Third-order phase transition and superconductivity in thin films

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ABSTRACT

We have found a new mean field solution in the BCS theory of superconductivity. This unconventional solution indicates the existence of superconducting phase transitions of third order in thin films, or in bulk matter with a layered structure. The critical temperature increases with decreasing thickness of the layer, and does not exhibit the isotope effect. The electronic specific heat is a continuous function of temperature with a discontinuity in its derivative.

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1 Introduction

The BCS theory of superconductivity [1] has been very successful in explaining properties of a large class of simple superconductors in terms of just two experimental parameters, namely the squared electron-phonon coupling constant $g$ and the Debye frequency $\omega_D$. The BCS theory in its simplest form is based on the following so-called BCS reduced grand canonical Hamiltonian,

$$H = \sum_{\mathbf{k},\sigma} \xi_\mathbf{k} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} - \frac{g}{V} \sum_{\mathbf{k},\mathbf{k}'} \Theta(h\omega_D - |\xi_\mathbf{k}|) \Theta(h\omega_D - |\xi_{\mathbf{k}'}|) a_{\mathbf{k},+}^\dagger a_{\mathbf{k},-}^\dagger a_{\mathbf{k}',-} a_{\mathbf{k}',+}$$  \hspace{1cm} (1)

where the quantities $\mathbf{k}$ and $\mathbf{k}'$ are wave vector variables, the quantity $\sigma = \pm$ is the spin projection, and the symbols $a_{\mathbf{k}\sigma}$ and $a_{\mathbf{k}\sigma}^\dagger$ are electron field operators. Furthermore,

$$\xi_\mathbf{k} = \frac{\hbar^2 k^2}{2m} - \mu$$  \hspace{1cm} (2)

where $\mu$ is the chemical potential and $m$ is the electron mass. Finally, $V$ is the volume of the system. The sum over $\mathbf{k}$ and $\mathbf{k}'$ in Eq. (1) is restricted by the conditions $|\xi_\mathbf{k}| \leq \hbar\omega_D$ and $|\xi_{\mathbf{k}'}| \leq \hbar\omega_D$, as indicated by the appropriate stepfunctions $\Theta$ in Eq. (1).

The Hamiltonian (1) represents by itself a great simplification of the net interaction between the electrons. Even so, in BCS theory one makes an additional technical simplification by adopting merely the mean field approximation in calculating physical properties of superconductors [2]. These simplifications notwithstanding, the BCS theory predicts a number of relations, some of which are even independent of the phenomenological parameters $g$ and $\omega_D$, which are surprisingly well obeyed by a large class of superconductors [3].

As is well known, before the BCS theory was developed, Ginzburg and Landau had proposed a theory of superconductivity, currently known as the Ginzburg-Landau theory [4]. The equations of this theory were derived from the phenomenological Landau theory of second-order phase transitions [5]. In accordance with the Landau theory, in all cases of second order phase transitions, one has to define the so-called order parameters, which characterise ordered structures of macroscopic fields appearing spontaneously in systems below a critical temperature $T_c$. Thus the order parameters equal zero for $T > T_c$ and acquire non-vanishing values for $T < T_c$. Later Gor’kov demonstrated [6] by using the Green function method, that the
Ginzburg-Landau theory is a limiting case of the BCS theory, provided that the order parameters are values of a complex function \( \varphi(x) \), which is proportional to the anomalous Green function \( \langle \psi_-(x)\psi_+(x) \rangle \) of the electron field operators \( \psi_\sigma(x) \), evaluated in the mean field approximation. The expression for the function \( \varphi(x) \) is thus the following,

\[
\varphi(x) = C \langle \psi_-(x)\psi_+(x) \rangle_{m_f} = \frac{C}{V} \sum'_{k,k'} \langle a_{k,-}a_{k',+} \rangle_{m_f} \exp i(k + k') \cdot x,
\]

where \( \langle ... \rangle_{m_f} \) denotes the statistical grand canonical ensemble average with the Hamiltonian (1) in the mean field approximation. From Eq. (3) one sees that ordered superconducting structures are characterised by the mean field correlation functions \( \langle a_{k,-}a_{k',+} \rangle_{m_f} \) corresponding to the Hamiltonian (1). Thus, the order parameters will be chosen to be related to these mean field correlation functions.

A very important theorem concerning mean field solutions to the BCS theory of superconductivity has been proved by Bogoliubov [7]. This theorem states that any mean field solution of the BCS Hamiltonian (1) becomes an exact solution in the thermodynamic limit. This means that the effects of quantal fluctuations about a given mean field give no contributions to thermodynamical potentials. This was also proven explicitly in [5] by a direct evaluation of the grandcanonical partition function corresponding to the Hamiltonian (1).

Although the BCS theory has existed for almost forty years, apparently only one of its mean field solutions corresponding to the Hamiltonian (1) has been considered so far. To the best of our knowledge, there have been no attempts to explore the possibility of finding more than one mean field solution with the Hamiltonian (1).

In this paper we report on our observation that there is at least one additional mean field solution to the system described by the Hamiltonian (1). We describe this solution explicitly below. The superconducting state corresponding to the new mean field solution can appear at non-zero temperature only in quasi-twodimensional systems such as thin films or layered structures of bulk material. Such layered structures are actually present in high \( T_c \) superconductors [9]. The new mean field solution described in this paper corresponds to a phase transition to a superconducting state with some rather unexpected properties. Specifically, it is a third-order phase transition which does not exhibit the isotope effect which is typical for the usual BCS...
theory. Thus, this phase transition cannot be described by the ordinary phenomenological Ginzburg-Landau theory, which describes phase transitions of second order.

2 The mean field approximation and the gap equation

In order to analyse the novel mean field solution to the BCS theory with the Hamiltonian (1) we first express the interaction Hamiltonian $H_I$ in (1) as a sum of two terms,

$$ H_I = H'_I + H''_I $$

where

$$ H'_I = -g \frac{V}{\sqrt{2}} \sum_{k,k'} \Theta(\hbar \omega_D - |\xi_k|) \Theta(\hbar \omega_D - |\xi_{k'}|) \delta_{|k|,|k'|} a_{k,+}^\dagger a_{-k,-}^\dagger a_{-k',+} a_{-k'+} $$

and

$$ H''_I = -g \frac{V}{\sqrt{2}} \sum_{k,k'} \Theta(\hbar \omega_D - |\xi_k|) \Theta(\hbar \omega_D - |\xi_{k'}|) (1 - \delta_{|k|,|k'|}) a_{k,+}^\dagger a_{-k,+}^\dagger a_{-k,-} a_{-k'+} $$

In the interaction term defined by Eq. (5) we introduce new summation indices $p$ and $q$ related to $k$ and $k'$ as follows,

$$ p = \frac{k + k'}{2}, \quad q = \frac{k - k'}{2} $$

The innocent looking change of summation variables introduced in (7) is very important, as it enables one to satisfy the condition $|k| = |k'|$ in the sum in Eq. (5) by any two perpendicular vectors $p$ and $q$. This will be seen to be quite essential for the definition of order parameters below.

The Hamiltonian (1) can now be written as follows,

$$ H = \sum_{k,\sigma} \xi_k a_{k,\sigma}^\dagger a_{k,\sigma} - g \frac{V}{\sqrt{2}} \sum_{p,q} \Theta(\hbar \omega_D - |\xi_{p+q}|) \delta_{|p+q|,|p-q|} a_{p+q,+}^\dagger a_{p,q,+}^\dagger a_{p-q,-} a_{p+q,-} a_{p+q,-} + H''_I $$

Let us note that it is enough to retain only one step function in the equation (8) above, since $\xi_{p+q} = \xi_{p-q}$ in the sum in Eq. (8).
We next introduce a general set of complex order parameters $b_{q,p}$ and $b^*_{q,p}$ by the following definitions,

$$b_{q,p} = g <a_{-(p+q),-}a_{(p+q),+} > \delta_{|p+q,|p-q|} \quad , \quad b^*_{q,p} = g <a^+_{(p+q),+}a^+_{-(p+q),-} > \delta_{|p+q,|p-q|} \quad (9)$$

The order parameters $b_{q,p}$ and $b^*_{q,p}$ are thus enumerated by two orthogonal vectors $p$ and $q$, which are restricted by the condition $|\xi_{p+q}| = |\xi_{p-q}| \leq \hbar \omega_D$.

We now define the following gap functions $\Delta_k$ and $\Delta^*_k$ in terms of the functions $b_{q,p}$ and $b^*_{q,p}$ introduced above,

$$\Delta_k = \frac{1}{V} \sum_{p,q} b_{q,p} \delta_{p-q,k} \quad , \quad \Delta^*_k = \frac{1}{V} \sum_{p,q} b^*_{q,p} \delta_{p-q,k} \quad (10)$$

Using the definitions (9) and (10), we decompose the Hamiltonian (8) as a sum of two terms,

$$H = H_{mf} + H_{fl} \quad (11)$$

where

$$H_{mf} = \frac{1}{gV} \sum_{p,q} b^*_{q,p} b_{-q,p} +$$

$$+ \sum_k \left\{ \xi_k (a^+_k a^+_k + a^+_k a^-_k) - (\Delta^*_k a^-_k a^+_k + \Delta_k a^+_k a^-_k) \right\} \quad (12)$$

is the mean field Hamiltonian, and the term

$$H_{fl} = -\frac{g}{V} \sum_{p,q} \Theta(h\omega_D - \xi_{p+q}) \left[ a^+_{-(p+q),-} a^+_{(p+q),-} - a^+_{(p+q),+} a^+_{(p+q),+} > \right]$$

$$\left[ a^-_{-(p-q),-} a^-_{(p-q),+} - a^-_{-(p-q),+} a^-_{(p-q),+} > \right] \delta_{|p+q,|p-q|} + H''_I \quad (13)$$

describes quantal fluctuations about the mean fields $b_{q,p}$ and $b^*_{q,p}$, cf. Eq. (9).

In view of the Bogoliubov theorem quoted above, the quantal fluctuation Hamiltonian (13) has no macroscopic effects in the thermodynamical limit. By neglecting it in all expressions, i.e. replacing the Hamiltonian (8) with the mean field Hamiltonian (12) one gets all physical quantities in the so-called mean-field approximation. From now on we use this approximation throughout.
The Hamiltonian \( H_{mf} \), eq. (12), can easily be diagonalized, and results then in the following partition function \( Z_{mf} \),

\[
Z_{mf} \equiv \text{Tr} \exp \left[ -\beta H_{mf} \right]
= \exp \left\{ -\frac{\beta}{gV} \sum_{p,q} b_{q,p}^* b_{-q,p} \right\} \left\{ \prod_k \left( e^{-\beta\xi_k} (1 + e^{\beta E_k}) (1 + e^{-\beta E_k}) \right) \right\},
\tag{14}
\]

where

\[
E_k = \left( \xi_k^2 + |\Delta_k|^2 \right)^{\frac{1}{2}}
\tag{15}
\]
is the quasiparticle energy spectrum.

Evaluating the correlation functions in the mean field approximation, one then gets the following relations from the equations (9),

\[
b_{q,p} = \frac{g}{2E_{p+q}} \Delta_{p+q} \text{th} \left( \frac{1}{2} \beta E_{p+q} \right).
\tag{16}
\]
The sets of equations (16) for the determination of the functions \( b_{q,p} \) and \( b_{q,p}^* \) are closely related to the so-called gap equations in the standard BCS-theory of superconductivity, as will be seen presently.

3 The solutions \( b_{q,p} \) and \( b_{q,p}^* \)

Using now equations (14) and (16), one gets the following equation for the gap function \( \Delta_k \),

\[
\Delta_k = \frac{g}{V} \sum_{p,q} \frac{\Delta_{p+q}}{2E_{p+q}} \text{th} \left( \frac{1}{2} \beta E_{p+q} \right) \delta_{p-q} \delta_{p+q} \text{th} \left( \frac{1}{2} \beta E_{p+q} \right) \Theta(\hbar \omega_D - |\xi_{p+q}|)
\tag{17}
\]

We now revert to the summation indices \( k' = p + q, k'' = p - q \) and carry out the summation over \( k'' \) with the result

\[
\Delta_k = \frac{g}{2V} \sum_{k'} \frac{\Delta_{k'}}{E_{k'}} \text{th} \left( \frac{1}{2} \beta E_{k'} \right) \delta_{|k'|,|k|} \Theta(\hbar \omega_D - |\xi_{k'}|)
\tag{18}
\]

The assumption that the gap function \( \Delta_{k'} \) is a function of the magnitude \( |k'| \) only, simplifies the relation (18) substantially, as follows,

\[
\Delta_k = \frac{gN_1}{2V} \frac{\Delta_k}{E_k} \text{th} \left( \frac{1}{2} \beta E_k \right)
\tag{19}
\]
where
\[ N_1 \equiv \sum_{\mathbf{k}'} \delta_{|\mathbf{k}'|,|\mathbf{k}|} \Theta(\hbar \omega_D - |\mathbf{k}'|) \] (20)

The quantity \( N_1 \) defined in Eq. (20) is the number of wave vectors \( \mathbf{k}' \) with given length \( |\mathbf{k}'|=|\mathbf{k}| \). The vectors \( \mathbf{k}' \) have the components given below,
\[ \mathbf{k}' = \left( \frac{2\pi}{L_1} n_1, \frac{2\pi}{L_2} n_2, \frac{2\pi}{L_3} n_3 \right) \] (21)

where \( n_1, n_2 \) and \( n_3 \) are integers, \( L_1, L_2 \) and \( L_3 \) are the lengths of the edges of the box into which the system is enclosed. The condition \( |\mathbf{k}'|=|\mathbf{k}| \) defines the surface of an ellipsoid with semiaxes \( a_1 = \frac{kL_1}{2\pi}, a_2 = \frac{kL_2}{2\pi}, \) and \( a_3 = \frac{kL_3}{2\pi}, \) i.e.
\[ \frac{n_1^2}{a_1^2} + \frac{n_2^2}{a_2^2} + \frac{n_3^2}{a_3^2} = 1 \] (22)

Thus the number of states \( N_1 \) is in fact equal to the surface area of the ellipsoid (22) which is determined by an elliptic integral. However for a very thin film, or layer with \( L_1 \ll L_2, L_1 \ll L_3 \) the number of states can be approximated by the surface area of a very thin disc of elliptical shape, with semiaxes \( a_2 = \frac{kL_2}{2\pi} \) and \( a_3 = \frac{kL_3}{2\pi} \). Thus the number of states \( N_1 \) is given by the following expression,
\[ N_1 = \frac{1}{2\pi} \frac{2\pi k^2 L_2 L_3}{(2\pi)^2} = \frac{1}{2\pi} k^2 L_2 L_3 \] (23)

Since the vectors \( \mathbf{k}' \) in the sum (18) are restricted by the inequalities below,
\[ E_F - \hbar \omega_D = \frac{\hbar k'^2}{2m} \leq \mathcal{E}_F + \hbar \omega_D \] (24)

and since \( \hbar \omega_D \ll \mathcal{E}_F \) we can replace the quantity \( k^2 \) in (23) by \( k_F^2 \), i.e.
\[ N_1 = \frac{1}{2\pi} k_F^2 L_2 L_3 \] (25)

By using the expression for the density of states of electrons with a single spin projection at the Fermi level \( N_0 \),
\[ N_0 = \frac{2mk_F}{(2\pi\hbar)^2} \] (26)

we can express the ratio \( \frac{N_1}{2V} \) as follows,
\[ \frac{N_1}{2V} = N_0 \sqrt{\mathcal{E}_F} \frac{\hbar}{\sqrt{2m}} \frac{\pi}{L_1} \] (27)
Using the last relation in Eq. (19) we obtain the formula,

$$\Delta_k = \Delta_k g N_0 \sqrt{\mathcal{E}_F \mathcal{E}_1} \left( \frac{1}{E_k} \right) \left( \frac{1}{2} \beta E_k \right),$$

(28)

where

$$\mathcal{E}_1 = \frac{\hbar^2 \pi^2}{2m L_1^2}$$

(29)

is the lower bound of the energy spectrum of free electrons in a thin box of volume $V = L_1 L_2 L_3$ with $L_2 \gg L_1$ and $L_3 \gg L_1$. From eq. (28) follows that the energy spectrum $E_k$ of the quasiparticles in the superconducting state with $\Delta_k \neq 0$ must satisfy the following relation,

$$1 = g N_0 \sqrt{\mathcal{E}_F \mathcal{E}_1} \left( \frac{1}{E_k} \right) \left( \frac{1}{2} \beta E_k \right),$$

(30)

which equation can be satisfied only if the temperature $T$ is bounded from above by the following critical temperature $T_c$,

$$T_c = \frac{1}{2k_B} g N_0 \sqrt{\mathcal{E}_F \mathcal{E}_1}.$$

(31)

The critical temperature $T_c$ defined by eq. (31) does not depend on the Debye frequency $\omega_D$ and hence it does not exhibit the isotope effect typical for the standard solution in BCS theory. The critical temperature also depends on the lowest bound $\mathcal{E}_1$ of the energy spectrum of the electrons in the superconducting material. For bulk materials $\mathcal{E}_1 \rightarrow 0$ so this kind of superconductivity does not exist in bulk samples. However for thin films the lower bound $\mathcal{E}_1$ is nonzero and given by Eq. (29). The critical temperature increases with decreasing thickness of the layer.

The solution to eq. (30) for the energy spectrum $E_k$ in the range of $k$ for which $\Delta_k \neq 0$, is a quantity $\eta(T)$ say, which is dependent on the temperature $T$ only,

$$E_k = (\xi_k^2 + |\Delta_k|^2)^{1/2} \equiv \eta(T)$$

(32)

One cannot obtain an explicit expression for the solution $\eta(T) = E_k$ of eq. (30) for general values of $T$ in the range $T < T_c$ but has to resort to numerical methods for these general values of $T$. However in the limiting cases $T \ll T_c$ and $T - T_c \ll T_c$, respectively, one readily obtains the following formulae from eq. (30),

$$\eta(T) \approx \eta_0 (1 - 2e^{-\beta \omega_0}); T \ll T_c,$$

(33)
and
\[ \eta(T) \approx \sqrt{3} \eta_0 \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}} ; T_c - T \ll T_c , \]
where
\[ \eta_0 = \eta(T = 0) = 2k_B T_c. \]
The ratio
\[ \frac{\eta_0}{k_B T_c} = 2 \]
is a universal constant, independent of the physical properties of the thin layer under consideration.

From eq. (32) we get the following expression for the gap function \( \Delta_k \),
\[ \Delta_k = \left(\eta^2 - |\xi_k|^2\right)^{\frac{1}{2}} \Theta(\eta - |\xi_k|). \] Combining eq. (37) with (36) one finally obtains an explicit expression for the order parameter \( b_{q,p} \),
\[ b_{q,p} = b_{-q,-p} = \frac{g}{2\eta_0} \left\{ \eta^2 - \left[ \frac{\hbar^2}{2m} (q^2 + p^2) - E_F \right] \right\}^{\frac{1}{2}} \Theta(\eta - \left| \frac{\hbar^2}{2m} (q^2 + p^2) - E_F \right|). \]
The last two formulae, (37) and (38), are of course consistent with the definition (10). The formulae (30) - (38) are valid under the following condition,
\[ \eta(T) \leq \hbar \omega_D \]
because for \( |\xi_k| \geq \hbar \omega_D \) the quasiparticle energy spectrum \( E_k \) must reduce to the energy spectrum of free electrons. Combining the relation (33) with the inequality (39) one obtains,
\[ T_c \leq \frac{\hbar \omega_D}{2k_B} = \frac{1}{2} T_D \]
where \( T_D \) is the Debye temperature. For the case under consideration we thus have an upper bound for the critical temperature. Critical temperatures \( T_c \) in the vicinity of this upper bound have in fact been observed in layered structures of high \( T_c \) superconductors [9].

The expressions (37) and (38) indicate unusual properties of the corresponding superconducting state. Namely, not all of the order parameters \( b_{q,p} \) with \( p \cdot q = 0 \) acquire spontaneously
non-vanishing values at the same time when \( T < T_c \). For \( T = T_c - 0 \) only one order parameter is non-vanishing at the opening of the energy gap \( \eta(T = T_c - 0) = 0^+ \). Decreasing the temperature from the value \( T_c \) the gap in the energy spectrum \( \eta(T) \) opens up more and more, whence more and more order parameters acquire non-vanishing values for \( T < T_c \).

4 Thermodynamical properties

We next calculate thermodynamical properties related to the novel solution analysed above. Using the standard method [2] we express the grand canonical potential \( \Omega_s(T) \) of the superconducting state by the formula

\[
\Omega_s(T) - \Omega_n(T) = \frac{2}{3} V N_0 \int_0^\eta d\eta' (\eta')^3 \frac{d}{d\eta'} \left[ \frac{1}{\eta'} t h \frac{1}{2} \eta' \right],
\]

where \( \Omega_n(T) \) is the normal-state grand canonical potential of the system if it were in a normal state at temperature \( T \). The integral (41) requires numerical analysis for general values of \( T \) in the appropriate range. However, similarly as in the previous cases (33) and (34) the following limiting cases are readily obtained,

\[
\Omega_s(T) - \Omega_n(T) = -\frac{1}{3} V N_0 \eta_0^2 \left[ 1 - \frac{\pi^2}{4} \left( \frac{T}{T_c} \right)^2 \right], T \ll T_c
\]

and

\[
\Omega_s(T) - \Omega_n(T) = -\frac{4\sqrt{3}}{5} V N_0 \eta_0^2 \left( 1 - \frac{T}{T_c} \right)^{5/2}, T_c - T \ll T_c
\]

Using the formulae (42) and (43) one can calculate the electronic specific heat \( C_s(T) \) and the critical magnetic field \( H_c(T) \) with the following results,

\[
C_s(T) = 4 V N_0 \eta_0 k_B (\beta \eta_0)^2 e^{-\beta \eta_0}, T \ll T_c,
\]

\[
H_c(T) = \left( \frac{8\pi}{3} N_0 \right)^{\frac{3}{2}} \eta_0 \left[ 1 - \frac{\pi^2}{8} \left( \frac{T}{T_c} \right)^2 \right], T \ll T_c.
\]

Likewise, in the limiting case corresponding to eq. (34) one obtains,

\[
\frac{C_s(T) - C_n(T)}{C_n(T)} = \frac{6\sqrt{3}}{\pi^2} \left( 1 - \frac{T}{T_c} \right)^{5/2}, T_c - T \ll T_c
\]
as well as
\[ H_c(T) = \left( \frac{32\pi^3}{5} N_0 \right)^\frac{1}{2} \eta_0 \left( 1 - \frac{T}{T_c} \right)^\frac{1}{2}, T_c - T \ll T_c \]  \tag{47}

where
\[ C_n(T) = \frac{2\pi^2}{3} VN_0 k_B^2 T \]  \tag{48}
is the normal-state electronic specific heat.

In the low-temperature region \( T \ll T_c \) the formulae (42) - (47) do not yield results which differ appreciably from the standard solution \[2\]. However, near the critical temperature, i.e. for \( T_c - T \ll T_c \) the differences are crucial. The formulae (43), (46) and (47) yield critical exponents which differ from those known for the standard solution. The electronic specific heat given by eq. (46) is a continuous function of \( T \) at \( T = T_c \), however with a discontinuous derivative at \( T = T_c \), in contradistinction to the standard case. The novel mean field solution considered here gives rise to a superconducting phase transition of third order, and can therefore not be described by the ordinary macroscopic Ginzburg-Landau theory of superconductivity, which is relevant for the phase transitions of second order.

5 Summary

The unconventional superconducting state which we have found within the mean field treatment of BCS theory can appear in thin films, or in layered structures in bulk material. Therefore, the existence of this novel feature of BCS theory can have relevance for high \( T_c \) superconductors or for the explanation of the fact that even some simple metals can become superconducting as thin films, but not as bulk material. The fact that the BCS Hamiltonian contains the possibility of two different superconducting structures, namely an unconventional superconducting state at a critical temperature \( T_{c1} \), and the well-known superconducting state at a critical temperature \( T_c \), offers the possibility of observing consecutive superconducting phase transitions in thin layered structures.
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