Ultra-small metallic grains

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- Introduction

- Superconducting metallic grains (nanoparticles): BCS (bulk) regime and fluctuation-dominated regime.

(I) Nanoparticles without spin-orbit scattering

Competition between pairing (superconductivity) and spin exchange correlations (ferromagnetism).

- Quantum phase diagram
- Transport
- Thermodynamics.

(II) Nanoparticles with spin-orbit scattering

Response to an external magnetic field: g-factor and level curvature

- Effects of pairing correlations on the g-factor and level curvature statistics.

- Conclusion
Introduction: ultra-small metallic grains (nanoparticles)

- Discrete energy levels extracted from non-linear conductance measurements (Ralph et al).
- Experiments on Al, Co, Au, Cu, and Ag grains.
- Ultra-small (nano-scale) grains: probe the quantum regime $T \ll \delta$ ($\delta$ = single-particle level spacing)

Superconducting grains

Consider materials that are superconductors in the bulk and characterized by a pairing gap $\Delta$. 

(i) Large Al grains (~ 10 nm) $\Delta \gg \delta$

The pairing gap is directly observed in the spectra of such grains with even number of electrons.

(ii) Small Al grains (~ 1 nm) $\Delta \leq \delta$

- BCS theory breaks down.
  “Superconductivity would no longer be possible” (Anderson)

A mesoscopic regime dominated by large fluctuations of the pairing gap (fluctuation-dominated regime).

Do signatures of pairing correlations survive the large fluctuations?

(I) Superconducting nanoparticles without spin-orbit scattering

An isolated chaotic grain with a large number of electrons is described by the universal Hamiltonian [Kurland, Aleiner, Altshuler, PRB 62, 14886 (2000)]

\[ H = \sum_i \varepsilon_i (a_{i\uparrow}^\dagger a_{i\uparrow} + a_{i\downarrow}^\dagger a_{i\downarrow}) + \frac{e^2}{2C} N^2 - G P^\dagger P - J_s S^2 \]

- Discrete single-particle levels \( \varepsilon_i \) (spin degenerate) and wave functions follow random matrix theory (RMT).
- Attractive BCS-like pairing interaction (\( P^\dagger = \sum_i a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger \) is the pair operator) with coupling \( G > 0 \).
- Ferromagnetic exchange interaction (\( \bar{S} \) is the total spin of the grain) with exchange constant \( J_s > 0 \).
- Corrections \( \sim O(1 / g) \) are small for large Thouless conductance \( g \).

Competition between pairing and exchange correlations: pairing favors minimal ground-state spin, while exchange favors maximal spin polarization.
A derivation from symmetry principles
[Y. A., H.A. Weidemuller, A. Wobst, PRB 72, 045318 (2005)]

\[ H = \sum_{\alpha\sigma} \varepsilon_{\alpha} a_{\alpha\sigma}^{\dagger} a_{\alpha\sigma} + \frac{1}{2} \sum_{\alpha\beta;\gamma\delta\sigma\sigma'} v_{\alpha\beta;\gamma\delta} a_{\alpha\sigma}^{\dagger} a_{\beta\sigma'}^{\dagger} a_{\gamma\sigma'} a_{\delta\sigma} \]

where \( v \) is the (screened) Coulomb interaction

- The randomness of the single-particle wave functions induces randomness in the two-body interaction matrix elements.

- Cumulants of the interaction matrix elements are determined by requiring invariance under a change of the single-particle basis (single-particle dynamics are chaotic).

**Averages:** There are three (two) invariants in the orthogonal (unitary) symmetry:

\[ \overline{v}_{\alpha\beta;\gamma\delta} = v_0 \delta_{\alpha\gamma} \delta_{\beta\delta} + J_s \delta_{\alpha\delta} \delta_{\beta\gamma} - G \delta_{\alpha\beta} \delta_{\gamma\delta} \]

\[ \iff \overline{v} = \frac{1}{2} (v_0 - J_s / 2) \hat{N}^2 - (v_0 / 2 - J_s) \hat{N} - J_s \hat{S}^2 - G \hat{P}^{\dagger} \hat{P} \]
Eigenstates of the universal Hamiltonian:

The eigenstates $|U\zeta; B\gamma SM>$ factorizes into two parts:

$U$ is a subset of doubly occupied and empty levels.

$B$ is a subset of singly occupied levels

(i) $|U\zeta>$ are zero-spin eigenstates of the reduced BCS Hamiltonian

(ii) $|B\gamma SM>$ are eigenstates of $\vec{S}^2$, obtained by coupling spin-1/2 singly-occupied levels in $B$ to total spin $S$ and spin projection $M$.

Exact solution: Richardson’s solution for the reduced BCS plus spin algebra.

For a review, see J. Dukelsky, S. Pittel, and G. Sierra, Rev. Mod. Phys. 76, 643 (2004)
Ground-state spin in the $\frac{J_s}{\delta} - \frac{\Delta}{\delta}$ plane (for an equally spaced single-particle spectrum)

Exact solution: coexistence of superconductivity and ferromagnetism in the fluctuation-dominated regime.


Mean-field approximation (S-dependent BCS) fails to reproduce coexistence.
Transport: Coulomb blockade conductance

A conductance peak is observed for each electron that tunnels into the dot.

- Single-particle energies and wave functions are described by RMT.

Mesoscopic fluctuations of $G_{\text{max}}$ and $\Delta_2$.
In sequential tunneling, there are two classes of transport processes:

(i) The electron tunnels into an empty level $\lambda$ and blocks it
After tunneling:

\[ S = \frac{3}{2} \]
(ii) The electron tunnels into a singly occupied level $\lambda$ and unblocks it.

Before tunneling:

\[ S=1 \]
After tunneling:

\[ S = \frac{1}{2} \]
Mesoscopic fluctuations of the conductance peaks

Single-particle energies and wave functions described by random matrix statistics (GOE).

Peak-spacing statistics ($T = 0.1\delta$)

![Peak-spacing distributions](image)

- Exchange suppresses bimodality while pairing enhances it.
Exchange interaction suppresses the peak-height fluctuations.

Mesoscopic signatures of coexistence of pairing and exchange correlations for $\Delta/\delta = 0.5$ and $J_s/\delta = 0.6$ : bimodality of peak spacing distribution (pairing) and suppression of peak height fluctuations (exchange).

Peak-height statistics ($T = 0.1\delta$)
Richardson’s solution becomes impractical at higher temperatures.

**A finite-temperature method:**

\[
H = \sum_i \varepsilon_i (a_{i\uparrow}^\dagger a_{i\uparrow} + a_{i\downarrow}^\dagger a_{i\downarrow}) - GP^\dagger P - J_s \vec{S}^2 = H_{BCS} - J_s \vec{S}^2
\]

(i) Exact spin projection method

\[
\text{Tr} e^{-\beta H} = \sum_S e^{\beta J_s S(S+1)} \text{Tr}_S e^{-\beta H_{BCS}}
\]

Trace over states with fixed spin \(S\)

\[
\text{Tr}_S X = (2S+1)(\text{Tr}_{S_z=S} X - \text{Tr}_{S_z=S+1} X)
\]

Trace with fixed spin component \(S_z\) (calculated by Fourier transform)

(ii) Functional integral representation (Hubbard-Stratonovich) for the reduced pairing Hamiltonian $H_{BCS}$:

$$e^{-\beta H_{BCS}} = \int D[\Delta(\tau), \Delta^*(\tau)] T e^{\beta \int_0^\beta d\tau(|\Delta(\tau)|^2/G+h[\Delta(\tau),\Delta^*(\tau)])}$$

one-body Hamiltonian in pairing field $\Delta(\tau)$

Expand $\Delta(\tau) = \Delta_0 + \sum_m \Delta_m e^{i\omega_m \tau}$

($\omega_m$ are Matsubara frequencies).

Integrate over $\Delta_0$ exactly (static path approximation) and over $\Delta_m$ by saddle point [i.e., random phase approximation (RPA)] around each static $\Delta_0$

(iii) Number-parity projection to capture odd-even effects.

$$P_\eta = \frac{(1 + \eta e^{i\pi N})}{2}$$

$\eta = 1(\eta = -1)$ describes a projection on even (odd) number of particles

Comparison with exact results for particular realizations of the single-particle spectrum

- The static path + RPA+number-parity projection is an accurate method yet very efficient.
Fluctuation-dominated regime: exchange correlations suppress the odd-even signatures of pairing correlations.

BCS regime: exchange correlations enhance the S-shoulder in the even case.
Spin susceptibility

- **Fluctuation-dominated regime**: exchange correlations enhance the fluctuations of the susceptibility.
- **BCS regime**: exchange correlations enhance re-entrant effect.

The exchange interaction enhances the mesoscopic fluctuations.
Spin-orbit scattering breaks spin symmetry but preserves time-reversal. The exchange interaction is suppressed but the pairing interaction remains unaffected.

We studied the response of energy levels in the nanoparticle to external magnetic field $B$: linear (g factor) and quadratic (level curvature) terms.

In the absence of pairing correlations, the single-particle levels are given by

$$\varepsilon_i \pm \frac{1}{2} g \mu_B B + \frac{1}{2} \kappa B^2 + ...$$

- Without spin orbit scattering, spin is a good quantum number and $g=2$.
- With spin-orbit scattering, spin is no longer conserved. The g factor is suppressed ($g<2$) and exhibits level-to-level fluctuations. In general, g has a tensor structure. The statistical distribution of the g factor was studied using random matrix theory.

[Brouwer, Waintal and Halperin (2000); Matveev, Glazman and Larkin (2000)]
• Recent advances (use of organic substrates) are providing much better control over the size and shape the metallic grain.

• Level and g-factor statistics in a gold grain are in agreement with the symplectic ensemble of RMT (Ralph et al, 2008).
**g factor and level curvature in the presence of interactions**

dl/dV curves in tunneling spectroscopy experiments measure the energy differences $\Delta E_{\Omega}$ between many-particle states with N+1 and N electrons.

We assume a one-bottleneck geometry: decay into the ground state before another electron is added.

For tunneling into the even ground state

$$\Delta E_{\Omega} = E_{\Omega}^{N+1} - E_{0}^{N}$$

Many-body levels of the odd nanoparticle are doubly degenerate (Kramers’ degeneracy), and they split in a magnetic field

$$\Delta E = \Delta E(0) \pm \frac{1}{2} g \mu_B B + \frac{1}{2} \kappa B^2 + ...$$

$g$ and $\kappa$ reduce to the single-particle level quantities in the constant-interaction model.
Universal Hamiltonian with strong spin-orbit scattering

\[ H = \sum_{i,\alpha} \varepsilon_i a_{i\alpha}^\dagger a_{i\alpha} - G P^\dagger P - BM_z \]

where \( \alpha = 1,2 \) is the Kramers doublet with energy \( \varepsilon_i \) and \( P^\dagger = \sum_i a_{i1}^\dagger a_{i2}^\dagger \)

Even ground state

\( G = 0 \)

(b) \( G \neq 0 \)

Odd state

(c) blocked orbital \( k_0 \)

(d) \( k_0' \)

\[ C_1 + C_2 + C_3 + \ldots \]

\[ C_1' + C_2' + C_3' + \ldots \]
For the even ground state:

$$\langle 0 | M^z | 0 \rangle = 0$$

by time-reversal symmetry

($M^z$ is odd under time reversal)

For the odd state:

$$\langle \Omega | M^z | \Omega' \rangle = M^{z}_{k_0\alpha,k_0\alpha'}$$

since

$$M^{z}_{m_1,m_1} + M^{z}_{m_2,m_2} = 0$$

by time-reversal symmetry

The many-particle g factor reduces to the single-particle g factor of the odd-particle blocked orbital $k_0$.

The g-factor distributions are not affected by pairing correlations.
Level curvature $\kappa$ (quadratic correction)

In second-order perturbation theory (even ground state to odd ground state)

$$\kappa = \sum_{\Omega' \neq 0} \frac{|\langle \Omega' | M_z | 0 \rangle_{N+1}|^2}{E_0^{N+1} - E_{\Omega'}^{N+1}} - \sum_{\Theta' \neq 0} \frac{|\langle \Theta' | M_z | 0 \rangle_N|^2}{E_0^N - E_{\Theta'}^N}$$

In the non-interacting case, $\kappa$ reduces to the single-level curvature

The single-level curvature distribution is symmetric around $\kappa = 0$. 

$$P\left(\frac{\kappa}{\langle |\kappa| \rangle}\right)^{0.5} = \begin{cases} 0.5 & \kappa / \langle |\kappa| \rangle < -2 \\ 0.4 & \kappa / \langle |\kappa| \rangle = -2 \\ 0.3 & \kappa / \langle |\kappa| \rangle = -2 \\ 0.2 & \kappa / \langle |\kappa| \rangle = -2 \\ 0.1 & \kappa / \langle |\kappa| \rangle = -2 \end{cases}$$
Results for the many-particle level curvature distributions

- Single-particle levels follow the Gaussian symplectic ensemble (GSE).
- Exact CI calculation versus a generalized BCS approach.

Similar qualitative behavior is observed in the exact results and in the BCS approximation: the curvature distribution is asymmetric and shifted towards negative values.

Many-particle level curvature distribution is highly sensitive to pairing correlations (even in the fluctuation-dominated regime)

Can be used as a tool to probe pairing correlations in the single-electron tunneling spectroscopy experiments.
Conclusion

- A superconducting nano-scale metallic grain is characterized by two regimes: BCS regime $\Delta / \delta \gg 1$ and fluctuation-dominated regime $\Delta / \delta \leq 1$.

(I) In the absence of spin-orbit scattering:
- Competition between pairing and spin exchange correlations
- Coexistence of superconductivity and ferromagnetism in the fluctuation-dominated regime
- Effects of exchange correlations on the odd-even signatures of pairing correlations are qualitatively different in the BCS and fluctuation-dominated regimes.

(II) In the presence of spin-orbit scattering:
- Spin exchange correlations are suppressed.
- $g$-factor statistics are unaffected by pairing correlations.
- Level curvature statistic is highly sensitive to pairing correlations.