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LEVEL STATISTICS AND PARITY EFFECT ON SMALL SUPERCONDUCTING SYSTEMS*

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In this paper we have calculated the variations of the gap $\Delta'(0,d)$ and transition temperature T_c' in small metallic grains as functions of grain size (or the level spacing d between discrete electronic states) for the cases of odd and even numbers of electrons by applying the random matrix theory to the mean field theory. We find the presence of enhancement of superconductivity and critical d_c, where the superconductivity of small grains breaks down. This agrees with Anderson's prediction (1959 *J. Phys. Chem. Solids* **11** 28). We find that in the grains, as the size is lowered, the transition temperature T_c' decreases and $\Delta'(0,d)/k_BT_c' \leq \pi e^{-\gamma}$ in odd numbers of electrons, and for Gaussian orthogonal and unitary ensembles in some regimes $\Delta'(0,d)/k_BT_c' > \pi e^{-\gamma}$ in even numbers of electrons.

Keywords: superconductivity, level statistics, parity effect
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I. INTRODUCTION

Bardeen–Cooper–Schrieffer (BCS) theory is a completely successful description of superconductivity in a bulk material. Usually superconducting samples are macroscopically large and can easily exchange electrons with external lead electrodes. But this is limited when the size of the superconductor decreases to a few nanometres. Some experiments[1,2] have shown that for small superconducting islands coupled to the lead electrodes via low transparent tunnel junctions, if the effective capacitance of the islands is small, the Coulomb interaction could block electron tunnelling across these junctions and thus fix the number of electrons on the islands. The low-temperature properties of superconducting islands with a fixed number of electrons N depend on the parity of this number: for even N all electrons can be paired, whereas for odd N at least one electron remains unpaired even at zero temperature and has an extra energy equal to a superconducting energy gap Δ. Therefore, at zero temperature the energy of a superconducting island with an odd number of electrons N is larger than that with even N by Δ. Golubev *et al.*[3] and Janko *et al.*[4] have made corrections to the conventional theory in the canonical ensemble and the grand canonical ensemble respectively after considering the parity of the number of electrons N.

Recently, Black, Ralph and Tinkham (BRT)[5,6] have constructed a new single-electron transistor (SET) in which the island, a single nano-scaled Al grain, is more than four orders of magnitude smaller in volume (the estimated radii lie between 2.5 and 13nm) than that of conventional SETs. Using this SET, BRT find the existence of the superconducting gap. Both the free-electron model and the direct observation give values of d (the level spacing between discrete electronic states) ranging from 0.02 to 0.3 meV; the latter is of the order of the bulk superconducting gap ($\Delta(0) = 0.18$meV for Al). The BRT experiments seem to arouse a great enthusiasm in the theoretical community.[7–9] However, in 1959 Anderson,[10] shortly after the establishment of the BCS theory, pointed out that superconductivity would be no longer possible if the level spacing $d \sim \Delta(0)$. Anderson's argument, although essentially correct, is not yet quite complete. Later, a few experiments[11,12] have found that certain superconductors, when composed of grains of a suitable size (in the range of 5–50nm), have transition temperatures T_c appreciably higher than that of the corresponding bulk material, i.e. the so-called enhancement of superconductivity. One of the explanations for the phenomena was suggested by Parmenter.[13] But there is a divergence problem in Parmenter's paper, i.e. both T_c' and/or $\Delta'(0,d)$ always increase with the decrease of the superconductor size. This would conflict with An-

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derson's argument and common sense. Von Delft *et al.*[7] used a uniformly spaced model and obtained the curve of $\Delta'(0,d)$ versus d, but there was no enhancement in their theory at all. Smith *et al.*[8] calculated the critical level spacings d^c for both odd and even numbers of electrons in the Gaussian orthogonal ensemble (GOE), but the variation of $\Delta'(0,d)$ versus d is not clear. Others[9] have shown the enhancement, but like those of Parmenter, the curves of $\Delta'(0,d)$ versus do not converge to zero. In this paper, we apply the random matrix theory to the na¨ive mean field theory for the odd and even numbers of electrons to explain: (1) theoretically the presence of enhancement for both T_c' and $\Delta'(0,d)$ in some small metallic grains; (2) that when the size of metallic grains becomes smaller, there aret critical level spacings d_c at which the superconductivity in small metallic grains would break down, i.e. both T_c' and $\Delta'(0,d)$ become zero.

II. MODEL AND DEDUCTION

A. The self-consistent equation

We adopt a model Hamiltonian having the standard reduced BCS form

$$\hat{H}-\mu\hat{N}=\sum_j(\varepsilon_j^0-\mu)(c_{j\uparrow}^+c_{j\uparrow}+c_{j\downarrow}^+c_{j\downarrow}) - \lambda d\sum_{ij}c_{i\uparrow}^+c_{i\downarrow}c_{j\downarrow}^+c_{j\uparrow}. \quad (1)$$

Here $c_{j\uparrow}^+$ and $c_{j\downarrow}^+$ create an electron in independent states $|j\uparrow\rangle$ and $|j\downarrow\rangle$ respectively, and the states are degenerate. We choose $\lambda^{-1}=\ln(2\omega_c/\Delta(0,0))$, where λ is the dimensionless coupling constant ω_c, the cutoff frequency d, level spacings, and μ the chemical potential. At this point, the self-consistent equation for metallic grains can be written as

$$\frac{1}{\lambda}=d\sum_i\frac{1}{2}\frac{\tanh\left\{\frac{1}{2}\beta[(\varepsilon_i-\mu)^2+\Delta'(T,d)^2]^{1/2}\right\}}{\sqrt{(\varepsilon_i-\mu)^2+\Delta'(T,d)^2}}, \quad (2)$$

where $\beta=1/k_BT$, whereas $\Delta'(T,d)$ is the gap in small metallic grains.

B. Two-point correlation functions

The two-point correlation function is defined as[8]

$$R(\varepsilon-\varepsilon')=d^2\Big\langle\sum_{i,j}\delta(\varepsilon-\varepsilon_i)\delta(\varepsilon'-\varepsilon_j)\Big\rangle. \quad (3)$$

We may set $\varepsilon'=0$, then we have

$$\begin{aligned}R(\varepsilon)&=d^2\Big\langle\sum_{i,j}\delta(\varepsilon-\varepsilon_i)\delta(\varepsilon_j)\Big\rangle\\&=d^2\Big\langle\sum_{i,j}\delta(\varepsilon-(\varepsilon_i-\varepsilon_j))\delta(\varepsilon_j)\Big\rangle\\&\approx d\Big\langle\sum_i(\varepsilon-(\varepsilon_i-\varepsilon_0))\Big\rangle. \quad (4)\end{aligned}$$

According to the random matrix theory, the two-point correlation function for the GOE, the Gaussian unitary ensemble (GUE) and the Gaussian symplectic ensemble (GSE) are[14]

$$R(x)=\begin{cases}1-\dfrac{\sin^2x}{x^2}-\dfrac{\mathrm{d}}{\mathrm{d}x}\left(\dfrac{\sin x}{x}\right)\displaystyle\int_x^\infty\frac{\sin t}{t}\mathrm{d}t & \text{(GOE)}\\ 1-\dfrac{\sin^2x}{x^2} & \text{(GUE)}\\ 1-\dfrac{\sin^2x}{x^2}+\dfrac{\mathrm{d}}{\mathrm{d}x}\left(\dfrac{\sin x}{x}\right)\displaystyle\int_0^x\frac{\sin t}{t}\mathrm{d}t & \text{(GSE)}\end{cases} \quad (5)$$

where $x=\pi(\varepsilon_i-\varepsilon_0)/d$.

C. Odd case

Here the chemical potential lies on the half-filled level, ε_0. We can write Eq.(2) as

$$\begin{aligned}\frac{1}{\lambda}&=\sum_i\frac{1}{2}\frac{\tanh\left\{\frac{1}{2}\beta[\varepsilon_i-\varepsilon_0)^2+\Delta'(T,d)^2]^{1/2}\right\}}{\sqrt{(\varepsilon_i-\varepsilon_0)^2+\Delta'(T,d)^2}}\\&=\int_{-\omega_c}^{\omega_c}\frac{\mathrm{d}\sum_i\delta(\omega-(\varepsilon-\varepsilon_0))\mathrm{d}\omega}{2\sqrt{\omega^2+\Delta'(T,d)^2}}\times\tanh\left\{\frac{1}{2}\beta[\omega^2+\Delta(T,d)^2]^{1/2}\right\}\\&=\int_0^{\pi\omega_c/d_c}\frac{R(x)\mathrm{d}x}{\sqrt{x^2+(\pi\Delta'(T,d)/d)^2}}\times\tanh\left\{\frac{\mathrm{d}}{2\pi}\beta[x^2+(\pi\Delta'(T,d)/d^2]^{1/2}\right\}, \quad (6)\end{aligned}$$

where $x=\pi\omega/d$, and d_c is the critical level spacing when $\Delta'(0,d_c)=0$ and/or $T_c'=0$.

At zero temperature, where $T=0$ and $\tanh\left\{\dfrac{\mathrm{d}}{2\pi}\beta[x^2+(\pi\Delta(0,d)/d^2]^{1/2}\right\}=1$, Eq.(6) changes to

$$\frac{1}{\lambda}=\int_0^{\pi\omega_c/d_c}\frac{R(x)}{\sqrt{x^2+(\pi\Delta'(0,d)/d)^2}}\mathrm{d}x. \quad (7)$$

Solving Eq.(7), we obtain

$$\frac{\Delta(0,d)}{\Delta(0,0)}=\exp\Big[\int_0^\infty\frac{(R(x)-1)\mathrm{d}x}{\sqrt{x^2+(\pi\Delta'(0,d)/d)^2}}\Big], \tag{8}$$

The gap in the bulk samples is now expressed as $\Delta(0,0)$.

At finite temperature, when $T=T_c'$ and $\Delta'(T,d)=0$, Eq.(7) can be written as

$$\frac{1}{\lambda}=\int_0^{\pi\omega_c/d}\frac{R(x)\mathrm{d}x}{x}\tanh\Big[\frac{\mathrm{d}}{2\pi}\beta_c x\Big]. \tag{9}$$

Therefore, we obtain

$$\frac{T_c'}{T_c}=\exp\Big[\int_0^\infty\frac{(R(x)-1)\mathrm{d}x}{x}\tanh(xd/2\pi k_BT_c')\Big]. \tag{10}$$

D. Even case

In this case the chemical potential is 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

$$\begin{aligned}\frac{1}{\lambda}=&d\sum_i\frac{1}{2}\frac{\tanh\Big\{\frac{1}{2}\beta\Big[\Big(\varepsilon_i-\frac{\varepsilon_1+\varepsilon_0}{2}\Big)^2+\Delta'(T,d)^2\Big]^{1/2}\Big\}}{\sqrt{\Big(\varepsilon_i-\frac{\varepsilon_1+\varepsilon_0}{2}\Big)^2+\Delta(T,d)^2}}\\ =&d\sum_i\frac{1}{2}\frac{\tanh\Big\{\frac{1}{2}\beta\Big[\Big(\varepsilon_i-\varepsilon_1+\frac{\varepsilon_1-\varepsilon_0}{2}\Big)^2+\Delta'(T,d)^2\Big]^{1/2}\Big\}}{\sqrt{\Big(\varepsilon_i-\varepsilon_1+\frac{\varepsilon_1-\varepsilon_0}{2}\Big)^2+\Delta'(T,d)^2}}.\end{aligned} \tag{11}$$

In Eq.(11) the distribution of $\varepsilon_i-\varepsilon_1$ is described by $R(x)$, and the distribution of $\varepsilon_1-\varepsilon_0$ is given by the nearest level spacing distribution $p(y)$. According to the random matrix theory,[14]

$$p(y)=\begin{cases}\frac{1}{2}y\exp\Big(-\frac{\pi}{4}y^2\Big), & \text{(GOE)}\\ \frac{32}{\pi^4}y^2\exp\Big(-\frac{4}{\pi^3}y^2\Big), & \text{(GUE)}\\ \Big(\frac{64}{9\pi}\Big)^3\Big(\frac{y}{\pi}\Big)^4\exp\Big(-\frac{64}{9\pi^3}y^2\Big), & \text{(GSE)}\end{cases} \tag{12}$$

where $y=\pi(\varepsilon_1-\varepsilon_0)/d$. Hence Eq.(11) can now be written as

$$\begin{aligned}\frac{1}{\lambda}=&\int_0^\infty\frac{p(y)\mathrm{d}y}{\sqrt{(y/2)^2+(\pi\Delta'(T,d)/d)^2}}\tanh\Big[\frac{d}{2\pi}\beta\frac{y}{2}\Big]\\ &+\int_0^{\pi\omega_c/d}\mathrm{d}x\int_0^\infty\frac{R(x)p(y)}{\pi\sqrt{(x+y/2)^2+(\pi\Delta'(T,d)/d)^2}}\\ &\times\tanh\Big[\frac{d}{2\pi}\beta[(x+y)/2)^2+(\pi\Delta'(T,d)/d)^2]\Big\}\mathrm{d}y.\end{aligned} \tag{13}$$

At zero temperature, $T=0$ and the terms of $\tanh\{\cdots\}$, from Eq.(13) we obtain

$$\begin{aligned}\frac{1}{\lambda}=&\int_0^\infty\frac{p(y)\mathrm{d}y}{\sqrt{(y/2)^2+(\pi\Delta'(0,d)/d)^2}}\\ &+\int_0^{\pi\omega_c/d}\mathrm{d}x\int_0^\infty\frac{R(x)p(y)}{\pi\sqrt{(x+y/2)^2+(\pi\Delta'(0,d)/d)^2}}\mathrm{d}y.\end{aligned} \tag{14}$$

That is

$$\begin{aligned}\frac{\Delta'(0,d)}{\Delta(0,0)}=&\exp\Big\{\int_0^\infty\frac{p(y)}{\sqrt{(y/2)^2+\pi\Delta'(0,d)^2/d^2}}\mathrm{d}y\\ &+\int_0^\infty\mathrm{d}x\int_0^\infty\frac{[R(x)-1]p(y)\mathrm{d}y}{\pi\sqrt{(x+y/2)^2+\pi\Delta(0,d)^2/d^2}}\\ &+\int_0^\infty\int_0^\infty\frac{p(y)}{\pi}\Big\{\frac{1}{\sqrt{(x+y/2)^2+\pi^2\Delta'(0,d)^2/d^2}}\\ &-\frac{1}{\sqrt{x^2+\pi^2\Delta'(0,d)^2/d^2}}\Big\}\mathrm{d}x\mathrm{d}y\Big\}.\end{aligned} \tag{15}$$

At a finite temperature, when $T=T_c'$, $\Delta'(T,d)=0$.

From Eq.(13), we obtain

$$\frac{1}{\lambda} = \int_0^{\infty} \frac{p(y)}{y/2} \tanh\left[\frac{d}{2\pi}\beta_c \frac{y}{2}\right] \mathrm{d}y + \int_0^{\pi\omega_c/d} \mathrm{d}x \int_0^{\infty} \frac{R(x)p(y)}{\pi(x+y/2)} \times \tanh\left[\frac{d}{2\pi}\beta_c(x+y/2)\right] \mathrm{d}y. \tag{16}$$

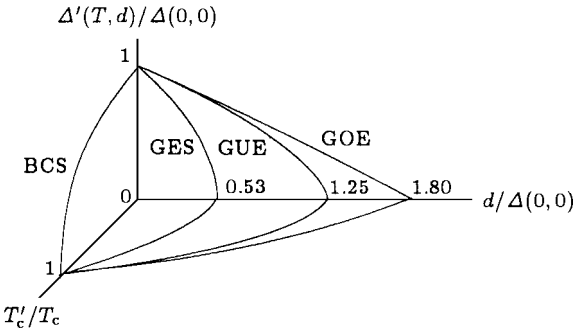


Fig.1. The granular gap $\Delta'(T,d)$ and the transition temperature T_c' decrease with d for an odd number of electrons.

The solution of Eq.(16) is

$$\frac{T_c'}{T_c} = \exp\left\{ \int_0^{\infty} \frac{p(y)}{y/2} \tanh\left(\frac{\mathrm{d}}{2\pi}\beta_c \frac{y}{2}\right) \mathrm{d}y + \int_0^{\infty}\int_0^{\infty} \frac{[R(x)-1]p(y)}{\pi(x+y/2)} \times \tanh\left[\frac{d}{2\pi}\beta_c(x+y/2)\right] \mathrm{d}x\mathrm{d}y + \int_0^{\infty}\int_0^{\infty} \frac{p(y)}{\pi}\left[\frac{\tanh\left[\frac{(x+y/2)d}{2\pi}\beta_c\right]}{x+y/2} - \frac{\tanh\left[\frac{xd}{2\pi}\beta_c\right]}{x}\right] \mathrm{d}x\mathrm{d}y \right\}. \tag{17}$$

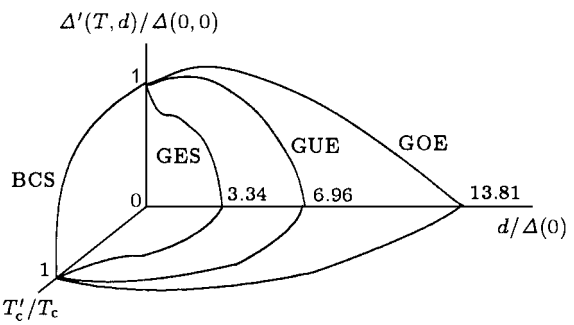


Fig.2. The granular gap $\Delta'(T,d)$ and the transition temperature T_c' decrease with d for an even number of electrons.

Ⅲ. ANALYSIS AND CONCLUSION

At first, we solve Eqs.(8) and (10) numerically and plot them in Fig.1, from which we can see that the superconductivity (both $\Delta'(0,d)$ and T_c') of metallic grains decreases with d monotonically, and finally vanishes at some critical level spacings d_c for the cases of GOE, GUE and GSE. For light metallic elements (governed by GOE),[15] for example Al, the superconductivity breaks down later than for heavy elements as the level spacings become broadened. For heavy metallic grains, the external magnetic field would improve the superconductivity so that the curves for the GUE in Fig.1 decline later than those for GSE. After a cumbersome analysis of the data in Fig.1, we find that in the regime of $d < 0.2\Delta(0)$, we have $\Delta'(0,d)/k_BT_c' \approx \pi \mathrm{e}^{-\gamma}$, and when $d > 0.2\Delta(0)$, we obtain $\Delta'(0,d)/k_BT_c' \leq \pi \mathrm{e}^{-\gamma}$. Here γ is the Euler constant.

Now we consider an even number of electrons. The numerical solutions of Eqs.(15) and (17) are plotted in Fig.2, from which one can see that both $\Delta'(0,d)$ and T_c' of metallic grains decrease with d no longer monotonically but vanish finally at some critical level spacings d_c respectively for GOE, GUE and GSE. In GOE, the transition temperature T_c' and energy gap $\Delta'(0,d)$ increase first, then decrease after reaching the top at $3.6\Delta(0,0)$ for T_c', and $2.7\Delta(0,0)$ for $\Delta'(0,d)$, and finally vanish at $d_c = 13.81\Delta(0,0)$. The increment is 17% for T_c' and 14% for $\Delta'(0,d)$, and $\Delta'(0,d)/k_BT_c' \leq \pi \mathrm{e}^{-\gamma}$ always exists. In GUE, both T_c' and $\Delta'(0,d)$ vanish at $d_c = 6.96\Delta(0,0)$ and when $d < 1.7\Delta(0,0)$, we have $\Delta'(0,d)/k_BT_c' > \pi \mathrm{e}^{-\gamma}$, and when $d > 1.7\Delta(0,0)$, we have $\Delta'(0,d)/k_BT_c' \leq \pi \mathrm{e}^{-\gamma}$. But the increment reduces to about 8% for T_c' and 6% for $\Delta'(0,d)$. As for GSE, T_c' and $\Delta'(0,d)$ vanish at $d_c = 3.34\Delta(0,0)$, and they never increase with d but have two points of inflection. Also, in the regime of $d \sim 0.6 - 1.7\Delta(0,0)$, there is $\Delta(0,d)/k_BT_c' > \pi \mathrm{e}^{-\gamma}$. We know that the GSE corresponds to the weak external magnetic field and GUE to the strong external magnetic field.[16] As a result, to some extent, external

magnetic fields may cause the enhancement of superconductivity.

From the above, one can conclude that there is (1) an enhancement in superconductivity for small metallic grains, especially small Al grains, and (2) the critical size (or critical level spacing d_c) at which superconductivity breaks down. Also, all the critical level spacings d_c for GOE, GUE and GSE, both in odd and even cases, are in good agreement with those in Ref.[17].

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