Boundary conditions for quasiclassical equations in the theory of superconductivity

C. J. Lambert*, R. Raimondi*†, V. Sweeney*†, and A. F. Volkov†

* School of Physics and Chemistry, Lancaster University, Lancaster LA1 4YB, U.K.
† Institute of Radioengineering and Electronics of the Russian Academy of Sciences, Moscow

(March 23, 2022)

In this paper we derive effective boundary conditions connecting the quasiclassical Green’s function through tunnel barriers in superconducting - normal hybrid (S-N or S-S’) structures in the dirty limit. Our work extends previous treatments confined to the small transparency limit. This is achieved by an expansion in the small parameter \( r^{-1} = T/2(1 - T) \) where \( T \) is the transparency of the barrier. We calculate the next term in the \( r^{-1} \) expansion for both the normal and the superconducting case. In both cases this involves the solution of an integral equation, which we obtain numerically. While in the normal case our treatment only leads to a quantitative change in the barrier resistance \( R_b \), in the superconductor case, qualitative different boundary conditions are derived. To illustrate the physical consequences of the modified boundary conditions, we calculate the Josephson current and show that the next term in the \( r^{-1} \) expansion gives rise to the second harmonic in the current-phase relation.

Pacs numbers: 72.10Bg, 73.40Gk, 74.50.+r

I. INTRODUCTION

In recent years there has been a great deal of work, both experimentally and theoretically, on the transport properties of mesoscopic superconducting - normal (N-S) hybrid structures. Various new effects have been observed including zero-bias anomalies in the differential conductance \( \hat{\sigma}_1 \), peculiar dependence on the magnetic field, re-entrant temperature behaviour \( \hat{\varepsilon}_2 \). All these phenomena are caused by the interplay of Andreev scattering at N-S interfaces and phase coherence in the mesoscopic region and are manifestations of the proximity effect, whereby superconducting correlations are induced in the normal region.

Among the various theoretical techniques used to deal with the above effects, the quasiclassical method has revealed itself as one of the most powerful approaches (see, for instance, \( \hat{\sigma}_3 \) - \( \hat{\varepsilon}_4 \)). This technique enables the study of thermodynamical and kinetic properties of superconductors (see \( \hat{\varepsilon}_5 \) and references therein), whose dimensions significantly exceed the Fermi wave length \( \lambda_F = 2\pi/k_F \) and where quantum size effects can be neglected. In the case of hybrid structures the quasiclassical equations of motion must be supplemented by appropriate boundary conditions in order to match the quasiclassical Green’s function \( \hat{\chi}_{\varepsilon} \) at N-S interfaces. These have been derived by Zaitsev \( \hat{\varepsilon}_6 \) in a general form which is valid in both the clean and dirty limits and take the form \( \hat{\varepsilon}_7 \)

\[
\hat{\chi} \left( R - \hat{R}\hat{\chi}^2 + \frac{T}{4}(\hat{s}_1 - \hat{s}_2)^2 \right) = \frac{T}{4}[\hat{s}_2, \hat{s}_1]. \tag{1}
\]

Here \( \hat{\chi} \) and \( \hat{\chi} \) are the antisymmetric and symmetric parts of the supermatrix Green’s function \( \hat{\chi} \), i.e.

\[
\hat{\chi}(\pm \mu) = \hat{\chi} \pm \hat{\chi}, \tag{2}
\]

where \( \mu = \cos(\theta) = p_\parallel/p \) and \( \theta \) is the angle between the velocity \( p/m \) of an incident electron and the vector normal to the interface. The reflection (R) and transmission (T) coefficients depend on \( \mu \) and are connected via the unitarity relation

\[
R(\mu) + T(\mu) = 1. \tag{3}
\]

As shown in \( \hat{\varepsilon}_8 \) the antisymmetric part \( \hat{\chi} \) is continuous at the interface, while the symmetric part \( \hat{\chi} \) experiences a jump determined by the commutator on the right hand side of eq.(1)

\[
[\hat{s}_2, \hat{s}_1] = \hat{s}_2\hat{s}_1 - \hat{s}_1\hat{s}_2. \tag{4}
\]

The matrix elements of \( \hat{\varepsilon}_9 \) are the retarded (advanced) Green’s functions \( \hat{\varepsilon}_9^R(A) \) and the Keldysh Green’s function \( \hat{\varepsilon}_9 \)

\[
\hat{\varepsilon}_9 = \begin{pmatrix} \hat{\varepsilon}_9^R & \hat{\varepsilon}_9^A \end{pmatrix}. \tag{5}
\]

Following the usual convention, we denote two-by-two matrices in the Nambu space by a “hat” (\( \hat{\varepsilon}_9 \)) symbol and the four-by-four supermatrices by a “check” (\( \hat{\varepsilon}_9 \)) symbol. The Keldysh Green’s function \( \hat{\varepsilon}_9 \) describes the kinetic effects and, by exploiting the normalization property, \( \hat{\varepsilon}_9^R \hat{\varepsilon}_9^A \) is related to the matrix distribution function \( \hat{\varepsilon}_9 \) via

\[
\hat{\varepsilon}_9 = \hat{\varepsilon}_9^R \hat{\varepsilon}_9^A. \tag{6}
\]

In what follows we will adopt the convention introduced by Larkin and Ovchinnikov, according to which the matrix \( \hat{\varepsilon}_9 \) can be chosen to be diagonal, with \( \hat{\varepsilon}_9 = f_0\hat{1} + f_\parallel\hat{\sigma}_z \).

The boundary conditions \( \hat{\varepsilon}_9 \) are valid in both the clean and dirty limit. We recall that in the dirty limit \( l \ll
The layout of our paper is as follows. As a preliminary step, in the next section, we consider the case of two normal regions separated by a barrier. In the following section we turn our attention to the superconducting case. In section IV we compute the Josephson current in the presence of the modified boundary conditions. Our conclusions are finally stated in section V. To simplify the notation in the following we will drop the explicit $\mu$ dependence of $r$, and only reinstate it whenever necessary.

II. NORMAL CONDUCTOR WITH A BARRIER

The case of two normal conductors (N-I-N) separated by a barrier was analyzed by Laikhtman and Luryi [11, 12]. We present here a derivation of the effective boundary conditions which differs from that presented in [11] and is applicable also to the more general case when one or both conductors are in the superconducting state (S-I-N and S-I-S). In the case of normal conductors, eq. (4) implies the following boundary condition

$$f_2(\mu) = T f_1(\mu) + R f_2(-\mu)$$

where $f_{1,2} = (f_0 + f_z)_{1,2}$ is the usual distribution function, as it is clear by recalling the definitions of the functions $f_0$ and $f_z$ in eq. (6) (see also [3]). Note also that, in the normal case, eq. (11) can be easily derived by means of simple counting arguments. By considering the symmetric ($s$) and antisymmetric ($a$) parts of $f$, one rewrites the boundary condition (11) in the form

$$- r a(0) = [s] \equiv s_2(0) - s_1(0),$$

where we have made use of the continuity of the anti-symmetric part $a$ at the boundary.

In order to find a spatial dependence of the distribution function, one has to solve the Boltzmann kinetic equation, in the relaxation time approximation in terms of $s$ and $a$ reads

$$s' = - a/\mu \equiv - b$$

$$\mu^2 b' = < s > - s$$

where to make our notation more compact $s' \equiv l \partial_z s$ and, we assume for simplicity that the mean free path, $l$, is the same on both sides of the barrier. Eliminating $s$ from eqs. (13, 14), we can write the equation for $b$ as

$$\mu^2 b'' - b = - < b > + B_0 \delta(z/l)$$

which is valid for all $z$. The function $B_0(\mu) \equiv B_0$ determines the jump in the derivative $b'$ at $z = 0$

$$B_0 = \mu^2 [b'] = [s > - s] = r \mu b(0, \mu) - < r \mu b(0, \mu) >$$

The subscript $\infty$ means that $|z| \gg l$ (the interface is located at $z = 0$, see Fig.1). However, close to the interface, one should keep all the terms in the expansion of $\hat{g}$ because the coefficients $R$ and $T$ entering the boundary condition (1) depend on $\mu$. In the dirty limit, all higher terms ($n \geq 2$) in the expansion of $\hat{g}$ decay exponentially away from the interface because the coefficients $R$ and $T$ enter the boundary condition (1) as $[\partial \mu s]$. In the dirty limit, all higher terms ($n \geq 2$) in the expansion of $\hat{g}$ decay exponentially with $z/l$, and it would be desirable to obtain a matching condition at the interface which involves the asymptotic functions $\hat{a}_\infty$ and $\hat{s}_\infty$ only. Such a problem was considered by Kupriyanov and Lukichev [14]. They showed that the boundary condition (1) reduces then to

$$\hat{a}_\infty = \hat{a}_{1\infty} \equiv \hat{a}_\infty$$

$$\hat{a}_\infty = 3/2 < \mu/r(\mu) > [\hat{s}_{2\infty}, \hat{s}_{1\infty}].$$

Here $r(\mu) = 2R(\mu)/T(\mu)$ and the angular brackets mean the angle averaging

$$< \mu/r(\mu) >= \int_0^1 d\mu \mu/r(\mu).$$

The main aim of the present paper is to show that eq. (5) is valid only to lowest order in an expansion in the small parameter $r^{-1}$, i.e. in the limit of a low transparency barrier, and consequently in the case of an arbitrary barrier transmission, eq. (5) can be used only for a qualitative description.

FIG. 1. Schematic picture of the structure studied in the text.

The subscripts $\infty$ or $\mu$ mean the angle averaging.

$\xi_{N,S}$, $l$ is the mean free path, $\xi_{N,S}$ are the coherence lengths in the N and S regions, respectively) the angular dependence of the matrix $\hat{g}$ can be taken into account by keeping only the first two terms in an expansion in Legendre polynomials $P_n(\mu)$. The first two terms in the expansion of $\hat{g}$ can be then related to each other. Far away from the interface this relation can be written down as

$$\hat{a}_\infty = - l \mu \hat{s}_\infty \partial_z \hat{s}_\infty.$$  

(7)
where the last equality follows from eq.(12). We single out the asymptotic part of \( b(z) \) and \( s(z) \)
\[
b(z) = b_\infty + \delta b(z), \quad s(z) = s_\infty + \delta s(z)
\]
(17)
in such a way that the functions \( b_\infty \) and \( s_\infty \) do not depend on \( \mu \) and are connected to each other via the relation (see eq.(12))
\[
b_\infty = -s'(\pm \infty).
\]
(18)

It follows from eq.(14) that the average of \(< \mu^2 b >\) does not depend on the coordinate (this amounts to the conservation of the current) and therefore can be evaluated from the asymptotic part
\[
< \mu^2 b > = \frac{1}{3} b_\infty = < \mu^2 b(0, \mu) >.
\]
(19)

As a result eq.(13) can now be written for the function \( \delta b \) decaying at \( |z| \to \infty \)
\[
\mu^2 \delta b'' - \delta b = -< \delta b > + B_0 \delta(z/l).
\]
(20)

By performing a Fourier transform, we obtain for the Fourier component \( \delta b_q \)
\[
\delta b_q = m_q (< \delta b > - B_0)
\]
(21)
and hence for the average
\[
< \delta b_q > = \frac{q^2}{1 - <m_q>} < m_q \mu^2 B_0 >,
\]
(22)

where \( m_q = 1/(1 + \mu^2 q^2) \), \(< m_q > = \arctan(q)/q \).

By performing the inverse Fourier transform, we find the magnitude of \( b(z, \mu) \) at \( z = 0 \)
\[
b(0, \mu) = b_\infty + \int_{-\infty}^{\infty} \frac{dq}{2\pi} m_q \left( \frac{q^2}{1 - <m_q>} < m_q r(\mu) \mu^3 b(0, \mu) > - r(\mu) \mu b(0, \mu) \right).
\]
(23)

Eq.(23) is an integral equation for \( b(0, \mu) \). It can be rewritten in the form
\[
\tilde{b}(\mu)(1 + r(\mu)/2) = 1 + \int_{0}^{1} d\mu_1 r(\mu_1)\mu_1 K(\mu, \mu_1)\tilde{b}(\mu_1)
\]
(24)

where
\[
\tilde{b}(\mu) = b(0, \mu)/b_\infty
\]

By a little manipulation of the boundary condition (12) we get
\[
- r\mu b(0, \mu) = [s_\infty] + [\delta s]
\]
(25)

where \([s_\infty] \equiv s(\infty) - s(-\infty)\).

Here the jump \([\delta s] = \delta s_2(0) - \delta s_1(0)\) and taking into account the continuity of \( \delta b \) at \( z = 0 \), we obtain from (13)
\[
[\delta s] = \int_{-\infty}^{\infty} dz \delta b(z) = \delta b_{q_0}
\]
(26)

where \( q_0 \equiv 0 \). By using eq.(21) to express \( \delta b_{q_0} \) and taking into account both eqs.(25) and (26), after angle averaging, we arrive at the desired effective boundary condition
\[
- 3 < r(\mu) \mu^3 \tilde{b}(\mu) > b_\infty = [s_\infty] .
\]
(27)

Once the solution of the integral equation \( \tilde{b}(\mu) \) is known, eq.(23) provides a relation between \( b_\infty \) and the jump of the symmetric part \([s_\infty] \). Such a relation is useful in evaluating the current density \( j \), which can be expressed in terms of \( b_\infty \) as
\[
j = \frac{\sigma}{2el} \int_{-\infty}^{\infty} dq b_\infty
\]
(28)

where \( \sigma = 2e^2 N_0 v F l/3 \) is the conductivity, \( N_0 \) being the single particle density of states per spin. If the symmetric part of the distribution function is in equilibrium on both sides of the barrier, then
\[
[s_\infty] = th[(\epsilon + eV)\beta] - th[(\epsilon - eV)\beta]
\]
(29)

where \( 2V \) is the voltage drop across the barrier, \( \beta = 1/2T \). As a result, the barrier resistance per unit area becomes
\[
R_b = (2V/j) = \frac{3l}{\sigma} < r(\mu) \mu^3 \tilde{b}(\mu) > .
\]
(30)

This formula gives a relationship between the barrier resistance \( R_b \) and the reflection and transmission coefficients. The function \( \tilde{b}(\mu) \) must be found from eq.(24). In the 3-dimensional case eq.(30) reads
\[
R_b = R_{60} < r(\mu) \mu^3 \tilde{b}(\mu) >
\]
(31)

where
\[
R_{60} = \frac{9\pi^2 \hbar}{k_F^2 e^2}.
\]

The integral equation (24) must be solved numerically, but before describing the numerical solution, it instructive to consider few limiting cases, where an analytical approach is possible.
A. Weak barrier

This means that \( r \ll 1 \) (this condition should be fulfilled for angles not too close to \( \pi/2 \)). Then, it is seen from eq. (24) that

\[
\tilde{b}(\mu) \approx 1
\]

(32)

and

\[
R_{bw} = R_{b0} < r\mu^3 >.
\]

(33)

For example, in the case of a thin barrier, modelled by a delta-like potential at \( z = 0 \), we have that

\[
r(\mu) = \frac{s^2}{\mu^2}
\]

(34)

and we obtain

\[
R_{bw} = R_{b0} \frac{s^2}{2}
\]

(35)

where \( s = \sqrt{2U_b w/(v_F \hbar)} \); \( U_b, w \), and \( v_F \) being the barrier height, barrier width, and Fermi velocity, respectively.

B. Strong barrier

This means that \( r \ll 1 \). To lowest order the solution to eq. (24) is obtained as

\[
\tilde{b}(\mu) = C/(r\mu)
\]

(36)

where \( C \) is a \( \mu \)-independent constant which can be determined by exploiting the fact that the average \( < \mu^2 b(0, \mu) > \) does not depend on \( z \). In fact, as follows from eq. (19)

\[
C = (3 < \mu/r >)^{-1}
\]

which lead to a barrier resistance equal to

\[
R_{bs} = R_{b0} (9 < \mu/r >)^{-1}.
\]

(37)

The above results coincides with that obtained by Ref. [10], as can be noted from eq. (4). For a thick barrier, we get

\[
R_{bs} = R_{b0} \frac{4}{9} s^2.
\]

(38)

We note that if we were to use, wrongly, eq. (37) in the case of a weak barrier, we would obtain the expression (38) instead of (36). The ratio of these two results, \( 9/8 \), is close to 1. However, this ratio does not contain any small parameter. This conclusion is in agreement with that of Ref. [11].

One can obtain a correction \( \tilde{b}_1(\mu) \) to the solution (36). To see this, we seek a solution in the form

\[
\tilde{b}_1(\mu) = \chi(\mu)/(r\mu).
\]

(39)

Substituting (39) into eq. (24), we obtain an integral equation for \( \chi(\mu) \)

\[
\frac{1}{3\mu r < \mu/r >} - 1 = -\frac{\chi(\mu)}{2\mu} + \int_0^1 d\mu K(\mu, \mu_1) \chi(\mu_1).
\]

(40)

It follows from eq. (40) that the function \( \chi \) is of the order 1, i.e. it is small compared to \( C \) in eq. (36). Therefore, in order to obtain the effective boundary condition connecting \( b_\infty \) and \([s_\infty]\) in the general case, we must solve the integral equation (24).

C. Numerical results

In the appendix we discuss how the integral equation is solved and here we merely illustrate the numerical results. Figure 2 shows the behaviour of the function \( \tilde{b}(\mu) \) for different values of the parameter \( s \). We see that at small and large \( s \) the numerics yield the expected behaviour discussed above. It is perhaps worth noting that for a planar barrier the Landauer formula yields

\[
R_{barrier} = \frac{\hbar}{2e^2} \left( \frac{2\pi}{k_F^2} \right) < \mu T(\mu) R(\mu) >^{-1}.
\]

(41)

which agrees with eq. (37) and is smaller than eq. (33) by a factor of 8/9. Figure 3 shows the behaviour of the barrier resistance as a function of \( s \) normalized to the \( s = 0 \) resistance.

In the next section, we now turn to the analysis of the more general case of a S-I-N or S-I-S interface.
III. GENERAL CASE: S-I-N AND S-I-S

In this section we analyze boundary conditions for the quasiclassical matrix Green’s function $\tilde{g}$ in the dirty limit. We will start with the boundary conditions for $\tilde{g}$ obtained by Zaitsev in the general case and, as in the preceding section, find a relation connecting the asymptotic values of $\tilde{g}$ at $|z| \gg l$ on the two sides of the barrier. In contrast to the previous case, the presence of anomalous components in the matrix Green’s function leads to a nonlinear equation governing $\tilde{g}$. In order to simplify the problem, we note that in the case of a weak barrier (i.e. $R \to 0$, $T \to 1$) the boundary condition for the symmetric parts $\delta_{1,2}$ reduces to a continuity condition at the interface. It is then physically relevant to confine our analysis to the most interesting case of a strong barrier and obtain a relation between $\tilde{a}$ and $\tilde{s}$ using the expansion in the small parameter $r^{-1}$.

By assuming that $r \gg 1$, eq.(1) can be cast in the form

$$\tilde{b}(0, \mu) \approx \frac{1}{2r\mu} [\delta s_2, \delta s_1] \left( 1 - \frac{1}{2r} (\delta s_2 - \delta s_1)^2 \right)$$

where as in the previous section we introduced the function $\tilde{b} = \tilde{a}/\mu$. Eq.(12) is valid up to terms of the order $r^{-2}$. From the equations for $\tilde{s}$ and $\tilde{b}$ (see below), one can obtain the relation corresponding to eq.(19), with $\tilde{b}$ replaced by the supermatrix $\tilde{b}$. We then proceed as before by writing $\tilde{s}$ and $\tilde{b}$ as the sum of a fast decaying and an asymptotic part

$$\tilde{s} = \tilde{s}_\infty + \delta \tilde{s}, \quad \tilde{b} = \tilde{b}_\infty + \delta \tilde{b}$$

where we assume $\delta \tilde{s} \ll \tilde{s}_\infty$. By multiplying eq.(12) by $\mu^2$ and using the representation (43), we perform the angle average of eq.(12) to obtain

$$\frac{1}{3} \tilde{b}_\infty = [\delta s_2, \delta s_1] \left( < \frac{\mu}{2r} > - < \frac{\mu}{4r^2} > (\delta s_2 - \delta s_1)^2 \right)$$

$$+ < \frac{\mu}{2r} (\delta s_2, \delta s_1) + [\delta s_2, \delta s_1] > .$$

Here $\delta s_{2,1} = \delta s_{2,1}(0^\pm)$. The problem is then reduced to the calculation of the functions $\delta s_{2,1}$. We start by writing the equation for $\tilde{g}$ in the space interval $0 < |z| \ll \xi_{N,S}$. It is then sufficient to retain only the gradient term and the collision integral in the self-consistent Born approximation for the impurity scattering. As a result the equation for $\tilde{g}$ reads

$$2\mu \tilde{g}' = \tilde{g} < \tilde{g} > - < \tilde{g} > \tilde{g} .$$

By rewriting eq.(15) in terms of $\tilde{b}$ and $\tilde{s}$ we get

$$2\mu^2 \tilde{b}' = \tilde{s} < \tilde{s} > - < \tilde{s} > \tilde{s}$$

$$2\tilde{s}' = \tilde{b} < \tilde{s} > - < \tilde{s} > \tilde{b}$$

together with the conditions deriving from the normalization condition $\tilde{g} \tilde{g} = 1$,

$$\tilde{s} \tilde{s} = 1, \quad \tilde{s} \tilde{s} + \tilde{b} \tilde{s} = 0 .$$

Using the expansion (43) we obtain the equations for the deviations $\delta \tilde{b}$ and $\delta \tilde{s}$ in the form

$$\mu^2 \delta \tilde{b}' = - \tilde{s}_\infty (\delta \tilde{s} - < \delta \tilde{s} >)$$

$$\delta \tilde{s}' = - \tilde{s}_\infty \delta \tilde{b}, \quad \tilde{s}' = - \tilde{s}_\infty \tilde{b}_\infty .$$

where we have used the relations

$$\delta \tilde{b} \tilde{s}_\infty + \tilde{s}_\infty \delta \tilde{b} = 0, \quad \tilde{s}_\infty \delta \tilde{s} + \delta \tilde{s} \tilde{s}_\infty = 0$$

$$\tilde{s}_\infty \tilde{s}_\infty = 1$$

which follow from (48). From eqs.(49,50) we finally get the equation for $\delta \tilde{b}$

$$\mu^2 \delta \tilde{b}'' - \delta \tilde{b} = - < \delta \tilde{b} > + \tilde{B}_0 \delta(z/l) .$$

One can easily check that the matrix $\tilde{B}_0$ is connected to the Fourier component $\delta \tilde{b}_{q_0}$ (where $q_0 \equiv 0$) by

$$\tilde{B}_0 = < \delta \tilde{b}_{q_0} > - \tilde{b}_{q_0} .$$

From eq.(53) we find the Fourier components

$$\delta \tilde{b}_{q} = m_q \left( \frac{q^2}{1 - < m_q >} < m_q \mu^2 \tilde{B}_0 > - \tilde{B}_0 \right)$$

and the value of $\delta \tilde{b}(0, \mu)$ at $z = 0$ reads
\[ \delta b(0, \mu) \equiv \tilde{b}(0, \mu) - b_{\infty} = -\int_{-\infty}^{\infty} \frac{dq}{2\pi} m_q \left( \frac{q^2}{1 - \langle m_q \rangle} - m_q \mu^2 \delta b_{q_0} - \delta b_{q_0} \right). \]

(56)

To close the above equation, we need to connect \( \tilde{b}(0, \mu) \) and \( b_{\infty} \). To lowest order in \( r^{-1} \), the boundary condition \([44]\) yields

\[ \tilde{b}(0, \mu) \approx (2r \mu)^{-1} [s_{2\infty}, \delta s_{1\infty}], \]

\[ b_{\infty} \approx 3 < \mu/2r > [s_{2\infty}, \delta s_{1\infty}]. \]

(57)

which when substituted into \([56]\) yields the equation

\[ \delta b_{q_0} = -\chi(\mu) \tilde{b}_{\infty} \]

(59)

then the function \( \chi \) satisfies the integral equation \([44]\) and the Fourier component \( \delta \tilde{b}_{q_0} \) is related to \( \delta \tilde{s}_{1,2} \) by integrating eq. \([50]\) from \(-\infty\) to 0 and from 0 to \( \infty \), to yield

\[ \delta \tilde{s}_2 = \tilde{s}_{2\infty} \delta \tilde{b}_{q_0}/2, \quad \delta \tilde{s}_1 = -\tilde{s}_{1\infty} \delta \tilde{b}_{q_0}/2. \]

(60)

Substituting eqs. \([60]\), \([50]\), and \([57]\) into eq. \([44]\) we finally obtain

\[ \frac{1}{3} \beta = [s_{2\infty}, \delta s_{1\infty}] \left( < \mu \frac{1}{2r} > - < \mu \frac{1}{4r^2} > (s_{2\infty} - \delta s_{1\infty})^2 \right) \]

\[ + 3 < \mu \frac{1}{2r} > < \mu \frac{1}{4r^2} > [s_{1\infty}, \tilde{s}_{2\infty} \delta s_{1\infty} \tilde{s}_{2\infty}]. \]

(61)

The above equation is the effective boundary condition for the matrix \( \tilde{g} \) in the dirty limit. The first term in \([61]\) coincides with the boundary condition obtained in Ref. \([10]\).

IV. THE JOSEPHSON EFFECT

As a simple application of the above boundary condition, we now derive an expression for the Josephson current. To this end we rewrite eq. \([61]\) in the following way

\[ \frac{1}{3} \beta = A[\tilde{g}_2, \tilde{g}_1] + B[\tilde{g}_2, \tilde{g}_1][\tilde{g}_2, \tilde{g}_1] \]

(62)

where we have identified the symmetric part \( \tilde{s} \) with the Green’s function \( \tilde{g} \) and dropped the \( \infty \) suffix and the curly brackets indicate the anticommutator

\[ \{\tilde{g}_2, \tilde{g}_1\} = \tilde{g}_2 \tilde{g}_1 + \tilde{g}_1 \tilde{g}_2. \]

The constants \( A \) and \( B \) can be read off from eq. \([61]\)

\[ A = < \mu/2r > -2 < \mu/4r^2 > 

\]

and

\[ B = < \mu/4r^2 > -3 < \mu \chi/2r > < \mu/2r >. \]

In deriving eq. \([62]\) we have made use of the normalization condition \( \tilde{g} \tilde{g} = 1 \). The current through the junction is determined by the formula

\[ I = -\frac{\sigma}{16e\ell} \int_{-\infty}^{\infty} dc \text{Tr}(\tilde{\sigma} \tilde{b}) \]

(63)

where \( \tilde{b} \) is the appropriate Keldysh component. In the absence of a voltage across the junction, the Keldysh component of the supermatrix \( \tilde{g} \) reduces to

\[ \tilde{g} = f_0(\tilde{g}^{R} - \tilde{g}^{A}) \]

(64)

where \( f_0 = 2\tanh(e/2T) \) is the equilibrium distribution function. The Keldysh component of the product of the commutator and the anticommutator reads

\[ ([\tilde{g}_2, \tilde{g}_1][\tilde{g}_2, \tilde{g}_1])_k = [\tilde{g}_2, \tilde{g}_1][\tilde{g}_2, \tilde{g}_1]_k + [\tilde{g}_2, \tilde{g}_1]_k [\tilde{g}_2, \tilde{g}_1] \]

(65)

with the Keldysh component of the commutator

\[ [\tilde{g}_2, \tilde{g}_1]_k = f_0(\tilde{g}_2^{R} + \tilde{g}_1^{R}) \]

(66)

and of the anticommutator

\[ \{\tilde{g}_2, \tilde{g}_1\}_k = f_0(\{\tilde{g}_2^{R} - \tilde{g}_1^{R}\} - \{\tilde{g}_2^{A} - \tilde{g}_1^{A}\}). \]

(67)

To calculate the current we represent the matrices in the Nambu space as

\[ \tilde{g}_{1,2}^{(A)} = G^{(A)} \tilde{\sigma}_x + i F^{(A)}(\cos(\phi_{1,2}) \tilde{\sigma}_y + \sin(\phi_{1,2}) \tilde{\sigma}_x) \]

where \( \phi_{1,2} \) are the phases of the superconducting order parameter on the two sides of the junction. The current in eq. \([63]\) can be written then as the sum of three terms
\[ I_A = -iI_{0,A} \sin(\phi_1 - \phi_2) \int_{-\infty}^{\infty} d\varepsilon f_0 (F_1^R F_2^R - F_1^A F_2^A), \]  

(68)

\[ I_B^{(1)} = -iI_{0,B} 2 \sin(\phi_1 - \phi_2) \int_{-\infty}^{\infty} d\varepsilon f_0 (F_1^R F_2^R G_1^R G_2^R - F_1^A F_2^A G_1^A G_2^A), \]  

(69)

and

\[ I_B^{(2)} = -iI_{0,B} \sin(2(\phi_1 - \phi_2)) \int_{-\infty}^{\infty} d\varepsilon f_0 ((F_1^R F_2^R)^2 - (F_1^A F_2^A)^2). \]  

(70)

In the above formulae, \( I_{0,A} = (eN_0 v_F/2) A \), \( I_{0,B} = (eN_0 v_F/2) B \), \( e \) is the electron charge, \( N_0 \) the single particle density of states per spin, and \( v_F \) the Fermi velocity. By using the expression for \( G^{R(A)} \) and \( F^{R(A)} \) at equilibrium

\[ G^{R(A)} = \frac{\epsilon}{\sqrt{(\epsilon)^2 - \Delta^2}}, \quad F^{R(A)} = \frac{\Delta}{\sqrt{(\epsilon)^2 - \Delta^2}}, \]

where \( \epsilon \equiv \epsilon \pm i0^+ \), and assuming that the gap \( \Delta \) is equal on both sides of the junction, we obtain, at \( T = 0 \), the following result for the current

\[ I = eN_0 v_F \Delta \pi \left[ (2A + B) \sin(\phi) - B \sin(2\phi) \right] \]  

(71)

where \( \phi = \phi_2 - \phi_1 \). Note that by confining ourselves to the lowest order in \( r^{-1} \), we would obtain for the Josephson current the standard result of tunneling theory

\[ I = (e^2 N_0 v_F < \mu/r >) \frac{\pi \Delta}{2e} \sin(\phi) = R_{bs} \frac{\pi \Delta}{2e} \sin(\phi) \]  

(72)

with \( R_{bs} \) given by eq. (68). Allowance for higher order terms in the barrier transparency leads then to higher harmonics in the current phase relation. This result has a simple physical interpretation. We know that in the case of a superconductor - normal metal - superconductor structure, the Josephson effect manifests itself with a triangular shape of the current - phase relation. For this case the Fourier decomposition has an infinite number of harmonics. Hence it is clear that higher order terms in the \( r^{-1} \) expansion must possess harmonics of higher order. It may be useful at this point to notice that very recently Josephson current measurements have been carried out in structures in which it is possible to control experimentally the barrier transparency. The experimental results show indeed that by tuning the barrier strength it is possible to observe higher harmonics \( 13 \).

V. CONCLUSIONS

We have analyzed the boundary condition for the quasiclassical matrix Green’s function \( \tilde{g} \) at the S-N or S-S’ boundaries in the dirty limit. Effective boundary conditions have been derived with the aid of an expansion in the barrier transmittance. The first term of the expansion reproduces the results previously derived by Kupriyanov and Lukichev \( 14 \). In the normal case, the boundary conditions for a barrier of arbitrary transparency may be obtained from the solution of an integral equation. In the superconducting case, due to the non-linear nature of the equations, we have been able to compute the next-to-leading term in the \( r^{-1} \) expansion. In this case the evaluation of this term also entails solving an integral equation. To illustrate the physical consequences of the modified boundary condition, we have calculated the Josephson current for a tunnel junction between two superconductors at equilibrium and shown that higher order harmonics arise. Given the relevance that the lowest order boundary expression (cf. eq. (11)) has played in the study of mesoscopic normal-superconducting hybrid structures, our result calls for a reexamination of the various effects occurring in mesoscopic hybrid structures. In particular, one may envisage a straightforward generalization of the circuit theory of Nazarov \( 14 \) to allow for the new boundary condition. This will be the subject of a future investigation.

ACKNOWLEDGMENTS

Financial support from the EPSRC is gratefully acknowledged.

APPENDIX A: SOLVING THE INTEGRAL EQUATION: TECHNICAL DETAILS

The variable \( \mu \) is discretized \( \mu_i = i\Delta_\mu \) with \( i = 1, ..., N \) and \( \Delta_\mu = 1/N \). By introducing a vector \( b_i = \hat{b}(\mu_i) \), the integral equation (24) acquires the matrix form

\[ b_i(1 + r_i/2) = 1 + \sum_{j=1}^{N} K_{ij} r_j \mu_j b_j \]  

(A1)

where \( r_i = r(\mu_i) \) and

\[ K_{ij} = \int_{-\infty}^{\infty} \frac{dq}{2\pi} m_q(\mu_i) m_q(\mu_j) \frac{q^2 \mu_i^2}{1 - < m_q }}>. \]  

(A2)

The solution \( b_i \) can then be obtained as

\[ b_i = \sum_{j=1}^{N} (A^{-1})_{ij} \]  

(A3)
where the matrix $A_{ij}$ is given by

$$A_{ij} = \left(1 + \frac{r_i}{2}\right)\delta_{ij} - \Delta_\mu K_{ij} r_j \mu_j. \quad (A4)$$