Small Superconducting Grain in the Canonical Ensemble

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By means of the Lanczos method we analyze superconducting correlations in ultrasmall grains at fixed particle number. We compute the ground-state properties and the excitation gap of the pairing Hamiltonian as a function of the level spacing δ. Both quantities turn out to be *parity dependent* and *universal* functions of the ratio δ/Δ (Δ is the BCS gap). We then characterize superconductivity in the canonical ensemble from the scaling behavior of correlation functions in energy space. [S0031-9007(98)06059-1]

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What is the size limit for a metal particle to have superconducting properties? Anderson [1] posed this question back in 1959 arguing that when the average level spacing δ (inversely proportional to volume of the grain) becomes of the order of the BCS gap Δ superconductivity should disappear. A related question is how to characterize "superconductivity" in small systems. The transition is washed out, for instance, by thermal fluctuations of the order parameter [2]. Moreover, the hallmarks of Cooper pair condensation like the zero resistance and the Meissner effect are absent when the grains are of submicron size.

In a series of recent experiments Ralph, Black, and Tinkham [3,4] studied the transport through nanometer-scale Al grains. These experiments revealed the existence of a spectroscopic gap larger than the average level spacing which could be driven to zero by applying a suitable magnetic field. This was convincingly interpreted as the reminiscence of superconductivity. As the grain size was further reduced (<5 nm) no trace of the gap in the spectrum was detected. The experimental results were found to be *parity dependent,* i.e., to depend on the electron number in the grain being even or odd.In the light of these experiments von Delft *et al.* [5] reconsidered the question posed by Anderson. They included the effect of a uniform finite level spacing in a parity dependent mean field theory [6], and found that the breakdown of superconductivity (in the BCS sense) occurs at a value of δ/Δ which is indeed parity dependent. In grains with an even number of electrons superconductivity persists down to smaller grain sizes as compared with the odd ones. This parity effect gets enhanced when the effect of level statistics [7] is included.

Because of the spontaneous breaking of the gauge symmetry, the BCS theory is most transparently formulated in the grand canonical ensemble [8] since it is easy to define the order parameter as the amplitude to create (or destroy) a Cooper pair in the condensate. In the canonical ensemble this quantity vanishes and the characterization of coherence is more difficult. Fortunately the use of the grand canonical ensemble is appropriate for many systems which are large enough to give small relative fluctuations of the electron number. This condition is not strictly met in the experiments of Refs. [3,4] where charging effects allow one to fix the number of electrons in the grain [9]. For these systems moreover quantum fluctuations of the pairing field may become so large to invalidate the mean field approach. In order to characterize the ground-state pair correlations, Matveev and Larkin [10] then proposed to use the parity gap Δ_P, an experimentally accessible quantity related to the extra ground-state energy of a system with an unpaired electron. Even the limit of very small grains Δ_P is very sensitive to superconducting fluctuations (for large grains it reduces to Δ).

Superconductivity in ultrasmall grains requires one to study the effect of finite level spacing at *fixed* particle number. We tackle this problem by Lanczos exact diagonalization. The purpose of this Letter is twofold. In the first part we characterize the superconducting correlations by studying the parity effect in the ground state (Figs. 1 and 2) and the spectroscopic gap (Fig. 3). The central question of defining superconductivity at fixed particle number is addressed in the second part where we discuss the scaling properties, *in energy space*, of the pairing model (Figs. 4 and 5).

The BCS pairing Hamiltonian for the small grain is

$$H = \sum_{\substack{n=1\\ \sigma=\pm}}^{\Omega} \epsilon_n c^\dagger_{n,\sigma} c_{n,\sigma} - \alpha\delta \sum_{m,n=1}^{\Omega} c^\dagger_{m,+} c^\dagger_{m,-} c_{n,-} c_{n,+} \,. \quad (1)$$

The indices m and n label the single particle energy levels with energy ϵ_m and annihilation operator $c_{m,\sigma}$. The quantum number $\sigma = \pm$ labels time reversed electron states. The number of (doubly degenerate) levels is fixed to Ω which is twice the Debye frequency ω_D in units of δ. Finally α is the dimensionless BCS coupling constant and $\delta \sim 1/N(0)V$ [$N(0)$ being the density of states at the Fermi energy and V the volume of the grain]. Since the Hamiltonian contains only pairing terms, an electron in a singly occupied level cannot interact with the other electrons (the unpaired electron is frozen). In the

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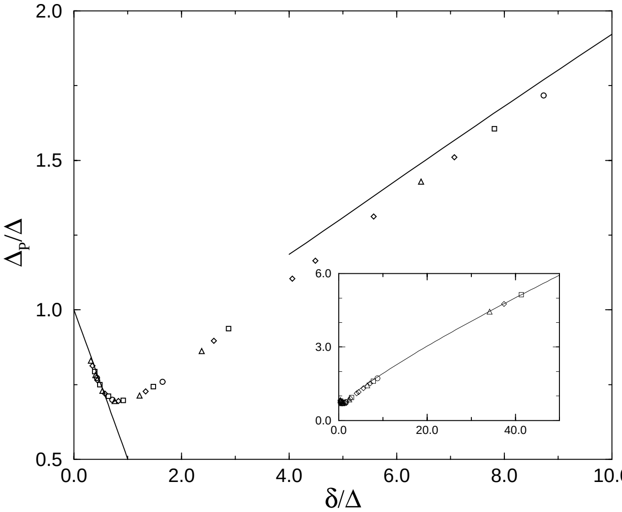

FIG. 1. The parity gap is plotted as a function of δ/Δ for systems with odd electron number. All the sets are evaluated at half filling ($\Omega = N$). In the inset the region of very large level spacing is plotted to compare with the asymptotic result of Matveev and Larkin. The parity gap is centered around $N = 17$ ($\circ$), $N = 19$ ($\Diamond$), $N = 21$ ($\Box$), and $N = 23$ ($\triangle$). In the limit of very small grains we obtained a quantitative agreement by using $\Delta_P \sim \delta/2 \ln(a\delta/\Delta)$ with $a \sim 1.35$.

following we will use the simplified model with equally spaced single particle levels $\epsilon_m = \delta m$ [5,10]. We will comment later about the effect of level statistics [11]. We study systems up to $\Omega = 25$ at half filling ($\Omega = N$) which corresponds to the usual case of attractive interaction in a shell $|\epsilon| < \omega_D$ centered at the Fermi energy.

The parity gaps.—We first consider the properties of the ground state by measuring the parity gaps introduced in Ref. [10]

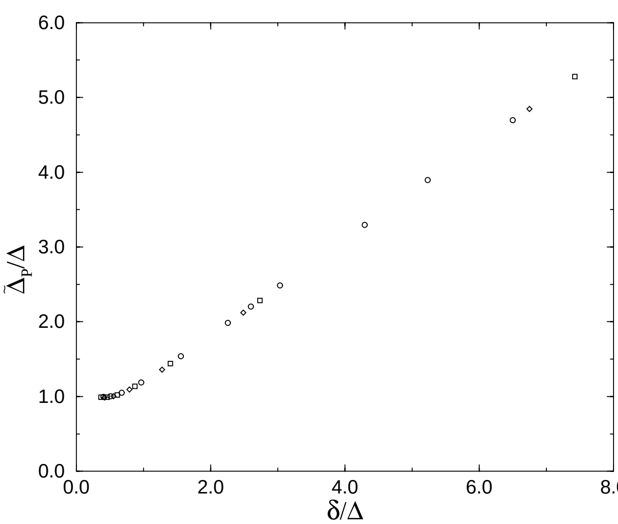

FIG. 2. The same as in Fig. 1 for an even number of particles. The parity gap is centered around $N = 18$ ($\circ$), $N = 20$ ($\Box$), and $N = 22$ ($\Diamond$).

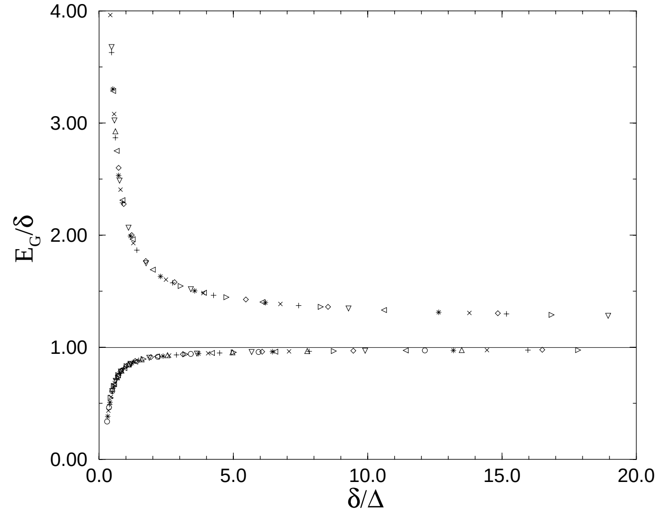

FIG. 3. The spectroscopic gap E_G is plotted as a function of δ/Δ for even and odd particle systems at half filling. [($\Diamond$) $\Omega = 9, 10$; ($\triangle$) $\Omega = 11, 12$; ($\triangleleft$) $\Omega = 13, 14$; ($\triangleright$) $\Omega = 15, 16$; ($\bigtriangledown$) $\Omega = 17, 18$; ($+$) $\Omega = 19, 20$; ($\times$) $\Omega = 21, 22$; ($\star$) $\Omega = 23, 24$; ($\circ$) $\Omega = 25$].

$$\Delta_P = E_{2N+1} - \frac{1}{2}(E_{2N} + E_{2N+2}),$$

$$\tilde{\Delta}_P = -E_{2N} + \frac{1}{2}(E_{2N+1} + E_{2N-1}).$$

Here E_N is the ground-state energy for a system with N electrons. By increasing the level spacing, $\tilde{\Delta}_P$ and Δ_P behave in a different way. The case $\delta \ll \Delta$ has been discussed in [5,10,12], $\Delta_P/\Delta \approx 1 - \delta/2\Delta$ and $\tilde{\Delta}_P/\Delta \approx 1 - \sqrt{\delta/\Delta}\exp(-2\pi\delta/\Delta)$. In the opposite limit, $\delta \gg \Delta$ the behavior of the parity effect is dominated by strong superconducting fluctuations [10] which give logarithmic

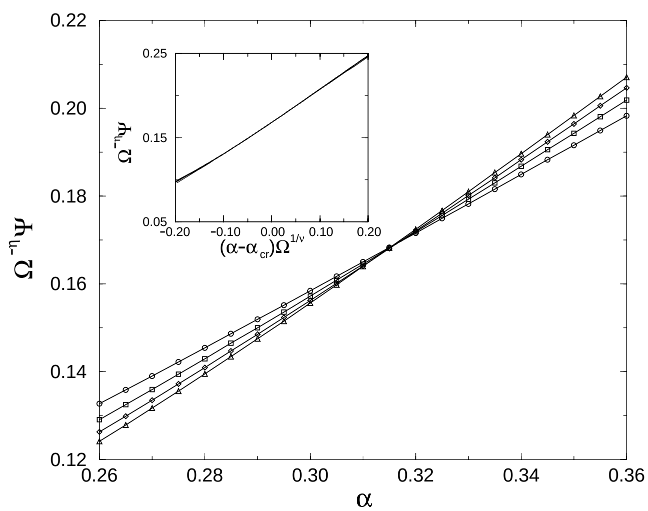

FIG. 4. Data for the pair mixing parameter Ψ, as a function of $\alpha = g/\delta$ and $\Omega = N =$ even, which show clearly a phase transition [$N = 8$ ($\circ$), $N = 12$ ($\Box$), $N = 16$ ($\Diamond$), $N = 20$ ($\triangle$)]. The inset shows the data collapse.

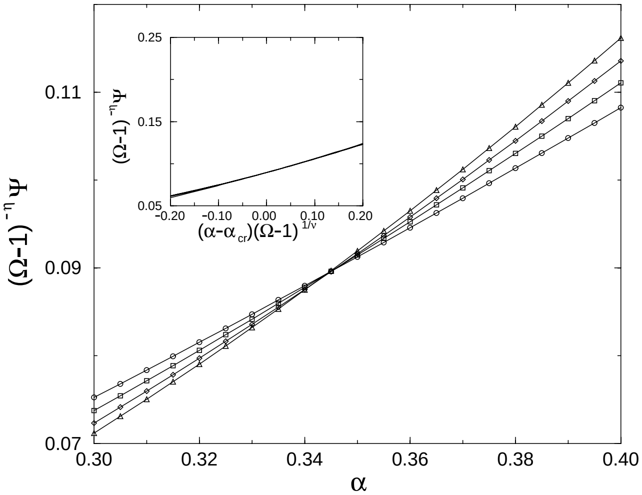

FIG. 5. The same as in Fig. 4 for odd systems [$N = 9$ (∘), $N = 13$ (◇), $N = 17$ (□), and $N = 21$ (△)].

corrections to the noninteracting result, i.e., $\Delta_P = \delta/2\ln(\delta/\Delta)$ (much larger than the BCS gap at the same level spacing). In Fig. 1 the results of the numerical diagonalization for Δ_P are presented as a function of δ/Δ. The two asymptotic behaviors discussed above are plotted for comparison. In Fig. 2 we plot $\tilde{\Delta}_P/\Delta$ which monotonically increases when the grain size is reduced, as expected [10]. Given the maximum number of levels we can account for, in the limit $\delta \ll \Delta$ we need to consider couplings up to $\alpha = 0.5$. In this regime we use the relation $\Delta = \omega_D/2\sinh(1/\alpha)$. Notice that our data, which refer to systems with a different number of electrons (from $N = 10$ to $N = 25$) collapse on a single curve for *all values* of the ratio δ/Δ. This suggests that Δ_P/Δ is a *universal function* of δ/Δ. One consequence of that is the systems we consider, although small compared with the superconducting grains used in the experiments where $N \sim 10^3-10^5$, may capture all the relevant features of the model, in particular in the interesting crossover region $\delta \sim \Delta$.

The spectroscopic gap.—Next we study the spectroscopic gap E_G between the ground state and the first excited many body level [3,4]. In the noninteracting case $E_G = \delta$ whereas in the BCS limit it either coincides with 2Δ (even-N grains) or it vanishes, $E_G \sim \delta^2/2\Delta$ (odd-N grains). In the first excited state for even-N grains two unpaired electrons occupy two single-particle levels close to the Fermi energy. In the odd-N grains the first excited state is obtained by moving the unpaired electron to the next single-particle level. In Fig. 3 E_G is plotted as function of the grain size. For small grains the effect of pairing correlations in the even case is still observable in a rather large range of δ/Δ for which odd grains have already reached the asymptotic behavior $E_G = \delta$. The crossover to the "strong coupling" regime occurs at values of δ/Δ which are different in the odd and in the even cases and roughly agree with the mean field critical values of Ref. [5], $\delta/\Delta \sim 4$ (even) and $\delta/\Delta \sim 1$ (odd). It is interesting to notice that the BCS regime is reached at (parity dependent) values of $\delta/\Delta \ll 1$ so there is an intermediate region of values $\delta/\Delta \leq 1$ where BCS theory describes well enough only the ground-state properties.

To summarize this first part we have shown the full crossover between a "weak coupling" regime (very small grains, where fluctuational superconductivity manifests itself via logarithmic renormalizations) and a "strong coupling" regime (very large grains). This situation is reminiscent of the antiferromagnetic Kondo problem. The level spacing δ is the low energy cutoff which tunes the system through the two regimes. The breakdown of the logarithmic renormalization marks the crossover to the superconducting phase. This provides a *quantitative* answer to Anderson's question [1] despite the fact that we have bypassed the very problem of defining superconductivity. We discuss this issue in the next section.

The order parameter.—Following the conventional wisdom up to now we meant by superconductivity a regime in which BCS results are qualitatively valid. This is not satisfactory in the canonical ensemble since the central quantity, the BCS order parameter, is always zero. In order to characterize superconductivity one has to consider higher order correlators. However, they will be nonzero for generic interaction, even for repulsive ones, so it is not straightforward to extract from them a quantity which plays the role of the "order parameter." Nevertheless a characterization of superconductivity in the canonical ensemble can be achieved by studying the scaling of correlations in the energy space: *a superconducting system displays long range energy correlations*. To this end we consider the pseudospin representation [13] of the Hamiltonian Eq. (1)

$$H = \sum_{n=1}^{\Omega} \epsilon_n (1 + 2S_n^z) - \alpha\delta \sum_{m,n=1}^{\Omega} S_m^+ S_n^- , \qquad (2)$$

where $S_n^+ = c_{n,+}^\dagger c_{n,-}^\dagger$ and $S_n^z = (1/2)(c_{n,+}^\dagger c_{n,+} + c_{n,-}^\dagger c_{n,-} - 1)$. Each energy level is represented by a site of a fictitious lattice and Eq. (2) is the Hamiltonian of a one dimensional spin-1/2 XY model with long range interaction in a nonuniform transverse field [14]. The number of pairs fixes the total S^z and for odd electron numbers one should simply remove the "site" occupied by the unpaired electron. In the absence of XY interaction the spins point in the z direction with a domain wall at the Fermi energy separating up and down spin regions. In the opposite limit (vanishing transverse field) the system possesses long range order in the XY plane [15]. The superconducting properties can be studied by defining the appropriate correlation functions (see also Ref. [16]).

Following Refs. [5,17] we consider the quantity

$$\Psi = \sum_{n=1}^{\Omega} u_n v_n \,, \tag{3}$$

where $v_n = \langle S_n^+ S_n^- \rangle^{1/2}$ and $u_n = \langle S_n^- S_n^+ \rangle^{1/2}$. In the noninteracting case $\Psi = 0$ since both u_n and v_n are step function symmetric around the Fermi energy and hence their product is zero. In the limit of very strong interaction the occupation probability for the pairs, as a function of the level position, is roughly uniform. In this case an estimate of the energy of this configuration, at half filling, is $\sim(2 - \alpha)\delta\Omega^2$. Note that for $\alpha > 2$ the system gains energy, due to pair mixing, from arbitrary high energy levels. So if we enlarge the phase space available for coherence (by progressively increasing Ω at fixed N/Ω) a "normal" system will not take advantage from the presence of extra levels whereas a "superconducting" does. In other words correlations are short ranged in energy in normal systems whereas a superconducting system displays long range energy correlations.

The finite size scaling ansatz for Ψ is

$$\Psi = \Omega^{\eta} F[(\alpha - \alpha_{\rm cr})\Omega^{1/\nu}], \tag{4}$$

where $\alpha_{\rm cr}$ is the critical point. In Figs. 4 and 5 the behavior of Ψ is shown for the even and the odd case, respectively. A scale invariant point is found whose value is parity dependent. By collapsing all the data on a single curve, shown for the even and the odd case in the inset of Figs. 4 and 5, respectively, it is possible to determine the exponent ν. We obtain $\alpha_{\rm cr} = 0.315 \pm 0.002$, $\eta = 0.94$, $1/\nu = 0.26$ for the even case and $\alpha_{\rm cr} = 0.345 \pm 0.002$, $\eta = 1.08$, $1/\nu = 0.35$ for the odd case. Both the magnitude of Ψ and the location of the critical point (see Figs. 4 and 5) confirm the natural conjecture that superconducting correlations are destroyed easier in the odd rather than in the even case.

We stress that the value of $\alpha_{\rm cr}$ does not correspond to a critical grain size below which superconductivity disappears [2] (note that the scaling in energy is performed at fixed level spacing). The study of the parity and the spectroscopic gaps shows that δ determines how far is a system with given pairing interaction from the BCS fixed point. This is reflected in the behavior of the correlations studied in this section. We propose that the finite size scaling in energy space of properly defined correlation functions [like that defined in Eq. (3)] can characterize quantitatively the superconductivity in the canonical ensemble.

The results presented here for the parity gap and the excitation gap are in good agreement with the analytical expressions of Refs. [10,12]. If the approximation of equally spaced levels is relaxed, mesoscopic fluctuations are expected to be important in the intermediate region $\delta \sim \Delta$ [10]. Nevertheless the very existence of the quantum phase transition and the scaling in energy space is not questioned since it does depend only on the interplay between kinetic energy and pairing interaction. A more detailed account including the role of level statistics and of an applied magnetic field [17–19] will be the subject of a forthcoming publication [20].

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