where use has been made of Eq. (3). Equation (8) exhibits the desired relation; namely, at a bias V where $\omega = 2eV/h = np$, the supercurrent has a dc component (a zero-slope region) whose amplitude varies as the magnitude of $J_n(2ev/hf)$ with rf voltage.

The rf voltage across the sample is proportional to the square root of the microwave power coupled into the cavity. The proportionality constant is fixed for all the data by fitting at one point only. Thus the argument of $J_1(2ev/hf)$ at which the first maximum occurs is 1.84 and so v is taken to be equal to $1.84(hf/2e)$ or about 35 μV at that point. From the known position of the sample in the cavity, the known mode pattern, and measurements of cavity Q, frequency and coupling, it is possible to estimate the rf voltage across the sample. The value estimated in this way is two orders of magnitude below the value obtained above from the fitting procedure. This discrepancy is not understood. It is similar to that obtaining between the data of Dayem and Martin[6] and the theory of Tien and Gordon[7] on the effect of microwaves on single-particle tunneling.

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[6] A. H. Dayem and R. J. Martin, Phys. Rev. Letters **8**, 245 (1962).

[7] P. K. Tien and J. P. Gordon, Phys. Rev. **129**, 647 (1963).

Discussion 34

KLEINMAN: Using the phonon assisted tunneling Hamiltonian that I discussed this morning and using the general techniques of Josephson, I've derived a phonon assisted tunneling of ground state pairs. To conserve momentum, the processes must involve the spontaneous omission of two phonons of equal and opposite wave vector. Thus to conserve energy we have $\hbar\omega = eV$ rather than $2eV$ as Josephson claims for photons. I think that's right because k is essentially zero for photons. The result I obtained is $J = J_0\alpha eV/2\Delta$, where J_0 is the discontinuity in the current at $eV = 2\Delta$ and α for lead is 0.58. This linear temperature independent leakage current has been observed by Rowell in lead where he finds values of alpha everywhere from 1 down to 0 and in tin by Taylor and aluminum by Giaever where alpha is less than 0.001. The experimental variation of alpha is at present a mystery. Because of the randomness of the phase of the spontaneously omitted phonons, the phase effects discussed by Josephson do not occur. The large value of alpha implies that if phonons a fixed phase are injected into the junctions the results may be even more spectacular than the microwave results we've just seen.

PIPPARD: I would like to ask Dr. Fiske if he has made any calculations of the resonant frequencies of the electromagnetic waves propagated between the plates. It seems to me that they ought to be at about $\frac{1}{10}$ the gap voltage, allowing for the very heavy inductive loading of these plates. I wonder in fact if these are not maser excited oscillations that he's observing, of the sort I think that Josephson's calculations would indicate ought to occur.

M. D. FISKE, *General Electric Research Laboratory:* I have not made such calculations. I think your suggestion of maser-type oscillations would be a very interesting one to consider.

Boundary Effects in Superconductors

P. G. DE GENNES

Faculté des Sciences, Orsay (S & O) France

I. INTRODUCTION

The present paper is concerned with the properties of layered structures of superconducting (and nonsuperconducting) materials, and with the related boundary problems. The basic experimental facts in this field are the following:

(a) for small superconducting samples surrounded by a nonmetallic substrate (e.g., films evaporated on glass), the transition temperature is very close to the bulk value. Tunneling experiments also show that the energy gap is close to the bulk value (derived for instance by ultrasonic attenuation).

(b) for "NS sandwiches" (thin superconducting film S deposited on a normal metal substrate N) the transition temperature may be significantly lower than in the bulk S material—or even vanish completely. Such effects were observed in the **Pb** Ag and **Sn** Ag systems.[1,2] However, as pointed out by Rose-Innes and Serin,[3] some of these experiments cannot be trusted entirely because of spurious atomic migration effects. To circumvent this difficulty one must deposit the films and keep them constantly at

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[1] D. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters **6**, 686 (1961).

[2] W. A. Simmons and D. H. Douglass, Phys. Rev. Letters **9**, 153 (1962).

[3] A. C. Rose-Innes and B. Serin, Phys. Rev. Letters **7**, 278 (1961).

low temperatures, as done by Hilsch.[4] The resulting samples have a very short electron mean free path l in the normal state (all the defects being quenched) and thus their coherence length is modified. This effect can be taken into account accurately if l is determined from resistivity measurements in the normal state.[5] Paradoxically, we expect more accurate results from such "dirty superconductor" sandwiches than from a "clean" NS system: In the former case the detailed atomic structure at the interface is less important and the large-scale motions of the superconducting electrons are ruled by a simple diffusion equation. In the latter case, on the other hand, the reflection and transmission properties of the transition region play an important role, and unfortunately they cannot be controlled at the present time. Thus in the following we shall restrict our attention to "dirty" systems.

(c) a thin (~1000 Å) normal slab N separating two superconductors S and S′ is able to carry a finite supercurrent from S to S′. These SNS′ junctions have been studied first in the pioneer work of Meissner.[6] Their interest is twofold: (1) from the dependence of the critical current on the thickness of the N slab one may obtain an estimate of V_N, the electron–electron interaction in N. (2) the SNS junctions have a wide range of critical currents and critical fields: this could be useful for some low-temperature devices. These properties are discussed in Sec. V.

II. ORDER PARAMETER AND EXCITATION SPECTRUM IN A NONHOMOGENEOUS SYSTEM

Let us first recall briefly how the excitation spectrum of a superconducting system is constructed by the self-consistent field method. We assume that the electrons are coupled by a point interaction $-V(\mathbf{r}_i)\delta(\mathbf{r}_i - \mathbf{r}_j)$. This is a good approximation, since the range of the exact interaction is of the order of a Fermi wavelength,[7] while the effects which we shall discuss take place on a much larger scale. Note that $V(\mathbf{r})$ will not be the same in the N and S regions. In the S regions, $V = V_S$ is positive (attractive interaction). In the N regions, $V = V_N$ may be of either sign, depending on a delicate balance between Coulomb repulsion and phonon-induced attraction. (If $V_N > 0$ the N material is also a superconductor at low enough temperatures $T < T_N$. However, as soon as $V_N \lesssim \frac{1}{2}V_S$, the corresponding transition temperature becomes so small that we never observe it.) One of the major interests of the thin-film experiments stems from the fact that, when done under suitable conditions to be discussed below, they may give us measurements of V_N.

To derive the Fermi-type excitations, we write down the equation[8] for the one-electron operator $\psi_\alpha^+(\mathbf{r})$

$$i\frac{\partial\psi_\alpha^+}{\partial t}(r) = \left[\frac{p^2}{2m} + U(r)\right]\psi_\alpha(r) - V(r) \times \sum_\beta \psi_\alpha^+(r)\psi_\beta^+(r)\psi_\beta(r) \qquad (2.1)$$

(α and β are spin indices; the origin of energies is at the Fermi level) and U is the one-electron potential, with different values in the two metals; it also includes the effects of impurities and boundaries. We linearize the last term of (2.1) according to the rule

$$V_n\psi_\alpha^+(r)\psi_\beta^+(r)\psi_\beta(r) \rightarrow V_n\langle\psi_\alpha^+(r)\psi_\beta^+(r)\rangle\psi_\beta(r) \,. \qquad (2.2)$$

The bracket denotes a thermal average. (The Hartree and exchange contribution which are essentially T-independent are incorporated in V). The only nonvanishing terms in (2.2) come from

$$V(\mathbf{r})\langle\psi_\downarrow^+(\mathbf{r})\psi_\uparrow^+(\mathbf{r})\rangle = -V(\mathbf{r})\langle\psi_\uparrow^+(\mathbf{r})\psi_\downarrow^+(\mathbf{r})\rangle = \Delta^+(\mathbf{r}) \,. \qquad (2.3)$$

We call $\Delta(\mathbf{r})$ the pair potential. We now look for eigenmodes of the linearized equation, of the form

$$\begin{aligned}\psi_\uparrow(\mathbf{r}t) &= \textstyle\sum_n (u_n(r)e^{-iE_nt}\gamma_{n\uparrow} + v_n^+(r)e^{iE_nt}\gamma_{n\downarrow}^+) \,,\\ \psi_\downarrow(\mathbf{r}t) &= \textstyle\sum_n (u_n(r)e^{-iE_nt}\gamma_{n\downarrow} - v_n^+(r)e^{iE_nt}\gamma_{n\uparrow}^+) \,,\end{aligned} \qquad (2.4)$$

where $\gamma_n^+\mu\gamma_n\mu$ are new fermion operators $[\gamma_{n\mu}^+\gamma_{m\sigma}] = \delta_{nm}\delta_{\mu\sigma}$, and the excitation energy E_n is restricted to positive values. u and v are the eigenfunctions of the following system of equations:

$$\begin{aligned}Eu &= [(1/2m)p^2 + U(r)]u + \Delta v \,,\\ Ev &= -[(1/2m)p^2 + U(r)]v + \Delta^+ u \,.\end{aligned} \qquad (2.5)$$

Once we have solved for the u's and v's, we must write down the self-consistency requirement obtained from Eqs. (2.3) and (2.4). The prescription for calculating the average in (2.3) is that the new fermion states γ_n^+ of energy E_n have their thermal equilibrium population given by the Fermi function $f(E_n) = 1/1 + \exp E_n/T$. This gives

$$\Delta(\mathbf{r}) \equiv V(\mathbf{r})\langle\psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r})\rangle = V(r) \times \textstyle\sum_n v_n^+(r)u_n(\mathbf{r})[1 - 2f(E_n)] \,. \qquad (2.6)$$

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[4] P. Hilsch, Z. Physik **167**, 511 (1962).

[5] Unfortunately we do not have such data for the films of Refs. 1 and 2.

[6] H. Meissner, Phys. Rev. **117**, 672 (1960).

[7] P. W. Anderson and P. Morel, Phys. Rev. **125**, 1263 (1962).

[8] We shall use a system where $\hbar = k_B = 1$.

To ensure the convergence of this equation, we cut off the interaction V when the excitation energy ϵ_n is higher than ω_D, the local Debye frequency, in agreement with the original BCS procedure. This prescription may be justified by a detailed calculation with the original retarded interaction, even for the nonhomogeneous systems which we consider here.

The pair potential $\Delta(r)$ will be space-dependent for these systems: typical variations of $\Delta(r)$ in an NS sandwich and in an SNS junction are represented on Fig. 1. This space dependence has a first important consequence: the eigenfunctions $u_n(\mathbf{r})$ $v_n(\mathbf{r})$ of Eq. (2.5) are *not* simply proportional to the one electron wave functions in the normal state $w_n(r)$ defined by

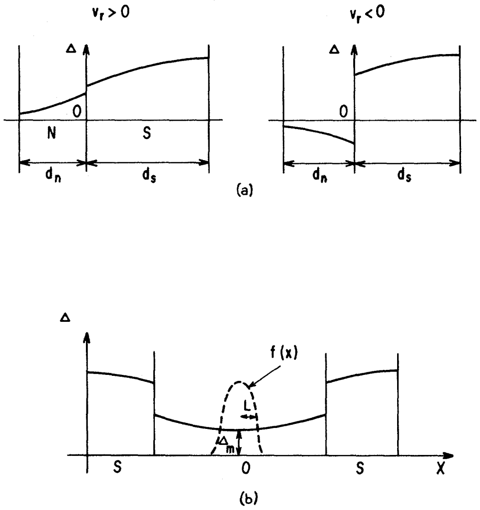

FIG. 1. Spatial dependence of the pair potential $\Delta(X)$ at temperatures close to the transition point in an NS sandwich (a), and in an SNS junction (b). For the sandwich, the two cases $V_N > 0$ and $V_N < 0$ have been represented. (b) also shows the function $f(X)$ corresponding to the wavefunction of a low-energy excitation.

$$[p^2/2m + U(\mathbf{r})]w_n = \epsilon_n w_n \,. \tag{2.7}$$

In more physical terms we may say that the optimum electron pairing is *not* obtained by pairing one electron in a state w_n, and another in the time-reversed state w_n. This procedure works only when $\Delta(\mathbf{r})$ may be taken as independent of r: in an infinite, pure metal or homogeneous alloy.[9]

The pair potential $\Delta(\mathbf{r})$ is a natural "order parameter" for our inhomogeneous systems. This is not the only possible choice, however: we could also use for instance the "condensation amplitude" $F(\mathbf{r})$ defined by

$$F(\mathbf{r}) = \langle \psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r})\rangle \,. \tag{2.8}$$

F is the probability amplitude of finding two electrons in the condensed state at point $\mathbf{r}$. There are two important properties which we shall now emphasize in connection with Δ and F.

(*a*) *boundary conditions*: On an atomic scale, $F(\mathbf{r})$ and $\Delta(\mathbf{r})$ are continuous functions of $\mathbf{r}$. But if, as usual, we are interested in a larger scale, and describe the interface between two metals as a sharp boundary, *neither F nor Δ are continuous on this surface.* Actually, as we shall see, for our dirty systems, the quantity which is continuous is $F(\mathbf{r})/N(\mathbf{r}) = \Delta(\mathbf{r})/N(\mathbf{r})V(\mathbf{r})$, where $N(\mathbf{r})$ is the local density of states (per energy unit and per volume unit) at the Fermi level.

(*b*) *relation between the pair potential and the energy gap E_0*: We define E_0 (a quantity independent of $(\mathbf{r})$ as the lowest excitation energy of the fermions in the self-consistent field Δ: i.e., the minimum positive eigenvalue of Eq. (2.5). We shall now prove the following theorem: when $\Delta(\mathbf{r})$ depends on only one space coordinate X, the energy gap E_0 is equal to the minimum value of $|\Delta(X)|$ in the sample.

This is a rather surprising result, since we might expect at first sight that E_0 is increased beyond $|\Delta|_{\min}$ by some sort of 0-point energy. In fact, this 0-point energy exists, but it is very small in the usual limit when the coherence length ξ is much larger than the Fermi wavelength.

To prove this statement, we first rewrite Eq. (2.5) in spinor form

$$\hat{\psi} = \begin{pmatrix} u \\ v \end{pmatrix}, \tag{2.9}$$

$$E\hat{\psi} = [T\sigma_z + \Delta(X)\sigma_x]\hat{\psi} = \mathcal{H}\hat{\psi}\,, \tag{2.10}$$

$$T = p^2/2m + U \,. \tag{2.11}$$

We choose Δ as real (this is allowed for a static, non magnetic problem). The general aspect of $\Delta(X)$ is represented on Fig. 1(b). The "potential well" corresponds to a minimum value Δ_m, and a spatial range δ (this in practice will be of the order of the coherence length ξ, or at least of the order of the thickness d of the film in which Δ_n is obtained). We want to use a variational principle to show that the minimum E is close to $|\Delta|_{\min}$. But the operator $\mathcal{H}$ is not positive definite (E and $-E$ are simultaneous eigenvalues). Thus we consider the operator $\mathcal{H}^2$, which, thanks to the properties of the Pauli matrices σ, can be written as

$$\mathcal{H}^2 = T^2 + \Delta^2 + i[T\Delta]\sigma_y \,. \tag{2.12}$$

Now, as a trial function, we choose the spinor

$$\hat{\psi}(r) = e^{ik_F Z} f(X)\hat{\varphi}_y \,, \tag{2.13}$$

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[9] $\Delta(\mathbf{r})$ is only approximately constant for an alloy. (For a detailed discussion of this point see Ref. 12.)

where $\hat{\varphi}_y$ is (either) one of the eigenfunctions of $\sigma_y(\sigma_y\hat{\varphi}_y = \pm\hat{\varphi}_y)$. The $0Z$ axis is perpendicular to the $0X$ direction (and otherwise arbitrary). Since our energies are counted from the Fermi level $E_F = k_F^2/2m$. We have simply

$$T\hat{\Psi} = e^{ik_F Z}\left(-\frac{1}{2m}\frac{\partial^2}{\partial X^2}\right)f(X)\hat{\varphi}_y\,. \qquad (2.14)$$

The particular choice of wave vector in (2.13) will lead to a function $f(X)$ with no nodes in the lowest state. We now compute the expectation value

$$E^2 = (\hat{\Psi}|\mathcal{H}^2|\hat{\Psi}) = \int dx f^+(X)\left[\left(-\frac{1}{2m}\frac{\partial^2}{\partial X^2}\right)^2 + |\Delta(X)|^2\right]f(X) \pm i\int f^+(X)\left[-\frac{1}{2m}\frac{\partial^2}{\partial X^2}\,,\ \Delta(X)\right]f(X)dx\,. \qquad (2.15)$$

If we choose for f a real function the third term vanishes; we shall now estimate the first and second terms, by inserting for $f(X)$ a smooth function as shown on Fig. 1(b), with a range L. Then the kinetic energy contribution will be of order $(1/2mL^2)^2$. For the potential energy, if $|\Delta|$ increases according to the law

$$|\Delta(X)|^2 = |\Delta|^2_{\min}(1 + X^2/\delta^2)\,,$$

then the second term of (2.15) is of order $|\Delta|^2_{\min}(1 + L^2/\delta^2)$ and

$$E^2 = |\Delta|^2_{\min}(1 + L^2/\delta^2) + (1/2mL^2)^2\,.$$

Taking the minimum of this expression with respect to the range L of our trial function we get

$$E^2 = |\Delta|^2_{\min}(1 + \mu^{\frac{2}{3}})\,,$$

where $\mu = \text{const} \times (1/2m\delta^2|\Delta|_{\min})$.

We now observe that μ is extremely small in practice: for instance when the variations of Δ take place in one coherence length

$$\delta \backsim v_F/|\Delta|_{\min}\,,$$

then $\mu \sim \lambda_F/\delta \sim 10^{-2}$ to 10^{-3}. Thus the lowest eigenvalue $|E|$ is very close to $\Delta_{\min}$ and the theorem is proven.

Let us now see what consequences this has for tunneling experiments performed on the outer faces of an (NS) sandwich: the minimum of $|\Delta(X)|$ is obtained on the edge of the N side. ($X = -d_n$) If we perform a tunneling experiment on this side we measure directly as a gap the pair potential at the surface. Some preliminary experiments in this field have been reported.[1] Unfortunately they measure only the absolute value of $|\Delta(-d_n)|$ and thus they do not provide a direct information on the sign of the electron electron interaction V_N in the normal metal. (However, as we shall see later on some examples we might derive the sign of V_N if the dependence of $|\Delta(-d_n)|$ on d_n was measured.) A particularly simple case is one where V_N is negligible: then $\Delta(-d_N) \to 0$ and there is no gap. The density of states to be expected in an extreme case of this sort has been computed (in the highly idealized limit of specular reflection of the electrons on the boundaries).[10] It may be that some negative results of tunneling experiments on superconductors with short coherence lengths ξ are due to this effect: if, below the oxide surface, there is a slab of thickness $\sim\xi$ where the BCS parameter NV is small (because of partial oxidation, say), then there will be a strong density of states at low energies due to excitations in the slab, and no gap will be observed.

Let us now consider another type of tunneling experiment on an NS sandwich: this time we perform the experiment on the S side. Here again the energy gap is $E_0 = |\Delta(-d_n)|$ much smaller in this case than the local pair potential $\Delta(d_S)$ (as is clear from Fig. 1). This identity of the gap on the two sides of a thin sandwich has apparently not been verified up to now. Of course, to get a significant tunnel current, at voltages just beyond E_0, on the S side, the thickness of the S slab must not exceed one coherence length, since the one-fermion excited states which may contribute in this range of voltages are rather localized in the N region. (A discussion of the spread out of the states on a simple example can be found in Ref. 10.)

Finally we turn to the case of an SnS junction: here the minimum of $|\Delta(X)|$ is obtained in the central plane $E_0 = \Delta_m = \Delta(0)$ [Fig. 1(b)]. Again, if we perform a tunneling experiment on the outer face of the S slabs, and if they are not much thicker than a coherence length, we should measure E_0 as a gap. The general conclusion is that the energy gap measured by a tunneling experiment on the outer surface of a layered system is not, in general, simply related to the value of the pair potential on this surface. (The only case where the two coincide, in the above example, is for tunneling on the N side of an NS sandwich).

III. SELF-CONSISTENT EQUATION FOR THE PAIR POTENTIAL

We now discuss the numerical determination of the pair potential $\Delta(X)$ for a layered structure. The naive method is to guess a shape of $\Delta(X)$, solve the eigenfunction problem (2.5) for this potential, insert

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[10] P. G. De Gennes and D. Saint-James, Phys. Letters **4**, 151 (1963).

the resulting u's and v's in the self-consistency requirement (2.6), obtain a new value for $\Delta(X)$ and iterate the process. The technique may be improved by the use of a variational principle, but even so it remains rather complicated. To reach a simpler situation we shall restrict our attention to the vicinity of the transition point T of the layered system, and we shall *assume* that the superconducting transition is always of second order: when this is true, the pair potential Δ is small at all points in space when the temperature is close to the transition point. Then it can be treated as a perturbation in the eigenvalue equations (2.5) and the self-consistency condition (2.6) becomes a linear integral equation for Δ, which is not too difficult to solve in practice.

This equation, due to Gor'kov[11] may be written as

$$\Delta(\mathbf{r}) = V(\mathbf{r}) \sum_{\omega} \int d_3\mathbf{r}' \Delta(\mathbf{r}') H_\omega(\mathbf{rr}') \,, \tag{3.1}$$

$$H_\omega(\mathbf{rr}') = T \sum_{\omega} \sum_{nm} \frac{1}{\epsilon_n - i\omega} \frac{1}{\epsilon_m + i\omega} \times w_n^+(\mathbf{r}) w_m^+(\mathbf{r}) w_n(\mathbf{r}') w_m(\mathbf{r}') \,, \tag{3.2}$$

where $\omega = 2\pi T(\nu + \frac{1}{2})$ and the sum $\sum_\omega$ represents a sum over all (positive or negative or 0) integers ν. The functions w_n are the one-electron wave functions in the normal state, defined by Eq. (2.7). They include the effects of impurity and boundary scattering. The one-electron Hamiltonian $\hat{T}$ being real we can choose the w's to be real. This choice of standing, rather than running waves is convenient as usual when impurity scattering is important; thus from now on we drop the stars in Eq. (3.2).

The main properties of the symmetric kernel $H_\omega(\mathbf{rr}')$ are the following.

A. Sum Rule

From the orthogonality of the (real) functions w's we get

$$\int H_\omega(\mathbf{rr}') d_3\mathbf{r}' = \sum_n \frac{1}{\epsilon_n^2 + \omega^2} |w_n(\mathbf{r})|^2 = N(\mathbf{r}) \int \frac{d\epsilon}{\epsilon^2 + \omega^2} = \frac{\pi}{|\omega|} N(\mathbf{r}) \,, \tag{3.3}$$

where $N(\mathbf{r})$ is the local density of states.[12]

B. Relation with a One-Electron Correlation Function[13]

Consider the sum

$$\mathcal{G}_\Omega(\mathbf{rr}') = \sum\nolimits_m \overline{w_n(\mathbf{r}) w_m(\mathbf{r}) w_n(\mathbf{r}') w_m(\mathbf{r}')} \, \delta(\epsilon_n - \epsilon_m + \Omega) \,, \tag{3.4}$$

where the average is taken over all states n with a fixed energy ϵ_n. When $\mathcal{G}$ is known, $H_\omega(\mathbf{rr}')$ can be derived simply according to (3.2). Now we observe that the Fourier transform

$$\mathcal{G}(\mathbf{rr}'t) = \int \frac{dt}{2\pi} e^{i\Omega t} \mathcal{G}_\Omega(\mathbf{rr}') \tag{3.5}$$

is a one-electron correlation function, namely

$$\mathcal{G}(\mathbf{rr}'t) = \overline{\delta(\mathbf{r}(0) - \mathbf{r})[\mathbf{r}(t) - \mathbf{r}']} \,, \tag{3.6}$$

where the average is over all one-electron states of energy ϵ_n (in practice at the Fermi energy) $\mathbf{r}(t) = e^{iTt}\mathbf{r}e^{-iTt}$ is the electron position operator in the Heisenberg representation; it describes the motion of an electron in the normal metal, with the Hamiltonian $\hat{T} = p^2/2m + U(\mathbf{r})$. Equation (3.6) is easily verified in the w_n representation. It is useful because the form of the correlation function or the right-hand side is immediately known in many cases. We shall now discuss this on some examples.

C. Value of Hω(rr′) for an Infinite "Dirty" Medium

When the electron mean free path l is small, the correlation function (3.6) spreads according to a diffusion equation

$$(\partial/\partial|t|)\mathcal{G}(\mathbf{rr}'t) - D\nabla^2\mathcal{G}(\mathbf{rr}'t) = \text{const} \times \delta(\mathbf{rr}')\delta(t) \,. \tag{3.7}$$

Here $D = \frac{1}{3} v_F l$ is the diffusion coefficient, v_F is the Fermi velocity. Equation (3.7) is valid when (1) uncertainty relations do not come into play (distances $|r - r'| \gg \lambda_F$) (2) the diffusion approximation applies ($|\mathbf{r} - \mathbf{r}'| \gg l$ and $t \gg l/v_F$).

Taking Fourier transforms we get

$$\mathcal{G}_\Omega(\mathbf{q}) = \int \mathcal{G}_\Omega(\mathbf{rr}') e^{i\mathbf{q}.(\mathbf{r}-{}'\mathbf{r})} d_3r' = \text{const} \left\{ \frac{1}{i\Omega + Dq^2} + \text{c.c.} \right\} . \tag{3.8}$$

When $\mathcal{G}$ is known we can derive H_ω by Eqs. (3.2) and (3.4),

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[11] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 1407 (1959) [English transl.: Soviet Phys.—JETP **10**, 998 (1960)]. See also C. Caroli, P. G. De Gennes, and J. Matricon, Phys. Cond. Matter **1**, 176 (1963).

[12] C. Caroli, P. G. De Gennes, and J. Matricon, J. Phys. Rad. **23**, 707 (1962).

[13] P. G. De Gennes and E. Guyon, Phys. Letters **3**, 168 (1963).

$$H_\omega(\mathbf{q}) = \int H_\omega(\mathbf{rr}')e^{iq.(\mathbf{r}-'\mathbf{r})}d_3r'$$
$$= \text{const} \times \int d\epsilon d\Omega \frac{1}{\epsilon - i\omega} \frac{1}{\epsilon + \Omega + i\omega}$$
$$\times \left\{\frac{1}{i\Omega + Dq^2} + \text{c.c.}\right\} = 2\pi N \frac{1}{2|\omega| + Dq^2}\,. \tag{3.9}$$

The constant in (3.9) has been obtained from the sum rule (3.3). Eq. (3.9) can also be obtained by the Green's function method—but the latter derivation is much more tedious and slightly less general.[14]

Since in the following we shall be concerned with situations where the pair potential Δ depends only on one space coordinate ($\Delta(X)$), it is of interest to write down the one-dimensional Fourier transform of $H_\omega(q)$,

$$H_\omega(XX') = \frac{1}{2\pi}\int H_\omega(q)e^{iq(X-X')}dq$$
$$= (\pi N/2|\omega|\xi_\omega)e^{-|X-X'|/\xi_\omega}\,. \tag{3.10}$$

$\xi_\omega = (D/2|\omega|)^{\frac{1}{2}}$ gives us the range of $H_\omega(XX')$. The largest range corresponds to $\omega = \omega_0 = \pi T$,

$$\xi_{\omega_0} = \xi = (D/2\pi T)^{\frac{1}{2}}\,. \tag{3.11}$$

ξ plays the role of a coherence length for our alloy (The dirty superconductor approximation requires $l \ll \xi$.)

D. Boundary Effects

The first, and most simple problem here is that of a *free surface* (the metal occupying, for instance, the half space $X > 0$); Eq. (3.7) for the correlation function remains valid. Since there is no electron flow out from the surface, we must have $D(d\mathcal{G}/dX)_{X=0} = 0$. This condition can be achieved by a method of images, and we get finally

$$H_\omega(XX') = \frac{\pi N}{2|\omega|\xi_\omega}[e^{-|X-X'|/\xi_\omega} + e^{-(X-X')/\xi_\omega}]\,. \tag{3.12}$$

Since
$[(\partial H_\omega/\partial X)(XX')]_{X=0} = 0$, we see in Eq. (3.1) that

$$(d\Delta/dX)_{X=0} = 0\,. \tag{3.13}$$

The pair potential has 0 slope at the surface.[15]

It is slightly more complicated to discuss the boundary problem for two metals A and B (separated by the plane $X = 0$) with different densities of state N_A, N_B and diffusion coefficients D_A, D_B. By the correlation function method or with Green's functions, we may show that in each of the metals $H_\omega(XX')$ is still ruled by the equation

$$2|\omega|H_\omega(XX') - D(X')(d^2/dX'^2)H_\omega(XX')$$
$$= 2\pi N(X)\delta(X - X')\,. \tag{3.14}$$

What are the boundary conditions on the surface? One of them can be obtained by a sum rule argument: we integrate (3.14) on X', obtaining

$$2|\omega|\int_{-\infty}^{\infty} H_\omega(XX')dX' - \left[D\frac{d}{dX'}H_\omega(XX')\right]_{X'=0+}^{X'=\infty}$$
$$- \left[D\frac{d}{dX'}H_\omega(XX')\right]_{X'=-\infty}^{X'=0-} = 2\pi N(X)\,. \tag{3.15}$$

The contributions for $X' = \infty$ vanish, and by comparison with (3.3) we get

$$\left[D(X)\frac{d}{dX'}H_\omega(XX')\right]_{X'=0-}^{X'=0+} = 0\,. \tag{3.16}$$

The other boundary condition will have the general form

$$[H_\omega(X,X')]_{X'=0+} = [\alpha H_\omega(X,X')$$
$$+ \beta(d/dX')H_\omega(X,X')]_{X'=0-}\,. \tag{3.17}$$

β/α is an effective length, which could be derived from the microscopic transport equation satisfied by H_ω, and which is familiar from similar neutron transport problems at the surface of a moderator. If there is no insulating barrier between A and B,[16] we know from the neutron case that β/α is comparable to the mean free path l. Since $(1/H_\omega)(d/dX')H_\omega \sim (1/\xi)$, the second term of (3.17) is of order l/ξ, and is negligible in our limit. Thus the second boundary condition will be simply of the form

$$H_\omega(X,0_+) = \alpha H_\omega(X,0_-)\,. \tag{3.18}$$

We now proceed to show that α is determined by the symmetry properties of $H_\omega(XX')$. From Eq. (3.14) we have

$$\left.\begin{array}{l} H_\omega(XX') = \dfrac{N_A\pi}{2|\omega|\xi_A}[e^{-|X-X'|/\xi_A} + \lambda e^{-(X+X')/\xi_A}]\,, \\ \qquad\qquad \begin{array}{l} X > 0 \\ X' > 0 \end{array} \text{(side A)}\,, \\ H_\omega(XX') = (N_B\pi/2|\omega|\xi_B)\mu e^{-X/\xi_A + X'/\xi_B}\,, \\ \qquad\qquad X > 0 \quad \text{(side A)}\,, \\ \qquad\qquad X' < 0 \quad \text{(side B)}\,. \end{array}\right\} \tag{3.19}$$

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[14] Note that the diffusion concept applies even for concentrated alloys.

[15] When the finite thickness of the metal–vacuum transition layer is taken into account, the condition is not exactly one of 0 slope; see Reference 12. On all physical effects, however, this leads only to corrections of order λ_F/ξ.

[16] More accurately, if the transmission coefficient of the barrier is much larger than l/ξ.

Here λ and μ are unknown parameters, to be determined from the boundary conditions (3.16), (3.18), which yield

$$(1-\lambda)N_{\mathrm{A}} = \mu N_{\mathrm{B}}\,, \quad (1+\lambda)(N_{\mathrm{A}}/\xi_{\mathrm{A}}) = \alpha\mu(N_{\mathrm{B}}/\xi_{\mathrm{B}})\,,$$

$$\mu = [2\xi_{\mathrm{B}}/(\xi_{\mathrm{B}}+\alpha\xi_{\mathrm{A}})](N_{\mathrm{A}}/N_{\mathrm{B}})\,,$$

$$H_\omega(XX') = (\pi/|\omega|)\,[N_A/(\xi_B+\alpha\xi_A)]e^{-X/\xi_A+X'/\xi_B} \qquad (X>0\,,\quad X'<0)\,.$$

We interchange X and X', repeat the argument and write that $H_\omega(XX')$ is symmetric; we get

$$[N_{\mathrm{A}}/\xi_{\mathrm{B}}+\alpha\xi_{\mathrm{A}})] = [N_{\mathrm{B}}/(\xi_{\mathrm{A}}+\alpha^{-1}\xi_{\mathrm{B}})]\,, \qquad \alpha = N_{\mathrm{A}}/N_{\mathrm{B}}\,. \tag{3.20}$$

Thus we conclude that $H_\omega(XX')/N(X')$ is continuous when X' crosses the boundary. If we now return to Eq. (3.1) for the pair potential, we observe that $\Delta(X)/V(X)$ obeys the same boundary conditions than $H_\omega(XX')$. Thus the boundary conditions for dirty superconductors are, from Eqs. (3.16) and (3.20),

$$\left.\begin{array}{ll}\Delta/NV & \text{continuous}\\ (D/V)(d/dX)\,\Delta & \text{continuous}\end{array}\right\}\text{at a metallic interface,}$$

$$d\Delta/dX = 0 \qquad \text{at a free surface.} \tag{3.21}$$

These conditions will play a crucial role in the following. Finally, it is sometimes of interest to translate these results in terms of the "Landau–Ginsburg wavefunction" ψ. For a dirty superconductor, the relation between ψ and Δ is[11]

$$\psi = [(\tfrac{1}{8}\,\pi)(n\tau/T)]^{\frac{1}{2}}\Delta\,, \tag{3.22}$$

where n is the number of electrons per cm^3, and $\tau = l/v_{\mathrm{F}}$ is the transport relaxation time. Comparing (3.22) and (3.21) we see that ψ is *not* continuous at a metallic interface.

IV. NS SANDWICHES: TRANSITION TEMPERATURE

We now consider a two-layer system of the type represented on Fig. 1. Our aim is to solve the integral equation (3.1) for the pair potential and see at what temperature T it has a nontrivial solution: this will give us the transition point (provided that the transition is of second order). Of course, this is a rather formidable task, and we shall perform it only in some limiting cases.

A. The Cooper Limit

We assume that the thicknesses $d_{\mathrm{N}}, d_{\mathrm{S}}$ of the slabs are much smaller than the respective coherence lengths $\xi_{\mathrm{N}}(T)\xi_{\mathrm{S}}(T)$ defined by Eq. (3.11). (Note that the ξ'_{S} are temperature dependent: in particular, if the transition point of the sandwich is low, the ξ'_{S} will be large and the requirement is mild.) Then the kernel $H_\omega(XX')$ is essentially constant when X or X' is varied in one of the slabs. There are three values to be derived:

$$H_\omega(NN)\,(\text{for both } X,X' \text{ in } N),\quad H_\omega(SN) = H_\omega(NS)\,,$$

$$\text{and } H_\omega(SS)\,.$$

They are derived from the equations

$$d_n H_\omega(NN) + d_{\mathrm{S}} H_\omega(NS) = N_{\mathrm{N}}(\pi/|\omega|)\,,$$

$$d_n H_\omega(SN) + d_{\mathrm{S}} H_\omega(SS) = N_{\mathrm{S}}(\pi/|\omega|)\,, \tag{4.1}$$

$$H_{\mathrm{NN}}/N_{\mathrm{N}} = H_{\mathrm{NS}}/N_{\mathrm{S}}\,, \qquad H_{\mathrm{SN}}/N_n = H_{\mathrm{SS}}/N_{\mathrm{S}}\,. \tag{4.2}$$

The group (4.1) is derived from the sum rule (3.3). The group (4.2) is derived from the boundary condition (3.20).

From (4.1) and (4.2) we get

$$\frac{H_\omega(\mathrm{NS})}{N_n N_{\mathrm{S}}} = \frac{H_\omega(\mathrm{NN})}{N_n^2} = \frac{H_\omega(\mathrm{SS})}{N_{\mathrm{S}}^2} \qquad \frac{\pi}{|\omega|}\frac{1}{N_n d_n + N_{\mathrm{S}} d_{\mathrm{S}}}\,. \tag{4.3}$$

We can then write down Eq. (3.1) for the pair potential Δ. Since $\Delta(X)$ will be constant in each slab in our limit, this becomes simply

$$\Delta_n = \sum_\omega V_n T\frac{\pi}{|\omega|}\frac{1}{N_n d_n + N_{\mathrm{S}} d_{\mathrm{S}}}(N_n^2 d_n \Delta_n + N_n N_{\mathrm{S}} d_{\mathrm{S}} \Delta_{\mathrm{S}})$$

$$\Delta_{\mathrm{S}} = \sum_\omega V_{\mathrm{S}} T\frac{\pi}{|\omega|}\frac{1}{N_n d_n + N_{\mathrm{S}} d_{\mathrm{S}}}(N_n N_{\mathrm{S}} d_n \Delta_n + N_{\mathrm{S}}^2 d_{\mathrm{S}} \Delta_{\mathrm{S}})\,. \tag{4.4}$$

We now require that (4.4) has a nontrivial solution. We shall write down the result only for the case where the frequency cutoff ω_0 of the interaction V is the same in N and S. (This is often close to the experimental situation, and greatly simplifies the algebra). When this cutoff is taken into account, we must effect the standard replacement

$$T\sum_\omega \frac{\pi}{|\omega|} \rightarrow \log\frac{1.14\,\omega_0}{T} = \frac{1}{\rho}\,, \tag{4.5}$$

and the nontrivial solution is obtained for

$$\rho = \frac{V_n N_n^2 d_n + V_{\mathrm{S}} N_{\mathrm{S}}^2 d_{\mathrm{S}}}{N_n d_n + N_{\mathrm{S}} d_{\mathrm{S}}}\,. \tag{4.6}$$

ρ plays the role of a "effective NV" in the BCS formula for T [Eq. (4.5)]. A formula of this type

(4.6) has been first derived by Cooper[17] by a very simple argument. [There is a difference however in the weighting factors which, according to (4.6) are $N_n\, d_n$ and $N_S\, d_S$, while the Cooper argument leads to d_n and d_S]. The main consequences of (4.6) are the following:

(1) when both V_S and V_n are attractive (positive), there is always a finite transition temperature T,

(2) when V_n is repulsive and $|V_n|d_n > V_S\, d_S \times (N_S/N_n)^2$, the system does never become superconducting. There are some experimental data on Ag Pb[1] and Ag Sn[2] sandwiches which might be interpreted in terms of Eq. (4.6). The thicknesses are in the 300-Å range. In these experiments the transition temperature seems to vanish rather sharply when d_n exceeds some critical value. This might suggest that V_{Ag} is repulsive. However, we do not think that any definite conclusion can be reached in the present state of affairs, since the intrinsic mean free path l (and thus the coherence length ξ) was not controlled. It is thus not clear whether the limit $\xi > d$ applies, and if not, as we shall see later, the conclusions might be very different.

Finally, we should mention the possible effects of a thin oxide layer separating the two films.[17] When the transmission of the oxide layer becomes small, the boundary condition (3.17) cannot be simplified, and we must compute the effective length β/α. This "oxide effect" is difficult to control, and is one of the main limitations for the determination of V_N in the Cooper limit.

B. Thick Films: the One-Frequency Approximation

We now consider NS sandwiches where the thicknesses $d_S\, d_N$ are somewhat larger than the corresponding coherence lengths $\xi_S\, \xi_N$. It turns out that in this situation we can obtain the shape of the pair potential $\Delta(X)$ in closed form if we make a slight simplification on the integral equation (3.1). The argument is as follows: the kernel $H_\omega(XX')$ has a range $\xi_\omega = (D/2|\omega|)^{\frac{1}{2}}$. For the lowest frequency $\omega = \pm\omega_0 = \pm\pi T$, the range $\xi_{\omega_0} = \xi$ is maximum. All the other frequencies' components have shorter ranges $\xi/\sqrt{3}$, $\xi/\sqrt{5}$, etc. The approximation amounts to retaining the lowest-frequency component H_{ω_0}, and replacing all the other ones by a δ function suitably normalized,

$$T\sum\nolimits_\omega H_\omega(XX') \to 2TH_{\omega 0}(XX') + CN(X)\delta(X-X'). \qquad (4.7)$$

From the sum rule (3.3) and the cutoff prescription $T\sum_\omega (\pi/|\omega|) \to \log(1.14\,\omega_0/T)$, we get

$$C = \log(1.14\,\omega_0/T) - 2\,.$$

Equation (3.1) for the pair potential becomes

$$\Delta(X)[1 - CN(X)V(X)] = 2V(X)T \times \int H_{\omega 0}(XX')\Delta(X')dX'\,. \qquad (4.8)$$

The main interest of this form is the following: in each slab we know that $H_{\omega 0}(XX')$ obeys the "diffusion equation" (3.14) with respect to X or X'. Applying the operator $2|\omega| - D(d^2/dX^2)$ to both sides of (4.8) we obtain

$$(1 - CVN)2\pi T\Delta - D(d^2\Delta/dX^2) = 2NV\Delta\,. \qquad (4.9)$$

Thus in this approximation, the pair potential in each slab is ruled by an elementary differential equation and the only problem left is to match the boundary conditions [to be derived from (4.8)]. How accurate is the approximation? We can get an estimate of the accuracy by returning to the case of an infinite dirty metal, where the solutions of (3.1) are plane waves $\Delta \sim e^{iqX}$. Making use of the Fourier transform (3.9), and performing the sum over ω, we get for this case the exact relation[13]

$$v \equiv (1/NV) - \log(1.14\,\omega_0/T) = \psi(\tfrac{1}{2}) - \psi(\tfrac{1}{2} + \tfrac{1}{2}y)\,,$$
$$y = Dq^2/2\pi T\,, \quad \psi(X) = \Gamma'(X)/\Gamma(X)\,. \qquad (4.10)$$

This has to be compared to the approximate relation derived from (4.9),

$$v = [-2y/(1+y)]\,. \qquad (4.11)$$

The two curves $v(y)$ are plotted on Fig. 2, both for $y > 0$ and for $y < 0$ (the latter corresponding to imaginary values of q, i.e., exponential decays which are of interest for our slab problems). Near $y = 0$, the exact slope dv/dy is equal to -2.44, while the approximate one is -2. (This means that the coefficients of the Landau–Ginsburg equation as deduced from the approximate form are correct within 20%). Near $y = -1$, the exact relation is

$$v = -1.39 + 2/(1+y)\,, \qquad (4.12a)$$

while the approximate one is

$$v = -2 + 2/(1+y)\,. \qquad (4.12b)$$

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[17] L. Cooper, Phys. Rev. Letters **6**, 698 (1961). Earlier theoretical discussions include: A. D. Misener and J. O. Wilhelm, Trans. Roy. Soc. Can. Sec. III **29**, 5 (1935); R. H. Parmenter, Phys. Rev. **118**, 1173 (1960). A recent phenomenological theory has been proposed by D. H. Douglass, Phys. Rev. Letters **9**, 155 (1962).

The singular term of v is exactly reproduced (Note that large $|v|$ corresponds to $N\,|V|$ small, a situation often realized in the normal slab.) Thus we conclude that the one-frequency approximation is satisfactory, except in the range $y > 1$. In practice, the positive y's will be encountered in the S slab, and the condition $y < 1$ means that the thickness of the S slab must be larger than one coherence length.

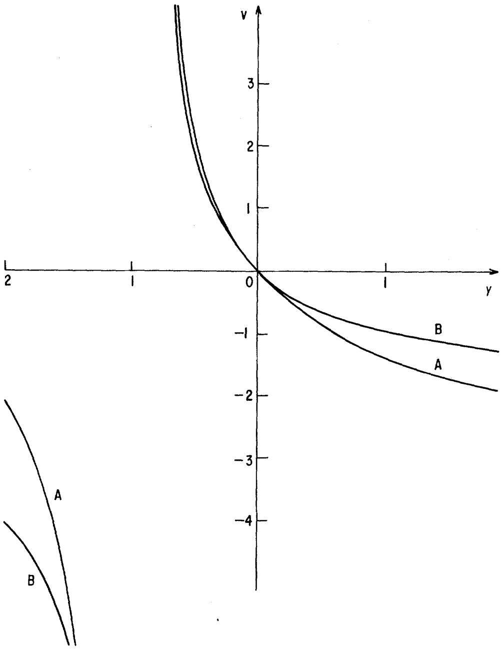

FIG. 2. Fourier transform of the kernel of the integral equation (3.1) for the pair potential in an infinite dirty material. Abscissa $y = Dq^2/2\pi T$ (q is the wave vector). Ordinate $v = (1/NV) - \log(1.14\,\omega_0/T)$. Curve A: exact (Eq. 4.10); Curve B: one-frequency approximation (Eq. 4.11). The region $y < -1$ corresponds to negative V (repulsive interactions).

We now discuss the boundary conditions to be applied to $\Delta(X)$ at a metallic interface when the approximate Eq. (4.8) is used. From the boundary conditions satisfied by $H_\omega(XX')$ [Eqs. (3.16) and (3.20)], we see that in the one-frequency approximation

$$\Delta(1 - CNV)/NV \quad \text{is continuous}\,,$$
$$(D/V)(1 - CNV)(d\Delta/dX) \quad \text{is continuous}\,. \tag{4.13}$$

These boundary conditions are slightly different from the exact ones (Eq. 3.21). In the exact solution, for instance, Δ/NV is continuous, but shows a rapid variation near the boundary because of the high-frequency terms in the kernel (3.1). This rapid variation is here approximated by an extra discontinuity. At a free surface we still have the condition $d\Delta/dX = 0$.

We are now able to write down the shape of $\Delta(X)$ for an (NS) sandwich (corresponding to Fig. 1) as the solution of Eq. (4.9) with the above boundary conditions,

$$\Delta(X)\,\frac{1 - CNV}{NV} = A\,\frac{\cos q(X - d_S)}{\cos qd_S}\,, \quad X > 0 \quad \text{(side S)}\,,$$
$$\Delta(X)\,\frac{1 - CNV}{NV} = A\,\frac{\cosh K(X + d_n)}{\cosh Kd_n}\,, \quad X < 0 \quad \text{(side N)}\,, \tag{4.14}$$

where A is an arbitrary constant, and

$$q^2 = \frac{2\pi T}{D_S}\left(-1 + \frac{2N_SV_S}{1 - CN_SV_S}\right) > 0\,, \tag{4.15a}$$

$$K^2 = \frac{2\pi T}{D_n}\left(+1 - \frac{2N_nV_n}{1 - CN_nV_n}\right) > 0\,. \tag{4.15b}$$

The solution (4.14) has 0 slope on the free surfaces. On the NS boundary there remains to satisfy the second equation (4.12). This yields

$$qtgqd_S = \eta KthKd_n\,, \tag{4.16}$$

where $\eta = D_nN_n/D_SN_S$.

Equation (4.16) is an implicit equation for the transition temperature T.[18] To discuss experimental data, it is sometimes preferable to invert the procedure: when N_S, V_S, N_n, D_n, D_S are known, and the transition temperature is measured, we know q from (4.15a). Then (4.16) gives K, from which we may derive by Eq. (4.15b) the unknown electron–electron interaction V_n in the normal metal. Finally we must check that we are in the range of validity of the one-frequency approximation ($d_S > \xi_S$); in practice this implies that T is not much lower than the transition point T_{S0} of the bulk S metal.

Two characteristic lengths are of interest in this boundary problem: (1) the depth of penetration of the pairs on the N side is K^{-1}. In the (usual) situation where V_N is small (or arbitrary sign), K^{-1} is close to $(D_n/2\pi T)^{\frac{1}{2}}$ (slightly larger if $V_N > 0$, slightly smaller if $V_N < 0$). The only case where K^{-1} may become anomalously large is when the metal N is also a superconductor ($V_N > 0$) and when T is just above T_{N0} (the transition temperature of the bulk N metal). (2) The "extrapolation length"

$$b = \frac{\Delta(0+)}{(d\Delta/dX)_{0+}} = \left(\frac{D_SN_S}{D_nN_n}\right) K^{-1}\coth Kd_n \tag{4.17}$$

defines the macroscopic boundary condition satisfied

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[18] More accurately, the largest root T of (4.16) is the transition temperature.

by the pair potential on the S side. Consider for instance the case $d_n \to \infty$ $(b \to b_\infty)$. Then, when N_S and N_n are comparable, we see from (4.8) that $b_\infty \sim K^{-1}$. On the other hand, if N is a semimetal or a heavily doped semiconductor, N_S/N_n may be of order 100, and λ_∞ is much larger than K^{-1}. Finally, when $N_n \to 0$ (insulator on the N side), b_∞ becomes infinite and we come back to the requirement $(d\Delta/dX)_{0+} = 0$.

In the limit where $d_S \gg \xi_S$ we may simplify (4.16) and write

$$q(d_S + b) = \tfrac{1}{2}\pi .$$

In this limit, q is small, and from (4.15a) we see that T is close to T_{SO}. Writing down the explicit value of C we obtain, in the one-frequency approximation,

$$T = T_{SO} - (1/\pi)D_S q^2 = T_{SO} - \tfrac{1}{4}\pi[D_S/(d_S + b)^2] . \tag{4.18}$$

[Note that in the right-hand side of (4.18) we may use the value of b corresponding to $T = T_{SO}$.] When $d_n \to \infty$ the transition temperature (4.18) reaches a lower limit

$$T_{\lim} = T_{SO} - \tfrac{1}{4}\pi[D_S/(d_S + b_\infty)^2] . \tag{4.19}$$

When d_n is finite, but still larger than K^{-1}, we may expand $b \cong b_\infty(1 + 2e^{-Kd_n})$ and we obtain

$$T = T_{\lim} + \pi D_S[b_\infty/(d_S + b_\infty)^3]e^{-2Kd_n} . \tag{4.20}$$

This exponential law of approach to $T_{\lim}$ has been first proposed, on experimental grounds, by Hilsch.[4] In the experiments by Hilsch (on Cu Pb sandwiches) the electron mean free path l_{Cu} was measured and could be varied (from 40 to 800 Å) by changing the evaporation temperature. The transition temperature could be described by a law of the form $T = T_{\lim} + Ce^{-2Kd_n}$ and the decay constant $2K$ was shown to be inversely proportional to $(l_{Cu})^{\frac{1}{2}}$. This in agreement with Eq. (4.15b) since $D = \frac{1}{3} v_F l$. For a Pb Cu sandwich with $l_{Cu} = 40$ Å, Hilsch measures $K^{-1} = 200$ Å. Taking $v_{F(Cu)} = 1.58\ 10^8$ cm/sec and $T = 7°$K, we have $(2\pi T/D_n)^{\frac{1}{2}} = 190$ Å, smaller than K^{-1}. Thus we expect the interaction v_{Cu} to be attractive, and in fact we compute from (4.15b) $(NV)_{Cu} \cong 0.05$. Of course this conclusion is very provisory: if a 10% uncertainty is allowed on K, $(NV)_{Cu}$ may range between -0.06 and 0.10. It is clear, however, that from such experiments we may derive important informations on the electron–electron interaction in "normal" metals.[19] There are two favorable points: (1) the significance of K is independent of the physical state of the NS boundary; for instance, if there was a thin oxide layer between N and S, the amplitude of the temperature shifts $T - T_{\lim}$ would be reduced, but the exponential factor in (4.20) would still hold with the same value of K.[20] (2) When the BCS parameter $(NV)_n$ is small, as will often be the case, the one-frequency approximation is very accurate on the N side [since (4.12a) and (4.12b) are very similar in the limit $y \to -1$]. In fact, in the discussion of reference 13, the complete Eq. (4.10) was used to relate K and $(NV)_{Cu}$ and the results were essentially identical to those derived from (4.12b) or (4.15b).

C. Thin Superconducting Layer on a Massive Normal Substrate

The only case which is not covered by the above discussions (A and B) corresponds to $d_S \ll \xi_S(T)$, $d_n > \xi_n(T)$. We shall discuss the limiting case $d_n \to \infty$, which is comparatively simple, since when $d_S \ll \xi_S$, $\Delta(X)$ and $H_\omega(XX')$ are nearly constant in the S region $(0 < X < d_S)$. It is then easy to determine $H_\omega(XX')$ from (3.14), (3.16), (3.20), and the equation for Δ finally reads

$$\Delta_S\left(1 - N_S V_S T \sum_\omega \frac{\pi}{|\omega|}\frac{N_S d_S}{D(\omega)}\right) = N_S V_S T \sum_\omega \frac{\pi}{|\omega|}\frac{N_n}{D(\omega)} \times \int_{-\infty}^{0} dX \Delta(X) e^{X/\xi_\omega} , \tag{4.21a}$$

$$\Delta(X) = N_n V_n T \sum_\omega \frac{\pi}{|\omega|}\left\{\Delta_S \frac{N_S d_S}{D(\omega)} e^{X/\xi_\omega} + \int_{-\infty}^{0} dX' \Delta(X') \frac{1}{2\xi_\omega}\left[e^{-|X-X'|/\xi_\omega} + \left(1 - \frac{N_S d_S}{2D(\omega)}\right) e^{(X+X')/\xi_\omega}\right]\right\} \quad (X < 0) , \tag{4.21b}$$

$$\Delta_S = \Delta(0 < X < d_S) ,$$

$$D(\omega) = N_n \xi_\omega + N_S d_S ,$$

$$\xi_\omega = (D_n/2|\omega|)^{\frac{1}{2}} .$$

Consider first the case $V_N = 0$. Then $\Delta(X) = 0$ for $X < 0$ and we get the equation for the transition

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[19] A preliminary discussion of these effects was given in reference 10. It was not realized, however, in this reference, that Eq. (4.10) applied even for repulsive interaction $V_n < 0$.

[20] In fact, for a typical Hilsch experiment ($d_{Pb} = 400$ Å), the theoretical value of $T_{SO} - T_{\lim}$ as derived from (4.16) assuming no oxide layer is $\sim$2°K, the experimental value is closer to 1°K.

point directly from (4.21a). After rearrangement, this becomes

$$\log\frac{T_{\mathrm{SO}}}{T}=\sum_{n\geq 0}\frac{1}{n+\frac{1}{2}}\times\left[1-\frac{1}{1+Z(2n+1)^{-\frac{1}{2}}}\right]=m(Z)\,, \tag{4.22}$$

$$Z=\frac{N_n\xi_n}{N_{\mathrm{S}}d_{\mathrm{S}}}=\frac{N_n}{N_{\mathrm{S}}d_{\mathrm{S}}}\left(\frac{D_n}{2\pi T}\right)^{\frac{1}{2}}. \tag{4.23}$$

we shall be mainly interested in the limit of low T, large Z, for which

$$m(Z)\rightarrow 2\log Z+\log 2\gamma+\beta/Z+\cdots\,, \tag{4.24}$$

where γ is Euler's constant ($\gamma = 1.78$) and $\beta = (\sqrt{2}-2)\zeta(\frac{1}{2}) = 0.86$. Then (4.22) may be cast into the explicit form

$$d_{\mathrm{S}}=\frac{d_1}{1-\beta[\frac{1}{2}\,\gamma(T/T_{\mathrm{SO}})]^{\frac{1}{2}}}\qquad \text{for } d_n=\infty\,,\quad d_{\mathrm{S}}\ll\left(\frac{D_n}{2\pi T}\right)^{\frac{1}{2}}, \tag{4.25}$$

$$d_1=\frac{N_n}{N_{\mathrm{S}}}\left(\frac{\gamma}{\pi}\,\frac{D_n}{T_{\mathrm{SO}}}\right)^{\frac{1}{2}}. \tag{4.26}$$

The diagram (d_{S},T) is represented on Fig. 3. Note that there is no second-order transition point when $d_{\mathrm{S}} < d_1$; thus the absence of all superconductivity points in a finite range of d_{S} does not necessarily show that the interaction V_n is repulsive. The physical origin of this surprising result may be understood qualitatively by an extension of the Cooper argument: the interaction V_{S} is reduced by a factor $\sim d_{\mathrm{S}}/(d_{\mathrm{S}} + \xi_n)$, where $\xi_n = (D_n/2\pi T)^{\frac{1}{2}}$ is the range of penetration of the pairs on the N side. The important point is that ξ_n becomes large when T is low: this tends to accelerate the decrease of T when d_{S} decreases, and leads to a critical thickness d_1. A similar argument can be applied to the nonlinear self-consistency equation for Δ_{S} at $T = 0$.

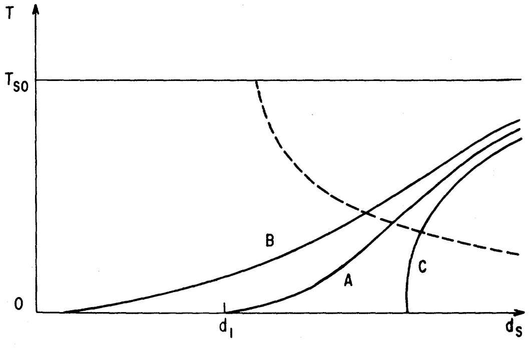

FIG. 3. Transition temperature of a thin film of superconducting material (thickness d_{S}) deposited on a massive normal substrate ($d_n = \infty$). Curve A corresponds to $V_{\mathrm{N}} = 0$ (no electron–electron interaction in N). Curve B cooresponds to a weak attractive interaction, and curve C to a weak repulsive interaction. The region of validity of the calculation of Sec. IV.C corresponds to $d_{\mathrm{S}} < \xi_{\mathrm{S}}(T)$, and is bounded by the dotted curve.

These considerations can be extended to the case of a small, nonvanishing V_{N} (or arbitrary sign) by applying the one-frequency approximation to (4.21b). The results are represented qualitatively on Fig. 3.

V. JUNCTIONS

Consider a thin normal layer N (of thickness $2a$) embedded in a superconducting metal S. We ask what is the maximum supercurrent density J_m which may cross this SNS junction. When $2a \gg \xi_{\mathrm{N}}$, we expect this current to be very small, while when $2a < \xi_{\mathrm{N}}$, J_m is certainly very large; the interest of these junctions is precisely that the critical current may be adjusted to (nearly) any desired value by a proper choice of the thickness $2a$.

We shall compute this critical current for temperatures T which are only slightly lower than T_{SO}. Then, in the S regions, the pair potential is ruled by the local Landau–Ginsburg equation[21]

$$\frac{T_{\mathrm{SO}}-T}{T_{\mathrm{SO}}}\Delta+L_1\frac{d^2\Delta}{dX^2}-R_1|\Delta|^2\Delta=0 \qquad (|X|>a)\,, \tag{5.1}$$

where, for a dirty superconductor,[11]

$$L_1=\tfrac{1}{8}\,\pi(D/T_{\mathrm{SO}})\,,\qquad R_1=\tfrac{7}{8}\,[\zeta(3)/(\pi T_{\mathrm{SO}})^2]\,. \tag{5.2}$$

The superfluid current is given by

$$J=-\frac{i}{2}\,C\left(\Delta^+\frac{d\Delta}{dX}-\Delta\frac{d\Delta^+}{dX}\right), \tag{5.3}$$

$$\text{where } C=\tfrac{1}{2}\,\pi e(N_{\mathrm{S}}\,D_{\mathrm{S}}/T_{\mathrm{SO}})\,. \tag{5.4}$$

The variations of Δ predicted by (5.1) take place within a characteristic distance $p \sim \xi_{\mathrm{S}}(T_{\mathrm{SO}}/T_{\mathrm{SO}} - T)^{\frac{1}{2}} \gg \xi_{\mathrm{S}}$. Since p is large, the effect of the N slab may be included by imposing appropriate boundary conditions to Eq. (5.1) on the planes $X = \pm a$. We shall now derive these conditions.

The major point is the following: in the region of the junction we may derive the shape of Δ from the linearized self-consistency equation (3.1), and even set $T = T_{\mathrm{SO}}$; all the corrections neglected by this

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[21] L. D. Landau and V. L. Ginsburg, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

procedure are of order $\xi_S/p = (1 - T/T_{S0})^{\frac{1}{2}} \ll 1$. Thus we return to (3.1), use the one-frequency approximation, and write down immediately the solutions for $|X| < a$:

$$\Delta(X) = [N_nV_n/(1 - CN_nV_n)](\cosh KX/\cosh Ka) \quad \text{(even)},$$

$$\Delta(X) = [N_nV_n/(1 - CN_nV_n)][\sinh KX/\sinh ka) \quad \text{(odd)}, \quad (5.6)$$

where K is given by Eq. (4.15b) with $T = T_{S0}$. The solutions for $T = T_S$ for $|X| > a$ are linear in X,

$$\Delta(X) = [N_SV_S/(1 - CN_SV_S)](\alpha(X/a) + 1 - \alpha), \quad X > a. \quad (5.7)$$

Equations (5.6) and (5.7) satisfy the first boundary condition (4.13a). The second one, (4.13b), yields finally

$$Ka \tanh Ka = \eta\alpha \quad \text{(even)},$$

$$Ka/\tanh K\alpha = \eta\alpha \quad \text{(odd)}. \quad (5.8)$$

These results may be rewritten in a form applicable to a solution of no given parity:

$$(d\Delta/dX)_a - (d\Delta/dX)_{-a} = \eta K \tanh Ka(\Delta_a + \Delta_{-a}),$$

$$(d\Delta/dX)_a + (d\Delta/dX)_{-a} = \eta K \coth Ka(\Delta_a - \Delta_{-a}). \quad (5.9)$$

The conditions (5.9) are to be imposed on the solutions of the Landau–Ginsburg equation (5.1). They can also be used to transform the expression of the current crossing the junction. Solving for $(d\Delta/dX)_a$ in (5.9) we get

$$J_{(X=a)} = -\frac{i}{2} C\left[\left(\frac{d\Delta}{dX}\right)_a \Delta_a^+ - \text{c.c.}\right]$$

$$= \frac{-i\eta CK}{2 \sinh 2Ka} (\Delta_a^+\Delta_{-a} - \Delta_{-a}\Delta_a^+). \quad (5.10)$$

Equation (5.10) is somewhat similar to the Josephson formula for the current through an insulating junction.[22] In most actual situations we will have $|\Delta_a| = |\Delta_{-a}|$, the two potentials differing only by a phase $\Delta_{-a} = \Delta_a e^{i\varphi}$. Then $J = J_m \sin\varphi$ with the maximum value J_m given by

$$J_m = \eta CK/\sinh 2Ka \, |\Delta_a|^2. \quad (5.11)$$

At this point, however, there is an important difference from the Josephson case. For an insulating junction, $|\Delta_a|$ is very close to $|\Delta_\infty|$, the value of the pair potential in the bulk S material. This is shown explicitly elsewhere.[23] For a metallic junction, on the other hand, $|\Delta_a|$ is much smaller than $|\Delta_\infty|$. As an example, we shall now compute $|\Delta_a|$ explicitly in the limit of a thick junction $Ka \gg 1$. In this case, the currents are small and we can neglect the phase of Δ in Eq. (5.1). Then multiplying (5.1) by $(d\Delta/dX)$ and integrating we obtain

$$L_1(d\Delta^2/dX) + \Delta^2(\epsilon - \tfrac{1}{2} R_1\Delta^2) = \tfrac{1}{2} \Delta_\infty^2\epsilon, \quad (5.12)$$

$$\epsilon = T_{S0} - T/T_{S0}, \quad \Delta_\infty^2 = \epsilon/R_1.$$

For a thick junction we may write the boundary condition (5.9) in the form (4.17),

$$\frac{1}{\Delta_a}\left(\frac{d\Delta}{dX}\right)_a = \frac{1}{b_\infty} = \frac{D_nN_n}{D_SN_S} K. \quad (5.13)$$

Inserting (5.13) in (5.12) we get a second-order equation for $|\Delta_a|^2$,

$$\tfrac{1}{2} R_1\Delta_a^4 - (L_1/b_\infty^2 + \epsilon)\Delta_a^2 + \tfrac{1}{2} \Delta_\infty^2\epsilon = 0. \quad (5.14)$$

When the N material is a metal b_∞, and $L_1^{\frac{1}{2}}$ are of the same order of magnitude, the term of order Δ_a^4 is negligible and the correct root corresponds to

$$\left|\frac{\Delta_a}{\Delta_\infty}\right|^2 = \frac{\epsilon}{2} \frac{b_\infty^2}{L_i}, \quad (5.15)$$

$$\frac{J_m}{e} \cong 4\eta^{-1} e^{-2Ka} \frac{N}{KR_1} \left(\frac{T_{S0} - T}{T_{S0}}\right)^2 \quad (Ka \gg 1). \quad (5.16)$$

We see that J_m is proportional to $(T_{S0} - T)^2$, while for an insulating junction, J_m is proportional only to $T_{S0} - T$.[23] As already pointed out, the great interest of the present metallic case is that Ka is a very flexible parameter, from the experimental point of view. Unfortunately, at the present time, the only experiments in this field are the early ones by Meissner,[6] where the mean free paths were not controlled. Qualitatively, for various nonmagnetic metals, Meissner found values of $K^{-1} \sim 10^3$ Å, a very reasonable figure as can be seen from Eq. (4.15b). It is very much to be hoped that more accurate data will soon be taken.

Once J_m is known, it is of course possible to derive an effective penetration depth δ for the junction currents, using the Ferrell Prange procedure.[24] δ is proportional to e^{Ka}. Consider for example a Pb Cu Pb junction with $l_{Cu} = 40$ Å and $K \sim 200$ Å^{-1} at 7°K. If the copper thickness is $2a \sim 4000$ Å, the penetration depth δ will be of order 1 mm, the critical current will be in the milliampere range. To force a normal current of the same magnitude through the junction, we

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[22] It is, in fact, possible to derive the Josephson formula in a completely self-consistent way by similar methods.[23]

[23] P. G. De Gennes, Phys. Letters **5**, 22 (1963).

[24] R. A. Ferrell and R. E. Prange, Phys. Rev. Letters **10**, 479 (1963).

would need an applied voltage of order 1 mV. Thus in such a case we expect interesting signals even for rather large thicknesses, for which the crystallographic state of the N slab can be accurately controlled.

We might finally mention the magnetic junctions such as Pb Fe Pb. They do not seem very promising for the following reason: if Γ is the energy difference between a state $(k\uparrow)$ with spin up and the time reversed state $(-k\downarrow)$ in the magnetic metal, the penetration range of the pairs in (N) is roughly $\hbar v_F/\Gamma$, and thus very small (of order 100 Å or less[25] in agreement with the experimental results of Meissner)[6]. Thus for the thicknesses of interest $2a \sim \hbar v_F/\Gamma$, it would be very difficult to prepare an N slab free from holes, and of well defined properties.

VI. CONCLUDING REMARKS

We have seen that the transition temperature T of "dirty" NS sandwiches can be related to the electron–electron interaction V_N in the normal metal. The best procedure is to deduce K from a plot of T vs normal slab thickness and then to relate K to V_N, since this method does not imply any specific assumption about the "transition" layer between the two metals (provided that this layer is smaller than K^{-1}). The experiments could be carried out with metals or semimetals on the N side (but for semimetals, the shift of T is comparatively smaller).

The strong dependence of T on the mean free paths l forbids the discussion of experiments where l was not measured. On the other hand, it probably explains the spectacular "aging effects" observed on the transition temperature of Sn Au sandwiches by Rose-Innes and Serin,[3] since a slow atomic diffusion at room temperature will react markedly on l in the vicinity of the interface, and on the transmission coefficient. It is remarkable to observe that, in a homogeneous alloy, the effect of impurity concentration on the transition temperature is weak, while it is strong in our inhomogeneous NS systems, where impurity scattering controls the leakage of superconducting pairs towards an unfavorable region.

Finally, we notice that V_N could also be derived from measurements of critical current vs thickness in the SNS junctions.

ACKNOWLEDGMENTS

We would like to thank J. Friedel, E. Guyon, D. Saint-James, and G. Sarma for various discussions on superconducting contacts.

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[25] P. G. De Gennes and G. Sarma, J. Appl. Phys. **34**, 1380 (1963).

Discussion 35

Lynton: This temperature dependence of the coherence length seems to be contrary to what I understand the BCS theory to predict. It also seems to imply that if one were at low temperatures where the penetration depth is essentially constant and had a superconductor for which the surface energy was barely negative, then at a somewhat lower temperature it would become positive. It would become a superconductor of the first kind.

de Gennes: What you have is a system of two films where the transition temperature is very low. If you were to be very naive, you would just say: "Well here is the transition temperature. The gap and the coherence length will be related to it by the *BCS* equation: $\xi \sim 0.18\ \hbar v_F/k_B T_C$. If T_c is small, ξ is large."

Blatt: I just wanted to ask whether this very nice correlation which you find between the correlation functions in the normal and the properties of the superconducting state is restricted to the temperature region close to the transition temperature where the nonlinear integral equation can be linearalized or whether it also extends down into the lower temperature range?

de Gennes: For the problem I described here (a self-consistent calculation of the gap) it holds only in the vicinity of the transition temperature. For the electromagnetic problem on the other hand it goes down to low temperatures. The reason is that for the electromagnetic problem there is always a small perturbation. We can define the perturbation for this problem while in the self-consistent calculation the gap becomes large and we cannot define the perturbation.

Jensen: I'd like to make the probably trivial observation that your method for predicting $N(0)V$ for normal metals could be checked using a low temperature superconductor instead of your normal metal and working in the intermediate region.

de Gennes: Absolutely. Actually we plan to do this on aluminum which is a very nice case of a "quasi-normal" metal.