

# Solid State Physics

Lecture notes by

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## INTRODUCTION

### What is Solid State Physics?

Typically properties related to crystals, i.e., **periodicity**.

### What is Condensed Matter Physics?

Properties related to solids and liquids including crystals. For example: liquids, polymers, carbon nanotubes, rubber,...

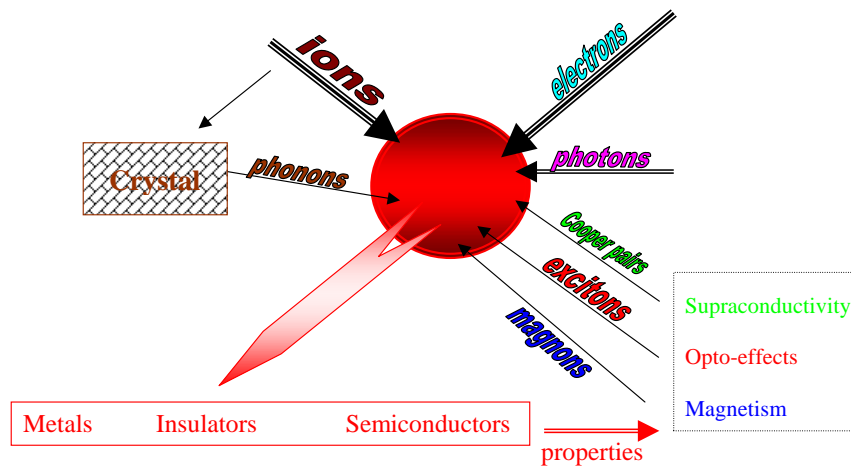
Historically, SSP was considered as the basis for the understanding of solids since many of the properties were

derived based on a periodic lattice. However it appeared that most of the properties are very similar independent of the presence or not of a lattice. **But** there are many exceptions, for example, localization due to disorder or the disappearance of the periodicity.

Even in crystals, liquid-like properties can arise, such as a Fermi liquid, which is an interacting electron system. The same is also true the other way around since liquids can form liquid crystals.

Hence, the study of SSP and CMP are strongly interrelated and can not be separated. These inter-correlations are illustrated below.

### The Big Bang of Condensed Matter Physics



## THE THEORY OF EVERYTHING

See ppt notes

### $H_2O$ - AN EXAMPLE

See ppt notes

### BINDING

What holds atoms together and also keeps them from collapsing?

We will start with the simplest molecule:  $H_2$  to ask what holds it together.

#### Van der Waals attraction

The Van der Waals force arises simply from the change in energy due to the cross Coulomb interactions between atom  $a$  and  $b$ , which is simply a dipole-dipole interaction.

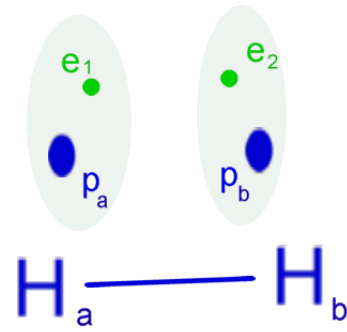


FIG. 1: Graphical representation of a  $H_2$  molecule

The total Hamiltonian can then be written as the sum between the non interacting H atoms and the cross terms due to Coulomb interactions. Hence,

$$H = (H_0) + (H_{int}) \quad (1)$$

with

$$H = \left( -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{1a}} - \frac{e^2}{r_{2b}} \right) + e^2 \left( \frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} \right) \quad (2)$$

Using standard perturbation theory it is then possible to evaluate the gain in energy due to  $H_{int}$ . This is left as an exercise. The result is

$$\Delta E \simeq \frac{-\alpha_a \alpha_b}{r_{ab}^6}, \quad (3)$$

where  $\alpha_x$  are the atomic polarizabilities.

#### Derivation of Van der Waals

Problem 1

#### Repulsion

We just saw that there is an attractive potential of the form  $-1/r^6$ . If there were only a Coulomb repulsion of strength  $1/r$  this would lead to the collapse of our molecule. In fact there is a very strong repulsion, which comes from the Pauli principle. For the general purpose this repulsive potential is often taken to be  $\sim 1/r^{12}$ ,

which leads to a total potential of the form

$$\phi(r) = -4\epsilon \left( \frac{\sigma^6}{r^6} - \frac{\sigma^{12}}{r^{12}} \right), \quad (4)$$

which is usually referred to as the Lennard-Jones potential. The choice of the repulsive term is somewhat arbitrary but it reflects the short range nature of the interaction and represents a good approximation to the full problem. The parameters  $\epsilon$  and  $\sigma$  depend on the molecule.

#### Crystals

What about crystals? Let's first think about what kind of energy scales are involved in the problem. If we assume that the typical distance between atoms is of the order of  $1\text{\AA}$  we have

$$e^2/1\text{\AA} \simeq 14.4\text{eV for the Coulomb energy and} \quad (5)$$

$$\hbar^2 \left( \frac{1}{1\text{\AA}} \right)^2 \simeq 3.8\text{eV for the potential in a } 1\text{\AA} \text{ quantum box} \quad (6)$$

In comparison to room temperature ( $300\text{K} \simeq 25\text{meV}$ ) these energies are huge. Hence ionic Crystals like NaCl are extremely stable, with binding energies of the order of 1eV.

### Ionic crystals

Some solids or crystals are mainly held together by the electrostatic potential and they include the alkali-halides like ( $\text{NaCl} \rightarrow \text{Na}^+\text{Cl}^-$ ).

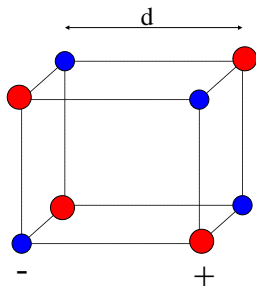


FIG. 2: A simple ionic crystal such as  $\text{NaCl}$

The energy per ion pair is

$$\frac{\text{Energy}}{N_{\text{ionpair}}} = -\alpha \frac{e^2}{d} + \frac{C}{d^n} = -\alpha \frac{14.4\text{eV}}{[d/\text{\AA}]} + \frac{C}{d^n} \quad \text{with } 6 < n \leq 12, \quad (7)$$

where  $\alpha$  is the Madelung constant and can be calculated from the crystal structure.  $C$  can be extracted experimentally from the minimum in the potential energy and typically  $n = 12$  is often used to model the effect of the Pauli principle. Hence, from the derivative of the potential we obtain:

$$d_0 = \left( \frac{12C}{e^2\alpha} \right)^{1/11} \quad (8)$$

so that

$$\frac{\text{Energy}}{N_{\text{ionpair}}} = \frac{11\alpha e^2}{12d_0} \quad (9)$$

How good is this model? See table below:

### Quantum mechanics as a bond

#### Hydrogen-like bonding

Let's start with one H atom. We fix the proton at  $r = 0$  then we know from basic quantum mechanics that

the ground state energy is then given by  $E^0 = -13.6\text{ eV}$ . What happens if we add one proton or  $H^+$  to the system which is  $R$  away. The potential energy for the electron is then

$$U(r) = -\frac{e^2}{r} - \frac{e^2}{|r-R|} \quad (10)$$

The lowest eigenfunction with eigenvalue  $-13.6\text{ eV}$  is

$$\xi(r) = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0}, \quad (11)$$

where  $a_0$  is the Bohr radius. But now we have two protons. If the protons were infinitely apart then the general solution to potential 10 is a linear superposition, i.e.,  $\psi(r) = \alpha\xi(r) + \beta\xi(r-R)$  with a degenerate lowest eigenvalue of  $E^0 = E^0 = -13.6\text{ eV}$ . When  $R$  is not infinite, the two eigenfunctions corresponding to the lowest eigenvalues  $E_b$  and  $E_a$  can be approximated by  $\psi_b = \xi(r) + \xi(r-R)$  and  $\psi_a = \xi(r) - \xi(r-R)$ . See figure 3.

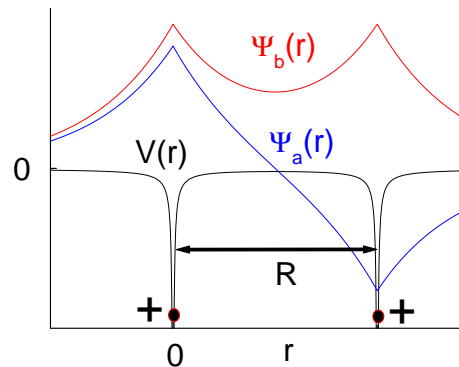


FIG. 3: The potential for two protons with the bonding and anti-bonding wave function of the electron

The average energy (or expectation value of  $E_b$ ) is

$$E_b = \langle \psi_b^* H \psi_b \rangle / \langle \psi_b^* \psi_b \rangle \quad (12)$$

$$= E^0 - \frac{A+B}{1+\Delta} \quad \text{with} \quad (13)$$

$$A = e^2 \int dr \xi^2(r) / |r-R| \quad (14)$$

$$B = e^2 \int dr \xi(r) \xi(|r-R|) / r \quad (15)$$

$$\Delta = \int dr \xi(r) \xi(|r-R|), \quad (16)$$

where  $\langle \cdot \rangle \equiv \int \cdot dr$  and similarly,

$$E_a = E^0 - \frac{A-B}{1-\Delta} \quad (17)$$

Hence, the total energy for state  $\psi_b$  is now

$$E_b^{total} = E_b + e^2/R \quad (18)$$

When plugging in the numbers  $E_b^{total}$  has a minimum at  $1.5\text{\AA}$ . See figure 4

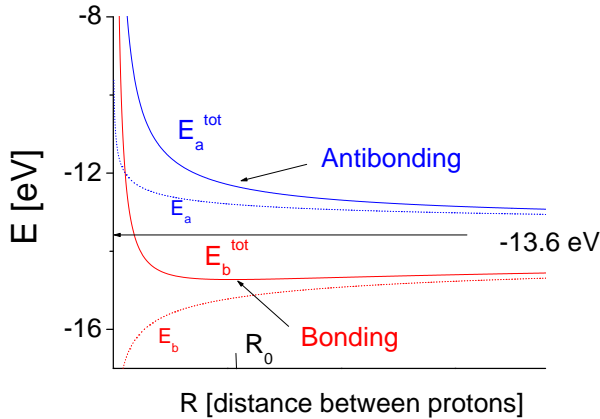


FIG. 4: The energies as a function of the distance between them for the bonding and anti-binding wave functions of the electron

This figure illustrates why they are called bonding and anti-bonding, since in the bonding case the energy is lowered when the distance between protons is reduced as long as  $R > R_0$ .

### Covalent bonding

Covalent bonds are very similar to Hydrogen bonds, only that we have to extend the problem to a linear combination of atomic orbitals for every atom.  $N$  atoms would lead to  $N$  levels, in which the ground state has a bonding wave-function.

### Metals

In metals bonding is a combination of the effects discussed above. The idea is to consider a cloud of electrons only weakly bound to the atomic lattice. The total electrostatic energy can then be written as

$$E_{el} = - \int dr n(r) \sum_R \frac{e^2}{r-R} + \sum_{R>R'} \frac{e^2}{R-R'} + 1/2 \cdot \int dr_1 dr_2 \frac{e^2 n(r_1) n(r_2)}{|r_1 - r_2|} \quad (19)$$

which corresponds to an ionic contribution of the form

$$E_{el} = - \frac{\alpha e^2}{2r_s} \text{ where } r_s = \left( \frac{3}{4\pi n} \right)^{1/3} \quad (20)$$

and  $\alpha$  is the Madelung constant. Deriving this requires quite a bit of effort. On top of this one has to add the kinetic energy of the electrons, which is of the form:

$$E_{kin} = \left( \frac{9\pi}{4} \right)^{2/3} \frac{3\hbar^2}{10mr_s^2} \quad (21)$$

And finally we have to add the exchange energy, which is a consequence of the Pauli principle. The expression for this term is given by

$$E_{ex} = - \left( \frac{9\pi}{4} \right)^{1/3} \frac{3}{4\pi r_s} \quad (22)$$

Putting all this together we obtain in units of the Bohr radius:

$$E = \left( - \frac{24.35a_0}{r_s} + \frac{30.1a_0^2}{r_s^2} - \frac{12.5a_0}{r_s} \right) \text{ eV/atom} \quad (23)$$

This last expressions leads to a minimum at  $r_s/a_0 = 1.6$ . We can now compare this with experimental values and the result is off by a factor between 2 and 6. What went wrong. Well, we treated the problem on a semiclassical level, without incorporating all the electron-electron interactions in a quantum theory. This is very very difficult, but in the large density case this can be estimated and a better agreement with experiments is obtained.

### Binding summary

There are essentially three effects which contribute to the binding of solids:

- Van der Waals (a dipole-dipole like interaction)
- ionic (Coulomb attraction between ions)
- Quantum mechanics (overlap of the wave-function)

In addition we have two effects which prevent the collapse of the solids:

- Coulomb
- Quantum mechanics (Pauli)

## STRUCTURE

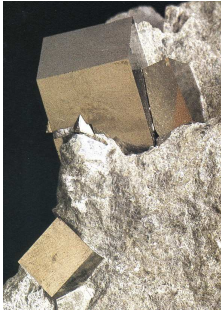


FIG. 5: Pyrite,  $FeS_2$  crystal with cubic symmetry.

## Illustrations

See ppt notes.

## Summary

Periodic solids can be classified into two main classes:

- Bravais lattices: Every point of the lattice  $\vec{R}$  can be reached from a linear combination of the primitive vectors:  $\vec{R} = n_1\hat{a}_1 + n_2\hat{a}_2 + n_3\hat{a}_3$ , where  $n_i$  are integers.
- Lattices with basis: Here every point in a primitive cell is described by a basis vector  $\vec{B}_i$  so that any point of the lattice can be reached through:  $\vec{R} = n_1\hat{a}_1 + n_2\hat{a}_2 + n_3\hat{a}_3 + \vec{B}_i$ .

In 3D there are 14 Bravais lattices and 230 symmetry groups for lattices with basis. In 2D there are 5 Bravais lattices and in 1D only 1.

This is the zoology of crystals and they all have names. It is important to remember that many of the physical properties cannot be deduced from the crystal structure directly. The same crystal structure could be a metal (Cu) or an insulator (Ca).

Miller indices can be obtained through the construction illustrated in the figure below:

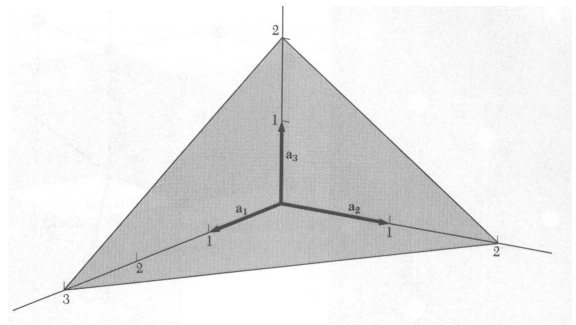


FIG. 6: Plane intercepts the axes at  $(3\hat{a}_1, 2\hat{a}_2, 2\hat{a}_3)$ . The inverse of these numbers are  $(1/3, 1/2, 1/2)$ , hence the smallest integers having the same ratio are 2,3,3, i.e., the Miller indices are  $(233)$ . For a negative intercept the convention is  $\bar{1}$ . (Picture from Ashcroft and Mermin)

## SCATTERING

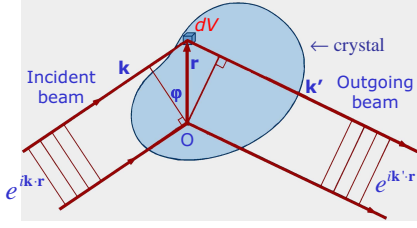
See supplement on diffraction.

In order to determine the structure of a crystal it is possible to observe the interference pattern produced by scattering particles with wave-length comparable to the lattice spacing, i.e., of the order of  $1\text{\AA}$ . There are three main classes of particles, which can be used:

- Photons, in particular X-rays, whose wave lengths are around  $1\text{\AA}$ . The probability to scatter off the crystal is not that large, hence they can penetrate quite deeply into the crystal. The main scattering occurs with the electrons. Hence, what is really observed with X-rays is the periodic distribution of electrons.
- Neutrons are also extensively used since they mainly interact with the nuclei and the magnetic moments.
- Electrons, have a very scattering probability with anything in the crystal, hence they do not penetrate very deep, but they are therefore an interesting tool to probe the surface structure.

All forms of scattering share very similar basic principles and can be applied to the scattering's theory of everything described in the next section.

## Scattering theory of everything



The total scattered wave off V is

$$A(\mathbf{q}) \propto \iiint_V d\mathbf{r}^3 n(\mathbf{r}) \cdot e^{i\mathbf{q} \cdot \mathbf{r}}$$

$$\mathbf{q} = \mathbf{k} - \mathbf{k}'$$

where  $n(\mathbf{r})$  is the distribution of scatterers

FIG. 7: Diffraction set-up (picture from G. Frossati)

This formulation can describe any scattering process in terms of the scattering amplitude  $A(\vec{q})$ . The entire

Physics is hidden in  $n(r)$ , which contains the information on the position of scatterers and their individual scattering distribution and probability. In the following we discuss the most important implications.

### 1D scattering pattern

Let's suppose we have a 1D crystal along direction  $\hat{y}$  with lattice spacing  $a$  and that the incoming wave  $e^{i\vec{k}_{in} \cdot \vec{r}}$  is perpendicular to the crystal along  $\hat{x}$ . We want to calculate the scattered amplitude along direction  $\vec{k}_{out}$ . By defining  $\vec{q} = \vec{k}_{out} - \vec{k}_{in}$ , we can write the scattering amplitude as

$$A(\vec{q}) = \int_V n(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d\mathbf{r}^3 \quad (24)$$

If we assume that the crystal is composed of point-like scatterers we can write:

$$n(x, y, z) = \frac{C}{N} \sum_{n=0}^{N-1} \delta(y - an) \delta(x) \delta(z), \quad (25)$$

where  $C$  is simply a constant. Hence, by inserting 25 into 24, and defining  $\vec{q} = (0, q, 0)$  we have

$$A(q) = \frac{C}{N} \sum_{n=0}^{N-1} e^{iqan} = \frac{C}{N} \frac{1 - e^{iaqN}}{1 - e^{iaq}} \xrightarrow{N \rightarrow \infty} \begin{cases} C & \text{when } q = 2\pi m/a \\ 0 & \text{when } q \neq 2\pi m/a \end{cases} = C \delta_{q, \vec{G}} \quad (26)$$

$\vec{G} = \hat{y} 2\pi m/a$  is the reciprocal lattice and  $m$  an integer. If we had a screen along  $\hat{y}$  we would see a diffraction pattern along  $I(q) = |A(q)|^2$ , since what is measured experimentally is the intensity. In this simple case the reciprocal lattice is the same as the real lattice, but with lattice spacing  $2\pi/a$  instead.

### Point-like scatterers on a Bravais lattice in 3D

We start again with the general form of  $A(\vec{q})$  from 24 and assume that our 3D crystal is formed by point-like scatterers on a Bravais lattice  $\vec{R}$ . Hence,

$$n(\vec{r}) = \frac{C}{N} \sum_{n=0}^{N-1} \delta^3(\vec{r} - \vec{R}_n), \quad (27)$$

and

$$A(\vec{q}) = \frac{C}{N} \sum_{n=0}^{N-1} e^{i\vec{q} \cdot \vec{R}_n} \xrightarrow{N \rightarrow \infty} \begin{cases} C & \text{when } \vec{q} \in \vec{G} \\ 0 & \text{when } \vec{q} \notin \vec{G} \end{cases} = C \delta_{\vec{q}, \vec{G}} \quad (28)$$

In this case the Bravais lattice (or Real-Space) is

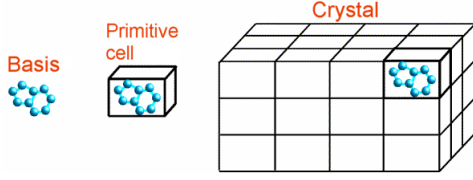
$$\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad (29)$$

and the reciprocal space  $\vec{G}_m$  (or k-space) can be deduced from  $e^{i\vec{R}_n \cdot \vec{G}_m} = 1$ , hence

$$\vec{G}_m = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3, \quad (30)$$

where

$$\vec{b}_1 = \frac{2\pi \vec{a}_2 \times \vec{a}_3}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|}, \quad \vec{b}_2 = \frac{2\pi \vec{a}_3 \times \vec{a}_1}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|} \quad \text{and} \quad \vec{b}_3 = \frac{2\pi \vec{a}_1 \times \vec{a}_2}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|} \quad (31)$$



General case of a Bravais lattice with basis

The most general form for  $n(\vec{r})$ , when the atoms sit on the basis  $\{\vec{u}_j\}$  along the Bravais lattice  $\vec{R}_n$  is

$$n(\vec{r}) = \frac{C}{N} \sum_{j=1, n=0}^{M, N-1} f_j(\vec{r} - \vec{R}_n - \vec{u}_j), \quad (32)$$

where  $f_j$  is the scattering amplitude for the atoms on site  $\vec{u}_j$  and is typically proportional to the number of electrons centered on  $\vec{u}_j$ . Now

$$\begin{aligned} A(\vec{q}) &= \frac{C}{N} \sum_{j=1, n=0}^{M, N-1} \int f_j(\vec{r} - \vec{R}_n - \vec{u}_j) e^{i\vec{q} \cdot \vec{r}} d^3 r \\ &= \frac{C}{N} \sum_{j=1, n=0}^{M, N-1} \int f_j(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d^3 r \cdot e^{i\vec{q} \cdot \vec{u}_j} \cdot e^{i\vec{q} \cdot \vec{R}_n} \end{aligned}$$

$$\begin{aligned} \text{with } \vec{r} &\rightarrow \vec{r} + \vec{R}_n + \vec{u}_j \\ &= CS(\vec{q}) \cdot \delta_{\vec{q}, \vec{G}}, \end{aligned} \quad (33)$$

where we have defined the structure factor  $S(\vec{q})$  as

$$S(\vec{q}) = \sum_{j=1}^M \int f_j(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d^3 r \cdot e^{i\vec{q} \cdot \vec{u}_j} \quad (34)$$

This is the most general form. It is interesting to remark that in most case, experiments measure the intensity  $I(\vec{q}) = |A(\vec{q})|^2$ , rather than the amplitude.

*Example: the structure factor of a BCC lattice*



The BCC crystal can be viewed as a cubic crystal with lattice  $a$  and a basis. Therefore, all lattice sites are described by

$$\vec{R}_n = n_1 a \hat{x} + n_2 a \hat{y} + n_3 a \hat{z} + \vec{u}_j, \quad (35)$$

where  $\vec{u}_1 = 0(\hat{x} + \hat{y} + \hat{z})$  and  $\vec{u}_2 = (a/2)(\hat{x} + \hat{y} + \hat{z})$ .

The structure factor then becomes:

$$S(\vec{q}) = \sum_{j=1,2} \int f_j(\vec{r}) e^{i\vec{q} \cdot \vec{r}} e^{i\vec{q} \cdot \vec{u}_j} d^3 r. \quad (36)$$

As a simplification we suppose that  $f_1 = f_2 = f$ , then

$$S(\vec{q}) = (1 + e^{(ia/2)\vec{q} \cdot (\hat{x} + \hat{y} + \hat{z})}) \tilde{f}(\vec{q}), \quad (37)$$

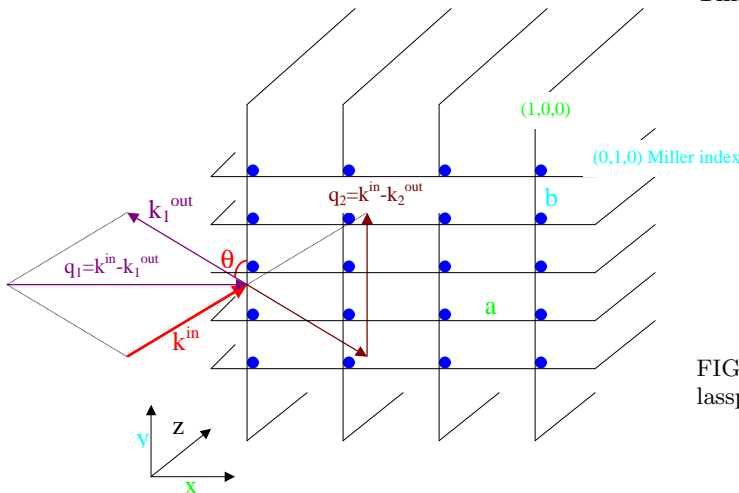
where  $\tilde{f}(\vec{q})$  is the Fourier transform of  $f$ . Hence,

$$A(\vec{q}) = S(\vec{q}) \cdot \delta_{\vec{q}, \vec{G}} = \tilde{f}(\vec{q}) \begin{cases} 2\delta_{\vec{q}, \vec{G}} & \text{if } q_1 + q_2 + q_3 \text{ is even} \\ 0 & \text{if } q_1 + q_2 + q_3 \text{ is odd} \end{cases} \quad (38)$$



### Bragg's law

Equivalence between Bragg's law for Miller planes and the reciprocal lattice.



From Bragg's law we know that for the planes perpendicular to  $\hat{x}$  or Miller index (1,0,0) the following diffraction condition applies:

$$n\lambda = 2a \sin(\theta). \quad (39)$$

hence,

$$n \frac{2\pi}{a} = 2 \sin(\theta) \cdot |k^{\vec{i}n}| = |\vec{q}_1|, \quad (40)$$

since  $k = 2\pi/\lambda$  and we supposed that  $k^{\vec{i}n}$  is perpendicular to  $\hat{z}$ . This condition is equivalent to  $\vec{q}_1 = \hat{x}2\pi/a \in \vec{G}$ . The same relation applies for the scattering of the plane perpendicular to  $\hat{y}$  or Miller index (0,1,0) the following diffraction condition applies:

$$n\lambda = 2b \cos(\theta). \quad (41)$$

hence,

$$n \frac{2\pi}{b} = 2 \cos(\theta) \cdot |k^{\vec{i}n}| = |\vec{q}_2|, \quad (42)$$

or  $\vec{q}_2 = \hat{y}2\pi/b \in \vec{G}$ .

### Summary of scattering

We have an incoming wave  $e^{ik^{\vec{i}n} \cdot \vec{r}}$  diffracting on some sample with volume  $V$  and with a scattering probability  $n(\vec{r})$  inside  $V$ . For X-ray  $n$  is typically given by the electron distribution whereas for neutrons it is typically the

nuclear sites. The scattered wave amplitude with wave number  $\vec{k}$  is then

$$A(\vec{k} - \vec{k}_{in}) \sim \int_V d^3r n(\vec{r}) e^{i(\vec{k} - \vec{k}_{in}) \cdot \vec{r}} \quad (43)$$

This leads to three typical cases:

- **Mono crystal diffraction:** Point-like Bragg peaks

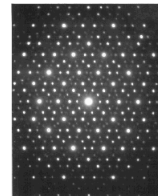


FIG. 8: Point-like Bragg peaks from a single crystal. (Ref: [lassp.cornell.edu/lifshitz](http://lassp.cornell.edu/lifshitz))

- **Powder diffraction:**

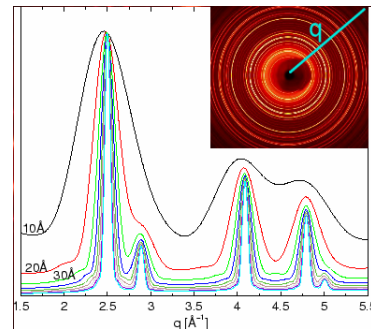


FIG. 9: Circle-like Bragg peaks from a powder with different grain sizes

- **Liquid diffraction:**

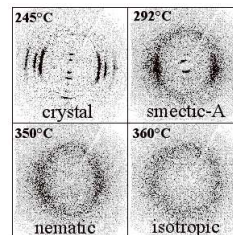


FIG. 10: Pattern evolution for a complex molecule evolving from a crystal-like structure to an isotropic liquid

The liquid diffraction is essentially the limiting case of the powder diffraction when the grain size becomes comparable to the size of an atom.

## PROPERTIES OF SOLIDS AND LIQUIDS

The Theory of everything discussed in the first section can serve as a guideline to illustrate which part of the Hamiltonian is important for a given property. For instance, when interested in the mechanical properties, the terms containing the electrons can be seen as a perturbation. However, when considering thermal conductivity, for example, the kinetic terms of the ions **and** the electrons are important.

In the following we will start by considering a few cases and we will start with the single electron approximation.

### single electron approximation

The single electron approximation can be used to derive the energy and density of the electrons. This simplest model will always serve as a reference and in some cases the result is very close to the experimental value. Alkali metals (Li, Na, K,...) are reasonably well described by this model, when we suppose that the outer shell electron/atom (there is 1 for Li, Na, K) is free to move inside the metal. This picture leads to the simple example of  $N$  electrons in a box. This box can be viewed as a uniform and positively charge background due to the atomic ions. We suppose that this box with size  $L \times L \times L$  has periodic boundary conditions, i.e.,

$$H = - \sum_{n=1}^N \frac{\hbar^2 \nabla_n^2}{2m_e} \text{ with } \Psi(0) = \Psi(L) \quad (44)$$

For one electron the solutions can be written as

$$\Psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \text{ with } E = \frac{\hbar^2 |\vec{k}|^2}{2m_e} \text{ and } \vec{k} = \frac{2\pi}{L}(n_1, n_2, n_3), \quad (45)$$

where  $n_i$  are the quantum numbers, which are positive or negative integers. Since electrons are Fermions we cannot have two electrons in the same state, except for the spin degeneracy. Hence each electron has to have different quantum numbers. This implies that  $2\pi/L$  is the minimum difference between two electrons in  $k$ -space, which means that 1 electron uses up

$$\left(\frac{2\pi}{L}\right)^D \quad (46)$$

of volume in  $k$ -space, if  $D$  is the dimension of the space. If we now want to compute the electron density (number of electrons per unit volume  $n_e = N/L^D$ ) in the ground state, which have  $k < k_F$  (Fermi sphere with radius  $k_F$ ), we obtain:

$$n_e = 2 \cdot V_{k_F}^D \cdot \left(\frac{L}{2\pi}\right)^D / L^D, \quad (47)$$

where the pre-factor 2 comes from the spin degeneracy. Hence,

$$n_e^{3D} = \frac{k_F^3}{3\pi^2} \text{ in } D = 3 \text{ since } V_{k_F}^D = \frac{4\pi}{3} k_F^3 \quad (48)$$

$$n_e^{2D} = \frac{k_F^2}{2\pi} \text{ in } D = 2 \text{ since } V_{k_F}^D = \pi k_F^2 \quad (49)$$

$$n_e^{1D} = \frac{2k_F}{\pi} \text{ in } D = 1 \text{ since } V_{k_F}^D = 2k_F, \quad (50)$$

where the maximum energy of the electrons is

$$E_F = \frac{\hbar^2 k_F^2}{2m_e} \text{ the Fermi energy} \quad (51)$$

This defines the Fermi energy: it is the highest energy when all possible states with energy lower than  $E_F$  are occupied, which corresponds to the ground state of the system. **This is one of the most important definitions in condensed matter physics.** The electron density can now be rewritten as a function of the Fermi energy, through eqs. (51) and (48) in 3D:

$$n(E_F) = \frac{(2mE_F)^{3/2}}{3\pi^2 \hbar^3}. \quad (52)$$

We now want to define the energy **density of states**  $D(E)$  as

$$n(E_F) \equiv \int_0^{E_F} D(E) dE \implies D(E) = \frac{\partial}{\partial E} n(E), \quad (53)$$

which leads to

$$D(E) = \frac{m\sqrt{2mE}}{\hbar^3 \pi^2} \text{ in 3D} \quad (54)$$

$$D(E) = \frac{m}{\hbar^2 \pi} \text{ in 2D} \quad (55)$$

$$D(E) = \sqrt{\frac{2m}{\hbar^2 \pi^2 E}} \text{ in 1D} \quad (56)$$

and illustrated below.

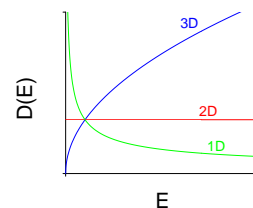


FIG. 11: Density of states in 1D, 2D and 3D

### Properties of the free electron model

Physical quantities at  $T=0$ :

- Average energy per electron:  $\frac{\langle E \rangle}{n} = \frac{3}{5} E_F$
- Pressure:  $P = -\frac{\partial \langle E \rangle V}{\partial V} = \frac{2}{5} n E_F$ , where  $\langle E \rangle V$  is the total energy.
- Compressibility  $\kappa^{-1} = -V \frac{\partial P}{\partial V} = \frac{2}{3} n E_F$

$$C_V = \frac{1}{V} \frac{\partial \langle E \rangle}{\partial T} \Big|_{\mu, V} = \frac{\pi^2}{3} k^2 T D(E_F) \quad (64)$$

Hence,  $\frac{C_V}{T} = \gamma$ , which is the Sommerfeld parameter.

Case 2:  $T \neq 0$ : In equilibrium

$$f_{FD} = \frac{1}{e^{(E-\mu)/kT} + 1}, \quad (57)$$

where the chemical potential is the energy to add one electron  $\mu = F_{N+1} - F_N$ .  $\mu = E_F$  at  $T=0$  and  $F$  is the free energy.

The Sommerfeld expansion is valid for  $kT \ll \mu$  and

$$\langle H \rangle = \int_0^\infty dE H(E) F_{FD}(E) \quad (58)$$

$$\simeq \int_0^\mu H(E) dE + \frac{\pi^2}{6} (kT)^2 H'(\mu) + \dots \quad (59)$$

$$\langle E \rangle = \int_0^\infty dE E D(E) F_{FD}(E) \quad (60)$$

$$\simeq \int_0^{E_F} E D(E) dE + \frac{\pi^2}{6} (kT)^2 D(E_F) + \dots \quad (61)$$

$$\langle n \rangle = n(T=0) \quad (62)$$

$$\Rightarrow \mu(T) \simeq E_F - \frac{\pi^2}{6} (kT)^2 \frac{D'(E_F)}{D(E_F)} + \dots \quad (63)$$

Physical quantities at  $T \neq 0$ : Specific heat

### Periodic potentials

The periodicity of the underlying lattice has important consequences for many of the properties. We will walk through a few of them by starting with the simplest case in 1D.

#### Kronig-Penney model

Let us first consider the following simple periodic potential in 1D.

$$H = -\frac{\hbar^2 \nabla^2}{2m} - V \sum_n \delta(x - na) \quad (65)$$

The solutions for  $na < x < na+a$  are simply plane waves and can be written as

$$\psi(x) = A_n e^{ikx} + B_n e^{-ikx}. \quad (66)$$

Now the task is to use the boundary conditions in order to determine  $A_n$  and  $B_n$ . We have two conditions:

$$(1) \quad \psi(na - \epsilon) = \psi(na + \epsilon) \text{ when } \epsilon \rightarrow 0 \text{ and} \quad (67)$$

$$(2) \quad \int_{na-\epsilon}^{na+\epsilon} (H - E) \psi(x) dx = 0 \implies -\frac{\hbar}{2m} (\psi'(na + \epsilon) - \psi'(na - \epsilon)) = V \psi(na).$$

Inserting 66 into condition (1) yields

$$\begin{cases} A_{n-1} e^{ikna} + B_{n-1} e^{-ikna} = A_n e^{ikna} + B_n e^{-ikna} = \psi(na) = \psi_n \\ A_{n-1} e^{ikna} e^{-ika} + B_{n-1} e^{-ikna} e^{ika} = \psi_{n-1} \end{cases} \quad (68)$$

$$\implies \begin{cases} e^{-ika} \psi_n - \psi_{n-1} = B_{n-1} e^{-ikan} (e^{-ika} - e^{ika}) \\ e^{ika} \psi_n - \psi_{n-1} = A_{n-1} e^{ikan} (e^{ika} - e^{-ika}) \end{cases} \quad (69)$$

$$\text{and } \begin{cases} e^{-ika} \psi_{n+1} - \psi_n = B_n e^{-ikan} e^{-ika} (e^{-ika} - e^{ika}) \\ e^{ika} \psi_{n+1} - \psi_n = A_n e^{ikan} e^{ika} (e^{ika} - e^{-ika}) \end{cases} \quad (70)$$

When taking the derivative of 66 then condition (2) implies

$$-\frac{\hbar}{2m} \left( ik \underbrace{A_n e^{ikan}}_{\frac{\psi_{n+1} - e^{-ika} \psi_n}{2i \sin(ka)}} - ik \underbrace{B_n e^{-ikan}}_{\frac{\psi_{n+1} - e^{ika} \psi_n}{-2i \sin(ka)}} - ik \underbrace{A_{n-1} e^{ikan}}_{\frac{e^{ika} \psi_n - \psi_{n-1}}{2i \sin(ka)}} + ik \underbrace{B_{n-1} e^{-ikan}}_{\frac{e^{-ika} \psi_n - \psi_{n-1}}{-2i \sin(ka)}} \right) = V \psi_n, \quad (71)$$

hence,

$$-\frac{\hbar^2}{2m} \frac{k}{2 \sin(ka)} \left( 2\psi_{n+1} + 2\psi_{n-1} + \psi_n \underbrace{(-e^{-ika} - e^{ika} - e^{ika} - e^{-ika})}_{-4 \cos(ka)} \right) = V\psi_n \quad (72)$$

and finally,

$$\psi_{n+1} + \psi_{n-1} = \underbrace{\left( -\frac{2m \sin(ka)}{\hbar^2 k} V + 2 \cos(ka) \right)}_W \psi_n, \quad (73)$$

Which can be rewritten as

$$\psi_{n+1} + \psi_{n-1} = W\psi_n \quad (74)$$

This equation is often called the tight binding equation as we will see in the next section. Finding a solution for this equation is trivial since

$$\psi_n = e^{ipn} \quad (75)$$

is a solution. This is easily verified by plugging (75) into (74), which yields

$$e^{ipn} e^{ipa} + e^{ipn} e^{-ipa} = W e^{ipn} \implies W = e^{ipa} + e^{-ipa} = 2 \cos(pa). \quad (76)$$

This equation has a solution only if

$$-2 \leq W \leq 2 \quad (77)$$

We now recall that the Eigenstate of the original Hamiltonian is given by  $E(k) = \frac{\hbar^2 k^2}{2m}$ , where  $e^{ikx}$  is the plane wave between two  $\delta$  functions, hence the dispersion relation is equal to  $E(k) = \frac{\hbar^2 k^2}{2m}$  as long as  $-2 \leq W \leq 2$ . This condition will create gaps inside the spectrum as illustrated in the graph below:

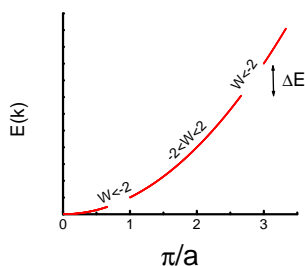


FIG. 12: Dispersion curve for the Kronig-Penney model

**Conclusion: a periodic potential creates gaps, which leads to the formation of a band structure.** This is a very general statement which is true for almost any periodic potential.

#### Tight binding approximation

Let us consider the general potential due to the arrangement of the atoms on a lattice:

$$H = -\frac{\hbar^2 \nabla^2}{2m} + \underbrace{\sum_n V_0(\vec{r} - \vec{R}_n)}_{V(\vec{r})} \quad (78)$$

This is a very general form for a periodic potential assuming that we only have one type of atoms. The periodicity is given by the lattice index  $\vec{R}_n$ . For a general periodic potential **Bloch's** theorem (see A& M for proof) tells us that a solution to this Hamiltonian can be written as

$$\psi_k(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_k(\vec{r}), \quad (79)$$

where  $u_k$  is a periodic function such that  $u_k(\vec{r} + \vec{R}_n) = u_k(\vec{r})$ . This implies that

$$\psi_k(\vec{r} + \vec{R}_n) = e^{i\vec{k} \cdot \vec{R}_n} \psi_k(\vec{r}) \quad (80)$$

Let us now suppose that the solution of the Hamiltonian  $H_{1atom} = -\frac{\hbar^2 \nabla^2}{2m} + V_0(\vec{r} - \vec{R}_n)$  with one atom is  $\phi_l(\vec{r} - \vec{R}_n)$  corresponding to the energy level  $\epsilon_l$ , i.e.,  $H_{1atom} \phi_l = \epsilon_l \phi_l$ . Now comes the important assumption, which allows us to simplify the problem: We suppose that

$$\langle \phi_l(r - R_m) | H | \phi_l(r - R_n) \rangle = -t_l \left( \sum_{\vec{i}=\hat{x},\hat{y},\hat{z}} \delta_{\vec{m},\vec{n}+\vec{i}} + \delta_{\vec{m},\vec{n}-\vec{i}} \right) + \epsilon_l \delta_{\vec{m},\vec{n}} \quad (81)$$

Hence, only the nearest neighbor in every direction is taken to be non-zero. Further, we assume that there is no overlap between levels of the one atom potential, which allows us to look for a general solution of the following form for each energy level  $\epsilon_l$ .

$$\psi_l(r) = \sum_{\vec{n}} c_{\vec{n}}^l \phi_l(r - R_{\vec{n}}) \quad (82)$$

with eigenvalue  $E_l(k)$ . To calculate  $E_l(k)$  we plug-in this Ansatz into eq. (82) and obtain an equation for the coefficients  $c_{\vec{n}}^l$ , which leads to the following equation when using the tight binding approximation given in eq. (81).

$$c_{\vec{m}}^l \epsilon_l - t_l \sum_{\vec{i}=\pm\hat{x},\hat{y},\hat{z}} c_{\vec{m}+\vec{i}}^l = E_l(k) c_{\vec{m}}^l \quad (83)$$

The solution of this equation are plane waves, which can be verified readily by taking  $c_{\vec{m}}^l = e^{i\vec{k}\cdot R_{\vec{m}}}$  and plugging it into the equation to obtain

$$E_l(k) = \epsilon_l - t_l (2 \cos(k_x a_x) + 2 \cos(k_y a_y) + 2 \cos(k_z a_z)), \quad (84)$$

where  $\vec{a}$  is the lattice constant in all 3 space directions:  $\vec{a} = R_{\vec{m}+\hat{a}} - R_{\vec{m}}$ . The energy diagram is illustrated in fig. . The degeneracy of each original single atomic energy level  $\epsilon_l$  is lifted by the coupling to the neighboring atoms and leads to a dispersion curve or electronic band structure.

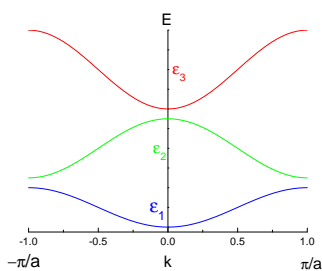


FIG. 13: Dispersion curve for the tight binding model

This tight binding approximation is very successful in describing the electrons which are strongly bound to the atoms. In the opposite limit where the electrons are more plane-wave like, the weak potential approximation is more accurate:

#### Combining Bloch's theorem with the tight binding approximation

The tight binding approximation is very general and can be applied to almost any system, including non-periodic ones, where the tight binding elements can be assembled in an infinite matrix. For the periodic case, on the other hand, it is possible to describe the system with a finite matrix in order to obtain the full dispersion relation. This is obtained by combining the Bloch theorem for periodic potentials, where the wave-function from (79) is again:

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})$$

Instead of writing (82) we write the Bloch-tight-binding solution as

$$\psi_l^k(r) = \sum_{\vec{n}} e^{i\vec{k}\cdot R_{\vec{n}}} c_{\vec{n}}^l \phi_l(r - R_{\vec{n}}),$$

which now depends explicitly on the wavevector  $\vec{k}$ . Using Bloch's theorem this implies that

$$c_{\vec{n}}^l = c_{\vec{m}}^l,$$

whenever  $\vec{n}$  and  $\vec{m}$  are related by a linear combination of Bravais vectors. Moreover, the tight binding equation in (83) is the same but with  $c_{\vec{n}}^l$  replaced by  $c_{\vec{n}}^l e^{i\vec{k}\cdot R_{\vec{n}}}$

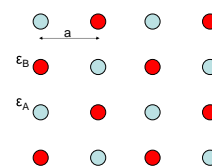


FIG. 14: Diatomic square crystal

We apply this to the simple example of a diatomic square lattice of lattice constant  $a$  with alternating atoms  $A$  and  $B$  shown in figure . We will further assume that we have only one band  $l$ . Hence, the Bloch-tight-binding solution is written as

$$\psi^k(r) = \sum_{\vec{n}} e^{i\vec{k}\cdot R_{\vec{n}}} c_{\vec{n}}^l \phi_l(r - R_{\vec{n}}),$$

where  $c_{\vec{n}}$  takes on only to possible values due to Bloch's theorem:  $c_A$  or  $c_B$ . This leads to the following simplified tight binding equations (assuming  $\langle \phi_l(r - R_n) | H | \phi_l(r - R_n) \rangle = \epsilon_A$  or  $\epsilon_B$  and  $t = -\langle \phi_l(r - R_n) | H | \phi_l(r - R_m) \rangle$  when  $n$  and  $m$  are nearest neighbors):

$$\begin{aligned} c_A \epsilon_A - t \sum_{\vec{i}=\pm\hat{x},\hat{y}} c_B e^{i\vec{a}\vec{k}\cdot\vec{i}} &= E(\vec{k}) c_A \\ c_B \epsilon_B - t \sum_{\vec{i}=\pm\hat{x},\hat{y}} c_A e^{i\vec{a}\vec{k}\cdot\vec{i}} &= E(\vec{k}) c_B \end{aligned}$$

It is now quite straightforward to rewrite these equations in matrix form:

$$\begin{pmatrix} \epsilon_A & -t \cdot g \\ -t \cdot g^* & \epsilon_B \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = E(\vec{k}) \begin{pmatrix} c_A \\ c_B \end{pmatrix},$$

with  $g = e^{i\vec{a}\vec{k}\cdot\hat{x}} + e^{-i\vec{a}\vec{k}\cdot\hat{x}} + e^{i\vec{a}\vec{k}\cdot\hat{y}} + e^{-i\vec{a}\vec{k}\cdot\hat{y}}$ . The dispersion relation or band structure is then simply given by obtaining the eigenvalues of  $H_{BTB}$ , where

$$H_{BTB} = \begin{pmatrix} \epsilon_A & -t \cdot g \\ -t \cdot g^* & \epsilon_B \end{pmatrix}.$$

#### Weak potential approximation

In this case we consider the effect of the periodic potential  $V(\vec{r})$  as a perturbation on the plane wave solution

$\psi_k^0(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$ , with corresponding energies  $\epsilon_k^0 = \frac{\hbar^2 k^2}{2m}$  and Hamiltonian  $H_0$ , i.e.,  $H_0 \psi_k^0(\vec{r}) = \epsilon_k^0 \psi_k^0(\vec{r})$ . Since the origin of this energy dispersion relation can be chosen from any site of the reciprocal lattice, we have  $\epsilon_{k+K}^0 = \epsilon_k^0$ , hence these energies are degenerate. This implies that we have to use a degenerate perturbation theory. The mathematical procedure is very similar to the tight binding approximation, but we now expand the solution  $\psi(\vec{r})$  of the full Hamiltonian  $H = H_0 + V(\vec{r})$  in terms of a sum of plane waves  $\psi_k^0(\vec{r})$ . Since  $\epsilon_{k+K}^0 = \epsilon_k^0$  we will only use two plane waves in this expansion:  $\psi_k^0(\vec{r})$  and  $\psi_{k+K}^0(\vec{r})$ . Hence,

$$\psi(\vec{r}) = \alpha \psi_k^0(\vec{r}) + \beta \psi_{k+K}^0(\vec{r}), \quad (85)$$

where the coefficients  $\alpha$  and  $\beta$  have to be determined in order to solve Schrödinger's equation:

$$(H - E)\psi(\vec{r}) = 0. \quad (86)$$

We can find the solution by first multiplying (86) by  $(\psi_k^0)^*(\vec{r})$  and then integrating the equation over the whole space which will lead to one equation, and we obtain a second equation by multiplying (86) by  $(\psi_{k+K}^0)^*(\vec{r})$  and then integrating of the whole space. This leads to

$$\begin{cases} \alpha \int d^3r (\psi_k^0)^*(\vec{r}) (H - E) \psi_k^0(\vec{r}) + \beta \int d^3r (\psi_k^0)^*(\vec{r}) (H - E) \psi_{k+K}^0(\vec{r}) = 0 \\ \alpha \int d^3r (\psi_{k+K}^0)^*(\vec{r}) (H - E) \psi_k^0(\vec{r}) + \beta \int d^3r (\psi_{k+K}^0)^*(\vec{r}) (H - E) \psi_{k+K}^0(\vec{r}) = 0 \end{cases}, \quad (87)$$

where (assuming normalized plane waves in the integrals)

$$\begin{cases} \int d^3r (\psi_k^0)^*(\vec{r}) (H - E) \psi_k^0(\vec{r}) = \int d^3r e^{-i\vec{k}\cdot\vec{r}} (H_0 + V(r) - E) e^{i\vec{k}\cdot\vec{r}} = \epsilon_k^0 + 0 - E \\ \int d^3r (\psi_k^0)^*(\vec{r}) (H - E) \psi_{k+K}^0(\vec{r}) = \int d^3r e^{-i\vec{k}\cdot\vec{r}} (H_0 + V(r) - E) e^{i(\vec{k}+\vec{K})\cdot\vec{r}} = \int d^3r e^{i\vec{K}\cdot\vec{r}} (\epsilon_{k+K}^0 + V(r) - E) = V_K \\ \int d^3r (\psi_{k+K}^0)^*(\vec{r}) (H - E) \psi_{k+K}^0(\vec{r}) = \epsilon_{k+K}^0 - E \\ \int d^3r (\psi_{k+K}^0)^*(\vec{r}) (H - E) \psi_k^0(\vec{r}) = V_{-K}, \end{cases} \quad (88)$$

and  $V_{\vec{K}} = \int d^3r e^{i\vec{K}\cdot\vec{r}} V(\vec{r})$  (the Fourier transform),  $\int d^3r e^{i\vec{K}\cdot\vec{r}} = 0$  (for  $K \neq 0$ ), and  $\int d^3r V(\vec{r}) = 0$ . With coefficients (88), equation (87) leads to the following couple of equations:

$$\begin{cases} \alpha(\epsilon_k^0 - E) + \beta V_K = 0 \\ \alpha V_{-K} + \beta(\epsilon_{k+K}^0 - E) = 0 \end{cases} \Rightarrow \begin{vmatrix} \epsilon_k^0 - E & V_K \\ V_{-K} & \epsilon_{k+K}^0 - E \end{vmatrix} = 0 \Rightarrow E = \frac{\epsilon_k^0 + \epsilon_{k+K}^0}{2} \pm \sqrt{\frac{(\epsilon_k^0 - \epsilon_{k+K}^0)^2}{4} + V_K V_{-K}}. \quad (89)$$

Finally if  $\epsilon_k^0 = \epsilon_{k+K}^0$ , we have  $E = \epsilon_k^0 \pm |V_K|$ , which leads to a splitting  $2|V_K|$  of the energy levels at these degenerate energies. For the example in figure , this weak potential approximation would give us a splitting of  $2|V_{K=2\pi/a}|$  at  $k = -\pi/a$  and  $k = K - \pi/a = \pi/a$ . This implies that the first order calculation of the energy splitting due to the weak periodic potential  $V(r)$  is equal to twice the fourier transform of this potential evaluated at

the wavevector which corresponds to the two dispersion curves which led to the degenerate energy level.

#### Localization

When, instead of having a purely periodic potential disorder is included into the system, we no more have

Bloch wave solutions but localization of the wave functions occur. This is particularly important in low dimensional systems and tends to suppress transport.

### Electronic properties due to periodic potential

#### Density of states

Density of states in 1D:

$$\begin{aligned}
D(E) &= \frac{\partial n}{\partial E} \simeq \frac{\delta n}{\delta E} \\
&= \frac{\delta n}{\delta k} \left| \frac{\partial E(k)}{\partial k} \right|^{-1} \times \underbrace{2}_{\text{spin}} \times \underbrace{2}_{\Sigma_{\pm k}} \\
&= \frac{1}{L} \frac{\delta N}{\delta k} \left| \frac{\partial E(k)}{\partial k} \right|^{-1} \times 4 \\
D(E) &= \frac{2}{\pi} \left| \frac{\partial E(k)}{\partial k} \right|^{-1}, \quad (90)
\end{aligned}$$

where we used that  $\delta E = (\partial E/\partial k)\delta k$  and  $\delta k = 2\pi/L$  for one electron, i.e.,  $\delta N = 1$ .

In three dimensions (D=3) we have:

$$\begin{aligned}
D(E) &= \frac{\partial n}{\partial E} \simeq \frac{\delta n}{\delta E} \\
&= \sum_{E(k)=E} \frac{\delta n}{\delta k} |\nabla_k E(k)|^{-1} \times \underbrace{2}_{\text{spin}} \\
&= \frac{2}{(2\pi)^3} \int_{E(k)=E} d^2k |\nabla_k E(k)|^{-1}, \quad (91)
\end{aligned}$$

where we used  $\delta E = (\nabla_k E(k)) \cdot \delta k$ ,  $\sum_{E(k)=E} (\delta k)^2 \rightarrow \int_{E(k)=E} d^2k$ , and  $\delta n/(\delta k)^3 = 1/(2\pi)^3$ . This result shows that the density of state in the presence of a periodic potential, i.e., for a crystal depends only on the slope of the dispersion relation or the band structure.

#### Average velocity

The average velocity of an electron in a periodic potential is given by the expectation value of the velocity, i.e.,

$$\langle v \rangle = \langle \psi | v | \psi \rangle, \quad (92)$$

where  $\psi$  is the wavefunction from the Hamiltonian with periodic potential  $V$ , i.e.,  $H = \frac{\hbar^2 \nabla^2}{2m} + V$ . From Bloch's theorem (79) we can write  $\psi(r) = e^{ikr} u_k(r)$ , where  $u_k(r)$  has the same periodicity as  $V(r)$ . From the Schrödinger

equation  $H\psi = E(k)\psi$  it follows that  $u_k$  is a solution of

$$\underbrace{\left( \frac{\hbar^2}{2m} (k - i\nabla)^2 + V - E(k) \right)}_{H_k - E(k)} u_k = 0. \quad (93)$$

In order to calculate  $\langle v \rangle$  we use first a first order perturbation in  $k + q$ , where  $q$  is very small. Therefore, the eigenvalue corresponding to  $H_{k+q}$  is  $E(k + q)$ , which is to first order

$$\begin{aligned}
E(k + q) &= E(k) + \langle u_k | H_{k+q} - H_k | u_k \rangle \\
&= E(k) + \langle \psi e^{ikr} | \frac{\hbar^2}{2m} (\underbrace{q^2}_{\rightarrow 0} + 2q(k - i\nabla)) | e^{-ikr} \psi \rangle \\
&= E(k) + \langle \psi e^{ikr} | \frac{\hbar^2}{m} q(k - i\nabla) | e^{-ikr} \psi \rangle \\
&= E(k) + \langle \psi | q \hbar \frac{\hbar}{m} (-i\nabla) | \psi \rangle \\
&= E(k) + q \hbar \langle \psi | v | \psi \rangle \\
&= E(k) + q \nabla_k E(k) \quad (\text{Taylor expansion}) \\
\Rightarrow \langle v \rangle &= \frac{1}{\hbar} \nabla_k E(k). \quad (94)
\end{aligned}$$

Hence, the expectation value of the velocity is determined by the slope of the dispersion relation. This also implies that the sign of the average velocity depends on the sign of  $\partial E/\partial k$ .

#### Response to an external field and existence of holes and electrons

The idea is to describe the average motion of an electron in the presence of an external field (electric,  $E_{el}$ , or magnetic,  $B$ ) in a semiclassical way. Hence, we want

$$m^* \frac{d}{dt} \langle v \rangle = F = (qE_{el} \text{ or } q\langle v \rangle \times B), \quad (95)$$

where  $m^*$  is an effective mass and  $q$  the charge. Using (95) and (94) we have

$$\begin{aligned}
m^* \frac{\partial \langle v \rangle}{\partial k} \dot{k} &= qE_{el} \\
\frac{1}{\hbar} m^* \frac{\partial^2 E}{\partial k^2} \dot{k} &= qE_{el} \\
\Rightarrow \hbar \dot{k} &= qE_{el} = F, \quad (96)
\end{aligned}$$

Where we defined the effective mass  $m^*$  as

$$m^* = \hbar^2 \left| \frac{\partial^2 E}{\partial k^2} \right|^{-1}. \quad (97)$$

If  $\frac{\partial^2 E}{\partial k^2}$  is negative we need to change the sign of  $q$  in order to remain consistent. Hence, when  $\frac{\partial^2 E}{\partial k^2} > 0$ , the charge

of an electron is  $q = -e$  but if  $\frac{\partial^2 E}{\partial k^2} < 0$  then  $q$  is positive ( $+e$ ). In this case we describe the particles as holes. They represent missing electrons. With these definitions of  $q$  and  $m^*$ , which is also called the band mass, the semiclassical equations of motion of single electrons in a periodic potential are simply given by eqs. (95) and (96).

In general, the effective mass is given by a tensor defined as

$$m_{\alpha\beta}^* = \hbar^2 \left| \frac{\partial^2 E}{\partial k_\alpha \partial k_\beta} \right|^{-1}, \quad (98)$$

where  $\alpha$  and  $\beta$  are the spatial directions. An important consequence of this semiclassical description of the motion of electrons is the dependence of the effective mass on the energy and the band structure. In some cases the effective mass can even diverge (when  $\frac{\partial^2 E}{\partial k^2} = 0$ ). Similarly the sign of the carriers also depends on the band structure and the energy of the carriers. By definition we call the bottom of an energy band and electronic band when  $\frac{\partial^2 E}{\partial k^2} > 0$  and a hole band when at the top of the energy band  $\frac{\partial^2 E}{\partial k^2} < 0$ .

#### Bloch oscillations

In the presence of an electric field and a periodic potential we can use the equation of motion (96), i.e.,

$$\hbar \dot{k} = -eE_{el} \Rightarrow k = -\frac{eE_{el}}{\hbar}t, \quad (99)$$

but in a periodic potential and in the tight binding approximation the energy is given by  $E(k) = -2t_0 \cos(ka)$ , where  $a$  is the lattice constant and  $t_0$  the nearest neighbor overlap integral. Hence, since  $v = \dot{r}$  and  $\langle v \rangle = \hbar^{-1} \partial E / \partial k$  we have

$$\langle r \rangle = \frac{2t_0}{eE_{el}} \cos\left(\frac{aeE_{el}t}{\hbar}\right). \quad (100)$$

This means that the average position of the electrons oscillates in time (Bloch oscillations). In artificial structures these Bloch oscillations are typically of the order of 1THz.

#### Semiclassical motion in a magnetic field

In the presence of a magnetic field ( $B$ ), we can describe the semiclassical trajectories in  $k$ -space using (96), i.e.,

$$\hbar \dot{k} = q\langle v \rangle \times B. \quad (101)$$

Hence, only the values of  $k$  perpendicular to the magnetic field will change, which we denote by  $k_\perp$ . The component parallel to the field,  $k_\parallel$  is not affected by  $B$ . During a small time difference

$$\delta t = t_2 - t_1 = \int_{t_1}^{t_2} dt = \int_{k_1=k(t_1)}^{k_2=k(t_2)} dk_\perp / |\dot{k}|. \quad (102)$$

Using (101) and (94) and since  $\dot{k}$  is perpendicular to  $\langle v \rangle$  and  $B$ ,  $(\dot{k}) \sim \partial E / \partial k_\parallel$  we obtain

$$\begin{aligned} \delta t &= \frac{\hbar^2}{qB} \int_{k_1}^{k_2} \frac{dk_\perp}{\partial E / \partial k_\parallel} \\ &= \frac{\hbar^2}{qB} \frac{d}{dE} \int_{k_1}^{k_2} k_\parallel dk_\perp. \end{aligned} \quad (103)$$

For a complete turn this leads to

$$T = \frac{\hbar^2}{qB} \frac{d}{dE} \oint_S k_\parallel dk_\perp. \quad (104)$$

Here  $S$  is the area enclosed by an orbit in  $k$ -space. This orbit corresponds to an equipotential line perpendicular to the magnetic field.

Let's suppose for simplicity that the effective mass tensor  $m^*$  is diagonal and given by

$$m^* = \begin{pmatrix} m_x & 0 & 0 \\ 0 & m_y & 0 \\ 0 & 0 & m_z \end{pmatrix} \quad (105)$$

and that the energy dispersion is harmonic (which is usually true at a band extremum, i.e.,

$$E(k) = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 k_z^2}{2m_z}. \quad (106)$$

If we assume that the magnetic field is along  $z$  and that the average effective mass perpendicular to  $B$  is given by  $m_\perp$ , we can rewrite (106) as

$$E(k) = \frac{\hbar^2 k_\perp^2}{2m_\perp} + \frac{\hbar^2 k_\parallel^2}{2m_\parallel}, \quad (107)$$

where  $k_\perp^2 = k_x^2 + k_y^2$ . Using (104) and (107) we then obtain

$$\begin{aligned} S &= \pi k_\perp^2 = \pi(2m_\perp E / \hbar^2) - \pi k_\parallel^2 m_\perp / m_\parallel \\ \Rightarrow \frac{dS}{dE} &= \frac{\pi 2m_\perp}{\hbar^2} \\ \Rightarrow \omega_c &= \frac{2\pi}{T} = \frac{qB}{m_\perp}, \end{aligned} \quad (108)$$

which is the cyclotron frequency. Hence, the cyclotron frequency depends on the average effective mass perpendicular to the magnetic field. This allows us to measure the effective mass along different directions, simply by changing the direction of the magnetic field and by measuring the cyclotron frequency.

#### Quantization of the cyclotron orbit: Landau levels

In quantum mechanics the energies of these cyclotron orbits become quantized. To see this we can write the



Hamiltonian of an electron in a magnetic field in the harmonic approximation (107) as

$$H = \frac{1}{2m_{\parallel}} P_{\parallel}^2 + \frac{1}{2m_{\perp}} (P_{\perp} + qA)^2, \quad (109)$$

where  $B = \nabla \times A \Rightarrow A = -By\hat{x}$  in the Landau Gauge if  $B$  is along  $\hat{z}$ . In analogy to the harmonic oscillator, the eigenvalues of (109) are then given by

$$E_{n,k_{\parallel}} = \frac{\hbar^2 k_{\parallel}^2}{2m_{\parallel}} + (n + 1/2)\hbar \underbrace{\frac{qB}{m_{\perp}}}_{\omega_c}. \quad (110)$$

These eigenvalues can be found by writing the wavefunction as  $\psi = e^{ik_x x} \phi_n(y - y_0) e^{ik_{\parallel} z}$  with  $y_0 = -\frac{\hbar k_x}{qB}$ , which leads to  $H\psi = \left( \frac{\hbar^2 k_{\parallel}^2}{2m_{\parallel}} + \frac{P_y^2}{2m_{\perp}} + \frac{1}{2}m_{\perp} \left( \frac{qB}{m_{\perp}} \right)^2 (y - y_0)^2 \right) \phi_n(y - y_0)$ . In the  $y$  direction this is simply the harmonic oscillator with eigenvalues  $(n + 1/2)\hbar\omega_c$  and in the direction parallel to the field we have a plane wave so that the total energy is given by (110). The quantized levels  $(n + 1/2)\hbar\omega_c$  due to the magnetic field are called the Landau levels.

### Magneto-oscillations

The quantization of the energy levels in the presence of a magnetic field will lead to oscillations of almost any experimental quantity (resistance, thermal conductivity, magnetization, ...) as a function of  $B$ . These oscillations can be understood by looking at the density of states due to the quantization (110). Indeed, (110) leads to a peak in the density of states whenever  $E = (n + 1/2)\hbar\omega_c$ . Therefore, whenever the component of the Fermi energy perpendicular to the magnetic field is equal to one of these quantized levels there is an extremum in the quantity measured. The distance between two of these extrema is given by

$$\begin{aligned} \hbar \frac{qB_1}{m_{\perp}} (n_1 + 1/2) &= E_F^{\perp} = \hbar \frac{qB_2}{m_{\perp}} (n_2 + 1/2) \\ \Rightarrow \frac{1}{B_1} - \frac{1}{B_2} &= \hbar \frac{q}{m_{\perp}} \left( \frac{E_F^{\perp}}{\hbar^2} \right)^{-1} (n_2 - n_1) \\ &= \frac{\hbar^2}{2\pi m_{\perp}} \cdot S \\ \Rightarrow \Delta \left( \frac{1}{B} \right) &= \frac{2\pi q}{\hbar} S^{-1}, \end{aligned} \quad (111)$$

where the maximum  $S$  is  $S = \oint k_{\parallel} dk_{\perp} = \pi(k_x^F)^2 = \pi(k_y^F)^2$  and  $E_F^{\perp} = \frac{\hbar^2 (k_x^F)^2}{2m_{\perp}} = \frac{\hbar^2 S}{2\pi m_{\perp}}$ . Hence, the Magneto-oscillations are periodic in  $1/B$  and the period depends on  $S$ . An example of these oscillations in resistance is shown in figure 15 as a function of  $B$  and  $1/B$ .

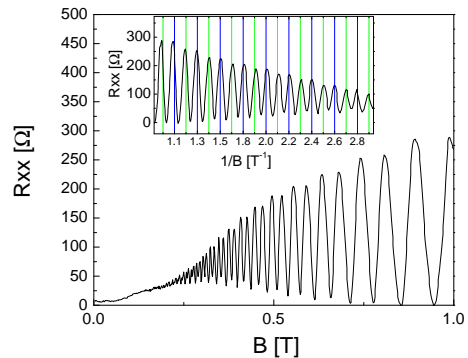


FIG. 15: Magneto-resistance oscillations in a *GaAs/AlGaAs* quantum well.

### PHONONS: LATTICE VIBRATIONS

In general:

$$M\ddot{u}_l = - \sum_m \phi_{lm} u_m, \quad (112)$$

where  $u_l$  are the deviations from the original lattice sites and  $\phi_{lm}$  are the elastic constants who have to obey this sum rule  $\sum_m \phi_{lm} = 0$  (translation invariance). In words, equ. 112 simply means that the force producing the deviation on lattice site  $l$  only depends on the deviations from the other lattice sites. No deviation=no force (equilibrium). This equation is very general and does not assume that we have a periodic lattice, but in order to calculate things we will use a periodic lattice and start with 1D. In fig. 16 we illustrate two typical displacement waves in 2D.

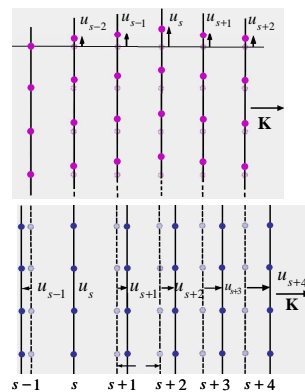


FIG. 16: Two types of lattice displacement waves in 2D, transverse and longitudinal modes

### Mono-atomic phonon dispersion in 1D

In 1D equ. 112 for nearest neighbors and using  $\sum_m \phi_{lm} = 0$  simply reduces to

$$M\ddot{u}_l = K(u_{l+1} - 2u_l + u_{l-1}) \quad (113)$$

in the simplest approximation, where only the nearest neighbors are important and where the elastic constants are the same. Further we assume that the equilibrium case has a lattice constant  $a$ . In this case the solution can be written as

$$\begin{aligned} u_l &= e^{ikla - i\omega t} \\ \implies M\omega^2 &= 2K(1 - \cos(ka)) = 4K \sin^2(ka/2) \quad (114) \\ \implies \omega &= 2\sqrt{\frac{K}{M}} |\sin(ka/2)| \end{aligned}$$

which is illustrated below. In this case there is only a

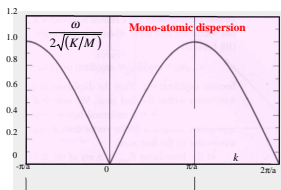


FIG. 17: Phonon dispersion for a mono-atomic lattice

single dispersion mode, which is called the acoustic mode or branch.

### Optical branch

The situation is quite different when there is an addition symmetry breaking in the problem. In the 1D case this occurs when there is a second species with a different mass, for example, or when there are two different elastic constants. Let us discuss the case where there are two different masses but only one elastic constant  $C$ :

$$\begin{cases} M_1\ddot{u}_l = C(u_{l+1} - 2u_l + u_{l-1}) \\ M_2\ddot{v}_l = C(v_{l+1} - 2v_l + v_{l-1}) \end{cases} \quad (115)$$

To solve this set of equation we use a solution of the form  $u_l = ue^{ikla - i\omega t}$  and  $v_l = ve^{ikla - i\omega t}$ , which inserted into eq. 115 leads to

$$\omega = \sqrt{C} \sqrt{\frac{M_1 + M_2 \pm \sqrt{M_1^2 - 2M_1M_2 \cos(ka) + M_2^2}}{M_1M_2}} \quad (116)$$

The following two limiting cases can easily be obtained in the limit of small  $k$ .

1. Acoustic mode:

$$\omega \simeq \sqrt{\frac{C}{2(M_1 + M_2)}} ka \quad (117)$$

2. Optical mode:

$$\omega \simeq \sqrt{\frac{2C(M_1 + M_2)}{M_1M_2}} \quad (118)$$

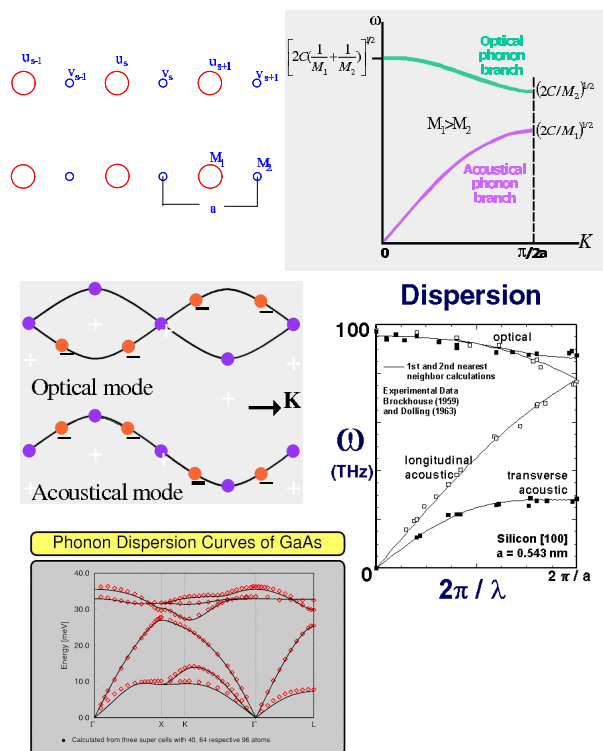


FIG. 18: Phonon dispersion for a di-atomic lattice and the more general 3D case

### Experimental determination of the phonon dispersion

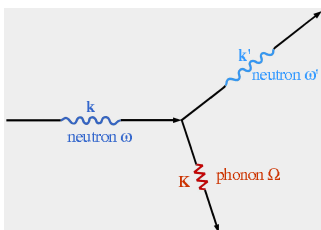
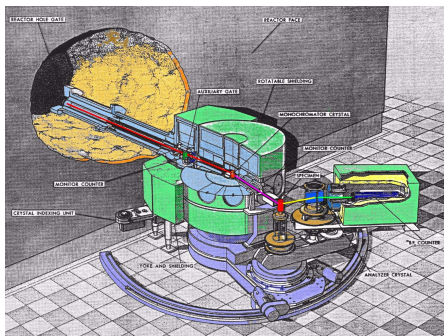
In order to determine the dispersion curve of the phonons there is essentially one trick. The idea is to look for inelastic scattering of other particles, which are typically photons or neutrons. The incoming particles scatter with phonons, thereby transferring some of their energy and momentum to phonons. From the energy and momentum of the out-coming particles it is then possible to infer the phonon absorption. This process can also be inverted in that the energy of the out-coming particle increases by absorption of a phonon. In general, the energy conservation can be expressed as

$$\underbrace{\hbar\omega_{in}(\vec{k}) - \hbar\omega'_{out}(\vec{k}')}_{\text{in/out particle}} = \underbrace{\pm\hbar\Omega(\vec{K})}_{\text{phonon}} \quad (119)$$

and the momentum conservation as

$$\hbar\vec{k} - \hbar\vec{k}' = \pm\hbar\vec{K} + \hbar\vec{G}, \quad (120)$$

where  $\vec{G}$  is a reciprocal lattice vector. A neutron scattering experiment is illustrated below.



### Origin of the elastic constant

From the TOE we have the potential term due to the interactions between ions.

$$H_{ions} = - \sum_i^{N_{ions}} \frac{\hbar^2 \nabla_i^2}{2m_i} + \sum_{i<j}^{N_{ions}} \frac{q_i q_j}{|r_i - r_j|} \quad (121)$$

This leads to a potential of the form

$$\phi(r_1, \dots, r_n) = \underbrace{\phi(r_1^0, \dots, r_n^0)}_{\text{Cohesive energy Equilibrium pos.}} + \underbrace{\sum_i \left( \frac{\partial \phi}{\partial r_i} \right)_{r_i^0}}_{\text{displacement } u_i} + \frac{1}{2} \underbrace{\sum_{i,j} \left( \frac{\partial^2 \phi}{\partial r_i \partial r_j} \right)_{r_i^0}}_{\phi_{i,j}} u_i u_j + \dots \quad (122)$$

The linear term has to be zero for stability reasons (no minimum in energy otherwise). The classical equation of motion is then simply given by equ. 112, because  $\vec{F} = -\vec{\nabla}\phi$ . To solve this equation in general, one can write a solution of the form

$$\vec{u}_l = \vec{\epsilon} \cdot e^{i\vec{k} \cdot \vec{R}_l - i\omega t}, \quad (123)$$

where  $\vec{R}_l$  are the lattice sites. One then has to solve for the dispersion relation  $\omega(\vec{k})$  in all directions, as illus-

trated in fig. 18. From 123 we have

$$m\omega^2 \vec{\epsilon} = \underbrace{\sum_m \phi_{l,m} e^{i\vec{k} \cdot (\vec{R}_l - \vec{R}_m)}}_{\hat{\phi}(k)} \cdot \vec{\epsilon} \quad (124)$$

where  $\hat{\phi}(k)$  is a  $3 \times 3$  matrix, since  $\phi_{lm}$  too. This leads to an eigenvalue equation for  $\omega^2$  with three eigenvalues:  $\omega_L^2$  (for  $\vec{k} \parallel \vec{\epsilon}$ ) and  $\omega_{T(1,2)}^2$  (for  $\vec{k} \perp \vec{\epsilon}$ ). Hence, we have on longitudinal mode and two transverse modes and all phonon modes can be described by a superposition of these.

If we have two different masses, we have two addi-

tional equations of the form (124). This leads to the general case, where one has two branches the optical one and the acoustic one and each is divided in longitudinal and transverse modes. The acoustic branch has always a dispersion going to zero at  $k = 0$ , whereas for the optical mode at  $k = 0$  the energy is non-zero. The acoustic phonons have a gapless excitation spectrum and can therefore be created at very low energy as opposed to optical phonons which require a minimum energy to be excited.

### Quantum case

While many of the properties, like the dispersion relation, can be explained in classical terms, which are simply vibrations of the crystal ions, others, such as statistical properties need a quantum mechanical treatment.

Phonons can simply be seen as harmonic oscillators which carry no spin (or spin 0). They can, therefore, be accurately described by bosons with energy

$$E_n(k) = \hbar\omega(k)(n + 1/2). \quad (125)$$

We can now calculate the density of states of phonons, or the number of states between  $\omega$  and  $\omega + d\omega$ , i.e.,

$$D(\omega)d\omega = \frac{1}{(2\pi)^3} \int_{\omega}^{\omega+d\omega} dk \quad (126)$$

but  $d\omega = \nabla_k \omega dk$ , hence

$$D(\omega) = \frac{1}{(2\pi)^3} \int_{\omega=const} \frac{dS_{\omega}}{|\nabla_k \omega|} \quad (127)$$

Let us now suppose that we have 3 low energy modes with linear dispersion, one longitudinal mode  $\omega_L(k) = c_L k$  and two transverse modes  $\omega_T(k) = c_T k$ , hence  $\nabla \omega_{L,T}(k) = c_{L,T}$ , which implies that  $\int dS = 4\pi k^2$ . This leads to a density of state

$$D_{L,T}(\omega) = \frac{k^2}{2\pi^2 c_{L,T}} = \frac{\omega^2}{2\pi^2 c_{L,T}^3} \quad (128)$$

or

$$D_{tot}(\omega) = \frac{\omega^2}{2\pi^2} \underbrace{\left( \frac{1}{c_L^3} + \frac{2}{c_T^3} \right)}_{\frac{1}{c^3}} \quad (129)$$

in the isotropic case.

From statistics we know that the probability to find a state at  $E = E_n$  is given by the Boltzmann distribution  $P_n \sim e^{-E_n/k_B T}$ , with normalization  $\sum P_n = 1$ . Hence,

$$P_n = e^{-n\hbar\omega/k_B T} (1 - e^{-\hbar\omega/k_B T}) \quad (130)$$

simply from the normalization condition. We can now calculate the average energy at  $\omega$ ,

$$\begin{aligned} E(\omega) &= \sum_n E_n P_n = (1 - e^{-\hbar\omega/k_B T}) \hbar\omega \sum_{n=0}^{\infty} (n + 1/2) (e^{-\hbar\omega/k_B T})^n \\ &= \hbar\omega \left( \frac{1}{2} + \underbrace{\frac{1}{e^{\hbar\omega/k_B T} - 1}}_{\langle n \rangle} \right) \end{aligned} \quad (131)$$

here  $\langle n \rangle$  is the expectation value of quantum number  $n$  at  $T$ , which is nothing else but the Bose-Einstein distribution. As is well known, Bosons obey the Bose-Einstein statistics, where the Bose-Einstein distribution function is given by

$$f_{BE} = \frac{1}{e^{E/k_B T} - 1} \quad (132)$$

**Important:** at  $T = 0$ ,  $f_{BE}$  is simply a delta function  $\delta(E)$ . This is the Bose-Einstein condensation, where the

zero energy state is totally degenerate (this does suppose that there are no interactions between bosons, with interactions the delta function will be a little broader). The total average energy can then be calculated from the density of states as:

$$\langle E \rangle = \int d\omega D(\omega) E(\omega) \quad (133)$$

This also allows us to calculate the specific heat  $C_V =$

$\frac{d}{dT}\langle E \rangle$  in the isotropic case and in the linear dispersion approximation  $D(\omega) \sim \omega^2/c^3$ , hence

$$\begin{aligned}
C_V &= \frac{d}{dT} \int_0^\infty d\omega D(\omega) E(\omega) \\
&= \frac{d}{dT} \int_0^\infty d\omega D(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \\
&= \frac{d}{dT} \frac{3}{2\pi^2} \underbrace{\frac{1}{c^3}}_{\frac{1}{3}\left(\frac{1}{c_L^3} + \frac{2}{c_T^3}\right)} \underbrace{\int_0^\infty d\omega \frac{\hbar\omega^3}{e^{\hbar\omega/k_B T} - 1}}_{\int_0^\infty d\omega \frac{x^3}{e^x - 1} \frac{(k_B T)^4}{\hbar^3}} \\
&= \frac{d}{dT} \frac{3(k_B T)^4}{2\pi^2 (c\hbar)^3} \underbrace{\int_0^\infty d\omega \frac{x^3}{e^x - 1}}_{\pi^4/15} \\
&= \frac{2\pi^2 k_B}{5} \left( \frac{k_B T}{\hbar c} \right)^3 \quad (134)
\end{aligned}$$

where we had defined the variable  $x = \hbar\omega/k_B T$  and where  $1/c^3$  is the average over the 3 acoustic modes.

The Debye model assumes a linear dispersion ( $\omega = ck$ ) and uses the analogy to electrons where ( $n = k_F^3/3\pi^2$ ) to define  $k_D$ . Since phonons have no spins one obtains:

$$\begin{aligned}
n &= \frac{k_D^3}{6\pi^2} \text{ and} \\
k_B \Theta_D &= \hbar\omega_D = \hbar ck_D \quad (\Theta_D: \text{Debye temperature}) \\
\Rightarrow C_V &= \frac{12\pi^4 k_B}{5} \left( \frac{T}{\Theta_D} \right)^3 \cdot n \quad (135)
\end{aligned}$$

The typical Debye temperature is of the order of 100K. Finally, combining this result with the contributions from electrons (64), we obtain the expression valid for low temperatures:

$$C_V = \underbrace{\gamma T}_{\text{electrons}} + \underbrace{\beta T^3}_{\text{phonons}} \quad (136)$$

## TRANSPORT (BOLTZMANN THEORY)

Transport allows us to calculate transport coefficients such as resistances and thermal conductivities. While several transport theories exist, Boltzmann's approach is the most powerful and applies to most situations in condensed matter. The main idea in Boltzmann theory is to describe the electrons by a distribution function  $g$ . In equilibrium  $g$  is simply the Fermi-Dirac distribution function  $f_{FD}$ . In general,  $g(r, k, t)$  and at  $t - dt$  it can be written as:

$$g(r - \dot{r}dt, k - \dot{k}dt, t - dt) \quad (137)$$

If the electrons flow without collisions, (137) =  $g(r, k, t) = f_{FD}$ . The situation changes if collisions (f. ex. between electrons, impurities, or phonons) are included. In this case

$$g(r, k, t) - g(r - \dot{r}dt, k - \dot{k}dt, t - dt) = \delta g_{coll}. \quad (138)$$

where  $g_{coll}$  describes the collisions.  $g_{coll} = 0$  without collisions. Expanding (137) to first order and using (138) we obtain

$$\underbrace{\dot{r} \frac{\partial g}{\partial r} + \dot{k} \frac{\partial g}{\partial k} + \frac{\partial g}{\partial t}}_{\frac{dg}{dt}} = \frac{dg}{dt} \Big|_{coll}. \quad (139)$$

This is Boltzmann's equation.

### Relaxation time approximation

Solving Boltzmann's equation is not easy in general and therefore approximations are used. The simplest one is the relaxation time ( $\tau$ ) approximation. In this approximation:

$$\begin{aligned}
\left. \frac{dg}{dt} \right|_{coll} &= -\frac{1}{\tau} (g - f_{FD}) \\
\Rightarrow \frac{dg}{dt} &= -\frac{1}{\tau} (g - f_{FD}) \quad (140)
\end{aligned}$$

It is quite intuitive to see from where this approximation comes from, since a kick at  $t = 0$  would lead to solution of the form

$$g(t) = \frac{e^{-t/\tau}}{\tau} + f_{FD} \rightarrow f_{FD} \text{ (when } t = \infty) \quad (141)$$

This is the basic framework, which allows us to evaluate the effect of external fields on the system and to estimate the linear response to them.

### Case 1: $\vec{F} = -e\vec{E}$

In this case we look for a response in current density and define the conductivity tensor in linear response as

$$\begin{aligned}
\vec{j} &= \sigma \vec{E} \\
\Rightarrow j_\alpha &= \sigma_{\alpha\beta} E_\beta = -2e \int \frac{d^3k}{(2\pi)^3} v_\alpha g(r, k, t). \quad (142)
\end{aligned}$$

Since we are interested in the case of a homogenous uniform electric field,  $\partial g/\partial t = 0$  and  $\partial g/\partial r = 0$  and

$\hbar \dot{k} = -eE$ , Boltzmann's equation (139) in the relaxation time approximation becomes

$$\begin{aligned} \underbrace{\dot{k} \frac{\partial g}{\partial k}}_{-\frac{e\vec{E}}{\hbar} \cdot \frac{\partial g}{\partial \epsilon} \cdot \frac{\partial \epsilon}{\partial \vec{k}}} &= -\frac{1}{\tau}(g - f_{FD}) \\ \Rightarrow g &= \frac{e\vec{E}\tau}{\hbar} \underbrace{\frac{\partial g}{\partial \epsilon}}_{\simeq -\frac{\partial f_{FD}}{\partial \mu}} \cdot \underbrace{\frac{\partial \epsilon}{\partial \vec{k}}}_{\hbar \vec{v}} + f_{FD} \end{aligned} \quad (143)$$

Here we used the first order approximation  $\partial g/\partial \epsilon \simeq -\partial f_{FD}/\partial \mu$ , which is justified if the correction  $g - f_{FD}$  is smoother than  $\partial f_{FD}/\partial \mu$ , which is close to a delta function when  $kT \ll E_F$ . Hence, using (143) to evaluate the current (142), we obtain

$$j_\alpha = 2e \int \frac{d^3k}{(2\pi)^3} v_\alpha e\tau \vec{E} \cdot \vec{v} \frac{\partial f_{FD}}{\partial \mu} + \underbrace{\sim \left( \int v_\alpha f_{FD} \right)}_{=0}, \quad (144)$$

which leads to

$$\sigma_{\alpha\beta} = \frac{\partial j_\alpha}{\partial E_\beta} = 2e^2 \int \frac{d^3k}{(2\pi)^3} v_\alpha v_\beta \frac{\partial f_{FD}}{\partial \mu} \tau(\epsilon) \quad (145)$$

This is one of the most important expressions for the conductivity. Since  $\partial f_{FD}/\partial \mu$  is almost a delta function for  $kT \ll E_F$  this expression shows that only electrons close to the chemical potential  $\mu$  will significantly contribute to transport. It is possible to evaluate (145) in simple cases.

Let's assume that  $\tau$  does not depend on the energy, then we can rewrite (145) as

$$\begin{aligned} \sigma_{\alpha\beta} &= 2e^2\tau \int \frac{d^3k}{(2\pi)^3} v_\alpha \frac{\partial \epsilon}{\hbar \partial k_\beta} \left( -\frac{\partial f_{FD}}{\partial \epsilon} \right) \\ &= e^2\tau \int \frac{d^3k}{(2\pi)^3} v_\alpha \left( -\frac{\partial f_{FD}}{\hbar \partial k_\beta} \right) \\ &= e^2\tau \int \frac{d^3k}{(2\pi)^3} \underbrace{\frac{\partial v_\alpha}{\partial k_\beta}}_{\hbar \delta_{\alpha\beta}/m^*} f_{FD}/\hbar - \underbrace{\int_{k_\perp \beta} f_{FD} v_\alpha}_{=0} \\ &= \frac{e^2\tau}{m^*} \underbrace{\int \frac{d^3k}{(2\pi)^3} f_{FD}}_n \delta_{\alpha\beta} \end{aligned} \quad (146)$$

- If  $\tau(\epsilon) = \tau$  we therefore obtain the most important formula of conductivity (the Drude formula)

$$\sigma_{\alpha\beta} = \frac{e^2\tau n}{m^*} \delta_{\alpha\beta} \quad (147)$$

Using the same approach but in the presence of a magnetic field,  $\vec{F} = -e\vec{E} - e\vec{v} \times \vec{B}$ , we can derive an equivalent expression for  $\sigma_{\alpha\beta}$ , but in this case the off-diagonal component is not zero anymore. (See assignment).

## Diffusion model of transport (Drude)

In the case where the scattering of electrons is dominated by inelastic diffusion, we can write a very simple form for the conductivity or resistivity tensor. Indeed, in a diffusive regime the average velocity is directly proportional to the external force and to the inverse effective mass. The proportionality coefficient is then simply the scattering probability  $1/\tau$ . Hence,

$$\frac{m^*}{\tau} \vec{v} = \vec{F} = -e\vec{E} - e\vec{v} \times \vec{B} \quad (148)$$

If we suppose that the magnetic field is small and in the  $\hat{z}$  direction and  $\vec{E}$  along  $\hat{x}$ , then eq. (148) becomes

$$\begin{aligned} \underbrace{e\vec{E}}_{eE_x} &= -\frac{m^*}{\tau} \vec{v} - \underbrace{e\vec{v} \times \vec{B}}_{\simeq j_y B/n} \\ E_x &= \frac{m^*}{ne^2\tau} j_x + \frac{B}{ne} j_y \end{aligned} \quad (149)$$

Since in general  $\vec{E} = \rho \vec{j}$  and because the resistivity along  $\vec{B}$  is not affected by the magnetic field we can write for  $\vec{B}$  in the  $\hat{z}$  direction,

$$\rho = \begin{pmatrix} \frac{m^*}{ne^2\tau} & \frac{B}{ne} & 0 \\ -\frac{B}{ne} & \frac{m^*}{ne^2\tau} & 0 \\ 0 & 0 & \frac{m^*}{ne^2\tau} \end{pmatrix} = \sigma^{-1} \quad (150)$$

This is the famous Drude formula in a magnetic field. This formula is in fact equivalent to the relaxation time approximation in the Boltzmann theory (147).

## Case 2: Thermal inequilibrium

We now consider the case, where we also have a spacial gradient. Hence (139) and (140) become

$$\underbrace{\dot{r} \frac{\partial g}{\partial r}}_{\simeq \vec{v} \cdot \frac{\partial f}{\partial \vec{r}}} + \underbrace{\dot{k} \frac{\partial g}{\partial k}}_{\simeq -e\vec{E} \cdot \vec{v} \frac{\partial f}{\partial \epsilon}} = -\frac{1}{\tau}(g - f_{FD}), \quad (151)$$

here we used again that  $g - f$  is smooth so that  $\partial(g - f)/\partial \epsilon \ll \partial f/\partial \epsilon$ . Moreover, since

$$\begin{aligned} f_{FD} &= \frac{1}{e^{(\epsilon - \mu(r))/kT(r)} + 1} \\ \Rightarrow \frac{\partial f}{\partial r} &= \frac{\partial f}{\partial \epsilon} \left( -\nabla_r \mu - (\epsilon - \mu) \frac{\nabla_r T}{T} \right) \\ \Rightarrow g &= \vec{v} \cdot \frac{\partial f}{\partial \epsilon} \tau \left( e\vec{G} + (\epsilon - \mu) \frac{\nabla_r T}{T} \right) + f_{FD} \end{aligned} \quad (152)$$

where we defined the generalized field  $e\vec{G} = e\vec{E} + \vec{\nabla}\mu(r)$  and the external forces are now  $-e\vec{E}$ ,  $\vec{\nabla}\mu(r)$  and  $\vec{\nabla}T(r)$ , corresponding to an external electrical field, a gradient in the chemical potential (f.ex. a density gradient), and a temperature gradient. The electrical current density is the same as before but is now expressed (in the linear response) in terms of the additional external fields:

$$\vec{j}_e = -2e \int \frac{d^3k}{(2\pi)^3} \vec{v}g \simeq L^{11}\vec{G} + L^{12} \left( -\frac{\vec{\nabla}T}{T} \right). \quad (153)$$

An expression for the thermal current can be deduced from the following thermodynamical relation  $dQ = TdS = dU - \mu dN$ , hence

$$\vec{j}_Q = 2e \int \frac{d^3k}{(2\pi)^3} (\epsilon - \mu) \vec{v}g \simeq L^{21}\vec{G} + L^{22} \left( -\frac{\vec{\nabla}T}{T} \right). \quad (154)$$

Here  $L^{\alpha\beta}$  are the linear transport coefficients and  $\sigma = L^{11}$ . We now want to evaluate these expressions in the low temperature limit, where we can use  $\partial f_{FD}/\partial\mu \simeq \delta(\epsilon - \epsilon_F)$ , hence the expression for  $\sigma$  in (145) can be written as

$$\sigma_{\alpha\beta}(x) = \frac{\partial j_\alpha}{\partial E_\beta} = 2e^2 \int \frac{d^3k}{(2\pi)^3} v_\alpha v_\beta \tau(x) \delta(\epsilon - x), \quad (155)$$

where  $\sigma_{\alpha\beta} = \sigma_{\alpha\beta}(\epsilon_F)$ . We will use this new function  $\sigma(x)$  to express the other transport coefficients. For instance in linear response,

$$\begin{aligned} e^2 L_{\alpha\beta}^{22} &= \frac{\partial j_Q}{\partial \left( -\frac{\vec{\nabla}T}{T} \right)_\beta} \\ &= 2e^2 \int \frac{d^3k}{(2\pi)^3} v_\alpha v_\beta (\epsilon - \mu)^2 \tau(\epsilon) \frac{\partial f}{\partial \mu} \\ &= \int dx \frac{\partial f}{\partial \mu} (\epsilon - \mu)^2 \sigma_{\alpha\beta}(\epsilon). \end{aligned} \quad (156)$$

Using that  $(\epsilon_F - \mu) \simeq \frac{\pi^2}{6} (kT)^2 D'(\epsilon_F)/D(\epsilon_F)$ , we obtain (derivation in assignment).

$$\begin{aligned} L_{\alpha\beta}^{22} &= \frac{\pi^2}{3e^2} (kT)^2 \sigma_{\alpha\beta}(\epsilon_F) \text{ and similarly} \\ L_{\alpha\beta}^{12} = L_{\alpha\beta}^{21} &= -\frac{\pi^2}{3e} (kT)^2 \sigma'_{\alpha\beta}(\epsilon_F) \\ L_{\alpha\beta}^{11} &= \sigma_{\alpha\beta}(\epsilon_F) \end{aligned} \quad (157)$$

### Physical quantities

- **Thermal conductivity** ( $\kappa$ ):  $j_Q = \kappa(-\nabla T)$

Is obtained from eqs. (153,154,157), by setting  $j_e = 0$ , hence at low temperatures,  $L^{11}\vec{G} + L^{12} \left( -\frac{\vec{\nabla}T}{T} \right) = 0$  and

$$\begin{aligned} j_Q &= \underbrace{(L^{12}(L^{11})^{-1}L^{12} - L^{22})}_{\sim O(T^4) \simeq 0} \left( -\frac{\vec{\nabla}T}{T} \right) \\ &= -\frac{L^{22}}{T} \nabla T \\ \Rightarrow \kappa_{\alpha\beta} &= \frac{\pi^2 k^2 T}{3} \frac{\sigma_{\alpha\beta}}{e^2} \end{aligned} \quad (158)$$

This is the well known Wiedemann-Franz law

- **Thermopower** ( $Q$ ):  $\vec{E} = Q\nabla T$  with  $j_e = 0$ . In this case

$$Q = \frac{L^{12}}{L^{11}T} = \frac{\pi^2 k^2 T}{3} \frac{\sigma'}{e \sigma} \quad (159)$$

- **Peltier effect** ( $\nabla T = 0$ ):  $j_Q = \Pi j_e \Rightarrow \Pi = L^{21}/L^{11} = TQ$

### Historical note:

**The Seebeck effect:** The discovery of thermoelectricity dates back to Seebeck [1] (1770-1831). Thomas Johann Seebeck was born in Revel (now Tallinn), the capital of Estonia which at that time was part of East Prussia. Seebeck was a member of a prominent merchant family with ancestral roots in Sweden. He studied medicine in Germany and qualified as a doctor in 1802. Seebeck spent most of his life involved in scientific research. In 1821 he discovered that a compass needle deflected when placed in the vicinity of a closed loop formed from two dissimilar metal conductors if the junctions were maintained at different temperatures. He also observed that the magnitude of the deflection was proportional to the temperature difference and depended on the type of conducting material, and does not depend on the temperature distribution along the conductors. Seebeck tested a wide range of materials, including the naturally found semiconductors ZnSb and PbS. It is interesting to note that if these materials had been used at that time to construct a thermoelectric generator, it could have had an efficiency of around 3% - similar to that of contemporary steam engines.

The Seebeck coefficient is defined as the open circuit voltage produced between two points on a conductor, where a uniform temperature difference of 1K exists between those points.

**The Peltier effect:** It was later in 1834 that Peltier[2] described thermal effects at the junctions of dissimilar conductors when an electrical current flows between the materials. Peltier failed however to understand the full implications of his findings and it wasn't until four years later that Lenz[3] concluded that there is heat adsorption or generation at the junctions depending on the direction of current flow.

**The Thomson effect:** In 1851, Thomson[4] (later Lord Kelvin) predicted and subsequently observed experimentally the cooling or heating of a homogeneous conductor resulting from the flow of an electrical current in the presence of a temperature gradient. This is known as the Thomson effect and is defined as the rate of heat generated or absorbed in a

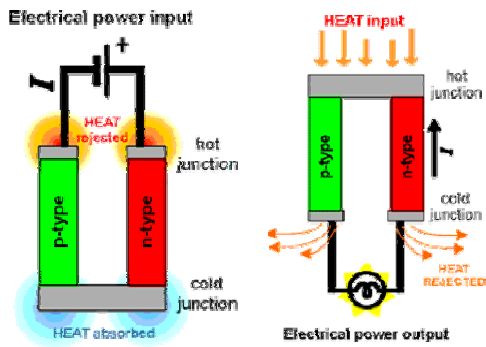


FIG. 20: Thermoelectric cooling (left): If an electric current is applied to the thermocouple as shown, heat is pumped from the cold junction to the hot junction. The cold junction will rapidly drop below ambient temperature provided heat is removed from the hot side. The temperature gradient will vary according to the magnitude of current applied. Thermoelectric generation (right): The simplest thermoelectric generator consists of a thermocouple, comprising a p-type and n-type thermoelement connected electrically in series and thermally in parallel. Heat is pumped into one side of the couple and rejected from the opposite side. An electrical current is produced, proportional to the temperature gradient between the hot and cold junctions.

single current carrying conductor subjected to a temperature gradient.

[1] Seebeck, T.J., 1822, Magnetische Polarisation der Metalle und Erzedurch Temperatur-Differenz. Abhandl. Deut. Akad. Wiss. Berlin, 265-373.

[2] Peltier, J.C., 1834, Nouvelles experiences sur la calorificite des courans electriques. Ann. Chem., LVI, 371-387.

[3] See Ioffe, A.F., 1957, Semiconductor Thermoelements and Thermoelectric Cooling, Infosearch, London.

[4] Thomson, W., 1851, On a mechanical theory of thermoelectric currents, Proc.Roy.Soc.Edinburgh, 91-98.

## SEMICONDUCTORS

Semiconductors are distinguished from metals in that they have a gap at the Fermi surface, and are distinguished from insulators in that the gap is smaller, which is ambiguous. But generally, if the gap is close to 1eV it's a standard semiconductor. If the gap is close to 3eV it's a wide band gap semiconductor and above 6eV it's usually called an insulator. Typically, the distinction is simply made from the temperature dependence of the conductivity. If  $\sigma \rightarrow 0$  for  $T \rightarrow 0$  it's a semiconductor or an insulator but the material is a metal if  $\sigma \rightarrow \sigma_0 > 0$ . However, even at room temperatures the conductivities of pure materials differ by many orders of magnitude ( $\sigma_{metal} \gg \sigma_{semi} \gg \sigma_{insu}$ ).

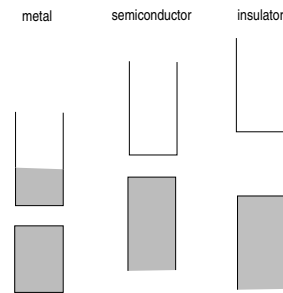


FIG. 21: There is no band gap at the Fermi energy in a metal, while there is a band gap in an insulator. Semiconductors on the other hand have a band gap, but it is much smaller than those found in insulators.

## Band Structure

Clearly the band structure of the semiconductors is crucial for the understanding of their properties and their device applications. Semiconductors fall into several categories, depending upon their composition, the simplest, *type IV* include silicon and germanium. The type refers to their valence.

The band structure is quite rich and shown in figure (22) for silicon. Germanium is very similar to Si and does

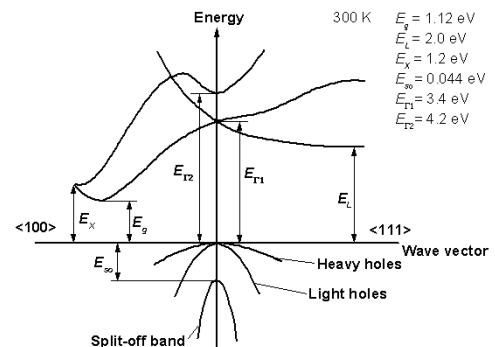


FIG. 22: Band structure of Si. (Figures from [ioffe.rssi.ru/SVA/NSM/Semicond](http://ioffe.rssi.ru/SVA/NSM/Semicond))

not have a direct gap either. In general the dispersion relation can be approximated with the use of the effective masses, noting that

$$\frac{1}{m_{ij}^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j}, \quad (160)$$

hence

$$E(\vec{k}) = E_c + \hbar^2 \left( \frac{k_x^2 + k_y^2}{2m_t^*} + \frac{k_z^2}{2m_l^*} \right) \quad (161)$$

for the conduction band and



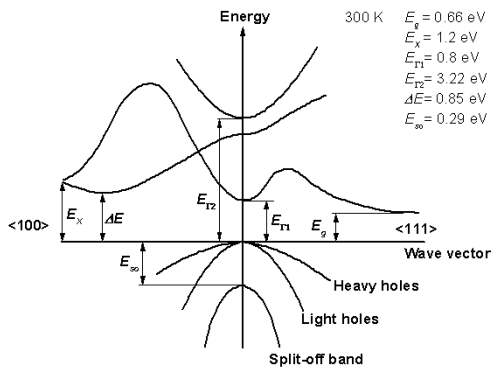


FIG. 23: Band structure of Ge.

$$E(\vec{k}) = E_v - \frac{\hbar^2 \vec{k}_h^2}{2m_h^*} - \frac{\hbar^2 \vec{k}_{lp}^2}{2m_{lp}^*} \simeq E_v - \frac{\hbar^2 \vec{k}^2}{2m_p^*} \quad (162)$$

for the valence band, where there are typically two bands, the heavy holes and the light holes. These dispersion relations are generally good approximations to the real system. In addition, the valence band has another band due to spin-orbit interaction. However, at zero wavenumber ( $\vec{k} = 0$ ) this band is not degenerate with the other two light and heavy hole bands.

	$m_n^*$	$m_p^*$	$m_t^*$	$m_l^*$	$m_h^*$	$m_{lp}^*$	gap [eV]
Si	0.36	0.81	0.19	0.98	0.49	0.16	1.12
Ge	0.22	0.34	0.0815	1.59	0.33	0.043	0.661
GaAs	0.063	0.53	0.063	0.063	0.51	0.082	1.424

TABLE I: The effective masses in units of the free electron mass for the conduction band, the valence band, the transverse and longitudinal part in the conduction band and the heavy and light hole mass in the valence band.

The situation in III-V semiconductors such as GaAs is similar but the gap is direct. For this reason GaAs makes more efficient optical devices than does either Si or Ge. A particle-hole excitation across the gap can readily recombine, emit a photon (which has essentially no momentum) and conserve momentum in GaAs; whereas, in an indirect gap semiconductor, this recombination requires the addition creation or absorption of a phonon or some other lattice excitation to conserve momentum. For the same reason, excitons live much longer in Si and especially Ge than they do in GaAs.

#### Electron and hole densities in intrinsic (undoped) semiconductors

At zero temperature, the Fermi energy lies in the gap, hence there are no holes ( $p = 0$ ) in the valence band and

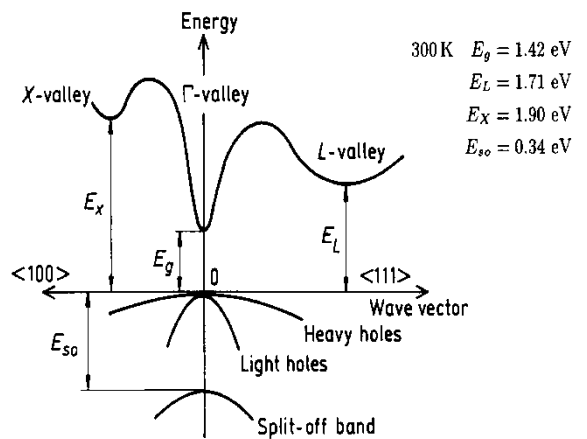


FIG. 24: Band structure of GaAs. Note the direct,  $\Gamma \rightarrow \Gamma$ , minimum gap energy. The nature of the gap can be tuned with Al doping.

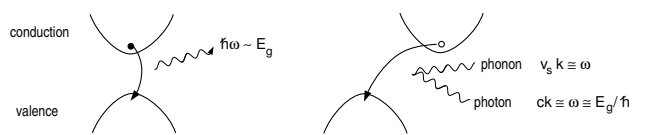


FIG. 25: A particle-hole excitation across the gap can readily recombine, emit a photon (which has essentially no momentum) and conserve momentum in a direct gap semiconductor (left) such as GaAs. Whereas, in an indirect gap semiconductor (right), this recombination requires the additional creation or absorption of a phonon or some other lattice excitation to conserve momentum.

no electrons in the conduction band ( $n = 0$ ). At non-zero temperatures, the situation is very different and the carrier concentrations are highly  $T$ -dependent since all of the carriers in an intrinsic (undoped) semiconductor are thermally induced.

In this case, the Fermi-Dirac distribution defines the temperature dependent density

$$n = \int_{E_c}^{E_{top}} D_C(E) f_{FD}(E) dE \simeq \int_{E_c}^{\infty} D_C(E) f_{FD}(E) dE \quad (163)$$

$$p = \int_{-\infty}^{E_v} D_V(E) (1 - f_{FD}(E)) dE \quad (164)$$

To proceed further we need forms for  $D_C$  and  $D_V$ . Recall that in the parabolic approximation  $E_k \simeq \frac{\hbar^2 \vec{k}^2}{2m^*}$  we found

material	$\tau_{exciton}$
GaAs	$1ns(10^{-9}s)$
Si	$19\mu s(10^{-5}s)$
Ge	$1ms(10^{-3}s)$

TABLE II:

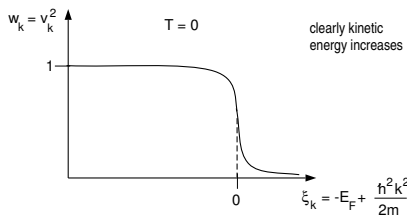


FIG. 26: Partially filled conduction band and hole band at non-zero temperature

that  $D(E) = \frac{(2m^*)^{3/2}}{2\pi^2\hbar^3} \sqrt{E}$ . Thus,

$$D_C(E) = \frac{(2m_n^*)^{3/2}}{2\pi^2\hbar^3} \sqrt{E - E_C} \quad (165)$$

$$D_V(E) = \frac{(2m_p^*)^{3/2}}{2\pi^2\hbar^3} \sqrt{E_V - E} \quad (166)$$

for  $E > E_C$  and  $E < E_V$  respectively, and zero otherwise  $E_V < E < E_C$ .

In an intrinsic (undoped) semiconductor  $n = p$ , and so  $E_F$  must lie in the band gap. Physically, this also means that we have two types of carriers at non-zero temperatures. Both contribute actively to physical properties such as transport.

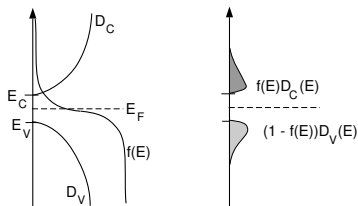


FIG. 27: The density of states of the electron and hole bands

If  $m_n^* \neq m_p^*$  (ie.  $D_C \neq D_V$ ), then the chemical potential,  $E_F$ , must be adjusted up or down from the center of the gap so that  $n = p$ .

Furthermore, the carriers which are induced across the gap are relatively (to  $k_B T$ ) high in energy since typically  $E_g = E_C - E_V \gg k_B T$ .

	$E_g$ (eV)	$n_i$ (cm <sup>-3</sup> ) (300° K)
Ge	0.67	$2.4 \times 10^{13}$
Si	1.1	$1.5 \times 10^{10}$
GaAs	1.43	$5 \times 10^7$

TABLE III: Intrinsic carrier densities at room temperature

$$\frac{1eV}{k_B} \simeq 10000^\circ K \gg 300^\circ K \quad (167)$$

Thus, assuming that  $E - \mu \gtrsim \frac{E_g}{2} \gg k_B T$

$$\frac{1}{e^{(E-\mu)/k_B T} + 1} \simeq \frac{1}{e^{(E-\mu)/k_B T}} = e^{-(E-\mu)/k_B T} \quad (168)$$

ie., Boltzmann statistics. A similar relationship holds for holes where  $-(E - \mu) \gtrsim \frac{E_g}{2} \gg k_B T$

$$1 - \frac{1}{e^{(E-\mu)/k_B T} + 1} = \frac{1}{e^{-(E-\mu)/k_B T} + 1} \simeq e^{(E-\mu)/k_B T} \quad (169)$$

since  $e^{(E-\mu)/k_B T}$  is small. Thus, the concentration of electrons  $n$

$$\begin{aligned} n &\simeq \frac{(2m_n^*)^{3/2}}{2\pi^2\hbar^3} e^{\mu/k_B T} \int_{E_C}^{\infty} \sqrt{E - E_C} e^{-E/k_B T} dE \\ &= \frac{(2m_n^*)^{3/2}}{2\pi^2\hbar^3} (k_B T)^{3/2} e^{-(E_C-\mu)/k_B T} \underbrace{\int_0^{\infty} x^{1/2} e^{-x} dx}_{\sqrt{\pi}/2} \\ &= 2 \left( \frac{2\pi m_n^* k_B T}{h^2} \right)^{3/2} e^{-(E_C-\mu)/k_B T} \\ &= N_{eff}^C e^{-(E_C-\mu)/k_B T} \end{aligned} \quad (170)$$

Similarly

$$p = 2 \left( \frac{2\pi m_p^* k_B T}{h^2} \right)^{3/2} e^{(E_V-\mu)/k_B T} = N_{eff}^V e^{(E_V-\mu)/k_B T} \quad (171)$$

where  $N_{eff}^C$  and  $N_{eff}^V$  are the partition functions for a classical gas in 3-d and can be regarded as "effective densities of states" which are temperature-dependent. Within this interpretation, we can regard the holes and electrons statistics as classical. This holds so long as  $n$  and  $p$  are small, so that the Pauli principle may be ignored - the so called *nondegenerate limit*.

In general, in the nondegenerate limit,

$$np = 4 \left( \frac{k_B T}{2\pi\hbar^2} \right)^3 (m_n^* m_p^*)^{3/2} e^{-E_g/k_B T} \quad (172)$$

this, the *law of mass action*, holds for both doped and intrinsic semiconductor so long as we remain in the nondegenerate limit. However, for an *intrinsic semiconductor*, where  $n = p$ , it gives us further information.

$$n_i = p_i = 2 \left( \frac{k_B T}{2\pi\hbar^2} \right)^{3/2} (m_n^* m_p^*)^{3/4} e^{-E_g/2k_B T} \quad (173)$$

(See table (II)). However, we already have relationships for  $n$  and  $p$  involving  $E_C$  and  $E_V$

$$n = p = N_{eff}^C e^{-(E_C-\mu)/k_B T} = N_{eff}^V e^{(E_V-\mu)/k_B T} \quad (174)$$

$$e^{2\mu/k_B T} = \frac{N_{eff}^V}{N_{eff}^C} e^{(E_V+E_C)/k_B T} \quad (175)$$

or

$$\mu = \frac{1}{2}(E_V + E_C) + \frac{1}{2}k_B T \ln \left( \frac{N_{eff}^V}{N_{eff}^C} \right) \quad (176)$$

$$\mu = \frac{1}{2}(E_V + E_C) + \frac{3}{4}k_B T \ln \left( \frac{m_p^*}{m_n^*} \right) \quad (177)$$

Thus if  $m_p^* \neq m_n^*$ , the chemical potential  $\mu$  in a semiconductor is temperature dependent.

### Doped Semiconductors

Since,  $\sigma \sim n\tau$ , so the conductivity depends linearly upon the doping (it may also effect  $\mu$  in some materials, leading to a non-linear doping dependence). A typical metal has

$$n_{metal} \simeq 10^{23}/(cm)^3 \quad (178)$$

whereas we have seen that a typical semiconductor has

$$n_i \simeq \frac{10^{10}}{cm^3} \quad \text{at } T \simeq 300^\circ K \quad (179)$$

Thus the conductivity of an intrinsic semiconductor is quite small!

To increase  $n$  (or  $p$ ) to  $\sim 10^{18}$  or more, dopants are used. For example, in Si the elements used as dopants are typically in the third or fifth column. Thus P or B

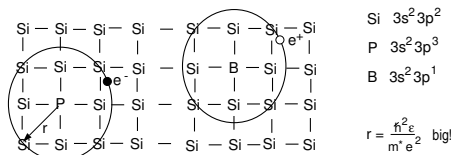


FIG. 28: The dopant, P, (left) donates an electron and the acceptor, B, donates a hole (or equivalently absorbs an electron).

will either donate or absorb an additional electron (with the latter called the creation of a hole).

In terms of energy levels

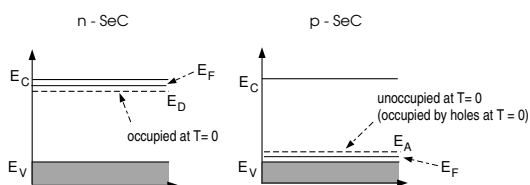


FIG. 29: Left, the density of states of a n-doped semiconductor with the Fermi level close to the conduction band and, right, the equivalent for a p-doped semiconductor.

### Carrier Densities in Doped semiconductor

The law of mass action is valid so long as the use of Boltzmann statistics is valid i.e., if the degeneracy is small. Thus, even for doped semiconductor

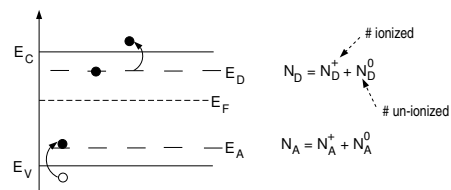


FIG. 30: Ionization of the dopants

$$np = N_{eff}^C N_{eff}^V e^{-\beta E_g} = n_i^2 = p_i^2, \quad (180)$$

where  $\beta = 1/k_B T$ . Using (177) we can define

$$\mu_i = \frac{1}{2}(E_V + E_C) + \frac{3}{4}k_B T \ln \left( \frac{m_p^*}{m_n^*} \right), \quad (181)$$

hence,

$$n = n_i e^{(-\mu_i - \mu)/k_B T} \quad \text{and} \quad p = n_i e^{(\mu_i - \mu)/k_B T} \quad (182)$$

To a good approximation we can assume that all donors and all acceptors are ionized. Therefore,

$$\begin{aligned} n - p &= N_D - N_A \quad \text{and} \quad np = n_i^2 \\ \Rightarrow n &= N_D - N_A + \frac{n_i^2}{n} \\ &= \frac{N_D - N_A}{2} + \frac{\sqrt{(N_D - N_A)^2 + 4n_i^2}}{2} \\ \Rightarrow n &\simeq N_D \quad \text{and} \quad p \simeq n_i^2/N_D \quad \text{for } N_D \gg N_A \\ p &\simeq N_A \quad \text{and} \quad n \simeq n_i^2/N_A \quad \text{for } N_A \gg N_D \end{aligned} \quad (183)$$

By convention, if  $n > p$  we have an n-type semiconductor,  $n^+$ -Si, or n-doped Si. The same is true for p. Quite generally, at large doping the semiconductor will behave like a metal, since the dopant will spill over into the conduction band (or valence band for holes). In this case there is no gap anymore for the carriers and the conductivity remains constant to the lowest possible temperatures. The main difference to a metal is only that the density of carriers is still very much lower (several orders of magnitude) than in a metal. At low doping the number of carriers in the conduction band (or valence band) vanishes at zero temperature and the semiconductor behaves like an insulator.

An effective way to describe a semiconductor at high temperature or high doping is to consider that  $n = N_D^{eff}$  and  $p = N_A^{eff}$ , where  $n$  and  $p$  are mobile negative and positive carriers, whereas  $N_D^{eff}$  and  $N_A^{eff}$  are effective positive and negative fixed charges, respectively. In this approximation, charge neutrality is automatically verified and we can use it to discuss heterogenous systems, where  $N_D^{eff}$  depends on position (but is fixed).

### Metal-Insulator transition

In n-type semiconductors, when  $E_F < E_C$ , carriers experience a gap  $\Delta = E_C - E_F$ . Hence at low temperatures the system is insulating. Indeed,

$$n = \underbrace{N_C}_{\sim T^{3/2}} e^{\frac{\mu - E_C}{k_B T}} \quad (184)$$

Since from Drude

$$\sigma = \frac{ne^2\tau}{m^*} \rightarrow 0 \text{ when } T \rightarrow 0. \quad (185)$$

When  $E_F > E_C$ , the semiconductor behaves like a metal. In this case we obtain again from Drude that  $\sigma = \frac{ne^2\tau}{m^*} > 0$  even for  $T \rightarrow 0$ , since the density does not vanish. In general,  $\tau$  also depends on temperature. Indeed, in the metallic phase the most important temperature dependence comes from  $\tau$ . To evaluate the contributions from different scattering mechanism we can consider  $1/\tau$  as the scattering probability. This follows directly from Boltzmann's equation, where

$$\left(\frac{dg}{dt}\right)_{coll} = \sum_{k'} (\Gamma(k'k) - \Gamma(kk')), \quad (186)$$

where

$$\Gamma(kk') = \underbrace{W(kk')}_{\text{prob. } k \rightarrow k'} \cdot \underbrace{g(k)}_{\# \text{ of states in } k} \cdot \underbrace{(1 - g(k'))}_{\# \text{ of empty states in } k'} \quad (187)$$

is the transition rate from state  $k$  to  $k'$ . Local equilibrium implies  $\Gamma_{kk'} = \Gamma_{k'k}$ , hence  $g = f_{FD}$ .

The most important scattering cases are the following:

- Impurity scattering (for a density of impurities  $n_I$ ):

$$\frac{1}{\tau_{e-imp}} \sim n_I \quad (188)$$

- Electron-electron scattering:

$$\frac{1}{\tau_{e-e}} \sim (T/T_F)^2 \quad (189)$$

- Electron-phonon scattering:

$$\frac{1}{\tau_{e-ph}} \sim (T/T_D)^5 \quad (190)$$

In general, the total scattering probability is the sum of all possible scattering probabilities, hence

$$\begin{aligned} \frac{1}{\tau_{tot}} &= \frac{1}{\tau_{e-imp}} + \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{e-ph}} \\ \Rightarrow \rho &= \frac{m^*}{e^2 n \tau} \simeq \rho_0 + A \left(\frac{T}{T_F}\right)^2 + B \left(\frac{T}{T_D}\right)^5 \end{aligned} \quad (191)$$

where the constants ( $\rho_0$ ,  $A$  and  $B$ ) depend on the material. In most metals and heavily doped semiconductors the temperature dependence of the resistivity is dominated by these three mechanisms, which means that the importance of impurities, electron-phonon and phonon-phonon interactions can be extracted from the temperature dependence of the resistivity.

A special case is the magnetic impurity case (Kondo), which gives rise to an additional term in  $1/\tau_K \sim -(T/T_K)^2$ .

### In practice

To determine the density (n-p) the Hall resistance can be used. The ratio  $\tau/m^*$  can then be obtained from the Drude conductivity and  $m^*$  can be obtained from magneto-oscillations due to the Landau levels. This can in principle be done for all temperatures, hence it is possible to extract  $m^*$ ,  $n(T)$ , and  $\tau(T)$  simply by using transport and to deduce the dominant scattering mechanisms in the systems under study.

### p-n junction

(See also pn junction supplement)

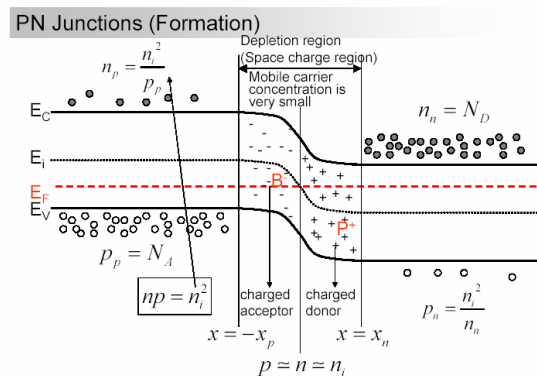


FIG. 31: Formation of a pn junction, with the transfer of charges from the n region to the p region and the alignment of the chemical potential so that  $\nabla \mu(\vec{r}) = 0$ . The depletion and accumulation regions are delimited by  $x_n$  and  $-x_p$ , respectively.

When two differently doped semiconductors are brought together they form a pn junction. In general, electrons from the more n-type doped region will transfer to the less doped or p-type region. This leaves a positively charged region on the n side and accumulation of negative charges on the p side. The potential

distribution can then be obtained by solving Poisson's equation

$$\frac{\partial^2 V(x)}{\partial x^2} = -\frac{e}{\epsilon_0} \rho(x) \quad (192)$$

where  $\rho(x) = -n(x) + p(x) + N_D(x) - N_A(x)$  is the charge distribution of the mobile carriers (electrons and holes) plus the fixed charges (donors and acceptors) and  $\epsilon_0$  is the dielectric constant.

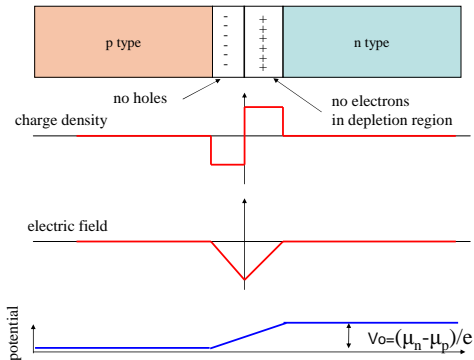


FIG. 32: Sketch of the charge density, the electric field and the internal potential distribution due the transfer of charges in a pn junction

The most important consequence of a pn-junction is the diode behavior. Indeed, when applying a negative bias on the n region, the conduction bands tend to align more and current can flow (forward bias). If the bias is positive the internal potential is increased and almost no current can flow (reverse bias). This leads to the well known asymmetry in the current-voltage characteristics of a diode. This is one of the most important elements of electronics. These ideas can be extended to three terminal devices such as a pnp junction or npn junction (which is equivalent to two pn junction put together). In this case we have a transistor, i.e., by varying the potential on the center element we can control the current through the device.

### ONE DIMENSIONAL CONDUCTANCE

Suppose that we have a perfect one-dimensional conductor (quantum wire) connected by two large electron reservoirs. In real life they would be electrical contacts. The left reservoir is fixed at chemical potential  $\mu_L$  and the right one at  $\mu_R$ . The current is then given as usual by

$$\begin{aligned} I = -env &= -e \int_{k_F^L}^{k_F^R} 2 \cdot \frac{dk}{2\pi} \overbrace{\frac{\hbar k}{m^*}}^v \\ &= -e \frac{\hbar(k_F^L)^2 - (k_F^R)^2}{2\pi m^*} \\ &= -\frac{2e}{h} \left( \underbrace{\mu_R}_{-eV_R} - \underbrace{\mu_L}_{-eV_L} \right) \\ &= \frac{2e^2}{h} (V_R - V_L) \end{aligned} \quad (193)$$

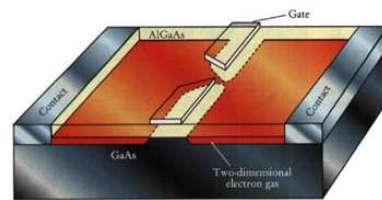


FIG. 33: Schematic cross-sectional view of a quantum point contact, defined in a high-mobility 2D electron gas at the interface of a GaAs-AlGaAs heterojunction. The point contact is formed when a negative voltage is applied to the gate electrodes on top of the AlGaAs layer. Transport measurements are made by employing contacts to the 2D electron gas at either side of the constriction. (Beenakker, PHYSICS TODAY, July 1996).

Hence  $I = (2e^2/h)\Delta V \Rightarrow R = h/2e^2$  and  $G = 2e^2/h$ , where  $R$  and  $G$  are the resistances and conductances, respectively. This result can seem surprising at first since it implies that the resistance does not depend on the length of the system. A very short quantum wire has the same resistance as an infinitely long wire. This result however, only applies for a perfect conductor. As soon as impurities lie in the wire this result has to be modified to take into account scattering by the impurities and then  $R$  would typically depend on the length of the system.

### MORE THAN ONE CHANNEL, THE QUANTUM POINT CONTACT

The previous result is specific to the purely one-dimensional case. In general the system can be extended to a system of finite width,  $W$ . In this case the electron energy is given by

$$\epsilon = \frac{\hbar^2 k_x^2}{2m^*} + \frac{\hbar^2 (\pi n/W)^2}{2m^*} \quad (194)$$

if the boundary of our narrow wire is assumed to be sharp, since in this case the wave function has to vanish

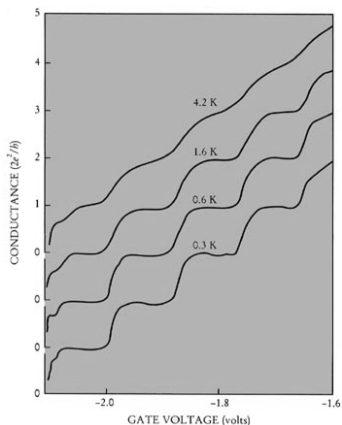


FIG. 34: Conductance quantization of a quantum point contact in units of  $2e^2/h$ . As the gate voltage defining the constriction is made less negative, the width of the point contact increases continuously, but the number of propagating modes at the Fermi level increases stepwise. The resulting conductance steps are smeared out when the thermal energy becomes comparable to the energy separation of the modes.

at the boundary (like for an electron in a box of width  $W$ ). In general, if

$$\frac{\hbar^2(\pi/W)^2}{2m^*} < E_F < \frac{\hbar^2(2\pi/W)^2}{2m^*} \quad (195)$$

then we recover the ideal case of a one-dimensional quantum wire, or single channel. If, however,

$$\frac{\hbar^2(N\pi/W)^2}{2m^*} < E_F < \frac{\hbar^2((N+1)\pi/W)^2}{2m^*} \quad (196)$$

we can have  $n$  channels, where each channel contributes equally to the total conductance. Hence in this case  $G = N \cdot 2e^2/h$ , where  $N$  is the number of channels. This implies that a system, where we reduce the width of the conductor will exhibit jumps in the conductance of step  $2e^2/n$ . Indeed, this is what is seen experimentally.

## QUANTUM HALL EFFECT

The quantum hall effect is a beautiful example, where the concept of a quantized conductance can be applied to (see additional notes on the quantum Hall effect).

## SUPERCONDUCTIVITY

The main aspects of superconductivity are

- Zero resistance (Kammerlingh-Onnes, 1911) at  $T < T_c$ : The temperature  $T_c$  is called the critical temperature.

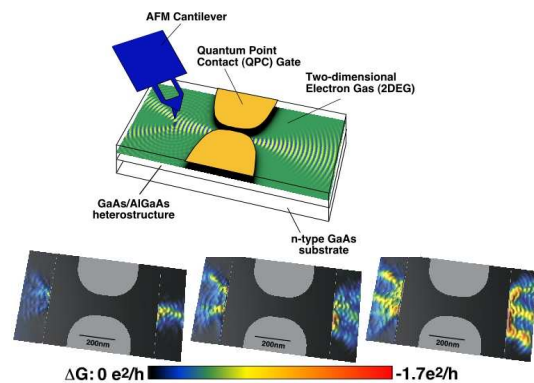


FIG. 35: Imaging of the channels using an AFM (1 to 3 channels from left to right). The images were obtained by applying a small negative potential on the AFM tip and then measuring the conductance as a function of the tip scan and then reconstruct the 2D image from the observed change in conductance. (From R.M. Westervelt).

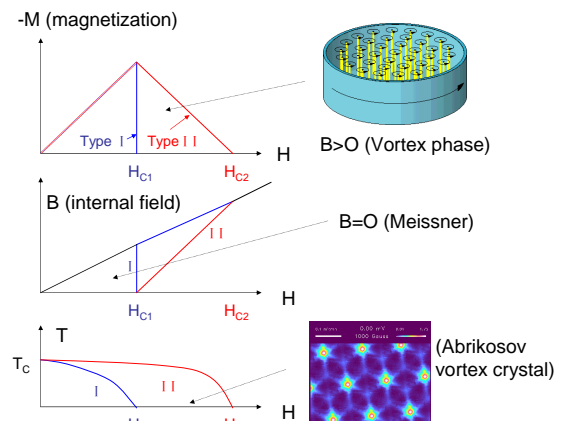


FIG. 36: Magnetic field dependence in a superconductor. (Vortex picture from AT&T '95)

- Superconductivity can be destroyed by an external magnetic field  $H_c$  which is also called the critical field (Kammerlingh-Onnes, 1914). Empirically,  $H_c(T) = H_c(0)(1 - (T/T_c)^2)$
- The Meissner-Ochsenfeld effect (1933). The magnetic field does not penetrate the sample, the magnetic induction is zero,  $B = 0$ . This effect distinguishes two types of superconductors, type I and type II. In Type I, no field penetrates the sample, whereas in type II the field penetrates in the form of vortices.
- Superconductors have a gap in the excitation spectrum.

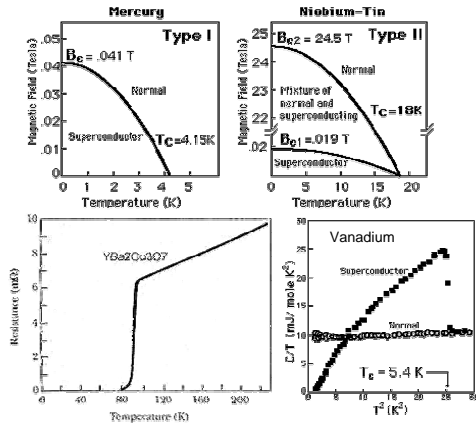


FIG. 37: The critical magnetic field, resistance and specific heat as a function of temperature. (Ref: superconductors.org)

The main mechanism behind superconductivity is the existence of an effective attractive force between electrons, which favors the pairing of two electrons of opposite momentum and spin. In conventional superconductors this effective attractive force is due to the interaction with phonons. This pair of electrons has now effectively zero total momentum and zero spin. In this sense this pair behaves like a boson and will Bose-Einstein condensate in a coherent quantum state with the lowest possible energy. This ground state is separated by a superconducting gap. Electrons have to jump over this gap in order to be excited. Hence when the thermal energy exceeds the gap energy the superconductor becomes normal.

The origin of the effective attraction between electrons can be understood in the following way:

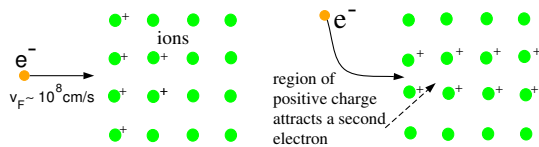


FIG. 38: Origin of the retarded attractive potential. Electrons at the Fermi surface travel with a high velocity  $v_F$ . As they pass through the lattice (left), the positive ions respond slowly. By the time they have reached their maximum excursion, the first electron is far away, leaving behind a region of positive charge which attracts a second electron.

When an electron flies through the lattice, the lattice deforms slowly with respect to the time scale of the electron. It reaches its maximum deformation at a time  $\tau \simeq \frac{2\pi}{\omega_D} \simeq 10^{-13}$  s after the electron has passed. In this time the first electron has travelled  $\simeq v_F \tau \simeq 10^8 \frac{\text{cm}}{\text{s}} \cdot 10^{-13} \text{s} \simeq 1000 \text{\AA}$ . The positive charge of the lattice deformation can then attract another electron without feeling the Coulomb repulsion of the first electron.

Due to retardation, the electron-electron Coulomb repulsion may be neglected!

The net effect of the phonons is then to create an attractive interaction which tends to pair time-reversed quasiparticle states. They form an antisymmetric spin

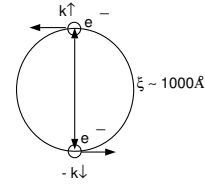


FIG. 39: To take full advantage of the attractive potential illustrated in Fig. 38, the spatial part of the electronic pair wave function is symmetric and hence nodeless. To obey the Pauli principle, the spin part must then be antisymmetric or a singlet.

singlet so that the spatial part of the wave function can be symmetric and nodeless and so take advantage of the attractive interaction. Furthermore they tend to pair in a zero center of mass (cm) state so that the two electrons can chase each other around the lattice.

Using perturbation theory it is in fact possible to show that to second order (electron-phonon-electron) the effect of the phonons effectively leads to a potential of the form

$$V_{e-ph} \sim \frac{(\hbar\omega_q)^2}{(\epsilon(k) - \epsilon(k-q))^2 - (\hbar\omega(q))^2} \quad (197)$$

This term can be negative, hence effectively produce an attraction between two electrons exceeding the Coulomb repulsion. This effect is the strongest for  $k = k_F$  and  $q = 2k_F$  since  $\epsilon(k_F) = \epsilon(-k_F)$  and  $\omega(2k_F) \simeq \omega_D$  (the Debye frequency). Hence electrons will want to form opposite momentum pairs ( $k_F, -k_F$ ). This will be our starting point for the microscopic theory of superconductivity à la BCS (Bardeen, Shockley and Schrieffer).

### BCS theory

To describe our pair of electrons (the Cooper pair) we will use the formalism of second quantization, which is a convenient way to describe a system of more than one particle.

$$H_{1particle} = \frac{p^2}{2m} \Rightarrow H_{1p}\psi(x) = E\psi(x) \quad (198)$$

Let's define

$$c_1^\dagger(x) \underbrace{|0\rangle}_{\text{vacuum}} = \psi(x) \text{ and } \langle 0|c_1(x) = \psi^*(x) \quad (199)$$

With these definitions,  $|0\rangle$  is the vacuum (or ground state), i.e., state without electrons.  $c_1^\dagger(x)|0\rangle$  corresponds

to one electron in state  $\psi(x)$  which we call 1.  $c^+$  is also called the creation operator, since it creates one electron from vacuum.  $c$  is then the annihilation operator, i.e.,  $c_1 c_1^+ |0\rangle = |0\rangle$ , which corresponds to creating one electron from vacuum then annihilating it again. Other properties include

$$c_1 |0\rangle = 0 \text{ and } c_1^+ c_1^+ |0\rangle = 0 \quad (200)$$

The first relation means that we cannot annihilate an electron from vacuum and the second relation is a consequence of the Pauli principle. We cannot have two electrons in the same state 1.

Hence,

$$\begin{aligned} c_1^+ c_1^+ = 0 &\Rightarrow (c_1^+ c_1^+)^+ = 0 \Rightarrow c_1 c_1 = 0 \\ &\Rightarrow (c_1^+ c_1) c_1^+ |0\rangle = c_1^+ |0\rangle \end{aligned} \quad (201)$$

This shows that  $c_1^+ c_1$  acts like a number operator. It counts the number of electrons in state 1. (Either 1 or 0).

We can now extend this algebra for two electrons in different states  $c_1^+ |0\rangle$  corresponds to particle 1 in state 1 and  $c_2^+ |0\rangle$  to particle 2 in state 2. The rule here is that  $c_i^+ c_j + c_j c_i^+ = \delta_{i,j}$ .

Finally we can write down the two particle hamiltonian as

$$H_{2p} = t_1 c_1^+ c_1 + t_2 c_2^+ c_2 - g c_1^+ c_1 c_2^+ c_2 \quad (202)$$

where  $t_i$  is the kinetic energy of particle  $i$  and  $g$  is the attraction between particle 1 and 2. We will also suppose that  $t_1 = t_2$  for the Cooper pair. The job now is to find the ground state of this Hamiltonian. Without interactions ( $g = 0$ ) we would simply have  $E = t_1 + t_2$ . The interaction term is what complicates the system since it leads to a quadratic term in the Hamiltonian. The idea is to simplify it by getting rid of the quadratic term. This is done in the following way. From eq. (202) we have

$$\begin{aligned} H &= t(c_1^+ c_1 + c_2^+ c_2) - g c_1^+ c_1 c_2^+ c_2 \\ &= t(c_1^+ c_1 + c_2^+ c_2) + g c_1^+ c_2^+ c_1 c_2 \\ &= t(c_1^+ c_1 + c_2^+ c_2) - g a (c_1 c_2 - c_1^+ c_2^+) + g a^2 \\ &\quad + \underbrace{g(c_1^+ c_2^+ + a)(c_1 c_2 - a)}_{\simeq 0 \text{ (Mean field approx.)}} \end{aligned} \quad (203)$$

$$\Rightarrow H_{MF} = t(c_1^+ c_1 + c_2^+ c_2) - g a (c_1 c_2 - c_1^+ c_2^+) + g a^2$$

We used the mean field approximation, which replaces  $c_1 c_2$  by its expectation value  $\langle a | c_1 c_2 | a \rangle = a \Rightarrow \langle a | c_1^+ c_2^+ | a \rangle = -a$ , where  $|a\rangle$  is the ground state of the Hamiltonian. The idea now is to diagonalize  $H_{MF}$ , i.e. a Hamiltonian in the form  $H = \sum_i c_i^+ c_i$ . The trick here is to use the Bogoliubov transformation:

$$\begin{aligned} &\begin{cases} c_1 = A_1 \cos(\theta) + A_2^+ \sin(\theta) \\ c_2^+ = -A_1 \sin(\theta) + A_2^+ \cos(\theta) \end{cases} \\ \Rightarrow &\begin{cases} A_1 = c_1 \cos(\theta) - c_2^+ \sin(\theta) \\ A_2^+ = c_1 \sin(\theta) + c_2^+ \cos(\theta) \end{cases} \end{aligned} \quad (204)$$

It is quite straightforward to see that  $A_i^+ A_j + A_j A_i^+ = \delta_{ij}$ ,  $A_i A_j + A_j A_i = 0$ , and  $A_i^+ A_j^+ + A_j^+ A_i^+ = 0$  using the properties of  $c_i$ . We can now rewrite  $H_{MF}$  in terms of our new operators  $A_i$ :

$$\begin{aligned} H_{MF} &= t(c_1^+ c_1 + c_2^+ c_2) - g a (c_1 c_2 - c_1^+ c_2^+) + g a^2 \\ &= t(A_1^+ \cos(\theta) + A_2 \sin(\theta))(\cos(\theta) A_1 + \sin(\theta) A_2^+) + \dots \\ &= (A_1^+ A_1 + A_2^+ A_2)(t \cos(2\theta) - g a \sin(2\theta)) \\ &\quad + t(1 - \cos(2\theta)) + g a \sin(2\theta) + g a^2 \\ &\quad + (A_1^+ A_2^+ - A_1 A_2) \underbrace{(t \sin(2\theta) + g a \cos(2\theta))}_{=0 \text{ to diagonalize } H_{MF}} \end{aligned} \quad (205)$$

Hence the diagonalization condition for  $H_{MF}$  fixes the angle  $\theta$  of our Bogoliubov transformation:

$$\tan(2\theta) = -\frac{g a}{t} \Rightarrow \sin(2\theta) = \frac{-g a}{\sqrt{t^2 + (g a)^2}} \quad (206)$$

Hence  $H_{MF}$  now becomes

$$H_{MF} = (A_1^+ A_1 + A_2^+ A_2) \sqrt{t^2 + (g a)^2} + (t - \sqrt{t^2 + (g a)^2}) + g a^2 \quad (207)$$

It is now immediate to obtain the solutions of the Hamiltonian, since we have the ground state  $|a\rangle$  and we have a diagonal Hamiltonian in terms of  $A_i$  hence the Ground state energy  $E_0$  is simply given by  $H_{MF}|a\rangle = E_0|a\rangle$  and  $A_i|a\rangle = 0$ . The first degenerate excited states are  $A_i^+|a\rangle$  with energy  $E_1$ , where  $H_{MF} A_i^+|a\rangle = E_1 A_i^+|a\rangle$  and the next energy level and state is  $A_1^+ A_2^+|a\rangle$ , with energy  $E_2$  given by  $H_{MF} A_1^+ A_2^+|a\rangle = E_2 A_1^+ A_2^+|a\rangle$ , hence

$$\begin{aligned} E_2 &= t + \sqrt{t^2 + (g a)^2} + g a^2 \\ E_1 &= t + g a^2 \\ E_0 &= t - \sqrt{t^2 + (g a)^2} + g a^2 \end{aligned} \quad (208)$$

If we take  $t \rightarrow 0$  and define  $\Delta = g a$  we have

$$\begin{cases} E_2 = \Delta + g a^2 \\ E_1 = g a^2 \\ E_0 = -\Delta + g a^2 \end{cases} \quad (209)$$

We can now turn to what  $a$  is since,

$$\begin{aligned} a &= \langle a | c_1 c_2 | a \rangle \\ &= -\cos(\theta) \sin(\theta) \langle a | A_1 A_1^+ | a \rangle \\ &= -\cos(\theta) \sin(\theta) \underbrace{\langle a | a \rangle}_{=1} \\ \Rightarrow a &= -\sin(2\theta)/2 \end{aligned} \quad (210)$$



Combining (206) and (210) we obtain

$$2a = \frac{ga}{\sqrt{t^2 + (ga)^2}} \quad (211)$$

which is the famous BCS gap ( $\Delta$ ) equation. Indeed, it has two solutions,

$$\begin{aligned} a = 0 &\Rightarrow \langle a|c_1c_2|a\rangle = 0 \Rightarrow \text{Normal} \\ a \neq 0 &\Rightarrow \underbrace{t^2 + (ga)^2 = g^2/4}_{\Delta=ga=\sqrt{g^2/4-t^2}} \Rightarrow \text{Superconductor} \end{aligned} \quad (212)$$

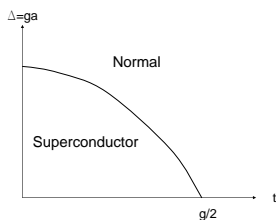


FIG. 40: The gap of a BCS superconductor as function of the kinetic energy.

This gives us the condition for superconductivity  $g \geq 2t$ . Hence the attraction between our two electrons has to be strong enough in order to form the superconducting gap  $\Delta$ . Typically,  $t$  is directly related to the temperature, hence there is a superconducting transition as a function of temperature.

We now want to find the expression for our superconducting wavefunction  $|a\rangle$ . The most general possible form is

$$|a\rangle = \alpha|0\rangle + \beta_1c_1^\dagger|0\rangle + \beta_2c_2^\dagger|0\rangle + \gamma c_1^\dagger c_2^\dagger|0\rangle \quad (213)$$

In addition the condition  $A_i|a\rangle = 0$  has to be verified, which leads after some algebra to

$$|a\rangle = \alpha(1 + \tan(\theta)c_1^\dagger c_2^\dagger)|a\rangle \quad (214)$$

This state clearly describes an electron pair, the Cooper pair and represents the superconducting ground state of the Hamiltonian. In our derivation we only considered two electrons, but this framework can be generalized to  $N$  electrons, where the generalized BCS Hamiltonian can be written as

$$H_{BCS} = \sum_{k,\sigma} t_k c_{k,\sigma}^\dagger \underbrace{c_{k,\sigma}}_{\text{spin}} - \sum_q V_q c_{k+q,\uparrow}^\dagger c_{-k+q,\downarrow}^\dagger c_{k,\uparrow} c_{-k,\downarrow} \quad (215)$$

Here  $V_q$  is positive and represents the effective phonon induced attraction between electrons at the Fermi level. It's maximum for  $q = 0$ . The second term describes the process of one electron with momentum  $k$  and another electron with momentum  $-k$  which are annihilated in order to create one electron with momentum  $k + q$  and

another one with momentum  $-k - q$ , hence momentum is conserved in this scattering process and a phonon with momentum  $q$  is exchanged.

How can we relate BCS theory to the observed Meissner effect? By including the vector potential  $\vec{A}$  into the BCS Hamiltonian it is possible to show that the current density is then given by

$$\vec{j} = \frac{ne^2}{mc} \vec{A} \quad (216)$$

The magnetic induction is  $\vec{B} = \vec{\nabla} \times \vec{A}$  as usual. This is in fact London's equation for superconductivity. We can now take the rotational on both sides of (216), hence

$$\begin{aligned} \vec{\nabla} \times \underbrace{\vec{j}}_{\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{j}} &= \frac{ne^2}{mc} \vec{\nabla} \times \vec{A} \\ \Rightarrow \vec{\nabla} \times \vec{\nabla} \times \vec{B} &= -\frac{4\pi ne^2}{mc^2} \vec{B} \\ \Rightarrow B_x &\sim e^{-x/\lambda_L} \end{aligned} \quad (217)$$

with  $\lambda_L = \sqrt{\frac{mc^2}{4\pi ne^2}}$  which is the London penetration length.

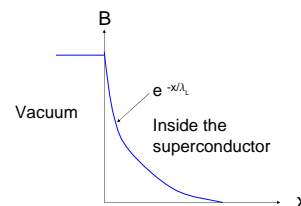


FIG. 41: The decay of the magnetic field inside the superconductor. The decay is characterized by the London penetration length  $\lambda_L$ .

If we had a perfect conductor, this would imply that the current would simply keep on increasing with an external field  $\vec{E}$ , hence

$$\begin{aligned} \frac{\partial \vec{j}}{\partial t} &= \frac{ne^2}{mc} \vec{E} \\ \Rightarrow \frac{\partial}{\partial t} \vec{\nabla} \times \vec{j} &= \frac{ne^2}{mc} \vec{\nabla} \times \vec{E} \\ \Rightarrow \frac{\partial}{\partial t} \vec{\nabla} \times \vec{\nabla} \times \vec{B} &= \frac{\partial}{\partial t} \frac{4\pi ne^2}{mc^2} \vec{B} \end{aligned} \quad (218)$$

This equation is automatically verified from (217). Hence, (217) implies both the Meissner effect and zero resistance, which are the main ingredients of superconductivity. (Reminder: Maxwell gives  $\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{j}$  and  $\vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}$ ).

A remarkable aspect of superconductivity is that one of the most fundamental symmetries is broken. Indeed, Gauge invariance is broken because  $\vec{j} \sim \vec{A}$ . What happens is that below  $T_c$  we have a symmetry breaking, which leads to new particles, the Cooper pairs. Mathematically, we have

$$\underbrace{U(2)}_{\text{Normal state}} = \underbrace{SU(2)}_{\text{SC state}} \otimes \underbrace{U(1)}_{\text{Gauge invariance}}, \quad (219)$$

where  $U(1) \Leftrightarrow c \rightarrow ce^{i\alpha}$  (Gauge invariance),  $U(2) \Leftrightarrow c \rightarrow Ac$  ( $A = e^{i\phi/2}a$ ) and  $a^+a = 1$ ,  $SU(2) \Leftrightarrow \phi = 0$ .