plain the experiments the field increments necessary for penetration must be of the order of magnitude of one tenth of an oersted.[7] The number of field penetrations per unit time is then dependent upon the dc sweep speed. On the basis of this model it can be shown[8] that the ac field penetration (and hence χ') depends on the number of times the surface is broken down by the dc field during an ac cycle. If there are many breakdowns the average internal ac field follows the external field and χ' will equal the slope of the magnetization curve. For many ac cycles per breakdown, χ' will appear diamagnetic since the ac fields are excluded most of the time. The above discussion assumes the ac amplitude to be comparable to or less than the field increments necessary for penetration. Under these conditions almost all break-ins are caused by the dc sweep field.

The results of Park[9] and Le Blanc[10] on "semireversible" superconductors provide an alternate explanation. They find that for small changes in the external field a minor hysteresis loop of negligible area, with slope $-\frac{1}{4}\pi$, is traversed, when the direction-of-field scan along the magnetization curve is reversed. Thus at fixed dc fields, the ac field reverses the scan direction and travels along the diamagnetic hysteresis loop. In a sweeping dc field when $\omega H_{ac} < dH_{dc}/dt$, the external field always scans in one direction and will not trace out the diamagnetic minor-hysteresis loop. Under these conditions[11] the susceptibility χ' measures dM/dH of the magnetization curve. While this model appears reasonable below H_{c2}, it is not clear how it can explain the diamagnetism in the H_{c2} to H_{c3} region where the mechanism which would cause hysteresis is not obvious.

Sensitive magnetization measurements with sufficient field resolution may be able to determine whether the proposed structure in the inset of Fig. 2(a) exists, and thereby distinguish between the two models.

It is worth noting that our experiments imply that resonance experiments on bulk superconductors may now be possible by choosing dc sweep rates and ac frequencies which allow the ac field to penetrate the sample.

[7] The increment size is expected to depend upon the sample, sample preparation, and the external field. In some samples we find large amounts of "noise" in the region between the initial- and upper-bulk critical fields. This noise can be observed in a swept dc field by looking at the signal coming out of the secondary coil with no ac field on the sample. These results would imply that in these samples the field increment necessary for breakdown is very irregular. Experiments to investigate the details of the increment size are underway.

[8] A. Paskin, P. P. Craig, D. G. Schweitzer, and M. Strongin (unpublished).

[9] J. G. Park, Rev. Mod. Phys. **36**, 87 (1964).

[10] M. A. R. Le Blanc, Phys. Letters **9**, 9 (1964).

[11] In these measurements, dM/dH does not change appreciably over one ac cycle. If the sweep rate is large enough so that dM/dH changes in this interval, correction terms must be considered which depend on the sweep rate and d^2M/dH^2.

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Magnetic Properties of Superconducting Films

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The general Gor'kov equations are solved for a superconducting film in a parallel magnetic field. The method determines the best pairing in the superconducting state without the need for *ad hoc* assumptions about pairing such as are used in other theories. The critical field $H_c(T)$ and energy gap $\Delta(H, T)$ are determined for temperatures near the transition temperature at zero field T_c. The energy gap in the quasiparticle excitation spectrum is shown to be approximately equal to the spatial average of the order parameter. For films whose thickness d is less than the coherence length ξ_T the Gor'kov equations are nonlocal and differ from the Ginzburg-Landau (GL) equations. In this range we find $H_c \propto d^{-3/2}$ in agreement with experiment. For films with $d > \xi_T$ the solution of the Gor'kov equations are the same as the GL results, as expected, since this is a local regime. We find that for all d (excepting ultrathin films) and in the temperature range $(1-T/T_c) < < 1$ the field dependence of the energy gap is the same as that given by the GL equations, i.e, $\Delta(H)/\Delta(0) = \{1-(H/H_c)^2\}^{1/2}$. Thus, nonlocal effects do not change the field dependence of the gap. Most of the experimental data are in accord with this equation. However, some recent results for aluminum films show deviations which we interpret as probably being due to the important role played by energy-level quantization of single-particle states in ultrathin films. The extension of the method to lower temperatures and higher fields is also discussed.

I. INTRODUCTION

We obtain *nonlocal* solutions of the Gor'kov[1] integral equations for the critical temperature $T_c(H)$ and order parameter $\Delta(H,T)$ [for $T < T_c(H)$] of a type-I superconducting film with equal magnetic fields H applied parallel to both film surfaces. Our derivation is restricted to the temperature range, $1-t \ll 1$, where $t = T/T_c(0)$ is the reduced temperature, and to sufficiently pure samples for which the film thickness d is considerably less than the mean free path l for scattering

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

due to bulk imperfections. Moreover, we assume specular scattering at the film boundaries. For bulk samples in fields such that the vector potential $\mathbf{A}(\mathbf{r})$ and the order parameter $\Delta(\mathbf{r})$ vary slowly with position $\mathbf{r}$ over distances of the order of the Bardeen-Cooper-Schrieffer (BCS)[2] coherence length ξ_0, Gor'kov has shown that his relations reduce to the well-known Ginzburg-Landau[3] (GL) differential equations in the temperature range we consider. Since the penetration depth, λ, becomes infinite as $t\rightarrow 1$, the condition $d/\lambda \ll 1$ (for which H is approximately equal to the externally applied field) is readily obtained for thin films. Under this condition the GL equations are easily solved for the critical field $H_c(T,d)$ and yield, for fixed T, $H_c \propto d^{-1}$. However, the data of Toxen[4] for indium films and of Blumberg[5] for tin show that experimentally, $H_c \propto d^{-3/2}$ for films such that $d \lesssim \xi_0$. Since Gor'kov's derivation of the *local* GL relations does not remain valid for such thin films the disagreement is not surprising.[6] A phenomenological derivation for $H_c(T,d)$ has been given by Toxen[4] and also by Hauser and Helfand.[7] These phenomenological results correctly reproduce the critical field data in both the local and nonlocal regimes. The Toxen method uses the GL equations to establish a connection between H_c and the bulk critical field H_{cb} and weak field susceptibility, obtaining the latter from a calculation of Schrieffer[6] who employed the nonlocal Pippard relation between current and vector potential. Assuming specular reflection, Toxen found [Eq. (15), Ref. 4]

$$H_c \approx 2.01 H_{cb}(\xi_0 \lambda_L^2/(d/2)^3)^{1/2}, \tag{1}$$

where λ_L is the London penetration depth. Assuming diffuse scattering at the boundaries, he found a result identical to Eq. (1) with the exception that the numerical coefficient, 2.01, is to be replaced by the quantity 2.31. Thus the results of Toxen indicate that the critical field does not depend strongly on the nature of the surface scattering assumed. Although the existence of residual resistance in the normal state in clean films requires some diffuse boundary scattering, we have considered only the case of specular scattering for mathematical convenience. The assumption of specular scattering has also been made by Nambu and Tuan,[8] whose work related to this problem will be discussed later, and by Thomson and Blatt[9] in their work on "shape resonances" in very thin films. The phenomenological theory has been treated in more detail by Liniger and Odeh.[10]

In the present analysis we derive an expression for $T_c(H)$ which is equivalent to Eq. (1) and, hence, in good agreement with the data. Our expression for H_c is equal to the right side of Eq. (1) except for a dimensionless multiplicative constant, of order unity, which results from the nature of our mathematical approximations. As will be shown in Sec. III, we obtain $T_c(H)$ by direct solution of the *microscopic*, *nonlocal* Gor'kov equations without invoking *ad hoc* assumptions about the nature of the Cooper pairs. Moreover, our method for deriving $T_c(H)$ can be extended in a straightforward way to apply to lower temperatures, i.e., higher fields, than we consider here. We emphasize, however, that as presented here, the method is restricted to films for which the assumption, $d/\lambda \ll 1$, is maintained. Otherwise, of course, the difference between the applied and actual fields must be taken into account.

As noted earlier we also obtain the order parameter $\Delta(H,T)$ for $H<H_c$. In Appendix D we prove that the spatial average of this quantity is the energy gap in the excitation spectrum. Within the limits of validity of the Gor'kov or BCS effective electron-electron interaction leading to superconductivity $|\bar{\Delta}(H,T)|$ is also the tunneling gap. However, effects due to the dynamical electron-phonon interaction (shown by Schrieffer, Scalapino, and Wilkins[11] to be essential for a detailed understanding of the tunneling density of states observed in lead by Rowell, Anderson, and Thomas[12]) are absent in the Gor'kov interaction. Thus, while our result for $|\bar{\Delta}(H,T)|$ is equal to the energy of the cutoff in the dentisy of states relative to the Fermi energy, the structure in the tunneling characteristics lies outside the scope of our treatment.

Recently Maki[13] and Nambu and Tuan[8] have given theoretical treatments of thin superconducting films in magnetic fields based upon a microscopic approach. Maki considered *dirty* films, i.e., $l \ll d$. He found $H_c \propto d^{-1}\tau^{-1/2}$, where τ is the mean free time for impurity scattering. Thus, his results and ours apply to different regimes which do not overlap.[13a] One might attempt to apply his result to clean films by arguing that $\tau \propto l$ and assuming $l \approx d$, obtaining $H_c \propto d^{-3/2}$. This argument is not wholly satisfying as has been noted by Toxen and Burns[14] and, more recently, by De Gennes and Tink-

[2] J. Bardeen, L. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

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

[4] A. M. Toxen, Phys. Rev. **127**, 382 (1962); **123**, 442 (1961).

[5] R. H. Blumberg, J. Appl. Phys. **33**, 1822 (1962).

[6] That the Gor'kov derivation of the GL equations does not apply to films of thickness $d \lesssim \xi_0$ when H is parallel to the film is perhaps most readily seen for the case of specular reflection where one may invoke the equivalence, noted by Schrieffer, of a film in uniform field to a bulk sample in a square-wave field which alternates sign as the position coordinate normal to the film changes by an amount equal to d. Thus $A(r)$ does not vary slowly over a distance $\sim\xi_0$. [J. R. Schrieffer, Phys. Rev. **106**, 47 (1957).]

[7] J. J. Hauser and E. Helfand, Phys. Rev. **127**, 386 (1963).

[8] Y. Nambu and S. F. Tuan, Phys. Rev. **133**, A1 (1964).

[9] C. J. Thompson and J. M. Blatt, Phys. Letters **5**, 6 (1963).

[10] W. Linger and F. Odeh, Phys. Rev. **132**, 1934 (1962).

[11] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963).

[12] J. M. Rowell, P. W. Anderson, and D. E. Thomas, Phys. Rev. Letters **10**, 334 (1963).

[13] K. Maki, Progr. Theoret. Phys. (Kyoto) **29**, 603 (1963).

[13a] *Note added in proof*. The existence of gapless superconductivity in dirty films is in marked contrast to our result for clean films where gapless superconductivity does not occur.

[14] A. M. Toxen and M. J. Burns, Phys. Rev. **130**, 1808 (1963).

ham.[15] In any event, we believe that an alternative approach, which deals with the nonlocal effects explicitly at a microscopic level is worthwhile. Nambu and Tuan consider the case $d \ll l$, $d \ll \lambda$ and assume specular reflection as we do. For weak fields at $T=0°$K they pair zero-field states of the form $\exp\{i(\mathbf{k}\cdot\mathbf{r})\}\sin(m\pi x/d)$, where m is a positive integer and $\mathbf{k}=(0,k_y,k_z)$ is a two-dimensional wave vector consistent with a film bounded by planes at $x=0$, d with $\mathbf{H}$ parallel to the z axis. They pair $(\mathbf{k}m\uparrow)$ with $(-\mathbf{k}m\downarrow)$ where the arrow indicates the z component of the electron spin. By a combined variational and perturbative (in H) approach, they deduce the empirical result, $H_c \propto d^{-3/2}$. For higher fields they argue that one should pair degenerate exact single-particle eigenstates in the presence of the field and deduce therefrom an effective coupling constant $g(H)$ and associated similarity law, obtaining $T_c(H)$ from the BCS relation, $\Delta(H,0)=1.75k_BT_c(H)$. (Here k_B is the Boltzmann constant.) *We find no such simple pairing, even for weak fields when* $[1-T_c(H)/T_c(0)]\ll 1$. In Appendix D we show that although the Green function G is approximately diagonal in the exact single-particle representation for small Δ, the Gor'kov pair-correlation function F is not. Although we do not know explicitly the proper states to pair in the presence of the field, optimal pairing is automatically provided for in Gor'kov's method. From physical considerations, we believe that the pairing of exact degenerate single-particle eigenstates is valid only for magnetic fields sufficiently large that $\hbar\omega_c > |\bar{\Delta}(H,T)|$ *and* $\hbar\omega_c > k_BT$, which does not hold in the region we consider (ω_c= cyclotron frequency).

In Sec. II we summarize our physical assumptions and define the problem. Section III together with Appendices A through C contains the derivation of our results. Further comparison with experiment is made in Sec. IV.

II. DEFINITION OF PROBLEM

1. Summary of Physical Assumptions

Thus far, as noted in the Introduction, we have assumed (1) T is near $T_c(0)$, i.e., $1-t\ll 1$; (2) the film is pure, i.e., $d\ll l$; (3) boundary scattering is specular; and (4) H is constant throughout the film and equal to the field applied parallel to the film surfaces, i.e., $d\ll\lambda$, which is consistent with assumption (1). In addition, we (5) limit the analysis to weak coupling superconductors, (6) assume, as did Gor'kov, that the magnetic field does not affect the superconducting interaction, *per se*, and (7) omit from consideration ultrathin films for which effects due to the quantization of the momentum variable normal to the major film surfaces become important. Such quantum effects, also noted by Nambu and Tuan, appear when the minimum energy separation between adjacent single-particle states in zero field (with a common value of wave vector parallel to the surfaces) becomes $\gtrsim k_BT_c$. That is, when

$$\pi^2\hbar^2/(md^2)\gtrsim k_BT_c, \tag{2}$$

where m is the electron mass and henceforth, we write T_c without an argument to mean $T_c(0)$. Equivalently, restating condition (7), we exclude from consideration films for which

$$d\lesssim 6(\xi_T/k_0)^{1/2}, \tag{3}$$

where k_0 is the Fermi wave vector and

$$\xi_T\equiv\hbar v_0/(\pi k_BT)=1.75\xi_0(T_c/T). \tag{4}$$

Here v_0 is the Fermi velocity and we have used the BCS relation for the coherence length,

$$\xi_0=0.18\hbar v_0/(k_BT_c). \tag{5}$$

Moreover, we have set T equal to T_c in establishing the equivalence of the approximate inequalities, (2) and (3).

2. Basic Hamiltonian and Choice of Gauge

Letting $\mathcal{H}$ be the Hamiltonian, μ the chemical potential, and N the particle-number operator, the Gor'kov effective Hamiltonian $\mathcal{H}'$ may be written

$$\mathcal{H}'\equiv\mathcal{H}-\mu N=\sum_\sigma\int d^3r\psi_\sigma^+(\mathbf{r})O(\mathbf{r})\psi_\sigma(\mathbf{r})$$
$$+\tfrac{1}{2}\sum_\sigma\int d^3r\int d^3r'\psi_\sigma^+(\mathbf{r})\psi_{-\sigma}^+(\mathbf{r}')$$
$$\times v(\mathbf{r}-\mathbf{r}')\psi_{-\sigma}(\mathbf{r}')\psi_\sigma(\mathbf{r}), \tag{6}$$

where

$$O(\mathbf{r})=\frac{\hbar^2}{2m}[-i\nabla_r+\alpha\mathbf{A}(\mathbf{r})]^2-\mu \tag{7}$$

and

$$\alpha\equiv|e|/\hbar c. \tag{8}$$

$O(\mathbf{r})$ is the single-particle Hamiltonian and e, the electronic charge. v is the Gor'kov interaction coupling electron pairs of opposite spin. Other interactions, contributing to the renormalization of the single-particle energies, are assumed contained in $O(\mathbf{r})$ where m may be regarded as an effective mass. $\psi_\sigma^+(\mathbf{r})$ is the usual fermion creation operator for a particle with z component of spin equal to σ. Gor'kov assumed

$$v(\mathbf{r}-\mathbf{r}')=-V\delta^3(\mathbf{r}-\mathbf{r}'), \tag{9}$$

where V is a positive constant subject to the BCS cutoff on the energy shell about the Fermi surface of width, $2\hbar\omega_D$, twice the Debye phonon energy.

[15] P. G. De Gennes and M. Tinkham (to be published). In this report which we received after the original version of this paper was submitted for publication, the authors state that assuming diffuse scattering, a film free of bulk imperfections does not behave like a dirty superconductor with an effective mean free path comparable to the thickness. However, when $d<l<[d\xi_0/(1-t)]^{1/2}$, they recover "ergodicity" which they consider to be a property of the dirty case.

We assume the film to be bounded by planes at $x=\pm d/2$ with the magnetic field directed along the positive z axis. We select the gauge

$$\mathbf{A}=(0,Hx,0). \tag{10}$$

This gauge satisfies the London conditions and ensures that the average current flow is zero. It is, apart from a trivial coordinate transformation resulting from a different choice of origin, identical with the gauge of Nambu and Tuan.

III. DERIVATION OF $T_c(H)$ AND $|\bar{\Delta}(H,T)|$

1. Review of the Gor'kov Theory

To establish our notation we recall that Gor'kov considers two imaginary time-correlation functions,

$$G(\mathbf{r},\mathbf{r}',\tau)\equiv\langle T_\tau\psi_\uparrow(\mathbf{r},\tau)\psi_\uparrow^+(\mathbf{r}',0)\rangle, \quad |\tau|\leq\beta$$
$$F(\mathbf{r},\mathbf{r}',\tau)\equiv\langle T_\tau\psi_\downarrow^+(\mathbf{r},\tau)\psi_\uparrow^+(\mathbf{r}',0)\rangle, \quad |\tau|\leq\beta. \tag{11}$$

Here, T_τ is the time-ordering operator; the field operators are in the Heisenberg picture with the replacement $t=-i\tau$, where t is the real time variable; and the brackets denote a thermal average, taken with respect to the partition sum, trace $\exp(-\beta\mathcal{H}')$. $\mathcal{H}'$ is given by Eq. (6) and $\beta\equiv(k_BT)^{-1}$. From the equations of motion of the field operators and their anticommutation properties Gor'kov obtains linearized equations of motion for the correlation functions which, in our notation, read

$$[\hbar(\partial/\partial\tau)+O(\mathbf{r})]G(\mathbf{r},\mathbf{r}',\tau)+\Delta^*(\mathbf{r})F(\mathbf{r},\mathbf{r}',\tau)=\delta(\tau)\delta^3(\mathbf{r}-\mathbf{r}'), \tag{12}$$
$$[\hbar(\partial/\partial\tau)-O^*(\mathbf{r})]F(\mathbf{r},\mathbf{r}',\tau)+\Delta(\mathbf{r})G(\mathbf{r},\mathbf{r}',\tau)=0,$$

where

$$\Delta(\mathbf{r})\equiv-V\langle\psi_\uparrow^+(\mathbf{r},0)\psi_\downarrow^+(r,0)\rangle=+VF(\mathbf{r},\mathbf{r},0). \tag{13}$$

G and F are Fourier analyzed. Thus, for G

$$G(\mathbf{r},\mathbf{r}',\tau)=\beta^{-1}\sum_\omega e^{-i\omega\tau}G_\omega(\mathbf{r},\mathbf{r}'), \tag{14}$$

where

$$\omega\equiv\omega_n=(2n+1)\pi/(\hbar\beta). \tag{15}$$

(n is an integer.)

2. Reduction to a One-Dimensional Problem

At this point we depart from the original Gor'kov theory, noting that for our choice of gauge, $\mathcal{H}'$ is invariant with respect to translations in the y and z directions, whence we may write

$$G_\omega(\mathbf{r},\mathbf{r}')=\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}G_{\mathbf{k}\omega}(x,x'), \tag{16}$$

where $\mathbf{k}$ is a two-dimensional wave vector, i.e., $\mathbf{k}=(0,k_y,k_z)$. A similar equation may be written for $F_\omega(\mathbf{r},\mathbf{r}')$. $G_{\mathbf{k}\omega}$ and $F_{\mathbf{k}\omega}$ satisfy coupled differential equations, of the form

$$[-i\hbar\omega+O_{\mathbf{k}}(x)]G_{\mathbf{k}\omega}(x,x')+\Delta^*(x)F_{\mathbf{k}\omega}(x,x')=\delta(x-x') \tag{17}$$
$$[-i\hbar\omega-O_{-\mathbf{k}}(x)]F_{\mathbf{k}\omega}(x,x')+\Delta(x)G_{\mathbf{k}\omega}(x,x')=0,$$

where

$$O_{\mathbf{k}}(x)\equiv(\hbar^2/2m)\left[-\frac{\partial^2}{\partial x^2}+k^2+2\alpha k_yA_y(x)+\alpha^2A_y{}^2(x)\right]-\mu, \tag{18}$$

and

$$\Delta(x)=V\sum_{\mathbf{k}}F_{\mathbf{k}}(x,x,0)=V\beta^{-1}\sum_{\mathbf{k}\omega}F_{\mathbf{k}\omega}(x,x). \tag{19}$$

In analogy with Gor'kov's method of deriving the GL relations, we seek functions $\tilde{G}_{\mathbf{k}\omega}(x,x')$ and $\tilde{F}_{\mathbf{k}\omega}(x,x')$ which satisfy the conditions

$$[-i\hbar\omega+O_{\mathbf{k}}(x)]\tilde{G}_{\mathbf{k}\omega}(x,x')=\delta(x-x'),$$
$$[-i\hbar\omega-O_{-\mathbf{k}}(x)]\tilde{F}_{\mathbf{k}\omega}(x,x')=\delta(x-x'). \tag{20}$$

Clearly

$$\tilde{F}_{\mathbf{k}\omega}(x,x')=-\tilde{G}_{-\mathbf{k}-\omega}(x,x'). \tag{21}$$

$\tilde{G}_{\mathbf{k}\omega}(x,x')$ is the one-dimensional normal-state Green function. Combining Eqs. (17) and (20), we obtain the coupled integral equations

$$G_{\mathbf{k}\omega}(x,x')=\tilde{G}_{\mathbf{k}\omega}(x,x')-\int ds\Delta^*(s)\tilde{G}_{\mathbf{k}\omega}(x,s)F_{\mathbf{k}\omega}(s,x'),$$
$$F_{\mathbf{k}\omega}(x,x')=-\int ds\Delta(s)\tilde{F}_{\mathbf{k}\omega}(x,s)G_{\mathbf{k}\omega}(s,x'). \tag{22}$$

3. Determination of $T_c(H)$

a. Small Δ Approximation

Since the gap parameter $\Delta(x)$ is a measure of pair correlation and hence of the order characterizing the superconducting state, by definition of $T_c(H)$, $\Delta(x)\to0$ as $T\to T_c(H)$ from below. This statement is valid, whether or not the space average of $\Delta(x)$ represents the gap in the excitation spectrum. Therefore, to determine $T_c(H)$ we may solve Eqs. (22) by expanding in powers of $\Delta(x)$, keeping only the first nonvanishing term. In this approximation Eqs. (22) combine, setting $x'=x$ and using Eqs. (19) and (21) to give the integral equation

$$\Delta(x)=(V/\beta)\int dsK(x,s)\Delta(s), \tag{23}$$

where

$$K(x,s)\equiv\sum_{\mathbf{k}\omega}\tilde{G}_{-\mathbf{k}-\omega}(x,s)\tilde{G}_{k\omega}(s,x). \tag{24}$$

Equation (23) has a solution only for the eigenvalue $T=T_c(H)$.

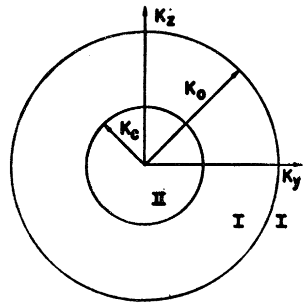

FIG. 1. Subdivision of the two-dimensional **k** space into two regions. In region I Re$Zd>1$; in II Re$Zd<1$, where Z is the root of Eq. (38) for which Re$Z>0$. The figure is drawn for the case of thin films ($d<\xi_T$). For this case region II is bounded by a circle of radius k_c, given by Eq. (45). Region I exhausts the remainder of k space. The circle $k=k_0$ is also shown. When $d>\xi_T$, region II does not exist.

b. Solution for the Normal-State Green Function and $K(x,s)$

Again by analogy with the Gor'kov derivation of the GL equations, we write

$$\tilde{G}_{\mathbf{k}\omega}(x,x')=e^{i\phi_{\mathbf{k}\omega}(x,x')}\tilde{G}_{\mathbf{k}\omega}{}^0(x,x'),\qquad(25)$$

where $\tilde{G}_{\mathbf{k}\omega}{}^0$ is the zero-field normal-state Green function. It satisfies the relation

$$[-i\hbar\omega+O_{\mathbf{k}}{}^0(x)]\tilde{G}_{\mathbf{k}\omega}{}^0(x,x')=\delta(x-x').\qquad(26)$$

The operator $O_{\mathbf{k}}{}^0(x)$ equals the right side of Eq. (18) when one sets $A_y=0$. Eqs. (20), (25), and (26) can be satisfied only if $\phi_{\mathbf{k}\omega}(x,x')$ is a solution of the following equation:

$$\left[2\alpha k_yA_y(x)+\alpha^2A_y{}^2(x)-i\frac{\partial^2\phi_{\mathbf{k}\omega}}{\partial x^2}+\left(\frac{\partial\phi_{\mathbf{k}\omega}}{\partial x}\right)^2\right]\tilde{G}_{\mathbf{k}\omega}{}^0-2i\frac{\partial\tilde{G}_{\mathbf{k}\omega}{}^0}{\partial x}\frac{\partial\phi_{\mathbf{k}\omega}}{\partial x}=0.\qquad(27)$$

ϕ must also satisfy an equation derivable from Eq. (27) by exchanging the variables x and x' throughout, including the (unwritten) arguments of ϕ and $\tilde{G}^0$. Finally, the boundary condition on ϕ is

$$\phi_{\mathbf{k}\omega}(x,x')|_{x'=x}=0.\qquad(28)$$

The solution to Eq. (26) for $\tilde{G}_{\mathbf{k}\omega}{}^0$ is

$$\tilde{G}_{\mathbf{k}\omega}{}^0=\sum_{m'}[-i\hbar\omega+\epsilon_{\mathbf{k}m'}{}^0]^{-1}u_{m'}{}^0(x)u_{m'}{}^0(x'),\qquad(29)$$

where

$$u_{m'}{}^0(x)\equiv(2/d)^{1/2}\sin[(m'\pi/d)(x+d/2)]\qquad(30)$$

and m' is a positive integer. $u_{m'}{}^0$ satisfies the zero-field single-particle Schrödinger equation

$$O_{\mathbf{k}}{}^0(x)u_{m'}{}^0(x)=\epsilon_{\mathbf{k}m'}{}^0u_{m'}{}^0(x),\qquad(31)$$

where

$$\epsilon_{\mathbf{k}m'}{}^0=(\hbar^2/2m)[\mathbf{k}^2+(m'\pi/d)^2]-\mu.\qquad(32)$$

Moreover, $u_{m'}{}^0(x)$ vanishes at the film boundaries, i.e., when $x=\pm\frac{1}{2}d$, corresponding to the assumption of specular reflection.

The following useful identities follow by inspection of Eq. (29):

$$\tilde{G}_{\mathbf{k}\omega}{}^0(x'x)=\tilde{G}_{\mathbf{k}\omega}{}^0(x,x')=[\tilde{G}_{-\mathbf{k}-\omega}{}^0(x,x')]^*.\qquad(33)$$

From the left-hand equality in (33) and Eq. (27), together with its counterpart with x and x' interchanged, one see that $\phi_{\mathbf{k}\omega}(x,x')$ is likewise invariant under the exchange of x and x'.

Since we have assumed $1-t\ll1$, the critical field cannot be very large, suggesting the convenience of writing the kernel $K(x,x')$, defined by Eq. (24), in the form

$$K(x,x')=K_0(x,x')+K_H(x,x'),\qquad(34)$$

where

$$K_0(x,x')\equiv\sum_{\mathbf{k}\omega}\tilde{G}_{-\mathbf{k}-\omega}{}^0(x,x')\tilde{G}_{\mathbf{k}\omega}{}^0(x',x).\qquad(35)$$

Combining Eqs. (24), (25), (34), and (35), one sees

$$K_H(x,x')=\sum_{\mathbf{k}\omega}\{\exp[i(\phi_{\mathbf{k}\omega}+\phi_{-\mathbf{k}-\omega})]-1\}\tilde{G}_{-\mathbf{k}-\omega}{}^0\tilde{G}_{\mathbf{k}\omega}{}^0.\qquad(36)$$

K_0 is readily determined from Eq. (29) and Eqs. (33). To obtain K_H, we must solve Eq. (27) for $\phi_{\mathbf{k}\omega}$. This task is simplified by noting that since K_H is a correction term, we may use a simpler approximate form for $\tilde{G}_{\mathbf{k}\omega}{}^0$ in Eq. (36) and Eq. (27) without introducing serious error. To determine the approximate $\tilde{G}_{\mathbf{k}\omega}{}^0$ we first observe that the exact function can be written in an alternate way:

$$\tilde{G}_{\mathbf{k}\omega}{}^0(x,x')=\frac{-(m/\hbar^2)}{Z\sinh(Zd)}\times\{\cosh[Z(x+x')]-\cosh[Z(|x-x'|-d)]\}.\qquad(37)$$

It is readily verified that the right side of Eq. (37), like that of Eq. (29), satisfies the differential Eq. (26) and vanishes at the film boundaries, i.e., when x or x' equals $\pm\frac{1}{2}$. The quantity Z appearing in Eq. (37) is a function of $\mathbf{k}$ and ω and is given by either root of the equation

$$Z^2=\mathbf{k}^2-k_0{}^2-i(2m\omega/\hbar)=k^2-k_0{}^2-i[2(2n+1)k_0/\xi_T].\qquad(38)$$

We have denoted the magnitude of the two-dimensional wave vector $\mathbf{k}$ by k and recall that k_0 is the magnitude of the wave vector on the usual Fermi surface in three dimensions. Of the two possible roots of Eq. (38) we shall consistently select the root for which Re$Z>0$. It is convenient to divide the two-dimensional k space into two regions, labeled I and II as shown in Fig. 1. By definition, in region I Re$Zd>1$; in region II Re$Zd<1$. The boundary between the regions is a circle of radius k_c where k_c is given below [see Eq. (45)]. From Eq. (37) we obtain two asymptotic forms for $\tilde{G}_{\mathbf{k}\omega}{}^0$ when Re$Zd\gg1$

and $\text{Re}Zd \ll 1$. We approximate $\tilde{G}_{\mathbf{k}\omega}{}^0$ by using the first asymptotic form throughout region I, and the second throughout region II. When $\text{Re}Zd \gg 1$, Eq. (37) reduces to

$$\tilde{G}_{\mathbf{k}\omega}{}^0 = (m/\hbar^2) Z^{-1} \exp(-Z|x-x'|). \quad (39)$$

We note that the right side of Eq. (39) is just the particular solution to Eq. (26) ignoring the boundary conditions. Since the solution is damped in a distance $\sim (\text{Re}Z)^{-1}$ we see intuitively that neglecting a fraction, $\sim (\text{Re}Zd)^{-1}$ of the film volume near the surfaces introduces little error when $\text{Re}Zd \gg 1$.[15a] The other asymptotic form, when $\text{Re}Zd \ll 1$, is

$$\tilde{G}_{\mathbf{k}\omega}{}^0 = \frac{(m/\hbar^2)}{Z_i \sin(Z_i d)} \times \{\cos[Z_i(x+x')] - \cos[Z_i(|x-x'|-d)]\}. \quad (40)$$

In the foregoing we have used ReZ and Z_i to denote the real and imaginary parts of Z, respectively.

Next we observe, upon examining Eq. (38), that when $k \geq k_0$, $\text{Re}Zd \geq (k_0/\xi_T)^{1/2} d$. As noted in Sec. II, however, we consider only films for which $d \gtrsim 6(\xi_T/k_0)^{1/2}$. Thus $\text{Re}Zd > 1$ everywhere in the $\mathbf{k}$ plane outside a circle of radius k_0. That is, region I extends from $k=\infty$ inward to some value k_c where $k_c < k_0$ as depicted in Fig. 1. For $k < k_0$, $\text{Re}Z < Z_i$ and we obtain from Eq. (38), neglecting terms $\sim (\text{Re}Z/Z_i)^2$,

$$Z_i = \pm (k_0^2 - k^2)^{1/2} \approx \pm [2k_0(k_0-k)]^{1/2}, \quad (k < k_0) \quad (41)$$

$$\text{Re}Z = -(2n+1)k_0/(Z_i \xi_T), \quad (k < k_0). \quad (42)$$

In Eq. (41) the sign of Z_i is to be chosen such as to make $\text{Re}Z > 0$ in accordance with our previously established convention. Note that Eq. (42) and the left-hand relation in Eqs. (41) become highly accurate when $(k_0-k)/k_0 \gg |2n+1|/(k_0\xi_T)$. We shall see later on that only the terms $n=0, -1$ contribute appreciably to the sum on n, i.e., on ω, in the expression (36) for K_H. Thus, since $k_0\xi_T$ is typically $\sim 10^4$, the relations cited are nearly exact everywhere within the circle $k=k_0$ except in a negligibly small region near the perimeter.

It is clear that the minimum value of ReZ occurs when $k=0$ where $\text{Re}Z = |2n+1|/\xi_T$. Again anticipating that only the terms $n=0, -1$ contribute to K_H, we are led to distinguish between two classes of film: (1) *Thick* films for which $d > \xi_T$. For this class $\text{Re}Zd \geq 1$ throughout the entire $\mathbf{k}$ plane, i.e., region II does not exist. The GL equations are valid for these films as is evident from the discussion given in Sec. I of the Gor'kov derivation. For completeness we shall proceed to solve the integral equations directly using the approximate form (39) for $\tilde{G}_{\mathbf{k}\omega}{}^0$ and summing on all $\mathbf{k}$ values in the expression (36) for K_H. (2) *Thin* films for which

$$6(\xi_T/k_0)^{1/2} \lesssim d < \xi_T \quad (43)$$

where the lower limit excludes *ultrathin* films. Here we must consider both regions I and II. However, we assert that the contributions from region II to the value of K_H are negligible compared with those from region I. In Appendix A we show that, under certain reasonable assumptions, in region II

$$\phi_{-\mathbf{k}-\omega}(x,x') = -\phi_{\mathbf{k}\omega}(x,x'). \quad (44)$$

From Eq. (36) we see that Eq. (44) implies that the contributions to K_H from region II vanish. For thin films we again use the approximate form (39) for $\tilde{G}_{\mathbf{k}\omega}{}^0$ to determine K_H, but restrict the sum on $\mathbf{k}$ in Eq. (36) to values lying in region I. Recalling once again that only the terms $n=0, -1$ contribute to K_H we may determine the radius k_c of the circle bounding the two regions from Eqs. (41) and Eq. (42). k_c satisfies the relation

$$(k_0 - k_c) = \gamma k_0 (d/\xi_T)^2, \quad (45)$$

where γ is a dimensionless constant, assumed to be of order unity, introduced to account for the approximate nature of $\tilde{G}_{\mathbf{k}\omega}{}^0$ and the cutoff procedure. An important test of the validity of the theory is that quantitative comparison of the theoretical value for $H_c(\gamma,T,d)$ with experiment yield $\gamma \sim 1$ and that the theory give the correct functional dependence of H_c on T and d.

An approximate solution for $\phi_{k\omega}$ in region I is obtained by retaining only the first and last terms in the left side of Eq. (27) and employing Eq. (39). From the discussion following Eq. (27) it follows that $\phi_{k\omega}$ satisfies the coupled equations,

$$2\alpha k_y H x \pm 2iZ[\partial\phi_{\mathbf{k}\omega}(x,x')/\partial x] = 0,$$
$$2\alpha k_y H x' \mp 2iZ[\partial\phi_{\mathbf{k}\omega}(x',x)/\partial x'] = 0, \quad (46)$$

where the upper of the double sign applies when $x > x'$ and the lower when $x < x'$. The solution to Eqs. (46) satisfying the boundary condition (28) and invariance under exchange of x and x' is

$$\phi_{\mathbf{k}\omega}(x,x') = [(i\alpha H k_y)/(2Z_{\mathbf{k}\omega})] |x^2 - x'^2|. \quad (47)$$

The neglect of the second term in Eq. (27) in obtaining the approximate Eqs. (46) is justified by noting that its magnitude is everywhere much less than that of the first term except in a negligibly small region of $\mathbf{k}$ space in which $|k_y/k_0| \lesssim d/r_c$, where r_c is the radius of the classical cyclotron orbit for an electron at the Fermi surface. The neglect of the third and fourth terms is discussed in Appendix B, where it is shown that neglect of the latter imposes a relatively mild restriction on the field strength which is satisfied near $t=1$. This condition is less stringent than the inequality (52) imposed for another reason, to be discussed later.

Equation (38), together with the convention of

[15a] *Note added in proof*. Since, as will be shown, the main contributions to K_H come from region I, we see from the discussion above that our results are insensitive to the detailed nature of the boundary scattering (e.g., diffuse versus specular), a conclusion arrived at earlier in Sec. I by appeal to Toxen's results. The assumption of specular scattering enters formally only in establishing that the contributions to K_H from region II are small.

selecting the root for which $\mathrm{Re}Z>0$, implies that Z satisfies the following identities:

$$Z_{-\mathbf{k}\omega}=Z_{\mathbf{k}\omega}=Z_{-\mathbf{k}-\omega}^{*}. \quad (48)$$

From the solution, Eq. (47), for ϕ in region I, Eqs. (48) imply that in this region ϕ satisfies the relations,

$$\phi_{-\mathbf{k}\omega}=\phi_{\mathbf{k}\omega}, \quad \phi_{-\mathbf{k}-\omega}=\phi_{\mathbf{k}\omega}^{*}. \quad (49)$$

Equations (33), (36), and (49) combine to yield

$$K_H(x,x')=\sum_{\mathbf{k}\omega}{}^{(\mathrm{I})}\{\exp[i2\,\mathrm{Re}\phi_{\mathbf{k}\omega}(x,x')]-1\} \times|\tilde{G}_{\mathbf{k}\omega}{}^0(x,x')|^2, \quad (50)$$

where the superscript (I) on the summation sign implies that the sum on $\mathbf{k}$ is restricted to region I. For sufficiently weak fields we may expand the exponential, keeping only the first term which contributes to K_H. From Eqs. (39), (48), (49), and (50) we see that the term in the expansion which is linear in Re $\phi_{\mathbf{k}\omega}$ does not contribute to K_H since it is odd in the variable $\mathbf{k}$. From the foregoing, Eqs. (39), (47), and (50) can be combined to obtain the following approximate expression for K_H:

$$K_H=-\tfrac{1}{2}(\alpha Hm/\hbar^2)^2\sum_{\mathbf{k}\omega}{}^{(\mathrm{I})}k_y{}^2Z_i{}^2|Z|^{-6} \times e^{-2\,\mathrm{Re}Z|x-x'|}(x^2-x'^2)^2. \quad (51)$$

In Appendix C we show that Eq. (51) is a good approximation to Eq. (50) when the field satisfies the condition

$$(|e|/\hbar c)Hd\xi_T<1. \quad (52)$$

Our analysis can be extended to encompass higher fields by combining Eqs. (39), (47), and (50) without expanding the exponential in Eq. (50).

c. *Solution of the Integral Equation*

Using Eq. (34), the integral equation for $\Delta(x)$, Eq. (23), may be rewritten in the form

$$\Delta(x)=(V/\beta)\int dx'K_0(x,x')\Delta(x') +(V/\beta)\int dx'K_H(x,x')\Delta(x'), \quad (53)$$

where K_0 is given by Eq. (35) and Eq. (29) and K_H by Eq. (51). We obtain an approximate solution to Eq. (53) by assuming $\Delta(x')=\Delta_0$ on the right, where Δ_0 is constant, and setting the average value $\bar{\Delta}_1$ of the resulting function, $\Delta_1(x)$, equal to Δ_0. That is, we assume

$$\bar{\Delta}_1\equiv d^{-1}\int_{-d/2}^{+d/2}dx\Delta_1(x)=\Delta_0. \quad (54)$$

The quantity Δ_0 cancels from the resulting expression and we may carry out the first double integral on the right using the orthonormality of the functions $u_m{}^0(x)$ which appear in the expression for $K_0(x,x')$. Moreover, the sum on ω can be carried out in this term using the relations,

$$\sum_{\omega}[\epsilon^2+(\hbar\omega)^2]^{-1}=\sum_{n}\{\epsilon^2+[\pi(2n+1)/\beta]^2\}^{-1} =\tfrac{1}{2}(\beta/\epsilon)\tanh(\tfrac{1}{2}\beta\epsilon), \quad (55)$$

where the second relationship is a well-known identity. Thus Eq. (53) can be expressed in the form

$$1=(V/d)\sum_{\mathbf{k}m}(2\epsilon_{\mathbf{k}m}{}^0)^{-1}\tanh(\tfrac{1}{2}\beta\epsilon_{\mathbf{k}m}{}^0) +V(\beta d)^{-1}\int dx\int dx'K_H(x,x'). \quad (56)$$

The first term on the right is of the well-known BCS form, and may be written

$$(V/d)\sum_{\mathbf{k}m}(2\epsilon_{\mathbf{k}m}{}^0)^{-1}\tanh(\tfrac{1}{2}\beta\epsilon_{\mathbf{k}m}{}^0) =N(0)V\int_0^{\hbar\omega_D}d\epsilon\epsilon^{-1}\tanh(\tfrac{1}{2}\beta\epsilon) =N(0)V\ln(1.14\hbar\omega_D\beta), \quad (57)$$

where $N(0)$ is the density of states for electrons of like spin at the Fermi surface and use has been made of the assumption of weak coupling in writing the second equality. Equation (57), together with the BCS relation, $[1/(N(0)V)]=\ln(1.14\hbar\omega_D\beta_c)$, enables us to express Eq. (56) in the form

$$\ln(T_c/T)=-(N(0)\beta d)^{-1}\int_{-d/2}^{+d/2}dx \times\int_{-d/2}^{+d/2}dx'K_H(x,x'). \quad (58)$$

We recall that Eq. (23) and, hence, Eq. (58) has a solution only when $T=T_c(H)$. Next we substitute the expression (51) for K_H in Eq. (58) and obtain

$$\ln\frac{T_c(0)}{T_c(H)}=\left(\frac{\pi}{24}\right)\frac{d^2}{\beta}(\alpha H)^2\left(\frac{m}{\hbar^2}\right)k_0{}^{-1} \times\sum_{\omega}\int_{0,k_c}^{\infty}dkk^3\frac{Z_i{}^2}{(\mathrm{Re}Z)^3|Z|^6}, \quad (59)$$

where the first lower limit on the integral in Eq. (59) applies to *thick* and the second to *thin* films. Since we have excluded *ultrathin* films it can be shown that the upper limit can be set equal to k_0. In fact, the entire contribution to the integral comes from the neighborhood of the lower limit. Within the new region of integration we may set $|Z|^2=Z_i^2$ and $k=k_0$, except in the difference, k_0-k, without introducing serious error. Moreover, since within the approximations described, the integrand in Eq. (59) may be written in the form

$$k_0{}^3(\mathrm{Re}Z)^{-3}Z_i{}^{-4}=\xi_T{}^3|2n+1|^{-3}[2k_0(k_0-k)]^{-1/2}, \quad (60)$$

we see, as mentioned earlier, that in the sum on ω, i.e., on n, only the terms $n=0, -1$ contribute appreciably. In obtaining Eq. (60) we have employed Eq. (42) and the second of Eqs. (41). Combining Eq. (59) and Eq. (60) and changing variables, letting $q=k_0-k$ we obtain

$$\ln\frac{T_c(0)}{T_c(H)}=\frac{\pi(mk_BT)(\alpha Hd)^2\xi_T^3}{12(2)^{1/2}k_0^{3/2}\hbar^2}\int_0^{k_0,\,q_c}dq\,q^{-1/2}, \quad (61)$$

where, from Eq. (45), $q_c=\gamma k_0(d/\xi_T)^2$. The upper limits on the integral in Eq. (61) apply, respectively, to thick and thin films. Finally, since $1-t\ll 1$, we may replace T by $T_c(0)$ on the right side of Eq. (61) and obtain,

$$[T_c(H)/T_c(0)]=1-(H/H_{c0})^2, \quad (62)$$

where

$$H_{c0}^{-2}=0.36(e/\hbar c)^2(\xi_0 d)^2\begin{cases}1, & \text{thick}\\ 0.57\gamma^{1/2}(d/\xi_0), & \text{thin}.\end{cases} \quad (63)$$

For convenience we recall that, by definition,

$$\text{thick film}\Rightarrow d>\xi_T,$$
$$\text{thin film}\Rightarrow 6(\xi_T/k_0)^{1/2}\lesssim d<\xi_T. \quad (64)$$

4. Determination of $|\bar{\Delta}(H,T)|$

When $T<T_c(H)$, i.e., $H<H_c(T)$, we must return to Eqs. (22). $\Delta(x)$ is again treated as an expansion parameter, but the nonlinear term $\sim\Delta^3$ is kept. As before, we solve for $\bar{\Delta}$, the spatial average of the gap parameter. From the foregoing, we see that $\bar{\Delta}$ satisfies the equation,

$$\bar{\Delta}=\bar{\Delta}[1+N(0)V\ln(T_c/T)]+(V/\beta d)\bar{\Delta}\int dx\int dx' K_H(x,x')-aN(0)V\bar{\Delta}|\bar{\Delta}|^2, \quad (65)$$

where $\bar{\Delta}=\bar{\Delta}(H,T)$ and

$$a\equiv[N(0)\beta d]^{-1}\sum_{\mathbf{k}\omega}\int dx\int dx'\int ds\int ds' \times\tilde{G}_{-\mathbf{k}-\omega}(x,x')\tilde{G}_{\mathbf{k}\omega}(x',s)\tilde{G}_{-\mathbf{k}-\omega}(s,s')\tilde{G}_{\mathbf{k}\omega}(s',x). \quad (66)$$

We need not calculate the quantity a since Eq. (65) can be manipulated into a form where a cancels. From the discussion in Sec. III.3.c, it is clear that Eq. (65) can be reduced to the form

$$\ln(T_c/T)-(H/H_{c0})^2-a|\bar{\Delta}(H,T)|^2=0. \quad (67)$$

When $H=0$, Eq. (67) reads

$$\ln(T_c/T)=a|\bar{\Delta}(0,T)|^2. \quad (68)$$

When $T=T_c(H)$, Eq. (67) reads

$$\ln(T_c/T)=(H_c/H_{c0})^2. \quad (69)$$

Combining Eqs. (67)–(69), we obtain the desired result,

$$|\bar{\Delta}(H,T)|/|\bar{\Delta}(0,T)|=[1-(H/H_c)^2]^{1/2}, \quad (70)$$

where H_c is obtained by solving Eq. (62) for H, setting $H=H_c$ and $T_c(H)=T$, and substituting for H_{c0} from Eq. (63). In Appendix D we identify $|\bar{\Delta}(H,T)|$ with the energy gap in the excitation spectrum of a single quasiparticle. We emphasize that Eq. (70) is valid only when $(d/\lambda)\ll 1$, i.e., when H is approximately equal to the applied field.

IV. COMPARISON WITH PHENOMENOLOGICAL THEORIES AND EXPERIMENT

1. The Critical Temperature, $T_c(H)$

Our result for $T_c(H)$ is given by Eqs. (62)–(64), which have been derived subject to the seven assumptions listed in Sec. II.1, together with the limitation on the field strength given by Eq. (52). We note that the Toxen relation, [Eq. (1)], can be manipulated into a form identical with Eq. (62) by using the BCS relationships for bulk critical field and London penetration depth near $t=1$. The identification of the result with Eq. (62) is completed by noting that when $H=H_c$, $T=T_c(H)$, and defining H_{c0} such that

$$H_{c0}^{-2}=0.12(e/\hbar c)^2 d^3\xi_0. \quad (71)$$

By comparing Eq. (71) with our thin-film result, given in Eq. (63), we may establish the value of the cutoff parameter γ which makes our result for $T_c(H)$ identical with that derived from Eq. (1). We find $\gamma=0.33$. As noted earlier, Eq. (1) is in good quantitative agreement with the data of Toxen[4] and of Blumberg[5] for indium and tin in the thin-film regime, where the law $H_c\propto d^{-3/2}$ is observed. Moreover, deviations from this law occur when $d\gtrsim\xi_T$, where a weaker dependence of H_c on d is observed in accord with our result. We remark, parenthetically, that Eq. (62) describes Toxen's thin-film data exceedingly well up to fields $\sim$1 kG which represent the limit of his data in the cases we examined. Such fields lie well outside the criterion [Eq. (52)] for the validity of the theory as presented here. The simplicity of the experimental law suggests that extension of the theory along lines suggested earlier may be worthwhile. The theory of Nambu and Tuan gives a similar result for H_c.

2. The Energy Gap, $|\Delta(H,T)|$

Our expression for $|\bar{\Delta}(H,T)|$ is given by Eq. (70), which is of the form derived earlier by Douglass[16] from the GL equations. Thus we conclude that nonlocal effects do not change the field dependence of the energy gap from the GL form. Our result for $H_c(T,d)$ is, of course, quite different from the GL result due to nonlocal effects when $d<\xi_T$. Morris and Tinkham[17] have determined the dependence of the energy gap on field for indium by measurements of the thermal conductivity. For a film with $t=0.63$ and $d\approx 650$ Å, they

[16] D. H. Douglass, Jr., Phys. Rev. Letters 6, 346 (1961); IBM J. Res. Develop. 6, 44 (1962).

[17] D. E. Morris and M. Tinkham, Phys. Rev. Letters 6, 600 (1961); also M. Tinkham, IBM J. Res. Develop. 6, 49 (1962).

fit their data reasonably well by the GL formula, Eq. (70). Also, they obtain $H_c=1.1$ kG, whereas from Eqs. (62)–(64) (setting $\gamma=0.33$), we find the theoretical value, $H_c=1.5$ kG. Considering that they cannot determine H_c accurately and that their measurement of d is only approximate, the agreement is considered satisfactory.

The field dependence of the tunneling gap in aluminum has been studied experimentally by Giaever and Megerle[18] and by Douglas.[19] Douglass[16] has compared the GL formula, treating H_c as an adjustable parameter, with Giaever's and Megerle's data taken at $T=1.05$°K on a film with $d=1600$ Å. He found qualitative agreement with the experimental points lying somewhat below the theoretical curve depicting $\Delta(H,T)/\Delta(0,T)$. Later,[19] his own data were found to fit the theory quantitatively under the conditions, $d/\lambda<\sqrt{5}$, $(0.75<t<1)$, and (500 Å$\leq d \leq$3000 Å). Recently, however, Meservey and Douglass[20] have carried out more detailed measurements on aluminum films using a criterion for determining H_c experimentally which differs from that employed earlier by Douglass. They conclude that when $d<\lambda$ there is *qualitative disagreement* between the observed behavior of $\Delta(H,T)$ and that deduced from the GL equations with H_c an experimentally determined parameter.

To summarize, the theoretical field dependence of the energy gap in superconducting films (near $t=1$) is well established both from the GL theory and from the present model. Also most of the experimental data (i.e., Refs. 17, 18, 19) are in approximate agreement with this field dependence. The major exception is the recent work on aluminum films by Meservey and Douglass,[20] who find a field dependence in disagreement with the theory. This disagreement becomes most pronounced for the thinnest films. It seems that this disagreement is probably due to energy-level quantization of single-particle states in zero field. As discussed in Sec. II, the quantization effect becomes important when $d\lesssim 6(\xi_T/k_0)^{1/2}$ [Eq. (3)], which implies that the effect is most pronounced for aluminum which has a large coherence length. A recent calculation of the field dependence of the energy gap for ultrathin films,[21] where quantization is important, does appear to yield a field dependence similar to that observed by Meservey and Douglass.

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APPENDIX A

We show that Eq. (44) follows from Eq. (27), using the asymptotic form [Eq. (40)] for $\tilde{G}_{\mathbf{k}\omega}{}^0$ in region II of the two-dimensional **k** space (see Fig. 1). That is,

$$\phi_{-\mathbf{k}-\omega}(x,x')=-\phi_{\mathbf{k}\omega}(x,x')\,. \qquad \text{(A1)}$$

The second term in Eq. (27) may be neglected, just as in region I. [See the discussion following Eq. (47).] From Eq. (40) the magnitude of the ratio of the fourth to fifth terms in Eq. (27) is $\sim|Z^{-1}\partial\phi/\partial x|$, a quantity which we assume to be $\ll 1$. (Recall that although $\mathrm{Re}Zd<1$ in region II, $|Z|d\gg 1$ and that ϕ is expected to vary slowly across the film.) Neglecting the second and fourth terms in Eq. (27), we obtain the following relations for $\phi_{\mathbf{k}\omega}$ and $\phi_{-\mathbf{k}-\omega}$:

$$\left[2\alpha k_y A_y(x)-i\frac{\partial^2\phi_{\mathbf{k}\omega}}{\partial x^2}\right]\tilde{G}_{\mathbf{k}\omega}{}^0 -2i\left(\frac{\partial\tilde{G}_{\mathbf{k}\omega}{}^0}{\partial x}\right)\left(\frac{\partial\phi_{\mathbf{k}\omega}}{\partial x}\right)=0\,, \qquad \text{(A2)}$$

$$\left[-2\alpha k_y A_y(x)-i\frac{\partial^2\phi_{-\mathbf{k}-\omega}}{\partial x^2}\right]\tilde{G}_{-\mathbf{k}-\omega}{}^0 -2i\left(\frac{\partial\tilde{G}_{-\mathbf{k}-\omega}{}^0}{\partial x}\right)\left(\frac{\partial\phi_{-\mathbf{k}-\omega}}{\partial x}\right)=0\,. \qquad \text{(A3)}$$

From the second of Eqs. (33) and the fact that $\tilde{G}_{\mathbf{k}\omega}{}^0$ is real in region II,

$$\tilde{G}_{-\mathbf{k}-\omega}{}^0=\tilde{G}_{\mathbf{k}\omega}{}^0\,. \qquad \text{(A4)}$$

Combining Eqs. (A2)–(A4) we obtain Eq. (A1), the desired result.

APPENDIX B

We show that in region I our solution for $\phi_{\mathbf{k}\omega}(x,x')$, Eq. (47), is consistent with the neglect of the third and fourth terms in Eq. (27). From (39), (41), (42), and (47), the magnitude, R of the ratio of the fourth to fifth terms in Eq. (27) satisfies

$$R\sim|\alpha H k_y x/Z^2|\lesssim \alpha H d/(k_0-k)\,. \qquad \text{(B1)}$$

We recall that the main contributions to the integral in the expression (59) for $\ln[T_c(0)/T_c(H)]$ occur when $(k_0-k)\sim k_0$ and $(k_0-k)\sim k_0(d/\xi_T)^2$ for thick and thin films, respectively. Thus, the field condition, Eq. (52), implies

$$R\lesssim\begin{cases}(k_0\xi_T)^{-1} & \text{(thick films)}\,,\\ [\xi_T/(k_0d^2)] & \text{(thin films)}\,.\end{cases} \qquad \text{(B2)}$$

From Eq. (43) and the fact that typically, $k_0\xi_T\sim 10^4$, we see that $R \ll 1$ in both cases. Moreover, this condition obtains for field strengths considerably greater than allowed by Eq. (52).

The ratio of the third to fifth terms in Eq. (27) is $\sim |Zx|^{-1}$. Since $|Zd| \gg 1$, this ratio is negligible throughout most of the film, excluding a small region of width $|Z|^{-1}$ about $x=0$, where Eq. (47) is not correct.

APPENDIX C

We establish that for fields satisfying Eq. (52), we may expand the exponential in Eq. (50) to obtain Eq. (51). From Eq. (47) we see

$$|2\,\mathrm{Re}\phi| \leq \alpha H d k_0 |(x-x')/Z_i| . \tag{C1}$$

From Eq. (39) we see that the quantity $|\tilde{G}_{\mathbf{k}\omega}{}^0(x,x')|^2$ which occurs in Eq. (50) is sharply peaked about $x=x'$. Thus $K_H(x,x')$ is large only when $|x-x'| \lesssim (\mathrm{Re}Z)^{-1}$, and from Eq. (41) and Eq. (42) we see,

$$|2\,\mathrm{Re}\phi| \lesssim \alpha H d \xi_T / |2n+1| . \tag{C2}$$

Since upper bounds have been used throughout and the expansion parameter is $(2\,\mathrm{Re}\phi)^2$, we conclude that Eq. (51) is a good approximation to Eq. (50) whenever

$$(|e|/\hbar c) H d \xi_T < 1 , \tag{C3}$$

which was to be proved.

APPENDIX D

We prove that $|\bar{\Delta}(H,T)|$ is the gap in the excitation spectrum. Since $\Delta(x)$ is small we may solve Eqs. (22) to obtain the following approximate expression for the Green function:

$$G_{\mathbf{k}\omega}(x,x') = \tilde{G}_{\mathbf{k}\omega}(x,x') - \int ds \int ds' \Delta^*(s)\Delta(s') \times \tilde{G}_{\mathbf{k}\omega}{}^0(x,s)\tilde{G}_{-\mathbf{k}-\omega}{}^0(s,s')\tilde{G}_{\mathbf{k}\omega}{}^0(s',x') . \tag{D1}$$

$\tilde{G}_{\mathbf{k}\omega}{}^0$ is given by Eq. (29) and $\tilde{G}_{\mathbf{k}\omega}$ by a similar expression obtained by omitting the superscript (0) on all quantities and adding a subscript (**k**) to the u functions. By definition, $u_{\mathbf{k}m}(x)$ is an exact single-particle eigenfunction in the presence of the field, i.e., $u_{\mathbf{k}m}$ is a (real) eigenfunction of the operator $O_k(x)$, defined by Eq. (18), belonging to the eigenvalue $\epsilon_{\mathbf{k}m}$ and satisfying the boundary conditions, $u_{\mathbf{k}m}(\pm d/2)=0$. We evaluate $G_{\mathbf{k}\omega}$ in the $u_{\mathbf{k}m}$ representation, where

$$G_{\mathbf{k}\omega}(m|m') \equiv \int dx \int dx' u_{\mathbf{k}m}(x) u_{\mathbf{k}m'}(x') G_{\mathbf{k}\omega}(x,x') . \tag{D2}$$

We obtain

$$G_{\mathbf{k}\omega}(m|m') = \delta_{mm'}\{[-i\omega+\epsilon_{\mathbf{k}m}]^{-1} - |\bar{\Delta}|^2[-i\omega+\epsilon_{\mathbf{k}m}{}^0]^{-1}[\omega^2+(\epsilon_{\mathbf{k}m}{}^0)^2]^{-1}\} , \tag{D3}$$

where $\bar{\Delta} \equiv \bar{\Delta}(H,T) = \bar{\Delta}_1$, which is defined in Eqs. (54). Since $\bar{\Delta}$ is small, Eq. (D3) may be expressed in the form

$$G_{k\omega}(m|m') = \delta_{mm'}[(i\omega+\epsilon_{\mathbf{k}m})/(\omega^2+E_{\mathbf{k}m}{}^2)] , \tag{D4}$$

where

$$E_{\mathbf{k}m} = (\epsilon_{\mathbf{k}m}{}^2 + |\bar{\Delta}|^2)^{1/2} , \tag{D5}$$

and ω is given by Eq. (15). From Eq. (D4) it is easy to show that the poles in the Fourier transform of the real-time Green function, i.e., the excitation energies, are given by Eq. (D5) and exhibit a gap of magnitude $|\bar{\Delta}(H,T)|$. Within our approximations the lifetime of the excitation is infinite.

Next, we show that although G is diagonal in the $u_{\mathbf{k}m}$ representation F is not. Within the approximation discussed,

$$F_{\mathbf{k}\omega}(m|m') = \bar{\Delta} \sum_l \int dx \int ds \times \left\{ \frac{u_{\mathbf{k}m}(x) u_{-\mathbf{k}l}(x) u_{-\mathbf{k}l}(s) u_{\mathbf{k}m'}(s)}{(i\omega+\epsilon_{\mathbf{k}l})(-i\omega+\epsilon_{\mathbf{k}m'})} \right\} . \tag{D6}$$

To see that $F_{\mathbf{k}\omega}(m|m')$ is not diagonal, we note

$$\int_{-d/2}^{+d/2} dx u_{\mathbf{k}m}(x) u_{-\mathbf{k}l}(x) \neq \delta_{ml} \tag{D7}$$

since $u_{\mathbf{k}m}(x)$ and $u_{-\mathbf{k}l}(x)$ are eigenfunctions of *different* Hamiltonians, $O_{\mathbf{k}}(x)$ and $O_{-\mathbf{k}}(x)$, respectively.