peratures where C^{es} and β^{es} are negligible, and provides no means of estimating these quantities at higher temperatures. Consequently, in order to obtain values of γ^{es} we are obliged to retain our assumptions, which have the virtues of generality and simplicity.

APPENDIX B: THEORETICAL CALCULATION OF $(\partial H_c^2/\partial p)_T$

We obtain the following expression for $(\partial H_c^2/\partial p)_T$ using the theory described in Sec. 5:

$$\left(\frac{\partial H_c^2}{\partial p}\right)_T=\frac{8\pi\Gamma T_c^2}{V}h\left[-\chi(\gamma^{en}-1)+\frac{d\ln T_c}{dp}\times\left(2-\frac{T}{T_c}\frac{h'}{h}\right)\right]. \quad \text{(B1)}$$

From Eq. (17), we see that $h\propto H_c^2$ and $h'\propto(\partial H_c^2/\partial T)_p$. It can be shown, using Eq. (B1), that when H_c^2 approaches its limiting behavior (i.e., Q is flattening off), $(\partial H_c^2/\partial p)_T$ also approaches its limiting behavior with R flattening off.

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Critical-Field Ratio H_{c3}/H_{c2} for Pure Superconductors Outside the Landau-Ginzburg Region. I. $T\simeq 0°K$*†

Chia-Ren Hu‡ and Victor Korenman
Center for Theoretical Physics and the Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742
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In this paper and a subsequent one (Paper II) we study the nucleation of superconductivity near a sample surface at temperatures outside the Landau-Ginzburg region. We develop a generalized image method to solve for the normal electron temperature Green's function for a semi-infinite sample with a specularly reflective plane boundary in an external magnetic field. Gor'kov's linearized gap equation is then obtained and studied for such a sample geometry. The pair wave function Δ is found to obey the Landau-Ginzburg boundary condition at all $T<T_c$, even though this boundary condition was originally suggested only for the Landau-Ginzburg region (i.e., when $T_c-T\ll T_c$). However, we also find that merely adding the boundary condition to the differential equation appropriate to the bulk case does not give the correct solution to the problem, except when $T_c-T\ll T_c$. At $T=0°K$, the integral gap equation is solved by a variational approach, yielding the critical-field ratio $H_{c3}/H_{c2}\geq 1.925$. This should be compared with Saint-James and de Gennes's result, $\sim$1.7, for T in the Landau-Ginzburg region. The small-T correction to the ratio near $T=0°K$ is found to be proportional to $T^2\ln T$ with a small coefficient. An upper bound is also found for the $T=0°K$ ratio to be 5.22, which is useful mainly in proving the existence of a ground state, so as to help justify the use of a variational approach.

I. INTRODUCTION

THE phenomenological Landau-Ginzburg (L-G) equation[1] is, because of its simplicity, a very powerful tool for studying the various phenomena of superconductivity.[2] It is well known,[2] however, that except for extremely dirty superconductors[3] this equation is applicable in only a limited temperature range near the critical temperature T_c, and for very pure superconductors this limitation becomes rather restrictive. In order to extend the description of superconducting phenomena beyond the "L-G region" (the temperature range in which the L-G equation is applicable), it is necessary to use the microscopic BCS[4] theory or Gor'kov's[5] generalization of it to space- and time-dependent cases. A recent example of such an extension is the elegant calculation by Helfand and Werthamer[6] of the bulk nucleation critical field H_{c2} for all impurity concentrations and all temperatures below T_c. The

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† This paper and the subsequent one (Paper II) are based on a thesis submitted by C.-R. Hu in partial fulfillment of the requirements for the Ph.D. degree in the Department of Physics and Astronomy of the University of Maryland (unpublished). The main results of Paper I were reported at the 1968 Annual Meeting of the American Physical Society [Bull. Am. Phys. Soc. 13, 109 (1968)].

‡ Present address: Department of Physics, University of Illinois, Urbana, Ill.

1 V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. 20, 1064 (1950).

2 Many applications of the L-G equation are discussed in P. G. de Gennes, *Superconductivity of Metals and Alloys*, translated by P. A. Pincus (W. A. Benjamin, Inc., New York, 1966).

3 K. Maki, Physics 1, 21 (1964); 1, 127 (1964); P. G. de Gennes, Physik Kondensierten Materie 3, 79 (1964).

4 J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

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

6 E. Helfand and N. R. Werthamer, Phys. Rev. 147, 288 (1966).

critical field H_{c2} is the largest magnetic field for which a localized superconducting region can exist deep inside a bulk sample. A superconductor is classified as type I or type II, according to whether H_{c2} is smaller or larger than the thermodynamic critical field H_c. In a type-I sample, localized interior superconducting regions are thermodynamically unstable but H_{c2} still has significance as a nucleation field. That is, it is the smallest field for which the sample can be kept metastably normal in a "supercooling" situation, when surface effects are not important.

There is yet another analogous critical field of interest for superconductors, called the surface nucleation critical field, H_{c3}. By using the L-G equation, Saint-James and de Gennes (SJdG)[7] have shown that when the magnetic field is parallel to the sample surface a localized superconducting region can be present near the surface (surface sheath) until the field reaches this significantly higher critical value, H_{c3}. They further found the ratio H_{c3}/H_{c2} to be equal to 1.695 for any given material. For all type-II materials and those type-I materials for which $H_{c3}>H_c$ the surface sheath will be present below H_{c3}. For those type-I materials for which $H_{c3}<H_c$, the field H_{c3} still has significance as the smallest field for which the sample can be kept metastably normal in a "supercooling" situation, when the field is parallel to a surface.

Although we may expect the above to remain qualitatively true even where the L-G equation is not accurate, it is not clear if the predicted value of H_{c3} (or ratio H_{c3}/H_{c2}) is correct outside the L-G region. In fact the experiments of Rosenblum and Cardona[8] and of Tomasch[9] indicate a deviation of the ratio from the predicted value of about 1.7. Suggestions that the deviation is a strong-coupling effect (the experiments were done on Pb) seem to have been ruled out by recent investigations.[10] We suspect the deviation to reflect the fact that the samples were outside the L-G region.

The present paper is an attempt to extend the calculation of H_{c3} by SJdG outside the L-G region. Unfortunately, the presence of a boundary in the problem sufficiently complicates matters that we have not been able to emulate Helfand and Werthamer and find H_{c3} for all temperatures and impurity concentrations. We have restricted ourselves to pure samples with a specularly reflecting surface and only treated two limiting temperature regions in detail. In this paper we consider the low-temperature limit, $T\simeq 0$, while in a subsequent paper (Paper II) we shift our attention to temperatures only slightly below the L-G region to compute the first few correction terms to the results obtained from the L-G equation.

Our work is based on Gor'kov's microscopic theory of superconductivity.[5] In Sec. II we construct the linearized gap equation (LGE) for our sample geometry by introducing a generalized image method to solve for the normal electron temperature Green's function appropriate for such a sample. In Sec. III we set up a variational calculation of H_{c3} at $T=0°$K. In Sec. IV the calculation of H_{c3} is extended to small but nonvanishing T by perturbation techniques. Section V contains a conclusion and comments while two appendices are devoted, respectively, to Gor'kov's equivalent-space-cutoff procedure[11] and an upper bound calculation of H_{c3}. This last is only of technical interest, needed to show that the variational calculation is valid.

II. LINEARIZED GAP EQUATION

Since H_{c3} is the critical field for a second-order phase transition, at which the pair wave function $\Delta(\mathbf{r})$ vanishes, we can start with the linearized version of Gor'kov's gap equation (LGE)[5]:

$$\Delta(\mathbf{r})=\int K(\mathbf{r},\mathbf{r}')\Delta(\mathbf{r}')d\mathbf{r}', \tag{1}$$

with

$$K(\mathbf{r},\mathbf{r}')\equiv|\lambda|T\sum_n G_\omega(\mathbf{r},\mathbf{r}')G_{-\omega}(\mathbf{r},\mathbf{r}'), \tag{2}$$

and $G_\omega(\mathbf{r},\mathbf{r}')$ being the normal electron temperature Green's function[12] of "frequency" $\omega=(2n+1)\pi T$. For a pure material in an external magnetic field with vector potential $\mathbf{A}(\mathbf{r})$, $\mathbf{G}_\omega$ satisfies

$$\{i\omega+(2m)^{-1}[\nabla_\mathbf{r}+ie\mathbf{A}(\mathbf{r})]^2+\mu\}G_\omega(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}'), \tag{3}$$

where $\mu=\epsilon_F$ is the chemical potential, or Fermi energy. We use units in which $\hbar=c=k_B=1$, where k_B is the Boltzmann constant. The Green's function should also satisfy the symmetry condition

$$G_\omega^*(\mathbf{r},\mathbf{r}')=G_{-\omega}(\mathbf{r}',\mathbf{r}). \tag{4}$$

For a sample with boundaries, boundary conditions (BC) are also needed to supplement Eq. (3). We shall be interested in a semi-infinite superconducting sample separated from a vacuum or an insulator by a specularly reflective plane boundary. If its work function is on the order of ϵ_F, which is in turn $\gg T_c$, the microscopic

[7] D. Saint-James and P. G. de Gennes, Phys. Letters **7**, 306 (1963). Extension of this work to superconductors in the dirty limit at all temperatures below T_c are independently worked out by Maki and by de Gennes. See Ref. 3.

[8] B. Rosenblum and M. Cardona, Phys. Letters **9**, 220 (1964); **13**, 33 (1964).

[9] W. J. Tomasch, Phys. Rev. **139**, A746 (1965).

[10] G. Eilenberger and V. Ambegaokar, Phys. Rev. **158**, 332 (1967); E. D. Yorke and A. Bardasis, *ibid.* **159**, 344 (1967). See also, E. D. Yorke, Ph.D. thesis, University of Maryland, 1967 (unpublished), and University of Maryland Technical Report No. 664 (unpublished).

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

[12] 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). This book also contains a good introduction to Gor'kov's microscopic theory of superconductivity. We have mainly followed this book in the choice of notation.

BC should be[13]

$$G_\omega(\mathbf{r},\mathbf{r}')|_{\mathbf{r}\text{ on bdry}}=0. \tag{5}$$

Another BC[13] which has been used is

$$\hat{n}\cdot[\nabla_{\mathbf{r}}+ie\mathbf{A}(\mathbf{r})]G_\omega(\mathbf{r},\mathbf{r}')|_{\mathbf{r}\text{ on bdry}}=0, \tag{6}$$

where $\hat{n}$ is a unit vector normal to the boundary. We believe this to be less realistic than Eq. (5) but it leads to the same kernel **K** and thus gives the same results for H_{c3} as when Eq. (5) is used [cf. remarks after Eq. (27)].

We shall use $\mathbf{g}_{0,\omega}$ and $\mathbf{g}_\omega$ to denote, respectively, the normal electron temperature Green's function for an infinite sample, without and with an external constant magnetic field H. Similarly, $\mathbf{G}_{0,\omega}$ and $\mathbf{G}_\omega$ will denote the corresponding Green's functions appropriate for the semi-infinite sample of interest.

The expression for $\mathbf{g}_{0,\omega}$ is well-known[12]:

$$g_{0,\omega}(\mathbf{r},\mathbf{r}')=g_{0,\omega}(|\mathbf{r}-\mathbf{r}'|)=-\frac{m}{2\pi}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\times\exp\left[\left(ip_F\frac{\omega}{|\omega|}-\frac{|\omega|}{v_F}\right)|\mathbf{r}-\mathbf{r}'|\right], \tag{7}$$

while $\mathbf{g}_\omega$ has been found by Gor'kov[11] to be

$$g_\omega(\mathbf{r},\mathbf{r}')=g_{0,\omega}(|\mathbf{r}-\mathbf{r}'|)\exp\left[-ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right], \tag{8}$$

to a very good approximation. (The integration path is a straight line connecting $\mathbf{r}'$ and $\mathbf{r}$.) To justify Eq. (8), Gor'kov pointed out that $\mathbf{g}_{0,\omega}$, which satisfies Eq. (3) with $\mathbf{A}=0$, also satisfies

$$\{i\omega+(2m)^{-1}[\nabla_{\mathbf{r}}+\tfrac{1}{2}ie\mathbf{H}\times(\mathbf{r}-\mathbf{r}')]^2+\mu\}\times\mathbf{g}_{0,\omega}(|\mathbf{r}-\mathbf{r}'|)=\delta(\mathbf{r}-\mathbf{r}'), \tag{9}$$

if the term quadratic in **H** can be neglected. This follows since

$$\nabla_{\mathbf{r}}g_{0,\omega}(|\mathbf{r}-\mathbf{r}'|)\propto(\mathbf{r}-\mathbf{r}')\perp\mathbf{H}\times(\mathbf{r}-\mathbf{r}'),$$

so that terms in Eq. (9) linear in **H** vanish. But Eq. (9) is just the result of inserting Eq. (8) into Eq. (3) for $\mathbf{g}_\omega$ and commuting the exponential integral to the left past the differential operator, which verifies Gor'kov's expression. The approximation involved in neglecting the terms quadratic in **H** is to ignore the curvature of the electron orbits over distances of importance in the problem. Equation (8) has been called the "semiclassical" approximation[6] because only the magnetic vector potential along the classical path of the electron contributes to the Green's function.

Without the external magnetic field, the Green's function $\mathbf{G}_{0,\omega}$, for a sample occupying the region $z\geq 0$ and satisfying the BC (5) at $z=0$, can be obtained by the ordinary image method:

$$G_{0,\omega}(\mathbf{r},\mathbf{r}')=g_{0,\omega}(|\mathbf{r}-\mathbf{r}'|)-R_{z'}g_{0,\omega}(|\mathbf{r}-\mathbf{r}'|)=g_{0,\omega}(|\mathbf{r}-\mathbf{r}'|)-g_{0,\omega}(|\mathbf{r}-R_{z'}\mathbf{r}'|), \tag{10}$$

where the reflection operator $R_{z'}$ changes z' to $-z'$. Equation (10) clearly satisfies Eq. (3) with **A** set to zero and the addition of a second source term in the unphysical region, while the BC Eq. (5) and the symmetry condition Eq. (4) are easily verified.

Abrikosov[14] combined the two procedures above to obtain an expression for the Green's function in a semi-infinite sample in the presence of a magnetic field as

$$G_\omega(\mathbf{r},\mathbf{r}')=G_{0,\omega}(\mathbf{r},\mathbf{r}')\exp\left[-ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]. \tag{11}$$

Although this satisfies the symmetry condition and the BC it is not correct since the terms linear in H no longer drop out in the analog of Eq. (9). This is because $\nabla_{\mathbf{r}}g_{0,\omega}(|\mathbf{r}-R_{z'}\mathbf{r}'|)$ is no longer normal to $\mathbf{H}\times(\mathbf{r}-\mathbf{r}')$ everywhere.

The correct expression for $\mathbf{G}_\omega$ is

$$G_\omega(\mathbf{r},\mathbf{r}')=g_{0,\omega}(|\mathbf{r}-\mathbf{r}'|)\exp\left[-ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]-g_{0,\omega}(|\mathbf{r}-R_{z'}\mathbf{r}'|)\exp\left[-ie\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]. \tag{12}$$

In Eq. (12),

$$\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}}\equiv\int_{\mathbf{r}'}^{\mathbf{r}_1}+\int_{\mathbf{r}_1}^{\mathbf{r}},$$

each following a straight path, where $\mathbf{r}_1$ is the intercept of the straight line connecting $\mathbf{r}$ and $R_{z'}\mathbf{r}'$ with the boundary surface. Explicitly, $\mathbf{r}_1$ has the components

$$\mathbf{r}_1\equiv((zx'+xz')/(z+z'),\,(zy'+yz')/(z+z'),\,0). \tag{13}$$

It is easy to see that the new path of integration involved in the image term is nothing but the classical orbit of an electron going from $\mathbf{r}'$ to $\mathbf{r}$, via a specular reflection on the boundary surface.

To justify Eq. (12), we first notice that it clearly satisfies the BC (5) and the symmetry condition (4). To show that it satisfies Eq. (3), we must prove that the image term in Eq. (12) satisfies Eq. (3) with the image source. For this purpose, it is convenient to rewrite the image term by using the identity

$$\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}=\int_{\mathbf{r}'}^{R_{z'}\mathbf{r}',\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}, \tag{14}$$

where

$$\int_{\mathbf{r}'}^{R_{z'}\mathbf{r}',\mathbf{r}}\equiv\int_{\mathbf{r}'}^{R_{z'}\mathbf{r}'}+\int_{R_{z'}\mathbf{r}'}^{\mathbf{r}},$$

[13] For a discussion of boundary conditions, see C.-R. Hu, thesis, University of Maryland, 1968 (unpublished).

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

and the vector potential has been extended into the negative-z region according to the following conditions:

(a) $\mathbf{H}(\mathbf{r}) = -\mathbf{H}(R_z\mathbf{r})$. (15)

(b) The gauge of $\mathbf{A}$ in the region $z<0$ is so related to that in the region $z\geq 0$ that the vector potential $\mathbf{A}$ itself is continuous across the boundary.

The proof of (14) is clear if one notices that the total flux enclosed by the difference of the two integration paths is always zero due to condition (a) and that the validity of Stokes's theorem is guaranteed by condition (b).

Using Eq. (14), and the further simple identity

$$\nabla_{\mathbf{r}} \int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{A}(\mathbf{s}) \cdot d\mathbf{s} = \mathbf{A}(\mathbf{r}) - \tfrac{1}{2}\mathcal{H}(\mathbf{r},\mathbf{r}_0) \times (\mathbf{r}-\mathbf{r}_0), \quad (16)$$

where

$$\mathcal{H}(\mathbf{r},\mathbf{r}_0) \equiv 2\int_0^1 \mathbf{H}(\mathbf{r}_0 + \theta(\mathbf{r}-\mathbf{r}_0))\theta d\theta \quad (17)$$

is a weighted average magnetic field along the straight line path, we find that we must prove the following relation to be merely an identity, in order to conclude that Eq. (3) is satisfied by Eq. (12):

$$\{i\omega + (2m)^{-1}[\nabla_{\mathbf{r}} + \tfrac{1}{2}ie\mathcal{H}(\mathbf{r},R_{z'}\mathbf{r}') \times (\mathbf{r}-R_{z'}\mathbf{r}')]^2 + \mu\} \times g_{0,\omega}(|\mathbf{r}-R_{z'}\mathbf{r}'|) = \delta(\mathbf{r}-R_{z'}\mathbf{r}'). \quad (18)$$

As before we neglect the term quadratic in $\mathbf{H}$ while a term linear in $\mathbf{H}$ vanishes identically. Due to the spatial dependence of $\mathcal{H}$, however, there is an additional term which did not appear in Gor'kov's analysis, i.e.,

$$(4m)^{-1}ie[\nabla_{\mathbf{r}} \times \mathcal{H}(\mathbf{r},R_{z'}\mathbf{r}')] \cdot (\mathbf{r}-R_{z'}\mathbf{r}') \times g_{0,\omega}(|\mathbf{r}-R_{z'}\mathbf{r}'|), \quad (19)$$

but which turns out to be of the same order as the neglected quadratic terms since $\mathcal{H}$ is slowly varying on the scale of p_F^{-1}, and can then also be dropped. Then Eq. (18) reduces to the equation which $g_{0,\omega}$ satisfies and our proof is complete.

Before we go on to use Eq. (12), we would like to make a few remarks about the range of applicability of our generalized method of images.

In the first place Eq. (12) is independent of the choice of gauge and also remains correct to the same degree of accuracy if $\mathbf{H}$ is not constant in space, as long as $\mathbf{H}$ does not vary over distances on an atomic scale.

Secondly, if Eq. (12) is replaced by the *sum* of the direct and image terms instead of the difference, the result is the Green's function for the same problem with the new boundary condition Eq. (6).

Finally the method can be extended to other geometries for which the usual method of images is applicable. When there are planar boundaries each image term can be associated with a path from the source point $\mathbf{r}'$ to the field point $\mathbf{r}$ via one or several specular reflections, and the integral phase factor for any term will follow that path. Our expression for the Green's function has the appealing feature that it conforms to our intuitive notion of the role of a propagator in carrying information from the source point. There is a contribution from each possible electron path and each contributes a phase factor related to the potential along its path.

Now that we have the proper Green's function, the corresponding kernel $\mathbf{K}$ of the LGE is found by using Eq. (2). The resulting expression clearly satisfies the BC:

$$K(\mathbf{r},\mathbf{r}')|_{z=0} = 0, \quad (20)$$

which in turn implies

$$\Delta(\mathbf{r})|_{z=0} = 0. \quad (21)$$

Now the kernel $\mathbf{K}$ contains four terms, the two "direct" terms which vary on the scale of the BCS coherence length, $\xi_0 \equiv v_F/2\pi T_c$, and two "cross terms" whose scale of variation is much smaller, p_F^{-1}. The pair wave function Δ, however, should be slowly varying, as it is in the bulk case, except in a small region near the boundary, $z \ll \xi_0$, where it has a rapidly varying component.[15] Since we are interested in global properties of the superconducting states we find, such as the critical field H_{c3}, we can ignore the exact behavior of Δ in the narrow surface region and consider an averaged value (averaged over distances large compared to p_F^{-1} but small compared to ξ_0). This "smoothed" pair wave function satisfies Eq. (1) but with a "smoothed" kernel from which the rapidly varying cross terms have been removed:

$$K(\mathbf{r},\mathbf{r}') = k_0(|\mathbf{r}-\mathbf{r}'|) \exp\left[-2ie\int_{\mathbf{r}'}^{\mathbf{r}} \mathbf{A}(\mathbf{s}) \cdot d\mathbf{s}\right] + k_0(|\mathbf{r}-R_{z'}\mathbf{r}'|) \exp\left[-2ie\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}} \mathbf{A}(\mathbf{s}) \cdot d\mathbf{s}\right], \quad (22)$$

where

$$k_0(|\mathbf{r}-\mathbf{r}'|) \equiv |\lambda| T \sum_n g_{0,\omega}(|\mathbf{r}-\mathbf{r}'|) g_{0,-\omega}(|\mathbf{r}-\mathbf{r}'|)$$
$$= |\lambda| T \left(\frac{m}{2\pi}\right)^2 \frac{1}{|\mathbf{r}-\mathbf{r}'|} \sum_n \exp\left[-\left(\frac{2|\omega|}{v_F}|\mathbf{r}-\mathbf{r}'|\right)\right]. \quad (23)$$

We can also write

$$K(\mathbf{r},\mathbf{r}') \equiv k(\mathbf{r},\mathbf{r}') + R_{z'}{}^{\mathbf{H}}k(\mathbf{r},\mathbf{r}'), \quad (24)$$

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[15] This rapidly oscillating component of the pair wave function near a sample surface has been found by Falk for finite and semi-infinite superconducting slabs, and for semi-infinite superconducting and normal metals in contact [D. S. Falk, Phys. Rev. **132**, 1576 (1963)]; by Leyendecker for the free surface of a normal metallic slab backed by a superconductor [A. J. Leyendecker, Ph.D. thesis, University of Maryland, 1967 (unpublished)]; and by Boyd in the vicinity of a tunneling barrier [R. G. Boyd, Phys. Rev. **167**, 407 (1968)]. All have assumed that there is no applied magnetic field. Boyd has restricted his attention to the neighborhood of a second-order phase transition, as we do in the present paper, but not Falk and Leyendecker.

where

$$k(\mathbf{r},\mathbf{r}')\equiv k_0(|\mathbf{r}-\mathbf{r}'|)\exp\left[-2ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]. \quad (25)$$

Equation (22), or (24), is the *sum* of a direct term and an image term and can be easily shown to satisfy the BC:

$$\mathfrak{D}_z K(\mathbf{r},\mathbf{r}')|_{z=0}\equiv[\nabla_z+2ieA_z(\mathbf{r})]K(\mathbf{r},\mathbf{r}')|_{z=0}=0, \quad (26)$$

which in term implies:

$$\mathfrak{D}_z\Delta(\mathbf{r})|_{z=0}=0. \quad (27)$$

It should be remembered that Eqs. (26) and (27) are actually the extrapolated behavior of the smoothed kernel and the smoothed pair wave function, respectively, from the region $p_F^{-1}\ll z\ll\xi_0$.

Equation (27) is exactly the BC proposed by Ginzburg and Landau to supplement the L-G equation, which is a valid description of a superconductor only when its temperature is very close to T_c. We now find that this BC can actually describe the behavior of the pair wave function near a specularly reflective sample boundary for all temperatures below T_c. (It can also be shown that this is still true even when the gap equation is not linearized, and when the system is not pure.)

We note also that should we have started with the microscopic BC (6) instead of (5), and the Green's function appropriate to it, the microscopi c kernel would have differed only in the sign of the rapidly oscillating terms so that the smoothed kernel would again be given by Eq. (22), and from this point on the two calculations will coincide.

We now go back to the kernel Eq. (22), and write down the corresponding LGE:

$$\Delta(\mathbf{r})=\int_{z'>0}k_0(|\mathbf{r}-\mathbf{r}'|)\exp\left[-2ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]\Delta(\mathbf{r}')d\mathbf{r}'$$
$$+\int_{z'>0}k_0(|\mathbf{r}-R_{z'}\mathbf{r}'|)$$
$$\times\exp\left[-2ie\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]\Delta(\mathbf{r}')d\mathbf{r}'. \quad (28)$$

Without the second term and the limitation $z'>0$ to the integration range, Eq. (28) would be the corresponding LGE for the infinite sample case, to which Helfand and Werthamer[6] applied the operator identity

$$\exp\left[-2ie\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]\exp[(\mathbf{r}'-\mathbf{r})\cdot\nabla_\rho]\Delta(\boldsymbol{\rho})|_{\rho=\mathbf{r}}$$
$$=\exp[(\mathbf{r}'-\mathbf{r})\cdot\mathfrak{D}_\rho]\Delta(\boldsymbol{\rho})|_{\rho=\mathbf{r}}, \quad (29)$$

where $\mathfrak{D}_\rho\equiv\nabla_\rho+2ie\mathbf{A}(\boldsymbol{\rho})$, to convert the LGE into a linear, homogeneous differential equation of infinite order. The equation was then solved by simultaneously diagonalizing the two scalar operators $\mathfrak{D}_r^2$ and $\mathfrak{D}_H(\equiv|H|^{-1}\mathbf{H}\cdot\mathfrak{D})$. For our case, we can easily generalize Eq. (31) to nonstraight paths as

$$\exp\left[-2ie\int_0^1\mathbf{A}(\mathbf{s})\cdot\frac{d\mathbf{s}(\tau)}{d\tau}d\tau\right]\exp[(\mathbf{r}'-\mathbf{r})\cdot\nabla_\rho]\Delta(\boldsymbol{\rho})|_{\rho=\mathbf{r}}$$
$$=T_\tau\exp\left[-\int_0^1 d\tau\frac{d\mathbf{s}(\tau)}{d\tau}\cdot\mathfrak{D}_\rho\right]\Delta(\boldsymbol{\rho})|_{\rho=\mathbf{r}}, \quad (30)$$

where $\mathbf{s}(\tau)$ is the parametric equation of an arbitrary given curve with $\mathbf{s}(0)=\mathbf{r}'$ and $\mathbf{s}(1)=\mathbf{r}$, and T_τ is an ordering operation which requires operators characterized by smaller τ to act first. (The generalization is required because different components of $\mathfrak{D}_\rho$ do not commute.) We then can also convert our LGE, Eq. (28), into a linear, homogeneous differential equation of infinite order, which reads

$$\Delta(\mathbf{r})=\int_{z'>0}d\mathbf{r}'k_0(|\mathbf{r}-\mathbf{r}'|)\exp[(\mathbf{r}'-\mathbf{r})\cdot\mathfrak{D}_\rho]\Delta(\boldsymbol{\rho})|_{\rho=\mathbf{r}}$$
$$+\int_{z'>0}d\mathbf{r}'k_0(|\mathbf{r}-R_{z'}\mathbf{r}'|)\exp[(\mathbf{r}_1-\mathbf{r})\cdot\mathfrak{D}_\rho]$$
$$\times\exp[(\mathbf{r}'-\mathbf{r}_1)\cdot\mathfrak{D}_\rho]\Delta(\boldsymbol{\rho})|_{\rho=\mathbf{r}}, \quad (31)$$

or, after separating the bulk term and the surface correction term,

$$\Delta(\mathbf{r})=\int d\mathbf{R}k_0(R)\exp[\mathbf{R}\cdot\mathfrak{D}_\mathbf{r}]\Delta(\mathbf{r})+\int_{z'<0}d\mathbf{r}'k_0(|\mathbf{r}-\mathbf{r}'|)$$
$$\times\exp[(R_{z'}\mathbf{r}_1-\mathbf{r})\cdot\mathfrak{D}_\rho]\{\exp[(R_{z'}\mathbf{r}'-R_{z'}\mathbf{r}_1)\cdot\mathfrak{D}_\rho]$$
$$-\exp[(\mathbf{r}'-R_{z'}\mathbf{r}_1)\cdot\mathfrak{D}_\rho]\}\Delta(\boldsymbol{\rho})|_{\rho=\mathbf{r}}. \quad (32)$$

Without the second term on the right-hand side, Eq. (32) is identical to the corresponding equation for the infinite sample case found by Helfand and Werthamer, which we shall refer to as Eq. (32′). With the extra term in it, Eq. (32), as well as Eq. (31), now implies that the exact BC, Eq. (27), is automatically satisfied.

Unfortunately, Eq. (31) or Eq. (32) can no longer be solved exactly in the way Helfand and Werthamer solved Eq. (32′), since they now involve three scalar operators $\mathfrak{D}_r^2$, $\mathfrak{D}_H$, and $\mathfrak{D}_n(\equiv\hat{n}\cdot\mathfrak{D}_\mathbf{r}$, where $\hat{n}$ is the unit vector normal to the surface) which can no longer be simultaneously diagonalized. Since, however, Eq. (32) has the peculiar property that it contains the BC, the possibility exists that it may be equivalent to Eq. (32′) with the BC Eq. (27) added as an independent requirement. This possibility is worth examining since an important feature of Helfand and Werthamer's solution[6] to the bulk nucleation problem is the discovery that the nucleation pair wave function at all temperatures is the same as that in the Landau-Ginzburg region. It is therefore interesting to see whether this is also the case here, which is likely to occur only if the differential equation for the bulk case, Eq. (32′), is recovered except for the addition of the Landau-Ginzburg BC. This possibility can be ruled out, however, as is shown in Ref. 18, in Sec. III.

We have also considered the possibility of solving Eq. (32) by a perturbational approach, using the solutions of Eq. (32′) with the BC Eq. (27) as a starting point. This approach is not fruitful however, since a divergence occurs in the zero-order calculation. The divergence arises since Eq. (32′) is equivalent to the first term of Eq. (28) with no restriction on the region of integration. But the zero-order solution with BC is strongly divergent for $z\to-\infty$, so that matrix elements of the zero-order kernel diverge as well. This divergence also strongly indicates (but does not yet rigorously prove) that the possibility mentioned in the last paragraph is untenable.

To find the critical field, then, we have resorted to a variational approach, as discussed in the next section. Only the special case $T=0°$K is considered, as only in this case can the integral equation be reduced to one dimension.

III. VARIATIONAL CALCULATION OF H_{c3} AT $T=0°$K

The present calculation follows very closely Gor'kov's variational calculation of H_{c2} at $T=0°$K.[11] Our starting point is Eq. (28) and we choose the constant magnetic field to be in the y direction. We take the gauge

$$\mathbf{A}(\mathbf{r})=H(z-z_0,0,0) \tag{33}$$

with z_0 variable, and then can limit our consideration to those solutions $\Delta(\mathbf{r})$ which do not depend on x.[16] To begin, we first reduce Eq. (23) to a simpler form by temporarily ignoring the frequency cutoff.

$$k_0(|\mathbf{r}-\mathbf{r}'|)=|\lambda|T(m/2\pi)^2[|\mathbf{r}-\mathbf{r}'|^2\times\sinh(2\pi Tv_F^{-1}|\mathbf{r}-\mathbf{r}'|)]^{-1}. \tag{34}$$

At $T=0°$K, this expression becomes:

$$k_0(|\mathbf{r}-\mathbf{r}'|)=(4\pi)^{-1}|\lambda|N(0)|\mathbf{r}-\mathbf{r}'|^{-3}, \tag{35}$$

where $N(0)=mp_F/2\pi^2$ is the electron density of states per unit energy interval at the Fermi level. Equation (28) therefore becomes, with $\xi_0(T)=v_F/2\pi T$,

$$[|\lambda|N(0)]^{-1}\Delta(\mathbf{r})=[4\pi\xi_0(T)]^{-1}\int_{z'>0}\left\{\frac{\exp\left[-2\pi i\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]}{|\mathbf{r}-\mathbf{r}'|^2\sinh[|\mathbf{r}-\mathbf{r}'|/\xi_0(T)]}+\frac{\exp\left[-2\pi i\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]}{|\mathbf{r}-R_{z'}\mathbf{r}'|^2\sinh[|\mathbf{r}-R_{z'}\mathbf{r}'|/\xi_0(T)]}\right\}\times\Delta(\mathbf{r}')d\mathbf{r}'\quad(\text{for } T\neq0) \tag{36}$$

and

$$[|\lambda|N(0)]^{-1}\Delta(\mathbf{r})=(4\pi)^{-1}\int_{z'>0}\left\{|\mathbf{r}-\mathbf{r}'|^{-3}\times\exp\left[-2\pi i\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]+|\mathbf{r}-R_{z'}\mathbf{r}'|^{-3}\times\exp\left[-2\pi i\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]\right\}\Delta(\mathbf{r}')d\mathbf{r}'\quad(\text{for } T=0). \tag{37}$$

The $\mathbf{r}'$ integrations in Eqs. (36) and (37) are logarithmically divergent since we did not introduce the proper frequency cutoff in Eq. (34). Gor'kov,[11] however, has established an equivalent space-cutoff procedure which can compensate the error. He first pointed out the existence of the identity

$$[|\lambda|N(0)]^{-1}=(4\pi^2\gamma\xi_0)^{-1}\int_0^{\omega_D}\frac{du}{u}\int\frac{\sin(uR/v_F)}{R^2}K_1\left(\frac{R\Delta_0}{v_F}\right)d\mathbf{R}, \tag{38}$$

where $\ln\gamma=C\cong0.577$ is Euler's constant, ω_D the Debye frequency, and $K_1(z)$ the first-order Bessel function of imaginary argument, which behaves as z^{-1} for small z. Letting $\omega_D\to\infty$, Eq. (38) becomes also logarithmically divergent. Thus by substituting this expression into Eq. (36) or (37) to eliminate $|\lambda|N(0)$, and then introducing proper space-cutoffs on both sides of the equation, we can get cutoff-independent finite results. So much is given in Gor'kov's original paper, but to get the correct answer, he somehow chose to identify

$$\mathbf{R}=2(\mathbf{r}-\mathbf{r}'), \tag{39}$$

so that the same space cutoff $|z-z'|>\delta$ could be used on both sides of the equation. We use this identification here and in Appendix A we show why Eq. (39) is necessary and correct. Then Eq. (38) with $\omega_D\to\infty$, $\mathbf{R}\to2(\mathbf{r}-\mathbf{r}')$, and with the space cutoff $|z-z'|>\delta$ introduced can be simplified to give

$$[|\lambda|N(0)]^{-1}=-\ln(e\epsilon/2\sqrt{h}), \tag{40}$$

[16] In the gauge $\mathbf{A}(\mathbf{r})=(Hz,0,0)$ we could consider pair wave functions of the form $\Delta(\mathbf{r})=\Delta_k(y,z)\exp(ikx)$. Identical equations are found using Eq. (33) for A with Δ not a function of x if $k\equiv-2eHz_0$. In the bulk case there is degeneracy in k or z_0. In our case the nucleation critical field retains a dependence on z_0, which is roughly the "center of gravity" of the state, because of the presence of the surface at $z=0$. H_{c3} should then be the maximum value of these critical fields among all nucleation modes characterized by $-\infty<z_0<\infty$.

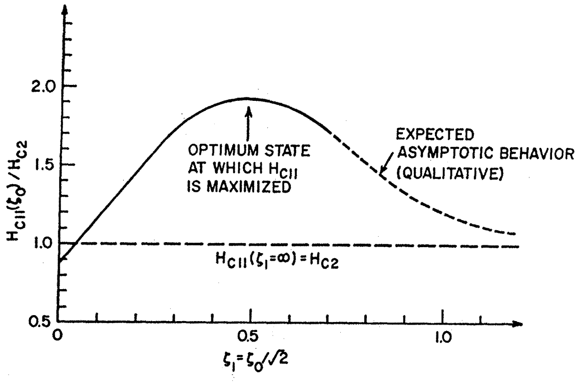

FIG. 1. The optimal variational value of the surface nucleation critical field H_{c11} as a function of the "center of nucleation" parameter ζ_0. The maximum of this curve is a lower bound to H_{c3}.

where $\xi_H\equiv(2eH)^{-1/2}$, $h\equiv(2eH)(v_F/2\pi_c)^2=(\xi_0/\xi_H)^2$, and $\epsilon\equiv\delta/\xi_H$. We can then change Eqs. (36) and (37) to

$$\Delta(\varrho)\ln\left(\frac{e\epsilon}{2\sqrt{h}}\right)=-\frac{\tilde{t}}{4\pi}\int_{\zeta'>0,|\zeta-\zeta'|>\epsilon}\left\{\frac{\exp[-\frac{1}{2}i(\zeta+\zeta'-2\zeta_0)(\xi-\xi')]}{|\varrho-\varrho'|^2\sinh(\tilde{t}|\varrho-\varrho'|)}+\frac{\exp\{-\frac{1}{2}i[(\zeta^2+\zeta'^2)/(\zeta+\zeta')-2\zeta_0](\xi-\xi')\}}{|\varrho-R_{\zeta'}\varrho'|^2\sinh(\tilde{t}|\varrho-R_{\zeta'}\varrho'|)}\right\}\Delta(\varrho')d\varrho'\quad(\text{for } T\neq0°\text{K})\quad(41)$$

and

$$\Delta(\varrho)\ln\left(\frac{e\epsilon}{2\sqrt{h}}\right)=-(4\pi)^{-1}\int_{\zeta'>0,|\zeta-\zeta'|>\epsilon}(|\varrho-\varrho'|^{-3}\times\exp[-\tfrac{1}{2}i(\zeta+\zeta'-2\zeta_0)(\xi-\xi')]+|\varrho-R_{\zeta'}\varrho'|^{-3}\times\exp\{-\tfrac{1}{2}i[(\zeta^2+\zeta'^2)/(\zeta+\zeta')-2\zeta_0](\xi-\xi')\})\Delta(\varrho')d\varrho',\quad(\text{for } T=0°\text{K})\quad(42)$$

where we have used the dimensionless variables $\varrho\equiv\mathbf{r}/\xi_H\equiv(\xi,\eta,\zeta)$, $\zeta_0\equiv z_0/\xi_H$, $\tilde{t}=th^{-1/2}$ with $t=T/T_c$, and have also carried out the path integrals with the vector potential given by Eq. (33). As we pointed out there, in this gauge, we can assume $\Delta(\varrho)$ to be independent of ξ but the explicit dependence on z_0 (or ζ_0) is clear in Eqs. (41) and (42). For calculating the surface nucleation critical field H_{c3}, we can limit ourselves to nucleation modes which are also independent of η (or y). We can then perform the η' and ξ' integrations successively in Eq. (42) to get

$$\Delta(\zeta)\ln\left(\frac{e\epsilon}{2\sqrt{h}}\right)=-\frac{1}{2}\int_{\zeta'>0,|\zeta-\zeta'|>\epsilon}\left\{\frac{\exp[-\frac{1}{2}|\zeta^2-\zeta'^2-2\zeta_0(\zeta-\zeta')|]}{|\zeta-\zeta'|}+\frac{\exp[-\frac{1}{2}|\zeta^2+\zeta'^2-2\zeta_0(\zeta+\zeta')|]}{|\zeta+\zeta'|}\right\}\Delta(\zeta')d\zeta',\quad(\text{for } T=0°\text{K})\quad(43)$$

which is a standard integral eigenvalue equation. The equivalent reduction of Eq. (41) is not possible.

The eigenvalue for this equation is $\ln(e\epsilon/2\sqrt{h})$. We are looking for the largest value of $H(H_{c3})$ such that there is a solution, and therefore the minimum eigenvalue. That there is a finite critical field is demonstrated in Appendix B where we find a strict lower bound to the eigenvalues of Eq. (43). The Hermiticity (here symmetry) of the kernel is easily demonstrated. We use a variational technique to estimate and bound[17] the lowest eigenvalue, choosing our trial wave function to be a normalized Gaussian centered on the surface

$$\Delta(\zeta)=(4\alpha/\pi)^{1/4}\exp(-\tfrac{1}{2}\alpha\zeta^2),\qquad(44)$$

where the width α and the parameter ζ_0[16] in the kernel are to be varied. After some mathematical manipulations, we then get

$$\frac{1}{2}\ln\left(\frac{e^2}{2\gamma h}\right)\leq\ln\left\{\left(\frac{\alpha+1}{2\alpha}\right)^{1/2}[(2\alpha)^{1/2}+(\alpha+1)^{1/2}]\right\}-\left(\frac{\alpha}{\alpha+1}\right)^{1/2}\ln(\sqrt{2}-1)-\sum_{i=1}^{5}J_i(\alpha,\zeta_0),\qquad(45)$$

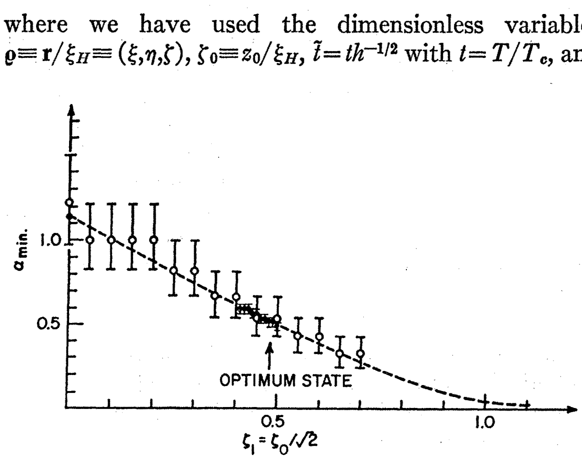

FIG. 2. The width, α_{min}, of the variational state giving the largest H_{c11} for a given value of ζ_0. The open circles are rough values with errors as indicated. The full circles show a refined calculation used to pinpoint the optimum state. The dashed curve shows the general trend.

[17] Strictly speaking, in order to show that the lowest eigenvalue is bounded above by any matrix element of the kernel, and thus that a variational value for this eigenvalue will be an upper bound to it, one must first demonstrate that the eigenfunctions of the kernel are a complete set. Separable kernels, for example, do not provide a complete set of eigenfunctions. A direct proof of completeness for an arbitrary Hermitian kernel is rarely possible and completeness is often merely assumed. On the other hand, a proper variational formulation of superconductivity can serve us as well as a proof of completeness. Two such treatments are those of G. Eilenberger [Z. Physik 182, 427 (1965); 190, 142 (1966); Phys. Rev. 153, 584 (1967)] and W. Silvert and L. N. Cooper [Phys. Rev. 141, 336 (1966)]. The former, considered as a minimum principle rather than a statement of stationarity, can be shown to justify our upper bound calculation, while the latter, again considered as a minimum principle, implies the former. These variational treatments of superconductivity will be discussed elsewhere by one of us (CRH) where it will be reconfirmed that they are indeed minimum principles. We wish to thank Dr. D. Falk for bringing the completeness question to our attention.

where

$$J_1(\alpha,\zeta_0)\equiv\int_0^\infty du\frac{\exp(\sqrt{2}\zeta_0u)-1}{u}\exp\left[-\frac{\alpha^2-1}{2\alpha}u^2\right]\left[1-\mathrm{erf}\left(\frac{\alpha+1}{(2\alpha)^{1/2}}u\right)\right],$$

$$J_2(\alpha,\zeta_0)\equiv\int_0^{\sqrt{2}\zeta_0}\frac{du}{u}\exp\left[-\frac{\alpha^2-1}{2\alpha}u^2\right]\left\{\exp(-\sqrt{2}\zeta_0u)\left[\mathrm{erf}\left(\alpha^{1/2}\zeta_0+\frac{u}{(2\alpha)^{1/2}}\right)-\mathrm{erf}\left(\frac{\alpha-1}{(2\alpha)^{1/2}}u\right)\right]\right.$$
$$\left.-\exp(+\sqrt{2}\zeta_0u)\left[\mathrm{erf}\left(\alpha^{1/2}\zeta_0+\frac{u}{(2\alpha)^{1/2}}\right)-\mathrm{erf}\left(\frac{\alpha+1}{(2\alpha)^{1/2}}u\right)\right]\right\},$$

$$J_3(\alpha,\zeta_0)\equiv\left(\frac{\alpha}{\alpha+1}\right)^{1/2}\int_0^\infty du\frac{\exp(\sqrt{2}\zeta_0u)-1}{u}\exp[-\tfrac{1}{2}(\alpha+1)u^2]\ \mathrm{erf}[2^{-1/2}(\alpha+1)^{1/2}u],$$

$$J_4(\alpha,\zeta_0)\equiv\int_0^{\sqrt{2}\zeta_0}\frac{du}{u}\left\{\exp[-\tfrac{1}{2}(\alpha-1)u^2-\sqrt{2}\zeta_0u]\left(\frac{2\alpha}{\pi}\right)^{1/2}f[\tfrac{1}{2}(\alpha-1),u]\right.$$
$$\left.-\exp[-\tfrac{1}{2}(\alpha+1)u^2+\sqrt{2}\zeta_0u]\left(\frac{\alpha}{\alpha+1}\right)^{1/2}\mathrm{erf}[2^{-1/2}(\alpha+1)^{1/2}u]\right\},$$

and

$$J_5(\alpha,\zeta_0)\equiv\int_{\sqrt{2}\zeta_0}^{2\sqrt{2}\zeta_0}\frac{du}{u}\left\{\exp[-\tfrac{1}{2}(\alpha-1)u^2-\sqrt{2}\zeta_0u]\left(\frac{2\alpha}{\pi}\right)^{1/2}f[\tfrac{1}{2}(\alpha-1),(u(2\sqrt{2}\zeta_0-u))^{1/2}]\right.$$
$$\left.-\exp[-\tfrac{1}{2}(\alpha+1)u^2+\sqrt{2}\zeta_0u]\left(\frac{\alpha}{\alpha+1}\right)^{1/2}\mathrm{erf}[(\tfrac{1}{2}(\alpha+1)u(2\sqrt{2}\zeta_0-u))^{1/2}]\right\},$$

with

$$f(a,b)=\int_0^b\exp[-ax^2]dx$$
$$=\left(\frac{\pi}{4a}\right)^{1/2}\mathrm{erf}(b\sqrt{a})\quad\text{for } a>0$$
$$=|a|^{-1/2}\exp(|a|b^2)F(b|a|^{1/2})\quad\text{for } a<0$$

and the function

$$F(x)=\exp(-x^2)\int_0^x\exp(x^2)dx$$

being called Dawson's integral.

Keeping $\zeta_0=0$ and only varying α to minimize the right-hand side of Eq. (45) is particularly simple and we obtain

$$\alpha_{\min}=1.1350;\ \tfrac{1}{2}\ln\left(\frac{e^2}{2\gamma h}\right)\leq 0.4145,$$

or

$$H_{c11}(\zeta_0=0)/H_{c2}\geq 0.8729,\ (\text{for } T=0°\text{K})\qquad(46)$$

where use has been made of the fact that at $T=0°$K, $h_{c2}=e^2/4\gamma$,[11,6] and the notation $H_{c11}(\zeta_0)$ refers to the critical field for nucleation of a state whose wave function is characterized by a particular value of ζ_0.[18]

For $\zeta_0\neq 0$, we used the 7094 computer of the University of Maryland to carry out all of the integrals in Eq. (45) for various values of α and ζ_0. Minimizing the eigenvalue with respect to α, we get the functional dependence of $H_{c11}(\zeta_0)$ on ζ_0 which is shown in Fig. 1. Further minimizing the eigenvalue with respect to ζ_0 then gives us

$$\alpha_{\min}=0.52,$$
$$(\zeta_0)_{\min}=0.68,$$
$$\tfrac{1}{2}\ln(e^2/2\gamma h)\leq 0.0192,$$

and

$$H_{c3}/H_{c2}\geq 1.925\quad(\text{for } T=0°\text{K}).\qquad(47)$$

In Fig. 2 we have also shown the dependence of the width parameter of the pair wave function, $\alpha_{\min}(\zeta_0)$, on the "center of nucleation" parameter ζ_0.[19,20]

We can now compare our results with the corresponding ones in the L-G region. There the exact calculation

[18] Using these bounds on $H_{c11}(\zeta_0)$ we can show that our LGE(34) is not equivalent to the equation of Helfand and Werthamer, Eq. (34′) plus a boundary condition. The exact solution of Eq. (34′) for $z_0=0$ is a Gaussian centered at $z=0$, and for this case the BC is immediately satisfied. Then $H_{c11}(\zeta_0)$ would be equal to H_{c2} and our variational calculation, using a Gaussian trial function, would give the exact value. But we see in Eq. (48) that our best variational result is $0.87H_{c2}$ so the two equations cannot be the same. This also makes it highly unlikely that the nucleation wave function found in the L-G region is the correct wave function also outside that region.

[19] That the parameter z_0 gives the position of the center of nucleation is rigorously true for the bulk nucleation cases, and is only roughly true for the surface nucleation cases. In the L-G region, it gives the point where the current density vanishes for surface as well as for bulk nucleation modes, but for lower temperature cases, even this is perhaps no longer true since the current density now depends on the pair wave function in a rather complicated nonlocal fashion.

[20] Notice that we have quantized the possible values of $u=\alpha/(1+\alpha)$ in numerical computation which gives the errors indicated in the figure.

by SJdG gives

$$(\zeta_0)_{\min}=0.768,$$
$$H_{c3}/H_{c2}=1.695 \quad (\text{for } T_c-T\ll T_c\text{, exact result}). \quad (48)$$

It is better, however, to compare our results with those from a similar variational calculation in the L-G region using the same trial wave function as we have used here,[21] which reads

$$\alpha_{\min}=0.603,$$
$$(\zeta_0)_{\min}=0.727,$$
$$H_{c3}/H_{c2}=1.658$$
$$(\text{for } T_c-T\ll T_c\text{, variational result}). \quad (49)$$

We therefore see that the variational critical field ratio H_{c3}/H_{c2} is roughly 16% higher at $T=0°\text{K}$ than in the L-G region. Using this percentage increase and the exact value of the ratio in the L-G region, we estimate that the exact value for H_{c3} at $T=0°\text{K}$ will probably be near $1.97H_{c2}$.

In Appendix B, we find an upper bound for the value of H_{c3} at $T=0°\text{K}$: $H_{c3}/H_{c2}\lesssim 5.22$, which, however, does not help us very much in pinpointing the exact value of H_{c3}.

IV. EXTENSION TO SMALL BUT NON-VANISHING TEMPERATURES

For $T\neq 0°\text{K}$, Eq. (41) should take the place of Eq. (42). Again, with $\Delta(\mathbf{\varrho})$ limited to $\Delta_T(\zeta)$ [the subscript T is added to distinguish it from the corresponding quantity at $T=0°\text{K}$, $\Delta_0(\zeta)$] we can simplify the equation slightly to get

$$\Delta_T(\zeta)\ln\left(\frac{e\epsilon}{2\sqrt{h_T}}\right)$$
$$=-\tfrac{1}{2}\int_{0,|\zeta-\zeta'|>\epsilon}^{\infty}[K_{1,T}(\zeta,\zeta')+K_{2,T}(\zeta,\zeta')]\Delta(\zeta')d\zeta', \quad (50)$$

with

$$K_{1,T}(\zeta,\zeta')=\tilde{t}\int_1^\infty du\frac{J_0[\frac{1}{2}(\zeta+\zeta'-2\zeta_0)(\zeta-\zeta')(u^2-1)^{1/2}]}{u\sinh(\tilde{t}|\zeta-\zeta'|u)},$$

and

$$K_{2,T}(\zeta,\zeta')$$
$$=\tilde{t}\int_1^\infty du\frac{J_0\{\frac{1}{2}[\zeta^2+\zeta'^2-2\zeta_0(\zeta+\zeta')](u^2-1)^{1/2}\}}{u\sinh(\tilde{t}|\zeta-\zeta'|u)}, \quad (51)$$

where J_0 is the Bessel function of order zero.

Following closely Gor'kov's corresponding calculation for H_{c2},[11] we let $h_T\equiv h_0+\delta h_T$, $\mathbf{K}_{i,T}\equiv\mathbf{K}_{i,0}+\delta\mathbf{K}_{i,T}$ for $i=1, 2$, where h_0 corresponds to the value of H_{c3} at $T=0°\text{K}$ as h_T does at finite T. We also define $\Delta_T(\zeta)\equiv\Delta_0(\zeta)+\lambda(\zeta)$. Equation (50) can then be symbolically written, to lowest order in $\tilde{t}$, as

$$\lambda(\zeta)\ln\left(\frac{e\epsilon}{2\sqrt{h_0}}\right)+\tfrac{1}{2}\int_0^\infty[K_{1,0}(\zeta,\zeta')+K_{2,0}(\zeta,\zeta')]\lambda(\zeta')d\zeta'$$
$$=\tfrac{1}{2}h_0^{-1}\delta h_T\Delta_0(\zeta)-\tfrac{1}{2}\int_0^\infty[\delta K_{1,T}(\zeta,\zeta')$$
$$+\delta K_{2,T}(\zeta,\zeta')]\Delta_0(\zeta')d\zeta', \quad (52)$$

so that

$$h_0^{-1}\delta h_T=\int_0^\infty\int_0^\infty[\delta K_{1,T}(\zeta,\zeta')+\delta K_{2,T}(\zeta,\zeta')]\Delta_0^*(\zeta)$$
$$\times\Delta_0(\zeta')d\zeta d\zeta',$$

when

$$\int_0^\infty|\Delta_0(\zeta)|^2d\zeta=1. \quad (53)$$

Symbolically, therefore,

$$h_0^{-1}\delta h_T=\langle\delta\mathbf{K}_{1,T}\rangle+\langle\delta\mathbf{K}_{2,T}\rangle. \quad (54)$$

Now for $|\zeta+\zeta'-2\zeta_0|\gg\tilde{t}$,

$$\delta K_{1,T}(\zeta,\zeta')=-\frac{\tilde{t}^2}{3}\frac{\exp[-\frac{1}{2}|\zeta^2-\zeta'^2-2\zeta_0(\zeta-\zeta')|]}{|\zeta+\zeta'-2\zeta_0|}, \quad (55)$$

and for $|(\zeta^2+\zeta'^2)/(\zeta+\zeta')-2\zeta_0|\gg\tilde{t}$,

$$\delta K_{2,T}(\zeta,\zeta')=-\frac{\tilde{t}^2}{3}\frac{\exp[-\frac{1}{2}|\zeta^2+\zeta'^2-2\zeta_0(\zeta+\zeta')|]}{|(\zeta^2+\zeta'^2)/(\zeta+\zeta')-2\zeta_0|}. \quad (56)$$

Within the regions $|\zeta+\zeta'-2\zeta_0|\lesssim\tilde{t}$, $|(\zeta^2+\zeta'^2)/(\zeta+\zeta')-2\zeta_0|\lesssim\tilde{t}$, for $\mathbf{K}_{1,T}$, $\mathbf{K}_{2,T}$, respectively, the expansion procedure is not valid and $\delta\mathbf{K}_{1,T}$, $\delta\mathbf{K}_{2,T}$ are therefore much more involved. However, it is not hard to see that within these regions, $\delta\mathbf{K}_{1,T}$ and $\delta\mathbf{K}_{2,T}$ are $\sim\tilde{t}$, so that the total contribution to $h_0^{-1}\delta h_T$ from these integration regions are $\sim\tilde{t}^2$. To the lowest order, which is $\sim\tilde{t}^2\ln\tilde{t}$, we therefore have:

$$\langle\delta\mathbf{K}_{1,T}\rangle=-\frac{\tilde{t}^2}{3}\int_0^\infty\int_0^\infty\frac{\exp[-\frac{1}{2}|\zeta^2-\zeta'^2-2\zeta_0(\zeta-\zeta')|]}{|\zeta+\zeta'-2\zeta_0|}$$
$$\times\Delta^*(\zeta)\Delta(\zeta')d\zeta d\zeta',$$
$$\langle\delta\mathbf{K}_{2,T}\rangle=-\frac{\tilde{t}^2}{3}\int_0^\infty\int_0^\infty\frac{\exp[-\frac{1}{2}|\zeta^2+\zeta'^2-2\zeta_0(\zeta+\zeta')|]}{|(\zeta^2+\zeta'^2)/(\zeta+\zeta')-2\zeta_0|}$$
$$\times\Delta^*(\zeta)\Delta(\zeta')d\zeta d\zeta',$$

where the integration regions are restricted as above. Using our trial wave function, Eq. (44), we can then get, to order $\tilde{t}^2\ln\tilde{t}$:

$$h_0^{-1}\delta h_T=w(\lambda)\tilde{t}^2\ln\tilde{t}+O(\tilde{t}^2),$$

and therefore,

$$H_{c3}(T)/H_{c3}(0)=1+w(\lambda)\tilde{t}^2\ln\tilde{t}+O(\tilde{t}^2)$$
$$=1+w(\lambda)[h_{c3}(0)]^{-1}t^2\ln t+O(t^2), \quad (57)$$

[21] See, for example, Refs. 2, 14.

with

$$w(\lambda)\equiv\tfrac{4}{3}[\exp(-\lambda^2)\,\mathrm{erf}(\lambda)+4\lambda\pi^{-1/2}\times\exp(-4\lambda^2)\int_0^1(2-u^2)^{1/2}\exp(2\lambda^2u^2)du]$$

and $\lambda=\zeta_0\sqrt{\alpha}$. (Here $\tilde{t}=\tilde{t}_{c3}\equiv th_{c3}^{1/2}$.)

Our variational result gives $\lambda\cong0.49$. A numerical integration then gives $w(\lambda)\cong1.39$. We thus get, using

$$[h_{c3}(0)]^{-1}=[h_{c2}(0)(h_{c3}(0)/h_{c2}(0))]^{-1}\cong[1.93\times e^2/4\gamma]^{-1}\cong0.50:$$

$$H_{c3}(T)/H_{c3}(0)\cong1+0.70t^2\ln t+O(t^2). \qquad (58)$$

Comparing this result with Gor'kov's corresponding result on H_{c2} at low temperatures[11] (which can be shown to be also the result of Helfand and Werthamer's calculation[6]),

$$H_{c2}(T)/H_{c2}(0)=1+\tfrac{2}{3}\tilde{t}_{c2}^2\ln\tilde{t}_{c2}+0(\tilde{t}_{c2}^2)\cong1+0.65t^2\ln t+0(t^2) \qquad (59)$$

(where $\tilde{t}_{c2}\equiv th_{c2}^{-1/2}$), we then obtain

$$H_{c3}(T)/H_{c2}(T)\cong1.93[1+0.05t^2\ln t+0(t^2)]. \qquad (60)$$

This is only a very rough estimation of the lowest-order correction term for the ratio H_{c3}/H_{c2} at small but nonvanishing temperatures. However, it indicates that the ratio H_{c3}/H_{c2} has a vanishing slope with respect to t at $t=0$, and that the coefficient of the correction term is very small, which means that most of the temperature dependences of H_{c3} and H_{c2} cancel one another in forming the ratio, leaving only a weak temperature dependence. We therefore expect H_{c3}/H_{c2} to be rather flat in the low-temperature region and not to drop very much until T becomes a large fraction of T_c.

V. CONCLUSION AND COMMENTS

Using a variational approach at $T=0$°K, we have studied Gor'kov's linearized gap equation appropriate to a pure superconducting sample separated from a vacuum or an insulator by a specularly reflective plane boundary, in an applied magnetic field parallel to this boundary. We found that the ratio of surface to bulk nucleation critical fields, H_{c3}/H_{c2}, is roughly 14% higher than that in the Landau-Ginzburg region, i.e., when $T_c-T\ll T_c$. A perturbational calculation was then made to find that for small but nonvanishing T, the percentage change of the ratio is roughly equal to 0.05 $(T^2/T_c^2)\ln(T/T_c)$, indicating that the ratio stays more or less constant in the low-temperature region. In a subsequent paper (Paper II), however, we shall show that the same linearized gap equation will also predict that when the temperature is decreased just below the Landau-Ginzburg region, the ratio H_{c3}/H_{c2} decreases at a non-negligible rate, from the value ~1.7 valid in the Landau-Ginzburg region. Combination of the two results therefore indicates that this ratio cannot be described by a monotonic function. Instead, it will possess a minimum somewhere between 0 and T_c. We suspect that the minimum will probably occur quite close to T_c, so that the ratio is essentially larger than 1.7, for $0\leq T\lesssim T_c$. [*Note added in proof*. The conclusions of Paper II are sensitive to the value of a certain expression which was incorrectly evaluated in the literature. Using the correct value, the minimum in H_{c3}/H_{c2} disappears and H_{c3}/H_{c2} seems to increase monotonically as T becomes smaller. See Paper II for a detailed discussion.]

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APPENDIX A: ON GOR'KOV'S EQUIVALENT-SPACE-CUTOFF PROCEDURE

In this appendix we show that Eq. (39) is required in Gor'kov's equivalent-space-cutoff procedure. We consider the special case $T=0$°K and the simplest space cutoff $|\mathbf{r}-\mathbf{r}'|>\delta$. The generalization of the proof to finite T and to other space cutoffs such as $|z-z'|>\delta$ (which we actually use) is then straightforward.

Gor'kov's procedure accomplishes two things. First the inconvenient limit of summation at finite ω_D which should appear in Eq. (23) and which would then modify Eqs. (34) through (37) is replaced by the more convenient spatial limitation $|\mathbf{r}-\mathbf{r}'|>\delta$. A value of δ can be found for which this replacement is essentially exact, as we note below. In addition, however, it is also convenient to eliminate the potential strength $\lambda N(0)$ in favor of other parameters, and this is accomplished by use of Eq. (38). In Eq. (38) one can let $\omega_D\to\infty$ if a spatial cutoff at $|\mathbf{R}|=\delta'$ is substituted and again δ' can be found such that the substitution is essentially exact. It is simplest, however, just to find the relationship between δ and δ' which will ensure that the errors in the two expressions will compensate one another when $\lambda N(0)$ is eliminated. Equivalently, one can set $\delta=\delta'$ and find the appropriate relationship between $\mathbf{R}$ in Eq. (38) and $(\mathbf{r}-\mathbf{r}')$ in Eqs. (36) and (37) which will lead to the same compensation.

Setting $\mathbf{R}=\alpha(\mathbf{r}-\mathbf{r}')$, letting $\omega_D\to\infty$, inserting the spatial cutoff and eliminating $\lambda N(0)$ between Eqs. (37)

and (38) gives the equation

$$\Delta(\mathbf{r})\frac{\alpha}{\pi\gamma\xi_0}\int_0^\infty\frac{du}{u}\int_{|\mathbf{r}-\mathbf{r}'|>\delta}\frac{\sin(\alpha u|\mathbf{r}-\mathbf{r}'|/v_F)}{|\mathbf{r}-\mathbf{r}'|^2}K_1\left(\frac{\alpha\Delta_0|\mathbf{r}-\mathbf{r}'|}{v_F}\right)$$

$$=\int_{z'>0,|\mathbf{r}-\mathbf{r}'|>\delta}d\mathbf{r}'\Delta(\mathbf{r}')\left\{\frac{\exp\left[-2ei\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]}{|\mathbf{r}-\mathbf{r}'|^3}+\frac{\exp\left[-2ei\int_{\mathbf{r}'}^{\mathbf{r}_1,\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]}{|\mathbf{r}-R_{z'}\mathbf{r}'|^3}\right\}. \quad \text{(A1)}$$

Each side of this equation differs from the corresponding exact expression. Let E_l and E_r be the "errors" in the left- and right-hand sides of Eq. (A1). If we can choose α such that $E_l=E_r$ then Eq. (A1) will be correct as it stands.

Now for δ sufficiently small we may include the spatial cutoff in the "correct" expressions introducing negligible errors of order δ since all the integrals converge. Then the "errors" are

$$E_l=\Delta(\mathbf{r})\frac{\alpha}{\pi\gamma\xi_0}\int_{\omega_D}^\infty\frac{du}{u}\int_{|\mathbf{r}-\mathbf{r}'|>\delta}d\mathbf{r}'\frac{\sin(\alpha u|\mathbf{r}-\mathbf{r}'|/v_F)}{|\mathbf{r}-\mathbf{r}'|^2}K_1\left(\frac{\alpha\Delta_0|\mathbf{r}-\mathbf{r}'|}{v_F}\right)$$
$$\simeq\Delta(\mathbf{r})\frac{2}{\pi}\int_{\omega_D}^\infty\frac{du}{u}\int_{|\mathbf{r}-\mathbf{r}'|>\delta}d\mathbf{r}'\frac{\sin(\alpha u|\mathbf{r}-\mathbf{r}'|/v_F)}{|\mathbf{r}-\mathbf{r}'|^3}$$
$$=-4\pi\Delta(\mathbf{r})\ln(\alpha\gamma\omega_D\delta v_F^{-1}), \quad \text{(A2)}$$

where one assumes $\omega_D\gg\Delta_0$ and $\omega_D\delta v_F^{-1}\ll1$, and

$$E_r=\int_{z'>0,|\mathbf{r}-\mathbf{r}'|>\delta}d\mathbf{r}'\Delta(\mathbf{r}')\frac{\exp\left[-2ei\int_{\mathbf{r}'}^{\mathbf{r}}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]}{|\mathbf{r}-\mathbf{r}'|^3}\times\exp\left[\frac{-2\omega_D}{v_F}|\mathbf{r}-\mathbf{r}'|\right]$$
$$\simeq\Delta(\mathbf{r})\int_{|\mathbf{r}-\mathbf{r}'|>\delta}d\mathbf{r}'\frac{\exp[-2\omega_D v_F^{-1}|\mathbf{r}-\mathbf{r}'|]}{|\mathbf{r}-\mathbf{r}'|^3}$$
$$=-4\pi\Delta(\mathbf{r})\ln(2\gamma\omega_D\delta v_F^{-1}) \quad \text{(A3)}$$

as the scales of variation of the integral phase factor and $\Delta(\mathbf{r})$ are $\sim\xi_0$ which is $\gg v_F/\omega_D$.

Comparing Eqs. (A2) and (A3) we see that $\alpha=2$ is required to make Eq. (A1) correct. Further, as we mentioned above, a particular choice, $\delta=v_F/2\gamma\omega_D$, will make the individual "errors" vanish as well and would be the correct choice for the cutoff if we were not eliminating $\lambda N(0)$ as well. Finally, we mention that for the cutoff $|z-z'|>\delta$ the appropriate value would be $\delta=v_F/2e\gamma\omega_D$, where e is the base of the natural logarithms.

APPENDIX B: UPPER BOUND FOR $H_{c11}(\zeta_0)$ AND H_{c3}

In this appendix, we show that for any given ζ_0, Eq. (45) implies the existence of a lower bound to its eigenvalue $\ln(\frac{1}{2}e\epsilon h^{-1/2})$, hence an upper bound to the nucleation critical field $H_{c11}(\zeta_0)$. The largest one among these upper bounds will then naturally give an upper bound to H_{c3}. We first cast Eq. (45) into the form

$$\Delta(|\zeta|)\ln\left(\frac{e\epsilon}{2\sqrt{h}}\right)=-\tfrac{1}{2}\Delta(|\zeta|)\int_{-\infty,|\zeta-\zeta'|>\epsilon}^{\infty}\frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_0(\zeta-\zeta')|]}{|\zeta-\zeta'|}d\zeta'$$
$$-\tfrac{1}{2}\int_{-\infty}^{\infty}\frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_0(\zeta-\zeta')|]}{|\zeta-\zeta'|}(\Delta(|\zeta'|)-\Delta(|\zeta|))d\zeta',$$

which then implies

$$\ln\left(\frac{e\epsilon}{2\sqrt{h}}\right)\int_{-\infty}^{\infty}|\Delta(|\zeta|)|^2d\zeta=-\tfrac{1}{2}\int_{-\infty}^{\infty}|\Delta(|\zeta|)|^2\int_{-\infty,|\zeta-\zeta'|>\epsilon}^{\infty}\frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_0(\zeta-\zeta')|]}{|\zeta-\zeta'|}d\zeta'$$
$$+\tfrac{1}{4}\int_{-\infty}^{\infty}\frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_0(\zeta-\zeta')|]}{|\zeta-\zeta'|}|\Delta(|\zeta|)-\Delta(|\zeta'|)|^2d\zeta d\zeta'.$$

The second term is positive definite, so we have

$$\ln\left(\frac{e\epsilon}{2\sqrt{h}}\right)\geq \int_{-\infty}^{\infty} I(|\zeta|,\zeta_0)|\Delta(|\zeta|)|^2 d\zeta \Big/ \int_{-\infty}^{\infty} |\Delta(|\zeta|)|^2 d\zeta,$$

where

$$I(|\zeta|,\zeta_0)=-\tfrac{1}{2}\int_{-\infty}^{\infty} d\zeta'|\zeta-\zeta'|^{-1} \times\exp[-\tfrac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_0(\zeta-\zeta')|]$$
$$=I_1(|\zeta|,\zeta_0)+I_2(|\zeta|,\zeta_0),$$

while

$$I_1(|\zeta|,\zeta_0)=-\tfrac{1}{2}\int_{-\infty}^{\infty} d\eta'|\eta-\eta'|^{-1}\exp[-|\eta^2-\eta'^2|],$$

with $\eta=(|\zeta|-\zeta_0)/\sqrt{2}$, $\eta'=(\zeta'-\zeta_0)/\sqrt{2}$, and

$$I_2(|\zeta|,\zeta_0)=\tfrac{1}{2}\int_0^{\infty} d\zeta'||\zeta|+\zeta'|^{-1} \times\{\exp[-\tfrac{1}{2}||\zeta|^2-\zeta'^2-2\zeta_0(|\zeta|+\zeta')|] -\exp[-\tfrac{1}{2}||\zeta|^2+\zeta'^2-2\zeta_0(|\zeta|+\zeta')|]\}.$$

The integral $I_1(|\zeta|,\zeta_0)$ has been studied by Gor'kov.[11] From this results, we get

$$I_1(|\zeta|,\zeta_0)=\tfrac{1}{2}\ln(\tfrac{1}{2}\gamma\epsilon^2)+\Phi[(|\eta|-\zeta_0)/\sqrt{2}],$$

where

$$\Phi(x)\equiv\exp[-x^2]\int_0^{|x|}\exp[x'^2]x'\ln[(|x|+x')/(|x|-x')]dx'\geq 0,\quad \text{for all } x.$$

We therefore get

$$\tfrac{1}{2}\ln(e^2/2\gamma h)\geq\int_{-\infty}^{\infty} I_2(|\zeta|,\zeta_0)|\Delta(|\zeta|)|^2 d\zeta \Big/ \int_{-\infty}^{\infty}|\Delta(|\zeta|)|^2 d\zeta. \quad \text{(B1)}$$

Up to now, all the steps we have taken are in close analogy with Gor'kov's corresponding calculation on H_{c2}. However, because of the simpler integral equation which Gor'kov worked with, he obtained $\frac{1}{2}\ln(e^2/2\gamma h_{c2})\geq 0$ instead of our Eq. (B1), from which he concluded $h_{c2}\leq h_{c2}^{\mathrm{UB}}$, where the upper bound h_{c2}^{UB} is equal to $e^2/2\gamma$. For our present case, we first notice that for $\zeta_0\leq 0$, we have $I_2\geq 0$ for all ζ. This implies that we can find $h_{c11}^{\mathrm{UB}}(\zeta_0)\leq h_{c2}^{\mathrm{UB}}$ for all $\zeta_0\leq 0$, which strongly suggests (but does not prove) that no surface nucleation modes with $\zeta_0\leq 0$ are physically more favorable than the bulk nucleation mode, a fact known to be true in the L-G region. For $\zeta_0>0$, I_2 is no longer positive definite. But if $\alpha(\zeta_0)>0$ exists such that $I_2(|\zeta|,\zeta_0)\geq-\alpha(\zeta_0)$ for all ζ, we can then have $h_{c11}^{\mathrm{UB}}(\zeta_0)=\frac{1}{2}(e^2/\gamma)\exp[2\alpha(\zeta_0)]$. That such a finite $\alpha(\zeta_0)$ does exist for any value $\zeta_0>0$ is assured by the fact that $I_2(|\zeta|,\zeta_0)$ is defined and continuous for all ζ, $-\infty<\zeta<\infty$, and as $|\zeta|\to\infty$, $I_2\to 0$. To estimate $\alpha(\zeta_0)$, however, we must employ numerical method. We omit the details here but only point out that (i) $\alpha(\zeta_0)$ is continuous, and $\to 0$ as $\zeta_0\to 0$ or ∞, and (ii) $\alpha=\min\alpha(\zeta_0)$ exists and is found to be $\cong 0.48$ so that $h_{c3}\leq 2.61(e^2/2\gamma)=5.22h_{c2}$.

Comparing our procedure in getting this upper bound for H_{c3} with Gor'kov's corresponding one for H_{c2}, we feel that our upper bound is looser than his, due to our replacement of $I_2(|\zeta|,\zeta_0)$ by its minimum value. Since Gor'kov's upper bound for H_{c2} is twice as large as the true value of H_{c2}, we expect that our upper bound to H_{c3} is more than twice larger than the true value of H_{c3}, indicating that most probably the exact value of H_{c3} is somewhere around $2H_{c2}$.