Step wise destruction of the pair correlations in micro clusters by a magnetic field

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The response of \( nm \)-size spherical superconducting clusters to a magnetic field is studied for the canonical ensemble of electrons in a single degenerate shell. For temperatures close to zero, the discreteness of the electronic states causes a step like destruction of the pair correlations with increasing field strength, which shows up as peaks in the susceptibility and heat capacity. At higher temperatures the transition becomes smoothed out and extends to field strengths where the pair correlations are destroyed at zero temperature.

The electron pair correlations in small systems where the single-particle spectrum is discrete and the mean level spacing is comparable with the pairing gap have recently been studied by means of electron transport through \( nm \)-scale Al clusters [1]. The pair correlations were found to sustain an external magnetic field of several Tesla, in contrast to much weaker critical field of \(\approx 1 \text{G} \) of bulk Al. A step wise destruction of the pair correlations was suggested [3]. It is caused by the subsequent excitation of quasi particle levels, which gain energy due to the interaction of their spin with the external field. This mechanism is very different from the transition to the normal state caused by a magnetic field applied to a macroscopic superconductor. Hence it is expected that physical quantities, as the susceptibility \( \chi \) and the specific heat capacity \( C \), which indicate the transition, behave very differently in the micro cluster. The present letter addresses this question.

For the micro clusters the energy to remove an electron is much larger than the temperature \( T \). The fixed number of the electrons on the cluster was demonstrated by the tunneling experiments [4]. Hence, one must study the transition from the paired to the unpaired state in the frame of the canonical ensemble. The small number of particles taking part in superconductivity causes considerable fluctuations of the order parameter, which modify the transition [2]. Consequences of particle number conservation for the pair correlations in micro clusters have also been discussed recently in [2,3], where a more complete list of references to earlier work can be found.

In order to elucidate the qualitative features we consider the highly idealized model of pair correlations between electrons in a degenerate level, which permits to calculate the canonical partition function. A perfect Al-sphere of radius \( R = (1-5)nm \) confines \( N \approx 2 \cdot 10^3 \sim 3 \cdot 10^5 \) free electrons. Its electron levels have good angular momentum \( l \). Taking the electron spin into account, each of these levels has a degeneracy of \( 2M \), where \( M = 2l + 1 \).

For a spherical oscillator potential, the average angular momentum at the Fermi surface is \( l \approx N^{1/3} \sim 1.4 \), where \( N \) is the number of free electrons. The distance between these levels is \( \Delta \sim 10 \text{meV} \) is much larger than the BCS gap parameter \( \Delta \), which is less than \( 1 \text{meV} \). Therefore, it is sufficient to consider the pair correlations within the last incompletely filled level. This single-shell model also applies to a hemisphere, because its spectrum consists of the spherical levels with odd \( l \), and to clusters with a superconducting layer covering an insulating sphere (cf. [2]) or hemisphere.

The single-shell model Hamiltonian

\[
H = H_{\text{pair}} - \omega(L_z + 2S_z),
\]

\[
H_{\text{pair}} = -GA^+A, \quad A^+ = \sum_{k \geq 0} a_k^+ a_k^-,
\]

consists of the pairing interaction \( H_{\text{pair}} \), which acts between the electrons in the last shell with the effective strength \( G \), and the interaction with the magnetic field. We introduced the Larmour frequency \( \hbar \omega = \mu_B B \), the Bohr magneton \( \mu_B \), the -components of the total orbital angular momentum and spin \( L_z \) and \( S_z \). The label \( k = \{ \lambda, \sigma \} \) denotes the \( z \)-projections of orbital momentum and spin of the electrons, respectively, and \( A^+ \) creates an electron pair on states \((k,k)\), related by the time reversal.

The magnetic susceptibility and heat capacity of the electrons are

\[
\chi = -\frac{\mu_B^2}{h^2V} \frac{\partial^2 F(T,\omega)}{\partial \omega^2}, \quad C = -\frac{\partial^2 F(T,\omega)}{\partial T^2},
\]

The free energy \( F \) derived from the Hamiltonian (1) gives only the paramagnetic part \( \chi_P \) of the susceptibility, because we left out the term quadratic in \( B \). For the fields we are interested in (magnetic length is small as compared to the cluster size), the latter can be treated in first order perturbation theory, generating the diamagnetic part of the susceptibility

\[
\chi_D = -\frac{m \mu_B^2}{h^2V} \frac{<x^2 + y^2>}{N^{2/3}} \sim -4 \cdot 10^{-6} N^{2/3},
\]

where \( m \) is the electron mass and \( V \) the volume of the cluster. It is nearly temperature and field independent [3]. The numerical estimate for Al assumes constant...
Here we have defined the parameter \( \Delta_n \), which measures the amount of pair correlations. Applying the mean field approximation and the grand canonical ensemble to our model, the thus introduced \( \Delta_n \) becomes the familiar BCS gap parameter \( \Delta \). Accordingly we also refer to \( \Delta_n \) as the "canonical gap". However, \( \Delta_n \) must be clearly distinguished from \( \Delta \) because it incorporates the correlations caused by the fluctuations of the order parameter \( \Delta \). For the case of a half filled shell and even \( N_{sh} \), the BCS gap is \( \Delta(0) \equiv \Delta(T=0, \omega=0) = GM/2 \). Ref. [1] found \( \Delta(0) = 0.3-0.4 \text{ meV} \) for Al-clusters with \( R = 5-10 \text{ nm} \), which sets the energy scale.

\[
E_\nu = -\frac{G}{4} (N_{sh} - \nu)(2M + 2 - N_{sh} - \nu),
\]
where \( N_{sh} \) is the number of particles in the shell. The seniority, which is the number of unpaired particles, is constrained by \( 0 \leq \nu \leq N_{sh} \) and \( \nu \leq M \). The degenerate states \( \{ \nu, i \} \) of given seniority \( \nu \) differ by their magnetic moments \( \mu_B m_{\nu, i} \), where \( i = \{ \Lambda \Sigma \} \) takes all values of the total orbital \( (L) \) and total spin \( (S) \) momenta and their total \( z \)-projections \( (\Lambda, \Sigma) \) that are compatible with the Pauli principle for \( \nu \) electrons. In presence of a magnetic field the states have the energy

\[
U_{\nu,i}(\omega) = E_\nu - \omega m_{\nu,i}, \quad m_{\nu,i} = (\Lambda + 2\Sigma)_{\nu,i},
\]
and the canonical partition function becomes

\[
Z = \sum_{\nu,i} \exp(-\beta U_{\nu,i})
= \sum_{\nu} \exp(-\beta E_\nu) \langle \Phi_\nu - \Phi_{\nu-2}(1 - \delta_{\nu,0}) \rangle,
\]

\[
\beta = 1/T, \quad \Phi_\nu = \sum_i \exp(-\beta \omega m_{\nu,i}).
\]

To evaluate the sums we take into account symmetry of the wave functions of the \( \nu \) unpaired electrons and reduce the sums (5) to products of sums over orbital projections of completely antisymmetric states (one column Young diagram, cf. [11]) with \( \nu/2 + \Sigma \) and \( \nu/2 - \Sigma \) electrons.

\[
\Phi_\nu = \sum_{\Sigma=\Sigma_{min}}^{\nu/2} 2(1 + \delta_{\Sigma,0})^{-1} \Phi_{\nu/2 + \Sigma} \Phi_{\nu/2 - \Sigma} \cosh(2\beta\omega\Sigma),
\]

\[
\Sigma_{min} = [1 - (-)^\nu]/4,
\]

\[
\Phi_k = \delta_{k,0} + (1 - \delta_{k,0}) \prod_{\mu=1}^{k} \sinh(\beta\omega \frac{2l+2+\mu}{2}) \sinh(\beta\omega \frac{2l-\mu}{2}).
\]

The derivation of (5-8) will be published separately [12].

The pair correlation energy is

\[
E_c(T, \omega) = \frac{1}{Z} \sum_{\nu} E_\nu \exp(-\beta E_\nu) \langle \Phi_\nu - \Phi_{\nu-2}(1 - \delta_{\nu,0}) \rangle
= -\Delta^2_c(T, \omega)/G.
\]

FIG. 1. Canonical gap \( \Delta_c(T, \omega) \) (full lines) and BCS gap \( \Delta(T, \omega) \) (dotted lines) vs. the Larmour frequency \( \omega \).

Let us first consider the destruction of the pair correlations at \( T = 0 \). The lowest state of each seniority multiplet has the maximal magnetic moment

\[
m_\nu = \frac{\mu_B}{4} (\nu(2M - \nu) - \frac{1}{2} [1 - (-)^\nu] + 4(1 - \delta_{\nu,0})).
\]

According to (6), (7) and (8) the state of lowest energy changes from \( \nu \) to \( \nu + 2 \) at

\[
\omega_{\nu+2} = \frac{2\Delta(0)}{M} \left[ \delta_{\nu,0} + \frac{M - \nu}{M - \nu - 1} (1 - \delta_{\nu,0}) \right].
\]

At each such step \( m_\nu \) increases according to (11). The pair correlations are reduced because two electron states are blocked. At the last step leading to the maximum seniority \( \nu_{max} \) all electron states are blocked. Hence the field \( B_c \) corresponding to \( \omega_c = \omega_{\nu_{max}} \) can be regarded as the critical one, which destroys the pairing completely at \( T = 0 \). For a half filled shell \( \omega_c = 3\Delta(0)/M \) for even electron number and \( 4\Delta(0)/M \) for odd \( (\nu_{max} = M - 1 \) and \( M \), respectively).

Fig. 2 illustrates the step wise destruction of pairing by blocking for the half filled shell \( M = 11 \) \( (l = 5) \). This mechanism was discussed in [4], where the crossing of states with different seniority could be observed. It is a well established effect in nuclear physics, where the states of maximum angular momentum, are observed as "High-K isomers" [13]. Fig. 2 also shows results for the mean

electron density. For \( nm \) scale clusters \( \chi_D \sim 10^{-3} \). It is much smaller than \( \chi_D \sim -1 \) for macroscopic superconductors, which show the Meissner effect. Since the magnetic field penetrates the cluster it can sustain a very high field of \( B \sim \text{Tesla} \). On the other hand, the \( \chi_D \) is three orders of magnitude larger than the Landau diamagnetic susceptibility observed in normal bulk metals.

The exact solutions to the pairing problem of particles in a degenerate shell were found in nuclear physics in terms of representations of the group \( SU_2 \). The eigenvalues \( E_\nu \) of \( H_{pair} \) are

\[
E_\nu = -\frac{G}{4} (N_{sh} - \nu)(2M + 2 - N_{sh} - \nu),
\]
field (BCS) approximation (cf. [3,10]) to the single shell model. The pair correlations are more rapidly destroyed. The quantum fluctuations of the order parameter stabilize the pairing.

We introduce $T_c$ as the temperature at which the mean field pair gap $\Delta(T_c, \omega = 0)$ takes the value zero when the magnetic field is absent. For the half filled shell $T_c = \Delta(0)/2$. Fig. 1 shows the mean field gap $\Delta(T, \omega)$. It behaves as expected from macroscopic superconductors: The frequency where $\Delta = 0$ shifts towards smaller values with increasing $T$. Fig. 2 shows that the temperature where $\Delta = 0$ shifts from $T_c$ to lower values for $\omega > 0$.

However, fig. 1 also demonstrates that the canonical gap $\Delta_c$ behaves differently. For $T = 0.8T_c$ there is a region above $\omega_c$ where there are still pair correlations. For $T = 2T_c$ this region extends to $2\omega_c$. The pair correlations fall off very gradually with $\omega$. Fig. 3 shows how these "temperature induced" pair correlations manifest themselves with increasing $T$. For $\omega = 0$ there is a pronounced drop of of $\Delta_c$ around $T_c$, which signalizes the break down of the static pair field. Above this temperature there is a long tail of dynamic pairing. For $\omega \geq \omega_c$ the dynamic pair correlations only built up with increasing $T$.

The temperature induced pairing can be understood in the following way: At $T = 0$, all electrons are unpaired when the state of maximum seniority becomes the ground state for $\omega > \omega_{crit}$. At $T > 0$ excited states with lower seniority enter the canonical ensemble, reintroducing the pair correlations.

Here we have adopted the terminology of nuclear physics, calling "static" the mean field (BCS) part of the pair correlations and "dynamic" the quantal and statistical fluctuations of the mean field (or equivalently of the order parameter). The "pair vibrations", which are oscillations of the pair field around zero [14], are well established in nuclei. Fluctuation induced superconductivity was discussed before [15]. The fluctuations play a particularly important role in the systems the size of which is smaller than the coherence length,

![FIG. 2. Canonical gap $\Delta_c(T, \omega)$ (full lines) and BCS gap $\Delta(T, \omega)$ (dotted lines) vs. the temperature $T$.](image)

![FIG. 3. Canonical gap $\Delta_c(T, \omega)$ vs. $\omega$.](image)

![FIG. 4. Susceptibility $\chi(T, \omega)$ vs. $\omega$.](image)

Fig. 2 shows a very small cluster ($M = 7$) with very pronounced steps. Already at $T = 0.1T_c$ the steps are noticeably washed out. In the single-shell model the step length is $\omega_0 - \omega_{n-2} \sim \Delta(0)/M$. Accordingly, no individual steps are recognizable at $T = 0.1T_c$ for the large cluster ($M = 23$) shown. Yet there is some irregularity around $\omega = 0.7\omega_c$, which is a residue of the discreteness of the electronic states. It is thermally averaged out for $T = 0.2T_c$. Hence only for $M < 50$ i.e. $N < 2 \cdot 10^4$ and $T < 0.1T_c$ the step wise change of $\Delta_c$ is observable.

The discreteness of the electronic levels has dramatic consequences for the the susceptibility at low tempera-
tures. As shown in the upper panel of fig. 4, $\chi_p$ has pronounced peaks at the frequencies where the states with higher seniority and magnetic moment take over. The paramagnetic contribution is very sensitive to the temperature and to the fluctuations of the order parameter. Using the BCS mean field approximation we find much more narrow peaks, which are one to two orders of magnitude higher. For the larger cluster in the lower panel the individual steps are no longer resolved, resulting in a peak of $\chi_p$ near $\omega = 0.7\omega_c$. Since for the considered temperatures it is unlikely to excite states with finite magnetic moment, $\chi_p$ is small at low $\omega$. It grows with $\omega$ because these states come down. It falls off at large $\omega$ when approaching the maximum magnetic moment of the electrons in the shell. The curve $T = 0.1T_c$ shows still a double peak structure, which is residue of the discreteness of the electron levels.

The deviation of real clusters from sphericity will attenuate the orbital part of $\chi_p$ and round the steps of $\Delta_c$ already at $T = 0$. The back-bending phenomenon observed in deformed rotating nuclei [13] is an example. How strongly the orbital angular momentum is suppressed needs to be addressed by a more sophisticated model than the present one. In any case, there will be steps caused by the reorientation of the electron spin, if the spin orbit coupling is small as in Al [1]. Most of the findings of the present paper are expected to hold qualitatively for these spin flips.

In summary, at a temperature $T < 0.1T_c$ an increasing external magnetic field causes the magnetic moment of small spherical superconducting clusters ($R < 5nm$) to grow in a step like manner. Each step reduces the pair correlations until they are destroyed. The steps manifest themselves as peaks in the magnetic susceptibility and the heat capacity. The steps are washed out at $T > 0.2T_c$. For $T \sim T_c$, reduced but substantial pair correlations persist to a higher field strength than for $T = 0$. This phenomenon of the temperature-induced pairing in a strong magnetic field is only found for the canonical ensemble.

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\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{Heat capacity $C(T, \omega)$ v.s. $\omega$.}
\end{figure}

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