

## Thermodynamic properties of a small superconducting grain

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The reduced BCS Hamiltonian for a metallic grain with a finite number of electrons is considered. The crossover between the ultrasmall regime, in which the level spacing  $d$  is larger than the bulk superconducting gap  $\Delta$  and the small regime, where  $\Delta \gtrsim d$ , is investigated analytically and numerically. The condensation energy, spin magnetization, and tunneling peak spectrum are calculated analytically in the ultrasmall regime, using an approximation controlled by  $1/\ln N$  as a small parameter, where  $N$  is the number of interacting electron pairs. The condensation energy in this regime is perturbative in the coupling constant  $\lambda$  and is proportional to  $dN\lambda^2 = \lambda^2 \omega_D$ . We find that also in a large regime with  $\Delta > d$ , in which pairing correlations are already rather well developed, the perturbative part of the condensation energy is larger than the singular, BCS part. The condition for the condensation energy to be well approximated by the BCS result is found to be roughly  $\Delta > \sqrt{d\omega_D}$ . We show how the condensation energy can, in principle, be extracted from a measurement of the spin magnetization curve and find a reentrant susceptibility at zero temperature as a function of magnetic field, which can serve as a sensitive probe for the existence of superconducting correlations in ultrasmall grains. Numerical results are presented, which suggest that in the large  $N$  limit the  $1/N$  correction to the BCS result for the condensation energy is larger than  $\Delta$ .

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### I. INTRODUCTION AND SUMMARY OF RESULTS

In the macroscopic limit, a system described by the reduced BCS Hamiltonian is well treated by the mean-field BCS method.<sup>1</sup> When the size of a superconducting sample becomes small, two related questions can be asked: what is the lower size limit for which superconducting properties are observable, and what is the lower size limit for the validity of the BCS theory?

In 1959 Anderson<sup>2</sup> considered the first question and argued that “superconductivity would no longer be possible” once the electron spectrum’s mean level spacing  $d$  becomes larger than the bulk superconducting gap  $\Delta$ . [ $1/d = \mathcal{N}(0)$ , the density of states per spin species near the Fermi energy, hence  $d \propto 1/\text{vol}$ .] This statement sets a lower limit for the size above which a grain still exhibits superconducting properties, but at the same time states that such a grain can well be much smaller than the superconducting coherence length. Superconductors in the regime where the level spacing is comparable to the gap energy have been studied for many years both theoretically (e.g., Ref. 3) and experimentally (e.g., Ref. 4, see also the review by Perenboom *et al.*<sup>5</sup>).

Recently, Ralph, Black, and Tinkham performed measurements on single superconducting nm-scale grains in the regimes of  $\Delta \gtrsim d$  and  $\Delta \lesssim d$ .<sup>6</sup> These experiments and the considerable amount of theoretical work they initiated<sup>7–18</sup> found various properties indicative of strong superconducting pairing correlations in grains with  $\Delta \gtrsim d$  (to be called “small grains”), but not in grains with  $\Delta < d$  (to be called “ultrasmall grains”), thus supporting Anderson’s criterion. These properties include (i) a parity-dependent gap in the excitation spectrum (the gap exists only for grains with an even number of electrons), which is driven to zero by magnetic field;<sup>6,8,9,15</sup> (ii) a difference of order  $\Delta$  in the ground-state energies of

even and odd grains;<sup>10,14</sup> and (iii) a first-order paramagnetic transition induced by a magnetic field.<sup>9,15</sup>

Though *ultrasmall* grains with  $\Delta < d$  do not have as strongly developed signatures of pairing correlations as the small grains with  $\Delta \gtrsim d$  mentioned above, pairing correlations nevertheless do exist in such grains, albeit in the form of weaker fluctuations, and they can affect various physical quantities. For example, Lorenzo *et al.*<sup>19</sup> found that pairing correlations affect the temperature dependence of the spin susceptibility of grains also in the ultrasmall regime.

The crossover regime between small and ultrasmall grains has also been studied in some detail numerically, using a simple reduced BCS model with a discrete set of single-particle levels.<sup>13,14,16,18</sup> In particular, it was found that the condensation energy  $E_{cond}$  (i.e., the energy gain of the exact ground state relative to the uncorrelated Fermi ground state) smoothly crosses over from being extensive (proportional to the size of the system) for  $\Delta > d$  to being intensive for  $\Delta < d$ .

One of the goals of the present paper is to obtain further insights into the crossover from the ultrasmall regime, which can be treated perturbatively in the dimensionless coupling ( $\lambda$ ) of the said reduced BCS model, to the small regime, which cannot. Our point of departure is an exact solution, due to Richardson and Sherman<sup>20,21</sup> of the reduced BCS model of present interest. By analyzing Richardson’s solution both analytically and numerically in the crossover regime, we elucidate in detail when and how perturbation theory in  $\lambda$  breaks down, how the answer depends on the system size, and how the standard BCS results are recovered in the bulk limit  $d \ll \Delta$ .

The bulk regime is of course well known to require a nonperturbative treatment; indeed, the BCS result for the condensation energy

$$E_{cond}^{BCS} = \Delta^2 / (2d) \quad (1)$$

is not analytical in  $\lambda$  as  $\lambda \rightarrow 0$ , since the bulk gap is given by

$$\Delta(\lambda) = \omega_D / \sinh(1/\lambda) \quad [\approx 2\omega_D e^{-1/\lambda} \quad \text{for } \lambda \ll 1], \quad (2)$$

where  $\omega_D = Nd$  is the bandwidth about the Fermi energy within which the pairing interaction acts (typically the Debye frequency). This nonanalyticity arises because BCS consider the thermodynamic limit of an infinite system size ( $N \rightarrow \infty$ ,  $d \rightarrow 0$  at fixed  $\omega_D$ ).

We shall argue that if instead one considers a system with a finite number of pairs, say  $N$ , the condensation energy  $E_{cond}(\lambda)$  is an analytical function about  $\lambda = 0$ , with a finite radius of convergence given approximately by  $\lambda^* = 1/\ln N$ . For  $\lambda < \lambda^*(1 - \lambda^*)$ , corresponding to  $\Delta < d$  [by Eq. (2)].<sup>22</sup>  $E_{cond}(\lambda)$  is found to be well approximated by the perturbative result

$$E_{cond}^{pert}(\lambda) = \ln 2 \cdot \lambda^2 \omega_D. \quad (3)$$

On the other hand, the BCS mean-field result  $E_{cond}^{BCS}$  of Eq. (1) is found to become reliable only for  $\lambda > 2\lambda^*$ , corresponding to roughly  $\Delta > \sqrt{\omega_D d}$ . Thus, we identify a substantial intermediate regime,

$$\lambda^* < \lambda < 2\lambda^*, \quad \text{i.e.,} \quad d < \Delta < \sqrt{\omega_D d}, \quad (4)$$

in which neither the perturbative result nor the BCS mean-field result adequately reproduces  $E_{cond}$  (though, roughly speaking, the sum  $E_{cond}^{pert} + E_{cond}^{BCS}$  does).

The existence of this intermediate regime implies that the regime of validity of the BCS mean-field approach for calculating  $E_{cond}$  is significantly smaller than realized hitherto: the crossover level spacing ( $d > \Delta^2 / \omega_D$ ) beyond which it becomes inadequate is considerably smaller than the scale ( $d > \Delta$ ) beyond which the BCS approach formally breaks down (in the sense of yielding no nontrivial solution to the self-consistency equation<sup>8</sup>) and up to which strong signatures for pairing correlations can still be observed, as mentioned above.

We are also able to pinpoint the reason for the failure of the BCS approach in the intermediate regime (4): we shall show in detail that  $E_{cond}^{BCS}$  incorporates only contributions to  $E_{cond}$  from the strongly pair-correlated, ‘‘condensed’’ levels within  $\Delta$  of the Fermi energy  $E_F$ , but neglects contributions from all the remaining, ‘‘weakly pair-fluctuating’’ levels that extend to a distance  $\omega_D$  from  $E_F$ . Although the latter levels are so weakly correlated that their contribution can be calculated perturbatively, essentially yielding  $E_{cond}^{pert}$ , this contribution turns out to be larger than  $E_{cond}^{BCS}$  as long as  $\Delta < \lambda \sqrt{\omega_D d}$  and is not negligible compared to the  $E_{cond}^{BCS}$  in the whole intermediate regime (4). (Note though, that  $E_{cond}^{pert}$  would largely cancel out when one considers energy differences between eigenstates that differ only in the specific placement of a small number of electrons in levels near  $E_F$ . An example would be the ground-state energy difference between an even and odd superconducting grain, for which the BCS approach would be adequate in the intermediate re-

gime.) Our results for the condensation energy in regimes I and II also show that the condensation energy is not a universal function of  $d/\Delta$ , but an explicit function of  $\omega_D$ .

It should be mentioned here that the question of how to recover the BCS gap equation from Richardson’s exact solution has been solved by Richardson himself<sup>23</sup> by effectively doing a  $1/N$  expansion around the bulk, thermodynamic limit. Our work differs from his in that we do an expansion in  $\lambda$  around the ultrasmall limit for a system of finite size, with  $\lambda < 1/\ln N$  as a small parameter.

Using the insights gained from our studies of the condensation energy, we also calculate various other thermodynamic properties of ultrasmall grains at zero temperature, using a controlled analytical approximation with  $\lambda < 1/\ln N$  as the small parameter. Specifically, we calculate the spin magnetization and susceptibility curves, and tunneling peak spectrum of ultrasmall grains and find that pairing correlations have their signature in all the above physical quantities, even in the regime  $\lambda < \lambda^*$  where pairing correlations are weakest.

The condensation energy can, in principle, be measured by integrating the spin magnetization as a function of magnetic field ( $H$ ) and comparing it to the linear curve of a normal grain. In fact, as we discuss in Sec. III, since the energy levels in the grain are not equally (or systematically) spaced, one needs to do the measurement on an ensemble of grains. Calculating the spin susceptibility of an ultrasmall grain, we find that for  $H \gg d/\mu_B$ , pairing fluctuations of levels far away from  $E_F$  result in a correction of the order  $\lambda^2 d/\mu_B H$  to the normal susceptibility. Interestingly, this correction persists for all fields  $H < \omega_D/\mu_B$ , i.e., well beyond the Clogston-Chandrasekhar field  $\mu_B H_{CC} = \Delta/\sqrt{2}$ ,<sup>24</sup> at which, for bulk systems, a first-order transition occurs from the superconducting ground state to a paramagnetic ground state. (Only for  $H > \omega_D/\mu_B$ , the grain becomes effectively ‘‘normal,’’ since then all the levels within  $\omega_D$  from the Fermi energy become unpaired.) The correction to the spin susceptibility results in a reentrant behavior of the differential susceptibility as a function of magnetic field, which could possibly serve as a sensitive probe to detect superconducting correlations in ultrasmall grains.<sup>19</sup> (The consequences of pairing correlations in the regime  $H > H_{CC}$  have also been studied by Aleiner and Altshuler,<sup>11</sup> who found an anomaly in the tunneling density of states.) Similarly, we argue below that in ultrasmall superconducting grains, pairing fluctuations involving levels far away from  $E_F$  are sufficiently strong that they also leave their mark in the specific heat (even for  $T \gg T_c$ ) and the tunneling peak spectrum.

All our calculations are done for grains with an even number of electrons. The results for grains with an odd number of electrons are similar in the ultrasmall regime and will be discussed shortly for each calculated quantity.

The paper is arranged as follows: In Sec. II we calculate the condensation energy of an ultrasmall superconducting grain in the regime  $\Delta < d$  and also analyze the intermediate regime of Eq. (4) for larger grains. In Sec. III the spin magnetization of ultrasmall grains as a function of magnetic field is calculated. It is shown that the condensation energy is given by integrating the magnetization from  $H = 0$  to

$\omega_D/\mu_B$ . In Sec. IV we calculate the differential spin susceptibility of ultrasmall grains as a function of magnetic field and find that it exhibits a reentrant behavior. In Sec. V the tunneling peak spectrum of an ultrasmall superconducting grain is calculated. In Sec. VI we present numerical results for the contribution of the ‘‘condensed’’ and ‘‘fluctuating’’ levels to the condensation energy.

The technical aspects of our calculations are collected in three appendices. In Appendix A a detailed derivation of the accuracy of the condensation energy approximation is given. In Appendix B the functional behavior of the prefactors of the series expansion of the approximate condensation energy is analyzed. In Appendix C the series expansion of the exact condensation energy is discussed.

## II. CONDENSATION ENERGY OF AN ULTRASMALL GRAIN

### A. Richardson’s equations

We consider the reduced BCS Hamiltonian

$$\hat{H} = \sum_{j,\sigma=\pm} \epsilon_j c_{j\sigma}^\dagger c_{j\sigma} - \lambda d \sum_{i,j} c_{i+}^\dagger c_{i-}^\dagger c_{j-} c_{j+} \quad (5)$$

for a grain with a given, finite number of electrons  $\bar{N}$ . The first term is the kinetic term, which we will refer to as  $\hat{H}_0$ , and the second term is the interaction Hamiltonian, denoted  $\hat{H}_I$ . The sum in  $\hat{H}_I$  is over all the levels inside the range  $E_F - \omega_D < \epsilon < E_F + \omega_D$ , which we designate as  $I$ . The Hamiltonian (5) is the usual BCS Hamiltonian used when discussing superconducting grains<sup>8–19</sup> and its validity is discussed in, e.g., Refs. 11, 25, and 26. (In particular, for the model to be valid the grain’s dimensionless conductance  $g$  must be much larger than one.) In all cases discussed below we consider states in which all levels below  $E_F - \omega_D$  are doubly occupied, while all levels above  $E_F + \omega_D$  are empty. Since the dynamics of electrons occupying levels outside the range  $I$  and their contribution to the total energy are trivially given by  $\hat{H}_0$ , we will not consider them henceforth.

Richardson and Sherman<sup>20,21</sup> showed that this Hamiltonian, with a finite number of electrons, can be solved exactly. They define for each single-particle eigenstate of  $\hat{H}_0$  the operator  $\xi_j = c_{j+}^\dagger c_{j+} - c_{j-}^\dagger c_{j-}$ . This operator, for any  $j$ , is a constant of motion of the Hamiltonian (5) and takes the value  $\pm 1$  if the level is singly occupied, and 0 otherwise. The many-body eigenstates of Eq. (5) can therefore be classified into different subspaces according to their value of the  $\xi_j$ ’s, i.e., according to the configuration of levels within  $I$  that are occupied by one electron only. The many-body eigenstates and the eigenenergies of Eq. (5) are then found separately<sup>20,21</sup> for each of the above subspaces.

The electrons in the singly occupied levels are not scattered to other levels by the interaction term, and the singly occupied levels are ‘‘blocked’’ to pair scattering, and we therefore designate them as  $B$ . The dynamics of the singly occupied levels is also trivially given by  $\hat{H}_0$ . Therefore, for each set  $B$  one has to solve the reduced Hamiltonian

$$\hat{H} = \sum_j^U 2\epsilon_j b_j^\dagger b_j - \lambda d \sum_{i,j}^U b_i^\dagger b_j. \quad (6)$$

Here  $b_j^\dagger = c_{j+}^\dagger c_{j-}^\dagger$  creates a pair of electrons in level  $j$ , and  $U$  is the set of paired levels within  $I$ , i.e., the set of all levels that belong to  $I$  but not to  $B$  (the notation, in general, follows Ref. 26). Below, sums over levels labeled by  $j$  are to be understood as sums over levels within  $U$ .

Once the configuration of unpaired electrons is given, Richardson and Sherman<sup>21</sup> (see Ref. 17 for a review) show that the eigenstates of the system are given by

$$|\alpha\rangle = \prod_{i \in B} c_{i\sigma_i}^\dagger |\Psi_k\rangle, \quad |\Psi_k\rangle = C \prod_{\nu=1}^k B_\nu^\dagger |0\rangle,$$

$$B_\nu^\dagger = \sum_j \frac{b_j^\dagger}{2\epsilon_j - E_\nu}, \quad (7)$$

where  $2k$  is the number of electrons occupying the unblocked levels, and  $|0\rangle$  is the state with all the levels below  $E_F - \omega_D$  fully occupied and all the levels above  $E_F - \omega_D$  empty (in our model  $|0\rangle$  is the vacuum state). The energy parameters  $E_\nu$  (with  $\nu = 1, \dots, k$ ) are the solutions of a set of  $k$  coupled nonlinear equations, the  $\nu$ th equation of which is given by

$$\frac{1}{\lambda d} + \sum_{\mu=1(\neq\nu)}^k \frac{2}{E_\mu - E_\nu} - \sum_j \frac{1}{2\epsilon_j - E_\nu} = 0. \quad (8)$$

The total energy of the system is given by<sup>20,21</sup>

$$E = \sum_j^B \epsilon_j + \sum_{\nu=1}^k E_\nu. \quad (9)$$

Since the ground state of a grain with an even number of electrons does not contain any singly occupied levels (i.e.,  $U=I$ ), the even ground-state energy is simply  $E_{g.s.} = \sum_{\nu=1}^k E_\nu$ . Its  $\lambda \rightarrow 0$  limit is  $E_{g.s.}(\lambda=0) = \sum_{\nu=1}^k 2\epsilon_\nu$ , where  $\{2\epsilon_\nu, \nu=1, \dots, k\}$  is the set of the  $k$  lowest-lying single-pair energies. [This is consistent with the observation, following from Eq. (8), that in the limit  $\lambda \rightarrow 0$  the set of  $E_\nu$ ’s reduces to a set of  $k$  single-pair energies  $2\epsilon_j$ , which, for the ground state, must have the lowest total energy possible.] Consequently, the interaction energy of the even ground state  $E_{int}(\lambda)$ , defined to be the reduction of the exact ground-state energy as the interaction is turned on from zero to some finite  $\lambda$ , can be written as

$$E_{int}(\lambda) \equiv E_{g.s.}(0) - E_{g.s.}(\lambda) = \sum \delta E_\nu, \quad (10)$$

where we introduced the energy differences  $\delta E_\nu \equiv 2\epsilon_\nu - E_\nu$ . A closely related quantity is the condensation energy  $E_{cond}(\lambda)$ , defined to be the energy gain of the exact even ground state relative to the uncorrelated Fermi ground state:

$$E_{cond}(\lambda) \equiv E_{F.g.s.}(\lambda) - E_{g.s.}(\lambda), \quad (11)$$

$$= \sum_{\nu=1}^k (2\epsilon_{\nu} - \lambda - E_{\nu}) = E_{int}(\lambda) - k\lambda d. \quad (12)$$

The  $\lambda$  contribution in the first sum in Eq. (12) is the Hartree self-energy of level  $j$  in the Fermi ground state.

### B. Perturbative results for $E_{cond}$ and $E_{int}$

Let us now consider the case in which the set  $I$  of interacting levels consists of  $2N$  equally spaced energy levels between  $E_F - \omega_D$  and  $E_F + \omega_D$ , occupied by  $2N$  electrons, so that  $k=N$ . Measuring the single-particle energies with respect to the bottom of the interacting band, we thus take  $\epsilon_j = jd$ , where  $j=1, \dots, 2N$  and  $d = \omega_D/N$ . (Note that  $N \neq \bar{N}$  the total number of electrons in the grain, which is of order  $2E_F/d$ , not  $2\omega_D/d$ .)

Using Eq. (8), the energy differences  $\delta E_{\nu}$  occurring in Eq. (10) can be rewritten as

$$\delta E_{\nu} \equiv 2\epsilon_{\nu} - E_{\nu} = \frac{\lambda d}{1 - \lambda a_{\nu}}, \quad (13)$$

where

$$a_{\nu} = d \left( \sum_{j=1(\neq \nu)}^{2N} \frac{1}{2\epsilon_j - E_{\nu}} - \sum_{\mu=1(\neq \nu)}^N \frac{2}{E_{\mu} - E_{\nu}} \right). \quad (14)$$

For small  $\lambda$ , it is natural to approximate  $\delta E_{\nu}$  by

$$\delta E_{\nu}^0 \equiv \lambda_{\nu} d, \quad \text{where} \quad \lambda_{\nu} \equiv \frac{\lambda}{1 - \lambda a_{\nu}^0}, \quad (15)$$

and  $a_{\nu}^0 \equiv a_{\nu}(\lambda=0)$  is given by

$$a_{\nu}^0 = \sum_{j=1(\neq \nu)}^{2N} \frac{1}{2j - 2\nu} - \sum_{\mu=1(\neq \nu)}^N \frac{2}{2\mu - 2\nu}. \quad (16)$$

The accuracy of this approximation is studied in Appendix A (by deriving an expression for  $\delta a_{\nu} = a_{\nu} - a_{\nu}^0$ ), where we find that the relative error in  $\delta E_{\nu}$  depends on both  $\lambda$  and  $N$ . Specifically, we find that for all  $\nu$ ,

$$\delta E_{\nu} / \delta E_{\nu}^0 = 1 + \mathcal{O}[1/(\ln N)^2] \quad \text{for} \quad \lambda < 1/(2 \ln N), \quad (17a)$$

$$\delta E_{\nu} / \delta E_{\nu}^0 = 1 + \mathcal{O}(1/c^2) \quad \text{for} \quad 1/(2 \ln N) < \lambda < 1/\ln N - c/(\ln N)^2, \quad (17b)$$

for any  $c > 1$ . Note that Eq. (17b) implies the emergence of a second scale near  $\lambda = 1/\ln N$ , namely,  $1/(\ln N)^2$ .

To the accuracy given by Eqs. (17a) and (17b), the interaction and condensation energies can be approximated by

$$E_{int}^0 = E_{cond}^0 + N\lambda d \approx \sum_{\nu=1}^N \delta E_{\nu}^0 = \sum_{\nu=1}^N \lambda_{\nu} d, \quad (18)$$

where  $\lambda_{\nu}$  is given in Eq. (15). This result coincides with that obtained by Matveev and Larkin [Eq. (17) of Ref. 10]; more-

over, our approach allows us to give a controlled estimate of the error introduced by this approximation, both for Eq. (18) and our explicit calculation of  $E_{int}$  and  $E_{cond}$  in Appendix B. Interestingly, Eq. (18) can be interpreted as a sum over the Hartree self-energies  $\lambda_{\nu} d$  of the lowest  $N$  levels, each of which is evaluated using its own level-specific ‘‘renormalized coupling constant’’  $\lambda_{\nu}$  (thus motivating our choice of notation). The emergence of such renormalized coupling constants has been noted before,<sup>27</sup> in particular by Matveev and Larkin<sup>10</sup> and Berger and Halperin.<sup>14</sup> Matveev and Larkin, for example, were concerned with perturbatively calculating a certain parity parameter that was essentially equal to  $\lambda_N d/2$  and found

$$\lambda_N^{ML} \approx \frac{\lambda}{1 - \lambda \ln(\omega_D/d)}, \quad (19)$$

in agreement with our result [Eq. (15)] for  $\lambda_N$  [see Eq. (B6) and the statement following it].

Now, calculating the interaction or condensation energies is considerably more involved than calculating the parity parameter of Matveev and Larkin, since, in contrast to their calculation, not only one but all  $N$  renormalized couplings  $\lambda_{\nu}$  enter in Eq. (18) for  $E_{int}^0$  or  $E_{cond}^0$ . This is a major complication, since their  $\nu$  dependence turns out to be sufficiently important to make it impossible to replace all  $\lambda_{\nu}$  by a single ‘‘effective coupling constant.’’

Nevertheless, progress can be made by expanding  $E_{int}^0$  or  $E_{cond}^0$  in powers of  $\lambda$  and analyzing the convergence properties of the resulting series. This is done in Appendix B (for  $E_{int}^0$ , but here we shall give the results for  $E_{cond}^0$ , which is slightly more convenient, since it lacks the Hartree term). It is found that the convergence radius of the power series for  $E_{cond}^0(\lambda)$  is

$$\lambda^* = 1/\ln N. \quad (20)$$

The regime of analyticity,

$$\lambda < \lambda^*, \quad \text{i.e.,} \quad \Delta < d, \quad (21)$$

[by Eq. (2)] will be called ‘‘regime I’’ below. Within regime I, we obtain an analytical expression for  $E_{cond}^0(\lambda)$  as a series in  $\lambda$ . We find (see Appendix B) that the series for  $E_{cond}^0$  does not have one parameter that describes the ratio between consecutive terms in the series. Denoting the  $m$ th term in the power series as  $E_{cond}^{0(m)}$ , we show that the low powers fulfill the relation  $E_{cond}^{0(m+1)}/E_{cond}^{0(m)} \approx m \cdot \lambda$  while the high powers fulfill the relation  $E_{cond}^{0(m+1)}/E_{cond}^{0(m)} \approx \lambda \cdot \ln N$ . This results in having two separate scales in  $\lambda$ . While the high powers dictate the convergence radius of the series to be  $\lambda^*$ , their contribution is large only for  $\lambda \geq \lambda^*(1 - \lambda^*)$  (see Appendix B), introducing the aforementioned second scale of  $1/(\ln N)^2$  near  $\lambda = 1/\ln N$ . As a result, for  $\lambda < \lambda^*(1 - \lambda^*)$  (i.e., in most of regime I),  $E_{cond}^0$  is well approximated by the contribution of the low powers that turn out to correspond simply to the second-order perturbative result (up to a relative correction of  $1/\ln N$ , see Appendix B):



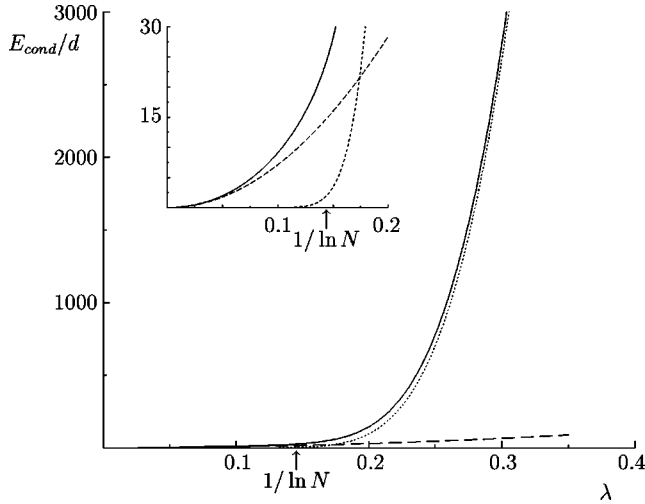


FIG. 1. The condensation energy of a grain with  $N=1024$ , in units of level spacing, is plotted as a function of  $\lambda$ . The solid line is the numerical solution of the exact Richardson equations. The dashed line is the second-order approximation. The dotted line is the BCS approximation. The BCS approximation is good for  $\lambda \gg \lambda^* \equiv 1/\ln N$ . In the inset the same graph is given for a small range of  $\lambda$  and a much smaller range for  $E_{cond}$ . The value at which the perturbative term equals the BCS term tends asymptotically to  $2/\ln N$  (see text), but here it is somewhat smaller since  $N$  is not very large.

$$E_{cond}^0 \simeq E_{cond}^{pert}(\lambda) = \ln 2 \cdot \lambda^2 \omega_D [1 + \mathcal{O}(1/\ln N)]$$

$$\text{for } \lambda < \lambda^* (1 - \lambda^*). \quad (22)$$

This is illustrated in Fig. 1. Intuitively speaking, this contribution can be attributed to pairing fluctuations involving all the levels in the range  $E_F - \omega_D < \epsilon < E_F + \omega_D$ .

### C. Analysis of the intermediate regime $\lambda^* < \lambda < 2\lambda^*$

Although we are not able to extend the analytical calculation to the regime of  $\lambda > \lambda^*$  (i.e.,  $\Delta > d$ ), we are able to draw some conclusions about the value of the condensation energy in the latter regime. First, we note that the perturbative result (22) for the condensation energy at  $\lambda = \lambda^*$  is larger than the BCS mean-field result (1) as a function of  $\lambda$ , i.e.,  $E_{cond}^{pert}(\lambda^*) \gg E_{cond}^{BCS}(\lambda)$ , as long as  $\Delta < \lambda \sqrt{\omega_D d}$ . In this regime  $E_{cond}^{BCS}(\lambda)$  is thus also much smaller than the actual condensation energy  $E_{cond}(\lambda)$  [since, assuming monotonicity of  $E_{cond}(\lambda)$  as function of  $\lambda$ , we have  $E_{cond}(\lambda) > E_{cond}^{pert}(\lambda^*)$  for  $\lambda > \lambda^*$ ]. In terms of  $\lambda$  and  $N$  the condition is  $\ln[\ln 2 \cdot (\lambda^*)^2/2] + 2/\lambda > \ln N$ , which, for large  $N$ , is roughly  $\lambda < 2\lambda^*$ . [Note that the exponential dependence of  $\Delta$  on  $\lambda$  causes a relatively small change in the condition for  $\lambda$  ( $< \lambda^*$  versus  $< 2\lambda^*$ ) to translate into a parametric change in the condition for  $\Delta$  ( $< d$  versus  $\lambda \sqrt{\omega_D d}$ ).] The  $E_{cond}^{pert}$  contribution in Eq. (24) becomes significantly smaller (by a factor  $\lambda^2$ ) than the  $E_{cond}^{BCS}$  contribution only for  $\Delta > \sqrt{\omega_D d}$ . Thus, we identify an intermediate regime

$$d < \Delta < \sqrt{\omega_D d}, \quad \text{i.e., } \lambda^* < \lambda < 2\lambda^* \quad (23)$$

[by Eq. (2)], to be called ‘‘regime II,’’ in which the BCS mean-field approach is severely inadequate for calculating  $E_{cond}$ , but which, according to the three properties mentioned in the introduction, nevertheless already features strongly developed pairing correlations. In other words, the condition for the adequacy of the BCS mean-field approximation ( $\lambda > 2\lambda^*$ , ‘‘regime III’’) is more restrictive than the condition for the existence of strongly developed pairing correlations ( $\lambda > \lambda^*$ ). Importantly, this also means that the BCS mean-field approach becomes inadequate already for much smaller level spacings  $d \approx \Delta^2/\omega_D$ , than those at which it formally breaks down (in the sense of yielding no nontrivial solution to the self-consistency equation), which occurs for  $d \gtrsim \Delta$ .

The inadequacy of the BCS approximation in regime II stems from the abundance of ‘‘fluctuating’’ levels compared to ‘‘condensed’’ levels. Each ‘‘condensed’’ level within a range  $\Delta$  from the Fermi energy contributes approximately  $\Delta/2$  to the condensation energy and having  $\Delta/d$ , such levels give the BCS term  $\Delta^2/2d$ . Though each ‘‘fluctuating’’ level outside this range contributes only an amount of order  $(d\lambda)^2/d$  to the condensation energy, there are  $\omega_D/d$  such levels, and for  $\Delta < \lambda \sqrt{\omega_D d}$  the total contribution  $\lambda^2 \omega_D$  of all fluctuating levels is larger than  $\Delta^2/2d$ . This sets an energy scale  $\sqrt{\omega_D d}$ , which  $\Delta$  has to exceed before the BCS approximation becomes reliable. The above interpretation of the relative contributions of ‘‘condensed’’ and ‘‘fluctuating’’ levels to the total condensation energy is confirmed by a detailed numerical analysis, see Sec. VI.

Second, by numerically analyzing Richardson’s equations (see Refs. 20, 21, 28, and 29 and a review in Ref. 26), we find that in the regime  $\lambda > \lambda^*$ , the condensation energy can be written as

$$E_{cond}(\lambda) = E_{cond}^{BCS}(\lambda) + \Delta + \alpha(\lambda) E_{cond}^{pert}(\lambda), \quad (24)$$

where  $\alpha(\lambda)$  is a function of  $\lambda$  of order unity. [A rather similar, but not identical, form was obtained in Eq. (44) of Ref. 18 from a fit to numerical results for  $E_{cond}(\lambda)$  obtained with the density-matrix renormalization group.] As will be discussed in more detail in Sec. VI, the first two terms in Eq. (24) represent the contributions of those levels lying within  $\Delta$  from  $E_F$  (to be called ‘‘condensed levels’’), while the last term is due to the remaining levels within  $\omega_D$  from  $E_F$  (to be called ‘‘fluctuating levels’’). According to Eq. (24), the size-independent correction to the BCS result (i.e., the leading-order  $1/N$  correction relative to the extensive, bulk result) is at least  $\Delta$ .

The numerical analyses carried out in Sec. VI and Appendix C also give evidence that  $E_{int}$  (and also  $E_{cond}$ ) is an analytical function on the positive real axis of  $\lambda$  with a radius of convergence around  $\lambda = 0$  of approximately  $1/\ln N$ . This is in agreement with our analytical treatment of the perturbative series in Appendixes B and C.

The results for the condensation energy of grains with an odd number of electrons are similar. In the ground state of an odd grain the state at the Fermi level is occupied by a single electron. Due to the considerations above, one does all the calculations neglecting this level, and therefore, when the

ground-state energy is concerned, a grain with an odd number of electrons is equivalent to a grain with an even number of electrons with a noninteracting level spectrum, which does not contain the single level at the Fermi energy and is otherwise identical. This change introduces only small quantitative changes in the results above.

One way in which one can, in principle, measure the interaction energy of an ultrasmall superconducting grain is by measurement of the specific heat. The interaction energy is then given by

$$E_{int} = \int_0^\infty [c_s(T) - c_n(T)] dT. \quad (25)$$

$c_{n(s)} = d\bar{E}_{n(s)}/dT$ , where  $\bar{E}_{n(s)}$  is the thermal average of the energy of a normal (superconducting) grain. While in macroscopic samples one obtains the leading-order (extensive) term of the interaction energy by performing the above integral from zero to  $T_c$ , in ultrasmall grains, since the fluctuations involve states in the whole range of  $E_F - \omega_D < \epsilon < E_F + \omega_D$ , one has to replace the upper limit of the integral by  $T_{max} \approx \omega_D$  in order to have a good estimate of  $E_{int}$ . At  $T > T_{max}$ , one expects that the interaction term in the Hamiltonian would play a negligible role, and  $(\bar{E}_s)$  and  $(\bar{E}_n)$  would be roughly the same. Another way to measure the interaction energy is by spin magnetization measurements, as we discuss in the next section.

### III. SPIN MAGNETIZATION OF AN ULTRASMALL GRAIN

Since the condensation energy of an ultrasmall grain has contributions from all the levels within the range of  $\omega_D$ , in order to measure it one has to probe all the levels within this range. One way to do this is to put an ultrasmall, preferably pancake-shaped grain in a magnetic field parallel to the flat direction. One can then neglect orbital magnetization and consider only the Pauli paramagnetism.<sup>30</sup>

The interaction energy can then be obtained by

$$E_{int} = \int_0^{\omega_D/\mu_B} (M_n - M_s) dH, \quad (26)$$

where  $M_{n(s)}$  is the magnetization of the normal (superconducting) grain. This is a general thermodynamic identity, relying only on the fact that the electrons further than  $\omega_D$  from  $E_F$  are noninteracting, so that  $M_n(H) = M_s(H)$  for  $\mu_B H > \omega_D$ . We now derive this relation for ultrasmall superconducting grains and calculate the magnetization of such grains for  $H \gg d/\mu_B$ .

We introduce the Zeeman term to the Hamiltonian (5) changing  $\epsilon_j \rightarrow \epsilon_j - \sigma \mu_B H$  (taking the  $g$  factor to equal 2). Each eigenstate of the Hamiltonian (5) is also an eigenstate of the modified Hamiltonian, with an energy  $E_H = E_{H=0} - \mu_B H(n_\uparrow - n_\downarrow)$ , where  $n_\uparrow(n_\downarrow)$  is the number of levels singly occupied by an electron with a spin in (opposite to) the direction of the magnetic field.

We consider, as above, an ultrasmall grain with an even number of electrons and neglect orders of  $\lambda$  higher than two

in the calculations of the eigenstate energies below. At  $T = 0$  and zero magnetic field the ground state of the system has no broken pairs, meaning there are no bare levels occupied with a single electron. Of all the states with  $l$  broken pairs, the one with the lowest energy will be denoted  $\psi_l$  and its energy  $E_l$ . One can show that  $\psi_l$  has all the  $l$  levels closest to  $E_F$  from above and all the  $l$  levels closest to  $E_F$  from below singly occupied, while all the other levels are not singly occupied. For  $H \neq 0$  all the electrons in the singly occupied levels will have their spin in the direction of the magnetic field. In this case  $E_l(H) = E_l(0) - 2l\mu_B H$ . For  $T = 0$  and finite  $H$  the ground state of the system is  $\psi_l$  with the smallest  $E_l(H)$  of all  $l$ 's. While for a large superconducting grain an abrupt transition from  $l=0$  to  $l=\Delta/(\sqrt{2}d)$  occurs at  $H = \Delta/(\sqrt{2}\mu_B)$ ,<sup>24</sup> in an ultrasmall grain the number of broken pairs in the ground state increases by one at a time as  $H$  is increased.<sup>15</sup> The magnetic field for which the transition of the ground state from  $\psi_{l-1}$  to  $\psi_l$  occurs is denoted  $H_l$ . For  $H_l < H < H_{l+1}$ ,  $\psi_l$  is the ground state of the grain with ground state energy  $E_l(0) - 2l\mu_B H$ , and therefore the magnetization equals  $2l\mu_B$ . The magnetization is a step function in  $H$ , with equal steps of magnitude  $2\mu_B$ . One needs only to find the values of  $H_l$  to get the magnetization curve. The above picture is also true for a normal grain. (By normal and superconducting grains we mean here similar grains, with the same single-particle noninteracting spectrum that differ only by the value of  $\lambda$ , which is zero for the normal grain and finite for the superconducting grain. The relation of the above to a realistic situation is discussed below.) From its definition as the solution of

$$E_l^{s/n}(H_l^{s/n}) = E_{l-1}^{s/n}(H_l^{s/n}), \quad (27)$$

(for both pair-correlated or normal grains),  $H_l^{s/n}$  is given by

$$2\mu_B H_l^{s/n} = E_l^{s/n}(0) - E_{l-1}^{s/n}(0). \quad (28)$$

It follows that

$$\sum_{l=1}^{l_{max}} 2\mu_B H_l^{s/n} = E_{l_{max}}^{s/n}(0) - E_0^{s/n}(0). \quad (29)$$

Taking  $l_{max} = \omega_D/d$  and subtracting the equation for normal grains from that for pair-correlated ones, we find

$$\sum_{l=1}^{l_{max}} 2\mu_B (H_l^s - H_l^n) = E_0^n(0) - E_0^s(0) = E_{int}, \quad (30)$$

where we took  $E_{l_{max}}^s(0) = E_{l_{max}}^n(0)$ , since at energies beyond  $l_{max}d = \omega_D$  the pairing interaction is no longer operative. But, as can be seen from Fig. 2 (drawn for equally spaced normal and pair-correlated grains), the sum on the left-hand side equals the area between the solid and dashed lines, and hence also equals the integral in Eq. (26).

Finding  $H_l$  amounts to solving Eq. (27). We first assume that the noninteracting energy levels in the grain are equally spaced. For a normal grain this equation then reduces to  $(2l-1)d - 2\mu_B H = 0$ , where the first term is the extra kinetic energy of the  $l$  state compared to the  $l-1$  state, and the second term is its gain in Zeeman energy. In an ultrasmall

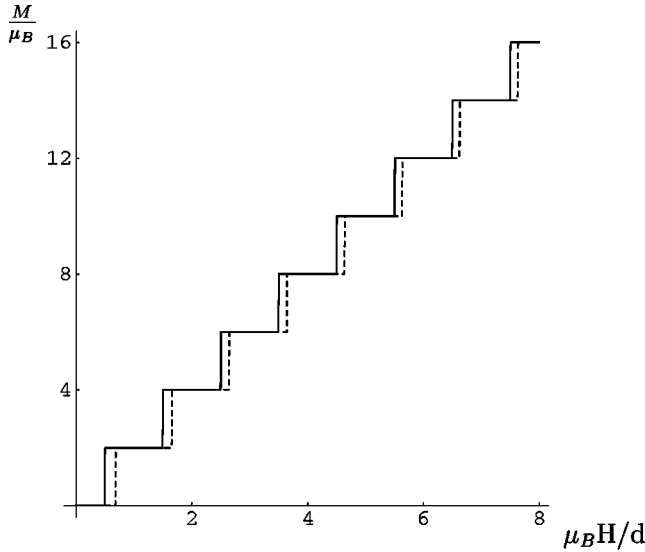


FIG. 2. Magnetization curve of normal (solid) and superconducting (dashed) grains with an equally spaced noninteracting spectrum. The width of the rectangles between the curves decreases with increasing magnetic field due to the decrease of the second-order term. The sum of all the areas of the rectangles equals  $E_{cond}/d$ .

superconducting grain one has to add the energy contributions due to  $\hat{H}_l$  to the different ground states. To second order in  $\lambda$ , one can show, by using either Richardson's equations or perturbation theory, that the difference in the interaction energies of  $\psi_l$  and  $\psi_{l-1}$  is

$$\lambda d + \frac{1}{2} \cdot \left( \sum_{j=2l-1}^{N+l-1} 1/j + \sum_{j=2l}^{N+l} 1/j \right) \lambda^2 d \approx \lambda d + \widehat{\ln}(2l, N) \lambda^2 d, \quad (31)$$

where we define  $\widehat{\ln}(i, j) \equiv \sum_{k=i}^j 1/k$ . Therefore, the equation for  $H_l$  is

$$(2l-1)d + \lambda d + \widehat{\ln}(2l, N) \lambda^2 d - 2\mu_B H = 0. \quad (32)$$

The above equation is true for all  $l < \omega_D/d$ , while for larger  $l$  the interaction term vanishes, and one obtains the same equation as for the normal grain.

The first term in the equation reflects the kinetic-energy cost of breaking the  $l$ th pair and is similar to the normal grain case. The second term reflects the "direct" (Hartree) energy cost of breaking a pair, coming from the diagonal part of the interaction term in the Hamiltonian (5). This term is not  $l$  dependent, and therefore is not reflected in the susceptibility, as we shall see in the next section. The third term is the result of the two levels, one  $l$  below  $E_F$  and one  $l$  above  $E_F$  becoming blocked to pairing fluctuations. Its magnitude is a decreasing function of  $l$ , since as the levels are further from  $E_F$  their contribution to the pairing fluctuations is smaller. This dependence on  $l$  is reflected in the susceptibility.

In Fig. 2 we plot the magnetization curve for a normal grain ( $\lambda=0$ ) and a superconducting grain with the same equally spaced noninteracting spectrum. Using Eq. (30), Eq.

(32), and the expressions above Eq. (32), one immediately confirms the equality (to second order in  $\lambda$ ) of the interaction energy, as was calculated in Appendix B, and the integral in Eq. (26).

So far we considered the idealized case of grains with equally spaced energy levels. In order to relate to experiment, we now relax this assumption. It is not possible to see the effects of superconducting correlations on the condensation energy by measuring only a single ultrasmall grain, since the fluctuations of the noninteracting energy levels cause larger shifts in the position of the  $H_l$ 's than those induced by the superconducting interaction. We therefore consider an ensemble of grains with the same noninteracting mean level spacing  $\tilde{d}$  and an energy spectrum that obeys Gaussian orthogonal ensemble (GOE) statistics. We assume that the pairing interaction constant in all the grains is the same, given by  $\lambda\tilde{d}$ , and calculate the mean spin magnetization of such an ensemble for  $H \gg \tilde{d}/\mu_B$ . For each grain, the equation (32) for  $H_l$  now becomes

$$\zeta_l + \lambda\tilde{d} + \widehat{\ln}(2l, N) \lambda^2 \tilde{d} - 2\mu_B H_l = 0. \quad (33)$$

$\zeta_l$  is the energy difference between the  $l$ th level above the Fermi energy and the  $l$ th level below it in that grain. The Hartree term is not affected by level statistics, and we neglect the change incurred by the second-order term due to the effects of level statistics, since this change is small compared to its mean value. We approximate the second-order term in Eq. (33) by  $\lambda^2 \tilde{d} \ln[\omega_D/(2\mu_B H)]$  (replacing  $l$  inside the logarithm by its mean value and replacing  $\widehat{\ln}$  by  $\ln$ ). We then obtain, for a given magnetic field, for each grain, an equation for  $l$ , the number of broken pairs. It is given by the maximum  $k$  that satisfies the equation

$$2\mu_B H - \lambda\tilde{d} - \lambda^2 \tilde{d} \ln[\omega_D/(2\mu_B H)] \geq \zeta_k. \quad (34)$$

The mean value of the magnetization of a grain at a given  $H$  is therefore

$$\bar{M}_s(H) = 2\mu_B^2 H/\tilde{d} - \lambda\mu_B - \lambda^2 \mu_B \ln[\omega_D/(2\mu_B H)]. \quad (35)$$

The variation around the mean value is given by the variation of the number of levels within the energy range given by the left side of Eq. (34). Since the level statistics of the grains is given by GOE statistics, the variation in the magnetization of one grain is approximately  $\delta\bar{M}_s(H) = \mu_B \ln[2\mu_B H/\tilde{d}]/\pi^2$  (see e.g., Ref. 31). This variation is indeed larger than the shift of the mean magnetization compared to that of a normal grain [Eq. (35)], but in an ensemble of  $n$  grains the variation reduces as  $1/\sqrt{n}$ , while the shift in the mean value does not change.

One can therefore, in principle, measure the interaction energy of ultrasmall superconducting grains by measuring the magnetization of an ensemble of such grains and calculating the integral in Eq. (26). While  $M_s$  is measured,  $M_n$  is given by the straight line starting from the origin with a slope equal to the measured ensemble magnetization at  $H$

$> \omega_D/\mu_B$ . The Hartree term in Eq. (35) shifts the magnetization of a pair-correlated grain relative to that of a normal grain by a constant, resulting in a parallel line not intersecting the origin. Its contribution to the integral is trivially  $\lambda \omega_D$ . The second-order term changes the slope of the magnetization and introduces a nonlinear correction to the normal Pauli susceptibility, which we discuss in the next section.

The consideration of grains with an odd number of electrons would lead to similar results in the regime  $\mu_B H \gg d$ . The magnetization graph for an odd grain would be similar to that in Fig. 2, only shifted by one unit down and half a unit to the left, not affecting the average quantities discussed.

In this section we were concerned with the magnetization at  $H \gg d/\mu_B$ , which depends on level statistics through their effect on energy levels far from  $E_F$ . The effect of level statistics is more dramatic for small magnetic fields  $H \lesssim d/\mu_B$ , for which the magnetization is due to the levels closest to  $E_F$ . In the next section we are interested in the magnetic susceptibility also in the regime where  $H \approx d/\mu_B$  and therefore consider the levels closest to  $E_F$  more carefully. A more rigorous treatment of level statistics that will also be valid in the regime of  $H \ll \tilde{d}/\mu_B$  is deferred to a future work.

#### IV. REENTRANCE OF THE SUSCEPTIBILITY

Measuring the interaction energy by a magnetization measurement might be a difficult task, since it requires very high magnetic fields of the order of  $\omega_D/\mu_B$ . As an alternative, we propose here a susceptibility measurement that would reveal the presence of superconducting correlations in ultrasmall grains and only requires magnetic fields of the order  $\tilde{d}/\mu_B$ .

Let  $\chi^{s/n}(H, T) = \partial \bar{M}^{s/n}(H, T) / \partial H$  denote the spin susceptibility as a function of magnetic field and temperature for a superconducting or normal grain, respectively. Lorenzo *et al.*<sup>19</sup> calculated  $\chi^s(0, T)$ , finding that even for ultrasmall grains it has a minimum at  $T \approx \tilde{d}$ , implying a reentrant behavior as a function of decreasing  $T$ . Since this reentrance differs from the monotonic increase expected for the Pauli susceptibility  $\chi^n(0, T)$  of normal grains, they suggested that it could be a sensitive probe to detect superconducting correlations in such grains.

In this section we discuss an analogous but complementary quantity, namely,  $\chi^s(H, 0)$ . We find that  $\chi^s(H, 0)$  has a maximum at  $H \approx \tilde{d}/\mu_B$  and decreases as  $1/H$  for  $H \gg \tilde{d}/\mu_B$  (see Fig. 3). Thus,  $\chi^s(H, 0)$  shows a reentrant behavior in ultrasmall superconducting grains, just as  $\chi^s(0, T)$  does. Since this again contrasts with the Pauli susceptibility  $\chi^n(H, 0)$  of normal grains,<sup>32,33</sup> measuring  $\chi^s(H, 0)$  as a function of  $H$  could possibly serve as a sensitive probe to detect superconducting correlations in ultrasmall grains.

For  $H \gg \tilde{d}/\mu_B$  we use Eq. (35) and obtain to first order in  $d/\mu_B H$ ,

$$\chi^s = \chi_0 + \lambda^2 \mu_B / H, \quad (36)$$

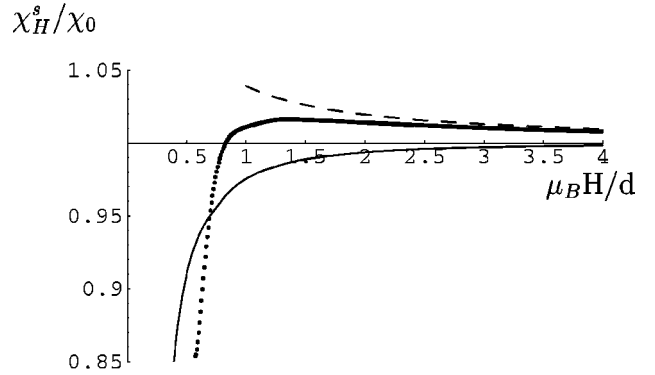


FIG. 3. Spin susceptibility as a function of magnetic field at  $T=0$  for  $\lambda=0.28$  is shown. As  $H$  decreases,  $\chi^s$  increases, until reaching a maximum of  $1.02\chi_0$  for  $H \approx 1.3\tilde{d}/\mu_B$ , implying a reentrant behavior.  $\chi^n(H)$  (thin solid line) and the high-field approximation obtained in Eq. (36) (dashed line) are given for comparison.

where  $\chi_0 = 2\mu_B^2/\tilde{d}$ . The susceptibility is a decreasing function of  $H$ , and the positive  $1/H$  correction to the normal grain susceptibility  $\chi^n$  [for  $H \gg \tilde{d}/\mu_B$ , to first order in  $d/\mu_B H$ , one obtains  $\chi^n = \chi_0$  (Refs. 32 and 33)] is smaller than the leading, normal term by  $\lambda^2 \tilde{d}/2\mu_B H = \lambda^2/2l$ .

The intuitive reason for why the correction is positive is as follows: For a given magnetic field, the magnetization of a pair-correlated grain is, on the average, smaller than that of a normal grain (see Fig. 2), because breaking pairs to increase the magnetization costs pairing energy. However, since the pairing energy per extra pair decreases the further the pairs involved lie from  $E_F$ , the difference between the two magnetization curves decreases with increasing  $H$ . Consequently, it requires a smaller  $H$  increment to break the next pair for a pair-correlated grain than a normal grain, implying a larger susceptibility for the former.

The result in Eq. (36) is already sufficient to establish the reentrant behavior of the susceptibility  $\chi^s(H, 0)$ , since as  $H$  is lowered below  $\tilde{d}$  and approaches zero,  $\chi^s(H, 0)$  decreases and approaches zero, too, due to level repulsion. Precisely at  $H=0$  the susceptibility  $\chi^s(H, 0)$  of an odd grain has an additional  $\delta(H)$ -like peak due to the contribution of the single, unpaired electron at  $E_F$ ; in fact, for finite  $T$  it is the contribution of this unpaired electron that is responsible for the reentrance of  $\chi^s(0, T)$  predicted in Ref. 19. However, for any nonzero  $H$  the spin of this electron is fully aligned with the magnetic field and hence makes no contribution to  $\chi^s(H > 0, 0)$ .

We now proceed with a calculation of  $\chi^s$ , which gives a quantitative estimate of the magnitude of the reentrance effect. We consider an ensemble of odd and even grains. For a normal grain,  $\chi^n(H)$  is proportional to the probability to have a pair of states ( $l$  pair),  $l$  above and  $l$  below  $E_F$  (denoted  $-l$ ) separated by  $\zeta_l \equiv \epsilon_l - \epsilon_{-l} = 2\mu_B H$  and is given by<sup>32,33</sup>

$$\chi^n = \frac{2\mu_B^2}{\tilde{d}} R \left( \frac{2\mu_B H}{\tilde{d}} \right), \quad (37)$$



where  $R(x)$  is the probability of finding two levels a spacing  $x$  apart regardless of the position of the other levels<sup>34</sup> [ $R(x) = 1 - \mathcal{O}(1/x^2)$  for  $x \gg 1$ ]. We now consider a single superconducting grain. The  $l$ th pair of this grain would contribute, without pairing interaction, to the value of the spin susceptibility at  $H = \zeta_l / (2\mu_B)$ . However, due to the extra energy cost of breaking a pair, which was discussed in the previous section, the  $l$  pair contributes to the susceptibility at a higher magnetic field. This shift is specific to each grain, as it is a function of the energies of the noninteracting levels further than  $i$  from the Fermi energy (the levels closer than  $l$  to  $E_F$  are singly occupied and therefore do not contribute to the interaction energy). While the energy of the  $l$  pair is arbitrary and later is taken to satisfy GOE statistics, we now make the approximation that the levels further than  $l$  from  $E_F$  are equally spaced with level spacing  $\tilde{d}$ , the first ones being  $\tilde{d}$  apart from the  $l$  levels. Due to the smallness of the fluctuations in the GOE ensemble we believe that the above approximation is not only proper for  $H \gg \tilde{d} / \mu_B$ , but also gives fairly good results for  $H \approx \tilde{d} / \mu_B$ . Under our approximation, which introduces a modification of Eq. (31) due to the arbitrariness of the energies of the  $l$  pair, we find that the  $l$  pair will contribute to  $\chi^s(H)$  at a  $\zeta_l$ -dependent field  $H(\zeta_l)$  given by

$$H = \frac{1}{2\mu_B} \left[ \zeta_l + \lambda \tilde{d} + \frac{1}{2} \cdot \left( \frac{1}{\zeta_l} + 2 \sum_{j=1}^{N-l} \frac{1}{\zeta_l + j} \right) \lambda^2 \tilde{d} \right]. \quad (38)$$

Therefore, for an ensemble of ultrasmall superconducting grains as considered,

$$\chi^s(H) = (2\mu_B^2 / \tilde{d}) P[2\mu_B H(\zeta) / \tilde{d}], \quad (39)$$

where  $H(\zeta)$  is given by Eq. (38) with  $\zeta_l$  replaced by  $\zeta$ , and

$$P[2\mu_B H(\zeta) / \tilde{d}] = R(\zeta / \tilde{d}) (2\mu_B d H / d\zeta)^{-1}. \quad (40)$$

The result for this calculation with  $\lambda = 0.28$  is given in Fig. 3.

For larger, but still small grains, where  $\Delta \gg \tilde{d}$ , the spin susceptibility is very different at  $H \lesssim \Delta / \mu_B$ . However, similar calculations<sup>35</sup> to those leading to Eq. (36) show that for  $\Delta^2 / (\tilde{d}\mu_B) < H < \omega_D / \mu_B$  one obtains the same result as in Eq. (36). The reason essentially is that in this regime enough levels are singly occupied, so the energy levels involved in the interaction are sufficiently far for the perturbative treatment to be valid.

## V. TUNNELING PEAK SPECTRUM

Superconducting correlations in ultrasmall grains are also reflected in their tunneling excitation spectrum. For a normal grain, the tunneling peak spectrum is simple, consisting of peaks at the single-particle excitation energies of the grain. When the pairing interaction is present, the spectrum is much more complex, containing peaks at the energies of all the many-body states of the grain with one electron added or removed. However, for a small coupling constant, most of these peaks are small (proportional to  $\lambda^2$ ), and we do not consider them here. Instead, we consider only the ‘‘primary’’

peaks, i.e., those that survive as  $\lambda \rightarrow 0$  and in this limit correspond to the tunneling peaks of the normal grain. A non-zero pairing interaction reduces their strength by a factor of  $1 - \lambda^2$  and shifts their energy. In this section we are concerned only with the energy shift of these primary peaks due to the pairing interaction. We show that this shift, being a decreasing function of energy, causes, for  $\epsilon \gg d$ , the mean spacing between the primary peaks to be smaller than in an equivalent normal grain and therefore introduces a positive correction to their density.

Consider a grain with equally spaced energy levels having an even number ( $2k$ ) of electrons and a ground state  $|\phi_{2k}^G\rangle$ , and consider the tunneling at positive energies into any eigenstates  $|\phi_{2k+1}\rangle$  with  $2k+1$  electrons. We assume that the Coulomb blockade energy is the same for the tunneling to all states with  $2k+1$  electrons, and henceforth neglect it, since we are interested here only in energy differences between tunneling peaks.

To first order in the tunneling Hamiltonian, tunneling will occur whenever there is a finite matrix element between any state  $|\psi_{2k+1}^s\rangle \equiv c_s^\dagger |\phi_{2k}^G\rangle$ , where  $s$  is an index labeling single noninteracting levels and any eigenstate  $|\phi_{2k+1}\rangle$  with  $2k+1$  electrons.

If the grain is normal,  $\lambda = 0$ , then the only relevant eigenstates with  $2k+1$  electrons are those in which all levels up to  $E_F$  are filled with two electrons, and one state  $s$ , above  $E_F$ , is occupied by one electron. We define  $|\phi_{2k+1}^s\rangle$  for either a superconducting or a normal grain as the lowest-energy many-body eigenstate of  $2k+1$  electrons for which the state  $s$  is singly occupied. For a normal grain  $|\psi_{2k+1}^s\rangle$  and  $|\phi_{2k+1}^s\rangle$  are identical. The spectrum of tunneling peaks in a normal grain would therefore be identical to the noninteracting single-particle energy spectrum of the grain. In a similar ultrasmall superconducting grain ( $\lambda \neq 0$ ), pair fluctuations will affect the tunneling spectrum in three ways. (i) The primary peaks are shifted and (ii) reduced in magnitude due to the fact that the overlap of the states  $|\psi_{2k+1}^s\rangle$  and  $|\phi_{2k+1}^s\rangle$  is smaller than one. (iii) Many small peaks emerge due to the small overlap (of order  $\lambda$ ) between  $|\psi_{2k+1}^s\rangle$  and all the other many-body eigenstates with  $2k+1$  electrons that are different from  $|\phi_{2k+1}^s\rangle$ . We will not consider effects (ii) and (iii) here and proceed with the calculation of the mean spacing between the primary peaks in ultrasmall superconducting grains, as a function of energy.

The tunneling of an electron into the  $l$ th level above the Fermi energy costs a total energy of

$$E(\phi_{2k+1}^l) - E(\phi_{2k}^G) = ld + \lambda d/2 + \lambda^2 d \widehat{\ln}(N, l)/2. \quad (41)$$

The first term is the kinetic-energy contribution. The second term is the Hartree term, and the factor of  $\frac{1}{2}$  is due to the fact that the number of pairs within  $\omega_D$  below  $E_F$  changes by, on average,  $-\frac{1}{2}$  when an electron is added to the grain (because we have assumed that the band of interacting electrons is spaced symmetrically about  $E_F$ , and  $E_F$  shifts upward by half a unit of  $d$  when an electron is added to the grain).

Tunneling an electron into the  $l$ th level also affects the interaction energy, which to second order in  $\lambda$  is reduced,

due to the blocking of level  $l$ , by  $\lambda^2 d \widehat{\ln}(N,l)/2 \approx \lambda^2 \ln(N/l)/2$ . (This second-order term can be found, using, e.g., perturbation theory, and calculating the difference in the second-order interaction energy of a Fermi state with  $2k$  electrons and the same state up to a single electron added to the  $l$ th level.) Both the kinetic energy and the Hartree term leave the distance between nearby tunneling energies unchanged ( $d$ ). However, the second-order term becomes smaller with increasing energy, and therefore the distance between tunneling energies is smaller than that of a similar normal grain. This reduction manifests itself in the mean spacing of the primary tunneling peaks in an ensemble of ultrasmall superconducting grains. One can obtain the mean primary peak spacing of such an ensemble by a similar procedure to the one we used in Secs. III and IV for the spin magnetization and susceptibility. Here we obtain the same result in a simpler way. We consider a grain with equally spaced energy levels as above. The difference between the tunneling energy to state  $|\phi_{2k+1}^l\rangle$  and to state  $|\phi_{2k+1}^{l+1}\rangle$  is approximately  $d + \lambda^2 d \{\ln[N/(l+1)] - \ln(N/l)\}/2 \approx d [1 - \lambda^2/(2l)]$ . The mean density of primary peaks in an ensemble for  $l \gg 1, \epsilon \gg d$ , including spin degeneracy, is therefore given by

$$\bar{N}(\epsilon) = \frac{2}{d} \cdot \frac{1}{1 - \lambda^2 d / (2\epsilon)}. \quad (42)$$

The functional behavior of the primary peak density resembles that of the magnetic susceptibility. In both cases the correction to the leading term reflects the change in interaction energy as levels further from the Fermi energy are blocked. Similar considerations for negative energies (tunneling electrons out of the grain, going from the ground state of  $2k$  electrons to states of  $2k-1$  electrons) will result in a similar shift of the tunneling peaks, and the tunneling spectrum being symmetric around  $E_F$ .

We now consider shortly the case of the tunneling process (at positive energies) changing a grain with an odd number of electrons to a grain with an even number of electrons. In the even-to-odd case described above, the change in the number of singly occupied noninteracting levels from zero to one induced an upward shift in the primary tunneling peak energies. Most primary tunneling peaks in the odd-to-even case correspond to a change in the number of singly occupied noninteracting levels from one to two and therefore an upward shift in the tunneling peak energies similar to the even-to-odd case. The only exception is the peak closest to the Fermi level, which is a result of tunneling into the singly occupied level, resulting in the even grain having no singly occupied levels. This induces a downward shift of this tunneling peak. The functional behavior of the mean peak spacing at  $\epsilon \gg d$  will be similar to Eq. (42) above.

We now relax the assumption of the noninteracting energy spectrum of the grain being equally spaced and consider the regime  $0 < \epsilon \ll d$ . Due to the positive shift in energy of the tunneling peaks as a result of the pairing interaction,  $\bar{N}(\epsilon)$  is smaller for ultrasmall superconducting grains compared to its value for similar normal grains (this can also be obtained by conservation of the number of primary peaks).

This can be seen as a first sign for the onset of the gap in the density of states in a macroscopic sample.

## VI. NUMERICAL ANALYSIS OF RICHARDSON'S EQUATIONS

In this section we analyze the solutions of Richardson's equations (8) for the ground state of a grain with equally spaced energy levels. The above equations for the energy parameters can be studied numerically.<sup>29</sup> The energy parameters are, in principle, complex, and one can show that they are either real or come in complex-conjugate pairs. If the ground state of the system is considered, it is found<sup>29</sup> that for  $\lambda \ll 1/\ln N$  all the energy parameters are real, monotonically decreasing functions of the coupling. Taking  $N$  to be even, we group all the energy parameters  $E_\nu$  into pairs labeled by an index  $a$ , starting from the largest two and counting downward:  $\{E_{N+2-2a}, E_{N+1-2a}\}$ , with  $a = 1, \dots, N/2$ . (The case of odd  $N$  can be treated analogously, except that  $E_1$  will then remain unpaired.) Each pair of energy parameters are real, until, for some  $\lambda_a$  (Fig. 1 of Ref. 29), the  $a$ th pair becomes a pair of complex-conjugate numbers, which they do in order of increasing  $a$  (i.e.,  $\lambda_a < \lambda_{a+1}$ ). At the transition point  $\lambda_a$ , the two energy parameters are equal to the value of the lower-energy parameter at  $\lambda = 0$ :

$$E_{N+2-2a} = E_{N+1-2a} = 2\epsilon_{N+1-2a}. \quad (43)$$

Each energy parameter is an analytic function for  $\lambda < \lambda_a$  and has a branch point at  $\lambda_a$ .

By solving Richardson's equations (8) for  $\nu = N$  and  $\nu = N-1$  with the conditions above (43) we find that

$$\lambda_1 = 1/(\widehat{\ln} N + a_1), \quad (44)$$

where  $\widehat{\ln} N = \sum_{j=1}^N 1/j$  and  $0 < a_1 < 1$ .

It would seem that the interaction energy

$$E_{int} = \sum_{\nu} (2\epsilon_{\nu} - E_{\nu}) \quad (45)$$

would be nonanalytical at this point. However, although  $E_N, E_{N-1}$  have a branch point at  $\lambda_1$ , their sum is analytical at this point, due to the cancellation of the singularities. The analyticity of the sum, as well as the result in Eq. (44), are derived<sup>35</sup> in the following way: We first define  $\xi$  and  $\eta$  to satisfy the equations  $E_N = 2\epsilon_{N-1} + \xi + i\eta$  and  $E_{N-1} = 2\epsilon_{N-1} + \xi - i\eta$ , using the fact that  $E_N$  and  $E_{N-1}$  are real (in which case  $\eta$  is imaginary) or complex conjugates of each other (in which case  $\eta$  is real). We insert the above definitions in Richardson's equations for  $\nu = N$  and  $\nu = N-1$  and obtain equations for  $\xi$  and  $\eta^2$  as a function of  $\lambda$  (similar equations are given in Refs. 29 and 26). We then expand  $\xi$  and  $\eta^2$  in a series in  $\delta\lambda = (\lambda - \lambda_1)$  and solve the equations for each order of  $\delta\lambda$  separately.  $\lambda_1$  is obtained by the solution to the zeroth order and yields Eq. (44). Solving for the next orders we find that the coefficients for both  $\xi$  and  $\eta^2$  of  $(\delta\lambda)^i$  are, up to a factor of order unity,  $(\ln N)^{2i}$ . This results in  $\xi$  and  $\eta^2$  being in fact expanded as a series in  $\delta\lambda \cdot (\ln N)^2$ . This result both reflects a scale of  $1/(\ln N)^2$  near

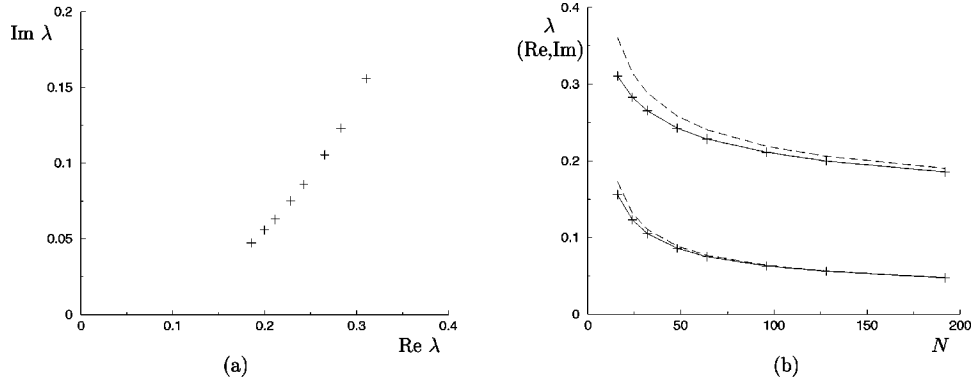


FIG. 4. (a) The singularity point of the complex coupling parameter closest to the origin is plotted for (from top right to bottom left)  $N=16, 24, 32, 48, 64, 96, 128,$  and  $192$ . Not plotted is their mirror image across the  $x$  axis, with negative imaginary parts. (b) The real (top) and imaginary (bottom) parts of the complex coupling parameter at the above singularity points are plotted as a function of  $N$ . The dashed lines are fits,  $1/\ln N$  for the real part and  $1.33/(\ln N)^2$  for the imaginary part. The error in both graphs is  $0.002$  (not plotted).

$\lambda = 1/\ln N$ , which we will return to later, and shows that the sum  $E_N + E_{N+1}$  can indeed be expanded perturbatively in  $\delta\lambda$ .

This result also suggests that  $E_{int}(\lambda)$  is analytical on the positive real axis. The only points at which one can suspect nonanalyticities to occur are the different  $\lambda_a$ 's. The reasonable assumption that for  $a > 1$  the behavior of  $E_{int}$  near  $\lambda_a$  is similar to that near  $\lambda_1$  discussed above, i.e., that the sum of the singular energy parameters is analytical, leads to the analyticity of  $E_{int}$  on the positive real axis. This is also supported by contour integration in the complex  $\lambda$  plane, as we discuss in Appendix C.

However,  $E_{int}$  is not an analytical function in the whole complex  $\lambda$  plane. By numerically analyzing Richardson's equations as a function of complex  $\lambda$ , we find that the interaction energy has singular points in the complex plane, the closest to the origin occurring at approximately

$$\lambda_{sing}(N) = 1/\ln N \pm 1.33i/(\ln N)^2. \quad (46)$$

In Fig. 4 we plot the real and imaginary parts of the closest singular points as a function of  $N$ , with the corresponding fits.

This numerical result suggests that the radius of convergence of the perturbation series for the interaction energy around  $\lambda = 0$  is roughly  $1/\ln N$ , in agreement with our analytical treatment of the perturbation series in Appendixes B and C. It also reflects a convergence radius of the order of  $1/(\ln N)^2$  for the sum  $E_N + E_{N-1}$  around  $\lambda = \lambda_1$ , in agreement with the  $1/(\ln N)^2$  scale mentioned above.

The second part of this section is devoted to establishing a connection between the analytical properties of Richardson's energy parameters and the BCS theory. In particular, we show that in the regime where  $d \ll \Delta$  the BCS result for the condensation energy (1) is closely related to the singular contribution of the complex energy parameters to the condensation energy, and that the points, on the positive real axis of  $\lambda$ , at which the energy parameters become complex, are related to the values of  $\lambda$  at which additional states become "condensed" (i.e., come to lie within  $\Delta$  of  $E_F$ ).

We separate the energy parameters into two groups  $R_\lambda$  and  $C_\lambda$ , containing those energy parameters that for a given  $\lambda$  are real or complex, respectively. We define the contribution of the complex energy parameters to the condensation energy (disregarding the Hartree term)

$$E_{cond}^{comp} = \sum_{\nu}^{C_\lambda} (2\epsilon_\nu - \lambda - E_\nu) \quad (47)$$

and find that  $|E_{cond}^{comp} - (\Delta^2/2d + \Delta)| < 3d$  for  $8 < N < 1024$  for all  $\lambda < 0.3$ . The relative correction decreases with  $N$  and  $\lambda$  and is  $0.1\%$  for  $N = 1024$  and  $\lambda = 0.3$ .

For those energy parameters that have already become complex at a given  $\lambda$ , we can separate the contribution of  $E_{2N+2-2a} + E_{2N+1-2a}$  to the condensation energy into two parts, one containing the decrease that each  $E_{2N+2-2a} + E_{2N+1-2a}$  underwent as  $\lambda$  is increased from 0 to  $\lambda_a$  (the perturbative regime), the other containing its further decrease for  $\lambda > \lambda_a$  (the singular regime).

Defining, for each energy parameter  $E_\nu$ , its value at the branch point as  $E_\nu^b$  [by Eq. (43),  $E_{2l}^b = E_{2l-1}^b = 2\epsilon_{2l-1}$ ], we write  $E_{cond}^{comp} = E_{cond}^{sing} + E_{comp}^{pert}$ , where

$$E_{cond}^{sing} = \sum_{\nu}^{C_\lambda} (E_\nu^b - E_\nu), \quad E_{comp}^{pert} = \sum_{\nu}^{C_\lambda} (2\epsilon_\nu - \lambda - E_\nu^b). \quad (48)$$

$E_{cond}^{sing}$  is the singular contribution to  $E_{cond}$  or  $E_{int}$ . (Note that the Hartree term is subtracted in  $E_{comp}^{pert}$  when calculating the condensation energy; for the analogous calculation of the interaction energy, this subtraction should be omitted.) Remarkably, our numerical analysis shows that this singular contribution is well approximated by the BCS expression for the condensation energy  $\{E_{cond}^{sing} = \Delta^2/2d[1 + \mathcal{O}(d/\Delta)^2]$  for  $64 < N < 1024$  for all  $\lambda < 0.3\}$  as is shown in Fig. 5(a). This suggests that the BCS approximation is equivalent to considering *only* the singular contribution to the condensation energy. By taking first the limit  $N \rightarrow \infty$ , one would indeed get the singular point of the interaction energy to be at the origin (46), and no contribution from the perturbative terms. In this

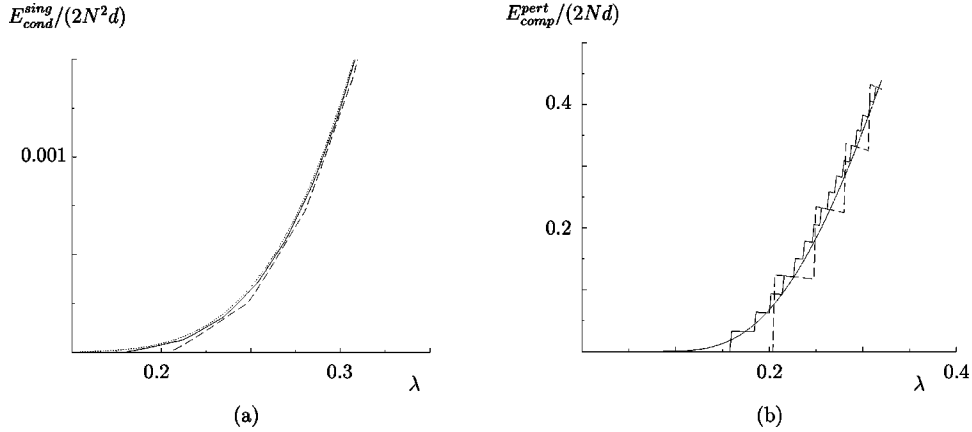


FIG. 5. The different contributions of the complex energy parameters to the condensation energy are plotted. (a) We show that  $E_{cond}^{sing}$  is well approximated by the BCS result by plotting  $E_{cond}^{sing}/(2N^2d)$  for  $N=64$  (dashed line) and  $N=128$  (solid line) and the function  $\exp(-2/\lambda)$  (dotted line) for comparison. Plots for larger  $N$  are not drawn since they are indistinguishable from  $\exp(-2/\lambda)$  in the resolution of this figure. (b)  $E_{comp}^{pert}/2Nd$  for  $N=64$  (dashed line, large steps) and  $N=256$  (solid line, small steps) is plotted and compared to  $\exp(-1/\lambda)$  (smooth solid line), showing that  $E_{comp}^{pert} \approx \Delta$ . Steps occur at points  $\lambda_a$  in which pairs of energy parameters become complex.

limit the Hartree term in the reduced Hamiltonian (5) vanishes, and the condensation energy equals the interaction energy.

These results suggest that the  $1/N$  correction to the BCS result in the large  $N$  limit is at least  $\Delta$ . However, one also has to add the contribution of the energy parameters in group  $R_\lambda$ , which correspond to the levels between  $E_F - \omega_D$  and  $E_F - \Delta$ . This contribution would give an additional correction of the order  $\lambda^2 \omega_D$ . Summing the above three contributions to  $E_{cond}$ , we obtain Eq. (24).

Since  $E_{cond}^{comp} \approx \Delta^2/2d + \Delta + \mathcal{O}(d)$  and  $E_{cond}^{sing} \approx \Delta^2/2d + \mathcal{O}(d)$ , we find that  $E_{comp}^{pert} \approx \Delta$  [see Fig. 5(b)]. This implies, since  $2\epsilon_\nu - E_\nu^b$  equals  $2d$  for even  $\nu$  and  $0$  for odd  $\nu$ , the approximate equation

$$2n_C(\lambda) \approx \frac{\Delta(\lambda)/d}{(1-\lambda)}, \quad (49)$$

where  $\Delta(\lambda)$  is given in Eq. (2), and  $n_C(\lambda)$  is the number of pairs of energy parameters  $\{E_{N+2-2a}, E_{N+1-2a}\}$  that have already turned complex for the given  $\lambda$ . Remarkably, Eq. (49) tells us that the associated number of bare levels  $\epsilon_{N+2-2a}$  and  $\epsilon_{N+1-2a}$ , namely,  $2n_C(\lambda)$  is just the number of bare levels within  $d$  of  $\Delta$  (up to a factor close to unity), i.e., the number of what we have called ‘‘condensed levels.’’ The reason for this nomenclature now becomes apparent, since we have just established that the singular, BCS part of  $E_{cond}$  arises precisely from those energy parameters that have evolved from these  $2n_C(\lambda)$  bare levels.

If we solve Eq. (49) for  $\lambda$ , the result gives a function, say  $\lambda_{approx}(n_C)$ , that actually depends on  $N$  and  $n_C$  only via the ratio  $N/n_C$  and that is plotted as a function of  $1/\ln(N/n_C)$  in Fig. 6 (thick bold line). This function can be used to approximately predict, for given  $N$  and  $n_C$ , at which value of the coupling constant the  $n_C$ th pair of energy parameters will become complex. For comparison, we plot in Fig. 6 also the actual value at which this happens, say  $\lambda(n_C)$ , for several

values of  $N$  (regular lines, obtained by numerically solving Richardson’s equations). We find that the difference can be well fit by

$$\lambda_{approx}(n_C) - \lambda(n_C) \approx 0.055/\ln N, \quad (50)$$

implying that the approximate prediction becomes very accurate for  $N \rightarrow \infty$ . Equation (50) represents a one-parameter fit that can be used for any combination of  $N$  and  $n_C$ , the quality of which is illustrated in more detail in the inset of Fig. 6.

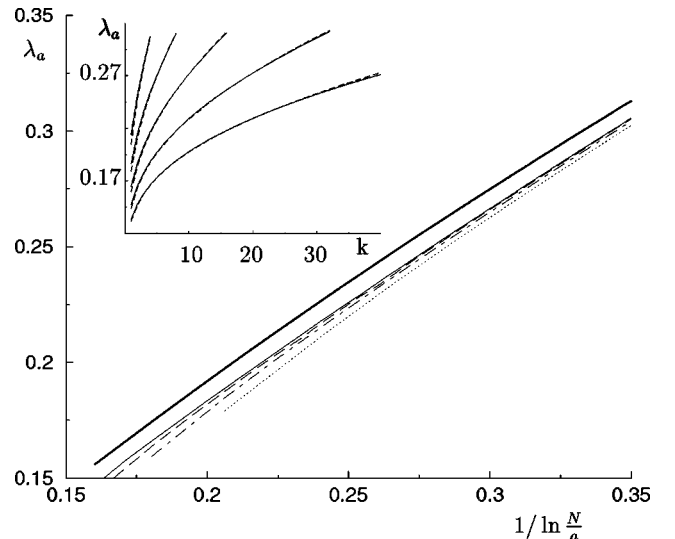


FIG. 6. The bottom four curves are plots of  $\lambda_a$  as a function of  $1/\ln(N/a)$  computed by changing  $a$  for fixed (from bottom up)  $N = 128, 256, 512, \text{ and } 1024$ . The topmost (thick, solid) curve is the solution to Eq. (49). In the inset we plot  $\lambda_a$  as a function of  $a$  for (from top left to bottom right)  $N = 64, 128, 256, 512, \text{ and } 1024$ . The numerical curves (dashed) are each fit with the solution to Eq. (49) minus  $0.055/\ln N$  (solid lines). The error in  $\lambda_a$  is  $0.0002$  and is not drawn.



Expanding  $\lambda_{approx}(n_C)$  to first order in  $\ln(N/n_C)$ , we find that

$$\lambda(n_C) = 1/\ln(N/n_C) \approx \frac{1}{\ln N} + \frac{\ln n_C}{(\ln N)^2}. \quad (51)$$

This equation shows, once again, that the scale of  $1/(\ln N)^2$  is present also for  $\lambda > \lambda^*$ , both in BCS theory and in the analytical properties of Richardson's equations.

## VII. CONCLUSIONS

Though many superconducting properties are limited to grains large enough that  $d < \Delta$ , pair correlations exist also in ultrasmall grains, where  $d > \Delta$ . We calculated the effect of pair correlations on the condensation energy, spin magnetization, and tunneling spectrum of ultrasmall superconducting grains. We found that the contribution of pair fluctuations to the condensation energy is much larger than the BCS result even for grains in which  $\Delta > d$ , and that the condition for the validity of the BCS approximation for calculating the condensation energy is  $\Delta > \sqrt{\omega_D d}$ . The interaction energy of ultrasmall grains can, in principle, be experimentally obtained through measuring their spin magnetization, which was calculated above. The pair correlations result in a positive correction to the differential spin susceptibility which is proportional to  $\lambda^2 d / (\mu_B H)$  for  $\mu_B H \gg d$ , and a positive correction to the mean tunneling peak density which is proportional to  $\lambda^2 d / \epsilon$  for  $\epsilon \gg d$ . The differential spin susceptibility at  $T=0$  of ultrasmall superconducting grains shows a reentrant behavior as a function of  $H$ , which could serve as a sensitive probe for the existence of superconducting correlations in such grains. We argued that the interaction energy is an analytical function of the coupling parameter, with a convergence radius of approximately  $1/\ln N$ . We showed that the BCS result for the condensation energy can be obtained from the singular part of Richardson's energy parameters, and that the correction to the BCS result in the regime where  $d \ll \Delta$  is at least  $\Delta$ .

## ACKNOWLEDGMENTS

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## APPENDIX A: ACCURACY OF THE ENERGY APPROXIMATION

In this appendix we show that the relative accuracy of the approximations in Eqs. (15) and (18) is as stated in Eq. (17). In this appendix we take  $d=1$ .

From Eqs. (16) and (14),  $\delta a_\nu = a_\nu - a_\nu^0$  is given by

$$\begin{aligned} \delta a_\nu = & - \sum_{j=1(\neq \nu)}^{2N} \frac{\delta E_\nu}{(2j-2\nu+\delta E_\nu)(2j-2\nu)} \\ & + \sum_{\mu=1(\neq \nu)}^N \frac{2(\delta E_\mu - \delta E_\nu)}{(2\mu-2\nu+\delta E_\nu - \delta E_\mu)(2\mu-2\nu)}. \end{aligned} \quad (A1)$$

For  $\lambda < 1/\ln N - c/(\ln N)^2$ , we assume (and later check for consistency) that  $0 < \delta E_\nu < 1/c$  for all  $\nu$ . Separating each sum in Eq. (A1) into a sum over the levels above and below  $\nu$ , one can see that  $|\delta a_\nu| < (1/c) \cdot 3 \cdot 2 \sum_s [2s(2s-1)]^{(-1)} \Rightarrow |\delta a_\nu| < 6/c$  (actually a more careful treatment can reduce the numerical factor multiplying  $1/c$  to be of order unity, but this is of no importance here).

Therefore, one can write

$$\delta E_\nu = \frac{\lambda}{1 - \lambda a_\nu^0 + \lambda b_\nu(\lambda)/c}, \quad (A2)$$

where  $|b_\nu(\lambda)| < 6$ . Manipulating the above equation, we obtain  $\delta E_\nu = \delta E_\nu^0 + R_\nu$  where

$$R_\nu = - \frac{\lambda^2 b_\nu(\lambda)}{c \cdot [1 - \lambda a_\nu^0 + \lambda b_\nu(\lambda)/c] \cdot (1 - \lambda a_\nu^0)}. \quad (A3)$$

The relative accuracy is therefore

$$r_\nu(\lambda) \equiv \left| \frac{R_\nu(\lambda)}{\delta E_\nu(\lambda)} \right| = \frac{\lambda |b_\nu(\lambda)|}{c \cdot (1 - \lambda a_\nu^0)}. \quad (A4)$$

Consider now  $\lambda < 1/\widehat{\ln} N - c/(\widehat{\ln} N)^2$ , and  $\nu = N$  (the highest-energy parameter). Since  $a_N^0 = (\widehat{\ln} N + \widehat{\ln} N - 1)/2 \approx \widehat{\ln} N$  we see that  $r_N < 6/c^2$ .

One can obtain from Eq. (16) that  $a_\nu^0$  increases monotonically with  $\nu$ , and by differentiating Eq. (A4) with respect to  $a_\nu^0$ ,  $r_\nu$  increases monotonically with  $a_\nu^0$ . We conclude that  $r_\nu < 6/c^2$  for all  $\nu$ , and therefore  $\delta E_\nu = \delta E_\nu^0 [1 + \mathcal{O}(1/c^2)]$  for all  $\nu$ . In the same way one finds that  $\delta E_\nu < 1/c$  for all  $\nu$ , consistent with our assumption above.

By summing over all  $\nu$ , one shows that

$$E_{int} = E_{int}^0 [1 + \mathcal{O}(1/c^2)], \quad (A5)$$

where  $E_{int}^0$  is given in Eq. (18).

To show that the accuracy of the above expression is  $1/(\ln N)^2$  in the regime  $\lambda < 1/(2 \ln N)$  one has to assume (and later show consistency) that  $\delta E_\nu < 1/\ln N$  for all  $\nu$  and proceed as above.

## APPENDIX B: APPROXIMATE FORMULA FOR THE MTH ORDER TERM OF THE INTERACTION ENERGY

In this appendix we expand Eq. (18) for the approximate interaction energy  $E_{int}^0$  in powers of  $\lambda$  and analyze the convergence properties of the resulting series. We begin by showing that the order- $\lambda^m$  contribution to  $E_{int}^0$  has the form

$$E_{int}^{0(m)} = d \lambda^m \sum_{\nu=1}^N (a_{\nu}^0)^{m-1}, \quad (\text{B1})$$

$$= \begin{cases} d \lambda^m b_m N (m-1)! & \text{for } m < \ln N, \\ d \lambda^m b'_m (\ln N)^{(m-1)} & \text{for } m > \ln N, \end{cases} \quad (\text{B2})$$

where  $b_m$  and  $b'_m$  are constants of order unity and then analyze the consequences of this result. Since we are not interested here in numerical factors of order unity, we will allow ourselves to make some crude approximations.

The expression obtained (18) for the interaction energy can be written as

$$E_{int}^0 = \sum_m E_{int}^{0(m)} = d \sum_m \left[ \lambda^m \sum_{\nu=1}^N (a_{\nu}^0)^{m-1} \right], \quad (\text{B3})$$

where  $a_{\nu}^0$  is given by Eq. (16). The first-order term is given trivially by  $E_{int}^{0(1)} = \lambda d N$ .

The second-order term of the interaction energy is given by

$$\begin{aligned} E_{int}^{0(2)} &= \lambda^2 d \sum_{i=1}^N \left[ \sum_{j=1(\neq i)}^{2N} \frac{1}{2(j-i)} - \sum_{j=1(\neq i)}^N \frac{1}{j-i} \right] \\ &= \lambda^2 d \sum_{i=1}^N \left[ \sum_{j=N+1}^{2N} \frac{1}{2(j-i)} \right]. \end{aligned} \quad (\text{B4})$$

This result can also be obtained by standard second-order perturbation theory (Ref. 26, and references therein). For large  $N$  one obtains  $E_{int}^{0(2)} \approx \ln 2 \lambda^2 d N = \ln 2 \lambda^2 \omega_D$ .

The calculation of the higher-order terms is more difficult. We now make some approximations that enable us to find the  $m$ th order within a factor of order unity.

First we manipulate the  $a_{\nu}^0$ 's (16) and obtain

$$a_{\nu}^0 = \frac{1}{2} \left[ \sum_{k=1}^{\nu-1} \frac{1}{k} - \sum_{k=1}^{N-\nu} \frac{1}{k} + \sum_{k=N-\nu+1}^{2N-\nu} \frac{1}{k} \right]. \quad (\text{B5})$$

This can be approximated by

$$a_{\nu}^0 = \frac{1}{2} \ln[2(N+1)/\nu - 1] - \ln[(N+1)/\nu - 1]. \quad (\text{B6})$$

For  $\nu \ll N$  one obtains  $a_{\nu}^0 \approx -\ln(N/\nu)/2$ , and for  $\nu \approx N$  (meaning  $N - \nu \ll N$ ) one obtains  $a_{\nu}^0 \approx \ln(N/\nu)$ .

We now make a crude approximation:

$$\sum_{\nu=1}^N (a_{\nu}^0)^{m-1} \approx \left[ 1 - \left( \frac{1}{2} \right)^{m-1} \right] \sum_{j=1}^N [\ln(N/j)]^{m-1}. \quad (\text{B7})$$

This approximation is proper only for the  $\nu$ 's that are either small or close to  $N$ . However, since these  $\nu$ 's contribute the most to the sum, we expect this approximation to be correct within a numerical factor of order unity. Indeed, for  $m=2$ , the last sum in Eq. (B7) approximately equals  $N$ , and the total result we obtain,  $0.5N$ , is different than the correct result  $\ln 2 \cdot N$  only by a factor of order unity. Increasing  $m$ ,

the approximation becomes better, since the relative contribution of the levels far from  $N$  decreases. For  $m > 2$  we neglect the factor  $(\frac{1}{2})^m$  in Eq. (B7). For  $m \gg \ln N$  only the  $j=1$  term in Eq. (B7) contributes, and  $E_{int}^{0(m)}$  is approximated by  $\lambda^m \cdot \ln N^{(m-1)}$ . For  $m \ll \ln N$  one can show that

$$(m-1)! N - \ln N^{(m-1)} < \sum_{j=1}^N [\ln(N/j)]^{m-1} < (m-1)! N \quad (\text{B8})$$

and therefore  $\sum_{j=1}^N [\ln(N/j)]^{m-1} \approx (m-1)! N$ .

Having thus established Eq. (B1), let us now examine its consequences. First, since the low powers in the series for  $E_{int}^0$  fulfill the relation  $E_{int}^{0(m+1)}/E_{int}^{0(m)} \approx m \cdot \lambda$ , whereas the high powers fulfill the relation  $E_{int}^{0(m+1)}/E_{int}^{0(m)} \approx \lambda \cdot \ln N$ , the series for  $E_{int}^0$  does not have a single parameter describing the ratio between consecutive terms in the series.

Second, while the high powers dictate the convergence radius of the series to be roughly  $1/\ln N$ , their contribution is larger than that of the low powers only for  $\lambda \geq 1/\ln N - 1/(\ln N)^2$ , introducing a scale of  $1/(\ln N)^2$  near  $\lambda = 1/\ln N$  (see also Sec. VI). This can be seen by estimating the partial sum of Eq. (B3) for  $m \geq \ln N$  using the result in Eq. (B2). Taking  $b'_m = 1$  for all  $m$  we get

$$\sum_{m=\ln N}^{\infty} \lambda^m (\ln N)^{m-1} = \frac{(\lambda \ln N)^{\ln N}}{\ln N (1 - \lambda \ln N)}. \quad (\text{B9})$$

For  $\lambda = 1/\ln N - c/(\ln N)^2$  for any  $c \geq 1$ , the above sum equals

$$\frac{(1 - c/\ln N)^{\ln N}}{c} \approx \frac{e^{-c}}{c}, \quad (\text{B10})$$

which is smaller than one, while the low orders are proportional to  $N$ .

Third, for  $\lambda < 1/\ln N - 1/(\ln N)^2$ , where the low powers dominate, one readily obtains

$$E_{int}^0 = \lambda N d + E_{int}^{0(2)} [1 + \mathcal{O}(1/\ln N)]. \quad (\text{B11})$$

Here the first-order term  $\lambda N d$  is the Hartree term, and the second-order term  $E_{int}^{0(2)} \approx \ln 2 \cdot \lambda^2 \omega_D$  is obtained from Eq. (B4). The order  $1/\ln N$  can be understood as follows. The third-order term is smaller than the second-order term by a factor of order  $\lambda$ , which is smaller than  $1/\ln N$ . All the higher orders are smaller than the second-order term by a factor of order  $1/(\ln N)^2$  or smaller, and since there are about  $\ln N$  such terms, their sum is also approximately  $1/\ln N$  smaller than the second-order term.

The corresponding perturbative result for the condensation energy  $E_{cond}^0 \equiv E_{cond}^{pert}$  now immediately follows by inserting Eq. (B11) into Eq. (11) (with  $k=N$ ). The result is given by Eq. (22), namely,  $E_{cond}^{pert}(\lambda) \approx \ln 2 \cdot \lambda^2 \omega_D$ .

### APPENDIX C: SERIES EXPANSION OF THE INTERACTION ENERGY

In Eq. (18) we obtained an expression for the interaction energy, whose accuracy for different regimes in the range

$\lambda < 1/\ln N$  was obtained in Appendix A. We then expanded the result in a series in  $\lambda$ . This series converges, in the regime  $\lambda < 1/\widehat{\ln} N$ , to the approximate result. We were not able to find a series that converges to the exact result for the interaction energy in the above regime. However, we obtained results that suggest that the interaction energy is analytical on the positive real axis of the coupling parameter and can be expanded in a series in  $\lambda$  with a finite convergence radius that equals  $1/(\widehat{\ln} N + b)$ , where  $b$  is of order unity (Sec. VI). As another check of the above statement we solved, numerically, Richardson's equations (8) for complex values of  $\lambda$  and calculated the integral

$$\int_C E_{int}(z) dz, \quad (C1)$$

where  $C$  is a contour circumventing the positive real axis (see Fig. 7).

The integral was calculated for various  $N$ 's in the range  $4 < N < 64$  (a few contours for each  $N$ , each extending to a different value of  $\text{Re } \lambda$ , up to  $\text{Re } \lambda = 0.7$ ). For all  $N$  the integrals were zero within the numerical error, which suggests that there are no singularities on the positive real axis.

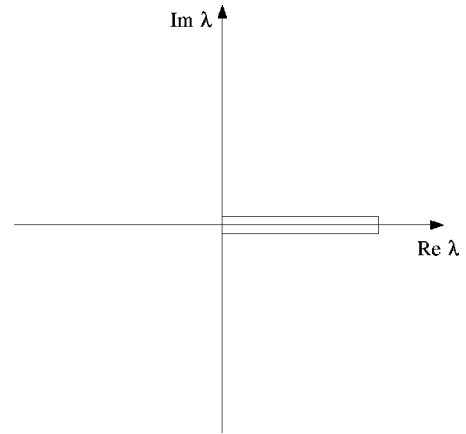


FIG. 7. An integration contour in the complex  $\lambda$  plane.

The exact interaction energy is given by Eq. (10). Expanding the exact expression as  $E_{int} = d \sum_{\lambda=1}^{\infty} \alpha_m \lambda^m$ , we find that

$$\alpha_m = \sum_{\nu} \left( (a_{\nu}^0)^{(m-1)} + \sum_{s=1}^{m-3} b_s (a_{\nu}^0)^s \right). \quad (C2)$$

The approximation we make in Eq. (18) is equivalent to taking only the highest power  $(m-1)$  in Eq. (C2) for each  $m, \nu$  and neglecting the sum in the brackets.

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