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Andreev Bound States, Surfaces and Subdominant Pairing in High T_c Superconductors

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A characteristic feature of the BCS theory of superconductivity is the quantum-mechanical coherence of particle and hole states. Direct observation of particle-hole coherence in unusual superconducting materials is a strong indication of traditional superconductivity. We use the Fermi liquid theory of superconductivity to study the implications of particle-hole coherence on properties of d-wave superconductors near surfaces. Typical surface phenomena are the suppression of the superconducting order parameter, surface bound states associated with Andreev reflection, anomalous screening currents, and spontaneous breaking of time-reversal symmetry. We review these phenomena and present new results for the effects of surface roughness.

It is generally accepted that high T_c cuprate superconductors are strongly correlated metals whose superconducting state is not well described by mean field theory or equivalent methods designed for weakly correlated electrons. On the other hand, theoretical methods for studying strongly correlated electrons, developed in the context of high T_c superconductivity, are still far from being able to calculate subtle effects such as the influence of surface roughness on superconducting properties. A theory which is not restricted to weakly correlated systems but nevertheless can be used to study a broad range of superconducting phenomena including the effects of surfaces is the Fermi liquid theory of superconductivity. The most useful formulation of this theory is in terms of *quasiclassical transport equations* derived in 1968 by Eilenberger[1] and Larkin & Ovchinnikov[2] for superconductors in equilibrium, and generalized to nonequilibrium phenomena a few years later[3; 4]. The Fermi liquid theory of superconductivity combines the motion of quasiparticles along classical trajectories (*external degrees of freedom*) with the quantum dynamics of *internal degrees of freedom* which are the spin and the particle-hole degrees of freedom. This combination of classical and quantum physics is the proper generalization of Landau's semi-classical transport equation for normal Fermi liquids to the superconducting state. Like Landau's theory the leading order terms in the expansion parameters of Fermi liquid theory are low-energy compared with the Fermi energy or long wavelength compared with the atomic scale, e.g. $1/k_f\xi_0$, where $\xi_0 = \hbar v_f/2\pi T_c$[5; 6]. The equations of the Fermi liquid theory of superconductivity consist of the quasiclassical transport equation for the quasiclassical propagator, $\check{g}(\vec{p}_f, \vec{R}; \epsilon, t)$, Eilenberger's normalization condition for $\check{g}$, the self-consistency equations for the self-energies, $\check{\sigma}(\vec{p}_f, \vec{R}; \epsilon, t)$, and boundary conditions at surfaces and interfaces[7; 8; 9; 10]. An important part of the self-energy is the superconducting order parameter $\check{\Delta}$; it establishes the coherence between particles and holes. We refer to recent reviews [5; 6] and the original publications [1; 2; 3] for the definitions and physical interpretation of the quasiclassical propagators and self-energies, and the detailed form of the quasiclassical transport equations and boundary conditions.

In quasiclassical theory an excitation approaches the surface along a classical (straight) incoming trajectory and is reflected into an outgoing trajectory. At a specular surface the outgoing trajectory is fixed by the conservation of parallel momentum (ideal reflection). Surfaces with roughness lead to a statistical distribution of outgoing trajectories. This classical picture for the kinematics of an excitation must be supplemented by the quantum equations for the internal degrees of freedom. The internal state along a classical trajectory is obtained by solving the quasiclassical matrix transport equations on this trajectory. The most important quantum effect in this context is Andreev reflection[11], which is caused by rotations of the internal state of an excitation from *particle-type* to *hole-type* (or vice versa). This may lead to a velocity reversal (retro-reflection) or to trapping of an excitation (Andreev bound states). Particle-hole rotation and Andreev reflection are controlled by the off-diagonal self-energy (order parameter), and carry information about the anisotropy and symmetry of the order parameter. A typical trajectory at a (120) surface of a $d_{x^2-y^2}$ superconductor is shown in Fig.1. For this trajectory repeated Andreev reflections lead to a bound state with excitation energy $\epsilon = 0$, a zero-energy bound state (ZBS), which is a robust feature of the spectrum depending only on the change in sign of the order parameter along the trajectory[12].

A quasiclassical study of surface effects in unconventionally paired superfluids (e.g. p-wave pairing in ^{3}He) was published by Ambegaokar et al.[13], who used deGennes' method of classical correlation functions[14] to study the suppression and reorientation of the order parameter. DeGennes' method is a predecessor of the full quasiclassical theory applicable to the limit $\Delta \to 0$. The order parameter and the tunneling spectra at ideal surfaces of a p-wave superconductor in the Balian-Werthamer state were calculated by Buchholtz and Zwicknagl[15]. These authors found surface bound states and, in particular, a ZBS for trajectories at perpendicular incidence; for the Balian-Werthamer state the conditions of the Atiyah-Patodi-Singer theorem are fulfilled only at perpendicular incidence. The ZBS shifts for all other angles of incidence.

The chances for observing zero-energy bound states are more favorable for d-wave pairing[16]. In this case the ZBS exists at an ideal surface for a whole range of angles. For (110) surfaces and $d_{x^2-y^2}$ pairing in bulk this range covers all angles of incidence, while the range collapses to zero at the (100) and (010) surfaces. These results were confirmed and extended by several authors[17; 18; 19]. The ZBS leads to a zero-bias conductance peak which was observed in tunneling experiments on cuprate high-T_c superconductors by several groups[20; 21; 22; 23; 24]. The zero-bias conductance peak has been identified convincingly as due to tunneling into the ZBS [25; 26; 27]. Hence, the existence of a ZBS associated with an unconventional d-wave order parameter in high-T_c superconductors seems well established by experiment as well as theory.

The order parameter near T_c is determined by the solution of the linearized gap-equation at T_c. The symmetry of this solution defines the dominant pairing channel; subdominant pairing channels may mix spontaneously in bulk superconductors below a transition temperature $T_{sub} < T_c$. However, no

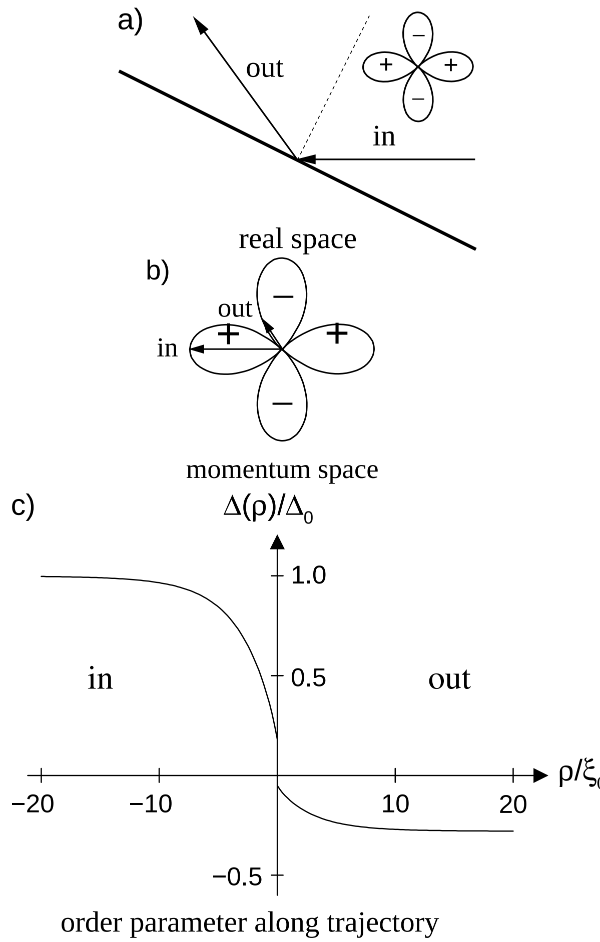

FIG. 1 Formation of an Andreev bound state at an ideal (120) surface. An excitation moving along the trajectory in Fig.1a experiences changes in the order parameter $\Delta(\vec{p}_f, \vec{R})$, where $\vec{p}_f$ is the momentum of the excitation, and $\vec{R}$ is the position. These changes are due to 1) the depletion of the order parameter near the surface and 2) the change in momentum direction of the excitation when hitting the surface. The change in momentum direction leads to a sign change of the order parameter as shown in Fig.1b. Fig.1c shows a sketch of the order parameter along the trajectory of the excitation.

such phase transition has been observed in high-T_c superconductors. Thus, either there is no attractive channel other than the dominant one, or the subdominant order parameter is blocked in bulk by the dominant order parameter. In the latter case, a subdominant superconducting order parameter which is not subject to surface pair breaking (s-wave pairing, etc.) may be stabilized at surfaces where the dominant order parameter is suppressed. This possibility has stimulated theoretical work by Matsumoto and Shiba[18] and Buchholtz et al.[19] on the mixing of subdominant pairing channels at surfaces. Of particular interest is the possibility of time-reversal symmetry breaking by the subdominant order parame-

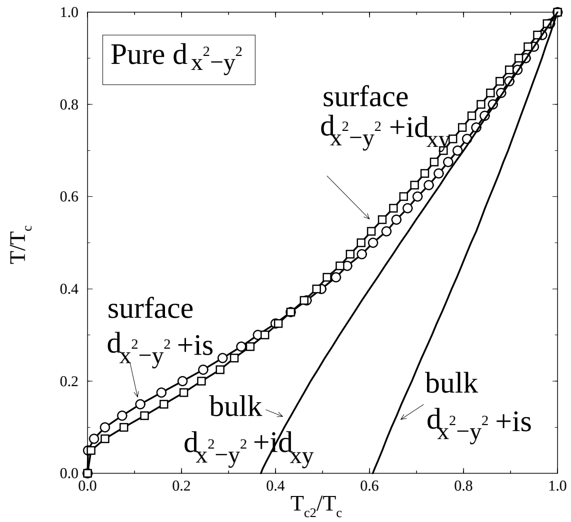

FIG. 2 Calculated phase diagram for the surfaces phases of type $d_{x^2-y^2}+is$ and $d_{x^2-y^2}+id_{xy}$ at an ideal (110) surface of a $d_{x^2-y^2}$–superconductor with a bulk transition temperature T_c. The bulk transition lines are also shown.

ter, as first discussed in the framework of Ginzburg-Landau theory by Sigrist et al.[28] This effect was studied in the full temperature range by Matsumoto and Shiba[18] who used the quasiclassical theory to calculate the structure of the order parameter, the quasiparticle excitation spectrum at the surface, and the spontaneous surface currents.

Fig.2 shows the phase diagram for the transition to a time-reversal breaking surface phase at the (110) surface of a $d_{x^2-y^2}$-superconductor, as calculated by Fogelström et al.[29]. The transition temperatures of the surface phases are given as a function of the strength of the subdominant pairing interaction, which we measure by the subdominant transition temperature T_{c2}. Also shown are the corresponding bulk transitions. We note that the order parameters with s or d_{xy} symmetry are not suppressed by an ideal (110) surface, whereas the bulk stable phase, of type $d_{x^2-y^2}$, is suppressed by the surface. As a result the sub-dominant order parameter can nucleate in a region of strong pair-breaking, and the corresponding surface phase spontaneously breaks time-reversal symmetry for $T < T_s$.

The tunneling density of states at a (110) surface is shown in Fig.3. This figure demonstrates the characteristic splitting of the ZBS due to time-reversal breaking surface phases, and the effects of surface roughness. Note the presence of two pairs of time-reversed Andreev bound states for the $d_{x^2-y^2}+id_{xy}$ surface phase. Surface roughness is described by Ovchinnikov's model.[8] The degree of surface roughness is measured by the parameter ρ[30], where the

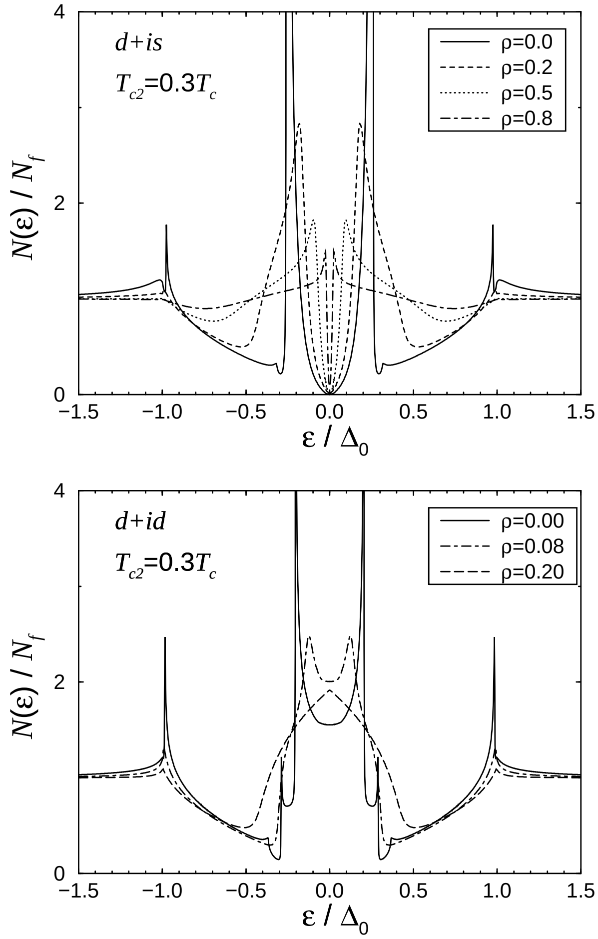

FIG. 3 Tunneling density of states at a (110) surface as function of energy (ϵ). Numerical results are presented for $T_{c2}/T_c = 0.3$, $T/T_c = 0.1$, various degrees of surface roughness (ρ), and two different subdominant order parameters.

ideal surface corresponds to $\rho = 0$. The state $d_{x^2-y^2}+id_{xy}$ is clearly more sensitive to surface roughness than the state $d_{x^2-y^2}+is$. An important consequence of time-reversal breaking surface states is a spontaneous surface current which flows within a depth of a few ξ_0. The two members of a pair of time reversed states, $d_{x^2-y^2}+is$ and $d_{x^2-y^2}-is$ or $d_{x^2-y^2}+id_{xy}$ and $d_{x^2-y^2}-id_{xy}$, lead to surface currents of opposite direction. Typical results for the current density at a flat surface, obtained from Fermi-liquid theory of superconductivity, are shown in Fig.4.

The current resulting from a subdominant order parameter of type s is an order of magnitude larger than from d_{xy}, and much less sensitive to surface roughness. Important differences between surface states $d_{x^2-y^2}+is$ and $d_{x^2-y^2}+id_{xy}$ are expected if the surface currents have to be matched along a

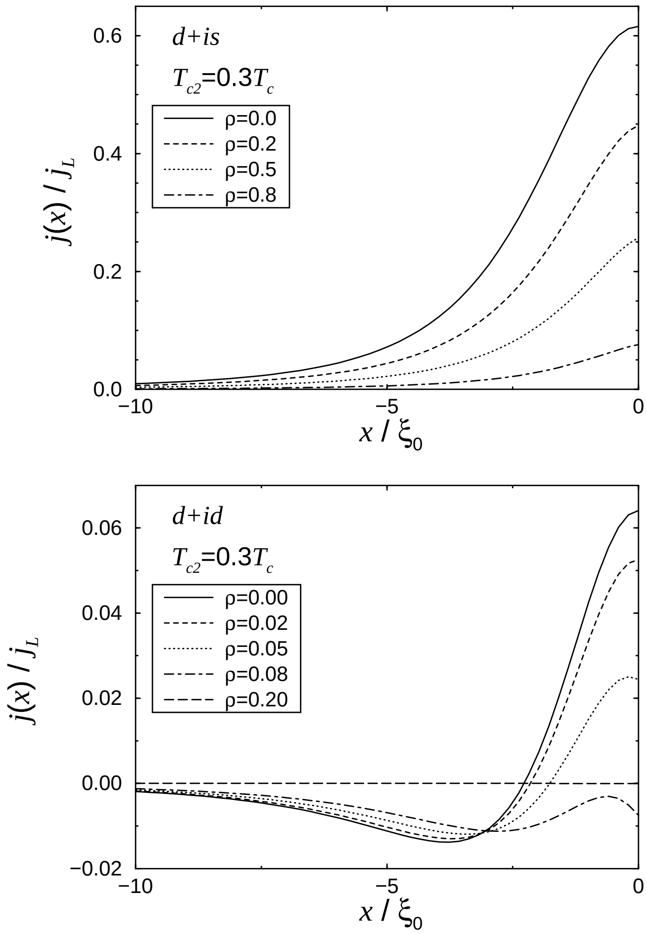

FIG. 4 Current density (normalized by Landau's critical current, $\jmath_L$) at a (110) surface as function of the distance from the surface. Numerical results are presented for $T_{c2}/T_c = 0.3$, $T/T_c = 0.1$, various degrees of surface roughness (ρ), and two different subdominant order parameters. Surface roughness is described by Ochchinnikov's model.

closed surface consisting of, say, a (110), (1-10), (-1-10) and (-110) surface. The differences follow from the different symmetries of the two states. For instance, the state $d_{x^2-y^2} + id_{xy}$ is invariant under the combined operation of time reversal and reflection $x \to -x$ (or $y \to -y$). As a consequence, the surface currents of the state $d_{x^2-y^2} + id_{xy}$ can be matched smoothely in the four corners to give a closed current loop. On the other hand, the state $d_{x^2-y^2} \pm is$ is invariant under the reflections $x \to -x$ and $y \to -y$, and the naive choice of a surface order parameter, namely the same state (e.g. $d_{x^2-y^2} + is$) on the (110), (1-10), (-1-10) and (-110) surface leads to surface currents with sinks (sources) at the corners. In order to have a single closed current loop for $d_{x^2-y^2} \pm is$-order, the surface states at adjacent surfaces have to be time-reversed. This requires at each corner a "defect" in the s-component at which $d_{x^2-y^2} \pm is$ changes into $d_{x^2-y^2} \mp is$. This defect covers an area $\approx \xi_0^2$ in the $x - y$ plane, and thus costs little energy compared to the energy gained by forming the surface phases. The symmetry of the stable surface phase is determined for macroscopic surfaces by the channel with maximum subdominant T_c. Measurements of the surface transition temperature and the symmetry of the surface phase[25] provide new insights into the pairing interaction and thus into the mechanism of superconductivity in the materials of interest.

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