

# Solid State Physics

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Last update: October 11, 2020

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# 1 Lattice structure

A *crystal* can be seen as the composition of two patterns: a lattice, which is a topological motive which represent the periodicity of the crystal, and a basis, which show the physical structure of the pattern tile.

A *Bravais lattice* is a set of points, connected by vectors, which are linear integer combinations of the primitive cell sides. Repeating the basis tile in each Bravais lattice point, the crystal is formed. A point on the Bravais lattice can be therefore represented, given the sides of the basis cells  $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ , as:

$$\vec{R} = m\vec{a}_1 + n\vec{a}_2 + l\vec{a}_3 \quad m, n, l \in \mathbb{Z}$$

The periodicity of the lattice result in the periodicity of each generic function  $f(\vec{r})$  defined on the lattice:

$$f(\vec{r}) = f(\vec{r} + \vec{R}(m, n, l)) \quad \forall m, n, l \in \mathbb{Z}$$

There can be multiple modes to create a basis tile (and therefore a Bravais lattice) given the element one want to stack. A concrete example can be seen in stacking cannon balls: there are two different ways to stack cannon balls (FCC and HCP), both stable and with the same efficiency in filling space.

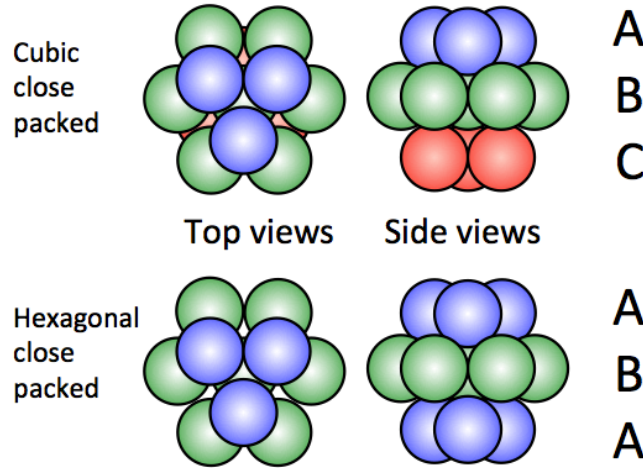


Figure 1: Cannon balls stacked in different ways

Given a crystal, sometimes is not trivial to find the basis cell. The *Wigner Seitz cell* is a easy-to-find basis unitary cell. To find it, it's enough to connect a selected atom with all the neighbors and draw the axis planes to each connection. The portion of space containing the initial atom and defined by all the drawn planes will be a unitary basis cell.

## 1.1 Reciprocal lattice

Remember that a generic function on a crystal is forced to have translational invariance:

$$f(\vec{r}) = f(\vec{r} + \vec{R})$$

But Fourier-expanding  $f$ , one obtain:

$$f(\vec{r}) = \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$$

and forcing the previous condition:

$$\begin{aligned} f(\vec{r}) &= f(\vec{r} + \vec{R}) \\ \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G}\cdot\vec{r}} &= \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G}\cdot(\vec{r}+\vec{R})} \\ \sum_{\vec{G}} f(\vec{G}) e^{i\vec{G}\cdot\vec{R}} &= 1 \end{aligned}$$

Since this relation must be valid for each function, and therefore for each value of  $f(\vec{G})$ , one obtain:

$$e^{i\vec{G}\cdot\vec{R}} = 1$$

This define a set of vectors  $\{\vec{G}\}$ , which are the vector appearing in the fourier expansion of a generic function defined over the lattice. This set of vectors, uniquely defined by the Bravais lattice vectors  $\{\vec{R}\}$ , is called *reciprocal lattice*. The primitive cells in the reciprocal lattice are called *Brillouin cells*. Experimentally, it's more simple to measure the reciprocal lattice instead than the direct one.

Can be proven that, given the basis of the direct lattice  $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$  a basis of the reciprocal lattice is:

$$\begin{cases} \vec{b}_1 = \frac{2\pi}{V} \vec{a}_2 \times \vec{a}_3 \\ \vec{b}_2 = \frac{2\pi}{V} \vec{a}_3 \times \vec{a}_1 \\ \vec{b}_3 = \frac{2\pi}{V} \vec{a}_1 \times \vec{a}_2 \end{cases}$$

where  $V$  is the volume of the primitive cell,  $V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ .

## 1.2 Bragg's Law

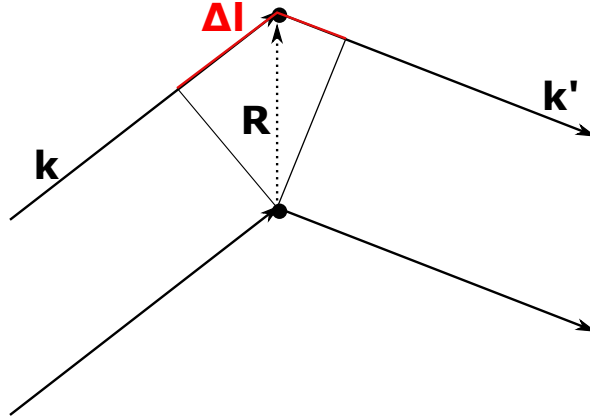


Figure 2: Bragg interference

Let's consider an electromagnetic wave, with wavevector  $\vec{k}$ , hitting the crystal and being scattered, with a new wavevector  $\vec{k}'$ . Considering an elastic scattering, must be valid  $|\vec{k}| = |\vec{k}'|$ .

Let's consider, as in figure 2, a generic couple of atoms in the Bravais lattice. The two scattered beams have an optical-path difference  $\Delta l$  which is:

$$\Delta l = \vec{R} \cdot \frac{\vec{k} - \vec{k}'}{k}$$

To have a constructive interference, the optical-path difference must be an integer multiple of the wavelength:

$$\begin{aligned} \Delta l = \vec{R} \cdot \frac{\vec{k} - \vec{k}'}{2\pi/\lambda} &\stackrel{!}{=} n\lambda \\ \vec{R} \cdot (\vec{k} - \vec{k}') &= 2\pi n \end{aligned}$$

which is the same condition of the reciprocal lattice! This means that **there is constructive interference if and only if the wavevector variation, i.e.  $\vec{k} - \vec{k}'$ , is a vector of the reciprocal lattice.**

$$\vec{k} - \vec{k}' = \vec{G}$$

What does this mean, figuratively? Let's square both terms:

$$\begin{aligned} (\vec{k}')^2 &= (\vec{k} - \vec{G})^2 \\ \vec{G}^2 - 2\vec{k}\vec{G} &= 0 \\ \vec{k} \cdot \hat{G} &= \frac{G}{2} \end{aligned}$$

which means that if the projection of  $\vec{k}$  on a reciprocal lattice  $\vec{G}$  falls in its middle point, then the wavevector  $\vec{k} + \vec{G}$  will be a maximum in the interference pattern.

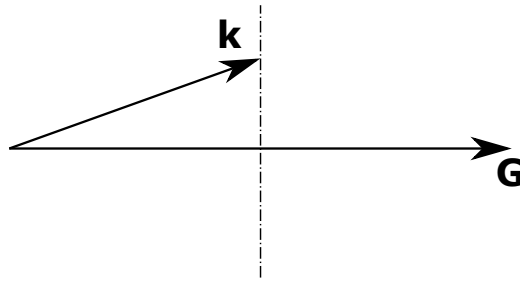


Figure 3: Bragg interference condition visualized

### 1.3 Rotation symmetries

The crystal in general can show rotation symmetries: which means, the crystal is invariant over rotation of an angle  $\phi$ . Not all angles are possible: consider a couple of points, and rotate each point with respect to the other of the rotation symmetry angle  $\phi$ .

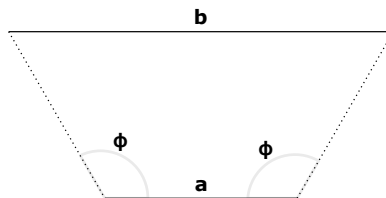


Figure 4: Rotation symmetries

If  $a$  is a basis side, then  $b$  must be a multiple of that side:

$$\begin{aligned} b &= ma \\ a - 2a \cos \phi &= ma \\ \cos \phi &= \frac{1 - m}{2} \\ \left| \frac{1 - m}{2} \right| &\leq 1 \\ m = 0, 1, 2, 3 \quad \phi &= \frac{2\pi}{6}, \frac{2\pi}{4}, \frac{2\pi}{3}, \frac{2\pi}{2} \end{aligned}$$

Therefore, the only possible rotational symmetries are

$$\phi = \frac{2\pi}{m} \quad m = 1, 2, 3, 4, 6$$

## 2 Motion equations

A crystal can be considered a collections of electrons ( $m, -e, n, \vec{r}_i$ ) and nuclei ( $M, Ze, N, \vec{R}_I$ ) where  $m \ll M$ .

The Hamiltonian of the system is therefore:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m} \sum_i \vec{\nabla}_i^2}_{T_e} + \underbrace{-\frac{\hbar^2}{2M} \sum_I \vec{\nabla}_I^2}_{T_N} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{V_{ee}} + \underbrace{\frac{1}{2} \sum_{I \neq J} \frac{Z^2 e^2}{|\vec{R}_I - \vec{R}_J|}}_{V_{NN}} - \underbrace{\sum_{i,I} \frac{Ze^2}{|\vec{R}_I - \vec{r}_i|}}_{V_{Ne}}$$

and the Shrödinger equation to be solved is:

$$\begin{aligned} \hat{H}\Psi_T(\vec{R}, \vec{r}) &= E\Psi_T(\vec{R}, \vec{r}) \\ (T_N + T_e + V_{ee} + V_{NN} + V_{Ne})\Psi_T(\vec{R}, \vec{r}) &= E\Psi_T(\vec{R}, \vec{r}) \end{aligned}$$

As we will consider later, the order of magnitude of the nuclei motion ( $\omega_n \approx \omega_{Debye} \approx 10^{14}$ ) is way slower than the electrons one ( $\omega_e \approx \omega_{plasma} = 10^{16}$ ). Therefore, we can proceed in the *BornOppenheimer approximation*:

$$\Psi_T(\vec{r}, \vec{R}) = \Phi_N(\vec{R})\Psi(\vec{r}, \vec{R}) \quad \text{s.t.} \quad \vec{\nabla}_{\vec{R}}\Psi(\vec{r}, \vec{R}) = 0$$

when  $\Phi_N$  govern the nuclei motions while  $\Psi$  the electrons one. Therefore, the Shrödinger equations becomes:

$$\Psi T_N \Phi_N + \Phi_N T_e \Psi + (V_{ee} + V_{NN} + V_{Ne})\Phi_N \Psi = E\Phi_N \Psi$$

which can be split into

$$\begin{cases} T_N \Phi_N + \mathcal{E}(\vec{R})\Phi_N = E\Phi_N \\ T_e \Psi + (V_{ee} + V_{NN} + V_{Ne})\Psi = \mathcal{E}(\vec{R})\Psi \end{cases}$$

Left-multiplying the second equation by  $\Psi$  and integrating, one obtain:

$$\mathcal{E}(\vec{R}) = V_{NN} + \langle \Psi | T_e + V_{ee} + V_{Ne} | \Psi \rangle$$

which means that the nuclei, in their interactions, see a potential which is given by  $V_{NN}$  plus another factor, called *screening term*: is the effect of electrons which permeate the space.

The nuclei motion is slow: considering an average temperature of  $300K$ , their quantum wavelength can be estimated as

$$\lambda = \frac{\hbar}{P} = \frac{\hbar}{\sqrt{2ME}} \approx \frac{\hbar}{\sqrt{2M(3/2k_B T)}} \approx \text{pm}$$

which is way smaller than the mean interatomic distance. This means that nuclei can be studied through the classical motion equation, following Newton rules. The nuclei equation can be therefore replaced with

$$M \frac{d^2 \vec{R}_I}{dt^2} = -\frac{\partial \mathcal{E}(\vec{R})}{\partial \vec{R}_I}$$

Finally, the equations which govern the motion of a crystal are:

$$\begin{cases} M \frac{d^2 \vec{R}_I}{dt^2} = -\frac{\partial \mathcal{E}(\vec{R})}{\partial \vec{R}_I} \\ T_e \Psi + (V_{ee} + V_{NN} + V_{Ne})\Psi = \mathcal{E}(\vec{R})\Psi \end{cases}$$

### 3 Lattice static

Multiple forces can be responsible of nuclei positioning, depending on charge, mass and distance of the nuclei. Crystalline bounds can be considered in 4 types: VanDerWaals, Ionic, Metallic, Covalent.

#### 3.1 Van der Waals forces

Van der Waals forces are given by the interaction of neutral systems, through dipole fluctuations. Their amplitude goes like  $R^{-6}$ . This can be proven throughout a simple toy-model: consider a couple of nuclei, each with a bounded electron which can harmonically oscillate around the nucleus.

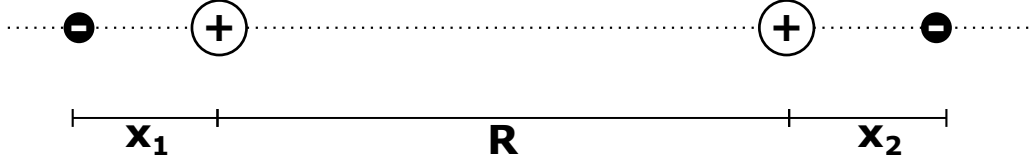


Figure 5: Van der Waals toy model

The interatomic interaction is given by:

$$H_I = \frac{e^2}{R} + \frac{e^2}{R + x_1 + x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R + x_2}$$

In the approximation  $x_1, x_2 \ll R$  and remembering the Taylor expansion  $\frac{1}{1+x} \approx 1 - x + x^2 + \dots$ , one obtain:

$$\begin{aligned} H_I &= \frac{e^2}{R} \left( 1 + 1 - \frac{x_1 + x_2}{R} + \left( \frac{x_1 + x_2}{R} \right)^2 - 1 + \frac{x_1}{R} - \left( \frac{x_1}{R} \right)^2 - 1 + \frac{x_2}{R} - \left( \frac{x_2}{R} \right)^2 \right) \\ &= \frac{2e^2 x_1 x_2}{R^3} \end{aligned}$$

This lead to an Hamiltonian in the form:

$$\begin{aligned} H &= \frac{p_1^2 + p_2^2}{2m} + k \frac{x_1^2 + x_2^2}{2} + \frac{2e^2 x_1 x_2}{R^3} \\ x_{S,A} &= \frac{x_1 \pm x_2}{\sqrt{2}}, \quad p_{S,A} = \frac{p_1 \pm p_2}{\sqrt{2}} \\ &= \frac{p_S^2 + p_A^2}{2m} + \underbrace{\frac{1}{2} \left( k + \frac{2e^2}{r^3} \right)}_{m\omega_+^2} x_S^2 + \underbrace{\frac{1}{2} \left( k - \frac{2e^2}{r^3} \right)}_{m\omega_-^2} x_A^2 \end{aligned}$$

which is clearly the equation for a couple of harmonic oscillators! We know that the ground state energy is

$$\begin{aligned} U &= \frac{\hbar}{2} (\omega_+ + \omega_-) \\ &= \frac{\hbar}{2} \sqrt{\frac{k}{m}} \left( \sqrt{1 + \frac{2e^2}{kr^3}} + \sqrt{1 - \frac{2e^2}{kr^3}} \right) \\ \omega_0 &= \sqrt{\frac{k}{m}}, \quad \sqrt{1+x} \approx 1 + \frac{x}{2} + \frac{x^2}{8} + \dots \\ &= \frac{\hbar\omega_0}{2} \left( 1 + \frac{e^2}{kr^3} + \frac{1}{8} \left( \frac{2e^2}{kr^3} \right)^2 + 1 - \frac{e^2}{kr^3} + \frac{1}{8} \left( \frac{2e^2}{kr^3} \right)^2 \right) \\ &= \hbar\omega_0 + \frac{\hbar\omega_0 e^4}{2k^2} \frac{1}{R^6} \end{aligned}$$

To be more precise, the potential is not harmonic. In fact, when approaching the atom, a repulsive force appears due to Pauli principle. There are different ways to model this attraction: some of the most used are the LennardJones potential ( $aR^{-12} - bR^{-6}$ ) or the BornMeyer one ( $ae^{-R} - bR^{-6}$ ). But the harmonic one is a good approximation for our example.

### 3.2 Ionic crystal

A ionic crystal is a crystal composed by cations and anions. The energy of the interaction between two generic atoms can be expressed as

$$U_{ij} = \lambda e^{-R_{ij}/\rho} + \frac{q_i q_j}{R_{ij}} \quad R_{ij} = |\vec{R}_i - \vec{R}_j|$$

where the first term is the Fermi repulsion and the second one is the Coulomb interaction. Considering the first term negligible for all atoms but the nearest neighbors, the energy associated to a single atom can be written as:

$$U_i = \sum_{j \neq i} U_{ij} = z \lambda e^{-R/\rho} - \frac{q^2}{R} \sum_{j \neq i} \frac{1}{p_{ij}}$$

where  $R$  is the nearest-neighbors distance and  $p_{ij}$  is a factor that consider the ratio between  $r_{ij}/R$  and the sign of  $q_i q_j$ . If the space is isotropic, the total energy of the crystal is:

$$\begin{aligned} U = N U_i &= N z \lambda e^{-R/\rho} - \frac{N q^2}{R} \underbrace{\sum_{j \neq i} \frac{1}{p_{ij}}}_{\alpha} \\ &= N z \lambda e^{-R/\rho} - \frac{N q^2}{R} \alpha \end{aligned}$$

where  $\alpha$  is the Madelung constant; observe that it doesn't depend on the lattice constant, but only on the crystal structure and ordering! Typical values are 1.6 – 1.7.

To find equilibrium, one must search for the minimum of  $U$ :

$$\begin{aligned} \frac{dU}{dR} &= 0 \\ -\frac{N z \lambda}{\rho} e^{-R/\rho} + \frac{N q^2}{R^2} \alpha &= 0 \\ e^{-R/\rho} &= \frac{q^2 \alpha \rho}{z \lambda R^2} \end{aligned}$$

which lead to a minimum energy of

$$U_0 = -\frac{N \alpha q^2}{R} \left( 1 - \frac{\rho}{R} \right)$$

## 4 Lattice dynamics

Some phenomena have no explanation if you doesn't consider lattice motion, e.g. specific heat dependence from T, melting, electrical properties, light scattering, ...

The atom positions can be split in equilibrium position and displacement, assumed way smaller:

$$\vec{r}_I(t) = \vec{R}_I + u(\vec{R}, t)$$



Considering a 1D crystal:

$$\begin{aligned}
U &= \frac{1}{2} \sum_{n,m} \Phi(|na + u_n - ma - u_m|) \\
&= \frac{1}{2} \sum_{n,m} \Phi(|(n-m)a + \underbrace{u_n - u_m}_{\varepsilon}|) \\
&\approx \frac{1}{2} \sum_{n,m} \Phi(|(n-m)a|) + \underbrace{\frac{1}{2} \sum_{n,m} \Phi' \varepsilon}_0 + \frac{1}{4} \sum_{n,m} \Phi'' \varepsilon^2 \\
&= U_0 + \frac{1}{4} \sum_{n,m} (u_n - u_m)^2 \Phi'' \\
&\quad \text{Assuming NN interaction} \\
&= U_0 + \frac{1}{2} \tilde{k} \sum_n (u_n - u_{n+1})^2
\end{aligned}$$

In a classical point of view, the equation of motion is:

$$\begin{aligned}
M\ddot{u}_n &= -\frac{dU}{du_n} \\
&= -\tilde{k}(u_n - u_{n+1}) + \tilde{k}(u_{n-1} - u_n) \\
&= \tilde{k}(u_{n+1} + u_{n-1} - 2u_n) \\
&= \tilde{k}a^2 u_n''
\end{aligned} \tag{1}$$

that is a wave equation, with solution  $e^{i(kx-\omega t)}$ . But this is an approximation:  $n$  is an integer and can't be interpreted as a continuum variable.

Let's consider, to detect dispersion relation, discrete coordinates:

$$\begin{aligned}
u_n &= \mathcal{E} e^{i(kna-\omega t)} \rightarrow u_{n+1} = u_n e^{ika} \\
-M\omega^2 &= \tilde{k}[e^{ika} + e^{-ika} - 2] \\
-M\omega^2 &= -4\tilde{k} \sin^2\left(\frac{ka}{2}\right) \\
\omega &= \sqrt{\frac{4\tilde{k}}{M}} \left| \sin \frac{ka}{2} \right|
\end{aligned} \tag{2}$$

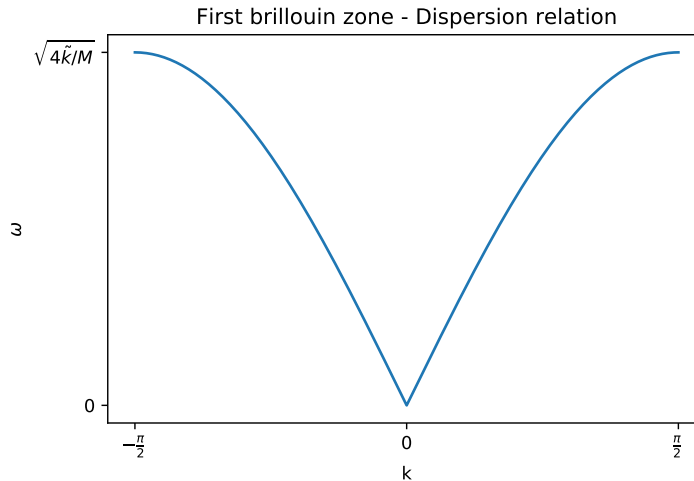


Figure 6: Eq. (2), visualized

The boundary condition, then, must be considered. For example, let's consider periodic boundary conditions:

$$\begin{aligned} u_N &= u_0 \\ e^{ikNa} &= 0 \\ k &= \frac{2\pi}{L}m \quad m \in \mathbb{Z} \end{aligned}$$

Considering only the first Brillouin zone, i.e.  $k \in [-\pi/2, \pi/2]$ , there are only  $N$  possible wavevectors! It's easy to demonstrate that the Brillouin zones are all equivalents, i.e. the wave with wavevector  $k$  and the wave with wavevector  $k + n\pi$  are, in our discretized space, the same wave.

This also allow to find the sound speed in a crystal: from eq. (1), can be deduced that:

$$v_s = \sqrt{\frac{\tilde{k}a^2}{M}}$$

that is compatible with the sound velocity classically (mechanically) derived.

#### 4.1 Crystal with a basis

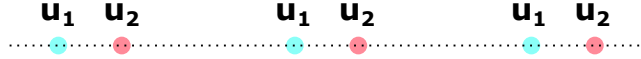


Figure 7: 1D crystal with basis.

Let's now consider a crystal with a biatomic basis. The energy of the system, considering two harmonic nearest-neighbors potential with constants  $\tilde{k}$  and  $\tilde{G}$  around the equilibrium positions, can be written as:

$$U = \frac{\tilde{k}}{2} \sum_n (u_1^n - u_2^n)^2 + \frac{\tilde{G}}{2} \sum_n (u_2^n - u_1^{n+1})^2$$

Considering the Newton motion equations:

$$\begin{cases} m \frac{d^2 u_1}{dt^2} = -\frac{\partial U}{\partial u_1} \\ m \frac{d^2 u_2}{dt^2} = -\frac{\partial U}{\partial u_2} \end{cases}$$

and supposing an oscillating solution,  $u_{1,2} = \varepsilon_{1,2} e^{i(kx - \omega t)}$ , one can find the dispersion relation:

$$\begin{cases} -m\ddot{u}_1^i = \tilde{k}(u_1^i - u_2^i) - \tilde{G}(u_2^{i-1} - u_1^i) \\ -m\ddot{u}_2^i = -\tilde{k}(u_1^i - u_2^i) + \tilde{G}(u_2^i - u_1^{i+1}) \\ m\omega^2 \varepsilon_1 = \tilde{k}(\varepsilon_1 - \varepsilon_2) - \tilde{G}(\varepsilon_2 e^{-ika} - \varepsilon_1) \\ m\omega^2 \varepsilon_2 = -\tilde{k}(\varepsilon_1 - \varepsilon_2) + \tilde{G}(\varepsilon_2 - \varepsilon_1 e^{ika}) \\ (m\omega^2 - \tilde{k} - \tilde{G})\varepsilon_1 = -(\tilde{k} + \tilde{G}e^{-ika})\varepsilon_2 \\ (m\omega^2 - \tilde{k} - \tilde{G})\varepsilon_2 = -(\tilde{k} + \tilde{G}e^{ika})\varepsilon_1 \end{cases}$$

Performing the product between the two lines and simplifying  $\varepsilon_1 \varepsilon_2$ :

$$\begin{aligned} (m\omega^2 - \tilde{k} - \tilde{G})^2 &= (\tilde{k} + \tilde{G}e^{-ika})(\tilde{k} + \tilde{G}e^{ika}) \\ m\omega^2 - \tilde{k} - \tilde{G} &= \pm \sqrt{\tilde{k}^2 + \tilde{G}^2 + 2\tilde{k}\tilde{G}\cos(ka)} \\ \omega^2 &= \frac{\tilde{k} + \tilde{G}}{m} \pm \frac{1}{m} \sqrt{\tilde{k}^2 + \tilde{G}^2 + 2\tilde{k}\tilde{G}\cos(ka)} \end{aligned} \quad (3)$$

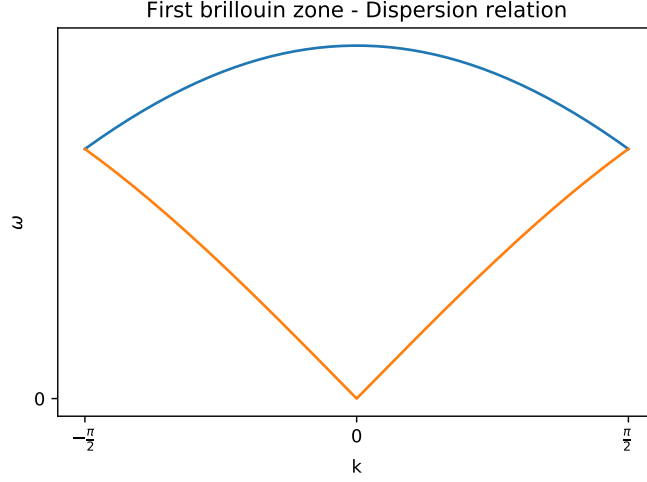


Figure 8: Eq. (3), visualized

From the last equation, two different solutions are present. Moreover, one can consider the ratio between the two amplitudes:

$$\begin{aligned} \frac{\varepsilon_1}{\varepsilon_2} &= -\frac{m\omega^2 - \tilde{k} - \tilde{G}}{\tilde{k} + \tilde{G}e^{ika}} \\ &= \mp \sqrt{\frac{\tilde{k} + \tilde{G}e^{-ika}}{\tilde{k} + \tilde{G}e^{ika}}} \end{aligned}$$

Observe that there are therefore 2 different branches: the branch in which all the atoms are in phase is called *acoustic branch*, and it's the same branch observed in the monoatomic crystal. The other one, called *optic branch*, is an higher-frequencies branch, which exists even at  $k = 0$ . In this case, the two different species oscillate in phase opposition, i.e.  $\varepsilon_1\varepsilon_2 < 0$ .

## 4.2 Three-dimensional crystal

Let's now consider a two-dimensional crystal, and an harmonic potential. The energy of the system can be written as:

$$\begin{aligned} U &= \frac{1}{2} \sum_{\vec{R}, \vec{R}'} [u_\mu(\vec{R}) - u_\mu(\vec{R}')] \Phi''_{\mu\nu}(\vec{R} - \vec{R}') [u_\nu(\vec{R}) - u_\nu(\vec{R}')] \\ &= \frac{1}{2} \sum_{\vec{R}, \vec{R}'} u_\mu(\vec{R}) D_{\mu\nu}(\vec{R} - \vec{R}') u_\nu(\vec{R}') \end{aligned}$$

where  $D$  is a matrix such that:

$$\begin{aligned} D_{\mu\nu}(\vec{R}) &= D_{\mu\nu}(-\vec{R}) \\ \sum_{\vec{R}} D_{\mu\nu}(\vec{R}) &= 0 \end{aligned}$$

where the last condition is granted by the definition of  $D(0)$ .

Recalling the Newton motion equations,

$$M\ddot{u} = -\frac{\partial U}{\partial u} \quad \rightarrow \quad M\ddot{u}(\vec{R}) = \sum_{\vec{R}'} D(\vec{R} - \vec{R}') u(\vec{R}')$$

and supposing a periodic oscillating solution,  $u = \vec{\varepsilon} e^{i(\vec{k} \cdot \vec{R} - \omega t)}$ :

$$-M\omega^2 \vec{\varepsilon} = - \underbrace{\sum_{\vec{R}'} D(\vec{R}') e^{-i\vec{k} \cdot \vec{R}'} \vec{\varepsilon}}_{D(\vec{k})}$$

which reduces to the eigenvalues equation:

$$D(\vec{k}) \vec{\varepsilon} = M\omega^2 \vec{\varepsilon}$$

But let's observe what the  $D(\vec{k})$  matrix is:

$$\begin{aligned} D(\vec{k}) &= \sum_{\vec{R}} D(\vec{R}) e^{i\vec{k} \cdot \vec{R}} \\ &= \frac{1}{2} \sum_{\vec{R}} D(\vec{R}) \left( e^{i\vec{k} \cdot \vec{R}} + e^{-i\vec{k} \cdot \vec{R}} \right) \\ &= \sum_{\vec{R}} D(\vec{R}) \cos(\vec{k} \cdot \vec{R}) \end{aligned}$$

From the last relation is clear that  $D$  is a real matrix! Therefore, it has 3 real eigenvalues: 3 (acoustic) branches are present!

Consider a crystal in  $d$  dimension with  $n$  atoms in basis: therefore,  $d$  acoustic branches and  $d(n-1)$  optical branches are present, for a total of  $nd$  branches. Pay attention that, if the crystal is somehow symmetric, some branches can be degenerate, which means some branches can collapse in a single branch (with multiplicity greater than 1).

### 4.3 Thermal properties

Consider the Hamiltonian of the system:

$$H = \sum_{\vec{R}} \frac{p^2}{2M} + \frac{1}{2} \sum_{\vec{R}, \vec{R}'} u(\vec{R}) D(\vec{R} - \vec{R}') u(\vec{R}') + U_0$$

remembering that both  $p$  and  $u$  are vector in the three-dimensional space. Consider  $d\Gamma$  a differential in the phase space, i.e.  $d\Gamma = d^3u_1 d^3p_1 \dots d^3u_N d^3p_N$ : the partition function of the system can be written as

$$\mathcal{Z} = \int d\Gamma \exp \left\{ -\beta \left( \sum_{\vec{R}} \frac{p^2}{2M} + \frac{1}{2} \sum_{\vec{R}, \vec{R}'} u(\vec{R}) D(\vec{R} - \vec{R}') u(\vec{R}') + U_0 \right) \right\}$$

Performing a substitution

$$\tilde{p} = \sqrt{\beta} p \quad \tilde{u} = \sqrt{\beta} u \quad d\tilde{\Gamma} = \beta^{3N} d\Gamma$$

$$\begin{aligned} \mathcal{Z} &= \int \beta^{-3N} d\tilde{\Gamma} \exp \left\{ - \sum_{\vec{R}} \frac{\tilde{p}^2}{2M} - \frac{1}{2} \sum_{\vec{R}, \vec{R}'} \tilde{u}(\vec{R}) D(\vec{R} - \vec{R}') \tilde{u}(\vec{R}') - \beta U_0 \right\} \\ &= \beta^{-3N} e^{-\beta U_0} \zeta \end{aligned}$$

where  $\zeta$  does not depend from  $\beta$ . From the partition function, the specific heat can be computed:

$$\begin{aligned}
c &= \frac{dU}{dT} = -\frac{d}{dT} \frac{\partial}{\partial \beta} \ln \mathcal{Z} \\
&= -\frac{d}{dT} \frac{\partial}{\partial \beta} (-3N \ln \beta - \beta U_0 + \ln \zeta) \\
&= -\frac{d}{dT} (-3Nk_B T - U_0) \\
&= \mathbf{3Nk_B}
\end{aligned}$$

This result work fine at high temperature; sadly, at low temperature the specific heat is non-constant and goes like  $T^3$ . This means that a most detailed, quantum, model must be considered.

#### 4.4 Phonons

Let's recall the mono-dimensional Hamiltonian for the oscillations:

$$H = \frac{1}{2}M \sum \left( \frac{du}{dt} \right)^2 + \frac{1}{2}\tilde{k} \sum (u_n - u_{n+1})^2$$

Consider a general solution, **expanding it in Fourier series**:

$$\begin{aligned}
u_n &= \sum_k c_k e^{i(kna - \omega t)} \\
&= \sum_k Q_k(t) e^{ikna}
\end{aligned}$$

The first term in the Hamiltonian can be therefore rewritten as:

$$\begin{aligned}
\sum_n \left( \frac{du}{dt} \right)^2 &= \sum_n \sum_{k,p} \dot{Q}_k \dot{Q}_p e^{i(k+p)na} \\
&= \sum_{k,p} \dot{Q}_k \dot{Q}_p \sum_n \left( e^{i(k+p)a} \right)^n \\
&= \sum_{k,p} \dot{Q}_k \dot{Q}_p \frac{1 - e^{i(k+p)Na}}{1 - e^{i(k+p)a}}
\end{aligned}$$

From the periodic boundary conditions,  $(k+p)Na$  is a multiple of  $2\pi$  and therefore the fraction is 0, but if also the denominator is 0; which is, if  $k = -p$ . Therefore,

$$\sum_n \left( \frac{du}{dt} \right)^2 = \sum_k \dot{Q}_k \dot{Q}_{-k}$$

Let's now consider the second term in the Hamiltonian:

$$\begin{aligned}
\sum_n (u_n - u_{n+1})^2 &= \sum_n \sum_{k,p} Q_k Q_p e^{i(k+p)na} (1 - e^{ika}) (1 - e^{ipa}) \\
&= \sum_{k,p} Q_k Q_p (1 - e^{ika}) (1 - e^{ipa}) \underbrace{\sum_n e^{i(k+p)na}}_{\text{As before}} \\
&= \sum_k Q_k Q_{-k} \cdot 4 \sin^2 \frac{ka}{2}
\end{aligned}$$

Observe than, since  $u_n$  must be real,  $Q_k = Q_{-k}^*$ , which means  $Q_k Q_{-k} = |Q_k|^2$ . Recalling the Hamiltonian,

$$H = \frac{1}{2}M \sum_k |\dot{Q}_k|^2 + \frac{1}{2} \frac{\tilde{k}}{N} \sum_k |Q_k|^2 \cdot 4 \sin^2 \frac{ka}{2}$$

Being  $\omega = \sqrt{\frac{4\tilde{k}}{M} \left| \sin^2 \frac{ka}{2} \right|}$ , one obtain a well-known Hamiltonian:

$$H = \frac{1}{2}M \sum_k \left( |\dot{Q}_k|^2 + \omega^2 |Q_k|^2 \right)$$

It's a set of N decoupled harmonic oscillators! The energy of the system is

$$E = \sum_k \hbar \omega_k \left( n_k + \frac{1}{2} \right)$$

or, in multiple dimension,

$$E = \sum_s \sum_{\vec{k}} \hbar \omega_{\vec{k}s} \left( n_{\vec{k}s} + \frac{1}{2} \right) \quad (4)$$

where  $s$  is an indices which run on the possible different (acoustic and optical) branches.

The system can be therefore considered as a collection of phonons, each one with an energy  $\hbar \omega_{s\vec{k}}$  and momentum  $\vec{p} = \hbar \vec{k}$ , non interacting between themself.

#### 4.5 $T > 0$

Let's consider now a warm system. To find the energy of the system, the Boltzmann distribution must be considered. Let's compute the partition function, using the previous found total energy formula:

$$\begin{aligned} \mathcal{Z} &= \sum_{\vec{n}} \exp \left\{ -\beta \sum_s \sum_{\vec{k}} \hbar \omega_{\vec{k}s} \left( n_{\vec{k}s} + \frac{1}{2} \right) \right\} \\ &= \sum_{\vec{n}} \prod_{s,\vec{k}} \exp \left\{ -\beta \hbar \omega_{\vec{k}s} \left( n_{\vec{k}s} + \frac{1}{2} \right) \right\} \\ &= \sum_{\vec{n}} \prod_{s,\vec{k}} \exp \left\{ -\beta \hbar \omega_{\vec{k}s} n_{\vec{k}s} - \frac{1}{2} \beta \hbar \omega_{\vec{k}s} \right\} \\ &= \prod_{s,\vec{k}} \sum_{n_{\vec{k}s}} \exp \left\{ -\beta \hbar \omega_{\vec{k}s} n_{\vec{k}s} - \frac{1}{2} \beta \hbar \omega_{\vec{k}s} \right\} \\ &= \prod_{s,\vec{k}} \frac{\exp \left\{ -\frac{1}{2} \beta \hbar \omega_{\vec{k}s} \right\}}{1 - \exp \left\{ -\beta \hbar \omega_{\vec{k}s} \right\}} \end{aligned}$$

The energy can be therefore computed as:

$$\begin{aligned}
U &= -\frac{\partial}{\partial\beta} \ln \mathcal{Z} \\
&= -\frac{\partial}{\partial\beta} \sum_{s,\vec{k}} \left( -\frac{1}{2}\beta\hbar\omega_{\vec{k}s} - \ln\left(1 - \exp\{-\beta\hbar\omega_{\vec{k}s}\}\right) \right) \\
&= -\sum_{s,\vec{k}} \left( -\frac{1}{2}\hbar\omega_{\vec{k}s} - \hbar\omega_{\vec{k}s} \frac{\exp\{-\beta\hbar\omega_{\vec{k}s}\}}{1 - \exp\{-\beta\hbar\omega_{\vec{k}s}\}} \right) \\
&= \sum_{s,\vec{k}} \hbar\omega_{\vec{k}s} \left( \frac{1}{2} + \frac{1}{\exp\{\beta\hbar\omega_{\vec{k}s}\} - 1} \right)
\end{aligned}$$

where the fraction, comparing this formula with eq. (4), represent the average number of phonons in the given state:

$$\langle n_{\vec{k}s} \rangle = \frac{1}{\exp\{\beta\hbar\omega_{\vec{k}s}\} - 1}$$

The latter is the well-known Bose-Einstein distribution, typical of bosons: therefore, phonons can be treated like bosons!

Consider a single phonon with momentum  $k$ . The total momentum of the crystal is:

$$\vec{P} = \sum_n m e^{ik(na)} = Nm\delta_{k,0}$$

which is, the total momentum of the crystal produced by a single phonon is 0, but if  $\vec{k} = 0$ . This last situation, however, correspond to a rigid translation of the crystal and therefore is not particularly interesting.

We can now want to compute the specific heat, which is nothing but the variation of energy due to temperature variation:

$$\begin{aligned}
c_V &= \frac{d}{dT} u \\
&= \frac{1}{V} \frac{d}{dT} \sum_{s,\vec{k}} \hbar\omega_{\vec{k}s} \left( \frac{1}{2} + \frac{1}{\exp\{\beta\hbar\omega_{\vec{k}s}\} - 1} \right)
\end{aligned}$$

Going to the continuous limit, with periodic boundary conditions  $\vec{k} = \frac{2\pi}{L}\vec{n}$ , one obtain:

$$\begin{aligned}
c_V &= \frac{1}{V} \left( \frac{L}{2\pi} \right)^3 \frac{d}{dT} \sum_s \int d\vec{k} \frac{\hbar\omega_{\vec{k}s}}{\exp\{\beta\hbar\omega_{\vec{k}s}\} - 1} \\
&= \frac{1}{(2\pi)^3} \frac{d}{dT} \sum_s \int d\omega g(\omega) \frac{\hbar\omega}{\exp\{\beta\hbar\omega\} - 1}
\end{aligned} \tag{5}$$

where the ground state energy as been neglected, as it's independent from the temperature, and where  $g_s(\omega)$  is the density of states.

## 4.6 Debye model

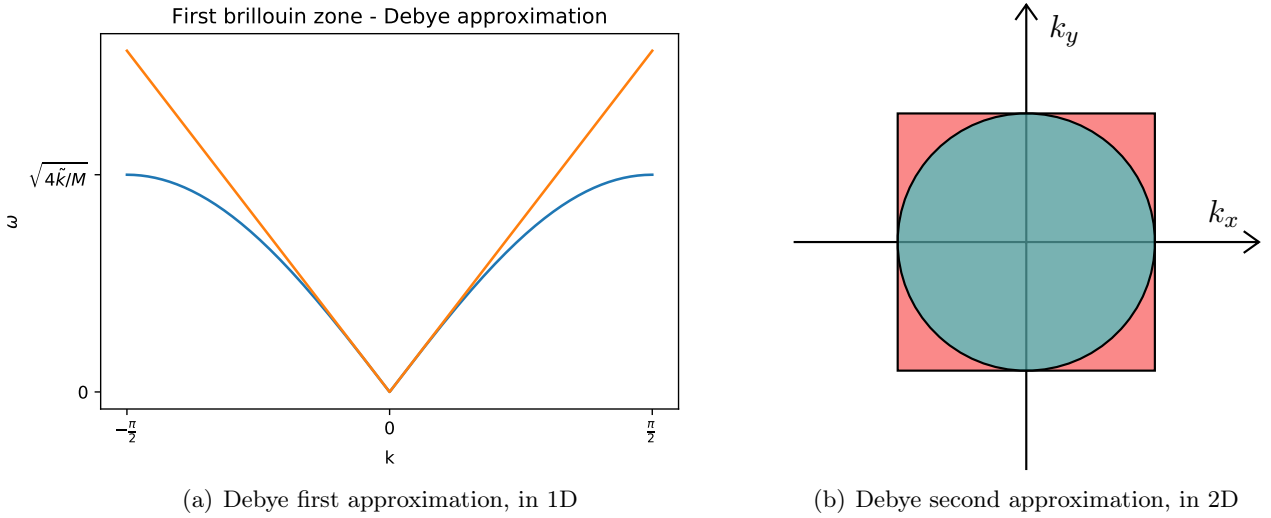


Figure 9: Debye approximations

To solve the integral in eq. (5), the density of states must be found. Debye propose an approximation which ease the computation of that function, which is represented in fig. 9: the idea is to approximate  $\omega = \frac{2v}{a} \left| \sin \frac{ka}{2} \right| \approx vk$ , where  $v$  is the phonon speed. This approximation it's allowed by the exponential factor in eq. (5): in fact, largest  $\omega$  contributes are very small, and therefore can be approximated.

Then, on the same spirit, a second approximation is done: the  $\vec{k}$  should move in a cubic space (square in 2 dimensions, red in fig. 9(b)). To ease the computation, however, Debye proposed to consider a spherical space (circular in 2 dimensions, blu in fig. 9(b)), neglecting the corners.

Under this assumption, the density of states is given by:

$$g(\omega) d\omega = \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{(2\pi)^3} \frac{1}{v^3} 4\pi\omega^2 d\omega$$

$$g(\omega) = \frac{V}{2\pi^2 v^3} \omega^2$$

Pay attention that this is the density of states *for each mode*, so if multiple modes are present the sum over  $s$  must be considered. Moreover, if there are different oscillation modes, the average inverse-of-the-speed-cubed can be considered:

$$v^{-3} = \frac{v_L^{-3} + 2v_T^{-3}}{3}$$

But what should the integration limit be? We know that in 3 dimensions there should be  $3N$  states, when  $N$  is the number of atoms in a crystal side. So let's impose the normalization of the density of state:

$$\sum_s \int_0^{\omega_D} d\omega g_s(\omega) = 3 \frac{V}{6\pi^2 v^3} \omega_D^3 \stackrel{!}{=} 3N$$

$$\omega_D = \sqrt[3]{\frac{6\pi^2 N}{V}} v = v \sqrt[3]{6\pi^2 n}$$

This result is very important: it gives an order of magnitude for the average frequency of phonons, for the average energy of phonons and for the average temperature of the system!  $\omega_D$  is called *Debye*



frequency.

$$\begin{aligned}\omega_D &= \sqrt[3]{\frac{6\pi^2 N}{V}} v \approx 10^{14} \text{Hz} \\ E_D &= \hbar\omega_D \approx 10^{-20} \text{J} \\ T_D &= \frac{\hbar\omega_D}{k_B} \approx 1000 \text{K}\end{aligned}$$

Now we can compute the specific heat of the system:

$$\begin{aligned}c_V &= \frac{1}{(2\pi)^3} \frac{d}{dT} \sum_s \int_0^{\omega_D} d\omega \frac{V}{2\pi^2 v^3} \omega^2 \frac{\hbar\omega}{\exp\{\beta\hbar\omega\} - 1} \\ &\propto \frac{d}{dT} \int_0^{\omega_D} d\omega \frac{\omega^3}{\exp\{\beta\hbar\omega\} - 1} \\ &\quad x = \beta\hbar\omega, \quad x_D = T_D/T \\ &\propto \frac{d}{dT} \beta^{-4} \int_0^{x_D} dx \frac{x^3}{e^x - 1}\end{aligned}\tag{6}$$

Let's consider the two cases: if  $T \ll T_D \rightarrow x_D \rightarrow \infty$ , the integral is a finite constant

$$\begin{aligned}c_V^\infty &\propto \frac{d}{dT} \beta^{-4} \int_0^\infty dx \frac{x^3}{\exp\{x\} - 1} \\ &\propto T^3\end{aligned}$$

On the other hand, if  $T \gg T_D \rightarrow x_D \rightarrow 0$ , the integral denominator can be approximated to  $e^x - 1 \approx x$ :

$$\begin{aligned}c_V^0 &\propto \frac{d}{dT} \beta^{-4} \int_0^{x_D} dx x^2 \\ &\propto \frac{d}{dT} T^4 \frac{T_D^3}{T^3} \\ &\propto \frac{d}{dT} T = \text{const}\end{aligned}$$

This behavior correspond to the observed one!

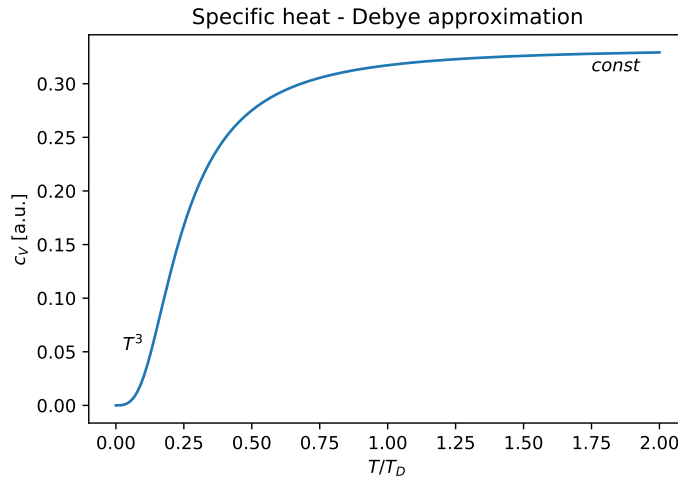


Figure 10: Eq. (6), visualized.

Consider that, in real systems, the dispersion relation does not follow Debye model, therefore a more general relation for the density of state must be found. Consider a shell, with radius  $\omega$  and

thickness  $d\omega$ . The density function is therefore:

$$g(\omega) d\omega = \sum_{\vec{k} \in \text{shell}} 1 = \frac{V}{(2\pi)^3} \int_{\text{shell}} d\vec{k}$$

Let  $\omega = \omega(\vec{k})$ , and decompose  $d^3\vec{k} = d^2k_{\parallel} dk_{\perp}$ , where the relation  $\parallel$  and  $\perp$  are defined with respect to  $\vec{\nabla}\omega$ . But this means that:

$$d^3\vec{k} = d^2k_{\parallel} \cdot dk_{\perp} = dS_{\omega} \cdot \frac{d\omega}{|\vec{\nabla}\omega|}$$

$$g(\omega) = \frac{V}{(2\pi)^3} \int_{\text{shell}} \frac{dS_{\omega}}{|\vec{\nabla}\omega|}$$

where  $S_{\omega}$  is the surface element. The gradient module appearing in the denominator can lead to various behavior of the density function, resulting for examples in spikes and valleys and leading to divergences in specific heat.

#### 4.7 Anharmonic terms

Until now, we've considered only an harmonic term keeping the atoms in their lattice positions. Such phenomena, however, are not explicable without considering the anharmonic perturbations to the potential: in particular, thermal expansion and thermal conduction.

**Thermal expansion** If the potential is harmonic, the minimum is always in the parabola vertex: no chance to see a displacement due to thermal expansion or compression. Let's instead consider a perturbation to the potential:

$$U(x) = cx^2 + gx^3 + fx^4 + \dots$$

$$\langle x \rangle = \frac{\int x e^{-\beta U} dx}{\int e^{-\beta U} dx}$$

$$e^{-\beta U} = e^{-\beta cx^2} e^{-\beta gx^3 - \beta fx^4 + \dots}$$

$$= \frac{\int x e^{-\beta cx^2} (1 - \beta gx^3 - \beta fx^4 + \dots)}{\int e^{-\beta cx^2} (1 - \beta gx^3 - \beta fx^4 + \dots)}$$

The last equation can be simplified by parity consideration (since the domain is symmetric, let's neglect odd terms):

$$\langle x \rangle = \frac{\int (-\beta gx^4) e^{-\beta cx^2}}{\int e^{-\beta cx^2}}$$

$$= \frac{-\frac{3}{4} \sqrt{\pi} \frac{9}{c^{5/2} \beta^{3/2}}}{\sqrt{\frac{\pi}{\beta c}}}$$

$$= -\frac{3gk_B}{4c^2} T$$

The last equation show a linear dependence of the expected position of each atom,  $\langle x \rangle$ , from the temperature: since from common experience we know temperature produce an expansion,  $g < 0$  since the coefficient is positive.

Let's define the expansion coefficients:

$$\alpha_L = \frac{1}{l} \left( \frac{dl}{dT} \right)_P \quad \alpha_V = \frac{1}{V} \left( \frac{dV}{dT} \right)_P \approx 3\alpha_L$$

To compute  $\alpha_L$ , we can consider the chain rule of the  $\{P, V, T\}$  ensemble:

$$\begin{aligned} \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V &= -1 \\ \left(\frac{\partial V}{\partial T}\right)_P &= - \underbrace{\left(\frac{\partial V}{\partial P}\right)_T}_{V/B} \left(\frac{\partial P}{\partial T}\right)_V \end{aligned}$$

where the bulk module  $B$  can be recognized. To compute the remaining term, consider the free energy of the system as the sum of the free energies of each oscillation mode:

$$\begin{aligned} F &= \sum_m f_m \\ &= - \sum_m \beta^{-1} \ln \mathcal{Z}_m \\ &= -\beta^{-1} \sum_m \ln \sum_n \exp\{-\beta \hbar \omega_m (n + 1/2)\} \\ &= -\beta^{-1} \sum_m \ln \frac{\exp\{-1/2\beta \hbar \omega_m\}}{1 - \exp\{-\beta \hbar \omega_m\}} \\ &= \beta^{-1} \sum_m \left( \frac{1}{2} \beta \hbar \omega_m + \ln(1 - \exp\{-\beta \hbar \omega_m\}) \right) \end{aligned}$$

Apparently, there is no dependence from the volume, so the pressure is zero. However, this is valid only in harmonic approximation: where there is an anharmonic perturbation,  $\omega = \omega(V)$ . Let's assume, for the sake of simplicity, that  $\omega \propto V^{-\gamma}$ .

From the latter, the pressure can be computed:

$$\begin{aligned} P &= -\frac{\partial F}{\partial V} = - \sum_m \left( \frac{1}{2} \hbar + \frac{\hbar \exp\{-\beta \hbar \omega_m\}}{1 - \exp\{-\beta \hbar \omega_m\}} \right) \frac{\partial \omega_m}{\partial V} \\ &= \underbrace{\sum_m \hbar \omega_m \left( \frac{1}{2} + \frac{1}{\exp\{\beta \hbar \omega_m\} + 1} \right)}_{U_{vib}} \frac{\gamma}{V} \end{aligned}$$

From this, the expansion coefficient can be computed:

$$\begin{aligned} \alpha_V &= \frac{1}{V} \left( \frac{dV}{dT} \right)_P \\ &= -\frac{1}{V} \frac{V}{B} \left( \frac{\partial}{\partial T} \frac{\gamma}{V} U_{vib} \right)_V \\ &= \frac{\gamma}{BV} c_V \end{aligned}$$

Moreover, observe that if anharmonic terms are present the harmonic constant,  $\tilde{k}$ , must be computed at the current minima position:

$$\begin{aligned} \tilde{k}' &= \frac{d^2 V}{dr^2} \Big|_{r=a'} = \frac{d^2 V}{dr^2} \Big|_{r=a} + \delta a \frac{d^3 V}{dr^3} \Big|_{r=a} \\ \tilde{k}' &= \tilde{k} + g \delta a \end{aligned}$$

Recalling the previous relations:

$$\omega = V^{-\gamma} \quad \rightarrow \quad \delta \omega = -\frac{\gamma \omega}{V} \delta V$$

$$\begin{aligned}
\omega &\propto \sqrt{\tilde{k}} \rightarrow \tilde{k} \propto \omega^2 \\
&\rightarrow \delta\tilde{k} \propto 2\omega\delta\omega \\
&\rightarrow g\delta a \propto \omega\delta\omega
\end{aligned}$$

and remembering the approximation  $\delta a = 1/3\delta V$ :

$$\begin{aligned}
\frac{1}{3}g\delta V &\propto -\omega\frac{\gamma\omega}{V}\delta V \\
\gamma &\propto -\frac{gV}{\omega^2} = -\frac{gV}{\tilde{k}}
\end{aligned}$$

which make sense remembering that  $g < 0$ .

**Thermal conduction on insulators** Insulators have not free electrons, so thermal conduction must be given by phonons. Let's consider the phonon flux:

$$\Phi = \sum_{\vec{k}_s} \hbar\omega_s(\vec{k}) \cdot \frac{\langle n_{\vec{k}_s} \rangle}{V} \cdot v_s^x(\vec{k})$$

where the flux for each mode is computed as the product between the energy of a phonon, the phonons density and the phonon  $\hat{x}$  group velocity.

Consider a non-equilibrium stationary system, and therefore a perturbation in the phonon number:  $\langle n \rangle = \langle n \rangle_{eq} + \delta n$ . Since the state is stationary,

$$\frac{\partial \delta n}{\partial t} = 0 = \left( \frac{\partial \delta n}{\partial t} \right)_{diff} + \left( \frac{\partial \delta n}{\partial t} \right)_{dec}$$

when the variation of  $\langle n \rangle$  has been split in two components: the variation due to diffusion and the variation due to photon decay.

For the diffusion process, one can write:

$$\left( \frac{\partial \delta n}{\partial t} \right)_{diff} \approx \frac{\partial n}{\partial x} \frac{\partial x}{\partial t} = -\frac{\partial n}{\partial T} \frac{\partial T}{\partial x} v^x$$

where the minus sign come from the fact that, if phonons are moving towards positive  $x$ , then  $n(x) = n(x_0 - vt)$ . On the other hand, for the decay process, let's introduce a relaxation time  $\tau$ :

$$\left( \frac{\partial \delta n}{\partial t} \right)_{dec} = -\frac{\delta n}{\tau}$$

This lead to:

$$\begin{aligned}
\frac{\partial \delta n}{\partial t} = 0 &= -\frac{\partial n}{\partial T} \frac{\partial T}{\partial x} v^x - \frac{\delta n}{\tau} \\
\delta n &= -\frac{\partial n}{\partial T} \frac{\partial T}{\partial x} \tau v^x
\end{aligned}$$

Returning to the flux, and observing that  $\langle n \rangle_{eq}$  cannot contribute to the flux since is equilibrium condition (while single  $\langle n_{\vec{k}_s} \rangle$  can be different from zero, the weighted sum is clearly zero):

$$\begin{aligned}
\Phi &= \sum_{\vec{k}_s} \hbar\omega_s(\vec{k}) \frac{\delta n_{\vec{k}_s}}{V} v_s^x(\vec{k}) \\
&= -\sum_{\vec{k}_s} \hbar\omega_s(\vec{k}) \frac{\partial n}{\partial T} \tau \frac{1}{V} (v_s^x(\vec{k}))^2 \frac{\partial T}{\partial x} \\
&= -\kappa \frac{\partial T}{\partial x}
\end{aligned}$$

which is fully compatible with experimental results! Moreover, assuming  $(v_s^x(\vec{k}))^2 \approx 1/3(v_s(\vec{k}))^2$ , one can compute:

$$\begin{aligned}\kappa &= \sum_{\vec{k}s} \hbar\omega_s(\vec{k}) \frac{\partial n}{\partial T} \tau \frac{1}{V} (v_s^x(\vec{k}))^2 \\ &= \frac{1}{V} \frac{\partial}{\partial T} \left( \sum_{\vec{k}s} \hbar\omega_s(\vec{k}) \langle n_{\vec{k}s} \rangle \right) \tau^{1/3} (v_s(\vec{k}))^2 \\ &= \frac{1}{3} c_V \langle v^2 \rangle \tau\end{aligned}$$

The behavior of  $\kappa$  can be studied in 2 parts:

$T \ll T_D$	$T \gg T_D$
$c_V \sim T^3$	$c_V \sim \text{const}$
$v^2 \sim \text{const}$	$v^2 \sim \text{const}$
$\tau \sim \text{const}$	$\tau \sim T^{-1}$
$\rightarrow \kappa \sim T^3$	$\rightarrow \kappa \sim T^{-1}$

#### 4.8 Phonons momentum

A phonon interact with other particles as if it had a momentum  $\hbar\vec{k}$ ; however, photons does not carry physical momentum, since they are described by coordinates *differences*.

We've already see that photon scattering is governed by the rule

$$\vec{k}' = \vec{k} + \vec{G}$$

Consider instead an inelastic photon diffraction, with the creation of a phonon with momentum  $\pm\vec{K}$ .

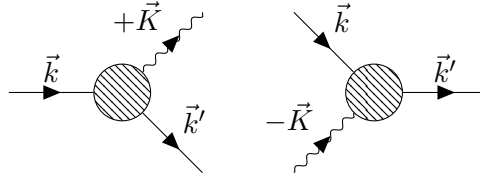


Figure 11: Photon diffraction with phonon creation. Straight lines represent photons, while wavy ones represent phonons.

$$\vec{k} = \vec{k}' + \vec{K} + \vec{G}$$

Moreover, to explain the thermal conductance properties, even phonon-phonon collisions must be considered:

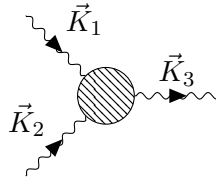


Figure 12: Phonon-phonon collision

Considering both energy and momentum conservation, one obtain:

$$\begin{cases} \hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3 \\ \vec{K}_1 + \vec{K}_2 = \vec{K}_3 + \vec{G} \end{cases}$$

Two cases can be distinguished. First cases, with  $\vec{G} = 0$ , is not particularly important, since the total momentum of the crystal does not vary and therefore this process doesn't contribute to the reaching of equilibrium. On the other hand considering a  $\vec{G} \neq 0$  case one obtain the so-called *unklapp scattering*: in this case, the total momentum is not conserved, so the process contribute to the reduction of the total momentum and the reaching of equilibrium.

## 5 Free electrons Fermi gas

Let's now move to the electronic part. Electrons are in a very complicated potential, periodic but full of holes in correspondence of the nuclei. In a first approximation, let's consider the positive charge as uniformly distributed, and therefore the electrons living in a rectangular potential well. The solutions of the Shrödinger equation in this potential are well-know:

$$\begin{cases} -\frac{\hbar^2 \nabla^2}{2m} \psi = E \psi \\ \psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}} \\ E_{\vec{k}} = \frac{\hbar^2 k^2}{2m} \end{cases}$$

which can be rewritten in terms of a number triplet of integer numbers considering that periodic boundary conditions impose:

$$\vec{k} = \frac{2\pi}{L} \vec{n}$$

Consider a state  $\vec{k}$ : from Pauli principle,  $0 \leq n_{\vec{k}} \leq 1$ , where  $n_{\vec{k}}$  is the occupation number of the state  $\vec{k}$ . Considering a Boltzmann-like distribution:

$$\langle n_{\vec{k}} \rangle = \frac{1}{e^{\beta(E-\mu)} + 1}$$

and, remembering that  $\mu = E_F$  (where  $E_F$  is the Fermi energy), one obtain:

$$\langle n(E) \rangle = \frac{1}{e^{\beta(E-E_F)} + 1}$$

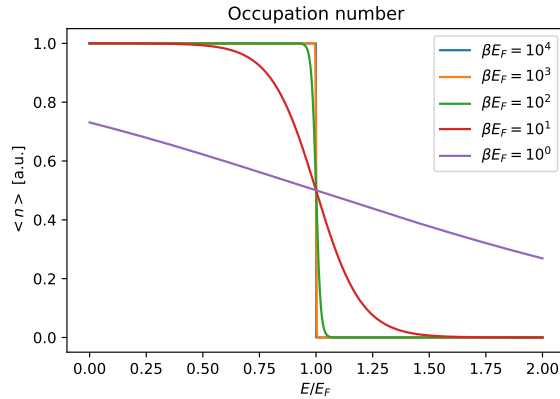


Figure 13: Occupation number as function of energy, for different  $\beta$ .

The occupation number is therefore a step-like function. In fact, typically the Fermi temperature is way higher than the room one, so the expectation value of  $n$  can be approximated to a Heaviside function.

Let's therefore consider a sphere, with radius  $k_F$ : inside the sphere, considering also the spin factor, there are:

$$N = 2 \cdot \frac{V_{sph}}{V_{state}} = 2 \cdot \frac{4/3\pi k_F^3}{(2\pi/L)^3}$$

states, and considering  $N$  must be equal to the number of free electrons in the crystal, Fermi quantities can be easily computed:

$$\begin{aligned} n &= \frac{N}{V} \sim 10^{28} \\ k_F &= \sqrt[3]{3\pi^2 n} \\ E_F &= \frac{\hbar^2 k_F^2}{2m} \sim \text{eV} \\ T_F &= \frac{E_F}{k_B} \sim 10^5 \text{K} \\ v_F &= \frac{\hbar k_F}{m_e} \sim 10^6 \text{m s}^{-1} \end{aligned}$$

Observe the high values of Fermi temperature and Fermi speed!  
From these relations, the total energy of the system can be computed:

$$\begin{aligned} E_0 &= 2 \sum_{|\vec{k}| \leq k_F} \frac{\hbar^2 k^2}{2m} \rightarrow 2 \frac{V}{(2\pi)^3} \int d\vec{k} \frac{\hbar^2 k^2}{2m} \\ &= 2 \frac{V}{(2\pi)^3} \int_0^{k_F} 4\pi k^2 dk \frac{\hbar^2 k^2}{2m} \\ &= \frac{V}{\pi^2} \frac{\hbar^2 k_F^5}{10m} \\ &= \frac{V}{\pi^2} \frac{\hbar^2 k_F^2}{2m} \frac{k_F^3}{5} \\ &= \frac{3}{5} N \mathcal{E}_F \end{aligned}$$

which means that the mean "per electron" energy is

$$e_0 = \frac{3}{5} \mathcal{E}_F \propto n^{2/3}$$

From the total energy it's possible to give an estimation of the internal pressure:

$$\begin{aligned} P &= -\frac{\partial E_0}{\partial V} = -\frac{\partial}{\partial V} \frac{3}{5} N \frac{\hbar^2}{2m} 3^{2/3} \pi^{4/3} \frac{N^{2/3}}{V^{2/3}} \\ &= \frac{2 \cdot 3^{2/3} \pi^{4/3}}{5} \frac{\hbar^2}{2m} \frac{N^{5/3}}{V^{5/3}} \\ &= \frac{2}{3} \frac{E_0}{V} \sim 10^7 \text{atm} \end{aligned}$$

Following the same model, the density of states as function of energy can be computed:

$$\begin{aligned} g(E) &= g(k) \frac{dk}{dE} \\ &= 2 \cdot \frac{4\pi k^2}{(2\pi)^3} \frac{d}{dE} \frac{\sqrt{2mE}}{\hbar} \\ &= \frac{V}{\pi^2} \frac{2mE}{\hbar^2} \frac{\sqrt{2m}}{2\hbar\sqrt{E}} \\ &= \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} \end{aligned}$$

Observe that

$$g(E_F) = \frac{3}{2} \frac{N}{E_F}$$

## 5.1 Electrons contribute to specific heat

Let's consider a  $T \neq 0$  system: therefore, the Boltzmann function can't be approximated to a Heaviside theta and its complete form must be considered:

$$f(E, T) = \frac{1}{e^{\beta(E-E_F)} + 1} \quad \text{s.t.} \quad \int_0^\infty f(E, T)g(E) dE = N \quad (7)$$

$$E_0(T) = \int_0^\infty E f(E, T)g(E) dE$$

Observing that the energy of electrons depend from temperature, they contribute to the specific heat:

$$\begin{aligned} c_V^e &= -\frac{1}{V} \frac{\partial}{\partial T} \int_0^\infty dE E f(E, T)g(E) \\ &= -\frac{1}{V} \int_0^\infty dE E g(E) \frac{\partial f(E, T)}{\partial T} \\ &= -\frac{1}{V} \int_0^\infty dE E g(E) \frac{\partial f(E, T)}{\partial T} - \frac{1}{V} E_F \underbrace{\frac{\partial}{\partial T} \int_0^{E_F} dE g(E) f(E, T)}_{0, \text{ by definition: see (7)}} \\ &= -\frac{1}{V} \int_0^\infty dE (E - E_F) g(E) \frac{\partial f(E, T)}{\partial T} \end{aligned}$$

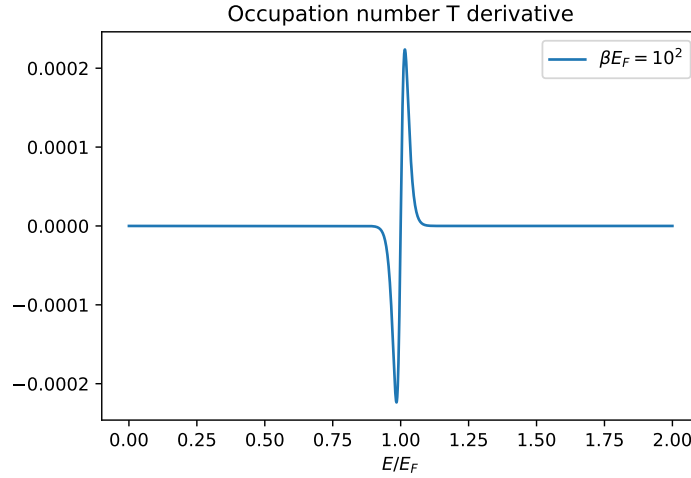


Figure 14:  $\frac{\partial f}{\partial T}$ , clearly non-negligible only around  $E_F$

Observing the form of the occupation number function, it's clear that its derivative with respect to  $T$  is different from 0 only strictly around  $E_F$  (where "strictly" is intended with respect to  $k_B T$ ). Therefore, in the last relation we can assume  $g(E) \approx g(E_F)^*$ :

$$c_V^e = -\frac{1}{V} g(E_F) \int_0^\infty dE (E - E_F) \frac{\partial f(E, T)}{\partial T}$$

---

\*Observe that the derivative does not carry a (-) sign, since there are two (-) deleting each other: one from  $\frac{\partial}{\partial e} \frac{1}{e+1}$  and one from  $\frac{\partial}{\partial T} \beta$



$$\begin{aligned}
c_V^e &= \frac{1}{V} g(E_F) \int_0^\infty dE (E - E_F) \frac{k_B \beta^2 (E - E_F) e^{\beta(E - E_F)}}{(e^{\beta(E - E_F)} + 1)^2} \\
&\quad x = \beta(E - E_F) \quad T_F \gg T \rightarrow x(E = 0) \approx -\infty \\
&= g(E_F) k_B \beta^{-1} \int_{-\infty}^\infty dx \frac{x^2 e^x}{(e^x + 1)^2} \\
&= \frac{\pi^2 k_B}{2} n \frac{T}{T_F}
\end{aligned}$$

There is, therefore, a linear dependence from  $T$  of the specific heat. This factor, however, is very small and negligible with respect to the total  $c_V$ .

## 5.2 Drude model

Drude model is a very simple approximation to study the behavior of electrons where a electric field is present. If we consider a totally-free electron, classical electrodynamic says that:

$$\langle \vec{P}(t + \Delta t) \rangle = \langle \vec{P}(t) \rangle - e \vec{E} \Delta t$$

But we shall consider that we're in a medium, so there is a scattering probability  $1/\tau$ : therefore

$$\begin{aligned}
\langle \vec{P}(t + \Delta t) \rangle &= \left( \langle \vec{P}(t) \rangle - e \vec{E} \Delta t \right) \left( 1 - \frac{\Delta t}{\tau} \right) \\
&\approx \langle \vec{P}(t) \rangle - e \vec{E} \Delta t - \frac{\Delta t}{\tau} \langle \vec{P}(t) \rangle
\end{aligned}$$

which means, sending  $\Delta t \rightarrow 0$  and remembering  $\vec{P} = m\vec{v}$ :

$$\frac{\partial \vec{v}}{\partial t} = -\frac{e \vec{E}}{m} - \frac{\vec{v}}{\tau}$$

When the system reaches the equilibrium, it becomes stationary, therefore:

$$\begin{aligned}
\frac{\partial \vec{v}}{\partial t} = 0 &\quad \rightarrow \quad \vec{v} = -\frac{\tau e \vec{E}}{m} \\
\vec{j} &= \underbrace{\frac{ne^2 \tau}{m}}_{\sigma} \vec{E}
\end{aligned}$$

from which the conductance can be computed!

**Numerical values** From this model, an estimation of the scattering time, of the Fermi velocity and of the mean free paths can be computed:

$$\tau \sim 10^{-9} - 10^{-14} \text{ s}$$

$$v_F \sim 10^6 \text{ m s}^{-1}$$

$$\lambda \sim 10^{-3} - 10^{-8} \text{ m}$$

But which are  $\tau$  due to? There are two scattering phenomena which mainly contributes to resistivity: collisions with phonons and collisions with lattice impurities. While the first is strongly temperature-dependent, and therefore is non-negligible at high (room) temperature, the second one can be considered constant over temperature and it's the most important term at low temperatures. Remember that the most valuable contribute to electron-phonons scattering is given by the umklapp scattering.

Another way to find the same result is to consider a Fermi-sphere shift: when a field is applied, the Fermi sphere is shifted by a quantity  $\frac{e \vec{E}}{\hbar} \tau$ .

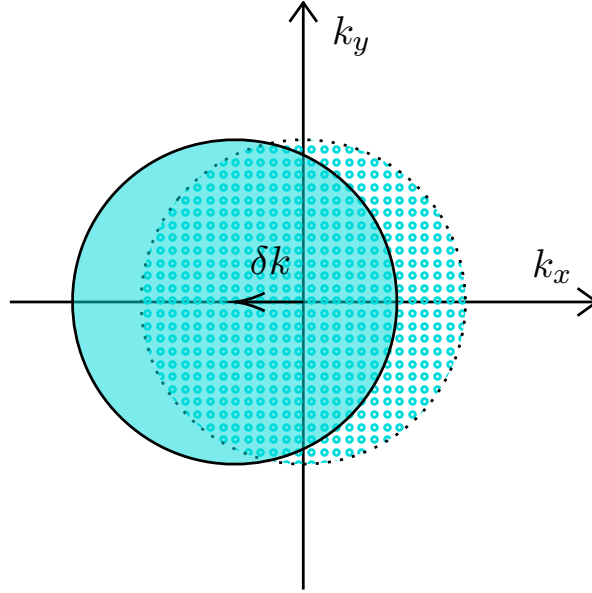


Figure 15: Fermi sphere shifted by an external field.

$$\begin{aligned}
 f(\vec{k}) &= f_0(\vec{k} + \frac{e\vec{E}}{\hbar}\tau) \\
 &= f_0(\vec{k}) + \frac{e\vec{E}}{\hbar}\tau f'_0(\vec{k}) \\
 &= f_0(\vec{k}) + \frac{e\vec{E}}{\hbar}\tau \frac{df_0}{dE} \frac{dE}{d\vec{k}}
 \end{aligned}$$

Remembering that  $\frac{df_0}{dE} \sim -\delta(E - E_F)$  and  $\frac{dE}{d\vec{k}} = \frac{\hbar^2 \vec{k}}{m} \approx \hbar v_{\parallel}$ , one obtain

$$f(\vec{k}) = f_0(\vec{k}) - e\vec{E}\tau v_{\parallel} \delta(E - E_F)$$

from which the current can be computed:

$$\begin{aligned}
 \vec{j} &= -\frac{e}{V} \int dE \vec{v}g(E) f(E, T) \\
 &= -\frac{e}{V} \int dE \vec{v}g(E) \left( f_0(\vec{k}) - e\vec{E}\tau v_{\parallel} \delta(E - E_F) \right)
 \end{aligned}$$

Since at equilibrium the current is zero, the  $f_0$  term does not contribute:

$$\begin{aligned}
 \vec{j} &= \frac{e}{V} \int dE \vec{v}g(E) e\vec{E}\tau v_{\parallel} \delta(E - E_F) \\
 &= \frac{e^2}{V} g(E_F) \vec{E} \tau v_{\parallel}^2 \\
 &= \frac{e^2}{V} \frac{3}{2} \frac{N}{E_F} \vec{E} \tau \frac{1}{3} \frac{2E_F}{m} \\
 &= \frac{e^2 n \tau}{m} \vec{E}
 \end{aligned}$$

which is the same result obtained before.

### 5.3 Thermal conductivity

As seen for phonons, the thermal conductivity can be expressed as:

$$\begin{aligned}\kappa &= \frac{1}{3} c_V \langle v^2 \rangle \tau \\ &= \frac{1}{3} \frac{\pi^2 k_B}{2} n \frac{T}{T_F} \cdot \frac{2k_B T_F}{m} \cdot \tau \\ &= \frac{\pi^2 k_B^2}{3m} n T \tau\end{aligned}$$

From this, the Lorentz number can be defined:

$$\mathcal{L} = \frac{\kappa}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} = 2.44 \cdot 10^{-8} \text{W } \Omega \text{K}^{-2}$$

which is a **universal ratio!** Experimental values are in good agreement with this, for almost all metals.

### 5.4 Screening effects

Until now and in the following, we suppose that electrons behave independently between them. However, electrons have a density of  $10^{29} \text{m}^{-3}$ , therefore the average distance is in the order of the Angstrom. How can the Coulomb interaction be screened?

#### 5.4.1 Plasmons

Consider a density perturbation in the electron distribution,  $\Delta n = n - n_0$ . Consider Drude model equation, Maxwell first law and continuity equation:

$$\begin{cases} m\dot{\vec{v}} = -e\vec{E} - \frac{m\vec{v}}{\tau} \\ \vec{\nabla} \cdot \vec{E} = -\frac{e\Delta n}{\epsilon_0} \\ \dot{\vec{n}} + \vec{\nabla} \cdot (n\vec{v}) = 0 \end{cases}$$

Start from the first, neglect the last term, multiply by  $n$  both side and take the divergence (consider, since  $\Delta n$  is small,  $\frac{dn}{dt} \approx 0$ ):

$$\begin{aligned}nm\dot{\vec{v}} &= -ne\vec{E} \\ \vec{\nabla} \cdot m \frac{d}{dt}(n\vec{v}) &= -\vec{\nabla} \cdot ne\vec{E}\end{aligned}$$

Considering now  $\vec{\nabla} \cdot n \approx 0$  and applying second and the third relations:

$$\begin{aligned}m \frac{d}{dt} \vec{\nabla} \cdot (n\vec{v}) &= -ne \vec{\nabla} \cdot \vec{E} \\ m \frac{d}{dt} \vec{\nabla} \cdot (n\vec{v}) &= -ne \vec{\nabla} \cdot \vec{E} \\ -m \frac{d}{dt} \dot{\vec{n}} &= ne \frac{e\Delta n}{\epsilon_0} \\ \ddot{\vec{n}} &= -\frac{ne^2}{m\epsilon_0} \Delta n\end{aligned}$$

which is the equation of an harmonic oscillation, with frequency:

$$\omega_P = \sqrt{\frac{ne^2}{m\epsilon_0}}$$

This frequency is called *plasma frequency*, and is the typical frequency of electron oscillations; this oscillation when they're seen as particles, are called *plasmas*. These are collective motion, that are the result of lots of electrons: in fact, their energy is in the order of

$$\omega_P \approx 10^{16}$$

$$E_P = \hbar\omega_P \approx 15\text{eV}$$

which is in the same order (if not greater) of the ionization energy of the atoms. This means that, if a single electron had all the energy, then it would ionize the atom!

#### 5.4.2 Screening: Thomas-Fermi model

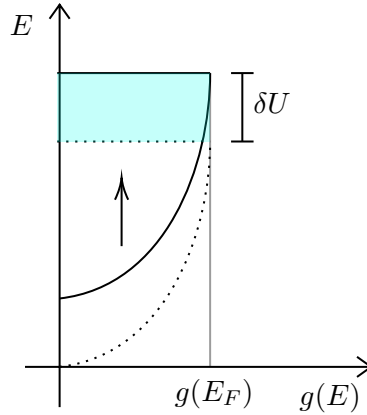


Figure 16: States migration for screening.

Let's consider, for example, a free non-equilibrium charge inserted in a metal. How the electrons around all the metal will see the field? The potential induced change the energy of each electron for  $\delta U = -e\Phi(\vec{r})$ : states whose energy goes above Fermi energy will migrate to restore equilibrium. The number of states interested by the shift are:

$$\delta n = -\delta U \cdot g(E_F) = e\Phi(\vec{r})g(E_F)$$

This induce a charge density

$$\rho = -e\delta n = -e^2\Phi(\vec{r})g(E_F)$$

Recalling Maxwell equations:

$$\nabla^2\Phi = -\frac{\rho}{\epsilon_0} = \frac{e^2g(E_F)}{\epsilon_0}\Phi$$

This equation have an exponential-decay solution: the field induced by the non-equilibrium charge it's exponentially screened by the nearest electrons. The typical length of this screening is:

$$\lambda_{TF} = \sqrt{\frac{\epsilon_0}{e^2g(E_F)}} \sim \text{\AA}$$

which is really short: any free charge is quickly screened, and interaction can take place only at very short range.

**Observation** As seen in the ManyBody course, this screening can be modelled with a Yukawa potential: defining the ThomasFermi momentum  $q_{TF} = \frac{2\pi}{\lambda_{TF}}$ , one can write

$$V(\vec{r}, \vec{r}') = \frac{e^2}{|\vec{r} - \vec{r}'|^2} e^{-q_{TF}|\vec{r} - \vec{r}'|}$$

### 5.4.3 Electron-electron scattering

The last result can be used to compute the electron-electron scattering typical time:

$$\tau = \frac{1}{v_F \sigma_{ee} n} = \frac{1}{v_F \lambda_{TF}^2 n}$$

and therefore the total scattering frequency per unit of volume is:

$$w = n \cdot \frac{1}{\tau} = v_F \lambda_{TF} n^2$$

This result turn out to being false: in fact, the fermionic nature of electrons must be considered. This means that not all electrons are subject to scattering, but only a small part in an interval that can be quantified by Fermi temperature:

$$w = v_F \lambda_{TF} n^2 \quad \rightarrow \quad w = v_F \lambda_{TF} \left( \frac{T}{T_F} n \right)^2$$

Typically, the ratio  $T/T_F$  is in the order of 0.01, so the squared term introduce a factor of  $10^{-4}$  in the scattering probability, i.e. a factor of  $10^4$  in  $\tau$ . This contributes to lead the electron-electron interaction to be negligible, and therefore the independent electrons approximation to be valid!

## 6 Band Theory

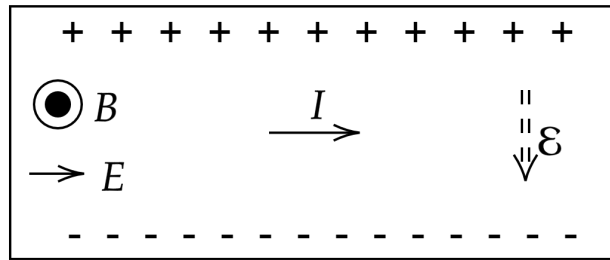


Figure 17: Hall effect

Consider the Hall effect: a metallic tile, of height  $h$  and depth  $b$ , in a electromagnetic field. The motion of the electrons and their interaction with the magnetic field induces an electric field  $\mathcal{E}$ . Consider the Hall coefficient:

$$R_H = \frac{\mathcal{E}bh}{IB} = \frac{vB \cdot bh}{vqn bh \cdot B} = \frac{1}{qn}$$

Experimental data shows that for small atoms, with only one free electron, Drude model gives a correct result; instead, for largest atoms, our model doesn't work. Moreover, sometimes a positive  $R_H$  is found, as if there are positive charges moving: how is it possible?

### 6.1 Quasi-free electrons approach

Consider the Schrödinger equation:

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) \right) \psi(\vec{r}) = E\psi(\vec{r})$$

where  $V(\vec{r})$  is a periodic potential, which follows the lattice structure. From the scattering theory and the Bloch theorem,  $\psi$  can be expanded as:

$$\psi(\vec{r}) = \sum_{\vec{G}} c_{\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}} = e^{i\vec{k}\vec{r}} u(\vec{r})$$

where  $u(\vec{r})$  is the so-called Bloch function, s.t.  $u(\vec{r} + \vec{R}) = u(\vec{r})$ .

**Informal observation** Consider a 1D crystal, and the border of the Brillouin zone:  $k = \pi/a$ , which correspond to the opposite border  $k' = -\pi/a$ . This means that the wavefunction must be a linear combination of this two momenta. In the simplest case,

$$\psi_{\pm} = e^{-i\frac{\pi}{a}x} \pm e^{+i\frac{\pi}{a}x} = \begin{cases} \cos^2(\frac{\pi}{a}x) \\ \sin^2(\frac{\pi}{a}x) \end{cases}$$

The two states have two different energies, even if they have the same momentum!

Let's expand both wavefunction and potential, remembering the periodicity:

$$\begin{cases} \psi(\vec{r}) = \sum_{\vec{q}} c_{\vec{q}} e^{i\vec{q}\vec{r}} \\ V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\vec{r}} \end{cases}$$

where  $\vec{G}$  is a reciprocal lattice vector. Insert this expansions in the Schrödinger equation:

$$\frac{\hbar^2}{2m} \sum_{\vec{q}} q^2 c_{\vec{q}} e^{i\vec{q}\vec{r}} + \sum_{\vec{q}} \sum_{\vec{G}} V_{\vec{G}} c_{\vec{q}} e^{i(\vec{q}+\vec{G})\vec{r}} = E \sum_{\vec{q}} c_{\vec{q}} e^{i\vec{q}\vec{r}}$$

Relabelling the (mute) variable  $\vec{q}$  on the second summation to  $\vec{q} - \vec{G}$  and considering that the equation must be valid for each  $\vec{r}$ :

$$\begin{aligned} \frac{\hbar^2}{2m} \sum_{\vec{q}} q^2 c_{\vec{q}} e^{i\vec{q}\vec{r}} + \sum_{\vec{q}} \sum_{\vec{G}} V_{\vec{G}} c_{\vec{q}-\vec{G}} e^{i\vec{q}\vec{r}} &= E \sum_{\vec{q}} c_{\vec{q}} e^{i\vec{q}\vec{r}} \\ \frac{\hbar^2 q^2}{2m} c_{\vec{q}} + \sum_{\vec{G}} V_{\vec{G}} c_{\vec{q}-\vec{G}} &= E c_{\vec{q}} \end{aligned}$$

Let relabel  $\vec{G}$  to  $\vec{G}'$  and consider  $\vec{k} = \vec{q} + \vec{G}$ , with  $\vec{G}$  s.t.  $\vec{k}$  is in the first Brillouin zone:

$$\frac{\hbar^2(\vec{k} - \vec{G}')^2}{2m} c_{\vec{k}-\vec{G}'} + \sum_{\vec{G}'} V_{\vec{G}'-\vec{G}} c_{\vec{k}-\vec{G}'} = E c_{\vec{k}-\vec{G}'}$$

The latter is called **central equation**. Firstly, let's neglect  $V$ : it remains

$$E = \frac{\hbar^2(\vec{k} - \vec{G}')^2}{2m}$$

For each  $\vec{k}$ , therefore, there are multiple solutions, at different  $\vec{G}'$ ! Moreover, if one study the crossing points, one obtain the Bragg interference condition.

Let's now consider a small perturbation: if the considered  $\vec{k}$  is far from crossing points, there is only one  $c_{\vec{k}-\vec{G}^*}$  which is non-negligible, and therefore the central equation becomes:

$$\begin{aligned} \frac{\hbar^2(\vec{k} - \vec{G}')^2}{2m} c_{\vec{k}-\vec{G}'} + V_{\vec{G}^*-\vec{G}'} c_{\vec{k}-\vec{G}^*} &= E c_{\vec{k}-\vec{G}'} \approx E_{\vec{k}-\vec{G}^*}^0 c_{\vec{k}-\vec{G}'} \\ c_{\vec{k}-\vec{G}'} &= -\frac{V_{\vec{G}^*-\vec{G}'}}{E_{\vec{k}-\vec{G}'}^0 - E_{\vec{k}-\vec{G}^*}^0} c_{\vec{k}-\vec{G}^*} \end{aligned}$$

which lead to:

$$\begin{aligned} E(\vec{k}) &= E_{\vec{k}-\vec{G}^*}^0 + \sum_{\vec{G}} V_{\vec{G}-\vec{G}^*} \frac{c_{\vec{k}-\vec{G}}}{c_{\vec{k}-\vec{G}^*}} \\ &= E_{\vec{k}-\vec{G}^*}^0 - \sum_{\vec{G}} \frac{V_{\vec{G}-\vec{G}^*} V_{\vec{G}^*-\vec{G}}}{E_{\vec{k}-\vec{G}}^0 - E_{\vec{k}-\vec{G}^*}^0} \end{aligned}$$

The perturbation, therefore, is small (second order in the already-small potential) and not interesting. Consider instead if you are near a crossing point: then you have two different non-negligible contributors:  $c_{\vec{k}-\vec{G}^*}$  and  $c_{\vec{k}-\vec{G}^+}$ . Following the same procedure and solving the system, one obtains:

$$E_{\vec{k}} = \frac{E_{\vec{k}-\vec{G}^*}^0 + E_{\vec{k}-\vec{G}^+}^0}{2} \pm \frac{1}{2} \sqrt{(E_{\vec{k}-\vec{G}^*}^0 - E_{\vec{k}-\vec{G}^+}^0)^2 + 4|V_{\vec{G}^*-\vec{G}^+}|^2}$$

which are two distinct solutions: this means that a gap opens in the energy structure, i.e. an energy band in which there are no electron slots!

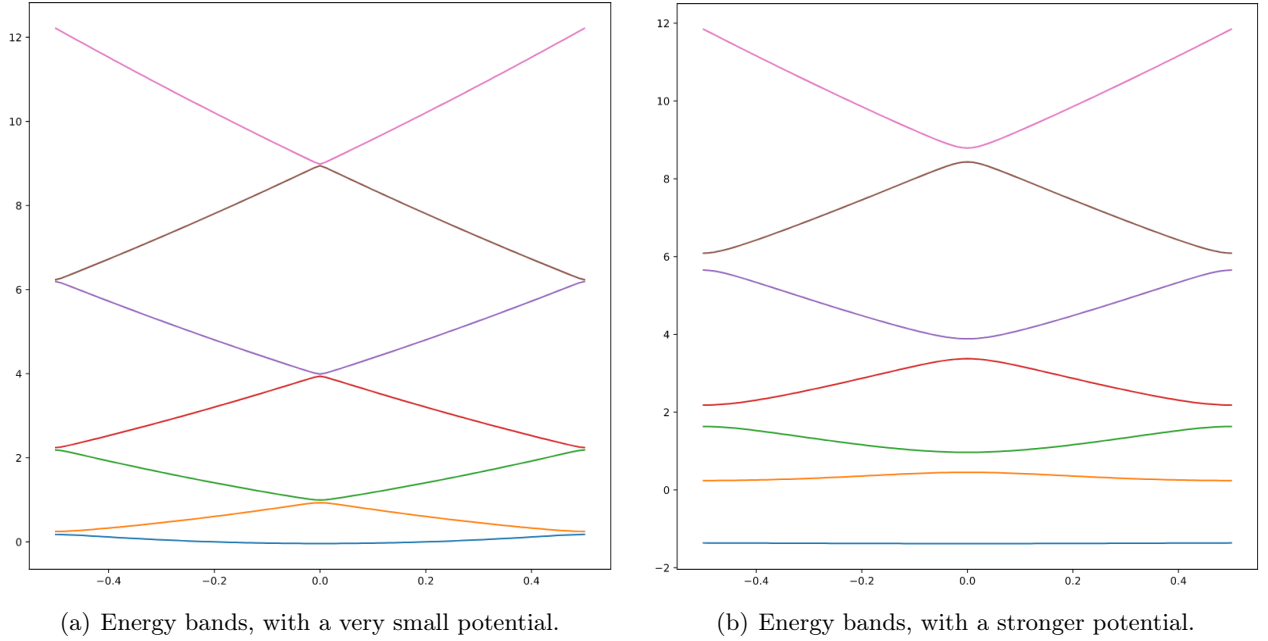


Figure 18: Energy bands (a.u.) in the first Brillouin zone.

This model works only when external electrons are nearly-free, like in a  $s$  orbital. On the other hand, when external atoms are tightly bound to the nucleus, a different model must be used.

## 6.2 Tight binding approximation

When the electrons are tightly bound to the atoms, a plane-wave expansion is not appropriate. Instead, the wavefunction of the electron can be expanded in a linear combination of atomic orbitals. Let  $\psi_n$  be the solutions of the Schrödinger equation for a single atom (i.e. the atomic orbitals):

$$\Psi(\vec{r}) = \sum_n \sum_{\vec{R}} c_{n\vec{R}} \psi_n(\vec{r} - \vec{R})$$

In a first approximation, consider only  $s$  orbitals, i.e. the simplest ones. Moreover, for the Bloch theorem,  $\Psi(\vec{r}) = e^{-i\vec{k}\cdot\vec{R}} \Psi(\vec{r} + \vec{R})$ . Therefore,

$$\Psi(\vec{r}) = \sum_{\vec{R}} c_{\vec{R}} \psi_0(\vec{r} - \vec{R}) \quad c_{\vec{R}} = e^{i\vec{k}\cdot\vec{R}}$$

Let's start from the eigenvalues equation, and multiplying both sides by  $\psi_0(\vec{r})^*$ , let's integrate:

$$\begin{aligned}\hat{H}\Psi(\vec{r}) &= E\Psi(\vec{r}) \\ \underbrace{\int d\vec{r} \psi_0(\vec{r})^* \hat{H}\Psi(\vec{r})}_A &= \underbrace{\int d\vec{r} \psi_0(\vec{r})^* E\Psi(\vec{r})}_B\end{aligned}$$

Solving  $A$  term: let's split the Hamiltonian in the atomic and potential terms and remember that  $\psi_0$  is an atomic Hamiltonian eigenstate with eigenvalue  $E_0$ .

$$\begin{aligned}\int d\vec{r} \psi_0(\vec{r})^* \hat{H}\Psi(\vec{r}) &= \sum_{\vec{R}} \int d\vec{r} \psi_0(\vec{r})^* (H_{atom} + V(\vec{r})) e^{i\vec{k}\cdot\vec{R}} \psi_0(\vec{r} - \vec{R}) \\ &= \sum_{\vec{R}} \int d\vec{r} \psi_0(\vec{r})^* (E_0 + V(\vec{r})) e^{i\vec{k}\cdot\vec{R}} \psi_0(\vec{r} - \vec{R}) \\ &= E_0 \left[ 1 + \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} \alpha_0(\vec{R}) \right] + \underbrace{\int d\vec{r} \psi_0(\vec{r})^* V(\vec{r}) \psi_0(\vec{r})}_\beta + \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} \underbrace{\int d\vec{r} \psi_0(\vec{r})^* V(\vec{r}) \psi_0(\vec{r} + \vec{R})}_{\gamma(\vec{R})}\end{aligned}$$

where the terms with  $\vec{R} = 0$  have been distinguished from the terms with  $\vec{R} \neq 0$ , and the overlapping function  $\alpha_0(\vec{R}) = \int d\vec{r} \psi_0(\vec{r})^* \psi_0(\vec{r} + \vec{R})$  has been defined. For the  $B$  term, instead:

$$\begin{aligned}\int d\vec{r} \psi_0(\vec{r})^* E\Psi(\vec{r}) &= E \int d\vec{r} \psi_0(\vec{r})^* \Psi(\vec{r}) \\ &= E \left[ 1 + \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} \alpha_0(\vec{R}) \right]\end{aligned}$$

This lead to:

$$E = E_0 + \frac{\beta + \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} \gamma(\vec{R})}{1 + \sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}} \alpha_0(\vec{R})}$$

Consider now that:

- $\alpha_0(\vec{R}) \approx 0 \forall \vec{R} \neq 0$
- $\gamma_{\vec{R}}$  is non-negligible only for nearest neighbors:  $\gamma_{\vec{R}} \approx \delta_{R,a} \gamma_{\vec{a}}$

Therefore, in first approximation:

$$E = E_0 + \beta + \sum_{\vec{a} \text{ NN}} e^{i\vec{k}\cdot\vec{a}} \gamma(\vec{a})$$

which in 1D becomes:

$$E = E_0 + \beta + 2\gamma(a) \cos(ka)$$

### 6.3 Electron velocity

Let's consider a Bloch wavefunction,  $\Psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r})$ , and the squared momentum operator:

$$\begin{aligned}(-i\vec{\nabla})^2 \Psi_{n\vec{k}} &= (-i\vec{\nabla}) \left[ e^{i\vec{k}\cdot\vec{r}} (\vec{k} - i\vec{\nabla}) u_{n\vec{k}} \right] \\ &= e^{i\vec{k}\cdot\vec{r}} (k^2 - 2i\vec{k}\cdot\vec{\nabla} + (-i\vec{\nabla})^2) u_{n\vec{k}} \\ &= e^{i\vec{k}\cdot\vec{r}} (\vec{k} - i\vec{\nabla})^2 u_{n\vec{k}}\end{aligned}$$



which means that the Schrödinger equation can be written in terms of  $u_{n\vec{k}}$ :

$$\begin{aligned}\hat{H}\Psi_{n\vec{k}} = E\Psi_{n\vec{k}} &\quad \rightarrow \quad \hat{H}_{\vec{k}}u_{n\vec{k}} = Eu_{n\vec{k}} \\ &\quad \text{with } \hat{H}_{\vec{k}} = \frac{\hbar^2}{2m}(\vec{k} - i\vec{\nabla})^2 + V(\vec{r})\end{aligned}$$

Let's consider a small deviation of  $\vec{k}$ : therefore

$$\begin{aligned}E(\vec{k} + \vec{q}) &= E(\vec{k}) + \vec{q}(\vec{\nabla} \cdot E(\vec{k})) \\ \hat{H}_{\vec{k}+\vec{q}} &= \frac{\hbar^2}{2m}(\vec{k} - i\vec{\nabla})^2 + 2\vec{q} \cdot \frac{\hbar^2}{2m}(\vec{k} - i\vec{\nabla}) + V(\vec{r}) = \hat{H}_{\vec{k}} + 2\vec{q} \cdot \frac{\hbar^2}{2m}(\vec{k} - i\vec{\nabla})\end{aligned}$$

But also (in first approx,  $u_{n\vec{k}} \approx u_{n(\vec{k}+\vec{q})}$ ):

$$\begin{aligned}E(\vec{k} + \vec{q}) &= \int u_{n\vec{k}}^* \hat{H}_{\vec{k}+\vec{q}} u_{n\vec{k}} d\vec{r} \\ &= E(\vec{k}) + \int u_{n\vec{k}}^* 2\vec{q} \frac{\hbar^2}{2m} (\vec{k} - i\vec{\nabla}) u_{n\vec{k}} d\vec{r} \\ &= E(\vec{k}) + 2\vec{q} \int u_{n\vec{k}}^* e^{-i\vec{k}\cdot\vec{r}} e^{i\vec{k}\cdot\vec{r}} \frac{\hbar^2}{2m} (\vec{k} - i\vec{\nabla}) u_{n\vec{k}} d\vec{r}\end{aligned}$$

but observe that, as shown before:

$$e^{i\vec{k}\cdot\vec{r}}(\vec{k} - i\vec{\nabla})u_{n\vec{k}} = -i\vec{\nabla}\Psi_{n\vec{k}}$$

and remembering that  $\frac{-i\hbar\vec{\nabla}}{m} = \hat{v}$ , one obtain

$$\begin{aligned}E(\vec{k} + \vec{q}) &= E(\vec{k}) + \vec{q} \int \Psi_{n\vec{k}}^* \hbar\hat{v}\Psi_{n\vec{k}} d\vec{r} \\ &= E(\vec{k}) + \vec{q}\hbar\langle\vec{v}\rangle\end{aligned}$$

Comparing the latter with the series expansion previously found:

$$\langle\vec{v}\rangle = \frac{\vec{\nabla} \cdot E(\vec{k})}{\hbar}$$

This last relation permit to compute the crystalline momentum of the electrons! Observe that, if the crystal is perfect,  $E \propto k^2$ , which means that the velocity have no theoretical upper limit. Sadly, in real crystals there are imperfections and phonons that limit the possible velocities.

## 6.4 External force on electrons

Let's now consider the effects of an external force on electrons. Let  $T_{\vec{R}}$  be the translational operator, i.e. such that

$$T_{\vec{R}}f(\vec{r}) = f(\vec{r} + \vec{R})$$

Remember that, by definition,  $T_{\vec{R}}V(\vec{r}) = V(\vec{r})$ . Let's apply the translational operator to the wavefunction, remembering the Block theorem:

$$\begin{aligned}T_{\vec{R}}\Psi_{n\vec{k}}(\vec{r}) &= \Psi_{n\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{R}}\Psi_{n\vec{k}}(\vec{r}) \\ \langle T_{\vec{R}} \rangle &= \int \Psi_{n\vec{k}}(\vec{r}) T_{\vec{R}}\Psi_{n\vec{k}}(\vec{r}) d\vec{r} = e^{i\vec{k}\vec{R}} \\ \frac{d}{dt} \langle T_{\vec{R}} \rangle &= i \frac{d\vec{k}}{dt} e^{i\vec{k}\vec{R}} \vec{R}\end{aligned}$$

Let's consider an Hamiltonian which contain a standard part plus an external force:

$$H = H_0 - \vec{F}_{ext}\vec{r}$$

$$\begin{aligned} [H, T_{\vec{R}}] &= [H_0, T_{\vec{R}}] - [\vec{F}_{ext}\vec{r}, T_{\vec{R}}] \\ &= 0 - (\vec{F}_{ext}\vec{r}T_{\vec{R}} - T_{\vec{R}}\vec{F}_{ext}\vec{r}) \end{aligned}$$

$$\begin{aligned} \langle [H, T_{\vec{R}}] \rangle &= \int d\vec{r} \Psi_{n\vec{k}}(\vec{r}) (T_{\vec{R}}\vec{F}_{ext}\vec{r} - \vec{F}_{ext}\vec{r}T_{\vec{R}}) \Psi_{n\vec{k}}(\vec{r}) \\ &= \int d\vec{r} \Psi_{n\vec{k}}(\vec{r}) T_{\vec{R}}(\vec{F}_{ext}\vec{r}\Psi_{n\vec{k}}(\vec{r})) - \vec{F}_{ext}\vec{r}T_{\vec{R}}\Psi_{n\vec{k}}(\vec{r}) \\ &= \int d\vec{r} \Psi_{n\vec{k}}(\vec{r}) \vec{F}_{ext}(\vec{r} + \vec{R}) e^{i\vec{k}\vec{R}} \Psi_{n\vec{k}}(\vec{r}) - \vec{F}_{ext}\vec{r} e^{i\vec{k}\vec{R}} \Psi_{n\vec{k}}(\vec{r}) \\ &= \int d\vec{r} \Psi_{n\vec{k}}(\vec{r}) (\vec{F}_{ext}(\vec{r} + \vec{R}) e^{i\vec{k}\vec{R}} - \vec{F}_{ext}\vec{r} e^{i\vec{k}\vec{R}}) \Psi_{n\vec{k}}(\vec{r}) \\ &= \vec{F}_{ext}\vec{R} e^{i\vec{k}\vec{R}} \end{aligned}$$

Consider now the Heisemberg equation for the evolution of operators in Heisemberg picture:

$$\begin{aligned} \frac{d\langle T_{\vec{R}} \rangle}{dt} &= \frac{i}{\hbar} \langle [H, T_{\vec{R}}] \rangle \\ i \frac{d\vec{k}}{dt} e^{i\vec{k}\vec{R}} \vec{R} &= \frac{i}{\hbar} \vec{F}_{ext}\vec{R} e^{i\vec{k}\vec{R}} \end{aligned}$$

$$\frac{d\vec{k}}{dt} = \frac{\vec{F}_{ext}}{\hbar}$$

## 6.5 Electrons momentum

Remembering that  $\Psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\vec{r}}$ , let's compute the expectation value of the momentum operator:

$$\begin{aligned} \langle P \rangle &= \int d\vec{r} \Psi_{n\vec{k}}^* (-i\hbar\vec{\nabla}) \Psi_{n\vec{k}} \\ &= \sum_{\vec{G}, \vec{G}'} c_{\vec{k}-\vec{G}}^* c_{\vec{k}-\vec{G}'} \int d\vec{r} e^{-i(\vec{k}-\vec{G})\vec{r}} (-i\hbar\vec{\nabla}) e^{i(\vec{k}-\vec{G}')\vec{r}} \\ &= \sum_{\vec{G}, \vec{G}'} c_{\vec{k}-\vec{G}}^* c_{\vec{k}-\vec{G}'} \hbar(\vec{k} - \vec{G}') \underbrace{\int d\vec{r} e^{i(-\vec{k}+\vec{G}+\vec{k}-\vec{G}')\vec{r}}}_{\delta_{\vec{G}, \vec{G}'}} \\ &= \sum_{\vec{G}} |c_{\vec{k}-\vec{G}}|^2 \hbar(\vec{k} - \vec{G}) \\ &= \hbar\vec{k} \sum_{\vec{G}} |c_{\vec{k}-\vec{G}}|^2 - \hbar \sum_{\vec{G}} \vec{G} |c_{\vec{k}-\vec{G}}|^2 \\ &= \hbar\vec{k} - \hbar\vec{G} \sum_{\vec{G}} |c_{\vec{k}-\vec{G}}|^2 \end{aligned}$$

where can be seen that the momentum of an electron is given by the expected relation,  $\hbar\vec{k}$ , plus an additive factor which consider the dispersion of the electron in the different Brillouin zones!

## 6.6 Effective mass

Let's search for an equivalent of the classical notion of mass, starting from the classical Newton relation

$$\vec{F} = m \frac{d\vec{v}}{dt}$$

Recalling the previous results:

$$\frac{d\vec{k}}{dt} = \frac{\vec{F}}{\hbar} \quad \langle \vec{v} \rangle = \frac{\vec{\nabla} \cdot E(\vec{k})}{\hbar}$$

and replacing in the Newton equation, one obtain:

$$\begin{aligned} \hbar \frac{d\vec{k}}{dt} &= m \frac{d}{dt} \frac{\vec{\nabla} \cdot E(\vec{k})}{\hbar} \\ \hbar \frac{d\vec{k}}{dt} &= m \left( \frac{d}{d\vec{k}} \frac{\vec{\nabla} \cdot E(\vec{k})}{\hbar} \right) \cdot \frac{d\vec{k}}{dt} \\ \frac{1}{m} &= \frac{\text{Hess } E(\vec{k})}{\hbar^2} \end{aligned}$$

where Hess is the Hessian matrix (with respect to  $\vec{k}$ ) operator. Observe that in one dimension the relation is simplified:

$$\frac{1}{m} = \frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial \vec{k}^2}$$

while in multiple dimensions the effective mass is a tensor. Moreover, remembering the various shapes that can be assumed by the energy as function of  $\vec{k}$  (e.g., fig. 18), observe that the mass can be zero, or can be negative!

Observe what happen to an electron subject to an electric field  $\vec{E}$ , in a 1D tight-binding approximation:

$$\begin{aligned} E &= E_0 + \beta + 2\gamma(a) \cos(ka) & \frac{\partial \vec{k}}{\partial t} &= \frac{-e\vec{E}}{\hbar} \\ v &= \frac{1}{\hbar} \frac{\partial}{\partial k} E(\vec{k}) = -\frac{2a\gamma(a)}{\hbar} \sin(ka) \\ &= -\frac{2a\gamma(a)}{\hbar} \sin\left(\frac{-e\vec{E}at}{\hbar}\right) \\ x &= \int v dt \propto \cos\left(\frac{-e\vec{E}at}{\hbar}\right) \end{aligned}$$

Observe the particular result: the mass changes continuously sign, and the electron oscillates even if the electric field is fixed in a given direction. If one compute the oscillation period, however, he found something in the order of  $10^{-7}$ s, which is much larger than the mean scattering time ( $10^{-9} - 10^{-14}$ s). This means that the oscillations doesn't really take place.

## 7 Electrons and holes

The full bands are inert; only the partially-filled ones contribute to electrical and thermal conduction. Moreover,

$$\begin{aligned} \int_{\text{full band}} &= 0 = \int_{\text{occupied}} + \int_{\text{unoccupied}} \\ \int_{\text{occupied}} &= - \int_{\text{unoccupied}} \end{aligned}$$

This means that the system can be rescaled such that the zero-energy is considered with the full band, the electrons above the band limit are the only electrons to be considered while the leaks under the band limit are considered as holes. A hole have the following properties:

- $\vec{k}_h = -\vec{k}_e$
- $E_h = E_0 - E_e$
- $\vec{v}_h = \vec{v}_e$

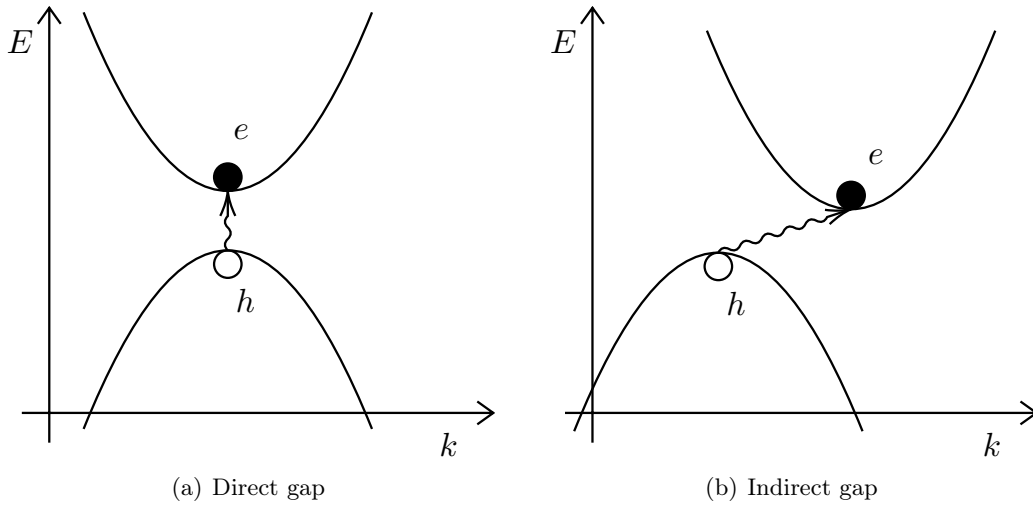


Figure 19: Hole creation from external excitation

Typically, the gap between bands is in the order of electronvolts, while the room temperature is in the order of 0.01 electronvolts. There may be a probability that an electron jump from the valence band to the conduction band! Let  $n$  be the electrons number (only electrons in conduction band are considered), and  $p$  the holes number. Consider a system that, at  $T = 0$ , shows a full-filled band. Therefore,  $p = n$ .

Consider, for simplicity, a direct gap. Let  $D$  be the density of states (and in particular, let  $D_e$  be the density of states in the higher band and  $D_h$  the density of states in the lower band) and  $f$  the occupation function.

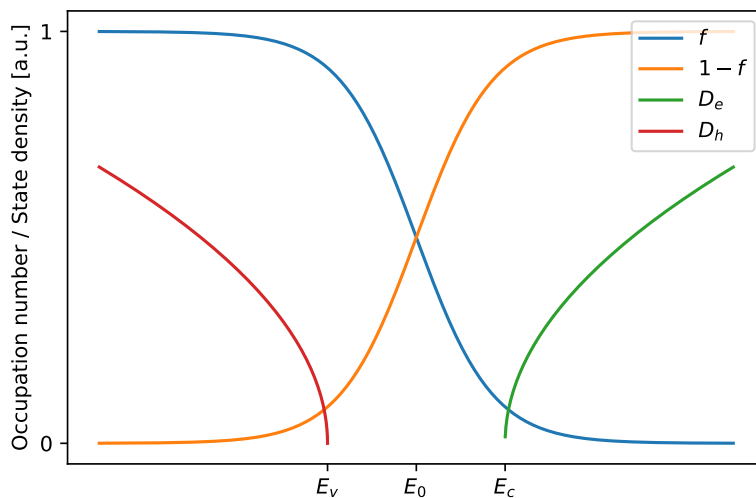


Figure 20: Holes and electrons densities

$$p = n$$

$$\int D_h(1 - f) dE = \int D_e f dE$$

In first approximation:

$$f = \frac{1}{e^{\beta(E-E_F)} + 1} \approx e^{-\beta(E-E_F)}$$

In a quadratic approximation, replying the behavior of the free-electrons Fermi gas, near the minima:

$$D_e = \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}$$

$$D_h = \frac{1}{2\pi^2} \left( \frac{2m_h^*}{\hbar^2} \right)^{3/2} \sqrt{E_v - E}$$

This means that:

$$n = \int D_e f dE = \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} \int dE \sqrt{E - E_c} e^{-\beta(E-E_F)}$$

$$= \frac{1}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} e^{-\beta(E_c-E_F)} \int dE \sqrt{E - E_c} e^{-\beta(E-E_c)}$$

$$= 2 \left( \frac{m_e^*}{2\hbar^2\pi\beta} \right)^{3/2} e^{-\beta(E_c-E_F)}$$

and similarly

$$p = 2 \left( \frac{m_h^*}{2\hbar^2\pi\beta} \right)^{3/2} e^{-\beta(E_F-E_v)}$$

The intrinsic concentration is therefore defined as (remember  $n = p = n_i$ ):

$$n_i = \sqrt{np} \propto e^{-1/2\beta(E_c-E_v)}$$

which depends only from the width of the gap between the bands!

Finally, the Fermi energy can be computed:

$$n = p$$

$$2 \left( \frac{m_e^*}{2\hbar^2\pi\beta} \right)^{3/2} e^{-\beta(E_c-E_F)} = 2 \left( \frac{m_h^*}{2\hbar^2\pi\beta} \right)^{3/2} e^{-\beta(E_F-E_v)}$$

$$E_F = \frac{E_v + E_c}{2} + \frac{3}{4} \frac{1}{\beta} \ln \frac{m_h^*}{m_e^*}$$

i.e. **the Fermi energy is the average energy between the two bands limits, plus a correction due to different bands curvature.**

## 7.1 Semiconductors

In a pure semiconductor (typically, metal of IV group), typically the gap is enough high to produce a negligible intrinsic concentration. Doping the semiconductor, with a donor or an acceptor, i.e. with a metal of the groups V or III, new extra level are created. This new level modify the Fermi energy of the crystal and produces more pairs electrons-holes.

In fact, e.g., for a donor the electron radius can be computed considering the effective mass and the dielectric constant:

$$a_0 = \frac{\hbar^2}{m e^2} \cdot 4\pi\epsilon_0 \quad \rightarrow \quad a_d = \frac{\hbar^2}{m^* e^2} \cdot 4\pi\epsilon_d \epsilon_0 \sim 30 - 80 \text{ \AA}$$

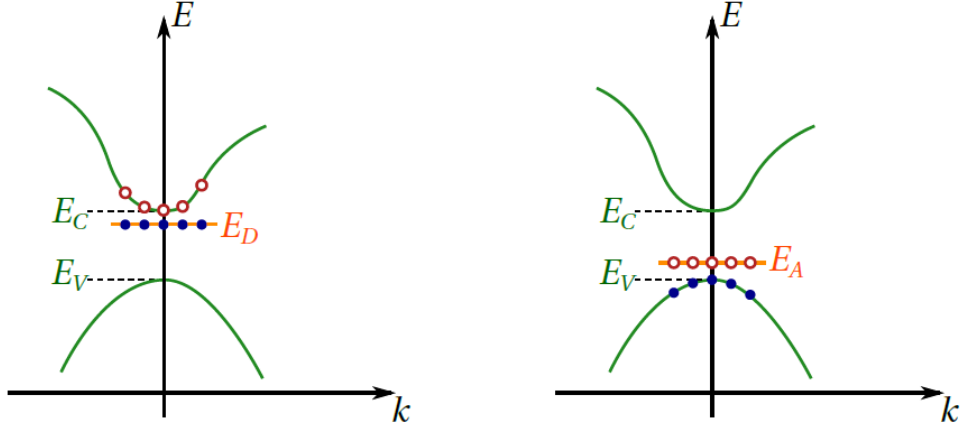


Figure 21: Donors and acceptors extra energy levels

For the energy level provided by the donor, 4 different states are possible:

- No electrons in the level; energy 0;
- 1 electron in the level; energy  $E_d$ ; two cases, with the two spins;
- 2 electrons in the level; energy  $2E_d + U$  where  $U$  is the Coulomb repulsion. Since the atom is a donor, this case have high energy and is therefore negligible.

Therefore, considering the Boltzmann distribution and being  $N_d$  the total density of the donors, the expectation value of the number of electrons in the donor level is:

$$\langle n_d^0 \rangle = N_d \frac{0 \cdot e^0 + 1 \cdot e^{-\beta(E_d - E_f)} + 1 \cdot e^{-\beta(E_d - E_f)}}{e^0 + e^{-\beta(E_d - E_f)} + e^{-\beta(E_d - E_f)}} = \frac{1}{\frac{1}{2}e^{\beta(E_d - E_f)} + 1}$$

Observe that  $E_d - E_f$  is negative! Therefore, at  $T \rightarrow 0$ , all electrons are in donors levels. Therefore, the expectation value of the electrons in the conduction band is:

$$\langle n_c \rangle = n_i + (N_d - \langle n_d^0 \rangle) = n_i + n_d^+$$

where  $n_i$  is the intrinsic concentration. Three cases can be distinguished:

- High temperature: electrons from valence band easy jump to conduction band. Therefore,  $n_i \gg n_d^+$  and the effects of the impurities are negligible;
- Intermediate temperature: all impurities are ionized, while electrons don't manage to jump from valence to conduction band. Therefore  $n_c \approx n_d^+ \approx N_d$ ;
- Low temperature: both donors and valence electrons are in their ground state. The Fermi energy is between  $E_d$  and  $E_c$ .

## 7.2 Mobility

The mobility is defined as the ratio between the speed and the electric field:

$$\mu = \frac{|v|}{|\mathcal{E}|}$$

The current can be written as

$$j = en\mu\mathcal{E} \quad \rightarrow \quad \sigma = en\mu$$

but, in a system with electron and holes,

$$\sigma = e(n\mu_e + p\mu_h)$$

Remembering that we've previously proven that  $\sigma \approx \frac{ne^2\tau}{m}$ :

$$\mu \sim \sigma \sim \tau \sim \frac{1}{v\Sigma}$$

where  $v$  is the electrons speed,  $v \sim \sqrt{T}$ , while  $\Sigma$  is the scattering cross section:

$$\Sigma \sim \begin{cases} v^{-4} \sim T^{-2} & \text{Low } T \\ n_{phon} \sim T & \text{High } T \end{cases} \quad \mu \sim \begin{cases} T^{3/2} & \text{Low } T \\ T^{-3/2} & \text{High } T \end{cases}$$

### 7.3 Real Fermi surfaces

Typically, Fermi surface is spherical while Brillouin zones are cubic, therefore the Fermi surface cross different zones! Using a proper folding, all the Brillouin zones can be transported to the first one.

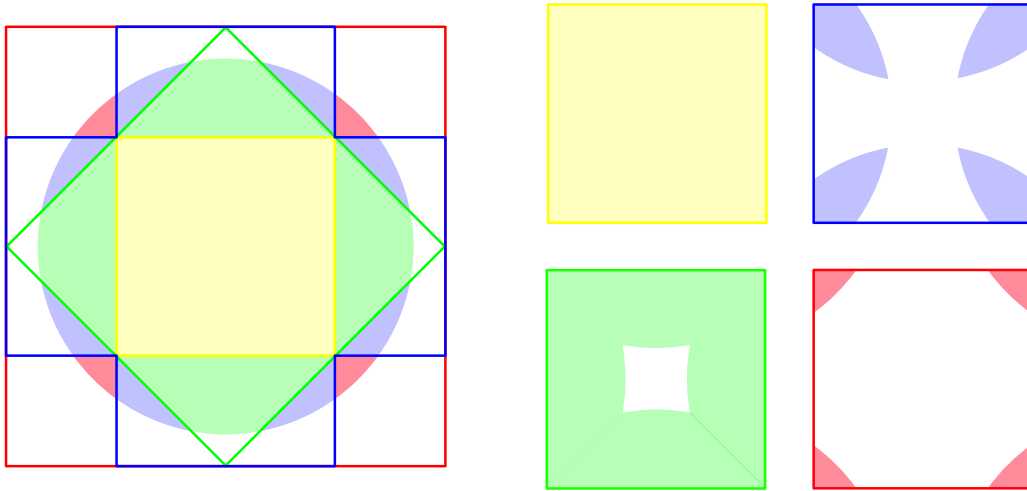


Figure 22: Fermi sphere in different Brillouin zones, and folding.

Moreover, for quasi-free electrons, the potential is modified such that the symmetry is respected and no spikes appears, i.e. the Fermi surface intersect the Brillouin zones surfaces perpendicularly.

Considering the electrons in the Fermi surface, let's introduce an electric field:

$$\begin{aligned} \hbar \frac{d\vec{k}}{dt} &= \vec{F}_{ext} = -e\vec{v} \times \vec{B} \\ &= -\frac{e}{\hbar} \vec{\nabla} E(\vec{k}) \times \vec{B} \end{aligned}$$

which means, the variation of  $\vec{k}$  are parallel to the Fermi surface (remember that at the Fermi surface  $E(\vec{k}) = E_F$  and therefore  $\vec{\nabla} E(\vec{k})$  is perpendicular to the surface itself). This means that an electron on the Fermi surface remain on the Fermi surface, following a circular path **in the momentum space**. Measuring therefore the orbits of electrons (in  $\vec{k}$  space!) the Fermi surface can be reconstructed.

## 8 Superconductors

Superconductors are systems that, at low temperature, present some particular behaviors. In particular:

- They're resistivity is zero. Current has been measured flowing around a superconductors for years;

- Meissner effect: they deflect the magnetic field, such that the field inside the superconductor is zero. In other words, the magnetization is equal and opposite to the external field,  $\vec{H} = -\vec{M}$ .

Superconductors of two different types can be distinguished, with respect to the sharpness of the transition.

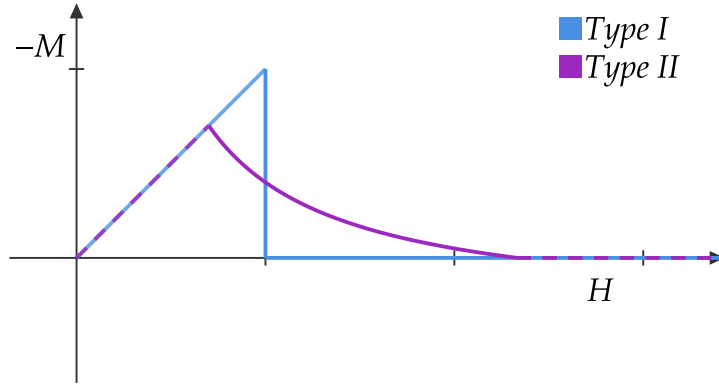


Figure 23: Semiconductors types

## 8.1 London equation

A phenomenological approach to superconductivity has been developed by London. The idea is to consider a density of *superconduction electrons*  $n_s$  which are moving with a speed  $\vec{v}$  and produces a superconduction current  $\vec{j}$ . This lead to:

$$\begin{aligned} \frac{\partial \vec{j}}{\partial t} &= \frac{\partial}{\partial t}(-en_s \vec{v}) = -en_s \frac{\partial \vec{v}}{\partial t} \\ &= -en_s \left( \frac{-e\mathcal{E}}{m} \right) = \frac{e^2 n_s}{m} \vec{\mathcal{E}} \end{aligned}$$

The quantity

$$\lambda_L = \frac{m}{e^2 n_s}$$

is called *London length* and, even if is not properly a length ( $[\lambda_L] = \text{H m}$ ), it's helpful in describing superconductors behavior. Considering the Maxwell equations:

$$\begin{aligned} \frac{\partial}{\partial t} (\vec{\nabla} \times \vec{j}) &= \vec{\nabla} \times \frac{\partial \vec{j}}{\partial t} = \vec{\nabla} \times \frac{1}{\lambda_L} \vec{\mathcal{E}} = -\frac{1}{\lambda_L} \frac{\partial \vec{B}}{\partial t} \\ \frac{\partial}{\partial t} \left( \vec{\nabla} \times \vec{j} + \frac{\vec{B}}{\lambda_L} \right) &= 0 \end{aligned}$$

The sum in the parenthesis is therefore constant in time; the Meissner hypothesis is that its value is zero. Therefore, the two London equations are:

$$\frac{\partial \vec{j}}{\partial t} = \frac{\vec{\mathcal{E}}}{\lambda_L} \quad \vec{\nabla} \times \vec{j} + \frac{\vec{B}}{\lambda_L} = 0$$



Recalling again the Maxwell equation:

$$\begin{aligned}\vec{\nabla} \times (\vec{\nabla} \times \vec{j}) &= \underbrace{\vec{\nabla}(\vec{\nabla} \cdot \vec{j})}_0, \text{ since } \vec{j} \propto \vec{\nabla} \times \vec{B} - \nabla^2 \vec{j} \\ &= \vec{\nabla} \times \left( -\frac{\vec{B}}{\lambda_L} \right) = -\frac{\mu_0}{\lambda_L} \vec{j} \\ \vec{\nabla} \times (\vec{\nabla} \times \vec{B}) &= \underbrace{\vec{\nabla}(\vec{\nabla} \cdot \vec{B})}_0 - \nabla^2 \vec{B} \\ &= \vec{\nabla} \times (\mu_0 \vec{j}) = -\frac{\mu_0}{\lambda_L} \vec{B}\end{aligned}$$

and defining  $\Lambda_L = \sqrt{\lambda_L/\mu_0}$ :

$$\nabla^2 \vec{j} = \frac{\vec{j}}{\Lambda_L^2} \quad \nabla^2 \vec{B} = \frac{\vec{B}}{\Lambda_L^2}$$

which are two skin-effect equations, with typical length  $\Lambda_L \approx 200\text{\AA}$ . This means that the external magnetic field and the external current are exponentially damped by the superconductor, which therefore is neutral in its center.

## 8.2 BSC theory

It's a microscopic theory to explain superconductivity at low temperature<sup>†</sup>. It's based on an hypothetical attraction between electrons. They therefore can form bound states (*Cooper pairs*) which are bosons and condensate following Bose-Einstein theory. Therefore, all pairs have the same wavefunction

$$\Psi(\vec{r}) = \sqrt{\rho} e^{i\theta}$$

Consider the probability current, that inside a superconductor must be zero. This leads to:

$$\begin{aligned}0 = \vec{j} &= -\frac{i\hbar}{2m}(\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^*) - \frac{q}{m} A \Psi^* \Psi \\ &= \frac{\hbar}{m}(\vec{\nabla} \theta - \frac{q}{m} A) \rho(\vec{r})\end{aligned}$$

$$\vec{\nabla} \theta = \frac{q}{m} A$$

Let's now consider a superconductive ring, and choose a path  $\Lambda$  inside it. From the last relation,

$$\begin{aligned}\int_{\Lambda} \vec{\nabla} \theta \, dl &= \int_{\Lambda} \frac{q}{m} A \, dl \\ \Delta \theta &= \frac{q}{\hbar} \Phi_B\end{aligned}$$

where  $\Phi_B$  is the flux of the magnetic field inside the ring. To keep the waveform coherence, the phase variation must be a multiple of  $2\pi$ :

$$\Delta \theta = 2\pi n \quad \rightarrow \quad \Phi_B = \frac{2\pi\hbar}{q} n$$

The last equation is particularly interesting, since it shows that **the magnetic flux inside a superconductive ring is quantized!** Moreover, studying the steps of the quantization, one can measure

<sup>†</sup>Superconductivity at high temperature exists, but still has not been explained.

$q = -2e$ , confirming the hypothesis that electrons gather in pairs! But how can the attractive force be provided? It's due to phonons!

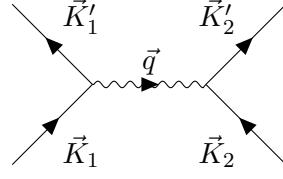


Figure 24: Electrons interaction mediated by a phonon.

The typical size of this pair can be exploited considering the typical Fermi speed,  $v_F$ , and the typical phonons frequency,  $\omega_D$ :

$$l \approx 2\pi \frac{v_F}{\omega_D} \approx 10^3 - 10^4 \text{ \AA}$$

which is remarkably large!

Moreover, it turns out that in a Cooper pair **the two electrons have opposite spin, and equal and opposite momentum  $\vec{k}_1 = -\vec{k}_2$ .**

### 8.3 Binding energy

In quantum mechanics, low attractions are typically not enough to make a bound state. But let's consider this specific case: the Schrödinger equation is:

$$\left[ -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + V(\vec{r}_1, \vec{r}_2) \right] \Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2)$$

Only electrons close to the Fermi surface, in a shell let's say with a thickness  $\hbar\omega_D$ , are interested by the attraction. In this case, the energy of the couple of electrons is given by their non-interacting energy plus an attractive perturbation:

$$E = 2E_F + \varepsilon$$

Let's expand  $\Psi$  and  $V$  in a generic superposition of states, remembering that  $\vec{k}_1 = -\vec{k}_2$ :

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{V} \sum_{\vec{k}} g(\vec{k}) e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)}$$

$$V(\vec{r}_1, \vec{r}_2) = \frac{1}{V} \sum_{\vec{k}_1, \vec{k}_2} V_{\vec{k}_1, \vec{k}_2} e^{i(\vec{k}_1 \vec{r}_1 - \vec{k}_2 \vec{r}_2)}$$

where  $\vec{k}$  is "near" the Fermi surface. Substituting in the Schrödinger equation:

$$\frac{1}{V} \sum_{\vec{k}} g(\vec{k}) \frac{\hbar^2}{m} k^2 e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} + \frac{1}{V^2} \sum_{\vec{k}_1, \vec{k}_2} g(\vec{k}) V_{\vec{k}_1, \vec{k}_2} e^{i\vec{k}(\vec{r}_1 - \vec{r}_2) + i(\vec{k}_1 \vec{r}_1 - \vec{k}_2 \vec{r}_2)} = \frac{2E_F + \varepsilon}{V} \sum_{\vec{k}} g(\vec{k}) e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)}$$

Let  $\vec{r}_- = \vec{r}_1 - \vec{r}_2$ ,  $\vec{r}_+ = \vec{r}_1 + \vec{r}_2$ , then multiply by  $e^{i\vec{k}'\vec{r}_-}$ :

$$\frac{1}{V} \sum_{\vec{k}} g(\vec{k}) \frac{\hbar^2}{m} k^2 e^{i(\vec{k} - \vec{k}')\vec{r}_-} + \frac{1}{V^2} \sum_{\vec{k}_1, \vec{k}_2} g(\vec{k}) V_{\vec{k}_1, \vec{k}_2} e^{i(\vec{k} - \vec{k}' + \frac{\vec{k}_1 - \vec{k}_2}{2})\vec{r}_- + i(\frac{\vec{k}_1 + \vec{k}_2}{2})\vec{r}_+} = \frac{2E_F + \varepsilon}{V} \sum_{\vec{k}} g(\vec{k}) e^{i(\vec{k} - \vec{k}')\vec{r}_-}$$

Integrate with respect to  $r_+$  and  $r_-$ . In the first and in the last term a  $\delta(\vec{k} - \vec{k}')$  appear, while in the central term appears both  $\delta(\vec{k} - \vec{k}' + \frac{\vec{k}_1 - \vec{k}_2}{2})$  and  $\delta(\frac{\vec{k}_1 + \vec{k}_2}{2})$ :

$$g(\vec{k}') \frac{\hbar^2}{m} (k')^2 + \frac{1}{V} \sum_{\vec{k}} g(\vec{k}) V_{\vec{k}' - \vec{k}, \vec{k} - \vec{k}'} = (2E_F + \varepsilon) g(\vec{k}')$$

Let's now define a constant potential:  $V_{\vec{k}_1 \vec{k}_2} = -V_0$ . Remember that all the  $\vec{k}$  considered are supposed to be contained in the  $\hbar\omega_D$  shell around  $E_F$ . Therefore:

$$g(\vec{k}') \frac{\hbar^2}{m} (k')^2 - \frac{V_0}{V} \sum_{\vec{k}} g(\vec{k}) = (2E_F + \varepsilon)g(\vec{k}')$$

$$g(\vec{k}') = \frac{\frac{V_0}{V} \sum_{\vec{k}} g(\vec{k})}{2E_{\vec{k}'} - 2E_F - \varepsilon}$$

$$\sum_{\vec{k}'} g(\vec{k}') = \sum_{\vec{k}'} \frac{\frac{V_0}{V} \sum_{\vec{k}} g(\vec{k})}{2E_{\vec{k}'} - 2E_F - \varepsilon}$$

$$\frac{V}{V_0} = \sum_{\vec{k}'} \frac{1}{2E_{\vec{k}'} - 2E_F - \varepsilon}$$

In the continuous limit,

$$\frac{V}{V_0} = V \int_{E_F}^{E_F + \hbar\omega_D} dE g(E) \frac{1}{2E - 2E_F - \varepsilon}$$

and remembering that in the considered shell  $g(E) \approx g(E_F)$ :

$$\frac{1}{V_0} = \frac{g(E_F)}{2} \ln \frac{2E_F + 2\hbar\omega_D - 2E_F - \varepsilon}{2E_F - 2E_F - \varepsilon}$$

$$= \frac{g(E_F)}{2} \ln \frac{\varepsilon - 2\hbar\omega_D}{\varepsilon}$$

$$\varepsilon = \frac{2\hbar\omega_D}{1 - \exp\left\{\frac{2}{V_0 g(E_F)}\right\}} \approx -2\hbar\omega_D e^{-\frac{2}{V_0 g(E_F)}}$$

The last results permit to observe some important effects:

- $\varepsilon$  is negative: it's a bound!
- $\varepsilon > 0$  for an arbitrary small value of  $V_0$ : there's not a thresholds!
- $\varepsilon$  cannot be expanded perturbatively.

Can be also demonstrated that:

$$T_C = 1.13 T_D e^{-\frac{2}{V_0 g(E_F)}}$$

and the London equations can be derived by the probability current equation.

Let's consider a 2-state model, i.e. a model with a superconducting state at energy 0 and a normal state at energy  $\Delta$ . The medium energy can be therefore written as:

$$\langle E \rangle = \frac{\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \approx \Delta e^{-\beta\Delta}$$

$$c_V = \frac{\partial E}{\partial T} \approx \frac{\Delta^2}{k_B T^2} e^{-\beta\Delta}$$

## 8.4 Josephson effect

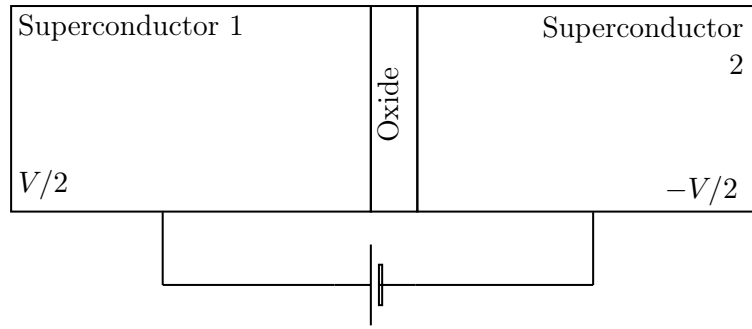


Figure 25: Josephson apparatus

Consider a couple of semiconductors, separated by an insulating material and with an induced potential difference  $V$ , and suppose a linear coupling between them. Consider  $\rho_1 \approx \rho_2 \approx \rho$  uniform, and therefore neglect the kinetic term in the Hamiltonian. Therefore:

$$i\hbar \frac{\partial \Psi_1}{\partial t} = H_1 \Psi_1 + K \Psi_2$$

$$i\hbar \frac{\partial}{\partial t} \sqrt{\rho_1} e^{i\theta_1} = \frac{qV}{2} \sqrt{\rho_1} e^{i\theta_1} + k \sqrt{\rho_2} e^{i\theta_2}$$

and similarly for the superconductor 2. Therefore, one can write  $\delta = \theta_2 - \theta_1$  which lead to:

$$\frac{d\rho_1}{dt} = \frac{d\rho_2}{dt} = J$$

$$J = \frac{2K\sqrt{\rho_1\rho_2}}{\hbar} \sin\left(\delta_0 - \frac{2e}{\hbar} \int V(t) dt\right)$$

This means that there is an high-efficiency oscillating current between the two superconductors! Moreover, observe that there is a (stationary) current even if  $V = 0$ , which is due to the difference in phase between the two superconductors!

## 8.5 SQUID

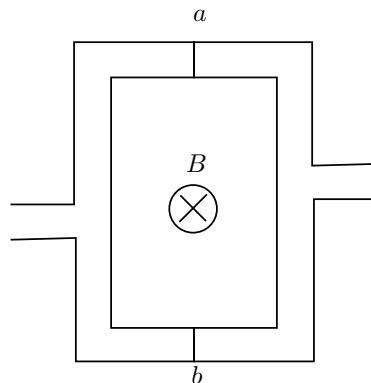


Figure 26: A SQUID apparatus

Consider a couple of superconductors, with the shape in fig. 26. Remembering that inside a superconductor  $\vec{\nabla}\theta = \frac{q}{\hbar}A$ . Integrate this relation around a path passing by  $a$ , and then by a path

passing by  $b$ . Being  $\delta_a$  and  $\delta_b$  the phase changes introduced by the junctions:

$$\begin{aligned}\Delta\theta \Big|_a &= \frac{q}{\hbar} \int_a A \, dl + \delta_a \\ \Delta\theta \Big|_b &= \frac{q}{\hbar} \int_b A \, dl + \delta_b\end{aligned}$$

Since the wavefunction must be coherent,

$$\Delta\theta \Big|_a - \Delta\theta \Big|_b = 2\pi n = \frac{q}{\hbar} \Phi_B + \delta_a - \delta_b$$

i.e., neglecting the  $2\pi$  additive factors:

$$\delta_{a,b} = \delta_0 \pm \frac{q}{2\hbar} \Phi_B$$

The total current flowing between the two superconductors, considering the current from both the junctions, is:

$$\begin{aligned}J &= J_0 \left[ \sin\left(\delta_0 + \frac{e}{2\hbar} \Phi_B\right) + \sin\left(\delta_0 - \frac{e}{2\hbar} \Phi_B\right) \right] \\ &= 2J_0 \sin \delta_0 \cos \frac{e\Phi_B}{2\hbar}\end{aligned}$$

which means, the current is maximum when:

$$\frac{e\Phi_B}{2\hbar} = \pi n \quad \Phi_B = \frac{2\hbar\pi}{e} n$$

and again a quantized magnetic flux is found. This can lead to high precision measurements of both the  $e/m$  ratio or the magnetic field.