

Bernoulli potential in type-I and weak type-II superconductors: II. Surface dipoleP. Lipavský,^{1,2} K. Morawetz,^{3,4} J. Koláček,¹ J. J. Mareš,¹ E. H. Brandt,⁵ and M. Schreiber³¹*Institute of Physics, Academy of Sciences, Cukrovarnická 10, 16253 Prague 6, Czech Republic*²*Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 12116 Prague 2, Czech Republic*³*Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany*⁴*Max-Planck-Institute for the Physics of Complex Systems, Noethnitzer Str. 38, 01187 Dresden, Germany*⁵*Max-Planck-Institute for Metal Research, D-70506 Stuttgart, Germany*

(Received 10 September 2003; revised manuscript received 30 January 2004; published 28 September 2004)

The Budd-Vannimenus theorem is modified to apply to superconductors in the Meissner state. The obtained identity links the surface value of the electrostatic potential to the density of free energy at the surface which allows one to evaluate the electrostatic potential observed via the capacitive pickup without the explicit solution of the charge profile.

DOI: 10.1103/PhysRevB.70.104518

PACS number(s): 74.25.Bt, 73.30.+y, 74.25.Nf, 74.25.Op

I. INTRODUCTION

The Hall voltage is commonly used to measure the concentration of charge carriers in conductors. In superconductors this method is not applied, because of a missing theoretical support. In this paper we show that the Bernoulli potential, which is closely related to the Hall voltage, can be used to the same end in superconductors.

Any ideal collisionless electric fluid should exhibit a finite Hall voltage, but superconductors seem to escape this theoretical conclusion. The zero Hall voltage was reported the first time by Kamerlingh Onnes and Hof¹ already in 1914. Though later analyses showed that their samples were in the mixed state which obscures an interpretation of their experiment, the zero Hall voltage was confirmed anyway.²

From a theoretical point of view, it was clear that there has to be a voltage balancing the magnetic pressure which acts on electrons via the Lorentz force. The report of Kamerlingh Onnes and Hof thus stimulated various speculations about the missing Hall voltage, see the critical review by Lewis.³ From various concepts proposed we mention the so-called contact potential—a potential step at the interface—which was expected to cancel the Hall voltage. Such a potential step might exist only if a charge dipole is formed at the interface of a superconductor. The surface dipole we discuss here is a similar concept.

The explanation of the zero Hall voltage turned out to be very simple. By contacts one monitors the differences in the Gibbs chemical potential, often called the electrochemical potential.⁴ The Gibbs potential is composed of three components: the electrostatic potential, the kinetic energy, and the correlation energy. None of these components is constant in the presence of diamagnetic currents, but their sum is constant in equilibrium in agreement with the observed zero Hall voltage.

To eliminate the kinetic and correlation energies, Hunt proposed to access the electrostatic potential with a contactless method called the Kelvin capacitive pickup.⁴ Capacitive measurements appeared soon and they successfully proved the existence of a nonzero electrostatic potential.^{5,6}

Both experiments^{5,6} were done at temperatures well below T_c , where the electrostatic potential has a simple form resembling the Bernoulli law⁷⁻⁹

$$e\varphi = -\frac{1}{2}mv^2, \quad (1)$$

where e is the elementary charge, positive for holes and negative for electrons. To avoid confusion we note that the electrostatic potential in equilibrium superconductors is called the Bernoulli potential for brevity, even if its actual form does not coincide with the Bernoulli law.

None of the early experimental data were sufficiently accurate to allow for a discussion of possible corrections to the plain Bernoulli potential (1). Nevertheless, the authors^{5,6} made some conclusions in this direction and we find it necessary to comment on them in more detail.

A. Bok and Klein

Bok and Klein⁵ claimed that their data agree with the plain Bernoulli potential (1). This conclusion has to be taken with reservations, however, because they measured the electrostatic potential as a function of the magnetic field B at the surface. They evaluated the velocity \mathbf{v} of the superconducting electrons (briefly called the condensate velocity) from the London condition $m\mathbf{v} = e\mathbf{A}$ and the exponential decay $\mathbf{A} = \mathbf{A}_0 e^{-x/\lambda_0}$, using $\mathbf{B} = \nabla \times \mathbf{A}$. At low temperatures, the London penetration depth depends on the density n of pairable electrons $\lambda_0^2 = m/(e^2\mu_0 n)$, therefore their experimental result can be expressed in terms of the magnetic pressure, $en\varphi = -B^2/(2\mu_0)$.

According to the above arguments, the relation of the electrostatic potential to the magnetic pressure seems to be a consequence of the plain Bernoulli potential and the London theory. As we show below, the relation to the magnetic pressure is very general and holds also under conditions when neither the plain Bernoulli potential nor the London theory applies.

In fact, Bok and Klein measured on indium which, being a type-I superconductor, is not fully covered by the London theory. Moreover, they swept the magnetic field from zero to the critical value, while the plain Bernoulli potential and the simple form of the London theory used above are restricted to low magnetic fields. At high fields, the condensate density

at the surface is suppressed what results in v^4 and higher-order contributions to the electrostatic potential.

Briefly, Bok and Klein have observed the magnetic pressure. But the link of their experiment to the Bernoulli potential (1) has to be taken with caution.

B. Brown and Morris

Brown and Morris have used a different setup which allowed them to achieve a much higher precision.⁶ They did not control the magnetic field but the current in a thin wire. This current was scaled with the critical current. They announced in 1968 that their data reveal about 20% deviations from the screened Bernoulli potential

$$e\varphi = -\frac{n_s}{n} \frac{1}{2} m v^2, \quad (2)$$

discussed in more detail below.

It should be noted that Brown and Morris expected deviations which were predicted from the BCS theory in the same year. Adkins and Waldrum had studied the electrostatic potential from changes of the BCS gap due to a current and they recovered the plain Bernoulli potential for zero temperature, while for finite temperatures they indicated a presence of additional contributions.⁹ They were not, however, capable to derive these contributions in an explicit form or to estimate their amplitudes.

Some corrections to the Bernoulli potential (1) were derived already before the BCS studies. Historically, the first example is the theory of Sorokin¹⁰ from 1949 which covers the majority of effects recovered later. Although this paper is mentioned by London,⁸ later it became forgotten. In 1964 van Vijfeijken and Staas¹¹ took into account that the electrostatic field acts on normal electrons and arrived at the so-called quasiparticle screening.

The quasiparticle screening is represented by the fraction of superconducting electrons n_s/n by which Eq. (2) differs from the simple Bernoulli law ((1)). In the experiment of Brown and Morris it accounts for 6% of the observed potential. In spite of its small magnitude, the quasiparticle screening is important with respect to the concept of the magnetic pressure. At finite temperatures one has to take into account that the London penetration depth also depends on the density of condensate, $\lambda^2 = m / (e^2 \mu_0 n_s) = \lambda_0^2 n / n_s$. Combining the screened Bernoulli potential ((2)) with the condensate velocity v found from the London theory, one finds that the electrostatic potential is temperature independent, i.e., it is given by the magnetic pressure with the density n of pairable electrons. Despite this importance of the quasiparticle screening, it should be noted, however, that the quasiparticle screening is not responsible for the 20% deviations announced by Brown and Morris and discussed above.

Corrections capable to explain the observed potential were obtained by Rickayzen,¹² who showed that the electrostatic potential includes a pairing contribution

$$e\varphi = -\frac{\partial n_s}{\partial n} \frac{1}{2} m v^2 = -\frac{n_s}{n} \frac{1}{2} m v^2 - 4 \frac{n_n}{n} \frac{\partial \ln T_c}{\partial \ln n} \frac{1}{2} m v^2. \quad (3)$$

The pairing term dominates close to the critical temperature T_c , because $n_s = n(1 - t^4)$, with $t = T/T_c$, while $n_n = n - n_s = n t^4$.

According to Eq. (3), from φ close to T_c one may deduce the density dependence of T_c , which would be very attractive with respect to designing materials. Indeed, this important material property is otherwise deducible only from measurements applying a hydrostatic pressure or adding impurities to crystals. Unlike the later methods, a measurement of the Hall voltage or, respectively, the Bernoulli potential does not affect the electronic bands, the phonon spectrum or the electron-phonon interaction, therefore it offers a uniquely clear information about the material.

All expectations were chilled by the next paper of Morris and Brown.¹³ They admitted that deviations announced in the previous paper were due an incorrect estimate of the critical current and presented new highly accurate data for a wide range of temperatures. The observed electrostatic potential is perfectly equal to the magnetic pressure and exhibits no pairing contribution. They reported that this behavior is common to both type-I and weak type-II superconductors and for the magnetic field up to the critical value.

C. Surface dipole

The disagreement between theory and experiment remained unexplained for a long time and the question of the charge transfer in superconductors was left aside until the discovery of the high- T_c materials. For these layered materials it was predicted^{14,15} that the superconducting transition induces a charge transfer from CuO_2 planes to charge reservoirs. This transfer caused merely by the pairing mechanism has been confirmed by bulk-oriented experiments like the positron annihilation,¹⁶ the x -ray absorption spectroscopy,¹⁷ and the nuclear magnetic resonance.¹⁸

Apparently, there are two groups of contradictory experimental results. The pairing contribution is absent in the surface potential but a charge transfer is observed at internal interfaces in the bulk.

As it was indicated recently,¹⁹ there is a charge transfer at the surface which is the interface of superconductor and vacuum. This transfer forms a surface dipole which causes a step φ_δ in the electrostatic potential. The value of the potential step has been evaluated from the Budd-Vannimenus theorem²⁰

$$e\varphi_\delta = n \frac{\partial f_{\text{el}}}{\partial n}, \quad (4)$$

where f_{el} is the electronic part of the free energy density (it does not include the electrostatic and magnetic parts). Rickayzen has obtained formula (3) from the general stability condition $e\varphi = -\partial f_{\text{el}} / \partial n$ and the free energy $f_{\text{el}} = n_s / 2 m v^2$. Using the same free energy one finds that the potential at the surface, $\varphi_0 = \varphi(0) + \varphi_\delta$, equals the screened Bernoulli potential (2). The surface dipole φ_δ thus explains the observed magnetic pressure.

In spite of the agreement between observed and theoretically derived voltage one should be reserved about claims that the theory correctly describes the profile of the electrostatic potential in superconductors. Arguments against the theory are similar to those already raised in relation to the interpretation of the measurement of Bok and Klein.

First, the measurement of Morris and Brown explores the entire range of magnetic fields from low up to critical values. The free energy employed by Rickayzen, however, applies in the limit of low magnetic fields only.

Second, materials studied by Morris and Brown are type-I and weak type-II materials so that their behavior is not fully covered by the London theory. As we have shown recently,²¹ even for low magnetic fields the electrostatic potential depends on the Ginzburg-Landau (GL) parameter κ . Rickayzen's formula is recovered for the extreme type-II superconductor $\kappa \rightarrow \infty$. For measured materials with $\kappa \approx 1/\sqrt{2}$ the potential $\varphi(0)$ at the surface is reduced by a factor $1/3$ compared to Rickayzen's formula.

Third, the surface dipole φ_δ derived from the free energy that covers only the low-field perturbation in the London approximation has the same shortcomings as Rickayzen's formula. Apparently, $\varphi(0)$ obtained from Rickayzen's formula can be far from the correct value and the same applies to φ_δ . Since the sum agrees with the experimental result, one can see that eventual errors tend to compensate each other in the resulting electrostatic potential. In this sense, the surface dipole φ_δ is consistent with the internal potential φ , since both are evaluated using the same free energy.

D. Plan of the paper

As demonstrated for Rickayzen's theory, the internal electrostatic potential φ and the surface dipole φ_δ ought to be derived from the same free energy. We have shown²¹ that for type-I and weak type-II superconductors, the GL theory yields the internal electrostatic potential which is quite different from the one predicted by Rickayzen's formula. In this paper we derive the surface dipole within the GL theory.

As in Ref. 19 we use the Budd-Vannimenus theorem. Here we employ this identity within Bardeen's extension²² of the GL theory. Bardeen's extension offers two advantages. First, it naturally interpolates between the GL theory close to T_c and the London theory at low temperatures. Second, it uses material parameters of the Gorter-Casimir two-fluid model, which have a transparent density dependence. In contrast, the parameters of the original GL theory are introduced in the limit $T \rightarrow T_c$ and T is replaced by T_c wherever possible. Since T is an independent thermodynamic variable while $\partial T_c / \partial n \neq 0$, one has to be careful when taking density derivatives. To evaluate the density dependence of the GL parameters, one has to recall the microscopic theory of Gorkov and take the density derivatives of the corresponding parameters before the limit $T \rightarrow T_c$ is applied.

The plan of the paper is as follows. In Sec. II we assume temperatures close to T_c and an infinitesimally weak magnetic field. In this limit we derive a modification of the Budd-Vannimenus theorem which takes into account a non-zero charge density near the surface. In Sec. III we discuss a

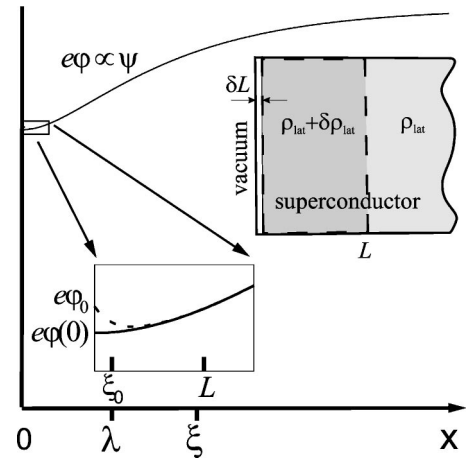


FIG. 1. Electrostatic potential at the surface. On the scale of the London penetration depth λ and the GL coherence length ξ , the electrostatic potential φ is linear in the GL wave function ψ . The schematic short-dashed line in the expanded detail shows the deviation of the potential from the GL value on the scale of the BCS coherence length ξ_0 . The surface potential φ_0 is the experimentally observed value, while $\varphi(0)$ is the internal GL potential extrapolated to the surface. In the inset, we show the virtual compression of the crystal lattice on the scale L , as it is employed in the Budd-Vannimenus theorem. The compression removes the lattice charge from the infinitesimal layer δL and correspondingly increases the charge density in the region framed by the long-dashed line.

general system in the Meissner state and show that the formula for the surface dipole derived in Sec. II applies to any temperature and magnetic field below critical values. Section IV includes a summary.

II. SURFACE DIPOLE

Let us first estimate the thickness of the surface dipole from thermodynamic considerations. The pairing correlation is weaker on the surface than in the bulk, what results in forces pulling the Cooper pairs inside. Such forces are always balanced by the electrostatic field. The full understanding of this effect will require microscopic studies which are not yet feasible. From the BCS studies it is known, however, that close to the surface on the scale of the BCS coherence length ξ_0 , the gap profile differs from the value given by the GL theory.²³ We thus expect that the surface dipole is somehow linked to this "microscopic" modulation of the gap profile.

To introduce the surface dipole on an intuitive level, let us assume that the system is close to the critical temperature. In this regime, the London penetration depth λ and the GL coherence length ξ are much larger than the BCS coherence length ξ_0 . Since the electrostatic potential induced by the diamagnetic current extends on scales of λ and ξ from the surface,²¹ the surface dipole is very narrow on these scales.

We can then define an intermediate scale L such that $\xi_0 \ll L \ll \xi, \lambda$, as sketched in Fig. 1. On the scale L , the GL wave function changes only negligibly, i.e., $\psi(x) \approx \psi(x \rightarrow 0) \equiv \psi(0)$ for $0 < x < L$. We note that the GL boundary condi-

tion $\partial_x \psi = 0$ supports the slow change of ψ close to the surface.

As shown by de Gennes,²³ the GL wave function is linearly proportional to the BCS gap, except for the surface region on the scale of the BCS coherence length ξ_0 . Following microscopic theories giving the electrostatic potential in terms of the BCS gap,^{14,15,24} we expect the electrostatic potential to have similar features, see Fig. 1.

For $\xi_0 \ll x < L$, the potential is well described by the GL value $\varphi(x)$. Since $L \ll \lambda, \xi$, the GL prediction of the electrostatic potential changes only negligibly in this region and it is convenient to introduce the extrapolated value $\varphi(x) \approx \varphi(x \rightarrow 0) \equiv \varphi(0)$. The extrapolation of the GL potential toward the surface, $\varphi(0)$, has to be distinguished from the true surface potential φ_0 . The difference $\varphi_\delta = \varphi_0 - \varphi(0)$ is caused by the surface dipole we aim to evaluate.

A. Budd-Vannimenus theorem at intermediate scale

Close to the critical temperature, we can take the intermediate region $x \sim L$ as a homogeneous “bulk” and follow the idea of Budd and Vannimenus.^{20,25} Let us assume a virtual compression of the crystal lattice such that the background or the lattice charge density is removed from the surface layer of an infinitesimal width δL . The perturbation of the lattice charge density in the infinitesimal layer $0 < x < \delta L$ is $\delta \rho_{\text{lat}} = -\rho_{\text{lat}}$. The compression leads to an increase of the charge density in the layer $\delta L < x < L$, where $\delta \rho_{\text{lat}} = \rho_{\text{lat}} \delta L / L$ is selected to conserve the total charge.

Now we recall the basic idea of the Budd-Vannimenus theorem. The lattice charge enters the jellium model of metals as an external parameter. If one changes this external parameter, the situation corresponds to doing work on the system

$$\delta \mathcal{W} = S \int dx \delta \rho_{\text{lat}} \frac{\partial f}{\partial \rho_{\text{lat}}} = S \int dx \delta \rho_{\text{lat}} \varphi, \quad (5)$$

where f is the density of the free energy including the electrostatic interaction, and S is the sample area. According to the Feynman-Hellmann theorem, the change of the electrostatic potential does not contribute to the work up to the first order in $\delta \rho_{\text{lat}}$. Now we can proceed with the algebra. We split the integral into three parts, $(0, \delta L)$, $(\delta L, \xi_0)$, and (ξ_0, L) . Since δL is an infinitesimal displacement, the potential in the layer $0 < x < \delta L$ can be replaced by the surface value φ_0 . The surface region $\delta L < x < \xi_0$ gives a negligible contribution of the order of ξ_0 / L . In the remaining bulk region $\xi_0 < x < L$, the electrostatic potential is nearly constant and equals $\varphi(0)$. The work thus reads

$$\delta \mathcal{W} = S \delta L \rho_{\text{lat}} [\varphi(0) - \varphi_0]. \quad (6)$$

The work increases the free energy \mathcal{F} of the system

$$\delta \mathcal{W} = \delta \mathcal{F} = - \frac{\partial (f_{\text{el}} S L)}{\partial (S L)} S \delta L = \left(-f_{\text{el}} + n \frac{\partial f_{\text{el}}}{\partial n} \right) S \delta L, \quad (7)$$

where f_{el} is the spatial density of the electronic free energy. Note that only the change of the electronic part in the “bulk” is assumed. The surface energy does not change as the sur-

face is merely shifted. The magnetic free energy changes negligibly, because the number of electrons in the layer L is not changed by the deformation. Since the condensate velocity changes on the scale $\lambda \gg L$, changes of the screening current vanish in the limit $L/\lambda \rightarrow 0$.

The first term in Eq. (7) results from the reduced volume, $S L \rightarrow S(L - \delta L)$, and the second one from the corresponding increase of the electron density, $n \rightarrow n(1 + \delta L/L)$. Equating Eqs. (6) and (7) we obtain a modification of the Budd-Vannimenus theorem

$$\rho_{\text{lat}} \varphi_\delta \equiv \rho_{\text{lat}} [\varphi_0 - \varphi(0)] = f_{\text{el}} - n \frac{\partial f_{\text{el}}}{\partial n}. \quad (8)$$

It describes the step of the potential at the surface due to the surface dipole in terms of the free energy. This relation is the main result of the present paper. In the remaining part we demonstrate how Eq. (8) can be used and show that it applies also at low temperatures, where the intermediate region cannot be defined.

Formula (8) differs from the original Budd-Vannimenus (BV) theorem in four points. First, in the original BV theorem one evaluates the total potential step at the surface. Its values are of the order of volts. Here we evaluate only the change of the potential step which appears as the system becomes superconducting. The typical magnitude of this change is of the order of nanovolts. Second, in the BV theorem the surface potential is related to the potential φ_∞ deep in the bulk. In Eq. (8), the extrapolation of the internal potential toward the surface $\varphi(0)$ appears instead. Third, in order to cover systems at finite temperatures, we use the free energy instead of the ground-state energy. Fourth, within the original Budd-Vannimenus approach, the electron charge density and the lattice charge density have to be equal because of the charge neutrality. In our approach, the density of electronic charge differs locally from the lattice charge density, $en \neq -\rho_{\text{lat}}$, due to the charge transfer induced by the magnetic fields.²¹

In the limit of extreme type-II superconductors and weak magnetic fields one can compare formula (8) with the surface dipole evaluated in Ref. 19. In this limit, the free energy simplifies to $f_{\text{el}} = f_\infty - n_s / 2mv^2$. The second term provides the current induced changes of the surface dipole derived in Ref. 19. Due to the bulk free energy f_∞ one finds from Eq. (8) a finite potential step also in the absence of diamagnetic currents.

For the purpose of the plot in Fig. 1, we have used a small magnitude of the potential step at the surface (the short-dashed line is rather close to the full line). In reality, even the current induced part of the step φ_δ might achieve a magnitude much larger than the internal potential $\varphi(0)$. A simple estimate of surface step for the experiment of Morris and Brown¹³ ranges from a few percent for $T = 0.6 T_c$ to about 30 times of the observed potential at $T = 0.97 T_c$, see Ref. 19. Since we assume the limit $T \rightarrow T_c$, the large values are more appropriate.

B. Application within the GL theory

Now we demonstrate how the relation (8) can be used within the GL theory. To this end we introduce the GL free energy

$$f_{\text{el}} = \frac{1}{2m^*} |(-i\hbar \nabla - e^* \mathbf{A})\psi|^2 + f_{\text{cond}}, \quad (9)$$

where ψ is the GL wave function, \mathbf{A} is the vector potential, $m^* = 2m$ and $e^* = 2e$ are the mass and the charge of the Cooper pair, and f_{cond} is the free energy of the condensate. It can be either the Gorter-Casimir free energy

$$f_{\text{cond}} = -\frac{1}{4} \gamma T_c^2 \frac{2}{n} |\psi|^2 - \frac{1}{2} \gamma T^2 \sqrt{1 - \frac{2}{n}} |\psi|^2 \quad (10)$$

used by Bardeen²² or the GL free energy

$$f_{\text{cond}} = \alpha |\psi|^2 + \frac{1}{2} \beta |\psi|^4. \quad (11)$$

The GL parameters $\alpha = \gamma(T_c^2 - T^2)/2n$ and $\beta = \gamma T^2/n^2$ depend on the temperature T and the electron density $n = n_n + 2|\psi|^2$, where n_n is the density of normal electrons. Finally, we add the electromagnetic energy so that the free energy reads

$$f = f_{\text{el}} + \varphi(\rho_{\text{lat}} + en) - \frac{\epsilon_0}{2} E^2 + \frac{1}{2\mu_0} B^2, \quad (12)$$

with the magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$ and the electric field $\mathbf{E} = -\nabla \varphi$. Here the standard local function expression for the two-point Coulomb interaction $1/2 \int \rho(\mathbf{r})\rho(\mathbf{r}')/4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'| d\mathbf{r}d\mathbf{r}' = \int (\varphi\rho - 1/2\epsilon_0 E^2) d\mathbf{r}$ was used. This form allows us to regard the scalar potential φ as an independent variable and simplifies the variational procedure employed below.

Variations of the free energy with respect to its independent variables \mathbf{A} , φ , ψ , n_n yield the equations of motion in Lagrange's form

$$-\nabla \frac{\partial f}{\partial \nabla \nu} + \frac{\partial f}{\partial \nu} = 0. \quad (13)$$

For $\nu = A$ the variational condition (13) yields the Ampere-Maxwell equation, for $\nu = \varphi$ the Poisson equation, for $\nu = \psi$ the GL equation, and for $\nu = n_n$ the condition of zero dissipation,

$$e\varphi = -\frac{\partial f_{\text{el}}}{\partial n}. \quad (14)$$

This condition allows one to evaluate the electrostatic potential in the bulk of the superconductor.²⁶ Of course, one can add any constant to the electrostatic potential.

Formula (14) does not cover the surface dipole on the scale ξ_0 , therefore at the surface it provides the extrapolated bulk value $\varphi(0)$. We can thus use Eq. (14) to rearrange the Budd-Vannimenus theorem (8) as

$$\rho_{\text{lat}}\varphi_0 = f_{\text{el}} + \varphi(0)(\rho_{\text{lat}} + en). \quad (15)$$

Now all terms on the right-hand side are explicit quantities which one obtains within the GL theory extended by the electrostatic interaction.²⁶

C. Convenient approximation

In customary GL treatments, the electrostatic potential and the corresponding charge transfer are omitted. For mag-

netic properties this approximation works very well, since the relative charge deviation $(\rho_{\text{lat}} + en)/\rho_{\text{lat}}$ is typically of the order of 10^{-10} , leading to comparably small corrections in the GL equation. With the same accuracy one obtains the electronic free energy f_{el} . Therefore it is possible to evaluate the surface potential using the approximation

$$\varphi_0 \approx -\frac{f_{\text{el}}}{en_{\infty}} \quad (16)$$

which follows from Eq. (15) if terms proportional to $(\rho_{\text{lat}} + en)/\rho_{\text{lat}}$ are neglected. By n_{∞} we have denoted the asymptotic value of n deep in the bulk, i.e., the density of pairable electrons, $\rho_{\text{lat}} = -en_{\infty}$.

Within approximation (16) one does not have to evaluate the potential profile and the related charge inside the superconductor. This is advantageous, in particular for systems of unknown material parameters $\partial T_c/\partial n$ and $\partial \gamma/\partial n$.

Turning the argument around, from Eq. (16) one can see that the electrostatic potential at the surface cannot be used to measure the material parameters $\partial T_c/\partial n$ and $\partial \gamma/\partial n$. This fact is already known from the experiment of Morris and Brown.¹³

III. MAGNETIC PRESSURE

So far we have discussed systems close to the critical temperature, when the validity conditions of the GL theory are well satisfied. In many cases, however, the GL theory is used beyond the limits of its nominal applicability. In these cases the GL coherence length ξ and/or the London penetration depth λ are comparable to, or even shorter than the BCS coherence length ξ_0 so that the intermediate scale L cannot be introduced.

It is possible, however, to follow the original formulation of Budd and Vannimenus and define L as the sample thickness, i.e., $L \gg \xi, \lambda$. In this case it is necessary to account for the energy of the magnetic field, since the infinitesimal compression δL shifts the screening layer inwards into the superconductor.

A. Budd-Vannimenus theorem

For $L \gg \xi, \lambda$, the charge removed from the surface is placed deep in the bulk (the region of the scale of ξ, λ gives a negligible contribution) so that the work on the charge reads

$$\delta \mathcal{W} = S \delta L (\varphi_{\infty} - \varphi_0) \rho_{\text{lat}}. \quad (17)$$

Compared to the previous treatment we have merely replaced the potential close to the surface by the value deep in the bulk. Similarly, the electronic part of the total free energy changes by

$$\delta \mathcal{F}_{\text{el}} = \left(-f_{\text{el}}^{\infty} + n \frac{\partial f_{\text{el}}^{\infty}}{\partial n} \right) S \delta L. \quad (18)$$

Finally, the shift of the screening layer by δL changes the magnetic energy by an amount $\delta \mathcal{F}_B = S \delta L B_0^2 / 2\mu_0$, given by

the magnetic pressure. Here B_0 is the value of the magnetic field at the surface.

From $\delta\mathcal{W} = \delta\mathcal{F}_{\text{el}} + \delta\mathcal{F}_B$ follows:

$$\rho_{\text{lat}}(\varphi_0 - \varphi_\infty) = \frac{B_0^2}{2\mu_0} + f_{\text{el}}^\infty + n_\infty \frac{\partial f_{\text{el}}^\infty}{\partial n}. \quad (19)$$

As L is the thickness of the sample one can use the charge neutrality $\rho_{\text{lat}} = -en_\infty$. Since the value of the potential deep in the sample is given by condition (14), using $e\varphi_\infty = -\partial f_{\text{el}}^\infty / \partial n$ from Eq. (19) one obtains

$$\varphi_0 = -\frac{B_0^2}{2\mu_0 en_\infty} - \frac{f_{\text{el}}^\infty}{en_\infty}. \quad (20)$$

The electrostatic potential observed at the surface is thus given by the magnetic pressure as observed by Morris and Brown.¹³

Note that deriving formula (20) we have not used many assumptions about the system. The condition of zero dissipation (14) is a general thermodynamic relation. The Budd-Vannimenus relation (19), however, is limited to systems with a homogeneous jelly-like background charge. This approximation is acceptable for conventional superconductors, where characteristic scales ξ_{BCS} , ξ , and λ are much larger than the elementary cell of the crystal. The applicability is questionable for the high- T_c materials which due to the layered structure and a short coherence length are far from the jellium model.

As noticed already by Bok and Klein,⁵ there is a simple argument for the formula like Eq. (20). If one assumes a slab with magnetic fields B_L and B_R on the left/right sides, the voltage difference gives

$$\rho_{\text{lat}}(\varphi_0^L - \varphi_0^R) = \frac{1}{2\mu_0}(B_L^2 - B_R^2). \quad (21)$$

The left-hand side of this relation represents the electrostatic force (per unit area) on the lattice

$$F_{\text{elst}} = \int_L^R dx E \rho_{\text{lat}} = \rho_{\text{lat}}(\varphi_0^L - \varphi_0^R). \quad (22)$$

The right-hand side is the Lorentz force $F_{\text{Lor}} = BJ$ with the mean magnetic field $B = 1/2(B_L + B_R)$ and the net current $J = \int_L^R dx j$ given by Ampere's rule, $B_L - B_R = \mu_0 J$. Since the electrostatic field provides the only mechanism by which the force is passed from the electrons to the lattice, the two forces have to be equal, $F_{\text{Lor}} = F_{\text{elst}}$. This argument was, however, overlooked in the later studies.

B. Test of the surface relation

The Budd-Vannimenus theorem provides the electrostatic potential (20) in terms of the magnetic field with no regard to the actual potential inside the superconductor. To link formula (20) with the more intuitive derivation from Sec. II, we show that Eq. (15) results in the surface potential (20) for any temperature.

For the assumed geometry, the GL equation has an integral of motion, see Bardeen.²² This integral can be obtained

quite generally by the Legendre transformation of the free energy

$$g = f - \sum_\nu \frac{\partial f}{\partial \nabla \nu} \nabla \nu. \quad (23)$$

Indeed, if the fields ν obey the equations of motion (13), the gradient $\nabla g = 0$ vanishes, i.e., $g = \text{const}$. Deep in the bulk all gradients vanish, therefore $g = f_{\text{el}}^\infty$.

From Eqs. (9)–(12) one finds

$$\sum_\nu \frac{\partial f}{\partial \nabla \nu} \nabla \nu = \frac{\hbar^2}{m^*} |\nabla \psi|^2 - \epsilon_0 E^2 + \frac{B^2}{\mu_0}. \quad (24)$$

With the help of Eqs. (23) and (24) and definition (12), one can express the electronic free energy as

$$f_{\text{el}} = f_{\text{el}}^\infty + \frac{\hbar^2}{m^*} |\nabla \psi|^2 - \frac{\epsilon_0 E^2}{2} + \frac{B^2}{2\mu_0} - \varphi(\rho_{\text{lat}} + en). \quad (25)$$

At the surface, the GL boundary condition demands that $\nabla \psi = 0$ what implies $E = 0$. The free energy at the surface thus reads

$$f_{\text{el}} = f_{\text{el}}^\infty + \frac{B^2}{2\mu_0} - \varphi(0)(\rho_{\text{lat}} + en). \quad (26)$$

From Eq. (26) and the surface relation (15) it follows that $\rho_{\text{lat}} \varphi_0 = B^2 / (2\mu_0) + f_{\text{el}}^\infty$. This value is identical to Eq. (20).

Apparently, we can reverse the procedure. Starting from the general Budd-Vannimenus relation (20) and the general integral of motion (23), we can derive the surface relation (15). Accordingly, the surface relation holds for any temperature, provided that the free energy is a functional of the GL wave function and its first derivative only, $f \equiv f[\psi, \nabla \psi]$. This functional can be an arbitrary one.

Perhaps we should explain why we have derived the surface dipole from the Budd-Vannimenus theorem on the intermediate scale, although the more general derivation from the integral of motion is available. There are two reasons. First, the intermediate scale provides at least a qualitative picture of the potential in the vicinity of the surface. This picture might be helpful if measurements sensitive to layers close to the surface will be designed.

Second, within the intermediate scale the surface dipole is treated as a property of the superconducting condensate, what encourages us to hope that formula (15) or its approximation (16) can be used to obtain the surface potential also for cases when the magnetic field has a component perpendicular to the surface. In particular, we expect that it will be applicable to the superconductors in the mixed state, especially to evaluate the electric field generated by vortices penetrating the surface.²⁷

IV. CONCLUSIONS

In conclusion, the Budd-Vannimenus theorem was modified so that it is applicable to the surface of a superconductor. It allows one to evaluate the electrostatic potential on the surface from the free energy and the bulk electrostatic potential nearby. Formula (16) offers the approximation of the

surface potential from the free energy without the actual knowledge of the bulk potential.

For plain surfaces we have recovered the experimentally established fact that the electrostatic potential equals the magnetic pressure divided by the density of pairable electrons. This experimental law was confirmed also for type-I and weak type-II superconductors, while the previous theoretical treatments were restricted to weak magnetic fields and extreme type-II superconductors. The presented theory is free of these limitations.

It was shown that thermodynamic corrections do not influence the surface electrostatic potential, measurable, e.g., via contactless capacitive pickup. Consequently, contrary to earlier expectations, the density dependence of the critical temperature cannot be estimated in this way. On the other hand, the relation between the surface electrostatic potential and the magnetic pressure shows, that such a measurement allows one to determine the density of charge carriers with-

out knowledge of any other material parameters.

In this paper we have derived only the amplitude of the potential step. The detailed profile of the electrostatic potential including its modulation at the surface can be obtained by a microscopic approach like the Bogoliubov-de Gennes theory extended recently to cover the electrostatic phenomena.²⁸⁻³¹ For microscopic calculations, the Budd-Vannimenus theorem can serve as a test of accuracy of the numerical procedure, similarly as it is used in the theory of metal surfaces.

ACKNOWLEDGMENTS

This work was supported by MŠMT program Kontakt ME601 and GAČR 202/03/0410, GAAV A1010312 grants. The European (ESF) program VORTEX is also acknowledged.

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