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Chapter 12

BCS Theory of Superconductivity

12.1 Binding and Dimensionality

Consider a spherically symmetric potential $U(r) = -U_0 \Theta(a - r)$. Are there bound states, i.e. states in the eigenspectrum of negative energy? What role does dimension play? It is easy to see that if $U_0 > 0$ is large enough, there are always bound states. A trial state completely localized within the well has kinetic energy $T_0 \approx \hbar^2/ma^2$, while the potential energy is $-U_0$, so if $U_0 > \hbar^2/ma^2$, we have a variational state with energy $E = T_0 - U_0 < 0$, which is of course an upper bound on the true ground state energy.

What happens, though, if $U_0 < T_0$? We again appeal to a variational argument. Consider a Gaussian or exponentially localized wavefunction with characteristic size $\xi \equiv \lambda a$, with $\lambda > 1$. The variational energy is then

$$E \approx \frac{\hbar^2}{m\xi^2} - U_0 \left( \frac{a}{\xi} \right)^d = T_0 \lambda^{-2} - U_0 \lambda^{-d}. \quad (12.1)$$

Extremizing with respect to $\lambda$, we obtain $-2T_0 \lambda^{-3} + dU_0 \lambda^{-(d+1)}$ and $\lambda = \left( \frac{dU_0}{2T_0} \right)^{1/(d-2)}$. Inserting this into our expression for the energy, we find

$$E = \left( \frac{2}{d} \right)^{2/(d-2)} \left( 1 - \frac{2}{d} \right) T_0^{d/(d-2)} U_0^{-2/(d-2)} \quad (12.2)$$

We see that for $d = 1$ we have $\lambda = 2T_0/U_0$ and $E = -U_0^2/4T_0 < 0$. In $d = 2$ dimensions, we have $E = (T_0 - U_0)/\lambda^2$, which says $E \geq 0$ unless $U_0 > T_0$. For weak attractive $U(r)$, the minimum energy solution is $E \to 0^+$, with $\lambda \to \infty$. It turns out that $d = 2$ is a marginal dimension, and we shall show that we always get localized states with a ballistic dispersion and an attractive potential well. For $d > 2$ we have $E > 0$ which suggests that we cannot have bound states unless $U_0 > T_0$, in which case $\lambda \leq 1$ and we must appeal to the analysis in the previous paragraph.
We can firm up this analysis a bit by considering the Schrödinger equation,

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi(x) + V(x) \psi(x) = E \psi(x) \]  

(12.3)

Fourier transforming, we have

\[ \varepsilon(k) \hat{\psi}(k) + \int \frac{d^dk'}{(2\pi)^d} \hat{V}(k - k') \hat{\psi}(k') = E \hat{\psi}(k) \]  

(12.4)

where \( \varepsilon(k) = \hbar^2 k^2 / 2m \). We may now write \( \hat{V}(k - k') = \sum_n \lambda_n \alpha_n(k) \alpha^*_n(k') \), which is a decomposition of the Hermitian matrix \( \hat{V}_{k,k'} \equiv \hat{V}(k - k') \) into its (real) eigenvalues \( \lambda_n \) and eigenvectors \( \alpha_n(k) \). Let’s approximate \( V_{k,k'} \) by its leading eigenvalue, which we call \( \lambda \), and the corresponding eigenvector \( \alpha(k) \). That is, we write \( \hat{V}_{k,k'} \approx \lambda \alpha(k) \alpha^*(k') \). We then have

\[ \hat{\psi}(k) = \frac{\lambda \alpha(k)}{E - \varepsilon(k)} \int \frac{d^dk'}{(2\pi)^d} \alpha^*(k') \hat{\psi}(k') \]  

(12.5)

Multiply the above equation by \( \alpha^*(k) \) and integrate over \( k \), resulting in

\[ \frac{1}{\lambda} = \int \frac{d^dk}{(2\pi)^d} \frac{|\alpha(k)|^2}{E - \varepsilon(k)} = \frac{1}{\lambda} = \int_0^\infty d\varepsilon \frac{g(\varepsilon)}{E - \varepsilon} |\alpha(\varepsilon)|^2 \]  

(12.6)

where \( g(\varepsilon) \) is the density of states \( g(\varepsilon) = \text{Tr} \delta(\varepsilon - \varepsilon(k)) \). Here, we assume that \( \alpha(k) = \alpha(k) \) is isotropic. It is generally the case that if \( V_{k,k'} \) is isotropic, i.e. if it is invariant under a simultaneous \( O(3) \) rotation \( k \rightarrow Rk \) and \( k' \rightarrow Rk' \), then so will be its lowest eigenvector. Furthermore, since \( \varepsilon = \hbar^2 k^2 / 2m \) is a function of the scalar \( k = |k| \), this means \( \alpha(k) \) can be considered a function of \( \varepsilon \). We then have

\[ \frac{1}{|\lambda|} = \int_0^\infty d\varepsilon \frac{g(\varepsilon)}{|E| + \varepsilon} |\alpha(\varepsilon)|^2 \]  

(12.7)

where we have we assumed an attractive potential \( \lambda < 0 \), and, as we are looking for a bound state, \( E < 0 \).

If \( \alpha(0) \) and \( g(0) \) are finite, then in the limit \( |E| \rightarrow 0 \) we have

\[ \frac{1}{|\lambda|} = g(0) |\alpha(0)|^2 \ln \left( \frac{1}{|E|} \right) + \text{finite} \]  

(12.8)

This equation may be solved for arbitrarily small \( |\lambda| \) because the RHS of Eqn. 12.7 diverges as \( |E| \rightarrow 0 \). If, on the other hand, \( g(\varepsilon) \sim \varepsilon^p \) where \( p > 0 \), then the RHS is finite even when \( E = 0 \). In this case, bound states can only exist for \( |\lambda| > \lambda_c \), where

\[ \lambda_c = 1 / \int_0^\infty d\varepsilon \frac{g(\varepsilon)}{\varepsilon} |\alpha(\varepsilon)|^2 \]  

(12.9)
Typically the integral has a finite upper limit, given by the bandwidth $B$. For the ballistic dispersion, one has $g(\varepsilon) \propto \varepsilon^{(d-2)/2}$, so $d = 2$ is the marginal dimension. In dimensions $d \leq 2$, bound states form for arbitrarily weak attractive potentials.

12.2 Cooper’s Problem

In 1956, Leon Cooper considered the problem of two electrons interacting in the presence of a quiescent Fermi sea. The background electrons comprising the Fermi sea enter the problem only through their Pauli blocking. Since spin and total momentum are conserved, Cooper first considered a zero momentum singlet,

$$|\Psi\rangle = \sum_k A_k (c^\dagger_{k\uparrow} c^\dagger_{-k\downarrow} - c^\dagger_{k\downarrow} c^\dagger_{-k\uparrow}) |F\rangle$$

(12.10)

where $|F\rangle$ is the filled Fermi sea, $|F\rangle = \prod_{|p|<k_F} c^\dagger_p c^\dagger_{-p} |0\rangle$. Only states with $k > k_F$ contribute to the RHS of Eqn. 12.10, due to Pauli blocking. The real space wavefunction is

$$\Psi(r_1, r_2) = \sum_k A_k e^{i\mathbf{k} \cdot (r_1 - r_2)} \left( |\uparrow_1 \downarrow_2\rangle - |\downarrow_1 \uparrow_2\rangle \right)$$

(12.11)

with $A_k = A_{-k}$ to enforce symmetry of the orbital part. It should be emphasized that this is a two-particle wavefunction, and not an $(N+2)$-particle wavefunction, with $N$ the number of electrons in the Fermi sea. Again, the Fermi sea in this analysis has no dynamics of its own. Its presence is reflected only in the restriction $k > k_F$ for the states which participate in the Cooper pair.

The many-body Hamiltonian is written

$$\hat{H} = \sum_{k, \sigma} \varepsilon_k c^\dagger_{k\sigma} c_{k\sigma} + \frac{1}{2} \sum_{k_1, \sigma_1, k_2, \sigma_2} \sum_{k_3, \sigma_3} \sum_{k_4, \sigma_4} \langle k_1 \sigma_1, k_2 \sigma_2 | v | k_3 \sigma_3, k_4 \sigma_4 \rangle c^\dagger_{k_1 \sigma_1} c^\dagger_{k_2 \sigma_2} c_{k_3 \sigma_3} c_{k_4 \sigma_4}. $$

(12.12)

We treat $|\Psi\rangle$ as a variational state, which means we set

$$\frac{\delta}{\delta A_k} \langle \Psi | \hat{H} | \Psi \rangle = 0,$$

(12.13)

resulting in

$$(E - E_0) A_k = 2\varepsilon_k A_k + \sum_{k'} V_{k,k'} A_{k'},$$

(12.14)

where

$$V_{k,k'} = \langle k\uparrow, -k\downarrow | v | k'\uparrow, -k'\downarrow \rangle = \frac{1}{V} \int d^3r \, v(r) \, e^{i(k-k') \cdot r}.$$

(12.15)
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Here $E_0 = \langle F | \hat{H} | F \rangle$ is the energy of the Fermi sea.

We write $\varepsilon_k = \varepsilon_F + \xi_k$, and we define $E \equiv E_0 + 2\varepsilon_F + W$. Then

$$W A_k = 2\xi_k A_k + \sum_{k'} V_{k,k'} A_{k'} \quad .$$

(12.16)

If $V_{k,k'}$ is rotationally invariant, meaning it is left unchanged by $k \to Rk$ and $k' \to Rk'$ where $R \in O(3)$, then we may write

$$V_{k,k'} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} V_{\ell}(k,k') Y_{\ell,m}(\hat{k}) Y_{\ell,m}^*(\hat{k}') \quad .$$

(12.17)

We assume that $V_{\ell}(k,k')$ is separable, meaning we can write

$$V_{\ell}(k,k') = \frac{1}{V} \lambda_{\ell} \alpha_{\ell}(k) \alpha_{\ell}^*(k') \quad .$$

(12.18)

This simplifies matters and affords us an exact solution, for now we take $A_k = A_{\ell,m}(\hat{k})$ to obtain a solution in the $\ell$ angular momentum channel:

$$W_{\ell} A_k = 2\xi_k A_k + \lambda_{\ell} \alpha_{\ell}(k) \cdot \frac{1}{V} \sum_{k'} \alpha_{\ell}^*(k') A_{k'} \quad ,$$

(12.19)

which may be recast as

$$A_k = \frac{\lambda_{\ell} \alpha_{\ell}(k)}{W_{\ell} - 2\xi_k} \cdot \frac{1}{V} \sum_{k'} \alpha_{\ell}^*(k') A_{k'} \quad .$$

(12.20)

Now multiply by $\alpha_k^*$ and sum over $k$ to obtain

$$\frac{1}{\lambda_{\ell}} = \frac{1}{V} \sum_k \left| \alpha_{\ell}(k) \right|^2 = \Phi(W_{\ell}) \quad .$$

(12.21)

We solve this for $W_{\ell}$.

We may find a graphical solution. Recall that the sum is restricted to $k$ such that $k > k_F$, and that $\xi_k \geq 0$. The denominator on the RHS of Eqn. 12.21 changes sign as a function of $W_{\ell}$ every time $\frac{1}{2} W_{\ell}$ passes through one of the $\xi_k$ values\(^1\). A sketch of the graphical solution is provided in Fig. 12.1. One sees that if $\lambda_{\ell} < 0$, i.e. if the potential is attractive, then a bound state exists. This is true for arbitrarily weak $|\lambda_{\ell}|$, a situation not usually encountered in three-dimensional problems, where there is usually a critical strength of the attractive potential in order to form a bound state\(^2\). This is a density of states effect — by restricting our attention to electrons near the

---

\(^1\)We imagine quantizing in a finite volume, so the allowed $k$ values are discrete.

\(^2\)For example, the $^2$He molecule is unbound, despite the attractive $-1/r^6$ van der Waals attractive tail in the interatomic potential.
Fermi level, where the DOS is roughly constant at \( g(\varepsilon_F) = m^* k_F / \pi^2 \hbar^2 \), rather than near \( k = 0 \), where \( g(\varepsilon) \) vanishes as \( \sqrt{\varepsilon} \), the pairing problem is effectively rendered two-dimensional. We can make further progress by assuming a particular form for \( \alpha_\ell(k) \):

\[
\alpha_\ell(k) = \begin{cases} 
1 & \text{if } 0 < \xi_k < B_\ell \\
0 & \text{otherwise}
\end{cases},
\]

(12.22)

where \( B_\ell \) is an effective bandwidth for the \( \ell \) channel. Then

\[
1 = \frac{1}{2} |\lambda_\ell| \int_0^{B_\ell} d\xi \frac{g(\varepsilon_F + \xi)}{|W_\ell| + 2\xi}.
\]

(12.23)

The factor of \( \frac{1}{2} \) is because it is the DOS per spin here, and not the total DOS. We assume \( g(\varepsilon) \) does not vary significantly in the vicinity of \( \varepsilon = \varepsilon_F \), and pull \( g(\varepsilon_F) \) out from the integrand. Integrating and solving for \( |W_\ell| \),

\[
|W_\ell| = \frac{2B_\ell}{\exp\left[4/|\lambda_\ell| g(\varepsilon_F)\right] - 1}.
\]

(12.24)

In the weak coupling limit, where \( |\lambda_\ell| g(\varepsilon_F) \ll 1 \), we have

\[
|W_\ell| \simeq 2B_\ell \exp\left(-\frac{4}{|\lambda_\ell| g(\varepsilon_F)}\right).
\]

(12.25)

As we shall see when we study BCS theory, the factor in the exponent is twice too large. The coefficient \( 2B_\ell \) will be shown to be the Debye energy of the phonons; we will see that it is only over a narrow range of energies about the Fermi surface that the effective electron-electron interaction is attractive. For strong coupling,

\[
|W_\ell| = \frac{1}{2} |\lambda_\ell| B_\ell g(\varepsilon_F).
\]

(12.26)
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Finite momentum Cooper pair

We can construct a finite momentum Cooper pair as follows:

\[ |\psi_q⟩ = \sum_k A_k (c^\dagger_{k+\frac{1}{2}q} c^\dagger_{-k+\frac{1}{2}q} - c^\dagger_{-k+\frac{1}{2}q} c^\dagger_{k+\frac{1}{2}q}) |F⟩. \] (12.27)

This wavefunction is a momentum eigenstate, with total momentum \( P = \hbar q \). The eigenvalue equation is then

\[ W A_k = (\xi_{k+\frac{1}{2}q} + \xi_{-k+\frac{1}{2}q}) A_k + \sum_{k'} V_{k,k'} A_{k'}. \] (12.28)

Assuming \( \xi_k = \xi_{-k} \),

\[ \xi_{k+\frac{1}{2}q} + \xi_{-k+\frac{1}{2}q} = 2 \xi_k + \frac{1}{4} q^\alpha q^\beta \frac{\partial^2 \xi_k}{\partial k^\alpha \partial k^\beta} + \ldots \] (12.29)

The binding energy is thus reduced by an amount proportional to \( q^2 \); the \( q = 0 \) Cooper pair has the greatest binding energy.3

Mean square radius of the Cooper pair

We have

\[ \langle r^2 \rangle = \frac{\int d^3r |\psi(r)|^2 r^2}{\int d^3r |\psi(r)|^2} = \frac{\int d^3k |\nabla_k A_k|^2}{\int d^3k |A_k|^2} \approx \frac{g(\varepsilon_F) \xi'(k_F)^2 \int d\xi |\frac{\partial A}{\partial \xi}|^2}{g(\varepsilon_F) \int d\xi |A|^2} \] (12.30)

with \( A(\xi) = -C/(|W|+2\xi) \) and thus \( A'(\xi) = 2C/(|W|+2\xi)^2 \), where \( C \) is a constant independent of \( \xi \). Ignoring the upper cutoff on \( \xi \) at \( B_\xi \), we have

\[ \langle r^2 \rangle = 4 \xi'(k_F)^2 \cdot \frac{\int du u^{-4}}{|W|} = \frac{4}{3} (\hbar v_\nu)^2 |W|^{-2}, \] (12.31)

where we have used \( \xi'(k_F) = \hbar v_\nu \). Thus, \( R_{\text{rms}} = 2\hbar v_\nu / \sqrt{3} |W| \). In the weak coupling limit, where \(|W|\) is exponentially small in \( 1/|\lambda| \), the Cooper pair radius is huge. Indeed it is so large that many other Cooper pairs have their centers of mass within the radius of any given pair. This feature is what makes the BCS mean field theory of superconductivity so successful. Recall in our discussion of the Ginzburg criterion in §11.4.5, we found that mean field theory was qualitatively correct down to the Ginzburg reduced temperature \( t_G = (a/R_s)^{2d/(4-d)} \), i.e. \( t_G = (a/R_s)^6 \) for \( d = 3 \). In this expression, \( R_s \) should be the mean Cooper pair size, and \( a \) a microscopic length (i.e. lattice constant). Typically \( R_s/a \sim 10^2 - 10^3 \), so \( t_G \) is very tiny indeed.

3We assume the matrix \( \frac{\partial}{\partial \alpha} \frac{\partial}{\partial \beta} \xi_k \) is positive definite.
12.3 Effective attraction due to phonons

The solution to Cooper’s problem provided the first glimpses into the pairing nature of the superconducting state. But why should $V_{k,k'}$ be attractive? One possible mechanism is an induced attraction due to phonons.

12.3.1 Electron-phonon Hamiltonian

In §5.12 we derived the electron-phonon Hamiltonian,

$$\hat{H}_{\text{el-ph}} = \frac{1}{\sqrt{V}} \sum_{k,k',\sigma,\lambda,G} g_\lambda(k,k') (a_{q\lambda}^\dagger + a_{-q\lambda}) c_{k\sigma}^\dagger c_{k'\sigma} \delta_{k',k+q+G},$$  \hspace{1cm} (12.32)

where $c_{k\sigma}^\dagger$ creates an electron in state $|k\sigma\rangle$ and $a_{q\lambda}^\dagger$ creates a phonon in state $|q\lambda\rangle$, where $\lambda$ is the phonon polarization state. $G$ is a reciprocal lattice vector, and

$$g_\lambda(k,k') = -i \left( \frac{\hbar}{2\Omega} \omega_\lambda(q) \right)^{1/2} \frac{4\pi Z e^2}{(q + G)^2 + \lambda_{\text{TF}}^{-2}} (q + G) \cdot \hat{e}_\lambda(q).$$  \hspace{1cm} (12.33)

is the electron-phonon coupling constant, with $\hat{e}_\lambda(q)$ the phonon polarization vector, $\Omega$ the Wigner-Seitz unit cell volume, and $\omega_\lambda(q)$ the phonon frequency dispersion of the $\lambda$ branch.

Recall that in an isotropic ‘jellium’ solid, the phonon polarization at wavevector $q$ either is parallel to $q$ (longitudinal waves), or perpendicular to $q$ (transverse waves). We then have that only longitudinal waves couple to the electrons. This is because transverse waves do not result in any local accumulation of charge density, and the Coulomb interaction couples electrons to density fluctuations. Restricting our attention to the longitudinal phonon, we found for small $q$ the electron-longitudinal phonon coupling $g_L(k,k+q) \equiv g_q$ satisfies

$$|g_q|^2 = \lambda_{\text{el-ph}} \cdot \frac{\hbar c_L q}{g(\varepsilon_F)},$$  \hspace{1cm} (12.34)

where $g(\varepsilon_F)$ is the electronic density of states, $c_L$ is the longitudinal phonon speed, and where the dimensionless electron-phonon coupling constant is

$$\lambda_{\text{el-ph}} = \frac{Z^2}{2M c_L^2 \Omega g(\varepsilon_F)} = \frac{2Z}{3} \frac{m^*}{M} \left( \frac{\varepsilon_F}{k_B \Theta_s} \right)^2,$$  \hspace{1cm} (12.35)

with $\Theta_s \equiv \hbar c_L k_F / k_B$. 


12.3.2 Effective interaction between electrons

Consider now the problem of two particle scattering $| k \sigma, -k - \sigma \rangle \rightarrow | k' \sigma, -k' - \sigma \rangle$. We assume no phonons are present in the initial state, i.e. we work at $T = 0$. The initial state energy is $E_i = 2\xi_k$ and the final state energy is $E_f = 2\xi_{k'}$. There are two intermediate states:

\begin{align}
|I_1\rangle &= |k' \sigma, -k' - \sigma \rangle \otimes |q \lambda \rangle \\
|I_2\rangle &= |k \sigma, -k' - \sigma \rangle \otimes |+q \lambda \rangle ,
\end{align}

with $k' = k + q$ in each case. The energies of these intermediate states are

\begin{align}
E_1 &= \xi_{-k} + \xi_{k'} + \hbar\omega_{-q\lambda} , \\
E_2 &= \xi_k + \xi_{-k'} + \hbar\omega_{q\lambda} .
\end{align}

The second order matrix element is then

\begin{align}
\langle k' \sigma, -k' - \sigma | \hat{H}_{\text{indirect}} | k \sigma, -k - \sigma \rangle &= \sum_n \langle k' \sigma, -k' - \sigma | \hat{H}_{\text{el-ph}} | n \rangle \langle n | \hat{H}_{\text{el-ph}} | k \sigma, -k - \sigma \rangle \\
& \quad \times \left( \frac{1}{E_i - E_n} + \frac{1}{E_f - E_n} \right) \\
&= |g_{k'k}|^2 \left( \frac{1}{\xi_{k'} - \xi_k - \omega_q + \xi_k - \xi_{k'} - \omega_q} \right) .
\end{align}

Here we have assumed $\xi_k = \xi_{-k}$ and $\omega_q = \omega_{-q}$, and we have chosen $\lambda$ to correspond to the longitudinal acoustic phonon branch. We add this to the Coulomb interaction $\hat{v}(|k - k'|)$ to get the net effective interaction between electrons,

\begin{align}
\langle k' \sigma, -k' - \sigma | \hat{H}_{\text{eff}} | k \sigma, -k - \sigma \rangle &= \hat{v}(|k - k'|) + |g_q|^2 \left( \frac{2\omega_q}{(\xi_k - \xi_{k'})^2 - (\hbar\omega_q)^2} \right) ,
\end{align}

where $k' = k + q$. We see that the effective interaction can be attractive, but only so long as $|\xi_k - \xi_{k'}| < \hbar\omega_q$. 

\footnote{The annihilation operator in the Hamiltonian $\hat{H}_{\text{el-ph}}$ can act on either of the two electrons.}
Another way to evoke this effective attraction is via the jellium model studied in §8.2 and §9.5.6. There we found the effective interaction between unit charges was given by

\[ V_{\text{eff}}(q, \omega) = \frac{4\pi e^2}{q^2 \epsilon(q, \omega)} \]

where

\[ \frac{1}{\epsilon(q, \omega)} \simeq \frac{q^2}{q^2 + q_{\text{TF}}^2} \left\{ 1 + \frac{\omega_q^2}{\omega^2 - \omega_q^2} \right\} , \]

where the first term in the curly brackets is due to Thomas-Fermi screening (§9.5.2) and the second from ionic screening (§9.5.6). Recall that the Thomas-Fermi wavevector is given by

\[ q_{\text{TF}} = \sqrt{\frac{4\pi e^2}{g(\epsilon_F)}} \]

where \( g(\epsilon_F) \) is the electronic density of states at the Fermi level, and that \( \omega_q = \Omega_{p,i} q / \sqrt{q^2 + q_{\text{TF}}^2} \), where \( \Omega_{p,i} = \sqrt{4\pi n_i^0 Z_i e^2 / M_i} \) is the ionic plasma frequency.

### 12.4 Reduced BCS Hamiltonian

The operator which creates a Cooper pair with total momentum \( q \) is \( b_{k,q}^\dagger b_{-k,-q}^\dagger \), where

\[ b_{k,q}^\dagger = c_{k+\frac{1}{2}q}^\dagger c_{-k-\frac{1}{2}q} \]

is a composite operator which creates the state \( |k + \frac{1}{2}q \uparrow, -k - \frac{1}{2}q \downarrow \rangle \). We learned from the solution to the Cooper problem that the \( q = 0 \) pairs have the greatest binding energy. This motivates consideration of the so-called reduced BCS Hamiltonian,

\[ \hat{H}_{\text{red}} = \sum_{k,\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k,k',\sigma\sigma'} V_{k,k'} b_{k,0}^\dagger b_{k',0} \]

The most general form for a momentum-conserving interaction is\(^5\)

\[ \hat{V} = \frac{1}{2V} \sum_{k,p,q,\sigma,\sigma'} \hat{u}_{\sigma\sigma'}(k, p, q) c_{k+q\sigma}^\dagger c_{p-q\sigma'}^\dagger c_{p\sigma'} c_{k\sigma} \]

Taking \( p = -k, \sigma' = -\sigma \), and defining \( k' \equiv k + q \), we have

\[ \hat{V} \to \frac{1}{2V} \sum_{k,k',\sigma} \hat{v}(k, k') c_{k'\sigma}^\dagger c_{-k'-\sigma}^\dagger c_{-k-\sigma} c_{k\sigma} \]

where \( \hat{v}(k, k') = \hat{u}_{\uparrow\downarrow}(k, -k, k' - k) \), which is equivalent to \( \hat{H}_{\text{red}} \).

\(^5\)See the discussion in Appendix I, §12.13.
If $V_{k,k'}$ is attractive, then the ground state will have no pair $(k \uparrow, -k \downarrow)$ occupied by a single electron; the pair states are either empty or doubly occupied. In that case, the reduced BCS Hamiltonian may be written as:

$$H^0_{\text{red}} = \sum_k 2\varepsilon_k b^\dagger_k b_k + \sum_{k,k'} V_{k,k'} b^\dagger_k b_{k'} \quad .$$  

(12.46)

This has the innocent appearance of a noninteracting bosonic Hamiltonian – an exchange of Cooper pairs restores the many-body wavefunction without a sign change because the Cooper pair is a composite object consisting of an even number of fermions. However, this is not quite correct, because the operators $b_{k,0}$ and $b_{k',0}$ do not satisfy canonical bosonic commutation relations. Rather,

$$[b_{k,0}, b^\dagger_{k',0}] = 0$$
$$[b_{k,0}, b^\dagger_{k,0}] = (1 - c^\dagger_{k\uparrow} c_{k\uparrow} - c^\dagger_{-k\downarrow} c_{-k\downarrow}) \delta_{kk'} \quad .$$  

(12.47)

Because of this, $\hat{H}_{\text{red}}^0$ cannot naively be diagonalized. The extra terms inside the round brackets on the RHS arise due to the Pauli blocking effects. Indeed, one has $(b^\dagger_{k,0})^2 = 0$, so $b^\dagger_{k,0}$ is no ordinary boson operator.

Suppose, though, we try a mean field Hartree-Fock approach. We write

$$b_{k,0} = \langle b_{k,0} \rangle + \frac{\delta b_{k,0}}{\langle b_{k,0} \rangle + (b_{k,0} - \langle b_{k,0} \rangle)} \quad .$$  

(12.48)

---

Footnotes:

6 Spin rotation invariance and a singlet Cooper pair requires that $V_{k,k'} = V_{-k,-k'} = V_{-k,k'}$.

7 Recall that the atom $^4$He, which consists of six fermions (two protons, two neutrons, and two electrons), is a boson, while $^3$He, which has only one neutron and thus five fermions, is itself a fermion.
and we neglect terms in $\hat{H}_{\text{red}}$ proportional to $\delta b_{k,0}^{\dagger} \delta b_{k',0}$. We have

$$\hat{H}_{\text{red}} = \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{k,k'} V_{k,k'} \left( \langle b_{k,0}^{\dagger} b_{k',0} \rangle + \langle b_{k,0} b_{k',0}^{\dagger} \rangle \right) + \delta b_{k,0}^{\dagger} \delta b_{k',0}^{\dagger} .$$

(12.49)

Dropping the last term, which is quadratic in fluctuations, we obtain

$$\hat{H}_{\text{MF}}^{\text{red}} = \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{k} \left( \Delta_k c_{k\uparrow}^{\dagger} c_{-k\downarrow}^{\dagger} + \Delta_k^{\ast} c_{-k\downarrow} c_{k\uparrow} \right) - \sum_{k,k'} V_{k,k'} \langle b_{k,0}^{\dagger} \rangle \langle b_{k',0} \rangle ,$$

(12.50)

where

$$\Delta_k = \sum_{k'} V_{k,k'} \langle c_{-k'\downarrow} \rangle \langle c_{k'\uparrow} \rangle , \quad \Delta_k^{\ast} = \sum_{k'} V_{k,k'}^{\ast} \langle c_{k'\uparrow} \rangle \langle c_{-k'\downarrow} \rangle .$$

(12.51)

The first thing to notice about $\hat{H}_{\text{MF}}^{\text{red}}$ is that it does not preserve particle number, i.e. it does not commute with $\hat{N} = \sum_{k,\sigma} c_{k\sigma}^{\dagger} c_{k\sigma}$. Accordingly, we are practically forced to work in the grand canonical ensemble, and we define the grand canonical Hamiltonian $\hat{K} \equiv \hat{H} - \mu \hat{N}$.

### 12.5 Solution of the mean field Hamiltonian

We now subtract $\mu \hat{N}$ from Eqn. 12.50, and define $\hat{K}_{\text{BCS}} \equiv \hat{H}_{\text{red}}^{\text{MF}} - \mu \hat{N}$. Thus,

$$\hat{K}_{\text{BCS}} = \sum_{k} \left( \begin{array}{c} \xi_k \\ \Delta_k \end{array} \right) \left( \begin{array}{c} \Delta_k^{\ast} \\ \xi_k \end{array} \right) + K_0 ,$$

(12.52)

with $\xi_k = \varepsilon_k - \mu$, and where

$$K_0 = \sum_{k} \xi_k - \sum_{k,k'} V_{k,k'} \langle c_{k\uparrow}^{\dagger} c_{-k'\downarrow} \rangle \langle c_{-k'\downarrow} \rangle .$$

(12.53)

is a constant. This problem may be brought to diagonal form via a unitary transformation,

$$\left( \begin{array}{c} c_{k\uparrow}^{\dagger} \\ c_{-k'\downarrow}^{\dagger} \end{array} \right) = U_k \left( \begin{array}{c} \cos \vartheta_k e^{i\phi_k} \\ \sin \vartheta_k e^{-i\phi_k} \end{array} \right) \left( \begin{array}{c} \gamma_{k\uparrow}^{\dagger} \\ \gamma_{-k'\downarrow}^{\dagger} \end{array} \right) .$$

(12.54)
In order for the $\gamma_{k\sigma}$ operators to satisfy fermionic anticommutation relations, the matrix $U_k$ must be unitary. We then have

$$
c_k \sigma = \cos \vartheta_k \gamma_k \sigma - \sigma \sin \vartheta_k e^{i\phi_k} \gamma^\dagger_{-k} \sigma
$$

$$
\gamma_k \sigma = \cos \vartheta_k c_k \sigma + \sigma \sin \vartheta_k e^{i\phi_k} c^\dagger_{-k} \sigma .
$$

(12.55)

**EXERCISE:** Verify that $\{\gamma_{k\sigma}, \gamma^\dagger_{k'\sigma'}\} = \delta_{kk'} \delta_{\sigma\sigma'}$.

We now must compute the transformed Hamiltonian. Dropping the $k$ subscript for notational convenience, we have

$$
\tilde{K} = U^\dagger K U = \begin{pmatrix}
\cos \vartheta & \sin \vartheta e^{i\phi} \\
-\sin \vartheta e^{-i\phi} & \cos \vartheta
\end{pmatrix} \begin{pmatrix}
\xi & \Delta \\
\Delta^* & -\xi
\end{pmatrix} \begin{pmatrix}
\cos \vartheta & -\sin \vartheta e^{i\phi} \\
\sin \vartheta e^{-i\phi} & \cos \vartheta
\end{pmatrix}
$$

(12.56)

$$
= \begin{pmatrix}
(\cos^2 \vartheta - \sin^2 \vartheta) \xi + \sin \vartheta \cos \vartheta (\Delta e^{-i\phi} + \Delta^* e^{i\phi}) & \Delta \cos^2 \vartheta - \Delta^* e^{2i\phi} \sin^2 \vartheta - 2\xi \sin \vartheta \cos \vartheta e^{i\phi} \\
\Delta^* \cos^2 \vartheta - \Delta e^{2i\phi} \sin^2 \vartheta - 2\xi \sin \vartheta \cos \vartheta e^{-i\phi} & (\sin^2 \vartheta - \cos^2 \vartheta) \xi - \sin \vartheta \cos \vartheta (\Delta e^{-i\phi} + \Delta^* e^{i\phi})
\end{pmatrix}.
$$

We now use our freedom to choose $\vartheta$ and $\phi$ to render $\tilde{K}$ diagonal. That is, we demand that

$$
2\xi \sin \vartheta \cos \vartheta = |\Delta| (\cos^2 \vartheta - \sin^2 \vartheta) .
$$

(12.57)

This says $\tan(2\vartheta) = |\Delta|/\xi$, which means

$$
\cos(2\vartheta) = \frac{\xi}{E} , \quad \sin(2\vartheta) = \frac{|\Delta|}{E} , \quad E = \sqrt{\xi^2 + |\Delta|^2} .
$$

(12.58)

The upper left element of $\tilde{K}$ then becomes

$$
(\cos^2 \vartheta - \sin^2 \vartheta) \xi + \sin \vartheta \cos \vartheta (\Delta e^{-i\phi} + \Delta^* e^{i\phi}) = \frac{\xi^2}{E} + \frac{|\Delta|^2}{E} = E ,
$$

(12.59)

and thus $\tilde{K} = \begin{pmatrix} E & 0 \\ 0 & -E \end{pmatrix}$. This unitary transformation, which mixes particle and hole states, is called a Bogoliubov transformation, because it was first discovered by Valatin.

Restoring the $k$ subscript, we have $\vartheta_k = \arg(\Delta_k)$, and $\tan(2\vartheta_k) = |\Delta_k|/\xi_k$, which means

$$
\cos(2\vartheta_k) = \frac{\xi_k}{E_k} , \quad \sin(2\vartheta_k) = \frac{|\Delta_k|}{E_k} , \quad E_k = \sqrt{\xi_k^2 + |\Delta_k|^2} .
$$

(12.60)

Assuming that $\Delta_k$ is not strongly momentum-dependent, we see that the dispersion $E_k$ of the excitations has a nonzero minimum at $\xi_k = 0$, i.e. at $k = k_F$. This minimum value of $E_k$ is called the superconducting energy gap.

---

8The most general $2 \times 2$ unitary matrix is of the above form, but with each row multiplied by an independent phase. These phases may be absorbed into the definitions of the fermion operators themselves. After absorbing these harmless phases, we have written the most general unitary transformation.
We may further write
\[
\cos \vartheta_k = \sqrt{\frac{E_k + \xi_k}{2E_k}} , \quad \sin \vartheta_k = \sqrt{\frac{E_k - \xi_k}{2E_k}} .
\] (12.61)

The grand canonical BCS Hamiltonian then becomes
\[
\hat{K}_{BCS} = \sum_{k,\sigma} E_k \gamma_k \gamma_{k\sigma} + \sum_{k} (\xi_k - E_k) - \sum_{k,k'} V_{k,k'} \langle c_{k\uparrow} \gamma_{k\sigma}^\dagger \gamma_{-k\downarrow} \rangle \langle c_{-k\downarrow} \gamma_{k\sigma}^\dagger \gamma_{k\uparrow} \rangle .
\] (12.62)

Finally, what of the ground state wavefunction itself? We must have \( \gamma_{k\sigma}^\dagger G \rangle = 0 \). This leads to
\[
|G\rangle = \prod_k \left( \cos \vartheta_k - \sin \vartheta_k \ e^{i\phi_k} \ c_{k\downarrow}^\dagger c_{-k\uparrow}^\dagger \right) |0\rangle .
\] (12.63)

Note that \( \langle G|G\rangle = 1 \). J. R. Schrieffer conceived of this wavefunction during a subway ride in New York City sometime during the winter of 1957. At the time he was a graduate student at the University of Illinois.

### Sanity check

It is good to make contact with something familiar, such as the case \( \Delta_k = 0 \). Note that \( \xi_k < 0 \) for \( k < k_F \) and \( \xi_k > 0 \) for \( k > k_F \). We now have
\[
\cos \vartheta_k = \Theta(k - k_F) , \quad \sin \vartheta_k = -\Theta(k_F - k) .
\] (12.64)

Note that the wavefunction \( |G\rangle \) in Eqn. 12.63 correctly describes a filled Fermi sphere out to \( k = k_F \). Furthermore, the constant on the RHS of Eqn. 12.62 is \( 2 \sum_{k < k_F} \xi_k \), which is the Landau free energy of the filled Fermi sphere. What of the excitations? We are free to take \( \phi_k = 0 \). Then
\[
k < k_F : \gamma_{k\sigma}^\dagger = \sigma \ c_{-k\downarrow} \\
k > k_F : \gamma_{k\sigma}^\dagger = c_{k\sigma}^\dagger .
\] (12.65)

Thus, the elementary excitations are holes below \( k_F \) and electrons above \( k_F \). All we have done, then, is to effect a (unitary) particle-hole transformation on those states lying within the Fermi sea.

### 12.6 Self-consistency

We now demand that the following two conditions hold:
\[
N = \sum_{k\sigma} \langle c_{k\sigma}^\dagger c_{k\sigma} \rangle \\
\Delta_k = \sum_{k'} V_{k,k'} \langle c_{-k'\downarrow} c_{k'\uparrow} \rangle .
\] (12.66)
the second of which is from Eqn. 12.51. Thus, we need

\[
\langle c_{k}^\dagger c_{k} \rangle = \langle (\cos \vartheta_{k} \gamma_{k}^\dagger - \sigma \sin \vartheta_{k} e^{-i\phi_{k}} \gamma_{-k}^\dagger) (\cos \vartheta_{k} \gamma_{k} - \sigma \sin \vartheta_{k} e^{i\phi_{k}} \gamma_{-k}^\dagger) \rangle
\]

\[
= \cos^{2} \vartheta_{k} f_{k} + \sin^{2} \vartheta_{k} \left(1 - f_{k}\right) = \frac{1}{2} - \frac{\xi_{k}}{2E_{k}} \tanh \left(\frac{1}{2} \beta E_{k}\right)
\]

where

\[
f_{k} = \langle \gamma_{k}^\dagger \gamma_{k} \rangle = \frac{1}{e^{\beta E_{k}} + 1} = \frac{1}{2} - \frac{1}{2} \tanh \left(\frac{1}{2} \beta E_{k}\right)
\]

is the Fermi function, with \( \beta = 1/k_{B}T \). We also have

\[
\langle c_{-k}^\dagger c_{k} \rangle = \langle (\cos \vartheta_{k} \gamma_{-k} - \sigma \sin \vartheta_{k} e^{i\phi_{k}} \gamma_{k}^\dagger) (\cos \vartheta_{k} \gamma_{k} - \sigma \sin \vartheta_{k} e^{-i\phi_{k}} \gamma_{-k}^\dagger) \rangle
\]

\[
= \sigma \sin \vartheta_{k} \cos \vartheta_{k} e^{i\phi_{k}} \left(2f_{k} - 1\right) = -\frac{\sigma \Delta_{k}}{2E_{k}} \tanh \left(\frac{1}{2} \beta E_{k}\right)
\]

Let’s evaluate at \( T = 0 \):

\[
N = \sum_{k} \left(1 - \frac{\xi_{k}}{E_{k}}\right)
\]

\[
\Delta_{k} = -\sum_{k'} V_{k,k'} \frac{\Delta_{k'}}{2E_{k'}}
\]

The second of these is known as the BCS gap equation. Note that \( \Delta_{k} = 0 \) is always a solution of the gap equation.

To proceed further, we need a model for \( V_{k,k'} \). We shall assume

\[
V_{k,k'} = \begin{cases} 
-v/V & \text{if } |\xi_{k}| < \hbar \omega_{D} \text{ and } |\xi_{k'}| < \hbar \omega_{D} \\
0 & \text{otherwise}
\end{cases}
\]

Here \( v > 0 \), so the interaction is attractive, but only when \( \xi_{k} \) and \( \xi_{k'} \) are within an energy \( \hbar \omega_{D} \) of zero. For phonon-mediated superconductivity, \( \omega_{D} \) is the Debye frequency, which is the phonon bandwidth.

### 12.6.1 Solution at zero temperature

We first solve the second of Eqns. 12.70, by assuming

\[
\Delta_{k} = \begin{cases} 
\Delta e^{i\phi} & \text{if } |\xi_{k}| < \hbar \omega_{D} \\
0 & \text{otherwise}
\end{cases}
\]
with \( \Delta \) real. We then have

\[
\Delta = +v \int \frac{d^3 k}{2\pi^3} \frac{\Delta}{2E_k} \Theta(\hbar \omega_D - |\xi_k|) \\
= \frac{1}{2} v g(\varepsilon_F) \int d\xi \frac{\Delta}{\sqrt{\xi^2 + \Delta^2}}.
\]

(12.73)

Cancelling out the common factors of \( \Delta \) on each side, we obtain

\[
1 = \frac{1}{2} v g(\varepsilon_F) \int_0^{\hbar \omega_D/\Delta} ds \ (1 + s^2)^{-1/2} = \frac{1}{2} v g(\varepsilon_F) \sinh^{-1}\left(\frac{\hbar \omega_D}{\Delta}\right).
\]

(12.74)

Thus, writing \( \Delta_0 \equiv \Delta(0) \) for the zero temperature gap,

\[
\Delta_0 = \frac{\hbar \omega_D}{\sinh\left(\frac{2}{g(\varepsilon_F)} v\right)} \approx 2 \hbar \omega_D \exp\left(-\frac{2}{g(\varepsilon_F)} v\right),
\]

(12.75)

where \( g(\varepsilon_F) \) is the total electronic DOS (for both spin species) at the Fermi level. Notice that, as promised, the argument of the exponent is one half as large as what we found in our solution of the Cooper problem, in Eqn. 12.25.

### 12.6.2 Condensation energy

We now evaluate the zero temperature expectation of \( \hat{K}_{\text{BCS}} \) from Eqn. 12.62. To get the correct answer, it is essential that we retain the term corresponding to the constant energy shift in the mean field Hamiltonian, \textit{i.e.} the last term on the RHS of Eqn. 12.62. Invoking the gap equation

\[
\Delta_k = \sum_{k'} V_{k,k'} \langle c_{-k\downarrow} c_{k'\uparrow} \rangle,
\]

we have

\[
\langle G | \hat{K}_{\text{BCS}} | G \rangle = \sum_k \left( \xi_k - E_k + \frac{|\Delta_k|^2}{2E_k} \right).
\]

(12.76)

From this we subtract the ground state energy of the metallic phase, \textit{i.e.} when \( \Delta_k = 0 \), which is

\[
2 \sum_k \xi_k \Theta(k_F - k).
\]

The difference is the condensation energy. Adopting the model interaction potential in Eqn. 12.71, we have

\[
E_s - E_n = \sum_k \left( \xi_k - E_k + \frac{|\Delta_k|^2}{2E_k} - 2\xi_k \Theta(k_F - k) \right)
\]

\[
= 2 \sum_k \left( \xi_k - E_k \right) \Theta(\xi_k) \Theta(\hbar \omega_D - \xi_k) + \sum_k \frac{\Delta_0^2}{2E_k} \Theta(\hbar \omega_D - |\xi_k|).
\]

(12.77)

---

\(^9\)We assume the density of states \( g(\varepsilon) \) is slowly varying in the vicinity of the chemical potential and approximate it at \( g(\varepsilon_F) \). In fact, we should more properly call it \( g(\mu) \), but as a practical matter \( \mu \approx \varepsilon_F \) at temperatures low enough to be in the superconducting phase. Note that \( g(\varepsilon_F) \) is the total DOS for both spin species. In the literature, one often encounters the expression \( N(0) \), which is the DOS per spin at the Fermi level, \textit{i.e.} \( N(0) = \frac{1}{2} g(\varepsilon_F) \).
where we have linearized about $k = k_F$. We then have

$$E_u - E_n = V g(\varepsilon_F) \Delta_0^2 \int_0^{\hbar \omega_D/\Delta_0} ds \left( s - \sqrt{s^2 + 1} + \frac{1}{2\sqrt{s^2 + 1}} \right) = \frac{1}{2} V g(\varepsilon_F) \Delta_0^2 \left( x^2 - x \sqrt{1 + x^2} \right) \approx -\frac{1}{4} V g(\varepsilon_F) \Delta_0^2 ,$$

where $x \equiv \hbar \omega_D/\Delta_0$. The condensation energy density is therefore $-\frac{1}{4} V g(\varepsilon_F) \Delta_0^2$, which may be equated with $-H_c^2/8\pi$, where $H_c$ is the thermodynamic critical field. Thus, we find

$$H_c(0) = \sqrt{2\pi g(\varepsilon_F) \Delta_0} ,$$

which relates the thermodynamic critical field to the superconducting gap, at $T = 0$. 

Figure 12.4: Top panel: BCS coherence factors $\sin^2 \vartheta_k$ (blue) and $\cos^2 \vartheta_k$ (red). Bottom panel: the functions $\xi_k$ (black) and $E_k$ (magenta). The minimum value of the magenta curve is the superconducting gap $\Delta_0$. 

CHAPTER 12. BCS THEORY OF SUPERCONDUCTIVITY
12.7 Coherence factors and quasiparticle energies

When $\Delta_k = 0$, we have $E_k = |\xi_k|$. When $\hbar \omega_D \ll \varepsilon_F$, there is a very narrow window surrounding $k = k_F$ where $E_k$ departs from $|\xi_k|$, as shown in the bottom panel of Fig. 12.4. Note the energy gap in the quasiparticle dispersion, where the minimum excitation energy is given by

$$\min_k E_k = E_{k_F} = \Delta_0.$$  (12.80)

In the top panel of Fig. 12.4 we plot the coherence factors $\sin^2 \vartheta_k$ and $\cos^2 \vartheta_k$. Note that $\sin^2 \vartheta_k$ approaches unity for $k < k_F$ and $\cos^2 \vartheta_k$ approaches unity for $k > k_F$, aside for the narrow window of width $\delta k \simeq \Delta_0 / \hbar v_F$. Recall that

$$\gamma^\dagger_{k\sigma} = \cos \vartheta_k c^\dagger_{k\sigma} + \sigma \sin \vartheta_k e^{-i\varphi_k} c_{-k-\sigma}.$$  (12.81)

Thus we see that the quasiparticle creation operator $\gamma^\dagger_{k\sigma}$ creates an electron in the state $|k\sigma\rangle$ when $\cos^2 \vartheta_k \simeq 1$, and a hole in the state $|-k-\sigma\rangle$ when $\sin^2 \vartheta_k \simeq 1$. In the aforementioned narrow window $|k - k_F| \lesssim \Delta_0 / \hbar v_F$, the quasiparticle creates a linear combination of electron and hole states. Typically $\Delta_0 \sim 10^{-4} \varepsilon_F$, since metallic Fermi energies are on the order of tens of thousands of Kelvins, while $\Delta_0$ is on the order of Kelvins or tens of Kelvins. Thus, $\delta k \lesssim 10^{-3} k_F$.

The difference between the superconducting state and the metallic state all takes place within an onion skin at the Fermi surface!

Note that for the model interaction $V_{k,k'}$ of Eqn. 12.71, the solution $\Delta_k$ in Eqn. 12.72 is actually discontinuous when $\xi_k = \pm \hbar \omega_D$, i.e. when $k = k^* \equiv k_F \pm \omega_D / v_F$. Therefore, the energy dispersion $E_k$ is also discontinuous along these surfaces. However, the magnitude of the discontinuity is

$$\delta E = \sqrt{(\hbar \omega_D)^2 + \Delta_0^2} - \hbar \omega_D \approx \frac{\Delta_0^2}{2 \hbar \omega_D}.$$  (12.82)

Therefore $\delta E / E_{k_F} \approx \Delta_0^2 / 2(\hbar \omega_D)^2 \propto \exp(-4/g(\varepsilon_F) v)$, which is very tiny in weak coupling, where $g(\varepsilon_F) v \ll 1$. Note that the ground state is largely unaffected for electronic states in the vicinity of this (unphysical) energy discontinuity. The coherence factors are distinguished from those of a Fermi liquid only in regions where $\langle c^\dagger_{k\uparrow} c_{-k\downarrow}\rangle$ is appreciable, which requires $\xi_k$ to be on the order of $\Delta_k$. This only happens when $|k - k_F| \lesssim \Delta_0 / \hbar v_F$, as discussed in the previous paragraph. In a more physical model, the interaction $V_{k,k'}$ and the solution $\Delta_k$ would not be discontinuous functions of $k$.

---

10Here we assume, without loss of generality, that $\Delta$ is real.
12.8 Number and Phase

The BCS ground state wavefunction $|G\rangle$ was given in Eqn. 12.63. Consider the state

$$|G(\alpha)\rangle = \prod_k (\cos \vartheta_k - e^{i\alpha} e^{i\phi_k} \sin \vartheta_k c_{k\uparrow} c_{k\downarrow}^\dagger) |0\rangle.$$  

(12.83)

This is the ground state when the gap function $\Delta_k$ is multiplied by the uniform phase factor $e^{i\alpha}$. We shall here abbreviate $|\alpha\rangle \equiv |G(\alpha)\rangle$.

Now consider the action of the number operator on $|\alpha\rangle$:

$$\hat{N} |\alpha\rangle = \sum_k \left( c_{k\uparrow} c_{k\uparrow}^\dagger + c_{k\downarrow}^\dagger c_{k\downarrow}\right) |\alpha\rangle$$

(12.84)

$$= -2 \sum_k e^{i\alpha} e^{i\phi_k} \sin \vartheta_k c_{k\uparrow} c_{k\uparrow}^\dagger \prod_{k' \neq k} \left( \cos \vartheta_{k'} - e^{i\alpha} e^{i\phi_{k'}} \sin \vartheta_{k'} c_{k'\uparrow} c_{k'\downarrow}^\dagger \right) |0\rangle$$

$$= \frac{2}{i} \frac{\partial}{\partial \alpha} |\alpha\rangle .$$

If we define the number of Cooper pairs as $\hat{M} = \frac{1}{2} \hat{N}$, then we may identify $\hat{M} = \frac{1}{i} \frac{\partial}{\partial \alpha}$. Furthermore, we may project $|G\rangle$ onto a state of definite particle number by defining

$$|M\rangle = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\alpha e^{-iM\alpha} |\alpha\rangle.$$  

(12.85)

The state $|M\rangle$ has $N = 2M$ particles, i.e. $M$ Cooper pairs. One can easily compute the number fluctuations in the state $|G(\alpha)\rangle$:

$$\frac{\langle \alpha | \hat{N}^2 | \alpha \rangle - \langle \alpha | \hat{N} | \alpha \rangle^2}{\langle \alpha | \hat{N} | \alpha \rangle} = 2 \int d^3k \sin^2 \vartheta_k \cos^2 \vartheta_k .$$

(12.86)

Thus, $(\Delta N)_{\text{RMS}} \propto \sqrt{\langle N \rangle}$. Note that $(\Delta N)_{\text{RMS}}$ vanishes in the Fermi liquid state, where $\sin \vartheta_k \cos \vartheta_k = 0$.

12.9 Finite temperature

The gap equation at finite temperature takes the form

$$\Delta_k = -\sum_{k'} V_{k,k'} \frac{\Delta_{k'}}{2E_{k'}} \tanh \left( \frac{E_{k'}}{2k_B T} \right).$$  

(12.87)
It is easy to see that we have no solutions other than the trivial one $\Delta_k = 0$ in the $T \to \infty$ limit, for the gap equation then becomes $\sum_{k'} V_{k,k'} \Delta_{k'} = -4k_B T \Delta_k$, and if the eigenspectrum of $V_{k,k'}$ is bounded, there is no solution for $k_B T$ greater than the largest eigenvalue of $-V_{k,k'}$.

To find the critical temperature where the gap collapses, again we assume the forms in Eqns. 12.71 and 12.72, in which case we have

$$1 = \frac{1}{2} g(\varepsilon_F) v \int_0^{\hbar \omega_D} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2}} \tanh\left(\frac{\sqrt{\xi^2 + \Delta^2}}{2k_B T}\right).$$

(12.88)

It is clear that $\Delta(T)$ is a decreasing function of temperature, which vanishes at $T = T_c$, where $T_c$ is determined by the equation

$$\int_0^{\Lambda/2} ds s^{-1} \tanh(s) = \frac{2}{g(\varepsilon_F) v},$$

(12.89)

where $\Lambda = \hbar \omega_D / k_B T_c$. One finds, for large $\Lambda$,

$$I(\Lambda) = \int_0^{\Lambda/2} ds s^{-1} \tanh(s) = \ln \left(\frac{1}{2} \Lambda\right) \tanh\left(\frac{1}{2} \Lambda\right) - \int_0^{\Lambda/2} ds \frac{\ln s}{\cosh^2 s}$$

$$= \ln \Lambda + \ln \left(2 e^{C}/\pi\right) + \mathcal{O}(e^{-\Lambda/2}),$$

(12.90)

where $C = 0.57721566 \ldots$ is the Euler-Mascheroni constant. One has $2 e^{C}/\pi = 1.134$, so

$$k_B T_c = 1.134 \hbar \omega_D e^{-2/g(\varepsilon_F) v}.$$  

(12.91)

Comparing with Eqn. 12.75, we obtain the famous result

$$2\Delta(0) = 2\pi e^{-C} k_B T_c \simeq 3.52 k_B T_c.$$  

(12.92)

As we shall derive presently, just below the critical temperature, one has

$$\Delta(T) = 1.734 \Delta(0) \left(1 - \frac{T}{T_c}\right)^{1/2} \simeq 3.06 k_B T_c \left(1 - \frac{T}{T_c}\right)^{1/2}.$$  

(12.93)

### 12.9.1 Isotope effect

The prefactor in Eqn. 12.91 is proportional to the Debye energy $\hbar \omega_D$. Thus,

$$\ln T_c = \ln \omega_D - \frac{2}{g(\varepsilon_F) v} + \text{const.}.$$  

(12.94)
If we imagine varying only the mass of the ions, via isotopic substitution, then \( g(\varepsilon_F) \) and \( v \) do not change, and we have

\[
\delta \ln T_c = \delta \ln \omega_D = -\frac{1}{2} \delta \ln M ,
\]

where \( M \) is the ion mass. Thus, isotopically increasing the ion mass leads to a concomitant reduction in \( T_c \) according to BCS theory. This is fairly well confirmed in experiments on low \( T_c \) materials.

### 12.9.2 Landau free energy of a superconductor

Quantum statistical mechanics of noninteracting fermions applied to \( \hat{K}_{\text{BCS}} \) in Eqn. 12.62 yields the Landau free energy

\[
\Omega_s = -2k_B T \sum_k \ln \left( 1 + e^{-E_k/k_B T} \right) + \sum_k \left\{ \xi_k - E_k + \frac{|\Delta_k|^2}{2E_k} \tanh \left( \frac{E_k}{2k_B T} \right) \right\} .
\]

The corresponding result for the normal state \( (\Delta_k = 0) \) is

\[
\Omega_n = -2k_B T \sum_k \ln \left( 1 + e^{-|\xi_k|/k_B T} \right) + \sum_k \left( \xi_k - |\xi_k| \right) .
\]
Thus, the difference is

\[ \Omega_s - \Omega_n = -2k_B T \sum_k \ln \left( \frac{1 + e^{-E_k/k_B T}}{1 - e^{-|\xi_k|/k_B T}} \right) + \sum_k \left\{ |\xi_k| - E_k + \frac{1}{2} \frac{\Delta_k^2}{E_k} \tanh \left( \frac{E_k}{2k_B T} \right) \right\} . \quad (12.98) \]

We now invoke the model interaction in Eqn. 12.71. Recall that the solution to the gap equation is of the form \( \Delta_k(T) = \Delta(T) \Theta(h \omega_D - |\xi_k|) \). We then have

\[ \frac{\Omega_s - \Omega_n}{V} = \frac{\Delta^2}{\nu} - \frac{1}{2} g(\varepsilon_F) \Delta^2 \left\{ \frac{\hbar \omega_D}{\Delta} \sqrt{1 + \left( \frac{\hbar \omega_D}{\Delta} \right)^2} - \left( \frac{\hbar \omega_D}{\Delta} \right)^2 + \sinh^{-1} \left( \frac{\hbar \omega_D}{\Delta} \right) \right\} \]

\[ - 2 g(\varepsilon_F) k_B T \int_0^\infty ds \ln \left( 1 + e^{-\sqrt{1+s^2} \Delta/k_B T} \right) + \frac{1}{6} \pi^2 g(\varepsilon_F) (k_B T)^2 . \]

(12.99)

We will now expand this result in the vicinity of \( T = 0 \) and \( T = T_c \). In the weak coupling limit, throughout this entire region we have \( \Delta \ll \hbar \omega_D \), so we proceed to expand in the small ratio, writing

\[ \frac{\Omega_s - \Omega_n}{V} = -\frac{1}{2} g(\varepsilon_F) \Delta^2 \left\{ 1 + 2 \ln \left( \frac{\Delta_0}{\Delta} \right) - \left( \frac{\Delta}{2\hbar \omega_D} \right)^2 + O(\Delta^4) \right\} \]

\[ - 2 g(\varepsilon_F) k_B T \int_0^\infty ds \ln \left( 1 + e^{-\sqrt{1+s^2} \Delta/k_B T} \right) + \frac{1}{6} \pi^2 g(\varepsilon_F) (k_B T)^2 . \]

(12.100)

where \( \Delta_0 = \Delta(0) = \pi e^{-C} k_B T_c \). The asymptotic analysis of this expression in the limits \( T \to 0^+ \) and \( T \to T_c^- \) is discussed in the appendix §12.14.

\[ T \to 0^+ \]

In the limit \( T \to 0 \), we find

\[ \frac{\Omega_s - \Omega_n}{V} = -\frac{1}{2} g(\varepsilon_F) \Delta^2 \left\{ 1 + 2 \ln \left( \frac{\Delta_0}{\Delta} \right) + O(\Delta^2) \right\} \]

\[ - g(\varepsilon_F) \sqrt{2 \pi (k_B T)^3} e^{-\Delta/k_B T} + \frac{1}{6} \pi^2 g(\varepsilon_F) (k_B T)^2 . \]

(12.101)

Differentiating the above expression with respect to \( \Delta \), we obtain a self-consistent equation for the gap \( \Delta(T) \) at low temperatures:

\[ \ln \left( \frac{\Delta}{\Delta_0} \right) = -\sqrt{2 \pi k_B T} \Delta - \Delta/k_B T \left( k_B T \right) + \ldots \)

(12.102)
Thus,
\[ \Delta(T) = \Delta_0 - \sqrt{2\pi \Delta_0 k_B T} e^{-\Delta_0/k_B T} + \ldots \] (12.103)

Substituting this expression into Eqn. 12.101, we find
\[ \frac{\Omega_s - \Omega_n}{V} = -\frac{1}{4} g(\varepsilon_F) \Delta_0^2 - g(\varepsilon_F) \sqrt{2\pi \Delta_0 (k_B T)^3} e^{-\Delta_0/k_B T} + \frac{1}{6} \pi^2 g(\varepsilon_F) (k_B T)^2 . \] (12.104)

Equating this with the condensation energy density, \(-H_c^2(T)/8\pi\), and invoking our previous result, \(\Delta_0 = \pi e^{-C} k_B T_c\), we find
\[ H_c(T) = H_c(0) \left\{ 1 - \frac{1}{2} e^{2C} \left( \frac{T}{T_c} \right)^2 \right\} , \] (12.105)

where \(H_c(0) = \sqrt{2\pi g(\varepsilon_F) \Delta_0}\).

\[ T \rightarrow T_c^- \]

In this limit, one finds
\[ \frac{\Omega_s - \Omega_n}{V} = \frac{1}{2} g(\varepsilon_F) \ln \left( \frac{T}{T_c} \right) \Delta^2 + \frac{7}{32} \zeta(3) \frac{g(\varepsilon_F)}{(k_B T)^2} \Delta^4 + O(\Delta^6) . \] (12.106)

This is of the standard Landau form,
\[ \frac{\Omega_s - \Omega_n}{V} = \tilde{a}(T) \Delta^2 + \frac{1}{2} \tilde{b}(T) \Delta^4 , \] (12.107)

with coefficients
\[ \tilde{a}(T) = \frac{1}{2} g(\varepsilon_F) \left( \frac{T}{T_c} - 1 \right) , \quad \tilde{b} = \frac{7}{16} \zeta(3) \frac{g(\varepsilon_F)}{(k_B T)^2} , \] (12.108)

working here to lowest nontrivial order in \(T - T_c\). The head capacity jump, according to Eqn. 1.44, is
\[ c_s(T^-) - c_n(T_c^+) = T_c \left[ \tilde{a}'(T_c) \right]^2 = \frac{4\pi^2}{7 \zeta(3)} g(\varepsilon_F) k_B T_c \] (12.109)

The normal state heat capacity at \(T = T_c\) is \(c_n = \frac{1}{3} \pi^2 g(\varepsilon_F) k_B^2 T_c\), hence
\[ \frac{c_s(T^-)}{c_n(T_c^+)} = \frac{12}{7 \zeta(3)} = 1.43 \] (12.110)

This universal ratio is closely reproduced in many experiments; see, for example, Fig. 12.6.
Figure 12.6: Heat capacity in aluminum at low temperatures, from N. K. Phillips, Phys. Rev. 114, 3 (1959). The zero field superconducting transition occurs at $T_c = 1.163$ K. Comparison with normal state $C$ below $T_c$ is made possible by imposing a magnetic field $H > H_c$. This destroys the superconducting state, but has little effect on the metal. A jump $\Delta C$ is observed at $T_c$, quantitatively in agreement BCS theory.

The order parameter is given by

$$\Delta^2(T) = -\frac{\tilde{a}(T)}{\tilde{b}(T)} = \frac{8\pi^2(k_B T_c)^2}{7\zeta(3)} \left(1 - \frac{T}{T_c}\right) = \frac{8e^{2C}}{7\zeta(3)} \left(1 - \frac{T}{T_c}\right) \Delta^2(0) ,$$

(12.111)

where we have used $\Delta(0) = \pi e^{-C} k_B T_c$. Thus,

$$\frac{\Delta(T)}{\Delta(0)} \approx 1.734$$

$$\left(\frac{8e^{2C}}{7\zeta(3)}\right)^{1/2} \left(1 - \frac{T}{T_c}\right)^{1/2} .$$

(12.112)

The thermodynamic critical field just below $T_c$ is obtained by equating the energies $-\tilde{a}^2/2\tilde{b}$ and $-H_c^2/8\pi$. Therefore

$$\frac{H_c(T)}{H_c(0)} = \left(\frac{8e^{2C}}{7\zeta(3)}\right)^{1/2} \left(1 - \frac{T}{T_c}\right) \simeq 1.734 \left(1 - \frac{T}{T_c}\right) .$$

(12.113)
12.10 Paramagnetic Susceptibility

Suppose we add a weak magnetic field, the effect of which is described by the perturbation Hamiltonian

\[
\hat{H}_1 = -\mu_B H \sum_{k,\sigma} \sigma c_{k\sigma}^\dagger c_{k\sigma} = -\mu_B H \sum_{k,\sigma} \sigma \gamma_{k\sigma}^\dagger \gamma_{k\sigma}.
\]  

(12.114)

The shift in the Landau free energy due to the field is then

\[
\Delta \Omega_s(T, V, \mu, H) = \Omega_s(T, V, \mu, H) - \Omega_s(T, V, \mu, 0).
\]

We have

\[
\Delta \Omega_s(T, V, \mu, H) = -k_B T \sum_{k,\sigma} \ln \left( \frac{1 + e^{-\beta E_k + \sigma \mu B H}}{1 + e^{-\beta E_k}} \right)
\]

\[
= -\beta (\mu_B H)^2 \sum_{k} \frac{e^{\beta E_k}}{(e^{\beta E_k} + 1)^2} + \mathcal{O}(H^4).
\]

(12.115)

The magnetic susceptibility is then

\[
\chi_s = -\frac{1}{V} \frac{\partial^2 \Delta \Omega_s}{\partial H^2} = g(\varepsilon_F) \mu_B^2 \mathcal{Y}(T),
\]

(12.116)

where

\[
\mathcal{Y}(T) = 2 \int_0^\infty d\xi \left( -\frac{\partial f}{\partial E} \right) = \frac{1}{2} \beta \int_0^\infty d\xi \text{sech}^2 \left( \frac{1}{2} \beta \sqrt{\xi^2 + \Delta^2} \right)
\]

(12.117)

is the Yoshida function. Note that \(\mathcal{Y}(T_c) = \int_0^\infty du \text{sech}^2 u = 1\), and \(\mathcal{Y}(T \to 0) \simeq (2\pi \beta \Delta)^{1/2} \exp(-\beta \Delta)\), which is exponentially suppressed. Since \(\chi_n = g(\varepsilon_F) \mu_B^2\) is the normal state Pauli susceptibility, we have that the ratio of superconducting to normal state susceptibilities is \(\chi_s(T)/\chi_n(T) = \mathcal{Y}(T)\). This vanishes exponentially as \(T \to 0\) because it takes a finite energy \(\Delta\) to create a Bogoliubov quasiparticle out of the spin singlet BCS ground state.

In metals, the nuclear spins experience a shift in their resonance energy in the presence of an external magnetic field, due to their coupling to conduction electrons via the hyperfine interaction. This is called the Knight shift, after Walter Knight, who first discovered this phenomenon at Berkeley in 1949. The magnetic field polarizes the metallic conduction electrons, which in turn impose an extra effective field, through the hyperfine coupling, on the nuclei. In superconductors, the electrons remain unpolarized in a weak magnetic field owing to the superconducting gap. Thus there is no Knight shift.

As we have seen from the Ginzburg-Landau theory, when the field is sufficiently strong, superconductivity is destroyed (type I), or there is a mixed phase at intermediate fields where magnetic flux penetrates the superconductor in the form of vortex lines. Our analysis here is valid only for weak fields.
12.11 Finite Momentum Condensate

The BCS reduced Hamiltonian of Eqn. 12.43 involved interactions between \( q = 0 \) Cooper pairs only. In fact, we could just as well have taken

\[
\hat{H}_{\text{red}} = \sum_{k,\sigma} \varepsilon_k c_k^{\dagger} c_k + \sum_{k,k',p} V_{k,k'} b_{k,p}^{\dagger} b_{k',p} .
\]

(12.118)

where \( b_{k,p} = c_{k+\frac{1}{2}p}^{\dagger} c_{-k+\frac{1}{2}p} \), provided the mean field was \( \langle b_{k,p} \rangle = \Delta_k \delta_{p,0} \). What happens, though, if we take

\[
\langle b_{k,p} \rangle = \langle c_{-k+\frac{1}{2}q} c_{k+\frac{1}{2}q} \rangle \delta_{p,q} ,
\]

(12.119)
corresponding to a finite momentum condensate? We then obtain

\[
\hat{K}_{\text{BCS}} = \sum_k \left( c_{k+\frac{1}{2}q}^{\dagger} c_{-k+\frac{1}{2}q} \right) \left( \begin{array}{cc} \omega_{k,q} + \nu_{k,q} & \Delta_{k,q} \\ \Delta_{k,q}^* & -\omega_{k,q} + \nu_{k,q} \end{array} \right) \left( \begin{array}{c} c_{k+\frac{1}{2}q} \\ c_{-k+\frac{1}{2}q} \end{array} \right) + \sum_k \left( \xi_k - \Delta_{k,q} \langle b_{k,q} \rangle \right)
\]

(12.120)

where

\[
\begin{align*}
\omega_{k,q} &= \frac{1}{2} \left( \xi_{k+\frac{1}{2}q} + \xi_{-k+\frac{1}{2}q} \right) \\
\nu_{k,q} &= \frac{1}{2} \left( \xi_{k+\frac{1}{2}q} - \xi_{-k+\frac{1}{2}q} \right) \\
\xi_{k+\frac{1}{2}q} &= \omega_{k,q} + \nu_{k,q} \\
\xi_{-k+\frac{1}{2}q} &= \omega_{k,q} - \nu_{k,q}
\end{align*}
\]

(12.121-12.122)

Note that \( \omega_{k,q} \) is even under reversal of either \( k \) or \( q \), while \( \nu_{k,q} \) is odd under reversal of either \( k \) or \( q \). That is,

\[
\omega_{k,q} = \omega_{-k,-q} = \omega_{-k,q} = \omega_{k,-q} , \quad \nu_{k,q} = -\nu_{-k,q} = -\nu_{k,-q} = \nu_{-k,-q} .
\]

(12.123)

We now make a Bogoliubov transformation,

\[
\begin{align*}
c_{k+\frac{1}{2}q}^{\dagger} &= \cos \vartheta_{k,q} \gamma_{k,q}^{\dagger} - \sin \vartheta_{k,q} e^{i\phi_{k,q}} \gamma_{-k,q} \\
c_{-k+\frac{1}{2}q}^{\dagger} &= \cos \vartheta_{k,q} \gamma_{-k,q}^{\dagger} + \sin \vartheta_{k,q} e^{i\phi_{k,q}} \gamma_{k,q}
\end{align*}
\]

(12.124)

with

\[
\begin{align*}
\cos \vartheta_{k,q} &= \sqrt{\frac{E_{k,q} + \omega_{k,q}}{2E_{k,q}}} \\
\sin \vartheta_{k,q} &= \sqrt{\frac{E_{k,q} - \omega_{k,q}}{2E_{k,q}}} \\
\phi_{k,q} &= \arg(\Delta_{k,q})
\end{align*}
\]

(12.125-12.126)
We then obtain
\[
\hat{K}_{\text{BCS}} = \sum_{k,\sigma} (E_{k,q} + \nu_{k,q}) \gamma_{k,q,\sigma}^\dagger \gamma_{k,q,\sigma} + \sum_k \left( \xi_k - E_{k,q} + \Delta_{k,q} \langle b_{k,q}^\dagger \rangle \right). \tag{12.127}
\]

Next, we compute the quantum statistical averages
\[
\langle c_{k+\frac{q}{2}q}^\dagger c_{k+\frac{q}{2}q} \rangle = \cos^2 \vartheta_{k,q} f(E_{k,q} + \nu_{k,q}) + \sin^2 \vartheta_{k,q} \left[ 1 - f(E_{k,q} - \nu_{k,q}) \right] = \frac{1}{2} \left( 1 + \frac{\omega_{k,q}}{E_{k,q}} \right) f(E_{k,q} + \nu_{k,q}) + \frac{1}{2} \left( 1 - \frac{\omega_{k,q}}{E_{k,q}} \right) \left[ 1 - f(E_{k,q} - \nu_{k,q}) \right] \tag{12.128}
\]
and
\[
\langle c_{k+\frac{q}{2}q}^\dagger c_{-k+\frac{q}{2}q} \rangle = -\sin \vartheta_{k,q} \cos \vartheta_{k,q} e^{-i\varphi_{k,q}} \left[ 1 - f(E_{k,q} + \nu_{k,q}) - f(E_{k,q} - \nu_{k,q}) \right] = -\frac{\Delta_{k,q}}{2E_{k,q}} \left[ 1 - f(E_{k,q} + \nu_{k,q}) - f(E_{k,q} - \nu_{k,q}) \right] \tag{12.129}
\]

### 12.11.1 Gap equation for finite momentum condensate

We may now solve the $T = 0$ gap equation,
\[
1 = -\sum_{k'} V_{k,k'} \frac{1}{2E_{k',q}} = \frac{1}{2} g(\varepsilon_v) v \int_0^{\hbar \omega_D} \frac{d\xi}{\sqrt{(\xi + b_q)^2 + |\Delta_{0,q}|^2}}. \tag{12.130}
\]
Here we have assumed the interaction $V_{k,k'}$ of Eqn. 12.71, and we take
\[
\Delta_{k,q} = \Delta_{0,q} \Theta(\hbar \omega_D - |\xi_k|). \tag{12.131}
\]
We have also written $\omega_{k,q} = \xi_k + b_q$. This form is valid for quadratic $\xi_k = \frac{\hbar^2 k^2}{2m^*} - \mu$, in which case $b_q = \hbar^2 q^2 / 8m^*$. We take $\Delta_{0,q} \in \mathbb{R}$. We may now compute the critical wavevector $q_c$ at which the $T = 0$ gap collapses:
\[
1 = \frac{1}{2} g(\varepsilon_v) v \ln \left( \frac{\hbar \omega_0 + b_q}{b_{qc}} \right) \Rightarrow b_{qc} \approx \hbar \omega_0 e^{-2/g(\varepsilon_v) v} = \frac{1}{2} \Delta_0, \tag{12.132}
\]
whence $q_c = 2 \sqrt{m^* \Delta_0 / \hbar}$. Here we have assumed weak coupling, i.e. $g(\varepsilon_v) v \ll 1$.

Next, we compute the gap $\Delta_{0,q}$. We have
\[
\sinh^{-1} \left( \frac{\hbar \omega_0 + b_q}{\Delta_{0,q}} \right) = \frac{2}{g(\varepsilon_v) v} + \sinh^{-1} \left( \frac{b_q}{\Delta_{0,q}} \right). \tag{12.133}
\]
Assuming $b_q \ll \Delta_{0,q}$, we obtain
\[
\Delta_{0,q} = \Delta_0 - b_q = \Delta_0 - \frac{\hbar^2 q^2}{8m^*}. \tag{12.134}
\]
12.11.2 Supercurrent

We assume a quadratic dispersion \( \varepsilon_k = \hbar^2 k^2 / 2m^* \), so \( v_k = \hbar k / m^* \). The current density is then given by

\[
\begin{align*}
 j &= \frac{2e\hbar}{m^*V} \sum_k (k + \frac{1}{2}q) \langle c_{k+\frac{1}{2}q\uparrow}^\dagger c_{k+\frac{1}{2}q\uparrow} \rangle \\
&= \frac{ne\hbar}{2m^*} q + \frac{2e\hbar}{m^*V} \sum_k k \langle c_{k+\frac{1}{2}q\uparrow}^\dagger c_{k+\frac{1}{2}q\uparrow} \rangle ,
\end{align*}
\]

where \( n = N/V \) is the total electron number density. Appealing to Eqn. 12.128, we have

\[
\begin{align*}
 j &= \frac{e\hbar}{m^*V} \sum_k k \left\{ \left[ 1 + f(E_{k,q} + \nu_{k,q}) - f(E_{k,q} - \nu_{k,q}) \right] \\
&\quad + \frac{\omega_{k,q}}{E_{k,q}} \left[ f(E_{k,q} + \nu_{k,q}) + f(E_{k,q} - \nu_{k,q}) - 1 \right] \right\} + \frac{ne\hbar}{2m^*} q \\
&= \frac{e\hbar}{m^*V} \sum_k k \left[ 1 + 2 \nu_{k,q} f'(E_{k,q}) \right] + \frac{ne\hbar}{2m^*} q .
\end{align*}
\]

We now write

\[
\begin{align*}
 j &= \frac{e\hbar}{m^*V} \sum_k k \left[ 1 + 2 \nu_{k,q} f'(E_{k,q}) \right] + \frac{ne\hbar}{2m^*} q \\
&= \frac{e\hbar}{m^*V} \sum_k k^2 f'(E_{k,q}) \\
&\quad + \frac{ne\hbar}{2m^*} q \int_0^\infty d\xi \frac{\partial f}{\partial E} ,
\end{align*}
\]

where we have set \( k^2 = k_F^2 \) inside the sum, since it is only appreciable in the vicinity of \( k = k_F \), and we have invoked \( g(\varepsilon) = m^* k_F^2 / \pi^2 \hbar^2 \) and \( n = k_F^3 / 3\pi^2 \). Thus,

\[
\begin{align*}
 j &= \frac{ne\hbar}{2m^*} \left( 1 + 2 \int_0^\infty d\xi \frac{\partial f}{\partial E} \right) q \equiv \frac{n_s(T) e\hbar q}{2m^*} .
\end{align*}
\]

This defines the superfluid density,

\[
\begin{align*}
 n_s(T) &= n \left( 1 + 2 \int_0^\infty d\xi \frac{\partial f}{\partial E} \right) .
\end{align*}
\]

Note that the second term in round brackets on the RHS is always negative. Thus, at \( T = 0 \), we have \( n_s = n \), but at \( T = T_c \), where the gap vanishes, we find \( n_s(T_c) = 0 \), since \( E = |\xi| \) and \( f(0) = \frac{1}{2} \). We may write \( n_s(T) = n - n_n(T) \), where \( n_n(T) = n \mathcal{Y}(T) \) is the normal fluid density.
Ginzburg-Landau theory

We may now expand the free energy near $T = T_c$ at finite condensate $q$. We will only quote the result. One finds

$$
\frac{\Omega_s - \Omega_n}{V} = \tilde{a}(T) |\Delta|^2 + \frac{1}{2} \tilde{b}(T) |\Delta|^4 + \frac{n \tilde{b}(T)}{g(\varepsilon_F)} \frac{\hbar^2 q^2}{2m^*} |\Delta|^2 ,
$$

(12.141)

where the Landau coefficients $\tilde{a}(T)$ and $\tilde{b}(T)$ are given in Eqn. 12.108. Identifying the last term as $\tilde{K} |\nabla \Delta|^2$, where $\tilde{K}$ is the stiffness, we have

$$
\tilde{K} = \frac{\hbar^2 n \tilde{b}(T)}{2m^* \varepsilon_F}. 
$$

(12.142)

### 12.12 Effect of Repulsive Interactions

Let’s modify our model in Eqns. 12.71 and 12.72 and write

$$
V_{k,k'} = \begin{cases} 
(v_c - v_p)/V & \text{if } |\xi_k| < \hbar \omega_D \text{ and } |\xi_{k'}| < \hbar \omega_D \\
v_c/V & \text{otherwise}
\end{cases}
$$

and

$$
\Delta_k = \begin{cases} 
\Delta_0 & \text{if } |\xi_k| < \hbar \omega_D \\
\Delta_1 & \text{otherwise}
\end{cases}
$$

(12.143)

(12.144)

Here $-v_p < 0$ is the attractive interaction mediated by phonons, while $v_c > 0$ is the Coulomb repulsion. We presume $v_p > v_c$ so that there is a net attraction at low energies, although below we will show this assumption is overly pessimistic. We take $\Delta_{0,1}$ both to be real.

At $T = 0$, the gap equation then gives

$$
\Delta_0 = \frac{1}{2} g(\varepsilon_F) (v_p - v_c) \int_0^{\hbar \omega_D} d\xi \frac{\Delta_0}{\sqrt{\xi^2 + \Delta_0^2}} - \frac{1}{2} g(\varepsilon_F) v_c \int_0^{\hbar \omega_D} d\xi \frac{\Delta_1}{\sqrt{\xi^2 + \Delta_1^2}},
$$

$$
\Delta_1 = -\frac{1}{2} g(\varepsilon_F) v_c \int_0^{\hbar \omega_D} d\xi \frac{\Delta_0}{\sqrt{\xi^2 + \Delta_0^2}} - \frac{1}{2} g(\varepsilon_F) v_c \int_0^{\hbar \omega_D} d\xi \frac{\Delta_1}{\sqrt{\xi^2 + \Delta_1^2}},
$$

(12.145)

where $\hbar \omega_D$ is once again the Debye energy, and $B$ is the full electronic bandwidth. Performing the integrals, and assuming $\Delta_{0,1} \ll \hbar \omega_D \ll B$, we obtain

$$
\Delta_0 = \frac{1}{2} g(\varepsilon_F) (v_p - v_c) \Delta_0 \ln \left( \frac{2\hbar \omega_D}{\Delta_0} \right) - \frac{1}{2} g(\varepsilon_F) v_c \Delta_1 \ln \left( \frac{B}{\hbar \omega_D} \right),
$$

$$
\Delta_1 = -\frac{1}{2} g(\varepsilon_F) v_c \Delta_0 \ln \left( \frac{2\hbar \omega_D}{\Delta_0} \right) - \frac{1}{2} g(\varepsilon_F) v_c \Delta_1 \ln \left( \frac{B}{\hbar \omega_D} \right).
$$

(12.146)
The second of these equations gives

\[ \Delta_1 = -\frac{\frac{1}{2} g(\varepsilon_F) v_C \ln(2\hbar \omega_D / \Delta_0)}{1 + \frac{1}{2} g(\varepsilon_F) v_C \ln(B / \hbar \omega_D)} \Delta_0. \] (12.147)

Inserting this into the first equation then results in

\[ \frac{2}{g(\varepsilon_F) v_p} = \ln \left( \frac{2\hbar \omega_D}{\Delta_0} \right) \cdot \left\{ 1 - \frac{v_C}{v_p} \cdot \frac{1}{1 + \frac{1}{2} g(\varepsilon_F) \ln(B / \hbar \omega_D)} \right\}. \] (12.148)

This has a solution only if the attractive potential \( v_p \) is greater than the repulsive factor \( v_C / [1 + \frac{1}{2} g(\varepsilon_F) v_C \ln(B / \hbar \omega_D)] \). Note that it is a renormalized and reduced value of the bare repulsion \( v_C \) which enters here. Thus, it is possible to have

\[ v_C > v_p > \frac{v_C}{1 + \frac{1}{2} g(\varepsilon_F) v_C \ln(B / \hbar \omega_D)}, \] (12.149)

so that \( v_C > v_p \) and the potential is always repulsive, yet still the system is superconducting!

Working at finite temperature, we must include factors of \( \tanh \left( \frac{1}{2} \beta \sqrt{\xi^2 + \Delta_0^2} \right) \) inside the appropriate integrands in Eqn. 12.145, with \( \beta = 1/k_B T \). The equation for \( T_c \) is then obtained by examining the limit \( \Delta_0, \Delta_1 \to 0 \), with the ratio \( r \equiv \Delta_1 / \Delta_0 \) finite. We then have

\[
\begin{align*}
\frac{2}{g(\varepsilon_F)} &= (v_p - v_C) \int_0^{\tilde{\Omega}} ds \ s^{-1} \ \tanh(s) - r v_C \int_0^{\tilde{B}} ds \ s^{-1} \ \tanh(s) \\
\frac{2}{g(\varepsilon_F)} &= -r v_C \int_0^{\tilde{\Omega}} ds \ s^{-1} \ \tanh(s) - v_C \int_0^{\tilde{B}} ds \ s^{-1} \ \tanh(s)
\end{align*}
\] (12.150)

where \( \tilde{\Omega} \equiv \hbar \omega_D / 2k_B T_c \) and \( \tilde{B} \equiv B / 2k_B T_c \). We now use

\[ \int_0^\Lambda ds \ s^{-1} \ \tanh(s) = \ln \Lambda + \ln \left( \frac{4 e^C}{\pi} \right) + \mathcal{O}(e^{-\Lambda}) \] (12.151)

to obtain

\[ \frac{2}{g(\varepsilon_F) v_p} = \ln \left( \frac{1.134 \hbar \omega_D}{k_B T_c} \right) \cdot \left\{ 1 - \frac{v_C}{v_p} \cdot \frac{1}{1 + \frac{1}{2} g(\varepsilon_F) \ln(B / \hbar \omega_D)} \right\}. \] (12.152)
Comparing with Eqn. 12.148, we see that once again we have 

\[ 2\Delta_0(T = 0) = 3.52 k_B T_c. \]

Note, however, that 

\[ k_B T_c = 1.134 \hbar \omega_0 e^{-1/(\lambda - \mu^*)}, \quad \Delta_0 = 2\hbar \omega_0 e^{-1/(\lambda - \mu^*)}, \quad \Delta_1 = -\frac{\mu^* \Delta_0}{\lambda - \mu^*}. \] (12.156)

Since \( \mu^* \) depends on \( \omega_D \), the isotope effect is modified:

\[ \delta \ln T_c = \delta \ln \omega_D \cdot \left\{ 1 - \frac{\mu^2}{1 + \mu \ln(B/\hbar \omega_D)} \right\}. \] (12.157)

12.13 Appendix I : General Variational Formulation

We consider a more general grand canonical Hamiltonian of the form

\[ \hat{K} = \sum_{k,\sigma} \left( \epsilon_k - \mu \right) c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{2V} \sum_{k,p,q,\sigma,\sigma'} \hat{u}_{\sigma\sigma'}(k, p, q) c_{k+p+q,\sigma'}^\dagger c_{p-q,\sigma}^\dagger c_{p,\sigma'} c_{k,\sigma}. \] (12.158)

In order that the Hamiltonian be Hermitian, we may require, without loss of generality,

\[ \hat{u}_{\sigma\sigma'}^*(k, p, q) = \hat{u}_{\sigma\sigma'}(k + p, q, q - p, -q). \] (12.159)

In addition, spin rotation invariance says that \( \hat{u}_{\uparrow\uparrow}(k, p, q) = \hat{u}_{\downarrow\downarrow}(k, p, q) \) and \( \hat{u}_{\uparrow\downarrow}(k, p, q) = \hat{u}_{\downarrow\uparrow}(k, p, q) \).

We now take the thermal expectation of \( \hat{K} \) using a density matrix derived from the BCS Hamiltonian,

\[ \hat{K}_{BCS} = \sum_k \left( c_{k\uparrow}^\dagger c_{-k\downarrow} \right) \left( \xi_k \Delta_k \Delta_k^* \right) \left( c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger \right) + K_0. \] (12.160)

The energy shift \( K_0 \) will not be important in our subsequent analysis. From the BCS Hamiltonian,

\[ \langle c_{k\sigma}^\dagger c_{k'\sigma'} \rangle = n_k \delta_{k,k'} \delta_{\sigma\sigma'}, \]

\[ \langle c_{k\sigma}^\dagger c_{k'\sigma'}^\dagger \rangle = \Psi_k^* \delta_{k',-k} \delta_{\epsilon_\sigma\epsilon_{\sigma'}}. \] (12.161)
where $\varepsilon_{\sigma\sigma'} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$. We don’t yet need the detailed forms of $n_k$ and $\Psi_k$ either. Using Wick’s theorem, we find

$$\langle \hat{K} \rangle = \sum_k 2(\varepsilon_k - \mu) n_k + \sum_{k,k'} W_{k,k'} n_k n_{k'} - \sum_{k,k'} V_{k,k'} \Psi_k^* \Psi_{k'} ,$$

(12.162)

where

$$W_{k,k'} = \frac{1}{V} \left\{ \hat{u}_{1\uparrow}(k,k',0) + \hat{u}_{1\downarrow}(k,k',0) - \hat{u}_{1\uparrow}(k,k',k'-k) \right\}$$

and

$$V_{k,k'} = -\frac{1}{V} \hat{u}_{1\downarrow}(k',-k',k-k') .$$

(12.163)

We may assume $W_{k,k'}$ is real and symmetric, and $V_{k,k'}$ is Hermitian.

Now let’s vary $\langle \hat{K} \rangle$ by changing the distribution. We have

$$\delta \langle \hat{K} \rangle = 2 \sum_k \left( \varepsilon_k - \mu + \sum_{k'} W_{k,k'} n_{k'} \right) \delta n_k + \sum_{k,k'} V_{k,k'} \left( \Psi_k^* \delta \Psi_{k'} + \delta \Psi_k^* \Psi_{k'} \right).$$

(12.164)

On the other hand,

$$\delta \langle \hat{K}_{BCS} \rangle = 2 \sum_k \left( \xi_k \delta n_k + \Delta_k \delta \Psi_k^* + \Delta_k^* \delta \Psi_k \right).$$

(12.165)

Setting these variations to be equal, we obtain

$$\xi_k = \varepsilon_k - \mu + \sum_{k'} W_{k,k'} n_{k'}$$

(12.166)

and

$$\Delta_k = \sum_{k'} V_{k,k'} \Psi_{k'}$$

(12.167)

These are to be regarded as self-consistent equations for $\xi_k$ and $\Delta_k$. 


12.14 Appendix II : Superconducting Free Energy

We start with the Landau free energy difference from Eqn. 12.100,

\[ \frac{\Omega_s - \Omega_n}{V} = -\frac{1}{4} g(\varepsilon_F) \Delta^2 \left\{ 1 + 2 \ln \left( \frac{\Delta_0}{\Delta} \right) - \left( \frac{\Delta}{2 \hbar \omega_D} \right)^2 + \mathcal{O}(\Delta^4) \right\} \]

\[-2 \ g(\varepsilon_F) \Delta^2 \ I(\delta) + \frac{1}{6} \pi^2 \ g(\varepsilon_F) \ (k_B T)^2 , \]

where

\[ I(\delta) = \frac{1}{\delta} \int_0^\infty ds \ln \left( 1 + e^{-\delta\sqrt{1+s^2}} \right) . \]

We now proceed to examine the integral \( I(\delta) \) in the limits \( \delta \to \infty \) (i.e. \( T \to 0^+ \)) and \( \delta \to 0^+ \) (i.e. \( T \to T^- \), where \( \Delta \to 0 \)).

When \( \delta \to \infty \), we may safely expand the logarithm in a Taylor series, and

\[ I(\delta) = \sum_{n=1}^\infty \frac{(-1)^{n-1}}{n\delta} K_1(n\delta) , \]

where \( K_1(\delta) \) is the modified Bessel function, also called the MacDonald function. Asymptotically, we have\(^{11}\)

\[ K_1(z) = \left( \frac{\pi}{2z} \right)^{1/2} e^{-z} \cdot \left\{ 1 + \mathcal{O}(z^{-1}) \right\} . \]

We may then retain only the \( n = 1 \) term to leading nontrivial order. This immediately yields the expression in Eqn. 12.101.

The limit \( \delta \to 0 \) is much more subtle. We begin by integrating once by parts, to obtain

\[ I(\delta) = \int_1^\infty dt \frac{\sqrt{t^2 - 1}}{e^{\delta t} + 1} . \]

We now appeal to the tender mercies of Mathematica. Alas, this avenue is to no avail, for the program gags when asked to expand \( I(\delta) \) for small \( \delta \). We need something better than Mathematica. We need Professor Michael Fogler.

Fogler says\(^{12}\): start by writing Eqn. 12.170 in the form

\[ I(\delta) = \sum_{n=1}^\infty \frac{(-1)^{n-1}}{n\delta} K_1(n\delta) = + \int_{C_1} dz \frac{\pi}{2\pi i} \frac{K_1(\delta z)}{\sin \pi z} \frac{K_1(\delta z)}{\delta z} . \]

\(^{11}\)See, e.g., the NIST Handbook of Mathematical Functions, §10.25.

\(^{12}\)M. Fogler, private communications.
Figure 12.7: Contours for complex integration for calculating $I(\delta)$ as described in the text.

The initial contour $C_1$ consists of a disjoint set of small loops circling the points $z = \pi n$, where $n \in \mathbb{Z}_+$. Note that the sense of integration is clockwise rather than counterclockwise. This accords with an overall minus sign in the RHS above, because the residues contain a factor of $\cos(\pi n) = (-1)^n$ rather than the desired $(-1)^{n-1}$. Following Fig. 12.7, the contour may now be deformed into $C_2$, and then into $C_3$. Contour $C_3$ lies along the imaginary $z$ axis, aside from a small semicircle of radius $\epsilon \to 0$ avoiding the origin, and terminates at $z = \pm iA$. We will later take $A \to \infty$, but for the moment we consider $1 \ll A \ll \delta^{-1}$. So long as $A \gg 1$, the denominator $\sin \pi z = i \sinh \pi u$, with $z = iu$, will be exponentially large at $u = \pm A$, so we are safe in making this initial truncation. We demand $A \ll \delta^{-1}$, however, which means $|\delta z| \ll 1$ everywhere along $C_3$. This allows us to expand $K_1(\delta z)$ for small values of the argument. One has

$$K_1(w) = \frac{1}{w^2} + \frac{1}{2} \ln w \left( 1 + \frac{1}{8} w^2 + \frac{1}{192} w^4 + \ldots \right) + (C - \ln 2 - \frac{1}{2}) + \frac{1}{16} (C - \ln 2 - \frac{5}{4}) w^2 + \frac{1}{384} (C - \ln 2 - \frac{5}{3}) w^4 + \ldots,$$

where $C \approx 0.577216$ is the Euler-Mascheroni constant. The integral is then given by

$$I(\delta) = \int_{\epsilon}^{A} \frac{du}{2\pi i} \frac{\pi}{\sinh \pi u} \left[ \frac{K_1(i\delta u)}{i\delta u} - \frac{K_1(-i\delta u)}{-i\delta u} \right] + \int_{-\pi/2}^{\pi/2} \frac{d\theta}{2\pi} \frac{\pi e^{i\theta}}{\sin(\pi e^{i\theta})} \frac{K_1(\delta e^{i\theta})}{\delta e^{i\theta}}.$$  \hspace{1cm} (12.175)

Using the above expression for $K_1(w)/w$, we have

$$\frac{K_1(i\delta u)}{i\delta u} - \frac{K_1(-i\delta u)}{-i\delta u} = \frac{i\pi}{2} \left( 1 - \frac{1}{8} \delta^2 u^2 + \frac{1}{192} \delta^4 u^4 + \ldots \right).$$  \hspace{1cm} (12.176)

At this point, we may take $A \to \infty$. The integral along the two straight parts of the $C_3$ contour is then

$$I_1(\delta) = \frac{i\pi}{\epsilon} \int_{\epsilon}^{\infty} \frac{du}{\sinh \pi u} \left( 1 - \frac{1}{8} \delta^2 u^2 + \frac{1}{192} \delta^4 u^4 + \ldots \right)$$

$$= -\frac{1}{4} \ln \tanh \left( \frac{1}{2} \pi \epsilon \right) - \frac{7}{64 \pi^2} \delta^2 + \frac{31}{512 \pi^4} \delta^4 + O(\delta^6).$$  \hspace{1cm} (12.177)
The integral around the semicircle is

\[
I_2(\delta) = \int_{-\pi/2}^{\pi/2} \frac{d\theta}{2\pi} \frac{1}{1 - \frac{1}{6}\pi^2 \epsilon^2 e^{2i\theta}} \left\{ \frac{1}{\delta^2 \epsilon^2} e^{2i\theta} + \frac{1}{2} \ln(\delta \epsilon e^{i\theta}) + \frac{1}{2}(C - \ln 2 - \frac{1}{2}) + \ldots \right\}
\]

\[
= \int_{-\pi/2}^{\pi/2} \frac{d\theta}{2\pi} \left(1 + \frac{1}{6}\pi^2 \epsilon^2 e^{2i\theta} + \ldots\right) \left\{ \frac{e^{-2i\theta}}{\delta^2 \epsilon^2} + \frac{1}{2} \ln(\delta \epsilon) + \frac{1}{2} \theta + \frac{1}{2}(C - \ln 2 - \frac{1}{2}) + \ldots \right\}
\]

\[
= \frac{\pi^2}{12 \delta^2} + \frac{1}{4} \ln \delta + \frac{1}{4} \ln \epsilon + \frac{1}{4}(C - \ln 2 - \frac{1}{2}) + O(\epsilon^2)
\]  \hspace{1cm} (12.178)

We now add the results to obtain \( I(\delta) = I_1(\delta) + I_2(\delta) \). Note that there are divergent pieces, each proportional to \( \ln \epsilon \), which cancel as a result of this addition. The final result is

\[
I(\delta) = \frac{\pi^2}{12 \delta^2} + \frac{1}{4} \ln \left(\frac{2\delta}{\pi}\right) + \frac{1}{4}(C - \ln 2 - \frac{1}{2}) - \frac{7}{64} \frac{\zeta(3)}{\pi^2} \delta^2 + \frac{31}{512} \frac{\zeta(5)}{\pi^4} \delta^4 + O(\delta^6)
\]  \hspace{1cm} (12.179)

Inserting this result in Eqn. 12.168 above, we thereby recover Eqn. 12.106.