed after the advent of quantum theory. Shortly after the discovery that the Pauli exclusion principle was needed to account for the bound electron states in atoms, Sommerfeld applied the same principle to the free electron gas of metals. As we shall see, this removes many thermal anomalies of the Drude model.

2.1 Ground-state properties of the electron gas

We calculate the ground-state properties of N electrons confined to a volume V . We use again the independent electron approximation (the electrons do not interact with one another). Thus to find the ground state of N electrons we first find the energy levels of a single electron in the volume V and then fill all the levels up consistent with the Pauli exclusion principle (no two electrons may occupy the same quantum state simultaneously).

As you should know, a single electron can be described by a wave function $\psi(\mathbf{r})$ and a specification of its spin state. The one electron wave function associated with the energy level \mathcal{E} satisfies the time-independent Schrödinger equation $\hat{H}\psi(\mathbf{r}) = \mathcal{E}\psi(\mathbf{r})$ with \hat{H} denoting the Hamiltonian operator. It is given by $\hat{H} = \hat{T} + \hat{V}$, the sum of operators corresponding to the kinetic and potential energy. If the electron has no interactions, one has $\hat{V} \equiv 0$ and thus $\hat{H} = \hat{T}$ and the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial^2 x} + \frac{\partial^2}{\partial^2 y} + \frac{\partial^2}{\partial^2 z} \right) \psi(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \mathcal{E}\psi(\mathbf{r}). \quad (14)$$

with \hbar denoting Planck's constant divided by 2π .

Solutions to Eq. 14 (neglecting for now boundary conditions) are of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad (15)$$

with energy

$$\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \quad (16)$$

where \mathbf{k} is any position independent vector. The electron is confined to a volume V by the attraction to the ions (V is the volume occupied by the solid); we choose the normalization in 15 such that

$$\int_V |\psi(\mathbf{r})|^2 d\mathbf{r} = 1. \quad (17)$$

The wave function $\psi_{\mathbf{k}}(\mathbf{r})$ constitutes a plane wave with wave vector \mathbf{k} and wave length $\lambda = 2\pi/k$. It is an eigenstate of the momentum operator $\mathbf{p} = (\hbar/i)(\partial/\partial\mathbf{r}) = (\hbar/i)\nabla$ with eigenvalue

$$\mathbf{p} = \hbar\mathbf{k}, \quad (18)$$

the momentum of an electron in the state $\psi_{\mathbf{k}}(\mathbf{r})$. The velocity $\mathbf{v} = \mathbf{p}/m$ is given by

$$\mathbf{v} = \frac{\hbar \mathbf{k}}{m}. \quad (19)$$

Here we assume for simplicity the volume to be a cube of side $L = V^{1/3}$. Since we are interested in bulk properties, the choice of the surface is usually not important. The most convenient choice is to remove the surface altogether by setting

$$\begin{aligned} \psi(x+L, y, z) &= \psi(x, y, z), \\ \psi(x, y+L, z) &= \psi(x, y, z), \\ \psi(x, y, z+L) &= \psi(x, y, z), \end{aligned} \quad (20)$$

the so-called *Born-van Karmann* (or periodic) *boundary condition*. The boundary condition 20 only permits certain discrete values of \mathbf{k} such that

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1. \quad (21)$$

The components of the wave vector must thus be of the form

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L} \quad (22)$$

with n_x , n_y and n_z integers. In k -space (a 3D space with coordinates k_x , k_y and k_z) the allowed wave vectors are those whose coordinates along the three axes are given by multiples of $2\pi/L$. A 2D version of this space is shown in Figure 4.

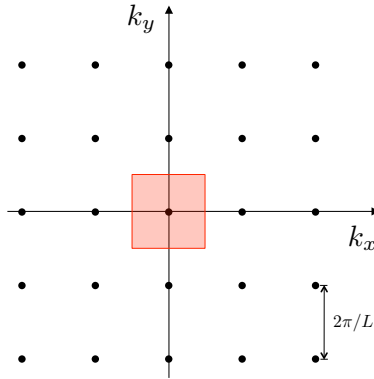


Figure 4: Points in (two-dimensional) k -space of the form $k_x = 2\pi n_x/L$, $k_y = 2\pi n_y/L$. Note the area per point is just $(2\pi/L)^2$.

Consider some arbitrary volume Ω in k -space with $\Omega \gg (2\pi/L)^3$. $(2\pi/L)^3$ is the volume per point. Then we know that this volume contains

$$\frac{\Omega}{(2\pi/L)^3} = \frac{\Omega V}{8\pi^3} \quad (23)$$

allowed values of \mathbf{k} , or, equivalently, the k -space density of levels is just

$$\frac{V}{8\pi^3}. \quad (24)$$

We are now in the position to build the ground state for the N electrons. Each one-electron level is specified by a wave vector \mathbf{k} and the projection of the electron's spin along an arbitrary axis (which can take either one of the two values $\hbar/2$ or $-\hbar/2$), i.e. each allowed \mathbf{k} -vector has two electronic levels. Since the energy of a one-electron level is proportional to k^2 , Eq. 16, for $N \gg 1$ the occupied region in k -space will be indistinguishable from a sphere, the so-called *Fermi sphere*, of radius k_F , the Fermi wave vector. The number of allowed \mathbf{k} -values within the Fermi sphere follows with Eq. 23 to be

$$\left(\frac{4\pi k_F^3}{3}\right) \left(\frac{V}{8\pi^3}\right) = \frac{k_F^3}{6\pi^2} V. \quad (25)$$

With 2 electrons per allowed k -value in order to accommodate N electrons we must have

$$N = 2 \frac{k_F^3}{6\pi^2} V = \frac{k_F^3}{3\pi^2} V. \quad (26)$$

In terms of the electron density $n = N/V$ this can be rewritten as

$$n = \frac{k_F^3}{3\pi^2}. \quad (27)$$

Thus in the ground state all k less than k_F are filled with electrons, leaving all k greater than k_F unoccupied.

The surface of the Fermi sphere that separates the occupied from the unoccupied levels is called the *Fermi surface*. The electrons occupying the highest levels have a momentum $\hbar k_F = p_F$, the *Fermi momentum*, and energy

$$\mathcal{E}_F = \frac{\hbar^2 k_F^2}{2m}, \quad (28)$$

the *Fermi energy*, and a velocity $v_F = p_F/m$, the *Fermi velocity*. This velocity is substantial (about 10^4 km/s), even though we are at the $T = 0$ ground state where classical particles have zero velocity. Even at room temperature classical particles with electronic mass are about 10 times slower.

To calculate the ground state energy of N electrons in a volume V we must add up the energies of all one-electron levels within the Fermi sphere:

$$E = 2 \sum_{k < k_F} \mathcal{E}(\mathbf{k}) = 2 \sum_{k < k_F} \frac{\hbar^2 k^2}{2m}. \quad (29)$$

We can replace the summation by an integration as follows. The volume of k -space per allowed \mathbf{k} -value is $\Delta \mathbf{k} = 8\pi^3/V$ (see Eq. 24). It is then convenient to write

$$E = \frac{V}{8\pi^3} \sum_{k < k_F} 2\mathcal{E}(\mathbf{k}) \Delta \mathbf{k} \quad (30)$$

Finally we can write to an excellent approximation

$$\frac{E}{V} = \frac{1}{8\pi^3} \int_{k < k_F} 2\mathcal{E}(\mathbf{k}) d\mathbf{k} = \frac{1}{4\pi^3} \int_{k < k_F} \frac{\hbar^2 k^2}{2m} d\mathbf{k} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}. \quad (31)$$

The energy per electron, E/N , in the ground state follows through division by N/V which gives (see Eq. 27):

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} \mathcal{E}_F = \frac{3}{5} k_B T_F \quad (32)$$

where we introduced the Fermi temperature T_F .

2.2 Thermal properties of the free electron gas: the Fermi-Dirac distribution

We next study the N -electron state at a finite temperature T . In that case we need to assign to each stationary state of energy E a weight $P_N(E)$ proportional to $e^{-E/k_B T}$:

$$P_N(E) = \frac{e^{-E/k_B T}}{\sum_{\alpha} e^{-E_{\alpha}^N/k_B T}}. \quad (33)$$

Here E_{α}^N is the energy of the α th stationary state of the N -electron system and the sum is over all such states. The denominator of Eq. 33 is the partition function and is related to the free energy $F = U - TS$ (U : internal energy, S : entropy) by

$$\sum_{\alpha} e^{-E_{\alpha}^N/k_B T} = e^{-F_N/k_B T} \quad (34)$$

This allows to rewrite Eq. 33 more compact:

$$P_N(E) = e^{-(E-F_N)/k_B T}. \quad (35)$$

We introduce now f_i^N , the probability of there being an electron in the particular one-electron level i when the N -electron system is in thermal equilibrium. This probability is found by summing over all N -electron state α' in which there is an electron in level i :

$$f_i^N = \sum_{\alpha'} P_N(E_{\alpha'}^N). \quad (36)$$

In Quantummechanics 2 you learned this year that f_i^N is given by the *Fermi-Dirac distribution*:

$$f_i^N = \frac{1}{e^{(\mathcal{E}_i - \mu)/k_B T} + 1}, \quad (37)$$

where μ denotes the chemical potential:

$$\mu = F_{N+1} - F_N. \quad (38)$$

In the following we will drop the explicit reference to the N dependence of f_i . N can always be computed from the f_i via

$$N = \sum_i f_i = \sum_i \frac{1}{e^{(\mathcal{E}_i - \mu)/k_B T} + 1}, \quad (39)$$

which determines N as a function of T and μ .

Let us first check whether we recover from Eq. 37 the ground state properties derived above. In the ground state only those levels are occupied with $\mathcal{E}(\mathbf{k}) \leq \mathcal{E}_F$. Hence we need $f_{\mathbf{k}s} = 1$ for $\mathcal{E}(\mathbf{k}) \leq \mathcal{E}_F$ and $f_{\mathbf{k}s} = 0$ for $\mathcal{E}(\mathbf{k}) > \mathcal{E}_F$ (k is the wave vector, s the spin quantum number and $\mathcal{E}(\mathbf{k})$ is given by Eq. 16). On the other hand, as $T \rightarrow 0$, the limiting form of the Fermi-Dirac distribution, Eq. 37, is $\lim_{T \rightarrow 0} f_{\mathbf{k}s} = 1$ for $\mathcal{E}(\mathbf{k}) \leq \mu$ and $\lim_{T \rightarrow 0} f_{\mathbf{k}s} = 0$ for $\mathcal{E}(\mathbf{k}) > \mu$. Hence

$$\lim_{T \rightarrow 0} \mu = \mathcal{E}_F. \quad (40)$$

We shall see shortly that μ remains equal to \mathcal{E}_F to a high degree of precision all the way up to room temperature.

The most important application of Fermi-Dirac statistics is the calculation of the electronic contribution to the constant volume specific heat of a metal:

$$c_v = \left(\frac{\partial u}{\partial T} \right)_V \quad (41)$$

with $u = U/V$. Here

$$U = 2 \sum_{\mathbf{k}} \mathcal{E}(\mathbf{k}) f(\mathcal{E}(\mathbf{k})). \quad (42)$$

We introduced the *Fermi function* $f(\mathcal{E})$ to emphasize that $f_{\mathbf{k}}$ depends on \mathbf{k} only through $\mathcal{E}(\mathbf{k})$:

$$f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E} - \mu)/k_B T} + 1}. \quad (43)$$

Divide both sides of Eq. 42 by V and replacing summation by integration (as in Eq. 31) gives

$$u = \int \frac{d\mathbf{k}}{4\pi^3} \mathcal{E}(\mathbf{k}) f(\mathcal{E}(\mathbf{k})). \quad (44)$$

Similarly from Eq. 39 we find a relation for $n = N/V$:

$$n = \int \frac{d\mathbf{k}}{4\pi^3} f(\mathcal{E}(\mathbf{k})) \quad (45)$$

which can be used to eliminate the chemical potential.

Both integrals, Eqs. 44 and 45, are of the form

$$\int \frac{d\mathbf{k}}{4\pi^3} F(\mathcal{E}(\mathbf{k})). \quad (46)$$

Since the integrands depend on \mathbf{k} only through $\mathcal{E} = \hbar^2 k^2/2m$ we can go to spherical coordinates and change variables from k to \mathcal{E} :

$$\int \frac{d\mathbf{k}}{4\pi^3} F(\mathcal{E}(\mathbf{k})) = \int_0^\infty \frac{k^2 dk}{\pi^2} F(\mathcal{E}(\mathbf{k})) = \int_{-\infty}^\infty d\mathcal{E} D(\mathcal{E}) F(\mathcal{E}). \quad (47)$$

Here

$$D(\mathcal{E}) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\mathcal{E}}{\hbar^2}} \quad (48)$$

for $\mathcal{E} > 0$ and zero otherwise. Since the integral 46 is an evaluation of the sum $(1/V) \sum_{\mathbf{k}_s} F(\mathcal{E}(\mathbf{k}))$ we know that $V D(\mathcal{E}) d\mathcal{E}$ gives the number of one-electron levels in the energy range \mathcal{E} to $\mathcal{E} + d\mathcal{E}$. $D(\mathcal{E})$ is thus the *density of levels* per unit volume.

Using Eqs. 27 and 28 we can write $D(\mathcal{E})$ in a more transparent way:

$$D(\mathcal{E}) = \frac{3}{2} \frac{n}{\mathcal{E}_F} \left(\frac{\mathcal{E}}{\mathcal{E}_F} \right)^{1/2} \quad (49)$$

for $\mathcal{E} > 0$ and zero otherwise. Of importance will be the density of levels at the Fermi energy which follows from Eqs. 48 or 49 to be

$$D(\mathcal{E}_F) = \frac{mk_F}{\hbar^2 \pi^2} = \frac{3}{2} \frac{n}{\mathcal{E}_F}. \quad (50)$$

With this notation we can rewrite Eqs. 44 and 45:

$$u = \int_{-\infty}^\infty d\mathcal{E} D(\mathcal{E}) \mathcal{E} f(\mathcal{E}) \quad (51)$$

and

$$n = \int_{-\infty}^\infty d\mathcal{E} D(\mathcal{E}) f(\mathcal{E}). \quad (52)$$

Note that these expressions are quite general as the free electron approximation enters only through $D(\mathcal{E})$. The expressions can thus also be used for more sophisticated models of independent electrons in metals.

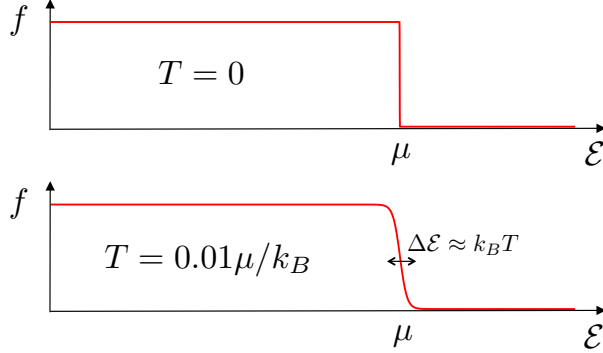


Figure 5: Fermi function $f(\mathcal{E}) = 1/(e^{\beta(\mathcal{E}-\mu)} + 1)$ vs. \mathcal{E} for a given value of μ at zero temperature (top) and at room temperature for a typical metal (bottom).

The integrals 51 and 52 are rather complex. One can, however, exploit the fact that in metals one has typically electron densities such that $k_B T/\mu \approx 0.01$. This means that the Fermi-Dirac distribution looks similar to the zero temperature distribution, see Fig. 5. f differs from zero temperature only in a small region of width $k_B T$ around $\mathcal{E} = \mu$. Thus the way in which integrals of the form $\int_{-\infty}^{\infty} H(\mathcal{E}) f(\mathcal{E}) d\mathcal{E}$ differs from zero temperature values $\int_{-\infty}^{\mathcal{E}_F} H(\mathcal{E}) d\mathcal{E}$ will entirely be determined by the form of $H(\mathcal{E})$ near $\mathcal{E} = \mu$. If H does not vary too much around μ one can calculate the integral through a Taylor expansion of H around that value. Without giving the rather lengthy derivation, the first two terms of this so-called *Sommerfeld expansion* are as follows:

$$\int_{-\infty}^{\infty} H(\mathcal{E}) f(\mathcal{E}) d\mathcal{E} = \int_{-\infty}^{\mu} H(\mathcal{E}) d\mathcal{E} + \frac{\pi^2}{6} (k_B T)^2 H'(\mu) + O\left(\frac{k_B T}{\mu}\right)^4. \quad (53)$$

To evaluate the specific heat of a metal for $T \ll T_F$ we apply now the Sommerfeld expansion to Eqs. 51 and 52:

$$u = \int_0^{\mu} \mathcal{E} D(\mathcal{E}) d\mathcal{E} + \frac{\pi^2}{6} (k_B T)^2 [\mu D'(\mu) + D(\mu)] + O(T^4) \quad (54)$$

and

$$n = \int_0^{\mu} D(\mathcal{E}) d\mathcal{E} + \frac{\pi^2}{6} (k_B T)^2 D'(\mu) + O(T^4). \quad (55)$$

We will see soon that the latter equation implies that μ differs from \mathcal{E}_F only by a term of order T^2 . This allows to write correctly to order T^2 :

$$\int_0^{\mu} H(\mathcal{E}) d\mathcal{E} = \int_0^{\mathcal{E}_F} H(\mathcal{E}) d\mathcal{E} + (\mu - \mathcal{E}_F) H(\mathcal{E}_F). \quad (56)$$

Using this expansion for the integrals 54 and 55 and replacing μ by \mathcal{E}_F in those terms that are already of order T^2 we find

$$u = \int_0^{\mathcal{E}_F} \mathcal{E} D(\mathcal{E}) d\mathcal{E} + \mathcal{E}_F \left((\mu - \mathcal{E}_F) D(\mathcal{E}_F) + \frac{\pi^2}{6} (k_B T)^2 D'(\mathcal{E}_F) \right) + \frac{\pi^2}{6} (k_B T)^2 D(\mathcal{E}_F) + O(T^4) \quad (57)$$

and

$$n = \int_0^{\mathcal{E}_F} D(\mathcal{E}) d\mathcal{E} + (\mu - \mathcal{E}_F) D(\mathcal{E}_F) + \frac{\pi^2}{6} (k_B T)^2 D'(\mathcal{E}_F) + O(T^4). \quad (58)$$

The first terms on the right sides of Eqs. 57 and 58 are the values of u and n in the ground state. Since we calculate the specific heat at constant V , n must be constant and is given by the first term on the rhs of Eq. 58. Subtracting n from from both sides, leads to:

$$0 = (\mu - \mathcal{E}_F) D(\mathcal{E}_F) + \frac{\pi^2}{6} (k_B T)^2 D'(\mathcal{E}_F). \quad (59)$$

This determines the deviation of μ from \mathcal{E}_F :

$$\mu = \mathcal{E}_F - \frac{\pi^2}{6} (k_B T)^2 \frac{D'(\mathcal{E}_F)}{D(\mathcal{E}_F)}. \quad (60)$$

Using Eq. 49 this gives

$$\mu = \mathcal{E}_F \left(1 - \frac{1}{3} \left(\frac{\pi k_B T}{2\mathcal{E}_F} \right)^2 \right) \quad (61)$$

which is indeed, as assumed above, a shift of the order T^2 (typically about 0.01 percent at room temperature).

Equation 59 sets the term in brackets in Eq. 57 to zero. Hence

$$u = u_0 + \frac{\pi^2}{6} (k_B T)^2 D(\mathcal{E}_F) \quad (62)$$

with u_0 being the energy density in the ground state. The specific heat of the electron gas is thus

$$c_v = \frac{\pi^2}{3} k_B^2 T D(\mathcal{E}_F). \quad (63)$$

For the free electron gas we use Eq. 50 and find:

$$c_v = \frac{\pi^2}{2} \left(\frac{k_B T}{\mathcal{E}_F} \right) n k_B \quad (64)$$

Compare this to the classical result for an ideal electron gas: $c_v = (3/2)nk_B$. The Fermi-Dirac statistics depresses the specific heat by a factor $(\pi^2/3)(k_B T/\mathcal{E}_F)$ which is proportional to T and even at room temperature only of the order 10^{-2} . This explains the absence of any observable contribution of the electronic degrees of freedom to the specific heat of a metal at room temperature.

The functional dependence of the specific heat, Eq. 63, can be easily understood (up to numerical coefficients) to result from the shape of the Fermi function, Figure 5. If one goes from $T = 0$ to some finite temperature T about $D(\mathcal{E}_F)k_B T$ electrons are excited by about $k_B T$ increasing the total thermal energy density by $D(\mathcal{E}_F)(k_B T)^2$.

The linear dependence of the specific heat can be tested provided that other degrees of freedom are negligible. The ionic degrees of freedom dominate the specific heat at high temperatures but well below room temperatures their contribution falls off as T^3 , faster than the electronic contribution proportional to T . The latter can thus be seen at a few degrees Kelvin.

2.3 The Sommerfeld theory of conduction in metals

We next apply the Sommerfeld theory to predict the conduction in metals. Following Sommerfeld we will replace in the Drude model the classical velocity distribution by the Fermi-Dirac distribution (we will here not try to justify why a quantummechanical distribution can be used in an otherwise classical theory but there are good reasons for such a procedure). Consider a small volume element of k -space about a point \mathbf{k} of volume $d\mathbf{k}$. According to Eq. 24 (allowing for two-fold spin degeneracy) the number of one-electron levels in this volume element are

$$\left(\frac{V}{4\pi^3}\right) d\mathbf{k}. \quad (65)$$

With the probability $f(\mathbf{k})$ of each level to be occupied we find the total number of electrons in that k -space volume element:

$$\frac{V}{4\pi^3} f(\mathcal{E}(\mathbf{k})) d\mathbf{k} \quad (66)$$

with $\mathcal{E}(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m$.

Since $\mathbf{v} = \hbar \mathbf{k} / m$ the number of electrons in a volume element $d\mathbf{v}$ about \mathbf{v} is the same as the number in a volume element $d\mathbf{k} = (m/\hbar)^3 d\mathbf{v}$ about $\mathbf{k} = m\mathbf{v}/\hbar$. Thus the number of electrons per unit volume of real space in a velocity space element of volume $d\mathbf{v}$ around \mathbf{v} is

$$\tilde{f}(\mathbf{v}) d\mathbf{v} \quad (67)$$

with

$$\tilde{f}(\mathbf{v}) = \frac{(m/\hbar)^3}{4\pi^3} \frac{1}{\exp\left[\left(\frac{1}{2}mv^2 - \mu\right)/k_B T\right] + 1} \quad (68)$$

This is dramatically different from the velocity distribution of a classical electron gas, the one assumed in the Drude model, namely

$$\tilde{f}_{\text{MB}}(\mathbf{v}) = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}. \quad (69)$$

Think e.g. about the difference in the limit $T \rightarrow 0$ between the classical case (all electrons come to rest) and the fermionic case (electrons keep moving to obey the Pauli exclusion principle).

Sommerfeld essentially used the classical treatment of Drude but with the velocity distribution 68. We shall not discuss why such an approach can be useful but simply mention some predictions that follow. The mean free path can be estimated, if we use $v_F = \hbar k_F/m$ as the typical electronic speed, to be $l = v_F \tau$ which predicts with Eq. 6 a mean free path of order 10 nm, even at room temperature. We next estimate the thermal conductivity, Eq. 11:

$$\kappa = \frac{1}{3} v^2 \tau c_v. \quad (70)$$

The correct specific heat, Eq. 64, is smaller than Drude's guess by a factor $k_B T/\mathcal{E}_F$. A correct estimate for v^2 is not the classical value of order $k_B T/m$ but $v_F^2 = 2\mathcal{E}_F/m$ which is larger to the classical value by a factor of order \mathcal{E}_F/m . Inserting this in 70 and eliminating the relaxation time τ in favor of the conductivity through Eq. 5 (the electric conductivity does not depend on the electronic velocity distribution), we find for the Lorenz number

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} \text{ watt ohm/K}^2. \quad (71)$$

This is remarkably close to Drude's result, Eq. 13, due to two compensating corrections of order $k_B T/\mathcal{E}_F$.

To conclude these two chapters we mention some of the failures and problems of the free electron model. The Wiedemann-Franz law, the great triumph of the free electron theory at high (room) temperature and at very low temperature, fails at intermediate temperatures. Often one finds a temperature dependence of the DC conductivity which can be only accounted for as an *ad hoc* dependence of τ on temperature (see Eq. 5). Some fundamental questions remain unsolved: what determines the number of conduction electrons? Why are some elements non-metals?

It turns out that the assumption that the ions have no significant effect on the motion of the electrons between collisions is responsible for most of the deficiencies of the Drude and Sommerfeld models. We shall see that a theory that takes properly into account the detailed field produced by a static array of ions produce much more reasonable results. As a first step, in the next chapter we study the arrangement of ions in regular periodic arrays or lattices.

3 Crystal lattices and reciprocal lattices

3.1 Crystal lattices

The ions in a metal are arranged in a periodic array. Here we survey some of the most important geometrical properties of periodic arrays in three-dimensional space. A fundamental concept to describe any crystalline solid is that of the *Bravais lattice*. It specifies the periodic array in which the repeated units (single atoms, groups of atoms, molecules, ions etc) are arranged. We give two equivalent definitions:

1. A Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.
2. A (three-dimensional) Bravais lattice consists of all points with position vectors \mathbf{R} of the form

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad (72)$$

where \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 are any three vectors not all in the same plane and n_1 , n_2 and n_3 range through all the integers.

The \mathbf{a}_i are called *primitive vectors* and are said to generate or span the lattice. An example of a two-dimensional Bravais lattice is given in Figure 6. Clearly the definition 1 is satisfied and the primitive vectors required for definition 2 are indicated in the figure. We note that the choice of the set of primitive vectors for a given Bravais lattice is not unique but that there are infinitely many non-equivalent choices.

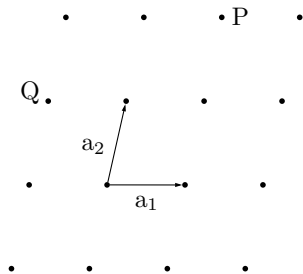


Figure 6: Example of a two-dimensional Bravais lattice with primitive vectors \mathbf{a}_1 and \mathbf{a}_2 . All points in the net can be reached via linear combinations of these vectors with integer coefficients, e.g. $\mathbf{P} = \mathbf{a}_1 + 2\mathbf{a}_2$ and $\mathbf{Q} = -\mathbf{a}_1 + \mathbf{a}_2$.

We discuss now three cubic lattices. The most simple one is the simple cubic lattice, Fig. 7(a). This geometry is rare among crystalline solids (polonium is the only known example of an element that shows the cubic form under normal conditions). Common are the *body-centered cubic* (bcc) lattice, Fig. 7(b), and

the *face-centered cubic* (fcc) lattice, Fig. 7(c) (e.g. bcc: Ar, Ag, Al, Au, Ca, Ce, Co, Cu; fcc: Ba, Cr, Cs, Fe, K). The bcc lattice can be obtained by placing an additional point in the cube center or by two simple cubic lattices displaced with respect to each other. The fcc lattice can be formed from the cubic lattice by adding an additional point at the center of each square face.

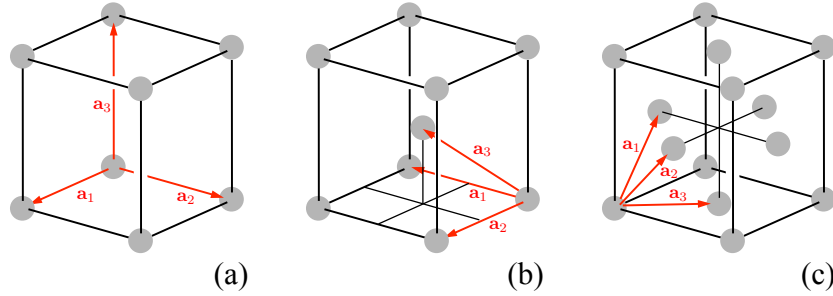


Figure 7: (a) The simple cubic three-dimensional Bravais lattice. (b) The body-centered cubic (bcc) Bravais lattice. (c) The face-centered cubic (fcc) Bravais lattice. For all three cases primitive vectors are indicated.

The points in a Bravais lattice that are closest to a given point are called its *nearest neighbors*. Since all points are equal, each point has the same number of nearest neighbors. This number is thus a property of the lattice and is called the *coordination number* of the lattice. The simple cubic lattice has coordination number 6, the bcc lattice 8 and the fcc lattice 12.

A volume of space that, when translated through all vectors in a Bravais lattice, fills all of space without either overlapping or leaving voids is called a *primitive cell* of the lattice. There is no unique way of choosing a primitive cell for a given Bravais lattice, see Figure 8 for several possible choices of primitive cells for a two-dimensional Bravais lattice. A primitive cell contains precisely one point (unless it is positioned such that there are points on the surface). The volume of a primitive cell is independent of the choice of the cell.

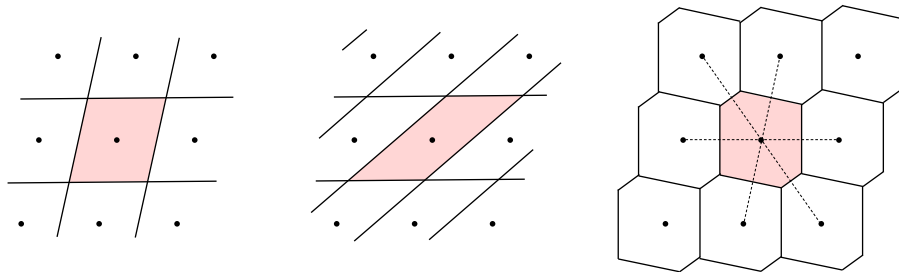


Figure 8: Three possible choices of the primitive cell for a single two-dimensional Bravais lattice. The choice to the right is the Wigner-Seitz cell (see main text).

The obvious choice for the primitive cell for a given set of primitive vectors, \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 , is the set of all points \mathbf{r} of the form

$$\mathbf{r} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3 \quad (73)$$

with $0 \leq x_i < 1$. This leads to a parallelepiped. This has often (e.g. bcc lattice, Figure 7(b)) not the full (e.g. cubic) symmetry of the lattice. It is, however, often important to work with cells that have the full symmetry of their Bravais lattice. There are two solutions to the problem. The first one is to fill space with nonprimitive cells, so-called *unit cells*, that fill space without any overlap when translated through some subset of the vectors of a Bravais lattice. Such a unit cell is then bigger than a primitive cell. An example is the full cube depicted in Figure 7(b) that has two times the volume of a primitive cell in a bcc lattice.

The second solution to the problem is to choose a primitive cell with the full symmetry of the Bravais lattice which is always possible. The most common choice is the *Wigner-Seitz cell*. The Wigner-Seitz cell about a lattice point is defined as the region of space that is closer to that point than to any other lattice point. The Wigner-Seitz cell for a two-dimensional Bravais-lattice is shown on the right of Figure 8 and for the bcc and fcc lattice in Figure 9.

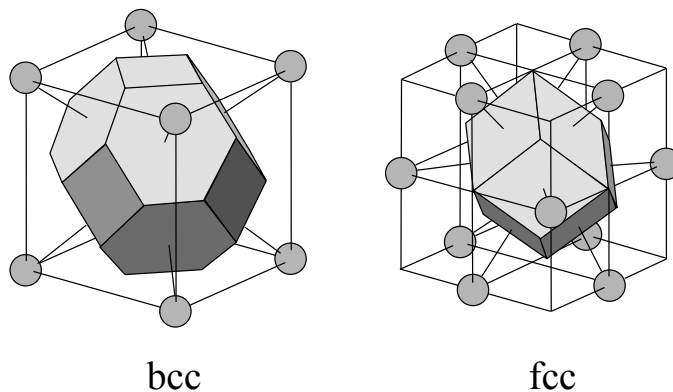


Figure 9: The Wigner-Seitz cells for the bcc and fcc Bravais lattice. In the bcc case one has a truncated octahedron, in the fcc case a rhombic dodecahedron.

A physical crystal can be described by giving its underlying Bravais lattice, together with a description of the arrangement of its atoms within a particular primitive cell. A *crystal structure* consists of identical copies of the same physical unit, called the *basis*, located at all the points of the Bravais lattice. This is also called *lattice with a basis*. To give a two-dimensional example: The vertices of a honeycomb are not a Bravais lattice since the lattice has to be rotated when going from one point to the neighbor to look exactly the same. However, the honeycomb can be represented by a two-dimensional Bravais lattice with a two-point basis, see Figure 10.

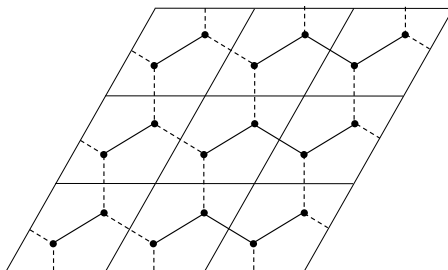


Figure 10: The honeycomb net drawn so as to emphasize that it is a Bravais lattice with a two-point basis.

We mention here two additional important crystal structures. The *diamond lattice* (formed by C atoms in diamond crystals) can be considered as a fcc lattice with the two point bases $\mathbf{0}$ and $(a/4)(\mathbf{e}_x + \mathbf{e}_y + \mathbf{e}_z)$. About 30 elements crystallize in the *hexagonal closed-packed* (hcp) structure. It can be obtained by stacking two-dimensional triangular nets.

3.2 The reciprocal lattice

We come to the definition of the reciprocal lattice which plays a fundamental role in most analytical studies. Consider a set of points \mathbf{R} constituting a Bravais lattice and a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$. For general \mathbf{k} such a plane will not have the periodicity of the Bravais lattice but for certain choices of \mathbf{k} it will. The set of all vectors \mathbf{K} that yield plane waves with the periodicity of a given Bravais lattice is known as its *reciprocal lattice*. \mathbf{K} belongs to the reciprocal lattice of a Bravais lattice of points \mathbf{R} , provided that the relation

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}} \quad (74)$$

holds for any \mathbf{r} , and for all \mathbf{R} of the Bravais lattice. Dividing Eq. 74 by $e^{i\mathbf{k}\cdot\mathbf{r}}$, we can characterize the reciprocal lattice as the set of wave vectors \mathbf{K} satisfying

$$e^{i\mathbf{k}\cdot\mathbf{R}} = 1 \quad (75)$$

for all \mathbf{R} of the Bravais lattice. The Bravais lattice that determines a given reciprocal lattice is often referred to as the *direct lattice*.

We prove now that the reciprocal lattice is itself a Bravais lattice. Let \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 be a set of primitive vectors of the direct lattice. Then the reciprocal lattice can be generated by the three primitive vectors

$$\begin{aligned} \mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\ \mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \\ \mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \end{aligned} \quad (76)$$

To verify that Eq. 76 gives a set of primitive vectors of the reciprocal lattice, note first that the \mathbf{b}_i satisfy

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}. \quad (77)$$

Now any \mathbf{k} can be written as a linear combination of the \mathbf{b}_i :

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3 \quad (78)$$

If \mathbf{R} is any direct lattice vector, then

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (79)$$

where the n_i are integers. Using 77 we find

$$\mathbf{k} \cdot \mathbf{R} = 2\pi(k_1n_1 + k_2n_2 + k_3n_3). \quad (80)$$

For $e^{i\mathbf{k} \cdot \mathbf{R}}$ to be unity for all \mathbf{R} , Eq. 75, $\mathbf{k} \cdot \mathbf{R}$ must be 2π times an integer for any choices of the integers n_i which requires the k_i to be integers as well. Thus condition 75 is fulfilled by just those vectors \mathbf{K} that are linear combinations of the \mathbf{b}_i with integral coefficients. By comparing with Eq. 72 one can see that the reciprocal lattice is a Bravais lattice with the \mathbf{b}_i being a set of primitive vectors. q.e.d.

We note here that one can show along similar lines that the reciprocal of a reciprocal lattice is the original direct lattice again.

We mention now three important examples of reciprocal lattices that can be verified using the above explicit construction. The reciprocal of a simple cubic Bravais lattice (with a cubic primitive cell of side a) is a simple cubic lattice (with a cubic primitive cell of side $2\pi/a$). The reciprocal lattice of the fcc lattice turns out to be the bcc lattice. And the reciprocal of the bcc lattice is the fcc lattice.

If v is the volume of a primitive cell in the direct lattice, then $(2\pi)^3/v$ is the volume of the primitive cell of the reciprocal lattice. The Wigner-Seitz primitive cell of the reciprocal lattice is known as the *first Brillouin zone*. When reference is made to the first Brillouin zone of a particular r -space Bravais lattice, what is meant is the Wigner-Seitz cell of the associated reciprocal lattice. For example, because the reciprocal of the bcc lattice is an fcc lattice, the first Brillouin zone of the bcc lattice, Figure 11(a), is just the fcc Wigner-Seitz cell. Conversely the first Brillouin zone of the fcc lattice, Figure 11(b), is just the bcc Wigner-Seitz cell.

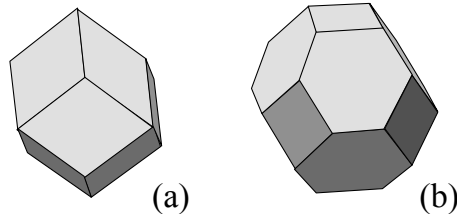


Figure 11: The first Brillouin zone of (a) the bcc lattice and (b) the fcc lattice.

There is an intimate relation between vectors in the reciprocal lattice and planes of points in the direct lattice. Given a particular Bravais lattice a *lattice plane* is defined by any plane that contains at least three non-collinear Bravais lattice points. In fact, it will then be itself a two-dimensional Bravais lattice containing infinitely many lattice points. By a *family of lattice planes* we mean an infinite set of parallel, equally spaced lattice planes, which together contain all the points of the three-dimensional Bravais lattice. This is not a unique construction, see the two examples for the simple cubic Bravais lattice in Figure 12. The reciprocal lattice allows to classify all possible families of lattice planes: For any family of lattice planes separated by distance d , there are reciprocal lattice vectors perpendicular to the planes, the shortest of which has a length $2\pi/d$ (and vice versa).

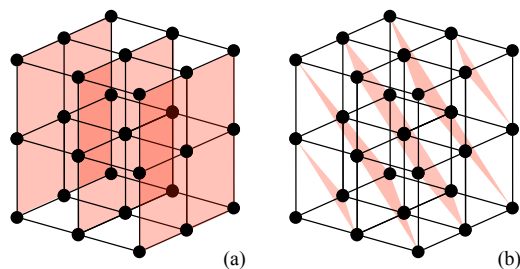


Figure 12: Two different ways of representing a simple cubic Bravais lattices as a family of lattice planes.

Reciprocal lattices and lattice planes play a role in the determination of crystal structures by X-ray diffraction. William Henry and William Laurence Bragg (father and son, Nobelprice 1915) found that cystalline substances show for certain sharply defined wavelength and incident directions intense peaks of scattered X-ray radiation. They accounted for this by regarding a crystal as made by parallel planes of ions, spaced a distance d apart (i.e. lattice planes). This led them to formulate the Bragg condition

$$n\lambda = 2d \sin \theta \quad (81)$$

where λ is the wave length, θ the angle of incidence and n is an integer. This condition means that reflected rays from successive planes interfere constructively, see Figure 13.

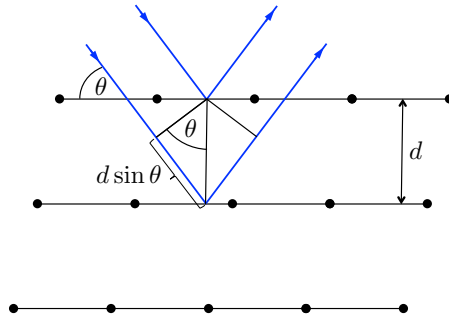


Figure 13: A Bragg reflection from a particular family of lattice planes. The path difference between the two depicted rays is $2d \sin \theta$.

Max van Laue came up with another yet equivalent formulation. He regarded the crystal as composed of identical microscopic objects placed at the sites \mathbf{R} of a Bravais lattice, each of which reradiates the incident radiation in all directions. Sharp peaks will be observed only in directions and at wave lengths for which the rays scattered from all lattice points scatter constructively. To find the condition consider first two scatterers separated by a displacement \mathbf{d} , see Figure 14. The incident ray comes in along a direction $\hat{\mathbf{n}}$ with wave length λ and wave vector $\mathbf{k} = 2\pi\hat{\mathbf{n}}/\lambda$. A scattered wave will be observed in direction $\hat{\mathbf{n}}'$ with wave vector $\mathbf{k}' = 2\pi\hat{\mathbf{n}}'/\lambda$, provided that the path difference between the two rays scattered by the two ions is an integral number of the wave length:

$$d \cos \theta + d \cos \theta' = \mathbf{d} \cdot (\hat{\mathbf{n}} - \hat{\mathbf{n}}') = m\lambda. \quad (82)$$

Multiplying both sides by $2\pi/\lambda$ one finds

$$\mathbf{d} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m. \quad (83)$$

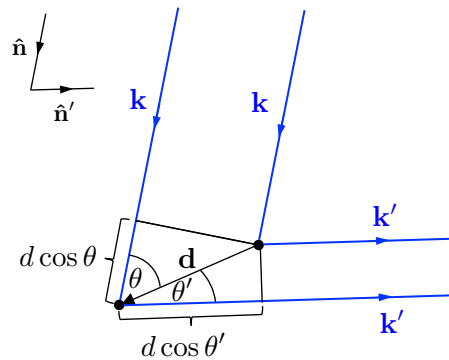


Figure 14: Two rays are scattered at two points separated by \mathbf{d} .

Now consider an array of scatterers at the sites of an Bravais lattice. The condition that all scattered rays interfere constructively is that Eq. 83 holds simultaneously for all values of \mathbf{R} that are Bravais lattice vectors, $\mathbf{R} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m$ which can be rewritten as

$$e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}} = 1. \quad (84)$$

Comparison with Eq. 75 tells us that the Laue condition for constructive interference will occur provided that the change in wave vector, $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, is a vector of the reciprocal lattice.

We give an alternative formulation of the Laue condition, stated entirely in terms of \mathbf{k} . We learned above that $\mathbf{k}' - \mathbf{k}$ is a reciprocal lattice vector and thus also $\mathbf{k} - \mathbf{k}'$ which we call now \mathbf{K} . The length of \mathbf{k} is denoted by $|\mathbf{k}| = k$. The condition $|\mathbf{k}| = |\mathbf{k}'|$ can be written as

$$k = |\mathbf{k} - \mathbf{K}|. \quad (85)$$

Squaring both sides of Eq. 85 yields $k^2 = k^2 - 2\mathbf{k} \cdot \mathbf{K} + K^2$ and thus

$$\mathbf{k} \cdot \hat{\mathbf{K}} = \frac{1}{2}K \quad (86)$$

with $\hat{\mathbf{K}} = \mathbf{K}/K$. In geometrical terms, the incident wave vector \mathbf{k} will satisfy the Laue condition if and only if the tip of the vector lies in a plane that is the perpendicular bisector of a line joining the origin of k -space to a reciprocal lattice point \mathbf{K} , see Figure 15. Such k -space planes are called *Bragg planes*. One can show that the k -space Bragg plane associated with a particular diffraction peak in the Laue formalism is parallel to the family of direct lattice planes in the Bragg formulation.

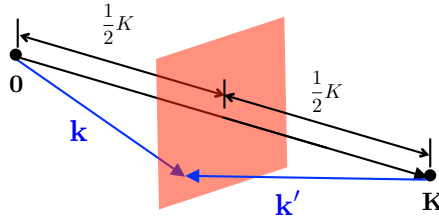


Figure 15: Geometrical interpretation of the Laue condition (see text).

4 Electron levels in a periodic potential

Ions in a metal are arranged in a periodic fashion as discussed in the previous chapter. This leads us to consider the problem of an electron in a periodic potential $U(\mathbf{r})$ with the periodicity of the underlying Bravais lattice, i.e.

$$U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \quad (87)$$

for all Bravais lattice vectors \mathbf{R} . We will still assume independent electrons but they are not free anymore. $U(\mathbf{r})$ can be thought of as an effective potential that contain both the interaction with the ions and the contributions from other electrons. Qualitatively a typical crystalline potential might be expected to have the form shown in Figure 16, resembling the individual atomic potentials as the ions are approached closely and flattening off in the region between ions.

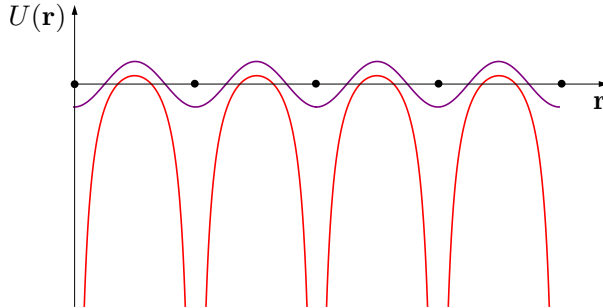


Figure 16: A typical periodic crystalline potential, plotted along a line of ions (red curve) and along a line between planes of ions (purple curve).

4.1 Bloch's theorem

We are thus led to examine the general properties of the Schrödinger equation for a single electron,

$$H\psi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \right) \psi(\mathbf{r}) = \mathcal{E}\psi(\mathbf{r}) \quad (88)$$

that follow from the fact that the potential U has the periodicity 87.

The stationary states of these so-called *Bloch electrons* have the following important property stated in the so-called *Bloch's theorem*: The eigenstates ψ of the one-electron Hamiltonian $H = -\hbar^2\nabla^2/2m + U(\mathbf{r})$, where $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$ for all \mathbf{R} in a Bravais lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (89)$$

where

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) \quad (90)$$

for all \mathbf{R} in the Bravais lattice.

Note that Eqs. 89 and 90 imply

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}). \quad (91)$$

Alternatively Bloch's theorem can be stated as follows: eigenstates of H can be chosen so that associated with each ψ is a wave vector \mathbf{k} such that

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi(\mathbf{r}) \quad (92)$$

for every \mathbf{R} in the Bravais lattice.

We will prove this theorem in a moment. But first let us ask: Which Bloch wave vectors \mathbf{k} are allowed? We impose again the Born-van Karmann boundary condition, this time for a volume commensurate with a primitive cell of the underlying Bravais lattice:

$$\psi(\mathbf{r} + N_i \mathbf{a}_i) = \psi(\mathbf{r}) \quad (93)$$

where the \mathbf{a}_i are three primitive vectors and the N_i are all integers of the order $N^{1/3}$ where $N = N_1 N_2 N_3$ is the total number of primitive cells in the crystal. From Bloch's theorem 91 follows then

$$\psi_{n\mathbf{k}}(\mathbf{r} + N_i \mathbf{a}_i) = e^{iN_i \mathbf{k} \cdot \mathbf{a}_i} \psi_{n\mathbf{k}}(\mathbf{r}) \quad (94)$$

for $i = 1, 2, 3$. Write $\mathbf{k} = x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3$ with the \mathbf{b}_i being primitive vectors of the reciprocal lattice, obeying Eq. 77. Hence

$$e^{2\pi i N_i x_i} = 1. \quad (95)$$

Consequently we must have

$$x_i = \frac{m_i}{N_i} \quad (96)$$

with m_i being an integer leading to the general form of the allowed *Bloch wave vectors*:

$$\mathbf{k} = \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3. \quad (97)$$

The volume $\Delta \mathbf{k}$ of k -space per allowed value of \mathbf{k} is thus

$$\Delta \mathbf{k} = \frac{\mathbf{b}_1}{N_1} \cdot \left(\frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3} \right) = \frac{1}{N} \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{V} \quad (98)$$

where we used in the last step that $2\pi/v$ is the volume of a reciprocal lattice primitive cell ($v = V/N$). This is precisely the result 24 that we found in the free electron case.

We come to the proof of Bloch's theorem. We do this by constructing explicit solutions and showing that these have the form 89. Any function obeying the Born-van Karman boundary condition 93 can be expanded in the set of all plane waves that satisfy that boundary condition and therefore have wave vectors \mathbf{q} of the form 97:

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}}. \quad (99)$$

On the other hand, $U(\mathbf{r})$ has the periodicity of the direct lattice and it can be expanded in plane waves with the periodicity of the lattice:

$$U(\mathbf{r}) = \sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K} \cdot \mathbf{r}} \quad (100)$$

where the \mathbf{K} 's are vectors in the reciprocal lattice. The Fourier coefficients $U_{\mathbf{K}}$ are related to $U(\mathbf{r})$ by

$$U_{\mathbf{K}} = \frac{1}{v} \int_{\text{cell}} U(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r}. \quad (101)$$

(Note: both equations are plane wave expansions, 3D analogues to Fourier series. Eq. 100 has the periodicity of the Bravais lattice whereas Eq. 99 has the whole crystal as one "repeat unit." As a result the \mathbf{q} 's are much more densely spaced in k -space than the \mathbf{K} 's.)

We now insert the expansions 99 and 100 into Schrödinger equation 88. The kinetic term is given by

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \sum_{\mathbf{q}} \frac{\hbar^2}{2m} q^2 c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \quad (102)$$

and the potential energy by

$$U(\mathbf{r}) \psi(\mathbf{r}) = \left(\sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \right) \left(\sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} \right) = \sum_{\mathbf{K}, \mathbf{q}} U_{\mathbf{K}} c_{\mathbf{q}} e^{i(\mathbf{K}+\mathbf{q})\cdot\mathbf{r}}.$$

Now introducing $\mathbf{q}' = \mathbf{K} + \mathbf{q}$ this can be rewritten as

$$U(\mathbf{r}) \psi(\mathbf{r}) = \sum_{\mathbf{K}, \mathbf{q}'} U_{\mathbf{K}} c_{\mathbf{q}'-\mathbf{K}} e^{i\mathbf{q}'\cdot\mathbf{r}} = \sum_{\mathbf{K}', \mathbf{q}} U_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} e^{i\mathbf{q}\cdot\mathbf{r}} \quad (103)$$

where in the second step we renamed \mathbf{K} as \mathbf{K}' and \mathbf{q}' as \mathbf{q} . The Schrödinger equation 88 becomes

$$\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\{ \left(\frac{\hbar^2}{2m} q^2 - \mathcal{E} \right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} \right\} = 0. \quad (104)$$

The plane waves form an orthogonal set, so the term in the curly brackets vanishes for each \mathbf{q} :

$$\left(\frac{\hbar^2}{2m} q^2 - \mathcal{E} \right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} = 0. \quad (105)$$

Choose each \mathbf{q} in the form $\mathbf{q} = \mathbf{k} - \mathbf{K}$ where \mathbf{K} is a reciprocal lattice vector so that \mathbf{k} lies in the first Brillouin zone:

$$\left[\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \mathcal{E} \right] c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}-\mathbf{K}'} = 0. \quad (106)$$

Now change variables $\mathbf{K}' \rightarrow \mathbf{K}' - \mathbf{K}$. One finally arrives at

$$\left[\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \mathcal{E} \right] c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0. \quad (107)$$

This is essentially the Schrödinger equation in momentum space.

For fixed \mathbf{k} in the first Brillouin zone the set of equations 107 for all reciprocal lattice vectors \mathbf{K} couples only those coefficients $c_{\mathbf{k}}$, $c_{\mathbf{k}-\mathbf{K}}$, $c_{\mathbf{k}-\mathbf{K}'}$, $c_{\mathbf{k}-\mathbf{K}''}$, ... whose wave vector differs from \mathbf{k} by a reciprocal vector. This leads to N independent problems with solutions that are superpositions of plane waves containing only the wave vector \mathbf{k} and wave vectors differing from \mathbf{k} by a reciprocal lattice vector:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}} \quad (108)$$

This can be rewritten as

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}} \quad (109)$$

This is of the Bloch form 89 with the periodic function $u(\mathbf{r})$ given by

$$u(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}}. \quad (110)$$

This finishes the proof of the Bloch theorem.

There are 2 quantum numbers that characterize the eigenstates 89 of the Bloch electrons, \mathbf{k} and n . $\hbar\mathbf{k}$ is called *crystal momentum* of the electron but is not really its momentum as $\psi_{n\mathbf{k}}$ is not an eigenstate of the momentum operator $(\hbar/i)\nabla$. Why does there also occur another quantum number, n ? The best way to understand this is to insert solutions in the Bloch form $\psi(\mathbf{r}) = u(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$ into Schrödinger equation 88. This leads to

$$H_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) = \left(\frac{\hbar^2}{2m} \left(\frac{1}{i} \nabla + \mathbf{k} \right)^2 + U(\mathbf{r}) \right) u_{\mathbf{k}}(\mathbf{r}) = \mathcal{E}_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) \quad (111)$$

with

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}). \quad (112)$$

Because of the periodic boundary conditions one can regard Eq. 111 as an Hermitian eigenvalue problem restricted to a single cell of the crystal. We expect on general grounds an infinite family of solutions with discretely spaced eigenvalues, which we label with the *band index* n . \mathbf{k} occurs only as a parameter in the Hamiltonian $H_{\mathbf{k}}$. We thus expect that each energy level varies continuously with \mathbf{k} leading to the description of the levels of an electron in a periodic potential in terms of a family of continuous functions $\mathcal{E}_{n\mathbf{k}}$ or $\mathcal{E}_n(\mathbf{k})$, each with the periodicity of the reciprocal lattice, called the *band structure* of the solid. For each n , the set of energy levels specified by $\mathcal{E}_n(\mathbf{k})$ is called an *energy band*. Because each $\mathcal{E}_n(\mathbf{k})$ is periodic in \mathbf{k} and continuous, it has an upper and a lower bound so that all the levels lie in the band of energies lying between these limits.

The ground state of N Bloch electrons can be similarly constructed as we did for free electrons, see below Eq. 24. But now the quantum levels are labelled by the quantum numbers n and \mathbf{k} , $\mathcal{E}_n(\mathbf{k})$ does not have the simple explicit free

electron form and \mathbf{k} must be confined to a single primitive cell of the reciprocal lattice to avoid double counting. When the lowest levels are filled by a specific number of electrons, two quite distinct types of configuration can result:

1. A certain number of bands is completely filled, the rest is empty. One can show (not in this lecture) that completely filled bands do not contribute to the thermal or electrical conductivity. The difference between the highest occupied level (the top of the highest occupied band) and the lowest unoccupied level (the bottom of the lowest empty band) is known as *band gap*. If the band gap is much larger than $k_B T$ (T : room temperature) one has an *insulator*, if it is comparable to $k_B T$ one has an *intrinsic semiconductor*.
2. A number of bands is partially filled. In that case the energy of the highest occupied level, the Fermi energy \mathcal{E}_F , lies within the range of one or more bands leading to a surface in k -space separating occupied from unoccupied levels. The set of all such surfaces is called the *Fermi surface*, a generalization of the Fermi sphere of free electrons. The parts of the Fermi surface arising from individual partly filled bands are known as *branches* of the Fermi surface. A solid has metallic properties provided that a Fermi surface exists.

4.2 Electrons in a weak periodic potential

Metals in group I, II, III and IV in the periodic table are often referred to as “nearly free electron metals” since it turns out that the conduction electrons can be described as moving in what amounts to an almost constant potential. The starting point of their description is thus the Sommerfeld free electron gas from Chapter 2, modified by the presence of a weak periodic potential. This suggests to go from plane waves, Eq. 15, to the expansion of the exact solution in plane waves, Eq. 108, where the coefficients $c_{\mathbf{k}-\mathbf{K}}$ and the energy of level \mathcal{E} are determined by the set of Eqs. 107.

In the free electron case all the $U_{\mathbf{K}}$'s are zero and Eq. 107 becomes

$$[\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0 - \mathcal{E}] c_{\mathbf{k}-\mathbf{K}} = 0 \quad (113)$$

with

$$\mathcal{E}_{\mathbf{q}}^0 = \frac{\hbar^2}{2m} q^2. \quad (114)$$

Eq. 113 requires for each \mathbf{K} either $c_{\mathbf{k}-\mathbf{K}} = 0$ or $\mathcal{E} = \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$. The latter can occur for only a single \mathbf{K} , unless it happens that some of the $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$ are equal to several different choices of \mathbf{K} . Without such a degeneracy one simply has

$$\mathcal{E} = \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0, \quad \psi_{\mathbf{k}} \sim e^{i(\mathbf{k}-\mathbf{K}) \cdot \mathbf{r}}. \quad (115)$$

If on the other hand there are m reciprocal lattice vectors $\mathbf{K}_1, \dots, \mathbf{K}_m$ satisfying

$$\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 = \dots = \mathcal{E}_{\mathbf{k}-\mathbf{K}_m}^0, \quad (116)$$

then when \mathcal{E} is equal to that common value there are m degenerate plane wave solutions. Since any linear combination of degenerate solutions is also a solution, one has complete freedom in choosing the coefficients $c_{\mathbf{k}-\mathbf{K}}$ for $\mathbf{K} = \mathbf{K}_1, \dots, \mathbf{K}_m$.

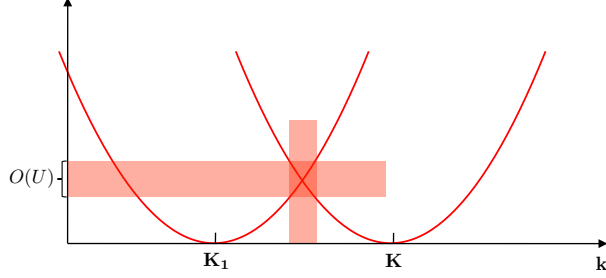


Figure 17: For the range of \mathbf{k} outside the indicated band, the free electron levels $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ and $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$ differ by an amount larger than $O(U)$.

Now suppose the $U_{\mathbf{K}}$ are not zero but very small. What happens? We have two cases, corresponding to the nondegenerate and the degenerate case for free electrons. Now the distinction is, however, not exact equality of several levels but only whether they are equal aside from terms of order U .

Case 1: Fix \mathbf{k} and consider a particular reciprocal lattice vector \mathbf{K}_1 such that the free electron energy $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ is far from the values $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$ for all other \mathbf{K} compared with U (see Figure 17):

$$|\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0| \gg U \quad (117)$$

for fixed \mathbf{k} and all $\mathbf{K} \neq \mathbf{K}_1$ (U refers here and in the following to a typical Fourier component of the potential). We wish to investigate the effect of the weak potential on that free electron level. Using the set of equations given by 107 and retaining only terms of order U^2 one finds after a few steps (not shown here)

$$\mathcal{E} = \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 + \sum_{\mathbf{K}} \frac{|U_{\mathbf{K}-\mathbf{K}_1}|^2}{\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0 - \mathcal{E}_{\mathbf{k}-\mathbf{K}}^0} + O(U^3). \quad (118)$$

This shows that weakly perturbed nondegenerate bands repel each other: A level $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$ with $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0 < \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ contributes a term in Eq. 117 that raises the value of \mathcal{E} whereas the opposite is true for a level $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0$ with $\mathcal{E}_{\mathbf{k}-\mathbf{K}}^0 > \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$. Most importantly, the shift is very small, of order U^2 .

Case 2: Suppose the value of \mathbf{k} is such that there are (without loss of generality) two (and only two) reciprocal lattice vectors \mathbf{K}_1 and \mathbf{K}_2 with $\mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0$ and $\mathcal{E}_{\mathbf{k}-\mathbf{K}_2}^0$ within order U of each other. The set of equations 107 reduces then to

$$\begin{aligned} (\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_1}^0) c_{\mathbf{k}-\mathbf{K}_1} &= U_{\mathbf{K}_2-\mathbf{K}_1} c_{\mathbf{k}-\mathbf{K}_2}, \\ (\mathcal{E} - \mathcal{E}_{\mathbf{k}-\mathbf{K}_2}^0) c_{\mathbf{k}-\mathbf{K}_2} &= U_{\mathbf{K}_1-\mathbf{K}_2} c_{\mathbf{k}-\mathbf{K}_1}. \end{aligned} \quad (119)$$

With the new variables $\mathbf{q} = \mathbf{k} - \mathbf{K}_1$ and $\mathbf{K} = \mathbf{K}_2 - \mathbf{K}_1$ this can be rewritten as

$$\begin{aligned} (\mathcal{E} - \mathcal{E}_{\mathbf{q}}^0) c_{\mathbf{q}} &= U_{\mathbf{K}} c_{\mathbf{q}-\mathbf{K}}, \\ (\mathcal{E} - \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0) c_{\mathbf{q}-\mathbf{K}} &= U_{-\mathbf{K}} c_{\mathbf{q}} = U_{\mathbf{K}}^* c_{\mathbf{q}}. \end{aligned} \quad (120)$$

Now $\mathcal{E}_{\mathbf{q}}^0 = \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0$ for some reciprocal lattice vector \mathbf{K} only when $|\mathbf{q}| = |\mathbf{q} - \mathbf{K}|$. This means that \mathbf{q} must lie on the plane bisecting the line joining the origin of k -space to the reciprocal lattice vector \mathbf{K} . In other words, the point \mathbf{q} lies in the Bragg plane determined by \mathbf{K} (see Figure 15 with $\mathbf{k} = \mathbf{q}$ and $\mathbf{k}' = \mathbf{q} - \mathbf{K}$). In short, a weak periodic potential has a major effect (i.e. an effect of order U) on only those free electron levels whose wave vectors are close to ones at which Bragg reflection occurs.

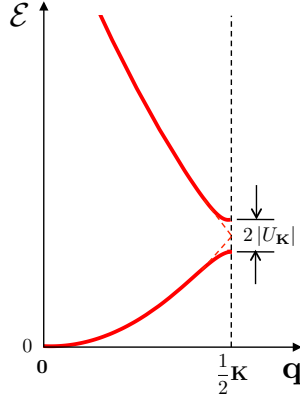


Figure 18: Plot of the two energy bands given by Eq. 121 for \mathbf{q} parallel to \mathbf{K} (the lower band corresponds to the minus sign and the upper band to the plus sign). The free electron values are denoted by the red dotted lines

Equations 120 have a solution when

$$\begin{vmatrix} \mathcal{E} - \mathcal{E}_{\mathbf{q}}^0 & -U_{\mathbf{K}} \\ -U_{\mathbf{K}}^* & \mathcal{E} - \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0 \end{vmatrix} = 0$$

leading to the quadratic equation $(\mathcal{E} - \mathcal{E}_{\mathbf{q}}^0)(\mathcal{E} - \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0) = |U_{\mathbf{K}}|^2$. The two roots

$$\mathcal{E} = \frac{1}{2}(\mathcal{E}_{\mathbf{q}}^0 + \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0) \pm \sqrt{\left(\frac{\mathcal{E}_{\mathbf{q}}^0 - \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0}{2}\right)^2 + |U_{\mathbf{K}}|^2} \quad (121)$$

give the dominant effect of the weak periodic potential on the energies of the two free electron levels $\mathcal{E}_{\mathbf{q}}^0$ and $\mathcal{E}_{\mathbf{q}-\mathbf{K}}^0$ when \mathbf{q} is close to the Bragg plane determined by \mathbf{K} , see Figure 18. If \mathbf{q} lies *on* the Bragg plane, $\mathcal{E}_{\mathbf{q}}^0 = \mathcal{E}_{\mathbf{q}-\mathbf{K}}^0$, Eq. 121 simplifies to

$$\mathcal{E} = \mathcal{E}_{\mathbf{q}}^0 \pm |U_{\mathbf{K}}|. \quad (122)$$

Thus at all points on the Bragg plane one level is uniformly raised by $|U_{\mathbf{K}}|$ and the other is uniformly lowered by the same amount.

We close this lecture by showing how in one dimension the electron bands can be constructed. Start with the electronic levels of a free electron which is a parabola in k (Figure 19(a)). The parabola is not (much) affected by a weak periodic potential except near Bragg “planes” which are found by drawing other free electron parabolas, e.g. centered around K (Fig 19(b)). Where they cross they need to be modified as discussed above (Figure 19(c)) which modifies the original free electron parabola as shown in Figure 19(d). Doing this for all Bragg planes we end up with Figure 19(e), the so-called *extended zone scheme*. Shifting all the pieces back into the first Brillouin zone through reciprocal lattice vectors we find the so-called *reduced-zone scheme* representation (Figure 19(f)). A highly redundant representation, the *repeated-zone scheme* (Figure 19(g)), periodically extends Figure 19(f) and is the most general representation of the electronic levels.

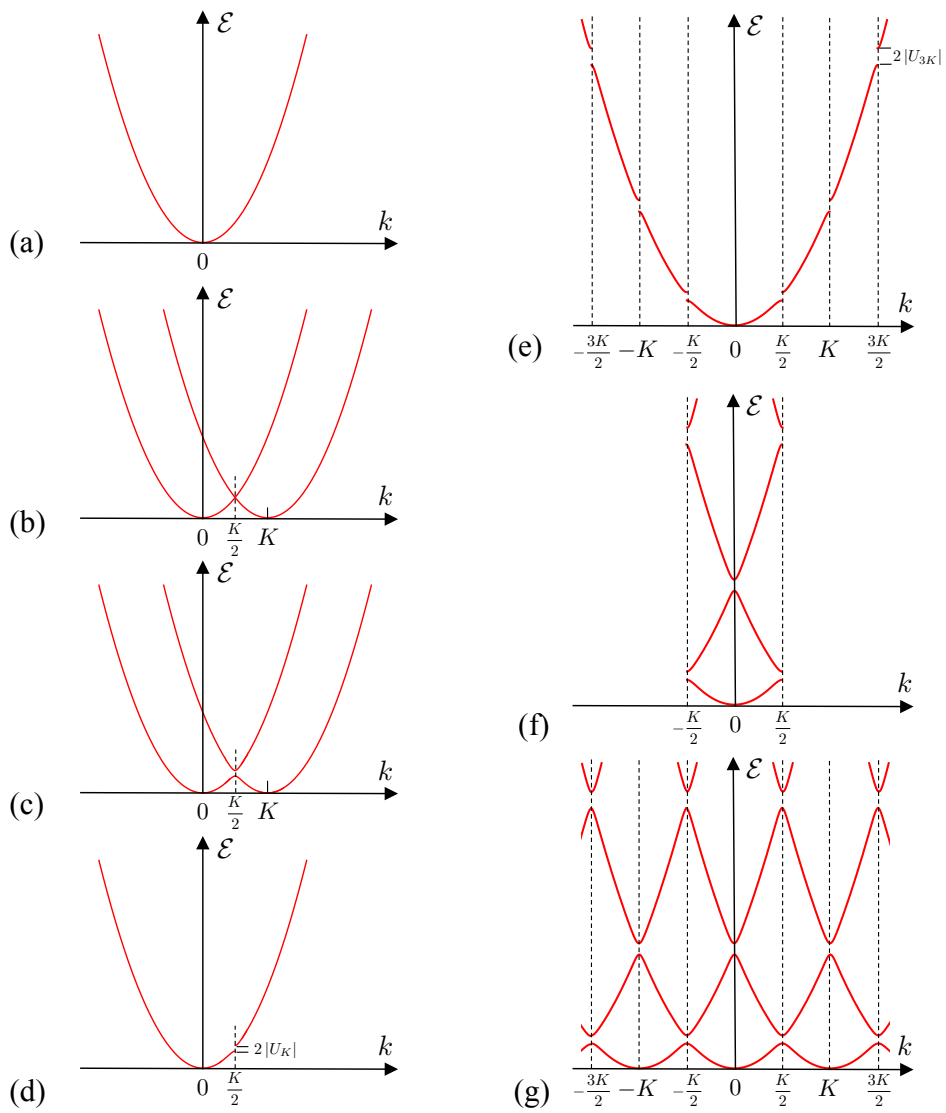


Figure 19: How to construct the energy bands for a 1D solid: from the free electron parabola (a) to the repeated-zone representation (g), see text for details.