Theory of thermoelectric phenomena in superconductors

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The theory of thermoelectric effects in superconductors is discussed in connection to the recent publication by Marinescu and Overhauser [Phys. Rev. B **55**, 11 637 (1997)]. We argue that the charge nonconservation arguments by Marinescu and Overhauser do not require any revision of the Boltzmann transport equation in superconductors. We show that the charge current proportional to the gradient of the gap, $|\Delta|$, found by Marinescu and Overhauser, is incompatible with the time-reversal symmetry, and conclude that their "electron-conserving transport theory" is invalid. Possible mechanisms responsible for the discrepancy between some experimental data and the theory by Galperin, Gurevich, and Kozub {Pis'ma Zh Éksp. Teor. Fiz. **17**, 687 (1973) [JETP Lett. **17**, 476 (1973)]} are discussed.

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I. INTRODUCTION

The purpose of the present paper is to discuss some aspects of the kinetic approach to the thermoelectric properties of superconductors. As early as 1944 Ginzburg[1] suggested that in the presence of a temperature gradient, there appears in a superconductor a normal current of the form given by

$$\mathbf{j}_n = -\alpha \nabla T.$$

It was also pointed out by Ginzburg that the total current in the bulk of a homogeneous isotropic superconductor vanishes because the normal current is offset by a supercurrent $\mathbf{j}_s$ so that the total current in the bulk is

$$\mathbf{j}_n + \mathbf{j}_s = 0.$$

This makes impossible the direct observation of the thermoelectric effect in a simply connected homogeneous isotropic superconductor. Ginzburg considered also simply connected anisotropic or inhomogeneous superconductors as systems where it is possible to observe thermoelectric phenomena by measuring the magnetic field produced by a temperature gradient. As indicated in Refs. 2–4 (see also Ref. 5), the best way to observe thermoelectric phenomena in superconductors, in particular, to measure the thermoelectric coefficient α is to make the superconductor a part of a bimetallic superconducting loop that may also contain weak links.

Using the approach based on the Boltzmann equation for the normal excitations, the calculation of the coefficient α for impurity scattering has been made in Refs. 2 and 3, see also reviews in Refs. 6–8. The expression for α has been later rederived in Ref. 9 using the Green's-function version of the nonequilibrium statistical operator approach. In that paper the role of paramagnetic impurities was also discussed. Based on the same method, an enhancement of the thermoelectric flux in superconductors containing nonmagnetic impurities with localized states near the Fermi energy was predicted in Ref. 10, see also Ref. 11. As was proved in Refs. 9–11, the expressions for α, obtained in Refs. 2 and 3 for the case of nonmagnetic impurities, remain valid for an arbitrary relation between the coherence length of the superconductor and the electron mean free path.

Recently, Marinescu and Overhauser[12] have proposed another method to calculate the transport coefficients α. In their approach, the principal contribution to the thermoelectric effect in superconductors comes from the dependence of the superconducting gap Δ on the temperature. For some typical interval of temperatures and impurity concentrations their results differ from that of Refs. 2 and 3 by several orders of magnitude. Therefore, it is desirable to discuss the validity of their results. In the present paper we compare these approaches. We also briefly discuss how the theoretical results are related to the existing experimental data.

II. THEORY OF MARINESCU AND OVERHAUSER

Marinescu and Overhauser in Ref. 12 have proposed a method which they call an "electron-conserving transport equation." They introduce distribution functions, $\tilde{g}_{\mathbf{k}\uparrow}$ and $\tilde{g}_{-\mathbf{k}\downarrow}$, which differ from the distribution functions for the BCS excitations $f_{\mathbf{p}\uparrow,\downarrow}$ (below, the spin index is dropped).

The nonequilibrium part of the distribution function [see Eq. (47) of Ref. 12] is

$$\delta g_{\mathbf{k}} = -\frac{\hbar \tau_s}{m}\left[\frac{\beta \epsilon_k^2 f_k(1-f_k)}{TE_k} - \frac{f_k \Delta}{E_k^2}\left(\frac{d\Delta}{dT}\right)\right]\mathbf{k}\cdot\nabla T. \quad (1)$$

Here, as in Ref. 12, $\beta = 1/k_B T$, $E_k = \sqrt{\Delta^2(T) + \epsilon_k^2}$, and $f_k = (e^{\beta E_k} + 1)^{-1}$, while $\epsilon_k = \hbar^2 k^2/2m - \epsilon_F$ is the one-electron energy measured with respect to the Fermi level, ϵ_F.

The relaxation time τ_s is related to the relaxation time τ_n for impurity scattering in the normal state: For quasiparticle transitions from $\mathbf{k}$ to $\mathbf{k}'$,

$$\tau_s^{-1} = \tau_n^{-1} |E_k/\epsilon_k| (u_k u_{k'} - v_k v_{k'})^2. \quad (2)$$

For future convenience, we write Eq. (1) as

$$\delta g_{\mathbf{k}} = \delta g_{\mathbf{k}}^{(I)} + \delta g_{\mathbf{k}}^{(II)},$$

$$\delta g_{\mathbf{k}}^{(I)} = -\frac{\hbar \tau_s}{m} \frac{\beta \epsilon_k^2}{T E_k} f_k(1-f_k)\mathbf{k}\cdot\nabla T,$$
$$\delta g_{\mathbf{k}}^{(II)} = \frac{\hbar \tau_s}{m} \frac{f_k \Delta}{E_k^2}\left(\frac{d\Delta}{dT}\right)\mathbf{k}\cdot\nabla T. \tag{3}$$

Accordingly, the electric current density is split as $\mathbf{j}=\mathbf{j}^{(I)} + \mathbf{j}^{(II)}$, where

$$\mathbf{j}^{(I)} = -\alpha^{(I)}\boldsymbol{\nabla} T, \quad \mathbf{j}^{(II)} = -\alpha^{(II)}\boldsymbol{\nabla} T$$

with

$$\alpha^{(I)} = \frac{4eN(0)}{3mk_B T^2}\int_{-\hbar\omega_D}^{\hbar\omega_D} d\epsilon\, \tau_s(\epsilon+\epsilon_F) f(1-f)\frac{\epsilon^2}{E},$$

$$\alpha^{(II)} = -\frac{4eN(0)}{3mk_B T^2}\int_{-\hbar\omega_D}^{\hbar\omega_D} d\epsilon\, \tau_s(\epsilon+\epsilon_F)\frac{k_B T^2 f\Delta}{E^2}\frac{d\Delta}{dT},$$

with $N(0)$ being the density of states per spin.

III. DISCUSSION

Now we are in position to discuss the results of Ref. 12. The first term, $\delta g_{\mathbf{k}}^{(I)}$ in Eq. (3) comes from the coordinate dependence of the temperature T entering the Fermi-Dirac distribution function, and therefore, is of true nonequilibrium origin. A nonequilibrium term exists in the distribution function found from the Boltzmann equation approach[2,3] [cited as Eq. (21) in Ref. 12] with a very important difference: $\delta g_{\mathbf{k}}^{(I)}$ is *even* under $\epsilon \to -\epsilon$ so that electrons above and below the Fermi surface do not tend to compensate each other as in Refs. 2 and 3. The opposite symmetry in ϵ is the reason why the thermoelectric current obtained by Marinescu and Overhauser is some five orders of magnitude larger than that in Refs. 2 and 3.

The origin of the second term, $g_{\mathbf{k}}^{(II)}$, is the $\mathbf{r}$ dependence of $\Delta = \Delta[(T(\mathbf{r})]$ as is obvious when $\delta g_{\mathbf{k}}^{(II)}$ is identically written in the following form:

$$\delta g_{\mathbf{k}}^{(II)} = \tau_s f_k \frac{\Delta(\mathbf{r})}{E_k^2}\left(\mathbf{v}\cdot \frac{\partial}{\partial \mathbf{r}}\Delta(\mathbf{r})\right), \quad \mathbf{v} = \frac{\hbar \mathbf{k}}{m}.$$

This means that in the approach of Ref. 12, $\delta g_{\mathbf{k}}^{(II)}$ would exist irrespective of the origin of dependence of $\Delta(\mathbf{r})$ on the coordinate $\mathbf{r}$. For instance, such dependence may be due to the variation of the chemical composition of the superconductor or to the spatial variation of the strain.

Even if the dependence $\Delta(\mathbf{r})$ is due to one of these equilibrium mechanisms, the theory[12] nevertheless predicts the current,

$$\mathbf{j} = -\beta \frac{\partial \Delta}{\partial \mathbf{r}}, \tag{4}$$

where $\beta = \alpha^{(II)}(d\Delta/dT)^{-1}$. In our opinion, such a current is forbidden. Below we give physical considerations supporting this statement.

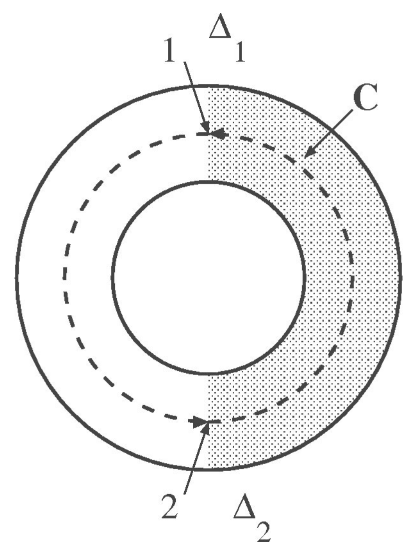

FIG. 1. The equilibrium of nonquantized magnetic flux.

It is well known that any linear-response process can be classified as either reversible or irreversible (dissipative)[13] (see Ref. 14 for a general discussion of nonequilibrium thermodynamics of superconductors, including thermoelectric phenomena). The basis for the classification is the time-reversal symmetry (T symmetry). For instance, the charge current $\mathbf{j}$ induced by the electric field $\mathbf{E}$, in a normal conductor, is irreversible. Indeed, the current changes its sign under time reversal whereas $\mathbf{E}$ remains intact, and the Ohm law, $\mathbf{j} = \sigma \mathbf{E}$, is not invariant relative to the T-symmetry transformation. Thermoelectric current, $\mathbf{j}^{(T)} = -\alpha \boldsymbol{\nabla} T$, is irreversible because the left-hand side changes its sign under time reversal whereas $\boldsymbol{\nabla} T$ does not. Another example is the supercurrent, $\boldsymbol{j}_s = 2eN_s \mathbf{v}_s$, proportional to the density of the Cooper pairs, N_s, and their velocity, $\mathbf{v}_s$. This relation is T invariant since both current and velocity are T-odd quantities. Consequently, supercurrent is reversible and compatible with thermal equilibrium.

From this point of view, the current in Eq. (4) is irreversible. Indeed, the gap function $\Delta(=|\Delta|)$ is unchanged by the time-reversal transformation $\psi \to \psi^*$, whereas the current changes its sign. Unlike the supercurrent, the irreversible current in Eq. (4) if existed would be accompanied by a steady entropy production. Being incompatible with equilibrium, the current must be equal to zero.

The contradiction with the T-symmetry arguments can be also demonstrated by the following gedanken experiment. Consider a ring built of two superconducting arms, left and right, both in thermal equilibrium. The arms are thick enough, so in their bulks the magnetic field is completely screened. The right arm is made of a chemically inhomogeneous superconductor with a position-dependent gap, $\Delta^{(r)}(\mathbf{r})$, varying along the arm from Δ_1 to Δ_2 if one moves counterclockwise, Fig. 1. The left arm is built of a homogeneous superconductor with the gap $\Delta^{(l)}$. The expression for the electric current, according to Eq. (4) and the theory of Ref. 12, reads

$$\mathbf{j}=\begin{cases}\dfrac{2e\hbar}{m}N_s^{(r)}\left[\boldsymbol{\nabla}\chi^{(r)}-\dfrac{2\pi}{\Phi_0}\mathbf{A}\right]-\beta\boldsymbol{\nabla}\Delta^{(r)} & \text{right arm,}\\ \dfrac{2e\hbar}{m}N_s^{(l)}\left[\boldsymbol{\nabla}\chi^{(l)}-\dfrac{2\pi}{\Phi_0}\mathbf{A}\right] & \text{left arm.}\end{cases} \tag{5}$$

Thus, there is an additional current in the right arm given by Eq. (4). Since the current vanishes in the bulk of the ring, $\mathbf{j}=0$, from Eq. (5) one gets the following equation for the phase χ,

$$(2\pi)^{-1}\boldsymbol{\nabla}\chi^{(r)}=\Phi_0^{-1}\mathbf{A}+(\beta m/2e\hbar N_s^{(r)})\boldsymbol{\nabla}\Delta^{(r)}(\mathbf{r}),$$

$$(2\pi)^{-1}\boldsymbol{\nabla}\chi^{(r)}=\Phi_0^{-1}\mathbf{A}. \tag{6}$$

Integrating the phase gradient along a contour C in the bulk of the ring shown in Fig. 1 and remembering that the phase gets an increment $2\pi n$, one gets for the total flux in the ring,

$$\Phi=n\Phi_0+\Phi^{(MO)}, \quad n=0,\pm 1,\ldots, \tag{7}$$

where the additional flux $\Phi^{(MO)}$ is

$$\Phi^{(MO)}=\frac{\beta m\Phi_0}{2e\hbar}\int_{\Delta_1}^{\Delta_2}\frac{d\Delta}{N_s^{(r)}(\Delta)}. \tag{8}$$

The lowest-energy state (at least for small values of $\Phi^{(MO)}$) corresponds to $n=0$, and, therefore, the *equilibrium* flux of the ring is predicted to be finite and equal to $\Phi^{(MO)}$. A similar conclusion was made in Ref. 15.

Clearly, the finite magnetic flux and a finite electric current generating the flux are not compatible with the underlying time-reversal symmetry of the Hamiltonian of the superconductors. It is true that the state of the system may have symmetry lower that the Hamiltonian: A ferromagnet gives an example of a system with spontaneously broken T symmetry. However, the underlying T symmetry guarantees the existence of two macroscopically allowed states related to each other by the T transform: for a magnet, theses are states with reversed magnetizations. In other words, the underlying T-reversal symmetry demands permission of any sign of the parameter that quantifies the spontaneous symmetry violation.

In the case under consideration, the sign of the flux in the ring is predetermined,[15] given the geometry and the material parameters. This contradicts the time-reversal symmetry, by which the existence of the two equilibrium states with the opposite magnetic flux is compulsory. Therefore, the current in Eq. (4), which is the source of the spurious flux, must be equal to zero. (Incidentally, a finite $\Phi^{(MO)}$ would mean that there are material-dependent corrections to the flux quantization phenomena.)

These are our general arguments for why we think that the current given by Eq. (4) should not exist. Of course, the absence of the equilibrium current which would be solely due to a spatial dependence of $|\Delta|$ is well known in the microscopic theory of superconductivity.[16] Therefore, in our opinion, the predictions of the theory[12,15] contradict the general principles, and this is why we believe that the transport theory suggested in Ref. 12 is invalid.

Although the derivation of the "charge conserving transport equation" has not been presented by Marinescu and Overhauser[12] in enough detail, let us try to specify those parts in their calculations which has lead to the above contradictions with general principles. In our opinion, it is mostly related to the transport Eq. (39) of their paper.

The equation is formulated for the function $g_{\mathbf{k}\uparrow}$, which gives the occupation number of *bare* electrons [see Eqs. (37) and (38) of Ref. 12]. The transport Eq. (39) is identical to that which would be obtained by the standard procedure based on the Liouville theorem.[13] As is clear from Eq. (46), the Hamilton function $H(\mathbf{r},\mathbf{p})$, which defines $\hbar\dot{\mathbf{k}}=-(\partial H/\partial\mathbf{r})$ and $\dot{\mathbf{r}}=(\partial H/\partial\hbar\mathbf{k})$, is taken in Ref. 12 to be the BCS excitation energy

$$H(\mathbf{r},\hbar\mathbf{k})=E_k(\mathbf{r})=\sqrt{\epsilon_k^2+|\Delta(\mathbf{r})|^2}.$$

We believe that this procedure is qualitatively unsatisfactory: Due to the electron-hole quantum coherence, the bare electrons are not good semiclassical eigenstates, and the motion of wave packets built of them cannot be described by the Hamilton equation, even approximately.

The main objection of Marinescu and Overhauser to the Boltzmann equation approach[6,7] is based on an apparent nonconservation of "bare electrons" and thus of electric charge in the course of the propagation of a wave packet. As is well known, the BCS Hamiltonian itself does not support detailed conservation of the "bare electrons" while the charge conservation takes place only after the quantum averaging over the quantum states, provided the complex pair potential $\Delta=|\Delta|e^{i\chi}$ satisfies the self-consistency condition (see the Appendix for the details). It has been specifically emphasized in Refs. 6 and 7 that the continuity equation,

$$e\frac{\partial N}{\partial t}+\operatorname{div}\mathbf{j}=0,$$

bears no explicit relation to the Boltzmann equation. In superconductors, the charge conservation law plays the role of a subsidiary equation allowing one to find the phase χ of the superconducting order parameter. Again, the conservation holds only as an average over different states and the self-consistency equation plays a crucial role to support the charge conservation. Thus, the objections of Marinescu and Overhauser do not undermine the Boltzmann equation approach. Furthermore, the same result for the transport coefficient was derived using the Green's-function method.[9]

IV. EXPERIMENTAL SITUATION

Let us briefly discuss experimental results. The thermoelectric flux through a closed loop has been first measured by Zavaritskii.[17] The results exhibited no serious discrepancies with the theory of Refs. 2 and 3. However, in the later experiments[18–21] the observed thermoelectric flux was much larger than the estimates from Refs. 2 and 3.

In our opinion, the notable discrepancy between different experimental results as well between some of those results and the microscopic theory[2,3,9–11] remains a challenging problem. We present a brief review of different suggestions regarding this problem, see also p. 1856 of Ref. 21, where a discussion of possible reasons for the discrepancy is presented.

Two possible suggestions can be made regarding the source of puzzling discrepancies between the theory and the experimental results.[18–21] The first is focused on the differences between the realistic circuits used in Refs. 18–21 and the simple theoretical model.[2,3]

The complications can arise, in particular, from the near-contact regions. In Ref. 22, a thermoelectric loop consisting of an impure branch with higher T_c and a pure branch with lower T_c (passive and active branches, respectively) was considered. It was shown that if (i) the electronic thermal conductance of the passive branch is much smaller than that of the active one, and (ii) there is finite thermal flux through the contact between these branches, then there exists a large contact thermoelectric contribution to the measured flux due to the phonon drag. The reason is that the phonon thermal flux in one of the materials cannot be transformed to the electronic one abruptly at the contact. Rather, the transformation takes place within a near-contact layer of finite thickness where the phonon flux within the active branch is *much larger* than that in its bulk. As a result, the contact contribution can exceed the predictions of Refs. 2 and 3 by a factor $\sim\epsilon_F/\Theta_D$, where ϵ_F is the Fermi energy while Θ_D is the Debye energy. However this enhancement, although substantial, seems to be still too small to explain the magnitude of the effect reported in Refs. 20 and 21.

Another suggestion is that the effects observed in Refs. 18–21 can be related to some temperature-dependent magnetic fluxes produced by external sources. A possible effect of such a sort was suggested in Ref. 23 and later considered in detail in Ref. 24. This effect is related to a spatial redistribution of a background magnetic flux due to the temperature dependence of the London penetration depth, λ, of the superconductor. Since the redistribution effect is proportional to λ/L, where L is a size of the circuit, while the ''true'' thermoelectric flux within the superconducting circuit is proportional to a smaller factor, $(\lambda/L)^2$, even very weak background fields can produce a temperature-dependent flux. Indeed, the effective near-surface area $\sim\lambda L$ becomes rather large in the vicinity of T_c, where $\lambda > 1$ μm. Then, the non-screened magnetic field of the Earth, for instance, may generate a temperature-dependent magnetic flux as big as $\sim 10^3\Phi_0$.

It is worthwhile to note that if the diameter d of the wires forming the loop is much less than L the ''redistribution'' effect can be suppressed by a small factor d/L. The reason is that the contributions of the ''inner'' and the ''outer'' parts of the wire to the redistribution effect have opposite signs. We believe that it is because of the suppression of the redistribution effect that the first observation of the thermoelectric flux[17] exhibited no serious discrepancies with the theory.

To avoid the ''redistribution'' effect, the authors of Refs. 20 and 21 exploited the experimental set where the thermoelectric circuit had a shape of a hollow toroid, the thermoelectric flux being concentrated within its cavity. The measuring coil was winded along the toroid. The main idea was that the background fields were screened out by the bulk of the toroid. In our opinion, there still existed a region between the coil and the bulk of the toroid where the background field can penetrate. In particular, this region included the near-surface layer of the thickness $\sim\lambda$. Thus the measured flux obviously included a contribution of this ''outer'' region. Consequently, a temperature dependence of the penetration length brought about a temperature-dependent contribution provided that there existed some background field. The fact that, as reported in Refs. 20 and 21, the effect vanished for a homogeneous sample, in our opinion, cannot serve as proof of the absence of the redistribution effect. Indeed, if the measuring circuit is fully symmetric the contributions due to different parts of the toroid are compensated. However, for an inhomogeneous sample this symmetry will be absent, and the effect of the background field will be restored.

We believe that to check experimentally the validity of the theoretical approach[2,3] it is practical, along with further studies of the thermoelectric flux under different geometries, to study thermoelectric effects of other types. Among these effects, there is a specific interplay of a temperature gradient and a supercurrent in a superconducting film. Due to such an interplay a difference between the populations of the electronlike and holelike branches of the quasiparticle spectrum is established.[25,26,8,27] As a result, a difference U_T between the electrochemical potential and the partial chemical potential of the quasiparticles appears. According to the experimental studies,[25,28] the measured values of U_T agree with the theoretical predictions. We would like to emphasize that the measurements of U_T are *local* and consequently are much less sensitive to the above-mentioned masking redistribution effect. Another way of local measurement is the thermoelectric modification of the Josephson effect in the superconductor–normal metal–superconductor junction predicted in Ref. 29. The theoretical predictions obtained by the Boltzmann equation approach agree with the experimental results.[30]

V. CONCLUSIONS

In our opinion, the theory of thermoelectric effect in superconductors suggested by Marinescu and Overhauser in Ref. 12 is not valid. We come to this conclusion because the main contribution to the thermoelectric coefficient α calculated in Ref. 12 can be attributed to the spatial dependence of the order parameter $\Delta(\mathbf{r})$, which is due to the temperature dependence of the gap $\Delta(T)$ when $T=T(\mathbf{r})$. As such, the spatial inhomogeneity of Δ does not disturb the thermal equilibrium. We have shown that the existence of an equilibrium current $\propto\boldsymbol{\nabla}\Delta$ contradicts the time-reversal symmetry, and, therefore, it cannot contribute to the thermoelectric coefficient α. In addition, being irreversible, the current found in Ref. 12 would lead to a steady entropy production in an inhomogeneous *equilibrium* superconductor in contradiction with thermodynamics.[13,14] It is our belief that ''the electron-conserving transport equation'' proposed in Ref. 12, from which the above unphysical results are inferred, is erroneous.

We have presented the conventional point of view [6,7,31] on the issue of the charge conservation in superconductors: It is an intrinsic feature of the BCS mean-field theory that the charge conservation may be violated, i.e., $\operatorname{div}\boldsymbol{j}_n\neq 0$, for any individual quasiparticle state ψ_n. However, the total electric current $\boldsymbol{j}$, which is the sum over the quasiparticle states, is *locally* conserved, i.e., $\mathrm{div}\,\boldsymbol{j}=0$, if and when the pair potential is self-consistent (see the Appendix for details). Therefore, the Boltzmann equation supports the local charge conservation, and we disagree with the opposite claims in Ref. 12.

The results[2,3] of the Boltzmann equation approach are consistent with the experimental studies of the thermoelectrically induced branch imbalance[28] and corrections to the critical current of the Josephson junction.[30] The results of the thermoelectricallyinduced magnetic flux through a closed loop exhibit substantial scatter. Whereas the results[17] are consistent with the theory,[2,3] the giant thermoelectric flux observed in Refs. 18–21 is still not understood. We think that it is a challenging problem which is still open, and it may require an account of additional sources of thermoelectrically induced magnetic flux. However, we are convinced that within the framework of the physical picture involving quasiparticle diffusion, the Boltzmann equation approach of Ref. 2 does not in principle require any revision.

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APPENDIX: CHARGE CONSERVATION

A quasiparticle in a superconductor is described by a two-component wave function $\boldsymbol{\psi}=\binom{u}{v}$, with u and v being the electron and hole components of the quasiparticle, respectively. The stationary wave function corresponding to the energy E is found from the Bogoliubov–de Gennes equation,[16] $\hat{\mathcal{H}}\boldsymbol{\psi}=E\boldsymbol{\psi}$, with the matrix Hamiltonian

$$\hat{\mathcal{H}}=\begin{pmatrix} \xi\left(\hat{\mathbf{p}}-\frac{e}{c}\mathbf{A}\right)+U(\mathbf{r}) & \Delta \\ \Delta^* & -\xi\left(\hat{\mathbf{p}}+\frac{e}{c}\mathbf{A}\right)-U(\mathbf{r}) \end{pmatrix}. \tag{A1}$$

Here $\xi(\mathbf{p})=\mathbf{p}^2/2m-\epsilon_F$. For definiteness, we consider an isotropic s-wave superconductor so that the order parameter $\Delta(\mathbf{r})$ does not depend on the momentum. Also, $\mathbf{A}$ is the vector potential, and U is the potential energy, e.g., due to impurities or the scalar electric potential.

Generally, the eigenenergy E in Eq. (A1) may be positive or negative. In the ground state (the condensate), the states with the negative energy are filled, and the positive-energy states are empty. As usual, the excitation is defined relative to the ground state, i.e., it occupies an $E>0$ state or empties an $E<0$ state. It is a property of Eq. (A1) that the eigenfunctions corresponding to the energy E and $-E$ are related to each other as[16]

$$\begin{pmatrix} u \\ v \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -v^* \\ u^* \end{pmatrix}.$$

This property allows one to express the contribution of the negative-energy states via the positive-energy ones, and, therefore, exclude the negative energies from consideration.[16,32]

We denote

$$\psi_n=\begin{pmatrix} u_n(\mathbf{r}) \\ v_n(\mathbf{r}) \end{pmatrix}$$

as the wave function of the excitation with the energy $E_n>0$ and $f_{n,\sigma}$ as the distribution function of excitation ($\sigma=\uparrow,\downarrow$ being the spin); here n stands for the quantum numbers other than spin. The observables can be expressed via u_n, v_n, and $f_{n,\sigma}$.[16,32]

The densities of charge, $Q(\mathbf{r})$, and electric current, $\mathbf{j}(\mathbf{r})$, are given by the following expressions:

$$Q=\sum_{E_n>0}(2e|v_n|^2+(f_{n\uparrow}+f_{n\downarrow})q_n),$$
$$\mathbf{j}=\sum_{E_n>0}(-1+f_{n\uparrow}+f_{n\downarrow})\boldsymbol{j}_n, \tag{A2}$$

where the partial charge, $q_n(\mathbf{r})$, and current, $\mathbf{j}_n(\mathbf{r})$, densities are

$$e^{-1}q_n=|u_n|^2-|v_n|^2,$$

$$e^{-1}\mathbf{j}_n=\mathrm{Re}(u_n^*\hat{\mathbf{v}}u_n-v_n^*\hat{\mathbf{v}}^*v_n), \quad \hat{\mathbf{v}}=\frac{1}{m}\left(\hat{\mathbf{p}}-\frac{e}{c}\mathbf{A}\right).$$

Indeed, as is rightly stated in Ref. 12, the effective charge of the excitation q_n is, generally, a function of the coordinate $\mathbf{r}$. Accordingly, the total charge of a wave packet built as a superposition of ψ_n's varies while the packet propagates in an inhomogeneous superconductor. Of course, this violates the charge conservation on the level of an *individual* excitation. However, it is well known that the local charge conservation is restored: (i) after summation over the states, i.e., one should consider only the total charge and current rather than q_n and $\boldsymbol{j}_n$; (ii) the pair potential $\Delta=|\Delta|e^{i\chi}$ is taken self-consistently rather than as an input. Below, we elaborate upon this point.

Unlike the exact Hamiltonian of interacting particles, the BCS *effective* Hamiltonian does not commute with the particle number operator because of the presence of the anomalous average term $\Delta\hat{c}^\dagger_{\mathbf{p}\uparrow}\hat{c}^\dagger_{-\mathbf{p}\downarrow}+\mathrm{H.c.}$ For this reason, the charge conservation is not an automatic property of BCS theory. From Eq. (A1),

$$\mathrm{div}\,\mathbf{j}_n=-4\,\mathrm{Im}\,\Delta^*u_nv_n^*, \tag{A3}$$

so that lack of *detailed* current conservation, i.e., $\mathrm{div}\,\mathbf{j}_n\neq 0$, is obvious.

For the total electric current density $\mathbf{j}$, one gets from Eqs. (A2) and (A3),

$$\mathrm{div}\,\mathbf{j}=4\,\mathrm{Im}\,\Delta^*(\mathbf{r})\boldsymbol{F}(\mathbf{r}),$$

where

$$F(\mathbf{r})=\sum_{E_n>0}(1-f_{n,\uparrow}-f_{n,\downarrow})u_n(\mathbf{r})v_n^*(\mathbf{r}).$$

As discussed in Ref. 31, the pair potential $\Delta(\Delta^*)$ serves as a source (sink) of the charge. Again, the charge conservation is not guaranteed if the potentials in Eq. (A1) are arbitrary inputs. However, the Gor'kov self-consistency condition demands that

$$\Delta(\mathbf{r})=gF(\mathbf{r}),$$

where g is the coupling constant. If the complex potential Δ is self-consistent, one readily sees that div $\mathbf{j}=0$, i.e., the local charge conservation.

These are our arguments against the point of view expressed by Marinesku and Overhauser that the Boltzmann equation scheme violates the local charge conservation. To avoid confusion, another point should be mentioned. The lack of the detailed current conservation does not mean the absence of unitarity. Indeed, it generally follows from the Bogoliubov–de Gennes equation that the *quasiparticle* current $\boldsymbol{j}^{(qp)}$,

$$\mathbf{j}_n^{(qp)}=\mathrm{Re}(u_n^*\hat{\mathbf{v}}u_n+v_n^*\hat{\mathbf{v}}^*v_n),$$

is a conserved quantity, i.e., div $\mathbf{j}_n^{(qp)}=0$, for any solution to the Bogoliubov–de Gennes equation. The conservation of $\mathbf{j}_n^{(qp)}$ leads, e.g., to the conservation of probabilities in the Andreev reflection problem.

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