Anomaly in the heat capacity of Kondo superconductors

Rok Žitko[1,2] and Thomas Pruschke[1]

[1]*Institute for Theoretical Physics, University of Göttingen, Friedrich-Hund-Platz 1, D-37077 Göttingen, Germany*
[2]*J. Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

Using numerical renormalization group, we study thermodynamic properties of a magnetic impurity described by the Anderson impurity model in a superconducting host material described by the BCS Hamiltonian. When the Kondo temperature in the normal state, T_K, is comparable to the critical temperature of the superconducting transition, T_c, the magnetic doublet state may become degenerate with the Kondo singlet state, leading to a ln 3 peak in the temperature dependence of the impurity contribution to the entropy. This entropy increase translates into an anomalous feature in the heat capacity which might have already been experimentally observed.

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I. INTRODUCTION

After many decades of research, conventional superconductors are still being actively studied both theoretically and experimentally.[1] An important experimental technique for studying long-range-ordered states consists of determining what destroys that order.[2] Superconductivity can be suppressed, for example, by doping the host material with magnetic impurities. Each magnetic impurity locally perturbs the superconducting order. This can lead to a significant cumulative effect and ultimately, at large concentrations, to a complete suppression of the superconductivity.[2]

In the normal state of a metal, the impurity magnetic moment tends to be screened by the Kondo effect.[3] In the superconducting state, however, the gap in the spectrum implies that there are no low-energy electrons to perform the screening.[2] The behavior thus depends on the ratio between the Kondo temperature T_K and the critical temperature T_c for superconducting transition. In the $T_K \ll T_c$ limit, there is no Kondo effect since the gap is fully formed on the relevant energy scale of T_K, while in the $T_K \gg T_c$ limit, the Kondo physics does not affect the superconducting transition since the impurities are already fully nonmagnetic (Kondo screened) on the scale of T_c. The nontrivial regime is thus $T_K \sim T_c$, when both effects compete. To study this competition and demonstrate the existence of the Kondo effect in superconductors, one can study, for example, the effects of the impurities on the density of states[4,5] or the thermodynamic[6,7] and transport properties.[8] With advances in the tunneling spectroscopy, focus has recently shifted to dynamic properties, i.e., variation in the local density of states induced by the presence of the impurity.[2,9,10]

The effect of impurities on the host is the central focus in the field of quantum impurity physics.[3,11] Studying thermodynamics of an impurity model is a common practice in this field, as one can extract many essential aspects of the impurity behavior (its magnetic properties, effective degrees of freedom, etc.). A reliable theoretical tool is the numerical renormalization group (NRG).[11–13] The NRG has been applied, for example, to study the subgap bound states in isotropic[14] and anisotropic[15] Kondo models and in the Anderson model[16] in both conventional and unconventional[17,18] su-

perconductors. In unconventional superconductors, the anomalous propagators may in many cases be ignored and the superconducting bath can then be described using a pseudogap local density of states.[19–22] Further NRG calculations focused on dynamical properties such as the spectral function[19,23–25] and more recently on the transport properties of quantum dots attached to superconducting leads.[26–30] Only few results of NRG calculations for thermodynamic quantities, such as the impurity contribution to the magnetic susceptibility and the entropy, have been published so far.[19,21,22,31] In this Brief Report we present a detailed investigation of the thermodynamic properties of an Anderson impurity in a BCS superconducting host. We find features in the thermodynamic behavior of magnetically doped superconductors (also known as the "Kondo superconductors") in the dilute-doping limit which appear to have been overlooked in theoretical treatments, but may have been already experimentally observed.

II. MODEL AND METHOD

A conceptually proper way of studying the thermodynamics of a magnetic impurity in a superconducting host would start from a microscopic Hamiltonian for a conduction bath with explicit attractive electron-electron interaction (quartic) terms. The NRG can only be applied to noninteracting continuum Hamiltonians or, more accurately, to Hamiltonians with at most quadratic (mean-field) terms. We thus focus on a mean-field BCS Hamiltonian, keeping in mind that this is only an effective low-temperature Hamiltonian and that its use in the NRG to compute temperature-dependent thermodynamic quantities is associated with a certain ambiguity. In a superconductor, the superconducting order is namely established gradually as the temperature is reduced below T_c. In this work, we will make the following approximation:

$$\langle O \rangle(T) = \langle O(\Delta = \Delta(T)) \rangle(T), \quad (1)$$

i.e., at temperature T we take results computed in a calculation with a constant Δ chosen such that $\Delta = \Delta(T)$. We will use a phenomenological approximation for the temperature dependence for the superconductor gap that is correct near $T = 0$ and $T = T_c$:

$$\Delta(T) \approx \delta_{\rm sc} T_c \tanh\left[\frac{\pi}{\delta_{\rm sc}}\sqrt{a\frac{\delta C}{C_N}\left(\frac{T_c}{T}-1\right)}\right], \qquad (2)$$

with $\delta_{\rm sc}=1.76$, $a=2/3$, and $\delta C/C_N=1.43$.

Even for a single impurity, the order parameter becomes a spatially varying function $\Delta(\mathbf{r})$.[2,32] In this work, we disregard any spatial variation in the order parameter. In fact, we neglect any variation in Δ, considering it as a fixed (but doping-concentration dependent) quantity. In ppm to percent doping range, the distance between the impurities is much smaller than the coherence length in conventional superconductors. Thus the assumption of spatially constant order parameter is justified when impurity-position-averaged thermodynamic properties are considered.[33]

The impurity contribution to an expectation value is commonly defined by taking the difference between the values for a doped system and for a clean system:

$$\langle O\rangle_{\rm imp} = \langle O\rangle - \langle O\rangle_0. \qquad (3)$$

The impurity contribution can be further decomposed into two parts: the "intrinsic" local effect of an impurity and the average effect of all the impurities on the bulk pairing order parameter Δ (which needs to be calculated self-consistently). It is the first contribution that we are interested in in this work.

We thus consider a single Anderson impurity embedded in a superconducting host described by the Hamiltonian $H = H_{\rm bath} + H_{\rm imp} + H_{\rm hyb}$. We model the fermionic bath with a BCS model:

$$H_{\rm bath} = \sum_{k,\sigma} \epsilon_k c^{\dagger}_{k\sigma} c_{k\sigma} - \Delta \sum_k (c^{\dagger}_{k\uparrow} c^{\dagger}_{-k\downarrow} + c_{-k\downarrow} c_{k\uparrow}), \qquad (4)$$

where $c_{k\sigma}$ are conduction-band operators, ϵ_k are single-particle energies, and Δ the BCS order parameter. For simplicity we assume that the band has a flat density of states in the normal state, $\rho(\omega)=1/2D$, where $2D$ is the width of the conduction band. In the original BCS approach, the order parameter Δ has to be determined self-consistently through $\Delta=V\sum_k\langle c_{-k\downarrow}c_{k\uparrow}\rangle$, where V is some phenomenological effective coupling constant and the summation is to be cut off by the Debye energy ω_D. In numerical calculations, however, we consider Δ to be some given parameter. The magnetic impurity Hamiltonian has the usual form

$$H_{\rm imp} = \left(\epsilon + \frac{U}{2}\right)(n-1) + \frac{U}{2}(n-1)^2, \qquad (5)$$

where ϵ is the impurity energy level, U is the electron-electron repulsion, and n is the level occupancy operator, $n=\sum_\sigma d^{\dagger}_\sigma d_\sigma$. Finally, the hybridization Hamiltonian is

$$H_{\rm hyb} = V\sum_{k\sigma}(d^{\dagger}_\sigma c_{k\sigma} + {\rm H.c.}). \qquad (6)$$

The coupling to the conduction band is characterized by the hybridization strength $\Gamma=\pi\rho V^2$.

Due to strong exchange scattering of conduction-band electrons on magnetic impurities,[3,34] magnetic impurity problems need to be solved using nonperturbative methods such as NRG. We performed the calculations with a discretization
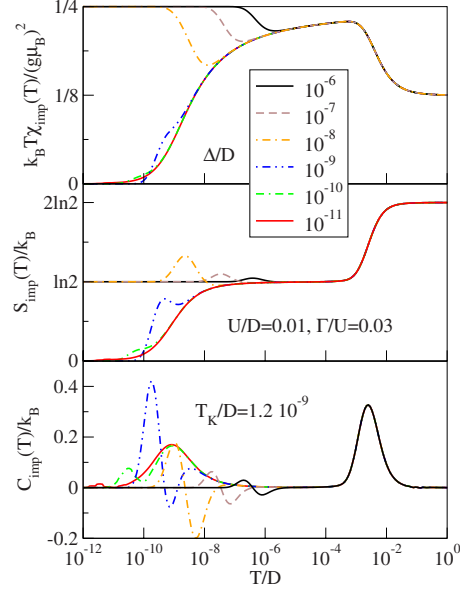

FIG. 1. (Color online) Thermodynamic properties of an Anderson impurity in a BCS superconductor, assuming a fixed value of Δ. The system is particle-hole symmetric: $\epsilon=-U/2$.

parameter $\Lambda=3$, four values of the twist parameter z, and the truncation energy cutoff of $E_{\rm cutoff}=10\omega_N$, where ω_N is the characteristic energy scale at the Nth NRG iteration. Only spin SU(2) symmetry can be explicitly used to simplify calculations with models of this class.

III. NUMERICAL RESULTS

We present results for the following thermodynamic quantities:

(1) the temperature-dependent impurity contribution to the magnetic susceptibility, $\chi_{\rm imp}(T)=(g\mu_B)^2/(k_BT)(\langle S_z^2\rangle-\langle S_z^2\rangle_0)$, where the subscript 0 refers to the clean system (where the Hamiltonian is simply the band Hamiltonian $H_{\rm band}$ without the impurity terms), S_z is the total system spin, g is the electronic gyromagnetic factor, μ_B is the Bohr magneton, and k_B is the Boltzmann constant;

(2) the temperature-dependent impurity contribution to the entropy, $S_{\rm imp}(T)=(E-F)/T-(E-F)_0/T$, where $E=\langle H\rangle$ and $F=-k_BT\ln{\rm Tr}(e^{-H/k_BT})$; and

(3) the temperature-dependent impurity contribution to the heat capacity, $C_{\rm imp}(T)=k_B(\langle H^2\rangle-\langle H\rangle^2)-k_B(\langle H^2\rangle-\langle H\rangle^2)_0$.

We first study the case of a constant gap parameter Δ, i.e., a fictitious gap parameter which does not change with the temperature. We computed thermodynamic properties for a range of Δ at fixed Kondo temperature (Fig. 1). [We use the definition of T_K by Wilson,[12] i.e., $k_BT_K\chi(T_K)/(g\mu_B)^2=0.07$ in the normal state.] For $\Delta\ll T_K$, we obtain the well-known results for an Anderson impurity in a normal metal exhibiting the formation of local moment at $T\sim U$ and the Kondo screening at $T\sim T_K$, with the system ultimately ending up in the strong-coupling fixed point.[13] The presence of the gap is hardly reflected in the impurity thermodynamic properties, although we observe a small feature at $T\sim\Delta$, when Kondo screening is interrupted and the remaining residual entropy is
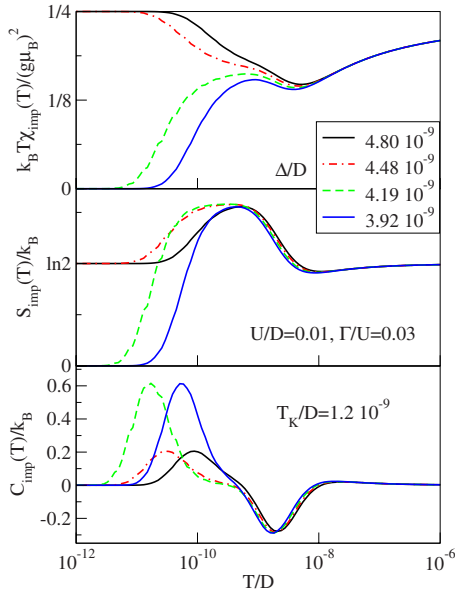
FIG. 2. (Color online) Closeup of the low-temperature region in the transition regime.
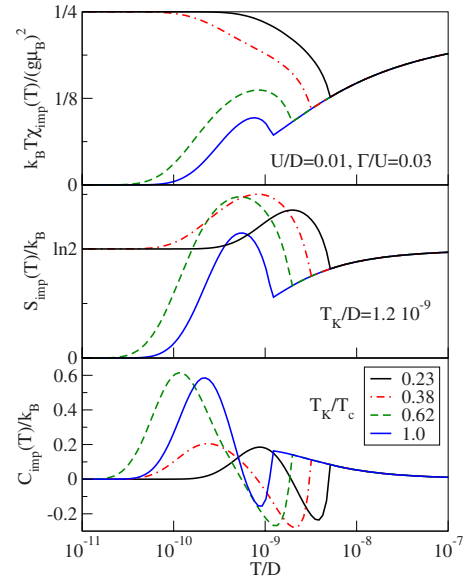

FIG. 3. (Color online) Thermodynamic properties of an Anderson impurity in a BCS superconductor, taking into account the temperature dependence of the gap.

released. For $\Delta \gg T_K$, the Kondo screening is again interrupted at $T \sim \Delta$, but this time the system ends up in the local-moment fixed point rather than the strong-coupling fixed point: the impurity spin decouples entirely, so we obtain Curie-Weiss behavior at low temperatures and a ln 2 residual entropy. We bring attention to the small bump in the impurity entropy above ln 2 at $T \sim \Delta$, which is mirrored in an S-shaped feature in the impurity heat capacity. For $\Delta \sim T_K$, the behavior is similar to that in the $\Delta \gg T_K$ regime, but the entropy increase at $T \sim \Delta$ becomes increasingly strong as the transition point is approached. The transition occurs for $\Delta/D = 4.31 \times 10^{-9}$, i.e., $\Delta/T_K = 3.6$, which is consistent with previously known results.[23] In Fig. 2 we show a closeup of the transition region. Near the transition, the entropy rises to exactly ln 3, forming a relatively broad plateau: at this point the magnetic doublet and the Kondo singlet states are degenerate, although this fixed point is unstable. The transition is clearly first order since the quantum numbers of the ground state change. We present results only for the particle-hole symmetric case, as asymmetry does not affect the results qualitatively.

We now turn to the case of BCS superconductors, where the gap is temperature dependent. The control quantity is in this case the ratio T_c/T_K, which is adjusted in experiments by changing the magnetic impurity species and concentration (within the limits set by the miscibility of metals) or by changing the doping x in the Kondo superconductor systems such as $(La_{1-x}Ce_x)Al_2$.

As previously described, we compute the thermodynamic quantity $\langle O \rangle(T)$ at temperature T from the NRG results for a fixed value of gap $\Delta = \Delta(T)$. The results of such a calculation for a range of the T_K/T_c ratios are shown in Fig. 3. For $T \gtrsim T_c$, the results are equivalent to those for a magnetic impurity in a normal metal. For $T < T_c$, the gap starts to open. On a logarithmic scale the features in thermodynamic quantities appear sharp (cusplike), but a closeup reveals that the change in slope is in fact continuous, albeit rapid. The results

are qualitatively equivalent to those obtained for fixed Δ; a notable difference, however, is the absence of the ln 3 plateau. The plateau is replaced by a rounded peak since the condition of exact degeneracy of the three many-particle states is satisfied only at a single temperature. The peak in the entropy is then reflected in a characteristic temperature variation in the impurity heat capacity, which has a positive and a negative part: this is the characteristic signature to be sought after in experiments. We emphasize that the impurity heat capacity may be negative since it is defined as the difference of two total heat capacities (which themselves are, of course, positive quantities). We note that for impurities in unconventional superconductors, the impurity specific heat is strictly positive.[21]

IV. DISCUSSION AND CONCLUSION

We find that in Kondo superconductor systems an anomaly appears in the impurity heat capacity for $T_K \sim T_c$. This is a large effect since the overall variation in the impurity heat capacity is on the order of k_B, and it occurs in a temperature interval of approximately 1 decade of the temperature scale. The positive part of the anomaly occurs at low temperatures, i.e., in the exponential tail of the BCS heat capacity. Thus the heat-capacity enhancement is sizable and should easily be observable. The negative part of the anomaly occurs in the temperature range where the heat capacity of a superconductor is enhanced. Thus the heat-capacity reduction would be more difficult to measure. Nevertheless, the magnitude of the effect $[(0.1-0.2)k_B$ per impurity] is large enough that this effect could nevertheless be detected. For 0.6 permil impurity concentration and assuming the density of states at the Fermi level of the host in the normal state to be one state per eV, we estimated the effect by summing our results to the BCS heat-capacity

curve in the case $T_K/T_c = 0.62$. We find that the reduction in the heat capacity relative to a clean superconductor is in the 10% range in the temperature interval $[0.3; 0.6]T_c$.

At high doping levels, the simple picture of independent impurities is no longer valid due to interactions between the impurities. Owing to their pair-breaking properties, magnetic impurities lead to a suppression of the superconducting transition temperature T_c.[2,35–38] In both the Abrikosov-Gorkov treatment[36] with classical impurity spins and the Nagaoka-Suhl-approximation treatment by Zittartz and Müller-Hartmann[4,38] with quantum impurity spins, the decrease in the critical temperature is found to be proportional to the concentration divided by $k_B\rho(0)$, where $\rho(0)$ is the density of states at the Fermi level in a pure normal-state metal. For impurity concentrations in the permil range, elemental superconductors with relatively high T_c such as lead or niobium are still superconducting. Another class of systems where these effects may be detected includes Kondo superconductor alloys. In fact, excess specific heat at low temperatures had already been observed in $(La_{1-x}Ce_x)Al_2$ alloy long ago.[6] Given the progress in both experimental and theoretical techniques, it would be interesting to revisit this problem focusing on the low-doping regime to detect the predicted reduction in the heat capacity before the onset of the enhancement and to look for possible semiquantitative agreement. We conclude by observing that a magnetic impurity in a bath may be considered as an open quantum system. Thus this problem is also of interest in the context of thermodynamics of nanosystems.[39]

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