Surface Induced Anomalous Superconductivity

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I. INTRODUCTION

Macroscopic effects of superconductivity are investigated using the Ginzburg-Landau (GL) phenomenological model for the free energy of the superconducting state characterized by a complex order parameter \( \psi \) and two parameters \( \alpha \) and \( \beta \). These parameter are, respectively, coefficients of the linear superconducting (SC) pair density term \( \propto |\psi|^2 \) and the quadratic pair interaction term \( \propto |\psi|^4 \). A variational process leads to coupled GL differential equations that characterize a minimum free energy state that depends on the surface energy density through additional parameters. In almost all cases the source of an applied magnetic field or a current is externally controllable and the free energy density. The sign of these parameters, which define distinct solution classes, and the ratio \( s(t) = \sqrt{\alpha/\beta} \) are governed by the characteristics of the surface energy density. In addition to the conventional bulk superconducting states with \((\alpha < 0, \beta > 0)\), anomalous superconducting states exist for all other sign combinations, including cases with \( \beta < 0 \) which may exist only when surface pair interactions are significant. All possible solutions of our generalized nonlinear, one dimensional GL equations are found analytically and applied to a thin superconducting slab which manifests the possibility of states exhibiting enhanced, diminished, and pre-wetting superconductivity. Critical currents are determined as functions of \( s(t) \) and surface parameters. The results are applied to critical current experiments on SNS systems.
$K \propto \psi^* \mathbf{p}^2 \psi = |\psi|^2 - i\mathbf{e} \cdot (\psi^* \mathbf{p} \psi)$, where the parameter $\epsilon = 1$, or 0 is used to keep track of the difference between the $K$ model and the standard GL model. In view of the divergence operation, the additional term is a surface term. The imaginary part of the divergence term is identically zero, but the real part changes the surface boundary conditions, and hence the character of the order parameter throughout the sample volume. It is shown that the real part of the divergence term in the $K$ model destroys superconductivity unless the surface energy is augmented by a term $c|\psi| |\nabla|\psi|$, where $c \geq \epsilon$ is a constant. Furthermore, a second order phase transition is possible only if $c = \epsilon$, and the transition temperature is higher for $c = \epsilon$ than for any value of $c > \epsilon$. For $c < \epsilon$ SC states do not exist for small values of the order parameter; however, first order phase transitions may exist.

In the GL theory $\alpha$ and $\beta$ are arbitrary parameters, assumed to be functions of the reduced temperature $t = T/T_c$. However, the explicit temperature dependence of $\alpha$ and $\beta$ is not given and thus has to be conjectured from experiments. Since we do not want to assume a priori an explicit temperature dependence, we first investigate the solutions of the GL equations consistent with the boundary conditions, independent of specific temperature models for $\alpha$ and $\beta$. For one dimensional systems with a uniform current density $j$, all possible physical solutions of the GL equations, with $\text{sgn}(\alpha) = \pm 1$ and $\text{sgn}(\beta) = \pm 1$ are found, and categorized. These solutions are then applied to a plane slab SC sample and the influence of the surface energy parameters $b_2$ and $b_4$ on the sample order parameter is studied, and unusual SC states, including “pre-wetting” surface states, are analyzed. Critical currents are shown as functions of $s(t)$. A temperature model is introduced for the fundamental ratio $s(t) = \sqrt{|\alpha(t)|/|\beta(t)|}$ to illustrate possible enhancement or reduction of the critical temperature. Finally, the critical current of a superconductor-normal-superconductor (SNS) layered system is calculated, and the results with $\alpha > 0, \beta > 0$ are shown to be in excellent agreement with critical current experiments.

II. GENERAL EQUATIONS

As originally formulated by Ginzburg and Landau, the free energy of a superconductor in a magnetic field $\mathbf{H}$ is a function of a coordinate dependent complex order parameter $\psi(\mathbf{r})$ and the vector potential $\mathbf{A}(\mathbf{r})$. We begin our development with a general energy functional $\mathcal{G}$ that encompasses a broad spectrum of models, including those leading to the stationary states of the Schrödinger equation and the GL equations for SC. It is

$$
\mathcal{G} = \int d^3r \left[ U(\mathbf{r}, |\psi(\mathbf{r})|) + K(\mathbf{r}) + \frac{1}{2\mu_0} |\nabla \times \mathbf{A'}(\mathbf{r})|^2 \right] + \frac{\hbar^2}{2m^*} \int_S d\mathbf{s} \cdot \hat{n} \Lambda(|\psi, \mathbf{A}|) + \frac{c}{2} \nabla |\psi|^2, 
$$

(2.1)

where $U$ is a potential energy density that depends only on functions of $\mathbf{r}$ and $|\psi(\mathbf{r})|$, $K(\mathbf{r})$ is the kinetic energy density, and $\mathbf{A'}$ is a linear function of $\mathbf{A}$. Specific forms of $U$ and $\mathbf{A'}$ will be detailed later. The second integral is over the surface $S$ enclosing the volume $V$. The unit vector $\hat{n}$ is normal to the surface at each point on $S$. The surface integrand function $\Lambda$, which has units of $(\text{length})^{-1}$, is assumed to contain all parameters that characterize not only the intrinsic aspects of the surface, but also external effects that link to the sample volume via the surface. It is shown below that the $c\nabla |\psi|^2$ term is necessary for a SC state to exist, and the value of $c$ determines whether a SC state exists and whether a phase transition to the SC state is first or second order. The boundary conditions for $\psi$ depend on $c$ and $\Lambda$, and a specific form for $\Lambda$ is introduced.

The kinetic energy density $K$ of a particle of effective mass $m^*$ and charge magnitude $e^*$ subject to a vector potential $\mathbf{A}$ is given by

$$
\frac{2m^*}{\hbar^2} K(\mathbf{r}) = \psi^* \mathbf{p}^2 \psi = |\mathbf{p} \psi|^2 - i\mathbf{e} \cdot (\psi^* \mathbf{p} \psi),
$$

(2.2)

where

$$
\mathbf{p} = -i\nabla + \frac{e^*}{\hbar} \mathbf{A},
$$

The first term in Eq. (2.2) is the form used in the standard GL functional. To distinguish the effects arising from the complex divergence term the parameter $\epsilon = 1$ or 0 is introduced. When $\epsilon = 0$ one recovers the standard GL model. As shown below, only the real part of the divergence term in $K$ contributes to $\mathcal{G}$.

Introducing the modulus-phase form

$$
\psi(\mathbf{r}) = |\psi(\mathbf{r})| \exp[i\theta(\mathbf{r})],
$$

(2.3)

the density $K$ assumes the form
\begin{equation}
\frac{2m^*}{\hbar^2} K(r) = \left[ \nabla |\psi| \cdot \nabla |\psi| + |\psi|^2 \mathbf{Q} \cdot \mathbf{Q} \right] - \imath c \nabla \cdot [|\psi|^2 \mathbf{Q} - \frac{\hbar}{2} \nabla |\psi|^2],
\end{equation}
where the vector \( \mathbf{Q} \) is the gauge invariant phase gradient
\begin{equation}
\mathbf{Q} = \nabla \phi + \frac{2\pi}{\phi_o} \mathbf{A},
\end{equation}
with \( \phi_o = \hbar/e^* \) the flux quantum. In the superconducting case, \( e^* = 2|\psi| > 0 \) is the SC pair charge. The magnetic field \( \mathbf{H} \) is given by
\begin{equation}
\mu_o \mathbf{H} = \nabla \times \mathbf{A} = \frac{\phi_o}{2\pi} \nabla \times (\mathbf{Q} - \nabla \phi).
\end{equation}
As will be shown, the term \( \nabla \cdot [|\psi|^2 \mathbf{Q}] \) may appear to be the divergence of a diffusion current, but it is not. It contributes to the surface energy. Using Eq. (2.4), the functional \( G \) is
\begin{equation}
G = \int d^3r \left[ U(|\psi|) + \frac{\hbar^2}{2m^*} \nabla |\psi| \cdot \nabla |\psi| + |\psi|^2 \mathbf{Q} \cdot \mathbf{Q} + \frac{1}{2\mu_o} [\nabla \times \mathbf{A}]^2 \right] + \int d^2 s \cdot [\hat{\mathbf{n}} \Lambda(|\psi|, \theta, \mathbf{A}) + \frac{1}{2}(a - 1) \nabla |\psi|^2], \quad \text{with} \quad a = 1 + c - \epsilon.
\end{equation}
The conventional GL free energy difference \( \Delta G = G_{sc} - G_0 \) between the superconducting and normal states is given by \( G \) in Eq. (2.7) with \( c = \epsilon = 0 \) and \( \mathbf{A}' = \mathbf{A} - \mathbf{A}_0 \), where \( \mathbf{A}_0 \) is the vector potential of the applied field \( \mathbf{H}_a \). Note that for the standard GL model \( \epsilon = 0 \) in \( K \propto \psi^* \psi = |p\psi|^2 - \imath c \nabla \cdot (\psi^* \mathbf{p} \psi) \). The vector potential \( \mathbf{A} \) that appears in \( \mathbf{Q} \) reduces to \( \mathbf{A}_a \) for single particle models, since a single charged particle does not interact with its own field.

The vectors \( \nabla \phi \) and \( \mathbf{A} \) in \( \mathbf{Q} \) are distinct mathematical entities. When a magnetic field is present \( \nabla \times \mathbf{A} \neq 0 \), whereas \( \nabla \times \nabla \phi = 0 \), except at vortex centers, where \( \nabla \times \nabla \phi \) is a sum of delta functions\(^8,9\). Thus \( \phi \) and \( \mathbf{A} \) must be considered as independent variables, and the minimum set of independent variables contains three elements, which we chose as \(|\psi|, \theta, \mathbf{A}\). As outlined the Appendix, setting the variation \( \delta G = 0 \), leads to the differential equations in the volume and corresponding surface boundary conditions. The variation with respect to \(|\psi|, \theta \) and \( \mathbf{A} \), respectively yield
\begin{equation}
\nabla^2 |\psi| = \frac{m^*}{\hbar^2} \frac{\partial U}{\partial |\psi|} + |\psi| \mathbf{Q} \cdot \mathbf{Q},
\end{equation}
\begin{equation}
\nabla \cdot [|\psi|^2 \mathbf{Q}] = 0,
\end{equation}
\begin{equation}
\frac{1}{\mu_o} \nabla \times (\nabla \times \mathbf{A}') = -\epsilon_s \frac{e^* \hbar}{m^*} |\psi|^2 \mathbf{Q},
\end{equation}
The parameter \( \epsilon_s = 0 \) for single particle models and \( \epsilon_s = 1 \) for models that include particle interaction terms, e.g. the GL model.

The corresponding surface boundary conditions are
\begin{equation}
[(a + 1) \nabla |\psi| + (a - 1)|\psi| \frac{\partial |\psi|}{\partial |\psi|}] \cdot \hat{\mathbf{n}} = - \frac{\partial \Lambda}{\partial |\psi|},
\end{equation}
\begin{equation}
2|\psi|^2 \mathbf{Q} \cdot \hat{\mathbf{n}} = \frac{\partial \Lambda}{\partial \theta},
\end{equation}
and
\begin{equation}
\frac{1}{\mu_o} \hat{\mathbf{n}} \times (\nabla \times \mathbf{A}') = \frac{\hbar^2}{2m^*} \nabla \Lambda.
\end{equation}
As outlined in the last paragraph of the Appendix, the minimum energy functional consistent with Eq. (2.8)- (2.13) assumes the form
\[ G_{\text{min}} = \int d^3r \left\{ U - \frac{1}{2} |\psi|^2 \partial U \left/ \partial |\psi| \right| + \frac{1}{2 \mu_s} |\nabla \times A|^2 \right\} + \frac{\hbar^2}{2m^*} \int \text{d}s \cdot \hat{n} \Lambda + \frac{1}{2} \hbar^2 |\nabla |\psi|^2|. \]  
(2.14)

Using the boundary condition (2.11) with \( a = 1 \), the expression for \( G_{\text{min}} \) can be written in the form
\[ G_{\text{min}} = \int d^3r \left\{ g(U) + \frac{1}{2 \mu_s} |\nabla \times A|^2 \right\} + \frac{\hbar^2}{2m^*} \int \text{d}s \cdot \hat{n} g(\Lambda), \]  
(2.15)

where
\[ g(F) = -|\psi|^3 \partial F \left/ \partial |\psi|^2 \right| \left[ \frac{F}{|\psi|^2} \right]. \]

Equation (2.15) shows the functional symmetry of the volume potential energy density \( U \) and the surface potential energy per unit area \( \left( \hbar^2/2m^* \right) \Lambda \) which determine \( G_{\text{min}} \). It is evident from this form of \( G_{\text{min}} \) that if \( U \) and \( \Lambda \) are expanded in powers of the particle density, the coefficient of leading term \(|\psi|^2\) does not contribute directly to \( G_{\text{min}} \). To proceed further one must introduce models for the functions \( U \) and \( \Lambda \).

For the potential energy density \( U \) we assume the form
\[ U(r, |\psi(r)|) = \alpha(r) |\psi(r)|^2 + \frac{1}{2} \beta(r) |\psi(r)|^4, \]  
(2.16)

where \( n_s^* \) is a constant reference particle density. As formulated, the parameters \( \alpha, \beta \), have units of energy. The function \( U \) in (2.16) encompasses both the Schrödinger quantum stationary state and GL superconductivity models. In the former case, \( \alpha(r) = V(r) - E \), and \( \beta = 0 \), with \( E \) the energy eigenvalue and \( V \) the potential. For the GL model, \( \alpha \) and \( \beta \) are independent of \( r \), \( n_s^* \) is the SC pair density at \( T = 0 \), and \( \psi(r) \) is the complex order parameter.

Since it is generally easier to solve the linear Schrödinger equation for the complex wave function \( \psi \) than the coupled nonlinear Eqs. (2.8) and (2.9), we do not pursue the coupled approach here; however, there are some advantages to this approach for interacting electron systems\(^8\).\(^9\). The remainder of the paper concerns superconducting systems with \( \alpha \) and \( \beta \) independent of the coordinate \( r \).

For mathematical expediency it is convenient to normalize the order parameter using a positive constant \( \psi_o \). Since the GL energy and resulting GL variational equations are independent of the value of \( \psi_o \), its choice is arbitrary. Using the scaled temperature notation \( t = T/T_c \), where \( T_c \) is the temperature at which a second order phase transition, with limit \( |\psi| \to 0 \), would occur in a bulk sample, we employ the implicit temperature dependent normalization
\[ f(r) = \frac{|\psi(r)|}{\psi_o(t)}, \quad \psi_o(t) = \sqrt{n_s^* s(t)}. \]  
(2.17)

The unitless temperature dependent function \( s(t) \) is defined by the fundamental length ratio
\[ s(t) = \frac{l_\beta(t)}{l_\alpha(t)} = \sqrt{\frac{|\alpha(t)|}{|\beta(t)|}}, \]  
(2.18)

where the lengths are defined as
\[ l_\alpha = \frac{\hbar}{\sqrt{2m^* |\alpha|}}, \quad l_\beta = \frac{\hbar}{\sqrt{2m^* |\beta|}}. \]  
(2.19)

In conventional superconductivity, with \( (\alpha < 0, \beta > 0) \), the length \( l_\alpha \) is referred to as the GL coherence length, usually denoted as \( \xi \). For a bulk superconductor with \( \Lambda = 0 \) the pair density for minimum energy \( |\psi_m(t = 0)|^2 = -\alpha(0)/\beta(0) = 1 \). Thus the maximum value of \( s(t) \) is \( s(0) = 1 \), i.e. \( l_\alpha(0) = l_\beta(0) \). When \( \Lambda \neq 0 \), anomalous SC states exist with \( s(t) > 1 \), even when \( t > 0 \); thus we retain the notation \( l_\alpha \) to denote a fundamental length that can assume values outside the range of the conventional coherence length \( \xi \). We also define a normalized, unitless, order parameter
\[ \chi(r) = \frac{|\psi(r)|}{\sqrt{n_s^*}} = s(t) f(r). \]  
(2.20)

Because the scaling parameter \( n_s^* \) is temperature independent, \( \chi \) is always physically meaningful; whereas \( f \) may become singular when the temperature dependent scaling parameter \( s(t) \to 0 \). Thus the function \( f \), although mathematically useful, is not in general a physical order parameter.
Since $\Delta G$ depends not only on the magnitudes, but also the signs of $\alpha$ and $\beta$, it is convenient to write $\alpha = |\alpha| \text{sgn}(\alpha)$, and $\beta = |\beta| \text{sgn}(\beta)$, where $\text{sgn}(\ldots) = \pm 1$. Using Eqs. (2.16)-(2.19), the equations (2.8)-(2.10) in the volume $V$ assume the form

$$l_0^2 \nabla^2 f = |\text{sgn}(\alpha)| + |\text{sgn}(\beta)| f^2 + l_0^2 Q \cdot Q f,$$

$$\nabla \cdot (f^2 Q) = 0,$$

$$\nabla \times [\nabla \times (Q - Q_a)] + \left(\frac{s}{\lambda_L}\right)^2 f^2 Q = \nabla \times [\nabla \times (V - \theta - \theta_0)].$$

(2.21)

(2.22)

(2.23)

with $\lambda_L = (1/e^*) \sqrt{m^*/(\mu_a n_s^*)}$ the London magnetic field penetration depth which is temperature independent. The inhomogeneous term in Eq. (2.23) is present when vortices, or 3D worm holes exist. Equation (2.23) may be written in the form

$$\nabla \times (H - H_a) = -\frac{|e|}{\epsilon \mu_0} \left(\frac{s}{\lambda_L}\right)^2 f^2 Q = -\frac{e^*}{m^*} |\psi|^2 Q. $$

(2.24)

The right hand side of Eq. (2.24) is the physical super current density $j$, which we write in terms of a unitless current density parameter $J$ by

$$j = -j_o J, \quad \text{where} \quad J = l_0 f^2 Q, \quad j_o = \frac{|e|}{\epsilon \mu_0} \left(\frac{s}{\lambda_L}\right)^2. $$

(2.25)

Although $J$ is a convenient parameter for mathematical reasons, it is not appropriate for physical interpretation since it is singular in the limit $s \to 0$. Thus we also define the unitless current parameter

$$k_j = \frac{m^* l_0}{e^* h n_s^*} j = -s^3(t) J. $$

(2.26)

For plotting, $k_j$ is a well behaved parameter that tracks the physical current density $j$.

The surface boundary conditions from Eqs. (2.11)-(2.13) are

$$[(a + 1)\nabla f + (a - 1) f \frac{\partial \nabla f}{\partial f}] \cdot \hat{n} = -\frac{1}{\psi_o^2} \frac{\partial \Delta(f, \theta)}{\partial f}, $$

(2.27)

where $a = 1 + c - \epsilon$, and

$$\hat{n} \times (H - H_a) = \frac{h^2}{2m^*} \nabla \Delta, $$

(2.28)

$$\frac{2m^*}{e^* h} j \cdot \hat{n} = -2\psi_o^2 f^2 Q \cdot \hat{n} = \frac{\partial \Delta(f, \theta)}{\partial \theta}. $$

(2.29)

Equation (2.22) is the continuity equation for $j$, and Eq. (2.29) is the boundary condition for the current normal to the surfaces. If $\Lambda(f, \theta)$ contains a product of $f$ and $\theta$, then the boundary conditions (2.27) and (2.29) are coupled.

From Eq. (2.14), the minimum free energy $\Delta G = G_{sc} - G_n$ for superconducting systems assumes the form

$$\Delta G_{min} = \frac{1}{2} \int_V d^3 r \left[ (A - A_a) \cdot j - \text{sgn}(\beta) n_s^* |\beta| s^4 f^4(r) \right] + \frac{h^2}{2m^*} \int d^3 s \cdot [\hat{n} \Delta + \frac{1}{2} an_s^* s^2 \nabla f^2]. $$

(2.30)

To proceed further one must formulate a model for the function $\Lambda(f, \theta)$, which determines the boundary conditions for $\psi$ and the minimum free energy. When currents are present a general form for $\Lambda(f, \theta)$ is not known. However, if the surface is that of a SNS junction, or Josephson junction, with tunneling supercurrent density $j \cdot \hat{n} = j_c \sin \Delta \theta$, it follows from Eq. (2.29) that $\Lambda$ must contain a term $\propto -j_c \cos \Delta \theta$, where $\Delta \theta$ is the phase difference across the link.

In the absence of transport currents, the superconducting sample in volume $V$ is in thermal equilibrium with the surrounding material. One may assume that the sample and its surface are characterized by an order parameter $\psi$, with $\Lambda$ a function of $|\psi| = \psi_o f$ only. As discussed after Eq. (2.15), the surface energy term $\Delta$ contributes to $\Delta G_{min}$}
only if $\Lambda$ deviates from the form $\Lambda \propto |\psi|^2$. Thus, to obtain the leading surface contribution for $J = 0$, we introduce the surface energy function $\Lambda$ as

$$\Lambda = \frac{1}{b_2} |\psi|^2 + \frac{1}{2b_4 n_s^2} |\psi|^4 = \psi_o^2 \left( \frac{1}{b_2} f^2 + \frac{1}{2b_4 s^2 f^4} \right).$$

(2.31)

The first term is the form introduced by de Gennes, where $b_2$ is a characteristic length for the surface. The second term represents the superconducting pair interaction energy, with $b_4$ a characteristic length. This term must be present in our approach for temperatures well below the critical temperature to be consistent with the retention of the $f^4$ term in the bulk free energy. The $f^4$ term may also be significant over most of the temperature range when the surface is strongly superconducting due to contact with a higher $T_c$ superconductor than the sample considered. Substituting the surface model (2.31) into Eq. (2.30), and using the boundary condition (2.27) to eliminate $1/b_2$ leads to the form

$$\Delta G_{\text{min}} = -\frac{1}{2} n_s^2 |\beta| s^2 \left\{ \text{sgn}(\beta) s^2 \int d^3 r f^4(r) + l_3^2 \int ds \cdot f^2 \left[ (a - 1) \left( \frac{\partial f}{\partial f} - \frac{\nabla f}{f} \right) + \hat{n} \frac{1}{b_4 s^2 f^2} \right] \right\}.$$  

(2.32)

Although the volume term with $\alpha$ cancelled and the surface term with $b_2$ was eliminated, $\Delta G_{\text{min}}$ remains an implicit function of $\alpha$ and $b_2$ since $f$ depends on them via Eqs. (2.21) and (2.27). If $a \neq 1$ ($c \neq c$), it will be shown that $\Delta G_{\text{min}}$ is greater than it is for $a = 1$. Furthermore, only $a = 1$ permits a second order phase transition. For $a = 1$ and $l_3^2/b_4 \geq 1$ the parameter $\beta$ can be negative and still have $\Delta G_{\text{min}} < 0$, i.e. the overall sample is in SC state. If $l_3^2/b_4 \ll 1$, the surface effect is negligible and the parameter $\beta$ must be positive for a SC state to exist. In the Gor'kov derivation of the GL equations from the microscopic BCS theory, $\beta$ is always positive. However, surface effects were not considered in the Gor'kov derivation.

As final observations for Section II, we examine the scaling roles of the fundamental lengths $l_o$ and $l_3$, and the uniform solution of Eq. (2.21). It is evident from Eqs. (2.21), (2.23), and the definition of $Q$ that $l_o$ scales the coordinate $r$, i.e. one may use $r \to r/l_o$. Multiplying Eq. (2.23) by $l_3^3$ to scale the coordinate, the only parameter in Eq. (2.23) is the experimentally observable parameter $\kappa = \lambda_o/l_o = \lambda_L/l_3$, where $\lambda_o = \lambda_L/s$ is equal to the Ginsburg-Landau penetration depth $\lambda_{GL}$ in conventional superconductivity. However, for the anomalous SC cases analyzed in section III, $\lambda_o$ can lie outside the range of the conventional $\lambda_{GL}$. The lengths $l_o$ and $l_3$ defined in Eq. (2.19) are positive real numbers. All signs consistent with the general GL Eq. (2.21) are in sgn($\alpha$) = ±1, and sgn($\beta$) = ±1, which dictate whether a solution $f$ is an oscillatory or non-oscillatory function of the coordinate $r$.

Consider the possibility of a uniform solution $f_u(r) = f_0$ of Eq. (2.21). Setting $\nabla^2 f = 0$ and using Eqs. (2.20) and (2.26) gives

$$Q_u = \pm q_u, \quad q_u = \frac{k_\perp}{l_3 \chi^2} = \frac{1}{b_4 s} \sqrt{|\text{sgn}(\alpha) s^2 + \text{sgn}(\beta) \chi^2|}.$$  

(2.33)

From the definition of $Q$, Eq. (2.5), the phase difference over path $r = 0$ to $r = d$ is

$$\theta(d)_u - \theta(0)_u = \frac{2\pi}{\phi_o} \int_0^d dr \cdot A \pm q_u d.$$  

(2.34)

Since the constant $q_u$ is real, the case with sgn($\alpha$) = sgn($\beta$) = 1 is excluded. Further restrictions are given in Eq. (3.16) below. Using Eq. (2.34), the uniform solution has the general form

$$\psi(r)_u = \exp \left( -\frac{2\pi i}{\phi_o} \int dr \cdot A \right) \left[ c_+ e^{iq_u r} + c_- e^{-iq_u r} \right].$$  

(2.35)

As will be shown, the uniform solution plays an important role in the general solution space. This solution appears, not only at a second order phase transition where $|\psi| \to 0$, but also well below the transition point where $|\psi|$ is large.

### III. ONE DIMENSIONAL SYSTEMS

#### Analytic Solution Classification

In this section a complete set of analytic solutions of the first GL equation is derived for one dimensional systems, which in accordance with Eq. (2.22) have uniform current density. In general Eqs. (2.21) and (2.23) are coupled since
Q remains multidimensional. However in SC microwires,\textsuperscript{12} and certain thin films of thickness $\leq \lambda_{GL}$ of arbitrary widths\textsuperscript{13}, the current density is approximately uniform. Consider a one dimensional system with coordinate $x$. Approximating the magnitude of the true current density by its mean value over all $x$, and using $J = l_\alpha f^2 Q$, the first GL equation (2.21) is

$$l_\alpha^2 \frac{d^2 f}{dx^2} = \text{sgn}(\alpha) f + \text{sgn}(\beta) f^3 + J^2 f^{-3},$$

subject to the boundary condition

$$\frac{1}{2} \left[ (a + 1) f^{-1} \frac{df}{dx} + (a - 1) \left( \frac{df}{dx} \right)^{-1} \frac{d^2 f}{dx^2} \right]_b = -\frac{1}{b_2} - \frac{1}{b_4} s^2 f^2|_b,$$  

where the subscript $b$ denotes the surface boundary. At this point the rationale for introducing the normalized function $f$ and current parameter $J$ is evident. Since one may use $x/l_\alpha$ as a normalized coordinate, the only parameter in Eq. (3.1) is $J$. The unitless current parameter $J$, together with $\text{sgn}(\alpha) = \pm 1$, and $\text{sgn}(\beta) = \pm 1$ completely characterize the solutions of Eq. (3.1).

When dealing with current carrying states, it is useful to introduce $N(x) = f^2(x)$. Equations (3.1) and (3.2) assume the forms

$$Nl_\alpha^2 \frac{d^2 N}{dx^2} = 2J^2 + 2N^2[\text{sgn}(\beta)N + \text{sgn}(\alpha)] + \frac{1}{2} \left( l_\alpha \frac{dN}{dx} \right)^2,$$

and

$$\frac{1}{2} \left[ \frac{1}{2}(a + 1) N^{-1} \frac{dN}{dx} + 2(a - 1)[J^2 + N^2(\text{sgn}(\beta)N + \text{sgn}(\alpha))] \left( l_\alpha^2 \frac{dN}{dx} \right)^{-1} \right]_b = -\frac{1}{b_2} - \frac{1}{b_4} s^2 N|_b,$$

which will be used below.

Integrating Eq. (3.1), assuming $J$ constant gives

$$2 \left( l_\alpha \frac{df}{dx} \right)^2 = \text{sgn}(\beta) f^4 + 2\text{sgn}(\alpha) f^2 - 2J^2 f^{-2} + C,$$

where $C$ is a constant of integration. All solutions of Eq. (3.5) may be expressed in terms of Jacobian elliptic functions $pq[u(x)|m|]$, which are periodic in the argument $u(x)$. In general when $J \neq 0$, determination of these functions requires the roots of a cubic equation in $f^2$. However, the process is considerably simplified by dividing the solutions into two classes: 1. Functions with at least one positive finite extremum at $x = x_0$, at which point $C$ is evaluated. 2. Functions with $f(x = x_0) = 0$, at which point $C$ is evaluated. In the first class only roots of a quadratic equation are required. For the second class only cases with $J = 0$ are possible, and these may also be resolved by a quadratic.

**Solutions with Finite, Positive Extrema**

If $f$ has at least one finite extremum point within each period, the constant $C$ may be evaluated at an extremum point $x_0$, where $df/dx = 0$. Thus, we write Eq. (3.5) in the form

$$2f^2 \left( l_\alpha \frac{df}{dx} \right)^2 = (f_0^2 - f_0^2)\{\text{sgn}(\beta)f^4 + [\text{sgn}(\beta)f_0^2 + 2\text{sgn}(\alpha)]f^2 + 2J^2 f^{-2}\},$$

where $f_0 = f(x_0)$ is an extremum to be determined from boundary conditions. A second extremum $f_1^2 = f^2(x_1)$, given in terms of $f_0$ by setting the factor $\{\ldots\} = 0$, may exist for both real and imaginary $f_1$.

Setting $N(x) = f^2(x)$, Eq. (3.6) assumes the form

$$\left( l_\alpha \frac{dN}{dx} \right)^2 = 2(N - N_0)\{\text{sgn}(\beta)N^2 + [\text{sgn}(\beta)N_0 + 2\text{sgn}(\alpha)]N + 2J^2 N_0^{-1}\},$$

Since the solutions are referenced to the extremum value $N_0 = N(x_0)$, it follows from Eq. (3.3) that the sign of the parameter $b_0$, given by
\[ b_0 = \frac{l_0^2 d^2 N}{dx^2} \bigg|_{x_0} = \frac{2}{N_0} [J^2 - C_0], \quad \text{with} \quad C_0 = -N_0^2[\text{sgn}(\beta)N_0 + \text{sgn}(-\alpha)], \quad (3.8) \]

determines whether \( N_0 \) is a maximum or a minimum.

For mathematical expediency, it is useful to make the following variable shift:
\[ N(x) = N_0 + \text{sgn}(b_0)\nu^2(x). \quad (3.9) \]

Equation (3.7) yields
\[ 2 \left( l_0 \frac{d\nu}{dx} \right)^2 = \text{sgn}(b_0)\text{sgn}(\beta)(\nu^2 - r_+)(\nu^2 - r_-), \quad (3.10) \]

which has roots
\[ r_\pm = \gamma \pm \Delta, \quad (3.11) \]

with
\[ \gamma = -\text{sgn}(b_0) \left[ \frac{3}{2} N_0 + \text{sgn}(\alpha)\text{sgn}(\beta) \right], \quad \Delta = \sqrt{\gamma^2 - b_0\text{sgn}(\beta)} = \sqrt{\frac{2}{N_0} |C_1 - J^2\text{sgn}(\beta)|}, \]
\[ C_0 = -N_0^2[\text{sgn}(\beta)N_0 + \text{sgn}(\alpha)], \quad C_1 = \frac{N_0}{2} \left[ \frac{N_0}{2} + \text{sgn}(\alpha)\text{sgn}(\beta) \right]^2. \]

For \( J = 0 \), one must use the magnitude of \( C_1 \) to obtain the correct result \( \Delta \geq 0 \). The solutions of Eq. (3.10) are the various elliptic function combinations, listed in (3.13) and (3.14), whose specific form is dictated by the characteristics of the roots shown in (3.12).

**Roots**: The array below shows the root ordering for all sign combinations that yield real \( N(x) \geq 0 \) solutions. The dashed line separates the positive \( \beta \) cases from the negative \( \beta \) cases.

| Case | \( \text{sgn}(\alpha) \) | \( \text{sgn}(\beta) \) | \( \text{sgn}(b_0) \) | Root Order | \( N_0 \) Range | \( J^2 \) Range |
|------|----------------|----------------|----------------|-------------|--------------|--------------|
| A    | -1            | 1              | -1            | \( r_+ > 0, \ r_- < 0 \) | \( 0 \leq N_0 \leq 1 \) | \( J^2 \leq C_0 \leq C_1 \) |
| B    | -1            | 1              | 1             | \( r_+ > r_- > 0 \) | \( 0 \leq N_0 \leq 2/3 \) | \( C_0 \leq J^2 \leq C_1 \) |
| C    | -1            | 1              | 1             | \( r_- < r_+ < 0 \) | \( N_0 \geq 2/3 \) | \( C_0 \leq J^2 \leq C_1 \) |
| D\pm | \pm1          | 1              | 1             | \( r_- = r_+ \) | \( 0 \leq N_0 < \infty \) | \( C_0 \leq C_1 \leq J^2 \) |
| E    | 1             | 1              | 1             | \( r_- < r_+ < 0 \) | \( 0 \leq N_0 < \infty \) | \( J^2 \leq C_1 \) |

---

For \( J \neq 0 \): The function \( \nu(x) \) are Jacobian elliptic functions of the form \( pq|u(x)|m \), shown in (3.13)

| Cases   | \( \nu(x) \)         | \( u(x) \)         | \( m \)         |
|---------|----------------------|-------------------|----------------|
| A, F, G | \( \sqrt{\frac{r_+}{r_+ + |r_-|}} \) sd(\(u|m\)) | \( \frac{x - x_0}{l_\alpha} \sqrt{\frac{r_+}{2}} \) | \( \frac{r_+ + |r_-|}{r_+ + |r_-|} \) |
| B, H, I | \( \sqrt{|r_-|} \) sn(\(u|m\)) | \( \frac{x - x_0}{l_\alpha} \sqrt{\frac{r_+}{2}} \) | \( \frac{r_-}{r_+} \) |
| C, E   | \( \sqrt{|r_+|} \) sc(\(u|m\)) | \( \frac{x - x_0}{l_\alpha} \sqrt{\frac{|r_-|}{2}} \) | \( 1 - \frac{|r_+|}{|r_-|} \) |
| D\pm   | \( \sqrt{|r_+|} \) sc(\(u|m\)) dn(\(u|m\)) | \( \frac{x - x_0}{l_\alpha} \sqrt{\frac{|r_-|}{2}} \) | \( \frac{1}{2} \left[ 1 + \frac{\text{Re}(r_+)}{|r_-|} \right] \) |
where \( |r_\pm| = -r_\pm \) if \( r_\pm < 0 \) for real roots, and \( |r_\pm| = \sqrt{r_+ r_-} = \sqrt{b_0} \) for the complex root case D. The function \( N(x) = f^2(x) \) is given by Eq. (3.9). Solutions for a conventional SC are cases A-C and D with \( \text{sgn}(\alpha) = -1 \) and \( \text{sgn}(\beta) = 1 \), which are the same as those given in Ref. 14. Solutions for the remaining 6 anomalous cases fall into the same solution classes, however \( \gamma, b_0, C_0, C_1 \) and \( \Delta \) are different functions of \( N_0 \), due to different values of \( \text{sgn}(\alpha) \) and \( \text{sgn}(\beta) \).

**Solutions with \( J = 0 \):** It follows from Eq. (3.6), with \( J = 0 \), that \( f(x) \) may be expressed directly in the form \( f(x) = f_0pq(u|m) \).

| Case | \( f(x)/f_0 \) | \( u(x) \) | \( m \) | \( N_0 \) Range | \( \text{sgn}(b_0) \) |
|------|----------------|-------------|------|----------------|------------------|
| A    | \( \text{cn} \) | \( \frac{x-x_0}{l_\alpha} \sqrt{\frac{1-N_0}{2}} \) | \( \frac{N_0}{2-N_0} \) | \( 0 \leq N_0 \leq 1 \) | \( -1 \) |
| C1   | \( \text{dn} \) | \( \frac{x-x_0}{l_\alpha} \sqrt{\frac{N_0}{2}} \) | \( \frac{2-N_0}{N_0} \) | \( 1 \leq N_0 \leq 2 \) | \( 1 \) |
| C2   | \( \text{cn} \) | \( \frac{x-x_0}{l_\alpha} \sqrt{\frac{N_0}{2} - 1} \) | \( \frac{0.5N_0 - 1}{N_0 - 1} \) | \( N_0 \geq 2 \) | \( 1 \) |
| E    | \( \text{dn} \) | \( \frac{x-x_0}{l_\alpha} \sqrt{\frac{N_0}{2} + 1} \) | \( \frac{0.5N_0 + 1}{N_0 + 1} \) | \( 0 \leq N_0 < \infty \) | \( 1 \) |
| F    | \( \text{dn} \) | \( \frac{x-x_0}{l_\alpha} \sqrt{\frac{1-N_0}{2}} \) | \( \frac{1-N_0}{1-0.5N_0} \) | \( 0 \leq N_0 \leq 1 \) | \( 1 \) |
| H1   | \( \text{dn} \) | \( \frac{x-x_0}{l_\alpha} \sqrt{\frac{N_0}{2}} \) | \( \frac{N_0 - 1}{0.5N_0} \) | \( 1 \leq N_0 \leq 2 \) | \( -1 \) |
| H2   | \( \text{cn} \) | \( \frac{x-x_0}{l_\alpha} \sqrt{\frac{N_0}{2} - 1} \) | \( \frac{0.5N_0}{N_0 - 1} \) | \( N_0 \geq 2 \) | \( -1 \) |
| I    | \( \text{cn} \) | \( \frac{x-x_0}{l_\alpha} \sqrt{\frac{N_0}{2} + 1} \) | \( \frac{0.5N_0}{N_0 + 1} \) | \( 0 \leq N_0 < \infty \) | \( -1 \) |

The zero current solutions in (3.14) may also be obtained from Eq. (3.13). The dashed line in (3.14) separates the \( \pm \) cases from the \( \mp \) cases. For \( \text{sgn}(\beta) = 1 \) cases, the \( \pm \) cases are possible only when superconductivity of the surface of the specimen is strongly enhanced through the boundary condition by introducing a significant quantity of pair interactions. For \( \text{sgn}(b_0) = +1 \), \( \text{sgn}(b_0) = -1 \), the function \( f_0 = f(x_0) \) is a minimum(maximum), respectively.

We emphasize that \( f^2 = N \) is employed only for mathematical convenience. It is particularly useful in numerical computation when one needs the precise range of \( N_0 \) which determines the parameter \( m \) in (3.14). However, the function \( \chi = sf \) is the normalized order parameter of physical interest, with \( |\psi|^2 = n_{\chi}^2 \) the actual superconducting pair density. Numerous treatises based on the GL model of superconductivity use the parameter \( f \) to illustrate the behavior of superconductors. In general, this is not a good parameter to use, except as an intermediate mathematical step. As seen in (3.14) the parameter \( f \) can become singular in cases C2, E, H2, and I, and is larger than unity in cases C1 and H1. As shown below, \( f \rightarrow \infty \) when \( s \rightarrow 0 \); whereas \( \chi = sf \) remains finite and well behaved. Similar comments apply to the use of the current parameter \( k \) in lieu of \( J \). Thus it is \( \chi \) or \( |\psi| \) and \( k \) that should generally be used for final illustration of superconducting effects.

It is interesting and useful to examine special solutions that appear at certain points in the \( (J,N_0,s) \) parameter space. At the end of Section II we determined the complex order parameter for the uniform solution \( \chi_u \). Now we determine \( \chi_u \) from the boundary conditions. Setting \( dN/dx = d^2N/dx^2 = 0 \) for all values of \( x \), Eq. (3.3) requires that \( J^2 = C_0 \), i.e. \( b_0 = 0 \). It follows, using Eq. (2.26), \( \chi = s\sqrt{N} \), and the boundary condition (3.2) with \( a = 1 \), that the \( (x_u, s_u) \) coordinates of the uniform solution \( \chi_u \) are

\[
\chi_u = s_u(0) = \sqrt{-b_4/b_2}, \quad s_u(k_j) = s_u(0) \sqrt{-\text{sgn}(\alpha)[\text{sgn}(\beta) + (k_j/\sqrt{N})^2]}.
\]

Since \( \chi/s = \sqrt{N} \), the argument of the root in Eq. (3.15) is \( 1/N_u \). For the uniform solution to exist for all \( x \), the \( \text{sgn}(b_2) = -\text{sgn}(b_4) \), and the order parameter \( \chi_u \) is independent of the current parameter \( k \); whereas \( s_u \) depends on
k_j. Because s is real and positive, Eq. (3.15) requires the \([\text{sgn}(\alpha), \text{sgn}(\beta)]\) combinations and \(k_j\) ranges shown in array (3.16).

\[
\begin{array}{ccc}
\text{Cases} & \text{sgn}(\alpha) & \text{sgn}(\beta) & k_j \text{Range} \\
\text{A|B, C} & -1 & 1 & k_j \geq 0 \\
\text{F|H} & 1 & -1 & 0 \leq k_j \leq \chi^3 \\
\text{G|I} & -1 & -1 & k_j \geq \chi^3 \\
\end{array}
\]

(3.16)

Applying the uniform solution condition \(b_0 = 0\) to the elliptic function solutions in (3.13) gives \(N(x) = N_0\), with \(m = 0\), at the boundaries of the solution case domains indicated in Eq. (3.16) by a vertical line. When \(k_j \neq 0\), the uniform solution point \(s_u\) approaches infinity in both the large and small limits of \(\chi\), corresponding, respectively, to weak and strong surface interaction limits.

Since \(s(t) = \sqrt{\frac{|\alpha(t)|}{\beta(t)}}\) by definition, Eq. (3.15) gives the relationship at \(t = t_u\) between the volume parameter ratio \(\alpha/\beta\) and the surfaces parameter ratio \(b_4, b_2\) as a function of the current parameter \(k_j\). For \(k_j = 0\), which requires that \(\text{sgn}(\alpha) = -\text{sgn}(\beta)\), it follows that

\[
\frac{\alpha(t_u)}{\beta(t_u)} = -\chi^2(t_u) = \frac{b_4}{b_2},
\]

(3.17)

where \(t_u\) is the normalized temperature at which \(s(t_u) = s_u\). For a bulk SC with \(k_j = 0\), the ratio \(\alpha(0)/\beta(0) = -1\) and \(\chi(0) = 1\). In contrast, the ratio \(\alpha(t_u)/\beta(t_u)\) given by Eq. (3.17) is generally not equal to \(-1\).

The uniform solutions and other special solutions follow from the general solutions listed in Eqs. (3.13) and (3.14). For \(J = 0\) they are listed in Eq. (3.18) below.

\[
\begin{array}{cccc}
\text{Case} & f(x)/f_0 & m & N_0 \\
\text{A, I} & \cos \left( \frac{x - x_0}{l_\beta} s \right) & 0 \to 0 \\
\text{E, F} & \cosh \left( \frac{x - x_0}{l_\beta} s \right) & 1 \to 0 \\
\text{A|C1} & 1 & 1 & 1 \\
\text{F|H1} & 1 & 0 & 1 \\
\text{C1|C2, D_} & \sec \left( \frac{x - x_0}{l_\beta} s \right) & 0 & 2 \\
\text{H1|H2} & \sech \left( \frac{x - x_0}{l_\beta} s \right) & 1 & 2 \\
\text{C2|E, H2|I} & \text{nc} \left[ \frac{x - x_0}{l_\beta - \chi(0)} \chi(0) \right] & 1 \to \infty \\
\end{array}
\]

(3.18)

The vertical line separating cases indicates that the special solution occurs at the boundary between the case solution domains. The solutions with \(N_0 \to 0\) are second order phase transition solutions which satisfy the linearized form of Eq. (3.1); those with \(N_0 = 1\) are the \(x\) independent uniform solutions; those with \(N_0 = 2\) satisfy the nonlinear form of Eq. (3.1); and those with \(N_0 \to \infty\) have \(s = 0\) and represent the transition between Jacobian elliptic functions with and without inflection.

**Solutions for \(J = 0\) with \(f(x = x_w) = 0\)**

When \(J = 0\), Eq. (3.5) assumes the form

\[
2 \left( \frac{d}{dx} \frac{df}{dx} \right)^2 = \text{sgn}(\beta) f^4 + 2 \text{sgn}(\alpha) f^2 + C = \text{sgn}(\beta) (f^2 - r_+)(f^2 - r_-),
\]

(3.19)

where
\[ r_\pm = -\text{sgn}(\alpha)\text{sgn}(\beta) \pm \sqrt{1 - C \text{sgn}(\beta)}. \]  

(3.20)

Although the constant \( C \) is arbitrary, the only solutions of interest that were not included in solutions with finite extrema are those for which \( f \) is zero at some point \( x_w \), with \( df/dx|x_w \neq 0 \). In such cases, the constant \( C \) is

\[ C = 2 \left( l_\alpha \frac{df(x_w)}{dx} \right)^2 \geq 0. \]  

(3.21)

The root ordering and corresponding solutions are given in Eq. (3.22) and (3.23) below.

| Case | \( \text{sgn}(\alpha) \) | \( \text{sgn}(\beta) \) | Root Order | \( C \) Range |
|------|----------------|----------------|-------------|-------------|
| A'   | -1           | 1             | \( r_+ > r_- > 0 \) | \( C < 1 \) |
| D'   | \pm 1         | 1             | \( r_- = r_+^* \) | \( C > 1 \) |
| E'   | 1            | 1             | \( r_- < r_+ < 0 \) | \( C < 1 \) |
| F', \( \Gamma \) | \pm 1 | -1 | \( r_+ > 0, r_- < 0 \) | \( 0 \leq C < \infty \) |

(3.22)

(3.23)

where \( r_\pm \) are given by Eq. (3.20), with \( |r_\pm| = -r_\pm \) if \( r_\pm < 0 \) for real roots, and \( |r_\pm| = \sqrt{r_+ r_-} = \sqrt{C} \) for case D'. In the application considered next, some of the functions in Eq. (3.23) are used to construct surface “pre-wetting” solutions which are zero at a point \( x_1 \) near a surface. Since \( f \geq 0 \) by definition, only that part of the elliptic function that is positive represents a physical solution. The slope of \( f^2(x) \) at \( x = x_1 \) is zero, thus establishing a smooth transition to the region with \( f = 0 \).

IV. APPLICATION: PLANE SLAB SAMPLE

The structure used in this section is a symmetric plane slab of thickness \( d \), with the origin \( x = 0 \) at its center. First we consider the zero current slab body solutions with \( N_0 = N(0) = f^2(0) \neq 0 \), then the corresponding current supporting solutions, followed by the currentless surface “pre-wetting” solutions with \( f(x_w) = 0 \).

Currentless Slab Solutions

For \( J = 0 \) there are eight solutions listed in (3.14). Since \( N(0) \) may become singular, we replace it with the well behaved normalized order parameter \( \chi^2(0) = s^2 N(0) \), and use \( l_\beta = sl_\alpha \). Applying the boundary condition (3.2) at \( x = 0.5d \), setting \( x_0 = 0 \), and defining \( u_* = u(x = 0.5d) \), leads to the boundary condition

\[ a\Omega_+ - \Omega_- + \frac{4}{b_4} \chi^2(0.5d) = -\frac{d}{b_2}. \]  

(4.1)

where

\[ \Omega_\pm = \frac{d}{2} \left[ \left( \frac{d\chi}{dx} \right)^{-1} \frac{d^2\chi}{dx^2} \pm \chi^{-1} \frac{d\chi}{dx} \right]_{0.5d}. \]
When \( a = 1 (c = e) \), it is seen in Eq. (4.1) that only the logarithmic derivative \( \chi^{-1}d\chi/dx \) is specified at the boundary. As mentioned, and as will be shown, \( a = 1 \) is the important case permitting second order phase transitions.

With considerable manipulation of the Jacobian elliptic functions, one may derive the following forms for \( \Omega_{\pm} \).

| Case | \( \Omega_{\pm} \) |
|------|------------------|
| A    | \( \frac{2u_s}{\text{sn}(2u_s)} \left[ 1 + \frac{1}{2}(1 \pm 1)[\text{cn}(2u_s) - \text{dn}(2u_s)] \right] \) |
| C1   | \( \frac{2u_s}{\text{sn}(2u_s)} \left[ 1 - \frac{1}{2}(1 \mp 1)[\text{cn}(2u_s) - \text{dn}(2u_s)] \right] \) |
| C2,E | \( \frac{2u_s}{\text{sn}(2u_s)} \left[ \text{dn}(2u_s) + \frac{1}{2}(1 \pm 1)[1 - \text{cn}(2u_s)] \right] \) |
| F    | \( \frac{2u_s}{\text{sn}(2u_s)} \left[ \text{cn}(2u_s) + \frac{1}{2}(1 \pm 1)[1 - \text{dn}(2u_s)] \right] \) |
| H1   | \( \frac{2u_s}{\text{sn}(2u_s)} \left[ \text{cn}(2u_s) - \frac{1}{2}(1 \pm 1)[1 - \text{dn}(2u_s)] \right] \) |
| H2,I | \( \frac{2u_s}{\text{sn}(2u_s)} \left[ \text{dn}(2u_s) - \frac{1}{2}(1 \pm 1)[1 - \text{cn}(2u_s)] \right] \) |

(4.2)

The argument \( u_s = u(x = 0.5d) \) and parameter \( m \) are easily transformed in (3.14) using \( \chi^2(0) = s^2N(0) \). The boundary conditions listed by Eqs. (4.1) contain the set \{ \( \chi(0), s(t), d/\alpha, d/b_2, d/b_4 \} \). Specifying the three scaled lengths, the boundary equations give the normalized order parameter \( \chi(0) \) at the slab center as a function of \( s \). In the boundary condition (4.1) the cases C and H in (3.13) split into subcases, defined in (3.14). The \( \text{sgn}(\alpha) \) and \( \text{sgn}(\beta) \) remain those of the parent case. The cases in (4.1) with \( \text{sgn}(b_0) = -1 \) have superconductivity at the surface reduced from that in the sample bulk; whereas cases with \( \text{sgn}(b_0) = 1 \) have enhanced surface superconductivity.

An alternative form of the boundary condition Eq. (3.2) is obtained by integrating the first GL Eq. (3.1) across the slab. Noting that \( df(x)/dx = -df(-x)/dx \) and \( f(x) = f(-x) \), one obtains for the case \( a = 1 \) the relation

\[
\frac{1}{b_2} + \frac{1}{b_4} s^2 f^2(0.5d) = -\frac{1}{l_\beta^2 f(0.5d)} \int_0^{0.5d} dx [\text{sgn}(\alpha)f(x) + \text{sgn}(\beta)f^3 + J^2 f^{-3}].
\]

(4.3)

Since Eq. (4.3) is exact within the GL model, it is difficult to reconcile it with a similar, but distinctly different expression involving the density of states given by de Gennes, who uses the same arguments to derive the GL equations.

Up to this point, all relations follow directly or indirectly from the free energy (2.7) with the models for \( U, \text{Eq. (2.16)}, \) and \( A, \text{Eq. (2.31)} \). No approximations, assumptions, or other conjectures have been made. To solve the boundary Eqs. (4.1) we assume that \( l_\beta \) is approximately temperature independent. Comparing the surface energy density with the volume condensation energy density, one notes that \( 1/b_2(t) \) and \( |\alpha(t)| \propto s^2(t) \) are both coefficients which scale \( |\psi|^2 \), and that \( 1/b_4 \) and \( |\beta| \) both scale \( |\psi|^4 \). Hence, by analogy, we conjecture that \( 1/b_2(t) \) may be a function of \( s^2(t) \) and \( b_4 \) is approximately independent of temperature. Since we have no model for \( b_2(t) \) we will neglect the temperature dependence and use \( b_2(t) \approx b_2 \), where \( b_2 \) is a controllable external parameter. [Assuming that \( 1/b_2(t) \propto s^2 \) leads to unreasonable results.]

The parameters \( b_2 \) and \( b_4 \) cannot be chosen arbitrarily. The free energy must be negative for a SC state to exist, which limits the range of \( b_4 \), and the boundary condition at a second order phase transition limits the value and sign of \( b_2 \). From Eq. (2.32), the normalized, minimum free energy for a symmetric slab is

\[
\Gamma_{\text{min}}(s) = (2\pi)^2 \frac{\Delta G_{\text{min}}}{K_d} = -\frac{1}{2} \left( \frac{d}{l_\beta} \right)^2 (\chi^4) \text{sgn}(\beta) - \frac{d}{b_4} \chi^4(0.5d) - 2(a - 1)\chi^2(0.5d)\Omega_-, \tag{4.4}
\]

where

\[
K_d^* = n^* V \left( \frac{1}{2m^*} \right) \left( \frac{d}{d} \right)^2, \quad (\chi^4) = \frac{2}{d} \int_0^{0.5d} dx \chi^4(x).
\]

The normalizing term \( K_d^* \) is the total kinetic energy of a non-interacting gas of SC pairs in volume \( V = \text{area} \times d \), with wavelength \( d \) at \( t = 0 \). The entire slab is in a SC state providing that the parameter \( \Gamma_{\text{min}}(s) < 0 \). It is clear
that if $a = 1$ ($c = e$) the inequality $\Gamma_{\text{min}} < 0$ can be satisfied when $\beta > 0$ for all $b_4 > 0$, or for $b_4 < 0$ in a restricted range. When $\beta < 0$ then $b_4$ must be positive, but not too large. For $a \neq 1$ the key factor determining whether a state is superconducting is the $\text{sgn}(\Gamma_{\text{min}})$. States that exhibit a second order phase transitions (SOPT) are defined by the zero limit entropy difference between $S$ and $N$ states,

$$
\lim_{\chi \to 0} \frac{\partial \Gamma_{\text{min}}}{\partial t} = \frac{\partial s}{\partial \chi} \lim_{\chi \to 0} \frac{\partial \Gamma_{\text{min}}}{\partial s} = 0.
$$

(4.5)

It can be shown that all states with $a \geq 1$ are potentially superconducting states, and in restricted $s(t)$ value domains states with $a \leq 1$ may be superconducting with a first order phase transition. However only states with $a = 1$ have second order phase transitions, as defined by Eq. (4.5). In this paper we focus on the SOPT states and states that are continuations of the SOPT states corresponding to the case $a = 1$.

When $J = 0$ the uniform solutions are $\chi_u = s_u = \sqrt{-b_4/b_2}$, which may exist for cases A, C1, F, and H1. The normalized energy for $a = 1$ has the value

$$
\Gamma_{\text{min}} = -\frac{1}{2} \left( \frac{b_1}{b_2} \right)^2 \left[ \left( \frac{d}{l_\beta} \right)^2 \text{sgn}(\beta) + \frac{2d}{b_4} \right],
$$

(4.6)

This exact analytical result for the uniform solution gives a simple check on the numerical results.

The point where $\chi(x) \to 0$ is interpreted as a second order phase transition point, and the corresponding $s$-value is obtained from Eq. (4.1) by letting $\chi(0)$ approach zero. As can be seen from Eq. (3.14) cases A and I give rise to a solution with maximum order parameter, while solutions E and F with minimum order parameter $\chi(0)$ in the center of the slab. Cases A and I, with $\text{sgn}(\alpha) = -1$, lead to a characteristic equation for $s = s_o$ in the limit $\chi(0) \to 0$. In this limit, from (3.18), $\chi(x) = \chi(0) \cos(\zeta x/d)$, and the characteristic equation (4.1) with $a = 1$ is

$$
\zeta_o \tan(0.5\zeta_o) = \frac{d}{b_2} \quad \text{with} \quad \zeta_o = \frac{d}{l_\beta} s_o.
$$

(4.7)

Similarly, for $a = 1$ the cases E and F, with $\text{sgn}(\alpha) = 1$, and $\chi(x) = \chi(0) \cosh(\zeta x/d)$ gives

$$
\zeta_o \tanh(0.5\zeta_o) = -\frac{d}{b_2}.
$$

(4.8)

As will be shown below, if $s$ is interpreted as a function of temperature, Eq. (4.7) gives rise to a reduction of $t_{cs}$ due to a pulling down of the order parameter at the surfaces of the slab, while Eq. (4.8) leads to an enhanced transition temperature $t_{cs} = T_{cs}/T_c$, as previously shown.4,15

Fig. 1 shows the E solution for $a = 1$ and for $a = 1 \pm 0.001$ near the transition point defined by $\chi \to 0$. The solid curves are the square of the normalized order parameter $\chi(0,s) \equiv \chi(0)$ plotted as a function of the length ratio $s(t) = l_\beta/l_o(t)$, and the dashed curves are the energy parameter $\Gamma_{\text{min}}(s)$. Only the curve for $a = 1$ satisfies the entropy condition (4.5) for a second order phase transition. For a fixed set of parameters, the $a = 1$ states always have a lower value of $\Gamma_{\text{min}}(s)$ than states with $a \neq 1$ at the same value of $s(t)$.

As we go below the second order phase transition point the order parameter increases, but the corresponding $s(t)$ value varies in different ways depending on the type of solution of the nonlinear equations, Eq. (4.1). As can be seen from Eq. (4.4), the minimum free energy $\Gamma_{\text{min}}$ can be positive or negative depending on $\text{sgn}(\beta)$ and the value of $b_4$, and implicitly on $b_2$ through $\chi$. In the conventional GL approach $\beta > 0$.

Figs. 2 and 3 show the zero current solutions of the nonlinear Eqs. (4.1) for $a = 1$ ($c = e$) with the scaled order parameter at the slab center $\chi(0)$ (solid lines), and the scaled minimum free energy $\Gamma_{\text{min}}$ (dashed lines), Eq. (4.4). In Figs. 2-10 the ratio $d/[b_2] = 0.01$. For a second order phase transition the sign of $b_2$ is dictated by the linearized Eqs. (4.7) and (4.8). The value of $d/l_\beta = 0.5$ in Figs. 2-10, i.e. the value of $|\beta|$ is fixed relative to the slab thickness $d$.

Figure 2 shows our results for cases A, C1, C2, and E, all for $\beta > 0$, obtained from Eq. (4.1) for various values of $b_2$ and $b_4$. The normalized energy function $\Gamma_{\text{min}}$ is shown by the broken lines and $\chi(0)$, the normalized order parameter at the center of the slab, defined by Eq. (2.20), is depicted by solid lines. In this particular situation $\Gamma_{\text{min}}$ is always negative, but very small; thus negative values of $b_4$ could drive the slab into the normal state with $\Gamma_{\text{min}} > 0$. The regions over which the different solution types are valid are separated by a bar, and as can be seen from the intersection of both A and C1 curves. Depending on the values of $b_2$ and $b_4$, the same type of solution can appear in different regions of the $\chi(0)$ versus $s$ diagram. Solutions A and C1 meet when $N_0 = 1$, at which point $\chi_u = s_u = \sqrt{-b_2/b_2} = 1/\sqrt{5}$ is a constant [See Eqs. (3.15)-(3.18)], independent of the coordinate $x$. As $s$ varies through this point, the slope of $\chi(x = d/2)$ changes sign as it goes through zero.
The point where $\chi(0) = 0$ is interpreted as the second order phase transition point and for a finite value of $b_2$ it occurs at a positive, non-zero value of $s$. For solution A, the order parameter at the surface of the slab is “pulled down” with respect to the center of the slab while for solution E it is “pulled up”. We shall interpret below the A case as a decrease of the superconducting transition temperature $T_c$ due to the proximity effect caused, for example, by a normal metal deposited on the surface of a thin film, while the opposite applies to case E. The symbol for the reference temperature is $T_c$, at which point $\chi(0) = 0$ occurs when $1/b_2 = 0$. For case A, as $s$ increases, $\chi(0) = s\sqrt{N_0}$ increases, which is interpreted as a decrease in temperature, away from the phase transition point.

For case E the value of $s$ decreases as the order parameter $\chi$ increases. For $s \to 0$ the value of $\chi(0)$ remains finite when $1/b_2 < 0$. This happens because $N_0 = N(0) = f^2(0) \to \infty$ when $s \to 0$. For $s = 0$ solution type E and C2 are satisfied by $N_0 \to \infty$ with Jacobian function parameter $m = 0.5$. The order parameter function $\chi(x)$ is, however, well behaved for $s = 0$ as seen in (3.18) for the C2/E point. As $\chi(0)$ increases, the function of type E switches to a C2 function and the $s$-value increases, as is the case for the A type solution, moving to lower temperatures, away from the phase transition point (lower A branch). The same interpretation is now applied to the upper curve as we go from type C2 to C1 to the upper A curve. Thus, if the phase transition point for the type E solution is interpreted as occurring at an enhanced transition temperature $T_{cs} > T_c$, then the point $s = 0$ anchors the temperature $T = T_c$

As one goes from the phase transition point along the E, C2, C1, and upper A branches, the parameter $N_0 = f^2(0)$ goes from zero to infinity at $s = 0$, with $\chi(0)$ finite, for the E branch. For the C2 section the function $N_0$ is also infinite at $s = 0$. As $s$ and $\chi(0)$ increase, C2 changes into C1 at $N_0 = 2$. At this point the Jacobian elliptic function becomes a trigonometric function [See Eq. (3.18)] and then changes again into an elliptic function in the C1 region. At the point where the C1 joins the upper A branch, $b_0 \propto d^2\chi/dx^2|_{x=0}$ changes sign, and the solution $\chi(x)$ becomes independent of $x$ at the intersection. In domains C2, and C1 the net slope of $\chi(x)$ at the surface $x = d/2$ is positive, while in the upper A domain it is negative.

The effect of changing the sign of the surface pair interaction parameter $b_4$ is also shown. When $b_4$ is negative it increases the net slope of $\chi(x)$ at the surface, enhancing superconductivity there by lowering the total energy of the slab. For solutions E, C2, and C1 the net slope at the slab surface $x = d/2$ is always positive, thus aiding superconductivity in the slab, while type A gives rise to a negative slope at $x = d/2$ which has an inhibiting effect on the superconducting state in the slab. As mentioned, where solutions A and C1 meet, the net slope of the order parameter is zero and $\chi(x)$ is constant, independent of $x$.

Figure 3 depicts solutions corresponding to Fig. 2 with $a = 1$, but with $\beta < 0$ for solutions F, H1, H2, and I. In order for these solutions to be superconducting the total minimized free energy difference $\Gamma_{\min}$, Eq. (4.4), must be negative. Equation (4.4) with $a = 1$ shows that this can be achieved only if $b_4 > 0$ with the surface term $(d/b_4)\chi^4(0.5d)$ larger than the volume term $0.5(d/l_0)^2(\chi^4)$. As for $\beta > 0$ cases, the surface parameter $b_2$ determines the point at which the second order phase transition occurs. Again, the results of Fig. 3 are exact solutions of our generalized GL equations and are completely independent of the temperature dependence of $s(t)$. Although the lower curve for solution type I can be interpreted in the same way as the lower A-type curve in Fig.2 was interpreted, the rest of Fig. 3 has some notable differences. The phase transition point $\chi(0) = 0$ on branch F can be interpreted as an enhancement of the transition point above the reference transition temperature $T_c$, defined by $s(t = 1) = 0$, because the order parameter at the surface is “pulled up” at $x = d/2$. Where F joins branch H1, the order parameter $\chi = \sqrt{-b_4/b_2} = 1/5$ is independent of $x$; thus the slope at the surface changes sign at this point and H1 becomes a “pull down” case before the reference temperature at $s = 0$ is reached. As the order parameter $\chi(0)$ increases from zero, its value is finite at $s = 0$ as it goes from F type to H1 and H2 and then to a different upper branch of the I solution. Along the H1, H2 and I curves, the order parameter $\chi(x = d/2)$ is always “pulled down” with respect to $\chi(0)$. At the point $\chi(0) = \sqrt{2}s$, where H1 and H2 join, $\chi(x)$ becomes a hyperbolic function, (3.18), and at $s = 0$, where H2 and I join, the value of $N_0 = f^2(0) \to \infty$. For the given parameter values, all of the solutions are superconducting, which depend on a positive $b_4$ of the pair interaction parameter near the surface.

Although the F solution is the only one with the order parameter “pulled up” at the surface, all solutions are superconducting. In particular, the H1 and H2 solutions are “pull down” cases existing above our reference point $T_c$ defined by $s(T = T_c) = 0$. Thus enhanced superconductivity can exist for $\beta < 0$ as long as the surface pair interaction parameter $1/b_4$ is large enough to overcome the unfavorable effect due to $\text{sgn}(\beta) = -1$ in the slab volume. This is the case for SNS or SS’S junctions where the N or S’ regions are embedded by a strong superconductor S.

The results depicted in Figs. 2 and 3, for the order parameter $\chi(x)$, defined by Eq. (2.20) as a function of the length ratio $s(t)$, defined by Eq. (2.18), with both $\chi(x)$ and $s(t)$ positive quantities by definition, are exact solutions of our generalized, nonlinear equations for a slab with $k_z = 0$. They do not depend on, or show how, $s(t)$ is related to the normalized temperature $t = T/T_c$, which is not included explicitly in the GL equations. Thus we must ascribe a temperature relation to $s(t)$ so that our model elucidates the arguments for an increase or decrease of the critical temperature. Since $s \geq 0$ by definition, the temperature function related to the E, F, and H solution types must be different from that of the A, C, and I solution types. We introduce the relation
\[ s_\pm(t) = \sqrt{\pm \left( \frac{t^2 - 1}{t^2 + 1} \right)}, \quad t = \frac{T}{T_c}, \] (4.9)

where the upper (lower) sign denotes the temperature model with \( t > 1 \) (\( t < 1 \)), respectively, and apply it to the exact results shown in Figs. 2 and 3. When \( \chi(0) = 0 \), the fundamental length ratios \( s_\pm(t) \) assume the values \( s_+(t_{cs}) \) for \( t_{cs} > 1 \), while \( s_-(t_{cs}) \) for \( t_{cs} < 1 \).

At the reference temperature \( t = 1 \), the fundamental ratio \( s(1) = 0 \). For this model there are two temperature ranges \( 0 < t < 1 \) and \( 1 < t < t_{cs} \), corresponding to the same value of \( s \) in the interval \( 1 \geq s \geq 0 \). For \( t_{cs} < 1 \), an increasing \( s(t) \) value corresponds to an increasing \( \chi(0) \) value such as seen in the lower branches A and I in Figs. 2 and 3. The explicit equation for \( s_-(t_{cs}) \) is (4.7), and fixed parameters \( d/l_\beta \) and \( d/b_2 \), from which \( t_{cs} < 1 \) is obtained using Eq. (4.9). For \( t_{cs} > 1 \), an increasing \( \chi(0) \) value corresponds to a decreasing \( s(t) \) value such as is depicted in Fig. 2 by the E branch and in Fig 3 by the F, H1, and H2 branches. In such cases the explicit equation for \( s_+(t_{cs}) \) is Eq. (4.8), from which \( t_{cs} > 1 \) is obtained using Eq. (4.9).

With these \( t_{cs} \) values, which are embedded in Eqs. (4.7) and (4.8), the results of Figs. 4 and 5 are calculated from the \( s(\chi(0)) \) values shown in Figs. 2 and 3 using Eq. (4.9). For the E, C2, C1, A curve in Fig. 4 and the F, H1, H2, I curve in Fig. 5, the \( \chi(0) \) curve is continuous and finite at \( t = 1 \), while \( N_0 = f^2(0) \) is infinite at this point. Again one sees that it is not the \( f(x) \) function which is the correct physical order parameter but the \( \chi(x) \) function.

The A/C1 boundary point in Fig. 4 and the F/H1 boundary point in Fig. 5 are the uniform solution points, with corresponding temperature \( t_u \). Temperature \( t_u \) may be found analytically using Eq. (3.15) with \( k_j = 0 \), and Eq. (4.9). The result is

\[ t_u(\pm) = \sqrt{\frac{1 + b_4/b_2}{1 \pm b_4/b_2}}, \] (4.10)

where the upper (lower) sign denotes \( t_u > 1 \) (\( t_u < 1 \)), respectively. Using Eq. (4.10), the temperature \( t_u = \sqrt{2/3} \) in Fig. 4, and \( t_u = \sqrt{13/12} \) in Fig. 5.

The conservative and convincing results shown by \( \chi(0,t) \) lend credence to our results that boundary conditions imposed on small superconducting specimens may change drastically their behavior, including increasing the transition temperature. Changing the slope of the order parameter at the surface of thin films in a magnetic field parallel to the surface effects also the magnetic field at which superconductivity nucleates.

Although the temperature model, Eq. (4.9), is not unique, it appears to be in accord with experimental results described by curve A (lower curve) in Fig.4 when the transition temperature of a thin superconducting film is depressed by bringing it in contact with normal metals (NSN). The upper curve in Fig. 4 is also a reasonable result for a weaker superconductor S in contact with a stronger superconductor S. The model temperature behavior is different for the N-metal of a SNS junction: \( s \propto \sqrt{T} \) (See Section IV).

**Current Supporting Slab Solutions**

Next we consider the non-zero current solutions for \( a = 1 \), which evolve continuously from the solutions plotted in Figs. 2 and 3 as the current parameter \( k_j \propto j \) increases from zero. Using the solutions from Eq. (3.13) in the boundary condition (3.4), with \( a = 1 \), yields the \( \chi(0) \) versus \( s(t) \) plots shown in Figs. 6-10. A typical nonlinear boundary equation that we solved is that for cases A, F, and G. It is

\[ \frac{1}{2 l_\beta} \frac{1}{\sqrt{\Delta}} \frac{b_0}{N_s} \frac{1}{\text{dn}^3(u_s)} + \frac{d}{b_4} s^2 N_s = - \frac{d}{b_2}, \] (4.11)

where

\[ N_s = N(x = 0.5d) = N_0 + \frac{b_0}{2 \Delta} \text{sd}^2(u_s), \quad u_s = \frac{1}{2 l_\beta} s \sqrt{\Delta}, \quad m = \frac{1}{2} \left( 1 + \gamma \right). \]

Figures 6 and 7 show the connectivity of all of the current carrying states A-E, with \( \text{sgn}(\beta) = 1 \), for various values of the unitless current parameter \( k_j \). The bars denote the boundaries separating solution types. The parameter set \( (d/l_\beta, d/b_2, d/b_4) \), and the \( k_j = 0 \) curves are those depicted in Fig. 2. In Fig. 6 the temperature \( t > 1 \) is decreasing to \( t = 1 \) as \( s \) decreases to \( s = 0 \). It is clear that a second order phase transition, characterized by \( \chi = 0 \), does not occur when \( k_j \neq 0 \). The upper curves in Fig. 6 show the physical order parameter decreasing for a fixed \( k_j \) as \( s \) and the corresponding temperature increase; whereas the lower part of the curves behave unphysically. At a fixed value
of \( s(t) \), increasing the current parameter \( k_j \) decreases the order parameter (starting from the \( k_j = 0 \) curve) until a critical, maximum current is reached, above which the order parameter does not exist. This critical point is given by an E(D+) solution for higher (lower) temperatures. In Fig. 7 the temperature \( t < 1 \) is decreasing from \( t = 1 \) as \( s \) increases from \( s = 0 \). Again, for a fixed \( s(t) \) there is a critical, maximum current parameter \( k_j \) above which the order parameter does not exist. The critical point is given by a D_-(A) solution for higher (lower) temperatures. In Fig. 7, the horizontal line \( \chi_u = \sqrt{1/5} \) is the value of the uniform solution, Eq. (3.15). The uniform solution is located at the A/C (A|B) boundary for higher (lower) temperatures.

Figure 8 shows the A solution, which has a second order phase transition for \( k_j = 0 \), for various values of \( k_j \). As \( s \) increases from \( s(t_o) \) the temperature \( t < 1 \) decreases. Other observations are analogous to those for Fig. 7.

Figures 9 and 10 show the connectivity of all of the current carrying states F, G, H, and I, with \( \text{sgn}(\beta) = -1 \), for various values of \( k_j \). The parameter set \( (d/\beta_0, s_u, b_2/d_6) \), and the \( k_j = 0 \) curves are those depicted in Fig. 3. In Figs. 9 and 10, the horizontal line is \( \chi_u = 1/5 \), Eq. (3.15), which is located at the F|H and G|I boundaries. Other significant observations are analogous to those for Figs. 6 and 7.

**Simple Analytic Solutions**

Here we return to the first order differential equation (3.7) to develop a simple algebraic model that very accurately fits the \( k_j = 0 \) curves for the cases A, F, H, and I, which have two finite extrema. Denoting the second extrema by \( N_1 \equiv N(x_1) \), where \( dN(x_1)/dx = 0 \), the term in the bracket \( \{ \ldots \} \) in Eq. (3.7) is zero. Using \( \chi^2 = s^2N \) and \( k_j = s^3J \) one obtains the exact relation between the extrema \( \chi_0 \equiv \chi(x_0) \) and \( \chi_1 \equiv \chi(x_1) \). It is

\[
\left[ \chi_0^2 + \chi_1^2 + 2\text{sgn}(\alpha)\text{sgn}(\beta)s^2 \right] \chi_0^2 \chi_1^2 + 2k_j^2\text{sgn}(\beta) = 0. \tag{4.12}
\]

Consider the \( k_j = 0 \) cases with \( \text{sgn}(\alpha)\text{sgn}(\beta) = -1 \). Equation (4.12) reduces to

\[
\chi_0^2(s) + \chi_1^2(s) = 2s^2, \quad \text{for } \chi_0^2 \chi_1^2 \neq 0. \tag{4.13}
\]

It is evident that as \( s \to 0 \), the second extremum \( \chi_1^2 = -\chi_0^2 \). Since \( \chi_0^2 \) is proportional to the physical electron pair density and is thus positive, \( \chi_1^2(s = 0) < 0 \) is purely mathematical and does not represent a SC state. Assume \( \chi_1^2 \) may be expanded in a power series in \( s^2 \). Taking the leading terms, we write

\[
\chi_1^2(s) = a_0 + a_1 s^2, \tag{4.14}
\]

which requires that

\[
\chi_0^2(s) = -a_0 + (2 - a_1)s^2. \tag{4.15}
\]

The expansion coefficients are obtained by evaluating \( \chi_0^2(s) \) at the SOPT point \( s = s_o \), given by Eq. (4.7) or (4.8), and at the uniform solution \( \chi_0 = s_u = \sqrt{-b_4/b_2} \), which gives

\[
a_0 = -s_u^2 \left[ 1 - \left( \frac{s_u}{s_o} \right)^2 \right]^{-1}, \quad a_1 = 1 + \left[ 1 - \left( \frac{s_u}{s_o} \right)^2 \right]^{-1}. \tag{4.16}
\]

When \( s_u < s_o \), the coefficient \( a_0 < 0 \) and \( a_1 > 2 \). This is the F case, and Eq. (4.15) lies within plot accuracy for all \( s \) of the exact F-H1-H2 curve shown in Fig. 3. When \( s_u > s_o \), the coefficient \( a_0 > 0 \) and \( a_1 < 2 \). This is the A case, and Eq. (4.15) lies within plot accuracy for all \( s \) of the exact A-C1 SOPT curve shown in Fig. 2. Other curves that do not have a SOPT may also be obtained using Eq. (4.15); however the coefficients cannot be analytically evaluated.

For \( k_j \neq 0 \) we have not found a simple expression for \( \chi_1(s, k_j) \) such that Eq. (4.12) produces the results shown in Figs. 8-10. It is evident from Fig. 10, for example, that an infinitesimal current completely changes the \( \chi(0, s) \) curve.

**Currentless Surface “Pre-Wetting” Solutions**

In this subsection we apply the solutions from Eq. (3.23), which exist only over a section of the slab. Substituting the solutions of Eq. (3.23) into the boundary condition (3.2), with \( a = 1 \) gives the equations to be solved for the integration constant \( C = 2(l_o ds/dx(x_w)^2 \) for a given value of the surface pre-wetting depth \( l_0 = 0.5d - x_w \). A typical equation is that for the E’ case:
\[
\frac{d}{l_\beta} s \sqrt{\frac{1 + \sqrt{1 - C}}{2}} \frac{dn(u_s)}{cn(u_s) sn(u_s)} + \frac{d}{b_4} s^2 (1 - \sqrt{1 - C}) sc^2(u_s) = -\frac{d}{b_2},
\]
(4.17)

where

\[ u_s = \frac{l_0}{l_\beta} s \sqrt{\frac{1 + \sqrt{1 - C}}{2}}, \quad m = \frac{2\sqrt{1 - C}}{1 + \sqrt{1 - C}}. \]

If the \( b_4 \) surface interaction term is neglected, cases A' and E' are elliptic function representations of the extensive numerical solutions of Eq. (3.5), with \( J = 0 \), evaluated in Ref. 15 by Indekeu and coworkers.

For all cases, when the argument \( u(x) \ll 1 \), the function \( f(x) \propto u(x) \). In this limit, i.e. when the pre-wetting depth \( l_0 \ll l_o \), the boundary condition (3.2) leads to \( l_0 = -b_2 \).

Cases A', E', F', and \( \Gamma \) exhibit second order phase transitions (SOPT) in the limit \( C \rightarrow 0 \). Then the boundary condition for A' and \( \Gamma \) reduces to the form

\[
\frac{d}{l_\beta} s_o(t) \cot \left( \frac{l_0 s_o(t)}{l_\beta} \right) = \frac{d}{b_2}, \quad \text{for } f(x_w) = 0,
\]
(4.18)

and for cases E' and F' it gives

\[
\frac{d}{l_\beta} s_o(t) \coth \left( \frac{l_0 s_o(t)}{l_\beta} \right) = \frac{d}{b_2}, \quad \text{for } f(x_w) = 0.
\]
(4.19)

It is interesting to compare the pre-wetting solution characteristic equations for \( l_0 = 0.5d \) with SOPT Eqs. (4.7) and (4.8) for the slab solution cases A, I and E, F. First note that in the A', \( \Gamma \) cases \( b_2 < 0 \); whereas \( b_2 > 0 \) for the A, I cases. At the reference temperature, where \( s(t = 1) \rightarrow 0 \), Eq. (4.7) for cases A, I requires \( 1/b_2 \rightarrow 0 \); whereas for A', \( \Gamma \), Eq. (4.18) gives \( |b_2| = l_0 \) at \( t = 1 \). Similar comments apply to cases E, F versus E', F'.

The pre-wetting solution normalized, minimum free energy, corresponding to Eq. (4.4), is

\[
\Gamma_{\text{min}}(s) = -\frac{1}{2} \left( \frac{d l_0}{l_\beta} \right) \frac{2}{l_0} \int_0^{0.5d} dx \chi^4(x) sgn(\beta) - \frac{d}{b_4} \chi^4(0.5d).
\]
(4.20)

As an application, consider a slab of normal, or SC, material between two superconducting reservoirs with a \( T_c \) higher than that of the slab. In the absence of a transport current, the order parameter is characterized by an A type solution in the interior of the reservoir with extremum value \( f_0 \leq 1 \). At the surface there will be some bending such that \( f(d/2) < f_0 \). For the slab we assume an E' type pre-wetting solution with surface value

\[
f^2(d/2) = \left( 1 - \sqrt{1 - C} \right) sc^2(u_s|m).
\]
(4.21)

Using Eq. (4.21) with elliptic function identities to write the elliptic functions in the derivative boundary condition (4.17) in terms of \( C \) leads to the expression

\[
C(s) = f^2(d/2) \left[ 2 \left( \frac{l_0}{b_2} \frac{1}{s} + \frac{l_0}{b_4} s f^2(d/2) \right)^2 - 2 - f^2(d/2) \right].
\]
(4.22)

The value of \( f(d/2) \) is a function of \( s(t) \), but if one fixes the values of \( f(d/2) \) in Eq. (4.22), the resulting \( C(s) \) may be inserted in Eq. (4.4), to determine the pre-wetting depth \( l_0 \) as a function of \( s(t) \).

Fig. 11 shows the pre-wetting depth \( l_0 \) plotted as a function of temperature, using \( t^2 = (1 - s^2)/(1 + s^2) \) for several values of \( f(d/2) \). Near \( T_c \) of the SC reservoirs the surface value \( f(d/2) \ll 1 \) and \( l_0/d \) approaches \( |b_2|/d = 0.2 \). As the temperature is decreased both \( f(d/2) \) and \( l_0 \) have the tendency to increase until \( l_0/d = 0.5 \), at which point we expect a transition to the E type.

V. TRANSPORT CURRENTS IN MULTIPLE LAYERED SYSTEMS

In the previous section we applied a boundary condition that was formulated from the surface energy characterized by the parameters \( b_2 \) and \( b_4 \), which were assumed to represent not only the surface properties, but also the material beyond the surface. Now we formulate a set of boundary conditions that relate parameters across a boundary, bypassing the intermediate surface parameters. These boundary conditions are then applied to a SNS system with transport currents, and the results are compared with recent experiments.
Crossing Boundaries

There are three basic quantities that are relevant at a boundary: the surface energy in \( G_{\text{min}} \), Eq. (2.15), the boundary condition (2.11) with \( a = 1 \), and the current density \( j \), Eq. (2.24). The surface energy density is proportional to the function

\[
g_* = \frac{1}{2m^*} |\psi|^2 \frac{\partial}{\partial |\psi|} \left[ \frac{\Lambda}{|\psi|^2} \right] = \frac{1}{m^*} \left[ \Lambda - \frac{1}{2} |\psi| \frac{\partial \Lambda}{\partial |\psi|} \right],
\]

and the boundary condition (2.11) may be written in the form

\[
\frac{1}{m^*} [\hat{n} \cdot \nabla |\psi|^2 + 2\Lambda] = 2g_*.
\]

Since \( g_* \) is the same when viewed from either side of the surface at the same point on the surface, with \( m^* \) changing value, in general, it follows that the right side of Eq. (5.2) must be continuous across the surface. Assuming that there is no generation or loss of particles at the surface, we conjecture that at the boundary between medium 1 and medium 2, the function \( \Lambda/m^* \) satisfies

\[
\frac{\Lambda(1)}{m^*(1)} = \frac{\Lambda(2)}{m^*(2)}.
\]

Continuity of \( g_* \) and \( \Lambda/m^* \) gives the continuity of the SC density gradient condition

\[
\frac{n_s^*(1)}{m^*(1)} \nabla \chi^2(1)|_b = \frac{n_s^*(2)}{m^*(2)} \nabla \chi^2(2)|_b.
\]

The second boundary condition is the continuity of the physical current density \( j \). Using the definition (2.26), continuity of \( j \) requires that

\[
\frac{n_s^*(1)}{m^*(1)} k_j(1) = \frac{n_s^*(2)}{m^*(2)} k_j(2).
\]

Aside from known material and geometry parameters, the functions on each side of Eq. (5.4) depend only on \( s(t), k_j \) and \( \chi(x_0) \), where \( x_0 \) is the reference point in the medium. Thus, if \( j \) and \( t \) are fixed and the model \( s_{\pm} \) is chosen for each medium, Eqs. (5.4) and (5.5) determine \( \chi(x_0(1)) \) in one medium as a function of the outer surface parameters. For a closed system, such as a ring constructed from two materials, the second constraint may be the flux quantization condition, which follows from Eq. (2.5), using Eqs. (2.25) and (2.26). It is

\[
- \oint d\lambda \cdot \left( \frac{k_j}{l_\beta \chi} \right) = 2\pi \left( n + \frac{1}{\phi_o} \phi(k_j) \right),
\]

where \( \phi \) is the flux enclosed by the contour \( l \). Equations (5.4) - (5.6) determine the numerical value of \( \chi(x_0) \) for each medium.

In lieu of imposing an outer boundary derivative condition in terms of presently unknown characteristic lengths \( b_2, b_4 \), one may set the “level” by simulating the outer surface with the imposition of a discontinuity in the physical pair density \( |\psi|^2 \) at the inner boundary. That is, we set

\[
n_s^*(1)\chi^2(1) = \eta n_s^*(2)\chi^2(2),
\]

where the parameter \( \eta \) is a measure of the size of the jump in \( |\psi|^2 \). Equations (5.4), (5.5), and (5.7) completely, and self-consistently determine the order parameter in each region of the system at a given value of \( k_j \) and \( s(t) \) if the transition temperature of the system is known.

Finally we note that the continuity of the current density \( j \), also relates the gradients of the phases of \( \psi(1) \) and \( \psi(2) \) via

\[
\frac{n_s^*(1)}{m^*(1)} \chi^2(1) Q(1) = \frac{n_s^*(2)}{m^*(2)} \chi^2(2) Q(2).
\]
A Periodic SNS Layered System

Here we analyze the experiments on SNS systems, AlAgAl and NbCuNb, as investigated by the Grenoble group\textsuperscript{7,17,18}. Although both the (F, H) and the (E, D\textsubscript{+}) solution pairs are possible candidates for the N slab (Compare Figs. 6 and 9), we choose the (E, D\textsubscript{+}) solutions because they are pull up solutions throughout the entire temperature range, and because the positive value of \( \beta \) is expected to give a lower energy state. We believe that this choice is more likely to be the correct physical solution than that previously used\textsuperscript{19}, which corresponds to the F solution. For simplicity, typical SC parameters and dimensions are used, similar to those used by Courtois et al.\textsuperscript{17} and Dubos et al.\textsuperscript{7,18}

We denote the superconducting layer (Al, Nb) properties by subscript “s” and those of the normal layer (Ag, Cu) by subscript “n” and use the \( N_0 \) notation of Eq. (3.12) for the extremum of the \( f^2 \) function in the \( s \) and \( n \) layer. Note that for case A, the restriction is \( 0 \leq N_0 \leq 1 \), while for \( E \) and \( D_+ \), it is \( 0 \leq N_0 \leq \infty \)

We assume that the current in the \( n \) layer \( k_{jn} = -s_n^2(t)J_n \) is phase-coherent and is treated as a pair current as it is in the superconducting layers. We define in the \( n \) layer “coherence” length \( \xi_n(t) = l_{an} = l_{\beta n}/s_n \), with \( l_{\beta n} = (\hbar/2\pi)(D/k_BT_c) \), where \( 3D = v_Fn/\ell_n = \xi_n^2/\tau, \) with \( D \) the diffusion constant, \( \ell_n \) the mean free path, \( v_F \) the Fermi velocity, and \( \tau \) the electron scattering time. The transition temperature of the SNS structure is \( T_c, k_B \) Boltzmann’s constant and \( s_n = \sqrt{t} = \sqrt{T/T_c} \).

In the \( s \) layer the coherence length is \( \xi_s(t) = l_{as} = l_{\beta s}(t)/s_s = \xi_s(0)(1 + t^2)/s_s \), with \( s_s = \sqrt{1-t^4} \). The effective penetration depth \( \lambda_{eff} = \Omega\lambda_L/\sqrt{1-t^4} \), where \( \lambda_L \) is the London penetration depth and \( \Omega = 0.65(\xi_0/\lambda_L)^{1/3} > 1 \) for Al, a Pippard superconductor, for which \( \xi_s^2(0) \gg \xi_0\lambda_L^2 \) (\( \xi_0 = \text{BCS coherence length} \) ) is satisfied. For \( Nb \) in the dirty limit \( \Omega = (\xi_0/\xi_s(0))^{1/2} > 1 \), with

\[
\xi_s(0) = \frac{\phi_o}{2\pi\sqrt{2\mu_0H_c(0)\lambda_{eff}(0)}},
\]

where \( \phi_o \) is the SC fluxoid quantum, \( H_c(t) = H_c(0)(1-t^2) \) is the thermodynamic critical field and \( \mu_0 \) the vacuum permeability. The Drude resistance of the \( n \) layer \( R_n = [m_n/(n_n\varepsilon_s^2\tau)](d_n/A) \), with \( d_n \) the thickness of the normal layer, \( A \) the cross-sectional area.

The physical current density \( j \) is the same in the \( n \) and \( s \) regions, and thus the relation between \( j \) and the normalized current densities in the \( n \) and \( s \) regions is

\[
J_n = \left( \frac{s_n}{s_s} \right)^3 \frac{1}{r} \frac{l_{\beta n}}{l_{\beta s}} J_s = \left( \frac{s_n}{s_s} \right)^3 \frac{1}{r} \frac{l_{\beta n}}{l_{\beta s}} \frac{\lambda_L}{\xi_s(0)(1 + t^2)} \sqrt{2H_c(t)\Omega s_s} j,
\]

where \( r = (m_s/m_n)(n_n/n_s) \). From the above, the physical critical current density \( j_c \), Eq. (2.26), leads to the energy expression

\[
e_{jc}A R_n = \frac{1}{2} \frac{h}{\tau} \left( \frac{d_n}{\ell_n} \right) k_{jc} = \frac{3}{2} \frac{d_n}{\ell_n} \left( \frac{d_n}{\ell_n} \right)^2 k_{jc}
\]

where \( \varepsilon = hD/\ell_n^2 \) is the Thouless energy.

It is our aim to calculate the largest (critical) current density \( k_{jc}(t) = \max|k_j| \) of a SNS structure as a function of temperature. The prefactor of \( k_{jc} \) depends solely on properties of the \( n \) layer, but the unitless current parameter \( k_{jc} \) tracks the physical critical current density \( j_c \) and is implicitly connected to the SC and normal region parameters. The \( E \) and \( D_+ \) solutions applicable to the \( n \) region, and \( A \) solution relevant to the \( s \) region are, using Eq. (3.13)

\[
A \quad N_s(x) = N_0 + \frac{1}{2} \frac{b_0}{\Delta} \Delta^2(u|m)
E \quad N_n(x) = N_0 + (1 + 3/2N_0 - \Delta) \Delta^2(u|m)
D_+ \quad N_n(x) = N_0 + \sqrt{b_0} sc^2(u|m) d^2(u|m).
\]

For simplicity, we set \( m_s/m_n = n_s/n_n = 1 \) which reduce Eqs. (5.4) and (5.7), respectively, to

\[
\frac{dN_n}{dx}|_b = \left[ \frac{s_n(t)}{s_n(t)} \right]^2 \frac{dN_s}{dx}|_b
\]

and

\[
19
\]
\[ N_n(b) = \eta \left( \frac{s_n(t)}{s_n(0)} \right)^2 N_s(b). \] (5.13)

Although the parameter \( \eta \) is set by “external” boundary conditions, we assume continuity of the physical pair density across the boundary, i.e. \( |\psi_n|^2 = |\psi_n|^2 \), with \( \eta = 1 \).

Since \( u \) and \( m \) are functions of \( N_0 \) and \( J \), it is possible to calculate for any pair \( (N_0, J) \) the values of \( N(x = d/2) = N_b \) and \( dN/dx \) at the interface between the \( n \) and \( s \) regions. The triple \( (N_0, J, N_b) \) comprise a surface, and it is then possible to plot \( J \) vs. \( N_0 \) for fixed \( N_b \).

The \( D_+ \) solutions for several values of \( N_b \) for a NbCuNb specimen at \( T = 0.35K \) are shown in Fig. 12. The \( D_+ \) solutions terminate on the right and the \( E \) solutions continue to \( J = 0 \) [not shown]. For fixed \( N_0 \) and \( N_b \) there exists a maximum \( J \) which is proportional to the critical current density \( j_c(0) \), provided boundary conditions (5.5), (5.12), and (5.13) are satisfied. Only the curve with \( N_b = 16.73 \) satisfies all three boundary conditions at \( T = 0.35K \); thus the maximum value of this curve, which occurs in the \( D_+ \) solution region at \( T = 0.35K \), corresponds to the unique \( j_c \). Similarly, Fig. 13 shows \( E \) solutions at \( T = 0.5K \) for the above NbCuNb specimen. The \( E \) solutions terminate on the left and continue as \( D_+ \) solutions [not shown]. Only the \( N_b = 11.63 \) curve satisfies all boundary conditions, and therefore its maximum value, which lies in the \( E \) solution region, is the correct unique solution for the critical current at \( T = 0.5K \). The general behavior depicted in Figs. 12 and 13 is consistent with results expected from Fig. 6 for constant temperature.

Critical current values \( k_{jc} \propto j_c \), Eq. (2.26), are plotted in Fig. 14 as a function of normalized temperature for the above NbCuNb and AlAgAl junctions with parameters listed in the captions for Figs. 12 and 14. The first three points on the left of each curve are \( D_+ \) solutions, and the remaining points are \( E \) solutions. The plotted points are exact solutions with all three boundary conditions satisfied. The solid line is an aid to the eye only, connecting the computed solutions. The extrapolated values of \( k_{jc} \) to \( T = 0K \) of the two junctions are \( 8.7 \times 10^{-3} \) and \( 5.6 \times 10^{-3} \), and are comparable to the maximum \( k_j \) value \( \sim 7 \times 10^{-3} \) in Fig. 6, although they were obtained with different external parameters. Similarly, the maximum value of \( k_j \) for the \( F \) type solution shown, in Fig. 9, is \( 8 \times 10^{-3} \). These results add credence to our earlier statements that it is \( k_j \propto j \), and not \( J \), that is a meaningful parameter.

In Ref. 18 the dimensionless parameter \( eI_cR_n/\varepsilon \), Eq. (5.10), is plotted versus \( k_BT/\varepsilon \), with \( \varepsilon \) a fitting parameter. These experiments indicate that this parameter extrapolated at \( T = 0K \) to the value 8.2. With the above parameters, the 0 K limiting value of \( eI_cR_n/\varepsilon \) for the NbCuNb junction is 47, and for the AlAgAl junction 257, indicating that this value depends strongly on the junction parameters of Eq. (5.10).

Figure 15 shows the experimental points, taken from Fig. 4 of Ref. 7, of critical currents of a NbCuNb junction with parameters similar to those of Fig. 12. The solid line is calculated from the \( k_{jc}(t) \) curve of Fig. 14 using Eq. (2.26) with \( e^* = 2|e|, m^*/n^*_e = 1.12 \times 10^{-58} \text{ kg m}^3 \), and \( A = 5.9 \times 10^{-14} \text{ m}^2 \). The latter curve is a convincing fit of our theory to the experimental points. Assuming that the extrapolation to \( T = 0K \) is meaningful, one obtains \( eI_cR_n/\varepsilon = 21 \), using \( I_c(0) = 2.5 \text{ mA}, \varepsilon = 24 \mu \text{ eV}, \) and \( R_n = 0.20 \Omega \).

VI. CONCLUSIONS

We have reformulated the GL theory by introducing the complete kinetic energy density, which requires a gradient term in the surface energy to support a SC state, thus replacing the standard GL energy density functional. The role of surface energy in determining the superconducting state of a sample was analyzed in detail. For a weakly superconducting surface, we have shown that the same phenomenological parameter \( b_2 \) can be used to describe a reduction or an enhancement of the transition temperature in moderately small to small superconductors. Plating a superconducting specimen with a normal metal or ferromagnetic substance reduces the transition temperature and is described by \( b_2 > 0 \). For \( b_2 < 0 \) an increase of \( T_c \) is perhaps brought about by elastic strain\(^{20} \), observed on tin whiskers, by severely cold working the surface of InBi foils\(^6 \), and by plating the specimen with a superconductor with a larger intrinsic \( T_c \) than the specimen, and by other means\(^{21-24} \). In recent theoretical studies\(^{25} \) the 3 Kelvin phase of Sr\(_2\)RuO\(_4\) is modeled with Ru metal inclusion as interface states with locally enhanced \( b_2 < 0 \) transition temperature. A negative \( b_2 \) value, or more precisely, a positive slope of the order parameter imposed at the surface of a normal slab, embedded between superconductors, induces superconductivity throughout the normal region if sufficiently thin. Nucleation fields for slabs for positive and negative slopes of the order parameter at the slab surfaces have been published previously\(^{16} \). They show that enhancements of \( H_{c3} \) for \( b_2 < 0 \) is also possible. Other practical surface treatments and theoretical microscopic explanations relating to \( T_c \) enhancements of superconductors are still to be discovered.

The parameter \( \beta \), characterizing SC pair interactions in a sample, is always positive when the surface is weakly superconducting. If the surface is strongly superconducting, that is, when SC pair interactions play a significant role, superconductivity of the system is also characterized by a parameter \( b_1 \). In this case, we have shown that the sample
may be in an anomalous superconducting state even when $\beta$ is negative. The parameter $b_2$ can be measured from SOPT experiments; whereas the parameter $b_4$ can be determined from the uniform state, if it can be detected, or perhaps from the minimum surface free energy.

For one dimensional systems with a uniform current density, all possible physical solutions of our generalized GL equations with $\text{sgn}(\alpha) = \pm 1$ and $\text{sgn}(\beta) = \pm 1$ were found and categorized. Although a commonly used parameter $f$ is mathematically expedient, it can be misleading when used to depict the SC order parameter when surface effects are significant, i.e. $f$ is not, in general, a physical order parameter.

Introducing a transport current modifies the solutions of the theory with arbitrary parameters $\alpha$ and $\beta$. Figures 6 - 10, in which the order parameter $\chi = \psi/\sqrt{\pi s}$ is plotted as a function of the fundamental length ratio $s = l_\beta/l_\alpha$, Eq. (2.26), relate to solutions with currents which are described by Eq. (3.14), while Eq. (3.23) and Fig. 11 are zero current pre-wetting solutions which evolve naturally in the present development. The current parameter $k_j$, Eq. (2.26), tracks the physical current density. Since $k_j$ remains finite as $s(t) \to 0$, the critical current remains finite in a normal region, where $s(t) = \sqrt{T}$, as $t \to 0$. In Figs. 12-15 the transport current results, applied to SNS junctions, are in excellent agreement with experiments over the entire wide temperature range of the measurements. The boundary condition for the gradient of the order parameter at the interface is derived from the surface energy functional. This boundary condition is consistent with that used in micronetworks$^{12}$. The continuity of the order parameter at the interface, assumed without formal justification, completes the set of boundary conditions necessary to set the “level” of the order parameter. Although this condition is consistent with that used in quantum mechanics, the level of the order parameter is set, in general, by an external boundary condition on its gradient.

It is often argued that the GL model equations apply only near $T_c$. However, this argument is weak, since the GL phenomenological model does not contain the temperature explicitly. The exact solutions given here for the order parameter are functions of the fundamental length ratio $s(t)$. It is true, if we write $s = \sqrt{T-T_c}$, as GL did, our results would be limited to temperatures near $T_c$. However, there is no compelling requirement that restricts the temperature dependence of the present theory to this limited temperature range. The Gor’kov derivation$^{10}$ of the GL equations uses a small energy gap expansion of the microscopic BCS theory$^{11}$, valid near $T_c$, but that does not exclude the possibility that the phenomenological order parameter theory gives reasonable physical results well below$^{26}$ $T_c$. However, it is prudent to relate $s(t)$ to the experimental results of the temperature dependence $l_\alpha(t)$ and $l_\beta(t)$.

**APPENDIX A: MINIMIZATION OF THE FUNCTIONAL $G$**

The energy functional Eq. (2.7) is

$$G = \int_V d^3r \left[ U(|\psi|) + \frac{\hbar^2}{2m^*} |\nabla|\psi| \cdot \nabla|\psi| + |\psi|^2 Q \cdot |\nabla|A'|^2 + \frac{1}{2\mu_0} (\nabla \times A')^2 \right] + \frac{\hbar^2}{2m^*} \int_S ds \cdot [\hat{n} \Lambda + (c - e)|\psi|\nabla|\psi|].$$

where $A' = A - A_a$.

The total variation of $G$ is

$$\frac{2m^*}{\hbar^2} \delta G = \int_V d^3r \left\{ \frac{m^*}{\hbar^2} \frac{\partial U}{\partial |\psi|} + |\psi|^2 Q \cdot \delta |\psi| + \nabla|\psi| \cdot \nabla \delta |\psi| + |\psi|^2 Q \cdot \nabla \delta \theta + \right.$$

$$\left. E_s \delta \Lambda \right\} + \frac{m^*}{\mu_0 \hbar^2} \int_S \frac{d\theta}{\phi_0} |\psi|^2 Q \cdot \delta A + \frac{m^*}{\mu_0 \hbar^2} \right\} + \int_S ds \cdot [\hat{n} \delta \Lambda + (c - e) \delta (|\psi| \nabla |\psi|)].$$

Consider the vector identities

$$\nabla f \cdot \nabla g = -f \nabla \cdot \nabla g + \nabla \cdot (f \nabla g)$$  \hspace{1cm} (A3)

$$B \cdot (\nabla \times A) = A \cdot (\nabla \times B) + \nabla \cdot [A \times B]$$  \hspace{1cm} (A4)

Using the vector identities for the volume terms involving $\nabla \delta |\psi|, \nabla \delta \theta, \nabla \times \delta A$, and applying the divergence theorem, one obtains from Eq. (A2) the variational form.
\[
\frac{2m^*}{\hbar} \delta G = 2 \int_V d^3r \left\{ \frac{m^*}{\hbar^2} \frac{\partial U}{\partial |\psi|} + |\psi| \mathbf{Q} - \nabla^2 |\psi| |\psi| - \nabla \cdot (|\psi|^2 \mathbf{Q}) \delta \theta + \right.
\]
\[
\left. \left[ \frac{2\pi}{\phi_0} |\psi|^2 \mathbf{Q} + \frac{m^*}{\mu_0 \hbar^2} \nabla \times (\nabla \times \mathbf{A}') \right] \cdot \delta \mathbf{A} \right\} +
\]
\[
\int ds \left\{ [(a+1)\nabla |\psi| + (a-1)\frac{\partial \nabla |\psi|}{\partial |\psi|}] + \frac{n}{\mu_0 \hbar^2} \frac{\partial A}{\partial |\psi|} |\psi| + [2|\psi|^2 \mathbf{Q} + \widehat{n} \frac{\partial A}{\partial \theta} |\psi| + \widehat{n} \frac{2m^*}{\mu_0 \hbar^2} (\nabla \times \mathbf{A}') \times \widehat{n} + \nabla A] \cdot \delta \mathbf{A} \right\},
\]
where \(a = 1 + c - \epsilon\). The variations \(\delta |\psi|, \delta \theta, \delta \mathbf{A}\) may be taken independently in \(V\) and on \(S\). Thus the coefficients of the variations are zero and one obtains Eqs. (2.8)-(2.13).

To obtain the form of the minimum free energy given by Eq. (2.14), use (A3) with \(g\) replaced by \(f\) to eliminate \(\nabla f \cdot \nabla f\), and use Eq. (2.8) to eliminate \(\nabla^2 |\psi|\).

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FIG. 1. The order parameter \(\chi(0)\) of the E solution for is plotted as a function of the fundamental length ratio \(s(t) = l_\parallel/l_\perp(t)\) for \(a = 1\) and for \(a = 1 \pm 0.001\), where \(a\) is a measure of the amount of \(\nabla \chi^2\) in the surface energy. The dashed curves are the energy parameter \(\Gamma_{\min}\), Eq. (4.4). Only the \(a = 1\) curve satisfies the entropy condition (4.5) for a second order phase transition.
FIG. 2. The order parameter $\chi(0)$ is plotted as a function of $s$ for positive $\beta$ cases A, C1, C2, and E for three surface parameter sets $(b_2,b_4)$. Also shown by dashed curves are the normalized, minimum free energy $\Gamma_{\text{min}}$. A superconducting state requires $\Gamma_{\text{min}} < 0$.

FIG. 3. The order parameter $\chi(0)$ is plotted as a function of $s$ for the negative $\beta$ cases F, H1, H2, and I for two surface parameter sets $(b_2,b_4)$. The dashed lines are the minimized energy $\Gamma_{\text{min}}$, Eq. (4.4). The superconducting state requires $\Gamma_{\text{min}} < 0$.

FIG. 4. The order parameter $\chi(0)$ for the cases shown in Fig. 2 are plotted as a function of the normalized temperature $t = T/T_c$ using Eq. (4.9).

FIG. 5. The order parameter $\chi(0)$ for the cases shown in Fig. 3 are plotted as a function of the normalized temperature $t = T/T_c$ using Eq. (4.9).

FIG. 6. The order parameter $\chi(0)$ is plotted as a function of $s$ for positive $\beta$ cases E and D for different values of the current parameter $k_j$. The $k_j = 0$ curves is that in Fig. 2, curve E.

FIG. 7. The order parameter $\chi(0)$ is plotted as a function of $s$ for positive $\beta$ cases A, B, C, and D for different values of the current parameter $k_j$. The $k_j = 0$ curve is that in Fig. 2, upper branch C2, C1, A.

FIG. 8. The order parameter $\chi(0)$ is plotted as a function of $s$ for positive $\beta$ case A (lower branch) for different values of the current parameter $k_j$. The $k_j = 0$ curve is the lower branch in Fig. 2.

FIG. 9. The order parameter $\chi(0)$ is plotted as a function of $s$ for positive $\beta$ cases F and H for different values of the current parameter $k_j$. The $k_j = 0$ curve is the F, H1, H2 curve in Fig. 3.

FIG. 10. The order parameter $\chi(0)$ is plotted as a function of $s$ for positive $\beta$ cases G and I for different values of the current parameter $k_j$. The $k_j = 0$ curve is the upper I branch in Fig. 3.

FIG. 11. Shown is the pre-wetting depth $l_0$ of the E' solution, Eq. (3.23), plotted as a function of temperature for fixed values of $f(d/2)$ at the NS interface of a SC reservoir.

FIG. 12. Normalized current $J$ vs. the minimum of the squared order parameter $f_0^2 = N_0$ in the $n$ region at constant temperature for various $N_0 = f_0^2$ values at the SN interface for the $D_+$ solution of NbCu at $T = 0.35$ K. The continuation of these curves on the right are E solutions [not shown]. Parameters: $d_n = 800 \text{ nm}$, $d_s = 200 \text{ nm}$, $l_{\beta n} = 61.3 \text{ nm}$, $l_{\beta s}(0) = 22.1 \text{ nm}$, $l_n = 48 \text{ nm}$, $\lambda_L = 39 \text{ nm}$, $\xi_0 = 38 \text{ nm}$, $T_c = 8.1$ K, $v_{F n} = 1.57 \times 10^6 \text{ m/s}$.

FIG. 13. Similar to Fig. 12, but for the E solution of NbCu at $T = 0.5$ K. The continuation of these curves on the left are $D_+$ solutions [not shown]. The parameters are the same as used in Fig. 12.

FIG. 14. Normalized critical current parameter $k_{jc} \propto j_c$, Eq. (2.26), plotted as a function of normalized temperature for a NbCuNb junction with the parameters of Fig. 12, and the same for an AlAgAl junction with parameters: $d_n = 1.48 \mu\text{m}$, $d_s = 2d_n$, $l_{\beta n} = 113 \text{ nm}$, $l_{\beta s}(0) = 487 \text{ nm}$, $l_n = 33 \text{ nm}$, $\lambda_L = 14.8 \text{ nm}$, $\xi_0 = 1.6 \mu\text{m}$, $T_c = 1.45$ K, $v_{F n} = 1.38 \times 10^6 \text{ m/s}$.

FIG. 15. Critical current $I_c$ plotted as a function of temperature $T$ of a NbCuNb junction. The experimental points are from Ref. 7, and the solid line is calculated from $k_{jc}$ of Fig. 14.
\( \chi^2(0) \)

- \( a = 1 \)
- \( d/l_{\beta} = 0.5 \)
- \( d/b_2 = -0.01 \)
- \( d/b_4 = 0.05 \)
- E-solution

\( s(t) \)

\( 0.24 \quad 0.25 \quad 0.26 \quad 0.27 \quad 0.28 \quad 0.29 \quad 0.3 \)
\[ s(t) \]

\[ \chi(0) \]

\[ 50\Gamma_{\text{min}} \]

\[ \frac{d}{b_2} = -0.01 \]
\[ \frac{d}{b_4} = 0.25 \]

\[ \frac{d}{b_2} = 0.01 \]
\[ \frac{d}{b_4} = 0.25 \]

\[ \frac{d}{l_\beta} = 0.5 \]
\[ t = \frac{T}{T_c} \]

[Graph showing \( \chi(0) \) vs. \( t = \frac{T}{T_c} \) with various curves and annotations such as \( d/b_2 = 0.01 \), \( d/b_4 = 0.05 \), \( d/b_2 = -0.01 \), \( d/b_4 = 0.05 \), and \( d/l_\beta = 0.5 \).]
\[ t = \frac{T}{T_c} \]

\[ \chi(0) \]

\[ \frac{d}{b_2} = 0.01 \]
\[ \frac{d}{b_4} = 0.25 \]

\[ \frac{d}{b_2} = -0.01 \]
\[ \frac{d}{b_4} = 0.25 \]

\[ \frac{d}{b} \]
\[ \beta = 0.5 \]
\[ s(t) \]

\[ \chi(0) = \text{sign}(\alpha) = 1 \]

\[ D \text{-solution} \]

\[ E \text{-solution} \]

\[ d/l_{\beta} = 0.5 \]
\[ d/b_2 = -0.01 \]
\[ d/b_4 = 0.05 \]

\[ k_j = 0 \]
\[ d/l_\beta = 0.5 \]
\[ d/b_2 = -0.01 \]
\[ d/b_4 = 0.05 \]
\[ \text{sign}(\alpha) = -1 \]
\[ s(t) \]

\[ \chi(0) \]

\[ d/l_B = 0.5 \]
\[ d/b_2 = -0.01 \]
\[ d/b_4 = 0.25 \]

\[ k_J = 0 \]

F-solution
H-solution
\[ s(t) \]

\[ \chi(0) \]

\[ d/l_\beta = 0.5 \]
\[ d/b_2 = -0.01 \]
\[ d/b_4 = 0.25 \]

\[ k_j = 0 \]
\[ k_j = 1.5e^{-2} \]

\[ 8.5e^{-3} \]
\[ 1e^{-2} \]
\[ 7e^{-3} \]
\[ 3e^{-3} \]

G-solution
I-solution
\[ t = \frac{T}{T_c} \]

\[ \frac{d}{l_\beta} = 5 \]
\[ \frac{d}{b_2} = -5 \]
\[ \frac{d}{b_4} = 1 \]

E' solution

f(d/2) = 0.9
$J$ vs $N_0$ for different $N_b$ values:

- $N_b = 16.73$
- $Nb$-Cu-Nb
- $T = 0.35$ K
- $D_+$ solution
$N_b = 11.63$

Nb–Cu–Nb

$T = 0.5 \text{ K}$

E solution
$k_c(T)$ vs $T/T_c$ for Nb–Cu–Nb $D^+$ and $E$ solutions and Al–Ag–Al $D^+$ and $E$ solutions.
$I_c [\text{A}]$ vs $T [\text{K}]$

- Nb-Cu-Nb $D_+$ and E solution