Pauli-Limited Superconductivity in Small Grains

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(January 3, 2022)

We report on an exploration of the mean-field phase diagram for Pauli-limited superconductivity in small metallic grains. Emphasis is placed on the crossover from the ultra-small grain limit where superconductivity disappears to the bulk thin-film limit as the single-particle level spacing in the grain decreases. We find that the maximum Zeeman coupling strength compatible with superconductivity increases with decreasing grain size, in spite of a monotonically decreasing condensation energy per unit volume.

I. INTRODUCTION

Mesoscopic physics may be broadly defined as the study of phenomena which depend fundamentally on the finite-size of a system, even when that size substantially exceeds characteristic length scales associated with microscopic degrees of freedom. By this definition, recent experiments in which strong parity effects are seen in superconducting islands containing $10^9$ electrons highlight the robustness of superconductor mesoscopics; pairing physics cannot occur in small grains when the limit $t_0$ is reached. Experimental realization of such ultra-small systems has opened the physics of superconductivity in small metallic grains. Emphasis is placed on the crossover from the ultra-small grain limit where superconductivity disappears to the bulk thin-film limit as the single-particle level spacing in the grain decreases. We find that the maximum Zeeman coupling strength compatible with superconductivity increases with decreasing grain size, in spite of a monotonically decreasing condensation energy per unit volume.

In this paper we address the influence of Zeeman coupling on superconductivity in such a model, emphasizing the crossover between the ultra-small grain regime and the bulk limit where the Chandrasekhar-Clogston paramagnetic limit, $Z < Z_C = \Delta_0/\sqrt{2}$, applies. Here $Z = g\mu_B B/2$ is the Zeeman coupling strength, $\mu_B$ is the Bohr magneton, and $B$ is the magnetic induction.

For a constant level spacing spectrum, the single particle energy levels measured from the Fermi energy are $\xi_n = (n - \alpha)\delta$. Here $n = 0, \pm 1, \pm 2, \ldots$, and parity dependence appears in the quantity $\alpha$ which has the value 0 if the number of electrons $N$ is odd and 1/2 if $N$ is even, corresponding respectively to chemical potentials pinned at and half-way between energy levels. The gap equation for a model in which pairing interactions occur only between identical orbitals differs from its BCS theory counterpart only in the discreteness of the quasiparticle level spectrum:

$$\frac{1}{\lambda} = \delta \sum_{n=1}^{M} \frac{1 - f(E_n + Z) - f(E_n - Z)}{E_n},$$

where $E_n = \sqrt{\Delta^2 + \xi_n^2}$, $\lambda$ is the dimensionless coupling constant and $\Delta$ is determined by solving these equations. The upper limit on this discrete sum comes from the energy cutoff used in BCS theory to model retarded attractive interactions and can be expressed in terms of $\Delta_0$ using the bulk solution of the zero temperature gap equation

$$\Delta_0 = 2M\delta \exp(-1/\lambda).$$

Since, at available fields, the magnetic flux through an ultra-small grains will typically be much smaller than $\Phi_0 = \hbar c/2e$, coupling to orbital degrees of freedom can normally be ignored. The electron spins still couple to the magnetic field $B$, however, splitting the single-particle energies, $\xi_n \rightarrow (n - \alpha)\delta \pm Z$.

For small superconducting particles it is essential that the occupation probabilities, $f$, in Eq. (1) be calculated in ensembles including states with only even or odd numbers of particles. These differ from Fermi occupation probabilities only for levels close to the chemical potential and only for temperatures $k_B T < \delta$; at $T=0$ the even restriction has no effect and the odd restriction has only the effect of removing the orbital at the Fermi energy, which cannot be paired, from the gap equation. This model was first studied by von Delft et al. to calculate the dependence of $\Delta(T)$ on $\delta$. They found that $\Delta(T)$ remains close to its bulk value until $\delta$ is close to a critical value $\delta_c$ which is parity dependent: $\delta_{c,\text{odd}}/\Delta_0 = 1/4e^\gamma \approx 0.89$ and $\delta_{c,\text{even}}/\Delta_0 = 2e^\gamma \approx 3.56$. Here $\gamma = 0.577215...$ is Euler’s
constant. As $\delta \rightarrow \delta_c$ from below, the critical temperature and the zero temperature gap both tend to zero. Later Braun et al. [4] and Balian et al. [5] extended this work to the case of finite Zeeman coupling. Ref. [4] concentrated on comparison between theory and the experiments by Ralph et al. [6] finding good qualitative agreement. Ref. [5] concentrated on the influence of using parity dependent distribution functions at finite temperature, predicting significant qualitative effects for such quantities as the superconducting and normal states.

We consider first the ultra-small grain limit. At $T = 0$, superconductivity is favored at low temperatures. Hence, as $Z$ is increased an additional pair of states $(n \uparrow, n \downarrow)$, is blocked from pairing every time $\alpha + Z/\delta$ passes through an integer value. It follows that

$$Z_2(T = 0, \delta) = (m - \alpha)\delta$$

where $m$ is the largest integer for which

$$\sum_{n = m}^{M} \frac{1}{n - \alpha} = \psi(M + 1 - \alpha) - \psi(m - \alpha) > \frac{1}{\lambda}.$$  

Here $\psi(x)$ is Euler’s psi function. Using $\psi(x) \sim \ln(x)$ for large arguments and replacing $M$ using Eq. (2) we find that $m$ is the largest integer for which

$$\delta/\Delta_0 < \frac{1}{2} \exp(-\psi(m - \alpha)).$$

The resulting $Z_2(T = 0, \delta)$ is plotted in Fig. 1 and Fig. 2 for even and odd $N$, respectively. In both cases the bulk value $Z_2(T = 0, \delta = 0) = 1/2$ is recovered as can be verified by letting $m$ become large in Eqs. (6) and (7).

B. First-order Transition Phase Boundary at $T = 0$

When $\Delta$ is finite, the pair-breaking condition $(Z > \sqrt{\xi_n^2 + \Delta^2})$ is not satisfied until larger values of $Z$ are reached compared to the $\Delta = 0$ case. Hence, at sufficiently low temperatures, states with finite $\Delta$ are favored over states with $\Delta = 0$, causing the superconductor-normal transition to be of first order. This physics is much the same as at finite $\delta$ and in the $\delta \rightarrow 0$ bulk thin film limit.

We consider first the ultra-small grain limit. At $T = 0$ the integral in Eq. (3) can be evaluated analytically.

$$\Omega_s - \Omega_n = \frac{\Delta^2}{\lambda \delta} - 2 \sum_{n = 1}^{M} \{\max(E_n, Z) - \max(\xi_n, Z)\}$$

The first form for the right hand side of Eq. (3) is exact whereas the second form only applies in the ultra-small
are thermally broadened and the condensation energies.

\[ \Omega_n\text{ and }Z_n \]

Examples at representative intermediate values of \( \delta \) and electron-number parity. As a consequence, like minimum grain sizes, Zeeman energies will have a broad distribution. Consequently, it is difficult to compare directly with specific data. Nevertheless our work appears to shed some light on the interpretation of both recent and older experiments.

In a pioneering early experiment, Giaever and Zeller found a violation of the Chandrasekhar-Clogston limit which, to our knowledge, is still not fully explained. These authors studied tunneling through an ensemble of Sn grains with a narrow size distribution. Interpreting their measurements using a Coulomb blockade picture, they concluded that most grains retained a superconducting gap up to magnetic fields that exceeded the Chandrasekhar-Clogston limit. The more recent experiments by Ralph, Black, and Tinkham also appear to find that the Chandrasekhar-Clogston limit can be exceeded. In the later tunneling experiments, a quasiparticle gap, is observed to decrease linearly with the Zeeman coupling strength \( Z \). The linear dependence arises from the Chandrasekhar-Clogston splitting of quasiparticle energies and is consistent with the mean-field theory employed in this paper. The linear decrease continues to Zeeman fields that exceed the Chandrasekhar-Clogston limit without the discontinuous drop which would be expected if \( \Delta \) dropped abruptly to zero. However, this observation is made at a value of \( \Delta_0/\delta \) which is smaller than those for which the Chandrasekhar-Clogston limit is exceeded in a model.
with equally spaced energy levels. The experiment could be explained by assuming that this particular sample happens to have a relatively large energy spacing at the Fermi energy.

The results presented in this paper are based on mean-field theory, and a few cautionary remarks concerning its validity are in order. For $T = 0$ and $Z \leq Z_2$, the mean-field condensation energy for $\delta \rightarrow \delta_c$ becomes microscopic: $\Omega - \Omega_0 \rightarrow -\delta [\ln(\delta_c/\delta)]^2/\zeta(3, \alpha)$. Thermal fluctuations will therefore be important unless the temperature is well below the bulk critical temperature and quantum fluctuations will be increasingly important as $\delta_c$ is approached. Clearly the ultrasmall grain in this regime will not exhibit anything approaching a true phase transition between normal and superconducting states. The phase boundaries found in mean-field-theory should be regarded as estimates for the locations of crossovers which become more gradual as $\delta$ increases.

This work was supported in part by NSF under Grant numbers DMR9714055 and PHY9407194, and in part by the Danish Research Academy. The authors would like to thank ITP, Santa Barbara for its hospitality. Discussions with F. Braun, J. von Delft, D. Ralph, M. Tinkham, and A. D. Zaikin are gratefully acknowledged.

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A critical examination of the assumption that pairing occurs only between identical orbitals will be presented elsewhere. M. C. Bonsager and A. H. MacDonald, in preparation, to be submitted to Physical Review B.

FIG. 1. The zero temperature limit of $Z_1$ (solid line) and $Z_2$ (long-dashed line) as a function of $\delta$ for an even number of electrons. The dashed line is the approximate expression $[\ln(\delta_c/\delta)]^2/\zeta(3, \alpha)$}
As in Fig. 1 but for an odd number of electrons. The discontinuities in $Z_2$ occur at $\delta/\Delta_0 = 0.3276, 0.1987, 0.1424, 0.1109, \ldots$ As it is the case for even $N$ (see Fig. 1), the function $Z_1(T = 0, \delta)$ has discontinuities in its first derivative at a series of $\delta$ given by $Z_1(\delta) = (n - \alpha)\delta, n = 2, 3, 4, \ldots$, i.e. where extrapolations of $Z_2$ (indicated by dotted lines) cross $Z_1$. These cusps are a consequence of discontinuities of the first derivative of the normal state energy with respect to $Z$. In most cases, the cusps are too small see in this figure, however.

The dependence of the free energy difference per particle $(\Omega_s - \Omega_n)/N$ on $\Delta$ at $(T = 0, Z = 0.65\Delta_0)$ for four different values of level spacing $\delta$ for an even number of electrons. The circles indicates cusps in the curves. The case $\delta/\Delta_0 = 1.4$ is special in the sense that it corresponds to Zeeman field below $Z_2(\delta)$ (see Fig. 1). For $Z > Z_2(1.4\Delta_0)$ this curve would also have a positive slope at $\Delta = 0$.

The same as in Fig. 3 but at finite temperature $T/T_{c0} = 0.2$, where $T_{c0}$ is the bulk critical temperature at $Z = 0$.

The functions $Z_1(T)$ and $Z_2(T)$ for both even and odd numbers of electrons. This figure is for $\delta/\Delta_0 = 0.4$. Temperatures are expressed in terms of the bulk critical temperature $T_{c0}$. For $\delta/\Delta_0 = 0.4$ $Z_1(T = 0)/\Delta_0$ is already close to its bulk value, $1/\sqrt{2}$. For both even and odd number of electrons the transition becomes first order near $T/T_{c0} = 0.56$, close to the corresponding bulk value. $Z_2$ shows the largest deviation from the bulk limit. For odd number of particles $Z_2(T = 0, \delta) < Z_2(T = 0, \delta \to 0)$ while for even number of particles $Z_2(T = 0, \delta) > Z_2(T = 0, \delta \to 0)$.
FIG. 6. The functions $Z_1(T)$ and $Z_2(T)$ for both even and odd numbers of electrons. This figure is for $\delta/\Delta_0 = 0.79$, a value sufficiently large to yield phase diagrams which differ substantially from their bulk counterparts. The transition becomes first order at $T/T_{c0} = 0.76$ for even $N$ and at $T/T_{c0} = 0.44$ for odd $N$. This illustration also reflects the dependence of the critical temperature $\delta$ and parity discussed by von Delft et al. For odd $N$ $T_c$ decreases monotonically with $\delta$ whereas for even $N$ it increases up to about $\delta/\Delta_0 \sim 2$ before it decreases.