# THE RATIO OF SURFACE TO BULK NUCLEATION CRITICAL FIELDS, $H_{c3}/H_{c2}$, FOR PURE SUPERCONDUCTORS IN THE NON-LANDAU-GINZBURG REGION

by

Chia-Ren Hu

Dissertation submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
1968

NGL-21-002-008

## ERRATA AND ADDENDA

1. P. 11, 1st row: In "$\nabla_x f(z)\Big|_{z=0} = 0$", "$\nabla_x$" should be "$\nabla_z$".

2. P. 19, last paragraph: Notice that $\omega \sim \pi T \sim \frac{2\pi T}{v_F} \frac{p_F}{m} \sim \frac{p_F}{m\xi_o}$. Also notice that even though at T = 0°K the zero field kernel becomes a long-range one, it will be seen later that the field dependent phase factors in the kernel for $H \quad H_{c2}$ will supply an effective damping so that we still have $|\vec{r}-\vec{r}\,'| \sim 0(\xi_H) \sim 0(\xi_o)$.

3. P. 20, Eq. (II-30): The factor "$\frac{1}{|\vec{r}-\vec{r}\,'|}$" should be "$\frac{1}{|\vec{r}-\vec{r}\,'|^2}$".

4. P. 22, 7th and 6th rows from below: "We thus have reduced ... L-G equation." should be changed to: "Solving Eq. (II-35) is therefore reduced to solving Eq. (II-37) alone, which is of the same type as the linearized L-G equation.". Also, same page, 5th row from below: "(II-36) and (II-37)" should be "(II-37) and (II-38)".

5. P. 27, Eq. (III-3): The lower limits of the two path integrations should be $\vec{r}\,'$. Also the line below Eq. (III-3): "where $\fint_{\vec{r}\,'}^{\vec{r}} \equiv \int_{\vec{r}\,'}^{\vec{r}} + \int_{\vec{r}\,'}^{\vec{r}}$ " should be changed to "where $\fint_{\vec{r}\,'}^{\vec{r}} \equiv \int_{\vec{r}\,'}^{\vec{r}_1} + \int_{\vec{r}_1}^{\vec{r}}$ ".

6. P. 31, 4th row from below: "the image term $G^{(o)}_{H,\omega}$"should be "the image term in $G^{(o)}_{H,\omega}$ ". Also same page, 2nd row from below: "phase integral" should be "path integral".

7. P. 35, footnote to be added at the end of the first sentence:

   "That a pair wave function will have a rapidly oscillating component near a sample surface has already been found by Falk in studying finite and semi-infinite superconducting slabs, and in studying semi-infinite superconducting and normal metals in contact (D. S. Falk, Phys. Rev. <u>132</u>, 1576 (1963)); by Leyendecker in studying the free surface side of a normal metallic slab backed by a superconductor (A. J. Leyendecker, Ph.D. Thesis, University of Maryland, 1967); and by Boyd in studying the vicinity of a tunneling barrier (R. G. Boyd, Phys. Rev. <u>167</u>, 407 (1968)); all assuming that no external magnetic field is applied to the sample. Boyd has restricted his attention to the neighborhood of a second order phase transition, as we did in this thesis, but Falk and Leyendecker have considered the general non-linear situations."

8. P. 35, Eq. (IV-1): "$k^{(o)}(|\vec{r}'R_z,\vec{r}'|)$" should be "$k^{(o)}(|\vec{r}-R_z,\vec{r}'|)$".

9. P. 36, Eq. (IV-4): In the first phase factor, the lower limit of integration should be $\vec{r}'$.

10. P. 39, 12th row from above: Insert "by" after "(IV-4)".

11. P. 41, Eq. (IV-9): "$\ln(\sqrt{2+1})$" should be $\ln(\sqrt{2} + 1)$".

12. P. 43, beginning of the 2nd paragraph: "the surface nucleation critical field $H_{c3}$" should be changed to "the critical field ratio $H_{c3}/H_{c2}$".

13. P. 51, 3rd row from below: "minimizing $H_{c/\!/}(\zeta_o)$" should be "maximizing $H_{c/\!/}(\zeta_o)$".

14. P. 61, 2nd row from below: In "$|\nabla_z\Delta(\vec{r})| \sim |\tilde{\nabla}_z\Delta(\vec{r})|$", "$\sim$" should be "=".

15. P. 70, 9th row from below: In "directions perpendicular to ...", "perpendicular" should be "parallel".

16. P. 72: Notice that Eq. (V-41) is not missing, but is embedded in the text.

17. P. 78, on the right hand side of Eq. (V-68): "$H_{c3}$" should be "$H_{c2}$".

18. P. 79, 2nd row in "Conclusion III": "to two orders in ..." should be "to two non-trivial orders in ...".

19. P. 80, 7th row from below: "see fig.  " should be "See fig. 5".

20. P. 86, Eqs. (IV-4) and (IV-5): the symbols "x" after "dz" should be multiplication signs.

21. P. 87, 11th row from below: "$\int \frac{d}{dz}\,[H-\varepsilon]\psi dz$" should be "$\int \frac{d\psi}{dz}\,[H-\varepsilon]\psi dz$".

22. P. 106, Eq. (A-2): "$e^{i\vec{k}\cdot\vec{r}}$" should be "$e^{i\vec{k}_\perp\cdot\vec{r}}$".

23. P. 107, Eq. (A-8): "$e^{i\vec{k}\cdot(r_\perp - r'_\perp)}$" should be "$e^{i\vec{k}_\perp\cdot(\vec{r}_\perp - \vec{r}'_\perp)}$".

24. P. 114, Eq. (C-2): "$-\!\!\!\!\!\!\int_{\vec{r}'}^{\vec{r}} A(\vec{s})\cdot d\vec{s} = \int_{\vec{r}'}^{\vec{r}} A(\vec{s})\cdot d\vec{s} + \int_{\vec{r}'}^{\vec{r}} A(\vec{s})\cdot d\vec{s}$ "

should be $-\!\!\!\!\!\!\int_{\vec{r}'}^{\vec{r}} A(\vec{s})\cdot d\vec{s} = \int_{\vec{r}'}^{\vec{r}_1} A(\vec{s})\cdot d\vec{s} + \int_{\vec{r}_1}^{\vec{r}} A(\vec{s})\cdot d\vec{s}$.

25. P. 118, 8th row from below: "$H_c(\zeta_o)$" should be "$H_{c/\!/}(\zeta_o)$".

26. P. 118, Footnote to be added to the sentence that ends in the 5th row from below:

"Since we do not have a completeness theorem for the set of all eigensolutions of a linear homogeneous integral equation, merely the existence of a ground state does not yet guarantee the validity of an upper bound estimation to the ground state eigenvalue by a variational technique. (The author wishes to thank Prof. D. S. Falk for pointing out this point to him.) We therefore need a suitable variational formulation of Gor'kov's theory of superconductivity, in order to justify our calculation at T = 0°K. One such variational formulation does exist (W. Silvert and L. N. Cooper, Phys. Rev. 141, 336 (1966)) which, however, is not what we need. Fortunately, the author has developed another variational formulation of Gor'kov's theory, the detail of which will be published in a later paper, which exactly served our purpose. Our variational estimation of $H_{c/\!/}(\zeta_o)$ and $H_{c3}$ at T = 0°K is therefore a valid procedure."

27. P. 123, in the right hand side of Eq. (D-1): the front negative sign should be dropped, and the limit of integration should be "$\zeta > 0$" and "$|\vec{\rho}-\vec{\rho}'|>\varepsilon$".

28. P. 128, 9th row from below: "$h_c^{U.B.}(\zeta_o)$" should be "$h_{c\parallel}^{U.B.}(\zeta_o)$".

29. P. 141, ref. 19: In "English transl. Soviet Phys. JETP 37, 593 ...), "37" should be "10".

30. P. 145, Fig. 2: Notice that $\zeta_1 = \sqrt{2}\,\zeta_o$ has been used to characterize the states, instead of $\zeta_o$ itself, for computational convenience.

31. P. 146, Fig. 4: Notice that the error bars are due to the fact that we have quantized the possible values of $u = \alpha/(1+\alpha)$ for numerical computation. We have also quantized the possible values of $\zeta_1$ as indicated.

# APPROVAL SHEET

Title of thesis: The Ratio of Surface to Bulk Nucleation Critical Fields, $H_{c3}/H_{c2}$, for Pure Superconductors in the Non-Landau-Ginzburg Region

Name of Candidate: Chia-Ren Hu

Doctor of Philosophy, 1968

Thesis and Abstract Approved: Victor Korenman

Victor Korenman
Assistant Professor
Department of Physics and Astronomy

Date Approved: June 17, 1968

# VITA

Name: Chia-Ren Hu

Permanent Address: 53 Lane 81, Amoy Street, Taipei, Taiwan,
The Republic of China

Degree and Date to be Conferred: Doctor of Philosophy, 1968

Date of Birth: May 25, 1939

Place of Birth: Shanghai, China

Secondary Education: Taiwan Provincial Chian-Kuo Middle School,
Taipei, Taiwan, China, 1952-1958.

| Collegiate Institutions Attended | Dates | Degree | Date of Degree |
|---|---|---|---|
| National Taiwan University | 1958-62 | B.S. | 1962 |
| University of Maryland | 1963-68 | Ph.D. | 1968 |

Major: Physics

Minor: Mathematics

Publications:

Chia-Ren Hu, R. A. Ferrell and V. Korenman, Bull. Am. Phys. Soc. Series II, Vol. 13, #1, 109 (1968).

Positions held:

Teaching Assistant, University of Maryland, 1963-1965

Research Assistant, University of Maryland, 1965-1968

# ABSTRACT

Title of Thesis: The Ratio of Surface to Bulk Nucleation Critical Fields, $H_{c3}/H_{c2}$, for Pure Superconductors in the Non-Landau-Ginzburg Region

Name of Author, Degree Sought, Date: Chia-Ren Hu, Doctor of Philosophy, 1968

Thesis directed by: Victor Korenman

The ratio of surface to bulk nucleation critical fields, $H_{c3}/H_{c2}$, for semi-infinite pure superconductors separated from a vacuum or an insulator by a specularly reflective plane boundary, is studied for both $T \simeq 0$°K and near the Landau-Ginzburg region (as defined by $T_c - T << T_c$). Gor'kov's microscopic formulation of superconductivity theory is employed. A generalized image method is first developed to obtain the normal electron temperature Green's function pertaining to the given sample geometry. The appropriate linearized gap equation for such a sample is then derived. For $T = 0$°K, this linear homogeneous integral equation is then solved by a variational method using a gaussian as the trial wave function. The result $H_{c3}/H_{c2} \geq 1.925$ is obtained, compared with Saint-James and de Gennes' result, $\sim 1.7$, for this ratio in the Landau-Ginzburg region. The result is then extended to small but non-vanishing T by a perturbational method, and the leading term in the temperature dependence of the ratio is found to be $0.05\ T^2 \ln T$ for small T. For $T \approx T_c$, two approaches are employed to calculate $H_{c3}/H_{c2}$. In the first approach, the conventional assumption that the pair wave function is everywhere slowly varying inside the sample is made. It leads to a simultaneous, microscopic derivation of the linearized Landau-Ginzburg equation and its supplementary boundary condition, for samples with a boundary, when $T_c - T << T_c$. This approach is shown to be not self-consistent for temperatures below the Landau-Ginzburg region. The second approach, allowing for the rapidly-varying nature of the pair wave function near the sample surface, is then used. We find the lowest two non-trivial orders in $(1-t)^{1/2}$ as corrections to the result $H_{c3}/H_{c2} = 1.7$, when T gets slightly below the Landau-Ginzburg region, and find that $H_{c3}/H_{c2}$ decreases as the temperature is lowered in this region. We speculate about the qualitative behavior of this ratio in the whole temperature region below $T_c$ and believe it to possess a minimum at some temperature not very far below Tc. Comparison between our calculation and some other presently existing theories are also made. Finally, two criteria concerning the optimum nucleation modes are studied.

# THE RATIO OF SURFACE TO BULK NUCLEATION CRITICAL FIELDS, $H_{c3}/H_{c2}$, FOR PURE SUPERCONDUCTORS IN THE NON-LANDAU-GINZBURG REGION

by

Chia-Ren Hu

Dissertation submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
1968

# ACKNOWLEDGEMENTS

I wish to express my sincere gratitude and thanks to Professor Richard A. Ferrell for suggesting this problem; and to both him and Professor Victor Korenman for their most helpful guidance and advice throughout the course of this research. I am particularly grateful to Professor Victor Korenman for his careful reading of the manuscript.

Mrs. Wendy Magi typed the manuscript; I would like to thank her for her excellent work.

Acknowledgements are due to the U.S. Air Force Office of Scientific Research for financial support of this work under Grant No.'s AF-AFOSR-735-65 and AFOSR-68-1459, and to the Computer Science Center of the University of Maryland for making the IBM-7094 computer available for numerical calculations under the NASA Grant NsG-398.

## TABLE OF CONTENTS

Chapter Page

APPENDIX

## LIST OF FIGURES

# CHAPTER I

## INTRODUCTION AND SUMMARY

The phenomenon of surface superconductivity was first predicted to exist by Saint-James and de Gennes in 1963,[1] on studying ideal superconducting samples in the Landau-Ginzburg (L-G) region, i.e. when the temperature T is very close to the critical temperature $T_c$. At that time, it was already well-known that the bulk superconducting states can only persist for magnetic field strengths below certain critical values, namely $H_c$ for type I superconductors, and $H_{c2}$ for type II superconductors, and it was assumed that above these critical fields the whole system will return to normal. But Saint-James and de Gennes discovered that for a quite large class of superconductors, including some type I superconductors and all type II superconductors, a thin sheath of superconducting region can continue to exist on some part of the sample near its surface, when the magnetic field strength is above these critical values, namely $H_c$ or $H_{c2}$, if the magnetic field is applied parallel to the surface. (For terminology and a good introductory course in superconductivity, the reader is recommended to the book by de Gennes[2]). This new superconducting state, called surface superconductivity, was predicted to persist until another critical field is reached, which is called $H_{c3}$.

We remind the readers that $H_c$, called the thermodynamic critical field, is the magnetic field at which the condensation energy of a homogeneous superconductor is exactly compensated by the total free energy increase due to the exclusion of magnetic flux from inside the whole sample. On the other hand, $H_{c2}$, called the upper critical field or the bulk nucleation critical field, is the magnetic field at and below which a localized superconducting region, usually a thin layer, can exist deep inside a bulk sample. A superconducting sample is classified as type I, or type II, depending on whether $H_{c2}$ is smaller, or greater, than $H_c$.

The newly discovered critical field, $H_{c3}$, can be defined in close analogy with the critical field $H_{c2}$. That is, it is the magnetic field at and below which, a localized superconducting region, usually a thin layer also, can exist near a sample surface, which is parallel to the field. It is therefore named as the surface nucleation critical field.

The phase transition, that occurs at $H = H_{c3}$, like the one at $H = H_{c2}$, is found to be of second order, which means that the superconducting pair amplitude, or the magnitude of the order parameter, will drop to zero continuously, before the surface (bulk) superconducting state disappears, as the magnetic field H reaches $H_{c3}$ ($H_{c2}$) from below. The magnitude of the order parameter is therefore infinitesimally small, everywhere inside the sample, for H in the vicinity of $H_{c3}$ ($H_{c2}$).

This fact allowed Saint-James and de Gennes to compute the exact value of $H_{c3}$ in the L-G region, with not too much difficulty. They found that the ratio of $H_{c3}$ to $H_{c2}$ is always equal to 1.695, or roughly 1.7, independent of the characteristic parameters of the sample, such as its critical temperature $T_c$, its zero temperature energy gap $\Delta_o$, its BCS coherence length $\xi_o$, and its L-G parameter $\kappa$, etc.. (see again ref.[2] for the definition of these quantities.)

For type I superconductors, with their $H_{c2}$ smaller than $H_c$, there also exists the possibility for $H_{c3}$ to be smaller than $H_c$. If this happens, surface superconductivity will not exist in such a sample. But if one reduces the magnetic field gradually from above to below $H_c$, and if non-uniformity of the sample, of the applied field, of the temperature distribution, and small external disturbances are all carefully avoided, a metastably supercooled normal state may be obtained until a lowest possible field is reached, which is defined as the supercooling critical field. For the case when H is perpendicular to the sample surface, this supercooling critical field is $H_{c2}$, since at this field the normal state becomes unstable against spontaneous nucleation of infinitesimal superconducting regions. But for the case when H is parallel to the surface, Saint-James and de Gennes pointed out that this supercooling critical field should then be $H_{c3}$, since for this case nucleation near the sample surface is easier, and therefore occurs earlier, than nucleation inside the bulk.

The discovery of surface superconductivity and the relationship $H_{c3} = 1.7 \times H_{c2}$ lead Saint-James and de Gennes to successfully explain a number of discrepancies between theories and experiments (such as the apparently too high values of the measured supercooling field of type I superconductors), and between experiments of different types (such as the disagreement between the values for the upper critical field of a type II superconductor, as determined by vanishing of the magnetic moment and the appearance of resistivity). (References on these can be found in their original paper.[1]) Their results are thus considered as well-established. (see the discussions in ref.[3] and the abundant references cited there.)

Subsequently, the result $H_{c3} = 1.7\ H_{c2}$ was further extended to all temperatures for dirty superconductors (i.e. when the electron mean free path due to impurities, $\ell$, is $<< \xi_o$), by Maki[4] and by de Gennes[5] independently.

Saint-James and de Gennes' theory is valid for weak coupling superconductors only, so are Maki's and de Gennes' extensions to dirty superconductors. Recently, however, Eilenberger and Ambegaokar[6], as well as Yorke and Bardasis[7] have shown that even for strong coupling superconductors,[8] the ratio $H_{c3}/H_{c2} \cong 1.7$ still holds in the L-G region.

The experiments of Rosenblum and Cardona[9], and of Tomasch[10] indicate, however, that they might have observed a deviation of the ratio $H_{c3}/H_{c2}$ from the predicted value 1.7. The samples they used are pure Pb and Pb with a few percent of Tl, which belong to the strong coupling category. Their conclusions were drawn from data for relatively pure samples outside the L-G region.

Since the possibility of this apparent deviation being due to strong coupling effects has been ruled out, we suspect that it could be because the samples are not in the L-G region nor in the dirty limit, especially since $H_{c3}$ in this case has never been explored.

It is to this question that we have addressed ourselves in this thesis. Unfortunately, to study superconductivity in the low temperature, pure limit is much more difficult than other cases. To study surface nucleation, we must consider samples with boundaries, which complicates the problem even more. We therefore can only calculate $H_{c3}$ for pure samples at two limiting temperature regions, i.e. for $T \overset{\sim}{=} 0^\circ K$, and for T near the L-G region. For the former case, $H_{c3}$ can only be estimated by a variational approach, which indicates that at $T = 0^\circ K$, the ratio $H_{c3}/H_{c2}$ is $\geq 1.93$ with a vanishing initial slope w.r.t. T; while for the latter case, the results we get for $H_{c3}$ are exact to order $(1-t)^{5/2}$, where $t \equiv T/T_c$ is the reduced temperature, which indicates that as T just begins to drop below the L-G region, the initial tendency of the ratio $H_{c3}/H_{c2}$ is to drop below its value in the L-G region, i.e. 1.7, with not a negligible rate. Comparing this conclusion with our low temperature results, we find that as T is further reduced below $T_c$, the ratio $H_{c3}/H_{c2}$ is necessary to increase, pass the value 1.7 again at some $T_x < T_c$, and finally approach some value roughly equal to, or slightly larger than, 1.93 horizontally, as T approaches $0^\circ K$. We emphasize that these results pertain to a semi-infinite sample separated from a vacuum or an insulator by a specularly reflective plane boundary parallel to the applied magnetic field.

Let us now briefly summerize the major contents of the later chapters:

In chapter II, we first review some previous work which is closely related to the present calculation. It includes the Saint-James and de Gennes' calculation of $H_{c3}$ in the L-G region,[1] with the dirty limit case[4,5] very briefly mentioned, Gor'kov's microscopic theory of superconductivity[11] which forms the basis of our present calculation, and Helfand and Werthermer's calculation of $H_{c2}$ at all temperatures below $T_c$[12] (for pure samples only), which serves as an illustration of the use of Gor'kov's theory, and as a guide to our present work.

In chapter III, we find the thermal Green's function[13] of a normal electron in our semi-infinite sample, by means of a generalized method of images.

In chapter IV, we use the thermal Green's functions found in the previous chapter to obtain Gor'kov's linearized gap equation[13] (LGE) appropriate for studying nucleation phenomena in such a sample. The lowest eigenvalue of this homogeneous integral equation is related to $H_{c3}$. A boundary condition (B.C.) is found from this equation, which the pair wave function order parameter must always satisfy. The equation is then shown to be not equivalent to Helfand and Werthamer's differential equation for $H_{c2}$,[12] plus any B.C.. Finally, the equation is used to calculate $H_{c3}$ and the ratio $H_{c3}/H_{c2}$ at T = 0°K and for $T \approx 0°K$, by variational and perturbational methods respectively. Some discussions on the current-carrying nucleation states are also made.

In chapter V, we turn to temperatures near L-G region. We first show that our LGE is equivalent to the linearized L-G equation[14], and the B.C. used by Saint-James and de Gennes[1] for calculating $H_{c3}$ in the L-G region, if (1-t) is negligible compared with 1. We then calculate corrections to $H_{c3}$ and $H_{c3}/H_{c2}$ to the first two non-vanishing orders in $(1-t)^{1/2}$, when the temperature is slightly below the L-G region. At the end of this chapter, we present a comparison of the results and conclusions of this chapter to some presently existing theories.

In chapter VI, we discuss two criteria that characterize the physically most favorable modes of nucleation, the proofs from first principles in the L-G region, and the possibility of extending them to, and using them at, lower temperatures.

Finally, in chapter VII, we collect all major conclusions and results from all previous chapters, together with a discussion on the possible extensions of the present calculation.

# CHAPTER II

# REVIEW OF PREVIOUS WORK AND FORMULATION OF THE PROBLEM

## $H_{c3}$ in the Landau-Ginzburg Region and in the Dirty Limit

We first review the work of Saint-James and de Gennes,[1] on the calculation of $H_{c3}$ in the L-G region (i.e. when $T_c - T << T_c$).

In the L-G region, it is well known (see for example ref.[2]) that superconductivity is governed by the phenomenological L-G equation,[14] which is in general non-linear. For discussing the nucleation problem, we assume the strength of superconductivity to be everywhere infinitesimally small, since we are asking for the field at which it is just possible for superconductivity to be present. We can therefore start from the linearized version of the L-G equation which we write in the following form:

$$-\frac{1}{4m}\,|\vec{\nabla}_r + 2ie\vec{A}(\vec{r})|^2\Delta(\vec{r}) = \frac{1}{\beta}(1-t)\Delta(\vec{r}), \qquad \text{(II-1)}$$

where m and e are the magnitudes of the electron mass and charge, and $t \equiv T/T_c$. We use units in which $\hbar = c = k_B = 1$, where $k_B$ is the Boltzmann constant.

This equation is written in a form first obtained by Gor'kov,[15] when he derived the L-G equations from his microscopic theory of superconductivity.[11] It differs from the conventional form by using (2m) and (2e) instead of the phenomenological effective mass and charge parameters: $m^*$ and $e^*$, and by using the microscopically defined "gap function", or better the "pair wave function order parameter", $\Delta(\vec{r})$ (see section 2 for microscopic definition), instead of a phenomenological order parameter $\psi(\vec{r})$. In fact, $\Delta(\vec{r})$ differs from $\psi(\vec{r})$ by a numerical constant. But normalization of $\Delta(\vec{r})$ or $\psi(\vec{r})$ does not interest us for our present calculation. $\beta$ is merely a temperature-independent constant. For pure samples, it is equal to $7\zeta(3)\varepsilon_F/6(\pi T_c)^2$,[15] with $\zeta(n)$ being the Reimann zeta function. If we introduce now the BCS coherence length[16] $\xi_o = v_F/(2\pi T_c)$(notice the slight difference from its conventional definition. Instead of 0.18, we have $(2\pi)^{-1}$ as the numerical factor), we observe that $\beta$ is of the order of $m\xi_o^{\,2}$.

The nucleation critical field is the field in which a local superconducting region can begin to grow, it is therefore the highest field in which eq. (II-1) has a non-zero solution. We first consider an infinite sample in a uniform magnetic field H along the positive y direction. Choose the gauge (called gauge A) such that $\vec{A}(\vec{r})$ = (HZ, 0, 0), we find the eigenfunctions to be of the form:

$$\Delta(\vec{r}) = \exp[i(k_x x + k_y y)]f(Z), \qquad \text{(II-2)}$$

where f(z) satisfies:

$$-\frac{1}{4m}\frac{d^2f(z)}{dz} + \frac{(2m)\omega_L^{\,2}}{2}(z-z_o)^2 f(z) = [\frac{(1-t)}{\beta} - \frac{k_y^{\,2}}{4m}]f(z), \qquad \text{(II-3)}$$

with $\omega_L = (2e)H/(2m)$, and $Z_o = -k_x/(2eH)$.

Eq. (II-3) is nothing but the Schrödinger equation of a harmonic oscillator of mass (2m) and characteristic frequency $\omega_L$, with the potential well centered at $z_o$. In order for eq. (II-3) to have a non-zero solution, the "eigenvalue" $[\frac{1-t}{\beta} - \frac{k_y^{\,2}}{4m}]$ must be equal to an odd integer multiple of $\frac{1}{2}\omega_L$, which relates H and T. The bulk nucleation critical field, $H_{c2}$, being defined as the largest field among all possible nucleation modes, for which eq. (II-3) has a non-zero solution is therefore given by the ground state solution of (II-3) with $k_y = 0$:

$$\frac{1}{2}\frac{eH_{c2}}{m} = \frac{1}{\beta}(1-t), \tag{II-4}$$

which is degenerate w.r.t. $z_o$ or $k_x$, as is expected from translational invariance.

We now turn to the case of a semi-infinite sample occupying the half-space $z \geq 0$ with $\vec{H}$ still parallel to y-axis. The region $z < 0$ is assumed to be a vacuum or an insulator. In this case eq. (II-1) is valid only in the region $z \geq 0$ and we must have a boundary condition (B.C.) on the surface $z = 0$ in order to find unique solution. It was suggested in G-L's original paper through general considerations on the total free energy of the sample, that the B.C. should be, to a good approximation:

$$[\nabla_z + 2ie\, A_z(\vec{r})]\Delta(\vec{r})\Big|_{z=o} = 0, \tag{II-5}$$

independent of the detailed nature of the surface.

A more rigorous justification of this B.C. will be supplied later. For the present moment, we can simply take it as a plausible assumption.

Going to the special gauge as before, we get again the type of solutions given by (II-2) with f(z) satisfying (II-3) in the region $z \geq 0$ together with the B.C.

$$\nabla_x f(z)\Big|_{z=0} = 0. \qquad \text{(II-6)}$$

This is equivalent to the quantum mechanical problem of a double harmonic oscillator (see, for example, Merzbacher,[17] Ch. 5). Defining the dimensionless variables:

$$\zeta = (2eH)^{1/2} z, \quad \zeta_o = (2eH)^{1/2} Z_o, \qquad \text{(II-7)}$$

the ground state with $k_y = 0$ has eigenvalue $\frac{1}{2}\varepsilon(\zeta_o)\omega_L$, and eigenfunction given by the parabolic cylinder function[20] (un-normalized):

$$f(z) = D_{\frac{1}{2}[\varepsilon(\zeta_o)-1]}(\sqrt{2}(\zeta-\zeta_o)), \qquad \text{(II-8)}$$

with $\varepsilon(\zeta_o) \to 1$ as $\zeta_o \to$ both o and $\infty$. $\varepsilon(\zeta_o)$ possesses a minimum at: $\zeta_o = \zeta_{oM} = 0.76818$ where $\varepsilon(\zeta_{oM}) = \varepsilon_o = \zeta_{oM}^{\,2} = 0.59010$.[1] Using the notation $H_{c/\!/}(\zeta_o)$ to denote the critical field for the particular nucleation mode characterized by $\zeta_o$. It is seen that the surface nucleation critical field $H_{c3}$ is given by the maximum value of $H_{c/\!/}(\zeta_o)$ as $\zeta_o$ varies between $-\infty$ and $+\infty$. The function $H_{c3}(T)$ is therefore given by

$$\frac{\varepsilon_o}{2}\,\frac{eH_{c3}}{m} = \frac{1}{\beta}\,(1-t). \qquad \text{(II-9)}$$

Comparing (II-4) with (II-9), we conclude that

$$H_{c3}/H_{c2} = \varepsilon_o^{-1} \cong 1.695. \qquad \text{(II-10)}$$

This is where the magic number 1.695 (often referred to as 1.7) came from. As is seen, it is intrinsicly related to the differential equation (II-1), and the B.C. (II-5).

It is worthwhile at this point to make the following few remarks:

1) An equivalent procedure in making these two calculations is the following:

We start by choosing the following gauge (gauge B) so that:

$$\vec{A}(\vec{r}) = (H(z-z_o), 0, 0). \qquad \text{(II-11)}$$

and we can then limit ourselves to eigenfunctions $\Delta(\vec{r})$ which are actually functions of z only, so far as the nucleation critical fields of the physically most favorable modes are concerned. Eq. (II-3) can then be reproduced (with $k_y = 0$), but this time it is an equation for $\Delta(z)$ itself. Eq. (II-6) also becomes the B.C. on $\Delta(z)$. All of the results of the first approach follow again in this new approach. In fact, it can be shown by general arguments based on gauge invariance and translational invariance along directions perpendicular to the surface, that this equivalent approach is always valid whether the system is in the L-G region or not. From now on, we shall always calculate things in this new gauge. The reader should always keep in mind the origin of the parameter $z_o$ in gauge B by referring back to gauge A.

2) For an infinite sample, the center of nucleation is exactly given by $z_o$. For a semi-infinite sample, this is still roughly true, except when $z_o < 0$, for which the pair wave function can at most peak sharper and sharper at the surface, when $z_o$ is further reduced. From now on, we shall always call $z_o$ "the center of nucleation" whether the system is in the L-G region or not. The reader is cautioned not to take its meaning too literally.

3) By looking at the solutions, we see that for both the infinite and the semi-infinite sample, the pair wave functions for the optimum modes possess the following property:

$$|[\vec{\nabla}_r + 2ie\vec{A}(\vec{r})]_i \Delta(\vec{r})| \sim O(\xi_H^{-1})|\Delta(\vec{r})|, \qquad \text{(II-12)}$$

everywhere inside the sample, where i = x, y, z, and

$$\xi_H(T) \doteq (2eH)^{-1/2}. \qquad \text{(II-13)}$$

In fact, by examining the differential equation, we can see that this property is possessed by all low lying nucleation modes, for all sample geometries and field arrangements, so long as T remains in the L-G region.$^{(i)}$

Since in the L-G region, $1-t<<1$, $\xi_H \sim \xi_o(1-t)^{-1/2}>>\xi_o$, we shall call the pair wave function "slowly varying at $\vec{r}$" if (II-12) is satisfied at $\vec{r}$, and "everywhere slowly varying" if (II-12) is satisfied everywhere inside the sample. This nomenclature will be used even when the temperature is slightly too small to be in the L-G region, i.e. when we are only "near" the L-G region. Notice that the statement (II-12) is gauge invariant.

It will be shown later that when T is only near the L-G region, the bulk nucleation modes still have this property everywhere inside the sample, but for surface nucleation modes, this property no longer holds within a distance of the order of $\xi_o$ from the surface, as terms of order $(1-t)^{3/2}$ gets no longer negligible compared with 1.

We now turn to the dirty limit case. i.e. when the impurity mean free path $\ell$ tends to zero compared with $\xi_o$. Without going through all of the details this time, we shall only point out that both de Gennes[5] and Maki[4] have shown that in the dirty limit, superconductivity is again governed by an equation of the type given by (II-1), for all temperatures below $T_c$ this time, except that a more complicated function of temperature should replace the factor $\frac{1}{\beta}(1-t)$ in the right hand side of (II-1). An immediate consequence of this discovery is that although both $H_{c2}$ and $H_{c3}$ change their temperature dependence, their ratio is nevertheless again given by the simple expression (II-10), and this time it is true for all temperatures below $T_c$!

## Gor'kov's Microscopic Theory of Superconductivity

To calculate $H_{c3}$ outside of the L-G region and the dirty limit, we must rely upon some microscopic theory of superconductivity. The best one available to serve our purpose is due to Gor'kov[11] since it allows spatially inhomogeneous situations.

We outline below the major steps that lead to Gor'kov's theory (see ref.[13] for a systematic introduction).

Employing the second quantization scheme, let $\psi_\alpha(\vec{r})$ and $\psi^+_\alpha(\vec{r})$ denote the electron annihilation and creation operators of spin state $\alpha$ in the Schrödinger representation. A model Hamiltonian was first proposed for the system of electrons in a pure metal to be:

$$\hat{H} = \int [-(\psi^+ \frac{|\vec{\nabla}+ieA|^2}{2m} \psi) + \frac{\lambda}{2} (\psi^+(\psi^+\psi)\psi)]\, d\vec{r},$$

where $(\psi^+\psi) = \psi^+_\alpha\psi_\alpha$, $\lambda = -|\lambda|$.

The second term in $\hat{H}$ is assumed to fully represent the phonon-mediated interaction that actually causes the appearance of superconductivity for most cases (Frohlich[18]). Its flat-spectrum, though very convenient to work with, is nevertheless too strong to give any finite result. A frequency cut-off at the Debye-frequency is therefore needed at later stages in order to make this model realistic.

The temperature Green's function of a single electron in the metal is then defined in the standard way (see ref. [13] Ch. 3 for a nice presentation.):

$$G_{\alpha\beta}(x_1,x_2) = - \mathrm{Sp}\{e^{(\Omega+\mu\hat{N}-\hat{H})/T}\, T_\tau(\tilde{\psi}_\alpha(x_1)\ \tilde{\bar{\psi}}_\beta(x_2))\}$$

$$\equiv -\langle T_\tau(\tilde{\psi}_\alpha(x_1)\ \tilde{\bar{\psi}}_\beta(x_2))\rangle ,$$

with $x \equiv (\vec{r},\tau)$ and $T_\tau$ being the imaginary time $\tau$ ordering operator. $\tilde{\psi}$ and $\tilde{\bar{\psi}}$ are defined as

$$\tilde{\psi}_\alpha(\vec{r},\tau) = e^{(\hat{H}-\mu\hat{N})\tau}\psi_\alpha(\vec{r})\ e^{-(\hat{H}-\mu\hat{N})\tau} ,$$

$$\tilde{\bar{\psi}}_\alpha(\vec{r},\tau) = e^{(\hat{H}-\mu\hat{N})\tau}\psi^+_\alpha(\vec{r})\ e^{-(\hat{H}-\mu\hat{N})\tau} ,$$

(Notice that $(\tilde{\psi}_\alpha(\vec{r},\tau))^+ = \tilde{\bar{\psi}}_\alpha(\vec{r},-\tau) \neq \tilde{\bar{\psi}}_\alpha(\vec{r},\tau))$ and $\Omega$ is given by $\mathrm{Sp}\{e^{(\Omega+\mu\hat{N}-\hat{H})/T}\} = 1$.

The Green's function possesses the following general property:

$$G^*_{\alpha\beta}(\vec{r},\tau;\ \vec{r}\,',\tau') = G_{\beta\alpha}(\vec{r}\,',-\tau';\ \vec{r},-\tau).$$

Or, since the temperature Green's function can only depend on $\tau-\tau'$,

$$G^*_{\alpha\beta}(\vec{r},\vec{r}\,';\ \tau-\tau') = G_{\beta\alpha}(\vec{r}\,',\vec{r};\ \tau-\tau').$$

The Green's function can be Fourier analyzed w.r.t. $\tau$ according to:

$$G(\tau) = T \sum_n e^{-i\omega_n \tau} G_{\omega_n} , \qquad \text{(II-15)}$$

so that

$$G_{\omega_n} = \int_o^{1/T} e^{i\omega_n \tau} G(\tau)\, d\tau , \qquad \text{(II-16)}$$

with $\omega_n = (2n+1)\pi T$. (II-14) then becomes

$$G^*_{\alpha\beta,\omega}(\vec{r},\vec{r}\,') = G_{\beta\alpha,-\omega}(\vec{r}\,',\vec{r}) . \qquad \text{(II-17)}$$

Gor'kov's major contribution is to discover that for the superconducting state, the following anomalous Green's functions are also non-vanishing:

$$F_{\alpha\beta}(x_1,x_2) = \langle T_\tau(\tilde{\psi}_\alpha(x_1)\ \tilde{\psi}_\beta\ (x_2))\rangle,$$

$$F^+_{\alpha\beta}(x_1,x_2) = \langle T_\tau(\tilde{\bar{\psi}}_\alpha(x_1)\ \tilde{\bar{\psi}}_\beta(x_2))\rangle .$$

These are related to one another by $F^*_{\alpha\beta}(\vec{r},\vec{r}\,';\tau) = F^+_{\beta\alpha}(r',r,\tau)$. Or, after Fourier transformation w.r.t. $\tau$, $F^*_{\alpha\beta,\omega}(\vec{r},\vec{r}\,') = F^+_{\beta\alpha,-\omega}(\vec{r}\,',\vec{r})$.

By applying the anti-commutation relations between $\psi$, $\psi^+$, and $\hat{H}$, and by introducing a generalized Hartree-Fock type of decoupling scheme, Gor'kov has been able to obtain the following coupled set of differential equations for these Green's functions:

$$(-\frac{\partial}{\partial\tau} + \frac{1}{2m}|\vec{\nabla}_r + ieA(\vec{r})|^2 + \mu)\ G(x,x') + \Delta(\vec{r})F^+(x,x') = \delta(x-x'),$$

$$(\frac{\partial}{\partial\tau} + \frac{1}{2m}|\vec{\nabla}_r - ieA(\vec{r})|^2 + \mu)F^+(x,x') - \Delta^*(\vec{r})\ G(x,x') = 0.$$

$$(\mu = \varepsilon_F = \frac{1}{2m}\ p_F{}^2), \qquad \text{(II-18)}$$

where the spin-dependence of the Green's functions has been separated out according to the recipe:

$$G_{\alpha\beta}(x,x') = \delta_{\alpha\beta}\mathcal{G}(x,x'),$$

$$F^{+}_{\alpha\beta}(x,x') = I_{\alpha\beta}\, F^{+}(xx'),$$

$$F_{\alpha\beta}(x,x') = -I_{\alpha\beta}F(x,x'),$$

with $I_{\alpha\beta}$ determined by $I_{\alpha\beta} = -I_{\beta\alpha}$, and $(I^2)_{\alpha\beta} = -\delta_{\alpha\beta}$. The "pair wave function" is in turn defined to be

$$\Delta(\vec{r}) = \lim_{\tau'\to\tau+} |\lambda| F(\vec{r},\tau;\, \vec{r},\tau'). \tag{II-19}$$

Eqs. (II-18) and (II-19) form a complete set of equations for the pair wave function $\Delta(\vec{r})$ to satisfy. The equations are seen to be non-linear in general. For studying the nucleation problem, we can again linearize them. This coupled set of equations can then be replaced by the following single integral equation:

$$\Delta(\vec{r}) = \int K^{(o)}(\vec{r},\vec{r}')\, \Delta(\vec{r}')d\vec{r}', \tag{II-20}$$

with

$$K^{(o)}(\vec{r},\vec{r}') \equiv |\lambda| T \sum_{n} G^{(o)}_{\omega}(\vec{r},\vec{r}')\, G^{(o)}_{-\omega}(\vec{r},\vec{r}'), \tag{II-21}$$

and $G^{(o)}_{\omega}(\vec{r},\vec{r}')$ being the normal electron temperature Green's function which therefore satisfies:

$$\{i\omega + \frac{1}{2m}|\vec{\nabla}_r + ie\vec{A}(\vec{r})|^2 + \mu\}\, G^{(o)}_{\omega}(\vec{r},\vec{r}') = \delta(\vec{r}-\vec{r}'), \tag{II-22}$$

with a similar equation on the variable $\vec{r}'$, which need not be considered if the general property (II-17) is satisfied.

Eq. (II-20) is usually called the "linearized gap equation (LGE)" and $K^{(o)}(\vec{r},\vec{r}\,')$ its kernel.

For a sample which possesses boundaries, eq. (II-22) is satisfied only within the sample, and we need B.C.'s to be satisfied by $G_\omega^{(o)}(\vec{r},\vec{r}\,')$ on the boundary surfaces. Referring back to the definition of Green's functions, we expect that the B.C. for $G_\omega^{(o)}(\vec{r},\vec{r}\,')$ should be the same as the microscopic B.C. for the normal conduction-electron wave functions. If the sample is separated by the boundary surface from a vacuum or an insulator, and if the boundary surface is specularly reflective in nature (i.e. perfectly smooth), we propose the following simple B.C. to be at least a very good approximation:

$$G_\omega^{(o)}(\vec{r},\vec{r}\,')\Big|_{\vec{r}\text{ on boundary}} = 0. \qquad \text{(II-23)}$$

Again there is a corresponding B.C. on $\vec{r}\,'$ which need not be considered if (II-17) is satisfied. In Appendix A we shall give a more detailed analysis of the choice of a proper B.C. We would like to mention another choice of the B.C. here which is also discussed in Appendix A:

$$\hat{n}\cdot[\vec{\nabla}_r + ie\vec{A}(\vec{r})]\, G_\omega^{(o)}(\vec{r},\vec{r}\,')\Big|_{\vec{r}\text{ on boundary}} = 0, \qquad \text{(II-24)}$$

where $\hat{n}$ is a unit vector normal to the boundary. It turns out that with this B.C. the problem is also solvable as a bonus case, and in fact, it gives the same results for $H_{c3}$.

It will be the text of the next chapter to solve for these Green's functions with these B.C.'s.

### $H_{c2}$ for Pure Samples at all Temperatures

We illustrate the use of the LGE by reviewing the calculation due to Helfand and Werthamer[12] of $H_{c2}$ at all temperatures below $T_c$. This work is also very helpful for guiding our later development. The original version of this paper covers both the pure and the impure cases. We shall only consider the pure case for simplicity.

To start, one needs the normal electron temperature Green's function $g^{(o)}_{H,\omega}(\vec{r},\vec{r}\,')$ for a pure sample in a uniform magnetic field $H(/\!/\hat{y})$, which has already been obtained by Gor'kov in 1960.[19] He pointed out that if one set:

$$g^{(o)}_{H,\omega}(\vec{r},\vec{r}\,') = g^{(o)}_{\omega}(\vec{r},\vec{r}\,') \exp\left[-ie\int_{\vec{r}\,'}^{\vec{r}} \vec{A}(\vec{s})\cdot d\vec{s}\right], \qquad \text{(II-25)}$$

where the path integral in the phase factor follows a straight line connecting $\vec{r}\,'$ and $\vec{r}$, then by using the following operator identity:

$$[\vec{\nabla}_r + ie\vec{A}(\vec{r})]\exp\left[-ie\int_{\vec{r}\,'}^{\vec{r}} \vec{A}(\vec{s})\cdot d\vec{s}\right] = \exp\left[-ie\int_{\vec{r}\,'}^{\vec{r}} \vec{A}(\vec{s})\cdot d\vec{s}\right]\times\left[\vec{\nabla}_r + \frac{ie}{2}\vec{H}\times(\vec{r}-\vec{r}\,')\right] \qquad \text{(II-26)}$$

(A generalization of this identity will be proved in Ch. III, see eq. (III-10) and the proof following it.), one can get the following differential equation for $g^{(o)}_{\omega}(\vec{r},\vec{r}\,')$:

$$\left[i\omega + \frac{1}{2m}\left|\vec{\nabla}_r + \frac{ie}{2}\vec{H}\times(\vec{r}-\vec{r}\,')\right|^2 + \mu\right] g^{(o)}_{\omega}(\vec{r},\vec{r}\,') = \delta(\vec{r}-\vec{r}\,'). \qquad \text{(II-27)}$$

This equation involves quantities of three different orders:

$$O(m^{-1}p_F^{\,2})|g^{(o)}_{\omega}|, \quad O\left(\frac{p_F}{m\xi_o}\right)|g^{(o)}_{\omega}|, \text{ and } O\left(\frac{1}{m\xi_o^{\,2}}\right)|g^{(o)}_{\omega}|$$

(for studying superconductivity, we require $|\vec{r}-\vec{r}\,'| \sim O(\xi_o)$, a fact which can be checked a posteriori, we also ignore the difference between $O(\xi_o)$ and $O(\xi_H) \equiv O\left(\frac{1}{\sqrt{2eH}}\right)$ here, since they are now being compared with $O(p_F^{-1})$). The $[i\omega\, g^{(o)}_{\omega}]$ term clearly belongs to the second order. To get a non-trivial solution, we must require $\left|\frac{1}{2m}|\vec{\nabla}_r|^2 \; g_\omega^{(o)}\right|$ $\sim O(m^{-1} \; p_F^{\,2})|g_\omega^{(o)}|$ so that the $\mu$ dependent term can be cancelled out. The dominant order in (II-27) is then the $2^{nd}$ order which comes from the cross terms in the expansion of $|\nabla_r + \frac{ie}{2}\vec{H} \times (\vec{r}-\vec{r}')|^2$. The $H^2$ term, being proportional to $(m\xi_o^{\,2})^{-1}$ which is a factor $(p_F\;\xi_o)^{-1} \sim 10^{-3}$ to $10^{-4}$ smaller than the dominant order, can therefore be neglected.

Under this approximation, Gor'kov finally observed that eq. (II-27) is simply satisfied by the corresponding zero-field Green's function:

$$g_\omega^{(o)}(\vec{r},\vec{r}') = g_\omega^{(o)}(|\vec{r}-\vec{r}'|) = -\frac{m}{2\pi}\frac{1}{|\vec{r}-\vec{r}'|} \exp\left[(ip_F\frac{\omega}{|\omega|} - \frac{|\omega|}{v_F}) x |\vec{r}-\vec{r}'|\right], \tag{II-28}$$

which satisfies (II-22) with $\vec{A}(\vec{r}) \equiv 0$. Indeed, if one substitutes (II-28) into (II-27), the cross terms (the only non-negligible H-dependent terms!) simply vanish due to the fact that

$$\vec{\nabla}_r \; g_\omega^{(o)}(|\vec{r}-\vec{r}'|) \propto (\vec{r}-\vec{r}') \perp \vec{H} \times (\vec{r}-\vec{r}')!$$

Having obtained the Green's function through (II-25) and (II-28), the kernel $k_H(\vec{r},\vec{r}')$ of the LGE for an infinite sample in a magnetic field H can then be obtained through (II-27):

$$k_H^{(o)}(\vec{r},\vec{r}') = k^{(o)}\;(|\vec{r}-\vec{r}'|)\exp[-2ie\int_{\vec{r}'}^{\vec{r}} \vec{A}(\vec{S})\cdot d\vec{S}] \tag{II-29}$$

where $k^{(o)}(|\vec{r}-\vec{r}'|)$ is the corresponding zero-field kernel :

$$k^{(o)}(|\vec{r}-\vec{r}'|) = \sum_n k_\omega^{(o)}(|\vec{r}-\vec{r}'|) = |\lambda|T(\frac{m}{2\pi})^2\frac{1}{|\vec{r}-\vec{r}'|} \sum_n \exp[-(\frac{2|\omega|}{v_F}|\vec{r}-\vec{r}'|)] \tag{II-30}$$

The Debye frequency cut-off is required to be properly taken care of in (II-30). However, if one ignores cut-off for the moment, (II-30) can then be reduced to the following simple form:

$$k^{(o)}(|\vec{r}-\vec{r}\,'|) = |\lambda| T(\frac{m}{2\pi})^2 [\frac{1}{|\vec{r}-\vec{r}\,'|^2 \text{ Sinh } (\frac{2\pi T}{v_F}|\vec{r}-\vec{r}\,'|)}]. \quad \text{(II-31)}$$

To introduce the frequency cut-off, we sum over $\omega_n$ only up to the Debye frequency $\omega_D$, $k^{(o)}(|\vec{r}-\vec{r}\,'|)$ then acquires an extra factor of $[1 - \exp(-\frac{2\omega_D}{v_F}|\vec{r}-\vec{r}\,'|)]$.

Having obtained the kernel for such a sample, one can now turn to the LGE itself:

$$\Delta(\vec{r}) = \int k^{(o)}(|\vec{r}-\vec{r}\,'|) \exp[-2ie \int_{\vec{r}\,'}^{\vec{r}} A(\vec{S})\cdot d\vec{S}]\Delta(\vec{r}\,')d\vec{r}\,'. \quad \text{(II-32)}$$

Helfand and Werthamer[12] then proved the following identity (assuming that $\Delta(\vec{r})$ is infinitely differentiable):

$$\exp[\mp 2ie \int_{\vec{r}\,'}^{\vec{r}} \vec{A}(\vec{S})\cdot d\vec{S}]\Delta(\vec{r}\,')$$

$$= \exp[\mp 2ie \int_{\vec{r}\,'}^{\vec{r}} \vec{A}(\vec{S})\cdot d\vec{S}] \times \exp[(\vec{r}\,'-\vec{r})\cdot\vec{\nabla}_\rho]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}}$$

$$= \exp[(\vec{r}\,'-\vec{r})\cdot\vec{\tilde{\nabla}}_\rho]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}},$$

$$\text{where } \vec{\tilde{\nabla}}_r \equiv \vec{\nabla}_r + 2ie\,\vec{A}(\vec{r}). \quad \text{(II-33)}$$

So that eq. (II-32) is changed to a differential equation of infinite order (with constant coefficients):

$$\Delta(\vec{r}) = \int d\vec{R}\, k^{(o)}(|\vec{R}|) \exp[\vec{R}\cdot\vec{\tilde{\nabla}}_r]\Delta(\vec{r}), \quad \text{(II-34)}$$

after a change of the dummy variable $(\vec{r}-\vec{r}\,')$ to $\vec{R}$.

By symmetry reasoning, the operator on the right hand side of (II-30) can only be a function of the following two scalar operators: $|\vec{\tilde{\nabla}}_r|^2$ and $\tilde{\nabla}_H (\equiv \frac{\vec{H}}{|\vec{H}|}\cdot\vec{\tilde{\nabla}}_r)$. That $\tilde{\nabla}_H$ will occur can be seen by expanding out the exponential operator in (II-34) and carrying out integrations over the directions of $\vec{R}$:

$$\Delta(\vec{r}) = a_o\Delta(\vec{r}) + \frac{1}{3!} a_2 |\vec{\tilde{\nabla}}_r|^2 \Delta(\vec{r})$$

$$+ \frac{1}{5!} a_4 \, [|\vec{\tilde{\nabla}}_r|^4 + (2eH)^2]\Delta(\vec{r})$$

$$+ \frac{1}{7!} a_6 \, [|\vec{\tilde{\nabla}}_r|^6 + 5(2eH)^2|\vec{\tilde{\nabla}}_r|^2 - 2(2eH)^2 \tilde{\nabla}_H{}^2]\Delta(\vec{r})$$

$$+ \ldots\ldots , \qquad \text{(II-35)}$$

where $a_n \equiv \int |\vec{R}|^n \, k^{(o)}(|\vec{R}|) \, d\vec{R}$. (II-36)

Since the two operators $|\vec{\tilde{\nabla}}_r|^2$ and $\tilde{\nabla}_H$ can be simultaneously diagonalized, eq. (II-34) can essentially be solved by finding the simultaneous eigenfunction of the following two eigenvalue equations:

$$-|\vec{\tilde{\nabla}}_r|^2 \, \Delta(\vec{r}) = \varepsilon(2eH)\Delta(\vec{r}), \qquad \text{(II-37)}$$

$$\tilde{\nabla}_H\Delta(\vec{r}) = \tilde{\nabla}_y\Delta(\vec{r}) = ik_y\Delta(\vec{r}), \qquad \text{(II-38)}$$

where the coordinate system is chosen as before.

In practice, one can set $k_y = 0$ for calculating nucleation critical fields, so that $\Delta(\vec{r})$ becomes independent of y. We thus have reduced the solution of the same type as the linearized L-G equation. Indeed, if one substitutes (II-36) and (II-37) with $k_y = 0$ into eq. (II-35), the following implicit equation for $H_{c2}(T)$ is then obtained:

$$1 = a_o(T) + \frac{\varepsilon}{3!} a_2(T) \times (2eH_{c2}) + \frac{1}{5!} (\varepsilon^2+1) \; a_4(T) \times (2eH_{c2})^2$$

$$+ \frac{\varepsilon}{7!} (\varepsilon^2+5) \; a_6(T) \times (2eH_{c2})^4 + \ldots . \qquad \text{(II-39)}$$

From the analysis in section I of this chapter, we know that

$\varepsilon = 1$ is the ground state eigenvalue of (II-37) (compare eqs. (II-1), (II-4) and (II-37)). The evaluation of $a_n(T)$ are well-known (see for example ref.[13], Ch. 7). The results for $a_o$, $a_2$ and $a_4$ are:

$$a_o = 1 - |\lambda| N(o) \ln \frac{T}{T_c} , \qquad \text{(II-40)}$$

$$a_2 = \frac{7}{2} \ \zeta(3) |\lambda| N(o) [\xi_o(T)]^2 , \qquad \text{(II-41)}$$

$$a_4 = \frac{93}{2} \ \zeta(5) |\lambda| N(o) [\xi_o(T)]^4 . \qquad \text{(II-42)}$$

where $N(o) = mP_F/(2\pi^2)$, and $\xi_o(T) = v_F/(2\pi T)$. We thus can invert eq. (II-39) to get $H_{c2}(T)$, say to second order in (1-t):

$$2eH_{c2} \cong (a_o-1)[\frac{1}{6} \ a_2]^{-1}[1 + \frac{2x(3!)^2}{5!} \ \frac{a_4}{a_2^{\ 2}} (a_o-1)]$$

$$\cong \frac{12}{7\ (3)} \ \xi_o^{\ -2} \ (1-t)[1 + 0.135 \ (1-t) + 0((1-t)^2)]$$

$$\text{(for } (1-t) \ll 1\text{)}, \qquad \text{(II-43)}$$

which agrees with Tewordt's calculation.[27]

For temperatures further below $T_c$, eq. (II-39) is no longer convenient. A closed form valid for all $T \leq T_c$ has been given by Helfand and Werthamer, which implicitly relates $H_{c2}$ and T, but at the expense of involving a two-dimensional integral which can not be evaluated by analytic method. For our purpose, we need only to write down the expansion of that expression near T = 0°K, to order $t^2 \ln t$. The result is:

$$h_{c2}(T) = \frac{e^2}{4\gamma} \ x[1 + \frac{2}{3} \ \tilde{t}_{c2}^{\ 2} \ \ln \tilde{t}_{c2} + 0(\tilde{t}_{c2}^{\,2})]$$

$$= \ 1.037 \ x \ [1 + 0.65 \ t^2 \ \ln t + 0(t^2)]$$

$$\text{(for } t \ll 1\text{)}, \qquad \text{(II-44)}$$

where $h_{c2}(T) \equiv 2eH_{c2}\,\xi_o^{\,2}$, $\tilde{t} \equiv t/(h)^{1/2}$ and $\ln \gamma = C = 0.577 \ldots$ is the Euler's constant.

We notice that eq. (II-44) has also been obtained by Gor'kov [19] using a variational approach.

Eqs. (II-43) and (II-44) will be used in Chapters IV and V, together with our corresponding results for $H_{c3}$, to get high and low temperature behaviors of the ratio $H_{c3}/H_{c2}$.

CHAPTER III

# THE NORMAL-ELECTRON TEMPERATURE GREEN'S FUNCTION

In this chapter, we want to obtain the normal-electron temperature Green's function for a pure semi-infinite sample separated from a vacuum or an insulator by a specularly reflective plane boundary, when a uniform magnetic field is applied parallel to this boundary.

According to section 2 of the last chapter, we should solve eq. (II-22) subject to the B.C. (II-23), and the general requirement (II-17). We choose the coordinate system as before, so that the sample is occupying the half-space $Z \geq 0$, with its boundary surface at $Z = 0$, and that the uniform magnetic field H is pointing along the positive y direction. We have used the notations $g^{(o)}_{H,\omega}(\vec{r},\vec{r}\,')$ and $g^{(o)}_{\omega}(\vec{r},\vec{r}\,')$ to denote normal-electron temperature Green's functions for an <u>infinite sample</u> when a uniform magnetic field is on and off, respectively. Let us now use the notations $G^{(o)}_{H,\omega}(\vec{r},\vec{r}\,')$, and $G^{(o)}_{\omega}(\vec{r},\vec{r}\,')$ to denote the corresponding temperature Green's functions when the sample geometry is as described in the beginning of this chapter. The Green's function $g^{(o)}_{\omega}$ is the simplest one, it is given by (II-28). The Green's function $g^{(o)}_{H,\omega}$ is shown in Ch. II, section 3 to be related to $g^{(o)}_{\omega}$ by (II-25), to a very good approximation. Physically, we say that the expression (II-5) for $g^{(o)}_{H,\omega}$ corresponds to the semi-classical approximation, where the curvature of the electron orbits are neglected, so that the only effect of the magnetic field is to cause a phase factor to be accumulated as the electron propagates. ( The curvature can be neglected because we are only interested in electrons which lie very close to the Fermi surface, so that their velocities are on the order of the Fermi velocity). We now turn to the Green's function $G_\omega^{(o)}$. Without the magnetic field, the ordinary method of images works, so that $G_\omega^{(o)}$ is simply given by:

$$G_\omega^{(o)}(\vec{r},\vec{r}\,') = g_\omega^{(o)}(\vec{r},\vec{r}\,')-R_{z'}\; g_\omega^{(o)}(\vec{r},\vec{r}\,')$$

$$= g_\omega^{(o)}(|\vec{r}-\vec{r}\,'|) - g_\omega^{(o)}(|\vec{r}-R_{z'}\vec{r}\,'|), \qquad \text{(III-1)}$$

where the reflection operator $R_{z'}$ changes z' to -z'.

This expression clearly satisfies the required differential equation (i.e. eq. (II-22) with $\vec{A} \equiv 0$), the B.C. (II-23) at z = o, and the general property (II-17). In fact, the second term in (III-1) satisfies the same differential equation as the first term does, except that the source is now at the image point, i.e. $\delta(\vec{r}-\vec{r}\,')$ is now changed to $\delta(\vec{r}-R_{z'}\vec{r}\,')$.

At this point, a simple suggestive question arises: Can we obtain the Green's function $G_{H,\omega}^{(o)}$ by somehow combining the semi-classical approximation that leads to $g_{H,\omega}^{(o)}$, and the method of images that leads to $G_\omega^{(o)}$? To answer this question, Abrikosov[3] in 1964 proposed the following expression for $G_{H,\omega}^{(o)}$:

$$G_{H,\omega}^{(o)}(\vec{r},\vec{r}\,') = G_\omega^{(o)}(\vec{r},\vec{r}\,') \exp[-ie \int_{\vec{r}\,'}^{\vec{r}} A(\vec{S})\cdot d\vec{S}], \qquad \text{(III-2)}$$

which, however, we do not believe to be correct. In fact, if we substitute (III-2) into (II-22), and follow the argument that leads to (II-27), we must now require $g_\omega^{(o)}(|\vec{r}-R_{z'}\vec{r}\,'|)$ to satisfy eq. (III-27) with $\delta(\vec{r}-\vec{r}\,')$ replaced by the image source $\delta(\vec{r}-R_{z'}\vec{r}\,')$. But this time the H-dependent cross terms no longer vanish since $\vec{\nabla}_r g_\omega^{(o)}(|\vec{r}-R_z,\vec{r}'|) \propto (\vec{r}-R_z,\vec{r}')$ is no longer perpendicular to $\vec{H} \times (\vec{r}-\vec{r}')$!

To make the image method work, we must therefore modify the phase factor of the image term in (III-3), so that Gor'kov's argument that this is the solution of the differential equation will again apply. We must not, however, lose the boundary condition (II-23) and the symmetry property (II-17), which eq. (III-2) does satisfy.

The correct expression for $G_{H,\omega}^{(o)}$, is the following:

$$G_{H,\omega}^{(o)}(\vec{r},\vec{r}') = g_\omega^{(o)}(|\vec{r}-\vec{r}'|) \exp[-ie \int_{\vec{r}}^{\vec{r}} A(\vec{S})\cdot d\vec{S}]$$

$$- g_\omega^{(o)}(|\vec{r}-R_z,\vec{r}'|) \exp[-ie \;{-}\!\!\!\!\!\!\int_{\vec{r}}^{\vec{r}} \vec{A}(\vec{S})\cdot d\vec{S}] \qquad \text{(III-3)}$$

where ${-}\!\!\!\!\!\!\int_{\vec{r}'}^{\vec{r}} \equiv \int_{\vec{r}'}^{\vec{r}} + \int_{\vec{r}'}^{\vec{r}}$ (each following a straight path), and $\vec{r}_1$ is the intercept of the straight line connecting $\vec{r}$ and $R_z,\vec{r}'$, with the boundary surface. Explicitly, $\vec{r}_1$ has the components $(\frac{zx'+z'x}{z+z'}, \frac{zy'+z'y}{z+z'}, 0)$. It is easy to see that the new path of integration involved in the phase factor of the image term is nothing but the classical orbit of an electron going from $\vec{r}'$ to $\vec{r}$, via a specular reflection on the boundary surface (see fig. 1a).

We now show one by one that eq. (III-3) does satisfy all of the requirements.

We first check the symmetry property eq. (II-17), as it is the easiest. For this purpose, we need only check the new phase factor involved in the image term, and the answer is clearly yes since $\vec{r}_1$ is a symmetric function of $\vec{r}$ and $\vec{r}'$.

We then check the B.C. (II-23). For this purpose we set $z=0$ so that $\vec r$ lies on the boundary. But with $z=o$, we get $\vec r_1 = \vec r$ and $\fint_{\vec r'}^{\vec r} = \int_{\vec r'}^{\vec r}$.

The phase factor of the image term therefore reduces to that of the direct term, and our expression for $G^{(o)}_{H,\omega}$ becomes identical in this case to that proposed by Abrikosov which satisfies the B.C., as it is proportional to the zero-field function.

Finally, we must check that eq. (III-3) satisfies the differential equation (II-22). There is no problem with the direct term. We, therefore, need only check that the image term satisfies eq. (II-22) with the image source. To achieve this, we would like to first convert the phase factor of the image term into the following form:

$$\exp[-ie \fint_{\vec r'}^{\vec r} A(\vec S)\cdot d\vec S], \qquad \text{(III-4)}$$

where $\fint_{\vec r'}^{\vec r} \equiv \int_{\vec r'}^{R_z \vec r'} + \int_{R_z \vec r'}^{\vec r}$, and the vector potential has been extended into the negative-z region according to the following recipe:

$$\vec H(\vec r) = -\vec H\,(R_z \vec r), \qquad \text{(III-5)}$$

i.e., the magnetic field in the negative-z region is exactly opposite to that in the positive-z region. For convenience, we also require that the gauge of $\vec A$ in the negative-z region is so related to that in the positive-z region that the vector potential $\vec A$ is continuous across the boundary.

Under this extension of $\vec A$ to the negative z-region, we now prove that expression (III-4) is identical to the phase factor of the image term in (III-3). The new path of integration involved in (III-4) is shown in fig. 1b. Comparing this path with the reflected path shown in fig. 1a appropriate for $\int\!\!\!\!-_{\vec{r}'}^{\vec{r}}$, it is easy to see that the total flux enclosed by these two paths is always zero due to (III-5), which means that

$$[\int\!\!\!\!-_{\vec{r}'}^{\vec{r}} - \int\!\!\!\!=_{\vec{r}'}^{\vec{r}}]A(\vec{S})\cdot d\vec{S} = [\int_{\vec{r}'}^{\vec{r}_1} + \int_{\vec{r}_1}^{R_z,\vec{r}'} + \int_{R_z,\vec{r}'}^{\vec{r}'}]A(\vec{S})\cdot d\vec{S}$$

$$= (\text{total flux enclosed}) = 0.$$

If we now define:

$$X(\vec{r},\vec{r}_o) \equiv -\int_{\vec{r}_o}^{\vec{r}} A(\vec{S})\cdot d\vec{S}, \tag{III-6}$$

we observe that the direct term and the image term of the Green's function $G_{H,\omega}^{(o)}$ can now be written as:

$$\exp\{ie[X(\vec{r},\vec{r}') - X(\vec{r}',\vec{r}')]\}g_\omega^{(o)}(|\vec{r}-\vec{r}'|), \tag{III-7}$$

and

$$\exp\{ie[X(\vec{r},R_z,\vec{r}') - X(\vec{r}', R_z,\vec{r}')]\}g_\omega^{(o)}(|\vec{r}-R_z,\vec{r}'|), \tag{III-8}$$

respectively.

We then prove the following identity:

$$\begin{aligned}
\vec{\nabla}_r X(\vec{r},\vec{r}_o) &= -\vec{\nabla}_r \int_o^1 \vec{A}(\vec{r}_o + \theta(\vec{r}-\vec{r}_o))\cdot(\vec{r}-\vec{r}_o)\, d\theta \\
&= -\int_o^1 \vec{A}(\vec{r}_o + \theta(\vec{r}-\vec{r}_o))d\theta - \int_o^1 \frac{\partial A_i(\vec{r}_o+\theta(\vec{r}-\vec{r}_o))}{\partial\vec{r}_o}(\vec{r}-\vec{r}_o)_i\, \theta d\theta \\
&= -\vec{A}(\vec{r}) + \int_o^1 \frac{\partial A(\vec{r}_o+\theta(\vec{r}-\vec{r}_o))}{\partial\theta}\, \theta d\theta \\
&\quad - \int_o^1 \frac{\partial A_i(\vec{r}_o+\theta(\vec{r}-\vec{r}_o))}{\partial\vec{r}_o}(\vec{r}-\vec{r}_o)_i\, \theta d\theta \\
&= -\vec{A}(\vec{r}) + \frac{1}{2}\vec{\bar{H}}(\vec{r},\vec{r}_o) \times (\vec{r}-\vec{r}_o),
\end{aligned} \tag{III-9}$$

where

$$\vec{\bar{H}}(\vec{r},\vec{r}_o) \equiv 2\int_o^1 \vec{H}(\vec{r}_o+\theta(\vec{r}-\vec{r}_o))\, \theta d\theta.$$

This result immediately leads to a generalization of eq. (II-26):

$$[\nabla_r + ie\vec{A}(\vec{r})] \exp[ieX(\vec{r},\vec{r}_o)]$$

$$= \exp[ieX(\vec{r},\vec{r}_o)] \times [\vec{\nabla}_r + \frac{ie}{2} \bar{\vec{H}}(\vec{r},\vec{r}_o) x (\vec{r}-\vec{r}_o)] \qquad \text{(III-10)}$$

Using this identity, we find that in order for eq. (III-8) to satisfy the differential equation (II-2) with the image source $\delta(\vec{r}-R_z,\vec{r}')$, the following equation must be proven to be merely an identity:

$$\{i\omega + \frac{1}{2m} [\vec{\nabla}_r + \frac{ie}{2} \bar{\vec{H}}(\vec{r},R_z,\vec{r}') x (\vec{r}-R_z,\vec{r}')]^2 + \mu\}$$

$$x\ g_\omega^{(o)} (|\vec{r}-R_z,\vec{r}'|) = \delta(\vec{r}-R_z,\vec{r}'). \qquad \text{(III-11)}$$

According to Gor'kov's[19] analysis, we again neglect the term quadratic in the magnetic field. To reduce eq. (III-11) into an identity, we must therefore get rid of the following two terms which are linear in the magnetic field:

$$\frac{ie}{2m} [\bar{\vec{H}}(\vec{r},R_z,\vec{r}') x (\vec{r}-R_z,\vec{r}')] \cdot \vec{\nabla}_r\ g_\omega^{(o)} (|\vec{r}-R_z,\vec{r}'|)$$

$$+ \frac{ie}{4m} [\vec{\nabla}_r \times \bar{\vec{H}}(\vec{r},R_z,\vec{r}')] \cdot (\vec{r}-R_z,\vec{r}')\ g_\omega^{(o)} (|\vec{r}-R_z,\vec{r}'|). \qquad \text{(III-12)}$$

The first term in (III-12) is again vanishing due to orthogonality. The second term comes about because of the non-commutativity between $\vec{\nabla}_r$ and $\bar{\vec{H}}(\vec{r},R_z,\vec{r}')$, and therefore is absent in Gor'kov's original analysis. Fortunately, this term can be simply dropped because it is small. To see this point, we notice that, as is pointed out in Ch. II, a term is not negligible if it is on the order of $\frac{p_F}{m\xi_o}$, where the factor $p_F$ can only be obtained by applying the operator $\vec{\nabla}_r$ on the Green's function itself. With $\vec{\nabla}_r$ operating on $\vec{\bar{H}}$, the second term in (III-12) is seen to be of the order of $\frac{1}{m\xi_o^2}$ which is a factor of $(p_F\xi_o)^{-1}$ $\sim 10^{-3}$ to $10^{-4}$ smaller than the dominant order, and is therefore negligible.

We thus have established mathematically that eq. (III-3) is indeed the correct expression for the Green's function $G^{(o)}_{H,\omega}$. We now want to give a heuristic argument to show that this expression is also a reasonable one from a physical point of view.

The Green's function is a propagator. It's role is to carry information from the "source point" $\vec{r}'$, to the "field point" $\vec{r}$. In the semi-classical approximation, we can picture the electrons carrying information along their classical orbits. Without a boundary and neglecting the curvatures of these orbits, the electrons can only arrive at $\vec{r}$ from $\vec{r}'$ via a straight path. With the boundary present, the electrons can also follow a reflected path. If there is no magnetic field, the "information receiver" at the "field point" can not tell the difference between an electron that came through a reflected path from one that came directly from the image point. This is because $g^{(o)}_{\omega}$ depends only on the total length travelled. And this is why the ordinary image method works! With the magnetic field on, the situation is different. Since the electron does accumulate phase as it propagates, the information receiver can now tell where this electron came from, and what orbit it has followed.

Since the image term $G^{(o)}_{H,\omega}$ is really due to those electrons which follow the reflected path, the phase factor that accompanies it should naturally involve a phase integral along the reflected trajectory! And this is indeed what we have found for the correct expression of $G^{(o)}_{H,\omega}$.

Finally, we want to make the following remarks about the expression (III-3):

i) We notice that our derivation of (III-3) is independent of any requirement that $\vec{H}$ be parallel to the boundary surface, so that (III-3) is still valid even if $\vec{H}$ is pointing in an arbitrary direction, including the case where $\vec{H}$ is perpendicular to the boundary except that for this case, the two phase factors become identical, and our expression for $G^{(o)}_{H,\omega}$ reduces to that given by Abrikosov.

ii) Our proof for (III-3) is also independent of whether $\vec{H}$ is a constant, in magnitude and/or in direction, so long as $|\nabla_r \vec{H}(\vec{r})|$ is negligible compared with $O(p_F)|\vec{H}|$. That is to say, as long as the magnetic field $\vec{H}$ does not vary significantly on the scale of atomic spacings.

iii) Since our proof is everywhere gauge invariant, we expect that (III-3) is true independent of the choice of gauge for $\vec{A}(\vec{r})$.

iv) We observe the following very interesting point that if we denote $G^{(o)}_{H,\omega}$ symbolically by

$$G^{(o)}_{H,\omega} \equiv g^{(o)}_{H,\omega} - R^{H}_{z'}\, g^{(o)}_{H,\omega} \,, \tag{III-13}$$

where $g^{(o)}_{H,\omega}$ is given by (II-25), and the generalized reflection operator $R^{H}_{z'}$ in the presence of magnetic field does a much more complicated job, we can define a new Green's function $\tilde{G}^{(o)}_{H,\omega}$ simply by changing the sign of the image term:

$$\tilde{G}^{(o)}_{H,\omega} \equiv g^{(o)}_{H,\omega} + R^{H}_{z'}\, g^{(o)}_{H,\omega} \,. \tag{III-14}$$

This new Green's function clearly satisfies the differential equation and the symmetry property. However, it no longer satisfies the B. C. (II-23), instead, it now satisfies the B.C. (II-24) on the surface z = 0!

v) We also observe that our generalized method of images clearly has the same range of applicability as the ordinary image method, no matter whether (II-23) or (II-24), or possibly a even more involved expression, is our B.C.. For example, a simple extension of our formulae (III-3) and (III-14) will be for the case of an infinite slab of finite thickness, where we can introduce infinitely many image points as in the ordinary image method case, and then properly take care of the phase factors of these image terms according to the same physical argument that leads to (III-3), as these various image terms clearly correspond to various possible paths that an electron can travel from $\vec{r}'$ to $\vec{r}$ via all sorts of multiple scatterings from the two boundary surfaces. These and other possible extensions of the generalized image method will be further explored in the future.

## CHAPTER IV

## THE LINEARIZED GAP EQUATION AND CALCULATION OF $H_{c3}$ FOR PURE SAMPLES NEAR T = 0°K

In the last chapter we have obtained the appropriate normal electron temperature Green's function $G^{(o)}_{H,\omega}$ for a pure semi-infinite sample separated from vacuum or insulator by a specularly reflective plane boundary, as is given by eq. (III-3). The kernel of the appropriate LGE for such a sample can therefore be obtained simply by substituting this Green's function into eq. (II-21). The so-obtained kernel clearly satisfies the same B. C. as the Green's function itself does, i.e. it must vanish when either $\vec{r}$ or $\vec{r}\,'$ lies on the boundary surface. This property of the kernel in turn implies that the pair wave function must also satisfy the same B. C., i.e. it must also vanish on the boundary surface. However, since the Green's function $G^{(o)}_{H,\omega}$ contains two rapidly oscillating terms both of which have characteristic wave lengths of the order of $P_F^{-1}$, the kernel thus obtained will have a smoothly varying part, with $\xi_o$ characterizing its spatial variation, and a rapidly oscillating part, with the same characteristic wave length as $G^{(o)}_{H,\omega}$. The former comes from the two direct terms in the multiplication of $G^{(o)}_{H,\omega}$ with $G^{(o)}_{H,-\omega}$, while the latter comes from the two cross terms. To study those energetically more favored modes of nucleation, it is reasonable to assume that the pair wave function is a rather smoothly varying function, with a characteristic length of its spatial dependence $\gtrsim \xi_o$, except in a very narrow region near the boundary, with a thickness of the order of $P_F^{-1}$, where the pair wave function must somehow drop to zero very rapidly, from its "inner value", in order to meet the microscopic boundary condition. Since the pair wave function is expected to extend much deeper into the sample (with a depth $\sim\xi_H \gtrsim \xi_o$) than this surface region (notice that $\xi_o P_F \sim 10^3$ to $10^4$ for pure samples!), we expect that all physically measurable quantities involved in such a nucleation problem, including $H_{c3}$, depend very little on the behavior of the pair wave function in this narrow surface region. It should therefore be sufficient to solve for the pair wave function in the region $Z >> P_F^{-1}$, and for this purpose, we can simply neglect those rapidly oscillating terms in the kernel and get:

$$\begin{aligned} K_H^{(o)}(\vec{r},\vec{r}\,') &= k^{(o)}(|\vec{r}-\vec{r}\,'|) \exp\left[-2ie \int_{\vec{r}\,'}^{\vec{r}} A(\vec{S})\cdot d\vec{S}\right] \\ &\quad + k^{(o)}(|\vec{r}\,'R_{z'}\vec{r}\,'|) \exp\left[-2ie -\!\!\!\!\!\!\int_{\vec{r}\,'}^{\vec{r}} A(\vec{S})\cdot d\vec{S}\right] \\ &\equiv k_H^{(o)}(\vec{r},\vec{r}\,') + R_{z'}^{H}\, k^{(o)}(\vec{r},\vec{r}\,'), \end{aligned} \tag{IV-1}$$

where $k_H^{(o)}$ has been defined in ch. II, section 2 by eq. (II-29).

We immediately recognize the similarity between (IV-1) and (III-14). Thus if we assume that (IV-1) is valid everywhere inside the sample, including the region $Z \lesssim P_F^{-1}$, we find that our approximate kernel satisfies the following B.C.:

$$\check{\nabla}_z K_H^{(o)}(\vec{r},\vec{r}\,')\Big|_{z=o} \equiv [\nabla_z + 2ieA_z(\vec{r})]\, K_H^{(o)}(\vec{r}\vec{r}\,')\Big|_{z=o} = 0. \tag{IV-2}$$

Using this kernel (i.e. eq. (IV-1)) in our LGE, we then see that the pair wave function must also satisfy a similar B.C.:

$$\check{\nabla}_z\, \Delta(\vec{r})\Big|_{z=o} = 0. \tag{IV-3}$$

The reader should keep in mind that eqs. (IV-2) and (IV-3) really describe the behavior of the kernel and the pair wave function in the region $P_F^{-1} \ll Z \ll \xi_o$.

It is worthwhile to remark here that should we have started with the microscopic B.C. (II-24) instead of (II-23), we would have to use (III-14) instead of (III-3) as the appropriate normal electron temperature Green's function. However, after neglecting those rapidly oscillating terms in the kernel, the result is easily seen to be given again by (IV-1). Eqs. (IV-2) and (IV-3) therefore remain valid. In fact, it is clear that the two calculations from here on coincide. This is why we claimed in Ch. II, section 2 that the B.C. (II-24) is a bonus case.

We now go back to the kernel (IV-1), and write down the corresponding LGE:

$$\Delta(\vec{r}) = \int_{z'>o} k^{(o)}(|\vec{r}-\vec{r}\,'|) \exp[-2ie \int_{\vec{r}}^{\vec{r}} \vec{A}(\vec{S})\cdot d\vec{S}]\Delta(\vec{r}\,')d\vec{r}\,'$$

$$+ \int_{z'>o} k^{(o)}(|\vec{r}-R_z,\vec{r}\,'|) \exp[-2ie \int\!\!\!\!\!-_{\vec{r}\,'}^{\vec{r}} \vec{A}(\vec{S})\cdot d\vec{S}]\Delta(\vec{r}\,')d\vec{r}\,'. \qquad \text{(IV-4)}$$

The first thing we would like to examine about this equation is to find out whether we can also convert this equation into a differential equation of infinite order as Helfand and Werthamer did to the LGE of an infinite sample case[12] (see ch. II, section 3). Indeed, the identity (II-33) discovered by Helfand and Werthamer can be generalized to curved path-integral cases:

$$\exp[-2ie \,\mathbb{P}\!\!\int_{\vec{r}\,'}^{\vec{r}} A(\vec{S})\cdot d\vec{S}]\exp[(\vec{r}\,'-\vec{r})\cdot\vec{\nabla}_\rho]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}}$$

$$= T\exp[-\,\mathbb{P}\!\!\int_{\vec{r}\,'}^{\vec{r}} d\vec{s}\cdot\vec{\tilde{\nabla}}_\rho]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}} \qquad \text{(IV-5)}$$

(A proof of this identity is given in Appendix B), where $\mathrm{P}\!\int_{\vec{r}'}^{\vec{r}}$ denotes the path integral along an arbitrary curved path connecting $\vec{r}'$ and $\vec{r}$, and T is a "time ordering operator" which requires operators characterized by earlier times to act earlier, where the "time" variable is defined to be proportional to the total length traveled along the path, i.e. $t(\vec{s}) \propto \int_{\vec{r}'}^{\vec{s}} |d\vec{S}|$, for any point on the path represented by the vector $\vec{S}$.

Using the identity (IV-5), we can now convert eq. (IV-4) into the following form:

$$\begin{aligned}\Delta(\vec{r}) \;=\; & \int_{z'>o} d\vec{r}'\; k^{(o)}(|\vec{r}-\vec{r}'|)\exp[(\vec{r}'-\vec{r})\cdot\vec{\tilde{\nabla}}_\rho]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}} \\ & + \int_{z'>o} d\vec{r}'\; k^{(o)}(|\vec{r}-R_z,\vec{r}'|)\exp[(\vec{r}_1-\vec{r})\cdot\vec{\tilde{\nabla}}_\rho] \\ & x\;\; \exp[(\vec{r}'-\vec{r}_1)\cdot\vec{\tilde{\nabla}}_\rho]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}},\end{aligned} \qquad \text{(IV-6)}$$

where $\vec{r}_1$ is the point of reflection on the boundary surface as is defined in ch. III. Eq. (IV-6) can also be written as

$$\begin{aligned}\Delta(\vec{r}) \;=\; & \int d\vec{\rho}\; k^{(o)}(|\vec{\rho}|)\exp[\vec{\rho}\cdot\vec{\tilde{\nabla}}_r]\Delta(\vec{r}) \\ & + \int_{z'<o} d\vec{r}'\; k^{(o)}(|\vec{r}-\vec{r}'|)\exp[(R_z,\vec{r}_1-\vec{r})\cdot\vec{\tilde{\nabla}}_\rho] \\ & x\;\{\exp[(R_z,\vec{r}'-R_z,\vec{r}_1)\cdot\vec{\tilde{\nabla}}_\rho]-\exp[(\vec{r}'-R_z,\vec{r}_1)\cdot\vec{\tilde{\nabla}}_\rho]\}\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}},\end{aligned} \qquad \text{(IV-7)}$$

which explicitly shows the bulk term and the surface correction term.

Unfortunately, eq. (IV-6) or (IV-7) can not be solved as easily as for the infinite sample case because it now involves the following three scalar operators: $|\vec{\tilde{\nabla}}_r|^2$, $\tilde{\nabla}_H (\equiv \frac{\vec{H}}{|\vec{H}|}\cdot\vec{\tilde{\nabla}}_r)$, and $\tilde{\nabla}_n (\equiv \hat{n}\cdot\vec{\tilde{\nabla}}_r$, where $\hat{n}$ is the unit vector normal to the surface) which can not be simultaneously diagonalized. However, we notice that eqs. (IV-6) and (IV-7) possess the very peculiar property that although they are differential equations defined on the half space $z \geq 0$, they do not require a separate B.C. on the boundary surface $z = 0$, since they still guarantee the automatic satisfaction of the B.C. (IV-3) as cen be easily checked. We decide, therefore, to study these equations a bit further. More specifically, we think that the following possibility ought to be checked:

Since an ordinary differential equation does not carry the information about what B.C. its solutions must satisfy, could it be possible then that eqs. (IV-6) and (IV-7) are redundant in the sense that they could be simplified to a significant extent so long as we "promise" to add the B.C. independently to it? Especially, since our LGE reduces to that of the infinite sample case as $z \gg \xi_0$, could it be possible then that eq. (IV-6) or (IV-7) represent nothing but Helfand and Werthamer's infinite order differential equation (i.e. eq. (II-35)), plus the B.C. (IV-3)? This conjecture sounds so plausible that one is very apt to accept it. However, it turns out to be wrong, and a rigorous justification of this conclusion can be supplied. To see this point, we first go to the special gauge named gauge B in ch. II, section 3. In this gauge we have $\vec{A}(\vec{r}) = (H(z-z_0), 0, 0)$ where the parameter $Z_0$ is closely related to the center of nucleation. Now should eq. (IV-6) or (IV-7) reduce to Helfand and Werthamer's equation plus the B.C., the problem could then be solved in close parallelism with ch. II, section 3, except that we now would have to solve (II-37) subjected to the B.C. (IV-3). We notice that for the particular mode of nucleation with $z_0=0$, the B.C. is trivially satisfied by all even solutions of (II-37) under no B.C., including the ground state solution which is nothing but the solution for the bulk nucleation mode. This means that should our eq. (IV-6) or (IV-7) be equivalent to Helfand and Werthamer's differential equation plus the B.C., we could then make the following conclusions:

(1) that $H_{c//}(z_o=0)$ should be equal to $H_{c2}$,

(2) that the spatial dependence of the pair wave function for the particular surface nucleation mode with $z_o=0$ should be the same as that of the bulk nucleation mode, which is simply the ground state solution of a simple harmonic oscillator type of wave equation, and therefore is given by a simple gaussian function.

In Appendix C, we studied our LGE (IV-4) a variational approach on the particular nucleation mode with $z_o=o$, at T = 0°K, using a gaussian of adjustable width as our trial wave function. We find a lower bound for $H_{c//}(z_o=0)$ which is slightly less than $\frac{8}{9} H_{c2}$. Now, should the exact solution for the pair wave function be also a gaussian according to conclusion (2) of the last paragraph, we ought to obtain the exact value of $H_{c11}(z_o=0)$ as our lower bound to it. But according to conclusion (1), the exact value of $H_{c//}(z_o=0)$ can not be less than $\frac{8}{9} H_{c2}$ because it is simply equal to $H_{c2}$! This therefore completes our proof that our LGE (IV-4) is not equivalent to Helfand and Werthamer's differential equation (II-35) plus any B.C..(as all choices of the B.C. other than (IV-3) have already been ruled out by the fact that our LGE (IV-4) implies that (IV-3) is satisfied.) This conclusion is also expected from another point of view: It is found that if one really proceeds to solve Helfand and Werthamer's differential equation together with the B.C., one will find that the solution is divergent except for the two special cases when $z_o$ is = 0 or ∞! However, this fact alone cannot serve as a rigorous justification of the conclusion. The physical origin of the divergence lies in the fact that Helfand and Werthamer's infinite-order differential equation "sees" the asymptotic behavior of the pair wave function for both $Z \to \pm\infty$ , while the B.C. (IV-3) impels the pair wave function to diverge as fast as $\exp(+cz^2)$ when $z \to -\infty$(notice that the solution is explicitly given by (II-8)), which cannot be overcome by the convergent factor in the kernel of (II-32) which drops at most as fast as $\exp(-C'|Z'|)$ when $Z' \to \pm\infty$.

We now understand that our LGE (IV-4) can not be solved by Helfand and Werthamer's trick. This practically rules out the possibility of solving (IV-4) at all temperatures below $T_c$, as inexact methods must be employed to attack the problem. We shall therefore only consider two limiting cases, one is when the temperature T is equal or very close to the absolute zero, which we shall consider in the remaining part of this chapter; the other is when the temperature T is only slightly below the L-G region, which is considered in the next chapter.

We now proceed to calculate $H_{c3}$ at $T \stackrel{\sim}{=} 0°K$. In Appendix C, we have reduced our LGE to the forms given by (C-12) for $T \neq 0°K$, and by (C-13) or even (C-14) for T = 0°K. We first consider the case when T = 0°K. Again, we choose our trial wave function to be a simple gaussian function of width $\frac{\sqrt{2}}{\sqrt{\alpha}}$, as is shown by (C-16). Denoting the kernel in Eq. (C-14) by $\bar{K}$, we shall vary the parameters $\alpha$ and $\zeta_o(=z_o/\xi_H)$ in $\langle\Delta|\bar{K}|\Delta\rangle/\langle\Delta|\Delta\rangle$ to find the smallest possible upper bound for the eigenvalue $\ln(\frac{1}{2}\,\epsilon\varepsilon h^{-1/2})$. Thus:

$$\ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right) \le -\left(\frac{4\alpha}{\pi}\right)^{1/2} \int_{\varepsilon}^{\infty}\int_{0}^{\zeta-\varepsilon} \frac{\exp[-\frac{1}{2}(\zeta-\zeta')\cdot|\zeta+\zeta'-2\zeta_o|]}{(\zeta-\zeta')} \exp[-\frac{\alpha}{2}(\zeta^2+\zeta'^2)]d\zeta' d\zeta$$

$$-\left(\frac{4\alpha}{\pi}\right)^{1/2}\int_{0}^{\infty}\int_{0}^{\zeta} \frac{\exp[-\frac{1}{2}|\zeta^2+\zeta'^2-2\zeta_o(\zeta+\zeta')]}{(\zeta+\zeta')} \exp[-\frac{\alpha}{2}(\zeta^2+\zeta'^2)]d\zeta' d\zeta.$$

We also change variables to $u = \frac{1}{\sqrt{2}}(\zeta+\zeta')$, $v = \frac{1}{\sqrt{2}}(\zeta-\zeta')$:

$$\ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right) \le -\left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{\varepsilon/\sqrt{2}}^{\infty} \frac{dV}{V}\exp[-\frac{\alpha}{2}V^2] \int_{V}^{\infty} \exp[-\frac{\alpha}{2}u^2 - v|u-\sqrt{2}\,\zeta_o|]du$$

$$-\left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{0}^{\infty} \frac{du}{u}\exp[-\frac{\alpha}{2}u^2]\int_{0}^{u} \exp[-\frac{\alpha}{2}u^2 - |\frac{1}{2}(u^2+v^2)-\sqrt{2}\,\zeta_o u|]dv. \tag{IV-8}$$

We can perform one more integration in this expression. However, the result is much more involved:

$$\ln\left(\frac{e}{\sqrt{2\gamma h}}\right) \le \ln\left[\sqrt{\left(\frac{\alpha+1}{2\alpha}\right)}(\sqrt{2\alpha} + \sqrt{\alpha+1})\right] - \sqrt{\left(\frac{\alpha}{1+\alpha}\right)}\ln(\sqrt{2+1}) - \sum_{i=1}^{5} J_i(\alpha,\zeta_o), \tag{IV-9}$$

where $J_1(\alpha,\zeta_o) \equiv \int_0^\infty dV \frac{\exp(\sqrt{2}\,\zeta_o v)-1}{V}\exp[-\frac{\alpha^2-1}{2\alpha}V^2][1-\text{erf}(\frac{\alpha+1}{\sqrt{2\alpha}}V)]$,

$$J_2(\alpha,\zeta_o) \equiv \int_0^{\sqrt{2}\zeta_o} \frac{dV}{V}\exp[-\frac{\alpha^2-1}{2\alpha}v^2]$$

$$\times\{\exp(-\sqrt{2}\zeta_o v)[\text{erf}(\sqrt{\alpha}\zeta_o - \frac{v}{\sqrt{2\alpha}}) - \text{erf}(\frac{\alpha-1}{\sqrt{2\alpha}}v)]$$

$$-\exp(+\sqrt{2}\zeta_o v)[\text{erf}(\sqrt{\alpha}\zeta_o + \frac{v}{\sqrt{2\alpha}}) - \text{erf}(\frac{\alpha+1}{\sqrt{2\alpha}}v)]\},$$

$$J_3(\alpha,\zeta_o) \equiv \sqrt{\left(\frac{\alpha}{\alpha+1}\right)}\int_0^\infty du\,\frac{\exp(\sqrt{2}\zeta_o u)-1}{u}\exp[-\frac{\alpha+1}{2}u^2]\text{erf}(\sqrt{\left(\frac{\alpha+1}{2}\right)}u),$$

$$J_4(\alpha,\zeta_o) \equiv \int_0^{\sqrt{2}\zeta_o} \frac{du}{u}\,[\exp(-\frac{\alpha-1}{2}u^2-\sqrt{2}\zeta_o u)\,\sqrt{\left(\frac{2\alpha}{\pi}\right)}f\,(\frac{\alpha-1}{2},\,u)$$

$$-\exp(-\frac{\alpha+1}{2}u^2+\sqrt{2}\zeta_o u)\sqrt{\left(\frac{\alpha}{\alpha+1}\right)}\text{erf}(\sqrt{\left(\frac{\alpha+1}{2}\right)}u)],$$

and

$$J_5(\alpha,\zeta_o) \equiv \int_{\sqrt{2}\zeta_o}^{2\sqrt{2}\zeta_o} \frac{du}{u} \, [\exp(-\frac{\alpha-1}{2} u^2 - \sqrt{2}\, \zeta_o u) \sqrt{\frac{2\alpha}{\pi}}\, f(\frac{\alpha-1}{2}, \sqrt{u(2\sqrt{2}\zeta_o - u)})$$

$$- \exp(-\frac{\alpha+1}{2} u^2 + \sqrt{2}\, \zeta_o u) \sqrt{\frac{\alpha}{\alpha+1}} \;\mathrm{erf}\; (\sqrt{\frac{\alpha+1}{2} u(2\sqrt{2}\zeta_o - u)})],$$

where $f(a,b) = \int_o^b \exp\,[-ax^2]\, dx$

$$= \begin{cases} \frac{\sqrt{\pi}}{2\sqrt{a}} \,\mathrm{erf}\, (\sqrt{a}\, b) & \text{for } a>0 \\ \frac{1}{\sqrt{|a|}} \exp\,(|a|b^2) F(\sqrt{|a|}\, b) & \text{for } a<0, \end{cases}$$

and the function $F(x) \equiv \exp(-x^2) \int_o^x \exp\,(x^2)dx$ is called Dawson's integral (see, for example, p. 298 of ref. 20).

We notice that $J_1$ and $J_2$ come from the first term in the R.H.S. of (IV-8), while $J_3$, $J_4$ and $J_5$ all from the second term.

Clearly, the integrals involved in these J functions can no longer be performed by analytic methods. We therefore evaluated these integrals numerically through a 7094 computer, for various values of $\alpha$ and $\zeta_o$. We then pin-pointed the minimum of the R.H.S. of (IV-9) to be located at:

$$\alpha_{min} = 0.52,$$

and

$$(\zeta_o)_{min} = 0.68, \qquad \text{(IV-10)}$$

and at this point

$$\ln(\frac{e}{\sqrt{2\gamma h}}) \leq 0.0192,$$

which predicts:

$$H_{c3}/H_{c2} \geq 1.925 \text{ at } T = 0°K, \qquad \text{(IV-11)}$$

using again the fact that $h_{c2} = \frac{e^2}{4\gamma}$ (see Appendix C).

We can now compare our results with those of the L-G case. There the exact calculation of Saint-James and de Gennes gives:

$$\left.\begin{aligned} &(\zeta_o)_{min} = 0.768 \\ \text{and} \quad &H_{c3}/H_{c2} = 1.695 \end{aligned}\right. \qquad \begin{aligned} &\text{at } T_c - T << T_c \\ &\text{(exact result).} \end{aligned} \tag{IV-12}$$

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 used here (see for example refs. 2, 3), which reads:

$$\left.\begin{aligned} &\alpha_{min} = 0.603 \\ &(\zeta_o)_{min} = 0.727 \\ \text{and} \quad &H_{c3}/H_{c2} \geq 1.658 \end{aligned}\right. \qquad \begin{aligned} &\text{at } T_c - T << T_c \\ &\text{(variational result).} \end{aligned} \tag{IV-13}$$

We notice that the surface nucleation critical field $H_{c3}$ is roughly 16% higher at T = 0°K than is the L-G region, i.e. when T is very close to $T_c$. Using this percentage increase and the exact value of $H_{c3}$ in the L-G region, we estimate that the exact value for $H_{c3}$ at T = 0°K will most probably be centered aroung 1.97 $H_{c2}$.

It is interesting to point out here that the pair wave function corresponding to this surface nucleation mode has a smaller $\zeta_o$, but a larger width at T = 0°K than in the L-G region!

Referring to Appendix E, we notice that we have also an upper bound for the value of $H_{c3}$ at T = 0°K which reads:

$$H_{c3}/H_{c2} \leq 5.22. \tag{IV-14}$$

As is pointed out in Appendix C, we expect that this upper bound is roughly two or more times larger than the exact value, so that its physical significance lies mainly in the fact that it allows us to feel safe in using a variational approach to estimate $H_{c3}$, instead of helping us very much in pinpointing the exact value.

We now turn to estimate the first order correction to the ratio of $H_{c3}/H_{c2}$ as T gets slightly above absolute zero. For this purpose, we can start with eq. (C-12) derived in Appendix C:

$$\Delta_T(\zeta)\ \ln\left(\frac{e\varepsilon}{2\sqrt{h_T}}\right) = -\frac{\tilde{t}}{4\pi}\int\limits_{\substack{\zeta'>0\\ |\zeta-\zeta'|>\varepsilon}}\left\{\frac{\exp[-i(\frac{\zeta+\zeta'}{2}-\zeta_o)(\xi-\xi')]}{|\vec{\rho}-\vec{\rho}\,'|^2\,\mathrm{Sinh}(\tilde{t}|\vec{\rho}-\vec{\rho}\,'|)}\right.$$

$$\left.+\frac{\exp[-i(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')}-\zeta_o)(\xi-\xi')]}{|\vec{\rho}-R_{z'}\vec{\rho}\,'|^2\ \mathrm{Sinh}(\tilde{t}|\vec{\rho}-R_{z'}\vec{\rho}\,'|)}\right\}\Delta_T(\zeta')d\vec{\rho}\,', \qquad \text{(IV-15)}$$

which is valid for T ≠ 0°K.

We shall follow very closely Gor'kov's work on the calculation of $H_{c2}$ at low temperatures.[19] In fact, we can also use the identity:

$$\int\int\frac{\exp[-ia\xi]}{|\vec{\rho}|^2\mathrm{Sinh}(b|\vec{\rho}|)}\,d\xi d\eta = 2\pi\int_1^{\pi}\frac{J_o(a\zeta\sqrt{u^2-1})}{u\ \mathrm{Sinh}(b\zeta u)}\,du,$$

as is used by him, where $\vec{\rho}\equiv(\xi,\eta,\zeta)$ as before, and $J_o$ is the zero$^{th}$ order Bessel function, to simplify our eq. (IV-15). We get:

$$\Delta_T(\zeta)\ln\left(\frac{e\varepsilon}{2\sqrt{h_T}}\right) = -\frac{\tilde{t}}{2}\left\{\int\limits_{\substack{\zeta'>0\\ |\zeta-\zeta'|>\varepsilon}}d\zeta'\Delta(\zeta')\int_1^{\infty}du\,\frac{J_o[(\frac{\zeta+\zeta'}{2}-\zeta_o)(\zeta-\zeta')\sqrt{u^2-1}]}{u\ \mathrm{Sinh}(\tilde{t}|\zeta-\zeta'|u)}\right.$$

$$\left.+\int\limits_{\zeta'>0}d\zeta'\Delta(\zeta')\int_1^{\infty}du\,\frac{J_o[(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')}-\zeta_o)(\zeta+\zeta')\sqrt{u^2-1}]}{u\ \mathrm{Sinh}(\tilde{t}(\zeta+\zeta')u)}\right\}\equiv -\frac{1}{2}\int_o^{\infty}[K_{1,T}(\zeta,\zeta') +$$

$$+K_{2,T}(\zeta,\zeta')]\Delta_T(\zeta')d\zeta'. \qquad \text{(IV-16)}$$

Let us then define $h_T \equiv h_o + \delta h$, $K_{i,T} \equiv K_{i,o} + \delta K_{i,T}$ for $i = 1,2$, where $h_o$ corresponds to the value of $H_{c3}$ at $T = 0°K$ as $h_T$ does to the value of $H_{c3}$ at finite T. We also define $\Delta_T(\zeta) \equiv \Delta_o(\zeta) + \lambda(\zeta)$, where $\Delta_o(\zeta)$ is the corresponding solution at $T = 0°K$ which has just been obtained. Eq. (IV-16) can then be symbolically written as, to lowest order in $\tilde{t}$:

$$\lambda(\zeta)\ln\left(\frac{e\varepsilon}{2}\,\frac{1}{\sqrt{h_o}}\right) + \frac{1}{2}\left\{\int_0^\infty [K_{1,0}(\zeta,\zeta') + K_{2,0}(\zeta,\zeta')]\lambda(\zeta')d\zeta'\right.$$

$$= \frac{1}{2}\,h_o^{-1}\,\delta h_T\Delta_o(\zeta) - \frac{1}{2}\left\{\int_0^\infty [\delta K_{1,T}(\zeta,\zeta') + \delta K_{1,T}(\zeta,\zeta')]\Delta_o(\zeta')d\zeta'\right]. \qquad \text{(IV-17)}$$

This is an inhomogeneous integral equation. Since it must possess non-trivial solutions for $\lambda(\zeta)$, we require that the source term (i.e. the R.H.S. of (IV-17)) is orthogonal to the solution of the corresponding homogeneous equation, which is simply $\Delta_o(\zeta)$. We therefore get

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

if $\Delta_o(\zeta)$ is properly normalized according to

$$\int_0^\infty |\Delta(\zeta)|^2\,d\zeta = 1.$$

Symbolically, we can write: $h_o^{-1}\,\delta h_T = \langle\delta K_{1,T}\rangle + \langle\delta K_{2,T}\rangle$.

Now for $|\zeta+\zeta'-2\zeta_o| >> \tilde{t}$, we have

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

and for $\left|\frac{\zeta^2+\zeta'^2}{\zeta+\zeta'} - 2\zeta_o\right| >> \tilde{t}$, we have

$$\delta K_{2,T}(\zeta,\zeta') = -\frac{\tilde{t}^2}{3}\,\frac{\exp[-\frac{1}{2}\,|\zeta^2+\zeta'^2-2\zeta_o(\zeta+\zeta')|]}{\left|\frac{\zeta^2+\zeta'^2}{\zeta+\zeta'} - 2\zeta_o\right|}\,.$$

Within the regions $|\zeta+\zeta' - 2\zeta_0| \lesssim \tilde{t}$ and $\left|\frac{\zeta^2+\zeta'^2}{\zeta+\zeta'} - 2\zeta_0\right| \lesssim \tilde{t}$, for $K_{1,T}$ and $K_{2,T}$ respectively, the expansion procedure is not valid, and $\delta K_{1,T}$, $\delta K_{2,T}$ are therefore much more complicated. However, it is not hard to see that within these regions, $\delta K_{1,T}$ and $\delta K_{2,T}$ are of the order of $\tilde{t}$, so that the contributions from these regions are of the order of $\tilde{t}^2$. If we are only interested in lowest order contributions, which are proportional to $\tilde{t}^2 \ln \tilde{t}$, we then have:

$$\langle\delta K_{1,T}\rangle = -\frac{\tilde{t}^2}{3} \mathop{\int_0^\infty\int_0^\infty}_{|\zeta+\zeta'-2\zeta_0| \geq \tilde{t}} \frac{\exp[-\frac{1}{2}|\zeta^2-\zeta'^2-2\zeta_0(\zeta-\zeta')|]}{|\zeta+\zeta'-2\zeta_0|} \Delta_0^*(\zeta)\Delta_0(\zeta')d\zeta d\zeta',$$

and

$$\langle\delta K_{2,T}\rangle = -\frac{\tilde{t}^2}{3} \mathop{\int_0^\infty\int_0^\infty}_{\left|\frac{\zeta^2+\zeta'^2}{\zeta+\zeta'} -2\zeta_0\right| \geq \tilde{t}} \frac{\exp[-\frac{1}{2}|\zeta^2+\zeta'^2-2\zeta_0(\zeta+\zeta')|]}{\left|\frac{\zeta^2+\zeta'^2}{\zeta+\zeta'} - 2\zeta_0\right|} \Delta_0^*(\zeta)\Delta_0(\zeta')d\zeta d\zeta'.$$

Using our variational trial wave function:

$$\Delta_0(\zeta) \cong \left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right)^{-1/2} \exp(-\frac{1}{2}\alpha\zeta^2),$$

we can now get a rough estimation of $\langle\delta K_{i,T}\rangle$ for $i = 1,2$. In fact, to order of $\tilde{t}^2 \ln \tilde{t}$, we have simply:

$$\frac{\sqrt{\pi}}{2\sqrt{\alpha}} \langle\delta K_{1,T}\rangle \cong -\frac{\tilde{t}^2}{3} \mathop{\int_0^\infty\int_0^\infty}_{|\zeta+\zeta'-2\zeta_0| \geq \tilde{t}} \frac{\exp[-\frac{\alpha}{2}(\zeta^2+\zeta'^2)]}{|\zeta+\zeta' - 2\zeta_0|} d\zeta d\zeta',$$

$$\frac{\sqrt{\pi}}{2\sqrt{\alpha}} \langle\delta K_{2,T}\rangle \cong -\frac{\tilde{t}^2}{3} \mathop{\int_0^\infty\int_0^\infty}_{\left|\frac{\zeta^2+\zeta'^2}{\zeta+\zeta'} -2\zeta_0\right| \geq \tilde{t}} \frac{\exp[-\frac{\alpha}{2}(\zeta^2+\zeta'^2)]}{\left|\frac{\zeta^2+\zeta'^2}{\zeta+\zeta'} -2\zeta_0\right|} d\zeta d\zeta'.$$

We can then evaluate $\langle\delta K_{1,T}\rangle$ in the new coordinate system: $u = \zeta+\zeta' - 2\zeta_o$, $v = \zeta-\zeta'$ to get: $\langle\delta K_{1,T}\rangle \cong \frac{4}{3}\,[\exp(-\alpha\zeta_o^{\,2})\,\mathrm{erf}(\sqrt{\alpha}\zeta_o)]\,\tilde{t}^2 \ln \tilde{t}$. The second matrix element $\langle\delta K_{2,T}\rangle$ can be evaluated in the polar coordinate system: $r^2 = \zeta^2+\zeta'^2$, $\theta = \tan^{-1}(\zeta'/\zeta)$ plus a subsequent change of variable from $\theta$ to $u = \cos\theta - \sin\theta$. The result is:

$$\langle\delta K_{2,T}\rangle \cong \frac{16}{3}\sqrt{\frac{\alpha\zeta_o^{\,2}}{\pi}}\,[\exp(-4\alpha\zeta_o^{\,2})\int_o^1 \sqrt{2-u^2}\,\exp(2\alpha\zeta_o^{\,2}u^2)\,du]\,\tilde{t}^2 \ln \tilde{t}.$$

If we now define $\lambda^2 = \alpha\zeta_o^{\,2}$ and

$w(\lambda) \equiv \frac{4}{3}[\exp(-\lambda^2)\mathrm{erf}(\lambda) + \frac{4\lambda}{\sqrt{\pi}}\exp(-4\lambda^2)\int_o^1 \sqrt{2-u^2}\,\exp(2\lambda^2u^2)\,du]$, we see that $\langle\delta(K_{1,T} + K_{2,T})\rangle = w(\lambda)\,\tilde{t}^2 \ln \tilde{t} + O(\tilde{t}^2)$, and thus $\frac{H_{c3}(T)}{H_{c3}(o)} = 1 + w(\lambda)\,\tilde{t}^2 \ln \tilde{t} + O(\tilde{t}^2)$, or $\frac{H_{c3}(T)}{H_{c3}(0)} = 1 + \frac{w(\lambda)}{h_{c3}(0)}\,t^2 \ln t + O(t^2)$.

From our earlier variational result at T = 0°K, we have found that (eq. (IV-10)):

$$\lambda \equiv \sqrt{\alpha}\,\zeta_o \cong 0.49.$$

A numerical integration then gives:

$$w(\lambda) \cong 1.39.$$

We also need:

$$[h_{c3}(0)]^{-1} = [\frac{h_{c3}(0)}{h_{c2}(0)} \times h_{c2}(0)]^{-1} \cong [1.93 \times \frac{e^2}{4\gamma}]^{-1} \cong 0.50.$$

Our result is therefore

$$\frac{H_{c3}(T)}{H_{c3}(0)} \cong 1 + 0.70\,t^2 \ln t + O(t^2).$$

Compare this result with Gor'kov's corresponding result[19] on $H_{c2}$ at low temperatures (which is also recovered in Helfand and Werthamer's calculation,[12] see Ch II, eq. (II-44).)

$$\frac{H_{c2}(T)}{H_{c2}(0)} = 1 + \frac{2}{3}\tilde{t}_{c2}^{2} \ln \tilde{t}_{c2} + O(\tilde{t}_{c2}^{2})$$

$$\cong 1 + 0.65\, t^{2} \ln t + O(t^{2}), \qquad \text{(IV-19)}$$

we then obtain:

$$\frac{H_{c3}(T)}{H_{c2}(T)} \cong 1.93\,[1 + 0.05\, t^{2} \ln t + O(t^{2})]. \qquad \text{(IV-20)}$$

This is only a very rough estimation of the lowest order correction term of the ratio $H_{c3}/H_{c2}$ due to slightly non-zero temperature. But it indicates that the ratio $H_{c3}/H_{c2}$ has a vanishing slope w.r.t. t at $t = 0$. We also notice 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 each other when they form the ratio $H_{c3}/H_{c2}$, leaving this ratio to be only very weakly temperature dependent. 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 $T_c$.

Finally, we would like to discuss briefly the current-carrying nucleation states. We do not attempt to solve this problem completely even at $T = 0°K$. Instead, we shall only make some remarks on this case, and supply some information available from our present calculation which we think are helpful to those who are interested in this problem and attempt to investigate it.

Clearly, in gauge A in which $\vec{A}(\vec{r}) \equiv (Hz, 0, 0)$, the most general current-carrying state has the following pair wave function:

$$\Delta(\vec{r}) = e^{ik_x x}\, e^{ik_y y}\, f(z). \qquad \text{(IV-21)}$$

In gauge B in which $\vec{A}(\vec{r}) \equiv (H(z-z_o), 0, 0)$, eq. (IV-21) is reduced to

$$\Delta(\vec{r}) = e^{ik_y y} \bar{\Delta}(z) \qquad \text{(IV-22)}$$

if we choose $Z_o = -k_x/(2eH)$. However, we must emphasize that for samples not in the L-G or dirty limit cases, the relation between $k_x$(or $z_o$), $k_y$, and the total current $\vec{I}$ carried by the sample is a complicated non-local expression involving seven or eight dimensional integrals which is very hard to carry out (see Ch. VI, eqs. (VI-25), (VI-27) for the current density). For $k_y = 0$ and $k_x$ (or $Z_o$) equal to its optimum value, we shall show in ch. VI that $\vec{I} = 0$. For $k_x$ and $k_y$ slightly deviated from these optimum values, some perturbational expansion procedure clearly can be applied to the current expression so that it will be simplified to some extent. The result is expected to be a polynomial in $k_x$ and $k_y$ with temperature- and magnetic field-dependent coefficients, which are, however, still very hard to evaluate. Besides, we must not forget that the magnetic field - the critical field for these current-carrying nucleation states, is still a function of T, $k_x$, and $k_y$.

For the present purpose, we shall be contented with characterizing the current-carrying states by $k_x$ and $k_y$, leaving the values of the total currents of these states implicit.

Eq. (IV-4) or eq. (IV-15), is correct for all nucleation states. For $k_y \neq 0$, the reduced one-or two-dimensional integral equation (e.g. eq. (IV-16) for $T \neq 0$, and eq. (C-14) for $T = 0$) must now be modified. The modification is, however, not very difficult, if the following point is observed: For $k_y = 0$ case, we evaluated the following two-dimensional integral in order to reduce our integral equation to a simpler form:

$$\iint \frac{\exp\,[-\,ia\xi]}{|\vec{\rho}|^2\,\mathrm{Sinh}(\tilde{t}|\vec{\rho}|)}\; d\xi d\eta, \qquad \text{(IV-23)}$$

with $a = (\frac{\zeta+\zeta'}{2} - \zeta_o)$, and $(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')} - \zeta_o)$, for the direct and the image terms of the kernel respectively. For $k_y \neq 0$ case, this integral is changed to

$$\iint \frac{\exp\,\{i[\bar{k}_y\eta - a\xi]}{|\vec{\rho}|^2\,\mathrm{Sinh}\,(\tilde{t}|\vec{\rho}|)}\; d\xi d\eta. \qquad \text{(IV-24)}$$

where $\bar{k}_y = k_y\xi_H$. Clearly, this integral can be reduced to that of the former case (i.e. (IV-23)), except for the change $a \to (a^2+\bar{k}_y{}^2)^{1/2}$, if we perform the following change of variables:

$$\xi' = (a^2 + \bar{k}^2)^{-1/2}\,[a\xi - \bar{k}_y\,\eta]$$

and

$$\eta' = (a^2 + \bar{k}^2)^{-1/2}\,[\bar{k}_y\xi + a\eta].$$

This indicates that to go from the $k_y = 0$ case to the $k_y \neq 0$ case, we need only make the following changes:

$$\Delta(\zeta) \to \bar{\Delta}(\zeta),$$

$$(\frac{\zeta+\zeta'}{2} - \zeta_o) \to [(\frac{\zeta+\zeta'}{2} - \zeta_o)^2 + \bar{k}_y{}^2]^{1/2}$$

and

$$(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')} - \zeta_o) \to [(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')} - \zeta_o)^2 + \bar{k}_y{}^2]^{1/2} \qquad \text{(IV-25)}$$

and eqs. (IV-16) and (C-14) will again become valid. Thus it is seen that the case with $k_y \neq 0$ is not much harder than the case with $k_y = 0$, and can be attacked by variational method, at least for $T \cong 0°\mathrm{K}$, in just the same way as we did in this chapter for the case with $k_y = 0$. This will lead us to the dependence of the parallel critical field on $k_x$ and $k_y$, i.e. the function $H_{c||}(k_x,k_y)$, at least for $T \cong 0°\mathrm{K}$. However, due to the fact that the expression for the current is too complicated for computational purposes, we shall not be able to obtain the dependence of the parallel critical field on the total current flowing inside the sample, which is of more physical interest. (We must remember, however, that the total current is always infinitesimal, so long as the gap equation is linearized.) This point combined with the fact that even $H_{c||}(k_x,k_y)$ can only be calculated by numerical method which requires enormous computer time, lead us to conclude that this problem is not rewarding enough to be worthwhile for us to carry out the computation. The case with $k_y = 0$, however, have been studied by us for quite a range of $k_x$, which is in fact a by-product of our variational calculation of the surface nucleation critical field $H_{c3}$. We therefore supply below all the information we have on these $k_y = 0$ nucleation states (corresponding to states with current flowing only in the direction perpendicular to the applied field, and parallel to the surface). These results are for T = 0°K only, and they are variational results using a gaussian function centered at the sample surface as our trial wave function:

$$\Delta(\zeta) = N \exp[-\frac{1}{2}\alpha\,\zeta^2]. \tag{IV-26}$$

In fig. 2 we first give some typical curves showing how the "eigenvalue" E.V. ($\equiv \ln[e/(2\gamma h)^{1/2}]$, see eq. (IV-9)), is minimized w.r.t. the parameter $\alpha$, for various values of $\zeta_o (= Z_o/\xi_H = -k_x\xi_H)$. The minimized E.V. is related to $H_{c||}(\zeta_o)$ through $h = (2eH)(v_F/2\pi T_c)^2$ as is defined in the beginning of Appendix C. The quantity $H_{c3}$ is of course obtained by further minimizing $H_{c||}(\zeta_o)$ w.r.t. the parameter $\zeta_o$. In fig. 3 we plot $H_{c||}(\zeta_o)/H_{c2}$ as a function of $\zeta_o$, and in fig. 4 we plot $\alpha_{min}$ (corresponding to $H_{c||}(\zeta_o)$) as a function of $\zeta_o$, which shows the dependence of the approximate pair-wave-function on the parameter $\zeta_o$, through eq. (IV-26). We also summarize these results in the following tables:

| $\zeta_1=2^{-1/2}\zeta_o$ | $u = \alpha/(1+\alpha)$ (error: $\pm$ 0.05) | $\alpha_{min}$ | E.V. = $\ln[e/(2\gamma h)^{1/2}]$ | $H_{c\|\|}(\zeta_o)/H_{c3}$ $=2\exp[-2\text{x}E.V.]$ |
|---|---|---|---|---|
| 0 | 0.55 | 1.22 | 0.415 | 0.872 |
| 0.05 | 0.50 | 1.00 | 0.344 | 1.005 |
| 0.10 | 0.50 | 1.00 | 0.273 | 1.159 |
| 0.15 | 0.50 | 1.00 | 0.209 | 1.317 |
| 0.20 | 0.50 | 1.00 | 0.154 | 1.470 |
| 0.25 | 0.45 | 0.82 | 0.107 | 1.615 |
| 0.30 | 0.45 | 0.82 | 0.073 | 1.728 |
| 0.35 | 0.40 | 0.67 | 0.045 | 1.828 |
| 0.40 | 0.40 | 0.67 | 0.030 | 1.884 |
| 0.45 | 0.35 | 0.54 | 0.020 | 1.922 |
| 0.50 | 0.35 | 0.54 | 0.021 | 1.918 |
| 0.55 | 0.30 | 0.43 | 0.025 | 1.902 |
| 0.60 | 0.30 | 0.43 | 0.037 | 1.857 |
| 0.65 | 0.25 | 0.33 | 0.056 | 1.788 |
| 0.70 | 0.25 | 0.33 | 0.073 | 1.728 |

(Notice that $H_{c||}(\zeta_o = \infty) = H_{c2}$ corresponds to E.V. = $\ln(2^{1/2}) = 0.3465$. The $\zeta_o = 0$ state is also studied in Appendix C, where we find the following set of more accurate data: u = 0.5316, $\alpha_{min}$ = 1.1350, E.V. = 0.4145, $H_{c||}(0)/H_{c2}$ = 0.8729).

To pinpoint the optimum state, we have studied the region $0.40 \leq 2^{-1/2} \zeta_o \leq 0.50$ in more detail and with better accuracy:

| $\zeta_1=2^{-1/2}\zeta_o$ | $u = \alpha/(1+\alpha)$ error: $\pm$ 0.01 | $\alpha_{min}$ | E.V. = $\ln[e/(2\gamma h)^{1/2}]$ | $H_{c\|\|}(\zeta_o)/H_{c3}$ $=2\exp[-2x\text{E.V.}]$ |
|---|---|---|---|---|
| 0.40 | 0.38 | 0.613 | 0.0286 | 1.889 |
| 0.41 | 0.37 | 0.587 | 0.0263 | 1.898 |
| 0.42 | 0.37 | 0.587 | 0.0243 | 1.905 |
| 0.43 | 0.37 | 0.587 | 0.0228 | 1.911 |
| 0.44 | 0.36 | 0.563 | 0.0213 | 1.917 |
| 0.45 | 0.36 | 0.563 | 0.0204 | 1.920 |
| 0.46 | 0.35 | 0.538 | 0.0196 | 1.923 |
| 0.47 | 0.35 | 0.538 | 0.0192 | 1.925 |
| 0.48 | 0.34 | 0.515 | 0.0192 | 1.925 |
| 0.49 | 0.34 | 0.515 | 0.0193 | 1.924 |
| 0.50 | 0.33 | 0.493 | 0.0197 | 1.923 |

We remark that our variational approach is not valid for large $\zeta_o$ states, for which our trial-wave-function is very poor. We therefore expect $\alpha \to 0$ as $\zeta_o \to \infty$. Near the optimum state, however, we believe that the chosen trial wave function should be quite good.

# CHAPTER V

## CALCULATION OF $H_{c3}$ FOR PURE SAMPLES NEAR THE LANDAU-GINZBURG REGION

In this chapter, we want to study $H_{c3}$ for pure samples in the high temperature limit. We have adopted two approaches in attacking this problem.

We first present an over-all view of these two approaches, as the details of them are quite tedious:

In both approaches, we shall start with the LGE found in Ch. IV, i.e. eq. (IV-4), which has been shown in the earlier chapters to be appropriate for studying surface nucleation in a sample described in the beginning of Ch. III. It is therefore only the ways we treat this equation which are different in the two approaches.

Two characteristic lengths are going to play very important roles in both approaches. We therefore restate their definitions: $\xi_o(T) = V_F/(2\pi T)$, and $\xi_H = (2eH)^{-1/2}$. Later we shall identify H with $H_{c3}(T)$, $\xi_H$ will then become a definite function of T. We have in this chapter limited ourselves to $T \sim T_c$. In this temperature range, we expect $H_{c3}(T) \propto (1-t)$ (assuming that our results will agree with Saint-James and de Gennes'[1] in the L-G region, a fact we can check <u>a posteriori</u>). We therefore have $\xi_H \propto \xi_o(1-t)^{-1/2} >> \xi_o$. A good expansion parameter is therefore given by the combination $(\xi_o/\xi_H)$ which is $\propto(1-t)^{1/2}$.

In Chapter II, section 1, we have made the following definition:

A function $F(\vec{r})$ is said to be "slowly varying" (henceforth referred to as "SV") at $\vec{r}$ if:

$$|\vec{\tilde{\nabla}}_r F(\vec{r})| \equiv |[\vec{\nabla}_r + 2ie\vec{A}(\vec{r})]\, F(\vec{r})| \sim \xi_H^{-1} |F(\vec{r})|. \qquad \text{(V-1)}$$

We now add the definition that a function $F(\vec{r})$ is "rapidly varying" (henceforth referred to as "RV") at $\vec{r}$ if:

$$|\vec{\tilde{\nabla}}_r F(\vec{r})| \sim \xi_o^{-1} |F(\vec{r})|. \qquad \text{(V-2)}$$

Both eqs. (V-1) and (V-2) are gauge invariant statements.

In our first approach, we shall only seek for those solutions of our LGE which are slowly varying everywhere inside the sample (henceforth referred to as "ESV") - a strong limitation which we do not know <u>a priori</u> whether it will lead us to anything. Using this limitation, however, we can expand our LGE in the way Gor'kov[15] obtained his microscopic derivation of the L-G equation. Our expansion parameter is $\xi_o/\xi_H \sim (1-t)^{1/2}$, as is his. We remind the reader of the result of Ch. II, section 3, that in the infinite sample case, as considered by Gor'kov in his derivation of the L-G equation, the expansion of the LGE to any order gives a finite order differential equation of constant coefficients, whose solutions are "ESV". Gor'kov's expansion is therefore self-consistent.

When we expand out our LGE to any order, we always find some extra terms (called surface layer terms), in addition to those in the corresponding differential equation found for an infinite sample to the same order (called bulk terms). The surface layer terms involve $\vec{r}$-dependent coefficients which are non-vanishing only for $Z \lesssim \xi_o$. They are therefore necessarily "RV" at $Z \lesssim \xi_o$. The solutions of such an equation are in general also "RV" at $Z \lesssim \xi_o$. To see whether such an equation does admit "ESV" solutions, we must examine whether these surface layer terms vanish when we enforce the "ESV" nature of its solutions. If they do, the conclusions are consistent with the original assumption, and are therefore valid. If not, the results must be abandoned.

In this way, and by expanding our LGE only to order $(\xi_o/\xi_H)^2$, or (1-t), we have obtained a gauge-invariant, completely microscopic, simultaneous derivation of both the linearized L-G equation, i.e. eq. (II.1), and the "standard B.C." for it (as Lüders[21] calls it), i.e. eq. (II-5). To see how the B.C. will also come out, the reader is reminded that in Ch. IV, we have pointed out that the exact LGE, eq. (II-4), implies the automatic satisfaction of the exact B.C. (IV-3), which is nothing but the "standard B.C." for the L-G equation.(ii) After the expansion in this approach, we shall show that this peculiar property is still retained (to the order of interest) by the complete differential equation including the surface layer terms. To second order the surface layer terms are then shown to give vanishing net effect to those "ESV" solutions of the complete differential equation using the fact that they must satisfy the exact B.C. The surface layer terms can therefore be dropped at the expanse that the exact B.C., eq. (IV-3), must now be added to the equation as an independent requirement.

In the next step of this approach, we extend our expansion of the LGE to order $(\xi_o/\xi_H)^3$ or (1-t) for $H_{c3}$. To this order, however, we find that the surface layer terms no longer vanish for nucleation states in the neighborhood of the optimum one. Our first approach is therefore invalid from this order on. We shall use the phrase

"L-G region" to mean the temperature region in which Saint-James and de Gennes' results are valid. Our first approach is therefore valid only in the L-G region. An exact criterion for the "L-G region" will be given later. For the present, it only means the temperature region in which the LGE need only be accurate to 0(1-t).

For T not in the L-G region, we need our second approach. In this approach, we assume that the pair wave function is made of two components: a "ESV" component, and a "RV" component vanishing except when $Z \lesssim \xi_o$. This assumption is valid because our LGE, eq. (IV-4), reduces to that of the infinite sample case when $Z >> \xi_o$. We can then expand our LGE as in our 1st approach, for the ESV component only. Separate the "SV"- and the "RV"- parts of the LGE, we get two coupled equations:

To any finite order in $(1-t)^{1/2}$, the "ESV" component, called the bulk component, is defined to satisfy the same differential equation as is satisfied by the complete pair wave function in an infinite sample case, i.e. eq. (II-35), with no $\vec{r}$-dependent surface layer terms. The "RV" component, called the surface layer component, will then satisfy an inhomogeneous integral equation with source terms proportional to the bulk component of the pair wave function and its derivatives. This integral equation can no longer be reduced to any differential equation, because it no longer contains any small expansion parameter such as $(\xi_o/\xi_H)$.

In the L-G region, it can be shown that the second equation admits only the trivial solution. The pair wave function therefore contains only the "ESV" component. Our first approach is therefore necessarily valid in this region. This proves that in the L-G region, the solutions of the L-G equation (II-1) plus the standard B.C. (II-5), exhaust all possible solutions of the exact LGE, eq. (IV-4).

In the non-L-G region, it is found that the second equation no longer admits the trivial solution. Our LGE is therefore a genuine integral equation to any order higher than the second, contrary to the infinite sample case, for which an approximate finite order differential equation can always be obtained by truncating eq. (II-35) to any order of interest.

In the non L-G region, we must then solve the two coupled equations. The coupling is rather implicit, as the first equation does not apparently involve the surface layer component. The coupling comes about because a B.C. is required for the bulk component to be well-defined. The most general B.C. that can be accepted is then discussed. In gauge B (see Ch. II, section 1, for definition), it can only contain an unknown constant. This constant is determined by the second equation, as there is only one value for this constant, for which the second equation admits finite solutions! The first equation is then solved together with this B.C., by a perturbation scheme. It is shown that this perturbation scheme is easily applied to two orders beyond the L-G region. This allows us to get a fourth and a fifth order correction term to $H_{c3}$ (not third and fourth, even though these are the extra orders considered in the LGE beyond those for the L-G region). Thus the lowest order correction to $H_{c3}$ is $\propto(1-t)^2$. Since $H_{c3}$ in the L-G region is already $\propto(1-t)$, it indicates that the L-G region can be defined by the criterion $(1-t) \ll 1$, so far as $H_{c3}$ is concerned.$^{(iii)}$

Our fourth order correction $(\sim(1-t)^2)$ of $H_{c3}$ turns out to be identical to that obtained by Lüders,[22] which predicts that the ratio $H_{c3}/H_{c2}$ should drop linearly from 1.7 as T gets slightly below $T_c$ (for pure sample with specularly reflective surface only). We, however, also find a fifth order term in $H_{c3}$ which in fact dominates the fourth order one for $(1-t) \gtrsim 10^{-2}$! This term also predicts that $H_{c3}/H_{c2}$ will drop below $T_c$ – with an even faster speed! Comparing these predictions with our low temperature results ($H_{c3}/H_{c2} \gtrsim 1.93$ with a vanishing initial slope), we find that $H_{c3}/H_{c2}$ for pure samples with specularly reflective surface cannot be described by a simple, monotonic function in the full temperature range $0 \leq T \leq T_c$.

We now begin to present the full details of the calculation.

## The First Approach

We first write down our LGE:

$$\begin{aligned}\Delta(\vec{r}) &= \int K_H^{(o)}(\vec{r},\vec{r}\,')\Delta(\vec{r}\,')\,d\vec{r}\,' \\ &= \int_{z'>o} k^{(o)}\,(|\vec{r}-\vec{r}\,'|)\,\exp[-2ie\int_{\vec{r}}^{\vec{r}\,'} A(\vec{s})\cdot d\vec{s}]\,\Delta(\vec{r}\,')d\vec{r}\,' \\ &\quad + \int_{z'>o} k^{(o)}(|\vec{r}-R_z\vec{r}\,'|)\,\exp[-2ie\int_{\vec{r}}^{\vec{r}\,'} A(\vec{s})\cdot d\vec{s}]\Delta(\vec{r})\,d\vec{r}\,'.\end{aligned} \qquad \text{(V-3)}$$

For $k^{(o)}$, we can use eq. (II-31), as the frequency cut-off needs not be taken care of at the present moment.

For $T \sim T_c$, $k^{(o)}(|\vec{R}|)$ vanishes for $|\vec{R}| \gg \xi_o$. For our present approach, we assume $\Delta(\vec{r})$ to be "ESV". As is mentioned in the outline, we attempt to expand eq. (V-3) into terms of different orders in $(\xi_o/\xi_H)$. For this purpose, we use the alternative form of eq. (V-3), i.e. eq. (IV-7):

$$\Delta(\vec{r}) = \int d\vec{R}\; k^{(o)}(|\vec{R}|)\, \exp[\vec{R}\cdot\vec{\tilde{\nabla}}_r]\Delta(\vec{r})$$

$$+ \int_{z'<o} d\vec{r}\; k^{(o)}(|\vec{R}|)\, \exp[(\vec{r}_2-\vec{r})\cdot\vec{\tilde{\nabla}}_s]$$

$$\times\{\exp[(R_z,\vec{r}\,'-\vec{r}_2)\cdot\vec{\tilde{\nabla}}_s]-\exp[(\vec{r}\,'-\vec{r}_2)\cdot\vec{\tilde{\nabla}}_s]\}\Delta(\vec{s})\Big|_{\vec{s}=\vec{r}}, \qquad \text{(V-4)}$$

where $\vec{R} = \vec{r}-\vec{r}\,'$, $\vec{r}_2 \equiv R_z,\vec{r}_1 = \frac{z}{z-z'}\vec{r}\,' - \frac{z'}{z-z'}\vec{r}$ with $\vec{r} = \vec{r} - \hat{z}(\hat{z}\cdot\vec{r})$ and $\vec{\tilde{\nabla}}_r = \vec{\nabla}_r + 2ie\,\vec{A}(\vec{r})$.

We remind the reader of the discovery in Ch. IV that both eqs. (V-3) and (V-4) imply the automatic satisfaction of the following exact B.C.:

$$[\vec{\nabla}_r + 2ie\,\vec{A}(\vec{r})]_z\,\Delta(\vec{r})\Big|_{z=o} = 0\;. \qquad \text{(V-5)}$$

In eq. (V-4), we can expand all of the exponential operators (as we did to eq. (II-34) to get (II-35), since $\vec{\tilde{\nabla}}_r$ acting on $\Delta(\vec{r})$ will give a factor of $\xi_H^{-1}$, while all lengths such as $|\vec{R}|$, $|\vec{r}_2-\vec{r}|$, $|R_z,\vec{r}\,'-\vec{r}_2|$ and $|\vec{r}\,'-\vec{r}_2|$ are of the order $\xi_o$ due to the short range nature of the zero-field kernel $k^{(o)}$.

After the expansion, we shall call all of those terms obtained from the first term at the R.H.S. of eq. (V-4), "the bulk terms"; while those from the second term at the R.H.S. of eq. (V-4) are "the surface layer terms". Notice that the bulk terms are also in the corresponding expansion for the infinite sample case (see eqs. (II-34), (II-35)), and they will involve differential operators acting on $\Delta(\vec{r})$, with constant coefficients. On the other hand, the surface layer terms are entirely due to the boundary, and they will involve differential operators acting on $\Delta(\vec{r})$, with space-dependent coefficients, non-vanishing only in the surface layer $Z \lesssim \xi_o$.

To second order, the expansion gives:

$$\Delta(\vec{r}) = a_o \Delta(\vec{r}) + \frac{1}{6} a_2 |\vec{\tilde{\nabla}}_r|^2 \Delta(\vec{r}) + \mathrm{SLT(II)}, \qquad \text{(V-6)}$$

where SLT(II), the surface layer terms to second order, are computed in Appendix F:

$$\mathrm{SLT(II)} = -2\chi_1(z)\tilde{\nabla}_z \Delta(\vec{r}) + 2z\chi_1(z)\tilde{\nabla}_z^2 \Delta(\vec{r}), \qquad \text{(V-7)}$$

with $\chi_1(z) \equiv \int_{z'<o} d\vec{r}'\, z'\, k^{(o)}(|\vec{r}-\vec{r}'|)$, and the constants $\{a_n\}$ are defined in Ch. II, eqs. (II-36), (II-40) through (II-42). To our present order of interest, we can write:

$$a_o \cong 1 + |\lambda|\, N(o)\, (1-t), \qquad \text{(V-8)}$$

$$a_2 \cong \frac{7}{2}\, \zeta(3)|\lambda|N(o)\, \xi_o^2 . \qquad \text{(V-9)}$$

Eq. (V-6) therefore becomes:

$$[\frac{1}{4m} |\vec{\tilde{\nabla}}_r|^2 + \frac{1}{\beta}(1-t)]\Delta(\vec{r}) - 2[\beta|\lambda|N(o)]^{-1}\chi_1(z)(\tilde{\nabla}_z - z\tilde{\nabla}_z{}^2)\Delta(\vec{r}) = 0. \qquad \text{(V-10)}$$

We notice that should the last term in the L.H.S. of this equation be absent, we would have got the linearized L-G equation, viz. eq. (II-1), whose solutions are "ESV". But with the extra surface layer terms in it, which are necessarily "RV" due to the appearance of $\chi_1(z)$, we are no longer sure that eq. (V-10) will still admit "ESV" solutions. However, we also notice that since Z is restricted to the neighborhood of Z=0 in these surface layer terms, we can further expand $\Delta(\vec{r})$ and its derivatives in a Taylor series, in the gauge in which $A_z \equiv 0$, $|\nabla_z \Delta(\vec{r})| \sim |\tilde{\nabla}_z \Delta(\vec{r})| \sim \xi_H^{-1}|\Delta(z)|$. Thus to order $\xi_H^{-2}$:

$$[\tilde{\nabla}_z - z\tilde{\nabla}_z^{\,2}]\Delta(\vec{r}) = [\nabla_z - z\nabla_z^{\,2}]\Delta(\vec{r})$$

$$\cong \{[\nabla_z \ \Delta(\vec{r})]_{z=o} + z[\nabla_z^{\,2} \ \Delta(\vec{r})]_{z=o} + \ldots\}$$

$$- Z[[\nabla_z^{\,2} \ \Delta(\vec{r})]_{z=o} + \ldots]$$

$$= [\nabla_z \ \Delta(\vec{r})]_{z=o} = [\tilde{\nabla}_z \ \Delta(\vec{r})]_{z=o}. \qquad \text{(V-11)}$$

On the other hand, if we apply $\tilde{\nabla}_z$ to both sides of eq. (V-6), and then set z = o, we get:

$$\tilde{\nabla}_z\Delta(\vec{r})\Big|_{z=o} = a_o[\tilde{\nabla}_z\Delta(\vec{r})]_{z=o} + \frac{1}{6}\, a_2[\tilde{\nabla}_z|\vec{\tilde{\nabla}}_r|^2\Delta(\vec{r})]_{z=o}$$

$$-2[\frac{d}{dz}\,\chi_1(z)]_{z=o} \times [\tilde{\nabla}_z\Delta(\vec{r})]_{z=o} - 2\chi_1(z) \times [\tilde{\nabla}_z^{\,2}\Delta(z)]_{z=o}$$

$$+ 2\,\chi_1(z)\ [\tilde{\nabla}_z^{\,2}\Delta(\vec{r})]_{z=o} \cong 0 \qquad \text{(V-12)}$$

to order $\xi_H^{-2}$, where use has been made of the identity $[\frac{d}{dz}\,\chi_1(z)]_{z=o} = \frac{1}{2}\,a_o$, as is given in Appendix F. This means that our approximate LGE, eq. (V-6) and hence eq. (V-10), still implies the automatic satisfaction of the exact B.C., as does the exact LGE eq. (V-3) or (V-4), except that this time it is true only to order $\xi_H^{-2}$.

Combining eqs. (V-11) and (V-12), we see that we can simply drop the surface layer terms in eq. (V-6) or (V-10) as their net result vanishes to the order of interest.

In this way we have proved that to second order, our LGE can simply be replaced by the linearized L-G equation:

$$-\frac{1}{4m}\ |\vec{\tilde{\nabla}}_r|^2\ \Delta(\vec{r}) = \frac{1}{\beta}\,(1-t)\ \Delta(\vec{r}). \qquad \text{(V-13)}$$

But during the process of deriving it, we have lost the information that the exact B.C. should always be satisfied, we therefore should now add the B.C. to equation (V-13), as an independent condition:

$$\tilde{\nabla}_z \Delta(\vec{r})\Big|_{z=0} = 0. \qquad \text{(V-14)}$$

This completes our simultaneous derivation of the linearized L-G equation and the "standard B.C.", for a sample with a boundary, with a solution which is "ESV", thereby justified the self-consistency of our initial assumption. As is seen, our derivation is gauge invariant,(iv) and completely microscopic.

From the derivation, we see that eq. (V-13) is valid everywhere inside the sample, in describing the pair wave function, except for $Z \lesssim P_F^{-1}$ where the kernel of our LGE is inaccurate (see the derivation of the kernel in Ch. IV, and also footnote(iii)).

We also notice that if we define a scalar product in the present problem by:

$$(f,g) \equiv \int_{z>0} d\vec{r}\; f^*(\vec{r})g(\vec{r}), \qquad \text{(V-15)}$$

then we observe that our exact LGE, eq. (V-3) or (V-4), is an hermitian equation, so are our final equations approximating the exact LGE, viz. eqs. (V-13) and (V-14), even though eqs. (V-6) and (V-10) do not look apparently like to have this property.

Before we go on to extend this approach to higher orders, we now want to caution the reader about the exact meaning of the phrase "to $n^{th}$ order". We have derived the linearized L-G equation (V-13) and the standard B.C. (V-14) by expanding our exact LGE to $2^{nd}$ order. But actually, these equations can already give $H_{c3}$ to $3^{rd}$ order (i.e. to $O[(1-t)^{3/2}]$). The reason is the following:

Eqs. (V-13) and (V-14) together are essentially equivalent to eq. (V-6), except that for the latter, we must restrict ourselves to "ESV" solutions. In eq. (V-6), the bulk terms are also accurate to 3rd order, since the lowest order term neglected there is already of 4th order. The surface layer terms are only accurate to 2nd order, but they are already sufficient to determine all global properties of $\Delta(\vec{r})$, one of which is $H_{c3}$, with a third order accuracy, because the surface layer terms are non-vanishing only in the region $Z \lesssim \xi_o$, and therefore become one order smaller after being averaged over the full range of $\Delta(\vec{r})$, which is $\sim\xi_H$.

This shows that Saint-James and de Gennes result for $H_{c3}$, which is proportional to (1-t), is already accurate to $O[(1-t)^{3/2}]$, indicating that the L-G region can be characterized by the criterion $(1-t) \ll 1$, so far as $H_{c3}$ is concerned.

Let us now be interested in $H_{c3}$ to 4th order. According to the analysis made above, we should now keep the bulk terms in the expansion of eq. (V-4) to 4th order, and the surface layer terms to 3rd order only. We therefore get:

$$\Delta(\vec{r}) = a_o\Delta(\vec{r}) + \frac{1}{6} a_2 |\vec{\tilde{\nabla}}_r|^2 \Delta(\vec{r}) + \frac{1}{5!} a_4 \, [|\vec{\tilde{\nabla}}_r|^4 + (2eH)^2] \, \Delta(\vec{r}) + \mathrm{SLT(III)}, \qquad (V\text{-}16)$$

where SLT(III) = SLT(II) + $\delta$[SLT(III)], and

$$\delta[\mathrm{SLT(III)}] = -\chi_{2,1}(z) |\vec{\tilde{\nabla}}_\perp|^2 \tilde{\nabla}_z \Delta(\vec{r}) - [Z^2 \chi_1(z) + \frac{1}{3} \chi_3(z)] \, \tilde{\nabla}_z^{\,3} \, \Delta(\vec{r}) + \chi_{2,2}^{(1)} (2ieH)\tilde{\nabla}_x \, \Delta(\vec{r}), \qquad (V\text{-}17)$$

with $\chi_{m,n}^{(\ell)}(z) \equiv \int_{z'<o} d\vec{r}\, \frac{(x-x')^m z'^n}{(z-z')^\ell}\, k^{(o)}\,(|\vec{r}-\vec{r}\,'|)$,

$$\chi_{m,n}(Z) \equiv \chi_{m,n}^{(o)}(Z) \text{ and } \chi_n(Z) \equiv \chi_{o,n}(Z), \tag{V-18}$$

as can all be found in Appendix F.

Just as we derived eq. (V-12) from eq. (V-6) (except that it becomes more tedious this time), we can again prove that eq. (V-16) together with (V-17), (V-18) implies the automatic satisfaction of the exact B.C. (V-5), to 3rd order in $(\xi_o/\xi_H)$.

Again we have to prove that SLT(III) $\equiv 0$ to the order of interest, in order to establish the self-consistency of our "ESV" assumption about $\Delta(\vec{r})$. (Notice that we should not prove $\delta$[SLT(III) $\equiv 0$, since SLT(II), with a third order accuracy, is no longer given by eq. (V-11) which is only correct to 2nd order.) What we are allowed to use in this proof are the "ESV" assumption, the exact B.C., and one more relation:

$$-|\vec{\tilde{\nabla}}_r|^2\, \Delta(\vec{r}) = \varepsilon(2eH)\Delta(\vec{r}), \tag{V-19}$$

with $\varepsilon$ being yet an unknown eigenvalue. This equation comes from the fact that should we be able to prove SLT(III) $\equiv 0$, then eq. (V-14) reduces to eq. (II-35) (truncated to 4th order), and can therefore be solved by the simultaneous eigenfunction of eqs. (II-37) and (II-38), together with the B.C. (V-5). Eq. (II-37) is just eq. (V-19), and eq. (II-38) is ignored since we shall only be interested in those solutions which are independent of y. As a self-consistency check, we are therefore allowed to use eq. (V-19) in advance.

We again go to the special gauges in which $A_z \equiv 0$, $\tilde{\nabla}_z\Delta(\vec{r}) = \nabla_z\Delta(\vec{r}) \sim \xi_H^{-1}\,\Delta(\vec{r})$, so that

$$\begin{aligned}
\mathrm{SLT(III)} &= -2\chi_1(z)\{[\nabla_z\Delta]_{z=o} + Z[\nabla_z^2\Delta]_{z=o} + \frac{z^2}{2}[\nabla_z^3\Delta]_{z=o} + \ldots\} \\
&+ 2z\chi_1(z)\ \{[\nabla_z{}^2\Delta]_{z=o} + z[\nabla_z{}^3\Delta]_{z=o} + \ldots\} \\
&- \chi_{2,1}(z)|\vec{\tilde{\nabla}}_\perp|^2\ \{[\nabla_z\Delta]_{z=o} + \ldots\} \\
&- [z^2\chi_1(z) + \frac{1}{3}\chi_3(z)]\ \{[\nabla_z{}^3\Delta]_{z=o} + \ldots\} \\
&+ \chi_{2,2}^{(1)}(z)\ (2ieH)\{\tilde{\nabla}_x[\Delta(\vec{r})]_{z=o} + \ldots\} \\
&\overset{\sim}{=} -2\chi_1(z)[\nabla_z\Delta]_{z=o} - \chi_{2,1}(z)|\vec{\tilde{\nabla}}_\perp|^2\ [\nabla_z\Delta]_{z=o} \\
&\quad - \frac{1}{3}\chi_3(z)[\nabla_z{}^3\Delta]_{z=o} + (2ieH)\chi_{2,2}^{(1)}(z)[\tilde{\nabla}_x\Delta]_{z=o}
\end{aligned} \tag{V-20}$$

to 3rd order in $(\xi_o/\xi_H)$.

The remaining steps are best done in the special gauge (called gauge B in Ch. II), in which $\vec{A}(\vec{r}) \equiv (H(z-z_o), 0, 0)$. In this gauge we can limit our interest to those pair wave functions which are functions of z only. Thus eq. (V-19) gives:

$$\nabla_z{}^2\Delta(z)\Big|_o = (2eH)[(2eH)z_o{}^2-\varepsilon]\Delta(o) \tag{V-21}$$

$$\begin{aligned}
\nabla_z{}^3\Delta(z)\Big|_o &= (2eH)](2eH)z_o{}^2-\varepsilon][\nabla_Z\Delta(2)]_o \\
&\quad - 2(2eH)^2\ Z_o\Delta(o).
\end{aligned} \tag{V-22}$$

We should also use the exact B.C. (V-5) which becomes $\nabla_z\Delta(z)\Big|_o = 0$ in gauge B. However, anticipating the later need, we shall first assume that $\Delta(z)$ satisfies (in gauge B) the following B.C.

$$\tilde{\nabla}_z\Delta(z)\Big|_o = \alpha\xi_H^{-1}\Delta(o), \tag{V-23}$$

with $\alpha$ assumed to be a second or smaller order quantity. By setting

$\alpha = 0$, we can certainly go back to the exact B.C. at any stage of our derivation.

Substituting (V-23) into (V-20), and remembering that $\alpha \sim O[(\xi_o/\xi_H)^2]$, we get:

$$\nabla_z{}^2\Delta(z)\Big|_o = \xi_H^{-2}\,[\zeta_o{}^2 - \varepsilon]\,\Delta(o), \tag{V-24}$$

and

$$\nabla_z{}^3\Delta(z)\Big|_o = -2\,\xi_H^{-3}\,\zeta_o\Delta(o). \tag{V-25}$$

where $\zeta_o = z_o/\xi_H$ as is used in earlier chapters.

We can now further simplify eq. (V-20) to give

$$\mathrm{SLT(III)} = \{-2\chi_1(z)\xi_H^{-1}\alpha + [\chi_{2,2}^{(1)}(z) + \frac{2}{3}\chi_3(z)]\,\xi_H^{-3}\,\zeta_o\}\Delta(o) \tag{V-26}$$

to third order in $(\xi_o/\xi_H)$.

Setting $\alpha = o$, we find that SLT(III) $\overset{\sim}{=} 0$ only if $\Delta(o) \sim O(\xi_o/\xi_H)$ or $\zeta_o \lesssim O(\xi_o/\xi_H)$, which correspond to the two limiting cases $\zeta_o \to \infty$ and $\zeta_o \to 0$, respectively. For the optimum mode, which is related to $H_{c3}$, we expect that $\zeta_o \sim \zeta_{oM} \overset{\sim}{=} 0.77$ (see Ch. II, section 1), so that SLT(III) does not vanish to third order in $(\xi_o/\xi_H)$. This shows that eq. (V-16), for $\zeta_o$ near the optimum value, does not admit "ESV" solutions, hence contradicting our original assumption.

Our first approach is therefore invalid if accuracy equal to or higher than $(\xi_o/\xi_H)^4$, or $(1-t)^2$, are required for $H_{c3}$.

## The Second Approach

In the 1st approach we have shown that the "ESV" assumption is invalid to 4th or higher order in $H_{c3}$. For this accuracy we therefore assume that

$$\Delta(\vec{r}) = \Delta^{B}(\vec{r}) + \Delta^{S.L.}(\vec{r}), \tag{V-27}$$

with $\Delta^B$ and $\Delta^{S.L.}$ being called the bulk component and the surface layer component of the pair wave function, respectively, so that $\Delta^B$ can be assumed as an "ESV" function, and $\Delta^{S.L.} \neq 0$ only for $Z \lesssim \xi_o$, which is therefore necessarily "RV" in this region.

This assumption comes from the fact that for $Z >> \xi_o$, our LGE becomes identical to that of the infinite sample case, whose solution has only the "ESV" component.

Using (V-27), we rewrite our LGE as:

$$\Delta^{B}(\vec{r}) + \Delta^{S.L.}(\vec{r})$$

$$= \int_{z'>o} K_H^{(o)}(\vec{r},\vec{r}\,')\Delta^{B}(\vec{r}\,')d\vec{r}\,' + \int_{Z'>0} K_H^{(o)}(\vec{r},\vec{r}\,')\Delta^{S.L.}(\vec{r}\,')d\vec{r}\,' \tag{V-28}$$

The 2nd term in the R.H.S. of (V-28) is easily seen to be "RV" and non-vanishing only for $Z \lesssim \xi_o$. For the first term, we can apply exactly the same expansion procedure as was elaborated before. This time, we shall be interested in $H_{c3}$ to order $(\xi_o/\xi_H)^5$, or $(1-t)^{5/2}$, as we shall soon see why. Thus, following the way eqs. (V-6) and (V-16) are obtained, we now have:

$$\int K_H^{(o)}(\vec{r},\vec{r}\,')\Delta^{B}(\vec{r}\,')d\vec{r}\,'$$

$$= a_o\Delta^{B}(\vec{r}) + \frac{1}{6}\,a_2|\tilde{\vec{\nabla}}_r|^2\,\Delta^{B}(\vec{r}) + \frac{1}{5!}\,a_4[|\tilde{\vec{\nabla}}_r|^4 + (2eH)^2]\Delta^{B}(\vec{r})$$

$$+ \mathrm{SLT(IV)}, \tag{V-29}$$

where SLT(IV) = SLT(III) + $\delta$[SLT(IV)], with SLT(III) given by eq. (V-17), except for the change $\Delta \rightarrow \Delta^B$, and

$$\begin{aligned}\delta[\mathrm{SLT(IV)}] = {} & Z\, \chi_{2,1}(z) \left|\vec{\tilde{\nabla}}_{\perp}\right|^{2} \tilde{\nabla}_{z}^{\,2}\, \Delta^{B}(\vec{r}) \\ & + \frac{1}{3}\left[z^{3}\, \chi_{1}(z) + z\, \chi_{3}(z)\right] \tilde{\nabla}_{z}^{\,4}\, \Delta^{B}(\vec{r}) \\ & + \left[z^{2}\, \chi_{2,1}^{(1)}(z) - 3z\, \chi_{2,2}^{(1)}(z)\right](2ieH)\, \tilde{\nabla}_{x}\, \tilde{\nabla}_{z}\, \Delta^{B}(\vec{r}) \\ & - \left[\frac{1}{2} z^{2}\, \chi_{2,2}^{(2)}(z) - z\, \chi_{2,3}^{(2)}(z)\right] (2ieH)^{2}\, \Delta^{B}(\vec{r}). \end{aligned} \tag{V-30}$$

We shall formally write eq. (V-29) as:

$$\int_{z'>0} K_{H}^{(o)}(\vec{r},\vec{r}\,')\, \Delta^{B}(\vec{r}\,')\, d\vec{r}\,' \equiv D^{B}\Delta^{B}(\vec{r}) + D^{S.L.}\, \Delta^{B}(\vec{r}), \tag{V-31}$$

where $D^{B}$ and $D^{S.L.}$ are differential operators which, when applied to $\Delta^{B}(\vec{r})$, give us the bulk terms and the surface layer terms in (V-29) respectively.

In view of our "ESV" requirement for $\Delta^{B}$, we now <u>define</u> it to satisfy the following differential equation:

$$\Delta^{B}(\vec{r}) = D^{B}\Delta^{B}(\vec{r}), \tag{V-32}$$

which is the same differential equation satisfied by the whole $\Delta(\vec{r})$ for an infinite sample case (see eq. (II-35)), when the same accuracy in $(1-t)^{1/2}$ is required.

Combining eqs. (V-28), (V-31) and (V-32), we find that $\Delta^{S.L.}$ must satisfy the following inhomogeneous integral equation:

$$\Delta^{S.L.}(\vec{r}) - \int_{z'>0} K_{H}^{(o)}(\vec{r},\vec{r}\,')\Delta^{S.L.}(\vec{r}\,')d\vec{r}\,' = D^{S.L.}\, \Delta^{B}(\vec{r}). \tag{V-33}$$

Eqs. (V-32) and (V-33) do not look like a genuine set of coupled equations as $\Delta^{S.L.}$ does not enter into eq. (V-32). However, we must remember that we want to define $\Delta^{B}$ through (V-32), which is not quite complete, since a finite order differential equation defined for $z \geq 0$

needs enough B.C.'s at $z = o$ in order to give a unique solution (assuming $\Delta(\vec{r}) \to 0$ as $z \to \infty$).

Since eq. (V-32) is nothing but eq. (II-35) (truncated to 4th order), we can follow the analysis there to solve it by the simultaneous eigenfunction of the following two eigenvalue equations:

$$-|\tilde{\vec{\nabla}}_r|^2 \; \Delta^B(\vec{r}) = \varepsilon(2eH)\Delta^B(\vec{r}), \tag{V-34}$$

$$\tilde{\nabla}_y \; \Delta^B(\vec{r}) = ik_y \; \Delta^B(\vec{r}). \tag{V-35}$$

Again we assume no y dependence in $\Delta^B$ so that (V-35) is trivially satisfied with $k_y = 0$. Eq. (V-34) is a 2nd order differential equation, it therefore needs only one B.C. relating $\nabla_z\Delta(\vec{r})$ and $\Delta(\vec{r})$ at $z = 0$.

Since $|\Delta|$ is infinitesimally small for a nucleation situation, the B.C. must be linear in both $\nabla_z\Delta(\vec{r})\big|_{z=o}$ and $\Delta(\vec{r})\big|_{z=o}$. Due to gauge invariance, we must require $\nabla_z\Delta(\vec{r})\big|_{z=o}$ to appear in the combination $\tilde{\nabla}_z\Delta(\vec{r})\big|_{z=o}$. Also, H can still enter into the B.C., but no longer $\vec{A}(\vec{r})$. If we further consider the translational invariance along directions perpendicular to the surface, we conclude that the following is the most general B.C. that eq. (V-34) should take:

$$\tilde{\nabla}_z\Delta^B(\vec{r})\Big|_{z=o} = \xi_H^{-1} \int \alpha(\vec{r}_\perp - \vec{r}_\perp{}')\Delta^B(\vec{r}\,')\Big|_{z'=o} \, d\vec{r}_\perp{}',$$

where

$$\vec{r}_\perp = \vec{r} - \hat{z}(\hat{z}\cdot\vec{r}) = (x,y,o). \tag{V-36}$$

In gauge B where $\vec{A}(\vec{r}) = (H(z-z_o),\ 0,\ 0)$ and $\Delta(\vec{r})$ can be limited to a function of Z alone without loss of generality, Eq. (V-36) becomes simply:

$$\nabla_z\Delta^B(z)\Big|_o = \alpha\xi_H^{-1} \; \Delta^B(o), \tag{V-37}$$

where $\alpha$ can in general be a function of H (which can be expressed through $\xi_H$), and $Z_o$ (which can be expressed through $\zeta_o = Z_o/\xi_H$). The $Z_o$-dependence of $\alpha$ in gauge B is equivalent to non-locality of eq. (V-36) in a general gauge, since, for example, in gauge A (see Ch. II, for definition) $Z_o$ plays the role of the x-directional wave number of $\Delta(\vec{r})$, $k_x$, except for a proportionality constant.

We must now find a self-consistent method to determine $\alpha$ - necessarily, through the 2nd equation, i.e. eq. (V-33). We first notice that eq. (V-33) is a Fredholm integral equation of the second kind (see for example ref.[23] for definition). It must therefore obey the following theorem (see Thm 3.7.2 of the reference cited above): "A Fredholm integral equation of the second kind can possess a finite solution only if its source term is orthogonal to all solutions of the corresponding homogeneous equation". Applying this theorem to eq. (V-33), and noticing that the corresponding homogeneous equation is nothing but our original LGE, whose solution is simply $\Delta(\vec{r})$ (not just $\Delta^B(\vec{r})$!), we thus get the following criterion for $\alpha$:

$$\int d\vec{r}\ \Delta^*(\vec{r})\ D^{S.L.}\ \Delta^B(\vec{r}) = 0. \qquad \text{(V-38)}$$

This looks like another self-consistency scheme, since $\Delta = \Delta^B + \Delta^{S.L.}$ can be determined only if $\alpha$ has been found through (V-38). However, the situation is not that bad if one makes an order analysis to eq. (V-38).

First we notice that $D^{S.L.}\ \Delta^B(\vec{r})$ is just the surface layer terms (SLT). To any order, we can simplify it in the way eq. (V-26) is obtained from eq. (V-17), since $\Delta^B$ in this approach behaves very much like the $\Delta$ in the first approach ($\Delta^B$ is ESV, eq. (V-34) corresponds to eq. (V-19), and eq. (V-37) corresponds to eq. (V-33), all of the three conditions used there to simplify eq. (V-17) are also available here). Thus to third order we get: (cf. eq. (V-26)

$$D^{S.L.}\Delta^B(\vec{r}) = \{-2\chi_1(z)\xi_H^{-1}\alpha + [\chi_{2,2}^{(1)}(z) + \frac{2}{3}\chi_3(z)]\xi_H^{-3}\Delta^B(o), \qquad \text{(V-39)}$$

(in gauge B)

and to lower than the third order, we have $D^{S.L.}\Delta^B(\vec{r}) \propto \alpha$. This means that to lower than the third order the L.H.S. of eq. (V-38) is $\propto \alpha$. Hence

$$\alpha^{(o)} = \alpha^{(1)} = 0 \qquad \text{(V-40)}$$

independent of what is $\Delta^*$ ($\alpha^{(n)}$ means $\alpha$ with $n^{th}$ order accuracy), and $\alpha^{(n)} \neq 0$ for $n \geq 2$, (V-41) since beginning with $\alpha^{(2)}$, an accuracy of $D^{S.L.}\ \Delta^B(\vec{r})$ with non-negligible $\alpha$-independent terms are required.

Thus in equation (V-38), the lowest order in

$$D^{S.L.}\ \Delta^B(\vec{r}) \equiv [f_1(z)\alpha + f_2(z)]\ \Delta^B(o) \text{ (in gauge B)}, \qquad \text{(V-42)}$$

is the 3rd order, while $f_1(z)$ is of 1st order and smaller. This indicates that if one is interested in $\alpha$ to $(2+n)^{th}$ order $(n \geq o)$, one needs $\Delta^*$ in eq. (V-38) only to $n^{th}$ order, and in fact:

$$\alpha^{(2+n)} = \frac{-\int dZ\ [\Delta^*_{(n)}(Z)\ f_2^{(3+n)}(z)]}{\int dZ\ [\Delta^*_{(n)}(z)\ f_1^{(1+n)}(z)]} \quad \text{(in gauge B)} \qquad \text{(V-43)}$$

where all parenthesized super- or subscripts denote the accuracy required.

Eq. (V-43) shows that for accuracy up to $\alpha^{(4)}$, one needs at most $\Delta^*_{(2)}$ which is still the result in the L-G region and has already been given in Ch. II, section 1. In fact, to this accuracy $\Delta = \Delta^B$ is "ESV", and since in (V-43) all integrals involve only the region $Z \lesssim \xi_o$, we can expand $\Delta_{(2)}(Z)$ to give:

$$\Delta_{(2)}(Z) \overset{\sim}{=} \Delta(o) + Z\,\Delta'(o) + \frac{Z^2}{2!}\,\Delta''(o)$$

$$= \Delta(o) \qquad \text{(in gauge B)}, \qquad \text{(V-44)}$$

where $\Delta'(o) = 0$ because of the exact B.C., and $\Delta''(o) = 0$ is valid only for the optimum mode (see Ch. VI for more detailed analysis on this point). Thus for $n \leq 2$,

$$\alpha^{(2+n)} = \frac{-\int dZ\; f_2^{(3+n)}(Z)}{\int dZ\; f_2^{(1+n)}(Z)} \qquad \text{(in gauge B)}, \qquad \text{(V-45)}$$

which requires no knowledge about $\Delta(\vec{r})$.

In practice, we shall only be interested in $\alpha^{(3)}$, with $n = 1$ in eq. (V-45), for reasons we shall soon explain. Eq. (V-45) then gives:

$$\alpha^{(3)} = \frac{-\int dZ\; f_2^{(4)}(Z)}{\int dZ\; f_1^{(2)}(Z)} \quad . \qquad \text{(V-46)}$$

To find $f_1^{(2)}$ and $f_2^{(4)}$, we have to extend eq. (V-39) to one order higher accuracy. This can be done by manipulating eq. (V-30) in the way we obtain eq. (V-26) from eq. (V-17) in gauge B, using eqs. (V-34), (V-37) and the "ESV" nature of $\Delta^B$. The result is

$$D^{S.L.}\Delta^B(\vec{r}) = \{-2\chi_1(Z)\,\xi_H^{-1}\,\alpha + [\chi_{2,2}^{(1)}(Z) + \tfrac{2}{3}\,\chi_3(Z)]\,\xi_H^{-3}\,\zeta_o$$

$$+ [\tfrac{1}{2}\,Z^2\,\chi_{2,2}^{(2)}(Z) - Z\chi_{2,3}^{(2)}(Z) - Z\chi_{2,2}^{(1)}(Z)]\,\xi_H^{-4}\}\;\Delta^B(o)$$

to 4th order in $(\xi_o/\xi_H)$, (in gauge B). (V-47)

Comparing eq. (V-47) with (V-42) to get $f_1^{(2)}$ and $f_2^{(4)}$, we then evaluate $\alpha^{(3)}$ in Appendix G using eq. (V-46). The result is:

$$\alpha^{(3)} = \left[\frac{31}{70}\,\frac{\zeta(5)}{\zeta(3)}\left(\frac{\xi_o}{\xi_H}\right)^2 \zeta_o + \frac{9}{64}\,\frac{\zeta(6)}{\zeta(3)}\left(\frac{\xi_o}{\xi_H}\right)^3\right], \qquad \text{(V-48)}$$

and the B. C. (V-37) becomes:

$$\frac{d}{d\zeta}\,\Delta^B(\zeta)\Big|_o = \left[\frac{31}{70}\,\frac{\zeta(5)}{\zeta(3)}\left(\frac{\xi_o}{\xi_H}\right)^2 \zeta_o + \frac{9}{64}\,\frac{\zeta(6)}{\zeta(3)}\left(\frac{\xi_o}{\xi_H}\right)^3\right]\Delta^B(o), \qquad \text{(V-49)}$$

to 4th order in the LGE, where $\zeta = Z/\xi_H$ as is defined in Appendix C.

We can now solve eq. (V-32) with the B. C. (V-49) to find $H_{c3}$ to 5th order in $(\xi_o/\xi_H)$ or $(1-t)^{1/2}$. (That this will give $H_{c3}$ to 5th order instead of 4th will soon be exhibited.)

We first prove that only up to this order, we can ignore any change in $\zeta_o$ for the optimum mode from its corresponding value in the L-G region, i.e. $\zeta_{oM} \cong 0.77$ as is found in Ch. II, section 1:

For $\alpha$ and $\delta\zeta_o = \zeta_o - \zeta_{oM}$ small, we have

$$\begin{aligned}\delta\varepsilon(\zeta_o,\alpha) = {} & \delta\zeta_o \times \left(\frac{\partial\varepsilon}{\partial\zeta_o}\right)_{\zeta_{oM},0} + \alpha \times \left(\frac{\partial\varepsilon}{\partial\alpha}\right)_{\zeta_{oM},0} \\ & + \frac{(\delta\zeta_o)^2}{2}\left(\frac{\partial^2\varepsilon}{\partial\zeta_o^2}\right)_{\zeta_{oM},0} + \alpha \times (\delta\zeta_o) \times \left(\frac{\partial^2\varepsilon}{\partial\zeta_o\partial\alpha}\right)_{\zeta_{oM},0} + \frac{\alpha^2}{2}\left(\frac{\partial^2\varepsilon}{\partial\alpha^2}\right)_{\zeta_{oM},0} \\ & + \ldots, \end{aligned} \qquad \text{(V-50)}$$

where $\delta\varepsilon(\zeta_o,\alpha) = \varepsilon(\zeta_o,\alpha) - \varepsilon(\zeta_{oM},0)$ is the change of the eigenvalue of eq. (V-34), which can in turn cause a change in $H_{c3}$ from its L-G value. First we notice that $\left(\frac{\partial\varepsilon}{\partial\zeta_o}\right)_{\zeta_{oM},0} = 0$ since $\varepsilon$ for the exact B.C. ($\alpha$=o) is minimized at $\zeta_{oM}$ (see Ch. II, section 1). Thus if we let $\alpha$ be given by eq. (V-48) which contains only 2nd and 3rd order terms, and if we are only looking for 2nd and 3rd order changes in $\delta\varepsilon$, we can then neglect the $\alpha^2$ term in (V-50). This allows us to reqrite (V-50) as:

$$\delta\varepsilon(\zeta_o,\alpha) = \alpha\left(\frac{\partial\varepsilon}{\partial\alpha}\right)_{\zeta_{oM},0} + \frac{(\delta\zeta_o)^2}{2} \text{ x } \left(\frac{\partial^2\varepsilon}{\partial\zeta_o^2}\right)_{\zeta_{oM},0} + \alpha\text{x } (\delta\zeta_o)\text{x}\left(\frac{\partial^2\varepsilon}{\partial\zeta_o\partial\alpha}\right)_{\zeta_{oM},0} \tag{V-51}$$

Minimize $\delta\varepsilon$ w.r.t. $\delta\zeta_o$ to find the optimum mode, we get:

$$(\delta\zeta_o)\text{x}\left(\frac{\partial^2\varepsilon}{\partial\zeta_o^2}\right)_{\zeta_{oM},0} + \alpha \text{ x } \left(\frac{\partial^2\varepsilon}{\partial\zeta_o\partial\alpha}\right)_{\zeta_{oM},0} = 0 \tag{V-52}$$

indicating that $\delta\zeta_o \propto \alpha$ is also of 2nd and 3rd order, which means that both the $(\delta\zeta_o)^2$ term and the $\alpha(\delta\zeta_o)$ term are negligible in eq. (V-51) and we have simply

$$\delta\varepsilon(\zeta_o,\alpha) = \alpha\text{x } \left(\frac{\partial\varepsilon}{\partial\alpha}\right)_{\zeta_{oM},0} \tag{V-53}$$

to second and third order. Clearly this proof will fail if either $\alpha$ contains 0th or 1st order term, or one more order in $\alpha$ and $\delta\varepsilon$ are considered.

Thus to our present order, one can use eq. (V-53) to compute $\delta\varepsilon$. To find $\left(\frac{\partial\varepsilon}{\partial\alpha}\right)_{\zeta_{oM},0}$, we trace back to the definition of $\alpha$, i.e. eq. (V-37), or

$$\left.\frac{d\Delta^B(\zeta)}{d\zeta}\right|_o = \alpha\Delta^B(o). \tag{V-54}$$

We then notice that $\Delta^B(\zeta)$ is the solution of eq. (V-54) which becomes $\left[-\frac{d^2}{d\bar{\zeta}^2} + \bar{\zeta}^2\right]\Delta^B(\bar{\zeta}) = \varepsilon\Delta^B(\bar{\zeta})$ under the new variable $\bar{\zeta} = \zeta - \zeta_o$. This differential equation is no longer $\zeta_o$-dependent, its solution is therefore uniquely characterized by the eigenvalue $\varepsilon$. Explicitly, we can then write $\Delta^B(\zeta,\zeta_o,\alpha) \equiv \Delta^B(\bar{\zeta},\varepsilon)$, with $\varepsilon$ being still a function of

$\zeta_o$ and $\alpha$.

If we now fix $\zeta_o = \zeta_{oM}$, we then have

$$\left.\frac{d\Delta^B}{d\zeta}\right|_{\substack{\zeta=0\\ \alpha<<1 \text{ fixed}}} = \left.\frac{d\Delta^B}{d\zeta}\right|_{\substack{\zeta=0\\ \alpha=0}} + \left.\frac{\partial^2\Delta^B}{\partial\zeta\partial\varepsilon}\right|_{\bar{\zeta}=-\zeta_o} \times \delta\varepsilon. \qquad \text{(V-55)}$$

Compare eqs. (V-54) and (V-55), and follow Lüders[22] to write:

$$C \equiv \left.\Delta^B\right|_{\substack{\bar{\zeta}=-\zeta_o\\ \alpha=0}} \Big/ \left.\frac{\partial^2\Delta^B}{\partial\bar{\zeta}\partial\varepsilon}\right|_{\substack{\bar{\zeta}=-\zeta_o\\ \alpha=0}}, \qquad \text{(V-56)}$$

we then get:

$$\delta\varepsilon = C\alpha , \qquad \text{(V-57)}$$

where use has been made of the fact that $\left.\frac{d\Delta^B}{d\zeta}\right|_{\substack{\zeta=0\\ \alpha=0}} = 0$ which follows trivially from the definition of $\alpha$.

We also notice that $\left.\Delta^B\right|_{\substack{\alpha=0\\ \zeta_o=\zeta_{oM}}}$ is exactly the appropriate solution for the optimum mode in the L-G region (in gauge B), it is therefore exactly the expression given in eq. (II-8), or

$$\left.\Delta^B(\bar{\zeta})\right|_{\substack{\alpha=0\\ \zeta_o=\zeta_{oM}}} = D_{\frac{1}{2}[\varepsilon_o-1]}(\sqrt{2}\,\bar{\zeta}). \qquad \text{(V-58)}$$

Thus

$$C = -D_{\frac{1}{2}(\varepsilon_o-1)}(-\sqrt{2}\,\zeta_{oM}) \Big/ \frac{\partial^2 D_{\frac{1}{2}(\varepsilon_o-1)}(-\sqrt{2}\,\zeta_{oM})}{\partial\varepsilon_o\partial\zeta_{oM}} \qquad \text{(V-59)}$$

with $\zeta_{oM}^2 = \varepsilon_o = 0.59010$, is an intrinsic property of the parabolic cylinder function. To find the numerical value of C is far from trivial, but fortunately, according to Lüders[22] it has been extimated by H. Schultens to be:

$$C = 1.36. \tag{V-60}$$

We shall assume this value to be correct.

From (V-57) and (V-48), we have:

$$\delta\varepsilon = C\left[\frac{31}{70}\,\frac{\zeta(5)}{\zeta(3)}\left(\frac{\xi_o}{\xi_H}\right)^2 \zeta_o + \frac{9}{64}\,\frac{\zeta(6)}{\zeta(3)}\left(\frac{\xi_o}{\xi_H}\right)^3\right]. \tag{V-61}$$

We can now evaluate $H_{c3}$ to 5th order in $(\xi_o/\xi_H)$:

First we substitute eq. (V-34) into eq. (V-32) to get:

$$(a_o - 1) \cong \frac{\varepsilon}{6}\, a_2\, \xi_H^{-2} - \frac{1}{5!}(\varepsilon^2 + 1)\, a_4\, \xi_M^{-4}\ , \tag{V-62}$$

which can be inverted to give:

$$2eH_{c3} = \xi_H^{-2} \cong (a_o - 1)\left[\frac{\varepsilon}{6}\, a_2\right]^{-1}\left[1 + \frac{(3!)^2}{5!}\,\frac{\varepsilon^2+1}{\varepsilon^2}\,\frac{a_4}{a_2^2}\,(a_o - 1)\right] \tag{V-63}$$

We then compare eq. (V-63) with the corresponding equation for $H_{c2}$:

$$2eH_{c2} \cong (a_o - 1)\left[\frac{1}{6}\, a_2\right]^{-1}\left[1 + \frac{2x(3!)^2}{5!}\,\frac{a_4}{a_2^2}\,(a_o - 1)\right]$$

(see eq. (II-43), (V-64)

to find:

$$H_{c3}/H_{c2} \cong \frac{1}{\varepsilon}\left[1 + \frac{(3!)^2}{5!}(\varepsilon^{-2} - 1)\,\frac{a_4}{a_2^2}\,(a_o - 1)\right]$$

$$\cong \frac{1}{\varepsilon_o}\left[1 - \frac{\delta\varepsilon}{\varepsilon_o} + \frac{(3!)^2}{5!}(\varepsilon_o^{-2} - 1\ \frac{a_4}{a_2^2}\,(a_o - 1)\right] \tag{V-65}$$

We can now use the Saint-James and de Gennes well-known result that $\varepsilon_o = 0.5901$, $\zeta_o = \varepsilon_o^{1/2}$, and the values for $a_o$, $a_2$, $a_4$ given in eqs. (II-40) through (II-42) to get:

$$\frac{H_{c3}}{1.695\ H_{c2}} \cong 1 + \frac{279}{245}\ \frac{\zeta(5)}{[\zeta(3)]^2}\ \left(\frac{1-\varepsilon_o^2}{\varepsilon_o^2} - \frac{2C}{3}\ \varepsilon_o^{-3/2}\right)(1-t)$$

$$- \frac{27}{56}\ \left(\frac{3}{7}\right)^{1/2} C\ \frac{\zeta(6)}{[\zeta(3)]^2}\ \varepsilon_o^{-5/2}\ (1-t)^{3/2}$$

$$\cong 1 - 0.105\ (1-t) - 1.031\ (1-t)^{3/2}. \qquad \text{(V-66)}$$

To find the temperature dependence of $H_{c3}$ itself, we use eq. (II-44) or

$$\frac{H_{c2}}{(1-t)} = - \left.\frac{dH_{c2}}{dt}\right|_{t=1} \times\ [1 + 0.135\ (1-t) + 0[(1-t)^2]]$$

where

$$- \left.\frac{dH_{c2}}{dt}\right|_{t=1} = \frac{12}{7\zeta(3)}\ \left(\frac{1}{2e\xi_o^2}\right), \qquad \text{(V-67)}$$

to get:

$$\frac{H_{c3}}{(1-t)} \cong - \left.\frac{dH_{c3}}{dt}\right|_{t=1} \times\ [1 + 0.030\ (1-t) - 1.031\ (1-t)^{3/2}]$$

with

$$- \left.\frac{dH_{c3}}{dt}\right|_{t=1} = 1.695\ \left[- \left.\frac{dH_{c2}}{dt}\right|_{t=1}\right]. \qquad \text{(V-68)}$$

The following are the conclusions of our present approach:

## Conclusion I

From eq. (V-40) we see that in the L-G region (i.e. when $(1-t \ll 1)$) $\Delta^{S.L.} \equiv 0$ and $\Delta \equiv \Delta^{B}$ is "ESV" so that to this order of accuracy all solutions of our exact LGE are also solutions of the linearized L-G equation plus the standard B.C..

## Conclusion II

From eq. (V-41) we find that below the L-G region (i.e. when (1-t) is no longer negligible compared with 1), none of the solutions of our LGE are "ESV", and a finite order differential equation plus an effective B. C. can at most describe the surface nucleation critical field $H_{c3}$, and the pair wave function in the region $Z>>\xi_o$. For the region $Z\lesssim\xi_o$ , $\Delta(\vec{r})$ is necessarily described by an non-local integral equation.

## Conclusion III

Using our 2nd approach, we have been able to calculate $H_{c3}$ to two orders in $(1-t)^{1/2}$ beyond the accuracy of Saint-James and deGennes' result for the L-G region. Besides, we could in principle have also obtained the exact behavior of $\Delta(\vec{r})$ in the surface region $Z\lesssim\xi_o$ to two non-trivial orders since to this accuracy eq. (V-33) can easily be solved by using Fourier cosine transforms. (To this accuracy $K_H^{(o)}$ in (V-33) can simply be replaced by $K^{(o)}$.) We did not carry out this calculation only because it requires tedious numerical integrations which seems to be not worthwhile judged from the present experimental need.

## Conclusion IV

Conclusion II should be subject to the following remark: From eq. (V-38) we find that to accuracy higher than 4th order in $\alpha$, or 6th order in $H_{c3}$, the effective B. C. can no longer be obtained without really solving a genuine integral equation.

## Conclusion V

Even though we have obtained two orders of correction terms for $H_{c3}/H_{c2}$ and for $H_{c3}$ alone, we believe that the region of validity of these results can not be significantly better than $(1-t)\lesssim 0.02$. as, for example, in eq. (V-66) the last term begins to dominate the second term at $(1-t)\sim 10^{-2}$, so that the neglected order is expected to become important after t is reduced by another $\Delta t\sim 10^{-2}$.

## Conclusion VI

In Ch. IV we have found that for $T\sim 0°K$, the ratio $H_{c3}/H_{c2}$ is roughly equal to (or may be slightly higher than) 1.93 with a vanishing initial slope. In the present chapter, however, we also found that as T is decreased slightly below the L-G region, the initial tendency of $H_{c3}/H_{c2}$ is to drop below 1.7 - the value in the L-G region. Combining the two predictions we therefore see that in the whole temperature region, $H_{c3}/H_{c2}$ can not be described by a monotonic function. We shall not, therefore, attempt to find any quantitative interpolation formula in the whole temperature range but will only try to guess its qualitative behavior in the intermediate temperatures, through a graphic method. (See fig. where we have also shown our high- and low temperature results as well as a comparison with Lüders' predictions.)

We now compare our results of this chapter with some presently existing theories:

On the microscopic derivation of the linearized L-G equation and its supplementary B. C. for a sample with a boundary: The original microscopic derivation of the L-G equation due to Gorkov[15] is only valid for an infinite sample. The "standard B. C." was obtained and justified by Ginzburg and Landau[14] and by deGennes[2,24] only through heuristic arguments.(v) Abrikosov[3], using his somewhat incorrect kernel for the LGE, had also arrived at our eq. (V-10), from which he proposed a different procedure from ours in obtaining the linearized L-G equation and the standard B.C., which, however, is rather misleading at lower temperatures since his procedure did not point out the necessity of a self-consistency check on the "ESV" assumption made at a very early stage of his derivation. Schöler and Lüders'[25,26] analysis is perhaps the first rigorous, microscopic treatment of this problem appropriate for a sample with a boundary, which is self-consistent. Since his method can also be generalized to lower temperatures we shall discuss it in the next paragraph.

On the generalization of the linearized L-G equation and obtaining an effective B. C. for temperatures slightly below the L-G region: A differential equation generalizing the L-G equation beyond the L-G region to describe the spatial dependence of the pair wave function is possible only if the exact behavior of the pair wave function within a distance $\sim \xi_o$ from the boundary is ignored. The B. C. for such a differential equation can therefore be at most effective. This picture has been un-ambiguously found in both Schöler and Lüders' (as cited above) and our theories, but not in Tewordt's[27] theory. The reason is that Tewordt's theory is not appropriate for a sample with a boundary, and he has ignored the possibility of a surface contribution to the total free energy of the sample. Obtained from applying variational principle to his free energy form, his generalization to the L-G equation can be considered as correct (except for the remark made in the beginning of this paragraph), but his B. C. is necessarily wrong. Schöler and Lüders' theory agrees with ours in many respects: (1) the pictures about the pair wave function conveyed through our conclusions I and II and partially stated in the beginning of this paragraph (except that Schöler and Lüders simply used $\Delta(\vec{r})$ to denote what we called $\Delta^B(\vec{r})$, and their variational approach did not make it clear when the exact pair wave function $\Delta(\vec{r})$ has been replaced by its major component $\Delta^B(\vec{r})$), (2) the generalized L-G equation for $\Delta^B$, and (3) its effective B. C. to the lowest non-trivial order, and perhaps also to the next two higher orders, but most probably not further, for reasons we shall soon explain. The major differences between the two theories are: (1) Their theory is not completely microscopic. Especially, they treated the boundary surface classically, instead of quantum mechanically as we did in our theory. (2) Their theory can not lead to our conclusion IV, and the second half of our conclusion III concerning the "RV" component of the pair wave function. Expecially, their theory seems to have contained a misleading concept that to any finite order in $(1-t)^{1/2}$, an effective B. C. can always be obtained without solving a genuine integral equation (one which does not contain a small expansion parameter such as $\xi_o/\xi_H$, and therefore can not be replaced by an finite order differential equation). What they will obtain for the effective B.C., we believe, is most probably nothing but our eq. (V-38) with $\Delta^*$ replaced by $\Delta^{B*}$, which is correct only if they limit their interest to the lowest three non-trivial orders, beyond the results for the L-G region. The reason is that their approach involved an expansion w.r.t. the operator $\frac{\vec{V}}{2|\omega|} \cdot \vec{\underset{\sim}{\nabla}}_r$ (where $|\vec{V}| = V_F$, $\omega = (2n+1)\pi T$, so that $\frac{\vec{V}}{2|\omega|} \lesssim \xi_o$), when it is yet acted on the complete pair wave function $\Delta \equiv \Delta^B + \Delta^{S.L.}$, instead of being merely on the "ESV" component $\Delta^B$. Their approach, with truncation of the expansion as a necessary step, can not treat the $\Delta^{S.L.}$ component properly, and therefore cannot give the correct effective B.C., whenever the exact behavior of the $\Delta^{S.L.}$ component becomes important in obtaining such a B. C., which occurs at n = 3 in eq. (V-43). This indicates why their approach cannot give correct results beyond the lowest three non-trivial orders in the correction terms to $H_{c3}$ and $H_{c3}/H_{c2}$ below the L-G temperature region.

*On the results of $H_{c3}$ calculation in the L-G region.* Both Schöler and Lüders'[25, 26] and our theory on $H_{c3}$ in the L-G region reduces to Saint-James and deGennes' prediction. Both theories have been able to make it clear that for pure samples with specularly reflective boundary surface, the L-G region for surface nucleation should be defined through the condition $(1-t) \ll 1$ so far as $H_{c3}$ is concerned. But one point not clear in Schöler and Lüders' theory is that the linearized L-G equation really cannot describe the correct behavior of the pair wave function within a distance of the order of Fermi wave length from the boundary surface, and the "standard B.C." describes actually the extrapolated behavior of the pair wave function from the region $P_F^{-1} \lesssim Z \lesssim \xi_o$. The L-G equation, however, will give correct description of the pair wave function in the region $Z \gtrsim P_F^{-1}$, contrary to the non-L-G region and non-linear L-G equation cases, for which the limitation must be $Z \gtrsim \xi_o$.

On the results of $H_{c3}$ calculation in the near L-G region: The first such attempt was made by Tewordt, but as mentioned before, his results must be abandoned. Lüders[22] then, using the theory by Schöler and Lüders (as cited before) on the generalization of the L-G equation and the B.C. to lower temperatures, has recalculated the ratio $H_{c3}/H_{c2}$ in the near L-G region. For specularly reflective boundary case, his result to lowest non-trivial order in $(1-t)^{1/2}$, agrees with ours. We, however, have computed $H_{c3}/H_{c2}$ and $H_{c3}$ alone to one more order accuracy (we believe that most probably Lüders can also obtain this result by extending his calculation to the next order, and will agree with us), which is found to dominate the Lüders' correction term for $T_c - T \lesssim 10^{-2}\ T_c$, indicating that both Lüders' result, and our extension to it, do not have a very good region of validity (perhaps good only for $1-t \lesssim 2 \times 10^{-2}$). But we also found that Lüders' 4th order correction term to $H_{c3}/H_{c2}$ has such a small coefficient mainly because it involves an almost cancellation of three contributions - two from the effects on $H_{c3}$ and $H_{c2}$ respectively, due to the 4th order correction term to the linearized L-G equation, and one from the correction to the standard B.C. which changes $H_{c3}$ alone, not $H_{c2}$. All of these three terms are proportional to (1-t), with coefficients roughly equal to 3.1, -1.6, -1.6, whose net result is roughly -0.1 as is shown in eq. (V-66). This indicates that perhaps the smallness of the Lüder term is in a sense accidental, and our extension to it might have a better range of validity than his result. (To say, $(1-t) \sim 0.05$; but not significantly better, we beleive, in view of our conclusion VI.)

# CHAPTER VI

# GENERAL CRITERIA FOR THE PHYSICALLY MOST FAVORABLE MODES OF NUCLEATION

In this chapter, we discuss two general criteria that characterize the physically most favored modes of surface nucleation. In principle, therefore, they can be used to reduce the number of variational parameters in a variational calculation. In practice, however, it turns out not to be quite the case as is discussed at the end of this chapter.

We shall call the two criteria "The vanishing overall surface current criterion" or simply "criterion A", and "The pair density peak position criterion" or simply "criterion B".(vii)

We first state the two criteria:

Criterion A: The optimum or physically most favorable state of surface nucleation is always such that the over-all surface supercurrent vanishes.

Criterion B: The optimum or physically most favorable mode of surface nucleation can be found by requiring that the peak position of the pair density is just about to depart from the boundary surface.

We first prove these two criteria in the L-G region from first principles. It also serves as an illustration of the meaning of these two criteria.

Proof of Criterion A in the L-G Region: The sample geometry, field arrangement, and coordinate system are all assumed to be the same as before. Since we are in the L-G region, the super-current density is described by the second phenomenological L-G equation:

$$\vec{j} = -\frac{2ie}{4m}\left(\psi^{*}\tilde{\nabla}_{r}\psi - \psi\,\tilde{\nabla}^{*}_{r}\psi^{*}\right), \qquad \text{(VI-1)}$$

where $\psi(\vec{r})$ differs from the pair wave function order parameter $\Delta(\vec{r})$ only by a multiplicative constant.[13]

The criterion A in our present case requires

$$\int_{S} d\vec{\sigma}\cdot\vec{j}(z) = 0, \qquad \text{(VI-2)}$$

where S is any cross section of the sample perpendicular to the surface. This is equivalent to the following statement:

$$\int_{S} d\vec{\sigma}\cdot[\psi^{*}\,\vec{\nabla}_{r}\psi - \psi\vec{\nabla}_{r}\psi^{*} - 4ie\vec{A}(\vec{r})|\psi|^{2}] = 0 \qquad \text{(VI-3)}$$

We clearly can not have a net current flowing perpendicular to the boundary surface. For studying physically most favored mode of nucleation, we can also require $\Delta(\vec{r})$ or $\psi(\vec{r})$ to have no y-dependence ($\hat{y}$ is the direction of the magnetic field!) so that $j_y \equiv 0$. Thus all we have to prove is:

$$\int_{z>o} dydz\; x\; \vec{j}_{x}(z) = 0, \qquad \text{(VI-4)}$$

for the optimum state of nucleation.

If we choose again to work in gauge B, eqs. (VI-4) simply becomes:

$$\int_{o}^{\infty} dz\; x\; (z-z_{o})\;\psi^{2}(z) = 0, \qquad \text{(VI-5)}$$

remembering that in this gauge $\psi$ is real, and can be considered as a function of z only.

It is in this form (i.e. eq. VI-5) that criterion A was first pointed out by Saint-James and de Gennes[1] to be valid in the L-G region.

The proof of (VI-5) from first principles is simple: first we write the first L-G equation (linearized) in the following shorthand form (see eq. II-3):

$$H\psi \equiv \psi''(z) + c(z-z_o)^2\,\psi(z) = \varepsilon\psi(z). \qquad \text{(VI-6)}$$

Differentiate both sides w.r.t. $z_o$ to get:

$$[H-\varepsilon]\,\frac{d\psi}{dz_o} = 2c\,(z-z_o)\psi, \qquad \text{(VI-7)}$$

where use has been made of $\frac{d}{dz_o}\varepsilon = 0$, for the optimum mode. Multiply both sides by $\psi$, and then integrate over z, we get:

$$\int (z-z_o)\,\psi^2\,dz \propto \int \psi[H-\varepsilon]\frac{d\psi}{dz_o}\,dz = \int \frac{d}{dz_o}\,[H-\varepsilon]\,\psi dz = 0$$

where Hermiticity of the operator H has been used, which can be easily proved using the standard B.C., $\left.\frac{d\psi}{dz}\right|_o = 0$ in our present gauge.

Criterion A is therefore established in the L-G region.

We now shift our attention to criterion B:

<u>Proof of Criterion B in the L-G region</u>: We first rephrase the criterion into the following mathematical statement:

$$\frac{d^2}{dz^2}\,|\psi(\vec{r})|^2\Big|_{z=o} = 0, \qquad \text{(VI-8)}$$

where $\psi$ corresponds to the optimum nucleation mode. In gauge B, $\psi$ is real, thus eq. (VI-8) becomes simply

$$\left.\frac{d^2\psi}{dz^2}\right|_{z=0} = 0. \qquad \text{(VI-9)}$$

To understand why eq. (VI-9) is equivalent to the original statement once we are in gauge B, let us consider the family of solutions characterized by the continuous parameter $z_o$. All solutions must satisfy the standard B.C. $\left.\frac{d\psi}{dz}\right|_o = 0$. If some mode has $\frac{d^2\psi}{dz^2} < 0$ at $z = o$, this mode has a local maximum, or peak, at $z = 0$. If another mode has $\frac{d^2\psi}{dz^2} > 0$, the point $z = o$ becomes a local minimum. Clearly the particular value $z_{oM}$ of $z_o$, which is determined by eq. (VI-9), separates these two classes of nucleation states. So if $z_o$ is continuously increased across $z_{oM}$ (the direction of change is hinted by the fact that $z_o = \infty$ corresponds to the bulk nucleation mode, which necessarily peaks deep inside the sample), the local peak begins to depart from the surface when $z_o$ is exactly equal to $z_{oM}$. Since the optimum nucleation mode corresponds to the ground state solution of eq. (VI-6), this local peak is also the only peak of the whole pair wave function.

The proof of eq. (VI-9) from first principles is also very simple in the L-G region:

We first point out the following simple identity:

$$\int_o^\infty \psi'\psi''\,dz = -\frac{1}{2}[\psi'(o)]^2 = 0. \qquad \text{(VI-10)}$$

Using eq. (VI-6), we convert this identity to:

$$\int_o^\infty \psi'[\varepsilon - c(z-z_o)^2]\psi\,dz = 0. \qquad \text{(VI-11)}$$

We now differentiate (VI-6) w.r.t. z:

$$\psi''' + 2c(z-z_o)\,\psi = [\varepsilon - c(z-z_o)^2]\,\psi'. \qquad \text{(VI-12)}$$

Multiply both sides of (VI-12) by $\psi$, integrate over z from 0 to $\infty$, and apply equation (VI-11) and the criterion A in the form of eq. (VI-5) to get:

$$\int_{0}^{\infty} \psi\psi''' \, dz = 0. \qquad \text{(VI-13)}$$

Partial integrate once and use eq. (VI-10) to get $\psi\psi''\big|_{o} = 0$, or simply eq. (VI-9), since we must assume $\psi(o) \neq 0$. ($\psi(o) = 0$ plus the B.C. $\psi'(o) = 0$ lead us to the trivial solution $\psi \equiv 0$, which we are not interested in.) We thus have justified criterion B in the L-G region. We notice that the proof above has used criterion A, so it is valid only for the optimum state. We also notice that this proof has used the standard B. C. ($\frac{d\psi}{dz}\big|_{o} = 0$ in gauge B), while in the proof for criterion A, a more general type of B.C., $\frac{d\psi}{dz}\big|_{o} = \alpha\psi(o)$, will be sufficient to serve the purpose (to justify the hermiticity of H), so long as $\alpha$ (real) does not depend on $z_o$. In fact, the criterion B simply no longer makes any sense if $\psi$ does not satisfy the standard B.C..

We now examine whether these criteria can be extended to lower temperatures. First we shall show that criterion A is in fact true for all temperatures below $T_c$ and also for all impurity concentrations, if the magnetic field is equal to the surface nucleation critical field. Abrikosov[3] has suggested that criterion A is actually true even at lower fields satisfying $H_{c2} \leq H \leq H_{c3}$. His line of reasoning goes as follows: The condensation energy for surface superconductivity is only a surface term (i.e. proportional to the surface area, but independent of the total volume). If a surface nucleation mode does not have a vanishing overall surface supercurrent the field strength inside the sample is necessarily different from the external field strength. The total free energy of the system is therefore raised by a magnetic term which is proportional to the total volume. For a bulk sample, no compensation of these two free energy terms could happen, as they belong to different orders. Such a surface state must therefore have a total free energy higher than the normal state, and can not exist physically.

This argument can be considered as rigorous. However, finding a microscopic proof to support it is always better than not. (For example, it can serve as a check of Gor'kov's microscopic theory of superconductivity.)

Unfortunately, our proof is only limited to the case when $H = H_{c3}$. All attempts to extend this proof to lower fields have failed. We now present our microscopic proof of criterion A as follows:

Proof of criterion A for all $T - T_c$, and for all impurity concentrations, at $H = H_{c3}$:$^{(viii)}$ Without averaging over impurity configuration, the linearized gap equation is as follows (Notations as in Ch. II):

$$\Delta(\vec{r}) = |\lambda| T \sum_{\omega} \int G_{\omega}^{(o)}(\vec{r},\vec{r}\,')\, G_{-\omega}^{(o)}(\vec{r},\vec{r}\,')\Delta(\vec{r}\,')d\vec{r}\,' \qquad \text{(VI-14)}$$

where the normal electron thermal Green's function $G_{\omega}^{(o)}$ satisfies:

$$\{i\omega + \frac{1}{2m}|\vec{\tilde{\nabla}}_r|^2 - v(\vec{r}) + \mu\}\, G_{\omega}^{(o)}(\vec{r},\vec{r}\,') = \delta(\vec{r}-\vec{r}\,'), \qquad \text{(VI-15)}$$

with $v(\vec{r}) = \sum_{\vec{r}_a} u\,(\vec{r}-\vec{r}_a)$ being the total interaction potential between an electron at $\vec{r}$ and all impurity atoms at $\{\vec{r}_a\}$.

With sample geometry, field direction, and coordinate system as before, we again employ gauge B where $\vec{A}(\vec{r}) = (H(z-z_o), 0, 0)$. The pair wave function $\Delta(\vec{r})$ is again limited to be a function of z only.

In equation (VI-14), we can either fix T, and consider H as the eigenvalue; or fix H, and let T be the eigenvalue. In any case, the optimum state is characterized by a stationary eigenvalue, when $z_o$ is varied. Thus when we vary $z_o$, both T and H can be considered as constants. Write eq. (VI-14) in the form:

$$\int |\Delta|^2 d\vec{r} \;=\; |\lambda| T \sum_{\omega} \iint \Delta^*(\vec{r}) G_{\omega}(\vec{r},\vec{r}\,') \; G_{-\omega}(\vec{r},\vec{r}\,') \Delta(\vec{r}\,') \; d\vec{r} \; d\vec{r}\,', \qquad \text{(VI-16)}$$

and vary $z_o$, to obtain, symbolically:

$$\int (\delta\Delta^*)\Delta + \int \Delta^*(\delta\Delta) = |\lambda| T \sum_{\omega} [\iint (\delta\Delta^*) G_{\omega}^{(o)} G_{-\omega}^{(o)} \Delta + \iint \Delta^* G_{\omega}^{(o)} G_{-\omega}^{(o)} (\delta\Delta)$$

$$+ \iint \Delta^* \; [\delta(G_{\omega} G_{-\omega})]\Delta]. \qquad \text{(VI-17)}$$

Varying (VI-14) and then taking scalar product with $\Delta$, we get:

$$\int \Delta^*(\delta\Delta) \;=\; |\lambda| T \sum_{\omega} [\iint \Delta^* [\delta(G_{\omega}^{(o)} G_{-\omega}^{(o)})]\Delta + \iint \Delta^* \; G_{\omega}^{(o)} G_{-\omega}^{(o)} (\delta\Delta)]. \qquad \text{(VI-18)}$$

Taking complex conjugate of it, we also get:

$$\int (\delta\Delta^*)\Delta = |\lambda| T \sum_{\omega} [\iint \Delta^* [\delta(G_{\omega}^{(o)} G_{-\omega}^{(o)})]\Delta + \iint (\delta\Delta^*) \; G_{\omega}^{(o)} G_{-\omega}^{(o)} \Delta]. \qquad \text{(VI-19)}$$

Combining (VI-17), (VI-18), and (VI-19), we then get:

$$|\lambda| T \sum_{\omega} \iint \Delta^*(\vec{r}) \delta[G_{\omega}^{(o)}(\vec{r},\vec{r}\,') G_{-\omega}^{(o)}(\vec{r},\vec{r}\,')]\Delta(\vec{r}\,') d\vec{r} \; d\vec{r}\,' \;=\; 0. \qquad \text{(VI-20)}$$

Now varying (VI-15), and using the fact that in gauge B, $\delta\vec{A} = - H\hat{x}$, we obtain:

$$\{i\omega + \frac{1}{2m} |\vec{\tilde{\nabla}}_r|^2 - V(\vec{r}) + \mu\}\delta G_{\omega}(\vec{r},\vec{r}\,') - \frac{ieH}{m} \tilde{\nabla}_x G_{\omega}(\vec{r},\vec{r}\,') \;=\; 0, \qquad \text{(VI-21)}$$

or equivalently:

$$\delta G_{\omega}(\vec{r},\vec{r}\,') \;=\; \frac{ieH}{m} \int G_{\omega}(\vec{r},\vec{s}) \tilde{\nabla}_{s_x} G_{\omega}(\vec{s},\vec{r}\,') \; d\vec{s} \; . \qquad \text{(VI-22)}$$

Taking complex conjugate of this equation, and interchange $\vec{r}$ and $\vec{r}\,'$, we get:

$$\delta G_{-\omega}(\vec{r},\vec{r}\,') = \frac{-ieH}{m} \int G_{-\omega}(\vec{s},\vec{r}\,')\, \tilde{\nabla}_{s_x}\, G_{-\omega}(\vec{r},\vec{s})\, d\vec{s} \qquad \text{(VI-23)}$$

where the symmetry property (II-17) has been used.

Substituting (VI-22), (VI-23) into eq. (VI-20), and changing $\omega$ to $(-\omega)$ in part of the expression, we obtain the following final expression:

$$\int d\vec{r}\, \{\frac{ieT}{m} (\tilde{\nabla}_{x'} - \tilde{\nabla}_{x}) x \sum_{\omega} \delta G_{\omega}^{(o)}(\vec{r},\vec{r}\,')\}\Big|_{\vec{r}\,'=\vec{r}} = 0, \qquad \text{(VI-24)}$$

where

$$\delta G_{\omega} = - \int G_{\omega}^{(o)}(\vec{r},\vec{1})\Delta(\vec{1}) G_{\omega}^{(o)}(\vec{m},\vec{r}\,')\Delta^{*}(m) G_{-\omega}^{(o)}(\vec{m},\vec{1})\, d\vec{1}\, d\vec{m}. \qquad \text{(VI-25)}$$

Now the current density is given by:

$$\vec{j}(\vec{r}) = \frac{ie}{m} (\vec{\tilde{\nabla}}_{r'} - \vec{\tilde{\nabla}}_{r}) G(x,x')\Big|_{\substack{\vec{r}\,' = \vec{r} \\ \tau' - \tau \to 0_{+}}}, \qquad \text{(VI-26)}$$

where $G(x,x')$ satisfies eq. (II-18).

Applying standard expansion technique to eq. (II-18), with the use of the normal state Green's function $G^{(o)}$, it can be shown that to lowest order in superconducting pair strength, $G_{\omega}(\vec{r},\vec{r}\,') = G_{\omega}^{(o)}(\vec{r},\vec{r}\,') + \delta G_{\omega}(\vec{r},\vec{r}\,')$, where $\delta G_{\omega}$ is exactly what is given in eq. (VI-25) (for detailed proof, see for example ref. 13 Ch. 7).

Since the current in a normal metal is always zero in a constant magnetic field, eq. (VI-26) is simply:

$$\vec{j}(\vec{r}) = \frac{ie}{m} (\vec{\nabla}_{r'} - \vec{\nabla}_{r}) \sum_{\omega} \delta G_{\omega}(\vec{r},\vec{r}\,')\Big|_{\vec{r}\,'=\vec{r}}, \qquad \text{(VI-27)}$$

to our orders of interest. Comparing (VI-27) with (VI-27), we therefore get: $\int d\vec{r}\, j_x(\vec{r}) = 0$. As for our sample geometry the current is necessarily independent of x, it becomes

$$\int dy\, dz\, j_x(\vec{r}) = 0, \qquad \text{(VI-28)}$$

or, the overall x-directional surface current vanishes.

As is in the L-G region, we again need not worry about y,z-directional currents. We thus have proved criterion A for lower temperatures, for all impurity concentrations, and at $H = H_{c3}$. However, the criterion is now described by eq. (VI-28), with $\vec{j}(\vec{r})$ given by eqs. (VI-27) and (VI-25), it is therefore much more complicated than the corresponding equation (VI-3) or (VI-5) for the L-G region.

We now turn our attention to criterion B. Should it also be possible to extend criterion B into lower temperatures, its mathematical form must still be given by equation (VI-8), indicating that this criterion is probably more useful than criterion A, if established. Since we have shown that <u>the pair wave function order parameter $\Delta(\vec{r})$ satisfies the exact B.C. at all temperatures</u>, the possibility of such an extention is therefore not zero. Unfortunately, all of our attempts in achieving such a proof have failed. Nor have we succeeded in disproving it. We are forced, therefore, to leave this equation open.

We now turn to discuss the significance of these two criteria. There is no doubt that these criteria help us to get a better understanding of the optimum nucleation modes. But we are more interested in their practical use, for example, as we have pointed out in the beginning of this chapter, they could help us to reduce the number of variational parameters in a variational calculation, in principle at least. We shall not be interested in the L-G region where exact solutions are possible. At lower temperatures, unfortunately, criterion A becomes too complicated to make its use advantageous. How good is then to approximate the exact criterion by the local expression (VI-5) (in gauge B), when the temperature is not in the L-G region? Examining our variational solution at T = 0, we find such an approximation is very bad indeed, as eq. (VI-5) requires, for the trial wave function $\exp[-\frac{1}{2}\alpha\zeta^2]$, that $\alpha\zeta_o^2 = \pi^{-1} \simeq 0.32$, while our variational result gives $\alpha\zeta_o^2 \simeq 0.24$, a roughly 25% deviation! As for criterion B, since it is not yet justified at low temperatures, there seems to be no grounds for using it. Besides, we have another doubt in using these criteria. As even though they have been proved to be satisfied by the exact solution, there is still no reason to believe that a trial wave function, which satisfies them, could give better estimate of the eigenvalues, especially if the criterion itself is a local property of the pair wave function - such as our criterion B, since it is more or less the global behavior of the pair wave function that determines the eigenvalues. Our conclusion is, therefore, that the two criteria will not lead us to a royal road in a variational calculation.

# CHAPTER VII

## CONCLUSION AND DISCUSSION

The surface nucleation critical field, $H_{c3}$, for a pure semi-infinite superconductor with a specularly reflective plane boundary, has been studied in two limiting temperature regions, namely, when the temperature is very close to absolute zero, and when it is only slightly below the Landau-Ginzburg region.

The basis of this calculation was Gor'kov's microscopic theory of superconductivity. However, first we had to develop a generalized image method to find the normal electron temperature Green's function in a sample described above, in order to obtain the appropriate linearized gap equation for studying such a nucleation problem. The resulting equation was a linear homogeneous integral equation whose lowest eigenvalue was related to $H_{c3}$. At absolute zero temperature, this equation was solved by a variational method using a simple Gaussian function centered at the surface as our trial wave function. It was found that in this case the ratio of $H_{c3}/H_{c2}$ should be roughly 14% (or slightly more) higher than the corresponding well-known result, namely 1.695 or roughly 1.7, in the Landau-Ginzburg region, as was predicted by Saint-James and de Gennes.[1] The result was then extended to slightly above absolute zero temperature by a perturbation method, which gave a vanishing initial slope to the ratio. It was therefore speculated that this ratio would stay significantly above 1.7 for quite a fraction of the temperature range between 0 and $T_c$.

In the high temperature limit (i.e. when $T \rightarrow T_c$), we have tried two approaches to attack the problem. The first approach was conventional, involving an assumption that the pair wave function was slowly varying in the whole sample, so that some expansion procedure could be applied to the equation. The approach, however, was shown to be valid only in the Landau-Ginzburg region which lead to a gauge invariant, completely microscopic, simultaneous derivation of the linearized Landau-Ginzburg equation and its supplementary B.C. for a sample with a specularly reflective boundary. For temperatures slightly below the Landau-Ginzburg region, we modified our first approach into our second approach so as to allow the pair wave function to vary rapidly at distances of the order of a BCS coherence length or less from the surface. The result contained two orders (the 2nd and the 3rd) in $(1 - T/T_c)^{1/2}$, correcting the value 1.7 for the ratio $H_{c3}/H_{c2}$ when the temperature is not in the Landau-Ginzburg region. The first correction term agreed with Lüders'[22] prediction which is obtained from a quite different approach. The second correction term was found to dominate the first for temperatures only 1% below $T_c$. We therefore speculated that our high temperature results, as well as Lüders' (in the specularly reflective surface case only), can not have a very wide range of validity. Both of our results are still interesting though, since they predicted that for samples with specularly reflective surface, the initial tendency of the ratio $H_{c3}/H_{c2}$ is to drop below 1.7 at a non-negligible rate. Combining our high and low temperature predictions, we find that this ratio does not behave monotonically in the whole temperature range below $T_c$, instead, it will possess a minimum at some temperature, say $T_m < T_c$, and then it will rise up to pass the value 1.7 again at some still lower temperature, say $T_x < T_m$, so that as $T \to 0°K$, the ratio can approach a value roughly equal to or slightly larger than 1.93 horizontally. Unfortunately, due to mathematical difficulties, our results can not be extended to the intermediate temperature range to give us a quantitative estimation of these two characteristic temperatures, namely $T_m$ and $T_x$. We can only speculate that probably these two temperatures will not lie very far below $T_c$.

On the other hand, we expect that it should also be rather difficult for our predictions to be checked experimentally, since to achieve this, simultaneous measurements of both $H_{c3}$ and $H_{c2}$ must be done in a relatively pure sample with negligible amounts of impurities and defects (a technical difficulty), whose surface must yet be specularly reflective in nature (another technical challenge). Besides, there is also the unavoidable fact that almost all pure superconductors are type I in nature (except for Vanadium, V[28], and Niobium, Nb,[29] whose pure samples are type II) which implies that the determination of $H_{c2}$ will in most cases involve supercooling situations, thereby making the distinction between 1.7 and 1.9 for the ratio $H_{c3}/H_{c2}$ an even harder task, let alone the detection of the mild temperature dependence of this ratio predicted in our present calculation. One way to get around this difficulty is to measure $H_c$ and then to use the theoretically predicted relations between $H_{c2}$ and $H_c$ to estimate the values of $H_{c2}$.[30] But then there is the question of how good are these relations themselves in describing the facts and how wide are their ranges of validity. Besides, these relations themselves will involve other characteristic parameters of the sample studied, which will also have to be determined experimentally, thus introduces more uncertainty into the final conclusions. In cases when strong coupling superconductors (such as pure lead) are used for such an experiment, the above mentioned method will be even less favorable because the predicted relations between $H_c$ and $H_{c2}$ could be totally inadequate for such a case, while our predictions about the ratio $H_{c3}/H_{c2}$ might still give a good qualitative or even semi-quantitative description of such a system. This point of view is reasonable in view of the fact that in the Landau-Ginzburg region, the ratio $H_{c3}/H_{c2}$ does not depend on the characteristic parameters of the system[1,5] and whether the system is weak- or strong coupling in nature,[6,7] while the ratio $H_{c2}/H_c$ clearly does.[19, 12, 31] From the above considerations, we expect that the best choice of a superconductor for performing such an experiment in order to check our predictions is vanadium, with niobium being the second. (Vanadium is a weak coupling superconductor,[28] while niobium is half way between weak- and strong coupling.[29]) The remaining difficulties for these metals are then only on how to make them into highly pure and defectless samples as is characterized by a large low-to-high-temperature resistivity ratio, and on how to make their surfaces to be specularly reflective in nature. But these are not completely impossible to overcome, we therefore still see some chance for our predictions to be seen experimentally.

In the introduction we have pointed out that both the works of Rosenblem and Cardona,[9] and of Tomasch[9] indicated that for relatively pure Pb, the ratio $H_{c3}/H_{c2} = 1.9$ fitted better to their experimental data than 1.7. But their data are too crude to be considered as a positive evidence of our prediction. De Sorbo[32] first reported that he had observed a consistent increase in the ratio $H_{c3}/H_{c2}$ from the value 1.7 for annealed pure-niobium samples (at $T = 4.2°K$, while $T_c \simeq 9.25°K$). In a subsequent paper[33], however, he reported that $H_{c3}/H_{c2} = 1.7_0$ was observed for pure Nb and for Nb containing oxygen in a concentration below the solubility limit (also measured at $T = 4.2°K$). We now want to point out the following two points concerning his work: (1) In his first paper,[32] $H_{c3}$ was identified as the smallest field at which the resistance of the sample attained the normal-state value. While in his second paper, he turned to use critical current measurement to obtain $H_{c3}$. As is pointed out by him, the former method can not give a good accuracy because the sample resistance restores to normal asymptotically. But we want to point out that his latter method will systematically give smaller values for $H_{c3}$. The reason is that theoretically the critical current is the largest current the system can carry without showing any resistance, and $H_{c3}$ is the field at which the critical current vanishes. But for practical reasons, he had to identify the critical current as the current which gives minimum detectable voltage. Besides, he also identified $H_{c3}$ as the field at which the critical current $I_c$ becomes equal to the normal current $I_n$ as the minimum detectable voltage is applied to the sample. It is easy to see that $H_{c3}$ measured in this way should always be smaller than the exact value. In fact, for H less than the "apparent $H_{c3}$", his measured values for $I_c$ (named by him as $J_c$ when divided by the cross sectional area of the sample, and $J_s$ when divided by the width of the current carrying superconducting surface sheath) should be quite accurate regardless of his "bad" definition for $I_c$. We can therefore extrapolate his data, at least crudely, down to $I_c = 0$, to find the "correct" value for $H_{c3}$. From the only plot of $J_c$ vs. H curve for an outgassed and annealed pure niobium sample published in his second paper, we found that while the "apparent $H_{c3}$" is $(1.7_1 \pm 0.03)\ H_{c2}$, the "correct $H_{c3}$" could very probably be some value within the range $(2.0 \pm 0.1)\ H_{c2}$. (2) While he did not describe the nature of surfaces of their samples, it is strongly doubtable that their sample could have almost specularly reflective surfaces, which can only be obtained, we believe, by careful polishing processes. His measurements are therefore most probably beyond the region of applicability of our theory. These two points indicate that his results do not consistute a disproof of our predictions.

Fischer[34,(ix)] recently published some accurate measurements of $H_{c3}$ (but not $H_{c2}$) for two pure Pb samples. He found that the curves of $H_{c3}$ vs. T are concave upward near $T_c$. However, he interpreted these data as to correspond to samples with surface roughness characterized by P = 0.48 and 1 respectively, so as to fit nicely for $T \gtrsim 1.5°K$ with Lüders' formula

$$\frac{H_{c3}(t)}{1.695\ H_{c2}(t)} = 1 + 0.382\ P\ (1-t)^{1/2} \quad (P>0)$$

for samples with rough surfaces, where the parameter P is so defined that P = 0 corresponds to a specularly reflective surface, and P = 1 indicates a completely diffuse scattering surface. We now want to point out that the set of Fischer's data corresponding to the sample assigned to P = 0.48 actually fits slightly better to our theory (which corresponds to P = 0!) than to Lüders', even though ours is only semi-quantitative. We first notice that Lüders' formula with P = 0.48 actually lies everywhere very close to our interpolated curve (see fig. 5 ). The deviation at low temperatures could be less if one remembers that our low temperature results are only lower bound estimations. The high temperature deviation of the two curves from each other is the major difference of the two theories. We then point out that Fischer also published in the same article a plot of $H_{c3}/(T_c-T)$ vs. T for the two samples of pure Pb mentioned before. Data are measured within the temperature range between ∿1.5°K and ∿5.9°K, but an interpolated point at $T_c \overset{\sim}{=} 7.2°K$ is also shown in the plot. For $T \gtrsim 5°K$ $H_{c2}$ is expected to be roughly proportional to $T_c-T$ (as is explained in the article). Thus for $T \gtrsim 5°K$, the plotted curves should reflect the behavior of $H_{c3}/H_{c2}$, which, according to Lüders' formula, should be proportional to $[1 + 0.382\ P\ (1-t)^{1/2}]$. But this is apparently not the case since the formula predicts an infinite slope at $T_c$, while the curves apparently do not show such a behavior. The curves are seen to be compatible with our predictions but no definite conclusions can be made on this point, especially since P is not measured independently.

Our conclusion is therefore that even Fischer's precision measurement of $H_{c3}$ can not be considered as a positive evidence for our theory, nor is it a disproof. It is therefore very desirable to see more precision measurements of $H_{c3}$ as well as $H_{c2}$ on high purity superconductors with extremely smooth surfaces, preferably on vanadium or niobium, in order to check our predictions.

We now turn to discuss some of the theoretical difficulties encountered in the present calculation, so that the readers may understand why we did not perform our calculation for a wider class of cases. In the meantime, we shall also point out some of the possible extensions of our present calculation.

We have mentioned before that it is only due to mathematical difficulties that we did not solve the problem at the intermediate temperature range. Our formulation of the problem is valid for all temperatures below $T_c$. In fact, a lower bound estimation of $H_{c3}$ is possible at all temperatures below $T_c$, except that too much computer time will be needed for it to be worth carrying out. The formalism for including the effect of non-magnetic impurities has been well established. Thus our formulation can certainly be generalized to include the effect of non-magnetic impurities. However, the solution of the resultant equations requires the finding of a new basis in which the kernel of the linearized gap equation for the pure limit case is diagonalized. This is equivalent to finding the exact solutions of all possible nucleation modes for the pure limit case - a situation which is possible for the infinite sample case, but not for the semi-infinite sample case as we have studied here. We therefore have given up the attempts to calculate $H_{c3}$ for all impurity concentrations. At low impurity concentrations, it is not hard to see from the general formalism that the lowest order correction to $H_{c3}/H_{c2}$ is a linear term in $\lambda \equiv \xi_0/l$ where $l$ is the electron mean free path due to impurities. It is not very easy to compute the coefficient of this correction term, but we can still speculate that the qualitative effect of impurities is to gradually reduce the mild temperature dependence of the ratio $H_{c3}/H_{c2}$ to a flat 1.7 as $\ell \to 0$. We also expect that this smoothing effect should be roughly half-done at $\ell \sim \xi_o$.

In our calculation we have also limited ourselves to specularly reflective surface. To generalize our microscopic calculation to samples with rough surfaces, a reasonable starting point will be to assume a roughly plane surface with small randomly-distributed bumps and kinks. We must require our normal electron Green's function to vanish on such a surface. Using this Greens function to construct our kernel for the linearized gap equation, we can then average the kernel over the statistical behavior of the surface roughness to reestablish translation invariance of the kernel along the surface. (This procedure is closely analogous to the treatment of randomly distributed impurities, see references cited in the last paragraph.) Using this procedure, it is clearly seen that a similar calculation of $H_{c3}/H_{c2}$ for the diffuse scattering surface case is much harder than for the specularly reflective surface case. However, we still think that such a fundamental study on the effect of surface roughness to $H_{c3}$ is possible, and we shall attempt to solve this problem in the future.

Another possible extension of our present calculation includes the calculation of $H_{c3}/H_{c2}$ for various types of sample geometries, such as infinite slabs of finite thickness,[1] cylinders of radius $\gg \xi_o$,[35] or even samples that occupy one or three quadrants of the space, - a study of the last case can probably cast light on the effect of large-scale surface roughness, or even periodic surface gratings. As is remarked at the end of our chapter IV, we expect that our generalized method of images can be successfully applied to these simple geometries to obtain the appropriate normal electron Green's function, and hence the linearized gap equation for such cases.

Our final generalization involves the study of the effects of dielectric or metallic coatings to the surface, and we expect that our generalized image method will also work for such cases, if properly simplified models are proposed for such systems. Experimentally, these surface effects have been studied by various groups.[36] Theoretically, calculations have been made only in the L-G region.[37] A microscopic study of such a problem is therefore quite desirable.

# APPENDIX A

## BOUNDARY CONDITION FOR A SPECULARLY REFLECTIVE SURFACE

In this Appendix, we analyze what is the exact effect of a "specularly reflective boundary surface" on the electron wave functions in a piece of metal, and therefore answer the question of what is the microscopic B.C. or B.C.'s that could be assigned to such a surface, so far as electron wave functions are concerned.

Consider a semi-infinite sample occupying the half-space $z \geq 0$. An electron of momentum $\vec{k}$, if not scattered by the boundary surface, is described by the plane wave $e^{i\vec{k}\cdot\vec{r}} \equiv e^{i\vec{k}_\perp\cdot\vec{r}} e^{ik_z r_z}$. Let $k_z < 0$ so that the electron is moving to the left. What is the scattered wave function if the boundary surface is present? The classical definition of "specular reflection" is that an electron coming toward the surface with momentum $(k_x, k_y, k_z)$ will leave the surface after scattering with momentum $(k_x, k_y, -k_z)$. Quantum mechanically the electron wave function can also gain a phase shift $e^{2i\phi}$ during the scattering process, where $\phi$ in general can still be an arbitrary real function of $\vec{k}$. An electron of momentum $\vec{k}$ (with $k_z < 0$) before scattering, should therefore be described by the following complete wave function:

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}_\perp\cdot\vec{r}} [e^{ik_z z} - e^{2i\phi(\vec{k})} e^{-ik_z z}], \quad (k_z \leq 0), \tag{A-1}$$

if it is in a sample with such a boundary. Let us now use the momentum after the scattering to characterize the wave function.

Since an overall phase factor is irrelevant to the wave function, expression (A-1) can also be written as:

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \sin[k_z z + \phi(\vec{k})], \quad (k_z \geq 0). \tag{A-2}$$

Collecting all $\psi_{\vec{k}}(\vec{r})$, of the form given in (A-2), for all $\vec{k}$ with $k_z \geq 0$, we get a complete orthogonal basis for the Hilbert space that contains all the states we are interested in. Let $\psi(\vec{r})$ be the wave function of an electron in the sample studied. Then, regardless of what state the electron is in, we must have:

$$\psi(\vec{r}) = \Sigma' A_{\vec{k}}\, e^{i\vec{k}_\perp\cdot\vec{r}} \sin[k_z z + \phi(\vec{k})], \tag{A-3}$$

where $\Sigma'$ means summing over all $\vec{k}$ with $k_z \geq 0$.

What B.C. does this $\psi(\vec{r})$ have to satisfy? To attempt to answer this question, we first notice that:

$$\psi(\vec{r})\Big|_{z=o} = \Sigma' A_{\vec{k}} \operatorname{Sin}[\phi(\vec{k})]\, e^{i\vec{k}_\perp\cdot\vec{r}}, \tag{A-4}$$

and

$$\frac{d}{dz}\psi(\vec{r})\Big|_{z=o} = \Sigma' A_{\vec{k}}\, k_z \cos[\phi(\vec{k})]\, e^{i\vec{k}_\perp\cdot\vec{r}}. \tag{A-5}$$

In general, no simple B. C. can be obtained from these two expressions by eliminating all $A_{\vec{k}}$'s. But if

$$k_z \cot\phi(\vec{k}) = f(\vec{k}_\perp) \tag{A-6}$$

is independent of $k_z$, we can eliminate $A_{\vec{k}}$'s by first applying an inverse Fourier transform to eq. (A-4) to get:

$$\Sigma'_{k_z} A_{\vec{k}} \sin[\phi(\vec{k})] = \frac{1}{(2\pi)^2}\int dx'dy'\, \psi(\vec{r}\,')\Big|_{z=o} e^{-i\vec{k}_\perp\cdot\vec{r}\,'},$$

and then substituting this result into eq. (A-5). We then get:

$$\frac{d}{dz}\ \psi(\vec{r})\Big|_{z=o} = \int S(\vec{r}_\perp-\vec{r}_\perp{}')\ \psi(\vec{r}\,')\Big|_{z'=o}\ d\vec{r}_\perp{}', \tag{A-7}$$

where

$$S(\vec{r}_\perp-\vec{r}_\perp{}') \equiv \frac{1}{(2\pi)^2}\ \Sigma_{\vec{k}_\perp}\ f(\vec{k}_\perp)\ e^{i\vec{k}\cdot(r_\perp-r_\perp')} \tag{A-8}$$

Thus all B.C.'s described by the general form (A-7) can be assigned to a specularly reflective boundary, which are not yet all that can be so assigned as eq. (A-6) is not necessarily true.

We remark that all B.C.'s of the form (A-7) satisfy the condition that no net total current (but not current density at a local point) flow out of or into the boundary surface. To prove it we can use the simple fact from (A-8):

$$S^*(\vec{r}_\perp-\vec{r}_\perp{}') = S(\vec{r}_\perp{}'-\vec{r}_\perp).$$

If $f(\vec{k}_\perp) = a^{-1}$ is further independent of $\vec{k}_\perp$, $S(\vec{r}_\perp-\vec{r}_\perp{}')$ then reduces to the local kernel $a^{-1}\ \delta(\vec{r}_\perp-\vec{r}_\perp{}')$, and the B.C. eq. (A-7) becomes:

$$\frac{d}{dz}\ \psi(\vec{r})\Big|_{z=o} = a^{-1}\ \psi(\vec{r})\Big|_{z=o} \tag{A-9}$$

Eq. (A-9) then guarantees us that even the current density normal to the boundary surface vanish everywhere on this surface.

If a is further set equal to zero, we then get

$$\psi(\vec{r})\Big|_{z=o} = 0. \tag{A-10}$$

This case can be realized by setting all $\phi(\vec{k}) = 0$.

Another situation is when $\phi(\vec{k}) \doteq \pi/2$ for all $\vec{k}$, we then get $a = \infty$, and eq. (A-9) becomes:

$$\frac{d}{dz}\ \psi(\vec{r})\Big|_{z=o} = 0. \tag{A-11}$$

Physically, the B.C. (A-10) is for the case when the surface is characterized by an infinite potential wall at $z = o$.

If an infinite potential wall is at $z = -a$ with "a" very small (more rigorously, "a" must be so small that $k_z a \ll 1$ for all $k_z$ that correspond to a non-negligible $A_{\vec{k}}$), we then have $\phi(\vec{k}) = k_z a$, and the B.C. is simply that given by eq. (A-9).

Equation (A-9) with a reasonably small "a", can also be crudely identified as the B.C. for a metal-insulator-metal sandwich, if the potential barrier established by the insulating layer is not only high compared with the energies of all states that participate in the expansion of $\psi(\vec{r})$ with a non-negligible probability amplitude, but also wide compared with the mean decay width of the electron wave function inside the barrier. And even in this limit, the identification can only be considered as an approximation, as the exact situation clearly can not be represented by a single parameter.

The B.C. (A-11) is even less realistic in the physical world. However, in the main text of this thesis, we shall also use it as a chosen B.C. to work with, not because it has any physical importance, but because it can lead us to a bonus soluble case (see Ch. II, eq. (II-24) and Ch. III, eq. (III-14), where the B.C. has been slightly changed to incorporate gauge invariance into the expression).

Finally, and most importantly, we analyze a realistic situation where a semi-infinite metallic sample is separated from a vacuum or an insulator by a perfectly smooth plane boundary. Such a boundary can be represented by a step potential:

$$V(z) = \begin{cases} 0 & \text{for } z>0 \\ V_o>0 & \text{for } z<0 \, . \end{cases} \qquad \text{(A-12)}$$

We shall only consider electrons in states with mean energy roughly equal to the Fermi energy $E_F$. (This is sufficient for studying superconductivity phenomenon, as only states in the neighborhood of the Fermi level with $|E-E_F| \lesssim \omega_D$, the Debye frequency, are involved in superconducting condensation, and we have $\omega_D << E_F$.) The quantity $V_o-E_F$ is usually called work function, whose magnitude is usually equal to a small fraction of $E_F$.

The electron wave functions and hence the phase shifts for such a case can be solved exactly, and the result gives

$$\begin{aligned} k_z \cot \phi(\vec{k}) &= \frac{1}{\hbar} \sqrt{2m(V_o-E_{\vec{k}})} \\ &\cong \frac{1}{\hbar} \sqrt{2m(V_o-E_F)} = a^{-1} \, . \end{aligned} \qquad \text{(A-13)}$$

The approximation makes $k_z \cot \phi(\vec{k})$ a $\vec{k}$-independent quantity, so that we again obtain the B.C. (A-9). Since the work function is usually equal to a small fraction of $E_F$, we find that "a" is roughly equal to a few Fermi wave lengths. This means that the electron wave functions can have an exponentially decreasing tail extending outside of the boundary surface to a distance roughly also equal to a few Fermi wave lengths. Since the electron mean wave length in the z direction can be any value between 0 and $0(p_F^{-1})$, the corresponding phase shift can therefore be any value from 0 to somewhat larger than $\pi/4$. This indicates that "a" is not small so far as electron wave functions are concerned. However, we must remember that we want to apply all of this to study properties of superconductivity, where the important characteristic length is the BCS coherence length $\xi_o$. For pure samples, this length $\xi_o$ is on the order $10^3$ to $10^4$ times $p_F^{-1}$. This implies that the only effect of a non-vanishing "a" in the B.C. (A-9) is to appear through the combination $a/\xi_o$, which is negligibly small.

We are therefore justified to consider the $a \to 0$ limit in the B.C. (A-9), and to use eq. (A-10) as the proper B.C., so long as we are studying superconductivity phenomenon for pure samples. It is concluded that if the sample is dirty enough so that the coherence length becomes much reduced, then the presence of a non-vanishing "a" in the more exact B.C. (A-9), should at least be examined, or proven to be not important if it happens to be the case.

## APPENDIX B

## GENERALIZATION OF HELFAND AND WERTHAMER'S IDENTITY

The identity found by Helfand and Werthamer[12] reads

$$\exp[\mp 2ie \int_{\vec{r}\,'}^{\vec{r}} A(\vec{s})\cdot d\vec{s}]\ \exp[(\vec{r}\,'-\vec{r})\cdot\vec{\nabla}_\rho]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}}$$

$$= \exp[(\vec{r}\,'-\vec{r})\cdot(\vec{\nabla}_\rho \pm 2ie\,\vec{A}(\vec{\rho}))]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}} \tag{B-1}$$

where the path integral follows a straight line connecting the end points. This identity can be generalized so that the path integration, instead of following a straight line, will now follow an arbitrary given curve. If the curve is given by the parametric equation $\vec{s} = \vec{s}(t)$ where $0 \leq t \leq 1$, so that $\vec{s}(o) = \vec{r}\,'$, $\vec{s}(1) = \vec{r}$, then the generalized identity reads:

$$\exp[\mp 2ie \int_o^1 dt\, \frac{d\vec{s}}{dt}\cdot\vec{A}(\vec{s})]\ \exp[-\int_o^1 dt\, \frac{d\vec{s}}{dt}\cdot\vec{\nabla}_\rho]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}}$$

$$= T_t \exp[-\int_o^1 dt\, \frac{d\vec{s}}{dt}\cdot(\vec{\nabla}_\rho \pm 2ie\,\vec{A}(\vec{\rho}))]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}} \tag{B-2}$$

where the time ordering operator $T_t$ requires that when we expand the exponential operator $\exp[-\int_o^1 dt\, D_\rho(t)]$, where $D_\rho(t) \equiv \frac{d\vec{s}}{dt}\cdot(\vec{\nabla}_p \pm 2ie\,\vec{A}(\vec{\rho}))$, we should always rearrange the operators $\{D_\rho(t)\}$, in any term involving a product of the form $D_\rho(t_1)\, D_\rho(t_2)\ldots$ $\ldots D_\rho(t_n)$, in order of decreasing t (i.e. to make $t_1 \geq t_2 \geq \ldots \geq t_n$). This means that operators characterized by earlier times must always operate earlier.

In the main text, we shall write eq. (B-2) in the following form, (see Ch. IV, eq. (IV-5):

$$\exp[\mp 2ie \int\!\!\!\!\!\mathrm{P}_{\vec{r}\,'}^{\vec{r}} d\vec{s}\cdot A(\vec{s})]\ \exp[(\vec{r}\,'-\vec{r})\cdot\vec{\nabla}_{\rho}]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}}$$

$$= \ T\ \exp\ [- \int\!\!\!\!\!\mathrm{P}_{\vec{r}\,'}^{\vec{r}} d\vec{s}\cdot(\vec{\nabla}_{\rho} \pm 2ie\vec{A}(\vec{\rho}))]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}} \qquad \text{(B-3)}$$

where $\int\!\!\!\!\!\mathrm{P}$ denotes a path integral along the given curve, and the "time" parameter for the operator T is now implicit.

In the following, we give a proof of eq. (B-2) which is a straight generalization of Helfand and Werthamer's original proof for eq. (B-1), (it includes the original proof as a special case):

First we define:

$$P(\theta) \ \equiv\ -\int_{\theta}^{1} dt\ \frac{d\vec{s}}{dt}\cdot\vec{\nabla}_{\rho} \quad ,$$

$$Q_{\pm}(\theta) \ \equiv\ -\int_{\theta}^{1} dt\ \frac{d\vec{s}}{dt}\cdot[\pm\ 2ie\ \vec{A}(\vec{\rho})],$$

and $V(\theta) \ \equiv\ T_t\{\exp[P(\theta) + Q_{\pm}(\theta)]\}\exp[-P(\theta)]$,

so that

$$dV(\theta)/d\theta \ = \ T_t\{\exp[P(\theta) + Q_{\pm}(\theta)]\}\frac{dQ_{\pm}(\theta)}{d\theta}\ \exp[-P(\theta)]$$

$$= \ V(\theta)\ \exp[P(\theta)]\ \frac{dQ_{\pm}(\theta)}{d\theta}\ \exp[-P(\theta)]. \qquad \text{(B-4)}$$

We then notice that:

$$\exp[P(\theta)]\ \frac{dQ_{\pm}(\theta)}{d\theta}\ \exp[-P(\theta)]$$

$$= \ \exp[\{\vec{s}(\theta) - \vec{s}(1)\}\cdot\vec{\nabla}_{\rho}]\ \frac{d\vec{s}(\theta)}{d\theta}\cdot\ [\pm\ 2ie\vec{A}(\vec{\rho})]\exp[-\{\vec{s}(\theta)-\vec{s}(1)\}\cdot\vec{\nabla}_{\rho}]$$

$$= \ \frac{d\vec{s}(\theta)}{d\theta}\cdot[\pm\ 2ie\ \vec{A}\cdot(\vec{\rho} + \vec{s}(\theta) - \vec{r})], \qquad \text{(B-5)}$$

which implies:

$$[\exp[P(\theta)\ \frac{dQ_{\pm}(\theta)}{d\theta}\ \exp[-P(\theta)],\ \exp[P(\theta')]\ \frac{dQ_{\pm}(\theta')}{d\theta'}\ \exp[-P(\theta')]] = 0,$$

so that eq. (B-4) can be integrated without worrying about $\theta$-ordering. Noticing that $V(1) = 0$, we get:

$$V(0) = \exp\{-\int_{o}^{1} d\theta\ \exp[P(\theta)]\ \frac{dQ_{\pm}(\theta)}{d\theta}\ \exp[-P(\theta)]\}.$$

Converting this equation into the form:

$$T_t\{\exp[P(0) + Q_{\pm}(0)]\}\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}}$$

$$= \exp\{-\int_{o}^{1} d\theta\ \exp[P(\theta)]\ \frac{dQ_{\pm}(\theta)}{d\theta}\ \exp[-P(\theta)]\}\ \exp[P(0)]\Delta(\vec{\rho})\Big|_{\vec{\rho}=\vec{r}},$$

we realize that this equation is nothing but eq. (B-2).

We notice that this proof holds for arbitrary $A(\vec{r})$. The magnetic field, therefore, does not have to be a constant.

# APPENDIX C

## VARIATIONAL CALCULATION OF $H_{c\parallel}$ $(\xi_o = 0)$ AT $T = 0°K$

We start from eq. (IV-4). In gauge B where $\vec{A}(\vec{r}) \equiv (H(z-z_o), 0, 0)$, we find

$$\int_{\vec{r}'}^{\vec{r}} \vec{A}(\vec{s})\cdot d\vec{s} = H[\frac{z+z'}{2} - z_o]\cdot(x-x'), \qquad \text{(C-1)}$$

and

$$-\!\!\!\!\!\!\int_{\vec{r}'}^{\vec{r}} \vec{A}(\vec{s})\cdot d\vec{s} = \int_{\vec{r}'}^{\vec{r}} A(\vec{s})\cdot d\vec{s} + \int_{\vec{r}'}^{\vec{r}} A(\vec{s})\cdot d\vec{s}$$

$$= H[\frac{z^2+z'^2}{2(z+z')} - z_o]\cdot(x-x'), \qquad \text{(C-2)}$$

where $\vec{r}_1 \equiv (\frac{zx'+z'x}{z+z'}, \frac{zy'+z'y}{z+z'}, 0)$ has been used.

Using (II-30) for $k^{(o)}(|\vec{r}-\vec{r}'|)$, we get the following form for our LGE:

$$\Delta(z) = |\lambda| T(\frac{m}{2\pi})^2 \sum_n \int_{z'>o} \{|\vec{r}-\vec{r}'|^{-2} \exp[-2|\omega| v_F^{-1} |\vec{r}-\vec{r}'|]$$

$$\text{x} \exp[-2ieH(\frac{z+z'}{2} - z_o)(x-x')] + |\vec{r}-R_{z'}\vec{r}'|^{-2} \exp[-2|\omega| v_F^{-1} |\vec{r}-R_{z'}\vec{r}'|]$$

$$\text{x} \exp[-2ieH(\frac{z^2+z'^2}{2(z+z')} - z_o)(x-x')]\}\Delta(z')\, d\vec{r}', \qquad \text{(C-3)}$$

where $\Delta(\vec{r})$ has been limited to be a function of z only.

Introducing the notations $N(o) = mP_F/(2\pi^2)$, $\xi_o(T) = v_F/(2\pi T)$, so that $\xi_o \equiv \xi_o(T_c)$, $\xi_H = (2eH)^{-1/2}$, we can then define the following dimensionless quantities:

$$t = T/T_c, \; h = (2eH)(v_F/2\pi T_c)^2 = (\xi_o/\xi_H)^2,$$

$$\tilde{t} = t h^{-1/2}, \; \vec{\rho} = \xi_H^{-1}\vec{r} \equiv (\xi, \eta, \zeta), \; \zeta_o = \xi_H^{-1} z_o,$$

$$\vec{\sigma} = \xi_H^{-1}\vec{s}, \text{ and } \vec{a}(\vec{\rho}) = 2e\vec{A}(\vec{r})\xi_H, \qquad \text{(C-4)}$$

so that (C-3) can be cast into the following more convenient form:

$$\Delta(\zeta) = (4\pi)^{-1}|\lambda|N(o)\tilde{t} \sum_n \int_{\zeta'>o} \{|\vec{\rho}-\vec{\rho}'|^{-2}\exp[-(2n+1)\tilde{t}|\vec{\rho}-\vec{\rho}'|]$$

$$\times \exp[-i(\frac{\zeta+\zeta'}{2} - \zeta_o)(\xi-\xi')] + |\vec{\rho}-R_{\zeta'}\vec{\rho}|^{-2} \exp[-(2n+1)\tilde{t}|\vec{\rho}-R_{\zeta'}\vec{\rho}'|]$$

$$\times \exp[-i(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')} - \zeta_o)(\xi-\xi')]\}\Delta(\zeta')\, d\vec{\rho}'. \qquad \text{(C-5)}$$

If we ignore the Debye frequency cut-off, the summation over n can then be carried out to give:

$$\Delta(\zeta) = (4\pi)^{-1}|\lambda|N(o)\tilde{t} \int_{\zeta'>o} \{\frac{\exp[-i(\frac{\zeta+\zeta'}{2} - \zeta_o)(\xi-\xi')]}{|\vec{\rho}-\vec{\rho}'|^2 \operatorname{Sinh}(\tilde{t}|\vec{\rho}-\vec{\rho}'|)}$$

$$+ \frac{\exp[-i(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')} - \zeta_o)(\xi-\xi')]}{|\vec{\rho}-R_{\zeta'}\vec{\rho}'|^2 \operatorname{Sinh}(\tilde{t}|\vec{\rho}-R_{\zeta'}\vec{\rho}'|)}\}\Delta(\zeta')d\vec{\rho}'. \qquad \text{(C-6)}$$

At T = 0°K, this equation reduces to:

$$\Delta(\zeta) = (4\pi)^{-1}|\lambda|N(o) \int_{\zeta'>o} \{\frac{\exp[-i(\frac{\zeta+\zeta'}{2} - \zeta_o)(\xi-\xi')]}{|\vec{\rho}-\vec{\rho}'|^3}$$

$$+ \frac{\exp[-i(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')} - \zeta_o)(\xi-\xi')]}{|\vec{\rho}-R_{\zeta'}\vec{\rho}'|^3}\} \Delta(\zeta')\, d\vec{\rho}' \qquad \text{(C-7)}$$

We now want to reestablish the proper frequency cut-off by introducing an equivalent space cut-off, say, $|\zeta-\zeta'| > \varepsilon$. That this is possible has already been established by Gor'kov.[19] Instead of finding the functional dependence between $\varepsilon$ and the Debye frequency $\omega_D$, he pointed out that the unknown cut-off parameter $\varepsilon$ could be eliminated by using the following identity:

$$\frac{1}{|\lambda|} = \frac{m^2\Delta_o}{4\pi^4}\int_o^{\omega_D}\frac{du}{u}\int\frac{\mathrm{Sin}(uR/v_F)}{R^2}K_1(R\Delta_o/v_F)\,d^3R, \qquad \text{(C-8)}$$

that determines $\Delta_o$, the zero temperature energy gap of an infinite superconductor in zero magnetic field. Writing in terms of dimensionless variables $\bar{R} = \xi_H^{-1}R$, $\tilde{t}_c = h^{-1/2}$, $\bar{u} = u/(2\pi T_c)$, and $\bar{\omega}_D = \omega_D/(2\pi T_c)$, eq. (C-8) becomes

$$[|\lambda|N(o)]^{-1} = (4\pi^2\gamma)^{-1}\tilde{t}_c\int_o^{\bar{\omega}_D}\frac{d\bar{u}}{\bar{u}}\int\frac{\mathrm{Sin}(\tilde{t}_c\bar{u}\bar{R})}{\bar{R}^2}K_1\left(\frac{\tilde{t}_c}{2\gamma}\bar{R}\right)d^3\bar{R}, \qquad \text{(C-9)}$$

where $\ln\gamma = c \simeq 0.577$ is Euler's constant.

Gor'kov pointed out that if one set $\bar{\omega}_D = \infty$ in (C-9), one could get an expression which is also logarithmically divergent at $\vec{\rho}\,'=\vec{\rho}$, if one identified $\vec{\bar{R}}$ as $\vec{\rho}-\vec{\rho}\,'$. He therefore proposed that one should use this expression with $\bar{\omega}_D = \infty$ to eliminate $|\lambda|N(o)$ in (C-6) or (C-7). One could then introduce proper space-cut-off's on both sides of the equation to get cut-off-independent finite results.

So much is given by Gor'kov, and indeed he has been able to obtain correct results on the calculation of $H_{c2}$ for pure samples at $T \simeq 0°K$, using this equivalent space-cut-off procedure. However, the application of this procedure is not yet so straight forward. Careful examination of Gor'kov's later expressions, after he has used this procedure, indicates that while he used the cut-off $|\zeta-\zeta'| > \varepsilon$ for eq. (C-7), he seems to have used the cut-off $\bar{R}_z > 2\varepsilon$ for eq. (C-9), and only in this way does he get the right results!

This means that one should identify

$$\bar{R} = 2(\vec{\rho}-\vec{\rho}\,'), \tag{C-10}$$

instead of simply $(\vec{\rho}-\vec{\rho}\,')$, in order to use the same space-cut-off $|\zeta-\zeta'| > \varepsilon$ for both sides of the equation.

In Appendix D we shall supply a rigorous justification of why the identification (C-10) is necessary and correct. Here let us simply accept it as the right way to do it. So let us set $\bar{\omega}_D = \infty$ in eq. (C-9) and introduce the cut-off $\bar{R}_z > 2\varepsilon$ to it, we can then carry out the integrations w.r.t. $\bar{u}$ and $\bar{R}$ to convert it into the following simple equation:

$$[|\lambda|N(o)]^{-1} = -\ln\left(\frac{e\tilde{t}_c\varepsilon}{2}\right) = -\ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right). \tag{C-11}$$

Eliminating $[|\lambda|N(o)]$ between this equation and (C-6) or (C-7), we get

$$\Delta(\zeta)\ \ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right) = -\frac{\tilde{t}}{4\pi}\int_{\substack{\zeta'>o\\ |\zeta-\zeta'|>\varepsilon}} \left\{\frac{\exp[-i(\frac{\zeta+\zeta'}{2}-\zeta_o)(\xi-\xi')]}{|\vec{\rho}-\vec{\rho}\,'|^2\ \mathrm{Sinh}(\tilde{t}|\vec{\rho}-\vec{\rho}\,'|)} + \frac{\exp[-i(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')}-\zeta_o)(\xi-\xi')]}{|\vec{\rho}-R_{\zeta'}\vec{\rho}\,'|^2\ \mathrm{Sinh}(\tilde{t}|\vec{\rho}-R_{\zeta'}\vec{\rho}\,'|)}\right\}\ \Delta(\zeta')\ d\vec{\rho}\,' \quad (\text{for } T \neq 0°K), \tag{C-12}$$

and

$$\Delta(\zeta)\ \ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right) = -\frac{1}{4\pi}\int_{\substack{\zeta'>o\\ |\zeta-\zeta'|>\varepsilon}} \left\{\frac{\exp[-i(\frac{\zeta+\zeta'}{2}-\zeta_o)(\xi-\xi')]}{|\vec{\rho}-\vec{\rho}\,'|^3} + \frac{\exp[-i(\frac{\zeta^2+\zeta'^2}{2(\zeta+\zeta')}-\zeta_o)(\xi-\xi')]}{|\vec{\rho}-R_{\zeta'}\vec{\rho}\,'|^3}\right\}\ \Delta(\zeta')\ d\vec{\rho}\,' \quad (\text{for } T = 0°K). \tag{C-13}$$

We now limit ourselves to eq. (C-13). Perform the $\eta'$ and $\xi'$ integrations successively, we obtain:

$$\Delta(\zeta)\ \ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right) = -\frac{1}{2}\int\limits_{\substack{\zeta'>o \\ |\zeta-\zeta'|>\varepsilon}} \left\{\frac{\exp[-|\frac{\zeta+\zeta'}{2}-\zeta_o|\cdot|\zeta-\zeta'|]}{|\zeta-\zeta'|}\right.$$

$$\left.+\frac{\exp[-|\frac{1}{2}(\zeta^2+\zeta'^2)-\zeta_o(\zeta+\zeta')|]}{|\zeta+\zeta'|}\right\}\ \Delta(\zeta')\ d\zeta' \qquad (\text{for } T = 0°K), \qquad (C\text{-}14)$$

which is a typical eigenvalue problem of integral equation type, with its eigenvalue being identified as "$\ln(\frac{e\varepsilon}{2\sqrt{h}})$". We therefore see that the lower is the eigenvalue of a particular eigenstate, the higher will be the critical field of the particular nucleation mode corresponding to that eigenstate. We should therefore look for the ground state solution of this eigenvalue problem if it exists. That such a ground state does exist for all $-\infty \leq \zeta_o \leq +\infty$ is then proved in Appendix E, by showing that there exists a lower bound to all eigenvalues corresponding to any fixed $\zeta_o$, and therefore an upper bound to the value of $H_c\ (\zeta_o)$ for the particular nucleation mode specified by the given value of $\zeta_o$. We are then very safe in using a variational approach to calculate the eigenvalue of this ground state, which can in turn give us a good estimate of $H_{c//}(\zeta_o)$, for any particular $\zeta_o$. In this appendix, we shall only consider the particular nucleation mode with $\zeta_o = 0$. Setting $\zeta_o = 0$ in (C-14) we get:

$$\Delta(\zeta)\ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right) = -\frac{1}{2}\int\limits_{\substack{\zeta'>o \\ |\zeta-\zeta'|>\varepsilon}} \left\{\frac{\exp[-\frac{1}{2}|\zeta^2-\zeta'^2|]}{|\zeta-\zeta'|}\right.$$

$$\left.+\frac{\exp[-\frac{1}{2}|\zeta^2+\zeta'^2|]}{|\zeta+\zeta'|}\right\}\ \Delta(\zeta')\ d\zeta' \qquad (\text{for } T = 0°K). \qquad (C\text{-}15)$$

We now follow the guidance of similar variational calculations in the L-G region,[19] and choose our trial wave function to be simply a gaussian function centered at the origin:

$$\Delta(\zeta) = N \exp[-\tfrac{1}{2}\alpha\,\zeta^2] \tag{C-16}$$

We then normalize this wave function according to

$$\int_0^\infty |\Delta(\zeta)|^2\, d\zeta = 1, \tag{C-17}$$

which gives

$$N = (\pi/4\alpha)^{-1/4}. \tag{C-18}$$

Using this trial wave function in (C-15), we get

$$\ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right) \le -\left(\frac{4\alpha}{\pi}\right)^{1/2} \int_\varepsilon^\infty \int_0^{\zeta-\varepsilon} \frac{\exp[-\frac{1}{2}(\zeta^2-\zeta'^2)]}{(\zeta-\zeta')} \exp[-\frac{\alpha}{2}(\zeta^2+\zeta'^2)]\,d\zeta' d\zeta$$

$$-\left(\frac{4\alpha}{\pi}\right)^{1/2} \int_0^\infty \int_0^\zeta \frac{\exp[-\frac{1}{2}(\zeta^2+\zeta'^2)]}{(\zeta+\zeta')} \exp[-\frac{\alpha}{2}(\zeta^2+\zeta'^2)]\,d\zeta' d\zeta .$$

Change to new variables $u = \frac{1}{\sqrt{2}}(\zeta+\zeta')$, $v = \frac{1}{\sqrt{2}}(\zeta-\zeta')$, we get

$$\ln\left(\frac{e\varepsilon}{2\sqrt{h}}\right) \le -\left(\frac{2\alpha}{\pi}\right)^{1/2} \int_{\varepsilon/\sqrt{2}}^\infty \int_v^\infty \frac{\exp[-uv]}{v} \exp[-\frac{\alpha}{2}(u^2+v^2)]\,du dv$$

$$-\left(\frac{2\alpha}{\pi}\right)^{1/2} \int_0^\infty \int_0^u \frac{1}{u} \exp[-\frac{(1+\alpha)}{2}(u^2+v^2)]\,dv du$$

$$= -\int_\varepsilon^\infty \exp[-\frac{(\alpha^2-1)}{2\alpha} v^2][1 - \mathrm{erf}(\frac{\alpha+1}{\sqrt{2\alpha}} v)]\,\frac{dv}{v}$$

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

We then use the following two formulae:

$$\int_\delta^\infty \frac{dx}{x} \exp[-px^2] = \frac{1}{2} E_1(p\delta^2) \cong -\ln(\sqrt{\gamma p}\,\delta) \quad (\text{for } \sqrt{p}\,\delta \ll 1), \tag{C-19}$$

(see eqs. (5.1.1), (5.1.11) of ref. 20),

and

$$\int_0^\infty \exp[-ax^2]\mathrm{erf}(\sqrt{b}x)\,\frac{dx}{x} = \frac{1}{2}\ln\left[\frac{\sqrt{a+b}+\sqrt{b}}{\sqrt{a+b}-\sqrt{b}}\right], \qquad \text{(C-20)}$$

which can be derived from the formula (see eq. (7.4.19) of ref. 20):

$$\int_0^\infty \exp[-at]\ \mathrm{erf}\ (\sqrt{bt})\ dt = \frac{1}{a}\sqrt{\frac{b}{a+b}}$$

by first integrating w.r.t. a, and then letting $t = x^2$.

Our result is:

$$\ln\left(\frac{e}{\sqrt{2\gamma h}}\right) \leq \ln\left[\sqrt{\frac{\alpha+1}{2\alpha}}\,(\sqrt{2\alpha}+\sqrt{\alpha+1})\right] - \sqrt{\frac{\alpha}{\alpha+1}}\ \ln(\sqrt{2}+1). \qquad \text{(C-21)}$$

The right hand side of this expression goes to intinity as both $\alpha \to 0$ and $\infty$, as it possesses a unique minimum which is determined by

$$\frac{\sqrt{2}}{\sqrt{2u}+1} - \frac{1}{\sqrt{u}} + \frac{\sqrt{u}}{1-u} = \ln\ (\sqrt{2}+1) \qquad \text{(C-22)}$$

where $u = [\alpha/(\alpha+1)]$.

Solving (C-22) numerically, we finally get:

$$u_{min} = 0.5316$$

or

$$\alpha_{min} = 1.1350 \qquad \text{(C-23)}$$

and

$$\ln\left(\frac{e}{\sqrt{2\gamma h}}\right) \leq 0.4145$$

or

$$\frac{H_{c/\!/}(\zeta_o=0)}{H_{c2}} \geq 0.8729 \quad \text{(for } T = 0°\text{K)} \qquad \text{(C-24)}$$

where we have used the fact that at T = 0°K, $h_{c2} = \frac{e^2}{4\gamma}$ (see eq. (II-44)). We thus have found a lower bound to $H_{c/\!/}(\zeta_o=o)$ which is slightly less then $\frac{8}{9} H_{c2}$.

We also notice that $\alpha_{min}$ is slightly greater than 1, which means that the pair wave function of the nucleation mode with $\zeta_o = 0$ is slightly wider than half of that of the bulk nucleation mode.

## APPENDIX D

## ON GOR'KOV'S EQUIVALENT CUT-OFF PROCEDURE

In Appendix C we have used Gor'kov's equivalent space-cut-off procedure to replace the standard Debye frequency cut-off in treating our LGE. The essential content of this equivalent cut-off procedure has been given in that appendix. As is pointed out there, Gor'kov has mysteriously identified $\bar{R}$ of (C-9) as $2(\vec{\rho}-\vec{\rho}\,')$, when he introduced the space-cut-off $|\zeta-\zeta'|>\varepsilon$ to both the LGE (eq. (C-6) or (C-7) for our present problem) and the identity found by him (eq. (C-9)), so that the two equations combined, by eliminating $|\lambda|N(o)$, will give the correct result, as if the standard Debye frequency cut-off has been used in the LGE. In this appendix, we address ourselves to supply a rigorous justification to this mysterious step. We guess that Gor'kov must also have found such a justification except that he did not bother to have the details published. Nevertheless, we still think this appendix to be worthwhile in assuring that nobody, when using this equivalent cut-off procedure, shall be misled.

We shall supply proof only for the simpler space-cut-off $|\vec{\rho}-\vec{\rho}\,'|>\varepsilon$. That a parallel but slightly more complicated proof exists also for the space-cut-off $|\zeta-\zeta'|>\varepsilon$, or any other space cut-off which aimed at an infinitesimal neighborhood of the origin, is then clear if one realizes that the only singular point of the integrands is at the origin.

Letting $\bar{\omega}_D \to \infty$ and setting $\bar{R} = g(\vec{\rho}-\vec{\rho}\,')$ in eq. (C-9), we eliminate $|\lambda|N(o)$ from this equation and eq. (C-7) and then introduce the cut-off $|\vec{\rho}-\vec{\rho}\,'|>\varepsilon$. We then get:

$$\Delta(\vec{\rho}) \times \frac{g\tilde{t}_c}{4\pi^2\gamma}\int_0^\infty \frac{d\bar{u}}{u}\int_{|\vec{\rho}-\vec{\rho}\,'|>\varepsilon} d\vec{\rho}\,' \, \frac{\mathrm{Sin}(g\tilde{t}_c\bar{u}|\vec{\rho}-\vec{\rho}\,'|)}{|\vec{\rho}-\vec{\rho}\,'|^2}\, K_1\!\left(\frac{g\tilde{t}_c}{2\gamma}|\vec{\rho}-\vec{\rho}\,'|\right)$$

$$= -\frac{1}{4\pi}\int_{\substack{\zeta_> \\ |\vec{\rho}-\vec{\rho}\,'|>\varepsilon}} \left\{\frac{\exp[-i\int_{\vec{\rho}\,'}^{\vec{\rho}} a(\vec{\sigma})\cdot d\vec{\sigma}]}{|\vec{\rho}-\vec{\rho}\,'|^3} + \frac{\exp[-i\,\fint_{\vec{\rho}\,'}^{\vec{\rho}} a(\vec{\sigma})\cdot d\vec{\sigma}]}{|\vec{\rho}-R_{z'}\vec{\rho}\,'|^3}\right\} \Delta(\vec{\rho}\,')d\vec{\rho}\,', \tag{D-1}$$

where we have gone back to the general gauge with notations following that of Appendix C.

Now should we have introduced the frequency cut-off in the correct way, the upper limit of the $\bar{u}$ integration in the L.H.S. of eq. (D-1) should be $\bar{\omega}_D = \omega_D/2\pi T_c$ instead of $\infty$, while the R.H.S. should have an extra factor of $[1 - \exp(-\frac{2\omega_D}{v_F}|\vec{r}-\vec{r}\,'|)]$, or in our dimensionless variables $[1 - \exp(-2\bar{\omega}_D\tilde{t}_c|\vec{\rho}-\vec{\rho}\,'|)]$, in the numerator of the first term of its integrand. Strictly speaking, we should also have an extra factor $[1 - \exp(-2\bar{\omega}_D\tilde{t}_c|\vec{\rho}-R_{z'}\vec{\rho}\,'|)]$ in the second term of this integrand, but this factor can be simply dropped without any harm since this term is not singular in the integration region. Similarly, the space cut-off $|\vec{\rho}-\vec{\rho}\,'|>\varepsilon$ need not be dropped even though it should be, because its existence will not do any harm either.

We can now compute the errors involved in both sides of eq. (D-1) due to the neglect of the proper frequency cut-off: Let us denote the error of the right (left) hand side by $\mathrm{ERR}_r$ ($\mathrm{ERR}_l$), where ERR = WRONG - CORRECT. We then have

$$\mathrm{ERR}_r = \frac{1}{4\pi}\int_{\substack{\zeta'>0\\ |\vec{\rho}-\vec{\rho}\,'|>\varepsilon}} \frac{\exp[-i\int_{\vec{\rho}\,'}^{\vec{\rho}} a(\vec{\sigma})\cdot d\vec{\sigma}]}{|\vec{\rho}-\vec{\rho}\,'|^3}\exp[-2\bar{\omega}_D\tilde{t}_c|\vec{\rho}-\vec{\rho}\,'|]\Delta(\vec{\rho}\,')d\vec{\rho}\,'.$$

But since $\bar{\omega}_D >> 1$ ($\bar{\omega}_D = \omega_D/2\pi T_c \sim 10$ to $10^2$ except for strong coupling superconductors such as Pb or Hg), and $\tilde{t}_c = h^{-1/2} \sim 1$, we can drop the limitation $\zeta' > 0$, approximate $\Delta(\rho')$ by $\Delta(\rho)$, and neglect the phase incoherence. We finally get:

$$\mathrm{ERR}_r \sim \frac{1}{4\pi}\Delta(\vec{\rho})\int_{|\vec{\rho}-\vec{\rho}\,'|>\varepsilon} |\vec{\rho}-\vec{\rho}\,'|^{-3}\exp[-2\bar{\omega}_D\tilde{t}_c|\vec{\rho}-\vec{\rho}\,'|]d\vec{\rho}\,' \sim -\ln(2\gamma\bar{\omega}_D\tilde{t}_c\varepsilon)\Delta(\vec{\rho}).$$

On the other hand,

$$\mathrm{ERR}_1 = \Delta(\vec{\rho}) \times \frac{g\tilde{t}_c}{4\pi^2\gamma}\int_{\bar{\omega}_c}^{\infty}\frac{d\bar{u}}{u}\int_{|\vec{\rho}-\vec{\rho}\,'|>\varepsilon} d\vec{\rho}\,'\frac{\mathrm{Sin}(g\tilde{t}_c\bar{u}|\vec{\rho}-\vec{\rho}|)}{|\vec{\rho}-\vec{\rho}\,'|^2}K_1(\frac{g\tilde{t}_c}{2\gamma}|\vec{\rho}-\vec{\rho}\,'|).$$

Again, since $\bar{u} \geq \bar{\omega}_c >> 1$, and $g\tilde{t}_c \sim 1$, only the integration region $\varepsilon<|\vec{\rho}-\vec{\rho}\,'| << 1$ are of interest to us. We can approximate $K_1(x)$ by $\frac{1}{x}$ (see, for example, eq. 9.6.11 of ref. 20) to get:

$$\mathrm{ERR}_1 \sim \Delta(\vec{\rho}) \times \frac{1}{2\pi^2}\int_{\bar{\omega}_D}^{\infty}\frac{d\bar{u}}{\bar{u}}\int_{|\vec{\rho}-\vec{\rho}\,'|>\varepsilon} d\vec{\rho}\,'\frac{\mathrm{Sin}(g\tilde{t}_c\bar{u}|\vec{\rho}-\vec{\rho}\,'|)}{|\vec{\rho}-\vec{\rho}\,'|^3}$$

$$= -\Delta(\vec{\rho}) \times \frac{2}{\pi}\int_{\bar{\omega}_D}^{\infty}\frac{d\bar{u}}{\bar{u}}\,\mathrm{si}(g\tilde{t}_c\bar{u}\varepsilon)$$

$$= -\Delta(\vec{\rho}) \times \frac{2}{\pi}\int_{g\bar{\omega}_D\tilde{t}_c\varepsilon}^{\infty}\frac{dx}{x}\,\mathrm{si}(x),$$

where $\mathrm{si}(x) \equiv -\int_x^{\infty}\frac{\sin t}{t}\,dt \equiv \mathrm{Si}(x) - \pi/2.$

But since

$$\int_{\delta}^{\infty} \frac{dx}{x}\, si(x) \;=\; si(x)\ln x \Big|_{\delta}^{\infty} + \int_{0}^{\infty} \ln x \,\frac{\sin x}{x}\, dx$$

$$= +\frac{\pi}{2}\ln\delta + \frac{\pi}{2}\ln\gamma \;=\; \frac{\pi}{2}\ln\gamma\delta,$$ [20]

we get $ERR_1 = -\ln(g\gamma\bar{\omega}_D\tilde{t}_c\varepsilon)$.

We thus see that $ERR_1 = ERR_r$ only if we set $g = 2$. So far we have proved the identification (C-10) only for the case $T = 0°K$, but it is easy to see that this proof can be extended to finite temperatures without much modification. Besides, the same proof can also be given for all sample geometries and field arrangements, since the whole proof is independent of the image terms in the kernel, and the details of the field (except for the conditions discussed at the end of Ch. III).

We also notice that should we have set $\varepsilon = (2\gamma\bar{\omega}_D\tilde{t}_c)^{-1}$ for the cut-off $|\vec{\rho}-\vec{\rho}\,'|>\varepsilon$, or $\delta = v_F/(2\gamma\omega_D)$ for the cut-off $|\vec{r}-\vec{r}\,'|>\delta$, we would have caused no error at all, and no compensation is therefore necessary through the use of eq. (C-8) or (C-9). If the cut-off $|\zeta-\zeta'|>\varepsilon$ or $|z-z'|>\delta$ is used, we should then take $\varepsilon = (2e\gamma\bar{\omega}_D\tilde{t}_c)^{-1}$ or $\delta = v_F/(2e\gamma\omega_D)$ to avoid any error.

# APPENDIX E

## UPPER BOUND OF $H_{c//}(\zeta_o)$ AND $H_{c3}$

In this appendix, we want to show that for any given $\zeta_o$, eq. (C-14) implies the existance of a lower bound to its eigenvalue $\ln(\frac{e\varepsilon}{2\sqrt{h}})$, or an upper bound to the nucleation critical field $H_{c//}(\zeta_o)$. The highest one among these upper bounds will then naturally give an upper bound to $H_{c3}$. To proceed, we first write (C-14) in the form:

$$\Delta(|\zeta|)\ \ln(\frac{e\varepsilon}{2\sqrt{h}}) = -\frac{1}{2}\int_{\substack{-\infty \\ |\zeta-\zeta'|>\varepsilon}}^{\infty} \frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_o(\zeta-\zeta')|}{|\zeta-\zeta'|}\,\Delta(|\zeta'|)d\zeta'$$

$$= -\frac{1}{2}\,\Delta(|\zeta|)\int_{\substack{-\infty \\ |\zeta-\zeta'|>\varepsilon}}^{\infty} \frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_o(\zeta-\zeta')|]}{|\zeta-\zeta'|}\,d\zeta'$$

$$-\frac{1}{2}\int_{-\infty}^{\infty} \frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_o(\zeta-\zeta')|]}{|\zeta-\zeta'|}\,(\Delta(|\zeta'|)-\Delta(|\zeta|))\ d\zeta'.$$

Multiply both sides by $\Delta(|\zeta|)$, and integrate over $\zeta$:

$$\ln\ (\frac{e\varepsilon}{2\sqrt{h}})\int_{-\infty}^{\infty}|\Delta(|\zeta|)|^2\ d\zeta$$

$$= -\frac{1}{2}\int_{\infty}^{\infty}|\Delta(|\zeta|)|^2\ d\zeta\ \mathrm{x}\int_{\substack{-\infty \\ |\zeta-\zeta'|>\varepsilon}}^{\infty} \frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_o(\zeta-\zeta')]}{|\zeta-\zeta'|}\,d\zeta'$$

$$+\frac{1}{4}\int_{-\infty}^{\infty} \frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_o(\zeta-\zeta')|]}{|\zeta-\zeta'|}\ |\Delta(|\zeta|)-\Delta(|\zeta'|)|^2\ d\zeta d\zeta'.$$

The second term is positive definite, so we can conclude that:

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

where

$$I(|\zeta|,\zeta_o) \equiv -\frac{1}{2}\int_{\substack{-\infty \\ |\zeta-\zeta'|>\varepsilon}}^{\infty} d\zeta'\,\frac{\exp[-\frac{1}{2}|\zeta|\zeta|-\zeta'|\zeta'|-2\zeta_o(\zeta-\zeta')|]}{|\zeta-\zeta'|}$$

$$= -\frac{1}{2}\int_{\substack{-\infty \\ |\zeta|-\zeta'|>\varepsilon}}^{\infty} d\zeta'\,\frac{\exp[-\frac{1}{2}||\zeta|^2-\zeta'^2-2\zeta_o(|\zeta|-\zeta')|]}{||\zeta|-\zeta'|}$$

$$+\frac{1}{2}\int_{0}^{\infty} d\zeta'\,\frac{1}{||\zeta|+\zeta'|}$$

$$\times\ \{\exp[-\tfrac{1}{2}||\zeta|^2-\zeta'^2-2\zeta_o(|\zeta|+\zeta')|]-\exp[-\tfrac{1}{2}||\zeta|^2+\zeta'^2-2\zeta_o(|\zeta|+\zeta')|]\}$$

$$\equiv I_1(|\zeta|,\zeta_o) + I_2(|\zeta|,\zeta_o).$$

For $I_1(|\zeta|,\zeta_o)$ we define $\eta = \frac{1}{\sqrt{2}}(|\zeta|-\zeta_o)$, $\eta' = \frac{1}{\sqrt{2}}(\zeta'-\zeta_o)$ to get:

$$I_1(|\zeta|,\zeta_o) = -\frac{1}{2}\int_{\substack{-\infty \\ |\eta-\eta'|\geq\varepsilon/\sqrt{2}}}^{\infty} d\eta'\,\frac{\exp[-|\eta^2-\eta'^2|]}{|\eta-\eta'|} .$$

This integral has been studied by Gor'kov.[19] From his results, we get:

$$I_1(|\zeta|,\zeta_o) = \frac{1}{2}\ln\left(\frac{\gamma\varepsilon^2}{2}\right) + \Phi\left(\frac{|\eta|-\zeta_o}{\sqrt{2}}\right) ,$$

where

$$\Phi(\eta) \equiv \exp[-\eta^2]\int_0^{|\eta|} \exp[\eta'^2]\eta' \ln \frac{|\eta|+\eta'}{|\eta|-\eta'}\, d\eta' \geq 0 \text{ for all } \eta.$$

We can therefore throw away the term involving $\Phi(\eta)$ again to get:

$$\ln\left(\frac{e}{\sqrt{2\gamma h}}\right) \geq \frac{\int_{-\infty}^{\infty} I_2(|\zeta|,\zeta_o)|\Delta(|\zeta|)|^2\, d\zeta}{\int_{-\infty}^{\infty} |\Delta(|\zeta|)|^2\, d\zeta}. \tag{E-1}$$

Up to here, we are in close analogy with Gor'kov's derivation of an upper bound to $H_{c2}$. In fact, the two terms that we have thrown away are very similar in form to the two terms that he has thrown away in his derivation. However, instead of obtaining (E-1), he found the simpler result $\ln(\frac{e}{\sqrt{2\gamma h}}) \geq 0$, from which he concludes that $h_{c2} \leq h_{c2}^{U.B.}$, where $h_{c2}^{U.B.} = e^2/2\gamma$ turns out to be twice as large as the exact value of $h_{c2}$.[12] (The superscript "U.B." means upper bound.)

We now go back to eq. (E-1). From the definition of $I_2$, it is easy to see that for all $\zeta_o \leq 0$, we have $I_2 \geq 0$. This implies that we can have $h_c^{U.B.}(\zeta_o) \leq e^2/2\gamma$ for all $\zeta_o \leq 0$, which strongly suggests (but doesn't prove) that no surface nucleation mode with $\zeta_o \leq 0$ is physically more favorable than the bulk nucleation mode, a fact known to be true in the L-G case.

For $\zeta_o > 0$, $I_2$ is no longer positive definite. However, if we can prove that there exist some $\alpha(\zeta_o) \geq 0$ such that $I_2(|\zeta|,\zeta_o) \geq -\alpha(\zeta_o)$ for all $0 \leq |\zeta| < \infty$, we can then conclude that:

$$\ln\left(\frac{e}{\sqrt{2\gamma h}}\right) \geq -\alpha(\zeta_o),$$

which implies that we can have:

$$h_c^{U.B.}(\zeta_o) = \frac{e^2}{2\gamma} e^{2\alpha(\zeta_o)} .$$

That such a value $\alpha(\zeta_o)$ exists for any given $\zeta_o > 0$ is easily seen from the fact that $I_2(|\zeta|,\zeta_o)$ is a well-defined and continuous function of $\zeta$ in the whole real line $(-\infty,\infty)$ and $I_2(|\zeta|,\zeta_o) \to +0$ as $|\zeta| \to \infty$ . To estimate $\alpha(\zeta_o)$, however, we must employ numerical method. This has been done using a CEIR computer of the physics department of the University of Maryland. Since these numerical values are not really very useful, we shall not give all the details except to point out that

i) $\alpha(\zeta_o) \to 0$ as both $\zeta_o \to 0$ and $\infty$,

ii) $\alpha(\zeta_o)$ is a continuous function of $\zeta_o$,

iii) $\alpha \equiv \underset{\zeta_o}{\mathrm{Min}}\ \alpha(\zeta_o)$ exists and is found to be $\alpha \overset{\sim}{=} 0.479 \pm 0.001$,

so that $\ln(\frac{e}{\sqrt{2\gamma h_{c3}}}) \geq -0.48$, and therefore $h_{c3} \leq 2.61 \frac{e^2}{2\gamma} = 5.22\ h_{c2}$.

Comparing our procedure in getting this upper bound for $H_{c3}$ with Gor'kov's one in getting an upper bound for $H_{c2}$, we feel that our upper bound is looser than his one, due to our replacement of $I_2(|\zeta|,\zeta_o)$ by $\underset{\zeta}{\mathrm{Min}}\ I_2(|\zeta|,\zeta_o)$, while knowing that it should be some weighted means of $I_2(|\zeta|,\zeta_o)$ w.r.t. $\zeta$ over the width of the pair wave function that determines $H_{c/\!/}(\zeta_o)$. Since Gor'kov's upper bound of $H_{c2}$ is exactly twice larger than 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 $H_{c3}$, which gives a rough estimate of $H_{c3}$ to be around $2H_{c2}$.

# APPENDIX F

## DERIVATION OF THE SURFACE LAYER TERMS

In this appendix, we present a systematic procedure to get the surface layer terms to the first few orders in the expansion of the LGE under the "everywhere slowly varying" assumption. What we want to expand is:

$$\mathrm{SLT} \equiv \int_{z'<0} d\vec{r}\,'\; k^{(o)}(|\vec{r}-\vec{r}\,'|)\, \exp\left[(\vec{r}_2-\vec{r})\cdot\vec{\tilde{\nabla}}_s\right]$$

$$\times \left\{\exp\left[(R_{z'}\;\; \vec{r}\,'-\vec{r}_2)\cdot\vec{\tilde{\nabla}}_s\right] - \exp\left[(\vec{r}\,'-\vec{r}_2)\cdot\vec{\tilde{\nabla}}_s\right]\right\} \Delta(\vec{s})\Big|_{\vec{s}=\vec{r}}. \qquad \text{(F-1)}$$

We use the notation SLT(I) (SLT(II), ...) to mean the expansion of SLT truncated at the 1st (2nd, ...) order in $(\xi_o/\xi_H)$, or equivalently, in the arguments of the exponential operators. The following functions will appear in the expansion:

$$\chi^{(\ell)}_{m,n}(Z) \equiv \int_{z'<0} d\vec{r}\,'\; \frac{(\chi-\chi')^{m} Z'^{\,n}}{(z-z')^{\ell}}\; k^{(o)}(|\vec{r}-\vec{r}\,'|)$$

$$\chi_{m,n}(Z) \equiv \chi^{(o)}_{m,n}(Z) \text{ and } \chi_n(Z) \equiv \chi_{o,n}(Z). \qquad \text{(F-2)}$$

They possess the following properties which are needed in the main text (with $a_n$ defined in Ch. II section 3, eq. II-36):

$$\frac{d}{dZ} \chi_{2n+1}(Z)\Big|_{Z=0+} = \frac{1}{2} a_{2n} ,$$

$$\frac{d}{dZ} \chi_{2m,2n+1}(Z)\Big|_{Z=0+} = \frac{(2m-1)!!\ (2n+1)!!}{2(2m+2n+1)!!} a_{2(m+n)} ,$$

$$\frac{d}{dZ} \chi^{(2\ell-1)}_{2m,2n} (Z)\Big|_{Z=0+} = \frac{(-n)(2m-1)!!\ [2(n-\ell)-1]!!}{[2(m+n-\ell)+1]!!} a_{2(m+n-\ell)} \qquad \text{(F-3)}$$

(n, m, $\ell$ integers; for the last equation, $n \geq \ell \neq 0$),

($(2n+1)!! = (2n+1)\,(2n-1)\ldots 1$, $(-1)!! \equiv 1$).

Other properties of $\chi$'s can be easily derived from their definitions.

Before we expand SLT, we first convert it into a more convenient form by using the commutation relations $[\tilde{\nabla}_i, \tilde{\nabla}_j] = 2ie\,\varepsilon_{ijk} H_k$, where i, j, k = x, y, or z, and $\varepsilon_{ijk}$ is the completely antisymmetric rank-3 tensor:

$$\begin{aligned} \text{SLT} = & \int_{z'<o} d\vec{r}'\ k^{(o)} (|\vec{r}-\vec{r}'|) \\ & \times \{\exp[(R_{z'}\vec{r}'-\vec{r})\cdot\vec{\tilde{\nabla}}_s] \exp[(2ieH) \frac{zz'}{z-z'} (x'-x)] \\ & - \exp[(\vec{r}'-\vec{r})\cdot\vec{\tilde{\nabla}}_s]\} \Delta(\vec{s})\Big|_{\vec{s}=\vec{r}}. \end{aligned} \qquad \text{(F-3)}$$

Expanding this expression, we get

i) $\text{SLT}(0) = 0.$

ii) $\text{SLT(I)} = \delta[\text{SLT(I)}] = -2\chi_1(Z)\ \tilde{\nabla}_z \Delta(\vec{r}).$

iii) $\text{SLT(II)} = \text{SLT(I)} + \delta[\text{SLT(II)}]$, with $\delta[\text{SLT(II)}] = 2Z\chi_1(Z)\tilde{\nabla}_z^{\ 2}\Delta(\vec{r}).$

iv) $\text{SLT(III)} = \text{SLT(II)} + \delta[\text{SLT(III)}]$, with

$$\delta[\mathrm{SLT(III)}] = \int_{z'<o} d\vec{r}\,'\; k^{(o)}(|\vec{r}-\vec{r}\,'|) \times \{\frac{1}{6}\,[R_{z'},\vec{r}\,'-\vec{r}]\cdot\vec{\tilde{\nabla}}_s]^3$$

$$-\frac{1}{6}\,[(\vec{r}\,'-\vec{r})\cdot\vec{\tilde{\nabla}}_s]^3 + (R_{z'},\vec{r}\,'-\vec{r})\;\vec{\tilde{\nabla}}_s(2ieH)\,\frac{zz'}{z-z'}\,(x'-x)\}\;\Delta(\vec{s})\Big|_{\vec{s}=\vec{r}}$$

$$= \int_{z'<o} d\vec{r}\,'\; k^{(o)}\;(|\vec{r}-\vec{r}\,'|) \times [\frac{1}{3}\,\{(\vec{r}\,'_\perp-\vec{r})\cdot\vec{\tilde{\nabla}}_s,\; (\vec{r}\,'_\perp-\vec{r})\cdot\vec{\tilde{\nabla}}_s,\; (-z')\vec{\tilde{\nabla}}_s\}_+$$

$$+\frac{1}{3}\,(-z')^3\;\vec{\tilde{\nabla}}_s^{\,3} + (2ieH)\,\frac{zz'}{z-z'}\,(x'-x)\;\vec{\tilde{\nabla}}_s]\;\Delta(\vec{s})\Big|_{\vec{s}=\vec{r}}$$

$$= -\chi_{2,1}(Z)\;|\vec{\tilde{\nabla}}_\perp|^2\;\tilde{\nabla}_z\;\Delta(\vec{r})$$

$$-\,(Z^2\chi_1(Z) + \frac{1}{3}\,\chi_3(Z))\;\tilde{\nabla}_z^{\,3}\;\Delta(\vec{r})$$

$$+\,\chi_{2,2}^{(1)}\,(Z)\;(2ieH)\;\tilde{\nabla}_x\;\Delta(\vec{r}),$$

where the notation $\{A, B, C, \ldots\}_+$ is defined to be the sum of all possible distinct ordering of the operators in the curved bracket. Thus

$\{A, B\}_+ = AB + BA,$

$\{A, A, B\}_+ = AAB + ABA + BAA,$

$\{A, A, B, B\}_+ = AABB + ABAB + BAAB + ABBA + BABA + BBAA\,,$

etc.. (Note that for correct counting we must consider $(Z\vec{\tilde{\nabla}}_s)$ and $(Z'\vec{\tilde{\nabla}}_s)$ to be distinct operators.)

v) SLT(IV) = SLT(III) + δ[SLT(IV)], with

$$\delta[\mathrm{SLT(IV)}] = \int_{z'<o} d\vec{r}'\ k^{(o)}(|\vec{r}-\vec{r}'|)\ \{\frac{1}{24}\ [(R_{z'},\ \vec{r}'-\vec{r})\cdot\vec{\tilde{\nabla}}_s]^4$$

$$-\frac{1}{24}\ [(\vec{r}'-\vec{r})\cdot\vec{\tilde{\nabla}}_s]^4 + \frac{1}{2}\ [(R_{z'},\ \vec{r}'-\vec{r})\cdot\vec{\tilde{\nabla}}_s]\ (2ieH)\ \frac{zz'}{z-z'}\ (x'-x)$$

$$+\frac{1}{2}\ (2ieH)^2\ (\frac{zz'}{z-z'})^2\ (x'-x)^2\}\ \Delta(\vec{s})\Big|_{\vec{s}=\vec{r}}$$

$$= \int_{z'<o} d\vec{r}'\ k^{(o)}(|\vec{r}-\vec{r}'|)\ [\frac{1}{12}\ \{(\vec{r}_\perp'-\vec{r})\cdot\vec{\tilde{\nabla}}_s,\ (\vec{r}_\perp'-\vec{r})\cdot\vec{\tilde{\nabla}}_s,\ (\vec{r}_\perp'-\vec{r})\cdot\vec{\tilde{\nabla}}_s,$$

$$(-Z')\tilde{\nabla}_{s_z}\}_+ + \frac{1}{12}\ \{(\vec{r}_\perp'-\vec{r})\cdot\vec{\tilde{\nabla}}_s,\ (-z')\tilde{\nabla}_{s_z},\ (-z')\tilde{\nabla}_{s_z},\ (-Z')\tilde{\nabla}_{s_z}\}_+ +$$

$$+\frac{1}{2}\ (2ieH)\ \frac{zz'}{z-z'}\ (x'-x)\ \{(x'-x)\tilde{\nabla}_{s_x},\ -\ (Z+Z')\tilde{\nabla}_{s_z}\}_+ +$$

$$+\frac{1}{2}\ (2ieH)^2\ (\frac{zz'}{z-z'})^2\ (x'-x)\}\Delta(\vec{s})\Big|_{\vec{s}=\vec{r}}$$

$$= \{Z\ \chi_{2,1}(z)|\tilde{\nabla}_\perp|^2\tilde{\nabla}_z^{\ 2} + \frac{1}{3}\ [Z^3\ \chi_1(Z) + Z\ \chi_3(Z)]\ \tilde{\nabla}_z^{\ 4}$$

$$+ (2ieH)[Z^2\ \chi_{2,1}^{(1)}(Z)\ -\ 3Z\ \chi_{2,2}^{(1)}(Z)]\ \tilde{\nabla}_x\tilde{\nabla}_z$$

$$-\frac{1}{2}\ (2ieH)^2\ [Z^2\ \chi_{2,2}^{(2)}(Z)\ -\ 2Z\chi_{2,3}^{(2)}(Z)]\}\ \Delta(\vec{r}),$$

where the following operator identity has been used:

$$\{A,A,B,B\}_+ = 6A^2B^2 + 12AB[B,A] + 3[B,A]^2\ ,$$

if [B,A] commutes with A and B.

# APPENDIX G

## EVALUATION OF $\alpha^{(3)}$

For this purpose, we need to evaluate two integrals: $I_1 = \int_o^\infty dZ\, f_1^{(2)}(Z)$ and $I_2 = \int_o^\infty dZ\, f_2^{(4)}(Z)$, where $f_1^{(2)}$ and $f_2^{(4)}$ are found by comparing eqs. (V-47) and (V-42) to be: $f_1^{(2)}(z) \equiv - 2\xi_H^{-1}\, \chi_1(Z)$, and

$$f_2^{(4)}(Z) \equiv \xi_H^{-3}\, \zeta_o\, [\chi_{2,2}^{(1)}(Z) + \frac{2}{3}\, \chi_3(Z)]$$

$$+ \xi_H^{-4}\, [\frac{1}{2}\, Z^2\, \chi_{2,2}^{(2)}(Z) - Z\, \chi_{2,3}^{(2)}\, (Z) - Z\, \chi_{2,2}^{(1)}(Z)].$$

Since $\chi_1(Z) = \int_{z'<o} d\vec{r}'\, Z'\, k^{(o)}\, (|\vec{r}-\vec{r}'|)$

$$= \int d\vec{R}_\perp \int_z^\infty dR_z\, (z-R_z)\, k^{(o)}\, (|\vec{R}|),$$

and $\int_o^\infty dZ \int_z^\infty dR_z\, (z-R_z)\, F(|R_z|)$

$$= \int_o^\infty dR_z \int_o^{R_z} dZ(z-R_z)\, F(|R_z|)$$

$$= \int_o^\infty dR_z\, (-\frac{1}{2}\, R_z^{\,2})\, F(|R_z|)$$

$$= -\frac{1}{4} \int dR_z\, R_z^{\,2}\, F(|R_z|),$$

we get

$$\int_o^\infty dZ\, \chi_1(z) = -\frac{1}{4} \int d\vec{R}\, R_z^{\,2}\, k^{(o)}(|\vec{R}|)$$

$$= -\frac{1}{12}\, a_2 \cong -\frac{7}{24}\, \zeta(3)\, \xi_o^{\,2} |\lambda|\, N(o)$$

so that $I_1 = \frac{7}{12}\,\zeta(3)\,\left(\frac{\xi_o^{\,2}}{\xi_H}\right)|\lambda|\,N(o)$. (The values of $a_2$ and $a_4$ have been given in eqs. (II-41), (II-42).)

Similarly, we get:

$$\text{(i)}\quad \int_o^\infty dZ\;\chi^{(1)}_{2,2}(Z) \;=\; \frac{1}{6}\int d\vec{R}\;R_z^{\,2}\;R_x^{\,2}\;k^{(o)}\;(|\vec{R}|)$$

$$=\;\frac{1}{15x6}\,a_4 \;\overset{\sim}{=}\; \frac{31}{60}\,\zeta(5)\;\xi_o^{\,4}\;|\lambda|N(o),$$

as:

$$\frac{1}{4\pi}\int d\Omega_R\;R_Z^{\,2}\;R_x^{\,2} \;=\; \frac{|\vec{R}|^4}{4\pi}\int_{-1}^{+1}\int_o^{2\pi}\cos^2\theta\;\sin^2\theta\;\cos^2\phi\;d\cos\phi\;d\phi$$

$$=\;\frac{|\vec{R}|^4}{4}\int_{-1}^{+1} x^2(1-x^2)\;dx \;=\; \frac{1}{15}\,|R|^4\;.$$

$$\text{(ii)}\quad \int_o^\infty dZ\;\chi_3(Z) \;=\; -\,\frac{1}{8}\int d\vec{R}\;R_z^{\,4}\;k^{(o)}\;(|\vec{R}|)$$

$$=\;-\,\frac{1}{8x5}\;a_4 \;\overset{\sim}{=}\; -\,\frac{93}{80}\;\zeta(5)\;\xi_o^{\,4}|\lambda|\;N(o).$$

$$\text{(iii)}\quad \int_o^\infty dZ\;[Z^2\;\chi^{(2)}_{2,2}(z)] \;=\; \frac{1}{30}\int_{R_z>o} d\vec{R}\;R_x^{\,2}\;R_z^{\,3}\;k^{(o)}\;(|\vec{R}|)$$

$$=\;\frac{1}{48x30}\;a_5 \;\overset{\sim}{=}\; \frac{21}{128}\;\zeta(6)\;\xi_o^{\,5}|\lambda|N(o),$$

$$\text{as}\quad a_5 \;\overset{\sim}{=}\; 4\pi|\lambda|T_c\;\left(\frac{m}{2\pi}\right)^2\int_o^\infty \frac{u^5}{\sinh(u/\xi_o)}\;du$$

$$=\;\frac{945}{4}\;\zeta(6)\;\xi_o^{\,5}|\lambda|\;N(o).$$

$$\text{(iv)}\quad \int_o^\infty dZ[Z\;\chi^{(2)}_{2,3}(Z)] \;=\; -\,\frac{1}{20}\int d\vec{R}\;R_x^{\,2}\;R_z^{\,3}\;k^{(o)}\;(|\vec{R}|)$$

$$=\;-\,\frac{3}{2}\int_o^\infty dZ\;\chi_{2,2}^{\;(2)}(Z).$$

(v) $$\int_o^\infty dZ\,[Z\,\chi_{2,2}{}^{(1)}(Z)] = \frac{1}{12}\int d\vec{R}\,R_x{}^2\,R_z{}^3\,k^{(o)}(|\vec{R}|)$$

$$= \frac{5}{2}\int_o^\infty dZ\,[Z^2\,\chi_{2,2}{}^{(2)}(Z)].$$

Combining the results in (i) through (v), we get:

$$I_2 = -\frac{31}{120}\,\zeta(5)\,\zeta_o\,\left(\frac{\xi_o{}^4}{\xi_H{}^3}\right)|\lambda|N(o) - \frac{21}{256}\,\zeta(6)\,\left(\frac{\xi_o{}^5}{\xi_H{}^4}\right)|\lambda|N(o).$$

From eq. (V-46) that $\alpha^{(3)} = -\,I_2/I_1$, we get:

$$\alpha^{(3)} = \frac{31}{70}\,\frac{\zeta(5)}{\zeta(3)}\,\left(\frac{\xi_o}{\xi_H}\right)^2\,\zeta_o + \frac{9}{64}\,\frac{\zeta(6)}{\zeta(3)}\,\left(\frac{\xi_o}{\xi_H}\right)^3.$$

## FOOTNOTES

(i) For high quantum nucleation states, we still have: $|[\vec{\nabla}_r + 2ie\vec{A}(\vec{r})]_i\Delta(\vec{r})| \sim \xi_o^{-1}(1-t)^{-1/2}|\Delta(\vec{r})| >> \xi_o^{-1}|\Delta(\vec{r})|$, but $\xi_H(T) \equiv (2eH)^{-1/2}$ is now further longer than $\xi_o(1-t)^{1/2}$. In order for (II-12) to be still true in this case, we should then interpret $O(\xi_H^{-1})$ as $O(\xi_{H_{c2}}^{-1})$ or $O(\xi_{H_{c3}}^{-1})$. This comment is still true for nucleation modes with $k_y \neq 0$, since from eq. (II-3), we see that $k_y$ is limited above by $[\frac{4m}{\beta}(1-t)]^{1/2} \sim \xi_o^{-1}(1-t)^{1/2}$.

(ii) We have used two names for this very one B.C. to emphasize the two different roles it is simultaneously playing. As a "standard B.C.", it is supposed to be modified in the non-L-G region, as Tewordt,[27] Lüders,[22] and we too (see our second approach) have all aimed at. On the other hand, as an "exact B.C.", it should in fact be valid at all temperatures!

(iii) The criterion (1-t) << 1 for the L-G region is also true if the pair wave function is concerned. But for the LGE one should only neglect third and higher order terms. This is understandable if one notices that to zero$^{th}$ order the LGE is merely an identity so that its first order is actually the lowest non-trivial order. We also notice that the L-G region is usually defined by both (1-t) << 1 and (1-t) << $\kappa^2$, where $\kappa \equiv \lambda(T)/\xi(T)$ is the ratio of the penetration depth to coherence length, both measured at T → $T_c$. For pure type I superconductors with $\kappa <<1$, the second requirement is much more restrictive than the first, indicating that the L-G region for nucleation situation is much wider than that for the bulk superconductivity states with finite order parameters, in case that such type of samples are concerned.

(iv) For convenience, we have derived eq. (V-11) in the special gauges characterized by $A_Z \equiv 0$, which is, however, not necessary. Thus, in a general gauge, we can proceed as follows:

Let $\phi(z) \equiv 2ie \int_o^Z A(z)dz$ (with its x, y dependence suppressed), then:

$$[\tilde{\nabla}_z - z\tilde{\nabla}_z^{\,2}]\Delta(\vec{r}) = \exp[-\phi(o)][\tilde{\nabla}_z - z\tilde{\nabla}_z^{\,2}]\Delta(\vec{r})$$

$$= \exp[-\phi(o)] \sum_{n=o}^{\infty} \frac{z^n}{n!} \{\nabla_z^{\,n}[\tilde{\nabla}_z - z\tilde{\nabla}_z^{\,2}]\Delta(\vec{r})\}_{z=o}$$

$$= \sum_{n=o}^{\infty} \frac{z^n}{n!} \{\tilde{\nabla}_z^{\,n} \exp[-\phi(z)][\tilde{\nabla}_z - z\tilde{\nabla}_z^{\,2}]\Delta(\vec{r})\}_{z=o}$$

$$\overset{\sim}{=} \sum_{n=o}^{\infty} \frac{z^n}{n!} \{[\frac{d^n}{dz^n} \exp(-\phi(z))]_{z=o} x[\tilde{\nabla}_z\Delta(\vec{r})]_{z=o} + n[\frac{d^{n-1}}{dz^{n-1}} \exp(-\phi(z))]_{z=o}$$

$$x[\tilde{\nabla}_z^{\,2}\Delta(\vec{r})]_{z=o} - [\frac{d^n}{dz^n} (z \exp(-\phi(z))]_{z=o} x[\tilde{\nabla}_z^{\,2}\Delta(\vec{r})]_{z=o}\}$$

$$= \exp\ [-\phi(z)][\tilde{\nabla}_z\Delta(\vec{r})]_{z=o}\ ,$$

which is slightly different from (V-11) (a result not very surprising since eq. (V-11) is not really gauge invariant), but will not affect our conclusions. In this derivation use has been made of the following generalized Leibniz's theorem:

$$\tilde{\nabla}_z^{\,n}[f(z)g(z)] = \sum_{m=o}^{n} C_m^n \times [\frac{d^m}{dz^m} f(z)] \times \tilde{\nabla}_z^{\,n-m} g(z),$$

which is very easy to justify by mathematical induction.

(v) According to a remark made by E. A. Shapoval (Soviet Phys. JETP 20, 675 (1965)), an unpublished microscopic derivation of this boundary condition was also given by Gor'kov.

(vi) I wish to thank Professor G. Lüders for sending me a copy of this note from which I learned the basic ideas of Schöler's thesis.

(vii) I wish to thank Dr. E. Helfand for pointing out to me the possibility of the existance of the second criterion.

(viii) A somewhat different version of such a proof has also been given by G. Lüders (see ref. 26, V).

(ix) I wish to thank Dr. G. Fischer for sending me the full detail of his work concerning his publication cited in ref. 34.

# REFERENCES

1. D. Saint-James and P. G. de Gennes, Phys. Letters 7, 306 (1963).
2. P. G. de Gennes, Superconductivity of Metals and Alloys, Translated by P. A. Pincus (W. A. Benjamin, Inc., New York 1966).
3. A. A. Abrikosov, J. Exptl. Theoret. Phys. (U.S.S.R.) 47, 720 (1964); English transl., Soviet Phys. JETP 20, 480 (1965).
4. K. Maki, Physics 1, 21 and 127 (1964).
5. P. G. de Gennes, Phys. kondens. Materie 3, 79 (1964).
6. G. Eilenberger and V. Ambegaokar, Phys. Rev. 158, 332 (1967).
7. E. D. Yorke and A. Bardasis, Phys. Rev. 159, 344 (1967). Also, Ph. D. Thesis, University of Maryland, 1967,and University of Maryland Technical Report No. 664.
8. G. M. Eliashberg, J. Exptl. Theoret. Phys. (U.S.S.R.) 38, 966 1966: English transl. Soviet Phys. JETP 11, 696 (1960). See also J. R. Schrieffer, D. J. Scalapino, and J. M. Wilkins, Phys. Rev. Letters 10, 526 (1963); D. J. Scalapino, J. R. Schrieffer, and J. M. Wilkins, Phys. Rev. 148, 263 (1966).
9. B. Rosenblum and M. Cardona, Phys. Letters 9, 220 (1964); 13, 33 (1964).
10. W. J. Tomasch, Phys. Rev. 139, A746 (1965).
11. L. P. Gor'kov, J. Exptl. Theoret. Phys. (U.S.S.R.) 34, 735 (1958); English transl. Soviet Phys. JETP 7, 505 (1958).
12. E. Helfand and N. R. Werthamer, Phys. Rev. 147, 288 (1966).

13. For a good review of the thermal Green's function, see: A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinsky, *Method of Quantum Field Theory in Statistical Physics*. Translated by R. A. Silverman (Prentice-Hall, Inc., Englewood Cliffs, New Jersey 1963). This book also contains a good introduction to Gor'kov's microscopic theory of superconductivity.

14. V. L. Ginzburg and L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 1064 (1950).

15. For pure samples, see L. P. Gor'kov, J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 1918 (1959); English transl. Soviet Phys. JETP **9**, 1364 (1959). For alloys, see L. P. Gor'kov, J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 1407 (1959); English transl. Soviet Phys. JETP **10**, 998 (1960).

16. J. Bardeen, L. N. Cooper and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957). See also ref. 2.

17. Eugen Merzbacher, *Quantum Mechanics*, (John Wiley and Sons, Inc., New York 1961).

18. H. Frölich, Phys. Rev., **79**, 845 (1950).

19. L. P. Gor'kov, J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 833 (1959); English transl., Soviet Phys. JETP **37**, 593 (1960).

20. *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, edited by M. Abramowitz and I. A. Stegun (U. S. Government Printing Office, Washington, D. C. 1964) Nat. Bur. Std. Appl. Math. Ser. 55.

21. G. Lüders, Z. Physik **209**, 219 (1968).

22. G. Lüders, Z. Physik **202**, 8 (1967).

23. F. Smithies, Integral Equations, (Cambridge Univ. Press, 1962).

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

25. E. Schöler, Thesis, Göttingen 1966. See also a revised English note of a talk delivered by G. Lüders at Theoretisch Physikalisches Seminar, Göttingen University, on May 9, 1967. (Limited distribution, not published.)$^{(vi)}$

26. See the series of papers by G. Lüders: Z. Naturforschg. 21a, 680 (I), 1415 (II), 1425 (III), 1842 (IV) (1966), 22a, 845 (V) (1967). These papers form the basis of Schöler's thesis.

27. L. Tewordt, Z. Physik 184, 319 (1965); and 185, 421 (1965).

28. R. Radebaugh and P. H. Keeson, Phys. Rev. 149, 209 (I) and 217 (II) (1966).

29. D. K. Finnemore, T. F. Stromberg, and C. A. Swenson, Phys. Rev. 149, 231 (1966). See also Rev. Mod. Phys. 36 (1964) where numerous articles can be found discussing this and related subjects.

30. See, for example, ref. 9.

31. See the numerous references cited in ref. 28, II.

32. W. DeSorbo, Phys. Rev. 134, A1119 (1964).

33. W. DeSorbo, Bull. Am. Phys. Soc. 9, 253 (1964); and W. DeSorbo, Phys. Rev. 135, A1190, (1964).

34. G. Fischer, Phys. Rev. Letters 20, 268 (1968).

35. D. Saint-James, Phys. Letters 15, 13 (1965); W. A. Litter and R. D. Parks, Phys. Rev. Letters 9, 9 (1962).

36. G. Deutscher, J. Phys. Chem. Solids 28, 241 (1967); C. F. Hempstead and Y. B. Kim, Phys. Rev. Letters 12, 145 (1964); and L. J. Barnes and H. J. Fink, Phys. Rev. 149, 186 (1966). See also a comment made in ref. 1 on this point.

37. P. Fulde and K. Maki, Phys. Cond. Matt. 5, 380, (1966); G. Deutscher, J. P. Huralt, F. Mennier and D. Saint-James, Phys. Letters 25A, 514 (1967).

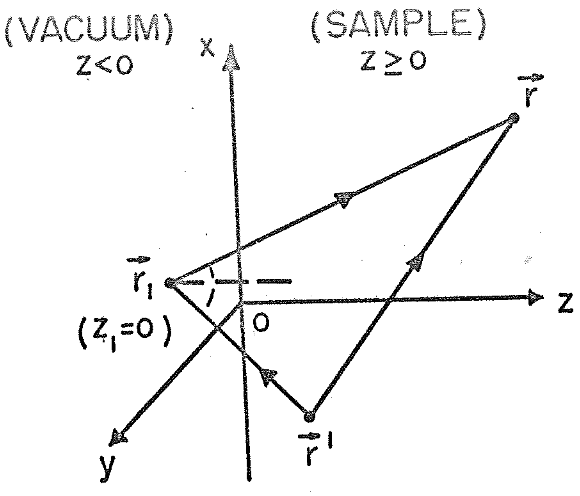
(VACUUM)
z<0
x
(SAMPLE)
z≥0
$\vec{r}$
$\vec{r}_1$
$(z_1=0)$
0
z
y
$\vec{r}'$

Fig. 1a

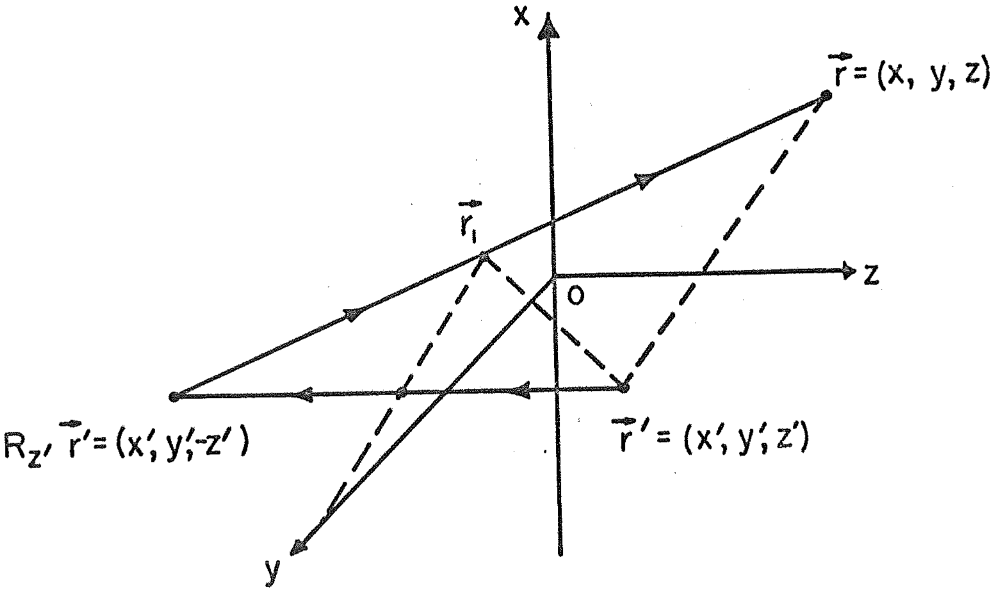
x
$\vec{r}=(x, y, z)$
$\vec{r}_1$
0
z
$R_{z'}\,\vec{r}'=(x', y', -z')$
$\vec{r}'=(x', y', z')$
y

Fig. 1b

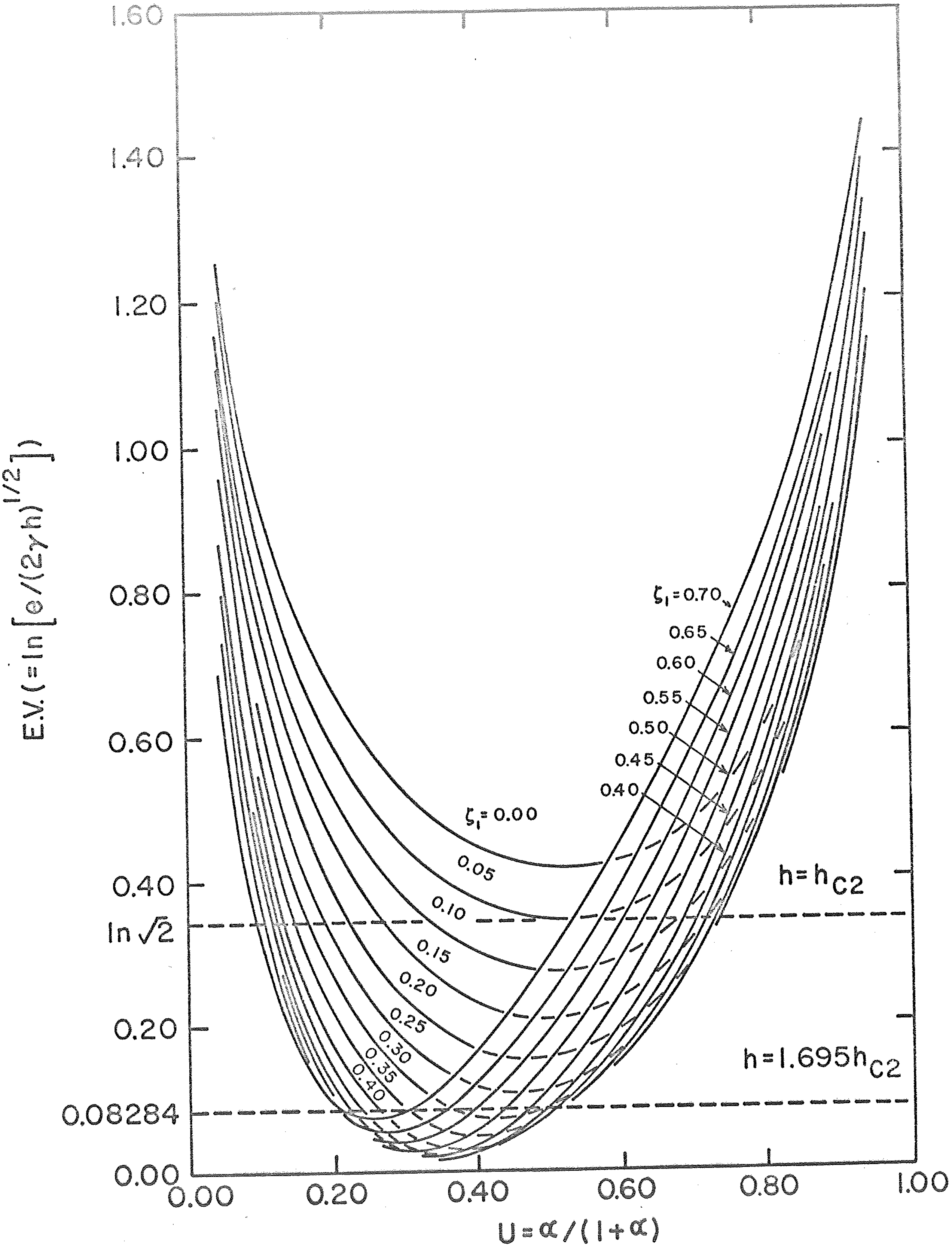
1.60
1.40
1.20
1.00
0.80
0.60
0.40
ln √2
0.20
0.08284
0.00
E.V.(=ln[e/(2γh)^1/2])
0.00
0.20
0.40
0.60
0.80
1.00
U=α/(1+α)
ζ1 = 0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
ζ1 = 0.70
0.65
0.60
0.55
0.50
0.45
0.40
h= hC2
h=1.695hC2

Fig. 2

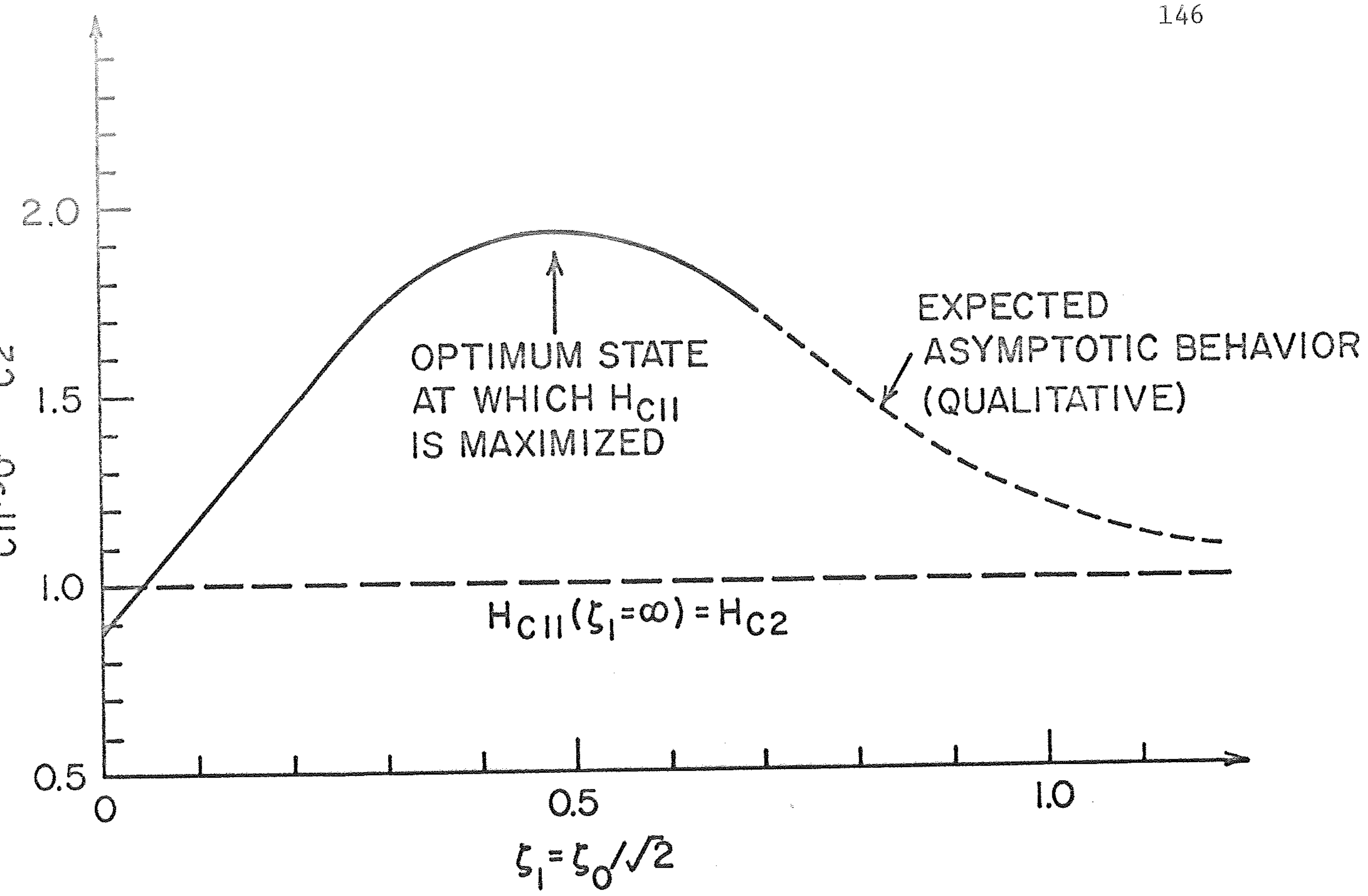
2.0
1.5
1.0
0.5
0
0.5
1.0
OPTIMUM STATE AT WHICH $H_{C11}$ IS MAXIMIZED
EXPECTED ASYMPTOTIC BEHAVIOR (QUALITATIVE)
$H_{C11}(\zeta_1=\infty)=H_{C2}$
$\zeta_1=\zeta_0/\sqrt{2}$

Fig. 3

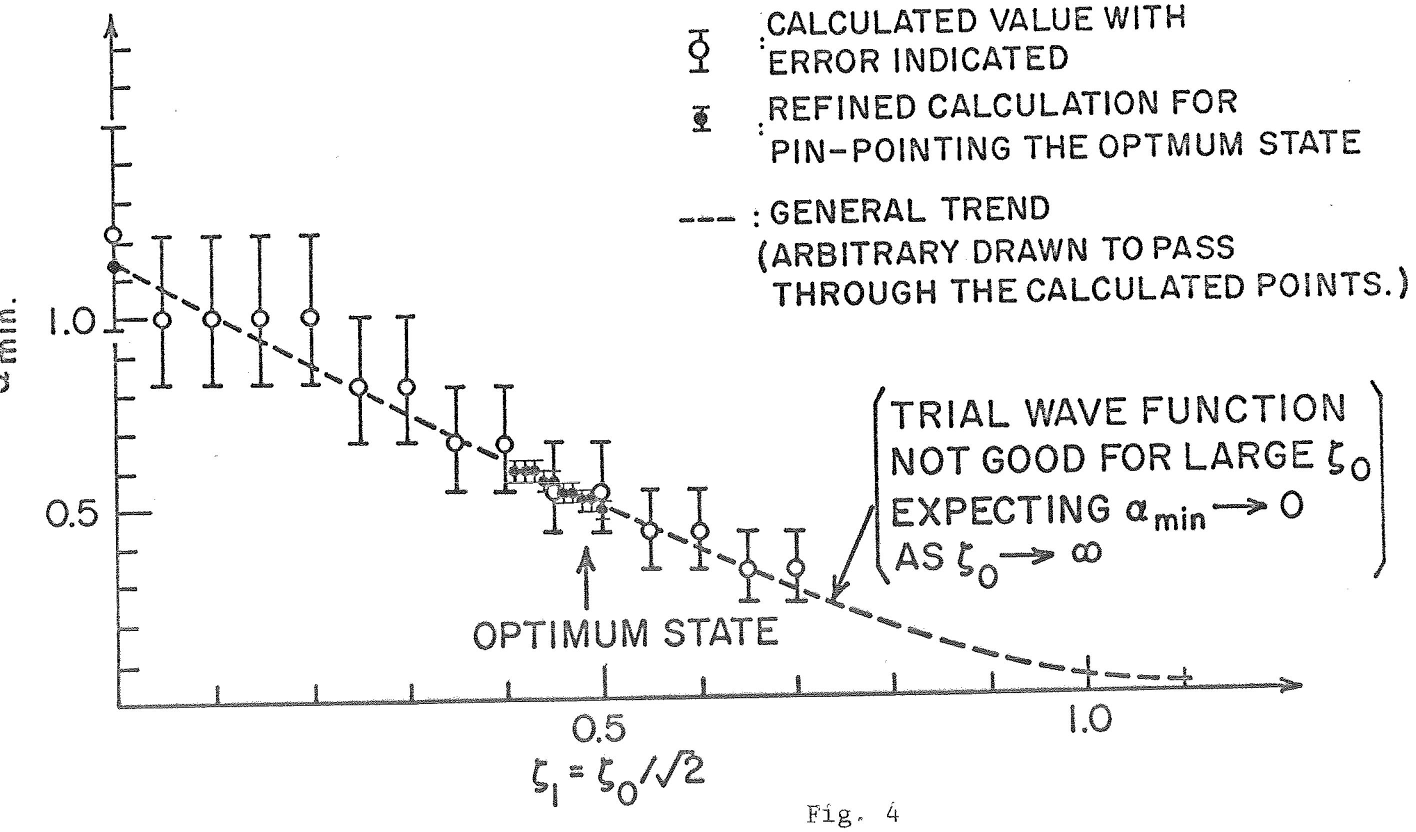
: CALCULATED VALUE WITH ERROR INDICATED
: REFINED CALCULATION FOR PIN-POINTING THE OPTMUM STATE
: GENERAL TREND (ARBITRARY DRAWN TO PASS THROUGH THE CALCULATED POINTS.)
TRIAL WAVE FUNCTION NOT GOOD FOR LARGE $\zeta_0$ EXPECTING $\alpha_{min}\to 0$ AS $\zeta_0\to\infty$
OPTIMUM STATE
min.
1.0
0.5
0.5
1.0
$\zeta_1=\zeta_0/\sqrt{2}$

Fig. 4

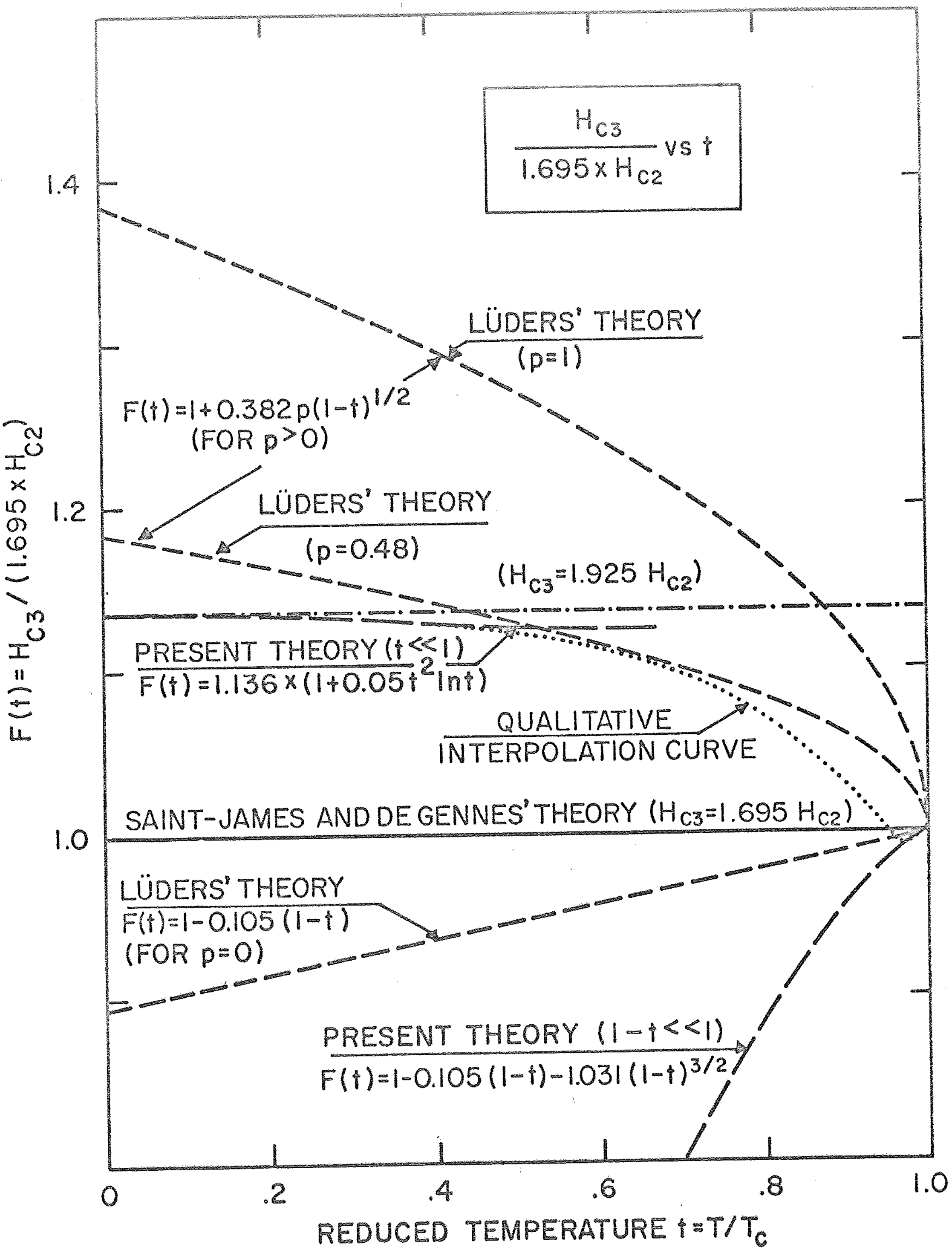
$\frac{H_{C3}}{1.695 \times H_{C2}}$ vs t
LÜDERS' THEORY
(p=1)
$F(t)=1+0.382p(1-t)^{1/2}$
(FOR p>0)
LÜDERS' THEORY
(p=0.48)
($H_{C3}$=1.925 $H_{C2}$)
PRESENT THEORY (t<<1)
$F(t)=1.136\times(1+0.05t^2 \ln t)$
QUALITATIVE
INTERPOLATION CURVE
SAINT-JAMES AND DE GENNES' THEORY ($H_{C3}$=1.695 $H_{C2}$)
LÜDERS' THEORY
$F(t)=1-0.105(1-t)$
(FOR p=0)
PRESENT THEORY (1-t<<1)
$F(t)=1-0.105(1-t)-1.031(1-t)^{3/2}$
$F(t)=H_{C3}/(1.695\times H_{C2})$
1.4
1.2
1.0
0
.2
.4
.6
.8
1.0
REDUCED TEMPERATURE $t=T/T_c$

Fig. 5