Condensed Matter I. Phys 631

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This lecture notes are based on "Introduction to Modern Solid State Physics" by Yuri M. Galperin. I am very grateful to Dr. Galperin for allowing me to use his materials, which the majority of this lecture notes is based upon. I am also very grateful to Peter Young for giving me his materials on De Haas-van Alphen effect.

Contents

PART 1

Basic concepts

LECTURE 1

Periodicity: Crystal Structures

In this lecture we review the general static properties of crystals, as well as possibilities to observe crystal structures. This material should be familiar from Phys 617. We emphasize basic principles of the crystal structure description. More detailed information can be obtained, e.g., from the books [**1, 4, 5**].

Most of solid materials possess crystalline structure that means *spatial periodicity* or *translation symmetry.* All the lattice can be obtained by repetition of a building block called *basis.* We assume that there are 3 non-coplanar vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ that leave *all the properties* of the crystal unchanged after the shift as a whole by any of those vectors. As a result, any lattice point $\mathbf{R}'$ could be obtained from another point $\mathbf{R}$ as

$$\mathbf{R}' = \mathbf{R} + m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3 \tag{1.1}$$

where m_i are integers. Such a lattice of building blocks is called the *Bravais lattice.* The crystal structure could be understood by the combination of the propertied of the building block (basis) and of the Bravais lattice. Note that

- There is no unique way to choose $\mathbf{a}_i$. We choose $\mathbf{a}_1$ as *shortest* period of the lattice, $\mathbf{a}_2$ as the shortest period not parallel to $\mathbf{a}_1$, $\mathbf{a}_3$ as the shortest period not coplanar to $\mathbf{a}_1$ and $\mathbf{a}_2$.
- Vectors $\mathbf{a}_i$ chosen in such a way are called *primitive.*
- The volume cell enclosed by the primitive vectors is called the *primitive unit cell.*
- The volume of the primitive cell is $\mathcal{V}_0$

$$\mathcal{V}_0 = (\mathbf{a}_1[\mathbf{a}_2\mathbf{a}_3]) \tag{1.2}$$

The natural way to describe a crystal structure is a set of *point group* operations which involve operations applied around a point of the lattice. We shall see that symmetry provide important restrictions upon vibration and electron properties (in particular, spectrum degeneracy). Usually are discussed:

- **Rotation**, C_n: Rotation by an angle $2\pi/n$ about the specified axis. There are *restrictions* for n. Indeed, for even n, if a is the lattice constant, the quantity $b = a + 2a\cos\phi = n'a$ (see Fig. 1) Consequently, $\cos\phi = (n'-1)/2$, where n' is some integer (See *problem* 2.2).

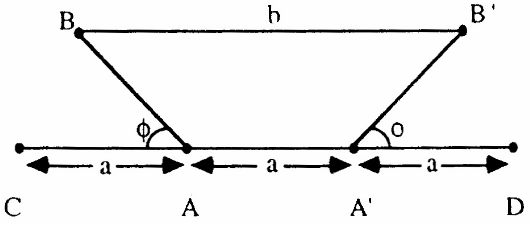


Figure 1. On the determination of rotation symmetry

- **Inversion**, I: Transformation $\mathbf{r} \to -\mathbf{r}$, fixed point is selected as origin (lack of inversion symmetry may lead to piezoelectricity);

- **Reflection**, σ: Reflection across a plane;
- **Improper Rotation**, S_n: Rotation C_n, followed by reflection in the plane normal to the rotation axis.

1.1. Examples

Now we discuss few examples of the lattices.

1.1.1. One-Dimensional Lattices - Chains

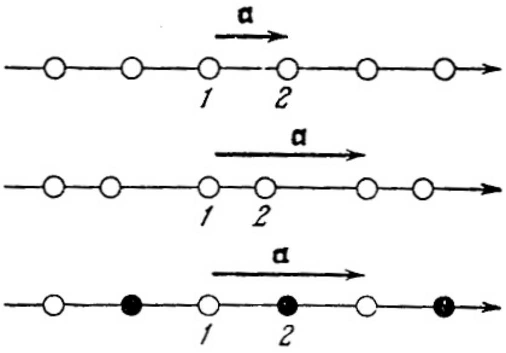


Figure 2. One dimensional lattices

1D chains are shown in Fig. 2. We have only 1 translation vector $|\mathbf{a}_1| = a$, $\mathcal{V}_0 = a$. White and black circles are the atoms of different kind. a is a *primitive* lattice with one atom in a primitive cell; b and c are *composite* lattice with two atoms in a cell.

1.1.2. Two-Dimensional Lattices

The are 5 basic classes of 2D lattices (see Fig. 3)

1.1.3. Three-Dimensional Lattices

There are 14 types of lattices in 3 dimensions. They are shown in Fig. 4. The types of lattices differ by the relations between the lengths a_i and the angles α_i.

We will concentrate on cubic lattices which are very important for many materials.

1.1.3.1. *Cubic and Hexagonal Lattices.* The *cubic* lattices are shown on the last row of Fig. 4. In the *primitive cubic* lattice there is 1 atom per primitive cell. In the *body centered cubic lattice* there are $1/8 \times 8 + 1 = 2$ atoms per cell. In the *face-centered lattice* there are $1/8 \times 8 + 1/2 \times 6 = 4$ atoms per cell. The row above the last on Fig. 4 shows hexagonal cell.

We shall see that discrimination between simple and complex lattices is important, say, in analysis of lattice vibrations.

1.1.4. The Wigner-Seitz cell

As we have mentioned, the procedure of choose of the elementary cell is not unique and sometimes an arbitrary cell does not reflect the symmetry of the lattice (see, e. g., Fig. 5, where specific choices for cubic lattices are shown). There is a very convenient procedure to choose the cell which reflects the symmetry of the lattice. The procedure is as follows:

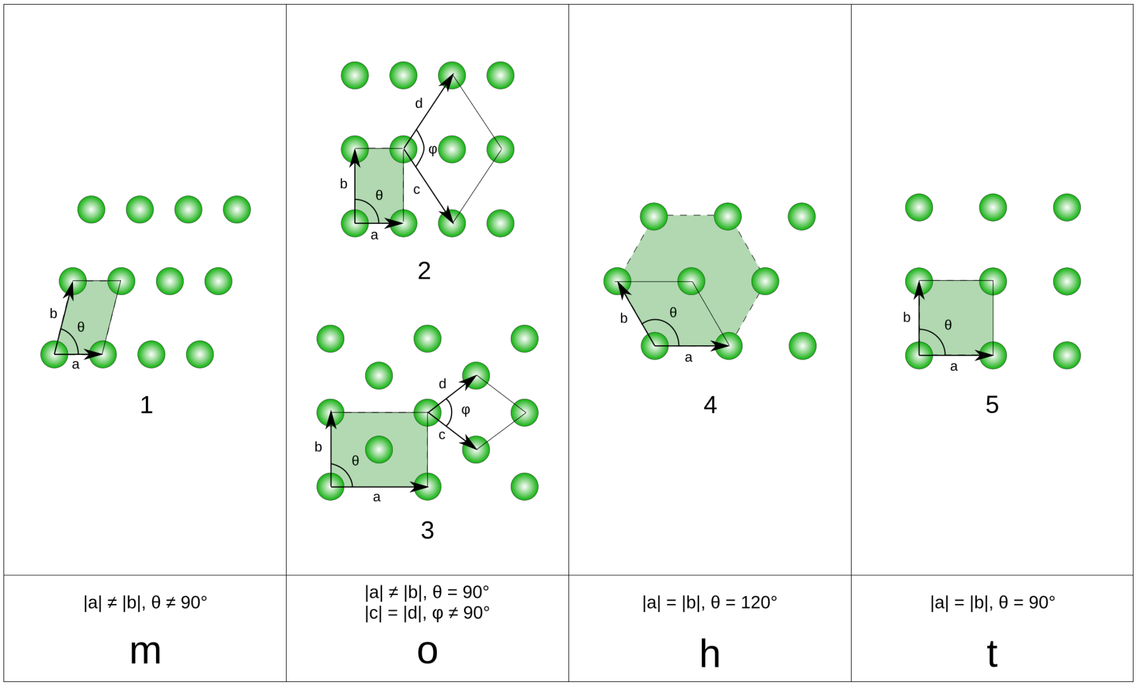


Figure 3. The five classes of 2D lattices. 1 – oblique (monoclinic), 2 – rectangular (orthorhombic), 3 – centered rectangular (orthorhombic), 4 – hexagonal, and 5 – square (tetragonal).
The figure is made by Prolineserver - Own work, CC BY-SA 3.0,
`https://commons.wikimedia.org/w/index.php?curid=3912829`

(a) Draw lines connecting a given lattice point to all neighboring points.
(b) Draw bisecting lines (or planes) to the previous lines.

The procedure is outlined in Fig. 6. For complex lattices such a procedure should be done for one of simple sublattices. We shall come back to this procedure later analyzing electron band structure.

1.2. The Reciprocal Lattice

The crystal periodicity leads to many important consequences. Namely, all the properties, say electrostatic potential V, are periodic

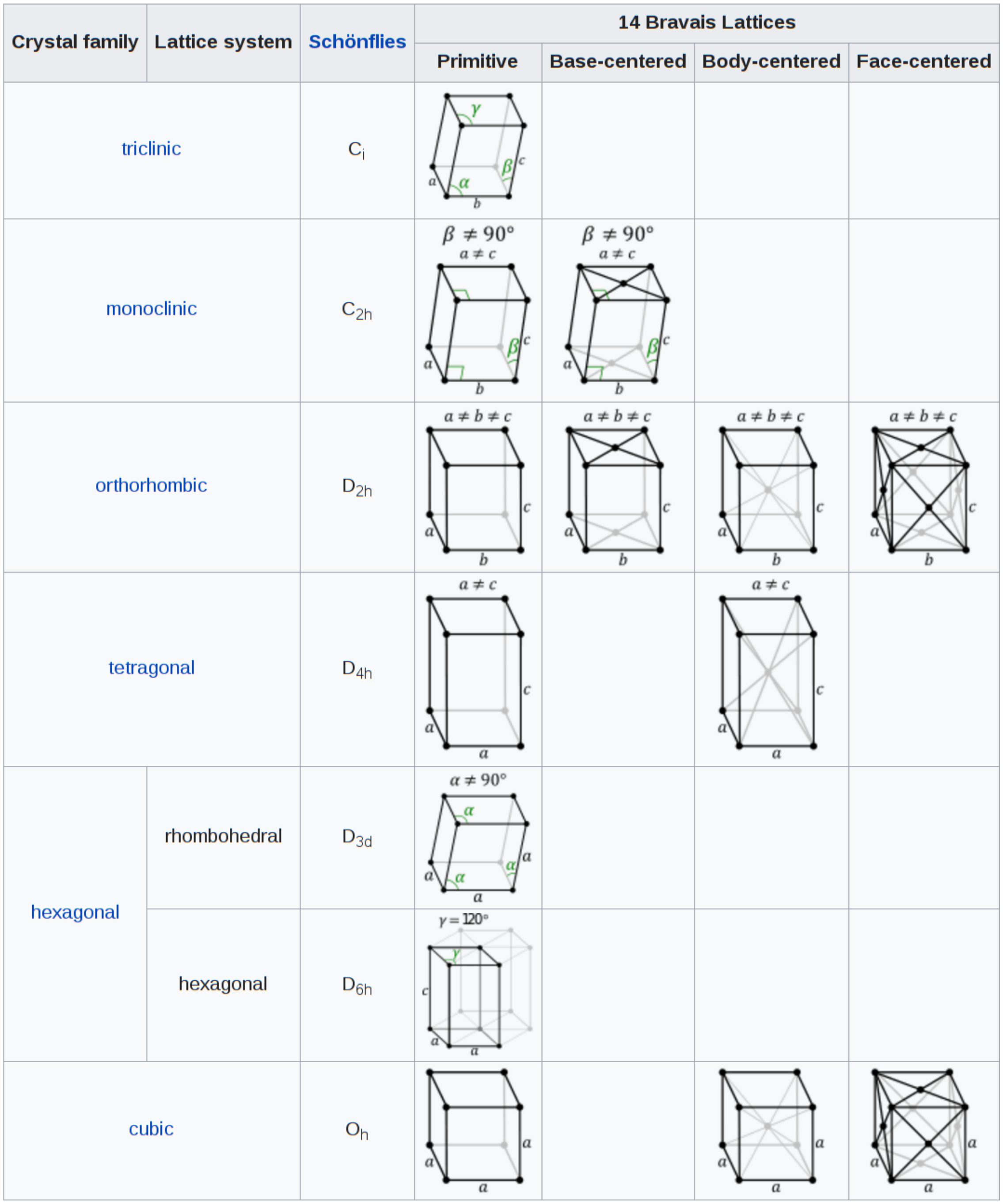
$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{a}_{\mathrm{n}}), \quad \mathbf{a}_n \equiv n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_2\mathbf{a}_3\,. \tag{1.3}$$

It implies the Fourier transform. Usually the *oblique* co-ordinate system is introduced, the axes being directed along $\mathbf{a}_i$. If we denote co-ordinates as ξ_s having periods a_s we get

$$V(\mathbf{r}) = \sum_{k_1,k_2,k_3=-\infty}^{\infty} V_{k_1,k_2,k_3} \exp\left[2\pi i \sum_s \frac{k_s\xi_s}{a_s}\right], \tag{1.4}$$

where k_1, k_2, and k_3 are integers. Then we can return to Cartesian co-ordinates by the transform

$$\xi_i = \sum_k \alpha_{ik} x_k \tag{1.5}$$



Crystal family	Lattice system	Schönflies	14 Bravais Lattices			
			Primitive	Base-centered	Body-centered	Face-centered
triclinic		C_i				
monoclinic		C_{2h}	$\beta \neq 90°$ $a \neq c$	$\beta \neq 90°$ $a \neq c$		
orthorhombic		D_{2h}	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$
tetragonal		D_{4h}	$a \neq c$		$a \neq c$	
hexagonal	rhombohedral	D_{3d}	$\alpha \neq 90°$			
	hexagonal	D_{6h}	$\gamma = 120°$			
cubic		O_h				

Figure 4. All 14 $3D$ Bravais lattices.
The figure is taken from the Wikipedia `https://en.wikipedia.org/wiki/Bravais_lattice`.

Finally we get

$$V(\mathbf{r}) = \sum_{\mathbf{b}} V_{\mathbf{b}} e^{i\mathbf{br}} . \tag{1.6}$$

From the condition of periodicity (1.3) we get

$$V(\mathbf{r} + \mathbf{a}_n) = \sum_{\mathbf{b}} V_{\mathbf{b}} e^{i\mathbf{br}} e^{i\mathbf{ba}_n} . \tag{1.7}$$

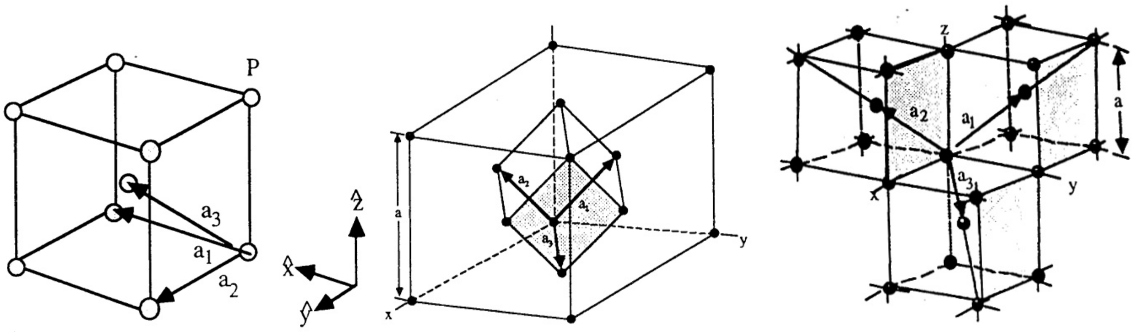


Figure 5. Primitive vectors for bcc (left panel) and fcc (middle panel) lattices. The right panel shows more symmetric choice of lattice vectors for bcc lattice.

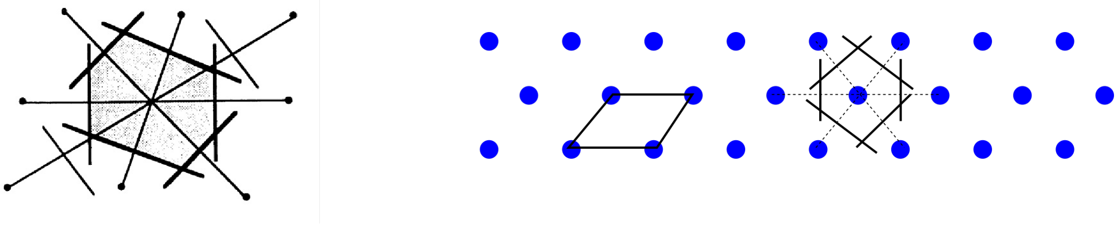


Figure 6. To the determination of Wigner-Seitz cell.

We see that $e^{i\mathbf{b}\mathbf{a}_n}$ should be equal to 1, that could be met at

$$\mathbf{b}\mathbf{a}_1 = 2\pi g_1, \quad \mathbf{b}\mathbf{a}_2 = 2\pi g_2, \quad \mathbf{b}\mathbf{a}_3 = 2\pi g_3 \tag{1.8}$$

where g_i are integers. It could be shown (see *Problem 2.4*) that

$$\mathbf{b}_{\mathrm{g}} \equiv \mathbf{b} = g_1\mathbf{b}_1 + g_2\mathbf{b}_2 + g_3\mathbf{b}_3 \tag{1.9}$$

where

$$\mathbf{b}_1 = \frac{2\pi[\mathbf{a}_2\mathbf{a}_3]}{\mathcal{V}_0}, \quad \mathbf{b}_2 = \frac{2\pi[\mathbf{a}_3\mathbf{a}_1]}{\mathcal{V}_0}, \quad \mathbf{b}_3 = \frac{2\pi[\mathbf{a}_1\mathbf{a}_2]}{\mathcal{V}_0}\,. \tag{1.10}$$

It is easy to show that scalar products

$$\mathbf{a}_i\mathbf{b}_k = 2\pi\delta_{i,k}\,. \tag{1.11}$$

Vectors $\mathbf{b}_k$ are called the basic vectors of the *reciprocal lattice*. Consequently, one can construct reciprocal lattice using those vectors, the elementary cell volume being $(\mathbf{b}_1[\mathbf{b}_2, \mathbf{b}_3]) = (2\pi)^3/\mathcal{V}_0$.

1.2.0.1. *Reciprocal Lattices for Cubic Lattices.* Simple cubic lattice (sc) has simple cubic reciprocal lattice with the vectors' lengths $b_i = 2\pi/a_i$. Now we demonstrate the general procedure using as examples body centered (bcc) and face centered (fcc) cubic lattices.

First we write lattice vectors for bcc as

$$\begin{aligned}\mathbf{a}_1 &= \frac{a}{2}(\mathbf{y}+\mathbf{z}-\mathbf{x})\,,\\ \mathbf{a}_2 &= \frac{a}{2}(\mathbf{z}+\mathbf{x}-\mathbf{y})\,,\\ \mathbf{a}_1 &= \frac{a}{2}(\mathbf{x}+\mathbf{y}-\mathbf{z})\end{aligned}$$

(1.12)

where unit vectors **x**, **y**, **z** are introduced (see the right panel of Fig.5). The volume of the cell is $\mathcal{V}_0 = a^3/2$. Making use of the definition (1.10) we get

$$\begin{aligned}\mathbf{b}_1 &= \frac{2\pi}{a}(\mathbf{y}+\mathbf{z})\,,\\ \mathbf{b}_2 &= \frac{2\pi}{a}(\mathbf{z}+\mathbf{x})\,,\\ \mathbf{b}_1 &= \frac{2\pi}{a}(\mathbf{x}+\mathbf{y})\end{aligned}$$

(1.13)

One can see from the middle panel of Fig. 5 that they form *a face-centered* cubic lattice. So we can get the Wigner-Seitz cell for bcc reciprocal lattice (later we will see that this cell bounds the 1st Brillouin zone for vibration and electron spectrum). It is shown in Fig. 7 (left panel). In a very similar way one can show that *bcc lattice is the reciprocal to the fcc one.* The corresponding Wigner-Seitz cell is shown in the right panel of Fig. 7.

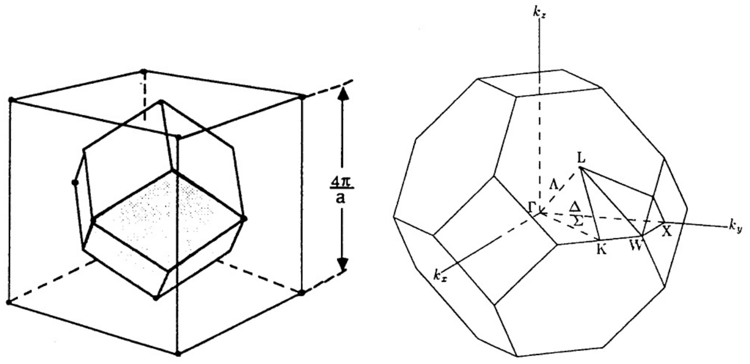


Figure 7. The Wigner-Seitz cell for the bcc (left panel) and for the fcc (right panel) lattices.

LECTURE 2
X-Ray Diffraction in Periodic Structures

2.1. The Laue Condition

Consider a plane wave of wave vector $\mathbf{k}$ and frequency ω at time t and coordinate $\mathbf{r}'$ is described as

$$\mathbf{F}(\mathbf{r}) = \mathbf{F}_0 \exp\left[i(\mathbf{k}\cdot\mathbf{r}' - \omega t)\right] \tag{2.1}$$

which acts upon a periodic structure. Each atom placed at the point $\boldsymbol{\rho}$ produces a scattered spherical wave

$$\mathbf{F}_{sc}(\mathbf{r}) = \mathbf{F}(\boldsymbol{\rho}) f \frac{e^{ikr}}{r} = \mathbf{F}_0 f \frac{e^{i\mathbf{k}\boldsymbol{\rho}} e^{i(kr-\omega t)}}{r} = \mathbf{F}_0 f \frac{e^{i(\mathbf{k}\boldsymbol{\rho}+kr)}}{r} e^{i\omega t} \tag{2.2}$$

where $r^2 = R^2 + \rho^2 - 2\boldsymbol{\rho}\mathbf{R}$, where $\mathbf{R}$ is the detector position (see Fig. 1). In a typical experiment $R \approx r \gg \rho$, so $r \approx R - \frac{\boldsymbol{\rho}\mathbf{R}}{R}$. In the denominator of Eq. (2.2) we replace r by R, as $r \approx R$ The phase needs more accurate treatment, as it is in exponent:

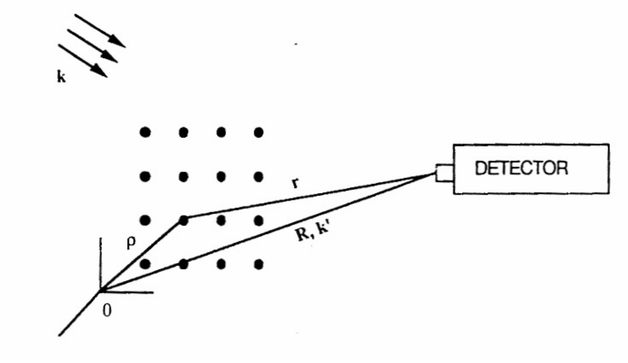


Figure 1. Geometry of scattering by a periodic atomic structure.

$$\mathbf{k}\boldsymbol{\rho} + kr = \mathbf{k}\boldsymbol{\rho} + kR - k\frac{\boldsymbol{\rho}\mathbf{R}}{R}. \tag{2.3}$$

Let's introduce vector $\mathbf{k}'$, which has the direction of $\mathbf{R}$ and the absolute value of $|\mathbf{k}|$. The vector $\mathbf{k}'$ is the scattered vector in the direction of $\mathbf{R}$.

$$\mathbf{k}' = \mathbf{R}\frac{k}{R}$$

then

$$k\frac{\boldsymbol{\rho}\mathbf{R}}{R} = \boldsymbol{\rho}\mathbf{k}'$$

Finally, the phase is

$$\mathbf{k}\boldsymbol{\rho} + kr = kR - \boldsymbol{\rho}\Delta\mathbf{k}, \quad \Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}.$$

So the scattered wave from a single atom is

$$\mathbf{F}_{sc}(\mathbf{r}) = f\mathbf{F}_0\frac{e^{i(kR-\omega t)}}{R}e^{-i\boldsymbol{\rho}\Delta\mathbf{k}}.$$

Now we can sum the contributions of all the atoms

$$\mathbf{F}_{sc}(\mathbf{R}) = \sum_{m,n,p} f_{m,n,p}\left(\mathbf{F}_0\frac{e^{i(kR-\omega t)}}{R}\right)\left[\exp(-i\boldsymbol{\rho}_{m,n,p}\Delta\mathbf{k})\right] \tag{2.4}$$

If all the atoms in the lattice are the same, then scattering factors $f_{m,n,p}$ are equal to each other and only the phase factors are important. Strong diffraction takes place when all phases are the same (constructive interference)

$$\boldsymbol{\rho}_{m,n,p}\Delta\mathbf{k} = 2\pi n \tag{2.5}$$

with integer n. The condition (2.5) for $\Delta\mathbf{k}$ is *just the same* as the definition of the reciprocal vectors. So, scattering is strong if the transferred momentum proportional to the reciprocal lattice factor. Note that the Laue condition (2.5) is just the same as the famous Bragg condition of strong light scattering by periodic gratings.

2.2. Scattering factor f_{mnp}

Now we come to the situation with complex lattices where there are more than 1 atoms per basis. To discuss this case we introduce

- The co-ordinate $\boldsymbol{\rho}_{mnp}$ of the initial point of unit cell (see Fig. 2).
- The co-ordinate $\boldsymbol{\rho}_j$ for the position of jth atom in the unit cell.

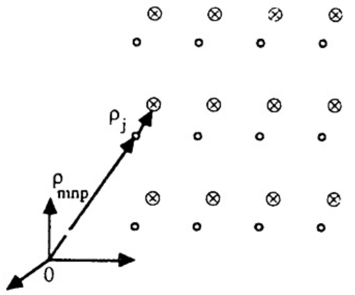


Figure 2. Scattering from a crystal with more than one atom per basis.

Coming back to our derivation (2.4)

$$\mathbf{F}_{sc}(\Delta\mathbf{k}) = \mathbf{F}_0\frac{e^{i(kR-\omega t)}}{R}\sum_{m,n,p}\sum_{j} f_j \exp\left[-i(\boldsymbol{\rho}_{m,n,p} + \boldsymbol{\rho}_j)\Delta\mathbf{k}\right] \tag{2.6}$$

where f_j are in general different for different atoms in the cell. Now we can extract the sum over the cell for $\Delta\mathbf{k} = \mathbf{G}$ which is called the *structure factor*:

$$S_{\mathbf{G}} = \sum_j f_j \exp\left[-i\boldsymbol{\rho}_j \mathbf{G}\right] . \tag{2.7}$$

The first sum is just the same as the result for the one-atom lattice.

$$\mathbf{F}_{sc}(\mathbf{G}) = \mathbf{F}_0 \frac{e^{i(kR-\omega t)}}{R} S_{\mathbf{G}} \sum_{m,n,p} \exp\left[-i\boldsymbol{\rho}_{m,n,p}\mathbf{G}\right]$$

So, we come to the rule

- *The X-ray pattern can be obtained by the product of the result for lattice sites times the structure factor.*

2.2.1. Example: The Diamond and Zinc-Blend Lattices

To make a simple example we discuss the lattices with a two-atom basis (see Fig. 3) which are important for semiconductor crystals. The co-ordinates of two basis atoms are (000) and (a/4)(111), so we have:

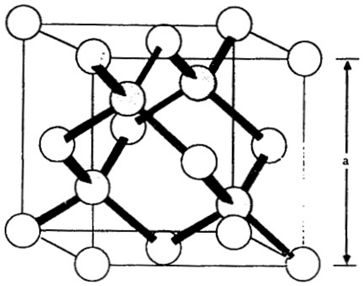


Figure 3. The two-atomic structure of inter-penetrating fcc lattices.

- 2 inter-penetrating fcc lattices shifted by a distance $(a/4)(111)$ along the body diagonal.
- If atoms are identical, the structure is called the *diamond* structure (elementary semiconductors: Si, Ge, and C).
- If the atoms are different, it is called the *zinc-blend structure* (GaAs, AlAs, and CdS).

For the diamond structure

$$\begin{aligned} \boldsymbol{\rho}_1 &= 0 \\ \boldsymbol{\rho}_2 &= \frac{a}{4}(\mathbf{x}+\mathbf{y}+\mathbf{z}) . \end{aligned} \tag{2.8}$$

We also have introduced the reciprocal vectors (see *Problem 2.5*)

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{a}(-\mathbf{x}+\mathbf{y}+\mathbf{z}) , \\ \mathbf{b}_2 &= \frac{2\pi}{a}(-\mathbf{y}+\mathbf{z}+\mathbf{x}) , \\ \mathbf{b}_3 &= \frac{2\pi}{a}(-\mathbf{z}+\mathbf{x}+\mathbf{y}) , \end{aligned}$$

the general reciprocal vector being

$$\mathbf{G} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3.$$

Consequently,

$$S_{\mathrm{G}} = f\left(1 + \exp\left[\frac{i\pi}{2}(n_1+n_2+n_3)\right]\right).$$

It is equal to

$$S_{\mathrm{G}} = \left[\begin{array}{ll} 2f\,, & n_1+n_2+n_3 = 4k\,; \\ (1\pm i)f\,, & n_1+n_2+n_3 = (2k+1)\,; \\ 0\,, & n_1+n_2+n_3 = 2(2k+1)\,. \end{array}\right. \tag{2.9}$$

So, the diamond lattice has some spots missing in comparison with the fcc lattice.

In the zinc-blend structure the atomic factors f_i are different and we should come to more understanding what do they mean. Namely, for X-rays they are due to Coulomb charge density and are proportional to the Fourier components of local charge densities. In this case one has instead of (2.9)

$$S_{\mathrm{G}} = \left[\begin{array}{ll} f_1+f_2\,, & n_1+n_2+n_3 = 4k\,; \\ (f_1 \pm i f_2)\,, & n_1+n_2+n_3 = (2k+1)\,; \\ f_1 - f_2\,, & n_1+n_2+n_3 = 2(2k+1)\,. \end{array}\right. \tag{2.10}$$

We see that one can extract a lot of information on the structure from X-ray scattering.

2.3. Temperature Dependent Effects

Now we discuss the role of thermal vibration of the atoms. The position of an atom is

$$\boldsymbol{\rho}(t) = \boldsymbol{\rho}_0 + \mathbf{u}(t)$$

where $\mathbf{u}(t)$ is the time-dependent displacement due to vibrations. So, we get an extra phase shift $\Delta\mathbf{k}\,\mathbf{u}(t)$ of the scattered wave. In the experiments, the average over vibrations is observed (the typical vibration frequency is 10^{12} s^{-1}). Since $u(t)$ is small,

$$\langle \exp(-i\mathbf{G}\mathbf{u})\rangle = 1 - i\,\langle \mathbf{G}\mathbf{u}\rangle - \frac{1}{2}\left\langle (\mathbf{G}\mathbf{u})^2\right\rangle + \dots$$

The second item is equal to zero, while the third is

$$\left\langle (\mathbf{G}\mathbf{u})^2\right\rangle = \frac{1}{3}\mathbf{G}^2\left\langle u^2\right\rangle$$

(the factor 1/3 comes from geometric average).

Finally, with some amount of cheating [1] we get

$$\langle \exp(-i\mathbf{G}\mathbf{u})\rangle \approx \exp\left[-\frac{\mathbf{G}^2\left\langle \mathbf{u}^2\right\rangle}{6}\right].$$

so we get (intensity is proportional to the square of the amplitude)

$$I_{sc} = I_0 e^{-G^2\left\langle u^2\right\rangle/3} \tag{2.11}$$

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[1] We have used the expression $1 - x = \exp(-x)$ which in general is not true. Nevertheless there is *exact* theorem $\langle \exp(i\varphi)\rangle = \exp\left[-\left\langle (\varphi)^2\right\rangle/2\right]$ for any Gaussian fluctuations with $\langle\varphi\rangle = 0$.

where I_0 is the intensity from the perfect lattice with points $\boldsymbol{\rho}_0$. From the pure classical considerations,[2]

$$\left\langle u^2 \right\rangle = \frac{3k_BT}{m\omega^2}$$

where ω is the lattice vibrations frequency (10^{13}–10^{14} s^{-1}). Thus,

$$I_{sc} = I_0 \exp\left[-\frac{k_BTG^2}{m\omega^2}\right]. \tag{2.12}$$

According to quantum mechanics, even at zero temperature there are zero-point vibrations with[3]

$$\left\langle u^2 \right\rangle = \frac{3\hbar}{2m\omega}\,.$$

In this case

$$I_{sc} = I_{0R} \exp\left[-\frac{\hbar G^2}{2m\omega}\right] \tag{2.13}$$

where I_{0R} is the intensity for a rigid classical lattice. For $T = 300K,\ G = 10^9 cm^{-1},\ \omega = 2\pi \cdot 10^{14}\ \mathrm{s}^{-1}$, $m = 10^{-22}$ g the exponential factor is ~ 0.99.

It means that vibrations do not destroy the diffraction pattern which can be studied even at high enough temperatures.

At the present time, many powerful diffraction methods are used, in particular, neutron diffraction. For low-dimensional structures the method of *reflection high energy electron diffraction* (RHEED) is extensively used.

2.4. Role of Disorder

The effect of the disorder is very different from the effect of temperature. The result for a $3D$ lattice is very complicated and is described by what is called *rocking curve* or *mosaicity.*

In order to understand the effect we will consider a $1D$ chain of scattering centers (atoms). The atoms are on average at distance a from each other. The disorder is modeled by assuming that the true distance is a little different. So that the distance between the atoms n and $n+1$ is $a + \delta a_n$, where δa_n are randomly distributed. For simplicity we will also assume that δa_n are independent from each other and distributed by Gauss distribution with $\langle \delta a_n \rangle = 0$ and $\langle (\delta a_n)^2 \rangle = \sigma$.

$$\mathcal{P}(\delta a_n) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(\delta a_n)^2}{2\sigma}}$$

- Notice, that this is very different from the thermal noise, as a typical shift of the N atom grows as $\sqrt{N}$.[4]

The scattering *intensity* is proportional to the amplitude squared, and we need to average the *intensity*!

- Although for a given crystal all δa_ns are fixed, we can consider a large crystal as a collection of small crystals each with its own δa_ns – this justifies the averaging.

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[2] $\langle E \rangle = m\omega^2 \left\langle u^2 \right\rangle / 2 = 3k_BT/2$.

[3] $\langle E \rangle = 3\hbar\omega/4$.

[4] Disorder means, that the lattice is not at equilibrium.

For a scattering vector k we thus need to compute (x_n is the position of the ns atom)

$$I_{sc} \propto \left\langle \left| \sum_n e^{ikx_n} \right|^2 \right\rangle = \langle \sum_{n,n'} e^{ik(x_n - x_{n'})} \rangle.$$

For our crystal $x_n = a(n-1) + \sum_{j=1}^{n-1} \delta a_j$, so we have

$$I_{sc} \propto \langle \sum_{n,n'} e^{ika(n-n') + ik\sum_{j=n'}^{n-1} \delta a_j} \rangle = \sum_{n,n'} e^{ika(n-n')} \langle e^{ik\sum_{j=n'}^{n-1} \delta a_j} \rangle = \sum_{n,n'} e^{ika(n-n')} \langle e^{\pm ik\delta a_j} \rangle^{|n-n'|}$$

The averaging is a simple Gaussian integral, the result is

$$I_{sc} \propto \sum_{n,n'} e^{ika(n-n') - \frac{k^2\sigma}{2}|n-n'|}.$$

Now let's look at around a reciprocal k_0, so $k = k_0 + \Delta k$, where $\Delta k \ll k_0$. In the first term in the exponent we have $e^{ika(n-n')} = e^{ia\Delta k(n-n')}$, as $k_0 a = 2\pi$. In the second term in the exponent σ is already small, so we can just substitute k_0 instead of k, so we have

$$I_{sc} \propto N \operatorname{Re} \sum_n e^{-(-i\Delta ka + \frac{k_0^2\sigma}{2})n} \approx 2N \operatorname{Re} \frac{1}{\frac{k_0^2\sigma}{2} - i\Delta ka} = \frac{Nk_0^2\sigma}{\left(\frac{k_0^2\sigma}{2}\right)^2 + (a\Delta k)^2}.$$

Notice:

- The typical spread of a peak is $\Delta k \sim \frac{k_0^2\sigma}{2a} \ll k_0$.
- In case $\sigma \to 0$ using $\frac{\delta}{\delta^2 + x^2} \xrightarrow[\delta \to 0]{} \pi\delta(x)$ we see, that the shape is just a δ-function.
- The shape is not Gaussian, but Lorenzian. It means much larger background.

The difference with the temperature case is in correlations. Let's introduce $\Delta x_n = x_n - (n-1)a$ and look at $\langle \Delta x_n \Delta x_{n'} \rangle$. We see, that it is not zero.

A finite note: without the disorder the peaks would be very sharp. In fact they would be so sharp that modern device resolution would not be enough to see them as the broadening due to the finite size of the sample would be too small.

2.5. Broadening due to finite size.

Another source of broadening is a finite size of the sample (important for small semiconductor samples). To get an impression let us consider a chain of N atoms separated by a distance a. We get

$$\left| \sum_{n=0}^{N-1} \exp(ina\Delta k) \right|^2 \propto \frac{\sin^2(Na\Delta k/2)}{\sin^2(a\Delta k/2)}. \tag{2.14}$$

This function has maxima at $a\Delta k = 2m\pi$ equal to N^2 (l'Hopital's rule) the width being $\Delta k' a = 2.76/N$ (see *Problem 2.6*).

2.6. Experimental Methods

Here we review few most important experimental methods to study scattering. Most of them are based on the simple geometrical *Ewald construction* (see Fig. 4) for the vectors satisfying the Laue condition. The prescription is as follows. We draw the *reciprocal lattice* (RL) and then an incident vector $\mathbf{k}$, $k = 2\pi/\lambda_X$ starting at the RL point. Using the tip as a center

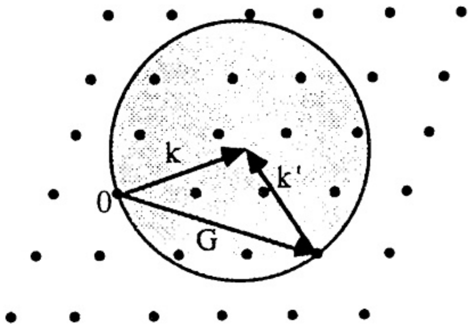

Figure 4. The Ewald construction.

we draw a sphere. The scattered vector $\mathbf{k}'$ is determined as in Fig. 4, the intensity being proportional to S_{G}.

2.6.1. The Laue Method

Both the positions of the crystal and the detector are *fixed*, a *broad* X-ray spectrum (from λ_0 to λ_1 is used). So, it is possible to find diffraction peaks according to the Ewald picture.

This method is mainly used to determine the *orientation* of a single crystal with a known structure.

2.6.2. The Rotating Crystal Method

The crystal is placed in a holder, which can rotate with a high precision. The X-ray source is fixed and monochromatic. At some angle the Bragg conditions are met and the diffraction takes place. In the Ewald picture it means the rotating of reciprocal basis vectors. As long as the X-ray wave vector is not too small one can find the intersection with the Ewald sphere at some angles.

2.6.3. The Powder or Debye-Scherrer Method

This method is very useful for powders or microcrystallites. The sample is fixed and the pattern is recorded on a film strip (see Fig. 5) According to the Laue condition,

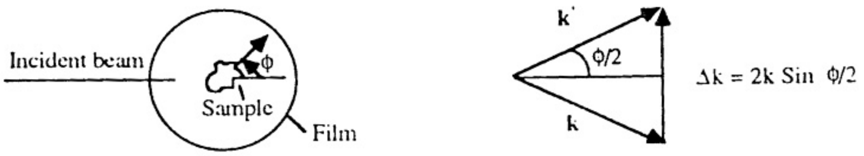

Figure 5. The powder method.

$$\Delta k = 2k \sin(\phi/2) = G.$$

So one can determine the *ratios*

$$\sin\left(\frac{\phi_1}{2}\right) : \sin\left(\frac{\phi_2}{2}\right) \ldots \sin\left(\frac{\phi_N}{N}\right) = G_1 : G_2 \ldots G_N.$$

Those ratios could be calculated for a given structure. So one can *determine* the structure of an unknown crystal.

2.6.4. Double Crystal Diffraction

This is a very powerful method which uses one very high-quality crystal to produce a beam acting upon the specimen (see Fig. 6).

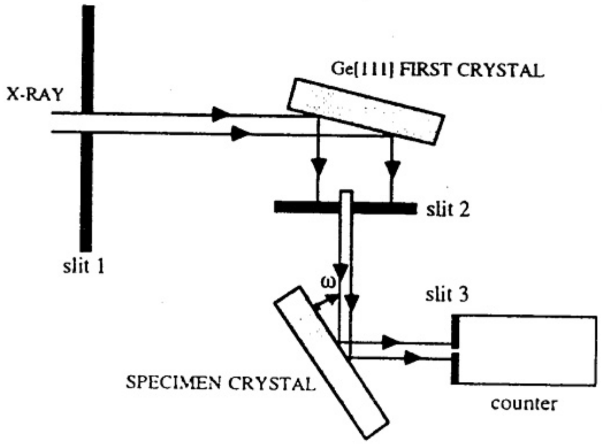

Figure 6. The double-crystal diffractometer.

When the Bragg angles for two crystals are the same, the narrow diffraction peaks are observed. This method allows, in particular, study epitaxial layer which are grown on the substrate.

2.7. Problems

2.1. Show that $(\mathbf{a}_1[\mathbf{a}_2\mathbf{a}_3]) = (\mathbf{a}_3[\ \mathbf{a}_1\mathbf{a}_2]) = (\mathbf{a}_2[\mathbf{a}_3\mathbf{a}_1])$.
2.2. Show that C_n with only $n = 1,\ 2,\ 3,\ 4,\ 6$ are available as crystal symmetries.
2.3. We have mentioned that primitive vectors are not unique. New vectors can be defined as

$$\mathbf{a}'_i = \sum_k \beta_{ik}\mathbf{a}_k,$$

Show that the condition

$$\det(\beta_{ik}) = \pm 1. \tag{2.15}$$

is a necessary condition.
2.4. Derive the expressions (1.10) for reciprocal lattice vectors.
2.5. Find the reciprocal lattice vectors for fcc lattice.
2.6. Find the width of the scattering peak at the half intensity due to finite size of the chain with N .
2.7. Show that for any Gaussian fluctuations of ϕ with $\langle\phi\rangle = 0$ the following is correct $\langle\exp(i\phi)\rangle = \exp\left[-\langle\phi^2\rangle/2\right]$.

PART 2

Lattice Vibrations: Phonons

LECTURE 3
Lattice Vibrations

In this lecture we consider the dynamic properties of crystal lattice, namely lattice vibrations and their consequences. One can find detailed theory in many books, e.g. in [**1, 2**].

3.1. Interactions Between Atoms in Solids

The reasons to form a crystal from free atoms are manifold, the main principle being

- Keep the charges of the same sign apart
- Keep electrons close to ions
- Keep electron kinetic energy low by quantum mechanical spreading of electrons

The full quantum mechanical treatment of both electrons and ions is impossible, however, there is a natural simplification one can employ.

- The ions are much heavier than electrons.
- This means, that the there is a huge difference between the time scales for the motion of electrons and ions: electrons are fast, ions are slow.

So we can consider the heavy atoms as being fixed. Consequently, the total energy appears dependent on the atomic configuration as on external parameters.

This procedure is still very complicated, and we discuss only main physical principles.

Let us start with the discussion of the nature of *repulsive* forces. There are two mechanisms for the repulsion:

- due to Coulomb repulsive forces between the ions with the same sign of the charge;
- due to inter-penetrating of electron shells at low distances. That penetration leads to the *increase* of kinetic energy due to Pauli principle – the kinetic energy of Fermi gas increases with its density. The quantum mechanical treatment leads to the law $V \propto \exp(-R/a)$ for the repulsive forces at large distances; at intermediate distances the repulsive potential is usually expressed as

$$\Delta V(R) = A/R^{12}. \tag{3.1}$$

There are several reasons for atom *attraction*. Although usually the bonding mechanisms are mixed, 4 types of bonds are specified:

- *Ionic (or electrostatic) bonding.* The physical reason is near complete transfer of the electron from the anion to the cation. It is important for the alkali crystals **NaCl**, **KI**, **CsCl**, etc. One can consider the interaction as the Coulomb one for point

Crystal	Ionicity
Si	0.0
SiC	0.18
Ge	0.0
ZnSe	0.63
ZnS	0.62
CdSe	0.70
InP	0.42
InAs	0.46
InSb	0.32
GaAs	0.31
GaSb	0.36

Table 1. Ionicity numbers for semiconductor crystals.

charges at the lattice sites. Because the ions at the first co-ordination group have opposite sign in comparison with the central one the resulting Coulomb interaction is an attraction.

To make very rough estimates we can express the interaction energy as

$$V_{ij} = \left[\begin{array}{ll} \lambda e^{-R/\rho} - \frac{e_*^2}{R} & \text{for nearest neighbors,} \\ \pm\frac{e_*^2}{R_{ij}} & \text{otherwise} \end{array} \right. \tag{3.2}$$

with $R_{ij} = Rp_{ij}$ where p_{ij} represent distances for the lattice sites; e_* is the effective charge. So the total energy is

$$U = L\left(z\lambda e^{-R/\rho} - \alpha\frac{e_*^2}{R}\right)$$

where z is the number of nearest neighbors while

$$\alpha = \sum_{i,j}{}' \frac{\pm}{p_{ij}}$$

is the so-called *Madelung constant.* For a linear chain

$$\alpha = 2\left(1 - \frac{1}{2} + \frac{1}{3} - \cdots\right) = 2\ln(1+x)|_{x=1} = 2\ln 2.$$

Typical values of α for 3D lattices are: 1.638 (zinc-blend crystals), 1.748 (NaCl).

- *Covalent (or homopolar) bonding.* This bonding appears at small distances of the order of atomic length 10^{-8} cm. The nature of this bonding is pure quantum mechanical; it is just the same as bonding in the H_2 molecule where the atoms share the two electron with anti-parallel spins. The covalent bonding is dependent on the electron orbitals, consequently they are *directed.* For most of semiconductor compounds the bonding is mixed – it is partly ionic and partly covalent. The table 1 shows the ionicity numbers (effective charge) for different bonds. Covalent bonding depends both on atomic orbital and on the distance – it exponentially decreases with the distance.
- *Van der Waal's (or dispersive) bonding.* This universal attractive force is important at relatively larger distances.

The physical reason is the polarization of electron shells of the atoms and resulting dipole-dipole interaction which behaves as

$$\Delta V(R) = -B/R^6. \tag{3.3}$$

The two names are due i) to the fact that these forces has the same nature as the forces in real gases which determine their difference with the ideal ones, and ii) because they are determined by the same parameters as light dispersion. This bonding is typical for inert gas crystals (Ar, Xe, Cr, molecular crystals). In such crystals the interaction potential is described by the Lennard-Jones formula

$$V(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] \tag{3.4}$$

the equilibrium point where $dV/dR = 0$ being $R_0 = 1.09\sigma$.

- *Metallic bonding.* Metals usually form closed packed fcc, bcc, or hcp structures where electrons are shared by all the atoms. The bonding energy is determined by a balance between the *negative* energy of Coulomb interaction of electrons and positive ions (this energy is proportional to e^2/a) and *positive* kinetic energy of electron Fermi gas (which is, as we will see later, $\propto n^{2/3} \propto 1/a^2$).

Taking all of this into account The most important thing for is that, irrespective to the nature of the bonding, the general form of the binding energy is like shown in Fig. 1. The energy has a minimum at some R_0 and this minimum is deep enough to hold the ions. If it is not so the crystal just does not form.

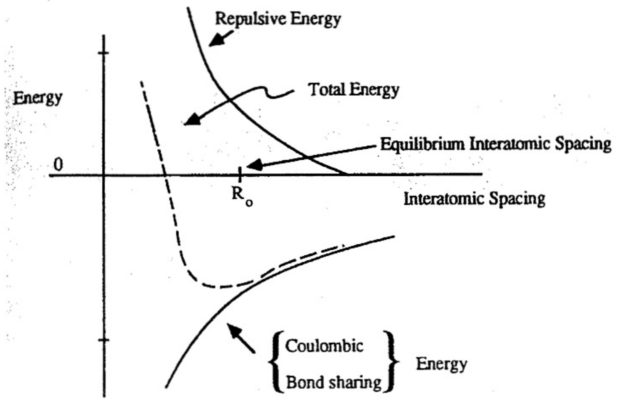

Figure 1. General form of binding energy.

3.2. Lattice Vibrations

For small displacement on an atom from its equilibrium position one can expand the potential energy near its minimal value where $\left(\frac{dV}{dR}\right)_{R_0} = 0$ (see Fig. 1)

$$\begin{aligned} V(R) &= V(R_0) + \frac{1}{2}\left(\frac{d^2V}{dR^2}\right)_{R_0}(R-R_0)^2 + \frac{1}{6}\left(\frac{d^3V}{dR^3}\right)_{R_0}(R-R_0)^3 + \cdots \\ &= V(R_0) + \frac{1}{2}C(R-R_0)^2 - \frac{1}{3}\gamma(R-R_0)^3, \end{aligned} \tag{3.5}$$

where

$$\left(\frac{d^2V}{dR^2}\right)_{R_0} \equiv C > 0, \quad \left(\frac{d^3V}{dR^3}\right)_{R_0} \equiv -2\gamma$$

we get the following expression for the restoring force for a given displacement $x \equiv R - R_0$

$$F = -\frac{dV}{dx} = -Cx + \gamma x^2 \tag{3.6}$$

The force under the limit $F = -Cx$ is called *quasi elastic.* The γx^2 term describes non-harmonicity of the lattice an is important for phonon-phonon interactions. It this term, for example which leads to the thermal expansion of a crystal.

3.2.1. One-Atomic Linear Chain

3.2.1.1. *Dispersion relation.* We start with the simplest case of one-atomic linear chain with nearest neighbor interaction (see Fig. 2) If one expands the energy near the equilibrium point

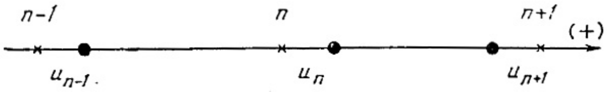

Figure 2. Vibrations of a linear one-atomic chain (displacements).

for the nth atom and use quasi elastic approximation (3.6) he comes to the Newton equation

$$m\ddot{u}_n + C(2u_n - u_{n-1} - u_{n+1}) = 0. \tag{3.7}$$

To solve this *infinite* set of equations let us take into account that the equation does not change if we shift the system *as a whole* by the quantity a times an integer. We can fulfill this condition automatically by searching the solution as

$$u_n = Ae^{i(qan-\omega t)}. \tag{3.8}$$

It is just a plane wave but for the *discrete co-ordinate na.* Immediately we get (see *Problem 7.1*)

$$\omega = \omega_m|\sin\frac{qa}{2}|, \quad \omega_m = 2\sqrt{\frac{C}{m}}. \tag{3.9}$$

The expression (3.9) is called the *dispersion law.* At larger q it differs from the dispersion relation for an homogeneous string, $\omega = sq$.

Another important feature is that if we replace the wave number q as

$$q \to q' = q + \frac{2\pi g}{a},$$

where g is an integer, the solution (3.8) does not change (because $\exp(2\pi i \times \text{integer}) = 1$). Consequently, it is impossible to discriminate between q and q' and it is natural to choose the region

$$-\frac{\pi}{a} \le q \le \frac{\pi}{a} \tag{3.10}$$

to represent the dispersion law in the whole q-space. This law is shown in Fig. 3. Note that there is the *maximal frequency* ω_m that corresponds to the *minimal* wave length $\lambda_{\min} = 2\pi/q_{\max} = 2a$. The maximal frequency is a typical feature of discrete systems vibrations.

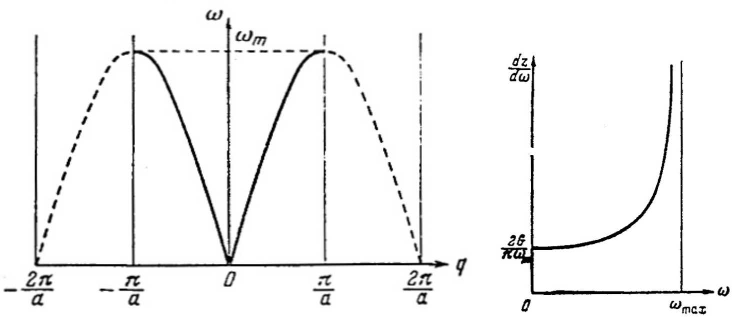

Figure 3. Left: Spectrum of vibrations of a linear one-atomic chain. Right the density of states for a linear one-atomic chain.

Now we should recall that any crystal is *finite* and the translation symmetry we have used fails. The usual way to overcome the problem is to take into account that actual number L of sites is large and to introduce *Born-von Karmann* cyclic boundary conditions

$$u_{n\pm L} = u_n \, . \tag{3.11}$$

This condition make a sort of ring of a very big radius that physically does not differ from the long chain.[1] Immediately, we get that the wave number q should be *discrete*. Indeed, substituting the condition (3.11) into the solution (3.8) we get $\exp(\pm iqaL) = 1,\ qaL = 2\pi g$ with an integer g. Consequently,

$$q = \frac{2\pi}{a}\frac{g}{L}, \quad -\frac{L}{2} < g < \frac{L}{2} \tag{3.12}$$

(it is convenient to consider L as a large even number). So, for a linear chain, the wave number q takes L discrete values in the interval $(-\pi/a,\ \pi/a)$. Note that this interval is just the same as the Wigner-Seitz cell of the one-dimensional reciprocal lattice.

3.2.1.2. *Density of States.* Because of the discrete character of the vibration states one can calculate *the number of states*, z, with different q in the frequency interval ω, $\omega + d\omega$. One easily obtains (see *Problem 7.2*)

$$\frac{dz}{d\omega} = \frac{2L}{\pi}\frac{1}{\sqrt{\omega_m^2 - \omega^2}} \, . \tag{3.13}$$

This function is called the *density of states* (DOS). It is plotted in the right of Fig. 3.

We shall see that DOS is strongly dependent on the dimensionality of the structure.

3.2.1.3. *Phase and Group Velocity.* Now we discuss the properties of long wave vibrations. Long wavelength means small q. At small q we get from Eq. (3.9)

$$\omega = sq \, , \tag{3.14}$$

where

$$s = a\sqrt{\frac{C}{m}} \tag{3.15}$$

---

[1] Note that for small structures of modern electronics this assumption need revision. Violation of this assumption leads to the specific interface modes.

is the sound velocity in a homogeneous elastic medium. In a general case, the sound velocity becomes q-dependent, i. e. there is the dispersion of the waves.

One can discriminate between the phase (s_p) and group (s_g) velocities. The first is responsible for the propagation of the equal phase planes while the last one describes the energy transfer. We have

$$\begin{aligned} s_p &= \frac{\omega}{|q|} = s\left|\frac{\sin(aq/2)}{aq/2}\right| , \\ s_g &= \left|\frac{d\omega}{dq}\right| = s|\cos(aq/2)| . \end{aligned} \tag{3.16}$$

Note, that the second formula is just one of the Hamiltonian equations.

At the boundaries of the interval we get $s_p = (2/\pi)s$ while $s_g = 0$ (boundary modes cannot transfer energy).

Another feature to note is that $\omega(q = 0) = 0$. This is not a coincidence this is the consequence of the Goldstone theorem.

3.2.2. Diatomic Chain. Acoustic and Optical branches.

We use this case to discuss vibrations of compound lattices. Let us consider the chain shown in Fig. 4 One can see that the elementary cell contains 2 atoms. If we assume the elastic constants to be $C_{1,2}$. If there is a reflection symmetry in the chain then $C_1 = C_2$. However, such symmetry can be broken then C_1 and C_2 are different.

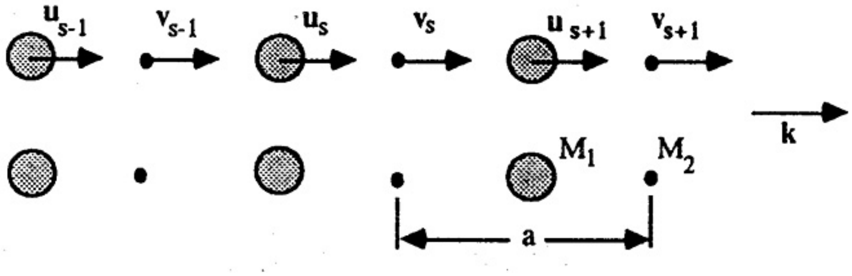

Figure 4. Linear diatomic chain.

We come to the following equations of motion:

$$\begin{aligned} m_1\ddot{u}_n &= -C_1(u_n - v_n) - C_2(u_n - v_{n-1}) , \\ m_2\ddot{v}_n &= -C_1(v_n - u_n) - C_2(v_n - u_{n+1}) . \end{aligned} \tag{3.17}$$

It is natural to use once more the translation symmetry condition and search the solution as

$$u_n = A_u e^{i(qan-\omega t)} , \quad v_n = A_v e^{i(qan-\omega t)} . \tag{3.18}$$

After substitution to Eqs. (3.17) we get the set of equations for the constants A_i. To formulate these equations it is convenient to express these equations in a matrix form introducing the vector $\mathbf{A} \equiv \begin{pmatrix} A_u & A_v \end{pmatrix}$ and the so-called *dynamic matrix*

$$\hat{D} = \begin{pmatrix} \frac{C_1+C_2}{m_1} & -\frac{C_1+C_2e^{-iaq}}{m_1} \\ -\frac{C_1+C_2e^{iaq}}{m_2} & \frac{C_1+C_2}{m_2} \end{pmatrix} \tag{3.19}$$

The equation for **A** has the form (see matrix notations in Appendix **??**)

$$\omega^2\mathbf{A} - \hat{D}\mathbf{A} = \hat{0}\,. \tag{3.20}$$

This is homogeneous equation; it has a solution only if

$$\det\,(\omega^2\hat{1} - \hat{D}) = 0\,. \tag{3.21}$$

This is just the equation which determines the eigenfrequencies. We get

$$\omega_{1,2}^2 = \frac{\omega_0^2}{2}\left[1 \mp \sqrt{1-\gamma^2\sin^2\frac{aq}{2}}\right] \tag{3.22}$$

where

$$\omega^2 = \frac{(C_1+C_2)(m_1+m_2)}{m_1m_2}\,, \qquad \gamma^2 = 16\left[\frac{C_1C_2}{(C_1+C_2)^2}\right]\left[\frac{m_1m_2}{(m_1+m_2)^2}\right]\,.$$

The frequencies $\omega_{1,2}$ are real because $|\gamma| \le 1$.

We see a very important difference with the case of monoatomic chain: there are 2 branches $\omega_{1,2}$ for a given value of q. The branches are shown in Fig. 5 The lower branch is called the *acoustic branch* while the upper one is called the *optical branch*. To understand the physical reason for these names let us consider the limits of zero and maximal q. We get

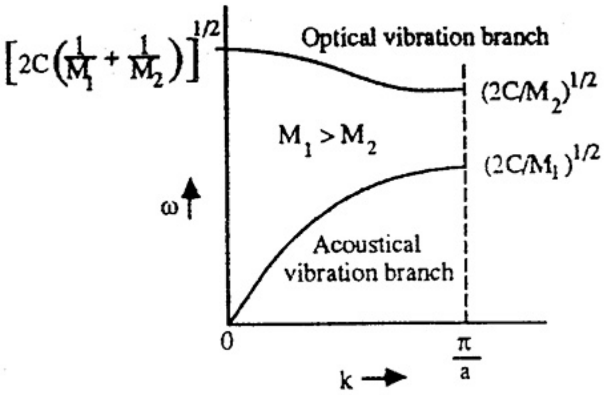

Figure 5. Optical and acoustic vibration branches.

$$\begin{aligned} &\omega_{ac}(0) = 0\,, && \omega_{ac}(\pi/a) = \tfrac{\omega_0}{\sqrt{2}}\sqrt{1-\sqrt{1-\gamma^2}}\,,\\ &\omega_{opt}(0) = \omega_0\,, && \omega_{opt}(\pi/a) = \tfrac{\omega_0}{\sqrt{2}}\sqrt{1+\sqrt{1-\gamma^2}}\,. \end{aligned} \tag{3.23}$$

So, we have the inequality chain

$$\omega_{opt}(0) = \omega_0 > \omega_{opt}(\pi/a) > \omega_{ac}(\pi/a) > \omega_{ac}(0) = 0\,.$$

What happens in the degenerate case when $C_1 = C_2$, $m_1 = m_2$? This situation is illustrated in Fig. 6 Now we can discuss the structure of vibrations in both modes. From the dispersion equation (3.20) we get

$$\mathcal{P}_{ac,opt} = \frac{u_n}{v_n}_{ac,opt} = \frac{A_u}{A_v} = \frac{C_1 + C_2e^{-iqa}}{(C_1+C_2) - m_1\omega_{ac,opt}^2}\,. \tag{3.24}$$

At very long waves ($q \to 0$) we get (*Problem 7.3*)

$$\mathcal{P}_{ac} = 1\,, \quad \mathcal{P}_{opt} = -\frac{m_2}{m_1} \tag{3.25}$$

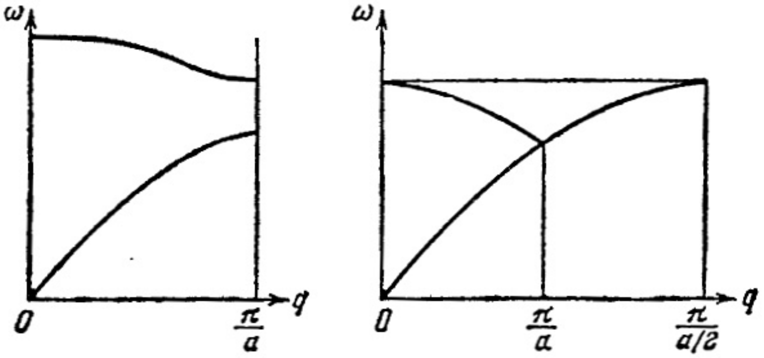

Figure 6. Degenerate case.

So, we see that in the acoustic mode all the atoms move next to synchronously, like in an acoustic wave in homogeneous medium. Contrary, in the optical mode; the gravity center remains unperturbed. In an ionic crystal such a vibration produce alternating *dipole moment*. Consequently, the mode is *optical active*. The situation is illustrated in Fig. 7.

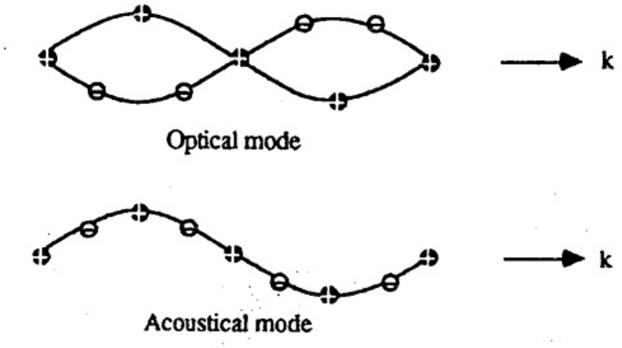

Figure 7. Transverse optical and acoustic waves.

LECTURE 4
Continuous Approximation for Lattice Vibrations

To elucidate the difference between acoustic and optical vibrations we discuss here the long wave limit in continuous approximation.

4.1. Acoustic vibrations

According to the theory of elasticity (see for example, Landau-Lifshitz, volume 7, Chapter III), one can write equations of motion as

$$\rho\frac{\partial^2\mathbf{u}}{\partial t^2} = (\Upsilon+\Lambda)\text{grad div}\,\mathbf{u} + \Upsilon\nabla^2\mathbf{u} \tag{4.1}$$

where ρ is the mass density while Υ, Λ are elastic constants. It is known that $\vartheta = \text{div}\,\mathbf{u}(\mathbf{r},t)$ is the relative *volume change* while $\boldsymbol{\varphi} = \frac{1}{2}\text{curl}\mathbf{u}$ is the rotation angle.

We are interested in the plane wave solutions $\mathbf{u} = \mathbf{A}\exp(i\mathbf{qr} - i\omega t)$ we get

$$\begin{aligned} \vartheta &= \text{div}\ \mathbf{u} = i\mathbf{qu}\,, \\ \boldsymbol{\varphi} &= \frac{i}{2}\mathbf{q}\times\mathbf{u}\,. \end{aligned} \tag{4.2}$$

So, we see that the compression ϑ wave is *longitudinal* while the $\boldsymbol{\varphi}$ rotation wave is transversal. These wave are the analogs of 3 acoustic modes in a crystal.

Taking into account that

$$\text{curl grad}\ \psi(\mathbf{r}) = 0, \quad \text{div curl}\ \mathbf{k}(\mathbf{r}) = 0, \quad \nabla^2 \equiv \text{div grad},$$

we can obtain the equations for the quantities ϑ, $\boldsymbol{\varphi}$:

$$\frac{\partial^2\vartheta}{\partial t^2} = s_l^2\nabla^2\vartheta\,, \tag{4.3}$$

$$\frac{\partial^2\boldsymbol{\varphi}}{\partial t^2} = s_t^2\nabla^2\boldsymbol{\varphi}\,, \tag{4.4}$$

where

$$s_l = \sqrt{\frac{2\Upsilon+\Lambda}{\rho}}\,, \quad s_t = \sqrt{\frac{\Upsilon}{\rho}}\,. \tag{4.5}$$

We can also calculate the number of the vibrations if we restrict ourselves with a cube with the side L and put zero boundary conditions. We get $\vartheta = A\sin(\omega t)\sin(q_x x)\sin(q_y y)\sin(q_z z)$

for each mode with $q_i = n_i \frac{\pi}{L}$. We have $\omega = qs = s\sqrt{q_x^2 + q_y^2 + q_z^2}$ for each branch. Consequently, the number of vibrations in the region R, $R + dR$ where $R = \sqrt{\sum_i n_i^2}$ is

$$g(\omega)\, d\omega = \sum_{l,t} \frac{4\pi R^2\, dR}{8} = \frac{\mathcal{V}}{2\pi^2}\left(\frac{1}{s_l^3} + \frac{2}{s_t^3}\right)\omega^2\, d\omega\,. \tag{4.6}$$

4.2. Optical vibrations

Consider a ionic crystal with 2 ions in a primitive cell with effective charges $\pm e^*$. Denoting the corresponding displacements as $\mathbf{u}_\pm$ and the force constant as κ we get the following equations of motion

$$\begin{aligned} M_+ \frac{d^2\mathbf{u}_+}{dt^2} &= -\kappa(\mathbf{u}_+ - \mathbf{u}_-) + e^*\mathbf{E}_e\,, \\ M_- \frac{d^2\mathbf{u}_-}{dt^2} &= -\kappa(\mathbf{u}_- - \mathbf{u}_+) - e^*\mathbf{E}_e \end{aligned} \tag{4.7}$$

where $\mathbf{E}_e$ is the effective electric field acting from the external sources and from other ions. Then, let us introduce reduced mass

$$\frac{1}{M_r} = \frac{1}{M_+} + \frac{1}{M_-}$$

and relative displacement $\mathbf{s} = \mathbf{u}_+ - \mathbf{u}_-$. Combining Eqs. (4.7) and considering only optical oscillations we obtain

$$M_r \frac{d^2\mathbf{s}}{dt^2} = -\kappa\mathbf{s} + e^*\mathbf{E}_e\,. \tag{4.8}$$

In this equation we do not know κ and $\mathbf{E}_e$. The electric field has three contributions: the external field, the one due to shift of the ions, and the one due to polarization of the electron clouds. The shift of the ions is exactly what is described by the above equation, but the contribution from the polarization of the electrons has to be accounted for explicitly. So if we denote the polarization of electrons by $\mathbf{P}_{el}$ we should use $\mathbf{E}_e = \mathbf{E} + 4\pi\mathbf{P}_{el}$.

From electrodynamics we know that

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}_{el} + 4\pi\mathbf{P}_{ion}.$$

($\mathbf{P}_{el} + \mathbf{P}_{ion}$ is the total polarization) The polarization $\mathbf{P}_{ion}$ is the dipole moment of ions per volume. The ion dipole moment per unit cell is $e^*\mathbf{s}$, so $\mathbf{P}_{ion} = \frac{e^*}{\mathcal{V}_0}\mathbf{s}$, and we have

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}_{el} + \frac{4\pi e^*}{\mathcal{V}_0}\mathbf{s} = \epsilon\mathbf{E}, \tag{4.9}$$

where ϵ is the dielectric constant.

The dielectric constant ϵ depends on the frequency of the field. Let's consider this dependence.

The contributions from electrons and ions the total polarization are very different. The ions are much heavier than electrons, so their frequency of motion is much smaller than that of electrons. So there is a large range frequencies of the external field where the frequency of the external field is mach larger than the typical frequency of ions and much smaller than the typical frequency of the electrons. If we apply a field of this frequency the ions will not have time to shift (so $\mathbf{s} = 0$), while the electrons will follow the field, as this field is almost static for electrons. If we denote the dielectric constant at such frequency as ϵ_∞, then we have from (4.9)

$$\mathbf{E} + 4\pi\mathbf{P}_{el} = \epsilon_\infty\mathbf{E}.$$

We then have

$$M_r\frac{d^2\mathbf{s}}{dt^2} = -\kappa\mathbf{s} + e^*\epsilon_\infty\mathbf{E}; \tag{4.10}$$

$$\mathbf{D} = \epsilon_\infty\mathbf{E} + \frac{4\pi e^*}{\mathcal{V}_0}\mathbf{s} = \epsilon\mathbf{E}. \tag{4.11}$$

Let's now consider $\mathbf{E} = \mathbf{E}_0$ to be time independent (at zero frequency). For such field we have

$$-\kappa\mathbf{s}_0 + e^*\epsilon_\infty\mathbf{E}_0 = 0; \tag{4.12}$$

$$\mathbf{D} = \epsilon_\infty\mathbf{E}_0 + \frac{4\pi e^*}{\mathcal{V}_0}\mathbf{s}_0 = \epsilon_0\mathbf{E}_0, \tag{4.13}$$

where ϵ_0 is the static dielectric constant. Eliminating $\mathbf{s}_0$ from these two equations we find

$$\kappa = \frac{4\pi e^{*2}}{\mathcal{V}_0}\frac{\epsilon_\infty}{\epsilon_0 - \epsilon_\infty}.$$

- Notice, that the stability requirement ($\kappa > 0$) means that $\epsilon_0 > \epsilon_\infty$.

Our equations now are

$$M_r\frac{d^2\mathbf{s}}{dt^2} = -\frac{4\pi e^{*2}}{\mathcal{V}_0}\frac{\epsilon_\infty}{\epsilon_0 - \epsilon_\infty}\mathbf{s} + e^*\epsilon_\infty\mathbf{E}; \tag{4.14}$$

$$\mathbf{D} = \epsilon_\infty\mathbf{E} + \frac{4\pi e^*}{\mathcal{V}_0}\mathbf{s}. \tag{4.15}$$

Now I want to analyze the transversal and longitudinal oscillations. First I point out, that the equation (4.14) is written for $\mathbf{q} = 0$ – they are uniform oscillations. In this sense there is no difference between the transversal and longitudinal modes. However, I can consider this equation as the equation in the limit $\mathbf{q} \to 0$. It will not change the equation in a considerable way, but will give me direction of propagation. We then can write

$$\mathbf{s} = \mathbf{s}_l + \mathbf{s}_t,$$

where $\mathbf{s}_l$ and $\mathbf{s}_t$ are longitudinal and transversal components:

$$\mathbf{s}_l = \mathbf{s}_{0l}e^{i\mathbf{q}\cdot\mathbf{r}}, \quad \mathbf{s}_{0l} \parallel \mathbf{q}, \qquad \text{and} \qquad \mathbf{s}_t = \mathbf{s}_{0t}e^{i\mathbf{q}\cdot\mathbf{r}}, \quad \mathbf{s}_{0t} \perp \mathbf{q},$$

So we see that

$$\operatorname{curl}\mathbf{s}_l = 0, \qquad \text{and} \qquad \operatorname{div}\mathbf{s}_t = 0.$$

From electrodynamics we also have

$$\operatorname{div}\mathbf{D} = 0, \qquad \operatorname{curl}\mathbf{E} = 0.$$

Taking div of the equation (4.15) we have $\epsilon_\infty \operatorname{div}\mathbf{E} = -\frac{4\pi e^*}{\mathcal{V}_0}\operatorname{div}\mathbf{s}_l$. Taking curl and div of the equation (4.14) we then have

$$M_r\frac{d^2}{dt^2}\operatorname{div}\mathbf{s}_l = -\frac{4\pi e^{*2}}{\mathcal{V}_0}\frac{\epsilon_0}{\epsilon_0 - \epsilon_\infty}\operatorname{div}\mathbf{s}_l;$$

$$M_r\frac{d^2}{dt^2}\operatorname{curl}\mathbf{s}_t = -\frac{4\pi e^{*2}}{\mathcal{V}_0}\frac{\epsilon_\infty}{\epsilon_0 - \epsilon_\infty}\operatorname{curl}\mathbf{s}_t.$$

So we see that

$$\frac{\omega_l^2}{\omega_t^2} = \frac{\epsilon_0}{\epsilon_\infty}. \tag{4.16}$$

This is called *Lyddane-Sax-Teller relation.*

- The stability now requires that $\omega_l > \omega_t$.

The ion motion in the transversal and longitudinal modes is shown in Fig. 1. Notice, that vector **q** shows the direction and period of *modulation*. We see that the two types of optical vibrations differ because of the long-range electric forces which are produced only by *longitudinal* modes. Consequently, they are called *polar*. The difference between the frequencies of polar and non-polar modes depends on the crystal ionicity and allows one to estimate the latter.

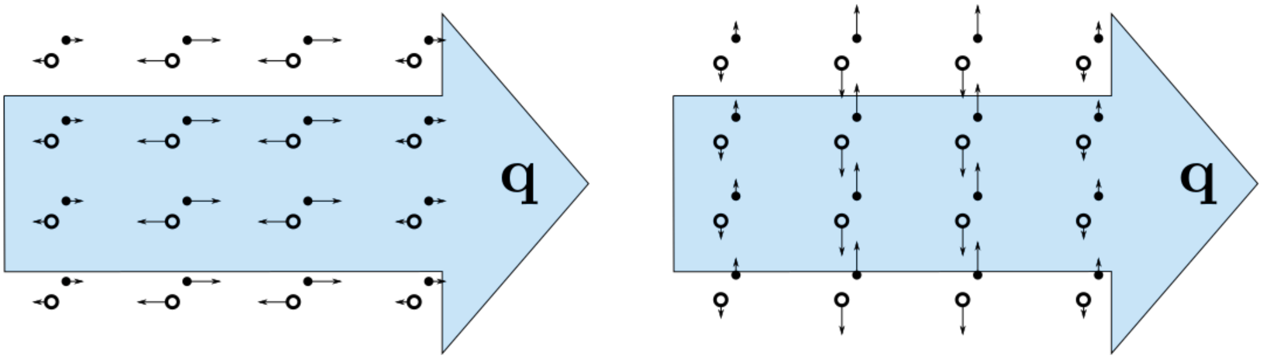

Figure 1. Longitudinal (left) and transverse (right) optical modes of vibration of a ion crystal.

LECTURE 5

Optical Vibration–Light Interaction. Vibrations in $3D$ lattices.

5.1. Optical Vibration–Light Interaction.

It is clear that optical vibrations in ionic compounds should interact with electromagnetic waves. To take this interaction into account one should add the Maxwell equations to the complete set of equations for the vibrations. Although the equation (4.14) was written for $\mathbf{q} = 0$ we will assume that it is good enough for any $\mathbf{q}$.

We have[1]

$$\ddot{\mathbf{s}} = -\omega_t^2 \mathbf{s} + \frac{e^* \epsilon_\infty}{M_r} \mathbf{E} \tag{5.1}$$

$$\operatorname{div} \left(\epsilon_\infty \mathbf{E} + \frac{M_r}{e^*} (\omega_l^2 - \omega_t^2) \mathbf{s} \right) = 0 \tag{5.2}$$

$$\nabla \times \mathbf{B} = \frac{1}{c} \left(\epsilon_\infty \dot{\mathbf{E}} + \frac{M_r}{e^*} (\omega_l^2 - \omega_t^2) \dot{\mathbf{s}} \right) \tag{5.3}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{5.4}$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \dot{\mathbf{B}} \tag{5.5}$$

We are interested in the transversal modes, so we search solutions proportional to $\exp(i\mathbf{qr} - i\omega t)$ with

$$\mathbf{E} \parallel \mathbf{s} \parallel \hat{x}\,, \quad \mathbf{B} \parallel \hat{y}\,, \quad \mathbf{q} \parallel \hat{z}\,. \tag{5.6}$$

so that

$$\mathbf{E} = E\hat{x} e^{iqz - i\omega t}, \qquad \mathbf{s} = s\hat{x} e^{iqz - i\omega t}, \qquad \mathbf{B} = B\hat{y} e^{iqz - i\omega t},$$

where E, B, and s are complex amplitudes.

In such geometry the equations (5.2) and (5.4) are satisfied automatically. The equation (5.5) gives the standard relation for the electromagnetic wave $qcE = \omega B$. Using this relation the last two equations read (Check!)

$$\begin{pmatrix} \omega^2 \epsilon_\infty - q^2 c^2 & \omega^2 (\omega_l^2 - \omega_t^2) \\ \epsilon_\infty & \omega^2 - \omega_t^2 \end{pmatrix} \begin{pmatrix} E \\ \frac{M_r}{e^*} s \end{pmatrix} = 0 \tag{5.7}$$

---

[1] We use the so-called Gaussian system of units.

This system has a non-trivial solution only if the determinant of the matrix is zero. This leads to the equation for the wave frequency

$$\epsilon_\infty \omega^4 - [q^2c^2 + \epsilon_\infty \omega_l^2]\omega^2 + \omega_t^2 q^2 c^2 = 0.$$

We then have two branches of propagating waves:

$$\omega_\pm^2 = \frac{\omega_l^2}{2}\left[1 + \frac{q^2c^2}{\epsilon_\infty \omega_l^2} \pm \sqrt{\left(1 + \frac{q^2c^2}{\epsilon_\infty \omega_l^2}\right)^2 - 4\frac{q^2c^2}{\epsilon_\infty \omega_l^2}\frac{\omega_t^2}{\omega_l^2}}\right] \tag{5.8}$$

This spectrum is shown in Fig. 1. It is informative to look at the spectrum (5.8) at small and large qc. Using (4.16) the results are

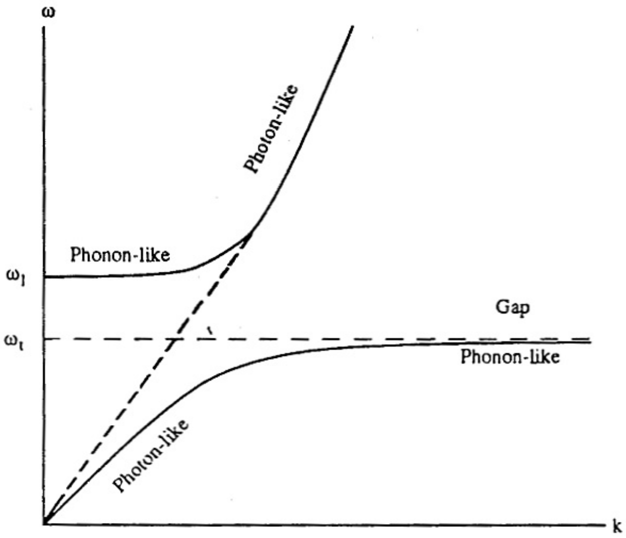

Figure 1. Coupled TO-photon modes. The broken lines – spectra without interaction.

$$\lim_{qc\to 0} \omega_\pm^2 = \begin{cases} \frac{q^2c^2}{\epsilon_0} \\ \omega_l^2 + q^2c^2\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) \end{cases}, \qquad \lim_{qc\to\infty} \omega_\pm^2 = \begin{cases} \omega_t^2 \\ \frac{q^2c^2}{\epsilon_\infty} \end{cases}$$

- The light is hybridized with phonons. At small q the lower branch is photon-like, while the upper branch is phonon-like, and at large q they switch. It can be seen from the eigen modes: at small q the weight of the eigen mode of the lower branch is mostly in E, etc.
- The light with the frequencies between ω_t and ω_l cannot penetrate the crystal, it is completely reflected.
- The velocity of light is larger at large q, than at small q.
- If $\omega_l = \omega_t$ (which means that $\epsilon_0 = \epsilon_\infty$) then the photon and phonon modes are decoupled. If ω_l and ω_t are almost the same, then the coupling is important only at the close vicinity of the intersection.

The coupled TO-vibration-photon modes are often called the *polaritons*. One can easily understand that longitudinal modes do not couple to the light.

5.2. Vibration modes of 3D lattices

Now we are prepared to describe the general case of 3D lattice. Assume an elementary cell with s different atoms having masses m_k. We also introduce the *main region* of the crystal as a body restricted by the sides $L\mathbf{a}_i$, the volume being $\mathcal{V} = L^3\mathcal{V}_0$ while the number of sites $N = L^3$. The position of each atom is

$$\mathbf{R}^k_{\mathbf{n}} = \mathbf{a}_{\mathbf{n}} + \mathbf{R}^k \,. \tag{5.9}$$

Here $\mathbf{R}^k$ determines the atom's position within the cell. Similarly, we introduce displacements $\mathbf{u}^k_{\mathbf{n}}$.

- The notation $\mathbf{u}^k_{\mathbf{n}}$ denotes the vector of displacement of the atom number k in the unit cell with coordinate $\mathbf{n}$.

The displacement-induced change of the potential energy Φ of the crystal is a function of all the displacements with a minimum at $\mathbf{u}^k_{\mathbf{n}} = 0$. So, we can expand it as

$$\Phi = \frac{1}{2}\sum_{all} \Phi_{\alpha,\beta}\begin{pmatrix} k, k' \\ \mathbf{n}, \mathbf{n}' \end{pmatrix} u^k_{\mathbf{n},\alpha} u^{k'}_{\mathbf{n}',\beta} + \frac{1}{6}\sum_{all} \Phi_{\alpha,\beta,\gamma}\begin{pmatrix} k, k', k'' \\ \mathbf{n}, \mathbf{n}', \mathbf{n}'' \end{pmatrix} u^k_{\mathbf{n},\alpha} u^{k'}_{\mathbf{n}',\beta} u^{k''}_{\mathbf{n}'',\gamma} \cdots \tag{5.10}$$

(Greek letters mean Cartesian projections). There are important relations between the coefficients Φ in Eq. (5.10) because the energy should not change if one shifts the crystal *as a whole.*

Let's restrict our consideration only to the quadratic (harmonic) terms.

(a) **Periodicity**: The coefficients depend only on the differences $\mathbf{n} - \mathbf{n}'$, $\mathbf{n} - \mathbf{n}''$, etc.

$$\Phi_{\alpha,\beta}\begin{pmatrix} k, k' \\ \mathbf{n}, \mathbf{n}' \end{pmatrix} = \Phi_{\alpha,\beta}\begin{pmatrix} k, k' \\ \mathbf{n} - \mathbf{n}' \end{pmatrix} . \tag{5.11}$$

(b) **Symmetry**: The coefficient do not change if one changes the order of columns in their arguments

$$\Phi_{\alpha,\beta}\begin{pmatrix} k, k' \\ \mathbf{n}, \mathbf{n}' \end{pmatrix} = \Phi_{\beta,\alpha}\begin{pmatrix} k', k \\ \mathbf{n}', \mathbf{n} \end{pmatrix} . \tag{5.12}$$

(c) **Translation of the whole lattice**: The Newton equations for the motion of the atoms are

$$m_k \ddot{u}^k_{\mathbf{n},\alpha} = \sum_{\mathbf{n}',k',\beta} \Phi_{\alpha,\beta}\begin{pmatrix} k, k' \\ \mathbf{n}, \mathbf{n}' \end{pmatrix} u^{k'}_{\mathbf{n}',\beta} \tag{5.13}$$

If we shift all atoms by the same vector $\mathbf{u}^k_{\mathbf{n}} = \mathbf{b}$, then we must get $\ddot{\mathbf{b}} = 0$. So the sums of the coefficients over all the subscripts vanish.

$$\sum_{\mathbf{n}',k'} \Phi_{\alpha,\beta}\begin{pmatrix} k, k' \\ \mathbf{n}, \mathbf{n}' \end{pmatrix} = 0 \tag{5.14}$$

As in 1D case, we search the solution as (it is more convenient to use symmetric form)

$$\tilde{u}^k_{\mathbf{n},\alpha} = \frac{1}{\sqrt{m_k}} A^k_\alpha(\mathbf{q}) e^{i(\mathbf{q}\cdot\mathbf{a}_{\mathbf{n}} - \omega t)} \,. \tag{5.15}$$

Here we introduce wave vector $\mathbf{q}$. Just as in 1D case, we can consider it in a restricted region

$$-\pi < \mathbf{q}\mathbf{a}_i < \pi \tag{5.16}$$

that coincides with the definition of the first Brillouin zone (or the Wigner-Seitz cell). The wave vector $\mathbf{q}$ is defined with the accuracy of an arbitrary reciprocal vector $\mathbf{G}$, the q-space is the same as the reciprocal lattice one.

Finally, we come to the equation (see (3.20))

$$\hat{D}\mathbf{A} = \omega^2 \mathbf{A} \tag{5.17}$$

with

$$D^{k,k'}_{\alpha,\beta}(\mathbf{q}) = \sum_{\mathbf{n}'} \frac{1}{\sqrt{m_k m_{k'}}} \Phi_{\alpha,\beta} \left(\begin{array}{c} k, k' \\ \mathbf{n} - \mathbf{n}' \end{array} \right) e^{i\mathbf{q}(\mathbf{a}_{\mathbf{n}'} - \mathbf{a}_{\mathbf{n}})} \tag{5.18}$$

(the combination $\mathbf{a}_{\mathbf{n}'} - \mathbf{a}_{\mathbf{n}}$ also depends only on $\mathbf{n} - \mathbf{n}'$, so the matrix $\hat{D}$ does not depend on $\mathbf{n}$ – this is a consequence of the periodicity, if it were not so the plane waves would not be the solution.)

The matrix equation (5.17) is in fact the same is the set of $3s$ equations for $3s$ complex unknowns A^k_α. Now we come exactly to the same procedure as was described in the previous subsection. In fact, the dispersion equation has the form (3.21).

Let us discuss general properties of this equation. One can show (see *Problem 7.5*) that

$$D^{kk'}_{\alpha\beta} = \left[D^{k'k}_{\beta\alpha} \right]^* , \tag{5.19}$$

i. e. the matrix $\hat{D}$ is *Hermitian*. Consequently, its eigenvalues are *real*. One can show that they are also *positive* using the fact that the potential energy to be minimal in the equilibrium.

The general solution is as follows. One should determine $3s$ eigenvalues of the matrix $\hat{D}$ for a given $\mathbf{q}$ to get the values of $\omega_j(\mathbf{q})$. These values have to be substituted into Eq. (5.17) to find corresponding complex amplitudes $A^k_{j,\alpha}(\mathbf{q})$ which are proportional to the eigenvectors of the dynamic matrix $\hat{D}$. One can show from its definition that in general case

$$\hat{D}(-\mathbf{q}) = \left[\hat{D}(\mathbf{q}) \right]^* . \tag{5.20}$$

That means important properties of solutions:

$$\omega_j(-\mathbf{q}) = \omega_j(\mathbf{q}) , \quad A^k_{j,\alpha}(-\mathbf{q}) = \left[A^k_{j,\alpha}(\mathbf{q}) \right]^* . \tag{5.21}$$

These properties are in fact the consequence of the *time reversibility* of the mechanical problem we discuss.

Finally, one can construct a set of iso-frequency curves/surfaces $\omega_j(\mathbf{q}) =$ const. which are periodic in $\mathbf{q}$-space the period being the reciprocal lattice vector $\mathbf{G}$. The symmetry of those curves/surfaces are determined by the lattice symmetry.

In the end of this section, we analyze the long wave properties of 3D lattice.

Acoustic branches: It is clear, that at $\mathbf{q} = 0$ the component of $\hat{D}$-matrix are *real*. If we put the real displacement $A^k_{j,\beta}/\sqrt{m_k}$ to be k-independent and use the property (5.14) we readily get $\omega_j(0) = 0$ for all the 3 components $\alpha = 1, 2, 3$. So, there are 3 acoustic branches and $3s$-3 optical ones.

Optical branches: To describe their behavior we should write down the dynamic equation for real displacements for $\mathbf{q} = 0$. In this case $\mathbf{u}^k_{j,\mathbf{n}}$ does not depend on $\mathbf{n}$ and the Newton equation (5.13) reads

$$-\omega^2_{j,\mathbf{q}=0} m_k u^k_{j,\alpha} = \sum_{\mathbf{n}',k',\beta} \Phi_{\alpha,\beta} \begin{pmatrix} k, k' \\ \mathbf{n}-\mathbf{n}' \end{pmatrix} u^{k'}_{j,\beta}$$

If we sum this equation over k and use (5.14) we get

$$\omega^2_{j,\mathbf{q}=0} \sum_k m_k u^k_{j,\alpha} = 0$$

For $\mathbf{q} = 0$ the frequency of the optical modes are not zero, so the center of mass for each unit cell for optical modes does not move.

A typical vibration spectrum is shown in Fig. 2

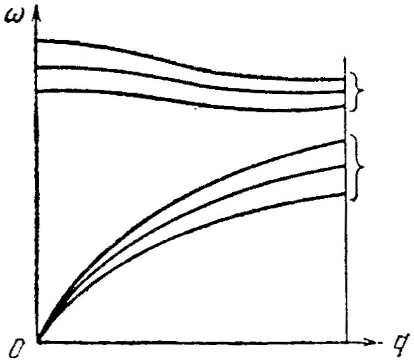

Figure 2. Typical vibration spectrum in 3D case.

LECTURE 6

Quantum Mechanics of Atomic Vibrations.

6.1. Normal Co-Ordinates for Lattice Vibrations

Now we formulate the dynamic equations in a universal form to prepare them to quantum mechanical description.

Let us introduce the eigenvectors $\mathbf{e}_{jk}(\mathbf{q})$ of the dynamical matrix $\hat{D}$ which correspond to the eigenvalues $\omega_j^2(\mathbf{q})$. According to the definition of eigenvectors,

$$\sum_{k'\beta} D_{\alpha\beta}^{kk'}(\mathbf{q}) e_{jk'\beta}(\mathbf{q}) = \omega_j^2(\mathbf{q}) e_{jk\alpha}(\mathbf{q})\,.$$

- Check out the indexes.

According to the properties of Hermitian matrices, the eigenvectors are orthogonal and normalized,

$$\sum_{\alpha k} e_{jk\alpha} e^*_{j'k\alpha} = \delta_{jj'} \qquad \sum_{j} e_{jk\alpha} e^*_{jk'\beta} = \delta_{kk'}\delta_{\alpha\beta}\,. \tag{6.1}$$

Also,

$$e_{jk\alpha}(\mathbf{q}) = e^*_{jk\alpha}(-\mathbf{q})\,. \tag{6.2}$$

The general displacements may differ from eigenvectors only by normalization. Consequently, it is convenient to expand the displacements in terms of the eigenvectors as

$$u^k_{\mathbf{n},\alpha}(t) = \frac{1}{\sqrt{Nm_k}} \sum_{\mathbf{q},j} e_{jk\alpha}(\mathbf{q}) a_j(\mathbf{q},t) e^{i\mathbf{q}\cdot\mathbf{a_n}}\,. \tag{6.3}$$

The amplitudes $a_j(\mathbf{q},t)$ are called the *normal co-ordinates* (or normal modes).

- As the displacements $u^k_{\mathbf{n},\alpha}(t)$ are real we must have $a(-\mathbf{q}) = a^*(\mathbf{q})$.
- This is an important constraint. If we forget about it we will over-count the number of degrees of freedom.
- Namely, as $a_j(\mathbf{q},t)$ are complex we seem to have doubled the number of degrees of freedom. However, the constraint $a_j(\mathbf{q},t) = a_j^*(-\mathbf{q},t)$ fixes half of these degrees of freedom. So this constraint is very important.

The total number of the amplitudes is $3sN$ ($3s$ values for the mode's number j and N for the discrete $\mathbf{q}$ number).

The total energy of vibration is the kinetic energy plus the potential energy. The kinetic energy of vibrations:

$$\mathcal{T} = \frac{1}{2}\sum_{\mathbf{n},k,\alpha} m_k (\dot{u}^k_{\mathbf{n},\alpha})^2 \,. \tag{6.4}$$

It is easy to show (see *Problem 7.6*) that it is equal to

$$\mathcal{T} = \frac{1}{2}\sum_{\mathbf{q},j} |\dot{a}_j(\mathbf{q},t)|^2 \,. \tag{6.5}$$

For the potential energy we use only the harmonic part. After some calculations (see *Problem 7.7*) we get

$$\Phi = \frac{1}{2}\sum_{\mathbf{q},j} \omega_j^2(\mathbf{q})\, |a_j(\mathbf{q},t)|^2 \,, \tag{6.6}$$

the Lagrangian of the lattice is then given by

$$\mathcal{L} = \mathcal{T} - \Phi = \frac{1}{2}\sum_{\mathbf{q},j} \left[|\dot{a}_j(\mathbf{q},t)|^2 - \omega_j^2(\mathbf{q})\, |a_j(\mathbf{q},t)|^2 \right] \,. \tag{6.7}$$

The quantities $a_j(\mathbf{q},t)$ are called the *complex normal co-ordinates.* We see that the total energy is the sum of the energies of almost independent oscillators. It is almost independent because there is the constraint $a_j(\mathbf{q},t) = a_j^*(-\mathbf{q},t)$.

Before we proceed, we need to resolve this constraint. It can be done by using the so-called *real normal co-ordinates.* Usually, it is done with the help of the so-called *Peierls transform.*

Let us introduce real *unconstrained* co-ordinates $Q_j(\mathbf{q})$ with the help of the transform

$$a_j(\mathbf{q}) = \frac{1}{2}\left[Q_j(\mathbf{q}) + Q_j(-\mathbf{q})\right] + \frac{i}{2}\left[Q_j(\mathbf{q}) - Q_j(-\mathbf{q})\right] \,. \tag{6.8}$$

We observe that the condition $a_j(\mathbf{q}) = a_j^*(-\mathbf{q})$ is automatically satisfied. Making use of the equality $\omega_j(-\mathbf{q}) = \omega_j(\mathbf{q})$ one can show that (see *Problem 7.8*) we get

$$\mathcal{L} = \frac{1}{2}\sum_{\mathbf{q},j} \left[\dot{Q}_j^2(\mathbf{q}) - \omega_j^2(\mathbf{q}) Q_j^2(\mathbf{q}) \right] \,. \tag{6.9}$$

Now we see, that this is a set (for each $\mathbf{q}$ and j) of real harmonic oscillators of mass equal to 1 and frequency $\omega_j(\mathbf{q})$. We then can introduce canonical momenta as (for each $\mathbf{q}$ and j)

$$P_j(\mathbf{q}) = \frac{\partial \mathcal{L}}{\partial \dot{Q}_j(\mathbf{q})} = \dot{Q}_j(\mathbf{q}) \,. \tag{6.10}$$

and write down the classical Hamilton of the system as

$$\mathcal{H}(Q,P) = \sum_{\mathbf{q},j} P_j(\mathbf{q})\dot{Q}_j(\mathbf{q}) - \mathcal{L} = \sum_{\mathbf{q},j} \left[\frac{P_j^2(\mathbf{q})}{2} + \omega_j^2(\mathbf{q}) \frac{Q_j^2(\mathbf{q})}{2} \right] \,. \tag{6.11}$$

As a result, we have expressed the classical Hamiltonian as the one for the set of independent oscillators.

At the end of this section we express the displacement in terms of the canonic variables (later we will need this expression)

$$u^k_{\mathbf{n},\alpha} = \frac{1}{\sqrt{Nm_k}} \sum_{\mathbf{q},j} \mathrm{Re}\left\{ e_{j\alpha k}(\mathbf{q}) \left[Q_j(\mathbf{q}) + \frac{i}{\omega_j(\mathbf{q})} P_j(\mathbf{q}) \right] e^{i\mathbf{q}\cdot\mathbf{a_n}} \right\} . \tag{6.12}$$

6.2. Quantization of Atomic Vibrations: Phonons

The quantum mechanical prescription to obtain the quantum Hamiltonian from the classical Hamiltonian function is to replace classical momenta by the momentum operators:

$$P_j(\mathbf{q}) \to \hat{P}_j(\mathbf{q}) = \frac{\hbar}{i} \frac{\partial}{\partial Q_j(\mathbf{q})} . \tag{6.13}$$

Consequently we come to the Schrödinger operator

$$\hat{\mathcal{H}}(\hat{P}, Q) = \sum_{\mathbf{q},j} \left\{ -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_j^2(\mathbf{q})} + \frac{1}{2} \omega_j^2(\mathbf{q}) Q_j^2(\mathbf{q}) \right\} . \tag{6.14}$$

It is a sum of the Schrödinger operators for independent oscillators with the mass equal to 1, co-ordinate $Q_j(\mathbf{q})$ and eigenfrequency $\omega_j(\mathbf{q})$. It is known that in such a case the total wave function is the product of the one-oscillator functions. So, let us start with one-oscillator equation for the wave function ψ

$$-\frac{\hbar^2}{2} \frac{\partial^2 \psi}{\partial Q^2} + \frac{1}{2} \omega^2 Q^2 \psi = \varepsilon \psi . \tag{6.15}$$

- This equation should be written for each j and $\mathbf{q}$:

$$-\frac{\hbar^2}{2} \frac{\partial^2 \psi_{j,\mathbf{q}}}{\partial Q_{j,\mathbf{q}}^2} + \frac{1}{2} \omega^2 Q_{j,\mathbf{q}}^2 \psi_{j,\mathbf{q}} = \varepsilon_{j,\mathbf{q}} \psi_{j,\mathbf{q}} .$$

Its solution is

$$\begin{aligned} \psi &= \psi_n(Q) = \left(\frac{\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} e^{-\omega Q^2/2\hbar} \mathrm{H}_n\left[\left(\frac{\omega}{\hbar}\right)^{1/2} Q\right] , \\ \varepsilon &= \varepsilon_n = \hbar\omega(n + 1/2) . \end{aligned} \tag{6.16}$$

- where again n is defined for each j, and $\mathbf{q}$, or $n \to n_{j,\mathbf{q}}$.

Here n is the oscillator's quantum number, $\mathrm{H}_n(\xi)$ is the Hermit polynomial which is dependent on the dimensionless co-ordinate

$$\xi = Q\sqrt{\omega/\hbar} . \tag{6.17}$$

In the following we will need the matrix elements of the operators Q and $\hat{P}$ defined as

$$\langle \alpha | \hat{A} | \beta \rangle \equiv \int_{-\infty}^{\infty} dQ \psi_\alpha^*(Q) \hat{A} \psi_\beta(Q) .$$

According to the table of integrals,

$$\begin{aligned}
\langle n'|\hat{Q}|n\rangle &= \sqrt{\frac{\hbar}{2\omega}} \times \begin{cases} \sqrt{n}\,, & \text{if } n' = n-1\,, \\ \sqrt{n+1} & \text{if } n' = n+1\,, \\ 0\,, & \text{otherwise}\,; \end{cases} \\
\langle n'|\hat{P}|n\rangle &= i\sqrt{\frac{\hbar\omega}{2}} \times \begin{cases} -\sqrt{n}\,, & \text{if } n' = n-1\,, \\ \sqrt{n+1} & \text{if } n' = n+1\,, \\ 0\,, & \text{otherwise}\,. \end{cases}
\end{aligned} \tag{6.18}$$

The important point:

- The number n completely specifies the state the oscillator is in. It means that if someone gives you the number n you will know the energy and the wavefunction of this state.
- So if someone gives you a set of numbers $n_{j,\mathbf{q}}$ for each j and $\mathbf{q}$, then you will know the the energy and the wavefunction of the crystal.
- This numbers $n_{j,\mathbf{q}}$ are called *occupation numbers*.

The equations introduced above describe the quantum mechanical approach to the lattice vibrations. In the following we employ this system to introduce a very general and widely used concept of *second quantization*.

LECTURE 7
Second Quantization. Measurement techniques.

7.1. Second Quantization

We now return to the problem described by the Hamiltonian (6.14). The full eigenstate of this operator is completely specified by the occupation numbers for each j and $\mathbf{q}$. We will denote these occupation numbers as $n_{j,\mathbf{q}}$. The corresponding wave function is $\psi_{\{n_{j,\mathbf{q}}\}}(\{Q_{j,\mathbf{q}}\})$.

It is clear that if I first increase the occupation number $n_{j,\mathbf{q}}$ by 1 and then occupation number $n_{j',\mathbf{q}'}$ by 1 or if I do that in the opposite order I will end up with the same wave function.[1] It means that the total wave function is the symmetrized product of the oscillator wave functions with occupation (quantum) numbers $n_{j,\mathbf{q}}$. The total energy of a state specified by a given numbers $n_{j,\mathbf{q}}$ is

$$E = \sum_{j,\mathbf{q}} \hbar\omega_j(\mathbf{q})(n_{j,\mathbf{q}} + 1/2).$$

- Notice, that if I increase one of the numbers $n_{j,\mathbf{q}}$ by one, the energy increases by $\hbar\omega_j(\mathbf{q})$, independently of the initial $n_{j,\mathbf{q}}$ and independently of any other occupation numbers.
- It then look like if I just added a particle of energy $\hbar\omega_j(\mathbf{q})$ to the system!
- These particles or quasiparticles are called phonons.

To describe quasiparticles it is convenient to introduce operators which act directly upon the occupation numbers $n_{j,\mathbf{q}}$. They are introduced as

$$\begin{aligned} b_{j,\mathbf{q}} &= \left(\frac{\omega_j(\mathbf{q})}{2\hbar}\right)^{1/2} \hat{Q}_j(\mathbf{q}) + i\left(\frac{1}{2\hbar\omega_j(\mathbf{q})}\right)^{1/2} \hat{P}_j(\mathbf{q})\,, \\ b^\dagger_{j,\mathbf{q}} &= \left(\frac{\omega_j(\mathbf{q})}{2\hbar}\right)^{1/2} \hat{Q}_j(\mathbf{q}) - i\left(\frac{1}{2\hbar\omega_j(\mathbf{q})}\right)^{1/2} \hat{P}_j(\mathbf{q})\,. \end{aligned} \tag{7.1}$$

One can show directly that

$$\begin{aligned} b_{j,\mathbf{q}}\psi_{\dots,n_{j,\mathbf{q}},\dots} &= \sqrt{n_{j,\mathbf{q}}}\psi_{\dots,n_{j,\mathbf{q}}-1,\dots}\,, \\ b^\dagger_{j,\mathbf{q}}\psi_{\dots,n_{j,\mathbf{q}},\dots} &= \sqrt{n_{j,\mathbf{q}}+1}\psi_{\dots,n_{j,\mathbf{q}}+1,\dots}\,, \end{aligned} \tag{7.2}$$

---

[1] It is a little bit more subtle than that. We will see it when we will discuss fermions.

- We see that the operator $b^\dagger_{j,\mathbf{q}}$ *increases* the occupation number $n_{j,\mathbf{q}}$ by one while the operator $b_{j,\mathbf{q}}$ *decreases* this number also by one.
- Consequently, the operators are called *creation* and *annihilation* operators for the quasiparticle $j, \mathbf{q}$.

Let us consider the properties of the creation and annihilation operators in more details. According to quantum mechanics

$$Q_{j,\mathbf{q}}\hat{P}_{j,\mathbf{q}} - \hat{P}_{j,\mathbf{q}}Q_{j,\mathbf{q}} \equiv [Q_{j,\mathbf{q}},\, \hat{P}_{j,\mathbf{q}}] = i\hbar\,. \tag{7.3}$$

Inserting in these commutation relations the definitions (7.1) we get

$$b_{j,\mathbf{q}}b^\dagger_{j,\mathbf{q}} - b^\dagger_{j,\mathbf{q}}b_{j,\mathbf{q}} = [b_{j,\mathbf{q}},\, b^\dagger_{j,\mathbf{q}}] = 1 \tag{7.4}$$

This relation could be generalized for the case of different modes because the modes with different $j, \mathbf{q}$ are independent under harmonic approximation. Consequently, the corresponding operators commute and we get

$$[b_{j,\mathbf{q}},\, b^\dagger_{j',\mathbf{q}'}] = \delta_{j,j'}\delta_{\mathbf{q},\mathbf{q}'}. \tag{7.5}$$

So we come to the picture of independent particles. To be more precise, they are called *quasiparticles.*[2]

- The quasiparticles obeying the commutation relations (7.5) are called *bosons*, they are described by the *Bose-Einstein* statistics.

Now we can insert the operators $b_{j,\mathbf{q}}$, $b^\dagger_{j,\mathbf{q}}$ into the Hamiltonian (6.14). We get

$$\mathcal{H} = \sum_{j,\mathbf{q}} \frac{\hbar\omega_j(\mathbf{q})}{2}\left[b_{j,\mathbf{q}}b^\dagger_{j,\mathbf{q}} + b^\dagger_{j,\mathbf{q}}b_{j,\mathbf{q}}\right] = \sum_{j,\mathbf{q}} \hbar\omega_j(\mathbf{q})\left[b^\dagger_{j,\mathbf{q}}b_{j,\mathbf{q}} + 1/2\right]\,. \tag{7.6}$$

Applying the product $b^\dagger_{j,\mathbf{q}}b_{j,\mathbf{q}}$ to the wave function $\psi_{\dots,n_{j,\mathbf{q}},\dots}$ we get

$$b^\dagger_{j,\mathbf{q}}b_{j,\mathbf{q}}\psi_{\dots,n_{j,\mathbf{q}},\dots} = n_{j,\mathbf{q}}\psi_{\dots,n_{j,\mathbf{q}},\dots}. \tag{7.7}$$

Consequently, the operator $b^\dagger_{j,\mathbf{q}}b_{j,\mathbf{q}}$ has eiqnevalues $n_{j,\mathbf{q}}$.

Finally, it is useful to remember matrix elements of the creation and annihilation operators:

$$\langle \dots, n'_{j,\mathbf{q}}, \dots |b_{j,\mathbf{q}}| \dots, n_{j,\mathbf{q}}, \dots\rangle = \sqrt{n_{j,\mathbf{q}}}\,\delta_{n'_{j,\mathbf{q}},n_{j,\mathbf{q}}-1}; \tag{7.8}$$

$$\langle \dots, n'_{j,\mathbf{q}}, \dots |b^\dagger_{j,\mathbf{q}}| \dots, n_{j,\mathbf{q}}, \dots\rangle = \sqrt{n_{j,\mathbf{q}}+1}\,\delta_{n'_{j,\mathbf{q}},n_{j,\mathbf{q}}+1}\,. \tag{7.9}$$

As will be demonstrated in the following:

- the normal vibrations behave as *particles* with the energy $\hbar\omega_j(\mathbf{q})$ and *quasimomentum* $\hbar\mathbf{q}$. The quasiparticles are called *phonons.* The part *quasi* is very important for some reasons which we will discuss in detail later.
- In particular, we have obtained the effective Hamiltonian as sum of the independent oscillator Hamiltonians under the *harmonic approximation* where only quadratic in displacement terms are kept.
- The higher order terms lead to an *interaction* between the introduced *quasiparticles.* In particular, phonons can scatter off each other, scatter electrons, etc.

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[2] We will see the reasons later.

- It will be shown that the conservation laws for the quasiparticle interaction differ from the ones for free particles, namely $\sum_i \hbar\mathbf{q}_i$ is conserved only with the accuracy of the arbitrary reciprocal lattice vector $\mathbf{G}$.

It is convenient to introduce operators for lattice vibrations. Using definitions of the operators $b_{j,\mathbf{q}}$ and $b_{j,\mathbf{q}}^\dagger$ and Eq. (6.12) we obtain

$$\hat{u}_{\mathbf{n},\alpha}^k(t) = \sqrt{\frac{\hbar}{2Nm_k}} \sum_{\mathbf{q},j} \frac{e_{j,\alpha,k}(\mathbf{q})}{\sqrt{\omega_j(\mathbf{q})}} \left[b_{j,\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{a}_\mathbf{n} - i\omega_j(\mathbf{q})t} + b_{j,\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{a}_\mathbf{n} + i\omega_j(\mathbf{q})t} \right] . \tag{7.10}$$

We also can build a state $|\cdots, n_{j,\mathbf{q},\dots}\rangle$ in the following way

$$|\cdots, n_{j,\mathbf{q}}, \cdots\rangle = \cdots \frac{\left(b_{j,\mathbf{q}}^\dagger\right)^{n_{j,\mathbf{q}}}}{\sqrt{n_{j,\mathbf{q}}!}} \cdots |0\rangle,$$

where the vacuum/empty state is defined as a state which is annihilated by any operator $b_{j,\mathbf{q}}$

$$b_{j,\mathbf{q}}|0\rangle = 0, \qquad \forall j \text{ and } \mathbf{q}.$$

7.2. Phonon Dispersion Measurement Techniques

Here we describe very briefly the main experimental techniques to measure the phonon spectra.

7.2.1. Neutron Scattering

In this method, neutron with the energy $E = p^2/2M_n,\ M_n = 1.67 \cdot 10^{-24}$ g are incident upon the crystal. The phonon dispersion is mapped exploiting the momentum-energy conservation law

$$\begin{aligned} E' - E &= \sum_{j,\mathbf{q}} \hbar\omega_j(\mathbf{q})(n'_{j,\mathbf{q}} - n_{j,\mathbf{q}}) , \\ \mathbf{p}' - \mathbf{p} &= -\sum_{j,\mathbf{q}} \hbar\mathbf{q}(n'_{j,\mathbf{q}} - n_{j,\mathbf{q}}) + \hbar\mathbf{G} . \end{aligned} \tag{7.11}$$

The processes involving finite $\mathbf{G}$ are called the *Umklapp* ones.

7.2.1.1. *Zero Phonon Scattering.* If no phonon are emitted or absorbed we have the same conditions as for X-ray scattering, the Laue condition $\mathbf{p}' - \mathbf{p} = \hbar\mathbf{G}$.

7.2.1.2. *One Phonon Scattering.* We get:

- Absorption:

$$\begin{aligned} E' &= E + \hbar\omega_j(\mathbf{q}) , \\ \mathbf{p}' &= \mathbf{p} + \hbar\mathbf{q} + \hbar\mathbf{G} . \end{aligned}$$

- Emission:

$$\begin{aligned} E' &= E - \hbar\omega_j(\mathbf{q}) , \\ \mathbf{p}' &= \mathbf{p} - \hbar\mathbf{q} + \hbar\mathbf{G} . \end{aligned}$$

Making use of the periodicity of the phonon spectra $\omega_j(\mathbf{q})$ we have

- Absorption:
$$\frac{\mathbf{p}'^2}{2M_n} = \frac{\mathbf{p}^2}{2M_n} + \hbar\omega_j\left(\frac{\mathbf{p}+\mathbf{p}'}{\hbar}\right),$$
- Emission
$$\frac{\mathbf{p}'^2}{2M_n} = \frac{\mathbf{p}^2}{2M_n} - \hbar\omega_j\left(\frac{\mathbf{p}-\mathbf{p}'}{\hbar}\right).$$

The equations allow one to analyze the phonon spectra.

7.2.2. Light Scattering

Usually the photons with $k \sim 10^5\ \mathrm{cm}^{-1}$ are used that corresponds to the photon energy ≈ 1 eV.

- Because this wave vector is small — much less than the size of the Brillouin zone — only central phonons contribute.
- The interaction with acoustic phonons is called *Brillouin scattering.*
- The interaction with optical modes is called the *Raman scattering.*

Once more one should apply the conservation laws. Introducing photon wave vector $\mathbf{k}$ we get

$$\begin{aligned}\omega' &= \omega \pm \omega_j(\mathbf{q}),\\ \eta\mathbf{k}' &= \eta\mathbf{k} \pm \mathbf{q} + \mathbf{G}\end{aligned}$$

where η is the refractive index,

- $+$ corresponds to a phonon absorption – the so-called anti-Stokes process.
- $-$ corresponds to an emission – Stokes process.

It is clear that $\omega_j(\mathbf{q}) \ll \omega$. Consequently, $|\mathbf{k}| \approx |\mathbf{k}'|$ and

$$q = 2\frac{\omega\eta}{c}\sin\frac{\theta}{2},$$

where θ is the scattering angle. The corresponding phonon frequency is determined as $\Delta\omega$.

- If $\Delta\omega = 0$, it means that $\mathbf{q} = \mathbf{G}$, so only specific θs are allowed – Laue/Bragg condition.

7.3. Problems

7.1. Derive the dispersion relation (3.9).
7.2. Derive the expression (3.13).
7.3. Derive Eq. (3.25).
7.4. Prove the relations (a), (b), and (c) of the Section 5.2.
7.5. Prove the relation (5.19).
7.6. Prove the equation (6.5).
7.7. Prove the expression (6.6) for the potential energy.
7.8. Prove the expression (6.9).
7.9. Prove the expression (7.2).

PART 3

Electrons in a Lattice.

LECTURE 8
Electrons in a Lattice. Band Structure.

In this lecture the properties of electron gas will be considered. Extra information can be found in many books, e. g. [**1, 2**].

8.1. General Discussion. Electron in a Periodic Field

To understand electron properties one should in general case solve the Schrödinger equation (SE) for the whole system of electrons and atoms including their interaction. There are several very important simplifications.

- The atomic mass M is much greater than the electron one m. So, for the beginning, it is natural to neglect the atomic kinetic energy, considering atoms as *fixed.* In this way we come to the SE for the many-electron wave function,

$$\left[-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + V(\mathbf{r},\mathbf{R})\right]\psi = \mathcal{E}\psi \tag{8.1}$$

  where atomic co-ordinates are considered as *external parameters*

$$\psi(\mathbf{r},\mathbf{R})\,, \quad \mathcal{E}(\mathbf{R})\,.$$

- We will see that the behavior of *interacting* electrons is very similar to the one of *non-interacting* particles (i. e. gas) in an external self-consistent field produced by the lattice ions and other electrons. It is very difficult to calculate this field but it is clear that it has *the same symmetry* as the lattice. So let us take advantage of this fact and study the general properties of the electron motion.

8.1.1. Electron in a Periodic Potential

Let us forget about the nature of the potential and take into account only the periodicity condition

$$V(\mathbf{r}+\mathbf{a}) = V(\mathbf{r})\,. \tag{8.2}$$

The one electron SE is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}). \tag{8.3}$$

- Notice, that for this equation in $1D$, if we change the notations $r \to \sqrt{\frac{\hbar^2}{2m}}t$, $\psi \to x$, and $\varepsilon \to \omega_0^2$ we will get

  $$\ddot{x} + (\omega_0^2 - V(t))x = 0.$$

  This is an oscillator with the parameter depending periodically on time. So there are conditions for the parametric resonance – these correspond to band gaps for electrons.

If the equation (8.3) has a solution $\psi(\mathbf{r})$ it should also have the solution $\psi(\mathbf{r}+\mathbf{a})$ corresponding to the *same energy.* Consequently, if the level ε is *non-degenerate* we get

$$\psi(\mathbf{r}+\mathbf{a}) = C\psi(\mathbf{r}), \quad C = \text{constant}. \tag{8.4}$$

According to the normalization condition $|C|^2 = 1$ one can write

$$C = e^{i\varphi(\mathbf{a})} \tag{8.5}$$

where φ is some real function of the lattice vector. Now we can apply the translation symmetry and make consequential displacements, $\mathbf{a}$ and $\mathbf{a}'$. We get

$$C(\mathbf{a})C(\mathbf{a}') = C(\mathbf{a}+\mathbf{a}') \tag{8.6}$$

that means the φ-function should be *linear*

$$\varphi(\mathbf{a}) = \mathbf{p}\cdot\mathbf{a}/\hbar. \tag{8.7}$$

It is clear that vector $\mathbf{p}$ is defined with the accuracy of $\hbar\mathbf{G}$ where $\mathbf{G}$ is the reciprocal lattice vector.

Finally, the general form of the electron wave function in a lattice is

$$\psi(\mathbf{r}) = e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}u_{\mathbf{p}}(\mathbf{r}) \tag{8.8}$$

where

$$u_{\mathbf{p}}(\mathbf{r}+\mathbf{a}) = u_{\mathbf{p}}(\mathbf{r}) \tag{8.9}$$

is a periodic function. The expression (8.8) is known as the *Bloch theorem.*

The meaning of this theorem is that

- due to the periodicity (8.9), we can consider only one cell of the lattice.

The Bloch function (8.8) is very similar to the plane wave, the difference being the presence of the modulation $u_{\mathbf{p}}(\mathbf{r})$. The vector $\mathbf{p}$ is called *quasimomentum* because it is defined with the accuracy $\hbar\mathbf{G}$.

- due to the periodicity of the quasimomentum, we can consider only one cell in the reciprocal lattice space.

8.2. The Model of Near Free Electrons

Let's first consider a limiting case where electrons are almost free. We start from 1D model for a very weak periodic potential $V(x)$, so

$$\hat{H} = \hat{H}_0 + \hat{V}, \qquad \hat{H}_0 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

We will consider the periodic potential as a perturbation. So at zeroth order in perturbation the states are just plane waves (we have in mind periodic boundary conditions for the sample boundaries)

$$|k\rangle = \frac{1}{\sqrt{L}} e^{ikx}\,, \quad k = p/\hbar\,, \tag{8.10}$$

the zeroth order energy being $\hat{H}_0|k\rangle = \varepsilon^{(0)}(k)|k\rangle$:

$$\varepsilon^{(0)}(k) = \hbar^2 k^2/2m\,. \tag{8.11}$$

The periodic potential with period a can be written as:

$$V(x) = \sum_{n\neq 0} V_n e^{2\pi i n x/a}. \tag{8.12}$$

The $n = 0$ term gives just a uniform shift of the energy, so we discard it.

The potential's matrix elements are

$$\langle k|\hat{V}|k'\rangle = \frac{1}{L}\int dx\, V(x) e^{-i(k-k')x} = \sum_{n\neq 0} V_n \delta\left(k - k' - \frac{2\pi n}{a}\right).$$

The first perturbation correction $\varepsilon^{(1)} = \langle k|\hat{V}|k\rangle = 0$, while the second one is

$$\varepsilon^{(2)}(k) = \sum_{k'\neq k} \frac{\langle k|\hat{V}|k'\rangle\langle k'|\hat{V}|k\rangle}{\varepsilon^{(0)}_k - \varepsilon^{(0)}_{k'}} = \sum_{n\neq 0} \frac{|V_n|^2}{\varepsilon^{(0)}(k) - \varepsilon^{(0)}(k - 2\pi n/a)} \tag{8.13}$$

We see that the perturbation theory works fine for all k except a close vicinity of $k = \pi m/a$. The problem is that at $k \to \pi m/a$ the zeroth order energies $\varepsilon^{(0)}(k) \approx \varepsilon^{(0)}(k - 2\pi m/a)$. So the denominator in (8.13) of the term with $n = m$ tends to zero. We then have two states that are degenerate. Consequently, one has to use the perturbation theory for *degenerate states*.

Let's consider a state which is very close to the dangerous momentum $k = \pi m/a + q$, where $q \ll \pi/a$. The component V_m of the potential will couple it to the state with momentum $k' = -\pi m/a + q$. We then should look for the wave function in the form

$$|\psi\rangle = A_+|\tfrac{\pi m}{a} + q\rangle + A_-| - \tfrac{\pi m}{a} + q\rangle$$

Acting on this state by the Hamiltonian we find

$$\hat{H}|\psi\rangle = A_+\varepsilon^{(0)}_{\frac{\pi m}{a}+q}|\tfrac{\pi m}{a} + q\rangle + A_-\varepsilon^{(0)}_{\frac{\pi m}{a}-q}| - \tfrac{\pi m}{a} + q\rangle + A_+\hat{V}|\tfrac{\pi m}{a} + q\rangle + A_-\hat{V}| - \tfrac{\pi m}{a} + q\rangle = \varepsilon_q|\psi\rangle$$

Multiplying this equation from the left and right by $\langle\frac{\pi m}{a} + q|$ and $\langle -\frac{\pi m}{a} + q|$, using the fact that those two states are orthogonal and that $\langle\frac{-\pi m}{a} + q|\hat{V}|\frac{\pi m}{a} + q\rangle = V_m$, we will get

$$\begin{pmatrix} \varepsilon^0_{\frac{\pi m}{a}+q} & V_m \\ V_m^* & \varepsilon^0_{-\frac{\pi m}{a}+q} \end{pmatrix} \begin{pmatrix} A_+ \\ A_- \end{pmatrix} = \varepsilon_q \begin{pmatrix} A_+ \\ A_- \end{pmatrix}$$

So ε_q are just eigenvalues of this matrix. We then have

$$\varepsilon_q = \frac{\varepsilon^{(0)}_{\pi m/a+q} + \varepsilon^{(0)}_{\pi m/a-q}}{2} \pm \sqrt{\left(\frac{\varepsilon^{(0)}_{\pi m/a+q} - \varepsilon^{(0)}_{\pi m/a-q}}{2}\right)^2 + |V_m|^2}.$$

Using Taylor expansion $\varepsilon^0_{\frac{\pi m}{a}\pm q} \approx \varepsilon_m \pm v_m q$ we find

$$\varepsilon_q = \varepsilon_m \pm \sqrt{v_m^2 q^2 + |V_m|^2}.$$

The branches must be chosen such, that the ε_q is increasing as q is increasing, so

$$\varepsilon_q - \varepsilon_m = \begin{cases} -\sqrt{v_m^2 q^2 + |V_m|^2}, & \text{for } q < 0 \\ \sqrt{v_m^2 q^2 + |V_m|^2}, & \text{for } q > 0 \end{cases}$$

So at $q = 0$ the spectrum has a gap

$$\Delta_m = \varepsilon_{q\to 0_+} - \varepsilon_{q\to 0_-} = 2|V_m|.$$

- Notice, that the group velocity $\frac{d\varepsilon_q}{dq} \to 0$, as $q \to 0$, from either side. This is a general situation that on the boundaries of BZ the group velocity is zero.

This situation is illustrated in Fig. 1

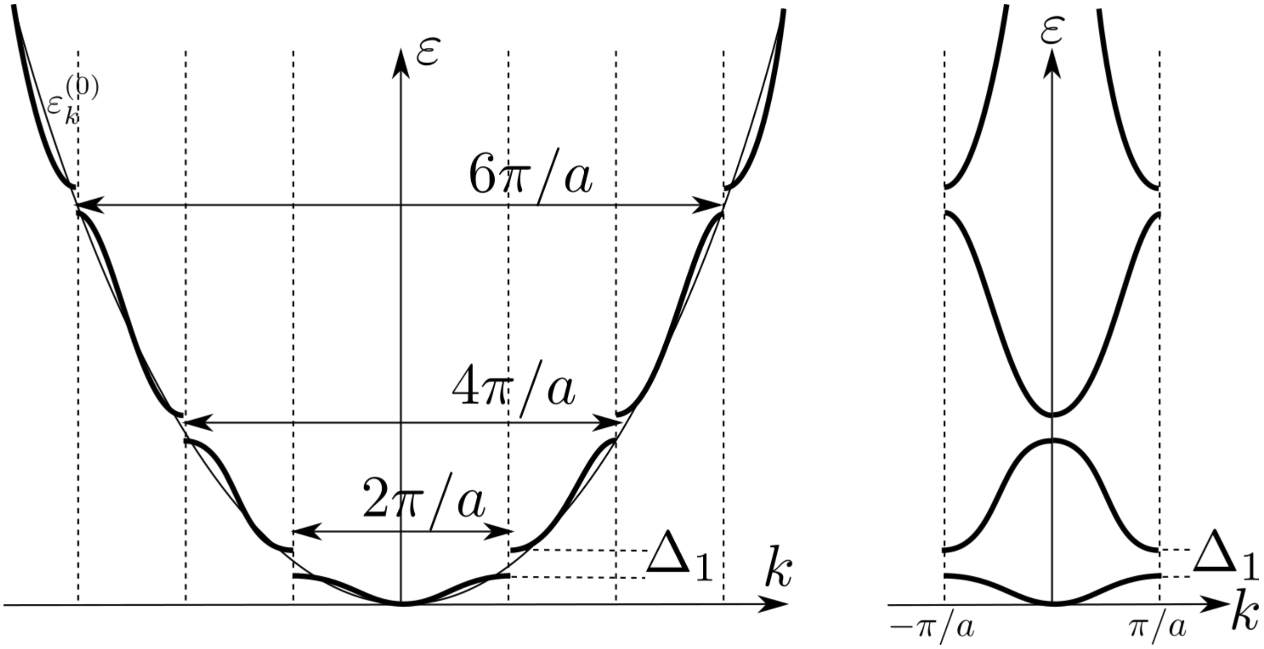

Figure 1. Energy spectrum in a weak periodic potential.

Because the energy spectrum is periodic in **k**-space, it is convenient to make use of the periodicity of ε in k-space and to subtract from each value of k the reciprocal lattice vector in order to come within BZ. So we come from the left panel of Fig. 1 to the right one. We a picture of bands with gaps in between, the gaps being small in comparison with the widths of the allowed bands.

Another often used construction is to imagine, that the BZ iz a circle. We then have energy bands as a set of smooth functions on a circle. In 3D the spectrum is defined on a torus in the momentum space.

8.2.1. $3D$ case.

In the 3D case the periodicity of the potential is taken into account by the expansion

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$$

where $\mathbf{G}$ is the reciprocal lattice vector, the perturbation theory being destroyed at

$$\varepsilon^{(0)}(\mathbf{k}) = \varepsilon^{(0)}(\mathbf{k} - \mathbf{G}) .$$

Substituting $\varepsilon^{(0)} = \hbar^2 k^2/2m$ we get

$$\mathbf{k} \cdot \mathbf{G} = \mathbf{G}^2/2 . \tag{8.14}$$

It is just the equation for the plane boundary of the BZ.

Thus the structure of BZ is important for understanding of electron properties.

LECTURE 9
Tight Binding Approximation, General properties. Summation over states.

9.1. Tight Binding Approximztion.

Here we consider an opposite limit of strong periodic potential. The electrons then at zeroth order are localized on the lattice sites. The corrections then lead to the electrons being able to hop from one site to another. This is so-called tight-binding-approximation.

- The simplest corresponding problem is quantum particle in a double well potential.
- Atomic orbitals are fuzzy.

Let us start with the 1D case and assume that the overlap of the electron shells is very small. Consequently, this overlap can be considered as perturbation.

We start with the potential

$$V(x) = \sum_n U(x - na)\,, \tag{9.1}$$

the SE equation being

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \sum_n U(x - na)\psi(x) = \varepsilon\psi(x)\,. \tag{9.2}$$

Let the exact wave functions be

$$\psi_p(x) = e^{ipx/\hbar}u_p(x)$$

with the eigenvalues $\varepsilon(p)$. We construct the so-called *Wannier* functions as

$$w_n(x) = \frac{1}{\sqrt{N}}\sum_p e^{-ipna/\hbar}\psi_p(x)\,, \tag{9.3}$$

where N is the total number of atoms in the chain while p belongs to the 1st BZ. One can check (*Problem 12.1*) that the inverse transform is

$$\psi_p(x) = \frac{1}{\sqrt{N}}\sum_n e^{ipna/\hbar}w_n(x)\,. \tag{9.4}$$

The Wannier functions are orthogonal and normalized (*Problem 12.2*).

It is important that the

- Wannier function w_n is large only near the nth ion position (without Bloch modulation it will be δ-function $\delta(x-na)$).
- Moreover, because of periodicity

$$w_n(x) = w_0(x-na)\,.$$

Now let's introduce the following notation

$$V(x) = U(x-na) + h_n(x), \qquad h_n = \sum_{n'\neq n} U(x-n'a)$$

and substitute the function (9.4) into the exact SE

$$\hat{H}\psi_p = \frac{1}{\sqrt{N}}\sum_n e^{ipna/\hbar}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x-na) + h_n(x)\right]w_n(x) = \frac{1}{\sqrt{N}}\varepsilon_p \sum_n e^{ipna/\hbar} w_n(x)$$

We get

$$\begin{aligned}\sum_n e^{ikan}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x-na)\right]w_n(x) \quad &+ \quad \sum_n h_n(x)e^{ikan}w_n(x) = \\ &= \quad \varepsilon(k)\sum_n e^{ikan}w_n(x)\,. \end{aligned} \tag{9.5}$$

Here we have introduced the electron wave vector $k \equiv p/\hbar$.

The product

$$h_n(x)\,e^{ikan}\,w_n(x)$$

is small because it contains only the items $U(x-ma)\,w_n(x)$ for $m\neq n$, and we can neglect it at the zeroth approximation. As a result we get

$$w_n^{(0)} = \Psi_0(x-na),$$

where $\Psi_0(x)$ is the wave function of a free atom. Consequently

$$\varepsilon^{(0)}(p) = \varepsilon_0\,.$$

Notice, that

- The zeroth order spectrum is highly degenerate.
- We could not have started from looking for a solution in the form of linear combinations of functions $\Psi_0(x-na)$, as these functions are not orthogonal to each other.

In the next approximation we put $w_n = w_n^{(0)} + w_n^{(1)}$ and find

$$\begin{aligned}\sum_n\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right. \quad &+ \quad U(x-na)-\varepsilon_0\big]\,e^{ikan}w_n^{(1)}(x) = \\ &= \quad -\sum_n h_n(x)e^{ikan}w_n^{(0)}(x) + (\varepsilon(k)-\varepsilon_0)\sum_n e^{ikan}w_n^{(0)}(x)\,. \end{aligned} \tag{9.6}$$

This is *non-uniform linear* equation for $w_n^{(1)}$. Since the Hamiltonian is Hermitian, Eq. (9.6) has a solution only if the r.h.s. is orthogonal to the solution of the corresponding *uniform* equation with the same boundary conditions. This solution is $w_n^{(0)}$.

As a result, we get

$$\varepsilon(k) - \varepsilon_0 = \frac{\sum_n h(n)e^{ikan}}{\sum_n I(n)e^{ikan}} \tag{9.7}$$

where

$$
\begin{aligned}
h(n) &= \int dx\, \Psi_0^*(x) h_n(x) \Psi_0(x-na)\,, \\
I(n) &= \int dx\, \Psi_0^*(x) \Psi_0(x-na)\,.
\end{aligned}
\tag{9.8}
$$

The atomic wave function can be chosen as real, so $h(-n) = h(n)$, $I(-n) = I(n)$, both functions rapidly decrease with increasing n (small overlap!). Finally, we get (*Problem 12.3*)

$$
\varepsilon(k) - \varepsilon_0 = h(0) - 2[h(0)I(1) - h(1)]\cos(ka)\,. \tag{9.9}
$$

9.1.1. $3D$ case.

The 3D case is more complicated if there are more than 1 atom in a primitive cell. First, atoms' positions are connected by the symmetry transforms which differ from a simple translation. Second, atomic levels for higher momenta are degenerate. We discuss here the simplest case with 1 atom per a primitive cell and for s-states of the atoms having spherical symmetry. In this case we come to a similar expression

$$
\varepsilon(\mathbf{k}) - \varepsilon_0 = \frac{\sum_{\mathbf{n}} h(\mathbf{n}) e^{i\mathbf{k}\cdot\mathbf{a}_\mathbf{n}}}{\sum_{\mathbf{n}} I(\mathbf{n}) e^{i\mathbf{k}\cdot\mathbf{a}_\mathbf{n}}}\,. \tag{9.10}
$$

In a bcc lattice taking into account nearest neighbors we get

$$
\mathbf{a} = (a/2)(\pm 1,\ \pm 1,\ \pm 1)\,,
$$

and

$$
\varepsilon(\mathbf{k}) - \varepsilon_0 = h(0) - 8W\cos(k_x a/2)\cos(k_y a/2)\cos(k_z a/2)\,, \tag{9.11}
$$

where $W = [h(0)I(1) - h(1)]$ is the characteristics of bandwidth. In a similar case of fcc lattice one gets (Check!)

$$
\varepsilon(\mathbf{k}) - \varepsilon_0 = h(0) - 4W\left[\cos(k_x a/2)\cos(k_y a/2) + \cos(k_y a/2)\cos(k_z a/2) + \cos(k_z a/2)\cos(k_x a/2)\right].
$$

In a sc lattice one gets (*Problem 12.4*)

$$
\varepsilon(\mathbf{k}) - \varepsilon_0 = h(0) - 2W\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right]\,. \tag{9.12}
$$

The physical meaning of the results is the spreading of atomic levels into narrow bands (Fig. 1)

The tight binding approximation is useful when the overlap is small (transition and rare earth metals). Another application is to produce starting empirical formulas having proper symmetry.

9.2. Some general properties of $\varepsilon_l(\mathbf{p})$.

The spectrum is given by the functions $\varepsilon_l(\mathbf{p})$, where l labels the band and $\mathbf{p}$ is quasimomentum.

The functions $\varepsilon_l(\mathbf{p})$ are periodic in the reciprocal space, so they have maximal and minimal values and form bands. These band can overlap or some energy gaps can exist.

Let us consider some other general properties of wave functions. If one writes down the complex conjugate to the Schrödinger equation and then replaces $t \to -t$ he gets the same

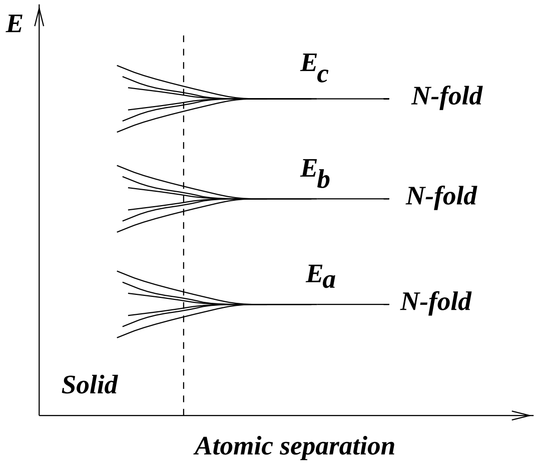

Figure 1. Spreading of atomic levels into bands

equation with the Hamiltonian $\mathcal{H}^*$. But it is known that Hamiltonian is a Hermitian operator and $\mathcal{H} = \mathcal{H}^*$. It means that if

$$\psi_{l\mathbf{p}}(\mathbf{r},t) = \exp\left[-i\varepsilon_l(\mathbf{p})t/\hbar\right]\psi_{l\mathbf{p}}(\mathbf{r})$$

is an eigenfunction of $\mathcal{H}$ the function $\psi^*_{l\mathbf{p}}(\mathbf{r},-t)$ is also the eigenfunction. At the same time, after the shift $\mathbf{a}$ these functions acquire different factors, $e^{\pm i\mathbf{pa}/\hbar}$ respectively. It means

$$\varepsilon_l(\mathbf{p}) = \varepsilon_l(-\mathbf{p})\,.$$

In the following we will specify the region of the reciprocal space in the same way as for lattice vibrations, namely, Brillouin zones (BZ). If the lattice symmetry is high enough the extrema of the functions $\varepsilon_l(\mathbf{p})$ are either in the center or at the borders of BZ.

Consider a state near a zone boundary. Let's apply a time reversal, and then shift by a zone length. We will end up with the state, just outside of the zone boundary. This state must have the same energy, as the original. So the derivative $\partial\varepsilon_p/\partial p$ at the zone boundary is zero – the group velocity is zero.

9.3. Summation over states.

As in the situation with lattice vibrations, we apply cyclic boundary conditions for the sample boundaries, so the vector $\mathbf{p}$ is a discrete variable:

$$p_i = \frac{2\pi\hbar}{L_i}n_i\,, \tag{9.13}$$

the number of states being

$$\sum_i \Delta n_i = \frac{\mathcal{V}}{(2\pi\hbar)^3}\sum_i \Delta p_i\,. \tag{9.14}$$

It means that the density of states is $\mathcal{V}/(2\pi\hbar)^3$. We will very often replace the sums over discrete states by the integrals

$$\mathcal{V}\sum_i \to \mathcal{V}\int\frac{2\,d^3p}{(2\pi\hbar)^3} \equiv \mathcal{V}\int(dp)\,.$$

Here we have taken into account that an electron has spin 1/2, the projection to a given axis being ±1/2 that doubles the number of states. Thus, the energy levels are specified as $\varepsilon_l(\mathbf{p})$ where $\mathbf{p}$ acquires N values where N is the number of primitive cells in the sample.

LECTURE 10
Main Properties of Bloch Electrons

10.1. Effective Mass

Let us discuss general properties on electrons in periodic potential. To make it as simple as possible we start with the case of a simple cubic crystal in the tight binding limit. From the expression (9.12)

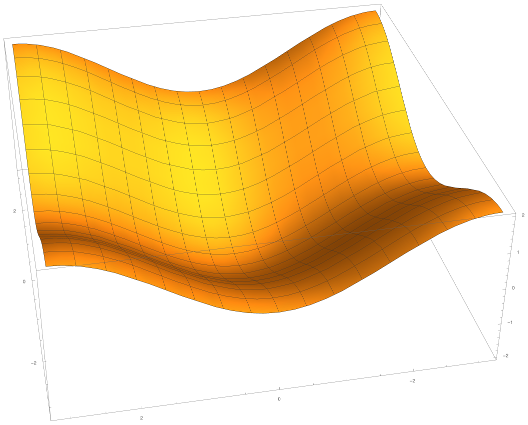

Figure 1. Energy band on a square lattice (2D simple cubic).

$$\varepsilon(\mathbf{k}) - \varepsilon_0 = h(0) - 2W\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right]$$

we see that there is a minimum $\mathbf{b}$ in the BZ center $\mathbf{k} = 0$. Near the minimum expanding (9.12) for small product $k_i a \ll 1$ we get

$$\varepsilon = \varepsilon_b + Wk^2a^2\,, \quad k = \sqrt{k_x^2 + k_y^2 + k_z^2}\,, \tag{10.1}$$

where ε_b is the energy of the minimum. So the spectrum is just the same as the one of a particle with the *effective mass*

$$m_n^*(b) = \left(\frac{\partial^2 \varepsilon}{\partial p_x^2}\right)_{\mathbf{b}}^{-1} = \frac{\hbar^2}{2Wa^2} \tag{10.2}$$

(the subscript n indicates that the material is of n-type, electron-like). Now we can analyze the BZ boundary $\mathbf{a}$ with $k_i \approx \pi/a$. Substituting $k_i' = \pi/a - k_i$ and expanding (9.12) in powers of $k_i' a \ll 1$ we get

$$\varepsilon = \varepsilon_a - W a^2 k'^2 \,. \tag{10.3}$$

In a similar way, we get the expression for the effective mass

$$m_n^*(a) = -\frac{\hbar^2}{2Wa^2} \tag{10.4}$$

that is *negative*. Very often such a quasiparticle is called a *hole* (see later) and we define its mass as the electron mass with opposite sign. So, in a simple cubic crystal the hole mass, $m_p^* = |m_n^*|$, near the band top is the same as the electron mass near its bottom.

In the general case one can expand the energy as in lth band near an extremum as

$$\varepsilon_l(\mathbf{k}) = \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2 \varepsilon(\mathbf{k})}{\partial k_\alpha \partial k_\beta}\right)_0 (k_\alpha - k_{\alpha 0})(k_\beta - k_{\beta 0}) \tag{10.5}$$

and introduce the *inverse effective mass* tensor

$$(m^{-1})_{\alpha\beta} = \left(\frac{\partial^2 \varepsilon(\mathbf{k})}{\partial k_\alpha \partial k_\beta}\right)_0 \tag{10.6}$$

This 2nd-order tensor can be transformed to its principal axes.

10.2. Wannier Theorem → Effective Mass Approach

Now we come to a very important concept of solid state physics which allows one to treat electrons in a periodic field like ordinary particles - to the so-called *effective mass* approach.

We know that the energy in a given band is periodic in the **k**-space that is the same as the reciprocal lattice space. So we can expand

$$\varepsilon_l(\mathbf{k}) = \sum_{\mathbf{a}} c_{\mathbf{a}} e^{i\mathbf{k}\cdot\mathbf{a}} \tag{10.7}$$

where **a** are lattice vectors (Check!). How does the operator

$$\exp\left(\mathbf{a}\cdot\nabla\right)$$

act upon a function? One can immediately show that it is just the operator, which shifts the co-ordinate by **a** (*Problem 12.5*):

$$\exp(\mathbf{a}\cdot\nabla)\psi(\mathbf{r}) = \psi(\mathbf{r}+\mathbf{a})\,. \tag{10.8}$$

Then we come to the very important formula:

$$\varepsilon_l(-i\nabla)\,\psi_{l,\mathbf{p}}(\mathbf{r}) = \sum_{\mathbf{a}} c_{\mathbf{a}} e^{\mathbf{a}\cdot\nabla}\psi_{l,\mathbf{p}}(\mathbf{r}) = \sum_{\mathbf{a}} c_{\mathbf{a}}\psi_{l,\mathbf{p}}(\mathbf{r}+\mathbf{a}) = \sum_{\mathbf{a}} c_{\mathbf{a}} e^{i\mathbf{p}\cdot\mathbf{a}}\psi_{l,\mathbf{p}}(\mathbf{r}) = \varepsilon_l(\mathbf{p})\,\psi_{l,\mathbf{p}}(\mathbf{r})\,. \tag{10.9}$$

In short

$$\varepsilon_l(-i\nabla)\,\psi_{l,\mathbf{p}}(\mathbf{r}) = \varepsilon_l(\mathbf{p})\,\psi_{l,\mathbf{p}}(\mathbf{r}), \qquad \text{or} \qquad \varepsilon_l(\hat{\mathbf{p}})\,\psi_{l,\mathbf{p}}(\mathbf{r}) = \varepsilon_l(\mathbf{p})\,\psi_{l,\mathbf{p}}$$

This relation is called the *Wannier theorem.* It is valid only if the spectrum is non-degenerate in the point **p**.

- Notice, that if $\epsilon_l(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}$, then what is written is the SE for a free particle.

So we come to the following prescription. As far as we know the spectrum $\varepsilon_l(\mathbf{k})$, we can replace $\mathbf{k} \to -i\nabla$ in the SE (which can also contain external fields) and analyze the electron's quantum dynamics. If we return to the situation where quadratic expansion is possible we come to the problem of a particle with (anisotropic) effective mass which can strongly differ from the free electron mass m_0.

- It is important to note that the prescription has essentially *single-band character*, it needs a very serious generalization if the bands are degenerate (or the gaps are narrow and interband transitions are possible).

It is important in many situations in semiconductor crystals and we will come back to this point in a later lecture.

10.3. Electron Velocity

Let us calculate quantum mechanical average electron velocity $\langle \mathbf{v} \rangle$ in a Bloch state $|\gamma\rangle \equiv |l, \mathbf{k}\rangle$. For a free electron one would obtain

$$\langle \mathbf{v} \rangle = \frac{1}{m_0} \langle \mathbf{p} \rangle = -\frac{i\hbar}{m_0} \langle \gamma | \nabla | \gamma \rangle = \frac{\hbar \mathbf{k}}{m_0} \,.$$

It is natural that for a quantum particle the average velocity is just the *group* velocity of the wave package representing quantum particle,

$$\mathbf{v} = \frac{\partial \varepsilon}{\partial \mathbf{p}} = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial \mathbf{k}} \tag{10.10}$$

(see *Problem 12.6*).

We see that if the spectrum is determined by quadratic expansion we get the usual expression for a particle with the mass m^*. In and external field we get the Newton equation

$$m^* \frac{\partial \mathbf{v}}{\partial t} = \mathbf{F} \,.$$

10.3.1. Electric current in a Bloch State. Concept of Holes.

Suppose that the electron has the charge $-e$ (we suppose e to be positive). The electric current is

$$\mathbf{j}_\gamma = -e \mathbf{v}_\gamma \,. \tag{10.11}$$

We know that $\varepsilon(-\mathbf{k}) = \varepsilon(\mathbf{k})$. Consequently, $\mathbf{v}(-\mathbf{k}) = -\mathbf{v}(\mathbf{k})$ and one can easily show that

$$\sum_{BZ} \mathbf{v}(\mathbf{k}) = 0 \tag{10.12}$$

where summation is performed inside the BZ. To get the total current one should multiply the equation (10.11) by 2 (number of spin projections).

- Taking into account relation (10.12) one can prove that *the total current of completely filled band vanishes.* It is a very important statement because it remains valid also in an external electric field (if the field is small enough and electrons are not transferred to higher bands).

If the band is only filled partly, the total current is determined by the difference of filled states with $\mathbf{k}$ and $-\mathbf{k}$. To formulate the current we introduce the occupation factor $\nu_n(\mathbf{k}, s)$

which is equal to 1 if the state with the quasimomentum $\hbar\mathbf{k}$ and spin s is *occupied* and 0 otherwise. One can also introduce the occupation number of *holes* as

$$\nu_p(\mathbf{k},s) = 1 - \nu_n(\mathbf{k},s)$$

which characterizes the probability of *empty* states. The current can be expressed as

$$\mathbf{j} = -e\sum_{\mathbf{k},s}\nu_n(\mathbf{k},s)\mathbf{v}(\mathbf{k}) = e\sum_{\mathbf{k},s}\nu_p(\mathbf{k},s)\mathbf{v}(\mathbf{k})$$

(the current of a completely filled band is zero!). So we can express the current of a partly full band as the current of *holes* with the charge $+e > 0$.

To get a more deep analogy let us calculate the *energy current* due to the flux of electrons and holes. Characterizing the energy current in a state $\mathbf{k}$ as $\mathbf{v}(\mathbf{k})[\varepsilon(\mathbf{k}) - e\varphi]$ where φ is the electric potential we get

$$\begin{aligned} \mathbf{w} &= \sum_{\mathrm{k},s}\nu_n(\mathbf{k},s)[\varepsilon(\mathbf{k}) - e\varphi]\mathbf{v}(\mathbf{k}) = \sum_{\mathrm{k},s}[1-\nu_p(\mathbf{k},s)][\varepsilon(\mathbf{k}) - e\varphi]\mathbf{v}(\mathbf{k}) = \\ &= \sum_{\mathrm{k},s}[\varepsilon(\mathbf{k}) - e\varphi]\mathbf{v}(\mathbf{k}) + \sum_{\mathrm{k},s}\nu_p(\mathbf{k},s)[-\varepsilon(\mathbf{k}) + e\varphi]\mathbf{v}(\mathbf{k}) \end{aligned} \tag{10.13}$$

The first term is zero as $\mathbf{v}(\mathbf{k}) = \frac{\partial\varepsilon_l(\mathbf{k})}{\partial\mathbf{k}}$.

So we see that holes can be considered as particles with the energy $-\varepsilon(\mathbf{k})$. The usual way to treat the quasiparticles near the top of the band where the expansion (10.3) is valid is to define the hole energy as

$$\varepsilon_p(\mathbf{k}) = \varepsilon_a - \varepsilon_n(\mathbf{k})\,, \quad m_p = -m_n > 0$$

where subscript n characterizes an electron variable. In such a way we come to the description of the particles with the charge e and effective mass m_p.

10.4. Band Filling and Classification of Materials

We have discussed the picture of allowed bands and forbidden gaps. Now we are prepared to discuss the actual presence of electrons in these bands.

One can discuss the following variants.

(a) There is one atom per cell and 1 electron per atom. Consequently, at $T = 0$ the band is *half-full*.
(b) One atom per cell and 2 electrons per atom. The band is full, there is a band gap and the next band is empty.
(c) There are two atoms per cell and each atom contributes 1 electron. The same as in the previous case.

In the case 1 the material has high conductivity at very low temperatures, it is a *metal*. The cases 2 and 3 correspond to *insulators*, their conductivity exponentially decreases at low temperatures. This is shown in Fig. 2.

- All this scheme is valid if the bands do not overlap. If the bans overlap the conduction is usually metallic (see Fig. 3). Such materials are often call *semimetals* if effective number of carriers is small. A typical example of semimetals is Bi.

The *semiconductors* are defined as insulators with small forbidden gaps. At finite temperatures some electrons are excited from the lower *valence* band to the upper, *conduction*

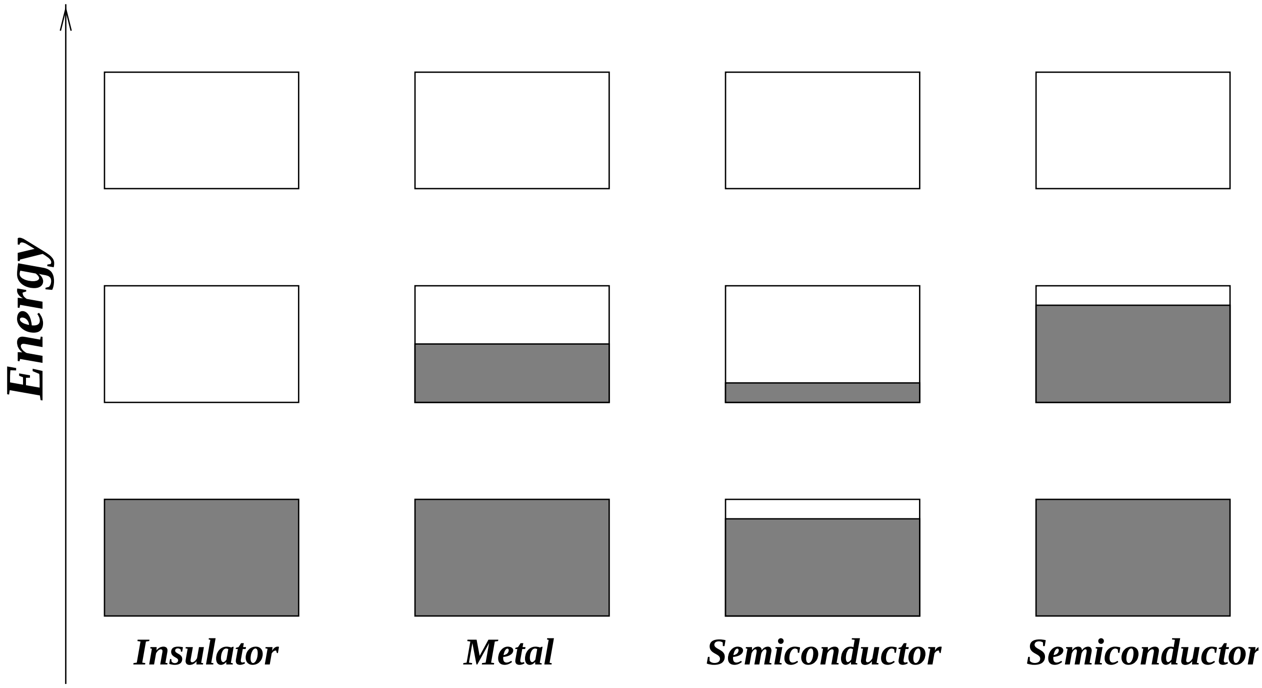

Figure 2. Electron occupation of bands (schematically).

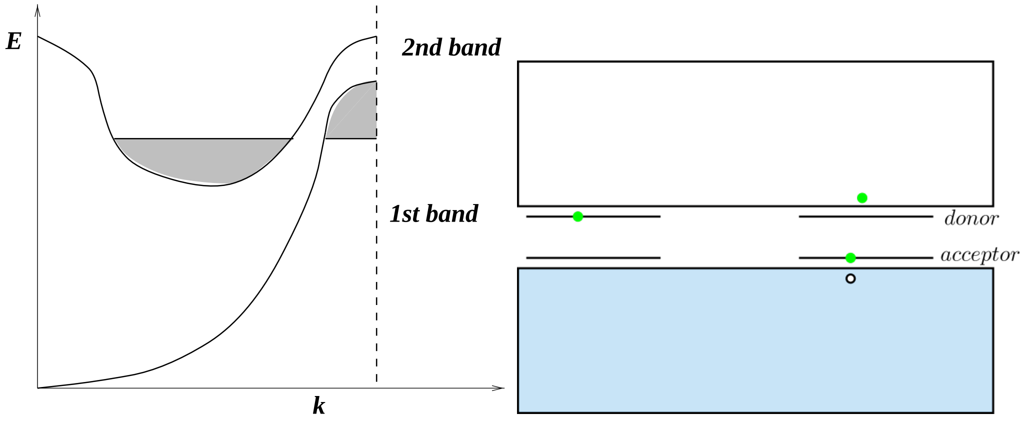

Figure 3. Left: the case of band overlap. Right: donors and acceptors.

one. So there are holes in the valence band and the electrons in the conduction one. Such semiconductor is called *intrinsic*.

(The electron and a hole may interact strong enough to produce a bound state, such state is called "an exciton".)

The modern way to produce materials for electronics is to *"dope"* semiconductor material with impurity atoms which introduce carriers in a controllable way.

The impurity level are usually situated in the forbidden gap. If the impurity level are situated near the bottom of conduction band the atom are ionized at low enough temperatures and provide extra electrons to the band (such impurities are called *donors*). Contrary, if the levels are near the top of the valence band they take electrons from the band producing holes (they are called *acceptors*).

We will come back to this classification later to describe special features of different materials.

LECTURE 11
Dynamics of Bloch Electrons

Now we discuss dynamic properties of Bloch electrons both classical and quantum.

11.1. Classical Mechanics

As we have seen, under the *one band approximation* the Bloch electron can be described as a particle with the classical Hamilton function

$$\mathcal{H}(\mathbf{p},\mathbf{r}) = \varepsilon(\mathbf{p}) + \mathcal{U}(\mathbf{r}), \qquad \mathbf{p} = \hbar\mathbf{k}.$$

Here $\mathcal{U}(\mathbf{r})$ is the total potential energy due to external fields. To take account of magnetic field one should replace the momentum $\mathbf{p}$ by the *kinematic* one[1]

$$\mathbf{p} \to \mathbf{P} = \mathbf{p} + \frac{e}{c}\mathbf{A}(\mathbf{r})$$

where $\mathbf{A}$ is the *vector-potential* of the magnetic field which is connected with the magnetic field $\mathbf{H}$ by the relation

$$\mathbf{H} = \operatorname{curl}\mathbf{A}.$$

Consequently, we have

$$\mathcal{H}(\mathbf{p},\mathbf{r}) = \varepsilon\left[\mathbf{p}+\frac{e}{c}\mathbf{A}(\mathbf{r})\right] + \mathcal{U}(\mathbf{r}), \qquad \mathbf{p} = \hbar\mathbf{k}$$

where

$$\mathcal{U}(\mathbf{r}) = U(\mathbf{r}) - e\varphi(\mathbf{r})\,,$$

U is the potential energy due to non-electric fields (like deformation), while φ is the electrostatic potential. To analyze the dynamics one should use classical Hamilton equations

$$\dot{\mathbf{r}} = \mathbf{v} = \frac{\partial\mathcal{H}}{\partial\mathbf{p}}, \qquad \dot{\mathbf{p}} = -\frac{\partial\mathcal{H}}{\partial\mathbf{r}}.$$

The first equation reduces to the one we have discussed earlier,

$$\mathbf{v} = \frac{\partial\varepsilon}{\partial\mathbf{p}}$$

while the second one needs more care because the vector-potential is $\mathbf{r}$-dependent. We get

$$\dot{p}_i = -\frac{\partial}{\partial x_i}\varepsilon\left[\mathbf{p}+\frac{e}{c}\mathbf{A}(\mathbf{r})\right] - \frac{\partial\mathcal{U}(\mathbf{r})}{\partial x_i}.$$

---

[1] Remember that we denote the electron charge as $-e$.

The first item is

$$-\frac{e}{c}\sum_k \frac{\partial \varepsilon}{\partial p_k}\frac{\partial A_k}{\partial x_i} = -\frac{e}{c}\sum_k v_k \frac{\partial A_k}{\partial x_i}.$$

We will consider for simplicity the case of a *homogeneous* magnetic field. It is convenient to choose the so-called *Landau gauge*

$$\mathbf{A} = \begin{pmatrix} 0 \\ Hx \\ 0 \end{pmatrix}, \qquad \mathbf{H} = H\hat{\mathbf{z}}. \tag{11.1}$$

In this case we have

$$-\frac{e}{c}v_y\frac{\partial A_y}{\partial x} = -\frac{e}{c}v_y H_z = -\frac{e}{c}\left[\mathbf{v}\times\mathbf{H}\right]_x .$$

As a result, we come to the very usual formula

$$\dot{\mathbf{p}} = (-e)\left(\mathbf{E}+\frac{1}{c}\left[\mathbf{v}\times\mathbf{H}\right]\right) - \nabla U(\mathbf{r}), \qquad \mathbf{E} = -\nabla\varphi(\mathbf{r}). \tag{11.2}$$

which is just the Newton law for the particle with the charge $-e$.

In the absence of external the electric field and the potential U, as one can easily show, energy is conserved. Indeed

$$\frac{d\varepsilon}{dt} = \frac{\partial\varepsilon}{\partial\mathbf{p}}\frac{\partial\mathbf{p}}{\partial t} + \frac{\partial\varepsilon}{\partial\mathbf{r}}\frac{\partial\mathbf{r}}{\partial t} = -2\frac{e}{c}\left(\mathbf{v}\left[\mathbf{v}\times\mathbf{H}\right]\right) = 0.$$

So we have 2 integrals of motion,

$$\varepsilon = \text{const}, \qquad p_z = \text{const}.$$

Thus we come to a geometric picture: one should take the surface $\varepsilon(\mathbf{p}) = \text{const}$ and intersect this surface by the plane $p_z = \text{const}$. The resulting line is just the electron orbit in $\mathbf{p}$-space.

It is clear that the result is strongly dependent on the *shape* of the surface $\varepsilon(\mathbf{p}) = \text{const}$. In semiconductors usually only the electrons near band extrema are important and all the orbits are *closed* lines.

The situation is much more rich in metals where the number of conduction electrons is large and (because of the Pauli principle) at small temperatures they occupy the states below the certain energy which is called the *Fermi level* ϵ_F. The electrons near the surface

$$\varepsilon(\mathbf{p}) = \epsilon_F$$

(the *Fermi surface*, FS) are most important for all the properties of metals. If the Fermi surface is confined within one BZ it is called *closed*. In general, FS can touch the boundaries of the BZ. In this case it is called *open*. The examples of closed and open FS in 2D case are shown in Fig. 1 while some FS in 3D case are shown in Fig. 2 and Fig. 3.

The closed orbits can be both electron- and hole-like. *Electron* orbits are the ones with the velocity $\mathbf{v} = \nabla_{\mathbf{p}}\varepsilon(\mathbf{p})$ is directed "*outside*" the orbit, the hole ones have to velocity directed "*inside*". It easy to show that it is just the same definition as we have used previously (see later). If the magnetic field is tilted with respect to the symmetry axes both closed and open orbits can exist (see Fig. 4).

To study the motion in momentum space one can introduce the element

$$dp \equiv \sqrt{(dp_x)^2 + (dp_y)^2}.$$

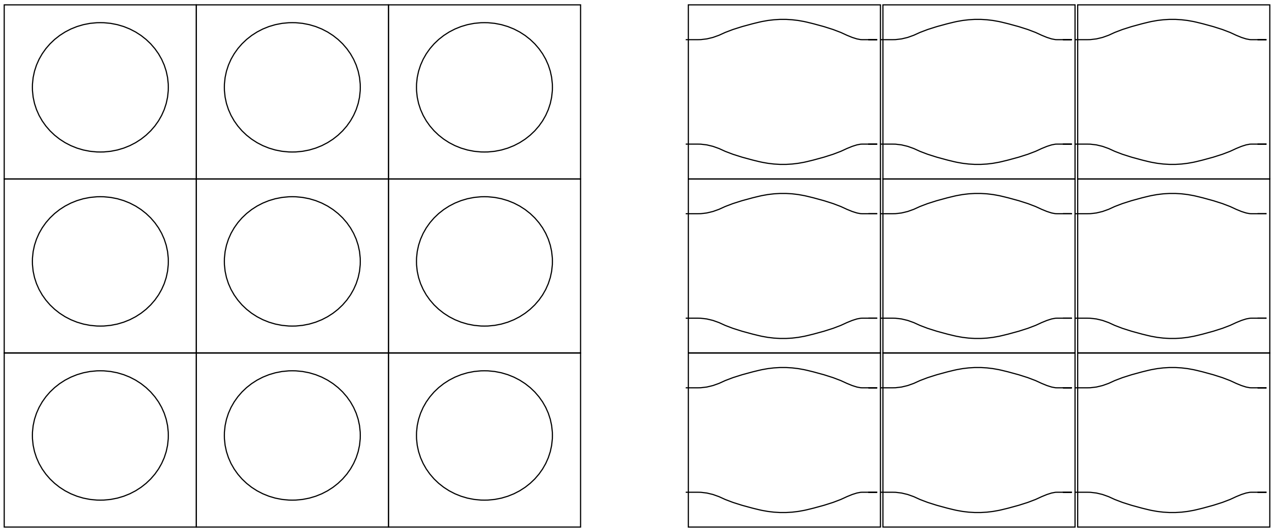

Figure 1. Closed and open FS in two-dimensional case (examples).

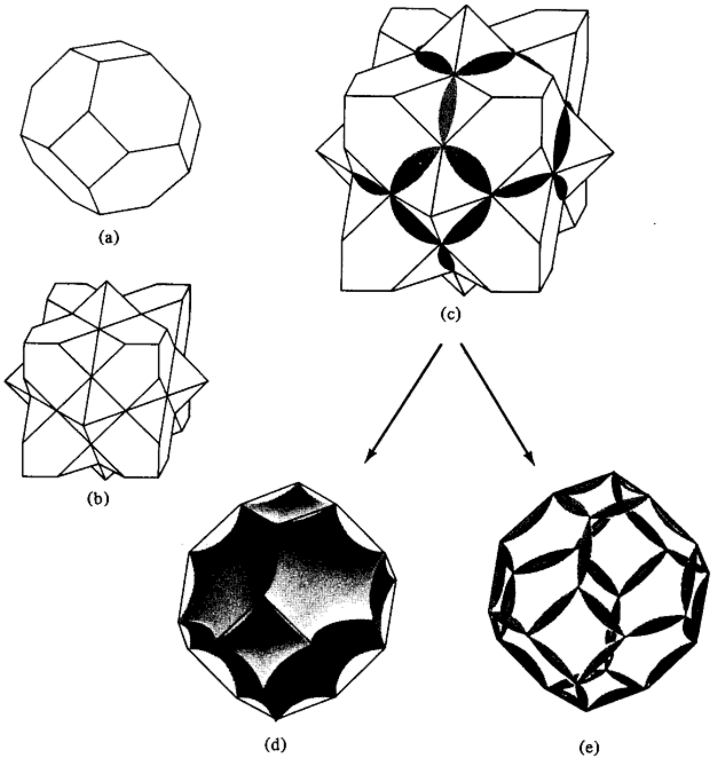

Figure 2. (a) 1st BZ for a fcc crystal (Al). (b) 2nd BZ for a fcc crystal. (c) The free electron sphere for a trivalent fcc Bravais lattice. It completely encloses the 1st zone, passing trough and beyond the 2nd zone into the third and (at the corners) ever slightly into the fourth. (d) Portion of the free electron surface in the second zone when translated into the 1st zone. The convex surface encloses holes. (e) portion of the free electron sphere in the 3d zone when translated into the 1st zone. The surface encloses electrons.

Taking squares of Eq. (11.2) for p_x and p_y and adding them we get

$$\frac{dp}{dt} = \frac{e}{c} H v_\perp, \qquad \text{or} \quad dt = \frac{c}{eH}\frac{dp}{v_\perp}.$$

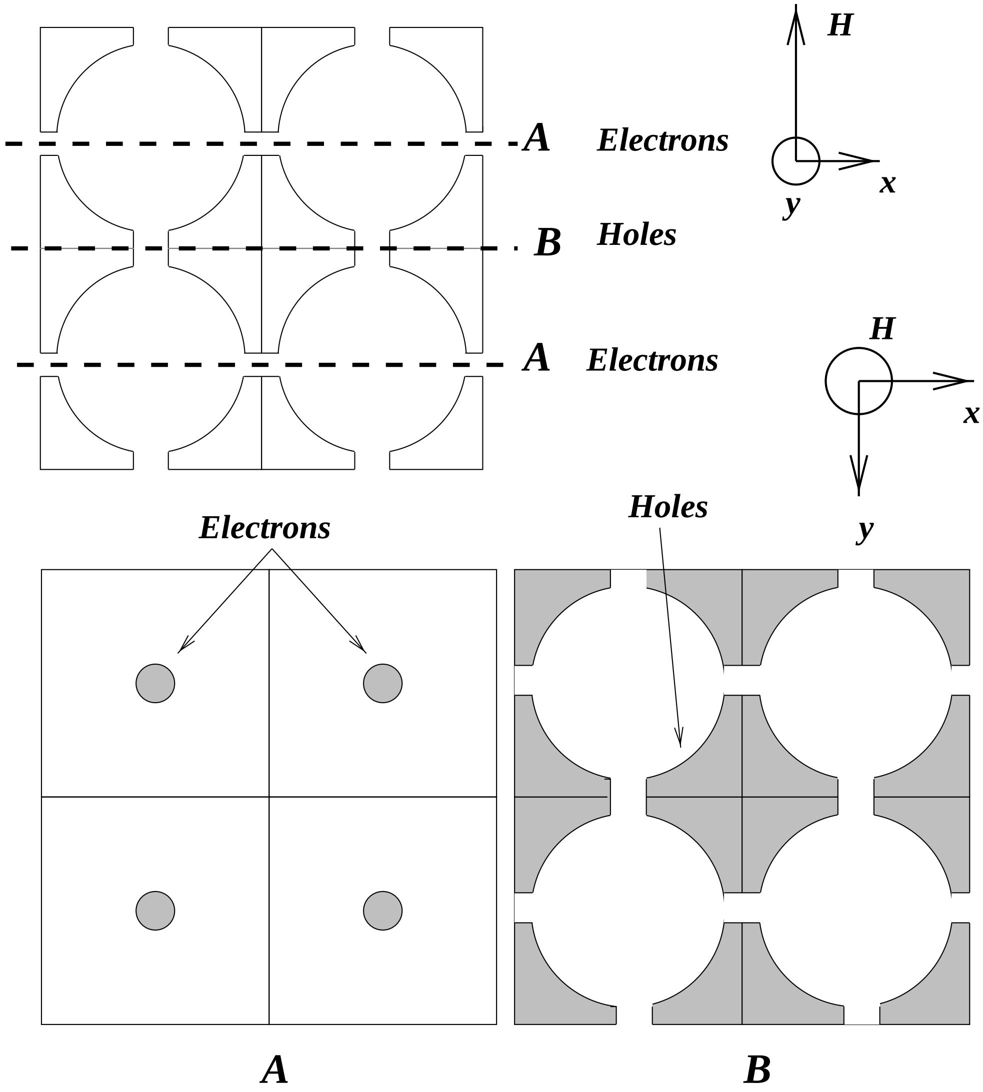

Figure 3. Possible FS for a cubic metal. Lower panel: Left part - electron orbits, right part - hole ones.

If the orbit is closed we immediately get the expression for the period through the integral along the orbit

$$T = \frac{c}{eH}\oint \frac{dp}{v_\perp}.$$

This period can be easily expressed in terms of the orbit's area S

$$S(p_z) = \left[\int dp_x\, dp_y\right]_{p_z=\text{const}}.$$

To do this integral we can take 2 contours corresponding to ε and $\varepsilon + d\varepsilon$, the width in $\mathbf{p}$-space in the normal direction being

$$d\varepsilon\, |\partial\varepsilon/\partial \mathbf{p}_\perp|^{-1} = d\varepsilon/v_\perp. \tag{11.3}$$

Thus

$$S = \int d\varepsilon \oint \frac{dp}{v_\perp}.$$

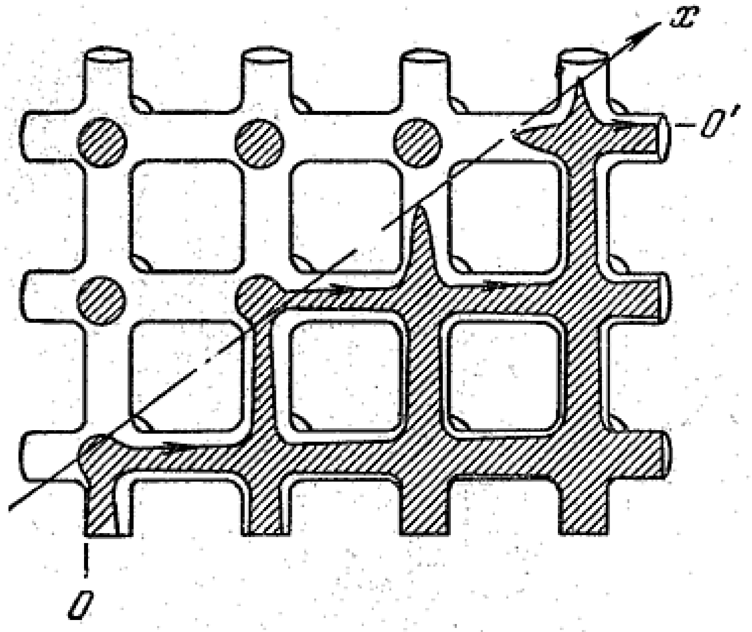

Figure 4. Electron orbits for tilted magnetic field.

Finally, we get the following formula for the *cyclotron frequency*

$$\omega_c = \frac{eH}{cm_c}, \text{ where } m_c(\varepsilon, p_z) = \frac{1}{2\pi}\left[\frac{\partial S}{\partial \varepsilon}\right]_{p_z}$$

is the *cyclotron effective mass.*

- The cyclotron mass can only be defined for closed orbits.

For a free electron $\varepsilon = (p_z^2 + \mathbf{p}_\perp^2)/2m_0$, and

$$S(p_z) = \pi \mathbf{p}_\perp^2 = 2\pi m_0 \varepsilon - \pi p_z^2, \text{ and } m_c = m_0.$$

Thus, in this case the cyclotron mass is constant. The same holds for all the quasiparticles with isotropic and quadratic spectrum $\varepsilon(\mathbf{p})$.

In order to find the trajectory in the real space, one can rewrite the equation of motion as

$$d\mathbf{p} = -\frac{e}{c}\left[d\mathbf{r} \times \mathbf{H}\right].$$

We see that the projection of the motion in the real space on the plane normal to $\mathbf{H}$ can be obtained by the substitution

$$x \to \frac{cH}{e} p_y, \qquad y \to \frac{cH}{e} p_x.$$

Also remains the motion along $\mathbf{z}$-axis with the velocity $v_z = \partial\varepsilon/\partial p_z$.

- In particular this means, that if the orbit is closed in momentum space it is also closed in the real space, and if it is open in the momentum space it is open in the real space

Now we discuss one very useful trick to calculate the properties of electrons in a magnetic field. Namely, let us introduce the *trajectory time* of the motion along the orbit as

$$dt_1 = \frac{c}{eH}\frac{dp}{v_\perp}, \qquad dt_1 = \frac{c}{eH}\frac{dp dp_\perp}{d\varepsilon}, \qquad dp dp_\perp = \frac{eH}{c} dt_1 d\varepsilon. \tag{11.4}$$

One should keep in mind that it is not the real time but some function of the point in the **p**-space. We get

$$\frac{2}{(2\pi\hbar)^3}\int dp_x\, dp_y\, dp_z = \frac{2}{(2\pi\hbar)^3}\frac{eH}{c}\int dp_z\, d\varepsilon\, dt_1$$

Here we have used the relation (11.3). This trick will be extensively used later.

11.1.1. Cyclotron resonance.

Now we discuss one of the ways to measure the characteristics of electron spectra. Let us assume that the electron with effective mass m moves in a weak a.c. electric field

$$\mathbf{E} = \mathbf{E}_0 \exp(-i\omega t), \qquad \mathbf{E}_0 \parallel \hat{\mathbf{x}}$$

and in a constant magnetic field $\mathbf{H} \parallel \hat{\mathbf{z}}$. Looking for a solution in the form $\mathbf{v}(t) = \mathbf{v}e^{i\omega t}$, we get

$$\begin{aligned} -i\omega m v_x &= -eE_x - \tfrac{e}{c} v_y H, \\ -i\omega m v_y &= \tfrac{e}{c} v_x H. \end{aligned}$$

To solve this set it is convenient to introduce the complex velocity $v \equiv v_x + iv_y$ and get

$$i(\omega - \omega_c)v = eE_x.$$

We see that at $\omega \to \omega_c$ the amplitude of velocity increases. It means that electron absorbs the energy from the electric field. To get more adequate theory of the *cyclotron resonance* one needs to take into account relaxation (we will come back to this problem later). The cyclotron resonance is a very useful tool to determine the cyclotron effective mass.

11.2. Quantum Mechanics of Bloch Electron

11.2.1. An electron with isotropic quadratic spectrum

We start our considerations with the simplest case of where the periodic potential can be taken into account by the effective mass approximation (we will denote is as m). We also use the Landau gauge (11.1). To get the SE[2] one can replace $\mathbf{p}$ in the classical Hamilton function with the operator $\hat{\mathbf{p}} = -i\hbar\nabla$

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2} + \left(\frac{\partial}{\partial y} + \frac{ieHx}{c}\right)^2 \psi + \frac{\partial^2\psi}{\partial z^2}\right] = \varepsilon\psi. \tag{11.5}$$

It is convenient to search the solution as

$$\psi(\mathbf{r}) = \varphi(x)e^{i(k_y y + k_z z)}.$$

Substituting this expression into (11.5) we get the equation for $\varphi(x)$ (Check!)

$$-\frac{\hbar^2}{2m}\frac{\partial^2\varphi}{\partial x^2} + \frac{1}{2}m\omega_c^2(x - x_0)^2\varphi = \varepsilon_1\varphi$$

---

[2] We ignore for a while the electron spin.

where ω_c is the cyclotron frequency,

$$x_0 = -a_H^2 k_y, \qquad a_H = \sqrt{\frac{c\hbar}{eH}}, \qquad \varepsilon_1 = \varepsilon - \frac{\hbar^2 k_z^2}{2m}.$$

The quantity a_H is often called the magnetic length or Landau length. Finally we came to the SE for a harmonic oscillator and we can write down both the energies and wave functions:

$$\varepsilon_1 = \varepsilon_N \equiv \hbar\omega_c(N + 1/2), \tag{11.6}$$

the so-called Landau levels,

$$\varphi(x) = \frac{1}{\sqrt{a_H}} \exp\left[-\frac{1}{2}\left(\frac{x - x_0}{a_H}\right)^2\right] \mathrm{H}_N\left(\frac{x - x_0}{a_H}\right) \tag{11.7}$$

where H_N is the Hermite polynomial. We see that the electron states in a magnetic field could be specified by the set of quantum numbers $\alpha = N, k_y, k_z$, the energy levels

$$\varepsilon_\alpha = \varepsilon_N + \frac{\hbar^2 k_z^2}{2m} \tag{11.8}$$

being dependent only on N, k_z.

One can ask: why the co-ordinates x and y are not equivalent? The reason is that the wave functions (11.7) correspond to the energy independent of k_y. Consequently, any function of the type

$$\sum_{k_y} C(k_y)\psi_{N,k_y,k_z}$$

corresponds to the same energy and one can chose convenient linear combinations to get correct asymptotic behavior.

11.2.2. General case.

The spectrum (11.8) has a very simple form for the case of any isotropic quadratic spectrum. Nevertheless it is possible to obtain important results even in the case of very complicated FS if we are interested in the Landau levels for large quantum numbers N. In this case one can expect that one can use the *Bohr-Sommerfeld* quantization procedure. Indeed, in the presence of magnetic field, as we have seen the *kinematic* momentum operator is

$$\mathbf{P} = -i\hbar\nabla + \frac{e}{c}\mathbf{A}.$$

Consequently,

$$P_x = -i\hbar\partial/\partial x, \qquad P_y = -i\hbar\partial/\partial y + (e/c)Hx,$$

the commutator being

$$[P_x, P_y] = i\pi\hbar\frac{eH}{c}.$$

One can see that the co-ordinate

$$Y = -\frac{c}{eH}P_x$$

is canonically conjugated to P_y,

$$[P_y, Y] = i\hbar.$$

Now we can directly apply the quantization rule

$$\left|\oint P_y\, dY\right| = \frac{c}{eH}\left|\oint P_y\, dP_x\right| = \frac{cS}{eH} = 2\pi\hbar\left[N + \gamma(N)\right].$$

Here $\gamma(N)$ is a slow function of N, $\quad 0<\gamma<1$. It is easy to show that the distance between the levels is just $\hbar\omega_c$. Indeed, neglecting $\gamma(N)-\gamma(N-1)$ we get

$$\frac{c}{eH}\frac{\partial S(\varepsilon)}{\partial\varepsilon}\Delta\varepsilon = 2\pi\hbar.$$

LECTURE 12
Second Quantization of Bosons and Electrons

Now we briefly discuss the way to describe many-electron states by the occupation numbers. Such a procedure was introduced for phonons which are *Bose* particles and we generalize that procedure for Bosons and Fermions.

- Indistinguishable particles in $3D$, $2D$, and $1D$.
- Why $2D$ and $1D$ are relevant (quantization of the transfer motion)?
- Composite particles (atoms) – dependence of the energy scale.

12.1. Bosons.

- We assume, that we have solved a one particle problem completely, i.e. we know all eigen states $\phi_p(\xi)$, where ξ is a set of coordinates and p is the set of quantum numbers – whatever they are.

In general case, the total wave function of bosons is symmetric with respect to the particles permutations. Thus it can be expressed as a symmetric product of individual one particle wave functions

$$\Phi_{n_1,n_2\dots} = \left(\frac{n_1!n_2!\dots}{N!}\right)^{1/2} \sum_P \varphi_{p_1}(\xi_1)\varphi_{p_2}(\xi_2)\dots\varphi_{p_N}(\xi_N)\,, \tag{12.1}$$

where p_i label the states (they do not need to be different) φ_{p_i}, the numbers n_i are the number of times the state φ_i is included in each term, number N is the total number of particles, and the sum is calculated over *all the permutations of the states* $\{p_i\}$.

From the form (12.1) we see, that different many-particle states are completely specified by the numbers n_i for each one-particle state. These numbers tell us how many particles are in a given one-particle state. They are called *occupation numbers.* So instead of (12.1) we can denote our states as

$$\Phi_{n_1,n_2\dots} = |n_1, n_2 \dots\rangle$$

The coefficient in (12.1) is introduced to make the total function normalized:

$$\langle n_1, n_2 \dots |\hat{F}| n_1, n_2 \dots\rangle = \int |\Phi|^2 \prod_i d\xi_i = 1.$$

The product $n_1!n_2!\dots$ appears in the numerator because we in reality need to permute only particles in *different* states.

- To better understand where the normalization factor comes from it is beneficial to start with just two states ϕ_1 and ϕ_2 with occupation numbers n_1 and n_2. The states ϕ_1 and ϕ_2 are orthogonal, so in the normalization integral the only nonzero terms are the ones that have the same set of coordinates for say functions ϕ_1 in the left and in the right. As states ϕ_1 and ϕ_2 are normalized, all those nonzero terms equal to 1. So the total integral equals to the number of nonzero terms. The number of nonzero terms is the number we can chose a set of n_1 coordinates out of $N = n_1 + n_2$, which is $\frac{N!}{n_1!n_2!}$.
- The extension to the arbitrary number of states simply follows.

Let's consider an arbitrary operator $\hat{F}$. As the functions (12.1) constitute a basis in the Hilbert space of many particle functions (with fixed total number of particles N) we need to know the matrix elements

$$\langle n_1', n_2' \dots |\hat{F}| n_1, n_2 \dots \rangle$$

We want to be able to compute these matrix elements between many-body states by computing matrix elements between one-particle states.

Assume that we have an arbitrary one-particle symmetric operator

$$\hat{F}^{(1)} = \sum_{a=1}^{N} \hat{f}_a^{(1)} \tag{12.2}$$

where $f_a^{(1)}$ acts only upon the functions of ξ_a. This operator can change the one-particle state only for one particle. So the only nonzero matrix elements of this operator will the following

$$\langle \dots n_i + 1, \dots, n_j - 1 \dots |\hat{F}^{(1)}| \dots n_i, \dots, n_j \dots \rangle \tag{12.3}$$

for all i and j. What it means is that the operator takes one particle from the one-particle state j and puts it in one-particle state i.

We assume that the one-particle matrix elements of the operator $\hat{f}^{(1)}$ are known:

$$f_{ik}^{(1)} = \int \varphi_i^*(\xi) f^{(1)}(\xi) \varphi_k(\xi)\, d\xi\,. \tag{12.4}$$

The computation of the matrix element (12.3) is very similar to the computation of the normalization factors, the result is (for $i \neq j$)

$$\langle \dots n_i + 1, \dots, n_j - 1 \dots |\hat{F}^{(1)}| \dots n_i, \dots, n_j \dots \rangle = f_{i,j} \sqrt{n_j} \sqrt{n_i + 1}. \tag{12.5}$$

- Notice, that apart from the one-particle matrix element the result depends only on the occupation numbers of the states i and j.

So let us introduce the operators b_i and $b_i^\dagger$ with the following matrix elements.

$$\langle n_k - 1 | b_i | n_k \rangle = \delta_{i,k} \sqrt{n_i}, \qquad \langle n_k + 1 | b_i^\dagger | n_k \rangle = \delta_{i,k} \sqrt{n_i + 1}.$$

So that the operator b_i annihilates a particle in the one-particle state i, the operator $b_i^\dagger$ creates a particle in the one-particle state i, and they both do nothing for other states. They are called annihilation and creation operators.

- The operator $b^\dagger$ is Hermitian conjugate to the operator b.

Using these operators we see, that the matrix element (12.5) is the same as the matrix element of an operator

$$f_{i,j} b_i^\dagger b_j.$$

Then the whole one particle operator $\hat{F}^{(1)}$ is

$$F^{(1)} = \sum_{ik} f^{(1)}_{ik} b^\dagger_i b_k \tag{12.6}$$

This is one-particle operator in the second quantization form.

In particular the operator of the total number of particles is (see *Problem 12.10*)

$$\hat{N} = \sum_{\text{all states}} b^\dagger_i b_i. \tag{12.7}$$

Computing the matrix elements one can see, that the operators b and $b^\dagger$ have the usual commutation relations (see *Problem 12.7*)

$$[b_i, b_j] = 0, \qquad [b^\dagger_i, b^\dagger_j] = 0, \qquad [b_i, b^\dagger_j] = \delta_{i,j} \tag{12.8}$$

Analogously a 2-particle symmetric operator

$$F^{(2)} = \sum_{a,b} f^{(2)}_{ab} \tag{12.9}$$

where $f^{(2)}_{ab}$ acts upon the functions of the variables ξ_a and ξ_b can be expressed as

$$F^{(2)} = \sum_{iklm} f^{ik}_{lm} b^\dagger_i b^\dagger_k b_l b_m \tag{12.10}$$

where

$$f^{ik}_{lm} = \int \varphi^*_i(\xi_1)\varphi^*_k(\xi_2) f^{(2)}(\xi_1, \xi_2)\varphi_l(\xi_1)\varphi_m(\xi_2)\, d\xi_1\, d\xi_2\,. \tag{12.11}$$

We can also write the wave function (12.1) in the second quantization form. For that we first consider just one one-particle state. Let's denote a normalized empty state as $|0\rangle$. This is a state with the following properties

$$\langle 0|0\rangle = 1, \qquad b|0\rangle = 0.$$

Then n-particle bosonic normalized state is (see *Problem 12.8*)

$$|n\rangle = \frac{1}{\sqrt{n!}}\left(b^\dagger\right)^n |0\rangle \tag{12.12}$$

Now we can define a state

$$|n_1, n_2, \dots\rangle = \frac{1}{\sqrt{n_1! n_2! \dots}}\left(b^\dagger_1\right)^{n_1}\left(b^\dagger_2\right)^{n_2}\dots|0\rangle. \tag{12.13}$$

One can show that the matrix elements calculated with this state for all operators are the same as before (see *Problem 12.9*)

- Notice, that this way we can construct the state with arbitrary total number of particles.

For arbitrary one particle energies ε_k we can construct a Hamiltonian in the second quantization language, which will act on the states with arbitrary number of particles.

$$\hat{H} = \sum_k \varepsilon_k b^\dagger_k b_k.$$

12.2. Fermions.

Now we turn to the Fermi statistics to describe electrons. According to the Pauli principle, the total wave function should be *anti-symmetric* over all the variables. So the occupation numbers could be 0 or 1. In this case we get instead of (12.1)

$$\Phi_{N_1 N_2 \dots} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \varphi_{p_1}(\xi_1)\varphi_{p_2}(\xi_2)\dots\varphi_{p_N}(\xi_N) \tag{12.14}$$

where all the numbers p_1, p_2, $\dots$, p_N are *different*. The symbol $(-1)^P$ shows that odd and even permutations enter the expression (12.14) with opposite signs (we take the sign '+' for the term with $p_1 < p_2 < \dots < p_N$). Note that the expression (12.14) can be expressed as the determinant of the matrix $\hat{M}$, $\Phi = \frac{1}{\sqrt{N!}} \det \hat{M}$ with the elements $M_{ik} = \varphi_{p_i}(\xi_k)$ which is often called the *Slater determinant.*

The diagonal matrix elements of the operator $F^{(1)}$ are

$$\bar{F}^{(1)} = \sum_i f_{ii}^{(1)} N_i \tag{12.15}$$

just as for the Bose particles. But off-diagonal elements are

$$\left(F^{(1)}\right)_{0_i 1_k}^{1_i 0_k} = \pm f_{ik}^{(1)} \tag{12.16}$$

where the sign is determined by the parity of the total number of particles in the states between the i and k ones. Consequently, for Fermi particles it is convenient to introduce the annihilation and creation operators as

$$\langle 0|c_i|1\rangle = \langle 1|c_i^\dagger|0\rangle = (-1)^{\sum_{l=1}^{i-1} N_l} . \tag{12.17}$$

We immediately get (Check!) the commutation rules for the Fermi operators:

$$\begin{aligned} \left\{c_i, c_k^\dagger\right\} &\equiv c_i c_k^\dagger + c_i^\dagger c_k = \delta_{ik} , \\ \{c_i, c_k\} &= \left\{c_i^\dagger, c_k^\dagger\right\} = 0 . \end{aligned} \tag{12.18}$$

In particular

$$(c_i^\dagger)^2 = 0,$$

so one cannot create two electrons in one state.

The product of Fermi operators are

$$c_i^\dagger c_i = N_i , \quad c_i c_i^\dagger = 1 - N_i . \tag{12.19}$$

One can express all the operators for Fermi particles exactly in the same way as the Bose ones, Eqs. (12.6), (12.10).

In particular the operator of a total number of particles is

$$\hat{N} = \sum_{\text{all states}} c_i^\dagger c_i \tag{12.20}$$

In the same way as for Bose particle we define an empty state as

$$\langle 0|0\rangle = 1, \qquad c_i|0\rangle = 0, \quad \forall i. \tag{12.21}$$

A Fermionic state with N particles is constructed as (see *Problem 12.11*)

$$|i_1, i_2, \dots, i_N\rangle = c_{i_1}^\dagger c_{i_2}^\dagger \dots c_{i_N}^\dagger |0\rangle \tag{12.22}$$

Again, if we know one particle energies ε_k we can construct a Hamiltonian for arbitrary number of particles.

$$\hat{H} = \sum_k \varepsilon_k c_k^\dagger c_k.$$

This Hamiltonian will act on a states with a fixed number of particle. But as we know the operator of a number of particles $\hat{N} = \sum_k c_k^\dagger c_k$, we can write a Hamiltonian with the number of particles not fixed, but instead we fix the chemical potential

$$\hat{\mathcal{H}} = \hat{H} - \mu\hat{N} = \sum_k (\varepsilon_k - \mu) c_k^\dagger c_k.$$

Another example is the tight binding model on a lattice. In $1D$ we have a state with energy ε_0 on each site of a chain. We also have a hopping amplitude between the nearest sites (we can also introduce a hopping between next nearest sites, etc.) The hoping means that we annihilate a fermion on a site i and create it on a site $i+1$, or in opposite direction. So the Hamiltonian is

$$\hat{H} = \sum_i \varepsilon_0 c_i^\dagger c_i + t\sum_i c_{i+1}^\dagger c_i + t\sum_i c_i^\dagger c_{i+1}. \tag{12.23}$$

It is a simple exercise to find the spectrum of this Hamiltonian (see *Problem 12.13*).

12.3. Problems

12.1. Derive Eq. (9.4).

12.2. Prove the orthogonality of the Wannier functions.

12.3. Derive expression (9.9) taking into account that $I(n)$ and $h(n)$ very rapidly decrease with increase of $|n|$.

12.4. Derive expression (9.12).

12.5. Prove the identity (10.8).

12.6. Prove the formula (10.10). Use Heisenberg equation $i\hbar\dot{\mathbf{r}} = [\mathbf{r}, \hat{H}]$. Consider the Hamiltonian given by the Wannier theorem and commute it with $\mathbf{r}$. Then average the result over a Bloch state $\psi_{l,\mathbf{p}}(\mathbf{r})$.

12.7. Prove (12.8).

12.8. Using (12.8) show that the state (12.12) is indeed normalized.

12.9. Using (12.8) compute the matrix elements of the operator (12.6) for the states (12.13).

12.10. Prove that the state (12.13) is an eigen state of the operator $\hat{N}$ defined in (12.7). What is the eigen value?

12.11. Prove that the state (12.22) is an eigen state of the operator $\hat{N}$ defined in (12.20). What is the eigen value?

12.12. We have $2P$ one particle states numbered $1, 2, \ldots, 2P$. We construct the following many particle Fermionic state

$$|\Psi\rangle = A\prod_{i=1}^{P}(u_i + v_i c_{2i-1}^\dagger c_{2i}^\dagger)|0\rangle,$$

where the complex numbers u_i and v_i are constrained by $|u_i|^2 + |v_i|^2 = 1$ for all i, and A is the normalization constant.

(a) Find A.
(b) Compute the average number of particles in this state.
(c) Compute the standard deviation of the number of particles.

12.13. Find the spectrum of the Hamiltonian (12.23). For that define the new annihilation operators $c_k = \frac{1}{\sqrt{N}} \sum_j e^{ijk} c_j$, where N is the number of sites on the chain. Show that they have the correct anticommutation relations (you need to check the normalization). Find the inverse of this transformation and rewrite the Hamiltonian (12.23) in terms of the new operators.

PART 4

Normal metals.

LECTURE 13

Statistics and Thermodynamics of Phonons

In this lecture we discuss thermodynamics of crystal lattice.

From the classical statistical physics, the average kinetic energy per degree of freedom is

$$\bar{\varepsilon}_k = \frac{1}{2}k_B T,$$

the total energy being

$$\bar{\varepsilon} = \bar{\varepsilon}_{\text{pot}} + \bar{\varepsilon}_{\text{kin}} = 2\bar{\varepsilon}_{\text{kin}}.$$

As a result, the total energy per mole is

$$\mathcal{E} = 3N_0 \cdot \bar{\varepsilon}_{\text{kin}} = 3RT,$$

where R is the Rydberg constant while N_0 is the Avogadro one. As a result, the specific heat is

$$c_V = 3R = 5.96 \text{ kal/K} \cdot \text{mole}. \tag{13.1}$$

This relation is violated at low temperatures as far as the temperature becomes less than the so-called *Debye* temperature (which is for most of solids is within the interval 100-400 K), namely it decreases with the temperature decrease. To understand this behavior one should apply quantum mechanics.

Let us calculate the average vibration energy from the point of view of quantum mechanics. We have seen that normal vibrations can be described as quasiparticles with the energy

$$\varepsilon_n = \hbar\omega(n + 1/2),$$

where we have omitted the indices $\mathbf{q}$ and j which characterize a given oscillator. The probability to find the oscillator in the state n is

$$w_n = \frac{e^{-\varepsilon_n/k_B T}}{\sum_n e^{-\varepsilon_n/k_B T}}.$$

The average energy is

$$\bar{\varepsilon} = \frac{\sum_n \varepsilon_n e^{-\varepsilon_n/k_B T}}{\sum_n e^{-\varepsilon_n/k_B T}}.$$

To demonstrate the way to calculate the average energy we introduce the *partition function* as

$$Z = \sum_{n=0} e^{-\varepsilon_n/k_B T}. \tag{13.2}$$

We get

$$\bar{\varepsilon} = -d\,\log(Z)/d\beta, \qquad \beta = 1/k_BT.$$

Form the definition (see *Problem 17.1*)

$$Z = \frac{e^{-\hbar\omega/2k_BT}}{1 - e^{-\hbar\omega/k_BT}}.$$

Making use of this formula we get

$$\bar{\varepsilon} = \frac{\hbar\omega}{2} + \hbar\omega\; N(\omega), \qquad N(\omega) = \frac{1}{e^{\hbar\omega/k_BT} - 1} \tag{13.3}$$

where $N(\omega)$ is the *Planck function.* The first item is energy-independent while the second one is just the average energy of bosons with zero chemical potential.

In general the Bose distribution has the form

$$\frac{1}{\exp\left[\frac{\varepsilon-\zeta}{k_BT}\right] - 1}$$

where ζ is *chemical potential* which is equal to the derivative of the free energy:

$$\left(\frac{\partial \mathcal{F}}{\partial N}\right)_{T,V} = \zeta.$$

Usually the chemical potential is determined by the conservation of the particles' number.

The Bose distribution function for bosons (and Fermi distribution for fermions) gives the average occupation number of a mode at given temperature and chemical potential.

The number of phonons is not conserved: they can be created or annihilated in course of interactions. Therefore their number at equilibrium should be determined from the condition of *equilibrium*, i. e. from the request of minimum of free energy — $\left(\frac{\partial \mathcal{F}}{\partial N}\right)_{T,V} = 0$. As a result, for phonons $\zeta = 0$. The Planck function determines the *equilibrium* number of phonons with a given frequency. Such a picture allows one to consider the phonons as *elementary excitations* over the zero-point vibration energy

$$\mathcal{E}_0 = (1/2)\sum_{j\mathbf{q}} \hbar\omega_j(\mathbf{q}).$$

To get the total energy one should sum (13.3) over all the momenta and vibration branches. It is convenient to express this sum through the DOS according to the general definition

$$g(\omega) = \sum_{j,\mathbf{q}} \delta\left[\omega - \omega_{j,\mathbf{q}}\right]\,. \tag{13.4}$$

This function is defined such that $g(\omega)d\omega$ counts the number of states in the interval $d\omega$. For any sum of the form $\sum_{j,\mathbf{q}} F(\omega_{j,\mathbf{q}})$ we can write

$$\sum_{j,\mathbf{q}} F(\omega_{j,\mathbf{q}}) = \int d\omega \sum_{j,\mathbf{q}} \delta\left[\omega - \omega_{j,\mathbf{q}}\right] F(\omega) = \int d\omega g(\omega) F(\omega).$$

For the energy we get

$$E = \int_0^\infty g(\omega)\hbar\omega N(\omega)\, d\omega.$$

In the first approximation let us assume that the frequencies of the optical branches are $\mathbf{q}$-independent and equal to ω_{j0}. Consequently, the summation is just the multiplication by the Planck function $N(\omega_{j0})$.

For acoustic modes we use the Debye model (see Section 2.2.4). Introducing the average sound velocity s_0 as

$$\frac{1}{s_0^3} = \frac{1}{3}\left(\frac{1}{s_l^3} + \frac{2}{s_t^3}\right)$$

we get the following contribution of acoustic modes

$$\mathcal{E}_{ac} = \frac{3\mathcal{V}\hbar}{2\pi^2 s_0^3}\int_0^\infty d\omega \frac{\omega^3}{e^{\hbar\omega/k_BT}-1}.$$

Let's consider this expression for very large T, then if we use $\frac{1}{e^{\hbar\omega/k_BT}-1} \approx \frac{k_BT}{\hbar\omega}$, we see, that the integral will diverge at the upper limit. We then have to cut it off by k_BT, the result will be $\sim T^4$ – which is wrong, as we must get the classical result (indeed $\hbar$ cancels out.)

The problem is that we have overcounted the number of states. The total number of modes/sates which we have is $3N$, by considering large temperatures we assumed that the phonon states go on forever in frequency. This is not the case, so we need to somehow account for the fact that there is no phonon states above a certain frequency. The simplest way to do that is to introduce an upper cutoff for the frequency integration – ω_D.

$$\mathcal{E}_{ac} = \frac{3\mathcal{V}\hbar}{2\pi^2 s_0^3}\int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_BT}-1}.$$

The upper cut off ω_D is the so-called Debye frequency. It must be determined from the condition of the total number of modes to be equal to $3N$ for all acoustic branches,

$$3N = \int_0^{\omega_D} g(\omega)\, d\omega.$$

From this equation

$$\omega_D = s_0\left(\frac{6\pi^2}{\mathcal{V}_0}\right)^{1/3}, \qquad q_D = \frac{\omega_D}{s_0}$$

where $\mathcal{V}_0$ is the cell volume. The order-of-magnitude estimate for the maximal wave vector q_D is π/a. So according to the so-called *Debye model* all the values of $\mathbf{q}$ are confined in a sphere with the radius q_D. Usually, the *Debye temperature* is introduced as

$$\Theta = \frac{\hbar\omega_D}{k_B} = \frac{\hbar s_0}{k_B}\left(\frac{6\pi^2}{\mathcal{V}_0}\right)^{1/3}.$$

The typical value of this temperature can be obtained from the rough estimate $a = 10^{-8}$ cm, $s_0 = 10^5$ cm/s. We get $\omega_D = 10^{13}$ s^{-1}, $\Theta = 100$ K. It is conventional also to introduce the temperatures corresponding to optical branches as

$$\Theta_j = \frac{\hbar\omega_{j0}}{k_B}.$$

These energies are of the order of $10^2 - 10^3$ K. Finally, we get the following expression for the internal energy

$$\mathcal{E} = \mathcal{E}_0 + Nk_BT\left[3\mathcal{D}\left(\frac{\Theta}{T}\right) + \sum_{j=4}^{3s}\frac{\Theta_j/T}{e^{\Theta_j/T}-1}\right] \tag{13.5}$$

where the *Debye function* $\mathcal{D}(z)$ is

$$\mathcal{D}(z) = \frac{3}{z^3}\int_0^z \frac{x^3\,dx}{e^x-1}. \tag{13.6}$$

At high temperatures, $T \gg \Theta_j$ (and, consequently, $T \gg \Theta$) we get $z \ll 1$ in Eq. (13.6) and then expand the integrand in powers of x. We see that $\mathcal{D}(0) = 1$. The item under the sum sign in Eq (13.5) are equal to 1, and we get for the sum $3s - 3$. consequently, we get the classical expression

$$\mathcal{E} = \mathcal{E}_0 + 3sNk_BT$$

that leads to the classical expression (13.1) for the specific heat. At low temperatures we immediately see that optical modes give exponentially small contributions and we can discard them. At the same time, we can replace the upper limit of the integral in (13.6) by infinity. Taking into account that

$$\int_0^\infty \frac{x^3\,dx}{e^x - 1} = \frac{\pi^4}{15}$$

we get

$$\mathcal{E} = \mathcal{E}_0 + \frac{\pi^2 \mathcal{V} (k_BT)^4}{10\hbar^3 s_0^3}$$

that leads to the following expression for the specific heat

$$c_V = \frac{12\pi^4 k_B}{5} \left(\frac{T}{\Theta}\right)^3 .$$

The Debye model is very good for low temperatures where only long wave acoustic modes are excited. The acoustic contribution to the specific heat can be expressed through the derivative of the Debye function. We have

$$\frac{c_{ac}}{3k_BN} = 3\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x\,dx}{(e^x - 1)^2} .$$

This function is shown in Fig. 1 left panel. One can see that really the border between the classical and quantum region corresponds to $T \leq \Theta/3$ rather that to $T \leq \Theta$. The physical reason is strong frequency dependence of phonon DOS. In real life, DOS behavior is much more complicated because of the real band structure effects. The experimental DOS for NaCl is shown in Fig. 1 (right upper), the dash curve showing Debye approximation.

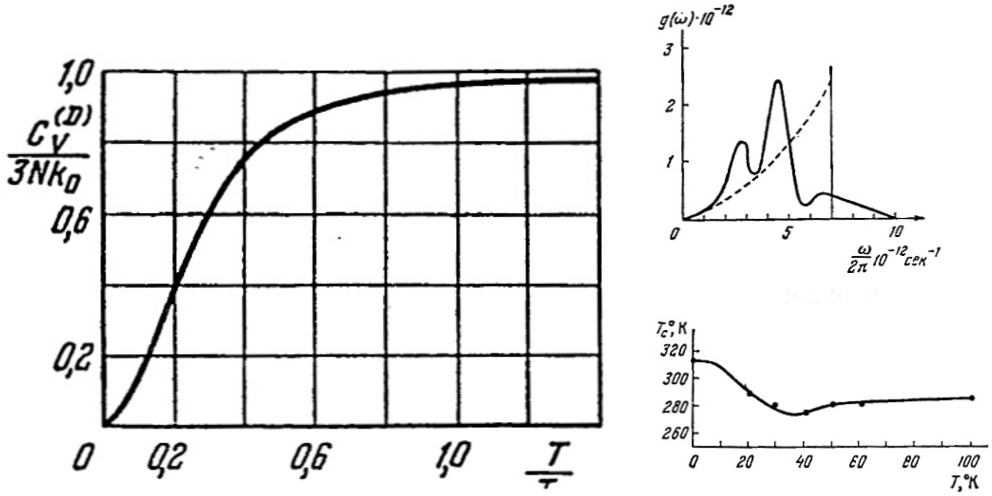

Figure 1. Left: Temperature dependence of acoustic contribution to the specific heat. Right: DOS (upper) and effective Debye temperature (lower) for NaCl .

Usually, people still fit the results on specific heat by Debye approximation but assume that the Debye temperature, Θ, is temperature dependent. The dependence $\Theta(T)$ is shown in Fig. 1 (right lower)

- Notice, that for the thermodynamics all we need from the phonon dispersion relation is the density of states.

LECTURE 14
Statistics and Thermodynamics of Electrons

14.1. Chemical potential.

Now we turn to the electron system in thermodynamic equilibrium. As we have seen, the electron state for a given energy band is characterized by the quantum number $\mathbf{k}$, the average number of electrons in this state being

$$f_0(\varepsilon_{\mathbf{k}}) = \frac{1}{\exp\left(\frac{\varepsilon_{\mathbf{k}}-\zeta}{k_B T}\right)+1} \,. \tag{14.1}$$

The function (14.1) is called the *Fermi-Dirac function.* The *chemical potential* ζ is determined by the normalization condition

$$N = \sum_{\mathbf{k}} \frac{1}{\exp\left(\frac{\varepsilon_{\mathbf{k}}-\zeta}{k_B T}\right)+1} \,. \tag{14.2}$$

The summation here should be done also over spin indices. The equation (14.2) defines the dependence of the chemical potential ζ on the electron density $n = N/\mathcal{V}$ and temperature.

It is also convenient to introduce the density of electron states with the formula similar to Eq. (13.4)

$$g(\varepsilon) = 2\sum_{\mathbf{k}} \delta\left(\varepsilon - \varepsilon_{\mathbf{k}}\right) \tag{14.3}$$

where we have taken into account spin degeneracy.

Notice, that this function can be written in the form

$$g(\varepsilon) = \mp\frac{2}{\pi}\,\mathrm{Im}\sum_{\mathbf{k}} \frac{1}{\varepsilon - \varepsilon_{\mathbf{k}} \pm i0}$$

For the density of electrons we get

$$n = \int_0^\infty g(\varepsilon) f_0(\varepsilon)\, d\varepsilon. \tag{14.4}$$

For the quadratic spectrum with the effective mass m we have (see *Problem 17.3*)

$$g(\varepsilon) = \frac{\sqrt{2}}{\pi^2}\frac{m^{3/2}}{\hbar^3}\sqrt{\varepsilon}\,. \tag{14.5}$$

- Notice, that this result depends on dimensionality.

- The singularity at the bottom of the band is different in $3D$, $2D$, and $1D$.

Inserting this formula to the normalization condition (14.4) and introducing the dimensionless chemical potential $\zeta^* = \zeta / k_B T$ we get the following equation for ζ^*

$$n = \frac{\sqrt{2}}{\pi^2} \frac{(m k_B T)^{3/2}}{\hbar^3} \mathcal{F}_{1/2}(\zeta^*)$$

where $\mathcal{F}_{1/2}(z)$ is a particular case of the *Fermi integrals*

$$\mathcal{F}_n(z) = \int_0^\infty \frac{x^n \, dx}{e^{x-z} + 1}.$$

14.1.1. Degenerated Electron Gas

Now we discuss the important limiting cases. The first one is the case for good metals or highly doped semiconductors in which the density of conduction electrons is large. The large density of conduction electrons means that $\zeta^* \gg 1$. That leads to the following approximate presentation for the Fermi function

$$f_0(\varepsilon) = \Theta(\zeta - \varepsilon)$$

where

$$\Theta(x) = \left| \begin{array}{ll} 1, & \text{if } x > 0, \\ 0, & \text{if } x < 0 \end{array} \right.$$

is the Heaviside unit step function. In this approximation we easily get

$$\zeta_0 = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}.$$

This quantity is often called the *Fermi level* because it is just the border between the full and empty states. We will also use this word and denote it as ϵ_F. To get temperature dependent corrections one should calculate the integral in Eq. (14.4) more carefully. One obtains (see *Problem 17.4*)

$$\zeta = \epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 \right].$$

Now we can check when our approximation is really good. To do it let us request that the second item in the brackets to be small. We get

$$\frac{\epsilon_F}{k_B T} = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2 m k_B T} \gg 1 \,. \tag{14.6}$$

So we see that the gas is degenerate at big enough electron density and small effective mass. Note that the criterion has the *exponential* character and inequality (14.6) can be not too strong (usually 5-7 is enough). In a typical metal $n \approx 10^{22}$ cm^{-3}, $m \approx 10^{-27}$ g, and at room temperature $\frac{\epsilon_F}{k_B T} \approx 10^2$.

14.1.2. Non-Degenerate Electron Gas

Now we discuss the situation when the electron density in the conduction band is not very high and the electrons are non-degenerate. It means that $\zeta < 0$, $\exp(-\zeta^*) \gg 1$. In this case the Fermi distribution tends to the *Maxwell-Boltzmann* distribution

$$f_0(\varepsilon) \approx e^{\zeta^*} e^{-\varepsilon / k_B T}$$

where

$$\zeta^* = \ln\left[\frac{4\pi^3\hbar^3 n}{(2\pi m k_B T)^{3/2}}\right],$$

$$e^{\zeta^*} = \frac{4\pi^3\hbar^3 n}{(2\pi m k_B T)^{3/2}}. \tag{14.7}$$

We see that the chemical potential of non degenerate electron gas is strongly temperature dependent. The degeneracy for room temperature is intermediate at $n \approx 10^{19}$ cm^{-3}.

14.1.3. Semiconductors.

These formulas are not very interesting in typical semiconductors because electrons are taken from impurities which can be partly ionized. So the dependence *n vs. T* remains unknown. To get insight into the problem let us consider the band scheme of a typical semiconductor with one donor level ε_D and one accepter one ε_A, Fig. 1 (the origin of energies is the bottom of the conduction band).

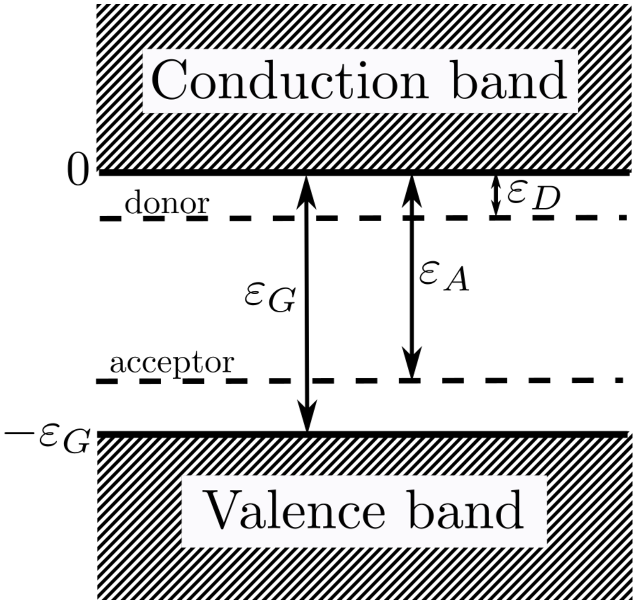

Figure 1. Band scheme of a typical semiconductor.

The most important feature is that in such situation we have both electrons (in the conduction band) and holes (in the valence band). The occupation factor for holes is

$$f_0^p(\varepsilon) = 1 - f_0(\varepsilon) = \frac{1}{e^{\frac{\zeta-\varepsilon}{k_BT}} + 1}.$$

It is natural to call the function $f^p(\varepsilon)$ as the Fermi function of holes.

According to our prescription for energies,

- the electron energy in the conduction band is $\varepsilon = \hbar^2 k^2/2m_n$,
- at the donor level $\varepsilon = -\varepsilon_D$,
- at the acceptor level $\varepsilon = -\varepsilon_A$,
- in the valence band $\varepsilon = -\varepsilon_G - \varepsilon^p$ where ε_G is the width of the forbidden gap and $\varepsilon^p = \hbar^2 k^2/2m_p$.

If we also introduce the *hole chemical potential*, $\zeta^p = -\varepsilon_G - \zeta$ we come to exactly the same form for the hole Fermi function as for electrons with the replacement $\varepsilon \to \varepsilon^p$, $\zeta \to \zeta^p$. To get the position of the chemical potential now we should apply the neutrality condition

$$\text{number of electrons} = \text{number of holes}$$

As we have holes in the donor level and in valence band, and electrons in the acceptor level and in the conduction band the above equation reads:

$$\int_{c.b.} g_n(\varepsilon) f_0(\varepsilon)\, d\varepsilon + \sum_A \frac{1}{e^{\frac{-\varepsilon_A - \zeta}{k_B T}} + 1} = \int_{v.b.} g_p(\varepsilon') f_0(\varepsilon')\, d\varepsilon' + \sum_D \frac{1}{e^{\frac{\varepsilon_D + \zeta}{k_B T}} + 1}\,.$$

This equation is strongly simplified if both electrons and holes obey the Boltzmann statistics. Denoting $A = \exp(\zeta/k_B T) \ll 1$ and assuming that $A \exp(\varepsilon_G/k_B T) \gg 1$ (ζ is negative and it is withing the gap) we get

$$\nu_n A + \frac{n_A}{\frac{1}{A}\exp\left(-\frac{\varepsilon_A}{k_B T}\right) + 1} = \nu_p A^{-1} e^{-\frac{\varepsilon_G}{k_B T}} + \frac{n_D}{A \exp\left(+\frac{\varepsilon_D}{k_B T}\right) + 1} \tag{14.8}$$

where n_D and n_A are the concentrations of donors and acceptors and we have introduced

$$\nu_{n,p} = \frac{(2\pi m_{n,p} k_B T)^{3/2}}{4\pi^3 \hbar^3}.$$

Even now we have a rather complicated situation which depends on the relation between the energies and the temperature. In the following we analyze few most important cases.

14.1.3.1. *Intrinsic semiconductor.* It is the simplest case where there is neither donors nor accepters. From the Eq. (14.8) using $n_A = n_D = 0$ we have

$$\begin{aligned} A &= \left(\frac{m_p}{m_n}\right)^{3/4} \exp\left(-\frac{\varepsilon_G}{2k_B T}\right), \\ \zeta &= -\frac{\varepsilon_G}{2} + \frac{3}{4} k_B T \ln\left(\frac{m_p}{m_n}\right). \end{aligned} \tag{14.9}$$

We see that the chemical potential in an intrinsic semiconductor is close to the middle of the forbidden gap.

- Notice, that if $m_p = m_n$, then the chemical potential does not depend on temperature.
- The sign of the temperature correction depends on which one is bigger m_p, or m_n.

Concentrations of the electrons and holes are the same

$$n_i = n_T \exp\left(-\frac{\varepsilon_G}{2k_B T}\right), \qquad n_T = \sqrt{\nu_n \nu_p}.$$

The concentration n_T for the room temperature and the free electron mass is $2.44 \cdot 10^{19}$ cm^{-3}, it scales as $(m_n m_p)^{3/4} T^{3/2}$.

14.1.3.2. *Extrinsic semiconductor.* Let us assume that only donors are present and $\varepsilon_G \gg \varepsilon_D$. In this case we get from Eq. (14.8)

$$\nu_n A \left(A e^{\frac{\varepsilon_D}{k_B T}} + 1\right) = n_D.$$

At very low temperatures the first term in the brackets is the most important one, and

$$A=\sqrt{\frac{n_D}{\nu_n}}e^{-\frac{\varepsilon_D}{2k_BT}}.$$

We see that the chemical potential is near the middle of the distance between the donor level and the bottom of the conduction band, the concentration in the conduction band being

$$n_n \approx \frac{n_D}{A}e^{-\frac{\varepsilon_D}{k_BT}}=\sqrt{\nu_n n_D}e^{-\frac{\varepsilon_D}{2k_BT}}.$$

At high temperatures we get

$$A=\frac{n_D}{\nu_n}, \qquad n_n \approx n_D.$$

The result is clear enough: at high temperature all the donors are ionized while at low temperatures electrons “freeze-out” into the donor states. The situation in accepter semiconductor is just the mirror one.

14.2. Specific Heat of the Electron System

We want to find the electronic contribution to the specific heat of a metal. The electrons are the degenerate Fermi gas. Normally we do not know the precise form of the density of states for all energies. What we are going to show, that the specific heat of a degenerate Fermi gas depends only on the density of states at the Fermi level.

In order to calculate the specific heat we need to compute

$$c_V=\left(\frac{\partial\mathcal{E}}{\partial T}\right)_{V,N}.$$

- Notice, that we need to take the derivative at fixed N – the number of particles (or n – the concentration), not at fixed ζ – the chemical potential.

However, when we use the Dirac-Fermi distribution function, we will have $\mathcal{E}$ at fixed chemical potential. So we need to compute $\mathcal{E}(T,\zeta)$ and $\zeta(T,n)$. Se we need to compute

$$\mathcal{E}=\int \varepsilon g(\varepsilon)f_0(\varepsilon)d\varepsilon \tag{14.10}$$

$$n=\int g(\varepsilon)f_0(\varepsilon)d\varepsilon. \tag{14.11}$$

Both of these integrals have the same form

$$I=\int \chi(\varepsilon)f_0(\varepsilon)d\varepsilon.$$

The Fermi-Dirac distribution function of a degenerate Fermi gas is almost a step function. It defers from the step function only at a small region of energies $|\varepsilon-\epsilon_F|\sim T\ll\epsilon_F$. Using this for any function $\chi(\varepsilon)$ regular in the above interval, we can write

$$\begin{aligned}I&=\int_0^\infty\frac{\chi(\varepsilon)d\varepsilon}{e^{(\varepsilon-\zeta)/T}+1}=\int_0^\zeta d\varepsilon\chi(\varepsilon)+\int_0^\zeta d\varepsilon\chi(\varepsilon)\left(\frac{1}{e^{(\varepsilon-\zeta)/T}+1}-1\right)+\int_\zeta^\infty\frac{\chi(\varepsilon)d\varepsilon}{e^{(\varepsilon-\zeta)/T}+1}\\&=\int_0^\zeta d\varepsilon\chi(\varepsilon)-\int_0^\zeta\frac{d\varepsilon\chi(\varepsilon)}{e^{(\zeta-\varepsilon)/T}+1}+\int_\zeta^\infty\frac{\chi(\varepsilon)d\varepsilon}{e^{(\varepsilon-\zeta)/T}+1}\\&=\int_0^\zeta d\varepsilon\chi(\varepsilon)-\int_0^\zeta\frac{d\varepsilon\chi(\zeta-\varepsilon)}{e^{\varepsilon/T}+1}+\int_0^\infty\frac{\chi(\zeta+\varepsilon)d\varepsilon}{e^{\varepsilon/T}+1}\end{aligned}$$

In the second integral the upper limit can be taken to be ∞, as $\zeta \gg T$ and the integral converges on $\varepsilon \sim T$. We then have

$$\int_0^\infty \frac{\chi(\varepsilon)d\varepsilon}{e^{(\varepsilon-\zeta)/T}+1} \approx \int_0^\zeta d\varepsilon\chi(\varepsilon) + \int_0^\infty \frac{[\chi(\zeta+\varepsilon)-\chi(\zeta-\varepsilon)]\,d\varepsilon}{e^{\varepsilon/T}+1}$$

$$\approx \int_0^\zeta d\varepsilon\chi(\varepsilon) + 2\chi'(\zeta)\int_0^\infty \frac{\varepsilon d\varepsilon}{e^{\varepsilon/T}+1} = \int_0^\zeta d\varepsilon\chi(\varepsilon) + 2T^2\chi'(\zeta)\int_0^\infty \frac{zdz}{e^z+1}$$

The last integral is $\int_0^\infty \frac{zdz}{e^z+1} = \pi^2/12$.

Let's use this result for (14.10) and (14.11). We start with the equation for the chemical potential (14.11). In this case $\chi(\varepsilon) = g(\varepsilon)$, so

$$n = \int_0^\zeta d\varepsilon g(\varepsilon) + 2T^2 g'(\zeta)\frac{\pi^2}{12}.$$

We expect that the $|\zeta - \epsilon_F| \sim T^2$, so in the second term we should use ϵ_F instead of ζ. So we have

$$n = \int_0^{\epsilon_F} d\varepsilon g(\varepsilon) + \int_{\epsilon_F}^\zeta d\varepsilon g(\varepsilon) + 2T^2 g'(\epsilon_F)\frac{\pi^2}{12}.$$

Now, by definition of ϵ_F the first term gives $\int_0^{\epsilon_F} d\varepsilon g(\varepsilon) = n$. The second term up to $\sim T^2$ is $\int_{\epsilon_F}^\zeta d\varepsilon g(\varepsilon) \approx (\zeta - \epsilon_F)g(\epsilon_F)$. So we get

$$\zeta = \epsilon_F - 2T^2\frac{g'(\epsilon_F)}{g(\epsilon_F)}\frac{\pi^2}{12}. \tag{14.12}$$

The same calculation for (14.10) gives ($\chi(\varepsilon) = \varepsilon g(\varepsilon)$)

$$\mathcal{E} = \mathcal{E}(T=0) + (\zeta - \epsilon_F)\epsilon_F g(\epsilon_F) + 2T^2(\varepsilon g(\varepsilon))'_{\varepsilon=\epsilon_F}\frac{\pi^2}{12},$$

where $\mathcal{E}(T=0) = \int_0^{\epsilon_F} \varepsilon g(\varepsilon)d\varepsilon$.

Using (14.12) we then have

$$\mathcal{E} = \mathcal{E}(T=0) + 2T^2 g(\epsilon_F)\frac{\pi^2}{12}.$$

- Notice, that fixing n means fixing ϵ_F, so to compute the specific heat we need to take the derivative of the above result at fixed ϵ_F.

We then have

$$c_V = Tg(\epsilon_F)\frac{\pi^2}{3}. \tag{14.13}$$

For the special case of parabolic dispersion we get:

$$c_V = \frac{\sqrt{2}}{3}\frac{m^{3/2}}{\hbar^3}\sqrt{\epsilon_F}k_B^2 T. \tag{14.14}$$

We see that $c_V \propto T$, it goes to zero at $T \to 0$ (the *Nernst theorem*). The physical meaning of Eq. (14.13) is very simple - only the electrons in the narrow layer $k_B T$ could be excited; their number being $g(\epsilon_F)k_B T$ while the contribution of each one to the specific heat being k_B.

It is interesting to compare electron and phonon contributions to specific heat. At room temperature and $\epsilon_F \approx 1$ eV we get that the electron contribution is only few percents in comparison with the phonon one. But *it is not the case at low temperatures* where the phonon contribution goes like T^3 while the electron one is $\propto T$.

For the Boltzmann statistics one can use the Boltzmann distribution function. The result is (see *Problem 17.5*)

$$c_V = (3/2)nk_B.$$

LECTURE 15

Paramagnetism of electrons

Now we will discuss the basic magnetic properties of electron gas. We start from the recalling of the main thermodynamic relations for magnetics.

15.1. Basic thermodynamic relations.

In a magnetic field **H** a sample acquires the magnetic moment **M**. For a volume dV one can introduce *magnetization*

$$d\mathbf{M} = \mathbf{M}(\mathbf{H})\, dV.$$

The derivative

$$\chi = \left(\frac{dM}{dH}\right)_{H=0}$$

is called magnetic susceptibility. It is a dimensionless quantity. According to the thermodynamics, the change of the internal energy is

$$d\mathcal{E} = dQ + dA$$

where $dQ = T\, dS$ is the transferred heat (S is the entropy) while dA is the work with the system, $dA = -\mathbf{M}\, d\mathbf{H}$. Finally

$$d\mathcal{E} = T\, dS - M\, dH.$$

Consequently, for the *free energy* $\mathcal{F} = \mathcal{E} - TS$ we get

$$d\mathcal{F} = -S\, dT - M\, dH,$$

and

$$S = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_H, \qquad M = -\left(\frac{\partial \mathcal{F}}{\partial H}\right)_T, \qquad \chi = -\left(\frac{\partial^2 \mathcal{F}}{\partial H^2}\right)_{T;H=0}.$$

So, the main quantity is the free energy.

15.2. Paramagnetism of Free Electrons (Pauli Paramagnetism).

Now we are prepared to discuss the magnetic susceptibility of a gas of near free electrons. In this case the orbital moment $l = 0$, $\quad j = s = 1/2$ and $g_L = 2$. Consequently, according to the classical result, one could expect quite big magnetic susceptibility, see Problem 17.10. *This statement strongly contradicts the experiment* – in fact the susceptibility is small. This very important problem was solved by *Pauli* in 1927 and it was just the beginning of quantum theory of metals. The key idea is that the electrons have Fermi statistics and one should calculate the average magnetic moment taking into account the Pauli principle.

To make such a calculation let us recall that the electron energy in a magnetic field depends on the magnetic moment (spin) orientation

$$\varepsilon_\pm = \varepsilon \mp \mu_B H,$$

where

$$\mu_B = \frac{e\hbar}{2m_e c}.$$

Consequently

$$M = M_+ - M_- = \frac{\mu_B}{2}\int \left[f_0(\varepsilon_+) - f_0(\varepsilon_-)\right] g(\varepsilon)\, d\varepsilon.$$

(the factor 1/2 is due to the fact that we have introduced the DOS $g(\varepsilon)$ including spin factor 2). For small magnetic fields we can expand the square brackets and get

$$\chi = \mu_B^2 \int \left(-\frac{\partial f_0(\varepsilon)}{\partial \varepsilon}\right) g(\varepsilon)\, d\varepsilon.$$

To get the final formula one should take into account that

$$\int \left(-\frac{\partial f_0(\varepsilon)}{\partial \varepsilon}\right) g(\varepsilon)\, d\varepsilon = \frac{\partial n}{\partial \zeta},$$

i. e. the derivative of electron concentration with respect to the chemical potential. This quantity is often called the *thermodynamic density of states.* So we get

$$\chi = \mu_B^2 \frac{\partial n}{\partial \zeta}\,.$$

Now the magnetic susceptibility can be calculated for any limiting case. For example, the temperature-dependent part for a strongly degenerate gas (see *Problem 17.6*)

We know that the electron concentration can be considered as a function of Fermi energy ϵ_F, so

$$\frac{\partial n}{\partial \zeta} = \frac{\partial n}{\partial \epsilon_F}\frac{\partial \epsilon_F}{\partial \zeta}.$$

By the definition of ϵ_F ($n = \int_0^{\epsilon_F} g(\epsilon) d\epsilon$) we have $\frac{\partial n}{\partial \epsilon_F} = g(\epsilon_F)$.

In the previous lecture we found

$$\zeta = \epsilon_F - 2T^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)}\frac{\pi^2}{12}.$$

With the same accuracy we can write

$$\epsilon_F = \zeta + 2T^2 \frac{g'(\zeta)}{g(\zeta)}\frac{\pi^2}{12} = \zeta + 2T^2 \frac{\pi^2}{12}\frac{\partial}{\partial \zeta}\log g(\zeta).$$

So that (again with the same accuracy)

$$\frac{\partial \epsilon_F}{\partial \zeta} = 1 + T^2 \frac{\pi^2}{6}\frac{\partial^2}{\partial \epsilon_F^2}\log g(\epsilon_F).$$

Finally

$$\chi = \mu_B^2 g(\epsilon_F)\left[1 + \left(\frac{T}{\epsilon_F}\right)^2 \frac{\pi^2}{6}\epsilon_F^2 \frac{\partial^2}{\partial \epsilon_F^2}\log g(\epsilon_F)\right].$$

The dimensionless number $\epsilon_F^2 \frac{\partial^2}{\partial \epsilon_F^2} \log g(\epsilon_F)$ depends on the first and second derivative of the density of states over the energy. For the case of pure parabolic dispersion we know that $g(\epsilon_F) \sim \sqrt{\epsilon_F}$, so $\epsilon_F^2 \frac{\partial^2}{\partial \epsilon_F^2} \log g(\epsilon_F) = -\frac{1}{2}$ and we have

$$\chi = \mu_B^2 g(\epsilon_F) \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 \right] . \tag{15.1}$$

We see very important features:

- At low temperatures the main part of magnetic susceptibility is temperature-independent.
- For electrons the role of characteristic energy plays the Fermi energy ϵ_F. For the Boltzmann gas we return to the result of Problem 17.10.
- For Pauli paramagnetism for $T \to 0$ we have a universal relation:
$$\frac{\chi T}{c_V} = \frac{3}{\pi^2} \mu_B^2 .$$
- The Bohr magneton μ_B here contains the true electron mass – not the band mass.

15.3. Paramagnetic Resonance (Electron Spin Resonance)

We take the opportunity to discuss here a very important tool of the modern solid state physics to investigate the properties of both the conduction electrons and the electrons belonging to impurity centers. As we have seen, in an atomic electron the level's splitting in the magnetic field is proportional to the Lande factor g_L. In a solid state electron there is also *spin-orbital interaction*, as well as the interaction with the lattice. So one could introduce instead of the Lande factor the so-called spectroscopic factor g_s which effectively describes the level's splitting. This factor is often called simply g-factor. In general case $g_s \neq 2$, it can be anisotropic and also depend on the magnetic field direction.

Under the external magnetic field the levels split. In simplest case, the electron level splits into doublet corresponding to $s = \pm 1$, in general case the splitting-can be much more complicated. It is important that in any case the selection rule for a *dipole magnetic transitions* $\Delta m = \pm 1$. So one can study *resonant absorption* of electromagnetic field in the sample obeying the condition

$$\hbar\omega = g_s \mu_B H .$$

Consequently, one can determine the behavior of g-factor which is a very instructive quantity. The position and width of the resonant peaks allows one to make many conclusions on the symmetry of the local field in a crystal, interaction with neighboring magnetic atoms and with the lattice vibrations, etc.

The very similar picture hold for atomic nuclei in a crystal, the corresponding approach is called the *nuclear magnetic resonance* (NMR).

15.3.1. Phenomenological theory of EPR.

Here we show a very simple theory of EPR (Bloch, 1946). If $\mathbf{M}$ is the magnetization vector and $\mathbf{L}$ is the mechanical angular momentum of a volume unit, we have the following equation of motion

$$\frac{d\mathbf{L}}{dt} = [\mathbf{M} \times \mathbf{H}]$$

(just the sum of equations for different particles). According to very general concepts of quantum mechanics

$$\mathbf{M} = \gamma \mathbf{L}, \quad \gamma = \frac{e g_s}{2mc}.$$

So we get the close vector equation for $\mathbf{M}$

$$\frac{d\mathbf{M}}{dt} = \gamma \left[\mathbf{M} \times \mathbf{H}\right] . \tag{15.2}$$

Phenomenologically, we also can add a dissipation

$$\frac{d\mathbf{M}}{dt} = \gamma \left[\mathbf{M} \times \mathbf{H}\right] + \alpha \left[\mathbf{M} \times \dot{\mathbf{M}}\right] \qquad \alpha > 0. \tag{15.3}$$

- The condition $\alpha > 0$ ensures, that we are dealing with dissipation.
- Notice, that without dissipation the magnetic moment will never align with the magnetic field.

To get explicit results let us assume that

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1 \exp(i\omega t), \qquad \mathbf{H}_1 \perp \mathbf{H}_0, \quad |\mathbf{H}_1| \ll |\mathbf{H}_0|$$

The solution can be expressed in the form

$$\mathbf{M} = \mathbf{M}_0 + \mathbf{M}_1 \exp(i\omega t), \qquad \mathbf{M}_0 \parallel \mathbf{H}_0.$$

In general $\mathbf{M}_1$ can have any direction, but $|\mathbf{M}_1| \sim |\mathbf{H}_1| \ll |\mathbf{H}_0|$.

Keeping only linear in H_1 and M_1 terms we get

$$i\omega \mathbf{M}_1 = \gamma \left[\mathbf{M}_1 \times \mathbf{H}_0\right] + \gamma \left[\mathbf{M}_0 \times \mathbf{H}_1\right] + i\omega\alpha \left[\mathbf{M}_0 \times \mathbf{M}_1\right] .$$

Taking the scalar product of this equation with $\mathbf{H}_0$ (and using $\mathbf{M}_0 \parallel \mathbf{H}_0$) we see that

$$\mathbf{M}_1 \cdot \mathbf{H}_0 = 0,$$

so the vector $\mathbf{M}_1$ is in the plane perpendicular to $\mathbf{H}_0$. There are two orthogonal vectors in this plane $\mathbf{H}_1$ and $\mathbf{H}_0 \times \mathbf{H}_1$. So we can write

$$\mathbf{M}_1 = a\mathbf{H}_1 + b\mathbf{H}_0 \times \mathbf{H}_1$$

Using $\mathbf{M}_0 = \chi_0 \mathbf{H}_0$ we can use the above decomposition in our equation

$$\left(i\omega a - \gamma b H_0^2 + i\omega\alpha\chi_0 b H_0^2\right) \mathbf{H}_1 = \left(-i\omega b - \gamma a + \gamma\chi_0 + i\omega\alpha\chi_0 a\right) \left[\mathbf{H}_0 \times \mathbf{H}_1\right].$$

As the LHS is orthogonal to the RHS we must have

$$\begin{aligned} i\omega a - (\gamma - i\omega\alpha\chi_0) b H_0^2 &= 0 \\ -i\omega b - (\gamma - i\omega\alpha\chi_0) a &= -\gamma\chi_0. \end{aligned}$$

The coefficient a is the response of $\mathbf{M}$ parallel to $\mathbf{H}_1$, so solving for it we get

$$\chi_{\parallel}(\omega) = a = \chi_0 \frac{1 - i\omega\alpha\chi_0/\gamma}{(1 - i\omega\alpha\chi_0/\gamma)^2 - (\omega/\gamma H_0)^2}.$$

We are interested in the case when the dissipation is small, so

$$\frac{1}{\gamma H_0} \gg \frac{\alpha\chi_0}{\gamma}, \quad \text{or} \quad \alpha\chi_0 H_0 \ll 1, \quad \text{or} \quad \alpha M_0 \ll 1.$$

Neglecting the terms quadratic in α we then can simplify our result

$$\chi_{\parallel}(\omega) = \chi_0 \frac{1 - i\alpha\chi_0 H_0 \omega/\omega_L}{1 - \left(\omega/\omega_L + i\alpha\chi_0 H_0\right)^2}$$

We see, that there is a resonance at $\omega = \omega_L = \gamma H_0$, and the width of this resonance is $\Delta\omega \sim \alpha M_0 \omega_L$.

For the limit $\alpha \to 0$ the above result can be written as

$$\chi_{\|}(\omega) = \frac{\chi_0 \omega_L^2}{\omega_L^2 - (\omega + i0)^2}.$$

We must keep $i0$ in the denominator, as it shows how the poles are to be understood.

- Both poles are in the lower half plane.
- All response functions must be retarded, so they must have no singularities in the upper half plane.

LECTURE 16

Diamagnetism of Electron gas. (Landau Diamagnetism).

16.1. Classical theory.

One can imagine that such a description holds for electrons. Indeed, a free electron's orbit moves along a circle in the plane normal to **H**, the radius being

$$r_c = \frac{mcv_\perp}{eH} = \frac{v_\perp}{\omega_c} \tag{16.1}$$

where

$$\omega_c = \frac{eH}{mc} \tag{16.2}$$

is the *cyclotron frequency*. Note that $\omega_c = 2\omega_L$, where the Larmor frequency ω_L was introduced earlier. The corresponding magnetic moment per volume is

$$\mu_z = n\frac{e}{2mc}L = n\frac{e}{2mc}mr_cv_\perp = n\frac{er_cv_\perp}{2c} = n\frac{mv_\perp^2/2}{H}\,.$$

Making use of the classical statistics, namely assuming $\overline{mv_\perp^2}/2 = k_BT$, we get

$$\mu_z = n\frac{k_BT}{H}, \qquad \chi = \frac{\mu_z}{H} = n\frac{k_BT}{H^2}\,.$$

It is clear that we have got a wrong equation, because it is charge-independent. It is interesting that the wrong result is due to the assumption that *all* the electrons have circular orbits. It appears that surface orbits which are not circles contribute to the surface current. So we will be more careful and show that according to classical physics one should get zero susceptibility for free electrons.

Let us introduce the *vector-potential* $\mathbf{A}(\mathbf{r})$ of the magnetic field as

$$\mathbf{H} = \mathrm{curl}\mathbf{A}\,.$$

For $\mathbf{H} \parallel \mathbf{z}$ we have $\mathbf{A} \parallel \mathbf{y}$, $\quad A_y = xH$. The classical Hamilton function is

$$\mathcal{H} = \frac{1}{2m}\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right)^2 + \mathcal{U}(\mathbf{r}) \tag{16.3}$$

where $\mathcal{U}(\mathbf{r})$ is the potential energy (remember that we denote the electron charge as $-e$). The partition function is

$$Z = \left[\int (dp) \int_{\mathcal{V}} (dr) \, \exp\left(-\frac{\mathcal{H}}{k_B T} \right) \right]^N \tag{16.4}$$

where N is the total number of particles. The free energy is, as usual,

$$\mathcal{F} = -k_B T \ln Z \, .$$

One can shift the integration variables $\mathbf{p}$ in Eq. (16.4) by $(e/c)\mathbf{A}(\mathbf{r})$. The shift is $\mathbf{p}$-independent, so the Jacobian of this transformation is 1. We come to the conclusion that the partition function is *field-independent* and $\chi = 0$.

16.2. Quantum mechanics.

Quantum mechanics changes the situation completely. Let's consider a thin ring of radius R with just one electron on it. If we thread magnetic field H through the ring we will have a gauge field A along the ring. The quantization condition then

$$L\left(p_n - \frac{e}{c} A \right) = 2\pi n \hbar,$$

where L is the ring circumference. The ground state corresponds to $n = 0$, so the momentum of the ground state is $p_0 L = \frac{e}{c} A L = \frac{e}{c} H S$, where S id the rings area, or $p_0 = \frac{e}{c}\frac{S}{L} H = \frac{e}{2c} R H$. The energy of the electron is $E = \frac{p_0^2}{2m} = \frac{e^2}{8mc^2} R^2 H^2$, so the magnetic moment of the ring is $M = -\frac{\partial E}{\partial H} = -\frac{e^2}{4mc^2} R^2 H = -\frac{e^2}{4\pi mc^2} S H$. The magnetic susceptibility per unit area then is $\chi = -\frac{e^2}{4\pi mc^2}$. We see, that quantum mechanics leads to non zero diamagnetism. The reason for the discrepancy with the classical result is the fact, that by "gauging away" the vector field A we change the boundary conditions for the wave function – the effect completely missed in the classical case.

To get the result for the bulk metal we start with a solution of quantum mechanical particle in a magnetic field. Let us apply a uniform magnetic field and assume that we have taken into account the periodic potential by the effective mass approximation. As was shown, the electron states in a magnetic field could be specified by the set of quantum numbers $\alpha = N, k_y, k_z$, the energy levels

$$\varepsilon_\alpha = \varepsilon_N + \frac{\hbar^2 k_z^2}{2m} = \hbar \omega_c (N + 1/2) + \frac{\hbar^2 k_z^2}{2m} \tag{16.5}$$

being dependent only on N, k_z.

To obtain thermodynamic functions one should calculate the density of states in a magnetic field. First we should count the number of the values k_y corresponding to the energy ε_α (the so-called *degeneracy factor*). As usual, we apply cyclic boundary conditions along y and z -axes and get

$$k_y = \frac{2\pi}{L_y} n_y, \quad k_z = \frac{2\pi}{L_z} n_z.$$

The wave functions in Landau gauge are the strips alone y-direction. The centers of the strips are at $x_0 = -a_H^2 k_y$, where $a_H = \sqrt{c\hbar/eH}$. The solution exists only in the region

$$0 < |x_0| < L_x.$$

So, the degeneracy factor is

$$n_y^{max} = \frac{L_y}{2\pi} k_y^{\max} = \frac{L_y}{2\pi a_H^2} x_0^{\max} = \frac{L_y L_x}{2\pi a_H^2}. \tag{16.6}$$

- This is very important relation which shows that one can imagine Landau states as cells with the area a_H^2. We will come back to this property later.
- The formula (16.6) can also be expressed in the following way

  $$n_y^{max} = \frac{\Phi}{\Phi_0},$$

  where Φ is the total magnetic field flux $\Phi = L_x L_y H$ and Φ_0 is the normal state flux quantum $\Phi_0 = \frac{hc}{e}$.

16.3. Quantum statistical mechanic.

Experiments can be done in two different ways,

(a) At fixed number of particles $\mathcal{N}$.
(b) At fixed chemical potential ξ.

The magnetization as the function of temperature T, magnetic field $\mathbf{H}$, and the number of particles $\mathcal{N}$ is (the volume is fixed throughout.)

$$\mathbf{M}(T, \mathbf{H}, \mathcal{N}) = -\left(\frac{\partial \mathcal{F}(T, \mathbf{H}, \mathcal{N})}{\partial \mathbf{H}}\right)_{T, \mathbf{H}, N},$$

where $\mathcal{F}(T, \mathbf{H}, \mathcal{N})$ is the free energy.

It is more convenient to do the calculations not at the fixed number of particles, but at fixed chemical potential. Then we define the thermodynamic potential $\Omega = \mathcal{F} - \xi\mathcal{N}$. Using this potential we will get

$$\mathbf{M}(T, \mathbf{H}, \xi) = -\left(\frac{\partial \Omega(T, \mathbf{H}, \xi)}{\partial \mathbf{H}}\right)_{T, V, \xi}. \tag{16.7}$$

These two magnetizations are the same, however, in order to compare them we will need to express the chemical potential ξ in (16.7) as a function of T, $\mathcal{N}$, and $\mathbf{H}$: $\xi(T, \mathbf{H}, \mathcal{N})$.

- If we are to calculate the magnetic susceptibility $\chi = \frac{\partial \mathbf{M}}{\partial \mathbf{H}}$, we have to be careful which experiment we are dealing with, as $\left(\frac{\partial \mathbf{M}}{\partial \mathbf{H}}\right)_{\mathcal{N}} \neq \left(\frac{\partial \mathbf{M}}{\partial \mathbf{H}}\right)_{\xi}$.

According the standard statistical mechanics for non-interacting electrons we have

$$\Omega = -T \sum_k \log\left(1 + e^{(\xi - \varepsilon_k)/T}\right), \tag{16.8}$$

where k enumerates the one particle states and ε_k is the energy of the one particle state k.

Instead of summation over the states in (16.8) we can integrate over the energy ε with the help of the density of states $g(\varepsilon)$

$$\Omega = -T \int d\varepsilon g(\varepsilon) \log\left(1 + e^{(\xi - \varepsilon)/T}\right).$$

As differentiation in (16.7) must be done at fixed ξ and T, the only parameter which changes with H is the density of states, so we have

$$M = T \int_0^\infty d\varepsilon \frac{\partial g(\varepsilon)}{\partial H} \log\left(1 + e^{(\xi - \varepsilon)/T}\right) \tag{16.9}$$

16.3.1. 2D case.

Let's analyze (16.9) for $2D$ electron gas (the plane is in x-y, the field along the z direction.) The density of states in this case is

$$g_{2D}(\varepsilon) = \frac{L_y L_x}{2\pi a_H^2}\sum_{n=0}^{\infty}\delta(\varepsilon - \hbar\omega_c(n+1/2)) = 2\frac{\mathcal{S}m}{2\pi\hbar}\omega_c\sum_{n=0}^{\infty}\delta(\varepsilon - \hbar\omega_c(n+1/2)).$$

(the first factor of 2 is for the spin)

- Notice, that m in this equation came from the dispersion relation, so it is the "band mass".

We now have

$$\frac{\partial g_{2D}(\varepsilon)}{\partial H} = \frac{e}{mc}\frac{\partial g_{2D}(\varepsilon)}{\partial\omega_c} = \frac{e}{mc}\left[\frac{g_{2D}}{\omega_c} - 2\frac{\mathcal{S}m}{2\pi\hbar}\sum_{n=0}^{\infty}\hbar\omega_c(n+1/2)\delta'(\varepsilon-\hbar\omega_c(n+1/2))\right]$$

$$(16.10) = \frac{e}{mc}\left[\frac{g_{2D}}{\omega_c} - 2\frac{\mathcal{S}m}{2\pi\hbar}\partial_\varepsilon\sum_{n=0}^{\infty}\hbar\omega_c(n+1/2)\delta(\varepsilon-\hbar\omega_c(n+1/2))\right]$$

Using the fact, that δ-function enforces that $\varepsilon = \hbar\omega_c(n+1/2)\equiv\varepsilon_n$ we can write

$$\frac{\partial g_{2D}(\varepsilon)}{\partial H} = \frac{e}{mc}\left[\frac{g_{2D}}{\omega_c} - 2\frac{\mathcal{S}m}{2\pi\hbar}\partial_\varepsilon\varepsilon\sum_{n=0}^{\infty}\delta(\varepsilon-\varepsilon_n)\right] = \frac{e}{mc\omega_c}\left[g_{2D} - \partial_\varepsilon(\varepsilon g_{2D})\right] = -\frac{e}{mc\omega_c}\varepsilon\partial_\varepsilon g_{2D}$$

So we have

$$M = -T\frac{e}{mc\omega_c}\int_0^\infty d\varepsilon\varepsilon g'_{2D}(\varepsilon)\log\left(1+e^{(\xi-\varepsilon)/T}\right).$$

- Notice, that if we now want to take the above equation for $H=0$, the density of states for free non-interacting fermions in 2D is ε-independent. So the integral is 0, as it should.

Let's now introduce two functions Z_ε — the number of states with energies below ε, and $\Phi(\varepsilon)$ such that

$$\frac{\partial Z_\varepsilon}{\partial\varepsilon} = g_{2D}(\varepsilon), \quad Z_{\varepsilon=0}=0, \quad \text{and} \quad \frac{\partial\Phi_\varepsilon}{\partial\varepsilon} = Z_\varepsilon(\varepsilon), \quad \Phi_{\varepsilon=0}=0.$$

Then we have

$$\varepsilon g'_{2D}(\varepsilon) = \partial_\varepsilon^2\left(\varepsilon Z_\varepsilon - 2\Phi_\varepsilon\right).$$

The magnetization then is

$$M = -T\frac{e}{mc\omega_c}\int_0^\infty d\varepsilon\partial_\varepsilon^2\left(\varepsilon Z_\varepsilon - 2\Phi_\varepsilon\right)\log\left(1+e^{(\xi-\varepsilon)/T}\right).$$

Integrating by parts twice and using

$$\partial_\epsilon\log\left(1+e^{(\xi-\varepsilon)/T}\right) = -\frac{1}{T}f_F, \qquad f_F = \frac{1}{e^{(\varepsilon-\xi)/T}+1} \text{ — Fermi distribution}$$

we get

$$(16.11) \qquad M = \frac{e}{mc\omega_c}\int_0^\infty d\varepsilon\left[\varepsilon Z_\varepsilon - 2\Phi_\varepsilon\right]\partial_\varepsilon f_F(\varepsilon).$$

So we need to compute the function $\varepsilon Z_\varepsilon - 2\Phi_\varepsilon$. Let's do it. First

$$g_{2D}(\varepsilon) = 2\frac{\mathcal{S}m}{2\pi\hbar}\omega_c\sum_{n=0}^{\infty}\delta(\varepsilon-\varepsilon_n).$$

Then

$$Z_\varepsilon = \int_0^\varepsilon g_{2D}(\varepsilon')d\varepsilon' = 2\frac{\mathcal{S}m}{2\pi\hbar}\omega_c \sum_{n=0}^{\infty}\theta(\varepsilon-\varepsilon_n), \qquad \theta(x) = \begin{cases} 0, & \text{if } x<0 \\ 1, & \text{if } x>0 \end{cases}$$

and

$$\Phi_\varepsilon = \int_0^\varepsilon Z_{\varepsilon'}d\varepsilon' = 2\frac{\mathcal{S}m}{2\pi\hbar}\omega_c \sum_{n=0}^{\infty}(\varepsilon-\varepsilon_n)\theta(\varepsilon-\varepsilon_n).$$

Finally we have

$$\varepsilon Z_\varepsilon - 2\Phi_\varepsilon = 2\frac{\mathcal{S}m}{2\pi\hbar}\omega_c \sum_{n=0}^{\infty}(2\varepsilon_n-\varepsilon)\theta(\varepsilon-\varepsilon_n) \tag{16.12}$$

Typically the experiments are done for the temperatures much lower than the chemical potential (this may be different in semiconductors). At such temperatures the chemical potential is very close to the Fermi energy, so $T \ll \varepsilon_F$. We still have two different cases $T \ll \hbar\omega_c$ – strong fields, and $T \gg \hbar\omega_c$ – weak fields.

16.3.1.1. *Strong field case.* The function $\partial_\varepsilon f_F(\varepsilon)$ is strongly peaked at $\varepsilon = \xi$, the width of this peak is $\sim T$. Let's start with $T = 0$. In this case $\partial_\varepsilon f_F(\varepsilon) \to -\delta(\varepsilon-\varepsilon_F)$, so the integral in (16.11) gives

$$M = -2\frac{e}{mc\omega_c}\left(\varepsilon_F Z_{\varepsilon_F} - \Phi_{\varepsilon_F}\right).$$

Using (16.12) we get

$$M = -4\mu_B\frac{H\mathcal{S}}{\Phi_o}\sum_{n=0}^{\infty}\left(2(n+1/2)-\frac{\varepsilon_F}{\hbar\omega_c}\right)\theta\left(\frac{\varepsilon_F}{\hbar\omega_c}-(n+1/2)\right). \tag{16.13}$$

Using $\varepsilon_F = \frac{N_e\pi\hbar^2}{m\mathcal{S}}$ (both spins are included) we can rewrite equation (16.13) as

$$\frac{M}{\mu_B N_e} = -2\frac{\hbar\omega_c}{\varepsilon_F}\sum_{n=0}^{\infty}\left(2(n+1/2)-\frac{\varepsilon_F}{\hbar\omega_c}\right)\theta\left(\frac{\varepsilon_F}{\hbar\omega_c}-(n+1/2)\right)$$

The behavior of this function is show on Fig. 1.

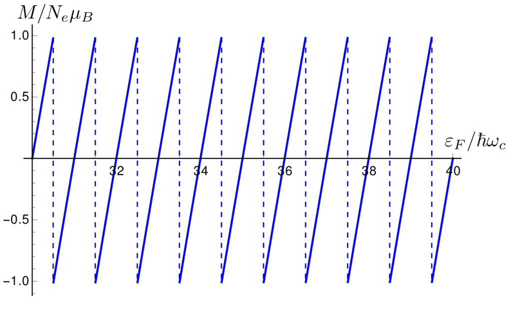

Figure 1. Magnetization per electron as a function of $\varepsilon_F/\hbar\omega_c$ for $2D$.

- One can see, that the magnetization is a periodic function of $1/H$.

Using the $\varepsilon_F = \frac{N_e\pi\hbar^2}{m\mathcal{S}}$ once more we see that

$$\frac{\varepsilon_F}{\hbar\omega_c} = \frac{N_e\Phi_0}{2\Phi} \equiv \nu.$$

The expression $2\Phi/\Phi_0$ gives the degeneracy of the Landau level (the factor of 2 is for the spin), so ν is the "filling factor" – how many Landau levels are filled (it can be fractional). The magnetization now can be written as

$$\frac{M}{\mu_B N_e} = -2\frac{1}{\nu}\sum_{n=0}^{\infty}\left(2(n+1/2)-\nu\right)\theta\left(\nu-(n+1/2)\right).$$

So we see, that the Magnetization jumps when a Landau level is half-filled.

We now can understand, what happens at finite, but still small temperatures $T \ll \hbar\omega_c$). In this case the function $\partial_\varepsilon f_F(\varepsilon)$ is still strongly peaked at ε_F, but have small width $\sim T$, as this width is much smaller than $\hbar\omega_c$ the convolution of $\partial_\varepsilon f_F(\varepsilon)$ with (16.12) will smear the sharp corners seen on Fig. 1, left, but will keep the periodic structure.

- So as long as $T \ll \hbar\omega_c$ the magnetization as a function of $1/H$ is a periodic function.

16.3.1.2. *Weak field case.* Now we consider the opposite limit $T \gg \hbar\omega_c$. According to (16.11) we need to compute the convolution of $\partial_\varepsilon f_F(\varepsilon)$ with (16.12). The width of the "bell" of the function $\partial_\varepsilon f_F(\varepsilon)$ is of the order of T. So the bell covers many periods of the function (16.12). So in the first approximation when we take the function $\partial_\varepsilon f_F(\varepsilon)$ to be constant the result will be zero and we need to go to the next approximation and take into account that although the function $\partial_\varepsilon f_F(\varepsilon)$ is very slow on the scale of $\hbar\omega_c$ it is not a constant. Here we will do exactly that. We have

$$M = 2\frac{\mathcal{S}}{\Phi_0}\int_0^\infty \sum_{n=0}^{\infty}(2\varepsilon_n-\varepsilon)\theta(\varepsilon-\varepsilon_n)\partial_\varepsilon f_F(\varepsilon)d\varepsilon.$$

The function that we need to integrate is not continuous, so I split the integral on sum of the integration over the intervals $[\varepsilon_k+0, \varepsilon_{k+1}-0]$ (± 0 means the point right after, or point right before.)

On each of these intervals the function

$$G(\varepsilon) \equiv \sum_{n=0}^{\infty}(2\varepsilon_n-\varepsilon)\theta(\varepsilon-\varepsilon_n)$$

is a linear function of ε. We then compute

$$G(\varepsilon_k+0) = \hbar\omega_c\frac{k+1}{2}, \qquad G(\varepsilon_{k+1}-0) = -\hbar\omega_c\frac{k+1}{2}.$$

As $G(\varepsilon)$ is a linear function on the interval $[\varepsilon_k+0, \varepsilon_{k+1}-0]$ we have

$$G(\varepsilon_k<\varepsilon<\varepsilon_{k+1}) = \frac{k+1}{2}(\hbar\omega_c - 2(\varepsilon-\varepsilon_k)).$$

We then have

$$M = 2\frac{\mathcal{S}}{\Phi_0}\sum_{k=0}^{\infty}\frac{k+1}{2}\int_{\varepsilon_k}^{\varepsilon_{k+1}}(\hbar\omega_c-2(\varepsilon-\varepsilon_k))\partial_\varepsilon f_F(\varepsilon)d\varepsilon.$$

Now in each integral I make the substitution $\varepsilon = \varepsilon_k + \tilde\varepsilon$, then I have

$$M = 2\frac{\mathcal{S}}{\Phi_0}\sum_{k=0}^{\infty}\frac{k+1}{2}\int_0^{\hbar\omega_c}(\hbar\omega_c-2\tilde\varepsilon)\partial_\varepsilon f_F(\varepsilon_k+\tilde\varepsilon)d\tilde\varepsilon.$$

- Notice, that if we neglect $\tilde\varepsilon$ in $\partial_\varepsilon f_F(\varepsilon_k+\tilde\varepsilon)$, thinking that this function is almost constant on the scale of $\hbar\omega_c$, then we would get exactly zero. So we need to take into account that $\partial^2 f_F(\varepsilon) \neq 0$.

Instead we do the following trick, we write $\hbar\omega_c - 2\tilde{\varepsilon} = \partial_{\tilde{\varepsilon}}(\hbar\omega_c\tilde{\varepsilon} - \tilde{\varepsilon}^2)$. And then take the integral by parts. We get

$$M = -2\frac{\mathcal{S}}{\Phi_0}\sum_{k=0}^{\infty}\frac{k+1}{2}\int_0^{\hbar\omega_c}(\hbar\omega_c\tilde{\varepsilon} - \tilde{\varepsilon}^2)\partial_\varepsilon^2 f_F(\varepsilon_k + \tilde{\varepsilon})d\tilde{\varepsilon}.$$

Now we neglect $\tilde{\varepsilon}$ in $\partial_\varepsilon^2 f_F(\varepsilon_k + \tilde{\varepsilon})$.

$$M = -2\frac{\mathcal{S}}{\Phi_0}\sum_{k=0}^{\infty}\frac{k+1}{2}\partial_\varepsilon^2 f_F(\varepsilon_k)\int_0^{\hbar\omega_c}(\hbar\omega_c\tilde{\varepsilon} - \tilde{\varepsilon}^2)d\tilde{\varepsilon}.$$

The integral is now a simple and we get

$$M = -\frac{1}{6}\frac{\mathcal{S}}{\Phi_0}(\hbar\omega_c)^2\sum_{k=0}^{\infty}(\varepsilon_k + \hbar\omega_c/2)\partial_\varepsilon^2 f_F(\varepsilon_k).$$

Now we convert the sum back to integration $\hbar\omega_c\sum_k = \int d\varepsilon$ and get

$$M = -\frac{1}{6}\frac{\mathcal{S}}{\Phi_0}\hbar\omega_c\int_0^{\infty}\varepsilon\partial_\varepsilon^2 f_F(\varepsilon_k)d\varepsilon.$$

Taking this integral by parts we get

$$M = \frac{1}{6}\frac{\mathcal{S}}{\Phi_0}\hbar\omega_c\int_0^{\infty}\partial_\varepsilon f_F(\varepsilon)d\varepsilon = -\frac{1}{6}\frac{\mathcal{S}}{\Phi_0}\hbar\omega_c$$

The diamagnetic susceptibility (per unit area) then is

$$\chi_{dia}^{2D} = -\frac{e^2}{12\pi mc^2}. \tag{16.14}$$

LECTURE 17
Diamagnetism of Electron gas. $3D$ case (De Haas-van Alphen effect).

17.1. $3D$ case.

For the $3D$ case we first consider the case of the weak fields and then the case of strong fields. For both cases we notice, that in the z direction — the direction of the field — the motion of electron is not effected by the magnetic field.

17.1.1. Weak field case.

In the momentum space we then look at the Fermi surface as a collection of N_z of $2D$ Fermi surfaces. Each of these $2D$ surfaces gives the same contribution (16.14) $\chi_{dia}^{2D} = -\frac{e^2}{12\pi mc^2}$ (multiplied by the area $\mathcal{S}$) to the total magnetization/susceptibility. So the total susceptibility will be

$$-\frac{e^2}{12\pi mc^2}\mathcal{S}N_z.$$

The number N_z is the number of states between $-p_F$ and p_F. As the states are quantized according to $L_z\Delta p = 2\pi\hbar$, we get $N_z = \frac{2p_F}{\Delta p} = \frac{p_F L_z}{\pi\hbar}$. So the susceptibility per unit volume ($\mathcal{V} = \mathcal{S}L_z$) is

$$\chi_{dia}^{3D} = -\frac{e^2 p_F}{12\pi^2 mc^2\hbar}$$

Using that the density of states at the Fermi energy for $3D$ electron gas is $g(\varepsilon_F) = \frac{p_F m}{\pi^2\hbar^3}$ we find that

$$\chi_{dia}^{3D} = -\frac{1}{3}\mu_B^2 g(\varepsilon_F) \tag{17.1}$$

If we compare this expression to the Pauli paramagnetic susceptibility, then we see, that it is 3 times smaller (and has different sign). However, we need to be careful. The Bohr magneton μ_B in (15.1) contains the bare electron mass m_0, while in the (17.1) μ_B contains the band mass m, so in general

$$\frac{\chi_{dia}^{3D}}{\chi_{para}^{3D}} = -\frac{1}{3}\left(\frac{m_0}{m}\right)^2.$$

17.1.2. Strong field case.

We again start with the case $T = 0$. We can calculate the magnetization at strong fields in the same spirit as the calculation for weak fields was done.

We consider the $3D$ Fermi sphere as a collection of the $2D$ Fermi discs – one for each p_z. For each of these discs we have the result given by (16.13),

$$M^{2D} = -4\mu_B \frac{H\mathcal{S}}{\Phi_o} \sum_{n=0}^{\infty} \left(2(n+1/2) - \frac{\varepsilon_F^{2D}}{\hbar\omega_c} \right) \theta \left(\frac{\varepsilon_F^{2D}}{\hbar\omega_c} - (n+1/2) \right).$$

so we just need to sum up contributions for all discs. In order to do that we need to remember, that ε_F in (16.13) is the $2D$ Fermi energy ε_F^{2D}, while we need to use ε_F^{3D}. So for the disc at some particular p_z we need to substitute $\varepsilon_F^{2D} = \varepsilon_F^{3D} - \frac{p_z^2}{2m}$ in (16.13) and sum over all p_z — which means taking the integral $L_z \int \frac{dp_z}{2\pi\hbar} \ldots$, So we have

$$M = -4\mu_B \frac{H\mathcal{S}L_z}{\Phi_o} \frac{1}{\hbar\omega_c} \int \frac{dp_z}{2\pi\hbar} \sum_{n=0}^{\infty} \left(2\hbar\omega_c(n+1/2) - \varepsilon_F^{3D} - \frac{p_z^2}{2m} \right) \theta \left(\varepsilon_F^{3D} - \frac{p_z^2}{2m} - \hbar\omega_c(n+1/2) \right).$$

Interchanging the order of summation and integration, and noticing, that θ-function enforces the limits of integration, as well as the upper limit of summation, to be finite, we get

$$\frac{M}{\mu_B N} = -4 \left(\frac{\hbar\omega_c}{\varepsilon_F^{3D}} \right)^{3/2} \sum_{n=0}^{n<\frac{\varepsilon_F}{\hbar\omega_c}-\frac{1}{2}} \left(\frac{\varepsilon_F}{\hbar\omega_c} - (n+1/2) \right)^{1/2} \left(\frac{5}{2}(n+1/2) - \frac{\varepsilon_F}{\hbar\omega_c} \right). \tag{17.2}$$

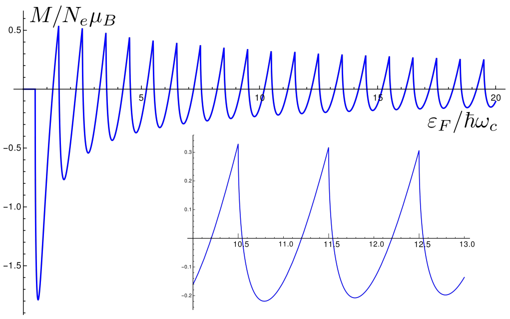

Figure 1. Magnetization per electron as a function of $\varepsilon_F/\hbar\omega_c$ for $3D$.

This result is shown on Fig. 1. One can see, that although the shape of the graph is very different from the $2D$ case the important features are intact,

- The signal is periodic (quasi-periodic) in $1/H$ with the period in both $2D$ and $3D$ given by $\Delta\left(\frac{1}{H}\right) = \frac{\hbar e}{mc}\frac{1}{\varepsilon_F}$. Using $\varepsilon_F = \frac{p_F^2}{2m}$, and introducing $A_F = \pi p_F^2$ – the maximal area of a cross section of the Fermi surface by a plane perpendicular to the magnetic field, we get

$$\Delta\left(\frac{1}{H}\right) = \frac{eh}{c}\frac{1}{A_F}. \tag{17.3}$$

- This periodic behavior comes from the fact that the as we increase the field the Landau levels periodically cross the Fermi energy.

We will see, that the property (17.3) is very general.

For finite, but still small temperatures $T \ll \hbar\omega_c$ we need to compute the convolution of (17.2) with the function $\partial_\varepsilon f_F(\varepsilon)$. This procedure will smooth out the sharp features of the result (17.2), but the result will still be periodic.

The oscillation of the magnetization as a function of magnetic field (at strong fields) is called the De Haas-van Alphen effect.

17.2. Bloch electrons.

So far we have derived equation (17.3) only for free electrons. The same result is also true for Bloch electrons (i.e. electrons in a periodic potential) as we shall now show. Already the fact that (17.3) does not depend on the electron mass, which could be altered to an effective mass by band structure effects, gives one a suspicion that this might be so. First we consider two dimensions.

17.2.1. Bloch electrons $2D$

The first stage in the proof of (17.3) is to derive an equation, (17.10) below, relating the period of an orbit of a Bloch electron in a magnetic field to the change in the area of the orbit in momentum space with energy. We start with the semi-classical equations of motion:

$$\mathbf{v}(\mathbf{p}) = \frac{\partial\epsilon(\mathbf{p})}{\partial\mathbf{p}} \tag{17.4}$$

$$\dot{\mathbf{p}} = (-e)\frac{1}{c}\mathbf{v}(\mathbf{p}) \times \mathbf{H}, \tag{17.5}$$

from which it follows that

$$|\dot{\mathbf{p}}| = \frac{eH}{c}\left|\left(\frac{\partial\epsilon(\mathbf{p})}{\partial\mathbf{p}}\right)_\perp\right|, \tag{17.6}$$

where $(\partial\epsilon(\mathbf{p})/\partial\mathbf{p})_\perp$ is the component of $\partial\epsilon(\mathbf{p})/\partial\mathbf{p}$ perpendicular to the field $\mathbf{H}$, i.e. its projection in the plane of the orbit. (Note this projection is not necessary in two dimensions considered here, but we include it so that our derivation of Eq. (17.10) below will also apply in three dimensions.) Hence the period of an orbit is given by

$$T = \oint \frac{dp}{|\dot{\mathbf{p}}|} = \frac{c}{eH}\oint \frac{dp}{|(\partial\epsilon(\mathbf{p})/\partial\mathbf{p})_\perp|}, \tag{17.7}$$

where dp is the magnitude of a small element of the orbit, and we integrate around the closed orbit.

If we consider two orbits whose difference in energy $\Delta\epsilon$ is small then the region between them in the p_x-p_y plane is a ribbon of width $\mathbf{\Delta}(\mathbf{p})$, see AM Fig. 12.9, where

$$\Delta\epsilon = \left|\left(\frac{\partial\epsilon(\mathbf{p})}{\partial\mathbf{p}}\right)_\perp\right| |\mathbf{\Delta}(\mathbf{p})|. \tag{17.8}$$

Hence the period T can be written as

$$T = \frac{c}{eH}\frac{1}{\Delta\epsilon}\oint |\mathbf{\Delta}(\mathbf{p})|\, dp. \tag{17.9}$$

The integral in the last equation is just the area between the two neighboring orbits, ΔA, and so

$$T = \frac{c}{eH}\left(\frac{\Delta A}{\Delta \epsilon}\right). \tag{17.10}$$

Note that with a free electron band structure, $\epsilon = p^2/2m,\ A = \pi p^2$, this gives $T = 2\pi/\omega_c$, where ω_c is the cyclotron frequency, as expected.

The second stage of the proof is to use another relationship involving the period of the orbits, the Bohr-Sommerfeld correspondence principle, which states that if ϵ_p and ϵ_{p+1} are two adjacent energy levels with quantum numbers p and $p+1$ where p is assumed large, then

$$\epsilon_{p+1} - \epsilon_p = \frac{h}{T}, \tag{17.11}$$

where T is the period of the motion of a semiclassical wavepacket on an orbit with energy centered on ϵ_p. This can be derived by noting that the wavepacket is built up out of adjacent energy levels, and its periodic motion comes from interference between different levels. This requires that the levels around ϵ_p be uniformly spaced with spacing $\hbar\omega = h/T$, where ω is the angular frequency of the orbit. (Note that the "correspondence principle" really only comes in with the further remark that T is also the period of a purely *classical* particle of the same energy.)

From Eq. (17.11) we substitute $T\Delta\epsilon = h = 2\pi\hbar$ into Eq. (17.10), and then find that the area between the semiclassical orbits of two adjacent Landau levels is given by

$$\Delta A = \frac{eh}{c}H. \tag{17.12}$$

This elegant result, first obtained by Onsager, can be reexpressed by stating that at large n the area A_n inside the Landau level n is given by

$$A_n = (n+\lambda)\frac{eh}{c}H \tag{17.13}$$

where λ is some number independent of n.

We can look at the result (17.13) in the following way: We have fixed area of the Fermi disc A_F, then the number of Landau levels inside the Fermi disc — the number n in (17.13) — is a function of the magnetic field $n = \frac{A_F c}{eh}\frac{1}{H} - \lambda$. So we see, that n changes by one if

$$\Delta\left(\frac{1}{H}\right) = \frac{eh}{c}\frac{1}{A_F},$$

which is the same as (17.3).

17.2.2. Bloch electrons $3D$

How does all this go over into three dimensions? One now needs to add p_z, so the semiclassical orbits, which were circles in two dimensions, are now cylinders. One such cylinder is shown in Fig. 2. As H increases the radius increases. However, one does not expect a dramatic change in the magnetization until the radius increases to p_F, (shown dashed in Fig. 2), beyond which the cylinder does not intersect the Fermi sphere at all.

The cylinders "pop out" of the Fermi sphere periodically with $1/H$. So one expects oscillatory behavior in the magnetization just as in two dimensions. This can be confirmed by a mathematical analysis, see e.g. Peierls, pp. 144-149. Clearly then, the periodicity of the magnetization with $1/H$ involves the *maximum* area formed by the intersection of the

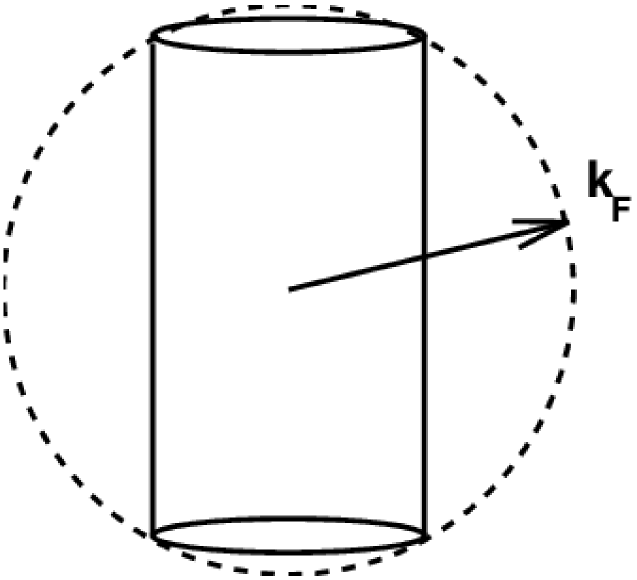

Figure 2. The dashed circle represents the Fermi sphere in three dimensions. The cylinder represents the semi-classical orbit corresponding to a single Landau level. As the strength of the magnetic field increases, the radius of the cylinder increases and will eventually exceed the Fermi wave vector, k_F. This "popping out" of the Landau levels from the Fermi surface leads to oscillatory behavior of the energy and magnetization at sufficiently low temperature.

Fermi sphere with a plane perpendicular to H. If one has a general Fermi surface from some complicated band structure, then it is also possible that, on varying p_z, the intersection of the Fermi surface with the plane of constant p_z might have a *minimum*. These orbits will also contribute to the oscillatory behavior because the part of the cylinder inside the Fermi sphere will decrease rapidly when the radius of the cylinder passes this extremal radius.

Thus we conclude that the magnetization will show oscillations with periods given by

$$\Delta\left(\frac{1}{H}\right) = \frac{eh}{c}\frac{1}{A_{\text{ext}}}, \tag{17.14}$$

where A_{ext} is the area of any *extremal* orbit in the plane perpendicular to the field. If there is more than one extremal area then several periods will be superimposed.

A determination of oscillations in M as a function of $1/H$ (the de Haas-van Alphen effect) for different orientations of the field has been the most successful method for mapping out the shape of the Fermi surface of metals. It is discussed in AM, Ch. 14.

Oscillations occur in other quantities as well. For example, the resistivity varies with magnetic field, an effect called magnetoresistance. At low temperature and in very clear samples, there are oscillations in the magnetorsistance as a function of $1/H$ (Shubnikov-de Haas effect) of the same origin as the oscillations in magnetization.

17.3. Summary of basic concepts.

In this section we discuss main concepts of the first, introductory part of the course and try to understand their range of applicability.

(a) The first concept was **translation symmetry** of crystalline materials. This concept allowed us to classify the structure of crystals and to formulate the basic theory of *lattice vibrations.* It was shown that *under harmonic approximation* one can introduce normal co-ordinates of lattice displacements which are independent.

- These displacements propagate as plane waves which are characterized by the *wave vector* $\mathbf{q}$ and frequency $\omega(\mathbf{q})$.
- The *dispersion law* $\omega(\mathbf{q})$ is *periodic* in $\mathbf{q}$-space, the period being the *reciprocal lattice vector* $\mathbf{G}$ which can be constructed from the basis $\mathbf{b}_i$ as $\mathbf{G} = \sum_i n_i \mathbf{b}_i$ where n_i are integers. Consequently, one can chose a basic volume in the reciprocal lattice space (the Brillouin zone, BZ).
- The properties of the dispersion law $\omega(\mathbf{q})$ are determined by the crystal structure, in particular, by the number s of atoms in a primitive cell. There are 3 acoustic branches and $3s - 3$ optical ones.

It is clear that the exact periodicity is not the case in real life because i) all the samples are finite, and ii) many important systems are inhomogeneous. Consequently, this approach do not take into account *surface states, interface states.* Moreover, the imperfections of the crystal lattice (defects, impurities) lead to violation of the translation symmetry and, as a result, to *scattering* of the waves. As a result, if the degree of disorder is large, the picture developed above needs important corrections. In particular, some *localized* modes can appear which are completely beyond the scope of Part 1.

(b)
- The properties of the lattice waves allowed us to introduce the central concept of solid state physics - **the concept of quasiparticles**. Namely, the lattice vibrations can be described as a set of quasiparticles (**phonons**) with quasimomentum $\hbar\mathbf{q}$ and energy $\hbar\omega_j(\mathbf{q})$.
- The only (but very important) difference is that (as we will see later) in all the interaction processes quasimomenta $\mathbf{q}$ are conserved only up to $\mathbf{G}$.
- They are Bose particles with zero chemical potential.
- The lattice anharmonicity leads to the interaction between quasiparticles. This interaction together with the scattering by defects lead to the *damping* of quasiparticles. It means that a quasiparticle is not exact eigenvalue of the total Hamiltonian of the system and the quasimomentum $\hbar\mathbf{q}$ is not exact quantum number. Physically, the quasiparticles have finite *mean free path* ℓ that is the characteristic distance of the wave function damping due to all the interactions.
- The length ℓ is very important property for all the transport phenomena. One can understand that the concept of quasiparticles can be valid only if

  $$q_{ph} \gg \frac{1}{\ell_{ph}}.$$

  Another formulation of this inequality is that the wave length $2\pi/q$ should be much less than the mean free path ℓ. Indeed, quantum system should have enough space to form a stationary state.
- In most situation this condition holds because the anharmonicity is rather weak (we will estimate it later). Nevertheless, there are some important situations where phonons could not be considered as independent quasiparticles. In particular, phonons can interact with electrons. In some situations this interaction

appears strong enough to form bound states -*polarons.* It is clear that in such a situation the concept of independent weakly interacting phonons fails.

(c) The translation symmetry influences strongly upon the electron system. As we have seen, the concept of **Bloch electrons** can be developed. The main advantages are:
   - The periodic potential created by the lattice and other electrons in the first approximation leads only to the *renormalization* of the electron spectrum from $\mathbf{p}^2/2m_0$ to more complicated function $\varepsilon(\mathbf{p})$ which is periodic in $\mathbf{p}$-space
$$\varepsilon(\mathbf{p}+\mathbf{G}) = \varepsilon(\mathbf{p}).$$
   - Again, we come to independent quasiparticles with the quasimomentum $\mathbf{k}=\mathbf{p}/\hbar$ confined in the BZ. As in the case of phonons, electrons have several energy bands, $\varepsilon_j(\mathbf{p})$.
   - The quasimomentum is conserved only up to $\mathbf{G}$.
   - The most important for applications feature is that one can treat the function
$$\mathcal{H}(\mathbf{p},\mathbf{r}) = \varepsilon_j\left(\mathbf{p}+\frac{e}{c}\mathbf{A}(\mathbf{r})\right)+U(\mathbf{r})-e\varphi(\mathbf{r})$$
as the Hamiltonian to describe the motion of a Bloch electron in external fields. This is very important statement because it allows one to analyze the electron motion in external fields.

The range of applicability of this picture is limited mainly by *one-band approximation* - it is implicitly assumed that *interband transitions* do not take place due to external fields. In particular this approach fails if the frequency ω of external field is close to the $|\varepsilon_i(\mathbf{p})-\varepsilon_j(\mathbf{p})|$ for a given $\mathbf{p}$. One can see that one cannot use the simplified effective mass approach for the case of *degenerate bands* in semiconductors (one should bear in mind that there are some special methods to treat this case, we will discuss some of them later).

Another criterion is that the typical spatial scale of motion, $\mathcal{L}$, should be greater than the lattice constant a. Indeed, the Bloch state is formed at the distances much greater than a, and external fields should not interfere with the formation of the electron state. The latter criterion is, in fact, dependent of the problem under consideration. Suppose that we are interested in the formation of a bound state Bloch electron+impurity with Coulomb potential. It is the typical problem of semiconductor physics. Substituting the Hamiltonian $\hat{\mathbf{p}}^2/2m+e\varphi=\hat{\mathbf{p}}^2/2m-e^2/\epsilon r$ with the effective mass m to the SE we get the effective *Bohr radius*
$$a_B=\frac{\hbar^2\epsilon}{me^2}=a_B^0\frac{m_0}{m}\epsilon=0.53\frac{m_0}{m}\epsilon,\ \text{Å}.$$
In this case the criterion for one-band approximation is $a_B \gg a$. This criterion can be mat only in materials with small effective mass and large dielectric constant ϵ. For the so-called deep levels, as well as for some interface states this approach is not valid.

The electron states as the phonon ones can be destroyed by the impurity scattering, as well as by electron-phonon and electron-electron interaction. Form the first glance, electron should interact with each other via very strong Coulomb forces and it is impossible for them to be near independent. Nevertheless, i) the total system is electrically neutral, and ii) electrons effectively screen electric fields. As a result, Coulomb interaction appears mostly included in the self-consistent potential and the remaining effects can be not important for many actual problems. We will come back to the electron-electron interaction in the following parts.

At the same time, there are important physical situations where the interaction play crucial role and change the ground state of the system. One example is the formation of the polaron (electron+phonon) states, another one is the formation of a superconductor states. The properties of superconductors will be discussed in a special Part.

Up to now, we have described the electron states as *stationary solutions* $\psi = e^{i\mathbf{kr}}u_k(\mathbf{r})$ of the SE. To describe the transport it is useful to form *packets* of the electrons with the quasimomenta $\mathbf{p}$, $\mathbf{p}+\Delta\mathbf{p}$. According to the uncertainty principle,

$$\Delta p \Delta r \approx \hbar.$$

Now, if we want to localize the quasiparticle, the uncertainty Δr should be, at least, less than the mean free path ℓ. The upper limit for Δp is p. So, we come to the criterion

$$p \gg \frac{\hbar}{\ell}.$$

For a typical metal $p \approx \hbar/a$, and we get $\ell \gg a$.

There is another important criterion which is connected with the *life-time* τ_φ with the respect of the phase destruction of the wave function. The energy difference $\Delta\varepsilon$ which can be resolved cannot be greater than $\hbar/\tau_\varphi$. In the most cases $\Delta\varepsilon \approx k_BT$, and we have

$$k_BT \gg \frac{\hbar}{\tau_\varphi}.$$

Note that elastic scattering does not contribute to the phase destruction.

The previous part of the course has outlined the physics of independent quasiparticles which are very often called the *elementary excitations*.

17.4. Problems

17.1. Calculate the partition function for a harmonic oscillator.

17.2. Compute the standard deviation for the occupation numbers at temperature T for both fermi and bose gases.

17.3. Prove the expression (14.5). Derive the density of states for the quadratic dispersion $\varepsilon = \frac{p^2}{2m}$ in $2D$ and in $1D$. See the difference!

17.4. Calculate temperature-dependent corrections to the chemical potential of a Fermi gas with quadratic dispersion for $3D$, $2D$ and $1D$ cases. Pay special attention to the $2D$ case.

17.5. Calculate specific heat for the Boltzmann gas.

17.6. Derive expression (15.1) for magnetic susceptibility.

17.7. Find "Pauli paramagnetic susceptibility" for Boltzmann gas.

17.8. Find "Landau diamagnetic susceptibility" for Boltzmann gas in the case of weak field.

17.9. Consider a classical gas of particles with fixed (in magnitude) classical angular momentum l. The magnetic moment of each particle is $\vec{M} = \mu_B\vec{l}$. Find the average magnetic moment per volume of this gas if the density of the particles is n, the temperature is T, and magnetic field is H. Find the magnetic susceptibility χ of this gas at small fields.

17.10. The same as the previous problem, but the angular momentum is quantum (the translational degrees of freedom of the particles are still classical).

PART 5

Classical Transport in Electron and Phonon Systems

LECTURE 18

The Boltzmann Equation for Electrons

18.1. General Form

Let's consider a gas (in particular electron gas) slightly out of equilibrium. We know that after some time it will equilibrate. This time of equilibration depends on the on the size of the system and growth with the system size. This means, that if we split our system in many much smaller subsystems (but each subsystem is still macroscopic), then each subsystem will almost equilibrate way before the whole system does – almost, because the whole system is still evolving, so does each subsystem.

In this situation we can introduce the distribution function (average occupation numbers) $f(\mathbf{r}, \mathbf{p}, t)$ for each (very small) subsystem. We then need to write the evolution equation for this function. This function is called *non-equilibrium distribution function.*

Let's for now ignore all equilibration processes: impurity scattering, electron-electron interaction, electron-phonon interaction, etc. We then have free Bloch particles (wave packets). The distribution function $f(\mathbf{r}, \mathbf{p}, t)$ at fixed $\mathbf{r}$ and $\mathbf{p}$ will still be evolving due to external fields. The Liouville's theorem, however, states that

$$\frac{df}{dt} = 0.$$

As was pointed out the equilibration is happening in each subsystem, where the function $f(\mathbf{r}, \mathbf{p}, t)$ can be taken to be $\mathbf{r}$ independent. The equilibration happens due to collisions in each of these small volumes. These collisions has to be included in the right hand side of the above equation. One can write

$$\frac{df}{dt} = I(f)$$

where $I(f) \equiv (\partial f/\partial t)_{\text{coll}}$ is called the *collision integral.* One can write the l.h.s. as

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{r}}\frac{\partial \mathbf{r}}{\partial t} + \frac{\partial f}{\partial \mathbf{p}}\frac{\partial \mathbf{p}}{\partial t}\,.$$

Using the Newton equation we can write the previous formula as

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} - e\left(\mathbf{E}+\frac{1}{c}\left[\mathbf{v}\times\mathbf{H}\right]\right)\frac{\partial f}{\partial \mathbf{p}}.$$

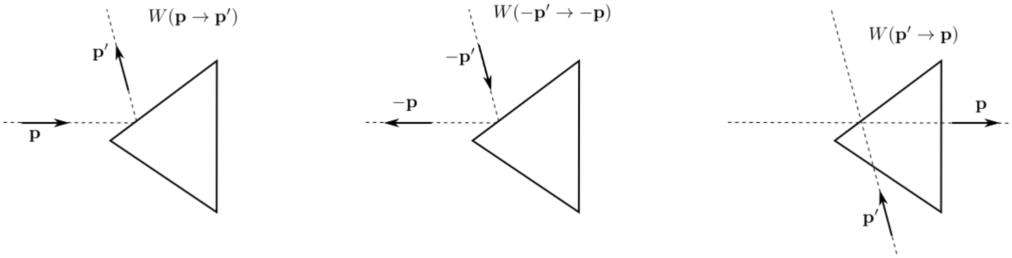

Figure 1. Left: scattering probability from state $\mathbf{p}$ to $\mathbf{p}'$, the time reversal process (middle) is scattering from state $-\mathbf{p}'$ to $-\mathbf{p}$. From the right panel it is obvious, that in general this is not the same as scattering from state $\mathbf{p}'$ to $\mathbf{p}$.

The collision integral describes transitions between the states with different $\mathbf{p}$ due to collisions. It can be specified if one knows the collision probability $W(\mathbf{p}\to\mathbf{p}')$ – the probability of a particle in a state of momentum $\mathbf{p}$ to scatter to the state of momentum $\mathbf{p}'$.

Indeed, the change of the distribution induced by the collisions is

$$\text{decrease:}\quad -\sum_{\mathbf{p}'} W(\mathbf{p}\to\mathbf{p}')f(\mathbf{p})\,[1-f(\mathbf{p}')] \to \text{“out” term},$$

$$\text{increase:}\quad \sum_{\mathbf{p}'} W(\mathbf{p}'\to\mathbf{p})f(\mathbf{p}')\,[1-f(\mathbf{p})] \to \text{ “in” term}.$$

The first term describes the scattering processes in which the electron *leaves* the state $\mathbf{p}$ while the second one describes the processes where an electron comes to the state $\mathbf{p}$ from other states $\mathbf{p}'$. The factors $[1-f(\mathbf{p})]$ takes account of the Pauli principle. So

$$I(f)=\sum_{\mathbf{p}'}\left\{W(\mathbf{p}'\to\mathbf{p})f(\mathbf{p}')\,[1-f(\mathbf{p})]-W(\mathbf{p}\to\mathbf{p}')f(\mathbf{p})\,[1-f(\mathbf{p}')]\right\}. \tag{18.1}$$

Finally, we get the *Boltzmann equation* for electrons

$$\frac{\partial f}{\partial t}+\mathbf{v}\frac{\partial f}{\partial \mathbf{r}}-e\left(\mathbf{E}+\frac{1}{c}\left[\mathbf{v}\times\mathbf{H}\right]\right)\frac{\partial f}{\partial \mathbf{p}}=I(f)\,. \tag{18.2}$$

18.1.1. Collision integral.

Let us investigate general properties of the collision integral. It is clear that if the system is in equilibrium the collision integral should vanish, $I(f_0)\equiv 0$. Making use of the relation

$$1-f_0(\varepsilon)=f_0(\varepsilon)\,\exp\left(\frac{\varepsilon-\zeta}{k_BT}\right)$$

we find that if

$$W(\mathbf{p}'\to\mathbf{p})\,\exp\left(\frac{\varepsilon}{k_BT}\right)=W(\mathbf{p}\to\mathbf{p}')\,\exp\left(\frac{\varepsilon'}{k_BT}\right)$$

where $\varepsilon=\varepsilon(\mathbf{p})$, $\varepsilon'=\varepsilon(\mathbf{p}')$, then indeed f_0 is the stationary solution. For any elastic scattering, the time reversal symmetry demands (see Figure 1)

$$W(\mathbf{p}\to\mathbf{p}')=W(-\mathbf{p}'\to-\mathbf{p}).$$

If in addition we have the inversion symmetry[1] (in the first Born approximation we always do) then $W(-\mathbf{p}' \to -\mathbf{p}) = W(\mathbf{p}' \to \mathbf{p})$, and we get

$$I(f) = \sum_{\mathbf{p}'} W(\mathbf{p} \to \mathbf{p}')\,[f(\mathbf{p}') - f(\mathbf{p})]\ . \tag{18.3}$$

We see that the Pauli principle is not important for elastic collisions because it is met automatically.

However, the Pauli principle will be important if we compute $W(\mathbf{p} \to \mathbf{p}')$ beyond Born approximation. In such calculation the scattering goes through an intermediate state. This state must be empty, so such processes will depend on the Fermi distribution. So generally, (18.3) contains the function $f(\mathbf{r}, \mathbf{p})$ inside the scattering probability W.

Now we will discuss one important collision mechanism to show the main properties of the transport, namely, the impurity scattering. This mechanism is important at low temperatures and in rather dirty materials.

18.2. Impurity scattering

As it is clear from the remark below (18.3) the Boltzmann equation becomes rather complicated if we have to compute W beyond Born approximation. Fortunately, Born approximation is sufficient for many problems (but not all). Under this approximation, the scattering probability for impurities is

$$W(\mathbf{p} \to \mathbf{p}') = \frac{2\pi}{\hbar}\,|V_{\mathbf{p}\mathbf{p}'}|^2\,\delta\,[\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{p}')] \tag{18.4}$$

where $V_{\mathbf{p}\mathbf{p}'}$ is the matrix elements of the impurity potential

$$V(\mathbf{r}) = \sum_i v(\mathbf{r} - \mathbf{R}_i) \tag{18.5}$$

which is the sum of the potentials v of the individual impurities between the Bloch states

$$\frac{1}{\sqrt{\mathcal{V}}} e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \qquad \mathbf{k} \equiv \frac{\mathbf{p}}{\hbar}.$$

Substituting (18.5) into the expression for matrix elements we get

$$\begin{aligned}
V_{\mathbf{k}\mathbf{k}'} &= \mathcal{V}^{-1} \sum_i \int v(\mathbf{r} - \mathbf{R}_i)\, e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}} u^*_{\mathbf{k}'}(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r})\, d^3r \\
&= \mathcal{V}^{-1} \sum_i e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_i} \int v(\mathbf{r}) u^*_{\mathbf{k}'}(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r})\, e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}} d^3r \\
&= \mathcal{V}^{-1} \sum_i e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_i} v_{\mathbf{k}'\mathbf{k}}\,.
\end{aligned}$$

Here we have assumed all the impurity atoms be of the same kind and their positions in the primitive cells are equivalent. So we have shifted the origin of the frame of reference for each cell by an appropriate lattice vector. Now we can calculate the scattering probability (18.4). We get

$$\frac{2\pi}{\hbar}\frac{1}{\mathcal{V}^2} \int \mathcal{V}(dp')\ |v_{\mathbf{p}'\mathbf{p}}|^2\ \delta\,[\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{p}')] \sum_{i,k} e^{i(\mathbf{k}-\mathbf{k}')(\mathbf{R}_i - \mathbf{R}_k)}$$

---

[1] What happens when there is no inversion symmetry is discussed in the paper by V. I. Belinicher and B. I. Sturman, `http://iopscience.iop.org/article/10.1070/PU1980v023n03ABEH004703/meta`

where we replaced the summation over the discrete quasimomenta by the integration

$$\sum_{\mathbf{p}'} \to \mathcal{V} \int (dp') \equiv \frac{2\mathcal{V}}{(2\pi\hbar)^3} \int d^3p' \,.$$

The last sum can be strongly simplified because the positions of the impurities are *random* the distance between them is much greater than interatomic spacing a, but much smaller, than the coarse grains that we used to define the non-equilibrium distribution function. So we can average over their impurity positions and the only terms important are the ones with $i = k$ (the other oscillate strongly, their contribution being very small). As a result,

$$\overline{\sum_{i,k} e^{i(\mathbf{k}-\mathbf{k}')(\mathbf{R}_i - \mathbf{R}_k)}} = N_{\text{imp}}$$

where N_{imp} is the number of impurities. Finally, we get the following collision integral

$$I(f) = \frac{2\pi}{\hbar} n_i \int \frac{2d^3p'}{(2\pi\hbar)^3} \left|v_{\mathbf{p}'\mathbf{p}}\right|^2 \delta\left[\varepsilon(\mathbf{p}) - \varepsilon(\mathbf{p}')\right] \left[f(\mathbf{p}^{'}) - f(\mathbf{p})\right] \tag{18.6}$$

where we introduced the impurity concentration as $n_i = N_{imp}/\mathcal{V}$.

Now we change the variables from $\mathbf{p}'$ to the energy ε' and the surface S' defined as $\varepsilon(\mathbf{p}') = \varepsilon'$. We get

$$\frac{2}{(2\pi\hbar)^3} d^3p' = \frac{2}{(2\pi\hbar)^3} dS'\, dp'_{\perp} = \frac{2}{(2\pi\hbar)^3} dS' \frac{d\varepsilon'}{|\partial\varepsilon'/\partial\mathbf{p}'|} = d\varepsilon' \, (ds'_{\varepsilon'})$$

where we have denoted

$$(ds_\varepsilon) \equiv \frac{2}{(2\pi\hbar)^3} \frac{dS}{v_\varepsilon}.$$

Note that the density of states is given by the expression

$$g(\varepsilon) = \int_{S_\varepsilon} (ds_\varepsilon)$$

where the integral is calculated over the surface of constant energy $\varepsilon(\mathbf{p})$. Using the above mentioned notations we can than apply the δ-function to integrate over the ε'. The result has a simple form

$$I(f) = \frac{2\pi}{\hbar} n_i \int_{S_{\varepsilon'=\varepsilon}} (ds_{\varepsilon'=\varepsilon}) \left|v_{\mathbf{p}'\mathbf{p}}\right|^2 \left[f(\mathbf{p}^{'}) - f(\mathbf{p})\right]. \tag{18.7}$$

Notice, that if the distribution function f depends only on energy, then for the impurity scattering the collision integral is 0. In particular it is zero for the equilibrium distribution. However, if we apply external field, such as electric field, then we expect a nonzero current, which means that we have more electrons moving to the, say, left than to the right. The distribution function then depends not only on energy, but also on the direction.

LECTURE 19

The transport relaxation time $1/\tau_{tr}$ and conductivity.

19.1. The Transport Relaxation Time

In the previous lecture we found the collision integral for the impurity scattering

$$I(f) = \frac{2\pi}{\hbar} n_i \int_{S_{\varepsilon'=\varepsilon}} (ds_{\varepsilon'=\varepsilon}) \left| v_{\mathbf{p}'\mathbf{p}} \right|^2 \left[f(\mathbf{p}') - f(\mathbf{p}) \right].$$

Notice

- If the distribution function depends on energy only, then the collision integral is zero. This is so because the collisions are absolutely elastic.
- Such collisions alone cannot lead to equilibration.
- In order to take the equilibrating processes into account (assuming they are negligible) we will assume that the true distribution function is close to the Fermi function.

Now we demonstrate a very useful representation of the collision integral that makes the solution of the Boltzmann equation rather simple. Let us assume that the deviation from equilibrium is small, so that

$$f = f_0 + f_1, \qquad |f_1| \ll f_0.$$

Because $I(f_0) = 0$ we have $I(f) = I(f_1)$. To get explicit results we assume that the spectrum $\varepsilon(\mathbf{p})$ is isotropic. Consequently $p = p'$, $\quad v_{\mathbf{p},\mathbf{p}'}$ depends only on the angle between $\mathbf{p}$ and $\mathbf{p}'$, the surface S is a sphere and the integration is in fact performed over the solid angle.

The function $f_1(\mathbf{p})$ must depend on the angle, as otherwise we will have just a function of ε, and the collision integral would be zero.

Let's take the function f_1 in the following form (first harmonic)

$$f_1 = -\mathbf{n} \cdot \mathbf{f}(\varepsilon), \quad \mathbf{n} \equiv \mathbf{p}/p \tag{19.1}$$

where $\mathbf{f}$ is a vector that depends only on ε. In this case

$$I(f) = \int \frac{d\Omega'}{4\pi} W(\epsilon, \theta) \left(\mathbf{n} \cdot \mathbf{f} - \mathbf{n}' \cdot \mathbf{f} \right).$$

where Ω' is the solid angle in the $\mathbf{p}'$-space, $\cos\theta = \mathbf{n}' \cdot \mathbf{n}$, and (Check!)

$$W(\varepsilon, \theta) = \pi \frac{n_i |v(\theta)|^2}{\hbar} g(\varepsilon). \tag{19.2}$$

Now let's use

$$\mathbf{n}' = \mathbf{n}(\mathbf{n}' \cdot \mathbf{n}) + \mathbf{n}'_\perp, \qquad \mathbf{f} = \mathbf{n}(\mathbf{f} \cdot \mathbf{n}) + \mathbf{f}_\perp,$$

where $\perp$ components are components perpendicular to $\mathbf{n}$. In this notations

$$\mathbf{n}' \cdot \mathbf{f} = (\mathbf{n}' \cdot \mathbf{n})(\mathbf{f} \cdot \mathbf{n}) + \mathbf{n}'_\perp \cdot \mathbf{f}_\perp$$

Let's call the angle between the vectors $\mathbf{n}'_\perp$ and $\mathbf{f}_\perp$ the second spherical angle ϕ. Then the last term is $|\mathbf{n}'_\perp||\mathbf{f}_\perp| \cos\phi$, as $d\Omega' = \sin(\theta) d\theta d\phi$, integration of this term over ϕ gives zero, and we have

$$\mathbf{n} \cdot \mathbf{f} - \mathbf{n}' \cdot \mathbf{f} \to \mathbf{n} \cdot \mathbf{f}(1 - \mathbf{n}' \cdot \mathbf{n}) = -f_1(1 - \cos(\theta)).$$

Finally we get

$$I(f) = -\frac{f_1}{\tau_{\mathrm{tr}}} = -\frac{f - f_0}{\tau_{\mathrm{tr}}(\varepsilon)}$$

where

$$\frac{1}{\tau_{\mathrm{tr}}(\varepsilon)} = \frac{1}{2} \int_0^\pi W(\varepsilon, \theta)\,(1 - \cos\theta)\, \sin\theta\, d\theta\,. \tag{19.3}$$

The quantity τ_{tr} is called the *transport relaxation time.* In many situations the Boltzmann equation is represented in the form

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} - e\left(\mathbf{E} + \frac{1}{c}\left[\mathbf{v} \times \mathbf{H}\right]\right)\frac{\partial f}{\partial \mathbf{p}} = -\frac{f - f_0}{\tau_{\mathrm{tr}}}\,. \tag{19.4}$$

It is called relaxation time approximation.

Here we have shown that this form is *exact* for elastic impurity scattering if the non-equilibrium function can be expressed as (19.1). One should remember that we have made several important simplifications:

- Isotropic spectrum;
- Elastic scattering;
- The form (19.1) for the non-equilibrium distribution function.

All these assumptions are important and in some cases they can be wrong. Nevertheless the form (19.4) allows one to get good order-of-magnitude estimates and we will extensively use it.

19.2. Conductivity.

19.2.1. DC Electric Conductivity

Let us apply the outlined approach to calculate the conductivity of a conductor. Namely, let us assume that a weak stationary electric field $\mathbf{E}$ is applied to the sample. The Boltzmann equation has the form

$$-e\left(\mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{p}}\right) = -\frac{f - f_0}{\tau_{\mathrm{tr}}}. \tag{19.5}$$

Because the field is weak we can assume that

$$f = f_0 + f_1\,, \quad f_1 \propto E\,,$$

In the linear response we can replace $f \to f_0$ in the l.h.s. and get $e(\mathbf{E} \cdot \mathbf{v})\,(-\partial f_0/\partial \varepsilon)$. Immediately we get

$$f_1 = e(\mathbf{E} \cdot \mathbf{v})\,\tau_{\mathrm{tr}}(\partial f_0/\partial \varepsilon)\,.$$

We see that it has just the form of (19.1) that justifies our approach. Now we calculate the current as

$$\mathbf{j} = -e\int (dp)\,\mathbf{v} f_1 = e^2\int (dp)\,\tau_{\rm tr}\,\mathbf{v}(\mathbf{E}\cdot\mathbf{v})\left(-\frac{\partial f_0}{\partial \varepsilon}\right) \tag{19.6}$$

(the function f_0 is even in $\mathbf{p}$ and does not contribute to the current). Again, we can average over the surface of a constant energy as

$$\int M(\mathbf{p})(dp) = \int d\varepsilon \int_{S_\varepsilon} M(\mathbf{p})\,(ds_\varepsilon) = \int d\varepsilon\, g(\varepsilon)\langle M(\mathbf{p})\rangle_\varepsilon$$

where

$$\langle M(\mathbf{p})\rangle_\varepsilon \equiv \frac{\int_{S_\varepsilon} M(\mathbf{p})\,(ds_\varepsilon)}{g(\varepsilon)}. \tag{19.7}$$

In the case of an isotropic spectrum the average (19.7) is just the average over the angles. Finally for the isotropic spectrum we get Ohm's law $\mathbf{j} = \sigma\mathbf{E}$ with

$$\sigma = e^2\int d\varepsilon\left(-\frac{\partial f_0}{\partial \varepsilon}\right) g(\varepsilon)D(\varepsilon) \tag{19.8}$$

where

$$D(\varepsilon) = \frac{1}{3}\left\langle v^2\tau_{\rm tr}\right\rangle_\varepsilon$$

is the partial *diffusivity* for the electrons with the given energy.

Indeed, consider a gas of electrons with the mean free time τ and mean free path $\ell = v\tau$. Let the density of electrons, n_e be non-uniform along the $\mathbf{x}$-axis. In this case the flux of the electrons through 1 cm^2 of the surface normal to $\mathbf{x}$ is equal

$$i_D(x) = \int n_e(x-\ell\cos\theta)\,v\cos\theta\,\frac{d\Omega}{4\pi},$$

where θ is the angle between $\mathbf{v}$ and $\mathbf{x}$ while ℓ is the electron mean free path, $\ell = v\tau_{\rm tr}$. Here we have taken into account that the electrons have arrived at the point with coordinate x from the point with the coordinate $x-\ell\cos\theta$ in a ballistic way. As a result, non-compensated current is

$$i_D = -\frac{\partial n_e}{\partial x}\frac{\ell v}{2}\int_{-1}^{1}\cos^2\theta\,d(\cos\theta) = -\frac{\ell v}{3}\frac{\partial n_e}{\partial x}.$$

According to the definition of the diffusivity (diffusion coefficient), we get $D = \ell v/3 = v^2\tau_{\rm tr}/3$.

In the case of Fermi statistics where $(-\partial f_0/\partial\varepsilon) = \delta(\varepsilon-\epsilon_F)$ we get the *Drude formula* (*Problem 24.2*)

$$\sigma_0 = e^2 D(\epsilon_F)g(\epsilon_F) = \frac{ne^2\tau_{\rm tr}}{m}. \tag{19.9}$$

The first expression is known as the *Einstein relation.*

If the degeneracy is not so strong, the energy dependence of the factor $D(\varepsilon)$ becomes important. This is just the case for semiconductors. We will come back to this problem after the analysis of important scattering mechanisms which determine the dependence $\tau_{\rm tr}(\varepsilon)$.

In general anisotropic case the Ohms law has the form

$$\mathbf{j} = \hat\sigma\mathbf{E}, \qquad \text{or} \quad j_i = \sum_k \sigma_{ik}E_k\,.$$

The *conductivity tensor* $\hat{\sigma}$ can be calculated with the help of the relation (19.8) if the *diffusivity tensor*

$$D_{ik} = \langle v_i I^{-1} v_k \rangle_\varepsilon$$

is known. Here the formal "inverse collision operator" is introduced which shows that one should in fact solve the Boltzmann equation.

19.2.2. AC Conductivity

Solving the Boltzmann equation for the perturbation $\propto \exp(-i\omega t)$ we obtain (see Problem 24.3)

$$\sigma(\omega) = \sigma_0 \frac{1}{\langle \tau_{\rm tr} \rangle} \left\langle \frac{\tau_{\rm tr}}{1 - i\omega\tau_{\rm tr}} \right\rangle . \tag{19.10}$$

Here angular brackets mean

$$\langle A \rangle = \frac{\int d\varepsilon\, \varepsilon^{3/2} A(\varepsilon)\, (\partial f_0/\partial \varepsilon)}{\int d\varepsilon\, \varepsilon^{3/2}\, (\partial f_0/\partial \varepsilon)} .$$

The real part of this expression,

$$\operatorname{Re} \sigma(\omega) = \sigma_0 \frac{1}{\langle \tau_{\rm tr} \rangle} \left\langle \frac{\tau_{\rm tr}}{1 + \omega^2 \tau_{\rm tr}^2} \right\rangle ,$$

represents ac loss in the sample, while imaginary part is the contribution to dielectric function. The typical scale for the momentum relaxation time is about 10^{-12}–10^{-14} s. Consequently, frequency dependence is important at microwave frequencies.

LECTURE 20

Thermoelectric Phenomena and energy transport.

20.1. Thermoelectric Phenomena

Now we demonstrate another kind of problems which appear if a *temperature gradient* s created in the sample. In this case the temperature is a slow function of co-ordinates and can be expressed as

$$T(\mathbf{r}) = T_1 + (\mathbf{r} - \mathbf{r}_1)\nabla T\,, \quad T_1 \equiv T(\mathbf{r}_1)\,.$$

If the characteristic scale of the spatial variation of the temperature, $T/|\nabla T|$, is large in comparison with the scale at which temperature is formed (that is usually the phonon mean free path, ℓ_{ph}) one can assume that at any point the distribution is close to the equilibrium one,

$$f_0(\varepsilon, \mathbf{r}) = \left[\exp\left(\frac{\varepsilon - \zeta(\mathbf{r})}{k_B T(\mathbf{r})}\right) + 1\right]^{-1} \tag{20.1}$$

Here we take into account that the chemical potential ζ is also coordinate-dependent, since it depends on the temparature. Consequently, we get

$$\nabla_{\mathbf{r}} f_0 = \left(-\frac{\partial f_0}{\partial \varepsilon}\right)\left[\nabla\zeta(\mathbf{r}) + \frac{\varepsilon - \zeta}{T}\nabla T(\mathbf{r})\right].$$

Thus in the l.h.s. of the Boltzmann equation we get

$$\left[(\mathbf{v}\cdot\nabla\zeta) + \frac{\varepsilon - \zeta}{T}\,(\mathbf{v}\cdot\nabla T)\right]\left(-\frac{\partial f_0}{\partial \varepsilon}\right).$$

Comparing this expression with the corresponding l.h.s. of Eq. (19.5) $-e(\mathbf{E}\cdot\mathbf{v})\partial_\epsilon f_0(\epsilon)$ of the Boltzmann equation in the case of electric field we observe that an additional effective $\delta\mathbf{E} = \nabla(\zeta/e)$ electric field appears, the total field being

$$\mathbf{E}^* = \nabla\left(\frac{\zeta}{e} - \varphi\right) = -\nabla\varphi^*.$$

The quantity $\varphi^* = \varphi - \zeta/e$ is called the *electrochemical potential.* This quantity rather the pure electric potential φ describes the transport. In the following we will assume that the static electric field includes this correction. Thus the first item leads to the extra contribution to the Ohmic current and finally $j = \sigma\mathbf{E}^*$.

For the second term, we can plug it into the equation

$$\mathbf{v}\cdot\nabla_{\mathbf{r}} f_0(\mathbf{r}) = \frac{\varepsilon-\zeta}{T}\left(\mathbf{v}\cdot\nabla T\right)\left(-\frac{\partial f_0}{\partial\varepsilon}\right) = -\frac{f-f_0}{\tau_{\rm tr}}$$

to get

$$f_1 = \tau_{\rm tr}\frac{\varepsilon-\zeta}{T}\left(\mathbf{v}\cdot\nabla T\right)\frac{\partial f_0}{\partial\varepsilon}\,. \tag{20.2}$$

- Notice, that this f_1 has exactly the form assumed in the derivation of the relaxation time approximation.

Now we substitute this expression into Eq. (19.6) and calculate the current. The result can be expressed as $\mathbf{j}_T = -\eta\nabla T$ with

$$\eta = -\frac{e}{T}\int d\varepsilon\, g(\varepsilon)D(\varepsilon)(\varepsilon-\zeta)\left(-\frac{\partial f_0}{\partial\varepsilon}\right), \qquad D(\varepsilon)=\frac{1}{3}\left\langle v^2\tau_{\rm tr}\right\rangle_\varepsilon\,. \tag{20.3}$$

This expression differs strongly from the corresponding expression for the conductivity by the factor $(\varepsilon-\zeta)$ under the integral. Indeed,

- If the temperature is zero, so $(-\partial f_0/\partial\varepsilon)=\delta(\varepsilon-\epsilon_F)$, then $\eta=0$.
- At finite temperatures, some electrons are excited above the Fermi level forming quasi-electron excitations and leaving quasi-hole ones below the Fermi level.
- Both quasiparticles are dragged by the temperature gradient in the *same* direction, but they have *different* charges. Consequently, there is almost exact compensation of the contributions, the remainder has the order of k_BT/ϵ_F.

Indeed, because $(-\partial f_0/\partial\varepsilon)$ is a sharp function we can expand the integrand as

$$g(\varepsilon)D(\varepsilon) = g(\epsilon_F)D(\epsilon_F) + (\varepsilon-\epsilon_F)\left[\frac{d}{d\varepsilon}\Big(g(\varepsilon)D(\varepsilon)\Big)\right]_{\varepsilon=\epsilon_F}\,.$$

Note that $\epsilon_F\equiv\zeta(T=0)$, and at small temperatures we can neglect the difference between ζ and ϵ_F.

The contribution of the first item vanishes after substitution to Eq. (20.3). To calculate the second contribution we extract the constant factor

$$(gD)'_F \equiv \Big[\big(d\big(g(\varepsilon)D(\varepsilon)\big)/d\varepsilon\Big]_{\epsilon_F}$$

out of the integral. In the remaining intergral, we introduce a new variable, $x\equiv(\varepsilon-\zeta)/k_BT$, and extend the limits of integration over x to $-\infty,\infty$. We are left with the integral

$$\eta = \frac{ek_B^2T}{4}(gD)'_F\int_{-\infty}^{\infty}\frac{x^2\,dx}{\cosh^2 x/2}$$

The results is

$$\eta = \frac{\pi^2}{9}\,ek_B^2T(gD)'_F\,.$$

This is the well known Cutler-Mott formula.

There are some important comments in connection with this formula.

- The thermoelectric coefficient is proportional to the *first* power of the charge. Consequently, it feels the type of the carriers and provides the way to determine it from the experiment.

- In the case of non-degenerate materials the thermoelectric coefficient is much more sensitive to the dependence of $D(\varepsilon)$ on the energy than the conductivity because in contains the derivative.
- If there are several kinds of carriers the behavior of thermoelectric coefficient becomes rich and very instructive to understand what happens.

Thermoelectric effects have important applications. Indeed, we have seen that in our simplest case the current can be written as

$$\mathbf{j} =\sigma \mathbf{E}^* - \eta \nabla T.$$

If the circuit is open $\mathbf{j} = 0$ and we obtain the *thermoelectric field*

$$\mathbf{E}^* = \alpha \nabla T, \qquad \alpha = \frac{\eta}{\sigma}.$$

The quantity α is called the *differential thermo-e.m.f.* or *Seebeck coefficient.* Indeed, the voltage across the sample is

$$V = \int_1^2 \alpha(d\mathbf{r} \cdot \nabla T) = \int_{T_1}^{T_2} \alpha(T)\, dT.$$

To measure this voltage one should prepare the *thermocouple*, i. e. system depicted in Fig. 1. It should contain 2 branches fabricated from different materials. The voltage measured between the leads is

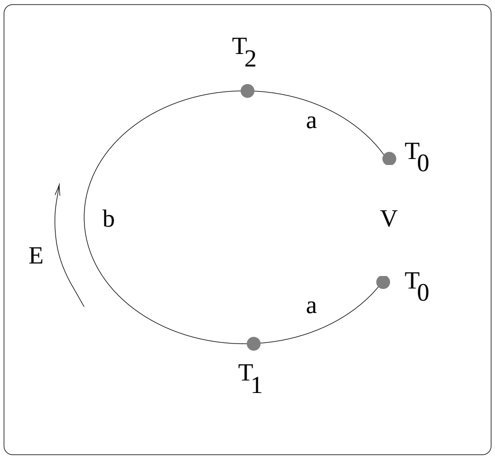

Figure 1. The scheme of thermocouple.

$$V_T = \int_{T_1}^{T_2} \left[\alpha_a(T) - \alpha_b(T)\right]\, dT.$$

We see that it is a relative effect, to measure absolute thermo-e.m.f. one branch is made of a superconductor.

20.2. Energy Transport

Now we discuss the energy transport in an electron system in the presence of electric field and temperature gradient. First we should define the energy flux. There are 2 conventional ways to express the charge and energy currents, $\mathbf{j}$ and $\mathbf{w}$, respectively. The first one is to express both currents through the field $\mathbf{E}^*$ and ∇T. In this way

$$\begin{aligned} \mathbf{j} &= \sigma\mathbf{E}^* - \eta\nabla T\,; \\ \mathbf{w} - \varphi^*\mathbf{j} &= \gamma\mathbf{E}^* - \beta\nabla T\,. \end{aligned} \tag{20.4}$$

The quantity $\mathbf{w} - \varphi^*\mathbf{j}$ has a physical meaning of the *heat* flux since we subtact the "convectional" energy flux $\varphi^*\mathbf{j} = (\zeta - \epsilon\varphi)\langle\mathbf{v}\rangle$ from the total energy flux.

More usual way is to express the electric field and the energy flux through the current $\mathbf{j}$ and ∇T. In this case we get

$$\begin{aligned} \mathbf{E}^* &= \rho\mathbf{j} + \alpha\nabla T\,; \\ \mathbf{w} - \varphi^*\mathbf{j} &= \Pi\mathbf{j} - \varkappa\nabla T\,. \end{aligned} \tag{20.5}$$

It is clear that

$$\rho = \frac{1}{\sigma}, \quad \alpha = \frac{\eta}{\sigma}, \quad \Pi = \frac{\gamma}{\sigma}, \quad \varkappa = \beta + \Pi\eta.$$

The quantity ρ is called *resistivity,* $\varkappa$ is called *thermal conductivity*, while Π is called the *Peltier coefficient.*

The physical nature of the differential thermo-e.m.f. has been already discussed. The nature of the Peltier coefficient can be visualized if one induces a current through the boundary between two materials at a given temperature. If $\Pi_1 \neq \Pi_2$ the fluxes are different and it means that some energy is taken from the contact or it is given to the contact. So, one has the way to cool, or to heat special regions. This is very important property for applications.

Due to fundamental *Onsager relations* all the thermoelectric coefficients can be expressed through only one, say differential thermo-e.m.f. α.

Assume that some generalized forces X_i are applied to the system. They induce currents

$$J_i = \sum_k Q_{ik} X_k$$

where the quantities Q_{ik} are called the *kinetic coefficients.* They are defined so that the entropy production can be expressed as

$$\dot{S} = -\sum_i J_i X_i\,.$$

The Onsager relations follow from the fact that the entropy production must be positive. Consequently, the tensor $\hat{Q}$ must be *symmetric*,[1]

$$Q_{ik} = Q_{ki}\,.$$

To apply the Onsager relations we have to specify forces and currents. In our case, both the divergence of the energy flux, $-\operatorname{div}\mathbf{w}$, and the Joule heating $\mathbf{j}\mathbf{E}^*$ contribute to the entropy production. Consequently,

$$\dot{S} = -\int \frac{\operatorname{div}\mathbf{w}}{T}\, d\mathcal{V} + \int \frac{\mathbf{j}\mathbf{E}^*}{T}\, d\mathcal{V}.$$

Integrating the first term by parts we get

$$\dot{S} = \int \mathbf{w}\nabla\left(\frac{1}{T}\right) d\mathcal{V} + \int \frac{\mathbf{j}\mathbf{E}^*}{T}\, d\mathcal{V}.$$

---

[1] In the presence of a magnetic field they should be generalized, see below.

We see that the generalized forces are

$$-\frac{\mathbf{E}^*}{T}, \qquad -\nabla\left(\frac{1}{T}\right).$$

Thus the kinetic coefficients for our problem are

$$\begin{array}{ll} -\sigma T, & -\eta T^2, \\ -\gamma T, & -\beta T^2. \end{array}$$

Applying the Onsager relations we obtain $\gamma = \eta T$. Using a similar approach for the Eqs. (20.5), we get $\Pi = \alpha T$. Combining the above eqialities we get $\varkappa = \beta - T\eta\alpha$.

The second contribution to the thermal conductivity is always small in the degenerate gas (*Problem* 24.6). Consequently, to analyze the thermal conductivity of a metal it is enough to calculate β.

In fact, $\varkappa$ is determined both by electrons and phonons. Here we are interested only in the electron contribution which is usually the main one in typical metals if the temperature is not too low.

One can estimate the coefficient β from the kinetic equation in a similar way as we have done to the thermo-e.m.f. We use the formula (20.2) for the distribution function and take into account that the energy flux transferred by one electron is $(\varepsilon - \zeta)\mathbf{v}$. As a result, instead of Eq. (20.3) we get

$$\varkappa \approx \beta = \frac{1}{T}\int d\varepsilon\, g(\varepsilon) D(\varepsilon)(\varepsilon-\zeta)^2 \left(-\frac{\partial f_0}{\partial \varepsilon}\right).$$

In the case of strong degeneracy we get

$$\varkappa = \frac{\pi^2}{9} k_B^2 T g(\epsilon_F) D(\epsilon_F).$$

It is interesting to calculate the ratio

$$\frac{\varkappa}{T\sigma} = \frac{\pi^2 k_B^2}{3e^2}.$$

This relation is called the *Wiedemann-Franz law* while its r.h.s. is called the *Lorenz number.* This law is derived under assumptions of isotropic spectrum and elastic scattering. One can show that only the last one is necessary.

So we see that all the characteristics of the d.c. transport are determined by the energy dependence of the quantity $D(\varepsilon)$, i.e. by the energy dependence of the transport relaxation time. If the relaxation time is described by a power law

$$\tau_{\mathrm{tr}}(\varepsilon, T) \propto T^a \varepsilon^r \quad \to \quad D(\varepsilon, T) \propto T^a \varepsilon^{r+1}$$

we get from Eq. (19.8) for the degenerate gas we have

$$\sigma \propto \int d\varepsilon D(\varepsilon) g(\varepsilon) \frac{\partial f}{\partial \varepsilon} \propto T^a.$$

For the Boltzmann gas with the distribution $f_0 \propto \frac{n_e}{T^{3/2}} \exp(-\varepsilon/k_B T)$ substituting $D(\varepsilon, T) = D_0(T)(\varepsilon/k_B T)^{r+1}$, $g(\varepsilon) = g(T)(\varepsilon/k_B T)^{1/2}$ we obtain

$$\sigma \propto T^{a+r}.$$

In the next section we will discuss the scattering processes in more detail and then we come back to the case of semiconductors to discuss the temperature dependencies of the kinetic coefficients.

LECTURE 21
Scattering mechanisms.

21.1. Scattering by Neutral and Ionized Impurities. Thomas-Fermi approximation.

In the following we will not perform very cumbersome calculations to solve the Boltzmann equation. Rather we will outline the main physics and obtain important estimates. The main goal is to learn how to make those estimates.

To study scattering it is convenient to determine the *scattering cross section.* The simplest idea one can use is that the atom is neutral and behaves as a hard sphere. Nevertheless, in many important situations it is not the case, the atom is *ionized* and has an electric charge.

The very important concept is that the electrons in the vicinity of the impurity atom rearrange to *screen the potential.*

We will assume, that the potential is screened at length much larger than the lattice constant (we will see later, that it is not so). We then can consider the local density of electrons $n_e(\mathbf{r})$, which is close to the electron density without the impurity and slowly varying with the distance. At every point the electrons are in local equilibrium.

This extra electron density results in the electric field which compensates/screens the electric field of the impurity. Consequently, one should calculate the electric potential which acts upon the electrons from the Poisson equation

$$\epsilon\nabla^2\varphi = -4\pi e\delta n_e$$

where $-e\delta n_e$ is the excess electric charge while ϵ is the dielectric constant. The boundary condition for this equation is

$$\varphi = \frac{Ze}{\epsilon r} \quad \text{at} \quad r \to 0, \qquad \varphi \to 0 \quad \text{at} \quad r \to \infty.$$

Now we should remember that in the presence of electric potential the chemical potential ζ is changed to the electrochemical one, $\zeta - e\varphi$. Consequently,

$$\delta n_e = n_e(\zeta - e\varphi) - n_e(\zeta) \approx -e\varphi\frac{\partial n_e}{\partial \zeta}. \tag{21.1}$$

Finally, the Poisson equation has the form

$$\nabla^2\varphi - \frac{\varphi}{r_s^2} = 0 \tag{21.2}$$

where

$$r_s = \left(\frac{4\pi e^2}{\epsilon} \frac{\partial n_e}{\partial \zeta} \right)^{-1/2} . \tag{21.3}$$

The solution of the Eq. (21.2) has the form (*Problem 24.7)*

$$\varphi = \frac{Ze}{r} e^{-r/r_s} , \tag{21.4}$$

so the quantity r_s is called the *screening length.*

Now let us estimate the screening length.

21.1.1. Degenerate electron gas

In a degenerate gas, we get $n_e \propto p_F^3 \propto \epsilon_F^{3/2}$ and $\zeta \approx \epsilon_F$. So

$$\frac{\partial n_e}{\partial \zeta} = \frac{3}{2} \frac{n_e}{\epsilon_F}$$

and

$$r_s = \left(\frac{6\pi e^2 n_e}{\epsilon \varepsilon_F} \right)^{-1/2} \equiv r_{TF} \, .$$

This is the so-called *Thomas-Fermi* length, r_{TF}. For a typical metal we get

$$\frac{1}{r_{TF}} \sim \left(e^2 \frac{p_F^3}{\hbar^3} \frac{m}{p_F^2} \right)^{1/2} = \frac{p_F}{\hbar} \left(\frac{e^2}{\hbar v_F} \right)^{1/2} .$$

The ratio $e^2/\hbar v_F$ has a clear physical meaning – it is just the ratio of the typical potential energy $e^2/\bar{r}$ to the typical kinetic energy $p_F^2/2m$. Indeed, in a typical metal, $\bar{r} \sim \hbar/p_F$ and

$$\frac{e^2/\bar{r}}{p_F^2/m} \sim \frac{e^2}{\hbar v_F} .$$

This ratio is or the order 1 because the metal is “glued” by the conduction electrons. Consequently, we get that the screening length in a typical metal is of the order of the interatomic distance a and one comes back to the model of hard spheres.

There two important things to be mentioned.

- We have assumed that the electron response is *local*, i. e. the electron density $n_e(\mathbf{r})$ feels the potential at the same point $\mathbf{r}$. In fact, it is not the case because the resulting electrical potential φ varies sharply in space, and the self-consistent approach (21.1) fails. In general,

  $$n_e'(\mathbf{r}) = -e \int K(\mathbf{r} - \mathbf{r}') \, \varphi(\mathbf{r}') \, d\mathcal{V}' \, .$$

  The function K cannot be derived from classical considerations because the typical spatial scale of the potential variation appears of the order of the de Broglie wave length $\hbar/p$. We may come back to this problem later in connection with the quantum transport. The function $K(r)$ reads (in the isotropic case)

  $$K(r) = -g(\epsilon_F) \frac{p_F^3}{(\pi\hbar)^3} \left[\frac{\cos(2k_F r)}{(2k_F r)^3} - \frac{\sin(2k_F r)}{(2k_F r)^4} \right] .$$

  We see that the response oscillates in space that is a consequence of the Fermi degeneracy (*Friedel oscillations*). These oscillations are important for specific effects but if we are interested in the distances much greater than k_F^{-1} the oscillations are smeared and we return to the picture of the spheres of atomic scale. So one can use the Thomas-Fermi approximation to get estimates.

- In the expression (21.1) we have assumed linear response to the external potential. In typical metals it is the case but in some semiconductors with small electron density one needs some generalizations (not enough electrons to screen). In particular this important for hopping transport in semiconductors.

21.1.2. Non-degenerate electron gas.

If the electrons are non-degenerate one should plug into the general expression (21.3) the Boltzmann distribution function

$$f_0(\varepsilon) = \exp\left(\frac{\zeta - \varepsilon}{k_B T}\right)$$

to get $\partial n_e/\partial\zeta = n_e/k_B T$. As a result

$$r_s \equiv r_D = \left(\frac{4\pi e^2 n_e}{\epsilon k_B T}\right)^{-1/2},$$

the quantity r_D is called the *Debye-Hukkel* length.

Using $n_e = 1/\bar{r}^3$ one gets

$$\frac{r_D}{\bar{r}} = \sqrt{\frac{k_B T}{4\pi e^2/\epsilon\bar{r}}},$$

So it is the ration of the typical kinetic energy $k_B T$, to the typical potential energy. The estimate differs from the Thomas-Fermi length by the presence $k_B T$ instead of the Fermi energy ϵ_F.

Now we can make a very rough estimate of the conductivity of a typical metal. We get

$$\sigma \sim \frac{n_e e^2 \tau}{m} \sim \frac{n_e e^2 \ell}{p_F} \sim \frac{n_e}{n_i}\frac{e^2}{p_F Q}.$$

Here we have taken into account that

$$\ell = \frac{1}{n_i Q}$$

where Q is the effective cross section. Making use of the estimates

$$Q \sim (\hbar/p_F)^2, \quad e^2 \sim \hbar v_F, \quad n_i/n_e \sim c_i$$

where c_i is the atomic impurity concentration (the numbers of electrons and atoms are the same) we get

$$\sigma \sim 10^{16}/c_i \ \mathrm{s}^{-1}.$$

To analyze the situation with the Boltzmann gas one should be more careful because the energy dependence of the relaxation time is important. In this case both a typical de Broglie wave length $\sim \hbar/p$ and the screening length r_s appear much greater than a typical interatomic distance, a. Consequently, while calculating the matrix element $|v(\theta)|$ for scattering against charged inpurities one can forget about the periodic potential and just calculate the matrix element of the potential (21.4) between the plane wave states. As a result, (*Problem 24.8*),

$$W(\theta) = 4\pi n_i v \left[\frac{e^2/\epsilon}{2\varepsilon(1-\cos\theta) + \hbar^2/2mr_s^2}\right]^2. \tag{21.5}$$

After substitution of the cross section in the definition of the transport relaxation time (19.3)[1] we get

$$\tau_{\rm tr} = \frac{\epsilon^2 m^2 v^3}{2\pi e^4 n_i \Phi(\eta)} = \frac{\sqrt{2m}\epsilon^2 \varepsilon^{3/2}}{\pi e^4 n_i \Phi(\eta)} \tag{21.6}$$

where

$$\Phi(\eta) = \ln(1+\eta) - \frac{\eta}{1+\eta}, \qquad \eta = \frac{4m^2v^2r_s^2}{\hbar^2} = \frac{8m\varepsilon r_s^2}{\hbar^2}.$$

We observe if the screening is neglected $r_s \to \infty$ than the the transport relaxation time $\tau_{\rm tr} \to 0$, and the transport relaxation rate diverges (long-range potential!). The function $\Phi(\eta)$ slowly depends on the energy, so

$$\tau_{\rm tr} \propto \varepsilon^{3/2}\,.$$

21.2. Electron-Electron Scattering. Phase space argument.

Now we estimate the electron-electron scattering. Although the problem seems very complicated, in the degenerate electron gas it is simplified considerably by the Pauli principle. The argument is that for a particle with the energy just above the Fermi energy, the conservation laws and the Pauli principle severely restrict the volume of the phase space for the scattering. This argument is called phase space argument. Here it is.

As usual, we start from the case of Fermi gas. Suppose that a particle is in a state 1 outside the Fermi sea, the first-order decay is shown on Fig. 1: Particle in the state 1 interacts with the particle in the state 2 inside the Fermi sphere, and both subsequently make transitions to states $1'$ and $2'$ outside the Fermi sphere (Pauli principle!).

Let's count the energy of the states from ε_F, say $\varepsilon_1 = \varepsilon_{\mathbf{p}_1} - \varepsilon_F$.

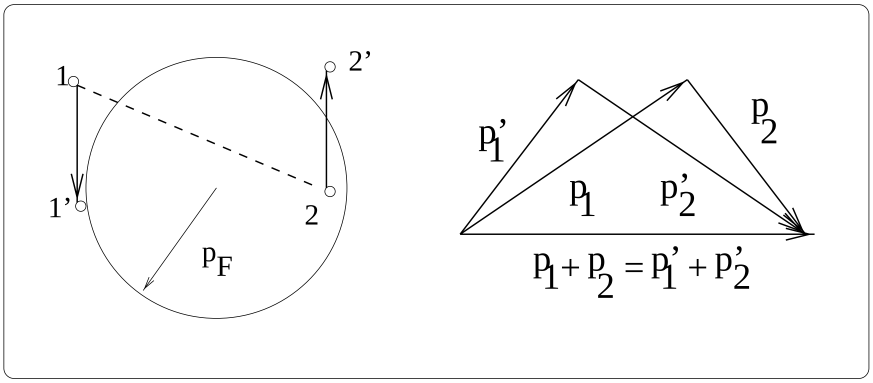

Figure 1. Scattering processes for electron-electron interaction.

According to the momentum and energy conservation laws,

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_{1'} + \mathbf{p}_{2'},$$
$$\varepsilon_1 + \varepsilon_2 = \varepsilon_{1'} + \varepsilon_{2'}.$$

The Pauli principle demands

$$\varepsilon_1, \varepsilon_{1'}, \varepsilon_{2'} > 0, \quad \varepsilon_2 < 0.$$

---

[1] $\tau_{tr}^{-1} = \frac{1}{2}\int_0^\pi W(\varepsilon,\theta)(1-\cos\theta)\sin\theta d\theta$.

Rewriting the energy conservation law in the form

$$\varepsilon_1 = \varepsilon_{1'} + \varepsilon_{2'} + |\varepsilon_2|$$

we see, that as all terms in the RHS are non-negative, none of these terms can exceed ε_1. So if the initial state 1 is close to the Fermi surface, then all other states $1'$, 2, and $2'$ will also be close to the Fermi surface.

The summation over the states, then can be done as follows

$$(dp) = \frac{1}{(2\pi\hbar)^3} p^2 dp d\Omega \approx \frac{p_F^2}{(2\pi\hbar)^3} dp d\Omega = \frac{p_F^2}{(2\pi\hbar)^3 v_F} d\varepsilon d\Omega,$$

where we used $d\varepsilon = v_F dp$.

The total scattering rate (the inverse life time) for the state 1 proportional to the number of resulting states $1'$, 2, $2'$ which satisfy the conservation laws and the Pauli principle. The conservation laws demand

$$W \propto \int \delta(\varepsilon_1 + \varepsilon_2 - \varepsilon_{1'} - \varepsilon_{2'}) \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_{1'} - \mathbf{p}_{2'}) \, (dp_2) \, (dp_{1'}) \, (dp_{2'}),$$

where the Pauli principle will determine the ranges of integration.

The integral over $(dp_{2'})$ takes care of the momentum δ-function. This tells us that if we know the states 1, $1'$, and 2, then, as momentum must be conserve, we have no freedom in choosing the state $2'$.

The energy conservation δ-function can be rewritten as

$$\varepsilon_1 + \varepsilon_2 - \varepsilon_{1'} - \varepsilon_{2'} = E - \frac{\mathbf{p}_{1'}^2}{2m} - \frac{(\mathbf{P} - \mathbf{p}_{1'})^2}{2m} = E - \frac{\mathbf{P}^2}{2m} - \frac{\mathbf{p}_{1'}^2}{m} + \frac{\mathbf{P} \cdot \mathbf{p}_{1'}}{m}$$

where E and $\mathbf{P}$ are the total energy and the momentum. So we see, that for given $\mathbf{p}_1$, $\mathbf{p}_2$, and $p_{1'}$ — the magnitude of $\mathbf{p}_{1'}$ — this δ-function after integration over $d\Omega_{1'}$ fixes the angle between $\mathbf{P}$ and $\mathbf{p}_{1'}$. The direction of the vector $\mathbf{p}_2$ is arbitrary, and the integration over $d\Omega_2$ gives just 4π. So we have

$$W \propto \int d\varepsilon_2 d\varepsilon_{1'}$$

and the Pauli principle will give the limits of integration. Let's find them.

The excitation energies $\varepsilon_{1'}$ and $\varepsilon_{2'}$ are positive, so $\varepsilon_1 + \varepsilon_2 > 0$, or

$$-\varepsilon_1 < \varepsilon_2 < 0.$$

The smallest excitation energy of the state $2'$ is zero, so the largest excitation energy of the state $1'$ is $\varepsilon_1 + \varepsilon_2$, so we have

$$0 < \varepsilon_{1'} < \varepsilon_1 + \varepsilon_2$$

We then have

$$W \propto \int_{-\varepsilon_1}^{0} d\varepsilon_2 \int_0^{\varepsilon_1 + \varepsilon_2} d\varepsilon_{1'} = \frac{\varepsilon_1^2}{2}.$$

So we see, that for an electron of energy ε life time $\tau = 1/W$ we have

$$\tau \propto \frac{1}{(\varepsilon - \varepsilon_F)^2}$$

The simplest way to estimate τ is to use the dimensionality approach. Indeed, the average potential and kinetic energies are of the order of ϵ_F. Consequently, the only quantity which is proportional to $(\varepsilon - \epsilon_F)^{-2}$ and has the time dimensionality is

$$\tau \sim \frac{\hbar \epsilon_F}{(\varepsilon - \epsilon_F)^2} . \tag{21.7}$$

We came to an important conclusion: the quasiparticles near the Fermi level, $|\varepsilon - \epsilon_F| \ll \epsilon_F$ can be treated as free partiicles provided

$$\frac{\hbar}{(\varepsilon - \epsilon_F)\tau} \approx \frac{\varepsilon - \epsilon_F}{\epsilon_F} \ll 1 .$$

The typical value for the quasiparticle energy is $k_B T \ll \epsilon_F$. This is why the electron-electron interaction can be treated in the leading approximation in a self-consistent approximation which results in a renormalization of the particle mass, $m_0 \to m^*$, and in a relatively weak damping with the rate τ^{-1}.

Substituting (21.7) in the Drude formula we easily get the estimate of the conductivity, limited by the electron-electron scattering

$$\sigma = \frac{ne^2\tau}{m} \sim \frac{n_e e^2 \hbar \epsilon_F}{m(k_B T)^2} \sim 10^{16} \left(\frac{\epsilon_F}{k_B T}\right)^2 \quad \mathrm{s}^{-1}.$$

Note that electron-electron interaction is the typically *inelastic* one. Electron-electron interaction is usually unimportant for the Boltzmann gas (not too many electrons!). One should also know that disorder drastically increases the electron-electron interaction. We may discuss this problem later.

LECTURE 22

Scattering mechanisms. Continued.

22.1. Scattering by Lattice Vibrations

Now we come to a very important point - to the electron phonon interaction which leads to many important consequences including superconductivity.

22.1.1. Interaction Hamiltonian (Estimates for Metals)

There are several mechanisms of electron-phonon interaction. We consider the mechanism when deformed lattice produces charge distribution which interacts with the electrons.

The deformed lattice creates a polarization $\mathbf{P}$, the electric charge being $\operatorname{div}\mathbf{P}$. Consequently, one can write down the interaction energy between an electron at a point $\mathbf{r}$ with lattice charge.

$$U(\mathbf{r}) = -e\int Q(\mathbf{r}-\mathbf{r}^{'})\operatorname{div}\mathbf{P}(\mathbf{r}')\,d\mathcal{V}' \,.$$

In the absence of screening, $Q(\mathbf{r}-\mathbf{r}^{'}) \propto |\mathbf{r}-\mathbf{r}'|^{-1}$ but *in a typical metal* the screening makes it local. As a result the estimate of $Q(\mathbf{r}-\mathbf{r}')$ is $Q(\mathbf{r}-\mathbf{r}') \approx a^2\delta(\mathbf{r}-\mathbf{r}')$.

The polarization $\mathbf{P}$ is of the order of $n_a e\mathbf{u}(\mathbf{r})$ where n_a is the atomic density which is of the order of the electron one, while $\mathbf{u}(\mathbf{r})$ is the displacement vector at point $\mathbf{r}$. Writing

$$\mathbf{u}(\mathbf{r},t) = \sum_{\mathbf{q}}\left[\mathbf{u}_{\mathbf{q}}\,e^{i\mathbf{q}\cdot\mathbf{r}-i\omega_{\mathbf{q}}t} + \mathbf{u}^*_{\mathbf{q}}\,e^{-i\mathbf{q}\cdot\mathbf{r}+i\omega_{\mathbf{q}}t}\right] ,$$

we get

$$\operatorname{div}\mathbf{P}(\mathbf{r},t) = n_a e\sum_{\mathbf{q}}\left[i\mathbf{q}\cdot\mathbf{u}_{\mathbf{q}}\,e^{i\mathbf{q}\cdot\mathbf{r}-i\omega_{\mathbf{q}}t} - i\mathbf{q}\cdot\mathbf{u}^*_{\mathbf{q}}\,e^{-i\mathbf{q}\cdot\mathbf{r}+i\omega_{\mathbf{q}}t}\right] .$$

We see that the $\mathbf{q}$th Fourier component of the quantity $\operatorname{div}\mathbf{P}(\mathbf{r})$ has the estimate $in_a e(\mathbf{q}\cdot\mathbf{u}_{\mathbf{q}}) \approx i(\omega_{\mathbf{q}}/s)n_a eu$. Here we consider the case of acoustic phonons when $q=\omega_{\mathbf{q}}/s$ and s is sound velocity.

Finally, we the following estimate for the Fourier component of the interaction energy

$$U_{\mathbf{q}} \sim ie^2a^2n_a\frac{\omega_{\mathbf{q}}}{s}u_{\mathbf{q}}\,. \tag{22.1}$$

In the following we use the second quantization scheme.

The interaction Hamiltonian is

$$\mathcal{H}_{\text{int}} = \int d^3r\hat{U}(\mathbf{r})\hat{n}(\mathbf{r})$$

where $\hat{n}(\mathbf{r}$ is the density of electrons at the point $\mathbf{r}$. Introducing Fermi creation and annihilation operators $a^\dagger_{\mathbf{k}}$ and $a_{\mathbf{k}}$ for each state $\mathbf{k}$ we have.

$$\mathcal{H}_{\text{int}} = \sum_{\mathbf{k}\mathbf{k}'} \langle \mathbf{k}'|\hat{U}(\mathbf{r})|\mathbf{k}\rangle a^\dagger_{\mathbf{k}'} a_{\mathbf{k}}.$$

For the operator $\hat{U}$ we use

$$\hat{\mathbf{u}}_{\mathbf{q}} \to \sqrt{\frac{\hbar}{2\omega_{\mathbf{q}} NM}}\, \mathbf{e}_{\mathbf{q}}\, b_{\mathbf{q}}\,, \quad \hat{\mathbf{u}}^*_{\mathbf{q}} \to \sqrt{\frac{\hbar}{2\omega_{\mathbf{q}} NM}}\, \mathbf{e}_{\mathbf{q}}\, b^\dagger_{\mathbf{q}}\,.$$

Here N is the number of atoms in the sample, M is the atomic mass, $\mathbf{e}_{\mathbf{q}}$ is the unit vector parallel to $\mathbf{u}_{\mathbf{q}}$. We have taken into account only one acoustic mode.

According to this approach, phonon system is characterized by number of phonons, $N_{\mathbf{q},j}$, having the wave vector $\mathbf{q}$ and belonging to the branch j, so the state is specified as $|N_{\mathbf{q},j}\rangle$. The so-called phonon annihilation (or creation) operators $b_{\mathbf{q}}, b^\dagger_{\mathbf{q}}$ are defined by the properties

$$b|N\rangle = \sqrt{N}\,|N-1\rangle \quad b^\dagger|N\rangle = \sqrt{N+1}\,|N+1\rangle\,,$$

the commutation rules being

$$bb^\dagger - b^\dagger b \equiv [b, b^\dagger]_- = 1\,.$$

The creation and annihilation operators for different modes *commute*. It is easy to check the following important properties of the creation and annihilation operators,

$$\begin{aligned} b^\dagger b\,|N\rangle &= N\,|N\rangle\,, \\ \langle N'|b|N\rangle = \sqrt{N}\,\delta_{N',N-1}\,, &\qquad \langle N'|b^\dagger|N\rangle = \sqrt{N+1}\,\delta_{N',N+1}\,. \end{aligned}$$

The interaction Hamiltonian in terms of electron creation and annihilation operators can be written as

$$\mathcal{H}_{\text{int}} = \sum_{\mathbf{k}\mathbf{k}'} \langle \mathbf{k}'|U(\mathbf{r})|\mathbf{k}\rangle a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} = \sum_{\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} \sum_{j\mathbf{q}} \left[C_j(\mathbf{q}) \langle \mathbf{k}^{'}|e^{i\mathbf{q}\mathbf{r}}|\mathbf{k}\rangle\, b_{\mathbf{q}} + C^*_j(\mathbf{q}) \langle \mathbf{k}^{'}|e^{-i\mathbf{q}\mathbf{r}}|\mathbf{k}\rangle\, b^\dagger_{\mathbf{q}} \right]\,.$$

Here $C_j(\mathbf{q})$ absorbs proportionality coefficients between the perturbation potential and normal coordinates. For $C(\mathbf{q})$ the following estimate can be used

$$C_{\mathbf{q}} \sim i\frac{e^2a^2n_a}{\sqrt{NM}}\frac{\omega}{s}\sqrt{\frac{\hbar}{\omega}} \sim i\sqrt{\frac{\hbar n_a \omega}{\mathcal{V} n_a M}}\frac{e^2a^2n_a}{s} \sim i\, n_a a^3 \frac{e^2}{a}\frac{1}{s\sqrt{M}}\sqrt{\frac{\hbar\omega}{\mathcal{V} n_a}} \sim i\sqrt{\frac{\hbar\omega}{\mathcal{V} m n_a}} p_F. \tag{22.2}$$

Here $n_a = N/\mathcal{V}$, we have taken into account that $n_a a^3 \sim 1$, $e^2/a \sim \epsilon_F \sim p_F^2/2m$, $s\sqrt{M} \sim v_F\sqrt{m}$.

From the properties of Bloch functions and lattice vibrations one can prove (Check!) that

$$\langle \mathbf{k}^{'}|e^{i\mathbf{q}\mathbf{r}}|\mathbf{k}\rangle = \sum_{\mathbf{G}} \delta(\mathbf{k}' - \mathbf{k} \mp \mathbf{q} - \mathbf{G}) \equiv \Delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} \tag{22.3}$$

where $\mathbf{G}$ are the reciprocal lattice vectors. Finally we can express the interaction Hamiltonian as

$$\begin{aligned} \mathcal{H}_{\text{int}} &= \sum_{j\mathbf{q}\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} \left[C_j(\mathbf{q}) \Delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}}\, b_{\mathbf{q}} + C^*_j(\mathbf{q}) \Delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}}\, b^\dagger_{\mathbf{q}} \right] \\ &= \sum_{j\mathbf{q}\mathbf{k}\mathbf{k}'} C_j(\mathbf{q}) \Delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}} a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} b_{\mathbf{q}} + \text{h.c.}\,. \end{aligned} \tag{22.4}$$

Here h.c. stands for Hermitian conjugate.

The form (22.4) is very illustrative to show the important transitions. We can specify the following processes

- Phonon emission:

$$\begin{array}{lcl}
\text{electron} & : & \text{scattered,}\quad \mathbf{k}\to\mathbf{k}'=\mathbf{k}-\mathbf{q}+\mathbf{G}\\
\text{phonon} & : & \text{created with the momentum } \hbar\mathbf{q}.\\
\text{operator form} & : & \sum_{\mathbf{G}} C^*_{\mathbf{q}}\, a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} b^\dagger_{\mathbf{q}}\, \delta(\mathbf{k}'-\mathbf{k}+\mathbf{q}-\mathbf{G})\,.\\
\text{matrix element} & : & M^+_{\mathbf{k},\mathbf{k}'} = C^*_{\mathbf{q}}\sqrt{N_{\mathbf{q}}+1}\langle\mathbf{k}'|e^{-i\mathbf{q}\mathbf{r}}|\mathbf{k}\rangle
\end{array} \tag{22.5}$$

- Phonon absorption

$$\begin{array}{lcl}
\text{electron} & : & \text{scattered,}\quad \mathbf{k}\to\mathbf{k}^{'}=\mathbf{k}+\mathbf{q}+\mathbf{G}\\
\text{phonon} & : & \text{absorbed with the momentum } \hbar\mathbf{q}.\\
\text{operator form} & : & \sum_{\mathbf{G}} C_{\mathbf{q}}\, a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} b_{\mathbf{q}}\, \delta(\mathbf{k}'-\mathbf{k}-\mathbf{q}-\mathbf{G})\\
\text{matrix element} & : & M^-_{\mathbf{k},\mathbf{k}'} = C_{\mathbf{q}}\sqrt{N_{\mathbf{q}}}\langle\mathbf{k}^{'}|e^{i\mathbf{q}\mathbf{r}}|\mathbf{k}\rangle
\end{array} \tag{22.6}$$

22.1.2. Transition Probability

We need to find the scattering rate for the electron to scatter from the state $\mathbf{k}$ to the state $\mathbf{k}-\mathbf{q}$. This scattering can proceed either by an emission or absorption of a phonon.

Emission: In the initial state we have an electron in the state $\mathbf{k}$ and $N_{\mathbf{q}}$ phonons in the state $\mathbf{q}$ and in the final state an electron in the state $\mathbf{k}-\mathbf{q}$ and $N_{\mathbf{q}}+1$ pnonons in the state $\mathbf{q}$.

Absorption: In the initial state we have an electron in the state $\mathbf{k}$ and $N_{-\mathbf{q}}$ phonon ins the state $-\mathbf{q}$ and in the final state an electron in the state $\mathbf{k}-\mathbf{q}$ and $N_{-\mathbf{q}}-1$ phonons in the state $-\mathbf{q}$.

Now we can construct the transition probabilities from the Fermi golden rule,

$$W_{fi} = \frac{2\pi}{\hbar}\,|M_{fi}|^2\,\delta(\varepsilon_f-\varepsilon_i)$$

where the subscripts i, f stand for the initial and final state, respectively.

For simplicity we assume here that $\mathbf{G}=0$, that is the case for the most interesting situations (see later). For the case (22.5) we get

$$W^+_{\mathbf{k}-\mathbf{q},\mathbf{k}} = \frac{2\pi}{\hbar}|C_{j\mathbf{q}}|^2(N_{\mathbf{q}}+1)\delta\left[\varepsilon(\mathbf{k}-\mathbf{q})+\hbar\omega_j(\mathbf{q})-\varepsilon(\mathbf{k})\right]\,.$$

The probability of the absorption process (22.6) is

$$W^-_{\mathbf{k}+\mathbf{q},\mathbf{k}} = \frac{2\pi}{\hbar}|C_{j\mathbf{q}}|^2 N_{\mathbf{q}}\delta\left[\varepsilon(\mathbf{k}+\mathbf{q})-\varepsilon(\mathbf{k})-\hbar\omega_j(\mathbf{q})\right].$$

for the absorption one. The total probability for the $\mathbf{k}\to\mathbf{k}-\mathbf{q}$ transitions for a given phonon brach is then:

$$\begin{aligned}
W_{\mathbf{k}-\mathbf{q}\leftarrow\mathbf{k}} &= (2\pi/\hbar)\,|C_{\mathbf{q}}|^2\\
&\times\Bigg\{\underbrace{(N_{\mathbf{q}}+1)\delta\left[\varepsilon(\mathbf{k}-\mathbf{q})-\varepsilon(\mathbf{k})+\hbar\omega_{\mathbf{q}}\right]}_{\text{emission}}+\underbrace{N_{-\mathbf{q}}\delta\left[\varepsilon(\mathbf{k}-\mathbf{q})-\varepsilon(\mathbf{k})-\hbar\omega_{\mathbf{q}})\right]}_{\text{absorption}}\Bigg\}\,.
\end{aligned} \tag{22.7}$$

To get the probability of the reverse transition, $W_{\mathbf{k}\leftarrow\mathbf{k}-\mathbf{q}}$, one should first replace $\mathbf{k}\to\mathbf{k}+\mathbf{q}$ and then $\mathbf{q}\to-\mathbf{q}$. We get

$$\begin{aligned} W_{\mathbf{k}\leftarrow\mathbf{k}-\mathbf{q}} &= (2\pi/\hbar)\,|C_{\mathbf{q}}|^2 \\ &\times\Big\{\underbrace{(N_{-\mathbf{q}}+1)\delta\left[\varepsilon(\mathbf{k}-\mathbf{q})-\varepsilon(\mathbf{k})-\hbar\omega_{\mathbf{q}}\right]}_{\text{emission}}+\underbrace{N_{\mathbf{q}}\delta\left[\varepsilon(\mathbf{k}-\mathbf{q})-\varepsilon(\mathbf{k})+\hbar\omega_{\mathbf{q}}\right]}_{\text{absorption}}\Big\}. \end{aligned} \tag{22.8}$$

To construct the transition rate *from* the state $\mathbf{k}$ one has to multiply Eq. (22.7) by the factor $f_{\mathbf{k}}(1-f_{\mathbf{k}-\mathbf{q}})$ and then sum over the phonon brancehs j and wave vectors $\mathbf{q}$. The transition rate *to* the state $\mathbf{k}$ is given by multiplication of Eq. (22.8) by the factor $f_{\mathbf{k}-\mathbf{q}}(1-f_{\mathbf{k}})$ with subsequent similar summation. Finally we come to the following collision integral

$$I=\frac{2\pi}{\hbar}\sum_{j\mathbf{q}}|C_j(\mathbf{q})|^2\left[F^{+}_{\mathbf{k},\mathbf{k}-\mathbf{q}}\delta(\varepsilon_{\mathbf{k}-\mathbf{q}}-\varepsilon_{\mathbf{k}}-\hbar\omega_{j\mathbf{q}})+F^{-}_{\mathbf{k},\mathbf{k}-\mathbf{q}}\delta(\varepsilon_{\mathbf{k}-\mathbf{q}}-\varepsilon_{\mathbf{k}}+\hbar\omega_{j\mathbf{q}})\right] \tag{22.9}$$

where

$$\begin{aligned} F^{+}_{\mathbf{k},\mathbf{k}-\mathbf{q}} &= f_{\mathbf{k}}(1-f_{\mathbf{k}-\mathbf{q}})N_{-\mathbf{q}j}-f_{\mathbf{k}-\mathbf{q}}(1-f_{\mathbf{k}})(N_{-\mathbf{q}j}+1), \\ F^{-}_{\mathbf{k},\mathbf{k}-\mathbf{q}} &= f_{\mathbf{k}}(1-f_{\mathbf{k}-\mathbf{q}})(N_{\mathbf{q}j}+1)-f_{\mathbf{k}-\mathbf{q}}(1-f_{\mathbf{k}})N_{\mathbf{q}j}\,. \end{aligned} \tag{22.10}$$

Now we start from rough estimates and then derive the relaxation rate more carefully.

22.1.3. Relaxation Time for Phonon Scattering. Rough Estimate.

To get a rough estimate we first understand that the maximal phonon frequency is ω_D that corresponds to $q_D\sim\pi/a\sim k_F$. One has the estimate $\hbar\omega_D\sim\hbar s\pi/a\sim sp_F$. So there are two limiting cases which differ by the relation between $\hbar\omega_D$ and k_BT.

22.1.3.1. *High temperature.* At high temperature

$$k_BT\gg\hbar\omega_D\,,$$

the most probable are the processes with high-frequency phonons, $\omega\approx\omega_D$, and we can use the classical limit for the Planck function

$$N_{\mathbf{q}}\approx\frac{k_BT}{\hbar\omega_{\mathbf{q}}}\approx\frac{k_BT}{\hbar\omega_D}\gg1.$$

We see that all the items in the collision integral have the same order.

As $q_D\sim p_F$ the scattering is "uniform over angles", so the transport time and the life time are almost the same — we can ignore $1-\cos\theta$ in the definition of the inverse transport time..

In order to estimate the integral over $\mathbf{q}$ we notice first, that both electronic states $\mathbf{k}$ and $\mathbf{k}\pm\mathbf{k}-\mathbf{q}$ must be close to the Fermi surface, as $\omega_D\ll\varepsilon_F$. However, the typical momentum transfer $\mathbf{q}$ is of the order of $q_D\sim p_F/\hbar$. The integral of the δ-function reads

$$2\pi\int\delta\left(\pm\frac{\hbar p_Fq}{m}\cos\vartheta+\frac{\hbar^2q^2}{2m}-\hbar sq\right)q^2dqd(\cos\vartheta),$$

where ϑ is the angle between $\mathbf{k}$ and $\mathbf{q}$, and I used the fact that $k\sim p_F/\hbar$ and $\epsilon_{\mathbf{k}}\sim\epsilon_{\mathbf{k}\pm\mathbf{q}}\sim\varepsilon_F$.

In this integral the terms $\frac{\hbar p_Fq}{m}$ and $\frac{\hbar^2q^2}{2m}$ are of the same order, as $q\sim p_F$, while the term $\hbar sq$ is much smaller, as $s\ll v_F=p_F/m$. We then can ignore the last therm under the δ-function.

As $\frac{\hbar p_F q}{m} \sim \frac{\hbar^2 q^2}{2m}$ the integral over $\cos\vartheta$ is almost not constrained and provides almost no constraint for the integration over dq. The integral over angle then gives $\frac{m}{\hbar p_F q}$, so we have

$$\sim \int \frac{mq^2\,dq}{\hbar p_F q} = \frac{m}{\hbar p_F}\int q\,dq.$$

We see, that indeed the main contribution to the integral comes form large q. As the largest q is q_D, we have

$$\sim \frac{mq_D^2}{\hbar p_F} \sim \frac{mp_F}{\hbar^3}.$$

Notice, that this result is just the density of states at ε_F. It reflects the fact that an electron close to ε_F can be scattered by a high temperature phonon to anywhere along the Fermi surface.

Using the estimate (22.2) for the coefficient $C_{\mathbf{q}}$ we get

$$\frac{1}{\tau_{\mathrm{tr}}} \sim \frac{1}{\hbar} p_F^2 \frac{\hbar\omega_D}{mn_a}\frac{k_BT}{\hbar\omega_D}\frac{mp_F}{\hbar^3} \sim \frac{k_BT}{\hbar}\,.$$

The estimate for conductivity is

$$\sigma = \frac{n_e e^2 \tau}{m} \sim \frac{p_F^2}{m\hbar}\frac{\epsilon_F}{k_BT} \sim 10^{16}\frac{\epsilon_F}{k_BT}\ \mathrm{s}^{-1}\,.$$

22.1.3.2. *Low temperature.* At low temperatures where

$$k_BT \ll \hbar\omega_D$$

the thermal phonons with $\hbar\omega \sim k_BT$ are most important, their wave vector being

$$q_T \sim k_BT/\hbar s\,.$$

We see that $q_T \ll k_F$. So these collisions are strongly *inelastic* - the change of the excitation energy (with respect to the Fermi level) is of the order of the excitation energy itself, while the change of momentum is relatively small. The δ-function in the conservation laws can be written as

$$\delta\left[\frac{\mathbf{p}^2}{2m} - \frac{(\mathbf{p}-\hbar\mathbf{q})^2}{2m} \pm \hbar\omega_{\mathbf{q}}\right] = \delta\left[\frac{\hbar\mathbf{pq}}{m} - \frac{\hbar^2q^2}{2m} \pm \hbar\omega_{\mathbf{q}}\right] = \frac{m}{\hbar pq}\,\delta\left[\cos\vartheta - \frac{\hbar q}{2p} \pm \frac{ms}{q}\right]\,.$$

We see that both the items under the δ-function are small (the second one is of the order $ms/p_F \sim s/v_F \ll 1$). The integral over $\mathbf{q}$ splits into the integral over the length of the wave vector and over the angles. Thus the δ-function gives 1 after the integration over the angles because is requests $|\cos\vartheta| \sim \hbar q_T/p_F \ll 1$. Finally, we get the following estimate ($|C|^2 \sim \frac{p_F^2\hbar\omega}{mn_a}$)

$$\frac{1}{\tau} \sim \frac{1}{\hbar}\frac{p_F^2\hbar\omega}{mn_a}\frac{m}{\hbar p_F q}q^3 \sim \frac{1}{\hbar}\frac{p_F^2\hbar\omega}{mn_a}\frac{ms}{p_F\hbar\omega}\left(\frac{\omega}{s}\right)^3 \sim \frac{1}{\hbar}\frac{p_F^2 k_BT}{m(p_F/\hbar)^3}\frac{ms}{p_F k_BT}\frac{(k_BT)^3}{\hbar^3 s^3} \sim \frac{k_BT}{\hbar}\left(\frac{k_BT}{\hbar\omega_D}\right)^2\,.$$

This is the good estimate for the escape relaxation time.

To compute the inverse transport time we need to also include $1-\cos\theta$, where θ is the angle between $\mathbf{k}$ and $\mathbf{k}' = \mathbf{k} \pm \mathbf{q}$. As $q \sim q_T \ll k, k' \sim p_F/\hbar$, this scattering angle is very small $\theta \sim \hbar q_T/p_F$, so

$$1 - \cos\theta \approx \theta^2/2 \sim (\hbar q/p_F)^2 \sim (k_BT/\hbar\omega_D)^2\,.$$

As a result,

$$\frac{1}{\tau_{\mathrm{tr}}} \sim \frac{k_B T}{\hbar} \left(\frac{k_B T}{\hbar \omega_D} \right)^4$$

and the conductivity acquires an extra factor $(\hbar\omega_D/k_BT)^4$

$$\sigma \sim 10^{16} \frac{\epsilon_F}{k_B T} \left(\frac{\hbar \omega_D}{k_B T} \right)^4 \ \mathrm{s}^{-1} \,.$$

We see that for small-angle scattering the transport time is much longer than the escape time. It is interesting that in the expression for the thermal conductivity one can study the relaxation of the energy flux. For the energy flux, every collision is effective and the proper estimate for the relaxation rate is the escape time τ. As a result, the Wiedemann-Franz law is not valid any more, and

$$\frac{\varkappa}{T\sigma} \sim \frac{k_B^2}{e^2} \left(\frac{k_B T}{\hbar \omega_D} \right)^2 \,.$$

22.1.4. Temperature Dependence of Resistivity in Metals

Now we review the temperature dependence of the conductivity of metals. We have assumed recently that only one scattering mechanism is important. In real life there is a mixture of the mechanisms, the interplay being temperature dependent. If we assume the mechanisms to be independent the *resistivities* ρ are approximately additive because one should sum the scattering *rates*. So, according to the results of Boltzmann equation, at low temperatures

$$\rho = c + \underbrace{aT^2}_{\text{e-e}} + \underbrace{bT^5}_{\text{e-ph}}$$

(except alkali metals) while at high temperatures phonon scattering is the most important and

$$\rho = AT.$$

The corresponding dependences of the thermal conductivity are

$$\varkappa^{-1} = dT^{-1} + fT + gT^2, \quad \text{and} \quad \varkappa = \text{ const} \,.$$

The temperature dependence of the resistivity of semiconductors is more tricky because the electron concentration is temperature dependent. We will come back to this problem later.

It is also important to know, that at very low temperatures quantum contribution to resistivity becomes important. This contribution cannot be analyzed with the help of the Boltzmann equation and we will also discuss it later.

22.1.5. Derivation of the Relaxation Time. Optional section

Now we outline the procedure of more rigorous derivation of the relaxation rate which includes the summation over $\mathbf{q}$

$$\sum_{\mathbf{q}} \to \frac{\mathcal{V}}{(2\pi)^3} \int_{q_{\min}}^{q_{\max}} q^2 \, dq \int_0^{\pi} \sin\vartheta \, d\vartheta \int_0^{2\pi} d\varphi$$

where $q_{\min}$ and $q_{\max}$ are determined by the conservation laws, $\vartheta \equiv (\widehat{\mathbf{q}, \mathbf{k}})$.

First, one should prove the relaxation time approximation, i.e. that

$$I(f_1) \propto f_1.$$

To prove it let us (as we have done earlier) search the solution as

$$f_1 = -\mathbf{n}\mathbf{f}(\varepsilon) = -f\cos(\widehat{\mathbf{f},\mathbf{k}}), \quad \mathbf{n}\equiv \mathbf{k}/k$$

and chose the polar axis $\mathbf{z}$ along the vector $\mathbf{k}$. In our notations

$$1-\cos\,(\widehat{\mathbf{k},\mathbf{k}-\mathbf{q}}) = (\mathbf{q}\cdot\mathbf{k})/qk = \cos\vartheta\,.$$

As in the case of impurity scattering, it is convenient to use the relation

$$\mathbf{f}\mathbf{q} = f_z q_z + \mathbf{f}_\perp \mathbf{q}_\perp\,,$$

or

$$\begin{aligned}
\cos(\widehat{\mathbf{f},\mathbf{q}}) &= \cos(\widehat{\mathbf{k},\mathbf{q}})\cos(\widehat{\mathbf{f},\mathbf{k}}) + \sin(\widehat{\mathbf{k},\mathbf{q}})\sin(\widehat{\mathbf{f},\mathbf{k}})\cos\varphi_{q,f}\\
&= \cos\vartheta\cos(\widehat{\mathbf{f},\mathbf{k}}) + \sin\vartheta\sin(\widehat{\mathbf{f},\mathbf{k}})\cos\varphi_{q,f}\,.
\end{aligned}$$

Now we can integrate this equation over $\varphi_{q,f}$ taking into account that the angle $(\widehat{\mathbf{f},\mathbf{k}})$ is $\varphi_{q,f}$-independent.(see Fig. 1). We get

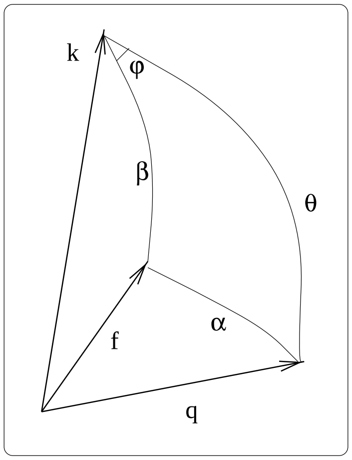

Figure 1. The arrangement of angles.

$$\int \cos(\widehat{\mathbf{f},\mathbf{q}})\,d\varphi = 2\pi\,\cos\vartheta\cos(\widehat{\mathbf{f},\mathbf{k}}).$$

The term $\cos(\widehat{\mathbf{f},\mathbf{k}})$ can be extracted from the integral over $\mathbf{q}$ and we have proved that $I(f_1)\propto f_1$.

Finally, after neglecting of the term proportional to s/v we get

$$\begin{aligned}
\frac{1}{\tau_{\mathrm{tr}}} &= -\frac{(2\pi)^2}{\hbar}\frac{\mathcal{V}}{(2\pi)^3}\int_{q_{\min}}^{q_{\max}} q^2\,dq\,|C(q)|^2\frac{m}{\hbar^2 kq}\frac{q}{k}\int_0^{\pi}\sin\vartheta\,\cos\theta\,d\vartheta\\
&\quad\times\left[N_q\delta\left(q/2k+\cos\theta\right)-(N_q+1)\delta\left(q/2k-\cos\theta\right)\right]\\
&= \frac{\mathcal{V}}{8\pi^2}\frac{m}{\hbar^2k^3}\int_{q_{\min}}^{q_{\max}}|C(q)|^2(2N_q+1)\,q^3dq\,. \qquad (22.11)
\end{aligned}$$

The result is determined by its limits determined by the conservation law and by the phonon spectrum. We have $q_{\min}=0$ while

$$q_{\max}=\min(q_D,2k), \qquad \omega_{\max}=\max(\omega_D,2ks)\,.$$

At high temperature, at $\hbar\omega_{\rm max} \leq k_BT$, as is was shown, $N_q \approx k_BT/\hbar s$ and we get

$$\frac{1}{\tau_{\rm tr}} \propto \frac{1}{k^3}\int^{q_D} q\,\frac{k_BT}{\hbar s q}q^3dq \propto \frac{Tq_D^4}{k^3}\left\{\begin{array}{ll} q_D^4 & \text{for } \; q_D < 2k \\ (2k)^4 & \text{for } \; q_D > 2k \end{array}\right. \propto T\left\{\begin{array}{l} \varepsilon^{-3/2} \\ \varepsilon^{1/2} \end{array}\right.$$

That is consistent with the rough estimates given above. The last case is important for semiconductors with low values of k. Remember that for the Boltzmann gas the typical value of $\hbar k$ is $\sqrt{mk_BT}$. Indeed,

$$\frac{\hbar s k}{k_BT} \approx \sqrt{\frac{ms^2}{k_BT}}, \qquad ms^2 \to 0.1 \;\; \text{K}.$$

In typical metals, $k \sim k_F \sim q_D$, and at low temperatures we meet the case $\hbar\omega_{\rm max} \leq k_BT$. This case is much more tricky because the collisions are *inelastic* and we cannot use the expression (19.3) for the relaxation time. Actually, one should linearize the collision integral (22.9). The main steps of the derivation are given below.

We transform the collision integral as follows. First we denote $f_{\mathbf{k}} = f_1 + \varphi_1$, $f_{\mathbf{k}-\mathbf{q}} = f_2 + \varphi_2$, where $f_{i,k}$ are equilibrium functions, and then linearize with respect to φ_i. We get

$$\begin{aligned} F^{+}_{\mathbf{k},\mathbf{k}-\mathbf{q}} &= f_{\mathbf{k}}(1-f_{\mathbf{k}-\mathbf{q}})N_{-\mathbf{q}} - f_{\mathbf{k}-\mathbf{q}}(1-f_{\mathbf{k}})(N_{-\mathbf{q}}+1) \\ &\to [\varphi_1(1-f_2) - \varphi_2 f_1]\,N - [\varphi_2(1-f_1) - \varphi_1 f_2]\,(N+1) \\ &= \varphi_1\,[N(1-f_2) + f_2(N+1)] - \varphi_2\,[Nf_1 + (N+1)(1-f_1)] \\ &= \varphi_1\,(N+f_2) - \varphi_2\,(N+1-f_1) \end{aligned}$$

for the phonon emission and

$$\begin{aligned} F^{-}_{\mathbf{k},\mathbf{k}-\mathbf{q}} &= f_{\mathbf{k}}(1-f_{\mathbf{k}-\mathbf{q}})(N_{\mathbf{q}}+1) - f_{\mathbf{k}-\mathbf{q}}(1-f_{\mathbf{k}})N_{\mathbf{q}} \\ &\to (\varphi_1(1-f_2) - \varphi_2 f_1)\,(N+1) - (\varphi_2(1-f_1) - \varphi_1 f_2)\,N \\ &= \varphi_1\,((N+1)(1-f_2) + f_2 N) - \varphi_2\,((N+1)f_1 + N(1-f_1)) \\ &= \varphi_1\,(N+1-f_2) - \varphi_2\,(N+f_1) \end{aligned}$$

for the absorption. Then we search solution in a form

$$\varphi(\mathbf{k}) = a(\mathbf{k})\left(-\frac{\partial f_0}{\partial\varepsilon}\right) = \frac{a(\mathbf{k})}{k_BT}f_0(1-f_0)$$

where $a(\mathbf{k})$ weakly depends on the energy, but strongly depends on the direction of $\mathbf{k}$. As a result, we have

$$k_BT\,F^{+}_{\mathbf{k},\mathbf{k}-\mathbf{q}} = a_1 f_1(1-f_1)(N+f_2) - a_2 f_2(1-f_2)(N+1-f_1) \to \text{emission}$$

To get a similar formula for absorption one should make a similar substitution. The result can be obtained from that above by the replacement $N \leftrightarrow N+1$, $f \leftrightarrow 1-f$,

$$a_1 f_1(1-f_1)\,(N+1-f_2) - a_2 f_2(1-f_2)\,(N+f_1)$$

and then replace $1 \leftrightarrow 2$ in the δ-functions to take into account the conservation law. Finally,

$$k_BT\,F^{-}_{\mathbf{k},\mathbf{k}-\mathbf{q}} = a_1 f_2(1-f_2)\,(N+1-f_1) - a_2 f_1(1-f_1)\,(N+f_2) \to \text{absorption}$$

Combining with the expression for the emission and absorption we get

$$\frac{(a_1-a_2)}{k_BT}\,[f_2(1-f_2)\,(N+1-f_1) + f_1(1-f_1)\,(N+f_2)]\;.$$

Fragments in the square brackets are

$$N+1-f_1=\frac{e^{\nu}}{e^{\nu}-1}-\frac{1}{e^{x}+1}=Nf_1\left(e^{x+\nu}+e^{\nu}-e^{\nu}+1\right)=N\frac{f_1}{f_2},$$

$$N+f_2=\frac{1}{e^{\nu}-1}+\frac{1}{e^{x+\nu}+1}=Nf_2\left(e^{x+\nu}+1+e^{\nu}-1\right)=(N+1)\frac{f_2}{f_1}$$

where $x=(\varepsilon-\zeta)/k_BT$, $\nu=\hbar\omega/k_BT$. Finally, we get in the brackets

$$Nf_1(1-f_2)+(N+1)f_2(1-f_1)=2Nf_1(1-f_2)$$

and the integrand in the collision integral becomes proportional to

$$\frac{2Nf_1(1-f_2)}{k_BT}(a_1-a_2).$$

We see that only thermal phonons are important since the integrand of the collision operator decreases exponentially at $\nu \gg 1$. As a result, we have proved the estimates made above. Unfortunately, the relaxation time approximation is not exact in this case and one should solve the Boltzmann equation numerically.

22.1.6. Umklapp-Processes. Optional section

It was a sort of cheating in our previous calculations of the electron-electron scattering. Indeed, suppose that we have only electrons which do not know anything about the lattice. How can the total momentum of the whole electron system relax?

To understand this important problem one should remember that there are processes where the quasimomentum is not conserved but there is a momentum transfer $\hbar\mathbf{G}$. To analyze the situation more carefully we write down the collision integral

$$\begin{aligned} I(f) \quad &= \quad -\int W_{\mathbf{p}_1\mathbf{p}_2}^{\mathbf{p}_1'\mathbf{p}_2'}\left[f_{\mathbf{p}_1}f_{\mathbf{p}_2}(1-f_{\mathbf{p}_1'})(1-f_{\mathbf{p}_2'})-f_{\mathbf{p}_1'}f_{\mathbf{p}_2'}(1-f_{\mathbf{p}_1})(1-f_{\mathbf{p}_2})\right] \\ &\times\,\delta(\varepsilon_1+\varepsilon_2-\varepsilon_1'-\varepsilon_2')\,(dp_2)\,(dp_1')\,. \end{aligned} \tag{22.12}$$

Here we assume that the momentum $\mathbf{p}_2'$ is determined by the conservation law

$$\mathbf{p}_1+\mathbf{p}_2=\mathbf{p}_1'+\mathbf{p}_2'+\hbar\mathbf{G}$$

and one should integrate over the remaining 2 variables. Because the process is inelastic we search the non-equilibrium function f_1 as

$$f_1(\mathbf{p})=a(\mathbf{p})\left(-\frac{\partial f_0}{\partial\varepsilon}\right)=\frac{a(\mathbf{p})}{k_BT}\,f_0(1-f_0)\,. \tag{22.13}$$

We have 4 terms proportional to a. The terms proportional to $a(\mathbf{p}_1)\equiv a_1$ are

$$-\frac{a_1}{k_BT}f_1(1-f_1)\left[f_2(1-f_1')(1-f_2')+f_1'f_2'(1-f_2)\right]$$

where all the functions are the equilibrium Fermi ones. Using the detailed balance equation

$$f_1f_2(1-f_1')(1-f_2')-f_1'f_2'(1-f_1)(1-f_2)=0$$

we transform the previous equation as (Check!)

$$-\frac{a_1}{k_BT}f_1f_2(1-f_1')(1-f_2')\,.$$

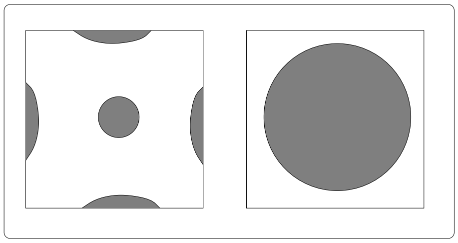

Figure 2. The Fermi surfaces of alkali metals and semimetals.

The same transformation can be done with all other terms and we get the following combinations in the collision integral (22.12).

$$\frac{1}{k_B T} f_1 f_2 (1-f_1^{'})(1-f_2^{'})(a_1+a_2-a_1^{\prime}-a_2^{'})\,.$$

If we assume that $a \propto p_i$ we get that the last bracket vanishes because of the momentum conservations. Consequently, we have no relaxation and a finite current in the absence of any field. To get a finite answer one should take into account the processes with finite $\mathbf{G}$, the so-called *Pierls Umklapp processes.*

We have seen that if $\mathbf{p}_1$ is close to the Fermi surface all other momenta are also close to the Fermi surface, all the vectors being in the BZ. Thus to get a finite resistance one should request

$$\max(|\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}_1^{'}-\mathbf{p}_2^{'}|) = \hbar G_{\min}$$

or

$$4\max p_F(\mathbf{n}) > \hbar G_{\min}\,.$$

This relation is definitely met if the FS reaches the boundary of the BZ. The same is true for the metals with near-spherical FS because the volume of the FS is equal to 1/2 of the BZ volume (half full band). It means that the radius of the FS is greater that 1/2 of the reciprocal lattice vector.

In semimetals like Bi the FS contains quasi-electron and quasi-hole valleys and electron-electron interaction is important for inter-valley transitions (see Fig. 2).

The situation is more complicated for electron-phonon collisions. We have assumed the phonons to be equilibrium. It means that we assume some effective mechanism to create equilibrium in the phonon gas, say, scattering of phonons by defects or phonon-phonon interaction including Umklapp processes. If the metal is very pure and the temperature is low the only scattering mechanism for phonons is their scattering by the electrons. Consequently, one should construct the Boltzmann equation for phonons

$$\frac{\partial N_{\mathbf{q}}}{\partial t} + \frac{\partial \omega(\mathbf{q})}{\partial \mathbf{q}}\frac{\partial N_{\mathbf{q}}}{\partial \mathbf{r}} = I_{ph}(N_{\mathbf{q}}).$$

The collision integral with electrons has the form

$$I_{ph-e} = \int W\left[f_1(1-f_2)(N_{\mathbf{q}}+1) - (1-f_1)f_2N_{\mathbf{q}}\right]\delta(\varepsilon_1-\varepsilon_2-\hbar\omega_{\mathbf{q}})\,(dp_1)$$

Again, we can search the solution for electrons as (22.13) and for phonon in the form

$$N_1(\mathbf{q}) = b(\mathbf{q})\left(-\frac{\partial N_0}{\partial(\hbar\omega)}\right) = \frac{b(\mathbf{q})}{k_B T}N_0(1+N_0).$$

As a result, we get

$$I \approx \int W f_{10}(1-f_{20})(N_{\mathbf{q}0}+1)(a_1-a_2-b)\,(dp_1)\,.$$

Again, if $a \propto p_i,\ b \propto \hbar q_i$ we get zero. Physically, it means the sum of electron and phonon quasimomenta conserve. As a result, we have a persistent motion of electrons accompanied by a "phonon wind". Again, we need the Umklapp processes to get finite electric and thermal conductivity. At high temperatures it is not a problem to find such processes. But at low temperatures the momenta of thermal phonons are small, and one can neglect the phonon quasimomenta in the conservation law

$$\mathbf{p}_1 - \mathbf{p}_2 - \hbar\mathbf{q} = \hbar\mathbf{G}\,.$$

So we come to the criterion

$$2\max p_F(\mathbf{n}) > \hbar G_{\min}$$

that cannon be met if the FS does not touch the BZ boundary. That changes all the kinetics because thermal phonons cannot take the electron momentum. Consequently, we need high-frequency phonons with $q \sim q_D$, their number being proportional to $\exp(-T_0/T)$ where $T_0 \sim \hbar\omega_D/k_B$. The resulting situation appears very tricky. To get an insight, let us come to the picture of extended BZs periodic in the reciprocal space. If the FS is open the electron momenta relaxation is just a diffusion along this surface and we have shown that

$$\tau_e \sim \frac{1}{\omega_D}\left(\frac{\hbar\omega_D}{k_B T}\right)^5 .$$

If the FS is closed, Umklapp processes mean *hops* between different branches. As a result, we get

$$\tfrac{1}{\tau_u} \sim \underbrace{\omega_D \left(\frac{k_B T_0}{\hbar\omega_D}\right)^3 e^{-T_0/T}}_{\text{number of phonons}} \cdot \underbrace{\frac{k_B T}{\hbar\omega_D}}_{\text{part of time}} \quad .$$

The last factor is just the part of time which electron spends near the region to which it can hop. Indeed, $\delta p \approx k_B T/s$, and $\delta p/p_F \sim k_B T/\hbar\omega_D$. The total relaxation time is a sum

$$\tau' = \tau_e + \tau_u$$

of the diffusion time over the closes surface and the time τ_u, the longest being most important. Note that here we add partial times rather than rates. The reason is that the scattering events take place sequentially.

As a result, we come to a crossover between the power and exponential temperature dependencies. Remember that all this physics is relevant only to very clean metals, otherwise impurity scattering is the most important at low temperatures.

LECTURE 23
Galvano- and Thermomagnetic Phenomena

23.1. The Physical Reason

The external magnetic field distort electron trajectories. Its influence is strong if the characteristic radius of cyclotron orbit, $r_c = v_\perp/\omega_c$, is less than the mean free path ℓ at which all the kinetic coefficients are formed. One can treat the distortion as an effective decrease of the mean free path ℓ. To estimate the influence of a weak magnetic field on the resistance one can compare the path between two scattering centers along the circle $r_c\phi$ (see Fig. 1) with the distance $2r_c \sin\phi/2$. The difference is $\sim r_c\phi^3$. If we put $r_c\phi \sim \ell$ we get

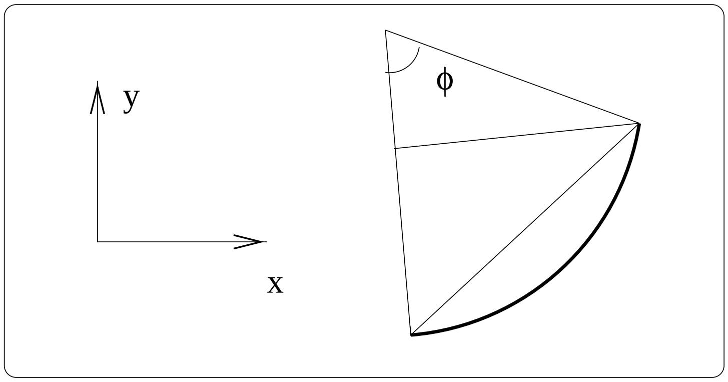

Figure 1. A trajectory fragment..

$$\Delta\rho/\rho \sim (\ell/r_c)^2 \sim (\omega_c\tau)^2 \, .$$

Another effect that one can expect is the creation of a current perpendicular to the electric and magnetic field direction. Indeed, under the influence of magnetic field an electron moves in the $[\mathbf{E}\times\mathbf{H}]$ direction by the distance

$$\sim r_c(1-\cos\phi) \approx (1/2)r_c\phi^2 \sim \ell(\ell/r_c) \sim \ell(\omega_c\tau) \, .$$

As a result, one can expect creation of off-diagonal components of the conductivity tensor with

$$|\sigma_{xy}| \sim \sigma_0(\omega_c\tau) \, .$$

To get the results in strong magnetic fields is more tricky and we will do it later.

23.2. Conductivity Tensor. Isotropic case. Relaxation time approximation.

In a magnetic field the Boltzmann equation reads

$$\left\{(\mathbf{v}\nabla_r) - e\left(E + \frac{1}{c}[\mathbf{v}\times\mathbf{H}]\right)\nabla_p\right\} f + \frac{f-f_0}{\tau_{\rm tr}} = 0\,.$$

We look for a solution as

$$f = f_0 + (\mathbf{v}\cdot\mathbf{G})\,, \quad |\mathbf{G}| \propto E\,.$$

We have

$$\left(-\frac{e}{c}[\mathbf{v}\times\mathbf{H}]\frac{\partial}{\partial\mathbf{p}} + \frac{1}{\tau_{\rm tr}}\right)(\mathbf{v}\cdot\mathbf{G}) = e\frac{\partial f_0}{\partial\varepsilon}(\mathbf{E}\cdot\mathbf{v})\,. \tag{23.1}$$

As we'll check, for a given ε the vector $\mathbf{G}$ is independent of the direction of $\mathbf{p}$ and depends only on the energy $\varepsilon = p^2/2m$. Since $\partial\varepsilon/\partial\mathbf{p} = \mathbf{v}$ we have

$$\frac{\partial(\mathbf{v}\cdot\mathbf{G})}{\partial\mathbf{p}} = \frac{\mathbf{G}}{m} + \mathbf{v}\left(\mathbf{v}\cdot\frac{d\mathbf{G}}{d\varepsilon}\right)\,.$$

Since

$$[\mathbf{v}\times\mathbf{H}]\cdot\mathbf{v}\left(\mathbf{v}\cdot\frac{d\mathbf{G}}{d\varepsilon}\right) = 0$$

we get

$$\frac{\mu}{c}\left([\mathbf{v}\times\mathbf{H}]\cdot\mathbf{G}\right) + (\mathbf{v}\cdot\mathbf{G}) = e\tau_{\rm tr}(\mathbf{v}\cdot\mathbf{E})\frac{\partial f_0}{\partial\varepsilon} \tag{23.2}$$

where

$$\mu(\varepsilon) = \frac{|e|\tau_{\rm tr}(\varepsilon)}{m} \tag{23.3}$$

is the partial electron *mobility*.

It is natural to look for a solution of the equation (23.2) in the form

$$\mathbf{G} = \alpha\mathbf{E} + \beta\mathbf{H} + \gamma[\mathbf{H}\times\mathbf{E}]\,.$$

Substitution this form to (23.2) and using the equality $([\mathbf{v}\times\mathbf{H}]\cdot\mathbf{H}) = 0$ we get

$$\alpha\frac{\mu}{c}([\mathbf{v}\times\mathbf{H}]\cdot\mathbf{E}) + \gamma\frac{\mu}{c}\left[(\mathbf{H}\cdot\mathbf{E})(\mathbf{v}\cdot\mathbf{H}) - H^2(\mathbf{v}\cdot\mathbf{E})\right]$$
$$+\alpha(\mathbf{v}\cdot\mathbf{E}) + \beta(\mathbf{v}\cdot\mathbf{H}) + \gamma(\mathbf{v}\cdot[\mathbf{H}\times\mathbf{E}]) = e\tau_{\rm tr}(\mathbf{v}\cdot\mathbf{E})\frac{\partial f_0}{\partial\varepsilon}\,.$$

Then we can collect the coefficients at $(\mathbf{v}\cdot\mathbf{E})$, $(\mathbf{v}\cdot\mathbf{H})$ and $(\mathbf{v}\cdot[\mathbf{H}\times\mathbf{E}])$. We have

$$\alpha - \gamma\frac{\mu}{c}H^2 = e\tau_{\rm tr}\left(\frac{\partial f_0}{\partial\varepsilon}\right)\,,$$
$$\gamma\frac{\mu}{c}(\mathbf{H}\cdot\mathbf{E}) + \beta = 0\,,$$
$$\alpha\frac{\mu}{c} + \gamma = 0\,. \tag{23.4}$$

As a result, (*Problem 24.9*)

$$\mathbf{G} = e\tau_{\rm tr}\frac{\partial f_0}{\partial\varepsilon}\frac{\mathbf{E} + (\mu/c)^2(\mathbf{H}\cdot\mathbf{E})\mathbf{H} + (\mu/c)[\mathbf{E}\times\mathbf{H}]}{1+\mu^2H^2/c^2}\,. \tag{23.5}$$

The quantity $\mu H/c$ is nothing else than the product $\omega_c\tau_{\text{tr}}$ We see that in the presence of magnetic field there is a current along the direction of $[\mathbf{E}\times\mathbf{H}]$. The conductivity tensor is easily calculated from the expression

$$j_i = -e\int \frac{2d^3p}{(2\pi\hbar)^3}\, v_i \sum_k v_k G_k\,.$$

For an isotopic spectrum, we get $\sigma_{zz}=\sigma_0$,

$$\sigma_{xx}=\sigma_{yy}=\frac{ne^2}{m}\left\langle\frac{\tau_{\text{tr}}}{1+\omega_c^2\tau_{\text{tr}}^2}\right\rangle,$$

while

$$\sigma_{xy}=-\sigma_{yx}=\frac{ne^2}{m}\left\langle\frac{\omega_c\tau_{\text{tr}}^2}{1+\omega_c^2\tau_{\text{tr}}^2}\right\rangle.$$

Here the average $\langle A\rangle$ is understood as

$$\langle A\rangle \equiv \frac{\int A(\mathbf{p})(-\partial f_0/\partial\varepsilon)\,(dp)}{\int(-\partial f_0/\partial\varepsilon)\,(dp)}\,.$$

Note that denominaator of this expression is nothing else then *thermodynamic density of states*,

$$g_T \equiv \partial n_e/\partial\zeta \tag{23.6}$$

where n_e is the electron density while ζ is the chemical potential.

23.3. Conductivity Tensor. Anisotropic case. Relaxation time approximation.

The major difference between the anisotropic and isotropic cases is how to sum over the states, or how we are to take the integrals $\int dp_x dp_y dp_z$. In order to do that in the anisotropic case we will do the following trick (magnetic field is along the z-direction): Let's consider a contour Γ_ε in p_x–p_y plane (at fixed p_z) given by the equation $\varepsilon(p_x,p_y)=\varepsilon$ – constant. Let' introduce the momentum differential dl along this contour, and momentum differential dp perpendicular to this contour, then $dp_xdp_y = dldp$. We then use $\frac{d\varepsilon}{dp}=v_\perp$, so $dp = d\varepsilon/v_\perp$ and have

$$\int dp_xdp_ydp_z \to \int \frac{1}{v_\perp} dl d\varepsilon dp_z.$$

In the absence of electric field the equation of motion is

$$\dot{\mathbf{p}} = -(e/c)[\mathbf{v}\times\mathbf{H}]$$

Considering the time evolution of $\varepsilon(\mathbf{p})$ with time $\frac{d\varepsilon}{dt}=\frac{\partial\varepsilon}{\partial\mathbf{p}}\dot{\mathbf{p}} = -(e/c)\mathbf{v}\cdot[\mathbf{v}\times\mathbf{H}]=0$. So the vector $\mathbf{p}$ evolves along a contour Γ_ε. We then have

$$dl = \frac{eH}{c} v_\perp dt.$$

We can now consider dt defined above not as the real time, but just as the parametrization of the contour Γ_ε. In particular if we include electric field the dt defined above is not time at all, but still it is a good parametrization of the contour Γ_ε. Having this in mind we will call it dt_1, then

$$\int dp_x dp_y dp_z \to \int \frac{1}{v_\perp} dl d\varepsilon dp_z \to \frac{eH}{c}\int dt_1 d\varepsilon dp_z, \qquad t_1 = \frac{c}{eH}\int \frac{dl}{v_\perp}.$$

Now we will consider the distribution function as a function of ε, t_1, and p_z: $f(\varepsilon, t_1, p_z)$, where we consider the quantities t_1, p_z, ε as independent variables.

In the presence of (time-independent) external fields we expect the function f to not depend on time explicitly. Then the l.h.s. of the Boltzmann equation can be written as

$$\frac{df}{dt} = \frac{\partial f}{\partial t_1}\frac{\partial t_1}{\partial t} + \frac{\partial f}{\partial p_z}\frac{\partial p_z}{\partial t} + \frac{\partial f}{\partial \varepsilon}\frac{\partial \varepsilon}{\partial t}$$

Since

$$\frac{\partial \varepsilon}{\partial t} = \mathbf{v}\cdot\frac{d\mathbf{p}}{dt} = -\mathbf{v}\cdot\left(\frac{e}{c}[\mathbf{v}\times\mathbf{H}] + e\mathbf{E}\right) = -e(\mathbf{v}\cdot\mathbf{E})\,, \quad \frac{dp_z}{dt} = -eE_z\,,$$

and in a *weak* (comparing to vH/c) electric field $\partial t_1/\partial t = 1$ we arrive at the Boltzmann equation

$$\frac{\partial f}{\partial t_1} - eE_z\frac{\partial f}{\partial p_z} - e(\mathbf{v}\cdot\mathbf{E})\frac{\partial f}{\partial \varepsilon} = I_{\text{col}}(f)\,. \tag{23.7}$$

As usual, we search the solution as

$$f = f_0 + a\left(-\frac{\partial f_0}{\partial \varepsilon}\right).$$

The function f_0 depends only on energy, and we get in the linear approximation in the case $E_z = 0$

$$\frac{\partial a}{\partial t_1} - I(a) = -e(\mathbf{v}\cdot\mathbf{E})\,. \tag{23.8}$$

We should solve this equation with proper boundary conditions. In the case of closed orbits it is just the periodicity while for open orbits the function should be finite. We need to analyze the solution of this equation in different cases.

To make estimates we use the relaxation time approximation to get

$$\frac{\partial a}{\partial t_1} + \frac{a}{\tau_{tr}} = -e\left(\mathbf{v}(t_1)\cdot\mathbf{E}\right)\,. \tag{23.9}$$

The general solution is

$$a(t_1) = \int_c^{t_1} -e\left(\mathbf{v}(t_2)\cdot\mathbf{E}\right)e^{-(t_1-t_2)/\tau_{tr}}\,dt_2.$$

If the orbits are *closed* one should apply the periodic conditions

$$a(t_1) = a(t_1 + \mathcal{T})$$

In this case one has to put $c = -\infty$ (*Problem 24.10*). The electric current is

$$j_i = -e\int v_i f\,(dp) = -\frac{2e^2H}{(2\pi\hbar)^3c}\int d\varepsilon\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\int dp_z\,dt_1\,v_i a(\varepsilon, p_z, t) =$$

$$= -\frac{2e^3H}{(2\pi\hbar)^3c}\int d\varepsilon\left(-\frac{\partial f_0}{\partial \varepsilon}\right)\int_{-p_F}^{p_F} dp_z\int_0^{\mathcal{T}} dt_1\,v_i(t_1)\int_{-\infty}^{t_1} dt_2\sum_k v_k(t_2)e^{-(t_1-t_2)/\tau_{tr}}E_k.$$

We see that the conductivity is a tensor with the components

$$\sigma_{ik} = -\frac{2e^3H}{(2\pi\hbar)^3c}\int d\varepsilon\left(-\frac{\partial f_0}{\partial\varepsilon}\right)\int_{-p_F}^{p_F} dp_z\int_0^{\mathcal{T}} dt_1\, v_i(t_1)\int_{-\infty}^{t_1} dt_2 v_k(t_2)e^{-(t_1-t_2)/\tau_{tr}}.$$

In the case $\mathbf{E}\perp\mathbf{H}$ we only need to consider i,k to be x,y-components. If the spectrum is isotropic,

$$v_x = v_\perp\cos\omega_c t_1, \quad v_y = -v_\perp\sin\omega_c t_1, \quad \omega_c = -\frac{eH}{mc}.$$

Now we can extract $v_\perp$ and analyze

$$\left\{\begin{array}{c} I_x \\ I_y \end{array}\right\} = \int_0^{\mathcal{T}} dt_1\left\{\begin{array}{c} \cos\omega_c t_1 \\ -\sin\omega_c t_1 \end{array}\right\}\int_{-\infty}^{t_1} dt_2\, e^{-(t_1-t_2)/\tau_{tr}}(E_x\cos\omega_c t_2 - E_y\sin\omega_c t_1)$$

It is convenient to employ an auxiliary integral

$$\begin{aligned}&\int_{-\infty}^{t_1} dt_2\, e^{t_2/\tau}\, e^{i\omega_c t_2} = e^{t_1/\tau}\, e^{i\omega_c t_1}\frac{\tau^{-1}-i\omega_c}{\tau^{-2}+\omega_c^2} = \\ &= e^{t_1/\tau}\frac{1}{\tau^{-2}+\omega_c^2}\left[(\tau^{-1}\cos\omega_c t_1 + \omega_c\sin\omega_c t_1) + i(\tau^{-1}\sin\omega_c t_1 - \omega_c\cos\omega_c t_1)\right].\end{aligned}$$

Finally, we come to the integral

$$\left\{\begin{array}{c} I_x \\ I_y \end{array}\right\} = \int_0^{\mathcal{T}} dt_1\left\{\begin{array}{c} \cos\omega_c t_1 \\ -\sin\omega_c t_1 \end{array}\right\}\left[E_x(\tau_{tr}^{-1}\cos\omega_c t_1 + \omega_c\sin\omega_c t_1) - E_y(\tau_{tr}^{-1}\sin\omega_c t_1 - \omega_c\cos\omega_c t_1)\right].$$

and get

$$\left\{\begin{array}{c} j_x \\ j_y \end{array}\right\} = -\frac{2e^3H}{(2\pi\hbar)^3c}\frac{\mathcal{T}}{2}\int d\varepsilon\left(-\frac{\partial f_0}{\partial\varepsilon}\right)\frac{1}{\tau_{tr}^{-2}+\omega_c^2}\left\{\begin{array}{c} \tau_{tr}^{-1}E_x + \omega_c E_y \\ -\omega_c E_x + \tau_{tr}^{-1}E_y \end{array}\right\}\int dp_z v_\perp^2.$$

We have used the integrals

$$\begin{aligned}&\int_0^{\mathcal{T}}\cos^2\omega_c t\, dt = \int_0^{\mathcal{T}}\sin^2\omega_c t\, dt = \frac{\mathcal{T}}{2}, \\ &\int_0^{\mathcal{T}}\cos\omega_c t\,\sin\omega_c t\, dt = 0.\end{aligned}$$

For degenerate electrons the integral over the energy enforces the internal integral to the Fermi surface, the last integral being

$$\int_{-p_F}^{p_F} v_\perp^2\, dp_z = \frac{1}{m^2}\int_{-p_F}^{p_F}\int(p_F^2 - p_z^2)\, dp_z = \frac{4}{3}\frac{p_F^2}{m^2}.$$

The final result is

$$\hat\sigma_\perp = \frac{n_e e^2}{m}\frac{1}{\tau_{tr}^{-2}+\omega_c^2}\left(\begin{array}{cc} \tau_{tr}^{-1} & \omega_c \\ -\omega_c & \tau_{tr}^{-1} \end{array}\right).$$

23.4. Weak Magnetic Field

In weak magnetic fields, when

$$\omega_c\tau_{tr} \ll 1$$

we get

$$\hat\sigma_\perp = \sigma_0\left(\begin{array}{cc} 1 & \omega_c\tau_{tr} \\ -\omega_c\tau_{tr} & 1 \end{array}\right).$$

The typical configuration to measure off-diagonal components of the conductivity tensor is shown in Fig. (2). In general

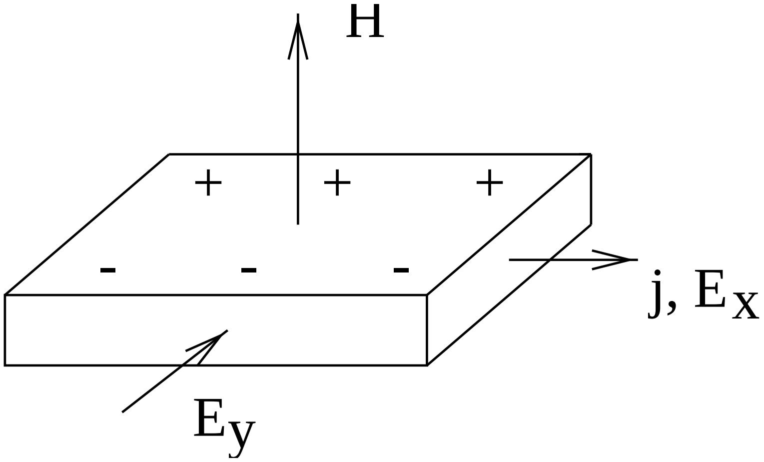

Figure 2. Arrangement to measure off-diagonal conductivity components.

$$j_x = \sigma_{xx}E_x + \sigma_{xy}E_y, \qquad (23.10)$$
$$j_y = \sigma_{yx}E_x + \sigma_{yy}E_y.$$

If the circuit in y-direction is open we have $j_y = 0$. As a result, a field

$$E_y = -\frac{\sigma_{yx}}{\sigma_{xx}}E_x \qquad (23.11)$$

appears, the current density being

$$j = j_x = \rho_{xx}E_x = \frac{\sigma_{xx}^2 + \sigma_{xy}^2}{\sigma_{xx}}E_x.$$

We have taken into account that

$$\sigma_{xx} = \sigma_{yy}, \qquad \sigma_{xy} = -\sigma_{yx}.$$

Thus

$$E_y = \frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2}j.$$

The creation of a transverse field directed along $[\mathbf{E}\times\mathbf{H}]$ is called the *Hall effect*. The *Hall coefficient* is defined as

$$R = \frac{E_y}{Hj_x} = \frac{\sigma_{xy}}{(\sigma_{xx}^2 + \sigma_{xy}^2)H}.$$

As we see, at weak magnetic field

$$R = \frac{\omega_c\tau_{tr}}{H\sigma_o} = \frac{1}{n_e ec}. \qquad (23.12)$$

We came to the conclusion that the Hall coefficient depends only on the electron density. It is not the case in real materials because we have canceled the factor τ_{tr} which in real life depends on the energy, directions, etc. In non-degenerate semiconductors the Hall coefficient becomes dependent on the scattering mechanisms. Usually, it is taken into account by introduction the *Hall factor* in Eq. (23.12). The *resistivity* component $\rho_{xx} = 1/\sigma_0$ in a weak field because $|\sigma_{xy}| \ll \sigma_{xx}$.

23.5. Strong Magnetic Field.

The results obtained above can be used to get estimates also in the case of high magnetic fields. But we will make more rigorous calculations because many results can be obtained for an arbitrary energy spectrum.

First, we introduce a specific perturbation theory to solve the Boltzmann equation in strong magnetic fields, i.e. expansion in power of $\gamma = (\omega_c \tau_{tr})^{-1}$. We write the function a as

$$a = \sum_k a_k , \qquad a_k \sim \gamma^k$$

and substitute the Boltzmann equation (23.8)

$$\begin{aligned} \partial a_0/\partial t_1 &= 0\,, \\ \partial a_1/\partial t_1 - I(a_0) &= -e(\mathbf{v}\mathbf{E})\,, \\ \partial a_2/\partial t_1 - I(a_1) &= 0\,,\ \ldots \end{aligned}$$

The solutions are:

$$\begin{aligned} a_0 &= C_0\,, \\ a_1 &= \int_0^{t_1} \left[I(a_0) - e\left(\mathbf{v}(t_2)\mathbf{E}\right)\right]\, dt_2 + C_1\,, \\ &\ldots \\ a_k &= \int_0^{t_1} I(a_{k-1})\, dt_2 + C_k \\ &\ldots \end{aligned}$$

Then we average all the equations over the time taking into account that $\overline{\partial a/\partial t_1} = 0$. As a result,

$$-\overline{I(a_0)} = -e(\overline{\mathbf{v}}\mathbf{E}), \qquad \overline{I(a_{k\neq 0})} = 0.$$

These equations determine the constant items C_i. Now we proceed with calculation of the conductivity tensor.

23.5.1. Closed Orbits

In this case $\overline{v_x} = \overline{v_y} = 0$, and C_0 depends only on $\overline{v_z} E_z$. Consequently, we are interested in a_1 and we can substitute (as we only interested in linear in E effect)

$$\frac{dp_x}{dt} = -\frac{e}{c} v_y H, \qquad \frac{dp_y}{dt} = \frac{e}{c} v_x H. \tag{23.13}$$

As a result,

$$a_1 = \frac{c}{H}\int_0^{t_1} dt_2 \left(E_y \frac{dp_x}{dt_2} - E_x \frac{dp_y}{dt_2}\right) - e\int_0^{t_1} dt_2\, v_z(t_2) E_z + \text{terms independent of } v_x \text{ and } v_y\,.$$

Now it is very simple to calculate σ_{xy}. Let us calculate, say, j_x for the Fermi gas. We have

$$\begin{aligned} j_x &= \frac{2He^2}{(2\pi\hbar)^3 c}\int dp_z \int_0^{\mathcal{T}} v_x(t_1) a_1\, dt_1 = \frac{2e}{(2\pi\hbar)^3}\int dp_z \int_0^{\mathcal{T}} a(t_1)\frac{dp_y}{dt_1}\, dt_1 \\ &= \frac{2e}{(2\pi\hbar)^3}\int dp_z \left[\int_0^{\mathcal{T}} dt_1 \left(p_x(t_1) - p_x(0)\right) E_y \frac{c}{H}\frac{dp_y}{dt_1} + \ \text{vanishing items}\right]. \end{aligned}$$

The result is

$$\sigma_{xy} = \frac{2ec}{(2\pi\hbar)^3 H}\int dp_z \int_0^{\mathcal{T}} dt_1\, p_x \frac{dp_y}{dt_1} = \frac{2ec}{(2\pi\hbar)^3 H}\underbrace{\int dp_z \oint p_x\, dp_y}_{\text{volume}} .$$

The result can be expressed through the densities of electron-like and hole-like excitations:

$$\sigma_{xy} = -\frac{ec}{H}(n_e - n_h).$$

The physical reason is that the Lorenz force has different signs for electrons and holes and the *Hall effect feels the sign of charge carriers.* It is very important that the result is independent on scattering mechanisms and the shape of the surfaces $\varepsilon =$ const. Actually, it is the most common way to determine the carriers' density.

Another conclusion is that there is no linear in γ contributions to the diagonal components of the conductivity tensor. Finally, we come to the following structure of the conductivity tensor

$$\sigma_{ik} = \begin{pmatrix} \gamma^2 a_{xx} & \gamma a_{xy} & \gamma a_{xz} \\ \gamma a_{yx} & \gamma^2 a_{yy} & \gamma a_{yz} \\ \gamma a_{zx} & \gamma a_{zy} & a_{zz} \end{pmatrix}$$

while the resistivity tensor $\hat{\rho} = (\hat{\sigma})^{-1}$ is

$$\rho_{ik} = \begin{pmatrix} b_{xx} & \gamma^{-1} b_{xy} & b_{xz} \\ \gamma^{-1} b_{yx} & b_{yy} & b_{yz} \\ b_{zx} & b_{zy} & b_{zz} \end{pmatrix} .$$

The case of compensated materials with $n_e = n_h$ (like Bi) needs a special treatment.

Note that the components of the conductivity tensor should meet the Onsager principle which in the presence of the magnetic field reads as

$$\sigma_{ik}(\mathbf{H}) = \sigma_{ki}(-\mathbf{H})$$

(the reason is that the Onsager principle is derived by use the symmetry with respect to time reversion. Under such a transform magnetic field changes its sign).

23.5.2. Open Orbits

The case of open orbits is more tricky. To understand what happens let us consider the case shown in Fig. 3. We observe that the trajectory in p_z-direction is infinite while in p_y direction it is finite. Taking the average of the equations of motion (23.13) we get

$$\overline{v_y} = -\frac{c}{eH}\lim_{T_1\to\infty}\left[\frac{p_x(T_1) - p_x(0)}{T_1}\right] \neq 0, \qquad \overline{v_x} = 0.$$

As a result, the quantity a_0 contains a component $\propto E_y$, and the component σ_{yy} is not small. As a result,

$$\sigma_{ik} = \begin{pmatrix} \gamma^2 a_{xx} & \gamma a_{xy} & \gamma a_{xz} \\ \gamma a_{yx} & a_{yy} & a_{yz} \\ \gamma a_{zx} & a_{zy} & a_{zz} \end{pmatrix} .$$

One can see from Fig. 3 that the conductivity tensor strongly depends on the tilt angle of the magnetic field, having a sharp crossover at $\theta \to 0$. The schematic angular dependencies of the Hall coefficient and transverse resistivity are shown in Fig. 4. .

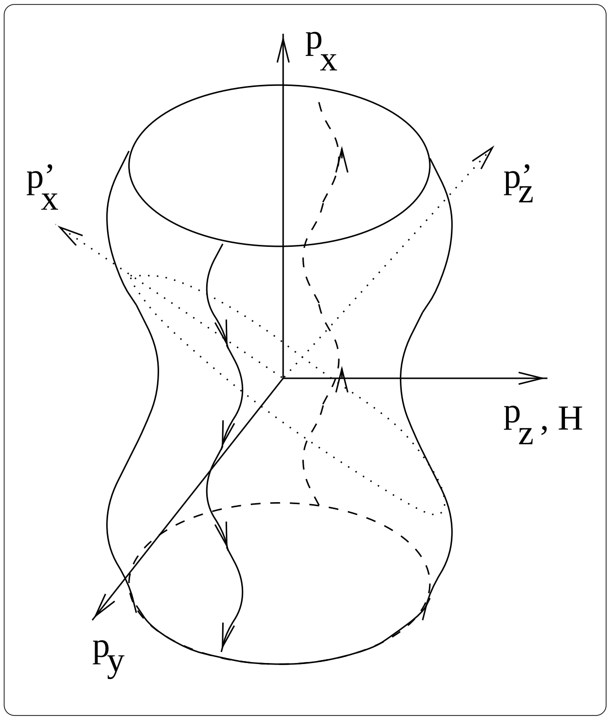

Figure 3. The case of open orbits..

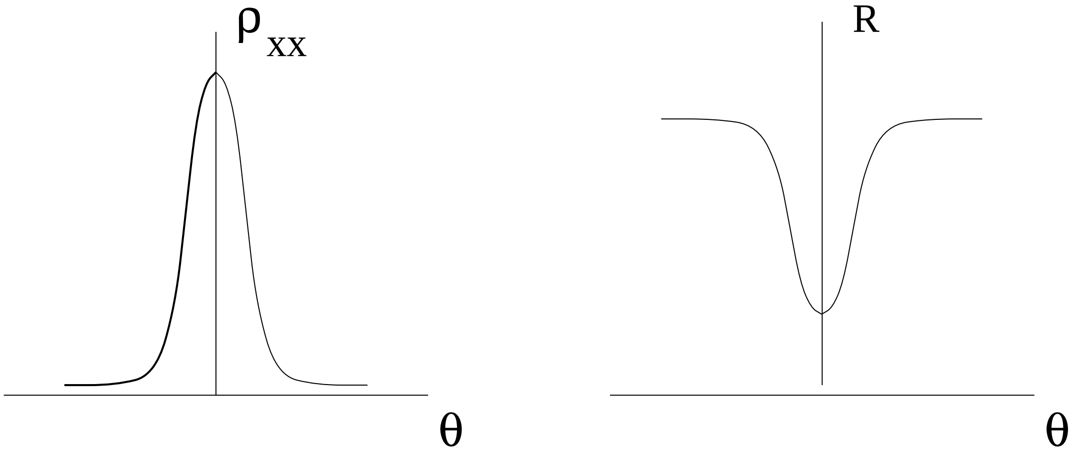

Figure 4. Crossover from closed to open orbits.

LECTURE 24

Thermomagnetic Effects. “Slow” perturbations.

24.1. Thermomagnetic Effects.

It is clear that the temperature gradient also produces electric currents, and a magnetic field leads to off-diagonal transport. As we have seen these currents are produced by the ”effective force” $(\varepsilon-\zeta)\nabla T/T$. As a result, all the kinetic coefficients become tensors. According to the Onsager principle

$$\rho_{ik}(\mathbf{H}) = \rho_{ki}(-\mathbf{H}), \qquad \varkappa_{ik}(\mathbf{H}) = \varkappa_{ki}(-\mathbf{H}), \qquad \Pi_{ik}(\mathbf{H}) = T\alpha_{ki}(-\mathbf{H}).$$

Consequently, we have 36 kinetic coefficients which obey 15 Onsager relations. It is clear that 21 independent components lead to a very complicated picture. These 21 components are further restricted by the lattice symmetries. The simplest case is for an isotropic material in a weak magnetic field. In this case one can write

$$\begin{aligned} \mathbf{j} &= \rho\mathbf{E} + R\,[\mathbf{H}\times\mathbf{j}] + \alpha\nabla T + N\,[\mathbf{H}\times\nabla T]\,, \\ \mathbf{w}-\mathbf{j}\zeta &= \Pi\mathbf{j} + B\,[\mathbf{H}\times\mathbf{j}] - \varkappa\nabla T + L\,[\mathbf{H}\times\nabla T]\ . \end{aligned} \tag{24.1}$$

According to the Onsager principle, $B = NT$. The expressions (24.1) describe many effects. For example, suppose that $\nabla_x T = 0$, $j_y = 0$, $w_y = 0$, but $j_x \neq 0$. In this case we get

$$\frac{\partial T}{\partial y} = \frac{B}{\varkappa} H j_x$$

(the *Ettingshausen effect*). Another effect is creation of a field E_y by the gradient $\partial T/\partial x$ (the *Nernst effect*)

$$E_y = NH(\partial T/\partial x).$$

All these effects have important applications. In high magnetic fields all the coefficients become field-dependent.

24.2. Response to “slow” perturbations

In this section we will discuss electron response to low-frequency perturbation which vary slowly in space.

Fro this approximation it is important to distinguish between τ_{tr} and τ_{in} – the transport time and the inelastic time. The transport time comes from the processes that change the electron's momentum, the inelastic time change the electron's energy. Typically the inelastic time is larger than transport time. In many cases $\tau_{\text{in}} \gg \tau_{\text{tr}}$.

Here we will first consider the case of slow perturbation for which

$$\omega\tau_{\text{tr}} \ll 1, \qquad q\ell \ll 1.$$

We will see, that the transport is defined by the diffusion constant $D \sim \tau_{\text{tr}}$. We then consider the case of very slow perturbations

$$\omega\tau_{\text{in}} \ll 1, \qquad q^2 D\tau_{\text{in}} \ll 1$$

Consider electron gas in a weak ac electric field $\mathbf{E}(\mathbf{r}, t)$. Let us separate odd and even in $\mathbf{p}$ parts of the electron distribution function,

$$f(\mathbf{p}) = f^+(\mathbf{p}) + f^-(\mathbf{p})\,, \quad f^\pm(-\mathbf{p}) = \pm f^\pm(\mathbf{p})\,.$$

The key point of the following consideration is that the relaxation rates for the odd and even in $\mathbf{p}$ components can be very much different. Indeed, elastic processes do not affect any function dependent only on the energy, and the average distribution function

$$F(\epsilon) = \langle f(\mathbf{p})\rangle_\epsilon \equiv \frac{\int (d\mathbf{p})\, f^+(\mathbf{p})\, \delta(\epsilon_{\mathbf{p}} - \epsilon)}{\int (d\mathbf{p})\, \delta(\epsilon_{\mathbf{p}} - \epsilon)}$$

is not effected by elastic scattering.

The function $F(\epsilon)$ will be the main object of study. The above consideration tells us, that in writing the Boltzmann equation we must consider all relaxation mechanisms for the function f^+, while for f^- we can keep only elastic processes (this assumes, that inelastic scattering is much weaker than elastic one.)

Assuming that inelastic processes are weak, we leave in the equation for f^- only elastic processes in the collision operator. As a result,

$$\frac{\partial f^-}{\partial t} + \mathbf{v}\frac{\partial f^+}{\partial \mathbf{r}} + e\mathbf{E}\frac{\partial f^+}{\partial \mathbf{p}} + \frac{f^-}{\tau_{\text{tr}}} = 0. \tag{24.2}$$

Such a procedure is not correct for f^+ because the main part of f^+ depends only on the electron energy. Thus one has to write

$$\frac{\partial f^+}{\partial t} + \mathbf{v}\frac{\partial f^-}{\partial \mathbf{r}} + e\mathbf{E}\frac{\partial f^-}{\partial \mathbf{p}} + I\{f^+\} = 0\,, \tag{24.3}$$

where the collision operator includes inelastic processes. Now let us assume

$$\omega\tau_{\text{tr}} \ll 1\,, \quad q\ell \ll 1$$

and solve Eq. (24.2),

$$f^-(\mathbf{p}) = -\tau_{\text{tr}}\mathbf{v}\frac{\partial f^+}{\partial \mathbf{r}} - e\tau_{\text{tr}}\mathbf{E}\frac{\partial f^+}{\partial \mathbf{p}}\,, \tag{24.4}$$

then substitute into Eq. 24.3 and average over the constant energy surface.

The most difficult term is

$$\int \tau_{\text{tr}}(\varepsilon)v_i(\varepsilon_{\mathbf{p}})v_j(\varepsilon_{\mathbf{p}})\frac{\partial^2 f^+}{\partial x_i \partial x_j}\delta(\varepsilon_{\mathbf{p}} - \varepsilon)(d\mathbf{p}).$$

However, one can show that if

$$eE\tau_{\text{tr}} \ll \bar{p}\,.$$

the difference between $f^+(\mathbf{p})$ and $F(\epsilon_\mathbf{p})$ can be neglected. Then substituting $F(\epsilon_\mathbf{p})$ in the integral we see, that the δ-function enforces it to be $F(\epsilon)$, which then can be pulled out of the integral.

Another important point is that in the absence of the electric field the function $f_0(\varepsilon)$ must be a solution. Assuming that $F_1 = F(\epsilon) - f_0(\epsilon) \sim E$ is small we will finally arrive to

$$\frac{\partial F_1}{\partial t} - D_{ik}(\epsilon)\frac{\partial^2 F_1}{\partial x_i \partial x_k} + \langle I\{F_1\}\rangle_\epsilon = eD_{ik}(\epsilon)\frac{\partial E_k}{\partial x_i}\frac{\partial f_0}{\partial \epsilon}\,, \tag{24.5}$$

where

$$D_{ik} = \langle v_i \tau_{\text{tr}} v_k\rangle_\epsilon .$$

The typical estimate for the third term in Eq. 24.3 is F_1/τ_{in} where τ_{in} is the *inelastic* relaxation time. Thus the solution of Eq. (24.5) depends on the dimensionless quantities

$$\omega\tau_{\text{in}}\,, \quad q^2 D\tau_{\text{in}}\,.$$

Because usually in semiconductors at low temperatures

$$\tau_{\text{in}} \gg \tau_{\text{tr}}$$

these quantities can be large even at $\omega\tau_{\text{tr}}, q\ell \ll 1$.

24.2.1. Very low frequancies, $\omega\tau_{\text{in}}$, $q^2D\tau_{\text{in}} \ll 1$.

In this case the third term in l.h.s. of Eq 24.5 is most important and one has to vanish this term. That can be done assuming that $F_1(\epsilon, \mathbf{r}, t) \propto f_0(\epsilon)$, or

$$F_1(\epsilon, \mathbf{r}, t) = A(\mathbf{r}, t) f_0(\epsilon)\,.$$

Multiplying this equation by the density of states $g(\epsilon)$ and integrating over the energies we get

$$A(\mathbf{r}, t) = n(\mathbf{r}, t)/n_0\,.$$

Here $n(\mathbf{r}, t)$ is the time- and position dependent electron density. In this way (in the isotropic case) we get

$$\frac{\partial n}{\partial t} - D\frac{\partial^2 n}{\partial x^2} = eD\frac{\partial E_x}{\partial x}\left(-\frac{\partial n_0}{\partial \zeta}\right)\,. \tag{24.6}$$

Here ζ is the chemical potential while

$$D_{ik} = \frac{1}{n_0}\int d\epsilon\, g(\epsilon)\, f_0(\epsilon) D_{ik}(\epsilon)\,.$$

Moving all the terms into l.h.s. we get instead of Eq. 24.6

$$\frac{\partial n}{\partial t} + \frac{1}{e}\frac{\partial}{\partial x}\left(-eD\frac{\partial n}{\partial x} + e^2 D\frac{\partial n}{\partial \zeta}E_x\right) = 0\,. \tag{24.7}$$

This is nothing else than the charge conservation law

$$e\frac{\partial n}{\partial t} + \text{div }\; \mathbf{j} = 0\,.$$

Indeed, due to Einstein relation

$$\sigma = e^2 D\frac{\partial n_0}{\partial \zeta}$$

we have a usual expression for the current density

$$j_x = \sigma E_x - eD\frac{\partial n}{\partial x}\,.$$

We conclude that at

$$\omega\tau_{\text{in}} \ll 1, \quad q^2\tau_{\text{tr}}\tau_{\text{in}}v_F^2 \ll 1$$

one can employ very simple diffusion description of the response.

24.3. Dielectric function at low frequencies.

In this section we will obtain a simplified expression for dielectric function at low frequencies. Let us assume that one applies an external field $\mathbf{E}$ with momentum $\mathbf{q}$ and frequency ω

$$\mathbf{E}_{\mathbf{q},\omega}e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t} + \text{h.c.}$$

Then all the quantities are $\propto e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t}$.

A test charged placed inside the metal will experience an electric field which consists of three parts: external field $\mathbf{E}$, polarization of the ions $4\pi\mathbf{P}$, and the field due to the conduction electrons $\mathbf{D}^e$. So

$$\mathbf{D}_{\mathbf{q},\omega} = \mathbf{E}_{\mathbf{q},\omega} + 4\pi\mathbf{P}_{\mathbf{q},\omega} + \mathbf{D}^e_{\mathbf{q},\omega}.$$

The combination $\mathbf{E}_{\mathbf{q},\omega} + 4\pi\mathbf{P}_{\mathbf{q},\omega}$ can be written as $\varepsilon_0\mathbf{E}_{\mathbf{q},\omega}$, so we have

$$\mathbf{D}_{\mathbf{q},\omega} = \varepsilon_0\mathbf{E}_{\mathbf{q},\omega} + \mathbf{D}^e_{\mathbf{q},\omega} = \varepsilon(\mathbf{q},\omega)\mathbf{E}_{\mathbf{q},\omega}.$$

It is the dielectric function $\varepsilon(\mathbf{q},\omega)$ which we want to find. In order to do that we need to express $\mathbf{D}^e_{\mathbf{q},\omega}$ through $\mathbf{E}_{\mathbf{q},\omega}$.

In order to do that, we will employ the Poisson and diffusion equations:

$$\nabla\cdot\mathbf{D}^e = -4\pi en, \qquad e\frac{\partial n}{\partial t} + \nabla\cdot(\sigma\mathbf{E} - eD\nabla n) = 0.$$

Notice, that it is $\mathbf{E}$ (not $\varepsilon_0\mathbf{E}$)in the diffusion equation, as the Ohm's law is defined as $\mathbf{j} = \sigma\mathbf{E}$.

Using the fact, that all quantities are $\propto e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t}$ these equations read

$$i\mathbf{q}\cdot\mathbf{D}_{\mathbf{q},\omega} = -4\pi en_{\mathbf{q},\omega}, \qquad e(-i\omega + q^2D)n_{\mathbf{q},\omega} + \sigma i\mathbf{q}\cdot\mathbf{E}_{\mathbf{q},\omega} = 0\,. \tag{24.8}$$

Taking $n_{\mathbf{q},\omega}$ from the diffusion equation and substituting it into the Poisson equation we get

$$i\mathbf{q}\cdot\mathbf{D}^e_{\mathbf{q},\omega} = \frac{4\pi\sigma}{-i\omega + Dq^2}i\mathbf{q}\cdot\mathbf{E}_{\mathbf{q},\omega}$$

In isotropic system the vectors $\mathbf{D}^e$ and $\mathbf{E}$ have the same direction, so we can write

$$\mathbf{D}^e_{\mathbf{q},\omega} = \frac{4\pi\sigma}{-i\omega + Dq^2}\mathbf{E}_{\mathbf{q},\omega}$$

and finally

$$\mathbf{D}_{\mathbf{q},\omega} = \varepsilon_0\left(1 + \frac{4\pi\sigma/\varepsilon_0}{-i\omega + Dq^2}\right)\mathbf{E}_{\mathbf{q},\omega}.$$

The quantity $4\pi\sigma/\varepsilon_0$ has the units of frequency, or inverse time. Using so called Maxwell relaxation time

$$\tau_m \equiv \epsilon_0/4\pi\sigma$$

we then write

$$\epsilon(\mathbf{q},\omega) = \epsilon_0 \frac{-i\omega + q^2 D + 1/\tau_m}{-i\omega + q^2 D}\,. \tag{24.9}$$

In the limit of static fields $\omega \to 0$

$$\epsilon(\mathbf{q},0) = \epsilon_0 \frac{q^2 + \varkappa^2}{q^2}$$

where

$$\varkappa^2 = \frac{4\pi\sigma}{\epsilon_0 D} = \frac{4\pi e^2}{\epsilon_0}\frac{\partial n_0}{\partial \zeta}$$

is the square of inverse static screening length.

(The Coulomb Law in momentum space is $\frac{Q}{q^2\epsilon(\mathbf{q},\omega)} = \frac{Q}{\epsilon_0(q^2+\varkappa^2)}$ in the static case.)

24.4. Few Words About Phonon Kinetics.

In most of our consideration we have assumed the phonon distribution to be equilibrium. Actually, phonon system form a thermal bath for electrons. Such a assumption is based on the belief that phonons have efficient enough scattering which brings them to the equilibrium. Consequently, the temperature T is just the temperature of the phonon system.

At the same time, phonon distribution can be non-equilibrium. In particular, it is the case when a temperature gradient exists. To analyze the phonon kinetics one can investigate the Boltzmann equation for phonons

$$\frac{\partial N}{\partial t} + \mathbf{s}_g \frac{\partial N}{\partial \mathbf{r}} = I_{ph}(N,f), \qquad \mathbf{s}_g \equiv \frac{\partial \omega}{\partial \mathbf{q}}$$

where the collision integral is determined by the scattering processes. The most important of them are

- *Phonon-phonon processes.* These processes are rather complicated in comparison with the electron-electron ones because the number of phonons is not conserved. Consequently, along with the scattering processes (2 → 2) there are processes (2 → 1) and (1 → 2). Scattering processes could be normal (N) or Umklapp ones. Their frequency and temperature dependencies are different ($\tau_N^{-1} \propto T\omega,\ \tau_U^{-1} \propto \exp(\Theta/T)$).
- *Scattering by static defects.* Usually it is the Rayleigh scattering (scattering by imperfections with the size less than the wave length, $\tau^{-1} \propto \omega^4$).
- *Scattering phonons by electrons.*

All these processes make the phonon physics rather complicated. We are not going to discuss it in detail. Rather we restrict ourselves with few comments.

Probably most important phenomenon is phonon contribution to thermal conductivity. Indeed, phonon flux transfers the energy and this contribution in many cases is the most important. If one introduced the phonon transport relaxation time, τ_{ph}, the phonon contribution can be derived in the same way as for electrons. The result is

$$\varkappa_{ph} = \int d\omega\, \hbar\omega\, g_{ph}(\omega)\, D_{ph}(\omega) \frac{\partial N_\omega}{\partial T}$$

where

$$D_{ph}(\omega) = \frac{1}{3}\langle s_g I^{-1} s_g \rangle_\omega$$

is the phonon diffusion coefficient. As we have discussed, N-processes cannot lead to finite thermal conductivity and one take into account defect scattering, or Umklapp-processes. Usually, the phonon thermal conductivity increases with the decrease of the temperature. Nevertheless, at low temperatures the phonon mean free path becomes of the order of the sample size, and boundary scattering appears very important. It is the case in many devices of modern electronics.

In very clean materials, the impurity scattering appears ineffective both for phonons and electrons. In this case at low temperatures (when Umklapp processes are not important) electron and phonon systems strongly interact (*electron-phonon drag*). As a result, the kinetics becomes rather complicated and very interesting.

24.5. Problems

24.1. An electron with an energy spectrum

$$\varepsilon(\mathbf{p}) = \frac{p_x^2}{2m_x} + \frac{p_y^2}{2m_y} + \frac{p_z^2}{2m_z}$$

is placed into a magnetic field parallel to **z**-axis. Find the cyclotron effective mass given by $\tilde{m} = \frac{1}{2\pi}\frac{dA}{d\varepsilon}$, see (17.10), and compare it with the density-of-states effective mass defined as

$$g(\varepsilon) = \frac{\sqrt{2} m_d^{3/2} \varepsilon^{1/2}}{\pi^2 \hbar^3} \, .$$

24.2. Derive the Drude formula.

24.3. Derive Eq. (19.10).

24.4. Assume that that the electrons obey Boltzmann statistics,

$$f_0(\varepsilon) = \exp\left(\frac{\zeta - \varepsilon}{T}\right) ,$$

and that

$$\tau_{\text{tr}}(\varepsilon, T) \propto \varepsilon^r \, .$$

Expressing the transport relaxation time as

$$\tau_{\text{tr}}(\varepsilon, T) = \tau_0(T)(\varepsilon/kT)^r$$

find the expressions for Drude conductance at $\omega\tau_0 \ll 1$ and $\omega\tau_0 \gg 1$.

24.5. Compare thermopower $\alpha = \eta/\sigma$ for degenerate and non-degenerate electron gas. Assume

$$\tau_{\text{tr}}(\varepsilon, T) = \tau_0(T)(\varepsilon/kT)^r \, .$$

24.6. Using the Wiedemann-Franz law compare the coefficients $\varkappa$ and β for a typical metal.

24.7. Derive the expression (21.4) for the screened Coulomb potential.

$$\varphi = \frac{Ze}{r} e^{-r/r_s} ,$$

24.8. Derive the expression (21.5).

$$W(\theta) = 4\pi n_i v \left[\frac{e^2/\epsilon}{2\varepsilon(1-\cos\theta) + \hbar^2/2mr_s^2}\right]^2$$

24.9. Derive the expression for the solution of the Boltzmann equation (23.5)

$$\mathbf{G} = e\tau_{\mathrm{tr}}\frac{\partial f_0}{\partial \varepsilon}\frac{\mathbf{E} + (\mu/c)^2(\mathbf{HE})\mathbf{H} + (\mu/c)[\mathbf{EH}]}{1+\mu^2H^2/c^2}\,.$$

Use this expression to calculate the conductivity tensor.

24.10. Derive the condition $c = -\infty$ for Eq. (23.8).

24.11. Using the expression (24.9) find imaginary part of $1/\epsilon(\mathbf{q},\omega)$ which is responsible for damping of the wave of electrical polarization.

LECTURE 25
Electrodynamics of Metals

In this lecture we discuss ac properties of metals.

25.1. Time and Spatial Dispersion

25.1.1. General Considerations

In general, the current density $\mathbf{j}(\mathbf{r},t)$ is determined by the electric field in the vicinity of the point $\mathbf{r}$ and at previous times $t_1 < t$

$$\mathbf{j}(\mathbf{r},t) = \int d\mathcal{V}_1 \int_{-\infty}^{t} dt_1\, \sigma(\mathbf{r}-\mathbf{r}_1, t-t_1)\, \mathbf{E}(\mathbf{r}_1,t_1)\,.$$

After Fourier transform we get

$$\mathbf{j}(\mathbf{q},\omega) = \sigma(\mathbf{q},\omega)\mathbf{E}(\mathbf{q},\omega)$$

where $\sigma(\mathbf{q},\omega)$ must be analytical function of ω in the upper half-plane of complex ω to keep the causality. Making use of the Boltzmann equation in the relaxation time approximation we get

$$\sigma_{ik}(\mathbf{q},\omega) = e^2 \int (dp) \frac{v_i v_k}{i(\mathbf{qv}-\omega)+\tau^{-1}} \left(-\frac{\partial f_0}{\partial \varepsilon}\right).$$

In the case $q \to 0,\ \omega \to 0$ we return to the expression for the static conductivity. We are interested in the diagonal conductivity. If the electric field is directed along the x direction, then we are interested in σ_{xx}, so

$$\sigma(\mathbf{q},\omega) \equiv \sigma_{xx}(\mathbf{q},\omega) = e^2 \int (dp) \frac{v_x^2}{i(\mathbf{qv}-\omega)+\tau^{-1}} \left(-\frac{\partial f_0}{\partial \varepsilon}\right).$$

We see that there are 3 parameters with the dimension of frequency: qv, ω, and τ^{-1}. At

$$qv,\ \omega \ll \tau^{-1}$$

we return to the static case.

Let's now change the integration $\int (dp)$ into $\int d\varepsilon g(\varepsilon) \frac{d\Omega}{4\pi}$. The function $\frac{\partial f_0(\varepsilon)}{\partial \varepsilon}$ is strongly peaked at the Fermi surface. The magnitude of the velocity does not depend strongly on ε at that region. In the case of spherical Fermi surface, the velocity $\mathbf{v}$ is just parallel to the momentum and its magnitude does not depend on the direction. So we have

$$\sigma(\mathbf{q},\omega) = e^2 \int d\varepsilon g(\varepsilon) \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \int \frac{d\Omega}{4\pi} \frac{v_x^2}{i(\mathbf{qv}-\omega)+\tau^{-1}}.$$

In the first integral we can substitute g_F instead of $g(\varepsilon)$, then we get

$$\sigma(\mathbf{q},\omega) = -ie^2 g_F \int \frac{d\Omega}{4\pi} \frac{v_x^2}{\mathbf{qv}-\omega-i\tau^{-1}}, \tag{25.1}$$

where the magnitude of $\mathbf{v}$ is v_F and the integration is over the direction of the vector $\mathbf{v}$.

25.1.2. Static conductivity $\tau^{-1} \gg \omega, qv_F$.

Let's first consider the static case:

$$\tau^{-1} \gg \omega, qv_F.$$

In this case in the denominator of (25.1) we can neglect both ω and $\mathbf{qv}$. Using $v_x = v_F \cos\theta$ we get

$$\sigma_{st} = e^2 g_F v_F^2 \tau \int \frac{d\Omega}{4\pi} \cos^2\theta = \frac{1}{3} e^2 g_F v_F^2 \tau = \frac{ne^2\tau}{m} \equiv \sigma_0.$$

This is the standard Drude formula.

25.1.3. Uniform dynamic conductivity $\omega \gg \tau^{-1}, qv_F$.

Now let's consider the case, when the magnetic field is almost uniform, but changing with large frequency

$$\omega \gg \tau^{-1}, qv_F.$$

In this case it is clear, that we can neglect τ^{-1} and $\mathbf{qv}$ in the denominator of (25.1). We then will have exactly the same integration as in the static case, except instead of τ^{-1} in the denominator, we will have ω (and i), so he result is

$$\sigma(\omega) = -\frac{\sigma_0}{i\omega\tau}. \tag{25.2}$$

The limiting case

$$\omega \gg qv, \ \tau^{-1}$$

is called the *time dispersion* one

We will return to this result later, but now we will consider the next case

25.1.4. Non-uniform dynamic conductivity $qv_F \gg \omega \gg \tau^{-1}$.

In this case τ^{-1} is the smallest parameter in the problem. The main contribution to the integral in (25.1) comes from the pole. In order to capture this contribution we can use

$$\frac{-i}{\mathbf{qv}-\omega-i\tau^{-1}} \to \pi\delta(\mathbf{qv}-\omega).$$

So we have

$$\sigma(\mathbf{q},\omega) = e^2 g_F \pi \int \frac{d\Omega}{4\pi} v_x^2 \delta(\mathbf{qv}-\omega).$$

There are two cases: $\mathbf{q} \parallel \mathbf{E}$, and $\mathbf{q} \perp \mathbf{E}$. Denoting the angle between $\mathbf{q}$ and $\mathbf{v}$ as θ we get

$$\sigma_{\parallel}(\mathbf{q},\omega) = e^2 g_F \pi v_F^2 \frac{1}{2}\int d\theta \sin(\theta)\cos^2(\theta)\delta(qv_F\cos(\theta)-\omega),$$
$$\sigma_{\perp}(\mathbf{q},\omega) = e^2 g_F \pi v_F^2 \frac{1}{4\pi}\int d\phi d\theta \sin(\theta)\sin^2(\phi)\sin^2(\theta)\delta(qv_F\cos(\theta)-\omega)$$

Taking the integrals we find

$$\sigma_{\parallel}(\mathbf{q},\omega) = \frac{3\pi}{2}\sigma_0\frac{(\omega\tau)^2}{(q\ell)^3} \tag{25.3}$$

$$\sigma_{\perp}(\mathbf{q},\omega) = \frac{3\pi}{8}\sigma_0\frac{1}{q\ell} \tag{25.4}$$

where $\ell = v_F\tau$.

- Notice, that neither result depends on τ ($\sigma_0 \sim \tau$).

25.1.5. Non-uniform static conductivity $qv_F \gg \tau^{-1} \gg \omega$.

In this case it is clear, that the result (25.4) for $\sigma_\perp$ still holds as it does not depend on ω, while the result (25.3) for $\sigma_\parallel$ needs to be corrected. In order to do that we use

$$\mathrm{Re}\,\frac{-iv_x^2}{\mathbf{qv}-\omega-i\tau^{-1}} \approx \mathrm{Re}\,\frac{-iv_x^2}{\mathbf{qv}-i\tau^{-1}} = \tau^{-1}\frac{v_F^2\cos^2\theta}{v_F^2 q^2\cos^2\theta+\tau^{-2}} \approx \tau^{-1}\frac{1}{q^2},$$

which gives

$$\sigma_{\parallel}(\mathbf{q},\omega\to 0) \approx 3\sigma_0\frac{1}{(q\ell)^2}.$$

Now we return to the time dispersion case (25.2).

25.2. Discussion of the time dispersion case (25.2). Plasmons.

The time dispersion result (25.2) is

$$\sigma(\omega) = -\frac{\sigma_0}{i\omega\tau}.$$

First, notice, that the result is imaginary, so it gives imaginary impedance, like that of inductance. Such impedance does not dissipate energy.

If we apply the Drude formula $\sigma_0 = \frac{ne^2\tau}{m}$, we get

$$\sigma(\omega) = i\frac{\epsilon}{4\pi}\frac{\omega_p^2}{\omega}, \qquad \text{where} \quad \omega_p^2 = \frac{4\pi n_e e^2}{\epsilon m} \tag{25.5}$$

is the *plasma frequency*.

This result is connected with the plasma oscillations in an electron gas. Indeed, the result above was derived for very small q. Let's consider the limit $q \to 0$. It means that the applied field is uniform in space. The field is along the $\hat{x}$ direction. All electrons uniformly shift by x in $\hat{x}$ direction. If S is the $y-z$ cross-section of the sample, then after such shift the excess charge $Q = \pm eSnx$ appeared at the ends of the sample, while inside the sample the net charge is still zero. Thus we have a capacitor with the capacitance $C = \frac{S\epsilon}{4\pi L_x}$. The potential energy of this capacitor is then $\frac{Q^2}{2C} = \frac{4\pi e^2 S L_x n^2}{2\epsilon} x^2$. The kinetic energy of the electron gas is $\frac{nmSL_x}{2}\dot{x}^2$, so the total energy is

$$E = \frac{4\pi e^2 S L_x n^2}{2\epsilon} x^2 + \frac{nmSL_x}{2}\dot{x}^2.$$

One can see, that this is the energy of a harmonic oscillator with frequency $\omega_p^2 = \frac{4\pi n_e e^2}{\epsilon m}$.

Let's consider the plasma oscillations more carefully. I will here consider only the longitudinal oscillations.

An electric field $\mathbf{E} = -\nabla\phi$, apart from the shift of the inner electrons (which is taken care of by the dielectric constant ϵ) gives rise to two effects: the polarization of the free electrons; and to current. Due to polarization the density of electrons becomes $n + \delta n(\mathbf{r}, t)$ which partially screens the applied electric field. The change of density leads to the change of the chemical potential $\zeta(\mathbf{r}, t)$, so that the electric current is induced by the unscreened part of the electric field

$$\tilde{\mathbf{E}} = -\nabla(\varphi - \zeta/e) = \mathbf{E} + (1/e)(\partial\zeta/\partial n)\nabla(\delta n) \to \tilde{\mathbf{E}}_{\mathbf{q},\omega} = \mathbf{E}_{\mathbf{q},\omega} + (eg_T)^{-1} i\mathbf{q}\delta n_{\mathbf{q},\omega}\,.$$

(the symbol → means Fourier transform, g_T is the density of states)

The current density then is

$$\mathbf{j}_{\mathbf{q},\omega} = \sigma(\mathbf{q},\omega)\tilde{\mathbf{E}}_{\mathbf{q},\omega}$$

We now use the Poisson equation

$$\mathrm{div}\,\mathbf{D} = \epsilon\,\mathrm{div}\,\mathbf{E} = -4\pi e(\delta n) \to i\epsilon\mathbf{q}\mathbf{E}_{\mathbf{q},\omega} = -4\pi e\delta n_{\mathbf{q},\omega}$$

and the continuity equation,

$$-e\frac{\partial n}{\partial t} + \mathrm{div}\,\mathbf{j} = 0 \to ie\omega\delta n_{\mathbf{q},\omega} + i\mathbf{q}\cdot\mathbf{j}_{\mathbf{q},\omega} = 0.$$

As a result, we come to two equations for $\delta n_{\mathbf{q},\omega}$ and $\mathbf{q}\mathbf{E}$:

$$\left(ie\omega - \frac{\sigma(\mathbf{q},\omega)}{eg_T}q^2\right)\delta n_{\mathbf{q},\omega} + i\sigma(\mathbf{q},\omega)\mathbf{q}\mathbf{E}_{\mathbf{q},\omega} = 0 \tag{25.6}$$

$$4\pi e\delta n_{\mathbf{q},\omega} + i\epsilon\mathbf{q}\mathbf{E}_{\mathbf{q},\omega} = 0 \tag{25.7}$$

These equations have a nontrivial solutions only if the determinant is zero. This condition gives the dispersion relation for the propagation of the charge density

$$i\omega - \frac{4\omega}{\epsilon}\sigma(\mathbf{q},\omega) - q^2\frac{\sigma(\mathbf{q},\omega)}{e^2 g_T} = 0.$$

Using $\sigma(\mathbf{q},\omega) = -\frac{\sigma_0}{i\omega\tau}$ and $\sigma_0 = \frac{ne^2\tau}{m}$ we get

$$\omega^2 = \omega_p^2 + \frac{n}{mg_T}q^2. \tag{25.8}$$

- The plasmons are gaped, with the gap ω_p and for small q the dispersion is quadratic.

Now let's assume, that the frequency and wave number of the *applied* electric field does not satisfy the relation (25.8). Any test charge placed in the metal will experience a field $\mathbf{D}$ which is the applied field $\mathbf{E}$ corrected by screening, so

$$\mathrm{div}\mathbf{D} = \epsilon\mathrm{div}\mathbf{E} + 4\pi\delta n \to i\mathbf{q}\mathbf{D}_{\mathbf{q},\omega} = i\epsilon\mathbf{q}\mathbf{E}_{\mathbf{q},\omega} + 4\pi\delta n_{\mathbf{q},\omega}$$

Taking $\delta n_{\mathbf{q},\omega}$ from (25.6) we get

$$\mathbf{D} = \epsilon_{\text{eff}}\mathbf{E}, \qquad \epsilon_{\text{eff}} = \epsilon + i\frac{4\pi\sigma(\mathbf{q},\omega)}{\omega + iD(\mathbf{q},\omega)q^2} \tag{25.9}$$

where I have denoted

$$D(\mathbf{q},\omega) = \frac{\sigma(\mathbf{q},\omega)}{e^2 g_T}.$$

It is useful to rewrite (25.9) in the following way

$$\sigma(\mathbf{q},\omega) = -\frac{i\omega}{4\pi}(\epsilon_{\text{eff}} - \epsilon) + \frac{Dq^2}{4\pi}(\epsilon_{\text{eff}} - \epsilon)$$

which shows, that the imaginary part of conductivity gives dielectric constant.

For the static field $\omega = 0$ equation (25.9) gives

$$\epsilon_{\text{eff}} = \epsilon\left(1 + \frac{4\pi e^2 g_T}{\epsilon}\frac{1}{q^2}\right) = \epsilon\frac{q^2 + \varkappa^{-2}}{q^2},$$

where

$$\varkappa = \left(\frac{4\pi e^2 g_T}{\epsilon}\right)^{-1/2}.$$

- The Coulomb interaction is given by $\frac{Q^2}{4\pi\epsilon_{\text{eff}}q^2}$, so in the static case we have $\frac{1}{4\pi\epsilon}\frac{4\pi Q^2}{q^2+\varkappa^{-2}}$. We see that $\varkappa$ is the screening length.

LECTURE 26
Skin Effect.

26.1. Skin Effect.

26.1.1. Normal Skin Effect.

Assume that the sample is placed in an external ac electromagnetic field. The Maxwell equations read

$$\operatorname{curl}\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t}, \qquad \operatorname{curl}\mathbf{H} = \frac{4\pi}{c}\mathbf{j}.$$

As a starting point we assume that $\mathbf{j} = \sigma\mathbf{E}$ and consider the arrangement shown in Fig. 1: $\mathbf{E} \parallel \mathbf{y}$, $\mathbf{H} \parallel \mathbf{z}$, the propagation direction is $\mathbf{x}$. Let all the fields be proportional to $\exp\left[i(qx-\omega t)\right]$. We get the following equations

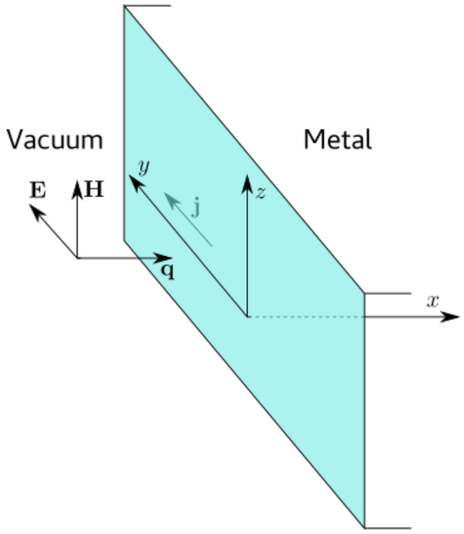

Figure 1. Arrangement for the calculation of the skin-effect.

$$iqE_y = i\frac{\omega}{c}H_z, \qquad -iqH_z = \frac{4\pi}{c}\sigma E_y.$$

Combining these equations we get

$$q^2 = 4\pi i\omega\sigma/c^2 \to q = \sqrt{4\pi i\omega\sigma/c^2} = (1+i)\sqrt{2\pi\omega\sigma/c^2} = q_1 + iq_2.$$

We see that the wave dumps in the metal, the penetration depth being

$$\delta = \frac{1}{q_2} = \frac{c}{\sqrt{2\pi\omega\sigma}}. \tag{26.1}$$

Usually the surface impedance is introduced as a sheet resistance of a surface layer

$$Z = E_y(0) / \int_0^\infty j_y \, dx \equiv R - iX.$$

The active (R) and reactive (X) components can be measured by monitoring the amplitude and phase of the reflected wave. The part R is responsible for the heating of the metal (surface quenching). Using the Maxwell equations we can rewrite

$$Z = \frac{E_y(0)}{-(c/4\pi)H_z|_0^\infty} = \frac{4\pi}{c}\frac{E_y(0)}{H_z(0)} = \frac{4\pi}{c^2}\frac{\omega}{q}.$$

Substituting (26.1) we get

$$R = X = \sqrt{\frac{2\pi\omega}{\sigma c^2}}.$$

26.1.2. Anomalous Skin Effect.

Let us consider the expression (26.1) in more detail. As the temperature decreases σ increases and in clean metals it can be large. So the skin depth decreases (at least at high frequencies). On the other hand, the mean free path ℓ *increases* with the decrease of the temperature. At some moment we will have $\delta < \ell$, which means that we cannot use the simple expression $\mathbf{j} = \sigma\mathbf{E}$ anymore. Indeed, this expression can be valid only if all the fields change slowly at the scale of ℓ.

Now we consider the case $\delta \ll \ell$ that leads to the *anomalous skin effect* (London, 1940). The picture of the fragment of the electron orbit near the surface is shown in Fig. 2. Only the electrons with small component v_x contribute to the interaction with the field (the other ones spend a very small part of time within the region where the field is present). Introducing the spherical co-ordinate system with the polar axis along $\mathbf{x}$ we estimate $d\theta \sim \delta/\ell$, and the solid angle element being

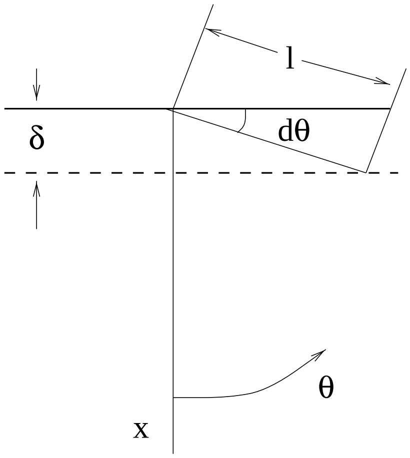

Figure 2. On the anomalous skin-effect.

$$d\Omega \sim 2\pi \, \sin\theta \, d\theta \approx 2\pi\delta/\ell, \qquad (\theta \approx \pi/2).$$

The effective density of electrons participating in the interaction is

$$n_{\text{eff}} \sim n_e \frac{d\Omega}{4\pi} \sim n_e \delta/\ell.$$

So, we come to the conclusion that the effective conductivity should also contain the factor $\sim \delta/\ell$.

The complex coefficient cannot be determined by these simple considerations, but it was obtained in (25.4) (the case $qv_F \gg \omega \gg \tau^{-1}$ for $\sigma_\perp$).

$$\sigma_{\text{eff}} = \sigma_0 \frac{b}{q\ell}$$

where q is the wave vector while $b = 3\pi/8 \sim 1$. This estimate means that the mean free path ℓ is replaced by $1/q$. Now we can use the expression

$$q = \sqrt{4\pi i \omega \sigma_{\text{eff}}/c^2}$$

and get (*Problem 26.1*)

$$q = \left[\frac{4\pi\omega\sigma_0 b}{c^2\ell}\right]^{1/3} e^{i\pi/3}. \tag{26.2}$$

Consequently,

$$\delta = \frac{1}{\operatorname{Im} q} = \frac{2}{\sqrt{3}} \left(\frac{c^2\ell}{4\pi\sigma_0\omega b}\right)^{1/3}. \tag{26.3}$$

The surface impedance could be found as

$$Z = \frac{4\pi\omega}{c^2 q} = \left(\frac{2}{ib}\right)^{1/3} \left(\frac{\pi\omega}{c^2}\right)^{2/3} \left(\frac{\ell}{\sigma_0}\right)^{1/3} (1 - \sqrt{3}).$$

We get: $Z \propto \omega^{2/3}$, $\quad X = R\sqrt{3}$. It is important that the conductivity σ_0 enters only in the combination σ_0/ℓ which is determined only by the electron spectrum.

The typical dependence of the surface conductance R on $\sqrt{\sigma_0}$ is shown in Fig. 3. This dependence is confirmed by the experiment.

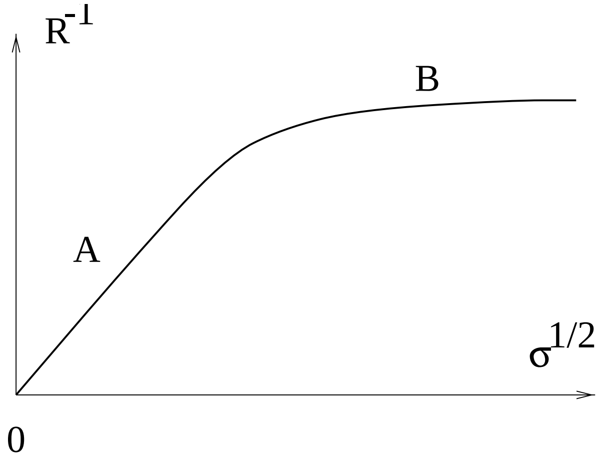

Figure 3. Dependence of the surface conductance on the bulk conductivity.

Finally, let us estimate the border between the normal skin effect and the anomalous one. From the criterion $\delta \approx \ell$ we get

$$\omega \sim c^2 p_F/(2\pi n_e e^2 \ell^3).$$

For $n_e \sim 10^{22}\ \text{cm}^{-3},\ \ p_F \sim 10^{-19}$ g·cm/s we ge

$$\omega \sim 10^{-2}\ell^{-3},\ \text{s}^{-1}$$

where ℓ is measured in cm. For $\ell \sim 10^{-3}$ m we get $\omega \sim 10^7\ \text{s}^{-1}$. We do not demonstrate here quite complicated procedure of solution of the Boltzmann equation.

26.2. Problems

26.1. Derive the equation (26.3).

$$\delta = \frac{1}{\operatorname{Im} q} = \frac{2}{\sqrt{3}} \left(\frac{c^2 \ell}{4\pi\sigma\omega_0 b} \right)^{1/3}.$$

LECTURE 27
Acoustical Properties of Metals.

27.1. Landau Attenuation.

There is another useful approach to study high-frequency properties of good conductors - to induce an acoustic wave and measure its attenuation (or its velocity). The main advantage is that acoustic wave propagate inside the conductors without sufficient damping.

The interaction between the acoustic waves and the electrons can be written as

$$\delta\varepsilon(\mathbf{p},\mathbf{r}) = \Lambda_{ik}(\mathbf{p})u_{ik}(\mathbf{r}) + e\varphi(\mathbf{r}),$$

where $\Lambda_{ik}(\mathbf{p})$ is some tensor which depends on the band structure.

The potential φ should be determined from the Poisson equation. As far as for good conductors $\omega \ll \sigma$ and $q \ll a^{-1}$ one can show that it is enough to request the *neutrality condition* $\delta n_e = 0$, so

$$\int (dp) f_0(\varepsilon_p) = \int (dp) f_0(\varepsilon_p + \Lambda_{ik}(\mathbf{p})u_{ik}(\mathbf{r}) + e\varphi(\mathbf{r})), \qquad \int (dp)\frac{\partial f_0}{\partial \varepsilon}\left[\Lambda_{ik}(\mathbf{p})u_{ik}(\mathbf{r}) + e\varphi(\mathbf{r})\right] = 0$$

so that

$$e\varphi(\mathbf{r}) = -\langle\Lambda_{ik}(\mathbf{p})\rangle_{\epsilon_F} u_{ik}(\mathbf{r}).$$

As a result, we get

$$\delta\varepsilon(\mathbf{p},\mathbf{r}) = \left[\Lambda_{ik}(\mathbf{p}) - \langle\Lambda_{ik}(\mathbf{p})\rangle_{\epsilon_F}\right] u_{ik}(\mathbf{r}) \equiv \lambda_{ik}(\mathbf{p})u_{ik}(\mathbf{r}).$$

We see that it is possible to produce an effective force varying as $\exp(i\mathbf{qr} - \omega t)$ and in such a way investigate the Fourier components of electronic response.

We again will look for the solution of the Boltzmann equation in the form $f = f_0 + a\left(-\frac{\partial f_0}{\partial \varepsilon}\right)$. The field u_{ik} is small, so in the term $\mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} = (\mathbf{v} \cdot \nabla\delta\varepsilon)\frac{\partial f_0}{\partial \varepsilon}$. We then get

$$\left[i(\mathbf{qv} - \omega) + \tau^{-1}\right] a = \sum_{ik} \lambda_{ik}(\mathbf{p})(\mathbf{v}\bigtriangledown)u_{ik}(\mathbf{r}).$$

If we express

$$\sum_{ik} \lambda_{ik}(\mathbf{p})u_{ik} = i\frac{1}{2}\sum_{ik} \lambda_{ik}(\mathbf{p})(q_i u_k + q_k u_i) = i\sum_{ik} \lambda_{ik}(\mathbf{p})q_i u_k = iq\lambda u$$

(where u is the displacement, $\lambda = \sum_{ik} \lambda_{ik}(\mathbf{p}) n_i e_k$, $\mathbf{e}$ is the polarization vector of the wave, while $\mathbf{n} = \mathbf{q}/q$) we obtain

$$\left[i(\mathbf{qv} - \omega) + \tau^{-1}\right] a = -(\mathbf{qv}) q \lambda u.$$

One can immediately express the absorbed power through the distribution function. Indeed,

$$Q = \int (dp)\, \dot{\varepsilon}\, f = \int (dp)\, \dot{\varepsilon}(\mathbf{p}) a(\mathbf{p}) \left(-\frac{\partial f_0}{\partial \varepsilon}\right) = \int d\varepsilon\, g(\varepsilon) \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \langle \dot{\varepsilon}(\mathbf{p}) a(\mathbf{p}) \rangle_{\varepsilon}.$$

This expression should also be averaged over the period $2\pi/\omega$ of the sound wave. This average is calculated in a complex form

$$\begin{aligned} \overline{A(t)B(t)} &= \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \left(Ae^{-i\omega t} + A^* e^{i\omega t}\right) \left(Be^{-i\omega t} + B^* e^{i\omega t}\right) \\ &= AB^* + A^*B = 2\,\mathrm{Re}\,(AB^*)\,. \end{aligned} \tag{27.1}$$

So, for Fermi electrons at low temperature we obtain

$$\begin{aligned} \bar{Q} &= 2g(\epsilon_F)\,\mathrm{Re}\,\langle (-i\omega\delta\varepsilon)^* a \rangle_{\epsilon_F} = 2\omega q^2 g(\epsilon_F) \lambda^2 |u|^2\, \mathrm{Re} \left\langle \frac{(\mathbf{qv})}{i(\mathbf{qv} - \omega) + \tau^{-1}} \right\rangle_{\epsilon_F} \\ &= 2\omega q^2 g(\epsilon_F) \lambda^2 |u|^2 \left\langle \frac{(\mathbf{qv})\tau^{-1}}{(\mathbf{qv} - \omega)^2 + \tau^{-2}} \right\rangle_{\epsilon_F}. \end{aligned}$$

The most interesting case is the one of the so-called short-wave sound

$$q\ell \gg 1$$

which can be met in pure conductors at low temperatures. In this case we see that only the electrons with

$$\mathbf{qv} \approx \omega \to v_{\mathbf{q}} \approx s \tag{27.2}$$

are important. For this condition we can write

$$\left\langle \frac{(\mathbf{qv})\tau^{-1}}{(\mathbf{qv} - \omega)^2 + \tau^{-2}} \right\rangle_{\epsilon_F} \approx \pi \frac{\omega}{q v_F} = \pi \frac{s}{v_F}.$$

As a result

$$Q \approx 2\omega q^2 g(\epsilon_F) \lambda^2 |u|^2 \pi \frac{s}{v_F}.$$

Usually, the attenuation coefficient is measured which is determined as

$$\Gamma = \frac{Q}{\mathcal{E}_{ac} s}$$

where $\mathcal{E}_{ac}$ is the energy density in the wave

$$\mathcal{E}_{ac} = 2\,\rho\omega^2 \overline{u(\mathbf{r},t)^2}/2 = 2\rho\omega^2 |u^2|$$

while ρ is the crystal density. We get

$$\Gamma = \frac{2\omega q^2 g(\epsilon_F) \lambda^2 |u|^2 \pi (s/v_F)}{2\rho\omega^2 |u^2| s} = \pi \frac{g(\epsilon_F)\lambda^2}{\rho s^2} q \frac{s}{v_F}.$$

- Notice, that this result does not depend on τ. This has a straightforward physical meaning: because $v_F \gg s$ most of electrons feel rapidly oscillating field produced by the acoustic wave, the average interaction being small. The electrons with $\mathbf{qv} \approx \omega$ move in resonance with the wave and they feel a slow varying field. The damping due to the resonant electrons is called the *Landau damping*, it has been analyzed at first for plasma waves.

Since λ is of the order of a typical electron energy, for rough estimates we can put $\lambda \sim \epsilon_F$, $\rho s^2 \sim M n_a s^2 \sim n_e \epsilon_F$. So

$$\pi \frac{g(\epsilon_F)\lambda^2}{\rho s^2} \sim 1$$

and $\Gamma/q \sim s/v_F \ll 1$. The coefficient Γ characterizes spatial decay of the wave:

$$\frac{\partial \mathcal{E}_{ac}}{\partial x} = -\Gamma \mathcal{E}_{ac} \, .$$

Thus, we have proved that acoustic waves have relatively small damping.

27.2. Giant Quantum Oscillations.

Quantum transport is out of the scope of this part of the course. Nevertheless, we will consider a very beautiful quantum effect of giant oscillations of the sound absorption.

As we know, in a quantizing magnetic field the energy spectrum consists of the Landau bands

$$\varepsilon(N, p_z) = \varepsilon_N + p_z^2/2m, \qquad \varepsilon_N = \hbar\omega_c(N + 1/2).$$

The energy-momentum conservation laws for the phonon absorption require

$$\varepsilon_{N'} + (p_z + \hbar q_z)^2/2m = \varepsilon_N + p_z^2/2m + \hbar\omega \to \hbar\omega_c(N' - N) + \hbar p_z q_z/2m = \hbar\omega.$$

For realistic sound frequency $\omega \ll \omega_c$ so this condition can be met only for $N' = N$, and we get

$$p_z = m\omega/q_z = msq/q_z = ms/\cos\theta \, , \quad \theta \equiv \angle(\mathbf{q}, \mathbf{H}). \tag{27.3}$$

Consequently, one can control the value of p_z changing the propagation direction.

The Landau bands are shown in Fig. 1. The value of p_z corresponding to the condition

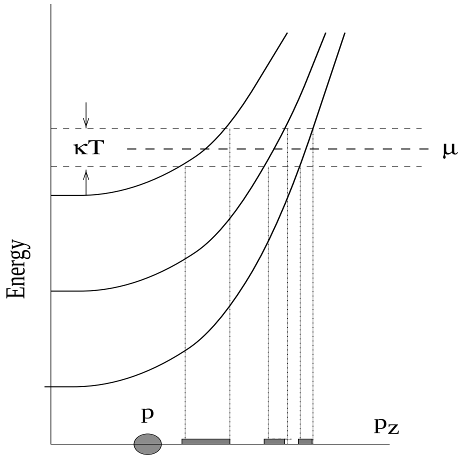

Figure 1. Landau levels.

(27.3) is denoted as p.

On the other hand, only the region near the FS (the layer of the thickness $\sim k_BT$) contributes to the absorption, the corresponding regions for p_z are hatched. If the value p is outside these regions, the absorption is very small. If magnetic field is changed the regions move along the p_z-axis. As a result, the attenuation coefficient Γ experiences giant oscillations. The typical experimental picture is shown in Fig. 2.

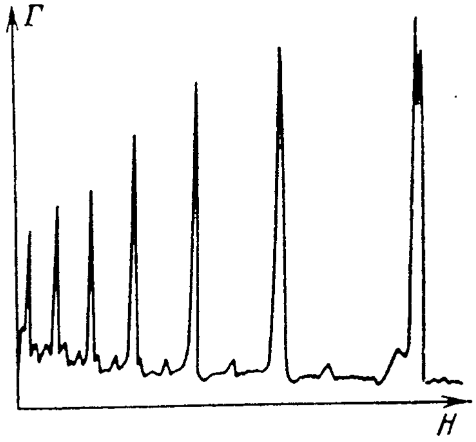

Figure 2. Giant oscillations of sound attenuation.

The giant oscillations provide a useful tool for investigation of the FS.

27.3. Geometric Oscillations

The short wave regime is very useful to study the Fermi surface. Indeed, only the electrons with $\mathbf{v}$ almost perpendicular to $\mathbf{q}$ are important. As a result, only small parts of the electron orbit in a magnetic filed contributes to attenuation.

To illustrate the situation we analyze the case

$$\mathbf{q} \perp \mathbf{H}, \qquad qr_c \ll 1, \qquad \omega_c\tau \gg 1.$$

An electronic orbit is shown in Fig. 3. The dashed lined show the planes where wave's phases are equal An electron spends different time near these planes, the longest being near the points 1 and 2. These points are the ones where the interaction is most important.

Now let us assume that a function is extreme for a given phase difference

$$\varphi = \int_{t_{(1)}}^{t_{(2)}} (\mathbf{qv})\, dt.$$

Then, if the number of wavelengths at the orbit's diameter is changed by an integer n the phase difference is changed by $2\pi n$. Let us direct the x-axis along $\mathbf{q}$. Then, from the equation of motion

$$\frac{dp_y}{dt} = \frac{e}{c} H v_x$$

we obtain

$$\varphi = \frac{cq}{eH}\left[p_y^{(2)} - p_y^{(1)}\right].$$

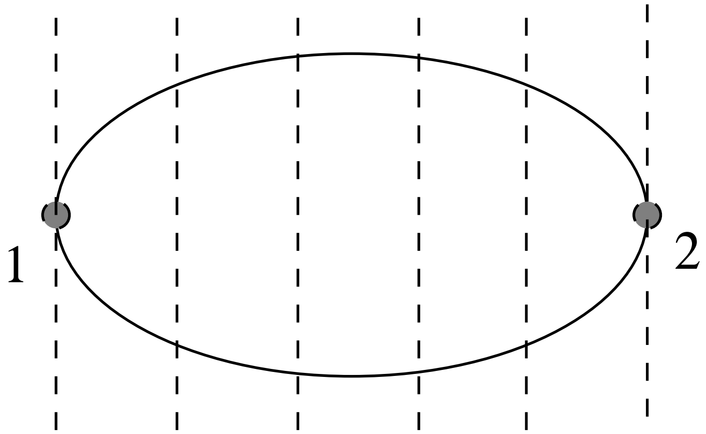

Figure 3. On the geometric oscillations.

Consequently, if $\varphi \gg 1$ the a-function oscillates with magnetic field, the period being

$$\Delta\left(\frac{1}{H}\right) = \frac{2\pi e}{cq}\frac{1}{p_y^{(2)} - p_y^{(1)}}.$$

In fact, the difference $p_y^{(2)} - p_y^{(1)}$ depends on p_z, and genuine oscillations correspond to the extreme cross sections with respect to $p_y^{(2)} - p_y^{(1)}$. As a result, the oscillations are relatively small (as in the case of the cyclotron resonance). The effect is more pronounced for open orbits.

The geometric oscillations provide a very powerful way to measure diameters of the FS.

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