Superconductivity in Small Samples

- What does "superconductivity" mean if the sample contains a fixed number of electrons?
- nm-sized samples
- pm-sized samples

References:
M. Tinkham, Intro to Superconductivity 2nd Ed
Ch. 7
J. van Delft, to appear in Physics Reports
http://www-thp.physik.uni-heidelberg.de/~vandelft/Kabil/physicsreports.ps

Conventional Electron-Beam Lithography:
70 x 20 x 2000 nm³ island

NSN tunneling transistor $10^3$ conduction electrons

- J. Hergeroth

Ralph Lecture 2
Small Samples and Charging

Coulomb Charging Energy $\sim \frac{e^2}{2C}$

For $100\text{nm} \times 100\text{nm}$ junction $C \approx 10^{-15} \text{F}$, $\frac{e^2}{k_B T C} \approx 1 \text{ K}$.

$3 \text{nm} \times 3 \text{nm}$ $C \approx 10^{-18} \text{F}$ $\frac{e^2}{k_B T C} \approx 1000 \text{ K}$.

Thermal Charge Fluctuations

For $k_B T < \frac{e^2}{2C}$, thermal fluctuations are suppressed.

Quantum Charge Fluctuations

are suppressed if the lifetime broadening of energy levels

$\frac{1}{\tau} < \frac{e^2}{2C}$

$\frac{1}{\tau} = RC$ lifetime of charge on capacitor

$\Rightarrow$ need $\frac{1}{RC} < \frac{e^2}{2C}$ or $R \gg \frac{2 \tau}{e^2}$

Conclusion - The charge on a metal grain is controllable to unit accuracy if

$k_B T < \frac{e^2}{2C}$ \quad $R \gg \frac{1}{C}$

Even if the total number of electrons $\gg 10^9$!

Tuning the Charge - Effects of Gate Voltage

Let $n_e$ be the number of excess charges on a metal island.

$E(n) = \frac{(ne)^2}{2C_e} - ne C_g V_g$

$= \frac{1}{2C_e} (ne - C_g V_g)^2 - \left(C_g V_g - \frac{1}{2C_e} \right)^2$

Ignore - doesn't depend on $n$

Units of charge - call this $Q_0 = C_g V_g$

For a given charge, energy depends quadratically on $Q_0$ (gate voltage)

\begin{align*}
E & \left( \frac{Q}{Q_0} \right) = 3 \\
-2 & \leq \frac{Q}{Q_0} \leq 2
\end{align*}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{graph.png}
\end{figure}
Is Superconductivity Still Possible With a Fixed Number of Electrons?

- BCS theory assumes a grand canonical ensemble. The ground state is written as a superposition of states with different numbers of electrons
  \[ |\Phi_6\rangle = \frac{1}{\Omega} \left(|u_1 + v_i c_i^+ c_i^\dagger \rangle |\text{vac}\rangle \right) \]

- The superconducting order parameter is normally defined as
  \[ \Delta_{\text{so}} = \lambda \langle \delta E \rangle \sum_i <c_{i\uparrow} c_{i\downarrow}> \]
  
  \[ = 0 \] for a fixed number of electrons.

- The superconducting phase is canonically conjugate to the electron number. If the electron number is fixed, then the phase is completely uncertain (No breaking of gauge invariance.)
In Reality - No Problem

The BCS pairing Hamiltonian can be solved exactly using a canonical ensemble (fixed # of electrons)
- R.W. Richardson (1960's -70's)

Attractive e-e interactions still lead to a pair-correlated ground state, with a gap to excitations. (Just like ordinary BCS theory)

(Important for many years in nuclear physics)

Can define a good order parameter

\[ \Delta_{ AVG} = \frac{1}{N} \sum_{i,j} \left( \langle i | c_i^+ c_j^+ i | \langle j | c_j c_i \rangle - \langle i | c_i^+ c_i^+ \rangle \langle j | c_i c_i \rangle \right) \]

The experiments I describe will demonstrate these pairing correlations.

Effects of Pairing - Even/Odd Effects

For Even # of Electrons:
- Ground State - Fully paired
- 1st Excited State - 1 broken pair (higher energy by \( 2\Delta \))

For Odd # of Electrons
- Ground state - 1 unpaired electron
- Relative to even-electron ground state, higher in energy by \( \Delta \) (plus changing energy)

\[ \frac{E}{E_c} \]

\[ \Delta \]

\[ n=0 \quad n=\pm 1 \quad n=\pm 2 \]

\[ Q_0 \]
Direct measurements of average charge on the island.

P. Lafarge et al.
PRL 70, 994 (93)
When raising $T$, why does the even-odd effect go away when $T \ll T_c$?

Thermally-excited quasiparticles - If a sample contains enough quasiparticles, no significant difference between even/odd.

Easy calculation - At what $T$ does a sample contain on average 1 quasiparticle. (Think about easiest case - no parity restrictions.)

$$\langle N_{q}(T) \rangle = \frac{1}{(Vol)} \int_{0}^{\infty} \rho_{3}(\varepsilon) f(\varepsilon, T) d\varepsilon$$

$$= \frac{1}{(Vol)} \int_{0}^{\infty} \rho_{3}(\varepsilon) e^{-\beta \Delta} d\varepsilon$$

$$= \frac{1}{(Vol)} \int_{0}^{\infty} \rho_{3}(\varepsilon) e^{-\beta \varepsilon} d\varepsilon$$

Results of a proper calculation:

Crossover temperature $T_0^*$

$$1 \sim N_{st} \sim \frac{\Delta}{k_{B}T_0^*}$$

$$\Rightarrow k_{B}T_0^* \sim \frac{\Delta}{\ln(N_{st})} \sim \frac{1.8 k_{B}T_{c}}{\ln(10^5)} \sim \frac{k_{B}T_{c}}{5}$$
How small a metal particle is required in order to resolve individual electronic states?

Need $\delta E > k_B T$.

$$\delta E = \frac{4\varepsilon_F}{3N} = \frac{2\pi^2 h^2}{mk_F \nu}$$

$$\nu = \frac{90 \text{ nm}^3}{\delta E / \text{meV}}$$

Suppose we want $\delta E > k_B (1 \text{ K}) \sim 0.1 \text{ meV}$.

$$\Rightarrow \nu < (10 \text{ nm})^3.$$
DEVICE CONCEPT

Without gate:

With gate:

Device Fabrication

1. Si₃N₄

2. 3-10 nm

3. Si₃N₄

4. Al

Al lead

Al lead Al particle

10 nm scale
TUNNELING VIA DISCRETE STATES

NORMAL METAL LEADS

Superconducting Particle

even to odd transitions (50 mK, 0.05 Tesla)

\[ V_g = -1216 \text{ mV} \]

\[ n_{e-1} \rightarrow n_e \]

\[ V_g = 166 \text{ mV} \]

\[ n_{e+1} \rightarrow n_e \]

\begin{align*}
\text{Energy (meV)} & \\ 
0.0 & \sim 1.5
\end{align*}

odd to even transitions

\[ V_g = -1177 \text{ mV} \]

\[ n_e \rightarrow n_{e-1} \]

\[ V_g = 110 \text{ mV} \]

\[ n_e \rightarrow n_{e+1} \]

\begin{align*}
\text{Energy (meV)} & \\ 
0.0 & \sim 1.5
\end{align*}
EVEN/ODD ELECTRON EFFECT IN MAGNETIC FIELD

For even number of electrons, the first tunneling state exhibits Zeeman spin splitting.
For odd number of electrons, the first state does not exhibit Zeeman splitting.

Independent Electron Picture:

![Energy levels diagram]

Magnetic field

Even particle

Odd particle

Occupied levels

Many-body Picture:

(Magnetic field fixed, nonzero)

Even particle

Odd particle

Kramers' doublet

Tunneling states

Singlet

Ground state

Kramers' doublet

Zeeman splitting with even-electron island

![Current vs. Voltage graph]

$I (\text{pA})$

$V (\text{mV})$

$0.03 \text{ Tesla}$

$3 \text{ Tesla}$

$3 \text{ Tesla}$

$2 \text{ Tesla}$

$1 \text{ Tesla}$

$0.03 \text{ Tesla}$

$\frac{dI}{dV} (\text{M} \Omega^{-1})$

$V (\text{mV})$

$3.4$ $3.6$ $3.8$ $4.0$ $4.2$ $4.4$
Magnetic field dependence for odd-electron particle

\[ I \text{ (pA)} \]

\[ V \text{ (mV)} \]

Even-to-odd tunneling:

Odd-to-even tunneling:

First two tunneling states are separated in energy by \( \sim 2\Delta \)
SUPERCONDUCTIVITY in nm-SCALE PARTICLES

\[ \Delta = 0.30 \text{ mev} \]

Superconductivity destroyed by spin pair breaking.

Transition is continuous, not first order.

\[ \begin{align*}
\text{What is the Lower Size Limit for} \\
\text{Superconductivity?}
\end{align*} \]

\[ \text{Anderson (1959)} \]
\[ \delta E_{\text{crit}} = \Delta_0 \]

\[ \text{von Delft, Zaikin, Golubev, Tichy (PRL 77, 3189 (96))} \]
\[ \text{Calculate } \Delta_{\text{even}}, \Delta_{\text{odd}} \text{ using MFT with uniform level spacings} \]
\[ \delta E_{\text{even, crit}} = 3.56 \Delta_0 \]
\[ \delta E_{\text{odd, crit}} = 0.89 \Delta_0 \]

\[ \text{Smith and Ambegaokar (PRL 77, 4962 (96))} \]
\[ \text{MFT with random level spacings} \]
\[ \langle \delta E_{\text{even, crit}} \rangle = 13.8 \Delta_0 \]
\[ \langle \delta E_{\text{odd, crit}} \rangle = 1.80 \Delta_0 \]

\[ \text{Matveev and Larkin (PRL 78, 3749 (97))} \]
\[ \text{Include quantum fluctuations of the order parameter} \]
\[ \text{Parity effects in ground state persist for } \delta E > \Delta_0. \]

\[ \text{Exact and DMRG solutions:} \]
\[ \text{Richardson (J. Math. Phys. 18, 1802 (77))} \]
\[ \text{Mastellone, Falci, Fazio (PRL 80, 4542 (98))} \]
\[ \text{Berger and Halperin (PRB 58, 5213 (98))} \]
\[ \text{Dukelsky and Sierra (PRL 83, 172 (99))} \]
\[ \text{Braun and von Delft (cond-mat/9907402)} \]
SIZE-DEPENDENCE OF SUPERCONDUCTIVITY?

\[ \text{energy (meV)} \]

\[ \text{radius (nm)} \]

○ measured \( \Delta \)

\( \times \) mean level spacing

(\text{von Delft et al. theory})

\[ \text{Note} \quad \delta_0 \equiv \frac{4\sqrt{2}}{\pi \Delta} \sim 2000 \text{ nm} \]

Cross-Over to a Fluctuation-Dominated Regime for Very Small Nanoparticles

No phase transition.
Qualitative change in behavior.

\[ \langle c_i^\dagger c_i^\dagger i c_i c_i \rangle - \langle c_i^\dagger c_i \rangle \langle c_i^\dagger c_i \rangle \]

(\text{exact solution: Richardson (1960's)})

Review: Jan von Delft, Habilitation thesis
Conclusions

• Superconducting pairing is allowed even in samples with a fixed number of electrons. (The use of a grand canonical ensemble in BCS theory is only a calculational convenience.)

• In micron-sized samples ($10^9$ electrons), superconducting pairing causes even-electron ground states to be energetically favorable.

• In nm-sized samples ($10^4$ electrons), pairing is visible directly in the "electron-in-a-box" level spectrum.

A paired ground state persists as long as

$$\Delta \geq 8E$$

$\uparrow$ the level spacing