$$= (\mathcal{H}_0)_{mn} - \frac{1}{4} \sum_{\substack{k k' q \\ \sigma\sigma'}} \frac{|\alpha_q|^2}{\Lambda} c^{\dagger}_{k'+q\sigma'} c_{k'\sigma'} c^{\dagger}_{k-q\sigma} c_{k\sigma}$$

$$\times \left(\frac{2\omega_q}{\omega_q^2 - (\epsilon_k - \epsilon_{k-q})^2} + \frac{2\omega_q}{\omega_q^2 - (\epsilon_{k'} - \epsilon_{k'+q})^2} \right)$$

$$= (\mathcal{H}_0)_{mn} - \sum_{\substack{k k' q \\ \sigma\sigma'}} \underbrace{\frac{\omega_q}{\omega_q^2 - (\epsilon_{k+q} - \epsilon_k)^2}}_{\text{attractive when positive}} \frac{|\alpha_q|^2}{\Lambda} c^{\dagger}_{k'+q\,\sigma'} c_{k'\sigma'} c^{\dagger}_{k-q\,\sigma} c_{k\sigma} \quad \text{—— (3)}$$

\# $\left(\begin{array}{l} \epsilon_k \sim v_F \hbar k \\ \Delta\epsilon_k \sim v_F \hbar q \\ \omega_q \sim c_{ph} q \end{array} \right)$

※ Typically (i.e., if we don't impose any condition on the direction of q ($|q| \sim O(q_D)$)), $|\epsilon_{k+q} - \epsilon_k| / \hbar\omega_q \sim v_F / c_{ph} \gg 1$. ..... \#

However, the terms in (3) for which $|\epsilon_{k+q} - \epsilon_k| > \hbar\omega_q$ doesn't contribute in lowering the total energy, because of the "wrong" sign.

Therefore, we can simply neglect them in calculating the ground state. (To be more precise, we'll consider the ground state in which only attractive part will contribute.) This suggests the following crude approximation:

- $\sum_{kk'q} \longrightarrow \sum_{kk'q} (|\epsilon_k - \epsilon_F|, |\epsilon_{k'} - \epsilon_F|, \hbar c q \le \hbar\omega_D) \equiv \sum'_{k,k',q}$
- $\frac{\omega_q}{\omega_q^2 - (\epsilon_{k+q} - \epsilon_k)^2} |\alpha_q|^2 \longrightarrow g/2 \; {}^{>0}$ (const)

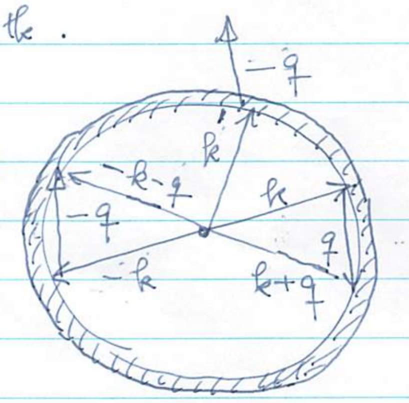
Then, we obtain

$$\tilde{\mathcal{H}} \approx \mathcal{H}_0 - \frac{g}{2\Lambda} \sum_{\substack{k,k',q \\ \sigma\sigma'}}^{\overbrace{\prime}^{\text{conditions on } k,\, k',\, q}} c^{\dagger}_{k'+q\sigma'} c_{k'\sigma'} c^{\dagger}_{k-q\sigma} c_{k\sigma}$$

For a reason similar to the one mentioned above, we may further restrict the wave number summation. Namely, the contribution from the term with $k' = -k$ should be larger than others because the volume of q that satisfy the condition

$$|\epsilon_{k'+q} - \epsilon_F|,\ |\epsilon_{k-q} - \epsilon_F| < \hbar\omega_D$$

would be largest when $k' = -k$.



($\because$ If $k' \neq -k$ as in the figure, $k'-q$ is likely out of the shell.)

Therefore, we may further reduce the Hamiltonian :

$$\tilde{\mathcal{H}} \Rightarrow \mathcal{H}_0 - \frac{g}{2\Lambda} \sideset{}{'}\sum_{\substack{k,k' \\ \sigma\sigma'}} c^+_{k'\sigma}\, c^+_{-k'\sigma'}\, c_{-k\sigma'}\, c_{k\sigma}$$

(we've put $k' = -k$ and redefined $k+q$ as k'.)

Finally, anticipating the conventional s-wave superconductivity for which antiparallel spins form pairs (Cooper pairs), we restrict the summation to the anti-parallel spins :

$$\boxed{\tilde{\mathcal{H}} \Rightarrow \mathcal{H}_{BCS} \equiv \mathcal{H}_0 - \frac{g}{\Lambda} \sideset{}{'}\sum_{k,k'} c^+_{k'\uparrow}\, c^+_{-k'\downarrow}\, c_{-k\downarrow}\, c_{k\uparrow}} \tag{1}$$

※ In fact, the approximations made above can be justified by a more logically smooth (but technically more involved) treatment such as the Hartree-Fock approximation.

o The typical magnitude of
the Fermi energy and the Debye frequency

$\hbar = 1.055 \times 10^{-34}$

$k_F \sim 1/a \sim 10^{10}$

$m \sim 9 \times 10^{-31} \sim 10^{-30}$

$v \sim 300$ (phonon)

$$\epsilon_F \sim \frac{\hbar^2 k_F^2}{m} \sim 10^{-68} \times 10^{20} / 10^{-30} \sim 10^{-18} \ (\mathrm{J})$$

$$\sim 10^5 \ (\mathrm{K})$$

$$\hbar\omega_D \sim \hbar v k_F \sim 10^{-34+2+10} \sim 10^{-22}$$

$$\sim 10 \ (\mathrm{K})$$

$\Longrightarrow \hbar\omega_D \ll \epsilon_F$ (typically)

Therefore, the "shell" in 8-9 is thin.
(The thickness is much smaller than the radius.)

A remark on the "crude" approximations

From the "raw" effective interaction (8-8-③) to the final form of the BCS Hamiltonian (8-9-①) we have made the following approximations:

① restrict the integration w.r.t. k, k' and q within the thin region near the fermi surface,
② replace the wave-number dependent coupling constant in (8-8-③) by a constant,
③ restrict the summation w.r.t. k, k' and q futher to the region satisfying $k' = -k$,
④ drop the contribution from the parallel spin pairs

These crude approximations/simplifications can be justified to a certain extent by "hand-waving" arguments. But further justication can be found in the variational approximation;
even if we apply the variational approximation to the "raw" effective Hamiltonian rather than the simplified BCS Hamiltonian, the results will be essentially the same. The calculation would be much more tedious but doable, though we will not get into more details in this course. It would be interesting to do it by numerical calculation for finite lattice systems.

Cooper Pair

- The effective interaction leads to formation of bound state of electron pairs, as we see below.

- We consider 2-electron problem, and show that we can form a bound state in the form

$$|\Phi\rangle = \sum_q{}' \theta_q \, c^{+}_{-q\downarrow} c^{+}_{q\uparrow} |0\rangle$$

$\longleftarrow$ vacuum

$\sum_q{}'$ is the summation within the shell $(\epsilon_F - \hbar\omega_D \sim \epsilon_F + \hbar\omega_D)$.

- The Schrödinger equation is $E|\Phi\rangle = \mathcal{H}|\Phi\rangle$:

$$\mathcal{H}_0 |\Phi\rangle = \sum_q{}' 2\epsilon_q \theta_q |q\rangle \quad \left(|q\rangle \equiv c^{+}_{-q\downarrow} c^{+}_{q\uparrow} |0\rangle \right)$$

$$V|\Phi\rangle = -\frac{g}{2\Lambda} \sum_{\substack{q k k' \\ \sigma\sigma'}}{}' \theta_q \left(c^{+}_{k'\sigma} c^{+}_{-k'\sigma'} c_{-k\sigma'} c_{k\sigma} \right) |q\rangle$$

$\longleftarrow$ We keep spin summation

$$c_{-k\sigma'} c_{k\sigma} |q\rangle = \left(-\delta_{kq} \delta_{\sigma\uparrow} \delta_{\sigma'\downarrow} + \delta_{k,-q} \delta_{\sigma'\uparrow} \delta_{\sigma\downarrow} \right) |0\rangle$$

$$V|\Phi\rangle = -\frac{g}{2\Lambda} \sum_{k'q}{}' \theta_q \left(-c^{+}_{k'\uparrow} c^{+}_{-k'\downarrow} + c^{+}_{k'\downarrow} c^{+}_{-k'\uparrow} \right) |0\rangle$$

$$= -\frac{g}{\Lambda} \sum_{k'q}{}' \theta_q \left(c^{+}_{-k'\downarrow} c^{+}_{k'\uparrow} \right) |0\rangle$$

$$= -\frac{g}{\Lambda} \sum_{kq}{}' \theta_q |k\rangle = -\frac{g}{\Lambda} \sum_{qk}{}' \theta_k |q\rangle$$

note that we go 1-step back from the BCS Hamiltonian.

$$E \sum_q{}' \theta_q |q\rangle = \sum_q{}' 2\epsilon_q \theta_q |q\rangle - \frac{g}{\Lambda} \sum_{qk}{}' \theta_k |q\rangle$$

For the coefficient of $|q\rangle$ $\rightarrow$

$$\boxed{E\theta_q = 2\epsilon_q \theta_q - \frac{g}{\Lambda} \sum_k \theta_k}$$

.... eigen value equation.

Switching from q to ϵ

$$C \equiv \frac{g}{\Lambda} \sum_{q'}{}' \theta_{q'} = g \int_{\epsilon_F - \hbar\omega_D}^{\epsilon_F + \hbar\omega_D} d\epsilon \, D(\epsilon)\, \theta(\epsilon)$$

$D = a^d \rho$
$= \begin{pmatrix} \text{DOS per} \\ \text{unit cell} \end{pmatrix}$

$$E \theta_q = 2\epsilon_q \theta_q - C$$

$$\theta_q = \frac{C}{2\epsilon_q - E}$$

$$C = g D_F \int_{\epsilon_F - \hbar\omega_D}^{\epsilon_F + \hbar\omega_D} d\epsilon \frac{C}{2\epsilon - E}$$

$$= g D_F \frac{C}{2} \Big[\log (2\epsilon - E) \Big]_{\epsilon_F - \hbar\omega_D}^{\epsilon_F + \hbar\omega_D}$$

$$= g D_F \frac{C}{2} \log \frac{2\epsilon_F + 2\hbar\omega_D - E}{2\epsilon_F - 2\hbar\omega_D - E}$$

defining $2\epsilon_F - 2\hbar\omega_D - E \equiv \Delta$

$$1 = g D_F \frac{1}{2} \log \frac{4\hbar\omega_D + \Delta}{\Delta}$$

$$e^{+2/gD_F} = \frac{4\hbar\omega_D}{\Delta} + 1$$

(※ The factor 2 difference from Kittel, but agrees with 青木)

$$\Delta = \frac{4\hbar\omega_D}{e^{2/gD_F} - 1}$$

(The amount of the energy reduction relative to the lowest non-perturbed energy, i.e. $2\epsilon_F - 2\hbar\omega_D$)

This can be interpreted as the binding energy of a cooper pair.

※ The reason why we can keep only antiparallel spin term ($\sigma \neq \sigma'$) in the BCS Hamiltonian.

Before dropping the parallel spin terms, the Hamiltonian was

$$\mathcal{H} = \mathcal{H}_0 - \frac{g}{\Lambda} \sum_{\substack{k k' \\ \sigma \sigma'}} C^{+}_{k'\sigma} C^{+}_{-k'\sigma'} C_{-k\sigma'} C_{k\sigma}$$

To form a parallel-spin version of Cooper pair we consider the wave function like

$$|\Phi\rangle = \sum_{q}{}' \theta_q C^{+}_{-q\uparrow} C^{+}_{q\uparrow} |0\rangle$$

However,

$$V|\Phi\rangle = -\frac{g}{\Lambda} \sum_{\substack{k k' \\ \sigma \sigma'}} \sum_{q} \theta_q C^{+}_{k'\sigma} C^{+}_{-k'\sigma'} C_{-k\sigma'} C_{k\sigma} \times C^{+}_{-q\uparrow} C^{+}_{q\uparrow} |0\rangle$$

$$= -\frac{g}{\Lambda} \sum_{k k' q} \theta_q C^{+}_{k'\uparrow} C^{+}_{-k'\uparrow} C_{-k\uparrow} C_{k\uparrow} C^{+}_{-q\uparrow} C^{+}_{q\uparrow} |0\rangle$$

$$= -\frac{g}{\Lambda} \sum_{k'} C^{+}_{k'\uparrow} C^{+}_{-k'\uparrow} \sum_{q k} \theta_q C_{-k\uparrow} C_{k\uparrow} C^{+}_{-q\uparrow} C^{+}_{q\uparrow} |0\rangle$$

$$\sum_{q k} \theta_q C_{-k\uparrow} C_{k\uparrow} C^{+}_{-q\uparrow} C^{+}_{q\uparrow} |0\rangle$$

$$= \sum_{q} \theta_q \Big(\underbrace{C_{-q\uparrow} C_{q\uparrow} C^{+}_{-q\uparrow} C^{+}_{q\uparrow}}_{(k=q)} + \underbrace{C_{q\uparrow} C_{-q\uparrow} C^{+}_{-q\uparrow} C^{+}_{q\uparrow}}_{(k=-q)} \Big) |0\rangle$$

$$= 0$$

Therefore, parallel spin pairs can't benefit from V in any way.. If we consider only anti-parallel spin pairs, we can set $\sigma' = -\sigma$.

Superconductivity

We have derived the BCS Hamiltonian.
The effective attraction among electrons was derived from the electron-phonon interaction through the 2nd order perturbation.

This effective coupling, as we see below, may change the electronic structure in a fundamental way beyond perturbation. In other words, the effective attraction is a relevant perturbation to the Fermi sea.

Gibbs-Bogoliubov-Feynman inequality

For any hermitian ops. $\mathcal{H}_0$ and Δ, we define

$$F(\eta) \equiv -\beta^{-1} \log e^{-\beta(\mathcal{H}_0 - \eta\Delta)}$$

Then, we can prove $F''(\eta) \equiv \frac{d^2F}{d\eta^2} \leq 0$ — ①

(This is equivalent to the 2nd law of thermodynamics.)

So, if we define $\Delta \equiv \mathcal{H}_0 - \mathcal{H}$, ① tells us that

$$F = F(1) \leq F(0) + F'(0)$$

$$= F_0 - \langle \Delta \rangle_0$$

$$= F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \equiv F_v$$

$$F_v = \langle \mathcal{H} \rangle_0 + F_0 - E_0$$

$$= \langle \mathcal{H} \rangle_0 - S_0 T$$

(E_0, S_0, F_0 are the energy, the entropy and the free-energy of the system $\mathcal{H}_0$.)

Proof of ①

It suffices to prove $F''(0) \leq 0$ because, for $\eta \neq 0$, by redefining $\mathcal{H}_0 - \eta\Delta \to \mathcal{H}_0$, the probrem is reduced to the case $\eta = 0$.

$$\chi \equiv -F''(0) = -\frac{d^2E}{d\eta^2}\bigg|_{\eta\to 0} \qquad \left(\Delta(\tau) \equiv e^{\tau\mathcal{H}_0}\Delta e^{-\tau\mathcal{H}_0}\right)$$

$$= \int_0^\beta d\tau \langle \Delta(\tau)\Delta(0)\rangle_0 - \beta\langle\Delta\rangle_0^2 \quad \text{— } \circledast$$

By choosing the basis where $\mathcal{H}_0$ is diagonal, i.e., $\mathcal{H}_0 = \sum_i E_i |i\rangle\langle i|$

$$\int_0^\beta d\tau \langle\Delta(\tau)\Delta(0)\rangle_0 = \int_0^\beta d\tau \langle e^{-(\beta-\tau)\mathcal{H}_0}\Delta e^{-\tau\mathcal{H}_0}\Delta\rangle_0$$

$$= Z_0^{-1}\int_0^\beta d\tau \sum_{ij} e^{-(\beta-\tau)E_i}\Delta_{ij}e^{-\tau E_j}\Delta_{ji}$$

$$(\Delta_{ij} \equiv \langle i|\Delta|j\rangle)$$

$$= Z_0^{-1}\left(\underbrace{\sum_i \beta e^{-\beta E_i}\Delta_{ii}^2}_{\#} + \sum_{\substack{i,j\\(i\neq j)}} \underbrace{\frac{e^{-\beta E_i} - e^{-\beta E_j}}{E_j - E_i}}_{\geq 0}\right)$$

$$\geq \beta\langle(\text{diag}\Delta)^2\rangle_0 \qquad \left((\text{diag}\Delta)_{ij} \equiv \delta_{ij}\Delta_{ii}\right)$$

$$\therefore \chi \geq \beta\left(\langle(\text{diag}\Delta)^2\rangle_0 - \langle\Delta\rangle_0^2\right)$$

$$= \beta\left(\langle(\text{diag}\Delta)^2\rangle_0 - \langle\text{diag}\,\Delta\rangle_0^2\right) \geq 0$$

$$F''(0) = -\chi \leq 0 \quad //$$

\# ... No degeneracy assumed. But it's easy to include degeneracy and the result is the same.

Proof of ⊛

$$F = -k_B T \log Z = -k_B T \log \mathrm{Tr}\, e^{-\beta(\mathcal{H}_0 - \eta\Delta)}$$

$$\left.\frac{d^2F}{d\eta^2}\right|_{\eta\to 0} = -k_B T\left(\frac{Z''}{Z} - \left(\frac{Z'}{Z}\right)^2\right)$$

$$\rho(\eta) \equiv e^{-\beta(\mathcal{H}_0-\eta\Delta)} = \left(e^{-\overbrace{\frac{\beta}{m}}^{\equiv \delta\tau}(\mathcal{H}_0-\eta\Delta)}\right)^m$$

$$= A^m \quad \left(A \equiv e^{-\delta\tau(\mathcal{H}_0-\eta\Delta)} \approx 1-\delta\tau(\mathcal{H}_0-\eta\Delta)\right)$$

$$\left.\frac{d^2}{d\eta^2}\rho(\eta)\right|_{\eta\to 0} = \sum_{k,l} A\cdots A\,A'A\cdots A\,A'A\cdots A\Big|_{\eta\to 0}$$

the k-th A the l-th A

$$= \sum_{k,l} A_0\cdots A_0\,\Delta\, A_0\cdots A_0\,\Delta\, A_0\cdots A_0\,(\delta\tau)^2$$

$$A_0 \equiv A|_{\eta\to 0} = e^{-\delta\tau\mathcal{H}_0}$$

$$Z'' = \mathrm{Tr}\left(\frac{d^2}{d\eta^2}\rho\right)\Big|_{\eta\to 0} = \sum_{k,l}\mathrm{Tr}\,(\underbrace{A_0\cdots A_0}_{m-k}\Delta\underbrace{A_0\cdots A_0}_{k-l-1}\Delta\underbrace{A_0\cdots A_0}_{l-1})(\delta\tau)^2$$

$$= \sum_{k,l}\mathrm{Tr}\,(\underbrace{A_0\cdots A_0}_{m-(k-l)-1}\Delta\underbrace{A_0\cdots A_0}_{k-l-1}\Delta)(\delta\tau)^2$$

$$= m\sum_{k=0}^{m-2}\mathrm{Tr}\,(\underbrace{A_0\cdots A_0}_{m-k-1}\Delta\underbrace{A_0\cdots A_0}_{k-1}\Delta)(\delta\tau)^2$$

$$\xrightarrow[\substack{m\to\infty \\ k\delta\tau\to\tau}]{} \beta\int_0^\beta d\tau\,\mathrm{Tr}\,e^{-\beta\mathcal{H}_0}\Delta(\tau)\Delta(0)$$

$$\therefore \left.\frac{d^2F}{d\eta^2}\right|_{\eta\to 0} = -\left(\int_0^\beta d\tau\,\langle\Delta(\tau)\Delta(0)\rangle_0 - \beta\langle\Delta\rangle_0^2\right)$$