Budd-Vannimenus theorem for superconductors

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

The Budd-Vannimenus theorem [1] links the value of the electrostatic potential at the surface of a metal to the energy per electron in the bulk. This simple consequence of the Feynman-Hellmann theorem turned out to be very useful in studies of metal surfaces [2] as it enables one to circumvent demanding calculations of the charge distribution at the surface. We will use this approach to evaluate the surface potential of superconductors within the Ginzburg-Landau (GL) theory.

Perhaps it is useful to start from a historical review. Within the pre-London approaches based on the ideal charged liquid [3], the electrostatic potential was assumed to balance the Lorentz and the inertial forces acting on currents. Since the current \(j = env\) flows along the surface and its amplitude falls off exponentially from the surface into the bulk, the electrostatic Bernoulli–type potential, \(e\varphi = -\frac{1}{2}mv^2\), falls off on the scale of the London penetration depth. From the Poisson equation, \(\rho = -\epsilon_0\nabla^2\varphi\), one finds that this corresponds to a charge accumulated in the layer penetrated by the magnetic field. Charge neutrality is maintained by the opposite surface charge. This picture has been confirmed by the London theory [4].

The electrostatic potential equals the Bernoulli potential only at zero temperature when all electrons are in the superconducting condensate. At finite temperatures, a part \(n_n\) of electrons remains in the normal state, while the rest \(n_s = n - n_n\) contributes to the supercurrent, \(j = en_nv\). As a consequence, the electrostatic potential reduces to \(e\varphi = -\frac{n_n}{n} \frac{1}{2}mv^2\) as shown by van Vijfeijken and Staas [5]. Jakeman and Pike [6] recovered this result from the time-dependent GL theory. Moreover, their approach describes the surface charge as a space charge localized on the Thomas-Fermi screening length.

The surface charge and the charge accumulated at the London penetration depth form a surface dipole due to which the electrostatic potential in the bulk differs from the potential out of the superconductor. This voltage difference, which like the resistance of the Hall effect is perpendicular to the current, is not accessible by contact measurements but it was observed by a contact-less capacitive pickup [7,8].

The first measurements [7,8] were not sufficiently accurate and created expectations that the surface voltage includes traces of the pairing mechanism. Rickayzen [9] used the thermodynamic approach and showed that the potential indeed has a pairing contribution, \(e\varphi = -\frac{3}{8}e\frac{1}{n}mv^2 - 4\frac{3}{8}n_0 \frac{\partial \ln T_c}{\partial n_0} \frac{1}{2}mv^2\). The first term results from the Lorentz and inertial forces, while the second one reflects the pairing. The pairing term dominates close to the critical temperature \(T_c\). If \(\varphi\) would be experimentally accessible, one could deduce from it the density dependence of \(T_c\). The highly accurate measurement by Morris and Brown [10], however, chilled all the expectations. The electrostatic potential revealed no pairing contribution.

The disagreement between the theory and experiment remained unexplained for a long time and the question of the charge transfer in superconductors was left aside till the discovery of the high-\(T_c\) materials. It was predicted [11,12] that in layered materials the superconducting transition induces a charge transfer from CuO2 planes to charge reservoirs. This transfer caused merely by the pairing mechanism has been experimentally confirmed by the positron annihilation [13], the x-ray absorption spectroscopy [14], and the nuclear magnetic resonance [15].

Apparently, there are two groups of contradictory experimental results. The pairing contribution is absent in the surface potential but it is observed in the bulk. As it was indicated recently [16], there is an additional surface dipole which cancels the pairing contribution to surface potential seen in capacitive measurements.

The approach presented in Ref. [16] employs the Budd-Vannimenus theorem, however, it has the same limitation as Rickayzen’s formula – the magnetic field is described within the London’s theory and it has to be weak not to perturb the density of the condensate. In contrast, the measurement of Morris and Brown [10] explores the entire range of the magnetic fields from weak fields up to the critical value. They found that the potential equals the magnetic pressure \(\varphi = \frac{1}{p_{\text{mag}}} \frac{1}{4n_0} B^2\), i.e., it is independent of the temperature and the used material enters merely via the charge density \(p_{\text{lat}}\) of its lattice, for both type-I and II superconductors.

Here we modify the Budd-Vannimenus theorem so that it is consistent with the GL theory. Its validity is not
restricted to weak magnetic fields. We will show that the surface potential is given by

$$\varphi_0 = \frac{f_{el}}{\rho_{lat}},$$

(1)

where $f_{el}$ is the surface value of the GL free energy (3). With the help of the modified Budd-Vannimenus theorem one can explain the experimental result of Morris and Brown under very general conditions.

The recent implementation of the GL theory has changed the picture of the surface charge. It is not localized on the scale of the Thomas-Fermi screening length as claimed by Jakeman and Pike, but it varies on scales of the GL coherence length [17]. As pointed out in Ref. [18], if the electrostatic potential is a local functional of the GL wave function, $\varphi[\psi]$, the GL boundary condition, $\nabla \psi = 0$ in the direction normal to the surface, implies the zero electric field at the surface, $E = -\nabla \varphi = \frac{\partial \varphi}{\partial \psi} \nabla \psi = 0$. Accordingly, no additional surface charge is needed to maintain the charge neutrality.

Since the surface charge is absent, it seems that the surface dipole on the Thomas-Fermi screening length is absent, too. There has to be yet another surface dipole, however. 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 understanding of this effect will require microscopic studies which are not yet feasible. We can merely speculate that the surface dipole is somehow linked to the gap profile at the surface [19], i.e., it is localized on the BCS coherence length.

![FIG. 1. Schematic picture of the electrostatic potential at the surface. On the scale of the London penetration depth $\lambda$ the potential $\varphi(x)$ is concave, which corresponds to charge accumulation. Below the GL coherence length $\xi$, the charge is depleted leading to a convex potential. Within the BCS coherence length $\xi_0$, the potential makes a sharp step due to the surface dipole. $\varphi_0$ is the true surface potential, while $\varphi(0)$ is the extrapolated GL value. The dashed line indicates the virtual compression of the lattice.](image)

To introduce the surface dipole on an intuitive level we first assume that the system is close to the critical temperature. In this regime, the London penetration depth $\lambda$ and the GL coherence length $\xi$ are much larger than the BCS coherence length $\xi_0$. 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, the vector potential, and the electrostatic potential change only negligibly, e.g., $\varphi(x) \approx \varphi(x \to 0) \equiv \varphi(0)$ for $\xi_0 < x < L$. The extrapolation of the bulk potential towards the surface, $\varphi(0)$, has to be distinguished from the true surface potential $\varphi_0$. The difference $\varphi_0 - \varphi(0)$ is caused by the surface dipole we aim to evaluate.

Close to the critical temperature we can follow the idea of Budd and Vannimenus [1]. Let us assume a virtual compression of the crystal lattice such that the lattice charge density is removed from the surface layer of an infinitesimal width $\delta L$. The perturbation of the lattice charge density in the infinitesimal layer $0 < x < \delta L$ is $\delta \rho_{lat} = -\rho_{lat}$. The compression leads to an increase of the charge density in the layer $\delta L < x < L$, where $\delta \rho_{lat} = \rho_{lat} \delta L/L$, in accordance with the charge conservation.

Let us remind the basic idea of the Feynman-Hellmann 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, $\delta W = S \int dx \delta \rho_{lat} \frac{\partial \psi}{\partial \rho_{lat}} = S \int dx \delta \rho_{lat} \varphi$, 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 $\delta \rho_{lat}$. Now we can proceed with the algebra. We split the integral into three parts. Since $\delta L$ is an infinitesimal displacement, the potential in the layer $0 < x < \delta L$ can be replaced by the surface value $\varphi_0$. The surface region $\delta L < x < \xi_0$ gives a negligible contribution of the order of $\xi_0/L$. In the remaining bulk region $\xi_0 < x < L$, the electrostatic potential is nearly constant and equals $\varphi(0)$. The work thus reads $\delta W = S \delta L \rho_{lat}(\varphi(0) - \varphi_0)$.

In the same time, the work increases the free energy $F$ of the system, $\delta W = \delta F$. We denote the spatial density of the electronic free energy by $f_{el}$. Lower case letters denote free energies per unit volume, i.e., their densities, while the calligraphic upper case letters denote the corresponding total values. The total free energy changes as $\delta F = -\frac{\partial f_{el}}{\partial (S \lambda)} \delta S \delta L = \left(-f_{el} + n \frac{\partial f_{el}}{\partial n} \right) S \delta L$. The first term results from the reduced volume, $SL \to S(L - \delta L)$, and the second one from the corresponding increase of the electron density by $n \to n(1 + \delta L/L)$. We thus obtain a modification of the Budd-Vannimenus theorem,

$$\rho_{lat}(\varphi_0 - \varphi(0)) = f_{el} - n \frac{\partial f_{el}}{\partial n}.$$  

(2)

This relation is our final result. It describes the step of the potential at the surface due to the surface dipole in terms of the free energy.

Formula (2) differs from the original Budd-Vannimenus theorem in three points. First, in the original Budd-Vannimenus theorem, the surface potential is related to
the potential \( \varphi_\infty \) deep in the bulk. In (2), the extrapolation of the internal potential towards the surface, \( \varphi(0) \), appears instead. Second, in order to cover systems at finite temperature, we use the free energy instead of the ground-state energy. Third, 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 on the scales \( \xi \) and \( \lambda \).

Let us demonstrate how the relation (2) can be used within the GL theory. To this end we introduce the GL free energy

\[
 f_{\text{el}} = \frac{1}{2m} \left| (-ih\nabla - e^* A) \psi \right|^2 + \alpha |\psi|^2 + \beta |\psi|^4, \tag{3}
\]

where \( \psi \) is the GL wave function, \( A \) is the vector potential and \( m^* = 2m \) and \( e^* = 2e \) are the mass and the charge of the Cooper pair. The GL parameters \( \alpha \) and \( \beta \) depend on the temperature and the electron density \( \nu = n_n + 2|\psi|^2 \).

Finally, we add the electromagnetic energy

\[
 f = f_{\text{el}} + \varphi(\rho_{\text{lat}} + en) - \frac{e_0}{2} E^2 + \frac{1}{2\mu_0} B^2, \tag{4}
\]

with the magnetic field \( B = \nabla \times A \) and the electric field \( E = -\nabla \varphi \).

Variations of the free energy with respect to its independent variables \( A, \varphi, \psi, n_n \) yield the equations of motion in Lagrange’s form

\[
 -\nabla \frac{\partial f}{\partial \nabla \nu} + \frac{\partial f}{\partial \nu} = 0. \tag{5}
\]

For \( \nu = A \) the variational condition (5) 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,

\[
 e\varphi = -\frac{\partial f_{\text{el}}}{\partial n}. \tag{6}
\]

This condition allows one to evaluate the electrostatic potential in the bulk of the superconductor [20]. Of course, one can add any constant to the electrostatic potential. The actual choice (6) simplifies the relations we deal with below. Another convenient choice would be to subtract the value of the potential in the non-magnetic state, i.e., deep inside the superconductor, so that \( \varphi \) approaches zero in the bulk.

Formula (6) does not cover the surface dipole on the scale \( \xi_0 \), therefore at the surface it provides the extrapolated bulk value \( \varphi(0) \). We can thus use (6) to rearrange the Budd-Vannimenus theorem (2) as

\[
 \rho_{\text{lat}} \varphi_0 = f_{\text{el}} + \varphi(0) (\rho_{\text{lat}} + en). \tag{7}
\]

Now all terms on the right hand side are explicit quantities which one obtains within the GL theory extended by the electrostatic interaction [20].

In customary GL treatments, the electrostatic potential and the corresponding charge transfer are omitted. This approximation works very well for magnetic properties since the relative charge deviation, \((\rho_{\text{lat}} + en)/\rho_{\text{lat}}\), is typically of the order of \(10^{-8}\) to \(10^{-4}\) leading to comparably small corrections in the GL equation. With the same accuracy one obtains the electronic free energy \( f_{\text{el}} \). Therefore it is possible to evaluate the surface potential using (1), which follows from (7) if terms proportional to \((\rho_{\text{lat}} + en)/\rho_{\text{lat}}\) are neglected.

So far we have restricted ourselves to systems close to the critical temperature when the validity conditions of the GL theory are well satisfied. In many cases, the GL theory is used beyond the limits of its nominal applicability, however. In these cases, the GL coherence length \( \xi \) and/or the London penetration depth \( \lambda \) are comparable to or even shorter than the BCS coherence length \( \xi_0 \). Although the above derivation does not apply to this case, it is possible to show that the Budd-Vannimenus theorem (7) provides physically consistent predictions in these cases, too.

We evaluate now the voltage which develops across a superconducting slab with the magnetic field parallel to the slab. For the slab geometry, the GL equation has an integral of motion, see Bardeen [21]. This integral can be obtained quite generally by the Legendre transformation of the free energy, \( g = f - \sum_\nu (\partial f/\partial \nabla \nu) \nabla \nu \). Indeed, if the fields \( \nu \) obey the equations of motion (5), the gradient \( \nabla g = 0 \) vanishes, i.e., \( g = \text{const} \). With the help of \( \sum_\nu (\partial f/\partial \nabla \nu) \nabla \nu = (\hbar^2/m^*) |\nabla \psi|^2 - e_0 E^2 + B^2/\mu_0 \), we can express the electronic free energy as

\[
 f_{\text{el}} = g + \frac{\hbar^2}{m^*} |\nabla \psi|^2 - \frac{e_0 E^2}{2} + \frac{B^2}{2\mu_0} - \varphi(\rho_{\text{lat}} + en). \tag{8}
\]

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

\[
 f_{\text{el}} = g + \frac{B^2}{2\mu_0} - \varphi(0)(\rho_{\text{lat}} + en). \tag{9}
\]

From the Budd-Vannimenus theorem (7) then follows \( \rho_{\text{lat}} \varphi_0 = g + B^2/(2\mu_0) \), and since \( g = \text{const} \), we obtain the potential difference across the surface as the difference of left and right magnetic pressures

\[
 \rho_{\text{lat}} (\varphi_0^L - \varphi_0^R) = \frac{B_0^2 - B_R^2}{2\mu_0}. \tag{10}
\]

Exactly this value of the voltage has been observed by Morris and Brown [10].

As noticed already by Bok and Klein [7], there is a simple argument for the formula (10). The left hand side represents the electrostatic force (per unitary area) on
the lattice, \( F_{\text{elst}} = \int_{\Omega} dE \rho_{\text{elst}} = \rho_{\text{elst}}(\varphi^L_0 - \varphi^R_0) \). The right hand side is the Lorentz force \( F_{\text{Lor}} = BJ \) with the mean magnetic field \( B = \frac{1}{2}(B_L + B_R) \) and the net current \( J = \int_{\Omega} dx j \) 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, \( F_{\text{Lor}} = F_{\text{elst}} \), which yields (10).

Turning the argument around, one can view the derivation of the Lorentz force as an alternative proof of formula (7). For the slab geometry, this is more general than the proof based on the Budd-Vannimenus approach, as the approach via the Lorentz force does not rely on the specific order of the characteristic lengths \( \xi_0 \ll \xi, \lambda \) needed above to define the intermediate length \( L \). Moreover, the Legendre transformation provides the integral of motion for any modification of the GL free energy which is of the form \( f_{\text{el}}[\psi, \nabla \psi] \).

On the other hand, within the Budd-Vannimenus approach the surface dipole is treated as a property of the superconducting condensate, what encourages us to hope that formula (7) or its approximation (1) 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 also to the superconductors in the mixed state, especially to evaluate the electric field generated by vortices penetrating the surface [22].

In conclusion, the Budd-Vannimenus theorem was modified to the surface of a superconductor. It allows one to evaluate the electrostatic potential of the surface from the free energy and the bulk electrostatic potential near the surface. Within approximation (1) one obtains the surface potential from the free energy without the actual knowledge of the bulk potential.

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