PHYSICAL REVIEW B

SOLID STATE

THIRD SERIES, VOL. 6, NO. 1 1 JULY 1972

Theory of Surface Energies in Pure Superconductors*

Chia-Ren Hu
Department of Physics, University of Southern California, Los Angeles, California 90007
(Received 12 November 1971)

The WKBJ variational scheme developed by Bardeen *et al.* which simplifies the Bogoliubov theory for inhomogeneous superconducting states, has been applied to study normal-superconducting phase boundaries in pure metals. The surface energy of a planar phase boundary at absolute-zero temperature is found for various values of the Ginzburg-Landau parameter. The order parameter and the magnetic field are also determined in this variational procedure. The present theory differs from the existing ones in its being microscopic and nonlocal, but the nonlocality of our theory is found to have small, though not negligible, effects. Near the transition temperature the free-energy expression for planar phase boundaries is examined by an asymptotic expansion method.

I. INTRODUCTION

A very basic concept in the theory of superconductivity is that additional energies must be associated with the formation of normal-superconducting (*NS*) phase boundaries. Such surface energies are the analog of surface tensions at liquid-vapor interfaces. As first noted by London, this concept must be introduced even to explain one of the most fundamental properties of superconductors, the Meissner effect. In fact, flux exclusion from superconductors would be impossible if no superconductors had positive surface energies to prevent flux penetration through the formation of many fine normal domains in the superconducting bulk. Superconductors with positive surface energies are now classified as type I, to distinguish them from type-II superconductors with negative surface energies whose magnetic properties are now known to be very different.

The early London theory on the electrodynamics of superconductors predicts a negative definite surface energy for all superconductors. The first theory which allows the possibility of a positive surface energy is the celebrated phenomenological theory of Ginzburg and Landau (GL).[1] This theory assumes that all superconductors are characterized by a single material constant—the GL parameter κ_{GL}. It predicts that a superconductor is type I or II depending on whether κ_{GL} is smaller or larger than a critical value $1/\sqrt{2}$.

The GL theory was proposed for the vicinity of the transition temperature T_c. A rather similar model was used by Bardeen[2] to investigate the surface energies for temperatures near absolute zero. Another model, based on the Gorter-Casimir two-fluid concept and qualitatively valid at all temperatures, was also briefly discussed. This last model, together with a variant to incorporate the existence of energy gaps in superconductors, was then investigated by Lewis[3] using variational methods.

These studies of the surface energies in superconductors were all done before the successful development of a microscopic theory of superconductivity by Bardeen, Cooper, and Schrieffer (BCS).[4] Since then, Gor'kov[5] and Bogoliubov[6] have formulated two alternative generalizations of the BCS theory to inhomogeneous problems. The microscopic theories, now well established as the correct theories of superconductivity phenomena, involve nonlocal integral equations in general and reduce to the local GL equations only when the sample is dirty, or, in the case of clean samples, when the temperature T is very close to T_c. The Bardeen-Lewis theories, being local and phenomenological in nature, must therefore be improved, especially for pure superconductors at low temperatures.

The microscopic theories of inhomogeneous superconductors have so far been applied successfully mostly to cases when a perturbative approach is possible due to the presence of certain small

parameters. Examples are when $T \simeq T_c$, when the sample is dirty, or when the order parameter is everywhere small. The theories have not been used to study the *NS*-wall energy for pure superconductors at low temperatures (except in some limiting cases[7]) because no perturbative approaches seem to be available. The hope for carrying out such a study arose only very recently when Bardeen, Kümmel, Jacobs, and Tewordt (BKJT)[8] reformulated the Bogoliubov theory into a WKBJ variational scheme, to study isolated vortex lines in pure superconductors. This method has since been applied by Kümmel[9] to study *NS* phase contacts in extreme type-I superconductors ($\kappa_{GL} = 0$), for which the magnetic field effects can be totally ignored. A general nonlocal theory of *NS*-phase boundaries valid for all κ_{GL} values is nevertheless still lacking.

In the original Bogoliubov theory of inhomogeneous superconductors, the particle and hole components of the elementary-excitation wave functions satisfy two coupled second-order linear differential equations which are now known as the Bogoliubov equations. These equations are much like the Schrödinger equations for a nonrelativistic spin-$\frac{1}{2}$ particle of charge $2e$ (e being the electron charge) moving in a vector potential $\vec{A}(\vec{r})$ and an off-diagonal complex pair potential $\Delta(\vec{r})$.[10] The vector potential $\vec{A}$ must be determined self-consistently via the Maxwell equations and a current expression. The pair potential Δ is to be determined by a relation now known as the gap equation. Both the current expression and the gap equation involve summations of quadratic forms of all eigensolutions of the Bogoliubov equations which render the exact solution of this set of equations a formidable task. The BKJT reformulation of this theory introduced two important ideas:

(i) The Bogoliubov equations are solved by a WKBJ method which reduces the two coupled second-order linear differential equations to two nonlinear first-order ones. We wish to emphasize that the main purpose of this step is to remove the rapidly oscillating factors in the wave functions, thereby making numerical solution of the equations much easier, rather than merely to reduce the orders of the equations.

(ii) The self-consistent conditions on Δ and $\vec{A}$ are replaced by a minumum principle on a Gibbs free-energy functional [cf. Eq. (2.2)], treating both Δ and $\vec{A}$ as trial functions. The forms of these functions must be guessed through physical arguments, allowing only a few adjustable parameters to be determined by the minimum principle.

This WKBJ variational scheme is a powerful tool for microscopic investigations of many basic problems concerning pure inhomogeneous superconductors at low temperatures, when no perturbative approaches are possible. One such problem is the properties of isolated vortex lines already studied by BKJT. The formation of *NS*-phase boundaries is another such problem, to which we address ourselves in the present paper.

The purposes of this work include (a) to formulate the *NS*-phase-boundary problem in the context of a microscopic theory, using the BKJT reformulation of the Bogoliubov theory; (b) to see how the surface energy arises in a nonlocal theory and, in particular, to see how nonlocality affects the formation of a phase wall; (c) to develop a systematic scheme for the numerical investigation of quantitative aspects of the problem; and (d) to provide a simpler, and therefore better, example for investigating a mysterious feature of the BKJT theory first discovered by Cleary,[11] namely, the appearance of a series of unexpected terms in the expansion of the BKJT free-energy expression in the vicinity of T_c,[12] besides those terms reproducing the GL[1] and Neumann-Tewordt theories.[13,14]

In Sec. II we show how the WKBJ method, as introduced by BKJT, must be generalized slightly in order to solve the Bogoliubov equations for the *NS*-wall problem. We then present formulas for calculating the density of states in such a system for energies both below and above the equilibrium gap.

In Sec. III, the BKJT expression for the Gibbs free energy is expressed in terms of the density of states, and is rewritten, together with the relevant equations to be solved for its calculation, in terms of dimensionless variables conveniently introduced for this problem. Being properly defined to contain no bulk energies, the minimum of this free-energy functional gives directly an upper-bound estimation of the desired surface energy of a planar *NS* wall.[15]

The wall energy of an ideal boundary, defined by mutually complementary step functions for the space dependence of the order parameter and the field, is calculated in Sec. III. This simple exercise serves as a qualitative guidance to a more elaborate numerical calculation of the surface energy at $T = 0$ which we present in Sec. IV. Simple trial functions of one adjustable parameter each are chosen for both Δ and $\vec{A}$. The results are compared with a corresponding variational study of the GL functional. Possible improvement of our zero-temperature calculation is discussed.

In Sec. VI, the microscopic free-energy expression for the planar-*NS*-wall problem is expanded near T_c, mainly to compare with a corresponding study of the isolated-vortex-line case by Cleary[11] and Jacobs.[12] In our expansion, as well as in theirs, the Ginzburg-Landau-Neumann-Tewordt[1,13,14] series is recovered together with another series

of mysterious anomalous terms as first discovered by Cleary. The terms in the latter series have orders in $(1-T/T_c)^{1/2}$ lying between those of the terms of the former. No attempts have been successful in resolving this puzzle, but we believe that the *NS*-wall problem is a simpler, and therefore better, example for investigating it. This follows since in the *NS*-wall problem, only Cartesian instead of cylindrical coordinates are needed, and one finds continuous rather than discrete spectrum below the gap.

Finally, a short conclusion is presented in Sec. VII, and two Appendixes are attached, one on some mathematical details, and the other presenting a general asymptotic-expansion formula useful for the high-temperature expansion.

II. SOLUTION OF BOGOLIUBOV EQUATIONS BY WKBJ METHOD

According to the BKJT theory,[8] the essential steps for studying an inhomogeneous state in a pure superconductor are the following:

(i) Variational forms must first be chosen for the pair potential $\Delta(\vec{r})$ and the magnetic field $\vec{h}(\vec{r})$ which may contain some adjustable parameters. In a special gauge the chosen form of $\vec{h}$ determines the vector potential $\vec{A}$.

(ii) The Bogoliubov equations, as stated below, must then be solved by the WKBJ method:

$$E_n U_n(\vec{r}) = [(2m_e)^{-1}(-i\vec{\nabla} - e\vec{A})^2 - E_F] \times U_n(\vec{r}) + \Delta(\vec{r})\, V_n(\vec{r}), \quad (2.1a)$$

$$E_n V_n(\vec{r}) = -[(2m_e)^{-1}(i\vec{\nabla} - e\vec{A})^2 - E_F] \times V_n(\vec{r}) + \Delta^*(\vec{r}) U_n(\vec{r}). \quad (2.1b)$$

In these equations, m_e, e, and E_F are the mass, charge, and Fermi energy of the electrons, and U_n, V_n are the particle and hole components of the quasiparticle wave functions that correspond to the eigenenergy E_n. Throughout this paper we let $\hbar = c$ = Boltzmann constant = 1.

(iii) The resultant quasiparticle spectrum E_n should next be used to evaluate the total Gibbs free energy of the system:

$$G_s = -2\beta^{-1} \sum_{E_n>0} \ln(2\cosh\tfrac{1}{2}\beta E_n) + \int \{V^{-1}|\Delta(\vec{r})|^2 + (8\pi)^{-1}[\vec{h}(\vec{r}) - \vec{H}_a]^2\}\, d^3r, \quad (2.2)$$

where $\beta = T^{-1}$, and V is the interaction parameter. For the *NS*-wall problem, the applied field H_a is equal to the thermodynamic critical field H_c. It is also convenient to remove all wall-independent energies from G_s and calculate

$$\Delta G = G_s - G_R, \quad (2.3)$$

where G_R is the corresponding free energy of a reference system made of a normal half-space and a *separate* superconducting half-space in the Meissner state. The field is H_c in the former and zero in the latter.

(iv) Finally, the free energy G_s (or equivalently the difference ΔG) should be minimized with respect to the adjustable parameters in Δ and $\vec{A}$. The final minimum value of the free-energy difference ΔG for the *NS*-wall problem is by definition an upper-bound estimation of the surface energy σ of the phase boundary.

In this section we first develop a form of the WKBJ method to solve the Bogoliubov equations (2.1) for the *NS*-wall problem. We then obtain formulas for calculating the density of states below as well as above the equilibrium gap $\Delta_\infty(T)$. To do so we must first know the qualitative behavior of Δ and h in such a system which is well known through GL-theory studies.[1,16] Far away from the wall, we expect $\Delta = 0$, $h = H_c$ in the normal side, and $\Delta = \Delta_\infty$, $h = 0$ in the superconducting side. In the wall region exact analytic solutions have been found for Δ and h only in the limiting cases $\kappa_{GL} = 0$ or ∞. In both cases a sharp edge exists at which Δ departs from zero which is actually a misleading feature not true for general κ_{GL} values. It can be shown that, for general κ_{GL}, the sharp edge must be rounded off into a Gaussian tail whose width is the geometric mean of the coherence length $\xi(T)$ and the penetration depth $\lambda(T)$ in the GL theory. For $\kappa_{GL} = 0$ the magnetic field does not penetrate into the S region in the scale $\xi(T)$, in which Δ rises up first linearly, then to saturate at the bulk value Δ_∞. For $\kappa_{GL} = \infty$, the field smoothly reduces to zero with a vanishing slope at the edge, while Δ rises up initially according to the square root of distance, both in the same scale $\lambda(T)$. For intermediate κ_{GL}, one expects h and Δ to vary at different scales, but both are likely to vary monotonically.

With the above picture in mind, we now seek the WKBJ method to solve the Bogoliubov equations (2.1) for the *NS*-phase wall. For the convenience of our variational solution, however, we ignore the possibility of a Gaussian tail, and assume that the N and S regions are always separated by a sharp edge. The original version of the WKBJ approximation, as developed by BKJT for the isolated-vortex problem,[8] must be modified in order to be applicable to the present problem. The reason is that in the single-vortex problem a gauge can be found in which the vector potential $A(\vec{r})$ is small everywhere [more precisely one has $|e\vec{A}(\vec{r})| \ll k_F$ for all $\vec{r}$]. One can, therefore, in that gauge ignore completely the A^2 term in Eqs. (2.1). The condition is clearly not satisfied in the *NS*-wall problem due to the presence of a normal region of macroscopic size in a finite magnetic field H_c.

Instead, in this problem one can at most find a gauge in which the vector potential is large in the normal region only. But in this gauge, as we shall see below, it is possible to modify the original BKJT version of the WKBJ method to properly take care of the large A^2 term in the normal region. We can then verify rigorously what we have expected from intuition. Namely, if only one ignores all effects associated with Landau-orbit quantization, which are usually small in superconductors anyway, then all results are independent of whatever happens in the normal region. This means that we could solve the problem essentially correctly by neglecting the A^2 term in Eqs. (2.1) irrespective of its large magnitude in the normal region. Another point of view to this less rigorous approach would be to imagine that we were considering a fictitious system. In this system no magnetic fields would be applied in the normal region except right at the boundary where their magnitudes would still be H_c. In such an alternative approach one could use the original version of the WKBJ approximation without modification, in a suitable gauge. Nevertheless, we do not adopt this alternative approach because we think that artifices should be avoided if only possible. A bonus reward of our more elaborate approach, as we shall see, is the discovery of a partial-Landau-orbit-quantization phenomenon, which leads to a continuous but oscillating density of states above the equilibrium gap.

We choose our coordinates such that the sharp edge of the phase boundary constitutes the xy plane with the z axis pointing from the N side to the S side. The magnetic field $\vec{h}$ is taken to be along the positive y axis, and the gauge is chosen such that the vector potential $\vec{A}$ has only an x component given by

$$A(z) \equiv A_x(z) = -\int_z^\infty h(z')\,dz' . \tag{2.4}$$

This is the gauge in which A stays small throughout the superconducting region. For $z<0$, we can write $A(z) = H_c(z - \lambda_{eff})$, where

$$\lambda_{eff} = H_c^{-1} \int_0^\infty h(z')\,dz' \tag{2.5}$$

is the effective penetration depth of the field in this problem.

In this choice of gauge, $\Delta(z)$ is real. It is clear that the eigensolutions of (2.1) are of the form

$$\begin{pmatrix} U \\ V \end{pmatrix} = e^{i(k_x x + k_y y)} \begin{pmatrix} f_+(z) \\ f_-(z) \end{pmatrix} . \tag{2.6}$$

The essential step of our modified WKBJ method consists of writing $\hat{f}(z) \equiv (f_+, f_-)^{tr}$ in the form

$$\hat{f}(z) = \begin{pmatrix} g_+(z)\phi_+(z) \\ g_-(z)\phi_-(z) \end{pmatrix} - \text{c.c.} , \tag{2.7}$$

where $\phi_\pm$ are the usual WKBJ solutions of the Schrödinger equations which are obtained from Eqs. (2.1) by setting $E_n = 0$ and by switching off the pair potential but not the vector potential:

$$\phi_\pm = [k_{z_0}^{(\pm)}(z)]^{-1/2} \exp\left[i \int_{z_t^{(\pm)}}^z k_{z_0}^{(\pm)}(z')\,dz' \right], \tag{2.8}$$

where the local wave numbers $k_{z_0}^{(\pm)}(z)$ are the positive solutions of

$$[k_x \mp eA(z)]^2 + k_y^2 + [k_{z_0}^{(\pm)}(z)]^2 = k_F^2 , \tag{2.9}$$

and $z_t^{(\pm)}$ are the classical turning points where $k_{z_0}^{(\pm)}(z) = 0$. For $z \to \infty$ we have $k_{z_0}^{(\pm)}(z) \to k_{z_0} = (k_F^2 - k_x^2 - k_y^2)^{1/2}$. We shall only consider states with real k_{z_0}, as mainly only these states are affected when one turns on the pair potential in the superconducting side. We anticipate that $g_\pm(z)$ are slowly varying in the atomic scale [more precisely, $|(d/dz) g_\pm(z)| \sim \xi(T)^{-1} |g_\pm(z)|$] for all solutions of (2.1) with $E \sim \Delta_\infty(T) \ll E_F$. Substituting Eq. (2.7) into (2.1) and consistently ignoring terms of order $(k_F\xi)^{-1}$ with respect to one, we obtain

$$E g_+ = -\frac{i}{m_e} k_{z_0}^{(+)}(z) \frac{d}{dz} g_+ + \Delta(z)\, Q_+(z) g_- , \tag{2.10a}$$

$$E g_- = +\frac{i}{m_e} k_{z_0}^{(-)}(z) \frac{d}{dz} g_- + \Delta(z) Q_-(z) g_+ , \tag{2.10b}$$

where the phase factors

$$Q_\pm(z) \equiv \exp\left[\pm 2ie\,(k_x/k_{z_0}) \int_z^\infty A(z')\,dz' \right] \tag{2.11}$$

are originally of a form

$$\exp\left[\mp i \int_{z_t^{(+)}}^z k_{z_0}^{(+)}\,dz' \pm i \int_{z_t^{(-)}}^z k_{z_0}^{(-)}\,dz' \right].$$

To obtain the simpler form (2.11) we have allowed E_F to have a very minute $\vec{k}_\parallel = (k_x, k_y)$ dependence, so that the Fermi energy at any $\vec{k}_\parallel$ always corresponds to an unperturbed particle or hole level.[17] Imagining the superconducting side to have a finite thickness D one must have

$$\int_{z_t^{(\pm)}}^D k_{z_0}^{(\pm)}(z')\,dz' = 2\nu_\pm \pi ,$$

where $\nu_\pm$ are integers. The phase factors then become $\exp\left[\pm i \int_z^D (k_{z_0}^{(+)} - k_{z_0}^{(-)})\,dz' \right]$. One further realizes that the factors $\Delta(z)$, which are multiplied by $Q_\pm$, vanish for $z<0$; and for $z>0$,

$$|e\vec{A}(\vec{r})| \lesssim eH_c\lambda_{eff} \sim \max\{[\xi(T)\lambda(T)]^{-1/2},\ \xi(T)^{-1}\} \ll k_F .$$

One can therefore use

$$k_{z_0}^{(\pm)}(z) \cong k_{z_0} \pm eA(z)\, k_x/k_{z_0} \quad (\text{for } z>0) \tag{2.12}$$

to obtain the forms in Eq. (2.11).

For $z<0$ the general solution of (2.10) is clearly of a form

$$\hat{g}=\begin{pmatrix} A\exp\left[im_eE\int_{z_t}^{z}(k_{z_0}^{(+)})^{-1}\,dz\right. \\ B\exp\left[-im_eE\int_{z_t}^{z}(k_{z_0}^{(-)})^{-1}\,dz\right] \end{pmatrix}, \tag{2.13}$$

where we have assumed that the classical turning points are in the normal side as is true for essentially all states of real k_{z_0} except for a negligible portion of the Fermi surface.

For $z>0$ it is convenient to let

$$\hat{g}=\begin{pmatrix} Q_+^{1/2} & \mathcal{J}_+ \\ Q_-^{1/2} & \mathcal{J}_- \end{pmatrix}. \tag{2.14}$$

If we further assume that

$$\hat{\mathcal{J}}=\begin{pmatrix} e^{i\eta(z)/2} \\ e^{-i\eta(z)/2} \end{pmatrix} e^{i\xi(z)}, \tag{2.15}$$

the quantities $\eta(z)$ and $\xi(z)$ must then satisfy

$$(2m_e)^{-1}k_{z_0}\frac{d\eta}{dz}+\Delta(z)\cos\eta=E+\frac{e}{m}k_xA(z), \tag{2.16a}$$

$$m_e^{-1}k_{z_0}\frac{d\xi}{dz}=i\Delta(z)\sin\eta. \tag{2.16b}$$

In obtaining Eqs. (2.16) we have again consistently ignored $(k_F\xi)^{-1}$ with respect to one. Equations (2.16) are seen to be essentially identical to Eqs. (4.17) and (4.18) in the paper of BKJT, except for the dimensionless quantities used there which we shall also introduce later.

In order to proceed further we must distinguish between two types of solutions of Eqs. (2.10): the "bound-state" solutions with $E<\Delta_\infty$ and the "scattering-state" solutions with $E>\Delta_\infty$.

A. Bound-State Solutions

For $E<\Delta_\infty$, Eq. (2.16a) should be solved together with the boundary condition $\eta\to\cos^{-1}E/\Delta_\infty$ as $z\to\infty$. [$\cos^{-1}$ is defined to be the principle branch. The other solution $\eta\to-\cos^{-1}E/\Delta_\infty$ is discarded because the corresponding solution of (2.16b) makes $\hat{g}$ grow exponentially as $z\to+\infty$.] One then sees that η is purely real and ξ, aside from a possible real integration constant, is purely imaginary. To match the solutions for $z<0$ with those for $z>0$, we first obtain from Eq. (2.13)

$$\hat{g}(0_-)=\exp\left(\alpha-\frac{im_eE}{eH_c}\sin^{-1}\frac{k_x}{(k_F^2-k_y^2)^{1/2}}\right)\times\begin{pmatrix} \exp\left(-\frac{\beta}{2}+\frac{\pi im_eE}{2eH_c}\right) \\ \exp\left(+\frac{\beta}{2}-\frac{\pi im_eE}{2eH_c}\right) \end{pmatrix}, \tag{2.17}$$

where we have set $A=e^{\alpha-\beta/2}$, $B=e^{\alpha+\beta/2}$, and we have ignored $eH_c\lambda_{eff}$ ($\sim\xi^{-1}$) with respect to k_x($\sim k_F$) in the arcsine function. It is then clear that continuity of $\hat{g}$ at $z=0$ implies

$$\alpha-\frac{im_eE}{eH_c}\sin^{-1}\frac{k_x}{(k_F^2-k_y^2)^{1/2}}=i\xi(0), \tag{2.18a}$$

$$\beta-\frac{\pi im_eE}{eH_c}=-i\eta(0)-\frac{2iek_x}{k_{z_0}}\int_0^\infty A(z)\,dz. \tag{2.18b}$$

Since A and B must both be real in order for $\hat{f}$ to satisfy the same boundary condition at the classical turning points for all $E\lesssim\Delta_\infty$ as when $E=0$, we may set $\mathrm{Im}\alpha=\frac{1}{2}m\pi$, $\mathrm{Im}\beta=n\pi$, with m and n being both even or both odd. Equation (2.18b) then implies that $\mathrm{Re}\beta=0$ and that, denoting $\eta(0)$ by η_0,

$$\frac{\pi m_eE}{eH_c}-\eta_0-\frac{2ek_x}{k_{z_0}}\int_0^\infty A(z)\,dz=n\pi. \tag{2.19}$$

The quantity η_0 may be obtained by solving Eq. (2.16a) in the region $z>0$ together with the boundary condition at $z=+\infty$, and is therefore uniquely related to $\vec{k}_\parallel$ and E. The density of states for $E<\Delta_\infty$ at given $\vec{k}_\parallel$ and spin, but including both electron and hole contributions, can be obtained from (2.19):

$$\rho_{\vec{k}_\parallel}(E)=\frac{m_e}{eH_c}-\frac{1}{\pi}\frac{d\eta_0(E)}{dE}. \tag{2.20}$$

The corresponding density of states of the standard reference system has contributions only from the normal half-space and may be obtained by requiring $g(0)$ of (2.17) real. The result is[18]

$$\rho_{\vec{k}_\parallel}^{(R)}(E)=\frac{m_e}{eH_c}=\frac{m}{\pi}\left[\int_{z_t^{(+)}}^{0}(k_{z_0}^{(+)})^{-1}\,dz+\int_{z_t^{(-)}}^{0}(k_{z_0}^{(-)})^{-1}\,dz\right]. \tag{2.21}$$

The difference in density of states between our NS system and the standard reference system, at given $\vec{k}_\parallel$, spin, and for $E<\Delta_\infty(T)$, is therefore simply

$$\Delta\rho_{\vec{k}_\parallel}(E)=-\frac{1}{\pi}\frac{d\eta_0(E)}{dE}. \tag{2.22}$$

By using Eq. (2.16a), which gives

$$\eta_0=\cos^{-1}\frac{E}{\Delta_\infty}\int_0^\infty\frac{2m}{k_{z_0}}\left(E+\frac{ek_x}{m}A(z)-\Delta(z)\cos\eta(z)\right)dz, \tag{2.23}$$

we can also write Eq. (2.22) as

$$\Delta\rho_{\vec{k}_\parallel}(E)=\frac{1}{\pi}\frac{1}{(\Delta_\infty^2-E^2)^{1/2}}+\frac{2m}{\pi k_{z_0}}\int_0^\infty\left(1+\Delta(z)\sin\eta\frac{d\eta}{dE}\right)dz, \tag{2.24}$$

which suggests, as is borne out later, that the

density of states for an *NS* system may diverge just below the equilibrium gap.

B. Scattering-State Solutions

We now consider solutions with $E > \Delta_\infty$. For $z < 0$, the most general solution is still given by (2.13). For $z > 0$, Eqs. (2.16) now require that both η and ξ be complex quantities. Following BKJT, we let $\eta = \eta_1 - i\eta_2$ and $\xi = \xi_1 - i\xi_2$, so that η_1, η_2, ξ_1, ξ_2 are all real functions of z. Equations (2.16) then become a set of four coupled equations as in the single-vortex problem:

$$\frac{k_{z0}}{2m_e}\frac{d\eta_1}{dz} + \Delta(z)\cos\eta_1\cosh\eta_2 = E + \frac{ek_x}{mc}A(z), \tag{2.25a}$$

$$\frac{k_{z0}}{2m_e}\frac{d\eta_2}{dz} = \Delta(z)\sin\eta_1\sinh\eta_2, \tag{2.25b}$$

$$\frac{k_{z0}}{m_e}\frac{d\xi_1}{dz} = \Delta(z)\cos\eta_1\sinh\eta_2, \tag{2.25c}$$

$$\frac{k_{z0}}{m_e}\frac{d\xi_2}{dz} = -\Delta(z)\sin\eta_1\cosh\eta_2. \tag{2.25d}$$

It is clear that if $(\eta_1, \eta_2, \xi_1, \xi_2)$ forms a set of solutions of these equations, so must also the set $(\eta_1, -\eta_2, -\xi_1, \xi_2)$ at the same E. Expression (2.15), therefore, now constitutes only a particular solution. The general solution is given by

$$\hat{\mathcal{J}} = A_+\hat{\mathcal{J}}_+ + A_-\hat{\mathcal{J}}_- \tag{2.26}$$

with

$$\hat{\mathcal{J}}_\pm = \begin{pmatrix} e^{(i\eta_1 \pm \eta_2)/2} \\ e^{(-i\eta_1 \pm \eta_2)/2} \end{pmatrix} e^{\pm i\xi_1 + \xi_2}, \tag{2.27}$$

where $(\eta_1, \eta_2, \xi_1, \xi_2)$ satisfy Eqs. (2.25) *and* the boundary conditions $\eta_1 \to 0$, $\eta_2 \to +\cosh^{-1}(E/\Delta_\infty)$ as $z \to 0$. (By $\cosh^{-1}$ we again mean the principle branch.) Since ξ_1 and ξ_2 still contain arbitrary integration constants, we may without loss of generality take $A_+ = e^{i\rho}$, $A_- = Ce^{i\rho}$, with real C and ρ. As before, we assume that the superconducting side has a finite thickness D and require our solutions to satisfy the same boundary condition at $z = D$ for all $E \sim \Delta_\infty \ll E_F$ as when $E = 0$. This is equivalent to requiring $\hat{g}_\pm$ real at $z = +D$ which gives $\rho = m\pi$ and

$$\xi_1(z = +D) = n\pi, \tag{2.28}$$

with m and n being integers. Without loss of generality we may take $m = 0$ which implies $\rho = 0$. Next we require the solutions for the regions $z > 0$ and $z < 0$ to match at $z = 0$. This gives, with $\Gamma \equiv (ek_x/k_{z0}) \times \int_0^\infty A(z)\,dz$,

$$A\exp\left[i\frac{m_eE}{eH_c}\left(\frac{\pi}{2} - \sin^{-1}\frac{k_x}{(k_F^2 - k_y^2)^{1/2}}\right)\right] = e^{\xi_{20}}\left\{\exp\left[\tfrac{1}{2}\eta_{20} + i(\tfrac{1}{2}\eta_{10} + \Gamma + \xi_{10})\right] + C\exp\left[-\tfrac{1}{2}\eta_{20} + i(\tfrac{1}{2}\eta_{10} + \Gamma - \xi_{10})\right]\right\}, \tag{2.29a}$$

$$B\exp\left[-i\frac{m_eE}{eH_c}\left(\frac{\pi}{2} + \sin^{-1}\frac{k_x}{(k_F^2 - k_y^2)^{1/2}}\right)\right] = e^{\xi_{20}}\left\{\exp\left[-\tfrac{1}{2}\eta_{20} - i(\tfrac{1}{2}\eta_{10} + \Gamma - \xi_{10})\right] + C\exp\left[\tfrac{1}{2}\eta_{20} - i(\tfrac{1}{2}\eta_{10} + \Gamma + \xi_{10})\right]\right\}, \tag{2.29b}$$

where we have used η_{10}, η_{20}, ξ_{10}, ξ_{20} to denote the values of η_1, η_2, ξ_1, ξ_2, respectively, at $z = 0$. Moving the left phase factors to the right, the right $e^{\xi_{20}}$ factors to the left, taking the imaginary parts of both sides, and bearing in mind that both A and B are real constants, we obtain

$$\sin(\xi_{10} - \Xi + \Theta) = Ce^{-\eta_{20}}\sin(\xi_{10} + \Xi - \Theta), \tag{2.30a}$$

$$\sin(\xi_{10} + \Xi + \Theta) = Ce^{+\eta_{20}}\sin(\xi_{10} - \Xi - \Theta), \tag{2.30b}$$

where

$$\Xi = \frac{\pi m_eE}{2eH_c} - \tfrac{1}{2}\eta_{10} - \Gamma$$

and

$$\Theta = \frac{m_eE}{eH_c}\sin^{-1}\frac{k_x}{(k_F^2 - k_y^2)^{1/2}}.$$

Equations (2.30a) and (2.30b) are the analog of Eqs. (4.25a) and (4.25b) of Ref. 8, but are trickier to analyze than the latter. Rewriting Eqs. (2.30) into the form

$$\tan\xi_{10}/\tan(\Theta - \Xi) = (Ce^{-\eta_{20}} + 1)/(Ce^{-\eta_{20}} - 1), \tag{2.31a}$$

$$\tan\xi_{10}/\tan(\Theta + \Xi) = (Ce^{\eta_{20}} + 1)/(Ce^{\eta_{20}} - 1), \tag{2.31b}$$

we can eliminate ξ_{10} to obtain

$$C^2 - 2C\sinh\eta_{20}(\sin2\Theta/\sin2\Xi) - 1 = 0. \tag{2.32}$$

Since Θ, Ξ, and η_{20} are fixed functions of $\vec{k}_\parallel$ and E (but not ξ_{10} which is why we eliminated it), and because Eq. (2.32) admits two real solutions for any set of real values of η_{20}, Θ, and Ξ, we conclude that there exist two linearly independent scattering states for each given set of values for $\vec{k}_\parallel$, E, and spin, satisfying the boundary conditions at $z = 0$ and at the classical turning points [at $z = D$ as well if (2.28) is further satisfied].

We denote the two solutions of Eq. (2.32) by C_1 and C_2. The corresponding two solutions for ξ_{10} of (2.30) will be denoted with the superscripts (1) and (2). These, combined with Eq. (2.28), allow us to determine the discrete energy eigenvalues and therefore the density of states of the scattering states. In doing so we need the relation

$$\xi_1(z=D) = \xi_{10} + \frac{m_e}{k_{z_0}} \int_0^D \Delta(z)\, \cos\eta_1\, \sinh\eta_2\, dz$$

$$= \xi_{10} + \frac{m_e D}{k_{z_0}} (E^2 - \Delta_\infty^2)^{1/2} + \frac{m_e}{k_{z_0}} \int_0^\infty [\Delta(z)\, \cos\eta_1\, \sinh\eta_2 - (E^2 - \Delta_\infty^2)^{1/2}]\, dz\,, \quad (2.33)$$

which follows from Eq. (2.25c).

The density of states for each of the two scattering modes follows from Eqs. (2.28) and (2.33):

$$\rho_{k_\parallel}^{(i)}(E) = \pi^{-1} \frac{d}{dE} \xi_{10}^{(i)} + \frac{m_e D}{\pi k_{z_0}} \frac{E}{(E^2 - \Delta_\infty^2)^{1/2}} + \frac{m_e}{\pi k_{z_0}} \frac{d}{dE} \int_0^\infty [\Delta(z)\, \cos\eta_1\, \sinh\eta_2 - (E^2 - \Delta_\infty^2)^{1/2}]\, dz\,. \quad (2.34)$$

In Appendix A it is shown that

$$\xi_{10}^{(1)} + \xi_{20}^{(2)} = 2\Xi + \Psi(E)\,, \quad (2.35)$$

where $\Psi(E)$ is a quasiperiodic function of period $eH_c/m \ll \Delta_\infty$ and averages to zero within each period. The sum of the density of states over the two scattering states (each being a coherent mixture of particle and hole) is therefore

$$\rho_{k_\parallel}(E) = \sum_{i=1,2} \rho_{k_\parallel}^{(i)}(E) \cong \frac{m_e}{eH_c} + \frac{2m_e D}{\pi k_{z_0}} \frac{E}{(E^2 - \Delta_\infty^2)^{1/2}} + \frac{1}{\pi} \frac{d}{dE} \left(-\eta_{10}(E) + \frac{2m_e}{k_{z_0}} \int_0^\infty [\Delta(z)\, \cos\eta_1 \times \sinh\eta_2 - (E^2 - \Delta_\infty^2)^{1/2}]\, dz \right), \quad (2.36)$$

where we have ignored a Ψ-dependent term (cf. Appendix A).

The first two terms are easily seen to constitute the corresponding density of states of the standard reference system:

$$\rho_{k_\parallel}^{(R)}(E) = \frac{m_e}{eH_c} + \frac{2m_e D}{\pi k_{z_0}} \frac{E}{(E^2 - \Delta_\infty^2)^{1/2}}\,. \quad (2.37)$$

The difference in density of states between our *NS* system and the standard reference system, at fixed $\vec{k}_\parallel$, spin, and for $E > \Delta_\infty$, is therefore

$$\Delta\rho_{k_\parallel}(E) = \frac{1}{\pi} \frac{d}{dE} \left(-\eta_{10}(E) + \frac{2m_e}{k_{z_0}} \times \int_0^\infty [\Delta(z)\, \cos\eta_1\, \sinh\eta_2 - (E^2 - \Delta_\infty^2)^{1/2}]\, dz \right). \quad (2.38)$$

A word about the neglected $\Psi(E)$ term: Its existence is clearly related to Landau-orbit quantization which is a subject that we wish to consistently neglect in this paper. *It is curious to notice, however, that Landau-orbit quantization does play a role here even though we are not dealing with closed orbits*! *The reason is that the elementary-excitation wave functions are actually made of linear combinations of open and closed orbits due to the possibility of multiple Andreev scattering*[19] *at the NS-phase boundary*. That the probability of finding a closed orbit is neither one nor zero explains why one gets a continuous but oscillating density-of-states function in the absence of sample-size quantization. Unfortunately our magnetic field strength is limited by the existing values for the thermodynamic critical field H_c of type-I superconductors which makes observation of this partial-Landau-quantization phenomenon difficult.

III. FREE ENERGY

In Sec. II we have obtained expressions for the difference in density of states at fixed $\vec{k}_\parallel$ and spin between our *NS* system and the standard reference system [i.e., Eq. (2.22) for $E < \Delta_\infty$ and Eq. (2.38) for $E > \Delta_\infty$]. Using them, the free-energy difference can be written

$$\Delta G[\Delta(\vec{r}), \vec{A}(\vec{r})] = -\frac{2\beta^{-1}}{(2\pi)^2} \int d^2k_\parallel \int_0^\infty dE \times \Delta\rho_{K_\parallel}(E)\, \ln(2\cosh\tfrac{1}{2}\beta E) + \frac{1}{V} \int_0^\infty [\Delta^2(z) - \Delta_\infty^2]\, dz + \frac{1}{8\pi} \int_0^\infty \{[h(z) - H_c]^2 - H_c^2\}\, dz\,. \quad (3.1)$$

Partial integration of the first term gives

$$+\frac{2\beta^{-1}}{(2\pi)^2} \int d^2k_\parallel \ln(2\cosh\tfrac{1}{2}\beta E) \int_E^\infty dE'\, \Delta\rho_{k_\parallel}(E') \Big|_0^\infty - \frac{1}{(2\pi)^2} \int d^2k_\parallel \int_0^\infty dE\, \tanh\tfrac{1}{2}\beta E \int_E^\infty dE'\, \Delta\rho_{k_\parallel}^*(E'),$$

of which the first term vanishes since the total number of single-particle states is unchanged when the system turns superconducting.[20]

For $E > \Delta_\infty$ we use Eq. (2.38) to find

$$\int_E^\infty dE'\, \Delta\rho_{k_\parallel}(E') = \pi^{-1} \eta_{10}(E) - \frac{2m}{\pi k_{z_0}} \times \int_0^\infty [\Delta(z)\, \cos\eta_1\, \sinh\eta_2 - (E^2 - \Delta_\infty^2)^{1/2}]\, dz\,.$$

For $E < \Delta_\infty$, Eq. (2.22) gives

$$\int_E^\infty dE'\, \Delta\rho_{k_\parallel}(E') = -\int_0^E dE'\, \Delta\rho_{k_\parallel}(E')$$

$$= \pi^{-1}[\eta_0(E) - \eta_0(0)],$$

where we have again observed the conservation of total number of states, anticipating the $k_{\parallel}$ integration in Eq. (3.1). Thus the free-energy functional can be rewritten as a sum of four terms,

$$\Delta G = \Delta G_B + \Delta G_S + \Delta G_P + \Delta G_M . \tag{3.2}$$

The first term comes from the bound-state contributions:

$$\Delta G_B = \frac{1}{4\pi^3}\int d^2k_{\parallel}\int_0^{\Delta_\infty} dE\,[\eta_0(0) - \eta_0(E)]\tanh\tfrac{1}{2}\beta E. \tag{3.3}$$

The second term is the scattering-state contributions:

$$\Delta G_S = \frac{1}{4\pi^3}\int d^2k_{\parallel}\int_{\Delta_\infty}^{\infty} dE\,\tanh\tfrac{1}{2}\beta E \times\left(\frac{2m_e}{k_{z_0}}\int_0^{\infty}[\Delta(z)\cos\eta_1\sinh\eta_2 - (E^2-\Delta_\infty^2)^{1/2}]\,dz - \eta_{10}(E)\right). \tag{3.4}$$

The third term, which depends on the pair potential only, corrects for the double counting of the interaction energy[2]:

$$\Delta G_P = V^{-1}\int_0^{\infty}[\Delta^2(z) - \Delta_\infty^2]\,dz . \tag{3.5}$$

Finally, the last term takes into account the magnetic energy:

$$\Delta G_M = (8\pi)^{-1}\int_0^{\infty}\{[h(z) - H_c]^2 - H_c^2\}\,dz . \tag{3.6}$$

It is more convenient to introduce the following dimensionless variables:

$$\Lambda = E/\Delta_\infty , \tag{3.7a}$$

$$\zeta = (2m\Delta_\infty/k_{z_0})\,z = (2/\pi)(k_F/k_{z_0})[z/\xi_\Delta(T)] , \tag{3.7b}$$

$$F(\zeta) = (ek_x/mc\Delta_\infty)\,A(z) = \tfrac{1}{2}\pi(k_x/k_F)[2eA(z)\,\xi_\Delta(T)] , \tag{3.7c}$$

$$\delta(\zeta) = \Delta(z)/\Delta_\infty , \tag{3.7d}$$

where

$$\xi_\Delta(T) = v_F/\pi\Delta_\infty(T) . \tag{3.7e}$$

[At $T=0$ this definition agrees with that of ξ_0, the BCS coherence length. Near T_c, $\xi_\Delta(T) = (\sqrt{6}/\pi)\xi(T)$ of the GL theory.] We also define $k_x = bk_\rho$, $k_\rho \equiv (k_x^2 + k_y^2)^{1/2} = k_F\cos\alpha$,

$$\Sigma_B = \sum_{b=\pm|b|}[\eta_0(0) - \eta_0(E)] = \pi - \sum_{b=\pm|b|}\eta_0(E) \tag{3.8a}$$

and

$$\Sigma_S = \sum_{b=\pm|b|}\{\int_0^{\infty}[\delta(\zeta)\cos\eta_1\sinh\eta_2 - (\Lambda^2-1)^{1/2}]\,d\zeta - \eta_{10}(E)\} , \tag{3.8b}$$

where in (3.8a) we have used the identity $\Sigma_{b=\pm|b|}\times\eta_0(0) = \pi$ which can be verified easily by Eq. (2.16a).

Using a method introduced by Cleary,[11] it can be established that as $\zeta\to\infty$,

$$\Sigma_S \to \Lambda^{-1}C + \Lambda^{-3}D(\alpha, b), \tag{3.9}$$

where

$$C = \int_0^{\infty}[1 - \delta^2(\zeta)]\,d\zeta ,$$
$$D(\alpha, b) = \int_0^{\infty}[\tfrac{1}{4}(1-\delta^4) - \delta^2F^2 - \delta'^2]\,d\zeta. \tag{3.10}$$

Equation (3.4) is therefore formally divergent and requires the usual Debye frequency cutoff to ensure finite result. Alternatively, we may follow the idea of Ref. 8 to combine ΔG_S and ΔG_P into a single convergent integral by using an identity for $[N(0)V]^{-1}$ [cf. Ref. 8, Eq. (8.16)]. We then obtain

$$\Delta G = \Delta G_B + \Delta G_{SP} + \Delta G_M , \tag{3.11}$$

where [with $N(0) = m^2v_F/2\pi^2$ being the usual electron density of states per spin at the Fermi surface]:

$$\Delta G_B = \tfrac{1}{2}\xi_\Delta N(0)\,\Delta_\infty^2\int_0^{\pi/2}\sin2\alpha\,d\alpha\int_0^1\frac{db}{(1-b^2)^{1/2}} \times\int_0^1 d\Lambda\,\Sigma_B\tanh\tfrac{1}{2}\beta\,\Delta_\infty\Lambda , \tag{3.12}$$

$$\Delta G_{SP} = \tfrac{1}{2}\xi_\Delta N(0)\,\Delta_\infty^2\int_0^{\pi/2}\sin2\alpha\,d\alpha\int_0^1\frac{db}{(1-b^2)^{1/2}} \times\int_1^{\infty} d\Lambda\left(\Sigma_S - \frac{C}{(\Lambda^2-1)^{1/2}}\right)\tanh\tfrac{1}{2}\beta\Delta_\infty\Lambda , \tag{3.13}$$

while for ΔG_M Eq. (3.6) is still the most convenient form.

To find $\eta_0(\Lambda)$ of Eq. (3.8a) we need to solve Eq. (2.16a), which in dimensionless variables becomes

$$\frac{d\eta}{d\zeta} + \delta(\zeta)\cos\eta = \Lambda + F(\zeta) \quad (\text{for } \Lambda < 1). \tag{3.14}$$

The boundary condition now reads $\eta(\infty) = \cos^{-1}\Lambda$.

For $E > \Delta_\infty$ (i.e., $\Lambda > 1$), Eqs. (2.25a) and (2.25b) are changed in dimensionless variables to

$$\frac{d\eta_1}{d\zeta} + \delta(\zeta)\cos\eta_1\cosh\eta_2 = \Lambda + F(\zeta) , \tag{3.15a}$$

$$\frac{d\eta_2}{d\zeta} = \delta(\zeta)\sin\eta_1\sinh\eta_2 , \tag{3.15b}$$

for which the boundary conditions are $\eta_2(\infty) = \cosh^{-1}\Lambda$, $\eta_1(\infty) = 0$. It is very convenient to introduce a third equation to be solved together with Eqs. (3.10a) and (3.10b):

$$\frac{d\eta_3}{d\zeta} = \delta(\zeta)\cos\eta_1\,e^{-\eta_2} - [\Lambda - (\Lambda^2-1)^{1/2}], \tag{3.15c}$$

with the corresponding boundary condition $\eta_3(\infty) = 0$. Equation (3.8b) can then be conveniently written

$$\Sigma_S = \sum_{b=\pm|b|}\eta_{30}(\Lambda) , \tag{3.16}$$

with again η_{30} denoting the value of η_3 at $\zeta = 0$.

Thus our program for calculating the free-energy difference is (i) we must solve the differential equation (3.14) for $0 < \Lambda < 1$ and (3.15a)–(3.15c) for $\Lambda > 1$ in the region $\zeta > 0$ as supplemented by the boundary conditions stated below the equations; (ii) Eqs. (3.8a) and (3.16) are then used to evaluate $\Sigma_{B,S}$; (iii) the free-energy difference is finally calculated using Eqs. (3.6) and (3.11)–(3.13).

IV. SURFACE ENERGY OF IDEAL BOUNDARY

In this section we consider an ideal phase boundary for which

$$\Delta(z) = \Delta_\infty \theta(z), \tag{4.1a}$$

$$h(z) = H_c \theta(-z), \tag{4.1b}$$

where

$$\theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0. \end{cases}$$

It is clear that for $E < \Delta_\infty$, $\eta_0 = \eta_\infty = \cos^{-1}\Lambda$; and for $E > \Delta_\infty$, $\eta_{10} = 0$, $\eta_{20} = \cosh^{-1}\Lambda$, $\eta_{30} = 0$. This gives, for the ideal boundary,

$$\Sigma_B = \pi - 2\cos^{-1}\Lambda, \tag{4.2a}$$

$$\Sigma_S = 0. \tag{4.2b}$$

Substituting these results into Eqs. (3.6), (3.12), and (3.13), one gets $\Delta G_S = \Delta G_M = 0$, and

$$\Delta G = \Delta G_B = \tfrac{1}{2}\pi \xi_\Delta(T) N(0) \Delta_\infty^2(T) \times \int_0^1 (\tfrac{1}{2}\pi - \cos^{-1}\Lambda) \tanh(\tfrac{1}{2}\beta\Delta_\infty\Lambda)\, d\Lambda. \tag{4.3}$$

This expression supplies an upper bound to the surface energy of a physical NS boundary.

At $T = 0$ it is

$$\sigma^{(\text{ideal boundary})} = \tfrac{1}{2}\pi(\tfrac{1}{2}\pi - 1)\xi_0 N(0)\Delta_\infty^2(0) \sim 1.79\xi_0[H_c^2(0)/8\pi], \tag{4.4}$$

which, as we shall see, is already a rather good approximation to the wall energy when $\kappa_{GL} = 0$.

At $T \sim T_c$, we obtain

$$\sigma^{(\text{ideal boundary})} = (\pi^2/32T_c) N(0) \xi_\Delta(T) \Delta_\infty^3(T) \propto (1 - T/T_c). \tag{4.5}$$

We notice that near T_c the surface energy of a physical boundary is, according to GL theory, proportional to $(1 - T/T_c)^{3/2}$. It is also worth noting that the surface energy for an ideal boundary would be infinitely large, if it were calculated from the GL theory, indicating that the microscopic theory suppresses rapid variations of the order parameter much less strongly than the GL theory.

V. NUMERICAL RESULTS AT $T = 0°K$

The ideal boundary studied in Sec. IV is expected to be unphysical. On the other hand, after a period of extensive search, we find that it is unlikely to extend our analytical result to any more realistic choice for the trial functions $\Delta(\vec{r})$ and $h(\vec{r})$. We therefore turn to solving this problem numerically using the IBM 360 computer of the University of Southern California. For the trial functions, we take the following simple functions which reasonably approximate the expected behavior of the boundary:

$$\Delta(z) = \Delta_\infty \tanh[dz/\xi_\Delta(T)], \tag{5.1}$$

$$h(z) = H_c e^{-sz/\xi_\Delta(T)}. \tag{5.2}$$

They are equivalent to

$$\delta(\zeta) = \tanh(a\zeta), \tag{5.3}$$

$$F(\zeta) = r e^{-c\zeta}, \tag{5.4}$$

with

$$a = \tfrac{1}{2}\pi d \sin\alpha, \tag{5.5}$$

$$c = \tfrac{1}{2}\pi d \sin\alpha, \tag{5.6}$$

and

$$r = -(\pi/2\sqrt{2}\,\kappa)\, bs^{-1} \cos\alpha. \tag{5.7}$$

In the last formula,

$$\kappa = \kappa(T) = [2\sqrt{2}\, e H_c(T) \xi^2(T)]^{-1} \tag{5.8}$$

is closely related to the GL parameter κ_{GL}. At $T = 0$ the relation is simply

$$\kappa(0) = 0.947\kappa_{GL}. \tag{5.9}$$

So far, we have completed our calculation of the surface energy only for zero temperature. At $T = 0$ and with the above chosen trial functions for Δ and h, we may first simplify our expression for the free-energy difference [Eqs. (3.6) and (3.11)–(3.13)] to

$$\Delta G(d, s, \kappa) = (8\pi)^{-1} H_c^2(0)\, \xi_0\, \tilde{\sigma}(d, s, \kappa), \tag{5.10}$$

where

$$\tilde{\sigma} = \int_0^{\pi/2} \sin 2\alpha\, d\alpha \int_0^1 \frac{db}{(1 - b^2)^{1/2}} K(a, c, r) - \frac{2\ln 2}{d} - \frac{3}{2s} \tag{5.11}$$

and

$$K(a, c, r) = \int_0^1 \Sigma_B\, d\Lambda + \int_1^\infty [\Sigma_S - (a\Lambda)^{-1}]\, d\Lambda. \tag{5.12}$$

The first step is to solve Eqs. (3.14) and (3.15a)–(3.15c), for $\Lambda \lessgtr 1$, respectively, in the region $\zeta > 0$ as supplemented by their respective boundary conditions at $\zeta = +\infty$. For large ζ, both $(1 - \delta)$ and F are small, and we can solve the equations analytically to first order in them. Using these asymptotic solutions at a suitably large positive ζ, the equations are numerically integrated back to origin to obtain $\eta_0(\Lambda)$ for $0 < \Lambda < 1$ and $\eta_{30}(\Lambda)$ for $\Lambda > 1$. Equa-

tions (3.8a) and (3.16) are then used to evaluate Σ_B and Σ_S. It can be shown that the following expressions are exact identities:

$$\Sigma_B(0) = 0, \tag{5.13}$$

$$\Sigma_S(1) = \Sigma_B(1) - \pi. \tag{5.14}$$

These equations, together with the asymptotic formula Eq. (3.9), serve as the best check on the accuracy of our results at this stage. By improving our computer program, we can satisfy Eqs. (5.13) and (5.14) up to at least five significant digits. In Figs. 1 and 2, the quantities $\Sigma_B(\Lambda)$ and $\Sigma_S(\Lambda)$ are plotted for six sets of values of a, c, and r. It is seen that the asymptotic formula for $\Sigma_S(\Lambda)$, namely, Eq. (3.9), is also obeyed very well. The next step is to calculate $K(a, c, r)$ using Eq. (5.12). The Λ integrals are performed numerically up to a certain value Λ_c, beyond which the asymptotic formula Eq. (3.9) is used in place of the exact Σ_S. The value of Λ_c is always adjusted to give a fixed accuracy in K. The α and b integrations in Eq. (5.11) can no longer be carried out straightforwardly by numerical method, since it takes too much computer time to do so. Instead, we calculate a loose mesh of values for $K(a, c, r)$ which are then fitted with simple analytic expressions to be used in Eq. (5.11). The errors so introduced may not be as bad as one might have suspected since numerical results on the mesh indicate that $K(a, c, r)$ is very simply behaved. In the third to fifth columns of Table I we have listed the value

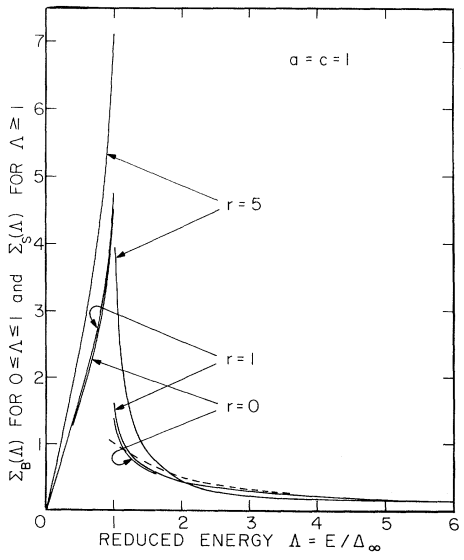

FIG. 1. Plot of $\Sigma_B(\Lambda)$ for $0 \le \Lambda \le 1$ and $\Sigma_S(\Lambda)$ for $\Lambda \ge 1$ at $a = c = 1$ and for three values of r. Dotted curve is the asymptotic behavior $(1/a\Lambda)$ of Σ_S at large Λ which is independent of c and r [see Eqs. (3.8a) and (3.8b) for the definitions of $\Sigma_{B,S}$].

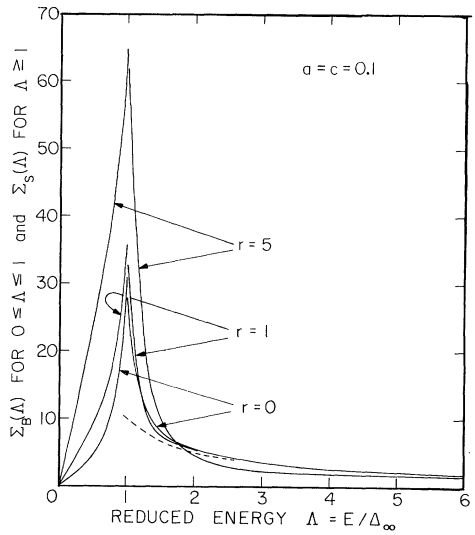

FIG. 2. Same as in Fig. 1 but with $a = c = 0.1$. Notice the different vertical scales between Figs. 1 and 2.

of K for $4 \times 4 \times 3 = 48$ sets of values for a, c, and r. Our first step is to fit the r dependence of K at each a and c by

$$K(r) = K_0 + p_1 r^2 + p_2 r^4. \tag{5.15}$$

(K is by definition an even function of r.) The values of p_1 and p_2 so obtained are listed in the sixth and seventh columns of the same table. The smallness of p_2 in all cases suggests that Eq. (5.15) must be very good at least in the regions of (a, c, r) studied. On the other hand, it is apparent from our numerical study that K depends monotonically on r. The negativeness of p_2, which implies that the expression in Eq. (5.15) will eventually reach a maximum and then turn around to approach negative infinity as r increases, indicates that it is necessarily wrong for large r. Fortunately, the turning points occur at $r \gtrsim 11$ in all cases, which does not pose a severe restriction on the validity range of our calculation (*vide infra*). Of course, a physically more acceptable approximation may be obtained by replacing $p_1 r^2 + p_2 r^4$ by, say, $p_1 r^2 \times (1 - p_2 r^2/p_1)^{-1}$. But this will prevent us later from performing the α and b integrations in (5.11) analytically, which can save us a great deal of computer time. We shall thus stick to Eq. (5.15). A surprising bonus in this fitting process is the discovery that $p_2/p_1 \cong -0.37 \times 10^{-2}$ is essentially independent of a and c (see the last column of Table I). This means that $\Delta K \equiv K(r) - K_0$ can be regarded as a separable function:

$$\Delta K \cong p_1(a/c, c)\, R(r), \tag{5.16}$$

where

$$R(r) \cong r^2(1 - 0.37 \times 10^{-2} r^2). \tag{5.17}$$

TABLE I. Numerical values of $K(a/c, c, r)$ [defined in Eq. (5.12)], their fitting coefficients p_1, p_2 [cf. Eq. (5.15)], and the ratio p_2/p_1.

a/c	c	$K(r=0)$	$K(r=2)$	$K(r=4)$	p_1	$-p_2\times10^2$	$-(p_2/p_1)\times10^2$
0.50	0.25	8.169	9.432	11.30	0.3206	0.1204	0.376
0.50	0.50	4.341	4.808	5.746	0.1185	0.0442	0.373
0.50	2.00	1.704	1.734	1.821	0.0076	0.0028	0.367
0.50	4.00	1.343	1.348	1.365	0.0013	0.0005	0.364
1.25	0.25	3.596	6.026	9.761	0.6168	0.2315	0.375
1.25	0.50	2.193	3.060	4.900	0.2200	0.0818	0.372
1.25	2.00	1.276	1.338	1.512	0.0157	0.0058	0.368
1.25	4.00	1.170	1.183	1.219	0.0033	0.0012	0.368
2.00	0.25	2.531	5.507	10.21	0.7553	0.2833	0.375
2.00	0.50	1.704	2.776	5.204	0.2720	0.1009	0.371
2.00	2.00	1.197	1.274	1.492	0.0195	0.0072	0.368
2.00	4.00	1.146	1.162	1.206	0.0041	0.0015	0.368
4.00	0.25	1.704	5.387	11.02	0.9348	0.3509	0.375
4.00	0.50	1.343	2.682	5.557	0.3398	0.1263	0.372
4.00	2.00	1.145	1.241	1.520	0.0244	0.0089	0.367
4.00	4.00	1.130	1.150	1.208	0.0051	0.0019	0.367

Since $r=0$ implies that $F(\zeta)\equiv0$, we expect K_0 to be a function of a only. The empirical formula

$$K_0(a)\cong 1.125+\frac{1}{a}\,\frac{0.935}{1+0.600a} \tag{5.18}$$

is found to have $\pm0.2\%$ accuracy. On the other hand, we came across another pleasant surprise when we found that $p_1(a/c, c)$ was again to a good approximation separable [the error is roughly the same as in (5.18)]:

$$p_1(a/c, c)\cong P(a/c)\,\Gamma(c)\,, \tag{5.19}$$

where, with $a/c\,(=d/s)$ denoted by ρ,

$$P(\rho)\cong 0.180\,[(1+0.959\rho)-(1-0.972\rho+0.926\rho^2)^{1/2}], \tag{5.20}$$

$$\Gamma(c)\cong(1+0.126c)/[c(1+1.695C+1.124c^2)]. \tag{5.21}$$

Substituting Eqs. (5.16)–(5.21) into Eq. (5.11) and using the definitions of a, c, and r in Eqs. (5.5)–(5.7), we can perform the b and α integrations by hand and obtain

$$\tilde{\sigma}(d, s)=[1.767+1.984d^{-2}\ln(1+0.943d)-1.386d^{-1}] + P(d/s)\,I(s)-1.5s^{-1}\,, \tag{5.22}$$

with

$$\begin{aligned}I(s)=\kappa^{-2}s^{-4}\{&-4.402\times10^2\,(1+8.185s^{-1})+4.402\times10^2\,(1+4.289s^{-2})\ln(1+2.662s+2.773s^2)\\&+1.115\,(1+1.277\times10^{-1}s^{-2})\tan^{-1}[1.001s/(1+1.331s)]\}\\&+\kappa^{-4}s^{-6}\{2.260\times10^{-4}\,(1+9.097s^{-1}+2.860s^{-2}-3.526s^{-3})\\&-1.507\times10^{-4}\,(1+8.236s^{-2}-9.907\times10^{-1}s^{-4})\ln(1+2.662s+2.773s^2)\\&-3.818\times10^{-3}\,(1-2.554\times10^{-1}s^{-2}-1.044\times10^{-1}s^{-4})\tan^{-1}[1.001s/(1+1.331s)]\}\,.\end{aligned} \tag{5.23}$$

We must still minimize $\tilde{\sigma}(d, s)$ with respect to d and s in order to obtain the surface energy [per unit area and in units of $(8\pi)^{-1}H_c^2(0)\,\xi_0$] of an NS-phase boundary at any given κ_{GL}. This is carried out numerically and the result is plotted in Fig. 3 (solid line). The difference between $\kappa=\kappa(0)$ and κ_{GL} indicated in Eq. (5.9) is already taken into account so that the horizontal axis is κ_{GL}. In Figs. 4 and 5 we also plot the value d_0 and s_0 of d and s that minimize $\tilde{\sigma}$ (solid lines). Figures 3–5 constitute the main results of this section.

In order to grasp a physical feeling of our results, we also perform an analogous variational calculation using the GL free-energy functional which, for pure superconductors, is presumably valid at the extreme neighborhood of T_c[1,16]:

$$\Delta G_{GL}(\psi, h)=(8\pi)^{-1}H_c^2(T)\,\xi_\Delta(T)\,\tilde{\sigma}_{GL}(\psi, h)\,, \tag{5.24}$$

$$\tilde{\sigma}_{GL}(\psi, h)=\int_0^\infty d\zeta\left[3.293\left(\frac{d\psi}{d\zeta}\right)^2+0.609\,\kappa_{GL}^{-2}a^2\psi^2-2\psi^2+\psi^4+(h-1)^2\right]. \tag{5.25}$$

In the above expression ψ is the (real) space-de-

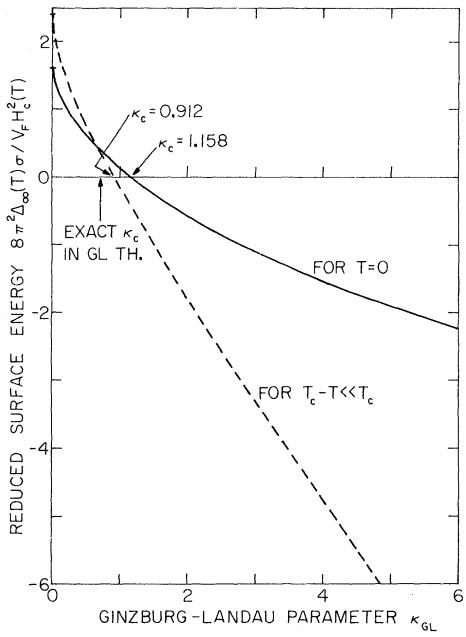

FIG. 3. Surface energy of a planar-phase wall, per unit area and in units of $v_F H_c^2(T)/8\pi^2\Delta_\infty(T)$, plotted against the Ginzburg-Landau parameter κ_{GL}. The solid curve is from our microscopic variational calculation performed for pure superconductors at $T=0$. The dashed curve, valid for $T_c - T \ll T_c$, is from a similar variational calculation using the Ginzburg-Landau free-energy functional.

pendent order parameter normalized to one in the superconducting bulk, h is the magnetic field normalized to one in the normal region, $\zeta = z/\xi_\Delta(T)$, and $a(\zeta) = -\int_\zeta^\infty h(\zeta)\,d\zeta$.[21]

The trial functions which correspond to Eqs.

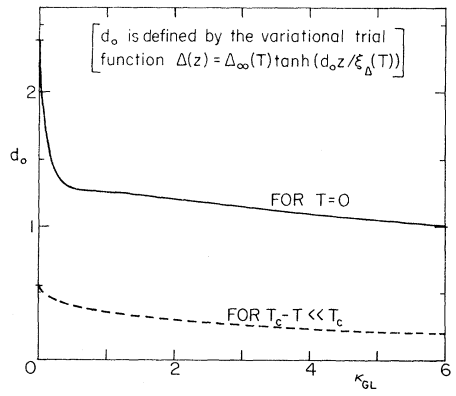

FIG. 4. Plot of d_0 vs κ_{GL}, where $\xi_\Delta(T)/d_0$ measures the thickness of the order-parameter transition region at the phase boundary, as determined by our variational calculations. As in Fig. 3, the solid curve pertains to our calculation at $T=0$ and the dashed curve is from a similar variational calculation for $T \cong T_c$.

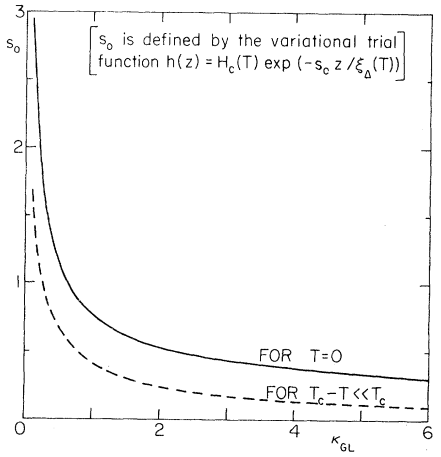

FIG. 5. Plot of s_0 vs κ_{GL}, where $\xi_\Delta(T)/s_0$ gives the effective penetration depth [cf. Eq. (2.5)] of the magnetic field at the phase boundary, as determined by our variational calculations. As in Fig. 3, the solid curve pertains to our calculation at $T=0$ and the dashed curve is from a similar variational calculation for $T \cong T_c$.

(5.1) and (5.2) are for the present case $\psi(\zeta) = \tanh(d\zeta)$ and $h(\zeta) = e^{-s\zeta}$. With them, Eq. (5.25) can be easily simplified to

$$\tilde{\sigma}_{GL}(d,s) = (2.195d + 0.667d^{-1}) + 0.609\,\kappa_{GL}^{-2}\,s^{-3} \times \int_0^\infty dx\, e^{-2x}\tanh^2(xd/s) - 1.5s^{-1}. \quad (5.26)$$

This expression, though much simpler, bears a striking resemblance to Eq. (5.22). One should particularly notice the separable functions of (d/s) and s that appeared in both expressions, suggesting that our earlier discovery of ΔK being a separable function of a/c, c, and r might not be purely accidental [cf. Eqs. (5.16) and (5.19)].

It is not difficult to minimize Eq. (5.26) with respect to d and s numerically. The results for $\tilde{\sigma}(\kappa_{GL})$, $d_0(\kappa_{GL})$, and $s_0(\kappa_{GL})$ are plotted in Figs. 3–5 as the dashed curves.

A comparison of the two sets of results for $T=0$ and $\sim T_c$ immediately reveals that our $T=0$ result for the surface energy is not good in the high-κ_{GL} limit. One expects in this limit that $|\tilde{\sigma}| \propto \kappa_{GL}$ but our results seem to indicate a $\kappa_{GL}^{1/2}$ dependence. This error is traced back to the difficulty in solving those nonlinear differential equations at very small values of a and/or c. In fact, our empirical expression for κ is obtained from fitting the numerical results in the region $r \lesssim 4$, $0.5 \lesssim (a/c) \lesssim 4.0$, and $0.25 \lesssim c \lesssim 4.0$. It turns out that the most severe restriction comes from c $(= \frac{1}{2}\pi s \sin\alpha) \gtrsim 0.25$. For $\sin\alpha = 0.5$ it already implies $s > \pi^{-1}$ or $\kappa \lesssim 5$. We must still remember that we need to integrate over $\sin\alpha$ from 0 to 1. At present our computer program cannot solve the equations for smaller

a/c and/or c, but we believe that this difficulty can be removed or at least relaxed after some further study.

An interesting related question is the critical value of κ_{GL} which separates type-I and type-II superconductors. At least four definitions exist for this κ_c (omitting the subscript GL for clarity). They are that (i) $H_{c2} = H_c$ (i.e., when $\kappa_1 = 1/\sqrt{2}$); (ii) the slope of the magnetization curve vs field diverges at H_{c2} (i.e., when $\kappa_2 = 1/\sqrt{2}$); (iii) $H_{c1} = H_c$; and (iv) the surface energy σ vanishes. We shall denote them, respectively, as κ_{c1}, κ_{c2}, κ_{c3}, and $\kappa_{c\infty}$, all being functions of temperature.

In the GL region ($T \sim T_c$) all four definitions agree giving $1/\sqrt{2} \sim 0.707$. Below the GL region there is no *a priori* reason that their values should still coincide. In fact, recent study by Jacobs[22] for temperatures just below the GL region, among others, has already indicated the contrary. Our numerical result for pure superconductors at $T = 0$ gives $\kappa_{c\infty}$ (at $T = 0$) ≤ 1.16. This should be compared with $\kappa_{c3}(0) \leq 0.74$ due to BKJT[6]; $K_{c1}(0) = 0.56$ due to Gor'kov,[23] Helfand and Werthamer[24]; and $\kappa_{c2}(0) = 0$ due to Maki and Tsuzuki[25] and Eilenberger.[26] (Only results for pure superconductors are quoted.) Our upper-bound estimation for $\kappa_{c\infty}(0)$ is most likely too high, but it still suggests $\kappa_{c\infty}(0) > \kappa_{c3}(0) > \kappa_{c1}(0) > \kappa_{c2}(0)$. For comparison we note that Jacobs found the order $\kappa_{c3} > \kappa_{c\infty} > \kappa_{c1} > \kappa_{c2}$ for pure superconductors at temperatures just below the GL region.

Besides the results on σ and $\kappa_{c\infty}$, we can draw one more conclusion from our numerical study.

We believe that the sharp drop of d_0 in the range $0 \leq \kappa_{GL} \lesssim 0.5$ is a genuine reflection of the nonlocal nature of our theory, and is peculiar to pure superconductors of very low κ near absolute zero temperature. We notice that when κ is small the magnetic field penetrates only very shallowly into the order-parameter wall region. The order parameter generally obeys a self-consistent integral equation with a kernel which depends on the field. For dirty superconductors or for pure superconductors near the transition temperature, the range of the kernel is much smaller than the order-parameter wall thickness, so that in most of the wall region, the order parameter does not "see" the penetrating field. For pure superconductors near absolute zero temperature, the range of the kernel is now comparable with the order-parameter wall thickness, and the latter must now depend more critically on exactly how much field has to penetrate the wall region. This, we believe, accounts for the sharp κ dependence of d_0 obtained when κ is small.

VI. EXPANSION OF MICROSCOPIC FREE ENERGY OF *NS*-PHASE BOUNDARY NEAR T_c

As stated in Sec. I, the BKJT theory, though elegant and rigorous, contains a mysterious feature which is not yet resolved. It was first discovered by Cleary,[11] and was investigated in more detail later by Jacobs.[12] It should be noted that the variational principle of BKJT was based on a general theory of Eilenberger[27] which was rigorously established. The WKBJ method used in solving the Bogoliubov equations is essentially equivalent to the semiclassical approximation [both ignoring quantities of order $(p_F \xi_0)^{-1}$ with respect to one],[28] which is also widely accepted among superconductivity theorists. One therefore expects that the BKJT theory, being formulated for all temperatures, should agree with the GL theory,[1] and its generalization by Neumann and Tewordt,[13,14] as T approaches T_c. (The latter theories have long been accepted as the correct theories near T_c.) Unfortunately, however, this was not exactly borne out in the study of Cleary and Jacobs. These authors found that near T_c, the free-energy expression of BKJT for an isolated-vortex line may be expanded into a power series in $[\Delta_\infty(T)/T] \propto (1-t)^{1/2}$, where $t \equiv T/T_c$. While the lowest two-integer power terms [proportional to $(1-t)$ and $(1-t)^2$, respectively] exactly reproduced the GL and Neumann-Tewordt theories, the half-integer power terms of orders $(1-t)^{1/2}$ and $(1-t)^{3/2}$, etc. were completely unexpected. Most serious is the term of order $(1-t)^{1/2}$. Being lower in order than the GL free energy, it seemingly has to vanish. But the investigations of Cleary and Jacobs strongly suggested the contrary. Jacobs then suggested (but not rigurously established) that probably the half-integer power terms would vanish when and only when the pair potential and the vector potential represented the true equilibrium solution (i.e., when they exactly minimized the BKJT free energy). This is not a completely satisfactory answer since if it were true, one might wonder why the Ginzburg-Landau–Neumann-Tewordt free energy should also be minimized by that "equilibrium" state.

The above dilemma was found by studying isolated-vortex lines in pure superconductors. The basic problem is most likely not confined to that particular situation. Since in the present paper the author has extended the BKJT theory to the plane-geometry case of a *NS*-phase boundary, it becomes extremely interesting to perform a parallel study in this situation. The basic techniques in this study will not be much different from those of Clearly and Jacobs. But the importance of the problem, and the fact that the present case is a simpler and therefore better one for investigating the dilemma, led us to decide on presenting the details to some extent.

To begin with, our expression for the Gibbs free energy of an *NS*-phase boundary is given by Eqs. (3.11)–(3.13). While ΔG_M should remain as it is,

we expand ΔG_B by writing the factor $\tanh\frac{1}{2}\beta\Delta_\infty\Lambda$ into its Taylor series. For expanding the scattering-state contribution ΔG_{SP}, we must first obtain the following expansion by extending Eqs. (3.9) and (3.10)[29]:

$$\Sigma_S - C/(\Lambda^2-1)^{1/2} = \tilde{D}(\alpha,b)\,\Lambda^{-3} + \tilde{E}(\alpha,b)\,\Lambda^{-5} + O(\Lambda^{-7}), \quad (6.1)$$

where

$$\tilde{D}(\alpha,b) = -\int_0^\infty [\delta'^2 + F^2\delta^2 + \tfrac{1}{4}(1-\delta^2)^2]\,d\xi, \quad (6.2)$$

$$\tilde{E}(\alpha,b) = -\int_0^\infty [(\delta'')^2 + \tfrac{5}{2}(\delta\delta')^2 - \tfrac{1}{8}(1-\delta^6) + \tfrac{3}{8}(1-\delta^2) + F^4\delta^2 + \tfrac{3}{2}F^2\delta^4 + (F'\delta)^2 + 6(F\delta')^2 + 8FF'\delta\delta']\,d\xi \quad (6.3)$$

(primes denote differentiations with respect to ξ).

The expansion of ΔG_{SP} is now a simple application of the general asymptotic expansion formula presented in Appendix B. Combining all the steps described above, we obtain

$$\Delta G = \sum_{i=1}^{\infty} \Delta G^{(i)} + \Delta G_M, \quad (6.4)$$

with

$$\Delta G^{(1)} = \tfrac{1}{4}\beta\xi_\Delta N(0)\,\Delta_\infty^3 \int_0^{\pi/2} \sin 2\alpha\, d\alpha \int_0^1 \frac{db}{(1-b^2)^{1/2}} \left[\int_0^1 \Lambda\Sigma_B\, d\Lambda + \int_1^\infty \Lambda\left(\Sigma_S - \frac{C}{(\Lambda^2-1)^{1/2}}\right) d\Lambda\right], \quad (6.5)$$

$$\Delta G^{(2)} = \tfrac{1}{8}\beta^2\xi_\Delta N(0)\,\Delta_\infty^4 \int_0^{\pi/2} \sin 2\alpha\, d\alpha \int_0^1 \frac{db}{(1-b^2)^{1/2}} \left(\tilde{D}(\alpha,b)\int_0^\infty u^{-3}(\tanh u - u)\,du\right), \quad (6.6)$$

$$\Delta G^{(3)} = -\frac{\beta^3}{48}\,\xi_\Delta N(0)\,\Delta_\infty^5 \int_0^{\pi/2} \sin 2\alpha\, d\alpha \int_0^1 \frac{db}{(1-b^2)^{1/2}} \left[\int_0^1 \Lambda^3\Sigma_B\, d\Lambda - \tilde{D}(\alpha,b) + \int_1^\infty \Lambda^3\left(\Sigma_S - \frac{C}{(\Lambda^2-1)^{1/2}} - \frac{\tilde{D}(\alpha,b)}{\Lambda^3}\right) d\Lambda\right], \quad (6.7)$$

and

$$\Delta G^{(4)} = \frac{\beta^4}{32}\,\xi_\Delta N(0)\,\Delta_\infty^6 \int_0^{\pi/2} \sin 2\alpha\, d\alpha \int_0^1 \frac{db}{(1-b^2)^{1/2}} \left(\tilde{E}(\alpha,b)\int_0^\infty u^{-5}[\tanh u - u + \tfrac{1}{3}u^3]\,du\right), \quad (6.8)$$

etc. We note that the leading term in $\Delta G^{(i)}$ is of order $(1-t)^{(i+1)/2}$ instead of $(1-t)^{i/2}$ as found in the isolated-vortex problem by Cleary and Jacobs.[30] This difference, however, is not unexpected and originates from the difference in geometry of the two problems.

Let us now investigate the two forms $\Delta G^{(2)}$ and $\Delta G^{(4)}$. To facilitate comparison with other theories, we first change the dimensionless variables back to natural variables and perform the α, b, and u integrations. This leads us to

$$\Delta G^{(2)} = \frac{7\beta^2}{8\pi^2}\,\zeta(3)N(0)\,\Delta_\infty^4 \int_0^\infty dz\,[\tfrac{1}{6}\pi^2\xi_\Delta^2(f'^2 + a^2f^2) + \tfrac{1}{2}(1-f^2)^2], \quad (6.9)$$

$$\Delta G^{(4)} = -\frac{31\zeta(5)}{32(\pi T)^4}\,N(0)\,\Delta_\infty^6 \int_0^\infty dz \left(\frac{\pi^4\xi_\Delta^4}{120}[3(f'')^2 + 3a^4f^2 + a'^2f^2 + 6a^2f'^2 + 8aa'ff'] + \frac{\pi^2\xi_\Delta^2}{12}\times[5(ff')^2 + 3a^2f^4] - \tfrac{1}{4}(1-\delta^6) + \tfrac{3}{4}(1-\delta^2)\right), \quad (6.10)$$

where f is nothing but δ considered as a function of z, and $a \equiv 2eA(z)$. Primes now denote differentiations with respect to z. Consider now the generalized GL theory of Tewordt[13] in which the Gibbs energy of a general inhomogeneous superconducting state is given. This theory has been nicely summarized in the paper of Neumann and Tewordt.[14] For the planar geometry case and when the sample is pure, the free-energy expression reduces to

$$\Delta G_{NT} = \Delta G_M + \Delta G_{NT}^{(2)} + \Delta G_{NT}^{(4)}, \quad (6.11)$$

where

$$\Delta G_{NT}^{(2)} = \frac{1}{4\pi}\,H_c^2 \int dz\,\{\kappa_3^{-2}\lambda_T^2[f'^2 + a^2f^2] + \tfrac{1}{2}(1-f^2)^2\} \quad (6.12)$$

and

$$\Delta G_{NT}^{(4)} = \frac{1}{4\pi}\,(1-t)\,H_c^2\,\Gamma \int dz\,\{\tfrac{2}{5}\kappa_3^{-4}\lambda_T^4[3(f'')^2 + 3a^4f^2 + (a'f)^2 + 6(af')^2 + 8aa'ff'] + \tfrac{2}{3}\kappa_3^{-2}\lambda_T^2[2(ff')^2 - 3(1-f^2)(f'^2 + a^2f^2)] + \tfrac{1}{3}f^2(1-f^2)^2\}. \quad (6.13)$$

In the above expressions, $\Gamma = -93\zeta(5)/98\zeta^2(3)$ is the ratio a_4/a_2^2 in Tewordt's theory. To compare the two free-energy expressions, one must first sub-

stitute into $\Delta G^{(2)}$ and $\Delta G_{NT}^{(2)}$ the expansions

$$\Delta_\infty(T) = \Delta_{\infty\,\mathrm{GL}}(T)\left[1 - (\tfrac{3}{4} + \tfrac{1}{2}\Gamma)(1-t)\right], \tag{6.14}$$

$$(\pi/\sqrt{6})\,\xi_\Delta(T) = \xi_{\mathrm{GL}}(T)\left[1 + (\tfrac{3}{4} + \tfrac{1}{2}\Gamma)(1-t)\right], \tag{6.15}$$

$$(4\pi)^{-1}H_c^2(T) = (4\pi)^{-1}H_{c\,\mathrm{GL}}^2(T)\left[1 - (1 + \tfrac{2}{3}\Gamma)(1-t)\right], \tag{6.16}$$

$$\lambda_T^2(T) = \lambda_{\mathrm{GL}}^2(T)\left[1 - (\tfrac{1}{2} + \Gamma)(1-t)\right], \tag{6.17}$$

$$\kappa_3(T) = \kappa_{\mathrm{GL}}\left[1 - (1 + \tfrac{4}{3}\Gamma)(1-t)\right], \tag{6.18}$$

where the quantities with the subscript GL are the corresponding quantities in the GL region [i.e., expanded to lowest order in $(1-t)$] which can all be found in, say, Ref. 31. Upon using only the lowest-order corresponding expressions in $\Delta G^{(4)}$ and $\Delta G_{\mathrm{NT}}^{(4)}$ one can then easily verify the following equality:

$$\frac{\Delta G^{(2)} - \Delta G_{\mathrm{NT}}^{(2)}}{(4\pi)^{-1}(1-t)\,H_{c\,\mathrm{GL}}^2\,\Gamma} = \frac{\Delta G_{\mathrm{NT}}^{(4)} - \Delta G^{(4)}}{(4\pi)^{-1}(1-t)\,H_{c\,\mathrm{GL}}^2\,\Gamma}$$

$$= \int dz\left[2\,\xi_{\mathrm{GL}}^2\,(f'^2 + a^2 f^2) + \tfrac{2}{3}(1-f^2)^2\right]. \tag{6.19}$$

This leads us to a similar conclusion as in Cleary's and Jacobs's studies of the isolated-vortex problem. Namely, our microscopic free energy for an *NS*-phase boundary to four orders in $(1-t)^{1/2}$ would precisely reproduce the Ginzburg-Landau–Neumann-Tewordt theory, had the former not contained the extra series of unexpected terms: $\Delta G^{(1)} + \Delta G^{(3)} + \cdots$.

The above work demonstrated that the dilemma discussed in the beginning of this section also exists in our extension of the BKJT theory to the planar-geometry case of an *NS*-phase wall. This shall be the sole purpose of this section since we have not made any progress in resolving this dilemma. The only statement about the unexpected terms that we can make with confidence at the present time is that they do not vanish identically for all trial functions Δ and h. This can be easily seen from our study of an ideal phase boundary presented in Sec. IV. Since the planar-*NS*-wall case is simpler to study than the isolated-vortex–line case in many senses as discussed in Sec. I, we hope that the work presented in this section could throw some light to the final breakthrough of this outstanding problem.

VII. CONCLUSION

In this paper we have developed a microscopic theory of the surface energy at a plane boundary between normal and superconducting phases. The theory applies to pure superconductors only, and is based upon a reformulation of the Bogoliubov theory of Bardeen *et al.* which features a WKBJ approximation in solving the Bogoliubov equations, and a replacement of the self-consistent conditions on the order-parameter and field distributions by a variational principle on a Gibbs free-energy expression. Numerical methods are required to solve some nonlinear coupled differential equations and to the final minimization of the free-energy expression which are carried out in this paper only for absolute-zero temperature. Results of this numerical study, together with a corresponding variational calculation of the surface energy near T_c using the Ginzburg-Landau free energy, indicate that the surface energy for pure superconductors may be expressed as the temperature-dependent factor $v_F H_c^2/8\pi^2\Delta_\infty$ multiplied by a dimensionless function $\bar{\sigma}(\kappa_{\mathrm{GL}})$ of the Ginzburg-Landau parameter κ_{GL}, with the latter having at most a weak temperature dependence as shown in Fig. 3. The nonlocal nature of our theory is expected to reveal its largest effects in pure low-κ_{GL} superconductors at very low temperatures. But in studying this case we find that only a rapid change of the thickness of the order-parameter transition region at the phase boundary, as κ_{GL} increases from zero, might be attributed to this origin. We remark in this connection that our theory is, in principle, valid for all κ_{GL} values, but at present our numerical method developed at $T=0$ involves tolerable errors only for $\kappa_{\mathrm{GL}} \lesssim 1$.

Near the transition temperature T_c, we have further substantiated an observation made by Cleary of a mysterious feature in the BKJT theory. Thus it appears that not only in the isolated-vortex problem studied by Cleary and Jacobs but also in the planar-phase-boundary case studied here, and perhaps in all other inhomogeneous states of superconductivity as well, the BKJT free-energy expression will reproduce the Ginzburg-Landau-Neumann-Tewordt free-energy expansion in $(1 - T/T_c)$ plus another series of unexpected terms that leads the first series by a factor $(1 - T/T_c)^{-1/2}$. We do not claim to have resolved this puzzle, but suggest that the planar-phase boundary is a better case for studying it.

ACKNOWLEDGMENTS

The author is indebted to Professor John Bardeen for suggesting this problem and for his constant interest and much helpful advice throughout the course of this investigation. He is also grateful to his colleague, Dr. Todd Smith, for many useful suggestions concerning the numerical computation.

APPENDIX A

The purpose of this Appendix is to derive Eq. (2.34) of the main text from Eqs. (2.30a), (2.30b), and (2.31). We first note that the two solutions

of Eq. (2.31) satisfy

$$C_1 C_2 = -1, \tag{A1}$$

$$C_1 + C_2 = 2\sinh\eta_{20}\,(\sin 2\Theta/\sin 2\Xi). \tag{A2}$$

Using these relations, and the fact that both $(C_1, \xi_{10}^{(1)})$ and $(C_2, \xi_{10}^{(2)})$ are solutions of Eqs. (2.31a) and (2.31b), we may derive

$$\tan\xi_{10}^{(1)}\tan\xi_{10}^{(2)} = -\tan(\Theta - \Xi)\tan(\Theta + \Xi), \tag{A3}$$

$$\tan\xi_{10}^{(1)} + \tan\xi_{10}^{(2)} = 2\coth\eta_{20}\tan(\Theta - \Xi)/(\sin 2\Theta/\sin 2\Xi - 1). \tag{A4}$$

Combining these equations, one arrives at the relation

$$\tan(\xi_{10}^{(1)} + \xi_{10}^{(2)}) = \coth\eta_{20}\tan 2\Xi. \tag{A5}$$

This equation may be analyzed as follows:

(i) It determines $\xi_{10}^{(1)} + \xi_{10}^{(2)}$ only up to an arbitrary integer multiple of π. This additive term has no physical meaning and may take any allowed value. But for the convenience in calculating the density of states, it is better chosen to give $\xi_{10}^{(1)} + \xi_{10}^{(2)}$ a continuous dependence on E.

(ii) As $E/\Delta_\infty \to \infty$, $\eta_{20} \to \infty$. Choosing the additive term to give the simplest result in this limit, we have

$$\xi_{10}^{(1)} + \xi_{10}^{(2)} \to 2\Xi \qquad \text{as } E/\Delta_\infty \gg 1. \tag{A6}$$

(iii) If we write

$$\xi_{10}^{(1)} + \xi_{10}^{(2)} = 2\Xi + \Psi, \tag{A7}$$

then Ψ vanishes whenever $2\Xi = \frac{1}{2}n\pi$ for any integer n.

(iv) If $\coth\eta_{20}$ is independent of Ξ, then it can be shown that Ψ is a periodic function of Ξ of period $\frac{1}{2}\pi$. A simple though not rigorous way to see this is through graphic method.

(v) Since $\Xi = \pi m_e E/2eH_c - \frac{1}{2}\eta_{10} - \Gamma$, and because η_{10} and η_{20} depend on E only in the scale Δ_∞, we conclude that Ψ is a quasiperiodic function of E with period $\sim eH_c/m_e \ll \Delta_\infty$. The period is nothing but the electron cyclotron frequency in the field H_c associated with Landau-orbit quantization (multiplied by $\hbar$).

(vi) Within each period one can ignore the E dependence of η_{10} and η_{20} which introduces a relative error $\sim eH_c/m_e\Delta_\infty \ll 1$. With this approximation Ψ can be shown to be an odd function about the center within each period. Thus if Ψ is multiplied by a function of E varying in the scale Δ_∞ and then integrated over a range $\gtrsim \Delta_\infty$, it usually can be neglected to lowest order in the above small parameter. This justifies our ignoring a term $+\pi^{-1}(d\Psi/dE)$ in Eq. (2.36), anticipating its role played in our calculation of the free-energy difference ΔG in Sec. III.

APPENDIX B

In this Appendix we present a general formula for finding the asymptotic expansion about $x = 0$ of the real function

$$f(x) = \int_1^\infty g(t)h(xt)\,dt, \tag{B1}$$

knowing the asymptotic expansions

$$g(t) = \sum_{n=1}^{\infty} a_n t^{-(2n+1)} \equiv \sum_n g^{(n)}(t), \tag{B2}$$

$$h(u) = \sum_{n=1}^{\infty} b_n u^{2n-1} \equiv \sum_n h^{(n)}(u). \tag{B3}$$

Before we present our formula we first make the following remarks:

(i) $f(x)$ is obviously an odd function since $h(u)$ is odd.

(ii) If one substitutes (B3) into (B1) and interchanges the summation and integration signs, one will end up with divergent integrals. This method therefore fails to give the expansion of $f(x)$.

(iii) If one substitutes (B2) into (B1), interchanges the summation with the integration, and then changes the integration variable from t to $u = xt$, one does not yet obtain the desired expansion because the lower limits of integration still depend on x. One must either follow Cleary[11] to perform partial integrations, or play the trick of Jacobs[12] in transforming the integrals. Both of these procedures become more complex when higher-order terms are handled. It is therefore desirable to see how the general expansion looks and why it is asymptotic. To do so we introduce the notations for partial sums and remainders:

$$S_g^{(n)}(t) \equiv \sum_{i=1}^{n} g^{(i)}(t), \tag{B4}$$

$$R_g^{(n)}(t) \equiv g(t) - S_g^{(n)}(t), \tag{B5}$$

with similar definitions for $S_h^{(n)}(u)$ and $R_h^{(n)}(u)$. In these notations the desired general formula may be written

$$f(x) = (\operatorname{sgn} x)\sum_{n=1}^{\infty}\Big[b_n|x|^{2n-1}\Big(\int_1^\infty t^{2n-1}R_g^{(n-1)}\,dt - \int_0^1 t^{2n-1}S_g^{(n-1)}\,dt\Big) + a_n|x|^{2n}\int_0^\infty u^{-(2n+1)}R_h^{(n)}(u)\,du\Big], \tag{B6}$$

which is manifestly odd but contains terms of even powers in $|x|$.

To prove Eq. (B6) we first observe the identities

$$f(x) = \sum_{i=1}^{n-1}\Big[\int_1^\infty R_g^{(i-1)}(t)h^{(i)}(xt)\,dt + \int_1^\infty g^{(i)}(t)R_h^{(i)}(xt)\,dt\Big] + \int_1^\infty R_g^{(n-1)}(t)h^{(n)}(xt)\,dt + R_f^{(2n)}(x), \tag{B7a}$$

$$= \sum_{i=1}^{n} \Big[\int_1^\infty R_g^{(i-1)}(t)\, h^{(i)}(xt)\, dt + \int_1^\infty g^{(i)}(t)\, R_h^{(i)}(xt)\, dt \Big] + R_f^{(2n+1)}(x), \qquad \text{(B7b)}$$

where the remainders are

$$R_f^{(2n)}(x) \equiv \int_1^\infty R_g^{(n-1)}(t)\, R_h^{(n)}(xt)\, dt,$$

$$R_f^{(2n+1)}(x) \equiv \int_1^\infty R_g^{(n)}(t)\, R_h^{(n)}(xt)\, dt.$$

The identities can be easily shown by repeatedly combining the last two terms until only one term is left.

Since Eqs. (B2) and (B3) are asymptotic expansions,[32] we have $R_g^{(n)}(t) = o(g^{(n)}(t))$ as $t \to \infty$ and $R_h^{(n)}(u) = o(h^{(n)}(u))$ as $u \to 0$. It is then possible to show that

$$R_f^{(2n)}(x) = o\Big(\int_1^\infty R_g^{(n-1)}(t)\, h^{(n)}(xt)\, dt \Big),$$

$$R_f^{(2n+1)}(x) = o\Big(\int_1^\infty g^{(n)}(t)\, R_h^{(n)}(xt)\, dt \Big),$$

both as $x \to 0$, provided that all $R_g^{(n)}$ and $R_h^{(n)}$ are continuous functions with no roots within the integration range, and that all infinite integrations converge uniformly for all $|x|$ less than some $x_0 \neq 0$. Under these conditions, therefore, Eqs. (B7) with $n \to \infty$ will furnish the desired asymptotic expansion of $f(x)$ at $x = 0$.

We must still evaluate the integrations in Eqs. (B7) for our definitions of $g^{(n)}$ and $h^{(n)}$:

$$\int_1^\infty R_g^{(i-1)}(t)\, h^{(i)}(xt)\, dt = b_n x^{2n-1} \int_1^\infty t^{2n-1} R_g^{(i-1)}(t)\, dt$$

and

$$\int_1^\infty g^{(i)}(t)\, R_h^{(i)}(xt)\, dt = (\operatorname{sgn} x)\, a_i |x|^{2i} \int_{|x|}^\infty u^{-(2i-1)} R_h^{(i)}(u)\, du$$

$$= (\operatorname{sgn} x) a_i A_i |x|^{2i} - a_i \sum_{k=i+1}^{\infty} b_k (2k - 2i - 1)^{-1} x^{2k-1},$$

where $A_i \equiv \int_0^\infty u^{-(2i+1)} R_h^{(i)}(u)\, du$.

Substituting these relations into Eq. (B7) with $n \to \infty$, we observe that

$$\sum_{i=1}^{\infty} \sum_{k=i+1}^{\infty} a_i b_k (2k - 2i - 1)^{-1} x^{2k-1} = \sum_{i=2}^{\infty} b_i x^{2i-1} \sum_{k=1}^{i-1} (2i - 2k - 1)^{-1} a_k$$

$$= \sum_{i=1}^{\infty} b_i x^{2i-1} \int_0^1 t^{2i-1} S_g^{(i-1)}(t)\, dt,$$

and we finally obtain our formula Eq. (B6).

---

*Work supported in part by the National Science Foundation under Grant No. GP-20458 and in part by the Research Corp.

[1]V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. 20, 1064 (1950) [*Men of Physics, L. D. Landau*, edited by D. ter Haar (Pergamon, Oxford, England, 1965)].

[2]J. Bardeen, Phys. Rev. 94, 554 (1954).

[3]H. W. Lewis, Phys. Rev. 104, 942 (1956).

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

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

[6]N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (Consultants Bureau, New York, 1959).

[7]W. N. Mathews, Jr., Ph. D. thesis, (University of Illinois, 1966) (unpublished). This work introduced the idea of a WKBJ approximation, but not the variational principle of the BKJT theory (Ref. 8). The self-consistent gap equation was solved by iteration method for the special case $\kappa_{GL} = 0$.

[8]J. Bardeen, R. Kümmel, A. E. Jacobs, and L. Tewordt, Phys. Rev. 187, 556 (1969).

[9]R. Kümmel, Physik Kondensierten Materie 10, 331 (1970); Phys. Rev. B 1, 784 (1971); 3, 3787 (1971).

[10]This anaolgy should not be taken too literally. For example, the pseudospins of Bogoliubov excitations are not accompanied by spin magnetic moments to interact with the magnetic field.

[11]R. M. Cleary, Phys. Rev. B 1, 1039 (1970).

[12]A more detailed study has been made by A. E. Jacobs, Phys. Rev. B 2, 3587 (1970).

[13]L. Tewordt, Z. Physik 180, 385 (1964); Phys. Rev. 137, A1745 (1965).

[14]L. Neumann and L. Tewordt, Z. Physik 189, 55 (1966).

[15]It should be noted that two definitions exist for the surface energy of a phase boundary which differ by a term equal to the surface energy in London theory. Our definition agrees with the quantity α_{ns} defined in Bardeen's paper (Ref. 2).

[16]For a comprehensive discussion, see D. Saint-James, E. J. Thomas, and G. Sarma, *Type II Superconductivity* (Pergamon, London, 1969).

[17]The error so introduced is of order $[k_F^2 \lambda(T) \xi(T)]^{-1} \ll 1$.

[18]In all density-of-states formulas, we ignore contributions, if any, from those Landau orbits which are totally confined within the normal region. Obviously such terms do not contribute to the free-energy difference ΔG that we wish to calculate.

[19]A. F. Andreev, Zh. Eksperim. i Teor. Fiz. 49, 655 (1965) [Sov. Phys. JETP 22, 455 (1966)].

[20]It follows from conservation of the total number of particles and particle-hole symmetry.

[21]Near T_c the natural length scale is the GL coherence length $\xi(T)$. But to conform with our low-temperature calculation we have converted it to the length $\xi_\Delta(T)$ which is defined at all T by Eq. (3.7e). This accounts for the noninteger numerical coefficients that appear in Eq. (5.25).

[22]A. E. Jacobs, Phys. Rev. B 4, 3022 (1971); Phys. Rev. Letters 26, 629 (1971).

[23]L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 37, 833 (1959) [Sov. Phys. JETP 10, 593 (1960)].

[24]E. Helfand and N. R. Werthamer, Phys. Rev. 147, 288 (1966).

[25]K. Maki and T. Tsuzuki, Phys. Rev. 139, A868 (1965).

[26]G. Eilenberger, Phys. Rev. 153, 584 (1967).

[27]G. Eilenberger, Z. Physik 182, 427 (1965).

[28]See Ref. 21 and A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinsky, *Methods of Quantum Field Theory*

in Statistical Physics, translated by R. A. Silverman (Prentice-Hall, Englewood Cliffs, N. J., 1963). See also C.-R. Hu and V. Korenman, Phys. Rev. 178, 684 (1969), and Ref. 22.

[29]We notice that Eqs. (6.1)–(6.3) are in fact identical to what is implied for the corresponding quantity in the vortex problem by the Eqs. (3)–(5) of Ref. 12 before the variable ρ is changed to x. We therefore suspect the existence of a transformation that could link the solutions of the two cases, but further study has yet to be made for a definite conclusion.

[30]Because of this we favor using the adjectives "unexpected" or "anomalous" rather than "nonanalytic" as is used by Jacobs (Ref. 12) to describe those terms in the expansion of BKJT free energy not predicted by the Ginzburg-Landau and Newmann-Tewordt theories.

[31]N. R. Werthamer, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Chap. 6.

[32]For the definitions of asymptotic expansion and the symbol "$\sim$", see, for example, A. Erdelyi, *Asymptotic Expansions* (Dover, New York, 1956).

PHYSICAL REVIEW B VOLUME 6, NUMBER 1 1 JULY 1972

Mössbauer Isomer Shifts in Sm^{149} Compounds

M. Eibschütz, R. L. Cohen, E. Buehler, and J. H. Wernick
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 23 September 1971)

The isomer shift (IS) of the 22.5-keV γ transition of Sm^{149} has been studied for various ionic, semiconducting, and metallic compounds using Mössbauer spectroscopy. We found changes as large as 0.9 mm/sec between trivalent and divalent compounds and 0.3 mm/sec between metallic and ionic trivalent compounds. The divalent compounds show a range of IS due to covalency effects, and the intermetallic compounds, which all have Sm in the trivalent state, show the extra electronic density due to the conduction electrons. The IS obtained for the semiconducting SmB_6, −0.4 mm/sec, and for the chalcogenide Sm_3S_4, −0.19 mm/sec, are anomalous. We calculated the difference in the mean-square charge radius between the 22.5-keV state and the ground state $\delta\langle r^2\rangle = 1.2\times10^{-3}$ fm^2. We also found the conduction-electron density at the nucleus of Sm metal $|\Psi|^2(\mathrm{CE}) = 0.95\times10^{26}$ cm^{-3}. The solid-state and nuclear results are discussed in the light of current theories.

INTRODUCTION

Isomer shifts (IS) in rare-earth nuclei have been observed during the past ten years, but relatively few measurements on IS of samarium compounds have been reported.[1] We have previously published the results[2] of measurements of the IS of SmB_6, and presented,[3] in abstract form, some results of IS measurements on divalent, trivalent, and intermetallic Sm compounds. This paper is the first extensive report of these measurements.

In particular, we present here measurements of the IS of Sm^{149} in various ionic, semiconducting, and metallic compounds, and determinations of the change of electronic density at the Sm nucleus due to chemical effects. The electronic structure of these materials is discussed in the light of the results. We have also determined the mean-square charge-radius change $\delta\langle r^2\rangle = \langle r_e^2\rangle - \langle r_g^2\rangle$ between the excited ($I = \frac{5}{2}$) and ground ($I = \frac{7}{2}$) states of Sm^{149} and will here compare the experimental value to that obtained from nuclear model calculations.

The shifts between centroids of Mössbauer spectra of various absorbers are usually described in terms of an electric monopole term, resulting from the electrostatic interaction energy between the nuclear charge density and the electronic density within the nuclear radius. This energy is different for different nuclear states, because of the effective nuclear charge-radius change $\delta\langle r^2\rangle$, and varies with effective electronic density, $|\Psi(0)|^2$, at the nucleus.[4,5]

The energy shift due to this interaction is given to a good accuracy by the formula[5,6]

$$\Delta E = E_1 - E_2 = \tfrac{2}{3}\pi\, Ze^2\left[\,|\Psi(0)|_1^2 - |\Psi(0)|_2^2\right]\delta\langle r^2\rangle\,, \tag{1}$$

where E_1 and E_2 are the nuclear excitation energies in compounds with total electron density at the nucleus $|\Psi(0)|_1^2$ and $|\Psi(0)|_2^2$, and Z is the nuclear charge. The nuclear mean charge radii $\langle r^2\rangle_{e,g}$ in the excited state (e) and ground state (g) are defined by the relation

$$\langle r^2\rangle = \int \rho(r)\, r^2\, dr \Big/ \int \rho(r)\, dr\,, \tag{2}$$

where $\rho(r)$ denotes the nuclear charge density, and the integral is taken over the nuclear volume. Relation (1) is exact to the first order, when the electron density is constant in the region of the nucleus[5,6] and relativistic electron densities are used.