Spin magnetization of small metallic grains

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Small metallic grains which satisfy the conditions of the universal Hamiltonian are considered. It is shown that for such grains the effects of the interactions in the spin channel and in the Cooper channel on their spin magnetization are well separated, thus allowing the determination of the interaction parameters within this model. In particular, the existence of pairing correlations in small grains and the sign of the interaction in the Cooper channel can be uniquely determined.

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I. INTRODUCTION

In general, the problem of disorder and interaction in electron systems is a very difficult one. However, it was shown[1–4] that for small diffusive metallic grains with large dimensional conductance $g=E_{\mathrm{Th}}/d$ the problem simplifies considerably. Here d is the mean level spacing and $E_{\mathrm{Th}}=\hbar D/L^2$ is the Thouless energy which is the inverse time to diffuse across the grain. D is the diffusion constant and L is the grain's size. The low energy physics of such small grains is described to leading order in $1/g$ by the "universal Hamiltonian,"[4] in which only the diagonal matrix elements of the interaction survive:

$$H=\sum_{n=1}^{\Omega/d}\sum_{\sigma}\epsilon_n c_{n,\sigma}^{\dagger}c_{n,\sigma}+E_c\hat{N}^2+J_c\hat{T}^{\dagger}\hat{T}+J_s\hat{S}^2. \qquad (1)$$

The index n spans a shell of Ω/d doubly degenerate time reversed states of energy ϵ_n, $\hat{N}=\sum_{n=1}^{\Omega/d}\sum_{\sigma}c_{n,\sigma}^{\dagger}c_{n,\sigma}$ is the number operator, $\hat{\boldsymbol{S}}=\frac{1}{2}\sum_{n=1}^{\Omega/d}\sum_{\sigma,\sigma'}c_{n,\sigma}^{\dagger}\boldsymbol{\sigma}_{\sigma,\sigma'}c_{n,\sigma'}$ is the total spin operator, and $\hat{T}=\sum_{n=1}^{\Omega/d}c_{n,-}c_{n,+}$ is the pair annihilation operator. E_c is the charging energy and $J_{c(s)}=\lambda_{c(s)}d$, where λ_c and λ_s are the dimensionless interaction parameters in the Cooper channel and in the spin channel, respectively. Ω is of the order of E_{Th}, and we take $\Omega/d=2g$. Recently, a similar problem of a ballistic grain with chaotic boundary conditions was addressed using renormalization group approach, and it was shown[5,6] that for weak interactions the low energy physics is indeed controlled by the universal Hamiltonian.

This relatively simple description of the low energy physics of diffusive metallic grains provides the opportunity to consider theoretically, and eventually experimentally, problems which in bulk systems are much harder to attack. One interesting problem is the question of whether metals such as gold, copper, and silver are superconducting or not at very low temperatures,[7] i.e., if their effective interaction in the Cooper channel is attractive or repulsive. While all these metals are not found to be superconducting down to currently accessible temperatures, it may well be that their effective electron-electron interaction is attractive but small. Since T_c depends exponentially on the interaction, such weak interaction will lead to unmeasurable T_c. However, small effective attractive interaction in such metals would affect other properties, like the proximity effect[8,7] and persistent currents,[9,10] which depend linearly on the interaction. Furthermore, the magnitude of the effective attractive interaction in these metals may be size dependent, as can be inferred from the apparent size dependence of T_c in many superconducting materials.[11–14] In particular, Platinum, which is not known to be a superconductor in bulk form, was recently reported to be superconducting at very low temperatures in granular form.[15]

While the determination of the effective interaction in bulk materials is a difficult task, it was already recognized that weak pairing correlations can be detected in small "superconducting" grains.[16–18] In these works it was shown that the existence of weak pairing correlations will result in measurable effects in the spin susceptibility[16,17] and specific heat[18] of the grains. All these works considered the reduced BCS Hamiltonian, in which only the pairing interaction exists. However, in a real system other interactions exist, and in order to experimentally determine the existence of pairing correlations one has to show that the measured effect is uniquely caused by the pairing interaction itself.

Small disordered metallic grains with $g\gg 1$ and not too strong interactions[5,6] are favorable from this point of view, as they satisfy the validity conditions of the universal Hamiltonian model, and therefore the constraints this model dictates on the interaction terms. In this paper we calculate the ensemble averaged differential spin susceptibility χ_s at $T=0$ of such isolated grains, and show that the effects of the different interaction terms are well separated, thus allowing an unequivocal determination of the existence of pairing correlations in such grains, and furthermore, a determination of the sign and magnitude of the effective interaction constants as they appear in the universal Hamiltonian. Actually, we consider the determination of λ_s and λ_c only. Since the grains are isolated, the charging energy E_c is not relevant, and could be determined by complementary tunneling experiments. We consider the regime of $|\lambda_c|,|\lambda_s|\ll 1$. Note, that for $\lambda_c<0$ two regimes exist, the perturbative regime and the superconducting regime, for which $|\lambda_c|>1/\ln[E_{\mathrm{Th}}/d]$.[17] We first consider the former, and then the latter regime.

II. THE PERTURBATIVE REGIME

Using the universal Hamiltonian, we assume that the spin-orbit interaction is small and neglect it.[4] This assumption

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should be verified when comparing our results with experiments, keeping in mind the specifics of spin-orbit interaction in small grains (see e.g., Refs. 19 and 20). Throughout the paper we will be interested in the ensemble averaged differential spin susceptibility at magnetic fields $H \gg d/\mu_B$. In this regime we can neglect level statistics and assume that the energy levels in the grains are equally spaced. Differences between grains with odd number and even number of electrons can be neglected in this regime as well, and for simplicity we consider grains with even number of electrons. For detailed considerations regarding the neglect of level statistics and even-odd effects see Sec. III of Ref. 17. In particular, ensembles of the order of 10^6 grains or larger are required for the shift in the magnetization (see below) to be larger than the fluctuations due to level statistics. We also neglect orbital magnetization. This can be achieved in pancake shaped grains (see e.g., Ref. 21), when the field is applied in the direction of the thin part. Practically, orbital magnetization cannot be completely avoided, but its relative magnitude can be experimentally determined by changing the direction of the applied magnetic field.

The spin magnetization of a grain is given by

$$M = \mu_B(n_+ - n_-), \tag{2}$$

where n_+ and n_- are the number of electrons with spin parallel and antiparallel to the magnetic field, respectively. We define l as the number of flipped spins, such that $n_+ - n_- = 2l$. It can be shown that among all states with l flipped spins, the one that has the lowest energy has all l states above E_F and l states below E_F singly occupied by electrons with spin parallel to the magnetic field. The number l that is realized at a given magnetic field is the one minimizing the total energy of the grain:

$$E(l) = E_0 + E^l_{\rm kin} + E^l_{\rm int} - 2l\mu_B H. \tag{3}$$

Here E_0 is the energy of the noninteracting Fermi state (with $l=0$, no singly occupied single particle states), $E^l_{\rm kin} = l^2 d$ is the kinetic energy cost of flipping l pairs, $E^l_{\rm int}$ is the energy due to the interaction, and $-2l\mu_B H$ is the Zeeman energy. In order to calculate $E^l_{\rm int}$ we use Richardson's exact solution.[22,23] Although this solution was derived for the reduced BCS Hamiltonian, it can be easily generalized to solve the universal Hamiltonian for isolated grains. The $\hat{N}^2$ term is then not relevant, and the only relevant extra term in the universal Hamiltonian compared to the reduced BCS Hamiltonian is the spin term.

Given l flipped spins, levels $g-l+1 \cdots g+l \equiv B$ are singly occupied, and do not participate in the pairing interaction.[24] Denoting $U = \Omega \backslash B$, and neglecting the spin term, Richardson's solution is given by a set of k coupled nonlinear equations, the νth equation of which is given by[23]

$$-\frac{1}{\lambda_c d} + \sum_{\mu=1(\neq\nu)}^{k} \frac{2}{E_\mu - E_\nu} - \sum_j^U \frac{1}{2\epsilon_j - E_\nu} = 0. \tag{4}$$

Here k is half the number of the "paired" electrons, and in our case $k = g - l$. The total energy of the system is given by

$$E_{\rm BCS} = \sum_j^B \epsilon_j + \sum_{\nu=1}^k E_\nu, \tag{5}$$

and the many-body wave function is also given in terms of the k energy parameters $\{E_\nu\}$ which solve the equations (4). Since the electrons participating in the pairing interaction have zero total spin, including the spin term and the Zeeman term does not change Richardson's equations, energy parameters, and orbital wave function. The spin and Zeeman terms do change the energy of the system, for a given l by $E_s = \lambda_s dl(l+1)$ and $E_Z = -2l\mu_B H$, respectively.

The total energy can therefore be written as

$$E(l) = \sum_j^B \epsilon_j + \sum_{\nu=1}^k E_\nu + \lambda_s dl(l+1) - 2l\mu_B H, \tag{6}$$

or, in accordance with Eq. (3),

$$E(l) = E_0 + l^2 d + \sum_{\nu=1}^k \delta E_\nu + \lambda_s dl(l+1) - 2l\mu_B H, \tag{7}$$

where $\delta E_\nu \equiv E_\nu - 2\epsilon_\nu$. Therefore, $E_{\rm int} = \lambda_s dl(l+1) + E_{\rm pair}$ where

$$E_{\rm pair} \equiv \sum_{\nu=1}^k \delta E_\nu \tag{8}$$

is the energy due to the interaction in the Cooper channel, and the problem reduces to finding $E_{\rm pair}(l)$. In Ref. 17 this was done to second order in the interaction λ_c. Here we use Richardson's exact solution for the determination of $E_{\rm pair}(l)$. This formalism allows a rigorous inclusion of the spin term. It also allows the possibility to give a general expression for $E_{\rm pair}(l)$, and then obtain the result to second order in λ_c as an expansion of the exact result.

Manipulating Eq. (4) one obtains[17]

$$\delta E_\nu = \frac{\lambda_c d}{1 + \lambda_c a_\nu}, \tag{9}$$

where

$$a_\nu = d\left(\sum_{j\neq\nu}^U \frac{1}{2\epsilon_j - E_\nu} - \sum_{\mu=1(\neq\nu)}^k \frac{2}{E_\mu - E_\nu}\right). \tag{10}$$

For the lowest energy solution, we approximate δE_ν by

$$\delta E^0_\nu \equiv \lambda_\nu d, \quad \text{where} \quad \lambda_\nu \equiv \frac{\lambda_c}{1 + \lambda_c a^0_\nu}, \tag{11}$$

and $a^0_\nu \equiv a_\nu(\lambda_c = 0)$ is given by

$$a^0_\nu = \sum_{j\neq\nu}^U \frac{1}{2j - 2\nu} - \sum_{\mu=1(\neq\nu)}^k \frac{1}{\mu - \nu}. \tag{12}$$

This approximation is exact to second order in λ_c, and its accuracy to higher orders in λ_c was studied in Ref. 17. $E_{\rm pair}$ can now be calculated to any order in λ_c by inserting expression (12) in Eq. (8). To second order in λ_c this gives

$$E_{\rm pair}(l) = \lambda_c d(g - l) + \frac{1}{2}\lambda_c^2 d \sum_{\nu=1}^{g-l} \ln\left[\frac{g + l + \nu}{2l + \nu}\right]. \tag{13}$$

Inserting Eq. (13) into Eq. (7) and differentiating with respect to l we obtain an equation for l that minimizes $E(l)$

$$2ld + \lambda_s d(2l+1) - \lambda_c d + \lambda_c^2 d \ln\left[\frac{g}{2l}\right] - 2\mu_B H = 0, \quad (14)$$

which results in

$$M = \frac{\mu_B[2\mu_B H/d - \lambda_c^2 \ln[E_{\mathrm{Th}}/(2\mu_B H)] + \lambda_c - \lambda_s]}{1+\lambda_s}. \quad (15)$$

In Eqs. (14) and (15), for the values inside the logarithm, we assume $l \ll g$ and replace l with its noninteracting value. The l that minimizes $E(l)$ as obtained from Eq. (14) is given by the condition that the energy gain from the Zeeman term when flipping another electron and creating two additional singly occupied states with spin up electrons is equal to the energy cost of flipping this electron, resulting from the kinetic energy, spin interaction, and pairing interaction. The kinetic part alone produces the noninteracting result [χ_0 in Eq. (16) below for the susceptibility]. The leading contribution of the spin part to the total energy is proportional to l^2, like the kinetic energy, and this results in an effective renormalization of the density of states. The second part of the spin term, as well as the leading part of the pairing interaction, contribute to the total energy terms which are linear in l, like the Zeeman term, and therefore result in a constant shift of the magnetization, and do not affect χ_s. The field dependent correction to χ_s comes from the higher orders of the pairing term, of which the second order gives the dominant contribution. This part gives a negative correction to the energy which is monotonically decreasing with increasing l, therefore contributing a positive, field dependent contribution to χ_s.

Differentiating with respect to H we obtain the ensemble averaged spin susceptibility for $d/\mu_B \ll H \ll E_{\mathrm{Th}}/\mu_B$,

$$\chi_s = \frac{\chi_0}{1+\lambda_s}\left(1 + \frac{\lambda_c^2 d}{2\mu_B H}\right). \quad (16)$$

This is our central result. The interaction in the spin channel results in an H independent shift of the susceptibility by a factor of $1/(1+\lambda_s)$. This gives the possibility to determine λ_s, by e.g. the Sommerfeld-Wilson ratio, that compares χ_s to the linear specific heat coefficient. The interaction in the Cooper channel results in a $1/H$ correction to χ_s. This correction is a finite size effect, as it is proportional to the level spacing. Moreover, *this correction unequivocally signals the presence of pairing correlations in small metallic grains*, as it does not result from the interaction in the spin channel or the charging energy, and all other interactions have $1/g$ smallness. Interestingly, the $1/H$ correction does not depend on the sign of the interaction, and therefore exists for attractive as well as repulsive interaction in the Cooper channel. Thus, measuring χ_s in small metallic grains at magnetic fields $H \gg d/\mu_B$ determines the magnitude of λ_c, but not its sign. In order to obtain the sign of λ_c one has to look at M/H. Unlike the case in the susceptibility, where the first order term in the interaction is not field dependent, and therefore does not contribute, here, to leading order in λ_c

$$\frac{M}{H} = \frac{\chi_0}{1+\lambda_s}\left[1 + \frac{(\lambda_c - \lambda_s)d}{2\mu_B H}\right], \quad (17)$$

and the $1/H$ correction does depend on the sign of λ_c. Once λ_s is either known or small, the sign of λ_c is easily determined. Note, that in principal the information given by χ_s and by M/H is equivalent. However, their high magnetic field behavior is different, and therefore both the sign and magnitude of λ_c can be obtained. (Actually, both can be obtained from the behavior of M/H. However, the susceptibility measurement is preferable for the determination of the magnitude of λ_c because it is independent of any other interaction. It is also a more precise measurement experimentally.) The magnetic field range for which our treatment is valid is given above Eq. (16), and depends on the specific metallic grain, as well as its size and its dimensionless conductance. For example, for Copper grains of size $5\times 50 \times 50$ nm^3 and $g=25$ the level spacing is roughly 0.06 K, the Thouless energy 1.5 K, and therefore the magnetic field range would be between 0.1 and 2.5 T.

III. THE SUPERCONDUCTING REGIME

So far we considered the perturbative regime, which for attractive interaction corresponds to $|\lambda_c| < 1/\ln[E_{\mathrm{Th}}/d]$ which is equivalent to $d > \Delta$ where Δ is the bulk gap in the mean field BCS approximation. In the crossover regime, where $d \approx \Delta$, the behavior of χ_s changes considerably in the low magnetic field regime, $\mu_B H \lesssim d$. However, the properties of χ_s at high magnetic field $\mu_B H \gg \Delta^2/d$ are similar to those in the perturbative regime,[17] and the interaction parameters can be similarly determined. The parameters of the universal Hamiltonian can also be determined in the "BCS regime," where $|\lambda_c| > 1/\ln[E_{\mathrm{Th}}/d]$ and the level spacing $d \ll \Delta$ and can therefore be neglected. In this regime λ_c is easy to determine, e.g. by measuring the excitation gap. In order to determine λ_s in this regime we revisit the spin magnetization of the system. For $\lambda_s=0$ it is well known[25,26] that the spin magnetization of a superconductor is zero below a value of $H=\Delta/(\sqrt{2}\mu_B)$, where a sharp step to the value of the spin magnetization of noninteracting electrons at the same H occurs. The area between the magnetization curves of the noninteracting and superconducting systems gives the condensation energy, $\Delta^2/(2d)$. We have already shown that finite λ_s changes the slope of the spin magnetization of noninteracting electrons [see Eq. (16) with $\lambda_c=0$]. Here we show that it also changes the value of H at which the step in the magnetization of a superconducting system occurs, as to keep the area between the magnetization curves to equal $\Delta^2/(2d)$. Thus, one can determine λ_s in the superconducting regime by the magnetic field value of the magnetization step. This value of H is where the normal and superconducting states have the same energy, i.e., when the equation

$$l^2 d + J_s l(l+1) + \frac{\Delta^2}{2d} - 2l\mu_B H = 0 \quad (18)$$

has one solution. This occurs when $l=\Delta/\sqrt{2d(d+J_s)}$, or when

$$H = \frac{\Delta}{\sqrt{2}\mu_B}\sqrt{1+\lambda_s}. \tag{19}$$

The shift in the magnetic field value of the spin magnetization step is a direct measure of λ_s in this regime.

IV. SUMMARY

We have thus shown that the determination of the interaction parameters in small metallic grains with not too large interactions can be done by measuring their ensemble averaged differential spin susceptibility. Such a measurement, done systematically as function of grain size, can shed light on the change of transition temperature with grain size in granular superconductors. Although our theory is valid for finite size grains, and cannot directly determine if a certain material is superconducting at low temperatures in bulk form, a systematic measurement of the interaction parameters as a function of grain size can suggest the bulk behavior as well.

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