Exact canonical and grand canonical descriptions of the pairing in spherical mesoscopic systems

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Abstract. The pairing in spherical nanograins with free electron numbers \(N < 10^5\) are treated in the exact manner on the basis of the single shell model (SSM) provided the Debye layer contains only one spherical shell. Such systems demonstrate the strengthening of the pairing gap (\(\Delta\)) and critical temperature as compared with the bulk values. The temperature variations of \(\Delta\) and \(\chi_P\) (paramagnetic susceptibility) are calculated vs strength of the magnetic field for the canonical ensemble (CE) and grand canonical one (GCE). Increasing of the field stimulates stepwise decreasing \(\Delta\) and oscillations in \(\chi_P\) which are smoothed by the temperature. For the electron numbers \(N < 10^5\) the BCS sharp temperature superconducting-normal phase transition in \(\Delta\) and \(\chi_P\) turns out to be essentially softened in CE and GCE. The temperature re-entrance of the superconductivity is considered for both CE and GCE at so strong magnetic fields which remove he pairing at \(T = 0\).

1. Introduction

As was shown about half a century ago \cite{1} the superconducting properties of a system can be described by using the exact solutions of the pairing Hamiltonian if the single particle level density of this system is such that in its Debye layer there is only one highly degenerated level. Until quite recently the existence of such systems was only an abstract possibility, however, studying the superconductivity of such symmetric systems as multielectron bubbles in liquid helium, metallic nanoshells, buckyballs and others has demonstrated that this one level model can find practical applications. In particularly such approach can be employed for some spherical clusters where high degeneracies of solitary levels are caused by high values of the shell orbital momenta \((l)\). The single shell model taking into account spherical symmetry (SSM) was worked out by Kerman \cite{2}.

The upper limit in \(N\) for applicability of SSM can be ascertained assuming that for metal clusters the Debye layer \(\varepsilon_D\) and the the Fermi energy \(\varepsilon_F\) are in the same relationship as in bulk systems i.e. \(\varepsilon_D/\varepsilon_F \sim 10^{-3}\). Then with employment of the maximum value of \(l_F\) which is possible for a given region of \(N\) and which for spherical systems, \(N^{1/3}\) the largest value of \(N\) to which SSM can be applied is assessed by means of the condition \(2(2l_F + 1) > N\varepsilon_D/\varepsilon_F\), that gives \(N < 10^5\) (here we suppose that the spin-orbit coupling is absent). The applicability of SSM to an actual system requires also preliminary studying its single electron spectrum as in the spherical mean field there can occur accidental concentration of the levels. It practically does not concern clusters with \(N \leq 10^3\) for which the averaged level spacing is more than \(\varepsilon_D\). One more important condition for SSM applicability consists in that the pairing that splits the
solitary Fermi level has to give such spectrum of the correlated states that covers the energy space only inside the Debye layer \( \varepsilon_F \pm \varepsilon_D \). Otherwise redistributions of electrons between unpaired states (outside \( \varepsilon_F \pm \varepsilon_D \)) and states with the pair correlations should be allowed for.

In many investigations on the superconductivity of spherical clusters performed both in the framework of the standard \( BCS \) theory and by using theories with the exact particle number conservation [3, 4, 5, 6, 7] it has been established that \( \Delta \) in small clusters can be much more than the bulk values for the same materials. For the cases when the \( SSM \) can be applied i.e. for \( N < 10^5 \) the ratio \( \Delta(SSM)/\Delta_{bulk} \) turns out to be equal to \( 2\lambda(\varepsilon_F/\varepsilon_D)(2l_F + 1)\sinh(1/\lambda)/3N \), \( \lambda \) being the \( BCS \) pairing coupling constant independent of \( N \). Thus, at maximum value of \( l_F \sim N^{1/3} \) this ratio increases as \( N^{-2/3} \) with decreasing \( N \). Such strengthening of \( \Delta \) in small clusters is caused by the high electron concentration on the Fermi shell and the independence of \( \lambda \) from \( N \).

The temperature evolution of \( \Delta \) and other thermodynamic quantities demonstrates the fundamental phenomenon in mesoscopic physics: in finite systems increasing the temperature does not lead to the second order phase transition that was established both for systems with uniform single electron spectra and in \( SSM \) [8, 9, 10]. Therefore for finite systems \( T_c \), the \( BCS \) critical temperature which is equal to \( \Delta(T = 0)/2 \) in \( SSM \) [2] marks only the temperature region where the most rapid decrease of \( \Delta \) takes place. Nevertheless in finite systems the absolute value of \( \Delta \) in this region is equal to about \( \Delta(T = 0)/2 \).

For all superconducting systems independently of their sizes the increasing magnetic field breaks off electron pairs and thereby decreases the pairing. For spherical systems this decreasing reveals some special feature on account of the angular momentum conservation in these systems. The stepwise decreasing of \( \Delta \) in relatively large spherical systems \( (N > 10^5) \) was predicted by Larkin [11]. Here we consider the temperature and magnetic variations of properties of small systems with \( N < 10^5 \) which can be treated in the framework of \( SSM \).

2. The partition function in \( SSM \)

Each eigenvalue of the pairing Hamiltonian in \( SSM \) is characterized by two numbers: \( N_{sh} \) the particle number in the shell (the number of superconducting particles in a system), \( N_{sh} \leq 2M/M = 2l_F + 1 \), and the seniority \( \nu \), the number of unpaired particles, \( 0 \leq \nu \leq N_{sh} \). If we put \( \varepsilon_F = 0 \) (without loss of generality) then in the absence of the magnetic field \( E_\nu(N_{sh}) = -(G/4) [ (M + 1 - \nu)^2 - (M + 1 - N_{sh})^2 ] \). In the exact theory there is no parameter like the \( BCS \) pairing gap, instead of this the canonical gap can be introduced so as in the Gor’kov theory

\[
\Delta_\nu^{(ex)} = \langle N_{sh}, \nu | A^+ | N_{sh} - 2, \nu \rangle = \left( -GE_\nu(N_{sh}) \right)^{1/2},
\]

\( \Delta_\nu^{(ex)} \) depends on \( \nu \) and for ground states of even systems \( (\nu = 0) \) and odd ones \( (\nu = 1) \) \( \Delta_\nu^{(ex)} \) is very close to the \( BCS \) pairing gap in \( SSM \)

\[
\Delta = GM/2, \quad G \simeq \lambda \varepsilon_F/N.
\]

The most interest for studying the superconductive properties of small clusters with \( N < 10^5 \) consists in investigation of their variations at increasing the temperature and magnetic field. To remain in the framework of \( SSM \) we have to use a rather narrow temperature range \( T < \varepsilon_D \), i.e. not more than \( 2T_c = \Delta \) and relatively small magnetic fields \( \omega < 4G = 8\Delta/M \), \( \omega \) is Larmor frequency.

In this approximation supposing that single-electron levels outside the Debye layer weakly contribute to quantities under consideration the canonical partition function of \( SSM \) taking into account the uniform magnetic field can be written in the form

\[
Z_{N_{sh}}(CE) = \sum_\nu d_\nu(\omega) \exp \left\{ -\beta E_\nu(N_{sh}) \right\},
\]

2
$d_\nu(\omega)$ depending on the field are calculated in [12]). They allow for that high degenerated states with $\nu > 0$ are split by the field. This splitting is governed practically only by paramagnetic term. The diamagnetic term is not considered in Eq.(2) as its effect is reduced to an additional energy monotonously increasing with $\omega^2$. Therefore the energy of each state with seniority $\nu$ is $E_\nu - \omega(L_z + g_S S_z)$ where $L_z$ and $S_z$ are total orbital and spin projections on the field direction in this state. The sum over all values of $L_z$ and $S_z$ gives $d_\nu(\omega)$.

The grand canonical partition function can be obtained by summing over all values of $N_{sh}$ in $SSM$

$$Z(GCE) = \sum_{N_{sh}=0}^{2M} Z_{N_{sh}}(CE) = \sum_\nu d_\nu \exp \left\{ \frac{\beta G}{4} (M + 1 - \nu)^2 \right\} \tilde{Z}_\nu,$$

$$\tilde{Z}_\nu = \sum_{-M+1-\nu \leq n \leq M+1-\nu} \frac{1 + (-1)^{\nu+n}}{2} \exp \left\{ -\frac{\beta G}{4} n^2 \right\}$$

The dependence on $N_{sh}$ enters in Eqs. (2),(3) via the factor $[\beta G (M + 1 - N)^2]/4$ so at small temperatures a term with $N_{sh} = M + 1$ prevails that provides the close values of thermodynamic quantities in $GCE$ and $CE$ at $N_{sh} = M + 1$.

3. Spherical superconducting nanograins in uniform magnetic field

As shown in Ref. [13] an increasing magnetic field causes alterations of the ground state structure. Generally, the energy of a $(\nu + 2)$-state with the maximum magnetic moment becomes lower than the energy of a $\nu$-state if the difference in the correlation energies is compensated by the magnetic field. Thus, the increase of the field reduces the paring gap in the ground state as the quantity of unpaired particles ($\nu$) in it successively increases. Figs. 1 show that at very low $T$ this pairing attenuation is a stepwise process. The point $\omega_g$ where the field produces the first electron pair break is the point of arising the gapless superconductivity ($\omega_g = \omega_{\nu=2} = G$ for even $N$). The last change in $\nu$ leading to $\nu_{\text{max}}$ (the maximum number of broken pairs) is accomplished at the critical value $\omega_c$ defined as $\Delta^{(\text{can})}(T = 0; \omega = \omega_c) = 0$; $\omega_c = 3G/2$ for even $N$. The temperature regime for observing the stepwise decrease of the canonical pairing gap

$(\Delta^{(\text{can})})$ with increasing $\omega$ can be estimated by using the condition: the temperature should be less than the step length that on the average equal to $\omega_{\nu} - \omega_{\nu-2} \sim 4T_c/M^2$, i.e. $T/T_c$ should be
Figure 2. The canonical paramagnetic susceptibility $\chi_P$ of a spherical $N$-even system with $N \sim 10^3$. Left panel: $\chi_P$ vs $\omega$ at different $T$. Right panel: $\chi_P$ vs $T$ at different $\omega$.

less than $4/M^2$. The drastic changes of the pairing gap in each point where the field breaks off a pair generates at such $T$ the delta-like peak in $\chi_P$ that is shown in Figs. 1, 2 where $\chi_P$ are given in units of $\chi(Pauli) = \mu_B^2 \rho_F/V$. The sharp peaks in $\chi_P$ is caused by the abrupt changes in the free energy $F$ that arise at each pair break while between these points $F$ is practically constant for a fixed very low $T$.

A rise in temperature at first joints all peaks together at $\omega_g < T < \omega_c$ and then at $T \to T_c$ tracks of the peaks disappear. However even at $\omega_g < T < \omega_c$ (e.g. at $T = 0.35T_c$, Fig. 2) the superposition of these peaks affects $\chi_P$ that explain maxima in these figures. Canonical calculations of $\chi_P$ show that such low and high temperature giant paramagnetism, developing at $\omega \sim \omega_g$ and $T < T_c$, is so large that practically completely compensates the diamagnetic contribution in the magnetic susceptibility of spherical superconducting nanograins.

However the most striking prediction of SSM is the re-entrance of the canonical pairing (Fig. 1b, on the right panel) at so strong magnetic fields which result in $\Delta^{can} = 0$ at $T = 0$, i.e. at $\omega > \omega_c$. The explanation of this phenomenon consists in that the spectrum of the excited states of the system turns out inverted in the strong magnetic field: the ground state contains the maximum quantity of unpaired particles ($\nu$ is maximum) whereas the state with maximum pair correlations possesses a much higher energy. Therefore increasing temperature has to balance the contributions of these states to the partition function and the temperature pairing gap will have a finite value. In so far as this phenomenon occurs both in $CE$ and $GCE$ the main role in its appearance plays the finite size of mesoscopic systems.

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