III.2. Microscopic Theory of Conventional Superconductivity

The occurrence of superconductivity relies on the formation of Cooper pairs so that the ground state of an otherwise fermion system becomes a bosonic condensate. In this section we first demonstrate that any infinitesimal attractive interaction between two electrons in the presence of a Fermi sea leads to a stable bound pair known as the Cooper pair [L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956)]. The original non-interacting ground state (*i.e.* the filled Fermi sea) becomes unstable against pair formation, and the finite binding energy of the Cooper pair provides a qualitative explanation for the presence of an energy gap in the excitation spectrum of superconductors. One possible origin for the attractive interaction between a pair of electrons is the electron-phonon interaction. This microscopic pairing mechanism can successfully account for the isotope effect and various thermodynamic and electrodynamic properties of simple superconductors [J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957)]. We shall discuss BCS theory in depth using the thermal Green's function approach by Gorkov [L. P. Gorkov, *Sov. Phys.* – JETP **7**, 505 (1958)]. It should be noted that in high-temperature superconducting cuprates, the simple-minded electron-phonon interaction and the microscopic BCS theory cannot provide a coherent picture to account for many complex and seemingly conflicting phenomena among different families of cuprate superconductors. The quest for the underlying pairing mechanism for high-temperature superconducting cuprates remains one of the greatest challenges in modern condensed matter physics.

[Cooper pairing]

Here we shall primarily focus on a simpler situation of adding two electrons to a filled Fermi sea and discuss how to obtain the pair binding energy when an attractive interaction is turned on between the two electrons *outside* the Fermi sea. We may also consider an alternative situation where an attractive interaction is introduced between two electrons *inside* the Fermi sea. The latter consideration must involve virtual interactions with states outside of the Fermi sea because all states within are already filled, and such consideration is more tedious in the formalism. In the interest of time we shall only outline the concepts and refer the details to references.

Let us assume that a bound pair of electrons is added to the Fermi sea at $T = 0$. If the added bound pair does not with interact with the electrons in the Fermi sea except obeying the Pauli exclusion principle, we may construct a two-electron wavefunction for the bound pair, and the lowest energy state of the wavefunction has zero total momentum relative to the Fermi sea. Anticipating an attractive potential, the two-particle wavefunction can be given by the following expressions, depending on whether the bound state is a singlet or a triplet:

$$\psi_0(\mathbf{r}_1,\mathbf{r}_2) = \sum_{|\mathbf{k}|>k_F} g_{\mathbf{k}} \cos\left[\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)\right](\alpha_1\beta_2-\alpha_2\beta_1); \qquad \text{(singlet)} \qquad \text{(III.97)}$$

$$= \sum_{|\mathbf{k}|>k_F} g_{\mathbf{k}} \sin\left[\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)\right](\alpha_1\beta_2+\alpha_2\beta_1), \quad (\alpha_1\alpha_2), \quad (\beta_1\beta_2). \qquad \text{(triplet)} \qquad \text{(III.98)}$$

For simplicity, we only consider the singlet situation in the following discussion. The Schrödinger's equation for the two-electron system with an electron-phonon interaction potential V is given by

$$(\mathcal{H}_0+V)\psi_0 = E\psi_0, \qquad \text{(III.99)}$$

where

$$\mathcal{H}_0\psi_0 = 2\sum_{|\mathbf{k}|>k_F} g_{\mathbf{k}}\,\varepsilon_{\mathbf{k}} \cos\left[\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)\right](\alpha_1\beta_2-\alpha_2\beta_1), \qquad \text{(III.100)}$$

($\varepsilon_{\mathbf{k}}$: the eigen-energy of the quasiparticles, E: the eigen-energy of the Cooper pairs),

so that

$$\left(\mathcal{H}_0 + V\right)\psi_0 = \sum_{|\mathbf{k}|>k_F} g_{\mathbf{k}} \left\{\left(2\varepsilon_{\mathbf{k}} + V\right)\cos\left[\mathbf{k}\bullet\left(\mathbf{r}_1 - \mathbf{r}_2\right)\right]\left(\alpha_1\beta_2 - \alpha_2\beta_1\right)\right\}, \tag{III.101}$$

$$\Rightarrow \quad E g_{\mathbf{k}} = \sum_{|\mathbf{k}'|>k_F} g_{\mathbf{k}'} \left\{2\varepsilon_{\mathbf{k}'}\delta_{\mathbf{k}\mathbf{k}'} + \frac{1}{\Omega}\int d^3\mathbf{r}\, e^{i(\mathbf{k}'-\mathbf{k})\bullet\mathbf{r}}\, V(\mathbf{r})\right\}$$

$$\equiv \sum_{|\mathbf{k}'|>k_F} g_{\mathbf{k}'} \left\{2\varepsilon_{\mathbf{k}'}\delta_{\mathbf{k}\mathbf{k}'} + V_{\mathbf{k}\mathbf{k}'}\right\}, \tag{III.102}$$

$$\Rightarrow \quad \left(E - 2\varepsilon_{\mathbf{k}}\right) g_{\mathbf{k}} = \sum_{|\mathbf{k}'|>k_F} g_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} . \tag{III.103}$$

The matrix elements $V_{\mathbf{k}\mathbf{k}'}$ defined in EQ. (III.102) characterize the strength of the potential for scattering a pair of electrons from $(\mathbf{k}',-\mathbf{k}')$ to $(\mathbf{k},-\mathbf{k})$. Thus, the above derivation implies that a bound pair exists if we can find a set of $g_{\mathbf{k}}$ that satisfies EQ. (III.103), or equivalently,

$$g_{\mathbf{k}} = \frac{1}{\left(E - 2\varepsilon_{\mathbf{k}}\right)} \sum_{|\mathbf{k}'|>k_F} g_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} . \tag{III.104}$$

Now consider a special case for the interaction potential $V_{\mathbf{k}\mathbf{k}'}$:

$$V_{\mathbf{k}\mathbf{k}'} = -V \qquad \text{for} \quad \varepsilon_{\mathbf{k},\mathbf{k}'} < \omega_D + \varepsilon_F ; \tag{III.105}$$
$$= 0 \qquad \text{for} \quad \varepsilon_{\mathbf{k},\mathbf{k}'} > \omega_D + \varepsilon_F ,$$

where $V > 0$ and ω_D is the cutoff energy associated with the Debye frequency as discussed in Part III.4. Inserting EQ. (III.105) into EQ. (III.104), we find

$$g_{\mathbf{k}} = V \sum_{|\mathbf{k}'|>k_F} \frac{g_{\mathbf{k}'}}{\left(2\varepsilon_{\mathbf{k}} - E\right)} \quad \Rightarrow \quad \sum_{|\mathbf{k}|>k_F} g_{\mathbf{k}} = V \sum_{|\mathbf{k}|>k_F} \sum_{|\mathbf{k}'|>k_F} \frac{g_{\mathbf{k}'}}{\left(2\varepsilon_{\mathbf{k}} - E\right)} = \sum_{|\mathbf{k}'|>k_F} g_{\mathbf{k}'} , \tag{III.106}$$

so that

$$\frac{1}{V} = \sum_{|\mathbf{k}|>k_F} \frac{1}{\left(2\varepsilon_{\mathbf{k}} - E\right)} = \int d\varepsilon \frac{\mathcal{N}(\varepsilon)}{\left(2\varepsilon - E\right)}, \tag{III.107}$$

where $\mathcal{N}(\varepsilon)$ is the density of states. If $\omega_D << \varepsilon_F$, we may further simplify EQ. (III.107) by making the assumption that $\mathcal{N}(\varepsilon) \approx \mathcal{N}(\varepsilon_F)$. Hence, we find the relation

$$\frac{1}{V} = \int_{\varepsilon_F}^{\varepsilon_F + \omega_D} d\varepsilon \frac{\mathcal{N}(\varepsilon)}{\left(2\varepsilon - E\right)} = \frac{1}{2}\mathcal{N}\left(\varepsilon_F\right) \ln\left[\frac{2\varepsilon_F - E + 2\omega_D}{2\varepsilon_F - E}\right]. \tag{III.108}$$

We note that EQ. (III.108) always holds for any small values of V as long as the condition $\left(2\varepsilon_F - E\right) > 0$ is satisfied, which implies that the eigen-energy of the pair is smaller than the sum of the two free particle energies and therefore a bound state is formed. In other words, the Fermi sea becomes unstable against the formation of a Cooper pair because solutions to $g_{\mathbf{k}}$ in EQ. (III.104) can always be found.

In the weak coupling limit, we have the condition $\mathcal{N}(\varepsilon)V \ll 1$, so that from EQ. (III.108) we obtain:

$$2\varepsilon_F - E + 2\omega_D = (2\varepsilon_F - E)\exp\left[\frac{2}{\mathcal{N}(\varepsilon_F)V}\right]$$

$$\Rightarrow \quad 2\omega_D = (2\varepsilon_F - E)\left[\exp\left(\frac{2}{\mathcal{N}(\varepsilon_F)V}\right) - 1\right] \approx (2\varepsilon_F - E)\exp\left(\frac{2}{\mathcal{N}(\varepsilon_F)V}\right),$$

$$\Rightarrow \quad E \approx 2\varepsilon_F - 2\omega_D \exp\left(\frac{-2}{\mathcal{N}(\varepsilon_F)V}\right). \tag{III.109}$$

Equation(III.109) implies that there is a bound state with a negative energy with respect to the Fermi surface. If we rewrite EQ. (III.109) into $E \equiv 2\varepsilon_F - \Delta_0$, we obtain an energy gap:

$$\Delta_0 \approx 2\omega_D \exp\left(\frac{-2}{\mathcal{N}(\varepsilon_F)V}\right). \tag{III.110}$$

For convenience, we may measure all energy scales relative to the Fermi level, so that we define

$$\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \varepsilon_F, \qquad E' = 2\varepsilon_F - E, \tag{III.111}$$

which yields

$$g_{\mathbf{k}} = V\sum_{|\mathbf{k}'|>k_F} \frac{g_{\mathbf{k}'}}{(2\xi_{\mathbf{k}} + E')}. \tag{III.112}$$

Clearly the weighting factor $(2\xi_{\mathbf{k}} + E')^{-1}$ in EQ. (III.112) has its maximum at $\xi_{\mathbf{k}} = 0$ because both $E' \geq 0$ and $\xi_{\mathbf{k}} \geq 0$. Thus, the electron states with a range of energy above ε_F are strongly involved in forming the bound state.

We may also examine the situation for an attractive interaction V between two electrons below the Fermi level. In this case, the two-electron wavefunction may be expressed as follows (assuming singlet state so that the spin indices may be neglected):

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \varphi_0(\mathbf{r}_1,\mathbf{r}_2) + \sum_{\lambda\neq 0} \varphi_\lambda(\mathbf{r}_1,\mathbf{r}_2)\frac{1}{E - E_\lambda}\langle\varphi_\lambda|V|\psi(\mathbf{r}_1,\mathbf{r}_2)\rangle, \tag{III.113}$$

where ψ satisfies the Schrödinger's equation for the interacting two-electron system $(\mathcal{H}_0 + V)\psi = E\psi$, φ_λ are the eigenfunctions of the non-perturbed Hamiltonian $\mathcal{H}_0$ so that $\mathcal{H}_0\varphi_\lambda = E_\lambda\varphi_\lambda$, and the states $\lambda \neq 0$ refer to the excited states outside of the filled Fermi sea. In a homogeneous system, the total momentum of the two-electron system is conserved, and therefore the two-electron wavefunction can be expressed in terms of a product of the center-of-mass wavefunction and the relative wavefunction

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \Omega^{-1/2} e^{i\mathbf{P}\cdot\mathbf{R}}\, \Omega^{-1/2}\, \psi_{\mathbf{P},\mathbf{k}}(\mathbf{r}), \tag{III.114}$$

where we have introduced the following definitions in EQ. (III.114) and assumed that the momenta of the two electrons are $\mathbf{k}_1$ and $\mathbf{k}_2$:

$$\mathbf{P} = \mathbf{k}_1 + \mathbf{k}_2 \qquad \mathbf{k} \equiv \frac{1}{2}(\mathbf{k}_1 - \mathbf{k}_2) \qquad (|\mathbf{k}_1| > k_F, |\mathbf{k}_2| > k_F)$$

$$\mathbf{R} \equiv \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \qquad \mathbf{r} \equiv (\mathbf{r}_1 - \mathbf{r}_2).$$

If we further define the eigen-energy of the Schrödinger's equation E as the sum of the kinetic energy of the center-of-mass and an effective eigen-value κ^2 so that

$$E = \frac{\kappa^2}{m} + \frac{|\mathbf{P}|^2}{4m}, \qquad \text{(III.115)}$$

we obtain the following *Bethe-Goldstone equation*:

$$\psi_{\mathbf{P},\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + \int_\Gamma \frac{d^3\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q}\cdot\mathbf{r}} \frac{m}{\kappa^2 - q^2} \langle \mathbf{q}|V|\psi_{\mathbf{P},\mathbf{k}}\rangle, \qquad \text{(III.116)}$$

where $\left|\frac{1}{2}\mathbf{P} \pm \mathbf{k}\right| < k_F \qquad \Gamma \equiv \left|\frac{1}{2}\mathbf{P} \pm \mathbf{q}\right| > k_F$

and $$\frac{\kappa^2 - q^2}{m} = \Omega^{-1} \langle \mathbf{k}|V|\psi_{\mathbf{P},\mathbf{k}}\rangle. \qquad \text{(III.117)}$$

It can be shown that the solution to the Bethe-Goldstone equation (see, for example, Section 36 of Fetter & Walecka) also yields an eigen-energy lower than the non-interacting two-particle energy, implying a bound pair, and the resulting energy gap for $\mathbf{P} = 0$ is approximately

$$\Delta_0 \equiv (2\varepsilon_F - E) \approx \frac{k_F^2}{m} \exp\left[-\frac{4\pi^2}{mk_F V}\right] = 2\varepsilon_F \exp\left[-\frac{2}{\mathcal{N}(\varepsilon_F)V}\right], \qquad \text{(III.118)}$$

where we have used the relation $\mathcal{N}(\varepsilon_F) = mk_F/(2m)$ for the free electron gas.

You may have noticed that the energy gap given in EQ. (III.118) differs somewhat from that given in EQ. (III.110). This discrepancy originates in different simplifications taken when proving the existence of a bound pair either inside or outside of the Fermi surface if there is a finite attractive interaction. The key point in the above discussion of Cooper pairing is that electrons of a filled Fermi sea becomes unstable under the formation of a bound pair near the Fermi level, regardless of whether the pair formation occurring inside or outside of the Fermi surface. The energy gap will be derived more rigorously in our later consideration of microscopic theory of superconductivity. Here we summarize several important points regarding Cooper pairing.

1) The bound energy of the Cooper pair given in either EQ. (III.110) or EQ. (III.118) has an essential singularity in the attractive potential V, and therefore cannot be obtained with perturbation theory.

2) The largest bounding energy (or the maximum superconducting gap) is obtained if the total momentum **P** of the Cooper pair is zero. In principle, Cooper pairing can still be retained up to a finite momentum.

3) The occurrence of a bound pair for an arbitrarily small attractive interaction potential V is crucially dependent on the presence of a Fermi sea, because in the absence of the medium we have $k_F \to 0$, or

equivalently $\mathcal{N}(\varepsilon_F) \to 0$, and therefore $\Delta_0 \to 0$ according to EQs. (III.110) and (III.118). In other words, a stable bound pair cannot exist in vacuum under an arbitrarily small attractive potential.

4) The condition for forming a bound pair as given in EQ. (III.107) can be rewritten as $I(E') = 1$ where

$$I(E') \equiv V \int d\xi \frac{\mathcal{N}(\xi)}{(2\xi + E')} \qquad (\xi \equiv \varepsilon - \varepsilon_F\,,\ \ E' \equiv 2\varepsilon_F - E\,). \tag{III.119}$$

It is clear from EQ. (III.119) that for all $E' > 0$ we have $I(E') < I(0)$. Given that $I(0)$ is a large number if V is finite, we can always find a value of $E' > 0$ associated with the condition $I(E') = 1$. In other words, a bound-pair state can always be found, which implies instability of the Fermi sea against the formation of a bound pair.

[Microscopic theory of superconductivity]

To derive the microscopic theory for superconductivity, we begin with the consideration of a model Hamiltonian that includes an on-site attractive electron-phonon interaction:

$$\hat{H} = \hat{H}_0 + \hat{V} = \int d^3\mathbf{x}\, \psi^\dagger_\alpha(\mathbf{x}) \left\{ \frac{1}{2m}\left[\frac{\nabla}{i} - e\mathbf{A}(\mathbf{x})\right]^2 - \mu \right\} \psi_\alpha(\mathbf{x}) - \frac{1}{2}\gamma \int d^3\mathbf{x}\, \psi^\dagger_\alpha(\mathbf{x}) \psi^\dagger_\beta(\mathbf{x}) \psi_\beta(\mathbf{x}) \psi_\alpha(\mathbf{x})\,, \tag{III.120}$$

where $\gamma > 0$. To solve the model Hamiltonian, we generalize the Hartree-Fock approximation as follows:

$$\begin{aligned}
\hat{V} &\approx -\gamma \int d^3\mathbf{x} \left[\left\langle \psi^\dagger_\alpha(\mathbf{x}) \psi_\alpha(\mathbf{x}) \right\rangle \psi^\dagger_\beta(\mathbf{x}) \psi_\beta(\mathbf{x}) - \left\langle \psi^\dagger_\alpha(\mathbf{x}) \psi_\beta(\mathbf{x}) \right\rangle \psi^\dagger_\beta(\mathbf{x}) \psi_\alpha(\mathbf{x}) \right] \\
&\quad - \frac{1}{2}\gamma \int d^3\mathbf{x} \left[\left\langle \psi^\dagger_\alpha(\mathbf{x}) \psi^\dagger_\beta(\mathbf{x}) \right\rangle \psi_\beta(\mathbf{x}) \psi_\alpha(\mathbf{x}) + \psi^\dagger_\alpha(\mathbf{x}) \psi^\dagger_\beta(\mathbf{x}) \left\langle \psi_\beta(\mathbf{x}) \psi_\alpha(\mathbf{x}) \right\rangle \right] \\
&\equiv \hat{V}_{HF} - \frac{1}{2}\gamma \int d^3\mathbf{x} \left[\left\langle \psi^\dagger_\alpha(\mathbf{x}) \psi^\dagger_\beta(\mathbf{x}) \right\rangle \psi_\beta(\mathbf{x}) \psi_\alpha(\mathbf{x}) + \psi^\dagger_\alpha(\mathbf{x}) \psi^\dagger_\beta(\mathbf{x}) \left\langle \psi_\beta(\mathbf{x}) \psi_\alpha(\mathbf{x}) \right\rangle \right].
\end{aligned} \tag{III.121}$$

The approximation given in EQ. (III.121) no longer conserves the number of particles, which may be justified by considering the condensate of Cooper pairs as a reservoir of bosons. We further note that the Hartree-Fock term is the same in both normal and superconducting states so does not affect the comparison of the two states. If we consider singlet superconductors, the indices α and β in EQ. (III.121) must refer to opposite spins. Thus, we may simplify the model Hamiltonian in EQ. (III.120) into the following effective Hamiltonian:

$$\hat{H}_{\text{eff}} = \hat{H}_0 - \gamma \int d^3\mathbf{x} \left[\left\langle \psi^\dagger_\downarrow(\mathbf{x}) \psi^\dagger_\uparrow(\mathbf{x}) \right\rangle \psi_\uparrow(\mathbf{x}) \psi_\downarrow(\mathbf{x}) + \psi^\dagger_\downarrow(\mathbf{x}) \psi^\dagger_\uparrow(\mathbf{x}) \left\langle \psi_\uparrow(\mathbf{x}) \psi_\downarrow(\mathbf{x}) \right\rangle \right], \tag{III.122}$$

which is the basis for the BCS theory. This theory is self-consistent because the ensemble average given in the angular brackets are evaluated with $\hat{H}_{\text{eff}}$ so that

$$\left\langle \psi^\dagger_\downarrow(\mathbf{x}) \psi^\dagger_\uparrow(\mathbf{x}) \right\rangle = \frac{\text{Tr}\left[e^{-\beta \hat{H}_{\text{eff}}} \psi^\dagger_\downarrow(\mathbf{x}) \psi^\dagger_\uparrow(\mathbf{x}) \right]}{\text{Tr}\left[e^{-\beta \hat{H}_{\text{eff}}} \right]}. \tag{III.123}$$

With EQ. (III.122) defined, the Heisenberg field operators become

$$\psi_{H\uparrow}(\mathbf{x},\tau)=e^{\hat{H}_{\text{eff}}\tau}\,\psi_{\uparrow}(\mathbf{x})\,e^{-\hat{H}_{\text{eff}}\tau}\,,\qquad \psi^{\dagger}_{H\downarrow}(\mathbf{x},\tau)=e^{\hat{H}_{\text{eff}}\tau}\,\psi^{\dagger}_{\downarrow}(\mathbf{x})\,e^{-\hat{H}_{\text{eff}}\tau}\,,\tag{III.124}$$

which satisfy the following linear equations of motion:

$$\frac{\partial\psi_{H\uparrow}}{\partial\tau}=-\left[\frac{1}{2m}\left(\frac{\nabla}{i}-e\mathbf{A}\right)^{2}-\mu\right]\psi_{H\uparrow}-\gamma\left\langle\psi_{\uparrow}\psi_{\downarrow}\right\rangle\psi^{\dagger}_{H\downarrow}\,,\tag{III.125}$$

$$\frac{\partial\psi^{\dagger}_{H\downarrow}}{\partial\tau}=\left[\frac{1}{2m}\left(-\frac{\nabla}{i}-e\mathbf{A}\right)^{2}-\mu\right]\psi^{\dagger}_{H\downarrow}-\gamma\left\langle\psi^{\dagger}_{\downarrow}\psi^{\dagger}_{\uparrow}\right\rangle\psi_{H\uparrow}\,.\tag{III.126}$$

We now define the single-particle Green's function

$$\mathcal{G}(\mathbf{x},\tau;\mathbf{x}',\tau')\equiv-\left\langle T_{\tau}\left[\psi_{H\uparrow}(\mathbf{x},\tau)\psi^{\dagger}_{H\uparrow}(\mathbf{x}',\tau')\right]\right\rangle\,,\tag{III.127}$$

the anomalous Green's functions

$$\mathcal{F}(\mathbf{x},\tau;\mathbf{x}',\tau')\equiv-\left\langle T_{\tau}\left[\psi_{H\uparrow}(\mathbf{x},\tau)\psi_{H\downarrow}(\mathbf{x}',\tau')\right]\right\rangle\tag{III.128}$$

$$\mathcal{F}^{\dagger}(\mathbf{x},\tau;\mathbf{x}',\tau')\equiv-\left\langle T_{\tau}\left[\psi^{\dagger}_{H\downarrow}(\mathbf{x},\tau)\psi^{\dagger}_{H\uparrow}(\mathbf{x}',\tau')\right]\right\rangle,\tag{III.129}$$

and the gap function

$$\Delta(\mathbf{x})\equiv\gamma\mathcal{F}(\mathbf{x},\tau^{+};\mathbf{x},\tau)=-\gamma\left\langle\psi_{\uparrow}(\mathbf{x})\psi_{\downarrow}(\mathbf{x})\right\rangle=\gamma\left\langle\psi_{\downarrow}(\mathbf{x})\psi_{\uparrow}(\mathbf{x})\right\rangle\,,\tag{III.130}$$

so that the derivative of $\mathcal{G}$ relative to τ yields

$$\begin{aligned}\frac{\partial}{\partial\tau}\mathcal{G}(\mathbf{x},\tau;\mathbf{x}',\tau')&=-\delta(\tau-\tau')\left\langle\left\{\psi_{H\uparrow}(\mathbf{x},\tau),\psi^{\dagger}_{H\uparrow}(\mathbf{x}',\tau')\right\}\right\rangle-\left\langle T_{\tau}\left[\frac{\partial}{\partial\tau}\psi_{H\uparrow}(\mathbf{x},\tau)\psi^{\dagger}_{H\uparrow}(\mathbf{x}',\tau')\right]\right\rangle\\&=-\delta(\tau-\tau')\,\delta(\mathbf{x}-\mathbf{x}')-\left[\frac{1}{2m}\left(\frac{\nabla}{i}-e\mathbf{A}\right)^{2}-\mu\right]\mathcal{G}(\mathbf{x},\tau;\mathbf{x}',\tau')+\gamma\left\langle\psi_{\uparrow}\psi_{\downarrow}\right\rangle\mathcal{F}^{\dagger}(\mathbf{x},\tau;\mathbf{x}',\tau'),\end{aligned}$$

$$\Rightarrow\left[-\frac{\partial}{\partial\tau}-\frac{1}{2m}\left(\frac{\nabla}{i}-e\mathbf{A}(\mathbf{x})\right)^{2}+\mu\right]\mathcal{G}(\mathbf{x},\tau;\mathbf{x}',\tau')+\Delta(\mathbf{x})\,\mathcal{F}^{\dagger}(\mathbf{x},\tau;\mathbf{x}',\tau')=\delta(\tau-\tau')\,\delta(\mathbf{x}-\mathbf{x}')\,.\tag{III.131}$$

Similarly, the derivative of $\mathcal{F}$ relative to τ becomes

$$\left[-\frac{\partial}{\partial\tau}-\frac{1}{2m}\left(\frac{\nabla}{i}-e\mathbf{A}(\mathbf{x})\right)^{2}+\mu\right]\mathcal{F}(\mathbf{x},\tau;\mathbf{x}',\tau')=\Delta(\mathbf{x})\,\mathcal{G}(\mathbf{x},\tau;\mathbf{x}',\tau'),\tag{III.132}$$

and the derivative of $\mathcal{F}^{\dagger}$ relative to τ is

$$\left[\frac{\partial}{\partial\tau}-\frac{1}{2m}\left(i\nabla-e\mathbf{A}(\mathbf{x})\right)^{2}+\mu\right]\mathcal{F}^{\dagger}(\mathbf{x},\tau;\mathbf{x}',\tau')=\Delta^{*}(\mathbf{x})\,\mathcal{G}(\mathbf{x},\tau;\mathbf{x}',\tau')\,.\tag{III.133}$$

We may consider EQs. (III.131) and (III.133) as a pair of coupled equations for $\mathcal{G}$ and $\mathcal{F}^{\dagger}$, which are known as the Gorkov equations. Alternatively, we may simplify the expressions in EQs. (III.131) – (III.133) in a matrix form. Specifically, we introduce a two-component field operator:

$$\Psi_{\hat{H}}(x) = \begin{pmatrix} \psi_{\hat{H}}(x) \\ \psi^{\dagger}_{\hat{H}}(x) \end{pmatrix}, \qquad x \equiv (\mathbf{x}, \tau). \tag{III.134}$$

Using EQs. (III.127) – (III.129) and (III.134), we may define a (2×2) matrix Green's function $\mathcal{G}(x, x')$:

$$\begin{aligned} \mathcal{G}(x, x') &\equiv -\left\langle T_{\tau}\left[\Psi_{\hat{H}}(x)\Psi^{\dagger}_{\hat{H}}(x')\right]\right\rangle \\ &= \begin{bmatrix} \mathcal{G}(x, x') & \mathcal{F}(x, x') \\ \mathcal{F}^{\dagger}(x, x') & -\mathcal{G}(x', x) \end{bmatrix}. \end{aligned} \tag{III.135}$$

Therefore, the corresponding equations of motion become

$$\mathcal{D}_x \mathcal{G}(x, x') = \mathbf{1}\delta(x - x'), \tag{III.136}$$

where
$$\mathcal{D}_x \equiv \begin{pmatrix} -\dfrac{\partial}{\partial\tau} - \dfrac{1}{2m}\left(\dfrac{\nabla}{i} - e\mathbf{A}(\mathbf{x})\right)^2 + \mu & \Delta(x) \\ \Delta^*(x) & -\dfrac{\partial}{\partial\tau} + \dfrac{1}{2m}\left(i\nabla - e\mathbf{A}(\mathbf{x})\right)^2 - \mu \end{pmatrix}. \tag{III.137}$$

Having derived the equations of motion for the single-particle and anomalous Green's functions, we can find the solutions to these Green's functions and discuss the corresponding physical properties. We first consider a simple situation of a time-independent Hamiltonian, so that the Green's functions only depend on $\tau - \tau'$. We may Fourier transform the Green's functions

$$\mathcal{G}(\mathbf{x}, \tau; \mathbf{x}', \tau') = \beta^{-1}\sum_{\nu} e^{-i\omega_{\nu}(\tau-\tau')}\mathcal{G}(\mathbf{x}, \mathbf{x}'; \omega_{\nu}), \tag{III.138}$$

$$\mathcal{F}^{\dagger}(\mathbf{x}, \tau; \mathbf{x}', \tau') = \beta^{-1}\sum_{\nu} e^{-i\omega_{\nu}(\tau-\tau')}\mathcal{F}^{\dagger}(\mathbf{x}, \mathbf{x}'; \omega_{\nu}), \tag{III.139}$$

where the Matsubara frequency for fermions is given by $\omega_{\nu} = (2n+1)\pi\beta^{-1}$. Therefore, the Gorkov equations EQs. (III.131) and (III.133) become

$$\left[i\omega_{\nu} - \frac{1}{2m}\left(\frac{\nabla}{i} - e\mathbf{A}(\mathbf{x})\right)^2 + \mu\right]\mathcal{G}(\mathbf{x}, \mathbf{x}'; \omega_{\nu}) + \Delta(\mathbf{x})\mathcal{F}^{\dagger}(\mathbf{x}, \mathbf{x}'; \omega_{\nu}) = \delta(\mathbf{x} - \mathbf{x}'), \tag{III.140}$$

$$\left[-i\omega_{\nu} - \frac{1}{2m}\left(i\nabla - e\mathbf{A}(\mathbf{x})\right)^2 + \mu\right]\mathcal{F}^{\dagger}(\mathbf{x}, \mathbf{x}'; \omega_{\nu}) - \Delta^*(\mathbf{x})\mathcal{G}(\mathbf{x}, \mathbf{x}'; \omega_{\nu}) = 0, \tag{III.141}$$

which must be solved together with the self-consistent condition in EQ. (III.130):

$$\Delta^*(\mathbf{x}) \equiv \gamma\mathcal{F}^{\dagger}(\mathbf{x}, \tau^+; \mathbf{x}, \tau) = -\gamma\left\langle\psi^{\dagger}_{\downarrow}(\mathbf{x})\psi^{\dagger}_{\uparrow}(\mathbf{x})\right\rangle = \frac{\gamma}{\beta}\lim_{\eta\to 0+}\sum_{\nu} e^{-i\omega_{\nu}\eta}\mathcal{F}^{\dagger}(\mathbf{x}, \mathbf{x}; \omega_{\nu}), \tag{III.142}$$

In general, the coupled equations in EQs. (III.140) – (III.142) are augmented by Maxwell's equation that relates the local field $\mathbf{h} = \nabla \times \mathbf{A}$ to the supercurrent and any other external currents used to generate the applied field. The solutions generally require numerical analysis, so we shall only consider limiting cases in the following.

If we assume an infinite bulk superconductor in zero field, the thermal Green's functions become translationally invariant so that EQs. (III.140) – (III.142) are rewritten into the following:

$$\left[i\omega_\nu + \frac{\nabla^2}{2m} + \mu\right]\mathcal{G}(\mathbf{x}-\mathbf{x}';\omega_\nu) + \Delta\,\mathcal{F}^\dagger(\mathbf{x}-\mathbf{x}';\omega_\nu) = \delta(\mathbf{x}-\mathbf{x}'), \tag{III.143}$$

$$\left[-i\omega_\nu + \frac{\nabla^2}{2m} + \mu\right]\mathcal{F}^\dagger(\mathbf{x}-\mathbf{x}';\omega_\nu) - \Delta^*\mathcal{G}(\mathbf{x}-\mathbf{x}';\omega_\nu) = 0, \tag{III.144}$$

$$\Delta^* = \frac{\gamma}{\beta}\lim_{\eta\to 0+}\sum_\nu e^{-i\omega_\nu \eta}\mathcal{F}^\dagger(\mathbf{x}=0;\omega_\nu). \tag{III.145}$$

Fourier transforming the thermal Green's functions into momentum space:

$$\mathcal{G}(\mathbf{x},\omega_\nu) = \int \frac{d^3\mathbf{k}}{(2\pi)^3}\, e^{i\mathbf{k}\cdot\mathbf{x}}\mathcal{G}(\mathbf{k},\omega_\nu), \qquad \mathcal{F}^\dagger(\mathbf{x},\omega_\nu) = \int \frac{d^3\mathbf{k}}{(2\pi)^3}\, e^{i\mathbf{k}\cdot\mathbf{x}}\mathcal{F}^\dagger(\mathbf{k},\omega_\nu), \tag{III.146}$$

we find that EQs. (III.143) and (III.144) take the following simple forms:

$$\left[i\omega_\nu - \left(\frac{k^2}{2m} - \mu\right)\right]\mathcal{G}(\mathbf{k};\omega_\nu) + \Delta\,\mathcal{F}^\dagger(\mathbf{k};\omega_\nu) \equiv \left[i\omega_\nu - \xi_\mathbf{k}\right]\mathcal{G}(\mathbf{k};\omega_\nu) + \Delta\,\mathcal{F}^\dagger(\mathbf{k};\omega_\nu) = 1, \tag{III.147}$$

$$\left[-i\omega_\nu - \left(\frac{k^2}{2m} - \mu\right)\right]\mathcal{F}^\dagger(\mathbf{k};\omega_\nu) - \Delta^*\mathcal{G}(\mathbf{k};\omega_\nu) \equiv \left[-i\omega_\nu - \xi_\mathbf{k}\right]\mathcal{F}^\dagger(\mathbf{k};\omega_\nu) - \Delta^*\mathcal{G}(\mathbf{k};\omega_\nu) = 0. \tag{III.148}$$

Solving EQs. (III.147) and (III.148), we obtain

$$\mathcal{G}(\mathbf{k};\omega_\nu) = \frac{-(i\omega_\nu + \xi_\mathbf{k})}{\omega_\nu^2 + \xi_\mathbf{k}^2 + |\Delta|^2}, \tag{III.149}$$

$$\mathcal{F}^\dagger(\mathbf{k};\omega_\nu) = \frac{\Delta^*}{\omega_\nu^2 + \xi_\mathbf{k}^2 + |\Delta|^2}. \tag{III.150}$$

In the absence of an applied field, the superconducting gap Δ can be taken as real without loss of generality. Therefore, $\mathcal{F}^\dagger(\mathbf{k};\omega_\nu) = \mathcal{F}(\mathbf{k};\omega_\nu)$ and EQs. (III.149) and (III.150) become

$$\mathcal{G}(\mathbf{k};\omega_\nu) = \frac{u_\mathbf{k}^2}{i\omega_\nu - E_\mathbf{k}} + \frac{v_\mathbf{k}^2}{i\omega_\nu + E_\mathbf{k}}, \tag{III.151}$$

$$\mathcal{F}^\dagger(\mathbf{k};\omega_\nu) = \mathcal{F}(\mathbf{k};\omega_\nu) = -u_\mathbf{k}v_\mathbf{k}\left[\frac{1}{i\omega_\nu - E_\mathbf{k}} + \frac{1}{i\omega_\nu + E_\mathbf{k}}\right], \tag{III.152}$$

where

$$E_\mathbf{k} \equiv \left(\xi_\mathbf{k}^2 + |\Delta|^2\right)^{1/2}, \tag{III.153}$$

$$u_\mathbf{k}v_\mathbf{k} = \frac{\Delta}{2E_\mathbf{k}}, \tag{III.154}$$

$$v_{\mathbf{k}}^2 = 1 - u_{\mathbf{k}}^2 = \frac{1}{2}\left(1 - \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}}\right). \tag{III.155}$$

Here $E_{\mathbf{k}}$ denotes the quasiparticle energy and $v_{\mathbf{k}}^2$ represents the distribution function for quasiparticles, as illustrated in Fig. III.2.1. Additionally, by inserting EQ. (III.150) into the self-consistent expression in EQ. (III.145) for the present uniform medium, we obtain

$$\Delta = \frac{\gamma}{\beta}\lim_{\eta\to 0+}\sum_{\nu} e^{-i\omega_\nu \eta}\mathcal{F}^{\dagger}\left(\mathbf{x}=0;\omega_\nu\right) = \frac{\gamma}{\beta}\sum_{\nu}\int\frac{d^3\mathbf{k}}{\left(2\pi\right)^3}\frac{\Delta}{\omega_\nu^2 + E_{\mathbf{k}}^2}. \tag{III.156}$$

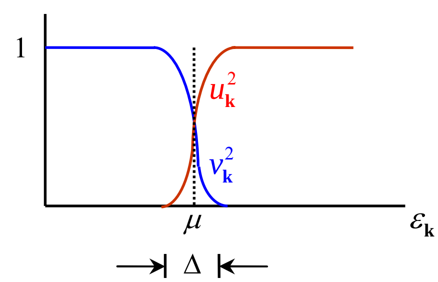

Fig.III.2.1 The dependence of the distribution functions $v_{\mathbf{k}}^2\left(=1-u_{\mathbf{k}}^2\right)$ and $u_{\mathbf{k}}^2$ of superconductors on the normal state energy $\varepsilon_{\mathbf{k}}$, assuming T = 0. The occupied state distribution function $v_{\mathbf{k}}^2$ exhibits a smooth energy spread on the order of the superconducting gap Δ around the chemical potential μ. This behavior differs from the Fermi liquid theory where a discontinuity in the distribution function, known as the quasiparticle residue Z_k, exists at the Fermi level.

For *s*-wave superconductors the superconducting energy gap Δ is independent of **k** and therefore can be cancelled out in EQ. (III.156), which leads to the following relation:

$$1 = \gamma\int\frac{d^3\mathbf{k}}{\left(2\pi\right)^3}\frac{1}{2E_{\mathbf{k}}}\tanh\left(\frac{1}{2}\beta E_{\mathbf{k}}\right) \approx \mathcal{N}\left(\varepsilon_F\right)\gamma\int_0^{\omega_D}\frac{d\xi}{\left(\xi^2+\Delta^2\right)^{1/2}}\tanh\left(\frac{\left(\xi^2+\Delta^2\right)^{1/2}}{2k_B T}\right), \tag{III.157}$$

where $\mathcal{N}\left(\varepsilon_F\right)$ denotes the density of states at the Fermi level. Therefore, this superconducting gap equation takes the following form in extreme temperature limits:

$$1 \approx \mathcal{N}\left(\varepsilon_F\right)\gamma\int_0^{\omega_D}\frac{d\xi}{\left(\xi^2+\Delta^2\right)^{1/2}}, \qquad \left(T\to 0\right) \tag{III.158}$$

$$1 \approx \mathcal{N}\left(\varepsilon_F\right)\gamma\int_0^{\omega_D}\frac{d\xi}{\xi}\tanh\left(\frac{\xi}{2k_B T_c}\right). \qquad \left(T\to T_c^-\right) \tag{III.159}$$

The temperature dependence of the superconducting gap can be obtained by numerically solving for Δ(T) in EQ. (III.157), although simpler analytical forms may be derived for special cases such as the weak coupling limit, which you will be asked to consider in Problem Set 4. The limiting behavior of Δ(T) satisfies the following temperature dependence:

$$\Delta(T) \approx \Delta_0 - \left(2\pi\Delta_0 k_B T\right)^{1/2} \exp\left(-\frac{\Delta_0}{k_B T}\right), \qquad \left(T \ll T_c\right) \qquad \text{(III.160)}$$

$$\Delta(T) \approx k_B T_c \pi \left(\frac{8}{7\zeta(3)}\right)^{1/2} \left(1-\frac{T}{T_c}\right)^{1/2} \approx 3.06 k_B T_c \left(1-\frac{T}{T_c}\right)^{1/2}, \qquad \left(T_c - T \ll T_c\right) \qquad \text{(III.161)}$$

To find an expression for T_c, we note that $\omega_D \gg 2k_B T_c$ so that the integral in EQ. (III.159) becomes

$$\int_0^{\omega_D} \frac{d\xi}{\xi} \tanh\left(\frac{\xi}{2k_B T_c}\right) = \int_0^{\omega_D/2k_BT} \frac{dz}{z} \tanh(z) = \ln(z)\tanh(z)\Big|_0^{\omega_D/2k_BT} - \int_0^{\omega_D/2k_BT} dz \ln(z) \operatorname{sech}^2(z)$$

$$\approx \ln\left(\frac{\omega_D}{2k_B T_c}\right) - \int_0^{\infty} dz \ln(z)\operatorname{sech}^2(z) \approx \ln\left(\frac{\omega_D}{2k_B T_c}\right) + \ln\left(\frac{4e^{\gamma_0}}{\pi}\right) = \ln\left(\frac{2e^{\gamma_0}\omega_D}{\pi k_B T_c}\right) \quad \left(\gamma_0 \approx 0.5772\right), \qquad \text{(III.162)}$$

so that

$$k_B T_c \approx \frac{2e^{\gamma_0}}{\pi} \omega_D \exp\left[-\left(\frac{1}{\mathcal{N}(\varepsilon_F)\gamma}\right)\right] \approx 1.13\, \omega_D \exp\left[-\left(\frac{1}{\mathcal{N}(\varepsilon_F)\gamma}\right)\right]. \qquad \text{(III.163)}$$

Therefore, we find that the superconducting transition temperature increases with the increasing electronic density of states at the Fermi level $\mathcal{N}(\varepsilon_F)$, electron-phonon coupling strength γ, and the Debye frequency ω_D of phonons. From EQs. (III.110) and (III.163), we also note that

$$\frac{\Delta_0}{k_B T_c} = \frac{\pi}{e^{\gamma_0}} \approx 1.76, \qquad \text{(III.164)}$$

which is a universal number in BCS superconductors. Moreover, for simple metals the Debye frequency is inversely proportional to the square root of the ionic mass M, *i.e.* $\omega_D \propto M^{-1/2}$ and therefore $T_c \propto M^{-1/2}$. The dependence of the superconducting transition temperature on the ionic mass of the superconductor is known as *the isotope effect*. In general, $T_c \propto M^{-\alpha}$ for conventional superconductors and typically $\alpha \le 0.5$. In the case of high-temperature superconductors, the isotope effect in the context of phonon-mediated pairing no longer holds. Specifically, the power α depends sensitively on the doping level, and for a given family of cuprate superconductors, it is found that $\alpha \approx 0$ near the optimal doping level where the cuprate exhibits maximum T_c, and α increases with decreasing doping level. Clearly the phonon-mediated pairing mechanism for conventional superconductors cannot account for the experimental findings in high-temperature superconducting cuprates.

Next, we compare the results of BCS theory with thermodynamic functions of superconductors. We first consider the change in the thermodynamic potential between the superconducting state (Ω_S) and the normal state (Ω_N) as the result of an attractive electron-phonon interaction Hamiltonian $\hat{H}_{e\text{-}ph}$:

$$\Omega_S - \Omega_N = \int_0^1 \frac{d\lambda}{\lambda} \left\langle \lambda \hat{H}_{e-ph} \right\rangle = -\frac{1}{2} \int_0^{\gamma} \frac{d\gamma'}{\gamma'} \int d^3\mathbf{x}\, \gamma' \left\langle \psi_\alpha^\dagger(\mathbf{x}) \psi_\beta^\dagger(\mathbf{x}) \psi_\beta(\mathbf{x}) \psi_\alpha(\mathbf{x}) \right\rangle$$

$$\approx -\int_0^{\gamma} d\gamma' \left(\frac{1}{\gamma'}\right)^2 \int d^3\mathbf{x} \left|\Delta(\mathbf{x})\right|^2, \qquad \text{(III.165)}$$

where we have used the definition of Δ in EQ. (III.142). For a uniform system, EQ. (III.165) can be simplified into the following expression:

$$\begin{aligned}\Omega_S-\Omega_N&=-\Omega\int_0^{\gamma}d\gamma'\left(\frac{1}{\gamma'}\right)^2\Delta^2\\&=\Omega\int_0^{\gamma}d\gamma'\frac{d(1/\gamma')}{d\gamma'}\Delta^2=\Omega\int_0^{\Delta}d\Delta'\frac{d(1/\gamma)}{d\Delta'}(\Delta')^2\ ,\end{aligned}\qquad\text{(III.166)}$$

where in the last line we have changed variables from the electron-phonon coupling coefficient γ to the superconducting gap Δ because they are related by EQ. (III.157). Inserting EQ. (III.157) into EQ. (III.166), we obtain

$$\begin{aligned}\frac{\Omega_S-\Omega_N}{\Omega}&=\mathcal{N}(\varepsilon_F)\int_0^{\omega_D}d\xi\int_0^{\Delta}d\Delta'(\Delta')^2\frac{\partial}{\partial\Delta'}\left\{\frac{1}{E'}\tanh\left(\frac{\beta E'}{2}\right)\right\}\\&=\mathcal{N}(\varepsilon_F)\int_0^{\omega_D}d\xi\left[\frac{\Delta^2}{E}\tanh\left(\frac{\beta E}{2}\right)-2\int_0^{\Delta}d\Delta'\frac{\Delta'}{E'}\tanh\left(\frac{\beta E'}{2}\right)\right]\\&=\frac{\Delta^2}{\gamma}-\left[2\mathcal{N}(\varepsilon_F)\int_0^{\omega_D}d\xi\int_0^{\Delta}d\Delta'\frac{\Delta'}{E'}\tanh\left(\frac{\beta E'}{2}\right)\right]\\&=\frac{\Delta^2}{\gamma}-\left[2\mathcal{N}(\varepsilon_F)\int_0^{\omega_D}d\xi\int_0^{E}dE'\tanh\left(\frac{\beta E'}{2}\right)\right]\\&=\frac{\Delta^2}{\gamma}-\left[\frac{4\mathcal{N}(\varepsilon_F)}{\beta}\int_0^{\omega_D}d\xi\ln\left(\frac{\cosh(\beta E/2)}{\cosh(\beta\xi/2)}\right)\right]\\&=\frac{\Delta^2}{\gamma}-\frac{4\mathcal{N}(\varepsilon_F)}{\beta}\int_0^{\omega_D}d\xi\left[\ln\left(1+e^{-\beta E}\right)+\frac{1}{2}\beta(E-\xi)\right]+\frac{4\mathcal{N}(\varepsilon_F)}{\beta}\int_0^{\omega_D}d\xi\ln\left(1+e^{-\beta\xi}\right).\end{aligned}\qquad\text{(III.167)}$$

At low temperatures where $\beta\omega_D\gg 1$, the last term of EQ. (III.167) may be approximated by

$$\frac{4\mathcal{N}(\varepsilon_F)}{\beta}\int_0^{\omega_D}d\xi\ln\left(1+e^{-\beta\xi}\right)\approx\frac{4\mathcal{N}(\varepsilon_F)}{\beta}\int_0^{\infty}d\xi\ln\left(1+e^{-\beta\xi}\right)=\frac{4\mathcal{N}(\varepsilon_F)}{\beta^2}\frac{\pi^2}{12}=\mathcal{N}(\varepsilon_F)\frac{\pi^2}{3}(k_BT)^2.\qquad\text{(III.168)}$$

In addition, the third term in EQ. (III.167) is

$$\begin{aligned}-2\mathcal{N}(\varepsilon_F)\int_0^{\omega_D}d\xi(E-\xi)&\approx-\mathcal{N}(\varepsilon_F)\left[\frac{1}{2}\Delta^2+\Delta^2\ln\left(\frac{2\omega_D}{\Delta}\right)\right]\\&=-\mathcal{N}(\varepsilon_F)\left[\frac{1}{2}\Delta^2+\Delta^2\ln\left(\frac{2\omega_D}{\Delta_0}\right)+\Delta^2\ln\left(\frac{\Delta_0}{\Delta}\right)\right]=-\mathcal{N}(\varepsilon_F)\left[\frac{1}{2}\Delta^2+\frac{\Delta^2}{\mathcal{N}(\varepsilon_F)\gamma}+\Delta^2\ln\left(\frac{\Delta_0}{\Delta}\right)\right]\\&=-\frac{1}{2}\mathcal{N}(\varepsilon_F)\Delta^2-\frac{\Delta^2}{\gamma}-\mathcal{N}(\varepsilon_F)\Delta^2\ln\left(\frac{\Delta_0}{\Delta}\right),\end{aligned}\qquad\text{(III.169)}$$

where we have used EQ. (III.110) with $\gamma = V/2$ in the second line of EQ. (III.169) and Δ_0 refers to the superconducting gap at $T = 0$. Inserting EQs. (III.168) and (III.169) into EQ. (III.167), we obtain

$$\frac{\Omega_S-\Omega_N}{\Omega}\approx-\frac{\Delta^2}{2}\mathcal{N}(\varepsilon_F)\left[1+2\ln\left(\frac{\Delta_0}{\Delta}\right)\right]+\mathcal{N}(\varepsilon_F)\frac{\pi^2}{3}(k_BT)^2-4k_BT\mathcal{N}(\varepsilon_F)\int_0^{\omega_D}d\xi\,\ln\left(1+e^{-\beta E}\right). \quad \text{(III.170)}$$

In the $T\to 0$ limit, EQ. (III.170) yields the thermodynamic potential difference

$$\frac{\Omega_S-\Omega_N}{\Omega}=-\frac{\Delta_0^2}{2}\mathcal{N}(\varepsilon_F). \quad \text{(III.171)}$$

Moreover, from EQ. (III.170) and the relation between the thermodynamic potential and the free energy, we arrive at the following for the free energy in the low temperature limit:

$$\frac{F_S-F_N}{\Omega}\approx-\frac{\Delta^2}{2}\mathcal{N}(\varepsilon_F)+\mathcal{N}(\varepsilon_F)\frac{\pi^2}{3}(k_BT)^2. \quad \text{(III.172)}$$

To find the specific heat in the $T\to 0$ limit, we approximate the last term in EQ. (III.170) by setting $\omega_D\to\infty$ and $\Delta\approx\Delta_0$ so that

$$\int_0^{\omega_D}d\xi\,\ln\left(1+e^{-\beta E}\right)\approx\int_0^{\infty}d\xi\,\ln\left\{1+\exp\left[-\beta\left(\xi^2+\Delta_0^2\right)^{1/2}\right]\right\}\approx\int_0^{\infty}d\xi\,\exp\left[-\beta\left(\xi^2+\Delta_0^2\right)^{1/2}\right]$$
$$\approx\int_0^{\infty}d\xi\,e^{-\beta\Delta_0\left(1+\frac{1}{2}\frac{\xi^2}{\Delta_0^2}\right)}=e^{-\beta\Delta_0}\int_0^{\infty}d\xi\,e^{-\frac{\beta\xi^2}{2\Delta_0}}=\frac{1}{2}e^{-\beta\Delta_0}\left(2\Delta_0\pi\beta^{-1}\right)^{1/2}. \quad \text{(III.173)}$$

Therefore,

$$\frac{\Omega_S}{\Omega}\approx\frac{\Omega_N(T=0)}{\Omega}-\frac{\Delta_0^2}{2}\mathcal{N}(\varepsilon_F)-2\mathcal{N}(\varepsilon_F)e^{-\beta\Delta_0}\left(2\pi\Delta_0\beta^{-3}\right)^{1/2}, \quad \text{(III.174)}$$

and the electronic specific heat in the superconducting state becomes

$$\frac{C_S}{\Omega}\approx 2\mathcal{N}(\varepsilon_F)\Delta_0k_Be^{-\Delta_0/(k_BT)}\left(\frac{2\pi\Delta_0}{k_BT}\right)^{1/2}, \qquad (T\to 0) \quad \text{(III.175)}$$

which confirms the phenomenology discussed in Part III.1.

To find the specific heat near T_c where $\beta\Delta\ll 1$, we consider the expression for thermodynamic potential in EQ. (III.166) and express the term $(1/\gamma)$ using EQ. (III.156) as follows:

$$\frac{1}{\gamma}=\frac{1}{\beta}\mathcal{N}(\varepsilon_F)\int_{-\omega_D}^{\omega_D}d\xi\sum_\nu\frac{1}{\omega_\nu^2+E_{\mathbf{k}}^2}=\frac{2}{\beta}\mathcal{N}(\varepsilon_F)\int_0^{\omega_D}d\xi\sum_\nu\frac{1}{\omega_\nu^2+\left(\xi^2+\Delta^2\right)}$$
$$=\frac{2}{\beta}\mathcal{N}(\varepsilon_F)\int_0^{\omega_D}d\xi\sum_\nu\left[\frac{1}{\omega_\nu^2+\xi^2}-\frac{\Delta^2}{\left(\omega_\nu^2+\xi^2\right)^2}+\cdots\right]. \quad \text{(III.176)}$$

Taking derivative of EQ. (III.176) relative to Δ and inserting the result into EQ. (III.166), we obtain

$$\frac{\Omega_S-\Omega_N}{\Omega}\approx-\frac{\mathcal{N}(\varepsilon_F)\Delta^4}{\beta}\int_0^{\omega_D}d\xi\sum_\nu\frac{1}{\left(\omega_\nu^2+\xi^2\right)^2}\approx-\frac{\mathcal{N}(\varepsilon_F)\Delta^4}{\beta}\sum_\nu\int_0^{\infty}d\xi\frac{1}{\left(\omega_\nu^2+\xi^2\right)^2}$$

$$= -\frac{\mathcal{N}(\varepsilon_F)\Delta^4}{\beta}\sum_{\nu}\frac{\pi}{4}\frac{1}{\omega_\nu^3} = -\frac{\mathcal{N}(\varepsilon_F)\Delta^4\beta^2}{2\pi^2}\sum_{\nu=0}^{\infty}\frac{1}{(2\nu+1)^3}$$

$$= -\frac{\mathcal{N}(\varepsilon_F)\Delta^4\beta^2}{2\pi^2}\frac{7\zeta(3)}{8}$$

$$= -\frac{8}{7\zeta(3)}\mathcal{N}(\varepsilon_F)(\pi k_B T_c)^2\frac{1}{2}\left(1-\frac{T}{T_c}\right)^2, \qquad \text{(III.177)}$$

where we have used EQ. (III.161) in the last line of EQ. (III.177). Hence, the specific heat difference at T_c becomes

$$\left.\frac{C_S - C_N}{\Omega}\right|_{T_c} \approx \frac{8}{7\zeta(3)}\mathcal{N}(\varepsilon_F)\left(\pi^2 k_B^2 T_c\right). \qquad \text{(III.178)}$$

Noting that

$$\frac{C_N}{\Omega} \approx \mathcal{N}(\varepsilon_F)\frac{2\pi^2}{3}\left(k_B^2 T\right), \qquad \text{(III.179)}$$

we find that

$$\left.\frac{C_S - C_N}{C_N}\right|_{T_c} \approx \frac{12}{7\zeta(3)} \approx 1.43. \qquad \text{(III.180)}$$

A schematic illustration of the electronic specific heat of a superconductor is shown in Fig. III.2.2. The discontinuity ratio as given in EQ. (III.180) is supposedly universal and independent of material properties, which is in reasonable agreement with empirical findings in simple conventional superconductors.

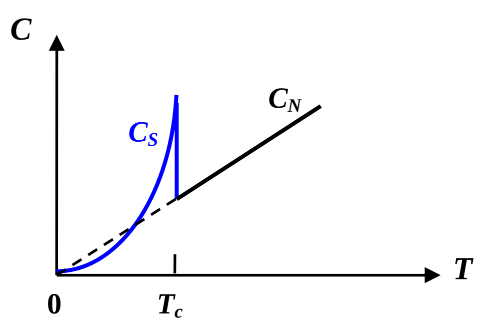

Fig.III.2.2 Schematic illustration of the electronic specific heat (C) of a BCS superconductor as a function of temperature (T), showing exponentially decreasing specific heat with decreasing temperature at $T \to 0$, a linear temperature dependence above T_c, and a discontinuity at T_c.

Overall, BCS theory has been successful in explaining the thermodynamic and electrodynamic properties of conventional superconductors where superconductivity is a well defined ground state mediated by the electron-phonon interaction. However, in the case of strongly correlated superconductors with a ground state not uniquely defined by superconductivity, such as in high-temperature superconducting cuprates and some of the heavy fermion superconductors, the predictability power of BCS theory diminishes, and a new paradigm of microscopic theory is needed to account for the pairing mechanism and the anomalous low-energy excitations.

One of the most powerful tools in the investigation of the pairing symmetry and low-energy excitations of novel superconductors is the quasiparticle tunneling spectroscopy, particularly the scanning tunneling spectroscopy (STS) that provides high spatial and energy resolution, and the angle-resolved photo-emission spectroscopy (ARPES) that provides complementary momentum and energy resolution. In the following section, we investigate the theory of quasiparticle tunneling in superconductors and discuss how to apply the theory to investigation of the pairing symmetry of unconventional superconductors.