2 Superconductivity

2.4 Mean Field Hamiltonian: Energy Gap and Quasiparticle Excitations

In the above variation calculation, it is not clear at all what is the meaning of $\Delta$. In fact, $\Delta$ is either called the ‘Superconducting Gap’ (more precisely the gap is related to $|\Delta|$) or the ‘Order Parameter’ of the superconductor. We are going to explain in this section, why $\Delta$ is the ‘gap’.

In order to discuss the gap of the system, we need to consider the excited states as well, not just the ground state as we did in the last section. Of course, to directly solve for the excited states are very hard because the Hamiltonian contains an interaction term. However, similar to the superfluid case, we can apply a ‘mean field’ approximation to the Hamiltonian and reduce it to quadratic form which can be readily diagonalized. This is the Bogoliubov approach to superconductivity, which closely resembles the Bogoliubov approach to superfluidity.

Consider the Hamiltonian

$$H = \sum_{k,\sigma} (\epsilon_k - \mu) c_{k\sigma}^\dagger c_{k\sigma} - V_0 \sum_{k,k'} c_{k\uparrow}^\dagger c_{-k\uparrow}^\dagger c_{-k'\downarrow} c_{k'\downarrow}$$

(1)

Our goal is to reduce the four body interaction term to two body terms. The key assumption in this approach is that we can replace $\sum_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger$ and $\sum_k c_{k\uparrow} c_{-k\downarrow}$ by their expectation values in the ground state, as we did for the superfluid. We have already defined these expectation values in the previous section

$$\langle \sum_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger \rangle = \sum_k v_k^* u_k = \frac{\Delta^*}{V_0}, \quad \langle \sum_k c_{k\uparrow} c_{-k\downarrow} \rangle = \sum_k u_k^* v_k = \frac{\Delta}{V_0}$$

(2)

If we write

$$\sum_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger = \frac{\Delta^*}{V_0} + \left( \sum_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger - \frac{\Delta^*}{V_0} \right), \quad \sum_k c_{k\uparrow} c_{-k\downarrow} = \frac{\Delta}{V_0} + \left( \sum_k c_{k\uparrow} c_{-k\downarrow} - \frac{\Delta}{V_0} \right)$$

(3)

and assume the second term – the fluctuation term – is small and keep only terms linear in such fluctuations, we can write the Hamiltonian as

$$H = \sum_{k,\sigma} (\epsilon_k - \mu) c_{k\sigma}^\dagger c_{k\sigma} - \sum_k \Delta c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger - \Delta^* c_{-k'\downarrow}^\dagger c_{k'\uparrow} + \text{constant}$$

(4)

This is the mean field or BCS form of the Hamiltonian.

A crucial feature of this Hamiltonian is that it only contains quadratic terms of the fermion creation and annihilation operators. It is different from the usual free fermion Hamiltonian of an insulator or metal in that it contains terms like $c_{k\uparrow}^\dagger c_{k\uparrow}^\dagger$ and $c_{k\downarrow} c_{-k\downarrow} c_{-k\downarrow}^\dagger$. Notice that in this Hamiltonian both $c_{k\uparrow}^\dagger$ and $c_{-k\downarrow}$ are coupled to $c_{k\uparrow}^\dagger$ and $c_{-k\downarrow}^\dagger$, we can write the Hamiltonian as

$$H = \sum_k \left( c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger \right) \begin{pmatrix} \epsilon_k - \mu & -\Delta \\ -\Delta^* & -\epsilon_k - \mu \end{pmatrix} \begin{pmatrix} c_{k\uparrow}^\dagger \\ c_{-k\downarrow}^\dagger \end{pmatrix}$$

(5)
where \((c_{\mathbf{k}}^{\uparrow}, c_{\mathbf{k}}^{\downarrow})\) is called a Nambu spinor. The Hamiltonian can be diagonalized for different \(\mathbf{k}\) separately and for each \(\mathbf{k}\) the eigenvalues of the matrix

\[
\begin{pmatrix}
\epsilon_{\mathbf{k}} - \mu & -\Delta \\
-\Delta^* & -(\epsilon_{\mathbf{k}} - \mu)
\end{pmatrix}
\]

are

\[
\pm E_{\mathbf{k}} = \pm \sqrt{(\epsilon_{\mathbf{k}} - \mu)^2 + |\Delta|^2}
\]

and the eigenvectors are

\[
\begin{pmatrix}
u_{\mathbf{k}} \\
v^*_{\mathbf{k}}
\end{pmatrix}
\]

where \(u_{\mathbf{k}}\) and \(v_{\mathbf{k}}\) are exactly given as above and in fact we are going to see that the BCS wave function is exactly the ground state of this mean field Hamiltonian (although it is not exactly the ground state of the original interacting Hamiltonian).

The eigenmodes of the mean field Hamiltonian are

\[
b_{\mathbf{k}}^{\uparrow} = u_{\mathbf{k}} c_{\mathbf{k}}^{\uparrow} - v_{\mathbf{k}} c_{\mathbf{k}}^{\downarrow}, \quad b_{\mathbf{k}}^{\downarrow} = v_{\mathbf{k}}^{*} c_{\mathbf{k}}^{\uparrow} + u_{\mathbf{k}}^{*} c_{\mathbf{k}}^{\downarrow}
\]

which are well defined fermion modes satisfying commutation relation

\[
\{b_{\mathbf{k}\sigma}, b_{\mathbf{k}'\sigma'}^{\dagger}\} = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'}, \quad \{b_{\mathbf{k}\sigma}, b_{\mathbf{k}'\sigma'}\} = 0, \quad \{b_{\mathbf{k}\sigma}^{\dagger}, b_{\mathbf{k}'\sigma'}^{\dagger}\} = 0
\]

Using these eigenmodes, the Hamiltonian can be written in a simple form

\[
H = \sum_{\mathbf{k}} E_{\mathbf{k}} (b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}}^{\dagger} + b_{-\mathbf{k}}^{\dagger} b_{-\mathbf{k}}^{\dagger})
\]

So the ground state satisfies the condition

\[
b_{\mathbf{k}}^{\dagger} |\Psi_{BCS}\rangle = 0, \quad b_{-\mathbf{k}}^{\dagger} |\Psi_{BCS}\rangle = 0
\]

It is straight forward to check that the BCS wave function defined by

\[
|\Psi_{BCS}\rangle = \prod_{\mathbf{k}} \left( u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{-\mathbf{k}}^{\dagger} \right) |0\rangle
\]

exactly satisfies these conditions.

To create excitations, we can apply \(b_{\mathbf{k}}^{\dagger}\) and \(b_{\mathbf{k}}^{\dagger}\) to the ground state, so that the wave function contains components like

\[
b_{-\mathbf{k}}^{\dagger} \left( u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{-\mathbf{k}}^{\dagger} \right) |0\rangle = c_{-\mathbf{k}}^{\dagger} |0\rangle, \quad b_{\mathbf{k}}^{\dagger} \left( u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{-\mathbf{k}}^{\dagger} \right) |0\rangle = c_{\mathbf{k}}^{\dagger} |0\rangle
\]

and each \(b_{\mathbf{k}}^{\dagger}\) or \(b_{\mathbf{k}}^{\dagger}\) costs energy

\[
E_{\mathbf{k}} = \sqrt{(\epsilon_{\mathbf{k}} - \mu)^2 + |\Delta|^2}
\]

The most important aspect of this formula is that, it is lower bounded by \(|\Delta|\) no matter what \(\mathbf{k}\) is. That is, all excitations above the ground state have a finite energy gap as long as \(|\Delta| > 0\). And this is exactly the reason why \(|\Delta|\) is called the superconducting gap. The value of \(|\Delta|\) can
be determined as in the previous section from the self consistency condition on the ground state expectation value. And we have

$$|\Delta| = 2\hbar \omega_D e^{-1/\lambda}$$  \hspace{1cm} (17)$$

where \(\lambda = Z E_F V_0/2\).

The face that superconductors have a gap makes it sharply different from superfluids, which is gapless. We are going to come back to this point later and discuss where the gapless modes have gone and why with a gap it can still conduct current without dissipation.

2.5 Spontaneous symmetry breaking

The parameter \(\Delta\) has another name – the order parameter of superconductor – indicating its relation to potential symmetry breaking in the superconducting state.

The original Hamiltonian of the system – with kinetic energy and interaction energy – has charge conservation symmetry. The total charge that’s being conserved is the number of electrons in the system and in this case it is indeed related to ‘charge’ conservation because each electron carries charge \(-e\).

$$N = \sum_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma}$$  \hspace{1cm} (18)$$

The electron creation and annihilation operators transform nontrivially under the \(U(1)\) symmetry generated by \(N\)

$$e^{i a N} c_{k\sigma}^\dagger e^{-a N} = e^{i a c_{k\sigma}^\dagger}, \quad e^{i a N} c_{-k\sigma} e^{-a N} = e^{-i a c_{k\sigma}}$$  \hspace{1cm} (19)$$

while the total Hamiltonian preserves the symmetry.

The BCS ground state on the other hand, does not. It is a superposition of all possible Cooper pair states, with particle number 0, \(\pm 2, \pm 4, \ldots\) (relative to a filled Fermi sea) and it has a nonzero expectation value on operators that break charge conservation symmetry

$$\langle \Psi_{BCS} | c_{r\uparrow} c_{r\downarrow}^\dagger | \Psi_{BCS} \rangle = v_k^* u_k$$  \hspace{1cm} (20)$$

If we define an order parameter to be the expectation value of \(c_{r\uparrow}^\dagger c_{r\downarrow}^\dagger\), we would find it to be

$$\langle \Psi_{BCS} | c_{r\uparrow}^\dagger c_{r\downarrow}^\dagger | \Psi_{BCS} \rangle = \frac{1}{L^3} \langle \Psi_{BCS} | \sum_{k,k'} e^{i(k+k')r} c_{k\uparrow}^\dagger c_{k'\downarrow}^\dagger | \Psi_{BCS} \rangle$$  \hspace{1cm} (21)$$

$$= \frac{1}{L^3} \langle \Psi_{BCS} | \sum_k c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger | \Psi_{BCS} \rangle = \frac{1}{L^3} \sum_k v_k^* u_k = \frac{\Delta^*}{L^3 V_0}$$  \hspace{1cm} (22)$$

where \(L^3\) is the volume of the system.

(If we are careful with the coefficient of the Fourier transformation, we can see that \(V_0\) is a quantity that scales as \(1/L^3\) with volume. Therefore, the order parameter is nonzero even in the thermal dynamic (infinite system size) limit. To see this, let’s define Fourier transform of fermion modes as

$$c_{r\sigma} = \frac{1}{\sqrt{L^3}} \sum_k e^{-ikr} c_{k\sigma}, \quad c_{k\sigma} = \frac{1}{\sqrt{L^3}} \int d^3 r e^{ikr} c_{r\sigma}$$  \hspace{1cm} (23)$$
The interaction term in real space reads (let’s take WLOG onsite interaction)

\[-U \int d^3r c_r^\dagger c_r^\dagger c_r c_r \]  \hspace{1cm} (24)

where \( U \) is independent of system size. Writing it in terms of the fermion modes in momentum space, we get

\[-\frac{U}{L^6} \sum_{k_1 k_2 k_3 k_4} \int d^3r e^{i(-k_1-k_2+k_3+k_4)} c_{k_1}^\dagger c_{k_2}^\dagger c_{k_3} c_{k_4} = -\frac{U}{L^3} \sum_{k_1+k_2=k_3+k_4} c_{k_1}^\dagger c_{k_2}^\dagger c_{k_3} c_{k_4} \]  \hspace{1cm} (25)

so that \( V_0 = \frac{U}{L^3} \) is inversely proportional to system size.

Of course, being a symmetry breaking ground state of a symmetric Hamiltonian, it can be mapped to all other ground states by a global symmetry transformation \( e^{i\alpha N} \)

\[ e^{i\alpha N} |\Psi_{BCS}\rangle = \prod_k \left( u_k e^{i2\alpha} v_k \right) c_{k_1}^\dagger c_{k_2}^\dagger - c_{k_3} c_{k_4} \]  \hspace{1cm} (26)

and correspondingly the order parameter changes to \( e^{-i2\alpha} \Delta \).

Similar to the superfluid case, we can form a symmetric wave function out of all the symmetry breaking ones as

\[ |\Psi_{sym}\rangle_{BCS} = \frac{1}{2\pi} \int d\alpha \prod_k \left( u_k + e^{i2\alpha} v_k \right) c_{k_1}^\dagger c_{k_2}^\dagger - c_{k_3} c_{k_4} \]  \hspace{1cm} (27)

On this symmetrized ground state, the expectation value of the order parameter will be zero but the correlator is not. That is, we need to calculate

\[ \langle \Psi_{sym} | c_{r_1}^\dagger c_{r_2}^\dagger c_{r_3} c_{r_4} | \Psi_{sym}\rangle \]  \hspace{1cm} (28)

It contains terms like

\[ \sum_{k,k'} \left( c_{k_1}^\dagger c_{k_2}^\dagger c_{k_3} c_{k_4} \right) \sum_{k,k'} e^{i(k+k')(r-r')} \]  \hspace{1cm} (29)

which could have nonzero expectation value. The first type of term contributes a constant term \( \frac{|\Delta|^2}{L^6 V_0} \) while the components in the second type of terms average to zero. Therefore, the correlation is finite even when \( r \) and \( r' \) are separated very far apart, which indicates spontaneous symmetry breaking in the system.

This spontaneous breaking of symmetry is the fundamental reason why the Meissner effect happens. Recall that when a single electron moves in a electromagnetic field, the phase factor of its wave function change by \( \int qA \cdot dl \). Similarly, if we have Cooper pairs moving in a electromagnetic field, the phase factor their wave function would also change, by \( \int (-2e)A \cdot dl \). Therefore, if the Cooper pairs are ‘condensed’ and we have a coherent superposition of all kinds of Cooper pair configurations, the phase change has to be quantized. Therefore, if magnetic field is to penetrate through a superconductor, it must come in quantized fluxes. If the magnetic field is too small to support the quantized flux, it cannot come into the superconductor at all and is completely screened.

This is very similar to the vortex quantization in a superfluid, but with two differences: 1. in a superconductor the electrons carry real charges, so the phase factor change can be induced by
real magnetic field. While both superconductors and superfluids break the charge conservation symmetry, the superconducting ground state preserves a $Z_2$ part of the symmetry. That is, the superconducting ground state is a superposition of only configurations with an even number of particles while the superfluid ground state contains all possible particle number configuration. Therefore, while in a superfluid, the vortex is quantized to integer multiples of $2\pi$, in a superconductor, magnetic fluxes are only quantized in integer multiples of $\pi$.

Another comment that I want to make is that: by considering the symmetry of the system, it seems rather strange that superconductors should be gapped. We found this gap by analyzing the mean field Hamiltonian of the superconductor, but the mean field Hamiltonian already breaks the charge conservation symmetry. On the other hand, if we start from the original Hamiltonian which preserves charge conservation symmetry, it seems that there should always be some gapless excitation if the ground state spontaneous breaks the symmetry which comes from the smooth variation of the order parameter field. This is actually stated as a theorem – the Goldstone theorem – that if a continuous symmetry is spontaneously broken in a system, there is always gapless excitations above the ground state. So is our conclusion about the gap in the superconductor wrong?

First of all, the gap we are talking about is not in contradiction to the Goldstone theorem because the gap is a single particle gap. It measures the energy needed to create one particle or remove one particle and hence break the Cooper pairs. As long as the Cooper pairs are in bound states, there should always be such a single particle gap. In superfluids, such a gapped excitation is missing because we cannot break each boson into halves and remove one half. The Goldstone modes are obtained by rotating the order parameter fields smoothly in space and this process cannot create or remove single electrons.

On the other hand, although generally we do expect the Goldstone mode to exist, superconductors are special. The reason is that, in a superconductor which carries real electromagnetic charge, there is real electromagnetic field. When real electromagnetic field is present, the Goldstone mode disappear due to a mechanism called the Higgs mechanism. This is the famous mechanism that is responsible for the Higgs boson and the mass of many fundamental particles. We are going to come back to this point later using the Landau Ginzburg theory for superconductivity.

### 2.6 Landau-Ginzburg theory

Having studied the microscopic BCS theory in detail, now let’s transition to the Ginzburg-Landau description which captures the key feature of superconductivity using a free energy functional of the order parameter field. The Landau Ginzburg theory of superconductivity turns out to be a highly useful formulation that allows us to deal with finite temperature, external field, and nonuniform (including interface) configurations in a much more simpler way than the fully microscopic approach like the BCS. In particular, it is extremely powerful in describing phase transitions. In the BCS theory discussed above, we basically talked about why attractive interaction can result in symmetry breaking BCS ground state wave function which indicates that we are in a superconducting phase. There are all kinds of factors that can destroy the superconducting phase: raising the temperature, increasing external magnetic field, doping of electrons / holes into the material, etc. The Landau Ginzburg theory will provide the adequate tool to describe the critical properties at the transition.
2.6.1 Spatially uniform and no external fields

As with the usual Landau’s approach to symmetry breaking phases, it assumes that superconductors are described by an order parameter field and the free energy of the system can be written as a functional of the order parameter field including simple polynomial terms of the field or derivatives of the field. The key requirement in writing down the functional is symmetry – the $U(1)$ charge conservation symmetry here.

As in the case of the superfluid, the order parameter field is a complex field $\psi(\mathbf{r})$ which changes its phase factor under the $U(1)$ symmetry transformation. From the previous discussion of the BCS model, we know that this is exactly the $\Delta$ field

$$\psi(\mathbf{r}) \sim \Delta(\mathbf{r}) = \langle c_{\mathbf{r}\uparrow}^\dagger c_{\mathbf{r}\downarrow}^\dagger \rangle$$

such that $\psi$ is mapped to $e^{i 2 \alpha} \psi$ under symmetry transformation by $\alpha$.

The free energy density functional, in the simplest form without spatial variation or external field but only the possibility of different temperatures, reads

$$f_s(T) = f_n(T) + a(T)|\psi|^2 + \frac{1}{2} b(T)|\psi|^4 + \ldots$$

so that $f_s$ is invariant under the $U(1)$ symmetry transformation. This has exactly the same function as in the superfluid phase and we know what would happen: $b(T)$ has to be always positive to ensure the system is stable. $a(T)$ can be positive or negative. When $a(T)$ is positive, the minimum of the free energy is achieved at $\psi = 0$ so that there is no symmetry breaking and no superconductivity; when $a(T)$ is negative, the minimum is achieved at $|\psi|^2 = -\frac{a(T)}{b(T)}$. The phase factor of $\psi$ is arbitrary. There is spontaneous symmetry breaking and the system is in the superconducting phase.

The subscript $s$ and $n$ refers to the superconducting and normal phase respectively, which makes sense because when $\psi = 0$, the system goes back to the normal phase.

At the critical temperature $T_c$, $a(T_c) = 0$. Around $T_c$, we can expand it to lowest order as

$$a(T) \approx \hat{a}(T - T_c)$$

while $b(T)$ is mostly a constant $b$. So that when $T > T_c$, $|\psi| = 0$; when $T < T_c$

$$|\psi|^2 = \frac{\hat{a}}{b}(T_c - T)$$

We can define the ‘condensation energy’ by comparing how much free energy is saved by going superconducting as compared to the normal state with $\psi = 0$ when $T < T_c$. Close to $T_c$, we have

$$f_s(T) - f_n(T) = -\frac{\hat{a}^2}{b}(T_c - T)^2 + \frac{1}{2} \frac{\hat{a}^2}{b}(T_c - T)^2 = -\frac{\hat{a}^2}{2 b}(T_c - T)^2$$

Taking the derivative of $f(T)$ with respect to $T$, we get the entropy of the system

$$s_s(T) - s_n(T) = \frac{\hat{a}^2}{b}(T - T_c)$$

which is zero at $T_c$. So in going across the phase transition, there is no discontinuity in entropy and hence no latent heat. This just confirms that the Ginzburg Landau theory describes a second-order phase transition.