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Mihail D. Croitoru, A. A. Shanenko, C. Kaun C., F. M. Peeters. Ultra-small metallic grains: effect of statistical fluctuations of the chemical potential on superconducting correlations and vice versa. *Journal of Physics: Condensed Matter*, 2012, 24 (27), pp.245701. 10.1088/0953-8984/24/27/275701 . hal-00732015

**HAL Id: hal-00732015**

**<https://hal.science/hal-00732015>**

Submitted on 28 Aug 2018

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# Ultra-small metallic grains: effect of statistical fluctuations of the chemical potential on superconducting correlations and vice versa

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## Abstract

Superconducting correlations in an isolated metallic grain are governed by the interplay between two energy scales: the mean level spacing  $\delta$  and the bulk pairing gap  $\Delta_0$ , which are strongly influenced by the position of the chemical potential with respect to the closest single-electron level. In turn superconducting correlations affect the position of the chemical potential. Within the parity projected BCS model we investigate the probability distribution of the chemical potential in a superconducting grain with randomly distributed single-electron levels. Taking into account statistical fluctuations of the chemical potential due to the pairing interaction, we find that such fluctuations have a significant impact on the critical level spacing  $\delta_c$  at which the superconducting correlations cease: the critical ratio  $\delta_c/\Delta_0$  at which superconductivity disappears is found to be increased.

(Some figures may appear in colour only in the online journal)

## 1. Introduction

In the past two decades quasi-low-dimensional superconductor systems have become a very active field of research due to their rich variety of physical properties and potential applications, which are superior to their three-dimensional homogeneous counterparts [1–15]. The technological advances in fabricating and controlling material structures of nanoscale size provided a whole range of opportunities for exploring experimentally these physical properties, induced by quantum confinement [16–27]. Quantum confinement results in the discretization of the electronic energy bands and its competition with the pairing correlations produces a nonuniform spatial distribution of the superconducting order parameter.

The discreteness of the single-particle energy levels due to electron confinement plays a fundamental role in the description of the superconducting state in a metallic

grain. A reduction of grain size leads to an increase of the spacing between the levels. Back in 1959, Anderson argued that when the average level spacing  $\delta$ , which is inversely proportional to the density of states at the Fermi level and the grain volume, becomes of the order of the BCS bulk gap  $\Delta_0$  then superconductivity should disappear [28]. Since the celebrated experiments by Ralph, Black, and Tinkham [16, 17] on Al superconducting grains, several groups have reported the fabrication of different metallic superconducting nanoparticles, some of them with crystalline perfection [18, 21, 25, 26]. Experiments have demonstrated clear signatures of superconducting pairing up to  $\delta \sim \Delta_0$ , whereas no such correlations survived for  $\delta \gg \Delta_0$ . This stimulated several theoretical investigations on the critical level spacing in nanograins at which superconducting correlations cease [1, 2, 29].

A mean-field model of a superconducting grain with equidistant energy levels was considered by von Delft

*et al* [1]. This model takes into account number-parity effects, which are of particular importance in small grains. They found that the superconducting gap vanishes abruptly at a certain critical value of the level spacing  $\delta_c$ , which depends on the parity-number of electrons in the grain, namely,  $\delta_c^o = 0.89\Delta_0$  in grains with an odd number of confined electrons, and  $\delta_c^e = 3.56\Delta_0$  in grains with an even number of electrons. Smith and Ambegaokar [2] extended the Delft's mean-field treatment of superconductivity in such small grains by taking into account the Wigner–Dyson distribution of energy levels as obtained within random matrix theory [30]. They found that for both odd and even cases randomness enhances pairing and that superconductivity persists beyond the critical level spacing as deduced from the equal level spacing model. It turns out that the critical level spacings at which pairing vanishes abruptly are increased to  $\delta_c^o = 1.80\Delta_0$  for an odd number of electrons, and  $\delta_c^e = 13.81\Delta_0$  for an even number of electrons. The treatments beyond the mean-field approximation [5–7] have shown that superconducting pairing persists beyond the critical level spacing, but only in the form of fluctuations, and the crossover between regimes of conventional and fluctuation-dominated superconductivity is smoothed out [5, 6].

In both mean-field models the chemical potential was chosen to lie halfway between the last filled and first empty levels for an even number of electrons (the even case), and on the half-filled level for an odd number of electrons (the odd case), which is a typical situation in a nanoparticle, when electron–electron correlation is neglected. However, the position of the chemical potential is of importance because the density of states in the vicinity of  $\mu$  strongly influences the superconducting correlations, and hence the final conclusion on the critical level spacing. The position of the chemical potential in its turn is affected by the correlations. To our knowledge, a thorough investigation of the influence of the superconducting pair correlations in a nanograin on the position of the chemical potential has not been reported in the literature.

Since in the most experiments only the average behavior of a large number of grains is obtained, the aim of the present paper is to study a statistical distribution of the chemical potential around its position, which it has in the absence of electron–electron correlations (henceforth,  $\mu_0$ -position). As an example, we extend the mean-field model, developed in [2], by weakening the  $\mu_0$  condition, and study how this effect can ostensibly modify the critical level spacing.

The layout of our paper is as follows. In section 2, we investigate the statistical distribution of the chemical potential induced by the pair correlations in a superconducting nanograin. In section 3, we show how the grain critical level spacing is affected by the statistical distribution of  $\mu$ . Finally, a short summary is given in section 4.

## 2. Grain size dependence of the chemical potential distribution

We describe the grain by the following reduced BCS Hamiltonian, where only the time-reversal states are paired

$$\hat{H} = \sum_{p,\sigma} \varepsilon_p a_{p,\sigma}^\dagger a_{p,\sigma} - \sum_{p,q} V_{p,q} a_{p\uparrow}^\dagger a_{p\downarrow}^\dagger a_{q\downarrow} a_{q\uparrow}. \quad (1)$$

Here  $p, q$  are integers numbering the single-particle energy levels  $\varepsilon_p$  and the operator  $a_{p,\sigma}$  ( $a_{p,\sigma}^\dagger$ ) annihilates (creates) an electron in state  $p$  with spin  $\sigma$ . The interaction matrix element  $V_{qp}$  is given by

$$V_{qp} = g \int d^3r |\varphi_q(\mathbf{r})|^2 |\varphi_p(\mathbf{r})|^2, \quad (2)$$

with  $g$  denoting the coupling constant and  $\varphi_q(\mathbf{r})$  the single-electron wavefunction. The first term in equation (1) contains the single-electron energies, and the second term is the attractive (when  $g > 0$ ) pairing interaction due to the exchange of virtual phonons. We have assumed that the electron–electron interaction is unaffected by quantum confinement and it is the same as in the bulk. In the bulk the real inter-electron potential is well approximated by a  $\delta$ -function pseudopotential. Employing such a simplified interaction requires a regularization, which makes the matrix elements non-zero only between states within the Debye window around the Fermi surface.

For a given value of the chemical potential the parity projected BCS self-consistency equation is [15, 31]

$$\Delta_q^\eta = \sum_{|\varepsilon_p - \mu| < \hbar\omega_D} V_{qp} \frac{\Delta_p^\eta}{2E_p} t_p \left[ 1 - \frac{\eta R_\pi t_q^{-2} (1 - t_p^{-2})}{1 + \eta R_\pi t_q^{-2}} \right], \quad (3)$$

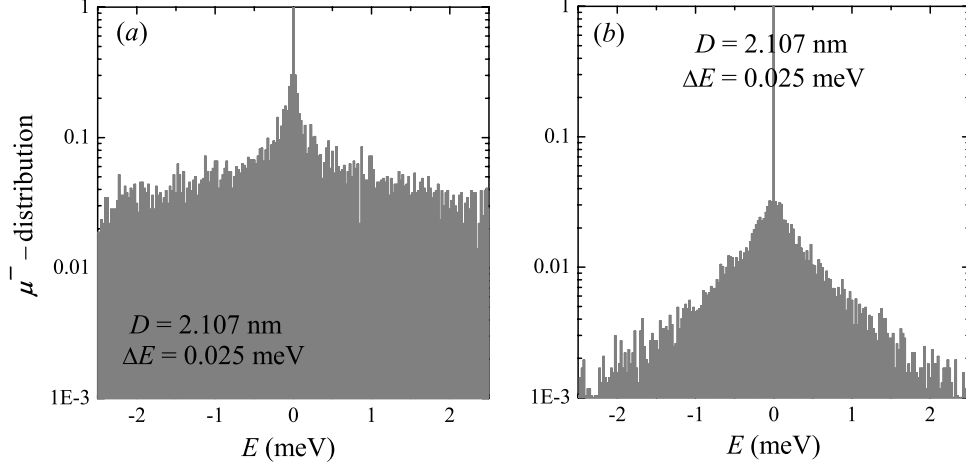
where  $t_p = \tanh(\beta E_p/2)$  with  $E_p$  the quasi-particle energy, which is given by a complicated expression but is well approximated by  $E_p = [(\varepsilon_p - \mu)^2 + |\Delta_p|^2]^{1/2}$ ,  $R_\pi/2 \equiv \prod_p t_p$  and  $\eta$  is the parity index ( $\eta = -1, 1$  for the odd and even cases, respectively).

For a given number  $N_e$  of electrons in the grain the chemical potential  $\mu$  is determined from equation

$$N_e = \sum_p f_p \left( 1 - \frac{\xi_p}{E_p} \right) + (1 - f_p) \left( 1 + \frac{\xi_p}{E_p} \right), \quad (4)$$

with  $\xi_p = (\varepsilon_p - \mu)$  and  $f_p = (1 - t_p)/2$ . The coupled set of equations (3) and (4) were solved numerically by iterations until full self-consistency was reached. At the first iteration the value of the chemical potential in the absence of superconducting correlations is taken.

Numerical calculations were performed with parameters typically for Sn, namely,  $\hbar\omega_D/k_B = 195$  K and  $gN(0) = 0.25$ , with  $N(0)$  the bulk density of states at the Fermi level, and we used the bulk electron density  $n_e = 148 \text{ nm}^{-3}$ . In the rest of the paper we consider a nearly cubic grain with  $L_x = D + a + v_1$ ,  $L_y = D - a + v_2$  and  $L_z = D + b$ , while varying the thickness of the grain  $D$ . Here  $a = 0.2$  nm;  $v_1, v_2$  are the random deviates with a normal (Gaussian) distribution used to generate a large sample of single-electron level configurations in a grain. The standard deviation for the normal distribution was chosen to be 0.1 nm.  $b$  is fixed to a value that keeps the volume of the grain constant for given  $D$  constant, i.e.  $b = (D + a)(D - a)D/L_x L_y$ . Parallelepiped-shaped grains were taken in order to avoid strong degeneracy of the single-electron levels typical for the highly symmetric samples. The single-electron wavefunction



**Figure 1.** The chemical potential probability distribution for a superconducting Sn ensemble of grains with thickness  $D = 2.107$  nm: (a) without Soloviev blocking; (b) with Soloviev blocking.

in such a grain reads

$$\varphi_p(x, y, z) = \prod_{l=x,y,z} \sqrt{\frac{2}{L_l}} \sin \left[ \pi j_l \frac{r_l}{L_l} \right], \quad (5)$$

where  $p = \{j_x j_y j_z\}$ . In this case the interaction matrix element, equation (2), acquires the form

$$V_{qp} = g \prod_{l=x,y,z} v_{q_l, p_l}, \quad (6)$$

where

$$v_{q_l, p_l} = \begin{cases} \frac{3}{2L_l}, & \text{if } q_l = p_l, \\ \frac{1}{L_l}, & \text{if } q_l \neq p_l. \end{cases} \quad (7)$$

The odd- $N$  BCS solution with lowest energy assigns a specific role to the twofold-degenerate individual level whose energy  $\varepsilon_p$  is closest to the chemical potential  $\mu$ . Throughout this paper, any quantity pertaining to this level is labeled by the index  $p = 0$ , and the level with second smallest quasi-particle energy is denoted by the index  $p = 1$ . For zero temperature,  $q \neq 0$  and  $\eta = -1$ , equation (3) is simplified to

$$\Delta_{q \neq 0} = \sum_{p(p \neq 0)} V_{qp} \frac{\Delta_p}{2E_p}, \quad (8)$$

and (for  $q = 0$ )

$$\Delta_{q=0} = \sum_{p(p \neq 0, 1)} V_{0,p} \frac{\Delta_p}{2E_p}. \quad (9)$$

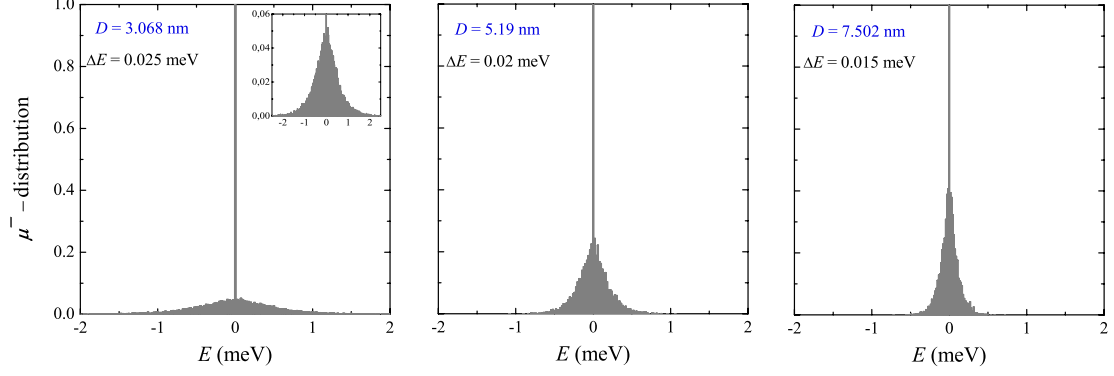
For convenience, we no longer mention explicitly that only single-electron states with  $|\varepsilon_p - \mu| < \hbar\omega_D$  are taken into account; i.e., the odd-ground state is obtained by creating a  $p = 0$  quasi-particle above the BCS vacuum. The only formal difference between equation (8) and the usual BCS model is the suppression of the term with  $p = 0$ . Nevertheless, this difference may lead to a significant decrease of the pairing [1, 31],

because the  $p = 0$  quasi-particle prohibits Cooper pair scattering involving  $p = 0$ . In nuclear physics, the above approximation is usually referred to as the blocking (Soloviev) approximation [32].

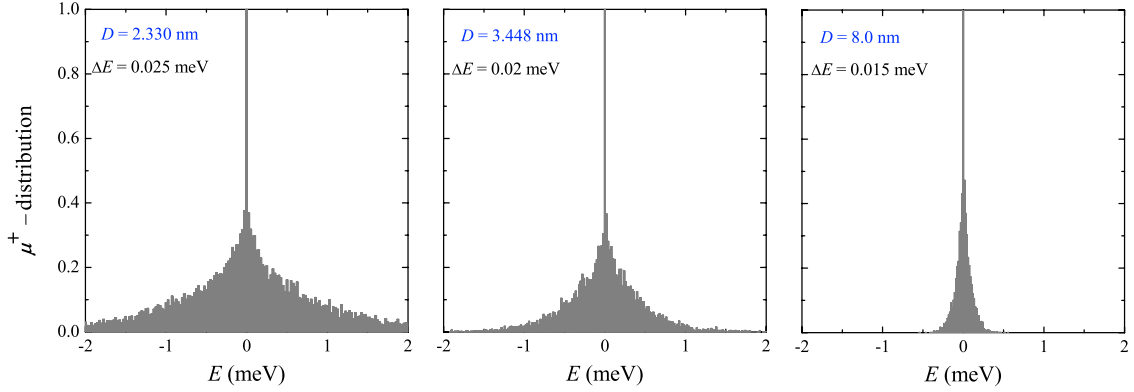
The gap  $\Delta_{q=0}$  does not enter in equation (8), which determines all the other gaps at sufficiently low temperatures. However, the presence of such a gap associated with the blocked level allows one to relax the requirement of  $\mu = \mu_0 = \varepsilon_0$  for the odd case [33]. We can expect that  $\mu - \varepsilon_0$  can be of the order of  $\Delta_{q=0} \sim \Delta_0$ . Indeed, this is seen from our numerical simulations.

Figures 1(a) and (b) show the probability distribution of the chemical potential in odd grains with  $D = 2.107$  nm without and with the blocking effect, respectively. The numerical simulations were performed with  $N = 2.0 \times 10^4$  energy level configurations and with energy steps  $\Delta E = 0.025$  meV (the number of discrete nodes for sampling the energy space is 200). The distribution is scaled by its maximum value. In the absence of superconducting correlations in the grains all single-electron level configurations result in a chemical potential pinned to the half-filled level  $\mu = \varepsilon_0$  for an odd number of electrons. The zero energy in the figure is the position of this level,  $\mu_0 = 0$ . One can see from figure 1(a) that switching on the inter-electron correlations leads to a chemical potential probability distribution that is different from the  $\delta(\mu - \mu_0)$ -function. However, as seen from figure 1(b), the blocking of the  $p = 0$  level weakens the effect of the redistribution of the chemical potential around  $\mu_0$  by weakening the pair correlations. It has a very sharp peak in the very vicinity of its average value (for  $|E| = |\mu - \mu_0| < \Delta E$ ). Nevertheless, for this particular case of  $D = 2.107$ , 66.5% of the configurations resulted in a chemical potential in the range  $|\mu - \mu_0| > \Delta E$ .

Figures 2(a)–(c) illustrate the probability distribution of the chemical potential in odd grains with thicknesses  $D = 3.068$ , 5.190, and 7.5 nm. The inset in the upper panel is a zoom of the lower part of the probability distribution for  $D = 3.068$  nm. It is seen that an increase of the grain size leads to a decrease of the distribution width and at the same time



**Figure 2.** The chemical potential probability distribution for a superconducting Sn ensemble of odd grains with thicknesses (a)  $D = 3.068$  nm; (b)  $D = 5.190$  nm; (c)  $D = 7.5$  nm.



**Figure 3.** The chemical potential probability distribution for a superconducting Sn ensemble of even grains with thickness (a)  $D = 2.330$  nm; (b)  $D = 3.448$  nm; (c)  $D = 8.0$  nm.

to a decrease of the relative height of the central peak in the probability distribution. For large grains the redistribution of the chemical potential due to the pair correlation is negligible and when calculating superconducting characteristics for the chemical potential one can use its value for the grain without correlation as an acceptable approximation. The reason is that in this case there are a lot of single-electron levels in the Debye window, which allows the system to conserve the particle-hole symmetry without a large perturbation of the chemical potential position.

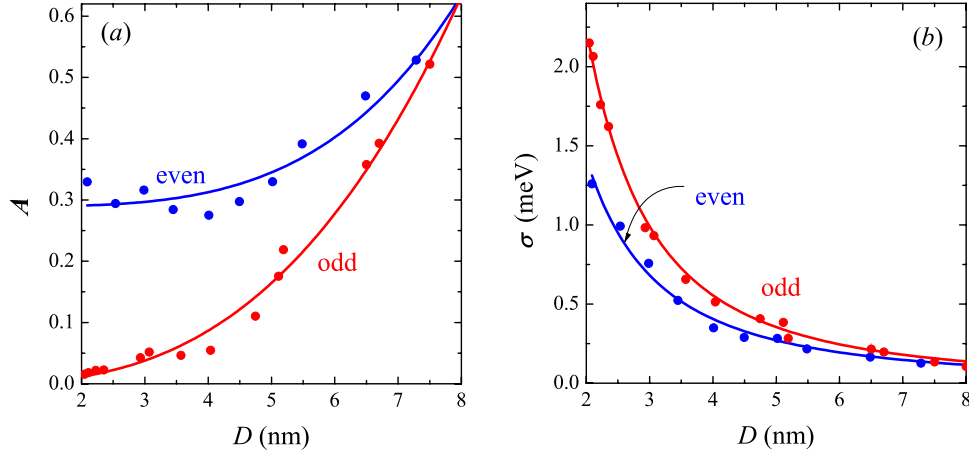
Figures 3(a)–(c) illustrate the probability distribution of the chemical potential in the even grain case with thicknesses  $D = 2.33$ ,  $3.448$ , and  $8.0$  nm. The behavior of the probability distribution is the same as in the odd case. The only noticeable difference is that the height of the redistribution does not approach zero when reducing the width of the sample (at least for the given range of the grain thicknesses).

To investigate the size dependence of the probability redistribution more qualitatively we fit part of the distribution, from which the central peak is removed, by a Gaussian function of the form

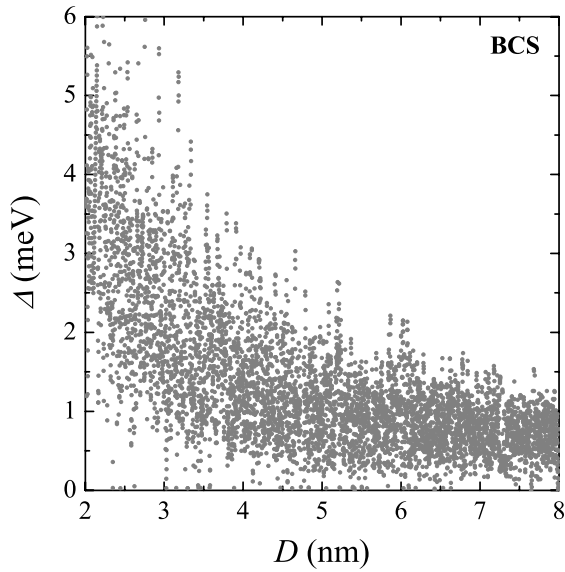
$$G(\mu, \sigma) = \frac{B}{\sigma \sqrt{\frac{\pi}{2}}} e^{-\left(\frac{\mu - \mu_0}{\sigma}\right)^2}. \quad (10)$$

Then the evolution of the chemical potential distribution with grain thickness can be represented with the found dependence of the fitting parameters  $\sigma$  and  $B$  on the grain thickness. The result is shown in figures 4(a) and (b). The upper panel here illustrates the relative height of the Gauss distribution (the height  $A = \frac{B}{\sigma \sqrt{\frac{\pi}{2}}}$  is normalized by the height of the central peak in the original distribution). The curve is obtained by fitting our numerical results with the function  $y = a + bx^c$ , with  $a = 0.0$ ,  $b = 0.005$  and  $c = 2.3$  in the odd case and with  $a = 0.28$ ,  $b = 6.6 \times 10^{-4}$  and  $c = 2.8$  in the even case. The lower panel shows the standard deviation  $\sigma$  as a function of the grain size. The results were fitted by the curves with:  $a = 0.0$ ,  $b = 9$  and  $c = -2$  (odd case),  $a = 0.0$ ,  $b = 4.9$  and  $c = -1.8$  (even case).

The dependence of the standard deviation of the Gauss distribution of the part of the original distribution is strongly correlated with the strength of the pair correlation, which is described by the mean value of the superconducting order parameter. This is seen from figure 5, where the order parameter as a function of the grain thickness is shown [15]. To plot this figure we performed calculations for a parallelepiped-shaped grain with  $L_x = D + a$ ,  $L_y = D - a$  and  $L_z = D$ , while varying the thickness of the grain  $D$ . Comparing this figure with the lower panel of figure 4 we can see that for  $D < 6$ – $8$  nm the average of the order parameter is approximately equals to  $2\sigma$ .



**Figure 4.** The relative height (panel (a)) and the standard deviation (panel (b)) of the normal distribution as a function of the grain size  $D$ .



**Figure 5.** The mean value of the superconducting order parameter versus the grain thickness  $D$ .

### 3. Critical level spacing

Let us now investigate the possible consequences of the chemical potential distribution on the critical level spacing in the superconducting grains.

*The odd case* ( $\eta = -1$ ): for the purpose of simplicity in the rest of our work we assume that quantum confinement does not modify the matrix elements  $V_{qp}$ , i.e. we disregard the spatial variations of the order parameter [9, 10], and  $V_{qp}$ 's are taken the same as in the bulk, namely  $V_{qp} = \frac{g}{V} = \lambda\delta$ , with  $\lambda$  the dimensionless coupling. This assumption results in  $\Delta_p(\delta, T) = \Delta(\delta, T)$ . Now, keeping this in mind and using equation (8), for  $k_B T/\Delta_0 \ll 1$  we obtain

$$1 = \lambda \delta \sum_{p(p \neq 0)} \frac{t_p}{2E_p}. \quad (11)$$

Adding and subtracting the energy  $\varepsilon_0$  of the single-electron level  $p = 0$ , which is closest to the chemical potential  $\mu$ , we

obtain

$$1 = \frac{\lambda \delta}{2} \int_{-\hbar\omega_D}^{\hbar\omega_D} d\omega \frac{t_\omega \sum_{p \neq 0} \delta(\omega - \varepsilon_p + \varepsilon_0)}{\sqrt{(\omega + \varepsilon_0 - \mu)^2 + |\Delta(\delta, T)|^2}}. \quad (12)$$

The position of the electron energy levels in a grain strongly depends on the boundary conditions and the interaction of the electrons inside a grain. However, disorder related to irregularities of the shape of individual grains, or internal defects inside a grain, plus the interaction with charged impurities in the insulating substrate, make a calculation of the energy levels a daunting task. To overcome this difficulty one usually performs a statistical description of the grain characteristics, instead of calculating the precise position of the energy levels in a specific dot. In this case the energy spectrum is characterized by the mean level spacing and by the level fluctuations [30, 34].

Thus we average equation (12) over disorder and shape irregularities

$$1 = \frac{\lambda}{2} \int_{-\hbar\omega_D}^{\hbar\omega_D} d\omega \frac{t_\omega R(\omega \frac{\pi}{\delta})}{\sqrt{(\omega + \varepsilon_0 - \mu)^2 + |\Delta(\delta, T)|^2}}, \quad (13)$$

where we introduce

$$R(\varepsilon)/\delta = \left\langle \sum_p \delta(\varepsilon - (\varepsilon_p - \varepsilon_0)) \right\rangle. \quad (14)$$

As shown in [2], this average can be related to the two-level correlation function (TLCF), describing the level fluctuations in the system. Since we consider the system without magnetic or spin-orbit interactions, which possess time-reversal and spin-rotation invariance, the TLCF given by RMT is that for a Gaussian orthogonal ensemble [30]

$$R(x) = 1 - \frac{\sin^2 x}{x^2} - \frac{d}{dx} \left( \frac{\sin x}{x} \right) \int_x^\infty dt \frac{\sin t}{t}. \quad (15)$$

Inserting equation (15) into (13), we arrive at the basic equation of the Smith-Ambegaokar model [2].

In the next step, we treat the position of the chemical potential statistically as was discussed in section 2<sup>4</sup>. As follows from that discussion, we have to model the statistical distribution of the chemical potential as the sum of two functions: one describing the central peak and another one for the redistributed part. However, since we are only interested in qualitative effects due to the redistribution of the chemical potential, we will neglect the central peak and approximate the redistribution part by the Gaussian function. Our approximation will result into an upper limit for the critical level spacing. The opposite situation, when we take into account only the central peak, leads to the Smith–Ambegaokar model.

So, the chemical potential is taken normally distributed around  $\varepsilon_0$ . In addition, we assume that  $(\varepsilon_p - \varepsilon_0)$  and  $(\varepsilon_0 - \mu)$  are independent random variables. Then, we obtain

$$1 = \lambda \int_0^{\hbar\omega_D} d\omega R\left(\frac{\pi\omega}{\delta}\right) \times \int_{-\infty}^{\infty} dy \frac{t_\omega G(y, \sigma)}{\sqrt{(\omega + y)^2 + |\Delta(\delta, T)|^2}}, \quad (16)$$

where  $G(y, \sigma)$  is the Gaussian distribution function of the chemical potential given by equation (10).

The critical level spacing  $\delta_c^0$  for the odd case is defined as the solution of equation (16) in the limit  $\Delta(\delta, T) \rightarrow 0$ , thus

$$\ln\left(\frac{2\hbar\omega_D}{\Delta_0}\right) = \int_0^{\pi\hbar\omega_D/\delta_c^0} dx R(x) \int_{-\infty}^{\infty} dy \frac{t_{x,y} G(y, \sigma)}{|x + \pi y/\delta_c^0|}, \quad (17)$$

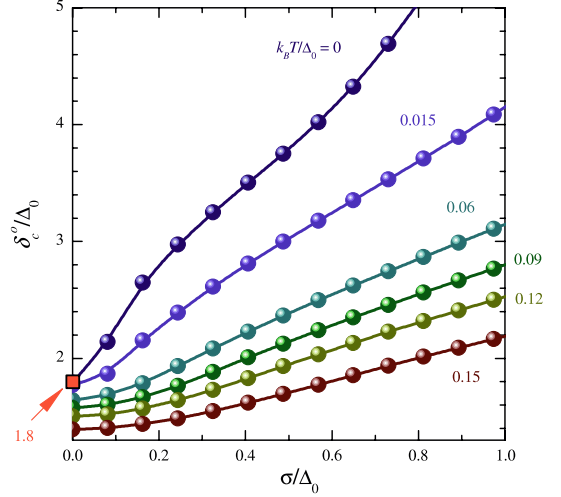
where we introduce the new variable  $x = \pi\omega/\delta$  and take into account that  $\lambda^{-1} = \ln(2\hbar\omega_D/\Delta_0)$  with  $\Delta_0 = \Delta(0, 0)$ . Here  $t_{x,y} = \tanh\left(\frac{\delta_c^0}{2\pi}\beta|x + \pi y/\delta_c^0|\right)$ . Equation (17) can only be solved numerically. When neglecting fluctuations of the chemical potential, i.e.,  $G(y, \sigma = 0) = \delta(y)$ , this equation reduces to (at  $T = 0$ )

$$\ln\left(\frac{2\hbar\omega_D}{\Delta_0}\right) = \int_0^{\pi\hbar\omega_D/\tilde{\delta}_c^0} dx \frac{R(x)}{x}. \quad (18)$$

This can be solved analytically resulting in the odd-case result of Smith and Ambegaokar [2], i.e.,  $\tilde{\delta}_c^0 = \pi e^{\gamma + \pi^2/16 - 7/4} \Delta_0 \approx 1.8\Delta_0$ , with  $\gamma$  the Euler constant.

The integrations in equation (17) are done numerically, from which we obtain the critical level spacing as  $\delta_c^0 = \delta_c^0(\sigma, T)$ . Figure 6 illustrates how the critical level spacing  $\delta_c^0$  depends on the standard deviation for the distribution of the chemical potential. The mean value of the chemical potential in the odd case is the energy of the half-filled level  $\varepsilon_0$ . Since,

<sup>4</sup> The physics behind this is as follows. The distribution of energy levels is a function of a certain number of statistical variables. Since the quasiparticle energy is defined according to the expression  $E_p = [(\varepsilon_p - \mu)^2 + |\Delta_p|^2]^{1/2}$ , the distribution of the chemical potential  $\mu$  is a function of the same statistical variables (levels) plus an additional variable due to the order parameter. This additional variable is a function of the statistics of the system wavefunctions. In the GOA ensemble the statistics of the levels is independent of the statistics of the wavefunctions [35].



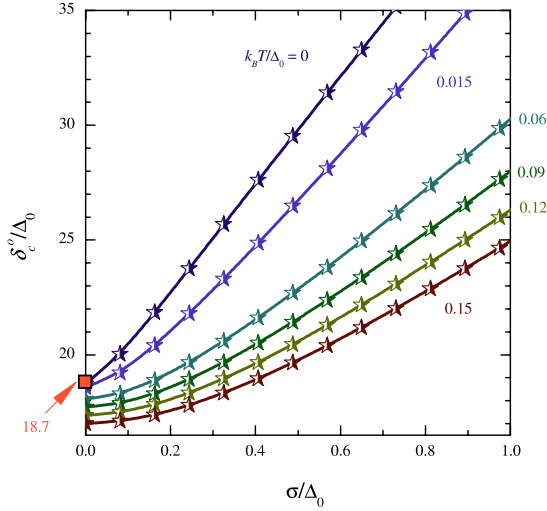
**Figure 6.** The odd case: the critical level spacing  $\delta_c^0$  versus the standard deviation  $\sigma$  of the chemical potential for different temperatures ranging from  $k_B T/\Delta_0 = 0$  to 0.15.

as it was shown in section 2, the deviation of the chemical potential from  $\varepsilon_0$  is due to electron correlations (for  $T \rightarrow 0$ ) characterized by  $\Delta$ , the standard deviation in this figure is normalized by  $\Delta_0$ . Note that fluctuations in the position of the chemical potential significantly enhance the critical level spacing, i.e., the regime of conventional superconductivity can persist in samples with smaller sizes. This effect can be explained as follows. The pair correlations are different from zero within a finite energy range around the chemical potential  $\mu$ , and are strongest exactly at  $\mu$  [31]. However, the unpaired particle which occupies the level  $\varepsilon_0$  forbids the formation of the pair state  $(\bar{0}, 0)$ , with  $\bar{0}$  the time-reversed counterpart. Consequently, when the chemical potential is pinned to the level  $\varepsilon_0$  we obtain the strongest decrease of the pairing correlations in the system. The redistribution of the chemical potential frees up phase space for the strongest pair scattering and so achieves a gain in interaction energy, and hence in the critical level spacing. This effect is suppressed by temperature because temperature diminishes the effect of Soloviev blocking. At finite- $T$  the peak in the pairing correlations at the chemical potential level diminishes and, hence, the effect of the redistribution of the chemical potential is weakened for increasing  $T$ .

*The even case ( $\eta = +1$ ):* the chemical potential is now distributed around the energy being halfway between the last filled level  $\varepsilon_0$  and the first empty level  $\varepsilon_1$ . The equation for the critical level spacing can be obtained as follows. We start with the chemical potential residing exactly at  $\mu_0 = (\varepsilon_0 + \varepsilon_1)/2$ , which yields

$$1 = \lambda\delta \sum_p \frac{t_p}{2\sqrt{(\varepsilon_p - \mu_0 + \mu_0 - \mu)^2 + |\Delta(\delta, T)|^2}}. \quad (19)$$

Then, for  $\varepsilon_p \neq \varepsilon_0$  and  $\varepsilon_p \neq \varepsilon_1$  we can write  $\varepsilon_p - \mu_0 = (\varepsilon_p - \varepsilon_1) + (\varepsilon_1 - \varepsilon_0)/2$ . Following similar arguments as for



**Figure 7.** The even case: the critical level spacing  $\delta_c^e$  versus  $\sigma$  for different temperatures from  $k_B T/\Delta_0 = 0$  to 0.15.

the odd case we found

$$\begin{aligned} \frac{1}{\lambda} = & \int_0^{\omega_D} d\omega \int_{-\infty}^{\infty} dz \frac{t_\omega R(\omega \frac{\pi}{d}) G(z, \sigma)}{\sqrt{(\omega + \frac{\varepsilon_1 - \varepsilon_0}{2} + z)^2 + |\Delta(\delta, T)|^2}} \\ & + \int_{-\infty}^{\infty} dz \frac{t_\omega G(z, \sigma)}{\sqrt{(\frac{\varepsilon_1 - \varepsilon_0}{2} + z)^2 + |\Delta(\delta, T)|^2}} \\ & + \int_{-\infty}^{\infty} dz \frac{t_\omega G(z, \sigma)}{\sqrt{(\frac{\varepsilon_0 - \varepsilon_1}{2} + z)^2 + |\Delta(\delta, T)|^2}}. \end{aligned}$$

The distribution of  $(\varepsilon_1 - \varepsilon_0)$  is given by the nearest level spacing distribution,  $P(y)$ . This distribution is well approximated by the ‘Wigner surmise’ expression [30]

$$P(y) = \frac{y}{2\pi} \exp\left(-\frac{y^2}{4\pi}\right), \quad (20)$$

where  $y = \pi(\varepsilon_1 - \varepsilon_0)/d$ . Assuming now that the distributions of  $(\varepsilon_p - \varepsilon_1)$ ,  $(\varepsilon_1 - \varepsilon_0)$  and  $(\frac{\varepsilon_0 + \varepsilon_1}{2} - \mu)$  can be treated independently, we obtain the following equation for the critical level spacing  $\delta_c^e$  in the even case:

$$\begin{aligned} \frac{1}{\lambda} = & 2\pi \int_0^{\infty} dy P(y) \int_0^{\infty} dz t_{y,z} G(z, \sigma) \\ & \times \left( \frac{1}{|y + 2\pi z/\delta_c^e|} + \frac{1}{|y - 2\pi z/\delta_c^e|} \right) \\ & + \int_0^{\pi\hbar\omega_D/\delta_c^e} dx R(x) \int_0^{\infty} dy P(y) \int_0^{\infty} dz t_{x,y,z} G(z, \sigma) \\ & \times \left( \frac{1}{|x + y/2 + \pi z/\delta_c^e|} + \frac{1}{|x + y/2 - \pi z/\delta_c^e|} \right). \end{aligned}$$

This equation is solved numerically and the results for  $\delta_c^e$  are shown in figure 7 as function of  $\sigma/\Delta_0$ . Now the mean value of the chemical potential is  $\mu_0$ . Notice that deviations of  $\mu$  from  $\mu_0$  result in a monotonic increase of the critical level spacing  $\delta_c^e$  with increasing standard deviation  $\sigma$ . This can be explained as follows. The pair correlations are strongest exactly at  $\mu$ .

The redistribution of the chemical potential shifts one of the neighboring levels (either  $\varepsilon_0$  or  $\varepsilon_1$ ) towards the maximum of the pairing correlation function—or in other words shifts one of them towards the chemical potential—where the pair scattering is stronger. At the same time the pair scattering that involves another neighboring level becomes weaker. However, an increase of the correlations on the former level exceeds the decrease on the latter one, resulting in a total gain in interaction energy and, hence, in the critical level spacing. As expected, temperature diminishes this effect. Notice that for  $T = 0$  and  $\sigma = 0$  we obtain  $\delta_c^e/\Delta_0 = 18.7$ , which is substantially larger than the approximate estimate  $\delta_c^e/\Delta_0 \approx 13.8$  found by Smith and Ambegaokar [2].

## 4. Conclusion

Concluding, we have studied the influence of the superconducting pair correlations in a grain on the probability distribution of the chemical potential. It is shown that pair correlations result in a redistribution of the chemical potential, which depends on the grain size. In the odd case, for ultra-small grains the effect of the redistribution is sufficiently suppressed due to the blocking effect.

We also investigated the possible effect of the statistical fluctuations of the chemical potential on the superconducting correlations in nanoparticles. A statistical description of the chemical potential is justified by the presence of a pairing gap in superconducting grains. The deviation of the chemical potential from a fixed value typical for normal metals frees up the phase space that becomes available for the scattering of Cooper pairs. As a result, the critical level spacing increases.

## Acknowledgments

This work was supported by the European Community under the Marie Curie IEF Action (Grant Agreement No. PIEF-GA-2009-235486-ScQSR), the Flemish Science Foundation (FWO-VI), the Belgian Science Policy (IAP), and the ESF network INSTANS. MDC and AAS are grateful to A Vagov for stimulating discussions.

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