An amendment of the BCS theory of superconductivity

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Abstract—Although the BCS theory of superconductivity is a well established theory, we have shown that the phenomenology predicted by this model is much richer than previously believed. By releasing the constraint that the attraction band is symmetric with respect to the chemical potential of the system, we observed that the energy gap may have more than one solution, the quasiparticle imbalance may appear in equilibrium, and the transition between the superconducting and the normal metal phases may be of the first order. The temperature of the superconductor-normal metal phase transition changes with the asymmetry of the attraction band and if we plot the phase transition temperature vs the chemical potential, we obtain a bell shaped curve, similarly to the superconducting dome, generally formed in high-Tc superconductors, but also in superconductors with narrow conduction bands.

While the pairing interaction is a microscopic characteristic of the system, determined by the effective interactions between constituent quasiparticles, the chemical potential is a macroscopic quantity, which can be changed by external conditions, like doping and pressure. Furthermore, if the conduction band of the system is narrow, then the attraction band is constrained to the conduction band and the chemical potential is not necessary in the center, as it happens in some of the bands in In-doped Pb,Sn_{1−x} and in MgB_{2}. For these reasons, the constraint that the attraction band is symmetric with respect to the chemical potential may be released.

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chemical potential of the system is $\mu_R$ and $\mu_R \neq \mu$, then the phenomenology predicted by the model changes dramatically: the energy gap changes and a quasiparticle imbalance appears in equilibrium. Furthermore, not only that the temperature of the superconductor-normal metal phase transition changes, but the phase transition changes qualitatively, becoming of the first order. If we denote the phase transition temperature by $T_{ph}$, to differentiate it from the BCS critical temperature $T_c$, and plot it vs the difference $\mu_R - \mu$, we observe that it has a maximum at $\mu_R - \mu = 0$ and decreases monotonically with $|\mu_R - \mu|$. For $|\mu_R - \mu| \geq 2\Delta_0$ the superconducting phase does not form anymore, i.e. $T_{ph} = 0$.

The difference $\mu_R - \mu$ is a measure of the asymmetry of the attraction band with respect to the chemical potential. The chemical potential may be influenced by pressure or doping, so if we assume that the asymmetry has a monotonic dependence on any of these parameters, then the phase transition temperature may form a maximum when plotted against that parameter, like the superconducting dome, generally observed in high-$T_c$ superconductors. Furthermore, in certain materials, like MgB$_2$ [4], [5] and In-doped Pb$_2$Sn$_{1-x}$ [6], the extremum of at least one of the conduction bands lies close enough to the chemical potential to lead to an asymmetric attraction band. In such materials, the asymmetric attraction band changes with pressure or doping.

We are not aware of any single-band superconductors with asymmetric attraction band. Nevertheless, this constitutes our first step in the study of the effects of such an asymmetry on the properties of the superconducting phase and the results, as mentioned above, are significant. The extension of these results to multi-band superconductors will constitute the subject of another study.

The main result of this paper is the dependence of the phase transition temperature on the asymmetry of the attraction band, $\mu_R - \mu$. Nevertheless, to make the paper more readable we shall introduce in Section II the basic concepts and notations, whereas the main result will be presented and discussed in Section III. The conclusions are presented in Section IV.

II. THE STANDARD BCS MODEL

Here we introduce briefly the basic notations and concepts. We denote by $|k\rangle$ the electron’s wavefunction, where $k$ is the electron’s wavevector and $s \equiv \uparrow, \downarrow$ is the electron’s spin. If $c_{ks}^\dagger$ and $c_{ks}$ are the electrons creation and annihilation operators, then the BCS Hamiltonian reads [1], [2]

$$\hat{H}_{BCS} = \sum_{ks} \epsilon_{ks}^{(0)} c_{ks}^\dagger c_{ks} + \sum_{kl} V_{kl} c_{k\uparrow}^\dagger c_{-l\uparrow}^\dagger c_{-l\downarrow}^\dagger c_{k\downarrow}^\dagger.$$  \hspace{1cm} (1)

Introducing the notation $b_k = \langle c_{-k\uparrow} c_{k\uparrow} \rangle$ (where by $\langle \cdot \rangle$ we denote the average) and replacing $c_{-k\downarrow} c_{k\downarrow}$ in (1) by the equivalent form $b_k + (c_{-k\uparrow} c_{k\uparrow} - b_k)$, keeping only the first order terms in the difference $(c_{-k\uparrow} c_{k\uparrow} - b_k)$, one arrives to a Hamiltonian which is quadratic in the operators $c_{ks}^\dagger$ and $c_{ks}$ and may be diagonalized (see for example [2] for a good introduction). After diagonalization, one obtains

$$\hat{H} = \mu \hat{N} + \sum_k (\xi_k - \epsilon_k + \Delta b_k) c_{ks}^\dagger c_{ks} + \sum_k \xi_k (\gamma_{k\uparrow} \gamma_{k\downarrow} + \gamma_{k\downarrow}^\dagger \gamma_{k\uparrow}^\dagger),$$  \hspace{1cm} (2)

where $\hat{N} = \sum_{ks} c_{ks}^\dagger c_{ks}$ is the particle number operator, $\xi_k \equiv \epsilon_{ks}^{(0)} - \mu$, $\epsilon_k \equiv \sqrt{\xi_k^2 + \Delta_k^2}$, $\Delta_k \equiv \sum_l V_{kl} b_l$ is the superconducting energy gap, and $\mu$ is a constant which will be identified with the center of the attraction band. The quasiparticle creation and annihilation operators introduced in (2) are $\xi_k = u_k \gamma_{k\uparrow} + v_k \gamma_{k\downarrow}^\dagger$, $\xi_k = u_k \gamma_{k\downarrow}^\dagger + v_k \gamma_{k\uparrow}$, $c_{k\uparrow} = -v_k \gamma_{k\uparrow}^\dagger + u_k \gamma_{k\downarrow}$, and $c_{k\downarrow} = -v_k \gamma_{k\downarrow} + u_k \gamma_{k\uparrow}^\dagger$, where $u_k$ and $v_k$ are

$$|v_k|^2 = 1 - |u_k|^2 = \frac{1}{2} \left(1 - \frac{\xi_k}{\epsilon_k}\right).$$  \hspace{1cm} (3)

To simplify the equations to be able to perform analytical calculations, one in general makes the assumption that $V_{kl} \equiv -V$ for any $k$ and $l$, such that both, $\xi_k^{(0)}$, $\epsilon_k^{(0)} \in I_V = (\mu - \hbar \omega_c, \mu + \hbar \omega_c)$. In such a case, the energy gap becomes independent of $k$,

$$\Delta = -V \sum_{k} \langle c_{-k\uparrow} c_{k\uparrow}\rangle.$$  \hspace{1cm} (4)

Replacing in (4) the electrons creation and annihilation operators by their expressions in terms of the quasiparticle operators,
The assumption that the formalism. The standard BCS results are obtained under such a case, the zero temperature solution

\[ \Delta = 0 \]

is the value of the energy gap at \( T = 0 \) to \( T = \infty \).

Similarly, the total energy of the system is

\[ \mathcal{H} = E_0 + \sum_k \xi_k (\gamma_{k0}^\dagger \gamma_{k0} + \gamma_{k1}^\dagger \gamma_{k1}), \]

where

\[ E_0 = \mu N + \sum_k (\xi_k - \epsilon_k) + \frac{\Delta^2}{V}. \]

and is plotted as the upper curve in Fig. 1. The solutions \( \Delta \) of Eqs. (10) for \( (\mu_R - \mu)/\Delta_0 = 0, 0.5, 1, 1.5, 1.9; \ \Delta_0 \) is the value of the energy gap at \( T = 0 \); whereas \( T_c \) is the BCS critical temperature for a symmetric band.

one arrives to the equation for the energy gap

\[ 1 = \frac{V}{2} \sum_k \frac{1 - n_{k0} - n_{k1}}{\epsilon_k}, \]

where \( n_{ki} = \langle \gamma_{ki}^\dagger \gamma_{ki} \rangle \).

Until now, the chemical potential of the system did not enter the formalism. The standard BCS results are obtained under the assumption that \( \mu \) is equal to the chemical potential. In such a case, the zero temperature solution \( \Delta(T = 0) = \Delta_0 \) is obtained by setting \( n_{ki} = 0 \) for any \( k \) and \( i = 0, 1 \) in (5). If the electrons single-particle energy spectrum have a constant density of states \( \sigma_0 \) for each spin projection, then in the low coupling limit \( (\sigma_0 V \ll 1) \), \( \Delta_0 = 2h\omega_c \exp[-1/(\sigma_0 V)] \).

Similarly, by setting \( \Delta = 0 \) in (5), one obtains the critical temperature \( T_c = (A/2\omega_c/k_B)e^{-1/(\sigma_0 V)} \), where \( A = 2e^\gamma/\pi \approx 1.13 \) and \( \gamma \approx 0.577 \) is the Euler’s constant (see [2] for details). The solution of (5) for \( T = 0 \) to \( T_c \) is plotted as the upper curve in Fig. 1.

III. SUPERCONDUCTIVITY FOR ASYMMETRIC ATTRACTION BAND

Let us denote the chemical potential of the system by \( \mu_R \) and generalize the results from the previous section by assuming that \( \mu_R \) may be different from \( \mu \). In such a case, the attraction band is not symmetric with respect to the chemical potential \( \mu_R \). To calculate the partition function, we follow [3] and write the (average) total particle number as

\[ N \equiv \langle \{n_{ki} \}, \mu | \hat{N} | \{n_{ki} \}, \mu \rangle = N_0 + \sum_{k, i} \frac{\xi_k}{\epsilon_k}, \]

where \( N_0 = N' + \sum_k 2\epsilon_k^2 \) and \( N' \) is the number of particles from outside of the energy interval \([\mu - \hbar \omega_c, \mu + \hbar \omega_c] \).

Similarly, the total energy of the system is

\[ \mathcal{H} = E_0 + \sum_k \epsilon_k (\gamma_{k0}^\dagger \gamma_{k0} + \gamma_{k1}^\dagger \gamma_{k1}), \]

where

\[ E_0 = \mu N + \sum_k (\xi_k - \epsilon_k) + \frac{\Delta^2}{V}. \]

and \( N \) is given by Eq. (6).

The partition function is

\[ \ln(\mathcal{Z})_\beta \mu = -\sum_{ki} [(1 - n_{ki}) \ln(1 - n_{ki}) + n_{ki} \ln n_{ki}] - \beta(E - \mu_R N), \]

where \( N \) and \( E \equiv \langle \mathcal{H} \rangle \) are given by (6) and (5). Maximizing \( \ln(\mathcal{Z})_\beta \mu \) with respect to the populations \( n_{ki} \) (see [3] for details), we obtain a system of equations which have to be solved self-consistently to determine the energy gap and the populations. If the electrons single-particle energy spectrum is \( \sigma_0 \) (is constant), this system reads

\[ \frac{2}{\sigma_0 V} = \int_{-\hbar \omega_c}^{\hbar \omega_c} \frac{1 - n_{k0} - n_{k1}}{\epsilon(\xi)} d\xi, \]

\[ n_{\xi i} = \frac{1}{e^{\beta(\epsilon(\xi) - (\mu_R - \mu - \xi)/\epsilon(\xi))} + 1}, \quad i = 0, 1 \]

\[ F \equiv \int_{-\hbar \omega_c}^{\hbar \omega_c} (1 - n_{k0} - n_{k1}) \frac{d\xi}{\epsilon(\xi)}. \]

The set (10) is symmetric under the interchange \( \mu_R - \mu \rightarrow \mu - \mu_R, \ F \rightarrow -F, \) and \( \xi \rightarrow -\xi \). So, by solving it for \( \mu_R - \mu > 0 \), we obtain all the solutions, including those for \( \mu_R - \mu < 0 \).

In Fig. 1 we present the solutions for the energy gap, obtained for different values of \( \mu_R - \mu \). We see that if \( \mu_R \neq \mu \), the energy gap is smaller than the standard BCS gap—which is the top black curve in Fig. 1—at any temperature and the phase transition temperature \( T_{ph} \) is also smaller that the BCS critical temperature \( T_c \). Nevertheless, eventually the most important feature that appears when \( \mu_R \neq \mu \) is that the phase transition
occurs abruptly, in the sense that the energy gap jumps from a finite value to zero, at $T_{ph}$.

In Fig. 2 we plot the phase transition temperature vs $\mu_R - \mu$. We see that the function $T_{ph}(\mu_R - \mu)$ has a maximum at $\mu_R = \mu$ and decreases to zero as $|\mu_R - \mu|$ increases to $2\Delta_0$. If $|\mu_R - \mu| \geq 2\Delta_0$, the energy gap cannot be formed anymore and the superconducting phase does not exist. If the difference $\mu_R - \mu$ varies monotonically with pressure or doping, then $T_{ph}$ plotted vs pressure or doping forms a kind of superconducting dome. A similar behavior was observed also in superconductors with asymmetric attraction band, for example in [6].

IV. Conclusions

We have briefly reviewed the BCS formalism for asymmetric attraction band proposed in [3] and we calculated the temperature of the superconductor-normal metal phase transition for $\mu_R - \mu$ taking values in the interval $[-2\Delta_0, 2\Delta_0]$, where $\Delta_0$ is the energy gap in the standard BCS theory, at zero temperature. For $|\mu_R - \mu| \geq 2\Delta_0$ the energy gap is zero at any temperature and therefore the superconducting phase cannot exist. The phase transition temperature is maximum when $\mu_R = \mu$ and decreases monotonically when $|\mu_R - \mu|$ increases. The phase transition is in general of the order 1, except for the case when $\mu_R = \mu$, when we obtain the standard BCS transition of the second order. If for a certain material the difference $\mu_R - \mu$ varies monotonically with pressure or doping, then the plot of the phase transition temperature vs these variables lead to a form similar to the superconducting dome or to the bell-shape form obtained in In-doped Pb$_x$Sn$_{1-x}$[6].

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