Oct. 31

Physics 212 – Statistical Mechanics

Superconductivity

In the previous lecture, I described the formalism for superfluidity. We saw that the superfluid state is described as a macroscopically occupied quantum wavefunction, or, more generally, by a macroscopic expectation value of a quantum field. The underlying theory has a $U(1)$ symmetry – the phase rotation symmetry of quantum mechanics. The field expectation value breaks this symmetry spontaneously. Then the phase transition to superfluidity is described by an $n = 2$ Landau free energy. I showed how this picture gives rise to frictionless fluid flow in the superfluid state.

Now I would like to generalize that description to the frictionless flow of current observed at very low temperatures in a metal – superconductivity. This is a flow of electric current without resistance. Our formalism will build on that for superfluidity, but with two new features. First, the current carriers in superconductor are electrons, which are fermions. We need to understand how fermions can give rise to a superfluid state with a macroscopic condensate. Second, the superconducting state is coupled to electromagnetism, and this changes its properties in an essential way. In this lecture, I will discuss the physics that leads to the formation of an electron superfluid. This is one of relatively few cases in which is possible be derive the Landau free energy explicitly from an underlying theory. That beautiful derviation is the BCS theory, due to John Bardeen, Leon Cooper, and Robert Schrieffer. It is one of major advances of 20th century physics.

It is amazing that, while magnetism is very special phenomenon limited to only a few elements in the periodic table, superconductivity occurs in a much larger number of elements, including most of the transition metals and actinides. Aluminum, mercury, and lead are important superconductors at sufficiently low temperature. So the explanation for superconductivity can only depend on generic properties of metals. The primary exceptions are magnetic elements, such as iron and nickel; even the next door neighbor copper does not have superconductivity.

The first question to ask is, what is the superconducting order parameter? This must be a bosonic quantum field. On the other hand, it must be build out of electrons. The expectation value of this field arises through a phenomenon called *fermion pair condensation*. In case of electrons in a metal, this is called *Cooper pairing*.

To derive fermion condensation in this lecture, I will rely on an an approximate Hamiltonian that encodes properties of electrons in a metal at low temperatures. In general, the wavefunctions of electrons is a metal are complicated, since the conduction electrons must avoid the more tightly bound valence electrons in each atom. However, the basic properties of electrons in metals are well described by a simpler picture, in which electrons are treated as free particles in wavefunctions of definite momentum. This model is called a “Fermi liquid”. It becomes exact at very low temperature, when the electron mass adjusted to an effective mass to agree with observations. Essentially, the Fermi liquid parameters model the averaged behavior of electrons over distances larger than a typical atomic spacing.

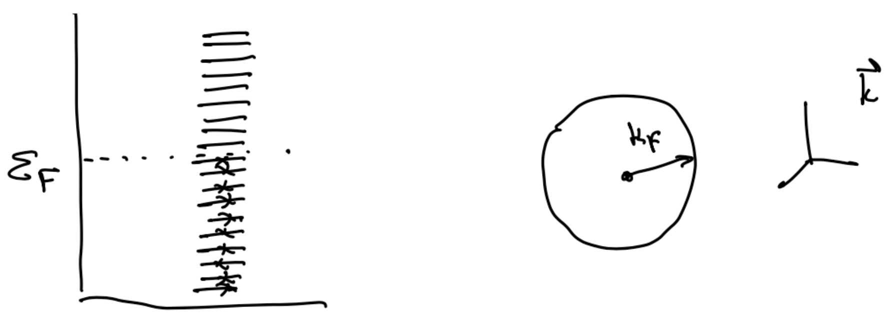
In my discussion here, I try to find the ground state of an interacting many-electron system at zero temperature. It will be clear in a moment why effects of temperature are not essential. I will consider the conduction electrons in a metal as a gas of free fermions with

$$E(k) = \frac{k^2}{2m} \tag{1}$$

and chemical potential μ. The occupation number for each quantum state is

$$n(k) = \frac{1}{e^{\beta(E(k)-\mu)}+1} \ , \tag{2}$$

in accord with Fermi-Dirac statistics. In the limit $T \to 0$, the quantum states are filled up to the energy μ and are empty above that level.



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The energy μ is called the *Fermi energy* ϵ_F, and the corresponding momentum is the *Fermi momentum* k_F. Typical values of ϵ_F in metals are of the order of 10 eV, corresponding to 100,000 °K. So at room temperature, and even more so at low temperatures, the motion of electron between energy levels happens only very close to the Fermi energy. In this case, we can approximate

$$E(k) = \epsilon_F + v_F\kappa \qquad v_F = \frac{k_F}{m} \ , \tag{4}$$

where

$$\kappa = |\vec{k}| - k_F \ . \tag{5}$$

At finite temperatures, the sharp discontinuity in the occupation number as a function of κ is smeared out, but only over a small interval $v_F|\kappa \ \sim kT$.

Naturally, electrons have Coulomb repulsion. This effect is mainly taken into account in the parameters of the Fermi liquid theory, as a shift in the mass of each electron as it moves through the sea of electrons and atoms. However, at low momentum transfers, there is another effect. An electron can deform the crystal lattice, and this deformation can be attractive to another electron. In the quantum theory, this effect is described as electron scattering by the exchange of *phonons*. It is very weakly attractive. Following BCS, I will model this effect by a pointlike attractive interaction of the electron fields. The electron quantum field is

$$\psi_s(x) = \int \frac{d^3k}{(2\pi)^3}\; e^{i\vec{k}\cdot\vec{x}}\; a_{ks} \qquad \psi_s^\dagger(x) = \int \frac{d^3k}{(2\pi)^3}\; e^{-i\vec{k}\cdot\vec{x}}\; a_{ks}^\dagger \tag{6}$$

where $a_{ks}^\dagger$ and a_{ks} are the electron creation and annihilation operators. The index s refers to the spin of the electron, which may be up ($\uparrow$) or down ($\downarrow$). Since electrons are fermions, their creation and annihilation operators should obey anticommutation relations

$$\{a_{ks}, a_{ps'}^\dagger\} = \delta_{ss'}\; (2\pi)^3 \delta(\vec{k} - \vec{p}) \tag{7}$$

Then

$$(a_{ks}^\dagger)^2\;\; |0\rangle = 0 \tag{8}$$

and we cannot put two electrons into a quantum state with the same momentum and the same spin.

The Fermi ground state is then

$$|\mathrm{Fermi}\rangle = \prod_s \prod_{k<k_F}\;\; a_{ks}^\dagger\, |0\rangle \;\; . \tag{9}$$

Acting with $a_{ks}^\dagger$, $k > k_F$, on this state creates an electron above the Fermi level. Acting with a_{ks}, $k < k_F$, creates a "hole" with positive charge and momentum $-\vec{k}$.

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Acting with $a^\dagger_{ks} a_{k's'}$ moves an electron from $\vec{k}'$ to $\vec{k}$, creating a particle-hole pair.

$$\tag{11}$$

Using this notation, the BCS effective Hamiltonian is

$$\mathcal{H} = \int \frac{d^3k}{(2\pi)^3} \sum_s \; v_F \kappa \; a^\dagger_{ks} a_{ks} - \lambda \int d^3x \sum_{s,s'} \; \psi^\dagger_s \psi_s(x) \, \psi^\dagger_{s'} \psi_{s'}(x) \; , \tag{12}$$

where λ represents a small positive coupling constant. The operator

$$\rho(x) = \sum_s \psi^\dagger_s(x) \psi_s(x) \tag{13}$$

is the electron density at x. The operator in $\mathcal{H}$

$$\psi^\dagger_s \psi_s \; \psi^\dagger_{s'} \psi_{s'} \tag{14}$$

has two roles. First, it introduces scattering among electrons and shifts their energies. For small λ this is a minor effect, and I will ignore it. But also, the operator contains terms of the form

$$a^\dagger_{ks} a_{ps} a^\dagger_{qs'} a_{rs'} \tag{15}$$

where k, q are above the Fermi level and p, r are below the Fermi level. This term removes two electrons from the filled levels below ϵ_F and introduces two electrons in empty states above ϵ_F. This term is off-diagonal in the original basis. If we diagonalize it, we will lower the energy of the ground state.

A particularly attract type of two-electron pair is one with opposite momentum and opposite spin

$$\tag{16}$$

This state has zero momentum and zero angular momentum – the same quantum numbers as the original free-particle ground state. This is a *Cooper pair*. To diagonalize the pair creation and annihilation terms, we can introduce an indefinite number of such pairs into the ground state.

Let

$$b_k^\dagger = a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger \qquad b_k = a_{-k\downarrow}^\dagger a_{k\uparrow}^\dagger \tag{17}$$

In terms of these operators, the original Fermi ground state is

$$|\mathrm{Fermi}\rangle = \prod_{k<k_F} b_k^\dagger \ |0\rangle \ . \tag{18}$$

BCS proposed the more general ground state

$$|\mathrm{BCS}\rangle = \prod_k \ (u_k + v_k b_k^\dagger) \ |0\rangle \ . \tag{19}$$

where u_k and v_k are functions of k that we will treat as variational parameters. The state is normalized as long as

$$|u_k|^2 + |v_k|^2 = 1 \ . \tag{20}$$

For a given k, $v_k = 1$ implies that the states $k = |\vec{k}|$ are occupied with electron pairs, and $u_k = 0$ implies that the states $k = |\vec{k}|$ are unoccupied. Intermediate values of u_k and v_k imply that the states are partially filled, actually as a linear combination of the filled and unfilled states. It is useful to substitute

$$u_k = \sin\theta_k \qquad v_k = \cos\theta_k \ . \tag{21}$$

Now I will compute the variational energy $\langle BCS|\,\mathcal{H}\,|BCS\rangle$ and minimize this energy with respect to the u_k and v_k. The expectation value of the kinetic term of $\mathcal{H}$ is

$$\begin{aligned}
\langle\mathrm{BCS}| \ &\int \frac{d^3k}{(2\pi)^3} \sum_s v_F\kappa \ a_{ks}^\dagger a_{ks}\,|\mathrm{BCS}\rangle \\
&= \int \frac{d^3k}{(2\pi)^3} \ 2v_F\kappa \ |v_k|^2 \\
&= \int \frac{d^3k}{(2\pi)^3} \ 2v_F\kappa \ \cos^2\theta_k
\end{aligned} \tag{22}$$

The term in the interaction part of the Hamiltonian that creates and destroys pairs has the expectation value

$$\begin{aligned}
\langle\mathrm{BCS}| \ &-2\lambda \int \frac{d^3q}{(2\pi)^3}\frac{d^3p}{(2\pi)^3} a_{q\uparrow}^\dagger a_{p\uparrow} a_{-q\downarrow}^\dagger a_{-p\downarrow}\,|\mathrm{BCS}\rangle \\
&= -2\lambda \int \frac{d^3q}{(2\pi)^3}\frac{d^3p}{(2\pi)^3} \ u_q v_q u_p v_p \\
&= -2\lambda \int \frac{d^3q}{(2\pi)^3}\frac{d^3p}{(2\pi)^3} \ \sin\theta_q\cos\theta_q\sin\theta_p\cos\theta_p
\end{aligned} \tag{23}$$

Then we can recast the Hamiltonian expectation value as

$$\langle \mathrm{BCS}| \ \mathcal{H} \ |\mathrm{BCS}\rangle$$
$$= \int \frac{d^3k}{(2\pi)^3} \ 2v_F\kappa \ (1+\cos 2\theta_k) - \frac{\lambda}{2}\int \frac{d^3q}{(2\pi)^3}\frac{d^3p}{(2\pi)^3} \ \sin 2\theta_q \ \sin 2\theta_p \ . \tag{24}$$

To get a feel for this expression, consider the minimization of just the kinetic term. We need

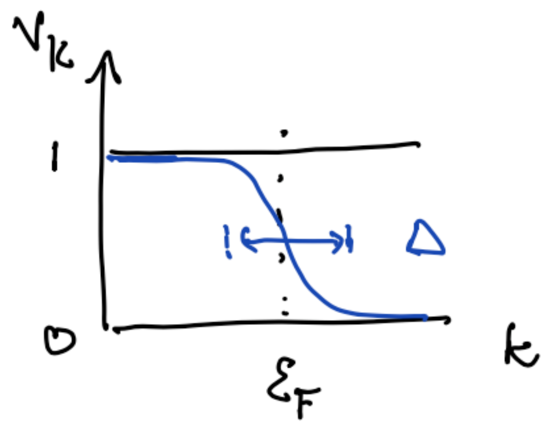
$$\frac{d}{d\theta_k}(1+cos2\theta_k) = -2\sin 2\theta_k = 0 \ . \tag{25}$$

that is,

$$\theta_k = 0 \ , \ \pi/2 \qquad \text{or} \qquad v_k = 0 \ , \ 1 \tag{26}$$

Again we find the Fermi ground state. Since the number of electrons is fixed, we should fill the states up to the Fermi level ($v_k = 1$) and then have $v_k = 0$ for $k > k_F$.

It is not hard to imagine that the interaction term will favor a solution in which v_k make a smooth transition from 1 to 0 around $k = k_F$,



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Now minimize the full $\langle H\rangle$ with respect to θ_k. Taking the derivative with respect to θ_q, we find

$$0 = -2v_F\kappa \ \sin 2\theta_k - 2\lambda\int \frac{d^3p}{(2\pi)^3}\cos 2\theta_k \ \sin 2\theta_p \ . \tag{28}$$

The solution of this equation is

$$\frac{\sin 2\theta_k}{\cos 2\theta_q} = -\frac{\Delta}{v_F\kappa} \tag{29}$$

where I have set

$$\Delta = \lambda\int \frac{d^3p}{(2\pi)^3} \ \sin 2\theta_p \tag{30}$$

Then the expressions for $\sin 2\theta_k$ and $\cos 2\theta_k$ are

$$\sin 2\theta_k = \frac{\Delta}{[(v_F\kappa)^2 + \Delta^2]^{1/2}} \qquad \cos 2\theta_q = -\frac{v_F\kappa}{[(v_F\kappa)^2 + \Delta^2]^{1/2}} \ . \tag{31}$$

Substituting the first expression into the expression for Δ, we generate the equation

$$\Delta = \lambda \int \frac{d^3p}{(2\pi)^3} \ \frac{\Delta}{[(v_F\rho)^2 + \Delta^2]^{1/2}} \ , \tag{32}$$

where $\rho = p - k_F$. The parameter Δ is called the *gap* in BCS, and the equation (32) is called the *gap equation*. This is a self-consistency equation that determines Δ.

The general form of (32) is familiar to us from the mean field theory of the Ising model. There is a solution $\Delta = 0$. However, if this equation has nontrivial solutions, those solution will generate broken-symmetry ground states of lower energy. It is clear that if there is one solution, there are two, $\pm|\Delta|$. I have been working with real-valued u_k and v_k, but, more generally, u_k and v_k can have quantum-mechanical phases, and then the solution space would be a circle

$$\Delta = e^{i\alpha}|\Delta| \ . \tag{33}$$

This is just the set of ground states that we found in the XY model.

The integral over momenta in the gap equation is spherically symmetric. Write the integral in a form appropriate to momenta near the Fermi energy,

$$\int \frac{d^3p}{(2\pi)^3} = \int d\rho \frac{k_F^2 d\Omega_p}{(2\pi)^3} = \frac{k_F^2}{2\pi^2 v_F} \ \int_{-k_F}^{k_F} d\rho \, v_F \tag{34}$$

Note that I have only estimated the limits of integration of the integral over ρ. This is reasonable, since the dominant contribution will come from $|\rho| << \epsilon_F$. Then the equation for Δ becomes

$$\Delta = \lambda \frac{k_F m}{2\pi^2} \int_{-k_F}^{k_F} d\rho \, v_F \ \frac{\Delta}{[(v_F\rho)^2 + \Delta^2]^{1/2}} \ . \tag{35}$$

We are looking for nontrivial solutions, so divide through by Δ. Then

$$1 = \lambda \frac{k_F m}{2\pi^2} \int_{-\epsilon_F}^{\epsilon_F} dx \ \frac{1}{[x^2 + \Delta^2]^{1/2}} \ . \tag{36}$$

In the limit $\Delta \to 0$, this integral is logarithmically divergent at small values of x. Then, for small Δ, (36) is well approximated by

$$1 = \lambda \frac{k_F m}{\pi^2} \log \frac{\epsilon_F}{\Delta} \ . \tag{37}$$

Notice that I have used the energy ϵ_F to estimate the cutoff of the logarithm at large energies.

The solution of this equation is

$$\Delta = \epsilon_F \ \exp\Big[-\frac{\pi^2}{k_F m} \cdot \frac{1}{\lambda}\Big] \ . \tag{38}$$

This solution has some remarkable properties. First, there is a solution for any value of λ, no matter how small. Second, the value of Δ, which is the energy scale at which the BCS state differs from the normal Fermi liquid ground state, is exponentially small for small values λ. This explains the two most important features of superconductivity. First, superconductivity occurs in almost every metal at low temperatures. We now see that it requires only an arbitrarily weak electron-electron interactions. Second, the value of the critical temperature for the transition to superconductivity is dramatically smaller than the Fermi energy. Both features are apparent in the solution for Δ.

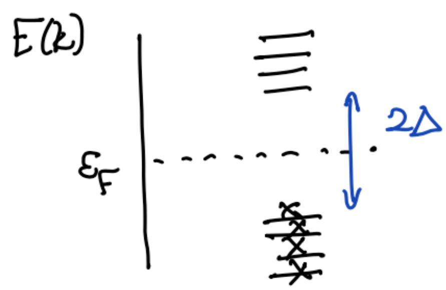
Some additional work is needed to find the spectrum of excitations of this ground state. With some computation, one can see that the operators

$$c_{k\uparrow} = (u_k a_{k\uparrow} - v_k a^\dagger_{-k\downarrow}) \quad \text{and} \quad c_{-k\downarrow} = (u_k a_{-k\downarrow} + v_k a^\dagger_{k\uparrow}) \tag{39}$$

annihilate the BCS ground state. Then the conjugate operators

$$c^\dagger_{k\uparrow} = (u_k a^\dagger_{k\uparrow} - v_k a_{-k\downarrow}) \quad \text{and} \quad c^\dagger_{-k\downarrow} = (u_k a^\dagger_{-k\downarrow} + v_k a_{k\uparrow}) \tag{40}$$

create electron excitations. The spectrum of excitations has the form



(41)

with a gap at the Fermi energy. All states below the gap are filled. The electron states above the gap have the energies

$$E(k) = \epsilon_F + [(v_F \kappa)^2 + \Delta^2]^{1/2} \tag{42}$$

The role of the gap in this expression is similar to the particle mass in the Dirac equation and, even more clearly, the mass for the fermion that we saw in the 2-dimensional Ising model.

The electrons excited above the gap can carry energy and electric charge, but the supercurrent is carried by a macroscopic wavefunction in a maneer similar to that in superfluidity. Define the quantum fields

$$\Phi(x) = \psi_\downarrow \psi_\uparrow(x) \qquad \Phi^\dagger(x) = \psi_\uparrow^\dagger \psi_\downarrow^\dagger(x) \ . \tag{43}$$

Notice that these fields create and annihilate pairs of fermions; hence, they are bosonic. The expectation value of $\Phi(x)$ in the BCS ground state is

$$\langle \Phi(x) \rangle = \int \frac{d^3k}{(2\pi)^3} u_k v_k \ . \tag{44}$$

Evaluating the integral,

$$\int \frac{d^3k}{(2\pi)^3} u_k v_k = \int \frac{d^3k}{(2\pi)^3} \cdot \frac{1}{2} \sin 2\theta_k = \frac{\Delta}{2\lambda} \tag{45}$$

Then

$$\langle \Phi(x) \rangle = \frac{\Delta}{2\lambda} \ . \tag{46}$$

Notice that the condensate field is proportional to Δ. Then $\Phi(x)$ is the order parameter for superconductivity. We have already remarked that Δ can have any quantum-mechanical phase. The circle of degenerate ground states noted above is then reflected in the possible phases of the superconducting order parameter. When we allow the phase of Φ to vary from point to point, this condensate can carry an electric charge current that can flow frictionlessly.

The phase transition to superconductivity will then be described by the Landau free energy of the form

$$G[\Phi] = \int d^3x \Big\{ \frac{1}{2m} |\vec{\nabla}\Phi|^2 + \frac{1}{2} a(T - T_c)|\Phi|^2 + \frac{1}{4} b|\Phi|^4 \Big\} \tag{47}$$

with $SO(2)$ or $U(1)$ symmetry. However, the coupling of the electron field to electromagnetism introduces some essential complications. I will discuss these in the next lecture. Lev Gorkov gave a derivation of this free energy from BCS theory that allows the parameters to be computed from first principles.

The mechanism of fermion pair condensation is a very general one that can apply whenever the Hamiltonian can contain off-diagonal terms that mix fermion pairs into the ground-state wavefunction. Fermion pair condensates are seen in nuclei, in neutron stars, and in the ground state of QCD, the theory of strong interactions, as well as in a variety of condensed matter systems. In the BCS theory, the gap equation involves a 1-dimensional integral that is logarithmically divergenct when Δ goes to zero. In other systems, the corresponding integral can be 3-dimensional and nonsingular in the $\Delta \to 0$ limit. Then we do not find a solution for any small coupling constant but only when the coupling is sufficiently strong.

In the BCS theory, the fermion pair has zero quantum numbers, but other systems include more general arrangements. In the low-temperature phase of He^3, the helium atoms pair at low temperature, but, because these atoms have a hard-core repulsion, the pair has a P-wave (orbital angular momentum 1) wavefunction. Then, by Fermi statistics, the spins of the helium atoms must be in a symmetric, spin 1 state. Then the pair condensate quantum field will have two spin-1 or vector indices, one giving the orbital angular momentum orientation, the second giving the spin orientation,

$$\Phi_{ij} \tag{48}$$

He^3 at low temperatures actually has two superfluid phases, called the A and B phases, with $\Phi_{ij} \propto \delta_{ij}$ in the B phase but taking a more general matrix form in the A phase. Similarly, in neutron stars, the fermion condensate has isospin 1 ("pion condensation"). Some high-temperature superconductors have electron pairing with a D-wave (spin 2) wavefunction. Fermion pair condensation makes many more strange physical systems possible.

Here is some extra material for those who are curious about it:

Here I will give the derivation of the equations (39) and (40) and the electron excitation spectrum (42).

First, rewrite the Hamiltonian by replacing the pair creation and annihilation terms by their expectation value plus the effects of additional excitations. For example

$$a^\dagger_{k\uparrow} a^\dagger_{-k\downarrow} \to u_k v_k + a^\dagger_{k\uparrow} a^\dagger_{-k\downarrow} \tag{49}$$

Drop the terms quartic in operators. These will be subdominant for small λ. This gives

$$\begin{aligned} \mathcal{H} = &\int \frac{d^3k}{(2\pi)^3}\; v_F\kappa (a^\dagger_{k\uparrow} a_{k\uparrow} + a^\dagger_{-k\downarrow} a_{k\downarrow}) \\ &- \int \frac{d^3k}{(2\pi)^3}\; \Delta\; (a^\dagger_{k\uparrow} a^\dagger_{-k\downarrow} + a_{-k\downarrow} a_{k\uparrow}) \end{aligned} \tag{50}$$

plus a constant that contributes to the BCS ground state energy. I have used the gap equation (32) in the second line. Compare this to the expression

$$\mathcal{H}_c = \int \frac{d^3k}{(2\pi)^3}\; [(v_F\kappa)^2 + \Delta^2]^{1/2}\; (c^\dagger_{k\uparrow} c_{k\uparrow} + c^\dagger_{-k\downarrow} c_{-k\downarrow}) \tag{51}$$

where the operators c_{ka} are defined as in (39) and (40). Being careful about the anticommutation of fermion operators, we find that this equals

$$\mathcal{H} = \int \frac{d^3k}{(2\pi)^3} \; [(v_F\kappa)^2 + \Delta^2]^{1/2} \Big\{ (u_k^2 - v_k^2)(a^\dagger_{k\uparrow} a_{k\uparrow} + a^\dagger_{-k\downarrow} a_{k\downarrow}) \\ - 2u_k v_k (a^\dagger_{k\uparrow} a^\dagger_{-k\downarrow} + a_{-k\downarrow} a_{k\uparrow}) \Big\} \; , \tag{52}$$

plus a constant. Putting in the expressions for u_k and v_k, this becomes

$$\mathcal{H} = \int \frac{d^3k}{(2\pi)^3} \; [(v_F\kappa)^2 + \Delta^2]^{1/2} \Big\{ -cos 2\theta_k \; (a^\dagger_{k\uparrow} a_{k\uparrow} + a^\dagger_{-k\downarrow} a_{k\downarrow}) \\ - \sin 2\theta_k \; (a^\dagger_{k\uparrow} a^\dagger_{-k\downarrow} + a_{-k\downarrow} a_{k\uparrow}) \Big\} \; , \tag{53}$$

which just reproduces the Hamiltonian (50). We find two sets of excitations above the BCS ground state with energies

$$E(k) = [(v_F\kappa)^2 + \Delta^2]^{1/2} \tag{54}$$

These are single-electron excitations with up and down spins. As with the Fermi ground state, removal of an electron from a filled state creates a hole that can then move as a free particle of positive charge.

More details of the BCS solution, including the analysis of the solution at $T > 0$, can be found in Michael TInkham's book *Introduction to Superconductivity*. This topic is also treated in textbooks on the application of quantum field theory techniques in many-particle systems, for example, the textbook of Fetter and Walecka.