Superconducting Thin Film in a Magnetic Field—Theory of Nonlocal and Nonlinear Effects. I. Specular Reflection*

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A self-consistent perturbation solution of the Gor'kov equations for a superconducting film in a strong parallel magnetic field is presented. The order parameter is assumed constant in space, but proper allowance is made for nonlocal effects, important when the thickness d is comparable to or smaller than the pair-correlation distance ξ, as is often realized in practice. Specular reflection simplifies the mathematical analysis: The usual momentum-space representation and impurity averaging procedures for Green's functions are shown to apply without essential modifications. Size quantization can be ignored as long as $p_F d^2/\xi \gg 1$. The Ginzburg-Landau and Maki local theories, valid in the vicinity of the transition temperature and in the dirty limit, respectively, are generalized. The modified equations for the current density, order parameter, free energy, and critical fields are studied in detail and compared with previous semiphenomenological extensions by Bardeen, Toxen, and others. An expression for the critical field H_c valid in the intermediate temperature and purity range is also obtained. The convergence of our perturbation expansion and the assumed constancy of the order parameter are shown to require $(e/c)H_c d\xi$ and $(e/c)H_c d^2 \ll 1$, respectively. An inconsistency in Rickayzen's alternative to Maki's theory is pointed out. The most important results, together with their ranges of validity, are indicated in the last section.

I. INTRODUCTION

A. Qualitative Features and History of the Problem

BECAUSE of its relative simplicity, a great deal of theoretical and experimental work has been devoted to the properties of a superconducting film placed in a uniform magnetic field of strength H applied parallel to its surface. Although the magnetization curve itself should be hard to trace because of the intrinsic smallness of the sample, the critical field H_c corresponding to the superconducting-normal transition is easily detected in transport and tunneling measurements. Good, sharp transitions are obtained when proper care is taken to ensure uniform film thickness and composition.

A bulk (type I) superconducting sample ideally behaves as a perfect diamagnet up to the thermodynamic critical field H_{cb}. The field drops to zero over a penetration depth λ, as implied by the well-known London equation,

$$(4\pi/c)\mathfrak{J} = -\lambda^{-2}\mathbf{A}, \tag{1.1}$$

relating the current density induced in the superconductor to the vector potential of the total field, $\mathbf{h}=\nabla\times\mathbf{A}$, in the transverse gauge ($\nabla\cdot\mathbf{A}=0$), chosen such that $\mathbf{A}$ has no component perpendicular to the surface.[1] This same constitutive equation leads to a reduced diamagnetic susceptibility when the film thickness d is less than λ. In the limit $d\ll\lambda$ London obtained

$$H_c/H_{cb} = (\sqrt{12})\lambda/d \tag{1.2}$$

by requiring that the work done in magnetizing the sample (the area under the magnetization curve) be equal to the superconducting condensation energy, i.e., the free-energy difference between the normal and superconducting states in zero field, $(8\pi)^{-1}H_{cb}^2$.

The Zeeman energy associated with the field inside the sample is, however, detrimental to the pairing of electrons in opposite time-reversed states which is the basic ingredient of the present (BCS) microscopic theory of superconductivity.[2] The electronic states adjust to the presence of the field by becoming more normal-like. This results in an effective field-dependent increase in the penetration depth and causes the magnetization curve to bend down, as shown in Fig. 1. One anticipates that below a certain critical thickness $d_c\sim\lambda$ the transition should change from first to second order. Above d_c one expects hysteresis associated with supercooling of the normal phase and superheating of the superconducting phase, as shown by the dotted part of the corresponding curve in Fig. 1. Such features are already contained in the appropriate solutions to the equations obtained by Ginzburg and Landau (GL)[3] by minimizing a phenomenological free-energy functional $\mathfrak{F}_S\{\psi, A\}$. The current equation,

$$(4\pi/c)\mathfrak{J} = -(\psi^2/\lambda^2)\mathbf{A}, \tag{1.3}$$

has the same structure as London's, except for the appearance of ψ, which leads to the above-mentioned nonlinear effects. The order parameter ψ, assumed real

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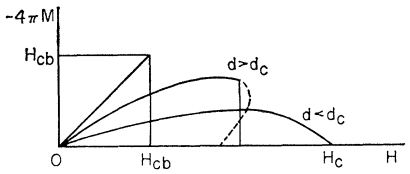

FIG. 1. Magnetization curves for a thin film in a parallel field. The transition is second order if the thickness is below a critical value d_c. Above d_c the sample undergoes a first-order thermodynamic transition, although superheating and supercooling are also possible. The area under each curve must remain equal to the condensation energy $(8\pi)^{-1}H_{cb}^2$.

and normalized to 1 in zero field, in turn obeys

$$(\lambda/\kappa)^2[\nabla/i-(2e/\hbar c)\mathbf{A}]^2\psi-\psi+\psi^3=0, \quad (1.4)$$

where $\kappa=\sqrt{2}(2e/\hbar c)H_{cb}\lambda^2$ is the so-called GL parameter ($\kappa<1/\sqrt{2}$ for type-I superconductors). In applying (1.4) to a thin film note that if d is much smaller than the characteristic distance λ/κ over which ψ varies, one may neglect the gradient term and average (1.4) over the volume V of the sample:

$$\psi^2=1-\tfrac{1}{2}(H_{cb}\lambda)^{-2}V^{-1}\int A^2(\mathbf{r})\,d^3r. \quad (1.5)$$

The critical field for a second-order transition is obtained by setting $\psi=0$ and $h=H_c$. The result[3]

$$H_c/H_{cb}=(\sqrt{24})\lambda/d \quad (1.6)$$

is larger than (1.2), calculated without taking nonlinearities into account, by a factor of $\sqrt{2}$.

Further complications arise if the vector potential does not vary slowly over the distance characterizing the extent of electron pair correlations. The existence of such a coherence length ξ, which should not be confused with λ/κ, was inferred by Pippard,[4] who showed that a proper interpretation of weak-field penetration measurements necessitated a nonlocal constitutive equation:

$$(4\pi/c)\mathfrak{J}(\mathbf{r})=-\int d^3r'\mathbf{K}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{A}(\mathbf{r}'). \quad (1.7)$$

He obtained good agreement with experiment by using a phenomenological kernel

$$\mathbf{K}_P(R)=(3/4\pi\xi_o\lambda_L^2)\mathbf{RR}e^{-R/\xi}/R^4$$

analogous to that describing the anomalous skin effect in normal metals. Just as in this case the range of integration in (1.7) is assumed to be over the volume of the sample if the electrons are diffusely scattered at the boundaries or over all space with $\mathbf{A}$ extended periodically outside the film in the case of specular reflection. Equation (1.7) reduces to the local London relation (1.1) whenever A varies slowly over the distance $\xi=(\xi_o^{-1}+l^{-1})^{-1}$, i.e., if λ or d, whichever is smaller, exceeds ξ. Here ξ_o and λ_L are the values of ξ and λ in pure material; a finite electronic mean free path l decreases the coherence length and increases the penetration depth. In his review of the subject just before the advent of the BCS theory,[2] Bardeen[5] proposed a nonlocal extension of the A-dependent term in the GL expression for $\mathfrak{F}_S$ leading to a current equation

$$(4\pi/c)\mathfrak{J}=-\psi^2\int d^3r'\mathbf{K}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{A}(\mathbf{r}'), \quad (1.8)$$

which reduces to (1.3) or (1.7) in the appropriate limits. The appropriate generalization of (1.5) is

$$\psi^2=1-V^{-1}\int d^3r\int d^3r'[\mathbf{A}(\mathbf{r})\cdot\mathbf{K}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{A}(\mathbf{r}')/2H_{cb}^2]. \quad (1.9)$$

Most of the phenomenological theories discussed above have been justified from a microscopic point of view in the past ten years. Thus, BCS showed that the Pippard kernel is a good approximation to the exact one with $\xi_o=0.18\hbar v_F/k_BT_c$, where T_c is the superconducting transition temperature and v_F the Fermi velocity. Later Gor'kov[6] derived the GL equations from his Green's-function formulation of the microscopic theory under a number of restrictions which are usually satisfied sufficiently close to T_c. In particular, he showed that the order parameter ψ can be identified with the amplitude Δ describing the center-of-mass motion of an electron pair normalized to its constant value Δ_o, appropriate to a bulk sample in zero field. Δ_o is equal to half the energy gap in the quasiparticle spectrum derived by BCS. Another consequence of Gor'kov's derivation is that the GL κ parameter is roughly given by the ratio $\lambda_L(0)/\xi$ of the London penetration depth at $T=0$ to the Pippard coherence length.

Recently Maki[7] developed a local theory describing the electronic spectrum of a dirty ($l\ll\xi_o$) superconducting film at all fields and temperatures, assuming the order parameter to be constant over the sample. Several authors[8–11] have arrived at expressions for H_c in the extreme nonlocal limit $d\ll\xi$, showing a $d^{-3/2}$ or stronger thickness dependence in contrast to the d^{-1} prediction of local theories.

Results pertaining to intermediate thicknesses have up to now been derived by phenomenological approaches.[12–16] Toxen's successful fits to his experimental

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[5] J. Bardeen, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. XV, p. 326. Note that ψ is assumed constant.

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[15] J. J. Hauser and E. Helfand, Phys. Rev. **127**, 387 (1962).

[16] W. Liniger and F. Odeh, Phys. Rev. **132**, 1934 (1963).

data on indium films[13,14] were obtained by using the GL results with λ replaced by an effective value adjusted to yield the correct weak-field susceptibility determined by (1.7), assuming specular reflection. A similar spirit occurs in Hauser and Helfand's work.[15] Extensive thin-film calculations based on (1.8) and (1.9) were performed by Liniger and Odeh,[16] assuming diffuse scattering at the boundaries. The most complete computations[13,14,16] were made using Pippard's kernel.

B. Scope and Outline of this Work

In the present and following papers we present a microscopic derivation of the properties of a superconducting thin film in a strong tangential magnetic field, including nonlocal effects. Bardeen's equations (1.8) and (1.9) are justified near T_c for all values of mean free path while a simple modification of Maki's depairing parameter ρ[7] extends the range of validity of his results outside the local limit. We obtain explicit analytic expressions for the second-order transition critical field $H_c(d, l, T)$ and the value $H_{cc}(l, T)$ corresponding to the critical thickness $d_c(l, T)$.

The calculations employ the thermodynamic Green's-function approach of Abrikosov and Gor'kov.[17] Magnetic field effects are calculated in perturbation theory. Rapid convergence is shown to require $(eH_cd/c)^2\xi_o\xi \ll 1$ or, equivalently, $1-t \ll 1$ or $d\xi_o/\xi^2$, whichever is smaller, near $T_c(t=T/T_c)$, and $(eHdl/c)^2 \ll 1$ or $l \ll \xi_o$ and $d\xi_o/l^2 \ll 1$ for a dirty film at all T. In both cases the restrictions involving d become important in the extreme nonlocal limit. A nonperturbative approach[10,11] is necessary to treat pure films at low temperatures. The order parameter is assumed constant over the sample. This should be a good approximation, provided that d is sufficiently small and that the field is perfectly aligned with the film faces (a small perpendicular component produces a vortex structure which can be avoided if extreme precautions are taken[18]). In the local limit near T_c, where $\lambda_L^{-2}=2(1-t)\lambda_L^{-2}(0)$, the first requirement is satisfied if $d \ll \lambda/\kappa$, i.e., $d^2 \ll \xi_o\xi(1-t)^{-1}$, using the results quoted in the first part of this section. From de Gennes's work on dirty superconductors,[19] we also know that the corresponding restriction in Maki's case is $d^2 \ll \xi_o l$. In either case, the condition on d is equivalent to the criterion

$$eH_cd^2/c \ll 1, \tag{1.10}$$

or $H_c \gg H_{c2}$, $H_{c2}=\sqrt{2}\kappa H_{cb}$ being the minimum supercooling field in bulk. We find that (1.10) is a sufficient condition in the extreme nonlocal limit as well, as first recognized by Shapoval.[11] Within the range of convergence of our perturbation expansion, however, (1.10) is automatically satisfied for $d<\xi$, so that it is an actual restriction in the local limit only.

Specular reflection at the film boundaries is assumed in the present paper. The corresponding unperturbed single-electron eigenfunctions are then simple products of exponentials and sines. The matrix elements of the perturbation can be expressed in terms of the Fourier components of A by means of elementary integrations. This approach has the advantage of allowing direct comparison with previous treatments[8,9] and to show unambiguously that only bulk parameters enter in the final equations, provided terms of order $(p_Fd)^{-1}$ and $(p_F^2d/\xi)^{-1}$ are systematically neglected. Since the Fermi momentum p_F is of the order of the inverse interatomic distance, these restrictions are not serious for typical films of superconductors with $d, \xi > 100$ Å.

A more elegant semiclassical approach, which makes no use of the explicit form of the single-particle states, is sketched in our previous communication.[20] The method is particularly well suited for a treatment of diffuse boundary scattering. A full exposition of the method is contained in a companion article,[21] to which we also relegate our comparison between theory and experiments. No essential differences between specular and diffuse reflection emerge from the analysis.

The generalized GL equations valid near T_c are obtained in Sec. II of the present paper. The derivation essentially parallels that of Gor'kov[6] for bulk superconducting alloys, the main difference occurring in our treatment of the explicit field-dependent contribution to the linearized equation for the pair amplitude. Nonlocal effects are automatically included by making a direct expansion in terms of $(e/mc)\mathbf{A}\cdot\mathbf{p}$ (up to second order) and keeping the exact spatial dependence of the vector potential. The final equations involve the bulk weak-field kernel K. Although we derive an expression for K valid near T_c which allows for nonisotropic scattering by impurities, it is necessary to ignore possible differences between the single-electron lifetime τ and the transport relaxation time τ_{tr} in comparing theory with experiments. With $\tau=\tau_{tr}$, K reduces to a rapidly converging sum of Pippard-like kernels.

In Sec. III the results of Sec. II are used to obtain the free energy and the critical quantities H_c and H_{cc} defined earlier. By neglecting contributions from Fourier components of A other than the first, the results can be cast in compact form, e.g., (1.6) holds with λ replaced by an effective-thickness-dependent λ_d, which is simply the inverse square root of the Fourier transform of K evaluated at π/d. Neglected terms entail a maximum error of 2%. Toxen's procedure[13,14] leads to a more complex definition of λ_d, but the final value is shown to agree with ours within the same accuracy for $d \gtrsim d_c$. This explains the success of his fits

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[18] M. Tinkham, in *Basic Problems in Thin Film Physics*, edited by R. Niedermayer and H. Mayer (Vandenhoek and Rupprecht, Gottingen, Germany, 1966).

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[21] R. S. Thompson and A. Baratoff (to be published).

to experiment. The equations determining the thermodynamic transition are also discussed.

An improved expression for H_c is obtained in Sec. IV. Assuming s-wave scattering, we average over impurities from the start and work directly with the renormalized frequency and order parameter.[17] If terms of order H^2 are retained, the resulting formula for H_c reduces to that given in Sec. II near T_c and to a simple generalization of Maki's equation valid down to $T=0$ in the dirty limit. In the intermediate range, considerable improvement is achieved by including terms in H^4, as shown by our comparison[20,21] with Toxen and Burns's data on In-Sn alloy films.[14] The convergence criteria and the restrictions mentioned earlier are readily ascertained from the structure of the perturbation expansion.

In the last section we show that additional contributions associated with the hitherto neglected spatial dependence of the order parameter are indeed negligible if (1.10) holds. In the local limit ($l \ll d$) Rickayzen's alternative[22] to Maki's theory is shown to be inconsistent.

The main results are summarized in the last section for the benefit of the reader who is not interested in the details of various derivations.

II. DERIVATION OF BARDEEN'S NONLOCAL GENERALIZED GL EQUATIONS

Although the approach developed in Sec. IV and in the companion article[21] provides a shortcut to the results obtained here, we think it is worth going first through a derivation which parallels Gor'kov's[6] as close as possible. The influence of finite thickness on impurity averaging and electrodynamics is examined in detail. One may suspect that discrete quantization effects would manifest themselves if the thickness d is smaller than the characteristic size ξ of a Cooper pair, i.e., throughout the range where nonlocal effects are important. This is not quite the case: As stated in the introduction, a description in terms of the bulk weak-field kernel and of macroscopic boundary conditions (specular or diffuse reflection), as embodied in (1.8) and (1.9), is adequate near T_c as long as $p_F d^2/\xi \gg 1$. The meaning of this peculiar condition is discussed in part D below.

A. Perturbation Expansion Near T_c

We take as our starting point Gor'kov's formulation of the microscopic theory, since it provides an adequate description of the isotropic weak-coupling superconductors and enables one to incorporate strong field and impurity effects in a natural way. In this scheme the electronic properties are completely specified by the single-particle Green's function G and the pair amplitude $F^\dagger$, which obey the following coupled integral equations[17]:

$$G(\mathbf{r},\mathbf{r}';\omega) = G_A(\mathbf{r},\mathbf{r}';\omega) - \int G_A(\mathbf{r},\mathbf{s};\omega)\Delta(\mathbf{s})F^\dagger(\mathbf{s},\mathbf{r}';\omega)\,d^3s, \quad (2.1)$$

$$F^\dagger(\mathbf{r},\mathbf{r}',\omega) = \int G_A(\mathbf{s},\mathbf{r};-\omega)\Delta^*(\mathbf{s})G(\mathbf{s},\mathbf{r}';\omega)\,d^3s. \quad (2.2)$$

In the finite temperature formalism the frequency variable ranges over the discrete values $\omega_\nu = (2\nu+1)\pi T$. The order parameter Δ must satisfy the self-consistency condition

$$\Delta^*(\mathbf{r}) = gT\sum_\omega F^\dagger(\mathbf{r},\mathbf{r};\omega), \quad (2.3)$$

where g is the strength of the effective electron-electron attraction. It is convenient to replace the BCS cutoff in momentum space by a frequency cutoff, i.e., carry the summation in (2.3) between $-\omega_D$ and ω_D, ω_D being the Debye frequency. This procedure gives results in agreement with BCS in the weak-coupling limit and corresponds to a more realistic model interaction, i.e., retarded rather than velocity-dependent.[23]

The normal-state Green's function G_A is in turn related to its counterpart in zero field G_0 via

$$G_A(\mathbf{r},\mathbf{r}';\omega) = G_0(\mathbf{r},\mathbf{r}';\omega) + \int G_0(\mathbf{r},\mathbf{s};\omega)[i(e/m^*c)A(\mathbf{s})\cdot\nabla_s + (e^2/2m^*c^2)A^2(\mathbf{s})]G_A(\mathbf{s},\mathbf{r}';\omega)\,d^3s, \quad (2.4)$$

where m^* is the effective mass of an electron. The A^2 term will be neglected from now on since the de Haas–van Alphen and related oscillatory effects which it is responsible for are not appreciable even above the critical field of typical materials because of thermal and lifetime broadening.

Equations (2.1), (2.2), and (2.4) are iterated with respect to the perturbations Δ and $(e/m^*c)\mathbf{A}\cdot\mathbf{p}$, then averaged over an assumed random distribution of impurities, using standard techniques.[17] Following the usual practice,[6] we assume that Δ and A may be averaged separately whenever they occur in a product because of the rapidly oscillating character of $G_0(\mathbf{r},\mathbf{r}';\omega)$. As far as Δ is concerned, Caroli *et al.*[24] have shown that this procedure introduces no appreciable errors, provided the valence difference between impurity and host is 0 or 1.

Although the semiclassical *Ansatz*

$$G_A(\mathbf{r},\mathbf{r}';\omega) = \exp\left(i\frac{e}{c}\int_{r'}^{r}\mathbf{A}\cdot d\mathbf{l}\right)G_0(\mathbf{r},\mathbf{r}';\omega)$$

is in fact adequate, and certainly quite useful whenever the vector potential cannot be treated as a perturbation,[10,11] the approximate expression for the phase used

[22] G. Rickayzen, Phys. Rev. **138**, A73 (1965).

[23] G. Rickayzen, *Theory of Superconductivity* (John Wiley & Sons, Inc., New York, 1965), p. 418.

[24] C. Caroli, P. G. de Gennes, and J. Matricon, J. Phys. Radium **23**, 707 (1962).

by Gor'kov,[6] i.e., $(e/c)\mathbf{A}(\mathbf{r})\cdot(\mathbf{r}-\mathbf{r}')$, is valid only if $d\gg\xi$ and $\mathbf{A}$ is sufficiently slowly varying. Since he obtained the GL equations by expanding the corresponding exponential to second order, a direct expansion of G_A should (and does) lead to the desired nonlocal generalization, since the exact spatial dependence of $\mathbf{A}$ can be taken into account.[25]

It is convenient to choose that gauge in which the averaged order parameter is real (and constant). With the boundaries of the film at $x=0$ and $x=d$, and $\mathbf{H}$ applied along the z axis, the average current density has a y-component only and so does the vector potential in the above-mentioned gauge. The problem is essentially one dimensional: Only the x dependence of the relevant quantities enters in nontrivial fashion. The even part of $A(x)$ turns out to be proportional to the net current along the film, which is zero in our case, so that both j and A are antisymmetric about $x=d/2$. At a second-order transition from the normal state, the field penetrates uniformly and $A=H_c(x-d/2)$. The situation is illustrated in Fig. 2.

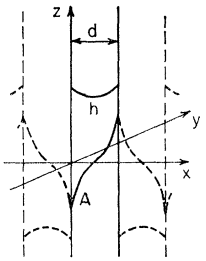

FIG. 2. Spatial dependence of the total magnetic field $h_z=h(x)$ and of the associated vector potential $A_y=A(x)$ in the gauge where the order parameter is real. A uniform field of strength H is applied in the z direction. The dotted curves show the periodic extensions of h and A appropriate to specular reflection at the boundaries of the film.

Since $\Delta(H, T)$ and A are bounded by $\Delta(0, T)$ and $H_c(T)d/2$, which in turn vanish at T_c, the lowest nontrivial terms in the perturbation expansion should provide an adequate description sufficiently close to the transition temperature. In this approximation the quantity appearing on the right side of the self-consistency equation,

$$1=gT\sum_{-\omega_D}^{\omega_D}F(\omega)/\Delta, \tag{2.5}$$

is given by

$$\begin{aligned}F(\omega)/\Delta\cong&\int\langle G_0(\mathbf{s},\mathbf{r};-\omega)G_0(\mathbf{s},\mathbf{r};\omega)\rangle d^3s-\Delta^2\\&\times\int\langle G_0(\mathbf{s},\mathbf{r};-\omega)G_0(\mathbf{s},\mathbf{u};\omega)G_0(\mathbf{v},\mathbf{u};-\omega)G_0(\mathbf{v},\mathbf{r},-\omega)\rangle d^3sd^3ud^3v+(e/im^*c)^2\\&\times\int\{\langle G_0(\mathbf{s},\mathbf{r};-\omega)G(\mathbf{s},\mathbf{u};\omega)[\partial_{u_y}G_0(\mathbf{u},\mathbf{v};\omega)][\partial_{v_y}G_0(\mathbf{v},\mathbf{r};\omega)]\rangle+2\text{ similar terms}\}\,A(u_x)A(v_x)d^3sd^3ud^3v,\end{aligned} \tag{2.6}$$

where the angular brackets refer to impurity averages. The first-order field-dependent terms vanish in the gauge where Δ is real.

Assuming from now on specular reflection at the film boundaries, it is natural to expand electromagnetic quantities in Fourier series, viz.,

$$A(x)=\sum_{j=0}^{\infty}A_j\cos(k_jx),\qquad k_j=j\pi/d. \tag{2.7}$$

The coefficients A_j decrease rather rapidly with j, e.g.,

$$\begin{aligned}A_j&=\frac{2}{d}\int_0^d H_c(x-\tfrac{1}{2}d)\cos\frac{j\pi x}{d}\,dx\\&=[(-1)^j-1/(\pi j)^2]2H_cd\end{aligned} \tag{2.8}$$

at $H=H_c$. Note that $A_j=0$ for j even by antisymmetry. The film is treated as a one-dimensional potential box. Since impurity averaging restores the symmetries of the problem, averaged Green's functions may be expanded in terms of the corresponding single-electron eigenfunctions, viz.,

$$G(\mathbf{r},\mathbf{r}';\omega)=\frac{2}{d}\sum_{nn'}\int\frac{d^2p_\perp}{(2\pi)^2}\sin\frac{n\pi x}{d}\sin\frac{n'\pi x'}{d}\exp[i\mathbf{p}_\perp\cdot(\mathbf{y}-\mathbf{y}')]G(nn',\mathbf{p}_\perp;\omega), \tag{2.9}$$

where $\mathbf{p}_\perp=(0, p_y, p_z)$, $\mathbf{y}=(0, y, z)$; n and n' range over positive integers (angular brackets will be omitted

[25] A similar spirit occurs in recent Russian work on nonlinear, nonlocal effects in bulk superconductors, e.g., A. I. Rusinov and E. A. Shapoval, Zh. Eksperim. i Teor. Fiz. **46**, 2227 (1964) [English transl.: Soviet Phys.—JETP **19**, 1504 (1964)] and T. K. Melik-Barkhudarov, Zh. Eksperim. i Teor. Fiz. **47**, 311 (1964) [English transl.: Soviet Phys.—JETP **20**, 208 (1965)].

when dealing with the average of a single quantity). The zero-field normal-state Green's function in the absence of impurities is, of course, diagonal in that representation.

$$G_0^{(0)}(nn', \mathbf{p}_\perp; \omega) = (i\omega - \epsilon_p)^{-1}\delta_{nn'}. \quad (2.10)$$

Here $\epsilon_p = (p^2/2m^*) - \mu$ is the energy of an electron of effective mass m^* and momentum $\mathbf{p} = (n\pi/d, \mathbf{p}_\perp)$, measured from the chemical potential (Fermi energy) $\mu = p_F^2/2m^*$.

B. Impurity Averaging

We wish to argue that the equations which, to order $(p_F l)^{-1}$, determine the self-energy and vertex corrections arising as a result of impurity scattering and averaging in a bulk sample,[6,17] are in fact applicable to a thin film, provided its thickness d is much larger than the inverse Fermi momentum, the range of the (screened) impurity potential r_i, and the mean separation of impurities d_i. These conditions are certainly realized in typical metal films with $d > 100$ Å. The restriction $d \gg d_i$ need not be serious even in the least favorable case where $d < l$ and the material is dirty, since the inequality $l \ll \xi_0$ can usually be satisfied in the dilute range where $l \gg d_i$.

A simple argument[26] shows that if terms of order d_i/d, r_i/d, etc., are neglected, the average zero-field normal-state Green's function is diagonal, i.e.,

$$G_0(nn', \mathbf{p}_\perp; \omega) = G_0(n, \mathbf{p}_\perp; \omega)\delta_{nn'},$$

where $G_0(n, \mathbf{p}_\perp; \omega) \equiv G_0(\mathbf{p}, \omega)$ is obtained from its counterpart for a pure film $G_0^{(0)}(\mathbf{p}, \omega) = (i\omega - \epsilon_p)^{-1}$ by a simple frequency renormalization: $\omega \to \tilde{\omega} = \eta\omega$, with $\eta = 1 + (2\tau\,|\,\omega\,|)^{-1}$.[17] The lifetime τ is determined by the scattering cross section σ for an electron at the Fermi surface

$$\tau^{-1} = n_i v_F \sigma = \tfrac{1}{2} n_i N(0) \int |\, u(\Theta)\,|^2\, d\Omega.$$

$n_i = N_i/V$ is the number density of impurities, $v_F = p_F/m^*$ the Fermi velocity, $N(0) = (2\pi^2)^{-1} m^* p_F$ the density of single-particle states at the Fermi surface, and u is a pseudopotential (t matrix) which, in Born approximation, gives rise to the same scattering amplitude as the actual potential. Note, on the other hand, that this simple form for G_0 would follow from

$$G_0^{(0)}(nn', \mathbf{p}_\perp; \omega) = G_0^{(0)}(\mathbf{p}, \omega)\left(\delta_{nn'} + G_0(nn', \mathbf{p}_\perp; \omega) n_i \int \frac{d^3p'}{(2\pi)^3} |\, u(\mathbf{p} - \mathbf{p}')\,|^2 G_0(\mathbf{p}', \omega)\right), \quad (2.11)$$

provided a constant term arising from integration over regions away from the Fermi surface is absorbed in the chemical potential by redefining the latter.[17] The exact relation for $G_0(nn', \mathbf{p}_\perp; \omega)$ obtained by substituting (2.9) and (2.10) into the integral equation for the average Green's function in position space,[17,22]

$$G_0(\mathbf{r}, \mathbf{r}'; \omega) = G_0^{(0)}(\mathbf{r}, \mathbf{r}'; \omega) + N_i \int G_0^{(0)}(\mathbf{r}, \mathbf{r}_1; \omega) \langle u(\mathbf{r}_1) u(\mathbf{r}_2) \rangle G_0(\mathbf{r}_1, \mathbf{r}_2; \omega) G_0(\mathbf{r}_2, \mathbf{r}'; \omega)\, d^3r_1 d^3r_2,$$

where

$$\langle u(\mathbf{r}_1) u(\mathbf{r}_2) \rangle = d^{-1} \sum_m \int \frac{d^2q_\perp}{(2\pi)^2} \exp[i\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)]\, |\, u(\hat{q})\,|^2, \qquad q_x = 2\pi m/d$$

results in a diagonal contribution which reduces to the expression on the right side of (2.11) if the sum over allowed values of p_x' is extended over negative as well as positive values and is approximated by the corresponding integral. There are additional off-diagonal ($n \neq n'$) contributions whose effect is difficult to estimate directly, but which we believe to be unimportant on the basis of our previous indirect argument.[26]

We feel justified in keeping only the diagonal contributions of more complicated averages, e.g., those over products of G_0's appearing in (2.6). If summations over internal momenta are treated as stated in the preceding paragraph, the resulting equations are identical to those first obtained by Gor'kov[6] for bulk samples, and the same diagrammatic representation may be used. Any contribution containing N times G_0 is given by the sum of all diagrams consisting of N solid lines connected in pairs by an arbitrary number of dotted lines, each carrying a factor $n_i\,|\,u(\hat{q})\,|^2$, momentum conservation being satisfied at every vertex. Each internal momentum $\mathbf{p}'$ contributes an integral

$$\int d^3p'/(2\pi)^3.$$

[26] For a pure film (2.10) holds because $G_0^{(0)}(\mathbf{r}, \mathbf{r}')$ is a Green's function in the mathematical sense. By the same token it may be viewed as a superposition of Green's functions $G_0^{(0)}(\mathbf{r}, \mathbf{r}_n')$ for an infinite metal, with $\mathbf{r}_n'$ ranging over $\mathbf{r}'$ and its images with respect to the boundaries of the film. Such a picture should retain its validity in the presence of impurities after averaging, provided $d \gg d_i, r_i$, since an electron then feels the influence of many impurities as it traverses the film: its propagation may be described in statistical terms. In a bulk sample the only effect of impurity averaging is to change ω to $\tilde{\omega}$ in the factor $\exp(-|\,\omega\,||\,\mathbf{r} - \mathbf{r}'\,|/v_F)$ appearing in $G_0^{(0)}(\mathbf{r}, \mathbf{r}')$[17]: $G_0(\mathbf{r}, \mathbf{r}')$, therefore, has the same functional dependence as in the pure case. This applies to a thin film as well if the above-mentioned conditions on d are met. Using the equivalence between the representations of the Green's function in terms of images and of eigenfunctions, we are led to the conclusions stated in the text. The innocuous restriction $p_F d \gg 1$ allows one to approximate sums over discrete values of p_x by integrals.

C. Field-Independent Terms

The evaluation of the first two terms on the right side of (2.6) follows Gor'kov's procedure very closely. Consider, for instance,

$$Q(\mathbf{r},\mathbf{r}';\omega)=\int\langle G_0(\mathbf{s},\mathbf{r};-\omega)G_0(\mathbf{s},\mathbf{r}';\omega)\rangle d^3s.$$

According to the considerations developed above, $Q(nn',\mathbf{p}_\perp;\omega)=\delta_{nn'}Q(\mathbf{p},\omega)$, where

$$Q(\mathbf{p},\omega)=G_0(\mathbf{p},-\omega)G_0(\mathbf{p},\omega)\times\left(1+n_i\int\frac{d^3p'}{(2\pi)^3}\,|\,u(\mathbf{p}-\mathbf{p}')\,|^2Q(\mathbf{p}',\omega)\right). \quad (2.12)$$

The diagrammatic representation of this equation is shown in Fig. 3(a). Denoting the second term in brackets by $L(\omega)$, and using (2.12), one obtains

$$\begin{aligned}L(\omega)&=n_i\int\frac{d^3p'}{(2\pi)^3}\,|\,u(\mathbf{p}-\mathbf{p}')\,|^2G_0(\mathbf{p}',-\omega)G_0(\mathbf{p}',\omega)\times[1+L(\omega)]\\&=n_iN(0)\int\frac{d\Omega}{4\pi}\,|\,u(\Theta)\,|^2\int\frac{d\epsilon}{\epsilon^2+\tilde\omega^2}[1+L(\omega)]\\&=[1+L(\omega)/2\,|\,\tilde\omega\,|\,\tau]=(2\,|\,\omega\,|\,\tau)^{-1}\end{aligned}$$

so that

$$Q(\mathbf{p},\omega)=G_0(\mathbf{p},-\omega)G_0(\mathbf{p},\omega)\eta \quad (2.13)$$

in terms of the quantities defined in the preceding section. The first contribution to (2.6) is therefore

$$Q(\mathbf{r},\mathbf{r};\omega)=\frac{2}{d}\sum_n\sin^2\frac{n\pi x}{d}\int\frac{d^2p_\perp}{(2\pi)^2}\frac{\eta}{\epsilon_p^2+\tilde\omega^2}. \quad (2.14)$$

The integral on the right may be transformed into one over ϵ extending from $-\mu+(n\pi/d)^2/2m^*$ to ∞. Since the integrand is peaked about $\epsilon=0$, the sum on n effectively extends up to $n_F=[p_Fd/\pi]\gg1$, each term being essentially independent of n[27]; the oscillating parts of $\sin^2(n\pi/d)$ cancel each other except within a negligible distance $\sim p_F^{-1}$ of the boundaries. The

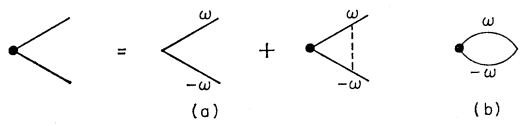

FIG. 3. (a) The integral equation (2.12) for $Q(\mathbf{p},\omega)$. (b) The diagram for the field-independent contribution to $F(\omega)$ linear in Δ; the vertex correction represented by the black dot introduces a factor $\eta=1+(2\tau\,|\,\omega\,|)^{-1}$.

[27] Strictly speaking, this is true only if the width of the peak is small, i.e., $|\,\tilde\omega\,|\ll(n_F/m^*)(\pi/d)^2=v_F\pi/d$. In general the value of the integral smoothly decreases from that given by the residue at $\epsilon=i\,|\,\tilde\omega\,|$, viz., $(m^*\eta/2\,|\,\tilde\omega\,|)$, to zero in an interval of width $(\pi v_F/d\,|\,\tilde\omega\,|)^{-1}$ about n_F. This smearing does not affect our conclusions as long as $p_Fd\gg1$ and $p_Fv_F/|\,\tilde\omega\,|\gg1$, however.

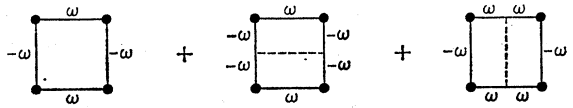

FIG. 4. Total contribution to the field-independent term proportional to Δ^3.

remaining contribution,

$$Q(\omega)=(n_F/d)(m^*\eta/2\,|\,\tilde\omega\,|)=\pi N(0)/|\,\omega\,|, \quad (2.15)$$

is unaffected by the presence of impurities and by the finite thickness of the film. It could be obtained by averaging (2.14) over the sample and approximating the sum by an integral. This procedure is consistent with the assumed constancy of Δ. The corresponding diagram is shown in Fig. 3(b).

The second term in (2.6) can now be easily evaluated. The three possible contributions are represented in Fig. 4. According to (2.13) impurity lines bridging any single vertex bring in a factor η. Diagrams with more than one line across the square give a zero contribution upon integration over the extra internal momentum, since both poles of the integrand occur in the same half-plane. The total contribution,

$$-2\pi N(0)\Delta^2\eta^4[2/(2\,|\,\tilde\omega\,|)^3-2/\tau(2\,|\,\tilde\omega\,|)^4]=-\pi N(0)(\Delta^2/2\,|\,\omega\,|^3), \quad (2.16)$$

is again the same as in bulk[6] and independent of impurity concentration.

D. Field-Dependent Term

The evaluation of the last term in (2.6) is only slightly more complicated than in the local limit.[6] The integral over u_x (or v_x) is directly expressed in terms of the Fourier components of the vector potential:

$$\frac{2}{d}\int_0^d\sin\frac{n'\pi u}{d}A(u)\sin\frac{n''\pi u}{d}\,du=\tfrac{1}{2}(A_{n'+n''}+A_{|n'-n''|}). \quad (2.17)$$

Since n' and n'' are typically of the same order as n_F, $k_{n'+n''}\sim p_F$; and $A_{n'+n''}$ is negligible for $p_Fd\gg1$, only $A_{|n'-n''|}$ need be retained.[8] The corresponding wavy-line insertion in any solid line of a diagram carrying momentum $\mathbf{p}$ must accordingly contribute a factor $\frac{1}{2}[(e/m^*c)A_jp_y]$ and an x component of momentum $\pm k_j$.

In the absence of scattering one obtains the three contributions represented in Fig. 5, diagram (a) corresponding to the term which is explicitly written out in (2.6). In addition to the simple η renormalization and vertex corrections obtained earlier, impurity averaging gives rise to the three types of diagrams shown in Fig. 6. Those like (a) and (b), which contain one or more dotted lines bridging one or both vector potential vertices, yield zero upon integration over the extra internal momentum, since all poles of the inte-

grand lie in the same half-plane. In order to sum the remaining diagrams like (c), it is convenient to introduce the quantity $Q(n, n+j, \mathbf{p}_\perp; \omega) \equiv Q_j(\mathbf{p}, \omega)$, which satisfies the integral equation represented in Fig. 7:

$$Q_j(\mathbf{p};\omega) = G_0(\mathbf{p}, -\omega)G_0(n+j, \mathbf{p}_\perp;\omega)\left(\eta G_0(\mathbf{p},\omega)(ep_yA_j/2m^*c) + n_i\int \frac{d^3p'}{(2\pi)^3} \mid u(\mathbf{p}-\mathbf{p}') \mid^2 Q_j(\mathbf{p}',\omega)\right). \quad (2.18)$$

Since the inhomogeneous term of (2.18) is proportional to p_y, we expect Q_j to have the same structure for the isotropic model considered here. Only the second term in the partial-wave expansion

$$\mid u(\Theta) \mid^2 = u_0 + u_1 \mathbf{p}\cdot\mathbf{p}'/p_F^2$$

can therefore contribute to the second bracketed term in (2.18), which we denote by $p_yL_j(\omega)$. Using (2.18) one obtains a direct equation for L_j:

$$L_j(\omega) = \frac{n_iu_1}{p_F^2}\int \frac{d^3p}{(2\pi)^3} p_y^2 G_0(\mathbf{p}, -\omega)G_0(n+j, \mathbf{p}_\perp;\omega)[\eta G_0(\mathbf{p},\omega)(eA_j/2m^*c) + L_j(\omega)].$$

Recalling that $G_0^{-1}(n+j, \mathbf{p}_\perp;\omega) = i\omega - \epsilon_p - k_jv_Fw$, where $w = \cos\theta$, θ being the angle $\mathbf{p}$ makes with the x axis, and performing the energy integration first, we obtain

$$L_j(\omega) = \frac{3}{\tau_1}\int_0^{2\pi}\frac{d\phi}{2\pi}\cos^2\phi\int_{-1}^{1}\frac{dw}{2}\frac{1-w^2}{2i\tilde{\omega}-k_jv_Fw}\left(\frac{eA_j}{2m^*c}\frac{\eta}{2\mid\tilde{\omega}\mid}+iL_j(\omega)\right) = \frac{eA_j}{2m^*c}\frac{f[k_j\xi(\omega)]}{2i\omega\tau_1}\left(2\mid\omega\mid+\tau^{-1}-\frac{f[k_j\xi(\omega)]}{\tau_1}\right)^{-1} \quad (2.19)$$

in terms of the inverse p-wave relaxation time

$$\tau_1^{-1} = n_im^*p_F(2\pi)^{-2}(4\pi/3)u_1 = \tfrac{1}{2}n_iN(0) \times\int \mid u(\Theta) \mid^2 \cos\Theta d\Omega,$$

the length $\xi(\omega) = v_F/(2\mid\omega\mid\eta)$, and the function

$$f(z) = \frac{3}{2}\int_0^1 \frac{1-w^2}{1+z^2w^2}\,dw = \frac{3}{2}\left[\left(1+\frac{1}{z^2}\right)\frac{\tan^{-1}z}{z} - \frac{1}{z^2}\right], \quad (2.20)$$

which also governs the k dependence of the conductivity in the normal state ($z=kl$ in that case, of course). It has the following limiting properties:

$$f(z) \cong 1-z^2/5, \qquad z\ll 1$$
$$\cong (3\pi/4z), \qquad z\gg 1. \quad (2.21)$$

The structure of the w integral shows that

$$Q(n, n-j, \mathbf{p}_\perp;\omega) = Q_j(\mathbf{p},\omega)$$

as well. It also reveals that, for $z\gg 1$, the main contribution to $f(z)$ comes from a narrow peak of width z^{-1}. In the extreme nonlocal limit ($d\ll\xi$) this corresponds to $p_x/p_F < d/\xi$, so that a large error is made by approximating the summation over $p_x = n\pi/d$ by an integral, as in the above treatment, unless enough allowed values of n, or rather w, fall within that peak This leads to the restriction $p_Fd^2/\xi\gg 1$ mentioned at the beginning of this section and in the introduction. This point has also been discussed by Shapoval.[11] The importance of size quantization was recognized by earlier workers,[8,9] but led to unnecessary complications due to their reliance on a BCS cutoff in momentum space.[2] Typically $(\xi/p_F)^{1/2} < 100$ Å, so that the above restriction is reasonably well satisfied in practice.

It is now straightforward to calculate all the field-dependent contributions, which are shown on Fig. 8. Thus the contribution from diagrams (a) and (d), obtained by summing over allowed values of k_j and multiplying by 2, take the liberty of choosing $\pm k_j$ into account:

$$2\sum_j\int \frac{d^3p}{(2\pi)^3}\left(\eta G_0(p,\omega)\frac{eA_j}{2m^*c} + L_j(\omega)\right)p_yG_0(n+j, \mathbf{p}_\perp;\omega)(eA_jp_y/2m^*c)G_0(\mathbf{p},\omega)\eta G_0(\mathbf{p},-\omega)$$

is eaily evaluated using the techniques employed above to find L_j:

$$-\pi N(0)\frac{1}{3}\left(\frac{ep_F}{m^*c}\right)^2\sum_j\frac{A_j^2f[k_j\xi(\omega)]}{(2\mid\omega\mid)^3}\left[1+(2\mid\omega\mid)^{-1}\left(\tau^{-1}-\frac{f[k_j\xi(\omega)]}{\tau_1}\right)\right]^{-1}. \quad (2.22)$$

Diagrams (c) and (g) make the same contribution, while (b), (e), and (f) yield twice that amount.

E. Order-Parameter Equation

Adding (2.15), (2.16) and four times (2.22), and substituting the result under the sum over frequencies in (2.5), we obtain the self-consistency equation for Δ to second order in the field. The density of states $N(0)$ and the coupling constant g can be eliminated by noting that

$$\pi T\sum_{-\omega_D}^{\omega_D}\mid\omega\mid^{-1} = 2\sum_{\nu=0}^{[\omega_D/(\pi T)]}(2\nu+1)^{-1} \cong \ln\frac{2\gamma\omega_D}{\pi T}, \quad (2.23)$$

provided that $\omega_D\gg\pi T$, using standard mathematical

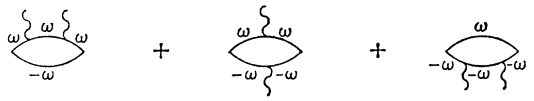

FIG. 5. Total contribution to $F(\omega)/\Delta$ to second order in the field in the absence of impurities.

results. In the particular case where $\Delta=0$ and $A=0$, the right side of (2.5) reduces to $N(0)g$ times (2.23): One obtains the well-known BCS result for the transition temperature T_c in the weak-coupling limit (this justifies our use of a frequency cutoff):

$$1=N(0)g\ln(2\gamma\omega_D/\pi T_c). \tag{2.24}$$

Substituting (2.24) for the right side of (2.5), subtracting the contribution from the term proportional to (2.23), and allowing the remaining rapidly converging frequency summations to run to infinity, one gets the desired form of the equation relating the order parameter to the Fourier components of the vector potential at any given temperature:

$$\ln\frac{T_c}{T}=\frac{7\zeta(3)}{8}\left(\frac{\Delta}{\pi T}\right)^2+\frac{1}{3}\left(\frac{2e\xi_T}{c}\right)^2\sum_j\sum_{\nu=0}^{\infty}\frac{A_j^2 f(k_j\xi_\nu)}{(2\nu+1)^2}$$
$$\times[2\nu+1+(2\pi T)^{-1}(1/\tau-f(k_j\xi_\nu)/\tau_1)]^{-1}, \tag{2.25}$$

where

$$\xi_T=(v_F/2\pi T)=0.88\xi_0(T_c/T),$$
$$\xi_\nu\equiv\xi(\omega_\nu)=[(2\nu+1)\xi_T^{-1}+l^{-1}]^{-1},$$

and

$$7\zeta(3)/8=1.05=\sum_{\nu=0}^{\infty}(2\nu+1)^{-3}.$$

Note that $\xi_\nu\gtrsim\xi$ (the Pippard coherence length defined in the introduction) and that only the first few terms in the sum over ν make an appreciable contribution. The local limit may therefore be defined by the condition $k_j\xi\ll1$ for the highest significant A_j. The function f can then be replaced by 1, and (2.25) reduces to the equation obtained by Gor'kov,[6] provided one neglects the spatial dependence of Δ and averages A^2 over the film. The connection is established by means of Parseval's theorem:

$$d^{-1}\int A^2dx\equiv\langle A^2\rangle_{\rm av}=\tfrac{1}{2}\sum_j A_j^2. \tag{2.26}$$

It is only in this limit that τ_1 enters through the simple combination $\tau^{-1}-\tau_1^{-1}=\tau_{\rm tr}^{-1}$, the inverse transport relaxation time which is proportional to the bulk residual resistivity of the material in the normal state. Unfortunately, there exists no easily measurable property from which one could separately determine τ (or τ_1). Furthermore, our calculation of the vertex correction $-f(k_j\xi_\nu)/\tau_1$ was done assuming isotropy, a rather unrealistic assumption in real metals. For the purpose of comparison with experiment, it therefore seems best to neglect all but s-wave corrections altogether, hence, to make no distinction between τ and $\tau_{\rm tr}$.

FIG. 6. New types of diagrams appearing as a result of impurity averaging.

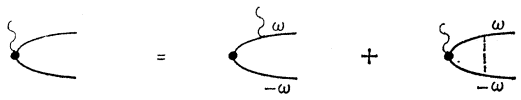

FIG. 7. The integral equation (2.18) for $Q_j(\mathbf{p},\omega)$.

The critical field for a second-order transition H_c is determined by setting $\Delta=0$ in (2.25) and substituting (2.8) for A_j. Since $A_j^2\propto j^{-4}$, a good approximation is to neglect all but the first ($j=1$) contribution:

$$\frac{1}{3}\left(\frac{8eH_cd}{\pi^2c}\right)^2\sum_{\nu=0}^{\infty}\frac{\xi_T\xi_\nu f(\pi\xi_\nu/d)}{(2\nu+1)^2}\approx\ln\frac{T_c}{T}. \tag{2.27}$$

The resulting error is 2% in the local limit [the factor $(8/\pi^2)^2$ should be replaced by $\frac{2}{3}$]. In the opposite case ($d\ll\xi$) it is only $\frac{1}{2}$%, and we obtain ($\ln t^{-1}\cong1-t$ near T_c):

$$(eH_c/c)^2=2.35(1-t)(\xi_0d^3)^{-1}, \tag{2.28}$$

a result independent of the mean free path as one would expect. It is interesting to compare (2.28) with the corresponding results of Nambu and Tuan,[8] and Casella and Miller,[9] which have the same form, but contain a cutoff parameter γ "of the order of unity". Setting $\gamma=1$ in their formulas, one finds that the values of the coefficient would be 3.49 and 2.21, respectively. The correct result was independently obtained by Shapoval in his second paper on specular reflection.[11]

The actual comparison of (2.27) and of the corresponding result for diffuse boundary scattering is taken up in our companion paper.[21] Although the exact range of validity of the nonlocal nonlinear theory developed here can only be determined from a knowledge of the structure of higher-order terms in the expansion in powers of A, it is appropriate to state the resulting limitations in compact form at this stage:

$$1-t\ll\min(1,\,d\xi_0/\xi^2). \tag{2.29}$$

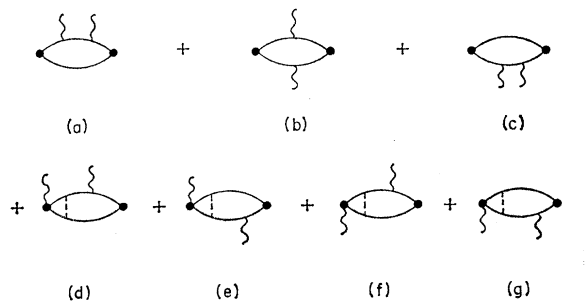

FIG. 8. Total contribution to $F(\omega)/\Delta$ to second order in the field after impurity averaging.

The replacement of $\ln t^{-1}$ by $1-t$ and ξ_T by $0.88\xi_o$ is certainly justified in this range. In addition, the assumed constancy of Δ requires

$$1-t \ll \xi_o \xi/d^2, \tag{2.30}$$

as mentioned in the Introduction.

F. Current Equation

An approximation for the average induced current density $\mathfrak{J}$ consistent with the terms retained in (2.6) is obtained by iterating (2.1) and (2.2) once, substituting the result for G into the exact expression[17]

$$\mathfrak{J}(x) = 2 \lim_{\mathbf{r}'\to\mathbf{r}} [(e/2im^*)(\partial_y - \partial_{y'}) - (e^2/m^*c)A(x)] T\sum_\omega G(\mathbf{r}, \mathbf{r}'; \omega), \tag{2.31}$$

and noting that the zero-order term, i.e., (2.31), with G replaced by G_A, must vanish, since the current in the normal state is zero if we continue to neglect the A^2 term in (2.4). The remainder is iterated once with respect to the perturbation $(e/m^*c)Ap_y$ and averaged over impurity configurations. Assuming again that A and Δ may be averaged separately, one obtains the desired result:

$$\mathfrak{J}(x) \cong T\sum_\omega \Delta^2 (e/im^*) \lim_{\mathbf{r}'\to\mathbf{r}} \int \{\langle (\partial_y - \partial_{y'}) G_0(\mathbf{r}, \mathbf{u}; \omega)[\partial_{u_y} G_0(\mathbf{u}, \mathbf{v}; \omega)] G_0(\mathbf{s}, \mathbf{v}; -\omega) G_0(\mathbf{s}, \mathbf{r}'; \omega)\rangle + 2 \text{ similar terms}\}$$
$$\times (e/im^*c) A(u_x)\, d^3u d^3v d^3s. \tag{2.32}$$

Writing the jth Fourier component of (2.32) as $\mathfrak{J}_j = \sum_\omega \mathfrak{J}_j(\omega)$, comparing (2.32) with the last term in (2.6), and using (2.17) with A replaced by $\mathfrak{J}$ one easily realizes that $\mathfrak{J}_j(\omega)$ is simply $2\Delta^2$ times the sum of the contributions from the diagrams shown on Fig. 8, provided that one of the wavy-line insertions is understood to carry factor (ep_y/m^*c) rather than the usual $\frac{1}{2}[(e/m^*c)A_j p_y]$ and that only the contribution from the jth Fourier component is retained. Modifying (2.22) accordingly, we obtain

$$\mathfrak{J}_j = -\tfrac{4}{3} N(0) \frac{(ev_F)^2}{c} A_j \left(\frac{\Delta}{\pi T}\right)^2 \sum_{\nu=0}^{\infty} \frac{f(k_j\xi_\nu)}{(2\nu+1)^2} [2\nu + 1 + (2\pi T)^{-1}(1/\tau - f(k_j\xi_\nu)/\tau_1)]^{-1}. \tag{2.33}$$

G. Normalized Nonlocal Equations

It is convenient to rewrite (2.33) as follows:

$$\mathfrak{J}_j = -(c/4\pi)\psi^2 K_j A_j, \tag{2.34}$$

where $\psi = \Delta/\Delta_o$, the order parameter normalized to its value in the absence of a field, i.e., the BCS temperature-dependent energy gap. We can then identify K_j as the Fourier transform of the weak-field (linear response) kernel evaluated at $k = k_j$. Because of the restrictions (2.29) and (2.30), the standard relations[17]

$$\tfrac{1}{2}\lambda_L^2(0)/\lambda_L^2(t) \cong \ln t^{-1} \cong (7\zeta(3)/8)(\Delta_o/\pi T)^2, \tag{2.35}$$

valid near T_c, may be used to eliminate Δ_o in favor of the London penetration depth λ_L of the pure material. Recalling the definition[2]

$$\lambda_L^{-2}(0) = (8\pi/3) N(0) (ev_F/c)^2, \tag{2.36}$$

we obtain

$$K(k) = \lambda_L^{-2}(t) \frac{8}{7\zeta(3)} \sum_{\nu=0}^{\infty} \frac{f(k\xi_\nu)}{(2\nu+1)^2}$$
$$\times [2\nu + 1 + (2\pi T)^{-1}(1/\tau - f(k\xi_\nu)/\tau_1)]^{-1}. \tag{2.37}$$

Although the vertex correction $-f(k\xi_\nu)/\tau_1$ is largely of academic interest as mentioned in our discussion of (2.26), it seems worthwhile to write down the exact result, since it shows how the transport relaxation time becomes replaced by the single-electron relaxation time as one goes from the local to the extreme nonlocal limit. To our knowledge, this has not been reported in the literature. In the local limit K reduces to $\lambda^{-2} = \lambda_L^{-2}\chi_o$, where χ_o is the function which describes the effect of impurities on the penetration depth in Gor'kov's derivation[6] ($\chi_o = 1$ in the pure limit). The function f defined by (2.20) also appears in the Fourier transform of the weak-field kernel proposed by Pippard on phenomenological grounds before the advent of the BCS theory, viz., $K_P(k) = \xi f(k\xi)/\xi_o$.[4] Neglecting all but s-wave vertex corrections from now on, we note that the bracketed term in (2.37) simply introduces a factor ξ_ν/ξ_T, so that K reduces to a rapidly converging sum of Pippard-like kernels. One easily verifies that, to order $(\Delta_o/\pi T)^2$, the result agrees with the expression for the weak-field kernel valid at all temperatures which is obtained by introducing a factor

$$\exp(-|r-r'|/l)$$

into the BCS kernel for a pure superconductor.[2]

Using the relation[17]

$$(8\pi)^{-1} H_{cb}^2 = (7\zeta(3)/16) N(0) \Delta_o^4/(\pi T)^2, \tag{2.38}$$

determining the bulk thermodynamic critical field near T_c, in conjunction with (2.35), one can rewrite (2.25) in normalized form:

$$\psi^2 = 1 - \sum_j (A_j/2H_{cb})^2 K_j. \tag{2.39}$$

The equivalence of (2.34) and (2.39) with Bardeen's generalized GL equations (1.8) and (1.9) is trivially established by substituting the Fourier representations of K, $\mathfrak{J}$, and A.

III. THERMODYNAMIC ANALYSIS AND PHENOMENOLOGY

A. Free Energy and the Thermodynamic Potential

The expression for the free-energy density appearing in the functional $\int dx\, F_S\{\psi, A(x)\}$, which yields (1.8) upon minimization with respect to ψ (or ψ^2), can be immediately written down:

$$F_S=F_N(0)+(8\pi)^{-1}\Big(H_{cb}^2(\psi^4-2\psi^2)+\psi^2A(x)\times\int dx'K(x-x')A(x')+h^2(x)\Big) \quad (3.1)$$

($\psi^2=0$ and $h=H$ outside the film, of course). To the required second and third terms, which can be identified with the condensation energy and the kinetic energy of the supercurrents, we have added the normal-state contribution and the field energy. Since $h=dA/dx\equiv A'$, variation with respect to A yields

$$A''(x)=\psi^2\int K(x-x')A(x')\,dx', \quad (3.2)$$

which is equivalent to (1.9) because of Maxwell's equation $h'=-4\pi\mathfrak{I}/c$. It is, however, important to realize that if one uses the Fourier representation (2.7), h exhibits jumps of magnitude H and $-H$ at $x=2md$ and $(2m+1)d$, respectively, when periodically continued outside the film as shown in Fig. 2. If, in addition, a net external current J per unit length flows in the y direction, A'' must contain δ-function contributions of strength $2H+4\pi J/c$ and $-2H+4\pi J/c$ at the same points. Adding them to the induced component (3.2) and Fourier transforming we obtain

$$-A_j=(8\pi J/cd)(k_j^2+\psi^2K_j)^{-1}, \quad j \text{ even} \quad (3.3)$$

$$=(4H/d)(k_j^2+\psi^2K_j)^{-1}, \quad j \text{ odd}. \quad (3.4)$$

The even part of A does indeed vanish in the case $J=0$ on which we continue to focus our attention.

In practice, it is the applied field H, rather than A, which is the experimentally controlled variable. Since no demagnetization effects are present in the simple geometry under study, no distinction between external and applied fields is necessary. The subsequent analysis parallels that developed by Ginzburg[28] in applying the GL theory to small samples (constant ψ). The thermodynamic potential which is minimum in equilibrium at fixed H is conveniently chosen as

$$G_S=\langle F_S\rangle_{\rm av}-(4\pi)^{-1}BH+(8\pi)^{-1}H^2, \quad (3.5)$$

$B\equiv\langle h\rangle_{\rm av}$ being the macroscopic magnetic induction in the film. The last term is solely added in order to ensure that $G\equiv 0$ when the sample is removed. It is convenient to consider ψ to be a variational parameter to be determined later. In order to obtain the explicit dependence of G_S on H note that the third term in $\langle F_S\rangle_{\rm av}$ may be written as

$$-(2c)^{-1}\langle\mathfrak{I}A\rangle_{\rm av}=(8\pi)^{-1}\langle(H-h)h\rangle_{\rm av},$$

using (1.8) and Maxwell's current equation, and integrating by parts. Substituting into (3.5) and subtracting $G_N=F_N(0)$ ($B=H$ in the normal state), one obtains

$$\Delta G=G_S-G_N=(8\pi)^{-1}H_{cb}^2(\psi^4-2\psi^2)-\tfrac{1}{2}MH, \quad (3.6)$$

which is formally the same as in Ginzburg's treatment.[28] Since

$$Bd=\int_0^d h\,dx=A(d)-A(0)=-2A(0)=-2\sum_j A_j,$$

the magnetization is given by

$$-4\pi M=H-B=H[1-(8/d^2)\sum_j(k_j^2+\psi^2K_j)^{-1}]$$

$$=H\psi^2(8/d^2)\sum_{j=1}^{\infty}K_j[k_j^2+\psi^2K_j)]^{-1}. \quad (3.7)$$

When $\psi=1$ the first expression agrees with Schrieffer's result[29] for weak fields. The second expression, obtained by using the identity

$$\sum_{j\,\text{odd}} j^{-2}=\pi^2/8,$$

is actually more convenient. Minimizing (3.6) with respect to ψ^2, one gets

$$\psi^2=1-(H/H_{cb})^2(4/d^2)\sum_j K_j(k_j^2+\psi^2K_j)^{-2}, \quad (3.8)$$

which is identical to (2.39) once (3.4) is substituted for A_j.

B. Determination of Critical Parameters

Nonlocality does not affect Ginzburg's qualitative results[28] concerning the behavior of ΔG and the classification of possible transitions.

The critical field above which the normal state is thermodynamically stable can in principle be determined by eliminating ψ between (3.8) and

$$2-\psi^2=(H/H_{cb})^2(8/d^2)\sum_j K_j[k_j^2(k_j^2+\psi^2K_j)]^{-1}, \quad (3.9)$$

which expresses the requirement $G_S=G_N$.

Since $\psi\to 0$ at a second-order phase transition the appropriate critical field is given by the corresponding limit of (3.8):

$$1=(H_c/H_{cb})^2(4/d^2)\sum_j K_j/k_j^4. \quad (3.10)$$

Note that (3.9) also reduces to (3.10) in that limit. When the film thickness is below a critical value d_c, (3.10) is the only simultaneous solution of (3.8) and

[28] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **34**, 113 (1958) [English transl.: Soviet Phys.—JETP **7**, 78 (1958)].

[29] J. R. Schrieffer, Phys. Rev. **106**, 47 (1957).

(3.9), so that the thermodynamic transition is in fact a second-order one. For $d>d_c$, (3.8) and (3.9) have a nontrivial solution corresponding to a first-order thermodynamic transition. Under favorable experimental conditions hysteresis associated with supercooling[30] and/or superheating can be observed. The normal phase can in principle be metastable down to the field H_c given by (3.10). The normalized version of (2.27) follows if one retains only the $j=1$ term in (3.10):

$$H_c/H_{cb}\approx(\pi^2/2)\lambda_d/d, \tag{3.11}$$

where

$$\lambda_d^{-2}=K_1\equiv K(\pi/d) \tag{3.12}$$

may be interpreted as an effective penetration depth whose thickness dependence reflects the net influence of nonlocality. As mentioned before the maximum error occurs in the local limit where $\lambda_d\to\lambda$ and the exact factor replacing $\frac{1}{2}\pi^2=4.93$ should be $\sqrt{(24)}=4.90$.

The critical thickness d_c is best characterized by the requirement that dM/dH be infinite at $H=H_c$. The physical meaning of this criterion is obvious from Fig. 1. Differentiating (3.7), setting $\psi=0$, and using (3.10) one gets

$$4\pi(dM/dH)_{H_c}=4H_{cb}^2(d\psi^2/dH^2)_{H_c},$$

where

$$H_{cb}^2(d\psi^2/dH^2)_{H_c}$$
$$=-(H_c/H_{cb})^{-2}[1-2(H_c/H_{cb})^2(4/d^2)\sum_j K_j^2/k_j^6]^{-1},$$

according to (3.8). Neglecting all but the $j=1$ term as before and using (3.11) we obtain

$$-4\pi(dM/dH)_{H_c}\approx(8/\pi^2)[(\pi^2/2)(\lambda_d/d)^2-1]^{-1}. \tag{3.13}$$

d_c is thus defined by the implicit equation $d_c\approx(\pi/\sqrt{2})\lambda_{d_c}$; the corresponding critical-field ratio

$$H_{cc}/H_{cb}\approx\pi/\sqrt{2}=2.22 \tag{3.14}$$

is, to a good approximation, unaffected by nonlocality. In the local limit the right sides of (3.13) and (3.14) should be replaced by (5/6) $(5\lambda^2/d^2-1)^{-1}$ and $(24/5)^{1/2}=2.19$, which shows that the maximum error is indeed small. It should be borne in mind that the constant ψ approximation is adequate provided that $H_c\gg H_{c2}=\sqrt{2}\kappa H_{cb}$. As a result, even our "exact" formula for H_{cc}/H_{cb} is only correct to zero order in κ^2, so that its usefulness is restricted to extreme type-I superconductors ($\kappa\ll1$).

C. Critique of Previous Semiphenomenological Theories

Several attempts to include nonlocal and nonlinear effects on the critical fields of small samples were all based on the same idea, namely that the GL results, e.g., (1.6) for the second-order transition of a thin film, still apply, provided λ is replaced by a thickness-dependent λ_d which describes nonlocal effects reasonably well in the weak-field limit. The generally good agreement obtained between theory and experiment suggested that such a separate treatment of nonlocal and nonlinear effects is justified. The analysis presented in the preceding sections shows that this is indeed a good approximation. We need only compare previous *Ansätze* for λ_d with our result (3.12).

It is appropriate to first estimate the error involved in using the Pippard kernel instead of the exact one.[13,14] For a given value of λ_L, both must, of course, agree in the pure, local limit ($k\xi_0$, $\xi_0/l\ll1$); in the dirty, local limit (kl, $l/\xi_0\ll1$) and in the extreme nonlocal limit ($k\xi\gg1$) the results of Sec. II imply that

$$K(k)=(\pi^2/7\zeta(3))(\xi_0/\xi_T)K_P(k)=1.33tK_P(k).$$

According to (3.11) this leads to a maximum 15% overestimate in the critical-field ratio.

We now discuss previous ways of defining λ_d for a given kernel. Douglass and Blumberg[12] used the very expedient and, hence, widely accepted, proposal due to Tinkham,[31] which consists of replacing the nonlocal $\mathcal{J}$-A relationship by the local London equation with λ replaced by the value corresponding to the effective mean free path l_d as determined by the normal-state resistivity of the sample. A critical examination of this procedure reveals serious inconsistencies, some of which were already discussed by Toxen and Burns.[14] We first note that according to Fuch's classical work on the subject[32] $l_d=l$ for specular reflection. One may, however, invoke the well-known insensitivity of the bulk weak-field penetration depth to the boundary condition used in calculating it[2] to argue that the diffuse-scattering result may be used instead. For a thin film the corresponding formulas for l_d are $(l^{-1}+\frac{3}{8}d^{-1})^{-1}$ if $l\ll d$ and $\frac{3}{4}d[\ln(l/\gamma d)+1]$ if $l\gg d$. Using the Pippard model for the sake of simplicity, one obtains the following asymptotic formulas for

$$\lambda_d^2=(\xi_0/\xi_d)\lambda_L^2=(\xi/\xi_d)\lambda^2(\xi_d^{-1}=\xi_0^{-1}+l_d^{-1}):$$
$$\lambda^2(1+\tfrac{3}{8}\xi/d) \qquad (d\gg\xi)$$
$$\tfrac{4}{3}(\xi_0\lambda_L^2/d)[\ln(l/\gamma d)+1]^{-1} \qquad (d\ll\xi). \tag{3.15}$$

By contrast our result, $\lambda_d^2=(\xi_0/\xi)[f(\pi/d)]^{-1}$, leads to

$$\lambda^2(1+(\pi^2/5)\xi^2/d^2) \qquad (d\gg\xi)$$
$$\tfrac{4}{3}\xi_0\lambda_L^2/d \qquad (d\ll\xi). \tag{3.16}$$

In view of what was said above, (3.15) should rather be compared with our result for diffuse scattering. Referring to Sec. II of the companion paper,[21] one obtains

$$\lambda^2(1+(9/8)\xi/d) \qquad (d\gg\xi)$$
$$(16/9)\xi_0\lambda_L^2/d \qquad (d\ll\xi). \tag{3.17}$$

[30] J. P. Baldwin, Rev. Mod. Phys. **36**, 317 (1964).

[31] M. Tinkham, Phys. Rev. **110**, 26 (1958).

[32] F. Fuchs, Proc. Cambridge Phil. Soc. **34**, 100 (1938).

The appearance of the same factor $\frac{4}{3}$ in both (3.15) and (3.16) for $d\ll\xi$ is purely coincidental. Note the absence of logarithmic terms in (3.16) and (3.17) and the slower increase of λ_d for $d\gg\xi$ in the specular case. We conclude that Tinkham's extrapolation or any of the widely used semiempirical interpolation formulas of the form $\lambda_d^2=\lambda^2(1+c\xi/d)$[33] are only crude approximations which could lead to significant errors either for $d\lesssim\xi$ or for $d\gg\xi$. We would also like to emphasize that it is unreasonable to expect any close connections between effective lengths describing nonlocal effects for different field configurations. In a resistivity measurement the current (or A) is symmetric with respect to the midplane of the film (it is in fact uniform for specular reflection), in contradistinction to the situation discussed here. By the same token no implications about the validity of his procedure can be drawn from Tinkham's observation[31] that the microwave power P_S absorbed in a superconducting film varies in such a way that the ratio of P_S over the same quantity in the normal state is independent of d and l at a given frequency. It only increases one's confidence in the theoretical considerations according to which the imaginary parts of the conductivities $\sigma_{S,N}(k,\omega)$ have the same k dependence in the dirty limit and in the anomalous skin-effect region.[2,34] As recognized by the Orsay group,[35] however, the use of l_d is justified in describing nonlocal effects on the magnetic properties of a thin film in a *transverse* field since the current is then symmetrically distributed across the film.

The procedure used by Toxen[13,14] in interpreting his own critical-field data is essentially based on the following *Ansatz* for λ_d, due to Ittner[36]:

$$1-(2\lambda_d/d)\tanh(d/2\lambda_d)=1-(8/d^2)\sum_j(k_j^2+K_j)^{-1}. \tag{3.18}$$

On the left side the reader will recognize the London expression for the susceptibility of a thin film[1] normalized to the full diamagnetic value $-(4\pi)^{-1}$. Referring to (3.7) one sees that the right side is the general expression for the weak-field susceptibility ratio. In the local limit (3.18) reduces to an identity:

$$(2\lambda/d)\tanh(d/2\lambda)\equiv(8/d^2)\sum_j(k_j^2+\lambda^{-2}). \tag{3.19}$$

The physical reasoning behind (3.18) is that it may be possible to simulate the net effect of the exact field distribution on the thermodynamic potential ΔG by using a simple London $\cosh(x/2\lambda_d)$ dependence with λ_d adjusted to give the correct B or M.

We shall now show that the value of λ_d defined by (3.18) is in fact very close to our result as long as $d\gtrsim d_c$. The hard computational work needed to solve (3.18) for λ_d can therefore be avoided. Each term of the sum in (3.18) may be expanded in powers of K_j/k_j^2 provided $K_j<k_j^2$, which is certainly satisfied if $K_1<k_1^2$. One obtains a double series whose general term is $(-1)^{n-1}K_j^n/k_j^{2n+2}$, where n runs from 1 to ∞ (the sum of the $n=0$ terms cancels against 1). Since

$$K_1^n/k_1^{2n+2}<\sum_j K_j^n/k_j^{2n+2}<K_1^n\sum_j k_j^{-2n-2}$$

and

$$\sum_j(k_1/k_j)^{2n+2}<\sum_j(k_1/k_j)^4=1.02k_1^4,$$

we may replace K_j by K_1 with a relative error less than 2% (the maximum error is actually 1.5% and occurs in the extreme nonlocal limit where $K_j\sim K_1k_1/k_j$). This estimate applies to the remaining series as well, since it is alternating. Summing it, we obtain

$$(2\lambda_d/d)\tanh(d/2\lambda_d)\approx(8/d^2)\sum_j(k_j^2+K_1). \tag{3.20}$$

Comparing with (3.19) we conclude that $\lambda_d^{-2}\approx K_1$, at least in the region $d\lesssim\pi\lambda_d$, where the expression on the left side of (3.20) varies so rapidly that the above-mentioned error has a negligible effect and where the geometric series converges. This completes the proof.

When $d\gg d_c$, one may replace the sum in (3.18) by an integral and set $\tanh(d/2\lambda_d)=1$ to obtain

$$\lambda_\infty=(2/\pi)\int_0^\infty dk[k^2+K(k)]^{-1},$$

which one readily recognizes as the exact expression for the effective penetration depth λ_b in a bulk sample.[2,4] It is important to keep in mind that the electrodynamics is local only if $\lambda\gg\xi$, i.e., $\lambda_L^2\xi_0\gg\xi^3$ or $1-t\ll\kappa^2\xi_0/\xi$. Otherwise $\lambda_b>\lambda$, and Toxen's λ_d diverges from the appropriate limiting value of (3.12), $1/\sqrt{K(0)}=\lambda$. This shows that Toxen's procedure would not yield a good value for the *second-order* (*supercooling*) transition critical field for $d>d_c$ if $1\gg1-t>\kappa^2\xi_0/\xi$, which may easily be realized in a pure extreme type-I superconductor.

In his work, however, Toxen was exclusively concerned with the *thermodynamic* critical field. He therefore substituted his result for λ_d into the GL analogs of (3.8) and (3.9):

$$\psi^2=1-(H_c/H_{cb})^2\times[1-(\lambda_d/\psi d)\sinh(\psi d/\lambda_d)]/[4\psi^2\cosh^2(\psi d/\lambda_d)],$$
$$(2-\psi^2)\psi^2=(H_c/H_{cb})^2\times[1-(2\lambda_d/\psi d)\tanh(\psi d/2\lambda_d)]. \tag{3.21}$$

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[33] One may argue that part of the thickness dependence may be due to increased scattering in the bulk of the film, e.g., from the boundaries of crystallites whose size would decrease with d. Unfortunately, it is hard to estimate the importance of such indirect effects. It should, however, be possible to separate the contribution due to genuine boundary scattering by comparing the dc resistivity of the film with that determining the decay of eddy currents, as suggested by P. Cotti [Physik Kondensierten Materie **3**, 40 (1964)].

[34] See, e.g., Appendix B in J. R. Waldram, Advan. Phys. **13**, 1 (1964).

[35] P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966), p. 226; E. Guyon, C. Caroli, and A. Martinet, J. Phys. (Paris) **25**, 683 (1964).

[36] W. Ittner, III, Phys. Rev. **119**, 1591 (1960).

Although it seems difficult to judge the validity of this procedure in the range just above d_c, we note that it does yield the correct behavior $H_c/H_{cb}\cong 1+\lambda_b/d(\psi\cong 1)$ for $d\gg d_c\sim\lambda_b$. Since it has just been shown to provide a good approximation for $d\gtrsim d_c(\psi=0)$, Toxen's scheme is probably adequate in the intermediate range as well.

The restrictions (2.29) and (2.30) must still apply, and it is somewhat surprising that Toxen's later attempt[37] to fit the temperature dependence of his critical-field data using the complete weak-field BCS kernel in conjunction with (3.18) and (3.21) results in rather good agreement down to $t=0.4$. Even if one ignores the importance of higher-order terms in A, one should use $K(\Delta, T)\equiv K[\psi\Delta_o(T), T]$ instead of $\psi^2K[\Delta_o(T), T]$. This distinction is especially important in the range $d<d_c$, where $\Delta\to 0$ at H_c while Δ_o/T is not small except close to T_c. Thus in the extreme nonlocal limit or the dirty, local limit the ratio of the kernel used by Toxen to the correct one behaves as $(\Delta_o/2T)^{-1}\tanh(\Delta_o/2T)$ when $\Delta\to 0$. The error made by using the wrong kernel leads one to overestimate H_c, while the omission of higher-order terms tends to give a lower value. The success of Toxen's fit must be due to a fortuitous cancellation of errors. In our opinion, a meaningful comparison with experiment should rather be based on the more systematic approach developed in the following section.

A final comment about Hauser and Helfand's approach[15] is in order. These authors start from expressions (3.6) for ΔG, which can be traced back to the following expression for the free-energy density:

$$F_S=(8\pi)^{-1}[H_{cb}^2(\psi^4-2\psi^2)+h^2]-(2c)^{-1}\mathfrak{J}A, \quad (3.22)$$

by going through the manipulations leading to (3.6) in reverse order. (3.22) is a reasonable *Ansatz*, provided that ψ is constant over the sample and that the explicit dependence of $\mathfrak{J}$ on A is linear (in order to ensure that $\delta\int F_S\{\psi, A\}d^3r/\delta A=-\mathfrak{J}/c$). They further assume that for sufficiently thin samples ($d<d_c$) M is proportional to ψ^2. Setting $\Delta G=0$ they observe that $(H_c/H_{cb})^2\propto 2-\psi^2$, and conclude that the actual critical field ($\psi=0$) can be obtained by multiplying the corresponding weak-field result ($\psi=1$) by $\sqrt{2}$, i.e.,

$$H_c/H_{cb}=(-2\pi\chi)^{-1/2},$$

where $-4\pi\chi$ is given by the expression on the right side of (3.18). The preceding discussion clearly shows that Hauser and Helfand essentially *assume* that (1.7) holds.

IV. IMPROVED PERTURBATION SCHEME

Going back to Sec. II, we note that (2.27) is obtained by retaining the first-order term in an expansion of $F(\omega)$ in powers of $(ev_FH_cd/c\omega)^2\eta^{-1}$. In this section we construct a direct expansion in terms of $(ev_FH_cd/c\tilde{\omega})^2$. This makes no difference in the pure limit, but in the opposite case ($l\ll\xi_o$) convergence is markedly improved, since $|\omega|\tau\ll 1$ and $\eta=\tilde{\omega}/\omega=1+(2\tau|\omega|)^{-1}\gg 1$ for the dominant contributions ($\omega_r<\pi T_c$). In that limit the corresponding expression for H_c is in fact valid down to $T=0$, as first realized by Maki.[7] We wish to emphasize that his work was restricted to the local limit ($l\ll d$) and assumed Δ to be constant over the film ($d^2\ll\xi_o l$). Since both conditions are hard to satisfy in practice, our nonlocal generalizations (4.17) and (4.18) are a significant improvement.

A. Average Impurity Self-Consistent Field

The basic idea of the method is to avoid all explicit calculations of vertex corrections by including the average effect of impurities *before* making any expansions. All the diagrams appearing as a result of the usual impurity averaging procedure[17] are generated by the iteration scheme illustrated in Fig. 9, which corresponds to the following integral equations for the averaged Green's functions:

$$G(\mathbf{r}, \mathbf{r}'; \omega)=G_A^{(0)}(\mathbf{r}, \mathbf{r}'; \omega)-\int G_A^{(0)}(\mathbf{r}, \mathbf{s}; \omega)\Delta(\mathbf{s})G(\mathbf{s}, \mathbf{r}'; \omega)d^3s$$
$$+\int G_A^{(0)}(\mathbf{r}, \mathbf{u}; \omega)[M_G(\mathbf{u}, \mathbf{v}, \omega)G(\mathbf{v}, \mathbf{r}'; \omega)-M_F(\mathbf{u}, \mathbf{v}; \omega)F^\dagger(\mathbf{v}, \mathbf{r}'; \omega)]d^3ud^3v, \quad (4.1)$$

$$F^\dagger(\mathbf{r}, \mathbf{r}'; \omega)=\int G_A^{(0)}(\mathbf{s}, \mathbf{r}; -\omega)\Delta^*(\mathbf{s})G(\mathbf{s}, \mathbf{r}'; \omega)d^3s$$
$$+\int G_A^{(0)}(\mathbf{u}, \mathbf{r}; -\omega)[M_F^\dagger(\mathbf{u}, \mathbf{v}; \omega)G(\mathbf{v}, \mathbf{r}'; \omega)+M_G(\mathbf{v}, \mathbf{u}; -\omega)F^\dagger(\mathbf{v}, \mathbf{r}'; \omega)]d^3ud^3v, \quad (4.2)$$

where

$$M_F(\mathbf{u}, \mathbf{v}; \omega)=n_i\int(2\pi)^{-3}d^3q\,|u(\hat{q})|^2\exp[i\mathbf{q}\cdot(\mathbf{u}-\mathbf{v})]F(\mathbf{u}, \mathbf{v}; \omega) \quad (4.3)$$

[37] A. M. Toxen, Rev. Mod. Phys. **36**, 308 (1964).

and similarly for M_G and $M_F^\dagger$. $G_A^{(0)}$ satisfies the same equation (2.4) as G_A, with G_0 replaced by $G_0^{(0)}$, the normal-state Green's functions for the pure film in zero field. We now make the same simplifying assumptions as in Sec. II.

We already noted there that it is difficult to extract any information concerning the angular dependence of the cross section for scattering by an impurity from experiment, so that it seems best to neglect the attendant complications altogether. Equivalently, we assume that the impurity pseudopotential may be represented by a δ function of strength u such that $\tau^{-1}=2\pi N(0)n_i u^2$. The self-energy corrections M_F and M_G acquire a similar structure, e.g., (4.3) becomes

$$M_F(\mathbf{u},\mathbf{v};\omega)=(2\pi N(0)\tau)^{-1}F(\mathbf{u},\mathbf{u};\omega)\delta(\mathbf{u}-\mathbf{v}). \quad (4.4)$$

Substituting into (4.1) and (4.2) we obtain the equations first written down by Larkin,[38] in which the average effect of s-wave scattering by impurities enters through a self-consistent field with an ordinary and an anomalous component proportional to $G(\mathbf{s},\mathbf{s};\omega)$ and $F(\mathbf{s},\mathbf{s};\omega)$, respectively. No distinction between F and $F^\dagger$ and the corresponding self-energies occurs in the gauge where Δ is real. As before, effects present in the normal state are absorbed by redefining the chemical potential; $M_G(M_F)$ is then odd (even) in ω.

We further assume, as Maki and Larkin do implicitly, that the spatial dependence of $G(\mathbf{s},\mathbf{s};\omega)$ and $F(\mathbf{s},\mathbf{s};\omega)$ is negligible whenever Δ is essentially constant over the sample. This crucial assumption will be examined in more detail in Sec. V, where it is argued that (1.10) is a sufficient condition. M_G and M_F are then constant and can be absorbed by renormalizing the frequency and the order parameter as follows:

$$\tilde{\omega}(\omega)=\omega+iM_G(\omega), \qquad \tilde{\Delta}(\omega)=\Delta+M_F(\omega). \quad (4.5)$$

Except for this change, the resulting equations are formally the same as Gor'kov's for a pure superconductor. In other words, one may start with (2.1), (2.2), and (2.4), replace Δ by $\tilde{\Delta}$, ω by $\tilde{\omega}$ in G_A and G_0,

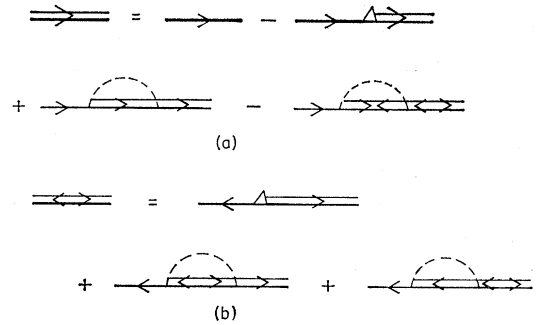

FIG. 9. The integral equations (4.1) and (4.2) for the impurity averaged one-electron Green's function (a) and electron pair amplitude (b).

[38] A. I. Larkin, Zh. Eksperim. i Teor. Fiz. **48**, 232 (1965) [English transl.: Soviet Phys.—JETP **21**, 153 (1965)].

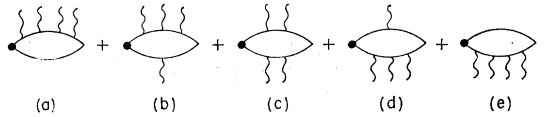

FIG. 10. Total contribution to $F(\omega)/\tilde{\Delta}$ to fourth order in the field; each black dot carries a factor $\tilde{\Delta}$.

and forget about impurity averaging from then on. The only difference from the zero-field case, investigated by Abrikosov and Gor'kov,[17] is that the renormalization constants $\tilde{\omega}/\omega$ and $\tilde{\Delta}/\Delta$ are no longer equal. All the interesting features of Maki's theory and of our generalization stem, as a matter of fact, from that very difference.

B. Linearized Equation for $F(\omega)$

The remainder of this paper is concerned exclusively with the determination of the critical field H_c corresponding to a second-order phase transition. It is then sufficient to retain only the lowest term in the expansion of G or F in powers of $\tilde{\Delta}$. A complete discussion of the generalized Maki theory, valid for all fields up to H_c, is contained in the companion paper.[21] For our present purposes the approximations

$$G(\mathbf{r},\mathbf{r}';\omega)\cong G_A(\mathbf{r},\mathbf{r}';\tilde{\omega}),$$

$$F(\mathbf{r},\mathbf{r}';\omega)\cong\int G_A(\mathbf{s},\mathbf{r};-\tilde{\omega})\tilde{\Delta}(\mathbf{s})G_A(\mathbf{s},\mathbf{r}';\tilde{\omega})d^3s, \quad (4.6)$$

are adequate. The superscript (0) has been suppressed for simplicity. As in Sec. II, G_A is in turn expanded in terms of $(e/m^*c)Ap_y$. According to (4.4) and the remarks that follow,

$$M_F(\omega)=(2\pi N(0)\tau)^{-1}F(\omega), \quad (4.7)$$

where $F(\omega)$ is obtained by setting $\mathbf{r}'=\mathbf{r}$ in (4.6), and similarly for $G(\omega)$. With $F(\omega)$ assumed constant, one may remove the constant $\tilde{\Delta}$ outside the integral over $\mathbf{s}$ and average $\mathbf{r}$ over the sample. The diagrammatic representation introduced in Sec. II can be used again; only contributions from diagrams with no impurity lines need be kept, however.

We first note that only the zero-order term G_0 in the expansion of G_A makes a nonvanishing contribution to $G(\omega)$, since higher-order terms have two or more poles in the same half plane. Thus $\tilde{\omega}=\omega+(2\tau)^{-1}\,\mathrm{sgn}\omega$ as in zero field.[39] By analogy with (2.15) and(2.22), one easily sees that

$$F(\omega)=\pi N(0)\tilde{\Delta}\left[|\tilde{\omega}|^{-1}-\tfrac{1}{2}\sum_j\left(\frac{ev_F}{c}\right)^2\frac{A_j^2 f[k_j\xi(\omega)]}{3|\tilde{\omega}|^3}\right] \quad (4.8)$$

to second order in H.

The diagrams contributing in fourth order are shown in Fig. 10. The black dot refers to the constant factor Δ. Without going into detail, we note that diagrams (b),

[39] This is only true in the framework of the approximation (4.6), i.e., for infinitesimally small Δ.

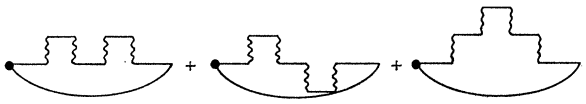

FIG. 11. Stairlike diagrams derived from Fig. 10(a) in the $j=1$ approximation.

(c), and (d) yield 4, 6, and 4 times the contribution of either (a) or (e), respectively: it is sufficient to evaluate (a) and multiply by 16. The general result is complicated since momentum conservation gives only one relation between the indices of the four Fourier components of A. For that same reason the error one makes by neglecting all but the lowest component $A_1=-(4/\pi^2)\,H_c d$ is larger than for the H^2 term. We nevertheless make this approximation for the sake of simplicity. It is then convenient to introduce new stairlike diagrams, each step contributing $\pm$ one unit of x momentum $k_1=\pi/d$ and a factor $(eA_1p_y/2m^*c)$. Thus the new diagrams derived from that shown in Fig. 10(a) are illustrated in Fig. 11. Those obtained by reflection about the base line have been omitted; they contribute an equal amount. The total fourth-order term is therefore

$$32\tilde{\Delta}\left(\frac{2ev_FH_cd}{\pi^2c}\right)^4 N(0)\int_0^{2\pi}\frac{d\varphi}{2\pi}\cos^4\varphi\int_{-1}^{1}\frac{dw}{2}(1-w^2)^2\int\frac{d\epsilon}{(\epsilon+i\tilde{\omega})(\epsilon-i\tilde{\omega})^2(\epsilon+v_Fk_1w-i\tilde{\omega})}$$
$$\times\{(\epsilon-i\tilde{\omega})^{-1}[(\epsilon+v_Fk_1w-i\tilde{\omega})^{-1}+(\epsilon-v_Fk_1w-i\tilde{\omega})^{-1}]+(\epsilon+2v_Fk_1w-i\tilde{\omega})^{-1}(\epsilon+v_Fk_1w-i\tilde{\omega})^{-1}\}.$$

We have neglected to include $k_1^2/2m^*$ in the denominators since it does not affect the final result, as shown in Sec. II. Picking up the residue at $\epsilon=-i\tilde{\omega}$, separating into partial fractions, and performing the angular integrations, one obtains

$$F^{(4)}(\omega)\approx 2\pi N(0)\tilde{\Delta}\left(\frac{2ev_FH_cd}{\pi^2c}\right)^4\frac{4f'[2k_1\xi(\omega)]-f'[k_1\xi(\omega)]}{|\tilde{\omega}|^5}, \tag{4.9}$$

where

$$f'(z)=5\int_0^{2\pi}\frac{d\phi}{2\pi}\cos^4\phi\int_0^1 dw\,\frac{(1-w^2)^2}{1+z^2w^2}$$
$$=(5/4)[f(z)-(1-f(z))/z^2] \tag{4.10}$$

is a new nonlocality function which, like $f(z)$, is normalized to 1 when $z=0$ and decreases as z^{-1} as $z\to\infty$. It is interesting to compare (4.9) to the exact result in the local limit,

$$F^{(4)}(\omega)=\pi N(0)\tilde{\Delta}(ev_F/c)^4(\langle A^4\rangle_{\rm av}/5\,|\,\tilde{\omega}\,|^5).$$

Since $\langle A^4\rangle_{\rm av}=(H_cd)^4/80$, our approximation yields an answer which is $80\times 6(2/\pi^2)^4=0.81$ times the correct one. The error is smaller, but hard to estimate, if nonlocality is important.

It is convenient to write $[\omega_\nu=(2\nu+1)\pi T]$

$$F_\nu=\pi N(0)(1-R_\nu)\tilde{\Delta}_\nu\,|\,\tilde{\omega}_\nu\,|^{-1}. \tag{4.11}$$

Keeping only the $j=1$ contribution in (4.8) and adding (4.9), one obtains

$$R_\nu\approx\tfrac{2}{3}\beta_\nu f(\pi\xi_\nu/d)-\tfrac{2}{5}\beta_\nu^2[4f'(2\pi\xi_\nu/d)-f'(\pi\xi_\nu/d)], \tag{4.12}$$

where $\beta_\nu=(4eH_cd\xi_\nu/\pi^2c)^2$. This should provide a reasonable approximation whenever β_ν^2 is sufficiently small. The structure of the complete series is easily surmised:

$$R_\nu=\sum_{n=1}^{\infty}(-1)^{n-1}(eH_cd\xi_\nu/c)^{2n}f_n(\pi\xi_\nu/d)(2n+1)^{-2}. \tag{4.13}$$

This last expression reduces to the exact result in the local limit ($f_n=1$), which one readily recognizes as the average of $1-(2eA\xi_\nu/c)^{-1}\tan^{-1}(2eA\xi_\nu/c)$ over the sample. By introducing appropriate nonlocality functions $f_n(z)$, whose behavior is qualitatively the same as that of $f(z)$, one can write the general result in this form.

C. Determination of H_c and Convergence Criteria

Substituting (4.11) into (4.7) and (4.5), one finds

$$F_\nu=\pi N(0)\Delta[(1-R_\nu)/(|\,\omega_\nu\,|+(2\tau)^{-1}R_\nu)]. \tag{4.14}$$

Recalling the self-consistency condition (2.5) and using (2.23) and (2.24) to eliminate $N(0)g$, we obtain

$$\ln\frac{T_c}{T}=2\pi T\sum_{\nu=0}^{\infty}\frac{\tilde{\omega}_\nu}{\omega_\nu}\frac{R_\nu}{\omega_\nu+(2\tau)^{-1}R_\nu}$$
$$=2\sum_{\nu=0}^{\infty}\frac{R_\nu\xi_T/\xi_\nu}{(2\nu+1)(2\nu+1+R_\nu\xi_T/l)} \tag{4.15}$$

which, with (4.12), yields the implicit equation for H_c given at the end of our preliminary note on the subject.[20] It is instructive to look at some limiting cases. Thus our previous result for H_c, (2.27), follows if one neglects R_ν in the denominator on the right side of (4.15) and retains only the leading contribution of order β_ν. Referring to (4.13) one easily verifies that the ratio of successive terms in the corresponding series is $(eH_cd\xi_\nu/c)^2[1+(2\omega_\nu\tau)^{-1}f(\pi\xi_\nu/d)]$, provided the inessential difference between different f_n's is neglected. Using the $\nu=0$ term in (2.27) to estimate H_c, one sees that (2.27) is a good approximation if

$$1-t\ll f(\pi\xi/d)(1+\xi_0/l)/[1+(\xi_0/l)f(\pi\xi/d)]. \tag{4.16}$$

In the local limit $(d\gg\xi)f\cong 1$ and (4.16) reduces to $1-t\ll 1$. In the opposite limit $(d\ll\xi)f(\pi\xi/d)\sim d/\xi$ and

the right side of (4.16) becomes $(d\xi_0/\xi^2)(1+d\xi_0/\xi l)^{-1}$, which is bounded by $d\xi_0/\xi^2$ or l/ξ, depending on whether $d/\xi<l/\xi_0$ or vice versa. In this last case $l\sim\xi$, however, since $d\ll\xi$ implies $l\ll\xi_0$. We conclude that (4.16) is equivalent to the simpler restrictions (2.29).

In the dirty limit $\xi_\nu\approx l$, so that R_ν becomes independent of ν and the ν summation can be carried out explicitly:

$$\ln\frac{T_c}{T}=\sum_{\nu=0}^{\infty}\frac{2\rho}{(2\nu+1)(2\nu+1+\rho)}$$
$$=\psi(\tfrac{1}{2}+\tfrac{1}{2}\rho)-\psi(\tfrac{1}{2}). \qquad (4.17)$$

Here $\psi(z)=\Gamma'(z)/\Gamma(z)$ is the logarithmic derivative of the Γ function[40] and $\rho=R_\nu\xi_T/l$ or

$$\rho=(\tau/3\pi T)(ev_F/c)^2$$
$$\times\sum_j A_j^2 f(k_j l)\approx\tfrac{2}{3}\xi_T l(4eH_c d/\pi^2 c)^2 f(\pi l/d), \qquad (4.18)$$

if we retain the leading contribution. This will be justified below. The first expression is a consequence of (4.8), while the second one obtains if one neglects all but the $j=1$ contribution, the resulting error being small, as shown in Sec. II. For $d\ll\xi$ or $d\gg\xi$ one recovers Maki's[7] and Shapoval's[11] results. According to (4.13), our neglect of higher-order terms is justified as long as $(eH_c dl/c)^2\ll 1$. The maximum value of H_c occurs at $T=0$. Using $\psi(\frac{1}{2})=\ln 4\gamma$ and $\psi(z)\cong\ln z$ $(z\gg 1)$,[40] and the BCS weak-coupling relations[2] $\Delta_0(0)=(\pi/\gamma)T_c=v_F/\pi\xi_0$, one finds

$$(4eH_c(0)d/\pi^2 c)^2\approx\tfrac{3}{2}[\pi\xi_0 l f(\pi l/d)]^{-1}. \qquad (4.19)$$

The expansion parameter is therefore small throughout the interval $0<t<1$, provided $l\ll\xi_0 f(\pi l/d)$. This condition is certainly satisfied in the local limit, since $l\ll\xi_0$ by assumption. In the opposite case $(d\ll l\ll\xi_0)$ one finds the restriction $d\xi_0/l^2\gg 1$. We conclude that our generalization of Maki's theory is valid, provided $l\ll\xi_0$ and

$$(l/\xi_0)l\ll d\ll(\xi_0 l)^{1/2}, \qquad (4.20)$$

where the second inequality ensures that Δ and $F(\omega)$ are constant over the film.

Our general result (4.15) is not useful for pure films at low temperatures because the expansion (4.13) does not converge in that range. That it can be summed in the local limit is of academic interest since the underlying assumption of a constant order parameter can only be satisfied if $d\ll\xi_0$, and the exact form of the f_n's in this extreme nonlocal case is not known at present (the error incurred by ignoring $j>1$ contributions increases rapidly with n). Nevertheless, (4.15), together with (4.12), offers a considerable improvement over (2.27) or (4.17) and (4.18) for moderately impure films $(l<\xi_0)$ at intermediate temperatures such that $(eH_c d\xi_\nu/c)^2\ll 1$ or, using (2.27) for a rough estimate,

$$\ln(T_c/T)\ll\min(\xi_T/\xi,\ d\xi_T/\xi^2). \qquad (4.21)$$

This is confirmed by our good fit to Toxen's critical field data for a In-4.6% Sn film[37] down to $t=0.4$, as shown in our preliminary note.[20] A more complete discussion is given in the companion paper.[21]

V. CONSTANT Δ ASSUMPTION

As mentioned before, the results obtained in Secs. II and IV are valid insofar that contributions associated with spatial variations of the order parameter Δ are negligible. Actually, the derivation of (4.15), (4.12), and (4.13) requires that this statement apply to $F(\mathbf{r},\ \mathbf{r};\ \omega)\equiv F(x,\ \omega)$ as well, a seemingly stronger condition. Using the analysis developed in the previous section, we include the effect of the lowest two components in the Fourier expansions of $\Delta(x)$ and $F(x,\omega)$, e.g.,

$$\Delta(x)=\sum_{m=0}^{\infty}\Delta_m\cos(2m\pi x/d), \qquad (5.1)$$

and estimate that $\Delta_1/\Delta_0\sim(eH_c d^2/c)^2$. One is thus led to the criterion (1.10) given in the introduction. As explained there, within the framework of our perturbation approach, (1.10) is a real restriction in the local limit only. It is then inconsistent to keep any terms beyond the leading one of order β_ν or $(eHd\xi_\nu/c)^2$ when substituting (4.12) and (4.13) into (4.15).

The formalism introduced at the beginning of Sec. IV also provides a clear interpretation of Rickayzen's treatment.[22] He assumed Δ constant, but allowed $F(x,\omega)$ to vary across the film. The self-consistency condition (2.3) implies that $\Delta(x)$ does vary appreciably, however, except near T_c, where the GL theory applies. We conclude that it is inconsistent to neglect the spatial dependence of Δ, but not that of $F(x,\omega)$.

A. Simple Criterion

It is assumed that $\Delta(\mathbf{r})$ depends on x alone and is symmetric about $x=d/2$, as implied by (5.1), in accordance with the Saint-James and de Gennes solution of the linearized GL equation for a sufficiently thin film in a parallel magnetic field.[41] Instead of (2.5) and (4.5), (4.7) has self-consistency conditions for each m:

$$\Delta_m=gT\sum_{-\omega_D}^{\omega_D}F_m(\omega), \qquad (5.2)$$

$$\tilde{\Delta}_m(\omega)=\Delta_m+(2\pi N(0)\tau)^{-1}F_m(\omega). \qquad (5.3)$$

[40] W. Magnus and F. Oberhettinger, *Special Functions of Mathematical Physics* (Chelsea Publishing Co., New York, 1947), p. 3.

[41] D. Saint-James and P. G. de Gennes, Phys. Letters **7**, 306 (1963).

$\tilde{\omega}$ remains equal to its constant, zero-field value in the framework of the linearized approximation (4.6). Since the strongest spatial dependence is expected at $H=H_c$, it seems reasonable to restrict one's attention to this case. The diagrammatic representation introduced in Secs. II and IV is easily adapted to the present situation. It is important to keep in mind the special status enjoyed by the $m=0$ components, e.g., the analog of (2.17) for Δ involves $\frac{1}{2}\Delta_{|n'-n''|}$ for $n'\neq n''$, and Δ_0 for $n'=n''$. Combining this result with the analog of (2.9), one obtains

$$F_m(\omega)=2\int(2\pi)^{-3}d^3pF_m(\mathbf{p},\omega),$$

$$F_0(\omega)=\int(2\pi)^{-3}d^3pF_0(\mathbf{p},\omega), \tag{5.4}$$

where

$$F_m(\mathbf{p},\omega)\equiv F(n,n+2m,\mathbf{p}_\perp;\omega)=F(n,n-2m,\mathbf{p}_\perp;\omega).$$

Since the perturbation $(e/m^*c)A(x)p_y$ couples different Fourier components, it is necessary to make simplifying assumptions in order to obtain manageable equations. We neglect all but the lowest component of A as before, retain only the $m=0$ and $m=1$ components of $F(x,\omega)$, $\Delta(x)$, and $\tilde{\Delta}(x)$, and work to second order in H. Typical contributions to $F_0(\mathbf{p},\omega)$ and $F_1(\mathbf{p},\omega)$ are illustrated in Figs. 12 and 13, respectively, where the black dot denotes $\tilde{\Delta}_0$, while the vertical bar with a black dot contributes a factor $\frac{1}{2}\tilde{\Delta}_1$. Diagrams (a) and (b) in Fig. 12 have been considered before. The contribution to $F_0(\omega)$ from diagrams like (c) is $2\times4=8$ times that of (c) (the factor 2 corresponds to reflection about the base line):

$$8(\tfrac{1}{2}\tilde{\Delta}_1)\left(\frac{2ev_FH_cd}{\pi^2c}\right)^2N(0)\,\frac{1}{2}\int_{-1}^{1}\tfrac{1}{2}(dw)\,(1-w^2)\int\frac{d\epsilon}{(\epsilon^2+\tilde{\omega}^2)\,(\epsilon+v_Fk_1w-i\tilde{\omega})\,(\epsilon+2v_Fk_1w-i\tilde{\omega})}$$
$$=-\pi N(0)\tfrac{1}{3}\beta(\omega)f_{01}(\pi\xi(\omega)/d)\tilde{\Delta}_1/\tilde{\omega},$$

where

$$f_{01}(z)=2f(2z)-f(z). \tag{5.5}$$

Going on to $F_1(\omega)$, we note that diagram (a) in Fig. 13 contributes [the factor 2 comes from (5.4) for $m=1$]

$$2\tfrac{1}{2}(\tilde{\Delta}_1)\left(\frac{2ev_FH_cd}{\pi^2c}\right)^2N(0)\int_{-1}^{1}\tfrac{1}{2}(dw)\int\frac{d\epsilon}{(\epsilon+i\tilde{\omega})\,(\epsilon+2v_Fk_1w-i\tilde{\omega})}=\pi N(0)\,g(2\pi\xi(\omega)/d)\tilde{\Delta}_1/\tilde{\omega},$$

where

$$g(z)=(\tan^{-1}z)/z. \tag{5.6}$$

The contribution from diagrams like (b) and (c) is $2\times4=8$ times that of their sum

$$8(\tfrac{1}{2}\tilde{\Delta}_1)\left(\frac{2ev_FH_cd}{\pi^2c}\right)^2N(0)\,\frac{1}{2}\int_{-1}^{1}\tfrac{1}{2}(dw)\,(1-w^2)\int\frac{d\epsilon}{(\epsilon+i\tilde{\omega})\,(\epsilon+2v_Fk_1w-i\tilde{\omega})^2}$$
$$\times[(\epsilon+v_Fk_1w-i\tilde{\omega})^{-1}+(\epsilon+3v_Fk_1w-i\tilde{\omega})^{-1}]=-\pi N(0)\tfrac{2}{3}\beta(\omega)f_{11}(\pi\xi(\omega)/d)\tilde{\Delta}_1/\tilde{\omega},$$

where

$$2f_{11}(z)=9f(3z)-8f(2z)+f(z). \tag{5.7}$$

Finally, diagram (d) contributes the same amount as diagram (c) of Fig. 12 with $\frac{1}{2}\tilde{\Delta}_1$ replaced by $\tilde{\Delta}_0$. Diagrams like that shown on Fig. 14 are ignored, since their contribution is proportional to $\tilde{\Delta}_2$, which we neglect in order to get a closed system of equations. Although this is a weak point in the argument, we believe that it leads to adequate estimates. Combining the results obtained above, one finds

$$F_0\cong\pi N(0)[(1-\tfrac{2}{3}\beta f)\tilde{\Delta}_0-\tfrac{1}{3}\beta f_{01}\tilde{\Delta}_1]/|\tilde{\omega}|,$$
$$F_1\cong\pi N(0)[-\tfrac{2}{3}\beta f_{01}\tilde{\Delta}_0+(g-\tfrac{2}{3}\beta f_{11})\tilde{\Delta}_1]/|\tilde{\omega}|. \tag{5.8}$$

Substituting into (5.3) one gets two equations for $\tilde{\Delta}_0$, $\tilde{\Delta}_1$ in terms of Δ_0, Δ_1; solving them and substituting back into (5.8), one obtains

$$F_0\cong\pi N(0)\,(N_0\Delta_0-\tfrac{1}{3}\beta f_{01}\,|\,\tilde{\omega}\,|\,\Delta_1)/D, \tag{5.9a}$$
$$F_1\cong\pi N(0)\,(-\tfrac{2}{3}\beta f_{01}\,|\,\tilde{\omega}\,|\,\Delta_0+N_1\Delta_1)/D, \tag{5.9b}$$

where

$$N_0=(1-\tfrac{2}{3}\beta f)[|\,\omega\,|+(2\tau)^{-1}(1-g+\tfrac{2}{3}\beta f_{11})]+\tau^{-1}(\tfrac{1}{3}\beta f_{01})^2,$$
$$N_1=(g-\tfrac{2}{3}\beta f_{11})\,(|\,\omega\,|+(2\tau)^{-1}\tfrac{2}{3}\beta f)+\tau^{-1}(\tfrac{1}{3}\beta f_{01})^2, \tag{5.10}$$

and

$$D=[|\,\omega\,|+(2\tau)^{-1}\tfrac{2}{3}\beta f][|\,\omega\,|+(2\tau)^{-1}(1-g+\tfrac{2}{3}\beta f_{11})]$$
$$-2(2\tau)^{-2}(\tfrac{1}{3}\beta f_{01})^2.$$

Substituting (5.9) into (5.2) one gets two homogeneous equations involving Δ_0 and Δ_1. Solving the second one

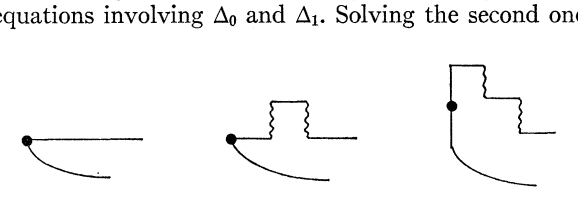

FIG. 12. Stairlike diagrams contributing to $F_0(\mathbf{p},\omega)$; the vertical bar with a black dot carries a factor $\frac{1}{2}\tilde{\Delta}_1$.

for Δ_1/Δ_0 and using the first one to eliminate $N(0)g$, one obtains

$$\Delta_1/\Delta_0 \cong -\Big(\sum_{\omega>0} \tfrac{2}{3}\beta f_{01}(\tilde{\omega}/D)\Big) \times \Big(\sum_{\omega>0} \{\tilde{\omega}[1-g-\tfrac{2}{3}\beta(f-f_{11})] - \tilde{\omega}\tfrac{1}{3}\beta f_{01}(\Delta_1/\Delta_0)\} D^{-1}\Big)^{-1}. \tag{5.11}$$

Since we are interested in the case where Δ_1/Δ_0 is small, the last term in the denominator of (5.11) may be safely neglected. Considerable simplification occurs for $d \gg \xi$ or $d \ll \xi$.

In the first case

$$f \cong f_{01} \cong f_{11} \cong 1 \quad \text{and} \quad 1-g \cong \tfrac{1}{3}[2\pi\xi(\omega)/d]^2.$$

If (1.10) holds, all the terms proportional to β in the denominator of (5.11) can be neglected, and the remaining expression has the same dependence on ω as the summand in the numerator, i.e., $(\tilde{\omega}D)^{-1}$. Thus

$$\Delta_1/\Delta_0 \approx -2(2/\pi^3)^2(eH_c d^2/c)^2 \ll 1. \tag{5.12}$$

In the second case $g \cong \frac{1}{4}d/\xi(\omega)$, $f \cong \frac{3}{4}d/\xi(\omega)$, but $f_{01} \cong \frac{3}{2}\pi^{-2}[d/\xi(\omega)]^2$ and $f_{11} \cong (8\pi^2)^{-1}[d/\xi(\omega)]^3$, as one easily infers from (5.6), (2.20), (5.5), and (5.7) and the asymptotic expression $\tan^{-1}z \cong \frac{1}{2}\pi - z^{-1}$. The denominator of (5.11) reduces to $\sum_{\omega>0}\tilde{\omega}/D$, and is again proportional to the numerator, since βf_{01} is independent of ω. One obtains

$$\Delta_1/\Delta_0 \approx (4/\pi^3)^2(eH_c d^2/c), \tag{5.13}$$

which again suggests that the spatial dependence of Δ is negligible if (1.10) holds. It is gratifying that (5.13) is consistent with the explicit dependence of Δ derived in that limit by Shapoval[11] for $eH_c d^2/c \gtrsim 1$, i.e., outside the range of convergence of our perturbation expansion.

For intermediate values of d one may use the convenient formula

$$\Delta_1/\Delta_0 \approx \tfrac{2}{3}\beta f_{01}(1-g)^{-1}, \tag{5.14}$$

which interpolates between (5.12) and (5.13), to show that $|\Delta_1|/\Delta_0 \lesssim (eH_c d^2/c)^2$; we conclude that (1.10) appears to be a sufficient criterion in general.

Using (5.14) to express Δ_1 in terms of Δ_0 in the equation obtained by substituting (5.9a) into (5.3), and eliminating $N(0)g$ with the help of (2.23) and (2.24), one obtains

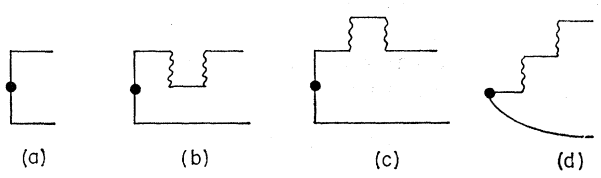

FIG. 13. Stairlike diagrams retained in the calculation of $F_1(\mathbf{p}, \omega)$.

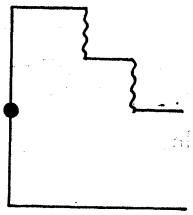

FIG. 14. Neglected stairlike diagram contributing to $F_1(\mathbf{p}, \omega)$; the vertical bar with a black dot carries a factor $\frac{1}{2}\bar{\Delta}_2$.

$$\ln(T_c/T) = 2\pi T \sum_{\omega>0} \tfrac{2}{3}\beta(\tilde{\omega}P/\omega D), \tag{5.15}$$

with

$$P = f[\omega + (2\tau)^{-1}(1-g+\tfrac{2}{3}\beta f_{11})] - \tfrac{1}{3}\beta f_{01}^2[(2\tau)^{-1} + \omega(1-g)^{-1}].$$

Equation (5.15) should be compared with (4.15) and (4.12), which determine H_c if Δ is assumed constant over the sample. Subtracting P/D from the corresponding expression derived from (4.15), with $R = \frac{2}{3}\beta$, viz., $f[\omega + (2\tau)^{-1}\frac{2}{3}\beta f]^{-1}$, one finds the correction arising from the neglected spatial dependence:

$$-\tfrac{1}{3}\beta[f_{01}^2/(1-g)][\omega/\omega + (2\tau)^{-1}\tfrac{2}{3}\beta f] \times [\omega + (2\tau)^{-1}(1-g+\tfrac{2}{3}\beta f)/D].$$

The last factor is essentially $[\omega + (2\tau)^{-1}\frac{2}{3}\beta f]^{-1}$, since one may neglect $\frac{2}{3}\beta f$ in the numerator and approximate D by $[\omega + (2\tau)^{-1}\frac{2}{3}\beta f][\omega + (2\tau)^{-1}(1-g)]$. The relative error made by assuming Δ constant and working to second order in H_c, i.e., retaining the leading term in (4.12), is therefore

$$\tfrac{1}{3}\beta[f_{01}^2/f(1-g)][\omega/\omega + (2\tau)^{-1}\tfrac{2}{3}\beta f], \tag{5.16}$$

which is bounded by $(eH_c d^2/c)^2$ if $d \gg \xi$ and by $(eH_c d^2/c)^2(d/\xi)$ if $d \ll \xi$. It is small in the local limit if (1.10) is satisfied and is always negligible in the extreme nonlocal limit as long as $\beta \ll 1$.

The inclusion of the next term in (4.12), which may be written as $-(6/5)\beta^2 f_2$, gives rise to a contribution

$$-(6/5)\beta^2 f_2(\omega/[\omega + (2\tau)^{-1}\tfrac{2}{3}\beta f]^2)$$

on the right side of (4.15). The error incurred by retaining the leading term only can therefore be estimated as

$$(9/5)\beta(f_2/f)[\omega/\omega + (2\tau)^{-1}\tfrac{2}{3}\beta f]. \tag{5.17}$$

Recalling that the asymptotic behaviors of f_2 and f are the same, we note that the ratio of (5.16) to (5.17) is of order $(d/\xi)^2$ if $d \gg \xi$ and $(d/\xi)^3$ in the opposite case. Our exact knowledge of the higher-order terms in (4.13) in the *local* limit is therefore mostly of academic interest. On the other hand, (4.15), together with (4.12), should provide reasonably accurate results when nonlocality is important.

B. Critique of Rickayzen's Theory

Rickayzen[22] arrived at the following equation for the critical field in the dirty local limit ($l \ll \xi_0, d$):

$$\ln(T_c/T) = \langle \psi[\tfrac{1}{2} + (\tau/3\pi T)(ev_F H_c x/c)^2] - \psi(\tfrac{1}{2}) \rangle_{\mathrm{av}}. \tag{5.18}$$

Since Δ was treated as constant in the derivation, our task is to criticize (5.18) as an alternative to Maki's equation for H_c,[7] obtained under the same assumptions, in which the average is taken inside the argument of the di-Γ function ψ. This difference results in a value of $H_c(0)$ greater than Maki's by a factor of 1.57. In either case the criterion (1.10) leads to the condition $d^2 \ll \xi_0 l$, which was first directly obtained by de Gennes.[19] Rickayzen's claim that (5.18) is valid in the opposite case, corresponding to surface superconductivity,[41] cannot be accepted and need not be discussed further. His apparently good fit to Toxen's data on a In-4.6% Sn film[37] is deceptive, since it can be shown to require an unrealistically small value of the mean free path.

The derivation of (5.18) is based on the following equations[22]:

$$1 = gT \sum_{\omega} \langle \lambda(\mathbf{r}, \omega) \rangle_{\mathrm{av}}, \tag{5.19}$$

$$\lambda(\mathbf{r}, \omega) = \lambda_0(\mathbf{r}, \omega) + (2\pi N(0)\tau)^{-1} \int K_0(\mathbf{r}, \mathbf{s}; \omega) \lambda(\mathbf{s}, \omega) d^3 s, \tag{5.20}$$

where

$$\lambda_0(\mathbf{r}, \omega) = \int K_0(\mathbf{r}, \mathbf{s}; \omega) d^3 s$$

and

$$K_0(\mathbf{r}, \mathbf{r}'; \omega) = G_0(\mathbf{r}', \mathbf{r}; -\omega) G_0(\mathbf{r}', \mathbf{r}; \omega) \times \exp[-i(2eH_c x/c)(y - y')], \tag{5.21}$$

which were obtained by looking for an instability in the two-particle normal-state propagator in the ladder approximation. We find it more instructive to consider the linearized equation (4.6) which, together with (2.3), (4.5), and (4.7) determine the order parameter in the limit $\Delta \to 0$. One readily verifies that $\lambda(\mathbf{r}, \omega) = F(x, \omega)/\Delta$; (5.20) follows if (4.5) and (4.7) are substituted into (4.6), while (5.19) obtains if (2.3) is averaged over the sample, in accordance with the assumed constancy of Δ. The *Ansatz*

$$G_A(\mathbf{r}, \mathbf{r}'; \omega) = G_0(\mathbf{r}, \mathbf{r}'; \omega) \exp[i(eHx/c)(y - y')]$$

leading to (5.21) is justified for $d \gg l$.[22] Rickayzen solved (5.20) approximately by neglecting the variation of λ over the range l of the kernel K_0:

$$\lambda(\mathbf{r}, \omega) \cong \lambda_0(\mathbf{r}, \omega)[1 + (2\pi N(0)\tau)^{-1} \lambda(\mathbf{r}, \omega)],$$

i.e.,

$$\lambda(x, \omega) \cong \pi N(0)[|\omega| + \tfrac{2}{3} v_F^2 \tau (eH_c x/c)^2]^{-1}, \tag{5.22}$$

using the well-known result for the Fourier transform of K_0 in zero field, viz., $\pi N(0)(|\tilde{\omega}| + \frac{1}{6} v_F^2 \tau q^2)^{-1}$ for $|\omega| \tau \ll 1$ and $ql \ll 1$. The above-mentioned identification allows one to check whether Δ is indeed constant. Substituting (5.22) into the equivalent of (2.3),

$$\Delta(x)/\Delta = gT \sum_{-\omega_D}^{\omega_D} \lambda(x, \omega), \tag{5.23}$$

and using (2.23) and (2.24), together with the definition of the di-Γ function implicit in (4.17), one finds

$$\Delta(x)/\Delta \cong \{\ln(2\gamma\omega_D/\pi T) - \psi[\tfrac{1}{2} + (\tau/3\pi T)(eH_c x/c)^2] + \psi(\tfrac{1}{2})\}[\ln(2\gamma\omega_D/\pi T_c)]^{-1}, \tag{5.24}$$

which leads to (5.18) upon averaging over the film. One easily verifies that the expression on the right of (5.25) is not close to 1 except in the GL range $1 - t \ll 1$. Thus it is inconsistent to use (5.19) in general, and we are led to the conclusion stated at the beginning of this section.

The results of Sec. IV pertaining to the local limit are recovered if $F(x, \omega)$ is assumed constant and Rickayzen's approach is modified accordingly. Since $\Delta(x)$ and $\tilde{\Delta}(x, \omega)$ are then constant as well, (5.20) or, equivalently, (4.6), is solved as follows:

$$F(\omega) = \tilde{\Delta}(\omega) \langle \lambda_0(x, \omega) \rangle_{\mathrm{av}} = \Delta[\langle \lambda_0(x, \omega) \rangle_{\mathrm{av}}^{-1} - (2\pi N(0)\tau)^{-1}]^{-1}. \tag{5.25}$$

$\lambda_0(x, \omega)$ may again be expressed in terms of the Fourier transform of K_0 in zero field,

$$K_0(\mathbf{q}, \omega) = \int \frac{d^3 p}{(2\pi)^3} G_0(\mathbf{p}, -\omega) G_0(\mathbf{q} - \mathbf{p}, \omega) = [2\pi N(0)/v_F q] \tan^{-1}(q v_F / 2\tilde{\omega})$$

by setting $q = 2eH_c x/c$ in accordance with (5.21). This result is not restricted to the dirty limit and is valid for $q \ll p_F$. Substituting into (5.25) and (2.5) one obtains (4.15) with

$$R_\nu = 1 - \left\langle \frac{\tan^{-1}(2eH_c x \xi/c)}{2eH_c x \xi_\nu/c} \right\rangle_{\mathrm{av}}. \tag{5.26}$$

As shown in the first part of this section, however, only the leading term in the expansion of (5.26) in powers of $2eH_c x \xi_\nu/c$, viz., $\frac{1}{3}(2eH_c \xi_\nu/c)^2 \langle x^2 \rangle_{\mathrm{av}} = (eH_c d \xi_\nu/3c)^2$, is meaningful, since the higher-order terms are smaller than the error due to the neglected spatial dependence of $F(x, \omega)$. In the dirty limit these higher-order terms are negligible even at $T = 0$, so that Maki's theory is certainly the correct one.

VI. SUMMARY

References to the most important equations derived in the course of this investigation are indicated below.

The restrictions ensuring constancy of the order parameter and rapid convergence limit the range of thickness in which various formulas apply from above and below, respectively. Nonlocal effects are governed by the function $f(z)$, defined in (2.20).

The generalized GL equations (2.34) and (2.39) valid close to T_c under the restrictions (2.29) and (2.30) involve the Fourier transform of the bulk weak-field kernel (2.37) evaluated at the discrete allowed wave vectors $k_j=j\pi/d$. The expressions (3.3) and (3.4) for the Fourier coefficients of the vector potential should enable one to include the effect of a net transport current. In its absence, the critical field H_c for a second-order transition is given by (2.27) or (3.11), while (3.14) gives the critical ratio below which the thermodynamic transition becomes first order.

Maki's equation (4.17) for H_c, generalized according to (4.18), is valid at all temperatures in the dirty limit ($l\ll\xi_0$) under the restrictions (4.20).

The expression (4.15), together with (4.12), valid in the range (4.21), provides the best answer for moderately impure samples at intermediate temperatures.

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Raman Scattering by Coupled Optical-Phonon–Plasmon Modes in GaAs

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Raman scattering by coupled optical-phonon–plasmon modes has been studied in five differently doped GaAs samples in order to determine the linewidths and polarization of the coupled modes. The linewidths have been related to a lifetime which is predominantly due to individual electron collisions, although evidence is presented for Landau damping in the purest sample studied. The polarization data show that the plasma Raman scattering is comparable in magnitude to the phonon Raman scattering. The excitation wavelength was 9698 Å from the ionized xenon laser.

I. INTRODUCTION

WE have studied Raman scattering from five differently doped GaAs samples in which the conduction-electron plasma frequency varied from one-quarter to twice the longitudinal optical-phonon frequency. Mooradian and Wright[1] (called MW hereafter) have performed the only previous experiment on a coupled electron plasma-phonon system, although there have been numerous theoretical papers.[2] MW showed that the frequency and damping of the coupled modes change as a function of carrier concentration or plasma frequency. At low plasma frequencies, the modes are only weakly coupled and there exists a reasonably pure plasma line and the longitudinal (LO) and transverse (TO) optical-phonon lines. At high plasma frequencies, the modes are again uncoupled with the LO phonon approaching the TO phonon frequency. For intermediate cases, the modes have mixed phonon-plasma character with the mixing being largest where the uncoupled dispersion curves would cross.

One motivation for the present experiment was to determine the linewidths of the coupled system. The linewidths have been related to a phenomenological damping constant which is predominantly determined by collision damping. However, evidence for Landau damping in the purest sample studied is presented. The polarization of the Raman scattered light has been determined in order to discriminate among the various mechanisms which can produce phonon[3] and/or plasmon Raman scattering.[4,5] The published results of MW were obtained with unoriented samples for which

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