The superconducting proximity effect, from metals to molecules

PhD  M. Kociak, M. Ferrier, L. Angers, F. Chiodi, A. Chepelianskii, C. Ojeda,
Post-doc  A. Rowe, P-E. Roche, A. Shailos, M. Monteverde
Interns  Yu. Kasumov, P. Delplace, E. Zakka-Bajjani
The group!  M. Ferrier, R. Deblock, S. Guéron, A. Kasumov, B. Reulet, H. Bouchiat,

With help from:
F. Fortuna, R. Weil, D. Debarre (Orsay)
F. Pierre, U. Gennsner, D. Mailly (Marcoussis)
O. Stéphan, M. Kociak, A. Gloter, C. Colliex (Orsay)
F. Ladieu, M. Ocio (Saclay), P. Poulin (Bordeaux), P. Launois (Orsay)
S. Nakamae (Saclay); M. Cazayous, Y. Gallais, A. Sacuto (Paris 7),
L. Buchaillot, V. Agache, A-S. Rollier (IEMN Lille); A.M. Bonnot (Grenoble)
O. Pietrement, E. Le Cam (IGR Villejuif); S. Lyonnais, J-L. Mergny (MNHN Paris), D. Klinov (Moscow)
F. Livolant, A. Leforestier, E. Raspaud (Orsay)
G. Montambaux, C. Texier, J-N. Fuchs (Orsay), D. Maslov (U. Florida)
J.C. Cuevas (Madrid),
M. Polianski (Copenhage), K. Tikhonov, M. Feigelman (Moscow)
The proximity effect can be induced in many systems:

- **The classical proximity effect**: in a metal ($\mu m^3$)

- **S-Molecular wire-S junctions** ($\mu m \times nm^2$): suspended carbon nanotubes, DNA molecules

- **S-Molecule-S junction** ($nm^3$): métallofullérène (molecule with spin)

- **S-Molecular plane-S junctions** ($\mu m^2 \times Å$): graphene
What is the Superconducting proximity effect?
Superconductor

$$\Psi_{BCS} = \Delta e^{i\phi}$$

Cooper pairs

Empty quasiparticle states

No single particle states at low energy: only paired electrons

Occupied quasiparticle states
**Superconductor/Normal junction**

Cooper pairs $S, \Delta e^{i\varphi}$

Single quasi-particles $N, I_e$

D diffusion constant $D = 1/3 v_F I_e$

Energy

Time reversed quasi-particles

**NS current** : two electrons passing from N to S

or

: one electron reflected into a hole (Andreev reflection)
Superconductor/Normal/Superconductor junction where $N$ is a clean (ballistic) metal.

Traversal time $\tau_e = \tau_h = L / v_F$, dephasing $e^{i\epsilon_n \tau / \hbar}$.

Resonance condition on accumulated phase:

$$\epsilon_n \tau_e / \hbar + \varphi_2 - \arccos(\epsilon_n / \Delta) - \epsilon_n \tau_h / \hbar - \varphi_1 - \arccos(\epsilon_n / \Delta) = 2\pi n$$

$$\epsilon_n (\varphi_1 - \varphi_2):$$ Andreev bound states in $N$.
Superconductor/Normal/Superconductor junction
N is a diffusive metal

D diffusion constant
D = 1/3 \( v_F l_e \)

Traversal time \( \tau_e = \tau_h \) varies! Typical \( \tau_D = L^2/D \)

Still, Andreev bound states exist also in diffusive N

Proximity effect is a consequence of these states
Density of states in N (long diffusive SNS junction)

Long junction: \( \xi_S = \left( \frac{\hbar D}{\Delta} \right)^{1/2} \) (\( E_{Th} \ll \Delta \))

- minigap \( \delta = 3.5 \ E_{Th} \)
- \( E_{Th} = \frac{\hbar}{\tau_D} = \frac{\hbar D}{L^2} \) Thouless energy
- \( \delta \ll \Delta \) in long junction

Small (« mini ») induced gap in the quasi-continuum of Andreev levels
The Andreev levels depend on S phase difference
(Minigap fully modulated)

Consequence: Supercurrent (if N quantum coherent)!

\[ I_s(\varphi) = \sum_n f_n(\varphi) \frac{\partial}{\partial \varphi} \varepsilon_n(\varphi) = I_c \sin \varphi + \ldots \]

Maximum supercurrent \( \sim I_c = 10 E_{Th}/eR_N << \Delta/eR_N \)
Some questions and answers in this presentation

Q1: Do Andreev bound states live long enough? Observe a supercurrent in a N metal?  
A1: Large supercurrents through coherent μm-long normal metals at low T

Q2: Can we take a snapshot of these Andreev states?  
A2: Measurement of $I(\varphi)$ at high frequencies  
\[ I(\varphi, \omega) = \Phi_{dc} + \Phi_{ac} \cos \omega t \]
\[ \varphi = 2\pi \Phi / \Phi_0 \]

Q3: What about supercurrents through molecules? Magnetic molecules?  
A3: Proximity effect through graphene and metallofullerenes
Q1: Do Andreev bound states live long enough? Can one measure a supercurrent in a N metal?
Three ways of making SNS junctions

1. **Angle evaporation:**
   - S and N without breaking vacuum
   - S=Al $T_c=1$ K

2. **Nb/Au bilayer:**
   - Then etch away Nb to get N
   - (coll LPN Marcoussy)
   - $T_c=8-9$ K

3. **N first, then use focused ion beam:**
   - To prepare interface and deposit W
   - (with A. Kasumov, coll. F. Fortuna CSNSM Orsay)
   - $T_c=3-5$ K, high $H_c$

**Note:** S doesn’t need to be bigger than N
S only needs to be bigger than $\xi_S$
Induced superconductivity at low temperature

Two long junctions with Nb: $T_c=9$ K, $\Delta=16$ K $\gg E_{Th}$

$\xi_s=0.07$ $\mu$m $<< L$

$E_{Th}=0.05$ K, minigap $\delta=0.18$ K

$E_{Th}=0.14$ K, $\delta=0.5$ K

$R=0$ when normal metal PHASE COHERENT:
No spin-flip or thermal fluctuations during $\tau_D$ (Even at $k_BT=10 \delta$!)
At low temperature, Zero R with a critical current

- $I_c(T=0) \sim 10 \frac{E_{Th}}{eR_N}, E_{Th} = \frac{\hbar D}{L^2}$ (S gap doesn’t come into play!)
- $I_c(T) : \sim \exp(-T/10E_{Th})$ understood (Dubos 2001)
- $I_c(H)$: depends on aspect ratio of N (Angers 2008, Cuevas 2008)
- Hysteresis in $V(I)$ curve? Still debated
Some questions and answers in this presentation

Q1: Do Andreev bound states live long enough? Observe a supercurrent in a N metal?  
A1: Large supercurrents through coherent $\mu$m-long normal metals at low T

Q2: Can we take a snapshot of these Andreev states?  
A2: Measurement of $I(\varphi)$ at high frequencies  
$$I(\varphi, \omega) = \varphi_{dc} + \varphi_{ac} \cos \omega t$$

Q3: What about supercurrents through molecules? Magnetic molecules?  
A3: Proximity effect through graphene and metallofullerenes
Snapshots of the Andreev levels: Dynamics of the proximity effect?

- All contributions at $t \to \infty$: $I_s(\phi) = -8.25 \frac{eE_{Th}}{R_N} \sum_n \frac{(-1)^n}{(n^2-1/4)} \sin(n\phi)$ (dc measurement)

- What about high frequency measurement ($t < \pi \tau_D$)?

Heikkila 2002
$I(\varphi)$ measured at $\omega=0$ with Hall bar (Strunk 2009)

Impose $\varphi$ with a ring geometry and Aharonov Bohm flux $\Phi$: $\varphi=2\pi\Phi/\Phi_0$, $\Phi_0=h/2e$

Non sinusoidal $I(\varphi)$ confirmed with high harmonics content at low $T$

Higher harmonics appear under rf irradiation, especially at high $T$
What happens at high frequency?

**dc:** \( I_s(\varphi) = \sum f_n(\varphi) \frac{\partial}{\partial \varphi} \varepsilon_n(\varphi) \)

- occupation
- energy of level

**ac:** \( \varphi(t) = 2\pi \Phi(t)/\Phi_0 = \varphi_{dc} + \varphi_{ac} \cos \omega t \)
  \( \Rightarrow \) delayed response
  \( I(t) \neq I_s(\varphi(t)) \)

\( l = \chi(\omega) (\Phi_{dc} + \Phi_{ac} \cos \omega t) \) with \( \chi = \chi' + i\chi'' \)

\( I_{ac}(t) = I_0 (\chi' \cos \omega t + \chi'' \sin \omega t) \)

- in phase
- out-of-phase: dissipation

Other way to see things:

\( I = Y(\omega)V, \ V = i\omega \Phi, \)
\( I = i\omega Y(\omega)\Phi, \) complex admittance of system

Goal: determine ac response experimentally
Measurement: SNS ring coupled to rf resonator

ac flux imposed by resonator

\[ i_{ac}(\omega_R) \rightarrow \Phi_{ac} = Mi_{ac} \rightarrow i_{ac} = (\chi' + i\chi'')Mi_{ac} \]

Change of resonator inductance and resonance frequency:

\[ L i_{ac}(\omega_R) \rightarrow L i_{ac}(\omega_R) + \chi'M^2i_{ac} \]

\[ 2\delta f/f = -\delta L/L = -\chi'M^2/L \]

Change of resonator quality factor due to dissipation

\[ \delta(1/Q): \text{losses: out-of-phase response } \chi'' \]
In practice: equivalent setup

\[ \Phi_{\text{ext}} = \Phi_{\text{dc}} + \Phi_{\text{ac}} \cos \omega t \]

inductive coupling

direct coupling
Use of multimode hf resonator

Bouchiat, Reulet, 1995

\[ f_1 = \frac{1}{\sqrt{LC}} = 380 \text{MHz} \]

\[ f_n = nf_1, \text{ up to } 8 \text{ GHz or more} \]

Then: couple SNS loop
In practice: the sample

- Put a Au wire in Nb resonator
- Find it and then grow a W ring around it
$E_{Th} \sim 50 \text{ mK}$
$I_c \sim \mu \text{A at low } T$

Response of single ring in a 20 cm long resonator
In phase response at 300 MHz: not purely harmonic, even at high T

\[-2\delta f/f = \chi' (\Phi_{\text{ext}}) \frac{M^2}{L}\]

\[I = \chi(\omega)(\Phi_{dc} + \Phi_{ac} \cos \omega t) \text{ with } \chi = \chi' + i\chi''\]

\[P = -120 \text{ dB (fW), average of 30 curves}\]

\[T = 450 \text{ mK, } I_c \sim 10 \mu A \text{ hysteretic at low T}\]

\[2\pi L I_c \sim \Phi_0\]

\[T = 670 \text{ mK, } I_c \sim 5 \mu A\]

\[T = 1 \text{ K} = 20E_{Th} = 6\delta\]

\[2\pi L I_c \sim \Phi_0/10\]

\[I(\phi)_{dc} = \sin \phi \text{ (within 1%) but } \chi' \text{ anharmonic!}\]

\[\chi' \neq \partial I / \partial \Phi \text{ at these frequencies!}\]
Out of phase response: dissipation

\[-\delta(1/Q) \sim \chi''\]

Losses greatest at \(\Phi_{\text{ext}} = \Phi_0/2\), when minigap closes (even though \(T \gg \delta\))
Frequency dependence of $\chi'$ and $\chi''$ (preliminary results)

$\chi(\omega=0) = \partial l / \partial \Phi$

Comparison with simplest dissipation model (relaxation time)

It seems as though relaxation time is longer than $\tau_D$: maybe $\tau_{e-ph}$ or $\tau_{e-e}$?

\[
\chi = \chi_0 / (1 + i \omega \tau) \\
\chi' = \chi_0 / (1 + \omega^2 \tau^2) \\
\chi'' = \omega \tau / (1 + \omega^2 \tau^2)
\]
Preliminary experiments: \( L = 1.5 \text{ \mu m}, f_{Th} = 1 \text{GHz}, E_{Th} = 50 \text{ mK} \)

Large dissipation: identify cause of relaxation (from T dependence)? Both linear and non-linear regime were accessed.

**Next:**
Directly measure \( I_c(T) \) at \( \omega = 0 \) to determine \( E_{Th} \) (cut resonator...)

**Then:** Adjust parameters to enable
Exploration at lower T (full harmonics content): need smaller \( I_c \), smaller \( L \)
Increase \( E_{Th} \) to see clear change in regime: \( \omega < \frac{E_{Th}}{\hbar} \)

**Possibly:**
Lower resonator frequency (to 10 MHz)
Observe crossover from mostly inductive to mostly dissipative

**Theory?? In progress...**
Some questions and answers in this presentation

Q1: Do Andreev bound states live long enough? Observe a supercurrent in a N metal? A1: Large supercurrents through coherent μm-long normal metals at low T

Q2: Can we take a snapshot of these Andreev states? A2: Measurement of I(\(\phi\)) at high frequencies

Between metals and molecules: Proximity effect in graphene


thin graphite (graphene multilayer)

graphene = single C plane
Why is graphene interesting?

Noble metals are (almost) all alike!
Not tunable
One accessible band
Massive carriers
\[ E = \hbar^2 k_F^2 / 2 m_e \]
\[ v_F \sim 10^6 \text{ m/s} \]

Conventional 2D electron gas (semi conductor heterojunction)
Tunable in transistor configuration
Electron-hole asymmetry
Massive carriers
\[ E_e = \hbar^2 k_F^2 / 2 m_e^* \]
Gap in DOS

Graphene
Tunable carrier density and type
Electron-hole asymmetry
Massless dispersion relation (Dirac cone)
\[ E = \hbar v_F k_F \]
\[ v_F \sim 10^6 \text{ m/s} \]
Dirac point: \( k_F = 0 \rightarrow \lambda_F = \infty \)
Semiclassical physics not valid!
Purely quantum physics...
Consequence on the Proximity effect?

Usual Andreev reflection at large doping

New: Specular Andreev reflection at zero doping (Beenakker 2006)

But: need zero doping ($E_F \ll \Delta$) and ballistic transport!
For starters: a tunable proximity effect in graphene

S=Pt/Ta contacts (T_c=2.5 K)

Resistance decreases upon annealing, full proximity effect at 4th step!

Can we relate R decrease to improved S/graphene contact?

No supercurrent!

Idea: « anneal » the device with a large dc current for a few minutes.
(Bachtold 2007)

T=50mK

dV/dI ()

V (mV)

annealing current
3 mA
6 mA
10 mA

Resistence decreases upon annealing, full proximity effect at 4th step!

Can we relate R decrease to improved S/graphene contact?
At $V_{dc} \neq 0$: Multiple Andreev reflections transfer Cooper pairs.

New MAR possible when $2\Delta = n eV$, $n$ Cooper pairs transferred.

Lower Resistance

Contrast of Multiple Andreev Reflection dips changes


Contrast of MAR in S/G/S

Contact transparency improves with annealing

No theory exists for S/disordered N/S or S/graphene/S
We induced supercurrent with large current annealing...
How do we know we’re still measuring graphene?

Field dependence of critical current corresponds to wide junction (and not to a metal chain)
Current annealing improves the quality of contacts

⇒ full Proximity effect in diffusive regime.

To improve graphene quality, achieve low doping, and ballistic regime, need cleaner samples:

⇒ suspend graphene!
Suspended 30 sheet graphene/ite (on N contacts)

Measure as deposited (bad contacts)

\[ R = 200 \text{ kOhms} \quad T=4.2 \text{ K} \]
Vibrational mode of the whole sheet seen on R

Higher energy phonon modes (5-20 meV) also detected (dynamical Coulomb blockade, Chepelianskii 2009)
Future work with graphene:

Improve the quality of graphene to reach uniform low doping regime, and ballisticity: with suspension and current annealing

Observe special proximity effect of graphene

Interplay of vibrations and superconductivity, proximity effect?

Understand electron-phonon coupling in suspended graphene (number of layers)

Hall effect and superconductivity with high Hc superconductor ($W_{\text{FIB}}$)
Supercurrent in **normal metals** $L > 1 \mu m$ at low $T$: large phase coherence length

Supercurrent in **graphene**? yes for $L = 0.3 \mu m$, not $L = 2 \mu m$

Proximity effect tests phase coherence!

Can proximity effect test spin state? What is the effect of magnetism on supercurrent?
Probing molecules with the proximity effect

Normal metal=universal, Molecules are each different! Molecule=resolved molecular levels $\delta E > k_B T$ (also called « quantum dots »)

Motivation: test interplay of superconductivity and spin at the simplest level

Simple?
In fact, rich physics!

Pairs can go through!

How? Coupling to leads $\Gamma$ broadens molecular levels
Pairs can go through a magnetic molecule

Small supercurrent if weak coupling to leads

Large supercurrent if strong coupling to leads

\[
\varepsilon_0 + U
\]

\[
\varepsilon_0
\]

\[
\varepsilon_0 + U
\]

\[
\varepsilon_0
\]

« π » state

\[
I = I_c \sin(\varphi + \pi)
\]

Small \( I_c \)

\[
\Delta > T_K
\]

Kondo temperature

\[
T_K = \frac{\sqrt{\Gamma U}}{2} \exp\left(\frac{\pi \varepsilon_0 (\varepsilon_0 + U)}{\Gamma U}\right)
\]

« 0 » state

Localized spin screened!

large \( I_c \sim 2\pi e\Delta/h \)

non sinusoidal \( I(\varphi) \)

\[
\Delta < T_K : \text{Kondo regime}
\]

Nature of proximity effect depends on gap, coupling, level position...
In practice: molecule=suspended metallofullerene dimer

A. Kasumov, K. Tsukagoshi, M. Kawamura, T. Kobayashi, Y. Aoyagi (RIKEN, Japan)
K. Senba, T. Kodama, H. Nishikawa, I. Ikemoto, K. Kikuchi, (Tokyo, Japan)

Effect of molecular magnetism on supercurrent
What is a metallofullerene?

A fullerene molecule with a metal atom inside.

$C_{82}$ fullerene  \hspace{1cm} \text{Gd atom}  \hspace{1cm} \text{Charge transfer} \rightarrow \text{Gd}^{3+}, C_{82}^{3-}$

$S = 7/2, s = 1/2$

$S = 3$ for single $\text{Gd}^{3+}@C_{82}^{3-}$

Dimer $\text{Gd}@C_{82}$: 2 coupled spins 7/2


- Paramagnetic above 3 K,
- Antiferromagnetic with $J=0.7$ K
- Dipolar coupling in dimer $J_d=0.1$ K

How do magnetic states influence transport?
Fabrication of electrodes for measurement and visualization

Ga\(^+\) (30 keV)

Used for nanotubes: too big! Decrease spacing between electrodes
Making electrodes with a nanometer sized gap

Alik Kasumov, Rikken, Thalès, CSNSM Orsay

Galium ions (30 keV)

FIB image

And finally insert molecule
A look at the sample...

Gd@C$_{82}$ dimer!

and measure...

Can pairs go through metallofullerene dimers?

Depending on magnetic state, proximity effect can develop

\[ T_{\text{prox}} = 0.7 \text{ K} \]
\[ H_{\text{prox}} = 1 \text{ T} \]

\[ T_c (\text{contacts}) > 4 \text{ K} \]
\[ H_c > 5 \text{ T} \]
Peaks in $dV/ dl$ at $V=2\Delta/ne$ ($\Delta=0.9$ meV): Multiple Andreev reflexion? 
Extra peaks related to the internal energy levels of the dimer, only visible with S electrodes?
Theoretical suggestion (Bergeret 2006)
Control magnetic state of dimer with externally imposed phase difference?

Test prediction in ring configuration

\[ \varphi = \frac{2\pi \Phi}{\Phi_0} \]
Conclusions and prospects

Molecular magnetic configuration affects the proximity effect.

Conversely: Control molecular magnetism with the superconducting phase?

$I(\varphi)$ relation in a ring configuration can test and change molecular configuration.

Many molecules to probe in this way:
metallofullerenes, (suspended) graphene, nanotubes
in dc and ac configuration
Develop appropriate small current detector...
1999-2009: Ten years of fun...

Tunneling spectroscopy of cobalt nanoparticles
M. Deshmukh, D. Ralph

Superconducting ropes of nanotubes
M. Kociak, M. Ferrier, A. Kasumov, H. Bouchiat

Suspended carbon nanotubes
M. Kociak, M. Ferrier, A. Shailos, A. Kasumov, H. Bouchiat

Suspended metallofullerenes
R. Deblock, A. Kasumov, H. Bouchiat

Suspended graphene
C. Ojeda, P. Delplace, M. Monteverde, A. Kasumov, M. Ferrier, H. Bouchiat

Dna
M. Kociak, A. Chepelianskii, A. Kasumov, M. Ferrier, H. Bouchiat

Proximity effect in metals
L. Angers, F. Chiodi, M. Ferrier, H. Bouchiat

Phase coherence, interactions in mesoscopic samples
M. Ferrier, L. Angers, E. Zakka-Bajjani, H. Bouchiat

... and many more to come!