# 2 Phenomenology and Microscopic Theory: Theoretical Foundations

**L. Pitaevskii** University of Trento Dept. of Physics, Trento, Italy



## 2.1 Off-Diagonal Long-Range Order and Superfluidity

Many important properties of superconductors follow from an understanding of the difference between the symmetry of the superconducting and normal states, i.e. an understanding of the nature of the order parameter arising from the phase transition between these states. Essential hints can be obtained from the deep physical analogy between two physical phenomena – superfluidity and superconductivity. For this reason it is instructive to examine some properties of a superfluid liquid.[1]

[1] In this and in the next chapter we use units such as the Boltzmann constant $k_B = 1$, so that temperature has dimensions of energy. We also use the CGS system of units. Operators are denoted by a circumflex. Hermitian conjugation is denoted by a † symbol.

Superfluidity was first discovered in liquid $^4$He at temperatures below 2.18 K. A superfluid has the property that it can flow through narrow capillaries or slits without exhibiting viscosity. The viscosity $\eta$ of a superfluid liquid is exactly zero. At $T = 0$ the liquid consists entirely of superfluid. At non-zero temperature part of the liquid behaves as a superfluid without viscosity; the remaining part behaves as a normal viscous liquid. However, these two parts fully interpenetrate each other. Thus the density of a superfluid can be written as a sum $\rho = \rho_s + \rho_n$ of superfluid and normal parts with associated hydrodynamic velocities $\mathbf{v}_s$ and $\mathbf{v}_n$. There is no friction between these two parts of the liquid.

We will not discuss here details of the theory of superfluidity. What is important for us is the relation of this phenomenon with the Bose–Einstein condensation of atoms in the superfluid liquid. It is well-known that Bose–Einstein condensation is associated with a thermodynamic state in which a finite number of atoms occupy a state with zero momentum, i.e. atoms "condense" in a $\mathbf{p} = \mathbf{0}$ state. Thus, the momentum distribution of atoms contains a delta-function term:

$$N(\mathbf{p}) = (2\pi\hbar)^3 n_0 \delta(\mathbf{p}) + n'(\mathbf{p}) . \qquad (2.1)$$

The distribution function $N(\mathbf{p})$ defines the number of atoms in the element of momentum space:

$$dN = N(\mathbf{p}) \frac{V d^3 p}{(2\pi\hbar)^3} . \qquad (2.2)$$

Thus, the number of atoms in the condensate is $N_0 = n_0 V$ where $n_0$ is the density of the condensate atoms. $N_0$ is proportional to the total number of atoms $N$ and depends on temperature. For an ideal Bose gas $n_0(T)$ can easily be calculated explicitly. For a general system it can be related to properties of the one-body density matrix of the system $\rho^{(1)}(\mathbf{r}_1, \mathbf{r}_2)$.

This matrix can be expressed in terms of the particle, creation and annihilation operators according to

$$\rho^{(1)}(\mathbf{r}_1, \mathbf{r}_2, t) = \langle \hat{\Psi}^\dagger(\mathbf{r}_2, t) \hat{\Psi}(\mathbf{r}_1, t) \rangle . \qquad (2.3)$$

(Here and below we will consider these operators in the time-dependent Heisenberg representation.) For a uniform system in equilibrium this function depends on the difference of coordinates $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ only and does not depend on time $t$. The momentum distribution can then be calculated as the Fourier transform of this function:

$$N(\mathbf{p}) = \int \rho^{(1)}(\mathbf{r}) e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar} d^3 x . \qquad (2.4)$$

The presence of the delta function in equation (2.1) requires that the one-body density matrix does not tend to zero as $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$, but to a constant value $n_0$:

$$\rho^{(1)}(\mathbf{r}_1 - \mathbf{r}_2) \to n_0, |\mathbf{r}_1 - \mathbf{r}_2| \to \infty . \qquad (2.5)$$

This equation expresses the existence of so-called off-diagonal long-range order. This is the symmetry property that distinguishes the superfluid and non-superfluid phases. (L.D. Landau 1951 [1], O. Penrose 1951 [2].)

Now, at large distances there can be no correlations between $\hat{\Psi}^\dagger$ and $\hat{\Psi}$ and therefore, the density matrix must have the property for $\rho^{(1)}(\mathbf{r}_1, \mathbf{r}_2, t) \to \left\langle \hat{\Psi}^\dagger(\mathbf{r}_2, t) \right\rangle \left\langle \hat{\Psi}(\mathbf{r}_1, t) \right\rangle$ for $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$. In the equilibrium uniform system that we have considered so far $\left\langle \hat{\Psi}(\mathbf{r}_1, t) \right\rangle = \left\langle \hat{\Psi}^\dagger(\mathbf{r}_2, t) \right\rangle = const = \sqrt{n_0}$ apart from an arbitrary phase. However, if the liquid moves, or if it is subjected to non-uniform and non-stationary external conditions, the asymptotic expression for the density matrix will now be a function of coordinates and time:

$$\rho^{(1)}(\mathbf{r}_1, \mathbf{r}_2, t) \to \Psi_0(\mathbf{r}_1, t) \Psi_0^*(\mathbf{r}_2, t) , \quad |\mathbf{r}_1 - \mathbf{r}_2| \to \infty , \qquad (2.6)$$

where we introduced the notations: $\Psi_0(\mathbf{r}, t) \equiv \left\langle \hat{\Psi}(\mathbf{r}, t) \right\rangle$, $\Psi_0^*(\mathbf{r}, t) \equiv \left\langle \hat{\Psi}^\dagger(\mathbf{r}, t) \right\rangle$.

The function $\Psi_0(\mathbf{r}, t)$ is interpreted as a wave function of the atoms in the condensate. It plays the role of the order parameter associated with the phase transition from the normal to the superfluid state. Its definition implies that the operator $\hat{\Psi}(\mathbf{r}, t)$ can be written in the form

$$\hat{\Psi}(\mathbf{r}, t) = \Psi_0(\mathbf{r}, t) + \hat{\Psi}'(\mathbf{r}, t) , \qquad (2.7)$$

with $\left\langle \hat{\Psi}'(\mathbf{r}_1, t) \right\rangle = 0$. One must not, however, take these definitions too literally. The operator $\hat{\Psi}$ has

no diagonal matrix elements with respect to the number of atoms $N$ since it generates a state with $N-1$ atoms which, by definition, is orthogonal to the $N$ atom state. Thus, strictly speaking, one must define $\Psi_0(\mathbf{r},t)=\left\langle N-1\left|\hat{\Psi}(\mathbf{r},t)\right|N\right\rangle$ where the state $N-1$ can be obtained from $N$ by adiabatically removing one atom. However, in the thermodynamic limit, where $N\to\infty$, the difference between these two states disappears and one can consider $\Psi_0$ as an average value. However, there is a "remnant" of this "off-diagonal" coupling. The Heisenberg matrix element between two stationary states depends on time according to $\langle N-1|\ldots|N\rangle \sim \exp\left[-\frac{it}{\hbar}\left(E(N)-E(N-1)\right)\right]$. Taking into account that $(E(N)-E(N-1))\approx\mu$, where $\mu$ is the chemical potential of the system, one finally gets:

$$\left\langle N-1\left|\hat{\Psi}(\mathbf{r},t)\right|N\right\rangle \propto e^{-i\mu t/\hbar}. \tag{2.8}$$

$\Psi_0(\mathbf{r},t)$ is a complex function. Its modulus defines the density of the condensate atoms according to $|\Psi_0(\mathbf{r},t)|^2=n_0(\mathbf{r},t)$. Thus, we may write

$$\Psi_0(\mathbf{r},t)=\sqrt{n_0(\mathbf{r},t)}e^{i\chi(\mathbf{r},t)}. \tag{2.9}$$

The phase of the order parameter also has a deep physical meaning. Note first of all that according to (2.8)

$$\frac{\partial\chi}{\partial t}=-\frac{\mu}{\hbar}. \tag{2.10}$$

It is natural to expect that this equation is valid not only at equilibrium where the chemical potential $\mu$ is independent of coordinates and time, but also if $\mu$ is a slowly varying function of $\mathbf{r}$ and $t$. The gradient of $\chi$ is also fundamental; to establish its significance let us calculate the particle current density for the condensate atoms. According to the general equation of quantum mechanics

$$\mathbf{j}_0=\frac{i\hbar}{2m}\left(\Psi_0\nabla\Psi_0^*-\Psi_0^*\nabla\Psi_0\right)=n_0\frac{\hbar}{m}\nabla\chi, \tag{2.11}$$

where $m$ is the mass of an atom. Thus, the condensate moves with a velocity

$$\mathbf{v}_s=\frac{\hbar}{m}\nabla\chi. \tag{2.12}$$

Since this motion can exist in a state of thermodynamic equilibrium characterized by the quantity $\Psi_0$, it is non-dissipative; this is the physical origin of the vanishing viscosity associated with the motion of the superfluid. Equation (2.12) therefore defines the velocity of the superfluid motion. We have already taken this into account in our definition of $\mathbf{v}_s$.

However, to avoid misunderstanding, we must emphasize that, although the velocity of the superfluid part of the liquid is the same as the condensate velocity, the density of the superfluid component $\rho_s$ and the density of the condensate $mn_0$ are not the same. This is clearly evident from the fact that at $T=0$ all of the liquid is superfluid, but not all its atoms are in the condensate. One may say that the condensate atoms in their motion carry other atoms creating an "effective"superfluid density.

Note that the appearance in the theory of a complex order parameter $\Psi_0$ with some phase $\chi$ implies a spontaneous breaking of the gauge symmetry in the superfluid state. One must remember, however, that the absolute value of the phase has no physical meaning. One can always add to $\chi$ an arbitrary constant and this constant, which cancels out in (2.6), can be dropped in the definition of $\Psi_0$. Observable physical quantities such as $\mu$ and $\mathbf{v}_s$ are defined by derivatives of the phase.

The difference in the behavior of normal and superfluid liquids is manifested in a very spectacular way in their properties under rotation. An ordinary liquid, placed in a cylindrical vessel rotating about its axes, rotates as whole with the vessel. The velocity field in the liquid is $\mathbf{v}=\Omega\times\mathbf{r}$, where $\Omega$ is the angular velocity; then curl $\mathbf{v}$ =2$\Omega$. This type of rotation is impossible for a superfluid. According to (2.12), for the superfluid flow one has curl $\mathbf{v}_s=0$ corresponding to potential flow. This equation is one of the most important results of the Landau theory of superfluidity. It says that a superfluid remains at rest even in a rotating vessel.

Such a state, however, becomes thermodynamically unfavorable for sufficiently large rates of rotation. The reason is that in a rotating coordinate frame thermodynamic equilibrium corresponds to a minimum of the thermodynamic potential $E_{\mathrm{rot}}=E-\mathbf{M}\cdot\Omega$, with $E$ and $\mathbf{M}$ being the energy and an-

gular momentum in a laboratory coordinate frame. As a result the state with $\mathbf{M} \cdot \Omega \rangle \mathbf{0}$ turns out to be energetically more favorable than that with $\mathbf{M} = \mathbf{0}$ for sufficiently large $\Omega$. The apparent contradiction between this statement and (2.12) is removed by assuming that the potential flow is lost only at certain lines of singularity in the liquid, so-called vortex lines (L. Onsager 1949 [3], R.P. Feynman 1955 [4]).

Let us consider the simplest case of a straight vortex line along the axis of a cylindrical vessel. In this case the streamlines are circles in planes perpendicular to the vortex line, with centers lying on the line. Integrating (2.12) around such a circle gives $\oint \mathbf{v}_s \cdot d\mathbf{l} = (\hbar/m)\,\delta\chi$, where $\delta\chi$ is the change in the circulation phase on going around the contour and returning to the original point. Since the wave function $\Psi_0$ is single valued, it must be an integer multiple of $2\pi$. Thus the circulation velocity is governed by

$$\oint \mathbf{v}_s \cdot d\mathbf{l} = \frac{2\pi\hbar}{m}\, s\,, \tag{2.13}$$

where $s$ is an integer. The integral on the l.h.s. of this equation gives $2\pi r v_s$, where $r$ is the distance from the axis so that

$$v_s = \frac{\hbar}{mr}\,. \tag{2.14}$$

Here we set $s = 1$ since it is not difficult to show that vortices with higher values are thermodynamically unstable.

Note that (2.13) is valid for integration on any contour enclosing the line. Since this must hold for arbitrarily small $\mathbf{r}$, it follows that the vorticity, curl $\mathbf{v}_s$ is concentrated on the axis according to

$$\text{curl}\,\mathbf{v}_s = \frac{2\pi\hbar}{m}\, s\delta^{(2)}(\mathbf{r})\,. \tag{2.15}$$

Here, $\mathbf{r}$ is a two-dimensional vector in a plane perpendicular to the line and $\delta^{(2)}(\mathbf{r})$ is the two-dimensional delta-function. We emphasize that the existence of such a vortex line as a stable object clearly demonstrates that the viscosity of the superfluid is zero. In the presence of even a small viscosity the vorticity will diffuse from the axis and will eventually spread over the whole volume.

The vortex line possesses an energy $\varepsilon_v$ and an angular momentum $M_v$. The appearance of the line is favorable if it decreases the energy $E_{\text{rot}} = E_0 + \varepsilon_v - \Omega M_v$, i.e. if $\Omega \rangle \Omega_c = \varepsilon_v / M_v$. To calculate this critical angular velocity we have to know $\varepsilon_v$ and $M_v$. The energy is simply the kinetic energy of rotation of the liquid:

$$\varepsilon_v = \frac{1}{2}\int \rho_s v_s^2\, dV = \pi L \rho_s \frac{\hbar^2}{m^2}\int \frac{dr}{r}\,, \tag{2.16}$$

where $L$ is the length of the cylinder. The integration with respect to $r$ has to be taken between the value $r \sim a$ of the order of an atomic distance, below which this macroscopic theory becomes invalid, and the radius $R$ of the cylinder. Because of the logarithmic divergence of the integral, the result is not sensitive to the precise value of $a$ and so

$$\varepsilon_v = \pi L \rho_s \frac{\hbar^2}{m^2}\log\left(\frac{R}{a}\right)\,. \tag{2.17}$$

The angular momentum can be calculated in a similar way:

$$\begin{aligned} M_v &= \int \rho_s v_s r \mathrm{d}V \\ &= \hbar \int \frac{\rho_s}{m}\mathrm{d}V = L\pi R^2 \rho_s \frac{\hbar}{m}\,. \end{aligned} \tag{2.18}$$

Thus

$$\Omega_c = \frac{\hbar}{mR^2}\log\left(\frac{R}{a}\right)\,. \tag{2.19}$$

As the angular velocity of the vessel increases further new vortex lines appear and eventually a "rigid body" type of rotation characteristic of an ordinary liquid with curl $\mathbf{v} = 2\,\Omega$ will result. According to (2.15), the mean vorticity is $\overline{\text{curl}\mathbf{v}_s} = \nu 2\pi\hbar/m$, where $\nu$ is the number of the vortex lines per unit area. Equating these values we obtain

$$\nu = \frac{m\Omega}{\pi\hbar}\,. \tag{2.20}$$

The thermal properties of a uniform body at low temperatures result from elementary excitations or quasiparticles. Every excitation has a definite momentum $\mathbf{p}$ and energy $\varepsilon$. The function $\varepsilon(p)$ characterizes the system. It is important to note that in a superfluid liquid the excitations are viewed as a sort of gas that can move through the rest of the liquid

with some velocity $\mathbf{v}_n$. Thus at every point in the superfluid there exist two independent motions with velocities $\mathbf{v}_s$ and $\mathbf{v}_n$. The gas of excitations possesses quite normal properties. Excitations can collide with the walls of a capillary and exchange momentum. The flow of the excitations is thus a viscous one and the excitations constitute the "normal part" of the liquid. The mass current, i.e. the momentum density, can be separated into superfluid and normal parts:

$$\mathbf{j} = \rho_s \mathbf{v}_s + \rho_n \mathbf{v}_n \,, \tag{2.21}$$

where $\rho_s$ and $\rho_n$ correspond to the densities of the normal and superfluid parts. Their sum is, of course, the total density of the liquid $\rho = \rho_s + \rho_n$.

One can calculate the normal density using the Galilean invariance. According to this principle the momentum $\mathbf{P}'$ and energy $E'$ of a body in a coordinate frame $K'$ which moves with a velocity $\mathbf{V}$, are related to $\mathbf{P}$ and $E$ in a stationary frame $K$ by

$$\mathbf{P}' = \mathbf{P} - M\mathbf{V}, \; E' = E - \mathbf{V}\cdot\mathbf{P} + \frac{1}{2}MV^2 \,. \tag{2.22}$$

By definition, the function $\varepsilon(p)$ is the dispersion law of the excitations in the frame where the superfluid part is at rest. Let us suppose that there is a single elementary excitation in the liquid with momentum $\mathbf{p}$ and energy $\varepsilon(p)$. In this case the momentum of the liquid is $\mathbf{P} = \mathbf{p}$ and the energy $E = E_0 + \varepsilon(p)$, where $E_0$ is the ground state energy. Let us now make a transformation to the frame moving with the velocity $\mathbf{V} = -\mathbf{v}_s$, where the superfluid velocity is $\mathbf{v}_s$. According to (2.22) we have

$$\begin{aligned} \mathbf{P}' &= M\mathbf{v}_s + \mathbf{p} \,, \\ E' &= E + \frac{1}{2}MV^2 + \varepsilon(p) + \mathbf{v}_s \cdot \mathbf{p} \,. \end{aligned} \tag{2.23}$$

From these equations we see that the momentum of the excitation in the new coordinate frame is still $\mathbf{p}$ but the energy is now

$$\tilde{\varepsilon}(p) = \varepsilon(p) + \mathbf{v}_s \cdot \mathbf{p} \,. \tag{2.24}$$

By definition the velocity of the normal part $\mathbf{v}_n$ is the velocity of the coordinate frame where the gas of excitations is in the thermodynamic equilibrium. In this frame the superfluid velocity is $(\mathbf{v}_s - \mathbf{v}_n)$ if $\mathbf{v}_s$ is the velocity in the laboratory frame. Thus, the equilibrium distribution function of the elementary excitations is

$$n(\mathbf{p}) = n_0\left[\varepsilon(p) + (\mathbf{v}_s - \mathbf{v}_n)\cdot\mathbf{p}\right] \,, \tag{2.25}$$

where $n_0[\varepsilon] = \left(\exp\frac{\varepsilon}{T} - 1\right)^{-1}$ is the Bose distribution function. Note that (2.25) has a meaning only if the argument of the function $n_0$ is positive for all values of $\mathbf{p}$. This results in a condition

$$|\mathbf{v}_s - \mathbf{v}_n| \langle \min \frac{\varepsilon(p)}{p} \,. \tag{2.26}$$

The l.h.s. of this equation defines the so-called Landau critical velocity.

Equation (2.25) is valid for an arbitrary coordinate frame. We now go to the frame where the superfluid part is at rest, $\mathbf{v}_s = 0$. In this frame $n(\mathbf{p}) = n_0\left[\varepsilon(p) - \mathbf{v}_n\cdot\mathbf{p}\right]$ and according to (2.21) the momentum density is $\mathbf{j} = \rho_n\mathbf{v}_n$. Thus, the density of the normal part can be calculated as

$$\rho_n\mathbf{v}_n = \int \mathbf{p} n_0\left[\varepsilon(p) - \mathbf{v}_n\cdot\mathbf{p}\right]\frac{d^3p}{(2\pi\hbar)^3} \,. \tag{2.27}$$

If the velocity $\mathbf{v}_n$ is small, we can expand the integrand. Integrating over the solid angle we obtain

$$\rho_n = -\frac{1}{6\pi^2}\int_0^\infty \frac{\mathrm{d}n_0}{\mathrm{d}\varepsilon} p^4 \mathrm{d}p \,. \tag{2.28}$$

This equation is one of the most important results of the Landau's theory of superfluidity [5].

## 2.2 Off-Diagonal Long-Range Order in Superconductors

We now turn our attention from Bose superfluids to superconductors. The early theories of superconductivity were phenomenological and we will follow this development. The full microscopic theory of superconductivity was constructed by J. Bardeen, L.N. Cooper and J.R. Schrieffer (BCS) in 1957 [6]. We will present this theory later. General ideas of this theory, however, provide a deep insight into the microscopic basis underlying the phenomenological theories.

According to the BCS theory the essence of the transition into the superconducting state is the formation of bound states, or pairs, involving two electrons with opposite values of their momenta. These pairs behave as Bose particles and exhibit a phenomenon analogous to the Bose–Einstein condensation. This analogy is sufficient to define the nature of the off-diagonal long-range order for superconductors.

Since the condensation takes place for the pairs, one must consider the two-particle density matrix for electrons

$$\rho^{(2)}_{\alpha\beta\gamma\delta}(\mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}'_2, t) = \langle\hat{\Psi}^\dagger_\gamma(\mathbf{r}_2, t)\hat{\Psi}^\dagger_\delta(\mathbf{r}'_2, t)\hat{\Psi}_\alpha(\mathbf{r}_1, t)\hat{\Psi}_\beta(\mathbf{r}'_1, t)\rangle\,. \quad (2.29)$$

Here $\hat{\Psi}^\dagger_\gamma(\mathbf{r}, t)$ and $\hat{\Psi}_\alpha(\mathbf{r}, t)$ are the electron creation and annihilation operators. These operators are spinors with indices $\alpha$ , $\beta$, etc. Let us consider this matrix for the particular values $\mathbf{r}_1 = \mathbf{r}'_1$ and $\mathbf{r}_2 = \mathbf{r}'_2$:

$$\rho^{(2)}_{\alpha\beta\gamma\delta}(\mathbf{r}_1, \mathbf{r}_2, t) = \langle\hat{\Psi}^\dagger_\gamma(\mathbf{r}_2, t)\hat{\Psi}^\dagger_\delta(\mathbf{r}_2, t)\hat{\Psi}_\alpha(\mathbf{r}_1, t)\hat{\Psi}_\beta(\mathbf{r}_1, t)\rangle\,. \quad (2.30)$$

The operator $\hat{\Psi}^\dagger_\gamma(\mathbf{r}_2, t)\hat{\Psi}^\dagger_\delta(\mathbf{r}_2, t)$ creates an electron pair. The condensate of the pairs involves the behavior of (2.30) for large separations, which we write in the form

$$\rho^{(2)}_{\alpha\beta\gamma\delta}(\mathbf{r}_1, \mathbf{r}_2, t) \to \Lambda^*_{\gamma\delta}(\mathbf{r}_2, t)\,\Lambda_{\alpha\beta}(\mathbf{r}_1, t)\,, \quad |\mathbf{r}_1 - \mathbf{r}_2| \to \infty\,, \quad (2.31)$$

where we introduced the function $\Lambda_{\alpha\beta}(\mathbf{r}, t)$ according to

$$\Lambda_{\alpha\beta}(\mathbf{r}, t) = \langle N-2 \left|\hat{\Psi}_\alpha(\mathbf{r}, t)\hat{\Psi}_\beta(\mathbf{r}, t)\right| N\rangle\,,$$
$$\Lambda^*_{\gamma\delta}(\mathbf{r}, t) = \langle N \left|\hat{\Psi}^\dagger_\gamma(\mathbf{r}, t)\hat{\Psi}^\dagger_\delta(\mathbf{r}, t)\right| N-2\rangle\,. \quad (2.32)$$

The state $|N-2\rangle$ in (2.32) is the state obtained by adiabatically removing two electrons from the initial state $|N\rangle$ of $N$ electrons. In the thermodynamic limit $N \to \infty$ the difference between these two states is negligible and one can consider the matrix element $\Lambda$ as an average value. However, for stationary conditions this function has the time dependence corresponding to the transition $N \to N-2$

$$\Lambda_{\alpha\beta}(\mathbf{r}, t) \propto e^{-2i\mu t/\hbar}\,, \quad (2.33)$$

where $\mu$ is the chemical potential of the electrons. In this chapter we consider only this stationary case. The function $\Lambda_{\alpha\beta}$ has the physical meaning of a wave function of the superconducting pairs. The spinor structure of $\Lambda_{\alpha\beta}$ is defined by the value of the spin of the pairs. For the majority of superconductors the bound states form with spin zero. The wave function of a particle with zero spin is proportional to an antisymmetric unit spinor tensor

$$I_{\alpha\beta} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\,. \quad (2.34)$$

In this case

$$\Lambda_{\alpha\beta}(\mathbf{r}, t) = I_{\alpha\beta}\Lambda(\mathbf{r}, t)\,. \quad (2.35)$$

The complex function $\Lambda(\mathbf{r}, t)$ is an order parameter of which the appearance distinguishes the superconducting state of the metal from the normal state.[2] Note that as in the case of superfluidity, the existence of the complex order parameter can be interpreted as spontaneous breaking of the gauge invariance.

The function $\Lambda$ can be represented in the form $\Lambda(\mathbf{r}, t) = |\Lambda(\mathbf{r})|\, e^{i\chi(\mathbf{r},t)}$. The gradient of the phase $\chi(\mathbf{r}, t)$ defines the velocity of the superconductive pairs

$$\mathbf{v}_s = \frac{\hbar}{2m}\nabla\chi\,, \quad (2.36)$$

where $m$ is the mass of an electron. (Compare (2.12). Here we have taken into account the fact that the mass of a pair is $2m$ . This equation, however, cannot be correct in the presence of a magnetic field, because it is not invariant with respect to a gauge transformation. We write the magnetic induction as

$$\mathbf{B} = \mathrm{curl}\,\mathbf{A}\,, \quad (2.37)$$

where $\mathbf{A}$ is the vector potential. We will restrict ourselves to the case of a time-independent magnetic field. In this case gauge invariance states that all observable physical quantities must remain unchanged

[2] This definition of the order parameter is due to L.P. Gor'kov [7].

by a transformation of the vector potential of the form

$$\mathbf{A} \to \mathbf{A} + \nabla\gamma\,, \tag{2.38}$$

where $\gamma(\mathbf{r})$ is an arbitrary function of the coordinates. The $\Psi$-operators of electrons must be transformed accordingly as

$$\begin{aligned}\hat{\Psi}_\alpha &\to \hat{\Psi}_\alpha \exp\left(ie\gamma/\hbar c\right)\,,\\ \hat{\Psi}^\dagger_\alpha &\to \hat{\Psi}^\dagger_\alpha \exp\left(-ie\gamma/\hbar c\right)\,.\end{aligned} \tag{2.39}$$

Then, according to (2.32), the order parameter transforms as

$$\Lambda \to \Lambda \exp\left(i2e\gamma/\hbar c\right)\,. \tag{2.40}$$

Thus, the order parameter is transformed in the same way as the wave function of a particle of charge $2e$. One can rewrite this equation in the form of the phase transformation:

$$\chi \to \chi + 2e\gamma/\hbar c\,. \tag{2.41}$$

Equation (2.36) is not invariant under such a transformation. To restore the required invariance, one must include a further term containing the vector potential

$$\mathbf{v}_s = \frac{\hbar}{2m}\left(\nabla\chi - \frac{2e}{\hbar c}\mathbf{A}\right)\,. \tag{2.42}$$

It is easy to check that this equation is invariant under the transformations (2.38) and (2.41). The superconducting current density, which is a directly observable physical quantity, is proportional to the velocity $\mathbf{v}_s$. In this chapter we will consider the simplest case of superconductors with cubic crystal symmetry. In this case the direction of the current coincides with that for the velocity and thus $\mathbf{j}_s = en_s\mathbf{v}_s$. The quantity $n_s$ defined in this way is called the number density of superconducting electrons. This density, of course, depends on temperature and disappears at the transition point. Using a microscopic theory we will later show that near this point $n_s$ is proportional to $|\Lambda|^2$. Finally one gets for the superconducting current density:

$$\mathbf{j}_s = \frac{e\hbar}{2m}n_s\left(\nabla\chi - \frac{2e}{\hbar c}\mathbf{A}\right)\,. \tag{2.43}$$

This is a fundamental equation for the phenomenological description of superconductors.

It is worth noting that $\mathbf{j}_s$ represents only part of the total current density. In a superconductor a normal current $\mathbf{j}_n$ can also flow, which results in the production of Joule heat and dissipation of energy. The total current density is $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n$. However, in the absence of the external electromagnetic forces the normal current will eventually decay. In a state of thermodynamic equilibrium only a superconducting current can exist.

The time derivative of the phase defines, according to (2.33), the chemical potential of the electrons

$$\frac{\partial\chi}{\partial t} = -\frac{2\mu}{\hbar} \tag{2.44}$$

(B.D. Josephson 1962 [8]).

## 2.3 The London Equation

The fundamental problem of how the magnetic field is distributed inside a superconductor can be solved using (2.43). Let us consider a uniform superconductor in the state of thermodynamic equilibrium. In this case there is no normal current and $\mathbf{j}_s = \mathbf{j}$. Applying the curl operator to both sides of (2.43) and using (2.37), we obtain the London equation

$$\operatorname{curl}\mathbf{j} = -\frac{e^2 n_s}{mc}\mathbf{B} \tag{2.45}$$

(F. London and H. London 1935 [9]). Using this equation we can calculate the current distribution resulting from a known distribution of the magnetic induction. In this sense for superconductors it plays an analogous role to that of Ohm's law $\mathbf{j} = \sigma\mathbf{E}$, for normal metals, where the latter defines the current density due to an electric field $\mathbf{E}$. To obtain the full system of equations we must incorporate the Maxwell equations

$$\operatorname{curl}\mathbf{B} = \frac{4\pi}{c}\mathbf{j} \tag{2.46}$$

and

$$\operatorname{div}\mathbf{B} = 0\,. \tag{2.47}$$

Let us substitute the current density $\mathbf{j}$ from (2.46) into (2.45). Taking into account that $\operatorname{curl}\operatorname{curl}\mathbf{B} = \operatorname{grad}\operatorname{div}\mathbf{B} - \Delta\mathbf{B} = -\Delta\mathbf{B}$, we obtain

$$\Delta\mathbf{B} = \frac{1}{\delta^2}\mathbf{B}\,, \tag{2.48}$$

where

$$\delta^2 = \frac{mc^2}{4\pi e^2 n_s} . \tag{2.49}$$

Equations (2.47) and (2.48) determine the magnetic field in a superconductor. These equations are sufficient to explain a fundamental property of a superconductor: the Meissner effect.

For simplicity, let us consider a superconductor occupying the half-space $x\rangle 0$. Then the problem is a one-dimensional one and the induction $\mathbf{B}$ depends only on the coordinate $x$. From (2.47) one gets $\mathrm{d}B_x/\mathrm{d}x = 0$ and (2.48) gives $B_x = 0$; i.e. the vector $\mathbf{B}$ is parallel to the surface. Equation (2.48) now becomes

$$\frac{\mathrm{d}^2\mathbf{B}}{\mathrm{d}x^2} = \frac{\mathbf{B}}{\delta^2} . \tag{2.50}$$

From the two solutions of this equation one must choose the one which decreases at $x \to \infty$:

$$\mathbf{B}(x) = \mathbf{H}_0 e^{-x/\delta} , \tag{2.51}$$

where the vector $\mathbf{H}_0$ is parallel to the surface. Outside the superconductor in the half-space $x < 0$ one has $\mathbf{B} = \mathbf{H} = \mathbf{H}_0$.

We see that a magnetic field decreases exponentially into the superconductor, penetrating a distance of the order of $\delta$. This distance is called the London penetration depth. A simple estimate shows that this distance is a macroscopical one that is much larger than the mean distance $\overline{r}$ between electrons in the metal. Indeed, we always have $n_s \leq n \sim \overline{r}^{-3}$. Then it follows from (2.49) that $\delta^2 \geq (\overline{r}/4\pi r_0)\overline{r}^2$, where $r_0 = e^2/mc^2$ is the "classical radius" of an electron. Thus, $\delta \gg \overline{r}$, since $\overline{r} \gg r_0$. Still the distance $\delta$ is small compared to the typical dimensions of samples ($\delta \sim 10^{-6} - 10^{-5}$ cm). The decrease of the magnetic induction described by (2.51) is a result of a "screening" of the external field by the superconducting currents. From (2.45) it follows that these currents flow within a surface layer of thickness $\delta$.

Note that for a bulk superconductor with characteristic dimensions $R\rangle\rangle\delta$ (2.51) defines the field distribution near the surface independent of the shape of the body. In this case, the axis $x$ must be directed along the internal normal to the surface.

Thus, the magnetic field does not penetrate deeply into a superconductor. The magnetic induction is $\mathbf{B} = 0$ inside the bulk of the body. One then says that a superconductor is an ideal diamagnetic, i.e. a body with magnetic permeability $\mu = 0$. Then, the usual equation $\mathbf{B} = \mu\mathbf{H}$ gives $\mathbf{B} = 0$ for any $\mathbf{H}$. Such a formal description is convenient, because it permits us to consider a superconductor as the particular case of ordinary magnetism.

In an external magnetic field a superconductor acquires a magnetic moment. Let us calculate this moment for the important example of a long cylinder. Let $\mathbf{H}_0$ be the external field parallel to its axis. From the condition that the tangential component of $\mathbf{H}$ is continuous on the surface it follows that $\mathbf{H} = \mathbf{H}_0$ both outside and inside the cylinder. It then follows that the magnetization (magnetic moment per unit volume) defined by

$$\mathbf{m} = (\mathbf{B} - \mathbf{H})/4\pi , \tag{2.52}$$

is $-\mathbf{H}_0/4\pi$ inside the body . Finally, we have for the total magnetic moment of the cylinder

$$\mathbf{M} = -V\frac{\mathbf{H}_0}{4\pi} , \tag{2.53}$$

where $V$ is its volume. This magnetic moment in the field $\mathbf{H}_0$ can be calculated also by differentiation of the energy of the system $\mathbf{M} = -\partial E/\partial\mathbf{H}_0$. Hence, a long cylinder in a field $\mathbf{H}_0$ has an additional magnetic energy

$$E_{\mathrm{mag}} = V\frac{\mathbf{H}_0^2}{8\pi} . \tag{2.54}$$

This energy is positive. The presence of a superconductor in a magnetic field increases the energy. In contrast the energy of a normal metal is practically independent of the field, because its permeability $\mu \approx 1$. It is clear that in a sufficiently strong magnetic field the superconducting state becomes thermodynamically less favorable than the normal state and at some critical field $H_c$ superconductivity will be destroyed. We will discuss this in detail in the next section.

The above derivation of the London equation is subject to some restrictions. In particular, (2.43) for the superconducting current is valid only under some conditions. First of all, the magnetic field must be weak compared to the critical field $H_c$. Further,

the equation is valid only if all quantities, the current density for example, vary sufficiently slowly in space. Microscopic theory shows that the characteristic distances over which such quantities vary must be large in comparison to the so-called correlation or coherence length

$$\xi_0 \sim \hbar v_F / T_c \,, \tag{2.55}$$

where $v_F$ is a characteristic Fermi velocity of the electrons in the metal (see Sects. 2.6 and 3.3.3 below). According to (2.51) the magnetic induction, and consequently the current, change on the scale of the penetration depth. Thus, we obtain the condition

$$\delta \gg \xi_0 \,. \tag{2.56}$$

This condition is always fulfilled near the transition point. The density of superconductive electrons $n_s \to 0$ as $T \to T_c$ and hence $\delta$ increases indefinitely. Whether the condition (2.56) is fulfilled far from $T_c$ depends on specific properties of the given superconductor. Superconductors in which the inequality (2.56) is fulfilled are called London superconductors. A phenomenological description of superconductors in the opposite limit $\delta \ll \xi_0$ was suggested by A.B. Pippard in 1953 [10]. In this case one speaks of Pippard superconductors.

Note that the existence of the inequality (2.56) does not affect the proof that $\mathbf{B} = 0$ inside a superconductor. The assumption that the field is not expelled would result in a contradiction.

In conclusion we consider the remarkable magnetic-flux quantization effect in a multiply-connected superconductor (F. London, 1950 [11]). This effect is also a consequence of (2.43) for the superconducting current. Let us consider a superconducting torus with dimensions that are large compared with both $\delta$ and $\xi_0$. A very important property of such a torus is that the magnetic flux through it cannot be changed without the destruction of superconductivity. Indeed, any change of $\Phi$ would induce an electromotive force $\mathcal{E}$ according to the equation of the electromagnetic induction $\mathcal{E} = -\frac{1}{c}\frac{d\Phi}{dt}$. In the absence of resistivity this, however, would result in an infinite current. This is impossible and therefore $\mathrm{d}\Phi/\mathrm{d}t = 0$. The flux remains constant when the external field changes or when the shape of the torus is altered. It is an adiabatic invariant of the system. Such invariants are subject to quantization in quantum theory.

Consider a closed contour inside the torus encircling its aperture and passing within the torus far from the surface. Then the magnetic induction $\mathbf{B} = \mathrm{curl}\,\mathbf{A}$ and the current density $\mathbf{j} = (c/4\pi)\,\mathrm{curl}\,\mathbf{B}$ are equal to zero on the contour. The vector potential, however, is not zero. Equation (2.43) takes the form:

$$\mathbf{A} = \frac{\hbar c}{2e} \nabla \chi \,. \tag{2.57}$$

Integrating along the contour we have

$$\oint \mathbf{A} \cdot \mathrm{d}\mathbf{l} = \frac{\hbar c}{2e} \delta\chi \,, \tag{2.58}$$

where $\delta\chi$ is the change in the phase of the wave function of the pairs on passing around the contour. Since this function must be single-valued, this change can only be an integer multiple of $2\pi$. On the other hand, the circulation of the vector $\mathbf{A}$ is equal to the magnetic flux $\phi$ through a surface spanning the contour, i.e. the flux through the torus:

$$\oint \mathbf{A} \cdot \mathrm{d}\mathbf{l} = \int \mathrm{curl}\,\mathbf{A} \cdot \mathrm{d}\mathbf{f} = \int \mathbf{B} \cdot d\mathbf{f} \equiv \phi \,. \tag{2.59}$$

Finally we have

$$\phi = s\phi_0 \quad , \quad \phi_0 = \frac{\pi\hbar c}{|e|} \,, \qquad s = 0, \pm 1, \pm 2 \,. \tag{2.60}$$

The quantity $\phi_0$ is the quantum of magnetic flux. It numerical value is $2 \times 10^{-7}\,\mathrm{G} \cdot \mathrm{cm}^2$. It is important to note that the factor 2 in (2.57) is due to the fact that the charge of a pair is $2e$. Thus an experimental check of the quantization rule (2.60) gives a direct prove of the existence of the electron pairing.

## 2.4 Thermodynamics of Superconductors in a Magnetic Field

In this section we will discuss effects of an external magnetic field on the phase transition between the normal and superconducting states. We will consider a long cylinder in a longitudinal external field

$H_0$. More complex behavior in a magnetic field of superconductors having an arbitrary shape will be considered in the next section.

We have already mentioned that in a sufficiently high magnetic field the superconducting state becomes unfavorable and so the magnetic field penetrates into the cylinder and superconductivity is destroyed. However, there are two kinds of behavior with respect to this field permeation, depending on the properties of the superconductor. Superconductors of the first kind undergo a sharp transition when the magnetic field reaches the *critical field* $H_c$ and the field penetrates throughout the cylinder destroying the superconductivity. In the superconductors of the second kind the magnetic field penetrates only at the surface. We will consider peculiar properties of such superconductors in Sect. 2.8.

In the absence of a magnetic field the phase transition between the normal and superconducting state is a second order phase transition; i.e., the normal phase becomes completely unstable below the *critical temperature* $T_c$, which, of course, depends on the pressure $P$, and the superconducting phase is unstable above $T_c$. Abrupt penetration of the magnetic field in a first kind superconductor implies that the phase transition in the field is a first order phase transition. In this case both the superconducting and normal phases can be characterized for some interval of the field around $T_c$ by their thermodynamic potentials $\Phi_s$ and $\Phi_n$. The phase with lower value of $\Phi$ is stable at a given $H_0$. The second one is metastable.

Superconductivity is a relatively weak phenomenon in the sense that its characteristic energy $T_c$ is small compared to the Fermi energy of the electrons $\varepsilon_F$. Therefore, the magnetic energy (2.54) is a small correction to the total energy of the superconductor. In this case one can easily write an equation for $\Phi_s$. Taking into account that a magnetic field does not penetrate into the superconductor and that small corrections to different thermodynamics potentials are the same if expressed in terms of the proper thermodynamic variables, we have

$$\Phi_s(T, P, H_0) = \Phi_{s0}(T, P) + V_{s0}(T, P)\frac{H_0^2}{8\pi}, \quad (2.61)$$

where $\Phi_{s0}(T, P)$ and $V_{s0}(T, P)$ are the thermodynamic potential and the volume of the superconductive cylinder in the absence of the magnetic field. On the other hand, the magnetic field penetrates into the cylinder in the normal state. However, the thermodynamic potential in this state does not depend on the field if one neglects the small paramagnetism or diamagnetism of a normal metal. Hence, $\Phi_n = \Phi_n(T, P)$.

At the critical field; i.e. on the transition line, the thermodynamic potentials of the normal and superconducting phases are equal:

$$\Phi_n(T, P) = \Phi_{s0}(T, P) + V_{s0}(T, P)\frac{H_c^2}{8\pi}. \quad (2.62)$$

Here, $H_c(T, P)$ is the critical field expressed in terms of temperature and pressure. $T_c(P)$ is the transition temperature in the absence of a magnetic field; i.e. $H_c(T_c, P) = 0$. At $T \to T_c$ the critical field tends to zero. The corresponding law will be established below (see (2.73)).

Since small corrections to all thermodynamic potentials are equal if expressed in corresponding variables, one can rewrite (2.62) also for the free energy

$$F_n(T, V) = F_{s0}(T, V) + V\frac{H_c^2(T, V)}{8\pi}. \quad (2.63)$$

The function $H_c(T, P)$ defines the fundamental properties of the first order transition – the latent heat and the change of the volume at the transition point. To calculate the latent heat note that by definition the entropy in the normal state is $S_n = -\left(\frac{\partial \Phi_n}{\partial T}\right)_P$ and in the superconducting state

$$\begin{aligned} S_s &= -\left(\frac{\partial \Phi_s}{\partial T}\right)_{P,H_0} \\ &= -\left(\frac{\partial \Phi_{s0}}{\partial T}\right)_P - \left(\frac{\partial V_{s0}}{\partial T}\right)_P \frac{H_0^2}{8\pi}. \end{aligned} \quad (2.64)$$

On the other hand, differentiation of (2.62) with respect to temperature gives

$$\begin{aligned} \left(\frac{\partial \Phi_n}{\partial T}\right)_P &= \left(\frac{\partial \Phi_{s0}}{\partial T}\right)_P + \left(\frac{\partial V_{s0}}{\partial T}\right)_P \frac{H_c^2}{8\pi}, \\ &\quad + V_{s0}\frac{\partial}{\partial T}\left(\frac{H_c^2}{8\pi}\right)_P. \end{aligned} \quad (2.65)$$

Using the expression for $S_n$ and (2.64) (taken at $H_0 = H_c$) we get the change in the entropy at the phase transition

$$S_s - S_n = \frac{V_s H_c}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)_P . \tag{2.66}$$

Correspondingly the latent heat of the transition $Q = T(S_n - S_s)$ is equal to (W.H. Keesom, 1924)

$$Q = -\frac{V_s H_c T}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)_P . \tag{2.67}$$

The critical field decreases with temperature, $\left(\frac{\partial H_c}{\partial T}\right)_P \langle 0$ so $Q\rangle 0$. Thus, heat is *absorbed* at the transition from the superconducting to the normal phase. Note that in the absence of a magnetic field (at $T = T_c$), the r.h.s. of (2.66) and (2.67) vanish with $H_c$ as they must, because the transition becomes second order. On the other hand, according to Nernst's theorem both $S_s$ and $S_n$ are zero at $T = 0$. Then it follows from (2.66) that $\left(\frac{\partial H_c}{\partial T}\right)_P \to 0$ as $T \to 0$.

Similarly one can calculate the change of volume of the cylinder at the phase transition. We recall the following thermodynamic identities

$$\begin{aligned} V_n &= \left(\frac{\partial \Phi_n}{\partial P}\right)_T , \\ V_s &= \left(\frac{\partial \Phi_s}{\partial P}\right)_T \\ &= \left(\frac{\partial \Phi_{s0}}{\partial P}\right)_T + \left(\frac{\partial V_{s0}}{\partial P}\right)_T \frac{H_0^2}{8\pi} . \end{aligned} \tag{2.68}$$

Differentiating (2.62) with respect to the pressure gives

$$\begin{aligned} \left(\frac{\partial \Phi_n}{\partial P}\right)_T &= \left(\frac{\partial \Phi_{s0}}{\partial P}\right)_T + \left(\frac{\partial V_{s0}}{\partial P}\right)_T \frac{H_c^2}{8\pi} \\ &\quad + V_{s0}\frac{\partial}{\partial P}\left(\frac{H_c^2}{8\pi}\right)_T . \end{aligned} \tag{2.69}$$

Putting $H_0 = H_c$ in (2.68) and combining it with (2.69) we have

$$V_s - V_n = -\frac{V_s H_c}{4\pi}\left(\frac{\partial H_c}{\partial P}\right)_P . \tag{2.70}$$

To find the change of the specific heat at the transition line, one must differentiate (2.66) with respect the temperature. Taking into account that $C_P = T(\partial S/\partial T)_P$ and neglecting the term with $(\partial V_s/\partial T)_P$, which is usually very small, we get the change in the specific heat at constant pressure as

$$\begin{aligned} C_s - C_n &= \frac{TV_s}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)_P^2 \\ &\quad + \frac{TV_s H_c}{4\pi}\left(\frac{\partial^2 H_c}{\partial T^2}\right)_P . \end{aligned} \tag{2.71}$$

In the absence of the magnetic field ($T = T_c$, $H_c = 0$) we find the change in specific heat at the second-order transition

$$C_s - C_n = \frac{T_c V_s}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)_P^2 \tag{2.72}$$

(A.J. Rutgers, 1933). It may be noted that in the Landau mean field theory for the second-order phase transition the specific heat has a finite discontinuity at the transition line. Equation (2.72) then implies that the derivative $(\partial H_c/\partial T)_P$ is finite, i.e. that the critical field tends to zero as

$$H_c = \text{constant} \times (T_c - T) \tag{2.73}$$

(we will discuss this problem in Sect. 2.6).

## 2.5 The Intermediate State of Superconductors

In the previous section we assumed that the superconducting body placed in the magnetic field is a cylinder with the external magnetic field $\mathbf{H}_0$ directed along its axis. In this section we discuss the general case of a superconductor of any shape. However, the qualitatively important features of this general case can be understood by studying a superconducting ellipsoid. In this case the magnetic field $\mathbf{H}$ inside the superconductor is uniform. Let the external field be parallel to one of the ellipsoid axes. The vectors $\mathbf{B}$ and $\mathbf{H}$ then have the same direction and one can write

$$n\mathbf{B} + (1-n)\mathbf{H} = \mathbf{H}_0 , \tag{2.74}$$

where $n$ is the so-called *demagnetizing factor*. This factor lies in the range $0 \le n \le 1$. For a sphere $n = 1/3$. Since $\mathbf{B} = \mathbf{0}$ inside the body, one has

$$\mathbf{H} = \frac{\mathbf{H}_0}{1-n} . \tag{2.75}$$

The field outside the ellipsoid is not uniform. We will not present here the corresponding equations. It is enough to note that in the equatorial plane of the ellipsoid the field **H** has the same value as in (2.75). This follows immediately from the fact that the field both at internal and external surfaces is tangential and that the tangential components of **H** are continuous. Obviously the magnetic field is greatest on the equator and this value is larger than $H_0$. When the external field reaches the value $H_0 = (1 - n)\, H_c$, the field at the surface reaches $H_c$. When $H_0$ increases further, the sample cannot remain in a pure (homogeneous) superconducting state. However, it cannot pass as a whole into the normal state, because then the field $H_0$ would be less than $H_c$ everywhere. At first sight one might assume that the superconductivity will be initially lost in a small "belt" near the equator, the size of which would gradually increase with increasing the field. A simple analysis shows, however, that such a picture is not self-consistent. Creation of the normal belt would decrease the field near the equator and such a belt cannot exist.

This paradoxical situation has the following solution. When the field reaches the value $H_c$ on the surface, the body is divided into thin parallel alternating normal and superconducting layers (L.D. Landau, 1937 [12]). For the case of an ellipsoid all of the body is in this *intermediate state* for external fields in the range

$$(1 - n)H_c \langle H_0 \langle H_c \,. \tag{2.76}$$

In view of this one can build a simple phenomenological theory for describing the intermediate state (R.E. Peierls, 1936 [13]; F.London, 1936 [14]). The crucial idea of this theory is to introduce a magnetic induction $\overline{\mathbf{B}}$ averaged over distances that are large compared to the layer thickness and a corresponding "field" $\overline{\mathbf{H}}$. Our goal is to establish relations between these quantities.

It is obvious from the symmetry considerations that these vectors are parallel to the direction of the external field and that the layers are also parallel to this direction. Note first of all that the equation $H = H_c$ must be fulfilled on the boundaries of the normal layers. Indeed, for such a condition the thermodynamic potentials of the normal and superconducting phases are equal and any displacement of the boundary does not change the thermodynamic potential; i.e. the surface is in *neutral* equilibrium with respect to this displacement. If $H \neq H_c$ one of the phases is energetically more favorable than another. Then the boundary would move in the direction of the less favorable phase.

Since we assumed that the layers are thin, one gets for the magnetic field $B = H = H_c$ everywhere in the normal layers. On the contrary, in the superconducting layers one has $B = 0$. This means that the average induction is

$$\overline{B} = xH_c \,, \tag{2.77}$$

where $x$ is the fraction of the normal phase, i.e. the fraction of the volume that is in the normal state. In addition, $H = H_c$ in the superconducting layers due to the boundary conditions for the tangential components. Hence, $\overline{H} = H_c$.

Combining these equations with (2.74), we have for the magnetic induction and the normal phase concentration:

$$\overline{B} = xH_c = \frac{H_0}{n} - \frac{1 - n}{n} H_c \,. \tag{2.78}$$

It follows from this equation that the averaged magnetic induction depends linearly on the external magnetic field in the interval (2.76). Thus $\overline{B} = 0$ at $H_0 = (1 - n)H_c$ and $\overline{B} = H_c$ at $H_0 = H_c$.

Analogous phenomena take place for a body of non-ellipsoidal shape. However, in this case the body contains regions in both the pure superconducting and pure normal states separated by regions in the intermediate state.

## 2.6 The Ginzburg–Landau Theory

In this section we present the Ginzburg–Landau (GL) theory of superconductivity (1950) [15]. This theory gives a quantitative description of superconductors near the transition point. This was the first theory to properly take into account the quantum nature of superconductivity and it has been used for the solution of numerous problems. It was constructed before the microscopic theory of superconductivity. When the microscopic theory was created it was shown that the Ginzburg–Landau equations can be derived from this theory. This derivation yielded a

physical interpretation of the basic quantities entering the Ginzburg–Landau theory. In particular, the microscopic derivation allows a calculation of the coefficients that enter in the GL theory.

The Ginzburg–Landau theory is based on general ideas associated with the Landau theory of second-order phase transitions. The crucial point of this theory is the expansion of the free energy of the system in powers of an "order parameter" that describes the difference in symmetry of the two phases. This order parameter differs from zero below the transition point and vanishes above. One assumes that the parameter is small near $T_c$ and changes slowly in space. For the case of a superconductor the order parameter is given by the complex wave function of the superconducting pairs $\Lambda$. The free energy of the system cannot depend on the phase of the function $\Lambda$, i.e. it must be invariant under the transformation $\Lambda \to \Lambda e^{i\beta}$ where $\beta$ is a constant. The expansion of the free energy in terms of $\Lambda$ and its gradients can be written in the form

$$f = f_n + d\,|\nabla\Lambda|^2 + A\,|\Lambda|^2 + \frac{B}{2}\,|\Lambda|^4 \;, \qquad (2.79)$$

where the phenomenological coefficients $d$, $A$ and $B$ are functions on the temperature and the density of the body. The coefficients $d$ and $B$ must be positive. However, the theory has a more natural form if one introduces a new quantity $\psi$ that is proportional to $\Lambda$ in a such way that the gradient term in (2.79) corresponds to the quantum mechanical kinetic energy of a particle of mass $2m$, i.e. $\frac{\hbar^2}{4m}\left|\nabla\psi\right|^2$, where $m$ is the mass of electron. Therefore, $\psi = \left(4m/\hbar^2 d\right)^{1/2}\Lambda$. We also introduce the notation $\left|\psi\right|^2 = \frac{n_s}{2}$. We will see below that for this definition of $\psi$ the quantity $n_s$ is just the density of superconducting electrons as it was introduced in (2.43) in Sect. 2.2. $\left|\psi\right|^2$ itself is then the density of superconducting pairs. Finally, in the absence of a magnetic field, one gets for the free energy of a superconductor:

$$F = F_n + \int\left(\frac{\hbar^2}{4m}\left|\nabla\psi\right|^2 + a\left|\psi\right|^2 + \frac{b}{2}\left|\psi\right|^4\right)\mathrm{d}V \;. \qquad (2.80)$$

Here, $F_n$ is the free energy at $\psi = 0$, i.e. $F_n$ is the free energy of the normal state.

Let us consider a uniform superconductor of volume $V$. Then

$$F = F_n + aV\left|\psi\right|^2 + \frac{bV}{2}\left|\psi\right|^4 \;. \qquad (2.81)$$

The equilibrium value of the order parameter can be found by minimization of $F$. The function $\psi$ can be chosen as real. The equation $\partial F/\partial\psi = 0$ has two solutions: $\psi = 0$ and $\psi^2 = -a/b$. The first corresponds to the normal state, the second to the superconducting state. At a given temperature the stable phase is one where the free energy has a minimum. One can easily check that $\partial^2 F/\partial\psi^2 = 2aV$ for the normal and $\partial^2 F/\partial\psi^2 = -6aV$ for the superconducting phases. Respectively, the solution corresponds to a minimum if this derivative is positive. Therefore the coefficient $a$ must be positive for $T \rangle T_c$ and negative for $T \langle T_c$. In the Landau theory of phase transitions it is assumed that the coefficient $a$ can be expanded near the point $T_c$ in integral powers of $(T - T_c)$. We therefore write

$$a = \alpha\,(T - T_c) \;, \qquad (2.82)$$

where $\alpha$ is a positive function and $|T - T_c| \ll T_c$. Thus for $T \langle T_c$ one gets

$$n_s = 2\left|\psi\right|^2 = \frac{2\alpha}{b}\,(T_c - T) \;. \qquad (2.83)$$

Substituting this into (2.81), we find

$$F_s = F_n - V\frac{a^2}{2b} = F_n - V\frac{\alpha^2}{2b}(T_c - T)^2 \,. \qquad (2.84)$$

Near the transition the second term on the r.h.s. of (2.84) is small. Thus the thermodynamic potential can be written as

$$\Phi_s = \Phi_n - V\frac{\alpha^2}{2b}(T_c - T)^2 \,. \qquad (2.85)$$

A comparison of this expression with (2.62) shows that $\left(a^2/2b\right) = H_c^2/8\pi$ and

$$H_c = \left(\frac{4\pi\alpha^2}{b}\right)^{1/2}(T_c - T) \;. \qquad (2.86)$$

Of course this equation is in accordance with (2.73). Differentiating both sides of (2.84) twice, we find the discontinuity of the specific heat:

$$C_s - C_n = VT_c\frac{\alpha^2}{b} \;. \qquad (2.87)$$

In accordance with the general theory of phase transitions, the specific heat of the less symmetric, i.e. superconducting, phase is higher.

The following remark should be made in connection with (2.80). The presence of the gradient term in the equation means that the Ginzburg–Landau theory contains a characteristic parameter, $\xi(t)$, with the dimensions of length. Let us consider a non-uniform distribution where the function $\psi(\mathbf{r})$ changes with distance. Such non-uniformity will significantly change the energy if the gradient term $(1/4m)\left|\nabla\psi\right|^2$ is of the order of $a\left|\psi\right|^2$. Thus, it is natural to define the length $\xi$ as

$$\xi(T) \sim \xi_0 \left(\frac{T_c}{T_c - T}\right)^{1/2} \gg \xi_0 . \tag{2.88}$$

This quantity is called the correlation or healing length. It defines a typical scale for the change of the wave function. We will see that the ratio $\hbar/(m\alpha T_c)^{1/2}$ is of the order of $\xi_0 \sim \hbar v_F/T_c$, see microscopic expressions for the coefficients of the Ginzburg–Landau equations. Thus, in the range of applicability of the Ginzburg–Landau theory

$$\xi(T) \sim \xi_0 \left(\frac{T_c}{T_c - T}\right)^{1/2} \gg \xi_0 . \tag{2.89}$$

Equation (2.89) is valid near the transition point. However, it must give the correct order of magnitude for $T \to 0$. Thus, the quantity $\xi_0$ has the physical meaning of the correlation length at zero temperature.

Let us now consider the behaviour in the presence of a magnetic field. The density of magnetic energy $\mathbf{B}^2/8\pi$ must be added in the integrand (2.80). But this is insufficient in that the gradient term in (2.80) is not invariant with respect to the gauge transformation (2.38)-(2.41) . To restore the invariance, one must substitute for $\left|\nabla\psi\right|^2$ the combination $\left|\left[\nabla - i\,(2e/\hbar c)\,\mathbf{A}\right]\psi\right|^2$, which is obviously gauge-invariant. The final expression for the free energy then takes the form:

$$F = F_n + \int\left(\frac{\hbar^2}{4m}\left|\left(\nabla - i\frac{2e}{\hbar c}\mathbf{A}\right)\psi\right|^2 + a\left|\psi\right|^2 + \frac{b}{2}\left|\psi\right|^4 + \frac{\mathbf{B}^2}{8\pi}\right)\mathrm{d}V . \tag{2.90}$$

Here, the magnetic induction must be expressed as $\mathbf{B} = \operatorname{curl}\mathbf{A}$. One can obtain the basic equations of the Landau–Ginzburg theory by varying this functional with respect to $\mathbf{A}$ and $\psi^*$. Carrying out first the variation with respect to $\mathbf{A}$, we find after a simple calculation:

$$\delta F = \int\left[c\frac{ie\hbar}{2m}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) + \frac{2e^2}{m}\left|\psi\right|^2\mathbf{A} + \frac{\operatorname{curl}\mathbf{B}}{4\pi}\right]\delta\mathbf{A}\,\mathrm{d}V + \int \operatorname{div}\,(\delta\mathbf{A}\times\mathbf{B})\,\frac{\mathrm{d}V}{4\pi} = 0 . \tag{2.91}$$

The second integral can be transformed into an integral over a remote surface and disappears. To minimize the free energy, the expression in the brackets must be equal to zero. This results in the Maxwell equation

$$\operatorname{curl}\mathbf{B} = \frac{c}{4\pi}\mathbf{j} , \tag{2.92}$$

provided that the current density is given by

$$\mathbf{j} = \frac{ie\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right) + \frac{2e^2}{mc}\left|\psi\right|^2\mathbf{A} . \tag{2.93}$$

According to the definition of $n_s$ we can substitute $\psi = \sqrt{n_s/2}\exp\left(i\chi\right)$. Then (2.93) becomes

$$\mathbf{j} = \frac{e\hbar}{2m}n_s\left(\nabla\chi - \frac{2e}{\hbar c}\mathbf{A}\right) . \tag{2.94}$$

Equation (2.94) coincides with (2.43). This justifies our identification of $2\left|\psi\right|^2$ with $n_s$. Variation of (2.90) with respect $\psi^*$ gives, after a simple integration by parts,

$$\delta F = \int\left[-\frac{\hbar^2}{4m}\left(\nabla - i\frac{2e}{\hbar c}\mathbf{A}\right)^2\psi + a\psi + b\left|\psi\right|^2\psi\right]\delta\psi^*\mathrm{d}V + \frac{\hbar^2}{4m}\oint\left(\nabla\psi - i\frac{2e}{\hbar c}\mathbf{A}\psi\right)\delta\psi^*\cdot\mathrm{d}\mathbf{S} = 0 . \tag{2.95}$$

The second integration is over the surface of the sample. The volume integral vanishes when

$$-\frac{\hbar^2}{4m}\left(\nabla - i\frac{2e}{\hbar c}\mathbf{A}\right)^2\psi + a\psi + b\left|\psi\right|^2\psi = 0 . \tag{2.96}$$

Equations (2.92) and (2.96) form the complete system of equations of the Ginzburg–Landau (GL) theory. It is interesting to note that in the original paper these equations were written with the electric charge $e$ instead of $2e$. The reason is that at that time the phenomenon of the pairing of electrons was not known. The correct version of the equations was established by L.P. Gor'kov (1959).

The surface integral in (2.95) yields the boundary condition

$$\left(\nabla\psi - i\frac{2e}{\hbar c}\mathbf{A}\psi\right)\cdot\mathbf{n} = 0 \tag{2.97}$$

on the surface of the superconductor, where $\mathbf{n}$ is the vector normal to the surface. This condition guarantees the absence of a supercurrent through the surface. It is worth noting that (2.97) does not imply that $\psi = 0$ on the surface as it would be natural to assume for a wave function. Actually $\psi$ decreases to zero within atomic distances at the surface. Such distances, however, cannot be considered on the basis of the GL theory.

The induction $\mathbf{B}$ does not need any special boundary conditions. Equations (2.92), (2.93) are valid in the entire space. (Outside the body, of course, $\mathbf{j} = 0$.) Thus the vector $\mathbf{B}$ is continuous at the surface.

The GL equations are non-linear with the result that the distribution of the field in the superconductor depends on its strength. Because of this the density of superconducting electrons in (2.94) depends on position even in a uniform superconductor. However, this effect is small if the field is weak; i.e. $B \ll H_c$. In this case one can assume that $n_s$ is constant and is given by (2.83). Then (2.94) is equivalent to the London equation (2.45) and the penetration of the magnetic field is described by (2.51), where the penetration depth is given by:

$$\delta = \left[\frac{mc^2 b}{8\pi e^2 \alpha\,(T_c - T)}\right]^{1/2}. \tag{2.98}$$

Note that this quantity has the same temperature dependence as the coherence length $\xi$. However the physical meaning of these parameters $\delta$ and $\xi$ is different. The parameter $\xi$ defines the scale of the spatial change of the wave function $\psi$, while $\delta$ defines the scale over which the magnetic field changes. The ratio of these two lengths, $\kappa$, does not depend on temperature:

$$\kappa = \frac{\delta}{\xi} = \frac{mcb^{1/2}}{(2\pi)^{1/2}\,\hbar\,|e|}. \tag{2.99}$$

Using (2.86) one can also express $\kappa$ in terms of the directly observable quantities:

$$\kappa = 2\sqrt{2}H_c\delta^2\frac{|e|}{\hbar c}. \tag{2.100}$$

The Ginzburg–Landau parameter $\kappa$ depends on the properties of the material and characterizes the superconductor. We will see in the next section that the behavior of superconductors in a magnetic field with small and large values of $\kappa$ is completely different. Actually in the framework of the GL theory $\kappa$ is the only parameter necessary to describe a superconductor. This can be seen after transforming the equations to dimensionless variables. It is convenient to introduce these variables as

$$\overline{\psi} = \psi\sqrt{\frac{b}{|a|}},\ \overline{\mathbf{r}} = \frac{\mathbf{r}}{\delta},\ \overline{\mathbf{A}} = \frac{\mathbf{A}}{H_c\delta},\ \overline{\nabla} = \frac{\partial}{\partial\overline{\mathbf{r}}},$$
$$\overline{\mathbf{B}} = \overline{\mathrm{rot}}\,\overline{\mathbf{A}} = \frac{\mathbf{B}}{H_c}, \tag{2.101}$$

with $\overline{\mathrm{rot}}\,\overline{\mathbf{A}} = \overline{\nabla}\times\overline{\mathbf{A}}$. Substituting these variables into (2.96) and (2.92) yields

$$\left(-i\overline{\nabla} - \kappa\overline{\mathbf{A}}\right)^2\overline{\psi} + \kappa^2\left(-\overline{\psi} + \left|\overline{\psi}\right|^2\overline{\psi}\right) = 0 \tag{2.102}$$

and

$$\kappa\overline{\mathrm{rot}}\,\overline{\mathrm{rot}}\,\overline{\mathbf{A}} = \frac{i}{2}\overline{\psi}\,\overline{\nabla}\,\overline{\psi}^* - \overline{\psi}^*\overline{\nabla}\overline{\psi} - \kappa\left|\overline{\psi}\right|^2\overline{\mathbf{A}}. \tag{2.103}$$

As said, the values of the parameter $\kappa$ differ widely among superconductors. The majority of the "good", or rather pure metals have a relatively small $\kappa \sim 0.01$ to 0.2. For superconducting alloys large values of $\kappa$ are typical. The new HTC superconductors are very anisotropic substances. Correspondingly the values for $\kappa$ depend on direction and can range from 50 to 500.

In conclusion, let us consider briefly the conditions for the applicability of the GL theory. As we have

already mentioned these equations are valid only near the transition, i.e. for $(T_c - T) \ll T_c$. However, this is insufficient for superconductors with small $\kappa$. The point is that the penetration depth $\delta$ must be large compared to the correlation length $\xi_0$ (see (2.55)–(2.56)). It is not difficult to show that this condition can be written as

$$(T_c - T) \ll \kappa^2 T_c \,. \tag{2.104}$$

The GL equations are also not valid too close to $T_c$, because the validity of the Landau mean-field theory of phase transitions breaks down in this region due to fluctuations of the order parameter. The associated theory gives the criterion (2.80)

$$(T_c - T) \gg \frac{b^2 T_c^2 m^3}{\hbar^6 \alpha} \,. \tag{2.105}$$

We will estimate the coefficients $\alpha$ and $b$ using the microscopical theory in Sect. 3.3.3. Substitution of the corresponding expressions in (2.105) shows that the r.h.s. of this inequality is very small for usual superconductors. However, this condition may be important for the HTC materials.

## 2.7 Surface Energy at the Boundary Between Normal and Superconducting Phases

As we showed in Sect. 2.4, a superconductor in the intermediate state is divided into alternating layers of normal and superconducting phases. The boundaries between these regions involve a surface energy. In this section we will calculate this energy with the help of the Ginzburg–Landau theory. This energy is an important characteristic of a superconductor and a knowledge of it is necessary for developing a full theory for the intermediate state. A positive value of this surface energy is a necessary condition of the stability of this state. However, we will see that this is not the case for sufficiently large values of the GL parameter $\kappa$. This result plays an important role in understanding type II superconductors.

To calculate the surface energy one must consider the structure of the transition layer between the normal and superconducting regions. In Sect. 2.4 this layer was considered as infinitesimally thin. Because the thickness of this layer is much less than the distances between layers, it is sufficient to consider a single boundary separating normal and superconducting half-spaces. Let us take the axis $x$ perpendicular to the layers and directed into the superconducting phase. All quantities under consideration will depend on the $x$ coordinate only; i.e. the problem is one-dimensional. We can assume that the induction vector $\mathbf{B}$ is directed along the $z$-axis. Then the vector-potential $\mathbf{A}$ can by chosen along the $y$-axis and

$$B = \frac{\mathrm{d}A}{\mathrm{d}x} \,. \tag{2.106}$$

We must solve the GL equations (2.92) and (2.96) for this one-dimensional problem subject to the boundary conditions for the $s$-$n$ boundary established in Sect. 2.4:

$$\begin{aligned} &x \to -\infty, \psi \to 0, B \to H_c \,, \\ &x \to \infty, \psi \to (|a|/b)^{1/2}, B \to 0 \,. \end{aligned} \tag{2.107}$$

Note that (2.106) defines $A$ only up to an arbitrary constant. We will fix this constant by the condition $A \to 0$ at $x \to \infty$.

Before proceeding with the calculations one must formulate the exact thermodynamic definition of the surface energy. This is a delicate problem. The main point is to use the correct thermodynamic potential. As a first step let us define the magnetic field strength $\mathbf{H}$ at every point of the body. To do this let us introduce the magnetization $\mathbf{m}$ by curl $\mathbf{m} = \mathbf{j}/c$. (This is possible because in the stationary case div $\mathbf{j} = 0$.) Then $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{m}$ and (2.92) takes the form

$$\operatorname{curl} \mathbf{H} = 0 \,. \tag{2.108}$$

In our one-dimensional problem this means that $dH/dx = 0$ and $H = \text{const}$. The boundary conditions yield

$$H = H_c \tag{2.109}$$

everywhere. Equation (2.109) is our condition for thermodynamic equilibrium together with the condition of constant temperature. Our problem is analogous to the condition of constant chemical potential $\mu$ at the liquid–gas phase transition. The thermodynamic potential must be written with respect to the variables $(T, H)$. The condition (2.109) can then

be imposed explicitly. (Note that in analogy to the definition of the surface tension at the liquid–gas boundary one must use the thermodynamic potential $\Omega$ with respect to the variables $T$, $\mu$; see, for example [16]). The free energy density $f$ is the thermodynamic potential with respect to the variables $T$, $\mathbf{B}$:

$$df = -SdT + \mathbf{H} \cdot d\mathbf{B}/4\pi \,, \tag{2.110}$$

(see [17]). We suppressed the gradient term here. We introduce a new thermodynamic potential

$$\widetilde{f} = f - \frac{\mathbf{H}.\mathbf{B}}{4\pi} \tag{2.111}$$

from which we obtain

$$d\widetilde{f} = -SdT - \mathbf{B}.d\mathbf{H}/4\pi \,. \tag{2.112}$$

Thus, $\widetilde{f}(T, \mathbf{H})$ is the desired thermodynamic potential with respect to the variables $T$, $\mathbf{H}$. Adding the gradient term we can write an expression for $\widetilde{f}$. Prior to doing this we introduce some simplifications. The point is that for the particular symmetry of our problem $\mathbf{A}.\nabla\,\psi = \psi\nabla.\mathbf{A} = 0$. As a result, the imaginary terms drop out of the GL equations and $\psi$ can be chosen as real. Taking this into account we get

$$\widetilde{f}\,(T, H_c) = f_n + \left[\frac{\hbar^2}{4m}\left(\psi'^2 + \frac{4e^2}{\hbar^2 c^2}A^2\psi^2\right) + a\psi^2 + \frac{b}{2}\psi^4 + \frac{B^2}{8\pi} - \frac{H_c B}{4\pi}\right] \tag{2.113}$$

(the prime denoting differentiation with respect to $x$). Using (2.86) and the boundary conditions (2.107) it is not difficult to show that the function $\widetilde{f}$ tends to the same constant value when $x \to \infty$ and $x \to -\infty$:

$$\widetilde{f} \to \widetilde{f}_\infty = f_n - \frac{a^2}{2b} = f_n - \frac{H_c^2}{8\pi}\,, \quad x \to \pm\infty \,. \tag{2.114}$$

This constant term gives a contribution proportional to the volume. For calculating the surface energy one has to subtract this contribution. Finally, the surface energy (or the surface tension) of the boundary between the normal and superconducting phases is $\int\left[\widetilde{f}\,(x) - \widetilde{f}_\infty\right]\mathrm{d}x$ or

$$\sigma_{sn} = \int_{-\infty}^{\infty}\left[\frac{\hbar^2}{4m}\left(\psi'^2 + \frac{4e^2}{\hbar^2 c^2}A^2\psi^2\right) + a\psi^2 + \frac{b}{2}\psi^4 + \frac{B^2}{8\pi} - \frac{H_c B}{4\pi} + \frac{H_c^2}{8\pi}\right]\mathrm{d}x \,. \tag{2.115}$$

This can be written as

$$\sigma_{sn} = \frac{H_c^2\delta}{8\pi}\int_{-\infty}^{\infty}\left[\frac{2}{\kappa^2}\overline{\psi}'^2 + \left(\overline{A}^2 - 2\right)\overline{\psi}^2 + \overline{\psi}^2 + \overline{\psi}^4 + \left(\overline{A}' - 1\right)^2\right]\mathrm{d}\overline{x} \,. \tag{2.116}$$

In the rest of this section we will omit the overbars, because only dimensionless quantities will be used. The GL equation (2.102) and (2.103) for our one-dimensional problem take the form:

$$\psi'' - \kappa^2\left[\left(\frac{1}{2}A^2 - 1\right)\psi + \psi^3\right] = 0 \tag{2.117}$$

and

$$A'' - A\psi^3 = 0 \,. \tag{2.118}$$

The boundary conditions (2.107) are

$$\psi = 0, B = A' = 1, \text{ for } x \to -\infty\,, \quad \text{and}$$
$$\psi = 1, A' = 0, \text{ for } x \to \infty \,.$$

Note that the boundary condition $A = 0$ at $x \to \infty$, which we imposed previously, follows from (2.118) and (2.119). This means that this condition and our restriction that $\psi$ is real are actually not independent. Equations (2.117) and (2.118) give

$$\frac{2}{\kappa^2}\psi'^2 + A'^2 - \left(A^2 - 2\right)\psi^2 - \psi^4 = \text{constant} \,. \tag{2.119}$$

This can be verified directly. One can also use a mechanical analogy. Equations (2.117) and (2.118) can be derived by minimization of the integral $\int_{x_1}^{x_2} L\mathrm{d}x$ with the "Lagrangian" $L = (2/\kappa^2)\psi'^2 + A'^2 + \left(A^2 - 2\right)\psi^2 + \psi^4$. Expression (2.119) is then the "energy", which is obtained from $L$ by changing the sign of the "potential energy". It follows from the boundary conditions that this energy must equal unity. Thus, we have

$$\frac{2}{\kappa^2}\psi'^2 + A'^2 - \left(A^2 - 2\right)\psi^2 - \psi^4 = 1 \,. \tag{2.120}$$

The expression (2.116) for the surface tension can be presented in different forms as

$$\sigma_{sn} = \frac{H_c^2\delta}{4\pi}\int\limits_{-\infty}^{\infty}\left[\frac{2}{\kappa^2}\psi'^2 + A'\left(A'-1\right)\right]\mathrm{d}x$$
$$= \frac{H_c^2\delta}{8\pi}\int\limits_{-\infty}^{\infty}\left[\left(A'-1\right)^2 - \psi^4\right]\mathrm{d}x\,. \qquad (2.121)$$

The first form is obtained with the help of (2.120), while the second follows from integrating the term $\psi'^2$ by parts and substituting $\psi''$ from (2.117).

Calculating $\sigma_{sn}$ requires numerical integration of the equations. An analytical result can be obtained in the limiting case $\kappa\langle\langle 1$ when $\delta(T)\langle\langle\xi(T)$. In this case the magnetic field penetrates only slightly into the superconducting phase. (It is not difficult to show that the penetration depth in this non-uniform problem is of the order $1/\sqrt{\kappa}$.[3]) The wave function $\psi$ is small in this region and gives only a small contribution to $\sigma_{sn}$. The main contribution arises from the region where $\psi$ changes rapidly, which is of the order of $1/\kappa$. The situation is illustrated in Fig. 2.1.

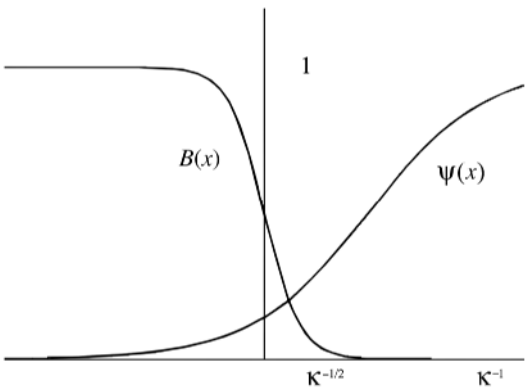


**Fig. 2.1.** Distribution of the magnetic field and order parameter in the transition layer between the normal and superconducting phases

There is no magnetic field in this region and one can put $A = 0$ in (2.120). Solving this equation for $\psi'$, we have

$$\psi' = \frac{\kappa}{\sqrt{2}}(1-\psi^2)\,. \qquad (2.122)$$

This equation has a simple solution

$$\psi = \tanh\left(\kappa x/\sqrt{2}\right)\,. \qquad (2.123)$$

We can now calculate the surface tension. It is convenient to use the second expression (2.121). However the integration must be taken from 0, because (2.123) was derived for distances $x \sim 1/\kappa\rangle\rangle 1$, which give the main contribution, and has no meaning for negative $x$. Then,

$$\sigma_{ns} = \frac{\sqrt{2}H_c^2\delta}{8\pi\kappa}\int\limits_{0}^{\infty}\left(1-\tanh^4 x\right)\mathrm{d}x$$
$$= \frac{4\sqrt{2}}{3\kappa}\frac{H_c^2}{8\pi}\,. \qquad (2.124)$$

It already follows from (2.124) that $\sigma_{ns}$ decreases as $\kappa$ increases. For sufficiently large $\kappa$ the surface tension becomes negative. This follows from the first expression (2.121). At large $\kappa$ one can neglect the first term in the integrand. (It is important that the transition region, where $\psi$ changes significantly, cannot be thinner than the penetration depth for the magnetic field, since any change in $B$ causes a change in $\psi$.) Then the integral is negative because $A' = B$ is positive and less than 1. In terms of unscaled quantities this means that $B\langle H_c$. Actually $\sigma_{sn}$ becomes zero for

$$\kappa = \frac{1}{\sqrt{2}}\,. \qquad (2.125)$$

This result was established By V. Ginzburg and L. Landau by means of a numerical calculation. Here we will present an analytical derivation. Let us introduce the notations

$$r = A' + \psi^2 - 1,\ s = 2\psi' + A\psi^2\,. \qquad (2.126)$$

Then the second expression (2.121) can be rewritten as

$$\sigma_{sn} = \frac{H_c^2\delta}{8\pi}\int\limits_{-\infty}^{\infty}\left[\left(A'-1\right) - \psi^2\right]r\mathrm{d}x\,. \qquad (2.127)$$

[3] Let us consider the distance $x \ll 1/\kappa$ and $\kappa^2A^2 \ll 1$. Then one can neglect the right-hand side of (2.117) and its solution matched to (2.123) is $\psi = \kappa x/\sqrt{2}$. Substituting this into (2.118), we find $A'' = \kappa^2x^2A/2$. It follows from this equation that the characteristic length of variation of $A$ is of the order of $1/\kappa^{1/2}$.

Correspondingly we can also rewrite (2.117) and (2.118) as

$$\left(\frac{2}{\kappa^2}-4\right)\psi'^2+s^2-2As+r^2 +2\left(1-\psi^2\right)r=0 \quad (2.128)$$

and

$$r'-\psi s=0\,. \quad (2.129)$$

It is now obvious that for $\kappa^2=1/2$ both (2.128) and (2.129) are fulfilled if

$$r=s=0\,. \quad (2.130)$$

Furthermore, these equations are compatible with the boundary conditions (2.119), because $r$ and $s$ are, according to these conditions, equal to zero both in the normal and superconducting phases. Finally, we have $\sigma_{sn}=0$ by virtue of (2.127).

## 2.8 Superconductors of the Second Kind

Results of the previous section explain the existence of two kinds of superconductors: superconductors of the first and second kinds or type I and type II. Superconductors of the first kind have a positive surface energy $\sigma_{sn}$. Superconductors with $\sigma_{sn}<0$ are superconductors of the second kind. Therefore, near $T_c$ superconductors with $\kappa\langle 1/\sqrt{2}$ are of the first kind and those with $\kappa\rangle 1/\sqrt{2}$ are of the second kind.

The main difference between these two types of superconductors is in the character of the phase transition. A sharp boundary between two phases is possible only if the surface tension of the interface is positive. Thus, our discussion of the phase transition in previous sections relates only to type I superconductors.

We now consider the phase transition in superconductors of the second kind. As in Sect. 2.4 we consider a cylindrical superconductor in a longitudinal magnetic field. For a superconductor of the first kind superconductivity is destroyed when the external magnetic field $H_0$ reaches the critical value $H_c$, which is defined by the thermodynamic properties of the material. For $H_0\rangle H_c$ the sample will be entirely in the normal state. For a sample with negative surface tension, however, it is favorable to have a "mixture" of normal and superconductive phases for magnetic fields around $H_c$. The loss in the volume energy can be compensated by a gain in surface energy. The magnetic field penetrates the superconductor over a range of fields $H_{c1}\langle H_0\langle H_{c2}$. The *thermodynamic* field $H_c$ must lie inside this interval. However, it has no special significance for the phase transition of superconductors of the second kind.

A cylindrical superconductor in this range of fields is said to be in the *mixed state*. The nature of this state was established by A.A. Abrikosov [18]. We will discuss thus in the next sections. However, the value of the upper critical field $H_{c2}$ can be calculated even without the detailed theory of the mixed state (V.L. Ginzburg, L.D. Landau, 1950 [15]). It is enough to note that just below $H_{c2}$ the value of $\psi$ in the superconducting regions must be small. Therefore this region can be described by a linearized Ginzburg–Landau equation. For the same reason we can also neglect perturbations of the external field. Omitting the non-linear ($|\psi|^2\psi$) term in (2.96) and assuming that the vector potential corresponds to the uniform external field $\mathbf{H}_0$, we have

$$\frac{1}{4m}\left(-i\hbar-\frac{2e}{c}\mathbf{A}_0\right)^2\psi=|a|\,\psi\,. \quad (2.131)$$

We assume that $T\langle T_c$, so that $a\langle 0$. We seek a solution where $\psi\to 0$ at infinity.

Equation (2.131) coincides with the Schrödinger equation for a particle of mass $2m$ and charge $2e$ in a magnetic field $\mathbf{H}_0$. The boundary conditions are also the same. The quantity $|a|$ plays the role of the energy. The minimum energy of a such particle in a uniform magnetic field is

$$\varepsilon_0=\frac{1}{2}\hbar\omega_B=\frac{1}{2}\frac{\hbar|e|H_0}{mc}\,. \quad (2.132)$$

Hence, equation (2.131) has a solution only if $|a|\rangle\hbar|e|B_0/2mc$ or equivalently if the magnetic field is less than an upper critical field

$$H_{c2}=\frac{2mc|a|}{\hbar|e|}=\frac{\phi_0}{2\pi\xi^2}\,. \quad (2.133)$$

Using (2.86) and (2.99) one can rewrite this equation in the form

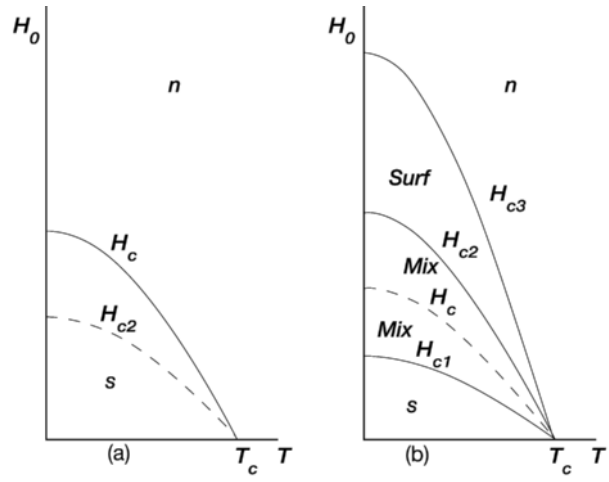


**Fig. 2.2.** Phase diagrams of superconductors of the first (**a**) and second (**b**) kinds

$$H_{c2} = \kappa\sqrt{2}H_c \tag{2.134}$$

(A.A. Abrikosov, 1952 [21]). Equation (2.134) confirms the above conclusion that for superconductors of the second kind, when $\kappa \rangle \sqrt{2}$, a superconducting order parameter can appear in a normal sample at fields larger than $H_c$.

Equation (2.134) defines the upper critical field for type II superconductors where $\kappa \rangle 1/\sqrt{2}$. However, this equation also has a meaning for type I superconductors when $H_{c2} \langle H_c$. Here $H_{c2}$ defines the "boundary for supercooling" of the normal state. For $H_0 \langle H_{c2}$ the thermodynamically unfavorable normal state becomes absolutely unstable because of the possibility of creating a superconducting nucleus. In the interval $H_{c2} \langle H_0 \langle H_c$ the normal phase is metastable.

In conclusion, we note that the condition for the appearance of superconducting regions is different near the surface of a superconductor. Here one has to use the boundary condition $\mathrm{d}\psi/\mathrm{d}x = 0$, where the $x$-axis is a normal to the surface. In this case (2.131) gives

$$H_0 \langle H_{c3} = 1.7 H_{c2} = 2.4 H_c \tag{2.135}$$

(D. Saint–James and P.G. de Gennes, 1963 [19]). For fields $H_{c2} \langle H_0 \langle H_{c3}$ one has a state with *surface* superconductivity. The density of superconducting electrons is different from zero for a surface layer with a thickness of the order of $\xi(T)$. The case where $H_{c2} \langle H_c \langle H_{c3}$ corresponds to a special kind of superconductor. The mixed phase does not exist in this case, but there is surface superconductivity for the interval $H_c \langle B_0 \langle H_{c3}$.

The phase diagrams for the superconductors of the first and the second kinds are shown schematically in Fig. 2.2(a) and (b), respectively.

## 2.9 Quantized Vortex Lines

In this section we will consider the structure of the mixed state. (For more details see [20].) The main problem is to understand how the magnetic field can penetrate into the bulk of the superconductor. Let us again consider a superconducting cylinder in a magnetic field $H_0$. It is natural to expect that the normal regions, with their accompanying magnetic field, are cylindrical tubes parallel to the field. To obtain the maximum gain in the (negative) surface energy, the number of these tubes must be as large as possible. However, there is a restriction. The magnetic flux inside such a tube must be an integral multiple $n$ of the flux quantum $\phi_0 = \pi\hbar c/|e|$ introduced in Sect. 2.3. As we will see later the total gain in surface energy is largest for $n = 1$, which results in the largest number of tubes. The proof follows immediately by applying the arguments of this section to each tube. This is obvious when there is no overlapping of the magnetic tubes, i.e. when their number is small enough, a condition which in any case will apply near the lower critical field $H_{c1}$.

Thus the magnetic tube must possess a minimal flux $\phi_0$. The magnetic field is concentrated inside the tube. At large distances from the tube it is shielded by the annular superconducting current flowing around the tube. This current is the analog of the superfluid velocity field surrounding the vortex lines in a superfluid liquid which we discussed in Sect. 2.1. We can then picture the mixed state as an array of quantized vortex lines. Such vortex lines were predicted by A.A. Abrikosov in 1957. Their existence is crucial for explaining the properties of type II superconductors.

Our first task is to calculate the lower critical field $H_{c1}$ for our superconducting cylinder. This field can be found from the condition that the penetration of a single vortex line becomes thermodynamically favorable. Again the problem is to choose the correct thermodynamical potential. The situation here is analogous to the one in Sect. 2.7. We must again define the magnetic strength $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$ at every point of the cylinder. Because of the symmetry of the problem, $\mathbf{H}$ is directed along the axis of the cylinder and on the boundary one has continuity of the tangential components $\mathbf{H} = \mathbf{H}_0$. The Maxwell equation curl $\mathbf{H} = 0$ will be satisfied if

$$\mathbf{H} = \mathbf{H}_0 \tag{2.136}$$

everywhere. As in Sect. 2.7 this means that we must consider the thermodynamic equilibrium at fixed $\mathbf{H}$ (as well as temperature and volume), i.e. use the thermodynamic potential

$$\tilde{F} = F - \frac{1}{4\pi}\int \mathbf{H}\cdot\mathbf{B}\mathrm{d}V\,, \tag{2.137}$$

where $F$ is the free energy. Taking into account equation (2.136), we can rewrite (2.137) as

$$\tilde{F} = F - \frac{H_0}{4\pi}\int B\mathrm{d}V\,. \tag{2.138}$$

There are two contributions in (2.138) in the presence of a vortex line. The magnetic induction inside the tube gives the magnetic energy in the external field $-H_0\int B\mathrm{d}V/4\pi = -H_0\phi_0 L/4\pi$. On the other hand, the presence of a vortex line increases the free energy of the superconducting media, $F = F_s + \varepsilon L$, where $\varepsilon$ is the energy per unit of length. Thus,

$$\tilde{F} = F_s + \varepsilon L - \phi_0 H_0 L/4\pi\,. \tag{2.139}$$

The presence of the vortex line is thermodynamically favorable if the contribution is negative; i.e. if $\varepsilon L - \phi_0 H_0 L/4\pi \langle 0$, or

$$H_0 \rangle H_{c1} = \frac{4\pi\varepsilon}{\phi_0}\,. \tag{2.140}$$

This is a general equation which defines the lower critical field $H_{c1}$ at arbitrary temperatures. Near the transition temperature $T_c$ one can calculate the energy $\varepsilon$ using the Ginzburg–Landau theory. In this approximation one must numerically integrate the set of equations (2.92)–(2.96). However, the problem can be solved analytically in the important case where

$$\delta \gg \xi \tag{2.141}$$

(near $T_c$ this means $\kappa \gg 1$). In this case one has a natural separation of the scales over which the quantities entering the problem vary. The coherence length $\xi$ determines the distance over which the order parameter varies from zero on the axis of the vortex to its constant bulk value deep in the superconducting phase. Thus, at distances $r \gg \xi$ the density of superconducting electrons is equal to its bulk value $n_s$. On the contrary, the magnetic induction $B(r)$ varies over the larger distances $\delta \gg \xi$. Thus most of the magnetic flux passes through the region where $n_s \cong$ const. This is important for the calculation of the energy $\varepsilon$. In this region we can use the London equation. We begin the calculation with (2.43).

The behavior of the magnetic field and the order parameter near the core of the vortex is shown schematically in the Fig. 2.3.

Substituting $\mathbf{j}_s$ from the Maxwell equation, we can rewrite (2.43) as:

$$\mathbf{A} + \delta^2 \mathrm{curl}\,\mathbf{B} = \phi_0\nabla\chi/2\pi\,. \tag{2.142}$$

The phase $\chi$ in the presence of a vortex line is not a single-valued function of the coordinates. For a vortex line with the minimum flux $\phi_0$, the phase increases by $2\pi$ on traversing a closed contour that encloses the line. (Actually for a single line the order parameter is proportional to $e^{i\varphi}$, where $\varphi$ is the angle in cylindrical coordinates.) Thus the integral along such a contour is

$$\oint \nabla\chi\cdot\mathrm{d}\mathbf{l} = 2\pi\,. \tag{2.143}$$

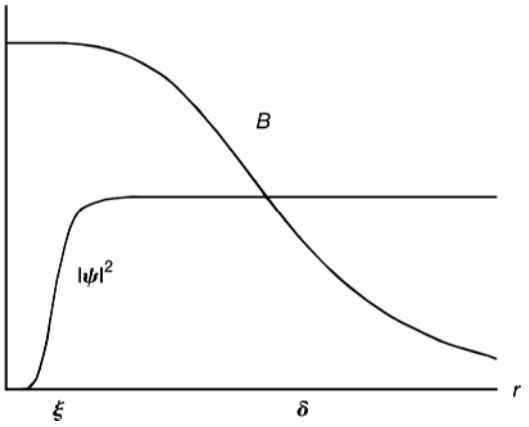


**Fig. 2.3.** Distribution of the magnetic field and order parameter near the core of the vortex line in a superconductor of the second kind

Integrating (2.142) we find

$$\oint \left(\mathbf{A} + \delta^2 \operatorname{curl} \mathbf{B}\right) \cdot \mathrm{d}\mathbf{l} = \phi_0 \,. \tag{2.144}$$

We will see below that for the calculation of the energy, relatively small distances from the axis are important. It is not difficult to check that in the range

$$\delta \gg r \gg \xi \tag{2.145}$$

the second term on the l.h.s. of (2.144) gives the main contribution. We take as the contour of integration in (2.144) a circle of radius $r$. For this geometry the vector curl $\mathbf{B}$ has only one component $(\operatorname{curl} \mathbf{B})_\varphi$ along the contour. The integration is then simple and we have

$$(\operatorname{curl} \mathbf{B})_\varphi = -\frac{\mathrm{d}B}{\mathrm{d}r} = \frac{\phi_0}{2\pi r \delta^2} \,. \tag{2.146}$$

Equation (2.146) has a very simple physical meaning. According to the Maxwell equation we have $(\operatorname{curl} \mathbf{B})_\varphi = \frac{4\pi}{c} e n_s v_{s\varphi}$. Equation (2.146) then gives $v_{s\varphi} = \hbar/2mr$ for the superfluid velocity as it must be for a vortex line in a superfluid of particles with mass $2m$. Integrating of (2.146) for the induction gives

$$B(r) = \frac{\phi_0}{2\pi\delta^2} \log \frac{\delta}{r} \,. \tag{2.147}$$

This equation is valid in the interval (2.145) with logarithmic accuracy. A more exact expression will be obtained in the next section.

We can now calculate the energy $\varepsilon$ of a vortex line. The magnetic part of the free energy corresponding to the London equations is given by the integral

$$F_B = \frac{1}{8\pi} \int \left[\mathbf{B}^2 + \delta^2 (\operatorname{curl} \mathbf{B})^2\right] \mathrm{d}V \,. \tag{2.148}$$

Indeed, by varying the expression with respect to $\mathbf{B}$ we immediately obtain the London equation (2.45). The coefficient follows from the condition that for $\delta = 0$ (2.148) coincides with the energy of the magnetic field in vacuum. The main contribution to the integral is due to the second term, which contains a logarithmic divergence. Substituting (2.146) into (2.148) and integrating in the range (2.145), we obtain for the energy per unit length of the vortex line

$$\varepsilon = \left(\frac{\phi_0}{4\pi\delta}\right)^2 \log\left(\frac{\delta}{\xi}\right) \,. \tag{2.149}$$

This expression also has only logarithmic accuracy, i.e. the constant under the logarithm is not defined. Equation (2.149) explains why only vortex lines with the minimum flux $\phi_0$ are most favorable. The energy of a line is proportional to the square of its magnetic flux. Thus the fragmentation of one line with the flux $n\phi_0$ into $n$ lines with flux $\phi_0$ results in an $n$-fold gain in energy. Substituting (2.149) in (2.140), we find the lower critical field

$$H_{c1} = \frac{\phi_0}{4\pi\delta^2} \log\left(\frac{\delta}{\xi}\right) \,. \tag{2.150}$$

It is worth noting that according to (2.147) near the axis, for $r \sim \xi$, the induction is $B(\xi) \approx 2H_{c1}$. Near $T_c$ in the Ginzburg–Landau region this equation can be expressed in terms of the parameter $\kappa$

$$H_{c1} = H_c \frac{\log \kappa}{\kappa\sqrt{2}} \,. \tag{2.151}$$

A comparison of (2.151) and (2.134) shows that for $\kappa \rangle\rangle 1$ the following inequalities are satisfied:

$$H_{c1} \ll H_c \ll H_{c2} \,. \tag{2.152}$$

Numerical solution of the Ginzburg–Landau equations allows us to calculate the coefficient under the logarithm. The result is:

$$H_{c1} = H_c \frac{\log(1.08\kappa)}{\kappa\sqrt{2}} \,. \tag{2.153}$$

Note that the more exact equation (2.153) is still only valid for large $\kappa$. For an arbitrary value of $\kappa$ the lower critical field near $T_c$ can be expressed as $H_{c1} = H_c h(\kappa)$. The function is $h(\kappa) = 1$ for $\kappa = 1/\sqrt{2}$. For this critical value of $\kappa$ one has $H_{c1} = H_{c2} = H_c$.

As the external field increases, the number of the vortex lines also increases. These lines form a two-dimensional lattice in the plane perpendicular to the axis of the cylinder. The density of the vortex lines and the symmetry of the lattice depend on the interaction between lines, which will be considered in the next section. Here we will present some qualitative considerations. If distances between the vortex lines are large compared to the radius of the cylinder, one can describe the superconductor in the mixed state in an averaged manner introducing the mean value of the induction $\bar{B}$ over the cross-section of the cylinder. Correspondingly one can define the magnetization $M = (\bar{B} - H)/4\pi = (\bar{B} - H_0)/4\pi$. The magnetization is related to $H_0$ by the equation $\partial\tilde{f}/\partial H_0 = -M$. Let us integrate this equation over $H_0$ from 0 to $H_{c2}$. We find

$$\int_0^{H_{c2}} M \mathrm{d}H_0 = -\left(f_n - f_{s0}\right) , \tag{2.154}$$

where $f_n$ is the free energy density of the normal metal and $f_{s0}$ is the free energy density of the superconductor in absence of the field. Both quantities do not depend on the field and one need not distinguish between $f$ and $\tilde{f}$. In the field range $0\langle H_0\langle H_{c1}$, the field does not penetrate into the cylinder and the magnetization is simply $M = -H_0/4\pi$. Then, $\int_{H_{c1}}^{H_{c2}} M \mathrm{d}H_0 = -\left(f_n - f_{s0}\right) + H_{c1}^2/8\pi$. According to equation (2.63), the quantity in the parenthesis is equal to $H_c^2/8\pi$. Thus, we finally obtain the important relation

$$\int_{H_{c1}}^{H_{c2}} M \mathrm{d}H_0 = \frac{1}{8\pi}\left(H_{c1}^2 - H_c^2\right) . \tag{2.155}$$

Notice also that every vortex carries the flux $\phi_0$, and hence the mean value of the induction over the cross-section of the cylinder is

$$\bar{B} = \nu\phi_0 , \tag{2.156}$$

where $\nu$ is the number of lines per unit area. This result is invalid near $H_{c2}$ where the cores of the vortex lines begin to overlap.

## 2.10 Vortex–Vortex Interactions

In this section we will examine the relation between the mean induction in a type II superconductor and the external field. According to (2.156) the induction is defined by the number of vortex lines per unit area. To calculate this number we have to take into account the interaction between the vortex lines. As a first step we have to find the magnetic induction through a loop of arbitrary radius surrounding the line without the restriction (2.145). Let us calculate the curl of both sides of (2.142). Note that

$$\mathrm{curl}\ \nabla\chi = 2\pi \mathbf{n}_z \delta(\mathbf{r}) , \tag{2.157}$$

where $\mathbf{r}$ is the two-dimensional radius-vector in the $x, y$ plane and $\mathbf{n}_z$ is a unit vector along the axis $z$. (We assume that the axis of the vortex line coincides with the $z$-axis.) Indeed, integrating $\nabla\chi$ along the contour encircling the line and transforming the integral by Stokes' theorem into an integral over a surface spanning the contour, we have according to (2.143)

$$\oint \nabla\chi \cdot \mathrm{d}\mathbf{l} = \int \mathrm{curl}\ \nabla\chi \cdot \mathrm{d}\mathbf{S} = 2\pi . \tag{2.158}$$

Since this equation must be satisfied for any such contour of integration, we have (2.157). Finally we obtain

$$\mathbf{B} + \delta^2 \mathrm{curl\ curl}\ \mathbf{B} = \mathbf{n}_z \phi_0 \delta(\mathbf{r}) . \tag{2.159}$$

In the presence of several vortex lines the r.h.s. of this equation contains a sum of $\delta$-functions corresponding to the positions of the lines. Using the vector identity $\mathrm{curl\ curl}\ \mathbf{B} = \nabla\mathrm{div}\ \mathbf{B} - \Delta\mathbf{B} = -\Delta\mathbf{B}$, we obtain

$$B - \delta^2 \Delta B = \phi_0 \delta(\mathbf{r}) . \tag{2.160}$$

This equation is valid at all distances

$$r \gg \xi . \tag{2.161}$$

Throughout all the space except the line $\mathbf{r} = 0$ equation (2.160) coincides with the London equation (2.45). The $\delta$-function on the r.h.s. defines

the character of the singularity of the solution at $r \to 0$. Actually this singularity has already been defined in the equation (2.147), which is valid at small $r$. The solution of this equation at $r \to \infty$ is $B(r) = \text{const}\, K_0(r/\delta)$, where $K_0$ is the Hankel function of an imaginary argument. The coefficient must be defined by matching with the solution (2.147). Note that $B(r)$ is finite. Using the asymptotic formula $K_0(x) \approx \log\left(2/\gamma x\right)$ for $x \ll 1$, where $\gamma = e^C \approx 1.78$ ($C$ is Euler's constant), we finally have

$$B(r) = \frac{\phi_0^2}{2\pi\delta^2} K_0(r/\delta) \,. \tag{2.162}$$

Using equation (2.162) we can rewrite (2.147) as

$$B(r) = \frac{\phi_0}{2\pi\delta^2} \log\frac{2\delta}{\gamma r}, \quad r \ll \delta \,. \tag{2.163}$$

In the opposite limit of large distances one can use the asymptotic expression $K_0(x) \approx (\pi/2x)^{1/2} e^{-x}$ for $x \gg 1$. Thus, at large distances from the axis of the vortex line the induction decreases according to

$$B(r) = \frac{\phi_0}{(8\pi r\delta^3)^{1/2}} e^{-r/\delta}, \quad r \gg \delta \,. \tag{2.164}$$

Accordingly the superconductive current density decreases as

$$j_\varphi = -\frac{c}{4\pi}\frac{\mathrm{d}B}{\mathrm{d}r} = \frac{c\phi_0}{8\left(2\pi^3 r\delta^5\right)^{1/2}} e^{-r/\delta} \,. \tag{2.165}$$

There is an important difference with respect to the vortex line in superfluid helium. In the latter case the superfluid velocity follows the $1/r$ law for arbitrarily large distances. This difference is due to the charged nature of the electron liquid. The motion of electrons creates a magnetic field, which in turn screens the current.

Let us apply the results obtained to the calculation of the energy of interaction of vortex lines. It is important that equation (2.160), which defines the distribution of the induction, is a linear one. It means that under the condition (2.161) the fields produced by different vortex lines are additive. Let us consider two vortex lines placed at $\mathbf{r}_1$ and $\mathbf{r}_2$ separated by a distance $d$ from each other. Then, $\mathbf{B} = \mathbf{B}_1 + \mathbf{B}_2$. The energy of the lines is given by (2.148). Let us transform the first term in the integrand by means of (2.159) which gives

$$\begin{aligned} &\mathbf{B}^2 + \delta^2 (\operatorname{curl}\mathbf{B})^2 \\ &= \delta^2\left[-\mathbf{B}\cdot\operatorname{curl}\operatorname{curl}\mathbf{B} + (\operatorname{curl}\mathbf{B})^2\right] \\ &+ \phi_0 B_z(\mathbf{r})\left[\delta(\mathbf{r}-\mathbf{r}_1) + \delta(\mathbf{r}-\mathbf{r}_2)\right] \,. \end{aligned} \tag{2.166}$$

The first term on the r.h.s. can be transformed into the form

$$\begin{aligned} &-\mathbf{B}\cdot\operatorname{curl}\operatorname{curl}\mathbf{B} + (\operatorname{curl}\mathbf{B})^2 \\ &= \operatorname{div}\,(\mathbf{B}\times\operatorname{curl}\mathbf{B}) \,. \end{aligned} \tag{2.167}$$

The volume integration of this term in (2.148) can be reduced to an integration over a remote surface. This integral disappears, because of the fast decrease of the field. We need not worry here about singularities of the field; they are taken into account properly by the $\delta$-functional terms in (2.166). Because we are interested here in the energy of interaction of the lines, we must take into account only the "mixed terms" of the type $B_{2z}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}_1)$. (Terms like $B_{1z}(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}_1)$ contribute to the self-energy of the vortex lines (2.149).) Now the integration in (2.148) is trivial. We have for the interaction energy

$$L\varepsilon_{\text{int}} = \frac{L\phi_0}{8\pi}\left(B_2(\mathbf{r}_1) + B_1(\mathbf{r}_2)\right) \,. \tag{2.168}$$

Both terms on the right contribute equally and using (2.162) we have

$$\varepsilon_{\text{int}}(d) = \frac{\phi_0}{4\pi} B(d) = \frac{\phi_0^2}{8\pi^2\delta^2} K_0\left(\frac{d}{\delta}\right) \,. \tag{2.169}$$

Now we can define the number $\nu$ of the vortex line per unit area in the thermodynamic equilibrium. When the interaction between the vortex lines is taken into account, this equilibrium corresponds to an ordered configuration of the lines, forming a two-dimensional lattice in the plane perpendicular to the cylinder axis. It is impossible to predict the symmetry of this lattice from general considerations. One has to compare the thermodynamic potentials for different configurations and choose the most favorable. For isotropic superconductors the most favorable lattice is formed from equilateral triangles with the vortex lines at their vertices. We will consider only this case.

The expression for the thermodynamic potential per unit volume $\tilde{f}$ can be written in the form

$$\tilde{f} = f_s + \nu\left(\varepsilon - \frac{1}{4\pi}\phi_0 H_0\right) + \frac{1}{2}\sum_{i,k}\varepsilon_{int}\left(|\mathbf{r}_i - \mathbf{r}_k|\right), \qquad (2.170)$$

where the summation of the interaction energies is over all filaments passing through a unit area. One can express the energy $\varepsilon$ in this equation according to (2.140): $\varepsilon = \phi_0 H_{c1}/4\pi$. For distances $d \gg \delta$, as will be the case well below the upper critical field $H_{c2}$, it is sufficient to consider only pairs of neighboring lines. One can also use the asymptotic expression for $\varepsilon_{\text{int}}$:

$$\varepsilon_{\text{int}} = \frac{\phi_0^2}{2^{7/2}\pi^{3/2}\delta^2}\left(\frac{\delta}{\mathrm{d}}\right)^{1/2} e^{-r/\delta}, \quad r \gg \delta \qquad (2.171)$$

(see (2.164)). For the triangular lattice each vortex has six nearest neighbors. Then,

$$\frac{1}{2}\sum_{i,k}\varepsilon_{\text{int}}\left(|\mathbf{r}_i - \mathbf{r}_k|\right) = 3\nu\varepsilon_{\text{int}}(d), \qquad (2.172)$$

where $d$ is the length of a side. The area of an equilateral triangle is $\left(\sqrt{3}/4\right)d^2$ and the number of lines is a half of the number of triangles in the lattice. Hence,

$$\nu = \frac{2}{d^2\sqrt{3}}. \qquad (2.173)$$

With the help of (2.172) and (2.173) we can write (2.170) in the form

$$\tilde{f}(l) = f_s + A\left[-\frac{H_0 - H_{c1}}{l^2} + \frac{3\phi_0}{2^{3/2}\pi^{1/2\delta}\delta^2}\frac{e^{-l}}{l^{5/2}}\right], \qquad (2.174)$$

where we introduced a dimensionless parameter $l = d/\delta \gg 1$ and $A = \phi_0/\left(2\pi\sqrt{3}\delta^2\right)$. Minimizing $\tilde{f}(l)$ with respect to $l$ yields $H_0$:

$$H_0 - H_{c1} = \frac{3\phi_0}{2^{5/2}\pi^{1/2\delta}\delta^2} l^{1/2} e^{-l}, \qquad (2.175)$$

where we omitted terms of higher order in $1/l$. By means of the equation $\bar{B} = \nu\phi_0$, one can express $l$ in terms of $\bar{B}$

$$l = \left(\frac{2\phi_0}{\sqrt{3}\delta^2\bar{B}}\right)^{1/2}. \qquad (2.176)$$

Equations (2.175)–(2.176) define the "magnetization curve", i.e. the function $\bar{B}(H_0)$ for a superconductor of the second kind. Notice that this function has an infinite derivative near $H_{c1}$. It is not difficult to check that

$$\frac{\mathrm{d}\bar{B}}{\mathrm{d}H_0} \propto \frac{1}{H_0 - H_{c1}} \log^{-3}\frac{1}{H_0 - H_{c1}}, \qquad (2.177)$$

as $H_0 \to H_{c1}$.

Results (2.175) and (2.176) are valid for a small density of the vortex lines, i.e. $d \gg \delta$. The problem can also be solved if $d \sim \delta \gg \xi$. The only difference is that we must use the general equation (2.169) for the interaction energy and not restrict the summation in (2.170) to nearest neighbors. The situation becomes completely different near the upper critical field $H_{c2}$. The disappearance of the superconductivity at $H_0 \to H_{c2}$ takes place as a phase transition of the second order. Accordingly the square of the modulus of the order parameter $|\psi|^2 \propto (H_{c2} - H_0)$. Similarly, the superconducting current and the magnetization $M$ are also proportional to $(H_{c2} - H_0)$:

$$-M = \frac{H_0 - \bar{B}}{4\pi} \propto H_{c2} - H_0. \qquad (2.178)$$

Let us estimate the mean distance between the vortex lines. For $H_0 \sim H_{c2}$ the mean induction $\bar{B} \sim H_{c2}$. It then follows from (2.78) and (2.133) that $\nu \sim 1/\xi^2$ and $d \sim \xi$, which means that the cores of vortex lines overlap. The linear equation (2.159) is no longer valid. However, (2.156) is still valid. Let us consider a closed contour near the surface of the cylinder. The change of the wave function on passing round the contour is $2\pi\nu S$, where $S$ is the cross–section area of the cylinder. One obtains from (2.94) that the magnetic flux is

$$\phi = \phi_0\nu S - \frac{2m}{e\hbar}\oint\frac{\mathbf{j}}{n_s}\cdot\mathrm{d}\mathbf{l}. \qquad (2.179)$$

It is possible to show using the symmetries of the vortex lattices that one can choose a contour sufficiently near the surface so that the integral in (2.179) is zero. Thus, we obtain (2.156) as an approximate equation.

## 2.11 Cooper Pairing

We now present the general ideas and methods of the microscopic theory of superconductivity developed by J. Bardeen, L.N. Cooper and J.R. Schrieffer.[4] As we have already mentioned, the main point of this theory is the formation of bound states or pairs of electrons due to their interaction. Obviously, to create a bound state the interaction must be attractive, which raises the problem of the origin of such an attraction.

Let us consider electron–electron scattering in a metal. We will consider two electrons with opposite values of the momenta, because just such electrons create the pairs. Let $\mathbf{p}$ and $-\mathbf{p}$ be the initial values of the momenta of the electrons and $\mathbf{p}'$ and $-\mathbf{p}'$ the final values . For simplicity, we will consider an isotropic model of the metal. The electron–electron interaction in metals has two different contributions. One is the Coulomb repulsion between electrons screened on the scale of the Debye radius $r_D$, which is of the order of an interatomic distance in good metals. The corresponding potential is $e^2 e^{-r/r_D}/\epsilon r$ and its Fourier component, describing electron–electron scattering, is

$$U_{\mathbf{q}} = \frac{4\pi e^2}{\epsilon\left(q^2 + (r_D)^{-2}\right)}, \tag{2.180}$$

where $\hbar\mathbf{q} = \mathbf{p} - \mathbf{p}'$ is the change of the momentum of an electron and $\epsilon$ is the dielectric constant of the lattice. The repulsive nature of this interaction is expressed by the positive sign of this Fourier component. The second contribution to the interaction is the electron–phonon interaction. The Hamiltonian of this interaction describes emission and absorption of a phonon by an electron. Electron–electron interaction arises in second-order perturbation theory, which describes processes of emission and absorption of virtual phonons. We will show that these processes result in an effective attraction between electrons (J. Bardeen, 1950 [24], H. Fröhlich (1950) [25].)

The general equation for the scattering amplitude in the second Born approximation is

$$V_{nm}^{(2)} = \frac{1}{2}\sum_i V_{ni} V_{im} \times \left[\frac{1}{E_n - E_i} + \frac{1}{E_m - E_i}\right], \tag{2.181}$$

where $m$ and $n$ are, correspondingly, the initial and final states and the sum is taken over all intermediate states $i$. In our case the initial state contains two electrons and has energy $2\varepsilon(\mathbf{p})$. The final state has energy $2\varepsilon(\mathbf{p}')$. There are two types of intermediate states allowed by momentum conservation. In the first of these, the electron with momentum $\mathbf{p}$ emits a phonon of momentum $\hbar\mathbf{q}$ and acquires the momentum $\mathbf{p} - \hbar\mathbf{q} = \mathbf{p}'$; the energy of this state is $\varepsilon(\mathbf{p}) + \varepsilon(\mathbf{p}') + \hbar\omega_q$, where $\omega_q$ is the frequency of the phonon with wave vector $\mathbf{q}$. In the second state, the electron with momentum $-\mathbf{p}$ emits a phonon with momentum $-\hbar\mathbf{q}$ and acquires a momentum $-\mathbf{p} - \hbar\mathbf{q} = -\mathbf{p}'$. Because $\varepsilon(-\mathbf{p}') = \varepsilon(\mathbf{p}')$, this state has the same energy. Then we can use the fact that matrix elements for emission and absorption of a phonon are complex-conjugates and depend only on $|\mathbf{q}|$. As a result, the contribution of the virtual phonons to the scattering amplitude is

$$V^{(2)}_{\mathbf{p}_1\mathbf{p}_1'} = \frac{1}{2}|M(q)|^2 \times \left[\frac{1}{\delta\varepsilon - \hbar\omega_q} + \frac{1}{-\delta\varepsilon - \hbar\omega_q}\right], \tag{2.182}$$

where $\delta\varepsilon = \varepsilon(\mathbf{p}') - \varepsilon(\mathbf{p})$ is the energy transfer. The total scattering amplitude is

$$V_{\mathbf{p}_1\mathbf{p}_1'} = U_{\mathbf{q}} + |M(q)|^2 \frac{\hbar\omega_q}{(\delta\varepsilon)^2 - (\hbar\omega_q)^2}. \tag{2.183}$$

The phonon contribution is negative when $|\delta\varepsilon| < \hbar\omega_q$. This corresponds to attraction. If the Coulomb part $U_{\mathbf{q}}$ is not too large, the total interaction will be attractive. Note that $\omega_q$ is in any case less than the Debye frequency $\omega_D$. In fact, the phonons with frequencies $\omega_q \sim \omega_D$ are most important. Qualitatively, attraction takes place when $|\delta\varepsilon| < \hbar\omega_D$.

These considerations explain the origin of the attractive interaction. However, there is a problem. The

[4] Here we give a concise introduction to this very rich subject. A more comprehensive presentation can be found in the excellent books [22] and [23].

smallness of the transition temperatures shows that this attraction is weak. According to a well-known theorem of quantum mechanics there is no bound state of two particles if the interaction is small. This problem was solved in the paper by Cooper in 1956 [26]. He showed that although this theorem is valid for free particles, it does not apply to the particles of a degenerated Fermi gas. The difference is due to the existence of the Fermi sphere. The formation of a bound state of two particles in vacuum for a weak interaction is prevented by the smallness of the density of states of these particles at small energy $\varepsilon$. This density of states $\sim \varepsilon^{1/2}$. The situation in the Fermi gas at $T = 0$ is different.

Let us consider two particles excited from the Fermi sphere with opposite momenta $\mathbf{p}_1 = -\mathbf{p}_2$. Their total energy $E$ must be larger than $2\varepsilon_F$ because of the Pauli principle. If as a result of the interaction the energy $E$ becomes less than $2\varepsilon_F$ the particles will be in a bound state. The difference $(2\varepsilon_F - E)$ is the binding energy. Thus in the case of the Fermi gas, the boundary that separates bound states from states of the continuous spectrum is $2\varepsilon_F$. However, the density of states at $2\varepsilon_F$ is not necessarily small and the above quantum mechanical theorem for particles in vacuum does not apply.

Let us consider an ideal Fermi gas. It is convenient to introduce excitation energies. An excitation in such a gas can be produced by transfer of a particle from the Fermi surface to a state of momentum $p \rangle p_F$. Thus, the excitation energy will be $\varepsilon(p) = \left(\frac{p^2}{2m} - \frac{p_F^2}{2m}\right) \approx v_F(p - p_F)$ for $p \rangle p_F$. Here we assumed that this energy is small. An excitation with $p \langle p_F$ can be created by transferring a particle from a state with momentum $p$ inside the Fermi sphere to the surface of the Fermi sphere. Then, $\varepsilon(p) = \left(\frac{p_F^2}{2m} - \frac{p^2}{2m}\right) \approx v_F(p_F - p)$ for $p \langle p_F$. From this point of view the gas has the elementary excitation spectrum

$$\varepsilon(\mathbf{p}) = v_F |p - p_F| \equiv |\eta_p| , \tag{2.184}$$

where we introduced a useful notation $\eta_p = v_F(p - p_F) = p_F(p - p_F)/m$. Let us suppose now that the particles interact by means of a weak attractive potential $U(|\mathbf{r}_1 - \mathbf{r}_2|)$. Then the binding energy will be small and the wave function will spread well beyond the range of the potential. One may take for the potential

$$U(|\mathbf{r}_1 - \mathbf{r}_2|) = -g\delta(\mathbf{r}_1 - \mathbf{r}_2) , g \rangle 0 . \tag{2.185}$$

The energy of the bound state of two excitations can be found from the Schrödinger equation

$$\left[\varepsilon(\hat{\mathbf{p}}_1) + \varepsilon(\hat{\mathbf{p}}_2) - g\delta(\mathbf{r}_1 - \mathbf{r}_2)\right]\Psi(\mathbf{r}_1, \mathbf{r}_2) = (E - 2\varepsilon_F)\Psi(\mathbf{r}_1, \mathbf{r}_2) . \tag{2.186}$$

Here we took into account that the excitations energies are defined with respect to the Fermi energy. We seek a bound state with zero total momentum. Then the wave function must be an invariant with respect to translations in space and can be written in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1 - \mathbf{r}_2) . \tag{2.187}$$

Let us transform (2.186) to the momentum representation by multiplying both sides with $e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$ and integrating over $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. We find

$$2[\varepsilon(\mathbf{p}) + \Delta]\Psi_{\mathbf{p}} = g , \tag{2.188}$$

where $\Psi_{\mathbf{p}} = \int e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}\Psi(\mathbf{r})\,\mathrm{d}^3x$ . Here, we introduced $2\Delta$ for the binding energy: $E - 2\varepsilon_F = -2\Delta$. One can rewrite (2.188) in the form

$$\Psi_{\mathbf{p}} = g\Psi_0/2[\varepsilon(\mathbf{p}) + \Delta] . \tag{2.189}$$

We integrate both sides of this equation with respect to the momentum. Taking into account that

$$\Psi_0 = \int \Psi_{\mathbf{p}} \frac{d^3p}{(2\pi\hbar)^3} \tag{2.190}$$

and integrating with respect to angles, we find the following equation for $\Delta$

$$\frac{g}{4\pi^2\hbar^3}\int \frac{p^2dp}{\varepsilon(\mathbf{p}) + \Delta} = 1 . \tag{2.191}$$

The integral (2.191) diverges. However, this divergence is non-physical. It is related to the substitution of the $\delta$-function for the real potential. The divergence can be eliminated by a renormalization of the coupling constant $g$ (which can be expressed in terms of the scattering amplitude of particles). We will not discuss this procedure. Instead we note that in our

problem the attractive interaction is due to the exchange of phonons that is possible only for particles sufficiently near the Fermi surface, $\varepsilon(\mathbf{p}) \leq \hbar\omega_D \ll \varepsilon_F$; here $\omega_D$ is the maximum (Debye) frequency of phonons. Thus, the main contribution to the integral (2.191) involves the interval

$$\Delta \ll v_F \left| p - p_F \right| \ll \hbar\omega_D \,. \tag{2.192}$$

One can substitute $p_F^2$ for the factor $p^2$ in the integrand and use (2.184) for $\varepsilon(\mathbf{p})$. Cutting off the integration at $\left|p - p_F\right| \sim \hbar\omega_D / v_F$, in place of (2.191) we have

$$\frac{gmp_F}{2\pi^2\hbar^3} \log\left(\hbar\omega_D/\Delta\right) = 1 \,. \tag{2.193}$$

Finally we obtain

$$\Delta = \hbar\omega_D \exp\left(-2/gv_F\right) \,, \tag{2.194}$$

where we introduced the notation

$$v_F = mp_F/\pi^2\hbar^3 \,. \tag{2.195}$$

The quantity $v_F$ is the number of states per unit energy (the density of states) of a particle on the Fermi surface which is given by

$$2\frac{d^3p}{(2\pi\hbar)^3} = \frac{p^2dp}{\pi^2\hbar^3} = \frac{mp}{\pi^2\hbar^3}d\varepsilon = v_F d\varepsilon \,. \tag{2.196}$$

The factor 2 is due to the twofold spin degeneracy. Equation (2.194) clearly shows that the Cooper pairing phenomenon depends on the finite value of the density of states near the Fermi surface. To simplify the notation, we did not write the spin indices of the wave function in the previous equations. A solution of (2.188) automatically corresponds to a pair with spin equal to zero, i.e. a singlet state. Indeed, the isotropic wave function (2.189) has the orbital angular momentum equal to zero and all states of two identical fermions with even values of the angular momentum are singlets. Note also that it is important that we considered particles with opposite momenta. One can easily check that the binding energy tends to zero quickly when the total momentum increases.

Note that for a particle in *two-dimensional* space the density of states is constant at small energy and a bound state can also be formed for an arbitrary weak attractive potential. The energy of the state is exponentially small with respect to the potential strength similar to (2.194).

Thus, we have shown that an attraction between particles must lead to the formation of bound pairs, regardless of how weak the attraction is. When the formation of pairs is energetically favorable, the state of non-paired particles is no longer a ground-state of the system. It must be rebuilt using pairs. To excite this new ground-state one has to break a pair. This requires the energy $2\Delta$, i.e. a gap in the excitation spectrum appears. Finally, the pairs in the rebuilt ground state behave like Bose particles and can accumulate on the lowest energy level in an analogy with the phenomenon of Bose–Einstein condensation. We have already used this analogy. In the next sections we will present a quantitative theory of superconductivity where these properties will be demonstrated explicitly.

## 2.12 Energy Spectrum of a Superconductor

We now undertake a study of the theory of superconductivity based on the Cooper pairing phenomenon. This theory was developed by J. Bardeen, L. Cooper and J.R. Schrieffer and is referred to as the "BCS theory" [6]. Here we will present a method for deriving the pairing which is due to N.N. Bogoliubov (1958) [27]. A similar method was also developed by J.G. Valatin (1958) [28].

The first step is to choose a proper model. The model must be sufficiently simple to allow an analytical solution and must take into account essential features of the Cooper pairing. We will consider electrons in a metal as a Fermi gas with a weak $\delta$-functional attraction (2.185) between particles. In the second quantization representation the Hamiltonian of the system can be written as

$$\hat{H} = \int \left[ -\frac{\hbar^2}{2m}\hat{\Psi}_\alpha^\dagger(\mathbf{r})\,\Delta\hat{\Psi}_\alpha(\mathbf{r}) - \frac{g}{2}\hat{\Psi}_\alpha^\dagger(\mathbf{r})\,\hat{\Psi}_\beta^\dagger(\mathbf{r})\,\hat{\Psi}_\beta(\mathbf{r})\,\hat{\Psi}_\alpha(\mathbf{r}) \right] \mathrm{d}^3x \,, \tag{2.197}$$

where $g\rangle 0$ and the $\hat{\Psi}$-operator can be represented as an expansion

$$\hat{\Psi}_\alpha(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{p},\sigma} \hat{a}_{\mathbf{p}\sigma} u_\alpha(\sigma) e^{i\mathbf{p}\cdot\mathbf{r}} . \qquad (2.198)$$

Here, $\hat{a}_{\mathbf{p}\sigma}$ is the annihilation operator for a Fermi particle with momentum $\mathbf{p}$ and spin projection $\sigma = \pm 1/2$, and $u_\alpha(\sigma)$ is the corresponding spinor amplitude. These amplitudes satisfy the completeness condition

$$u_\alpha(\sigma) u^*_\alpha(\sigma') = \delta_{\sigma\sigma'} . \qquad (2.199)$$

Also, the operators obey the anticommutation rules

$$\hat{a}_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}'\sigma'} + \hat{a}_{\mathbf{p}'\sigma'}\hat{a}_{\mathbf{p}\sigma} = 0 ,$$
$$\hat{a}_{\mathbf{p}\sigma}\hat{a}^\dagger_{\mathbf{p}'\sigma'} + \hat{a}^\dagger_{\mathbf{p}'\sigma'}\hat{a}_{\mathbf{p}\sigma} = \delta_{\sigma\sigma'}\delta_{\mathbf{p}\mathbf{p}'} . \qquad (2.200)$$

Substituting (2.198) into (2.198) transforms the Hamiltonian into the form

$$\hat{H} = \sum_{\mathbf{p},\sigma} \frac{p^2}{2m} \hat{a}^\dagger_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}\sigma} - \frac{g}{V} \sum_{\mathbf{p}_1\mathbf{p}_2\mathbf{p}'_1} \hat{a}^\dagger_{\mathbf{p}'_1+}\hat{a}^\dagger_{\mathbf{p}'_2-}\hat{a}_{\mathbf{p}_2-}\hat{a}_{\mathbf{p}_1+} , \qquad (2.201)$$

where $\mathbf{p}'_2 = \mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}'_1$ and the suffixes + and − replace the spin variables $+1/2$ and $-1/2$. Note that the products $\hat{a}^\dagger_{\mathbf{p}'_1\sigma_1}\hat{a}^\dagger_{\mathbf{p}'_2\sigma_2}$ with $\sigma_1 = \sigma_2$ are canceled in the second sum in (2.201) due to the anticommutation relations (2.200). Physically, the Bose condensation analogy is related to the fact that the $\delta$-function potential acts only between pairs of particles in an $l = 0$ state. Such pairs have total spin equal zero, thus $\sigma_1 = -\sigma_2$. The model of a superconductor based on this Hamiltonian is known as the BCS model.

The next simplifying step is based on the crucial role of the Cooper pairing. Taking into account that this pairing exists only for particles with opposite values of the momentum, we will retain in the second sum in (2.201) only the terms with $\mathbf{p}_1 = -\mathbf{p}_2 \equiv \mathbf{p}$ and $\mathbf{p}'_1 = -\mathbf{p}'_2 \equiv \mathbf{p}'$. We will also use the "grand canonical" Hamiltonian $\hat{H}' = \hat{H} - \mu\hat{N}$, where $\mu$ is the chemical potential of the gas, and $\hat{N} = \sum_{\mathbf{p},\sigma} \hat{a}^\dagger_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}\sigma}$ the particle number operator.

This permits us to relax the condition requiring the conservation of the number of particles. We can substitute $\mu = \varepsilon_F = p_F^2/2m$ with sufficient accuracy. Then we obtain the *reduced* Hamiltonian

$$\hat{H}' = \sum_{\mathbf{p},\sigma} \eta_p \hat{a}^\dagger_{\mathbf{p}\sigma}\hat{a}_{\mathbf{p}\sigma} - \frac{g}{V} \sum_{\mathbf{p}\mathbf{p}'} \hat{a}^\dagger_{\mathbf{p}'+}\hat{a}^\dagger_{-\mathbf{p}'-}\hat{a}_{-\mathbf{p}-}\hat{a}_{\mathbf{p}+} , \qquad (2.202)$$

where, as in (2.184),

$$\eta_p = \frac{p^2}{2m} - \mu \approx v_F(p - p_F) . \qquad (2.203)$$

As we explained in the previous section, the Cooper instability changes the spectrum of elementary excitations. An initially surprising result is that the annihilation and creation operators $\hat{a}, \hat{a}^\dagger$ are no longer represent elementary excitations (even approximately). We now denote the operators that destroy and create *excitations* by $\hat{b}$ and $\hat{b}^\dagger$ and assume they are related to the destruction and creation operators for particles $\hat{a}$ and $\hat{a}^\dagger$ by the following (Bogoliubov) transformation:

$$\hat{a}_{\mathbf{p}+} = u_p\hat{b}_{\mathbf{p}+} + v_p\hat{b}^\dagger_{-\mathbf{p}-} ,$$
$$\hat{a}_{\mathbf{p}-} = u_p\hat{b}_{\mathbf{p}-} + v_p\hat{b}^\dagger_{-\mathbf{p}+} , \qquad (2.204)$$

where $u_p$ and $v_p$ can be chosen as real functions. (N.N. Bogoliubov used an analogous transformation in his theory of dilute Bose gas [29].) The operators $\hat{b}$, $\hat{b}^\dagger$ must obey the same anticommutation rules (2.200). As a result, the parameters $u$ and $v$ must be normalized according to

$$u_p^2 + v_p^2 = 1 . \qquad (2.205)$$

The ground state of the system $|0\rangle$ is defined as the state where there are no elementary excitations:

$$\hat{b}_{\mathbf{p}\sigma}|0\rangle = \langle 0|\hat{b}^\dagger_{\mathbf{p}\sigma} = 0 . \qquad (2.206)$$

For an excited state the average of the operator $\hat{b}^\dagger_{\mathbf{p}\sigma}\hat{b}_{\mathbf{p}\sigma}$ defines the average number of excitations:

$$\langle \hat{b}^\dagger_{\mathbf{p}\sigma}\hat{b}_{\mathbf{p}\sigma}\rangle = n_{\mathbf{p}\sigma} , \qquad (2.207)$$

where here and below $\langle \ldots \rangle$ means averaging with respect to the grand canonical ensemble with the Hamiltonian $H'$. The commutation relations then give

$$\langle \hat{b}_{\mathbf{p}\sigma}\hat{b}^\dagger_{\mathbf{p}\sigma}\rangle = 1 - n_{\mathbf{p}\sigma} . \qquad (2.208)$$

Let us express the Hamiltonian $H'$ in terms of the quasiparticle operators $\hat{b}$. Substituting (2.204) into (2.201) and using the anticommutation relations, we obtain

$$\begin{aligned} H' = & 2\sum_{\mathbf{p}} \eta_p v_p^2 \\ & + \sum_{\mathbf{p}} \eta_p \left(u_p^2 - v_p^2\right) \left(\hat{b}^\dagger_{\mathbf{p}+}\hat{b}_{\mathbf{p}+} + \hat{b}^\dagger_{\mathbf{p}-}\hat{b}_{\mathbf{p}-}\right) \\ & + 2\sum_{\mathbf{p}} \eta_p u_p v_p \left(\hat{b}^\dagger_{\mathbf{p}+}\hat{b}_{-\mathbf{p}-} + \hat{b}^\dagger_{\mathbf{p}-}\hat{b}_{\mathbf{p}+}\right) \\ & - \frac{g}{V}\hat{D}^\dagger\hat{D}\,, \end{aligned} \tag{2.209}$$

where we introduced the notation

$$\begin{aligned} \hat{D} = \sum_{\mathbf{p}} \Big[ & u_p^2 \hat{b}_{-\mathbf{p}-}\hat{b}_{\mathbf{p}+} - v_p^2 \hat{b}^\dagger_{\mathbf{p}+}\hat{b}^\dagger_{-\mathbf{p}-} \\ & + u_p v_p \left(1 - \hat{b}^\dagger_{\mathbf{p}+}\hat{b}_{\mathbf{p}+} - \hat{b}^\dagger_{-\mathbf{p}1}\hat{b}_{-\mathbf{p}-}\right)\Big]\,. \end{aligned} \tag{2.210}$$

Let us calculate the average energy of the system. There is no problem to average terms that are quadratic in the $b$-operators. The diagonal matrix element are non-zero only for the products (2.207) and (2.208). In calculating the fourth-order term we will neglect fluctuations of the quantity $\hat{D}$; i.e. we will substitute $\left\langle \hat{D}^\dagger\hat{D}\right\rangle$ for $\left\langle \hat{D}\right\rangle^2$. Such a procedure corresponds to the well-known mean field approximation. Thus, we obtain

$$\begin{aligned} E = \langle H'\rangle = \sum_{\mathbf{p}} \eta_p \Big[ & 2v_p^2 + \left(u_p^2 - v_p^2\right) \\ & \times \left(n_{\mathbf{p}+} + n_{\mathbf{p}-}\right)\Big] - \frac{g}{V}\left\langle \hat{D}\right\rangle^2\,, \end{aligned} \tag{2.211}$$

with

$$\left\langle \hat{D}\right\rangle = \sum_{\mathbf{p}} u_p v_p \left(1 - n_{\mathbf{p}+} - n_{\mathbf{p}-}\right)\,. \tag{2.212}$$

The coefficients $u_p$ and $v_p$ will be determined by minimizing the energy $E$. This minimization according to the general rule of thermodynamics must be performed at constant entropy. In terms of the distribution function of the elementary excitations obeying the Fermi statistics, the entropy can be written as

$$\begin{aligned} S = -\sum_{\mathbf{p}\sigma} \Big[ & n_{\mathbf{p}\sigma} \log n_{\mathbf{p}\sigma} \\ & + \left(1 - n_{\mathbf{p}\sigma}\right) \log\left(1 - n_{\mathbf{p}\sigma}\right)\Big]\,. \end{aligned} \tag{2.213}$$

It follows from (2.213) that minimizing the energy for a given entropy is equivalent to minimizing for given occupation numbers of the excitations $n_{\mathbf{p}\sigma}$. Varying expression (2.212) and taking into account that according to (2.205) $u_p\delta u_p = -v_p\delta v_p$, we find

$$\begin{aligned} \delta E = & -2\left(1 - n_{\mathbf{p}+} - n_{\mathbf{p}-}\right) \\ & \times \left[2\eta_p u_p v_p - \Delta\left(u_p^2 - v_p^2\right)\right]\frac{\delta u_p}{v_p}\,, \end{aligned} \tag{2.214}$$

where we introduced an important quantity

$$\begin{aligned} \Delta &= \frac{g}{V}\left\langle \hat{D}\right\rangle \\ &= \frac{g}{V}\sum_{\mathbf{p}} u_p v_p \left(1 - n_{\mathbf{p}+} - n_{\mathbf{p}-}\right)\,. \end{aligned} \tag{2.215}$$

The condition $\delta E = 0$ yields

$$2\eta_p u_p v_p = \Delta\left(u_p^2 - v_p^2\right)\,. \tag{2.216}$$

Equations (2.205) and (2.216) allow us to express the parameters $u_p$, and $v_p$ in terms of $p$ and $\Delta$:

$$\begin{aligned} u_p^2 &= \frac{1}{2}\left(1 + \frac{\eta_p}{\sqrt{\left(\Delta^2 + \eta_p^2\right)}}\right)\,, \\ v_p^2 &= \frac{1}{2}\left(1 - \frac{\eta_p}{\sqrt{\left(\Delta^2 + \eta_p^2\right)}}\right)\,. \end{aligned} \tag{2.217}$$

Using these expressions in (2.215) we find

$$\frac{g}{2V}\sum_{\mathbf{p}} \frac{1 - n_{\mathbf{p}+} - n_{\mathbf{p}-}}{\sqrt{\left(\Delta^2 + \eta_p^2\right)}} = 1\,. \tag{2.218}$$

The quantity $\Delta$ plays a crucial role in the theory. It defines the energy spectrum of the elementary excitation. The characteristic feature of theory is the dependence of the spectrum on the distribution of the excitations. It is worth noting that this does not change equation (2.213) for the entropy. This equation is combinatorial in character and requires only that an excitation can be characterized by definite momentum and spin projection.

We will define the energy of an elementary excitations using Landau's theory of a Fermi liquid. According to this theory one can find the energy $\varepsilon_\sigma(p)$ of an excitation with momentum $p$ and spin projection $\sigma$ by varying the total energy with respect to the distribution function $n_{\mathbf{p}\sigma}$:

$$\delta E = \sum_{\mathbf{p}\sigma} \varepsilon_\sigma(p)\, \delta n_{\mathbf{p}\sigma} . \tag{2.219}$$

The expression for the energy is given by (2.212) and the variation with respect to $n_{\mathbf{p}\sigma}$ can be carried out at constant $u_p$ and $v_p$ due to our minimization with respect to these variables. A simple calculation gives

$$\varepsilon_\sigma(p) = \sqrt{\Delta^2 + \eta_p^2} . \tag{2.220}$$

The most important property of (2.220) is that the excitation energy cannot be less than $\Delta$. This means that the excited states of the system are separated from its ground state by an *energy gap*. The existence of this gap is closely related to the Cooper pairing considered in the previous section. The energy $2\Delta$ needed to create a pair of excitations can be interpreted as the "binding energy" of the Cooper pair. This energy is needed in order to break the pair. The excitation energy (2.220) does not depend on the projection of the spin and we will omit the index $\sigma$. If $\Delta = 0$ we have $\varepsilon(p) = |\eta_p|$, which corresponds to (2.184) for the excitation energy of the normal Fermi gas.

The gap $\Delta$ is an experimentally observable quantity. It can be measured in experiments on microwave and sound absorption. The function $\varepsilon(p)$ is presented schematically in Fig. 2.4. The dashed line shows for comparison the spectrum (2.184) of the normal Fermi gas. In a state of thermodynamic equilibrium the distribution function $n_{\mathbf{p}\sigma}$ does not depend on the spin projection and is given by the Fermi distribution

$$n_{\mathbf{p}+} = n_{\mathbf{p}-} \equiv n(\varepsilon) = \left[\exp\left(\frac{\varepsilon(p)}{T}\right) + 1\right]^{-1} . \tag{2.221}$$

Note that this expression is nothing more than the distribution of Fermi particles with zero chemical potential. The reason is that we used the "grand canonical" Hamiltonian $\hat{H}' = \hat{H} - \mu\hat{N}$ and the value $\mu$ is subtracted from the quasi-particle energy. Substituting (2.220) and (2.221) in (2.218) and changing from a summation to an integration over $\mathbf{p}$-space, we can finally write the equation for the gap in the form

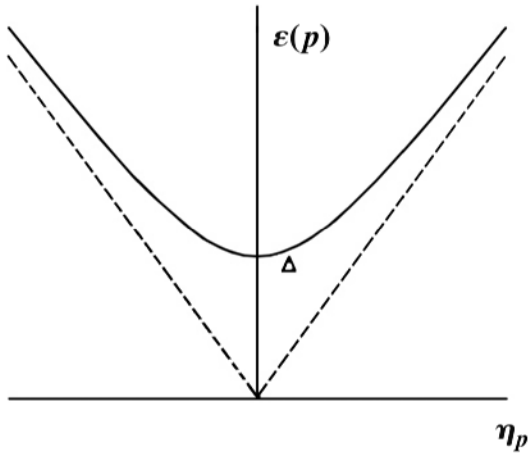


**Fig. 2.4.** Energy spectrum of a normal metal (*dashed line*) and a superconductor (*solid line*). $\Delta$ is the energy gap

$$\frac{g}{2}\int \frac{1-2n(\varepsilon)}{\varepsilon(p)}\frac{d^3p}{(2\pi\hbar)^3} = 1 . \tag{2.222}$$

Note that

$$1 - 2n(\varepsilon) = \tanh\left(\frac{\varepsilon}{2T}\right) . \tag{2.223}$$

It is obvious that (2.222) has a solution only if $g\rangle 0$, since $n_p \leq 1/2$. If the interaction is repulsive the Cooper pairs are not created and electrons remain in the normal state. The magnitude of the gap $\Delta$ depends on the temperature through the distribution function $n_p$. We will construct an approximate solution of (2.222) in the next section.

## 2.13 Thermodynamic Properties of Superconductors

### 2.13.1 Temperature Dependence of the Energy Gap

In this section we solve (2.222) for the gap $\Delta$. At $T = 0$ there are no quasi-particles and $n_p = 0$. Then (2.222) takes the form

$$\frac{g}{2}\int \frac{1}{\varepsilon(p)}\frac{d^3p}{(2\pi\hbar)^3} = 1 , \tag{2.224}$$

or

$$\frac{g}{4\pi^2\hbar^3}\int_0^\infty \frac{p^2\mathrm{d}p}{\sqrt{\Delta_0^2+\eta_p^2}} = 1\,. \tag{2.225}$$

Here, we introduced $\Delta_0$ for the value of $\Delta\,(T)$ at $T=0$. When $g$ is small, equation (2.225) has a solution only if the integral is larger. When $\Delta_0 \to 0$, the integral diverges logarithmically near the point $\eta_p = 0$. This means that at small $\Delta_0$ only values $p \approx p_F$ are important. Within logarithmic accuracy we can substitute $p^2 \to p_F^2$ in the numerator and cut the integration off at $|\eta| \sim \tilde{\varepsilon}$. The value of the cut off parameter $\tilde{\varepsilon}$ depends on the nature of the physical system. In the superconducting metal, where attraction is due to the exchange of phonons, $\tilde{\varepsilon}$ is of the order of the maximum frequency of phonons, $\tilde{\varepsilon} \sim \hbar\omega_D$, where $\omega_D$ is the Debye frequency of the metal.[5] Equation (2.225) then becomes

$$\frac{gp_F^2}{2\pi^2\hbar^3 v_F}\int_0^{\hbar\omega_D} \frac{d\eta_p}{\sqrt{\Delta_0^2+\eta_p^2}} = 1\,. \tag{2.226}$$

Integration gives

$$\frac{gp_F^2}{2\pi^2\hbar^3 v_F}\log\left(\frac{2\hbar\omega_D}{\Delta_0}\right) = 1\,. \tag{2.227}$$

Finally

$$\Delta_0 = 2\hbar\omega_D \exp\left(-2/gv_F\right)\,, \tag{2.228}$$

where $v_F = mp_F/\pi^2\hbar^3$ is the density of states near the Fermi surface.

According to (2.228) the gap $\Delta_0$ is exponentially small with regard to $\hbar\omega_D$. The function $\Delta_0\,(g)$ has an essential singularity as a function of the coupling constant at $g=0$ and cannot be expanded in powers of this parameter. Actually, the BCS theory corresponds to the sum of an infinite number of terms in the perturbation theory series.

We will begin the investigation of the temperature dependence of the gap by a calculation of the transition temperature $T_c$ at which $\Delta$ is zero. Since $\Delta = 0$ for $T = T_c$ we can easily transform (2.222) to the form

$$\frac{gv_F}{2}\int_0^{\hbar\omega_D/2T_c} \tanh x\,\frac{dx}{x} = 1\,. \tag{2.229}$$

Integrating by parts and taking into account that $\tanh\,(\hbar\omega_D/2T_c) \approx 1$, we obtain

$$\frac{gv_F}{2}\left[\log\left(\hbar\omega_D/T_c\right) - I/2\right] = 1\,, \tag{2.230}$$

where

$$I = \int_0^\infty \frac{\log x}{\cosh^2(x/2)}\mathrm{d}x = 2\log\left(\pi/2\gamma\right)\,,$$
$$\gamma = e^C = 1.78\,. \tag{2.231}$$

(To obtain rapid convergency of the integral, the limit was extended to $\infty$.) Hence the transition temperature is

$$T_c = \frac{\gamma}{\pi}\Delta_0 = 0.57\Delta_0 = 1.14\hbar\omega_D \exp\left(-2/gv_F\right)\,, \tag{2.232}$$

with $\Delta_0$ given by (2.228). The behavior of $\Delta$ near $T_c$ can be found in an analogous way. One gets

$$\frac{gv_F}{2}\int_0^{\hbar\omega_D}\tanh\left(\frac{\eta}{2T}\right)\frac{\mathrm{d}\eta}{\eta} + \tag{2.233}$$
$$\frac{gv_F}{2}\int_0^{\hbar\omega_D}\left[\tanh\left(\frac{\varepsilon}{2T}\right)\frac{1}{\varepsilon} - \tanh\left(\frac{\eta}{2T}\right)\frac{1}{\eta}\right]\mathrm{d}\eta = 1\,.$$

Note that the first integral on the l.h.s. differs from the integral (2.229) only in that $T_c$ is replaced by $T$. This permits us to rewrite (2.234) as

$$\log\frac{T_c}{T} = \int_0^\infty\left[\tanh\left(\frac{\eta}{2T}\right)\,\frac{1}{\eta} - \tanh\left(\frac{\varepsilon}{2T}\right)\frac{1}{\varepsilon}\right]\mathrm{d}\eta\,. \tag{2.234}$$

[5] Recent progress in experimental techniques has permitted one to trap and cool rarefied Fermi gases of neutral atoms. In such a system the coupling constant $g$ is proportional to the $s$-wave atom–atom scattering length. If this length is negative, the gas at low temperature undergoes a phase transition to a superfluid state. In this case $\tilde{\varepsilon} \sim \mu$. A consistent theory of this phenomenon was given in [30].

The limit of integration is again extended to $\infty$. If $\Delta$ is small, one can expand the r.h.s. with respect to $\Delta^2$ obtaining

$$\log \frac{T_c}{T} = -\frac{\Delta^2}{8T^2} I_1 \,, \tag{2.235}$$

with $I_1 = \int_0^\infty \frac{d}{dx}\left(\frac{\tanh x}{x}\right)\frac{dx}{x} = -\frac{7\zeta(3)}{\pi^2}$. Then, near the transition point we obtain to first order in $(T_c - T)$

$$\frac{T_c - T}{T_c} - \frac{7\zeta(3)}{8\pi^2 T_c^2}\Delta^2 = 0 \,, \tag{2.236}$$

or finally

$$\begin{aligned}\Delta(T) &= T_c \left[\frac{8\pi^2}{7\zeta(3)}\left(1 - \frac{T}{T_c}\right)\right]^{1/2} \\ &= 3.06 T_c \left(1 - \frac{T}{T_c}\right)^{1/2} .\end{aligned} \tag{2.237}$$

Let us now consider the limit of low temperature. Rewriting (2.222) in the form

$$\frac{g}{2}\int \frac{1}{\varepsilon(p)}\frac{d^3p}{(2\pi\hbar)^3} - 1 = g\int \frac{n(\varepsilon)}{\varepsilon}\frac{d^3p}{(2\pi\hbar)^3} \,, \tag{2.238}$$

we note that the first term on the left differs from that at $T = 0$ only in that $\Delta_0$ is replaced by $\Delta(T)$. According to (2.227) this means that the l.h.s. of the equation is $(g\nu_F/2)\log(\Delta_0/\Delta)$ . The integral on the r.h.s. converges rapidly due to the exponential decrease of $n_p$ far from the Fermi surface. Because of this we can safely substitute $d^3p \to 4\pi m p_F d\eta_p$ and extend the limits of integration $\eta_p$ to $\pm\infty$. After the change of variable $\eta_p = x\Delta$ the equation takes the form

$$\log(\Delta_0/\Delta) - 2\int_0^\infty \frac{n\left(\Delta\sqrt{1+x^2}\right)}{\sqrt{1+x^2}}\mathrm{d}x = \frac{2}{g\nu_F} \,. \tag{2.239}$$

At low temperatures ($T \ll \Delta_0$) the distribution function is exponentially small and small values of $x$ give the main contribution to the integral. Using the approximate expressions

$$n(\varepsilon) \approx e^{-\varepsilon/T} ts, \varepsilon \approx \Delta_0 + \eta^2/2\Delta_0 \tag{2.240}$$

and integrating, we find

$$\Delta \approx \Delta_0 \left[1 - \sqrt{(2\pi T/\Delta_0)}\exp\left(-\frac{\Delta_0}{T}\right)\right] . \tag{2.241}$$

### 2.13.2 Thermodynamic Functions

In this section we discuss the thermodynamics properties of the electron gas in a superconductor. We begin with the derivation of several useful relations for the grand canonical thermodynamic potential

$$\Omega(T, V, \mu) = -T\log\left[\mathrm{Tr}\left(e^{-\hat{H}'/T}\right)\right] . \tag{2.242}$$

Let us calculate the derivative of $\Omega$ with respect to the coupling constant $g$. According to the general theorem concerning the differentiation of thermodynamic potentials, one has

$$\left(\partial\Omega/\partial g\right)_{T,V,\mu} = \left\langle\left(\partial\hat{H}'/\partial g\right)_\mu\right\rangle . \tag{2.243}$$

From (2.209) and (2.212) we have $\left(\partial\hat{H}'/\partial g\right)_\mu = -\hat{D}^\dagger\hat{D}/V$ and

$$\left(\partial\Omega/\partial g\right)_{T,V,\mu} = -V\Delta^2/g^2 \,. \tag{2.244}$$

We recall that thermodynamic derivatives of different thermodynamic potentials are equal when expressed in terms of the appropriate variables. For example, the thermodynamic identity for the free energy

$$dF = -SdT - PdV + \mu dN + \left(\frac{\partial F}{\partial g}\right)_{T,V,N} dg \tag{2.245}$$

can be rewritten as

$$\begin{aligned}d\Omega = d(F - \mu N) &= -SdT - PdV \\ &- Nd\mu + \left(\frac{\partial F}{\partial g}\right)_{T,V,N} dg \,.\end{aligned} \tag{2.246}$$

Thus $\left(\partial F/\partial g\right)_{T,V,N} = \left(\partial\Omega/\partial g\right)_{T,V,\mu}$. Hence

$$\left(\partial F/\partial g\right)_{T,V,N} = -V\Delta^2/g^2 \,. \tag{2.247}$$

The energy gap $\Delta$ is defined by equation (2.222) and depends on $p_F$ as a parameter. In (2.247) $p_F$ must be expressed as a function of $N$ (not $\mu$!) according to the ideal-gas equation

$$\frac{N}{V} = \frac{p_F^3}{3\pi^3\hbar^3}\,. \tag{2.248}$$

Let us integrate (2.247) over $g$ from 0 to $g$. Taking into account that at $g = 0$ the gap $\Delta = 0$ and the free energy refers to the normal metal at the same temperature, we find:

$$F_s = F_n - V\int_0^g \frac{\Delta^2}{g^2}\mathrm{d}g\,. \tag{2.249}$$

At absolute zero the free energy coincides with the energy and $\Delta = \Delta_0$. From (2.228) we have

$$d\log\Delta_0 = d\Delta_0/\Delta_0 = (2/\nu_F)\,dg/g^2\,. \tag{2.250}$$

Substituting into (2.249) and integrating we find the difference between the ground state energies of the superconducting and normal states:

$$E_s = E_n - V\nu_F\Delta_0^2\,. \tag{2.251}$$

We note, a simple physical meaning of this equation: $E_n - E_s = \Delta_0\delta N$, where $\delta N = V\nu_F\Delta_0$ is of the order of the number of electrons in the energy interval $\Delta_0$. This equation shows that the superconducting state is more stable than the normal state as it must be under the given conditions. A comparison with (2.63) gives the expression for the critical field:

$$\frac{H_c^2}{8\pi} = \nu_F\Delta_0^2\,. \tag{2.252}$$

Let us now consider the opposite case $T \to T_c$. Differentiating (2.235) with respect to $g$ and taking into account (2.235) we find

$$\frac{7\zeta(3)}{4\pi^2T^2}\Delta d\Delta = \frac{2}{\nu_F}\frac{dg}{g^2}\,. \tag{2.253}$$

Substituting this equation in (2.249) and calculating the integral, we get

$$F_s = F_n - V\frac{7\zeta(3)}{32\pi^2T^2}\nu_F\Delta^4\,. \tag{2.254}$$

Substituting here the limiting expression (2.237), we finally obtain

$$F_s = F_n - V\frac{2mp_FT_c}{7\zeta(3)\,\hbar^3}\left(1 - \frac{T}{T_c}\right)^2\,. \tag{2.255}$$

Calculation of the specific heat according to $C_V = -T\left(\partial^2F/\partial T^2\right)$ gives the discontinuity in the specific heat at the transition point:

$$C_s - C_n = V\frac{4mp_FT_c}{7\zeta(3)\,\hbar^3}\,. \tag{2.256}$$

The specific heat of the normal state in the model under consideration is simply the specific heat of the ideal Fermi gas of the same density, i.e. $C_n = Vmp_FT/3\hbar^3$. Thus, the ratio of the specific heats at the transition point is

$$\left(\frac{C_s}{C_n}\right)_{T=T_c} = \frac{12}{7\zeta(3)} + 1 = 2.43\,. \tag{2.257}$$

To calculate the specific heat in the low temperatures region, it is more convenient to use (2.219) for the variation of the energy with respect to the distribution function. Changing from a summation to an integration we can write

$$C = \frac{\partial E}{\partial T} = 2\int \varepsilon\frac{\partial n}{\partial T}\frac{Vd^3p}{(2\pi\hbar)^3} \approx \frac{2Vp_F}{\pi^2\hbar^3}\int_0^\infty \varepsilon\frac{\partial n}{\partial T}\mathrm{d}\eta\,. \tag{2.258}$$

Then, we can use the approximate form (2.240) and an integration gives

$$C = V\frac{\sqrt{2}mp_F\Delta_0^{5/2}}{\pi^{3/2}\hbar^3T^{3/2}}\exp\left(-\frac{\Delta_0}{T}\right)\,. \tag{2.259}$$

In concluding this section we calculate the number of superconductive electrons $n_s$. According to the definition, $n_s = n - n_n = n - \rho_n/m$, where $n$ is the total density and the normal mass density $\rho_n$ is given by (2.28). With the usual simplifications and using equation (2.248) for the total density we transform this equation to the form

$$\frac{n_n}{n} = -2\int_0^\infty \frac{dn}{d\varepsilon}\mathrm{d}\eta\,. \tag{2.260}$$

There is a very useful expression which relates the normal density and the gap $\Delta(T)$. To derive it, we

differentiate (2.239) with respect to temperature. After changing back to an integration over $\eta$, we find by comparison with (2.260):

$$\frac{n}{n_n} = 1 - \frac{\Delta}{T\Delta'}\,, \tag{2.261}$$

where $\Delta' = d\Delta/dT$. The result (2.261) allows us to write down the equations for the temperature dependence of $n_n$ for different limiting cases without additional calculations. We obtain directly from (2.241) and (2.237):

$$\frac{n_n}{n} = \left(\frac{2\pi\Delta_0}{T}\right)^{1/2} e^{-\Delta_0/T}\,,\ T \to 0 \tag{2.262}$$

and

$$\frac{n_s}{n} = \frac{2}{T_c}\,(T_c - T)\ ,\ T_c - T \ll T_c\,. \tag{2.263}$$

### 2.13.3 Microscopic Meaning of the GL Equations

One of the important results of the BCS theory is that it allows us to understand the microscopic meaning of the coefficients in the phenomenological Ginzburg–Landau equations (L.P. Gor'kov, 1959 [31]). First of all, a comparison of (2.237) for the temperature dependence of the gap near $T_c$ with (2.263) allows us to find the relation between $\Delta$ and $\psi = \sqrt{n_s/2}$:

$$\psi = \sqrt{n}\left(\frac{7\zeta\,(3)}{8\pi^2}\right)^{1/2}\frac{\Delta}{T_c}\,. \tag{2.264}$$

Furthermore, comparison of (2.86) and (2.256) for the discontinuity in the specific heat gives

$$\frac{\alpha^2}{b} = \frac{4mp_F}{7\zeta\,(3)\,\hbar^3}\,. \tag{2.265}$$

Comparison of (2.82) and (2.263) gives a second equation

$$\frac{\alpha}{b} = \frac{n}{T_c} = \frac{p_F^3}{3\pi^2\hbar^3 T_c}\,. \tag{2.266}$$

Solving these equations with respect to $\alpha$ and $b$, we find

$$\alpha = \frac{12\pi^2 m T_c}{7\zeta\,(3)\,p_F^2} = 7.04T_c/\mu,\ b = \frac{\alpha T_c}{n}\,, \tag{2.267}$$

where $\mu$ is the chemical potential of the ideal Fermi gas, $\mu = p_F^2/2m$. Substitution this value of $b$ in (2.98) for the GL parameter $\kappa$ gives

$$\kappa = 1.09\,\frac{T_c mc}{\mu^{1/2} n^{1/2}\hbar\,|e|}\,. \tag{2.268}$$

Note also that the quantity $\xi_0$ which gives the correlation length at $T = 0$ is

$$\xi_0 = \frac{\hbar}{(m\alpha T_c)^{1/2}} = \frac{\hbar\mu^{1/2}}{T_c(7m)^{1/2}} \sim \frac{\hbar v_F}{T_c}\,. \tag{2.269}$$

Expression (2.85) for the critical field can now be written in the form

$$H_c = 2.44\left(\frac{mp_F}{\hbar^3}\right)^{1/2}(T_c - T)\,. \tag{2.270}$$

Let us now express the condition (2.105) for the validity of the GL theory in terms of the microscopic theory. Substitution from (2.267) gives:

$$\frac{T_c - T}{T_c} \gg \left(\frac{T_c}{\mu}\right)^4\,. \tag{2.271}$$

With the possible exception of high temperature superconductors very close to $T_c$, this inequality is generally satisfied in practice ((2.271)).

The theory of superconductivity which we have developed is of course quite crude. Real metals are anisotropic bodies and the energy spectrum of their electrons depends on the interaction with the crystal lattice. To some extent this fact can be taken into account by replacing the free electron mass in the above equations by some effective mass $m^*$. Further, the BCS Hamiltonian is only a crude approximation of the real electron–phonon Hamiltonian. Finally, the theory assumes that the coupling constant $g$ is small $(gv_F \ll 1)$. According to (2.232) this condition requires

$$\log\,(\hbar\omega_D/T_c) \gg 1\,. \tag{2.272}$$

In practice this condition is satisfied only with limited accuracy. A more sophisticated theory of superconductivity, which is free of these defects, will be presented in other chapters of this book. It is remarkable, however, that even the simple theory based on the BCS model in many respects gives a good description of the properties of superconductors, both qualitatively and quantitatively.

## 2.14 Elements of the Theory of Green's Functions

### 2.14.1 General Properties of Green's Functions

The Green's function method is an important part of the modern theory of superconductivity. This method permits a formulation of the theory in a very transparent and convenient form and provides a powerful tool to solve more complicated problems in superconductivity.

In this section we will introduce basic notions of the Green's function theory. Of course, our review cannot replace a systematic textbook (see, for example, [32] and [33]). However, we hope that our presentation can serve as a useful introduction to the subject.

The Green's function $G_{\alpha\beta}$ of a system of fermions at $T = 0$ is defined as

$$G_{\alpha\beta}(X_1, X_2) = -i\left\langle \hat{\mathrm{T}}\hat{\Psi}_\alpha(X_1)\,\hat{\Psi}^\dagger_\beta(X_2)\right\rangle , \qquad (2.273)$$

where $\langle \ldots \rangle$ denotes averaging with respect the ground state of the system. Here and below $\hat{\Psi}_\alpha(X)$ and $\hat{\Psi}^\dagger_\alpha(X)$ are the annihilation and creation and creation operators for electrons in the time-dependent Heisenberg representations and $X$ denotes the time $t$ and coordinates $\mathbf{r}$, $\hat{\Psi}_\alpha(X) \equiv \hat{\Psi}_\alpha(\mathbf{r}, t)$. As in the previous section we will use the grand canonical Hamiltonian $\hat{H}' = \hat{H} - \mu\hat{N}$. Then[6]

$$\hat{\Psi}_\alpha(\mathbf{r}, t) = \exp\left(i\hat{H}'t\right)\hat{\Psi}_\alpha(\mathbf{r}) \times \exp\left(-i\hat{H}'t\right) , \qquad (2.274)$$

where $\hat{\Psi}_\alpha(\mathbf{r})$ is the operator in the time-independent Schrödinger representation. The symbol $\hat{\mathrm{T}}$ is the time ordering operator: the operators to the right of this symbol are to be arranged from right to left in the order of increasing times of their arguments. The products are also to be multiplied by the factor $(-1)^P$, where $P$ is the number of permutations of the fermionic operators needed to obtain the chronological product from their original order. In our case of two operators we have explicitly

$$G_{\alpha\beta}(X_1, X_2) = \left\{ \begin{array}{l} -i\left\langle \hat{\Psi}_\alpha(X_1)\,\hat{\Psi}^\dagger_\beta(X_2)\right\rangle , \text{ for } t_1 \rangle t_2 \\ i\left\langle \hat{\Psi}^\dagger_\beta(X_2)\,\hat{\Psi}_\alpha(X_1)\right\rangle , \text{ for } t_1 \langle t_2 \end{array} \right\} . \qquad (2.275)$$

In the absence of a magnetic field, the spin dependence of the Green's function reduces to a unit spin-matrix:

$$G_{\alpha\beta}(X_1, X_2) = \delta_{\alpha\beta} G(X_1, X_2) . \qquad (2.276)$$

If, as we assume, the system is in stationary external fields, then Green's function depends only on the difference $t = t_1 - t_2$ of its time arguments. If in addition the system is microscopically homogeneous in space, Green's function depends only on the difference $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and

$$G(X_1, X_2) = G(X_1 - X_2) \equiv G(t, \mathbf{r}) . \qquad (2.277)$$

This condition is not valid for the electrons in the lattice of a real metal. However, it is valid for a model of a uniform superconducting gas, and then it is convenient to go to the Fourier representation

$$G(t, \mathbf{r}) = \int G(\omega, \mathbf{p})\, e^{i(\mathbf{p}\cdot\mathbf{r} - \omega t)} \frac{\mathrm{d}\omega d^3 p}{(2\pi)^3} , \qquad (2.278)$$

with

$$G(\omega, \mathbf{p}) = \int G(t, \mathbf{r})\, e^{-i(\mathbf{p}\cdot\mathbf{r} - \omega t)} \mathrm{d}t d^3 r . \qquad (2.279)$$

From a knowledge of the Green's function one can calculate the one-body density matrix of the system

$$\rho^{(1)}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, t) = \left\langle \hat{\Psi}^\dagger_\beta(\mathbf{r}_2, t)\,\hat{\Psi}_\alpha(\mathbf{r}_1, t)\right\rangle . \qquad (2.280)$$

For a uniform system in the ground state we have according to (2.275)

$$\rho^{(1)}_{\alpha\beta}(\mathbf{r}) = \delta_{\alpha\beta}\rho^{(1)}(\mathbf{r}) = -i\delta_{\alpha\beta} G(t \to -0, \mathbf{r}) , \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 . \qquad (2.281)$$

The Fourier expansion of the density matrix defines the momentum distribution of the particles

$$N(\mathbf{p}) = \int \rho^{(1)}(\mathbf{r})\, e^{i\mathbf{p}\cdot\mathbf{r}} d^3 r . \qquad (2.282)$$

Taking into account (2.281) and (2.279) we find:

[6] In order to simplify the equation, we will use below units such that $\hbar = 1$. However, we will include $\hbar$ in final results.

$$N(\mathbf{p}) = -i\int_{-\infty}^{\infty} G(\omega, \mathbf{p})\, e^{-i\omega t}\frac{d\omega}{2\pi}\,, \qquad t \to -0\,. \tag{2.283}$$

Important properties of Green's function can be established by inserting a complete set of states and rewriting it in the form (see (2.275))

$$G(X_1, X_2) = -\frac{i}{2}\sum_m \left\langle 0\left|\hat{\Psi}_\alpha(X_1)\right|m\right\rangle\left\langle m\left|\hat{\Psi}^\dagger_\alpha(X_2)\right|0\right\rangle\,, \qquad \text{for } t_1 \rangle t_2\,. \tag{2.284}$$

Since the operator $\hat{\Psi}^\dagger_\alpha$ creates an electron, $|m\rangle$ is a state of the system of $N+1$ electrons. The state $|0\rangle$ is the ground state of the system of $N$ electrons. For $t_1 \langle t_2$ we have an analogous equation. The crucial point is that the time and coordinate dependence of the matrix elements can be found from general considerations. First of all, the time dependence of $\left\langle 0\left|\hat{\Psi}_\alpha(X_1)\right|m\right\rangle$ has to correspond to the time-dependence of matrix elements in the Heisenberg representation, i.e. $\langle 0|\ldots|m\rangle \sim e^{i\omega_{0m}t}$. Since we use the grand canonical Hamiltonian $H'$, the frequencies are

$$\omega_{0m} = E'_0(N) - E'_m(N+1) = E_0(N) - E_m(N+1) + \mu\,. \tag{2.285}$$

Further, for a uniform system any transformation of the form $\mathbf{r} \to \mathbf{r}+\mathbf{a}$ can only change the wave function of the system by a constant phase factor. This means that $\left\langle 0\left|\hat{\Psi}_\alpha(X_1)\right|m\right\rangle \sim e^{i\mathbf{p}_m\cdot\mathbf{r}}$, where $\mathbf{p}_m$ is a constant vector interpreted as the momentum of the state $|m\rangle$. Thus

$$\left\langle 0\left|\hat{\Psi}_\alpha(X_1)\right|m\right\rangle = \left\langle m\left|\hat{\Psi}^\dagger_\beta(X_2)\right|0\right\rangle^* = \left\langle 0\left|\hat{\Psi}_\alpha(0)\right|m\right\rangle e^{i(\omega_{0m}t+\mathbf{p}_m\cdot\mathbf{r})}\,. \tag{2.286}$$

Substituting into (2.275) gives

$$G(t,\mathbf{r}) = -\frac{i}{2}\left\{\begin{array}{l}\sum\limits_m A_m e^{i(\omega_{0m}t+\mathbf{p}_m\cdot\mathbf{r})}\,, \text{ for } t_1\rangle t_2\\ -\sum\limits_{m'} B_{m'} e^{-i(\omega_{0m'}t-\mathbf{p}_{m'}\cdot\mathbf{r})}\,, \text{ for } t_1\rangle t_2\end{array}\right\}\,, \tag{2.287}$$

where the summation with respect to $m$ is over states with $N+1$ particles and the summation with respect to $m'$ is over states with $N-1$ particles and we introduced the notation

$$A_m = \left|\left\langle 0\left|\hat{\Psi}_\alpha(0)\right|m\right\rangle\right|^2\,, \quad B_{m'} = \left|\left\langle m'\left|\hat{\Psi}_\alpha(0)\right|0\right\rangle\right|^2\,, \quad \omega_{0m'} = E_{m'}(N-1) - E_0(N) + \mu\,. \tag{2.288}$$

Note that the coefficients $A_m$ and $B_{m'}$ are real and positive. It is convenient to transform the energy differences $\omega_{0m}$ and $\omega_{m0}$ taking into account that our system contains a large number of particles. In the first case we can write

$$E_0(N) + \mu \approx E_0(N+1)\,, \quad \omega_{0m} \approx E_0(N+1) - E_m(N+1) \equiv -\varepsilon_m\,, \tag{2.289}$$

and analogously

$$\omega_{0m'} = E_{m'}(N-1) - E_0(N-1) \equiv \varepsilon_{m'}\,. \tag{2.290}$$

It is obvious in view of the definition of the ground state ($E_m \rangle E_0$) that the quantities $\varepsilon_m$ and $\varepsilon_{m'}$ are positive.

Let us now calculate $G(\omega, \mathbf{p})$ according to (2.279). The spatial integration gives delta functions. In performing the integration over $t$, one must add to $\omega$ an infinitesimal imaginary part to insure convergence. This imaginary part must be positive for integration from 0 to $\infty$ and negative for integration from $-\infty$ to 0. Then

$$G(\omega,\mathbf{p}) = \frac{(2\pi)^3}{2}\times\sum_m\left\{\frac{A_m}{\omega-\varepsilon_m+i0}\delta(\mathbf{p}-\mathbf{p}_m) + \frac{B_m}{\omega+\varepsilon_m-i0}\delta(\mathbf{p}+\mathbf{p}_m)\right\}\,. \tag{2.291}$$

We do not distinguish now the summation over $m$ and $m'$, since it cannot result in a misunderstanding.

Equation (2.292) has an important physical meaning. It shows that the poles of the Green's function give the energy levels of the system. However, in the thermodynamic limit the energy levels of a macroscopical body become continuous. This corresponds to the change of the summation over $m$ into an integration. Still if the system has well-defined elementary excitations with the dispersion relation $\varepsilon(\mathbf{p})$ between states $m$ (2.292) there is a state with one excitation of the momentum $\mathbf{p}$ and energy $\varepsilon = \varepsilon(\mathbf{p})$. This state gives an "individual" pole contribution to the sum. Thus, the excitation dispersion relation $\varepsilon(\mathbf{p})$ is determined by the equation

$$G^{-1}(\varepsilon(\mathbf{p}), \mathbf{p}) = 0 . \tag{2.292}$$

On the contrary, for the states which contain several excitations with total momentum $\mathbf{p}$, the energy of the system is not uniquely determined by the value of $\mathbf{p}$ and the total energy of these excitations covers a continuous range of values in the thermodynamic limit. In this case the pole is removed by the integration over $m$.

### 2.14.2 Green's Function of an Ideal Fermi Gas

We begin our discussion of Green's function for a non-superconducting Fermi system with the calculation of Green's function $G^{(0)}$ of an ideal Fermi gas. Recall first that the operators $\hat{\Psi}_\alpha(\mathbf{r}, t)$ and $\hat{\Psi}^\dagger_\alpha(\mathbf{r}, t)$ at coinciding times obey the commutation rules

$$\hat{\Psi}_\alpha(\mathbf{r}, t)\hat{\Psi}^\dagger_\beta(\mathbf{r}', t) + \hat{\Psi}^\dagger_\beta(\mathbf{r}', t)\hat{\Psi}_\alpha(\mathbf{r}, t) = \delta_{\alpha\beta}\delta(\mathbf{r} - \mathbf{r}') , \tag{2.293}$$

and

$$\hat{\Psi}_\alpha(\mathbf{r}, t)\hat{\Psi}_\beta(\mathbf{r}', t) + \hat{\Psi}_\beta(\mathbf{r}', t)\hat{\Psi}_\alpha(\mathbf{r}, t) = \hat{\Psi}^\dagger_\alpha(\mathbf{r}, t)\hat{\Psi}^\dagger_\beta(\mathbf{r}', t) + \hat{\Psi}^\dagger_\beta(\mathbf{r}', t)\hat{\Psi}^\dagger_\alpha(\mathbf{r}, t) = 0 . \tag{2.294}$$

The grand canonical Hamiltonian of an ideal gas is

$$\hat{H}'_0 = \int \hat{\Psi}^\dagger_\alpha(\mathbf{r}, t)\left[-\frac{\nabla^2}{2m} - \mu\right]\hat{\Psi}_\alpha(\mathbf{r}, t)\,\mathrm{d}^3x . \tag{2.295}$$

The equation of motion for the operator $\hat{\Psi}_\alpha(\mathbf{r}, t)$ can be obtained according to the general rule as

$$i\frac{\partial}{\partial t}\hat{\Psi}_\alpha = -\left(\hat{H}'_0\hat{\Psi}_\alpha - \hat{\Psi}_\alpha\hat{H}'_0\right) . \tag{2.296}$$

The commutator on the r.h.s. of this equation is calculated by means of (2.293) and (2.294). As a result we obtain the "Schrödinger-like equation":

$$i\frac{\partial}{\partial t}\hat{\Psi}_\alpha(\mathbf{r}, t) = \left(-\frac{\nabla^2}{2m} - \mu\right)\hat{\Psi}_\alpha(\mathbf{r}, t) . \tag{2.297}$$

Let us differentiate Green's function (2.273) with respect to $t_1$. Here, we have to take into account that Green's function has a discontinuity at $t_1 = t_2$. According to (2.275) one has

$$\left[G_{\alpha\beta}\right] = G_{\alpha\beta}|_{t_1=t_2+0} - G_{\alpha\beta}|_{t_1=t_2-0} = -i\left\langle\hat{\Psi}_\alpha(\mathbf{r}_1, t_1)\hat{\Psi}^\dagger_\beta(\mathbf{r}_2, t_1) + \hat{\Psi}^\dagger_\beta(\mathbf{r}_2, t_1)\hat{\Psi}_\alpha(\mathbf{r}_1, t_1)\right\rangle . \tag{2.298}$$

Equation (2.293) then gives $\left[G_{\alpha\beta}\right] = -i\delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2)$. Differentiation of this discontinuity gives a contribution $\left[G_{\alpha\beta}\right]\delta(t_1 - t_2)$ and

$$i\frac{\partial}{\partial t}G^{(0)}_{\alpha\beta} = -i\left\langle T\frac{\partial\hat{\Psi}_\alpha(X_1)}{\partial t_1}\hat{\Psi}^\dagger_\beta(X_2)\right\rangle - i\delta_{\alpha\beta}\delta(\mathbf{r}_1 - \mathbf{r}_2)\,\delta(t_1 - t_2) . \tag{2.299}$$

Substituting (2.297) we finally obtain

$$\left(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m} + \mu\right)G^{(0)}(t, \mathbf{r}) = \delta(\mathbf{r})\,\delta(t) . \tag{2.300}$$

The Fourier transform of this equation gives

$$G^{(0)}(\omega, \mathbf{p}) = \left(\omega - \frac{p^2}{2m} + \mu + i0sgn\,\omega\right)^{-1} , \tag{2.301}$$

where the infinitesimal imaginary part, which is important only near the pole, is chosen according to (2.292). Comparing with (2.292) we also find that

$$\varepsilon(p) = \left|\frac{p^2}{2m} - \mu\right| , \tag{2.302}$$

as it must be in the absence of an interaction. Near the Fermi surface this equation can be rewritten as $\varepsilon(p) = p_F\left|p - p_F\right|/m$.

Green's function of a normal Fermi system in the presence of an interaction cannot be calculated in a general form. However, the energy spectrum of such a system is qualitatively similar to the spectrum of the ideal Fermi gas. Near the Fermi surface it can be presented as

$$\varepsilon\left(p\right) = p_F\left|p - p_F\right|/m^*\,, \tag{2.303}$$

where $m^*$ is the effective mass of an elementary excitation which depends on the interaction. The corresponding Green's function is

$$G\left(\omega, \mathbf{p}\right) = \frac{Z}{\omega - p_F\left(p - p_F\right)/m^* + i0sgn\,\omega} + g\left(\omega, \mathbf{p}\right), \tag{2.304}$$

where $g\left(\omega, \mathbf{p}\right)$ is a function that is regular at $\omega = \varepsilon\left(p\right)$. One can show also that the "constant of renormalization" $Z$ is restricted according to $0 \langle Z \leq 1$. The transition from the normal state to the superconducting state, of course, changes the situation completely.

### 2.14.3 Two-Particle Green's Function

It is impossible to obtain a closed equation similar to (2.300) for Green's function of a system in the presence of an interaction. However, one can derive an equation that connects the Green's function (2.273) with a more complicated two-body Green's function. To derive this equation, we consider the simplest case where the electrons interact by means of the two-body potential $U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right)$. One must then add to the Hamiltonian (2.295) the two-body term

$$\hat{V}_2 = \frac{1}{2}\int \hat{\Psi}^\dagger_\beta\left(\mathbf{r}_2, t\right)\hat{\Psi}^\dagger_\alpha\left(\mathbf{r}_1, t\right)U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) \times \hat{\Psi}_\alpha\left(\mathbf{r}_1, t\right)\hat{\Psi}_\beta\left(\mathbf{r}_2, t\right)\mathrm{d}^3x_1\mathrm{d}^3x_2\,. \tag{2.305}$$

Keeping in mind, however, future applications to the BCS model of superconductivity, we can simplify $V_2$ by assuming a $\delta$-functional interaction (2.185). We then have

$$\hat{V}_2 = -\frac{g}{2}\int \hat{\Psi}^\dagger_\beta\left(\mathbf{r}, t\right)\hat{\Psi}^\dagger_\alpha\left(\mathbf{r}, t\right)\hat{\Psi}_\alpha\left(\mathbf{r}, t\right)\hat{\Psi}_\beta\left(\mathbf{r}, t\right)\mathrm{d}^3x\,. \tag{2.306}$$

The time dependence of the $\Psi$-operator is now defined by the equation (2.296), where $\hat{H}'_0$ has to be changed to $\hat{H}' = \hat{H}'_0 + \hat{V}_2$. Calculating the commutator gives instead of (2.297) the operator equation

$$i\frac{\partial}{\partial t}\hat{\Psi}_\alpha\left(\mathbf{r}, t\right) = \left(-\frac{\nabla^2}{2m} - \mu - g\hat{\Psi}^\dagger_\beta\left(\mathbf{r}, t\right)\hat{\Psi}_\beta\left(\mathbf{r}, t\right)\right)\hat{\Psi}_\alpha\left(\mathbf{r}, t\right) \tag{2.307}$$

with which we can calculate $\partial G_{\alpha\beta}/\partial t$. Using (2.307) and noting that the discontinuity of Green's function does not depend on the interaction, instead of (2.300) we easily obtain

$$\left(i\frac{\partial}{\partial t_1} + \frac{\nabla^2_1}{2m} + \mu\right)G_{\alpha\beta}\left(X_1 - X_2\right) - ig\left\langle\hat{\mathrm{T}}\hat{\Psi}^\dagger_\gamma\left(X_1\right)\hat{\Psi}_\gamma\left(X_1\right)\hat{\Psi}_\alpha\left(X_1\right)\hat{\Psi}^\dagger_\beta\left(X_2\right)\right\rangle = \delta_{\alpha\beta}\delta\left(X_1 - X_2\right)\,, \tag{2.308}$$

where $\delta\left(X_1 - X_2\right) = \delta\left(\mathbf{r}_1 - \mathbf{r}_2\right)\delta\left(t_1 - t_2\right)$. The $T$-product on the l.h.s. of this equation is a particular case of the *two-particle* Green's function

$$K_{\gamma\delta;\alpha\beta}\left(X_3, X_4; X_1, X_2\right) = \left\langle\hat{\mathrm{T}}\hat{\Psi}_\gamma\left(X_3\right)\hat{\Psi}_\delta\left(X_4\right)\hat{\Psi}^\dagger_\alpha\left(X_1\right)\hat{\Psi}^\dagger_\beta\left(X_2\right)\right\rangle\,. \tag{2.309}$$

There is no general prescription to express the two-particle Green's function $K$ in the terms of the one-particle Green's function $G$. Still, for many problems this is possible by using valid approximations.

## 2.15 Green's Function of a Superconductor

The power of the Green's functions method in the theory of superconductivity is associated first of all with the possibility of providing a rigorous formulation of the phenomenon of Bose condensation of Cooper pairs, which we used earlier.[7] Consider the following operator that creates a pair of electrons

$$\hat{\Psi}^\dagger_\alpha\left(X_1\right)\hat{\Psi}^\dagger_\beta\left(X_2\right)\,. \tag{2.310}$$

[7] The technique described below is due to L.P. Gor'kov (1958) [7]. A compact matrix formulation of Green's theory of superconductivity was developed by Y. Nambu [34].

When this operator acts on the ground state wave function of a system of $N$ electrons, $\hat{\Psi}_\alpha^\dagger(X_1)\,\hat{\Psi}_\beta^\dagger(X_2)\,|N\rangle$ it creates, generally speaking, a superposition of excited states of the system. However, in the presence of the condensate of the Cooper pairs, a pair can be added to the condensate. Because of the large number of pairs, such an addition does *not* excite the system; i.e. in the presence of the Bose condensate the operator (2.310) has a non-vanishing matrix element between ground states of system, which differ only by the numbers of electrons:

$$\langle N+2|\hat{\Psi}_\alpha^\dagger(X_1)\,\hat{\Psi}_\beta^\dagger(X_2)\,|N\rangle\,. \tag{2.311}$$

In the thermodynamic limit the difference between these two states is negligible and this quantity can be considered as an average of the operator (2.310). The appearance of such "anomalous averages" is a special feature of a superconducting system.

Let us consider the two-particle Green's function $K$ defined according to (2.309). The average of the products of the $\Psi$-operators can be written according to the matrix multiplication rule. However, for the reconstruction of the ground state of the system in lowest approximation only the "anomalous" matrix elements (2.311) are important. The BCS theory corresponds to the following approximation of the function $K$:

$$\begin{aligned} &K_{\gamma\delta;\alpha\beta}(X_3,X_4;X_1,X_2)\\ &\approx\left\langle N|\hat{\mathrm{T}}\hat{\Psi}_\gamma(X_3)\,\hat{\Psi}_\delta(X_4)\,|N+2\right\rangle\\ &\quad\times\left\langle N+2|\hat{\mathrm{T}}\hat{\Psi}_\alpha^\dagger(X_1)\,\hat{\Psi}_\beta^\dagger(X_2)\,|N\right\rangle\,. \end{aligned} \tag{2.312}$$

Thus, in a natural way, so-called anomalous Green's functions appear:

$$F_{\alpha\beta}(X_1,X_2)=\left\langle N|T\hat{\Psi}_\alpha(X_1)\,\hat{\Psi}_\beta(X_2)\,|N+2\right\rangle\,, \tag{2.313}$$

and

$$F_{\alpha\beta}^+(X_1,X_2)=\left\langle N+2|T\hat{\Psi}_\alpha^\dagger(X_1)\,\hat{\Psi}_\beta^\dagger(X_2)\,|N\right\rangle\,. \tag{2.314}$$

We must make an important remark here. In addition to the anomalous matrix elements (2.311), the function $K$ also contains "normal" terms, for example matrix elements of the operator $\hat{\Psi}_\alpha(X_1)\,\hat{\Psi}_\beta^\dagger(X_2)$. They are not at all small compared with the anomalous terms. (On the contrary, the anomalous functions $F$ and $F^+$ are proportional to the gap $\Delta$ and consequently are exponentially small with respect to the coupling constant $g$.) However, we will nonetheless ignore these non-anomalous matrix elements in lowest approximation, because they do not cause the *qualitative* change in the nature of the ground state of the system (which is not the case for the anomalous terms). They only give "regular" corrections to the chemical potential and the effective mass.

Note that the wave function of the superconducting pair$\Lambda_{\alpha\beta}(\mathbf{r},t)$, which we introduced in Sect. 2.2, is expressed in terms of $F_{\alpha\beta}$ as

$$\Lambda_{\alpha\beta}(\mathbf{r},t)=F_{\alpha\beta}(X,X)\,,\ X=(\mathbf{r},t)\,. \tag{2.315}$$

Like $\Lambda_{\alpha\beta}$, the function $F_{\alpha\beta}$ is proportional to the antisymmetric unit spinor of rank two $I_{\alpha\beta}$:

$$\begin{aligned} F_{\alpha\beta}(X_1,X_2)&=I_{\alpha\beta}F(X_1,X_2)\,,\\ F_{\alpha\beta}^+(X_1,X_2)&=I_{\alpha\beta}F^+(X_1,X_2)\,. \end{aligned} \tag{2.316}$$

The difference in the spinor structures of $G_{\alpha\beta}$ and $F_{\alpha\beta}$ is related to the fact that $G_{\alpha\beta}$ is a mixed contracovariant spinor while $F_{\alpha\beta}$ is a contravariant one. Note also that due to the commutation relations (2.294) the functions (2.316) are symmetrical in $X_1$ and $X_2$:

$$\begin{aligned} F(X_1,X_2)&=F(X_2,X_1)\,,\\ F^+(X_1,X_2)&=F^+(X_2,X_1)\,. \end{aligned} \tag{2.317}$$

In the absence of an external field the functions $G$, $F$ and $F^+$ depend only on the coordinate difference $X=X_1-X_2$. Then the function

$$F(0)=\Lambda \tag{2.318}$$

is a constant. Note also that $F^+(0)=\Lambda^*$.

Our notation here is different from the one that we used previously. Here, we use the grand canonical Hamiltonian $H'$. Because of this, (2.315) for $\Lambda_{\alpha\beta}$ does not contain the factor $e^{-2i\mu t}$, which we had in (2.33).

Let us now derive equations for the BCS model of a superconductor. Using the decomposition (2.312)

and taking into account that $I^2 = -1$, we can rewrite (2.308) in the form

$$\left(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m} + \mu\right) G(X) + ig\Lambda F^+(X) = \delta(X) \ . \quad (2.319)$$

This equation contains the second unknown function $F^+$. To derive the equation of motion for this function, we require the equation of motion for $\hat{\Psi}^\dagger_\alpha$, which is the Hermitian conjugation of (2.307):

$$i\frac{\partial}{\partial t}\hat{\Psi}^\dagger_\alpha(\mathbf{r}, t) = \left(\frac{\nabla^2}{2m} + \mu + g\hat{\Psi}^\dagger_\alpha(\mathbf{r}, t)\,\hat{\Psi}^\dagger_\beta(\mathbf{r}, t)\right)\hat{\Psi}_\beta(\mathbf{r}, t) \ . \quad (2.320)$$

Differentiating (2.314) with respect to $t_1$ gives an equation with the *anomalous two-particle* Green's function

$$\left\langle \hat{\mathrm{T}}\hat{\Psi}^\dagger_a(X_1)\,\hat{\Psi}^\dagger_\gamma(X_1)\,\hat{\Psi}_\gamma(X_1)\,\hat{\Psi}^\dagger_\beta(X_2)\right\rangle = iI_{\alpha\beta}\Lambda^* G(X_1 - X_2) \ . \quad (2.321)$$

As a result, we obtain the following equation for $F^+(X)$:

$$\left(i\frac{\partial}{\partial t} - \frac{\nabla^2}{2m} - \mu\right) F^+(X) - ig\Lambda^* G(X) = 0 \ . \quad (2.322)$$

A delta-function term similar to the right-hand side of (2.319) does not arise here, since the function $F^+(X_1, X_2)$, unlike $G(X_1, X_2)$, is continuous at $t_1 = t_2$. Equations (2.319) and (2.322) can be easily solved in the momentum representation. Taking the Fourier components of these equations, we obtain

$$\begin{aligned}(\omega - \eta_p)\, G(P) + ig\Lambda F^+(P) &= 1 \ , \\ (\omega + \eta_p)\, F^+(P) - ig\Lambda^* G(P) &= 0 \ , \end{aligned} \quad (2.323)$$

where $P = (\mathbf{p}, \omega)$ and $\eta_p = p^2/2m - \mu$. Eliminating $F^+(P)$ from (2.323) gives the formal solution

$$G(P) = \frac{\omega + \eta_p}{\omega^2 - \varepsilon^2(p)} = \frac{u_p}{\omega - \varepsilon(p)} + \frac{v_p}{\omega + \varepsilon(p)} \ , \quad (2.324)$$

where

$$\varepsilon(p) = \sqrt{\Delta^2 + \eta_p^2} \ . \quad (2.325)$$

Here, we used the notation

$$\Delta = g\,|\Lambda| \ , \quad (2.326)$$

and $u_p$ and $v_p$ are given by (2.217). The solution (2.324) is only a formal one, since it does not define the way to pass around the poles. In this section we consider only the case of zero temperature. The case of finite temperatures will be considered in the next section by a different method. At $T = 0$ the way to pass around the poles is given by the general equation (2.292). Adding infinitesimal imaginary parts according to this equation we obtain

$$G(P) = \frac{u_p}{\omega - \varepsilon(p) + i0} + \frac{v_p}{\omega + \varepsilon(p) - i0} = \frac{\omega + \eta_p}{(\omega - \varepsilon(p) + i0)(\omega + \varepsilon(p) - i0)} \ . \quad (2.327)$$

Comparing this with (2.292) also shows that $\varepsilon(p)$ is the energy of elementary excitations. Thus we have recovered equation (2.220) for the spectrum. Equation (2.326) establishes a relation between the gap in the spectrum and the anomalous Green's function of a superconductor. Substituting (2.327) gives

$$F^+(P) = \frac{ig\Lambda}{(\omega - \varepsilon(p) + i0)(\omega + \varepsilon(p) - i0)} \ . \quad (2.328)$$

Then, rewriting (2.318) in momentum space, we find

$$\Lambda^* = \int F^+(P)\,\frac{d\omega d^3p}{(2\pi)^4} \ . \quad (2.329)$$

Substituting (2.328), we can integrate with respect to $\omega$ by closing the contour with an infinite semicircle in the upper or lower half plane. The integral is expressed in terms of the residue at the pole:

$$\Lambda^* = \Lambda^* \frac{g}{2}\int \frac{1}{\varepsilon(p)}\,\frac{d^3p}{(2\pi)^3} \ . \quad (2.330)$$

Thus we recapture (2.224) for the gap $\Delta_0$ at $T = 0$. The function

$$F^+(\mathbf{r}) = \int F^+(P)\, e^{-i\mathbf{p}\cdot\mathbf{r}}\,\frac{d\omega d^3p}{(2\pi)^4} = \Lambda^*\frac{g}{2}\int \frac{e^{-i\mathbf{p}\cdot\mathbf{r}}}{\varepsilon(p)}\,\frac{d^3p}{(2\pi)^3} \quad (2.331)$$

describes Cooper pairs and has the physical meaning of a pair wave function. It follows from (2.331) that this function decreases for large $r$ as $\sin\left(p_F r/\hbar\right) e^{-r/\xi_0}$, with

$$\xi_0 = \frac{\hbar p_F}{m\Delta_0} . \tag{2.332}$$

Thus, the coherence length $\xi_0$ introduced in (2.55) has the physical meaning of the size of a Cooper pair. Since $\Delta_0$ is exponentially small, the coherence length is very large in comparison to the interelectronic spacings $\hbar/p_F$.

So far we have considered a superconductor in the absence of a magnetic field. The introduction of the magnetic field is achieved by replacing the operator $\nabla$ in (2.307) by $(\nabla - ie\mathbf{A}/c)$ and correspondingly by $(\nabla + ie\mathbf{A}/c)$ in (2.320). In the presence of a stationary magnetic field Green's functions depend on $\mathbf{r}_1$ and $\mathbf{r}_2$ separately, but continue to depend on $t_1$ and $t_1$ only through the difference $t = t_1 - t_2$. We can keep the old spin structure of the Green's functions, since direct interaction of the magnetic field with spin magnetic momenta of electrons is small and can be neglected. Finally, the equations for the Green's functions in the field take the form:

$$\left(i\frac{\partial}{\partial t} + \frac{1}{2m}\left(\nabla_1 - ie\mathbf{A}\left(\mathbf{r}_1\right)/c\right)^2 + \mu\right) \times G\left(X_1, X_2\right) + ig\Lambda\left(\mathbf{r}_1\right) F^+\left(X_1, X_2\right) = \delta\left(X_1 - X_2\right) \tag{2.333}$$

and

$$\left(i\frac{\partial}{\partial t} + \frac{1}{2m}\left(\nabla_1 + ie\mathbf{A}\left(\mathbf{r}_1\right)/c\right)^2 + \mu\right) F^+ \times \left(X_1, X_2\right) - ig\Lambda^*\left(\mathbf{r}_1\right) G\left(X_1, X_2\right) = 0 . \tag{2.334}$$

It is not difficult to show that these equations are invariant with respect to the gauge transformation

$$\mathbf{A}\left(\mathbf{r}\right) \to \mathbf{A}\left(\mathbf{r}\right) + \nabla\gamma\left(\mathbf{r}\right) , \tag{2.335}$$

$$G\left(X_1, X_2\right) \to G\left(X_1, X_2\right) \times \exp\left[\frac{ie}{\hbar c}\left(\gamma\left(\mathbf{r}_1\right) - \gamma\left(\mathbf{r}_2\right)\right)\right] , \tag{2.336}$$

$$F^+\left(X_1, X_2\right) \to F^+\left(X_1, X_2\right) \times \exp\left[-\frac{ie}{\hbar c}\left(\gamma\left(\mathbf{r}_1\right) + \gamma\left(\mathbf{r}_2\right)\right)\right] . \tag{2.337}$$

Accordingly, one has

$$\Delta^*\left(\mathbf{r}\right) \to \Delta^*\left(\mathbf{r}\right) \exp\left[-\frac{2ie}{\hbar c}\gamma\left(\mathbf{r}\right)\right] . \tag{2.338}$$

However, the momentum cut-off actually breaks the gauge invariance. A consistent gauge-invariant theory can be formulated only by using a realistic electron–phonon interaction.

## 2.16 Temperature Green's Functions

There are several approaches to using Green's function methods to solve finite-temperature problems. We will present here the general and elegant method of so-called imaginary-time temperature Green's functions. This method is based on introducing a new imaginary-time representation for the $\Psi$-operators of the electrons. So far we used these operators in the ordinary time-dependent Heisenberg representation ( 2.274). The imaginary-time operators $\hat{\Psi}\left(\mathbf{r}, \tau\right)$ and $\hat{\Psi}^+\left(\mathbf{r}, \tau\right)$ can be obtained from the Heisenberg operators $\hat{\Psi}_\alpha\left(\mathbf{r}, t\right)$ and $\hat{\Psi}^\dagger_\alpha\left(\mathbf{r}, t\right)$ by replacing the variable $t$ by the imaginary variable $(-i\tau)$:

$$\hat{\Psi}_\alpha\left(\mathbf{r}, \tau\right) = \exp\left(\hat{H}'\tau\right) \hat{\Psi}_\alpha\left(\mathbf{r}\right) \exp\left(-\hat{H}'\tau\right) ,$$
$$\hat{\Psi}^+_\alpha\left(\mathbf{r}, \tau\right) = \exp\left(\hat{H}'\tau\right) \hat{\Psi}^\dagger_\alpha\left(\mathbf{r}\right) \exp\left(-\hat{H}'\tau\right) . \tag{2.339}$$

We will denote the imaginary-time operators by oblique ("Italic") letters. We emphasize that the operator $\hat{\Psi}^+_\alpha\left(\mathbf{r}, \tau\right)$ is not the Hermitian-conjugate of the operator $\hat{\Psi}_\alpha\left(\mathbf{r}, \tau\right)$; actually $\left(\hat{\Psi}_\alpha\left(\mathbf{r}, \tau\right)\right)^\dagger = \hat{\Psi}^+_\alpha\left(\mathbf{r}, -\tau\right)$. The temperature Green's function $\mathcal{G}$ is defined in terms of these operators.[8] The definition includes averaging with respect to the statistical distribution:

$$\mathcal{G}_{\alpha\beta}\left(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2\right) = - \left\langle \hat{\mathrm{T}}_\tau \hat{\Psi}_\alpha\left(\mathbf{r}_1, \tau_1\right) \hat{\Psi}^+_\beta\left(\mathbf{r}_2, \tau_2\right) \right\rangle , \tag{2.340}$$

[8] The mathematical technique based on using these Green's functions was introduced by T. Matsubara in 1955 [35], see also Abrikosov et al. [36].

where $\hat{T}_\tau$ is the symbol for "$\tau$-chronological ordering". It arranged the operators from right to left in order of increasing $\tau$. The sign is changed for every interchange of Fermi operators. The brackets $\langle \ldots \rangle$ mean averaging over the grand canonical distribution:

$$\langle \ldots \rangle = \mathrm{tr}\left\{ \exp\left( \frac{\Omega - \hat{H}'}{T} \right) \ldots \right\} , \qquad (2.341)$$

where tr denotes the sum of the diagonal matrix elements, and $\Omega$ is the grand canonical thermodynamic potential, which we already used in Sect. 3.3. Like $G_{\alpha\beta}$ the function $\mathcal{G}_{\alpha\beta}$ in the absence of a magnetic field is proportional to a unit spinor: $\mathcal{G}_{\alpha\beta} = \delta_{\alpha\beta}\mathcal{G}$. Thus,

$$\mathcal{G}(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2) = -\frac{e^{\beta\Omega}}{2}\mathrm{tr}\left\{ e^{-\beta\hat{H}'}\hat{T}_\tau \hat{\Psi}_\alpha(\mathbf{r}_1, \tau_1)\hat{\Psi}^+_\alpha(\mathbf{r}_2, \tau_2) \right\} . \qquad (2.342)$$

Here and below $\beta$ means the inverse temperature:

$$\beta = 1/T . \qquad (2.343)$$

Next, we will prove an important property of the temperature Green's functions. The function $\mathcal{G}$ depends only on the "time" difference $\tau = \tau_1 - \tau_2$. Consider the case $\tau_1 \langle \tau_2$. Then, according to (2.339) and (2.342):

$$\mathcal{G}(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2) = -\frac{e^{\beta\Omega}}{2}\mathrm{tr} \times \left\{ e^{-\beta\hat{H}'} e^{\tau_2\hat{H}'}\hat{\Psi}^\dagger_\alpha(\mathbf{r}_2)\, e^{-(\tau_2-\tau_1)\hat{H}'}\hat{\Psi}_\alpha(\mathbf{r}_1) e^{-\tau_2\hat{H}'} \right\} . \qquad (2.344)$$

A cyclic permutation of operators in the trace reduces this equation to:

$$\mathcal{G}(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2) = \frac{e^{\beta\Omega}}{2}\mathrm{tr} \times \left\{ e^{-(\beta+\tau)\hat{H}'}\hat{\Psi}^\dagger_\alpha(\mathbf{r}_2)\, e^{\tau\hat{H}'}\hat{\Psi}_\alpha(\mathbf{r}_1) \right\} ts,\ \tau\langle 0 . \qquad (2.345)$$

Analogous transformations give for $\tau\rangle 0$:

$$\mathcal{G}(\mathbf{r}_1, \tau_1; \mathbf{r}_2, \tau_2) = -\frac{e^{\beta\Omega}}{2}\mathrm{tr} \left\{ e^{-\tau\hat{H}'}\hat{\Psi}^\dagger_\alpha(\mathbf{r}_2)\, e^{-(\beta-\tau)\hat{H}'}\hat{\Psi}_\alpha(\mathbf{r}_1) \right\} ,\ \tau\rangle 0 . \qquad (2.346)$$

These equation show that indeed $\mathcal{G}$ is a function only of $\tau$. Moreover, comparison of (2.346) and (2.346) gives an important symmetry relation:

$$\mathcal{G}(\tau\langle 0) = -\mathcal{G}(\tau + \beta) . \qquad (2.347)$$

Hence, it is sufficient to consider the variable $\tau$ in the interval

$$-\beta \le \tau \le \beta . \qquad (2.348)$$

Then (2.347) expresses $\mathcal{G}$ for negative $\tau$ through its value for $\tau\rangle 0$.

The function $\mathcal{G}$ defines the thermodynamic properties of the system. For example, one can calculate the density of the system from the equation

$$2\mathcal{G}(\mathbf{r}; \mathbf{r}; \tau \to -0) = -\left\langle \hat{\Psi}^\dagger_\alpha(\mathbf{r})\hat{\Psi}_\alpha(\mathbf{r}) \right\rangle = -\frac{N}{V} . \qquad (2.349)$$

The density $N/V$ can be expressed in terms of the chemical potential $\mu$, volume $V$ and temperature $T$. One can calculate the potential $\Omega$ by integration of the equation $N = -(\partial\Omega/\partial N)_{T,V}$ .

The periodicity condition (2.348) allows us to represent the temperature Green's function as a Fourier *series* with respect to $\tau$ (as opposed to a Fourier integral) of the form

$$\mathcal{G}(\mathbf{r}_1, \mathbf{r}_2, \tau) = T\sum_{n=-\infty}^{\infty} e^{-i\zeta_n\tau}\mathcal{G}(\mathbf{r}_1, \mathbf{r}_2, \zeta_n) ; \qquad (2.350)$$

this greatly simplifies the application of the formalism. The symmetry condition (2.347) will be automatically fulfilled if

$$\zeta_n = (2n+1)\pi T ,\ n = 0, \pm 1, \pm 2, \pm 3, \ldots \qquad (2.351)$$

The inverse transformation is

$$\mathcal{G}(\mathbf{r}_1, \mathbf{r}_2, \zeta_n) = \int_0^\beta e^{i\zeta_n\tau}\mathcal{G}(\mathbf{r}_1, \mathbf{r}_2, \tau)\, \mathrm{d}\tau . \qquad (2.352)$$

In a spatially-uniform system $\mathcal{G}(\mathbf{r}_1, \mathbf{r}_2, \zeta_n)$ depends only on the coordinate difference $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. Then

$$\mathcal{G}(\mathbf{r}, \zeta_n) = \int e^{i\mathbf{p}\cdot\mathbf{r}}\mathcal{G}(\mathbf{p}, \zeta_n)\frac{d^3p}{(2\pi)^3} . \qquad (2.353)$$

In concluding this section note that differentiation of (2.339) gives the equation of motion for $\Psi$

$$-\frac{\partial}{\partial\tau}\hat{\Psi}_\alpha = -\left(\hat{H}_0'\hat{\Psi}_\alpha - \hat{\Psi}_\alpha\hat{H}_0'\right), \quad (2.354)$$

which can be obtained from (2.296) by $t \to -i\tau$. An equation of the same form is valid also for $\Psi^+$. For an ideal gas we find instead of (2.300):

$$\left(-\frac{\partial}{\partial\tau} + \frac{\nabla^2}{2m} + \mu\right)\mathcal{G}^{(0)}(\mathbf{r},\tau) = \delta(\mathbf{r})\,\delta(\tau)\,. \quad (2.355)$$

The Fourier transform of this equation gives

$$\mathcal{G}^{(0)}(\mathbf{p},\zeta_n) = \frac{1}{i\zeta_n - \eta_p}\,. \quad (2.356)$$

Since this function has no poles on the real axes of $\zeta_n$, it is uniquely defined by (2.355) without any additional conditions.

## 2.17 Temperature Green's Functions for a Superconductor

Equations for the temperature Green's functions of a superconductor can be derived in the same way as was done for $T = 0$. An equation for the imaginary-time $\Psi$-operator can be obtained from (2.307) and (2.320) by replacing $t \to -i\tau$. Differentiating (2.340) for the Green's function leads to the two-particle temperature Green's function

$$\mathcal{K}_{\gamma\delta;\alpha\beta}(X_3,X_4;X_1,X_2) = \left\langle \hat{\mathrm{T}}_\tau\hat{\Psi}_\gamma(X_3)\,\hat{\Psi}_\delta(X_4)\,\hat{\Psi}^+_\alpha(X_1)\,\hat{\Psi}^+_\beta(X_2)\right\rangle, \quad (2.357)$$

where $X = (\mathbf{r},\tau)$ and $\langle\ldots\rangle$ denotes the statistical average. In the superconducting state, the system is characterized by the existence of the anomalous averages

$$\mathcal{F}^+_{\alpha\beta}(X_1,X_2) = \left\langle \hat{\mathrm{T}}_\tau\hat{\Psi}^+_\alpha(X_1)\,\hat{\Psi}^+_\beta(X_2)\right\rangle = I_{\alpha\beta}\mathcal{F}^+(X_1,X_2)\,, \quad (2.358)$$

and a similar form for $\mathcal{F}_{\alpha\beta}$. Instead of the decomposition (2.312) we then have

$$K_{\gamma\delta;\alpha\beta}(X_3,X_4;X_1,X_2) = \mathcal{F}_{\gamma\delta}(X_3,X_4)\,\mathcal{F}^+_{\alpha\beta}(X_1,X_2)\,. \quad (2.359)$$

As a result we obtain for $\mathcal{G}$ the equation

$$\left(-\frac{\partial}{\partial\tau} + \frac{\nabla^2}{2m} + \mu\right)\mathcal{G}(X) + \Delta\mathcal{F}^+(X) = \delta(X)\,. \quad (2.360)$$

The equation for $\mathcal{F}^+$ is derived analogously to (2.322). Thus, we obtain

$$\left(\frac{\partial}{\partial\tau} + \frac{\nabla^2}{2m} + \mu\right)\mathcal{F}^+(X) - \Delta^*\mathcal{G}(X) = 0\,, \quad (2.361)$$

where

$$\Delta^* = g\mathcal{F}^+(0)\,. \quad (2.362)$$

One can easily solve this equation by Fourier transformation. Then,

$$\mathcal{F}^+(X) = T\sum_{n=-\infty}^{\infty}\int e^{i(\mathbf{p}\cdot\mathbf{r}-\zeta_n\tau)} \times \mathcal{F}^+(\mathbf{p},\zeta_n)\,\frac{d^3p}{(2\pi)^3}\,, \quad (2.363)$$

with $\zeta_n$ defined by (2.351). The system of equations (2.360) to (2.362) takes the form

$$\begin{aligned}(i\zeta_n - \eta_p)\,\mathcal{G}(\mathbf{p},\zeta_n) + \Delta\mathcal{F}^+(\mathbf{p},\zeta_n) &= 1\,,\\ (i\zeta_n + \eta_p)\,\mathcal{F}^+(\mathbf{p},\zeta_n) + \Delta^*\mathcal{G}(\mathbf{p},\zeta_n) &= 0\,,\end{aligned} \quad (2.364)$$

with

$$\Delta^* = gT\sum_{n=-\infty}^{\infty}\int \mathcal{F}^+(\mathbf{p},\zeta_n)\,\frac{d^3p}{(2\pi)^3}\,. \quad (2.365)$$

The solutions of (2.364) are

$$\mathcal{G}(\mathbf{p},\zeta_n) = -\frac{i\zeta_n + \eta_p}{\zeta_n^2 + \varepsilon^2}\,,\quad \mathcal{F}^+(\mathbf{p},\zeta_n) = \frac{\Delta^*}{\zeta_n^2 + \varepsilon^2}\,, \quad (2.366)$$

where again $\varepsilon = \sqrt{\Delta^2 + \eta_p^2}$. Equation (2.365) for $\Delta^*$ is reduced to

$$\frac{gT}{(2\pi)^3}\sum_{n=-\infty}^{\infty}\int\frac{d^3p}{\zeta_n^2 + \varepsilon(p)^2} = 1\,. \quad (2.367)$$

The sum with respect to $n$ is given by

$$\sum_{n=-\infty}^{\infty}\left[(2n+1)^2\pi^2 + x^2\right]^{-1} = \frac{1}{2x}\tanh\frac{x}{2}\,. \quad (2.368)$$

Finally we obtain the gap equation

$$\frac{g}{2}\int\frac{1}{\varepsilon}\tanh\frac{\varepsilon}{2T}\frac{d^3p}{(2\pi)^3} = 1\,, \quad (2.369)$$

which coincides with (2.222).

## References


1. L.D. Landau and E.M. Lifshitz, *Statisticheskaya Fizika* (Fizmatgiz, Moscow, 1951); In: *Statistical Physics* (Pergamon Press, Oxford 1958) Sect. 133
2. O. Penrose, Phylos. Mag. **42**, 1373 (1951)
3. L. Onsager, Nuove Cimento **6**, Suppl. 2, 249 and 281 (1949)
4. R.P. Feynman, In: *Progress in Low Temperature Physics*, ed. by C.J. Gorter (North-Holland, Amsterdam 1955)
5. L.D. Landau, J. Phys. (USSR) **5**, 71 (1941)
6. J. Bardeen, L.N. Cooper, and J.R. Schrieffer, Phys. Rev. **106**, 162; **108**, 1175 (1957)
7. L.P. Gor'kov, Sov. Phys. JETP **7**, 505 (1958)
8. B.D. Josephson, Phys. Lett. **1**, 251 (1962); Rev. Mod. Phys. **36**, 216 (1964)
9. F. London and H London, Proc. Roy. Soc. **149**, 71 (1935); Physica **2**, 341 (1935)
10. A.B. Pippard, Proc. Roy. Soc. A **216**, 547 (1953)
11. F. London, In: *Superfluids* (Wiley, New York 1950) Vol. 1
12. L.D. Landau, Phys. Z. (USSR) **11**, 129 (1937)
13. R.E. Peierls, Proc. Roy. Soc. A **155**, 613 (1936)
14. F. London, Physica **3**, 450 (1936)
15. V.L Ginzburg and L.D. Landau, Zh. Exp. Teor. Fiz. **20** 1064 (1950)
16. L.D. Landau and E.M. Lifshitz, In: *Statistical Physics, Part 1*, 3rd edn. (Pergamon Press, Oxford 1986)
17. L.D. Landau and E.M. Lifshitz, In: *Electrodynamics of Continuous Media*, 2nd edn. (Pergamon Press, Oxford 1984)
18. A.A. Abrikosov, Zh. Exp. Teor. Fiz. **32**, 1442 (1957)
19. D. Sain-James and P.G. De Gennes, Phys. Lett. **7**, 306 (1963)
20. A.A. Abrikosov, In: *Fundamentals of the Theory of Metals* (North-Holland, Amsterdam, 1988)
21. A.A. Abrikosov, Dokl. AN SSSR **86**, 489 (1952)
22. J.R. Schrieffer, In: *Theory of Superconductivity* (W.A. Benjamin, New York 1964)
23. P.G. de Gennes, In: *Supercpnductivity of Metals and Alloys* (W.A. Benjamin, New York 1966)
24. J. Bardeen, Phys. Rev. **79**, 167; **80**, 567 (1950)
25. H. Fröhlich, Phys. Rev. **79**, 1189 (1956)
26. L.N. Cooper, Phys. Rev. **104**, 845 (1950)
27. N.N. Bogoliubov, Sov. Phys. JETP **7**, 41 (1958); Nuovo Cimento **7**, 794 (1958)
28. J.G. Valatin, Nuovo Cimento **7**, 843 (1958)
29. N.N. Bogoliubov, J. Phys. (USSR) **11**, 23 (1947)
30. L.P. Gor'kov, T.K. Melik-Barkhudarov, Sov. Phys. JETP **13**, 1018 (1961)
31. L.P. Gor'kov, Sov. Phys. JETP **9**, 1364 (1959)
32. E.M. Lifshitz, L.P. Pitaevskii, In: *Statistical Physics, Part 2* (Pergamon Press, Oxford 1986)
33. A.A. Abrikosov, L.P. Gor'kov and I.E. Dzyaloshinski, In: *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, NJ, 1963)
34. Y. Nambu, Phys. Rev. **117** 648 (1960)
35. T. Matsubara, Prog. Theor. Phys. **14**, 351 (1955)
36. A.A. Abrikosov, L.P. Gor'kov and I.E. Dzyaloshinski, Sov. Phys. JETP **9**, 636 (1959)