Lecture 16 (Feb. 24)

BCS Theory of Superconductivity

- **Bound states**: Consider a ballistic particle in an attractive potential \( V(\mathbf{r}) \). The Schrödinger equation is

\[
-\frac{h^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r}) \psi(\mathbf{r}) = E \psi(\mathbf{r})
\]

Fourier transform to obtain

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

with \( \mathcal{E}(\mathbf{k}) = \hbar^2 k^2 / 2m \). Since \( \hat{V}(\mathbf{k}, \mathbf{k}') = \hat{V}(\mathbf{k} - \mathbf{k}') \) is a Hermitian matrix, we may express it as a sum over its eigenspace projectors, viz.

\[
\hat{V}(\mathbf{k} - \mathbf{k}') = \sum_n \lambda_n \alpha_n(\mathbf{k}) \alpha_n^*(\mathbf{k}')
\]

Let's approximate the above sum by the contribution from the lowest eigenvalue, which we call \( \lambda \). Thus, we take

\[
\hat{V}(\mathbf{k}, \mathbf{k}') \approx \lambda \alpha(\mathbf{k}) \alpha^*(\mathbf{k}')
\]

Such a potential is called *separable*. We then have

\[
\hat{\mathcal{E}}(\mathbf{k}) \hat{\psi}(\mathbf{k}) + \lambda \alpha(\mathbf{k}) \int \frac{d^d k}{(2\pi)^d} \alpha^*(\mathbf{k}') \hat{\psi}(\mathbf{k}') = E \hat{\psi}(\mathbf{k}')
\]

which entails

\[
\hat{\psi}(\mathbf{k}) = \frac{\lambda \alpha(\mathbf{k})}{E - \mathcal{E}(\mathbf{k})} \int \frac{d^d k'}{(2\pi)^d} \alpha^*(\mathbf{k}') \hat{\psi}(\mathbf{k}')
\]
Now multiply by $\alpha(t)$ and integrate to obtain

$$-\frac{1}{\lambda} = \int \frac{d^d k}{(2\pi)^d} \frac{|\alpha(k)|^2}{E(k)-E}$$

If $\hat{V}_{k,k'}$ is isotropic, i.e. if $\hat{V}(iH - iH') = \hat{V}(R_{k} - R_{k'})$ where $R \in SO(d)$, then the lowest eigenvector $\alpha(k)$ is generally isotropic, i.e. we may write $\alpha(k) = \alpha(E(k))$, which is a function only of the magnitude of $k$. Then with $g(E) = \int \frac{d^d k}{(2\pi)^d} \delta(E - E(k)) = \text{DOS}$, we have

$$\left( \star \right) \quad \frac{1}{|\lambda|} = \int dE \frac{g(E)}{|E| + E} |\alpha(E)|^2$$

where we assume $\lambda < 0$ and $E < 0$. If $\alpha(E)$ and $g(E)$ are finite as $E \to 0$, then we have, as $E \to 0^-$,

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

where $B$ is the bandwidth (i.e. $g(E) = 0$ for $E > B$). This equation has a solution for arbitrarily small values of $|\lambda|$, since the RHS diverges logarithmically as $E \to 0^-$. Thus, as $\lambda \to 0^-$ we have

$$E(\lambda) = -cB \exp \left( -\frac{1}{g(0) |\alpha(0)|^2 |\lambda|} \right)$$

where $c > 0$ is a constant. If $g(E) \propto E^p$ with $p > 0$, then the RHS of $(\star)$ is finite as $E \to 0^-$. In this
case, a bound state solution with $E < 0$ exists only for $|\lambda| > \lambda_c$, where

$$\lambda_c = \frac{1}{\Z} \int_0^\infty d\varepsilon \frac{g(\varepsilon)}{\varepsilon} |\alpha(\varepsilon)|^2$$

For a ballistic dispersion, $g(\varepsilon) \propto \varepsilon^{-(d-2)/2}$, so $g(0)$ vanishes for $d > 2$ and is finite for $d = 2$.

For $d < 2$, $g(\varepsilon \to 0^+) \to 0^+$ diverges as $g(\varepsilon) \propto \varepsilon^{-p}$ with $p = 1 - \frac{1}{2} d$, i.e. $p = \frac{1}{2}$ in $d = 1$. The RHS of (1) then diverges as $|E|^{1-p}$ as $E \to 0^-$ and so $E(\lambda) = -c |\lambda|^{1/p}$ as $\lambda \to 0^-$.

**Cooper's problem (1956):** Cooper considered the problem of two electrons with a weak attraction in the presence of a quiescent Fermi sea, described by a variational wavefunction

$$|\Psi\rangle = \frac{1}{\sqrt{A}} \sum_{k \in \mathbb{K}_F} A_k (c^+_\uparrow c^+_\downarrow - c^+_\downarrow c^+_\uparrow) |F\rangle$$

where $|F\rangle$ is the filled Fermi sphere. Note that $|\Psi\rangle$ has total momentum $\hat{K} = 0$ and total spin $S = 0$ (i.e. a singlet). The electrons in the Fermi sea only enter the problem through Pauli blocking. In real space, the wavefunction for Cooper's pair is
\[ \Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \sum_{|k| > k_F} A_k e^{i \mathbf{K} \cdot (\mathbf{x}_1 - \mathbf{x}_2)} (|\uparrow_1 \downarrow_2\rangle - |\downarrow_1 \uparrow_2\rangle) \]

where \( A_k = A_{-k} \). The Hamiltonian is

\[ \hat{H} = \sum_{|k| > k_F} C_{k\sigma}^+ C_{k\sigma} + \frac{1}{2} \sum_{k_1, k_2} \langle k_1 \sigma_1, k_2 \sigma_2 | V | k_3 \sigma_3, k_4 \sigma_4 \rangle \times C_{k_1 \sigma_1}^+ C_{k_2 \sigma_2}^+ C_{k_3 \sigma_3} C_{k_4 \sigma_4} \]

We treat \( |\Psi\rangle \) as a variational state, so we set

\[ \delta \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \delta \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} - \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \cdot \frac{\langle \Phi | \Phi \rangle}{\langle \Phi | \Phi \rangle} = 0 \]

We take the variation \( \text{wrt} \ \hat{A}_k^\dagger \). We have

\[ \langle \Psi | \Psi \rangle = \sum_{|k| > k_F} A_k^\dagger A_k \]

\[ \langle \Psi | \hat{H} | \Psi \rangle = E_0 + \sum_{|k| > k_F} 2 \varepsilon_k |A_k|^2 + \frac{1}{2} \sum_{k, k'} V_{k, k'} A_k^\dagger A_{k'} \]

where \( E_0 = \langle \Phi | \hat{H} | \Phi \rangle \) and

\[ V_{k, k'} = \langle k_1, -k_1 | V | k'_1, -k'_1 \rangle = \frac{1}{\sqrt{V}} \int d^3x \ v(x) e^{i (\mathbf{k} - \mathbf{k'}) \cdot \mathbf{x}} \]

Thus, we obtain the eigenvalue equation

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

Now define \( \Sigma_k = \Sigma_F + \varepsilon_k \) and \( E = E_0 + 2\Sigma_F + W \), so that

\[ 2\Sigma_k A_k + \sum_{k'} V_{k, k'} A_{k'} = W A_k \]
Assuming $\psi(\xi) = \psi(1\xi1)$, we may write

$$V_{w,w'}^{(k)} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} V_{l}^{(k,k')} Y_{l,m}(\xi) Y_{l,m}^{*}(\xi)$$

We further assume separability, i.e.

$$V_{l}^{(k,k')} = \frac{1}{\sqrt{\lambda_{l}}} \alpha_{l}^{\dagger}(k) \alpha_{l}^{*}(k')$$

and we seek a solution $A_{k} = A_{k} Y_{l,m}(\xi)$ in the angular momentum $l$ channel. This results in

$$2\xi_{k} A_{k} + \frac{1}{\sqrt{\lambda_{l}}} \sum_{k'}^{l} \alpha_{l}^{\dagger}(k') A_{k'} = W_{k} A_{k}$$

This may be recast as

$$A_{k} = \frac{\lambda_{l} \alpha_{l}(k)}{W_{k} - 2\xi_{k}} \cdot \frac{1}{\sqrt{\lambda_{l}}} \sum_{k'}^{l} \alpha_{l}^{\dagger}(k') A_{k'}$$

Now multiply by $\alpha_{l}^{\dagger}(k)$ and sum over $|k| < k_{F}$ to obtain

$$\frac{1}{\lambda_{l}} = \frac{1}{\sqrt{\lambda_{l}}} \sum_{k}^{l} |\alpha_{l}(k)|^{2} W_{k} - 2\xi_{k} = \Phi(W_{k})$$

We can solve this graphically. Since $|k| > k_{F}$, $\xi_{k} > 0$. The denominator passes through zero as $W_{k}$ passes through each value of $\xi_{k}$. As we see from the plot below, when $\lambda_{l} < 0$ there is a bound state solution with $W_{k} < 0$. This is true for arbitrarily weak attractive $\lambda_{l}$.
We saw previously how in $d=3$ dimensions bound states require a critical attraction strength. The difference here is that we are not interested in states near $K=0$, where the DOS vanishes as $\sqrt{E}$, but rather in states near $|k|=k_F$, where $g(E_F) = m^*k_F/\pi^2\hbar^2$ is constant, as it is for a $d=2$ system near $E=0$.

To solve further, assume $\alpha_\epsilon(k) = \Theta(B_\epsilon - \xi_k)$ so

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

Now assume $g(E_F + \xi) \approx g(E_F)$, integrate, and find

\[
|W_\epsilon| = \frac{2 B_\epsilon}{\exp(4/|\lambda_\epsilon| g(E_F)) - 1}
\]

In the weak coupling limit, where $|\lambda_\epsilon| g(E_F) \ll 1$,
As we shall see when we study BCS theory, the factor of 4 in the exponent is twice too large. For strong coupling, $|\lambda_2|g(\epsilon_F) \gg 1$, and

$$W_1 = -2B_2 e^{-4/|\lambda_2|g(\epsilon_F)}$$

The energy scale $B_2$ will be shown to be the Debye energy of the phonons for conventional phonon-mediated superconductivity. The effective attractive interaction exists only over a very thin energy shell about the Fermi surface. Two additional features of the Cooper problem:

- One can construct a finite momentum Cooper pair, viz.

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \sum_k A_k \left[ \begin{array}{c} c_{k+\frac{1}{2}T}^\dagger \ c_{-k+\frac{1}{2}T}^\dagger \ c_{-k+\frac{1}{2}T} \ c_{-k-\frac{1}{2}T} \end{array} \right] |F\rangle$$

The total momentum is $\overrightarrow{P} = \hbar \overrightarrow{q}$. This results in the eigenvalue equation

$$(\frac{3}{2} \delta_k + \frac{3}{2} \delta_{-k} + \overline{\delta}_k A_{\delta_k} + \sum_{k'} V_{kk'} A_{k'} = WA_k$$

Now

$$(\frac{3}{2} \delta_k + \frac{3}{2} \delta_{-k} + \overline{\delta}_k) = 2 \delta_k + \frac{4}{\hbar^2} \frac{\partial^2 f_k}{\partial \phi \partial \eta}$$
and thus the binding energy is reduced by $O(q^2)$. The $\tilde{q}=0$ Cooper pair has the greatest binding energy.

- The mean square radius of the Cooper pair is

$$\langle \vec{r}^2 \rangle = \frac{\int d^3r |\Psi(\vec{r})|^2 \vec{r}^2}{\int d^3r |\Psi(\vec{r})|^2} = \frac{\int d^3k |\tilde{\Omega}_{\#} A_{\#}|^2}{\int d^3k |A_{\#}|^2}$$

$$\approx \frac{g(\varepsilon_F) \xi(k_F)^2 \int d\xi \left| \partial A/\partial \xi \right|^2}{g(\varepsilon_F) \int d\xi \left| A(\xi) \right|^2}$$

We have $A(\vec{r}) = -C \lambda \alpha(\vec{r})/(|W| + 2 \xi)$, and $\xi(k) = \hbar v_F$. For weak binding, $W \rightarrow 0^-$, and we have

$$\langle \vec{r}^2 \rangle \approx \frac{4}{3} (\hbar v_F)^2 |W|^{-2}$$

Thus, for weak attractive interactions, $W \rightarrow 0^-$ and the radius of the Cooper pair diverges. This is why BCS turns out to be such a successful mean field theory. The Ginzburg criterion (§11.4.5) says that mean field theory is qualitatively accurate down to a reduced temperature

$$T_G = T_c - T_c = \left( \frac{\sigma}{R} \right)^{2d/(4-d)}$$

where $\sigma$ is a microscopic length (e.g., the lattice constant).
and \( R_* \) the mean Cooper pair size. Typically we have \( R_*/a \approx 10^2 - 10^3 \), so in \( d=3 \), \( t_G \approx 10^{-6} - 10^{-9} \).

**Phonon-mediated attraction**

Please read §12.3 for details. The electron-phonon Hamiltonian for small momentum transfer and longitudinal phonons is

\[
\hat{H}_{\text{el-ph}} = \frac{1}{\sqrt{V}} \sum_{\mathbf{k},q} \sum_{\sigma} \mathcal{g}_{\mathbf{q}} (a_{\mathbf{k}+\mathbf{q},\sigma}^+ + a_{-\mathbf{k}+\mathbf{q},\sigma}) c_{\mathbf{k}+\mathbf{q},\sigma}^+ c_{-\mathbf{k},\sigma}
\]

with \( \mathcal{g}_{\mathbf{q}} = \lambda_{\text{el-ph}} \hbar c_{\mathbf{q}} / g(\varepsilon_F) \). We compute an effective indirect electron-electron interaction by working to second order in \( \hat{H}_{\text{el-ph}} \). Starting with a pair of electrons in states \( |\mathbf{k}_0,-\mathbf{k}-\sigma\rangle \), we transition to either of the two intermediate states

\[
\begin{align*}
|I_1\rangle &= |\mathbf{k}_0,-\mathbf{k}-\sigma\rangle \otimes |-\mathbf{q}\rangle \\
|I_2\rangle &= |\mathbf{k}_0,-\mathbf{k}^\prime-\sigma\rangle \otimes |1+\mathbf{q}\rangle
\end{align*}
\]

where \( \mathbf{q} = \mathbf{k}^\prime - \mathbf{k} \). Another application of \( \hat{H}_{\text{el-ph}} \) takes us to \( |\mathbf{k}^\prime_0,-\mathbf{k}^\prime-\sigma\rangle \). The intermediate state energies are given by

\[
\begin{align*}
E_1 &= \frac{1}{2} \frac{\hbar}{m_{\text{eff}}} + \frac{1}{2} \hbar \omega_{-\mathbf{q}} \\
E_2 &= \frac{1}{2} \frac{\hbar}{m_{\text{eff}}} + \frac{1}{2} \hbar \omega_{\mathbf{q}}
\end{align*}
\]
The second order matrix element is then

\[
\langle \mathbf{k}' \sigma, -\mathbf{k}' - \sigma | \hat{H}_{\text{indirect}} | \mathbf{k} \sigma, -\mathbf{k} - \sigma \rangle = \sum_n \langle \mathbf{k}' \sigma, -\mathbf{k}' - \sigma | \hat{H}_{\text{el-ph}} | n \rangle 
\]

\[
\times \langle n | \hat{H}_{\text{el-ph}} | \mathbf{k} \sigma, -\mathbf{k} - \sigma \rangle \times \left( \frac{1}{E_f - E_n} + \frac{1}{E_i - E_n} \right)
\]

\[
= |g_{\sigma}|^2 \left( \frac{1}{\delta_{\mathbf{k}} - \delta_{\mathbf{k}'} - \hbar \omega_q^2} + \frac{1}{\delta_{\mathbf{k}} - \delta_{\mathbf{k}'} - \hbar \omega_q^2} \right)
\]

Adding in the direct Coulomb interaction \( \hat{U}(\hat{\sigma}) = \frac{4\pi e^2}{\hbar^2} \),
we obtain the effective interaction

\[
\langle \mathbf{k} \sigma, -\mathbf{k} - \sigma | \hat{H}_{\text{eff}} | \mathbf{k} \sigma, -\mathbf{k} - \sigma \rangle = \hat{U}(\hat{\sigma}) + |g_{\sigma}|^2 \times \left( \frac{2 \kappa \hbar \omega_q^2}{(\delta_{\mathbf{k}} - \delta_{\mathbf{k}'} + \hbar \omega_q^2)^2} \right)
\]

Thus for \( |\delta_{\mathbf{k}} - \delta_{\mathbf{k}'}| < \hbar \omega_q^2 \) the second term is negative
and can dominate the first, yielding an effective attraction.

• Reduced BCS Hamiltonian: The operator that creates
a Cooper pair with total momentum \( \frac{\mathbf{q}}{2} \) is \( b_{\mathbf{k}, \frac{\mathbf{q}}{2}}^+ + b_{-\mathbf{k}, \frac{-\mathbf{q}}{2}}^+ \)

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

Since \( \frac{\mathbf{q}}{2} = 0 \) pairs have the greatest binding energy, we
consider the reduced BCS Hamiltonian,

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

We may assume \( V_{\mathbf{k}, \mathbf{k}'} = V_{\mathbf{k}, -\mathbf{k}'} = V_{-\mathbf{k}, \mathbf{k}'} \), which is required
by spin rotational invariance. Since

$$2 \begin{pmatrix} C_{k\uparrow}^+ & C_{-k\downarrow} \\ b_{k,0}^+ & b_{k,0} \end{pmatrix} \begin{pmatrix} C_{k\uparrow} \\ C_{-k\downarrow} \end{pmatrix} \mid \psi \rangle = \begin{pmatrix} C_{k\uparrow}^+ C_{k\uparrow} + C_{-k\downarrow}^+ C_{-k\downarrow} \end{pmatrix} \mid \psi \rangle$$

provided all the pair states \((\uparrow, \downarrow)\) in \(\mid \psi \rangle\) are either empty or doubly occupied. Thus, we consider

$$\hat{H}_{\text{red}} = \sum_k 2 \varepsilon_k b_{k,0}^+ b_{k,0} + \sum_k V_k b_{k,0}^+ b_{k',0}$$

This has the alluring appearance of a noninteracting bosonic Hamiltonian, which would render it exactly solvable. However, \(b_{k,0}\) is a composite operator that is not a true boson in that it doesn't satisfy bosonic commutation relations. If \(\beta_k^+\) is a bosonic creation operator, then \([\beta_k, \beta_{k'}^+] = [\beta_k^+, \beta_{k'}^+] = 0\), \([\beta_k, \beta_{k'}^+] = \delta_{kk'}\). But while \([b_{k,0}, b_{k',0}^+] = [b_{k,0}^+, b_{k',0}^+] = 0\), \([b_{k,0}, b_{k',0}^+] = (1 - C_{k\uparrow}^+ C_{k\uparrow} - C_{-k\downarrow}^+ C_{-k\downarrow}) \delta_{kk'}\)

Furthermore, \((b_{k,0}^+)^2 = (b_{k,0})^2 = 0\). So we need another approach, as \(\hat{H}_{\text{red}}\) can't be diagonalized by any known methods.

Mean field theory: While \(b_{k,0}\) doesn't satisfy bosonic commutation relations, it is still a
composite boson and can take on an expectation value. So let's do the mean field thing and write

\[ b_{k,0}^{*} = \langle b_{k,0}^{*} \rangle + \left( b_{k,0}^{*} - \langle b_{k,0}^{*} \rangle \right) \]

\[ \delta b_{k,0}^{*} \]

We now have

\[ \hat{H}_{\text{red}} = \sum_{k,\sigma} E_k \hat{c}_{k\sigma}^{\dagger} \hat{c}_{k\sigma} + \sum_{k,k',\sigma} V_{k,k'} \left( -\langle \hat{b}_{k,0}^{*} \rangle \langle \hat{b}_{k,0} \rangle + \langle \hat{b}_{k,0}^{*} \rangle \hat{b}_{k,0} + \hat{b}_{k,0}^{*} \langle \hat{b}_{k,0} \rangle + \frac{\delta b_{k,0}^{+} \delta b_{k,0}^{*}}{(\text{flucts})^2} \right) \]

Thus our mean field Hamiltonian is

\[ \hat{H}_{\text{red}}^{\text{MF}} = \sum_{k,\sigma} E_k \hat{c}_{k\sigma}^{\dagger} \hat{c}_{k\sigma} + \sum_{k,k',\sigma} \left( \Delta_k \hat{c}_{k\sigma}^{\dagger} \hat{c}_{-k'\sigma} + \Delta_k^* \hat{c}_{-k'\sigma}^{\dagger} \hat{c}_{k\sigma} \right) \]

\[ - \sum_{k,k',\sigma} V_{k,k'} \langle \hat{c}_{k\sigma}^{\dagger} \hat{c}_{-k'\sigma}^{\dagger} \rangle \langle \hat{c}_{-k'\sigma} \hat{c}_{k\sigma} \rangle \]

where

\[ \Delta_k = \sum_{k'} V_{k,k'} \langle \hat{c}_{-k'\sigma} \hat{c}_{k'\sigma}^{\dagger} \rangle \quad \Delta_k^* = \sum_{k'} V_{k,k'}^* \langle \hat{c}_{k'\sigma}^{\dagger} \hat{c}_{-k'\sigma} \rangle \]

One highly noteworthy aspect of \( \hat{H}_{\text{red}} \) is that it does not conserve particle number! Therefore we need to work in the grand canonical ensemble, with

\[ \hat{H}_{\text{BCS}} = \hat{H}_{\text{red}}^{\text{MF}} - \mu \hat{N} \]

\[ \hat{N} = \sum_{k,\sigma} \hat{c}_{k\sigma}^{\dagger} \hat{c}_{k\sigma} \]