

Self-consistent microscopic theory of surface superconductivity

Robert J. Troy* and Alan T. Dorsey

Department of Physics, University of Virginia, McCormick Road, Charlottesville, Virginia 22901
(Received 23 November 1994; revised manuscript received 1 February 1995)

The electronic structure of the superconducting surface sheath in a type-II superconductor in magnetic fields $H_{c2} < H < H_{c3}$ is calculated self-consistently using the Bogoliubov-de Gennes equations. We find that the pair potential $\Delta(x)$ exhibits pronounced Friedel oscillations near the surface, in marked contrast with the results of Ginzburg-Landau theory. The local density of states near the surface shows a significant depletion near the Fermi energy due to the development of local superconducting order. We suggest that this structure could be unveiled by scanning-tunneling-microscopy studies performed near the edge of a superconducting sample.

The study of surface superconductivity was initiated some thirty years ago by the seminal work of Saint-James and de Gennes,¹ who predicted that a magnetic field parallel to a superconductor-vacuum interface would nucleate a superconducting "surface sheath" before the onset of superconductivity in the bulk of the material. By solving the linearized Ginzburg-Landau (GL) equations subject to the boundary condition that the *normal derivative* of the order parameter vanishes at the interface, they found an approximately Gaussian order parameter profile localized within a coherence length ξ of the interface; the critical field for this surface superconductivity is $H_{c3} = 1.69H_{c2}$, where H_{c2} is the bulk critical field for the Abrikosov flux-lattice phase.¹⁻³ This phenomenon has been confirmed by measurements which observe a vanishing surface resistance at fields above H_{c2} (for a review of the early experiments, see Refs. 2 and 3). Due to the presence of the superconducting nucleus there is also a depletion of states near the Fermi energy, which is reflected in a suppression of the tunneling conductivity at low bias, an effect which has been observed in certain Pb-Bi and Sn-In alloys.⁴

While the theory of surface superconductivity is quite complete within the framework of GL theory, there remain several interesting unanswered questions and problems which can only be addressed within a microscopic theory. (1) In a microscopic theory the natural boundary condition for the quasiparticle wave functions is that they vanish at the superconductor-vacuum interface, so that superconducting pair potential also vanishes at the interface. If we naively apply this microscopic boundary condition to the macroscopic GL equations, and solve the linearized GL equations subject to the boundary condition that the *order parameter* vanishes at the interface (rather than its *derivative*) we find $H_{c3} = H_{c2}$; i.e., there is no surface superconductivity. However, we cannot go back and infer that the microscopic equations do not possess surface superconducting solutions; by the same token, it cannot be taken for granted that the surface-superconducting solutions of GL theory (with the zero derivative boundary condition) prove the existence of surface-superconducting solutions of the microscopic theory. The two approaches, valid at different length scales,

utilize different boundary conditions, and it is generally difficult to connect the two.⁵ Whether surface superconductivity exists within a realistic microscopic model of superconductors remains an open question. (2) The GL equations are derived using the *quasiclassical phase approximation*, which neglects the effects of Landau-level quantization of the electronic states, and is valid in low fields. In very high magnetic fields the Landau-level quantization can become important. Recent theoretical work has predicted de Haas-van Alphen oscillations in $H_{c2}(T)$, as well as possible reentrant superconductivity in very high magnetic fields.⁶ Might there be reentrant surface superconductivity which precedes the reentrant bulk superconductivity? Again, the answer would require a microscopic calculation which does not invoke the quasiclassical phase approximation. (3) On a parallel note, Landau-level quantization in the presence of a surface produces magnetic edge states, which have been the subject of intensive study in the context of the integer and fractional quantum Hall effects.⁷ Understanding the role that edge states play in surface superconductivity may help us in answering the basic question: Why is superconductivity favored at a surface? (4) In the mixed state of type-II superconductors the spatial variation of the pair potential can produce a rich structure in the local density of states (LDOS),^{8,9} which can be measured directly using a scanning-tunneling microscope (STM).¹⁰ Analogous structure in the LDOS will be produced by the superconducting surface sheath, which should be observable using a STM. Such STM studies would provide the first direct image of the surface sheath, and provide valuable information about the pair potential profile and *local* electronic structure; all of the previous experimental studies have only explored *averaged* properties, such as the pair potential averaged over the sample.²⁻⁴ We note that previous attempts at a microscopic theory of surface superconductivity have been confined to analytical¹¹⁻¹³ or numerical¹⁴ solutions of the linearized gap equation. All of these works invoke the quasiclassical phase approximation, and make approximations which are equivalent to assuming that the derivative of the pair potential vanishes at the surface; they therefore do not address the issues which we have raised above. There have been no

calculations of the LDOS.

In this paper we will discuss our first attempts at addressing some of the questions raised above by numerically solving the microscopic Bogoliubov-de Gennes (BdG) equations² self-consistently, in a magnetic field with realistic boundary conditions at the superconductor-vacuum interface. We retain fully the Landau-level (and edge-state) structure. To make the calculations computationally tractable we assume a two-dimensional geometry, which is also a good approximation for many layered superconductors (see below). Our results show that the microscopic BdG equations do indeed admit a superconducting solution localized near the surface, for fields $H > H_{c2}$. The pair potential vanishes at the surface, but rises rapidly and eventually looks like the GL solution; there is a narrow “boundary layer” near the surface in which the GL solutions break down. However, unlike the GL solution we find large-amplitude Friedel-like oscillations in the pair potential. Our LDOS calculations show a suppression at low energies in the regions where the pair potential is a maximum; it should be possible to resolve this structure in a STM measurement. The remainder of this paper is organized as follows: Following a brief review of the BdG formalism, we will discuss our numerical methods. We will then present our results for the self-consistent pair potential and the LDOS, for a particular choice of parameters. Further details of these calculations will appear in Ref. 15.

I. THE BOGOLIUBOV-de GENNES EQUATIONS

The BdG equations² for the quasiparticle amplitudes $u_i(\mathbf{r})$ and $v_i(\mathbf{r})$ with excitation energy $\epsilon_i > 0$ (measured relative to the Fermi energy) are

$$\begin{pmatrix} \mathcal{H}_e & \Delta(\mathbf{r}) \\ \Delta^*(\mathbf{r}) & -\mathcal{H}_e^* \end{pmatrix} \begin{pmatrix} u_i(\mathbf{r}) \\ v_i(\mathbf{r}) \end{pmatrix} = \epsilon_i \begin{pmatrix} u_i(\mathbf{r}) \\ v_i(\mathbf{r}) \end{pmatrix}, \quad (1)$$

with $\Delta(\mathbf{r})$ is the pair potential. The single-particle electron Hamiltonian is

$$\mathcal{H}_e = \frac{1}{2m^*} \left[-i\hbar\nabla - \frac{e}{c}\mathbf{A}(\mathbf{r}) \right]^2 + V(\mathbf{r}) - E_F, \quad (2)$$

where E_F is the Fermi energy, $V(\mathbf{r})$ is the surface potential, and $\mathbf{A}(\mathbf{r})$ is the vector potential (we do not consider any effects of spin). Any effects of the band structure of the material are subsumed into the effective mass m^* . The pair potential must be determined self-consistently from the solutions of the BdG equations as

$$\Delta(\mathbf{r}) = g \sum_{\epsilon_i \leq \hbar\omega_D} v_i^*(\mathbf{r})u_i(\mathbf{r})[1 - 2f(\epsilon_i)], \quad (3)$$

where g is the BCS attractive coupling, ω_D is the Debye frequency, and $f(\epsilon)$ is the Fermi function. The vector potential must also be determined self-consistently using Ampère’s law with the current density determined by the quasiparticle wave functions.^{2,9} Once the quasiparticle wave functions have been computed self-consistently, we can calculate the thermally broadened local density of

states,

$$N(\mathbf{r}, E) = - \sum_i \left[|u_i(\mathbf{r})|^2 f'(E - \epsilon_i) + |v_i(\mathbf{r})|^2 f'(E + \epsilon_i) \right], \quad (4)$$

with $f'(\epsilon) = \partial f / \partial \epsilon$. This quantity is proportional to the local differential tunneling conductance which is measured in a STM experiment.

We now take the magnetic field $\mathbf{H} = H\hat{z}$ to be parallel to the vacuum-superconductor interface at $x = 0$, with the superconductor occupying the half-space $x > 0$. As we will eventually be interested in modeling quasi-two-dimensional materials, we will neglect dispersion in the z direction. Assuming the interface to be perfectly impenetrable, we have $u(x = 0) = v(x = 0) = 0$ [and therefore $\Delta(x = 0) = 0$]. In the Landau gauge $\mathbf{A} = (0, Hx, 0)$ the BdG equations are translationally invariant in the y direction, and so we factor out this dependence as

$$\Delta(\mathbf{r}) = e^{i2X_0y/l^2} \Delta(x), \quad (5)$$

$$\begin{pmatrix} u(\mathbf{r}) \\ v(\mathbf{r}) \end{pmatrix} = e^{i(x_0 \pm X_0)y/l^2} \begin{pmatrix} u_{x_0,n}(x) \\ v_{x_0,n}(x) \end{pmatrix}. \quad (6)$$

Here $l^2 = \hbar c / eH$ is the magnetic length, X_0 is the orbit center for the pair potential, $-\infty < x_0 < \infty$ is the orbit center for u ($-x_0$ is the orbit center for v), and $n = 0, 1, 2, \dots$ is a Landau-level index which counts the number of nodes of the wave functions; the sums in Eqs. (3) and (4) are over all (x_0, n) . We are left with a set of coupled one-dimensional equations for $u_{x_0,n}(x)$ and $v_{x_0,n}(x)$. Because of our boundary condition at $x = 0$ the corresponding eigenvalues $\epsilon_n(x_0, X_0)$ will depend upon the positions of the orbit centers, unlike the bulk case in which the energies are degenerate with respect to x_0 . The effort involved in solving these equations can be substantially reduced by finding both positive and negative energy solutions for $x_0 > 0$ and taking advantage of the transformation^{2,9} $\epsilon \rightarrow -\epsilon$, $u(\mathbf{r}) \rightarrow v^*(\mathbf{r})$, $v(\mathbf{r}) \rightarrow -u^*(\mathbf{r})$ to convert the negative energy solutions for $x_0 > 0$ into positive energy solutions for $x_0 < 0$.

II. METHOD OF SOLUTION

The BdG equations are solved iteratively, as follows. We start with an initial guess for the amplitude and the phase of the pair potential, taken from GL theory, for instance. We then fix the orbit center x_0 and calculate the wave functions and energies in the range $0 < \epsilon < \hbar\omega_D$, by writing the BdG equations as a set of finite-difference equations. The lattice spacing is determined so that variations on the scale of π/k_F can be resolved. The resulting matrix equations are sparse, and can be diagonalized using standard packages (we use LAPACK). This process is then repeated for new values of x_0 . The range of values of x_0 is determined so that the highest energy states (of energy $\hbar\omega_D$) are approaching their bulk behavior, i.e., becoming independent of x_0 , which occurs

at $x_0 = l[2(E_F + \hbar\omega_D)/\hbar\omega_c]^{1/2}$, with $\hbar\omega_c = \hbar eH/m^*c$ the cyclotron energy. The spacing between these points is again determined by requiring that structure on the scale of π/k_F can be resolved. Once all of the wave functions have been determined, the amplitude of the pair potential is recalculated from Eq. (3) by summing over x_0 and n . The phase of the pair potential is also recalculated by using the self-consistency condition for the vector potential.^{2,9} The entire process is then repeated until the relative error in the order parameter between successive iterations is less than 0.02.

Several cases were tested to determine the reliability of the algorithm. When $\Delta(\mathbf{r}) = 0$ we have reproduced the wave functions and spectrum for electrons in a constant magnetic field in the presence of an impenetrable surface.¹⁶ The eigenvalues for states with orbit centers at the surface ($x_0 = 0$, $X_0 = 0$) were within 1% of those found analytically; for x_0 large the usual bulk Landau levels were obtained. We have also used several different initial guesses for the pair potential, including the GL form and a constant pair potential. The final results are insensitive to the form of the initial pair potential, but convergence is expectedly slower for the constant pair potential. In the results shown here we have used a Gaussian profile centered near the surface $x = 0$ for the initial pair potential amplitude, and we have used for our initial X_0 the value obtained in GL theory.²

III. RESULTS

We have chosen to model a layered (i.e., two-dimensional) material whose parameters obey the weak-coupling BCS relations. We took the Fermi surface to be cylindrical with $m_{x-y}^* \ll m_z^*$ and $m_{x-y}^* = 2m$, where m is the electron mass. Assuming the zero temperature gap $\Delta(0) = 1.1$ meV and the zero temperature coherence length $\xi(0) = 100$ Å yields a Fermi velocity of $v_F = \pi\Delta(0)\xi(0)/\hbar = 5.27 \times 10^6$ cm/s, $k_F^{-1} = 11.0$ Å, and $E_F = 15.8$ meV. With $\hbar\omega_D = 15$ meV and $gN(0) = 0.30$, the zero field critical temperature is $T_c = 7.25$ K, and the zero temperature quasiclassical critical field is $H_{c2}(0) = 0.722\phi_0/2\pi\xi^2(0) = 2.38$ T.¹⁷ These parameters are similar to those used by Gygi and Schlüter in their study of the core structure of vortices in NbSe₂,⁹ which showed good agreement with STM measurements.¹⁰ Our Fermi energy is probably unrealistically low; it was chosen to make our computations tractable, and thus represents a compromise between numerical efficiency and realistic modeling. We do not expect any qualitative changes in our results for larger values of E_F .

We have chosen to present results for a temperature of 2 K ($T/T_c = 0.28$), and a magnetic field of 4 T [$H/H_{c2}(T) = 1.83$], so that $l = 128$ Å and $\hbar\omega_c = 0.23$ meV. With the parameters given above this means that we must keep a total of 134 bulk Landau levels. Using the criteria stated above, we need 350 lattice points in a sample $30l$ wide. A second impenetrable wall is placed at $x = 30l$ to aid in normalization, but we ignore any nucleation at that surface. The finite difference version of the BdG equations is then a 700×700 matrix equation.

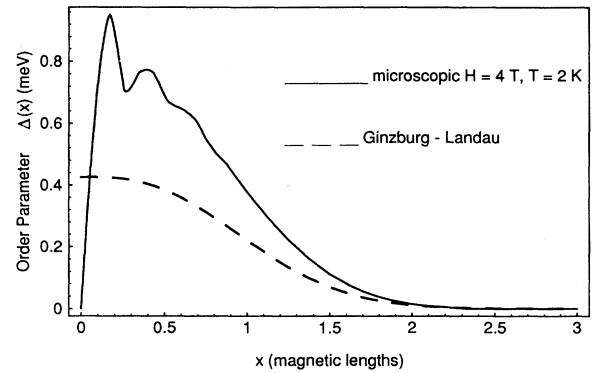


FIG. 1. The pair potential amplitude calculated from the BdG equations, compared with the GL result (Ref. 18), at $H/H_{c2}(T) = 1.83$ and $T/T_c = 0.28$. The BdG solution vanishes at the surface and exhibits strong Friedel oscillations as a result of the impenetrable wall at $x = 0$.

The range of x_0 is not limited to lie within the sample; indeed, the states with $x_0 < 0$ are precisely the edge states. We use 800 orbit centers ranging from $x_0 = -35l$ to $35l$, which ensures that all of the states in question have attained their bulk values. Convergence was reached after five iterations, requiring 10 h on an IBM RS 6000/370 workstation.

IV. DISCUSSION

Our result for the amplitude of the self-consistent pair potential is given in Fig. 1; this result is plotted against the GL theory result, taken from Ref. 18. The pair potential does indeed vanish at the material surface and exhibits large Friedel oscillations away from the surface, with a period which is approximately $\pi/k_F = 34$ Å. Such oscillations of the pair potential near a surface also occur in zero field,^{5,15} and in the vicinity of a magnetic

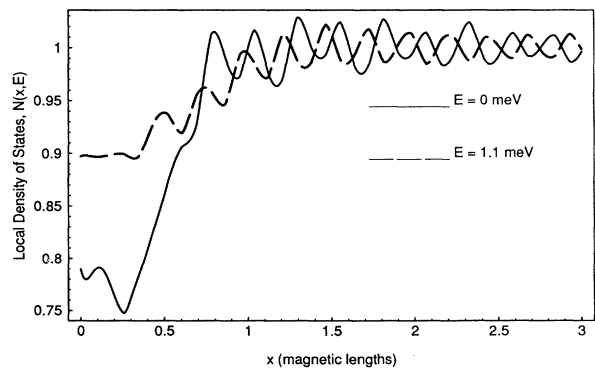


FIG. 2. Thermally averaged local density of states as a function of position (normalized to the normal local density of states), at $H/H_{c2}(T) = 1.83$ and $T/T_c = 0.28$. For $E = 0$ the electron states have been pushed away from the material surface by the nucleation of the pair potential. At higher energies ($E = 1.1$ meV) the effect becomes smaller, and vanishes altogether at very high energies.

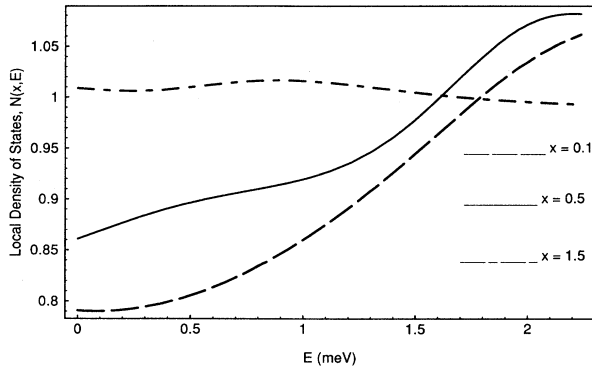


FIG. 3. Thermally averaged local density of states as a function of energy (normalized to the normal local density of states), at $H/H_{c2}(T) = 1.83$ and $T/T_c = 0.28$. Close to the surface ($x = 0.1, 0.5$) there is a significant depletion in the LDOS at low energies, as well as an enhancement at energies above the bulk gap of $\Delta(0) = 1.1$ meV. When $x = 1.5$ the LDOS approaches its bulk normal-state value.

impurity,¹⁹ and are the result of pair-breaking by the surface and impurity. The self-consistent orbit center for the pair potential is $X_0 = 0.19l$, which is close to the position of the first maximum of the amplitude of the pair potential. The existence of a surface sheath at these relatively high magnetic fields is not inconsistent with variational calculations at $T = 0$,^{12,13} which give $H_{c3}(0) \geq 1.95H_{c2}(0)$. We have repeated our calculations at a field of 4.5 T, and find that the maximum amplitude of the pair potential is decreased. Likewise, increasing the temperature results in a smaller amplitude. We have not been able to pin down $H_{c3}(T)$ using our method, as achieving self-consistency becomes delicate when the pair potential is small. The phase boundary is best determined by direct numerical solution of the linearized gap equation,²⁰ which will also enable us to attack the question of reentrant behavior in H_{c3} .

The resulting change in the electronic structure can be seen in the thermally broadened local density of states, $N(x, E)$, which we have plotted at constant energy, Fig. 2, and constant position, Fig. 3. In Fig. 2 we see that at low energies the wave functions have a reduced amplitude in the vicinity of the maximum of the pair potential. Due to the presence of local superconducting order,

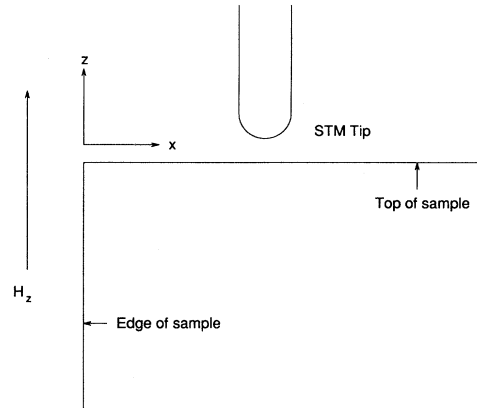


FIG. 4. Schematic diagram for the proposed STM measurement of the local density of states. The magnetic field is parallel to the edge of the sample; the pair potential will vary spatially in the x direction, with a maximum at about a coherence length from the surface. The STM tip would be swept across the top of the sample, and measure the local density of states $N(E, x)$, which will exhibit a depletion at low energies in regions where the pair potential is the largest.

in Fig. 3 we see that close to the surface there is a suppression in the density of states at low energies, with a corresponding enhancement at energies above the bulk gap. Farther from the surface we obtain the bulk normal density of states. We expect that this structure could be resolved by a STM measurement which would scan from the interior of a sample to a surface parallel to the applied magnetic field; we have illustrated this schematically in Fig. 4. Such a measurement would provide the first direct observation of the superconducting surface sheath.

ACKNOWLEDGMENTS

We would like to thank Dr. S. Girvin, Dr. A. MacDonald, Dr. C.-Y. Mou, and Dr. J. D. Shore for useful discussions, and Dr. W. Pesch for bringing Ref. 14 to our attention. This work was supported by NSF Grant No. DMR 92-23586 and Jeffress Trust Grant J-289. A.T.D. gratefully acknowledges the Alfred P. Sloan Foundation for financial support.

* Present address: St. Anne's Belfield School, 2132 Ivy Road, Charlottesville, VA 22901

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