Two pairing parameters in superconducting grains

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Unlike bulk superconductivity, where one energy scale, the energy gap, characterizes pairing correlations, we show that in small superconducting grains there exist two different such quantities. The first characterizes collective properties of the grain, such as the condensation energy, and the second single-particle properties. To describe these two energy scales, we define two corresponding pairing parameters, and show that although both reduce to the bulk gap for large grains, this occurs at different size scales.

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I. INTRODUCTION

The question of how superconductivity is affected by small sample size, raised already by Anderson in 1959,[1] has experienced a recent revival of interest, which started with the experimental work of Ralph, Black, and Tinkham.[2,3] In these experiments it was shown that small superconducting grains, with size much smaller than the coherence length, but level spacing d smaller than the bulk gap Δ, have a gap of order 2Δ in their tunneling spectrum, and grains in the regime $d \gtrsim \Delta$ (to be called ‘‘ultrasmall’’ regime) do not. Since the pairing parameter is the basic quantity in bulk superconductivity, several efforts have been made to define pairing parameters which are relevant in the regime of small grains,[4–9] and reduce to Δ in the bulk limit. The need for such new definitions arises for two apparent reasons: (i) for ultrasmall grains, in which $d > \Delta$, the quantity Δ has no direct physical meaning; (ii) in both ultrasmall grains, and small grains for which $d \lesssim \Delta$, if the grains are isolated the appropriate ensemble is the canonical one, in which the usual definition of Δ that is used in the grand canonical ensemble [see $\Delta_{\rm g.c.}$ in Eq. (3)] is trivially zero. In this paper we show that there is a third, fundamental reason for the inadequacy of $\Delta_{\rm g.c.}$ to describe pairing correlations in small superconducting grains. Unlike the situation in bulk superconductors, in which all the various superconducting properties can be characterized by one energy scale Δ, in general there exist two distinct energy scales that characterize pairing correlations, and the difference between them becomes important particularly for small grains. The first such energy scale, which we denote by $\Delta_{\rm s.p.}$, characterizes single-particle properties, such as excitation energies and parity effects. The second, denoted as $\Delta_{\rm col}$, characterizes collective properties, such as the condensation energy [see Eqs. (10) and (17)], to which pairing correlations of all the levels up to $\omega_{\rm D}$ contribute. The reason why these two scales are in general distinct is that levels far from the Fermi energy, namely those with energy $|\varepsilon - E_{\rm F}|$ between Δ and the Debye frequency $\omega_{\rm D}$ (to be called ‘‘not condensed’’ or ‘‘distant’’ levels), make a more significant contribution to collective properties than to single-particle ones. (For a discussion on the role of the distant levels in superconducting grains and persistent currents in normal metal rings see Refs. 10 and 11.) The contribution of the distant levels to physical properties turns out to be proportional to the level spacing; in the large grain limit where the level spacing becomes exceedingly small, this contribution can thus be neglected. In this limit, the single-particle and collective properties are therefore both determined by the correlations of only the ‘‘condensed levels,’’ i.e., those within Δ of $E_{\rm F}$, so that the two scales $\Delta_{\rm col}$ and $\Delta_{\rm s.p.}$ become identical.

Previous attempts[4,6–9] to define, in terms of pair correlation functions, a pairing parameter adequate to describe small grains in the canonical ensemble resulted in parameters characterizing collective properties of the grain, but not single-particle ones. We shall discuss a particular definition for such a collective parameter, denoted $\Delta_{\rm col}$, which is purposefully chosen such that $\Delta_{\rm col}$ reduces to Δ in the bulk limit. For small grains, we show the correspondence of this definition to collective properties such as the condensation energy. We then define a single-particle parameter $\Delta_{\rm s.p.}$ and show the correspondence of this definition to single-particle properties of the grain. In the bulk limit both $\Delta_{\rm col}$ and $\Delta_{\rm s.p.}$ reduce to Δ as expected, but at a different size scale (see Fig. 1). For the single-particle properties, we find $\Delta_{\rm s.p.} \gg \Delta$ in the ultrasmall regime $(d > \Delta)$, and $\Delta_{\rm s.p.} \simeq \Delta$ for larger grains. In

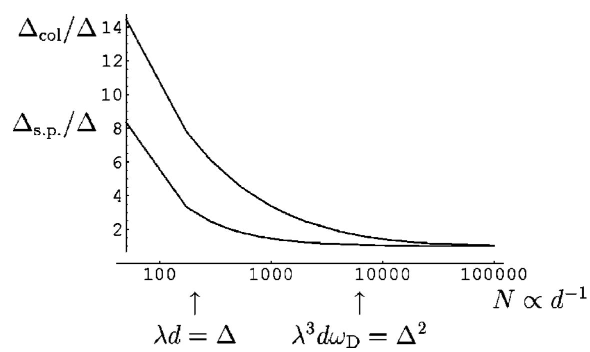

FIG. 1. The two pairing parameters, $\Delta_{\rm col}$ (top curve) and $\Delta_{\rm s.p.}$ (bottom curve), normalized to the value of the bulk gap, are sketched as function of $N = \omega_{\rm D}/d$ (proportional to the inverse grain size), for $\lambda = 0.12$. $\Delta_{\rm s.p.} \gg \Delta$ for $N < 250$, which correspond to $\lambda d = \Delta$. $\Delta_{\rm col} > \Delta, \Delta$s.p. both in the ultrasmall regime, and in the intermediate regime, up to $N \simeq 7500$ which corresponds to $\lambda^3 d\omega_{\rm D} = \Delta^2$.

contrast, for the collective properties we find $\Delta_{\rm col} \gg \Delta$ not only in the ultrasmall regime, but also in an "intermediate regime"[10] in which $\Delta > d > \Delta^2/\omega_{\rm D}$. Regarding the relation between collective and single-particle parameters, we find $\Delta_{\rm col} \gg \Delta_{\rm s.p.}$ in both the ultrasmall and the intermediate regimes. Note that both the range of the intermediate regime, and the value of the pairing parameters and the various superconducting properties obtained below, depend explicitly on $\omega_{\rm D}$. This $\omega_{\rm D}$ dependence, as well as the very existence of the intermediate regime, are direct manifestations of the contribution of the pairing correlations of the distant levels. Finally, we discuss some possible strategies for measuring the single-particle and collective quantities in small grains. Throughout the paper, except when discussing the parity effect, we assume for simplicity an even number of electrons in the grain.

II. PAIRING CORRELATIONS IN THE GRAND CANONICAL ENSEMBLE

We consider the reduced BCS Hamiltonian

$$\hat{H} = \sum_{j,\sigma=\pm} \epsilon_j c^\dagger_{j\sigma} c_{j\sigma} - \lambda d {\sum_{i,j}}' \, c^\dagger_{i+} c^\dagger_{i-} c_{j-} c_{j+} \, . \tag{1}$$

where the second sum (the pairing interaction) is restricted to energies within $\omega_{\rm D}$ of $E_{\rm F}$, and $+$ $(-)$ denote spin up (down). The Hamiltonian (1) is the usual BCS Hamiltonian used when discussing superconducting grains[9] and its validity is discussed in, e.g., Refs. 12,13, and 9. For a grain with a given, finite number of electrons this Hamiltonian has an exact solution, obtained by Richardson,[14,15] and independently by Gaudin.[16] In the macroscopic limit, where the canonical and grand canonical ensembles produce the same results, Richardson's solution reduces to the BCS solution.[17,18] As a result of the pairing interaction, the ground state of a superconductor is different from the noninteracting Fermi state. It is a coherent superposition of various paired many-body noninteracting states, defined as Slater determinant of real one-electron wave functions. The coherence means that the amplitudes for all these states in the superposition are real, up to an overall, global phase factor. This is true both for the BCS wave function in the grand canonical formalism,

$$|{\rm BCS}\rangle = \prod_j \, (u_j + v_j b^\dagger_j)|{\rm Vac}\rangle, \tag{2}$$

where $b_j \equiv c_{j-}c_{j+}$, and for the exact wave function given by Richardson's solution.[15] (In the grand canonical formalism, the above coherence relates to noninteracting many-body states with a given number of pairs. One can add a constant phase between states of different number of pairs, which is referred to as the superconducting phase.) A particular characteristic of the structure of the ground state of a superconductor is that the occupation probability of levels above the Fermi energy is *nonzero*, and that of levels below the Fermi energy is smaller than unity. A measure of the pairing correlations, which exploits both the non-Fermi-like occupation probability and the phase coherence mentioned above, is given by the pair amplitude, which in the grand canonical ensemble is given by

$$\Delta_{\rm g.c.} \equiv \lambda d \sum_j \, \langle c_{j-} c_{j+} \rangle. \tag{3}$$

For any many-body BCS-like eigenstate, characterized by the set $\{f_{j\sigma}\}$ of the occupation probabilities of the BCS quasiparticles, one obtains[19]

$$\Delta_{\rm g.c.}(\{f_{j\sigma}\}) = \lambda d \sum_j \, u_j v^*_j (1 - f_{j+} - f_{j-}). \tag{4}$$

Specifically, for the ground state given in Eq. (2), for which $f_{j\sigma}=0$ for all j, we obtain

$$\Delta_{\rm g.c.}({\rm g.s.}) = \lambda d \sum_j \, u_j v_j \, , \tag{5}$$

which gives in the bulk limit $\Delta_{\rm g.c.}({\rm g.s.}) = \omega_{\rm D}/\sinh(1/\lambda) \equiv \Delta$. The mean occupation of level j is given by v_j^2, and $u_j^2 + v_j^2 = 1$. Note that the nature of $\Delta_{\rm g.c.}$ is collective, being a sum of the contributions of all levels. As a result of the phase coherence mentioned above, all the contributions to the sum in Eq. (5) come with the same phase.

III. COLLECTIVE PAIRING PARAMETER $\Delta_{\rm col}$

We now turn to the definition of the collective canonical pairing parameter. A natural extension of the concept of long-range order in the bulk, suggests the following definition for a canonical pairing parameter:

$$|\Delta_{\rm col}|^2 \equiv (\lambda d)^2 \int \, dr_1 dr_2 F(r_1, r_2), \tag{6}$$

where $F(r_1, r_2)$ is a function characterizing pairing correlations, which is given by

$$F(r_1,r_2) \equiv \langle \psi^\dagger_+(r_1)\psi^\dagger_-(r_1)\psi_-(r_2)\psi_+(r_2)\rangle - \langle \psi^\dagger_+(r_1)\psi_+(r_2)\rangle\langle \psi^\dagger_-(r_1)\psi_-(r_2)\rangle. \tag{7}$$

We will show that this definition for the collective canonical pairing parameter is adequate, as it has the following properties: (i) it is meaningful for a canonical ensemble; (ii) in the bulk limit it is equivalent to the grand canonical definition (3) *for any given BCS eigenstate;* (iii) it is related to the condensation energy and to the mean occupation of the noninteracting levels not only in the bulk limit, but also in the opposite limit of ultrasmall grains [see Eqs. (10) and (11) below].

Expanding each of the ψ operators in the basis of the noninteracting single-particle eigenstates, we obtain

$$|\Delta_{\rm col}|^2 = (\lambda d)^2 \sum_{ij} \, (\langle b^\dagger_i b_j\rangle - \langle c^\dagger_{i+} c_{j+}\rangle\langle c^\dagger_{i-} c_{j-}\rangle). \tag{8}$$

Since the terms in each of the brackets are number conserving, they are meaningful in the canonical ensemble, which is used below for the evaluation of $|\Delta_{\rm col}|^2$ for small grains.

However, in the macroscopic limit, one can use the grand canonical ensemble to evaluate $|\Delta_{\rm col}|^2$ within the BCS approximation. By using the Bogoliubov transformation and the BCS wave functions, we find that for any many-body BCS-like eigenstate

$$|\Delta_{\rm col}|^2=(\lambda d)^2\sum_{ij} u_i v_i^* u_j^* v_j(1-f_{i+}-f_{i-})(1-f_{j+}-f_{j-})$$
$$=|\Delta_{\rm g.c.}|^2, \tag{9}$$

where the last equality is a result of Eq. (4). The canonical pairing parameter is equal, in the bulk limit, to the grand canonical pairing parameter for any many-body state, and therefore both definitions are equivalent in this limit. Our definition for $\Delta_{\rm col}$ differs slightly from that given in Ref. 8. The difference lies in the last term in Eq. (8), which results in the exact equivalence to $\Delta_{\rm g.c.}$ in Eq. (9).

We now turn to the opposite limit of ultrasmall grains. By examining Richardson's exact solution,[14,15] it was shown that pairing correlations, however small [i.e., even for $\lambda \ll 1/\ln(\omega_{\rm D}/d)$] manifest themselves both in the form of the ground-state wave function and in a finite condensation energy $E_{\rm cond}$.[10] Here we make the connection between these two effects and the canonical pairing parameter. In particular, we shall show that to leading order in λ

$$E_{\rm cond}=\frac{|\Delta_{\rm col}|^2}{2\lambda d}, \tag{10}$$

where $|\Delta_{\rm col}|^2$ is evaluated for the exact ground state [this result differs from the known bulk result $E_{\rm cond}=\Delta^2/(2d)$ by the occurrence of λ in the denominator, which is discussed below]. Also, $\Delta_{\rm col}$ is related to the sum of the pairing correlations in all the levels, as are reflected in their occupation probabilities, since we shall show that

$$|\Delta_{\rm col}|^2=\frac{2\ln 2}{\lambda}\Delta_{\rm occ}^2, \tag{11}$$

where

$$\Delta_{\rm occ}\equiv\lambda d\sum_j \overline{u_j}\,\overline{v_j}, \tag{12}$$

with $\overline{v_j^2}\equiv\langle b_j^\dagger b_j\rangle$ and $\overline{u_j^2}=1-\overline{v_j^2}$. The quantity $\Delta_{\rm occ}$, which has been defined in analogy to $\Delta_{\rm g.c.}$, reflects the non-Fermi-like mean occupation probability in the many-body ground state of the noninteracting single-particle levels.

These results are found as follows: To obtain the value of $|\Delta_{\rm col}|^2$ in the ground state we use Richardson's equations and expressions for the wave functions,[15] to write the ground state to leading order in λ, in terms of the amplitudes of the various noninteracting many-body states appearing in it:

$$\phi_{\rm g.s.}(1,\ldots,N)=1$$
$$\phi_{\rm g.s.}(1,\ldots,N;\neq j,k)=\frac{\lambda d}{2(\epsilon_k-\epsilon_j)}. \tag{13}$$

The first line refers to the amplitude that all the levels below the Fermi energy are occupied by pairs (noninteracting ground state of the system). The second line is the amplitude for the noninteracting many-body state which is the same as the noninteracting ground state, except for one pair excitation from level j to level k. The amplitudes of all the other many-body noninteracting states are zero to first order in λ.

From Eq. (13), to zeroth order in λ, the two terms in Eq. (8) cancel each other. The second term in Eq. (8) has no contribution to first order in λ. The contribution to the first term which is first order in λ comes from the fact that there is finite amplitude for levels above the Fermi energy to be occupied, and is given, using Eq. (13), by $\lambda d/2(\epsilon_j-\epsilon_i)$ for each $j>, i<$ [by $<(>)$ we refer to levels below (above) the Fermi energy]. Since the sum in Eq. (8) is unrestricted, we get a factor of 2, and to leading order in λ

$$|\Delta_{\rm col}|^2=(\lambda d)^3\sum_{i<,j>}\frac{1}{\epsilon_j-\epsilon_i}. \tag{14}$$

The condensation energy was calculated in Ref. 10. In order to compare it with $\Delta_{\rm col}$ of Eq. (14) we present here its value for a general spectrum, which to leading order in λ is given by

$$E_{\rm cond}=(\lambda d)^2\sum_{i<,j>}\frac{1}{2\epsilon_j-2\epsilon_i}. \tag{15}$$

This result is obtained directly from Richardson's equations, and leads to Eq. (10).

Evaluating Eq. (14) for equally spaced spectrum, we obtain

$$|\Delta_{\rm col}|^2=2\ln 2\cdot\lambda^3 d\,\omega_{\rm D}. \tag{16}$$

The large magnitude (linear in $\omega_{\rm D}$) of this result is due to the fact that all the amplitudes in Eq. (13) have the same phase (which is a consequence of the coherence discussed in Sec. II), so that all the terms in Eq. (14) are added with the same sign.

In Ref. 10 we have shown that $E_{\rm cond}\simeq E_{\rm cond}^{\rm BCS}+E_{\rm cond}^{\rm pert}$, where $E_{\rm cond}^{\rm BCS}=\Delta^2/2d$ is the contribution of the condensed levels, and $E_{\rm cond}^{\rm pert}\approx\lambda^2\omega_{\rm D}$ is the contribution of the distant (not-condensed) levels, which can be calculated perturbatively. Similarly, $|\Delta_{\rm col}|^2$ is a sum of the contributions of all levels below $\omega_{\rm D}$, too, and is related to the condensation energy in both the BCS and the perturbative regimes. Therefore it is natural to hypothesize that $|\Delta_{\rm col}|^2$ (similarly to $E_{\rm cond}$) can to a good approximation be written as the sum of a bulk contribution from the condensed levels and a perturbative contribution from the distant levels, i.e., $|\Delta_{\rm col}|^2\simeq 2\ln 2\lambda^3 d\omega_{\rm D}+\Delta^2$. This would imply that $\Delta_{\rm col}\gg\Delta$ in both the ultrasmall and intermediate regimes (see Fig. 1). Note that the expression for the condensation energy in Eq. (10) is different from the bulk expression of the condensation energy in terms of Δ, namely $E_{\rm cond}^{\rm bulk}=\Delta^2/2d$, by a factor of λ in the denominator. Since we have shown that in the bulk limit $\Delta_{\rm col}=\Delta_{\rm g.c.}$, we conclude that $\Delta_{\rm col}$ and the condensation energy have a different functional dependence on λ. The above hypothesis results in

$$E_{\mathrm{cond}}=\frac{|\Delta_{\mathrm{col}}|^2}{2f(\lambda)d}, \tag{17}$$

where $f(\lambda)$ is a monotonic function of λ, which equals λ for $\lambda \ll 1/\ln N$ and unity for $\lambda \gg 1/\ln N$ (bulk limit).

We now turn to derive the relation (11) between Δ_{col} and the mean occupation probabilities. In the exact ground state, $\overline{v_j^2}$ is given by

$$\sum_{\{f_1 \ldots f_N | j \in\}} |\phi(f_1, \ldots, j, \ldots, f_N)|^2, \tag{18}$$

where $\{f_1 \cdots f_N | j \in\}$ is any configuration of N levels out of the $2N$ noninteracting single-particle levels, that includes the level j. To leading order in λ, using Eq. (13), we obtain for levels j above E_{F}

$$\overline{v_j^2}=(\lambda d)^2 \sum_{i<} \frac{1}{4(\epsilon_j-\epsilon_i)^2}. \tag{19}$$

Using the approximation of constant level spacing, we find that

$$\overline{v_j^2}=\frac{\lambda^2 d}{4\epsilon_j}, \tag{20}$$

where ϵ_j is measured from the Fermi energy. This important result shows that the mean occupation $\overline{v^2}(\epsilon)$ is proportional to ϵ^{-1}, unlike the usual BCS result, where for $\epsilon \gg \Delta$ the mean occupation is proportional to ϵ^{-2}. Since the occupation probability for a single level is, by Eq. (20), proportional to the level spacing, this term can be neglected in the bulk limit. However, in finite-size grains, we find that in both the ultrasmall *and intermediate* regimes (i.e., $\Delta < \lambda\sqrt{d\omega_{\mathrm{D}}}$), the occupation probability for energies of the order of ω_{D} is in fact larger than that given by the BCS approximation.

As a result of Eq. (19), to first order in λ we find that $\overline{v_j}=\lambda d\sqrt{\Sigma_{i<}1/4(\epsilon_j-\epsilon_i)^2}$ and $\overline{u_j}=1$. For equally spaced levels, one therefore obtains from Eq. (20) that

$$\Delta_{\mathrm{occ}}=\lambda d \sum_j \overline{u_j}\,\overline{v_j}=\lambda^2\sqrt{d\omega_{\mathrm{D}}}, \tag{21}$$

which yields the relation between Δ_{occ} and Δ_{col} given in Eq. (11). To summarize: the condensation energy, pairing parameter, and mean level occupation all receive significant contributions from the weak pairing correlation of the distant (not-condensed) levels up to the Debye frequency. As a result, their magnitude is much larger than that given by the BCS approximation, not only in the ultrasmall regime, but also in the intermediate regime where $\Delta^2/\omega_{\mathrm{D}} < d < \Delta$.

IV. SINGLE-PARTICLE PAIRING PARAMETER $\Delta_{\mathrm{s.p.}}$

Unlike the collective properties considered above, other superconducting properties, such as the excitation energy and the parity effect [quantified by the Matveev-Larkin (ML) parameter, see Ref. 5], are related to the blocking of, say, only one or two levels to pairing correlations. Therefore they do not depend on the correlations between all possible pairs of levels in the grain, but only on the correlations between these selected levels and all the other levels. As a result, *their values in small grains are much smaller than one would get by using the bulk analogy with* Δ_{col} *as the pairing parameter*. We therefore define

$$\Delta_{\mathrm{s.p.}}^i \equiv \lambda d \sum_j (\langle b_i^\dagger b_j\rangle + \langle b_i b_j^\dagger\rangle), \tag{22}$$

where the sum is over the noninteracting single-particle levels and i is a selected such level. Since one frequently deals with the lowest energy levels, we define

$$\Delta_{\mathrm{s.p.}} \equiv \Delta_{\mathrm{s.p.}}^{\bar{i}} \tag{23}$$

for $\bar{i}$ being the level closest to the Fermi energy (for our considerations the cases that $\bar{i}$ is below or above E_{F} are equivalent, and we take $\bar{i}$ to be below E_{F}).

In the bulk limit, using the BCS approximation, we obtain for the ground state

$$\Delta_{\mathrm{s.p.}}^i = 2\lambda d u_i v_i \sum_j u_j v_j, \tag{24}$$

and specifically

$$\Delta_{\mathrm{s.p.}} = \lambda d \sum_j u_j v_j = \Delta. \tag{25}$$

We now turn to the ultrasmall regime, and evaluate $\Delta_{\mathrm{s.p.}}$ in the ground state to second order in λ. Using Eq. (13) we obtain

$$\Delta_{\mathrm{s.p.}}^i = \lambda d + \sum_{j>} \frac{(\lambda d)^2}{\epsilon_j - \epsilon_i}, \tag{26}$$

and for the equally spaced spectrum

$$\Delta_{\mathrm{s.p.}} = \lambda d + \lambda^2 d \ln\frac{\omega_{\mathrm{D}}}{d}. \tag{27}$$

Let us now consider the excitation energy, say E_{exc}, of the first excited state of an (even) superconducting grain. This state can be described by having the two levels nearest to E_{F} singly occupied with probability unity, thus breaking one pair, and the other $N-1$ pairs occupying the remaining $2N-2$ levels according to Richardson's exact solution.[15] The excitation energy has two different contributions. (i) The kinetic energy cost d of occupying a level of higher energy with probability unity, and (ii) a pairing energy cost, which is given by $\Delta_{\mathrm{s.p.}}$. Note that the latter has (iia) a diagonal part, given by λd, which is related to the excess energy of two electrons occupying the same spatial noninteracting eigenstate, and (iib) an off-diagonal part due to the blocking of the two singly occupied levels to pairing correlations. Adding these contributions gives

$$E_{\mathrm{exc}} = d + \Delta_{\mathrm{s.p.}} \approx d + \lambda d + \lambda^2 d \ln\frac{\omega_{\mathrm{D}}}{d}, \tag{28}$$

where the last expression is valid for a grain with equally spaced spectrum. Similarly, the ML parameter[5] is given by

$$\Delta_{ML}=\frac{1}{2}\Delta_{\text{s.p.}}. \tag{29}$$

Note that the pairing contribution to the energy cost of the first excitation equals $2\Delta_{\text{s.p.}}$ in the bulk limit, whereas it equals $\Delta_{\text{s.p.}}$ in an ultrasmall grain, and the same factor of 2 appears in the ML parameter. This reflects the fact that in the bulk limit each level is correlated with all the other levels, while in the ultrasmall grain, the dominant correlations are between levels on different sides of the Fermi energy.

V. MEASUREMENT STRATEGIES FOR Δ_{col} AND $\Delta_{\text{s.p.}}$

A possible measurement of the collective correlations of a superconducting grain was discussed in Ref. 10. It was shown that the condensation energy can be obtained from specific heat or spin magnetization measurements, where an explicit calculation was done for the latter.

In distinction with the case of bulk superconductivity, where the single-particle properties are easiest to measure through the lowest excitations of the system, in small grains the energy of the first excited state is given by Eq. (28), in which $\Delta_{\text{s.p.}}$ is only a small correction to the level spacing. Matveev and Larkin suggested to measure their pairing parameter by the parity-induced alternation of Coulomb blockade peak spacings in small grains. Here we suggest the possibility that for an ensemble of small, weakly coupled grains, $\Delta_{\text{s.p.}}$ could be measured through their spin magnetization as a function of magnetic field at zero temperature. We assume that the coupling between the grains is weak enough such that the equilibrium properties of the system can be approximated by summing over the individual grains, but strong enough so tunneling between grains in a large enough ensemble (of say 50 grains) occurs within the time of the experiment.

For a single-grain, the spin magnetization shows steps at values that correspond to the Zeeman energy being equal the energy required to break a pair, of which the first is at $E_{\text{exc}}=d+\Delta_{\text{s.p.}}$ [by Eq. (28)], which is dominated by the large *single-grain* level spacing d. In order to avoid having to worry about the latter, we consider an ensemble of weakly connected superconducting grains, which would have an effective joint level spacing d_{ens} that is much smaller than d if the ensemble is large, $d_{\text{ens}}\ll d$ (we neglect the charging energy. Note that the charging energy was found to be much smaller[20,21] than what naive estimates give. Since the tunneling between the grains is weak, the relevant ensemble is the canonical one). Then the ground state of the unconnected system is given by each of the grains having an even number of electrons, being in its ground state. The first excited state of the system is given by moving one electron between two grains, so that afterwards the first has a single-occupied level just below E_{F}, and the second has a singly occupied level just above E_{F}. For a system of "normal" noninteracting grains the energy of such an excitation is of the order of the single-particle level spacing of the whole ensemble of grains, d_{ens}. However, in a system of ultrasmall superconducting grains, since two singly occupied levels are created in two different grains, the energy of such an excitation would be given by $\Delta_{\text{s.p.}}$ (which is $\gg d_{\text{ens}}$). Since the first step in the spin magnetization is at the energy of the first excited state of the system, in such a measurement we predict a gap of value $\Delta_{\text{s.p.}}$. (In a similar measurement in grains with $d<\Delta$, the measured gap would be given by Δ). Thus $\Delta_{\text{s.p.}}$ can be interpreted as the superconducting gap as measured by single-particle properties. In principle, performing such a measurement as a function of the grain size would monitor the change of $\Delta_{\text{s.p.}}$, from being much larger than Δ for ultrasmall grains to equaling Δ for large ones. Note by that reducing the grain size one *increases* this gap $\Delta_{\text{s.p.}}$.

Finally, we would like to note that the logarithmic dependence of the correlation (second) term of $\Delta_{\text{s.p.}}$ in Eq. (27) is manifested in the interaction correction to the ensemble averaged magnetic response of small metallic grains, when considered within the BCS model.[11]

VI. SUMMARY

We have shown that various superconducting properties can be classified to two groups, one containing those properties which are single particle in nature, and the other containing those properties which are collective, a result of the summed contributions of many levels. Unlike the case in bulk superconductivity, where both these properties are characterized by one energy parameter Δ, in general, and in particular in small grains, two different energy parameters, $\Delta_{\text{s.p.}}$ for the former group and Δ_{col} for the latter one, characterize superconducting properties.

In bulk superconductivity the relevant contribution to the various superconducting properties comes from the "condensed" levels, within Δ of E_{F}. However, in small grains the contribution of all levels up to ω_{D} is significant, and this results in the existence of these two different parameters, as well as in the fact that $\Delta_{\text{col}}\gg\Delta_{\text{s.p.}}\gg\Delta$ in the ultrasmall regime and $\Delta_{\text{col}}\gg\Delta$ also in the intermediate regime. Experimental possibilities to measure the two pairing parameters were discussed.

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