



This is the accepted manuscript made available via CHORUS, the article has been published as:

Thermodynamics of ultrasmall metallic grains in the presence of pairing and exchange correlations: Mesoscopic fluctuations

Konstantin N. Nesterov and Y. Alhassid

Phys. Rev. B **87**, 014515 — Published 29 January 2013

DOI: [10.1103/PhysRevB.87.014515](https://doi.org/10.1103/PhysRevB.87.014515)

Thermodynamics of ultra-small metallic grains in the presence of pairing and exchange correlations: mesoscopic fluctuations

Konstantin N. Nesterov and Y. Alhassid
*Center for Theoretical Physics, Sloane Physics Laboratory,
Yale University, New Haven, Connecticut 06520, USA*
(Dated: December 3, 2012)

We study the mesoscopic fluctuations of thermodynamic observables in nano-sized metallic grains whose single-particle dynamics is chaotic and whose dimensionless Thouless conductance is large. Such a grain is modeled by the universal Hamiltonian describing the competition between exchange and pairing correlations. The exchange term is taken into account exactly by a spin projection method, and the pairing term is treated in the static-path approximation together with small-amplitude quantal fluctuations around each static fluctuation of the pairing field. Odd-even particle-number effects induced by pairing correlations are taken into account using a number-parity projection. We find that the exchange interaction shifts the number-parity effects in the heat capacity and spin susceptibility to lower temperatures, and may suppress the re-entrant behavior of the spin susceptibility for an odd number of electrons in the grain. If the exchange coupling constant is sufficiently large and the pairing gap is similar to or smaller than the single-particle mean level spacing, the number-parity effects are suppressed by mesoscopic fluctuations and the fluctuations of the spin susceptibility may be particularly large.

PACS numbers: 74.78.Na, 74.25.Bt, 75.75.-c, 05.30.Fk

I. INTRODUCTION

The physics of nano-sized metallic grains has attracted much attention following a series of experiments by Ralph, Black and Tinkham,¹⁻³ in which individual energy levels of ultra-small aluminum grains were resolved by single-electron tunneling spectroscopy. Recent advances have made it possible to achieve better control over the size of the grain, which is important for quantitative measurements. In recent experiments, very high quality spectra of individually synthesized gold nanoparticles were obtained.⁴

Typical grains used in the spectroscopic experiments are in the ballistic regime, i.e., their size is smaller than the mean free path and electron transport is determined by scattering from the boundaries of the grain rather than from impurities. When the boundaries are sufficiently irregular, the single-particle dynamics is chaotic. This induces sample-specific fluctuations of observables, and the meaningful quantities are the statistical distributions of these observables; see Ref. 5 and references therein. The single-particle energies and wave functions follow the statistics of the random matrix theory (RMT)⁶ in a Thouless energy window E_{Th} around the Fermi energy, where E_{Th} is determined by the time it takes for an electron to move across the grain.

When E_{Th} is much larger than the single-particle mean level spacing δ , the grain is described by the so-called universal Hamiltonian.^{7,8} This Hamiltonian contains three interaction terms: a “classical” charging energy term, a pairing term that is characterized by a pairing gap Δ , and exchange term that depends on the total spin of the grain and is characterized by a coupling constant J_s . These three interaction terms are universal, i.e., they are independent of the particular realization of the single-particle

Hamiltonian.

When the pairing term is suppressed, (i.e., when only charging and exchange terms contribute), thermodynamic observables of the universal Hamiltonian can be calculated in closed form using a spin projection method.⁹ In Refs. 10 and 11, a Hubbard-Stratonovich transformation^{12,13} was employed to calculate in closed form observables such as the tunneling density of states and spin susceptibility.

In the absence of the exchange term, the universal Hamiltonian has the form of the Bardeen-Cooper-Schrieffer (BCS)¹⁴ Hamiltonian. In the bulk limit $\Delta/\delta \gg 1$, an attractive pairing interaction leads to superconductivity. Effects of the BCS interaction in nano-sized metallic grains were studied extensively; see Ref. 15 and references therein. Anderson argued¹⁶ that the smallest possible size of a system that can be a superconductor is determined by the condition $\Delta/\delta \sim 1$. In the experiments of Ref. 1-3, a pairing gap was clearly observed in the excitation spectra of the largest aluminum grains containing an even number of electrons, while it was impossible to resolve such a gap in the smaller grains. This, however, does not necessarily mean that pairing correlations disappear in the smaller grains. It was proposed that thermodynamic properties could be a more suitable tool to probe this fluctuation-dominated regime, in which $\Delta/\delta \lesssim 1$.¹⁷ Signatures of pairing correlations in this regime are the dependence of observables on the number-parity of electrons in the grain. A good example is the reentrant behavior (i.e., a local minimum) of the spin susceptibility with decreasing temperature in an odd grain.^{17,18} Odd-even effects in the heat capacity and magnetic susceptibility were experimentally observed in small clusters of metallic grains.¹⁹

BCS theory breaks down when $\Delta/\delta \lesssim 1$ and fluctua-

tions of the gap order parameter (beyond its mean-field BCS value) are important. In the static path approximation (SPA),^{20–22} only static fluctuations of the gap are taken into account. A better approximation, the SPA plus random phase approximation (RPA), takes into account small-amplitude time-dependent quantal fluctuations of the order parameter around each static field.^{23–28} Number-parity effects can be studied by using an exact number-parity projection.^{29–31} The heat capacity and spin susceptibility of a metallic grain (without exchange correlations) as functions of temperature were studied in the SPA+RPA method together with number-parity projection in Ref. 32 as well as by quantum Monte Carlo methods^{33,34} and by Richardson’s solution.^{17,34–36} In all of those calculations, number-parity effects were clearly identified in both the heat capacity and spin susceptibility of the grain. Signatures of pairing correlations were also found in the spin susceptibility as a function of magnetic field.^{37,38}

The exchange interaction competes with the BCS-like pairing interaction. Exchange tends to maximize spin polarization while pairing correlations tend to minimize the spin. It is known that, depending on the values of Δ/δ and J_s/δ , the ground state of a system can be superconducting, ferromagnetic, or one in which pairing and ferromagnetic correlations coexist.^{39,40} The effects of mesoscopic fluctuations on this competition were studied in Ref. 41.

The effect of both pairing and exchange correlations on the thermodynamic properties of the grain (heat capacity and spin susceptibility) was studied in Ref. 42 for the case of an equally-spaced single-particle spectrum by using a quantum Monte-Carlo method. These thermodynamic quantities can also be calculated directly from the eigenvalues of the universal Hamiltonian using Richardson’s solution, modified to take into account the exchange interaction.⁴⁰ The combined effect of exchange and pairing interactions on the spin susceptibility as a function of magnetic field at zero temperature was studied in Ref. 43.

In this work we study the general problem of mesoscopic fluctuations of thermodynamic properties of the grain in the presence of both pairing and exchange correlations assuming spin-orbit coupling is negligible. The quantum Monte Carlo method and Richardson’s solution mentioned above are computationally intensive, and are less practical in calculating the mesoscopic fluctuations of thermodynamic properties for which many realizations of the grain must be studied. Richardson’s solution also becomes less tractable at larger values of the pairing gap or at higher temperatures, where a very large number of energy eigenvalues are required.

Here we use a more efficient method to calculate the heat capacity and spin susceptibility of the grain at finite temperature. The exchange interaction is taken into account exactly using a spin projection method,^{9,44} and the corresponding spin-projected partition functions are calculated in the SPA+RPA approach. Number-parity effects are captured by a number-parity projection. This

approach is particularly suitable for studying the mesoscopic fluctuations.

The outline of the paper is as follows. In Sec. II we discuss the universal Hamiltonian and briefly review the conditions of its validity. In Sec. III we discuss the calculation of the canonical partition function, and use it to evaluate the heat capacity and spin susceptibility of a system described by the universal Hamiltonian. We also discuss the stability of the RPA, which is unstable below a certain critical value of the temperature. In Sec. IV we present our results and discuss their physical significance. We conclude in Sec. V.

II. MODEL

In a chaotic grain, the statistical fluctuations of single-particle energies and wave functions follow random matrix theory (RMT)⁶ at energy scales below E_{Th} . In the absence of spin-orbit scattering and orbital magnetic field, the relevant ensemble is the Gaussian orthogonal ensemble (GOE). In general, the matrix elements of the electron-electron interaction in the basis of eigenstates of the non-interacting part of the Hamiltonian have a complex structure that depends on the particular realization of the one-body Hamiltonian. In the limit of a large Thouless conductance $g_{\text{Th}} = E_{\text{Th}}/\delta \gg 1$, these matrix elements can be decomposed into an average and fluctuating parts.^{7,8} The average interaction terms together with the one-body Hamiltonian are referred to as the universal Hamiltonian.^{7,8} The fluctuating (non-universal) part of the interaction forms an induced two-body ensemble⁴⁵ whose matrix elements are suppressed by $1/g_{\text{Th}}$.

For a fixed number of electrons, the universal Hamiltonian has the form

$$\hat{H} = \sum_{i,\sigma=\uparrow,\downarrow} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} - g \hat{P}^\dagger \hat{P} - J_s \hat{\mathbf{S}}^2, \quad (1)$$

where

$$\hat{P}^\dagger = \sum_i c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger, \quad \hat{P} = \sum_i c_{i\downarrow} c_{i\uparrow}, \quad (2)$$

and $\hat{\mathbf{S}}$ is the total spin. The single-particle levels are distributed as the eigenvalues of a GOE random matrix with a mean single-particle level spacing δ . The universal interaction terms are invariant under orthogonal transformations of the single-particle basis, allowing us to write the one-body part in a diagonal form. If the particle number N is not fixed, then the charging term $E_c \hat{N}^2$ should also be included in (1). The bandwidth of the model $\sim N_{\text{sp}}\delta$, where N_{sp} is the number of single-particle levels, should satisfy the conditions $N_{\text{sp}}\delta \gg \Delta$ and $N_{\text{sp}}\delta \gg kT$ at temperature T .

The condition of a large Thouless conductance $g_{\text{Th}} \gg 1$ guarantees that the number of single-particle levels that follow RMT statistics within a Thouless energy window around the Fermi energy is sufficiently large, and that

the fluctuating non-universal correction to the interaction can be ignored. We assume that the Thouless energy is larger than the bandwidth so that RMT is applicable in the full model space. This implies the conditions $E_{\text{Th}} \gg kT$ and $E_{\text{Th}} \gg \Delta$. For ballistic grains, the latter assumption is equivalent to $L \ll \xi_0$, where L is the linear size of the grain and ξ_0 is the superconducting coherence length. This condition also allows us to ignore the spatial fluctuations of the gap Δ within the grain, i.e., to treat the grain as a zero-dimensional object with respect to the fluctuations of the order parameter.

The pairing constant g in the universal Hamiltonian depends on the number of single-particle orbitals in the model space. To reduce the computational effort, we choose N_{sp} to be smaller than the number of orbitals within the physical window of the Debye frequency around the Fermi energy. In doing so we renormalize the value of g according to^{34,46}

$$\frac{g}{\delta} = \frac{1}{\text{arcsinh}\left(\frac{N_{\text{sp}}/2}{\Delta/\delta}\right)}, \quad (3)$$

where we have taken the Fermi level to be in the middle of the single-particle spectrum (i.e., we assume half-filling). Depending on the temperature, we choose N_{sp} to be between 30 and 60 in our calculations to insure the condition $N_{\text{sp}}\delta \gg kT$. In our studies $\Delta/\delta \lesssim 5.0$ so the condition $N_{\text{sp}}\delta \gg \Delta$ is also satisfied.

To study the mesoscopic fluctuations of thermodynamic observables, we generate a large number (~ 1000) of realizations of the single-particle spectrum in (1) and calculate these observables for each of them.

III. THEORY

In this section, we present approximate analytical results for the partition function and the spin susceptibility of a system described by (1) for a given realization of the single-particle spectrum. First, we show that both quantities can be related to the S_z -projected partition function in the absence of exchange (S_z is the spin projection along the z axis). Second, we present an auxiliary-field path-integral formalism for treating the pairing interaction and explain how the integral is evaluated in the SPA+RPA method. Third, we discuss the inclusion of number-parity projection.

A. Spin-projection method

The universal Hamiltonian (1) commutes with the total spin and particle-number operators. Consequently, the corresponding partition function at temperature $T =$

$1/\beta$ can be written as

$$\begin{aligned} Z(J_s) &= \text{Tr} e^{-\beta \hat{H}} = \text{Tr} e^{-\beta(\hat{H}_{\text{BCS}} - J_s \hat{S}^2)} \\ &= \sum_S e^{\beta J_s S(S+1)} \text{Tr}_S \left(e^{-\beta \hat{H}_{\text{BCS}}} \right), \end{aligned} \quad (4)$$

where Tr_S is the trace restricted to states with fixed spin S , and \hat{H}_{BCS} is the BCS-like pairing Hamiltonian

$$\hat{H}_{\text{BCS}} = \sum_{i,\sigma=\uparrow,\downarrow} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} - g \hat{P}^\dagger \hat{P}. \quad (5)$$

Similarly, the spin susceptibility (at zero external Zeeman field) can be written as

$$\begin{aligned} \chi &= 4\beta\mu_B^2 \langle \hat{S}_z^2 \rangle = \frac{4\beta\mu_B^2}{3} \langle \hat{S}^2 \rangle \\ &= \frac{4\beta\mu_B^2}{3} \frac{\sum_S S(S+1) e^{\beta J_s S(S+1)} \text{Tr}_S \left(e^{-\beta \hat{H}_{\text{BCS}}} \right)}{Z(J_s)}, \end{aligned} \quad (6)$$

where \hat{S}_z is the spin component operator along the z direction and μ_B is the Bohr magneton.

For a scalar operator (i.e., an operator that is rotational invariant in spin space) \hat{X} ^{9,44}

$$\text{Tr}_S \hat{X} = (2S+1) \left(\text{Tr}_{S_z=S} \hat{X} - \text{Tr}_{S_z=S+1} \hat{X} \right), \quad (7)$$

where $\text{Tr}_{S_z=M}$ denotes the trace restricted to states with a fixed spin component $S_z = M$ (while the spin quantum number is no longer fixed). Using Eq. (7), we can express the partition function (4) and spin susceptibility (6) of a system described by the Hamiltonian (1) in terms of the S_z -projected partition function of the corresponding system in the absence of exchange interaction

$$Z(J_s) = \sum_S (2S+1) e^{\beta J_s S(S+1)} (Z_{S_z=S} - Z_{S_z=S+1}) \quad (8)$$

and

$$\begin{aligned} \chi &= \frac{4\beta\mu_B^2}{3} \frac{1}{Z(J_s)} \sum_S S(S+1)(2S+1) \\ &\quad \times e^{\beta J_s S(S+1)} (Z_{S_z=S} - Z_{S_z=S+1}). \end{aligned} \quad (9)$$

Here

$$Z_{S_z=M} = \text{Tr}_{S_z=M} \left(e^{-\beta \hat{H}_{\text{BCS}}} \right) \quad (10)$$

is the S_z -projected partition function of the BCS-like Hamiltonian (5).

B. Auxiliary-field path-integral formulation

In the following we consider a partition function of the type

$$Z_\lambda = \text{Tr}_\lambda \hat{U}, \quad (11)$$

where \hat{U} is the propagator of the BCS Hamiltonian

$$\hat{U} = e^{-\beta(\hat{H}_{\text{BCS}} - \mu\hat{N})}, \quad (12)$$

and Tr_λ denotes a trace with certain restrictions (e.g., fixed S_z). Using the auxiliary-field path-integral representation of the propagator \hat{U} , we discuss the static path approximation (SPA) as well as quantal RPA-like corrections around each static fluctuation. We have included a $\mu\hat{N}$ term into the propagator (12) because further calculations of (10) will be carried out in the grand-canonical formalism.

The interaction term in the BCS Hamiltonian (5) can be decoupled by means of a Hubbard-Stratonovich transformation.^{12,13} In this transformation we express the propagator (12) as a functional integral over a complex auxiliary field $\tilde{\Delta}(\tau)$ that depends on imaginary time τ ($0 \leq \tau \leq \beta$) as follows^{25,26,30}

$$\hat{U} = \int \mathcal{D}[\tilde{\Delta}, \tilde{\Delta}^*] e^{-\int_0^\beta d\tau |\tilde{\Delta}(\tau)|^2/g} \hat{U}_{\tilde{\Delta}}. \quad (13)$$

Here

$$\hat{U}_{\tilde{\Delta}} = \mathcal{T} e^{-\int_0^\beta d\tau \hat{H}_{\tilde{\Delta}}(\tau)} \quad (14)$$

is the propagator for the one-body Hamiltonian

$$\hat{H}_{\tilde{\Delta}} = \sum_i \left[\left(\epsilon_i - \mu - \frac{g}{2} \right) (c_{i\downarrow}^\dagger c_{i\downarrow} + c_{i\uparrow}^\dagger c_{i\uparrow}) - \tilde{\Delta} c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger - \tilde{\Delta}^* c_{i\downarrow} c_{i\uparrow} + \frac{g}{2} \right] \quad (15)$$

and \mathcal{T} denotes time ordering. The measure $\mathcal{D}[\tilde{\Delta}, \tilde{\Delta}^*]$ is defined to preserve the normalization (i.e., $\hat{U} = 1$ when $\hat{U}_{\tilde{\Delta}} \equiv 1$)

$$\mathcal{D}[\tilde{\Delta}, \tilde{\Delta}^*] = \lim_{M \rightarrow \infty} \prod_{m=1}^M \int \frac{\Delta\beta}{2\pi g} d\tilde{\Delta}_m d\tilde{\Delta}_m^*, \quad (16)$$

where $\Delta\beta = \frac{\beta}{M}$.

The auxiliary field $\tilde{\Delta}(\tau)$ can be separated into its static and τ -dependent parts by a Fourier series

$$\tilde{\Delta}(\tau) = \Delta_0 + \sum_{r \neq 0} \Delta_r e^{i\omega_r \tau}, \quad (17)$$

where $\omega_r = 2\pi r/\beta$ (r integer) are the bosonic Matsubara frequencies. In the SPA, $\tilde{\Delta}(\tau)$ is replaced by Δ_0 in the Hamiltonian (15) and the propagator (14) is approximated by

$$\hat{U}_{\tilde{\Delta}} \approx \hat{U}_{\Delta_0} = e^{-\beta \hat{H}_{\Delta_0}}, \quad (18)$$

where \hat{H}_{Δ_0} is the Hamiltonian (15) for a static field $\tilde{\Delta} = \Delta_0$. The BCS theory can be derived by applying the saddle-point approximation to the SPA integral.

The time-dependent part of (15) can be written as

$$\hat{V}(\tau) = - \sum_{i,r \neq 0} e^{i\omega_r \tau} \left(\Delta_r c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger + \Delta_{-r}^* c_{i\downarrow} c_{i\uparrow} \right). \quad (19)$$

Since we are interested in the correction to the SPA propagator (18), it is natural to use an interaction representation of $\hat{V}(\tau)$ with respect to the unperturbed static Hamiltonian \hat{H}_{Δ_0}

$$\hat{V}_{\text{int}}(\tau) = e^{\tau \hat{H}_{\Delta_0}} \hat{V}(\tau) e^{-\tau \hat{H}_{\Delta_0}}. \quad (20)$$

To obtain the expression for \hat{V}_{int} , it is convenient to work in the Δ_0 -dependent basis that diagonalizes the static Hamiltonian \hat{H}_{Δ_0} . We will refer to this basis as the quasiparticle representation (even though this is strictly the case only for the saddle-point value of Δ_0). For a given value of Δ_0 , the quasiparticle operators are related to the original particle operators via the Bogoliubov transformation

$$\begin{cases} c_{i\uparrow} = u_i a_{i\uparrow} + v_i e^{i\theta} a_{i\downarrow}^\dagger, \\ c_{i\downarrow} = u_i a_{i\downarrow} - v_i e^{i\theta} a_{i\uparrow}^\dagger. \end{cases} \quad (21)$$

Here

$$u_i^2 = \frac{1}{2}(1 + \gamma_i), \quad v_i^2 = \frac{1}{2}(1 - \gamma_i), \quad \theta = \arg \Delta_0, \quad (22)$$

where

$$\gamma_i = \frac{\epsilon_i - \mu - \frac{g}{2}}{E_i}, \quad (23)$$

and E_i are the quasiparticle energies

$$E_i = \sqrt{\left(\epsilon_i - \mu - \frac{g}{2} \right)^2 + |\Delta_0|^2}. \quad (24)$$

In this quasiparticle basis, \hat{H}_{Δ_0} and $\hat{V}(\tau)$ have the following forms

$$\hat{H}_{\Delta_0} = \sum_i \left[\epsilon_i - \mu - E_i + E_i (a_{i\uparrow}^\dagger a_{i\uparrow} + a_{i\downarrow}^\dagger a_{i\downarrow}) \right] \quad (25)$$

and

$$\hat{V}(\tau) = -\frac{1}{2} \sum_{i,r \neq 0} e^{i\omega_r \tau} \left[\Lambda_{ir} a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger + \Lambda_{i,-r}^* a_{i\downarrow} a_{i\uparrow} + \frac{|\Delta_0|}{E_i} (\Delta_r e^{-i\theta} + \Delta_{-r}^* e^{i\theta}) (1 - a_{i\downarrow}^\dagger a_{i\downarrow} - a_{i\uparrow}^\dagger a_{i\uparrow}) \right] \quad (26)$$

with

$$\Lambda_{ir} = (\gamma_i + 1)\Delta_r + (\gamma_i - 1)e^{2i\theta} \Delta_{-r}^*. \quad (27)$$

The dependence of $\hat{V}(\tau)$ on θ can be eliminated by an appropriate gauge transformation of Δ_r and the quasiparticle operators. Therefore, the integrand in the SPA integral depends only on the absolute value of Δ_0 .

The form of $\hat{V}_{\text{int}}(\tau)$ in the quasiparticle basis is the same as of $\hat{V}(\tau)$ in Eq. (26) with a and a^\dagger replaced by

$$a_{i\sigma}(\tau) = a_{i\sigma} e^{-E_i \tau}, \quad a_{i\sigma}^\dagger(\tau) = a_{i\sigma}^\dagger e^{E_i \tau}. \quad (28)$$

In the interaction representation

$$\hat{U}_{\tilde{\Delta}} = \hat{U}_{\Delta_0} \hat{U}_{\text{int}}, \quad (29)$$

where

$$\hat{U}_{\text{int}} = \mathcal{T} e^{-\int_0^\beta d\tau \hat{V}_{\text{int}}(\tau)}. \quad (30)$$

As a result, the partition function (11) can be written as

$$Z_\lambda = \frac{\beta}{g} \int_0^\infty d|\Delta_0|^2 e^{-\frac{\beta}{g} |\Delta_0|^2} Z_\lambda(\Delta_0) C_\lambda(\Delta_0), \quad (31)$$

where

$$Z_\lambda(\Delta_0) = \text{Tr}_\lambda \hat{U}_{\Delta_0} \quad (32)$$

is the partition function for a static value Δ_0 of the pairing field and

$$C_\lambda(\Delta_0) = \int \mathcal{D}'[\Delta_r, \Delta_r^*] e^{-(\beta/g) \sum_{r \neq 0} |\Delta_r|^2} \langle \hat{U}_{\text{int}} \rangle_{\lambda, \Delta_0} \quad (33)$$

is the quantum correction. The average in (33) is defined with respect to the static-field propagator

$$\langle \hat{A} \rangle_{\lambda, \Delta_0} = \frac{\text{Tr}_\lambda (\hat{U}_{\Delta_0} \hat{A})}{\text{Tr}_\lambda \hat{U}_{\Delta_0}}, \quad (34)$$

and the integration measure is

$$\mathcal{D}'[\Delta_r, \Delta_r^*] = \prod_{r \neq 0} \frac{\beta d\Delta_r d\Delta_r^*}{2\pi g}. \quad (35)$$

The expression (31) for the partition function Z_λ is exact. In the SPA $C_\lambda = 1$ or, equivalently, $\hat{V}(\tau) = 0$. The SPA+RPA approximation is obtained by evaluating the integral over Δ_r and Δ_r^* in (33) in the saddle-point approximation assuming small-amplitude fluctuations. To this end, we write

$$\ln \langle \hat{U}_{\text{int}} \rangle_{\lambda, \Delta_0} \approx \frac{1}{2} \int_0^\beta \int_0^\beta d\tau d\tau' \langle \mathcal{T} \hat{V}_{\text{int}}(\tau) \hat{V}_{\text{int}}(\tau') \rangle_{\lambda, \Delta_0}, \quad (36)$$

where we have assumed that $\int_0^\beta d\tau \langle \hat{V}_{\text{int}}(\tau) \rangle_{\lambda, \Delta_0} = 0$. This is valid provided the projection in Tr_λ conserves the quasiparticle occupation number, which is the case for the S_z -projected trace but not for the canonical (particle-projected) trace. The RPA correction factor (33) is then given by

$$C_\lambda^{\text{RPA}}(\Delta_0) = \int \mathcal{D}'[\Delta_r, \Delta_r^*] e^{-\frac{\beta}{g} \sum_{r \neq 0} |\Delta_r|^2} \times \exp \left(\frac{1}{2} \int_0^\beta \int_0^\beta d\tau d\tau' \langle \mathcal{T} \hat{V}_{\text{int}}(\tau) \hat{V}_{\text{int}}(\tau') \rangle_{\lambda, \Delta_0} \right). \quad (37)$$

Higher-order corrections can be obtained by including more terms in the cumulant expansion (36).

C. Canonical and number-parity projections

The canonical partition function can be related to the grand-canonical partition by particle-number projection.⁵ However, an exact particle-number projection “inside” the integral (31) for each value of the static field Δ_0 leads to a complicated expression since the particle-number operator \hat{N} does not commute with the static Hamiltonian \hat{H}_{Δ_0} .⁴⁷

In the following we will carry out the particle-number projection in the saddle-point approximation. However, to account for important odd-even effects, we project on the number parity of electrons. The trace in (11) will be restricted to S_z and the number-parity quantum number η ($\eta = +1$ for an even number of particles and $\eta = -1$ for an odd number), i.e., $\lambda = \eta, S_z$.

The canonical partition function for N particles can be obtained from (11) by particle-number projection

$$Z_{N, \lambda} = \int_{-\pi}^{\pi} \frac{d\alpha}{2\pi} e^{-i\alpha N} \text{Tr}_\lambda \left(e^{-\beta \hat{H}_{\text{BCS}} + i\alpha \hat{N}} \right) \\ = \int_{-i\pi/\beta}^{i\pi/\beta} \frac{\beta d\mu}{2\pi i} \int_0^\infty \frac{\beta d|\Delta_0|^2}{g} e^{-\beta [F_\lambda(\mu, \Delta_0) + \mu N]} C_\lambda(\Delta_0), \quad (38)$$

where

$$e^{-\beta F_\lambda(\mu, \Delta_0)} = e^{-(\beta/g) |\Delta_0|^2} Z_\lambda(\Delta_0). \quad (39)$$

Here $Z_\lambda(\Delta_0)$ and $C_\lambda(\Delta_0)$ are calculated for a chemical potential μ . We denote by F the grand-canonical free energy (without the restriction λ) given by

$$e^{-\beta F(\mu, \Delta_0)} = e^{-(\beta/g) |\Delta_0|^2} \text{Tr} e^{-\beta \hat{H}_{\Delta_0}} \\ = e^{-(\beta/g) |\Delta_0|^2} \prod_i 4e^{-\beta(\epsilon_i - \mu)} \cosh^2 \frac{\beta E_i}{2}. \quad (40)$$

We exchange the order of integrations in (38) and for each value of Δ_0 evaluate the integral over μ by the saddle-point approximation. The latter is applied to the function $e^{-\beta [F(\mu, \Delta_0) + \mu N]}$ considering the remaining part, $e^{-\beta (F_\lambda - F)} C_\lambda(\Delta_0)$, as a pre-factor that does not affect the saddle-point integration. We then obtain⁴⁸

$$Z_{N, \lambda} \approx \int_0^\infty \frac{\beta d|\Delta_0|^2}{g} \\ \times \left(\frac{2\pi}{\beta} \left| \frac{\partial^2 F}{\partial \mu^2} \right| \right)^{-1/2} e^{-\beta [F_\lambda(\mu, \Delta_0) + \mu N]} C_\lambda(\Delta_0), \quad (41)$$

where

$$\frac{\partial^2 F}{\partial \mu^2} = - \sum_i \frac{\beta E_i (\epsilon_i - \mu - \frac{g}{2})^2 + |\Delta_0|^2 \sinh(\beta E_i)}{2E_i^3 \cosh^2\left(\frac{\beta E_i}{2}\right)} \quad (42)$$

and μ is a Δ_0 -dependent chemical potential determined by

$$N = - \frac{\partial F}{\partial \mu} = \sum_i \left(1 - \frac{\epsilon_i - \mu - \frac{g}{2}}{E_i} \tanh \frac{\beta E_i}{2} \right). \quad (43)$$

The number-parity projection is carried out using the projector

$$\hat{P}_\eta = \frac{1}{2} \left(1 + \eta e^{i\pi \hat{N}} \right), \quad (44)$$

where $\eta = \pm 1$, depending on the number-parity of electrons. If this operator is inserted in the grand-canonical trace, only states with even (odd) number of particles will be taken into account for $\eta = 1$ ($\eta = -1$).

D. Number-parity and S_z -projected static partition function

Here we discuss the calculation of the static partition function (32), when λ corresponds to the projections on number parity and S_z , i.e., $\lambda = \eta, S_z$.

The trace over states with fixed S_z can be calculated exactly through a discrete Fourier transform as long as the maximal value of S_z is finite. The corresponding projection operator is

$$\hat{P}_{S_z} = \frac{1}{2S_{\max} + 1} \sum_{m=-S_{\max}}^{S_{\max}} e^{i\phi_m (\hat{S}_z - S_z)}, \quad (45)$$

where S_{\max} is the maximal possible value of the spin and $\phi_m = 2\pi m / (2S_{\max} + 1)$ are quadrature points. We use this operator in accordance with the number-parity projection, i.e., the values of m are integers or half-integers for even or odd number of electrons, respectively. Because our goal is to obtain an expression for the canonical partition function, the value of S_{\max} is determined by the number of particles, rather than by the size of the Hilbert space.

The spin projection operator \hat{S}_z commutes with \hat{H}_{Δ_0} so we can write

$$\text{Tr} \left(\hat{P}_\eta e^{i\phi_m \hat{S}_z} e^{-\beta \hat{H}_{\Delta_0}} \right) = \text{Tr} \left(\hat{P}_\eta e^{-\beta \hat{H}_{\Delta_0} + i\phi_m \hat{S}_z} \right). \quad (46)$$

The second-quantized form of \hat{S}_z and \hat{P}_η remains invariant under Bogoliubov transformation (21). Consequently, the projected partition function for a static pairing field Δ_0 is given by

$$Z_{\eta, S_z}(\Delta_0) = \sum_m \frac{e^{-i\phi_m S_z}}{2S_{\max} + 1} \frac{Z^{(0, \phi_m)}(\Delta_0) + \eta Z^{(i\pi, \phi_m)}(\Delta_0)}{2}, \quad (47)$$

where

$$\begin{aligned} Z^{(0, \phi_m)}(\Delta_0) &= \text{Tr} \left(e^{-\beta \hat{H}_{\Delta_0} + i\phi_m \hat{S}_z} \right) \\ &= \prod_i e^{-\beta(\epsilon_i - \mu - E_i)} \left| 1 + e^{-\beta E_i - \frac{i\phi_m}{2}} \right|^2 \end{aligned} \quad (48)$$

and

$$\begin{aligned} Z^{(i\pi, \phi_m)}(\Delta_0) &= \text{Tr} \left(e^{i\pi \hat{N}} e^{-\beta \hat{H}_{\Delta_0} + i\phi_m \hat{S}_z} \right) \\ &= \prod_i e^{-\beta(\epsilon_i - \mu - E_i)} \left| 1 - e^{-\beta E_i - \frac{i\phi_m}{2}} \right|^2. \end{aligned} \quad (49)$$

The last two expressions were obtained using the grand-canonical formalism.

E. The RPA correction

The RPA correction factor (37) is calculated in the Appendix A. For $\lambda = \eta, S_z$ it is given by

$$C_\lambda^{\text{RPA}}(\Delta_0) = \prod_{r>0} [\det A(\omega_r)]^{-1}, \quad (50)$$

where

$$A(\omega_r) = \begin{pmatrix} 1 - g \sum_i \frac{2E_i \gamma_i^2 f_{\lambda i}}{4E_i^2 + \omega_r^2} & g \sum_i \frac{\omega_r \gamma_i f_{\lambda i}}{4E_i^2 + \omega_r^2} \\ -g \sum_i \frac{\omega_r \gamma_i f_{\lambda i}}{4E_i^2 + \omega_r^2} & 1 - g \sum_i \frac{2E_i \gamma_i^2 f_{\lambda i}}{4E_i^2 + \omega_r^2} \end{pmatrix} \quad (51)$$

and

$$f_{\lambda i} = \frac{1}{\beta} \frac{\partial \ln Z_\lambda(\Delta_0)}{\partial E_i}. \quad (52)$$

Here $\omega_r = 2\pi r / \beta$ are the positive bosonic Matsubara frequencies and γ_i are given by Eq. (23). Each factor in the product (50) is obtained after a Gaussian integration over $\Delta_r, \Delta_r^*, \Delta_{-r}$ and Δ_{-r}^* . This integral converges if and only if the real parts of both eigenvalues of the matrix $A(\omega_r)$ are positive. Since $A(\omega_r)$ is a 2×2 real matrix, this is equivalent to

$$\det A(\omega_r) > 0 \quad \text{and} \quad \text{tr} A(\omega_r) > 0. \quad (53)$$

For a given Δ_0 , the RPA breaks down below a certain temperature for which one of the conditions in (53) is not satisfied. It is then necessary to include higher-order cumulants in the expansion (36). The highest temperature for which the RPA breaks down for at least one value of Δ_0 is known as the SPA+RPA critical temperature T_* . The SPA+RPA approach is thus valid for temperatures above T_* . Numerical simulations show that T_* increases with the BCS gap Δ and becomes of the order of δ for $\Delta/\delta \sim 5$. It has been recently proposed⁴⁹ that the above instability can be avoided by treating non-perturbatively a low-energy collective mode.

In Appendix B we show that the RPA correction factor (50) can be written as

$$C_\lambda^{\text{RPA}}(\Delta_0) = \prod_i \frac{\Omega_i}{2E_i} \frac{\sinh(\beta E_i)}{\sinh\left(\frac{\beta \Omega_i}{2}\right)}, \quad (54)$$

where $\pm\Omega_i$ are the eigenvalues of the $2N_{\text{sp}} \times 2N_{\text{sp}}$ RPA matrix (N_{sp} is the number of single-particle orbitals)

$$\begin{pmatrix} 2E_i \delta_{ij} - \frac{g}{2} f_{\lambda i}(\gamma_i \gamma_j + 1) & -\frac{g}{2} f_{\lambda i}(\gamma_i \gamma_j - 1) \\ \frac{g}{2} f_{\lambda i}(\gamma_i \gamma_j - 1) & \frac{g}{2} f_{\lambda i}(\gamma_i \gamma_j + 1) - 2E_i \delta_{ij} \end{pmatrix}. \quad (55)$$

Expression (54) is more practical since it does not contain an infinite product and we have used it in our calculations below.

The relations (50) and (54) are valid not only for the restricted partition function (11) with $\lambda = \eta, S_z$, but also for the grand-canonical partition function^{25,26,30} and for the number-parity-projected partition function.³⁰ In all of these cases, the correct $Z_\lambda(\Delta_0)$ must be used in (52) to define $f_{\lambda i}$. These expressions, however, are not applicable for the canonical projection.

F. Summary

In summary, we use Eqs. (8) and (9) to express the N -particle partition function Z_N and spin susceptibility χ of a system described by the universal Hamiltonian (1) in terms of the number-parity and S_z -projected partition function Z_{N,η,S_z} of a system described by the BCS-like pairing Hamiltonian (5) (note that in Eqs. (8) and (9) we replace Z_{S_z} by Z_{N,η,S_z}). The partition function Z_{N,η,S_z} is calculated in the SPA+RPA using

$$Z_{N,\eta,S_z} \approx \int_0^\infty \frac{\beta d|\Delta_0|^2}{g} \left(\frac{2\pi}{\beta} \left| \frac{\partial^2 F}{\partial \mu^2} \right| \right)^{-1/2} \times e^{-(\beta/g)|\Delta_0|^2} e^{-\beta\mu N} Z_{\eta,S_z}(\Delta_0) C_{\eta,S_z}^{\text{RPA}}(\Delta_0). \quad (56)$$

Here Δ_0 denotes a static fluctuation of the order parameter and η is the number parity ($\eta = 1$ for even N and -1 for odd N). The partition function $Z_{\eta,S_z}(\Delta_0)$ and the RPA correction $C_{\eta,S_z}^{\text{RPA}}(\Delta_0)$ are given by Eqs. (47) and (50) or (54), respectively. The second partial derivative $\partial^2 F / \partial \mu^2$ is given by Eq. (42), and the chemical potential μ for a given static fluctuation Δ_0 is determined from Eq. (43). The heat capacity C is obtained numerically from the partition function $Z_N(T)$ as a function of temperature.

IV. RESULTS AND DISCUSSION

A. Accuracy of the method

We first discuss the accuracy of the number-parity projected SPA and SPA+RPA methods. To this end,

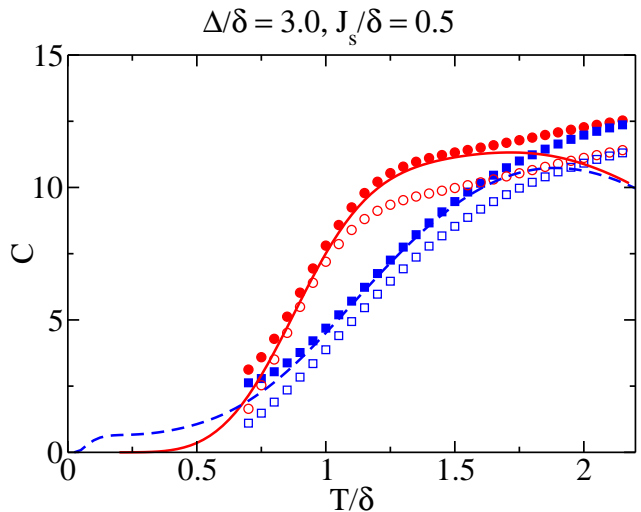


FIG. 1. Heat capacity C versus T/δ for an even and odd grain with $\Delta/\delta = 3.0$, $J_s/\delta = 0.5$ and for a specific realization of the GOE single-particle spectrum in (1). The results calculated in the number-parity projected SPA (open symbols) and SPA+RPA (solid symbols) for even (circles) and odd (squares) grains are compared with exact canonical results obtained by Richardson's solution (solid line for the even grain and dashed line for the odd grain). The results based on Richardson's solution use all eigenvalues below a cutoff of $\sim 30\delta$ and are no longer accurate for temperatures above $T \sim 1.5\delta$.

we have used the exact solution of the Hamiltonian (1), modifying Richardson's solution for the spectrum of the BCS-like Hamiltonian^{35,36} to include the exchange interaction.⁴⁰ The number of many-body eigenstates that contribute to the partition function increases rapidly with temperature and so does the required computational effort. In practice, we compute only the energy eigenvalues below a cutoff of $\sim 30\delta$. These exact calculations are then accurate at sufficiently low temperatures where the contribution of eigenstates with energy above 30δ is negligible.

The comparison between the exact and approximate calculations is demonstrated for a given realization of the single-particle spectrum in Figs. 1 and 2 for the heat capacity and spin susceptibility, respectively. We show results for both even and odd number of electrons.

We observe that the number-parity projected SPA+RPA (solid symbols) improves significantly the number-parity projected SPA (open symbols) and provides accurate results for both the heat capacity and spin susceptibility. In particular, the RPA correction is important for the spin susceptibility at moderate to high values of the exchange coupling J_s/δ . The example shown on Fig. 2 demonstrates that the number-parity projected SPA results can be qualitatively wrong, whereas the inclusion of the RPA correction factor gives much more accurate results.

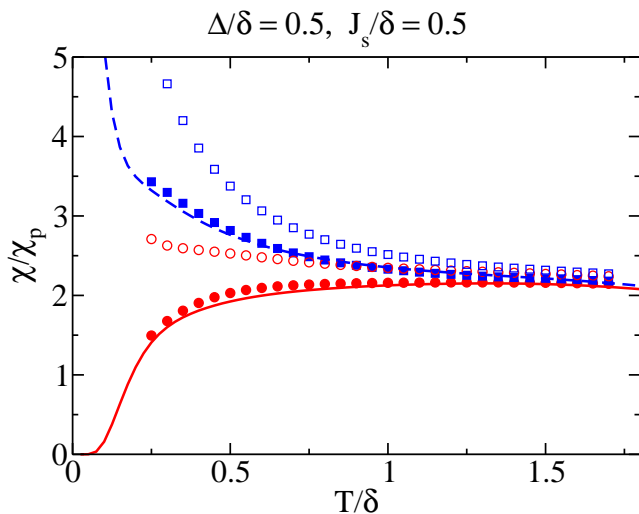


FIG. 2. As in Fig. 1 but for the spin susceptibility χ normalized by the Pauli susceptibility $\chi_P = 2\mu_B^2/\delta$ versus T/δ and for a grain with $\Delta/\delta = 0.5$, $J_s/\delta = 0.5$. Symbols and lines follow the same convention as in Fig. 1.

B. Heat capacity

There are two major number-parity dependent signatures of pairing correlations in the heat capacity: the heat capacity for an even particle number is suppressed at low temperatures and enhanced at intermediate temperatures when compared with the heat capacity for an odd particle number (see Richardson's solution results in Fig. 1). The low temperature effect is not accessible by the method we are using because the RPA becomes unstable at low temperatures, and we concentrate below on number-parity effects in the intermediate temperature region. It is known that, in the absence of exchange, the characteristic temperature of this region is determined by the scale that is the largest between δ and Δ .³⁴ In the BCS regime (i.e., large Δ/δ), this effect occurs around the BCS critical temperature, while in the fluctuation-dominated regime $\Delta/\delta \lesssim 1$ it occurs at temperatures higher than the BCS critical temperature. The even-odd effect becomes more prominent when the size of the grain, and consequently Δ/δ increase. The heat capacity for even particle number starts displaying a shoulder around $\Delta/\delta \approx 3.0$, which eventually develops into a sharp peak in the bulk limit $\Delta/\delta \gg 1$. Here we investigate how this picture is affected by a non-zero exchange interaction and by mesoscopic fluctuations.

The results for the heat capacity are shown versus T/δ and both number parities in Fig. 3 for $\Delta/\delta = 0.5, 1.0, 3.0$ and $J_s/\delta = 0, 0.4, 0.8$. The symbols and vertical bars are average values \overline{C} and standard deviations δC , respectively, calculated from an ensemble of 1000 random matrices describing the one-body part of (1). The lines (solid for even and dashed for odd number of electrons) are obtained for the equally-spaced single-particle spectrum in (1) with level spacing δ . Fig. 4 shows the stan-

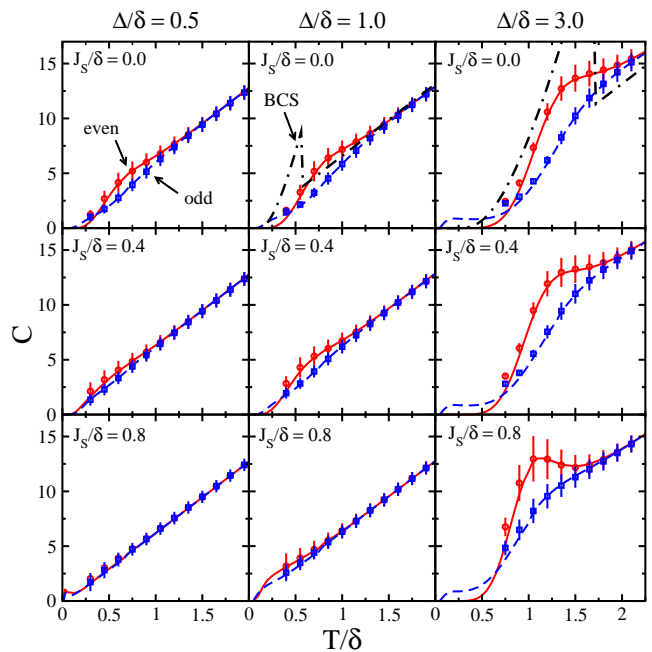


FIG. 3. The heat capacity C versus temperature T/δ for an even grain (solid lines, circles) and for an odd grain (dashed lines, squares). Results are shown for grains with $\Delta/\delta = 0.5$ (left column), $\Delta/\delta = 1.0$ (middle column) and $\Delta/\delta = 3.0$ (right column) and with $J_s/\delta = 0$ (top row), $J_s/\delta = 0.4$ (middle row) and $J_s/\delta = 0.8$ (bottom row). The symbols and vertical bars describe, respectively, the average value \overline{C} and standard deviation δC of the heat capacity (where an ensemble of single-particle spectra are sampled from the GOE). The lines correspond to an equally-spaced single-particle spectrum in (1) and the dash-dotted lines are the grand-canonical BCS results (where applicable).

dard deviation δC versus T/δ for the same cases as in Fig. 3.

We observe that the exchange interaction can suppress the odd-even effects in the heat capacity and shift them to lower temperatures. This is particularly evident if $\Delta/\delta \lesssim 1$. For $\Delta/\delta = 3.0$, a higher value of the exchange coupling constant is required to make a visible change. Even for $J_s/\delta = 0.8$ (which is close to the Stoner instability threshold), the number-parity effect is shifted to lower temperatures slightly. Only the right side of the even number-parity shoulder is suppressed, whereas the left side is not. As a result, the shoulder transforms into a peak.

This behavior is consistent with the ground-state phase diagram⁴⁰ of the grain, according to which the ground state for an even particle number is fully paired for small J_s/δ and the value of J_s/δ required to polarize the grain increases with Δ/δ . For $\Delta/\delta = 3.0$, this value of J_s/δ is close to the Stoner instability threshold. For smaller values of J_s/δ , the excited states with non-zero spin become important only at sufficiently high temperatures. At lower temperatures, the dominant contribution to the heat capacity comes from the zero spin levels whose en-

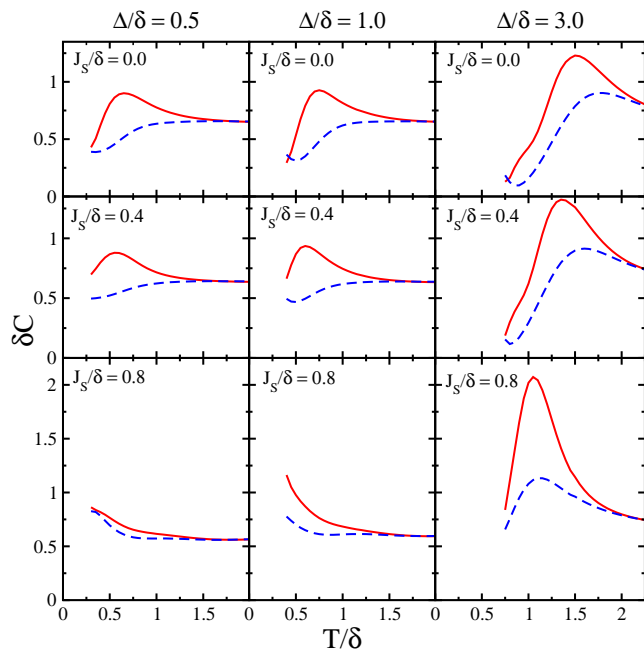


FIG. 4. The standard deviation δC of the heat capacity (shown by vertical bars in Fig. 3) versus temperature T/δ for an even grain (solid lines) and for an odd grain (dashed lines) with the same values of Δ/δ and J_s/δ as in Fig. 3.

ergy is independent of J_s/δ . This is consistent with the weak dependence on J_s/δ of the left side of the even-case shoulder for $\Delta/\delta = 3.0$. At temperatures that correspond to the right side of the even-case shoulder, non-zero spin configurations are more important and lead to visible change in the heat capacity. For $\Delta/\delta \lesssim 1$, the excitation energies of the states with non-zero spin are lower and the heat capacity is more sensitive to exchange correlations at lower temperatures.

In an ultra-small grain, the mesoscopic fluctuations of observables can be significant. For example, if an odd-even signature of pairing correlations is studied by carrying out measurements in many samples with unknown number parity and then determining the distribution of the observable, such a number-parity effect may be washed out when the fluctuations are large. As can be seen from our results, this can happen if Δ/δ is sufficiently small or J_s/δ is sufficiently large. In the absence of exchange, this occurs at $\Delta/\delta \lesssim 0.5$, and, for $J_s/\delta \sim 0.5$, number-parity effects already disappear below $\Delta/\delta \sim 1$. However, for $\Delta/\delta = 3.0$, the odd-even effect is not suppressed by the fluctuations even at relatively large J_s/δ .

As can be seen in Fig. 4 the mesoscopic fluctuations of the heat capacity at high temperatures are only weakly dependent on the pairing gap, exchange coupling constant and the number parity. At intermediate temperatures, when the heat capacity is enhanced for an even particle number, the fluctuations in the even case are stronger than in the odd case and are characterized by

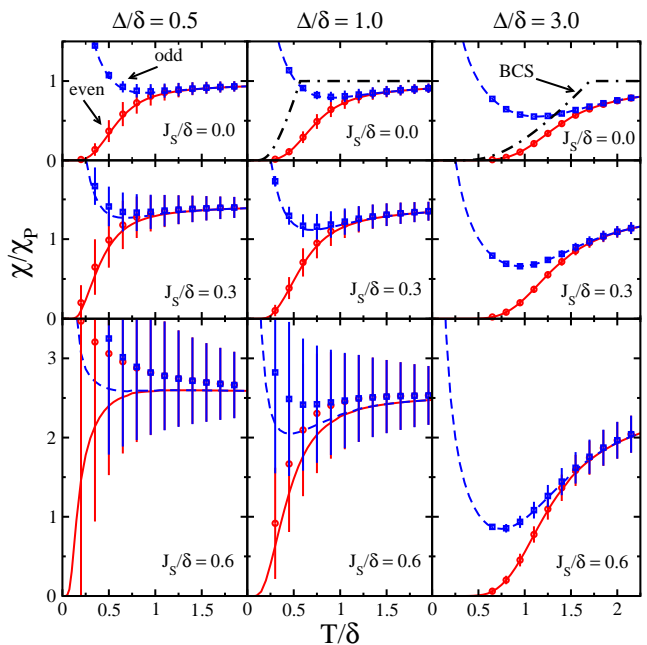


FIG. 5. The spin susceptibility χ in the units of the Pauli susceptibility $\chi_P = 2\mu_B^2/\delta$ versus temperature T/δ for even and odd grains with $\Delta/\delta = 0.5$ (left column), $\Delta/\delta = 1$ (middle column) and $\Delta/\delta = 3.0$ (right column) and with $J_s/\delta = 0$ (top row), $J_s/\delta = 0.3$ (middle row) and $J_s/\delta = 0.6$ (bottom row). Symbols and lines follow the same convention as in Fig. 3 but for the spin susceptibility.

a peak. The position and height of this peak are almost independent of Δ/δ for $\Delta/\delta \lesssim 1$, but increase with Δ/δ for $\Delta/\delta > 1$. In the presence of exchange correlations, the peak is shifted to lower temperatures. This is consistent with a similar shift of the odd-even signature in the heat capacity. In addition the peak height increases with J_s for $\Delta/\delta > 1$.

C. Spin susceptibility

It is known that pairing correlations (in the absence of exchange) suppress the spin susceptibility for both number parities. For an odd particle number, this suppression together with the low-temperature Curie-like divergence ($\sim 1/T$) leads to a reentrant behavior. For an even particle number, the spin susceptibility increases monotonically with temperature. Exchange correlations and mesoscopic fluctuations may affect this picture.

We express the spin susceptibility χ in the units of the Pauli susceptibility $\chi_P = 2\mu_B^2/\delta$, where μ_B is the Bohr magneton. For given values of Δ/δ and J_s/δ , the ratio χ/χ_P is expected to be a universal function of T/δ . In the high-temperature limit, χ/χ_P does not depend on Δ/δ . For an equally-spaced single-particle spectrum and in the absence of exchange it approaches 1 in the high temperature limit.

The results for the spin susceptibility versus T/δ are

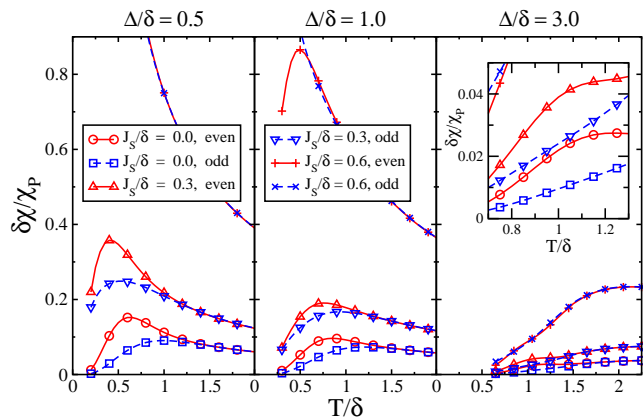


FIG. 6. The standard deviation $\delta\chi/\chi_P$ of the spin susceptibility (shown by vertical bars in Fig. 5) versus temperature T/δ for an even grain (solid lines) and for an odd grain (dashed lines) with the same values of Δ/δ and J_s/δ as in Fig. 5.

shown (for both number parities) in Fig. 5 for $\Delta/\delta = 0.5, 1.0, 3.0$, and $J_s/\delta = 0, 0.3, 0.6$. Symbols and lines follow the same convention as in Fig. 3. The standard deviation $\delta\chi/\chi_P$ is shown in Fig. 6 versus T/δ .

The most visible effect of the exchange interaction is the enhancement of χ/χ_P as higher spin states are shifted down in energy. Exchange correlations can also shift the odd-even effects to lower temperatures and even eliminate the odd-case reentrant behavior for $\Delta/\delta \lesssim 1$. However, at larger values of Δ/δ , exchange enhances the reentrant behavior. This effect is similar to what we observed for the even-case heat capacity where a shoulder changes into a peak for larger values of Δ/δ (see the right column of Fig. 3).

The mesoscopic fluctuations of χ/χ_P increase with decreasing Δ/δ or increasing J_s/δ . In the fluctuation-dominated regime $\Delta/\delta \lesssim 1$, they can become especially strong at larger values of J_s/δ and can hinder the observation of odd-even effects. When compared to the heat capacity results, higher values of J_s/δ or smaller values of Δ/δ are required to hinder the odd-even effects.

The large mesoscopic fluctuations of the spin susceptibility for $\Delta/\delta \lesssim 1$ and large values of J_s/δ may be attributed to the large dispersion of the magnetization of the system. This is confirmed by studying spectra of individual samples in that regime using Richardson's method. Examples are shown in Fig. 7. Large spin susceptibility values are obtained in samples in which the excitation energies of states whose spin is different from the ground-state spin are particularly low. The probability to have such a sample is enhanced when pairing correlations are weaker and/or exchange correlations are larger.

At relatively large values of Δ/δ , the fluctuations increase monotonically with temperature (see right column of Fig. 6). However, for $\Delta/\delta \lesssim 1$, the fluctuations in the spin susceptibility have a maximum at smaller values of J_s/δ . It is not clear if this is the case at large values J_s/δ

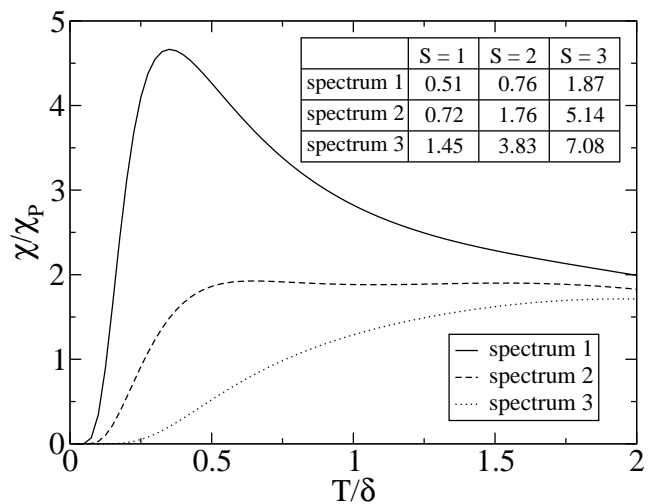


FIG. 7. The spin susceptibility χ/χ_P for an even grain with $\Delta/\delta = 0.5$ and $J_s/\delta = 0.5$ for three different RMT realizations of the single-particle spectrum in (1). The table shows (for each of the three realizations) the lowest excitation energy E_S/δ for a given spin S .

because we cannot access very low temperatures by our method. However, we expect the fluctuations to remain strong in the limit $T \rightarrow 0$ in the odd case because of the Curie-like behavior $\sim S_0/T$, where S_0 is fluctuating ground-state spin.

We note that the equally-spaced single-particle spectrum does not always describe the average behavior of the spin susceptibility. In the regime where the mesoscopic fluctuations are strong, the spin susceptibility calculated for the equally-spaced spectrum (solid lines in Fig. 5) is smaller than the spin susceptibility obtained by averaging over all samples (circles) and may be qualitatively different (see, e.g., the case $\Delta/\delta = 0.5$ and $J_s/\delta = 0.6$ in Fig. 5).

V. CONCLUSIONS

In conclusion, we have studied the thermodynamic properties of ultra-small chaotic metallic grains with a large dimensionless Thouless conductance in the presence of both superconducting and ferromagnetic correlations. We have used the so-called universal Hamiltonian (1) as our model, in which the one-body part is sample-specific and modeled by random-matrix theory, while the dominating interaction terms are universal. Sample-to-sample fluctuations of the interaction are suppressed and ignored in the limit of large dimensionless Thouless conductance. The exchange interaction has been taken into account exactly by means of a spin projection method, while the pairing interaction has been treated in a path integral approach in which all static fluctuations of the pairing gap and small-amplitude time-dependent fluctuations around each static value of the gap are taken into

account (SPA+RPA method). Particle-number projection is approximated in the saddle-point approximation while number-parity effects are preserved using an exact number-parity projection. The method is efficient and very accurate when compared to exact canonical calculations. However, it cannot be used at very low temperatures, when the RPA correction becomes unstable. This limitation can potentially be overcome using the method developed in Ref. 49.

We have found that the exchange interaction shifts the number-parity dependent signatures of pairing correlations (such as the enhancement of heat capacity in the even grain and the reentrant behavior of the spin susceptibility in the odd grain) to lower temperatures. In the fluctuation-dominated regime $\Delta/\delta \lesssim 1$, these signatures are suppressed by exchange correlations. However, at sufficiently large values of Δ/δ , exchange correlations have the opposite effect, i.e., the heat capacity of the even grain develops a peak and the reentrant behavior of the spin susceptibility in the odd grain is enhanced.

Mesoscopic fluctuations of thermodynamic observables can further hinder the odd-even effects for sufficiently small Δ/δ and large J_s/δ . The mesoscopic fluctuations of the spin susceptibility are especially large in the fluctuation-dominated regime $\Delta/\delta \lesssim 1$ for values of J_s/δ above ~ 0.5 because of the large dispersion of the magnetization.

It would be interesting to extend our work to the study of granular metals,⁵⁰ i.e., arrays of metallic nanoparticles that are coupled via tunnel junctions. For weakly coupled grains and when the charging energy E_C satisfies $E_C \gg \Delta$, the majority of grains are in the Coulomb-blockade regime $kT \ll E_C$ with suppressed inter-grain tunneling. These Coulomb-blockaded grains provide the dominant contribution to the thermodynamic properties of the granular metal at low temperatures. Therefore, the values of thermodynamic observables of a granular metal (per grain) at $kT \ll E_C$ can be effectively calculated by averaging the observables of individual grains over different random-matrix realizations and the number parity of electrons. We note that number-parity effects must still be taken into account since they lead to effects that could be missed in grand-canonical calculations. An example is the Curie-like divergence in the average spin susceptibility.

ACKNOWLEDGMENTS

We thank Sebastian Schmidt for useful discussions. This work was supported in part by the U.S. DOE grant No. DE-FG02-91ER40608, and by the facilities and staff of the Yale University Faculty of Arts and Sciences High Performance Computing Center.

Appendix A: Calculation of the RPA correction factor

In this appendix we calculate the RPA correction factor (37) with λ denoting simultaneous projections on the number-parity η and spin component S_z . The corresponding projection operators, given by Eqs. (44) and (45), respectively, have the same form in both single-particle and Δ_0 -dependent quasiparticle representations. This indicates that they commute with the quasiparticle occupation number operator $a_{i\sigma}^\dagger a_{i\sigma}$ for each i and σ . Therefore, if $\hat{V}_{\text{int}}(\tau)$ is written in the quasiparticle representation according to (26) with τ -dependent operators, non-zero contributions to the correlator of $\hat{V}_{\text{int}}(\tau)$ in (37) are possible only from the product of $a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger$ and $a_{i\downarrow} a_{i\uparrow}$ and from the product of two terms of the form $1 - a_{i\downarrow}^\dagger a_{i\downarrow} - a_{i\uparrow}^\dagger a_{i\uparrow}$ taken from both $\hat{V}_{\text{int}}(\tau)$ and $\hat{V}_{\text{int}}(\tau')$. In the latter case, the two terms are τ -independent and identical. Thus time-ordering can be omitted, and integration over τ vanishes because of the $e^{i\omega_r\tau}$ factor. Consequently, we obtain

$$\begin{aligned} & \frac{1}{2} \int_0^\beta \int_0^\beta d\tau d\tau' \left\langle \mathcal{T} \hat{V}_{\text{int}}(\tau) \hat{V}_{\text{int}}(\tau') \right\rangle_{\lambda, \Delta_0} \\ &= \frac{1}{4} \sum_i \sum_{r, r' \neq 0} \Lambda_{ir} \Lambda_{ir'}^* \int_0^\beta \int_0^\beta d\tau d\tau' e^{i\omega_r\tau - i\omega_{r'}\tau'} B_i(\tau, \tau'), \end{aligned} \quad (\text{A1})$$

where

$$B_i(\tau, \tau') = \left\langle \mathcal{T} a_{i\uparrow}^\dagger(\tau) a_{i\downarrow}^\dagger(\tau) a_{i\downarrow}(\tau') a_{i\uparrow}(\tau') \right\rangle_{\lambda, \Delta_0}. \quad (\text{A2})$$

Wick's theorem cannot be applied directly to the correlator $B_i(\tau, \tau')$ because of the projections. To proceed, we use the following two identities

$$\left\langle a_{i\downarrow} a_{i\uparrow} a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger \right\rangle_{\lambda, \Delta_0} = e^{2\beta E_i} \left\langle a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger a_{i\downarrow} a_{i\uparrow} \right\rangle_{\lambda, \Delta_0} \quad (\text{A3})$$

and

$$\begin{aligned} & (1 - e^{2\beta E_i}) \left\langle a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger a_{i\downarrow} a_{i\uparrow} \right\rangle_{\lambda, \Delta_0} \\ &= -1 + \left\langle a_{i\downarrow}^\dagger a_{i\downarrow} \right\rangle_{\lambda, \Delta_0} + \left\langle a_{i\uparrow}^\dagger a_{i\uparrow} \right\rangle_{\lambda, \Delta_0}. \end{aligned} \quad (\text{A4})$$

The second identity follows directly from the first one and the anti-commutation relations. To derive the first identity, we write the projected average (34) of an observable \hat{A} at a given static field in the form

$$\left\langle \hat{A} \right\rangle_{\lambda, \Delta_0} = \sum_{\phi_\lambda} \tilde{C}_{\phi_\lambda} \left\langle \hat{A} \right\rangle_{\phi_\lambda}, \quad (\text{A5})$$

where \tilde{C}_{ϕ_λ} are certain coefficients and

$$\left\langle \hat{A} \right\rangle_{\phi_\lambda} = \frac{\text{Tr} \left(\hat{U}_{\Delta_0} e^{i\phi_\lambda \hat{S}_z} \hat{A} \right)}{\text{Tr} \left(\hat{U}_{\Delta_0} e^{i\phi_\lambda \hat{S}_z} \right)}. \quad (\text{A6})$$

The sum in (A5) is over quadrature points ϕ_λ suitable for the projection λ . In deriving (A5) we have used expressions (44) and (45) for the projection operators and replaced $e^{i\pi\hat{N}}$ by $e^{2i\pi\hat{S}_z}$ (N and $2S_z$ have the same parity). The expectation value in (A6) is grand canonical with respect to the one-body Hamiltonian $\hat{H}_{\Delta_0} - i\phi_\lambda\hat{S}_z/\beta$ (\hat{H}_{Δ_0} commutes with \hat{S}_z), and therefore can be calculated using

Wick's theorem. We find

$$\begin{aligned} \left\langle a_{i\downarrow}a_{i\uparrow}a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger \right\rangle_{\phi_\lambda} &= (1 - n_{i\uparrow}^{\phi_\lambda})(1 - n_{i\downarrow}^{\phi_\lambda}) \\ &= e^{2\beta E_i} n_{i\uparrow}^{\phi_\lambda} n_{i\downarrow}^{\phi_\lambda} = e^{2\beta E_i} \left\langle a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger a_{i\downarrow} a_{i\uparrow} \right\rangle_{\phi_\lambda}. \end{aligned} \quad (\text{A7})$$

where

$$n_{i\sigma}^{\phi_\lambda} = \left\langle a_{i\sigma}^\dagger a_{i\sigma} \right\rangle_{\phi_\lambda} = \frac{1}{e^{\beta E_i \mp i\phi_\lambda/2} + 1}. \quad (\text{A8})$$

Using Eqs. (A5) and (A7), we obtain the relation (A3).

We can now evaluate the integrals on the r.h.s. of Eq. (A1) with the help of Eq. (28) and the identities (A3) and (A4) to find

$$\begin{aligned} \int_0^\beta \int_0^\beta d\tau d\tau' e^{i\omega_r\tau - i\omega_{r'}\tau'} B_i(\tau, \tau') &= \left\langle a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger a_{i\downarrow} a_{i\uparrow} \right\rangle_{\lambda\Delta_0} \int_0^\beta \int_0^\beta d\tau d\tau' e^{i\omega_r\tau - i\omega_{r'}\tau'} e^{2E_i(\tau - \tau')} [\theta(\tau - \tau') + \theta(\tau' - \tau)e^{2\beta E_i}] \\ &= \left\langle a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger a_{i\downarrow} a_{i\uparrow} \right\rangle_{\lambda\Delta_0} \int_0^\beta d\tau e^{(i\omega_r + 2E_i)\tau} \left[-\frac{e^{-(i\omega_{r'} + 2E_i)\tau} - 1}{i\omega_{r'} + 2E_i} - \frac{1 - e^{2\beta E_i} e^{-(i\omega_{r'} + 2E_i)\tau}}{i\omega_{r'} + 2E_i} \right] = \frac{\beta\delta_{rr'}}{i\omega_r + 2E_i} f_{\lambda i}, \end{aligned} \quad (\text{A9})$$

where

$$f_{\lambda i} = 1 - \left\langle \left(a_{i\downarrow}^\dagger a_{i\downarrow} + a_{i\uparrow}^\dagger a_{i\uparrow} \right) \right\rangle_{\lambda\Delta_0} = \frac{1}{\beta} \frac{\partial \ln Z_\lambda(\Delta_0)}{\partial E_i}. \quad (\text{A10})$$

Introducing the real $\sigma_1(\tau)$ and imaginary $\sigma_2(\tau)$ parts of $\Delta(\tau)e^{-i\theta}$, we change variables

$$\Delta_r = e^{i\theta}(\sigma_{1r} + i\sigma_{2r}), \quad (\text{A11})$$

where σ_{kr} is the Fourier transform of $\sigma_k(\tau)$ ($\sigma_{k,-r} =$

σ_{kr}^*). The quantity Λ_{ir} in Eq. (27) can then be written as

$$\Lambda_{ir} = 2e^{i\theta} (\gamma_i\sigma_{1r} + i\sigma_{2r}) \quad (\text{A12})$$

and the integration measure as

$$\mathcal{D}'[\Delta_r, \Delta_r^*] = \mathcal{D}'[\sigma_{1r}, \sigma_{2r}] = \prod_{r>0} \frac{\beta^2 d\sigma_{1r} d\sigma_{1r}^* d\sigma_{2r} d\sigma_{2r}^*}{\pi^2 g^2}. \quad (\text{A13})$$

Consequently, the RPA correction factor is given by

$$\begin{aligned} C_\lambda^{\text{RPA}}(\Delta_0) &= \int \mathcal{D}'[\sigma_{1r}, \sigma_{2r}] \exp \left[-(2\beta/g) \sum_{r>0} \left(\left(1 - g \sum_i \frac{2E_i \gamma_i^2 f_{\lambda i}}{4E_i^2 + \omega_r^2} \right) |\sigma_{1r}|^2 + \left(1 - g \sum_i \frac{2E_i f_{\lambda i}}{4E_i^2 + \omega_r^2} \right) |\sigma_{2r}|^2 + \right. \right. \\ &\quad \left. \left. + g \sum_i \frac{\omega_r \gamma_i f_{\lambda i}}{4E_i^2 + \omega_r^2} (\sigma_{1r} \sigma_{2r}^* - \sigma_{1r}^* \sigma_{2r}) \right) \right] = \prod_{r>0} [\det A(\omega_r)]^{-1}. \end{aligned} \quad (\text{A14})$$

where the matrix $A(\omega_r)$ is defined in (51). Note that in general Eq. (50) is valid as long as Eq. (A3) holds or the projection operator in Z_λ conserves the quasiparticle occupation numbers.

Appendix B: Relation of the RPA correction factor to the RPA matrix

As a function of ω , $\det A(\omega)$ in (A14) has poles at $\omega = \pm 2iE_i$, which could be either first or second order. A second-order pole at $\pm 2iE_i$ can only arise from prod-

ucts of two terms that contribute to the matrix elements of $A(\omega)$ and have $(4E_i^2 + \omega_r^2)$ in their denominators. However, when the sum of these products is written as a ratio of polynomials, a partial cancellation between denominator and numerator results in first-order poles.

Since all the poles of $A(\omega)$ are first order, its determinant can be written as

$$\det A(\omega) = \frac{P(\omega)}{\prod_i (\omega^2 + 4E_i^2)}, \quad (\text{B1})$$

where $P(\omega)$ is a polynomial of degree $2N_{\text{sp}}$ (N_{sp} is the number of single-particle orbitals). The roots of $P(\omega)$ and $\det A(\omega)$ come in pairs $\pm i\Omega_i$ ($\det A(\omega)$ is a function of ω^2), and the leading coefficient of $P(\omega)$ is equal to one. Thus $P(\omega) = \prod_i (\omega^2 + \Omega_i^2)$ and

$$\det A(\omega_r) = \prod_i \frac{\omega_r^2 + \Omega_i^2}{\omega_r^2 + 4E_i^2}. \quad (\text{B2})$$

Using (A14) and the infinite product representation

$$\begin{cases} \eta_+ = \frac{g}{2} \sum_i \left[\frac{f_{\lambda_i} \gamma_i}{2E_i - \Omega} (\gamma_i \eta_+ + \eta_-) + \frac{f_{\lambda_i} \gamma_i}{2E_i + \Omega} (\gamma_i \eta_+ - \eta_-) \right] = g \sum_i \frac{2E_i \gamma_i^2 f_{\lambda_i}}{4E_i^2 - \Omega^2} \eta_+ + g \sum_i \frac{\Omega \gamma_i f_{\lambda_i}}{4E_i^2 - \Omega^2} \eta_- , \\ \eta_- = \frac{g}{2} \sum_i \left[\frac{f_{\lambda_i}}{2E_i - \Omega} (\gamma_i \eta_+ + \eta_-) - \frac{f_{\lambda_i}}{2E_i + \Omega} (\gamma_i \eta_+ - \eta_-) \right] = g \sum_i \frac{\Omega \gamma_i f_{\lambda_i}}{4E_i^2 - \Omega^2} \eta_+ + g \sum_i \frac{2E_i f_{\lambda_i}}{4E_i^2 - \Omega^2} \eta_- . \end{cases} \quad (\text{B5})$$

Eqs. (B5) can be rewritten in the form

$$B(\Omega) \begin{pmatrix} \eta_+ \\ \eta_- \end{pmatrix} = 0, \quad (\text{B6})$$

where $B(\Omega)$ is a 2×2 matrix satisfying $\det B(\Omega) = \det A(i\Omega)$. In general, $\begin{pmatrix} \eta_+ \\ \eta_- \end{pmatrix} \neq 0$ and Eq. (B6) implies $\det B(\Omega) = 0$. Therefore, $\omega = i\Omega$ is a root of $\det A(\omega)$. Since the eigenvalues of the RPA matrix (55) come in pairs $\pm\Omega$ and their number is equal to the number of roots of $\det A(\omega)$, we conclude that all of the Ω_i in Eq. (54) are eigenvalues of (55) and vice versa.

The approximation used to calculate the correction factor (50) breaks down when at least one of the matrices $A(\omega_r)$ has an eigenvalue with negative real part and the corresponding Gaussian integral diverges. As discussed in Sec. III E, the necessary and sufficient conditions for the SPA+RPA to be applicable are that all matrices $A(\omega_r)$ have positive traces and determinants [see Eqs. (53)]. It is clear from (B2) that $\det A(\omega_r)$ can be made negative only when at least one of the Ω_i is complex. Moreover, such Ω_i must be purely imaginary; otherwise Ω_i^* also appears in the product of Eq. (B2) making the combined contribution from Ω_i and Ω_i^* positive. When Ω_i is purely imaginary, its complex conjugate

$\sinh x = x \prod_{r>0} (1 + x^2/\pi^2 r^2)$, we obtain the expression (54) for the RPA correction factor.

Next, we show that $\pm\Omega_i$ are the eigenvalues of the $2N_{\text{sp}} \times 2N_{\text{sp}}$ RPA matrix (55). Indeed, considering one of the eigenvalues Ω of this matrix and denoting its corresponding eigenvector by $(\chi_{1i} \chi_{2i})^T$, we have

$$\begin{cases} \chi_{1i} = \frac{g}{2} \frac{f_{\lambda_i}}{2E_i - \Omega} \sum_j ((\gamma_i \gamma_j + 1)\chi_{1j} + (\gamma_i \gamma_j - 1)\chi_{2j}) , \\ \chi_{2i} = \frac{g}{2} \frac{f_{\lambda_i}}{2E_i + \Omega} \sum_j ((\gamma_i \gamma_j - 1)\chi_{1j} + (\gamma_i \gamma_j + 1)\chi_{2j}) . \end{cases} \quad (\text{B3})$$

Defining

$$\begin{cases} \eta_+ = \sum_j (\chi_{1j} + \chi_{2j}) \gamma_j , \\ \eta_- = \sum_j (\chi_{1j} - \chi_{2j}) , \end{cases} \quad (\text{B4})$$

we obtain

belongs to the same ‘‘pair’’ $\pm\Omega_i$ of eigenvalues of the RPA matrix and does not give a separate contribution to the product in (B2). As the temperature decreases and an RPA frequency becomes purely imaginary, the first determinant that becomes singular is the one with the smallest ω_r , i.e., $\omega_1 = 2\pi T$. Consequently, all determinants $\det A(\omega_r)$ are positive if $|\Omega_i| < 2\pi T$ for all purely imaginary RPA frequencies Ω_i . There is a critical temperature T_* below which this condition is no longer satisfied for some value of the static gap Δ_0 .

In principle, the condition $|\Omega_i| < 2\pi T$ is necessary but not sufficient. Simulations show that for a small static field Δ_0 , the eigenvalues of $A(\omega_r)$ may form a complex-conjugate pair such that $\det A(\omega_r)$ positive, while their real parts may be negative. This can happen at temperatures of the order or lower than T_* .

-
- ¹ D. C. Ralph, C. T. Black, and M. Tinkham, Phys. Rev. Lett. **74**, 3241 (1995).
- ² C. T. Black, D. C. Ralph, and M. Tinkham, Phys. Rev. Lett. **76**, 688 (1996).
- ³ D. C. Ralph, C. T. Black, and M. Tinkham, Phys. Rev. Lett. **78**, 4087 (1997).
- ⁴ F. Kueemeth, K. I. Bolotin, S. F. Shi, and D. C. Ralph, Nano Lett. **8**, 4506 (2008).
- ⁵ Y. Alhassid, Rev. Mod. Phys. **72**, 895 (2000).
- ⁶ M. L. Mehta, *Random Matrices*, 2nd ed. (Academic, New York, 1991).
- ⁷ I. L. Kurland, I. L. Aleiner, and B. L. Altshuler, Phys. Rev. B **62**, 14886 (2000).
- ⁸ I. L. Aleiner, P. W. Brouwer, and L. I. Glazman, Phys. Rep. **358**, 309 (2002).
- ⁹ Y. Alhassid and T. Rupp, Phys. Rev. Lett. **91**, 056801 (2003).
- ¹⁰ I. S. Burmistrov, Y. Gefen, and M. N. Kiselev, JETP Lett. **92**, 179 (2010).
- ¹¹ I. S. Burmistrov, Y. Gefen, and M. N. Kiselev, Phys. Rev. B **85**, 155311 (2012).
- ¹² R. L. Stratonovich, Dokl. Akad. Nauk SSSR [Sov. Phys. - Dokl.] **115**, 1097 (1957).
- ¹³ J. Hubbard, Phys. Rev. Lett. **3**, 77 (1959).
- ¹⁴ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
- ¹⁵ J. von Delft and D. C. Ralph, Phys. Rep. **345**, 61 (2001).
- ¹⁶ P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
- ¹⁷ A. Di Lorenzo, R. Fazio, F. W. J. Hekking, G. Falci, A. Mastellone, and G. Giaquinta, Phys. Rev. Lett. **84**, 550 (2000).
- ¹⁸ G. Falci, R. Fazio, F. W. J. Hekking, and A. Mastellone, J. Low Temp. Phys. **118**, 355 (2000).
- ¹⁹ Y. Volokitin, J. Sinzig, L. J. de Jongh, G. Schmid, M. N. Vargaftik, and I. Moiseev, Nature **384**, 621 (1996).
- ²⁰ B. Muhlshlegel, D. J. Scalapino, and R. Denton, Phys. Rev. B **6**, 1767 (1972).
- ²¹ Y. Alhassid and J. Zingman, Phys. Rev. C **30**, 684 (1984).
- ²² B. Lauritzen, P. Arve, and G. F. Bertsch, Phys. Rev. Lett. **61**, 2835 (1988).
- ²³ A. K. Kerman and S. Levit, Phys. Rev. C **24**, 1029 (1981).
- ²⁴ A. K. Kerman, S. Levit, and T. Troudet, Ann. Phys. (NY) **148**, 436 (1983).
- ²⁵ G. Puddu, P. Bortignon, and R. Broglia, Ann. Phys. (NY) **206**, 409 (1991).
- ²⁶ B. Lauritzen, A. Anselmino, P. Bortignon, and R. Broglia, Ann. Phys. (NY) **223**, 216 (1993).
- ²⁷ R. Rossignoli and N. Canosa, Phys. Lett. B **394**, 242 (1997).
- ²⁸ H. Attias and Y. Alhassid, Nucl. Phys. A **625**, 565 (1997).
- ²⁹ A. L. Goodman, Nucl. Phys. A **352**, 30 (1981).
- ³⁰ R. Rossignoli, N. Canosa, and P. Ring, Phys. Rev. Lett. **80**, 1853 (1998).
- ³¹ R. Balian, H. Flocard, and M. Veneroni, Phys. Rep. **317**, 252 (1999).
- ³² G. Falci, A. Fubini, and A. Mastellone, Phys. Rev. B **65**, 140507 (2002).
- ³³ K. Van Houcke, S. M. A. Rombouts, and L. Pollet, Phys. Rev. B **73**, 132509 (2006).
- ³⁴ Y. Alhassid, L. Fang, and S. Schmidt, cond-mat/0702304.
- ³⁵ R. W. Richardson, Phys. Lett. **3**, 277 (1963).
- ³⁶ R. W. Richardson, Phys. Rev. **159**, 792 (1967).
- ³⁷ M. Schechter, Y. Imry, Y. Levinson, and J. von Delft, Phys. Rev. B **63**, 214518 (2001).
- ³⁸ V. N. Gladilin, V. M. Fomin, and J. T. Devreese, Phys. Rev. B **70**, 144506 (2004).
- ³⁹ Z. J. Ying, M. Cuoco, C. Noce, and H. Q. Zhou, Phys. Rev. B **74**, 012503 (2006).
- ⁴⁰ S. Schmidt, Y. Alhassid, and K. Van Houcke, Europhys. Lett. **80**, 47004 (2007).
- ⁴¹ G. Falci, R. Fazio, and A. Mastellone, Phys. Rev. B **67**, 132501 (2003).
- ⁴² K. Van Houcke, Y. Alhassid, S. Schmidt, and S. M. A. Rombouts, arXiv:1011.5421.
- ⁴³ M. Schechter, Phys. Rev. B **70**, 024521 (2004).
- ⁴⁴ Y. Alhassid, S. Liu and H. Nakada, Phys. Rev. Lett. **99**, 162504 (2007).
- ⁴⁵ Y. Alhassid, H. A. Weidenmuller, and A. Wobst, Phys. Rev. B **72**, 045318 (2005).
- ⁴⁶ S. D. Berger and B. I. Halperin, Phys. Rev. B **58**, 5213 (1998).
- ⁴⁷ If particle-number projection is carried out after the functional integral (31) is calculated, large errors are almost unavoidable because the canonical projection involves an oscillating sum or an integral of quantities whose only approximate values are known. For the same reason, S_z projection is done for each value of Δ_0 rather than after calculating the integral.
- ⁴⁸ Y. Alhassid, G. F. Bertsch, L. Fang, and S. Liu, Phys. Rev. C **72**, 064326 (2005).
- ⁴⁹ P. Ribeiro, and A. M. García-García, Phys. Rev. Lett. **108**, 097004 (2012).
- ⁵⁰ I. S. Beloborodov, A. V. Lopatin, V. M. Vinokur, and K. B. Efetov, Rev. Mod. Phys. **79**, 469 (2007).