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Critical-Field Ratio H_{c3}/H_{c2} for Pure Superconductors outside the Ginzburg-Landau Region. II. $T \simeq T_c$*†

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In Paper I we found the appropriate generalization of Gor'kov's linearized gap equation for a pure, semi-infinite weak-coupling superconductor in a magnetic field, separated from vacuum or an insulator by a specularly reflecting surface. In that paper we used the gap equation to study the surface-nucleation critical field H_{c3} at $T \simeq 0°\mathrm{K}$. Here we study the region $T \simeq T_c$ and find the first three nontrivial terms in an expansion of the ratio $H_{c3}(T)/H_{c2}(T)$ to be $1.695[1+0.614(1-t)-0.577(1-t)^{3/2}]$, where $t \equiv T/T_c$. The term linear in $1-t$ has been found previously, but the last term is new. For T close enough to T_c we show that the system is accurately described by the linearized Ginzburg-Landau equation with the usual boundary condition and thus regain the results of Saint-James and de Gennes. At lower temperatures the pair wave function has a slowly varying component which satisfies a finite-order differential equation and a surface component which does not. An analysis of the surface component gives an effective boundary condition on the slowly varying part; from this condition the field H_{c3} is derived. In combination with the results of Paper I we propose an interpolation formula for the entire temperature range below T_c. A comparison with the available experimental data is encouraging.

I. INTRODUCTION

In Paper I[1] we obtained the proper linearized gap equation (LGE) for studying the surface nucleation critical field H_{c3} for a semi-infinite pure superconductor separated from vacuum or an insulator by a specularly reflecting plane boundary. The result is a linear integral equation whose minimum eigenvalue is related to H_{c3}. Because of complications related to the presence of a boundary, we are unable to solve this equation at arbitrary temperature. In I,[1] we showed that at zero temperature the LGE could be put into a form amenable to a variational treatment and we found a lower bound estimate of the ratio H_{c3}/H_{c2} to be 1.925. By perturbation theory we were then able to estimate the leading term in the temperature dependence of the ratio to be $H_{c3}(T)/H_{c2}(T)-H_{c3}(0)/H_{c2}(0) \simeq 0.05(T^2/T_c^2) \times \ln(T/T_c)H_{c3}(0)/H_{c2}(0)$. The vanishing slope and small coefficient of this correction suggests that the ratio H_{c3}/H_{c2} may well remain in the neighborhood of 1.9 for a substantial portion of the temperature range below T_c.

For temperatures close to T_c, the smallness of the magnetic fields of interest leads to the existence of a small, dimensionless parameter proportional to $(1-T/T_c)^{1/2}$ in terms of which an expansion of our LGE becomes possible. Indeed, it is by means of just such an expansion that Gor'kov[2] was able to show the validity of the Ginzburg-Landau (GL) equation[3] in the interior of a pure superconductor for temperatures sufficiently close to critical (the GL region). Further, using this equation and taking account of the surface by means of a boundary condition, Saint-James and de Gennes (SJdG)[4] showed that $H_{c3}/H_{c2}=1.695$ in the GL region.[5] It will be our purpose in the following to analyze our LGE (which already incorporates the effects of the boundary) near T_c to determine, first, whether it reproduces the results of SJdG and, further, the corrections to these results for temperatures slightly beyond the GL region. In particular, we will demonstrate that the boundary condition used by SJdG fully incorporates the effect of the boundary to the same order of approximation as is involved in deriving the GL equation, and will find the modification of the boundary condition needed in higher orders.

In Sec. II we begin the discussion by expanding our LGE in powers of $(1-T/T_c)^{1/2}$ under the assumption

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[1] C.-R. Hu and V. Korenman, Phys. Rev. **178**, 684 (1969). We will henceforth refer to this paper as I and refer to equations from I, as I followed by the equation number.

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

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

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

[5] The validity of the GL equation for impure superconductors in a wide temperature range was shown in L. P. Gor'kov', Zh. Eksperim. i Teor. Fiz. **37**, 1407 (1959) [English transl.: Soviet Phys.—JETP **10**, 998 (1960)]. The ratio 1.695 for H_{c3}/H_{c2} holds whenever the GL equation does.

that the pair wave function $\Delta(\mathbf{r})$ is everywhere slowly varying (*vide infra*). We then demonstrate that in the lowest order of expansion this assumption is self-consistent, and that the GL equation and SJdG boundary condition emerge as consequences. In higher order, however, the slowly varying condition cannot be maintained, and in Sec. III we repeat the expansion allowing $\Delta(\mathbf{r})$ to contain both a slowly varying component and a component which is rapidly varying, but which is nonzero only in the vicinity of the boundary. Although the complete pair wave function $\Delta(\mathbf{r})$ always satisfies the SJdG boundary condition, the slowly varying part in general satisfies a modified condition which is determined from an analysis of the behavior of the boundary component. From this analysis we find corrections to the SJdG value of H_{c3}/H_{c2} proportional to $1-T/T_c$ and $(1-T/T_c)^{3/2}$. In Sec. IV our results are compared with previous calculations of these corrections. In Sec. V the correction terms are combined with the results of I, and we propose an interpolation formula giving H_{c3}/H_{c2} at all temperatures below T_c. This formula is then compared with the available experimental data and shows encouraging agreement.

II. EXPANSION OF LINEARIZED GAP EQUATION ASSUMING Δ TO BE SLOWLY VARYING

Our analysis is based on the LGE found in I[1] [see Eq. (I-28)]:

$$\Delta(\mathbf{r})=\int_{z'>0} d\mathbf{r}'k_0(|\mathbf{r}-\mathbf{r}'|)\exp\left[-2ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]\Delta(\mathbf{r}')$$
$$+\int_{z'>0} d\mathbf{r}'k_0(|\mathbf{r}-R_{z'}\mathbf{r}'|)$$
$$\times\exp\left[-2ie\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]\Delta(\mathbf{r}'),\quad(1)$$

where the integral phase factor in the second term involves a path along straight lines from $\mathbf{r}'$ to $\mathbf{r}$ via $\mathbf{r}_1$, while that in the first involves a simple straight-line path. The sample is taken to occupy the half-space $z>0$, $R_z\mathbf{r}$ denotes reflection of $\mathbf{r}$ in the sample surface, and the point $\mathbf{r}_1$ is the intersection with the $z=0$ plane of the straight line joining $\mathbf{r}$ and $R_{z'}\mathbf{r}'$. The kernel $\mathbf{k}_0$ is

$$k_0(\mathbf{r})\equiv|\lambda|T(m/2\pi)^2R^{-2}\sum_n e^{-2|\omega_n|R/v_F},\quad(2)$$

with $\omega_n\equiv(2n+1)\pi T$, where we have taken $\hbar=c=k_B=1$, and λ is the interaction strength in the BCS model. We remind the reader that Eq. (1) describes the behavior of a "smoothed" pair wave function [see remarks after (I-21)], where variations on the scale of the interatomic spacing p_F^{-1} have been averaged out. Our assumption of specular reflection requires the exact Δ to vanish at the boundary, but the smoothed Δ, which we shall always consider henceforth, is readily shown from Eq. (1) to satisfy the boundary condition (BC)

$$\hat{n}_z\cdot\mathfrak{D}(\mathbf{r})\Delta(\mathbf{r})|_{z=0}=0,\quad(3)$$

where

$$\mathfrak{D}(\mathbf{r})\equiv\nabla+2ie\mathbf{A}(\mathbf{r})\quad(4)$$

is the gauge-invariant gradient operator.

From Eq. (2) we see that the range of $\mathbf{k}_0$ is given by

$$\xi_0(T)\equiv v_F/2\pi T,\quad[\xi_0\equiv\xi_0(T_c)].\quad(5a)$$

A second length in the problem is ξ_H:

$$\xi_H\equiv(2eH)^{-1/2}.\quad(5b)$$

We will henceforth be concerned only with values of H equal to the nucleation field H_{c3}, whereupon ξ_H will become a definite function of T diverging at T_c. In fact, under the assumption that the temperature variation of H_{c3} in the GL region is that found by SJdG, which assumption we can verify *a posteriori*, $\xi_H\propto\xi_0(1-t)^{-1/2}\gg\xi_0$, where $t\equiv T/T_c$. The lengths ξ_H and ξ_0 will set the scale by which we measure the variation of $\Delta(\mathbf{r})$. More precisely, a function $F(\mathbf{r})$ will be called "slowly varying" (SV) at $\mathbf{r}$ if it satisfies the gauge-invariant condition

$$|\mathfrak{D}(\mathbf{r})F(\mathbf{r})|\lesssim\xi_H^{-1}|F(\mathbf{r})|,\quad(6)$$

and "rapidly varying" (RV) at $\mathbf{r}$ if

$$|\mathfrak{D}(\mathbf{r})F(\mathbf{r})|\sim\xi_0^{-1}|F(\mathbf{r})|.\quad(7)$$

Further, a function will be called "everywhere slowly varying" (EVS) if Eq. (6) holds for all values of $\mathbf{r}$ inside the sample.

In Gor'kov's[2] microscopic derivation of the GL equation for infinite samples he assumed that the pair wave function $\Delta(\mathbf{r})$ is ESV for T near T_c. The LGE for the infinite sample case is the first term of Eq. (1) with no restriction on the domain of integration. Under the ESV assumption one can expand $\Delta(\mathbf{r}')$ in a Taylor series about $\mathbf{r}$, expand the exponential, and find the infinite-order differential equation with constant coefficients[6]

$$\Delta(\mathbf{r})=a_0\Delta(\mathbf{r})+(3!)^{-1}a_2\mathfrak{D}(\mathbf{r})^2\Delta(\mathbf{r})$$
$$+(5!)^{-1}a_4[\mathfrak{D}(\mathbf{r})^4+(2eH)^2]\Delta(\mathbf{r})+(7!)^{-1}a_6[\mathfrak{D}(\mathbf{r})^6$$
$$+5(2eH)^2\mathfrak{D}(\mathbf{r})^2-2(2eH)^2\mathfrak{D}_H(\mathbf{r})^2]\Delta(\mathbf{r})+\cdots\quad(8)$$

with

$$\mathfrak{D}_H(\mathbf{r})\equiv(\mathbf{H}\cdot\mathfrak{D}(\mathbf{r}))/H\quad(9)$$

and

$$a_n\equiv\int R^nk_0(R)d\mathbf{R}.\quad(10)$$

The assumed ESV nature of $\Delta(\mathbf{r})$ and the range of the

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[6] See, for example, L. Tewordt, Z. Physik. **184**, 319 (1965); E. Helfand and N. R. Werthamer, Phys. Rev. **147**, 288 (1966).

kernel mentioned above together ensure that successive terms on the right-hand side of Eq. (8) are reduced by a factor $(\xi_0/\xi_H)^2 \propto (1-t)$, so that retention of a given number of terms will give accuracy in any computed quantity up to the corresponding order in $1-t$. In particular, retention of only the first two terms yields the linearized GL equation, while the fact that Eq. (8), truncated at any finite order, does admit ESV solutions, demonstrates the self-consistency of the original assumption.

The LGE for the present case, Eq. (1), differs from that for the infinite medium case only for points within about ξ_0 of the boundary. Although the boundary provides a mechanism for spoiling the slowly varying nature of the solution we will first study Eq. (1) under the assumption that it still admits ESV solutions for the pair-wave function, and check the self-consistency of that assumption at a later stage.

It is convenient to continue our discussion in terms of an alternative form of the LGE found in I [see (I-32)] in which the inherent surface terms are separated out:

$$\begin{aligned}\Delta(\mathbf{r}) = &\int d\mathbf{R}\, k_0(|\mathbf{R}|) \exp[\mathbf{R}\cdot\mathfrak{D}(\mathbf{r})]\Delta(\mathbf{r}) \\ &+\int_{z'<0} d\mathbf{r}' k_0(|\mathbf{r}-\mathbf{r}'|) \exp[(R_{z'}\mathbf{r}_1-\mathbf{r})\cdot\mathfrak{D}(\boldsymbol{\rho})] \\ &\times\{\exp[(R_{z'}\mathbf{r}'-R_{z'}\mathbf{r}_1)\cdot\mathfrak{D}(\boldsymbol{\rho})] \\ &\qquad -\exp[(\mathbf{r}'-R_{z'}\mathbf{r}_1)\cdot\mathfrak{D}(\boldsymbol{\rho})]\}\Delta(\boldsymbol{\rho})|_{\rho=\mathbf{r}}. \qquad (11)\end{aligned}$$

Under the ESV assumption about $\Delta(\mathbf{r})$ the first term of Eq. (11) will reproduce the expansion of Eq. (8) while the second term will be the contribution from the vicinity of the boundary. Since $\mathfrak{D}(\mathbf{r})$ acting on $\Delta(\mathbf{r})$ is equivalent to a factor $\sim\xi_H^{-1}$, successive terms in the expansion of the exponential will contain successively higher powers of ξ_0/ξ_H, so that we have a natural expansion of the LGE. To second order we have

$$\Delta(\mathbf{r}) = a_0\Delta(\mathbf{r}) + \tfrac{1}{6}a_2\mathfrak{D}(\mathbf{r})^2\Delta(\mathbf{r}) + \mathrm{SLT}(II), \qquad (12)$$

where the coefficients a_n in the "bulk terms" are defined in Eq. (10). The "surface-layer terms" (SLT) to this order are[7]

$$\mathrm{SLT}(II) = -2\chi_1(z)\mathfrak{D}_z(\mathbf{r})\Delta(\mathbf{r}) + 2z\chi_1(z)\mathfrak{D}_z(\mathbf{r})^2\Delta(\mathbf{r}), \quad (13)$$

where

$$\chi_1(z) \equiv \int_{z'<0} d\mathbf{r}' z' k_0(|\mathbf{r}-\mathbf{r}'|). \qquad (14)$$

Finally the constants a_n are well known.[8] We shall give their values below.

We may now demonstrate the self-consistency of the ESV assumption and also the validity of the SJdG approach to this order. We first point out that since the boundary condition, Eq. (3), is implied by Eq. (11), it should also be implied by the expansion of Eq. (11) to any order. That this is so to the present order is easily verified by applying $\mathfrak{D}_z(\mathbf{r})$ to Eq. (12), setting $z=0$, and using the identity $[d\chi_1(z)/dz]|_{z=0} = \frac{1}{2}a_0$, which follows from Eqs. (10) and (14). The result is

$$\mathfrak{D}_z(\mathbf{r})\Delta(\mathbf{r})|_{z=0} = \tfrac{1}{6}a_2\mathfrak{D}_z\mathfrak{D}(\mathbf{r})^2\Delta(\mathbf{r}) \simeq 0$$

to the order considered. The demonstration is completed by showing that SLT (II) vanishes to this order, since the remaining equation admits ESV solutions.

The vanishing of SLT (II) is most easily shown in a gauge where[9] $A_z=0$ so that a Taylor-series expansion of Δ and its spatial derivatives with respect to z becomes a natural expansion in powers of ξ_0/ξ_H which can be truncated at the order of interest. The Taylor series about $z=0$ is appropriate since the surface terms vanish for $z \gtrsim \xi_0$ due to the z dependence of χ_1. Then we have

$$\begin{aligned}\mathrm{SLT}\ (II) = &-2\chi_1(z)\{[\nabla_z\Delta(\mathbf{r})]_{z=0} + z[\nabla_z{}^2\Delta(\mathbf{r})]_{z=0} + \cdots\} \\ &+2z\chi_1(z)\{\nabla_z{}^2\Delta(\mathbf{r})|_{z=0} + \cdots\} \\ = &-2\chi_1(z)\mathfrak{D}_z(\mathbf{r})\Delta(\mathbf{r})|_{z=0} = 0, \qquad (15)\end{aligned}$$

where we have imposed the boundry condition. Thus we have shown, to order $(\xi_0/\xi_H)^2 \propto 1-t$, that the LGE admits ESV solutions, that these solutions satisfy the GL equation throughout the sample, and that the entire effect of the boundary is contained in the simple boundary condition, Eq. (3), which is just that assumed by SJdG. The critical field H_{c3} found by SJdG is then correct to order $1-t$, except for the possibility (ruled out in the next section) that a non-ESV mode of nucleation might be more favorable and lead to a higher nucleation field.

To look for corrections to this result one must expand the LGE to higher order. We remark that in the context of ESV solutions the first correction to H_{c3} will be of order $(\xi_0/\xi_H)^4 \propto (1-t)^2$, although corrections to Eq. (12) of order $(\xi_0/\xi_H)^3$ will appear. This is because the bulk terms are all of even order [cf. Eq. (8)] while the surface-layer terms, though including odd-order terms, are only nonzero for z within about ξ_0 of the boundary. The critical field H_{c3} being a global property of the system, the effect of the surface-layer terms is reduced by the ratio of ξ_0 to the full width of the pair wave function $\sim\xi_H$, so that they contribute in one-order higher than their nominal size. Then to compute H_{c3} to order $(\xi_0/\xi_H)^4$ we consider the equation

$$\begin{aligned}\Delta(\mathbf{r}) = &a_0\Delta(\mathbf{r}) + \tfrac{1}{6}a_2\mathfrak{D}(\mathbf{r})^2\Delta(\mathbf{r}) \\ &+(5!)^{-1}a_4[\mathfrak{D}(\mathbf{r})^4 + (2eH)^2]\Delta(\mathbf{r}) + \mathrm{SLT}(III), \quad (16)\end{aligned}$$

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[7] For a detailed derivation see C.-R. Hu, thesis, University of Maryland, 1968 (unpublished).

[8] See, for example, A. A. Abrikosov, L. P. Gor'kov', and I. E. Dzyaloshinsky, *Methods of Quantum Field Theory in Statistical Physics*, translated by R. A. Silverman (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

[9] That this conclusion is in fact gauge invariant is shown in Footnote (iv) of Ref. 7.

where[7]

$$\mathrm{SLT}(III)=\mathrm{SLT}(II)-\chi_{2,1}(z)\mathfrak{D}_\perp{}^2\mathfrak{D}_z\Delta(\mathbf{r})-[z^2\chi_1(z)+\tfrac{1}{3}\chi_3(z)]\mathfrak{D}_z{}^3\Delta(\mathbf{r})+2ieH\chi_{2,2}{}^{(1)}(z)\mathfrak{D}_x\Delta(\mathbf{r}), \tag{17}$$

$$\chi_{m,n}{}^{(l)}(z)\equiv\int_{z'<0}d\mathbf{r}'[(x-x')^m z'^n/(z-z')^l]\times k_0(|\mathbf{r}-\mathbf{r}'|) \tag{18a}$$

$$\chi_{m,n}(z)\equiv\chi_{m,n}{}^{(0)}(z),\quad \chi_n(z)\equiv\chi_{0,n}(z), \tag{18b}$$

and we have chosen H to be along the y axis. We define the symbol $\mathfrak{D}_\perp\equiv\mathfrak{D}-\hat{e}_z\mathfrak{D}_z$.

It is again straightforward to verify that the boundary condition Eq. (3) is implied by Eq. (16), to order $(\xi_0/\xi_H)^3$, which is the order of interest. For the ESV assumption to be justified it will be necessary to demonstrate that the rapidly varying surface terms SLT(III) vanish to this order, at least for the class of functions $\Delta(\mathbf{r})$ which satisfy the remaining equation and are otherwise candidates for the optimum-nucleation mode. These functions will be eigenfunctions of the operator $\mathfrak{D}(\mathbf{r})^2$ satisfying the boundary condition Eq. (3). In looking for the optimum-nucleation mode we may consider functions with no y dependence and, if we work in the gauge $\mathbf{A}=H(z-z_0,\ 0,\ 0)$, can ignore x dependence as well (cf. Ref. 16 of I) so long as we maximize the computed H_{c3} with respect to variations in z_0. We remark parenthetically that should we be able to find appropriate eigenfunctions, which would satisfy Eq. (3) and

$$-\mathfrak{D}(\mathbf{r})^2\Delta_n(\mathbf{r})=\xi_H{}^{-2}\epsilon_n(z_0/\xi_H)\Delta_n(\mathbf{r}), \tag{19}$$

and which would allow SLT (III) to vanish, we would compute H_{c3} by solving the equation which follows from Eq. (16):

$$1=a_0(T)-\tfrac{1}{6}a_2(T)\xi_H{}^{-2}\epsilon_n+(5!)^{-1}a_4(T)(\epsilon_n{}^2+1)\xi_H{}^{-4} \tag{20}$$

for H as a function of T and maximizing H with respect to both n and z_0.

Since the functions of interest will satisfy Eq. (19), we may use this equation in evaluating SLT(III). Thus, in the special gauge mentioned above, Eq. (19) implies

$$\nabla_z{}^2\Delta(z)|_{z=0}=\xi_H{}^{-2}[(z_0/\xi_H)^2-\epsilon]\Delta(0),$$
$$\nabla_z{}^3\Delta(z)|_{z=0}=\xi_H{}^{-2}[(z_0/\xi_H)^2-\epsilon][\nabla_z\Delta(z)]_{z=0}-2\xi_H{}^{-4}z_0\Delta(0). \tag{21}$$

We may also use the boundary condition Eq. (3), but anticipating the needs of Sec. III, write it in a generalized form which, in this gauge, is

$$\nabla_z\Delta(z)|_{z=0}=\alpha\xi_H{}^{-1}\Delta(0), \tag{22}$$

where α is assumed to be of order $(\xi_0/\xi_H)^2$ or smaller.

Combining Eqs. (21) and (22) we find

$$\nabla_z{}^2\Delta(z)|_0=\xi_H{}^{-2}(\zeta_0{}^2-\epsilon)\Delta(0),$$
$$\nabla_z{}^3\Delta(z)|_0=-2\xi_H{}^{-3}\zeta_0\Delta(0), \tag{23}$$

to order $(\xi_0/\xi_H)^4$, where $\zeta_0\equiv z_0/\xi_H$. Using Eqs. (22) and (23), we now evaluate Eq. (17) to order $(\xi_0/\xi_H)^3$ by making use of the same Taylor expansion which led to Eq. (15). The result is

$$\mathrm{SLT}(III)=\{-2\chi_1(z)\alpha\xi_H{}^{-1}+[\chi_{2,2}{}^{(1)}(z)+\tfrac{2}{3}\chi_3(z)]\xi_H{}^{-3}\zeta_0\}\Delta(0). \tag{24}$$

Then even with $\alpha=0$, SLT(III) will not be zero unless ζ_0 is of order ξ_0/ξ_H or $\Delta(0)$ is of that order compared to values of Δ away from the surface. Now in the GL region, $\zeta_0\simeq0.77$ for the optimum mode[4] while the boundary value of the nucleation wave function is comparable to its value elsewhere, so that neither of these quantities can be expected to become of higher order here. We conclude then that the rapidly varying boundary terms cannot be made to vanish for the pair wave functions of interest, and thus, that our original assumption that an ESV solution of the LGE Eq. (11) exists at H_{c3} is untenable, if accuracy to order $(\xi_0/\xi_H)^4\sim(1-t)^2$ or better is required.

III. EXPANSION OF LGE WITHOUT THE SLOWLY VARYING ASSUMPTION

Since the pair wave function has been shown to contain a rapidly varying part near the boundary, we look for a solution of the LGE of the form

$$\Delta(\mathbf{r})=\Delta^B(\mathbf{r})+\Delta^{\mathrm{SL}}(\mathbf{r}), \tag{25}$$

where the "bulk component" Δ^B is ESV while the "surface-layer component" Δ^{SL} vanishes except in the boundary region $z\lesssim\xi_0$. Writing the LGE Eq. (1) or Eq. (11) symbolically as $\Delta=\int\mathbf{K}\Delta$, we notice that $\int\mathbf{K}\Delta^{\mathrm{SL}}$ is rapidly varying and vanishes away from the boundary, while $\int\mathbf{K}\Delta^B$ has an ESV component and an RV component, which can be separated out by the expansion procedure used in Sec. II. Symbolically we set

$$\int\mathbf{K}\Delta^B\equiv\mathbf{O}^B\Delta^B+\mathbf{O}^{\mathrm{SL}}\Delta^B, \tag{26}$$

where $\mathbf{O}^B$ and $\mathbf{O}^{\mathrm{SL}}$ are differential operators which reproduce the bulk-and-surface-layer terms to a given order when operating on Δ. Thus, for example, $\mathbf{O}^B\Delta(\mathbf{r})$ to sixth order is the right-hand side of Eq. (8) while $\mathbf{O}^{\mathrm{SL}}\Delta(\mathbf{r})$ to third order is the right-hand side of Eq. (17) combined with Eq. (13).

The LGE now takes the form

$$\Delta^B+\Delta^{\mathrm{SL}}=\int\mathbf{K}\Delta^{\mathrm{SL}}+\mathbf{O}^B\Delta^B+\mathbf{O}^{\mathrm{SL}}\Delta^B. \tag{27}$$

We further specify Δ^B by requiring it to satisfy the same equation the full pair wave function satisfies in the infinite-sample case

$$\Delta^B = \mathbf{O}^B \Delta^B\,, \tag{28}$$

whereupon the surface-layer component must satisfy the inhomogeneous integral equation

$$\Delta^{\mathrm{SL}}(\mathbf{r}) - \int_{z'>0} d\mathbf{r}' K(\mathbf{r},\mathbf{r}')\Delta^{\mathrm{SL}}(\mathbf{r}') = \mathbf{O}^{\mathrm{SL}}\Delta^B\,. \tag{29}$$

Equation (29) cannot be approximated by a differential equation of finite order since it no longer contains a small expansion parameter.

The pair of equations (28) and (29) is a coupled set, though the influence of Δ^{SL} on Eq. (28) may not be immediately apparent. The coupling arises because Eq. (28) is insufficient to determine $\Delta^B(\mathbf{r})$ without the imposition of boundary conditions. The boundary condition is determined by the requirement that the inhomogeneous term of Eq. (29) be orthogonal to the solution of the corresponding homogeneous equation, so that finite solutions of the inhomogeneous equation may exist.

In particular, Eq. (28) will be an eigenvalue equation involving the commuting operators $\mathfrak{D}(\mathbf{r})^2$ and $\mathfrak{D}_H(\mathbf{r})$ [cf. Eq. (8)] and its solution can be expected to be a simultaneous eigenfunction of these two operators. Requiring $\Delta(\mathbf{r})$ to be normalizable leaves one boundary condition needed at $z=0$. Since $\Delta(\mathbf{r})$ is infinitesimal at the nucleation point, the boundary condition must be linear in $\Delta^B(\mathbf{r})|_{z=0}$ and $\nabla_z\Delta^B(\mathbf{r})|_{z=0}$, while gauge invariance requires ∇_z to appear as the combination $\mathfrak{D}_z(\mathbf{r})$. Finally, taking account of translational invariance in the boundary plane, we find the most general boundary condition at $z=0$ to be

$$\mathfrak{D}_z(\mathbf{r})\Delta^B(\mathbf{r})|_{z=0} = \xi_H^{-1}\int \alpha(\mathbf{r}_\perp - \mathbf{r}_\perp{}')\Delta^B(\mathbf{r}')|_{z'=0}d\mathbf{r}'\,, \tag{30}$$

where $\mathbf{r}_\perp$ is a point in the boundary surface. We will work, henceforth, in the gauge mentioned after Eq. (18), where there is no dependence of Δ on x, and assume that, as in the GL region and in computations of H_{c2},[4,6] the nucleation pair wave function does not depend on y. Then Eq. (30) becomes[10]

$$\nabla_z\Delta^B(z)|_{z=0} = \alpha\xi_H^{-1}\Delta^B(0)\,, \tag{31}$$

which contains only the single constant α (which can, however, depend on ξ_H and $\zeta_0 \equiv z_0/\xi_H$).[11] Given α as a function of H and ζ_0, the eigenvalues of $\mathfrak{D}(\mathbf{r})^2$ may be found and from them H_{c3} through the analog of Eq. (20). The effective-boundary-condition parameter α, however, is determined by the solution of Eqs. (28) and (29) and the orthogonality requirement which takes the form

$$\int_{z>0} d\mathbf{r}\, \Delta^*(\mathbf{r})\mathbf{O}^{\mathrm{SL}}\Delta^B(\mathbf{r}) = 0\,, \tag{32}$$

since the solution to the homogeneous equation corresponding to Eq. (29) is the full pair wave function Δ.

Although this coupled set of equations appears rather formidable, it can be solved to any given order in ξ_0/ξ_H by means of a finite-iteration procedure. Since Δ^B satisfies Eq. (19) as well as Eq. (31), $\mathbf{O}^{\mathrm{SL}}\Delta^B$ can be expanded in a Taylor series about $z=0$, just as the surface-layer terms were expanded in Sec. II, and various orders in ξ_0/ξ_H identified. Thus, from Eq. (24), $\mathbf{O}^{\mathrm{SL}}\Delta^B$ to second order is proportional to $\alpha^{(1)}$ so that Eq. (32), to second order, has the trivial solution

$$\alpha^{(0)} = \alpha^{(1)} = 0\,, \tag{33}$$

where $\alpha^{(n)}$ denotes the value of α accurate to nth order in ξ_0/ξ_H.

If we write generally

$$\mathbf{O}^{\mathrm{SL}}\Delta^B(\mathbf{r}) \equiv [\alpha f_1(z) + f_2(z)]\Delta^B(0)\,, \tag{34}$$

then from Eq. (24) we see that the leading term in $f_1(z)$ is of first order while the leading term in $f_2(z)$ is of third order, so that one may find $\alpha^{(n+2)}$ from Eq. (32) knowing $\Delta^*(\mathbf{r})$ only to order n. More precisely

$$\alpha^{(n+2)} = -\int_0^\infty dz\, \Delta^*_{(n)}(z) f_2{}^{(n+3)}(z) \Big/ \int_0^\infty dz\, \Delta^*_{(n)}(z) f_1{}^{(n+1)}(z)\,, \tag{35}$$

where parenthesized subscripts and superscripts denote the accuracy required. This is an iterative solution since f_1 and f_2 are easily found to all orders while $\Delta^*_{(n)}$ can be found from Eqs. (27)–(29) and (31) using the nth-order value for α.

The situation is particularly simple if we limit our attention to $\alpha^{(4)}$ [which, as we shall see, allows a calculation of H_{c3} to sixth order in $(1-t)^{1/2}$]. Equation (33) guarantees that $\Delta_{(2)}(\mathbf{r})$ be just the SJdG result

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[10] We stress that this is the boundary condition on the slowly varying part of the pair wave function $\Delta(\mathbf{r})$. It can be considered as the boundary condition on the extrapolation of the pair wave function from $z \gg \xi_0$ to the boundary $z=0$. The complete pair wave function still satisfies Eq. (3), at least as far as we are concerned in this work. On the true microscopic level, the remarks before Eq. (3) should be kept in mind.

[11] The ζ_0 dependence of α in our special gauge is equivalent to the nonlocality of Eq. (30) in a general gauge. For example, in the gauge in which $A_x = zH$, $A_y = A_z = 0$, we might look for solutions of the form $\Delta(\mathbf{r}) = f(z)e^{ikx}$. Then Eq. (30) for $\Delta(\mathbf{r})$ will become Eq. (31) for $f(z)$ with $\alpha \equiv \int \alpha(\mathbf{r}_\perp - \mathbf{r}_\perp{}')e^{-ik(x-x')}d\mathbf{r}_\perp{}'$, which depends on z_0 through the relation $k = -z_0/\xi_H{}^2$. See Ref. 16 of I.

for the GL region, which is ESV.[12] Then, in our special gauge,

$$\Delta_{(2)}(z)\simeq\Delta_{(2)}(0)+z\Delta_{(2)}'(0) +(z^2/2!)\Delta_{(2)}''(0)=\Delta_{(2)}(0) \quad (36)$$

to second order, considering the integration range in Eq. (35). We have set $\Delta_{(2)}'(0)$ equal to 0 because of the boundary condition, while $\Delta_{(2)}''(0)=0$ is valid for the optimum nucleation mode.[13] Using Eq. (36), then, Eq. (35) implies

$$\alpha^{(n)}=-\int_0^\infty dz\, f_2^{(n+1)}(z)\bigg/\int_0^\infty dz\, f_1^{(n-1)}(z) \quad (37)$$

for $n=2$, 3, or 4. To determine α to higher order, one would have to solve the integral equation Eq. (29) to find an expression for Δ^{SL} to insert in Eq. (35).

When we have also found the eigenvalues of $\mathfrak{D}(\mathbf{r})^2$ as a function of α and thus of ξ_0/ξ_H, it is straightforward to find the temperature dependence of H_{c3} to a corresponding order. Thus, from Eqs. (8) and (19) the analog of Eq. (20) to sixth order is

$$a_0-1-(a_2/3!)\epsilon\xi_H^{-2}+(a_4/5!)(1+\epsilon^2)\xi_H^{-4} -(a_6/7!)(\epsilon^3+5\epsilon)\xi_H^{-6}=0, \quad (38)$$

where we have explicitly assumed a zero eigenvalue for $\mathfrak{D}_H(\mathbf{r})$, or no y dependence of $\Delta^B(\mathbf{r})$.

This is easily inverted to give $\xi_H^{-2}=2eH_{c3}$ accurate to sixth order in $(1-t)^{1/2}$ as

$$2eH_{c3}=\frac{3!(a_0-1)}{\epsilon a_2}\left\{1+\frac{(3!)^2}{5!}\frac{a_4}{a_2^2}\frac{1+\epsilon^2}{\epsilon^2}(a_0-1) +2\left[\frac{(3!)^4}{(5!)^2}\frac{a_4^2}{a_2^4}\frac{(1+\epsilon^2)^2}{\epsilon^4} -\frac{(3!)^2}{7!}\frac{a_6}{a_2^3}\frac{\epsilon^2+5}{\epsilon^2}\right](a_0-1)^2\right\}, \quad (39)$$

which relies heavily on the fact (*vide infra*) that $a_0-1 \propto 1-t$. Note that ϵ still depends on ξ_H through its dependence on α, but that this dependence can be taken care of in Eq. (39) in an iterative fashion. It is clear from Eq. (39) that accuracy in ϵ to fourth order will allow H_{c3} to be computed to sixth order. Since the accuracy of ϵ is, in principle, the same as that of the value of α used to compute it, we see that the sixth is the highest order to which we can compute H_{c3} without solving an integral equation to find the surface part of the pair wave function.

In the following we shall compute ϵ only to third order, which allows an evaluation of H_{c3} to fifth order. The term in $(a_0-1)^3$ in Eq. (39) is then extraneous. We note further that H_{c2} is determined by Eq. (39) also,[14] with $\epsilon=1$ and can therefore write, now to third order,

$$H_{c3}/H_{c2}=\epsilon_0^{-1}[1-\delta\epsilon/\epsilon_0 +(3!)^2(5!)^{-1}(\epsilon_0^{-2}-1)a_4a_2^{-2}(a_0-1)], \quad (40)$$

where $\epsilon=\epsilon_0+\delta\epsilon$, ϵ_0 is the GL value of ϵ, and we anticipate that $\delta\epsilon$ is of at least second order.

To find $\delta\epsilon$ as a function of α we follow the calculation of Lüders,[15] who showed that

$$\delta\epsilon=C\alpha \quad (41)$$

to second order in ξ_0/ξ_H. Here $C=\partial\epsilon/\partial\alpha$ is evaluated at $\alpha=0$ and $\zeta_0=\zeta_{0M}$, the optimum value of ζ_0 in the GL region. In Appendix A we show that Eq. (41) is also correct to the next higher order—the order we shall now consider. Lüders also showed how the constant C could be related to the properties of the eigenfunctions of $\mathfrak{D}(\mathbf{r})^2$ with the SJdG boundary condition. We discuss this relation in Appendix A as well. Schultens[16] used this relation in a numerical evaluation of C which recently was found to be incorrect.[17] He has since reevaluated this constant to find

$$C=0.762. \quad (42)$$

An independent rough calculation of C by one of us (CRH) gives a value close to the above, and we will take Eq. (42) to be correct.

The final ingredient for the evaluation of Eq. (40) is the value of $\alpha^{(3)}$ which is to be found from Eq. (37). In Appendix B we show that

$$\alpha^{(3)}=\left[\frac{31}{70}\frac{\zeta(5)}{\zeta(3)}\left(\frac{\xi_0}{\xi_H}\right)^2\zeta_0+\frac{9}{64}\frac{\zeta(6)}{\zeta(3)}\left(\frac{\xi_0}{\xi_H}\right)^3\right], \quad (43)$$

where ζ (n) is the Riemann ζ function. Then, using Eqs. (15), (16), (41), (42), and (43), the values $\epsilon_0=0.59010$, $\zeta_{0M}=\epsilon_0^{1/2}$ found by SJdG,[4] and the values[8]

$$a_0=1-|\lambda|N(0)\ln(T/T_c)\simeq1+|\lambda|N(0)(1-t),$$
$$a_2=\tfrac{7}{2}\zeta(3)|\lambda|N(0)[\xi_0(T)]^2\simeq\tfrac{7}{2}\zeta(3)|\lambda|N(0)\xi_0^2,$$

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[12] This justifies our remark after Eq. (15) that no non-ESV solutions need be considered in determining H_{c3} to second order. Our coupled equations require Δ^{SL} to vanish to this order and provide a simultaneous microscopic proof of the GL equation and the SJdG boundary condition for temperatures sufficiently close to T_c.

[13] This is easily verified in the solution of Ref. 4. A proof of this statement from first principles is also contained in Chap. VI of Ref. 7.

[14] When there is no boundary, $\epsilon=1$ is the lowest eigenvalue of Eq. (19). See also Ref. 6.

[15] G. Lüders, Z. Physik **202**, 8 (1967).

[16] Quoted by Lüders. See Ref. 15 and G. Lüders, revised english note of a talk delivered at Theoretische Physikalisches Seminar, Gottingen University, 1967 (unpublished). We wish to thank Professor Lüders for sending us a copy of this note.

[17] G. Lüders (private communication). Our original calculations as well as those of Lüders in Ref. 15 were based on the earlier incorrect value of C. It was on the basis of this value that we predicted in Ref. 7 that H_{c3}/H_{c2} had a minimum at a temperature below T_c. We would also like to point out that the correct value of C was actually obtained much earlier by Ebneth and Tewordt [see Ref. 21, Eq. (8)] who evaluated the combination $C/2\epsilon_0^{1/2}=0.496$.

and

$$a_4 \simeq (93/2)\zeta(5)|\lambda|N(0)\xi_0^4 \tag{44}$$

were found. We can evaluate Eq. (40) as

$$\begin{aligned} H_{c3}/1.695H_{c2} \simeq & 1 \\ & +(279/245)\zeta(5)\zeta(3)^{-2}(\epsilon_0^{-2}-1-\tfrac{2}{3}C\epsilon_0^{-3/2})(1-t) \\ & -(27/56)(3/7)^{1/2}C\zeta(6)\zeta(3)^{-5/2}\epsilon_0^{-5/2}(1-t)^{3/2} \\ & =1+(1.530-1.202C)(1-t)-0.758C(1-t)^{3/2}. \end{aligned} \tag{45}$$

For C given by Eq. (42) we find

$$H_{c3}/1.695H_{c2} \simeq 1+0.614(1-t)-0.577(1-t)^{3/2}. \tag{46}$$

The temperature dependence of H_{c3} itself may be found directly through Eq. (39) (where careful note of the temperature dependence of a_2 and a_0 is required) or by using the known relation[6]

$$\begin{aligned} 7\zeta(3)e\xi_0^2H_{c2}(t) & \\ & =6(1-t)\{1+0.135(1-t)+O[(1-t)^2]\} \end{aligned} \tag{47}$$

so that

$$\begin{aligned} 7\zeta(3)e\xi_0^2H_{c3}(t) = & 6(1.695)(1-t) \\ & \times[1+0.749(1-t)-0.577(1-t)^{3/2}]. \end{aligned} \tag{48}$$

To summarize, then, we have shown that: (a) To order $1-t$ in H_{c3}, all relevant solutions to our exact LGE are ESV solutions to the linearized GL equation subject to the SJdG boundary condition, so that we reproduce the well-known results of SJdG. (b) When accuracy to higher order is required, no solutions of the LGE are ESV, and a finite-order differential equation plus a boundary condition can, at most, describe the pair wave function outside the surface region (i.e., for $z \gg \xi_0$), although it can yield a value for H_{c3}. In the surface region $\Delta(\mathbf{r})$ is necessarily described by a nonlocal integral equation which no longer contains a small expansion parameter. (c) The effective boundary condition on the ESV part of the pair wave function is determined by an expression which involves $\Delta(\mathbf{r})$ in the surface region. The critical field H_{c3} can be found from the boundary condition. To order $(1-t)^3$ in H_{c3}, the boundary condition can be found without actually knowing the surface part of Δ. To higher order, solution of the integral equation for Δ near the surface is required.

We have, further, computed corrections to H_{c3} of order $(1-t)^2$ and $(1-t)^{5/2}$, beyond the results in the GL region. Further corrections can be computed, in principle to any order, but the mathematical difficulties increase rapidly.

Finally, we note that the solution of the integral equation Eq. (29) for Δ in the surface region is easily obtained numerically to two nontrivial orders in $(1-t)^{1/2}$. To this accuracy the kernel may be replaced by the corresponding zero-field kernel and the equation solved by means of a Fourier cosine transformation.

IV. COMPARISON WITH PREVIOUS WORK

The GL equation was proposed on phenomenological grounds as a unified description of various properties of superconductors. It was later derived microscopically by Gor'kov[2,5] through an expansion, at temperatures near T_c, of an integral equation obtained by him earlier, which is a valid microscopic description of an *infinite* superconductor at all temperatures. The usual boundary condition [i.e., Eq. (3)] for the GL equation was proposed by Ginzburg and Landau,[3] and by de Gennes[18] only through heuristic arguments.[19] We know of only three attempts[20–22] prior to ours to provide a rigorous, microscopic derivation of the GL equation and boundary condition for a finite geometry at temperatures near the nucleation point. In two of these developments[21,22,15] the authors also were able to generalize the GL equation and BC to temperatures slightly outside the GL region, and use them in the calculation of the temperature dependence of the critical-field ratio H_{c3}/H_{c2} in this temperature regime. In the following we compare the present work with these earlier discussions.

Abrikosov,[20] using his somewhat incorrect kernel for the LGE [see remarks after (I-11)], has also arrived at our Eqs. (12) and (13), from which he proposed a procedure different from ours to obtain a simultaneous derivation of the linearized GL equation and the BC. His derivation is not completely satisfactory since it included no check on the self-consistency of the ESV assumption about the gap function made at an early stage. He made no attempt to extend the discussion to lower temperatures, where the effective BC must be modified.

In the work of Ebneth and Tewordt,[21] the authors first derived the generalization of the GL equation to fourth order [in $\xi_0/\xi_H \propto (1-t)^{1/2}$] for an *infinite* sample. They then obtained a unique expression for the free-energy density to the same order by requiring it to be real and by requiring the Euler-Lagrange equation obtained by varying the free energy to agree with the generalized GL equation to the order considered. Taking the free energy of a sample with boundaries to be just

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[18] P. G. de Gennes, Rev. Mod. Phys. **36**, 225 (1964); *Superconductivity of Metals and Alloys*, translated by P. A. Pincus (W. A. Benjamin, Inc., New York, 1966).

[19] According to a remark by E. A. Shapoval {Zh. Eksperim. i. Teor. Fiz. **47**, 1007 (1964) [English transl.: (Soviet Phys.—JETP **20**, 675 (1965)]}, an unpublished microscopic derivation of this boundary condition has also been found by Gor'kov.

[20] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **47**, 720 (1964) [English transl.: Soviet Phys.—JETP **20**, 480 (1965)].

[21] G. Ebneth and L. Tewordt, Z. Physik **185**, 421 (1965) and earlier references cited therein. There are a number of misprints which should be noted. Thus α should be $(\pi/2\gamma)(\xi_0/l)$ rather than $(\pi\gamma/2)(\xi_0/l)$ and a factor of 3 is missing from the numerator of the right-hand side of Eq. (11.) The numerical value for δ at large α is also in doubt as the theory actually predicts $H_{c3}/H_{c2} \cong 1.695[1+0.548\alpha^{-1}(1-t)]$ as $\alpha \to \infty$.

[22] E. Schöler, thesis, Gottingen, 1966 (unpublished). Also the series of papers by G. Lüders: Z. Naturforsch. **21a**, 680 (1966); **21a**, 1415 (1966); **21a**, 1425 (1966); **21a**, 1824 (1966); **22a**, 845 (1967). See also Ref. 15 for a brief account of this work.

the integral of this free-energy density over the corresponding finite volume, they then varied this expression to obtain, along with the generalized GL equation, the generalized BC to the same order. Using these they were then able to compute $H_{c3}(t)/H_{c2}(t)$ to order $1-t$. In the limit of infinite mean free path, the result is identical to the corresponding term in our Eq. (46).

Now it is clear that this procedure can only be correct insofar as the true pair wave function $\Delta(\mathbf{r})$ satisfies the generalized GL equation everywhere, and we have demonstrated that this cannot be the case. In computing H_{c3} to fourth order, however, Δ is required only to second order, and we have found in Sec. III that Δ^{SL}, the part of Δ which fails to satisfy this requirement, appears first in third order for a sample with a specularly reflecting surface. This accounts for the agreement we noted in lowest order, but agreement with our results in any higher order is not to be expected. In fact the procedure of Ebneth and Tewordt cannot give rise to half-integer powers of $1-t$ in the expansion of H_{c3} while the next term in our Eq. (46) is proportional to $(1-t)^{3/2}$.

Perhaps the first rigorous, microscopic treatment of the bounded-sample problem is that of Schöler and Lüders.[22] This work agrees with ours in many respects, although the approach is quite different. They obtain the same equation as we do for the major component of the pair wave function (our Δ^B) and an effective boundary condition on this component which is determined by an analysis of the effect of the boundary surface. Their BC (and thus the value for H_{c3} computed by Lüders[15,17]) agrees with ours to the order they computed it (the first nontrivial order), so that they have derived the linearlized GL equation and the usual boundary condition for T sufficiently close to T_c, as well as the first correction term for lower T. An extension of the work of Schöler and Lüders to impure samples by Usadel and Schmidt,[23] furthermore, agrees with the corresponding expression found by Ebneth and Tewordt[21] to this same order. As we shall explain below, we expect that the treatment of Schöler and Lüders will agree with ours for three nontrivial orders but no farther.

The major differences in the two treatments are as follows: We have treated the boundary surface quantum mechanically while Schöler and Lüders treat it by means of a classical scattering analysis. Though perhaps less "microscopically correct," their analysis does have the advantage of being applicable to diffuse scattering as well as the specular reflection we have had to assume.

Of more importance is a difference in the two treatments of the rapidly varying component of the pair wave function, which will lead to disagreements in higher orders. In particular, in Schöler-Lüders an effective boundary condition can be found to any finite order in $(1-t)^{1/2}$ by iteration. We have found that for terms of order $(1-t)^{7/2}$ and higher in H_{c3}, the solution of an integral equation exact to all orders [i.e., Eq. (29) for Δ^{SL}] is required before the boundary condition can be found. We believe that the effective BC which Schöler and Lüders will obtain is given by our Eq. (32) with Δ^* replaced by Δ^{B*}, which is correct only for the three lowest nontrivial orders of expansion. The reason is that their approach involves an expansion-and-truncation procedure which does not treat the SL component correctly. The boundary condition is then not correct when Δ^{SL} becomes important in its determination, as it does at $n=3$ in our Eq. (35). Thus Schöler and Lüders only can calculate correctly modifications of H_{c3} to the first three nontrivial orders.

V. SUMMARY, DISCUSSION, AND COMPARISON WITH EXPERIMENT

In Paper I we studied the ratio $H_{c3}(T)/H_{c2}(T)$, for a pure superconductor with a specularly reflecting plane surface, near $T=0°$K. The result was

$$H_{c3}(T)/H_{c2}(T)\simeq 1.93[1+0.05t^2\ln t+O(t^2)]. \quad (49)$$

The coefficient 1.93 (more precisely 1.925) is a variational lower bound to the true value of the ratio at $T=0°$K while the coefficient 0.05 is estimated by first-order perturbation theory, using the $T=0$ variational wave function. This low-temperature value for the ratio of the critical fields is substantially higher than the value 1.695 which was found by SJdG[4] in cases where the GL equation may be used to describe the superconducting state. Further, the rather slow temperature dependence of Eq. (49) suggests that the ratio will remain well above 1.7 for a substantial portion of the temperature range below T_c. We note that the similar variational calculation by Gor'kov[24] of H_{c2} near $T=0$ has a stronger temperature dependence than Eq. (49), yet agrees rather well with the exact calculation of Helfand and Werthamer[25] for $t\lesssim 0.15$. We may hope that the temperature dependence of Eq. (49) is correct in a similar range.

Starting from the same basic formulation, we computed above the ratio of the critical fields for T near T_c to two nontrivial orders in $(1-t)^{1/2}$ beyond the result of the SJdG calculation. Our result is given by Eq. (46), where the coefficients are now exact rather than best-variational values. It is difficult to estimate the range of validity of Eq. (46), but from the coefficients we may expect that it will be relatively accurate for $1-t$ on the order of a few tenths.

A convenient interpolation formula which reduces to Eq. (46) for $t\simeq 1$, and which reproduces the value and

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[23] K.-D. Usadel and M. Schmidt (unpublished). We thank the authors for sending us a copy of their work before publication.

[24] L. P. Gor'kov', Zh. Eksperim. i Teor. Fiz. 37, 833 (1959) [English transl.: Soviet Phys.—JETP 10, 593 (1960)].

[25] E. Helfand and N. R. Werthamer, Ref. 6.

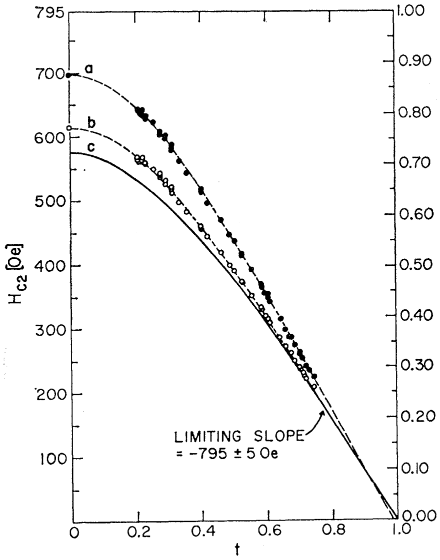

FIG. 1. $H_{c2}(t)$ computed from measured values of $H_{c3}(t)$ in pure Pb (see Ref. 35). Curve a computed according to $H_{c3}(t)=1.695\,H_{c2}(t)$. Curve b according to Eq. 50a. The point at $t=0$ is an extrapolation and curves a and b are extrapolated linearly to $t=1$. The right-hand scale shows H_{c2} normalized by its negative slope at $t=1$. Curve c is Helfand and Werthamer's (Ref. 25) theoretical calculation for this normalized field.

zero slope of Eq. (49) at $t=0$ is

$$H_{c3}(T)/1.695H_{c2}(T)=1+0.614(1-t)-0.577(1-t)^{3/2}-0.007(1-t)^2+0.106(1-t)^{5/2}. \quad (50a)$$

We may also take account of the fact that the $t=0$ value used above is only a lower bound to generalize Eq. (50a) to

$$H_{c3}(T)/1.695H_{c2}(T)=1+0.614(1-t)-0.577(1-t)^{3/2}-(5.687-2.951r_0)(1-t)^2+(4.650-2.360r_0)(1-t)^{5/2}, \quad (50b)$$

where r_0 is the true ratio of the critical fields at $t=0$, $r_0\geq 1.925$.

The experimental situation is not yet completely clear. The difficulty is that Eqs. (46) and (49) apply only to pure weak-coupling superconductors with perfectly specular reflecting surfaces. Unfortunately most pure superconductors are type I, so that H_{c2}, and perhaps H_{c3}, can only be measured in supercooling experiments, which are quite difficult. Pure vanadium and niobium are type-II superconductors, although niobium has almost strong coupling character. It would seem that vanadium would be the first choice for checking our results, with niobium a close second, since strong coupling effects do not seem to greatly affect the behavior of the ratio of the critical fields.[26]

In fact, measurements of the critical field ratio of Nb have been reported recently by Webb[27] and by Ostenson and Finnemore,[28] while Fischer[29] has shown us the data from his preliminary measurements on this same material. Webb's measurements were on high-purity Nb with an apparently very good surface. The experimental values of H_{c3}/H_{c2} are qualitatively quite similar to our interpolation formula Eq. (50a), though they seem to be systematically smaller than theory predicts. In particular Webb finds near T_c that $H_{c3}/H_{c2}\simeq 1.67\,[1+0.48(1-t)]$, while the ratio is extrapolated to a value of 1.89 at $T=0$. There is considerable scatter in the data.

Fischer's sample was less pure, with a residual resistance ratio better than 50 and $\xi_0/l\simeq\frac{1}{3}$, but his data show much less scatter than those of Webb. The measurements only covered the temperature range $0.3\lesssim t\lesssim 0.85$ but strongly indicate a limiting value of H_{c3}/H_{c2} smaller than 1.695 at $t=1$. The experimental points again fall consistently below our Eq. (50a). Impurity effects could account for the discrepancy at lower temperatures but not near T_c.

The experiment of Ostenson and Finnemore, on high-purity Nb, is apparently the most accurate of the above in the immediate vicinity of T_c. Although agreeing with Webb's values for $t\lesssim 0.9$, the ratio H_{c3}/H_{c2} is found to drop exponentially to unity in the range $0.9\lesssim t\lesssim 1$. The conclusion seems inescapable that theory and experiment disagree.

Now it is known[30] that the critical field H_{c2} in pure niobium and vanadium does not follow the Helfand-Werthamer[25] temperature dependence, and indeed this deviation is found again in the measurements of Fischer.[29] It has been suggested[31,32] that the deviation is due to Fermi surface anisotropy, and anisotropy of the measured H_{c2} has been reported.[33] Since we have not taken account of possible anisotropy in our development, our predictions may not be applicable to niobium or vanadium at all. It appears then that experiments on Type-I materials will be required for a definitive verification of our theoretical results. If, however, Ostenson and Finnemore[28] are correct in attributing the drop of H_{c3}/H_{c2} near T_c to critical fluctuation effects, agreement very near T_c may not be found in any material.[34]

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[26] G. Eilenberger and V. Ambegaokar, Phys. Rev. **158**, 332 (1967); E. D. Yorke and A. Bardasis, *ibid.* **159**, 344 (1967).

[27] G. W. Webb, Solid State Commun. **6**, 33 (1968)

[28] J. E. Ostenson and D. K. Finnemore, Phys. Rev. Letters **22** 188 (1969).

[29] G. Fischer (private communication).

[30] D. K. Finnemore, T. F. Stromberg, and C. A. Swenson, Phys. Rev. **149**, 231 (1966).

[31] N. R. Werthamer and W. L. McMillan, Phys. Rev. **158**, 415 (1967).

[32] P. C. Hohenberg and N. R. Werthamer, Phys. Rev. **153**, 493 (1967).

[33] D. E. Farrell, B. S. Chandrasekhar, and S. Huang, Phys. Rev. **176**, 562 (1968).

[34] We no not, however, believe that the explanation in terms of fluctuations is correct. One of us (CRH) has shown that the results of Ref. 28 can be fully accounted for in the present theory in a model where the coupling constant $|\lambda|$ is slightly depressed near the sample surface. In such a model the effective transition temperature is lowered in the surface region and the ratio of critical fields as a function of temperature is correspondingly modified. A discussion of the fluctuation explanation and details of the model calculation will be presented in a future publication.

Perhaps the best experimental verification of the present work yet available comes from analysis of measurements of H_{c3} performed by Fischer[35] in pure Pb. Fischer originally analyzed his data in terms of Lüders' expression[15] for H_{c3}/H_{c2} in the presence of diffuse scattering at the surface and found a good fit for a value of the "diffuseness" parameter $p=0.48$. Now the error in the constant[17] C mentioned above changes Lüders' formulas in such a way that the parameter p becomes 0.85 for a good fit to Fischer's data, while later study of his samples[29] points to almost complete specular reflection $p \simeq 0$. We have, accordingly, reanalyzed Fischer's experimental data in terms of our Eq. (50), which is appropriate when $p=0$.

In Fig. 1, curve a gives values of $H_{c2}(t)$ computed from Fischer's H_{c3} values according to the SJdG relation $H_{c3}=1.695\ H_{c2}$. Curve b gives corresponding values computed using Eq. (50a). The points at $t=0$ follow from Fischer's extrapolation $H_{c3}(0)=1181 \pm 4$ Oe, which we believe to be accurate. The data have been extrapolated linearly to $t=1$. Note that curve b passes through the point $t=1$, $H_{c2}=0$, in agreement with the theoretical prediction[25] that $H_{c2}(t)$ is very nearly linear near $t=1$. Curve a fails to have this property.

The right-hand scale of Fig. 1 shows values of $h^*(t)$, $H_{c2}(t)$ normalized by its negative slope at $t=1$. The normalizing slope (which must be the same for curves a and b) is taken from our extrapolation of curve b to be 795 ± 5, in excellent agreement with a different extrapolation[35] by Fischer. Finally, curve c is Helfand and Werthamer's[25] theoretical prediction for $h^*(t)$ in pure materials. We choose to compare with h^* rather than with H_{c2} itself since the latter is greatly modified by strong coupling effects while h^* has been shown[31] to change by at most 2%, due to the strong coupling characteristic of niobium, and perhaps will not be modified by much more than that due to the stronger coupling in lead.

It is clear from Fig. 1 that Eq. (50a) is far more satisfactory for interpreting the H_{c3} data than is the SJdG relationship for the ratio of the critical fields. Taking account of the fact that Eq. (50a) is based on a lower bound for the $t=0$ ratio, and using the more general result Eq. (50b), essentially perfect agreement with the theoretical curve for $h^*(t)$ is obtained for a value of r_0, the ratio of critical fields at $t=0$, equal to 2.06. Allowing for a possible 5% deviation due to strong coupling effects, this suggests that r_0 is the range $1.95 < r_0 < 2.15$, which is consistent with the estimate of 1.97 which we made in I on the basis of quite different considerations. The over-all agreement is encouraging and we consider it good evidence for the correctness of the theoretical development. Note that possible critical fluctuation effects would not be seen here since the measurements of H_{c3} did not extend beyond $t \simeq 0.8$. We look forward to the simultaneous measurement of H_{c3} and H_{c2} by supercooling techniques for the final verification of our work.

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APPENDIX A: EVALUATION OF ε AS A FUNCTION OF α

The eigenvalue ϵ is a function both of $\alpha(\zeta_0)$ and (explicity) of ζ_0 and, for any given $\alpha(\zeta_0)$, the optimum mode is determined by minimizing ϵ with respect to ζ_0 [see Eq. (39)]. For small α we may anticipate a small change in the optimum ζ_0 and expand ϵ as

$$\epsilon=\epsilon_0+\alpha(\partial\epsilon/\partial\alpha)+\tfrac{1}{2}(\delta\zeta_0)^2(\partial^2\epsilon/\partial\zeta_0{}^2)+\alpha\delta\zeta_0(\partial^2\epsilon/\partial\alpha\partial\zeta_0),$$

where ϵ_0 is the minimum ϵ for $\alpha=0$, and the term linear in $\delta\zeta_0$ consequently vanishes. The derivatives are evaluated at $\alpha=0$, $\zeta_0=\zeta_{0M}$, the value of ζ_0 where ϵ has its minimum for $\alpha=0$. Terms quadratic in α are neglected since they do not contribute in the third order. Minimizing ϵ at finite α, taking account of the dependence of α on ζ_0, we find

$$(\partial\alpha/\partial\zeta_0)(\partial\epsilon/\partial\alpha)+\delta\zeta_0(\partial^2\epsilon/\partial\zeta_0{}^2)+\alpha(\partial^2\epsilon/\partial\alpha\partial\zeta_0)=0$$

We see from Eq. (43) that $\partial\alpha/\partial\zeta_0$ is of the same order as α, so $\delta\zeta_0$ is also of second order and *all* the quadratic terms may be neglected in evaluating ϵ to third order. Then we have

$$\delta\epsilon\equiv\epsilon-\epsilon_0=\alpha(\partial\epsilon/\partial\alpha)_{\alpha=0,\zeta_0=\zeta_{0M}}\equiv C\alpha. \qquad (41)$$

We have limited our attention to third order in $\delta\epsilon$ so as to be able to use this simple form.

Another expression for C is found by considering the eigenvalue equation (19) which may be written

$$[-d^2/d\zeta^2+(\zeta-\zeta_0)]\Delta(\zeta)=\epsilon\Delta(\zeta),$$

where $\zeta\equiv z/\xi_H$. At constant ζ_0 the solutions are characterized by the eigenvalue ϵ. Then, for α sufficiently small

$$d\Delta/d\zeta|_{\zeta=0}=d\Delta/d\zeta|_{\zeta=0,\alpha=0}+C\alpha\partial^2\Delta/\partial\zeta\partial\epsilon|_{\zeta=0,\epsilon=\epsilon_0},$$

where we have used the relation $\delta\epsilon=C\alpha$, which is certainly true at constant ζ_0. Comparison with the boundary condition $d\Delta/d\zeta|_{\zeta=0}=\alpha\Delta(0)$ yields the required relation $C=\Delta(0)/[\partial^2\Delta/\partial\zeta\partial\epsilon]$ evaluated at

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[35] G. Fischer, Phys. Rev. Letters **20**, 268 (1968).

$\zeta=0$, $\epsilon=\epsilon_0$, and $\zeta_0=\zeta_{0M}$. We note that Δ here is the solution of the surface-nucleation problem in the GL region which is known to be[4]

$$\Delta(\zeta)=D_{\frac{1}{2}(\epsilon_0-1)}[\sqrt{2}(\zeta-\zeta_0)].$$

Then we have

$$C=-D_{\frac{1}{2}(\epsilon_0-1)}(-\sqrt{2}\zeta_{0M})\bigg/\left[\frac{\partial^2 D_{\frac{1}{2}(\epsilon_0-1)}(-\sqrt{2}\zeta_{0M})}{\partial\epsilon_0\partial\zeta_{0M}}\right],$$

which is an intrinsic property of these parabolic cylinder functions. It is this expression which has been evaluated by Schultens.[16,17]

APPENDIX B: EFFECTIVE-BOUNDARY-CONDITION PARAMETER TO THIRD ORDER

To find $\alpha^{(3)}$ we must first evaluate $\mathbf{O}^{\mathrm{SL}}\Delta^B$ to fourth order. A tedious but straightforward expansion of the surface term in Eq. (11) yields[7]

$$\begin{aligned}\mathbf{O}^{\mathrm{SL}}\Delta^B(\mathbf{r})=\mathrm{SLT}(III)&+z\chi_{2,1}(z)\mathfrak{D}_\perp^2\mathfrak{D}_z^2\Delta^B(\mathbf{r})\\&+\tfrac{1}{3}[z^3\chi_1(z)+z\chi_3(z)]\mathfrak{D}_z^4\Delta^B(\mathbf{r})\\&+[z^2\chi_{2,1}^{(1)}(z)-3z\chi_{2,2}^{(1)}(z)]\xi_H^{-2}\mathfrak{D}_x\mathfrak{D}_z\Delta^B(\mathbf{r})\\&-[\tfrac{1}{2}z^2\chi_{2,2}^{(2)}(z)-z\chi_{2,3}^{(2)}(z)]\xi_H^{-4}\Delta^B(\mathbf{r}),\end{aligned}$$

where SLT(III) is defined in Eqs. (13) and (17) while the various χ's are defined by Eqs. (18). Now using Eqs. (19) and (22) and in our special gauge, the above is expanded in a Taylor series around $z=0$ and the term proportional to α separated out to give

$$\begin{aligned}f_1^{(2)}(z)&=-2\chi_1(z)\xi_H^{-1}\\f_2^{(4)}(z)&=[\chi_{2,2}^{(1)}(z)+\tfrac{2}{3}\chi_3(z)]\xi_H^{-3}\zeta_0\\&\quad+[\tfrac{1}{2}z^2\chi_{2,2}^{(2)}(z)-z\chi_{2,3}^{(2)}(z)-z\chi_{2,2}^{(1)}(z)]\xi_H^{-4}.\end{aligned}$$

These may be substituted in Eq. (37) and the integrations performed to finally give Eq. (43).

PHYSICAL REVIEW VOLUME 185, NUMBER 2 10 SEPTEMBER 1969

Alfvén-Wave Propagation in Solid-State Plasmas. III. Quantum Oscillations of the Fermi Surface of Bismuth*†

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We have measured the quantum oscillations of Alfvén-wave mass densities in pure bismuth. To fit the experimental results, we use a four-energy-band model, corresponding to three equivalent nonparabolic ellipsoidal electron Fermi surfaces and one nonparabolic ellipsoidal hole Fermi surface. This enables us to evaluate the number of carriers, the carrier masses, the two energy gaps, the Fermi energy, and the overlap energy. These experiments yield a value for the energy gap E_{G2} of 250±50 meV. The value of the overlap energy is increased over the previously reported value of 36.0 meV. We find a value of 38.2±0.15 meV necessary. The other numerical parameters used are taken from previous values with some refinement. They are $n=(2.92\pm0.05)\times10^{17}$ cm^{-3}, $m_1=0.00651$, $m_2=1.362$, $m_3=0.0297$, $m_4=\pm0.1635$, $M_1=0.0644$, $M_3=0.696$, $E_F=26.6\pm0.18$ meV, and $E_{G1}=15.0$ meV. In addition, estimates are made for the lattice dielectric constant for several orientations.

I. INTRODUCTION

THE phase velocity of Alfvén waves in solids is determined by two quantities, the strength of the magnetic field and the mass density of the charge carriers. In a classical description the mass density is unaffected by a magnetic field. The quantization of electron energy into Landau levels brought about by a magnetic field causes the Fermi energy to oscillate in value as a function of the magnetic field.[1,2] This oscillation causes the number of carriers and, hence, the mass density also to oscillate with the magnetic field. The deviation of the mass density from its classical value is the subject of this paper.

Buchsbaum and Galt[3] pointed out that Alfvén waves could propagate in certain solid-state plasmas. Since then, Alfvén-wave propagation in bismuth has been

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