Solid State Theory I

Alexander Shnirman

Institute TKM, Karlsruhe Institute of Technology, Karlsruhe, Germany

(Dated: February 13, 2017)

Contents

I. GENERAL INFORMATION

Literature:

1) G. Czycholl, Theoretische Festkörperphysik.

2) C. Kittel, Quantum Theory of Solids.

3) N.W. Ashcroft and N.D. Mermin, Solid State Physics.

4) A. A. Abrikosov, Fundamentals of the theory of metals.

5) J.M. Ziman, Principles of the Theory of Solids.

Superconductivity:

6) J.R. Schrieffer, Theory of Superconductivity. (Chapters 1-4)

7) M. Tinkham, Introduction to Superconductivity.

II. BORN-OPPENHEIMER APPROXIMATION

If we are interested in not very high energies it is meaningful to split an atom into, on one hand, an *ion*, which contains the nucleus and the strongly coupled electrons and, on the other hand, the weakly coupled electrons. For simplicity we consider a situation when there is one weakly coupled electron per atom. Then ions have charge $+e$ and the electrons $-e$.

The Hamiltonian of N ions and N electrons reads:

$$H = H_{\rm el} + H_{\rm ion} + H_{\rm el-ion} \ , \tag{1}$$

where

$$H_{\rm el} = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \ , \tag{2}$$

$$H_{\rm ion} = \sum_n \frac{\vec{P}_n^{\,2}}{2M} + \sum_{n<m} V_{\rm ion}(\vec{R}_n - \vec{R}_m) \ , \tag{3}$$

$$H_{\rm el-ion} = \sum_{i,n} V_{\rm el-ion}(\vec{r}_i - \vec{R}_n) \ . \tag{4}$$

Here $\vec{p}_i \equiv -i\hbar\partial/\partial\vec{r}_i$ and $\vec{P}_n \equiv -i\hbar\partial/\partial\vec{R}_n$.

Rather simple-mindedly we could assume $V_{\rm ion}(\vec{R}_n - \vec{R}_m) = \frac{e^2}{|\vec{R}_n - \vec{R}_m|}$ and $V_{\rm el-ion}(\vec{r}_i - \vec{R}_n) = -\frac{e^2}{|\vec{r}_i - \vec{R}_n|}$. These interaction potentials are, of course, a bit naive. There will be corrections due to the fact that ions have structure (are not point-like particles).

Ions are much heavier than electrons: $m/M \ll 10^{-3}$. Thus electrons move much faster. The Born-Oppenheimer approximation is appropriate.

First one solves the problem for the electrons only considering the positions of ions fixed. The wave function of the electrons (the coordinates $\vec{R}_n$ are parameters) $\psi^{\rm el} = \psi^{\rm el}(\vec{r}_1, \ldots, \vec{r}_N; \vec{R}_1, \ldots, \vec{R}_N)$ satisfies the Schrödinger equation

$$[H_{\rm el} + H_{\rm el-ion}]\psi^{\rm el}_\alpha = E^{\rm el}_\alpha \psi^{\rm el}_\alpha \ . \tag{5}$$

α numbers all the eigenstates. We only need the ground state.

The eigenenergies are functions of ions' coordinates: $E^{\rm el}_\alpha(\vec{R}_1, \ldots, \vec{R}_N)$.

The wave function of the total system is assumed to have a form (this is an ansatz): $\psi = \sum_\alpha \phi_\alpha(\vec{R}_1, \ldots, \vec{R}_N)\psi^{\rm el}_\alpha(\vec{r}_1, \ldots, \vec{r}_N; \vec{R}_1, \ldots, \vec{R}_N)$.

The Schrödinger equation reads:

$$H\psi \ = \ [H_{\rm el} + H_{\rm ion} + H_{\rm el-ion}] \sum_\alpha \phi_\alpha \psi^{\rm el}_\alpha = [H_{\rm el} + H_{\rm el-ion}] \sum_\alpha \phi_\alpha \psi^{\rm el}_\alpha + H_{\rm ion} \sum_\alpha \phi_\alpha \psi^{\rm el}_\alpha \tag{6}$$

$$= \ \sum_\alpha E^{\rm el}_\alpha \phi_\alpha \psi^{\rm el}_\alpha + \sum_\alpha (H_{\rm ion}\phi_\alpha)\psi^{\rm el}_\alpha + \sum_\alpha \sum_n \frac{1}{2M}\left[\phi_\alpha(\vec{P}^2_n \psi^{\rm el}_\alpha) + 2(\vec{P}_n\phi_\alpha)(\vec{P}_n\psi^{\rm el}_\alpha)\right] \tag{7}$$

We project $(E - H)\psi = 0$ upon $\psi^{\rm el}_\beta$. This gives

$$\psi^{{\rm el},*}_\beta H\psi = E\phi_\beta = E^{\rm el}_\beta \phi_\beta + H_{\rm ion}\phi_\beta + \sum_\alpha A_{\beta\alpha} \ , \tag{8}$$

where

$$A_{\beta\alpha} = \sum_n \frac{1}{2M}\left[\phi_\alpha(\psi^{{\rm el},*}_\beta \vec{P}^2_n \psi^{\rm el}_\alpha) + 2(\vec{P}_n\phi_\alpha)(\psi^{{\rm el},*}_\beta \vec{P}_n \psi^{\rm el}_\alpha)\right] \tag{9}$$

Our aim is to argue that the terms $A_{\beta,\alpha}$ can be neglected due to the smallness of the ratio m/M. Since the interaction between ions and electrons depends only on the distance between them: $V_{\rm el-ion}(\vec{r}_i - \vec{R}_n)$, so does the wave function $\psi^{\rm el}$. Thus $|P\psi^{\rm el}| \sim |p\psi^{\rm el}|$. So, for example, we can estimate the first term of $A_{\beta\alpha}$ as

$$\sum_n \frac{P^2_n}{2M}\psi^{\rm el} \approx \frac{1}{M}\sum_i \frac{p^2_i}{2}\psi^{\rm el} \approx \frac{m}{M}E^{\rm el}_{\rm kin} \ . \tag{10}$$

The electronic kinetic energy can be, in turn, estimated from the characteristic atomic energy

$$\epsilon_0 = \frac{e^2}{2a_0} = \frac{me^4}{\hbar^2} \approx 13,6{\rm eV} \approx 0.2 \cdot 10^{-10}{\rm erg} \ ,$$

where $a_0 = \frac{\hbar^2}{me^2} \approx 0.5 \cdot 10^{-8} cm$ is the Bohr radius. The estimate reads $E^{\rm el}_{\rm kin}/N \sim \epsilon_0$. Thus the first term of (9) is estimated as $N(m/M)\epsilon_0$.

To estimate the second term of $A_{\beta\alpha}$ as well as the energy per ion stored in $E^{\rm el}_\beta\phi_\beta + H_{\rm ion}\phi_\beta$ we think of each ion as of a harmonic oscillator in a potential well described by the spring constant, K, of the order $K \sim \epsilon_0/a_0^2$. This is because shifting an ion by a distance of order a_0, i.e., by a distance of order of the distance between the ions and the electrons should cost approximately one electronic energy. Then the characteristic energy of an ion is given by $\epsilon_i \sim \hbar\sqrt{K/M} \sim \epsilon_0\sqrt{m/M}$. Since the potential and the kinetic energy of an oscillator are equal we obtain an estimate for the momentum of the ion: $P^2/M \sim \epsilon_i \sim \epsilon_0\sqrt{m/M}$. Thus $P \sim \sqrt{M\epsilon_i} \sim \sqrt{\epsilon_0\sqrt{Mm}} \sim (M/m)^{1/4}\sqrt{\epsilon_0 m} \sim (M/m)^{1/4}p$, where p is the characteristic electron momentum $p \sim \sqrt{\epsilon_0 m} \sim \hbar/a_0$.

Thus, we can estimate the second term of (9) as $NpP/M \sim N(m/M)^{3/4}\epsilon_0$. Finally, the ionic energy stored in $E^{\rm el}_\beta\phi_\beta + H_{\rm ion}\phi_\beta$ is estimated as $NP^2/M \sim N(m/M)^{1/2}\epsilon_0$. This energy is larger than both terms of (9).

Neglecting (9) we obtain the approximate Schrödinger equation for the ions:

$$[H_{\rm ion} + E^{\rm el}(\vec{R}_1, \ldots, \vec{R}_N)]\phi = E\phi \tag{11}$$

Thus the total interaction potential for the ions reads

$$V^{\rm total}_{\rm ion} = \sum_{n<m} V_{\rm ion}(\vec{R}_n - \vec{R}_m) + E^{\rm el}(\vec{R}_1, \ldots, \vec{R}_N)\ . \tag{12}$$

This potential should have an absolute minimum when the ions take places in the lattice of the solid. (We do not even try to prove it). The electrons adjust themselves to the instantaneous state of the ions.

At low temperatures it is sufficient to consider only small deviations of the ions from the lattice positions. These are called "phonons".

One arrives then for the ion positions at

$$H_{\rm ion} + E^{\rm el}(\vec{R}_1, \ldots, \vec{R}_N) = H^0_{\rm ion} + H_{\rm phonon}\ . \tag{13}$$

while for the electrons one has

$$H_{\rm el-ion} = H^0_{\rm el-ion} + H_{\rm el-phonon} \tag{14}$$

III. BRAVAIS AND RECIPROCAL LATTICES

To be written.

IV. BLOCH THEOREM

Potential of ions are periodic with periods being the vectors of the Bravais lattice.

$$H = -\frac{\hbar^2}{2m}\Delta + U(\vec{r}) \ , \tag{15}$$

with $U(\vec{r}+\vec{R}) = U(\vec{r})$ and $\vec{R} \in$ Bravais Lattice.

We look for eigenstates:

$$H\psi = E\psi \tag{16}$$

Bloch Theorem: eigenstates have the following form:

$$\psi_{n.\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_{n,k}(\vec{r}) \ , \tag{17}$$

where $u_{n,k}(\vec{r})$ is periodic, i.e., $u_{n,\vec{k}}(\vec{r}+\vec{R}) = u_{n,\vec{k}}(\vec{r})$. In addition $\vec{k} \in$ first Brillouin zone while $n \in \mathbf{Z}$.

A. 1-st proof

We define translation operator $T_{\vec{R}}$ so that $T_{\vec{R}} f(\vec{r}) = f(\vec{r}+\vec{R})$.

1) $T_{\vec{R}}$ is unitary. (Unitary operators satisfy $U^{-1} = U^{\dagger}$). We have obviously

$$T_{\vec{R}}^{-1} = T_{-\vec{R}} \tag{18}$$

To obtain $T_{\vec{R}}^{\dagger}$ we note the following

$$\begin{aligned} \langle \phi_1 | \, T_{\vec{R}} \, | \phi_2 \rangle &= \int d^3 r \phi_1^*(\vec{r}) T_{\vec{R}} \phi_2(\vec{r}) \\ &= \int d^3 r \phi_1^*(\vec{r}) \phi_2(\vec{r}+\vec{R}) \\ &= \int d^3 r \phi_1^*(\vec{r}-\vec{R}) \phi_2(\vec{r}) \\ &= \int d^3 r (T_{-\vec{R}} \phi_1(\vec{r}))^* \phi_2(\vec{r}) \end{aligned} \tag{19}$$

Thus $T_{\vec{R}}^{\dagger} = T_{-\vec{R}} = T_{\vec{R}}^{-1}$.

2) $T_{\vec{R}}$ commutes with H, $[T_{\vec{R}}, H] = 0$.

$$T_{\vec{R}} H\psi = H(\vec{r}+\vec{R})\psi(\vec{r}+\vec{R}) = H(\vec{r})\psi(\vec{r}+\vec{R}) = H T_{\vec{R}}\psi \tag{20}$$

3) All operators $T_{\vec{R}}$ form an Abelian group, i.e., commute with each other.

$$T_{\vec{R}_1} T_{\vec{R}_2} \psi = T_{\vec{R}_2} T_{\vec{R}_1} \psi = \psi(\vec{r} + \vec{R}_1 + \vec{R}_2) \tag{21}$$

$$T_{\vec{R}_1} T_{\vec{R}_2} = T_{\vec{R}_2} T_{\vec{R}_1} = T_{\vec{R}_1 + \vec{R}_2} \tag{22}$$

This means that the set of operators H, $T_{\vec{R}}$ (all of them) have common eigenstates (a full set of them).

$$H\psi = E\psi \tag{23}$$

$$T_{\vec{R}}\psi = c_{\vec{R}}\psi \tag{24}$$

From unitarity follows $|c_{\vec{R}}| = 1$. From commutativity of $T_{\vec{R}}$: $c_{\vec{R}_1} c_{\vec{R}_2} = c_{\vec{R}_1 + \vec{R}_2}$.

$\vec{R}$ are the vectors of Bravais lattice. Thus $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$. This gives

$$c_{\vec{R}} = (c_{\vec{a}_1})^{n_1} (c_{\vec{a}_2})^{n_2} (c_{\vec{a}_3})^{n_3} \tag{25}$$

We define $c_{\vec{a}_j} = e^{2\pi i x_j}$. Then

$$c_{\vec{R}} = e^{2\pi i (n_1 x_1 + n_2 x_2 + n_3 x_3)} \tag{26}$$

Now we start using the reciprocal lattice. We define $\vec{k} = \sum x_j \vec{b}_j$ where $\vec{b}_j$ are the elementary vectors of the reciprocal lattice. Then we can rewrite as follows

$$c_{\vec{R}} = e^{i\vec{k}\vec{R}} \tag{27}$$

Indeed, $\vec{k} \cdot \vec{R} = \sum_{jl} x_j n_l \vec{b}_j \cdot \vec{a}_l = 2\pi \sum_j x_j n_j$ (for reciprocal lattice we have $\vec{b}_j \cdot \vec{a}_l = 2\pi\delta_{jl}$).

Thus we obtain

$$T_{\vec{R}}\psi = e^{i\vec{k}\cdot\vec{R}}\psi \ , \tag{28}$$

i.e., each eigenvector is characterized by a vector $\vec{k}$. Thus we have

$$\psi = e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) \ , \tag{29}$$

where $u(\vec{r} + \vec{R}) = u(\vec{r})$. (We can define u as $e^{-i\vec{k}\cdot\vec{r}}\psi$).

Thus all the eigenstates are split into families characterized by different vectors $\vec{k}$. Actually only $\vec{k}$ belonging to the first Brillouin zone (Wigner-Seitz unit of the reciprocal lattice) (or any other primitive unite of the reciprocal lattice) give different families. This follows from $e^{i(\vec{k}+\vec{K})\vec{R}} = e^{i\vec{k}\vec{R}}$. Indeed, if $\vec{k}$ is outside the first Brillouin zone, then we can find $\vec{K}$ in the reciprocal lattice so that $\vec{q} = \vec{k} - \vec{K}$ is in the first Brillouin zone. Then we use

$$\psi = e^{i\vec{k}\cdot\vec{r}}u(\vec{r}) = e^{i\vec{q}\cdot\vec{r}}e^{-i\vec{K}\cdot\vec{r}}u(\vec{r}) = e^{i\vec{q}\cdot\vec{r}}\tilde{u}(\vec{r}) \ , \tag{30}$$

where $\tilde{u}(\vec{r}) \equiv e^{-i\vec{K}\cdot\vec{r}}u(\vec{r})$ and $\tilde{u}(\vec{r}+\vec{R}) = \tilde{u}(\vec{r})$.

In each family introduce index n counting the states of the family. The functions u depend, then, on $\vec{k} \in$ first B.Z. and on n. Thus, finally

$$\psi = e^{i\vec{k}\cdot\vec{r}}u_{n,\vec{k}}(\vec{r}) \tag{31}$$

B. Born-von Karmann boundary conditions

The B-v-K conditions read:

$$\psi(\vec{r} + N_j\vec{a}_j) = \psi(\vec{r}) \ , \tag{32}$$

for $j = 1, 2, 3$ and $N_1, N_2, N_3 \gg 1$. The total number of primitive cells is then $N_1N_2N_3$.

This limits the possible values of $\vec{k}$. Namely we must have $e^{iN_j\vec{k}\cdot\vec{a}_j} = 1$. With $\vec{k} = \sum x_j\vec{b}_j$ where $\vec{b}_j$ are the elementary vectors of the reciprocal lattice we obtain $x_j = m_j/N_j$.

Although it would be better to chose all allowed values of $\vec{k}$ within the first Brillouin zone it is simpler here to use a different primitive cell in the reciprocal lattice. Namely we can chose $m_j = 0, 1, ..., N_j - 1$. This gives

$$\vec{k} = \sum_j \frac{m_j}{N_j}\vec{b}_j \ , \tag{33}$$

for $m_j = 0, 1, ..., N_j - 1$. There are $N = N_1N_2N_3$ allowed vectors $\vec{k}$.

The volume in the reciprocal lattice per one vector $\vec{k}$:

$$\begin{aligned} \Delta k_1\Delta k_2\Delta k_3 = \Delta\vec{k}_1 \cdot (\Delta\vec{k}_2 \times \Delta\vec{k}_3) = \frac{\vec{b}_1}{N_1} \cdot \left(\frac{\vec{b}_2}{N_2} \times \frac{\vec{b}_3}{N_3}\right) \\ = \frac{1}{N}\frac{(2\pi)^3}{v} \ , \end{aligned} \tag{34}$$

where $v \equiv \frac{V}{N} = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$.

To calculate a sum over the whole primitive cell (1-st B.Z.) we use

$$\sum_{\vec{k}} = \int \frac{d^3k}{\Delta k_1 \Delta k_2 \Delta k_3} = \frac{Nv}{(2\pi)^3} \int d^3k = \frac{V}{(2\pi)^3} \int d^3k \tag{35}$$

C. 2-nd proof

We expand both the wave function and the potential in the basis of momentum states, i.e., plane waves. Thus:

$$\psi(\vec{r}) = \sum_{\vec{q}} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}} \tag{36}$$

The boundary conditions, e.g., those of Born-von Karmann make the set of $\vec{k}$-vectors discrete:

$$\vec{k} = \sum_j \frac{m_j}{N_j} \vec{b}_j \ , \tag{37}$$

where $m_j \in \mathbf{Z}$. The sum is not limited to the first Brillouin zone.

The potential energy is a periodic function (Bravais-lattice). Thus it can be expanded as

$$U(\vec{r}) = \sum_{\vec{Q}} U_{\vec{Q}} e^{i\vec{Q}\cdot r} \ , \tag{38}$$

where $\vec{Q}$ runs over the reciprocal lattice. We have

$$U_{\vec{Q}} = \frac{1}{v} \int_{P.U.} dV\, U(\vec{r}) e^{-i\vec{Q}\cdot\vec{r}} \ , \tag{39}$$

where the integration is over a primitive unit of the Bravais lattice and v is the volume of the primitive unit. Since U is real (hermitian) we have $U_{-\vec{Q}} = U^*_{\vec{Q}}$.

The Schrödinger equation now reads

$$\begin{aligned} E\psi &= E \sum_{\vec{q}} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}} = \left(-\frac{\hbar^2}{2m} \nabla^2 + U \right) \psi \\ &= \sum_{\vec{q}} \frac{\hbar^2 q^2}{2m} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}} + \sum_{\vec{Q},\vec{q}} U_{\vec{Q}} c_{\vec{q}}\, e^{i(\vec{Q}+\vec{q})\cdot\vec{r}} \\ &= \sum_{\vec{q}} \frac{\hbar^2 q^2}{2m} c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}} + \sum_{\vec{Q},\vec{q}} U_{\vec{Q}} c_{\vec{q}-\vec{Q}}\, e^{i\vec{q}\cdot\vec{r}} \ , \end{aligned} \tag{40}$$

where in the last line we substituted $\vec{q} \to \vec{q} - \vec{Q}$. The coefficients in front of each harmonics must sutisfy this equation. Thus

$$\left(E - \frac{\hbar^2 q^2}{2m} \right) c_{\vec{q}} = \sum_{\vec{Q}} U_{\vec{Q}} c_{\vec{q}-\vec{Q}} \ . \tag{41}$$

We see that only $\vec{q}$'s related by a vector of the reciprocal lattice influence each other. Each such family can be characterized by a vector in the 1-st Brillouin zone. Thus, in each family we introduce $\vec{k}$ and all the $\vec{q}$'s in the family are given by $\vec{k}+\vec{K}$, where $\vec{K}$ runs over the reciprocal lattice. This gives

$$\left(E - \frac{\hbar^2(\vec{k}+\vec{K})^2}{2m}\right) c_{\vec{k}+\vec{K}} = \sum_{\vec{Q}} U_{\vec{Q}} c_{\vec{k}+\vec{K}-\vec{Q}} \ . \tag{42}$$

The number of equations for each $\vec{k} \in$ 1-st B.Z. is infinite as $\vec{K}$ runs over the whole reciprocal lattice.

We will use index n to count solutions of Eq. (42). The solution number n is a set $c_{n,\vec{k}+\vec{K}}$ for all vectors $\vec{K} \in$ reciprocal lattice. Since Eq. (42) is a Schrödinger equation and the sets $c_{n,\vec{k}+\vec{K}}$ are the wave functions, they are orthonormal, i.e.,

$$\sum_{\vec{K}} c^*_{n_1,\vec{k}+\vec{K}} c_{n_2,\vec{k}+\vec{K}} = \delta_{n_1,n_2} \ , \tag{43}$$

and complete

$$\sum_{n} c^*_{n,\vec{k}+\vec{K}_1} c_{n,\vec{k}+\vec{K}_2} = \delta_{\vec{K}_1,\vec{K}_2} \ . \tag{44}$$

(Note that $\vec{K}$ serves here as coordinate of the wave function.)

The eigenstates in the coordinate representation then read

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{K}} c_{n,\vec{k}+\vec{K}}\, e^{i(\vec{k}+\vec{K})\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{K}} c_{n,\vec{k}+\vec{K}}\, e^{i\vec{K}\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r}) \ , \tag{45}$$

where

$$u_{n,\vec{k}}(\vec{r}) \equiv \sum_{\vec{K}} c_{n,\vec{k}+\vec{K}}\, e^{i\vec{K}\cdot\vec{r}} \ . \tag{46}$$

Now, if we slightly change $\vec{k}$, only the LHS of the equation (42) slightly changes. One can expect that in each family n the states and the eigen-energies change smoothly. We obtain bands.

D. Properties of the Bloch states

- Bloch states are orthonormal.

We obtain

$$\int d^3r\, \psi^*_{n_1,\vec{k}_1}(\vec{r})\psi_{n_2,\vec{k}_2}(\vec{r}) = \sum_{\vec{K}_1,\vec{K}_2} c^*_{n_1,\vec{k}_1+\vec{K}_1} c_{n_2,\vec{k}_2+\vec{K}_2} \int d^3r\, e^{i(\vec{k}_2+\vec{K}_2-\vec{k}_1-\vec{K}_1)}$$
$$= V \sum_{\vec{K}_1,\vec{K}_2} c^*_{n_1,\vec{k}_1+\vec{K}_1} c_{n_2,\vec{k}_2+\vec{K}_2} \delta_{\vec{k}_2+\vec{K}_2,\vec{k}_1+\vec{K}_1} \ , \qquad (47)$$

Since $\vec{k}_1$ and $\vec{k}_2$ both are in the 1-st B.Z. we have $\delta_{\vec{k}_2+\vec{K}_2,\vec{k}_1+\vec{K}_1} = \delta_{\vec{k}_1,\vec{k}_2}\delta_{\vec{K}_1,\vec{K}_2}$. Thus

$$\int d^3r\, \psi^*_{n_1,k_1}(\vec{r})\psi_{n_2,k_2}(\vec{r}) = V\delta_{\vec{k}_1,\vec{k}_2} \sum_{\vec{K}_1} c^*_{n_1,\vec{k}_1+\vec{K}_1} c_{n_2,\vec{k}_1+\vec{K}_1}$$
$$= V\delta_{\vec{k}_1,\vec{k}_2}\, \delta_{n_1,n_2} \ . \qquad (48)$$

In the thermodynamic limit $V \to \infty$ we have $V\delta_{\vec{k}_1,\vec{k}_2} \to (2\pi)^3\delta(\vec{k}_1 - \vec{k}_2)$.

- Basis of Bloch states is complete.

$$\sum_n \sum_{\vec{k}\in 1.\mathrm{B.Z}} \psi^*_{n,\vec{k}}(\vec{r}_1)\psi_{n,\vec{k}}(\vec{r}_2)$$
$$= \sum_n \sum_{\vec{k}\in 1.\mathrm{B.Z}} \sum_{\vec{K}_1,\vec{K}_2} c^*_{n,\vec{k}+\vec{K}_1} c_{n,\vec{k}+\vec{K}_2}\, e^{-i\vec{K}_1\cdot\vec{r}_1} e^{i\vec{K}_2\cdot\vec{r}_2} e^{i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)}$$
$$= \sum_{\vec{k}\in 1.\mathrm{B.Z}} \sum_{\vec{K}} e^{i(\vec{k}+\vec{K})\cdot(\vec{r}_2-\vec{r}_1)} = V\delta(\vec{r}_2 - \vec{r}_1) \ . \qquad (49)$$

- Crystal momentum

  The vector $\hbar\vec{k}$ is not the momentum and the Bloch states are not eigenstates of the momentum operator. Indeed

$$\vec{p}\psi_{n,\vec{k}} = -i\hbar\vec{\nabla}\psi_{n,\vec{k}} = \hbar\vec{k}\psi_{n,\vec{k}} + e^{i\vec{k}\cdot\vec{r}}\vec{\nabla}u_{n,\vec{k}} \ . \qquad (50)$$

  The vector $\hbar\vec{k}$ is called "crystal momentum".

- Discreetness of states indexed by n.

  The Schrödinger equation for a given $\vec{k}$

$$\left(E - \frac{\hbar^2(\vec{k}+\vec{K})^2}{2m}\right) c_{\vec{k}+\vec{K}} = \sum_{\vec{Q}} U_{\vec{Q}} c_{\vec{k}+\vec{K}-\vec{Q}} \qquad (51)$$

  can be rewritten for the function

$$u_{\vec{k}}(\vec{r}) \equiv \sum_{\vec{K}} c_{\vec{k}+\vec{K}}\, e^{i\vec{K}\cdot\vec{r}} \ . \qquad (52)$$

as

$$\left(E - \frac{\hbar^2(\vec{k} - i\vec{\nabla})^2}{2m}\right) u_{\vec{k}}(\vec{r}) = U(\vec{r}) u_{\vec{k}}(\vec{r}) \ , \tag{53}$$

accompanied by the periodic boundary conditions $u_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r})$. The problem thus must be solved in one primitive unit of the Bravais lattice and can give only discreet spectrum.

- The eigenenergies $E_{\vec{n},\vec{k}}$ are continuous (and analytic) functions of $\vec{k}$. Quite clear from the Schrödinger equation (53). No proof provided.

- Extension to the whole reciprocal lattice.

  One can extend the definition of Bloch states $\psi_{n,\vec{k}}$ for $\vec{k}$ not necessarily being in the 1-st. B.Z. Then this function is a periodic function of $\vec{k}$ with the periods given by the reciprocal lattice.

V. ALMOST FREE ELECTRONS.

We start from the Schrödinger equation

$$\left(E_{n,\vec{k}} - \frac{\hbar^2(\vec{k} + \vec{K})^2}{2m}\right) c_{n,\vec{k}+\vec{K}} = \sum_{\vec{Q}} U_{\vec{Q}} c_{n,\vec{k}+\vec{K}-\vec{Q}} \tag{54}$$

for the coefficients of the function

$$u_{n,\vec{k}}(\vec{r}) \equiv \sum_{\vec{K}} c_{n,\vec{k}+\vec{K}} \, e^{i\vec{K}\cdot\vec{r}} \ . \tag{55}$$

Renaming $\vec{K}_1 \equiv \vec{K}$ and $\vec{K}_2 \equiv \vec{K} - \vec{Q}$ we obtain

$$\left(E_{n,\vec{k}} - \frac{\hbar^2(\vec{k} + \vec{K}_1)^2}{2m}\right) c_{n,\vec{k}+\vec{K}_1} = \sum_{\vec{K}_2} U_{\vec{K}_1-\vec{K}_2} c_{n,\vec{k}+\vec{K}_2} \tag{56}$$

We start from the limit of free electrons $U = 0$. The solutions of (56) are trivial: for each n there is $\vec{K}_n$ such that

$$E_{n,\vec{k}} = \epsilon^{(0)}_{n,\vec{k}} \equiv \frac{\hbar^2(\vec{k} + \vec{K}_n)^2}{2m} \tag{57}$$

and $c_{n,\vec{k}+\vec{K}_l} = \delta_{n,l}$.

Now consider $U \neq 0$. First, $U_{\vec{Q}=0}$ gives a total shift of energy. Thus, we take it into account and put $U_{\vec{Q}=0} = 0$. There are two possibilities:

1) For a given $\vec{k}$ there are no other vectors of the reciprocal lattice $\vec{K}_l$ such that $\epsilon^{(0)}_{l,\vec{k}} \approx \epsilon^{(0)}_{n,\vec{k}}$ (more precisely the difference of the two energies of order or smaller than U). Then we are in the situation of the non-degenerate perturbation theory. This gives for $l \neq n$

$$c_{n,\vec{k}+\vec{K}_l} = \frac{U_{\vec{K}_l - \vec{K}_n}}{\epsilon^{(0)}_{n,\vec{k}} - \epsilon^{(0)}_{l,\vec{k}}} + O(U^2) \tag{58}$$

and for the band energy we obtain

$$E_{n,\vec{k}} = \epsilon^{(0)}_{n,\vec{k}} + \sum_{l \neq n} \frac{U_{\vec{K}_n - \vec{K}_l} U_{\vec{K}_l - \vec{K}_n}}{\epsilon^{(0)}_{n,\vec{k}} - \epsilon^{(0)}_{l,\vec{k}}} + O(U^3) \tag{59}$$

The bands repel each other.

2) There are some (at least one in addition to $\vec{K}_n$) vectors $\vec{K}_l \neq \vec{K}_n$ such that $\epsilon^{(0)}_{l,\vec{k}} \approx \epsilon^{(0)}_{n,\vec{k}}$. We denote all m such vectors (incluing $\vec{K}_n$) by $\vec{K}_l$ with $l = 1, \ldots, m$. The degenerate perturbation theory tells us to solve the following system of m equations ($j = 1, \ldots, m$):

$$\left(E_{\vec{k}} - \frac{\hbar^2 (\vec{k} + \vec{K}_j)^2}{2m} \right) c_{\vec{k}+\vec{K}_j} = \sum_{i=1}^{m} U_{\vec{K}_j - \vec{K}_i} c_{\vec{k}+\vec{K}_i} \tag{60}$$

Double degeneracy. Consider a special (but probably the most important) case when

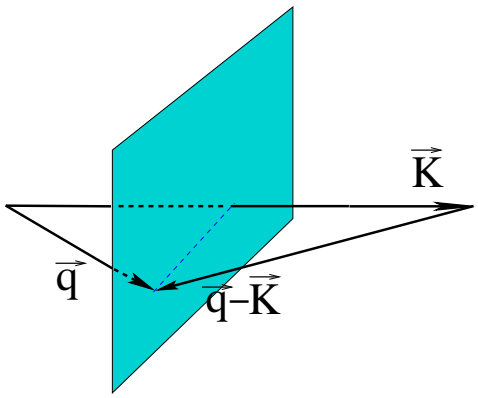

FIG. 1: Bragg plane.

the degeneracy is between two energies corresponding to vectors $\vec{K}_1$ and $\vec{K}_2$. First we note that the condition on $\vec{k}$ for this to happen coincides with the one for the Bragg scattering of the X-rays. Namely, the condition of degeneracy reads $|\vec{k} + \vec{K}_1| = |\vec{k} + \vec{K}_2| = |\vec{k} + \vec{K}_1 - (\vec{K}_1 - \vec{K}_2)|$. Introducing $\vec{q} \equiv \vec{k} + \vec{K}_1$ and $\vec{K} \equiv \vec{K}_1 - \vec{K}_2$ ($\vec{K} \in$ reciprocal lattice) we see that the relation between the wave vectors in the expanded band picture $\vec{q} = \vec{k} + \vec{K}_1$ and $\vec{q} - \vec{K} = \vec{k} + \vec{K}_2$ is like between the wave vectors of the incident and the reflected waves in

the Bragg scattering. Both have to end at the so called "Bragg plane" as depicted in Fig. 1. In particular the condition on $\vec{q}$ reads $|\vec{q}\cdot\vec{K}| = \frac{1}{2}|\vec{K}|$.

The eigenvalues are determined as zeros of the determinant of the following matrix

$$\begin{pmatrix} E_{\vec{k}} - \epsilon^{(0)}_{1,k} & -U_{\vec{K}} \\ -U_{-\vec{K}} & E_{\vec{k}} - \epsilon^{(0)}_{2,k} \end{pmatrix} \tag{61}$$

The solutions read

$$E_{\vec{k}} = \frac{\epsilon^{(0)}_{1,k} + \epsilon^{(0)}_{2,k}}{2} \pm \sqrt{\left(\frac{\epsilon^{(0)}_{1,k} - \epsilon^{(0)}_{2,k}}{2}\right)^2 + |U_{\vec{K}}|^2} \tag{62}$$

In particular, the splitting exactly at the Bragg plain, where $\epsilon^{(0)}_{1,k} = \epsilon^{(0)}_{2,k}$ is given by $E_{2,k} - E_{1,k} = 2|U_{\vec{K}}|$.

A. Example in 1D

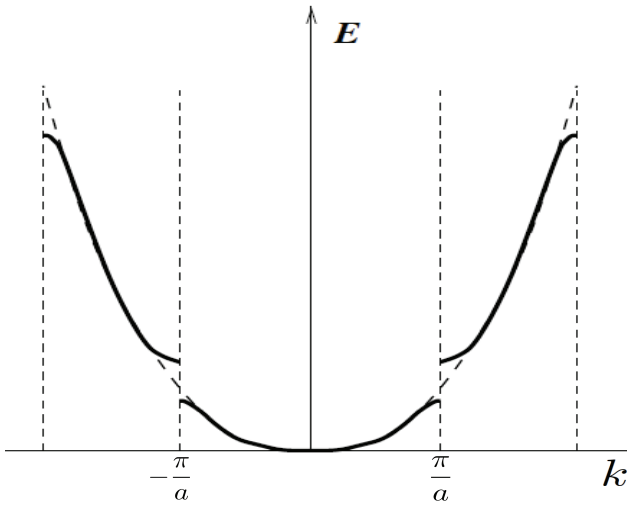

FIG. 2: Extended zone scheme in 1D.

Extended, reduced, and periodic zone schemes.

B. Lattice with basis, structure factor

Assume there are identical ions in positions $\vec{d}_j$ (basis) in each primitive cell of the Bravais lattice characterized by vector $\vec{R}$. Each ion creates a potential $\phi(\vec{r}-\vec{R}-\vec{d}_j)$, so that

$$U(\vec{r}) = \sum_{\vec{R}} \sum_{j} \phi(\vec{r}-\vec{R}-\vec{d}_j) \ . \tag{63}$$

The resulting potential $U(\vec{r})$ is still periodic with periods being the vectors of the Bravais lattice, $U(\vec{r}+\vec{R}) = U(\vec{r})$.

We need

$$\begin{aligned} U_{\vec{K}} &= \frac{1}{v}\int_{P.U.} dV\, U(\vec{r}) e^{-i\vec{K}\cdot\vec{r}} = \frac{1}{v}\int_{P.U.} dV e^{-i\vec{K}\cdot\vec{r}} \sum_{\vec{R}} \sum_{j} \phi(\vec{r}-\vec{R}-\vec{d}_j) \\ &= \frac{1}{v}\int_{all\ \ space} dV e^{-i\vec{K}\cdot\vec{r}} \sum_{j} \phi(\vec{r}-\vec{d}_j) = \frac{1}{v}\phi(\vec{K}) S^*_{\vec{K}} \ , \end{aligned} \tag{64}$$

where

$$\phi(\vec{K}) \equiv \int_{all\ \ space} \phi(\vec{r}) e^{-i\vec{K}\cdot\vec{r}} \ , \tag{65}$$

and

$$S_{\vec{K}} = \sum_{j} e^{i\vec{K}\cdot\vec{d}_j} \ . \tag{66}$$

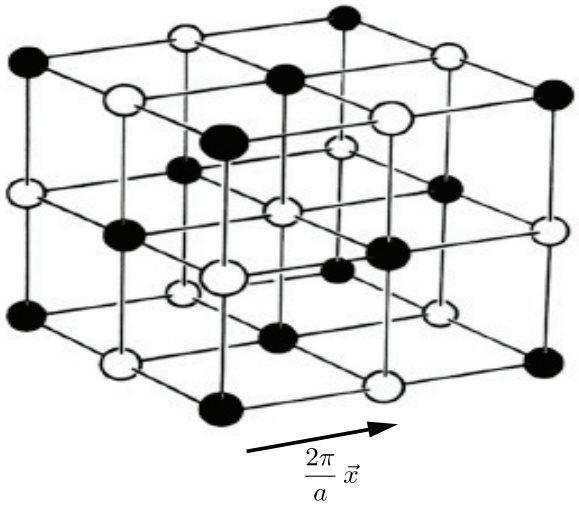

FIG. 3: Only black points are allowed.

The structure factor provides a nice way to recover the proper Bravais lattice. This is important both in Bragg scattering and in the Bloch theory. Assume we have a "bcc" lattice

with basis vectors $\vec{a}_1 = a\vec{x}$, $\vec{a}_2 = a\vec{y}$, and $\vec{a}_3 = \frac{a}{2}(\vec{x} + \vec{y} + \vec{z})$. We (wrongly) decide to treat it as a "cs" lattice with $\vec{a}_1 = a\vec{x}$, $\vec{a}_2 = a\vec{y}$, and $\vec{a}_3 = a\vec{z}$ and with two identical ions per unit cell with $\vec{d}_1 = 0$ and $\vec{d}_2 = \frac{a}{2}(\vec{x} + \vec{y} + \vec{z})$. The (wrong) reciprocal lattice is given by $\vec{K} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$, where $\vec{b}_1 = (2\pi/a)\vec{x}$, $\vec{b}_2 = (2\pi/a)\vec{y}$, and $\vec{b}_3 = (2\pi/a)\vec{z}$. We obtain for the structure factor

$$S_{\vec{K}} = \sum_j e^{i\vec{K}\cdot\vec{d}_j} = 1 + e^{\pi(m_1+m_2+m_3)} \ . \tag{67}$$

Possible results are either 0 or 2. The correct reciprocal lattice is only those $\vec{K}$ for which $S = 2$. It is easy to see that it is an "fcc" lattice (Fig. 3). Indeed no Bragg scattering appear for points (vectors $\vec{K}$) with $S = 0$. Also no no zone gap appear at Bragg planes corresponding to such vectors!

VI. BANDS, FERMI SURFACE, ISOLATORS, SEMICONDUCTORS, METALS.

Index n counts bands. Number of state in a band is $2\times$ the number of vectors $\vec{k}$ in the 1-st. B.Z., i.e., $2N$.

Bands can overlap in energy.

VII. TIGHT BINDING

A. Wannier functions

One can show that the Bloch states can be presented in a different form:

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \ , \tag{68}$$

where

$$\begin{aligned} w_n(\vec{r}) = \frac{1}{N} \sum_{\vec{k}\in 1.\ \text{B.Z.}} \psi_{n,\vec{k}}(\vec{r}) \ &= \ \frac{V}{N} \int_{1.\ \text{B.Z.}} \frac{d^3k}{(2\pi)^3} \psi_{n,\vec{k}}(\vec{r}) \\ &= \ v \int_{1.\ \text{B.Z.}} \frac{d^3k}{(2\pi)^3} \psi_{n,\vec{k}}(\vec{r}) \ . \end{aligned} \tag{69}$$

By operation of translation we obtain

$$w_n(\vec{r} - \vec{R}) = \frac{1}{N} \sum_{\vec{k}\in 1.\ \text{B.Z.}} \psi_{n,\vec{k}}(\vec{r} - \vec{R}) = \frac{1}{N} \sum_{\vec{k}\in 1.\ \text{B.Z.}} e^{-i\vec{k}\cdot\vec{R}} \psi_{n,\vec{k}}(\vec{r}) \ . \tag{70}$$

Indeed, substituting Eq.(70) into Eq.(68) we obtain

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \frac{1}{N} \sum_{\vec{q}\in 1.\ \mathrm{B.Z.}} e^{-i\vec{q}\cdot\vec{R}} \psi_{n,\vec{q}}(\vec{r}) = \sum_{\vec{q}\in 1.\ \mathrm{B.Z.}} \delta_{\vec{k},\vec{q}}\, \psi_{n,\vec{q}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r}) \ . \tag{71}$$

It is easy to check that the Wannier functions of different bands n are orthogonal. Also orthogonal are the Wannier functions of the same band but shifted to different $\vec{R}$'s.

B. Schrödinger equation for Wannier functions

Assume the total potential is a sum of atomic ones (for a simple Bravais lattice with one atom per unit):

$$U(\vec{r}) = \sum_{\vec{R}} U_a(\vec{r} - \vec{R}) \ . \tag{72}$$

Then from

$$H\psi_{n,\vec{k}} = \left(-\frac{\hbar^2 \Delta}{2m} + \sum_{\vec{R}} U_a(\vec{r} - \vec{R}) \right) \psi_{n,\vec{k}} = E_{n,\vec{k}} \psi_{n,\vec{k}} \tag{73}$$

we obtain

$$E_{n,\vec{k}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) = \left(-\frac{\hbar^2 \Delta}{2m} + \sum_{\vec{R}_1} U_a(\vec{r} - \vec{R}_1) \right) \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \ . \tag{74}$$

In the r.h.s. we separate the terms with $\vec{R}_1 = \vec{R}$ from those where $\vec{R}_1 \neq \vec{R}$:

$$\begin{aligned} E_{n,\vec{k}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \ &= \ \sum_{\vec{R}} \left(-\frac{\hbar^2 \Delta}{2m} + U_a(\vec{r} - \vec{R}) \right) e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \\ &+ \ \sum_{\vec{R}} \sum_{\vec{R}_1 \neq \vec{R}} U_a(\vec{r} - \vec{R}_1) e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \\ &= \ \sum_{\vec{R}} \left(-\frac{\hbar^2 \Delta}{2m} + U_a(\vec{r} - \vec{R}) \right) e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \\ &+ \ \sum_{\vec{R}} \Delta U(\vec{r}, \vec{R}) e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \ , \end{aligned} \tag{75}$$

where $\Delta U(\vec{r}, \vec{R}) \equiv \sum_{\vec{R}_1 \neq \vec{R}} U_a(\vec{r} - \vec{R}_1) = U(\vec{r}) - U_a(\vec{r} - \vec{R})$.

C. Linear Combination of Atomic Orbitals (LCAO)

Simplest approximation for the Wannier function $w = \sum_m b_m \phi_m$ where ϕ_m are the atomic orbitals, such that $H_a \phi_m = E_{a,m} \phi_m$. This can be, e.g., a multiplet of the orbital momentum

L with $2L+1$ degenerate states (we omit the band index n). This gives

$$\sum_m b_m(E_{\vec{k}} - E_{a,m}) \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \phi_m(\vec{r} - \vec{R}) = \sum_m b_m \sum_{\vec{R}} \Delta U(\vec{r}, \vec{R}) e^{i\vec{k}\cdot\vec{R}} \phi_m(\vec{r} - \vec{R}) \ , \tag{76}$$

We have restricted our Hilbert space to linear combinations of atomic orbitals $\phi_m(\vec{r} - \vec{R})$ shifted to all vectors of the Bravais lattice. While we cannot guarantee that Eq. (76) holds exactly (in the whole Hilbert space) we can choose the coefficients b_m and the energy $E_{\vec{k}}$ so that Eq. (76) holds in our restricted space. That is we demand that Eq. (76) projected on all $\phi_m(\vec{r} - \vec{R})$ holds. Due to the periodicity of the l.h.s. and the r.h.s. of Eq. (76) it is sufficient to project only on $\phi_m(\vec{r})$.

Projecting on $\phi_l(\vec{r})$ we obtain

$$\begin{aligned} &(E_{\vec{k}} - E_{a,l}) b_l + \sum_m b_m (E_{\vec{k}} - E_{a,m}) \sum_{\vec{R}\neq\vec{0}} e^{i\vec{k}\cdot\vec{R}} \int d^3 r \phi_l^*(\vec{r}) \phi_m(\vec{r} - \vec{R}) \\ &= \sum_m b_m \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \int d^3 r \phi_l^*(\vec{r}) \Delta U(\vec{r}, \vec{R}) \phi_m(\vec{r} - \vec{R}) \ , \end{aligned} \tag{77}$$

Introducing

$$I_{l,m}(\vec{R}) \equiv \int d^3 r \phi_l^*(\vec{r}) \phi_m(\vec{r} - \vec{R}) \tag{78}$$

and

$$h_{l,m}(\vec{R}) \equiv \int d^3 r \phi_l^*(\vec{r}) \Delta U(\vec{r}, \vec{R}) \phi_m(\vec{r} - \vec{R}) \tag{79}$$

we obtain

$$\begin{aligned} &(E_{\vec{k}} - E_{a,l}) b_l + \sum_m b_m (E_{\vec{k}} - E_{a,m}) \sum_{\vec{R}\neq\vec{0}} e^{i\vec{k}\cdot\vec{R}} I_{l,m}(\vec{R}) \\ &= \sum_m b_m \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} h_{l,m}(\vec{R}) \ , \end{aligned} \tag{80}$$

This is a homogeneous matrix equation on coefficients b_m. To have solutions one has to demand that the determinant of the matrix vanishes, This determines the band energies $E_{n,\vec{k}}$. The number of bands is equal to the number of states in the multiplet.

D. Single orbital (s states), one band

We obtain

$$E_{\vec{k}} = E_a + \frac{\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} h(\vec{R})}{1 + \sum_{\vec{R}\neq\vec{0}} e^{i\vec{k}\cdot\vec{R}} I(\vec{R})} \ , \tag{81}$$

Assume that only nearest neighbors matrix elements, do not vanish (and also $h(0)$). It is important to note that $I(\vec{R}) \ll 1$. Thus

$$E_{\vec{k}} \approx E_a + h(0) + \sum_{\vec{R}\in \text{n.n.}} (h(\vec{R}) - h(0)I(\vec{R}))e^{i\vec{k}\cdot\vec{R}} \ , \tag{82}$$

Then, for different Bravais lattices with one ion per primitive cell we obtain:

1) 1-D lattice with step a.

$$E_k = E_a + h(0) + 2W\cos(ak) \ , \tag{83}$$

where W $= h(a) - h(0)I(a)$.

2) sc-lattice, $\vec{a}_1 = a\vec{x}, \vec{a}_2 = a\vec{y}, \vec{a}_3 = a\vec{z}$, $\phi(\vec{r})$ is rotationally symmetric:

$$E_{\vec{k}} = E_a + h(0) + 2W\left(\cos(ak_x) + \cos(ak_y) + \cos(ak_z)\right) \ , \tag{84}$$

where W $= h(a) - h(0)I(a)$.

3) bcc-lattice. One of the possible choices of the primitive basis is: $\vec{a}_1 = a\vec{x}, \vec{a}_2 = a\vec{y}, \vec{a}_3 = \frac{1}{2}a(\vec{x} + \vec{y} + \vec{z})$, however the nearest neighbors are at $\vec{R} = \frac{a}{2}(\pm x \pm y \pm z)$. Altogether 8 neighbors each at distance $\sqrt{3}a/2$. We obtain

$$E_{\vec{k}} = E_a + h(0) + 8W\cos(ak_x/2)\cos(ak_y/2)\cos(ak_z/2) \ , \tag{85}$$

where W $= h(\sqrt{3}a/2) - h(0)I(\sqrt{3}a/2)$. (Interesting exercise: show that the reciprocal lattice in fcc).

E. Alternative formulation of tight-binding method

Each primitive cell is characterized by states $\left|\vec{R}, m\right\rangle$. Index m can count either states of the same atom or states of different atoms in the cell. For example in graphen we would have $m = A, B$, where A and B denote sub-lattices. The overlaps of different states vanish: $\langle R_1, m_1|\,|R_2, m_2\rangle = \delta_{\vec{R}_1,\vec{R}_2}\delta_{m_1,m_2}$. One postulates a tunneling Hamiltonian

$$H = \sum_{\vec{R}_1,m_1}\sum_{\vec{R}_2,m_2} t_{m_1,m_2}(\vec{R}_1 - \vec{R}_2)\left|\vec{R}_2, m_2\right\rangle\left\langle\vec{R}_1, m_1\right| \tag{86}$$

The Hamiltonian is hermitian, i.e., $t_{m_1,m_2}(\vec{R}) = t^*_{m_2,m_1}(-\vec{R})$.

The Bloch states:

$$\psi_{\vec{k}} = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\sum_m b_m\left|\vec{R}, m\right\rangle \ . \tag{87}$$

The Wannier w.f.: $w = \sum_m b_m \left|\vec{R}, m\right\rangle$.

The energies and the coefficients b_m are determined by substituting the Bloch wave function into the Schrödinger equation: $H\psi_{\vec{k}} = E_{\vec{k}}\psi_{\vec{k}}$.

We obtain

$$\begin{aligned} H\psi_{\vec{k}} &= \sum_{\vec{R}_1,m_1}\sum_{\vec{R}_2,m_2} t_{m_1,m_2}(\vec{R}_1-\vec{R}_2)\left|\vec{R}_2,m_2\right\rangle\left\langle\vec{R}_1,m_1\right|\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\sum_m b_m\left|\vec{R},m\right\rangle \\ &= \sum_{\vec{R}_1,m_1}\sum_{\vec{R}_2,m_2} e^{i\vec{k}\cdot\vec{R}_1} b_{m_1}\, t_{m_1,m_2}(\vec{R}_1-\vec{R}_2)\left|\vec{R}_2,m_2\right\rangle \\ &= E_{\vec{k}}\sum_{\vec{R}_2} e^{i\vec{k}\cdot\vec{R}_2}\sum_{m_2} b_{m_2}\left|\vec{R}_2,m_2\right\rangle \end{aligned} \tag{88}$$

Comparing coefficients in front of $\left|\vec{R}_2,m_2\right\rangle$ we obtain

$$\sum_{\vec{R}_1,m_1} e^{i\vec{k}\cdot\vec{R}_1} b_{m_1}\, t_{m_1,m_2}(\vec{R}_1-\vec{R}_2) = E_{\vec{k}} e^{i\vec{k}\cdot\vec{R}_2} b_{m_2}\ . \tag{89}$$

With $\vec{R} \equiv \vec{R}_1 - \vec{R}_2$

$$\sum_{\vec{R},m_1} e^{i\vec{k}\cdot\vec{R}} b_{m_1}\, t_{m_1,m_2}(\vec{R}) = E_{\vec{k}} b_{m_2}\ . \tag{90}$$

We again have reduced the problem to a matrix equation.

Examples:

1) 1-D, m=0 (1 state per primitive cell)

$$E_{\vec{k}} = \sum_{\vec{R}} t_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \tag{91}$$

For nearest neighbors tunneling $E_{\vec{k}} = 2t(1)\cos(ka)$.

2) Exercise: graphen.

VIII. DYNAMICS OF BLOCH ELECTRONS

A. Semi-classical equation of motion of Bloch electrons

We want to describe the evolution of electron's wave function when a weak and slowly changing external field is added. That is the Hamiltonian now reads

$$H = \frac{\left(-i\hbar\vec{\nabla} + \frac{e}{c}\vec{A}(\vec{r})\right)^2}{2m} + U(\vec{r}) - e\phi(\vec{r})\ , \tag{92}$$

where (the signs are consistent with negative charge, that is $e = |e| > 0$, but the charge of the electron is $-e < 0$.) The potential $U(\vec{r})$ is periodic while $\vec{A}$ and ϕ change little on the scale of primitive cell of the Bravais lattice (slow fields).

Our aim to prove that the electrons in the band n are governed by the following effective Hamiltonian

$$H_{\text{eff},n} = \epsilon_n \left(-i\vec{\nabla} + \frac{e}{\hbar c}\vec{A} \right) - e\phi \ . \tag{93}$$

B. Wave packet argument

We localize the electron of a certain band n into a wave packet:

$$\Phi(\vec{r}) = \int d^3k \, g(\vec{k}) \psi_{n,\vec{k}}(\vec{r}) = \int d^3k \, g(\vec{k}) u_{n,\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}. \tag{94}$$

The function $g(\vec{k})$ is centered around a certain quasi-impuls $\vec{k}_0$ and has a width Δk such that the width of the wave packet in the real space Δr is small enough. The two are related as $\Delta k \Delta r \sim 1$.

The time evolution of the wave packet is given by

$$\Phi(\vec{r}, t) = \int d^3k \, g(\vec{k}) u_{n,\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r} - i\epsilon_{n,\vec{k}} t/\hbar}. \tag{95}$$

We expand around $\vec{k}_0$ and $\epsilon_{n,\vec{k}_0}$. We assume one can approximate $u_{n,\vec{k}}(\vec{r}) \approx u_{n,\vec{k}_0}$ in the whole interval of Δk. Then

$$\Phi(\vec{r}, t) \approx u_{n,\vec{k}_0}(\vec{r}) e^{i\vec{k}_0\cdot\vec{r} - i\epsilon_{n,\vec{k}_0} t/\hbar} \int d^3\delta k \, g(\vec{k}) e^{i\delta\vec{k}\cdot\left(\vec{r} - \frac{\partial\epsilon_{n,\vec{k}}}{\partial\vec{k}} t/\hbar\right)}. \tag{96}$$

Thus we conclude that the wave packet propagates with the velocity

$$\vec{v} = \frac{\partial\vec{r}}{\partial t} = \frac{1}{\hbar}\frac{\partial\epsilon_{n,\vec{k}}}{\partial\vec{k}} \ . \tag{97}$$

Assume now the electron is influenced by an electric field $\vec{E}$. The work done by the field pro unit of time is $-e\vec{E}\cdot\vec{v}$. This work is "used" to change the energy of the electron. Thus we obtain

$$\frac{\partial\epsilon}{\partial t} = \frac{\partial\epsilon_{n,\vec{k}}}{\partial\vec{k}} \frac{d\vec{k}}{dt} = \hbar\vec{v}\frac{d\vec{k}}{dt} = -e\vec{E}\cdot\vec{v} \ . \tag{98}$$

Thus we obtain

$$\hbar\frac{d\vec{k}}{dt} = -e\vec{E} \ . \tag{99}$$

The quasi-momentum $\hbar k$ satisfies the same equation as the usual momentum for free electrons!

C. Proof for potential perturbation (not for vector potential)

We consider the following problem

$$H = \frac{\left(-i\hbar\vec{\nabla}\right)^2}{2m} + U(\vec{r}) + U_{\rm ext}(\vec{r}) = H_0 + U_{\rm ext}(\vec{r}) \ , \tag{100}$$

Here U is the periodic lattice potential and $U_{\rm ext} = -e\phi$ is the external and weak potential. More precisely what has to be weak is the external electric field, i.e., $\sim \vec{\nabla} U_{\rm ext}$.

We want to solve the time-dependent Schrdinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{101}$$

We expand $\psi(t)$ in basis of Wannier functions

$$\psi(t) = \sum_{n,\vec{R}} a_{n,\vec{R}}(t) w_n(\vec{r} - \vec{R}) \tag{102}$$

Recall the representation of a Bloch wave function

$$\psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \ . \tag{103}$$

In this case $a_{n,\vec{R}} = e^{i\vec{k}\cdot\vec{R}}$. Wannier functions are given by

$$w_n(\vec{r}) = \frac{1}{N} \sum_{\vec{k}\in 1.\ \rm B.Z.} \psi_{n,\vec{k}}(\vec{r}) \ . \tag{104}$$

and

$$w_n(\vec{r} - \vec{R}) = \frac{1}{N} \sum_{\vec{k}\in 1.\ \rm B.Z.} e^{-i\vec{k}\cdot\vec{R}} \psi_{n,\vec{k}}(\vec{r}) \ . \tag{105}$$

First we investigate how H_0 acts on the (shifted) Wannier functions using the fact $H_0\psi_{n,\vec{k}} = \epsilon_{n,k}\psi_{n,k}$.

$$H_0 w_n(\vec{r} - \vec{R}) = \frac{1}{N} \sum_{\vec{k}\in 1.\ \rm B.Z.} e^{-i\vec{k}\cdot\vec{R}} H_0\psi_{n,\vec{k}}(\vec{r}) = \frac{1}{N} \sum_{\vec{k}\in 1.\ \rm B.Z.} e^{-i\vec{k}\cdot\vec{R}} \epsilon_{n,k}\psi_{n,\vec{k}}(\vec{r}) \ . \tag{106}$$

We use now the Wannier expansion (103) and obtain

$$\begin{aligned} H_0 w_n(\vec{r} - \vec{R}) \ &= \ \sum_{\vec{R}_1} \frac{1}{N} \sum_{\vec{k}\in 1.\ \rm B.Z.} \epsilon_{n,k} e^{i\vec{k}\cdot(\vec{R}_1 - \vec{R})} w_n(\vec{r} - \vec{R}_1) \\ &= \ \sum_{\vec{R}_1} \epsilon_n(\vec{R}_1 - \vec{R}) w_n(\vec{r} - \vec{R}_1) \ , \end{aligned} \tag{107}$$

where

$$\epsilon_n(\vec{R}) \equiv \frac{1}{N} \sum_{\vec{k}\in 1.\ \mathrm{B.Z.}} \epsilon_{n,k} e^{i\vec{k}\cdot\vec{R}} \ . \tag{108}$$

The Schrödinger equation now reads:

$$\begin{aligned} & i\hbar\frac{\partial\psi}{\partial t} = i\hbar\sum_{n,\vec{R}} \dot{a}_{n,\vec{R}}(t) w_n(\vec{r}-\vec{R}) \\ & = H\psi = (H_0+U_{\mathrm{ext}})\psi = \sum_{n_2,\vec{R}_2} a_{n_2,\vec{R}_2}(t)(H_0+U_{\mathrm{ext}}) w_{n_2}(\vec{r}-\vec{R}_2) \\ & = \sum_{n_2,\vec{R}_2} a_{n_2,\vec{R}_2}(t) \sum_{\vec{R}_1} \epsilon_{n_2}(\vec{R}_1-\vec{R}_2) w_{n_2}(\vec{r}-\vec{R}_1) + \sum_{n_2,\vec{R}_2} a_{n_2,\vec{R}_2}(t) U_{\mathrm{ext}} w_{n_2}(\vec{r}-\vec{R}_2) \ . \end{aligned} \tag{109}$$

The Wannier functions form a complete orthonormal basis. Thus we just compare the coefficients:

$$\begin{aligned} i\hbar\dot{a}_{n,\vec{R}} \ &= \ \sum_{\vec{R}_2} a_{n,\vec{R}_2} \epsilon_n(\vec{R}-\vec{R}_2) \\ &+ \ \sum_{n_2,\vec{R}_2} a_{n_2,\vec{R}_2} \int d^3r \, w_n^*(\vec{r}-\vec{R}) U_{\mathrm{ext}}(\vec{r}) w_{n_2}(\vec{r}-\vec{R}_2) \ . \end{aligned} \tag{110}$$

The first term in the r.h.s. of (110) is rewritten as follows

$$\begin{aligned} & \sum_{\vec{R}_2} a_{n,\vec{R}_2} \epsilon_n(\vec{R}-\vec{R}_2) = \sum_{\vec{R}_1} \epsilon_n(\vec{R}_1) a_{n,\vec{R}-\vec{R}_1} = \sum_{\vec{R}_1} \epsilon_n(\vec{R}_1) e^{-i\vec{R}_1\cdot(-i\vec{\nabla})} a_{n,\vec{R}} \\ & = \epsilon_n(\vec{k}\to -i\vec{\nabla}) a_{n,\vec{R}} \ . \end{aligned} \tag{111}$$

Here we have used $a_{n,\vec{R}-\vec{R}_1} = e^{-\vec{R}_1\cdot\vec{\nabla}} a_{n,\vec{R}}$. That is already here we consider $a_{n,\vec{R}}$ as a "good" function in all the space, i.e., $a_{n,\vec{r}}$.

The second term of the r.h.s. of (110) is approximated as

$$\sum_{n_2,\vec{R}_2} a_{n_2,\vec{R}_2} \int d^3r \, w_n^*(\vec{r}-\vec{R}) U_{\mathrm{ext}}(\vec{r}) w_{n_2}(\vec{r}-\vec{R}_2) \approx U_{\mathrm{ext}}(\vec{R}) a_{n,\vec{R}} \ . \tag{112}$$

That is only diagonal matrix elements of U_{ext} are left. Since U_{ext} is slowly changing in space, i.e,. it changes very little on the scale of promitive cell, while the Wannier functions are localized on the scale of a cell this approximation is justified.

Thus, the SE for the "envelope" wave function $a_{n,\vec{R}}$ reads

$$i\hbar\dot{a}_{n,\vec{R}} = \left[\epsilon_n(-i\vec{\nabla}) + U_{\mathrm{ext}}(\vec{R})\right] a_{n,\vec{R}} \ . \tag{113}$$

If we now "forget" that $a_{n,\vec{R}}$ is defined only in the locations $\vec{R}$ and define it in the whole space, $a_{n,\vec{r}}$ we obtain a Schrödinger equation with the effective Hamiltonian $H_{\text{eff},n} = \epsilon_n(-i\vec{\nabla}) + U_{\text{ext}}(\vec{r})$. In presence of vector potential it becomes (with no proof given here)

$$H_{\text{eff},n} = \epsilon_n\left(-i\vec{\nabla} + \frac{e}{\hbar c}\vec{A}\right) - e\phi \ . \tag{114}$$

D. Effective mass

We see that the operator $\epsilon_n(-i\vec{\nabla})$ plays the role of the kinetic energy. The free kinetic energy reads $\epsilon_{\text{free}} = \frac{\hbar^2(\vec{k})^2}{2m}$. In many cases the relevant values of crystal momenta lay around an extremum of $\epsilon_n(\vec{k})$ at $\vec{k} = \vec{k}_0$. Then one can expand to the second order

$$\epsilon_n(\vec{k}) \approx \epsilon(\vec{k}_0) + \frac{1}{2}\left(\frac{\partial^2\epsilon_n}{\partial k_\alpha \partial k_\beta}\right)_{\vec{k}=\vec{k}_0}(k_\alpha - k_{0,\alpha})(k_\beta - k_{0,\beta}) \ . \tag{115}$$

In analogy to the free case the tensor

$$\left(m^{*-1}\right)_{\alpha,\beta} = \frac{1}{\hbar^2}\left(\frac{\partial^2\epsilon_n}{\partial k_\alpha \partial k_\beta}\right)_{\vec{k}=\vec{k}_0} \tag{116}$$

is called the effective mass tensor. In the simplest case when the tensor is proportional to the unity matrix, i.e., $\left(m^{*-1}\right)_{\alpha,\beta} = (1/m^*)\delta_{\alpha,\beta}$ one cane introduce the effective (band) mass m^*.

For example in a simple cubic lattice we have

$$\epsilon(\vec{k}) = const. - 2W\left(\cos(ak_x) + \cos(ak_y) + \cos(ak_z)\right) \ , \tag{117}$$

where in comparison to what we did earlier we change the definition of W so that $W > 0$. The energy has a minimum at $\vec{k}_0 = 0$ and the effective mass is obtained from $Wa^2k^2 = \hbar^2k^2/(2m^*)$ and is given by

$$m^* = \frac{\hbar^2}{2Wa^2} \ . \tag{118}$$

1. *Example*

Consider a semiconductor with fully occupied valance band and an empty conductance band. The conductance band is characterized by an effective mass $m^* \approx 0.1m$. That is

$E_{\rm cond}(\vec{k}) = E_{\rm cond} + \hbar^2 k^2/(2m^*)$, where $E_{\rm cond}$ is the bottom of the conduction band. An impurity (dopant ion) creates a potential

$$U_{\rm ext} = -\frac{e^2}{\epsilon|r|} \ , \tag{119}$$

where $\epsilon \approx 10$ is the dielectric constant. The dynamics of an extra electron added to the conduction band will be governed by an effective Hamiltonian which has the form of the Hydrogen atom one, but with different parameters:

$$H_{\rm eff} = E_{\rm cond} - \frac{\hbar^2 \vec{\nabla}^2}{2m^*} - \frac{e^2}{\epsilon|r|} \ . \tag{120}$$

The energy levels are known

$$E_n = E_{\rm cond} - \frac{m^* e^4}{2\epsilon^2 \hbar^2} \frac{1}{n^2} \tag{121}$$

The binding energy

$$\frac{m^* e^4}{2\epsilon^2 \hbar^2} = \frac{m^*}{m} \frac{1}{\epsilon^2} \, {\rm Ry} \ , \tag{122}$$

where Ry $\approx$ 13eV. Thus we obtain a binding energy of order 10^{-3}Ry. The size of he bound state, i.e., the new Bohr radius is given by $\frac{\epsilon\hbar^2}{e^2 m^*} \approx 10^2 a_0$. Thus we obtain Hydrogen-like bound states in the energy gap.

E. Classical equations of motion

Considering now the effective Hamiltonian classically, i.e., replacing $-i\hbar\vec{\nabla}$ with $\vec{p}$ we obtain

$$H = \epsilon_n \left(\frac{\vec{p}}{\hbar} + \frac{e}{c\hbar} \vec{A} \right) - e\phi(\vec{r}) \tag{123}$$

This Hamiltonian is useful for description of dynamics of wave packets.

The equations of motion read

$$\begin{aligned} \frac{d}{dt} \vec{r} &= \vec{\nabla}_p H \\ \frac{d}{dt} \vec{p} &= -\vec{\nabla}_r H \end{aligned} \tag{124}$$

The first equation gives

$$v_j = \frac{d}{dt} r_j = \frac{\partial H}{\partial p_j} = \frac{1}{\hbar} \left(\frac{\partial \epsilon_n(\vec{k})}{\partial k_j} \right)_{\vec{k} = \frac{\vec{p}}{\hbar} + \frac{e}{c\hbar}\vec{A}} \ . \tag{125}$$

The second equation reads

$$\begin{aligned}\frac{d}{dt}\,p_j &= -\frac{e}{c}\sum_i v_i\,\frac{\partial A_i}{\partial r_j} + e\nabla_j\phi \\ &= -\frac{e}{c}\sum_i v_i\left(\frac{\partial A_i}{\partial r_j} - \frac{\partial A_j}{\partial r_i} + \frac{\partial A_j}{\partial r_i}\right) + e\nabla_j\phi \\ &= -\frac{e}{c}\left(\vec{v}\times\vec{B}\right)_j - \frac{e}{c}\sum_i v_i\,\frac{\partial A_j}{\partial r_i} + e\nabla_j\phi \end{aligned} \tag{126}$$

Using

$$\frac{d}{dt}A_j = \frac{\partial A_j}{\partial t} + \sum_i \frac{\partial A_j}{\partial r_i}v_i \tag{127}$$

we obtain

$$\frac{d}{dt}\left(p_j + \frac{e}{c}A_j\right) = -\frac{e}{c}\left(\vec{v}\times\vec{B}\right)_j + \frac{e}{c}\frac{\partial A_j}{\partial t} + e\nabla_j\phi\ . \tag{128}$$

Introducing $\vec{p}_{\rm kin} = \vec{p} + \frac{e}{c}\vec{A}$ and recalling that $\vec{E} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t} - \vec{\nabla}\phi$ we obtain

$$\frac{d}{dt}\,\vec{p}_{\rm kin} = -\frac{e}{c}\left(\vec{v}\times\vec{B}\right) - e\vec{E}\ . \tag{129}$$

F. Only electric field

The equations of motion read

$$v_j = \frac{1}{\hbar}\left(\frac{\partial\epsilon_n(\vec{k})}{\partial k_j}\right)_{\vec{k}=\frac{\vec{p}}{\hbar}}\ . \tag{130}$$

$$\frac{d}{dt}\,\vec{p} = -e\vec{E}\ . \tag{131}$$

This gives

$$\begin{aligned}\frac{dv_j}{dt} &= \frac{1}{\hbar}\,\frac{d}{dt}\left(\frac{\partial\epsilon_n(\vec{k})}{\partial k_j}\right) = \frac{1}{\hbar}\sum_i\left(\frac{\partial^2\epsilon_n(\vec{k})}{\partial k_j\partial k_i}\right)\frac{dk_i}{dt} \\ &= \frac{1}{\hbar^2}\sum_i\left(\frac{\partial^2\epsilon_n(\vec{k})}{\partial k_j\partial k_i}\right)(-eE_i) = \sum_i (m^{*-1})_{ji}(-eE_i)\ . \end{aligned} \tag{132}$$

Or, one can invert the effective mass tensor and obtain

$$\sum_j (m^*)_{ij}\dot{v}_j = -eE_i = F_i\ . \tag{133}$$

These relations once again show the role of the effective mass. The mass tensor can have negative eigenvalues. Then, the acceleration of the electron has an opposite to the force ($\vec{F} = -e\vec{E}$) direction.

Bloch oscillations!!

G. Concept of holes

Consider an almost full band. As an example take the sc lattice.

$$\epsilon(\vec{k}) = const. - 2W\left(\cos(ak_x) + \cos(ak_y) + \cos(ak_z)\right) \ , \tag{134}$$

Near the top of the band, where the unoccupied states are, at $\vec{k}_0 = \frac{\pi}{a}(1,1,1)$ the effective mass is negative

$$m^* = -\frac{\hbar^2}{2Wa^2} \ . \tag{135}$$

Instead one can introduce holes. The unoccupied states are now called occupied by holes, while occupied states are unoccupied by holes. So a hole is an absence of an electron.

This is useful since the fully occupied by electrons band does not contribute to the current. The current provided by the band n (we do not use the band index as we limit ourselves here to a single band) is given by

$$\vec{j} = -\frac{e}{V}\sum_s \sum_{\vec{k}\in 1.\mathrm{B.Z}} n(\vec{k},s)\,\vec{v}(\vec{k},s) = -e\sum_s \int_{1.\mathrm{B.Z}} \frac{d^3k}{(2\pi)^3} n(\vec{k},s)\,\vec{v}(\vec{k},s) \ , \tag{136}$$

where $n(\vec{k},s)$ is the occupation number of the state with crystal momentum $\vec{k}$ and spin $s = \pm 1/2$ (in the band n). The velocity's components are given by

$$v_\alpha(\vec{k},s) = \frac{1}{\hbar}\frac{\partial\epsilon(\vec{k},s)}{\partial k_\alpha} \ . \tag{137}$$

Here we generalized the band energy $\epsilon(\vec{k})$ to depend on the spin index $\epsilon(\vec{k},s)$. We did not yet consider spin-orbit coupling. Thus $\epsilon(\vec{k})$ does not depend on the spin s. In general case, when the SO coupling is present, it does. The time reversal symmetry requires in general case $\epsilon(\vec{k},s) = \epsilon(-\vec{k},-s)$. Thus $v(-\vec{k},-s) = -v(\vec{k},s)$. In the absence of spin-orbit coupling $\epsilon(\vec{k}) = \epsilon(-\vec{k})$ and $v(-\vec{k}) = -v(\vec{k})$.

The occupation numbers are between 0 and 1. For the fully occupied band $n(\vec{k},s) = 1$. Thus we have

$$j_\alpha = -e\sum_s \int_{1.\mathrm{B.Z}} \frac{d^3k}{(2\pi)^3}\, v_\alpha(\vec{k},s) = -\frac{e}{\hbar}\sum_s \int_{1.\mathrm{B.Z}} \frac{d^3k}{(2\pi)^3}\frac{\partial\epsilon(\vec{k},s)}{\partial k_\alpha} = 0 \ . \tag{138}$$

The integral vanishes since $\epsilon(\vec{k},s)$ is periodic with the period given by the vectors of the reciprocal lattice.

For the holes we have the occupation numbers $n_h(\vec{k},s) = 1 - n(\vec{k},s)$. A hole characterized by $\vec{k}, s$ moves with the same velocity as the electron with $\vec{k}, s$. This follows just from the fact that Schrödinger equation for the state do not depend on whether the state is occupied.

Then we obtain for the current density

$$\begin{aligned}\vec{j} &= -e\sum_s \int_{\text{1.B.Z}} \frac{d^3k}{(2\pi)^3} n(\vec{k},s)\,\vec{v}(\vec{k},s) = e\sum_s \int_{\text{1.B.Z}} \frac{d^3k}{(2\pi)^3}\left[1 - n(\vec{k},s)\right]\,\vec{v}(\vec{k},s) \\ &= e\sum_s \int_{\text{1.B.Z}} \frac{d^3k}{(2\pi)^3} n_h(\vec{k},s)\,\vec{v}(\vec{k},s)\ . \end{aligned} \tag{139}$$

Thus we can say that the charge of the hole is $+e$.

Finally we recall the equation of motion

$$\sum_j (m^*)_{ij}\dot{v}_j = -eE_i\ . \tag{140}$$

Defining the hall effective mass as $m_h^* \equiv -m^*$ we obtain

$$\sum_j (m_h^*)_{ij}\dot{v}_j = eE_i\ . \tag{141}$$

Thus if the electronic effective mass is negative it is more convenient to use the picture of holes. They have positive charge and positive mass.

Thus far we characterized holes by the crystal momentum and the spin of the absent electron $\vec{k}, s$. It is more logical to say that the hole has a crystal momentum $\vec{k}_h = -\vec{k}$ and spin $s_h = -s$. We also define the energy of the hole as $\epsilon_h(\vec{k}_h, s_h) = const. - \epsilon(\vec{k}, s)$. For the constant it is convenient to chose the upper edge of the band. Then we can have the usual relation

$$\vec{v}_h(\vec{k}_h, s_h) = \frac{1}{\hbar}\frac{\partial \epsilon_h(\vec{k}_h, s_h)}{\partial \vec{k}_h} = \frac{1}{\hbar}\frac{\partial \epsilon(\vec{k}, s)}{\partial \vec{k}} = \vec{v}(\vec{k}, s)\ . \tag{142}$$

It is now easy to check that the usual relation is satisfied for the hole effective mass m_h^*.

IX. BLOCH ELECTRONS IN MAGNETIC FIELD

For $\vec{p}_{\text{kin}} = \vec{p} + \frac{e}{c}\vec{A}$ we obtained

$$\frac{d}{dt}\vec{p}_{\text{kin}} = -\frac{e}{c}\left(\vec{v}\times\vec{B}\right) - e\vec{E}\ . \tag{143}$$

Recalling also that the effective Hamiltonian reads

$$H = \epsilon_n\left(\frac{\vec{p}}{\hbar} + \frac{e}{c\hbar}\vec{A}\right) - e\phi(\vec{r}) \tag{144}$$

we conclude that the Bloch wave vector is related to $\vec{p}_{\rm kin}$, i.e., $\hbar\vec{k} = \vec{p}_{\rm kin}$.

This gives for the case $\vec{E} = 0$

$$\frac{d}{dt}\,\vec{k} = -\frac{e}{\hbar c}\left(\vec{v}(\vec{k}) \times \vec{B}\right) \ , \tag{145}$$

where

$$\frac{dr_j}{dt} = v_j(\vec{k}) = \frac{1}{\hbar}\,\frac{\partial \epsilon_n(\vec{k})}{\partial k_j} \ . \tag{146}$$

First, we observe that the energy is conserved:

$$\frac{d\epsilon}{dt} = \hbar\vec{v}\cdot\frac{d\vec{k}}{dt} = 0 \ . \tag{147}$$

Second, the vector $d\vec{k}/dt$ is perpendicular to $\vec{B}$, i.e. $k_z = const.$ if z is the direction of $\vec{B}$. Thus, in the $k-$space the motion is along lines of equal energy which belong to planes perpendicular to $\vec{B}$. One obtains these lines by cutting the equal-energy surfaces (e.g., the Fermi surface) by planes $\perp \vec{B}$.

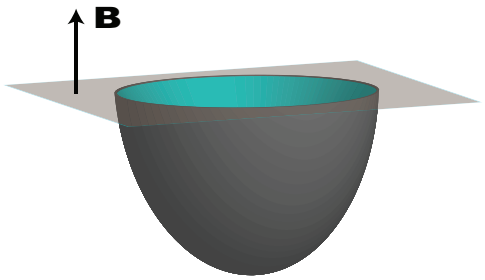

FIG. 4: Fermi surface cut by a plane perpendicular to $\vec{B}$.

Next we consider the trajectory in the real space. We obtain

$$\vec{B}\times\dot{\vec{k}} = -\frac{e}{\hbar c}\,\vec{B}\times\left(\vec{v}(\vec{k})\times\vec{B}\right) = -\frac{e}{\hbar c}\left(\vec{v}(\vec{k})(\vec{B})^2 - \vec{B}(\vec{B}\cdot\vec{v}(\vec{k}))\right) = -\frac{eB^2}{\hbar c}\,\vec{v}_\perp \ , \tag{148}$$

where $\vec{v}_\perp$ is the component of the velocity perpendicular to $\vec{B}$. Dividing by $|\vec{B}|$ we obtain

$$\vec{b}\times\dot{\vec{k}} = -\frac{eB}{\hbar c}\,\vec{v}_\perp \ , \tag{149}$$

where $\vec{b} \equiv \vec{B}/|\vec{B}|$. Integrating over time from 0 to t we obtain

$$\vec{b}\times(\vec{k}_\perp(t) - \vec{k}_\perp(0)) = -\frac{Be}{\hbar c}\,(\vec{r}_\perp(t) - \vec{r}_\perp(0)) \ , \tag{150}$$

Thus the trajectory in the $\vec{r}-$space is obtained from the trajectory in $\vec{k}-$space by a $\pi/2$ rotation around the axis of the magnetic field and a rescaling by a factor $-\hbar c/(eB)$.

A. Closed and open orbits

If the orbit in the k-space is closed, then also the orbit in the r-space is closed (see Fig. 5**a**). However, there exist situations when the orbit in the k-space is open (see Fig. 5**b**).

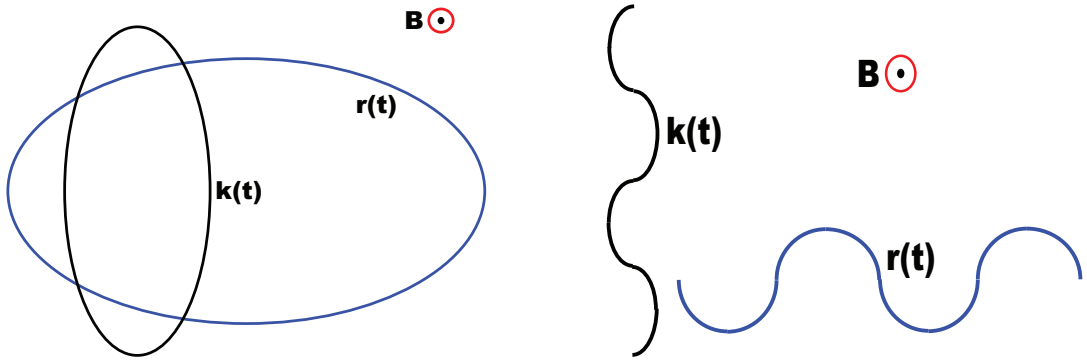

FIG. 5: **a)** Closed trajectories;**b)** Open trajectories.

This happens when the Fermi surface reaches the border of the Brillouin zone.

B. Cyclotron frequency

Assume the direction of the magnetic field is z, i.e., $\vec{b} = \vec{z}$. Also assume that all the orbits are closed. We write the equations of motion

$$\vec{z} \times \dot{\vec{k}} = -\frac{eB}{\hbar c}\,\vec{v}_\perp \tag{151}$$

in components:

$$\dot{k}_x = -\frac{eB}{\hbar c} v_y \quad , \quad \dot{k}_y = \frac{eB}{\hbar c} v_x \ . \tag{152}$$

From here we obtain

$$(dk_x)^2 + (dk_y)^2 = \frac{e^2B^2}{\hbar^2 c^2}(v_x^2 + v_y^2)(dt)^2 \tag{153}$$

Introducing the length element along the trajectory in the reciprocal space $dk \equiv \sqrt{(dk_x)^2 + (dk_y)^2}$ we obtain

$$\frac{dk}{dt} = \frac{|e|B}{\hbar c} v_\perp \ , \tag{154}$$

where $v_\perp \equiv \sqrt{v_x^2 + v_y^2}$. The inverted relation reads

$$dt = \frac{\hbar c}{|e|B}\,\frac{dk}{v_\perp} \ , \tag{155}$$

For the period of the orbit we obtain

$$T = \frac{\hbar c}{|e|B} \oint \frac{dk}{v_\perp} = \frac{\hbar^2 c}{|e|B} \oint \frac{dk}{\left|\frac{\partial \epsilon}{dq}\right|} \ , \tag{156}$$

where dq is the differential of the wave vector perpendicular to the trajectory (and laying in the plane of the trajectory, i.e., $k_z = const.$). This gives

$$T = \frac{\hbar^2 c}{|e|B} \oint dk \frac{dq}{\left|\frac{\partial \epsilon}{dq}\right| dq} = \frac{\hbar^2 c}{|e|B} \oint dk \frac{dq}{d\epsilon} \ . \tag{157}$$

We choose the differential dq so that at any point of the trajectory $k(t)$ we have $d\epsilon = const.$, i.e., $d\epsilon$ is independent of $k(t)$. We identify the integral along the trajectory in the $k-$space

$$\int dk dq = dS \ , \tag{158}$$

where S is the area of the closed orbit. Thus

$$T = \frac{\hbar^2 c}{|e|B} \frac{\partial S}{\partial \epsilon}\Big|_{k_z = const} \ . \tag{159}$$

One can also define the "cyclotron mass"

$$m^* \equiv \frac{\hbar^2}{2\pi} \frac{\partial S(\epsilon, k_z)}{\partial \epsilon} \ , \tag{160}$$

so that the cyclotron frequency is equal to

$$\omega_c = \frac{2\pi}{T} = \frac{|e|B}{m^*(\epsilon, k_z)c} \tag{161}$$

For a simple parabolic band the cyclotron mass is equal to the effective mass. In more complicated cases they are different (exercise).

C. Semiclassical quantization (Bohr-Sommerfeld) of orbits

We have seen that the effective Hamiltonian

$$H = \epsilon_n \left(\frac{\vec{p}}{\hbar} + \frac{e}{c\hbar} \vec{A} \right) \tag{162}$$

is obtained by substitution

$$\hbar \vec{k} \to \vec{p} + \frac{e}{c} \vec{A} \ . \tag{163}$$

We obtain

$$\oint \vec{p}\cdot d\vec{r} = \oint \left(\hbar\vec{k} - \frac{e}{c}\vec{A}\right)\cdot d\vec{r} \tag{164}$$

From

$$\vec{z}\times(\vec{k}_\perp(t) - \vec{k}_\perp(0)) = -\frac{Be}{\hbar c}\left(\vec{r}_\perp(t) - \vec{r}_\perp(0)\right) , \tag{165}$$

multiplying both sides from the left with $\vec{z}\times$ we obtain

$$\hbar\vec{k}_\perp = -\frac{e}{c}\,\vec{r}_\perp \times \vec{B} + const. . \tag{166}$$

Thus

$$\begin{aligned}\oint \vec{p}\cdot d\vec{r} &= -\frac{e}{c}\oint\left(\vec{r}_\perp\times\vec{B} + \vec{A}\right)\cdot d\vec{r} \\ &= \frac{e}{c}\,\vec{B}\cdot\oint \vec{r}_\perp\times d\vec{r} - \frac{e}{c}\oint\vec{A}\cdot d\vec{r} \\ &= \frac{e}{c}\left(2\Phi - \Phi\right) = \frac{e}{c}\,\Phi ,\end{aligned} \tag{167}$$

where Φ is the magnetic flux through the closed orbit (in $\vec{r}$-space). The quantization condition reads $\oint\vec{p}\cdot d\vec{r} = 2\pi\hbar\left(n+\frac{1}{2}\right)$. This means

$$\Phi = \frac{hc}{e}\left(n+\frac{1}{2}\right) = \Phi_0\left(n+\frac{1}{2}\right) , \tag{168}$$

where $\Phi_0 \equiv hc/|e|$ is the flux quantum. The allowed areas of the orbits in the $\vec{r}$-space read

$$A_n = \frac{\Phi_0}{B}\left(n+\frac{1}{2}\right) . \tag{169}$$

and in the $\vec{k}-$space

$$S_n = \frac{B^2e^2}{\hbar^2c^2}A_n = \frac{B^2e^2}{\hbar^2c^2}\frac{\Phi_0}{B}\left(n+\frac{1}{2}\right) = \frac{2\pi B|e|}{\hbar c}\left(n+\frac{1}{2}\right) . \tag{170}$$

Comparing now with

$$m^* \equiv \frac{\hbar^2}{2\pi}\,\frac{\partial S(\epsilon,k_z)}{\partial\epsilon} , \tag{171}$$

and

$$\omega_c = \frac{2\pi}{T} = \frac{|e|B}{m^*(\epsilon,k_z)c} . \tag{172}$$

We see that the energy difference between the levels n and $n+1$ is

$$\epsilon(n+1,k_z) - \epsilon(n,k_z) = \frac{1}{\frac{\partial S(\epsilon,k_z)}{\partial\epsilon}}\left(S_{n+1} - S_n\right) = \frac{\hbar^2}{2\pi m^*}\,\frac{2\pi B|e|}{\hbar c} = \hbar\omega_c \tag{173}$$

Thus we obtain the Landau levels quasi-classically. In what follows we will obtain Landau levels for a parabolic band exactly.

D. Magnetic susceptibility

Magnetization: $\vec{M}$

$$\vec{B} = \vec{H} + 4\pi\vec{M} \tag{174}$$

Susceptibility

$$\chi = \left(\frac{\partial M}{\partial H}\right)_{\vec{H}=0} \tag{175}$$

For small $\vec{H}$ we have $\vec{M} = \chi\vec{H}$. Then $\vec{B} = (1 + 4\pi\chi)\vec{H} = \mu\vec{H}$. Finally

$$\vec{M} = \frac{\chi}{\mu}\,\vec{B} = \frac{\chi}{1 + 4\pi\chi}\,\vec{B}\ . \tag{176}$$

If $\chi \ll 1$ we have $\vec{M} \approx \chi B$.

Internal energy

$$dU = dQ + dA = TdS - \vec{M}d\vec{H} \tag{177}$$

Free energy

$$F = U - TS \quad , \quad dF = -SdT - \vec{M}d\vec{H} \tag{178}$$

From here

$$M = -\left(\frac{\partial F}{\partial H}\right)_T \tag{179}$$

and

$$\chi = -\left(\frac{\partial^2 F}{\partial H^2}\right)_{T,H=0} \tag{180}$$

Thus we need the free energy $F = -k_{\rm B}T \ln Z$, where $Z = \sum_i e^{-E_i/(k_{\rm B}T)}$.

1. Grand canonical ensemble

In the grand canonical ensemble we have instead $\Omega = -k_{\rm B}T \ln Z_\Omega$, where $Z_\Omega = \sum_N \left[e^{\mu N} \sum_i e^{-E_{i,N}/(k_{\rm B}T)}\right]$. For free Fermions this gives

$$\Omega = -k_{\rm B}T \sum_k \ln\left[1 + \exp\left(\frac{\mu - \epsilon_k}{k_{\rm B}T}\right)\right]\ . \tag{181}$$

E. Bohr-van-Leeuven Theorem

No magnetization due to classical motion of electrons.

Classical partition function:

$$Z = \left[\int d^3r d^3p \, \exp\left(-\frac{H}{k_{\rm B}T} \right) \right]^N \tag{182}$$

and

$$H = \frac{\left(\vec{p} + \frac{e}{c}\vec{A}(\vec{r}) \right)^2}{2m} + U(\vec{r}) \tag{183}$$

Integration over $\vec{p}$ eliminates the effect of $\vec{A}$.

X. PARAMAGNETISM PAULI AND DIAMAGNETISM LANDAU

A. Pauli paramagnetism

$$H = H_0 + H_{\rm Zeeman} \ . \tag{184}$$

$$H_{\rm Zeeman} = -\frac{g\mu_{\rm B}\vec{B}\vec{\sigma}}{2} \ , \tag{185}$$

where $g = 2$, $\mu_{\rm B} = \frac{e\hbar}{2mc}$.

The energy enters into the expression for Ω as $\mu - \epsilon$. Thus for spin "up" we can say that the chemical potential is $\mu + \mu_{\rm B}B$ while for spin "down" it is $\mu - \mu_{\rm B}B$.

For the potential Ω we thus obtain

$$\Omega = \frac{1}{2}\left(\Omega_0(\mu + \mu_{\rm B}H) + \Omega_0(\mu + \mu_{\rm B}H) \right) = \Omega_0 + \frac{1}{2}\mu_{\rm B}^2 H^2 \frac{\partial^2 \Omega_0}{\partial \mu^2} \ . \tag{186}$$

We obtain

$$\chi_{\rm para} = -\frac{1}{V}\left(\frac{\partial^2 \Omega}{\partial H^2} \right)_{T,H=0,\mu} = -\frac{1}{V}\mu_{\rm B}^2 \frac{\partial^2 \Omega_0}{\partial \mu^2} \ . \tag{187}$$

(Ω should be divided by the volume to get the magnetization as density).

At $T = 0$ all states up to $E = E_F$ are occupied where $E = \epsilon \pm \mu_{\rm B}B$. In other words for electrons with $\sigma_z = +1$ we have all states up to $\epsilon = E_F + \mu_{\rm B}B$ occupied. For $\sigma_z = -1$ we have all states up to $\epsilon = E_F - \mu_{\rm B}B$ occupied. The difference of total densities is given by

$$n_+ - n_- = \int_0^{E_F + \mu_{\rm B}B} \nu(\epsilon) d\epsilon - \int_0^{E_F - \mu_{\rm B}B} \nu(\epsilon) d\epsilon \approx 2\mu_{\rm B}B\nu(E_F) \ , \tag{188}$$

where $\nu(\epsilon)$ is the density of states (pro spin). The magnetization is given by

$$M = \mu_{\rm B}(n_+ - n_-) = 2\mu_{\rm B}^2 B\nu \ . \tag{189}$$

Finally

$$\chi = 2\mu_{\rm B}^2\nu = \mu_{\rm B}^2\nu_s \ , \tag{190}$$

where $\nu_s \equiv 2\nu$ is the total density of states at the Fermi energy (including spin).

B. Landau levels

Consider now free electrons or equivalently a parabolic band. The magnetic field $\vec{B} \parallel \vec{z}$. The vector potential is, e.g., $\vec{A} = (0, Bx, 0)$. The Hamiltonian reads

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \left(\frac{\partial}{\partial y} + \frac{ieB}{\hbar c}\,x\right)^2 + \frac{\partial^2}{\partial z^2}\right) \tag{191}$$

Ansatz

$$\psi = \phi(x)e^{ik_y y}e^{ik_z z} \tag{192}$$

This gives

$$H\psi = -\frac{\hbar^2}{2m}\left[\frac{\partial^2\phi}{\partial x^2} + \left(ik_y + \frac{ieB}{\hbar c}\,x\right)^2\,\phi - k_z^2\,\phi\right]\,e^{ik_y y}e^{ik_z z} = E\phi\,e^{ik_y y}e^{ik_z z} \tag{193}$$

Thus

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\phi}{\partial x^2} + \left(ik_y + \frac{ieB}{\hbar c}\,x\right)^2\,\phi\right] = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)\phi \tag{194}$$

$$-\frac{\hbar^2}{2m}\,\frac{\partial^2\phi}{\partial x^2} + \frac{\hbar^2}{2m}\left(k_y + \frac{eB}{\hbar c}\,x\right)^2\,\phi = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)\phi \tag{195}$$

$$-\frac{\hbar^2}{2m}\,\frac{\partial^2\phi}{\partial x^2} + \frac{e^2B^2}{2mc^2}\left(x + \frac{\hbar c}{eB}k_y\right)^2\,\phi = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)\phi \tag{196}$$

$$-\frac{\hbar^2}{2m}\,\frac{\partial^2\phi}{\partial x^2} + \frac{m\omega_c^2}{2}\,(x - x_0)^2\,\phi = \left(E - \frac{\hbar^2 k_z^2}{2m}\right)\phi \ , \tag{197}$$

where $x_0 \equiv -\frac{\hbar c}{eB}k_y$ and $\omega_c = \frac{|e|B}{mc}$. We can also introduce $l_B^2 \equiv \frac{\hbar c}{|e|B}$. Thus $x_0 = l_B^2 k_y$.

The energy levels

$$E = \frac{\hbar^2 k_z^2}{2m} + \hbar\omega_c\left(n + \frac{1}{2}\right) \ . \tag{198}$$

C. Degeneracy of the Landau Level

The degeneracy is obtained by introducing the volume $V = L_x L_y L_z$ and introducing the periodic boundary conditions in the y and z directions. Then $k_z = \frac{2\pi n_z}{L_z}$ and $k_y = \frac{2\pi n_y}{L_y}$. The k_y values are also limited by the fact that $x_0 \equiv -\frac{\hbar c}{eB} k_y \in [0, L_x]$. Thus the number of states for a given k_z is given by $\frac{L_y}{2\pi}(k_y^{\max} - k_y^{\min}) = \frac{L_x L_y}{2\pi}\frac{eB}{\hbar c}$. The number of states in an interval dk_z for each Landau level is thus given by

$$dn_n = \frac{L_x L_y}{2\pi}\frac{eB}{\hbar c}\frac{L_z}{2\pi}dk_z = \frac{eBV}{(2\pi)^2\hbar c}dk_z \tag{199}$$

D. Landau diamagnetism

The energy levels

$$E = \frac{\hbar^2 k_z^2}{2m^*} + \hbar\omega_c\left(n + \frac{1}{2}\right) \ . \tag{200}$$

with $\omega_c = \frac{eB}{m^* c}$ (it is now important to differentiate m^* from m).

The number of states for a given k_z is given by $\frac{L_x L_y}{2\pi}\frac{eB}{\hbar c}$. The number of states in dk_z at the level n

$$dn_n = \frac{L_x L_y}{2\pi}\frac{eB}{\hbar c}\frac{L_z}{2\pi}dk_z = \frac{eBV}{(2\pi)^2\hbar c}\, dk_z \ . \tag{201}$$

We obtain

$$\begin{aligned}
\Omega &= -k_{\rm B}T\,\frac{L_x L_y}{2\pi}\frac{eB}{\hbar c}\sum_{n,k_z}\ln\left(1+\exp\left(\frac{\mu - \frac{\hbar^2 k_z^2}{2m^*} - \hbar\omega_c\left(n+\frac{1}{2}\right)}{k_{\rm B}T}\right)\right) \\
&= -k_{\rm B}T\,\frac{eBV}{(2\pi)^2\hbar c}\sum_n \int_{-\infty}^{\infty} dk_z \ln\left(1+\exp\left(\frac{\mu - \frac{\hbar^2 k_z^2}{2m^*} - \hbar\omega_c\left(n+\frac{1}{2}\right)}{k_{\rm B}T}\right)\right) \\
&= -\frac{k_{\rm B}TeBV}{(2\pi)^2\hbar c}\sum_{n=0} F\left(n+\frac{1}{2}\right)
\end{aligned} \tag{202}$$

where

$$F(x) \equiv \int_{-\infty}^{\infty} dk_z \ln\left(1+\exp\left(\frac{\mu - \frac{\hbar^2 k_z^2}{2m^*} - \hbar\omega_c x}{k_{\rm B}T}\right)\right) \tag{203}$$

We also introduce

$$f(y) \equiv \int_{-\infty}^{\infty} dk_z \ln\left(1+\exp\left(\frac{y - \frac{\hbar^2 k_z^2}{2m^*}}{k_{\rm B}T}\right)\right) \ . \tag{204}$$

We use the variant of the Euler-Maclaurin formula

$$\sum_{n=0}^{\infty} F\left(n+\frac{1}{2}\right) = \int_0^{\infty} dx F(x) + \frac{1}{24}F'(0) + \dots \ , \tag{205}$$

We obtain

$$\int_0^\infty dx F(x) = \frac{1}{\hbar\omega_c} \int_{-\infty}^{\mu} dy f(y) \ . \tag{206}$$

Thus the integral contribution to Ω reads

$$\Omega_{int} = -\frac{k_{\rm B}TeBV}{(2\pi)^2\hbar c} \frac{1}{\hbar\omega_c} \int_{-\infty}^{\mu} dy f(y) = -\frac{k_{\rm B}Tm^*V}{(2\pi\hbar)^2} \int_{-\infty}^{\mu} dy f(y) = \Omega_0 \ . \tag{207}$$

We also obtain

$$F'(0) = -\hbar\omega_c f'(y=\mu) \tag{208}$$

and the correction

$$\begin{aligned} \delta\Omega \ &= \ \frac{1}{24} \frac{k_{\rm B}TeBV}{(2\pi)^2\hbar c} \hbar\omega_c f'(\mu) = \frac{1}{24} \frac{k_{\rm B}TeBV}{(2\pi)^2\hbar c} \ \hbar\omega_c \frac{\partial^2}{\partial\mu^2} \int_{-\infty}^{\mu} f(y)dy \\ &= \ -\frac{1}{24} (\hbar\omega_c)^2 \frac{\partial^2}{\partial\mu^2}\Omega_0(\mu) = -\frac{1}{24} \left(\frac{\hbar eH}{m^*c}\right)^2 \frac{\partial^2}{\partial\mu^2}\Omega_0(\mu) \ . \end{aligned} \tag{209}$$

Thus

$$\chi_{\rm dia} = -\frac{1}{V} \left(\frac{\partial^2\Omega}{\partial H^2}\right)_{T,H=0,\mu} = \frac{1}{V} \frac{e}{12m^*c} \frac{\partial^2}{\partial\mu^2}\Omega_0(\mu) \ . \tag{210}$$

Comparing with

$$\chi_{\rm para} = -\frac{1}{V}\mu_{\rm B}^2 \frac{\partial^2\Omega_0}{\partial\mu^2} \ . \tag{211}$$

and with $\mu_{\rm B} = \frac{e\hbar}{2mc}$ we obtain

$$\chi_{\rm dia} = -\frac{1}{3} \left(\frac{m}{m^*}\right)^2 \chi_{\rm para} \tag{212}$$

E. van Alphen - de Haas effect

The correction to $\delta\Omega$ in Eq. (209) is proportional to H^2. The next correction is an oscillating function of H with amplitude $\propto H^{5/2}$. The magnetization $M = -\partial\Omega/\partial H$ is also oscillating and the amplitude of oscillations at low temperatures may become bigger than the non-oscillating contribution. This is the van Alphen - de Haas effect (predicted theoretically by Landau).

Qualitative explanation of oscillations due to changing occupation of Landau levels as function of H.

XI. BOLTZMANN EQUATION, ELASTIC SCATTERING ON IMPURITIES.

A. Kinematics

For quasiclassical description of electrons we introduce the Boltzmann distribution function $f_n(\vec{k},\vec{r},t)$. This is the probability to find an electron in state $n,\vec{k}$ at point $\vec{r}$ at time t. More precisely is f/V the probability density to find an electron in state $n,\vec{k}$ in point $\vec{r}$. This means the probability to find it in a volume element dV is given by fdV/V.

We consider both $\vec{k}$ and $\vec{r}$ defined. This means that we consider wave packets with both $\vec{k}$ and $\vec{r}$ (approximately) defined. The uncertainty relation $\Delta k\Delta r \sim 1$ allows us to choose both Δk and Δr small enough.

The electron density and the current density are given by

$$n(\vec{r},t) = \frac{1}{V}\sum_{n,\vec{k},\sigma} f_n(\vec{k},\vec{r},t) \tag{213}$$

$$\vec{j}(\vec{r},t) = -\frac{e}{V}\sum_{n,\vec{k},\sigma} \vec{v}_{\vec{k}} f_n(\vec{k},\vec{r},t) \tag{214}$$

The equations of motion

$$\frac{d}{dt}\vec{r} = \vec{v}_{\vec{k}} = \frac{1}{\hbar}\left(\frac{\partial \epsilon_n(\vec{k})}{\partial \vec{k}}\right) , \tag{215}$$

$$\hbar\frac{d\vec{k}}{dt} = -e\vec{E} - \frac{e}{c}\left(\vec{v}\times\vec{B}\right) . \tag{216}$$

determine the evolution of the individual $\vec{k}(t)$ and $\vec{r}(t)$ of each wave packet.

If the electrons would only obey the equations of motion the distribution function would satisfy

$$f_n(\vec{k}(t),\vec{r}(t),t) = f_n(\vec{k}(0),\vec{r}(0),0) \tag{217}$$

Thus, the full time derivative would vanish

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\vec{k}}\cdot\vec{\nabla}_k f + \dot{\vec{r}}\cdot\vec{\nabla}_r f = 0 \tag{218}$$

However, there are processes which change the distribution function. These are collisions with impurities, phonons, other electrons The new equation reads

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\vec{k}}\cdot\vec{\nabla}_k f + \dot{\vec{r}}\cdot\vec{\nabla}_r f = \left(\frac{\partial f}{\partial t}\right)_{\text{Coll}} , \tag{219}$$

where $\left(\frac{\partial f}{\partial t}\right)_{\text{Coll}} = I[f]$ is called the collision integral.

Using the equations of motion we obtain the celebrated Boltzmann equation

$$\frac{\partial f}{\partial t} - \frac{e}{\hbar}\left(\vec{E} + \frac{1}{c}\left(\vec{v}\times\vec{B}\right)\right)\cdot\vec{\nabla}_k f + \vec{v}_k\cdot\vec{\nabla}_r f = I[f]\ . \tag{220}$$

B. Collision integral for scattering on impurities

The collision integral describes processes that bring about change of the state of the electrons, i.e., transitions. There are several reasons for the transitions: phonons, electron-electron collisions, impurities. Here we consider only one: scattering on impurities.

Scattering in general causes transitions in which electron which was in the state $n_1, \vec{k}_1$ is transferred to the state $n_2, \vec{k}_2$. We will suppress the band index as in most cases we consider scattering within a band. The collision integral has two contribution: "in" and "out": $I = I_{\rm in} + I_{\rm out}$.

The "in" part describes transitions from all the states to the state $\vec{k}$:

$$I_{\rm in}[f] = \sum_{\vec{k}_1} W(\vec{k}_1,\vec{k}) f(\vec{k}_1,\vec{r})[1 - f(\vec{k},\vec{r})]\ , \tag{221}$$

where $W(\vec{k}_1,\vec{k})$ is the transition probability per unit of time (rate) from state $\vec{k}_1$ to state $\vec{k}$ given the state $\vec{k}_1$ is initially occupied and the state $\vec{k}$ is initially empty. The factors $f(\vec{k}_1)$ and $1 - f(\vec{k})$ take care for the Pauli principle.

The "out" part describes transitions from the state $\vec{k}$ to all other states:

$$I_{\rm out}[f] = -\sum_{\vec{k}_1} W(\vec{k},\vec{k}_1) f(\vec{k},\vec{r})[1 - f(\vec{k}_1,\vec{r})]\ , \tag{222}$$

The collision integral should vanish for the equilibrium state in which

$$f(\vec{k}) = f_0 = \frac{1}{\exp\left[\frac{\epsilon(\vec{k})-\mu}{k_{\rm B}T}\right] + 1}\ . \tag{223}$$

This can be rewritten as

$$\exp\left[\frac{\epsilon(\vec{k})-\mu}{k_{\rm B}T}\right] f_0 = 1 - f_0\ . \tag{224}$$

The requirement $I_{\rm in}[f_0] + I_{\rm out}[f_0]$ is satisfied if

$$W(\vec{k},\vec{k}_1)\exp\left[\frac{\epsilon(\vec{k}_1)}{k_{\rm B}T}\right] = W(\vec{k}_1,\vec{k})\exp\left[\frac{\epsilon(\vec{k})}{k_{\rm B}T}\right]\ . \tag{225}$$

We only show here that this is sufficient but not necessary. The principle that it is always so is called "detailed balance principle". In particular, for elastic processes, in which $\epsilon(\vec{k}) = \epsilon(\vec{k}_1)$, we have

$$W(\vec{k}, \vec{k}_1) = W(\vec{k}_1, \vec{k}) \ . \tag{226}$$

In this case (when only elastic processes are present we obtain)

$$\begin{aligned} I[f] &= \sum_{\vec{k}_1} W(\vec{k}_1, \vec{k}) f(\vec{k}_1)[1 - f(\vec{k})] - \sum_{\vec{k}_1} W(\vec{k}, \vec{k}_1) f(\vec{k})[1 - f(\vec{k}_1)] \\ &= \sum_{\vec{k}_1} W(\vec{k}_1, \vec{k}) \left(f(\vec{k}_1) - f(\vec{k}) \right) \ . \end{aligned} \tag{227}$$

Thus, Pauli principle does not play a role in this case.

C. Relaxation time approximation

We introduce $f = f_0 + \delta f$. Since $I[f_0] = 0$ we obtain

$$I[f] = \sum_{\vec{k}_1} W(\vec{k}_1, \vec{k}) \left(\delta f(\vec{k}_1) - \delta f(\vec{k}) \right) \ . \tag{228}$$

Assume the rates W are all equal and $\sum_{\vec{k}_1} \delta f(\vec{k}_1) = 0$ (no change in total density), then $I[f] \sim -\delta f(\vec{k})$. We introduce the relaxation time τ such that

$$I[f] = -\frac{\delta f}{\tau} \ . \tag{229}$$

This form of the collision integral is more general. That is it can hold not only for the case assumed above. Even if this form does not hold exactly, it serves as a simple tool to make estimates.

More generally, one can assume τ is $\vec{k}$-dependent, $\tau_{\vec{k}}$. Then

$$I[f(\vec{k})] = -\frac{\delta f(\vec{k})}{\tau_{\vec{k}}} \ . \tag{230}$$

We will keep writing τ even if we mean that it is actually $\tau_{\vec{k}}$.

D. Condutivity

Within τ-approximation we determine the electrical conductivity. Assume oscillating electric field is applied $\vec{E}(t) = \vec{E}e^{-i\omega t}$. The Boltzmann equation reads

$$\frac{\partial f}{\partial t} - \frac{e}{\hbar}\,\vec{E}\cdot\vec{\nabla}_k f + \vec{v}_k\cdot\vec{\nabla}_r f = -\frac{f-f_0}{\tau}\ . \tag{231}$$

Since the field is homogeneous we expect homogeneous response $\delta f(t) = \delta f e^{-i\omega t}$. This gives

$$-\frac{e}{\hbar}\,\vec{E}\cdot\vec{\nabla}_k f = \left(i\omega - \frac{1}{\tau}\right)\,\delta f\ . \tag{232}$$

In the l.h.s. we replace f with f_0. This gives

$$-\frac{e}{\hbar}\,\frac{\partial f_0}{\partial\epsilon}\hbar\vec{v}_k\cdot\vec{E} = \left(i\omega - \frac{1}{\tau}\right)\,\delta f\ . \tag{233}$$

Thus we obtain

$$\delta f = \frac{e\tau}{1-i\omega\tau}\,\frac{\partial f_0}{\partial\epsilon}\,\vec{v}_{\vec{k}}\cdot\vec{E} \tag{234}$$

For the current density we obtain $\vec{j}(t) = \vec{j}e^{-i\omega t}$, where

$$\begin{aligned}\vec{j} &= -\frac{e}{V}\sum_{\vec{k},\sigma}\vec{v}_k\delta f(\vec{k}) \\ &= -\frac{2e^2}{V}\sum_{\vec{k}}\frac{\tau}{1-i\omega\tau}\,\frac{\partial f_0}{\partial\epsilon}\,(\vec{v}_{\vec{k}}\cdot\vec{E})\,\vec{v}_{\vec{k}} \\ &= -2e^2\int\frac{d^3k}{(2\pi)^3}\,\frac{\tau}{1-i\omega\tau}\,\frac{\partial f_0}{\partial\epsilon}\,(\vec{v}_{\vec{k}}\cdot\vec{E})\,\vec{v}_{\vec{k}}\ .\end{aligned} \tag{235}$$

We define the conductivity tensor σ via $j_\alpha = \sum_\alpha \sigma_{\alpha,\beta}E_\beta$. Thus

$$\sigma_{\alpha,\beta} = -2e^2\int\frac{d^3k}{(2\pi)^3}\,\frac{\tau}{1-i\omega\tau}\,\frac{\partial f_0}{\partial\epsilon}\,v_\alpha v_\beta\ . \tag{236}$$

At low enough temperatures, i.e., for $k_{\rm B}T \ll \mu$,

$$\frac{\partial f_0}{\partial\epsilon} \approx -\delta(\epsilon-\mu) - \frac{\pi^2}{6}\,(k_{\rm B}T)^2\delta''(\epsilon-\mu)\ , \tag{237}$$

Assuming τ is constant and the band energy is isotropic (effective mass is simple) we obtain

$$\begin{aligned}\sigma_{\alpha,\beta} &= -\frac{2e^2\tau}{1-i\omega\tau}\int\nu(\epsilon)d\epsilon\frac{d\Omega}{4\pi}\,\frac{\partial f_0}{\partial\epsilon}\,v_\alpha v_\beta \\ &= \frac{2e^2\tau\nu(\mu)}{1-i\omega\tau}\int\frac{d\Omega}{4\pi}\,v_\alpha v_\beta = \frac{2e^2\tau\nu(\mu)}{(1-i\omega\tau)}\frac{v_F^2}{3}\,\delta_{\alpha,\beta}\ .\end{aligned} \tag{238}$$

For dc-conductivity, i.e., for $\omega = 0$ we obtain

$$\sigma_{\alpha,\beta} = \frac{2e^2\tau\nu(\mu)v_F^2}{3}\,\delta_{\alpha,\beta} = \frac{e^2\tau\nu_s(\mu)v_F^2}{3}\,\delta_{\alpha,\beta}\ , \tag{239}$$

where $\nu_s = 2\nu$ is the total density of states.

E. Determining the transition rates

Impurities are described by an extra potential acting on electrons

$$U_{\rm imp}(\vec{r}) = \sum_j v(\vec{r} - \vec{a}_j) \ , \tag{240}$$

where $\vec{a}_j$ are locations of the impurities.

In the Born approximation (Golden Rule) the rates are given by

$$W(\vec{k}_1, \vec{k}) = \frac{2\pi}{\hbar} \left| U_{{\rm imp},\vec{k}_1,\vec{k}} \right|^2 \delta(\epsilon(\vec{k}_1) - \epsilon(\vec{k})) \ , \tag{241}$$

where the delta function is meaningful since we use W in a sum over $\vec{k}_1$. Thus far we normalized the Bloch wave function to the volume V. That is $\langle \psi_k^* | \, \psi_k \rangle = V$ (this also means that the Wannier functions were not normalized to unity but to $v = V/N$). For the matrix element in the Golden Rule we need state normalized to 1. Thus we have

$$U_{{\rm imp},\vec{k}_1,\vec{k}} = \frac{1}{V} \sum_j \int dV \, v(\vec{r} - \vec{a}_j) u^*_{\vec{k}_1}(\vec{r}) u_{\vec{k}}(\vec{r}) e^{i(\vec{k}-\vec{k}_1)\vec{r}} \tag{242}$$

We assume all impurities are equivalent. Moreover we assume that they all have the same position within the primitive cell. That is the only random thing is in which cell there is an impurity. Then $\vec{a}_j = \vec{R}_j + \delta\vec{a}$. Shifting by $\vec{R}_j$ in each term of the sum and using the periodicity of the functions u we obtain

$$\begin{aligned} U_{{\rm imp},\vec{k}_1,\vec{k}} &= \frac{1}{V} \sum_j e^{i(\vec{k}-\vec{k}_1)\vec{R}_j} \int dV \, v(\vec{r} - \delta\vec{a}) u^*_{\vec{k}_1}(\vec{r}) u_{\vec{k}}(\vec{r}) e^{i(\vec{k}-\vec{k}_1)\vec{r}} \\ &= \frac{1}{V} \, v_{\vec{k}_1,\vec{k}} \sum_j e^{i(\vec{k}-\vec{k}_1)\vec{R}_j} \end{aligned} \tag{243}$$

This gives

$$\left| U_{{\rm imp},\vec{k}_1,\vec{k}} \right|^2 = \frac{1}{V^2} \left| v_{\vec{k}_1,\vec{k}} \right|^2 \sum_{j,l} e^{i(\vec{k}-\vec{k}_1)(\vec{R}_j - \vec{R}_l)} \ . \tag{244}$$

This result will be put into the sum over $\vec{k}_1$ in the expression for the collision integral I. The locations $\vec{R}_j$ are random. Thus the exponents will average out. What remains are only diagonal terms. Thus we replace

$$\left| U_{{\rm imp},\vec{k}_1,\vec{k}} \right|^2 \to \frac{1}{V^2} \left| v_{\vec{k}_1,\vec{k}} \right|^2 N_{\rm imp} \ , \tag{245}$$

where $N_{\rm imp}$ is the total number of impurities. In other terms what we perform is the averaging over positions of the impurities.

This gives for the collision integral

$$\begin{aligned} I[f] &= \sum_{\vec{k}_1} W(\vec{k}_1,\vec{k}) \left(f(\vec{k}_1) - f(\vec{k}) \right) \\ &= \frac{2\pi}{\hbar} \frac{N_{\rm imp}}{V^2} \sum_{\vec{k}_1} |v_{\vec{k}_1,\vec{k}}|^2 \, \delta(\epsilon(\vec{k}_1) - \epsilon(\vec{k})) \left(f(\vec{k}_1) - f(\vec{k}) \right) \\ &= \frac{2\pi}{\hbar} \, n_{\rm imp} \int \frac{d^3k_1}{(2\pi)^3} \, |v_{\vec{k}_1,\vec{k}}|^2 \, \delta(\epsilon(\vec{k}_1) - \epsilon(\vec{k})) \left(f(\vec{k}_1) - f(\vec{k}) \right) \ , \end{aligned} \tag{246}$$

where $n_{\rm imp} \equiv N_{\rm imp}/V$.

We introduce the surface S defined by $\epsilon(\vec{k}_1) = \epsilon(\vec{k})$ and then

$$\frac{d^3k}{(2\pi)^3} = \frac{dS dk_\perp}{(2\pi)^3} = \frac{dS d\epsilon}{(2\pi)^3 \left| \frac{\partial \epsilon}{\partial k_\perp} \right|} \tag{247}$$

Now we can integrate over energy and we obtain

$$I[f(\vec{k})] = \frac{2\pi}{\hbar} \, n_{\rm imp} \int \frac{dS(\vec{k}_1)}{(2\pi)^3 \left| \frac{\partial \epsilon(\vec{k}_1)}{\partial k_\perp} \right|} \, |v_{\vec{k}_1,\vec{k}}|^2 \, \left(f(\vec{k}_1) - f(\vec{k}) \right) \ . \tag{248}$$

Note that the density of states is given by

$$\nu = \int \frac{dS}{(2\pi)^3 \left| \frac{\partial \epsilon}{\partial k_\perp} \right|} \tag{249}$$

F. Transport relaxation time

As we have seen the correction to the distribution function due to application of the electric field was of the form $\delta f \sim \vec{E} \cdot \vec{v}_k$. In a parabolic band (isotropic spectrum) this would be $\delta f \sim \vec{E} \cdot \vec{k}$. So we make an ansatz

$$\delta f = -\vec{n}_k \cdot \vec{g}(\epsilon) \ , \tag{250}$$

where $\vec{n}_k \equiv \vec{k}/|\vec{k}|$. For isotropic spectrum conservation of energy means $|\vec{k}| = |\vec{k}_1|$, the matrix element $v_{\vec{k}_1,\vec{k}}$ depends on the angle between $\vec{k}_1$ and $\vec{k}$ only, the surface S is a sphere. Then we obtain

$$\nu = \int \frac{dS}{(2\pi)^3 \left| \frac{\partial \epsilon}{\partial k_\perp} \right|} = \nu \int \frac{d\Omega}{4\pi} \ . \tag{251}$$

Thus

$$\frac{dS}{(2\pi)^3 \left| \frac{\partial \epsilon}{\partial k_\perp} \right|} = \nu \frac{d\Omega}{4\pi} \tag{252}$$

and

$$I[\delta f] = \frac{2\pi}{\hbar}\, n_{\rm imp} \int \nu \frac{d\Omega_1}{4\pi} |v_{\vec{k}_1,\vec{k}}|^2 \left(\delta f(\vec{k}_1) - \delta f(\vec{k})\right)$$
$$= \frac{2\pi}{\hbar}\, n_{\rm imp}\nu|\vec{g}| \int \frac{d\Omega_1}{4\pi} |v(\theta_{\vec{k},\vec{k}_1})|^2 \left(\cos\theta_{\vec{k},\vec{g}} - \cos\theta_{\vec{k}_1,\vec{g}}\right) . \quad (253)$$

We choose direction $\vec{k}$ as z. Then the vector $\vec{k}_1$ is described in spherical coordinates by $\theta_{\vec{k}_1} \equiv \theta_{\vec{k},\vec{k}_1}$ and $\phi_{\vec{k}_1}$. Analogously the vector $\vec{g}$ is described by $\theta_{\vec{g}} = \theta_{\vec{k},\vec{g}}$ and $\phi_{\vec{g}}$. Then $d\Omega_1 = \sin\theta_{\vec{k}_1} d\theta_{\vec{k}_1} d\phi_{\vec{k}_1}$.

From simple vector analysis we obtain

$$cos\theta_{\vec{g},\vec{k}_1} = \cos\theta_{\vec{g}} \cos\theta_{\vec{k}_1} + \sin\theta_{\vec{g}} \sin\theta_{\vec{k}_1} \cos(\phi_{\vec{g}} - \phi_{\vec{k}_1}) . \quad (254)$$

The integration then gives

$$I[\delta f] = \frac{n_{\rm imp}\nu}{2\hbar}\, |\vec{g}| \int \sin\theta_{\vec{k}_1} d\theta_{\vec{k}_1} d\phi_{\vec{k}_1} |v(\theta_{\vec{k}_1})|^2 \times$$
$$\times \left(\cos\theta_{\vec{g}} - \cos\theta_{\vec{g}} \cos\theta_{\vec{k}_1} - \sin\theta_{\vec{g}} \sin\theta_{\vec{k}_1} \cos(\phi_{\vec{g}} - \phi_{\vec{k}_1})\right)$$
$$= \frac{\pi n_{\rm imp}\nu}{\hbar}\, |\vec{g}| \cos\theta_{\vec{g}} \int \sin\theta_{\vec{k}_1} d\theta_{\vec{k}_1} |v(\theta_{\vec{k}_1})|^2 (1 - cos\theta_{\vec{k}_1}) . \quad (255)$$

Noting that $|\vec{g}| \cos\theta_{\vec{g}} = \vec{g} \cdot \vec{n}_k = -\delta f$ we obtain

$$I[\delta f] = -\frac{\delta f}{\tau_{\rm tr}} , \quad (256)$$

where

$$\frac{1}{\tau_{\rm tr}} = \frac{\pi n_{\rm imp}\nu}{\hbar} \int d\theta\, |v(\theta)|^2 \sin\theta (1 - cos\theta) \quad (257)$$

Note that our previous "relaxation time approximation" was based on total omission of the "in" term. That is in the τ-approximation we had

$$I[f] = \sum_{\vec{k}_1} W(\vec{k}_1, \vec{k}) \left(\delta f(\vec{k}_1) - \delta f(\vec{k})\right) \approx -\delta f(\vec{k}) \sum_{\vec{k}_1} W(\vec{k}_1, \vec{k}) . \quad (258)$$

Thus

$$\frac{1}{\tau} = \sum_{\vec{k}_1} W(\vec{k}_1, \vec{k}) = \frac{\pi n_{\rm imp}\nu}{\hbar} \int d\theta\, |v(\theta)|^2 \sin\theta . \quad (259)$$

The difference between $\tau_{\rm tr}$ (transport time) and τ (momentum relaxation time) is the factor $(1 - cos\theta)$ which emphasizes backscattering. If $|v(\theta)|^2 = const.$ we obtain $\tau_{\rm tr} = \tau$.

G. Local equilibrium, Chapman-Enskog Expansion

Instead of global equilibrium with given temperature T and chemical potential μ in the whole sample, consider a distribution function $f(\vec{r},\vec{k})$ corresponding to space dependent $T(\vec{r})$ and $\mu(\vec{r})$:

$$f_0 = \frac{1}{\exp\left[\frac{\epsilon_k-\mu(\vec{r})}{k_{\rm B}T(\vec{r})}\right]+1} \ . \tag{260}$$

This state is called local equilibrium because also for this distribution function the collision integral vanishes: $I[f_0]=0$. However this state is not static. Due to the kinematic terms in the Bolzmann equation (in particular $\vec{v}_k\cdot\vec{\nabla}_r f$) the state will change. Thus we consider the state $f=f_0+\delta f$ and substitute it into the Bolzmann equation. This gives (we drop the magnetic field)

$$\frac{\partial \delta f}{\partial t} - \frac{e}{\hbar}\,\vec{E}\cdot\vec{\nabla}_k(f_0+\delta f) + \vec{v}_k\cdot\vec{\nabla}_r(f_0+\delta f) = I[\delta f] \ . \tag{261}$$

We collect all the δf terms in the r.h.s.:

$$-\frac{e}{\hbar}\,\vec{E}\cdot\vec{\nabla}_k f_0 + \vec{v}_k\cdot\vec{\nabla}_r f_0 = I[\delta f] + \frac{\partial \delta f}{\partial t} + \frac{e}{\hbar}\,\vec{E}\cdot\vec{\nabla}_k\delta f - \vec{v}_k\cdot\vec{\nabla}_r\delta f \ . \tag{262}$$

We obtain

$$\vec{\nabla}_r f_0 = -\frac{\partial f_0}{\partial \epsilon_k}\,\left(\vec{\nabla}_r\mu + \frac{(\epsilon_k-\mu)}{T}\,\vec{\nabla}_r T\right) \tag{263}$$

and

$$-\frac{\partial f_0}{\partial \epsilon_k}\,\vec{v}_k\,\left((\vec{\nabla}_r\mu + e\vec{E}) + \frac{\epsilon_k-\mu}{T}\,\vec{\nabla}_r T\right) = I[\delta f] + \frac{\partial \delta f}{\partial t} + \frac{e}{\hbar}\,\vec{E}\cdot\vec{\nabla}_k\delta f - \vec{v}_k\cdot\vec{\nabla}_r\delta f \ . \tag{264}$$

In the stationary state, relaxation time approximation, and neglecting the last two terms (they are small) we obtain

$$-\frac{\partial f_0}{\partial \epsilon_k}\,\vec{v}_k\,\left((\vec{\nabla}_r\mu + e\vec{E}) + \frac{\epsilon_k-\mu}{T}\,\vec{\nabla}_r T\right) = -\frac{\delta f}{\tau_{\rm tr}} \ , \tag{265}$$

$$\delta f = \frac{\partial f_0}{\partial \epsilon_k}\,\vec{v}_k\,\tau_{\rm tr}\,\left((\vec{\nabla}_r\mu + e\vec{E}) + \frac{\epsilon_k-\mu}{T}\,\vec{\nabla}_r T\right) \ . \tag{266}$$

Thus we see that there are two "forces" getting the system out of equilibrium: the electrochemical field: $\vec{E}_{\rm el.ch.}\equiv\vec{E}+(1/e)\vec{\nabla}\mu$ and the gradient of the temperature $\vec{\nabla}T$. More precisely one introduces the electrochemical potential $\phi_{\rm el.ch.}$ such that $\vec{E}_{\rm el.ch.}=\vec{E}+(1/e)\vec{\nabla}\mu = -\vec{\nabla}\phi_{\rm el.ch.} = -\vec{\nabla}\phi + (1/e)\vec{\nabla}\mu$. Thus $\phi_{\rm el.ch.}=\phi-(1/e)\mu$.

On top of the electric current

$$\vec{j}_E(\vec{r},t) = -\frac{e}{V}\sum_{\vec{k},\sigma}\vec{v}_{\vec{k}}\delta f(\vec{k},\vec{r},t) \tag{267}$$

we define the heat current

$$\vec{j}_Q(\vec{r},t) = \frac{1}{V}\sum_{\vec{k},\sigma}(\epsilon_k-\mu)\vec{v}_{\vec{k}}\delta f(\vec{k},\vec{r},t) \tag{268}$$

This expression for the heat current follows from the definition of heat $dQ = dU - \mu dN$.

This gives

$$\begin{pmatrix}\vec{j}_E\\ \vec{j}_Q\end{pmatrix} = \begin{pmatrix}K_{11} & K_{12}\\ K_{21} & K_{22}\end{pmatrix}\begin{pmatrix}\vec{E}_{\text{el.ch.}}\\ \vec{\nabla}T/T\end{pmatrix} \tag{269}$$

For the electrical current density we obtain

$$\begin{aligned}\vec{j}_E &= -\frac{e}{V}\sum_{\vec{k},\sigma}\vec{v}_k\delta f(\vec{k})\\ &= -\frac{e}{V}\sum_{\vec{k},\sigma}\tau_{\text{tr}}\frac{\partial f_0}{\partial\epsilon}\left[\vec{v}_{\vec{k}}\cdot\left(e\vec{E}_{\text{el.ch.}}+\frac{\epsilon_k-\mu}{T}\vec{\nabla}T\right)\right]\vec{v}_{\vec{k}}\ .\end{aligned} \tag{270}$$

Thus for K_{11} we obtain

$$K_{11\alpha\beta} = -\frac{e^2}{V}\sum_{\vec{k},\sigma}\tau_{\text{tr}}\frac{\partial f_0}{\partial\epsilon}v_{k,\alpha}v_{k,\beta}\ . \tag{271}$$

For K_{12} this gives

$$K_{12\alpha\beta} = -\frac{e}{V}\sum_{\vec{k},\sigma}\tau_{\text{tr}}\frac{\partial f_0}{\partial\epsilon}(\epsilon_k-\mu)v_{k,\alpha}v_{k,\beta}\ . \tag{272}$$

For the heat current density we obtain

$$\begin{aligned}\vec{j}_Q &= \frac{1}{V}\sum_{\vec{k},\sigma}(\epsilon_k-\mu)\vec{v}_k\delta f(\vec{k})\\ &= \frac{1}{V}\sum_{\vec{k},\sigma}\tau_{\text{tr}}\left(\epsilon_k-\mu\right)\frac{\partial f_0}{\partial\epsilon}\left[\vec{v}_{\vec{k}}\cdot\left(e\vec{E}_{\text{el.ch.}}+\frac{\epsilon_k-\mu}{T}\vec{\nabla}T\right)\right]\vec{v}_{\vec{k}}\ .\end{aligned} \tag{273}$$

Thus for K_{21} we obtain

$$K_{21\alpha\beta} = \frac{e}{V}\sum_{\vec{k},\sigma}\tau_{\text{tr}}\left(\epsilon_k-\mu\right)\frac{\partial f_0}{\partial\epsilon}v_{k,\alpha}v_{k,\beta}\ . \tag{274}$$

For K_{22} this gives

$$K_{22\alpha\beta} = \frac{1}{V}\sum_{\vec{k},\sigma}\tau_{\text{tr}}\frac{\partial f_0}{\partial\epsilon}(\epsilon_k-\mu)^2\,v_{k,\alpha}v_{k,\beta}\ . \tag{275}$$

1) K_{11} is just the conductivity calculated earlier.

2) $K_{12} = -K_{21}$. This is one of the consequences of Onsager relations. **Thermo-power etc.** $K_{12} \neq 0$ only if density of states asymmetric around μ (no particle-hole symmetry).

3) For K_{22} we use

$$\frac{\partial f_0}{\partial \epsilon} \approx -\delta(\epsilon - \mu) - \frac{\pi^2}{6} (k_{\rm B}T)^2 \delta''(\epsilon - \mu) \ , \tag{276}$$

This gives

$$\begin{aligned} K_{22\alpha\beta} &= \frac{1}{V} \sum_{\vec{k},\sigma} \tau_{\rm tr} \frac{\partial f_0}{\partial \epsilon} (\epsilon_k - \mu)^2 \, v_{k,\alpha} v_{k,\beta} \\ &= 2\tau_{\rm tr} \int \nu(\epsilon) d\epsilon \frac{d\Omega}{4\pi} \frac{\partial f_0}{\partial \epsilon} (\epsilon - \mu)^2 v_\alpha v_\beta \\ &= -2\tau_{\rm tr} \frac{\pi^2}{3} (k_{\rm B}T)^2 \nu \int \frac{d\Omega}{4\pi} v_\alpha v_\beta = -\frac{2\pi^2}{9} (k_{\rm B}T)^2 \nu v_F^2 \tau_{\rm tr} \delta_{\alpha,\beta} \ . \end{aligned} \tag{277}$$

Thus, for thermal conductivity κ defined via $\vec{j}_Q = -\kappa \vec{\nabla} T$ we obtain

$$\kappa = -\frac{K_{22}}{k_{\rm B}T} = \frac{2\pi^2}{9} k_{\rm B}^2 T \nu v_F^2 \tau_{\rm tr} \tag{278}$$

Comparing with the electrical conductivity

$$\sigma = \frac{2}{3} \nu v_F^2 \tau_{\rm tr} \tag{279}$$

We obtain the Wiedemann-Franz law:

$$\frac{\kappa}{\sigma} = \frac{k_{\rm B}^2 T}{e^2} \frac{\pi^2}{3} \ . \tag{280}$$

H. Onsager relations

The relation

$$\begin{pmatrix} \vec{j}_E \\ \vec{j}_Q \end{pmatrix} = \begin{pmatrix} K_{11} & K_{12} \\ K_{21} & K_{22} \end{pmatrix} \begin{pmatrix} \vec{E}_{\rm el.ch.} \\ \vec{\nabla} T/T \end{pmatrix} \tag{281}$$

can be slightly rewritten to fit Onsager's logic.

The entropy production is given by

$$\dot{S} = \int dV \, \frac{\vec{j}_E \cdot \vec{E}}{T} - \int dV \, \frac{\vec{\nabla} \cdot \vec{j}_Q}{T} \tag{282}$$

The last term expresses the heat brought to dV by the heat currents. We perform partial integration in the last term and obtain

$$\dot{S} = \int dV \, \frac{\vec{j}_E \cdot \vec{E}}{T} + \int dV \, \vec{j}_Q \cdot \vec{\nabla} \frac{1}{T} \tag{283}$$

Thus

$$\dot{S} = \int dV \left(\vec{j}_E \cdot \vec{X}_E + \vec{j}_Q \cdot \vec{X}_Q \right) \tag{284}$$

with $\vec{X}_E = \frac{\vec{E}}{T}$ and $\vec{X}_Q = -\frac{\vec{\nabla} T}{T^2}$.

The linear response relations read

$$\begin{pmatrix} \vec{j}_E \\ \vec{j}_Q \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} \\ Q_{21} & Q_{22} \end{pmatrix} \begin{pmatrix} \vec{X}_E \\ \vec{X}_Q \end{pmatrix} = \begin{pmatrix} Q_{11} & Q_{12} \\ Q_{21} & Q_{22} \end{pmatrix} \begin{pmatrix} \frac{\vec{E}}{T} \\ -\frac{\vec{\nabla} T}{T^2} \end{pmatrix} \tag{285}$$

The Onsager theorem states that the matrix Q_{ij} is symmetric.

XII. MAGNETO-CONDUCTANCE, HALL EFFECT

A. Hall effect

We consider a situation when a relatively strong magnetic field $\vec{B}$ is applied and, on top of that, a weak electric field $\vec{E}$. For simplicity we consider $\epsilon = \hbar^2 k^2/(2m)$, where m can be the band mass.

The Boltzmann equation reads

$$\frac{\partial f}{\partial t} - \frac{e}{\hbar} \left(\vec{E} + \frac{1}{c} \left(\vec{v} \times \vec{B} \right) \right) \cdot \vec{\nabla}_k f + \vec{v}_k \cdot \vec{\nabla}_r f = I[f] \ . \tag{286}$$

We assume $I[f] = -\frac{\delta f}{\tau}$ (by τ we mean $\tau_{\rm tr}$). As long as we do not consider very high magnetic fields where Landau quantization is important we still have the Fermi distribution function f_0 for $\vec{E} = 0$. However we no longer can neglect the magnetic force (Lorentz) acting on the δf function. Thus the stationary Boltzmann equation for δf reads:

$$-\frac{e}{\hbar} \vec{E} \cdot \vec{\nabla}_k f_0 = I[\delta f] + \frac{e}{\hbar c} \left(\vec{v}_k \times \vec{B} \right) \cdot \vec{\nabla}_k \delta f \ , \tag{287}$$

or

$$-e \vec{E} \cdot \vec{v}_k \left(\frac{\partial f_0}{\partial \epsilon} \right) = -\frac{\delta f}{\tau} + \frac{e}{\hbar c} \left(\vec{v}_k \times \vec{B} \right) \cdot \vec{\nabla}_k \delta f \ , \tag{288}$$

We look for a solution in the form (in analogy to the calculation of conductivity)

$$\delta f = \tau e \vec{X} \cdot \vec{v}_k \left(\frac{\partial f_0}{\partial \epsilon} \right) \tag{289}$$

We obtain (using $\vec{v} = \hbar \vec{k}/m$)

$$\vec{\nabla}_k \delta f = \frac{\hbar \tau e}{m} \left(\frac{\partial f_0}{\partial \epsilon} \right) \vec{X} + \tau e \left(\vec{X} \cdot \vec{v}_k \right) \left(\frac{\partial^2 f_0}{\partial \epsilon^2} \right) \hbar \vec{v}_k \tag{290}$$

The second term multiplied in the Boltzmann equation by $\vec{v} \times \vec{B}$ gives zero. Thus we obtain

$$-e\,\vec{E}\cdot\vec{v}_k\left(\frac{\partial f_0}{\partial \epsilon}\right) = -e\,\vec{X}\cdot\vec{v}_k\left(\frac{\partial f_0}{\partial \epsilon}\right) + \frac{e}{\hbar c}\left(\vec{v}_k\times\vec{B}\right)\cdot\frac{\hbar\tau e}{m}\left(\frac{\partial f_0}{\partial \epsilon}\right)\vec{X}\ , \tag{291}$$

or

$$\vec{E}\cdot\vec{v}_k = \vec{X}\cdot\vec{v}_k - \frac{\tau e}{mc}\left(\vec{v}_k\times\vec{B}\right)\cdot\vec{X}\ , \tag{292}$$

or

$$\vec{E}\cdot\vec{v}_k = \vec{X}\cdot\vec{v}_k - \omega_c\tau\left(\vec{v}_k\times\vec{b}\right)\cdot\vec{X}\ , \tag{293}$$

where $\vec{b}\equiv\vec{B}/|B|$. Note that now we assumed both e and m positive. However we should also be ready to change the sign of one of them if we have holes. We make an ansatz for $\vec{X}$:

$$\vec{X} = |\vec{E}|(\alpha\vec{e}+\beta\vec{b}+\gamma(\vec{e}\times\vec{b}))\ , \tag{294}$$

where $\vec{e}\equiv\vec{E}/|E|$.

This gives

$$\begin{aligned}
\vec{e}\cdot\vec{v}_k &= \alpha\vec{e}\cdot\vec{v}_k + \beta\vec{b}\cdot\vec{v}_k + \gamma(\vec{e}\times\vec{b})\cdot\vec{v}_k \\
&- \omega_c\tau(\vec{v}_k\times\vec{b})(\alpha\vec{e}+\beta\vec{b}+\gamma(\vec{e}\times\vec{b})) \\
&= \alpha\vec{e}\cdot\vec{v}_k + \beta\vec{b}\cdot\vec{v}_k + \gamma(\vec{e}\times\vec{b})\cdot\vec{v}_k \\
&- \omega_c\tau\left[\alpha(\vec{b}\times\vec{e})\cdot\vec{v}_k + \gamma(\vec{e}\times\vec{b})\cdot(\vec{v}_k\times\vec{b})\right] \\
&= \alpha\vec{e}\cdot\vec{v}_k + \beta\vec{b}\cdot\vec{v}_k + \gamma(\vec{e}\times\vec{b})\cdot\vec{v}_k \\
&- \omega_c\tau\left[-\alpha(\vec{e}\times\vec{b})\cdot\vec{v}_k + \gamma\vec{v}_k\vec{e} - \gamma(\vec{b}\vec{e})(\vec{v}_k\vec{b})\right]\ .
\end{aligned} \tag{295}$$

We collect coefficients in front of $\vec{e}\cdot\vec{v}_k$, $\vec{b}\cdot\vec{v}_k$, and $(\vec{e}\times\vec{b})\cdot\vec{v}_k$. This gives

$$\begin{aligned}
&\alpha - 1 - \omega_c\tau\gamma = 0 \\
&\beta + \omega_c\tau\gamma(\vec{e}\cdot\vec{b}) = 0 \\
&\gamma + \omega_c\tau\alpha = 0
\end{aligned} \tag{296}$$

We thus obtain

$$\begin{aligned}
\alpha &= \frac{1}{1+\omega_c^2\tau^2} \\
\gamma &= -\frac{\omega_c\tau}{1+\omega_c^2\tau^2} \\
\beta &= \frac{\omega_c^2\tau^2}{1+\omega_c^2\tau^2}\,(\vec{e}\cdot\vec{b})
\end{aligned} \tag{297}$$

Thus

$$\vec{X} = \frac{1}{1+\omega_c^2\tau^2}\left(\vec{E} - \omega_c\tau(\vec{E}\times\vec{b}) + \omega_c^2\tau^2(\vec{E}\cdot\vec{b})\vec{b}\right) \tag{298}$$

The current density is given by

$$\vec{j} = \sigma_0\vec{X} \ , \tag{299}$$

where $\sigma_0 = \frac{2}{3}\, e^2\nu_F\tau v_F^2$ (with ν being density of states per spin). With $\nu(\epsilon) \propto \sqrt{\epsilon}$ we obtain $n = 2(2/3)\epsilon_F\nu_F$ we obtain

$$\sigma_0 = \frac{ne^2\tau v_F^2}{2\epsilon_F^2} = \frac{ne^2\tau}{m^*} \ . \tag{300}$$

This gives for the conductivity tensor (choosing $\vec{b} = \vec{z}$)

$$\sigma = \frac{\sigma_0}{1+\omega_c^2\tau^2}\begin{pmatrix} 1 & -\omega_c\tau & 0 \\ \omega_c\tau & 1 & 0 \\ 0 & 0 & 1+\omega_c^2\tau^2 \end{pmatrix} \ . \tag{301}$$

The inverse tensor of resistivity reads

$$\rho = \sigma^{-1} = \rho_0\begin{pmatrix} 1 & \omega_c\tau & 0 \\ -\omega_c\tau & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \ , \tag{302}$$

where $\rho_0 \equiv \frac{1}{\sigma_0}$.

Thus from $E_\alpha = \sum_\beta \rho_{\alpha\beta} j_\beta$ follows

$$\vec{E} = \rho_0(\vec{j} - \omega_c\tau\vec{b}\times\vec{j}) \tag{303}$$

Hall effect. Hall coefficient

$$R = \frac{E_\perp}{Bj} = \rho_0\,\frac{\omega_c\tau}{B} \tag{304}$$

With $\omega_c = \frac{eB}{m^*c}$ we obtain

$$R = \frac{m^*}{e^2n\tau}\,\frac{eB}{m^*c}\,\frac{\tau}{B} = \frac{1}{enc} \ . \tag{305}$$

Note that for the hall coefficient R the sign of the charge is important.

B. Magnetoresistance

We obtained $\rho_{xx} = \rho_{yy} = \rho_{zz} = \rho_0 = const.$. Thus no magnetoresistance.

In general one should distinguish two cases

1. Closed orbits

We have obtained for the parabolic band (with only closed orbits)

$$\sigma = \frac{\sigma_0}{1+\omega_c^2\tau^2}\begin{pmatrix} 1 & -\omega_c\tau & 0 \\ \omega_c\tau & 1 & 0 \\ 0 & 0 & 1+\omega_c^2\tau^2 \end{pmatrix} . \tag{306}$$

At high magnetic fields $\omega_c\tau \gg 1$ we obtain

$$\sigma \sim \sigma_0 \begin{pmatrix} \frac{1}{\omega_c^2\tau^2} & -\frac{1}{\omega_c\tau} & 0 \\ \frac{1}{\omega_c\tau} & \frac{1}{\omega_c^2\tau^2} & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{307}$$

2. Open orbits

For open orbits the situation is different. Imagine the open orbit is in direction k_y, Then there is a finite average velocity v_x. Thus change of v_x is possible exactly as in the case of no magnetic field. This gives

$$\sigma \sim \sigma_0 \begin{pmatrix} 1 & -\frac{1}{\omega_c\tau} & 0 \\ \frac{1}{\omega_c\tau} & \frac{1}{\omega_c^2\tau^2} & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{308}$$

For the resistivity tensor we obtain

$$\rho \sim \rho_0 \begin{pmatrix} 1/2 & \omega_c\tau/2 & 0 \\ -\omega_c\tau/2 & \omega_c^2\tau^2/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{309}$$

Thus strong magnetoresistance. Namely 1) The Hall coefficient R is 2 times smaller; 2) ρ_{yy} is greatly enhanced. Since open orbits appear usually only for certain directions of the magnetic field, one can expect strong dependence of $\hat{\rho}$ or R on the direction of $\vec{B}$.

C. Quantum Hall Effect (QHE)

Qualitative discussion: Fig. 6.

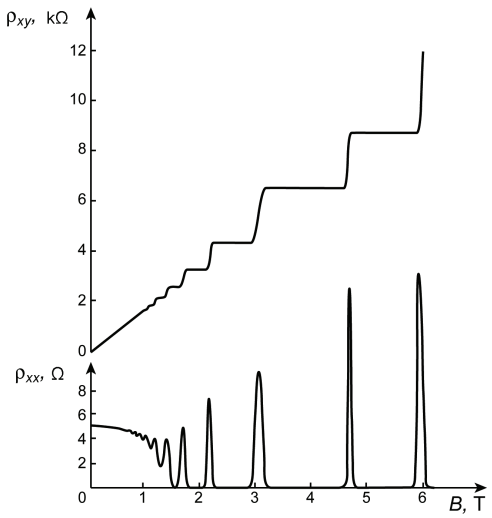

FIG. 6: Quantum Hall Effect.

XIII. FERMI GAS

We consider a collection (gas) of N free electrons (fermions with spin 1/2). The ground state is given by

$$|\phi_0\rangle = \prod_{|k|<k_F,\sigma} a^\dagger_{k,\sigma} |0\rangle \tag{310}$$

(some order of states should be chosen).

The value of k_F is determined by the number of particles N. Namely

$$N = \left(\sum_{|k|<k_F,\sigma} 1 \right) = 2 \left(\sum_{|k|<k_F} 1 \right) = \frac{2V}{(2\pi)^3} \int d^3k = V \cdot \frac{k_F^3}{3\pi^2} \tag{311}$$

Thus $k_F = (3\pi^2 n)^{1/3}$, where $n \equiv N/V$ is the density of electrons.

$$\begin{aligned} \langle\phi_0| \hat{\rho}(r) |\phi_0\rangle &= \sum_\sigma \langle\phi_0| \hat{\Psi}^\dagger_\sigma(r) \hat{\Psi}_\sigma(r) |\phi_0\rangle \\ &= \sum_\sigma \sum_{k,k'} \frac{e^{-ik'r}}{\sqrt{V}} \cdot \frac{e^{ikr}}{\sqrt{V}} \langle\phi_0| \hat{a}^\dagger_{k,\sigma} \hat{a}_{k',\sigma} |\phi_0\rangle \\ &= \sum_\sigma \sum_{k,k'} \frac{e^{-ik'r}}{\sqrt{V}} \cdot \frac{e^{ikr}}{\sqrt{V}} \delta_{k,k'} \theta(k_F - |k|) = n \end{aligned} \tag{312}$$

A. One-particle correlation function

$$G_\sigma(r-r') = \langle\phi_0|\,\hat{\Psi}^\dagger_\sigma(r)\hat{\Psi}_\sigma(r')\,|\phi_0\rangle \tag{313}$$

Meaning: amplitude to remove an electron with spin σ at r' and insert it back at r. Clearly $G_\sigma(0) = n/2$. So we define $g_\sigma(r-r')$ such that $G_\sigma(r-r') = (n/2)g_\sigma(r-r')$ and $g_\sigma(0) = 1$.

$$\begin{aligned} G_\sigma(r-r') &= \frac{1}{V}\sum_{k,k'} e^{-ikr+ik'r'}\,\langle\phi_0|\,\hat{a}^\dagger_{k,\sigma}\hat{a}_{k',\sigma}\,|\phi_0\rangle \\ &= \int_{|k|<k_F}\frac{d^3k}{(2\pi)^3}e^{-ik(r-r')} = \frac{n}{2}\cdot\frac{3(\sin x - x\cos x)}{x^3}\ , \end{aligned} \tag{314}$$

where $x \equiv k_F|r-r'|$.

B. Two-particle correlation function

Probability to find a particle at r' with spin σ' if at r there is already a particle with spin σ.

$$\begin{aligned} g_{\sigma,\sigma'}(r-r') &= \left(\frac{2}{n}\right)^2\langle\phi_0|\,\hat{\Psi}^\dagger_\sigma(r)\hat{\Psi}^\dagger_{\sigma'}(r')\hat{\Psi}_{\sigma'}(r')\hat{\Psi}_\sigma(r)\,|\phi_0\rangle \\ &= \left(\frac{2}{n}\right)^2[\langle\phi_0|\,\hat{\rho}_\sigma(r)\hat{\rho}_{\sigma'}(r')\,|\phi_0\rangle - \delta(r-r')\delta_{\sigma,\sigma'}\cdot n)] \end{aligned} \tag{315}$$

We obtain

$$g_{\sigma,\sigma'}(r-r') = \left(\frac{2}{n}\right)^2\frac{1}{V^2}\sum_{k,k',q,q'} e^{-i(k-k')r}\cdot e^{-i(q-q')r'}\,\langle\phi_0|\,\hat{a}^\dagger_{k,\sigma}\hat{a}^\dagger_{q,\sigma'}\hat{a}_{q',\sigma'}\hat{a}_{k',\sigma}\,|\phi_0\rangle \tag{316}$$

If $\sigma \neq \sigma'$ the calculation is simple

$$g_{\sigma,\sigma'}(r-r') = \left(\frac{2}{Vn}\right)^2\sum_{k,q}\langle\phi_0|\,\hat{n}_{k,\sigma}\hat{n}_{q,\sigma'}\,|\phi_0\rangle = 1 \tag{317}$$

If, however, $\sigma = \sigma'$, then we use Wick's theorem (in this case it is not difficult to prove)

$$\langle\phi_0|\,\hat{a}^\dagger_{k,\sigma}\hat{a}^\dagger_{q,\sigma}\hat{a}_{q',\sigma}\hat{a}_{k',\sigma}\,|\phi_0\rangle = (\delta_{k,k'}\delta_{q,q'} - \delta_{k,q'}\delta_{q,k'})n_{k,\sigma}n_{q,\sigma} \tag{318}$$

Thus

$$g_{\sigma,\sigma}(r-r') = \left(\frac{2}{Vn}\right)^2 \sum_{|k|<k_F,|q|<k_F} \left(1-e^{-i(k-q)(r-r')}\right) = 1 - \frac{9(\sin x - x\cos x)^2}{x^6}$$
$$= 1 - g_\sigma^2(r-r') = 1 - \frac{4}{n^2}G_\sigma^2(r-r') \ , \tag{319}$$

where again $x = k_F|r-r'|$.

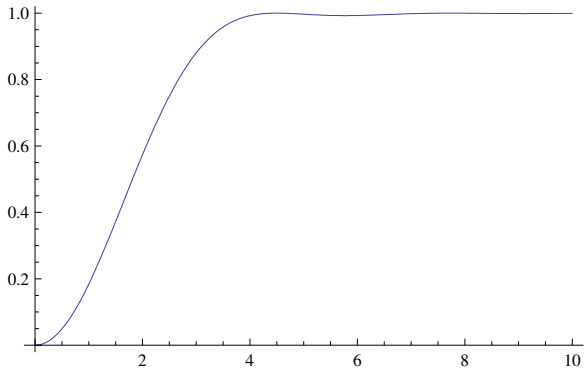

FIG. 7: Function $g_{\sigma,\sigma}(x)$.

There is a "hole" due to the Pauli principle. One can check that

$$n\int d^3r(g_{\sigma,\sigma}(r)-1) = -1 \tag{320}$$

Exactly one electron is missing. The radius of the hole $\sim k_F^{-1}$. From the density we obtain the volume taken by one electron $\delta V = 1/n$. Radius of a sphere corresponding to δV is obtained from $1/n = \delta V = (4\pi/3)r_F^3$. Thus, indeed, $r_F = \left(\frac{3}{4\pi n}\right)^{1/3} = \left(\frac{9\pi}{4}\right)^{1/3} k_F^{-1}$. In what follows it will be useful to introduce a dimensionless parameter by dividing r_F by the Bohr radius $a_0 = \hbar^2/(m_e e^2)$ and obtain

$$r_s \equiv \frac{r_F}{a_0} = \left(\frac{9\pi}{4}\right)^{1/3} \frac{m_e e^2}{\hbar^2 k_F} \tag{321}$$

C. Jellium model, energy of the ground state

We consider now the gas of interacting electrons. There are N electrons in volume V. The positively charged N ions are distributed homogeneously over the volume V. One neglects the crystalline structure and considers ions as an absolutely homogeneous charge density

$n = N/V$. Thus the Hamiltonian of the electrons reads

$$\begin{aligned}\hat{H} &= \sum_\sigma \int d^3r \left\{ -\frac{\hbar^2}{2m} \hat{\Psi}^\dagger_\sigma(r) \Delta \hat{\Psi}_\sigma(r) + \hat{\Psi}^\dagger_\sigma(r) U^{(1)}(r) \hat{\Psi}_\sigma(r) \right\} \\ &+ \sum_{\sigma_1,\sigma_2} \frac{1}{2} \int\int d^3r_1 d^3r_2 \, \hat{\Psi}^\dagger_{\sigma_1}(r_1) \hat{\Psi}^\dagger_{\sigma_2}(r_2) U^{(2)}(r_1 - r_2) \hat{\Psi}_{\sigma_2}(r_2) \hat{\Psi}_{\sigma_1}(r_1) \ , \end{aligned} \tag{322}$$

where

$$U^{(2)}(r_1 - r_2) = \frac{e^2}{|r_1 - r_2|} \quad \text{and} \quad U^{(1)}(r) = -\int d^3r' n(r') \frac{e^2}{|r - r'|} \tag{323}$$

Since the density of ions $n(r')$ does not depend on r', we obtain, that $U^{(1)}(r)$ is also r-independent (except for boundary effects) and is given by $U^{(1)}(r) = -nU_0$, where $U_0 = \int d^3r \frac{e^2}{|r|}$. This integral would diverge if $V \to \infty$.

We want to calculate the average value of the Hamiltonian in the free electrons' ground state

$$E = \langle \phi_0 | \, H \, | \phi_0 \rangle \ . \tag{324}$$

That is we do not look for the real ground state of H, but take the simple one ($|\phi_0\rangle$) and calculate the expectation value of the energy.

1. Kinetic energy

$$\begin{aligned} E_{\text{kin}} &= \langle \phi_0 | \sum_\sigma \int d^3r \left\{ -\frac{\hbar^2}{2m} \hat{\Psi}^\dagger_\sigma(r) \Delta \hat{\Psi}_\sigma(r) \right\} | \phi_0 \rangle \\ &= \sum_{|k| < k_F, \sigma} \frac{\hbar^2 k^2}{2m} = \frac{3}{5} N E_F = \frac{3}{5} N \frac{\hbar^2 k_F^2}{2m} = N \epsilon_{\text{kin}} \ , \end{aligned} \tag{325}$$

where $\epsilon_{\text{kin}} = (3/5)\, E_F$ is the kinetic energy per electron.

2. Potential energy

$$E_{\text{pot}} = \langle \phi_0 | \sum_\sigma \int d^3r \left\{ \hat{\Psi}^\dagger_\sigma(r) U^{(1)}(r) \hat{\Psi}_\sigma(r) \right\} | \phi_0 \rangle = -n^2 V U_0 = -nNU_0 \ . \tag{326}$$

3. Interaction energy

$$
\begin{aligned}
E_{\rm int} &= \langle\phi_0| \sum_{\sigma_1,\sigma_2} \frac{1}{2} \int\int d^3r_1 d^3r_2\, \hat\Psi^\dagger_{\sigma_1}(r_1)\hat\Psi^\dagger_{\sigma_2}(r_2) U^{(2)}(r_1-r_2)\hat\Psi_{\sigma_2}(r_2)\hat\Psi_{\sigma_1}(r_1)\,|\phi_0\rangle \\
&= \sum_{\sigma_1,\sigma_2} \frac{1}{2} \int\int d^3r_1 d^3r_2\, U^{(2)}(r_1-r_2)\ \langle\phi_0|\ \hat\Psi^\dagger_{\sigma_1}(r_1)\hat\Psi^\dagger_{\sigma_2}(r_2)\hat\Psi_{\sigma_2}(r_2)\hat\Psi_{\sigma_1}(r_1)\,|\phi_0\rangle \\
&= \frac{1}{2} \int\int d^3r_1 d^3r_2\, U^{(2)}(r_1-r_2) \sum_{\sigma_1,\sigma_2} \frac{n^2}{4}\, g_{\sigma_1,\sigma_2}(r_1-r_2) \\
&= \frac{1}{2} \int\int d^3r_1 d^3r_2\, U^{(2)}(r_1-r_2) \left(n^2 - \sum_\sigma G_\sigma(r_1-r_2)^2 \right)
\end{aligned}
\tag{327}
$$

The first term in called the Hartree term. It gives

$$
E_{\rm Hartree} = n^2 V U_0/2 = nNU_0/2 = N^2U_0/(2V)\ . \tag{328}
$$

It does not exactly cancel $E_{\rm pot}$ as sometimes (wrongly) stated. To get a full cancellation one has to consider the energy of the ion charges interacting with themselves (not included in the model). This one is also given by $E_{\rm ion-ion} = n^2VU_0/2$. More logical within the current model would be to say that $E_{\rm pot} + E_{\rm Hartree} = -n_{\rm el}n_{\rm ion}VU_0 + n_{\rm el}^2VU_0/2$ is minimized by $n_{\rm el} = n_{\rm ion} = n$. The minimal value of $E_{\rm pot} + E_{\rm Hartree}$ is given by $-n^2VU_0/2$.

The second term is called Fock or exchange contribution

$$
\begin{aligned}
E_{\rm Fock} &= -\frac{1}{2} \int\int d^3r_1 d^3r_2\, U^{(2)}(r_1-r_2) \sum_\sigma G_\sigma(r_1-r_2)^2 \\
&= -\frac{V}{2} \int d^3r\, U^{(2)}(r) \sum_\sigma G_\sigma(r)^2 \\
&= -N\frac{9n}{4} \int d^3r \frac{e^2}{|r|} \left[\frac{\sin k_F|r| - k_F|r|\cos k_F|r|}{(k_F|r|)^3} \right]^2 \\
&= -N\epsilon_{\rm exch}\ ,
\end{aligned}
\tag{329}
$$

where

$$
\epsilon_{\rm exch} = -\frac{9\pi n e^2}{k_F^2} \int_0^\infty dx\, \frac{(\sin x - x\cos x)^2}{x^5} = -\frac{3e^2}{4\pi}\, k_F\ . \tag{330}
$$

Thus the total energy balance reads

$$
\frac{E}{N} = \epsilon_{\rm kin} + \epsilon_{\rm exch} = \left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right] \frac{e^2}{2a_0} \tag{331}
$$

Minimum is reached for $r_s \approx 4.83$. This value corresponds to Alkali metals. Around these values of r_s the ground state of the Fermi see type is a good approximation.

For much bigger values, $r_s \to \infty$, which corresponds to a dilute limit, the energy per electron approaches zero. It turns out one can find a better ground state with a smaller energy per electron: the Wigner crystal. In this state the electron avoid each other and. thus, minimize the interaction energy.

For $r_s \to 0$ the energy per electron becomes positive, thus it seems the system is unstable, i.e., the electrons would be "better off" out of the system. This is however not so. In this limit the Fermi gas is a very good approximation. The positive kinetic energy is still compensated by the (infinite) negative energy (work function) $[E_{\rm pot} + E_{\rm Hartree}]/nV = -nU_0/2$.

XIV. FERMI LIQUID

A. Spectrum of excitations of the ideal Fermi gas

We begin again with the ideal Fermi gas (no interactions). The Fermi distribution function (the average occupation of a level with energy ϵ_k) reads

$$n_F = \frac{1}{e^{\frac{\epsilon_k - \mu}{k_{\rm B}T}} + 1} \tag{332}$$

Here $\epsilon_k = \frac{\hbar^2 k^2}{2m}$. In general the density $n = N/V$ is fixed. Thus the chemical potential is temperature dependent, $\mu(T)$. We define $\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \mu(0)$. One can obtain $k_F = (3\pi^2 n)^{1/3}$.

At $T = 0$ the Fermi function is a step function $n_F = \theta(\epsilon_F - \epsilon_k)$. At $T > 0$ the step gets smeared. This can be thought of as a result of excitation of "quasiparticles". Namely, assume we transfer one electron with energy $\epsilon_1 < \epsilon_F$ to a state with energy $\epsilon_2 > \epsilon_F$. The energy we have to pay is equal to $\epsilon_2 - \epsilon_1$. We say that we create two quasiparticles: 1) one of the particle (electron) type with energy $\xi_1 = \epsilon_2 - \epsilon_F$ and the other of the antiparticle (hole) type with energy $\xi_2 = \epsilon_F - \epsilon_1$. (One uses here the name "hole" again, although these holes have little to do with the holes introduced earlier for band electrons with negative effective mass and/or almost filled bands). If both ϵ_1 and ϵ_2 are close to ϵ_F we obtain

$$\begin{aligned} \xi_1 &= \frac{p_1^2}{2m} - \frac{p_F^2}{2m} \approx (p_1 - p_F)p_F/m = v_F(p_1 - p_F) \\ \xi_2 &= \frac{p_F^2}{2m} - \frac{p_2^2}{2m} \approx (p_F - p_2)p_F/m = v_F(p_F - p_2) \end{aligned} \tag{333}$$

It is instructive to study the dependence of the total energy $\hbar\omega \equiv \xi_1 + \xi_2$ on the total

momentum $\hbar\vec{q} \equiv \vec{p}_1 - \vec{p}_2$. It is easy to show that

$$\begin{aligned} &\text{for} \quad q < 2k_F \qquad 0 < \hbar\omega < \frac{\hbar^2 q(q+2k_F)}{2m} \\ &\text{for} \quad q > 2k_F \qquad \frac{\hbar^2 q(q-2k_F)}{2m} < \hbar\omega < \frac{\hbar^2 q(q+2k_F)}{2m} \ . \end{aligned} \tag{334}$$

Provide picture. Exercise: structure factor, reveals the spectrum of quasiparticle - hole continuum.

B. Landau hypothesis

Fermi liquid is a state (one of the possible states) of fermions (electrons or He^3 particles) with interactions. The interactions can be strong. Nevertheless Landau proposed the following: **At low temperatures (when there are not many excitations) the excitation spectrum of the Fermi liquid has the same form as that of the free Fermi gas.** Namely, the excitations are characterized by their momentum. There exists a special momentum p_F related to the density of the liquid. The energy of quasiparticles reads $\xi_1 = v_F(p_1 - p_F)$ and of quasiholes $\xi_2 = v_F(p_F - p_2)$. Now v_F is just a parameter with dimensions of velocity. One can also introduce an effective mass via $m^* v_F = p_F$. This effective mass has nothing to do with the band effective mass.

The Landau Hypothesis can be proved by the diagrammatic technique (course TKM 2). Here we just provide a motivating argument about weakness of relaxation in a Fermi gas with weak interaction. We consider an initial state with a filled Fermi see and in addition we have an electron (quasiparticle) with momentum $\vec{p}_1$ and energy ϵ_1 ($\xi_1 = \epsilon_1 - \epsilon_F > 0$). We assume $p_1 \sim p_F$ and $\xi_1 \to 0$. More precisely $\xi_1 \ll \epsilon_F$. The only possible scattering process should take an electron below the Fermi level with energy $\epsilon_2 < \epsilon_F$. Two "new" electrons will be created with energies $\epsilon_1' > \epsilon_F$ and $\epsilon_2' > \epsilon_F$. We have $\epsilon_1 + \epsilon_2 = \epsilon_1' + \epsilon_2'$ or $\xi_1 + \xi_2 = \xi_1' + \xi_2'$ with $\xi_1 > 0$, $\xi_2 < 0$, $\xi_1' > 0$, and $\xi_2' > 0$. The energy ξ_2' is given by the energy conservation. Two energies ξ_2 and ξ_1' are "free". We obtain $|\xi_2| < \xi_1$ and $\xi_1' < \xi_1$. Thus, the volume of the phase space available for the scattering process can be estimated from above to be smaller than $\nu^2\xi_1^2$, where ν is the density of states at the Fermi level. Of course one also has to take into account the conservation of momentum. In 3D this does not change the result and one arrives at the scattering rate: $\gamma \sim \xi_1^2/\epsilon_F \ll \xi_1$. Thus, it is the filled Fermi sphere which prevents particle from scattering. This is why quasiparticles with a given momentum have

long lifetimes. In a Fermi liquid the quasiparticles will have energies of order $k_{\rm B}T$. Thus they are "good" quasiparticles and the Fermi liquid description holds as long as $k_{\rm B}T \ll \epsilon_F$.

1. Implications

One of the important implications of the Landau hypothesis is the fact that the specific heat is still given by the formula similar to that of the free gas:

$$C_V = \frac{\pi^2}{3} k_{\rm B}^2 T \nu_s(\mu) \ , \tag{335}$$

where ν_s is the (total including spin) density of states at the Fermi energy. However in a Fermi liquid it is given by

$$\nu_s = \frac{p_F m^*}{\pi^2 \hbar^3} \ . \tag{336}$$

Here instead of the free mass we have the effective mass.

C. Gas model

Once having postulated the quasiparticles near the Fermi momentum p_F with the effective mass m^* we can "go back" and postulate a gas of (quasi) particles with mass m^* which fill the whole Fermi see. We describe it by the distribution function $n_{\vec{p},\sigma}$ such that at $T = 0$ all states with $p < p_F$ are occupied. At low temperatures this description is equivalent to the one with quasiparticles. We postulate that the energy eigenstates are product states characterized just by the occupation numbers $\hat{n}_{p,\sigma} = 0, 1$, with $n_{p,\sigma} \equiv \langle \hat{n}_{p,\sigma} \rangle$. Then the entropy of the system is given by

$$S = -k_{\rm B} \sum_{p,\sigma} \left[n_{p,\sigma} \ln n_{p,\sigma} + (1 - n_{p,\sigma}) \ln(1 - n_{p,\sigma}) \right] \ . \tag{337}$$

This expression follows from the definition $S = -k_{\rm B} \sum_s w_s \ln w_s$, where s denote the microscopic states characterized by which one-particle states are occupied and which are not. The probability of a particular microscopic state w_s is given by the product of occupation probabilities n_p for occupied one-particle states and $1 - n_p$ for unoccupied ones.

Proof: Assume we have already computed the entropy $S_{\{p\}}$ for a set of momenta $\{p\} = (p_1, p_2, \ldots, p_N)$. That is only the states from $\{p\}$ can be occupied by particles. We have $S_{\{p\}} = -k_{\rm B} \sum_s w_s \ln w_s$, where s is restricted to the appropriate occupation states of $\{p\}$.

We want to add to the set another momentum q. The new macroscopic states have the probabilities $w_s n_q$ if the state q is occupied and $w_s(1-n_q)$ if it is not. Then

$$\begin{aligned} S_{\{p\},q} &= -k_{\rm B}\sum_s \left[w_s n_q \ln\left[w_s n_q\right] + w_s(1-n_q)\ln\left[w_s(1-n_q)\right]\right] \\ &= S_{\{p\}} - k_{\rm B}\left[n_q \ln n_q + (1-n_q)\ln(1-n_q)\right] \ . \end{aligned} \tag{338}$$

Thus, the expression for the entropy follows from the combinatorics and has nothing to do with the energy of the states characterized by the occupation numbers.

In a free Fermi gas the (average) energy would read $E = \sum_{p,\sigma} \epsilon_p n_{p,\sigma}$. From this follows the variation of energy for a variation of the occupation probabilities δn, namely $\delta E = \sum_{p,\sigma} \epsilon_p \delta n_{p,\sigma}$.

In the Fermi liquid theory one uses a slightly more general relation. One considers the distribution function as a matrix in the spin space $\hat{n}_p = n_{p,\alpha\beta}$. While in the free gas it was sufficient to fix a spin quantization axis and to consider only diagonal matrices $n_{p,\sigma} \equiv n_{p,\sigma\sigma}$, in the Fermi liquid theory the spin-spin interaction between the quasiparticles makes a more general consideration necessary. Thus the basic relation reads

$$\delta E = \sum_{p,\alpha\beta} \epsilon_{p,\alpha\beta}\, \delta n_{p,\beta\alpha} = {\rm Tr} \sum_p \hat{\epsilon}_p\, \hat{\delta} n_p \ . \tag{339}$$

The trace is over spin variables. The relation (339) serves in the Fermi liquid theory as the definition of quasiparticle energy $\hat{\epsilon}_p$. That is creating a particle with momentum p would cause $\delta\hat{n}_p$ and a respective change in E. However in the Fermi liquid the energy is not given by a sum of single particle energies: $E \neq {\rm Tr}\sum_p \hat{\epsilon}_p \hat{n}_p$. Rather $\hat{\epsilon}_p$ is a functional of the occupation numbers for all momenta $\{p\}$: $\hat{\epsilon}_p = \hat{\epsilon}_p(\delta\hat{n}_{p_1}, \delta\hat{n}_{p_2}, \ldots)$. Here by $\delta\hat{n}_p$ we mean the deviation from the $T = 0$ step function.

We rewrite the entropy in the matrix form

$$S = -k_{\rm B}{\rm Tr}\sum_p \left[\hat{n}_p \ln \hat{n}_p + (1-\hat{n}_p)\ln(1-\hat{n}_p)\right] \ . \tag{340}$$

Using $\delta N = {\rm Tr}\sum_p \delta\hat{n}_p$ we look for a maximum of entropy for a given average energy and average number of particles. Thus we maximize $S' = S + \alpha E + \beta N$. From the condition $\delta S' = 0$ we obtain

$$\hat{n}(p) = \left[\exp\left(\frac{\hat{\epsilon}_p - \mu}{k_{\rm B}T}\right) + 1\right]^{-1} \ , \tag{341}$$

where μ and T are related to α and β. (To prove it is better to diagonalize $\hat{n}_p$ for each p.)

Have we obtained the usual Fermi occupation probability? Not really. Since $\hat{\epsilon}_p$ depends on occupation numbers of all other states, we cannot independently determine $\hat{n}_p$.

At $T = 0$ we can define $\epsilon_F \equiv \mu(T = 0)$. Note: It is a remarkable fact that the relation $k_F = (3\pi^2 n)^{1/3}$ holds also in the Fermi liquid, i.e., the value of $p_F = \hbar k_F$ is unchanged (proof of this is not simple).

D. Landau function f

If one varies the occupation probabilities one obtains for the energy functional $\epsilon_{p,\sigma}$

$$\delta\hat{\epsilon}_p = \frac{1}{V}\sum_{p'} \hat{f}(p,p')\,\delta\hat{n}_{p'} \ . \tag{342}$$

The same with indexes reads

$$\delta\epsilon_{p,\alpha\beta} = \frac{1}{V}\sum_{p'} f(p,p')_{\alpha\beta;\gamma\delta}\,\delta n_{p',\gamma\delta} \ . \tag{343}$$

In the Landau theory one postulates the function $\hat{f}(p,p')$ to be independent of $\delta\hat{n}_p$. Thus one postulates that the "quasiparticle energy" $\hat{\epsilon}_p$ is a linear functional, while the total energy E is the quadratic functional of $\delta\hat{n}_p$. Here, again, $\delta\hat{n}_p$ are the deviations from the $T = 0$ step function. Thus we obtain

$$\hat{\epsilon}_p - \epsilon_F = v_F(p - p_F)\,\hat{1} + \frac{1}{V}\sum_{p'} \hat{f}(p,p')\delta\hat{n}_{p'} \ . \tag{344}$$

Obviously the function $\hat{f}(p,p')$ is symmetric: $f(p,p')_{\alpha\beta,\gamma\delta} = f(p',p)_{\gamma\delta,\alpha\beta}$.

Only the momenta at the Fermi surface are important. Thus it is convenient to use the function $\nu_F\hat{f}(p,p')$. Then in an integration over p' only the angular dependence will remain. Usually the function $\hat{f}(p,p')$ has spin-independent part and a spin-dependent part:

$$\nu_F\,\hat{f} = F(\theta)\hat{1} + G(\theta)\,\vec{\sigma}\vec{\sigma}' \ . \tag{345}$$

Here θ is the angle between p and p'. The form with explicit spin indexes reads

$$\nu_F\,f_{\alpha\beta,\gamma\delta} = F(\theta)\delta_{\alpha\beta}\delta_{\gamma\delta} + G(\theta)\vec{\sigma}_{\alpha\beta}\vec{\sigma}_{\gamma\delta} \ . \tag{346}$$

The second term has the usual form of exchange interaction.

E. Zero sound

Here we disregard the spin degree of freedom. The Landau function f modifies the Boltzmann equation. Namely, assume we have an r-dependent deviation from equilibrium:

$$n(p,r,t) = n_0(p) + \delta n(p,r,t) \ . \tag{347}$$

We use ϵ_p as a Hamilton function of the particle and conclude that the equation of motion (with the external force $\vec{F}_{\rm ext}$, e.g., $-e\vec{E}$) reads

$$\frac{d}{dt}\vec{p} = \vec{F}_{\rm ext} - \frac{\partial \epsilon_p}{\partial \vec{r}} \ . \tag{348}$$

We obtain

$$\frac{\partial \epsilon_p}{\partial \vec{r}} = \frac{\partial \delta\epsilon_p}{\partial \vec{r}} = \frac{1}{V}\sum_{p'} f(p,p')\frac{\partial \delta n_{p'}}{\partial \vec{r}} \tag{349}$$

(we omit the spin indexes). Analogously

$$\frac{d}{dt}\vec{r} = \frac{\partial \epsilon_p}{\partial \vec{p}} \ . \tag{350}$$

The Boltzmann equation reads

$$\frac{\partial n}{\partial t} + \dot{\vec{r}}\frac{\partial n}{\partial \vec{r}} + \dot{\vec{p}}\frac{\partial n}{\partial \vec{p}} = I[n] \tag{351}$$

We retain only first order terms (omitting thus a correction to $\dot{\vec{r}} \approx v_F\vec{n}$) and we assume $F_{\rm ext} = 0$:

$$\frac{\partial \delta n}{\partial t} + v_F\vec{n}\,\frac{\partial \delta n}{\partial \vec{r}} - \frac{\partial \delta\epsilon_p}{\partial \vec{r}}\,\frac{\partial n_0}{\partial \vec{p}} = I[n] \tag{352}$$

Here $\vec{n}$ is a unity vector in the direction of $\vec{p}$.

We consider oscillations with high frequency $\omega\tau \gg 1$. Then one can neglect the collision integral. Taking into account that $\partial n_0/\partial\vec{p} = -v_F\vec{n}\delta(\epsilon_p^0 - \epsilon_F)$ we obtain

$$\frac{\partial \delta n}{\partial t} + v_F\vec{n}\,\frac{\partial \delta n}{\partial \vec{r}} + v_F\vec{n}\delta(\epsilon - \epsilon_F)\frac{1}{V}\sum_{p'} f(p,p')\frac{\partial \delta n_{p'}}{\partial \vec{r}} = 0 \ . \tag{353}$$

We look for a solution of the type $\delta n = x(\vec{n})\delta(\epsilon_p^0 - \epsilon_F)e^{i(\vec{k}\vec{r}-\omega t)}$, where $x(\vec{n})$ is an unknown function of the direction $\vec{n}$. We obtain

$$(\omega - v_F\vec{n}\vec{k})x(\vec{n}) = v_F\vec{n}\vec{k}\int \frac{d\Omega_{n'}}{4\pi}\nu_F\, f(\theta_{\vec{n},\vec{n}'})x(\vec{n}') \ . \tag{354}$$

We chose direction of $\vec{k}$ as $\vec{z}$ and introduce $s \equiv \omega/(kv_F)$. This gives

$$(s - \cos\theta)x(\theta,\phi) = \cos\theta \int F(\theta_{\vec{n},\vec{n}'})x(\theta',\phi')\frac{d\Omega_{n'}}{4\pi} \ . \tag{355}$$

Simplest case: $F = F_0 = const.$ If $s > 1$, i.e., the sound velocity ω/k bigger than v_F we have a solution of the form

$$x(\theta) = const \cdot \frac{\cos\theta}{s - \cos\theta} \ . \tag{356}$$

Discuss: shape of the deformation.

To find s substitute (356) into (355). The condition reads

$$F_0 \int_0^\pi \frac{2\pi \sin\theta d\theta}{4\pi} \frac{\cos\theta}{s - \cos\theta} = 1 \ . \tag{357}$$

With $y = -cos\theta$ we obtain

$$-F_0 \int_{-1}^{1} \frac{dy}{2} \frac{y}{s+y} = -F_0 + F_0 \frac{s}{2} \ln\frac{s+1}{s-1} = 1 \ . \tag{358}$$

Solutions exist for $F_0 > 0$. Discuss the case $F_0 \to 0$, $s \to 1$. The deviation from equilibrium only for small θ.

XV. PHONONS

We come back to the potential energy $V_{\rm ion}$ (see Eq. (12)) describing the interaction energy of slow ions due to their direct Coulomb repulsion and due to the electronic ground state energy.

The positions of ions are given by

$$\vec{r}_n^{\,k} = \vec{R}_n + \vec{a}^{\,k} \ , \tag{359}$$

where $\vec{R}_n$ are the Bravais lattice vectors. The superscript k stands for the ion number k in the unit cell. The deviations are denoted by $\vec{u}_n^k$ or in components by $u^k_{n,\alpha}$, where $\alpha = x, y, z$. As $u^k_{n,\alpha} = 0$ is the absolute minimum of the potential energy we can expand and obtain

$$V_{\rm ion} = V_0 + \frac{1}{2} \sum_{n,n',\alpha,\beta,k,k'} \Phi^{k,k'}_{n,n';\alpha,\beta} \, u^k_{n,\alpha} \, u^{k'}_{n',\beta} \tag{360}$$

The equations of motion:

$$m_k \ddot{u}^k_{n,\alpha} = - \sum_{n',\beta,k'} \Phi^{k,k'}_{n,n';\alpha,\beta} u^{k'}_{n',\beta} \tag{361}$$

The coefficients $\Phi^{k,k'}_{n,n';\alpha,\beta}$ have certain symmetries:

1) Translational symmetry

$$\Phi^{k,k'}_{n,n';\alpha,\beta} = \Phi(\vec{R}_n - \vec{R}_{n'})^{k,k'}_{\alpha,\beta} \tag{362}$$

2) Symmetry (partial derivatives are symmetric)

$$\Phi^{k,k'}_{n,n';\alpha,\beta} = \Phi^{k',k}_{n',n;\beta,\alpha} \tag{363}$$

3) Homogeneous shift should not produce any force

$$\sum_{n',k'} \Phi^{k,k'}_{n,n';\alpha,\beta} = 0 \tag{364}$$

It is very useful to introduce amplitudes $A^k_{n,\alpha} \equiv \sqrt{m_k}\, u^k_{n,\alpha}$. We look for solutions of the following form

$$A^k_{n,\alpha} = A^k_\alpha(q)\, e^{i\left(\vec{q}\vec{R}_n - \omega t\right)} \tag{365}$$

or equivalently

$$u^k_{n,\alpha} = \frac{A^k_\alpha(q)}{\sqrt{m_k}}\, e^{i\left(\vec{q}\vec{R}_n - \omega t\right)} \tag{366}$$

The eigenmodes are found from

$$\det(\omega^2\, \hat{1} - \hat{D}) = 0\ , \tag{367}$$

where the matrix $\hat{D}$ is given by

$$\begin{aligned} D^{k,k'}_{\alpha,\beta}(\vec{q}) &= \sum_{n'} D^{k,k'}_{n,n';\alpha,\beta}\, e^{-i\vec{q}\left(\vec{R}_n - \vec{R}_{n'}\right)} \\ &= \sum_{n'} \frac{1}{\sqrt{m_k m_{k'}}}\, \Phi^{k,k'}_{n,n';\alpha,\beta}\, e^{-i\vec{q}\left(\vec{R}_n - \vec{R}_{n'}\right)} = \frac{1}{\sqrt{m_k m_{k'}}}\, \Phi(\vec{q})^{k,k'}_{\alpha,\beta}\ . \end{aligned} \tag{368}$$

We have introduced the Fourier transform, which is defined via $B(q) = \sum_n B_n e^{-iqR_n}$ and $B_n = (1/N)\sum_q B(q) e^{iqR_n}$. Here N is the total number of the Bravais cells in the lattice ($N = N_1 N_2 N_3$). The wave vector q belongs to the first Brillouin zone. It is quantized due to the finite size of the crystal.

Easy to show that $D^{k,k'}_{\alpha,\beta}(\vec{q}) = [D^{k',k}_{\beta,\alpha}(\vec{q})]^*$. This means that the matrix $\hat{D}$ is hermitian and that $3M$ solutions exist, where M is the number of ions in a unit cell. We denote solutions by the subscript j: $\omega_j(\vec{q})$ and $e^k_{j,\alpha}$. The eigenvectors $e^k_{j,\alpha}$ should be normalized (see below).

Also easy to show that $D^{k,k'}_{\alpha,\beta}(-\vec{q}) = [D^{k,k'}_{\alpha,\beta}(\vec{q})]^*$. This means that

$$\omega_j(-\vec{q}) = \omega_j(\vec{q}) \quad \text{and} \quad e^k_{j,\alpha}(-\vec{q}) = [e^k_{j,\alpha}(\vec{q})]^* \ . \tag{369}$$

Now consider the limit $\vec{q} \to 0$. From the property $\sum_{n',k'} \Phi^{k,k'}_{n,n';\alpha,\beta} = 0$ follows that there are 3 modes for which $\omega_j(0) = 0$. In this modes $e^k_{j,\alpha}(0)/\sqrt{m^k}$ is independent of k. That is all ions are shifted exactly the same, i.g., $u^k_{n,\alpha}$ is independent of k.

All other $3(M-1)$ modes are optical. We obtain from the equation of motion for $\vec{q} = 0$:

$$\omega^2(0)\, m_k \, \frac{A^k_\alpha(0)}{\sqrt{m_k}} = \sum_{n',\beta,k'} \Phi^{k,k'}_{n,n';\alpha,\beta} \frac{A^{k'}_\beta(0)}{\sqrt{m_{k'}}} \ . \tag{370}$$

Using again $\sum_{n,k} \Phi^{k,k'}_{n,n';\alpha,\beta} = 0$ and assuming $\omega(0) \neq 0$ we sum over n, k and obtain

$$\sum_k m_k \, \frac{A^k_\alpha(0)}{\sqrt{m_k}} = \sum_k m_k \, u^k_\alpha(0) = 0 \tag{371}$$

Thus in optical modes the center of mass is constant.

Acoustic modes are divided into 1 longitudinal and 2 transversal.

A. Quantization of phonon modes.

The kinetic energy of vibrations reads

$$T = \frac{1}{2} \sum_{n,k,\alpha} m_k (\dot{u}^k_{n,\alpha})^2 = \frac{1}{2} \sum_{n,k,\alpha} (\dot{A}^k_{n,\alpha})^2 \ . \tag{372}$$

The potential energy reads

$$U = \frac{1}{2} \sum_{n,n',\alpha,\beta,k,k'} \Phi^{k,k'}_{n,n';\alpha,\beta} \, u^k_{n,\alpha} \, u^{k'}_{n',\beta} = \frac{1}{2} \sum_{n,n',\alpha,\beta,k,k'} D^{k,k'}_{n,n';\alpha,\beta} \, A^k_{n,\alpha} \, A^{k'}_{n',\beta} \ . \tag{373}$$

The Fourier transform of the D matrix $D^{k,k'}_{\alpha,\beta}(\vec{q})$ is a Hermitian matrix. Thus, it has $3M$ orthonormal eigenvectors $e^k_{j,\alpha}(\vec{q})$ with real eigenvalues $\omega^2_j(\vec{q})$:

$$\sum_{\alpha,k} e^k_{j,\alpha} [e^k_{j',\alpha}]^* = \delta_{j,j'} \ . \tag{374}$$

Another property is

$$e^k_{j,\alpha}(-\vec{q}) = [e^k_{j,\alpha}(\vec{q})]^* \tag{375}$$

We expand the amplitudes $A^k_{n,\alpha}(\vec{q})$ using the eigenvectors $e^k_{j,\alpha}(\vec{q})$:

$$A^k_\alpha(\vec{q}, t) = \sum_j \sqrt{N} Q_j(\vec{q}, t) e^k_{j,\alpha}(\vec{q}) \ . \tag{376}$$

The normalizing factor $\sqrt{N}$ is chosen to simplify the later expressions. We obtain

$$A^k_{n,\alpha}(t) = \frac{1}{N}\sum_{\vec{q}} A^k_\alpha(\vec{q},t)\, e^{i\vec{q}\vec{R}_n} = \frac{1}{\sqrt{N}}\sum_{j,\vec{q}} e^k_{j,\alpha}(\vec{q})\, Q_j(\vec{q},t)\, e^{i\vec{q}\vec{R}_n} \ , \tag{377}$$

where N is the total number of unit cells ($N = N_1N_2N_3$). Since $A^k_{n,\alpha}(t)$ is real we must have $Q_j(-\vec{q},t) = [Q_j(\vec{q},t)]^*$.

Using othonormality of the vectors $e^k_{j,\alpha}(\vec{q})$ we obtain

$$T = \frac{1}{2}\sum_{j,\vec{q}} \left|\dot{Q}_j(\vec{q},t)\right|^2 = \frac{1}{2}\sum_{j,\vec{q}} \dot{Q}_j(\vec{q})\dot{Q}_j(-\vec{q}) \ , \tag{378}$$

and for the potential energy we obtain

$$U = \frac{1}{2}\sum_{j,\vec{q}} \omega_j^2(\vec{q})\, |Q_j(\vec{q},t)|^2 = \frac{1}{2}\sum_{j,\vec{q}} \omega_j^2(\vec{q})\, Q_j(\vec{q})Q_j(-\vec{q}) \ . \tag{379}$$

To formulate a Lagrangian theory it would be better to have real coordinates instead of complex $Q_j(\vec{q})$. Alternatively one can use $Q_j(\vec{q})$ and $Q_j(-\vec{q})$ as independent variables.

To simplify we will suppress the index j and use $Q(\vec{q}) = Q_q$.

The conjugated variables:

$$P_q = \frac{\partial T}{\partial \dot{Q}_q} = \dot{Q}_{-q} \ . \tag{380}$$

The Hamiltonian:

$$H = \frac{1}{2}\sum_q P_q P_{-q} + \frac{1}{2}\sum_{j,\vec{q}} \omega_q^2\, Q_q Q_{-q} \ . \tag{381}$$

We introduce the creation and annihilation operators:

$$\begin{aligned} a^\dagger_q &= \frac{1}{\sqrt{2\omega_q}}\left(\omega_q Q_{-q} - iP_q\right) \ , \\ a_q &= \frac{1}{\sqrt{2\omega_q}}\left(\omega_q Q_q + iP_{-q}\right) \ . \end{aligned} \tag{382}$$

The inverse relations

$$\begin{aligned} Q_q &= \frac{a_q + a^\dagger_{-q}}{\sqrt{2\omega_q}} \ , \\ P_q &= i\sqrt{\frac{\omega_q}{2}}(a^\dagger_q - a_{-q}) \ . \end{aligned} \tag{383}$$

This gives

$$H = \sum_q \omega_q \left(a^\dagger_q a_q + \frac{1}{2}\right) \ . \tag{384}$$

It is important to express the physical field $u^k_{n,\alpha}$

$$
\begin{aligned}
u^k_{n,\alpha} &= \frac{A^k_{n,\alpha}}{\sqrt{m_k}} = \frac{1}{\sqrt{N m_k}} \sum_{j,\vec{q}} e^k_{j,\alpha}(\vec{q})\, Q_j(\vec{q})\, e^{i\vec{q}\vec{R}_n} \\
&= \frac{1}{2\sqrt{N m_k}} \sum_{j,\vec{q}} \left[Q_j(\vec{q})\, e^k_{j,\alpha}(\vec{q})\, e^{i\vec{q}\vec{R}_n} + Q_j(-\vec{q})\, e^k_{j,\alpha}(-\vec{q})\, e^{-i\vec{q}\vec{R}_n} \right] \\
&= \frac{1}{\sqrt{2N m_k}} \sum_{j,\vec{q}} \frac{1}{\sqrt{\omega_q}} \left[a_{j,\vec{q}}\, e^k_{j,\alpha}(\vec{q})\, e^{i\vec{q}\vec{R}_n} + a^\dagger_{j,\vec{q}} [e^k_{j,\alpha}(\vec{q})]^*\, e^{-i\vec{q}\vec{R}_n} \right] \ . \qquad (385)
\end{aligned}
$$

B. Phonon density of states

$$
D(\omega) = \sum_j \int \frac{d^3q}{(2\pi)^3}\, \delta(\omega - \omega_j(q)) = \sum_j \int \frac{dS}{(2\pi)^3}\, \frac{1}{|\vec{\nabla}_q\, \omega_j|} \qquad (386)
$$

Van-Hove singularities: $\vec{\nabla}_q\, \omega_j = 0$.

For $\vec{q} \to 0$ we consider only acoustic phonons. We obtain

$$
\omega_s = c_s(\vec{n}_q)|\vec{q}| \ , \qquad (387)
$$

where $s = 1, 2, 3$ counts the acoustic modes.

Then

$$
D(\omega) = \sum_s \int \frac{d\Omega_q}{(2\pi)^3}\, \frac{q^2(\omega)}{c_s(\vec{n}_q)} = \omega^2 \sum_s \int \frac{d\Omega_q}{(2\pi)^3}\, \frac{1}{c^3_s(\vec{n}_q)} = \frac{3\omega^2}{2\pi^2} \left\langle \frac{1}{c^3_s} \right\rangle \ , \qquad (388)
$$

where

$$
\left\langle \frac{1}{c^3_s} \right\rangle \equiv \frac{1}{3} \sum_s \int \frac{d\Omega_q}{4\pi}\, \frac{1}{c^3_s(\vec{n}_q)} \ . \qquad (389)
$$

C. Specific heat

Bose function:

$$
n_{j,q} = \frac{1}{e^{\beta\hbar\omega_{j,q}} - 1} \ , \qquad (390)
$$

where $\beta \equiv (k_{\rm B}T)^{-1}$. The chemical potential $\mu = 0$ since the number of phonons is not fixed and in the ground state there are no phonons.

The internal energy

$$
U = \sum_{j,q} \hbar\omega_{j,q} \left(n_{j,k} + \frac{1}{2} \right) = U_0 + \sum_{j,q} \hbar\omega_{j,q}\, n_{j,k} \ . \qquad (391)
$$

Specific heat

$$C_V = \frac{1}{V}\,\frac{\partial U}{\partial T}\Big|_V \ . \tag{392}$$

Two universal properties:

1) Maximal frequency of phonons

2) Linear dependence of $\omega(q)$ at small q and ω (sound waves)

allow for high- and low-temperature expansions.

1. High temperatures

$k_{\rm B}T \gg \hbar\omega_{max}$ (only for acoustic phonons).

$$\frac{1}{e^x - 1} = \frac{1}{x}\left(1 - \frac{x}{2} + \frac{x^2}{12} + \dots\right) \quad , \quad x \ll 1 \ . \tag{393}$$

$$\begin{aligned} C_V &= \frac{1}{V}\,\frac{\partial}{\partial T}\sum_{s,q}\hbar\omega_{s,q}\,\frac{k_{\rm B}T}{\hbar\omega_{s,q}}\left(1 - \frac{1}{2}\,\frac{\hbar\omega_{s,q}}{k_{\rm B}T} + \frac{1}{12}\left(\frac{\hbar\omega_{s,q}}{k_{\rm B}T}\right)^2 + \quad \dots\right) \\ &= 3k_{\rm B}\frac{N}{V}\left(1 - \frac{1}{12}\,\frac{\hbar^2\langle\omega_{s,q}^2\rangle}{(k_{\rm B}T)^2} + \dots\right) \ , \end{aligned} \tag{394}$$

(the first term is Dulong-Petit law) where

$$\langle\omega_{s,q}^2\rangle = \frac{1}{3N}\sum_{s,q}\omega_{s,q}^2 \tag{395}$$

If the temperature is also higher than the maximum frequency of he optical phonons, then $3 \to 3M$. All phonons contribute.

2. Low temperatures

$k_{\rm B}T \ll \hbar\omega_{max}$ (only acoustic phonons relevant).

$$\frac{1}{e^x - 1} \approx e^{-x} \quad , \quad x \gg 1 \ . \tag{396}$$

$$C_V \ = \ \frac{1}{V}\,\frac{\partial}{\partial T}\sum_{s,q}\hbar\omega_{s,q}n_{s,q} = \frac{\partial}{\partial T}\sum_s\int_0^\infty d\omega D(\omega)\hbar\omega\frac{1}{e^{\beta\hbar\omega} - 1}$$

$$= \frac{3}{2\pi^2}\left\langle\frac{1}{c_s^3}\right\rangle\frac{\partial}{\partial T}\sum_s\int\limits_0^\infty d\omega\,\frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1} = \frac{3}{2\pi^2}\left\langle\frac{1}{c_s^3}\right\rangle\frac{\partial}{\partial T}\sum_s\frac{1}{\hbar^3\beta^4}\int\limits_0^\infty dx\,\frac{x^3}{e^x-1}$$
$$= \frac{3}{2\pi^2}\left\langle\frac{1}{c_s^3}\right\rangle\frac{4k_{\rm B}^4T^3}{\hbar^3}\int\limits_0^\infty dx\,\frac{x^3}{e^x-1} = \frac{3}{2\pi^2}\left\langle\frac{1}{c_s^3}\right\rangle\frac{4k_{\rm B}^4T^3}{\hbar^3}\,\frac{\pi^4}{15}\ . \tag{397}$$

D. Debye and Einstein approximations

How to interpolate between low and high temperatures.

Simplified model.

For acoustic phonons - Debye model. For optical phonons - Einstein model.

1. Debye

The dispersion law $\omega = cq$ postulated for all q. Instead of the first Brillouin zone one takes a sphere so that the number of q's in this sphere is equal to N. That is the radius of the sphere q_D is given by

$$\frac{4\pi}{3}q_D^3\cdot\frac{V}{(2\pi)^3} = N \tag{398}$$

Debye frequency $\omega_D = cq_D$

Debye temperature $k_{\rm B}\Theta_D = \hbar\omega_D$

This gives

$$C_V = \frac{1}{V}\frac{\partial}{\partial T}\sum_{s,q}\hbar\omega_{s,q}n_{s,q} = 3\frac{\partial}{\partial T}\int\limits_0^{q_D}\frac{4\pi q^2dq}{(2\pi)^3}\,\frac{\hbar cq}{e^{\beta\hbar cq}-1}$$
$$= 3\int\limits_0^{q_D}\frac{4\pi q^2dq}{(2\pi)^3}\,\frac{(\hbar cq)^2e^{\beta\hbar cq}}{\left(e^{\beta\hbar cq}-1\right)^2}\left(-\frac{\partial\beta}{\partial T}\right)$$
$$= 3\frac{1}{k_{\rm B}T^2}\,\frac{4\pi(\hbar c)^2}{(2\pi)^3}\,\frac{1}{(\beta\hbar c)^5}\int\limits_0^{\Theta_D/T}dx\,\frac{x^4e^x}{(e^x-1)^2}$$
$$= 9k_{\rm B}\frac{N}{V}\left(\frac{T}{\Theta_D}\right)^3 f(T/\Theta_D)\ , \tag{399}$$

where

$$f(y) = \int\limits_0^{1/y}dx\,\frac{x^4e^x}{(e^x-1)^2}\ . \tag{400}$$

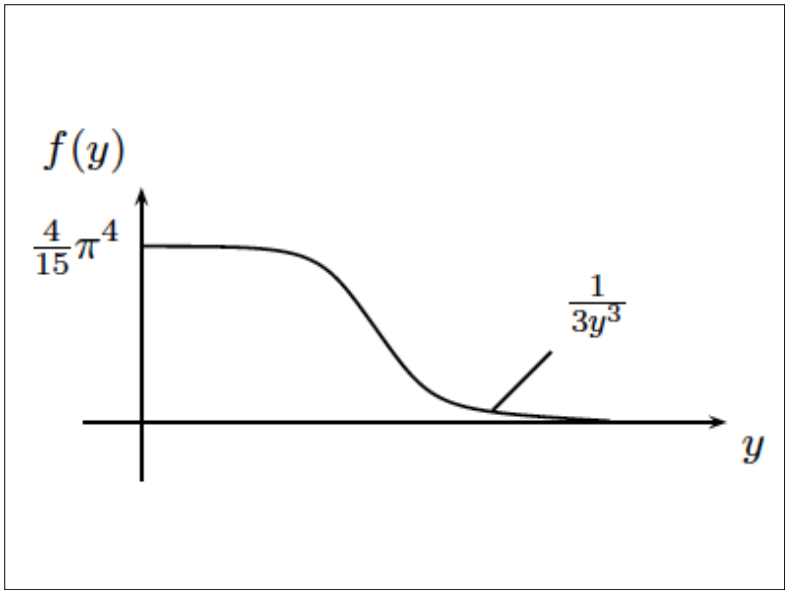

FIG. 8: Function f.

2. Einstein

Optical phonons. Neglect dispersion

$$\omega(\vec{q}) = \omega_0 \ . \tag{401}$$

$$U = U_0 + (3M-3)N\frac{\hbar\omega_0}{e^{\frac{\hbar\omega_0}{k_\mathrm{B}T}}-1} \ . \tag{402}$$

$$C_V = \frac{1}{V}\frac{\partial U}{\partial T} = (3M-3)\frac{N}{V}k_\mathrm{B}\frac{\left(\frac{\hbar\omega_0}{k_\mathrm{B}T}\right)^2 e^{\frac{\hbar\omega_0}{k_\mathrm{B}T}}}{\left(e^{\frac{\hbar\omega_0}{k_\mathrm{B}T}}-1\right)^2} \ . \tag{403}$$

E. Neutron scattering

The spectrum of phonons can be measured by scattering of neutrons on the material. One measures the differential cross-section:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{d\Omega d\omega}\frac{\delta N_f(\Omega,\omega)}{N_i} \ , \tag{404}$$

where N_i is the flux density of the incident neutrons (number of particles per area and time), $\delta N_f(\Omega,\omega)$ is the flux (number per time) of neutrons scattered into the solid angle interval

$d\Omega$ around Ω with energy transfer in the interval $\hbar d\omega$ around $\hbar\omega$. The energy transfer is given by

$$\hbar\omega = \frac{\hbar^2}{2M_n}(k_f^2 - k_i^2) = E_i - E_f \ , \tag{405}$$

where k_i and k_f are the initial and final wave vectors of the neutrons. E_i and E_f are the initial and final energies of the crystal.

Golden rule:

$$\delta N(\Omega,\omega) = \delta N(\vec{k}_i \to \vec{k}_f) = \sum_{i,f} \frac{e^{-\beta E_i}}{Z}\, W(\vec{k}_i, i \to \vec{k}_f, f)\, V n_i\, \frac{V}{(2\pi)^3}\, d^3k_f \ , \tag{406}$$

where n_i is the density of incident neutrons, $N_i = n_i v_i = n_i \frac{\hbar k_i}{M_n}$. With

$$d^3k_f = k_f^2 dk_f d\Omega = k_f\, \frac{M_n}{\hbar^2}\, (\hbar d\omega) d\Omega \tag{407}$$

we obtain

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{M_n}{2\pi\hbar}\right)^2 \frac{V^2}{2\pi}\, \frac{k_f}{k_i} \sum_{i,f} \frac{e^{-\beta E_i}}{Z}\, W(\vec{k}_i, i \to \vec{k}_f, f) \tag{408}$$

To calculate the rate W we take the interaction potential of the neutrons with the ions to be $u_0\delta(\vec{r}_{\text{neutron}} - \vec{r}_{\text{ion}})$ (neutrons interact mostly with nuclei). With $\vec{r} = \vec{r}_{\text{neutron}}$ and $\vec{r}_{\text{ion}} = \vec{r}_n = \vec{R}_n + \vec{u}_n$ (for simplicity we assume one ion per elementary cell, i.e., only acoustic phonons)

$$U(\vec{r}) = \sum_{n,k} u_0 \delta(\vec{r} - \vec{r}_n) \ . \tag{409}$$

Here u_0 has dimensions $E \cdot L^3$, $u_0 = \int d^3r U$.

Golden rule:

$$W(\vec{k}_i, i \to \vec{k}_f, f) = \frac{2\pi}{\hbar} |\langle i, k_i | U | f, k_f \rangle|^2\, \delta(E_f - E_i + \hbar\omega) \tag{410}$$

$$\begin{aligned} \langle i, k_i | U | f, k_f \rangle &= \frac{1}{V} \int d^3r\, \langle i | e^{i(\vec{k}_f - \vec{k}_i)\cdot\vec{r}} \sum_{n,k} u_0 \delta(\vec{r} - \vec{r}_n) | f \rangle \\ &= \frac{u_0}{V} \sum_n \langle i | e^{i(\vec{k}_f - \vec{k}_i)\cdot\vec{r}_n} | f \rangle = \frac{u_0}{V} \sum_n \langle i | e^{i\vec{q}\cdot\vec{r}_n} | f \rangle \ , \end{aligned} \tag{411}$$

where $\vec{q} \equiv \vec{k}_f - \vec{k}_i$.

This gives

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{M_n}{2\pi\hbar}\right)^2 \frac{V^2}{2\pi}\, \frac{k_f}{k_i} \sum_{i,f} \frac{e^{-\beta E_i}}{Z}\, \frac{2\pi}{\hbar}\, \frac{u_0^2}{V^2} \sum_{n,n'} \langle i | e^{i\vec{q}\cdot\vec{r}_n} | f \rangle \langle f | e^{-i\vec{q}\cdot\vec{r}_{n'}} | i \rangle\, \delta(E_f - E_i + \hbar\omega)$$

$$
\begin{aligned}
&= \left(\frac{M_n}{2\pi\hbar}\right)^2 \frac{u_0^2}{\hbar}\,\frac{k_f}{k_i}\,\sum_{i,f}\frac{e^{-\beta E_i}}{Z}\sum_{n,n'}\int\frac{dt}{2\pi\hbar}\langle i|e^{i\vec{q}\cdot\vec{r}_n}|f\rangle\langle f|e^{-i\vec{q}\cdot\vec{r}_{n'}}|i\rangle e^{i\frac{(E_f-E_i+\hbar\omega)t}{\hbar}} \\
&= \left(\frac{M_n}{2\pi\hbar}\right)^2 \frac{u_0^2}{\hbar}\,\frac{k_f}{k_i}\,\sum_{i,f}\frac{e^{-\beta E_i}}{Z}\sum_{n,n'}\int\frac{dt}{2\pi\hbar}\langle i|e^{i\vec{q}\cdot\vec{r}_n}|f\rangle\langle f|e^{-i\vec{q}\cdot\vec{r}_{n'}(t)}|i\rangle e^{i\omega t} \\
&= \left(\frac{M_n}{2\pi\hbar}\right)^2 \frac{u_0^2}{\hbar^2}\,\frac{k_f}{k_i}\,\sum_{i}\frac{e^{-\beta E_i}}{Z}\sum_{n,n'}\int\frac{dt}{2\pi}\langle i|e^{i\vec{q}\cdot\vec{r}_n}\,e^{-i\vec{q}\cdot\vec{r}_{n'}(t)}|i\rangle e^{i\omega t} \\
&= \left(\frac{M_n}{2\pi\hbar}\right)^2 \frac{u_0^2}{\hbar^2}\,\frac{k_f}{k_i}\sum_{n,n'}\int\frac{dt}{2\pi}\langle e^{i\vec{q}\cdot\vec{r}_n}\,e^{-i\vec{q}\cdot\vec{r}_{n'}(t)}\rangle e^{i\omega t}
\end{aligned}
\tag{412}
$$

Using $\rho(\vec{r}) = \sum_{n,k}\delta(\vec{r}-\vec{r}_n)$ we obtain $\sum_{n,k} e^{i\vec{q}\cdot\vec{r}_n} = \int d^3r\,\rho(\vec{r})e^{i\vec{q}\cdot\vec{r}} = \rho_{-\vec{q}}$.

Thus

$$
\begin{aligned}
\frac{d^2\sigma}{d\Omega d\omega} &= \left(\frac{M_n}{2\pi\hbar}\right)^2 \frac{u_0^2}{2\pi\hbar^2}\,\frac{k_f}{k_i}\int\frac{dt}{2\pi}\,\langle\rho_{-\vec{q}}(0)\rho_{\vec{q}}(t)\rangle e^{i\omega t} \\
&= \left(\frac{M_n}{2\pi\hbar}\right)^2 \frac{u_0^2}{2\pi\hbar^2}\,\frac{k_f}{k_i}\,S(\vec{q},\omega)\ ,
\end{aligned}
\tag{413}
$$

where

$$
S(\vec{q},\omega) \equiv \int\frac{dt}{2\pi}\,\langle\rho_{-\vec{q}}(0)\rho_{\vec{q}}(t)\rangle e^{i\omega t} = \sum_{n,n'}\int\frac{dt}{2\pi}\langle e^{i\vec{q}\cdot\vec{r}_n}\,e^{-i\vec{q}\cdot\vec{r}_{n'}(t)}\rangle e^{i\omega t}\ . \tag{414}
$$

We obtain

$$
\begin{aligned}
S(\vec{q},\omega) &= \sum_{n,n'}\int\frac{dt}{2\pi}\,\langle e^{i\vec{q}\cdot(\vec{R}_n+\vec{u}_n)}\,e^{-i\vec{q}\cdot(\vec{R}_{n'}+\vec{u}_{n'}(t))}\rangle e^{i\omega t} \\
&= \sum_{n,n'} e^{i\vec{q}\cdot(\vec{R}_n-\vec{R}_{n'})}\int\frac{dt}{2\pi}\,\langle e^{i\vec{q}\cdot\vec{u}_n}\,e^{-i\vec{q}\cdot\vec{u}_{n'}(t)}\rangle e^{i\omega t} \\
&= N\sum_n e^{-i\vec{q}\cdot\vec{R}_n}\int\frac{dt}{2\pi}\,\langle e^{i\vec{q}\cdot\vec{u}_0}\,e^{-i\vec{q}\cdot\vec{u}_n(t)}\rangle e^{i\omega t}\ .
\end{aligned}
\tag{415}
$$

Next we consider the average

$$
\langle e^{i\vec{q}\cdot\vec{u}_0}\,e^{-i\vec{q}\cdot\vec{u}_n(t)}\rangle\ , \tag{416}
$$

We use the formula obtained earlier

$$
u_{n,\alpha} = \frac{\sqrt{\hbar}}{\sqrt{2Nm}}\sum_{j,\vec{q}}\frac{1}{\sqrt{\omega_q}}\left[a_{j,\vec{q}}\,e_{j,\alpha}(\vec{q})\,e^{i\vec{q}\vec{R}_n} + a^\dagger_{j,\vec{q}}\,[e_{j,\alpha}(\vec{q})]^*\,e^{-i\vec{q}\vec{R}_n}\right]\ . \tag{417}
$$

We also use a relation

$$
\langle e^{i\phi_1}\,e^{-i\phi_2}\rangle = e^{-2W}e^{\langle\phi_1\phi_2\rangle}\ , \tag{418}
$$

where $4W = \langle\phi_1\phi_1 + \phi_2\phi_2\rangle$. This relation holds if the operators ϕ_1 and ϕ_2 satisfy the Wick theorem. They do if $\phi_{1/2}$ is linear in a and $a^\dagger$.

Proof

Thus we obtain

$$\langle e^{i\vec{q}\cdot\vec{u}_0}\, e^{-i\vec{q}\cdot\vec{u}_n(t)}\rangle = e^{-2W} e^{\langle[\vec{q}\cdot\vec{u}_0(0)][\vec{q}\cdot\vec{u}_n(t)]\rangle}\ , \tag{419}$$

where $2W = \langle[\vec{q}\cdot\vec{u}_0(0)]^2\rangle = \langle[\vec{q}\cdot\vec{u}_n(t)]^2\rangle$. The last equation follows from stationarity and translational symmetry.

Thus we obtain

$$S(\vec{q},\omega) = Ne^{-2W}\sum_n e^{-i\vec{q}\cdot\vec{R}_n}\int\frac{dt}{2\pi}\, e^{\langle[\vec{q}\cdot\vec{u}_0(0)][\vec{q}\cdot\vec{u}_n(t)]\rangle}\, e^{i\omega t} \tag{420}$$

F. Results

One can expand the exponent

$$e^{\langle[\vec{q}\cdot\vec{u}_0(0)][\vec{q}\cdot\vec{u}_n(t)]\rangle} = 1 + \langle[\vec{q}\cdot\vec{u}_0(0)][\vec{q}\cdot\vec{u}_n(t)]\rangle + \frac{1}{2}\langle[\vec{q}\cdot\vec{u}_0(0)][\vec{q}\cdot\vec{u}_n(t)]\rangle^2 + \dots \tag{421}$$

and obtain

$$S = S_0 + S_1 + \dots\ , \tag{422}$$

where

$$S_0 = N^2 e^{-2W}\delta(\omega)\sum_{\vec{K}}\delta_{\vec{q},\vec{K}}\ , \tag{423}$$

where $\vec{K}$ are the vectors of the reciprocal lattice. Physical meaning: 1) $\omega = 0$ elastic processes, no energy transfer. 2) $\vec{q} = \vec{K}$ - von Laue condition. Indeed $\vec{q} = \vec{k}_f - \vec{k}_i$. 3) The factor e^{-2W} is called Debye-Waller factor. It shows that the motion of ions reduces (smears) the scattering probability. Also zero point motion contributes: $W \neq 0$ for $T = 0$. One obtains

$$W = \frac{1}{2}\langle[\vec{q}\cdot\vec{u}_0(0)]^2\rangle = \frac{\hbar}{4Nm}\sum_{j,\vec{k}}\frac{|\vec{q}\cdot\vec{e}_j(\vec{k})|^2}{\omega_k}\ [2n_B(\omega_k)+1] \tag{424}$$

where $n_B(\omega) = (e^{\beta\hbar\omega}-1)^{-1}$ is the Bose function.

Consider now 1-Phonon processes. We obtain

$$S_1(\vec{q},\omega) = Ne^{-2W}\sum_s\frac{\hbar|\vec{q}\cdot\vec{e}_s(\vec{q})|^2}{2m\omega_s(\vec{q})}\left[n_{\vec{q},s}\delta(\omega-\omega_s(\vec{q})) + (n_{-\vec{q},s}+1)\delta(\omega+\omega_s(\vec{q}))\right] \tag{425}$$

The two terms correspond to emission and absorption of phonons by a neutron.

XVI. PLASMA OSCILLATIONS, THOMAS-FERMI SCREENING

A. Plasma oscillations

Consider a gas of charged particles (charge e, density n_0) in an oppositely charged static background. The Maxwell equation that governs the dynamics reads

$$\vec{\nabla} \cdot \vec{E} = 4\pi\rho \ . \tag{426}$$

It is equivalent to

$$\vec{\nabla} \times \vec{B} - \frac{1}{c}\frac{\partial \vec{E}}{\partial t} = \frac{4\pi}{c}\vec{j} \tag{427}$$

for $\vec{B} = 0$ together with the continuity equation: $\dot{\rho} + \vec{\nabla} \cdot \vec{j} = 0$.

In Fourier space this gives $i\vec{q} \cdot \vec{E}(\vec{q}, \omega) = 4\pi\rho$ and, with the continuity equation $\vec{q} \cdot \vec{j} = \omega\rho$ this gives (all fields are longitudinal) $i\omega\vec{E}(\vec{q}, \omega) = 4\pi\vec{j}(\vec{q}, \omega)$.

Equation of motion

$$m\frac{d^2\vec{r}}{dt^2} = e\vec{E} \tag{428}$$

and $\vec{j} = en_0\vec{v}$ lead to $-i\omega m\vec{j} = n_0 e^2\vec{E}$. This gives

$$\omega_p^2 = \frac{4\pi n_0 e^2}{m} \tag{429}$$

One can also associate the dielectric constant via $\rho = -\vec{\nabla} \cdot \vec{P} = -i\vec{q} \cdot \vec{P}$. Thus (everything longitudinal)

$$P = \frac{i\rho}{q} = i\,\frac{j}{\omega} = -\frac{n_0 e^2}{\omega^2 m}E = -\frac{1}{4\pi}\frac{\omega_p^2}{\omega^2}E \tag{430}$$

Thus

$$D = \epsilon E = E + 4\pi P = E\left(1 - \frac{\omega_p^2}{\omega^2}\right) \tag{431}$$

and

$$\epsilon(\omega) = \left(1 - \frac{\omega_p^2}{\omega^2}\right) \ . \tag{432}$$

B. Thomas-Fermi screening

One studies reaction of the electrons on an external charge/potential. The Poisson equation for the external charge/potential reads

$$q^2\phi^{ext}(\vec{q}) = 4\pi\rho^{ext}(\vec{q}) \tag{433}$$

For the full charge/potential

$$q^2\phi = 4\pi\rho \tag{434}$$

The dielectric constant is defined by

$$4\pi\rho^{ext} = \vec{\nabla}\cdot\vec{D} = i\vec{q}\cdot\vec{D} = i\vec{q}\epsilon(q)\vec{E} = i\vec{q}\epsilon(q)(-i\vec{q}\phi) = \epsilon(q)q^2\phi \tag{435}$$

Thus

$$\epsilon(q)\phi = \phi^{ext} \tag{436}$$

We introduce susceptibility $\chi(q)$ by

$$\rho^{ind} = \rho - \rho^{ext} = \chi(q)\phi(q) \tag{437}$$

That is the charge density is induced by the full potential. Then

$$\frac{q^2}{4\pi}(\phi - \phi^{ext}) = \chi\phi \quad \text{and} \quad \epsilon = 1 - \frac{4\pi}{q^2}\,\chi \tag{438}$$

The idea how to calculate χ is as follows. If the potential ϕ is a slowly changing function of coordinate, then it adds to the local chemical potential and locally one has an electrochemical potential $\mu+e\phi$ (charge of electron is $-e$). The electron density is then $n(\vec{r}) = n_0(\mu+e\phi(\vec{r}))$, where

$$n_0(\mu) = \frac{2}{V}\sum_k \frac{1}{e^{\beta(\epsilon_k-\mu)}-1} = 2\int d\epsilon\,\nu(\epsilon)\,\frac{1}{e^{\beta(\epsilon-\mu)}-1} \tag{439}$$

In linear response

$$\rho^{ind} = -e(n_0(\mu+e\phi) - n_0(\mu)) = -e^2\phi\frac{\partial n_0}{\partial\mu} \approx -e^2\phi[2\nu(\mu)] \tag{440}$$

Thus we obtain

$$\chi = -e^2\frac{\partial n_0}{\partial\mu} \quad \text{and} \quad \epsilon = 1 + \frac{4\pi e^2}{q^2}\,\frac{\partial n_0}{\partial\mu} \tag{441}$$

We define

$$k_{TF}^2 \equiv 4\pi e^2\,\frac{\partial n_0}{\partial\mu} = 4\pi e^2[2\nu] = 4\pi e^2\nu_s \tag{442}$$

Thus

$$\epsilon = 1 + \frac{k_{TF}^2}{q^2} \tag{443}$$

In real space this means the following. If a point charge Q is introduces as an external charge. Then

$$\phi^{ext}(\vec{r}) = \frac{Q}{r} \to \phi^{ext}(q) = \frac{4\pi Q}{q^2} \tag{444}$$

and

$$\phi = \frac{\phi^{ext}}{\epsilon} = \frac{4\pi Q}{q^2 + k_{TF}^2} \tag{445}$$

The inverse Fourier transform gives

$$\phi(\vec{r}) = \frac{Q}{r}\, e^{-r\, k_{TF}} \tag{446}$$

It is important to notice (although we did not prove it) that ϵ is independent of ω up to $\hbar\omega \sim E_F = \mu$. Thus, electrons screen instantaneously.

C. Dielectric constant of a metal

We have now ions and electrons and want to calculate their total dielectric constant defined via

$$\epsilon(\omega, \vec{q})\phi^{total}(\omega, \vec{q}) = \phi^{ext}(\omega, \vec{q}) \tag{447}$$

One can apply the following logic. Consider the potential/charge of ions as part of the external one. Then

$$\epsilon^{el}\phi^{total} = \phi^{ext} + \phi^{ion} \tag{448}$$

Another logic is to consider electrons as external. Then

$$\epsilon_0^{ion}\phi^{total} = \phi^{ext} + \phi^{el} \tag{449}$$

Since $\phi^{total} = \phi^{ext} + \phi^{ion} + \phi^{el}$ we add the two equations and obtain

$$(\epsilon^{el} + \epsilon_0^{ion})\phi^{total} = \phi^{total} + \phi^{ext} \tag{450}$$

or

$$(\epsilon^{el} + \epsilon_0^{ion} - 1)\phi^{total} = \phi^{ext} \tag{451}$$

or

$$\epsilon = \epsilon^{el} + \epsilon_0^{ion} - 1\ . \tag{452}$$

For electrons one takes Thomas-Fermi

$$\epsilon^{el}(\omega, q) = 1 + \frac{k_{TF}^2}{q^2} \tag{453}$$

For ions - dielectric constant of plasma oscillations

$$\epsilon_0^{ion}(\omega, q) = 1 - \frac{\Omega_p^2}{\omega^2}\ , \tag{454}$$

where $\Omega_p^2 = \frac{4\pi n^{ion}(Ze)^2}{M^{ion}}$. Thus

$$\epsilon = 1 - \frac{\Omega_p^2}{\omega^2} + \frac{k_{TF}^2}{q^2} \ . \tag{455}$$

This way we took into account the bare ions. Thus the notation ϵ_0^{ion}. Alternatively we can obtain the same if we consider ions "dressed" by screening electrons. That is "dressed" ions respond to a potential already screened by electrons:

$$\phi^{total} = \frac{1}{\epsilon_{dr}^{ion}} \phi_{screened}^{ext} = \frac{1}{\epsilon_{dr}^{ion}} \frac{1}{\epsilon^{el}} \phi^{ext} \tag{456}$$

Thus we obtain

$$\epsilon = \epsilon_{dr}^{ion} \epsilon^{el} = \epsilon^{el} + \epsilon_0^{ion} - 1 \tag{457}$$

This gives

$$\epsilon_{dr}^{ion} = \frac{1 - \frac{\Omega_p^2}{\omega^2} + \frac{k_{TF}^2}{q^2}}{1 + \frac{k_{TF}^2}{q^2}} = 1 - \frac{\Omega_p^2}{\omega^2 \left(1 + \frac{k_{TF}^2}{q^2}\right)} = 1 - \frac{\omega^2(q)}{\omega^2} \ , \tag{458}$$

where

$$\omega^2(q) \equiv \frac{\Omega_p^2}{1 + \frac{k_{TF}^2}{q^2}} = \frac{\Omega_p^2}{k_{TF}^2 + q^2} \, q^2 \tag{459}$$

For $q \ll k_{TF}^2$ this gives sound with

$$c = \frac{\Omega_p}{k_{TF}} \tag{460}$$

We return back to the total dielectric constant and obtain

$$\epsilon = \epsilon_{dr}^{ion} \epsilon^{el} = \left(1 + \frac{k_{TF}^2}{q^2}\right) \left(1 - \frac{\omega^2(q)}{\omega^2}\right) \tag{461}$$

or

$$\frac{1}{\epsilon(\omega, q)} = \frac{q^2}{(q^2 + k_{TF}^2)} \ \frac{\omega^2}{(\omega^2 - \omega^2(q))} \tag{462}$$

D. Effective electron-electron interaction

Unscreened Coulomb interaction gets screened

$$\frac{4\pi e^2}{q^2} \to \frac{4\pi e^2}{\epsilon q^2} = \frac{4\pi e^2}{(q^2 + k_{TF}^2)} \ \left(1 + \frac{\omega^2(q)}{\omega^2 - \omega^2(q)}\right) \tag{463}$$

Effective interaction between electrons $V_{\vec{k},\vec{k}'}^{eff}$ is obtained by the following substitution

$$\vec{q} = \vec{k} - \vec{k}' \qquad \hbar\omega = \epsilon_k - \epsilon_{k'} \tag{464}$$

At $\omega \ll \omega(q)$ - overscreening, attraction with retardation.

XVII. ELECTRON-PHONON INTERACTION, FRÖLICH-HAMILTONIAN

A. Derivation without taking into account screening

For simplicity we consider one ion per Primitive Unit (Primitive Cell) of the Bravais Lattice. Thus only acoustic phonons. The potential felt by an electron (neglecting screening by other electrons) is given by

$$U(\vec{r}) = \sum_n V^{ion}(\vec{r} - \vec{R}_n - \vec{u}_n) \approx \sum_n V^{ion}(\vec{r} - \vec{R}_n) - \sum_n \vec{\nabla} V^{ion}(r - \vec{R}_n)\vec{u}_n \ , \tag{465}$$

where $\vec{u}_n$ is the deviation of the ion with the equilibrium position $\vec{R}_n$. In the second quantization this becomes

$$\delta H = -\sum_\sigma \int dV \Psi^\dagger_\sigma(\vec{r}) \sum_n \left[\vec{\nabla} V^{ion}(r - \vec{R}_n)\right] \vec{u}_n \Psi_\sigma(\vec{r}) \tag{466}$$

With $\Psi_\sigma(\vec{r}) = \frac{1}{\sqrt{V}} \sum_k \psi_{k,\sigma}(\vec{r}) c_\sigma$ and $\Psi^\dagger_\sigma(\vec{r}) = \frac{1}{\sqrt{V}} \sum_k \psi^*_{k,\sigma}(\vec{r}) c^\dagger_\sigma$ and assuming the Bloch functions are spin independent we obtain

$$\delta H = -\sum_{k_1,k_2,\sigma} \langle k_1 | \, el.ph. \, | k_2 \rangle \, c^\dagger_{k_1,\sigma} c_{k_2,\sigma} \tag{467}$$

with

$$\langle k_1 | \, el.ph. \, | k_2 \rangle = \sum_n \vec{u}_n \frac{1}{V} \int dV \, \psi^*_{k_2}(\vec{r}) \left[\vec{\nabla} V^{ion}(\vec{r} - \vec{R}_n)\right] \psi_{k_1}(\vec{r}) \tag{468}$$

We expand

$$\vec{\nabla} V^{ion}(\vec{r} - \vec{R}_n) = \frac{1}{V} \sum_{\vec{p}} (i\vec{p}) V^{ion}_p e^{i(\vec{r} - \vec{R}_n)\vec{p}} \tag{469}$$

Then

$$\langle k_1 | \, el.ph. \, | k_2 \rangle = \frac{1}{V} \sum_n \sum_p (i\vec{p}\vec{u}_n) V^{ion}_p e^{-i\vec{p}\vec{R}_n} \frac{1}{V} \int dV \, \psi^*_{k_1}(\vec{r}) \psi_{k_2}(\vec{r}) e^{i\vec{p}\vec{r}} \tag{470}$$

We now use the second quantized form for $\vec{u}_n$:

$$\vec{u}_n = \sum_{j,\vec{q}} \frac{\sqrt{\hbar}}{\sqrt{2NM\omega_{j,q}}} \left[a_{j,\vec{q}} + a^\dagger_{j,-\vec{q}}\right] \vec{e}_j(\vec{q}) \, e^{i\vec{q}\vec{R}_n} \ . \tag{471}$$

Substituting and using

$$\sum_n e^{i(\vec{q} - \vec{p})\vec{R}_n} = N \sum_{\vec{G}} \delta_{\vec{p},\vec{q}+\vec{G}} \ , \tag{472}$$

where $\vec{q} \in$ 1.B.Z and $\vec{G}$ are vectors of the reciprocal lattice, we obtain

$$\begin{aligned}\langle k_1|\, el.ph.\, |k_2\rangle \;&=\; \frac{1}{V}\sum_{j,q,G} V^{ion}_{q+G}\frac{i\sqrt{N\hbar}\left[(\vec{q}+\vec{G})\vec{e}_{j,q}\right]}{\sqrt{2M\omega_{j,q}}}\left[a_{j,\vec{q}}+a^{\dagger}_{j,-\vec{q}}\right]\\ &\times\; \frac{1}{V}\int dV\,\psi^{*}_{k_1}(\vec{r})\psi_{k_2}(\vec{r})e^{i(\vec{q}+\vec{G})\vec{r}}\end{aligned} \tag{473}$$

For the matrix element we obtain

$$\begin{aligned}&\frac{1}{V}\int dV\,\psi^{*}_{k_1}(\vec{r})\psi_{k_2}(\vec{r})e^{i(\vec{q}+\vec{G})\vec{r}} = \frac{1}{V}\int dV\,u^{*}_{k_1}(\vec{r})u_{k_2}(\vec{r})e^{i(\vec{k}_2-\vec{k}_1+\vec{q}+\vec{G})\vec{r}}\\ &= \frac{1}{N}\sum_{n} e^{i(\vec{k}_2-\vec{k}_1+\vec{q}+\vec{G})\vec{R}_n}\frac{1}{V_{P.U.}}\int\limits_{P.U.} dV\,u^{*}_{k_1}(\vec{r})u_{k_2}(\vec{r})e^{i(\vec{k}_2-\vec{k}_1+\vec{q}+\vec{G})\vec{r}}\end{aligned} \tag{474}$$

We use again the relation (472) which can be written as

$$\frac{1}{N}\sum_{n} e^{i(\vec{k}_2-\vec{k}_1+\vec{q}+\vec{G})\vec{R}_n} = \sum_{\vec{G}'}\delta_{\vec{k}_1,\vec{k}_2+\vec{q}+\vec{G}-\vec{G}'} \tag{475}$$

Here, however, the possible choices for $\vec{G}'$ are severely limited. For each $\vec{G}$ only one term in the sum remains (one value of $\vec{G}'$) such that $\vec{k}_2, \vec{k}_1, \vec{q} \in$ 1.B.Z. It is more convenient, thus, to write

$$\frac{1}{N}\sum_{n} e^{i(\vec{k}_2-\vec{k}_1+\vec{q}+\vec{G})\vec{R}_n} = \delta_{q,k_1-k_2+K}\ , \tag{476}$$

where $\vec{K}_{\vec{k}_1,\vec{k}_2} \in$ R.L. is chosen so that $\vec{q} = \vec{k}_1 - \vec{k}_2 + \vec{K} \in$ 1.B.Z. Obviously, this choice is unique. This gives

$$\frac{1}{V}\int dV\,\psi^{*}_{k_1}(\vec{r})\psi_{k_2}(\vec{r})e^{i(\vec{q}+\vec{G})\vec{r}} = \delta_{q,k_1-k_2+K}\,\frac{1}{V_{P.U.}}\int\limits_{P.U.} dV\,u^{*}_{k_1}(\vec{r})u_{k_2}(\vec{r})e^{i\left[\vec{G}+\vec{K}\right]\cdot\vec{r}}\ . \tag{477}$$

Thus we obtain

$$\delta H = \sum_{k_1,k_2,q,j,\sigma} M(\vec{k}_1,\vec{k}_2,\vec{q},j)\,c^{\dagger}_{k_1,\sigma}c_{k_2,\sigma}\left[a_{j,\vec{q}}+a^{\dagger}_{j,-\vec{q}}\right]\ , \tag{478}$$

where

$$\begin{aligned}M(\vec{k}_1,\vec{k}_2,\vec{q},j) \;&=\; -\frac{1}{V}\sum_{\vec{G}} V^{ion}_{q+G}\frac{i\sqrt{N\hbar}\left[(\vec{q}+\vec{G})\vec{e}_{j,q}\right]}{\sqrt{2M\omega_{j,q}}}\delta_{q,k_1-k_2+K}\\ &\times\; \frac{1}{V_{P.U.}}\int\limits_{P.U.} dV\,u^{*}_{k_1}(\vec{r})u_{k_2}(\vec{r})e^{i(\vec{G}+\vec{K})\cdot\vec{r}}\ .\end{aligned} \tag{479}$$

Once again, $\vec{K}$ is uniquely chosen so that $\vec{q} \in$ 1.B.Z.

B. Including screening

Our naive derivation assumed no screaning and thus $V_p^{ion} = \frac{4\pi e^2}{p^2}$. Less naively we should include screening by substituting $V_p^{ion} = \frac{4\pi e^2}{(p^2+k_{TF}^2)} \approx \frac{4\pi e^2}{k_{TF}^2}$. This means $V^{ion}(\vec{r}) = 4\pi e^2 a_{TF}^2 \delta^3(\vec{r})$.

C. Direct derivation with screening

The polarization $\vec{P}(\vec{r}) = en\vec{u}(\vec{r})$ (assume $Z = 1$) creates a charge density $\rho^{ion} = -\vec{\nabla} \cdot \vec{P}$.

The interaction of an electron with this charge density is given by

$$U(\vec{r}) = -e \int d^3 r_1 Q(\vec{r} - \vec{r}_1) \rho^{ion}(\vec{r}_1) = e^2 n \int d^3 r_1 Q(\vec{r} - \vec{r}_1) \vec{\nabla} \vec{u}(\vec{r}_1) \ , \tag{480}$$

where

$$Q(\vec{k}) = \frac{4\pi}{k_{TF}^2} \ . \tag{481}$$

In the continuous limit

$$\vec{u}(\vec{r}) = \sum_{j,\vec{q}} \frac{\sqrt{\hbar}}{\sqrt{2NM\omega_{j,q}}} \left[a_{j,\vec{q}} + a_{j,-\vec{q}}^\dagger \right] \vec{e}_j(\vec{q}) \, e^{i\vec{q}\vec{r}} \ . \tag{482}$$

Thus

$$\delta H = \sum_{k_1,k_2,\sigma} \langle k_1 | \, el.ph. \, | k_2 \rangle \, c_{k_1,\sigma}^\dagger c_{k_2,\sigma} \tag{483}$$

with

$$\langle k_1 | \, el.ph. \, | k_2 \rangle = \frac{1}{V} e^2 n \int d^3 r \int d^3 r_1 \psi_{k_2}^*(\vec{r}) Q(\vec{r} - \vec{r}_1) \vec{\nabla} \vec{u}(\vec{r}_1) \psi_{k_1}(\vec{r}) \tag{484}$$

$$\begin{aligned} \langle k_1 | \, el.ph. \, | k_2 \rangle \ &= \ \frac{1}{V} e^2 n \sum_{j,q} Q(q) \frac{i\sqrt{\hbar} \, [\vec{q} \cdot \vec{e}_{j,q}]}{\sqrt{2NM\omega_{j,q}}} \left[a_{j,\vec{q}} + a_{j,-\vec{q}}^\dagger \right] \\ &\times \ \int dV \, \psi_{k_1}^*(\vec{r}) \psi_{k_2}(\vec{r}) e^{i\vec{q}\cdot\vec{r}} \ . \end{aligned} \tag{485}$$

With $n = N/V$ we reproduce the previous result. We only lost the "umklapp" processes due to the continuous approximation for $\vec{u}(\vec{r})$.

D. Phonon induced interaction between electrons

We simplify somewhat. We "forget" about "umklapp" processes, and also use plane waves instead of Bloch functions. For each $\vec{q}$ only one phonon mode (longitudinal with $\vec{e}_{j,q} \parallel \vec{q}$) contributes. Then

$$H_{el-ph} = \sum_{k,q,\sigma} M(\vec{q})\, c^{\dagger}_{k+q,\sigma} c_{k,\sigma} \left[a_{\vec{q}} + a^{\dagger}_{-\vec{q}} \right] \ , \tag{486}$$

where

$$M(\vec{q}) \ = \ -iV^{ion}_{q} \frac{1}{V} \frac{\sqrt{N\hbar}}{\sqrt{2M\omega_q}}\, q \ . \tag{487}$$

with $V^{ion}_{q} = 4\pi e^2 a^2_{TF}$.

Consider a process in which an electron with momentum $\vec{k}_1$ emits virtually a phonon with momentum $\vec{q}$, so that its new momentum is $\vec{k}_1 - \vec{q}$. Then an electron with momentum $\vec{k}_2$ absorbs the photon and its momentum becomes $\vec{k}_2 + \vec{q}$.

In the initial state the energy is $E_0 = \epsilon_{\vec{k}_1} + \epsilon_{\vec{k}_2}$. In the virtual state the energy is $E_1 = \epsilon_{\vec{k}_1 - \vec{q}} + \epsilon_{\vec{k}_2} + \hbar\omega_q$.

The second order amplitude of this process reads

$$\frac{|M(\vec{q})|^2}{E_0 - E_1} = \frac{|M(\vec{q})|^2}{\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1 - \vec{q}} - \hbar\omega_q} \tag{488}$$

Another process which interferes with the first one is as follows. Electron with momentum $\vec{k}_2$ emits a phonon with momentum $-\vec{q}$. Then electron with momentum $\vec{k}_1$ absorbs the phonon. The amplitude reads

$$\frac{|M(\vec{q})|^2}{\epsilon_{\vec{k}_2} - \epsilon_{\vec{k}_2 + \vec{q}} - \hbar\omega_q} \tag{489}$$

Conservation of energy requires $\epsilon_{\vec{k}_1} + \epsilon_{\vec{k}_2} = \epsilon_{\vec{k}_1 - \vec{q}} + \epsilon_{\vec{k}_2 + \vec{q}}$.

The total amplitude reads

$$\begin{aligned} & \frac{|M(\vec{q})|^2}{\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1 - \vec{q}} - \hbar\omega_q} + \frac{|M(\vec{q})|^2}{\epsilon_{\vec{k}_2} - \epsilon_{\vec{k}_2 + \vec{q}} - \hbar\omega_q} \\ = \ & \frac{2|M(\vec{q})|^2 \hbar\omega_q}{(\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1 - \vec{q}})^2 - (\hbar\omega_q)^2} \end{aligned} \tag{490}$$

We observe that if $|\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1 - \vec{q}}| \ll \omega_q$ the sign of the interaction matrix element is negative, i.e., we obtain attraction.

1. Comparison

We should compare the phonon mediated interaction

$$\frac{2|M(\vec{q})|^2\hbar\omega_q}{(\epsilon_{\vec{k}_1}-\epsilon_{\vec{k}_1-\vec{q}})^2-(\hbar\omega_q)^2} \tag{491}$$

where

$$M(\vec{q}) \;=\; -iV_q^{ion}\,\frac{1}{V}\,\frac{\sqrt{N\hbar}}{\sqrt{2M\omega_q}}\,q\;. \tag{492}$$

with $V_q^{ion}=4\pi e^2a_{TF}^2$, with the one obtained earlier (a factor $1/V$ needed)

$$\frac{1}{V}\,\frac{4\pi e^2}{q^2}\to\frac{1}{V}\,\frac{4\pi e^2}{\epsilon q^2}=\frac{1}{V}\,\frac{4\pi e^2}{(q^2+k_{TF}^2)}\,\left(1+\frac{\omega^2(q)}{\omega^2-\omega^2(q)}\right) \tag{493}$$

Neglecting q^2 in comparison with k_{TF}^2 we see that we have to compare

$$*=2|M(\vec{q})|^2\,\frac{\omega_q}{\hbar}=\;\frac{1}{V^2}\,2(4\pi e^2a_{TF}^2)^2\,\frac{N\hbar}{2M\omega_q}\,q^2\,\frac{\omega_q}{\hbar} \tag{494}$$

with

$$**=\;\frac{1}{V}\,4\pi e^2a_{TF}^2\omega_q^2 \tag{495}$$

We obtain

$$\begin{aligned}*&=\;\frac{1}{V^2}\,(4\pi e^2a_{TF}^2)^2\,\frac{N}{M}\,q^2=\;\frac{1}{V^2}\,(4\pi e^2a_{TF}^2)^2\,\frac{N}{M}\frac{\omega_q^2}{c_s^2}=\;\frac{1}{V^2}\,(4\pi e^2a_{TF}^2)^2\,\frac{N}{M}\frac{\omega_q^2}{\Omega_p^2a_{TF}^2}\\&=\;\frac{1}{V^2}\,(4\pi e^2a_{TF}^2)^2\,\frac{N}{M}\frac{\omega_q^2}{a_{TF}^2}\,\frac{M}{4\pi n_ie^2}=**\end{aligned} \tag{496}$$

XVIII. BCS THEORY OF SUPERCONDUCTIVITY

A. Phonon induced interaction between electrons

$$H_{el-ph}=\sum_{k,q,\sigma}M(\vec{q})\,c^\dagger_{k+q,\sigma}c_{k,\sigma}\left[a_{\vec{q}}+a^\dagger_{-\vec{q}}\right]\;, \tag{497}$$

where

$$M(\vec{q}) \;=\; -iV_q^{ion}\,\frac{1}{V}\,\frac{\sqrt{N\hbar}}{\sqrt{2M\omega_q}}\,q\;. \tag{498}$$

with $V_q^{ion}=4\pi e^2a_{TF}^2$.

The total interaction amplitude reads

$$V_{k_1,k_2,q} = \frac{2|M(\vec{q})|^2\hbar\omega_q}{(\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1-\vec{q}})^2 - (\hbar\omega_q)^2} = \frac{g_{k_1,k_2,q}}{V} \tag{499}$$

(Introduction of g is convenient since g does not contain extensive quantities like V or N - check this. g has dimensions $energy \times volume$). This amplitude is only taken on-shell as far as electrons are concerned. Thus

$$(\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1-\vec{q}})^2 = (\epsilon_{\vec{k}_2} - \epsilon_{\vec{k}_2+\vec{q}})^2$$

.

That is the effective second quantized interaction between electrons due to phonons reads

$$H_{el-el-ph} = \frac{1}{2V}\sum_{k_1,\sigma_1,k_2,\sigma_2,q} g_{k_1,k_2,q}\, c^\dagger_{k_1+q,\sigma_1}\, c^\dagger_{k_2-q,\sigma_2}\, c_{k_2,\sigma_2}\, c_{k_1,\sigma_1} \tag{500}$$

The noninteracting Hamiltonian reads

$$H_0 = \sum_{k,\sigma} \epsilon_k c^\dagger_{k,\sigma}\, c_{k,\sigma} \tag{501}$$

B. Cooper problem (L. Cooper 1955)

The interaction is attractive and considerable as long as the energy transfer $|\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1-\vec{q}}| \ll \hbar\omega_q \leq \hbar\omega_D$. We simplify the model as follows:

$$g_{k_1,k_2,q} = \begin{cases} -g & \text{if} \quad |\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1-\vec{q}}| \leq \hbar\omega_D \\ 0 & \text{if} \quad |\epsilon_{\vec{k}_1} - \epsilon_{\vec{k}_1-\vec{q}}| > \hbar\omega_D \end{cases} \tag{502}$$

Cooper considered a pair of electrons above the filled Fermi sphere. That is the Fermi sphere is given by

$$|\Phi_0\rangle = \prod_{k\leq k_F,\sigma} c^\dagger_{k,\sigma}\,|0\rangle \ , \tag{503}$$

Cooper explored the following state

$$|\Phi\rangle = \sum_{k_1>k_F,\sigma_1,k_2>k_F,\sigma_2} \psi(k_1,\sigma_1,k_2,\sigma_2) c^\dagger_{k_1,\sigma_1} c^\dagger_{k_2,\sigma_2}\,|\Phi_0\rangle \tag{504}$$

The wave function $\psi(k_1,\sigma_1,k_2,\sigma_2)$ is antisymmetric, i.e, $\psi(k_1,\sigma_1,k_2,\sigma_2) = -\psi(k_2,\sigma_2,k_1,\sigma_1)$ (indeed the second quantization is organized so that even if we use here not an antisymmetric function, only the antisymmetric part will be important). We use $\psi(k_1,\sigma_1,k_2,\sigma_2) =$

$\alpha(k_1,k_2)\chi(\sigma_1,\sigma_2)$. Further we restrict ourselves to the states with zero total momentum, $\vec{k}_1+\vec{k}_2=0$. We also restrict ourselves to the layer of states with energies $[E_F, E_F+\hbar\omega_D]$. Any pair out of this layer interacts with any other pair. Thus

$$|\Phi\rangle = \sum_{E_F<\epsilon_k<E_F+\hbar\omega_D,\sigma_1,\sigma_2} \alpha(\vec{k})\chi(\sigma_1,\sigma_2)c^\dagger_{k,\sigma_1}c^\dagger_{-k,\sigma_2}|\Phi_0\rangle \tag{505}$$

The Schrödinger equation reads

$$E|\Phi\rangle = (H_0+H_{el-el-ph})|\Phi\rangle \tag{506}$$

We count the energy from the energy of the filled Fermi sphere. Then

$$\begin{aligned} E|\Phi\rangle &= \sum_{k,\sigma_1,\sigma_2} 2\epsilon_k\alpha(\vec{k})\chi(\sigma_1,\sigma_2)c^\dagger_{k,\sigma_1}c^\dagger_{-k,\sigma_2}|\Phi_0\rangle \\ &- \frac{g}{V}\sum_{k,\sigma_1,\sigma_2,q}\alpha(\vec{k})\chi(\sigma_1,\sigma_2)c^\dagger_{k+q,\sigma_1}c^\dagger_{-k-q,\sigma_2}|\Phi_0\rangle \end{aligned} \tag{507}$$

This gives

$$(2\epsilon_k-E)\alpha(k) = \frac{g}{V}\sum_{E_F<\epsilon_{k_1}<E_F+\hbar\omega_D}\alpha(k_1) \tag{508}$$

We denote

$$C \equiv \frac{1}{V}\sum_{E_F<\epsilon_{k_1}<E_F+\hbar\omega_D}\alpha(k_1) \tag{509}$$

and obtain

$$\alpha(k) = \frac{gC}{(2\epsilon_k-E)} \tag{510}$$

Summing this equation we obtain

$$C = \frac{1}{V}\sum_{E_F<\epsilon_{k_1}<E_F+\hbar\omega_D}\frac{gC}{(2\epsilon_k-E)} \tag{511}$$

We obtain equation for E

$$1 = \int_{E_F}^{E_F+\hbar\omega_D} d\epsilon \frac{\nu(\epsilon)g}{(2\epsilon-E)} \tag{512}$$

Approximating the density of states by a constant $\nu(\epsilon)=\nu_0$ (this is density of states per spin) we obtain

$$\frac{1}{g\nu_0} = \frac{1}{2}\ln\frac{E_F+\hbar\omega_D-E/2}{E_F-E/2} \tag{513}$$

Thus

$$\frac{2E_F+2\hbar\omega_D-E}{2E_F-E} = e^{\frac{2}{g\nu_0}} \tag{514}$$

$$(2E_F - E)(e^{\frac{2}{g\nu_0}} - 1) = 2\hbar\omega_D \tag{515}$$

For weak coupling $g\nu_0 \ll 1$ we obtain

$$2E_F - E = 2\hbar\omega_D e^{-\frac{2}{g\nu_0}} \tag{516}$$

$$E = 2E_F - 2\hbar\omega_D e^{-\frac{2}{g\nu_0}} \tag{517}$$

The binding energy per electron is then found from $E = 2E_F - 2\Delta$

$$\Delta = \hbar\omega_D e^{-\frac{2}{g\nu_0}} \tag{518}$$

1. Symmetry

Since $\alpha(k) = \alpha(-k)$, i.e, symmetric, the spin part of the wave function χ must be antisymmetric - singlet.

C. BCS state (J. Bardeen, L. Cooper, and R. Schrieffer (BCS), 1957)

1) Everything done in the grand canonical ensemble. The grand canonical partition function

$$Z_\Omega = \sum_{n,N} e^{-\beta(E_{n,N} - \mu N)} \tag{519}$$

shows that at $T = 0$ one has to minimize $H_G = H - \mu N$.

We obtain

$$H_G = \sum_{k,\sigma} (\epsilon_k - \mu) c^\dagger_{k,\sigma}\, c_{k,\sigma} - \frac{1}{2}\,\frac{g}{V} \sum_{k_1,\sigma_1,k_2,\sigma_2,q} c^\dagger_{k_1+q,\sigma_1}\, c^\dagger_{k_2-q,\sigma_2}\, c_{k_2,\sigma_2}\, c_{k_1,\sigma_2} \tag{520}$$

where the interaction term works only if the energy transfer $\epsilon_{k_1+q} - \epsilon_{k_1}$ is smaller than the Debye energy $\hbar\omega_D$.

Although the Hamiltonian conserves the number of particles, BCS constructed a trial wave function which is a superposition of different numbers of particles:

$$|BCS\rangle = \prod_k (u_k + v_k c^\dagger_{k,\uparrow} c^\dagger_{-k,\downarrow})\,|0\rangle \ . \tag{521}$$

with the purpose to use u_k and v_k as variational parameters and minimize $\langle BCS|\, H_G\, |BCS\rangle$.

For this purpose one can introduce a reduced BSC Hamiltonian. Only terms of this Hamiltonian will contribute to the average with BCS trial functions. The reduced Hamiltonian is the one in which $k_1 = -k_2$ and $\sigma_1 = -\sigma_2$:

$$H_{\rm BCS} = \sum_{k,\sigma}(\epsilon_k - \mu)c^\dagger_{k,\sigma}\, c_{k,\sigma} - \frac{1}{2}\,\frac{g}{V}\,\sum_{k,q,\sigma}\, c^\dagger_{k+q,\sigma}\, c^\dagger_{-k-q,-\sigma}\, c_{-k,-\sigma}\, c_{k,\sigma}\ . \tag{522}$$

Renaming $k' = k + q$ we obtain

$$H_{\rm BCS} = \sum_{k,\sigma}(\epsilon_k - \mu)c^\dagger_{k,\sigma}\, c_{k,\sigma} - \frac{1}{2}\,\frac{g}{V}\,\sum_{k,k',\sigma}\, c^\dagger_{k',\sigma}\, c^\dagger_{-k',-\sigma}\, c_{-k,-\sigma}\, c_{k,\sigma}\ , \tag{523}$$

or

$$H_{\rm BCS} = \sum_{k,\sigma}(\epsilon_k - \mu)c^\dagger_{k,\sigma}\, c_{k,\sigma} - \frac{g}{V}\,\sum_{k,k'}\, c^\dagger_{k',\uparrow}\, c^\dagger_{-k',\downarrow}\, c_{-k,\downarrow}\, c_{k,\uparrow}\ , \tag{524}$$

Also the condition on k and k' gets simplified. We just demand that

$$\mu - \hbar\omega_D < \epsilon_k, \epsilon_{k'} < \mu + \hbar\omega_D\ . \tag{525}$$

1. Averages

Normalization:

$$\begin{aligned} 1 \;&=\; \langle BCS|\,|BCS\rangle = \langle 0|\prod_{k_2}(u^*_{k_2} + v^*_{k_2}c_{-k_2,\downarrow}c_{k_2,\uparrow})\prod_{k_1}(u_{k_1} + v_{k_1}c^\dagger_{k_1,\uparrow}c^\dagger_{-k_1,\downarrow})\,|0\rangle \\ &=\; \prod_k(|u_k|^2 + |v_k|^2)\ . \end{aligned} \tag{526}$$

We further restrict ourselves to real u_k and v_k such that $u_k^2 + v_k^2 = 1$. Thus only one of them is independent. The following parametrization is helpful: $u_k = \cos\phi_k$, $v_k = \sin\phi_k$.

We obtain

$$\begin{aligned} &\langle BCS|\, c^\dagger_{k,\uparrow}\, c_{k,\uparrow}\,|BCS\rangle \\ &= \langle 0|\prod_{k_2}(u_{k_2} + v_{k_2}c_{-k_2,\downarrow}c_{k_2,\uparrow})c^\dagger_{k,\uparrow}\, c_{k,\uparrow}\prod_{k_1}(u_{k_1} + v_{k_1}c^\dagger_{k_1,\uparrow}c^\dagger_{-k_1,\downarrow})\,|0\rangle \\ &= v_k^2 \end{aligned} \tag{527}$$

$$\begin{aligned} &\langle BCS|\, c^\dagger_{k,\downarrow}\, c_{k,\downarrow}\,|BCS\rangle \\ &= \langle 0|\prod_{k_2}(u_{k_2} + v_{k_2}c_{-k_2,\downarrow}c_{k_2,\uparrow})c^\dagger_{k,\downarrow}\, c_{k,\downarrow}\prod_{k_1}(u_{k_1} + v_{k_1}c^\dagger_{k_1,\uparrow}c^\dagger_{-k_1,\downarrow})\,|0\rangle \\ &= v_{-k}^2 \end{aligned} \tag{528}$$

$$\begin{aligned}
&\langle BCS|\ c^\dagger_{k',\uparrow} c^\dagger_{-k',\downarrow} c_{-k,\downarrow} c_{k,\uparrow} |BCS\rangle \\
&= \langle 0| \prod_{k_2} (u_{k_2} + v_{k_2} c_{-k_2,\downarrow} c_{k_2,\uparrow})\, c^\dagger_{k',\uparrow} c^\dagger_{-k',\downarrow} c_{-k,\downarrow} c_{k,\uparrow} \prod_{k_1} (u_{k_1} + v_{k_1} c^\dagger_{k_1,\uparrow} c^\dagger_{-k_1,\downarrow}) |0\rangle \\
&= u_k v_k u_{k'} v_{k'} \qquad (529)
\end{aligned}$$

This gives

$$\langle BCS| H_{\rm BCS} |BCS\rangle = 2\sum_k (\epsilon_k - \mu) v_k^2 - \frac{g}{V} \sum_{k,k'} u_k v_k u_{k'} v_{k'} \qquad (530)$$

We vary with respect to ϕ_k

$$\frac{\partial}{\partial \phi_k} \langle BCS| H_{\rm BCS} |BCS\rangle = 4(\epsilon_k - \mu) v_k u_k - 2\frac{g}{V}(u_k^2 - v_k^2) \sum_{k'} u_{k'} v_{k'} = 0\ . \qquad (531)$$

We introduce $\Delta = \frac{g}{V} \sum_{k'} u_{k'} v_{k'}$ and obtain

$$2(\epsilon_k - \mu) v_k u_k = \Delta (u_k^2 - v_k^2)\ . \qquad (532)$$

Trivial solution: $\Delta = 0$. E.g., the Fermi sea: $u_k = 0$ and $v_k = 1$ for $\epsilon_k < \mu$ and $u_k = 1$ and $v_k = 0$ for $\epsilon_k > \mu$.

We look for nontrivial solutions: $\Delta \neq 0$. Then from

$$(\epsilon_k - \mu) \sin 2\phi_k = \Delta \cos 2\phi_k \qquad (533)$$

we obtain

$$\sin 2\phi_k = 2u_k v_k = \frac{\Delta}{\sqrt{\Delta^2 + (\epsilon_k - \mu)^2}} \qquad (534)$$

$$\cos 2\phi_k = u_k^2 - v_k^2 = \frac{\epsilon_k - \mu}{\sqrt{\Delta^2 + (\epsilon_k - \mu)^2}} \qquad (535)$$

Then from definition of $\Delta = \frac{g}{V} \sum_k u_k v_k$ we obtain the self-consistency equation

$$\Delta = \frac{g}{2V} \sum_k \frac{\Delta}{\sqrt{\Delta^2 + (\epsilon_k - \mu)^2}} \qquad (536)$$

or

$$\begin{aligned}
1 \ &= \ \frac{g}{2V} \sum_k \frac{1}{\sqrt{\Delta^2 + (\epsilon_k - \mu)^2}} = \frac{g\nu_0}{2} \int\limits_{-\hbar\omega_D}^{\hbar\omega_D} d\xi \frac{1}{\sqrt{\Delta^2 + \xi^2}} \\
&= \ g\nu_0 \int\limits_0^{\hbar\omega_D/\Delta} dx \frac{1}{\sqrt{1 + x^2}} = g\nu_0\ \ln(\sqrt{1+x^2} + x)\Big|_0^{\hbar\omega_D/\Delta} \approx g\nu_0 \ln \frac{2\hbar\omega_D}{\Delta} \qquad (537)
\end{aligned}$$

We have assumed $\Delta \ll \hbar\omega_D$.

This gives

$$\Delta = 2\hbar\omega_D e^{-\frac{1}{\nu_0 g}} \qquad (538)$$

2. Total energy

We want to convince ourselves that the total energy of the new state is smaller that the energy of the trivial solution (fully filled Fermi sphere).

$$\begin{aligned} E_{BCS} &= \langle BCS|\, H_{\rm BCS}\, |BCS\rangle = 2\sum_k (\epsilon_k - \mu) v_k^2 - \frac{g}{V}\sum_{k,k'} u_k v_k u_{k'} v_{k'} \\ &= 2\sum_k (\epsilon_k - \mu) v_k^2 - \Delta \sum_k u_k v_k \ , \end{aligned} \tag{539}$$

whereas

$$E_{Norm} = \langle Norm|\, H_{\rm BCS}\, |Norm\rangle = 2\sum_k (\epsilon_k - \mu)\theta(\mu - \epsilon_k) \ . \tag{540}$$

We obtain

$$\Delta E = E_{BCS} - E_{Norm} = 2\sum_k (\epsilon_k - \mu)(v_k^2 - \theta(\mu - \epsilon_k)) - \Delta \sum_k u_k v_k \ , \tag{541}$$

With $\xi_k = \epsilon_k - \mu$,

$$v_k^2 = \sin^2\phi_k = \frac{1 - \cos 2\phi_k}{2} = \frac{1}{2} - \frac{\xi_k}{2\sqrt{\Delta^2 + \xi_k^2}} \tag{542}$$

and

$$u_k v_k = \frac{\Delta}{2\sqrt{\Delta^2 + \xi_k^2}} \tag{543}$$

we obtain

$$\Delta E = \sum_k \left(2\xi_k \left[\frac{1}{2} - \frac{\xi_k}{2\sqrt{\Delta^2 + \xi_k^2}} - \theta(-\xi_k) \right] - \frac{\Delta^2}{2\sqrt{\Delta^2 + \xi_k^2}} \right) \tag{544}$$

$$\begin{aligned} \Delta E &= 2V \int_0^{\hbar\omega_D} \nu_0 d\xi \left(\xi \left[\frac{1}{2} - \frac{\xi}{2\sqrt{\Delta^2 + \xi^2}} - \theta(-\xi) \right] - \frac{\Delta^2}{2\sqrt{\Delta^2 + \xi^2}} \right) \\ &= 2V \int_0^{\hbar\omega_D} \nu_0 d\xi \left[\xi - \frac{\xi^2}{\sqrt{\Delta^2 + \xi^2}} - \frac{\Delta^2}{2\sqrt{\Delta^2 + \xi_k^2}} \right] \\ &= 2V\nu_0\Delta^2 \int_0^{\hbar\omega_D/\Delta} dx \left(x - \sqrt{1 + x^2} + \frac{1}{2\sqrt{1 + x^2}} \right) \end{aligned} \tag{545}$$

The last integral is convergent and for $\hbar\omega_D \gg \Delta$ can be taken to ∞. The integral gives $-1/4$. Thus

$$\Delta E = -V\,\frac{\nu_0 \Delta^2}{2} \ . \tag{546}$$

Roughly energy Δ per electron in window of energies of order Δ.

D. Excitations

We want to consider the BCS ground state as vacuum and find the quasiparticle excitations above it. Let us start with the normal state, i.e., $v_k = \theta(-\xi_k)$ and $u_k = \theta(\xi_k)$. For $\xi_k > 0$ we have

$$c_{k,\sigma} \left| Norm \right\rangle = 0 \tag{547}$$

while for $\xi_k < 0$

$$c^\dagger_{k,\sigma} \left| Norm \right\rangle = 0 \tag{548}$$

we introduce

$$\alpha_{k,\sigma} \equiv \begin{cases} c_{k,\sigma} & \text{if} \quad \xi_k < 0 \\ \pm c^\dagger_{-k,-\sigma} & \text{if} \quad \xi_k > 0 \end{cases} \tag{549}$$

or equivalently

$$\alpha_{k,\sigma} = u_k c_{k,\sigma} \pm v_k c^\dagger_{-k,-\sigma} \tag{550}$$

(the sign to be chosen).

We see, thus, that $\alpha_{k,\sigma} \left| Norm \right\rangle = 0$, whereas

$$\alpha^\dagger_{k,\sigma} = u_k c^\dagger_{k,\sigma} \pm v_k c_{-k,-\sigma} \tag{551}$$

creates an excitation of energy $|\xi_k|$.

For the BCS state we obtain

$$\alpha_{k,\sigma} \left| BCS \right\rangle = (u_k c_{k,\sigma} \pm v_k c^\dagger_{-k,-\sigma}) \prod_q (u_q + v_q c^\dagger_{q,\uparrow} c^\dagger_{-q,\downarrow}) \left| 0 \right\rangle \tag{552}$$

We see that the proper choice of sign is

$$\alpha_{k,\sigma} = u_k c_{k,\sigma} - \sigma v_k c^\dagger_{-k,-\sigma} \tag{553}$$

and

$$\alpha_{k,\sigma} \left| BCS \right\rangle = 0 \ . \tag{554}$$

The conjugated (creation) operator reads

$$\alpha^\dagger_{k,\sigma} = u_k c^\dagger_{k,\sigma} - \sigma v_k c_{-k,-\sigma} \tag{555}$$

One can check the commutation relations

$$\left\{ \alpha_{k,\sigma}, \alpha^\dagger_{k',\sigma'} \right\}_+ = \delta_{k,k'} \delta_{\sigma,\sigma'} \tag{556}$$

$$\{\alpha_{k,\sigma}, \alpha_{k',\sigma'}\}_+ = 0 \quad \left\{\alpha^\dagger_{k,\sigma}, \alpha^\dagger_{k',\sigma'}\right\}_+ = 0 \tag{557}$$

The inverse relations read:

$$c_{k,\sigma} = u_k \alpha_{k,\sigma} + \sigma v_k \alpha^\dagger_{-k,-\sigma} \quad , \quad c^\dagger_{k,\sigma} = u_k \alpha^\dagger_{k,\sigma} + \sigma v_k \alpha_{-k,-\sigma} \tag{558}$$

1. Mean field

We adopt the mean field approximation for the BCS Hamiltonian.

$$H_{\rm BCS} \;=\; \sum_{k,\sigma} (\epsilon_k - \mu) c^\dagger_{k,\sigma}\, c_{k,\sigma} - \frac{g}{V} \sum_{k,k'} c^\dagger_{k',\uparrow}\, c^\dagger_{-k',\downarrow}\, c_{-k,\downarrow}\, c_{k,\uparrow} \tag{559}$$

Note that in the interaction the terms with $k = k'$ are absent, since the matrix element of the electron-phonon interaction is proportional to the momentum transfer $q = k - k'$. Thus the only averages we can extract in the interaction term are $\langle c_{-k,\downarrow}\, c_{k,\uparrow}\rangle$ and $\langle c^\dagger_{k,\uparrow}\, c^\dagger_{-k,\downarrow}\rangle$.

We use

1)

$$\begin{aligned} c^\dagger_{k,\uparrow}\, c^\dagger_{-k,\downarrow} \;&=\; (u_k \alpha^\dagger_{k,\uparrow} + v_k \alpha_{-k,\downarrow})(u_k \alpha^\dagger_{-k,\downarrow} - v_k \alpha_{k,\uparrow}) \\ &=\; u_k^2 \alpha^\dagger_{k,\uparrow} \alpha^\dagger_{-k,\downarrow} - v_k^2 \alpha_{-k,\downarrow} \alpha_{k,\uparrow} + u_k v_k (1 - \alpha^\dagger_{k,\uparrow} \alpha_{k,\uparrow} - \alpha^\dagger_{-k,\downarrow} \alpha_{-k,\downarrow}) \end{aligned} \tag{560}$$

2)

$$c_{-k,\downarrow} c_{k,\uparrow} = u_k^2 \alpha_{-k,\downarrow} \alpha_{k,\uparrow} - v_k^2 \alpha^\dagger_{k,\uparrow} \alpha^\dagger_{-k,\downarrow} + u_k v_k (1 - \alpha^\dagger_{k,\uparrow} \alpha_{k,\uparrow} - \alpha^\dagger_{-k,\downarrow} \alpha_{-k,\downarrow}) \tag{561}$$

In the BCS ground state we obtain $\langle c_{-k,\downarrow}\, c_{k,\uparrow}\rangle = v_k u_k$ and $\langle c^\dagger_{k,\uparrow}\, c^\dagger_{-k,\downarrow}\rangle = v_k u_k$. We use

$$AB = \langle A\rangle \langle B\rangle + \langle A\rangle (B - \langle B\rangle) + (A - \langle A\rangle) \langle B\rangle + (A - \langle A\rangle)(B - \langle A\rangle)$$

and neglect the last term. The mean field Hamiltonian reads

$$\begin{aligned} H^{\rm MF}_{\rm BCS} \;&=\; \sum_{k,\sigma} (\epsilon_k - \mu) c^\dagger_{k,\sigma}\, c_{k,\sigma} + \frac{g}{V} \sum_{k,k'} \langle c^\dagger_{k',\uparrow}\, c^\dagger_{-k',\downarrow}\rangle \langle c_{-k,\downarrow}\, c_{k,\uparrow}\rangle \\ &-\; \frac{g}{V} \sum_{k,k'} \langle c^\dagger_{k',\uparrow}\, c^\dagger_{-k',\downarrow}\rangle\, c_{-k,\downarrow}\, c_{k,\uparrow} - \frac{g}{V} \sum_{k,k'} c^\dagger_{k',\uparrow}\, c^\dagger_{-k',\downarrow} \langle c_{-k,\downarrow}\, c_{k,\uparrow}\rangle \\ &=\; \sum_{k,\sigma} \xi_k c^\dagger_{k,\sigma}\, c_{k,\sigma} - \sum_k \Delta c_{-k,\downarrow}\, c_{k,\uparrow} - \sum_k \Delta c^\dagger_{k,\uparrow}\, c^\dagger_{-k,\downarrow} + V \frac{\Delta^2}{g} \end{aligned} \tag{562}$$

Substituting the expressions for c operators in terms of α operators we obtain a diagonal Hamiltonian (exercise)

$$H = \sum_{k,\sigma} E_k \alpha^\dagger_{k,\sigma}\, \alpha_{k,\sigma} + const.\ , \tag{563}$$

where $E_k = \sqrt{\Delta^2 + \xi_k^2}$.

For proof one needs

3)

$$\begin{aligned} & c^\dagger_{k,\uparrow}\, c_{k,\uparrow} + c^\dagger_{-k,\downarrow}\, c_{-k,\downarrow} = (u_k \alpha^\dagger_{k,\uparrow} + v_k \alpha_{-k,\downarrow})(u_k \alpha_{k,\uparrow} + v_k \alpha^\dagger_{-k,\downarrow}) \\ & + (u_k \alpha^\dagger_{-k,\downarrow} - v_k \alpha_{k,\uparrow})(u_k \alpha_{-k,\downarrow} - v_k \alpha^\dagger_{k,\uparrow}) \\ & = (u_k^2 - v_k^2)(\alpha^\dagger_{k,\uparrow}\alpha_{k,\uparrow} + \alpha^\dagger_{-k,\downarrow}\alpha_{-k,\downarrow}) + 2v_k^2 + 2u_k v_k(\alpha^\dagger_{k,\uparrow}\alpha^\dagger_{-k,\downarrow} + \alpha_{-k,\downarrow}\alpha_{k,\uparrow}) \end{aligned} \tag{564}$$

2. Nambu formalism

Another way to get the same is to use the Nambu spinors. First we obtain

$$H^{\rm MF}_{\rm BCS} = \sum_k \begin{pmatrix} c^\dagger_{k,\uparrow} & c_{-k,\downarrow} \end{pmatrix} \begin{pmatrix} \xi_k & -\Delta \\ -\Delta & 0 \end{pmatrix} \begin{pmatrix} c_{k,\uparrow} \\ c^\dagger_{-k,\downarrow} \end{pmatrix} + \sum_k \xi_k c^\dagger_{k,\downarrow}\, c_{k,\downarrow} + V\frac{\Delta^2}{g} \tag{565}$$

Next we rewrite $\sum_k \xi_k c^\dagger_{k,\downarrow}\, c_{k,\downarrow} = \sum_k \xi_k (1 - c_{k,\downarrow}\, c^\dagger_{k,\downarrow}) = \sum_k \xi_k (1 - c_{-k,\downarrow}\, c^\dagger_{-k,\downarrow})$. This gives

$$H^{\rm MF}_{\rm BCS} = \sum_k \begin{pmatrix} c^\dagger_{k,\uparrow} & c_{-k,\downarrow} \end{pmatrix} \begin{pmatrix} \xi_k & -\Delta \\ -\Delta & -\xi_k \end{pmatrix} \begin{pmatrix} c_{k,\uparrow} \\ c^\dagger_{-k,\downarrow} \end{pmatrix} + \sum_k \xi_k + V\frac{\Delta^2}{g} \tag{566}$$

The eigenvalues of the matrix $\begin{pmatrix} \xi_k & -\Delta \\ -\Delta & -\xi_k \end{pmatrix}$ read $\pm E_k$, where $E_k = \sqrt{\Delta^2 + \xi_k^2}$. For the eigenvectors we get

$$\begin{pmatrix} \xi_k & -\Delta \\ -\Delta & -\xi_k \end{pmatrix} \begin{pmatrix} u_k \\ -v_k \end{pmatrix} = E_k \begin{pmatrix} u_k \\ -v_k \end{pmatrix} \tag{567}$$

and

$$\begin{pmatrix} \xi_k & -\Delta \\ -\Delta & -\xi_k \end{pmatrix} \begin{pmatrix} v_k \\ u_k \end{pmatrix} = -E_k \begin{pmatrix} v_k \\ u_k \end{pmatrix} \tag{568}$$

Thus

$$U^\dagger \begin{pmatrix} \xi_k & -\Delta \\ -\Delta & -\xi_k \end{pmatrix} U = \begin{pmatrix} E_k & 0 \\ 0 & -E_k \end{pmatrix}\ , \tag{569}$$

where

$$U \equiv \begin{pmatrix} u_k & v_k \\ -v_k & u_k \end{pmatrix} \tag{570}$$

We obtain

$$H^{\rm MF}_{\rm BCS} = \sum_k \begin{pmatrix} c^\dagger_{k,\uparrow} & c_{-k,\downarrow} \end{pmatrix} UU^\dagger \begin{pmatrix} \xi_k & -\Delta \\ -\Delta & -\xi_k \end{pmatrix} UU^\dagger \begin{pmatrix} c_{k,\uparrow} \\ c^\dagger_{-k,\downarrow} \end{pmatrix} + \sum_k \xi_k + V\frac{\Delta^2}{g} \tag{571}$$

Diagonalizing the 2×2 matrix for each k we obtain

$$H^{\rm MF}_{\rm BCS} = \sum_k \begin{pmatrix} \alpha^\dagger_{k,\uparrow} & \alpha_{-k,\downarrow} \end{pmatrix} \begin{pmatrix} E_k & 0 \\ 0 & -E_k \end{pmatrix} \begin{pmatrix} \alpha_{k,\uparrow} \\ \alpha^\dagger_{-k,\downarrow} \end{pmatrix} + \sum_k \xi_k + V\frac{\Delta^2}{g} \tag{572}$$

Using again the commutation relations for the α operators we obtain

$$H^{\rm MF}_{\rm BCS} = \sum_{k,\sigma} E_k \alpha^\dagger_{k,\sigma}\, \alpha_{k,\sigma} + \sum_k (\xi_k - E_k) + V\frac{\Delta^2}{g}\ . \tag{573}$$

E. Finite temperature

We obtained the energy spectrum $E_k = \sqrt{\Delta^2 + \xi_k^2}$ in the mean-field approximation assuming that $\langle c_{-k,\downarrow} c_{k,\uparrow} \rangle = v_k u_k$, where the averaging is in the ground state, i.e., there are no quasi-particles excited. For $T > 0$ some quasi-particles get excited and the value of $\langle c_{-k,\downarrow} c_{k,\uparrow} \rangle$ changes. Namely, we obtain

$$\langle c_{-k,\downarrow} c_{k,\uparrow} \rangle = v_k u_k (1 - 2n_k)\ , \tag{574}$$

where $n_k = f(E_k) = \frac{1}{e^{\beta E_k}+1}$.

If we still want to have the Hamiltonian diagonalized by the Bogolyubov transformation, we have to redefine Δ as

$$\Delta = \frac{g}{V}\sum_k \langle c_{-k,\downarrow} c_{k,\uparrow} \rangle = \frac{g}{V}\sum_k u_k v_k (1 - 2n_k) \tag{575}$$

Then, however, Δ is temperature dependent and thus $E_k = \sqrt{\Delta^2 + \xi_k^2}$ is also temperature dependent. We must do everything self-consistently.

From

$$u_k v_k = \frac{\Delta}{2\sqrt{\Delta^2 + \xi_k^2}} \tag{576}$$

we obtain the new self-consistency equation

$$\Delta = \frac{g}{2V}\sum_k \frac{\Delta}{\sqrt{\Delta^2+\xi_k^2}}\,\tanh\frac{\beta E_k}{2} \tag{577}$$

To find the critical temperature T_c we assume that $\Delta(T_c)=0$. This gives

$$1 = \frac{g}{2V}\sum_k \frac{1}{|\xi_k|}\,\tanh\frac{\beta|\xi_k|}{2} = g\nu_0\int_0^{\hbar\omega_D} d\xi\,\frac{\tanh\frac{\beta\xi}{2}}{\xi} = g\nu_0\int_0^{\beta\hbar\omega_D/2} dx\frac{\tanh x}{x} \tag{578}$$

Assuming $\hbar\omega_D/(2k_{\rm B}T_c)\gg 1$ we obtain

$$1 \approx g\nu_0 \ln\frac{\hbar\omega_D}{k_{\rm B}T_c} \tag{579}$$

or

$$k_{\rm B}T_c = \hbar\omega_D e^{-\frac{1}{g\nu_0}} = \frac{\Delta(T=0)}{2} \tag{580}$$

More precise calculation gives

$$k_{\rm B}T_c = 1.14\hbar\omega_D e^{-\frac{1}{g\nu_0}} = \frac{\Delta(T=0)}{1.76} \tag{581}$$

For $T\sim T_c$ and $T<T_c$ one can obtain

$$\Delta(T) \approx 3.06 k_{\rm B}T_c\sqrt{1-\frac{T}{T_c}} \tag{582}$$

1. More precise derivation

We have to minimize the grand canonical potential $\Omega = U-\mu N - TS = \langle H_{BCS}\rangle - TS$. For the density matrix we take (the variational ansatz)

$$\rho = \frac{1}{Z}\,e^{-\beta\sum_{k,\sigma}E_k n_{k,\sigma}}\ , \tag{583}$$

where $n_{k,\sigma}=\alpha^\dagger_{k,\sigma}\alpha_{k,\sigma}$ are the occupation number operators of the quasi-particles while E_k are the energies of the quasiparticles (to be determined). Here

$$\alpha_{k,\sigma} = u_k c_{k,\sigma} - \sigma v_k c^\dagger_{-k,-\sigma} \tag{584}$$

with $v_k=\sin\phi_k$ and $u_k=\cos\phi_k$ and ϕ_k is another variational parameter.

We thus obtain

$$\begin{aligned}\langle H^{MF}_{BCS}\rangle &= \sum_{k,\sigma}\xi_k c^\dagger_{k,\sigma}\,c_{k,\sigma} - \frac{g}{V}\sum_{k,k'}\langle c^\dagger_{k',\uparrow}\,c^\dagger_{-k',\downarrow}\rangle\,\langle c_{-k,\downarrow}\,c_{k,\uparrow}\rangle \\ &= \sum_k 2\xi_k\left[(u_k^2-v_k^2)f(E_k)+v_k^2\right] - \frac{g}{V}\left(\sum_k u_k v_k(1-2f(E_k))\right)^2\end{aligned} \tag{585}$$

For the entropy we have

$$S = -2k_{\rm B}\sum_k \left[f(E_k)\,\ln f(E_k) + (1-f(E_k))\,\ln(1-f(E_k))\right] \tag{586}$$

We vary with respect to ϕ_k and with respect to E_k independently. This gives

$$\begin{aligned}\frac{\partial\Omega}{\partial\phi_k} &= 4\xi_k u_k v_k(1-2f(E_k)) \\ &- \frac{2g}{V}\left(\sum_k u_k v_k(1-2f(E_k))\right)(1-2f(E_k))\,(u_k^2-v_k^2) = 0\end{aligned} \tag{587}$$

Introducing

$$\Delta = \frac{g}{V}\sum_k \langle c_{-k,\downarrow}c_{k,\uparrow}\rangle = \frac{g}{V}\sum_k u_k v_k(1-2n_k) \tag{588}$$

we obtain the old equation

$$\xi_k \sin 2\phi_k = \Delta\cos 2\phi_k \tag{589}$$

Thus all the formula remain but with new Δ.

$$\begin{aligned}\frac{\partial\Omega}{\partial E_k} &= \frac{\partial\langle H^{MF}_{BCS}\rangle}{\partial E_k} - T\frac{\partial S}{\partial E_k} \\ &= 2\xi_k(u_k^2-v_k^2)\frac{\partial f}{\partial E_k} + 4\Delta u_k v_k\frac{\partial f}{\partial E_k} - T\frac{\partial S}{\partial E_k} \\ &= 2\sqrt{\xi_k^2+\Delta^2}\,\frac{\partial f}{\partial E_k} - 2E_k\,\frac{\partial f}{\partial E_k} = 0.\end{aligned} \tag{590}$$

Thus we obtain

$$E_k = \sqrt{\xi_k^2+\Delta^2} \tag{591}$$

F. Heat capacity

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V\ . \tag{592}$$

Using for S Eq. (586) we obtain

$$C_V = -2k_{\rm B}T\sum_k(-\beta E_k)\frac{\partial f}{\partial T} = 2\sum_k E_k\,\frac{\partial f}{\partial T} \tag{593}$$

Let's introduce $g(x) = \frac{1}{e^x+1}$. Then $f(E_k) = g(\beta E_k)$.

$$\frac{\partial f}{\partial E_k} = \beta g' \tag{594}$$

$$\frac{\partial f}{\partial T} = g' \cdot \left(E_k \frac{\partial \beta}{\partial T} + \beta \frac{\partial E_k}{\partial T} \right) = g' \cdot \left(-E_k \frac{\beta}{T} + \beta \frac{\partial E_k}{\partial T} \right) = \frac{\partial f}{\partial E_k} \left(-\frac{E_k}{T} + \frac{\Delta}{E_k} \frac{\partial \Delta}{\partial T} \right) \tag{595}$$

Thus

$$C_V = 2 \sum_k E_k \left(-\frac{E_k}{T} + \frac{\Delta}{E_k} \frac{\partial \Delta}{\partial T} \right) \frac{\partial f}{\partial E_k} \tag{596}$$

First, we analyze at $T \to T_c$. There $E_k \approx \xi_k$.

With

$$\frac{\partial f}{\partial E} \approx -\delta(E) - \frac{\pi^2}{6} (k_{\rm B}T)^2 \delta''(E) \ , \tag{597}$$

and

$$\Delta(T) \approx 3.06 k_{\rm B} T_c \sqrt{1 - \frac{T}{T_c}} \tag{598}$$

We obtain for $T = T_c - 0$

$$\begin{aligned} C_V(T_c - 0) &= 2\nu_0 \int d\xi \left(-\frac{\xi^2}{T} \right) \frac{\partial f}{\partial \xi} + \nu_0 \int d\xi \frac{\partial \Delta^2}{\partial T} \frac{\partial f}{\partial \xi} \\ &= \frac{2\pi^2 \nu_0 k_{\rm B}^2}{3} T_c + (3.06)^2 \nu_0 k_{\rm B}^2 T_c = C_V(T_c + 0) + \Delta C_V \end{aligned} \tag{599}$$

Thus one obtains

$$\frac{\Delta C_V}{C_V(T_c + 0)} \approx 1.43 \tag{600}$$

Jump in $\frac{\partial \Delta}{\partial T}$ leads to jump in C_V (see Fig. 9).

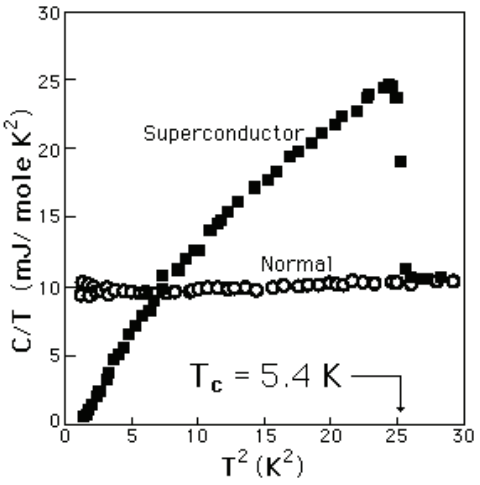

FIG. 9: Heat capacitance of vanadium.

For $k_{\rm B}T \ll k_{\rm B}T_c \sim \Delta(0)$ one obtains $C_V \propto e^{-\frac{\Delta}{k_{\rm B}T}}$.

G. Isotope effect.

We see that $T_c \propto \Delta(T=0) \propto \omega_D \propto M^{-1/2}$, where M is the ion mass. This dependence can be observed by using materials with different isotope content. It was one of the major motivations for the phonon mechanism of attraction.

XIX. ELECTRODYNAMICS OF SUPERCONDUCTORS.

A. London equations

The zero resistivity and the Meissner effect are closely related.

Assume the electrons are accelerated without resistance:

$$m\dot{\vec{v}} = e\vec{E} \tag{601}$$

With $\vec{j} = ne\vec{v}$ we obtain

$$\Lambda\dot{\vec{j}} = \vec{E}\ , \tag{602}$$

where $\Lambda = \frac{m}{ne^2}$.

The Maxwell equation reads:

$$\vec{\nabla} \times \vec{E} = -\frac{1}{c}\dot{\vec{B}} \tag{603}$$

Thus we obtain

$$\frac{\partial}{\partial t}\left(\Lambda\vec{\nabla} \times \vec{j} + \frac{1}{c}\vec{B}\right) = 0 \tag{604}$$

But inside the superconductor both $\vec{B} = 0$ and $\vec{j} = 0$. Thus F. London and H. London postulated:

$$\Lambda\vec{\nabla} \times \vec{j} + \frac{1}{c}\vec{B} = 0 \tag{605}$$

1. Time-independent situation

An external magnetic field is applied. We consider magnetization currents explicitly, thus we use microscopic Maxwell equation:

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c}\vec{j} \tag{606}$$

This gives

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{B}) = \vec{\nabla} \cdot (\vec{\nabla} \cdot \vec{B}) - (\vec{\nabla}^2)\vec{B} = -(\vec{\nabla}^2)\vec{B} = \frac{4\pi}{c}\vec{\nabla} \times \vec{j} \tag{607}$$

Substituting the London equation we obtain

$$(\vec{\nabla}^2)\vec{B} = \frac{4\pi}{c^2\Lambda}\vec{B} \tag{608}$$

One introduces the London penetration depth $\lambda_L = \sqrt{\frac{c^2\Lambda}{4\pi}} = \sqrt{\frac{c^2 m}{4\pi n e^2}}$.

B. Another form of London equations

$$\vec{B} = \vec{\nabla} \times \vec{A} \tag{609}$$

With this the London equation

$$\Lambda\vec{\nabla} \times \vec{j} + \frac{1}{c}\vec{B} = 0 \tag{610}$$

reads

$$\Lambda\vec{\nabla} \times \vec{j} + \frac{1}{c}\vec{\nabla} \times \vec{A} = 0 \tag{611}$$

If both $\vec{\nabla} \cdot \vec{j} = 0$ and $\vec{\nabla} \cdot \vec{A} = 0$ (Coulomb gauge) this gives

$$\vec{j} = -\frac{1}{\Lambda c}\vec{A} \tag{612}$$

In this form the London equation is convenient to connect to the microscopic theory.

C. Microscopic derivation of London equation

$$H_{kin} = \frac{\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2}{2m} \tag{613}$$

with $\vec{p} = -i\hbar\vec{\nabla}$.

In second quantized form

$$H_{kin} = \sum_\sigma \int dV\, \Psi^\dagger_\sigma(r) \frac{\left(-i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}\right)^2}{2m} \Psi_\sigma(r) = H_{0,kin} + H_1 + O(A^2)\ , \tag{614}$$

where

$$H_1 = -\frac{e}{mc}\sum_\sigma \int dV\, \Psi^\dagger_\sigma(r)\, \vec{A}\vec{p}\Psi_\sigma(r) \tag{615}$$

(the order of operators $\vec{A}$ and $\vec{p}$ unimportant since $\vec{\nabla} \cdot \vec{A} = 0$).

The first order correction to the BCS ground state $|0\rangle = |BCS\rangle$ is

$$|\Phi_1\rangle = \sum_{l \neq 0} |l\rangle \frac{\langle l| H_1 |0\rangle}{E_0 - E_l} \tag{616}$$

Current. Velocity

$$\vec{v} = \frac{\left(\vec{p} - \frac{e}{c}\vec{A}\right)}{m} \tag{617}$$

Current density

$$\begin{aligned} \vec{j} &= e \sum_\sigma \Psi^\dagger_\sigma(r) \frac{\left(\vec{p} - \frac{e}{c}\vec{A}\right)}{m} \Psi_\sigma(r) = e \sum_\sigma \Psi^\dagger_\sigma(r) \frac{\vec{p}}{m} \Psi_\sigma(r) - \frac{e^2}{cm} \vec{A} \sum_\sigma \Psi^\dagger_\sigma(r) \Psi_\sigma(r) \\ &= \vec{j}_p + \vec{j}_d \end{aligned} \tag{618}$$

(In $\vec{j}_p$ one has to symmetrize: half $\vec{p}$ works to the right and half to the left). The $\vec{j}_d$ contribution immediately gives the London equation

$$\vec{j}_d = -\frac{e^2 n}{mc} \vec{A} \tag{619}$$

Another contribution linear in $\vec{A}$ could come from $\vec{j}_p$:

$$\langle \vec{j}_p \rangle = \langle \Phi_1 | \vec{j}_p | 0 \rangle + \langle 0 | \vec{j}_p | \Phi_1 \rangle \tag{620}$$

To calculate $|\Phi_1\rangle$ we need $\langle l| H_1 |0\rangle$, where $|l\rangle$ is an excited state.

We assume

$$A = \vec{a}_q e^{i\vec{q}\vec{r}} \tag{621}$$

and $\vec{q} \cdot \vec{a}_q = 0$.

Using $\Psi_\sigma = \frac{1}{\sqrt{V}} \sum_k c_k e^{ikr}$ we obtain

$$H_1 = -\frac{\hbar e}{mc} \sum_{k,\sigma} c^\dagger_{k+q,\sigma} c_{k,\sigma} (\vec{k}\vec{a}_q) \tag{622}$$

We use

$$c_{k,\sigma} = u_k \alpha_{k,\sigma} + \sigma v_k \alpha^\dagger_{-k,-\sigma} \quad , \quad c^\dagger_{k,\sigma} = u_k \alpha^\dagger_{k,\sigma} + \sigma v_k \alpha_{-k,-\sigma} \tag{623}$$

and conclude that

$$\langle l| c^\dagger_{k+q,\sigma} c_{k,\sigma} |0\rangle = \sigma u_{k+q} v_k \langle l| \alpha^\dagger_{k+q,\sigma} \alpha^\dagger_{-k,-\sigma} |0\rangle \tag{624}$$

but also

$$\begin{aligned}\langle l|\, c^{\dagger}_{-k,-\sigma}c_{-k-q,-\sigma}\,|0\rangle &= -\sigma u_k v_{k+q}\,\langle l|\,\alpha^{\dagger}_{-k,-\sigma}\alpha^{\dagger}_{k+q,\sigma}\,|0\rangle \\ &= \sigma u_k v_{k+q}\,\langle l|\,\alpha^{\dagger}_{k+q,\sigma}\alpha^{\dagger}_{-k,-\sigma}\,|0\rangle \end{aligned} \tag{625}$$

Thus in both cases $|l\rangle$ the same, i.e., the same two quasiparticles created.

For this particular $|l\rangle$ we obtain

$$\begin{aligned}\langle l|\, H_1\,|0\rangle &= -\frac{\hbar e}{mc}\left((\vec{k}\vec{a}_q)\sigma u_{k+q}v_k + ((-\vec{k}-\vec{q})\vec{a}_q)\sigma u_k v_{k+q}\right) \\ &= -\frac{\hbar e}{mc}\,(\vec{k}\vec{a}_q)\sigma\;(u_{k+q}v_k - u_k v_{k+q}) \end{aligned} \tag{626}$$

For $\vec{q}\to 0$ we see that the matrix element vanishes. Together with the fact that $|E_0 - E_l| > 2\Delta$ this gives "rigidity" and

$$\langle \vec{j}_p\rangle = 0 \tag{627}$$

D. Pippard vs. London, coherence length.

The matrix element (626) vanishes for $q\to 0$. Let us analyze it more precisely. We have

$$u_{k+q}v_k - u_k v_{k+q} = \sqrt{\frac{1}{2}+\frac{\xi_{k+q}}{2E_{k+q}}}\sqrt{\frac{1}{2}-\frac{\xi_k}{2E_k}} - \sqrt{\frac{1}{2}+\frac{\xi_k}{2E_k}}\sqrt{\frac{1}{2}-\frac{\xi_{k+q}}{2E_{k+q}}} \tag{628}$$

For $\xi_k \ll E_k \sim \Delta$ we obtain

$$u_{k+q}v_k - u_k v_{k+q} \approx \frac{1}{2\Delta}\,(\xi_{k+q}-\xi_k) \approx \frac{\hbar v_F q}{2\Delta} \tag{629}$$

This introduces the coherence length:

$$\xi \equiv \frac{\hbar v_F}{\Delta} \tag{630}$$

(one usually defines $\xi_0 = \frac{\hbar v_F}{\pi\Delta}$).

The more general than London relation is called Pippard relation:

$$j_\alpha(\vec{r}) = -\sum_\beta \int d^3r' Q_{\alpha,\beta}(\vec{r}-\vec{r}')A_\beta(\vec{r}') \tag{631}$$

where the kernel Q decays on the distance of order ξ. ξ is the size of a Cooper pair.

Two limits: $\xi < \lambda_L$ - London limit, $\xi > \lambda_L$ - Pippard limit.

E. Superconducting density

At $T = 0$ we obtained

$$\vec{j} = -\frac{e^2 n}{mc}\vec{A} \tag{632}$$

Here n is the total electron density. Note that transition to pairs does not change the result. Namely the substitution $n \to n/2$, $m \to 2m$, and $e \to 2e$ leaves the result unchanged.

At $T > 0$ not all the electrons participate in the super current. One introduces the superconducting density $n_s(T)$ and the normal density $n_n(T)$, such that $n_s + n_n = n$. Thus

$$\vec{j_s} = -\frac{e^2 n_s}{mc}\vec{A} \tag{633}$$

Calculations show that near the critical temperature, i.e., for $T_c - T \ll T_c$

$$\frac{n_s}{n} \approx 2\left(1 - \frac{T}{T_c}\right) \tag{634}$$

(**arguments with moving liquid**)

The new penetration depth is defined as

$$\lambda_L(T) = \sqrt{\frac{c^2 m}{4\pi n_s e^2}} \approx \frac{\lambda_L(T=0)}{\sqrt{2}}\left(1 - \frac{T}{T_c}\right)^{-1/2} \tag{635}$$

F. Critical field

One applies external magnetic field H. It is known that the field is expelled from the superconductor (Meissner effect). That is inside the superconductor $B = 0$. When the field reaches the critical field H_c the superconductivity is destroyed and the field penetrates the metal.

Naive (but correct) argument: The total (free) energy of a cylindrical superconductor consists of the bulk free energy F_s and the energy of the induced currents screening the external magnetic field. We have $B = 0 = B_{\text{ext}} + B_{\text{induced}}$ (recall that $H = B_{\text{ext}}$). The energy of the induced currents is given by $B^2_{\text{induced}}/(8\pi)$. Thus the total energy of a superconductor reads $F_s + H^2/(8\pi)$. For $H = H_c$ the free energy of a superconductor and of a normal metal should be equal

$$F_s + \frac{H_c^2}{8\pi} = F_n \ . \tag{636}$$

The less naive thermodynamic argument involves the free enthalpy $G = F - HB/(4\pi)$ (see the book by Abrikosov).

At zero temperature ($F = U - TS$) we have

$$F_n - F_s = \frac{\nu_0 \Delta^2}{2} \tag{637}$$

Thus we find

$$H_c(T=0) = 2\sqrt{\pi\nu_0}\Delta(T=0) \tag{638}$$

In particular also for H_c we have the isotope effect, $H_c \propto M^{-1/2}$.

For $T \to T_c - 0$ one obtains (no proof)

$$H_c(T) = 1.735 H_c(0)\left(1 - \frac{T}{T_c}\right) \tag{639}$$

G. Order parameter, phase

Thus far Δ was real. We could however introduce a different BCS groundstate:

$$|BCS(\phi)\rangle = \prod_k (u_k + e^{i\phi} v_k c^\dagger_{k,\uparrow} c^\dagger_{-k,\downarrow}) \, |0\rangle \ . \tag{640}$$

Exercise: check that

$$|BCS(N)\rangle = \int_0^{2\pi} \frac{d\phi}{2\pi} \, |BCS(\phi)\rangle \, e^{-iN\phi} \tag{641}$$

gives a state with a fixed number of electrons N.

We obtain for Δ

$$\Delta = \frac{g}{V} \sum_k \langle c_{-k,\downarrow} c_{k,\uparrow} \rangle = \frac{g}{V} \sum_k u_k v_k e^{i\phi} = |\Delta| e^{i\phi} \tag{642}$$

Usual gauge transformation:

$$\vec{A} \to \vec{A} + \vec{\nabla}\chi \tag{643}$$

$$\Psi \to \Psi e^{\frac{ie}{\hbar c}\chi} \tag{644}$$

We identify

$$\frac{\phi}{2} = -\frac{e}{\hbar c}\chi \tag{645}$$

Thus

$$\vec{A} \to \vec{A} - \frac{\hbar c}{2e}\vec{\nabla}\phi \tag{646}$$

and

$$\vec{j}_s = -\frac{e^2 n_s}{mc}\left(\vec{A} - \frac{\hbar c}{2e}\vec{\nabla}\phi\right) \tag{647}$$

H. Ginsburg-Landau Theory

Theory works for $T \approx T_c$.

One introduces the order parameter

$$\Psi = \sqrt{\frac{n_s}{2}}\, e^{i\phi} \tag{648}$$

1. Landau Theory

One postulates for the free energy

$$\int dV\, F = \int dV\, \left\{ F_n + a|\Psi|^2 + \frac{b}{2}|\Psi|^4 \right\} \tag{649}$$

In order to describe the phase transition one postulates $a = \alpha\tau$, where

$$\tau = \frac{T - T_c}{T_c} \tag{650}$$

and $\alpha > 0$, $b > 0$.

By varying we obtain $|\Psi|^2$:

$$a + b|\Psi|^2 = 0 \tag{651}$$

For $\tau < 0$ this gives

$$|\Psi|^2 = -\frac{\alpha\tau}{b} = \frac{\alpha}{b}\,\frac{T_c - T}{T_c} \tag{652}$$

For $\tau > 0$ we have $|\Psi|^2 = 0$. Phase transition.

We define

$$\Psi_0^2 \equiv -\frac{a}{b}\ . \tag{653}$$

2. Ginsburg-Landau Theory, equations

Theory for inhomogeneous situations, currents and magnetic fields. One postulates for the free energy

$$\int dV\, F = \int dV\, \left\{ F_n + a|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{1}{4m}\left|\left(-i\hbar\vec{\nabla} - \frac{2e}{c}\vec{A}\right)\Psi\right|^2 + \frac{\vec{B}^2}{8\pi} \right\} \tag{654}$$

Here, for a while, we consider the superconductor on its own. Thus $\vec{B}$ is the field induced by the currents in the superconductor itself. Below we will include the external field.

Here we have to vary with respect to Ψ regarding Ψ^* as independent. This gives

$$\frac{1}{4m}\left(-i\hbar\vec{\nabla}-\frac{2e}{\hbar c}\vec{A}\right)^2\Psi+a\Psi+b|\Psi|^2\Psi=0 \tag{655}$$

Varying with respect to $\vec{A}$ (using $\mathrm{div}[\mathbf{a}\cdot\mathbf{b}]=\mathbf{b}\cdot\mathrm{rot}\mathbf{a}-\mathbf{a}\cdot\mathrm{rot}\mathbf{b}$) gives

$$\nabla\times\vec{B}=\frac{4\pi}{c}\vec{j} \tag{656}$$

with

$$\vec{j}=-\frac{2ie\hbar}{4m}\left(\Psi^*\vec{\nabla}\Psi-\Psi\vec{\nabla}\Psi^*\right)-\frac{(2e)^2}{2mc}|\Psi|^2\vec{A} \tag{657}$$

For $\Psi=\Psi_0 e^{i\phi(\vec{r})}$ we obtain again the London equation

$$\vec{j}_s=-\frac{4e^2}{2mc}\Psi_0^2\left(\vec{A}-\frac{\hbar c}{2e}\vec{\nabla}\phi\right)=-\frac{e^2n_s}{mc}\left(\vec{A}-\frac{\hbar c}{2e}\vec{\nabla}\phi\right) \tag{658}$$

Thus we obtain the London penetration depth

$$\lambda_{\mathrm{L}}=\sqrt{\frac{c^2m}{4\pi n_s e^2}}=\sqrt{\frac{c^2m}{8\pi\Psi_0^2e^2}}\ . \tag{659}$$

3. Coherence length

Coherence length is obtained by considering small fluctuations of the amplitude of Ψ. So we assume $\vec{A}=0$, and $\Psi=\Psi_0+\delta\Psi$ (both real), and $\Psi_0^2=-a/b$. Then we obtain

$$-\frac{\hbar^2}{4m}\nabla^2\delta\Psi+\delta\Psi(a+3b\Psi_0^2)=0\ . \tag{660}$$

In the normal state $\Psi_0=0$ and $a>0$ we obtain solutions of the type $e^{\pm x/\xi}$, where

$$\xi=\frac{\hbar}{\sqrt{4ma}} \tag{661}$$

In the superconducting state $\Psi_0^2=-a/b$, $a<0$

$$-\frac{\hbar^2}{4m}\nabla^2\delta\Psi+\delta\Psi(a+3b\Psi_0^2)=-\frac{\hbar^2}{4m}\nabla^2\delta\Psi-2a\delta\Psi=0\ . \tag{662}$$

We still define the coherence length as in the normal case

$$\xi=\frac{\hbar}{\sqrt{4m|a|}}\ . \tag{663}$$

However the solutions look like $e^{\pm\sqrt{2}x/\xi}$.

4. External field

If a superconductor is placed in an external magnetic field $\vec{H}_0$ the proper free energy reads

$$\int dV\, F_H = \int dV\, F - \frac{1}{4\pi}\,\vec{H}_0 \int dV\, \vec{B}\ . \tag{664}$$

Here $\vec{B}$ is the total magnetic field, $\vec{B} = \vec{H}_0 + \vec{B}_i$. Here $\vec{B}_i$ is the field induced by currents in the superconductor. Thus

$$\int dV\, F_H = \int dV\, \left\{ F_n + a|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{1}{4m}\left|\left(-i\hbar\vec{\nabla} - \frac{2e}{c}\vec{A}\right)\Psi\right|^2 + \frac{\vec{B}^2}{8\pi} - \frac{\vec{H}_0\cdot\vec{B}}{4\pi}\right\}\ . \tag{665}$$

Note, that this gives the same Ginsburg-Landau equations. Indeed $B^2/(8\pi) - BH_0/(4\pi) = B_i^2/8\pi + const.$ and we vary, actually, the field B_i.

In the normal state we have $B = H_0$ and $F_H = F_n - H_0^2/(8\pi)$. Deep in the superconductor $B = 0$ and $F_H = F_n + a|\Psi|^2 + \frac{b}{2}|\Psi|^4 = F_n - \frac{a^2}{2b} = F_n - \frac{(\alpha\tau)^2}{2b}$. Thus we obtain the critical field H_c, i.e., the value of H_0 above which the normal state has a lower free energy. We obtain $H_c^2/(8\pi) = \frac{(\alpha\tau)^2}{2b}$ and

$$H_c = \sqrt{\frac{4\pi a^2}{b}}\ . \tag{666}$$

5. Reduced Ginsburg-Landau equations

We define

$$\Psi' = \Psi/\Psi_0 \quad , \quad r' = r/\lambda_{\rm L} \quad , \quad B' = B/(H_c\sqrt{2}) \quad , \quad A' = A/(\lambda_{\rm L}H_c\sqrt{2}) \tag{667}$$

We obtain the Ginsburg-Landau equations in the reduced form (omitting the primes)

$$\left(-i\kappa^{-1}\vec{\nabla} - \vec{A}\right)^2\Psi - \Psi + |\Psi|^2\Psi = 0\ , \tag{668}$$

$$\vec{\nabla}\times(\vec{\nabla}\times\vec{A}) = -\frac{i}{2\kappa}\left(\Psi^*\vec{\nabla}\Psi - \Psi\vec{\nabla}\Psi^*\right) - |\Psi|^2\vec{A}\ , \tag{669}$$

where

$$\kappa = \frac{\lambda_{\rm L}}{\xi}\ . \tag{670}$$

Thus, everything depends on κ.

The free energy in these units reads

$$\int dV\, F_H = \int dV\, F_n + \frac{H_c^2}{4\pi}\int dV\, \left\{ -|\Psi|^2 + \frac{1}{2}|\Psi|^4 + \left| \left(-\frac{i\vec{\nabla}}{\kappa} - \vec{A} \right) \Psi \right|^2 + \vec{B}^2 - 2\vec{H}_0 \cdot \vec{B} \right\} . \tag{671}$$

Integrating by part, disregarding the boundary, using the Ginsburg-Landau equations, and adding an unimportant constant we obtain

$$\int dV\, F_H = \int dV\, F_n + \frac{H_c^2}{4\pi}\int dV\, \left\{ -\frac{1}{2}|\Psi|^4 + (\vec{B} - \vec{H}_0)^2 \right\} . \tag{672}$$

I. Surface energy

Let us estimate the surface energy of an interface between superconducting and normal phases. We assume $H_0 = H_c$, i.e., both phases are possible. In the normal phase we have the critical magnetic field $B = H_c$ ($B' = 1/\sqrt{2}$). In the superconducting phase $B = 0$ and $\Psi = \Psi_0$ ($\Psi' = 1$). The order parameter varies on the scale ξ (κ^{-1}). The magnetic field varies on the scale λ_L (1).

We consider a quasi-one dimensional situation. All the quantities depend only on x. $\vec{A}$ is along y ($\vec{A} = A(x)\vec{y}$) and, thus, $\vec{B}$ is along z. We can take Ψ to be real. Then

$$\kappa^{-2}\nabla^2\Psi + (1 - A^2)\Psi - \Psi^3 = 0 , \tag{673}$$

$$\nabla^2 A - \Psi^2 A = 0 . \tag{674}$$

Consider 2 cases:

a) $\xi \gg \lambda_L$ ($\kappa \ll 1$)(superconductor of the 1-st type). In this case there is a layer on the interface of thickness ξ where the magnetic field vanishes and the order parameter vanishes, i.e., the state is normal. We see that there is an additional cost of $\sim \xi \frac{H_c^2}{8\pi}$ per unit of area. The logic: the work of expelling the magnetic field has been performed but no energy reduction through the order parameter appearance. Thus the surface energy is positive in this case and the system avoids interfaces.

b) $\xi \ll \lambda_L$ ($\kappa \gg 1$)(superconductor of the 2-nd type). In this case there is a layer of thickness λ_L where the magnetic field is present and also the order parameter has its bulk value. The surface energy is then negative and equal $\sim -\lambda_L \frac{H_c^2}{8\pi}$. The logic: magnetic field not expelled in the layer, thus no energy cost. The energy is reduced by having the superconducting order parameter. Thus the system likes to have interfaces.

The critical value of κ at which the surface energy vanishes is given by $\kappa_c = 1/\sqrt{2}$.

J. Higgs mechanismus

We consider again the GL free energy density (action):

$$\begin{aligned} F &= a|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{1}{4m}\left|\left(-i\hbar\vec{\nabla} - \frac{2e}{c}\vec{A}\right)\Psi\right|^2 + \frac{\vec{B}^2}{8\pi} \\ &= a|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{1}{4m}\left[\left(-i\hbar\vec{\nabla} - \frac{2e}{c}\vec{A}\right)\Psi\right]\left[\left(i\hbar\vec{\nabla} - \frac{2e}{c}\vec{A}\right)\Psi^*\right] + \frac{(\vec{\nabla}\times\vec{A})^2}{8\pi} \ . \end{aligned} \tag{675}$$

Consider small fluctuations around the real solution $\Psi_0 = \sqrt{-a/b}$.

$$\Psi(\vec{r}) = \Psi_0 + \phi_1(\vec{r}) + i\phi_2(\vec{r}) \ , \tag{676}$$

where ϕ_1 and ϕ_2 are real. Considering also $\vec{A}(\vec{r})$ to be small we expand the action to second order in ϕ_1, ϕ_2 and $\vec{A}$:

$$\begin{aligned} \delta F^{(2)} &= \frac{1}{4m}\left[\left(\frac{2e}{c}\right)^2\Psi_0^2\left(\vec{A}\right)^2 + \hbar^2\left(\vec{\nabla}\phi_1\right)^2 + \hbar^2\left(\vec{\nabla}\phi_2\right)^2 - 2\hbar\left(\frac{2e}{c}\right)\Psi_0\left(\vec{A}\vec{\nabla}\phi_2\right)\right] \\ &- 2a\phi_1^2 + \frac{(\vec{\nabla}\times\vec{A})^2}{8\pi} + \text{higher orders} \ . \end{aligned} \tag{677}$$

We still have the gauge freedom:

$$\vec{A}' = \vec{A} + \vec{\nabla}\chi \quad , \quad \Psi' = \Psi\exp\left[\frac{2ie}{\hbar c}\chi\right] \ . \tag{678}$$

To keep $\vec{A}'$ small we perform an infinitesimal gauge transformation, which then reduces to $\Psi' \approx \Psi(1+i\tilde{\chi}) = (\Psi_0 + \phi_1 + i\phi_2)(1+i\tilde{\chi})$, where $\tilde{\chi} \equiv \frac{2ie}{\hbar c}\chi$. In terms of the deviations we obtain

$$\phi_1' = \phi_1 - \phi_2\tilde{\chi} \quad , \quad \phi_2' = \phi_2 + \phi_1\tilde{\chi} + \Psi_0\tilde{\chi} \ . \tag{679}$$

It is actually sufficient to keep only the term $\Psi_0\tilde{\chi}$. Thus, we can always find a gauge transformation such that $\phi_2' = 0$. Dropping the primes we obtain

$$\begin{aligned} \delta F^{(2)} &= \frac{\hbar^2}{4m}\left(\vec{\nabla}\phi_1\right)^2 - 2a\phi_1^2 \\ &+ \frac{(\vec{\nabla}\times\vec{A})^2}{8\pi} + \frac{1}{4m}\left(\frac{2e}{c}\right)^2\Psi_0^2\left(\vec{A}\right)^2 + \text{higher orders} \ . \end{aligned} \tag{680}$$

Thus we obtain two modes. The first mode, ϕ_1, called also Higgs mode, has a characteristic length, which coincides with the coherence length ξ. The second mode is described by field

$\vec{A}$. The transversal components of $\vec{A}$ are characterized by the London penetration depth (cf. Eq. (659)), i.e.,

$$\lambda_L^{-2} = \frac{8\pi}{4m}\left(\frac{2e}{c}\right)^2 \Psi_0^2 = \frac{4\pi e^2 n_s}{mc^2} \ . \tag{681}$$

This can also be seen as the photon mass. Our theory has no time-dependence, but is otherwise complete with respect to the transversal components of the field $\vec{A}$. This means, in the relativistic dispersion relation $E^2 = \mu^2 c^4 + c^2 p^2$ we should take $E = \hbar\omega = 0$. Then $p^2 = -\mu^2 c^2$. Since $p^2 < 0$, we obtain spatial decay, i.e., penetration depth. Identifying $p^2 = -\hbar^2 \lambda_L^{-2}$, we obtain the photon mass

$$(\mu c^2)^2 = \hbar^2 \frac{4\pi e^2 n_s}{m} = (\hbar\omega_{ps})^2 \ . \tag{682}$$

Here

$$\omega_{ps}^2 = \frac{4\pi e^2 n_s}{m} \tag{683}$$

is the plasma frequency of the superconducting electronic liquid. At $T = 0$ it coincides with the usual plasma frequency.

The variation of (680) with respect to the longitudinal component of $\vec{A}$ results simply in $\vec{A}_{\|} = 0$. Thus, unlike in full Higgs case, no longitudinal photon appears at $\omega = 0$. In order to treat the longitudinal modes (plasmons) properly we have to introduce time-dependence and the scalar potential. This is beyond the scope of this text.

K. Flux quantization

In the bulk of a superconductor, where $\vec{j}_s = 0$, we obtain

$$\vec{A} - \frac{\hbar c}{2e}\vec{\nabla}\phi = 0 \tag{684}$$

$$\oint \vec{A}d\vec{l} = \frac{\hbar c}{2e}\oint \vec{\nabla}\phi d\vec{l} = \frac{\hbar c}{2e} 2\pi n = \frac{hc}{2e} n = n\Phi_0 \tag{685}$$

This quantization is very important for, e.g., a ring geometry. If the ring is thick enough (thicker than λ_L) the total magnetic flux threading the ring is quantized.

L. Josephson effect

We consider now a tunnel junction between two superconductors with different phases ϕ_L and ϕ_R. The Hamiltonian reads

$$H = H_{BCS,L} + H_{BCS,R} + H_T \ , \tag{686}$$

where the tunneling Hamiltinoan reads

$$H_T = \sum_{k_1,k_2,\sigma} T \left[R^\dagger_{k_1,\sigma} L_{k_2,\sigma} + L^\dagger_{k_2,\sigma} R_{k_1,\sigma} \right] \ . \tag{687}$$

Here $R_{k,\sigma} \equiv c^{(R)}_{k,\sigma}$ is the annihilation operator of an electron in the left superconductor. Two important things: 1) microscopically the electrons and not the quasiparticles tunnel; 2) tunneling conserves spin.

A gauge transformation $L_{k,\sigma} \to e^{i\phi_L/2} L_{k,\sigma}$ and $R_{k,\sigma} \to e^{i\phi_R/2} R_{k,\sigma}$ "removes" the phases from the respective BCS wave functions (making v_k, u_k, and Δ real) and renders the tunneling Hamiltonian

$$H_T = \sum_{k_1,k_2,\sigma} T \left[R^\dagger_{k_1,\sigma} L_{k_2,\sigma} e^{-i\phi/2} + L^\dagger_{k_2,\sigma} R_{k_1,\sigma} e^{i\phi/2} \right] \ , \tag{688}$$

where $\phi \equiv \phi_R - \phi_L$.

Josephson [1] used (688) and calculated the tunneling current. We do so here for a time-independent phase difference ϕ. The current operator is given by time derivative of the number of particles in the right lead $N_R = \sum_{k,\sigma} R^\dagger_{k,\sigma} R_{k,\sigma}$

$$I = -e\dot{N}_R = -\frac{ie}{\hbar}[H_T, N_R] = \frac{ie}{\hbar} \sum_{k_1,k_2,\sigma} T \left[R^\dagger_{k_1,\sigma} L_{k_2,\sigma} e^{-i\phi/2} - L^\dagger_{k_2,\sigma} R_{k_1,\sigma} e^{i\phi/2} \right] \ . \tag{689}$$

The first order time-dependent perturbation theory gives for the density matrix of the system in the interaction representation

$$\rho(t) = T e^{-i\int_{-\infty}^{t} dt' H_T(t')} \rho_0 \tilde{T} e^{i\int_{-\infty}^{t} dt' H_T(t')} \approx \rho_0 - i\int_{-\infty}^{t} dt' [H_T(t'), \rho_0] \ . \tag{690}$$

For the expectation value of the current this gives

$$\langle I(t) \rangle = \mathrm{Tr}\{\rho(t) I(t)\} = -i\int_{-\infty}^{t} dt' \, \mathrm{Tr}\left\{[H_T(t'), \rho_0] I(t)\right\} = -i\int_{-\infty}^{t} dt' \, \mathrm{Tr}\left\{[I(t), H_T(t')] \, \rho_0\right\} \ . \tag{691}$$

We use

$$\begin{aligned}
&\langle BCS|\, c^\dagger_{k,\uparrow}(t_1)\, c^\dagger_{-k,\downarrow}(t_2)\, |BCS\rangle \\
&= \langle BCS|\, \Big(u_k \alpha^\dagger_{k,\uparrow}(t_1) + v_k \alpha_{-k,\downarrow}(t_1)\Big)\, \Big(u_k \alpha^\dagger_{-k,\downarrow}(t_2) - v_k \alpha_{k,\uparrow}(t_2)\Big)\, |BCS\rangle \\
&= v_k u_k e^{-iE_k(t_1-t_2)} \ , \qquad (692)
\end{aligned}$$

and

$$\begin{aligned}
&\langle BCS|\, c_{k,\uparrow}(t_1)\, c_{-k,\downarrow}(t_2)\, |BCS\rangle \\
&= \langle BCS|\, \Big(u_k \alpha_{k,\uparrow}(t_1) + v_k \alpha^\dagger_{-k,\downarrow}(t_1)\Big)\, \Big(u_k \alpha_{-k,\downarrow}(t_2) - v_k \alpha^\dagger_{k,\uparrow}(t_2)\Big)\, |BCS\rangle \\
&= -v_k u_k e^{-iE_k(t_1-t_2)} \ , \qquad (693)
\end{aligned}$$

After some algebra we obtain (from the anomalous correlators, the rest gives zero)

$$\begin{aligned}
\langle I(t)\rangle =& \ - \ 2eT^2 e^{-i\phi} \int_{-\infty}^{t} dt' \sum_{k_1,k_2} v_{k_1} u_{k_1} v_{k_2} u_{k_2} \left[e^{-i(E_{k_1}+E_{k_2})(t-t')} - e^{i(E_{k_1}+E_{k_2})(t-t')}\right] \\
&+ \ 2eT^2 e^{i\phi} \int_{-\infty}^{t} dt' \sum_{k_1,k_2} v_{k_1} u_{k_1} v_{k_2} u_{k_2} \left[e^{-i(E_{k_1}+E_{k_2})(t-t')} - e^{i(E_{k_1}+E_{k_2})(t-t')}\right] \\
&= \ 8eT^2 \sin(\phi) \sum_{k_1,k_2} \frac{v_{k_1} u_{k_1} v_{k_2} u_{k_2}}{E_{k_1}+E_{k_2}} = 2eT^2 \sin(\phi) \sum_{k_1,k_2} \frac{\Delta^2}{E_{k_1} E_{k_2} (E_{k_1}+E_{k_2})} \\
&= \ 2\pi^2 T^2 \nu^2 e \Delta \hbar^{-1} \sin(\phi) = I_c \sin(\phi) \ , \qquad (694)
\end{aligned}$$

where the Josephson critical current is given by

$$I_c = \frac{g_T e \Delta}{4\hbar} = \frac{\pi \Delta}{2eR_T} \ , \qquad (695)$$

where $g_T = 2 \times 4\pi^2 T^2 \nu^2$ is the dimensionless conductance of the tunnel junction (factor 2 accounts for spin), while the tunnel resistance is given by $R_T = \frac{h}{e^2}\frac{1}{g_T}$. This is the famous Ambegaokar-Baratoff relation [2] (see also erratum [3]).

Thus we have obtained the first Josephson relation $I = I_c \sin\phi$. We have introduced the variable ϕ as the difference of two phases $\phi = \phi_R - \phi_L$. The gauge invariant definition reads

$$\phi = \phi_R - \phi_L - \frac{2e}{\hbar c} \int_L^R \vec{A} d\vec{l} \, . \qquad (696)$$

As a shortest way to the second Josephson relation we assume that an electric field exists in the junction and that it is only due to the time-dependence of $\vec{A}$. Then we obtain

$$\dot{\phi} = -\frac{2e}{\hbar c} \int_L^R \left[\frac{\partial}{\partial t}\vec{A}\right] d\vec{l} = \frac{2e}{\hbar} \int_L^R \vec{E} d\vec{l} = -\frac{2e}{\hbar} V \ , \qquad (697)$$

where V is the voltage. Here we all the time treated e as the charge of the electron, i.e., $e < 0$. Usually one uses e as a positive quantity. Then

$$\dot{\phi} = \frac{2eV}{\hbar} \ . \tag{698}$$

An alternative way to derive this is to start with a difference of (time-dependent) chemical potentials

$$H = H_L + H_R - eV_L(t) \sum_{k,\sigma} L^\dagger_{k,\sigma} L_{k,\sigma} - eV_R(t) \sum_{k,\sigma} R^\dagger_{k,\sigma} R_{k,\sigma} + H_T \ , \tag{699}$$

where $V_{L/R}$ are the applied electro-chemical potentials (in addition to the constant chemical potential μ, which is included in H_L and H_R). A transformation with

$$U = e^{\frac{e}{\hbar}\hat{N}_L \int^t V_L(t')dt'} \, e^{\frac{e}{\hbar}\hat{N}_R \int^t V_R(t')dt'} \tag{700}$$

In the new Hamiltonian

$$\tilde{H} = i\dot{U}U^{-1} + UHU^{-1} \ . \tag{701}$$

the terms with V_L and V_R are cancelled and instead the electronic operators are replaced by, e.g,

$$L \to ULU^{-1} = Le^{i\phi_L/2} \ , \tag{702}$$

where $\phi_L = const. - \frac{2e}{\hbar} \int^t V_L(t')dt'$ and, thus, $\dot{\phi} = \dot{\phi}_R - \dot{\phi}_L = -\frac{2e}{\hbar}V$.

M. Macroscopic quantum phenomena

1. *Resistively shunted Josephson junction (RSJ) circuit*

Consider a circuit of parallelly connected Josephson junction and a shunt resistor R. A Josephson junction is simultaneously a capacitor. An external current I_{ex} is applied. The Kirchhoff rules lead to the ecquation

$$I_c \sin\phi + \frac{V}{R} + \dot{Q} = I_{ex} \ . \tag{703}$$

As $Q = CV$ and $V = \frac{\hbar}{2e}\dot{\phi}$. Thus we obtain

$$I_c \sin\phi + \frac{\hbar}{2eR}\,\dot{\phi} + \frac{\hbar C}{2e}\,\ddot{\phi} = I_{ex} \ . \tag{704}$$

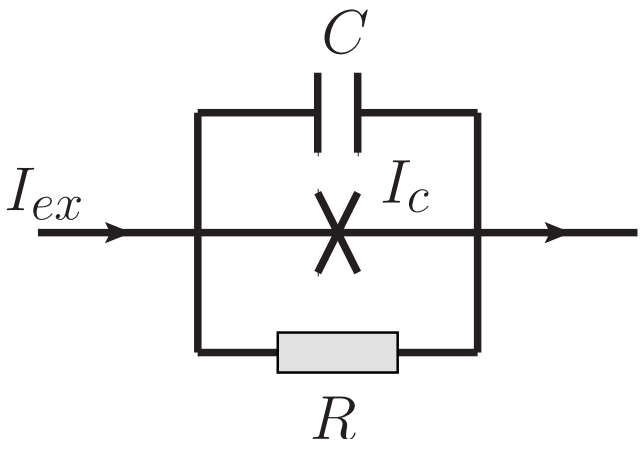

FIG. 10: RSJ Circuit.

It is very convenient to measure the phase in units of magnetic flux, so that $V = \frac{1}{c}\dot{\Phi}$ (in SI units $V = \dot{\Phi}$):

$$\Phi = \frac{c\hbar}{2e}\,\phi = \frac{\Phi_0}{2\pi}\,\phi \quad , \quad \phi = 2\pi\frac{\Phi}{\Phi_0}\ . \tag{705}$$

Then the Kirchhoff equation reads

$$I_c \sin\left(2\pi\frac{\Phi}{\Phi_0}\right) + \frac{\dot{\Phi}}{cR} + \frac{C\ddot{\Phi}}{c} = I_{ex}\ , \tag{706}$$

or in SI units

$$I_c \sin\left(2\pi\frac{\Phi}{\Phi_0}\right) + \frac{\dot{\Phi}}{R} + C\ddot{\Phi} = I_{ex}\ . \tag{707}$$

There are two regimes. In case $I_{ex} < I_c$ there exists a stationary solution $\phi = \arcsin(I_{ex}/I_c)$. All the current flows through the Josephson contact as a super-current. Indeed $V \propto \dot{\phi} = 0$. At $I_{ex} > I_c$ at least part of the current must flow through the resistor. Thus a voltage develops and the phase starts to "run".

2. Particle in a washboard potential

The equation of motion (707) can be considered as an equation of motion of a particle with the coordinate $x = \Phi$. We must identify the capacitance with the mass, $m = C$, the inverse resistance with the friction coefficient $\gamma = R^{-1}$. Then we have

$$m\ddot{x} = -\gamma\dot{x} - \frac{\partial U}{\partial x}\ , \tag{708}$$

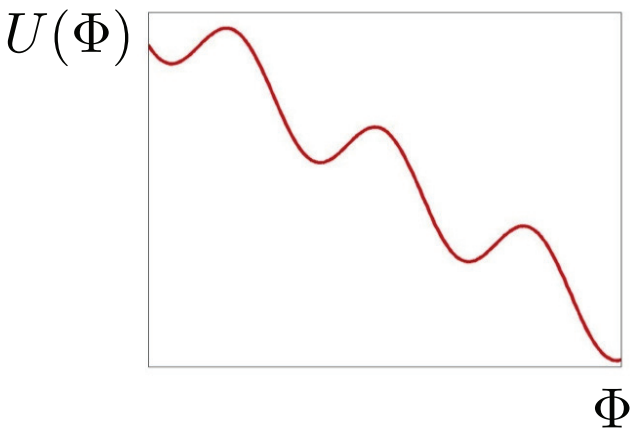

FIG. 11: Washboard potential.

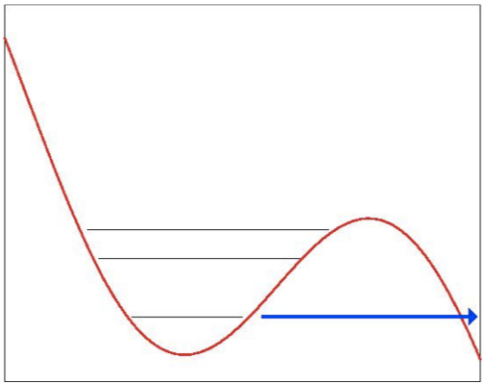

FIG. 12: Macroscopic Quantum Tunneling (MQT).

where for the potential we obtain

$$U(\Phi) = -E_J \cos\left(2\pi \frac{\Phi}{\Phi_0}\right) - I_{ex}\Phi \ , \tag{709}$$

where

$$E_J \equiv \frac{I_c \Phi_0}{2\pi} = \frac{\hbar I_c}{2e} \tag{710}$$

is called the Josephson energy. The potential energy $U(\Phi)$ has a form of a washboard and is called a washboard potential. In Fig. 11 the case $I_{ex} < I_c$ is shown. In this case the potential has minima and, thus, classically stationary solutions are possible.

When the external current is close to the critical value a situation shown in Fig. 12 emerges. If we allow ourselves to think of this situation quantum mechanically, then we would conclude that only a few quantum levels should remain in the potential well. Moreover a tunneling process out of the well should become possible. This tunneling process was named

Macroscopic Quantum Tunneling because in the 80-s and the 90-s many researchers doubted the fact one can apply quantum mechanics to the dynamics of the "macroscopic" variable Φ. It was also argued that a macroscopic variable is necessarily coupled to a dissipative bath which would hinder the tunneling. Out these discussions the famous Caldeira-Leggett model emerged [4, 5].

3. Quantization

We write down the Lagrangian that would give the equation of motion (708 or 707). Clearly we cannot include the dissipative part in the Lagrange formalism. Thus we start from the limit $R \to \infty$. The Lagrangian reads

$$L = \frac{C\dot{\Phi}^2}{2} - U(\Phi) = \frac{C\dot{\Phi}^2}{2} + E_J \cos\left(2\pi\frac{\Phi}{\Phi_0}\right) + I_{ex}\Phi \ . \tag{711}$$

We transform to the Hamiltonian formalism and introduce the canonical momentum

$$Q \equiv \frac{\partial L}{\partial \dot{\Phi}} = C\dot{\Phi} \ . \tag{712}$$

The Hamiltonian reads

$$H = \frac{Q^2}{2C} + U(\Phi) = \frac{Q^2}{2C} - E_J \cos\left(2\pi\frac{\Phi}{\Phi_0}\right) - I_{ex}\Phi \ . \tag{713}$$

The canonical momentum corresponds to the charge on the capacitor (junction). The usual commutation relations should be applied

$$[\Phi, Q] = i\hbar \ . \tag{714}$$

In the Hamilton formalism it is inconvenient to have an unbounded from below potential. Thus we try to transform the term $-I_{ex}\Phi$ away. This can be achieved by the following canonical transformation

$$R = \exp\left[-\frac{i}{\hbar}Q_{ex}(t)\Phi\right] \ , \tag{715}$$

where $Q_{ex}(t) \equiv \int^t I_{ex}(t')dt'$. Indeed the new Hamiltonian reads

$$\tilde{H} = RHR^{-1} + i\hbar\dot{R}R^{-1} = \frac{(Q - Q_{ex}(t))^2}{2C} - E_J \cos\left(2\pi\frac{\Phi}{\Phi_0}\right) \ . \tag{716}$$

The price we pay is that the new Hamiltonian is time-dependent. The Hamiltonian (716) is very interesting. Let us investigate the operator

$$\cos\left(2\pi\frac{\Phi}{\Phi_0}\right) = \cos\left(\frac{2e}{\hbar}\,\Phi\right) = \frac{1}{2}\,\exp\left[\frac{i}{\hbar}\,2e\,\Phi\right] + h.c. \tag{717}$$

We have

$$\exp\left[\frac{i}{\hbar}\,2e\,\Phi\right]\,|Q\rangle = |Q+2e\rangle \quad , \quad \exp\left[-\frac{i}{\hbar}\,2e\,\Phi\right]\,|Q\rangle = |Q-2e\rangle \ . \tag{718}$$

Thus in this Hamiltonian only the states differing by an integer number of Cooper pairs get connected. The constant offset charge remains undetermined. This, however, can be absorbed into the bias charge Q_{ex}. Thus, we can restrict ourselves to the Hilbert space $|Q = 2em\rangle$.

4. Phase and Number of particles (Cooper pairs)

We consider again the states $|BCS(\phi)\rangle$ and $|BCS(N)\rangle$ introduced above (see Eqs. 640 and 641):

$$|BCS(\phi)\rangle = \prod_k (u_k + e^{i\phi} v_k c^\dagger_{k,\uparrow} c^\dagger_{-k,\downarrow})\,|0\rangle \ . \tag{719}$$

$$|BCS(N)\rangle = \int_0^{2\pi} \frac{d\phi}{2\pi}\,|BCS(\phi)\rangle\, e^{-iN\phi} \tag{720}$$

It is easy to see that the operator $A^\dagger = e^{-i\phi}$ increases the number of Cooper pairs by one

$$A^\dagger\,|BCS(N)\rangle = \int_0^{2\pi} \frac{d\phi}{2\pi}\,|BCS(\phi)\rangle\, e^{-i(N+1)\phi} = |BCS(N+1)\rangle \ . \tag{721}$$

We have seen that the excitations above the BCS ground state have an energy gap Δ. Thus, if $T \ll \Delta$ no excitations are possible. The only degree of freedom left is the pair of conjugate variables N, ϕ with commutation relations $[N, e^{-i\phi}] = e^{-i\phi}$. Indeed the ground state energy is independent of ϕ. This degree of freedom is, of course, non-existent if the number of particles is fixed. Thus a phase of an isolated piece of a superconductor is quantum mechanically smeared between 0 and 2π and no dynamics of the degree of freedom N, ϕ is possible. However in a bulk superconductor the phase can be space dependent $\phi(\vec{r})$. One can still add a constant phase to $\phi(\vec{r}) + \phi_0$ without changing the state. More precisely the phase ϕ_0 is smeared if the total number of particles is fixed. However the difference of phases, i.e., the phase gradient can be well defined and corresponds to a super-current.

5. Josephson energy dominated regime

In this regime $E_J \gg E_C$, where $E_C = \frac{(2e)^2}{2C}$ is the Cooper pair charging energy. Let us first neglect E_C completely, i.e., put $C = \infty$. Recall that C plays the role of the mass. Then the Hamiltonian reads $H = -E_J \cos\left(2\pi \frac{\Phi}{\Phi_0}\right)$. On one hand it is clear that the relevant state are those with a given phase, i.e., $|\Phi\rangle$. On the other hand, in the discrete charge representation the Hamiltonian reads

$$H = -\frac{E_J}{2} \sum_m \left(|m+1\rangle \langle m| + |m\rangle \langle m+1| \right) \ . \tag{722}$$

The eigenstates of this tight-binding Hamiltonian are the Bloch waves $|k\rangle = \sum_m e^{ikm} |m\rangle$ with the wave vector k belonging to the first Brillouin zone $-\pi \leq k \leq \pi$. The eigenenergy reads $E_k = -E_J \cos(k)$. Thus we identify $k = \phi = \frac{2\pi\Phi}{\Phi_0}$.

6. Charging energy dominated regime

In this regime $E_J \ll E_C$. The main term in the Hamiltonian is the charging energy term

$$H_C = \frac{(Q - Q_{ex}(t))^2}{2C} = \frac{(2em - Q_{ex})^2}{2C} \ . \tag{723}$$

The eigenenergies corresponding to different values of m form parabolas as functions of Q_{ex} (see Fig. 13). The minima of the parabolas are at $Q_{ex} = 0, 2e, 4e, \ldots$. The Josephson tunneling term serves now as a perturbation $H_J = -E_J \cos\left(2\pi \frac{\Phi}{\Phi_0}\right)$. It lifts the degeneracies, e.g., at $Q_{ex} = e, 3e, 5e, \ldots$.

If a small enough external current is applied, $Q_{ex} = I_{ex} t$ the adiabatic theorem holds and the system remains in the ground state. Yet, one can see that between the degeneracies at $Q_{ex} = e, 3e, 5e, \ldots$ the capacitance is charged and discharged and oscillating voltage $V = \partial E_0 / \partial Q_{ex}$ appears. Here $E_0(Q_{ex})$ is the energy of the ground state. The Cooper pairs tunnel only at the degeneracy points. In between the Coulomb blockade prevents the Cooper pairs from tunneling because this would cost energy.

---

[1] B. D. Josephson, Physics Letters **1**, 251 (1962).

[2] V. Ambegaokar and A. Baratoff, Phys. Rev. Lett. **10**, 486 (1963).

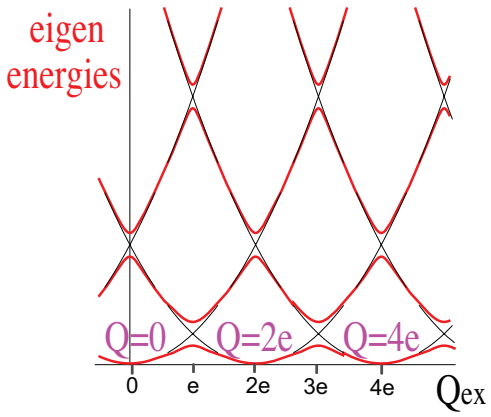

FIG. 13: Eigen levels in the coulomb blockade regime. Different parabolas correspond to different values of $Q = 2em$. The red lines represent the eigenlevels with the Josephson energy taken into account. The Josephson tunneling lifts the degeneracy between the charge states.

[3] V. Ambegaokar and A. Baratoff, Phys. Rev. Lett. **11**, 104 (1963).

[4] A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1981).

[5] A. O. Caldeira and A. J. Leggett, Annals of Physics **149**, 374 (1983).