Boundary condition for Ginzburg-Landau theory of superconducting layers

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Electrostatic charging changes the critical temperature of superconducting thin layers. To understand the basic mechanism, it is possible to use the Ginzburg-Landau theory with the boundary condition derived from the minimum free energy. We compare the two boundary conditions and use the Budd-Vannimenus theorem as a test of approximations.

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I. INTRODUCTION

Much experimental effort is devoted to find superconducting materials with critical temperatures as high as possible. It is well known that the critical temperature depends on the charge carrier density. The charge carrier density can be changed by doping and to some extent it can also be changed by electrostatic charging. Consequently it is an attractive task to determine, how electrostatic charging evoked by an applied electric field changes the critical temperature of superconductors. Generally the experiments revealed that it is easier to increase \( T_c \) than to decrease it\(^{1,2} \). The Ginzburg-Landau (GL) theory with the de Gennes boundary condition can be used to understand this behavior\(^3\).

The aim of this paper is to show how a superconductor screens the external electric field and to which extent the boundary condition derived from the minimum free energy principle is compatible with the de Gennes boundary condition.

Charges at a solid surface partially leak out of the surface. This creates a surface dipole. The Budd-Vannimenus theorem\(^4\) describes the step in the surface potential due to this surface dipole as a simple expression of the bulk free energy density. Therefore it is well suited to test the approximations used in this paper.

In the first chapter we explain the model and the parts considered in the free energy of the superconductor and solve the Euler-Lagrange equations for the GL and charge carrier wave function and the surface potential. In chapter III the corresponding equations outside the superconductor are solved and in chapter IV the continuity requirements determine the remaining constants. Chapter V presents the numerical values which are compared with the de Gennes boundary condition in chapter VI. Finally we conclude in chapter VII.

II. FREE ENERGY IN THE SUPERCONDUCTOR

We start with the free energy

\[
F = \int \left( f_{TF} + f_{GC} + f_{GL} + f_{elst} \right) \, d\mathbf{r},
\]

where we include only the terms most relevant for the above specified problem.

The first term \( f_{TF} \) is the Thomas-Fermi internal energy, for which we use the LDA (local-density approximation)

\[
f_{TF} = \frac{3}{5} \left( \frac{3}{4} \pi^2 \right)^{\frac{2}{3}} \frac{\hbar^2}{2m} n_s^{\frac{5}{3}}.
\]

The second term \( f_{GC} \) represents the condensation energy for which we use the formula following from the Gorter-Casimir two fluid model\(^5,6\)

\[
f_{GC} = \frac{1}{4} \gamma T_c^2 \left( \frac{n_s}{n} + 2 \frac{T^2}{T_c} \sqrt{1 - \frac{n_s}{n}} \right).
\]

The electrostatic energy density term reads

\[
f_{elst} = \frac{1}{2} \varepsilon_0 \mathbf{E}^2 + \varepsilon \varphi \delta n,
\]

in the form suitable for performing variations. For simplicity we exclude the magnetic field and it’s related kinetic energy of the screening current. We take the vector potential \( \mathbf{A} \) to be zero and write the GL gradient term as

\[
f_{GL} = \frac{\hbar^2}{2m} \psi_n^2 | \nabla \psi |^2.
\]

Here we have chosen the GL wave function \( \psi \) normalized with respect to the total charge carrier density \( n \). In the spirit of the Thomas-Fermi approximation the charge carriers are described by a wave function \( \psi_n \) with \( n = \psi_n^2 \) and the superconducting fluid density used in the formula for the condensation energy\(^3\) reads

\[
n_s = 2 \psi_n^2 \psi^2.
\]
In short, the free energy is expressed by three independent variables: the scalar potential \( \phi \) determining the electric field \( \mathbf{E} = - \nabla \phi \), the charge carrier wave function \( \psi \) and the charge carrier wave function \( \psi_n \). We assume that the material parameters, the critical temperature \( T_c \) and the Sommerfeld parameter \( \gamma \) depend on the charge carrier’s density \( n \), by using the approximations

\[
\gamma(n) = \gamma_0 \left( 1 + \frac{n - n_{lat}}{n_{lat}} \frac{\partial \ln \gamma}{\partial \ln n} \right), \tag{7}
\]

\[
T_c(n) = T_{c0} \left( 1 + \frac{n - n_{lat}}{n_{lat}} \frac{\partial \ln T_c}{\partial \ln n} \right), \tag{8}
\]

where \( n_{lat} \) is the crystal lattice density. In the following we shall use three characteristic length:

(i) the Thomas-Fermi screening length \( \lambda_{TF}^2 = \frac{3a \sqrt{\pi}}{2m} E_F \),
(ii) the Bohr radius \( a_B = \frac{4 \pi e^2 h^2}{me^2} \)
(iii) and the coherence length \( \xi_0^2 = \frac{\hbar^2 n_{lat}}{4 n_{lat} \lambda_{TF}^2 n_{lat}} \).

From the charge neutrality requirement we know that \( \psi_{\infty} = \sqrt{n_{lat}} \) (here and in the following the subscript \( \infty \) denotes the magnitude far from the surface). To keep things simple, we use the approximations

\[
\psi_n = \sqrt{n_{lat}} (1 + \delta \psi_n) \tag{9}
\]

\[
\psi = \psi_{\infty} (1 + \delta \psi) \tag{10}
\]

\[
e \phi = E_F (\phi_{\infty} + \delta \phi) \tag{11}
\]

and suppose that the deviations of the three independent variables from the optimum values are small. In a homogeneous superconductor far from the surface all these deviations have a zero value and the derivatives of the free energy formula (11) with respect to them must be also zero. From these requirements we get the magnitudes of the optimum superfluid fraction

\[
\frac{\psi_{\infty}}{\psi_{\infty}} = \sqrt{1 - t^4} \tag{12}
\]

and the optimum magnitude of the scalar potential

\[
\varphi_{\infty} = 1 - \frac{2 \lambda_{TF}^2}{\pi^2 a_B^2 \xi_0^2} \left[ 2 \left(1 - t^4\right) \frac{\partial \ln T_c}{\partial \ln n} + \left(1 + t^4\right) \frac{\partial \ln \gamma}{\partial \ln n} \right]. \tag{13}
\]

The electrostatic potential energy of the charge carrier thus equals the Fermi energy

\[
E_F = \frac{\hbar^2}{2m} \left(3n^2 n\right)^{2/3}, \tag{14}
\]

with a small (lower than gap) correction represented by the second term in (13).

Using the second order expansion of the free energy (11), from the variation we get three linear Euler-Lagrange (EL) equations for the three independent variables,

\[
\left( 1 - t^4 \right) \xi_0^2 \nabla^2 \delta \phi + \delta \psi_n = 0, \tag{15}
\]

\[
(2 + 4t^4) \frac{\partial \ln T_c}{\partial \ln n} \left( \frac{\partial \ln T_c}{\partial \ln n} + 2 \frac{\partial \ln \gamma}{\partial \ln n} \right) - \frac{\pi^2 a_B^2 \xi_0^2}{12 \lambda_{TF}^2} \delta \psi_n + 2 \left(1 - t^4\right) \frac{\partial \ln T_c}{\partial \ln n} \delta \psi - \frac{\pi^2 a_B^2 \xi_0^2}{16 \lambda_{TF}^2} \delta \phi = 0. \tag{17}
\]

Close to the planar surface we can assume exponential dependencies of the deviations and from the EL equations (15-17) we get a second order equation for the square of the expected penetration depth \( \lambda \). Two solutions arise out of it.

Observing that \( \lambda_{TF} a_B \ll \xi_0 \), we find a first approximate solution \( \lambda \) in the form of the coherence-like length

\[
\xi_t = \xi_0 \frac{2t^2}{1 - t^4}. \tag{18}
\]

In this solution the scalar potential is constant and local charge neutrality is preserved. Only the deviation of the wave function \( \delta \psi \) is nonzero (\( C_\xi \) will denote its magnitude).

A very small penetration depth characterizes the second solution such that this solution can be simplified. Using the same approximation as above, we find that the second penetration depth equals the Thomas-Fermi screening length \( \lambda_{TF} \). In this solution the scalar potential displays a sharp step (\( C_{TF} \) will denote its magnitude) and from the Poisson equation (15) follows that the charge carrier's density changes accordingly. The sharp step on the GL wave function \( \psi \) is negligibly small due to the factor \( \lambda_{TF}^2 / \xi_t^2 \) which enters the resulting formula. It corresponds to the well known fact that the GL wave function \( \psi \) cannot abruptly change.

The general solution can be written as a sum of the two above described solutions:

\[
\delta \phi = C_{TF} \exp \left( -\frac{x}{\lambda_{TF}} \right) \tag{19}
\]

\[
\delta \psi_n = -\frac{3}{4} C_{TF} \exp \left( -\frac{x}{\lambda_{TF}} \right) \tag{20}
\]

\[
\delta \psi = \frac{3 \lambda_{TF}^2 t^4}{(1 - t^4) \xi_t^2} \frac{\partial \ln T_c}{\partial \ln n} C_{TF} \exp \left( - \frac{x}{\xi_t} \right) + C_\xi \exp \left( - \frac{x}{\xi_t} \right). \tag{21}
\]

Here \( C_{TF} \) describes the step of the scalar potential in units of \( E_F / e \) according to (11). Using (19) - (21) we can calculate the free energy

\[
\mathcal{F} = \int \left( \frac{3}{5} + \frac{2(1 + t^4) \lambda_{TF}^2}{\pi^2 a_B^2 \xi_0^2} \right) \, dx - \frac{3}{4} \lambda_{TF} C_{TF}^2 + \frac{8 \lambda_{TF}^4 (1 - t^4)}{\pi^2 a_B^2 \xi_\tau^2} C_\xi^2 + \frac{48 t^4 \lambda_{TF}^5}{\pi^2 a_B^2 \xi_t^2} \frac{\partial \ln T_c}{\partial \ln n} C_{TF} C_\xi. \tag{22}
\]
For a semi-infinite medium the first term gives an infinite contribution which is not influenced by the surface conditions, so we do not need to deal with it. The last three terms correspond to the surface energy, which according to the principle of minimum free energy should take an extremum. The minimum of the free energy is obtained for

$$C_\xi = -\frac{3\lambda_{TF}\xi_0}{4e_0^2} \frac{\partial n_{TF}}{\partial \ln n_{TF}},$$

in which case the derivative of the wave function $\psi$ at the surface is zero. For $\alpha = 1, 2$ we get $C_\xi = -0.00044 C_{TF}$. As expected, the deviation of the GL wave function $\delta \psi$ is much smaller compared to the sharp steps on the scalar potential $\delta \varphi$ and on the charge carrier wave function $\delta \psi_n$.

We see that the principle of minimum free energy entails the GL boundary condition. Towards the surface the GL wave function $\delta \psi$ displays a small gradual change, only very close to the surface its derivative jumps to zero. The solution is complete, if the parameter $C_{TF}$ is determined. It can be derived from the requirement of continuity with a solution minimizing the total free energy including the one of the vacuum outside.

### III. FREE ENERGY OUTSIDE THE SLAB

Now we approximate the free energy density outside the superconductor by

$$\mathcal{F} = \int (f_W + f_{GL} + f_{elst}) \, d\mathbf{r}.$$  

We include the electrostatic term, the GL gradient correction and the von Weizsäcker kinetic energy functional

$$f_W = \frac{\hbar^2}{2m} |\nabla \psi|_2^2.$$  

In the limit of rapidly varying densities this kinetic energy term is dominant and when describing charge carriers tunneling outside the superconductor this term cannot be omitted. We have not included this term into the formula describing the free energy inside. The reason is that inside the superconductor the Thomas-Fermi internal energy plays the dominant role and moreover, as it is shown e.g. in the book of Dreizler and Grosz, in the limit of nearly homogeneous systems the second order term of the gradient expansion provides a better approximation. It has the same structure as the von Weizsäcker kinetic energy functional, but its coefficient is nine times lower. We suppose that for the rough estimates presented here this relatively small correction can be neglected.

In the vacuum far from the surface the scalar potential reaches the magnitude of the work function $\varphi_W$, so that we can approximate

$$\varphi = E_F \left( \varphi_W + \delta \varphi \right).$$  

The density of the tunneling charge carriers quickly drops to zero. Using an analogous notation as above we write

$$\psi_n = \sqrt{n_{out}} \delta \psi_n$$  

supposedly that $\delta \psi_n$ is small. For the wave function $\psi$ we use the approximation

$$\psi = \tilde{\psi}_\infty + \delta \psi,$$

where $\tilde{\psi}_\infty$ represents the superfluid fraction in the vacuum far from the surface. Let us remind that $\psi$ is normalized to the charge carrier density, see (40), so that $\tilde{\psi}_\infty$ does not need to be zero. The free energy density in the vacuum thus reads

$$f_{out} = \frac{8\lambda^2_{TF}}{\pi^2 a_B} \left( 2 (\nabla \delta \psi_n)^2 + \delta \psi_n^2 (\nabla \delta \psi)^2 \right)$$

$$- \frac{3}{4} \lambda^2_{TF} (\nabla \delta \varphi)^2 + (\varphi_W + \delta \varphi) \delta \psi_n^2$$

and we can write the Euler-Lagrange equations.

The variation with respect to the wave function $\psi$ gives the condition

$$\delta \psi_n^2 \nabla^2 \delta \psi = 0.$$  

We see that $\delta \psi$ remains constant or changes linearly.

The proximity effects indicate that the correlated charge carriers can remain correlated even if they are tunneling. For simplicity we suppose, that the superfluid fraction of the charge carriers tunneling outside the material does not change, so we take $\delta \varphi = \varphi(0)$. The two other Euler-Lagrange equations read

$$2 \varphi_W \delta \psi_n - \frac{32\lambda^4_{TF}}{\pi^2 a_B} \nabla^2 \delta \psi_n = 0$$  

$$\delta \psi_n^2 + \frac{3}{2} \lambda^2_{TF} \nabla^2 \delta \varphi = 0.$$  

In the same way as above we can try the exponential solution

$$\delta \psi_n = K_n \exp \left( \frac{x}{\lambda_W} \right)$$  

$$\delta \varphi = K \varphi \exp \left( \frac{2x}{\lambda_W} \right),$$

where $\lambda_W$ denotes the tunneling length which follows from the Euler-Lagrange equation (32) as

$$\lambda_W = \frac{\sqrt{6} \varphi_W}{K_n}.$$  

The work function can be determined from (31) as

$$\varphi_W = \frac{16\lambda^2_{TF}}{\pi^2 a_B^2 \lambda_W^2}.$$  

In this way we have an approximate solution outside the superconductor, which should be linked to the solution inside.
IV. CONTINUITY REQUIREMENTS

At the surface the continuity of the wave function $\psi_n$ and the continuity of the scalar potential $\varphi$ with its derivative (continuity of the electric field) must be ensured. We get three conditions

$$
\frac{2\lambda^2_{TF}}{\pi^2 a_B^2} \left( 2 (1 - t^2) \frac{\partial h T_e}{\partial \ln n} + (1 + t^2) \frac{\partial \ln \gamma}{\partial \ln n} \right) - 1 + C_{TF} = K_e - \frac{8\lambda^2_{TF}}{3\pi^2 a_B^2} K_e^2 \tag{37}
$$

$$
- C_{TF} = \frac{2K_e K_n}{\sqrt{-6K_e}} + E_a \tag{38}
$$

$$
1 - \frac{3}{4} C_{TF} = K_n \tag{39}
$$

where the term $E_a$ representing the applied electric field is included into the condition of continuity for the electric field. From the continuity requirements \((37)-(39)\) we obtain the equation

$$
\frac{2\lambda^2_{TF}}{\pi^2 a_B^2} \left( 2 (1 - t^2) \frac{\partial h T_e}{\partial \ln n} + (1 + t^2) \frac{\partial \ln \gamma}{\partial \ln n} \right) - \frac{\lambda^2_{TF}}{144\pi^2 a_B^2} (C_{TF} - E_a)^2 \frac{24 (C_{TF} - E_a)^2 (-4 + 3C_{TF})^2}{(C_{TF} - E_a)^2} - 1 + C_{TF} = 0, \tag{40}
$$

determining the step of the scalar potential $C_{TF}$.

V. NUMERICAL VALUES

The sixth order equation \((40)\) can be numerically solved. For small applied electric fields the linear expansion

$$
C_{TF} = C_{TF0} + \zeta E_a \tag{41}
$$

is applicable and for lead at temperature $t=0.9$ we get the numerical solution

$$
C_{TF} = 0.457 - 0.53 E_a. \tag{42}
$$

The numerical estimate for the tunneling length follows to be from \((35)\) $\lambda_W = 3.17 \lambda_{TF}$ and the work function according to \((36)\) $\varphi_W = 1.43$ eV. Taking into account how many simplifications we have used, it is surprising that the obtained results seem to be quite reasonable. The estimated magnitude of the work function is comparable with the experimentally determined value of $\varphi_W = 4.25$ eV.\(^8\)

The sharp step of the scalar potential can be estimated from the modified Budd-Vannimenus theorem\(^4\) according to which

$$
\epsilon (\varphi_\infty - \varphi_0) = \left( \frac{\partial f_{el}}{\partial n} - \frac{f_{el}}{n} \right), \tag{43}
$$

Here $f_{el}$ denotes the spatial density of the electronic free energy, which can be roughly approximated by the Thomas-Fermi internal energy $f_{TF}$ defined in \((2)\). Then the Budd-Vannimenus theorem \((43)\) predicts a sharp step, $C_{TF} = \frac{\varphi}{\varphi_0}$, of the scalar potential in units of $E_F/e$. The numerical solution \((42)\) gives a comparable result what strongly supports the applicability of the here used approximations.

We saw that the numerical values of the measurable quantities are reasonable. In Fig. \(1\) the scalar potential is plotted. As expected, inside the superconductor the scalar potential acquires the Fermi energy value, while in the vacuum outside it reaches the work function value $\varphi_w$. The dashed and dotted lines correspond to the experimentally accessible applied electric field $E_a = \pm 0.01 E_{TF} \approx \pm 1.7 \times 10^7$ V/cm. As it is seen in Fig. \(2\) the external electric field is screened on the Thomas-Fermi screening length. In the figure \(3\) deviations of the charge carrier densities from the equilibrium values are plotted. We can see that the magnitudes of these deviations are small. Close to the surface the superfluid density $n_s$ decreases and this decrease is compensated by an increase of the normal fluid density $n_n$. The total charge carrier density $n$ shows no change on the scale of the coherence length.

VI. COMPARISONS WITH DE GENNES FORMULA

Now we compare the GL boundary condition following from the minimum free energy principle with the de Gennes boundary condition\(^2\)

$$
\frac{\nabla \psi}{\psi} \bigg|_0 \frac{\nabla A}{A} \bigg|_0 = \frac{1}{b} = \frac{1}{b_0} + \frac{E_a}{U_s}. \tag{44}
$$
FIG. 2: Charge density ρ. To make the screening visible, the dashed and dotted lines correspond to the applied electric field $E_a = \pm 0.3$.

FIG. 3: Deviations of charge carrier densities. To ensure visibility, the dashed and dotted lines correspond to the applied field $E_a = \pm 0.1$.

determined by which the derivative of the gap at the surface is not exactly zero even without external electric field. The zero field extrapolation length $b_0$ is around 1 cm (almost infinity from the microscopic point of view). The effective potential $U_s$ determines how the extrapolation length $b$ changes if an external electric field $E_a$ is applied. According to the minimum free energy principle, $U_s$ gives $U_s = 1.35 \times 10^7$ V. From the minimum free energy we know, however, that the derivative at the surface should be zero. In Fig. 4 we see how the deviation of the wave function $\psi$ at the surface decreases with the derivative determined by the parameter $\zeta$. From this we get the extrapolation length $b_0 \approx 2.8$ mm, a value comparable with the one estimated by de Gennes. Only very close to the surface (on the distance of Thomas-Fermi screening length) the derivative of the wave function $\psi$ approaches zero (see insert of the Fig. 4).

In figure 4 we can also observe how the extrapolation length changes if an electric field $E_a$ is applied. By substituting $b = -\xi_0/C_\zeta$ into (44) and using (23) with the approximation (41) we get a simple expression for the effective potential $U_s$

$$
\frac{1}{U_s} = \frac{3\xi^2 T_F}{2\xi_0^2} \frac{\partial \ln T_c}{\partial \ln n} \frac{e}{E_F}.
$$

This formula is similar to the de Gennes formula (15). We should notice, however, that in this formula the extrapolation parameter $\zeta/2$ of (11) appears instead of the surface ratio $\eta$ which enters the de Gennes formula (15).

VII. CONCLUSIONS

It was shown in this paper that the minimum free energy principle entails a zero derivative of the wave function $\psi$ at the surface of the superconductor. On the scale of the coherence length, however, even if no external electric field is applied, the derivative is nonzero.
and its magnitude corresponds to the de Gennes estimate. Only on the Thomas-Fermi screening length scale it approaches zero. In the presence of an external electric field the extrapolation length changes according to equation (44), with the effective potential given by equation (47). This formula is similar to formula (45) following from the de Gennes theory. The agreement with the Budd-Vannimenus theorem and the numerical estimates support the applicability of the proposed approach.

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