Lectures on Superconductivity

Richard Hlubina
Comenius University, Bratislava, Slovakia

Contents

1 Basic notions **2**

2 Ginzburg-Landau theory **7**

3 Magnetic properties of type I superconductors **11**

4 Magnetic properties of type II superconductors **14**

5 Pairing instability **19**

6 BCS theory **23**

7 Spectroscopy of the superconducting state **28**

8 Josephson effect **32**

1 Basic notions

Experimental facts
Most metals exhibit at low temperatures a thermodynamic transition to a new condensed state (superconductor) with the following properties:

1. Critical temperature T_c
   The thermodynamic transition at zero applied magnetic field is of second order (specific heat jump) and occurs at a temperature $T = T_c$. Typical transition temperatures of elemental metals are below T_c(Nb)=9.3 K. Commercially used alloys: $T_c(Nb_3Sn)$=18 K, $T_c(Nb_3Ge)$=23 K. Post-high T_c era materials have substantially higher transition temperatures: $T_c(Rb_3C_{60})$=28 K, $T_c(MgB_2)$=39 K, and the current record holder is $T_c(HgBa_2Ca_2Cu_3O_8)$=133 K.

2. Dissipationless conductivity
   Below T_c, the resistance of a superconducting wire is not measurable and for all practical purposes can be taken $R = 0$. (This is true except extremely close to T_c, where fluctuation effects can lead to finite conductivity.) In pure superconductors, R jumps from a finite value above T_c to $R = 0$ in a narrow temperature range (10^{-5} K in pure gallium, e.g.).

3. Persistent currents
   Imagine a ring from a normal metal threaded by a flux Φ. Suppose there is no current flowing in the ring at negative times. At time $t = 0$, let us instantaneously switch off the flux in the ring. This induces an e.m.f. $-d\Phi/dt$ in the ring. If the resistivity of the ring is R and its inductance is L, then the induced current in the ring satisfies
   $$\Phi\delta(t) = -\frac{d\Phi}{dt} = RI + L\frac{dI}{dt},$$
   with the solution $I(t) = I_0 \exp(-t/\tau)$, where $I_0 = \Phi/L$ and $\tau = L/R$. By Lenz's law, the current initially keeps the flux in the ring unchanged, but it decays with a time constant τ. In a superconductor $R = 0$ and therefore a persistent current develops. Measurements of τ are among the most sensitive methods of determining the resistance of a superconductor. Note also that in a superconductor $d(\Phi + LI)/dt = 0$, i.e. the total magnetic flux threading the ring $\Phi + LI$ (fluxoid) is constant in time.

4. Meissner-Ochsenfeld effect
   Superconductors behave as ideal diamagnets. If an external magnetic field is applied to a superconductor, the magnetic field inside the superconductor vanishes. This means that finite surface currents have to flow in superconductors which shield the effect of external fields. Perfect conductivity can thus be thought of as a consequence of ideal diamagnetism: the superconductor screens the magnetic field around itself and therefore carries a transport current. The existence of supercurrents is therefore an equilibrium property.

5. Critical magnetic field B_c
Superconductivity can be destroyed by an application of a succiciently strong magnetic field. The details are different for the so-called type-I and type-II superconductors, see later. The simplest case is that of a long cylindrical type-I superconductor in a parallel magnetic field B. In that case, there exists a well-defined critical field B_c, above which superconductivity is destroyed. The critical field $B_c(T)$ decreases with increasing temperature and $B_c(T_c) = 0$.

London theory

Heuristic argument for $T = 0$: the Lagrangian of a particle with mechanical momentum $m\mathbf{v}$ and charge q in presence of electromagnetic potentials $\varphi(\mathbf{r}, t)$ and $\mathbf{A}(\mathbf{r}, t)$ is $L(\mathbf{r}, \mathbf{v}, t) = \frac{1}{2}m\mathbf{v}^2 + q\mathbf{A} \cdot \mathbf{v} - q\varphi$, as can be checked by showing that $\frac{d}{dt}\left(\frac{\partial L}{\partial \mathbf{v}}\right) = \frac{\partial L}{\partial \mathbf{r}}$ is equivalent to the Newton equation of motion $m\mathbf{a} = q(\mathbf{E}+\mathbf{v}\times\mathbf{B})$. The corresponding canonical momentum of the particle is $\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = m\mathbf{v} + q\mathbf{A}$. In absence of applied fields, if $\mathbf{v}$ is interpreted as the drift velocity, we have $\mathbf{v} = 0$ and therefore $\mathbf{p} = 0$. Now we make the assumption that, if we switch on a finite $\mathbf{A}$, the superconductor wavefunction is rigid and retains $\mathbf{p} = 0$. Therefore $\mathbf{v} = -q\mathbf{A}/m$, or alternatively, the current density $\mathbf{j} = nq\mathbf{v}$ (where n is the electron density) satisfies the London equation

$$\mathbf{j} = -\frac{ne^2}{m}\mathbf{A}, \tag{1}$$

where we have taken into account that the electron charge $q = -e$, $e > 0$. This equation (not gauge invariant!) describes the response of superconductors to transverse fields. The response of superconductors to longitudinal fields is well described by the Thomas-Fermi theory of metallic screening,

$$\rho = -\frac{ne^2}{mv_s^2}\varphi, \tag{2}$$

where $v_s^2 = m^{-1}\partial p/\partial n = v_F^2/3$ is the sound velocity in an electron liquid, φ is the scalar potential and the charge density ρ is related to the current density $\mathbf{j}$ by charge conservation,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0. \tag{3}$$

Note that neither Eq. 1, nor Eq. 2 are gauge invariant. However, making use of the definitions $\mathbf{B} = \nabla \times \mathbf{A}$ and $\mathbf{E} = -\nabla\varphi - \partial\mathbf{A}/\partial t$, we can write the following gauge-invariant equations (London equations), which describe the macroscopic electrodynamics of superconductors:

$$\begin{aligned} \nabla \times \mathbf{j} &= -\frac{ne^2}{m}\mathbf{B}, \\ \frac{\partial \mathbf{j}}{\partial t} &= \frac{ne^2}{m}\mathbf{E} - v_s^2\nabla\rho. \end{aligned} \tag{4}$$

The first London equation follows by taking the rotation of Eq. 1, while the second one obtains by adding the time derivative of Eq. 1 and the gradient of Eq. 2. Note that the second London equation describes the acceleration of the superconducting current by an applied electric field.

Combined with the Maxwell equations (with c the speed of light, $c^{-2} = \epsilon_0\mu_0$):

$$\begin{aligned}
\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} &= 0, \\
\nabla \times \mathbf{B} &= \mu_0 \mathbf{j} + \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t}, \\
\nabla \cdot \mathbf{E} &= \frac{\rho}{\epsilon_0}, \\
\nabla \cdot \mathbf{B} &= 0,
\end{aligned}$$

the London equations describe completely the longitudinal and transverse fields in superconductors, respectively:

$$\begin{aligned}
\left(\nabla^2 - \frac{1}{v_s^2}\frac{\partial^2}{\partial t^2}\right)\rho &= \frac{1}{\lambda_{TF}^2}\rho, \\
\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{B} &= \frac{1}{\lambda_L^2}\mathbf{B},
\end{aligned} \tag{5}$$

where $\lambda_{TF} = v_s/\omega_p$ is the Thomas-Fermi screening length (for longitudinal fields), and $\lambda_L = c/\omega_p$ is the London penetration depth. Taking an explicit form for the plasma frequency, $\omega_p^2 = ne^2/(m\epsilon_0)$, we thus have

$$\frac{1}{\lambda_L^2} = \frac{ne^2\mu_0}{m}$$

Typical values of the London penetration depth in elemental superconductors are hundreds of Å. For instance, λ_L(Al)=160 Å, and λ_L(Sn)=350 Å. In the cuprates, because of the small charge carrier density and heavy mass, the London penetration depth is much larger: $\lambda_L \sim$1500 Å.

In the static limit, Eqs. 5 describe the screening of longitudinal and transverse fields by superconductors. For instance, a parallel field B_0 enters a semiinfinite London superconductor in the form $B_0 \exp -(x/\lambda_L)$.

Sketch of a microscopic picture

Modern view of a superconductor is as follows. Below T_c, a kind of two-electron molecules are formed (Cooper pairs), with a binding energy $\Delta \sim T_c$. The Cooper pairs, being bosons, may condense into a single quantum-mechanical state, and once this happens, the superconducting state is formed.

The size of the Cooper pair ξ_0 (also called the Pippard coherence length for reasons to become clear later on) can be estimated as follows. The Cooper pairs form out of electrons at the Fermi surface with Fermi velocity v_F. Localizing such electrons in a region of order ξ_0 costs therefore an energy $\sim \hbar v_F/\xi_0$ and equating this to Δ yields

$$\xi_0 \sim \frac{\hbar v_F}{\Delta}$$

for the size of the Cooper pair. Since $\Delta \ll \varepsilon_F$ where ε_F is the Fermi energy, ξ_0 is much larger than the average distance between the electrons, leading to overlapping Cooper pairs. Therefore the two-electron molecule picture is not fully applicable. Note that ξ_0 decreases with the binding energy Δ, ranging from ξ_0(Sn)=3000 Å, to $\sim$ 15 Å, in the cuprates.

At $T = 0$ we expect that the condensation energy is of the order $N(0)\Delta^2/2$, since $N(0)\Delta$ electrons gain energy of the order Δ (where $N(0) \sim n/\varepsilon_F$ is the density of states at the Fermi energy per unit volume). This yields an estimate of the critical field at zero temperature, $B_c \sim \Phi_0/(\lambda_L \xi_0)$, where $\Phi_0 = h/(2e)$ is the elementary flux quantum.

Two-fluid model

So far we have considered only $T = 0$. At finite temperatures a fraction of the Cooper pairs is broken and the unpaired electrons provide a dissipative channel, e.g. for finite frequency electric fields. Within the so-called two-fluid model, the gas of unpaired electrons is called the normal fluid (density $n_N(T)$), as opposed to the superconducting fluid(density $n_S(T)$), which is formed by the condensate of the Cooper pairs and is responsible for the Meissner effect and other hallmarks of the superconducting state. It is assumed that $n_N + n_S = n$ and that $n_S(T)$ is a monotonically decreasing function such that $n_S(0) = n$ and $n_S(T_c) = 0$.

The two characteristic length scales of a superconductor have the following temperature dependence. The London penetration depth $\lambda_L^{-2}(T) = \frac{n_S e^2 \mu_0}{m}$ measures the number of condensed electrons and therefore becomes strongly temperature dependent, $\lambda \to \infty$ as $T \to T_c$, as it should be, since above T_c the material should not screen transverse fields. On the other hand, the Pippard coherence length ξ_0 is essentially temperature independent (this is a nontrivial consequence of the BCS theory).

Thermodynamic aspects

Consider a solenoid with N turns of length L and diameter r_1, inside which there is a cylindrical superconductor with radius r_0. The magnetic field inside the solenoid is $B = \mu_0 NI/L$. Let us denote the free energy densities (in absence of magnetic fields) in the normal and superconducting states as f_N and f_S, respectively. In the normal state the magnetic field penetrates the volume of the superconductor, and therefore the (Helmoltz) free energy of the system superconductor+magnetic field is

$$F_N(B) = V(f_N + \frac{B^2}{2\mu_0}) + V_{\text{ext}}\frac{B^2}{2\mu_0},$$

where $V = \pi r_0^2 L$ is the volume of the superconductor and $V_{\text{ext}} = \pi(r_1^2 - r_0^2)L$ is the free space volume within the coil. Let us consider what happens if we make the cylinder superconducting, while keeping the current in the coil constant. In the superconducting state the same field B exists only within the space between the coil and superconductor, and therefore

$$F_S(B) = V f_S + V_{\text{ext}}\frac{B^2}{2\mu_0}.$$

On the other hand, the flux across the coil has shrunk from $\Phi_N = B\pi r_1^2$ in the normal state to $\Phi_S = B\pi(r_1^2 - r_0^2)$ in the superconducting state. This induces a voltage U in the coil which is, by Lenz's law, parallel to the current I. In the process of its transformation from normal to superconducting, the cylinder has therefore done work W on the external circuit:

$$W(B) = \int_N^S UIdt = -NI\int_N^S d\Phi = NIB\pi r_0^2 = V\frac{B^2}{\mu_0}.$$

At $B = B_c$ we must have $F_N = F_S + W$ and therefore

$$f_N - f_S = \frac{B_c^2}{2\mu_0},$$

i.e. the free energy density (at zero applied field) in the superconducting state is reduced w.r.t. the normal state.

The above example shows that in situations when the externally controlled parameter is the field strength $\mathbf{H}$ (defined from the equation $\nabla\times\mathbf{H} = \mathbf{j}_{\text{coil}}$, i.e. the field determined by the external currents in absence of the sample) and not the flux density $\mathbf{B}$, the Helmholtz free energy is not a natural object to study. Let us define instead the Gibbs free energy

$$G(H) = F(B) - \int d^3\mathbf{r}BH.$$

In our example $H = NI/L$ everywhere inside the coil both in the normal and superconducting states and therefore

$$\begin{aligned} G_N(H) &= V(f_N - \frac{\mu_0 H^2}{2}) - V_{\text{ext}}\frac{\mu_0 H^2}{2}, \\ G_S(H) &= Vf_S - V_{\text{ext}}\frac{\mu_0 H^2}{2}. \end{aligned}$$

One finds readily that the transition occurs at $H_c = B_c/\mu_0$, i.e. the Gibbs free energy takes automatically into account the work done on the external coils.

Thus, the boundary between the normal and superconducting phases lies along the line $H = H_c(T)$ in the H-T plane. The difference of entropies between the normal and superconducting state along the boundary can be calculated from $S = -\partial G/\partial T$. We find that, per unit volume,

$$S_N - S_S = -\mu_0 H_c(T)\frac{\partial H_c(T)}{\partial T}.$$

Two points are worth mentioning: (i) the entropy of the normal state is higher than that of the superconductor and the transition is of first order in finite fields, and (ii) the difference vanishes only at $T = T_c$, i.e. in zero applied field, in which case the transition is of second order with a specific heat jump (obtained from $c = T\partial S/\partial T$),

$$c_S - c_N = \mu_0 T_c\left(\frac{\partial H_c(T)}{\partial T}\right)^2.$$

Exercise
Using the London theory, calculate the current and magnetic field distribution in an infinite cylindrical superconductor carrying a total current I.

2 Ginzburg-Landau theory

This is a long-wavelength theory for the condensate of Cooper pairs. The crucial notion is that of a macroscopic wavefunction $\psi(\mathbf{r})$ describing the center-of-mass motion of the Cooper pairs. The scalar complex field ψ plays the role of the order parameter in the general Landau sense: above the transition temperature, $\psi = 0$, while below T_c, $|\psi|^2$ corresponds to the density of Cooper pairs.

The theory describes time independent phenomena and is well justified close to T_c (where it can be derived from microscopic theory). It starts by assuming the (Helmholtz) free energy density of a superconductor

$$f_S = f_N + \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m^*}\,|(-i\hbar\nabla + 2e\mathbf{A})\psi|^2 + \frac{1}{2\mu_0}(\nabla\times\mathbf{A})^2, \tag{6}$$

where $\alpha = a(T - T_c)$ and a, β are positive constants. The first two terms form the well-known symmetry breaking potential which is minimized, for $T < T_c$, by $|\psi|^2 = \psi_\infty^2 = -\alpha/\beta$, leading to a thermodynamic field

$$\frac{B_c^2}{2\mu_0} = f_N - f_S = \frac{\alpha^2}{2\beta}.$$

The derivative term corresponds to the kinetic energy of particles (Cooper pairs) with mass m^* and charge $-2e$ in an external field $\mathbf{A}$. (The Hamiltonian of a particle in an external field is $H(\mathbf{r},\mathbf{p},t) = \mathbf{v}\cdot\mathbf{p} - L(\mathbf{r},\mathbf{v},t) = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\varphi$ and the canonical quantization requires $\mathbf{p} = -i\hbar\nabla$.)

Variation of Eq. 6 with respect to ψ^* yields

$$\frac{1}{2m^*}(-i\hbar\nabla + 2e\mathbf{A})^2\psi + \beta|\psi|^2\psi = -\alpha\psi, \tag{7}$$

which is a Schrödinger-like equation for a particle with energy $-\alpha$ in an external magnetic field. An important difference is the nonlinear term on the left-hand side.

Variation of Eq. 6 with respect to $\mathbf{A}$ yields the Maxwell equation $\nabla\times\mathbf{B} = \mu_0\mathbf{j}$, where

$$\mathbf{j} = -\frac{4e^2}{m^*}|\psi|^2\mathbf{A} + i\frac{e\hbar}{m^*}(\psi^*\nabla\psi - \psi\nabla\psi^*) \tag{8}$$

is the superconducting current. Introducing the representation of ψ in terms of an amplitude and a phase, $\psi = |\psi|e^{i\theta}$, the supercurrent can be written as

$$\mathbf{j} = -\frac{2e}{m^*}|\psi|^2(\hbar\nabla\theta + 2e\mathbf{A}) = -\frac{4e^2}{m^*}|\psi|^2(\mathbf{A} + \frac{\Phi_0}{2\pi}\nabla\theta). \tag{9}$$

The second form can be recognized as the London equation with a (local) penetration depth $\lambda^{-2} = \frac{4e^2|\psi|^2\mu_0}{m^*}$. In small fields we expect $\lambda^{-2} = \frac{4e^2\psi_\infty^2\mu_0}{m^*} = \frac{4e^2\mu_0|\alpha|}{m^*\beta}$. Note that the GL expression is invariant under the gauge transformation

$$\begin{aligned}\mathbf{A} &\rightarrow \mathbf{A} + \nabla\chi\\ \theta &\rightarrow \theta - \frac{2\pi}{\Phi_0}\chi\end{aligned}$$

Moreover, if we write Eq. 7 in terms of a dimensionless complex function f defined as $\psi = f\psi_\infty$, then we obtain

$$\xi^2(-i\nabla + \frac{2\pi}{\Phi_0}\mathbf{A})^2 f + f^3 = f,$$

where $\xi = \frac{\hbar}{\sqrt{2m^*(-\alpha)}}$ is seen to be a typical lengthscale, over which the function f (and therefore also the macroscopic wavefunction ψ) can change. This is therefore an analogue of the Pippard coherence length and is called the Ginzburg-Landau coherence length.

When the macroscopic wavefunction ψ is expressed in terms of the dimensionless function f, the kinetic term in the GL free energy takes a physically transparent form

$$\frac{1}{2m^*}\left|(-i\hbar\nabla + 2e\mathbf{A})\psi\right|^2 = \frac{1}{2}\frac{\mu_0\lambda^2}{|f|^2}\mathbf{j}^2 + \frac{B_c^2\xi^2}{\mu_0}\nabla\left(|f|^2\right) \tag{10}$$

which demonstrates that the kinetic term is a sum of the kinetic energy of the currents and of the amplitude modulation of the wavefunction. Let us note in passing that within the GL theory, B_c can be expressed in terms of the characteristic lengths λ and ξ,

$$B_c = \frac{1}{2\pi\sqrt{2}}\frac{\Phi_0}{\lambda\xi}.$$

It is instructive to estimate the values of the parameters α, β and of the characteristic lengths ξ, λ in the limit $T = 0$. [It should be pointed out, however, that such a jump to $T = 0$ is not rigorously justified.] First, if we take the mass of the Cooper pair $m^* = 2m$ and boldly assume that at $T = 0$ all electrons are condensed (i.e. $|\psi|^2 = -\alpha/\beta = n/2$), then we recover the London penetration depth from the GL expression. Moreover, assuming that the condensation energy $B_c^2/(2\mu_0) = \alpha^2/\beta \sim N(0)\Delta^2$, we find $-\alpha \sim \Delta^2/\varepsilon_F$ and $\beta \sim |\alpha|/n$. Therefore at low temperatures the Ginzburg-Landau coherence length approaches the Pippard coherence length $\sim \hbar v_F/\Delta$.

Note that the temperature dependence of the penetration depth is qualitatively the same in both, the London and the Ginzburg-Landau theory. On the other hand, the T-dependence of the coherence length is different in these theories, since close to T_c both λ and ξ diverge as $(T_c - T)^{-1/2}$, but the important GL parameter

$$\kappa = \frac{\lambda}{\xi} = \sqrt{\frac{(m^*)^2\beta}{2e^2\mu_0\hbar^2}} \sim \frac{c}{v_F}\frac{\Delta}{\hbar\omega_p}$$

is only weakly T-dependent.

Boundary conditions
Equations 7 and 8 together with the Maxwell equations form a closed set of equations for ψ and $\mathbf{A}$. The boundary conditions can be determined by requiring that no current flows across the surface of a superconductor. Denoting the normal to the surface as $\mathbf{n}$, one finds readily that if the condition

$$(-i\hbar\nabla + 2e\mathbf{A})\psi \cdot \mathbf{n} = \frac{i\hbar}{b}\psi$$

is satisfied at the surface, then $\mathbf{j} \cdot \mathbf{n} = 0$ and no supercurrent flows across the surface. The real length scale b depends on the type of the interface and can be determined from microscopic theory. As can be seen easily in absence of applied fields, small b implies a large suppression of the order parameter at the surface. Microscopic theory for conventional superconductors shows that, for a contact with insulators $b \to \infty$, for a superconductor-magnet interface $b = 0$, and for a contact with normal metals b has a finite value.

Flux quantization

Consider a massive superconducting ring threaded by a magnetic flux. Surface currents in the ring screen the magnetic field so that well inside the ring we have vanishing magnetic fields and currents. Consider a closed path C which encircles the hole of the ring and is well inside the ring, so that no current flows along C. From Eq. 9 it follows that $\Phi_0 \nabla\theta = -2\pi\mathbf{A}$ along C. Taking a line integral along C of this equation we find

$$\Phi_0 \oint_C \nabla\theta \cdot d\mathbf{r} = -2\pi \oint_C \mathbf{A} \cdot d\mathbf{r} = -2\pi\Phi,$$

where Φ is the flux across a surface spanned on C. However, since the wavefunction ψ has to be single valued, we must have $\oint_C \nabla\theta \cdot d\mathbf{r} = 2\pi n$ where n is an integer. Therefore we have $\Phi = -n\Phi_0$ and the flux Φ is quantized in units of $\Phi_0 = h/(2e) = 2.07 \times 10^{-15}$ Wb.

Critical current of a thin wire

We have already seen that the Ginzburg Landau theory differs from the London theory by introducing a new field, the phase of the superconductor $\theta(\mathbf{r})$, and that this makes the theory gauge invariant. Another difference with respect to the London theory is that the modulation of the amplitude of ψ is allowed. Due to this latter feature, the theory predicts the existence of critical current densities, a non existent concept within the London theory.

In order to show this in the simplest possible context, let us consider the critical current of a thin superconducting wire, i.e. a wire with radius a such that $a \ll \lambda, \xi$. Since $a \ll \xi$, we can neglect the spatial modulation of the amplitude $|\psi|$ and since $a \ll \lambda$, we can take a constant vector potential within the wire [we work in the gauge where $\mathbf{A} = (0, 0, A(r))$]. Consider the case when the supercurrent is fed into the wire by maintaining a finite phase difference $\Delta\theta$ between the ends of the wire. This leads to an externally prescribed gauge invariant phase gradient $\mathbf{q} = \nabla\theta + \frac{2e}{\hbar}\mathbf{A}$. The free energy of the wire then is

$$f_S(q) = f_N + |\psi|^2 \left[\alpha + \frac{\hbar^2 q^2}{2m^*}\right] + \frac{\beta}{2}|\psi|^4.$$

Minimizing $f_S(q)$ with respect to $|\psi|^2$ we find that the minimimum is realized for $|\psi|^2 = \psi_\infty^2(1 - q^2\xi^2)$. Note that the maximally allowed gradient is $q = \xi^{-1}$ and beyond this value superconductivity is destroyed. Inserting the expression for $|\psi|^2$ into Eq. 9 we find that the current flowing in presence of the phase gradient q is

$$j(q) = -\frac{\Phi_0}{2\pi\mu_0\lambda^2}(1 - q^2\xi^2)q.$$

This function acquires a maximum for $q = (\xi\sqrt{3})^{-1}$ and the magnitude of the maximally allowed current is

$$j_c = \frac{1}{3\pi\sqrt{3}}\frac{\Phi_0}{\mu_0\lambda^2\xi}.$$

This form could have been guessed directly from Eq. 9. Replacing the Ginzburg Landau parameters λ, ξ by the microscopic λ_L, ξ_0, we obtain from here a low temperature estimate $j_c \sim nev_c$ with a maximal drift velocity $v_c \sim \frac{\Delta}{\hbar k_F}$, as could also have been guessed.

Surface energy

Consider an infinite superconductor in an applied field $H_c = B_c/\mu_0$ along the z axis. The two states, completely superconducting and completely normal, have the same Gibbs free energy and are in equilibrium. Now let us consider a planar interface (in the $x = 0$ plane) dividing the normal and superconducting phases. Let us calculate the surface energy of such an interface.

We choose a gauge $\mathbf{A} = (0, A(x), 0)$ and a real $\psi(x)$ and look for a solution satisfying the boundary conditions $\psi(-\infty) = 0$, $\psi(\infty) = \psi_\infty$, $A'(-\infty) = B_c$, and $A(\infty) = 0$, since the current $j_y = -4e^2\psi^2 A/m^*$ flows only in the neighborhood of the $x = 0$ plane.

The surface energy is equal to the difference between the Gibbs free energy of the state with the interface, $G_{NS} = \int d^3\mathbf{r}[f_S(\mathbf{r}) - BH_c]$, and that of the completely normal state, $G_N = \int d^3\mathbf{r}[f_N - B_cH_c/2]$. The surface energy per unit area is therefore

$$\gamma = \int_{-\infty}^{\infty} dx \left[\alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m^*}\left|(-i\hbar\nabla + 2e\mathbf{A})\psi\right|^2 + \frac{1}{2\mu_0}(B - B_c)^2\right].$$

Integrating the GL Eq. 7 by parts (the surface term is easily seen to vanish) we find a useful identity (valid only for a solution of the GL equation)

$$0 = \int_{-\infty}^{\infty} dx \left[\alpha|\psi|^2 + \beta|\psi|^4 + \frac{1}{2m^*}\left|(-i\hbar\nabla + 2e\mathbf{A})\psi\right|^2\right],$$

and therefore the surface energy per unit area can be simplified to

$$\gamma = \int_{-\infty}^{\infty} dx \left[\frac{1}{2\mu_0}(B - B_c)^2 - \frac{\beta}{2}|\psi|^4\right] = \frac{B_c^2}{2\mu_0}\int_{-\infty}^{\infty} dx \left[\left(1 - \frac{B}{B_c}\right)^2 - \left(\frac{\psi}{\psi_\infty}\right)^4\right].$$

From here one can see that the surface energy is positive, if the first term dominates, i.e. if B is quickly screened (this happens for $\lambda \ll \xi$, the so-called type-I superconductors). This situation is usual in classical physics: surface formation costs energy. On the other hand, if the second term dominates, i.e. if ψ heals quickly to its normal state value (which occurs for $\xi \ll \lambda$, type-II superconductors), then it is energetically favourable to generate interfaces. Let us finally note that the surface energy density can be written in terms of a new length δ, $\gamma = \delta B_c^2/(2\mu_0)$. The above argument shows that δ scales roughly as the difference of ξ and λ.

A more quantitative analysis: If we introduce dimensionless units, $\psi = \psi_\infty f$ and $A = B_c\lambda g$, then the GL equations for f and g and the expression for δ read

$$\begin{aligned}
\lambda^2 g'' &= f^2 g, \\
\xi^2 f'' &= f(f^2 - 1 + g^2/2), \\
\delta &= \int_{-\infty}^{\infty} dx \left[(1 - \lambda g')^2 - f^4\right].
\end{aligned}$$

The boundary conditions are $\lambda g'(-\infty) = 1$, $g(\infty) = 0$, $f(-\infty) = 0$, and $f(\infty) = 1$.

Limit $\lambda \ll \xi$: For $x < 0$ we have $f = 0$ and $g = x/\lambda$. For $x > 0$ we have $g = 0$ and $\xi^2 f'' = f(f^2 - 1)$ with the solution $f(x) = \tanh[x/(\sqrt{2}\xi)]$. Simple integration gives $\delta = 4\sqrt{2}\xi/3$.

Limit $\xi = 0$: For $x < 0$ we have $f = 0$ and $g = x/\lambda - \sqrt{2}$. For $x > 0$ we have $f^2 = 1 - g^2/2$ and therefore $\lambda^2 g'' = g(1 - g^2/2)$. The first integral of this equation is $\lambda g' = -g\sqrt{1 - g^2/4}$ and therefore

$$\delta = \int_{-\sqrt{2}}^{0} \frac{dg}{g'} \left[(1 - \lambda g')^2 - (1 - \frac{g^2}{2})^2 \right] = -\frac{8(\sqrt{2} - 1)}{3} \lambda.$$

3 Magnetic properties of type I superconductors

Superconducting sphere in a magnetic field

Let us consider a superconducting sphere with a diameter R in an external field $\mathbf{B_0}$. Let the origin of the coordinate system conincide with the center of the sphere. For sufficiently small B_0 the sphere is in the Meissner state and $\mathbf{B} = 0$ inside the sphere. The field outside the sphere satisfies the Maxwell equations $\nabla \cdot \mathbf{B} = 0$ and $\nabla \times \mathbf{B} = 0$ with the boundary conditions $\mathbf{B} \to \mathbf{B_0}$ at large distance from the sphere and $\mathbf{B} \cdot \mathbf{r} = 0$ for $\mathbf{r}$ at the surface of the sphere $r = R$. (The latter condition being dictated by the continuity of the normal component of $\mathbf{B}$ across the superconductor surface.) One verifies easily that

$$\mathbf{B} = \mathbf{B_0} + \frac{R^3}{2} \nabla \left(\frac{\mathbf{B_0} \cdot \mathbf{r}}{r^3} \right) = \mathbf{B_0} + \frac{R^3}{2} \frac{\mathbf{B_0} r^2 - 3(\mathbf{B_0} \cdot \mathbf{r})\mathbf{r}}{r^5}$$

satisfies all the above requirements. The field in the interior of the superconductor vanishes as a result of the shielding effect of the screening currents at the surface of the superconductor with the linear current density $\mathbf{J} = \mathbf{r} \times \mathbf{B}/(\mu_0 r)$.

The tangential part of the magnetic field at the surface of the superconductor increases from zero at the poles to $3B_0/2$ at the equator. This has interesting consequences: if the applied field lies in the range $2B_c/3 < B_0 < B_c$, the field at the equator is larger than critical and the sphere should become normal. However, the field inside a normal sphere is homogeneous and equal to $B_0 < B_c$ everywhere. Thus the sphere can be neither fully normal, nor fully superconducting. Obviously, the character of the resulting so-called intermediate state is determined not only by microscopic parameters, but also by the sample geometry.

Intermediate state of a thin film

In what follows we study the intermediate state in a simple geometry. Namely, we consider a superconducting film of thickness d in a perpendicular field with flux density B. Since the flux has to go through the film, some regions must go normal. Let us assume that the fractions of the normal and superconducting phases are ρ_N and ρ_S, respectively, and $\rho_N + \rho_S = 1$. Since the whole applied flux has to cross the sample, the field B_0 in the normal regions must be $B_0 = B/\rho_N$.

Let us look for the optimal fraction of the normal state. We have to minimize the

Helmholtz free energy

$$f = \rho_S f_S + \rho_N \left(f_S + \frac{B_c^2}{2\mu_0} + \frac{B_0^2}{2\mu_0} \right) = f_S + \frac{1}{2\mu_0} \left(\rho_N B_c^2 + \frac{B^2}{\rho_N} \right) \tag{11}$$

with respect to ρ_N. The minimum occurs for $\rho_N = B/B_c$ and therefore the optimal fraction is realized when the field in the normal regions is equal to the critical field, $B_0 = B_c$. The corresponding free energy at the minimum is $f = f_S + BB_c/\mu_0$.

The above calculation specifies neither the spatial arrangement of the phases, nor their dimensions. In what follows we will, following Landau, assume a laminar structure and determine its characteristic size. Let us note in passing that for $B \ll B_c$ a phase with a regular array of normal tubes might be more stable, while for $B \to B_c$ a regular array of superconding tubes is likely.

Let us denote the widths of the normal and superconducting lamelae as D_N and D_S, respectively. The modulation length $D = D_N + D_S$ will be determined by a competition of two effects: surface energy (per unit area of the film)

$$F_1 = \frac{2d}{D}\gamma = \frac{d\delta}{D}\frac{B_c^2}{\mu_0}$$

which is minimized by large laminae, and by the cost of forming a modulated magnetic field above and below the film, F_2. The latter can be estimated as follows. In the intermediate state, in the vicinity of the N regions, the magnetic field has an energy density $B_c^2/(2\mu_0)$, while close to the S regions this energy vanishes. Therefore the average energy density in the intermediate state is $\rho_N B_c^2/(2\mu_0) = BB_c/(2\mu_0)$. On the other hand, the energy density of a uniform magnetic field is $B^2/(2\mu_0)$. Therefore the average excess energy density is $B(B_c - B)/(2\mu_0)$. The spatial extent L of the field modulation in a direction perpendicular to the film can be estimated by the smaller of the lengths D_N, D_S, i.e. $L = \rho_N \rho_S D$, and therefore

$$F_2 = 2L\frac{B(B_c - B)}{2\mu_0} = D\frac{B^2(B_c - B)^2}{\mu_0 B_c^2}$$

Note that F_2 is minimized by a development of fine laminae with $D \to 0$. Minimizing the full energy $F_1 + F_2$, we find an optimal size of the laminae

$$D = \frac{\sqrt{d\delta}}{\rho_N \rho_S} = \sqrt{d\delta}\frac{B_c^2}{B(B_c - B)}.$$

Note that D is essentially given by a geometric mean of the macroscopic length d and of the microscopic parameter $\delta \sim \xi$. Moreover, for both $B \to 0$ and $B \to B_c$ the length D diverges.

The corresponding minimal value of the free energy per unit area of the film is therefore $F = F_1 + F_2 = 2\sqrt{d\delta}\frac{B(B_c-B)}{\mu_0}$. In principle, we should have taken the contributions F_1 and F_2 into account in Eq. 11 which was used for the determination of the optimal fraction ρ_N. However, note that $F \propto \sqrt{d}$ and therefore F is, for $d \gg \delta$, much smaller than the bulk energy in Eq. 11 (which must be $\propto d$). Therefore for sufficiently thick films the fraction of the normal state remains $\rho_N = B/B_c$ with only small corrections.

Pippard nonlocal electrodynamics
Superconductors are characterized by two length scales, the coherence length ξ_0 and the London penetration depth λ_L. Both the London electrodynamics and the Ginzburg-Landau theory assume that the current at point $\mathbf{r}$ depends only on the vector potential at the same point, see Eqs. 1,8. Let us specialize in this paragraph to the simpler case of the London electrodynamics. Since the supercurrent is a flow of Cooper pairs, instead of Eq. 1, $\mathbf{j}(\mathbf{r})$ should be given (in the London gauge $\nabla \cdot \mathbf{A} = 0$) by the vector potential in the neighborhood of $\mathbf{r}$ with radius of the order of ξ_0,

$$j_i(\mathbf{r}) = -\frac{1}{\mu_0 \lambda_L^2} \int d^3\mathbf{r}' K_{ij}(\mathbf{r}' - \mathbf{r}) A_j(\mathbf{r}'),$$

where $K_{ij}(\mathbf{R})$ is an appropriate kernel with the normalization $\int d^3\mathbf{R} K_{ij}(\mathbf{R}) = \delta_{ij}$. Pippard has proposed the following simple form,

$$K_{ij}(\mathbf{R}) = \frac{3}{4\pi\xi_0} \frac{R_i R_j}{R^4} e^{-R/\xi_0}.$$

The power R^n in the denominator is fixed uniquely to $n = 4$. In fact, for $n \geq 5$ the kernel cannot be normalized, because of the divergence at $R \to 0$, while for $n \leq 3$ the contribution of the region $R \to 0$ would vanish, which is unphysical.

In the London limit $\xi_0 \ll \lambda_L$ the vector potential changes on a much larger scale than the Cooper pair size and therefore the nonlocal correction can be neglected. This case is well described by the London equations. It is realized in strong coupling type-II superconductors. It is worth pointing out that also weak coupling superconductors with $\xi_0 > \lambda_L$ can be described by local electrodynamics, if they have a sufficiently short mean free path l. In fact, for $l \ll \xi_0$, the spatial range of the Pippard kernel, ξ_0, should be replaced by l, and then the criterion for the applicability of local electrodynamics is $l \ll \lambda_L$. Let us also point out that sufficiently close to T_c, all superconductors have local electrodynamics, since $\lambda_L \to \infty$ whereas ξ_0 stays finite in that limit.

In the Pippard limit $\xi_0 \gg \lambda_L$ (realized in type-I superconductors at low temperatures) the electrodynamics of superconductors becomes nonlocal. Nevertheless, for qualitative purposes it is possible to describe the response of such superconductors by means of local electrodynamics with an effective penetration depth λ. This length scale depends in general on the sample geometry. For illustrative purposes, let us consider the case of bulk samples. It will checked a posteriori that in that case λ satisfies the inequalities $\lambda_L \ll \lambda \ll \xi_0$. In fact, consider a semiinfinite Pippard superconductor in a parallel field B_0. Then the vector potential is $A \sim B_0\lambda$ in a surface layer with a thickness of order λ. Therefore only a fraction $\sim \xi_0^2\lambda$ of the effective Pippard volume ξ_0^3 contributes to the surface current which reads

$$j \sim -\frac{1}{\mu_0 \lambda_L^2} \frac{\lambda}{\xi_0} B_0 \lambda.$$

On the other hand, from the Maxwell equation we have $B_0/\lambda \sim \mu_0 j$. Comparing the two expressions we find an estimate

$$\lambda \sim (\lambda_L^2 \xi_0)^{1/3},$$

consistent with $\lambda_L \ll \lambda \ll \xi_0$.

4 Magnetic properties of type II superconductors

Nucleation in the bulk: B_{c2}
Let us consider a superconductor in an external field B along the z axis, slightly below the second order transition to the superconducting state. In that case $|\psi| \ll \psi_\infty$ and the GL equation can be linearized,

$$\frac{1}{2m^*}\left[-\hbar^2\nabla^2 + 4e^2B^2x^2 - 4ie\hbar Bx\frac{\partial}{\partial y}\right]\psi = |\alpha|\psi.$$

Here we have taken into account that, because of the weakness of superconductivity, the magnetic field is equal to the external field and we have chosen the gauge $\mathbf{A} = (0, Bx, 0)$.

We search for a solution in the form $\psi(x, y, z) = \chi(x)e^{ik_y y}e^{ik_z z}$ and obtain an equation for $\chi(x)$ of the form

$$\left[-\frac{\hbar^2}{2m^*}\frac{d^2}{dx^2} + \frac{1}{2}m^*\omega_c^2(x - x_0)^2\right]\chi = \left(|\alpha| - \frac{\hbar^2 k_z^2}{2m^*}\right)\chi.$$

This is an equation for a linear harmonic oscillator with frequency $\omega_c = 2eB/m^*$, centered around $x_0 = -\hbar k_y/(2eB)$. The GL equation therefore possesses solutions only if $|\alpha|$ is larger than the ground state energy of the harmonic oscillator, $\hbar\omega_c/2$. Therefore the maximal admissible field B_{c2} in which superconductivity can appear is

$$B_{c2} = \frac{\Phi_0}{2\pi\xi^2} = \sqrt{2}\kappa B_c.$$

Note that for materials with $\kappa > 1/\sqrt{2}$ the upper critical field $B_{c2} > B_c$ and the normal metal - superconductor transition is of second order. These materials are called type-II materials. For $\kappa < 1/\sqrt{2}$, under decreasing the field, the normal metal - superconductor transition occurs (in a first-order fashion) at B_c. In this case of type-I superconductors, B_{c2} merely corresponds to a minimal field, in which an 'undercooled' normal conductor can exist.

Before proceeding let us point out that the ground state is macroscopically degenerate since the 'energy' $|\alpha|$ does not depend on k_y. For fields smaller than B_{c2}, this degeneracy will be lifted by the cubic term of the Ginzburg-Landau equation.

Superconducting vortex
Let us consider what happens in a bulk superconducting sample (of cylindrical shape, for simplicity), as we increase the external magnetic field from $B = 0$ (along the axis of the cylinder). We expect that if the magnetic field increases beyond some threshold field B_{c1}, magnetic flux will start to enter into the superconductor. We expect that the flux enters in the form of filaments, and that each filament carries a total flux Φ_0 (smaller values are not allowed for a spatially localized flux, due to flux quantization). In what follows we calculate the value of B_{c1} within the GL theory.

We consider a filament with cylindrical symmetry and choose a cylindrical coordinate system with the z axis along the cylinder. We assume that the wavefunction is $\psi(r, \varphi, z) = \psi_\infty f(r)e^{-i\varphi}$. Note that we have chosen a wavefunction whose phase winds by

2π when going once around the filament, as appropriate for a wavefunction carrying one flux quantum. We expect that the magnetic field is screened towards the interior of the superconductor (i.e. for $r \to \infty$) by currents circulating in the φ direction and we assume $\mathbf{A} = (0, A(r), 0)$. Therefore the current density is $\mathbf{j} = (0, j(r), 0)$, where

$$j(r) = -\frac{f^2}{\mu_0 \lambda^2} \left(A - \frac{\Phi_0}{2\pi r} \right).$$

One checks easily that the magnetic field $\mathbf{B} = (0, 0, B(r))$ with $B(r) = (rA)'/r$ (where the prime denotes a derivative w.r.t. r) and also that $\nabla \times \mathbf{B} = (0, -B', 0)$. Therefore the Maxwell equation $\nabla \times \mathbf{B} = \mu_0 \mathbf{j}$ reduces to a single scalar equation

$$\frac{dB}{dr} = \frac{d}{dr} \left[\frac{1}{r} \frac{d}{dr} (rA) \right] = \frac{f^2}{\lambda^2} \left(A - \frac{\Phi_0}{2\pi r} \right). \tag{12}$$

On the other hand, the GL equation for ψ can be written as

$$\xi^2 \left[-\left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} \right) + \left(\frac{1}{r} - \frac{2\pi A}{\Phi_0} \right)^2 \right] f + f^3 = f. \tag{13}$$

The functions $f(r)$ and $A(r)$ have to be determined from Eqs. 12,13. The boundary conditions for $A(r)$ are as follows. Integrating $B(r) = r^{-1}(rA)'$ we find $A(r) = r^{-1} \int_0^r d\rho \rho B(\rho) + \text{const}/r = \Phi(r)/(2\pi r) + \text{const}/r$, where $\Phi(r)$ is the flux within a disc with radius r. We have to choose the gauge with const $= 0$ in order that $A = \Phi_0/(2\pi r)$ for $r \to \infty$, as required by the vanishing of the current far from the filament. Requiring that the magnetic field B_0 at $r = 0$ is finite, we therefore find $A(r) = B_0 r/2$ for $r \to 0$.

Now let us specify the boundary conditions for f. The Maxwell equation Eq. 12 can be integrated for small r as follows:

$$B(r) = B_0 - \frac{\Phi_0}{2\pi\lambda^2} \int_0^r d\rho \frac{f^2(\rho)}{\rho}.$$

Thus in order that $B(r)$ is regular, we need $f \to 0$ for $r \to 0$. Trying $f \propto r^n$ we find from Eq. 13 that $n = 1$. Finally, for $r \to \infty$ we require $f = 1$, since far away from the vortex the state of the superconductor should be unaffected by its presence.

Let us consider the London limit $\lambda \gg \xi$. In that case the function f differs noticeably from unity only for $r \sim \xi$ and for $r \gg \xi$ we can set $f = 1$ and obtain, by taking the rotor of Eq. 12,

$$\left(\nabla^2 - \frac{1}{\lambda^2} \right) B = \frac{1}{r} (rB')' - \frac{1}{\lambda^2} B = -\frac{\Phi_0}{\lambda^2} \delta_2(\mathbf{r}), \tag{14}$$

where the right-hand side has been obtained making use of an auxiliary expression $\nabla \times \frac{\mathbf{e}_\varphi}{\sqrt{r^2+a^2}} = \frac{a^2}{r(r^2+a^2)^{3/2}} \mathbf{e}_z$ in which $\mathbf{e}_\varphi$ and $\mathbf{e}_z$ are unit vectors in the φ and z directions, respectively, and at the end the limit $a \to 0$ was taken. The exact solution of Eq. 14 is

$$B(r) = \frac{\Phi_0}{2\pi\lambda^2} K_0 \left(\frac{r}{\lambda} \right),$$

where K_0 is a zeroth-order Hankel function with the asymptotics

$$
\begin{aligned}
K_0\left(\frac{r}{\lambda}\right) &\approx \sqrt{\frac{\pi\lambda}{2r}}e^{-r/\lambda}, \\
K_0\left(\frac{r}{\lambda}\right) &\approx \ln\left(\frac{\lambda}{r}\right) + 0.12,
\end{aligned}
$$

valid for $r \gg \lambda$ and $\xi \ll r \ll \lambda$, respectively. The divergence of $B(r)$ is cut off at $r \sim \xi$.

Lower critical field B_{c1}

In the presence of a vortex, the Gibbs free energy (per unit length of the vortex) increases with respect to the homogeneous case by $\delta G = \int d^2\mathbf{r}[\delta f(\mathbf{r}) - HB(\mathbf{r})] = \varepsilon - H\Phi_0$, where we have used that the total flux carried by the vortex is $\int d^2\mathbf{r}B(\mathbf{r}) = \Phi_0$ due to flux quantization and we have denoted the Helmholtz free energy per unit length as ε. The lower critical field is defined as a minimal field for which vortex generation is possible and therefore $B_{c1} = \mu_0\varepsilon/\Phi_0$.

Let us split the integral for the vortex line energy into two parts, $\varepsilon = \varepsilon_< + \varepsilon_>$, corresponding to $r < \xi$ and $r > \xi$, respectively. For $r > \xi$, we can put $f = 1$ and obtain

$$
\varepsilon_> = \frac{1}{2\mu_0}\int d^2\mathbf{r}\left[\mathbf{B}^2 + (\mu_0\lambda)^2\mathbf{j}^2\right] = \frac{1}{2\mu_0}\int d^2\mathbf{r}\left[\mathbf{B}^2 + \lambda^2(\nabla\times\mathbf{B})^2\right],
$$

where in the latter form we have used the Maxwell equation (in the static case). Simple transformations show that $\int d^2\mathbf{r}(\nabla\times\mathbf{B})^2 = \oint d\mathbf{S}\cdot\mathbf{B}\times(\nabla\times\mathbf{B}) + \int d^2\mathbf{r}\mathbf{B}\cdot[\nabla\times(\nabla\times\mathbf{B})]$, where the first integral on the right hand side is taken over the surface of the superconducting region and $d\mathbf{S}$ is a surface element pointing out of the superconductor in the normal direction. Making use of $\nabla\times(\nabla\times\mathbf{B}) = -\mathbf{B}/\lambda^2$ we thus find

$$
\varepsilon_> = \frac{\lambda^2}{2\mu_0}\oint d\mathbf{S}\cdot\mathbf{B}\times(\nabla\times\mathbf{B}) \tag{15}
$$

There are two contributions to this surface integral. Since the magnetic field falls off exponentially at large distances, the integral at infinity vanishes and only the contribution from $r = \xi$ remains. Therefore $\varepsilon_> = -\frac{\pi\lambda^2\xi}{\mu_0}B(\xi)B'(\xi) \approx \frac{\Phi_0^2}{4\pi\mu_0\lambda^2}\ln\kappa$, where in the last form we have made use of the asymptotic form of $B(\xi)$ valid for $\kappa \gg 1$.

Let us turn now to the contribution $\varepsilon_<$ of the vortex core. The Helmholtz free energy density $\delta f(\mathbf{r})$ reads as

$$
\delta f(\mathbf{r}) = \frac{B_c^2}{\mu_0}\left[\frac{1}{2} - f^2 + \frac{1}{2}f^4 + \xi^2(f')^2 + \xi^2 f^2\left(\frac{1}{r} - \frac{2\pi A}{\Phi_0}\right)^2\right] + \frac{B^2}{2\mu_0}.
$$

Notice that the GL equation multiplied by f reads

$$
-f^2 + f^4 - \frac{\xi^2}{r}f(rf')' + \xi^2 f^2\left(\frac{1}{r} - \frac{2\pi A}{\Phi_0}\right)^2 = 0.
$$

Integrating by parts one can show that $\int_0^\infty drr[f(rf')'/r] = \int_0^\infty drr[-(f')^2]$, since the surface term vanishes, and therefore the quantities in square brackets are effectively equal.

Thus one can effectively write $\delta f(\mathbf{r}) = [(1-f^4)B_c^2 + B^2]/(2\mu_0)$. Since the magnetic field saturates in the vortex core to $B \sim \frac{\Phi_0}{2\pi\lambda^2}\ln\kappa$, it follows that $\varepsilon_<$ is dominated by the condensation energy loss $\varepsilon_< \sim B_c^2\xi^2/\mu_0$, which is smaller than $\varepsilon_>$ by a factor $\ln\kappa$. Therefore in the London limit we have $\varepsilon \approx \varepsilon_>$ and the lower critical field is

$$B_{c1} \approx \frac{\Phi_0}{4\pi\lambda^2}\ln\kappa = \frac{B_c}{\sqrt{2}\kappa}\ln\kappa.$$

Note that in the London limit we have $B_{c1} \ll B_c \ll B_{c2}$, i.e. the magnetic flux enters the superconductor for much lower fields than B_c (or, in other words, the Meissner region shrinks), but the material remains superconducting to much higher fields than B_c.

Interaction between the vortices
Let us consider two parallel vortices at $\mathbf{r}_1$ and $\mathbf{r}_2$ in an infinite superconductor. The total field at point $\mathbf{r}$ is then (due to the linearity of the Maxwell equations)

$$\mathbf{B}(\mathbf{r}) = \frac{\Phi_0}{2\pi\lambda^2}\left[K_0\left(\frac{|\mathbf{r}-\mathbf{r}_1|}{\lambda}\right) + K_0\left(\frac{|\mathbf{r}-\mathbf{r}_2|}{\lambda}\right)\right] = \mathbf{B}_1(\mathbf{r}) + \mathbf{B}_2(\mathbf{r}).$$

Making use of Eq. 15, the (dominant) London contribution to the Helmholtz free energy of the vortex pair is

$$\varepsilon_{1+2} = \frac{\lambda^2}{2\mu_0}\sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2}\oint d\mathbf{S}_i \cdot \mathbf{B}_j \times (\nabla \times \mathbf{B}_k) \approx -\frac{\lambda^2}{2\mu_0}\sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2}\mathbf{B}_j(\mathbf{r}_i)\cdot\oint d\mathbf{S}_i \times (\nabla \times \mathbf{B}_k),$$

where we have denoted the surfaces of the normal cores of vortices 1 and 2 as S_1 and S_2. Notice that a large contribution comes only from $i=k$ and that $\oint d\mathbf{S}_i \times (\nabla \times \mathbf{B}_i) = -\frac{1}{\lambda^2}\vec{\Phi_0}$ where we have introduced a vector $\vec{\Phi_0} = (0,0,\Phi_0)$. Therefore

$$\varepsilon_{1+2} = \frac{\Phi_0}{2\mu_0}\sum_{ij}B_j(\mathbf{r}_i) = \frac{\Phi_0}{2\mu_0}\sum_{i=1,2}B_i(\mathbf{r}_i) + \frac{\Phi_0}{\mu_0}B_1(\mathbf{r}_2) = 2\varepsilon + \frac{\Phi_0^2}{2\pi\mu_0\lambda^2}K_0\left(\frac{|\mathbf{r}_1-\mathbf{r}_2|}{\lambda}\right)$$

the first term describes the sum of the vortex energies, while the second corresponds to the interaction energy ε_{12} between the vortices. The interaction between the vortices is seen to be repulsive.

The force $\mathbf{f}_2$ acting on a unit length of the vortex 2 can be calculated as

$$\mathbf{f}_2 = -\frac{\partial \varepsilon_{12}}{\partial \mathbf{r}_2} = -\frac{\Phi_0}{\mu_0}\frac{\partial B_1(\mathbf{r}_2)}{\partial \mathbf{r}_2}.$$

Since the $\mathbf{B}$ field only has a z component, this can be written using the Maxwell equation $\nabla \times \mathbf{B} = \mu_0\mathbf{j}$ in the form $\mathbf{f}_2 = \mathbf{j}_1(\mathbf{r}_2) \times \vec{\Phi_0}$. Summing the forces from all current sources we thus find the net force acting on the unit length of a vortex,

$$\mathbf{f} = \mathbf{j} \times \vec{\Phi_0}, \tag{16}$$

where $\mathbf{j}$ is the net supercurrent density flowing at the location of the studied vortex.

Intermediate fields $H_{c1} < H < H_{c2}$
The result Eq. 16 is very important and has many consequences. First, it follows that

in equilibrium the net current density at the position of a vortex should vanish. This immediately suggests that the vortices will tend to form regular arrays.

If the average magnetic field in a superconductor is B, we can define the magnetization M of the superconductor from $B = \mu_0 H + M$. In what follows we will discuss the shape of the function $M = M(H)$.

For $H < H_{c1}$ we trivially have $M = -\mu_0 H$. In what follows, let us calculate the magnetization for $H_{c1} < H \ll H_{c2}$, when the vortices are well separated and the London limit is still applicable. The Gibbs free energy per unit length of N parallel vortex lines in an applied field H is $G = N(H_{c1} - H)\Phi_0 + 2^{-1}\sum_{ij} F_{ij}$. This expression should be minimized with respect to N in order to find an average actual magnetic field B inside the sample with cross-section S, $BS = N\Phi_0$, or $B = n\Phi_0$ where n is the fluxon density. Let us assume now that the vortices form a triangular lattice (which maximizes the distances between the vortices for their given density) with lattice constant a. If we consider magnetic fields slightly above H_{c1}, the vortices will be far apart, $a \gg \lambda$, and because of the exponential decay of the interaction energy it will be sufficient to keep only the interactions $F(a)$ between nearest neighbors on the lattice. Since the area corresponding to one vortex is $\sqrt{3}a^2/2$, the Gibbs free energy per unit volume will be

$$g = \frac{2\Phi_0}{\sqrt{3}}\left[\frac{H_{c1} - H}{a^2} + \frac{3\Phi_0}{2\pi\mu_0\lambda^2 a^2}\sqrt{\frac{\pi\lambda}{2a}}e^{-a/\lambda}\right].$$

Minimizing w.r.t. a we obtain the condition

$$\frac{a}{\lambda} = \ln\left[\frac{3\Phi_0}{4\sqrt{2\pi}\lambda^2\mu_0(H - H_{c1})}\right]$$

and the average magnetic field inside the sample is $B = 2\Phi_0/(a^2\sqrt{3})$. This means that the magnetization drops very fast above H_{c1}.

In the vicinity of H_{c2}, magnetization has to be calculated from the full GL theory with a small parameter ψ. The result is $M = -\mu_0 \frac{H_{c2} - H}{(2\kappa^2 - 1)\beta_A}$, where β_A is a numerical parameter characterizing the shape of the vortex lattice. For the globally stable triangular lattice $\beta_A = 1.16$.

Finally, let us show that the area under the $-M(H)$ curve is $\int_0^{H_{c2}}(-M)dH = \frac{B_c^2}{2\mu_0}$, irrespective of the value of κ. This follows from

$$\begin{aligned} G_N(H_{c2}) &= G_N(0) - \int_0^{H_{c2}} BdH = G_S(0) - \frac{\mu_0 H_{c2}^2}{2} + \frac{B_c^2}{2\mu_0} \\ G_S(H_{c2}) &= G_S(0) - \int_0^{H_{c2}} BdH = G_S(0) - \frac{\mu_0 H_{c2}^2}{2} + \int_0^{H_{c2}}(-M)dH \end{aligned}$$

since $G_N(H_{c2}) = G_S(H_{c2})$.

A second consequence of Eq. 16 is that in presence of a transport current, the vortices will move. As a consequence, since in this case $d\Phi/dt$ is nonzero, electric fields will be generated, leading to dissipative effects. This can be prevented if the vortices are pinned to particular positions within the crystal. For instance the vortices will like to sit in places where superconductivity cannot develop, since this will minimize the energy cost associated with the destruction of superconductivity in the vortex core.

5 Pairing instability

Phonon mediated interaction between electrons
Now we turn to the microscopic description of superconductivity. Let us start with a description of the effective interaction between the electrons in a metal. For the sake of simplicity, we consider the jellium model (with a deformable ionic background). The Hamiltonian for Coulomb interactions between the electrons reads

$$H_{\text{Coulomb}} = \frac{1}{8\pi\epsilon_0}\int d^3\mathbf{r}\int d^3\mathbf{r}'\rho^e(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\rho^e(\mathbf{r}') = \frac{1}{2\Omega}\sum_{\mathbf{q}}\frac{1}{\epsilon_0 q^2}\rho^e_{\mathbf{q}}\rho^e_{-\mathbf{q}},$$

where $\rho^e(\mathbf{r})$ is the electron density and the second form obtains introducing the Fourier transform $\rho^e(\mathbf{r}) = \frac{1}{\Omega}\sum_{\mathbf{q}}\rho^e_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r})$ in a system of volume Ω with periodic boundary conditions and the Fourier transform of the bare Coulomb force, $V_{\mathbf{q}} = \frac{1}{\epsilon_0 q^2}$.

It is well known that any charge immersed into an electron liquid will be quickly surrounded by a compensating charge accumulation of the electrons and of the ionic charge, leading to a screening of the bare charge interaction $V_{\mathbf{q}}$. In what follows we present the simplest theory of screening.

Namely, let us assume that we introduce into the electron liquid a small plane-wave like external charge $\delta\rho_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}-i\omega t)$. This will result in a development of screening charge densities $\rho^e_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}-i\omega t)$ and $\rho^i_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}-i\omega t)$ of the electrons and ions, respectively. Thus the total charge density will be $\rho_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}-i\omega t)$, where $\rho_{\mathbf{q}} = \delta\rho_{\mathbf{q}}+\rho^e_{\mathbf{q}}+\rho^i_{\mathbf{q}}$. The potential generated by the external charge will therefore be $\phi_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r}-i\omega t)$, where $\phi_{\mathbf{q}}$ is given by the Poisson equation,

$$\phi_{\mathbf{q}} = \frac{\rho_{\mathbf{q}}}{\epsilon_0 q^2} = \frac{\delta\rho_{\mathbf{q}}}{\epsilon_0\epsilon(q,\omega)q^2},$$

where in the latter expression we have defined a wavevector and frequency dependent dielectric constant which can be calculated from $\epsilon(q,\omega) = \delta\rho_{\mathbf{q}}/\rho_{\mathbf{q}}$. For small external charges, the screening charges will depend linearly on the total charge $\rho_{\mathbf{q}}$,

$$\begin{aligned}\rho^e_{\mathbf{q}} &= \chi^e(q,\omega)\rho_{\mathbf{q}},\\ \rho^i_{\mathbf{q}} &= \chi^i(q,\omega)\rho_{\mathbf{q}},\end{aligned}$$

where we have defined the polarizabilities $\chi^{e,i}(q,\omega)$ of the electrons and of the ions. The dielectric constant is then $\epsilon(q,\omega) = 1-\chi^e(q,\omega)-\chi^i(q,\omega)$.

In what follows we calculate the electronic polarizability $\chi^e(q,\omega)$. To this end, let us write down a suitable generalization of the London equation Eq. 4 to the case of a normal metal,

$$\frac{\partial\mathbf{j}^e}{\partial t} = -\frac{\mathbf{j}^e}{\tau}+\frac{ne^2}{m}\mathbf{E}-v_s^2\nabla\rho^e,$$

where the first term on the right hand side cuts off the acceleration of the current by an applied $\mathbf{E}$ field and τ is the corresponding charge transport relaxation time. If we take the divergence of this equation and make use of the continuity equation, we obtain

$$\left(\frac{1}{\tau}+\frac{\partial}{\partial t}\right)\frac{\partial\rho^e}{\partial t} = v_s^2\nabla^2\rho^e-\frac{ne^2}{m\epsilon_0}\rho,$$

where we have used that $\nabla \cdot \mathbf{E} = \rho/\epsilon_0$ with $\rho(\mathbf{r})$ the total charge density. Taking the Fourier transform of the resulting equation we thus find

$$\chi^e(q,\omega) = \frac{\omega_p^2}{\omega(\omega + i\gamma) - v_s^2 q^2},$$

where $\gamma = \frac{1}{\tau}$. The ionic susceptibility can be written in an analogous way, but with ionic parameters. In particular, the ionic plasma frequency reads $\Omega_p = \frac{nZe^2}{M\epsilon_0}$, where we have assumed that the ions carry the charge Ze and their mass is M. Since $\omega_p \gg \Omega_p$, we will see a posteriori that for the frequencies of interest, the ionic susceptibility can be approximated by its high-frequency limit, $\chi^i(q,\omega) = \frac{\Omega_p^2}{\omega^2}$.

Consequence 1. The electron-phonon system can exhibit spontaneous oscillations if the condition $\epsilon(q,\omega) = 0$ is satisfied. In the long wavelength limit, $q \to 0$, there are two solutions to this equation. The first is a high energy solution, $\omega \gg v_s q, \gamma$, in which case $\chi^e(q,\omega) \approx \frac{\omega_p^2}{\omega^2}$. In this case the solution is $\omega \approx \omega_p$, i.e. the usual plasmon. The second solution corresponds to the low-energy limit $\omega \ll v_s q$, in which case $\chi^e(q,\omega) \approx \frac{k_s^2}{q^2}$ where $k_s = \frac{\omega_p}{v_s}$ is the inverse screening length. This solution reads $\omega_q = \frac{\Omega_p q}{\sqrt{q^2+k_s^2}}$ which reduces to $\omega_q = vq$ in the long-wavelength limit and therefore corresponds to a longitudinal sound mode with the sound velocity

$$\frac{v}{v_F} \approx \sqrt{\frac{Zm}{3M}},$$

known as the Bohm-Staver formula. (In good qualitative agreement with experiment.) Note that $v \ll v_s$, i.e. the phonons are slow when compared with the electrons.

Consequence 2. For frequencies ω of the order of the phonon frequency, i.e. for $\omega \ll v_s q$, the effective interaction between plane wave like charge distributions is

$$V(q,\omega) = \frac{1}{\epsilon_0 q^2} \frac{1}{1 + (k_s/q)^2 - (\Omega_p/\omega)^2} = \frac{1}{\epsilon_0(q^2 + k_s^2)} \left[1 + \frac{\omega_q^2}{\omega^2 - \omega_q^2} \right].$$

The second form shows clearly that the effective interaction is a sum of two contributions: screened Coulomb interaction $\frac{1}{q^2+k_s^2}$, and an effective electron-electron interaction due to the interaction of the electrons with phonons $\propto \frac{\omega_q^2}{\omega^2-\omega_q^2}$. For a given q, the net interaction is attractive for $\omega < \omega_q$ and otherwise it is repulsive.

Cooper instability

In what follows we study the influence of a weak attractive interaction on the electron system. First we study a simplified problem: We consider a fully occupied Fermi sea (states with $k < k_F$ are completely occupied) and ask the question what happens to two additional electrons introduced into such a system. We will assume that the Fermi sea is intact and its only role is to prevent the additional electrons from occupying the states with $k < k_F$. We consider a state with total momentum zero,

$$|\psi\rangle = \sum_{p>k_F} \alpha_{\mathbf{p}} c^\dagger_{\mathbf{p}\uparrow} c^\dagger_{-\mathbf{p}\downarrow} |FS\rangle = \frac{1}{2\Omega} \sum_{p>k_F} \alpha_{\mathbf{p}} \left(c^\dagger_{\mathbf{p}\uparrow} c^\dagger_{-\mathbf{p}\downarrow} - c^\dagger_{\mathbf{p}\downarrow} c^\dagger_{-\mathbf{p}\uparrow} \right) |FS\rangle$$

where $|FS\rangle$ is the fully occupied Fermi sea. The second form, valid for $\alpha_{\mathbf{p}} = \alpha_{-\mathbf{p}}$ (which we assume), shows explicitly that the added Cooper pair is in a singlet state (total spin $S = 0$).

Let us model the electron system by the following BCS model Hamiltonian:

$$H = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} - \frac{1}{\Omega} \sum_{\mathbf{k}}{}' \sum_{\mathbf{k}'}{}' V_{\mathbf{k}\mathbf{k}'} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow}. \tag{17}$$

The first term is the usual kinetic energy, while the second (interaction) term requires some discussion. The primes on the summation over $\mathbf{k}$ and $\mathbf{k}'$ mean that we assume that the interaction is nonvanishing only within the energy shells $|\varepsilon_{\mathbf{k}}| < \hbar\omega_0$ and $|\varepsilon_{\mathbf{k}'}| < \hbar\omega_0$, respectively, where the quasiparticle energy $\varepsilon_{\mathbf{k}}$ is normalized so that $\varepsilon_{\mathbf{k}} = 0$ on the Fermi surface. The energy scale $\hbar\omega_0$ is taken to be on the order of the Debye energy, and therefore $\hbar\omega_0 \ll \varepsilon_F$. In order that the Hamiltonian is Hermitian, we have to require $V_{\mathbf{k}\mathbf{k}'} = V^*_{\mathbf{k}'\mathbf{k}}$. Moreover, we require $V_{\mathbf{k}\mathbf{k}'} = V_{\mathbf{k}-\mathbf{k}'} = V_{-\mathbf{k}\mathbf{k}'}$ in order that the interaction term can be written as

$$\frac{1}{\Omega} \sum_{\mathbf{k}}{}' \sum_{\mathbf{k}'}{}' V_{\mathbf{k}\mathbf{k}'} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} = \frac{1}{4\Omega} \sum_{\mathbf{k}}{}' \sum_{\mathbf{k}'}{}' V_{\mathbf{k}\mathbf{k}'} \left(c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} - c^\dagger_{\mathbf{k}\downarrow} c^\dagger_{-\mathbf{k}\uparrow} \right) \left(c_{-\mathbf{k}'\downarrow} c_{\mathbf{k}'\uparrow} - c_{-\mathbf{k}'\uparrow} c_{\mathbf{k}'\downarrow} \right),$$

which, being expressed in terms of singlet pair creation and annihilation operators, is explicitly spin-rotation invariant. Finally, let us note that in Eq. 17 we have taken into account only scatterings of Cooper pairs with zero total momentum. A generic interaction term would involve scattering of pairs with all total momenta $\mathbf{q}$. We will see explicitly later that pairs with $\mathbf{q} = 0$ gain most energy and that is why we do not consider other pairs with $\mathbf{q} \neq 0$.

Let us look for a solution of the Schrödinger equation $H|\psi\rangle = E|\psi\rangle$. If we neglect the action of H on $|FS\rangle$, then the Schrödinger equation can be written as

$$\sum_{p>k_F}{}' (2\varepsilon_{\mathbf{p}} - E) \alpha_{\mathbf{p}} c^\dagger_{\mathbf{p}\uparrow} c^\dagger_{-\mathbf{p}\downarrow} |FS\rangle - \frac{1}{\Omega} \sum_{p>k_F}{}' \sum_{k>k_F}{}' V_{\mathbf{k}\mathbf{p}} \alpha_{\mathbf{p}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} |FS\rangle = 0,$$

where we have assumed $\alpha_{\mathbf{p}} = 0$ for $\varepsilon_{\mathbf{p}} > \hbar\omega_0$. Taking the scalar product of this equation with $\langle FS| c_{-\mathbf{p}\downarrow} c_{\mathbf{p}\uparrow}$ and interchanging the summation indices $\mathbf{k}$ and $\mathbf{p}$ in the second term, we obtain a set of equations for the coefficients $\alpha_{\mathbf{p}}$:

$$(2\varepsilon_{\mathbf{p}} - E)\alpha_{\mathbf{p}} = \frac{1}{\Omega} \sum_{k>k_F}{}' V_{\mathbf{p}\mathbf{k}} \alpha_{\mathbf{k}}.$$

In order to further simplify the discussion, we assume $V_{\mathbf{p}\mathbf{k}} = V$, which is a reasonable approximation for the electron-phonon problem. In this case nothing depends on the angular variables and we can replace the sums by integrals, $\Omega^{-1} \sum'_{k>k_F} = N(0) \int_0^{\hbar\omega_0} d\varepsilon_k$. We have

$$\alpha_p = \frac{\lambda}{2\varepsilon_p - E} \int_0^{\hbar\omega_0} d\varepsilon_k \alpha_k$$

where we have introduced a dimensionless coupling constant $\lambda = N(0)V$. Taking the integral $\int_0^{\hbar\omega_0} d\varepsilon_p$ of both sides, we obtain an equation for the eigenvalue E:

$$\frac{1}{\lambda} = \int_0^{\hbar\omega_0} \frac{d\varepsilon}{2\varepsilon - E}.$$

Assuming $\lambda \ll 1$, we obtain from here $E = -2\hbar\omega_0 e^{-2/\lambda}$. Note that $E < 0$, i.e. the energy of the Cooper pair is lower than in absence of interactions (which is zero). This suggests that it will be energetically favourable to promote electrons from inside the Fermi sea into Cooper pairs above the Fermi surface. Hence the system should become unstable with respect to pair formation.

Another point worth mentioning is that the instability occurs for an arbitrarily small attraction, $\lambda > 0$, and that the energy gain is nonalytic in λ. This suggests that the pairing transition cannot be described by any finite order of perturbation theory and a new, nonperturbative solution has to be looked for.

Exercise
Calculate the size of the Cooper pair $\xi^2 = \frac{\langle\psi|R^2|\psi\rangle}{\langle\psi|\psi\rangle}$.

Magnetic interaction between electrons
Imagine a test spin density $\mathbf{S_q}$ introduced into a magnetic medium. To lowest order in the coupling constant g, this will generate a magnetic field $\mathbf{B_q} = g^2\chi(\mathbf{q})\mathbf{S_q}$ in the medium, which in turn is felt by (another) spin density $\mathbf{S_{-q}}$, leading to an energy $-\mathbf{B_q}\cdot\mathbf{S_{-q}}$. Counting each term only once, the total Hamiltonian of the system can be written

$$H_{\rm mag} = -\frac{g^2}{2\Omega}\sum_{\mathbf{q}}\chi(\mathbf{q})\mathbf{S_q}\cdot\mathbf{S_{-q}} = -\frac{g^2}{8\Omega}\sum_{\mathbf{q}}\chi(\mathbf{q})\sum_{\mathbf{k},\mathbf{k}'}\vec{\sigma_{\alpha\beta}}\cdot\vec{\sigma_{\gamma\delta}}c^\dagger_{\mathbf{k+q}\alpha}c_{\mathbf{k}\beta}c^\dagger_{\mathbf{k}'-\mathbf{q}\gamma}c_{\mathbf{k}'\delta},$$

where in the latter form we have used $\mathbf{S_q} = \frac{1}{2}\sum_{\mathbf{k}}\vec{\sigma_{\alpha\beta}}c^\dagger_{\mathbf{k+q}\alpha}c_{\mathbf{k}\beta}$ and $\vec{\sigma} = (\sigma^x, \sigma^y, \sigma^z)$ are the Pauli matrices. Making use of the identity $\vec{\sigma_{\alpha\beta}}\cdot\vec{\sigma_{\gamma\delta}} = 2\delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta}$ and specializing to the case when the scattering takes place only between Cooper pairs with zero total momentum, we then have

$$H_{\rm mag} = -\frac{g^2}{8\Omega}\sum_{\mathbf{k},\mathbf{k}'}\chi(\mathbf{k}'-\mathbf{k})c^\dagger_{\mathbf{k}'\alpha}c^\dagger_{-\mathbf{k}'\beta}(2c_{-\mathbf{k}\alpha}c_{\mathbf{k}\beta} - c_{-\mathbf{k}\beta}c_{\mathbf{k}\alpha}) = \frac{g^2}{8\Omega}\sum_{\mathbf{k},\mathbf{k}'}\chi(\mathbf{k}'-\mathbf{k})\left(3S^\dagger_{\mathbf{k}'}S_{\mathbf{k}} - \mathbf{T}^\dagger_{\mathbf{k}'}\cdot\mathbf{T}_{\mathbf{k}}\right),$$

where the last form uses the following definitions of the singlet and triplet Cooper pair annihilation operators, respectively:

$$\begin{aligned}
S_{\mathbf{k}} &= \frac{1}{\sqrt{2}}(c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} - c_{-\mathbf{k}\uparrow}c_{\mathbf{k}\downarrow}),\\
T^1_{\mathbf{k}} &= c_{-\mathbf{k}\uparrow}c_{\mathbf{k}\uparrow},\\
T^0_{\mathbf{k}} &= \frac{1}{\sqrt{2}}(c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} + c_{-\mathbf{k}\uparrow}c_{\mathbf{k}\downarrow}),\\
T^{-1}_{\mathbf{k}} &= c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\downarrow},
\end{aligned}$$

and we have made use of the identity $\sum_{\alpha\beta}c^\dagger_{\mathbf{k}'\alpha}c^\dagger_{-\mathbf{k}'\beta}(2c_{-\mathbf{k}\alpha}c_{\mathbf{k}\beta} - c_{-\mathbf{k}\beta}c_{\mathbf{k}\alpha}) = \mathbf{T}^\dagger_{\mathbf{k}'}\cdot\mathbf{T}_{\mathbf{k}} - 3S^\dagger_{\mathbf{k}'}S_{\mathbf{k}}$.

Note that the magnetic interactions are attractive for triplet Cooper pairs. Ferromagnetic fluctuations are believed to cause, e.g., the superfluidity of ^{3}He and superconductivity of Sr_2RuO_4.

On the other hand, magnetic interactions appear to be repulsive for singlet Cooper pairs. However, under certain conditions $H_{\rm mag}$ is attractive also in the singlet channel. This is often the case if the susceptibility is strongly peaked at a finite momentum. In particular, this mechanism is believed to be operative in the high-T_c superconductors.

6 BCS theory

BCS wavefunction

The Cooper pairs, being pairs of fermions, behave approximately as bosons. Because of the analogy between superfluidity and superconductivity, one might therefore expect that a superconductor with $2N$ electrons might be viewed as a Bose condensate of N Cooper pairs, $|\psi(N)\rangle = \left[\sum_{\mathbf{p}} \alpha_{\mathbf{p}} c^\dagger_{\mathbf{p}\uparrow} c^\dagger_{-\mathbf{p}\downarrow}\right]^N |0\rangle$, where $|0\rangle$ is the true vacuum (i.e. a state without electrons). For reasons of computational simplicity, BCS considered instead a linear combination of wavefunctions with different pair numbers,

$$\sum_{N=0}^{\infty} \frac{1}{N!}|\psi(N)\rangle = \exp\left[\sum_{\mathbf{p}} \alpha_{\mathbf{p}} c^\dagger_{\mathbf{p}\uparrow} c^\dagger_{-\mathbf{p}\downarrow}\right]|0\rangle = \prod_{\mathbf{p}} \exp\left[\alpha_{\mathbf{p}} c^\dagger_{\mathbf{p}\uparrow} c^\dagger_{-\mathbf{p}\downarrow}\right]|0\rangle = \prod_{\mathbf{p}}\left[1 + \alpha_{\mathbf{p}} c^\dagger_{\mathbf{p}\uparrow} c^\dagger_{-\mathbf{p}\downarrow}\right]|0\rangle,$$

where the second equation is due to the fact that Cooper pair creation operators commute between each other, while the last equation follows from $(c^\dagger_{\mathbf{p}\uparrow} c^\dagger_{-\mathbf{p}\downarrow})^2 = 0$ due to the Pauli principle. Finally, BCS wrote the wavefunction in the form

$$|\psi_{\rm BCS}\rangle = \prod_{\mathbf{k}} (u^*_{\mathbf{k}} + v^*_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow})|0\rangle = (\prod_{\mathbf{k}} u^*_{\mathbf{k}}) \prod_{\mathbf{k}} \left(1 + \frac{v^*_{\mathbf{k}}}{u^*_{\mathbf{k}}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow}\right)|0\rangle, \tag{18}$$

where the latter form shows the explicit connection with the above arguments, if we take $v^*_{\mathbf{k}}/u^*_{\mathbf{k}} = \alpha_{\mathbf{k}}$. Note that now it is possible to require that the wavefunction is normalized. In fact, let us compute

$$\langle\psi_{\rm BCS}|\psi_{\rm BCS}\rangle = \prod_{\mathbf{k}} \langle 0|(u_{\mathbf{k}} + v_{\mathbf{k}} c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow})(u^*_{\mathbf{k}} + v^*_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow})|0\rangle = \prod_{\mathbf{k}} \left(|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2\right).$$

Therefore the BCS wavefunction is normalized, if we require $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$ for all $\mathbf{k}$ (which we assume from now on). The average number of particles in $|\psi_{\rm BCS}\rangle$ is

$$\begin{aligned}
\langle N\rangle &= \sum_{\mathbf{k}} \langle\psi_{\rm BCS}|(c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow} + c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\downarrow})|\psi_{\rm BCS}\rangle \\
&= \sum_{\mathbf{k}} \langle 0|(u_{\mathbf{k}} + v_{\mathbf{k}} c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow})(c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow} + c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\downarrow})(u^*_{\mathbf{k}} + v^*_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow})|0\rangle = 2\sum_{\mathbf{k}} |v_{\mathbf{k}}|^2.
\end{aligned}$$

In a macroscopic system this quantity is proportional to the volume. At weak coupling we expect that the occupation numbers change with respect to the noninteracting case appreciably only in the vicinity of the Fermi surface. Therefore we expect that $|v_{\mathbf{k}}| \to 1$ well inside the Fermi sea and $|v_{\mathbf{k}}| \to 0$ far above the Fermi energy.

Now let us calculate the variance of the particle number, $\sqrt{\langle (N-\bar{N})^2\rangle} = \sqrt{\langle N^2\rangle - \langle N\rangle^2}$. We have

$$\begin{aligned}
\langle N^2\rangle &= \sum_{\mathbf{k}\neq\mathbf{p}} \langle (c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow} + c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\downarrow})(c^\dagger_{\mathbf{p}\uparrow} c_{\mathbf{p}\uparrow} + c^\dagger_{-\mathbf{p}\downarrow} c_{-\mathbf{p}\downarrow})\rangle + \sum_{\mathbf{k}} \langle (c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow} + c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\downarrow})^2\rangle \\
&= 4\sum_{\mathbf{k}\neq\mathbf{p}} |v_{\mathbf{k}}|^2 |v_{\mathbf{p}}|^2 + 4\sum_{\mathbf{k}} |v_{\mathbf{k}}|^2 = 4\sum_{\mathbf{kp}} |v_{\mathbf{k}}|^2 |v_{\mathbf{p}}|^2 + 4\sum_{\mathbf{k}} \left(|v_{\mathbf{k}}|^2 - |v_{\mathbf{k}}|^4\right).
\end{aligned}$$

Therefore we have

$$\sqrt{\langle (N-\bar{N})^2\rangle} = 2\sqrt{\sum_{\mathbf{k}} |v_{\mathbf{k}}|^2 |u_{\mathbf{k}}|^2} \propto \sqrt{\Omega}$$

and the variance becomes negligible in a macroscopic system.

Off-diagonal long range order
One can check easily that for the BCS wavefunction, the following anomalous average is nonvanishing, $b_{\mathbf{k}} = \langle\psi_{\rm BCS}|c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}|\psi_{\rm BCS}\rangle = u_{\mathbf{k}}v_{\mathbf{k}}^*$ (except for cases when either $v_{\mathbf{k}}$ or $u_{\mathbf{k}}$ are zero). Within the original formulation of BCS theory, this was a consequence of the technical trick of going from $|\psi(N)\rangle$ to $|\psi_{\rm BCS}\rangle$. However, according to the modern interpretation of superconductivity, this condition is taken to be fundamental and the superconducting state is defined as a novel symmetry breaking state, in which the expectation value of a pair destruction operator acquires a nonzero value, $\langle c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}\rangle = b_{\mathbf{k}} \neq 0$. Such states are said to possess off-diagonal long range order.

Self-consistent solution
Now we develop a method for calculating the thermodynamic properties of superconductors. To this end, let us consider the operator identity $c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} = b_{\mathbf{k}} + (c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} - b_{\mathbf{k}})$ which states that the pair destruction operator is equal to its mean value plus the fluctuation around the mean. Let us insert this identity and its Hermitian transpose into Eq. 17. We assume that the fluctuations are small and therefore we neglect the term of the type (fluctuation)^2. This way the Hamiltonian simplifies to

$$H = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} \left(c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}\uparrow} + 1 - c_{\mathbf{k}\downarrow}c_{\mathbf{k}\downarrow}^\dagger\right) - \frac{1}{\Omega}\sum_{\mathbf{k}}{}^{'}\sum_{\mathbf{k}'}{}^{'} V_{\mathbf{k}\mathbf{k}'}\left(c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger b_{\mathbf{k}'} + b_{\mathbf{k}}^* c_{-\mathbf{k}'\downarrow}c_{\mathbf{k}'\uparrow} - b_{\mathbf{k}}^* b_{\mathbf{k}'}\right),$$

where the kinetic energy term has been rewritten in a form which will be convenient later. Let us introduce an important energy scale (gap function) $\Delta_{\mathbf{k}} = \Omega^{-1}\sum_{\mathbf{k}'}' V_{\mathbf{k}\mathbf{k}'}b_{\mathbf{k}'}$. Note that since $V_{\mathbf{k}\mathbf{k}'} = V_{-\mathbf{k}\mathbf{k}'}$, the gap function is even, $\Delta_{\mathbf{k}} = \Delta_{-\mathbf{k}}$. Making use of $\Delta_{\mathbf{k}}$, the Hamiltonian can be written in a compact form

$$H = \sum_{\mathbf{k}}{}^{'} \begin{pmatrix} c_{\mathbf{k}\uparrow}^\dagger & c_{-\mathbf{k}\downarrow} \end{pmatrix} \begin{pmatrix} \varepsilon_{\mathbf{k}} & -\Delta_{\mathbf{k}} \\ -\Delta_{\mathbf{k}}^* & -\varepsilon_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix} + \sum_{\mathbf{k}}{}^{'}(b_{\mathbf{k}}^*\Delta_{\mathbf{k}} + \varepsilon_{\mathbf{k}}) + \sum_\sigma \sum_{|\varepsilon_{\mathbf{k}}|>\hbar\omega_0} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}, \tag{19}$$

known as the reduced BCS Hamiltonian. The first term is a quadratic form in creation and annihilation operators, while the second term is a constant which is important in defining the condensation energy. The last term is the kinetic energy outside the shell $\pm\hbar\omega_0$ around the Fermi surface. For $\Delta \ll \hbar\omega_0$, which will be seen to be the case for $\lambda \ll 1$ where the theory is controlled, the expectation value of this term is equal both in the normal and superconducting states. Therefore this term will not be considered any more.

Since the operator part of Eq. 19 is quadratic, it can be diagonalized. To this end, let us consider a transformation from the bare electrons to a new set of quasiparticles created by the operators $\gamma_{\mathbf{k}0}^\dagger$ and $\gamma_{\mathbf{k}1}^\dagger$,

$$\begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix} = \begin{pmatrix} u_{\mathbf{k}} & v_{\mathbf{k}}^* \\ -v_{\mathbf{k}} & u_{\mathbf{k}}^* \end{pmatrix} \begin{pmatrix} \gamma_{\mathbf{k}0} \\ \gamma_{-\mathbf{k}1}^\dagger \end{pmatrix}.$$

This transformation is canonical, i.e. it transforms fermion operators to fermion operators (satisfying the canonical commutation relations), if the transformation matrix is unitary, i.e. for $|u_{\mathbf{k}}|^2+|v_{\mathbf{k}}|^2=1$. Let us note in passing that the inverse transformation reads

$$\begin{pmatrix} \gamma_{\mathbf{k}0} \\ \gamma^{\dagger}_{-\mathbf{k}1} \end{pmatrix} = \begin{pmatrix} u^*_{\mathbf{k}} & -v^*_{\mathbf{k}} \\ v_{\mathbf{k}} & u_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c^{\dagger}_{-\mathbf{k}\downarrow} \end{pmatrix}.$$

Let us choose the transformation so that the Hamiltonian is diagonal,

$$\begin{pmatrix} u^*_{\mathbf{k}} & -v^*_{\mathbf{k}} \\ v_{\mathbf{k}} & u_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} \varepsilon_{\mathbf{k}} & -\Delta_{\mathbf{k}} \\ -\Delta^*_{\mathbf{k}} & -\varepsilon_{\mathbf{k}} \end{pmatrix} \begin{pmatrix} u_{\mathbf{k}} & v^*_{\mathbf{k}} \\ -v_{\mathbf{k}} & u^*_{\mathbf{k}} \end{pmatrix} = \begin{pmatrix} E_{\mathbf{k}} & 0 \\ 0 & -E_{\mathbf{k}}. \end{pmatrix}$$

Here we have used that the eigenvalues of the matrix in Eq. 19 are $\pm E_{\mathbf{k}}$ with $E_{\mathbf{k}} = \sqrt{\varepsilon^2_{\mathbf{k}}+|\Delta_{\mathbf{k}}|^2}$. The first eigenvalue has to be chosen positive and the second negative, if we want to describe the ground state of the superconductor as a vacuum for the particles γ (Bogoliubons), since the final diagonalized Hamiltonian reads

$$H = \sum_{\mathbf{k}}{}' E_{\mathbf{k}}(\gamma^{\dagger}_{\mathbf{k}0}\gamma_{\mathbf{k}0} + \gamma^{\dagger}_{\mathbf{k}1}\gamma_{\mathbf{k}1}) + \sum_{\mathbf{k}}{}'(b^*_{\mathbf{k}}\Delta_{\mathbf{k}} + \varepsilon_{\mathbf{k}} - E_{\mathbf{k}}). \tag{20}$$

This means that, within mean field description, a superconductor can be thought of as a gas of free fermions with the spectrum $E_{\mathbf{k}}$ and with the ground state energy given by the last term in Eq. 20. The ground state wavefunction $|\psi\rangle$ must satisfy the conditions $\gamma_{\mathbf{k}0}|\psi\rangle = \gamma_{\mathbf{k}1}|\psi\rangle = 0$ for all $\mathbf{k}$. One verifies easily that the BCS wavefunction $|\psi_{\rm BCS}\rangle$, Eq. 18, satisfies these constraints.

In order to completely solve the problem, we need to determine the functions $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ from

$$\begin{aligned} (|u_{\mathbf{k}}|^2-|v_{\mathbf{k}}|^2)\varepsilon_{\mathbf{k}} + u_{\mathbf{k}}v^*_{\mathbf{k}}\Delta^*_{\mathbf{k}} + u^*_{\mathbf{k}}v_{\mathbf{k}}\Delta_{\mathbf{k}} &= E_{\mathbf{k}}, \\ 2u_{\mathbf{k}}v_{\mathbf{k}}\varepsilon_{\mathbf{k}} + v^2_{\mathbf{k}}\Delta_{\mathbf{k}} - u^2_{\mathbf{k}}\Delta^*_{\mathbf{k}} &= 0. \end{aligned}$$

The solution to these equations reads (with $u_{\mathbf{k}}$ chosen to be real)

$$\begin{aligned} u_{\mathbf{k}} &= \sqrt{\frac{1}{2}\left(1+\frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}}\right)}, \\ v_{\mathbf{k}} &= \frac{\Delta^*_{\mathbf{k}}}{|\Delta_{\mathbf{k}}|}\sqrt{\frac{1}{2}\left(1-\frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}}\right)}. \end{aligned}$$

Note that $u_{\mathbf{k}} = u_{-\mathbf{k}}$ and $v_{\mathbf{k}} = v_{-\mathbf{k}}$, since both $\varepsilon_{\mathbf{k}}$ and $\Delta_{\mathbf{k}}$ are even functions. Moreover, deep inside the Fermi sea $|v_{\mathbf{k}}| = 1$, while far above the Fermi energy $u_{\mathbf{k}} = 1$, precisely as required in the discussion of $|\psi_{\rm BCS}\rangle$.

So far, we have determined all quantities in terms of the function $\Delta_{\mathbf{k}}$, which remains undetermined, however. In what follows we construct an equation for $\Delta_{\mathbf{k}}$. To this end, let us calculate

$$b_{\mathbf{k}} = \langle c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}\rangle = \langle(-v^*_{\mathbf{k}}\gamma^{\dagger}_{\mathbf{k}0}+u_{\mathbf{k}}\gamma_{-\mathbf{k}1})(u_{\mathbf{k}}\gamma_{\mathbf{k}0}+v^*_{\mathbf{k}}\gamma^{\dagger}_{-\mathbf{k}1})\rangle = u_{\mathbf{k}}v^*_{\mathbf{k}}\left[1-\langle\gamma^{\dagger}_{\mathbf{k}0}\gamma_{\mathbf{k}0}\rangle - \langle\gamma^{\dagger}_{-\mathbf{k}1}\gamma_{-\mathbf{k}1}\rangle\right],$$

the last equation follows from the fact that the mixed expectation values vanish. Since the Bogoliubons are free particles, we have $\langle\gamma^{\dagger}_{\mathbf{k}i}\gamma_{\mathbf{k}i}\rangle = f(E_{\mathbf{k}}) = \frac{1}{\exp(E_{\mathbf{k}}/T)+1}$, i.e. $f(x)$ is the usual Fermi-Dirac distribution function. Making use of the relation $u_{\mathbf{k}}v_{\mathbf{k}}^* = \Delta_{\mathbf{k}}/(2E_{\mathbf{k}})$ we therefore have $b_{\mathbf{k}} = [1 - 2f(E_{\mathbf{k}})]\,\Delta_{\mathbf{k}}/(2E_{\mathbf{k}})$. Inserting this relation into the definition of the gap function $\Delta_{\mathbf{k}}$ we thus finally find

$$\Delta_{\mathbf{k}} = \frac{1}{\Omega}\sum_{\mathbf{k}'}{}' V_{\mathbf{k}\mathbf{k}'}\frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}}\tanh\left(\frac{E_{\mathbf{k}'}}{2T}\right), \tag{21}$$

which is a self-consistent equation for $\Delta_{\mathbf{k}}$. Equation 21 is known as the gap equation and it represents the central equation of the BCS theory.

Application: conventional s-wave superconductors
In what follows let us solve the gap equation for the simple model potential $V_{\mathbf{k}\mathbf{k}'} = V$ which is a reasonable approximation for conventional phonon-mediated superconductivity. In that case Δ can be taken constant and we have

$$\frac{1}{\lambda} = \int_0^{\hbar\omega_0}\frac{d\varepsilon}{\sqrt{\varepsilon^2+\Delta^2}}\tanh\left(\frac{\sqrt{\varepsilon^2+\Delta^2}}{2T}\right),$$

where $\lambda = N(0)V$ is the coupling constant. Note that the gap $\Delta(T)$ is a function of T. At $T = 0$ we have from here the exact result $\Delta(0) = \hbar\omega_0/\sinh(1/\lambda) \approx 2\hbar\omega_0\exp(-1/\lambda)$, the latter equality holding at weak coupling, $\lambda \ll 1$. The critical temperature T_c can be calculated from

$$\frac{1}{\lambda} = \int_0^{\hbar\omega_0}\frac{d\varepsilon}{\varepsilon}\tanh\left(\frac{\varepsilon}{2T_c}\right) = \int_0^{\frac{\hbar\omega_0}{2T_c}}\frac{dx\tanh x}{x} \approx \ln\left(\frac{1.13\hbar\omega_0}{T_c}\right),$$

since at T_c the gap is infinitesimally small. The last equation holds for $\hbar\omega_0 \gg T_c$. When inverted, this yields $T_c \approx 1.13\hbar\omega_0\exp(-1/\lambda)$, valid in the limit $\lambda \ll 1$. Comparing the values of T_c and $\Delta(0)$ we find

$$\frac{\Delta(0)}{T_c} \approx 1.76,$$

i.e. within the BCS theory the ratio does not depend on the material parameters ω_0 and λ. For weak coupling superconductors, this prediction is in good agreement with experiment.

Let us also mention that the Debye frequency scales with the ion mass like $\omega_0 \propto M^{-1/2}$, whereas λ is independent of M, as can be explicitly seen within the jellium model, where $\lambda = N(0)V \sim \frac{n}{\varepsilon_F}\frac{e^2}{\epsilon_0 k_s^2}$. Therefore theory predicts $T_c \propto M^{-1/2}$ (so-called isotope effect), which scaling has been experimentally verified on samples containing different isotopic compositions of the same substance.

Exercise
(Bogoliubov) Calculate the critical temperature for a system with the following interaction among the Cooper pairs: $V_{\mathbf{kp}} = V_1F_1(\mathbf{k},\mathbf{p}) - V_2F_2(\mathbf{k},\mathbf{p})$, where $F_i(\mathbf{k},\mathbf{p}) = 1$ for $|\varepsilon_{\mathbf{k}}|, |\varepsilon_{\mathbf{p}}| < \hbar\omega_i$ and $F_i(\mathbf{k},\mathbf{p}) = 0$ otherwise. The V_1 part corresponds to an attractive interaction with a cutoff $\hbar\omega_1$, while V_2 is a repulsive interaction with a cutoff $\hbar\omega_2 \gg \hbar\omega_1$. This is a more realistic description of the screened Coulomb interaction.

Condensation energy
Let us first consider the condensation energy at $T = 0$, i.e. the difference of the ground

state energy densities of a superconductor $E_{\rm GS}^{SC}$ (see Eq. 20) and of the normal metal, $E_{\rm GS}^{N} = \Omega^{-1}\sum'_{\mathbf{k}}(\varepsilon_{\mathbf{k}} - |\varepsilon_{\mathbf{k}}|)$, i.e. $\frac{B_c^2}{2\mu_0} = E_{\rm GS}^{N} - E_{\rm GS}^{SC}$. Note that the contribution of the occupied states with energy $< \varepsilon_F - \hbar\omega_0$ is (being equal in both states) not included. Therefore we have

$$\frac{B_c^2}{2\mu_0} = \frac{1}{\Omega}\sum_{\mathbf{k}}{}' \left(E_{\mathbf{k}} - |\varepsilon_{\mathbf{k}}| - b_{\mathbf{k}}^*\Delta_{\mathbf{k}}\right) = \frac{1}{\Omega}\sum_{\mathbf{k}}{}' \left(E_{\mathbf{k}} - |\varepsilon_{\mathbf{k}}| - \frac{|\Delta_{\mathbf{k}}|^2}{2E_{\mathbf{k}}}\right) = \frac{1}{\Omega}\sum_{\mathbf{k}}{}' \frac{(E_{\mathbf{k}} - |\varepsilon_{\mathbf{k}}|)^2}{2E_{\mathbf{k}}},$$

where in the third equation we have used $b_{\mathbf{k}}^* = \Delta_{\mathbf{k}}^*/(2E_{\mathbf{k}})$ valid for $T = 0$. Evaluating the last integral in the simple s-wave model we obtain

$$\frac{B_c^2}{2\mu_0} = \frac{1}{2}N(0)\int_{-\hbar\omega_0}^{\hbar\omega_0} d\varepsilon \frac{\left(\sqrt{\varepsilon^2+\Delta^2} - |\varepsilon|\right)^2}{\sqrt{\varepsilon^2+\Delta^2}} \approx N(0)\Delta^2\int_0^\infty dx \frac{\left(\sqrt{x^2+1} - x\right)^2}{\sqrt{x^2+1}} = \frac{1}{2}N(0)\Delta^2,$$

in agreement with our previous qualitative argument. In the approximate step we have replaced the upper integration limit $\hbar\omega_0$ by infinity, since the integrand falls down for large ε as $\propto \varepsilon^{-3}$ and the introduced error is negligible for $\Delta \ll \hbar\omega_0$.

Thermodynamics

The entropy per unit volume of the system of free Bogoliubons described by Eq. 20 is

$$S = -\frac{2}{\Omega}\sum_{\mathbf{k}}\left[(1-f_{\mathbf{k}})\ln(1-f_{\mathbf{k}}) + f_{\mathbf{k}}\ln f_{\mathbf{k}}\right],$$

with $f_{\mathbf{k}}$ the Fermi-Dirac distribution function. When evaluated numerically, the entropy density of the superconducting state is seen to be substantially lower than its value in the normal state, $S_N = \frac{2\pi^2}{3}N(0)T$. This can be shown explicitly for the s-wave superconductor case at low temperatures, $T \ll \Delta$. In fact, in that limit $f_{\mathbf{k}} \approx e^{-E_{\mathbf{k}}/T} \ll 1$ and we have

$$S \approx \frac{2}{\Omega}\sum_{\mathbf{k}} f_{\mathbf{k}}\ln\frac{1}{f_{\mathbf{k}}} = \frac{4N(0)}{T}\int_\Delta^\infty \frac{dE E^2}{\sqrt{E^2-\Delta^2}}e^{-E/T} \approx \frac{2N(0)\Delta\sqrt{2\Delta}}{T}e^{-\Delta/T}\int_\Delta^\infty \frac{dE}{\sqrt{E-\Delta}}e^{-\frac{E-\Delta}{T}},$$

where in the last equation we have used the fact that the integral is dominated by $E-\Delta \sim T$. The last integral reduces to $\sqrt{\pi T}$ and therefore

$$S \approx 2\sqrt{2\pi}N(0)\Delta\sqrt{\frac{\Delta}{T}}e^{-\Delta/T},$$

much smaller than S_N at low temperatures. This means that the superconducting state is more ordered than the normal state. The electronic contribution to the specific heat (per unit volume) at constant volume $c_V = T(dS/dT)_V$ is therefore also exponentially small at low temperatures,

$$c_V \approx 2\sqrt{2\pi}N(0)\Delta\left(\frac{\Delta}{T}\right)^{3/2} e^{-\Delta/T},$$

much smaller than its normal state value $c_V^N = \frac{2\pi^2}{3}N(0)T$. Therefore, by means of a measurement of the electronic part of c_V, one can determine the excitation gap Δ.

7 Spectroscopy of the superconducting state

Excited states
Equation 19 shows that the BCS state can be thought of as a direct product of many particle ground states built of two single particle states $\mathbf{k}\uparrow$ and $-\mathbf{k}\downarrow$. For every $\mathbf{k}$, the ground state is a linear combination of an empty and a full (two-particle) state. One can check easily that the wavefunctions of the excited states are

$$\begin{aligned}
\gamma^\dagger_{\mathbf{k}0}|\psi_{\rm BCS}\rangle &= c^\dagger_{\mathbf{k}\uparrow}\prod_{\mathbf{p}\neq\mathbf{k}}(u^*_{\mathbf{p}}+v^*_{\mathbf{p}}c^\dagger_{\mathbf{p}\uparrow}c^\dagger_{-\mathbf{p}\downarrow})|0\rangle,\\
\gamma^\dagger_{-\mathbf{k}1}|\psi_{\rm BCS}\rangle &= c^\dagger_{-\mathbf{k}\downarrow}\prod_{\mathbf{p}\neq\mathbf{k}}(u^*_{\mathbf{p}}+v^*_{\mathbf{p}}c^\dagger_{\mathbf{p}\uparrow}c^\dagger_{-\mathbf{p}\downarrow})|0\rangle,\\
\gamma^\dagger_{\mathbf{k}0}\gamma^\dagger_{-\mathbf{k}1}|\psi_{\rm BCS}\rangle &= (-v_{\mathbf{k}}+u_{\mathbf{k}}c^\dagger_{\mathbf{k}\uparrow}c^\dagger_{-\mathbf{k}\downarrow})\prod_{\mathbf{p}\neq\mathbf{k}}(u^*_{\mathbf{p}}+v^*_{\mathbf{p}}c^\dagger_{\mathbf{p}\uparrow}c^\dagger_{-\mathbf{p}\downarrow})|0\rangle.
\end{aligned}$$

The first two (single quasiparticle) states contain a definite number of electrons in the $\mathbf{k}\uparrow$,$-\mathbf{k}\downarrow$ sector, while the last state has again an indefinite particle number in that sector. Therefore e.g. the excited state $\gamma^\dagger_{\mathbf{k}0}|\psi_{\rm BCS}\rangle$ can be thought of either as a result of adding the electron $\mathbf{k}\uparrow$ to the ground state, or as removing the electron $-\mathbf{k}\downarrow$ from it.

Moreover, notice that the states $|\psi_{\rm BCS}\rangle$ and $\gamma^\dagger_{\mathbf{k}0}\gamma^\dagger_{-\mathbf{k}1}|\psi_{\rm BCS}\rangle$ (with excitation energies 0 and $2E_{\mathbf{k}}$, respectively) contain an even number of particles, whereas $\gamma^\dagger_{\mathbf{k}0}|\psi_{\rm BCS}\rangle$ and $\gamma^\dagger_{-\mathbf{k}1}|\psi_{\rm BCS}\rangle$ (both with excitation energy $E_{\mathbf{k}}$) have an odd number of electrons. Therefore in an experiment which does not change the total particle number in the sample (e.g., optical spectroscopy), at $T=0$ the minimum excitation gap is 2Δ, whereas in an experiment which does change the electron number (like tunneling), the minimum excitation gap is Δ.

Electron spectral function
Let us start with a description of spectroscopies which change the electron number. To this end we define (for the sake of simplicity we restrict ourselves to $T=0$ in this paragraph) the spectral function for addition of electrons,

$$A^>_\sigma(\mathbf{k}\omega)=\sum_n\left|\langle n|c^\dagger_{\mathbf{k}\sigma}|0\rangle\right|^2\delta\left[\omega-(E_n-E_0)\right],$$

where $|0\rangle$ is an N-electron ground state with energy E_0 and $|n\rangle$ are all $N+1$ electron states with energies E_n. The function $A^>_\sigma(\mathbf{k}\omega)$ measures the weight with which an added particle $\mathbf{k}\sigma$ raises the energy of the system by ω. This function can in principle be measured by inverse photoemission. Similarly we define the electron removal spectral function,

$$A^<_\sigma(\mathbf{k}\omega)=\sum_n\left|\langle n|c_{\mathbf{k}\sigma}|0\rangle\right|^2\delta\left[\omega-(E_0-E_n)\right],$$

where $|n\rangle$ are all $N-1$ electron states. This function can be measured in photoemission experiments.

Let us also define the full spectral function $A_\sigma(\mathbf{k}\omega)=A^>_\sigma(\mathbf{k}\omega)+A^<_\sigma(\mathbf{k}\omega)$. One checks easily that for noninteracting electrons $A_\sigma(\mathbf{k}\omega)=\delta[\omega-(\varepsilon_{\mathbf{k}}+\mu)]$, as should have been expected. In this case only one of the functions $A_\sigma^{>,<}(\mathbf{k}\omega)$ is nonzero for a given $\mathbf{k}$: for $k > k_F$, it is $A_\sigma^{>}(\mathbf{k}\omega)$ and otherwise $A_\sigma^{<}(\mathbf{k}\omega) \neq 0$.

Now let us turn to the superconducting state. The matrix elements are calculated readily if we express the c operators in terms of the γ operators. In the electron addition case we have $E_n - E_0 = E_\mathbf{k} + \mu$, whereas in the electron removal case $E_n - E_0 = (E_\mathbf{k} + \mu) - 2\mu$, since one Cooper pair had to be annihilated. Here we have assumed that the energy of the Cooper pair is 2μ, which will be proved in the next section. Summarizing, we find the BCS expression for the spectral function

$$A_\sigma(\mathbf{k}\omega) = |u_\mathbf{k}|^2 \delta\left[\omega - (\mu + E_\mathbf{k})\right] + |v_\mathbf{k}|^2 \delta\left[\omega - (\mu - E_\mathbf{k})\right].$$

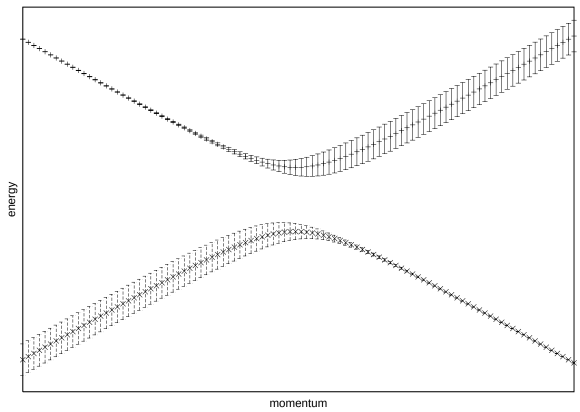

Figure 1: Spectral weight $A(\mathbf{k}, \omega)$ in the k-ω plane. Its magnitude is proportional to the error bar.

Consequence 1. For a given momentum $\mathbf{k}$ close to the Fermi surface, one can both add and remove electrons with a finite weight. No single particle excitations are possible at energies between $\mu - \Delta$ and $\mu + \Delta$.

Consequence 2. For a given energy ω, there are two momenta contributing to spectral weight, one inside and the other one outside the Fermi surface. The total weight of these two contributions is $|u_\mathbf{k}|^2 + |v_\mathbf{k}|^2 = 1$.

Consequence 3. The spectral weight does not depend on the spin label σ (in a singlet superconductor) and the index σ will be dropped.

In some cases (like diffuse tunneling), one is interested in a momentum integrated spectral weight, $N_S(\omega) = \frac{1}{\Omega}\sum_\mathbf{k} A(\mathbf{k}\omega)$, usually called the tunneling density of states. In the particle-hole symmetric case, i.e. when there is an equal number of states above and below the Fermi surface in an energy window $\pm\Delta$ around μ (applicable e.g. to low-T_c superconductors), this can be written as $N_S(\omega) = N(0)\int_{-\infty}^{\infty} d\varepsilon A(\mathbf{k}\omega)$ which can be simplified considerably due to the identity $|u(\varepsilon)|^2 = |v(-\varepsilon)|^2$. In that case the superconducting tunneling density of states (with ω measured with respect to μ) is even, $N_S(\omega) = N_S(-\omega)$, and simplifies for $\omega > 0$ to

$$\frac{N_S(\omega)}{N(0)} = \int_0^\infty d\varepsilon \delta\left(\omega - \sqrt{\varepsilon^2 + \Delta^2}\right) = \mathrm{Re}\left[\frac{\omega}{\sqrt{\omega^2 - \Delta^2}}\right].$$

Note that the absence of states at $|\omega| < \Delta$ is compensated by the divergence of $N_S(\omega)$ at $\omega = \Delta + 0^+$, so that the total number of states $\int d\omega N(\omega)$ is conserved. This BCS prediction is in good agreement with experiments on normal metal/superconductor tunnel junctions.

Ultrasound attenuation

As an example of a calculation of a response function for experiments which do not change the particle number, let us study the attenuation of longitudinal sound waves in a superconductor. In the clean limit when the electron mean free path l is longer than the wavelength of the sound, $ql \gg 1$, the impurity scattering of electrons is irrelevant and to lowest order the Hamiltonian for electron-phonon coupling reads

$$H_{\rm ep} = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{q}\neq 0} D_{\mathbf{q}} \rho_{-\mathbf{q}} (a_{\mathbf{q}} + a^\dagger_{-\mathbf{q}}),$$

where $\rho_{\mathbf{q}} = \sum_{\mathbf{k}} (c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{k}+\mathbf{q}\uparrow} + c^\dagger_{-\mathbf{k}-\mathbf{q}\downarrow} c_{-\mathbf{k}\downarrow})$ is the Fourier transform of the electron density, $a_{\mathbf{q}}$ annihilates a phonon with momentum $\mathbf{q}$, and $D_{\mathbf{q}}$ is the electron-phonon coupling constant. In the long wavelength limit, $q\xi_0 \ll 1$, $D_{\mathbf{q}}$ can be shown to be essentially the same both in the normal and in the superconducting states.

Let us assume that there are $N_{\mathbf{q}}$ phonons in the sound wave. The probabilities per unit time of phonon absorption and emission are given by the Fermi golden rule:

$$\begin{aligned} W_a &= \frac{2\pi |D_{\mathbf{q}}|^2 N_{\mathbf{q}}}{\hbar\Omega} \frac{1}{Z} \sum_{n,m} e^{-\beta E_n} \left|\langle m|\rho_{-\mathbf{q}}|n\rangle\right|^2 \delta(E_m - E_n - \hbar\omega_{\mathbf{q}}), \\ W_e &= \frac{2\pi |D_{\mathbf{q}}|^2 (N_{\mathbf{q}}+1)}{\hbar\Omega} \frac{1}{Z} \sum_{n,m} e^{-\beta E_n} \left|\langle m|\rho_{\mathbf{q}}|n\rangle\right|^2 \delta(E_m - E_n + \hbar\omega_{\mathbf{q}}), \end{aligned}$$

where $|n\rangle$ and $|m\rangle$ are eigenstates of the electronic system. Let us assume a macroscopic population of phonons $N_{\mathbf{q}} \gg 1$ and neglect terms of order $1/N_{\mathbf{q}}$. In the expression for W_e, let us interchange the summation indices n and m and make use of $\rho_{\mathbf{q}} = \rho^\dagger_{-\mathbf{q}}$. Then the population of phonons is described by the equation $\dot{N}_{\mathbf{q}} = -\alpha N_{\mathbf{q}}$ with the attenuation rate

$$\alpha = \frac{2\pi |D_{\mathbf{q}}|^2}{\hbar\Omega} \left(1 - e^{-\hbar\omega_{\mathbf{q}}/T}\right) \frac{1}{Z} \sum_{n,m} e^{-\beta E_n} \left|\langle m|\rho_{-\mathbf{q}}|n\rangle\right|^2 \delta(E_m - E_n - \hbar\omega_{\mathbf{q}}).$$

Let us note in passing that this expression can be written, making use of $\delta(E) = \int \frac{dt}{2\pi\hbar} \exp(iEt/\hbar)$, as a Fourier transform of the density-density correlation function,

$$\alpha = \frac{2\pi |D_{\mathbf{q}}|^2}{\hbar\Omega} \left(1 - e^{-\hbar\omega_{\mathbf{q}}/T}\right) \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} e^{-i\omega_{\mathbf{q}} t} \langle \rho_{\mathbf{q}}(0) \rho^\dagger_{\mathbf{q}}(t)\rangle,$$

where $\rho_{\mathbf{q}}(t) = \exp(iHt/\hbar)\rho_{\mathbf{q}} \exp(-iHt/\hbar)$.

In discussing the response functions of superconductors, the following two identities are helpful:

$$\begin{aligned} c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{p}\uparrow} + c^\dagger_{-\mathbf{p}\downarrow} c_{-\mathbf{k}\downarrow} &= (u^*_{\mathbf{k}} u_{\mathbf{p}} - v^*_{\mathbf{k}} v_{\mathbf{p}}) \gamma^\dagger_{\mathbf{k}0} \gamma_{\mathbf{p}0} + (u_{\mathbf{k}} u^*_{\mathbf{p}} - v_{\mathbf{k}} v^*_{\mathbf{p}}) \gamma^\dagger_{-\mathbf{p}1} \gamma_{-\mathbf{k}1} \\ &+ (u^*_{\mathbf{k}} v^*_{\mathbf{p}} + v^*_{\mathbf{k}} u^*_{\mathbf{p}}) \gamma^\dagger_{\mathbf{k}0} \gamma^\dagger_{-\mathbf{p}1} + (u_{\mathbf{k}} v_{\mathbf{p}} + v_{\mathbf{k}} u_{\mathbf{p}}) \gamma_{-\mathbf{k}1} \gamma_{\mathbf{p}0} + 2\delta_{\mathbf{kp}} |v_{\mathbf{k}}|^2, \quad (22) \\ c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{p}\uparrow} - c^\dagger_{-\mathbf{p}\downarrow} c_{-\mathbf{k}\downarrow} &= (u^*_{\mathbf{k}} u_{\mathbf{p}} + v^*_{\mathbf{k}} v_{\mathbf{p}}) \gamma^\dagger_{\mathbf{k}0} \gamma_{\mathbf{p}0} - (u_{\mathbf{k}} u^*_{\mathbf{p}} + v_{\mathbf{k}} v^*_{\mathbf{p}}) \gamma^\dagger_{-\mathbf{p}1} \gamma_{-\mathbf{k}1} \\ &+ (u^*_{\mathbf{k}} v^*_{\mathbf{p}} - v^*_{\mathbf{k}} u^*_{\mathbf{p}}) \gamma^\dagger_{\mathbf{k}0} \gamma^\dagger_{-\mathbf{p}1} - (u_{\mathbf{k}} v_{\mathbf{p}} - v_{\mathbf{k}} u_{\mathbf{p}}) \gamma_{-\mathbf{k}1} \gamma_{\mathbf{p}0}. \quad (23) \end{aligned}$$

The combinations of the u and v functions (in the brackets) are called coherence factors. For the present case, the type I coherence factors, Eq. 22, are relevant. One observes that the electronic states $|n\rangle$ and $|m\rangle$ can either differ by two quasiparticles (the second two terms in Eq. 22), or they contain the same number of quasiparticles (the first two terms in Eq. 22). In the limit when $\hbar\omega_{\mathbf{q}} \ll \Delta$ (which is valid except extremely close to T_c), conservation of energy requires that $|n\rangle$ and $|m\rangle$ have the same number of particles. Therefore we have

$$\rho_{-\mathbf{q}} = \sum_{\mathbf{k}} \left[(u^*_{\mathbf{k}} u_{\mathbf{k}-\mathbf{q}} - v^*_{\mathbf{k}} v_{\mathbf{k}-\mathbf{q}}) \gamma^\dagger_{\mathbf{k}0} \gamma_{\mathbf{k}-\mathbf{q}0} + (u_{\mathbf{k}} u^*_{\mathbf{k}-\mathbf{q}} - v_{\mathbf{k}} v^*_{\mathbf{k}-\mathbf{q}}) \gamma^\dagger_{-\mathbf{k}+\mathbf{q}1} \gamma_{-\mathbf{k}1} + \dots \right] = \sum_{\mathbf{k}} \rho_{-\mathbf{q}}(\mathbf{k}),$$

where the dots denote the pair creation and annihilation terms which are irrelevant in the present context. For $|n\rangle$, $|m\rangle$ which are eigenstates of Eq. 20, one can see immediately that $|\langle m|\rho_{-\mathbf{q}}|n\rangle|^2 = \sum_{\mathbf{k}} |\langle m|\rho_{-\mathbf{q}}(\mathbf{k})|n\rangle|^2$. The only nonzero contribution to the attenuation rate due to $\rho_{-\mathbf{q}}(\mathbf{k})$ therefore comes from processes in which $|n\rangle$ contains a $\mathbf{k}-\mathbf{q}, 0$ particle and no $\mathbf{k}, 0$ particles [which happens with probability $f_{\mathbf{k}-\mathbf{q}}(1-f_{\mathbf{k}})$] or from processes in which $|n\rangle$ contains a $-\mathbf{k}, 1$ particle and no $-\mathbf{k}+\mathbf{q}, 1$ particles. Changing the summation variable $\mathbf{k}$ in the contribution of the latter processes to $-\mathbf{k}+\mathbf{q}$ (and making use of the fact that both $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are even), one finds that both contributions are equal. Furthermore, making use of the identity

$$\left(1 - e^{-\hbar\omega_{\mathbf{q}}/T}\right) f_{\mathbf{k}-\mathbf{q}}(1-f_{\mathbf{k}}) \delta(E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{q}} - \hbar\omega_{\mathbf{q}}) = (f_{\mathbf{k}-\mathbf{q}} - f_{\mathbf{k}}) \delta(E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{q}} - \hbar\omega_{\mathbf{q}}),$$

we find

$$\alpha = \frac{4\pi|D_{\mathbf{q}}|^2}{\hbar} \frac{1}{\Omega} \sum_{\mathbf{k}} |u^*_{\mathbf{k}} u_{\mathbf{k}-\mathbf{q}} - v^*_{\mathbf{k}} v_{\mathbf{k}-\mathbf{q}}|^2 (f_{\mathbf{k}-\mathbf{q}} - f_{\mathbf{k}}) \delta(E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{q}} - \hbar\omega_{\mathbf{q}}).$$

Now, since $q\xi_0 \ll 1$ and $\hbar\omega_{\mathbf{q}} \ll \Delta$, we can neglect $\mathbf{q}$ in the coherence factor and we obtain

$$\begin{aligned} \alpha &= 4\pi|D_{\mathbf{q}}|^2 \omega_{\mathbf{q}} \frac{1}{\Omega} \sum_{\mathbf{k}} \left(|u_{\mathbf{k}}|^2 - |v_{\mathbf{k}}|^2\right)^2 \frac{f_{\mathbf{k}-\mathbf{q}} - f_{\mathbf{k}}}{E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{q}}} \delta(E_{\mathbf{k}} - E_{\mathbf{k}-\mathbf{q}}) \\ &= 4\pi|D_{\mathbf{q}}|^2 \omega_{\mathbf{q}} N(0) \int_{-\infty}^{\infty} d\varepsilon \left(\frac{\varepsilon}{E}\right)^2 \left(-\frac{\partial f}{\partial E}\right) \int_{-1}^{1} dt \delta\left(\sqrt{(\varepsilon + \hbar v_F q t)^2 + \Delta^2} - \sqrt{\varepsilon^2 + \Delta^2}\right), \end{aligned}$$

where t is the cosine of the angle between $\mathbf{k}$ and $\mathbf{q}$. Taking first the integral over t we obtain

$$\alpha = \frac{8\pi|D_{\mathbf{q}}|^2 v N(0)}{\hbar v_F} \int_0^{\infty} \frac{d\varepsilon \varepsilon}{E} \left(-\frac{\partial f}{\partial E}\right) = \frac{8\pi|D_{\mathbf{q}}|^2 v N(0)}{\hbar v_F} \int_{\Delta}^{\infty} dE \left(-\frac{\partial f}{\partial E}\right) = 2\alpha_N f(\Delta)$$

where we introduced $\alpha_N = 4\pi|D_{\mathbf{q}}|^2 v N(0)/(\hbar v_F)$ and we have used that $\omega_{\mathbf{q}} = vq$ with the sound velocity v. Note that since $f(0) = 1/2$, the attenuation rate equals α_N in the normal state. Thus we conclude that in the superconducting state the attenuation rate is depressed with respect to α_N by a factor $2f(\Delta)$.

8 Josephson effect

Relation between phase and pair number
Let us discuss the connection between the wavefunction with a fixed pair number,$|\psi(N)\rangle$, and the BCS wavefunction $|\psi_{\rm BCS}\rangle$ in more detail. Let us first note that, if we perform a global $U(1)$ gauge transformation, $c^\dagger_{\mathbf{k}\sigma} \to e^{i\varphi}c^\dagger_{\mathbf{k}\sigma}$ and $c_{\mathbf{k}\sigma} \to e^{-i\varphi}c_{\mathbf{k}\sigma}$ for all $\mathbf{k}$ and σ, the Hamiltonian Eq. 17 remains unchanged, while the BCS wavefunction changes to

$$|\psi_{\rm BCS}(\theta)\rangle = \prod_{\mathbf{k}}(u^*_{\mathbf{k}} + v^*_{\mathbf{k}}e^{i\theta}c^\dagger_{\mathbf{k}\uparrow}c^\dagger_{-\mathbf{k}\downarrow})|0\rangle,$$

where $\theta = 2\varphi$ is the phase of a Cooper pair. Note that $|\psi_{\rm BCS}(\theta)\rangle$ is in general physically different from the original $|\psi_{\rm BCS}\rangle$ (i.e. it differs not only by an overall phase factor). Therefore the BCS wavefunction breaks the global $U(1)$ gauge invariance of the Hamiltonian Eq. 17. It is obvious that the part $|\psi(N)\rangle$ of $|\psi_{\rm BCS}(\theta)\rangle$ which contains precisely N Cooper pairs is proportional to $e^{iN\theta}$. Therefore we can obtain $|\psi(N)\rangle$ by the following projection,

$$|\psi(N)\rangle = \int_0^{2\pi}\frac{d\theta}{2\pi}e^{-iN\theta}|\psi_{\rm BCS}(\theta)\rangle,$$

and the two sets of states, namely $|\psi(N)\rangle$ with different N and $|\psi_{\rm BCS}(\theta)\rangle$ with different θ are seen to be analogs of the eigenstates of the x and p operators in quantum mechanics. In fact, the 'wavefunction' of the state $|\psi(N)\rangle$ in the θ representation is seen to be $e^{-iN\theta}/(2\pi)$ and therefore the operator of the pair number can be written $\hat{N} = i\frac{\partial}{\partial\theta}$ in the phase representation. Therefore we have the commutation relation

$$[\hat{N}, \hat{\theta}] = i$$

and the pair of operators $\hat{N}, \hbar\hat{\theta}$ are canonically conjugate:

$$\begin{aligned} \hat{N} &\leftrightarrow \hat{x} \\ \hbar\hat{\theta} &\leftrightarrow \hat{p}. \end{aligned}$$

It follows furthermore that the uncertainties of the phase and particle number will have to satisfy the Heisenberg principle, $\Delta N\,\Delta\theta > 1$. Nevertheless, a macroscopic superconductor with an average number $N \gg 1$ of Cooper pairs which weakly interchanges pairs with a reservoir of the Cooper pairs (e.g. with another macroscopic superconductor), can have a well defined phase $\Delta\theta \ll 1$ and, at the same time, a negligible pair number fluctuation $\Delta N/N$. Therefore the operators $\hat{N}$ and $\hat{\theta}$ can be replaced by the corresponding classical fields.

Josephson equations
In the preceding discussion we have made use of Hamiltonians in which a term $\mu N_{\rm el}$ was subtracted, where μ is the chemical potential and $N_{\rm el}$ is the operator of the electron number. In situations where the electron number can change it is therefore important to add the term $\mu N_{\rm el}$ back to the Hamiltonian. With this proviso, let us calculate the time dependence of the operator $c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}$:

$$i\hbar\frac{\partial}{\partial t}c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} = [c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}, H + \mu N_{\rm el}] = 2\mu c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} + [2\varepsilon_{\mathbf{k}}c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} - \Delta_{\mathbf{k}}(1 - n_{\mathbf{k}\uparrow} - n_{-\mathbf{k}\downarrow})],$$

where for the Hamiltonian we have taken Eq. 19 and we have used the commutation relations $[c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}, n_{\mathbf{k}\uparrow} + n_{-\mathbf{k}\downarrow}] = 2c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}$ and $[c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}, c^\dagger_{\mathbf{k}\uparrow}c^\dagger_{-\mathbf{k}\downarrow}] = 1 - n_{\mathbf{k}\uparrow} - n_{-\mathbf{k}\downarrow}$ (which shows that the Cooper pairs are not strictly bosons). Taking the expectation value of this equation of motion and making use of $\langle n_{\mathbf{k}\uparrow}\rangle = \langle n_{-\mathbf{k}\downarrow}\rangle = \frac{1}{2} - \frac{\varepsilon_{\mathbf{k}}}{2E_{\mathbf{k}}}\tanh\left(\frac{E_{\mathbf{k}}}{2T}\right)$ we find

$$i\hbar\frac{\partial}{\partial t}\langle c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}\rangle = 2\mu\langle c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}\rangle$$

and therefore $\langle c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}\rangle = b_{\mathbf{k}}e^{-2i\mu t/\hbar}$. Denoting the phase of the Cooper pair as θ we thus find

$$\dot{\theta} = -\frac{2\mu}{\hbar}. \tag{24}$$

This is the Josephson equation for the time development of phase. One of its consequences is that the energy of a Cooper pair is 2μ. Note that, if we denote the true Hamiltonian as $\tilde{H} = H + 2\mu\hat{N}$ and if we assume that $\tilde{H} = \tilde{H}(\hat{N}, \hat{\theta})$ is a function of $\hat{N}$ and $\hat{\theta}$, the Josephson equation 24 can be thought of as the Hamiltonian equation of motion, $i\hbar\dot{\theta} = [\hat{\theta}, \tilde{H}(\hat{N}, \hat{\theta})] = -i\frac{\partial\tilde{H}}{\partial N}$, where in the last equation we have made use of the N representation of the operator $\hat{\theta}$. The equation of motion for the canonically conjugate coordinate N reads as

$$\dot{N} = \frac{1}{i\hbar}[\hat{N}, \tilde{H}(\hat{N}, \hat{\theta})] = \frac{1}{\hbar}\frac{\partial\tilde{H}}{\partial\theta}. \tag{25}$$

In what follows we will show that the physical content of Eq. 25 is very close to the Ginzburg-Landau equation 8.

Josephson effect

Let us consider two macroscopic superconductors with phases θ_1 and θ_2. Let us bring them in a weak contact with each other (e.g., by forming a narrow channel connecting the two, or by separating them by a very thin insulating barrier). Let us assume that the energy of the system depends on the relative phase, $E = E(\theta_1 - \theta_2)$. Then the current flowing from superconductor 1 to 2 is $I = 2e\dot{N}_1 = \frac{2e}{\hbar}\frac{\partial E}{\partial\theta_1} = -\frac{2e}{\hbar}\frac{\partial E}{\partial\theta_2} = -2e\dot{N}_2$, since the charge carried by a Cooper pair $-2e$. Introducing $\theta = \theta_1 - \theta_2$, we can write the Josephson equation for the current,

$$I = \frac{2e}{\hbar}\frac{\partial E(\theta)}{\partial\theta}. \tag{26}$$

Let us make the reasonable assumption that for $\theta = 0$ (i.e. homogeneous phase), the energy $E(\theta)$ is minimized. Then for $\theta = 0$ no currents are expected to flow. However, if $E(\theta)$ is not a constant function (which should not be the case, since the superconductors are in contact), this equation shows that in the presence of a finite phase difference, currents flow across the weak link (also called Josephson junction). This is the so called Josephson effect.

Let us for a while consider a single macroscopic superconductor. Let us divide the sample into small but microscopic pieces with phases θ_i. The above discussion suggests that in presence of an inhomogeneous distribution of phases currents will flow, in qualitative agreement with Eq. 8.

Both of the above examples, that of a Josephson junction and that of a bulk superconductor, imply that a dissipationless current flows in a superconductor in case of an inhomogeneous phase distribution. As emphasized by Anderson, this is an emergent property associated with the spontaneous breaking of the global $U(1)$ gauge symmetry and with the off-diagonal long range order.

Dissipationless transport of charge (or matter in case of superfluidity) is a phenomenon which we are not used to in daily life and therefore looks mysterious. There is however another emergent property, dissipationless transport of force, to which we are perfectly accustomed and which we do not perceive as mysterious, although it is completely analogous to superconductivity and superfluidity. In fact, pushing a rigid body at one end, also the other end of the body moves. The dissipationless transport of force is caused by the rigidity of the solid, which is an emergent property associated with the breaking of translational symmetry: once we fix one part of the body, the rest of it has one preferred position and any deformation field $\mathbf{u}$ leads to an elastic energy increase $\propto |\nabla \mathbf{u}|^2$.

Let us return to the Josephson junction. Making use of Eq. 24, the time evolution of the phase difference at the junction can be written

$$\dot{\theta} = \frac{2eV}{\hbar}, \tag{27}$$

where we have noted that $\mu_2 - \mu_1 = e(\varphi_1 - \varphi_2) = eV$ and V is the voltage difference which is positive for currents flowing from 1 to 2. The internal consistency of Eqs. 26 and 27 can be checked by considering the following experiment. Let us prepare the junction in a state with phase difference $\theta = \theta_0$ and change the phase difference to $\theta = 0$. The junction will lose the energy

$$E(\theta_0) - E(0) = \int_0^{\theta_0} d\theta \frac{\partial E(\theta)}{\partial \theta} = \frac{\hbar}{2e} \int_0^{\theta_0} d\theta I = \int dt V I,$$

where in the second and third equality, we have used Eqs. 26 and 27, respectively. The lost energy is precisely equal to the heat dissipated in the transformation process, as one should expect.

Tunnel junctions

Now let us calculate the phase dependent part of the energy of a junction between two superconductors connected by a thin planar tunneling barrier. The Hamiltonian of the system is $H = H_1 + H_2 + H_T$, where H_1 and H_2 describe the superconductors 1 and 2 and

$$H_T = \sum_{\mathbf{kq}} \left[t_{\mathbf{kq}} (c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{q}\uparrow} + c^\dagger_{-\mathbf{q}\downarrow} c_{-\mathbf{k}\downarrow}) + \text{h.c.} \right].$$

Here and in what follows we assume that the indices $\mathbf{q}$ and $\mathbf{k}$ describe the left and the right superconductor, respectively. H_T is the so-called tunneling Hamiltonian which describes the transfer of electrons from 1 to 2 and vice versa with amplitude $t_{\mathbf{kq}}$. Note that the operator multiplying $t_{\mathbf{kq}}$ can be written in terms of the γ operators using the coherence factors Eq. 22.

Because H_T is assumed to be small, it will be treated within perturbation theory. Let us first note that the first order correction vanishes, since H_T changes the occupation numbers of the γ particles in a given superconductor. The second-order contribution to the energy is

$$\begin{aligned}\delta E &= -2\sum_{\mathbf{kq}}|t_{\mathbf{kq}}|^2|u^*_{\mathbf{k}}u_{\mathbf{q}}-v^*_{\mathbf{k}}v_{\mathbf{q}}|^2\left[\frac{f_{\mathbf{q}}(1-f_{\mathbf{k}})}{E_{\mathbf{k}}-E_{\mathbf{q}}}+\frac{f_{\mathbf{k}}(1-f_{\mathbf{q}})}{E_{\mathbf{q}}-E_{\mathbf{k}}}\right]\\ &\quad -2\sum_{\mathbf{kq}}|t_{\mathbf{kq}}|^2|u_{\mathbf{k}}v_{\mathbf{q}}+v_{\mathbf{k}}u_{\mathbf{q}}|^2\left[\frac{(1-f_{\mathbf{k}})(1-f_{\mathbf{q}})}{E_{\mathbf{k}}+E_{\mathbf{q}}}-\frac{f_{\mathbf{k}}f_{\mathbf{q}}}{E_{\mathbf{k}}+E_{\mathbf{q}}}\right],\end{aligned}$$

where the first line comes from processes in which already existing quasiparticles were virtually transferred across the junction, whereas the second line describes processes where a pair of quasiparticles, one in each superconductor, is virtually created or annihilated. At $T=0$, only this latter type of processes contributes. The overall factor 2 comes from two spin degrees of freedom. Making use of

$$\begin{aligned}|u^*_{\mathbf{k}}u_{\mathbf{q}}-v^*_{\mathbf{k}}v_{\mathbf{q}}|^2 &= |u_{\mathbf{k}}|^2|u_{\mathbf{q}}|^2+|v_{\mathbf{k}}|^2|v_{\mathbf{q}}|^2-\frac{\Delta^*_{\mathbf{k}}\Delta_{\mathbf{q}}+\Delta_{\mathbf{k}}\Delta^*_{\mathbf{q}}}{4E_{\mathbf{k}}E_{\mathbf{q}}},\\ |u_{\mathbf{k}}v_{\mathbf{q}}+v_{\mathbf{k}}u_{\mathbf{q}}|^2 &= |u_{\mathbf{k}}|^2|v_{\mathbf{q}}|^2+|v_{\mathbf{k}}|^2|u_{\mathbf{q}}|^2+\frac{\Delta^*_{\mathbf{k}}\Delta_{\mathbf{q}}+\Delta_{\mathbf{k}}\Delta^*_{\mathbf{q}}}{4E_{\mathbf{k}}E_{\mathbf{q}}},\end{aligned}$$

we find that the phase dependent part of δE is

$$\delta E(\theta)=-\sum_{\mathbf{kq}}|t_{\mathbf{kq}}|^2\frac{\Delta^*_{\mathbf{k}}\Delta_{\mathbf{q}}+\Delta_{\mathbf{k}}\Delta^*_{\mathbf{q}}}{2E_{\mathbf{k}}E_{\mathbf{q}}}\left[\frac{1-f_{\mathbf{k}}-f_{\mathbf{q}}}{E_{\mathbf{k}}+E_{\mathbf{q}}}-\frac{f_{\mathbf{q}}-f_{\mathbf{k}}}{E_{\mathbf{k}}-E_{\mathbf{q}}}\right].$$

In the simplest case of a Josephson junction between identical s-wave superconductors we have $\Delta_{\mathbf{k}}=\Delta e^{i\theta_1}$ and $\Delta_{\mathbf{q}}=\Delta e^{i\theta_2}$ and therefore

$$\delta E(\theta)=-E_c\cos\theta,$$

which is the celebrated Josephson formula for the energy of a tunnel junction. Note that the minimum of energy is realized for $\theta=0$, in agreement with our expectations. Assuming a featureless tunneling, $|t_{\mathbf{kq}}|=t$, the energy E_c can be calculated from

$$E_c=\frac{\hbar\Delta^2}{\pi e^2R_N}\int_0^\infty\frac{d\varepsilon_1}{E_1}\int_0^\infty\frac{d\varepsilon_2}{E_2}\frac{E_1\tanh\frac{E_2}{2T}-E_2\tanh\frac{E_1}{2T}}{E_1^2-E_2^2}=\frac{\pi}{4}\frac{\hbar\Delta}{\pi e^2R_N}\tanh\left(\frac{\Delta}{2T}\right),$$

where we have used the expression for the normal state resistance, $R_N=\frac{\hbar}{4\pi e^2N(0)^2t^2}$. Making use of Eq. 26, we find that the superconducting current $I(\theta)=I_c\sin\theta$. Therefore the maximal dissipationless current which can flow across the junction is

$$I_cR_N=\frac{\pi}{2}\frac{\Delta}{|e|}\tanh\left(\frac{\Delta}{2T}\right).$$

Exercise
Prove the formula for the normal state resistance.