

Theory of Nonhomogeneous Superconductors*

WILLIAM SILVERT† AND LEON N. COOPER‡

Brown University, Providence, Rhode Island

(Received 9 June 1965)

A variational principle is developed for calculating the properties of nonhomogeneous superconducting systems at finite temperatures. The quantity varied is the energy-gap function as it occurs in the Gor'kov equations, and the correct Green's function is obtained by minimization of the thermodynamic potential. The calculation may be simplified by expanding the potential in powers of the energy-gap function or by a technique of analytic continuation. The former is easier but can be used only near the transition temperature, while the latter is valid at all temperatures. The variational procedure is used to calculate the transition temperatures of superposed-film systems, using a one-parameter model to describe the intermetallic potential barrier. The results agree well with the experimental data and indicate that barrier effects are important. The theory is valid for all mean free paths and is in accord with the phenomenological analysis of Hilsch and Hilsch.

INTRODUCTION

A NUMBER of experiments have revealed various effects due to the proximity of one superconductor to another or to a normal material. These can be attributed to the fact that the electron-electron interaction is not homogeneous over such specimens but varies from one material to the other. The usual theory¹ is not directly applicable to such situations, and in this paper we develop a variational form of the Gor'kov theory² which is applicable to nonhomogeneous systems. This variational procedure is then used to calculate the transition temperatures of superposed films, and the theory is found to agree well both with available experimental data and with previous theoretical work.

The Hamiltonian for a superconductor can be written in the form $H = H_1 + H_2$, where H_1 and H_2 are respectively the one- and two-body components. The usual Hartree and Hartree-Fock contributions to the interaction can be incorporated in H_1 as self-consistent fields characteristic of the normal state, and H_2 then contains only the residual interaction terms necessary to give superconductivity (e.g., the BCS reduced interaction). The superconducting state can then be expressed in terms of the eigenstates of H_1 alone.

In the BCS type of calculation, the representation of the superconducting state is in terms of explicit product wave functions of the electron pairs. With each eigenstate of H_1 , $|n\rangle$, a unique conjugate state $|\bar{n}\rangle$ is prescribed, and the ground state is obtained by minimization of the free energy of a trial state formed from two-particle wave functions $|n, \bar{n}\rangle$, with amplitudes given by a pairing probability h_n . The pairing pre-

scription can often be obtained from simple physical arguments, e.g., time-reversal invariance.

In nonhomogeneous systems, difficulties can arise if the symmetry properties of H_1 and H_2 are different. For dirty bulk superconductors this is not a problem, for reasons which were pointed out by Anderson.³ But when macroscopic nonhomogeneities occur, it is frequently impossible to find an explicit pairing which adequately describes the physical state of the system. Consider, for example, an idealized model of semi-infinite slabs of superconducting and normal metals in perfect contact. We take H_1 to be the free-electron Hamiltonian, so the single-particle eigenstates are plane waves. There is no way to pair these plane-wave states so that they give a higher pairing density in the superconductor than in the normal metal. We must instead choose a single-particle representation which anticipates the localized nature of the superconducting correlations.

The use of Green's functions avoids this problem, since the pair wave functions need not be written down explicitly in terms of a predetermined choice of single-particle functions. The correlation properties are characterized by an "anomalous Green's function," $\langle \psi_{\uparrow}(x)\psi_{\downarrow}(x') \rangle$, which gives a unique singlet-state pairing without requiring that it have the same spatial variation as H_1 . The quantity varied in the minimization of the thermodynamic potential is in fact the "energy-gap function" $\Delta(\mathbf{r})$ which represents the degree of pairing present at each point in the system. It is, furthermore, generally more convenient to work with the "normal" Green's function than it is to determine the explicit eigenstates of H_1 .

VARIATIONAL FORMULATION OF THE GOR'KOV THEORY

The Gor'kov Equations

Two types of Green's function are important in the Gor'kov formulation of the theory of superconductivity. One of these, $G(\mathbf{r}, t; \mathbf{r}', t') = -\langle T \psi_{\uparrow}(\mathbf{r}, t) \psi_{\uparrow}^{\dagger}(\mathbf{r}', t') \rangle$, is the

* Supported in part by Advanced Research Projects Agency, the U. S. Atomic Energy Commission, and the National Science Foundation. Parts of this paper are based on a thesis submitted by William Silvert in partial fulfillment of the requirements for the Ph.D. degree in physics at Brown University.

† Present address: Michigan State University, East Lansing, Michigan.

‡ Alfred P. Sloan Research Fellow.

¹ J. Bardeen, L. Cooper, and J. Schrieffer, *Phys. Rev.* **108**, 1175 (1957), afterwards referred to as BCS.

² L. P. Gor'kov, *Zh. Eksperim. i Teor. Fiz.* **34**, 735 (1958) [*English transl.: Soviet Phys.—JETP* **7**, 505 (1958)].

³ P. W. Anderson, *J. Phys. Chem. Solids* **11**, 26 (1959).

usual single-particle Green's function (T is the time-ordering operator and the angular brackets denote a thermal average over states). The "anomalous Green's function," $F(\mathbf{r}, t; \mathbf{r}', t') = \langle \psi_{\uparrow}(\mathbf{r}, t) \psi_{\downarrow}(\mathbf{r}', t') \rangle$, is a unique feature of the superconducting state which represents the "condensation" of bound pair states.

At finite temperatures it is easiest to evaluate the Green's functions by the Matsubara technique of imaginary-time Fourier transforms,⁴ which for fermion operators take the form

$$G(t) = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} e^{\omega t} G_{\omega},$$

where $\omega = (2n+1)\pi/\beta$ and the Fourier coefficients are given by

$$G_{\omega} = \frac{1}{2i} \int_{-\beta}^{i\beta} e^{-\omega t} G(t) dt.$$

The superconducting Green's functions can be expressed in terms of the normal Green's function $G^{(0)}$ and an "energy-gap function" $\Delta(\mathbf{r})$ which will be defined later⁵;

$$G_{\omega}(\mathbf{r}, \mathbf{r}') = G_{\omega}^{(0)}(\mathbf{r}, \mathbf{r}') - \int d\mathbf{r}_1 \int d\mathbf{r}_2 G_{\omega}^{(0)}(\mathbf{r}, \mathbf{r}_1) \Delta(\mathbf{r}_1) G_{-\omega}^{(0)}(\mathbf{r}_2, \mathbf{r}_1) \times \Delta^*(\mathbf{r}_2) G_{\omega}(\mathbf{r}_2, \mathbf{r}') \quad (1)$$

and

$$F_{\omega}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}_1 G_{\omega}(\mathbf{r}, \mathbf{r}_1) \Delta(\mathbf{r}_1) G_{-\omega}^{(0)}(\mathbf{r}', \mathbf{r}_1). \quad (2)$$

It is useful to have a formal expansion of the Green's function in powers of $\Delta(\mathbf{r})$, which may be obtained by iterating Eq. (1), giving

$$G_{\omega}(\mathbf{r}, \mathbf{r}') = \sum_{m=0}^{\infty} G_{\omega}^{(m)}(\mathbf{r}, \mathbf{r}'), \quad (3)$$

$$F_{\omega}(\mathbf{r}, \mathbf{r}') = \sum_{m=1}^{\infty} F_{\omega}^{(m)}(\mathbf{r}, \mathbf{r}'),$$

where

$$G_{\omega}^{(m)}(\mathbf{r}, \mathbf{r}') = - \int d\mathbf{r}_1 \int d\mathbf{r}_2 G_{\omega}^{(0)}(\mathbf{r}, \mathbf{r}_1) \Delta(\mathbf{r}_1) G_{-\omega}^{(0)}(\mathbf{r}_2, \mathbf{r}_1) \times \Delta^*(\mathbf{r}_2) G_{\omega}^{(m-1)}(\mathbf{r}_2, \mathbf{r}') \quad (4)$$

and

$$F_{\omega}^{(m)}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}_1 G_{\omega}^{(m-1)}(\mathbf{r}, \mathbf{r}_1) \Delta(\mathbf{r}_1) G_{-\omega}^{(0)}(\mathbf{r}', \mathbf{r}_1). \quad (5)$$

It is also convenient to define the pair correlation

⁴ T. Matsubara, *Progr. Theoret. Phys. (Kyoto)* **14**, 351 (1955).
⁵ L. P. Rapoport and A. G. Krylovetskii, *Dokl. Akad. Nauk SSSR* **145**, 771 (1962) [English transl.: *Soviet Phys.—Doklady* **7**, 703 (1963)].

amplitude $\chi(\mathbf{r}) = F(\mathbf{r}, t; \mathbf{r}, t)$ with the corresponding components $\chi_{\omega}^{(m)}(\mathbf{r}) = F_{\omega}^{(m)}(\mathbf{r}, \mathbf{r})$. It can be shown that these expansions are convergent as long as $|\Delta(\mathbf{r})| < \pi/\beta = \pi kT$, which relation holds for a bulk superconductor when $T > 0.53T_c$.⁶

The energy-gap function $\Delta(\mathbf{r})$ introduced above is a phonon-mediated self-energy term of the form

$$\Delta(\mathbf{r}) = V(\mathbf{r})F(\mathbf{r}, t; \mathbf{r}, t) = V(\mathbf{r})\chi(\mathbf{r}), \quad (6)$$

where $V(\mathbf{r})$ is the effective electron-electron interaction; we use the convention that a positive sign of V corresponds to an attractive interaction. The function $\Delta(\mathbf{r})$ represents the energy associated with each pair condensation process, and Eq. (6) can be derived by standard field-theoretic arguments. It can also be obtained from a variational principle by expressing the thermodynamic potential in terms of the Green's function, which is the procedure which we shall follow.

The Thermodynamic Potential

We consider the difference $\Omega(T, \mathcal{V}, \mu)$ between the thermodynamic potentials of the superconducting and normal states.⁷ (T = temperature; \mathcal{V} = volume; μ = chemical potential.) This quantity can be expressed in terms of the single-particle Green's function, and, in order to render explicit the dependence of Ω on $\Delta(\mathbf{r})$, we follow this procedure; for an arbitrary trial energy-gap function we calculate the Green's functions G and F from the Gor'kov equations (1) and (2) of the preceding section. Since in this calculation we do not need to introduce explicitly the interaction, we can use Eq. (6) to define a fictitious interaction, $V_f[\Delta] = \Delta/\chi[\Delta]$, which obeys the equation $\Delta(\mathbf{r}) = V_f(\mathbf{r})F(\mathbf{r}, t; \mathbf{r}, t)$. By doing so we can calculate the thermodynamic potential of a system which has this fictitious interaction, and then we simply correct the potential-energy term to obtain the correct thermodynamic potential. For the system characterized by the energy-gap function $\Delta(\mathbf{r})$ and the interaction $V_f(\mathbf{r})$, the Ω function will be given by the relation

$$V_f(\mathbf{r}) \frac{\delta \Omega_f}{\delta V_f(\mathbf{r})} = \frac{1}{\beta} \sum_{\omega} \Delta^*(\mathbf{r}) F_{\omega}(\mathbf{r}, \mathbf{r}) = \Delta^*(\mathbf{r}) \chi(\mathbf{r}), \quad (7)$$

where the symbol Ω_f indicates that we are using the fictitious interaction $V_f(\mathbf{r})$, and not the correct interaction $V(\mathbf{r})$.⁸ Using the expansion $\chi = \sum \chi^{(m)}$, where

⁶ W. Silvert, doctoral dissertation, Brown University, 1964 (unpublished).

⁷ This is related to the free energy by $\Omega = U - TS - \mu N = F - \mu N = -kT \ln Z$, where μ is the chemical potential, N the particle number, and Z the grand partition function. See for example T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), pp. 66, 72.

⁸ A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963), p. 70. See also Eqs. (1) and (2).

$\chi^{(m)}(\mathbf{r}) = F^{(m)}(\mathbf{r}, t; \mathbf{r}, t)$ is a homogeneous functional of $\Delta(\mathbf{r})$ of order $2m-1$, we obtain by replacing $\Delta(\mathbf{r})$ by $\lambda\Delta(\mathbf{r})$,

$$\begin{aligned} \frac{\partial \Omega_f}{\partial \lambda} &= \int \frac{\delta \Omega_f}{\delta V_f(\mathbf{r})} \frac{\partial V_f(\mathbf{r})}{\partial \lambda} d\mathbf{r} \\ &= - \int \Delta^*(\mathbf{r}) \chi(\mathbf{r}) \frac{\partial}{\partial \lambda} \left[\frac{\Delta(\mathbf{r})}{\chi(\mathbf{r})} \right] d\mathbf{r} \\ &= - \frac{1}{\lambda} \sum_{m=1}^{\infty} (2m-2) \int d\mathbf{r} \Delta^*(\mathbf{r}) \chi^{(m)}(\mathbf{r}). \end{aligned}$$

Integrating this gives

$$\begin{aligned} \Omega_f &= \int_0^1 \frac{\partial \lambda}{\lambda} \sum_{m=1}^{\infty} (2m-2) \int d\mathbf{r} \Delta^*(\mathbf{r}) \chi^{(m)}(\mathbf{r}) \\ &= \sum_{m=1}^{\infty} \left(1 - \frac{1}{m} \right) \int d\mathbf{r} \Delta^*(\mathbf{r}) \chi^{(m)}(\mathbf{r}). \end{aligned}$$

The next step is to obtain Ω for the real interaction $V(\mathbf{r})$. Since the potential energy is the only term in Ω which depends directly on the interaction, we obtain

$$\begin{aligned} \Omega &= \Omega_f + \int [V_f(\mathbf{r}) - V(\mathbf{r})] |\chi(\mathbf{r})|^2 d\mathbf{r} \\ &= \int d\mathbf{r} \left\{ \sum_{m=1}^{\infty} \left(2 - \frac{1}{m} \right) \Delta^*(\mathbf{r}) \chi^{(m)}(\mathbf{r}) - V(\mathbf{r}) |\chi(\mathbf{r})|^2 \right\}. \quad (8) \end{aligned}$$

In writing down Eq. (8) for the thermodynamic potential we have neglected the BCS cutoff in the interaction, which must be included if the theory is not to contain divergences.¹ Following the argument of Morel and Anderson⁹ that the excitation of localized phonon modes leads to a short-range retarded electron-electron interaction, we see that by writing down the instantaneous point interaction $V(\mathbf{r})$ we have neglected the energy dependence of the energy-gap function. This effectively means that the phonon Green's function is approximated by the expression $\mathfrak{D}(\mathbf{r}, t; \mathbf{r}', t') = C\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$. A more realistic interaction is obtained by writing $\mathfrak{D}(\mathbf{r}, t; \mathbf{r}', t') = C\delta(\mathbf{r}-\mathbf{r}')D(t-t')$, where $D(t)$ has the imaginary-time Fourier transform

$$D_\omega = \left\langle \frac{\omega^2_{\text{phonon}}}{\omega^2 + \omega^2_{\text{phonon}}} \right\rangle_{\text{phonons}}. \quad (9)$$

In the weak-coupling case this may be approximated by the step-function retardation factor $D_\omega = \theta(\omega_D - |\omega|)$, where ω_D is the cutoff frequency and is related to the Debye temperature by $\hbar\omega_D = k\Theta$. This introduces a cutoff into the ω summations at the point $|n| = \mathfrak{N}$

$\equiv \omega_D/2\omega(n=0) = \Theta/2\pi T$. This cutoff will be used in further calculations, where, unless otherwise indicated, all summations over ω run from $n = -\mathfrak{N}$ to $+\mathfrak{N}$.

We should now like to verify that the variational procedure leads to the same result as the usual calculation of the self-energy, Eq. (6). It can be shown for the field-free case that in minimizing Ω the phase of $\Delta(\mathbf{r})$ may be set equal to zero.⁶ Because $\int d\mathbf{r} \Delta^*(\mathbf{r}) \chi(\mathbf{r})$ is a symmetric homogeneous functional of $\Delta(\mathbf{r})$, Euler's theorem may be applied to Eq. (8), and we obtain

$$\frac{\delta \Omega}{\delta \Delta(\mathbf{r})} = 2 \int [\Delta(\mathbf{r}') - V(\mathbf{r}') \chi(\mathbf{r}')] \frac{\delta \chi(\mathbf{r}')}{\delta \Delta(\mathbf{r})} d\mathbf{r}'. \quad (10)$$

The "stationarity" requirement $\delta \Omega / \delta \Delta = 0$ is therefore equivalent to the expression given previously for the self-energy, $\Delta(\mathbf{r}) = V(\mathbf{r}) \chi(\mathbf{r})$.

The functional derivative $\Gamma(\mathbf{r}, \mathbf{r}') = \delta \chi(\mathbf{r}') / \delta \Delta(\mathbf{r})$ occurring in the above expression plays an important role in superconductivity calculations. It is the time-averaged scalar response function of the system, as may be seen from the Fourier components

$$\Gamma_\omega(\mathbf{r}, \mathbf{r}') = \delta \chi_\omega(\mathbf{r}') / \delta \Delta(\mathbf{r}) = |G_\omega(\mathbf{r}, \mathbf{r}')|^2 - |F_\omega(\mathbf{r}, \mathbf{r}')|^2. \quad (11)$$

Of particular importance is the normal response function occurring in the expansion of Γ in powers of $\Delta(\mathbf{r})$,

$$\Gamma_\omega^{(0)}(\mathbf{r}, \mathbf{r}') = |G_\omega^{(0)}(\mathbf{r}, \mathbf{r}')|^2. \quad (12)$$

The functional equation $\Delta = V\chi[\Delta]$ is of fundamental importance in the theory of superconductivity and is equivalent to the BCS integral equation for the energy gap. In systems for which this equation, which is customarily referred to as the "consistency condition," can be solved exactly, the superconducting properties can be obtained by direct calculation; but this is usually possible only for the simplest systems, and in most cases it is necessary to use approximation techniques such as the variational method developed here.

The Variational Method

From the preceding calculation we have seen how to define a functional $\Omega[\Delta(\mathbf{r})]$ such that $\Omega[\Delta] \geq \Omega_0$, where Ω_0 is the thermodynamic potential of the superconducting system measured relative to the normal state and corresponds to an energy-gap function which obeys the consistency condition $\Delta = V\chi[\Delta]$. The method outlined above can be used to calculate Ω at any finite temperature,¹⁰ and, as we shall see in the next section, it can be extrapolated to absolute zero. However, the convenience of the series expansion in powers of $\Delta(\mathbf{r})$ makes it particularly useful to apply the variational method to the study of second-order phase transitions, where $\Delta(\mathbf{r})$

¹⁰ Using the convergence property alluded to previously, $\Omega[\lambda\Delta]$ is an analytic function of λ in the finite region $|\lambda| < \pi kT / |\Delta_{\text{max}}|$, and it can be shown that there are no singularities on the real axis (Ref. 6). Therefore the integration over λ from 0 to 1 can be performed by analytic continuation.

⁹ P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

vanishes continuously. In such cases it is necessary only to consider the quadratic functional

$$\begin{aligned}\Omega^{(1)}[\Delta] &= \int d\mathbf{r} \{ \Delta(\mathbf{r}) \chi^{(1)}(\mathbf{r}) - V(\mathbf{r}) |\chi^{(1)}(\mathbf{r})|^2 \} \\ &= \int \chi^{(1)}(\mathbf{r}) [\Delta(\mathbf{r}) - V(\mathbf{r}) \chi^{(1)}(\mathbf{r})] d\mathbf{r}. \quad (13)\end{aligned}$$

For example, since $\Omega^{(1)}[\Delta] < 0$ implies $\Omega_0 < 0$ and is therefore a sufficient condition for the stability of the superconducting state, a lower bound to the critical temperature is the temperature $T[\Delta]$ at which $\Omega^{(1)}[\Delta]$ vanishes.¹¹

Example: Bulk Superconductor

The preceding calculations are greatly simplified in the case of a pure bulk superconductor, which can be treated by Fourier transform techniques.² The normal Green's function is $G_\omega^{(0)}(\mathbf{k}) = (i\omega - \epsilon_{\mathbf{k}})^{-1}$, and if we define the quantity

$$\gamma_\omega(\mathbf{k}) = \Delta G_{-\omega}^{(0)}(\mathbf{k}) \Delta G_\omega^{(0)}(\mathbf{k}) = \Delta^2 / (\omega^2 + \epsilon_{\mathbf{k}}^2),$$

we see from either Eq. (1) or Eqs. (3) and (4) that

$$\begin{aligned}G_\omega(\mathbf{k}) &= G_\omega^{(0)}(\mathbf{k}) \sum_{m=0}^{\infty} [-\gamma_\omega(\mathbf{k})]^m = \frac{G_\omega^{(0)}(\mathbf{k})}{1 + \gamma_\omega(\mathbf{k})} \\ &= \frac{-i\omega - \epsilon_{\mathbf{k}}}{\omega^2 + \epsilon_{\mathbf{k}}^2 + \Delta^2}.\end{aligned}$$

As noted previously, $G_\omega(\mathbf{k})$ is a well-defined function of Δ , even though the series expansion has the finite radius of convergence given by $\Delta < (\omega^2 + \epsilon_{\mathbf{k}}^2)^{1/2}$. The expansion of $G(\mathbf{r}, t; \mathbf{r}', t')$ therefore has the radius of convergence $\Delta < \omega (n=0) = \pi kT$ but can still be determined for all values of Δ .

The pair correlation function is

$$\begin{aligned}\chi &= (2\pi)^{-3} \int d\mathbf{k} \beta^{-1} \sum_\omega F_\omega(\mathbf{k}) \\ &= N \int_{-\infty}^{\infty} d\epsilon \beta \Delta \sum_{\pi=-\pi}^{\pi} \frac{1}{(\beta\omega)^2 + (\beta E)^2} \\ &= N \Delta \int_0^{\infty} \frac{d\epsilon}{E} \left[\tanh\left(\frac{1}{2}\beta E\right) - \frac{2}{\pi} \tan^{-1}\left(\frac{E}{\omega_D}\right) \right] \\ &\approx N \Delta \int_0^{\omega_D} \frac{d\epsilon}{E} \tanh\left(\frac{1}{2}\beta E\right),\end{aligned}$$

where N is the density of states at the Fermi level

¹¹ More precisely, $T[\Delta]$ is the least upper bound of the set of temperatures at which $\Omega^{(1)}[\Delta] < 0$. The equation $\Omega^{(1)} = 0$ also has the extraneous solution $\chi^{(1)} = 0$, which corresponds to an infinite temperature.

and $E^2 = \epsilon^2 + \Delta^2$. At absolute zero this reduces to $\chi = N \Delta \sinh^{-1}(\omega_D/\Delta)$, and Ω can be obtained directly from Eqs. (7) and (8). Minimization of Ω with respect to Δ gives the equation for the $T=0$ energy-gap,

$$\Delta - V\chi = \Delta[1 - NV \sinh^{-1}(\omega_D/\Delta)] = 0.$$

This then gives the correct ground-state energy,

$$\Omega_0 = -2N\omega_D^2 / (e^{2/NV} - 1).$$

Finally, the bulk transition temperature is given by the vanishing of the quadratic functional

$$\begin{aligned}\Omega^{(1)} &= \chi^{(1)}[\Delta - V\chi^{(1)}] \\ &= \chi^{(1)}\Delta \left[1 - NV \int_0^{\omega_D} \frac{d\epsilon}{\epsilon} \tanh\left(\frac{1}{2}\beta\epsilon\right) \right],\end{aligned}$$

giving $T_0 = 1.14 \Theta e^{-1/NV}$. These are, of course, all results obtained originally by BCS.¹

TRANSITION TEMPERATURES OF SUPERPOSED FILMS

Idealized Model

We consider first a superposed film system for which the single-particle Hamiltonian H_1 is translationally invariant and contains no scattering. While this idealized model has no direct physical applicability, it reveals a number of interesting features which tend to be obscured in a more comprehensive analysis.

The Green's function for a pure metal in the absence of interactions is¹²

$$G_\omega^{(0)}(R) = -\frac{2m}{4\pi R} e^{i k R} \operatorname{sgn} \omega e^{-|\omega| R/v}, \quad (14)$$

where $R = |\mathbf{r} - \mathbf{r}'|$, m is the effective mass, and k and v are the Fermi momentum and velocity (we set $\hbar = 1$ except where otherwise dictated by convention). From (12) we get the normal response function

$$\Gamma_\omega^{(0)}(R) = \left(-\frac{2m}{4\pi R} \right)^2 e^{-2|\omega| R/v}. \quad (15)$$

The linear term in the correlation amplitude is given by

$$\begin{aligned}\chi^{(1)}(\mathbf{r}) = \chi^{(1)}(z) &= \int d\mathbf{r}_1 \Gamma_\omega^{(0)}(\mathbf{r} - \mathbf{r}_1) \Delta(\mathbf{r}_1) \\ &= \int dz_1 H(z - z_1) \Delta(z_1), \quad (16)\end{aligned}$$

where the Fourier coefficients of the one-dimensional

¹² L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959) [English transl.: Soviet Phys.—JETP **9**, 1364 (1959)].

normal response function are

$$H_\omega(z) = \int dx \int dy 1/\omega^{(0)} ([x^2 + y^2 + z^2]^{1/2}) \\ = \frac{\pi N}{v} E_1 \left(\left| \frac{2\omega z}{v} \right| \right) \quad (17)$$

and the E function occurring in the above expression is one of the generalized exponential integrals¹³

$$E_m(u) = \int_1^\infty e^{-ut} t^{-m} dt. \quad (18)$$

From the consistency condition we see that the energy-gap function can be discontinuous at a boundary,¹⁴ and with this in mind we consider a trial function which takes a constant value Δ in the superconducting region (denoted by S) and is zero in the normal region (N). For an NS boundary represented by the trial function $\Delta(z) = \Delta\theta(z)$ this gives

$$\chi^{(1)}(z) = \frac{\pi N \Delta}{\beta v} \sum_\omega \int_0^\infty E_1 \left(\left| \frac{2\omega}{v} (z-z') \right| \right) dz' \\ = N \Delta \begin{cases} \frac{1}{2} f(z), & z < 0, \\ f(0) - \frac{1}{2} f(z), & z > 0, \end{cases}$$

where

$$f(z) = \frac{1}{\beta} \sum_\omega \frac{\pi}{|\omega|} E_2 \left(\left| \frac{2\omega z}{v} \right| \right) \\ = \sum_\omega \left| \frac{1}{2n+1} \right| E_2(|z|/\Xi_\omega),$$

and $\Xi_\omega = v/2|\omega|$ plays the role of an energy-dependent coherence length. The correlation and energy-gap functions are sketched in Fig. 1 for both this trial function and for a rough solution of the consistency condition with $V_N = 0$. We note that the slope of the correlation amplitude becomes infinite at the boundary. This is a consequence of the degree of singularity of the response function and is a general feature of systems in which the interaction is discontinuous, as is shown in the Appendix.

The penetration of superconducting coherence into the normal metal is characterized by the falloff distance

$$\Lambda = \int_0^\infty f(z) dz / f(0) \approx 1.2 \Xi / \ln(\beta \omega_D),$$

where $\Xi = \Xi_{\omega(n=0)} = \hbar v / 2\pi k T$ is the bulk coherence length as usually defined. At the bulk critical temperature the ratio of Λ to Ξ is roughly equal to $\rho = NV$, which

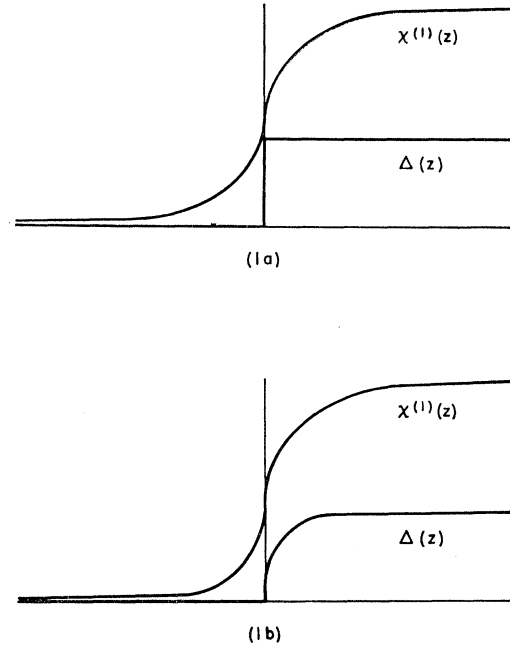


FIG. 1. Behavior of the correlation amplitude and energy-gap function at an intermetallic boundary. (a) Approximate trial function. (b) Rough solution of consistency condition, $V_{\text{normal}} = 0$.

is typically 0.3. For values of z greater than Ξ , the falloff function has the asymptotic form

$$f(z)/f(0) \approx 2\rho(\Xi/z)e^{-(z/\Xi)},$$

as has previously been shown by Falk.¹⁵

A similar method can be used to obtain the falloff at temperatures below the transition point. Independent calculations by Falk¹⁵ and one of the authors¹⁶ have shown that at absolute zero $\chi(z)$ falls off as $1/z$ in the asymptotic region. This is faster than the falloff obtained by Parmenter,¹⁷ who uses a different theoretical approach. His method is to let the BCS pairing probability $h_{\mathbf{k}}$ be a function of position, so that the pair wave functions are of the form

$$\varphi(\mathbf{r}, \mathbf{r}') = h_{\mathbf{k}}(\mathbf{r} + \mathbf{r}') e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')/2};$$

but this procedure permits violation of the exclusion principle, a problem similar to that which arises in the boson model of superconductivity. In the Green's-function formalism the commutation properties of the operators $\psi(x)$ and $\psi^\dagger(x)$ guarantee that the exclusion principle is not violated.

A superconducting film of thickness D on a semi-infinite normal substrate can be represented by the interaction

$$V(z) = V, \quad |z| < D \\ = 0, \quad |z| > D,$$

¹⁵ D. S. Falk, Phys. Rev. **132**, 1576 (1963).

¹⁶ W. Silvert, Rev. Mod. Phys. **36**, 251 (1964).

¹⁷ R. H. Parmenter, Phys. Rev. **118**, 1173 (1960).

¹³ H. C. van de Hulst, Astrophys. J. **107**, 220 (1948).

¹⁴ P. G. de Gennes, Rev. Mod. Phys. **36**, 225 (1964).

where the boundary condition $\partial\chi^{(1)}/\partial z|_{z=0}=0$ for the free surface is satisfied by use of the image method. The transition temperature of this system is determined by the consistency condition

$$\chi^{(1)}(z) = V \int_{-D}^D H(z-z')\chi^{(1)}(z')dz'.$$

Without attempting to solve this integral equation exactly, we obtain a lower bound to T_c by using a trial function which is constant in S and zero in N . This gives

$$\begin{aligned} \chi^{(1)}(z) &= \Delta \int_{-D}^D H(z-z')dz' \\ &= \Delta N [f(0) - \frac{1}{2}f(D+z) - \frac{1}{2}f(D-z)], \quad |z| < D. \end{aligned}$$

By using the approximation $f(D+z) + f(D-z) \approx 2f(D)$ and setting $\Omega^{(1)}=0$, we obtain an equation for $T[\Delta]$,

$$V[f(0) - f(D)] = 1. \quad (19)$$

In the limit $D \rightarrow \infty$ the bulk transition temperature is given by $Vf(0)=1$, where $f(0) = \psi(N + \frac{3}{2}) - \psi(\frac{1}{2})$ and ψ is the digamma function. For finite values of D , substitution of this expression for $f(0)$ in (19) gives

$$f(D) = \ln(T_0/T[\Delta]).$$

If $D \gtrsim \hbar v/\omega_D$, $f(D)$ is independent of cutoff and we get

$$\ln \frac{T_0}{T[\Delta]} = \int_0^{\hbar v/DkT[\Delta]} \ln \tanh x \, dx.$$

Model of a Real Film

A realistic model of a superposed film system must include effects arising from finite mean free path and the presence of an insulating boundary layer between the metals. Considering first the effects of scattering, we begin with the Abrikosov-Gor'kov normal response function as derived by Werthamer for isotropic scattering^{18,19}

$$\Gamma_{\omega}^{(0)}(q) = H_{\omega}(q) = \frac{2\pi N}{v} \left[\frac{q}{\tan^{-1}\xi_{\omega}q} - \frac{1}{l} \right]^{-1}, \quad (20)$$

where

$$\frac{1}{\xi_{\omega}} = \frac{2|\omega|}{v} + \frac{1}{l} + \frac{1}{\xi_{\omega}} + \frac{1}{l}$$

and l is the electronic mean free path. In the limit $l \rightarrow \infty$ this agrees with the result previously obtained for a pure metal, Eqs. (15) and (17). By expanding the quantity $q/\tan^{-1}\xi_{\omega}q$ and Fourier transforming to coordinate space we obtain a kernel of the diffusion type,

$$H_{\omega}^{\text{diff}}(z, z') = \frac{\pi N}{2|\omega|\xi_{\omega}} e^{-|z-z'|/\xi_{\omega}}, \quad (21)$$

where $\xi_{\omega} = (\frac{1}{3}\zeta_{\omega}\xi_{\omega})^{1/2}$ is the thermal- and impurity-scattering-limited coherence length. In dirty films, where impurity scattering is dominant, this reduces to the de Gennes-Guyon result.²⁰

If we write the exact kernel in the form $H_{\omega} = H_{\omega}^{\text{diff}} + H_{\omega}^{\text{corr}}$, where H_{ω}^{corr} contains the correction to the diffusion approximation, we see that this correction term consists primarily of a logarithmic singularity of range roughly equal to ξ_{ω} , such as Eq. (17) exhibits. The main effect of this term is that the slope of the correlation amplitude becomes infinite at an intermetallic boundary, which means that $\chi_{\omega}^{(1)}$ can change rapidly within a distance $\sim \xi_{\omega}$. This shows up as an apparent discontinuity across the boundary. The relative magnitude of this change is on the order of $\zeta_{\omega}/\xi_{\omega}$, so the effect is small for very dirty systems.

A distinction must be made between this procedure and the diffusion approximation introduced by de Gennes and Guyon²⁰ and subsequently developed by de Gennes¹⁴ and by Werthamer.¹⁹ These authors have made two assumptions which restrict the validity of their results: (i) that the mean free path is so short ($l \ll \xi_{\omega}$) that the ζ_{ω} can all be set equal to l , and (ii) that H can be set equal to H^{diff} for all values of $|z-z'|$ of interest. The first assumption is not a necessary one, and it is clearly not valid for any but very dirty films; by retaining the exact form of ζ_{ω} in calculating the coherence length, the formal separation of the kernel into diffusion and correction terms can be carried out for all ranges of mean free path. The dependence of the coherence length on mean free path will of course be weaker than the $l^{1/2}$ behavior characteristic of a true diffusion process. Assumption (ii) is valid only when the energy-gap function is slowly changing over distances on the order of the mean free path; this condition clearly does not hold when the effect of boundaries is being studied. By the formal procedure of writing $H = H^{\text{diff}} + (H - H^{\text{diff}})$ we can use the diffusion kernel as a starting point in calculating the properties of any system; but it must be remembered that ξ_{ω} equals the diffusion length only in the limit of short mean free paths, and that the short-range properties of $H^{\text{corr}} \equiv H - H^{\text{diff}}$ lead to boundary conditions different from those associated with diffusion processes.

In most systems of physical interest, the boundary behavior of $\chi^{(1)}$ described above tends to be overshadowed by effects associated with the creation of an intermetallic barrier, such as oxidation, chemisorption, and various diffusion effects. Consequently, it becomes quite difficult to arrive at meaningful continuity conditions, and we shall treat the question of behavior at the boundary in a semiempirical fashion. Elsewhere in the system H^{corr} may be neglected, and we therefore obtain a quite generally applicable form of the diffusion approximation, valid even for clean films.

Two useful sum rules may be obtained from Eq. (20),

¹⁸ A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **35**, 1558 (1958) and **36**, 319 (1959) [English transl.: Soviet Phys. —JETP **8**, 1090 (1959) and **9**, 220 (1959)].

¹⁹ N. R. Werthamer, Phys. Rev. **132**, 2440 (1963).

²⁰ P. G. de Gennes and E. Guyon, Phys. Letters **3**, 168 (1963).

both of which are independent of the foregoing approximations. The first, which de Gennes¹⁴ has derived from quite general arguments, is

$$\int \Gamma_{\omega}^{(0)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \int_{-\infty}^{\infty} H_{\omega}(z, z') dz' = \frac{\pi N(\mathbf{r})}{|\omega|}, \quad (22)$$

where $N(\mathbf{r})$ is the local density of states. Since $H^{\text{diff}}(z, z')$ also obeys this sum rule, it follows that $\int_{-\infty}^{\infty} H_{\omega}^{\text{corr}}(z, z') dz' = 0$, which is a more formal justification for neglecting H^{corr} in regions where $\Delta(z)$ is not rapidly changing. The second sum rule is a direct corollary of the first; from Eq. (16) for the correlation amplitude we get

$$\int_{-\infty}^{\infty} \phi_{\omega}(z) dz = \frac{\pi}{|\omega|} \int_{-\infty}^{\infty} \Delta(z) dz, \quad (23)$$

where $\phi_{\omega} = \chi_{\omega}^{(1)}/N$ is the Fourier component of the correlation amplitude per electron at the Fermi surface.

In the region of validity of the diffusion approximation we can use the procedure suggested by Werthamer¹⁹ and de Gennes¹⁴ of converting the integral expression

$$\chi_{\omega}^{(1)}(z) = \int_{-\infty}^{\infty} H_{\omega}^{\text{diff}}(z, z') \Delta(z') dz'$$

into the differential equation

$$(1 - \xi_{\omega}^2 \partial^2 / \partial z^2) \chi_{\omega}^{(1)}(z) = \pi N \Delta(z) / |\omega|. \quad (24)$$

The z dependence of $N(z)$ and $\xi_{\omega}(z)$ is suppressed to indicate that these quantities change only at the boundaries, where the diffusion equation does not apply.

A simple and general lower bound to the transition temperature of any system may be obtained by choosing for a trial function $\Delta(\mathbf{r}) = \text{const}$. The sum rule (22) immediately gives $\phi_{\omega} = \pi / |\omega|$, or $\chi^{(1)}(\mathbf{r}) = \Delta N(\mathbf{r}) \sum_n |2n+1|^{-1}$. Since the Debye cutoff frequency varies from metal to metal, we get a position dependence of the form $\chi^{(1)}(\mathbf{r}) = \Delta N(\mathbf{r}) \ln[1.14\beta\omega_D(\mathbf{r})]$. If a constant ω_D is assumed, we obtain the result

$$T[\Delta] = 1.14 \Theta e^{-1/\rho_{\text{av}}},$$

where

$$\rho_{\text{av}} = \int N^2(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} / \int N(\mathbf{r}) d\mathbf{r}.$$

Such a trial function is of limited applicability, but for very thin films it provides a useful approximation.¹⁴ More accurate approximations may be obtained with the trial function introduced previously. We shall characterize the superconducting region (S) by a constant energy-gap Δ and unprimed quantities (e.g., $N, \xi_{\omega}, l, V, \rho = NV$), and the normal region (N) by a zero energy-gap and primed symbols. The boundary condition $\partial \chi_{\omega}^{(1)} / \partial z = 0$ is used at free surfaces.¹⁴ For a superposed film system the coordinate system is defined so that the superconducting region is the slab $0 < z < D$,

and the normal region $D < z < D + D'$. The general solution of the diffusion equation obeying the free surface boundary condition is

$$\begin{aligned} \chi_{\omega}^{(1)}(z) &= \frac{\pi N \Delta}{|\omega|} \left(1 - C_{\omega} \cosh \frac{z}{\xi_{\omega}} \right) \quad \text{in } S \\ &= \frac{\pi N' \Delta}{|\omega|} C_{\omega'} \cosh \frac{D + D' - z}{\xi_{\omega'}} \quad \text{in } N'. \end{aligned}$$

The constants C_{ω} and $C_{\omega'}$ are related by the sum rule and can be expressed symmetrically in the form

$$C_{\omega} \xi_{\omega} \sinh(D/\xi_{\omega}) = C_{\omega'} \xi_{\omega'} \sinh(D'/\xi_{\omega}') = \alpha_{\omega},$$

where the α_{ω} are characteristic lengths which depend both on the properties of the two metals and on the localized behavior of the correlation amplitude in the interface region.

If we assume that the short-range component of the response function H^{corr} can be neglected, and that there is no barrier present between the two metals, then $\phi(z)$ is continuous. From this additional condition we obtain the value

$$\frac{1}{\alpha_{\omega}^{\text{max}}} = \frac{1}{\xi_{\omega} \tanh(D/\xi_{\omega})} + \frac{1}{\xi_{\omega'} \tanh(D'/\xi_{\omega}')}.$$

Both the presence of a barrier and the short-range correction to the diffusion approximation have the effect of reducing α_{ω} below the above maximum, and for an infinite barrier we obtain the limiting value $\alpha_{\omega}^{\text{min}} = 0$.

The transition temperature is given by the vanishing of the quadratic term in the energy functional,

$$\begin{aligned} \Omega^{(1)} &= \Delta \int_0^D \chi^{(1)}(z) dz - V \int_0^D [\chi^{(1)}(z)]^2 dz \\ &\quad - V' \int_D^{D+D'} [\chi^{(1)}(z)]^2 dz. \end{aligned}$$

Substitution of the preceding expression for $\chi^{(1)}(z)$ into $\Omega^{(1)} = 0$ gives

$$\rho K^2 - [1 + (4\rho J_1/D)] K + (2J_1 + J_2 + J_2') = 0, \quad (25)$$

where

$$\begin{aligned} K &= \sum_{n=0}^{\infty} \frac{1}{n + \frac{1}{2}}, \quad J_1 = \sum_{n=0}^{\infty} \frac{\alpha_{\omega}}{2n+1}, \\ J_2 &= \rho \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \frac{2C_{\omega}}{2n+1} \frac{2C_{\omega'}}{2n'+1} \int_0^D \cosh \frac{z}{\xi_{\omega}} \cosh \frac{z}{\xi_{\omega'}} dz, \\ J_2' &= \frac{N' \rho'}{N} \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \frac{2C_{\omega'}}{2n+1} \frac{2C_{\omega'}}{2n'+1} \\ &\quad \times \int_0^{D'} \cosh \frac{z}{\xi_{\omega'}} \cosh \frac{z}{\xi_{\omega'}} dz. \end{aligned} \quad (26)$$

The temperature dependence is implicit, occurring through the cutoff $\mathfrak{N} = \Theta/2\pi T$ and through the lengths ξ_ω and α_ω .

Thin-Film Limit

When the film thicknesses are much less than the coherence lengths, the α_ω may be replaced by a constant,

$$\alpha_\omega = \alpha \leq \alpha^{\max} = DD'/(D+D').$$

The J sums are expressible in terms of K ,

$$J_1 = \alpha K/2, \quad J_2 = \rho \alpha^2 K^2/D, \quad J_2' = N' \rho' \alpha^2 K^2/ND', \quad (27)$$

and substituting in Eq. (25) we obtain the solution²¹

$$K = \frac{1}{\rho} \frac{1 - \alpha/D}{1 - 2\alpha/D + (\alpha^2/D^2)(1 + \epsilon D/D')} \equiv \frac{1}{\rho_{\text{eff}}}, \quad (28)$$

where $\epsilon \equiv N' \rho' / N \rho$. The lower bound to the transition temperature found with this trial function is therefore²² $T[\Delta] = 1.14 \Theta e^{-1/\rho_{\text{eff}}}$. For $V' = 0$ this reduces to the result obtained previously by one of the authors,²³ and $\rho_{\text{eff}} = \rho_{\text{eff}}^0 = \rho [1 - (\alpha/D)]$ obeys the inequality

$$\rho \frac{D}{D+D'} < \rho_{\text{eff}}^0 < \rho.$$

The general result (28) can be written

$$\ln \frac{T_0}{T_c} \leq \frac{1 - \epsilon}{\rho} \left/ \left(\frac{D}{D'} + \epsilon \right) \right., \quad (29)$$

where equality corresponds to the limit $\alpha = \alpha^{\max}$. If the normal film is sufficiently thin, i.e., $N'^2 V' D' \ll N^2 V D$, we obtain the approximate expression used by Simmons and Douglass²⁴

$$T_c = T_0 [1 - b(D'/D)]. \quad (30)$$

The quantity b depends on the nature of interface and obeys the inequality $\rho b \leq 1 - \epsilon$.

For systems consisting of a very thin superconducting film on a thick normal substrate, the behavior of the correlation amplitude in the interface region is the essential factor determining the superconducting properties. The transition temperature is given by Eq. (28), and if $\alpha = \alpha^{\max} = D$, we get $T_c = 0$ for the case $V' = 0$.²⁵

²¹ There is also the extraneous root $K = 0$, which corresponds to the $T = \infty$ solution mentioned in footnote 11.

²² The appropriate Debye frequency for this trial function is that of the superconducting metal, since the pairing self-energy is set equal to zero in the normal region.

²³ L. N. Cooper, Phys. Rev. Letters **6**, 689 (1961).

²⁴ W. A. Simmons and D. H. Douglass, Jr., Phys. Rev. Letters **9**, 153 (1962).

²⁵ By expanding α_ω^{\max} in powers of D/ξ' , de Gennes (Ref. 14) has established that $T[\Delta]$ vanishes in this limit for $D < 1.9 \xi'(T_0)$.

Thick and Intermediate Films

If $D > \xi_\omega (n = \mathfrak{N})$, which is typically on the order of $\hbar v/\omega_D \sim 100 \text{ \AA}$, then the J sums are independent of cutoff and depend on temperature only through the coherence length. It is convenient to separate these terms from the cutoff-dependent K sum by formally solving Eq. (25) for K , getting

$$K = \frac{1}{2\rho} \left[1 + \frac{4\rho J_1}{D} + R^{1/2} \right], \quad (31)$$

where

$$R = 1 + \left(\frac{4\rho J_1}{D} \right)^2 - \frac{4\rho}{D} (J_2 + J_2'). \quad (32)$$

(The positive root is taken, since the negative root gives the extraneous solution $T = \infty$. This can easily be seen by letting D go to infinity, where the roots are $K = 1/\rho$ and $K = 0$, respectively.) An approximate expression for R can be obtained by using the inequalities

$$\cosh x \cosh y > \frac{1}{2} \cosh(x+y), \quad \sinh x \sinh y < \frac{1}{2} \sinh(x+y)$$

to obtain

$$J_2 > 4\rho \sum_{n=0}^{\mathfrak{N}} \sum_{n'=0}^{\mathfrak{N}} \frac{\alpha_\omega}{2n+1} \frac{\alpha_{\omega'}}{2n'+1} \frac{1}{\xi_\omega + \xi_{\omega'}} \\ \approx \frac{4\rho}{\xi} \sum_{n=0}^{\mathfrak{N}} \sum_{n'=0}^{\mathfrak{N}} \frac{\alpha_\omega}{2n+1} \frac{\alpha_{\omega'}}{2n'+1} \\ \times \frac{(2n+1)^{1/2} \times (2n'+1)^{1/2}}{(2n+1)^{1/2} + (2n'+1)^{1/2}} > \frac{2\rho}{\xi} J_1^2,$$

where $\xi = \xi_\omega (n=0)$. The above inequality actually provides a fair approximation to J_2 ; consider for example the thick-film limit, where $(\alpha_\omega^{\max})^{-1} = \xi_\omega^{-1} + \xi_{\omega'}^{-1}$. This dependence suggests that α_ω can be written in the form $\alpha_\omega = \alpha (2n+1)^{-1/2}$, and we obtain $J_1 = 1.7\alpha$ and $J_2 = 7.2\rho\alpha^2/\xi = 1.2(2\rho J_1^2/\xi)$. Similarly, the remaining sum may be approximated by the expression $J_2' \sim (2\epsilon\rho/\xi') J_1^2$. For fairly thick films we can therefore express K entirely in terms of J_1 by using

$$R \approx 1 - \frac{8\rho^2 J_1^2}{D} \left(\frac{2}{D} - \frac{1}{\xi} - \frac{\epsilon}{\xi'} \right).$$

For sufficiently thick films this can be further simplified by noting that the second term is quite small, and consequently $R \sim 1$. Furthermore, by substituting the limiting expressions (27) into Eq. (32), we find that for small values of V' , the value of R for thin films is also unity. This suggests that we set $R = 1$ over the entire range of thicknesses and determine the critical temperature from the equation $K = (1/\rho) + (2J_1/D)$, or $\ln(T_0/T_c) = 2J_1/D$.

For thick films the α_ω depend mainly on the coherence lengths, and these in turn are proportional to $T^{-1/2}$ in

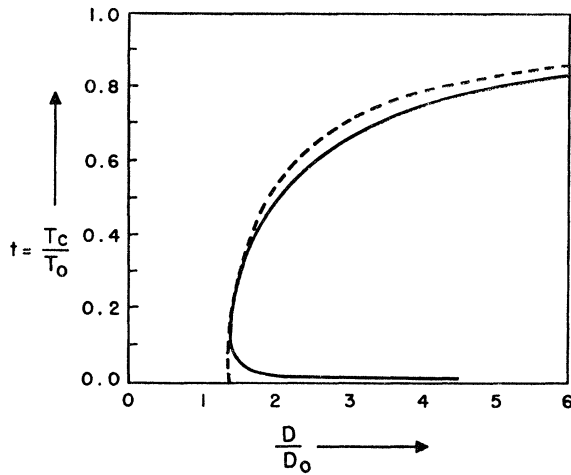


FIG. 2. Plot of reduced critical temperature, $t = T_c/T_0$, versus thickness of superconducting film. Solid line: theoretical curve, Eq. (33). Broken line: semiempirical curve of Hilsch and Hilsch, Eq. (34), $D_0/D_{s0} = 0.75$.

dirty films. We can therefore write the sum J_1 as the product of a temperature-independent length $D_0/2$ and $t^{-1/2}$, where $t = T_c/T_0$ is the reduced temperature. The resulting equation for the critical temperature is

$$t^{1/2} \ln(1/t) = D_0/D; \quad (33)$$

this is plotted in Fig. 2. The unphysical behavior of the curve for values of t less than ~ 0.15 reflects the breakdown of the thick-film approximation, as may be seen in the following way: setting $\alpha_\omega = \alpha_\omega^{\max}$ we obtain $D_0 \sim 3\xi(T_0) \sim 3t^{1/2}\xi(T)$, so that in the low-temperature range the temperature-dependent coherence length becomes larger than the film thickness. The sum J_1 therefore ceases to vary as $t^{-1/2}$ and goes over to the logarithmic temperature dependence characteristic of the thin-film limit, Eq. (27). Since the lowest value of t reported to date is 0.16, we expect Eq. (33) to provide a good description of the available data.²⁶

COMPARISON WITH EXPERIMENT

Hilsch and Hilsch have recently published a phenomenological theory of superposed thin films in which the reduced transition temperature t is expressed as a function of the thickness of the superconducting film D and two parameters; a characteristic length D_{s0} and a universal constant B .²⁶ The relationship is of the form

$$1 - t^2 = [B + (1 - B)(D/D_{s0})]^{-1}, \quad (34)$$

where B and D_{s0} are obtained by fitting this expression to the data. Using the Hilsch value of $B = 0.2$ and setting $D_0 = 0.75D_{s0}$, Eqs. (33) and (34) are plotted together in Fig. 2. The two curves agree well within the experimental scatter, and both provide an excellent fit to the data over the entire experimental range.

Although it is in principle necessary to know the α_ω in order to calculate D_0 , an indication of the importance of the barrier effects can be obtained by assuming $\alpha_\omega = \sigma\alpha_\omega^{\max}$, where σ is an empirical parameter. In the limit $D' = \infty$ we obtain

$$\frac{1}{D_0^*} = \frac{0.3}{\sigma} \left[\frac{1}{\xi(T_0)} + \frac{1}{\xi'(T_0)} \right].$$

This is quite different from the result derived by Hilsch and Hilsch from their phenomenological theory.

The Hilsch data gives remarkably consistent σ values; for the Sn-Cu and Pb-Cu systems they lie between 0.4 and 0.5, while the corresponding values of D_0^* range from 100 to 3000 Å. The fact that σ is virtually independent of mean free path suggests that these low values are due mostly to the formation of a boundary layer between the metals. This is in part substantiated by the dependence of D_0^* on order of deposition for dirty Pb-Cu and Pb-Pt systems,²⁷ where the relative oxidizabilities of the two metals is probably the dominant factor.

The dependence of D_0 on normal film thickness is roughly given by

$$\frac{1}{D_0} \sim \frac{0.3}{\sigma} \left[\frac{1}{\xi(T_0)} + \frac{1}{\xi'(T_0) \tanh D'/\xi'(T_0)} \right] \leq \frac{1}{D_0^*} + \frac{0.3}{\sigma} \frac{1}{D'}.$$

Using $\sigma = \frac{1}{2}$ we obtain good agreement with the Hilsch results for Sn-Cu and Sn-Ag, but for Pb-Cu and Pb-Ag they obtain a somewhat larger coefficient multiplying $1/D'$. Since this coefficient appears to depend on the choice of metals but not on their mean free paths, changes in R involving the sums J_2 and J_2' may be responsible.

Because the thick-film approximation breaks down at low temperatures, it is not likely that the Hilsch formula can be extrapolated to this region. For systems with transition temperatures near absolute zero there should be little of the mean free path dependence seen above, while such parameters as the strength of the interaction in the normal metal should have much greater importance. In particular, if the "normal" metal is actually a superconductor with a low transition temperature, the t -versus- D curve must level off and intersect the t axis. This effect has been seen by Hauser and Theuerer in Pb-Al systems, which follow the Hilsch curve very closely down to within one degree of the transition temperature of bulk Al.²⁸ Consequently, for systems with low-transition temperatures ($t \lesssim 0.1$) as well as for those formed from very thin films, Eq. (29) is applicable.

Because mean free path data is missing from many of the early papers on proximity effects, it is useful to analyze these experiments from a thin-film standpoint.

²⁶ P. Hilsch and R. Hilsch, Z. Physik **180**, 10 (1964).

²⁷ P. Hilsch, Z. Physik **167**, 511 (1962). J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. **136**, A637 (1964).

²⁸ J. J. Hauser and H. C. Theuerer, Phys. Letters **14**, 270 (1965).

Simmons and Douglass²⁴ have studied the effect of thin silver films on the transition temperature of tin, and they obtain a curve of the type described by Eq. (30) with $b=0.5$ for the Sn-Ag system. If we assumed that $\sigma=1$, this would give a value of NV in silver roughly the same as that of tin. The inference that a barrier is present is confirmed by the observation that an oxide layer is formed during evaporation. The very low value of $b=0.06$ found for the Pb-Ag systems of Smith *et al.*²⁹ gives further evidence of barrier formation. On the other hand, Sn-Co is reported by Simmons and Douglass to have $b\sim 25$. This reflects a strong effective repulsion between electrons of opposite spin in a ferromagnet due to the energy gained in the breaking of a singlet pair state.

CONCLUSION

The variational form of the Gor'kov theory developed above makes possible the study of systems in which the electron-electron interaction varies over the dimensions of the system. This procedure can be used when the interaction changes discontinuously, as has been seen by studying superposed films. With the simplest trial functions we have calculated transition temperatures which agree with the experimental data in both the thick and thin film limits and over a wide range of mean free paths.

ACKNOWLEDGMENT

One of the authors (WS) wishes to acknowledge support received from the National Science Foundation under grant GP-1532 during the completion at Michigan State University of his contribution to this work.

APPENDIX: EFFECT OF A DISCONTINUOUS INTERACTION

The superconducting Green's functions possess the following properties of a many-body wave function³⁰: single-valuedness, analyticity at all points at which the Hamiltonian is analytic, and absolute and quadratic integrability of the function and of its first derivative. For example, consider the behavior of the pair correlation amplitude $\chi_\omega(\mathbf{r})$ in the vicinity of a point \mathbf{r}_0 at which $V(\mathbf{r})$ is discontinuous. Using the expansion (3-5) for $\chi_\omega(\mathbf{r})=F_\omega(\mathbf{r},\mathbf{r})$, we obtain

$$\chi_\omega(\mathbf{r}) = \int \Gamma_\omega^{(0)}(\mathbf{r},\mathbf{r}')\Delta_\omega(\mathbf{r}')d\mathbf{r}' + \dots, \quad (\text{A1})$$

where the remaining terms are well behaved. Since the correct energy-gap for the system is given by the consistency condition $\Delta=V\chi$, and $\chi(\mathbf{r})$ is a continuous function, the problem is one of specifying the properties of (A1) when $\Delta_\omega(\mathbf{r})$ is discontinuous at $\mathbf{r}=\mathbf{r}_0$. These are in turn determined by the $1/R^2$ singularity of $\Gamma_\omega^{(0)}(\mathbf{r},\mathbf{r}')$ for small values of $R=|\mathbf{r}-\mathbf{r}'|$, which comes from the $1/R$ singularity in the Green's function; cf. Eqs. (12), (14), and (15).

We need consider only the one-dimensional case, for which the kernel has a logarithmic singularity such as is exhibited by Eq. (17). The behavior of the correlation amplitude is characterized by the function $\varphi(z)=\int_{-\delta}^{\delta} \ln|z-z'|\theta(z')dz'$. This obeys the continuity condition

$$|\varphi(\epsilon)-\varphi(-\epsilon)| = \int_0^\delta \ln\left|\frac{z+\epsilon}{z-\epsilon}\right| dz = 2\epsilon\left(1+\ln\frac{\delta}{\epsilon}\right) \xrightarrow{\epsilon\rightarrow 0} 0,$$

which is a necessary property of the wave function. If, however, we calculate the derivative

$$\left.\frac{d\varphi(z)}{dz}\right|_{z=0} = \lim_{\epsilon\rightarrow 0} \left[\frac{\varphi(\epsilon)-\varphi(-\epsilon)}{2\epsilon}\right],$$

we find that it is infinite. In this fashion we can also establish that the divergence is logarithmic, so that $d\varphi/dz$ is both absolutely and quadratically integrable.

We can also obtain this result directly from the Gor'kov equation for F , which in the free-electron approximation is

$$(i\omega + \nabla^2/2m + \mu)F_\omega(\mathbf{r},\mathbf{r}') = \Delta_\omega(\mathbf{r})G_{-\omega}(\mathbf{r}',\mathbf{r}).$$

Neglecting terms which are bounded and integrable, we obtain for the derivative

$$\begin{aligned} \frac{\partial F_\omega(\mathbf{r},\mathbf{r}')}{\partial[(\mathbf{r}_z+\mathbf{r}'_z)/2]} &\sim \int^{\mathbf{r}} \Delta_\omega(\boldsymbol{\rho})G_{-\omega}(\mathbf{r}',\boldsymbol{\rho})d\boldsymbol{\rho}_z \\ &\quad + \int^{\mathbf{r}'} \Delta_\omega(\boldsymbol{\rho})G_{-\omega}(\mathbf{r},\boldsymbol{\rho})d\boldsymbol{\rho}_z. \end{aligned}$$

If \mathbf{r} and \mathbf{r}' are the points $(0, 0, Z\pm\zeta)$, this gives

$$\begin{aligned} \frac{\partial F_\omega(\mathbf{r},\mathbf{r}')}{\partial Z} &\sim \int^{Z+\zeta} \frac{\Delta_\omega(z)dz}{|z|} + \int^{Z-\zeta} \frac{\Delta_\omega(z)dz}{|z|} \\ &\sim [\Delta_\omega(Z+\zeta) - \Delta_\omega(Z-\zeta)] \ln\zeta. \end{aligned}$$

When V , and hence Δ , is discontinuous across the $z=0$ plane, the derivative $\partial F(\mathbf{r},\mathbf{r}')/\partial Z$ diverges logarithmically as $\zeta\rightarrow 0$, and $\partial\chi/\partial z$ is infinite.

²⁹ P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters **6**, 686 (1961).

³⁰ E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (Dover Publications, Inc., New York, 1958), p. 198.