the interior of the superconductor against external fields, also decay exponentially with distance into the solid. For an order of magnitude estimate of the London penetration depth, we set \( m \) equal to the electron mass and take \( n_s \) to be the atomic density, i.e., we assume that each atom provides a superconducting electron. For Sn, for example, one obtains \( \lambda_L = 260 \text{ Å} \). An important element of the microscopic theory of superconductivity is that it is not electrons but electron pairs, so-called Cooper pairs, which are the current carriers. This can be included in the London equations if, instead of \( n_s \), one uses half of the electron density \( n_e/2 \). Because the London equations describe the Meissner-Ochsenfeld effect particularly well, a microscopic theory of superconductivity should be able to provide, among other things, an equation of the type (10.10b). This, and an explanation of the vanishing resistance at sufficiently low temperature \( T < T_c \), is the central concern of the BCS theory mentioned above. Because superconductivity is evidently a widespread phenomenon, the theory must also be sufficiently general; it should not hinge on one special metallic property. In the following sections the basic aspects of the microscopic theory of superconductivity will be treated in a somewhat simplified form.

### 10.3 Instability of the “Fermi Sea” and Cooper Pairs

From the previously mentioned fundamental experiments on the phenomenon of superconductivity, it is clear that we are dealing with a new phase of the electron gas in a metal which displays the unusual property of “infinitely high” conductivity. An important contribution to our understanding of this new phase was made by Cooper [10.6] who, in 1956, recognised, that the ground state \( (T=0\text{ K}) \) of an electron gas (Sect. 6.2) is unstable if one adds a weak attractive interaction between each pair of electrons. Such an interaction had already been discussed by Fröhlich [10.7] in the form of the phonon-mediated interaction. As it passes through the solid, an electron, on account of its negative charge, leaves behind a deformation trail affecting the positions of the ion cores. This trail is associated with an increased density of positive charge due to the ion cores, and thus has an attractive effect on a second electron. The lattice deformation therefore causes a weak attraction between pairs of electrons (Fig. 10.7a). This attractive electron-electron interaction is retarded because of the slow motion of the ions in comparison with the almost instantaneous Coulomb repulsion between electrons; at the instant when an electron passes, the ions receive a pull which, only after the electron has passed, leads to a displacement and thereby to a polarization of the lattice (Fig. 10.7b). The lattice deformation reaches its maximum at a distance from the first electron which can be estimated from the electron velocity (Fermi velocity \( v_F \sim 10^8 \text{ cm/s} \)) and the maximum phonon vibration period (\( 2\pi/\omega_p \sim 10^{-13} \text{ s} \)). The two electrons correlated by the lattice deformation thus have an approximate separation of about 1000 Å. This then corresponds to the “size” of a Cooper pair (which is also estimated in Sect. 10.7 using a different method). The extremely long interaction range of the two electrons correlated by a lattice deformation explains why the Coulomb repulsion is insignificant; it is completely screened out over distances of just a few Ångstroms.

Quantum mechanically, the lattice deformation can be understood as the superposition of phonons which the electron, due to its interaction with the lattice, continuously emits and absorbs. To comply with energy conservation, the phonons constituting the
lattice deformation may only exist for a time \( t = 2\pi/\omega \) determined by the uncertainty relation; thereafter, they must be absorbed. One thus speaks of “virtual” phonons.

The ground state of a non-interacting Fermi gas of electrons in a potential well (Chap. 6) corresponds to the situation where all electron states with wave vector \( \mathbf{k} \) within the Fermi sphere \( [E^0_F(T = 0K) = h^2k_F^2/2m] \) are filled and all states with \( E > E^0_F \) are unoccupied. We now perform a Gedankenexperiment and add to this system two electrons \([k_1, E(k_1)] \) and \([k_2, E(k_2)]\) in states just above \( E^0_F \). A weak attractive interaction between these two electrons is switched on in the form of phonon exchange. All other electrons in the Fermi sea are assumed to be non-interacting, and, on account of the Pauli exclusion principle, they exclude a further occupation of states with \( |k| < k_F \). Due to phonon exchange the two additional electrons continually change their wave vector, whereby, however, momentum must be conserved:

\[
k_1 + k_2 = k_1^* + k_2^* = K.
\]

Since the interaction in \( k \)-space is restricted to a shell with an energy thickness of \( h\omega_D \) (with \( \omega_D = \text{Debye frequency} \)) above \( E^0_F \), the possible \( k \)-states are given by the shaded area in Fig. 10.8. This area and therefore the number of energy-reducing phonon exchange processes — i.e., the strength of the attractive interaction — is maximum for \( K = 0 \). It is therefore sufficient in what follows to consider the case \( k_1 = -k_2 = k \), i.e., electron pairs with equal and opposite wave vectors. The associated two particle wave function \( \psi(r_1, r_2) \) must obey the Schrödinger equation

\[
-\frac{\hbar^2}{2m} \left( \Delta_1 + \Delta_2 \right) \psi(r_1, r_2) + V(r_1, r_2) \psi(r_1, r_2) = E \psi(r_1, r_2) = (\varepsilon + 2E^0_F) \psi(r_1, r_2).
\]

\( \varepsilon \) is the energy of the electron pair relative to the interaction-free state \((V = 0)\), in which
10.3 Instability of the “Fermi Sea” and Cooper Pairs

Each of the two electrons at the Fermi level would possess an energy $E_F^0 = \hbar^2 k_F^2/2m$. The two-particle function in this case consists of two plane waves

$$\left( \frac{1}{\sqrt{L^3}} e^{i k_1 \cdot r_1} \right) \left( \frac{1}{\sqrt{L^3}} e^{i k_2 \cdot r_2} \right) = \frac{1}{L^3} e^{i k \cdot (r_1 - r_2)} .$$

We note that (10.19) implies that the two electrons have opposite spin (compare Sect. 8.3). The most general representation of a two-particle state for the case of a non-vanishing interaction ($V \neq 0$) is given by the series

$$\psi(r_1 - r_2) = \frac{1}{L^3} \sum_k g(k) e^{i k \cdot (r_1 - r_2)} ,$$

which depends only on the relative coordinate $r = r_1 - r_2$. The summation is confined to pairs with $k = k_1 = -k_2$, which, because the interaction is restricted to the region $\hbar \omega_D$ (Fig. 10.9), must obey the condition

$$E_F^0 < \frac{\hbar^2 k^2}{2m} < E_F^0 + \hbar \omega_D .$$

The quantity $|g(k)|^2$ is the probability of finding one electron in state $k$ and the other in $-k$, that is, the electron pair in $(k, -k)$. Due to the Pauli principle and the condition (10.21a) we have

$$g(k) = 0 \quad \text{for} \quad \left\{ \begin{array}{ll} k < k_F \\ k > \sqrt{2m(E_F^0 + \hbar \omega_D)/\hbar^2} . \end{array} \right.$$  

Inserting (10.20) in (10.18), multiplying by $\exp(-i k' \cdot r)$ and integrating over the normalization volume yields

$$\frac{\hbar^2 k^2}{m} g(k) + \frac{1}{L^3} \sum_{k'} g(k') V_{kk'} = (\varepsilon + 2E_F^0) g(k) .$$

The interaction matrix element

$$V_{kk'} = \int V(r) e^{-i(k-k') \cdot r} d^3r$$

describes scattering of the electron pair from $(k, -k)$ to $(k', -k')$ and vice versa. In the simplest model this matrix element $V_{kk'}$ is assumed to be independent of $k$ and attractive, that is, $V_{kk'} < 0$.

Fig. 10.9. Diagram to illustrate the simplest attractive interaction between two electrons which leads to Cooper pairing within BCS theory. The interaction potential is assumed to be constant ($= -V_0$) in the dashed region of $k$ space, i.e., between the energy shells $E_F^0 + \hbar \omega_D$ and $E_F^0 - \hbar \omega_D$ ($\omega_D$ is the Debye frequency of the material). For the case of one extra Cooper pair considered here only the $k$-space with $E > E_F$ is of interest.
\[ V_{kk'} = \begin{cases} -V_0(V_0 > 0) & \text{for } E_F^0 < \left( \frac{\hbar^2 k^2}{2m}, \frac{\hbar^2 k'^2}{2m} \right) < E_F^0 + \hbar \omega_D \\ 0 & \text{otherwise} \end{cases} \] (10.24)

It thus follows from (10.22) that

\[ \left( -\frac{\hbar^2 k^2}{m} + \varepsilon + 2E_F^0 \right) g(k) = -A, \quad \text{where} \]

\[ A = \frac{V_0}{L^3} \sum_{k'} g(k') \] (10.25a)

is independent of \( k \).

After summing (10.25a) over \( k \) and comparing with (10.25b), consistency demands that

\[ 1 = \frac{V_0}{L^3} \sum_{k} \frac{1}{\varepsilon + \hbar^2 k^2/m - 2E_F^0}. \] (10.26)

We replace the sum over \( k \) by the integral

\[ L^{-3} \sum_k \frac{1}{(2\pi)^3} \int dk \] (10.27)

and keep in mind that the sum as well as the integral extends only over the manifold of states of one spin type. We have already encountered such summations in the context of exchange interaction between electrons (Sect. 8.4). With reference to Sect. 7.5 we split the integral over the entire \( k \)-space into an integral over the Fermi sphere and the energy and obtain from (10.26)

\[ 1 = \frac{V_0}{(2\pi)^3} \int \frac{dS_E}{|\text{grad}_k E(k)|} \frac{dE}{2E - \varepsilon - 2E_F^0} \quad \text{with} \quad E = \frac{\hbar^2 k^2}{2m}. \] (10.28)

Since the integral over the energy extends only over the narrow interval between \( E_F^0 \) and \( E_F^0 + \hbar \omega_D \), the first part of the integral can be considered as a constant. This constant is the density of states for one spin type (7.41) at the Fermi level which we shall denote as \( Z(E_F^0) \) here and in the following parts of the chapter. By performing the integration we obtain

\[ 1 = V_0 \frac{Z(E_F^0 + \hbar \omega_D)}{Z(E_F^0)} \int_{E_F^0}^{E_F^0 + \hbar \omega_D} \frac{dE}{2E - \varepsilon - 2E_F^0} = \frac{1}{2} V_0 Z(E_F^0) \ln \frac{\varepsilon + 2\hbar \omega_D}{\varepsilon} \quad \text{or} \]

\[ \varepsilon = \left( \frac{2\hbar \omega_D}{1 - \exp \left( \frac{2}{V_0 Z(E_F^0)} \right)} \right). \] (10.29a)

For the case of a weak interaction, \( V_0 Z(E_F^0) \ll 1 \), it follows that

\[ \varepsilon = -2\hbar \omega_D e^{-2/V_0 Z(E_F^0)}. \] (10.30)

In Sect. 10.4 the electronic interaction between electrons in the Fermi sea due to the non-interacting sea is imagined as a weak pairwise interaction, \((r_1, r_2)^{\dagger}\), where \( r_1 \) and \( r_2 \) are the pair forming states and \( (r_1, r_2)^{\dagger} \) is the pair of states. The interaction is achieved through a reduction in the available binding energy. The binding energy is the pair state energy.

\[ E_{\text{kin}} = 2E_F - 2\hbar \omega_D. \]
There thus exists a two-electron bound state, whose energy is lower than that of the fully occupied Fermi sea \((T=0)\) by an amount \(\varepsilon = E - 2E_F^0 < 0\). The ground state of the non-interacting free electron gas, as treated in Sect. 6.2, becomes unstable when a minute attractive interaction between electrons is "switched on". It should be noted that the energy reduction \(\varepsilon\) (10.30) results from a Gedankenexperiment in which the Fermi-sea for states with \(\hbar^2k^2/2m < E_F^0\) is assumed to be fixed and only the effect of the attraction between two additional electrons in the presence of the Fermi-sea is treated. In reality the instability leads to the formation of a high density of such electron pairs, so called Cooper pairs \((k, -k)\), via which the system tries to achieve a new lower-energy ground state. This new ground state is identical to the superconducting phase, as we shall see.

In the aforegoing treatment it was important that the Pauli principle applies to both electrons. The two-particle wavefunction (10.19) was symmetric in spatial coordinates \((r_1, r_2)\) under exchange of electrons 1 and 2, but the whole wavefunction including spins must be antisymmetric (the most general formulation of the Pauli principle). The spin part of the wavefunction, not indicated in (10.19), must therefore be antisymmetric. The Cooper pair therefore comprises two electrons with opposite wave vectors and opposite spins \((k_\uparrow, -k_\downarrow)\). In this connection one often speaks of singlet pairs. It should be noted that a more complicated electron-electron coupling could lead to parallel spin pairs, so-called triplets. Models of this type have been discussed, but experimental proof of the existence of such states has not yet been found. Triplet pairs have however been found in liquid \(^3\)He. At low temperatures this system behaves like a degenerate Fermi gas.

### 10.4 The BCS Ground State

In Sect. 10.3 we saw how a weak attractive interaction, resulting from electron-phonon interaction, leads to the formation of "Cooper pairs". The energy reduction of the Fermi sea due to a single pair was calculated in (10.29). Such a Cooper pair must be imagined as an electron pair in which the two electrons always occupy states \((k_\uparrow, -k_\downarrow), (k_\uparrow', -k_\downarrow')\) and so on, with opposed \(k\)-vectors and spin. The scattering of the pair from \((k_\uparrow, -k_\downarrow)\) to \((k_\uparrow', -k_\downarrow')\) mediated by \(V_{kk'}\) leads to an energy reduction on the formation of a Cooper pair (Fig. 10.10). Due to this energy reduction ever more Cooper pairs are formed. The new ground state of the Fermi sea after pair formation is achieved through a complicated interaction between the electrons. The total energy reduction is not obtained by simply summing the contributions (10.29) of single Cooper pairs. The effect of each single Cooper pair depends on those already present. One must thus seek the minimum total energy of the whole system for all possible pair configurations, taking into account the kinetic one-electron component and the energy reduction due to "pair collisions", i.e., the electron-phonon interaction. Since an excitation above \(E_F^0\) is necessary, the pairing is associated with an increase in kinetic energy. The kinetic component can be given immediately: If \(w_k\) is the probability that the pair state \((k_\uparrow, -k_\downarrow)\) is occupied, the kinetic component \(E_{\text{kin}}\) is

\[
E_{\text{kin}} = 2 \sum_k w_k \xi_k , \quad \text{with} \quad \xi = \hbar^2k^2/2m - E_F^0 . \tag{10.31}
\]

The total energy reduction due to the pair collisions \((k_\uparrow, -k_\downarrow) \leftrightarrow (k_\uparrow', k_\downarrow')\) can be most
easily calculated via the Hamiltonian $\mathcal{H}$ which explicitly takes account of the fact that the "annihilation" of a pair $(k\uparrow, -k\downarrow)$ and the "simultaneous creation" of a pair $(k'\uparrow, -k'\downarrow)$, i.e. a scattering from $(k\uparrow, -k\downarrow)$ to $(k\uparrow, -k\downarrow)$, leads to an energy reduction of $V_{kk'}$ (Sect. 10.3 and Fig. 10.10). Since a pair state $k$ can be either occupied or unoccupied, we choose a representation consisting of two orthogonal states $|1\rangle_k$ and $|0\rangle_k$, where $|1\rangle_k$ is the state in which $(k\uparrow, -k\downarrow)$ is occupied, and $|0\rangle_k$ is the corresponding unoccupied state. The most general state of the pair $(k\uparrow, -k\downarrow)$ is thus given by

$$|\psi\rangle_k = u_k |0\rangle_k + v_k |1\rangle_k .$$

(10.32)

This is an alternative representation of the Cooper pair wavefunction (10.19). Hence $w_k = u_k^2$ and $1 - w_k = u_k^2$ are the probabilities that the pair state is occupied and unoccupied, respectively. We shall assume that the probability amplitudes $v_k$ and $u_k$ are real. It can be shown in a more rigorous theoretical treatment that this restriction is not important. In the representation (10.32) the ground state of the many-body system of all Cooper pairs can be approximated by the product of the state vectors of the single pairs

$$|\phi_{BCS}\rangle = \prod_k (u_k |0\rangle_k + v_k |1\rangle_k) .$$

(10.33)

This approximation amounts to a description of the many-body state in terms of non-interacting pairs, i.e., interactions between the pairs are neglected in the state vector. In the two dimensional representation

$$|1\rangle_k = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_k , \quad |0\rangle_k = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_k$$

(10.34)

one can use the Pauli matrices

$$\sigma^{(1)}_k = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_k , \quad \sigma^{(2)}_k = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_k$$

(10.35)

to describe the "creation" or "annihilation" of a Cooper pair:

The operator

$$\sigma^+_k = \frac{1}{2} (\sigma^{(1)}_k + i \sigma^{(2)}_k)$$

(10.36a)

transforms the unoccupied state $|0\rangle_k$ into the occupied state $|1\rangle_k$, while

$$\sigma^-_k = \frac{1}{2} (\sigma^{(1)}_k - i \sigma^{(2)}_k)$$

(10.36b)

transforms the state $|1\rangle_k$ into $|0\rangle_k$. From the representations (10.34 - 36) one can deduce the following properties:

$$\sigma^+_k |1\rangle_k = 0 , \quad \sigma^+_k |0\rangle_k = |1\rangle_k ,$$

(10.37a)

$$\sigma^-_k |1\rangle_k = |0\rangle_k , \quad \sigma^-_k |0\rangle_k = 0 .$$

(10.37b)

The matrices $\sigma^+_k$ and $\sigma^-_k$ are formally identical to the spin operators introduced in Sect. 8.7. Their physical interpretation as "creator" and "annihilator" of Cooper pairs...
is however completely different from that in Sect. 8.7, where the reversal of a spin was described.

Scattering from \((k \uparrow, -k \downarrow)\) to \((k' \uparrow, -k' \downarrow)\) is associated with an energy reduction by an amount \(V_{kk'}\). In the simple BCS model of superconductivity (as in Sect. 10.3) this interaction matrix element \(V_{kk'}\) is assumed to be independent of \(k, k'\), i.e. constant. We relate this to the normalization volume of the crystal, \(L^3\), by setting it equal to \(V_0/L^3\). The scattering process is described in the two-dimensional representation as annihilation of \(k (\sigma_k^-)\) and creation of \(k' (\sigma_k'^+)\). The operator that describes the corresponding energy reduction is thus found to be \(- (V_0/L^3) \sigma_k^+ \sigma_k^-\). The total energy reduction due to pair collisions \(k \rightarrow k'\) and \(k' \rightarrow k\) is given by summing over all collisions and may be expressed in operator terminology as

\[
\mathcal{H} = -\frac{1}{L^3} V_0 \sum_{kk'} \frac{1}{2} (\sigma_k^+ \sigma_k^- + \sigma_k'^+ \sigma_k'^-) = -\frac{V_0}{L^3} \sum_{kk'} \sigma_k^+ \sigma_k'^- .
\]  

(10.38)

Since \(V_0\) is restricted to the shell \( \pm \hbar \omega_0 \) around \(E_F\), the sum over \(k, k'\) likewise includes only pair states in this shell. In the sum, scattering in both direction is considered; the right-hand side of (10.38) follows when one exchanges the indices.

The energy reduction due to collisions is given from perturbation theory as the expectation value of the operator \(\mathcal{H}(10.38)\) in the state \(| \phi_{BCS}\rangle\) (10.33) of the many-body system

\[
\langle \phi_{BCS} | \mathcal{H} | \phi_{BCS}\rangle = -\frac{V_0}{L^3} \left[ \prod_p (u_{pp} | 0\rangle + v_{pp} | 1\rangle) \sum_{kk'} \sigma_k^+ \sigma_k'^- \prod_q (u_q | 0\rangle + v_q | 1\rangle) \right] .
\]  

(10.39)

In evaluating (10.39), one should note that the operator \(\sigma_k^+ (\sigma_k'^-)\) acts only on the state \(| 1\rangle_k\) \(| 0\rangle_k\). The explicit rules are given in (10.37). Furthermore, from (10.34) we have the orthonormality relations

\[
k \langle 1 | 1\rangle_k = 1 , \quad k \langle 0 | 0\rangle_k = 1 , \quad k \langle 1 | 0\rangle_k = 0 .
\]  

(10.40)

We thus obtain

\[
\langle \phi_{BCS} | \mathcal{H} | \phi_{BCS}\rangle = -\frac{V_0}{L^3} \sum_{kk'} v_k u_{k'} u_k v_{k'} .
\]  

(10.41)

According to (10.31, 41) the total energy of the system of Cooper pairs can therefore be represented as

\[
W_{BCS} = 2 \sum_k v_k^2 \xi_k - \frac{V_0}{L^3} \sum_{kk'} u_k v_k u_{k'} v_{k'} .
\]  

(10.42)

The BCS ground state at \(T = 0\)K of the system of Cooper pairs is given by the minimum, \(W_{BCS}^0\), of the energy density \(W_{BCS}\). By minimizing (10.42) as a function of the probability amplitudes \(u_k\) and \(v_k\) we obtain the energy of the ground state \(W_{BCS}^0\) and the occupation and non-occupation probabilities \(w_k = u_k^2\) and \((1 - w_k) = u_k^2\). Because of the relationship between \(v_k\) and \(u_k\), the calculation is greatly simplified by setting

\[
v_k = \sqrt{w_k} = \cos \theta_k ,
\]  

(10.43 a)
\[ u_k = \sqrt{1 - w_k} = \sin \theta_k \]  \hspace{1cm} (10.43b)

which guarantees that
\[ u_k^2 + v_k^2 = \cos^2 \theta_k + \sin^2 \theta_k = 1 \]  \hspace{1cm} (10.43c)

The quantity to be minimized can be written
\[ W_{\text{BCS}} = \sum_k 2 \xi_k \cos^2 \theta_k - \frac{V_0}{L^3} \sum_{kk'} \cos \theta_k \sin \theta_k' \cos \theta_k' \sin \theta_k' \]
\[ = \sum_k 2 \xi_k \cos^2 \theta_k - \frac{1}{4} \frac{V_0}{L^3} \sum_{kk'} \sin 2 \theta_k \sin 2 \theta_k'. \]  \hspace{1cm} (10.44)

The condition for the minimum of \( W_{\text{BCS}} \) then reads
\[ \frac{\partial W_{\text{BCS}}}{\partial \theta_k} = -2 \xi_k \sin 2 \theta_k - \frac{V_0}{L^3} \sum_{kk'} \cos 2 \theta_k \sin 2 \theta_k' = 0 \]  \hspace{1cm} (10.45a)
\[ \xi_k \tan 2 \theta_k = -\frac{1}{2} \frac{V_0}{L^3} \sum_{kk'} \sin 2 \theta_k'. \]  \hspace{1cm} (10.45b)

We let
\[ \Delta = \frac{V_0}{L^3} \sum_{kk'} u_{k'} v_{k'} = \frac{V_0}{L^3} \sum_{kk'} \sin \theta_k' \cos \theta_k', \]  \hspace{1cm} (10.46)
\[ E_k = \sqrt{\xi_k^2 + \Delta^2} \]  \hspace{1cm} (10.47)

and obtain from standard trigonometry
\[ \frac{\sin 2 \theta_k}{\cos 2 \theta_k} = \tan 2 \theta_k = -\frac{\Delta}{\xi_k} \]  \hspace{1cm} (10.48)
\[ 2 u_k v_k = \sin 2 \theta_k = \frac{\Delta}{E_k} \]  \hspace{1cm} (10.49)
\[ v_k^2 - u_k^2 = -\xi_k/E_k. \]  \hspace{1cm} (10.50)

Thus the occupation probability, \( w_k = v_k^2 \), of a pair state \((k^\uparrow, -k^\downarrow)\) in the BCS ground state at \( T = 0 \) K is given by
\[ w_k = v_k^2 = \frac{1}{2} \left( 1 - \frac{\xi_k}{E_k} \right) = \frac{1}{2} \left( 1 - \frac{\xi_k}{\sqrt{\xi_k^2 + \Delta^2}} \right). \]  \hspace{1cm} (10.51)

This function is plotted in Fig. 10.11. At \( T = 0 \) K(l) it has a form similar to the Fermi function at finite temperature and a more exact analysis shows that it is like the Fermi distribution at the finite critical temperature \( T_c \). It should be noted that this form of
10.4 The BCS Ground State

Fig. 10.11. The BCS occupation probability $v_k^2$ for Cooper pairs in the vicinity of the Fermi energy $E_F$. The energy is given as $\xi_k = E(k) - E_F$, i.e., the Fermi energy ($\xi_k = 0$) serves as a reference point. Also shown for comparison is the Fermi-Dirac distribution function for normally conducting electrons at the critical temperature $T_c$ (dashed line). The curves are related to one another by the BCS relationship between $\Delta (0)$ and $T_c$ (10.67).

$\psi^2$ results from the representation in terms of single-particle states with well-defined quantum numbers $k$. This representation is not particularly appropriate for the many-body problem; for example, one does not recognize the energy gap in the excitation spectrum of the superconductor (see below). On the other hand, it can be seen in the behavior of $\psi^2_k$ that the Cooper pairs which contribute to the energy reduction of the ground state are constructed from one-particle wavefunctions from a particular $k$-region, corresponding to an energy shell of $\pm \Delta$ around the Fermi surface.

The energy of the superconducting BCS ground state $\mathcal{W}_{BCS}^0$ is obtained by inserting in $\mathcal{W}_{BCS} - \mathcal{W}_{BCS}^0$ relationships (10.48-51) which follow from the minimization. The result is

$$\mathcal{W}_{BCS}^0 = \sum_k \xi_k (1 - \xi_k / E_k) - L^3 \frac{\Delta^2}{V_0}.$$  \hspace{1cm} (10.52)

The condensation energy of the superconducting phase is obtained by subtracting from $\mathcal{W}_{BCS}^0$ the energy of the normal conducting phase, i.e., the energy of the Fermi-sea without the attractive interaction $\mathcal{W}_a = \sum_{|k| < \xi_k} 2 \xi_k$. In analogy to (10.26, 28) we now go from a sum in $k$-space to an integral \((L^{-3} \sum_k \int dk/8 \pi^2)\). After some calculation, the specific condensation energy density is obtained as

$$\frac{\mathcal{W}_{BCS}^0 - \mathcal{W}_a^0}{L^3} = \left( \frac{\Delta^2}{V_0} - \frac{\Delta^2}{V_0} \right) - \frac{1}{2} Z(E_F^0) \Delta^2 = - \frac{1}{2} Z(E_F^0) \Delta^2.$$  \hspace{1cm} (10.53)

Thus, for finite $\Delta$, there is always a reduction in energy for the superconducting state, whereby $\Delta$ is a measure of the size of the reduction. One can visualize (10.53) by imagining that $Z(E_F^0)$ electron pairs per unit volume from the energy region $\Delta$ below the Fermi level all “condense” into a state at exactly $\Delta$ below $E_F^0$. Their average gain in energy is thus $\Delta/2$.

The decisive role of the parameter $\Delta$ is clear from the following: The first excitation state above the BCS ground state involves the breaking up of a Cooper pair due to an external influence. Here an electron is scattered out of $(k\uparrow)$ leaving behind an unpaired electron in $(k\downarrow)$. In order to calculate the necessary excitation energy, we rewrite the ground state energy $\mathcal{W}_{BCS}^0$ (10.52) as follows
\[ W_{\text{BCS}}^0 = \sum_k \xi_k \left(1 - \frac{\xi_k}{E_k}\right) - \frac{L^3 \Delta^2}{V_0} \]

\[ = \sum_k E_k \left(u_k^2 - v_k^2\right) - \sum_k E_k \left(u_k^2 - v_k^2\right)^2 - \frac{L^3 \Delta^2}{V_0} \]

\[ = 2 \sum_k E_k u_k v_k^2 + \sum_k E_k [u_k^2 (1 - u_k^2) - v_k^2 (1 + v_k^2)] - \frac{L^3 \Delta^2}{V_0} \]

\[ = \Delta \sum_k u_k v_k - \frac{L^3 \Delta^2}{V_0} + \sum_k E_k v_k^2 (u_k^2 - 1 - v_k^2) = -2 \sum_k E_k v_k^4 . \quad (10.54) \]

If \((k', -k'')\) is occupied, i.e., \(v_{k'}^2 = 1\), then the first excited state \(W_{\text{BCS}}^1\) is achieved by breaking up the pair, i.e., \(v_{k'}^2 = 0\), and therefore

\[ W_{\text{BCS}}^1 = -2 \sum_{k \neq k'} E_k v_k^4 . \quad (10.55) \]

The necessary excitation energy is the difference between the energies of the initial and final states

\[ \Delta E = W_{\text{BCS}}^1 - W_{\text{BCS}}^0 = 2E_k' = 2\sqrt{\xi_{k'}^2 + \Delta^2} . \quad (10.56) \]

The first term in the square-root, \(\xi_{k'}^2\), describes the kinetic energy of the two electrons "scattered" out of the Cooper pair. Since \(\xi_{k'} = h^2 k'^2 / 2m - E_F^0\), this can be arbitrarily small, i.e., the excitation requires a minimum finite energy

\[ \Delta E_{\text{min}} = 2\Delta . \quad (10.57) \]

The excitation spectrum of the superconducting state contains a gap of \(2\Delta\), which corresponds to the energy required to break up a Cooper pair. Equation (10.56) describes the excitation energy of the two electrons that result from the destruction of a Cooper pair. If we imagine that a single electron is added to the BCS ground state, then it can naturally find no partner for Cooper pairing. Which energy state can this electron occupy? From (10.56) we conclude that the possible states of this excited system are given by \(E_k = (\xi_k^2 + \Delta^2)^{1/2}\). If the unpaired electron is at \(\xi_k = 0\) it thus has an energy which lies at least \(\Delta\) above the BCS ground state (Fig. 10.12). However it can also occupy states with finite \(\xi_k\); for \(\xi_k^2 \gg \Delta^2\) the one-electron energy levels

\[ E_k = \sqrt{\xi_k^2 + \Delta^2} \approx \xi_k = \frac{h^2 k^2}{2m} - E_F^0 \quad (10.58) \]

Fig. 10.12. (a) Simplified representation of the excitation spectrum of a superconductor on the basis of one-electron energies \(E_k\). In the BCS ground state, the one-electron picture collapses: At \(T = 0\) K all Cooper pairs occupy one and the same ground state (like Bosons). This state is therefore energetically identical to the chemical potential, i.e., the Fermi energy \(E_F^0\). The energy level drawn here can thus be formally interpreted as the "many-body energy of one electron" (total energy of all particles divided by the number of electrons). Note that a minimum energy of \(2\Delta\) is necessary to split up a Cooper pair. (b) Density of states for excited electrons in a superconductor \(D_s\) relative to that of a normal conductor. \(E_k = 0\) corresponds to the Fermi energy \(E_F^0\).
become occupied. These are exactly the levels of the free electron gas (of a normal conductor). Thus, for energies well above the Fermi energy ($\xi_k^2 > \Delta^2$), the continuum of states of a normal conductor results. To compare the density of states in the energy range $\Delta$ about the Fermi level for excited electrons $D_s(E_k)$ in a superconductor with that of a normal conductor $D_n(\xi_k)$ (Sect. 6.1), we note that in the phase transition no states are lost, i.e.

$$D_s(E_k) dE_k = D_n(\xi_k) d\xi_k .$$  \hspace{1cm} (10.59a)

Because we are only interested in the immediate region $\Delta$ around $E_F^0$, it is sufficient to assume that $D_n(\xi_k) = D_n(E_F^0) = \text{const.}$ According to (10.56) it then follows that

$$\frac{D_s(E_k)}{D_n(E_F^0)} = \frac{d\xi_k}{dE_k} = \begin{cases} \frac{E_k}{\sqrt{E_k^2 - \Delta^2}} & \text{for } E_k > \Delta \\ 0 & \text{for } E_k < \Delta . \end{cases}$$  \hspace{1cm} (10.59b)

This function possesses a pole above $\Delta$ and for $E_k > \Delta$ converts, as expected, to the density of states of a normal conductor; it is depicted in Fig. 10.12b.

It should again be emphasised that the illustration in Fig. 10.12 does not express the fact that the breaking up of a Cooper pair requires a minimum energy $2\Delta$. It says only that the “addition” of an unpaired electron to the BCS ground state makes possible the occupation of one-particle states which lie at least $\Delta$ above the BCS ground state energy (for one electron). The density of states in the vicinity of the minimum energy single-particle states is singular (Fig. 10.12b).

The “addition” of electrons to the BCS ground state can be realized in an experiment by the injection of electrons via an insulating tunnel barrier (Panel IX). Such tunnel experiments are today very common in superconductor research. They may be conveniently interpreted with reference to diagrams such as Fig. 10.12b.

We wish now to determine the gap $\Delta$ (or $2\Delta$) in the excitation spectrum. For this we combine (10.49) with (10.46, 47), and obtain

$$\Delta = \frac{1}{2} \frac{V_0}{L^3} \sum_k \frac{\Delta}{E_k} = \frac{1}{2} \frac{V_0}{L^3} \sum_k \frac{\Delta}{\sqrt{\xi_k^2 + \Delta^2}} .$$  \hspace{1cm} (10.60)

As in (10.26, 28), the sum in $k$-space is replaced by an integral ($L^{-3} \sum_k \rightarrow \int dk/8\pi^3$). We note that we are summing again over pair states, i.e., that instead of the one-particle density of states $D(E_F^0 + \xi)$ we must take the pair density of states $Z(E_F^0 + \xi) = \frac{1}{2} D(E_F^0 + \xi)$.

Furthermore, in contrast to Sect. 10.3, the sum is taken over a spherical shell $\pm \hbar \omega_D$ located symmetrically around $E_F^0$. We then have

$$1 = \frac{V_0}{2} \frac{\hbar \omega_D}{-\hbar \omega_D} \int_{\sqrt{\xi^2 + \Delta^2}} Z(E_F^0 + \xi) d\xi .$$  \hspace{1cm} (10.61a)

In the region $[E_F^0 - \hbar \omega_D, E_F^0 + \hbar \omega_D]$ where $V_0$ does not vanish, $Z(E_F^0 + \xi)$ varies only slightly, and, due to the symmetry about $E_F^0$, it follows that

$$\frac{1}{V_0 Z(E_F^0)} = \int_{\xi}^{\hbar \omega_D} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2}} .$$  \hspace{1cm} (10.61b)
In the case of a weak interaction, i.e., $V_0 Z(E_F) \ll 1$, the gap energy is thus

$$
\Delta = \frac{\hbar \omega_D}{\sinh \left[ \frac{1}{V_0 Z(E_F)} \right]} \approx 2 \hbar \omega_D e^{-1/V_0 Z(E_F)}.
$$

This result bears a noticeable similarity to (10.30), i.e., to the binding energy $\varepsilon$ of two electrons in a Cooper pair in the presence of a fully occupied sea. As in (10.30), one sees that even a very small attractive interaction, i.e., a very small positive $V_0$, results in a finite gap energy $\Delta$, but that $\Delta$ cannot be expanded in a series for small $V_0$. A perturbation calculation would thus be unable to provide the result (10.63). For the sake of completeness, it should also be mentioned that superconductors have now been discovered that have a vanishingly small gap energy.

### 10.5 Consequences of the BCS Theory and Comparison with Experimental Results

An important prediction of the BCS theory is the existence of a gap $\Delta$ (or $2\Delta$) in the excitation spectrum of a superconductor. The tunnel experiments described in Panel IX provide direct experimental evidence for the gap. Indications for the existence of a gap are also present in the behavior of the electronic specific heat capacity of a superconductor at very low temperature. The exponential behavior of this specific heat capacity (10.3) is readily understandable for a system whose excited states are reached via excitation across an energy gap. The probability that the excited state is occupied is then proportional to an exponential Boltzmann expression, which also appears in the specific heat capacity (temperature derivative of the internal energy) as the main factor determining its temperature dependence.

A further direct determination of the energy gap $2\Delta$ is possible using spectroscopy with electromagnetic radiation (optical spectroscopy). Electromagnetic radiation is only absorbed when the photon energy $\hbar \omega$ exceeds the energy necessary to break up the Cooper pair, i.e., $\hbar \omega$ must be larger than than the gap energy $2\Delta$. Typical gap energies for classical superconductors lie in the region of a few meV. The appropriate experiments must therefore be carried out with microwave radiation. The curves in Fig. 10.13 result from an experiment in which the microwave intensity $I$ is measured by a bolometer after multiple reflection in a cavity made of the material to be examined. With an external magnetic field, the material can be driven from the superconducting state (intensity $I_S$) to the normal state (intensity $I_N$). This allows the measurement of a difference quantity $(I_S - I_N)/I_N$. At a photon energy corresponding to the gap energy $2\Delta$, this quantity drops suddenly. This corresponds to an abrupt decrease in the reflectivity of the superconducting material for $\hbar \omega > 2\Delta$, whereas for photon energies below $2\Delta$ the superconductor reflects totally since there are no excitation mechanisms.

At all temperatures above $T = 0$ K there is a finite possibility of finding electrons in the normal state. As the temperature rises, more and more Cooper pairs break up; thus a temperature increase has a destructive effect on the superconducting phase. The