

Short notes of Condensed Matter Physics

Federico Manzoni
Dipartimento di Fisica università La Sapienza
manzoni.1759892@studenti.uniroma1.it
Federico13.Manzoni97@gmail.com

Abstract: This short work is intended as introductory notes to the study of condensed matter physics by treating some specific basic topics useful for advanced study in this field. We follow [1] in general, [2] for chapter 2, [3] for chapter 3 and [4], [5] for chapter 4.

Contents

1	Bravais lattice and X-rays scattering	2
1.1	Bravais lattice, basis, reciprocal lattice and Miller indexes	2
1.2	Bragg's and Von Laue's formulation of X-rays scattering	4
1.2.1	Bragg's formulation	4
1.2.2	Von Laue's formulation	5
1.2.3	Equivalence of the Bragg's and Von Laue's formulations	5
1.3	X-rays scattering experimental methods without basis	6
1.3.1	Von Laue method	6
1.3.2	Rotating crystal method	6
1.3.3	Debye-Scherrer method	6
1.4	X-rays scattering experimental methods with basis	7
2	Lattice vibrations and phonons	8
2.1	Normal modes development	8
2.2	Phonons and specific heat	11
2.2.1	Einstein model	11
2.2.2	Debye model	12
3	Band structure of solids	13
3.1	Bloch theorem	13
3.1.1	Proof of Bloch theorem	13
3.2	Weak potential approximation	14
3.3	Tight Binding	15
4	Semiclassical theory of Bloch electrons	18
4.1	Motion in a DC electric field and in uniform magnetic field	19
4.2	Specific heat of Bloch electrons in solid	20
4.2.1	Sommerfeld expansion	20
4.2.2	Electronic specific heat	22
4.3	Semiclassical theory of transport phenomena in metals	23
5	Semiconductors	26
5.1	Intrinsic semiconductors	26
5.2	Extrinsic semiconductors	27

1 Bravais lattice and X-rays scattering

1.1 Bravais lattice, basis, reciprocal lattice and Miller indexes

A Bravais¹ lattice is an ideal model of crystal solids, spanned by a 1,2 or 3 primitive vectors (depending on the number of the system's dimensions). The simplest is the simple cubic (SC) lattice; example of others lattices are the FCC (face centered cubic) or the BCC (base centered cubic); generally speaking it exist 17 Bravais lattices in 3D systems. A vector belongs at the Bravais lattice if is in the form

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3,$$

in which n_1, n_2, n_3 are integers and $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the basis vectors. Some example (lattice with size a):

- SC $\Rightarrow a_1 = a\hat{x}, a_2 = a\hat{y}, a_3 = a\hat{z}$;
- FCC $\Rightarrow a_1 = \frac{a}{2}(\hat{z} + \hat{y}), a_2 = \frac{a}{2}(\hat{x} + \hat{z}), a_3 = \frac{a}{2}(\hat{x} + \hat{y})$;
- BCC $\Rightarrow a_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), a_2 = \frac{a}{2}(\hat{x} + \hat{z} - \hat{y}), a_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$.

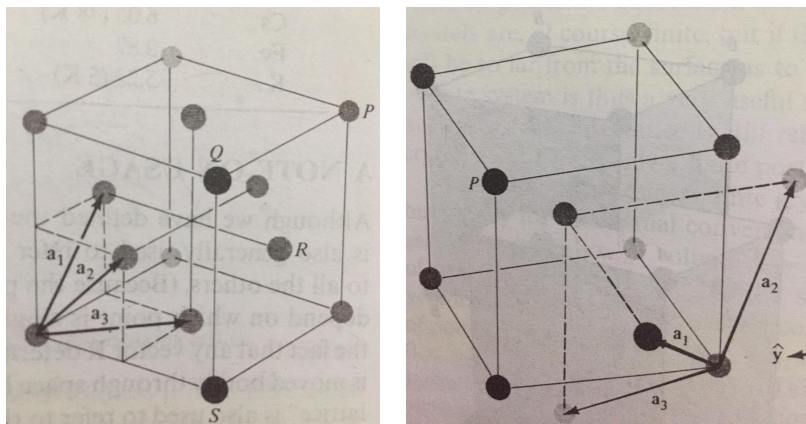


Figure 1: More symmetrical choice for primitive vectors for FCC (left) and BCC (right).

A prerogative of the Bravais lattices is that each of their points is identical from wherever they are observed (for example the honeycomb is not a Bravais lattice).

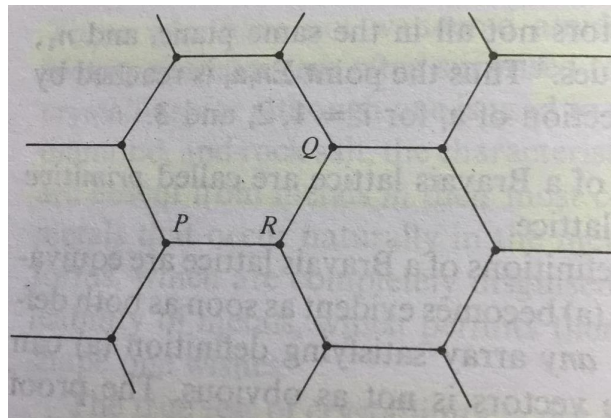


Figure 2: Honeycomb, it is not a Bravais lattice because the P point is not equivalent to the R point.

The simplest crystal is a crystal with only one kind of atom (or molecule or other) in which a Bravais lattice is sufficient for describe the system. A more complex crystal is a crystal with different kinds of atoms (or molecules or other) that needs a Bravais lattice with a basis. A basis can be constructed starting from the displacement of the different atoms that form the crystal; for example two atom displaced of $\frac{a}{2}$ along the diagonal of the cube can be described with two vectors that form the basis $\vec{d}_0 = (0, 0, 0)$; $\vec{d}_1 = a(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

¹Auguste Bravais was a French physicist known for his work in crystallography and the conception of Bravais lattices

The basis means that at each point of the basis I have to construct the associated Bravais lattice in order to have more interpenetrated lattice that correctly describes the solid under exam. We define unit (or primitive) cell a cell with one reticular site and conventional cell, a cell with n reticular sites. The volume of the two cells is related by

$$V_{uni} = \frac{V_{con}}{n}.$$

The unit cell is the smallest mineral's unit that still has the characteristic symmetry properties of the same mineral. We can always choose a cell that has the fully symmetries of the system and also one reticular site, this cell is called Wigner-Seitz cell.

Every real lattice (BL) have a correspondence in Fourier space, a reciprocal lattice (RL). Consider a plane wave with the same periodicity of the BL

$$e^{i\vec{K}\cdot(\vec{r}+\vec{R})} = e^{i\vec{K}\cdot\vec{r}} \Rightarrow e^{i\vec{K}\cdot\vec{R}} = 1,$$

so a vector, \vec{K} , belongs to the reciprocal lattice if

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

Since \vec{K} has to be of the form $\vec{K} = m_1b_1 + m_2b_2 + m_3b_3$ where

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

the condition $e^{i\vec{K}\cdot\vec{R}} = 1$ became (noting that $a_i b_j = 2\pi\delta_{ij}$)

$$e^{i2\pi(m_1n_1+m_2n_2+m_3n_3)} = 1 \Rightarrow m_1, m_2, m_3 \text{ are integers},$$

so the RL is a BL. It's obvious that the reciprocal lattice of the reciprocal lattice is the starting real lattice (because if we do two times Fourier transform we obtain the starting function). The Wigner-Seitz cell of the reciprocal lattice is called first Brillouin² zone (FBZ). Some examples of reciprocal lattice (real lattice with size a):

- SC \Rightarrow SC (size $\frac{2\pi}{a}$),
- FCC \Rightarrow BCC (size $\frac{4\pi}{a}$),
- BCC \Rightarrow FCC (size $\frac{4\pi}{a}$).

The volume of the BL and the RL are related, in fact

$$V_{RL} = \frac{(2\pi)^3}{V_{BL}}.$$

We define the lattice plane as a plane that connects an infinity number of reticular sites and a family of reticular planes as a set of parallel planes whose distance from each other is d . An important theorem says that for each family of lattice planes there exists a set of vectors of the reciprocal lattice perpendicular to the family of planes and the shortest has modulo $K = \frac{2\pi}{d}$. Since a reciprocal lattice vector is of the form $\vec{K} = h\vec{b}_1 + m\vec{b}_2 + l\vec{b}_3$, we can use the three coefficients to classify the lattice planes, these coefficients are called Miller³ indices so the Miller indices are three integers co-prime numbers (h, m, l) . In general given the RL's primitive vectors we can write $\vec{K} = h\vec{b}_1 + m\vec{b}_2 + l\vec{b}_3$ and so

$$|K| = \sqrt{h^2|b_1|^2 + m^2|b_2|^2 + l^2|b_3|^2 + 2hmb_1 \cdot b_2 + 2hmb_1 \cdot b_3 + 2mlb_2 \cdot b_3},$$

using the above formula we can collect, using Miller indices, the K vectors based on their length. For a orthogonal RL's primitive vectors we have

$$|K| = \sqrt{h^2|b_1|^2 + m^2|b_2|^2 + l^2|b_3|^2},$$

²Léon Brillouin was a French physicist. He made contributions to quantum mechanics, radio wave propagation in the atmosphere, solid state physics, and information theory.

³William Hallows Miller was a Welsh mineralogist and laid the foundations of modern crystallography.

which is simpler. In the case of cubic lattice (SC, FCC, BCC) (more generally for lattice that have orthogonal primitive vectors) we can use the Miller indices in a simple way (h, m, l) to collect the lattice planes. We know that between lattice planes and lattice vectors a one-to-one relationship exists. We know that

$$K = \frac{2\pi n}{d} = \frac{2\pi n}{a} \sqrt{h^2 + m^2 + l^2} \Rightarrow d = \frac{a}{\sqrt{h^2 + m^2 + l^2}}$$

where d is the distance between two lattice planes of the same family.

- SC $\Rightarrow h, m, l$ any integer number,
- FCC $\Rightarrow h + m + l$ even number,
- BCC $\Rightarrow h, m, l$ all odd or all even.

(the lattices in the list are reciprocal lattices). Thanks to the ratio between the increasing length K vectors we can understand if the RL is a SC or a FCC or a BCC or other type of lattices; we report some examples:

- SC $\Rightarrow \frac{K_1}{K_1} = 1.00, \frac{K_2}{K_1} = \sqrt{2} = 1.41, \frac{K_3}{K_1} = \sqrt{3} = 1.71, \frac{K_4}{K_1} = 2.00, \frac{K_5}{K_1} = \sqrt{5} = 2.23,$
- BCC $\Rightarrow \frac{K_1}{K_1} = 1.00, \frac{K_2}{K_1} = \frac{2}{\sqrt{3}} = 1.16, \frac{K_3}{K_1} = \frac{2\sqrt{2}}{\sqrt{3}} = 1.63, \frac{K_4}{K_1} = \frac{\sqrt{11}}{\sqrt{3}} = 1.92,$
- FCC $\Rightarrow \frac{K_1}{K_1} = 1.00, \frac{K_2}{K_1} = \sqrt{2} = 1.41, \frac{K_3}{K_1} = \sqrt{3} = 1.71, \frac{K_4}{K_1} = 2.00, \frac{K_5}{K_1} = \sqrt{6} = 2.45.$

So when we measure the K , for example with the DS method (see below), through the sequenced ratios we are able to understand what lattice it is.

1.2 Bragg's and Von Laue's formulation of X-rays scattering

Hitting a crystal with X-rays (the range of wavelength comparable with the characteristic distance in a crystal, order $10^{-10}m \approx 10^4 eV$) there are some elastic scattering between the X-rays and the atoms sitting in the reticular sites. This scattering can be described in two formulation. To study X-rays scattering of a crystal is fundamental because the bright points that are produced by scattering give us important information about the reciprocal lattice of the system and consequently on the real lattice of the crystal.

1.2.1 Bragg's formulation

In the Bragg's formulation⁴ the scattering is due to lattice planes that work like mirrors; in order to see something it's necessary that two rays interact constructively and that the difference of path of two rays must be an integer number of wavelength

$$\Delta l = 2d \sin(\theta) = n\lambda,$$

n is called reflection index. This formulation doesn't explain why the lattice planes work like mirrors and so it's not the better formulation to understand the reason why X-rays are scattered.

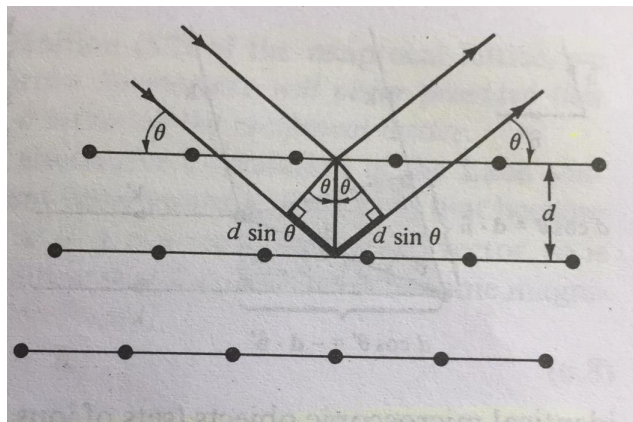


Figure 3: Geometric construction for Bragg scattering.

⁴This formulation was investigated by William Henry Bragg and his son William Lawrence Bragg. They were both physicist and both won the Nobel prize in 1915.

1.2.2 Von Laue's formulation

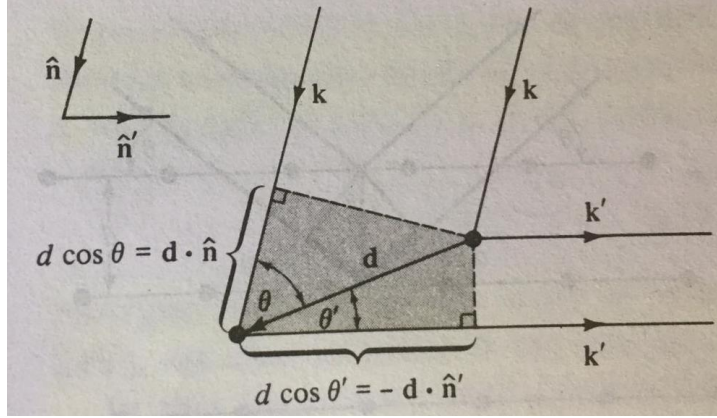


Figure 4: Geometric construction for Von Laue scattering. Note that the vector \vec{d} is a Bravais lattice vector, so $\vec{d} = \vec{R}$

In Von Laue's formulation⁵ the starting point is that the process is elastic and in each lattice site there is an atom that is able to absorb the radiation that hits the system and reemits isotropically. For the two rays to constructively interfere, their optical path difference must be an integer multiple of wavelengths, so from the figure,

$$\Delta l = R \cos(\theta) + R \cos(\theta') = \vec{R} \cdot (\hat{n} - \hat{n}') = m\lambda \Rightarrow \vec{R} \cdot (\vec{k} - \vec{k}') = 2\pi m,$$

in the last passage we have multiply by $\frac{2\pi}{\lambda}$, in which λ is the wavelength of the X-ray. The above equation can be rewrite

$$e^{i\vec{R} \cdot (\vec{k} - \vec{k}')} = 1,$$

so the condition in Von Laue formulation is that the difference between the wavenumber of incoming ray and the wavenumber of outgoing rays is a reciprocal lattice vector

$$\vec{k} - \vec{k}' = \vec{K}.$$

By rearranging the above equation we have that (remember that the process is elastic, so $(k')^2 = (k)^2$)

$$\vec{k}' = \vec{k} - \vec{K} \Rightarrow (k')^2 = (k)^2 + (K)^2 - 2\vec{K} \cdot \vec{k} \Rightarrow (K)^2 = 2\vec{K} \cdot \vec{k} \Rightarrow \vec{k} \cdot \hat{K} = \frac{K}{2},$$

so the projection of the incoming wave vector along the direction of a reciprocal lattice vector must be equal to half of the reciprocal lattice vector.

1.2.3 Equivalence of the Bragg's and Von Laue's formulations

Consider the construction

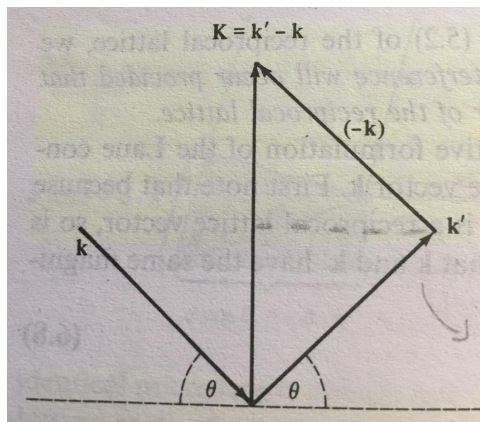


Figure 5: Geometric construction for the equivalence between Bragg's and Von Laue's formulation.

⁵Max Von Laue was a German physicist who received the Nobel Prize in Physics in 1914 for his discovery of the diffraction of X-rays by crystals.

From the figure we have that

$$K = 2k\sin(\theta),$$

the vector \vec{K} it will not be the shortest but will generally be an integer multiple of the shortest $K = \frac{2\pi n}{d}$ and $k = \frac{2\pi}{\lambda}$, so

$$\frac{2\pi n}{d} = 2k\sin(\theta) \Rightarrow \frac{2\pi n}{d} = 2\frac{2\pi}{\lambda}\sin(\theta) \Rightarrow 2d\sin(\theta) = n\lambda.$$

The two formulations are equivalent and so a Von Laue's diffraction peak corresponds to a Bragg's reflection peak and the reflection index is nothing but the ratio between the vector of the reciprocal lattice, which corresponds to the difference between the incoming and outgoing wave vector, and the shortest reciprocal lattice vector.

1.3 X-rays scattering experimental methods without basis

An interesting construction is the Ewald sphere; it's a sphere centered on the reticular site hit by the X-rays radiation and with a radius equal to the amplitude of the propagation vector of the radiation. If a reticular site lies on the surface of this sphere we see a bright spot corresponding to this reticular site.

There are different methods to do an experiment with X-rays that help us to understand how it is done: the reciprocal lattice of a crystal; the most important is the Debye-Scherrer method.

1.3.1 Von Laue method

In the Von Laue method we change the wavelength and therefore the propagation vector; the Ewald sphere changes its radius with continuity and we see a bright spot for each reticular site touched by the surface of the sphere.

1.3.2 Rotating crystal method

In this method we rotate the crystal around a fixed axis; rotating the crystal we move the reticular sites and when one of them intersects the surface of the Ewald sphere we see a bright spot.

1.3.3 Debye-Scherrer method

In the Debye⁶-Scherrer⁷ (DS) method we use a polycrystal or powders; this brings to have a lot of crystal randomly oriented. Hitting the system with a fixed wavelength radiation, λ , we obtain an average value of K (we lose the information on the direction of K but the magnitude is sufficient to understand how the reciprocal lattice of the system is done). The value of K is related to the scattering angles throughout the relation

$$K = 2k\sin\left(\frac{\phi}{2}\right) = 2k\sin(\theta),$$

in which $k = \frac{2\pi}{\lambda}$ is the wave vector of the incoming ray and $\phi = 2\theta$ is the scattering angle measured with respect to the incident beam direction. We note that K increases with increasing $\phi = 2\theta$.

We report the first 10 K , sorted according to their length and using Miller indexes (in the DS method a set with different indexes but with the same $\sqrt{h^2 + m^2 + l^2}$ gives us only one scattering peak) in the case of SC, FCC and BCC

<i>SC</i>	<i>BCC</i>	<i>FCC</i>
100	111	110
110	200	200
111	220	211
200	311	220
210	222	301
211	400	222
220	331	321
221, 300	420	400
301	422	411, 330
311	333, 511	420

Table 1: The first 10 triads of Miller indices for RL are reported in order of length of K . (the lattices in the table are reciprocal lattices)

⁶Peter Debye was a Dutch-American physicist and physical chemist, and Nobel laureate in Chemistry. He is most known for the Debye model that we will study later.

⁷Paul Scherrer was a Swiss physicist.

1.4 X-rays scattering experimental methods with basis

In case the lattice shows a basis we have to study two different cases:

- basis with n equal kind of atoms or molecules,
- basis with n difference kind of atoms or molecules,

we define the structure factor as

$$S_{\vec{K}} = \sum_{j=1}^n f_j(\vec{K}) e^{i\vec{K} \cdot \vec{d}_j},$$

the functions $f_j(\vec{K})$ are the form factor and depend only by the electron distribution of the atom or the molecule. We are adding several plane waves so we can have:

- $S_{\vec{K}} \neq 0 \Rightarrow$ we see a bright point,
- $S_{\vec{K}} = 0 \Rightarrow$ we see a missing point.

The case of missing point is due to the interference between scattered waves by different reticular sites. In case of basis with n equal kind of atoms or molecules we have that all the form factor are the same so that it is factorized and it is possible that the sum is zero. In the case with n different kind of atoms or molecules we have that the form factor are different one to each other and so it's very unlikely that the sum is zero. So in the first case we can have missing points, while in the second is very unlikely. In order to calculate it, we can put $\vec{K} = h\vec{b}_1 + m\vec{b}_2 + l\vec{b}_3$ specialized to the case examined, we calculate the scalar product and then try to understand for which (m_1, m_2, m_3) the structure factor is zero. Generally the first base vector is always taken to be null.

2 Lattice vibrations and phonons

Now we'll study the lattice vibrations, previously from the point of view of classical mechanics and then from the quantum point of view.

2.1 Normal modes development

We now studying the lattice vibrations; the simplest model is those one with mass and spring with the harmonic approximation so we develop the potential until the second order with Taylor, we use also the adiabatic approximation to study only the ions motion. The electron typical velocity is order $10^6 \frac{m}{s}$ while the ions typical velocity is order $10^3 \frac{m}{s}$, so they are stationary for the electrons and we can study their motion independently of the motion of the electrons. An ideal crystal is created by the infinite repetition, without overlapping or holes, of a fundamental unit. A real crystal has a finite volume and is delimited by its surface. The presence of a free surface violates the invariance by translating the crystal. However, it is clear that this cannot change the physical properties of a macroscopic crystal significantly. It is therefore customary to adopt, in the description of the real crystals, fictitious boundary conditions that restore the translational invariance. These conditions are the periodic conditions of Born-von Karman. The idea is to develop the problem in the regime of small oscillations since for Lindemann's criterion if the oscillations were comparable with the lattice constant (spacing between one reticular site and another) then the crystal would fall apart.

The classic Lagrangian of small oscillations in the harmonic approximation is

$$L = \frac{1}{2} \sum_n \sum_l \sum_\alpha m_l (\dot{u}_{n,l}^\alpha)^2 - \frac{1}{2} \sum_{n,n'} \sum_{l,l'} \sum_{\alpha,\alpha'} K_{l,l'}^{\alpha,\alpha'}(n,n') u_{n,l}^\alpha u_{n',l'}^{\alpha'}$$

where the sum on n (and n') runs on the sites of the Bravais lattice identified by the vectors position \vec{R}_n , the sum on l (e l') runs on the vectors of the base that identify the position of the different atoms within each elementary cell, \vec{r}_l , so that the equilibrium position of an atom is identified by the vector $\vec{R}_n + \vec{r}_l$ and the vector $\vec{u}_{n,l}$ indicates the deviation from the equilibrium position of the atom and the index α indicates the cartesian components of the vector. The constant term in the harmonic development of the Lagrangian has been set to be null and the matrix $K_{l,l'}^{\alpha,\alpha'}(n,n')$ is the coupling between all the atoms. So the position of each atom is specified by

$$\vec{x}_{n,l} = \vec{R}_n + \vec{r}_l + \vec{u}_{n,l}(t).$$

The matrix $K_{l,l'}^{\alpha,\alpha'}(n,n')$ has same important symmetries

- Sufficiently good potential \Rightarrow independence of order of differenzation $\Rightarrow K_{l,l'}^{\alpha,\alpha'}(n,n') = K_{l',l}^{\alpha',\alpha}(n',n)$;
- Inversion symmetry of BL $\Rightarrow K_{l,l'}^{\alpha,\alpha'}(n,n') = K_{l',l}^{\alpha',\alpha}(n',n)$,

this two symmetry allow us to say that the matrix $K_{l,l'}^{\alpha,\alpha'}(n,n')$ is symmetric and is also important remember that the coupling only depends on the relative distance of two lattice sites. The Lagrangian above gives rise to an unsolvable coupled problem $DNp \times DNp$ (DNp is equal to the number of degrees of freedom of the system) in which D is the dimension of the system, N is the number of elementary cells in the crystal and p is the number of atoms contained in an elementary cell. The solution is easier if we pass into Fourier transform, and given that the matrix $K_{l,l'}^{\alpha,\alpha'}(n,n')$ is real its Fourier transform is such that

$$\tilde{K}_{l,l'}^{\alpha,\alpha'}(-\vec{k}) = \tilde{K}_{l',l}^{\alpha',\alpha}(\vec{k}) = [\tilde{K}_{l',l}^{\alpha',\alpha}(\vec{k})]^*$$

so it's hermitian and so its eigenvalues are all real; the original problem is reduced to a more easily algebraic problem $Dp \times Dp$. Doing this we are looking for a plane waves solutions that are superposition of the normal modes solutions

$$u_{n,l}^\alpha = \sum_{\vec{k}} A_{\vec{k},l}^\alpha e^{i[\omega_s(\vec{k})t - \vec{k}(\vec{R}_n + \vec{r}_l)]}$$

to find the normal modes solutions we have to impose that the matrix associated with the algebraic system $Dp \times Dp$ has zero determinant or, equivalently, solve the eigenvalue problem

$$\det(K_{l,l'}^{\alpha,\alpha'}(n,n') - \omega_s^2 m_l) = 0$$

Being a $Dp \times Dp$ problem we have to find Dp eigenvalues for each fixed allowed \vec{k} , that we call $\omega_s(\vec{k})$, and since the allowed wavevectors \vec{k} are N (adopting Born-Von Karman boundary conditions) we find all the degrees of freedom that we need, DNp . In a D -dimensional crystal with periodic boundary conditions, the normal

modes are characterized by the wavevector \vec{k} and by the branch index s which assumes Dp values. Among the different branches of the oscillation spectrum there are D that in the limit of large wavelength correspond to ordinary elastic waves, whose frequency drop to zero linearly with $\vec{k} \rightarrow 0$ and are called acoustic modes while the remaining $D(p-1)$ modes are called optical modes because they interact with the EM field and characterize the optical properties of the solid.

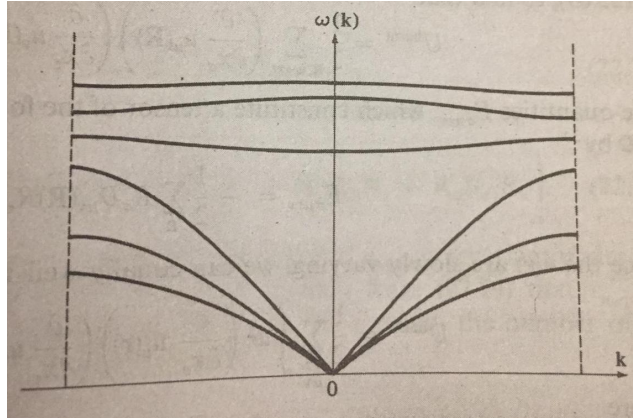


Figure 6: Dispersion relations in the case of $D = 3$ and $p = 2$.

To recap, to solve equations of motion deriving from the previous Lagrangian we move on Fourier space and so we want to find a plane wave solutions (that are superposition of the normal mode solutions). Using the ansatz we obtain an homogeneous system that has non trivial solution only if the determinant of the coefficient matrix is zero. Imposing that the determinant of coefficient matrix is zero, we obtain the relationship between the proper frequencies, ω_s , and the propagation vector \vec{k} ; the number of proper frequencies must be equal to the number of degrees of freedom of the system. The degrees of freedom depend on the dimension of the system and also from the number of different kind of atoms (or molecules) that build the system, DNp (D is the dimension of the system, p is the number of atoms per fundamental cell and N is the number of fundamental cells). D of the normal modes are acoustic (goes to zero linearly with $\vec{k} \rightarrow 0$) while the remaining are optical.

To solve exercise in which the dispersion relationship is required we write the equations of motion $\vec{F} = m\vec{a}$ for every atom or molecule in the lattice. For example, we consider one dimension for the sake of simplicity, let us consider the system in figure below.

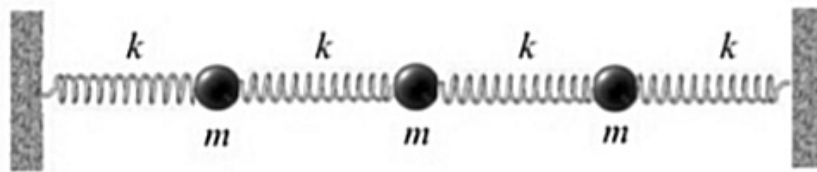


Figure 7: Example of coupled system we are considering.

We have four springs with the same elastic constant and three masses dubbed, respectively, a, b, c ; the equations of motion are

$$\begin{aligned} m\ddot{x}_a &= -kx_a + k(x_b - x_a); \\ m\ddot{x}_b &= -k(x_b - x_a) + k(x_c - x_b); \\ m\ddot{x}_c &= -kx_c - k(x_c - x_b); \end{aligned}$$

where \ddot{x}_i are the displacement vectors of the three masses. Note that the mass attached to springs not anchored feels only force due to relative displacement since walls are considered with infinite mass.

Once we have a system of equations of motion, we write a solution of the form $u_n = Ae^{i(\omega t - qna)}$; where u is the displacement respect the equilibrium position. In the case of more kind of atoms (or molecules) we have different displacement v_n and, theoretically, we should have an extra displacement (due to the different position of the basis) that is reabsorbed in the definition of the amplitude constant of the plane wave solution,

so $v_n = B e^{i(\omega t - qna)}$. To find the sound velocity it's necessary to approximate the dispersion relation of the sound modes (the relation between the frequency and the propagation vector, so the solved determinant of the coefficient matrix) for small q with Taylor development. To do this is important remind those Taylor approximations:

- $\sin^2(x) \approx x^2$;
- $\sqrt{1-x} \approx 1 - \frac{x}{2}$;
- $\cos^2(x) \approx (1 - \frac{x^2}{2})^2$.

Is important also remember this trigonometric relation

$$1 - \cos(x) = 2\sin^2\left(\frac{x}{2}\right).$$

Developing dispersion relation, we find a linear relationship between the frequencies and q , and the coefficient is the sound velocity. This treatment is a classical treatment based on the normal modes development we now move to quantize the elastic field of the solid and what we find is the phonons, the quanta of elastic field.

2.2 Phonons and specific heat

Our goal is to find the correct specific heat of a solid; we know experimentally the Dulong-Petit (DP) law (limit for $T \rightarrow \infty$) for which the specific heat goes to

$$c_{v,DP} = \frac{DNpk_b}{V} = \frac{Dpk_b}{V_N} = nDpk_b$$

where D is the dimension of the system, Dp is the number of branches (depending on the number of atom or molecule basis), N is the number of cells, V is the total volume and V_N is the volume of one cell; for example

- $D = 1$, 1 - base system, $V_N = a \Rightarrow c_{v,DP} = \frac{k_b}{a}$;
- $D = 1$, 2 - basis system, $V_N = a \Rightarrow c_{v,DP} = \frac{2k_b}{a}$;
- $D = 1$, 3 - basis system, $V_N = a \Rightarrow c_{v,DP} = \frac{3k_b}{a}$;
- $D = 2$, 1 - base system, $V_N = a^2 \Rightarrow c_{v,DP} = \frac{2k_b}{a^2}$;
- $D = 2$, 2 - basis system, $V_N = ab \Rightarrow c_{v,DP} = \frac{4k_b}{ab}$;
- $D = 3$, 1 - basis system, $V_N = a^3 \Rightarrow c_{v,DP} = \frac{3k_b}{a^3}$.

On the other hand, in the limit $T \rightarrow 0$ the specific heat goes to zero as T^D .

To find the specific heat we start from the internal energy for unit volume u ; we can treat the system of phonons like a non interacting bosons gas, and so $c_v = \frac{\partial u}{\partial T}$. The internal energy for unit volume can be written as

$$u = \frac{1}{V} \sum_q \sum_s \hbar\omega_s(q) \left[\frac{1}{e^{\beta\hbar\omega_s(q)} - 1} + \frac{1}{2} \right],$$

where q is the propagation vector (or the reciprocal lattice vector) and s is the branch index. The fact that the occupation number is given by the Bose statistic is due to the fact that the phonons are the quanta of elastic vibration, and since the elastic deformation is additive nothing prevents you from creating more phonons that deform in the same way and therefore with the same energy, in addition, the chemical potential is zero because the number of phonons in the system is not conserved.

We can transform the sum over q in an integral

$$\frac{1}{V} \sum_q \rightarrow \int dq_x dq_y dq_z \frac{1}{(2\pi)^3},$$

we have, in the end (and generalizing to arbitrary dimensions)

$$u = \sum_s \int_{FBZ} \frac{d^D q}{(2\pi)^D} \hbar\omega_s(q) \left[\frac{1}{e^{\beta\hbar\omega_s(q)} - 1} + \frac{1}{2} \right].$$

The specific heat is

$$c_v = \frac{\partial}{\partial T} \sum_s \int_{FBZ} \frac{d^D q}{(2\pi)^D} \hbar\omega_s(q) \left[\frac{1}{e^{\beta\hbar\omega_s(q)} - 1} + \frac{1}{2} \right] = \frac{\partial}{\partial T} \sum_s \int_{FBZ} \frac{d^D q}{(2\pi)^D} \hbar\omega_s(q) \left[\frac{1}{e^{\beta\hbar\omega_s(q)} - 1} \right].$$

Now we want to simplify our life so we discuss two models that describe the specific heat.

2.2.1 Einstein model

In Einstein model the frequencies $\omega_s(q)$ are replaced with an average value ω_E ; so (remembering that s take all the Dp values)

$$c_v = \frac{\partial}{\partial T} \frac{1}{(2\pi)^D} Dp \left[\frac{\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1} \right] \int_{FBZ} d^D q = \frac{1}{(2\pi)^D} Dp \left[\frac{(\hbar\omega_E)^2 e^{\frac{\hbar\omega_E}{k_b T}}}{k_b T^2 (e^{\frac{\hbar\omega_E}{k_b T}} - 1)^2} \right] \int_{FBZ} d^D q$$

Einstein model is a good approximation only for the optical modes (or branches). To understand if a given temperature is small or big in the Einstein model we have to compare the given temperature with the Einstein temperature

$$T_E = \frac{\hbar\omega_E}{k_b} \approx O(10^{2\div 3} K),$$

in the two limits we can approximate the exponential and so

- $T \gg T_E \Rightarrow e^{\beta\hbar\omega_E} - 1 \approx \beta\hbar\omega_E \Rightarrow c_v = \frac{Dp}{(2\pi)^D} \frac{(2\pi)^D}{a^D} \frac{(\hbar\omega_E)^2}{k_b T^2 (\beta\hbar\omega_E)^2} = \frac{Dp}{a^D} k_b = c_{v,DP}$ (cubic lattice case) ;
- $T \ll T_E \Rightarrow e^{\beta\hbar\omega_E} - 1 \approx e^{\beta\hbar\omega_E} \Rightarrow c_v \sim e^{-\beta\hbar\omega_E}$.

The Einstein model is wrong at low temperature.

2.2.2 Debye model

In Debye model we consider for the acoustic modes $\omega_a^{(s)} = c_S^{(s)} q$, where $c_S^{(s)}$ is the sound velocity in the crystal of the s -th acoustic branch, and we perform the integration on an ipersphere with radius q_d (Debye radius),

$$c_v = \frac{\partial}{\partial T} \sum_s \int_0^{q_d} \int \frac{q^{D-1} dq d\Omega}{(2\pi)^D} \frac{\hbar c_S^{(s)} q}{e^{\beta\hbar c_S^{(s)} q} - 1},$$

where the sum over s now is the sum on acoustic branches only. The value of Debye radius is found by the request that the ipersphere has the same volume of the first Brilluoin zone; they are explained in the case of cubic first Brilluoin zone:

- $D = 3 \Rightarrow \frac{4\pi}{3} q_d^3 = V_{FBZ} = \frac{(2\pi)^3}{a^3} \Rightarrow q_d = \frac{1}{a} (6\pi^2)^{\frac{1}{3}}$;
- $D = 2 \Rightarrow \pi q_d^2 = V_{FBZ} = \frac{(2\pi)^2}{a^2} \Rightarrow q_d = \frac{2\sqrt{\pi}}{a}$;
- $D = 1 \Rightarrow 2q_d = V_{FBZ} = \frac{2\pi}{a} \Rightarrow q_d = \frac{\pi}{a}$.

Using the change of variable $x = \beta\hbar c_S^{(s)} q$ (at fixed Ω) we obtain

$$c_v = \frac{\partial}{\partial T} \sum_s \frac{1}{(2\pi)^D \beta^{D+1} \hbar^D (c_S^{(s)})^D} \int_0^{\beta\hbar c_S^{(s)} q_d} \frac{x^D}{e^x - 1} dx d\Omega,$$

defining the Debye average sound velocity $\frac{1}{\langle c_d \rangle^D} = \frac{1}{D} \frac{\Gamma(\frac{D}{2})}{2\pi^{\frac{D}{2}}} \sum_s \int \frac{d\Omega}{(c_S^{(s)})^D}$, we have

$$c_v = \frac{\partial}{\partial T} \frac{D}{(2\pi)^D \beta^{D+1} \hbar^D \langle c_d \rangle^D} \frac{2\pi^{\frac{D}{2}}}{\Gamma(\frac{D}{2})} \int_0^{\beta\hbar \langle c_d \rangle q_d} \frac{x^D}{e^x - 1} dx,$$

where $\Theta(\beta\hbar \langle c_d \rangle q_d)_D := \int_0^{\beta\hbar \langle c_d \rangle q_d} \frac{x^D}{e^x - 1} dx$ is the generalized Debye function. We define the Debye temperature as

$$T_d = \frac{\hbar\omega_d}{k_b} = \frac{\hbar \langle c_d \rangle q_d}{k_b} \approx O(10^{2\div 3} K),$$

and we have the two limits

- $T \gg T_d \Rightarrow \Theta(\beta\hbar \langle c_d \rangle q_d)_D \rightarrow \frac{(\beta\hbar \langle c_d \rangle q_d)^D}{D} \Rightarrow c_v \rightarrow c_{v,DP}$;
- $T \ll T_d \Rightarrow \Theta(\beta\hbar \langle c_d \rangle q_d)_D \rightarrow \Gamma(D+1) \zeta(D+1) \Rightarrow c_v \sim T^D$.

Now we specialized our results at the physical interesting cases, so for $D = 1$, $D = 2$ and $D = 3$:

- $D = 1 \Rightarrow c_v = \frac{\partial}{\partial T} \frac{1}{(2\pi)\beta^2 \hbar \langle c_d \rangle} \frac{2\pi^{\frac{1}{2}}}{\Gamma(\frac{1}{2})} \int_0^{\beta\hbar \langle c_d \rangle q_d} \frac{x}{e^x - 1} dx = \frac{\partial}{\partial T} \frac{1}{\pi\beta^2 \hbar \langle c_d \rangle} \int_0^{\beta\hbar \langle c_d \rangle q_d} \frac{x}{e^x - 1} dx$
- $D = 2 \Rightarrow c_v = \frac{\partial}{\partial T} \frac{2}{(2\pi)^2 \beta^3 \hbar^2 \langle c_d \rangle^2} \frac{2\pi^{\frac{2}{2}}}{\Gamma(\frac{2}{2})} \int_0^{\beta\hbar \langle c_d \rangle q_d} \frac{x^2}{e^x - 1} dx = \frac{\partial}{\partial T} \frac{1}{\pi\beta^3 \hbar^2 \langle c_d \rangle^2} \int_0^{\beta\hbar \langle c_d \rangle q_d} \frac{x^2}{e^x - 1} dx$
- $D = 3 \Rightarrow c_v = \frac{\partial}{\partial T} \frac{3}{(2\pi)^3 \beta^4 \hbar^3 \langle c_d \rangle^3} \frac{2\pi^{\frac{3}{2}}}{\Gamma(\frac{3}{2})} \int_0^{\beta\hbar \langle c_d \rangle q_d} \frac{x^3}{e^x - 1} dx = \frac{\partial}{\partial T} \frac{3}{2\pi^2 \beta^4 \hbar^3 \langle c_d \rangle^3} \int_0^{\beta\hbar \langle c_d \rangle q_d} \frac{x^3}{e^x - 1} dx$

In general we adopt both models, Einstein model for optical branches and Debye model for acoustic branches; so the internal energy (and the specific heat) is the sum of contributions due to both models.

3 Band structure of solids

In this section we'll study the band structure of solids, it explains why some materials are insulators and other conductors and also the electronic properties of solids. An insulator is a material in which the bands are filled while a metal (a conducting material) has no all bands filled. To construct the band structure we use the Weak potential approximation and the tight binding method. Remember that in anisotropic system the current density is

$$J_i = \sigma_{ij} E_j$$

in which $\sigma_{ij} = \frac{1}{\rho_{ij}} = qn\mu_{ij} = \frac{q^2 n \tau}{m_{ij}}$ ($\mu_{ij} = \frac{q\tau}{m_{ij}}$ is the mobility and m_{ij} is the mass tensor). The density of electrons is $n = \frac{N_e}{V_{uni}}$ in which N_e is the number of electrons with which each atom contributes and V_{uni} is the volume of the unit cell.

3.1 Bloch theorem

The starting point is the Bloch⁸ theorem, a general result for Schrödinger equation with a periodic potential. The theorem states that the solution of this type of Schrödinger equation, and consequently the eigenstates of one-electron periodic hamiltonian (we use the independent electron approximation), have the two equivalent form

$$\begin{aligned}\psi(\vec{r})_{n,\vec{k}} &= e^{i\vec{k}\cdot\vec{r}} u(\vec{r})_{n,\vec{k}} \\ \psi(\vec{r} + \vec{R})_{n,\vec{k}} &= e^{i\vec{k}\cdot\vec{R}} \psi(\vec{r})_{n,\vec{k}}\end{aligned}$$

in which n is the band index (like the n in the case of hydrogen atom takes all the positive integers numbers), the quantum number \vec{k} is the quasi-momentum (or crystal momentum and is the quantum number characteristic of the translational operator of the solids) and \vec{R} is a Bravais lattice vector. The important thing is that the function $u(\vec{r})_{n,\vec{k}}$ has the same periodicity of the potential of the system (obviously the periodicity is the Bravais lattice vector). Using the Bloch form to simplify the initial general one electron Schrödinger equation we obtain a secular equation for the function $u(\vec{r})_{n,\vec{k}}$ with the boundary condition (dictated by the periodicity):

$$\begin{aligned}H_{\vec{k}} u(\vec{r})_{\vec{k}} &= E_{\vec{k}} u(\vec{r})_{\vec{k}}, \\ u(\vec{r})_{\vec{k}} &= u(\vec{r} + \vec{R})_{\vec{k}}.\end{aligned}$$

This equation has, in general, an infinite number of solutions for every fixed \vec{k} ; this solutions are labelled by the band index, n , and they have a discretely spaced eigenvalues (but they are so many that the band looks like a continuous). So for every n the eigenvalues and the eigenstates are function of the quasi-momentum \vec{k} and we call the set of functions $E_{n,\vec{k}}$ band structure.

3.1.1 Proof of Bloch theorem

Consider the operator that translates by an amount equal to a vector of the Bravais lattice considered, $T(\vec{R})$. This operator commute with the one-electron periodic hamiltonian, $H = -\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})$, because the potential part is periodic in the Bravais lattice ($U(\vec{r} + \vec{R}) = U(\vec{r})$) while the kinetic term is a larger set that also includes the operator $T(\vec{R})$. So is possible diagonalize simultaneously H and $T(\vec{R})$

$$\begin{aligned}H\psi &= E\psi, \\ T(\vec{R})\psi &= c(\vec{R})\psi.\end{aligned}$$

Since $T(\vec{R})$ is a translation operator its eigenvalues are of the form

$$c(\vec{R}) = e^{\frac{i\vec{R}\cdot\vec{p}}{\hbar}} = e^{i\vec{R}\cdot\vec{k}},$$

in which $\vec{k} = \frac{\vec{p}}{\hbar}$, it's important to emphasize that \vec{p} it is not the momentum because it only generates a restricted set of translations and is called quasi-momentum. So we can write

$$T(\vec{R})\psi(\vec{r}) = \psi(\vec{r} + \vec{R}) = c(\vec{R})\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r})$$

QED

⁸Felix Bloch was a Swiss-American physicist and Nobel physics laureate in 1952.

3.2 Weak potential approximation

We rewrite the general one electron Schrödinger equation as

$$\left(\frac{\hbar^2}{2m} (\vec{k} - \vec{K})^2 - E \right) c_{\vec{k}-\vec{K}} + \sum_{\vec{K}'} U_{\vec{K},-\vec{K}'} c_{\vec{k}-\vec{K}'} = 0,$$

the above equations are nothing but the original Schrödinger equation in momentum space simplified by the fact that the Fourier components of the potential must be only plane waves with an impulse equal to a vector of the reciprocal lattice. The idea is to use perturbation theory applied to a free electron system in which is present a weak periodic external potential due to the ions of the solids.

At this point we consider two cases, the first one is the case of some free electron levels that are non degenerate compared with the typical magnitude of the Fourier coefficients of the external potential and the second one is the case of some free electron levels that are degenerate compared with the typical magnitude of the Fourier coefficients of the external potential. In the first case we can use non degenerate perturbation theory stopping development on the first non-trivial order in external potential; fixed one \vec{k} and considered the lattice vector \vec{K}' the correction is

$$E = E_{\vec{k}-\vec{K}'}^0 + \sum_{\vec{K}} \frac{|U_{\vec{K}-\vec{K}'}|^2}{E_{\vec{k}-\vec{K}'}^0 - E_{\vec{k}-\vec{K}}^0}.$$

Energy is similar to that of a free electron but corrected to a quantity of $O(U^2)$, the first order is just a trivial shift in energy so we can "neglect" it. In the second case we must use degenerate perturbation theory and we can stop the development at first order in the external potential; fixed one \vec{k} and a set of $i = 1, \dots, m$ reciprocal lattice vector in which the energy is degenerate (in the sense specified above) the correction is

$$E - E_{\vec{k}-\vec{K}_i}^0 c_{\vec{k}-\vec{K}_i} = \sum_{j=1}^m U_{\vec{K}_j-\vec{K}_i} c_{\vec{k}-\vec{K}_j}.$$

The above equations are the general equation for a system of m quantum levels. If we use these equations in the case of two degenerate free electron levels we obtain that the two levels are spaced by an amount equal to $2|U_{\vec{K}_2-\vec{K}_1}|$, so near the boundaries of the first Brillouin zone, due to the ions periodic potential, GAPS are open. In fact taken two free electron levels we have, using the above equation and remembering that we choose $U_{\vec{0}} = 0$,

$$\begin{aligned} (E - E_{\vec{k}-\vec{K}_1}^0) c_{\vec{k}-\vec{K}_1} &= U_{\vec{K}_2-\vec{K}_1} c_{\vec{k}-\vec{K}_2} \Rightarrow (E - E_{\vec{q}}^0) c_{\vec{q}} = U_{\vec{K}} c_{\vec{q}-\vec{K}}, \\ (E - E_{\vec{k}-\vec{K}_2}^0) c_{\vec{k}-\vec{K}_2} &= U_{\vec{K}_1-\vec{K}_2} c_{\vec{k}-\vec{K}_1} \Rightarrow (E - E_{\vec{q}-\vec{K}}^0) c_{\vec{q}-\vec{K}} = U_{-\vec{K}} c_{\vec{q}}, \end{aligned}$$

in which we called $\vec{q} = \vec{k} - \vec{K}_1$ and $\vec{K} = \vec{K}_2 - \vec{K}_1$. The above system is a homogeneous one so we must impose that the determinant of the coefficient matrix is zero (remembering that $U_{-\vec{K}} = U_{\vec{K}}^*$ because the potential is real)

$$\begin{aligned} (E - E_{\vec{q}}^0)(E - E_{\vec{q}-\vec{K}}^0) &= |U_{\vec{K}}|^2 \Rightarrow E^2 - E E_{\vec{q}-\vec{K}}^0 - E_{\vec{q}}^0 E + E_{\vec{q}}^0 E_{\vec{q}-\vec{K}}^0 - |U_{\vec{K}}|^2 = 0 \\ \Rightarrow E_{\pm} &= \frac{(E_{\vec{q}}^0 + E_{\vec{q}-\vec{K}}^0) \pm \sqrt{(E_{\vec{q}}^0 - E_{\vec{q}-\vec{K}}^0)^2 + 4|U_{\vec{K}}|^2}}{2}, \end{aligned}$$

when the two levels are degenerate in the classical sense of the term (that is, in case that the levels are on the boundary of the FBZ) we obtain

$$E_{\pm} = E_{\vec{q}}^0 \pm |U_{\vec{K}}| \Rightarrow E_{GAP} = E_+ - E_- = 2|U_{\vec{K}}|$$

that is the GAP.

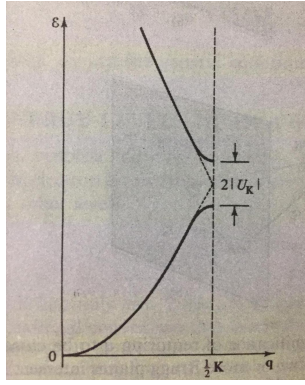


Figure 8: Example of GAP for two degenerate free electron levels.

3.3 Tight Binding

In the tight binding method we consider the hamiltonian in the form

$$H = H_{atomic} + \Delta U(\vec{r}),$$

so we imagine that the total hamiltonian is more or less like the atomic hamiltonian of the constituent atoms of the solid; when the electrons are very close to the nuclei the levels are very close to the atomic levels, when the electrons are quite far from the nuclei the levels are appreciably different from atomic levels. Understood this, we looking for an eigenstates of the total hamiltonian of the form of a superposition of atomic orbitals that respect the Bloch form

$$\psi(\vec{r})_{n,\vec{k}} = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \psi(\vec{r} - \vec{R})_{n,\vec{k}}.$$

Now, any Bloch function can be written as

$$\psi(\vec{r})_{n,\vec{k}} = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi(\vec{r} - \vec{R})_{n,\vec{k}},$$

in which the function ϕ are known as Wannier functions (the proof is based on the Fourier expansion of the Bloch function ψ in plane waves with wave vectors in the real lattice) and the Wannier functions can be chosen as LCAO functions

$$\phi(\vec{r} - \vec{R}) = \sum_j b_j \psi_j(\vec{r} - \vec{R}),$$

in which, now, ψ_i are atomic eigenfunctions.

Taking the Schrödinger equation for the total hamiltonian H and using the above development for the eigenfunctions we obtain

$$(H_{atomic} + \Delta U(\vec{r}) - E_{\vec{k}}) \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \sum_j b_j \psi_j(\vec{r} - \vec{R}) = 0,$$

now, we multiply scalarly for a generic atomic eigenfunction $\psi_n(\vec{r})$

$$\begin{aligned} & \int \psi_n^*(\vec{r}) (H_{atomic} + \Delta U(\vec{r}) - E_{\vec{k}}) \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \sum_j b_j \psi_j(\vec{r} - \vec{R}) d\vec{r} = \\ & = \int \psi_n^*(\vec{r}) (E_n + \Delta U(\vec{r}) - E_{\vec{k}}) \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \sum_j b_j \psi_j(\vec{r} - \vec{R}) d\vec{r} = 0 \Rightarrow \\ & \Rightarrow \int \psi_n^*(\vec{r}) \left(E_n + \Delta U(\vec{r}) - E_{\vec{k}} \right) \left(\sum_j b_j \psi_j(\vec{r}) + \sum_{\vec{R} \neq 0} e^{i\vec{k}\cdot\vec{R}} \sum_j b_j \psi_j(\vec{r} - \vec{R}) \right) d\vec{r} = 0 \Rightarrow \\ & \Rightarrow (E_n - E_{\vec{k}}) b_n + \sum_j b_j \int \psi_n^*(\vec{r}) \Delta U(\vec{r}) \psi_j(\vec{r}) d\vec{r} + \\ & + \sum_{\vec{R} \neq 0} e^{i\vec{k}\cdot\vec{R}} \sum_j b_j \left((E_n - E_{\vec{k}}) \int \psi_n^*(\vec{r}) \psi_j(\vec{r} - \vec{R}) d\vec{r} + \int \psi_n^*(\vec{r}) \Delta U(\vec{r}) \psi_j(\vec{r} - \vec{R}) d\vec{r} \right) = 0 \end{aligned}$$

These are the equations that determinate the band structure, is easy to see that the problem easily becomes very complicated. In the above equations appear three integrals that we rename:

- $\beta_j = - \int \psi_n^*(\vec{r}) \Delta U(\vec{r}) \psi_j(\vec{r}) d\vec{r} \Rightarrow$ Shift integral;
- $\alpha_j = \int \psi_n^*(\vec{r}) \psi_j(\vec{r} - \vec{R}) d\vec{r} \Rightarrow$ overlap integral;
- $\gamma_j = - \int \psi_n^*(\vec{r}) \Delta U(\vec{r}) \psi_j(\vec{r} - \vec{R}) d\vec{r} \Rightarrow$ transfer integral.

The shift integral is just a number while the overlap and the transfer integrals are functions of the real lattice vector \vec{R} ; all of them are small quantity compared with the typical size of the atomic levels so the band structure can be seen as small deformation of an atomic levels.

We can rewrite the tight binding equations as

$$(E_n - E_{\vec{k}})b_n - \sum_j b_j \beta_j + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \sum_j b_j \left((E_n - E_{\vec{k}}) \alpha_j - \gamma_j \right) = 0,$$

depending on the type of orbitals that are carried by the solid atoms we obtain a different set of equations; for example for the p orbitals (that are triply degenerate) we obtain a 3×3 homogeneous system and its eigenvalues are the 3 bands and the solutions of the system are the three coefficients of the LCAO superposition. We focus our attention on the case in which each lattice sites host s orbitals; in this case we have

$$\begin{aligned} (E_s - E_{\vec{k}})b_s - \beta_s b_s + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} b_s \left((E_s - E_{\vec{k}}) \alpha_s - \gamma_s \right) &= 0 \Rightarrow \\ \Rightarrow \left((E_s - E_{\vec{k}}) - \beta_s + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \left((E_s - E_{\vec{k}}) \alpha_s - \gamma_s \right) \right) b_s &= 0 \Rightarrow \\ \Rightarrow (E_s - E_{\vec{k}}) - \beta_s + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \left((E_s - E_{\vec{k}}) \alpha_s - \gamma_s \right) &= 0 \Rightarrow E_{\vec{k}} = E_s - \frac{(\beta_s + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \gamma_s)}{1 + \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \alpha_s}. \end{aligned}$$

If the case under examination (s orbital) the overlap integral is neglectable so

$$E_{\vec{k}} = E_s - \beta_s - \sum_{\vec{R} \neq 0} e^{i\vec{k} \cdot \vec{R}} \gamma_s.$$

It is important to underline that even if the orbitals considered are not s type, it is always possible, provided that an appropriate number of n th-neighbors and an appropriate signs in the transfer integrals are considered, to write the resulting band as if the orbitals were all s type. So the tight binding is a very powerful method. We report some trigonometric identities useful in calculations of the bands structure

$$\begin{aligned} \cos(a - b) &= \cos(a)\cos(b) + \sin(a)\sin(b); \\ \cos(a + b) &= \cos(a)\cos(b) - \sin(a)\sin(b). \end{aligned}$$

We can expand the band near the stationary point and we can write

$$E_{\vec{k}} = const + \frac{\hbar^2}{2} \sum_{i,j} m_{ij}^{-1} k_i k_j,$$

in which m_{ij}^{-1} is the inverse mass tensor (we treat better this part in the section on the semiclassical theory of Bloch electrons); so we can expand with Taylor the band and comparing the development with the equation above we can derive the components of the mass tensor. This derivation of the mass tensor is right if we want, or to know the tensor at the gamma point, $\Gamma = (k_x = 0; k_y = 0; k_z = 0)$; in general we have

$$m_{ij}^{-1}(\vec{k} = P) = \frac{1}{\hbar^2} \left. \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j} \right|_{\vec{k}=P}.$$

We can also calculate the velocity of the Bloch electrons

$$\vec{v} = \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}}.$$

We mention the one-dimensional case in which there are two atoms, one of which carries s orbitals and the other p orbitals; the two bands are (γ is the transfer integral between p and s orbitals)

$$E_{k_p, k_s} = \frac{E_p + E_s}{2} \pm \sqrt{\left(\frac{E_p + E_s}{2} \right)^2 + 4\gamma^2 \sin^2 \left(\frac{ka}{2} \right)},$$

in the case $E_{GAP} = E_p - E_s \gg \gamma$ we can expand the square root, so bands are

$$E_{k_p} = E_p + \frac{4\gamma^2}{E_p - E_s} \sin^2\left(\frac{ka}{2}\right);$$
$$E_{k_s} = E_s - \frac{4\gamma^2}{E_p - E_s} \sin^2\left(\frac{ka}{2}\right).$$

4 Semiclassical theory of Bloch electrons

The semiclassical theory of Bloch electrons is based only on the knowledge of the band structure of the solid. First we write the electron wave function as Bloch's eigenfunctions wave packet

$$\psi_n(\vec{r}, t) = \int g(\vec{k}' - \vec{k}) \psi_{n, \vec{k}}(\vec{r}) e^{-\frac{iE_n(\vec{k}')t}{\hbar}} d\vec{k}',$$

in which the functions $g(\vec{k}' - \vec{k})$ weighs the wavevectors that contribute to the wave packet and is peaked in \vec{k} . Since the size of the FBZ is order $10^{10}m^{-1}$ we assume that the spread of the wave packet is small compared with the FBZ size; for the uncertainty principle the size of the distribution in real space is large compared to the typical scale of the Bravais lattice (order $10^{-10}m$). The semiclassical model describes the response of the electrons to external EM field when this varies slowly on the scale of the Bravais lattice (that is, when its wavelength is much larger than the typical size of the BL). We note also that the group velocity of the wave packet is

$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar} \frac{\partial E_n(\vec{k})}{\partial \vec{k}},$$

for the Ehrenfest theorem this velocity is the mean velocity of Bloch electrons.

The semiclassical model describes the electrons treating classically the EM field and quantum mechanically the matter, and so, according to

$$\begin{aligned} \dot{\vec{r}} &= \vec{v}_n(\vec{k}) = \frac{1}{\hbar} \frac{\partial E_n(\vec{k})}{\partial \vec{k}}; \\ \hbar \dot{\vec{k}} &= -e[\vec{E}(\vec{r}, t) + \frac{1}{c} \vec{v}_n(\vec{k}) \times \vec{H}(\vec{r}, t)]. \end{aligned}$$

We note, again, that $\hbar \dot{\vec{k}}$ is not the momentum because it varies not under the total external force (we are not considering the strength exerted by the ions).

We can develop the dispersion relation close to a minimum or a maximum and we have an expansion of the form (for a minimum) $E(\vec{k}) = E(\vec{k}_0) + \frac{A}{2}(\vec{k} - \vec{k}_0)^2$ in which \vec{k}_0 is the singular point and A is the hessian matrix of $E(\vec{k})$, so that

$$\vec{v} = \frac{1}{\hbar} A \vec{k} \Rightarrow \vec{a} = \frac{d\vec{v}}{dt} = \frac{1}{\hbar} A \dot{\vec{k}} = \frac{A \vec{F}}{\hbar^2},$$

in which \vec{F} is the external force. By comparison we define $A = \hbar^2 m^{-1}$ and so we can write

$$E_{\vec{k}} = E_{const} + \frac{\hbar^2}{2} \sum_{i,j} m_{ij}^{-1} k_i k_j,$$

in which $m_{ij}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j}$ is known as inverse mass tensor and it determines the dynamics of the object under examination. It is always possible to diagonalize the inverse mass tensor (along the crystallographic axes); the fact that the mass is tensor makes us understand that crystals are highly anisotropic objects and that the electrons in a crystal (we call them Bloch electrons) are completely different from free electrons.

We also note that if a solid has a filled band then these are inert from the energy and current point of view, infact

$$\begin{aligned} \vec{j} &= -en\vec{v}(\vec{k}) = -2e \int_{full\ band} \frac{d\vec{k}}{(2\pi)^3} \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}} = 0; \\ u &= nE(\vec{k}) = 2 \int_{full\ band} \frac{d\vec{k}}{(2\pi)^3} E(\vec{k}) = 0, \end{aligned}$$

in which n is the density of electrons (the Fermi distribution does not appear because the band is full and therefore all the levels are occupied). We note that

$$\begin{aligned} 0 &= -2e \int_{zone} \frac{d\vec{k}}{(2\pi)^3} \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}} = -2e \int_{occupied\ zone} \frac{d\vec{k}}{(2\pi)^3} \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}} - 2e \int_{unoccupied\ zone} \frac{d\vec{k}}{(2\pi)^3} \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}} \\ &\Rightarrow -2e \int_{occupied\ zone} \frac{d\vec{k}}{(2\pi)^3} \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}} = 2e \int_{unoccupied\ zone} \frac{d\vec{k}}{(2\pi)^3} \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}}, \end{aligned}$$

for which study the zones of the bands occupied by electrons or the zones of the bands not occupied by electrons (the lack of electrons generates a hole of positive charge) are totally equivalent for the purposes of electronic properties; the holes picture and the electrons picture are equivalent.

4.1 Motion in a DC electric field and in uniform magnetic field

In a uniform static electric field the semiclassical equations become

$$\begin{aligned}\dot{\vec{r}} &= \vec{v}_n(\vec{k}) = \frac{1}{\hbar} \frac{\partial E_n(\vec{k})}{\partial \vec{k}}; \\ \hbar \dot{\vec{k}} &= -e\vec{E},\end{aligned}$$

and so

$$\begin{aligned}\vec{k}(t) &= \vec{k}(0) - \frac{e\vec{E}t}{\hbar}; \\ \dot{\vec{r}} &= \vec{v}_n(\vec{k}) = \vec{v}_n\left(\vec{k}(0) - \frac{e\vec{E}t}{\hbar}\right).\end{aligned}$$

Since the velocity is a periodic function in the reciprocal lattice it's a bounded function of time and in some cases is also oscillatory. This strange behavior (AC current in a DC field) is due to the potential of the ions which in the semiclassical model is no longer explicit. To see this behavior one electron must travel a distance in \vec{k} -space larger than the typical FBZ size but even with very intense fields and large relaxation time (the typical time after which the system returns to equilibrium thanks to collision) the distance that one electron can cover is small compared with typical FBZ size.

In the case of uniform magnetic field the semiclassical equations are

$$\begin{aligned}\dot{\vec{r}} &= \vec{v}_n(\vec{k}) = \frac{1}{\hbar} \frac{\partial E_n(\vec{k})}{\partial \vec{k}}; \\ \hbar \dot{\vec{k}} &= -\frac{e}{c} \vec{v}_n(\vec{k}) \times \vec{H}\end{aligned}$$

follows that, since the cross product produce a vector perpendicular to both addends, the external force has zero component along the magnetic field's lines and so the component of \vec{k} along the magnetic field's lines is a motion constant; moreover, since Lorenz force due to magnetic field do not work, also the energy $E_n(\vec{k})$ is a motion constant. The solution of the equation are determinate by those two conservation laws, electrons move along curves (in general not closed) given by the intersection of surfaces of constant energy (the Fermi surface for a particular band, remember that the Fermi surface is defined as $E_n(\vec{k}) = E_F$) and planes perpendicular to the magnetic field's lines.

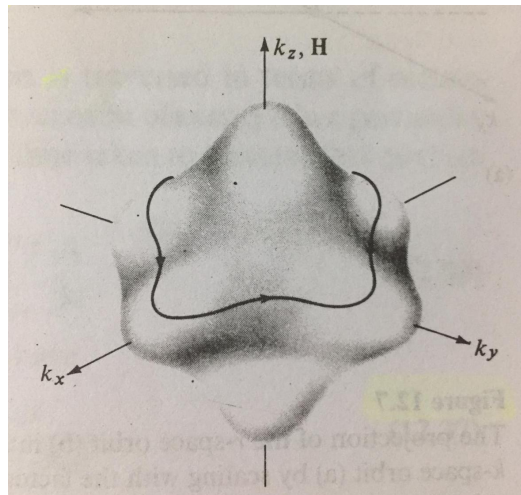


Figure 9: Intersection between Fermi surface and planes perpendicular to the magnetic field's lines. The orbit is completely different from the case of electrons in vacuum.

Consider the case of a closed orbit, the projection of the real space in a plane perpendicular to the magnetic field's lines can be found taking the vector product of the second above equation with a magnetic field's vector

$$\hat{H} \times \hbar \dot{\vec{k}} = -\frac{e}{c} \hat{H} \times \dot{\vec{r}} \times \vec{H},$$

remembering that $a \times b \times c = b(a \cdot c) - c(a \cdot b)$ we have

$$\hat{H} \times \dot{\vec{k}} = -\frac{e}{c\hbar} [\dot{\vec{r}}(\hat{H} \cdot \vec{H}) - \vec{H}(\hat{H} \cdot \dot{\vec{r}})] = -\frac{eH}{c\hbar} [\dot{\vec{r}} - \hat{H}(\hat{H} \cdot \dot{\vec{r}})] = -\frac{eH}{c\hbar} \dot{\vec{r}}_{\perp}$$

in which $\dot{\vec{r}}_{\perp}$ is the component perpendicular to the magnetic field. Integrating the above equation we obtain

$$\vec{r}_{\perp}(t) - \vec{r}_{\perp}(0) = -\frac{c\hbar}{He} \hat{H} \times (\vec{k}(t) - \vec{k}(0)),$$

since the vector $\vec{k}(t) - \vec{k}(0)$ is always (at each time) perpendicular to magnetic field's lines (it's due to the conservation law previously exposed), the vector product rotate by 90° the orbit in \vec{k} -space around the magnetic field vector. In the end, the orbit in real space is the orbit in \vec{k} -space rotate by 90° around the magnetic field vector and scaled by a factor $\frac{\hbar c}{eH}$. We note also that from the first of the semiclassical equations in the case of motion in uniform magnetic field we can derive the component of the real orbit along the axis parallel to the magnetic field's lines (for example along the z axis)

$$z(t) = z(0) + \int_0^t v_z(t) dt = z(0) + \int_0^t \frac{1}{\hbar} \frac{\partial E_n(\vec{k})}{\partial k_z} dt,$$

and the motion can be not uniform. We conclude that the motion in a uniform magnetic field of a Bloch electrons is completely different from the case of electrons in vacuum subject to uniform magnetic field.

4.2 Specific heat of Bloch electrons in solid

In this section we will introduce the Sommerfeld expansion and use it to calculate thermodynamic quantities of interest, like the specific heat. First, we define again the density of states (DOS). A lot of the quantities of interest are of the form

$$Q = g \sum_{n, \vec{k}} Q_n(\vec{k})$$

in the limit of large crystal the allowed \vec{k} are very dense and the sum can be replaced by an integral

$$q = \lim_{V \rightarrow \infty} \frac{Q}{V} = g \sum_n \int_{FBZ} \frac{d\vec{k}}{(2\pi)^3} Q_n(\vec{k})$$

in which g is the spin degeneracy (for electrons $g = 2$). This type of integral can be rewrite in the form

$$q = \int Q(E) G(E) dE,$$

on condition you define the DOS in the form (comparing with the second equation)

$$G(E) = \sum_n G_n(E) = \sum_n \int_{FBZ} \frac{d\vec{k}}{(4\pi^3)} \delta(E - E_n(\vec{k}))$$

DOS counts how many states are there at a certain energy E .

4.2.1 Sommerfeld expansion

The typical integral which allows us to calculate thermodynamic quantities of interest is of the form

$$q = \int_{-\infty}^{\infty} dE H(E) f(E),$$

in which the function $f(E)$ is the Fermi distribution

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

and $H(E)$ is a function that vanishes in the limit $E \rightarrow -\infty$. Defining the function

$$R(E) = \int_{-\infty}^E H(z) dz$$

we can rewrite the first integral in the form

$$q = \int_{-\infty}^{\infty} f(E) dR(E) \Rightarrow q = R(E)f(E) \Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} R(E) \left(-\frac{df(E)}{dE} \right) dE = \int_{-\infty}^{\infty} R(E) \left(-\frac{df(E)}{dE} \right) dE,$$

the term $R(E)f(E) \Big|_{-\infty}^{\infty} = 0$ because $R(-\infty) = 0$ and $f(\infty) = 0$. Whereas the term in parentheses in the integral above is very spiky around $E = \mu$ (so much so that it behaves like a Dirac delta) it is a good idea to expand with Taylor the $R(E)$ function around the point μ

$$q = \sum_{l=0}^{\infty} \frac{1}{l!} R^{(l)}(\mu) \int_{-\infty}^{\infty} (E - \mu)^l \left(-\frac{df(E)}{dE} \right) dE,$$

since the function in parentheses is an even function of $(E - \mu)$, all the odd derivatives disappear so

$$q = \sum_{s=0}^{\infty} \frac{1}{(2s)!} R^{(2s)}(\mu) \int_{-\infty}^{\infty} (E - \mu)^{2s} \left(-\frac{df(E)}{dE} \right) dE.$$

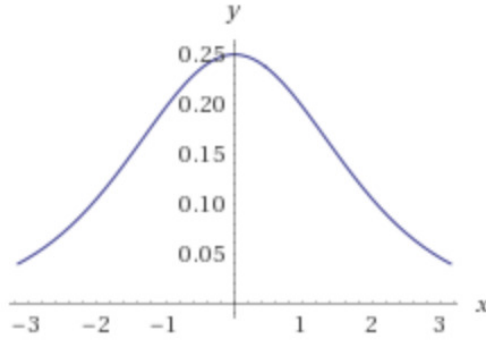


Figure 10: Plot of the function in parenthesis, $x = E - \mu$. It's an even function.

Now the remaining integral can be written as

$$\frac{1}{(2s)!} \int_{-\infty}^{\infty} (E - \mu)^{2s} \left(-\frac{df(E)}{dE} \right) dE \equiv a_s (k_b T)^{2s}$$

in which $a_s = \frac{1}{(2s)!} \int_{-\infty}^{\infty} x^{2s} \frac{e^x}{(e^x + 1)^2}$. So, in the end, we can write (noting that $R^{(0)}(\mu) = \int_{-\infty}^{\mu} H(E) dE$ and $R^{(2s)}(\mu) = H^{2s-1}(\mu)$)

$$q = \int_{-\infty}^{\mu} H(E) dE + \sum_{s=1}^{\infty} a_s H^{2s-1}(\mu) (k_b T)^{2s}.$$

The above expression is the Sommerfeld expansion (SE); it's based on the fact that the Fermi distribution even at high temperatures, it keeps its Heaviside theha shape almost unaltered, so the limiti of SE lies in the fact that at a certain temperature the Fermi distribution will deviate greatly from its shape a $T = 0$. The power of the SE lies in the fact that the typical temperatures at which the Fermi distribution differs appreciably from its original shape are of the order of $\frac{E_F}{k_b} \sim 10^4 K$ so when the solid is gone.

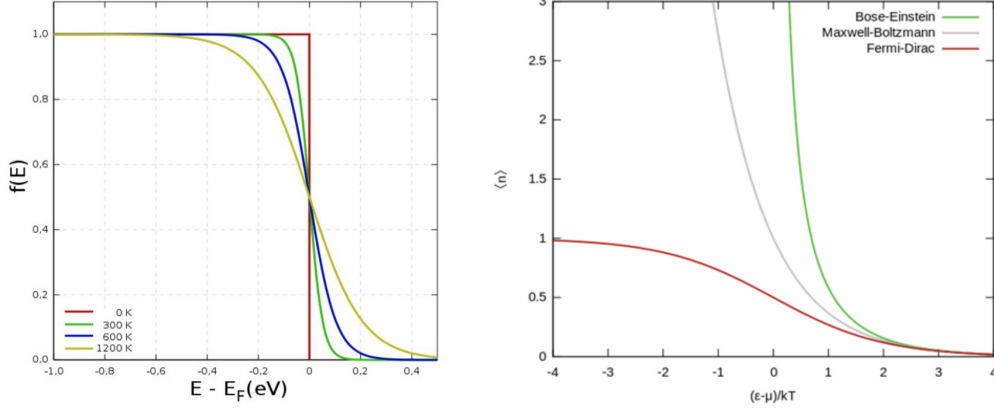


Figure 11: Graph of the Fermi distribution for various temperatures (left). Comparison of various nature's statistics (right).

The expansion until the fourth order is

$$\int_{-\infty}^{\infty} dE H(E) f(E) = \int_{-\infty}^{\mu} H(E) dE + \frac{\pi^2}{6} H'(\mu) (k_b T)^2 + \frac{7\pi^4}{360} H'''(\mu) (k_b T)^4 + O(T^6)$$

4.2.2 Electronic specific heat

Generally we never go beyond the fourth expansion order, but we will stop at the second to calculate the corrections to the chemical potential and the electronic specific heat. The energy density and the density of electron can be evaluated as

$$u = \int_{-\infty}^{\infty} E G(E) f(E) dE$$

$$n = \int_{-\infty}^{\infty} G(E) f(E) dE$$

so using SE (in the first case $H(E) = EG(E)$ in the second one $H(E) = G(E)$) we obtain

$$u = \int_{-\infty}^{\mu} EG(E) dE + \frac{\pi^2}{6} (\mu G'(\mu) + G(\mu)) (k_b T)^2,$$

$$n = \int_{-\infty}^{\mu} G(E) dE + \frac{\pi^2}{6} G'(\mu) (k_b T)^2,$$

We assume that the chemical potential corrections are $O(T^2)$ so, since the correction in electron density are already $O(T^2)$ we can write

$$n = \int_{-\infty}^{\mu} G(E) dE + \frac{\pi^2}{6} G'(E_F) (k_b T)^2,$$

moreover if $\mu - E_F$ is small, using the integral mean theorem, we have, $\int_{-\infty}^{\mu} G(E) dE = \int_{-\infty}^{E_F} G(E) dE + \int_{E_F}^{\mu} G(E) dE \approx \int_{-\infty}^{E_F} G(E) dE + G(E_F)(\mu - E_F)$; so

$$n = \int_{-\infty}^{E_F} G(E) dE + G(E_F)(\mu - E_F) + \frac{\pi^2}{6} G'(E_F) (k_b T)^2 = n_0 + G(E_F)(\mu - E_F) + \frac{\pi^2}{6} G'(E_F) (k_b T)^2,$$

in which n_0 is the quantity calculated at $T = 0$. Since the electron density does not depend on the temperature we must have

$$G(E_F)(\mu - E_F) + \frac{\pi^2}{6} G'(E_F) (k_b T)^2 = 0 \Rightarrow \mu = E_F - \frac{\pi^2}{6} (k_b T)^2 \frac{G'(E_F)}{G(E_F)}$$

the correction depend on the sign of the derivative of the DOS.

Doing the same kind of simplifications in the case of energy density we obtain

$$u = u_0 + E_F G(E_F)(\mu - E_F) + \frac{\pi^2}{6} E_F G'(E_F) (k_b T)^2 + \frac{\pi^2}{6} G(E_F) (k_b T)^2$$

$$= u_0 + E_F [G(E_F)(\mu - E_F) + \frac{\pi^2}{6} G'(E_F) (k_b T)^2] + \frac{\pi^2}{6} G(E_F) (k_b T)^2$$

$$= u_0 + \frac{\pi^2}{6} G(E_F) (k_b T)^2$$

given that $[G(E_F)(\mu - E_F) + \frac{\pi^2}{6}G'(E_F)(k_b T)^2] = 0$; and in which u_0 is the quantity calculated at $T = 0$. We can calculate, now, the specific heat

$$c_v = \frac{\partial u}{\partial T} = \frac{\pi^2}{3}G(E_F)k_b^2 T,$$

the electronic specific heat is linear in T in the limit of "low" temperature. In the section on phonons we have seen that in $3 - D$ system the specific heat due to the ions oscillation (due to the phonons) goes to zero like T^3 , so the total specific heat goes like

$$c_v^{tot} = c_v^{el} + c_v^{phon} = aT + bT^3.$$

If we plot the quantity $\frac{c_v^{tot}}{T}$ vs T^2 we can extrapolate the electronic specific heat (given by the intercept of the right line multiplied by T) and the phonon specific heat (given by the slope of the right line multiplied by T^3).

4.3 Semiclassical theory of transport phenomena in metals

Whenever a system is put out of equilibrium, it will host processes that tend to bring it back to equilibrium. These processes are called transport phenomena. The causes that produce the non-equilibrium conditions will henceforth be called forces. There are two possibilities: if the forces are removed after producing the non-equilibrium conditions, the system will relax back to equilibrium. Once equilibrium is regained, the transport processes will stop. If the system is permanently forced out of equilibrium, the transport processes will continuously attempt to restore equilibrium, without stopping. If the forces are stationary, a steady non-equilibrium states will be reached and the system will host steady transport processes.

When characterising the non-equilibrium state of a metal, within a semiclassical picture, one is led to consider the distribution of conduction electrons with a given quasi-momentum \vec{k} . The distribution function $g_n(\vec{r}, \vec{k}, t)$ is such that the number of electrons belonging to the n -th band, with quasi-momentum \vec{k} in the infinitesimal volume element $d\vec{k}$ of reciprocal space and whose position \vec{r} is comprised within the infinitesimal volume element $d\vec{r}$, at time t , is

$$dN_n = g_n(\vec{r}, \vec{k}, t) \frac{d\vec{r}d\vec{k}}{(2\pi)^3}.$$

We can define the concept of local equilibrium in the infinitesimal volume element as the condition such that the distribution function is of the form

$$g_n^0(\vec{r}, \vec{k}, t) = \frac{1}{e^{\beta(\vec{r}, t)[E_n(\vec{k}) - \mu(\vec{r}, t)]} + 1},$$

it corresponds to the Fermi distribution function for given local and instantaneous values of the chemical potential μ and temperature T , $E_n(\vec{k})$ indicates the dispersion of Bloch electrons belonging to the n -th band.

In a system of independent particles, the distribution function is conserved along the time evolution of the system (Liouville's theorem)

$$\frac{dg_n(\vec{r}, \vec{k}, t)}{dt} = \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial \vec{r}} \cdot \frac{d\vec{r}}{dt} + \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial \vec{k}} \cdot \frac{d\vec{k}}{dt} + \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial t} = \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial \vec{r}} \cdot \vec{v}_n + \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial \vec{k}} \cdot \dot{\vec{k}} + \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial t} = 0,$$

using the semiclassical equations of motion for Bloch electrons in the case of EM field we obtain

$$\frac{1}{\hbar} \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial \vec{r}} \cdot \frac{\partial E_n(\vec{k})}{\partial \vec{k}} - \frac{e}{\hbar} \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial \vec{k}} \cdot [\vec{E}(\vec{r}, t) + \frac{1}{c\hbar} \frac{\partial E_n(\vec{k})}{\partial \vec{k}} \times \vec{H}(\vec{r}, t)] + \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial t} = 0.$$

Of course, in a perfect Fermi gas, where all interactions between the electrons are neglected (so no collision), no relaxation to equilibrium is possible for $g_n(\vec{r}, \vec{k}, t)$. To describe relaxation process, we are forced to consider collisions between the electrons (or with other degrees of freedom); in such case $\frac{dg_n(\vec{r}, \vec{k}, t)}{dt} \neq 0$ and so

$$\frac{1}{\hbar} \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial \vec{r}} \cdot \frac{\partial E_n(\vec{k})}{\partial \vec{k}} - \frac{e}{\hbar} \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial \vec{k}} \cdot [\vec{E}(\vec{r}, t) + \frac{1}{c\hbar} \frac{\partial E_n(\vec{k})}{\partial \vec{k}} \times \vec{H}(\vec{r}, t)] + \frac{\partial g_n(\vec{r}, \vec{k}, t)}{\partial t} = I_{coll}(g_n(\vec{r}, \vec{k}, t)).$$

The above equation is the Boltzmann equation, describing the evolution of a given system under arbitrary non-equilibrium conditions, where the collision integral, $I_{coll}(g_n(\vec{r}, \vec{k}, t))$, is a non-linear functional of $dg_n(\vec{r}, \vec{k}, t)$; the resulting equation in a non-linear integro-differential equation, which is quite difficult to treat in general.

So, collisions are the mechanisms that restores equilibrium, or allows the system to reach a steady state under stationary non equilibrium conditions. For Bloch electrons, quasi-momentum is a conserved quantity in equilibrium, so the interaction with a perfectly periodic crystal lattice cannot produce relaxation. Collisions arise when electrons are scattered by imperfections of the lattice (crystal defects, impurities, vacancies, etc), by

lattice vibrations (electron-phonon interactions), or by other electrons, when the electron-electron interaction is taken into account.

To solve the Boltzmann equation is important remember that in many circumstances, the empirical experience shows that, if a system is weakly out of equilibrium, the relaxation is exponential, and is governed by a characteristic relaxation time, which is the characteristic time scale of the fastest collision mechanism. In any case, the assumption of an exponential relaxation, will usually provide a first crude description of the relaxation to equilibrium (or to a steady non-equilibrium state). Mathematically this means to write the collision integral as

$$I_{coll}(g_n(\vec{r}, \vec{k}, t)) = -\frac{(g_n(\vec{r}, \vec{k}, t) - g_n^0(\vec{r}, \vec{k}, t))}{\tau},$$

where $\tau \equiv \tau_n(\vec{r}, \vec{k})$ is the relaxation time. This expression guarantees that $g_n(\vec{r}, \vec{k}, t)$ relaxes exponentially to its (local) equilibrium value. In weak non-equilibrium conditions the band index n is not involved in the relaxation process and will be omitted the index. Therefore Boltzmann's equation becomes (simplifying the notation, pay attention that we write g_n^0 as g_0)

$$\frac{1}{\hbar} \frac{\partial g}{\partial \vec{r}} \cdot \frac{\partial E}{\partial \vec{k}} - \frac{e}{\hbar} \frac{\partial g}{\partial \vec{k}} \cdot [\vec{E}(\vec{r}, t) + \frac{1}{c\hbar} \frac{\partial E}{\partial \vec{k}} \times \vec{H}(\vec{r}, t)] + \frac{\partial g}{\partial t} = -\frac{(g - g_0)}{\tau}.$$

Considering situations where the forces that bring the system out of equilibrium are weak enough, so that g deviates but slightly from the equilibrium value; so we can approximate the derivatives with respect to the position and the quasi momentum considering the linear response

$$\begin{aligned} \frac{\partial g}{\partial \vec{r}} &\approx \frac{\partial g_0}{\partial T} \frac{\partial T}{\partial \vec{r}} + \frac{\partial g_0}{\partial \mu} \frac{\partial \mu}{\partial \vec{r}}; \\ \frac{\partial g}{\partial \vec{k}} &\approx \frac{\partial g_0}{\partial E} \frac{\partial E}{\partial \vec{k}}, \end{aligned}$$

and Boltzmann's equation becomes (for simplicity we consider absent temperature and chemical potential gradients)

$$\begin{aligned} -\frac{e}{\hbar} \frac{\partial g_0}{\partial E} \frac{\partial E}{\partial \vec{k}} \cdot [\vec{E}(\vec{r}, t) + \frac{1}{c\hbar} \frac{\partial E}{\partial \vec{k}} \times \vec{H}(\vec{r}, t)] + \frac{\partial g}{\partial t} &= -\frac{(g - g_0)}{\tau} \\ \Rightarrow -\frac{e}{\hbar} \frac{\partial g_0}{\partial E} \frac{\partial E}{\partial \vec{k}} \cdot \vec{E}(\vec{r}, t) + \frac{\partial g}{\partial t} &= -\frac{(g - g_0)}{\tau} \\ \Rightarrow -e \frac{\partial g_0}{\partial E} \vec{v} \cdot \vec{E}(\vec{r}, t) + \frac{\partial g}{\partial t} &= -\frac{(g - g_0)}{\tau}, \end{aligned}$$

given the first semiclassical equation. This equation shows that a stationary non-equilibrium state is reached in the presence of absent temperature and chemical potential gradients, and constant electric field, in which the deviation of g from its equilibrium value g_0 is linear in the forces that keep the system out of equilibrium. Non-linear corrections will arise beyond the linear response theory. We point out that the magnetic field disappeared from the linearized Boltzmann equation. This does not mean that the magnetic field disappears altogether, because it still determines the time evolution of \vec{k} through the semiclassical equations of motion for Bloch electrons.

To illustrate how the transport properties of a metal can be described within the approach developed so far, let us consider the case of a uniform electric field is present, which depends on time as a simple harmonic

$$\vec{E}(t) = \vec{E}_\omega e^{i\omega t},$$

Let us call $\delta g \equiv g - g_0$ the deviation of the distribution from its equilibrium value. We can look for a solution of the Boltzmann equation in which δg has the same time dependence as the electric field,

$$\delta g(t) = \delta g_\omega e^{i\omega t}.$$

When T and μ are constant, g_0 does not depend on time, so that

$$\frac{\partial g}{\partial t} = \frac{\partial \delta g}{\partial t} = i\omega \delta g_\omega e^{i\omega t}$$

and the Boltzmann equation becomes

$$-e \frac{\partial g_0}{\partial E} \vec{v} \cdot \vec{E}_\omega + i\omega \delta g_\omega = -\frac{\delta g_\omega}{\tau} \Rightarrow \delta g_\omega = \frac{e}{i\omega + \frac{1}{\tau}} \frac{\partial g_0}{\partial E} \vec{v} \cdot \vec{E}_\omega.$$

The value of the current density \vec{j} (the transport phenomenon that is induced by the electric field) is found calculating the average value of the velocity with the non-equilibrium distribution g , times the charge of an electron (that the average velocity vanishes when calculated with the equilibrium distribution g_0)

$$\vec{j}(t) = -2e \int_{FBZ} \vec{v} \delta g \frac{d\vec{k}}{(2\pi)^3},$$

using the explicit solution for δg , we find $\vec{j}(t) = \vec{j}_\omega e^{i\omega t}$

$$\vec{j}(t) = -2e^2 \int_{FBZ} \frac{1}{i\omega + \frac{1}{\tau}} \frac{\partial g_0}{\partial E} \vec{v} (\vec{v} \cdot \vec{E}_\omega) \frac{d\vec{k}}{(2\pi)^3} e^{i\omega t} \Rightarrow \vec{j}_\omega = -2e^2 \int_{FBZ} \frac{1}{i\omega + \frac{1}{\tau}} \frac{\partial g_0}{\partial E} \vec{v} (\vec{v} \cdot \vec{E}_\omega) \frac{d\vec{k}}{(2\pi)^3},$$

since the quantity $\frac{\partial g_0}{\partial E}$ forces the integrand to be evaluated at the Fermi surface, τ becomes a constant $\tau(E_F)$ so

$$\vec{j}_\omega = -\frac{2e^2}{i\omega + \frac{1}{\tau}} \int_{FBZ} \frac{\partial g_0}{\partial E} \vec{v} (\vec{v} \cdot \vec{E}_\omega) \frac{d\vec{k}}{(2\pi)^3}.$$

From the above equations, given that $j_i = \sigma_{ij} E_j$, we can find the conductivity tensor

$$\begin{aligned} \sigma_{ij} &= -\frac{2e^2}{i\omega + \frac{1}{\tau}} \int_{FBZ} \frac{\partial g_0}{\partial E} v_i v_j \frac{d\vec{k}}{(2\pi)^3} = -\frac{2e^2}{i\omega + \frac{1}{\tau}} \int_{FBZ} \frac{\partial g_0}{\partial E} \frac{1}{\hbar^2} \frac{\partial E}{\partial k_i} \frac{\partial E}{\partial k_j} \frac{d\vec{k}}{(2\pi)^3} \\ &= -\frac{2e^2}{i\omega + \frac{1}{\tau}} \int_{FBZ} \frac{1}{\hbar^2} \frac{\partial g_0}{\partial E} \frac{\partial E}{\partial k_i} \frac{\partial E}{\partial k_j} \frac{d\vec{k}}{(2\pi)^3} = \frac{2e^2}{i\omega + \frac{1}{\tau}} \int_{FBZ} g_0 \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j} \frac{d\vec{k}}{(2\pi)^3} \\ &= \frac{2e^2}{i\omega + \frac{1}{\tau}} \int_{FBZ} g_0 m_{ij}^{-1} \frac{d\vec{k}}{(2\pi)^3}, \end{aligned}$$

in the penultimate step we integrated by parts (considering that the integrand is periodic so that the contribution evaluated at the boundaries of the first Brillouin zone vanishes). The Fermi distribution function g_0 selects the occupied states. However, the inverse mass tensor is a periodic function, its integral over the entire first Brillouin zone vanishes so, again, filled band are inert.

For free electrons the inverse mass tensor is proportional to the identity matrix $m_{ij}^{-1} = \frac{\delta_{ij}}{m}$, where m is the free electron mass; so $\sigma_{ij} = \sigma \delta_{ij}$ with

$$\sigma = \frac{2e^2}{m(i\omega + \frac{1}{\tau})} \int_{occupied} \frac{d\vec{k}}{(2\pi)^3} = \frac{ne^2\tau}{m} \frac{1}{1 + i\omega\tau},$$

given that the integral over the occupied states yielding the conduction electron density n . In the limit of DC current ($\omega \rightarrow 0$) we obtain the Drude conductivity (the Drude model electrons in solids as a perfect gas)

$$\sigma = \frac{ne^2\tau}{m}.$$

5 Semiconductors

We pay attention on a particular type of solid, a solid that is neither conductor nor insulator; we're talking about semiconductor. In semiconductor solids, like Si or Ge, the GAP between valence band and conducting band is more or less a few eV or fraction of eV. The peculiarity of semiconductor materials is that when they are thermally excited some inert electrons can cross the GAP and became conducting electrons. We'll study pure (intrinsic) semiconductors and doped (extrinsic) semiconductors.

5.1 Intrinsic semiconductors

A $T = 0$ we identify the conduction and the valence band; when we thermally excited the electrons of the material only the electrons that are close to the Fermi energy (those one that are close to the top of the valence band) can be excited. The excited electrons cross the GAP to go to the bottom of the conducting band (their energy are close to the minimum of the conducting band) and leaves a empty spaces in the valence band, we call this empty spaces of electrons "holes"; we can describe our system using the electrons in the conducting band or the holes in the valence band. Since electrons and holes are close to singular point we can develop their dispersion relation using Taylor expansion

$$E_{\vec{k}}^{electrons} = E_c + \frac{1}{2} \sum_{i,j} \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j} k_i k_j,$$

$$E_{\vec{k}}^{holes} = E_c - \frac{1}{2} \sum_{i,j} \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j} k_i k_j.$$

that we can rewrite as

$$E_{\vec{k}}^{electrons} = E_c + \frac{\hbar^2}{2} \sum_{i,j} m_{e,ij}^{-1} k_i k_j,$$

$$E_{\vec{k}}^{holes} = E_c - \frac{\hbar^2}{2} \sum_{i,j} m_{h,ij}^{-1} k_i k_j.$$

in which $m_{ij}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j}$ is known as inverse mass tensor. Holes are identical to electrons but they have a negative mass tensor, so we can move the minus sign from mass to acceleration and consider the holes as electrons with positive charge.

Two important quantities in semiconductors physic are the density of holes in valence band, p_v , and electrons in conducting band, n_c ,

$$n_c(T) = \int_{E_c}^{\infty} G_c(E) f(E) dE,$$

$$p_v(T) = \int_{-\infty}^{E_v} G_v(E) (1 - f(E)) dE,$$

here $f(E)$ is the Fermi-Dirac distribution and $G(E)$ is the density of state. To evaluate this two integrals we make the assumption (remembering that $k_b T = 25 meV$ at room temperature) that $E_c - \mu, \mu - E_v \gg k_b T$, so

$$n_c(T) \approx \int_{E_c}^{\infty} G_c(E) e^{-\frac{(E-\mu)}{k_b T}} dE \Rightarrow n_c(T) \approx N_c(T) e^{-\frac{(E_c-\mu)}{k_b T}},$$

$$p_v(T) \approx \int_{-\infty}^{E_v} G_v(E) e^{-\frac{(\mu-E)}{k_b T}} dE \Rightarrow p_v(T) \approx P_v(T) e^{-\frac{(\mu-E_v)}{k_b T}},$$

in which we had multiplied the first equation for $e^{\frac{E_c}{k_b T}} e^{-\frac{E_c}{k_b T}}$, the second for $e^{\frac{E_v}{k_b T}} e^{-\frac{E_v}{k_b T}}$ and we also defined $N_c(T)$ and $P_v(T)$ as

$$N_c(T) = \int_{E_c}^{\infty} G_c(E) e^{-\frac{(E-E_c)}{k_b T}} dE \Rightarrow N_c(T) = \frac{\sqrt{2\pi m_e^3}}{2\pi^2 \hbar^3} (k_b T)^{\frac{3}{2}},$$

$$P_v(T) = \int_{-\infty}^{E_v} G_v(E) e^{-\frac{(E_v-E)}{k_b T}} dE \Rightarrow P_v(T) = \frac{\sqrt{2\pi m_h^3}}{2\pi^2 \hbar^3} (k_b T)^{\frac{3}{2}}.$$

The above integrals are evaluated starting from the calculation of the DOS, $G_j(E) = \int \frac{d\vec{k}}{4\pi^3} \delta(E - E_{\vec{k},j})$, moreover, $m_e = (m_{e,xx}m_{e,yy}m_{e,zz})^{\frac{1}{3}}$ and $m_h = (m_{h,xx}m_{h,yy}m_{h,zz})^{\frac{1}{3}}$. Now, if we consider the product $n_c(T)p_v(T)$, the dependence from the chemical potential disappear

$$n_c(T)p_v(T) = N_c(T)P_v(T)e^{-\frac{E_c - E_v}{k_bT}} = N_c(T)P_v(T)e^{-\frac{E_{GAP}}{k_bT}} \equiv n_i^2,$$

this equation is known as mass action law.

In the case of pure semiconductor the only electrons that can cross the GAP are those one that are in the valence band and so the number density of electrons in conducting band and the number of density of holes in valence band must be equal

$$n_c(T) = p_v(T) \equiv n_i(T);$$

so we obtain

$$n_i(T) = \sqrt{N_c(T)P_v(T)}e^{-\frac{E_c - E_v}{2k_bT}} = \sqrt{N_c(T)P_v(T)}e^{-\frac{E_{GAP}}{2k_bT}} = \frac{1}{4} \left(\frac{2k_bT}{\pi\hbar^2} \right)^{\frac{3}{2}} (m_e m_h)^{\frac{3}{4}} e^{-\frac{E_{GAP}}{2k_bT}}.$$

We are now interested to the chemical potential; if we consider the ratio between $n_c(T)$ and $p_v(T)$

$$1 = \frac{n_c(T)}{p_v(T)} = \frac{N_c(T)}{P_v(T)} e^{-\frac{E_c + E_v - 2\mu}{k_bT}} \Rightarrow \mu = \frac{E_c + E_v}{2} - \frac{k_bT}{2} \ln \left(\frac{N_c(T)}{P_v(T)} \right).$$

Using the equations for $N_c(T)$ and $P_v(T)$ we have for the chemical potential

$$\mu = E_v + \frac{E_{GAP}}{2} - \frac{3k_bT}{4} \ln \left(\frac{m_e}{m_h} \right) \equiv \mu_i,$$

we note that at $T = 0$ the chemical potential is exactly in the middle between the two bands.

In the intrinsic regime, the components of the conductivity tensor along the principal axes are

$$\begin{aligned} \sigma_{xx} &= en_i(\mu_{e,xx} + \mu_{h,xx}) = e^2 n_i \tau \left(\frac{1}{m_{e,xx}} + \frac{1}{m_{h,xx}} \right); \\ \sigma_{yy} &= en_i(\mu_{e,yy} + \mu_{h,yy}) = e^2 n_i \tau \left(\frac{1}{m_{e,yy}} + \frac{1}{m_{h,yy}} \right); \\ \sigma_{zz} &= en_i(\mu_{e,zz} + \mu_{h,zz}) = e^2 n_i \tau \left(\frac{1}{m_{e,zz}} + \frac{1}{m_{h,zz}} \right), \end{aligned}$$

in general

$$\sigma_{ij} = en_i(\mu_{e,ij} + \mu_{h,ij}) = e^2 n_i \tau \left(\frac{1}{m_{e,ij}} + \frac{1}{m_{h,ij}} \right).$$

Remember that the resistivity is the inverse of the conductivity, $\rho_{ij} = \frac{1}{\sigma_{ij}}$.

We emphasize that what has been done up to the law of mass action (included) has a completely general validity and does not depend on the type of semiconductor.

5.2 Extrinsic semiconductors

An extrinsic semiconductor is a semiconductor with some impurities and they contribute a significant amount of the conducting electrons. The process of inserting impurities is said "doping" and the semiconductor material is said "doped". The process consists in the insertion of atoms of different valence with respect to those one constituting the material, for example in the case of homogeneous Si (that have valence 4), we can insert atom like B (valence 3) or As (valence 5). The impurity with less valence respect to the atoms of the materials are called acceptors because they form less bonds and so they bring some holes and so they can accept some electrons, while the impurity with more valence respect to the atoms of the materials are called donors because they are able to form more bonds and so they bring some electrons. In this case the density of carriers are not the same, so we define $\Delta n = n_c - p_v$. We consider only semiconductors doped with atoms with valence +1 or -1 respect to the atoms of the semiconductor material.

A semiconductor is

- if the semiconductor is doped with acceptors (more holes than electrons, so $\Delta n < 0$) \Rightarrow p -type;
- if the semiconductor is doped with donors (more electrons than holes, so $\Delta n > 0$) \Rightarrow n -type.

Multiplying the definition of Δn for p_v we obtain

$$\Delta n p_v = n_c p_v - p_v^2 \Rightarrow \Delta n p_v = n_i^2 - p_v^2,$$

in the last passage we use the definition of n_i . Multiplying, instead, the definition of Δn for n_c we have

$$\Delta n n_c = -n_c p_v + n_c^2 \Rightarrow \Delta n n_c = -n_i^2 + n_c^2.$$

Solving the first equation for p_v and the second for n_c we found

$$p_v = \frac{-\Delta n + \sqrt{(\Delta n)^2 + 4n_i^2}}{2};$$

$$n_c = \frac{\Delta n + \sqrt{(\Delta n)^2 + 4n_i^2}}{2};$$

At this point we expand our solutions in the regimes in which $\frac{\Delta n}{n_i}$ is small and $\frac{\Delta n}{n_i}$ is large, so

$$n_c \approx \frac{\Delta n}{2} + n_i;$$

$$p_v \approx -\frac{\Delta n}{2} + n_i,$$

for $\frac{\Delta n}{n_i}$ small, and

$$n_c \approx \frac{\Delta n}{2} + \frac{|\Delta n|}{2} \left(1 + \frac{2n_i^2}{(\Delta n)^2}\right);$$

$$p_v \approx -\frac{\Delta n}{2} + \frac{|\Delta n|}{2} \left(1 + \frac{2n_i^2}{(\Delta n)^2}\right),$$

for $\frac{\Delta n}{n_i}$ large. The latter case is to be studied more closely, in fact we have

$$\Delta n \text{ large and positive} \Rightarrow n_c \approx \Delta n, p_v \approx \frac{n_i^2}{\Delta n} \Rightarrow \text{Extreme } n \text{ - type};$$

$$\Delta n \text{ large and negative} \Rightarrow n_c \approx \frac{n_i^2}{|\Delta n|}, p_v \approx |\Delta n| \Rightarrow \text{Extreme } p \text{ - type}.$$

The quantity $\frac{\Delta n}{n_i}$ is important because measures the impurity in the semiconductor and can be expressed as a function of chemical potential, in fact

$$n_c = N_c(T) e^{-\beta(E_c - \mu_i)} e^{\beta(\mu - \mu_i)} = n_i e^{\beta(\mu - \mu_i)}$$

$$p_v = P_v(T) e^{-\beta(\mu_i - E_v)} e^{-\beta(\mu - \mu_i)} = n_i e^{-\beta(\mu - \mu_i)}$$

so

$$\frac{\Delta n}{n_i} = \frac{n_c - p_v}{n_i} = 2 \sinh[\beta(\mu - \mu_i)],$$

so we can classify the doped semiconductors as

- n -type if $\mu > \mu_i$;
- p -type if $\mu < \mu_i$.

The effect of the impurities is to form new levels called donors and acceptors levels and the energy of the donors levels is slightly below E_c while the energy of the acceptors levels is slightly above E_v ; so is far easier thermally to excite an electron into the conduction band from a donor level or a hole into the valence band from an acceptor level, in other words, doping a semiconductor causes the material to have a smaller GAP. We are interested to the density number of electrons (holes) in the donors (acceptors) levels; calling respectively N_a and N_d the density of acceptors and donors we have

$$n_d = \langle n \rangle N_d = N_d \frac{\sum_j N_j e^{-\beta(E_j - \mu N_j)}}{\sum_j e^{-\beta(E_j - \mu N_j)}};$$

$$p_a = \langle p \rangle N_a = N_a \frac{\sum_j N_j e^{-\beta(\mu N_j - E_j)}}{\sum_j e^{-\beta(\mu N_j - E_j)}},$$

where $\langle n \rangle$ is the mean number of electrons in donors levels when there is only 1 donor impurity (in other words, $\langle n \rangle$ is the mean number of electrons in donors levels per unit density of donors), in the same way $\langle p \rangle$ is the

mean number of holes in acceptors levels when there is only 1 acceptor impurity (so, $\langle p \rangle$ is the mean number of holes in acceptors levels per unit density of acceptors). Since both electrons and holes are fermions they must obey to Pauli principle and so we can have at maximum 2 electrons (holes) in each donor (acceptor) level, moreover due to the coulombian repulsion the configuration with 2 electrons (holes) in the same level is strongly depleted by the Boltzmann factor; doing all the calculation we obtain (remembering that we are neglecting all spin contributions to the hamiltonian)

$$n_d = \frac{N_d}{\frac{1}{2}e^{\beta(E_d - \mu)} + 1};$$

$$p_a = \frac{N_a}{\frac{1}{2}e^{\beta(\mu - E_a)} + 1}.$$

At $T = 0$, N_a electrons (per unit volume) dropped from the donors levels to the acceptors levels (we have N_a holes (per unite volume) in the acceptors levels), so we have $N_d - N_a$ electrons (per unit volume) in the donors levels. When T increases, at thermal equilibrium, the electrons will be redistributed in all possible levels but, since the total number of electrons must be the same, the number density $n_c + n_d$ must exceed it's value at $T = 0$ (the value $N_d - N_a$) by the number of empty levels in the valence and acceptors levels (so the number of holes in those levels)

$$n_c + n_d = N_d - N_a + p_v + p_a.$$

At this point, we restrict us to the case in which $E_d - \mu \gg k_b T$ and $\mu - E_a \gg k_b T$ and we note that this condition is more restrictive than the condition adopted in the intrinsic case because the GAP between acceptors and donors levels is smaller than the GAP between valence and conducting band. Using this ansatz (called fully ionize regime) we have

$$n_d = \frac{N_d}{\frac{1}{2}e^{\beta(E_d - \mu)} + 1} \ll N_d;$$

$$p_a = \frac{N_a}{\frac{1}{2}e^{\beta(\mu - E_a)} + 1} \ll N_a,$$

therefore

$$n_c = N_d - N_a + p_v \Rightarrow n_c - p_v = \Delta n = N_d - N_a,$$

so in all the above equations we can replace Δn with $N_d - N_a$, we obtain

$$\Delta n = N_d - N_a \text{ large and positive} \Rightarrow n_c \approx N_d - N_a, p_v \approx \frac{n_i^2}{N_d - N_a} \Rightarrow \text{Extreme } n\text{-type};$$

$$\Delta n = N_d - N_a \text{ large and negative} \Rightarrow n_c \approx \frac{n_i^2}{|N_d - N_a|}, p_v \approx |N_d - N_a| \Rightarrow \text{Extreme } p\text{-type}.$$

Finally, remembering that $\Delta n = 2n_i \sinh[\beta(\mu - \mu_i)]$ and that in the extreme n -type we have $\mu \gg \mu_i$ and that in the extreme p -type we have $\mu \ll \mu_i$ we can find the chemical potential in the limit of extreme doped semiconductor

- extreme n -type if $\mu \gg \mu_i \Rightarrow \sinh[\beta(\mu - \mu_i)] = e^{\beta(\mu - \mu_i)} \Rightarrow \frac{N_d - N_a}{n_i} = e^{\beta(\mu - \mu_i)} \Rightarrow \mu = \mu_i + k_b T \ln\left(\frac{N_d - N_a}{n_i}\right);$
- extreme p -type if $\mu \ll \mu_i \Rightarrow \sinh[\beta(\mu - \mu_i)] = e^{\beta(\mu_i - \mu)} \Rightarrow \frac{N_d - N_a}{n_i} = e^{\beta(\mu_i - \mu)} \Rightarrow \mu = \mu_i - k_b T \ln\left(\frac{N_d - N_a}{n_i}\right).$

Fanally, in the extrinsic regime, the components of the conductivity tensor along the principal axes are

$$\sigma_{xx} = e(n_c \mu_{e,xx} + p_v \mu_{h,xx}) = e^2 \tau \left(\frac{n_c}{m_{e,xx}} + \frac{p_v}{m_{h,xx}} \right);$$

$$\sigma_{yy} = e(n_c \mu_{e,yy} + p_v \mu_{h,yy}) = e^2 \tau \left(\frac{n_c}{m_{e,yy}} + \frac{p_v}{m_{h,yy}} \right);$$

$$\sigma_{zz} = e(n_c \mu_{e,zz} + p_v \mu_{h,zz}) = e^2 \tau \left(\frac{n_c}{m_{e,zz}} + \frac{p_v}{m_{h,zz}} \right),$$

in general

$$\sigma_{ij} = e(n_c \mu_{e,ij} + p_v \mu_{h,ij}) = e^2 \tau \left(\frac{n_c}{m_{e,ij}} + \frac{p_v}{m_{h,ij}} \right).$$

Remember that the resistivity is the inverse of the conductivity, $\rho_{ij} = \frac{1}{\sigma_{ij}}$.

References

- [1] N. Ashcroft, D. Mermin. Solid state physics. 1976.
- [2] S. Caprara. Eccitazioni elementari dei solidi, <http://www2.phys.uniroma1.it/doc/caprara/SCaprara/sergio-caprara-IIQUANT.html>
- [3] S. Caprara. Notes on tight binding, <http://www2.phys.uniroma1.it/doc/caprara/SCaprara/SC-note-tb-CMP.pdf>,
- [4] S. Caprara. Notes on transport theory, <http://www2.phys.uniroma1.it/doc/caprara/SCaprara/SC-note-transport-CMP.pdf>
- [5] S. Caprara. Notes on sommerfeld expansion, <http://www2.phys.uniroma1.it/doc/caprara/SCaprara/SC-note-sommerfeld-CMP.pdf>