Superfluid $^3$He and heavy-fermion superconductors near surfaces and interfaces

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We discuss various model boundary conditions that supplement the quasi-classical equations of superconductivity, and we review their application to superfluid $^3$He and unconventional superconductors in contact with walls and interfaces.

Nous discutons différentes conditions aux limites modèles, qui complètent les équations classiques de supraconductivité, et passons en revue leurs applications à $^3$He superfluide et aux supraconducteurs non conventionnels en contact avec des parois et des interfaces.


1. Introduction

The Bardeen–Cooper–Schrieffer (BCS) theory (weak-coupling theory) and its extensions, such as Eliashberg’s strong-coupling theory, are invaluable for calculating phenomena in superconductors and superfluid $^3$He. These theories owe their quantitative success in part to expansion parameters like $1/k_F\xi_0$, $k_B T_c/\hbar\omega_{\text{phon}}$, and $\sqrt{m/M}$, which are indeed small, in the order of $10^{-1}$–$10^{-2}$ in conventional superconducting materials and in $^3$He. Moreover, these theories are useful tools in basic materials research. Theoretical interpretation of measurements in the superconducting state can yield information on fundamental material parameters. For example, McMillan and Rowell’s analysis (1) of tunneling data gives detailed information about the electron–phonon coupling, information that is difficult to obtain by other means. In this paper we argue that superconducting and superfluid phenomena are valuable aids for measuring material parameters of interfaces and surfaces. Typical parameters of interest are the (in general) spin-dependent electronic transmissivity and reflectivity of boundaries and the degree of roughness of surfaces and interfaces. Systems of interest include interfaces between conventional and unconventional superconductors, superconductors in contact with magnetic materials, $^3$He in contact with walls, and the interface between $^3$He and a saturated $^3$He–$^4$He mixture. Finally, the superconducting or superfluid phenomena that we have in mind as probes of the interface are proximity effects, surface depairing of the order parameter, Josephson coupling in S–N–S junctions or other weak-link geometries, and size effects in the tunneling density of states of artificially fabricated thin films and layered structures.

An accurate and tractable theory of superconductors, including a realistic description of surfaces and interfaces, is necessary for the above program. Recently, substantial progress has been made in this direction by incorporating surface and interface scattering into the quasi-classical theory of superconductivity and superfluidity. There is a large amount of literature on surface and interface effects based on Gorkov’s equations with appropriate boundary conditions. However, even with modern computers these equations can be solved only for a restricted number of situations, unless simplifying assumptions are made that often spoil the accuracy of the results. In particular, Gorkov’s equations are too complicated to be solved in any realistic geometry with a spatially varying order parameter or magnetic field, because they carry too much irrelevant quantum-mechanical detail.

The quasi-classical approach of Eilenberger (2) and Larkin and Ovchinnikov (3) is the most efficient and most powerful formulation of the weak- and strong-coupling theories of superconductivity (and superfluid $^3$He). Together with its extensions to nonequilibrium phenomena (4), the newer theory has been successfully applied to a variety of problems that would otherwise be unmanageable. The quasi-classical theory has proven superior in both numerical and analytical calculations. The original formulation by Eilenberger and Larkin and Ovchinnikov, however, does not cover electron scattering at surfaces and interfaces. To include surface scattering and interface transmission, one must supplement the quasi-classical theory with boundary conditions that connect the quasi-classical propagators for the scattered quasi-particles; this boundary condition depends on the reflection and transmission amplitudes and roughness parameters of the interface. Such boundary conditions have been derived by various authors for a number of model boundaries. We discuss them in Sect. 2 and review a number of applications to superfluid $^3$He and unconventional superconductors.

2. Boundary conditions

The quasi-classical theory reduces the full quantum-mechanical wave equations (or Gorkov’s equations) to ordinary differential equations along classically allowed paths. The classical paths are straight trajectories of high-speed particles, for nearly all applications in bulk superconductors or superfluid $^3$He. The trajectories are labeled by a direction $\hat{p}$ (the hat indicates a unit vector) for quasi particles near the Fermi surface with momentum $\sim p_F\hat{p}$. Interfaces and surfaces as well as impurities scatter quasi particles and change the directions of their momenta. This effect is incorporated into the theory by boundary conditions relating quasi-classical propagators along different directions. A smooth interface, for example, conserves the compo-
ment of momentum parallel to the surface; the corresponding boundary condition then couples the propagators for sets of only four momentum directions with one another. A diffusive interface, on the other hand, mixes propagators with all momentum directions. At present, no all-encompassing boundary condition is known for the quasi-classical theory, and one has to rely on models for the surface scattering that depend upon a small number of phenomenological parameters. Our expectation is that such descriptions of boundaries are reasonably accurate. Below we discuss several models of boundaries and interfaces suitable for superfluid $^{3}\text{He}$ and heavy-fermion superconductors.

The boundary conditions for the quasi-classical equations are well established in two limiting cases, in the normal state and just below $T_{c}$ where terms that are linear in the order parameter provide an adequate description. In the normal state, the quasi-classical theory leads to Boltzmann–Landau’s transport equation, where the boundary conditions have been studied extensively (5). The linearized theory of superconductivity can be mapped onto a classical ballistics problem and the boundary conditions lifted from the corresponding theory, as shown by deGennes (6). DeGennes’ correlation–function method, including surface effects, has been formulated in terms of Boltzmann’s transport equation for a classical distribution function by Lüders and Usadel (7). An important feature of the boundary conditions for Boltzmann’s equation and deGennes’ theory is that they are linear in the distribution function. This simplification is unfortunately lost in the fully developed superconducting state, which we are interested in here. The distribution functions in the most general quasi-classical theory are replaced by quasi-classical propagators satisfying boundary conditions that are nonlinear, counterintuitive, and therefore difficult to interpret. It is a useful check on these more complicated boundary conditions that they must become linear in the limit $T \rightarrow T_{c}$, and must reproduce the known boundary conditions of Boltzmann’s equation. Before discussing the boundary conditions, we briefly introduce the basic notation and equations of the standard quasi-classical theory.

The central objects of the theory, the quasi-classical propagators, are $4 \times 4$ Nambu matrices $\hat{g}^{A,R,K}(\rho, R, \epsilon)$, where $\rho$ is the matrix the transport-like equations (Eilenberger’s equations), and $\mathbf{R}$ is the normal vector to the interface.

\[ \varepsilon \tau - \hat{A}, \hat{g} \] + $i\mathbf{v}_F \cdot \nabla \hat{g} = 0 \]

and are normalized according to

\[ \hat{g} \otimes \hat{g} = -\pi^2 \hat{1} \]

We faithfully follow the notation of Serene and Rainer (8) and use $\hat{g}$ as the generic symbol for quasi-classical propagators of the various kinds. The operation $\otimes$ stands for a combination of conventional matrix multiplication, the following operation in the energy and time variables:

\[ \hat{f}(\epsilon, t) \otimes \hat{g}(\epsilon, t) = \hat{f} \left( \epsilon - \frac{1}{2\tau} \frac{\partial}{\partial \tau}, t \right) \times \hat{g} \left( \epsilon + \frac{1}{2\tau} \frac{\partial}{\partial \tau}, t \right) \mid \bigg|_{t_1 = t_2 = t} \]

and a specific assignment of Keldysh indices

\[ (\hat{f} \otimes \hat{g})^{A,R,K} = \hat{f}^{A,R} \hat{g}^{A,R} \]

\[ (\hat{f} \otimes \hat{g})^{K} = \hat{f}^{R} \hat{g}^{K} + \hat{f}^{K} \hat{g}^{A} \]

\[ \hat{f} \otimes \hat{g} \]

The symbol $[\hat{f}, \hat{g}]$ denotes the commutator $\hat{f} \otimes \hat{g} - \hat{g} \otimes \hat{f}$, and the matrix $\Delta(\hat{p}, R)$ represents the self-consistent order-parameter field. We omit impurity scattering terms, external perturbations, and strong-coupling effects and assume a spherical Fermi surface. None of these simplifications leads to any relevant restrictions on the generality of the theory.

The following short description of boundary conditions for the quasi-classical propagators introduces the various models, lists the respective boundary conditions, and discusses briefly their physical motivation. For their formal derivation, we refer the reader to the original literature.

### 2.1. Transparent interfaces

The simplest boundary is a transparent interface that the quasi particles pass without being reflected or scattered. The quasi-classical propagators are then continuous across the interface:

\[ \hat{g}(\hat{p}_\text{in}, R_b) = \hat{g}(\hat{p}_\text{out}, R_b) \]

The superscripts $\text{l}$ and $\text{r}$ label the left and right sides of an interface, and $R_b$ (the index $b$ stands for boundary) is a point at the interface; we have omitted all unnecessary labels and variables. Although the propagators are continuous, the bulk materials parameters are, in general, discontinuous across the boundary and may lead, e.g., to different types of pairing on the two sides and a discontinuous change in the order parameter at the interface.

### 2.2. Specular walls

A specular wall reflects all impinging quasi particles and conserves energy and momentum parallel to the wall. The propagators are continuous along their classical trajectories, which leads at the point of reflection to the boundary condition

\[ \hat{g}(\hat{p}_\text{in}, R_b) = \hat{g}(\hat{p}_\text{out}, R_b) \]

where $\hat{p}_\text{in}$ and $\hat{p}_\text{out}$ denote a pair of incoming and outgoing momentum directions, i.e., $\hat{p}_\text{out} = \hat{p}_\text{in} - 2\Delta(\hat{p}_\text{in}, \mathbf{n})$ with $\mathbf{n}$ being the surface normal. The two boundary conditions [6] and [7] are special limits of the more general condition given in Sect. 2.3.

### 2.3. Semitransparent smooth interfaces (spin conserving)

A smooth interface conserves the parallel component of momentum in processes in which an incoming quasi particle from direction $\hat{p}_\text{in}$, for example, is reflected into the direction $\hat{p}_\text{out}$ or transmitted into the deflected direction $\hat{p}_\text{def}$ (see Fig. 1). The reflection probability $R$ depends on the incoming direction and is, within the framework of the quasi-classical theory, a phenomenological material parameter describing the interface. The quasi-classical propagators are, in general, discontinuous along the reflected and deflected trajectories, with the discontinuities determined by $R$. The first correct boundary condition for this type of interface was published by Zaitsev (9). The same result was derived independently by Kieselmann (10) using a quite different approach. Zaitsev’s and Kieselmann’s boundary condition relates the quasi-classical propagators for the four kinematically connected momentum directions, $\hat{p}_\text{in}, \hat{p}_\text{out}, \hat{p}_\text{def} = \hat{p}_\text{in}, \hat{p}_\text{def}$ (see Fig. 1), and can be written very compactly in terms of the differences, $\hat{d}^{1} = \hat{g}^{1}(\hat{p}_\text{out}) - \hat{g}^{1}(\hat{p}_\text{in})$, and the sums, $\hat{s}^{1} = \hat{g}^{1}(\hat{p}_\text{out}) + \hat{g}^{1}(\hat{p}_\text{in})$.

\[ \hat{d}^{1} + \hat{d}^{2} = 0 \]

\[ \hat{d}^{1} + \hat{d}^{2} = 0 \]

\[ \hat{d}^{1}(\mathbf{s}^\tau)^2 = i \frac{1 - R}{1 + R} \left[ \hat{s}^{1}, \mathbf{s}^\tau \otimes \left( \mathbf{\pi} - \frac{i}{2} \mathbf{s}^\tau \right) \right] \]
unconventional pairing are discussed in Sect. 3.

The boundary conditions [8] and [9] are nontrivial because they are nonlinear. Both derivations, by Zaitsev and Kieselmann, use nonstandard tricks to eliminate superfluous quantum-mechanical details from the microscopic theory of interface scattering. Zaitsev (9) has applied the boundary condition to smooth interfaces with spin-dependent scattering by quasi-particles. For a weakly transmitting interface, the authors expanded the boundary model to calculate tunneling spectra of proximity junctions (10). Applications to systems with unconventional pairing are discussed in Sect. 3.

2.4. Semitransparent smooth interfaces (spin active)

The work of Zaitsev and Kieselmann has been generalized to smooth interfaces with spin-dependent scattering by Millis et al. (2). In their theory, the interface scattering matrix for quasi particles is a phenomenological parameter. The four components \( S_{ij} \) of the \( S \) matrix are Nambu matrices in the spin and particle-hole degrees of freedom of quasi particles. For a weakly transmitting interface, the authors obtain the following boundary condition in terms of the \( S \) matrix:

\[
[10] \quad \hat{g}^{\dagger}(\hat{p}_{\text{in}}) - \hat{S}_{11}^{-1} \hat{g}^{\dagger}(\hat{p}_{\text{out}}) \hat{S}_{11} = \frac{-i}{2\pi} \left[ \hat{S}_{21} \hat{g}^{\dagger}(\hat{p}_{\text{out}}) + i\pi \hat{S}_{21} \right]
\]

\[
[11] \quad \hat{g}^{\dagger}(\hat{p}_{\text{out}}) - \hat{S}_{22} \hat{g}^{\dagger}(\hat{p}_{\text{in}}) \hat{S}_{22} = \frac{i}{2\pi} \left[ \hat{S}_{21} \hat{g}^{\dagger}(\hat{p}_{\text{in}}) + i\pi \hat{S}_{21} \right]
\]

If the matrices \( \hat{S}_{ab} \) commute with the \( \hat{g}^{\dagger} \)'s, as is the case for spin-conserving interfaces, one obtains directly from [10] and [11] the boundary conditions [8] and [9], expanded to first order in the transmission amplitude \( T \) (note that \( \hat{S}_{12} \hat{S}_{21} = T = 1 - R \) for a spin-conserving interface). The generalized magnetic boundary condition is important for heavy-fermion superconductors with a strong spin-orbit mixing. Here the classification of Cooper pairs as singlet or triplet pairs breaks down and must be replaced by what is called pseudosinglet or psuedotriplet pairs for crystals with inversion symmetry (11). An interface between two metals with different amounts of spin-orbit mixing are pseudospin active even if the interface potential conserves real spin. In this sense, even a vacuum interface between, e.g., Al and UPt3 is expected to be spin active. We drop the prefix pseudo hereafter. The magnetic boundary condition is also important for describing conventional superconductors in contact with magnetic materials and for determining the order parameter of superfluid \(^3\)He near a magnetically polarizable surface.

2.5. Diffusive walls

The first attempt to incorporate boundary roughness into the quasi-classical theory is due to Buchholtz and Rainer (12). They describe the effect of surface scattering formally by a surface \( T \) matrix, and they average the quasi-classical propagators over an ensemble of surface configurations. This procedure leads to a boundary condition for the propagators that involves an effective \( T \) matrix \( \hat{R}(\hat{p}, \mathbf{R}; \epsilon, l) \):

\[
[12] \quad \left[ \hat{g}(\hat{p}), \hat{g}(\hat{p}) \right]_\Sigma \left( 1 + \frac{i\text{sgn}(\hat{p} \cdot \hat{n})}{\pi} \hat{g}(\hat{p}) \right) = 0
\]

Equation [12] is a more recent version (13) of the boundary condition of ref. 12; it eliminates spurious unphysical solutions that were present in the older version. The effective \( T \) matrix in [12] is a function of the quasi-classical propagators and a set of material parameters characterizing the surface. Any specific model for the boundary determines the form of these functional dependences. In ref. 12, the quasi-classical \( T \) matrix was calculated for Falkovskii’s randomly rippled wall model (14), which is a two-parameter model for a fully reflecting wall with an arbitrary degree of roughness. The two material parameters describe the average height and wavelength of the surface ripples. Applications of this model to transport properties of normal metal films can be found in a recent review by Falkovskii (5), an application to unconventional pairing has been published by Buchholtz (15) and is discussed here.

2.6. Semitransparent diffusive interfaces

The simplest model for an interface with roughness is probably the thin dirty layer proposed by Culetto et al. (16). Interface roughness is simulated in this model by a disordered layer of thickness \( d \) and a quasi-particle mean free path, \( l \). For small values of \( d \), as compared with the coherence length, the only relevant parameter is the ratio \( d/l \), and one can formally let \( d \) and \( l \) go to zero keeping \( d/l = \rho \) constant. This leads to a one-parameter model for rough interfaces in which the relation between quasi-classical propagators on the two sides of the interface is given in terms of a nonlinear differential equation for an auxiliary interface propagator, \( \hat{g}_1 \):

\[ [13] \quad \hat{g}_1(\hat{p}, \mathbf{R}_s) = \hat{g}_1(\hat{p}, 0) \]

\[ [14] \quad \hat{g}_1(\hat{p}, \mathbf{R}_s) = \hat{g}_1(\hat{p}, 1) \]

\[ [15] \quad \int \frac{d\Omega'}{4\pi} \hat{g}_1(\hat{p}', \xi), \hat{g}_1(\hat{p}, \xi) \int \frac{d^2\mathbf{R}}{4\pi} \hat{g}_1(\hat{p}'', \xi), \hat{g}_1(\hat{p}, \xi) \int \frac{d\Omega''}{4\pi} \left[ 2\pi i \frac{\hat{g}_1(\hat{p}, \xi)}{\rho} \frac{d}{d\xi} \hat{g}_1(\hat{p}, \xi) = 0 \right] \]

For \( \rho = 0 \) (\( l = \infty \), this boundary condition turns into the continuity condition [5] for a transparent interface; and for \( \rho = \infty \) (\( l = 0 \), [13]–[15] describe a nontransparent, diffusively re-
flecting interface. One can combine the thin dirty layer with the models 2.2–2.4 and thereby generalize these models to include interface roughness. For example, a thin dirty layer augmented by a specular wall models a fully reflecting wall with an arbitrary degree of diffusiveness (17). A semitransparent smooth interface (as in Sects. 2.3 and 2.4) coated on one or both sides with thin dirty layers is a model for an interface with complex reflection and transmission properties described by an interface $S$ matrix and a roughness parameter. The thin dirty layer model has been applied to study consequences of interface roughness on the proximity effect in conventional superconductors in the original paper (16). Its application to unconventional pairing is reviewed in this paper.

2.7. Thick interdiffusion layers

The quasi-classical equations can be generalized to systems with strong variations in quasi-particle parameters like $v_F$, $k_F$, etc. This is possible as long as the variations take place on a length scale that is large compared with the atomic scale (e.g., $|\nabla v_F|/v_F << k_F$). The generalized theory (18) is capable of describing an interface where material parameters change gradually (within many atomic layers) from one metal to the other. Such gradual changes can be caused by strong interdiffusion of the two metals. We know of no calculations using the model of a thick interdiffusion layer. We include this model in our listing because it is of interest for future applications in the theory of unconventional (and also conventional) superconductors.

Spatial variations of the Fermi velocity, the impurity concentration, and the pairing interaction are taken into account simply by replacing $v_F$ in the standard quasi-classical theory by $v_F(R)$, etc. Only spatial variations of the Fermi momentum, which need a more careful treatment, lead to an additional term in the transport-like equation. The generalized equation is

$$[\varepsilon^2 - \hat{\Delta}, \hat{g}] + i[v_F(R) \cdot \nabla \hat{g} + i \frac{v_F(R)}{k_F(R)} \times [\nabla k_F(R) - (\hat{p} \cdot \nabla k_F(R)) \hat{p}] \cdot \partial \hat{g} = 0$$

The last term on the left-hand side is due to deviations of the classical trajectories from straight lines.

3. Applications

In this section we review the relatively small number of papers employing the various model boundary conditions for the quasi-classical theory to study systems exhibiting unconventional pairing. Our expectation is that the discoveries of superconductivity in heavy-fermion superconductors, as well as recent advances in fabrication of artificial superconducting and magnetic materials, will generate many more applications of quasi-classical methods in interpreting the properties of these exotic materials.

The first application of quasi-classical methods to systems exhibiting unconventional pairing was the calculation by Ambegaokar et al. (19), using deGennes’ formulation in terms of classical correlation functions, of the effects of surface scattering of quasi particles on the order parameter of superfluid $^3$He near both perfectly reflecting and fully diffusive walls. This calculation showed the surface depairing effect on an unconventional (non-s-wave) order parameter and provided microscopic support for orientation effects of boundaries on the $l$ vector in $^3$He–A. Kjällman et al. (20) used the same linearized quasi-classical theory to study the distortion of the superfluid order parameter and the reduction of the transition temperature of $^3$He in narrow slabs and cylindrical channels (i.e., dimensions in the order of the coherence length) with diffuse scattering at the walls. Recently, Tokuyasu et al. (2) investigated thin slabs of a superconductor in contact with a fully reflecting, magnetically active interface, as a model for a thin superconducting film deposited on a ferromagnetic insulator. For conventional superconducting films of thickness $d$, this restricted geometry combined with magnetic wall leads to a reduction in the superconducting transition temperature, which depends on a single surface “pair-breaking” parameter, $\sigma \sim \tan(\theta/2)k_F/d$, where $\theta$ is a material parameter describing the strength of the spin-flip reflection probability.

The first implementation of the full (not linearized) quasi-classical theory to study surface pair breaking in a system with unconventional pairing was carried out by Buchholz and Zwicknagl (21) for a model $p$-wave superconductor (Balian–Werthamer state) in contact with a specular wall. These authors calculated the distortion of the order parameter near the wall, the most dramatic effect being the suppression of the component of the order parameter perpendicular to the wall. They also calculated the local density of states (observable in tunneling experiments) and the spectrum of surface states that are bound to the wall by the order-parameter field. The order parameter, as calculated by Buchholz and Zwicknagl, was used by Kieselman and Rainer (22) to determine the reflection probabilities of Andreev scattering at the wall. The results of ref. 21 were generalized for superfluid $^3$He–B to include diffusive scattering by Buchholz (15), using the randomly rippled wall model, and by Zhang et al. (17), using the thin dirty layer model. The results for the order parameter were essentially identical in both models and showed clearly the additional depairing effect, on the parallel components of the order parameter, that results from surface roughness. Starting from the results of ref. 17, Zhang et al. (23) studied the effect of surface roughness on Andreev scattering. More recently, Zhang et al. (24) have added surface supercurrents to the calculation of the surface order parameter to investigate the role that superflow may have in inducing phase transitions at surfaces, analogous to the vortex phase transitions known to exist in rotating $^3$He–B.

The effects of transmission of quasi particles through a nonmagnetic interface separating a conventional (s-wave) superconductor and a triplet $p$-wave superconductor have been studied by Ashauer et al. (25). These authors calculate the suppression of the conventional superconductivity by a bulk unconventional superconductor in a proximity contact. Ashauer (26) has also examined the proximity effect between $^3$He and a $^3$He–$^4$He mixture and has calculated the superfluid contribution to the surface tension and its dependence on the hypothetical transition temperature of the mixture. Lee and Rainer (27) have used the same model of a $^3$He–$^4$He mixture interface to calculate the critical Josephson current of a weak link provided by pores filled with the mixture.

The Josephson effect in unconventional superconductors has been investigated by Millis et al. (28, 29) using the quasi-classical model for a spin-active smooth interface. For a weak link connecting a conventional, singlet superconductor to an unconventional, triplet superconductor, these authors obtain the result of Sauls that Josephson tunneling, with critical currents of

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3D. Rainer, lecture notes 1980.

4T. Tokuyasu, D. Rainer, and J. A. Sauls. Submitted to Phys. Rev. B.
conventional magnitude, is possible if the interface is time-reversal invariant and rotationally symmetric, provided that the spin-orbit transmission amplitude is comparable to the spin-independence amplitude. This result is relevant for triplet models of the superconducting order parameter of heavy-fermion metals.

Finally, we remark that the boundary condition for a perfectly reflecting, smooth magnetic surface has been used by Toku-yasu et al. to model thin superconducting slabs in contact with ferromagnetic insulating substrates. These authors calculate the tunneling density of states, which reveals a spin splitting of the gap edge resulting from the exchange field in the ferromagnet and the tunneling of conduction electrons into the classically forbidden insulating region.

4. Conclusions

We have summarized our work with various collaborators on the boundary conditions for the quasi-classical theory and some applications to systems exhibiting unconventional pairing. In contrast to conventional superconductors, surface effects are much more important in these exotic materials because of surface depairing. Finally, we remark that our results for unconventional superconductors assume that these materials are accurately described as Fermi liquids with $T_c \ll T_F$. In heavy-fermion metals it is not yet clear if this condition is satisfied; if not, we will have to wait for the development of a more general microscopic theory of superconductivity.