Effect of Level Statistics on Superconductivity in Ultrasmall Metallic Grains

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We examine the destruction of superconducting pairing in metallic grains as their size is decreased for both even and odd numbers of electrons. This occurs when the average level spacing d is of the same order as the BCS order parameter Δ. The energy levels of these grains are randomly distributed according to random matrix theory, and we must work statistically. We find that the average value of the critical level spacing is larger than that for the model of equally spaced levels for both parities, and derive numerically the probability densities $P_{o,e}(d)$ that a grain of mean level spacing d shows pairing. [S0031-9007(96)01831-5]

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A recent experiment by Black, Ralph, and Tinkham (BRT) [1] involving the observation of a superconducting gap in ultrasmall Al grains (of size between 5 and 13 nm) has led to the reconsideration of an old but fundamental theoretical question—how small can a superconductor be? It is also of interest that in a previous experiment [2] on a smaller Al grain, the same group saw no sign of a gap (although, as they noted, there are experimental difficulties in observing an energy gap of similar magnitude to the average level spacing). von Delft *et al.* [3] have considered a simple mean-field model for such a grain which uses the standard BCS pairing interaction and assumes equal level spacing for analytical simplicity. Even-odd parity effects [4,5], which can be seen in samples at least 10^4 times larger [6,7], and are of paramount importance here, are included in their model. They find that the superconducting gap at zero temperature should cease at critical level spacing $d_c^o = 0.89\Delta(0)$ in odd grains, and $d_c^e = 4d_c^o$ in even grains, where $\Delta(0)$ is the zero-temperature bulk gap. They also note that although the mean-field result is subject to several types of correction, it does give a criterion for when pair correlations will cease to exist. It is therefore surprising that in the data of BRT from sample 4, an odd grain, that a gap is still seen although the sample is very close to the odd critical level-spacing. We also note that BRT's data shows no variation of the gap with level spacing d, suggesting that their samples are still on the flat part of the $\Delta(d)$ curve.

In this paper we consider the effect on the mean-field theory of relaxing the condition of equal level spacing. It is by now well known that the level spacing in small metallic grains is the Wigner-Dyson (WD) distribution [8] obtained from random matrix theory (RMT) [9]. This was first conjectured by Gor'kov and Eliashberg [10], and later proved by Efetov [11]. The reason for considering this effect is that most of the other corrections to mean-field theory seem to lead to a reduction in d_c; on the other hand, level statistics effects lead to larger values of $\langle d_c \rangle$, as we shall see.

The first thing we shall do is to reproduce the results of von Delft *et al.* [3] for d_c^o and d_c^e. We do this to demonstrate how the positioning of the energy levels enters into the calculation, and how this leads to the factor of 4 in the result $d_c^e = 4d_c^o$. Our starting point is the mean-field self-consistency equation

$$\frac{1}{\lambda} = d \sum_{|i|<\omega_c/d} \frac{1}{2E_i}(1 - 2f_i), \tag{1}$$

where $E_i = \sqrt{(\epsilon_i - \mu)^2 + \Delta^2}$, with ϵ_i the ith energy level, μ the chemical potential, ω_c the Debye energy, d the level spacing, and λ the BCS interaction. The occupation factor f_i differs for even or odd parity ensembles

$$f_i = \frac{f_i^+ Z_+ \pm f_i^- Z_-}{Z_+ \pm Z_-}, \tag{2}$$

where $f_i^{\pm} = \pm(e^{\beta E_i} \pm 1)^{-1}$ and $Z_\pm = \prod(1 \pm e^{-\beta E_i})$. We will work at zero temperature, so that $f_i = 1/2$ if the chemical potential lies on a level, and zero otherwise. In the case of equal level spacing the chemical potential lies halfway between the last filled and first empty levels in the even case, and on the half-filled level in the odd case, as shown in Fig. 1. For the case of the critical level spacing, the solution has $\Delta(T = 0) = 0$, so that one has

$$\frac{1}{\lambda} = \sum_{i=1}^{\omega_c/d_c^e} \frac{1}{i + 1/2}; \qquad \frac{1}{\lambda} = \sum_{i=1}^{\omega_c/d_c^0} \frac{1}{i}. \tag{3}$$

These can be rewritten in terms of the digamma function to yield

$$\frac{1}{\lambda} = \psi(\omega_c/d_c^e) - \psi(1/2) \approx \ln(\omega_c/d_c^e) - \psi(1/2),$$
$$\frac{1}{\lambda} = \psi(\omega_c/d_c^0) - \psi(1) \approx \ln(\omega_c/d_c^o) - \psi(1). \tag{4}$$

Finally, since we know that $\psi(1) = -\gamma$, $\psi(1/2) = -\gamma - 2\ln 2$, where γ is the Euler-Mascheroni constant,

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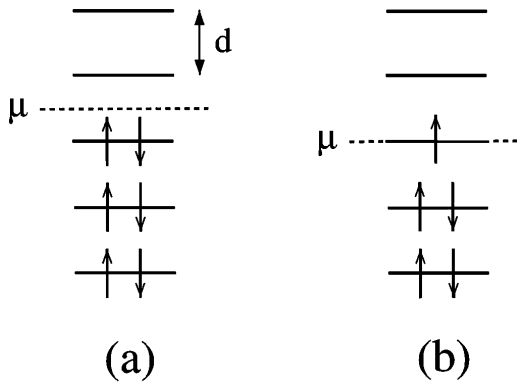

FIG. 1. The positioning of the chemical potential relative to the electronic energy levels in a superconducting grain with (a) an even number of electrons; (b) an odd number of electrons. In the even case the chemical potential lies halfway between the last filled and first empty level; in the odd case it lies on the half-filled level. Although illustrated for the equal level spacing case, the same occurs for randomly spaced levels.

it follows that

$$d_c^o = \tfrac{1}{4} e^{\gamma} \omega_c e^{-1/\lambda} = \tfrac{1}{2} e^{\gamma} \Delta(0) \approx 0.89\Delta(0); \quad d_c^e = 4 d_c^o . \tag{5}$$

We see that the factor of 4 between d_c^e and d_c^o comes from the fact that $\psi(1) - \psi(1/2) = 2\ln 2$, and thus ultimately from the positioning of the chemical potential relative to the energy levels. Furthermore if we write this out as a series for $2\ln 2$,

$$2\ln 2 = \psi(1) - \psi(1/2) = \left(\frac{2}{1} - \frac{2}{2}\right) + \left(\frac{2}{3} - \frac{2}{4}\right) + \left(\frac{2}{5} - \frac{2}{6}\right) + \ldots, \tag{6}$$

we see that only a few terms are needed before we are close to the final answer. In other words, the value of this particular factor is determined by a few energy levels near to the Fermi surface.

Let us now see how we can extend the above approach to the case of nonequally spaced energy levels. Consider first the odd case, so that the chemical potential lies on the half-filled level ϵ_0. The gap equation can then be written as

$$\frac{1}{\lambda} = d \sum_i \frac{1}{2\sqrt{(\epsilon_i - \epsilon_0)^2 + \Delta^2}} = \int_{-\omega_c}^{\omega_c} \frac{d\omega}{2\sqrt{\omega^2 + \Delta^2}}\, d \sum_i \delta(\omega - \epsilon_i + \epsilon_0). \tag{7}$$

We can then take the average of this equation over the disorder ensemble, so that all the statistical information about the level spacing occurs in the average over the sum of delta functions. This can be related to the two-level correlation function (TLCF) of the system as follows. The TLCF is defined by

$$R(\epsilon - \epsilon') = d^2 \left\langle \sum_{i,j} \delta(\epsilon - \epsilon_i)\delta(\epsilon' - \epsilon_j) \right\rangle. \tag{8}$$

Since this is a function only of the energy difference, $\epsilon - \epsilon'$, we may set $\epsilon' = 0$ to obtain the result

$$\begin{aligned} R(\epsilon) &= d^2 \left\langle \sum_{i,j} \delta(\epsilon - \epsilon_i)\delta(\epsilon_j) \right\rangle \\ &= d^2 \left\langle \sum_{i,j} \delta(\epsilon - \epsilon_i + \epsilon_j)\delta(\epsilon_j) \right\rangle \\ &\approx d \left\langle \sum_i \delta(\epsilon - \epsilon_i + \epsilon_0) \right\rangle . \end{aligned} \tag{9}$$

The averaged odd-gap equation can finally be written as

$$\frac{1}{\lambda} = \int_0^{\pi\omega_c/d} \frac{dx}{\sqrt{x^2 + (\pi\Delta/d)^2}} R(x), \tag{10}$$

where $x = \pi\omega/d$. Since the system has time-reversal invariance, the TLCF given by RMT is that for the orthogonal ensemble [9],

$$R(x) = 1 - \frac{\sin^2 x}{x^2} - \frac{d}{dx}\left(\frac{\sin x}{x}\right) \int_x^{\infty} dt\, \frac{\sin t}{t}, \tag{11}$$

and the average critical level spacing $\langle d_c^o \rangle$ is then the solution of

$$\frac{1}{\lambda} = \int_0^{\pi\omega_c/d} \frac{R(x)}{x}. \tag{12}$$

This integral can then be performed analytically to give

$$\langle d_c^o \rangle = \pi e^{\gamma + \pi^2/16 - 7/4} \Delta(0) = 1.80\Delta(0), \tag{13}$$

and we see that the average odd critical level spacing is a factor 2 larger than in equal level spacing model.

Next let us consider the even case. The chemical potential is now halfway between the last filled level, ϵ_0, and the first filled level, ϵ_1. It follows that the gap equation can now be written in the form

$$\frac{1}{\lambda} = d \sum_i \frac{1}{2\sqrt{(\epsilon_i - \frac{\epsilon_0 + \epsilon_1}{2})^2 + \Delta^2}}, \tag{14}$$

where the sum over i includes both ϵ_0 and ϵ_1. For ϵ_i not equal to ϵ_0 or ϵ_1, we can rewrite

$$\epsilon_i - \frac{\epsilon_0 + \epsilon_1}{2} = (\epsilon_i - \epsilon_1) + \frac{\epsilon_1 - \epsilon_0}{2}. \tag{15}$$

We know from the odd case that the distribution of the $\epsilon_i - \epsilon_1$ is described by the TLCF, $R(x)$. The distribution of the $\epsilon_1 - \epsilon_0$ is given by the nearest level spacing distribution, $P(y)$. There is no analytic expression for $P(y)$, but it is well approximated by the "Wigner surmise" [9],

$$P(y) = \frac{y}{2\pi} e^{-y^2/4\pi}, \tag{16}$$

where $y = \pi(\epsilon_1 - \epsilon_0)/d$. Let us now assume that the distributions of $\epsilon_i - \epsilon_1$ and $\epsilon_1 - \epsilon_0$ may be treated independently. The actual distribution function we need is a three-level function for ϵ_0, ϵ_1, and ϵ_i, but such a function is not discussed in the RMT literature. The equation for the critical level spacing, d_c^e, is then

$$\frac{1}{\lambda} = \int_0^\infty dy\, P(y)\,\frac{2\pi}{y} + \int_0^{\pi\omega_c/d_c^e} dx \int_0^\infty dy\,\frac{R(x)P(y)}{x + y/2}, \quad (17)$$

where the first term comes from the levels ϵ_0 and ϵ_1, which have to be treated separately, and the second term comes from all other levels. Note that if we were to replace the denominator $x + y/2$ by x in the second term we should recover the odd integral. It follows that we should evaluate the difference between the second term and the odd integral, from which we obtain the result

$$\langle d_c^e\rangle = \exp(\pi - 2I/\pi)\,\langle d_c^0\rangle, \quad (18)$$

where I is the integral

$$I = \int_0^\infty dt\, t^2 e^{-t^2\pi} \int_0^\infty \frac{1}{x(x+t)} \times \left[1 - \frac{\sin^2 x}{x^2} + \mathrm{si}(x)\,\frac{d}{dx}\left(\frac{\sin x}{x}\right)\right]. \quad (19)$$

This integral cannot be performed analytically, and has the numerical value $I \approx 1.7343$. We can therefore summarize the results for the mean critical spacings in terms of the bulk BCS gap $\Delta(0)$ or the critical spacing for equidistant levels in odd grains d_c^o by

$$\langle d_c^o\rangle = 1.80\Delta(0) \approx 2.0 d_c^o,$$
$$\langle d_c^e\rangle = 7.67\langle d_c^o\rangle \approx 15.5 d_c^o\ . \quad (20)$$

We see that the consideration of level statistics not only makes both the odd and even critical level spacings larger, it also increases the ratio between them. The reason for this is that both the individual gap equations, and the difference between the gap equations, involve the inverse of energy level spacings. The fluctuations to smaller level spacings are thus weighted more than those to larger than average level spacings, i.e., $\langle 1/\delta E\rangle > 1/\langle \delta E\rangle$.

In the analytic discussions above we have evaluated the mean value of the critical level spacing. We note that the mean is only one statistical measure of a probability distribution, and may not actually be the one we want. We would therefore like to look at the probability distributions $P_{o,e}(d)$ of there being a superconducting gap in odds and even grains with average level spacing d. We might imagine an experiment in which many grains of the same nominal size are produced and examined for the presence of a superconducting gap; the experimental results would then yield $P_{e,o}(d)$. To obtain $P_{e,o}(d)$ we proceed numerically, obtaining sets of energy levels $\{\epsilon_i\}$ by diagonalizing $N \times N$ random matrices. Since the eigenvalues produced have a semicircular density of states [9],

$$\rho(\epsilon) = \frac{1}{\pi}\sqrt{2N - \epsilon^2}\;\theta(2N - \epsilon^2), \quad (21)$$

where $\theta(x)$ is the Heaviside function, we use the rescaling

$$\epsilon \to \frac{1}{2\pi}\left[2N \sin^{-1}(\epsilon/\sqrt{2N}) + \epsilon\sqrt{2N - \epsilon^2}\right] \quad (22)$$

to obtain eigenvalues with average spacing unity [12]. From the gap equations we see that the criterion for a grain to have a nonzero superconducting gap is (all energies now in units of d)

$$\frac{1}{\lambda} < \sum_{|\epsilon_i - \mu| < \omega_c/d} \frac{1}{2|\epsilon_i - \mu|}, \quad (23)$$

where $\mu = \epsilon_0$ in the odd case, and $\mu = (\epsilon_0 + \epsilon_1)/2$ in the even case. As in the analytical calculations, d enters only in the upper cutoff ω_c/d. We choose the value $\lambda = 0.193$ corresponding to $\omega_c/d_c^o = 100$ in the equal level spacing case, and d is measured in units of this d_c^o. For d points from 0.5 to 1.0 we use 1000 realizations of 500×500 matrices; for d points from 1.0 to 4.0 we use 1000 realizations of 300×300 matrices; and for d-points from 4.0 to 20.0 we use 10 000 realizations of 100×100 matrices. We note that for larger d, where we need more realizations to get good statistics, we are fortunate in that we require smaller matrices. The results are shown in Fig. 2.

We see that for both odd and even cases there is a significant chance of superconductivity persisting beyond

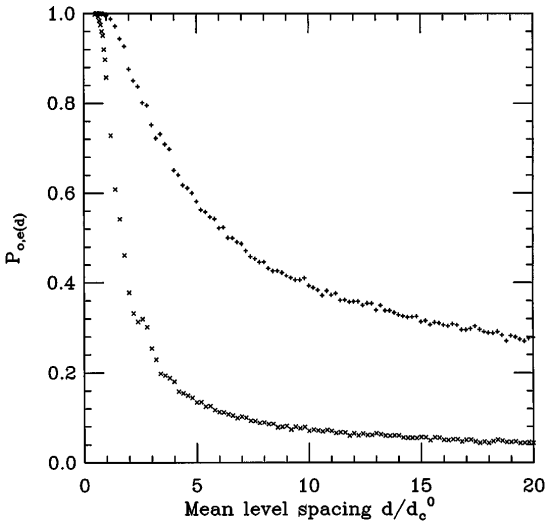

FIG. 2. The probability densities $P_{e,o}(d)$ of a metallic grain with mean level spacing d, and an even (+ symbols) or odd (× symbols) number of electrons, having a nonzero superconducting energy gap. d is measured relative to $d_c^0 = 0.89\Delta(0)$, the critical level spacing for the equidistant model with an odd number of electrons.

the critical level spacings deduced from the equal level spacing model. Both curves also show long tails which we believe are due to the nonzero probability of finding two levels very close together. These long tails make it hard to estimate the mean value of the critical spacing from the numerical data—though it is worth noting that Fig. 2 is quite consistent with the analytic results in Eq. (20). The long tails also imply that the mean is perhaps not the best measure for a typical critical spacing. If instead we use the value of d where $P(d) = 0.5$, we get about $1.7d_c^o$ for the odd case, and $6.5d_c^o$ for the even case. So, using this measure we recover a factor of order 4 between the two critical spacings.

Let us now discuss the implications of the above calculation for experiment. First let us ask the question of what the BRT experiment actually measures for the cases of even and odd grains. In both these cases, since an electron tunnels onto and then off the island, the result involves some sort of comparison between odd and even states. So do we see the odd gap, even gap, or some mixture thereof? We will always work in the zero-temperature limit, which is effectively where the experiment is performed. Consider the case of the even grain. The lowest state an electron can tunnel into is the first unoccupied level, so the energy cost should be the energy difference between ground states of the system with $2N$ and $2N + 1$ electrons. From the $T = 0$ limit of Eq. (4.9) of Ref. [4], this is given by

$$E(2N + 1) - E(2N) = \mu + \Delta . \tag{24}$$

To see which Δ is involved, note that Δ arose from formulas (2.19) of Ref. [4] which give

$$\begin{aligned}\Omega_o - \Omega_e &= \frac{1}{\beta} \ln\left(\frac{Z_+ + Z_-}{Z_+ - Z_-}\right) \\ &= \frac{1}{\beta} \ln\left(\frac{1 + (1 - 2N_{\mathrm{eff}} e^{-\beta\Delta_e})}{1 - (1 - 2N_{\mathrm{eff}} e^{-\beta\Delta_o})}\right). \end{aligned} \tag{25}$$

At zero temperature we see that it is the odd gap, Δ_o, that is measured.

For the case of an odd grain, the lowest state for the electron to go into is the singly occupied state, and we measure the energy difference

$$E(2N + 2) - E(2N + 1) = \mu - \Delta_o . \tag{26}$$

It follows that the lower branch of the odd grain curve should be the mirror image of the even grain curve, so that Δ_o appears in experiments on both even and odd grains. We note that the first excited state of an odd grain is obtained by putting the extra electron into the first unoccupied state, thus giving a state with two unpaired electrons. This should have an energy roughly 2Δ above the ground state, but the evaluation is complicated by the quasiparticles reducing the phase space for pairing correlations [13].

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