QUANTUM FLUCTUATIONS IN SUPERCONDUCTING DOTS
AT FINITE TEMPERATURES

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We study the thermodynamics of ultrasmall metallic grains with level spacing $\delta$ comparable or smaller than the pairing correlation energy, at finite temperatures, $T \gtrsim \delta$. We describe a method which allows to find quantum corrections to the effect of classical fluctuations. We present results for thermodynamic quantities in ordered grains and for the reentrant odd susceptibility in disordered grains.

1. Outline of the problem

Superconducting coherence in finite systems has recently received a renewed attention since the series of experiments of Ralph Black and Tinkham (RBT). They succeeded to perform tunneling spectroscopy on individual nanoscale Al grains where $E_C$, the charging energy, is very large (up to 500 K), enforcing the conservation of the total number of electrons $N$. They observed spectroscopic features related to superconductivity, which also depended on the parity ($N$ being odd or even) of the grains.

The question of the size limit for a metal particle to have superconducting properties was posed since the early days of BCS theory by Anderson. It was argued that when the average level spacing $\delta \sim 1/(N(0)V)$ becomes of the order of the BCS gap $\Delta$, superconductivity should disappear.

In small metallic grains, thermal fluctuations wash out the hallmarks of Cooper pair condensation, like the zero resistance and the complete Meissner effect. However, other features related to superconductivity can be clearly observed. In micrometer size samples charging effects determine the Coulomb Blockade and parity effects, but superconducting correlations are still strong (the typical energy scale is the BCS $\Delta$). For ultrasmall grains ($\delta \geq \Delta$, “superconducting dots”) at low temperature, quantum fluctuations due to both large $E_C$ and finite $\delta$ tend to suppress superconducting properties.

Theoretical analysis by parity dependent mean field theories found that the
breakdown of BCS superconductivity occurs at a value of $\delta/\Delta$ which depends on parity. The use of the mean field grand-canonical approach is appropriate when the grains are large enough to give small relative fluctuations of the electron number (this condition is not strictly met in the experiments) and it breaks down completely in superconducting dots at $T = 0$. In the canonical ensemble the BCS pair amplitude is zero and in order to characterize pairing correlations different quantities have to be studied, for instance the odd-even staggering between the ground state energies at different $N$.

They studied the BCS Hamiltonian

$$
\mathcal{H} = \sum_{n,\sigma} (\epsilon_n - \sigma \mu_B H) c_{n,\sigma}^{\dagger} c_{n,\sigma} - \lambda \sum_{m,n=1}^{\Omega} c_{m,+}^{\dagger} c_{m,-}^{\dagger} c_{n,-} c_{n,+} .
$$

where $\{m,n\}$ span a shell of $\Omega$ doubly degenerate time reversed ($\sigma = \pm$) single particle energy levels (energy $\epsilon_n$ and annihilation operator $c_{n,\sigma}$), and $\lambda$ is the BCS coupling constant. The effect of a magnetic field $H$ is accounted for by the Zeeman term ($\mu_B$ is the Bohr magneton).

For equally spaced $\epsilon_m = m\delta$, it was found that even in ultrasmall grains pairing correlations manifest with non-perturbative fluctuations and that the low-energy physics can be expressed by universal functions of $\delta/\Delta$ ($\Delta$ plays the role of an energy scale analogous to the Kondo temperature), allowing a quantitative description of the full crossover regime.

The model Eq.(1) was further studied with various methods until it was recognized that it has been exactly solved long ago by Richardson and Sherman. The connections of this solution with conformal field theories and off-shell Bethe Ansatz has been recently exploited, and may yield exact expressions for the correlation functions.

It is in general very difficult to achieve experimentally unambiguous evidence of the presence of strong pairing correlations in ultrasmall grains. However the spin susceptibility in grains with $N$ odd $\chi_o(T)$ was found to show a striking reentrant behavior (see Fig.1). This qualitative difference with normal metal grains is a signature of pairing and persists even in ultrasmall grains. It is due to the interplay of pairing which tends to suppress $\chi_o(T)$ for decreasing $T$, and parity which determines a Curie $1/T$ contribution which eventually prevails.

The result was obtained by combining a parity-projected path-integral approach in the static-path approximation (SPA) with low temperature results obtained by massive use of the exact solution. In this paper we describe how to study quantum corrections to the SPA with a functional procedure which has been named RPA'. The RPA' also allows to study the thermodynamics of weakly disordered grains at finite temperature, in an efficient and reliable way. This is an important virtue because experiments should be carried out in ensembles of grains, where a distribution of shape and volume has to be considered.

We remark that the Hamiltonian Eq.(1) describes universal properties of small grains in the metallic regime (weak disorder) if we choose $\epsilon_m$ as the eigenvalue of a random matrix of the Gaussian Orthogonal Ensemble (GOE), since we ignore here spin-orbit effects. A set of mono dispersed grains should be studied along these lines. This makes practically impossible the use of the exact solution as in the work of Di Lorenzo et al. Some effects of disorder have been previously studied using a parity-projected mean field approach valid for large grains, and at $T = 0$.

To clarify the virtues and differences of various approaches we sketch the procedure we employ. We start from a path-integral formulation of the problem which we consider the grand-canonical ensembles of odd or even grains. We express the partition function as a path integral over a quantum auxiliary field $\Delta(\tau)$. The SPA consists in retaining only the contribution of all constant $\Delta(\tau) = \Delta^{(s)}$, which is
maximal if $\Delta(s) = \Delta$, the BCS gap. Thus the SPA describes exactly classical fluctuations. We account for quantum fluctuations by allowing for non constant paths $\Delta(\tau)$. The RPA consists in retaining Gaussian fluctuations along the static path by first fixing $\Delta(s)$, then evaluating Gaussian fluctuations and finally integrating over $\Delta(s)$.

More accurate approximation schemes are also possible. All these methods break down at low temperatures, in a more or less spectacular way. In this paper we use study the thermodynamics at finite temperature beyond the SPA. We present results on the specific heat and on the odd spin susceptibility for equally spaced $\epsilon_n$. We finally check that the reentrant behavior of $\chi_o$ persists in disordered grains.

2. Functional formulation

The spin susceptibility and the specific heat of a grain with an even (e) or an odd (o) number $N$ of electrons is defined starting from the partition functions $Z(T, N)$, which should be evaluated in the canonical ensemble. With the help of a parity projection technique, the grand partition function of an even or odd system can be expressed as

$$Z_{e/o}(T, \mu) = \frac{1}{2} \sum_{N=0}^{\infty} e^{\mu N/T} \left[ 1 \pm e^{i\pi N} \right] Z(T, N)$$

$$\equiv \frac{1}{2} \left( Z_+ \pm Z_- \right).$$

Here, the partition function $Z_+$ is the usual grand partition function at temperature $T$ and chemical potential $\mu_+ = \mu$. The grand partition function $Z_-$ describes an auxiliary ensemble at temperature $T$ and chemical potential $\mu_- = \mu + i\pi T$; it is a formal tool, necessary to include parity effects. In the calculation, the chemical potential $\mu$ will be placed between the topmost occupied level and the lowest unoccupied level in the even case, while it will be at the singly occupied level in the odd case.

The method we use to perform the calculation is based on the functional formalism and the Hubbard-Stratonovic (HS) approach, where the two-body interaction $c^\dagger_{m,+} c_{n,-} - c_{n,+} c^\dagger_{m,-}$ is reduced to a one-body interaction with a time dependent external field $\Delta(\tau)$, which has to be averaged over a Gaussian weight. So that the problem switches to the treatment of the interaction vertex between the fermionic and the HS field. The functional integral over the fermionic degrees of freedom is Gaussian and can be easily performed. After this step the grand partition functions $Z_\pm$ read

$$Z_\pm = N \int D^2 \Delta \exp \left\{ \frac{\beta}{2} \int d\tau \left[ \sum_m \left( \text{Tr} \ln \hat{G}^{-1}_{m,\pm} - \frac{\epsilon_m - \mu + \mu_B H}{T} - \frac{\Delta^2}{\lambda} \right) \right] \right\},$$

where, $\beta = 1/T$ and $N$ is the normalization factor of the Gaussian “measure” introduced by the HS procedure. The matrix Green function $\hat{G}_{m,\pm}$ is given by

$$\hat{G}^{-1}_{m,\pm} = \begin{pmatrix} -\partial_\tau - \epsilon_m + \mu + \mu_B H & \Delta(\tau) \\ \Delta^\dagger(\tau) & -\partial_\tau + \epsilon_m - \mu + \mu_B H \end{pmatrix} \delta(\tau - \tau').$$

It is worth to stress that the $\{\pm\}$ ensembles are characterized by different time-periodicity of the Green function: in the $\{-\}$ case the adding term to the chemical
potential $i\pi T$ has been re-absorbed by the gauge transformation on the fermionic variables $c_{m,\sigma}(\tau) = \exp(i\pi T \tau) d_{k,\sigma}$ changing, in this way, the periodic boundary condition. In particular the fermionic (bosonic) Matsubara periodicity is associated to the $Z_+$ ($Z_-$) partition function.

In order to deal with the non-linear functional integral (8), it is useful to extract the static term by the HS field, i.e. $\Delta(\tau) = \Delta(\omega_0) + \sum_{n\neq 0} \Delta(\omega_n) \exp(-i\omega_n t) \equiv \Delta^{(s)} + \delta \Delta(\tau)$. The SPA approximation consists in taking into account the only static contribution $\Delta^{(s)}$, so that the functional integral is therefore reduced to an ordinary integral over the class of “straight paths” in the time interval $[0, \beta]$. It is worth to notice that $\Delta^{(s)}$ is just the average point of the path (the centroid in Feynman language) and for this reason some analogies with the Feynman variational approach can be found. As in the variational case, the SPA can be improved by taking into account small-amplitude (quadratic) fluctuation around the centroid. This is the so-called RPA', introduced by Wang et al. and refined later by Keiter et al. in order to study the Anderson model (for an exhaustive review on this approximation see also Refs. 12, 21). In particular it turns out that RPA' corresponds to a ring-diagram summation equivalent to the standard random phase approximation (RPA), except that only non-zero-frequency transfers at the vertices are retained in the ring-diagrams, while all zero-frequency transfers are treated exactly.

The logarithm term in Eq. (3) can be expanded in the following way

$$
\ln \hat{G}^{-1}_{m,\pm} = \ln \hat{G}^{-1}_{m,\pm} + \sum_{\ell=1}^{\infty} \frac{(-1)^{\ell-1}}{\ell} \left( \hat{G}^{(s)}_{m,\pm} \hat{V}^{\ell} \right),
$$

where

$$
\hat{V} = \begin{pmatrix} 0 & \delta \Delta(\tau) \\ \delta \Delta^\dagger(\tau) & 0 \end{pmatrix} \delta(\tau - \tau').
$$

Performing the trace operation and paying attention to the fact that the zero frequency are ruled out from the sums, it is easy to find the first order contribution vanish. So the static path $\Delta^{(s)}$ is a local extreme of the integrand. The leading correction to the SPA is quadratic in the fluctuation around the centroid. In RPA' the partition function reads

$$
Z_\pm = N \int d\Delta^{(s)} \exp \left[ \varphi_{\pm}^{\text{SPA}}(\Delta^{(s)}) + \delta^2 \varphi_{\pm}(\Delta^{(s)}) \right],
$$

where

$$
\varphi_{\pm}^{\text{SPA}}(\Delta^{(s)}) = -\frac{s}{\lambda T} + \sum_{m,\sigma} \left[ \ln 2 \left( \frac{\cosh \frac{E_m + \sigma \mu H}{2T}}{\sinh \frac{E_m + \sigma \mu H}{2T}} \right) - \frac{\xi_m}{2T} \right],
$$

with $E_m^2 = \xi_m^2 + s$ and $\xi_m = \epsilon_m - \mu$, is the standard SPA contribution. The quantum fluctuation correction to the free energy is

$$
\exp \left[ \delta^2 \varphi_{\pm}(\Delta^{(s)}) \right] = \int D^2[\delta \Delta] \exp \left\{ -\delta^2 S_\pm[\delta \Delta(\tau)] \right\},
$$

where the functional $\delta^2 S_\pm[\delta \Delta]$ contains products of two Green’s functions. The path integral can be easily evaluated after the standard sum procedure over (fermionic
and bosonic) Matsubara frequency has been performed. After some algebra the following expression is found

\[ \delta^2 \varphi_{\pm}(\Delta^{(s)}) = -\frac{1}{2} \sum_{\omega_n > 0} \ln \left[ A_{\pm}^2(\omega_n) - B_{\pm}^2(\omega_n) \right]. \]  

where

\[ A_{\pm}(\omega_n) = \sum_{m, \sigma} g_m(\omega_n) \tanh \frac{1}{2T} \frac{E_m + \sigma \mu_B H}{\Delta}, \quad g_m(\omega_n) = \frac{E_m^2 + E_m^2}{2E_m(\omega_n^2 m + 4E_m^2)}, \]

\[ B_{\pm}(\omega_n) = \sum_{m, \sigma} f_m(\omega_n) \tanh \frac{1}{2T} \frac{E_m + \sigma \mu_B H}{\Delta}, \quad f_m(\omega_n) = \frac{s}{2E_m(\omega_n^2 m + 4E_m^2)}. \]

By means of expressions (6-9), the thermodynamical quantity of the model can be numerically evaluated with a CPU time much shorter than what needed for the exact solution. This makes possible the analysis of the effect of a statistical distribution of non-interacting levels. In the next section we will show our results for even specific heat and for the reentrant susceptibility in the ordered level spacing case and we compare them with previous results both analytic and exact. This comparison, besides, allows to test the reliability of the RPA’ in dealing with the quantum fluctuations in ultrasmall grains. Finally we will show results for disordered superconducting dots.

3. Results

Results obtained with RPA’ are shown in Figs.1-3. We notice first of all that for \( \chi_o(T) \) (Fig.1) the RPA’ curves (full lines) move away from the SPA curves (dotted-dashed) towards the exact result (dashed curve). So the quantum corrections are appreciable and give the expected trend. The difference between RPA’ and exact curves can be mainly attributed to differences between canonical ensemble and parity-projected grand canonical ensemble. The agreement at lower temperature

![Fig. 1. Spin susceptibility for an odd grain vs. temperature in units of \( \delta \). Solid line: RPA’; dashed line: exact; dot-dashed: SPA](image_url)
Fig. 2. (a) Specific heat for an even grain vs. temperature in units of $\delta$. (b) Rescaled specific heat $c_v \delta/\gamma T$ vs. temperature in units of $\delta$ (see text.). Solid curves are the RPA' results whereas dashed curves are the exact results. Thin lines represent the asymptotic behavior at large $T$ in the canonical (dashed) and in the grandcanonical (solid) ensemble.

is due to the fact that essentially only the classical Curie contribution is important. At very low temperature the SPA gives wrong results for the contribution of the “condensate” which is by itself small, whereas the RPA’ breaks down. For even grains $\chi_e(T)$ vanishes exponentially for $T \to 0$.

The specific heat for even grains is shown in Fig.2a. For large enough coupling an anomaly develops. This is not the case for odd grains, as expected, because the odd electron reduces the phase space for pairing to be active. At lower temperatures the RPA’ data seem to reach the data obtained by diagonalization with a good quantitative accuracy, at even lower temperatures RPA’ breaks down. While is not surprising that the Richardson and the parity projected RPA’ curves do not match each other at high temperature: the former arise from a correct canonical analysis, the latter come from the parity projection technique, which relies on the grand-canonical treatment. As shown by Denton et al.\cite{28} for a normal metal particle, the specific heat in the grand-canonical case is larger than in the canonical case, asymptotically is $\frac{1}{2} k_B$ higher, because there are more excitations allowed when the electron number is not conserved. In order to point out this behavior, in Fig.2b $c_v \delta/\gamma T$ is shown, where $\gamma = 2\pi^2/3$ is the Sommerfeld coefficient of the specific heat for an electron gas in the grand-canonical ensemble.

Experimental investigation on thermodynamic properties of ultrasmall superconducting grains can only be performed in large ensembles rather than in individual grains. In the case of the susceptibility it is of course not possible to prepare an ensemble of all odd grains. However at temperatures where the Curie contribution prevails the susceptibility of even grains is already exponentially small. A similar line of reasoning applies for the measurement of the even specific heat anomaly, which however seems to be less promising. Two questions can be raised for what concerns the physics of ensembles of grains. The first one concerns interaction between neighboring grains with possible electron tunneling. However for small enough grains large charging energies, as the ones in the RBT\cite{1} experiment, prevent charge transfer, except for very special situations. Another question is the effect of the disorder. To discuss this issue we considered samples of monodispersed grains, i.e. grains differ in the shape but not in the volume. This has striking consequences in small metallic grains, since shape irregularities over lengths $\sim \lambda_F$ are enough
Quantum fluctuations in superconducting dots at finite temperatures

Fig. 3. Effects of a GOE statistical distribution of energy levels on the reentrant behavior of $\chi_o(T)$. Solid lines represent the canonical ($\Delta = 0$) and RPA ($\delta/\Delta = 1$) results for equally spaced noninteracting single-particle levels, while dots are the result for GOE distributed single-particle levels.

to affect the spectrum at the Fermi energy. Gorkov and Eliashberg incorporated the effect of the disordered boundary conditions into the Hamiltonian, where they appear as random matrix elements which determine a statistical distribution of the energy level. For vanishing magnetic field the proper ensemble is the GOE. The thermodynamics of normal disordered grains was studied by Denton et al. We applied the RPA to this problem. Results are shown in Fig2., where points represent ensemble averages over 200 samples of random Hamiltonians belonging to the GOE. The spectra were obtained by diagonalizing $500 \times 500$ matrices with random elements and taking the central 100 levels of the resulting semicircular distribution, in order to prevent undesired border effects. Results show that $\chi_o(T)$ is clearly reentrant even in disordered samples.

4. Conclusions

We have discussed some thermodynamic properties of ultrasmall superconducting grains at $T > \delta$ using the RPA’ approximation. Comparison with results in the SPA, which accounts exactly for classical fluctuations, allows to estimate the effect of quantum fluctuations. Comparison with the behavior of the exact solution results at $T \sim \delta$ allows to estimate differences between results in the grand canonical and in the canonical ensemble.

The RPA’ turns out to be an efficient and reliable method. It can be successfully applied to problems for which the exact solution is not useful in practice. An example is the study of the effect of a statistical distribution of noninteracting levels on the thermodynamics. We considered the odd susceptibility $\chi_o(T)$ which was found to show a characteristic reentrant behavior for grains with a regular spectrum. This is a promising quantity for experimental detections of pairing correlations in ultrasmall grains. We checked that the reentrant behavior is well preserved even in samples containing a large number of monodispersed grains, whose spectrum has statistical properties described by the GOE.

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