9. Cooper - Problem:

The task of a quantum theory of superconductivity is twofold. On the one hand, a microscopic theory must be able to derive the phenomenological theories of London as well as of Ginzburg and Landau. On the other hand, it has to derive the material parameters as, for instance, the Landau coefficients α and β and their respective temperature dependencies. In particular, it has to connect the phase transition from a normal conductor to a superconductor to microscopic processes.

In section 1.2 we reported about the experimental result that superconductivity occurs for transition metals, which are not ferromagnetic, and intermetallic compounds of transition metals. Those materials are known to be bad conductors in the normal conducting state. Conversely, materials with a large conductivity have not been observed to be superconducting at temperatures above 0.1 K. To such good conductors belong precious metals ("Edelmetalle") like copper (Cu), silver (Ag), gold (Au) and alkali metals like lithium (Li), sodium (Na), potassium (K) and cesium (Cs). The preferred occurrence of superconductivity in bad conductors indicates that the mobility of electrons in the normal conducting state is not decisive for the emergence of superconductivity. Instead, those findings indicate that for superconductivity the coupling of electrons to the crystal lattice are important. Due to this coupling to the crystal lattice the electrons no longer scatter below the critical temperature of superconductivity. Or, in other words, there must be a microscopic mechanism, which immediately cancels the scattering of electrons and forces them back to their propagation direction.

In order to clarify the interaction mechanism, which leads to superconductivity, it is useful to consider the magnitude of the interaction energy $k_B T_c \simeq 10^{-3}$ eV. It is much smaller than the Coulomb interaction, which typically occurs in crystals and is of the order of eV. Fröhlich discovered that the small interaction energy $k_B T_c$

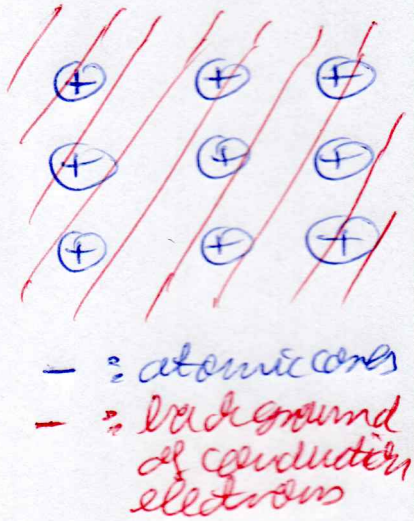
between electrons arises from an indirect coupling via phonons, which represent quantised sound waves. In 1950 Fröhlich recognised that the motion of an electron in a crystal lattice deforms slightly the periodic arrangement of positively charged ions in form of atomic cores. Such a deformation affects the motion of neighbouring electrons, yielding the aforementioned indirect coupling between two electrons. Microscopically this amounts to a virtual exchange of phonons, where one electron emits a virtual phonon, which is subsequently absorbed by a neighbouring electron. This phonon exchange leads effectively to an attractive interaction between the two electrons, which depends on their respective energies and their distance. It turns out that this attractive interaction becomes largest if both electrons have the same energy. This is, in particular, valid for electrons at the Fermi edge. This indirect coupling of electrons via phonons is most obviously proven by the isotope effect of the critical temperature, which was already briefly discussed at the end of Chapter 1.

Based on the idea of Fröhlich, later on Bardeen, Cooper, and Schrieffer worked out in 1957 their quantum theory of superconductivity. In the following chapter we provide a self-contained introduction into this so-called BCS theory. But before we come to that, we have to report about the Cooper problem from 1956. Namely, Cooper showed that an electron gas becomes unstable under the impact of a weak, attractive interaction. Consequently, the electrons go over into a new stable state, which turns out to have a lower total energy than the initial state. This is the same mechanism, which drives one a normal conductor performs a transition to a superconductor. Due to the indirect phonon coupling between the electrons an energetically lower state emerges, once the attractive interaction overcomes the thermal energy. The elementary process of this lowering of energy can be most clearly

investigated for the case of two electrons, which are coupled by an attractive interaction.

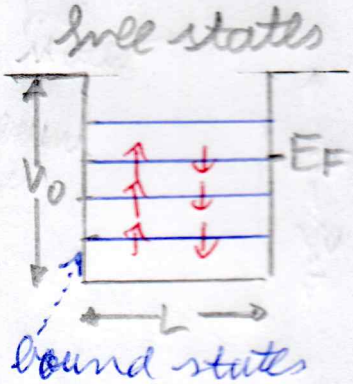
9.1 Model of Free Electron Gas:

According to the jellium ("Gelee") model a metal consists of a periodic arrangement of positively charged atomic cores which are glued together by a background of conduction electrons. The latter are assumed to be uniformly distributed over the whole metal. Within the jellium model one yields cohesion energies, which are in the eV range.



9.1.1 Model Assumptions:

For the conduction electrons one makes a mean-field assumption that they belong to a potential box of finite extension L and the constant depth V_0. Then the conduction electrons have a finite probability to stay also outside of the potential box.



Within the model of the free electron gas one performs subsequently the limiting procedure $V_0 \to \infty$. Thus, the probability to find a conduction electron at the boundary goes to zero and we obtain in the end a Dirichlet boundary condition. With this we obtain the Hamilton operator

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \Delta_i + U(\vec{x}) \qquad (9.1)$$

with the potential

$$U(\vec{x}) = \begin{cases} 0 \,; & \text{inside the metal} \\ \infty \,; & \text{outside the metal} \end{cases} \qquad (9.2)$$

9.1.2 Discussion:

On the one hand, the free electron gas model seems to be an oversimplifying model as, for instance, the attractive Coulomb interaction with the atomic cores

and the repulsive Coulomb interaction between the electrons is neglected. On the other hand, it turns out that the free electron gas represents a reasonable approximation:

1) The conduction electrons are screened from the attractive Coulomb interaction with the atomic cores due to inner, tightly bound electrons.
2) Due to the Pauli exclusion principle electrons with spin avoid each other. This reduces the repulsive Coulomb interaction among the conduction electrons.
3) Based on the Landau quasi-particle concept the Coulomb interaction effects can be approximately taken into account by using in (9.1) for the mass of the conduction electrons not the bare value but some appropriately renormalised value.

9.1.3 Dirichlet Boundary Conditions:

One has to solve the time-independent Schrödinger equation for the many-body Hamilton operator (9.1) by taking into account the Dirichlet boundary conditions. The solution of this eigenvalue problem reads

1) Eigenfunctions:

$$\psi_{n_1 n_2 n_3}(x,y,z) = \sqrt{\frac{8}{L_1 L_2 L_3}} \sin(k_1 x) \sin(k_2 y) \sin(k_3 z) \quad (9.3)$$

2) Quantization conditions:

$$k_i = \frac{\pi}{L_i} n_i \; ; \; n_i \geq 1 \; ; \; i = 1,2,3 \quad (9.4)$$

3) Eigenvalues:

$$E_{n_1 n_2 n_3} = \frac{\hbar^2}{2m} \pi^2 \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) \quad (9.5)$$

At zero temperature all the energy states (9.5) are filled by two electrons, one with spin up and one with spin down up to the Fermi energy E_F. Thus, the number of conduction electrons is given by

$$N = 2 \sum_{n_1 \geq 1} \sum_{n_2 \geq 1} \sum_{n_3 \geq 1} 1 \quad (9.6)$$

where the sums over the quantum numbers n_1, n_2, n_3 are restricted by the condition

$$E_F \geq E_{n_1 n_2 n_3} \tag{9.7}$$

with taking into account (9.5). In the thermodynamic limit $L_1, L_2, L_3 \to \infty$ the discrete sums in (9.6) go over into the integral

$$N = 2 \frac{V}{\pi^3} \frac{1}{8} \int_{0 \leq |\vec{k}| \leq k_F} d^3k \tag{9.8}$$

where the wave vector integral was originally restricted to first octant in $\vec{k}$-space due to (9.4). Furthermore, we have introduced the volume $V = L_1 L_2 L_3$ and the Fermi wave vector k_F is defined according to

$$E_F = \frac{\hbar^2 k_F^2}{2m} \tag{9.9}$$

Thus, the density of conduction electrons

$$n = \frac{N}{V} \tag{9.10}$$

turns out to be related to the Fermi wave vector

$$n = \frac{1}{4\pi^3} \frac{4\pi}{3} k_F^3 \quad \Rightarrow \quad k_F = (3\pi^2 n)^{1/3} \tag{9.11}$$

and to the Fermi energy:

$$E_F \overset{(9.9),(9.11)}{=} \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \tag{9.12}$$

9.1.4 Periodic Boundary Conditions:

A slightly different but equivalent description of the free electron gas, which is more popular in solid-state physics, is based on substituting the Dirichlet boundary conditions by periodic boundary conditions:

$$\psi(x,y,z) = \psi(x+L_1, y, z) = \psi(x, y+L_2, z) = \psi(x, y, z+L_3) \tag{9.13}$$

Then the solutions of the time-independent Schrödinger equation with the many-body Hamilton operator (9.1) are not given by (9.3)–(9.5) but by

1) Eigenfunctions: $\psi_{n_1 n_2 n_3}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$ (9.14)

2) Quantization conditions: $k_i = \frac{2\pi}{L_i} n_i ; n_i \in \mathbb{Z}$ (9.15)

3) Eigenvalues: $E_{n_1 n_2 n_3} = \frac{\hbar^2}{2m} 4\pi^2 \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right)$ (9.16)

Filling up again each energy state with spin up and spin down electrons yields

$$N = 2 \sum_{n_1} \sum_{n_2} \sum_{n_3} 1 \qquad (9.17)$$

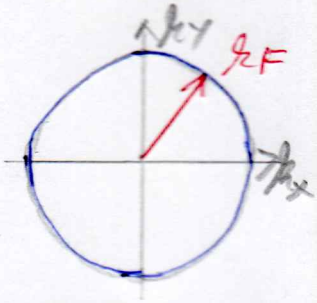
where the sums over the quantum numbers n_1, n_2, n_3 are only restricted by (9.7) with (9.15). The thermodynamic limit $L_1, L_2, L_3 \to \infty$ now amounts to convert (9.16) to the integral

$$N = 2 \frac{V}{8\pi^3} \int_{0 \le |\vec{k}| \le k_F} d^3k \qquad (9.18)$$

with k_F being again defined by (9.9). We remark that in the thermodynamik limit the expressions (9.8) and (9.18) for the Dirichlet and the periodic boundary conditions coincide. Thus, (9.10)–(9.12) are also valid for periodic boundary conditions.

9.2 Two Electrons with Attractive Interaction:

In the following we discuss the Cooper pair problem, which involves the following assumptions.



1) In an isotropic metal at zero temperature the conduction electrons occupy all the states within the Fermi sphere, according to the free electron gas model discussed in the preceding section.

2) We consider two additional electrons, which are added to this filled Fermi sphere, and we assume that between them an attractive interaction is present.

3) Furthermore, we assume that there is no interaction between the filled Fermi sphere and the two additional electrons. But we have to take into account the Pauli exclusion principle, which leads to the conditions

$$|\vec{k}_1| > k_F, \quad |\vec{k}_2| > k_F \qquad (9.19)$$

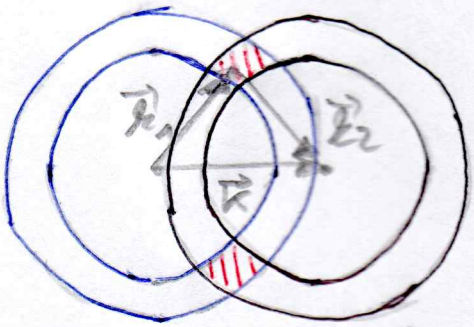
9.2.1 Cooper Pairs:

Without interaction the wave function of a pair of distinguishable electrons would read according to the free electron gas model

$$\psi_{\vec{k}_1, \vec{k}_2}(\vec{r}_1, \vec{r}_2) = \frac{e^{i\vec{k}_1\vec{r}_1}}{\sqrt{V}} \frac{e^{i\vec{k}_2\vec{r}_2}}{\sqrt{V}} \qquad (9.20)$$

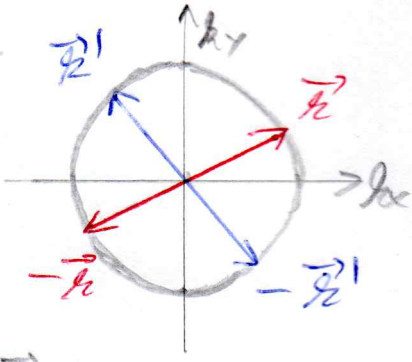
Switching on the interaction between two electrons has the effect that they are scattered into states with different wave vectors $\vec{k}'_1, \vec{k}'_2$. But due to the conservation of momentum the total momentum remains unchanged despite of the scattering:

$$\vec{K} = \vec{k}_1 + \vec{k}_2 = \vec{k}'_1 + \vec{k}'_2 \qquad (9.21)$$



Later on we show that an attractive interaction between the electrons can only occur in $\vec{k}$-space within a thin shell around the Fermisphere whose thickness is given by the Debye energy $\hbar\omega_D$, which is about a factor 100 smaller than the Fermi energy. The magnitude of the interaction is then characterized by the number of transitions, which are possible und the restriction (9.21) and are colored in red in the adjacent figure. The sketch shows that the number of transitions has a quite sharp maximum for the case $\vec{K} = \vec{0}$, i.e. when both Fermi spheres overlap. In contrast to that all other states $\vec{K} \neq \vec{0}$ are negligible. Therefore, we restrict ourselves from now on to electron pairs with antiparallel wave vectors:

$$\vec{k}_1 = +\vec{k}, \quad \vec{k}_2 = -\vec{k} \qquad (9.22)$$



Thus, inserting (9.22) in (9.20) we conclude that the center of mass of such Cooper pairs does not move as the wave function only depends on the relative coordinate vector:

$$\psi_{\vec{k}}(\vec{r}_1, \vec{r}_2) = \psi_{\vec{k}}(\vec{r}_1 - \vec{r}_2) = \frac{1}{V} e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} \qquad (9.23)$$

But we have to take into account, in principle, according to the restriction (9.19), all wave vectors $\vec{k}$, whose absolute value is larger than the Fermi wave vector k_F. Thus, we have to consider the physical wave function as a superposition of the states (9.23) with yet unknown superposition coef-

ficients $c(\vec{k})$. Thus, as the free electron gas model allows for discrete wave vectors $\vec{k}$, either (9.4) for Dirichlet or (9.15) for periodic boundary conditions, we get

$$\psi(\vec{r}_1,\vec{r}_2)=\psi(\vec{r}_1-\vec{r}_2)=\frac{1}{V}\sum_{|\vec{k}|>k_F} c(\vec{k})\, e^{i\vec{k}(\vec{r}_1-\vec{r}_2)} \qquad (9.24)$$

Note that the superposition coefficients $c(\vec{k})$ represent the Fourier coefficients of the Fourier decomposition (9.25). Indeed, the Fourier transformed of the wave function (9.25)

$$\psi(\vec{k})=\int d^3r\, \psi(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}} \qquad (9.25)$$

yields

$$\psi(\vec{k})=\Theta(|\vec{k}|-k_F)\, c(\vec{k}) \qquad (9.26)$$

9.2.2 Schrödinger Equation in Spatial Representation:

In spatial representation the time-independent Schrödinger representation for the pair of distinguishable electrons reads as follows:

$$\left\{-\frac{\hbar^2}{2m}(\Delta_1+\Delta_2)+V(\vec{r}_1,\vec{r}_2)\right\}\psi(\vec{r}_1,\vec{r}_2)=E\,\psi(\vec{r}_1,\vec{r}_2) \qquad (9.27)$$

Here the potential energy $V(\vec{r}_1,\vec{r}_2)$ can only depend on the relative coordinate vector $\vec{r}_1-\vec{r}_2$ due to the Newton "actio = -reactio" axiom:

$$V(\vec{r}_1,\vec{r}_2)=V(\vec{r}_1-\vec{r}_2) \qquad (9.28)$$

9.2.3 Convolution Theorem:

The convolution theorem states that a multiplication in real space corresponds to a convolution in Fourier space. In order to prove this, we consider the term

$$V(\vec{r}_1,\vec{r}_2)\,\psi(\vec{r}_1,\vec{r}_2) \overset{(9.24),(9.28)}{=} V(\vec{r}_1-\vec{r}_2)\,\psi(\vec{r}_1-\vec{r}_2) \qquad (9.29)$$

As (9.29) only depends on the relative coordinate vector $\vec{r}_1-\vec{r}_2$, we consider in analogy to (9.25) its Fourier transform

$$(V\psi)(\vec{r})=\int d^3r\, V(\vec{r})\,\psi(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}} \qquad (9.30)$$

Inserting (9.24) in (9.30) yields

$$(V\psi)(\vec{r})=\int d^3r\, V(\vec{r})\,\frac{1}{V}\sum_{|\vec{k}'|>k_F} c(\vec{k}')\, e^{i\vec{k}'\vec{r}}\, e^{-i\vec{k}\vec{r}} \qquad (9.31)$$

Interchanging integration and summation we obtain

$$(V\psi)(\vec{r})=\frac{1}{V}\sum_{|\vec{k}'|>k_F} c(\vec{k}')\left\{\int d^3r\, V(\vec{r})\, e^{-i(\vec{k}-\vec{k}')\vec{r}}\right\} \qquad (9.32)$$

In the brackets we recognise the Fourier transformed of the potential in analogy to (9.25)

$$V(\vec{k}) = \int d^3r\, V(\vec{r})\, e^{-i\vec{k}\vec{r}} \tag{9.33}$$

Therefore, (9.32) reduces to

$$(V\Psi)(\vec{k}) = \frac{1}{V} \sum_{|\vec{k}'|>k_F} V(\vec{k}-\vec{k}')\, c(\vec{k}') \tag{9.34}$$

Note that the matrix element $V(\vec{k},\vec{k}') = V(\vec{k}-\vec{k}')$ describes the scattering of an electron pair with wave vectors $\vec{k}'$ and $-\vec{k}'$ to another electron pair of wave vectors $\vec{k}$ and $-\vec{k}$.

9.2.4 Schrödinger Equation in Fourier Space:

The Schrödinger equation in real space (9.27) is converted into Fourier space by the following manipulations:

1) Inserting (9.24) into (9.27)
2) Multiplying (9.27) with $e^{-i\vec{k}(\vec{r}_1-\vec{r}_2)}$ and integrating over space

Both manipulations yield at first

$$\int d^3r_1 \int d^3r_2\, e^{-i\vec{k}(\vec{r}_1-\vec{r}_2)} \frac{-\hbar^2}{2m}(\Delta_1+\Delta_2) \frac{1}{V} \sum_{|\vec{k}'|>k_F} c(\vec{k}')\, e^{i\vec{k}'(\vec{r}_1-\vec{r}_2)}$$
$$+ \int d^3r_1 \int d^3r_2\, e^{-i\vec{k}(\vec{r}_1-\vec{r}_2)} \left[V(\vec{r}_1-\vec{r}_2) - E \right] \Psi(\vec{r}_1-\vec{r}_2) = 0 \tag{9.35}$$

In the first line we use $\Delta_{1,2} \to -\vec{k}'^2$ and in both lines we perform the substitution $\vec{r}'(\vec{r}_1) = \vec{r}_1 - \vec{r}_2$, yielding

$$\frac{1}{V} \sum_{|\vec{k}'|>k_F} c(\vec{k}') \frac{\hbar^2 \vec{k}'^2}{m} \int d^3r\, e^{i(\vec{k}'-\vec{k})\vec{r}}$$
$$+ \int d^3r\, V(\vec{r})\Psi(\vec{r})\, e^{-i\vec{k}\vec{r}} - E \int d^3r\, \Psi(\vec{r})\, e^{-i\vec{k}\vec{r}} = 0 \tag{9.36}$$

Taking into account (9.25), (9.26), (9.30), and (9.34) we obtain

$$\sum_{|\vec{k}'|>k_F} \frac{\hbar^2 \vec{k}'^2}{m} c(\vec{k}')\, \delta_{\vec{k},\vec{k}'} + \frac{1}{V} \sum_{|\vec{k}'|>k_F} V(\vec{k}-\vec{k}')\, c(\vec{k}')$$
$$= E\, \Theta(|\vec{k}| - k_F)\, c(\vec{k}) \tag{9.37}$$

Provided that we choose a wave vector $\vec{k}$ with the property $|\vec{k}| > k_F$, (9.37) reduces to

$$\underbrace{\frac{\hbar^2 \vec{k}^2}{m} c(\vec{k})}_{\text{kinetic energy}} + \underbrace{\frac{1}{V} \sum_{|\vec{k}'|>k_F} V(\vec{k}-\vec{k}')\, c(\vec{k}')}_{\text{potential energy}} = \underbrace{E\, c(\vec{k})}_{\text{total energy}} \tag{9.38}$$

9.2.5 Cooper Approximation:

The Schrödinger equation in Fourier representation (9.38) is not exactly solvable for a general interaction potential. In order to achieve at least an approximative solution, Cooper introduced the following assumptions:

1) The matrix element $V(\vec{k}-\vec{k}')$ is assumed to be homogeneous, isotropic and attractive according to

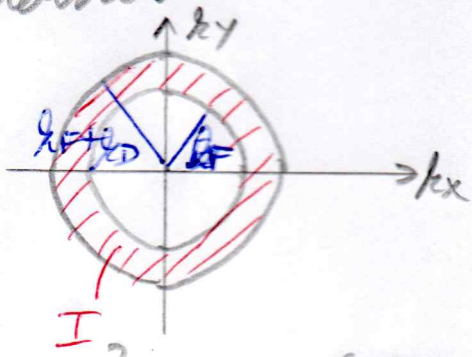
$$V(\vec{k}-\vec{k}') = -g \tag{9.39}$$

with $g>0$. If (9.39) was valid for all $\vec{k}, \vec{k}'$, the corresponding spatial representation of the interaction potential would read

$$V(\vec{r}_1-\vec{r}_2) = -g\,\delta(\vec{r}_1-\vec{r}_2) \tag{9.40}$$

This means that electrons only interact with each other if they are at the same space point.

2) Furthermore, it is assumed that (9.39) only occurs for wave vectors $\vec{k}, \vec{k}'$, which lie in a shell around the Fermi energy E_F with the width of the Debye energy $\hbar\omega_D$:



$$I = \left\{ \vec{k} : \frac{\hbar^2 k_F^2}{2m} \le \frac{\hbar^2 k^2}{2m} \le \frac{\hbar^2 k_F^2}{2m} + \hbar\omega_D \right\} \tag{9.41}$$

Thus, both assumptions can be summarized as

$$V(\vec{k}-\vec{k}') = \begin{cases} -g\,; & \vec{k} \in I \text{ and } \vec{k}' \in I \\ 0\,; & \text{otherwise} \end{cases} \tag{9.42}$$

9.2.6 Eigenvalue Problem:

Inserting the Cooper assumption (9.42) into (9.38), the case $\vec{k} \notin I$ yields

$$\left(\frac{\hbar \vec{k}^2}{m} - E\right) c(\vec{k}) = 0 \quad \Rightarrow \quad c(\vec{k}) = 0\,; \quad \vec{k} \notin I \tag{9.43}$$

However, in the case $\vec{k} \in I$ we get

$$\frac{\hbar^2 \vec{k}^2}{m} c(\vec{k}) - \frac{g}{V} \sum_{\vec{k}' \in I} c(\vec{k}') = E\, c(\vec{k})\,; \quad \vec{k} \in I \tag{9.44}$$

Thus, solving for the Fourier coefficients $c(\vec{k})$ we obtain

$$c(\vec{k}) = \frac{g}{\frac{\hbar^2 k^2}{m} - E} \frac{1}{V} \sum_{\vec{k}' \in I} c(\vec{k}')\,; \quad \vec{k} \in I \tag{9.45}$$

Summing (9.45) over all allowed wave vectors $\vec{k} \in I$

leads to an eigenvalue equation for the total energy E

$$\sum_{\vec{k}\in\vec{k}} c(\vec{k}) = g\,\frac{1}{V}\sum_{\vec{k}\in I}\frac{1}{\frac{\hbar^2\vec{k}^2}{m}-E}\sum_{\vec{k}'\in I} c(\vec{k}') \qquad (9.46)$$

Provided that the constant

$$c = \frac{1}{V}\sum_{\vec{k}\in I} c(\vec{k}) \overset{(9.24),\,(9.43)}{=} \psi(\vec{0}) \qquad (9.47)$$

is non-vanishing, the implicit for the energy eigenvalue E reads

$$\frac{1}{g} = \frac{1}{V}\sum_{\vec{k}\in I}\frac{1}{\frac{\hbar^2\vec{k}^2}{m}-E} \qquad (9.48)$$

9.2.7 Thermodynamic Limit:

In the thermodynamic limit that the spatial extensions L_1, L_2, L_3 of the potential box diverge, the distances between the wave vectors (9.15) become infinitesimally small. This justifies to approximately evaluate sums over wave vectors like in (9.48) by corresponding integrals:

$$\sum_{\vec{k}} f(\vec{k}) \approx \int d^3k\, z(\vec{k})\, f(\vec{k}) \qquad (9.49)$$

Here the homogeneous, isotropic density of states of the wave vectors for periodic boundary conditions (9.15) is given by

$$z(\vec{k}) = \frac{V}{(2\pi)^3} \qquad (9.50)$$

From (9.48) – (9.50) we conclude

$$\frac{1}{g} = \int_I \frac{d^3k}{(2\pi)^3}\,\frac{1}{\frac{\hbar^2\vec{k}^2}{m}-E} \qquad (9.51)$$

As the integrand only depends on the absolute value of the wave vector, (9.51) reduces to

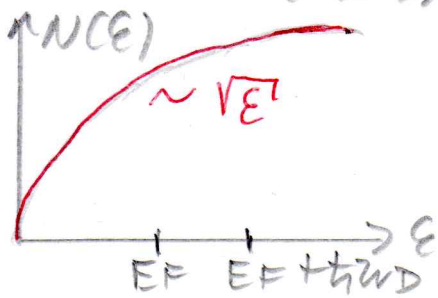
$$\frac{1}{g} = \frac{1}{2\pi^2}\int_I dk\,\frac{k^2}{\frac{\hbar^2k^2}{m}-E} \qquad (9.52)$$

Introducing as a new integration variable $\varepsilon(k) = \frac{\hbar^2k^2}{2m}$ we get

$$\frac{1}{g} = \int_{E_F\le\varepsilon\le E_F+\hbar\omega_D} d\varepsilon\,\frac{N(\varepsilon)}{2\varepsilon-E} \qquad (9.53)$$

with the density of states

$$N(\varepsilon) = \frac{2}{\sqrt{\pi}}\left(\frac{m}{2\pi\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon} \qquad (9.54)$$



A corresponding shift of the energy variables

$$\varepsilon' = \varepsilon - E_F, \quad E' = E - 2E_F \tag{9.55}$$

simplifies (9.53) according to

$$\frac{1}{g} = \int_0^{\hbar\omega_D} d\varepsilon' \, \frac{N(E_F+\varepsilon')}{2\varepsilon' - E'} \tag{9.56}$$

Without any interaction g we would expect that the two additional electrons at the Fermi edge have the energy $2E_F$. Therefore, $E' = E - 2E_F$ directly represents the energy reduction, which occurs due to presence of the attractive interaction $-g$.

Furthermore, we can take advantage of the respective scales of the involved energies. As the Fermi energy E_F is about 100 times larger than the Debye energy $\hbar\omega_D$, the density of states (9.54) is changing only tinily within the integration boundary in (9.56). Therefore, we can approximate (9.56) according to

$$\frac{1}{gN(E_F)} \approx \int_0^{\hbar\omega_D} d\varepsilon' \, \frac{1}{2\varepsilon' - E'} \tag{9.57}$$

The remaining integral is now elementary and can be straight-forwardly evaluated:

$$\frac{1}{gN(E_F)} = \left[\frac{1}{2}\ln(2\varepsilon' - E')\right]_0^{\hbar\omega_D} = \frac{1}{2}\ln\frac{E' - 2\hbar\omega_D}{E'}$$

$$e^{\frac{2}{gN(E_F)}} = \frac{E' - 2\hbar\omega_D}{E'} \Rightarrow E' = -\frac{2\hbar\omega_D}{e^{\frac{2}{gN(E_F)}} - 1} \tag{9.58}$$

Thus, we conclude that the binding energy $E' = E - 2E_F$ is, indeed, negative.

9.2.8 Discussion:

The binding energy (9.58) depends on three parameters. At first, the Debye energy $\hbar\omega_D$ sets the energy scale. Furthermore, both the density of states at the Fermi edge $N(E_F)$ and the interaction strength g reduce via the exponential function the Debye energy $\hbar\omega_D$ to the binding energy E'. Furthermore, we can read off from (9.58) two interesting special cases:

1) In case of a strong coupling $N(E_F)\,g \gg 1$ we get

the usual perturbative result

$$E' = -\hbar\omega_D N(E_F)\, g \qquad (9.59)$$

that the binding energy E' is proportional to the interaction strength $(-g)$.

2) For a weak coupling $N(E_F)g \ll 1$ we obtain instead

$$E' = -2\hbar\omega_D \cdot e^{-2/N(E_F)g} \qquad (9.60)$$

which represents a non-perturbative result as the function $f(x) = e^{-1/x}$ has a vanishing Taylor series. Note that the binding energy (9.60) is of the order of both the energy associated to the critical temperature of superconductivity $k_B T_c$ and the gap parameter Δ according to the BCS theory, see (1.4) and (4.146).

Let us discuss exemplarily the case of lead (Pb). There we have $N(E_F)g = 0.39 < 1$. Thus, for such a conventional superconductor we are in the weak-coupling regime. Furthermore, we have for lead a Debye temperature of $T_D = 96\,K$, which amounts to a Debye energy $\hbar\omega_D$ of $8\,meV$. The corresponding Fermi energy E_F is given by $9\,eV$. Thus, the energy shell around the Fermi edge, which is affected by the attractive interaction, is, indeed, quite small. With this we obtain from (9.60) the binding energy E' to be $-0.095\,meV$. Thus, we conclude that we have to deal here with a hierarchy of three energies, which amount for lead to be: $|E'| = 0.095\,meV \ll \hbar\omega_D = 8\,meV \ll E_F = 9\,eV$.

9.2.9 Summary:

1) Two electrons with an attractive interaction yield with the above assumptions a bound state, as the binding energy E' turns out to be negative.
2) This bound state exists for any arbitrarily small attractive interaction.
3) The binding energy E' depends non-perturbatively on the interaction strength g, thus for small g we can not obtain a Taylor series.

Thus, the conclusion of the Cooper problem is that the Fermi sphere becomes unstable for any attractive interaction between two electrons.

9.2.10 Spin Singlet/Triplet State:

Previously we have mentioned for the Fermi sphere that we have to take into account the Pauli exclusion principle by occupying each wave vector twice, once with a spin up and once with a spin down electron. Correspondingly, we have now also to include the spin degree of freedom for the two additional electrons outside the Fermi sphere.

To this end we decompose (9.24) into a symmetric and an antisymmetric spatial contribution. Adding a corresponding function, we can obtain a total wave function, which is antisymmetric. Henceforth we introduce the spin functions

$$\alpha_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \beta_i = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad ; \quad i = 1, 2 \tag{9.61}$$

corresponding to spin up ("↑") and spin down ("↓"), respectively. With this the singlet state reads

$$\psi_S(\vec{r}_1, \vec{r}_2) = \frac{1}{V} \sum_{\vec{k} \in I} C(\vec{k}) \cos[\vec{k}(\vec{r}_1 - \vec{r}_2)] \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 - \alpha_2 \beta_1) \tag{9.62}$$

which is symmetric in space but antisymmetric in spin. Indeed, we obtain for the spin operator

$$\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z} \tag{9.63}$$

the eigenvalue equation

$$\hat{S}_z \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 - \alpha_2 \beta_1) = 0 \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 - \alpha_2 \beta_1) \tag{9.64}$$

so the state (9.62) has, indeed, the multiplicity one. Correspondingly, the triplet state is given by

$$\psi_T(\vec{r}_1, \vec{r}_2) = \frac{1}{V} \sum_{\vec{k} \in I} \sin[\vec{k}(\vec{r}_1 - \vec{r}_2)] \begin{pmatrix} \alpha_1 \alpha_2 \\ \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 + \alpha_2 \beta_1) \\ \beta_1 \beta_2 \end{pmatrix} \tag{9.64}$$

which is antisymmetric in space and symmetric in spin. The eigenvalue equations for the spin operator

$$\hat{S}_z \begin{pmatrix} \alpha_1 \alpha_2 \\ \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 + \alpha_2 \beta_1) \\ \beta_1 \beta_2 \end{pmatrix} = \begin{pmatrix} \alpha_1 \alpha_2 \\ 0 \cdot \frac{1}{\sqrt{2}} (\alpha_1 \beta_2 + \alpha_2 \beta_1) \\ \beta_1 \beta_2 \end{pmatrix} \tag{9.65}$$

indicate the multiplicity three. Note that singlet and triplet state (9.62) and (9.65) differ in their behaviour with respect to an exchange of coordinates $\vec{r}_1$ and $\vec{r}_2$:

$$\psi_S(\vec{r}_1,\vec{r}_2) = \psi_S(\vec{r}_2,\vec{r}_1) \Rightarrow \lim_{\vec{r}_1\to\vec{r}_2} \psi_S(\vec{r}_1,\vec{r}_2) \neq 0 \quad (9.67)$$

$$\psi_T(\vec{r}_1,\vec{r}_2) = -\psi_T(\vec{r}_2,\vec{r}_1) \Rightarrow \lim_{\vec{r}_1\to\vec{r}_2} \psi_T(\vec{r}_1,\vec{r}_2) = 0 \quad (9.68)$$

Now we have to take into account that the attractive interaction (9.39) amounts via (9.40) that both electrons have to be at the same space point. Therefore, we conclude from (9.67) and (9.68) that a singlet state is more preferable for producing a Cooper pair than a triplet state. This has the consequence that a Cooper pair consists of two electrons with opposite wave vector and opposite spin.

9.2.11 Remark:

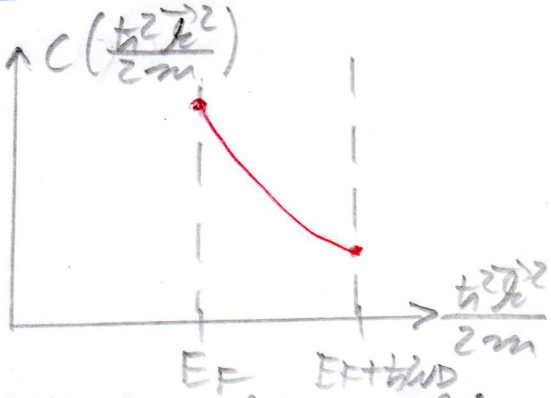
Note that these findings only hold for conventional superconductors, where a homogeneous and isotropic interaction (9.39) is a valid approximation. However this no longer holds for high T_c superconductors as there the above assumptions have to be revised step by step:

1) The isotropy of the matrix elements $V(\vec{k},\vec{k}')$ no longer holds as anisotropies are quite relevant for high T_c superconductors.
2) For high T_c superconductors the density of states can not be considered to be constant within the interaction shell around the Fermi edge.

9.2.12 Cooper Pair Wave Function:

Now we discuss properties of the Cooper pair wave function, which follows from (9.45) and (9.47)

$$C(\vec{k}) = \frac{g}{\frac{\hbar^2\vec{k}^2}{m} - E}\, C, \quad \vec{k}\in I \quad (9.69)$$



Here the energy E is determined via (9.55) by the binding energy (9.58). Furthermore, the coefficient C is

fixed by the normalisation condition, which reads in spatial representation

$$1 = \int d^3r_1 \int d^3r_2 \, |\psi(\vec{r}_1, \vec{r}_2)|^2 \qquad (9.70)$$

Indeed, inserting (9.24) in (9.70) yields a first

$$1 = V \int d^3r \, \frac{1}{V} \sum_{\vec{k} \in I} c^*(\vec{k}) e^{-i\vec{k}\vec{r}} \, \frac{1}{V} \sum_{\vec{k}' \in I} c(\vec{k}') e^{i\vec{k}'\vec{r}} \qquad (9.71)$$

$$= \frac{1}{V} \sum_{\vec{k} \in I} \sum_{\vec{k}' \in I} c^*(\vec{k}) c(\vec{k}') \int d^3r \, e^{i(\vec{k}'-\vec{k})\vec{r}} = \sum_{\vec{k} \in I} |c(\vec{k})|^2$$

Thus, inserting (9.69) in the normalisation condition in Fourier space (9.71), we get

$$1 = c^2 \sum_{\vec{k} \in I} \frac{g^2}{\left(\frac{\hbar^2 \vec{k}^2}{m} - E\right)^2} \Rightarrow c = \frac{1}{g} \cdot \sqrt{\frac{1}{\sum_{\vec{k} \in I} \frac{1}{\left(\frac{\hbar^2 \vec{k}^2}{m} - E\right)^2}}} \qquad (9.72)$$

As the Cooper pair wave function is determined by (9.69) and (9.72), we can now embark on calculating any observable from it.

9.2.13 Cooper Pair Width:

The square of the Cooper pair width follows from

$$\langle (\vec{r}_1 - \vec{r}_2)^2 \rangle = \int d^3r_1 \int d^3r_2 \, (\vec{r}_1 - \vec{r}_2)^2 |\psi(\vec{r}_1, \vec{r}_2)|^2 \qquad (9.73)$$

Converting (9.73) from the spatial into the Fourier representation yields similar to (9.71)

$$\langle (\vec{r}_1 - \vec{r}_2)^2 \rangle = \frac{1}{V} \sum_{\vec{k} \in I} \sum_{\vec{k}' \in I} \int d^3r \, \vec{r} e^{-i\vec{k}\vec{r}} \cdot \vec{r} e^{i\vec{k}'\vec{r}} c^*(\vec{k}) c(\vec{k}') \qquad (9.74)$$

Here we can perform the substitutions $\vec{r} \to i \vec{\nabla}_k$ and $\vec{r} \to -i \vec{\nabla}_{k'}$, respectively, so (9.74) reduces to

$$\langle (\vec{r}_1 - \vec{r}_2)^2 \rangle = \sum_{\vec{k} \in I} |\vec{\nabla}_{\vec{k}} c(\vec{k})|^2 \qquad (9.75)$$

Inserting (9.69) and (9.72) into (9.75) we obtain

$$\langle (\vec{r}_1 - \vec{r}_2)^2 \rangle = \frac{\frac{1}{V} \sum_{\vec{k} \in I} \left| \vec{\nabla}_{\vec{k}} \frac{1}{\frac{\hbar^2 \vec{k}^2}{m} - E} \right|^2}{\frac{1}{V} \sum_{\vec{k} \in I} \frac{1}{\left(\frac{\hbar^2 \vec{k}^2}{m} - E\right)^2}} \qquad (9.76)$$

At this stage of the calculation we, finally, perform the thermodynamic limit (9.49), (9.50) and get for the square of Cooper pair width Fourier integrals:

$$\langle(\vec{v}_1-\vec{v}_2)^2\rangle = \frac{\int_I \frac{d^3k}{(2\pi)^3} \left|\vec{\nabla}_{\vec{k}} \frac{1}{\frac{\hbar^2\vec{k}^2}{m}-E}\right|^2}{\int_I \frac{d^3k}{(2\pi)^3} \frac{1}{\left(\frac{\hbar^2\vec{k}^2}{m}-E\right)^2}} \tag{9.77}$$

Introducing the substitution $\varepsilon(\vec{k}) = \hbar^2\vec{k}^2/2m$ and taking into account the chain rule

$$\vec{\nabla}_{\vec{k}}\, f(\varepsilon(\vec{k})) = \vec{\nabla}_{\vec{k}}\varepsilon(\vec{k})\frac{\partial f(\varepsilon(\vec{k}))}{\partial\varepsilon(\vec{k})} = \frac{\hbar^2\vec{k}}{m}\frac{\partial f(\varepsilon(\vec{k}))}{\partial\varepsilon(\vec{k})} \tag{9.78}$$

converts the wave vector integrals in (9.77) to corresponding energy integrals

$$\langle(\vec{v}_1-\vec{v}_2)^2\rangle = \frac{8\hbar^2}{m}\frac{\int_{E_F\le\varepsilon\le E_F+\hbar\omega_D} d\varepsilon\; N(\varepsilon)\frac{\varepsilon}{(2\varepsilon-E)^4}}{\int_{E_F\le\varepsilon\le E_F+\hbar\omega_D} d\varepsilon\; N(\varepsilon)\frac{1}{(2\varepsilon-E)^2}} \tag{9.79}$$

The shift of the energy variables (9.55) reduces (9.79) to

$$\langle(\vec{v}_1-\vec{v}_2)^2\rangle = \frac{8\hbar^2}{m}\frac{\int_0^{\hbar\omega_D} d\varepsilon'\; \frac{N(E_F+\varepsilon')(E_F+\varepsilon')}{(2\varepsilon'-E')^4}}{\int_0^{\hbar\omega_D} d\varepsilon'\; \frac{N(E_F+\varepsilon')}{(2\varepsilon'-E')^2}} \tag{9.80}$$

As the integration range of the Debye energy $\hbar\omega_D$ is quite small in comparison with the Fermi energy E_F, we can approximate (9.80) according to

$$\langle(\vec{v}_1-\vec{v}_2)^2\rangle = \frac{8\hbar^2 E_F}{m}\frac{\int_0^{\hbar\omega_D} d\varepsilon'\; \frac{1}{(2\varepsilon'-E')^4}}{\int_0^{\hbar\omega_D} d\varepsilon'\; \frac{1}{(2\varepsilon'-E')^2}} \tag{9.81}$$

The remaining integrals are elementary and can directly be evaluated:

$$\langle(\vec{v}_1-\vec{v}_2)^2\rangle = \frac{4\hbar^4 k_F^2}{m^2}\frac{\left[-\frac{1}{6}\frac{1}{(2\varepsilon'-E')^3}\right]_0^{\hbar\omega_D}}{\left[-\frac{1}{2}\frac{1}{2\varepsilon'-E'}\right]_0^{\hbar\omega_D}}$$

$$= \frac{4\hbar^4 k_F^2}{3m^2}\frac{\frac{1}{(2\hbar\omega_D-E')^3}-\frac{1}{(-E')^3}}{\frac{1}{2\hbar\omega_D-E'}-\frac{1}{-E'}} \tag{9.82}$$

Inserting the weak-coupling approximation for the binding energy E' from (9.60) in (9.82) we obtain the following result:

$$\langle(\vec{v}_1-\vec{v}_2)^2\rangle = \frac{4\hbar^4 k_F^2}{3m^2(2\hbar\omega_D)^2}\cdot\frac{\dfrac{1+3e^{-\frac{2}{N(E_F)g}}+3e^{-\frac{4}{N(E_F)g}}}{e^{-\frac{6}{N(E_F)g}}\left(1+e^{-\frac{2}{N(E_F)g}}\right)^3}}{\dfrac{1}{e^{-\frac{2}{N(E_F)g}}\left(1+e^{-\frac{2}{N(E_F)g}}\right)}} \tag{9.83}$$

In the limit of weak-coupling this reduces to

$$\langle(\vec{v}_1-\vec{v}_2)^2\rangle = \frac{4\hbar^4 k_F^2}{3m^2E'^2} \tag{9.84}$$

where we have, again, used the weak-coupling binding energy E' from (9.60). From (1.4) and (9.60) we conclude that the binding energy E' can be expressed in terms of the critical temperature of superconductivity T_c:

$$|E'| = \frac{2}{1.18}\, k_B T_c \tag{9.85}$$

Furthermore, we introduce the Fermi velocity

$$v_F = \frac{p_F}{m} = \frac{\hbar}{m} k_F \tag{9.86}$$

Thus, finally, the Cooper pair width follows as

$$\sqrt{\langle(\vec{v}_1-\vec{v}_2)^2\rangle} = \frac{1.18}{\sqrt{3}}\,\frac{\hbar v_F}{k_B T_c} \approx 0.68\,\frac{\hbar v_F}{k_B T_c} \tag{9.87}$$

Comparing this result (9.87) with the coherence length ξ, which we have already estimated in (14.147), we read off

$$\sqrt{\langle(\vec{v}_1-\vec{v}_2)^2\rangle} \approx 3.78\,\xi \tag{9.88}$$

Thus, the Cooper pair width corresponds to the coherence length ξ, which represents one of the two fundamental length scales governing the Ginzburg-Landau theory.