Theoretical Description of the Superconducting State of Nanostructures at Intermediate Temperatures: A Combined Treatment of Collective Modes and Fluctuations

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A rigorous treatment of the combined effect of thermal and quantum fluctuations in a zero-dimensional superconductor is considered one of the most relevant and still-unsolved problems in the theory of nanoscale superconductors. In this Letter, we notice that the divergences that plagued previous calculations are avoided by identifying and treating nonperturbatively a low-energy collective mode. In this way, we obtain for the first time closed expressions for the partition function and the superconducting order parameter which include both types of fluctuation and are valid at any temperature and to leading order in δ/Δ_0, where δ is the mean level spacing and Δ_0 is the bulk energy gap. Our results pave the way for a quantitative description of superconductivity in nanostructures at finite temperature and pairing in hot nuclei.

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Superconductivity in nanostructures has attracted the attention of the condensed matter community since the early days of the Bardeen-Cooper-Schriffer (BCS) theory [1]. Later, it was observed [2] that the superconducting transition in nanowires and small particles became broader as the grain size decreased due to thermal and quantum fluctuations. The use of path integral techniques [3,4] led to a quantitative description of thermal fluctuations, especially in zero-dimensional superconductors [3] where the static phase approximation (SPA) is applicable. For one-dimensional systems, the theoretical treatment of quantum fluctuations of [5] provided a semiquantitative description (up to a numeric prefactor) of the broadening of the transition observed in [2]. The field received an important impetus in the mid-1990s after the experiments of Ralph *et al.* on single, isolated Al nanoparticles [6] 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, Richardson's formalism [7] made it possible to find exact solutions for the low-energy excitations of the reduced BCS Hamiltonian [8]. However, a theoretical analysis that takes into account thermal and quantum fluctuations simultaneously is still an open problem in the field. In [9], this problem was addressed by combining the SPA, which models thermal fluctuations, with the random phase approximation (RPA), which accounts for quantum fluctuations to leading order in δ/Δ_0. However, it was found that the resulting partition function had singularities at low temperature. Progress in this problem is especially timely, as recent experiments, taking advantage of advances in the growth and control of nanostructures, have put the basis to quantitatively test the limits of superconductivity in the nanoscale [10,11]. On the theoretical side, a satisfactory description of both effects is broadly considered [12] as a key step to open new avenues of research.

The main goal of this Letter is to put forward a theoretical analysis free of divergences and valid at all temperatures that combines thermal and quantum fluctuations to leading order in δ/Δ_0 in a zero-dimensional superconductor. These results are of interest for other strongly interacting fermionic systems. For instance, for the quantitative description of pairing in heavy nuclei, it is necessary to take into account quantum and thermal fluctuations [13] (see also [14] for a recent review). In the context of cold atomic gases, a similar effect becomes important as a result of the interplay between pairing and the optical potential that traps the atomic gas [15].

Technical details of the calculation are postponed to a forthcoming publication [16]. Here, we summarize the main results, their limits of applicability, and the key technical aspects. Moreover, we also provide explicit results of the order parameter in two simple cases: a constant spectral density and two highly degenerate shells.

Model, approximations, and main results.—We consider the BCS Hamiltonian:

$$H = \sum_{\alpha,\sigma} \varepsilon_\alpha c^\dagger_{\alpha,\sigma} c_{\alpha,\sigma} - \delta g \Big(\sum_{\alpha,\alpha'} c_{\alpha,1} c^\dagger_{-\alpha,-1} c_{-\alpha',-1} c_{\alpha',1} \Big),$$

where α and $-\alpha$ label one-particle states related by time reversal symmetry with energies $\varepsilon_\alpha = \varepsilon_{-\alpha}$, δ is the mean level spacing, $\sigma = \pm 1$ is the spin label, and g is the dimensionless coupling constant. The partition function of the model is given by $Z = \mathrm{Tr}[e^{-\beta H}]$. The fermionic degree of freedom can be integrated exactly by introducing a complex valued Hubbard-Stratonovich field $\Delta(\tau, r)$ which results in a partition function $Z/Z_0 = \int \mathcal{D}\Delta^\dagger \mathcal{D}\Delta e^{-S[\Delta]}$, where Z_0 is the partition function for free electrons. The main goal of the paper is to evaluate Z including thermal and quantum fluctuations. The main approximations in our calculation are (a) the grain size is zero-dimensional, namely, the coherence length ξ is larger 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 the second order is justified. At $T = 0$, this corresponds with the usual RPA around the saddle point solution Δ_0 which is valid in the limit $\delta/\Delta_0 < 1$. (c) We assume that, for $\delta/\Delta_0 < 1$, Coulomb interactions can be accounted by a simple redefinition of g. Recent experiments [11] 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.

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

$$Z/Z_0 = \int_0^\infty ds_0^2 e^{-\beta(\mathcal{A}_0[s_0] + \mathcal{A}_1[s_0])}, \tag{1}$$

where

$$\mathcal{A}_0[s_0] = (\delta g)^{-1} s_0^2 - \frac{2}{\beta} \int_D d\varepsilon \varrho(\varepsilon) \times \ln\left[\cosh\left(\frac{\beta\xi}{2}\right) / \cosh\left(\frac{\beta|\varepsilon|}{2}\right)\right], \tag{2}$$

$$\mathcal{A}_1[s_0] = \frac{1}{2} \int d\nu \left[n_B(\nu) - \frac{1}{\beta\nu}\right] \times \frac{1}{2\pi i} \{\ln[\tilde{C}(\nu + i0^+)] - \ln[\tilde{C}(\nu - i0^+)]\}, \tag{3}$$

where $\xi = \sqrt{s_0^2 + \varepsilon^2}$; $\varrho(\varepsilon) = \sum_\alpha \delta(\varepsilon - \varepsilon_\alpha)$ is the spectral density of the one-body problem; $n_{\frac{F}{B}}(z) = \frac{1}{e^{\beta z} \pm 1}$ are, respectively, the Fermi and Bose functions; and

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

with $r(\xi) = \frac{1}{2\xi} \tanh(\frac{\beta\xi}{2})$ and $\int_D = \int_{-E_D}^{E_D}$. For $T = 0$, we recover the RPA results [9], and, for $T \gg T_c$, Z is given by the SPA of [3].

Calculation Highlights.—We give an overview of the calculation leading to (1) with special emphasis on the main differences with respect to the techniques of [9]. A comprehensive account of technical details will be provided elsewhere [16].

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 [9] considered indeed small corrections $\delta\Delta(\tau)$ to a static solution $\Delta(0)$, $\Delta(\tau) = \Delta(0) + \delta\Delta(\tau)$. Then, $\Delta(0)$ is integrated out exactly and the integral over $\delta\Delta(\tau)$ is carried out in the Gaussian approximation. 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 $\Xi_{ij} = \frac{\delta S}{\delta X_i \delta X_j}|_{\Delta(\tau)=\Delta(0)}$ [with $X_{1,2} = \Delta(\tau), \bar{\Delta}(\tau)$] is always positive. However, it was found in [9] that some eigenvalues of Ξ acquire a negative real part as the temperature is lowered. As a consequence, divergences occur and the theory breaks down, thus preventing 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 nonperturbatively. 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 $\phi(\tau) = \frac{2\pi}{\beta} M\tau + \phi_0 + \delta\phi(\tau)$, where $\delta\phi(\tau)$ and $\delta s(\tau)$ are small fluctuations around the static values s_0 and ϕ_0, and $M \in \mathbb{Z}$ accounts for phase configurations with nontrivial winding numbers. Note that a simple gradient expansion of the action generates, up to second order in $\partial_\tau\phi(\tau)$, a contribution of the form $\frac{i}{2\pi}\langle N\rangle_{s_0} \int d\tau \partial_\tau \phi(\tau) + \frac{1}{4\delta} \int d\tau [\partial_\tau\phi(\tau)]^2$ (where $\langle N\rangle_{s_0}$ is the average number of electrons in the dot for a fixed s_0) [17,18]. A collective mode can be explicitly identified with an exact zero mode by noticing that such a contribution is time-translation-invariant $[\phi(\tau) \to \phi(\tau + \tau_0)]$. The identification of this collective mode, which is evident only in polar coordinates, is nevertheless crucial. If treated perturbatively, it will lead to the negative eigenvalues and divergences observed in [9]. By contrast, following the above decomposition, we restrict Ξ to a subspace where the zero modes were removed; therefore, its eigenvalues always have a positive real part and no divergences arise. In other words, unlike [19], where the full low-energy sector has divergences, in our model, the Gaussian integration is accurate for all nonzero modes, provided that $\delta\phi(\tau)$ and $\delta s(\tau)$ are small. We can then treat separately the collective mode and integrate exactly over the static phase ϕ_0. This is the key difference between our method and that of [9]. As a consequence, our results provide a quantitative, free-of-divergences, description of the combined quantum and thermal fluctuations at any temperature. Finally, we note that only the $M = 0$ contribution is considered here and, instead, we keep the full gradient dependence of the action. The reason for that is that, at $T = 0$, the $M \neq 0$ contributions are related to odd-even effects [18] not addressed in this Letter. At $T \neq 0$, the action of paths with $M \neq 0$ is proportional to M^2 [17], and consequently its contribution to the partition function is not important.

The described procedure leads to the partition function

$$Z = \int_{-\pi}^{\pi} \frac{d\phi_0}{2\pi} \int_0^\infty ds_0^2 e^{-\beta \mathcal{A}_0[s_0]} \times \int \mathcal{D}'\tilde{s}^2 \mathcal{D}'\phi \times e^{-1/2\sum_{m\neq 0} \begin{pmatrix} \tilde{s}^2_{-m} \\ \phi_{-m}\end{pmatrix} \cdot \begin{pmatrix} \Xi_m^{s^2s^2} & \Xi_m^{s^2\phi} \\ \Xi_m^{\phi s^2} & \Xi_m^{\phi\phi}\end{pmatrix} \begin{pmatrix}\tilde{s}^2_m \\ \phi_m\end{pmatrix}}, \tag{5}$$

where $\Xi_m^{s^2s^2} = \beta^{-1}\frac{1}{2s_0^2}\frac{\sum_\alpha c_\alpha(1-\{(2\varepsilon_\alpha)^2/[\Omega_m^2+(2\xi_\alpha)^2]\})}{[\sum_\alpha c_\alpha]^2}$, $\Xi_m^{\phi\phi} = \beta\sum_\alpha c_\alpha \frac{2s_0^2\Omega_m^2}{\Omega_m^2+(2\xi_\alpha)^2}$, and $\Xi_m^{s^2\phi} = -\Xi_m^{\phi s^2} = \frac{\sum_\alpha c_\alpha\{\Omega_m(2\varepsilon_\alpha)/[\Omega_m^2+(2\xi_\alpha)^2]\}}{\sum_\alpha c_\alpha}$, with $c_\alpha = \frac{[n_f(-\xi_\alpha)-n_f(\xi_\alpha)]}{2\xi_\alpha}$ and $\tilde{s}_m^2 = (\beta\sum_\alpha c_\alpha)s_m^2$. ϕ_m and s_m^2 are the mth Matsubara component of $\delta\phi(\tau)$ and $\delta s^2(\tau)$ [defined as $Y_m = \frac{1}{\beta}\int d\tau e^{i\Omega_m\tau}Y(\tau)$, $Y = \delta\phi, \delta s^2$]. $\mathcal{D}'$ stands for the integration over the nonzero Matsubara components, and Ξ_m is normalized such that $\det\Xi_{m\to\infty} = 1$. $\mathcal{A}_0[s_0]$ is an extensive part of the action coming from the integration of the electronic degrees of freedom, and $\mathcal{A}_1[s_0]$ in Eqs. (1) and (3) is the spectral determinant resulting from the Gaussian integration over the fluctuations around the mean-field solution. From these considerations, one can interpret $-\frac{1}{\pi}\,\mathrm{Im}\tilde{C}(\nu + i0^+)$, given in Eq. (4), as the density of states of the fluctuating modes.

Results.—The natural order parameter for the superconducting (sc) transition is the connected pair correlation function $\Delta_C^2 = (g\delta)^2\sum_{\alpha\alpha'}\langle c^\dagger_{\alpha'1}c^\dagger_{\alpha'-1}c_{\alpha-1}c_{\alpha1}\rangle_C$. An explicit expression for Δ_C is obtained in a standard way by adding source terms to the action S and deriving, with respect to them,

$$\Delta_C^2 = \bar{\Delta}^2 - (\delta g)^2\int_D d\varepsilon\varrho(\varepsilon)[\langle\langle n_{\mathrm{sc}}(\xi)^2\rangle\rangle - \langle\langle n_{\mathrm{sc}}(\xi)\rangle\rangle^2], \tag{6}$$

where

$$\bar{\Delta}^2 = \left\langle\left\langle s_0^2\left[(\delta g)\int_D d\varepsilon\varrho(\varepsilon)r(\xi)\right]^2\right\rangle\right\rangle, \tag{7}$$

$n_{\mathrm{sc}}(\xi) = \frac{1}{2}[1 - \frac{\varepsilon}{\xi}\tanh(\frac{\beta\xi}{2})]$, and the average $\langle\langle\cdots\rangle\rangle$ is defined as $\langle\langle O\rangle\rangle = \frac{Z_0}{Z}\int_0^\infty ds_0^2 e^{-\beta(\mathcal{A}_0[s_0]+\mathcal{A}_1[s_0])}O$. In the literature, other parameters have been considered to study deviations from mean-field results: for example, $\langle\langle s_0^2\rangle\rangle$ [3] and $\Delta_P^2 = (g\delta)^2\sum_{\alpha\alpha'}[\langle c^\dagger_{\alpha'1}c^\dagger_{\alpha'-1}c_{\alpha-1}c_{\alpha1}\rangle_g - \langle c^\dagger_{\alpha'1}c^\dagger_{\alpha'-1}c_{\alpha-1}c_{\alpha1}\rangle_{g=0}]$ [9]. The latter can be simply related to (7) by $\Delta_P^2 = \bar{\Delta}^2 - g\delta(\delta g)\int_D d\varepsilon\varrho(\varepsilon)\times[\langle\langle n_{\mathrm{sc}}(\xi)^2\rangle\rangle - n_f(\varepsilon)^2]$. For simplicity, we assume $\Delta_C \approx \bar{\Delta}$, as other terms in (6) do not play a significant role and make the calculation slightly more involved. Δ_C becomes the bulk gap for $\delta \to 0$ and it is expected to be closely related to the spectral gap at finite δ. We focus on two especially simple situations: (a) a constant spectral density and (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 [16].

Constant spectral density.—In this case, $\varrho(\varepsilon) = 1/\delta$ and the partition function (5) cannot be simplified further, so we carry out the calculation of Δ_C (6) numerically. In Fig. 1, we depict $\Delta_C(T)$ for different values of δ. As was expected, no divergences arise at low temperatures. For zero temperature, $\Delta_C(0)$ is equal to the RPA result [9] that predicts a leading correction $\Delta_C(0) = \Delta_0(1 + \alpha\delta/E_D)$, with α a constant of the order unity. For $T \gg T_C$, Δ_C agrees with the SPA [3] that describes thermal but not quantum fluctuations (see Fig. 2). Results from Richardson's formalism [7,20] at $T = 0$ are similar, but a direct comparison is not possible, as Δ_C is not exactly the spectral gap. In Fig. 2, we depict the difference between (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 Δ_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 within a mean-field approach.

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

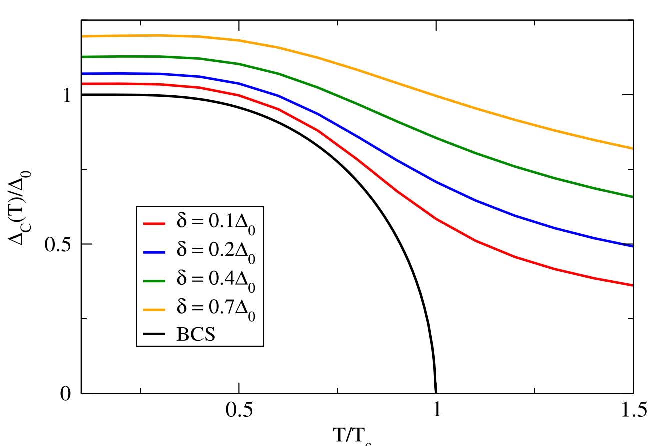

FIG. 1 (color online). $\Delta_C(T)$ (6) for a constant spectral density $\rho(\varepsilon) = 1/\delta$. $\Delta_C(T)$ combines thermal and quantum fluctuations. It reduces to the RPA (SPA) for $T \ll T_C$ ($T \gg T_c$).

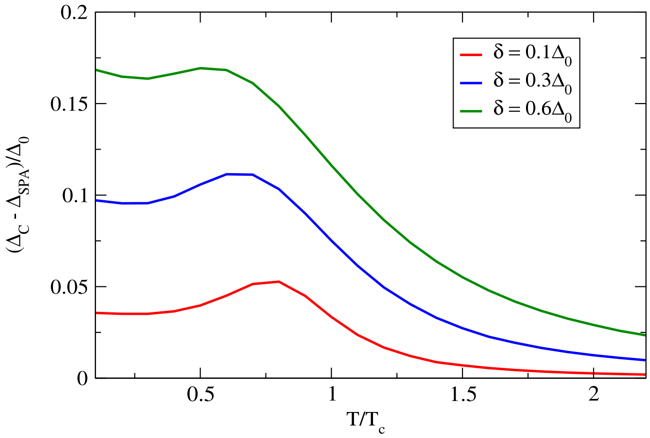

FIG. 2 (color online). Difference between $\Delta_C(T)$ (6) and the SPA prediction [3] which only takes into account thermal fluctuations for different δ's. It is assumed that $\rho(\epsilon) \approx 1/\delta$. For low temperatures, the difference is just the usual RPA correction that describes quantum fluctuations at $T = 0$. However, the peak observed close to T_c is due to the nontrivial interplay of thermal and quantum fluctuations which is beyond the reach of SPA and RPA separately.

$\delta \ll \Delta_0$, where, in this case, $\delta = 2E_D/N_l$. With this simplification, we find an explicit expression for $\mathcal{A}_1$. For two shells with energy at $\pm\varepsilon_0$ {i.e., $\varrho(\varepsilon) = \frac{N_l}{2}[\delta(\varepsilon - \varepsilon_0) + \delta(\varepsilon + \varepsilon_0)]$}, $\mathcal{A}_0$ and $\mathcal{A}_1$ in (1) are given by

$$\mathcal{A}_0[s_0] = \delta g\left\{ s_0^2 - \frac{4\varepsilon_0 \coth(\frac{\varepsilon_0\beta_c}{2}) \log[\frac{\cosh[(1/2)\beta\sqrt{\varepsilon_0^2+s_0^2}]}{\mathrm{sech}[(\beta|\varepsilon_0|)/2]}]}{\beta}\right\},$$

$\mathcal{A}_1[s_0] = \frac{1}{\beta}\ln[\frac{\beta\xi_0^2 \mathrm{csch}^2(\beta\xi_0)\sinh(\beta s_0)}{s_0}]$, where $\xi_0 = \sqrt{s_0^2 + \varepsilon_0^2}$ and $\beta_c = T_c^{-1} = \frac{2\coth^{-1}(E_D g/\varepsilon_0)}{\varepsilon_0}$. For $T = 0$, the first correction to the mean-field result coincides with the RPA prediction, $\Delta_C = \Delta_0(1 + \frac{g\delta}{\Delta_0}\{\sqrt{1 + (\frac{\varepsilon_0}{\Delta_0})^2} - \frac{1}{2}[1 + (\frac{\varepsilon_0}{\Delta_0})^2]\})$, where $\Delta_0 = \sqrt{E_D^2 g^2 - \varepsilon_0^2}$. In the limit $T \gg T_c$, it is also possible to obtain explicit expressions of Δ_C by expanding the action in powers of s_0. To the lowest order in δ, the SPA result $\Delta_C \simeq \sqrt{\frac{\delta g \tanh^2(\beta\varepsilon_0/2)\coth^2(\beta_c\varepsilon_0/2)}{\beta[1-\tanh(\beta\varepsilon_0/2)\coth(\beta_c\varepsilon_0/2)]}}$ is recovered. Higher-order terms include deviations from the SPA due to quantum fluctuations.

In summary, we have shown for the first time that thermal and quantum fluctuations can be combined in a single theoretical framework. We have cured divergences that plagued previous calculations by integrating exactly a zero-energy mode. As a result, we obtain explicit expressions for Z and $\Delta_C(T)$ valid for all temperatures and to leading order in δ/Δ_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. Natural extensions of this work include the calculation of odd-even effects, magnetic susceptibilities and the differential conductance, and the outcome of STM experiments [16].

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