

Superconductivity with *p*- and *d*-Wave Pairing

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I. Introduction

We shall survey the properties of a hypothetical superconducting system, in which the pairs would be formed with an angular momentum different from zero. This problem is a generalization of the B.C.S. theory (1), and is conveniently described with a reduced Hamiltonian

$$H \equiv \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} V_{\mathbf{k}\mathbf{k}'} c_{-\mathbf{k}\sigma'}^{\dagger} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}'\sigma} c_{-\mathbf{k}'\sigma'}, \quad (1)$$

where

$$V_{\mathbf{k}\mathbf{k}'} \equiv \sum_l (2l + 1) P_l(\hat{k} \cdot \hat{k}') V_l(k, k'). \quad (2)$$

Here $c_{\mathbf{k}\sigma}^{\dagger}$ is the fermion creation operator for a plane wave of momentum \mathbf{k} and spin σ , and the interaction is truncated to particles of total momentum zero. In the B.C.S. theory, only the $l = 0$ term of the expansion (2) of $V_{\mathbf{k}\mathbf{k}'}$ in spherical harmonics is considered; when this term is attractive, although it is a small part of the real interaction, it causes the particles to bind in pairs of total linear momentum, total spin, and angular momentum zero, which condense. The more general case of interaction (2) has been studied in a number of papers which we shall review.

As presented here, this problem looks rather academic, but it has in fact some physical interest. Superconductivity with $l \neq 0$ may perhaps exist in nature in two different circumstances: metals and liquid He³.

A. METALS

It has been shown in Anderson's lectures that the interaction between electrons arising from the exchange of one phonon has a short range, of the order of magnitude of the lattice spacing. If this range was zero, the Fourier transform of the potential would be a constant, so that Eq. (2) would contain only the term $l = 0$ considered in the B.C.S. theory. Since the range of the potential is the lattice spacing, its Fourier transform may vary in momentum space over distances of the order of the inverse lattice spacing, that is of the Fermi momentum. Therefore, for $k \simeq k' \simeq k_F$, the first few $l \neq 0$ terms in Eq. (2) may be as large as the $l = 0$ one. It is thus interesting to study the properties of such a system, in order to be able to recognize it experimentally (if it exists), and to know in which conditions it may be observed.

In fact, the model problem (1) and (2) is an oversimplification of the real one. In particular, the interaction between electrons is retarded, and is furthermore not invariant by rotation (as well as the kinetic energy ε_k). But since the qualitative predictions of the theory are not affected by these facts, we shall simply discuss here the model (1, 2), in particular in the case of an $l = 1$ attraction.

B. LIQUID He³

Another Fermi system to which the B.C.S. theory may be extended is liquid He³ (2). Here, the interaction (2) between atoms, for momenta k and k' close to k_F , is repulsive for $l = 0$ and $l = 1$, and attractive for $l = 2$. This point is easy to understand: if a potential $V(r)$ is strongly repulsive for $r < r_1$ and has a long but weak attractive tail (for $r_1 < r < r_2$), its Fourier transform $V(q)$ has the shape represented in Fig. 1. Then, since (as functions of the angle $\widehat{k, k'}$, and therefore of $q = |\mathbf{k} - \mathbf{k}'| \simeq 2k_F \sin [\frac{1}{2}\widehat{k, k'}]$) P_0 is positive, P_1 decreases, and P_2 has a minimum, it is clear from Fig. 1 that V_0 and V_1 are positive and V_2 is negative, provided the density (proportional to k_F^3) is large enough, which is the case in liquid He³. The more detailed treatments confirm this rough argument. Liquid He³ at low temperature is well described by the Landau theory. The relevant interaction is that between quasi particles, and it is also repulsive for $l = 0, 1$, and attractive for $l = 2$.

We shall only consider here the case of an attractive potential in a single partial wave $l = 1$ (3) or $l = 2$ (2). In fact, it can be shown that, when several waves are present in Eq. (2), only the most attractive partial

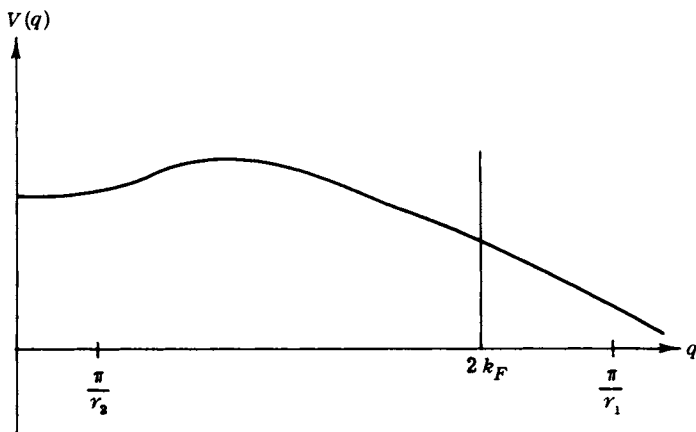


FIG. 1. Variation of the potential $V(q)$ in momentum space.

wave is relevant, at least for a weak coupling. In particular, all partial waves in the gap equation decouple at $T = T_c$, so that the critical temperature depends only on the strength of the most attractive one.

II. The *p*-Wave Pairing

A. THEORY

Equation (2) has the form

$$V_{\mathbf{k}\mathbf{k}'} = -3 \hat{k} \cdot \hat{k}' V_1(k, k'), \tag{3}$$

where \hat{k} is the unit vector in the direction \mathbf{k} . Contrarily to the B.C.S. case, the pairing must not be performed between states of opposite spins. Note that the gap matrix

$$\Delta_{\mathbf{k}\sigma\sigma'} \equiv - \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \langle c_{\mathbf{k}'\sigma} c_{-\mathbf{k}'\sigma'} \rangle \tag{4}$$

plays the role of a bound pair wave function. If $V_{\mathbf{k}\mathbf{k}'}$ has the form of

Eq. (3), the spatial part of ψ is a combination of spherical harmonics $l = 1$, that is of k_x, k_y, k_z ; its spin part is expected to be a combination of the triplet wave functions. We need therefore a kind of pairing in which all three components of the triplet, $\uparrow\uparrow, \downarrow\downarrow$, and $\uparrow\downarrow + \downarrow\uparrow$ are allowed. Pairing spins of the same direction would give only the two first components, and pairing opposite spins would give only the third component of the triplet (and the singlet). It is therefore necessary to introduce a more complicated pairing, which mixes all four operators $c_{\mathbf{k}\uparrow}, c_{\mathbf{k}\downarrow}, c_{-\mathbf{k}\uparrow}^\dagger$, and $c_{-\mathbf{k}\downarrow}^\dagger$.

It is convenient for this purpose to use a matrix notation (4); (also see Kadanoff, this volume). Generalizing the 2×2 matrix Green's function which involves both normal and abnormal Green's functions, we define the 4×4 matrix Green's function $\mathcal{G}_{\mathbf{k}}$, for operators

$$\mathcal{G}_{\mathbf{k}} \equiv \begin{pmatrix} c_{\mathbf{k}\uparrow} \\ c_{\mathbf{k}\downarrow} \\ c_{-\mathbf{k}\uparrow}^\dagger \\ c_{-\mathbf{k}\downarrow}^\dagger \end{pmatrix}$$

at time t , and

$$\mathcal{G}_{\mathbf{k}}^\dagger \equiv (c_{\mathbf{k}\uparrow}^\dagger \quad c_{\mathbf{k}\downarrow}^\dagger \quad c_{-\mathbf{k}\uparrow} \quad c_{-\mathbf{k}\downarrow})$$

at time 0.

The equation of motion for $\mathcal{G}_{\mathbf{k}}$ is obtained by the usual method as

$$(\omega - \mathcal{E}_{\mathbf{k}}) \mathcal{G}_{\mathbf{k}} = 1, \quad (6)$$

where $\mathcal{E}_{\mathbf{k}}$ is the 4×4 matrix

$$\mathcal{E}_{\mathbf{k}} \equiv \left(\begin{array}{cc|cc} \varepsilon_{\mathbf{k}} & 0 & & \\ 0 & \varepsilon_{\mathbf{k}} & \Delta_{\mathbf{k}\sigma\sigma'} & \\ \hline (\Delta_{\mathbf{k}\sigma\sigma'})^\dagger & & -\varepsilon_{\mathbf{k}} & 0 \\ & & 0 & -\varepsilon_{\mathbf{k}} \end{array} \right), \quad (7)$$

so that the spectral density is $\delta(\omega - \mathcal{E}_{\mathbf{k}})$.

Through Eq. (4), ψ depends on the anomalous part of the matrix $\langle \mathcal{G}_{\mathbf{k}} \mathcal{G}_{\mathbf{k}}^\dagger \rangle$, which is determined self consistently in terms of the spectral density by

$$\langle \mathcal{G}_{\mathbf{k}} \mathcal{G}_{\mathbf{k}}^\dagger \rangle = \int_{-\infty}^{+\infty} d\omega f(\omega) \delta(\omega - \mathcal{E}_{\mathbf{k}}) = f(\mathcal{E}_{\mathbf{k}}) \equiv \frac{1}{2} (1 + \text{th } \frac{1}{2} \beta \mathcal{E}_{\mathbf{k}}). \quad (8)$$

It remains now to solve the coupled Eqs. (4, 7, 8).

Let us first consider in this formalism the case when (2) contains only even *l*'s. The gap matrix (4) has then the form

$$\Delta_{\mathbf{k}\sigma\sigma'} = \begin{pmatrix} 0 & \Delta_{\mathbf{k}} \\ -\Delta_{\mathbf{k}} & 0 \end{pmatrix}, \quad (9)$$

and it is easy to see that

$$\mathcal{E}_{\mathbf{k}}^2 = \varepsilon_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2 = E_{\mathbf{k}}^2 \quad (10)$$

is proportional to the unit matrix. The calculation of $\text{th } \frac{1}{2} \beta \mathcal{E}_{\mathbf{k}}$ in (8) is thus greatly simplified, since

$$\begin{aligned} \text{th } \frac{1}{2} \beta \mathcal{E}_{\mathbf{k}} &= \mathcal{E} \left(1 - \frac{1}{3} \mathcal{E}^2 + \frac{2}{15} \mathcal{E}^4 - \dots \right) = \mathcal{E} \left(1 - \frac{1}{3} E^2 + \frac{2}{15} E^4 - \dots \right) \\ &= \mathcal{E}_{\mathbf{k}} \text{th } \frac{1}{2} \beta E_{\mathbf{k}}/E_{\mathbf{k}}, \end{aligned} \quad (11)$$

and the gap equation

$$\Delta_{\mathbf{k}} = -\frac{1}{2} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \Delta_{\mathbf{k}'} \text{th } \frac{1}{2} \beta E_{\mathbf{k}'}/E_{\mathbf{k}'} \quad (12)$$

follows.

Returning to the case $l = 1$, we make the statement (which will be verified later) that $\mathcal{E}_{\mathbf{k}}^2$ is still proportional to the unit matrix. Since

$$\mathcal{E}_{\mathbf{k}}^2 = \varepsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}\sigma\sigma'} (\Delta_{\mathbf{k}\sigma\sigma'})^\dagger \quad (= E_{\mathbf{k}}^2) \quad (13)$$

this assumption amounts to suppose that Δ is proportional to a unitary matrix. Then (11) holds, and we get as a consequence of (7) and (8)

$$\langle c_{\mathbf{k}\sigma} c_{-\mathbf{k}\sigma'} \rangle = \frac{1}{2} \Delta_{\mathbf{k}\sigma\sigma'} \text{th } \frac{1}{2} \beta E_{\mathbf{k}}/E_{\mathbf{k}}, \quad (14)$$

which together with (4) leads to the gap equation

$$\Delta_{\mathbf{k}\sigma\sigma'} = -\frac{1}{2} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \Delta_{\mathbf{k}'\sigma\sigma'} \text{th } \frac{1}{2} \beta E_{\mathbf{k}'}/E_{\mathbf{k}'}. \quad (15)$$

It is easy to check that Eq. (15) [with $V_{\mathbf{k}\mathbf{k}'}$ given by (3)] admits as a solution

$$\Delta_{\mathbf{k}\sigma\sigma'} = \delta_k \begin{pmatrix} -k_x + i k_y & k_z \\ k_z & k_x + i k_y \end{pmatrix} \quad (16)$$

in which

$$\delta_k = \frac{1}{2} \sum_{\mathbf{k}'} V_1(k, k') \delta_{k'} \text{th } \frac{1}{2} \beta E_{k'}/E_k. \quad (17)$$

is the same as the gap equation (12) which would correspond to an s -wave potential $V_1(k, k')$. Finally, we verify that Eq. (12) is satisfied, since (16) implies $\Delta\Delta^\dagger = |\delta_k|^2$. Moreover, as is well known, the present Green's functions treatment is equivalent to the variational approach of B.C.S.-Bogoliubov (1), and it may be shown that the solution (16, 17) leads to the lowest free energy, so that the statement is fully justified.

B. COMPARISON WITH THE B.C.S. CASE

The quasi-particle energy

$$E_k = (\varepsilon_k^2 + |\delta_k|^2)^{1/2} \quad (18)$$

has the same form as in the B.C.S. theory, and the resulting properties (gap, specific heat, tunneling characteristics) will therefore be the same. It is also easy to show that the state with p -wave pairs would present no Meissner effect.

The isotropy of this state and of the energy (18) can be understood by rewriting (16) as

$$\Delta_{\mathbf{k}\sigma\sigma'} \propto \sum_m \langle \frac{1}{2} \frac{1}{2} \sigma\sigma' | 1m \rangle Y_{1m'}(\mathbf{k}) \langle 1m 1m' | 00 \rangle \quad (19)$$

which shows that $\Delta_{\mathbf{k}\sigma\sigma'}$ behaves like the wave function of a pair with total spin 1, orbital angular momentum 1, coupled together to a total angular momentum zero. (In the B.C.S. case, both total spin and orbital angular momentum vanish.)

Although the pairs are isotropic, they have a spin 1. As a first consequence, there exists a set of low lying collective states, constructed by rotating the spins with respect to the angular variables. These states, which have no equivalent in the B.C.S. theory, would, however, be difficult to detect.

A more remarkable difference with the B.C.S. case is the spin susceptibility (Fig. 2). In the B.C.S. case, it is necessary to provide a finite energy in order to flip a spin, since a pair must be broken, so that the spin susceptibility vanishes at $T = 0$. Here 1/3 of the pairs are in a state $m_s = 0$ and behave like B.C.S. pairs, but the remaining 2/3 are coupled to a spin component $m_s = \pm 1$; applying a weak magnetic field changes the population of these pair states, without breaking the pairs, so that 2/3 of the particles behave as if they were free, and the spin

susceptibility at $T = 0$ is predicted to be $2/3$ of the normal spin susceptibility. It is curious to note the agreement between the predictions of this $l = 1$ theory with experiments performed in Sn and Hg (Fig. 2).

It is thus tempting to conclude that in these materials $V_{\mathbf{k}\mathbf{k}'}$ is more attractive for the p -wave than for the s -wave, since other experiments

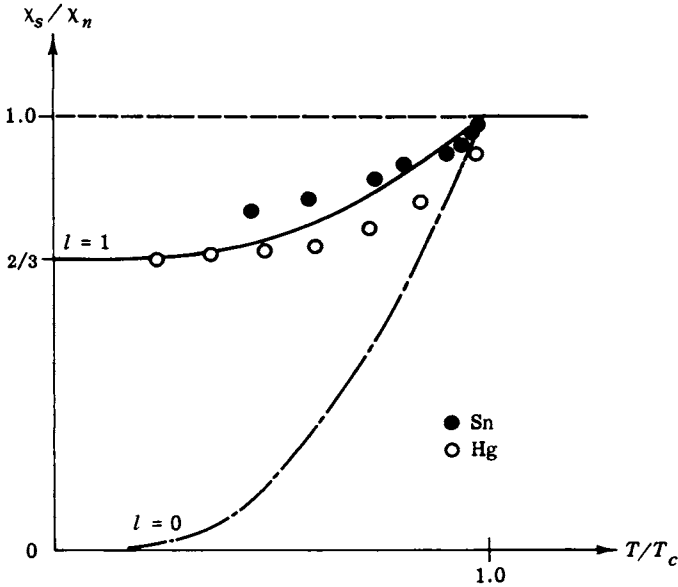


FIG. 2. Spin susceptibility χ of a superconductor with $l = 0$ and $l = 1$.

do not allow the distinction between s - and p -wave pairing. However, the experimental situation is not very clear; it is now believed that the anomalous Knight shift experiments are not a measurement of the spin susceptibility of conduction electrons only, and the agreement is probably a coincidence.

On the other hand, another difference with the B.C.S. case comes from the fact that the radial pair wave function has $l = 1$ instead of $l = 0$, so that the pairs are more loosely bound. As a consequence, impurities will have an important effect. The dirty superconductor theorem (see Anderson's lectures) does not apply here, since it is based on two hypotheses: the scattering is invariant by time reversal (which is true for nonmagnetic impurities), and the interaction is local (which is

true in the B.C.S. case, but not here). Each nonmagnetic impurity, as well as dislocation, surface effects, etc. ... will have a strong effect, comparable with a magnetic impurity in the B.C.S. case. Since the density of nonmagnetic impurities is very large, they will affect considerably the critical temperature, contrary to the s -wave case.

The observation of superconductivity with p -wave pairing, which is expected to occur if the particles attract more in the p -wave than in the s -wave, is therefore probably very difficult, since very pure and perfect samples are needed. The simplest way of distinguishing such a state from an s -wave state is to detect strong impurity effects.

III. The d -Wave Pairing

In the case of an $l = 2$ attractive potential

$$V_{\mathbf{k}\mathbf{k}'} = -5 P_2(\hat{k} \cdot \hat{k}') V_2(k, k'), \quad (20)$$

the solutions of the gap equations (10, 12) have an angular dependance (2) of the form

$$\Delta_{\mathbf{k}} = \sum_m c_m Y_{2m}(\hat{k}). \quad (21)$$

Anderson and Morel found that the solution of lowest energy is obtained for the combination

$$c_1 = c_{-1} = 0 \quad c_2 = -c_{-2} = c_0/\sqrt{2},$$

that is for

$$\Delta_{\mathbf{k}} \propto k_x^2 + j k_y^2 + j^2 k_z^2 \quad (j^3 = 1). \quad (22)$$

Contrary to the case $l = 1$, most predicted properties differ from those of $l = 0$. First, the gap vanishes, since (22) is equal to zero in the directions $k_x = \pm k_y = \pm k_z$. It results that the specific heat will behave like T^3 at low temperature, instead of $e^{-1/T}$. The state is anisotropic, somewhat as in the case of a ferromagnet or a solid, and the energy $E_{\mathbf{k}}$ of the elementary excitations depends on the direction \mathbf{k} ; the symmetry of the state is that of a cube, as seen in (22). The detection of such a superfluid phase of He_3 is therefore expected to be easy.

Two problems have been raised by this theory. The first one is purely

theoretical, and concerns the treatment of the model Hamiltonian (1, 2): Gorkov and Galitskii (5), using another method than above, have found a ground state with different properties (in particular isotropy). It is therefore interesting to compare both methods and find which one is correct. The second problem is to explain why the predicted phase has not yet been observed experimentally.

A. THE METHOD OF GORKOV AND GALITSKII

In terms of normal and abnormal Green's functions $G_{\mathbf{k}}$ and $F_{\mathbf{k}}$, Eqs. (6, 9) are rewritten as

$$\begin{aligned} (\omega - \varepsilon_{\mathbf{k}}) G_{\mathbf{k}} - \Delta_{\mathbf{k}} F_{\mathbf{k}}^+ &= 1 \\ (\omega + \varepsilon_{\mathbf{k}}) F_{\mathbf{k}}^+ - \Delta_{\mathbf{k}}^* G_{\mathbf{k}} &= 0. \end{aligned} \tag{23}$$

These equations may also be obtained without introducing anomalous Green's functions F . Consider the hierarchy of equations satisfied by the higher order Green's functions $G, G^{(2)}, G^{(3)}, \dots$. Rewriting them in terms of the connected parts $G, C^{(2)}, C^{(3)}, \dots$ defined as usual, we neglect $C^{(3)}$ in the equation satisfied by $C^{(2)}$, and assume that the correlation function $C^{(2)}$ for states of opposite momenta and spins is factorizable into $F_{\mathbf{k}}^+ F_{\mathbf{k}'}$. Then, Eq. (23) are recovered as the two first equations of the hierarchy.

This way of presenting the B.C.S. theory has been generalized by G.G. Assuming a nonseparable $C^{(2)}$, of the form $\sum_m F_{\mathbf{k}m}^+ F_{\mathbf{k}'m}$, and still neglecting $C^{(3)}$, Eq. (23) are replaced by

$$(\omega - \varepsilon_{\mathbf{k}}) G_{\mathbf{k}} - \sum_m \Delta_{\mathbf{k}m} F_{\mathbf{k}m}^+ = 1 \tag{24a}$$

$$\sum_m F_{\mathbf{k}'m} \{(\omega + \varepsilon_{\mathbf{k}}) F_{\mathbf{k}m}^+ - \Delta_{\mathbf{k}m}^* G_{\mathbf{k}}\} = 0, \tag{24b}$$

where

$$\Delta_{\mathbf{k}m} = - \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \int_{-\infty}^{+\infty} d\omega \varrho_{\mathbf{k}'m} f(\omega) \tag{25}$$

[$\varrho_{\mathbf{k}m}$ is the spectral density associated with $F_{\mathbf{k}m}(\omega)$]. The quasi-particle energy [introduced by solving Eq. (24)] is now

$$E_{\mathbf{k}}^2 = \varepsilon_{\mathbf{k}}^2 + \sum_m |\Delta_{\mathbf{k}m}|^2, \tag{26}$$

and $\Delta_{\mathbf{k}m}$ is a solution of

$$\Delta_{\mathbf{k}m} = -\frac{1}{2} \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \Delta_{\mathbf{k}'m} \operatorname{th} \frac{1}{2} \beta E_{\mathbf{k}'}/E_{\mathbf{k}'}. \quad (27)$$

This gap equations (26, 27) differs from the usual one (10, 12), if m takes several values. In particular, for $l = 2$ (Eq. 20), G.G. find

$$\Delta_{\mathbf{k}m} = Y_{lm}(\hat{k}) (4\pi/5)^{\frac{1}{2}} \Delta_k \quad (28)$$

$$E_k^2 = \varepsilon_k^2 + |\Delta_k|^2 \quad (29)$$

$$\Delta_k = \frac{1}{2} \sum_{k'} V_2(k, k') \Delta_{k'} \operatorname{th} \frac{1}{2} \beta E_{k'}/E_{k'}. \quad (30)$$

Contrary to the solution of A.M. [Eqs. (10, 22)] this solution is isotropic. The gap is Δ_k and does not vanish. Equation (30) has the same form as in the $l = 0$ case, which gives a free energy lower than in the theory of A.M. (Fig. 3). The critical temperatures are the same in both theories.

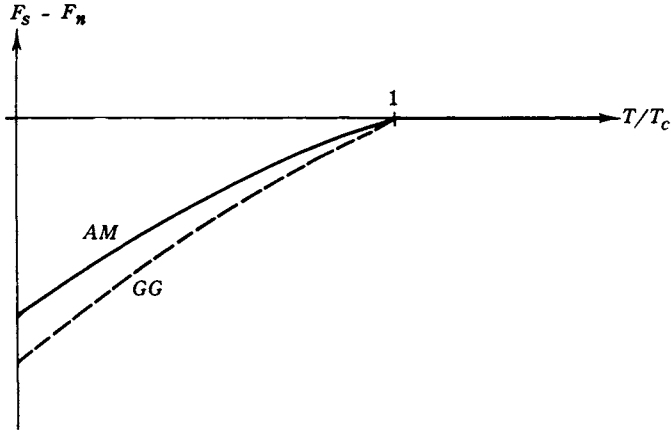


FIG. 3. Free energy of a superconducting system with $l = 2$, as predicted in the theories of Anderson and Morel, and Gorkov and Galitskii.

If the treatment of G.G. was variational, we would conclude from Fig. 3 that it is a better approximation than the A.M. solution (which is variational, as is well known). This, however, is not the case (6).

In fact, one can prove that in the limit of an infinite volume, the ground state energy per unit volume given by the A.M. theory is asymptotically exact for the model Hamiltonian (1) considered here, whereas the energy given by the G.G. theory is lower by a finite amount from the exact ground state energy.

The method of G.G., although it appears like a natural extension of the B.C.S. theory, is therefore not correct. It is interesting to try to understand why this is so, and why $C^{(2)}$ cannot be taken as separable when $C^{(3)}$ is neglected. Let us consider the third equation in the hierarchy, which must be satisfied by $C^{(3)}$. We do not write it explicitly, but represent each term by a diagram (Fig. 4), dropping the terms in $1/\Omega$.

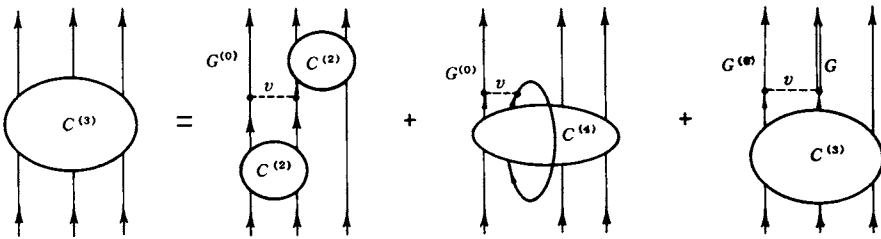


FIG. 4. Third equation of the hierarchy.

From this equation, it is clear that $C^{(3)}$ and $C^{(4)}$ cannot both be small if $C^{(2)}$ is large. In particular, the B.C.S. theory is asymptotically exact for $\Omega \rightarrow \infty$ [as seen by considering the hierarchy of coupled equations, written now in terms of both normal and anomalous Green's functions and corresponding connected parts (7)]. In this case, $C^{(3)} = 0$, which implies that $C^{(4)}$ is such that the two first terms of Fig. 4 compensate exactly. In this formalism without anomalous Green's functions, such a cancellation appears as a coincidence [since $C^{(3)} = 0$, but $C^{(4)} \neq 0$ in the B.C.S. case]; it becomes impossible if $C^{(2)}$ is not separable, so that $C^{(3)}$ cannot be neglected in the second equation (24b) of the hierarchy [giving $C^{(2)}$].

It remains, however, an open question whether the treatment of G.G. would be correct in the case of a Hamiltonian more general than (1).

B. ADEQUACY OF THE MODEL

The theories (2, 5) based on the reduced Hamiltonian (1) predict a critical temperature between 0.1 and 0.05°K. However, liquid He³ has been studied down to 0.008°K, and no transition has been found. The model used is therefore too crude to describe liquid He³, and several attempts, none completely successful, have been made to explain the absence of transition.

The predicted temperature is reduced, but not enough, if lifetime effects are taken into account (8). Due to collisions, quasi particles are not stable, and the pairing may take place only during their lifetime. This effect is taken into account by introducing a peaked spectral density instead of the δ -function density used above, with a width taken from scattering experiments.

On the other hand, nonmagnetic impurities as well as elastic scattering have a strong effect, as in the case $l = 1$, and experiments have always been performed in impure liquid He³. It is also possible that three-particle correlations, which are much more important for liquid He³ than for an electron gas in a metal, tend to destroy the formation of pairs. Because no precise calculation has been done, theory and experiment do not yet agree.

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