Survival of parity effects in superconducting grains at finite temperature

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We study the thermodynamics of a small, isolated superconducting grain using a recently developed quantum Monte Carlo method. This method allows us to simulate grains at any finite temperature and with any level spacing in an exact way. We focus on the pairing energy, pairing gap, condensation energy, heat capacity, and spin susceptibility to describe the grain. We discuss the interplay between finite size (mesoscopic system), pairing correlations, and temperature in full detail.

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The bulk properties of a superconductor are well described by the standard BCS theory. When the system size is reduced, however, its mesoscopic behavior is strongly dictated by the finite electron number. For such small systems with a fixed number of particles, the BCS theory is no longer applicable since the BCS order parameter is identically zero. Therefore, it cannot determine the lower size limit for which the system exhibits superconducting properties. It was suggested by Anderson[1] that the superconductivity would disappear once the average level spacing d ($\propto 1/V$, V being the volume of the system) of the electron spectrum becomes larger than the bulk superconducting gap Δ. Due to a series of experiments by Ralph, Black, and Tinkham (RBT) (Ref. 2) on the transport through a single superconducting nm-scale Al grain, a lot of authors shed new light on Anderson's suggestion. In their experiments, RBT found a spectroscopic gap larger than the average level spacing, which goes to zero when applying a suitable magnetic field. The measurements also revealed a peculiar parity effect: grains with an even number of electrons have a larger gap in the spectrum than grains with an odd electron number. These observations were regarded as signs of "superconductivity," in the sense that there is a pair-correlated ground state. Properties indicative of strong pairing correlations were only found in grains with $d \lesssim \Delta$. So Anderson's answer turned out to be uncomplete, since it does not differentiate between odd and even numbers of electrons. A large number of theoretical studies tried to characterize the ground state correlations and superconductivity of such small systems in a qualitative way and tried to predict the critical level spacing at which the superconductivity breaks down. An extended review can be found in Ref. 3. In this report we study the competition between pairing, finite size, and finite temperature in an exact way, with all quantum correlations taken into account.

To model small superconducting grains, one uses the reduced BCS Hamiltonian[4]

$$H = \sum_{\sigma=\pm, j=1}^{\Omega} (\epsilon_j - \sigma\mu_B h) c^\dagger_{j,\sigma} c_{j,\sigma} - \lambda d \sum_{j,j'=1}^{\Omega} B^\dagger_j B_{j'}, \qquad (1)$$

where $B^\dagger_j = c^\dagger_{j,+} c^\dagger_{j,-}$. The operator $c^\dagger_{j,\sigma}$ creates an electron in the single-particle state $|j,\sigma\rangle$. The quantum number j labels the Ω single-particle levels with energies ϵ_j, and σ labels time-reversed states. Since the pairing interaction only scatters time-reversed pairs of electrons within an energy ω_D of the Fermi level ϵ_F, electrons outside the cutoff are not taken into account. The parameter λ is the dimensionless BCS coupling constant and is related to Δ and ω_D via the bulk gap equation $\sinh(1/\lambda) = \omega_D/\Delta$.[5] We take $\lambda = 0.224$, close to that of Al.[6] The Zeeman term couples an external magnetic field h to the electrons and μ_B is the Bohr magneton. Throughout the paper, we will consider a half-filled band with fixed width $2\omega_D$ and $\Omega = 2\omega_D/d$ doubly degenerate and uniformly spaced levels with energies $\epsilon_j = jd$. We will only discuss the case without magnetic field h.

To study the crossover from the bulk to the few electron limit, a number of authors originally used a parity-projected grand canonical (g.c.) BCS approach.[4,7–11] The parity effect can be explained with this variational technique. However, an artificial sharp transition to the normal state appears at some critical level spacing and temperature, which is impossible for a finite system. Since the electron number fluctuations are strongly suppressed by charging effects in the experiments of RBT, it is clear that a canonical formalism is needed to describe the grains properly. A number of canonical techniques were used to tackle this problem. Unfortunately, exact diagonalization techniques (e.g., Lanczos[12]) can only handle systems with a very small number of electrons. In order to go to larger model spaces, the particle number projection was combined with the static path approximation plus random-phase approximation treatment[13,14] and with variational wave functions.[6] Dukelsky and Sierra developed a particle-hole version of the density-matrix renormalization-group method to study the crossover.[15,16] All these canonical techniques reveal the parity effect at low enough temperatures, and make clear that the abrupt crossover is just an artefact of the g.c. approach. It turned out that small grains with $d \lesssim \Delta$ are indeed characterized by strong superconducting pairing correlations. As the grain size decreases, quantum fluctuations of the order parameter start to play a crucial role. These fluctuations make the crossover completely smooth without any sign of critical level spacing. Only when the grain is not too small ($d \ll \Delta$) the fluctuations in the order parameter can be neglected, making the mean field description of superconductivity appropriate. In the canonical picture, pairing correlations still exist at arbitrary large values of d/Δ, though in the form of weak fluctuations. Qualitative differences between the pairing correlations in the bulk and

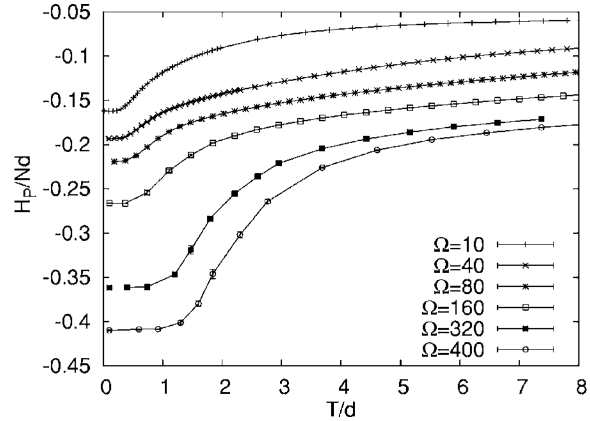

FIG. 1. The temperature dependence of the pairing energy per electron for grains with an even number $N=\Omega$ of electrons. Simulations were performed for different grain sizes Ω. The energy and temperature scale is set by the level spacing d.

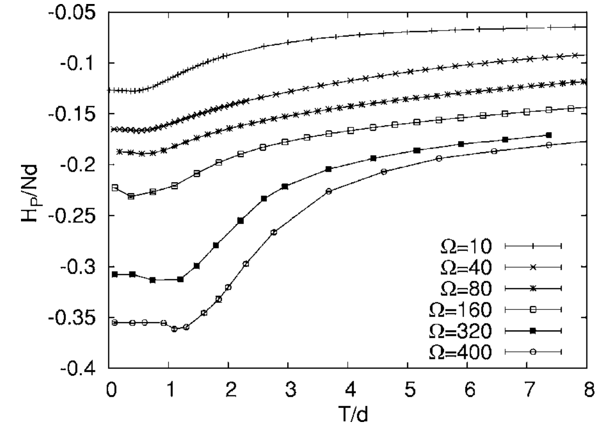

FIG. 2. The pairing energy per electron as a function of temperature for an odd grain with different sizes. Simulations were performed for grains with $N=\Omega+1$ electrons.

the few-electron regime make it still possible to speak of the superconducting regime ($d \ll \Delta$) and the fluctuation-dominated regime ($d \gtrsim \Delta$).[3]

It was only after the appearance of most of these works that one became aware of the fact that the reduced BCS model has an exact solution, worked out decades ago by Richardson in the context of nuclear physics.[17] In Ref. 18, Sierra *et al.* compare the previously mentioned treatments with the exact solution. Using this exact solution to study the finite temperature behavior for a large number of many-particle states is difficult due to the exponential scaling of the number of eigenstates that need to be considered. Gladilin *et al.* developed an approximation based on the Richardson solution to get finite temperature information.[19] In Ref. 3 it was already suggested by von Delft and Ralph that quantum Monte Carlo (QMC) techniques could be helpful to investigate the BCS pairing model at finite temperature. Recently we developed a new quantum Monte Carlo method[20,21] that is able to simulate the BCS model for any fixed number of particles without a sign problem. The method allows calculating thermodynamic properties in an exact way, up to a controllable statistical error. Simulations can be performed at any finite temperature and any level spacing d/Δ for large system sizes. Because our method allows a projection on specific symmetries such as the total spin projection, we can calculate the susceptibility and magnetization.

We performed simulations of grains with different sizes (Ω equal to 10, 40, 80, 160, 320, and 400). These half-filled model spaces lead, respectively, to ratios d/Δ of 8.68, 2.17, 1.09, 0.54, 0.27, and 0.22. Figures 1 and 2 show the thermal averages of the pairing energy $H_P=-\lambda d\Sigma_{j,j'=1}^{\Omega} B_j^\dagger B_{j'}$ per particle as a function of temperature for even and odd grains. The energy scale is set by the level spacing d. By comparing both figures, one notices that at low enough temperatures (typically $T \lesssim d$) the even electron system has more pairing energy than the odd system. This is due to the single unpaired electron, which blocks the Fermi level in the odd case. Around $T \approx d$ a small dip appears in the odd pairing energy. Qualitatively, this can be explained as follows: due to the thermal energy, the single unpaired electron is moved one level upward, making the Fermi level available to pair scattering. This is reflected in a slight decrease of the pairing energy in Fig. 2. To measure the real correlation energy due to pairing in the system, the "canonical" pairing gap

$$\Delta_{\rm can}^2 = (\lambda d)^2 \sum_{m,n=1}^{\Omega} \left(\langle B_m^\dagger B_n \rangle - \langle B_m^\dagger B_n \rangle_{\lambda=0} \right), \qquad (2)$$

was introduced in Eq. (92) of Ref. 3. The second term subtracts the thermal average of the pairing interaction for the noninteracting system. When going to the thermodynamic limit, $\Delta_{\rm can}$ becomes equivalent to the BCS bulk gap Δ.[3] Figure 3 shows the even and odd canonical gap for different system sizes. It follows very clearly that the temperature scale at which the parity effect appears is set by the level spacing d, and this for all grain sizes. The crossover temperature is given by $T_{cr}=\Delta \ln N_{\rm eff}$, with $N_{\rm eff}$ the effective number of states available for excitation ($N_{\rm eff}=\sqrt{8\pi T\Delta}/d$ in the limit $d \ll \Delta$).[22] This is in qualitative agreement with Fig. 3, where

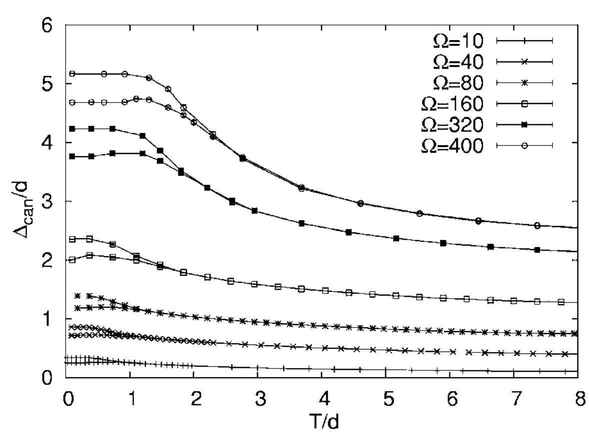

FIG. 3. The canonical pairing gap as a function of temperature. For each number of levels Ω the gap is calculated for an even ($N=\Omega$) and an odd ($N=\Omega+1$) number of electrons. Only at low enough temperature one can distinguish between the gap of the even grain (upper curve) and the odd grain (lower curve) of the same size Ω.

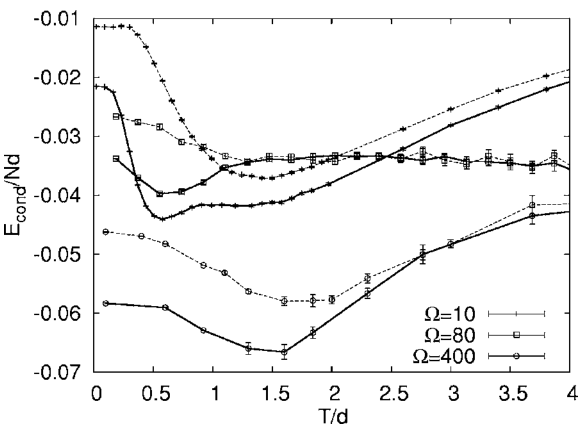

FIG. 4. The condensation energy per particle as a function of T/d for system sizes $\Omega=10$, 80, and 400. Even (odd) grain data points are connected by a solid (dashed) line.

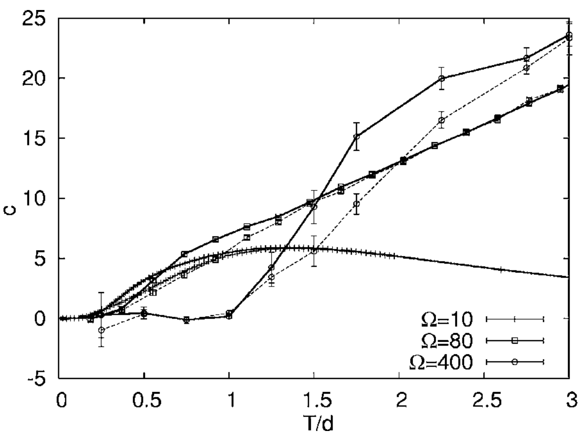

FIG. 5. The heat capacity $c=\partial\langle H\rangle/\partial T$ as a function of T/d for system sizes $\Omega=10$, 80, and 400. Even (odd) grain data points are connected by a solid (dashed) line. Around temperatures $T\approx 0.5d$ for $\Omega=10$, 80, and $T\approx d$ for $\Omega=400$ the heat capacity of the even grain (with $N=\Omega$ electrons) exceeds the odd ($N=\Omega+1$) specific capacity.

the crossover temperature decreases as the grain size is reduced. One should, of course, keep in mind that the temperature is shown in units of the level spacing which is considerably smaller for the largest grains. Figure 3 shows that pairing correlations persist even for ultrasmall grains and that a reduction of the grain size leads to a suppression of these correlations.

The condensation energy $E_{cond}=\langle\psi|H|\psi\rangle-\langle FS|H|FS\rangle$ is the energy difference of the state $|\psi\rangle$, where all quantum correlations are included, and the uncorrelated Fermi sea $|FS\rangle$. Figure 4 shows the thermal average of the condensation energy per particle for a number of even and odd grains as a function of temperature. These energy differences were obtained by calculating the thermal averages of the Hamiltonian over correlated states $|\psi\rangle$ and over the Fermi states $|FS\rangle$ separately. Below temperatures of the order d, the even grains have a larger condensation energy (in absolute value). Both even and odd grains have a minimal condensation energy around $T\approx d$. In agreement with Ref. 3, our calculations give an almost intensive condensation energy for the smallest grains ($d\gg\Delta$), while the condensation energy of grains with $d\ll\Delta$ increases (in absolute value) inversely proportional to d.

Figure 5 shows the heat capacity as a function of temperature for sizes $\Omega=10$, 80, and 400. Around the crossover temperature where the parity effect becomes visible (see Figs. 3 and 4), a slight parity effect also appears in the heat capacity. Here the even heat capacity exceeds the odd one. At higher temperatures the odd and even results become indistinguishable again. For the $\Omega=10$ grain size, the finite model space makes the Shottky peak visible when the temperature becomes of the order of the level spacing.

The spin susceptibility of a grain is defined by

$$\chi(T) = - \left.\frac{\partial \mathcal{F}(T,h)}{\partial h^2}\right|_{h=0}$$

$$= \frac{1}{T}(\langle M^2\rangle - \langle M\rangle^2). \tag{3}$$

Here $\mathcal{F}=-T\ln Z$ is the free energy of the grain, with Z the canonical partition function. The susceptibility is proportional to the fluctuation of the "magnetization" $M=-\mu_B\sum_{\sigma,n}\sigma c^\dagger_{n,\sigma}c_{n,\sigma}$ at finite temperature T. The spin susceptibility of a single isolated grain has been studied by Di Lorenzo *et al.*[23] They found that the pairing correlations affect the temperature dependence of the spin susceptibility. In particular, if the number of electrons in the grain is odd, the spin susceptibility shows a reentrant behavior as a function of T for any value of the ratio d/Δ. They show that this behavior persists even in the case of ultrasmall grains, where the level spacing is much larger than the BCS gap. Since this reentrance behavior is absent in normal metallic grains, they suggested that this quantity can be measured and used as a unique signature of pairing correlations in small and ultrasmall grains. The susceptibility was calculated by combining an analytic analysis in the limiting cases $\Delta\gg d$ and $\Delta\ll d$ with a static path approximation for intermediate values. By means of exact canonical methods based on Richardson's solution, they also got exact results at low temperatures. With the aid of our QMC method, we are now able to solve the problem exactly for the whole temperature range. Figures 6 and 7 show the temperature dependence of the spin susceptibility for a number of even and odd grains, respectively. The susceptibility is normalized to its bulk high temperature value $\chi_P=2\mu_B^2/d$. Our results are completely in line with those of Di Lorenzo *et al.*[23] At low temperatures the even susceptibility remains exponentially small, while for an odd grain the unpaired spin gives rise to an extra paramagnetic contribution to the spin susceptibility ($\chi\simeq\mu_B^2/T$). The minima in the odd spin susceptibilities coincide with a small increase of the pairing correlations (see Figs. 2 and 3), with a mimimal condensation energy (see Fig. 4), and with a parity effect in the heat capacity (see Fig. 5). For the smallest odd grain no reentrant behavior is visible in Fig. 7. This is an effect of the finite model space. If the BCS coupling constant is increased a little, a reentrance effect appears also in this case.

In conclusion, we solved the BCS pairing problem at a finite temperature exactly via quantum Monte Carlo simula-

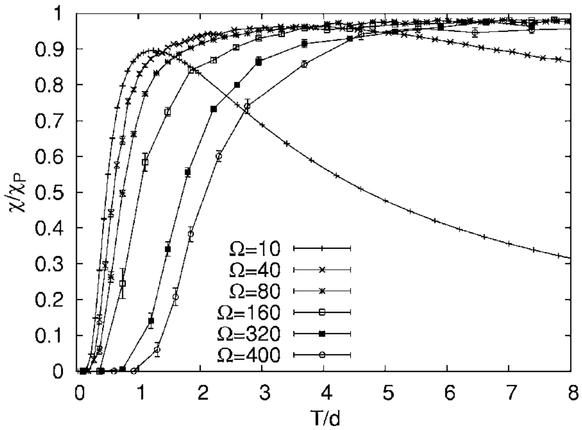

FIG. 6. The spin susceptibility normalized to its bulk high temperature value χ_P as a function of T/d for a number of even grains. Each grain contains $N=\Omega$ electrons, with Ω the model space size.

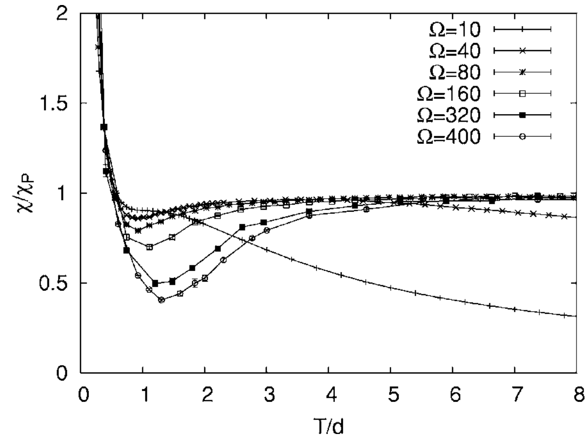

FIG. 7. The spin susceptibility as a function of T/d for a number of odd grains (containing $N=\Omega+1$ electrons). The grain size is determined by the model space size Ω.

tion. We studied odd and even grains with a large number of electrons and arbitrary level spacings. Our exact results confirm predictions of previous approximate calculations, showing that the physics of ultrasmall superconducting grains is well described by a pairing model with exact particle number projection and that parity effects are visible in thermodynamic properties.

The number of unpaired electrons in a grain can be increased by an external magnetic field. Frauendorf *et al.* showed that at zero temperature a magnetic field attenuates the pairing, but for a mesoscopic system in a strong magnetic field the pairing correlations may come back after heating.[24] Such a reentrance of pairing correlations has also been discussed by Balian *et al.*[11] Work on this problem of how an external field can influence the thermodynamic properties of a single superconducting grain is in progress.

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