Combined effect of thermal and quantum fluctuations in superconducting nanostructures: a path integral approach

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We study the combined effect of thermal and quantum fluctuations in a zero dimensional superconductor. By using path integral techniques, we obtain novel expressions for the partition function and the superconducting order parameter which include both types of fluctuations. Our results are valid for any temperature and to leading order in $\delta/\Delta_0$ where $\delta$ is the mean level spacing and $\Delta_0$ is the bulk energy gap. We avoid divergences at low temperatures, previously reported in the literature, by identifying and treating non-perturbatively a low-energy collective mode. In the low and high temperature limit our results agrees with those from the random phase (RPA) and the static path approximation (SPA) respectively.

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Superconductivity in nanostructures has attracted the attention of theorists [1] and experimentalists [2] since the early days of the Bardeen-Cooper-Schrieffer (BCS) theory. Explicit calculations [3] soon showed that, even within a mean field formalism, finite size effects had a profound impact on the superconducting state. Experimentally it was also observed [4, 5] that the superconducting transition in nanowires and small particles became broader as the grain size decreases due to thermal and quantum fluctuations. The use of path integral techniques [5] led to a quantitative description of thermal fluctuations specially in zero dimensional superconductors [6] where the SPA is applicable. By contrast semi-phenomenological models [8] that combined quantum and thermal fluctuations provided only a qualitative description of the broadening of the transition observed in superconducting nanowires. The field received an important impetus in the mid nineties after the experiments of Ralph et al. on single, isolated Al nanoparticles [9] that showed for the first time that superconductivity survived in single particles down to a few nanometers. These experiments also stimulated the theoretical interest in ultrasmall superconductors. At zero temperature, the Richardson’s formalism [10], originally introduced in the context of nuclear physics, made possible to find exact solutions for the low energy excitations of the reduced BCS Hamiltonian [11]. However a theoretical analysis that takes into account thermal and quantum fluctuations simultaneously is still an open problem in the field. In [10] this problem was addressed by combining the SPA, that models thermal fluctuations, with the RPA, that accounts for quantum fluctuations to leading order in $\delta/\Delta_0$. However it was found that the resulting partition function had singularities at low temperature. Progress in this problem are specially timely as recent experiments, taking advantage of advances in the growth and control of nanostructures, have put the basis to test quantitatively the limits of superconductivity in the nanoscale [12, 13, 15, 17, 18].

The main goal of this paper is to put forward a theoretical analysis free of divergences and valid at all temperatures that combines thermal fluctuations and quantum fluctuations to leading order in $\delta/\Delta_0$ in a zero dimension superconductor. These results are of interest for other strongly interacting Fermi systems beyond the realm of superconductivity in nanostructures. Typical examples include hot nuclei (see [19] and references therein), and trapped cold atomic gases [20]. Technical details of the calculation are postponed to a forthcoming publication [23]. Here we summarize the main results, their limits of applicability and some technical aspects. Moreover we also provide explicit results of the order parameter in two simple cases: a constant spectral density and a single, highly degenerate, shell.

Model, approximations and main results

We consider the BCS Hamiltonian:

$$H = \sum_{\alpha, \sigma} \varepsilon_\alpha c_{\alpha, \sigma}^\dagger c_{\alpha, \sigma} - \frac{\delta g}{2} \left( \sum_{\alpha, \alpha'} I(\alpha, \alpha') c_{\alpha, 1}^\dagger c_{-\alpha, -1} c_{-\alpha', -1} c_{\alpha', 1} \right),$$

where $\alpha, -\alpha$ label one-particle states related by time reversal symmetry with energies $\varepsilon_\alpha = \varepsilon_{-\alpha}$, $\delta$ is the mean level spacing, $\sigma = \pm 1$ is the spin label, $g$ the dimensionless coupling constant, $I(\alpha, \alpha') = L^d \int d^d r \Psi_{\alpha}^2(r) \Psi_{\alpha'}^2(r)$ with $\Psi_\alpha$ an eigenstate of the one-body problem and $L$ the system size. The partition function of the model is given by $Z = \text{Tr} \left[ e^{-\beta H} \right]$. Fermionic degree of freedom can be integrated exactly by introducing a complex valued Hubbard-Stratonovich field $\Delta(\tau, r)$ which results in
For ever, even in a grand canonical formalism, it is possible to sensitive to odd-even effects are considered. How-
with the usual RP A around the saddle point solution second order is justified. At $\Delta(0)$ which is valid in the limit $\delta/\Delta_0 < 1$; c) the interacting region in the BCS Hamiltonian is restricted to a narrow interval $[-E_D, E_D]$ around the chemical potential where $E_D$ is the Debye energy. We assume that $I(\alpha, \alpha') = L^d d^d r \Psi_0^2(r) \Psi_0^2(r) \approx 1$ is independent on $\alpha, \alpha'$ and $I(\alpha, \alpha') = 0$ outside the interacting region. This is a good approximation as it was shown in \[14\] that the $\alpha$ dependence is only important for $\xi < L$; d) we assume that for $\delta/\Delta_0 < 1$ Coulomb interactions can be accounted by a simple redefinition of $g$. Recent experiments \[13\] suggest that, at least for Pb and Sn grains, this is a good approximation up to sizes $\delta \sim \Delta_0$ or $L \sim 5$nm.

We also note that, for the sake of simplicity, no observable sensitive to odd-even effects are considered. However, even in a grand canonical formalism, it is possible to take them into account \[21\], at least for low temperatures, by simply blocking the level closest to the Fermi energy.

The main result of this letter is the following expression for $Z$, valid at all temperatures, that includes simultaneously thermal and quantum fluctuations,

$$\frac{Z}{Z_0} = \int D\Delta D\delta e^{-S[\Delta]}$$
(2)

where $Z_0$ is the partition function for free electrons. The main goal of the paper is to evaluate (2), including thermal and quantum fluctuations. The main approximations in our calculation are: a) the grain size is zero dimensional, namely, the coherence length $\xi$, is smaller than the system size. As a consequence, $\Delta(\tau, r)$ only depends on imaginary time $\Delta(\tau, r) \approx \Delta(\tau)$; b) the time dependence is sufficiently weak so that an expansion to second order is justified. At $T = 0$ this corresponds with the usual RPA around the saddle point solution $\Delta_0$ which is valid in the limit $\delta/\Delta_0 < 1$; c) the interacting region in the BCS Hamiltonian is restricted to a narrow interval $[-E_D, E_D]$ around the chemical potential where $E_D$ is the Debye energy. We assume that $I(\alpha, \alpha') = L^d d^d r \Psi_0^2(r) \Psi_0^2(r) \approx 1$ is independent on $\alpha, \alpha'$ and $I(\alpha, \alpha') = 0$ outside the interacting region. This is a good approximation as it was shown in \[14\] that the $\alpha$ dependence is only important for $\xi < L$; d) we assume that for $\delta/\Delta_0 < 1$ Coulomb interactions can be accounted by a simple redefinition of $g$. Recent experiments \[13\] suggest that, at least for Pb and Sn grains, this is a good approximation up to sizes $\delta \sim \Delta_0$ or $L \sim 5$nm.

We also note that, for the sake of simplicity, no observable sensitive to odd-even effects are considered. However, even in a grand canonical formalism, it is possible to take them into account \[21\], at least for low temperatures, by simply blocking the level closest to the Fermi energy.

The main result of this letter is the following expression for $Z$, valid at all temperatures, that includes simultaneously thermal and quantum fluctuations,

$$\frac{Z}{Z_0} = \int_0^\infty ds_0^2 e^{-\beta(A_0(s_0) + A_1(s_0))}$$
(3)

where

$$A_0(s_0) = (\delta g)^{-1} s_0^2$$
(4)

$$A_1(s_0) = \frac{1}{2} \int d\nu \left[ n_b(\nu) - \frac{1}{\beta \nu} \right]$$

$$\times \ln \left( \frac{C(\nu + i0^+)}{C(\nu - i0^+)} \right)$$

$$\times \frac{2}{\pi i},$$

$$\xi = \sqrt{s_0^2 + 2}, \quad g(\varepsilon) = \sum_\alpha \delta(\varepsilon - \varepsilon_\alpha)$$

is the spectral density of the one-body problem, $n_f(z) = \frac{1}{e^{\varepsilon_f + 1} - 1}$ and $n_b(\varepsilon) = \frac{1}{e^{\varepsilon_f + 1}}$ are the Fermi and Bose function respectively and

$$C(z) = (-z^2 + 4s_0^2)(-z^2) \left[ \int_D d\varepsilon g(\varepsilon) \frac{r(\xi)}{-z^2 + (2\xi^2)^2} \right]^2$$

$$+ (-z^2) \left[ \int_D d\varepsilon g(\varepsilon) \frac{2\varepsilon r(\xi)}{-z^2 + (2\xi^2)^2} \right]^2,$$

with $r(\xi) = \frac{1}{\pi} \tanh(\frac{\xi}{2})$ and $\int_D = \int_{-E_D}^{E_D}$. For $T = 0$ we recover the approximations \[10\] and, for $T \gg T_c$, $Z$ is given by the SPA of \[8\].

**Calculation Highlights**

We give an overview of the calculation leading to (3) with special emphasis on the main differences with respect to the techniques of \[10\]. A detailed account of technical details will be provided elsewhere \[23\].

The task is to evaluate simultaneously the contribution to the partition function $Z$ of thermal fluctuations, taken into account by integrating exactly over the static component of $\Delta(\tau)$ (SPA) and quantum fluctuations, arising as small (imaginary) time dependent Gaussian corrections (RPA) to SPA. Previous approaches to this problem \[10\] considered indeed small corrections to a static solution $\Delta(0)$, $\Delta(\tau) = \Delta(0) + \delta\Delta(\tau)$ where $\delta\Delta(\tau)$ is the second derivative matrix for the fluctuations $\delta\Delta(\tau)$. Then $\Delta(0)$ is integrated out exactly but the integral over $\delta\Delta(\tau)$ is carried out in the Gaussian approximation only. It is therefore assumed that any small correction around any $\Delta(0)$ is still a local minimum of the action, namely, the real part of the eigenvalues of $\delta\Delta(\tau)$ is always positive. However it was found in \[10\] that some eigenvalues of $\delta\Delta(\tau)$ acquire a negative real part as the temperature is lowered. As a consequence divergences occur and the theory breaks down, preventing thus the combined study of quantum and thermal fluctuations. Divergences in this context usually suggest the existence of a collective zero mode that must be treated non-perturbatically.

In order to identify this collective mode we separate phase and amplitude fluctuations by using polar coordinates $\Delta(\tau) = s(\tau) e^{i\phi(\tau)}$, with $s(\tau) = s_0 + \delta s(\tau)$ and $\phi(\tau) = \phi_0 + \delta\phi(\tau)$, where $\delta\phi(\tau)$ and $\delta s(\tau)$ are small fluctuations around the static values $s_0, \phi_0$ and $s_0 = \frac{4\pi M}{\xi^2} M (M \in \mathbb{Z})$ accounts for phase configurations with non-trivial winding numbers. Only the $a_0 = 0$ is considered, contributions from different values of $a_0$, known to be related to odd-even effects \[21\] are not addressed here. The identification of this collective mode is nevertheless crucial, if treated perturbatively it will lead to the negative eigenvalues and divergences observed in \[10\]. By contrast, following the above decomposition, the eigenvalues of $\delta\phi(\tau)$ and $\delta s(\tau)$ in our case have always a positive real part and therefore no divergences arise. We can then treat separately the collective mode and integrate exactly over the static phase $\phi_0$. This is the key difference between our method
and that of \[\text{16}\]. As a consequence our results provide a quantitative, free of divergences, description of the combined quantum and thermal fluctuations at any temperature.

**Results**

The natural order parameter for the superconducting transition is the connected pair correlation function \[\Delta^2_C = (g\delta)^2 \sum_{\alpha\alpha'} \langle c_{\alpha'}^\dagger c_{\alpha} c_{\alpha'} c_{\alpha} \rangle \]. An explicit expression for \[\Delta_C\] is obtained in a standard way by adding source terms to the action \[\text{2}\] and deriving with respect to them,\[
\Delta_C^2 = \bar{\Delta}^2 - (\delta g)^2 \int_D \bar{d} \bar{g}(\varepsilon) \left[ \left\langle \left\langle n_{sc}(\xi)^2 \right\rangle \right\rangle - \left\langle \left\langle n_{sc}(\xi) \right\rangle \right\rangle^2 \right],
\]
where
\[
\bar{\Delta}^2 = \left\langle \left\langle s^2 \left( (\delta g) \int_D \bar{d} \bar{g}(\varepsilon) \bar{r}(\xi) \right)^2 \right\rangle \right\rangle,
\]
\[n_{sc}(\xi) = \frac{1}{\xi} \left[ 1 - \frac{1}{\xi} \tanh \left( \frac{\xi}{2} \right) \right],\]
and the average \[\langle \langle \ldots \rangle \rangle\] is defined as
\[
\langle \langle O \rangle \rangle = \frac{Z_0}{\mathcal{Z}} \int_0^{\infty} ds_0^2 e^{-\beta(A_0|s_0|+A_1|s_0|)} O.
\]

In the literature other parameters have been considered to study deviations from mean-field results: for example \[\langle \langle s_0^2 \rangle \rangle \] and \[\Delta^2_b = (g\delta)^2 \sum_{\alpha\alpha'} \left[ \langle c_{\alpha'}^\dagger c_{\alpha} c_{\alpha'} c_{\alpha} \rangle - \langle c_{\alpha'}^\dagger c_{\alpha'} c_{\alpha} c_{\alpha} \rangle \right]_{g=0} \]. The latter can be simply related to \[\Delta^2\] by \[\Delta^2_b = \bar{\Delta}^2 - g\delta (\delta g) \int_D \bar{d} \bar{g}(\varepsilon) \left[ \langle \left\langle n_{sc}(\xi)^2 \right\rangle \rangle - n_f(\varepsilon)^2 \right].\]

For simplicity we assume \[\Delta_C \approx \Delta\] as other terms in \[\text{6}\] do not play a significant role and make the calculation slightly more involved. \[\Delta_C\] becomes the bulk gap for \[\delta \to 0\], and it is expected to be closely related to the spectral gap at finite \[\delta\]. We focus on two specially simple situations: a) a constant spectral density, b) only one level, usually called shell, in the interacting region with a degeneracy \[N_l \gg 1\] such that \[\delta/\Delta_0 \ll 1\] where \[\delta = 2E_D/N_l\]. Physically this corresponds to a spherical or cubic grain in which, due to geometrical symmetries, the spectrum is highly degenerate. Other geometries can be easily studied but calculations are more involved. We postpone this study to a future publication \[\text{22}\].

**Constant spectral density**

In this case \[\bar{g}(\varepsilon) = 1/\delta\] and the partition function \[\text{24}\] cannot be simplified further so we carry out the calculation of \[\Delta_C\] \[\text{6}\] numerically. In Fig.2 we depict \[\Delta_C(T)\] for different values of \[\delta\]. As was expected, no divergences arise at low temperatures. For zero temperature \[\Delta_C(0)\] is equal to the RPA result \[\text{16}\] that predicts a leading correction \[\Delta_C(0) = \Delta_0(1 + \alpha \delta/E_D)\] with \[\alpha\] a constant of order the unity. For \[T \gg T_C\], \[\Delta_C\] agrees with the SPA \[\text{6}\] that describes thermal but not quantum fluctuations (see Fig.2). Results from Richardson’s formalism \[\text{10, 22}\] at \[T = 0\] are similar but a direct comparison is not possible as \[\Delta_C\] is not exactly the spectral gap. In Fig.2 we depict the difference between \[\text{7}\] and the SPA prediction. Deviations at low temperatures are mostly due to the RPA correction, however it is clearly observed that, for intermediate temperatures, differences from SPA results increase as a consequence of the combined effect of thermal and quantum fluctuations. Previously this region was not accessible to analytical calculations. We note that the observed enhancement of \[\Delta_C\] by quantum and thermal fluctuations is not an indication that superconductivity is more robust. In fact fluctuations always weaken long range order causing phase slips and the broadening of the transition. The gap is enhanced because fluctuations induce pairing in circumstances which are not allowed by a mean field formalism.

**Shell models**

The calculation of the partition function greatly simplifies by assuming that there are only two degenerate levels (shells) in the interaction region. We note that quantum fluctuations are still small, and therefore our formalism is still applicable, provided that the degeneracy of the level \[N_l/2\] is large enough such that \[\delta \ll \Delta_0\] where in this case \[\delta = 2E_D/N_l\]. With this simplification it is possible to find an explicit expression for \[A_1\]. For two shells with energy at \[\pm \varepsilon_0\] (i.e. \[\bar{g}(\varepsilon) = \frac{N_l}{2} [\delta (\varepsilon - \varepsilon_0) + \delta (\varepsilon + \varepsilon_0)]\]}
We have studied the combined effect of thermal and quantum fluctuations in a zero dimensional superconductor. For the first time we have obtained explicit expressions for $Z$ and $\Delta_C(T)$ valid for all temperatures and to leading order in $\delta/\Delta_0$. For intermediate temperatures both fluctuations contribute substantially to $\Delta_C(T)$. These results provide a solid theoretical framework to describe quantitatively pairing in confined geometries at finite temperature beyond the mean field approximation. A problem of current interest in condensed matter, nuclear and cold atom physics.

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