# Ultra-small metallic grains

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- (I) Nanoparticles without spin-orbit scattering Competition between pairing (*superconductivity*) and spin exchange correlations (*ferromagnetism*).
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- (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.
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## Introduction: ultra-small metallic grains (nanoparticles)

- Discrete energy levels extracted from non-linear conductance measurements (Ralph et al).
- Experiments on AI, 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.



- The Bardeen-Cooper-Schrieffer (BCS) theory is valid (BCS regime)
- (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 ?

For a review, see J. von Delft and D.C. Ralph, Phys. Rep 345, 61 (2001).

#### (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)]

$$H = \sum_{i} \varepsilon_{i} (a_{i\uparrow}^{\dagger} a_{i\uparrow} + a_{i\downarrow}^{\dagger} a_{i\downarrow}) + \frac{e^{2}}{2C} N^{2} - G P^{\dagger} P - J_{s} \vec{S}^{2}$$

- Discrete single-particle levels  $\mathcal{E}_i$  (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 ( S is the total spin of the grain) with exchange constant  $J_s > 0$ .
  - Corrections ~ 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)]

$$H = \sum_{\alpha\sigma} \varepsilon_{\alpha} a^{\dagger}_{\alpha\sigma} a_{\alpha\sigma} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta\sigma\sigma'} \mathbf{v}_{\alpha\beta;\gamma\delta} a^{\dagger}_{\alpha\sigma} a^{\dagger}_{\beta\sigma'} a_{\gamma\sigma'} a_{\delta\sigma}$$

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:

$$\overline{\mathbf{v}}_{\alpha\beta;\gamma\delta} = \mathbf{v}_0 \delta_{\alpha\gamma} \delta_{\beta\delta} + J_s \delta_{\alpha\delta} \delta_{\beta\gamma} - G \delta_{\alpha\beta} \delta_{\gamma\delta}$$
  
$$\Leftrightarrow \overline{V} = \frac{1}{2} (\mathbf{v}_0 - J_s/2) \hat{N}^2 - (\mathbf{v}_0/2 - J_s) \hat{N} - J_s \hat{S}^2 - G \hat{P}^{\dagger} \hat{P}$$

#### Eigenstates of the universal Hamiltonian:

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

- U is a subset of doubly occupied and empty levels.
- *B* is a subset of singly occupied levels

(i)  $|U\varsigma\rangle$  are zero-spin eigenstates of the *reduced BCS Hamiltonian* 



#### Quantum phase diagram

Z. Ying et al, Phys. Rev. B 74, 012503 (2006)

S. Schmidt, Y.A., K. van Houcke, Europhys. Lett., 80, 47004 (2007)

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



Conductance in a metallic grain [S. Schmidt and Y.A, PRL 101, 207003 (2008)]

In sequential tunneling, there are two classes of transport processes:

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

Before tunneling:



## After tunneling:



(ii) The electron tunnels into a singly occupied level  $\lambda$  and unblocks it

Before tunneling:



## After tunneling:



S=1/2

#### Mesoscopic fluctuations of the conductance peaks

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

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



• Exchange suppresses bimodality while pairing enhances it.

## Peak-height statistics ( $T = 0.1\delta$ )



• 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).

#### Thermodynamics

#### K. Nesterov and Y.A., PRB 87, 014515 (2013)

Richardson's solution becomes impractical at higher temperatures.

A finite-temperature method:

Т

$$H = \sum_{i} \mathcal{E}_{i} (a_{i\uparrow}^{\dagger} a_{i\uparrow} + a_{i\downarrow}^{\dagger} a_{i\downarrow}) - GP^{\dagger}P - J_{s}\vec{S}^{2} = H_{BCS} - J_{s}\vec{S}^{2}$$
(i) Exact spin projection method  

$$Tre^{-\beta H} = \sum_{s} e^{\beta J_{s}S(S+1)}Tr_{s}e^{-\beta H_{BCS}}$$
Trace over states with fixed spin S  

$$Tr_{s}X = (2S+1)(Tr_{S_{z}=S}X - Tr_{S_{z}=S+1}X)$$
Trace with fixed spin component  $S_{z}$  (calculated by Fourier transform)

See Y.A., Liu and Nakada, PRL 99, 162504 (2007).

(ii) Functional integral representation (Hubbard-Stratonovich) for the reduced pairing Hamiltonian  $H_{BCS}$ :  $\int_{-\int d\tau (|\Lambda(\tau)|^2/G+h[\Lambda(\tau)]\Lambda^*(\tau)])}^{\beta}$ 

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

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.

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

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

See also R. Rossignoli, N. Canosa and P. Ring, Phys. Rev. Lett. 80, 1853 (1998); G. Falci, A. Fubini, and A. Mastellone, Phys. Rev. B 65, 140507 (2002). 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.

## Heat capacity



Fluctuation-dominated regime: exchange correlations suppress the oddeven 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.

## (II) Superconducting nanoparticles with spin-orbit scattering K. Nesterov and Y.A. (2014)

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

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

- 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.</li>
   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  $\Delta E_{\Omega} = E_{\Omega}^{N+1} - E_{\Omega}^{N}$ 

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

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

g and  $\kappa$  reduce to the single-particle level quantities in the constant-interaction model.

Universal Hamiltonian with strong spin-orbit scattering

$$H = \sum_{i,\alpha} \varepsilon_i a_{i\alpha}^{\dagger} a_{i\alpha} - G P^{\dagger} P - B M_z$$

where  $\alpha = 1,2$  is the Kramers doublet with energy  $\mathcal{E}_i$  and  $P^{\dagger} = \sum a_{i1}^{\dagger} a_{i2}^{\dagger}$ 



g-factor (linear correction)

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:

 $\langle \Omega | M_z | \Omega' \rangle = M_{k_0 \alpha, k_0 \alpha'}^z$ 

since  $M_{m1,m1}^{z} + M_{m2,m2}^{z} = 0$  by time-reversal symmetry

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

g-factor distributions are not affected by pairing correlations.

#### Level curvature K (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, κ reduces to the single-level curvature

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



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 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 characterize by two regimes: BCS regime  $\Delta / \delta >> 1$  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 fluctuationdominated 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