

## Bardeen-Cooper-Schrieffer Theory of Finite-Size Superconducting Metallic Grains

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(Received 11 October 2007; published 5 May 2008)

We study finite-size effects in superconducting metallic grains and determine the BCS order parameter and the low energy excitation spectrum in terms of the size and shape of the grain. Our approach combines the BCS self-consistency condition, a semiclassical expansion for the spectral density and interaction matrix elements, and corrections to the BCS mean field. In chaotic grains mesoscopic fluctuations of the matrix elements lead to a smooth dependence of the order parameter on the excitation energy. In the integrable case we observe shell effects when, e.g., a small change in the electron number leads to large changes in the energy gap.

DOI: [10.1103/PhysRevLett.100.187001](https://doi.org/10.1103/PhysRevLett.100.187001)

PACS numbers: 74.20.Fg, 05.45.Mt, 74.78.Na

Since experiments by Ralph, Black, and Tinkham [1] on Al nanograins in the mid-1990s, there has been considerable interest in the theory of ultrasmall superconductors (see [2,3] for earlier studies). In particular, finite-size corrections to the predictions of the Bardeen-Cooper-Schrieffer (BCS) theory for bulk superconductors [4] have been studied [5–10] within the exactly solvable Richardson model [11]. Pairing in specific potentials, such as a harmonic oscillator potential [12] and a rectangular box, [13,14] and mesoscopic fluctuations of the energy gap [15,16] have been explored as well. Nevertheless, a comprehensive theoretical description of the combined effect of the discrete energy spectrum and fluctuating interaction matrix elements has not yet emerged.

In the present Letter we develop a framework based on the BCS theory and semiclassical techniques that permit a systematic analytical evaluation of the low energy spectral properties of superconducting nanograins in terms of their size and shape. Leading finite-size corrections to the BCS mean field can also be taken into account in our approach. Our main results are as follows. For chaotic grains, we show that the order parameter is energy dependent. The energy dependence is universal; i.e., its functional form is the same for all chaotic grains. The matrix elements are responsible for most of the deviation from the bulk limit. In integrable grains, we find that the superconducting gap is strongly sensitive to shell effects, namely, a small modification of the grain size or number of electrons can substantially affect its value.

We start with the BCS Hamiltonian  $H = \sum_{n\sigma} \epsilon_n c_{n\sigma}^\dagger c_{n\sigma} - \sum_{n,n'} I_{n,n'} c_{n\uparrow}^\dagger c_{n\downarrow}^\dagger c_{n'\downarrow} c_{n'\uparrow}$ , where  $c_{n\sigma}$  ( $c_{n\sigma}^\dagger$ ) annihilates (creates) an electron of spin  $\sigma$  in state  $n$ ,

$$I_{n,n'} = I(\epsilon_n, \epsilon_{n'}) = \lambda V \delta \int \psi_n^2(r) \psi_{n'}^2(r) dV \quad (1)$$

are matrix elements of a short-range electron-electron interaction,  $\lambda$  is the BCS coupling constant, and  $\psi_n$  and  $\epsilon_n$  are eigenstates and eigenvalues of the one-body mean field Hamiltonian of a free particle of mass  $m$  in a clean grain of volume  $V$ . Eigenvalues  $\epsilon_n$  are measured from the Fermi level  $\epsilon_F$  and the mean level spacing  $\delta = 1/\nu_{\text{TF}}(0)$ , where  $\nu_{\text{TF}}(0) = 2 \frac{V}{4\pi^2} (\frac{2m}{\hbar^2})^{3/2} \sqrt{\epsilon_F}$  is the spectral density at the Fermi level in the Thomas-Fermi approximation.

Our general strategy can be summarized as follows: (i) use semiclassical techniques to compute the spectral density  $\nu(\epsilon) = \sum_n \delta(\epsilon - \epsilon_n)$  and  $I(\epsilon, \epsilon')$  as series in a small parameter  $1/k_F L$ , where  $k_F$  is the Fermi wave vector and  $L \simeq V^{1/3}$  is the size of the grain (ii) solve the BCS gap equation in orders in  $1/k_F L$  (iii) evaluate the low energy spectral properties of the grain such as the energy gap, excitation energies, and Matveev-Larkin parameter [5] including finite-size corrections to the BCS mean field. The results thus obtained are strictly valid in the region,  $k_F L \gg 1$  (limit of validity of the semiclassical approximation),  $\delta/\Delta_0 < 1$  (limit of validity of the BCS theory), and  $l \gg \xi \gg L$  (condition of quantum coherence) where  $\xi = \hbar v_F/\Delta_0$  is the superconducting coherence length,  $v_F$  is the Fermi velocity,  $l$  is the coherence length of the single-particle problem and  $\Delta_0$  is the bulk gap. We note that in Al grains [9]  $\xi \approx 1600$  nm and  $l > 10000$  nm for temperatures  $T \leq 4$  K. Therefore the region  $l \gg \xi \gg L$  is accessible to experiments.

Since the matrix elements  $I(\epsilon, \epsilon')$  are energy dependent the BCS order parameter  $\Delta(\epsilon)$  also depends on energy. The self-consistency equation for  $\Delta(\epsilon)$  reads

$$\Delta(\epsilon) = \int_{-E_D}^{E_D} \frac{\Delta(\epsilon')I(\epsilon, \epsilon')}{2\sqrt{\epsilon'^2 + \Delta(\epsilon')^2}} \nu(\epsilon') d\epsilon', \quad (2)$$

where  $E_D$  is the Debye energy. In the limit  $V \rightarrow \infty$ , the spectral density in the  $2E_D$  energy window near the Fermi level can be taken to be energy independent and given by the Thomas-Fermi approximation,  $\nu(\epsilon) = \nu_{\text{TF}}(0)$ , matrix elements are also energy independent,  $I(\epsilon, \epsilon') = \lambda\delta$ , and the gap is equal to its bulk value,  $\Delta_0 = 2E_D e^{-1/\lambda}$ . As the volume of the grain decreases the mean level spacing increases and eventually both  $\nu(\epsilon)$  and  $I(\epsilon, \epsilon')$  deviate from the bulk limit.

*Semiclassical evaluation of  $\nu(\epsilon)$ .*—The spectral density in a 3d grain,

$$\nu(\epsilon') \simeq \nu_{\text{TF}}(0)[1 + \bar{g}(0) + \tilde{g}_l(\epsilon')] \quad (3)$$

consists of a monotonic part,  $\bar{g}(0) = \pm \frac{S\pi}{4k_F V} + \frac{2C}{k_F^2 V}$  and an oscillatory contribution  $\tilde{g}_l(\epsilon')$ . Here  $S$  and  $C$  denote the surface area and mean curvature of the grain, respectively, and upper (lower) signs stand for Neumann (Dirichlet) boundary conditions. The oscillatory contribution, to leading order, is given by the Gutzwiller trace formula [17,18],

$$\tilde{g}_l(\epsilon') = \Re \frac{2\pi}{k_F^2 V} \sum_p^l A_p e^{i(k_F L_p + \beta_p + \epsilon' k_F L_p / 2\epsilon_F)}, \quad (4)$$

where both the amplitude  $A_p$  and the topological index  $\beta_p$  depend on classical quantities only [18]. The summation is over a set of classical periodic orbits  $p$  of length  $L_p$ . For isolated grains Dirichlet is the most natural choice, but we also include Neumann to illustrate the dependence of our results on boundary conditions. Only orbits shorter than the quantum coherence length  $l$  of the single-particle problem are included. This effectively accounts for inelastic scattering and other factors that destroy quantum coherence. Here we focus on the limit  $l \gg \xi$ , the case  $l \sim \xi$  will be discussed elsewhere [19]. In Eq. (4) classical actions  $\hbar k(\epsilon')L_p$  are expanded as  $k(\epsilon') \approx k_F + \epsilon' k_F / 2\epsilon_F$ . The amplitude  $A_p$  increases by a factor  $(k_F L)^{1/2} \gg 1$  for each of the symmetry axes of the grain.

*Semiclassical evaluation of  $I(\epsilon, \epsilon')$ .*—For integrable systems  $I(\epsilon, \epsilon')$  depends on details of the system. In a rectangular box it is simply  $I(\epsilon, \epsilon') = \lambda\delta$  but in most other geometries an explicit expression in terms of classical quantities is not available. In the chaotic case the situation is different. As a result of the quantum ergodicity theorem [20] it is well justified to assume that for systems with time reversal symmetry (the only ones addressed in this Letter),  $\psi_n^2(\vec{r}) = \frac{1}{V}(1 + O(1/k_F L))$ . In order to explicitly determine deviations from the bulk limit we replace  $\psi_n^2(\vec{r})$  in  $I_{n,n'}$  with  $\langle \psi^2(\vec{r}) \rangle_{\epsilon_n}$ , where  $\langle \dots \rangle_{\epsilon}$  stands for an energy average around  $\epsilon$ . The single-particle probability density is thus effectively averaged over a small energy window resembling the effect of a finite coherence length.

Substituting  $\langle \psi^2(\vec{r}) \rangle_{\epsilon}$  into  $I_{n,n'}$ , we obtain  $I(\epsilon, \epsilon') = \frac{\lambda}{V} \times [1 - (\frac{S\pi}{4k_F V})^2 + \bar{I}(\epsilon_F, \epsilon, \epsilon')]$ , where  $\bar{I}(\epsilon_F, \epsilon, \epsilon') = \bar{I}^{\text{short}}(\epsilon_F) + \bar{I}^{\text{long}}(\epsilon_F, \epsilon - \epsilon')$  can be split into two parts

coming from short and long orbits. Short orbits involve a single reflection at the grain boundary and result in a monotonic contribution

$$\bar{I}^{\text{short}}(\epsilon_F) = \frac{\pi S}{4k_F V}, \quad (5)$$

while the contribution of long orbits depends on the energy difference  $\epsilon - \epsilon'$

$$\bar{I}^{\text{long}}(\epsilon_F, \epsilon - \epsilon') = \frac{1}{V} \Pi_l \left( \frac{\epsilon - \epsilon'}{\epsilon_F} \right), \quad (6)$$

with  $\Pi_l(w) = \int \sum_{\gamma(r)}^l D_\gamma^2 \cos[wk_F L_\gamma] dr$ , where the sum is over all nonzero classical paths (not periodic orbits)  $\gamma(r)$  starting and ending at a given point  $r$  inside the grain [21] and the amplitude  $D_\gamma$  is defined in Refs. [17,19,21]. The integral stands for an average over all points  $r$  inside the grain. The explicit evaluation of  $\Pi_l(w)$  for a given geometry requires, in principle, the knowledge of all classical paths  $L_\gamma$  up to length  $l$ . However, for  $l \gg L$ , one can use a *sum rule* for classical closed orbits [22] to obtain

$$\Pi_l(w) = \left( \frac{2\pi}{k_F} \right)^2 \frac{\sin(wk_F l)}{wk_F}. \quad (7)$$

*Solution of the gap equation.*—First, let us consider chaotic grains. Here we present only the final answer for the 3d case deferring a more detailed account, including the 2d case, to Ref. [19]. Writing the gap function  $\Delta(\epsilon)$  formally as a series in  $1/k_F L$ ,

$$\Delta(\epsilon) = \Delta_0 [1 + f^{(1)} + f^{(2)} + f^{(3)}(\epsilon)], \quad (8)$$

substituting it into Eq. (2), and using the above expressions for the density of states and interaction matrix elements, we derive

$$f^{(1)} = \frac{1 \pm 1}{\lambda} \frac{\pi S}{4k_F V}, \quad (9)$$

where  $\pm$  stands for the Neumann (+) and Dirichlet (−) boundary conditions. Note that to leading order the combined effect of the interaction matrix elements and the density of states have very different consequences on the gap, depending on the kind of boundary conditions. For Dirichlet, the leading finite-size corrections to the gap vanishes.

The second order  $(1/(k_F L)^2)$  correction reads

$$\lambda f^{(2)} = \frac{2C}{k_F^2 V} + 2 \left( \mp 1 + \frac{1 \pm 1}{\lambda} \right) \left( \frac{\pi S}{4k_F V} \right)^2 + \bar{g}(0),$$

where

$$\bar{g}(0) = \frac{2\pi}{k_F^2 V} \sum_p^l A_p W(L_p/\xi) \cos(k_F L_p + \beta_p) \quad (10)$$

and,

$$W(L_p/\xi) = \frac{\lambda}{2} \int_{-\infty}^{\infty} dt \frac{\cos(L_p t/\xi)}{\sqrt{1+t^2}} \quad (11)$$

exponentially suppresses periodic orbits longer than  $\xi$ .

The third order correction (included in the definition of  $\delta$ ) is energy dependent,

$$f^{(3)}(\epsilon) = \frac{\pi\lambda\delta}{\Delta_0} \left[ \frac{\Delta_0}{\sqrt{\epsilon^2 + \Delta_0^2}} + \frac{\pi}{4} \right]. \quad (12)$$

Note that (i)  $\delta/\Delta_0 \ll 1$  is an additional expansion parameter, therefore the contribution (12) can be comparable to lower orders in the expansion in  $1/k_F L$  and (ii) the order parameter  $\Delta(\epsilon)$  has a maximum at the Fermi energy ( $\epsilon = 0$ ) and slowly decreases on an energy scale  $\epsilon \sim \Delta_0$  as one moves away from the Fermi level. One can also show that mesoscopic corrections given by Eqs. (9), (10), and (12), always enhance  $\Delta(0)$  as compared to the bulk value  $\Delta_0$ . Figure 1 shows the gap function  $\Delta(\epsilon)$  for Al grains of different sizes  $L$ , where we used (see [1])  $k_F \approx 17.5 \text{ nm}^{-1}$ ,  $\lambda \approx 0.18$ , and  $\delta \approx 7279/N \text{ meV}$ , where  $N$  is the number of particles.

Several remarks are in order: (a) the smoothing of the spectral density energy dependence in Eq. (10) caused by a cutoff function  $W$  is a superconductivity effect not related to the destruction of quantum coherence, (b) the energy dependence of the gap is universal in the sense that it does not depend on specific grain details, (c) the matrix elements  $I(\epsilon, \epsilon')$  play a crucial role, e.g., they are responsible for most of the deviation from the bulk limit in Fig. 1, (d) the requirement  $\xi \gg L$  used to derive Eq. (7) is well justified for nanograins since  $L \sim 10 \text{ nm}$ , while  $\xi \sim 10^4 \text{ nm}$ .

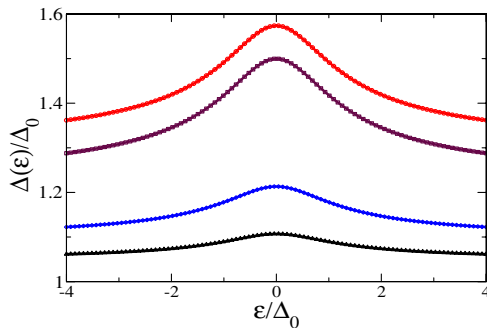


FIG. 1 (color online). Superconducting order parameter  $\Delta(\epsilon)$  in units of the bulk gap  $\Delta_0$  for chaotic Al grains ( $k_F = 17.5 \text{ nm}^{-1}$ ,  $\delta = 7279/N$ ,  $\Delta_0 \approx 0.24 \text{ meV}$ ) as a function of energy  $\epsilon$  counted from the Fermi level. Different curves correspond to grain sizes (top to bottom)  $L = 6 \text{ nm}$ ,  $k_F L = 105$ ,  $\delta/\Delta_0 = 0.77$  (Dirichlet and Neumann boundary conditions),  $L = 8 \text{ nm}$ ,  $k_F L = 140$ ,  $\delta/\Delta_0 = 0.32$  (Dirichlet), and  $L = 10 \text{ nm}$ ,  $k_F L = 175$ ,  $\delta/\Delta_0 = 0.08$  (Dirichlet). The leading contribution comes from the energy dependent matrix elements  $I(\epsilon, \epsilon')$  obtained from Eqs. (5) and (6). Note that the order parameter is always larger than its bulk value  $\Delta_0$  and has a single maximum at the Fermi level.

We now turn to the integrable case. Probably the simplest example is that of a rectangular box, since in this case the interaction matrix elements are simply  $I(\epsilon, \epsilon') = \lambda\delta$ . The calculation is simplified as now the order parameter is energy independent. We have

$$\Delta = \Delta_0[1 + f^{(1)} + f^{(3/2)} + f^{(2)}], \quad (13)$$

where  $f^{(n)} \propto (k_F L)^{-n} \lambda^{-1}$ . We obtain  $\lambda f^{(1)} = \bar{g}(0) + \bar{g}^{(1)}(0)$ ,  $\lambda f^{(3/2)} = \sum_{i,j \neq i} \bar{g}_{i,j}^{(3/2)}(0)$ ,  $\lambda f^{(2)} = \sum_i \bar{g}_i^{(2)}(0) + f^{(1)}$ ,  $[f^{(1)} - \bar{g}(0)]$ , where  $\bar{g}^{(k)} \propto (k_F L)^{-k}$  denotes the oscillating part of the spectral density and indexes  $i$  and  $j$  take values 1, 2, and 3 in three dimensions. Explicit expressions for  $\bar{g}^{(k)}$ ,  $\bar{g}_i^{(k)}$ , and  $\bar{g}_{i,j}^{(k)}$  in terms of periodic orbits for a rectangular box can be found in Ref. [18] [the cutoff function in our case is given by Eq. (11)]. We note that: (i) Eq. is also obtained by expanding the standard expression of the bulk gap  $\Delta = 2E_D \exp(-\nu_{\text{TF}}(0)/\nu(0)\lambda)$  in powers of  $(k_F L \lambda)^{-1}$  with  $\nu(0)$  given by Eq. (3). (ii) Unlike the chaotic case, the leading smooth correction to the bulk limit does not vanish for any boundary condition, (iii) smooth and oscillating corrections are of comparable magnitudes.

*Shell effects and fluctuations.*—Motivated by previous studies for other fermionic systems such as nuclei and atomic clusters (see, e.g., Ref. [23]), we investigate shell effects in metallic nanograins. In particular, we are interested in the fluctuations of the BCS gap with the number of electrons on the grain. As an illustration let us consider a cubic geometry. This is a natural choice since shell effects increase with the symmetry of the grain. To determine the gap, we solve the gap Eq. (2) numerically and determine the Fermi energy for a given number of electrons  $N$  by inverting the relation  $2 \int^{\epsilon_F} \nu(\epsilon) d\epsilon = N$ . We find a good agreement between numerical results and the semiclassical expansion; see Fig. 2. We also observe that a slight modification of the grain size (or equivalently the number of electrons  $N$  or the mean level spacing  $\delta$ ) can result in substantial changes in the value of the gap, see Fig. 2. The typical magnitude of fluctuations of the gap,  $\frac{\Delta}{\Delta_0} \approx$

$\sqrt{\frac{\pi\delta}{4\Delta_0}}$  [16] is consistent with our results (see Fig. 2).

*Low energy excitations.*—Having solved the gap Eq. (2), one can evaluate low energy properties of the grain taking into account finite-size corrections to the BCS mean field approximation. For example, the energy cost for breaking a Cooper pair in an isolated grain is [24],

$$\Delta E = 2\Delta(0) - \delta, \quad (14)$$

where  $\Delta(0)$  is the solution of Eq. (2) taken at the Fermi energy and is given by Eqs. (8) and (13) for chaotic and rectangular shapes, respectively. We note that the correction to the mean field ( $-\delta$ ) has been evaluated [10] for constant interaction matrix elements. Nevertheless, since the deviation of matrix elements from a constant energy independent value is itself of order  $(k_F L)^{-1}$ , Eq. (12) is

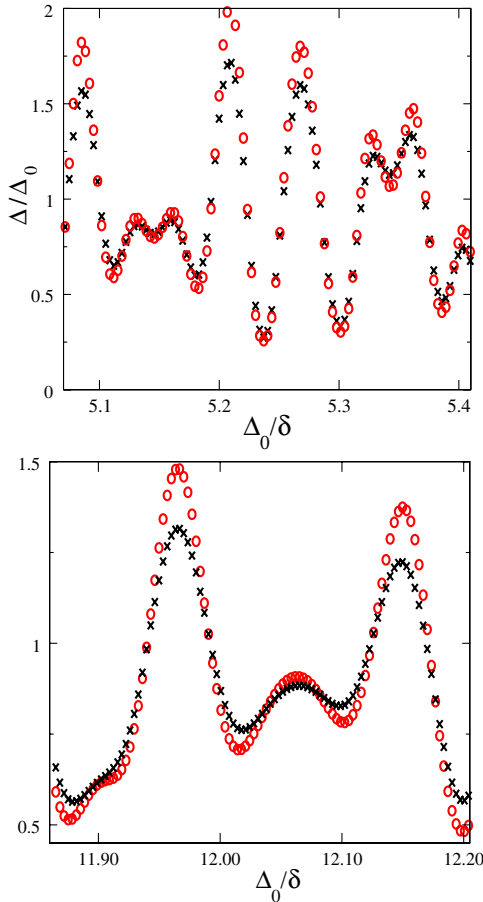


FIG. 2 (color online). Superconducting order parameter  $\Delta$  in units of the bulk gap  $\Delta_0$  for a cubic Al grain as a function of the ratio  $\Delta_0/\delta$ , where  $\delta$  is the mean level spacing. Black crosses correspond to the exact numerical solution of the gap Eq. (2), while the red circles represent the semiclassical analytical expression.

accurate up to terms of order  $(\delta/\Delta_0)(k_FL)^{-1}$ , which are negligible as compared to the ones we kept in Eqs. (8) and (13).

Similarly, the Matveev-Larkin parity parameter [5] reads  $\Delta_p \equiv E_{2N+1} - \frac{1}{2}(E_{2N} + E_{2N+2}) = \Delta(0) - \frac{\delta}{2}$ , where  $E_N$  is the ground state energy for a superconducting grain with  $N$  electrons. Quasiparticle energies are  $\sqrt{\epsilon^2 + \Delta(\epsilon)^2}$  plus corrections to mean field, which can be determined using the approach of Ref. [10].

We see that finite-size corrections to the BCS mean field approximation are comparable to the energy dependent correction (8) obtained within mean field, but have an opposite sign. We also note that our approach of expanding around the bulk BCS ground state is applicable only when  $\delta \ll \Delta_0$ , i.e., when corrections to the BCS mean field approximation are small [25].

To conclude, we have determined the low energy excitation spectrum for small superconducting grains as a function of their size and shape by combining the BCS

mean field, semiclassical techniques and leading corrections to the mean field. For chaotic grains the nontrivial energy dependence of the interaction matrix elements leads to a universal smooth dependence (12) of the gap function on excitation energy. In the integrable case we found that small changes in the number of electrons can substantially modify the superconducting gap.

A.M.G. thanks Jorge Dukelsky for fruitful conversations and acknowledges financial support from a Marie Curie Outgoing Action, Contract No. MOIF-CT-2005-007300. K.R. and J.D.U. acknowledge conversations with Jens Siewert and financial support from the Deutsche Forschungsgemeinschaft (No. GRK 638). E.A.Y. was supported by the Alfred P. Sloan Research Foundation and NSF Grant No. NSF-DMR-0547769.

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