Surface superconductivity controlled by electric field

Pavel Lipavský¹,², Jan Koláček², and Klaus Morawetz³,⁴

¹ Institute of Physics, Academy of Sciences, Cukrovarnická 10, 16253 Prague 6, Czech Republic kolacek@fzu.cz
² Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 12116 Prague 2, Czech Republic lipavsky@fzu.cz
³ University of Applied Science Münster, Stegerwaldstrasse 39, 48565 Steinfurt, Germany morawetz@fh-muenster.de
⁴ International Center for Condensed Matter Physics, Universidade de Brasília, 70904-910, Brasília-DF, Brazil

Summary. We discuss an effect of the electrostatic field on superconductivity near the surface. First, we use the microscopic theory of de Gennes to show that the electric field changes the boundary condition for the Ginzburg-Landau function. Second, the effect of the electric field is evaluated in the vicinity of \( H_{c3} \), where the boundary condition plays a crucial role. We predict that the field effect on the surface superconductivity leads to a discontinuity of the magnetocapacitance. We estimate that the predicted discontinuity is accessible for nowadays experimental tools and materials. It is shown that the magnitude of this discontinuity can be used to predict the dependence of the critical temperature on the charge carrier density which can be tailored by doping.

1.1 Introduction

The surface of a superconductor is an important region in which the superconductivity nucleates and which represents a natural barrier for penetrating or escaping vortices. It is desirable to control surface properties so that the nucleation can be stimulated or suppressed. An even more attractive task is to open or shut the penetration barrier for vortices. A promising tool of the surface control is the gate voltage for which we can benefit from the extensive technological experience with field effect transistors.

Unfortunately, the interaction of the electric field applied to the metal surface with the superconducting condensate is very weak. Indeed, the superconducting condensate does not interact with the electrostatic potential as shown by Anderson [2]. The condensate feels only the indirect effects like
changes of the local density of states or eventual changes of the surface crystal structure.

It is very likely that it will become possible to enhance the field effect on the superconductivity by a proper surface treatment. To this end it would be of great advantage to understand how the field interacts with the condensate and to have reliable experimental methods directly aiming to measure the strength of this interaction.

To support the experimental effort in this direction, in this chapter we provide a phenomenological theory of Ginzburg-Landau (GL) type supplemented with the de Gennes boundary condition derived from the microscopic Bardeen, Copper, and Schrieffer (BCS) theory. It will be shown that the boundary condition captures the field effect on the condensate while the GL equation determines how the condensate responds to the field-affected boundary condition.

The field effect on the superconductivity has been measured under various conditions, nevertheless its actual strength is not yet accurately established. The most pronounced field effects are observed on thin layers, in which it is possible to increase or lower their critical temperature \([1, 7, 8, 19, 28]\). These samples are so thin that the applied field considerably changes the total density of electrons and the observed effect can be interpreted in terms of the modified bulk properties. With thicker samples one meets the problem that the potential field effect is restricted to the surface and the underlying bulk overrides its contribution.

At the end of this chapter we discuss the field effect on the surface superconductivity near the third critical magnetic field \(H_{c3}\). In this regime the bulk superconductivity is absent and the surface superconductivity crucially depends on the boundary condition. We will show that the field effect can be observed via the discontinuity in the magnetocapacitance \([20, 21]\).

### 1.2 Limit of large Thomas-Fermi screening length

To introduce the field effect on the superconductivity we start from the theory employed by Shapiro and Burlachkov \([3, 23–27]\) and by Chen and Yang \([4]\). It is justified for high-\(T_c\) superconductors in which the GL coherence length \(\xi\) is very short, while the hole density is low leading to relatively large Thomas-Fermi screening length \(\lambda_{TF}\). In these materials \(\lambda_{TF} \sim \xi\), which allows us to introduce field induced effects via local changes of the parameters of the GL theory.

Let us assume the jelly model in which the electric charge of electrons is compensated by a smooth positively charged background. Both charges are restricted to the half space \(x > 0\). The electric field applied to the surface is exponentially screened \(E(x) = E e^{-x/\lambda_{TF}}\) inside the metal. According to the Gauss equation \(\epsilon \text{div} E = \rho\), the induced electron density \(\delta n = \rho/e\) reads

\[
\delta n(x) = \frac{\epsilon E}{e \lambda_{TF}} e^{-x/\lambda_{TF}}.
\]  (1.1)
In the GL equation

\[
\frac{1}{2m^*} (-i\hbar \nabla - e^* A)^2 \psi + \alpha \psi + \beta |\psi|^2 \psi = 0,
\]

(1.2)

the change of the electron density leads to changes of the GL parameters \(\alpha\) and \(\beta\). According to the Gor’kov theory [9] \(\beta = \frac{6\pi^2 k_B^2 T_c}{\xi(3)E_F}\). It is thus a robust parameter in which \(\delta n\) can create relative changes of the order of \(\delta \beta/\beta \sim \delta n/n\). These changes can be neglected. The other parameter \(\alpha = \alpha'(T - T_c)\) is a difference of two large constituents. Here, \(\alpha' = \frac{6\pi^2 k_B^2 T_c}{\xi(3)E_F}\) is modified also only negligibly as \(\delta \alpha'/\alpha' \sim \delta n/n\). But, for temperatures close to the critical temperature, \(T \to T_c\), even small changes in \(T_c\) lead to large relative changes of \(\alpha\) eventually even changing its sign. The GL equation with the dominant part of the field effect thus reads

\[
\frac{1}{2m^*} (-i\hbar \nabla - e^* A)^2 \tilde{\psi} + \alpha \tilde{\psi} - \alpha' \frac{\partial T_c}{\partial n} \delta n \psi + \beta |\tilde{\psi}|^2 \tilde{\psi} = 0.
\]

(1.3)

We have denoted the field affected GL function as \(\tilde{\psi}\). Initially we shall use the customary GL condition \(\frac{\partial}{\partial x} \tilde{\psi} = 0\) for this equation.

Let us assume now that this theory holds also for conventional superconductors where one always finds a sharp inequality \(\lambda_{TF} \ll \xi\). Below we confirm the result obtained with this unjustified assumption by using the well justified microscopic approach of de Gennes.

We split the GL function according to \(\tilde{\psi} = \psi + \delta \psi\), where \(\delta \psi(x) = \delta \psi e^{-x/\lambda_{TF}}\) is the part of field induced perturbation which changes on the short scale \(\lambda_{TF}\) and \(\psi\) covers the rest changing on the larger scale \(\xi\). Our aim is to establish approximative \(\delta \psi\) and to eliminate it, so that in the second step we will be left with the GL equation for the slowly varying function \(\psi\).

The short scale component has an enormously large space gradient which dominates its contribution to the GL equation,

\[
-\frac{\hbar^2}{2m^*} \nabla^2 \delta \psi(x) - \alpha' \frac{\partial T_c}{\partial n} \delta n \psi(x) \approx 0.
\]

(1.4)

Since in this approximation the function \(\delta \psi\) is nonzero only in the narrow layer \(x \sim \lambda_{TF}\), we can neglect the space dependence of \(\psi\) and use its surface value. Performing derivatives one finds

\[
\delta \psi = -\frac{2m^* \lambda_{TF}^2}{\hbar^2} \alpha' \frac{\partial T_c}{\partial n} \frac{eE}{e\lambda_{TF}} \psi(0).
\]

(1.5)

Besides the very local contribution expressed by the function \(\delta \psi\), the electric field induces also a perturbation on the scale of the GL coherence length \(\xi\). Indeed, the GL boundary condition demands the zero derivative of the total function

\[
\frac{\partial}{\partial x} (\psi + \delta \psi) = 0
\]

(1.6)
and the local part has a nonzero derivative
\[ \frac{\partial}{\partial x} \delta \psi(x)|_{x=0} = -\frac{\delta \psi}{\lambda_{TF}}. \] (1.7)

From the GL boundary condition (1.6) and relations (1.5) and (1.7) one thus finds the boundary condition for \( \psi \)
\[ \frac{\partial \psi}{\partial x} \bigg|_{x=0} = \frac{2m^*}{\hbar^2} \alpha' \frac{\partial T_c}{\partial n} \epsilon E \psi(0). \] (1.8)

This relation can be interpreted as a field-affected GL boundary condition.

In usual problems handled by the GL theory one ignores the exact gap profile at the surface and focuses on its behavior deeper in the bulk on the scale \( \xi \). In the same spirit we can ignore the short scale component \( \delta \psi \) using the approximation \( \tilde{\psi} \approx \psi \). Doing so, we have to keep in mind that the short scale component leads to the field-affected boundary condition (1.8). Solving the GL equation (1.2) with the boundary condition (1.8) one obtains the GL function where the field effect manifests itself on the scale \( \xi \).

1.3 de Gennes approach to the boundary condition

The limit of large screening length does not apply to conventional superconductors. In fact, in metals the Thomas-Fermi screening is smaller than the interatomic distance and the jelly model is not justified to describe the interaction of the surface with the electric field. Naturally, the gradient correction represented by the kinetic energy of GL theory is not a sufficient approximation of the non-local part of the BCS interaction kernel.

To access short screening lengths, Shapiro and Burlachkov [3, 23–27] have employed a more sophisticated version of the GL theory in which the ‘kinetic energy’ is not a mere parabolic function of the gradient but includes all derivatives up to infinite order in a form of the di-gamma function. Since high order gradients are important only in the short scale component, the above approach can be easily modified in this way. One merely replaces the kinetic energy in (1.4) by the corresponding di-gamma expression.

Although this high order gradient correction is elegant and simple, it is likely not sufficient to cover changes on the sub-Ångström scale, i.e., on the scale typical for majority of metals. Apparently, one should employ the microscopic approach of Bogoliubov-de Gennes type pioneered by Koyama [13] and other groups [11, 15–17, 29–32]. Beside microscopic details of the gap near the surface, one has to take into account that the simple exponential decay of the charge from a sharp surface is not a very realistic model of metals, because electrons tunnel out of the metal. Realistic studies of the surface are problematic, however, even in the normal state, namely due to the nontrivial exchange-correlation interaction at the strong gradient of the electron density innate to all surfaces.
Instead of improving the above approach, it is advantageous to formulate
the boundary condition directly from the microscopic theory of de Gennes [5].
De Gennes did not assume the electric field explicitly. His result, however,
does not specify the forces forming the surface so that the applied field can
be included.

Gor’kov has shown that the BCS gap $\Delta$ and the GL function are propor-
tional to each other, $\psi = \text{const} \times \Delta$. Using an extrapolation of the BCS gap
from the bulk towards the surface, de Gennes has arrived at the boundary
condition of the form

$$\left. \frac{1}{\psi(0)} \frac{\partial \psi}{\partial x} \right|_{x=0} = \left. \frac{1}{\Delta_0} \frac{\partial \Delta}{\partial x} \right|_{x=0} = \frac{1}{b},$$

(1.9)

where $b$ is called the extrapolation length.

Within the BCS theory, the extrapolation length is given by the formula

$$\frac{1}{b} = \frac{1}{\xi^2(0) N_0 V} \int_{-\infty}^{\infty} dx \frac{\Delta(x)}{\Delta_0} \left[ 1 - \frac{N(x)}{N_0} \right],$$

(1.10)

derived by de Gennes (Eq. (7-62) in Ref. [5]). Here $N(x)$ is the local density
of states at the Fermi level and $N_0$ is its bulk limit. The notation of the gap
is different. While $\Delta(x)$ is the true local value of the BCS gap, $\Delta_0$ is the fake
surface value after all short scale components have been removed, i.e., it is
a value extrapolated from the near vicinity to the surface. Finally, $V$ is the
BCS interaction and $\xi(0)$ is the GL coherence length at ‘zero’ temperature.
In pure metals it is linked to the BCS coherence length $\xi_0$ as $\xi(0) = 0.74 \xi_0$.

De Gennes estimated a typical value of $b \sim 1$ cm at metal surfaces in
vacuum. This value is very large on the scale of the GL coherence length,
therefore this contribution is usually neglected. The approximation, $1/b \approx 0$,
corresponds to the original GL condition $\frac{\partial}{\partial x} \psi = 0$.

Our aim is to include the effect of electric fields on the extrapolation
length $b$. We denote as $b_0$ the extrapolation length in the absence of the
applied electric field and $\delta(1/b) = 1/b - 1/b_0$ reflects variation of the inverse
length. The electrostatic potential corresponding to the electric field modifies
the potential profile near the surface. It results in a change of the density of
states $\delta N(x)$. The density of states affects the gap function and creates its
deviation $\delta \Delta(x)$. In the linear approximation from (1.10) we find the change
of the inverse extrapolation length as

$$\delta \left( \frac{1}{b} \right) = \frac{1}{\xi^2(0) N_0 V} \int_{-\infty}^{\infty} dx \left\{ \frac{\delta \Delta(x)}{\Delta_0} \left[ 1 - \frac{N(x)}{N_0} \right] - \frac{\Delta(x) \delta N(x)}{\Delta_0 N_0} \right\}. \quad (1.11)$$

To estimate this change we recall the local density approximation in which
the local density of states is a function of the local density, $N(x) = N[\rho(x)]$.
Since the charge density $\delta \rho(x)$, which screens the applied electric field, spreads
over a layer of a few Ångströms near the surface, the perturbed density of state is restricted to this very narrow layer, too. We can thus neglect the $x$-dependence of $\Delta(x)$ in the second term and write

$$\delta \left( \frac{1}{b} \right) = \frac{1}{\xi^2(0) N_0 V} \left\{ \int_{-\infty}^{\infty} dx \frac{\delta \Delta(x)}{\Delta_0} \left[ 1 - \frac{N(x)}{N_0} \right] - \frac{\Delta(0) \delta N^{(2)}}{\Delta_0 N_0} \right\}, \quad (1.12)$$

where

$$\delta N^{(2)} = \int_{-\infty}^{\infty} dx \delta N(x) \quad (1.13)$$

is the total change of the density of states per area.

To estimate the second term we assume that the local density of states achieves the bulk value on the scale of a few Ångströms. Since the gap function changes on the scale of the BCS coherence length which is much larger, we can expect that in the region of non-zero function $1 - N(x)/N_0$ the gap function keeps its shape. Assuming that $\delta \Delta(x) \approx \Delta(0) \delta c$, the last $x$-integration becomes identical to the integral in the de Gennes condition (1.10) so that (1.12) simplifies to

$$\delta \left( \frac{1}{b} \right) = \frac{\delta c}{b} - \frac{1}{\xi^2(0) N_0 V} \frac{\Delta(0) \delta N^{(2)}}{\Delta_0 N_0}. \quad (1.14)$$

The relative change of the gap $\delta c$ can be estimated from the GL theory. The GL function obtained with the boundary condition of a large but finite extrapolation length $b$ can be written as a sum of the constant bulk term $\psi_\infty = \sqrt{-\alpha/\beta}$ and a small perturbation $\psi'$, i.e. $\psi = \psi_\infty + \psi'$. For the moment we ignore the magnetic field and assume a real GL function so that the GL equation reads $\xi^2 \nabla^2 \psi - \psi + \psi^3/\psi_\infty^2 = 0$. Since $\psi'$ is proportional to $1/b$, we keep its linear terms only, $\xi^2 \nabla^2 \psi' + 2\psi' = 0$. This equation has the exponential solution $\psi'(x) = -\psi_\infty e^{-\sqrt{2}x/\xi}/(\sqrt{2}b)$. Since the GL coherence length $\xi$ is much smaller than the extrapolation length $b$, the exponential is small compared to the constant term. Assuming that the GL function provides us with the order of magnitude estimate of the gap function, we find that $\delta c = \delta \Delta(0)/\Delta_0 \approx \delta \psi(0)/\psi_0 = - (\xi/\sqrt{2}) \delta (1/b)$. After substitution of this estimate into Eq. (1.14) we obtain

$$\delta \left( \frac{1}{b} \right) = - \frac{1}{1 + \frac{\xi}{\sqrt{2}b}} \frac{\Delta(0)}{\Delta_0} \frac{1}{\xi^2(0) N_0 V} \frac{1}{N_0} \frac{\delta N^{(2)}}{N_0}. \quad (1.15)$$

We can assume, that the induced density of states per area is linearly proportional to the applied electric field,

$$\delta N^{(2)} = E g \quad (1.16)$$
so that the modified inverse length is of the form
\[ \delta \left( \frac{1}{b} \right) = \frac{E}{U_s}, \]  
(1.17)
where \( U_s \) has a dimension of a potential. According to (1.15) this effective potential is given by
\[ \frac{1}{U_s} = -\eta \xi^2(0) \frac{1}{N_0} \frac{g}{V N_0}. \]  
(1.18)
We have introduced a dimensionless parameter
\[ \eta = \frac{1}{1 + \sqrt{2} b \Delta(0) \Delta_0}, \]  
(1.19)
which captures the effects of the gap profile near the surface. According to de Gennes’ estimate [5], the surface ratio \( \eta \) is of the order of unity.

Let us note, that a boundary condition similar to the de Gennes boundary condition described above can be derived also from the minimum free energy principle [12].

1.4 Link to the limit of large screening length

To draw a link between the de Gennes-type formula (1.18) and the field-affected GL boundary condition (1.8) obtained in the limit of large Thomas-Fermi screening lengths, we evaluate the coefficients of the de Gennes formula in the jelly model. As above we assume that in the absence of the electric field the extrapolation length diverges, \( 1/b_0 = 0 \).

For zero electric field the density of states is step-like, \( N(x) = N_0 \) for \( x > 0 \) and \( N(x) = 0 \) elsewhere. Now we include the electric field. It is exponentially screened due to the induced electron density given by (1.1). We employ the local density approximation and assume that the local density of states is a function of the local density of electrons
\[ N(x) = N_0 + \frac{\partial N_0}{\partial n} \delta n(x). \]  
(1.20)
This approximation yields a simple change of the density of states per area
\[ \delta N^{(2)} = \frac{\partial N_0}{\partial n} \int_0^\infty dx \delta n(x). \]  
(1.21)
The induced density of electrons per area is given by the Gauss law
\[ \epsilon E = -e \int_0^\infty dx \delta n(x). \]  
(1.22)
From relations (1.16), (1.21) and (1.22) we find the coefficient of the density of states
\[ g = -\frac{\partial N_0}{\partial n} \epsilon. \] (1.23)

To be able to compare the BCS formula with the de Gennes-type one, we have to express both expressions in terms of the same parameters. We thus convert the parameters of de Gennes-type formula to their phenomenological counterparts.

The GL coherence length \( \xi = \frac{\hbar}{\sqrt{-2m^*\alpha}} \) depends on the temperature according to \( \xi = \xi(0)/\sqrt{1 - T/T_c} \), where \( \xi(0) \) is the ‘zero’ temperature value. From \( \alpha = \alpha'(T - T_c) \) one finds
\[ \frac{1}{\xi^2(0)} = \frac{2m^*\alpha'T_c}{\hbar^2}. \] (1.24)

Finally, we have to express the BCS interaction potential \( V \) in terms of the critical temperature. In the BCS critical temperature
\[ T_c = 0.85 \Theta_D e^{-\frac{1}{\Theta_D}} \] (1.25)
we assume that the Debye temperature \( \Theta_D \) and the BCS interaction \( V \) are independent of the electron density. This corresponds to approximations we have tacitly used above ignoring the electric field effect on the phonon spectrum. The density dependence of the critical temperature follows thus from the density dependence of the density of states
\[ \frac{\partial T_c}{\partial n} = 0.85 \Theta_D e^{-\frac{1}{\Theta_D}} \frac{1}{N_0^2V} \frac{\partial N_0}{\partial n} = T_c \frac{1}{N_0^2V} \frac{\partial N_0}{\partial n}. \] (1.26)

We will use this relation to express density derivatives of the density of states in terms of the density derivative of the critical temperature.

Now we can rewrite the effective potential in terms of phenomenological parameters. Using \( \xi(0) \) from (1.24) in equation (1.18) we find
\[ \frac{1}{U_s} = -\eta \frac{2m^*\alpha'}{\hbar^2} T_c \frac{1}{N_0^2V} g. \] (1.27)
Next we substitute \( g \) from (1.23)
\[ \frac{1}{U_s} = \eta \frac{2m^*\alpha'}{\hbar^2} T_c \frac{1}{N_0^2V} \frac{\partial N_0}{\partial n} \epsilon. \] (1.28)

The group of terms around \( \partial N_0/\partial n \) can be substituted with the help of (1.26) so that we obtain
\[ \frac{1}{U_s} = \eta \frac{2m^*\alpha'}{\hbar^2} \frac{\partial T_c}{\partial n} \epsilon. \] (1.29)

The boundary condition we have obtained now from the de Gennes-type formula
Surface superconductivity controlled by electric field

\[ \frac{\partial \psi}{\partial x} \bigg|_{x=0} = \frac{E}{U_s} \psi(0) = \eta \frac{2m^* \alpha'}{\hbar^2} \frac{\partial T_c}{\partial n} \frac{e E}{e} \psi(0) \]  

(1.30)

differs from the large screening length limit (1.8) by the factor \( \eta \). Of course, a heuristic derivation of the field-effect from the GL equation cannot cover the factor \( \eta \) which depends on the gap profile on a scale smaller than the GL coherence length.

In summary, the electric field applied to the surface of the superconductor modifies the GL wave function near the surface. This effect is conveniently described by the GL theory, where the GL equation remains unaffected by the field and the entire electric field effect is covered by a modified boundary condition. In the next section we discuss an experiment which can be used to measure the predicted field effect on the GL boundary condition.

1.5 Electric field effect on surface superconductivity

We will investigate now the magneto-capacitance for magnetic fields near the surface critical field \( B_{c3} \). We focus on this region since we expect that the bias voltage affecting only the surface has a relatively large effect on the surface superconductivity. In this section we show how the electric field affects the nucleation of superconductivity [20].

1.5.1 Nucleation of surface superconductivity

At the surface critical field \( B_{c3} \) the superconductivity nucleates in the surface region. At the nucleation point the GL wave function \( \psi \) is infinitely small, therefore we can work with the linearized GL equation, omitting the cubic term in the equation (1.2)

\[ \frac{1}{2m^*} (-i\hbar \nabla - e^* A)^2 \psi + \alpha \psi = 0. \]  

(1.31)

The solution is restricted by the boundary condition (1.9).

The electrode is a superconductor which fills the half space \( x > 0 \). We assume a homogeneous applied magnetic field \( B_a = (0, 0, B_a) \). Since an ‘infinitely’ large electrode has translation invariance along the \( y \) direction, we use the Landau gauge of the form

\[ A = (0, B_a x, 0). \]  

(1.32)

Nucleation is possible if (1.31) has a nonzero solution, i.e. if the parameter \(-\alpha\) becomes equal to an eigenvalue \( \varepsilon \) of the kinetic energy given by \[ \frac{1}{2m^*} (-i\hbar \nabla - e^* A)^2 \psi = \varepsilon \psi. \] Since \( \alpha \) changes with temperature, \( \alpha = \alpha'(T - T_c) \), the eigenvalue \( \varepsilon \) of the kinetic energy determines the nucleation temperature \( T^* \) according to \[ T^* - T_c = -\varepsilon/\alpha'. \] To avoid dual notation for
the same quantity, we will treat the equation as an eigenvalue for $\alpha$. Since $\alpha$ is negative, the nucleation temperature $T^*$ is always below the critical temperature $T_c$ in the absence of the magnetic field. Note that we are looking for maximal $\alpha$.

Assuming the translation invariance along the $y$ and $z$ axes we can write the wave function as

$$\psi(x, y, z) = \psi(x) e^{iky} e^{iqz}. \quad (1.33)$$

Using (1.33) in the GL equation (1.31) we get a one-dimensional equation

$$\frac{\hbar^2}{2m^*} \left( -\left( \frac{\partial}{\partial x} \right)^2 + \left( k - \frac{e^* B_a}{\hbar} x \right)^2 + q^2 \right) \psi + \alpha \psi = 0. \quad (1.34)$$

Any non-zero value of $q$ results in the kinetic energy $q^2\hbar^2/2m$ which lowers the value of $\alpha$ reducing the nucleation temperature. The nucleation happens at the first possible occasion, i.e., at the highest allowed temperature. We thus take $q = 0$. Similarly, we have to find the wave vector $k$ from the requirement of the highest nucleation temperature.

### 1.5.2 Solution in dimensionless notation

It is advantageous to express the $x$-coordinate with the help of the dimensionless coordinate $\tau$

$$x = \tau l + 2l^2 k, \quad (1.35)$$

with the magnetic length

$$l^2 = \frac{\hbar}{2e^* B_a} \quad (1.36)$$

and the momentum $\tau_0 = -2kl$. The wave function is then proportional to the parabolic cylinder function of Whittaker [18]

$$\psi(x) = N D_{\nu} \left( \frac{x}{l} + \tau_0 \right), \quad (1.37)$$

which solves the differential equation (1.31) in the dimensionless notation

$$\frac{d^2 D_{\nu}(\tau)}{d\tau^2} = \left( \frac{\tau^2}{4} - \nu - \frac{1}{2} \right) D_{\nu}(\tau). \quad (1.38)$$

The dimensionless boundary condition is

$$\frac{D'_{\nu}(\tau_0)}{D_{\nu}(\tau_0)} \bigg|_{\tau_0 = -2kl} = \frac{\xi}{b} \sqrt{\nu + \frac{1}{2}}, \quad (1.39)$$

where the prime denotes a derivative with respect to $\tau_0$. The parameter

$$\nu = -\frac{1}{2} - \frac{\alpha m^*}{e^* \hbar B_a} \quad (1.40)$$
plays the role of an eigenenergy.

The boundary condition (1.39) links \( \nu \) and \( \tau_0 \). Since we are looking for the minimal \( \nu \), we take the solution of (1.39) as a function \( \nu(\tau_0) \). Besides the obvious numerical search we can give directly a nonlinear equation for this desired minimum given by \( \nu'(\tau_0) = 0 \). For this purpose we differentiate (1.39) with respect to \( \tau_0 \) arriving at

\[
\left. \frac{D_{\nu+1}(\tau_0)}{D_\nu(\tau_0)} \right|_{\tau_0 = -2\sqrt{(\tilde{\nu} + \frac{1}{2})(1 + \frac{\xi^2}{b^2})}} = -\sqrt{\left( \tilde{\nu} + \frac{1}{2} \right) \left( 1 + \frac{\xi^2}{b^2} \right)} - \frac{\xi}{b} \sqrt{\tilde{\nu} + \frac{1}{2}}.
\]

(1.41)

where \( \tilde{\nu} \) is the minimal value of \( \nu \).

Solving equation (1.41) we find the minimal \( \nu \) to each given \( \tau_0 \), i.e., \( \tilde{\nu}[\tau_0] \).

Since \( \tau_0 = -2kl \), we find in this way the eigenenergy as a function of momentum \( k \). The GL wave function (1.37) is now specified except for its amplitude \( \mathcal{N} \). We discuss this amplitude below. In figure 1.1 we see how the shape of the GL wave function evolves with inverse extrapolation length \( 1/b \), i.e. how it depends on the external bias. For positive electric fields attracting charge carriers to the surface, the superconducting density is pushed from the surface into the bulk while for oppositely directed electric fields the superconductivity is even more squeezed near the surface.

The lowest eigenvalue \( \tilde{\nu} \) corresponds to the highest attainable critical magnetic field

\[
B_{c3} = \frac{-m^* \tilde{\alpha}}{\hbar e*(\tilde{\nu} + \frac{1}{2})} \equiv \frac{B_{c2}}{2\tilde{\nu} + 1},
\]

(1.42)

where \( B_{c2} \) is the upper critical field. In figure 1.2 we present the result for the surface critical field (1.42) versus the external bias. Without external bias the known GL solution [22] with \( B_{c3}/B_{c2} = 1.69461 \) is reproduced. We see that the external bias can enhance or decrease the surface critical value.

According to the GL wave function (1.33), the current flows only in the \( y \) direction. Its net value given by the \( x \) integral of the current density equals the \( k \) derivative of the eigenenergy. Thus, for the minimal \( \nu \) the net current
is zero. Current distributions for three different boundary conditions with extrapolation lengths $\xi/b = 0, +1$ and -1 are plotted in the fig. (1.3) as bold, dashed and dash dot lines. Since there is no net current circulating around the sample, as is seen in the inset of the fig. (1.3), the magnetic field is reduced only in the region of nucleation. Each surface thus acts independently.

1.5.3 Surface energy

With the help of the GL wave function we can now calculate the surface energy

$$\sigma = \int_0^\infty dx \left[ \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{[B_0 - B(x)]^2}{2\mu_0} + \frac{[i\hbar \nabla + e^* A] \psi|^2}{2m^*} \right]. \quad (1.43)$$

Here we neglect the free energy of the magnetic field, but the term $\sim |\psi|^4$ which determines the amplitude of the GL wave function cannot be omitted even near the nucleation line.

Since the applied field changes the shape of the GL wave function only weakly while its amplitude changes rapidly near the critical point, we fix the shape to be the nucleation function (1.37) and use the amplitude $N$ as a variational parameter. Briefly we substitute $\psi = ND_\nu$ into (1.43) which gives

$$\sigma = (\alpha - \tilde{\alpha}) N^2 I_2 + \frac{1}{2} \beta N^4 I_4, \quad (1.44)$$

where $\tilde{\alpha} = -(\hbar e^* B/2m^*) (2\tilde{\nu}(E,B) + 1)$ is the maximal eigenvalue corresponding to the nucleation temperature under given magnetic and electric
Fig. 1.2. The surface critical field $B_{c3}$ versus extrapolation length. The exact solution (1.42) is the solid line and its slope at $\xi/b = 0$ is shown by the dotted line. The inset shows the ratio of integrals (1.45) and (1.46).

field, while $\alpha = \alpha'(T - T_c)$ is the GL parameter given by the actual sample temperature. The quadratic and quartic terms in (1.44) are weighted by dimensionless integrals

$$I_2 = \int_{\tau_0}^{\infty} d\tau D_2^2(\tau), \quad (1.45)$$

$$I_4 = \int_{\tau_0}^{\infty} d\tau D_4^4(\tau). \quad (1.46)$$

In the normal state, $\alpha > \tilde{\alpha}$ and the minimum of the surface energy is $\mathcal{N}^2 = 0$ giving $\sigma = 0$. In the superconducting state $\alpha < \tilde{\alpha}$ and the minimum of $\sigma$ (1.44) is at $\mathcal{N}^2 = -(\alpha - \tilde{\alpha})I_2/(\beta I_4)$ giving the surface energy

$$\sigma = -\frac{I_2^2 (\alpha - \tilde{\alpha})^2}{2\beta}. \quad (1.47)$$

At the critical point $\alpha = \tilde{\alpha}$ and the surface energy vanishes. The surface energy and its first derivatives with respect to the electric and magnetic field are continuous at the critical point. The second derivatives are discontinuous.
Fig. 1.3. Distribution of the current density for boundary conditions with extrapolation lengths $\xi/a = 0, +1$ and $-1$ are plotted in bold, dashed and dash dot lines. The inset shows the corresponding reduction of magnetic field.

In the next chapter we show how this discontinuity appears in the magneto-capacitance.

1.6 Magneto-capacitance

We assume a capacitor in which the first electrode is a superconducting and the second electrode is a normal metal. Our aim is to evaluate the contribution of the surface superconductivity to the capacitance.

The capacitance of the capacitor with one superconducting electrode reads

$$\frac{1}{C_s} = \frac{1}{C_n} + \frac{1}{\epsilon^2 S \partial E^2},$$  \hspace{1cm} (1.48)

where $S$ is the area of the capacitor, $C_n$ is the capacitance when both electrodes are normal, $\epsilon$ is the permittivity of the ionic background in the superconductor. This follows from the inverse capacitance given by the second derivative of the total energy $W$ with respect to the charge $Q$, $1/C = \partial^2 W/\partial Q^2$. The charge $Q$ is linked to the electric field $E$ at the surface of the superconductor via the Gauss law $\epsilon E = Q/S$. Since energies of normal and superconducting states differ by the surface energy $W_s = W_n + S\sigma$, one arrives at equation (1.48) for the difference in capacitances.
1.6.1 Discontinuity in magneto-capacitance

Now we can evaluate the jump of the capacitance, which appears as the magnetic field $B$ exceeds the critical value $B_{c3}$. Since $\alpha_E \to \alpha$ for $B \to B_{c3}$, the discontinuity of the inverse capacitance equals

$$\frac{1}{C_s} - \frac{1}{C_n} = -\frac{\hbar^2 e^2 B_{c3}^2 I_2^2}{c^2 m^* S \beta I_4} \left( \frac{\partial \tilde{\nu}}{\partial E} \right)^2,$$

(1.49)

where we have used $\partial \alpha_E / \partial E = -(\hbar e^* B/m^*)(\partial \tilde{\nu} / \partial E)$.

To evaluate the slope $\partial \tilde{\nu} / \partial E$ we recall the numerical result shown Fig. 1.2. The tangential dotted line yields $B_{c3}/B_{c2} = 1/(2\tilde{\nu} + 1) = 1.69 - 1.69\xi/b$ which follows also from an explicit variational calculation, see Eq. 20 in [20]. Since $\partial(1/b)/\partial E = 1/U_n$, for $1/b \to 0$ we find $(\partial \tilde{\nu} / \partial E)^2 = 0.087 \xi^2 / U_n^2$. From relation (1.29) thus follows

$$\left( \frac{\partial \tilde{\nu}}{\partial E} \right)^2 = 0.087 \frac{4m^* e^2}{\hbar^2 (e^*)^2} \xi^2 \beta \eta^2 \left( \frac{\partial \ln T_c}{\partial \ln n} \right)^2.$$

(1.50)

We have used the relation $\beta = \alpha' T_c / n$ which holds for Gor’kov values of GL parameters. Substituting (1.50) into (1.49) we arrive at

$$\frac{1}{C_s} - \frac{1}{C_n} = -0.348 \frac{I_2^2}{I_4} \frac{B_{c3}^2}{\hbar^2 S \xi^2 \beta \eta^2} \left( \frac{\partial \ln T_c}{\partial \ln n} \right)^2.$$

(1.51)

The GL coherence length $\xi = \hbar / \sqrt{2m^* \alpha}$ relates to the surface critical field, see (1.42). For $1/b \to 0$ it yields $\xi^2 = 1.69\hbar/(e^* B_{c3})$. Moreover, according to (1.36) we can express $B_{c3}$ via the magnetic length, therefore

$$\frac{1}{C_s} - \frac{1}{C_n} = -0.712 \frac{1}{(e^*)^2 S I} \beta \eta^2 \left( \frac{\partial \ln T_c}{\partial \ln n} \right)^2.$$

(1.52)

We have used $I_2^2/I_4 = 2.42$, which is the value at $1/b = 0$.

Since the GL parameter $\beta$ can be fitted from experimental results, relation (1.52) allows one to establish $\eta (\partial \ln T_c / \partial \ln n)$. This material parameter describes the change of the critical temperature with the electron density.

1.6.2 Estimates of magnitude

For an estimate we assume some typical numbers. The most sensitive measurements of capacitance performed in the $C \sim \mu F$ range are capable to monitor changes $\delta C/C \sim 10^{-6}$ with error bars at $\delta C/C \sim 10^{-7}$. From the capacitance $C = \epsilon_d S/L$ one sees that a 1000Å-thick dielectric layer with $\epsilon_d = 10^3 \epsilon_0$ has an optimal area of $S = 10 \text{ mm}^2$ which is about the usual size of such samples [10].

To estimate $\beta$ we use Gor’kov’s relation $\beta = 6\pi^2 k_B T_c^2 / (7\zeta(3)E_F n)$. For Niobium $T_c = 9.5 \text{ K}$ and $n = 2.2 \times 10^{28} / \text{m}^3$. The free electron model used by
Gor’kov than gives the Fermi energy $E_F = 4.6 \times 10^{-19}$ J. The corresponding GL parameters then is $\beta = 1.2 \times 10^{-53}$ Jm$^3$. The logarithmic derivative is estimated in [14] as $\partial \ln T_c/\partial \ln n = 0.74$. Since $\eta$ is not known, we take $\eta = 1$ according to the simple theory. Finally we need the third critical magnetic field $B_{c3}$ to estimate the magnetic length $l$. From $B_{c3} = 1.69 B_{c2}$ and the experimental value $B_{c2} = 0.35$ T [6] one finds $B_{c3} = 0.59$ T, which yields $l = 325 \, \text{Å}$. With these values from equation (1.52) we obtain the discontinuity $1/C_s - 1/C_n = -2.8 \times 10^{-4}$ F$^{-1}$. Since the capacitance was estimated to be $\sim 10^{-6}$ F, the corresponding relative change $C_s/C_n - 1 \sim 3 \times 10^{-10}$ is too small to be observed. A slightly more optimistic estimation can be found in Ref. [21].

In high-$T_c$ materials the GL parameter $\beta$ is by three to four orders of magnitude larger than in conventional metals due to larger $T_c$ and lower density of holes giving also lower Fermi energy. Moreover, the logarithmic derivative of the critical temperature is about $\partial \ln T_c/\partial \ln n = -4.82$ as estimated in Ref. [14]. Finally, higher critical surface magnetic field $B_{c3}$ allows to reduce the magnetic length to values limited rather by experimental facility. For a typical field of 10 T the magnetic length is 79 Å. These factors together provide an enhancement to values $1/C_s - 1/C_n = -52$ F$^{-1}$ or $C_s/C_n - 1 \sim 5 \times 10^{-5}$ which is an experimentally accessible discontinuity.

1.7 Summary

We have shown that the electric field applied to the surface of the superconductor modifies the boundary condition of the GL wave function. Since the surface superconductivity is sensitive to this boundary condition, we have discussed the influence of the electric field. From the surface energy we predict that a planar capacitor with one normal electrode and the other electrode to be superconducting reveals a discontinuity of the capacitance at the third critical field $B_{c3}$. This discontinuity is too small for capacitors from conventional superconductors but it is large enough to be observed in capacitors with ferroelectric dielectric layers of a width of 1000 Å and non-conventional superconductor electrodes.

References

1. C. H. Ahn, J. M. Triscone, and J. Mannhart. Nature, 424:1015, 2003.
2. P. W. Anderson. J. Phys. Chem. Solids, 11:26, 1959.
3. L. Burlachkov, I. B. Khalfin, and B. Ya. Shapiro. Phys. Rev. B, 48:1156, 1993.
4. J. L. Chen and T. J. Yang. Physica C, 231:91, 1994.
5. P. G. de Gennes. Superconductivity of Metals and Alloys. Benjamin, New York, 1966.
6. D. K. Finnemore, T. F. Stromberg, and C. A. Swenson. Phys. Rev., 149:231, 1966.
7. T. Frey, J. Mannhart, J. G. Bednorz, and E. J. Williams. *Phys. Rev. B*, 51:3257, 1995.
8. R. E. Glover and M. D. Sherrill. *Phys. Rev. Lett.*, 5:248, 1960.
9. L. P. Gor’kov. Zh. Ekspert. Teor. Fiz., 36:1918, 1959. [Sov. Phys. JETP 9, 1364 (1959)].
10. Ch. S. Hwang. *J. Appl. Phys.*, 92:432, 2002.
11. X.-Y. Jin and Z.-Z. Gan. *European Phys. J. B*, 37(4):489, 2004.
12. J. Koláˇcek, P. Lipavský, K. Morawetz, and E. H. Brandt. *Phys. Rev. B*, 79:174510, 2009.
13. T. Koyama. *J. Phys. Soc. Jpn.*, 70:2102, 2001.
14. P. Lipavský, J. Koláˇcek, K. Morawetz, E. H. Brandt, and T. J. Yang. *Bernoulli potential in superconductors*. Springer, Berlin, 2007. Lecture Notes in Physics 733.
15. M. Machida and T. Koyama. *Physica C*, 378-381(Part 1):443, 2002.
16. M. Machida and T. Koyama. *Phys. Rev. Lett.*, 90:077003, 2003.
17. M. Machida and T. Koyama. *Physica C*, 388-389:659, 2003.
18. W. Magnus, F. Oberhettinger, and R. P. Soni. *Formulas and theorems of the special functions of modern physics*. Springer, Berlin, 1966.
19. D. Matthey, S. Gariglio, and J. M. Triscone. *Appl. Phys. Lett.*, 83:3758, 2003.
20. K. Morawetz, P. Lipavský, J. Koláˇcek, and E. H. Brandt. *Phys. Rev. B*, 78:054525, 2008.
21. K. Morawetz, P. Lipavský, and J. J. Mares. *New J. of Phys.*, 11:023032, 2008.
22. D. Saint-James and P. G.de Gennes. *Phys. Lett.*, 7:306, 1963.
23. B. Ya. Shapiro. *Phys. Lett.*, 105A:374, 1984.
24. B. Ya. Shapiro. *Solid State Commun.*, 53:673, 1985.
25. B. Ya. Shapiro. *Phys. Rev. B*, 48:16722, 1993.
26. B. Ya. Shapiro and I. B. Khalfin. *Physica C*, 209-99, 1993.
27. B. Ya. Shapiro, I. B. Khalfin, and L. Burlachkov. *Physica B*, 194:1893, 1994.
28. X. X. Xi, C. Doughty, A. Walkenhorst, C. Kwon, Q. Li, and T. Venkatesan. *Phys. Rev. Lett.*, 68:1240, 1992.
29. G.-Q. Zha, S.-P. Zhou, B.-H. Zhu, and Y.-M. Shi. *Phys. Rev. B*, 73:104508, 2006.
30. B.-H. Zhu, S.-P. Zhou, Y.-M. Shi, G.-Q. Zha, and K. Yang. *Phys. Rev. B*, 74:014501, 2006.
31. B.-H. Zhu, S.-P. Zhou, Y.-M. Shi, G.-Q. Zha, and K. Yang. *Phys. Lett. A*, 355(3):237, 2006.
32. B.-H. Zhu, S.-P. Zhou, G.-Q. Zha, and K. Yang. *Phys. Lett. A*, 338(3-5):420, 2005.