The superconducting proximity effect, from metals to molecules

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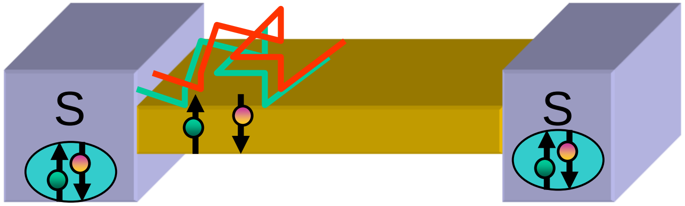
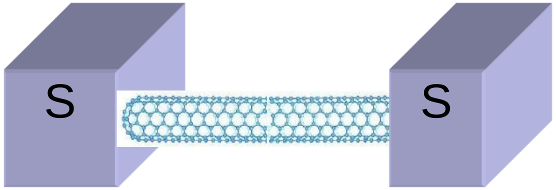
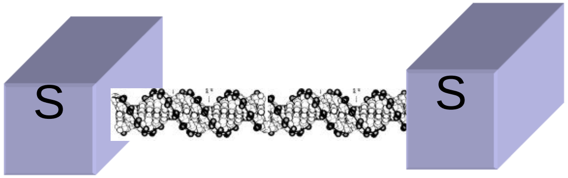
The proximity effect can be induced in many systems

- **The classical proximity effect**: in a metal (μm^3)

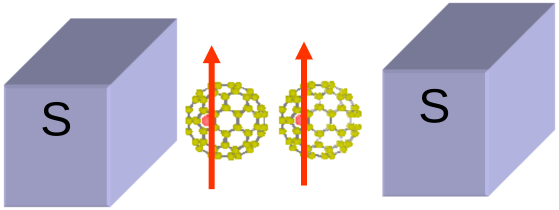


- **S-Molecular wire-S** junctions ($\mu m \times nm^2$) :
  suspended carbon nanotubes, DNA molecules

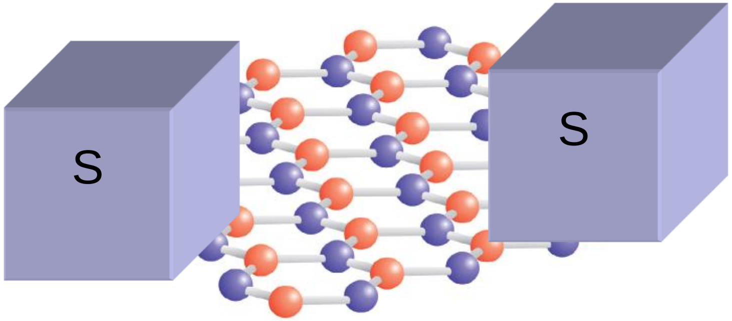




- **S-Molecule-S junction** (nm^3): métallofullérène (molecule with spin)

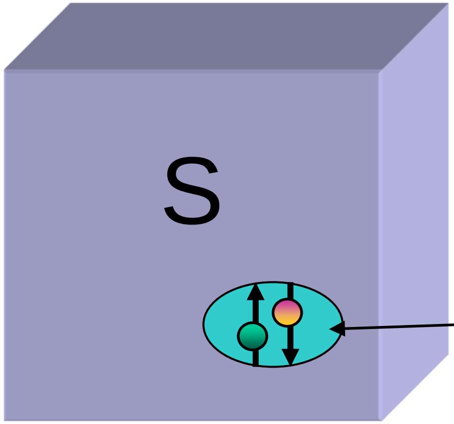


- **S-Molecular plane-S** junctions (μm^2xÅ) :
  graphene

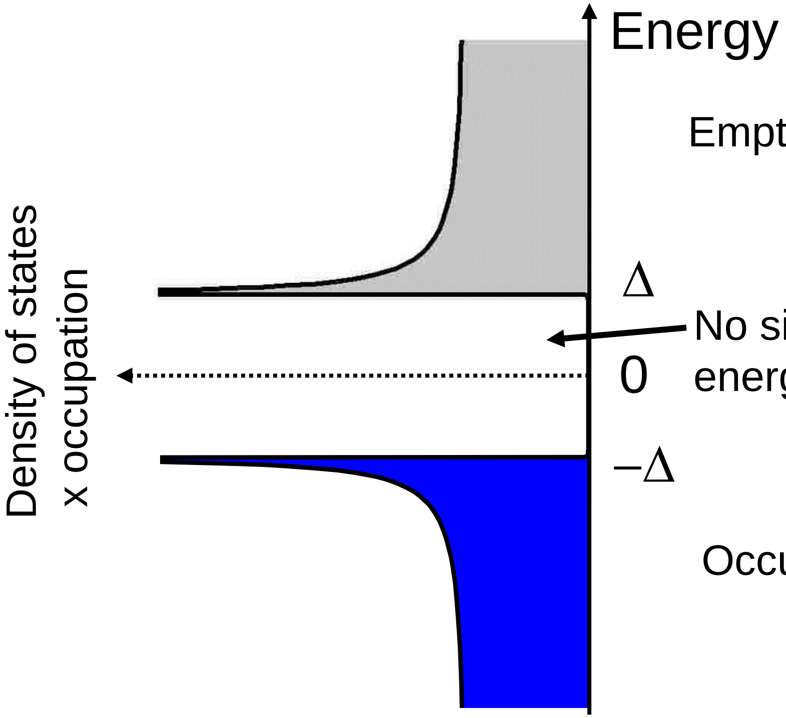


What is the Superconducting proximity effect?

Superconductor



$\psi_{BCS}=\Delta e^{i\varphi}$,
Cooper pairs

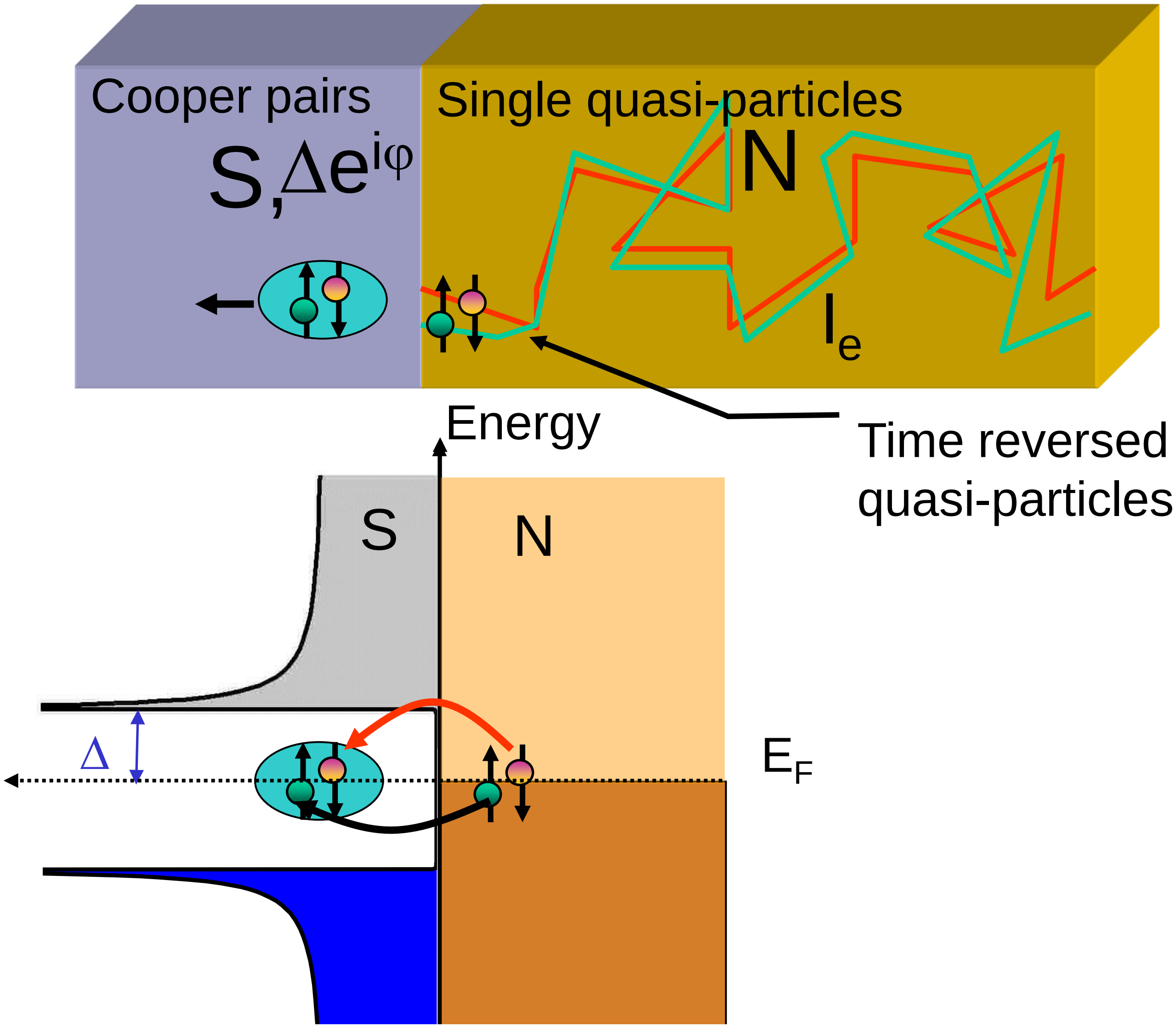


Empty quasiparticle states

No single particle states at low energy: only paired electrons

Occupied quasiparticle states

Superconductor/Normal junction

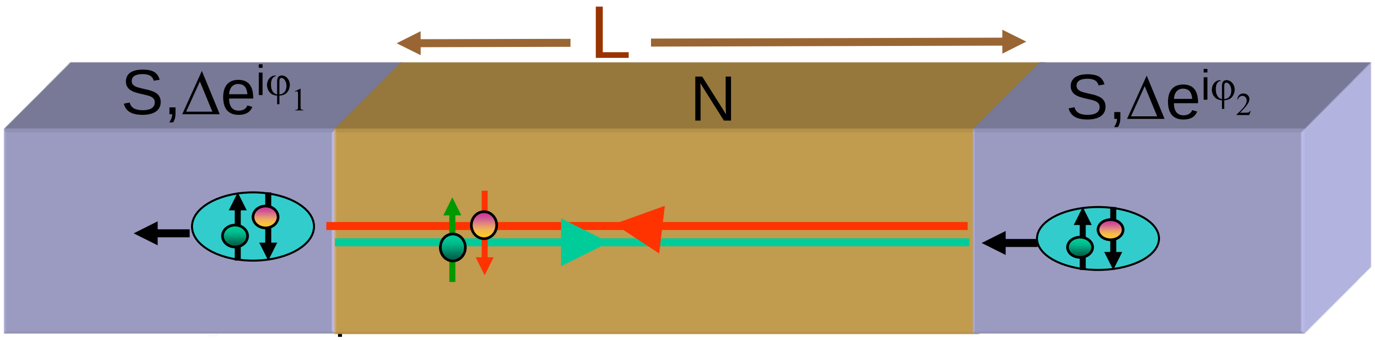


Time reversed quasi-particles

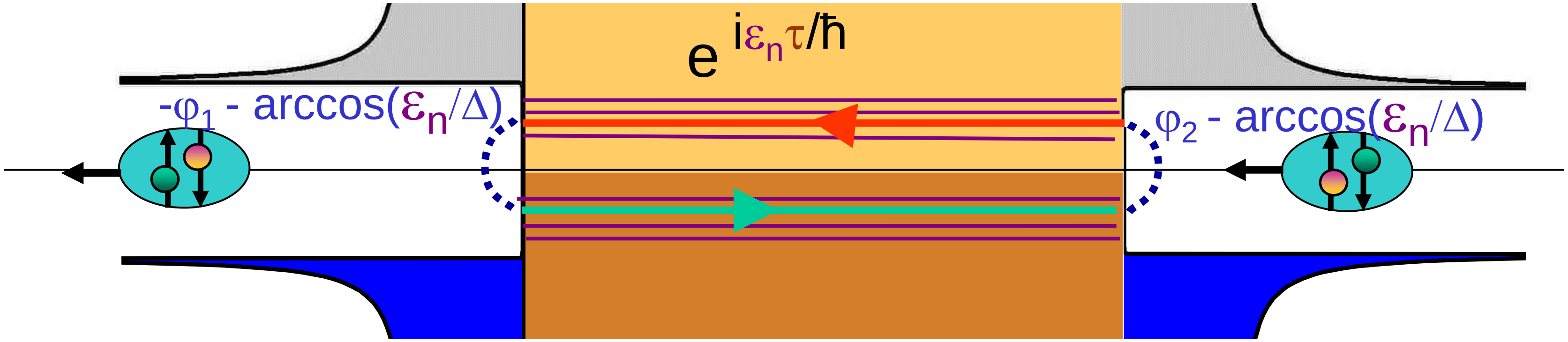
D diffusion constant
$D = 1/3 \; v_F \; l_e$

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 $e^{i\varepsilon_n\tau/\hbar}$



Resonance condition on accumulated phase:

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

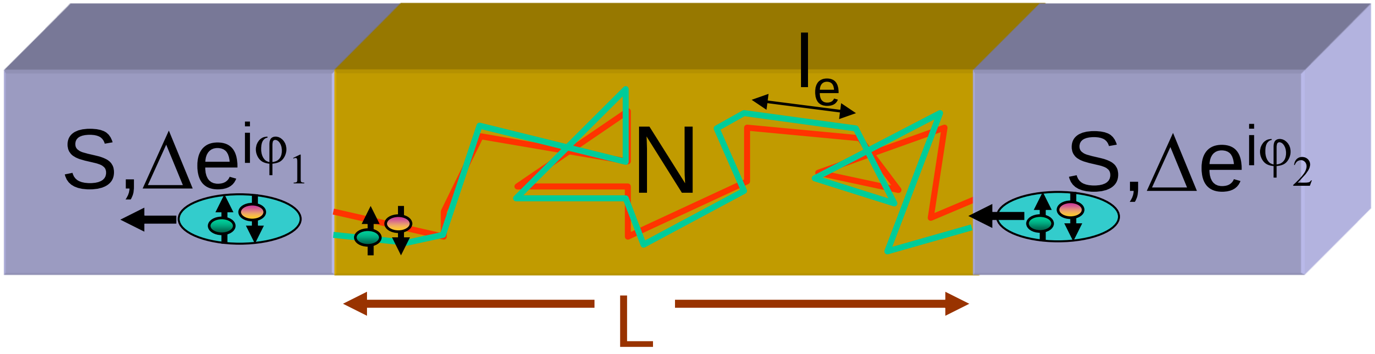
$\varepsilon_n(\varphi_1-\varphi_2)$: Andreev bound states in N

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 $\tau_D=L^2/D$

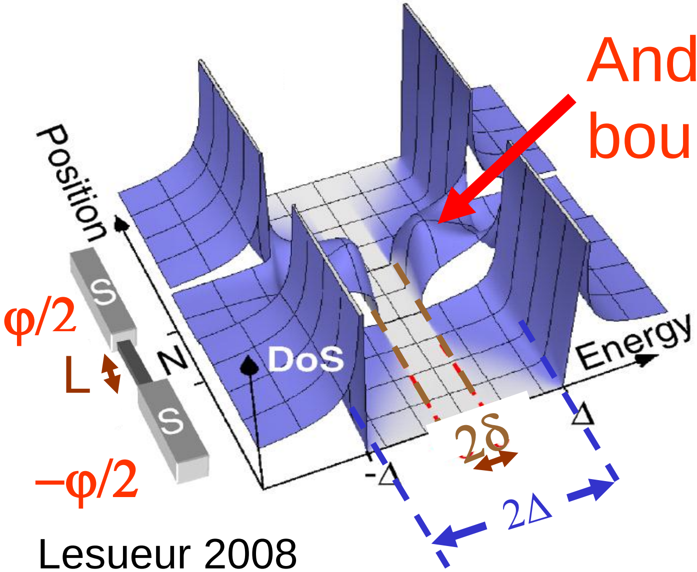
Still, Andreev bound states exist also in diffusive N

Proximity effect is a consequence of these states

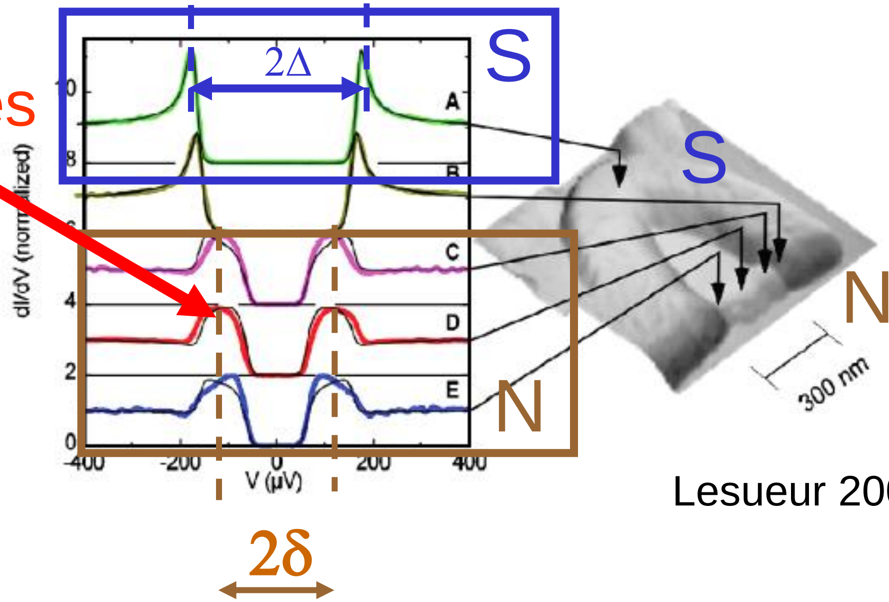
Property n°1 Density of states in N (long diffusive SNS junction)

Long junction: $L \gg \xi_S = (\hbar D/\Delta)^{1/2}$ $(E_{Th} \ll \Delta)$

Andreev bound states



Lesueur 2008



Lesueur 2008

- minigap $\delta = 3.5\, E_{Th}$
- $E_{Th} = \hbar/\tau_D = \hbar D/L^2$ Thouless energy
- $\delta \ll \Delta$ in long junction

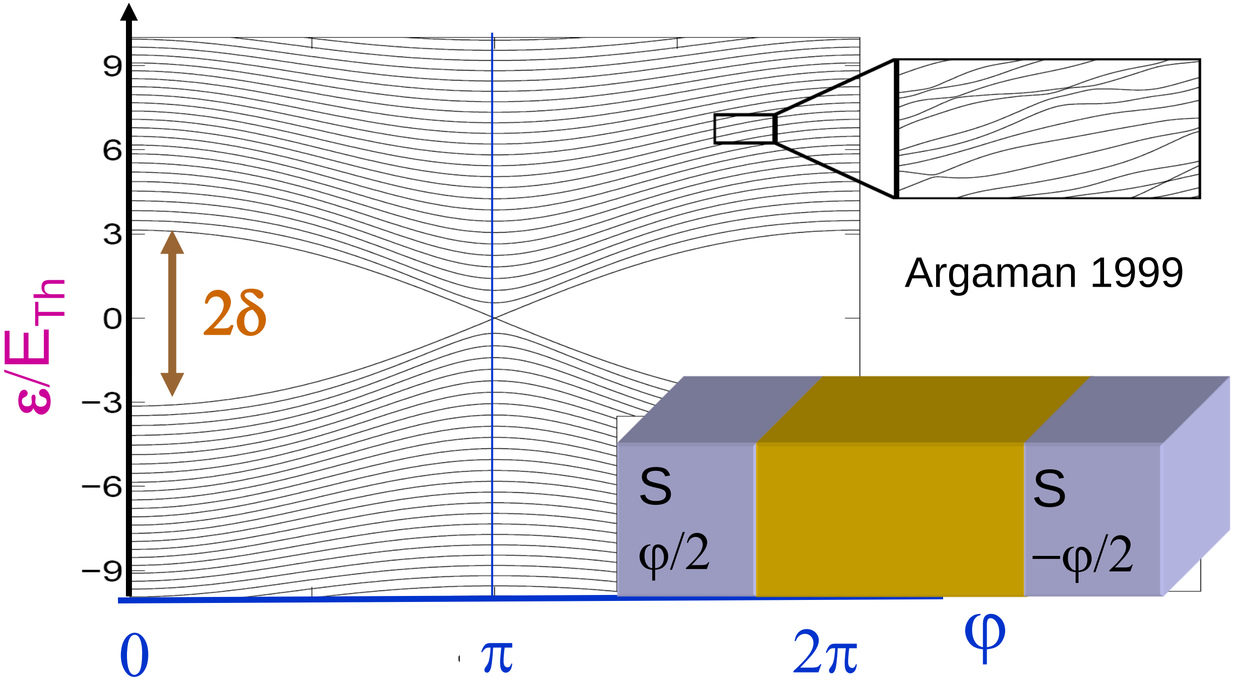
Small (« mini ») induced gap in the quasi-continuum of Andreev levels

Property n°2

Supercurrent flows through N

The Andreev levels depend on S phase difference

(Minigap fully modulated)



Argaman 1999

Consequence: Supercurrent (if N quantum coherent)!

$$I_s(\varphi)=\sum_n f_n(\varphi)\;\frac{\partial}{\partial\varphi}\varepsilon_n(\varphi)=I_c\sin\varphi+\dots$$

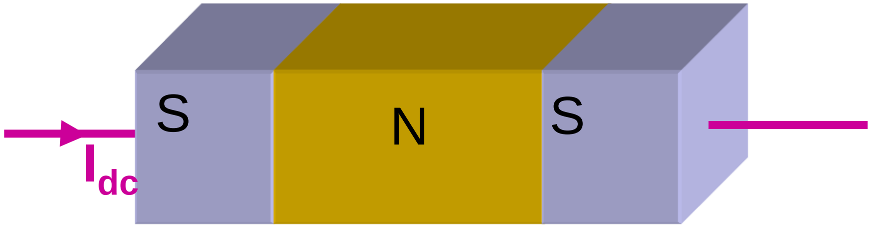
occupation

energy of level

Maximum supercurrent ~$I_c=10\ E_{Th}/eR_N << \Delta/eR_N$

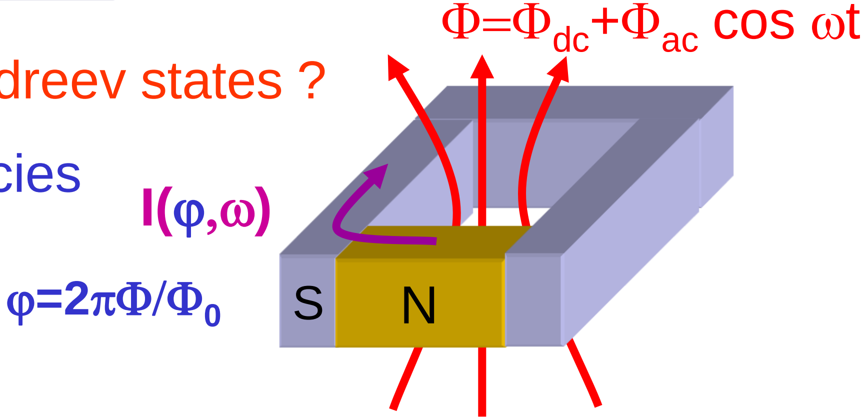
Some questions and answers in this presentation

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



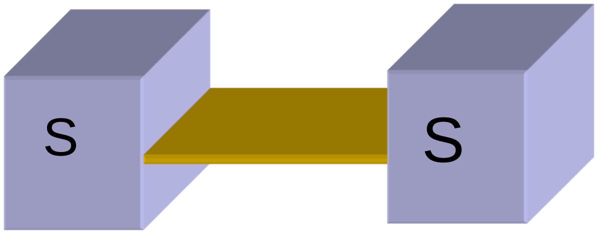
Q2: Can we take a snapshot of these Andreev states ?

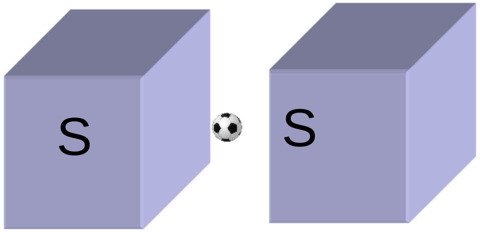
A2: Measurement of I(φ) at high frequencies



Q3: What about supercurrents through molecules ? Magnetic molecules?

A3: Proximity effect through graphene and metallofullerenes

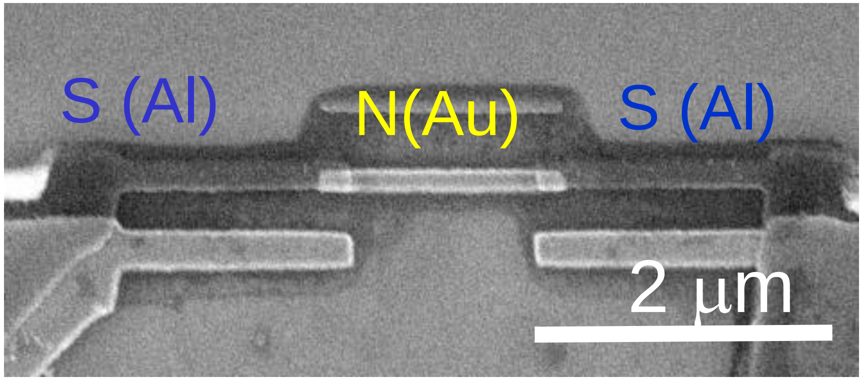




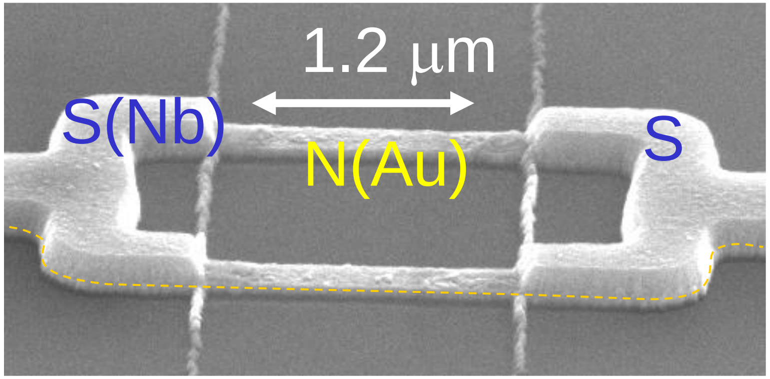
Q1: Do Andreev bound states live long enough? Can one measure a supercurrent in a N metal?

Three ways of making SNS junctions

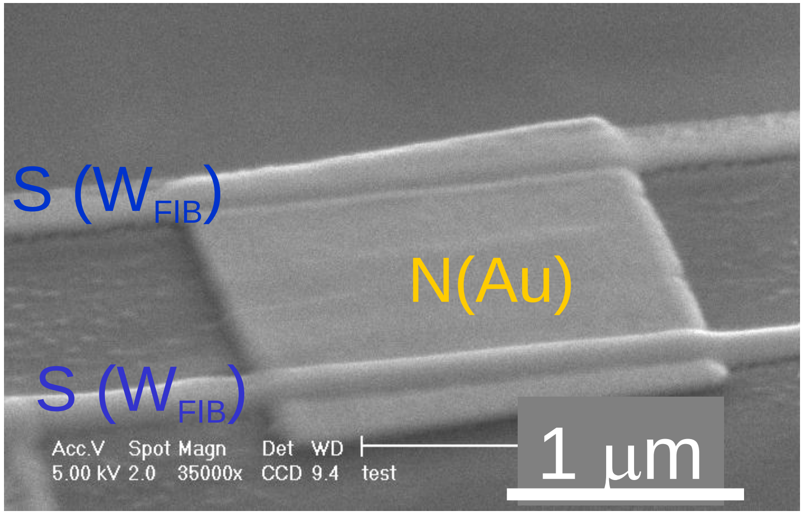
Thesis L. Angers, F. Chiodi



Angle evaporation:
S and N without breaking vacuum
S=Al T_c=1K



Nb/Au bilayer, then etch away Nb to get N
(coll LPN Marcoussy)
T_c=8-9 K



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 ξ_S

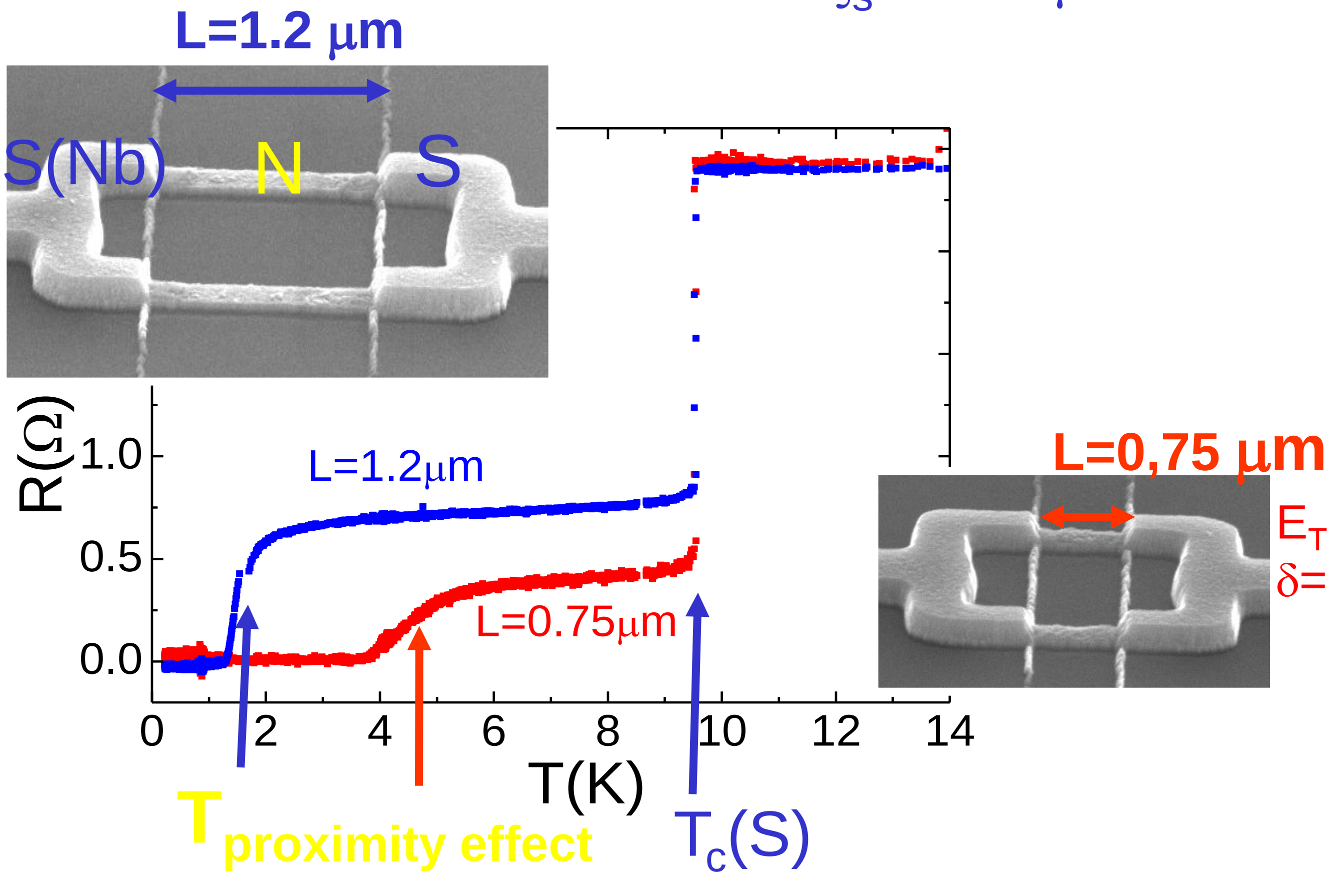
Induced superconductivity at low temperature

Two long junctions with Nb: T_c=9 K, Δ=16 K>>E_{Th}

ξ_s=0.07 μm <<L

E_{Th}=0.05 K

minigap δ=0.18 K



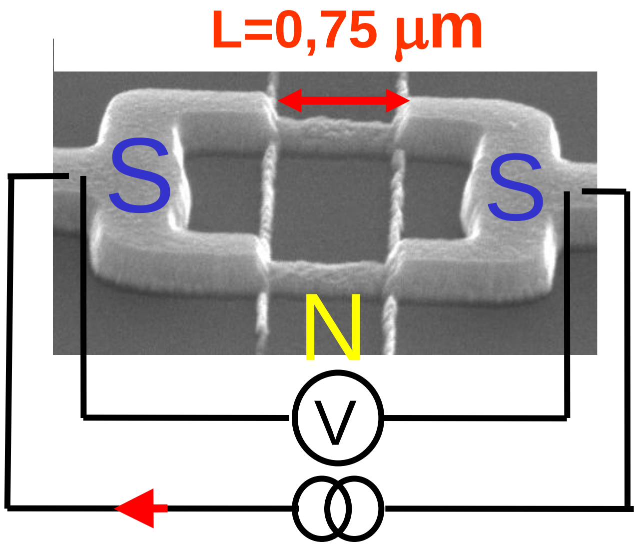
E_{Th}=0.14 K

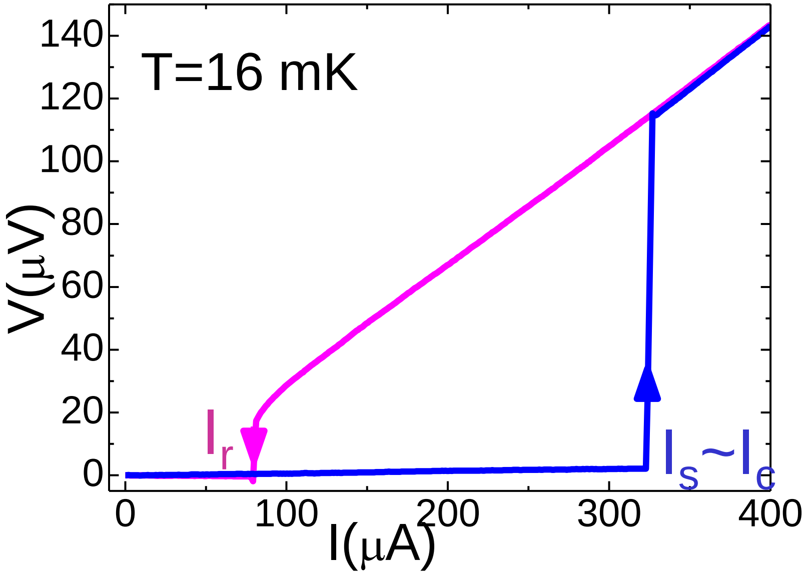
δ=0.5 K

R=0 when normal metal PHASE COHERENT:

No spin-flip or thermal fluctuations during τ_D (Even at k_BT=10 δ!)

At low temperature, Zero R with a critical current





- I_c(T=0) ~10 E_{Th}/eR_N ,E_{Th}= $\hbar D/L^2$ (S gap doesn't come into play!)
- I_c(T) : ~ 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

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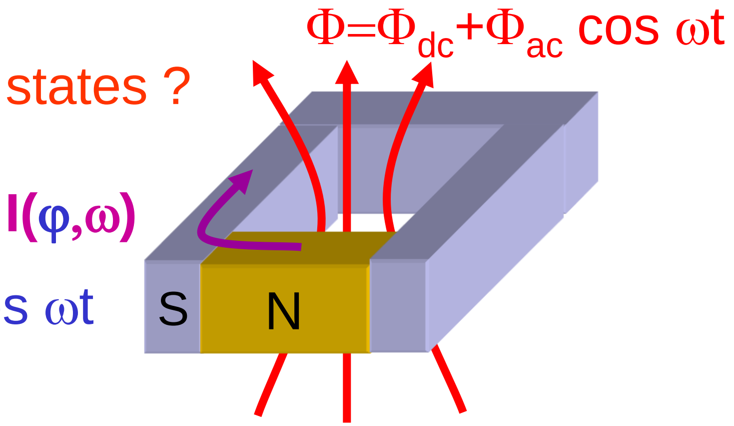
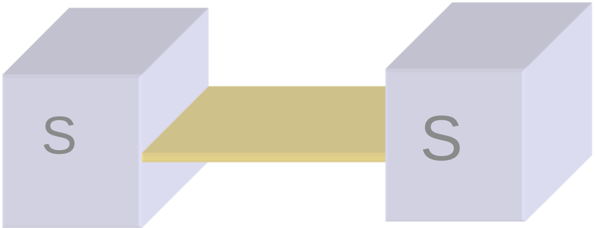
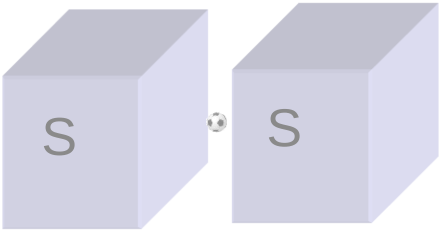


$\varphi_{dc}+\varphi_{ac}$ cos ωt

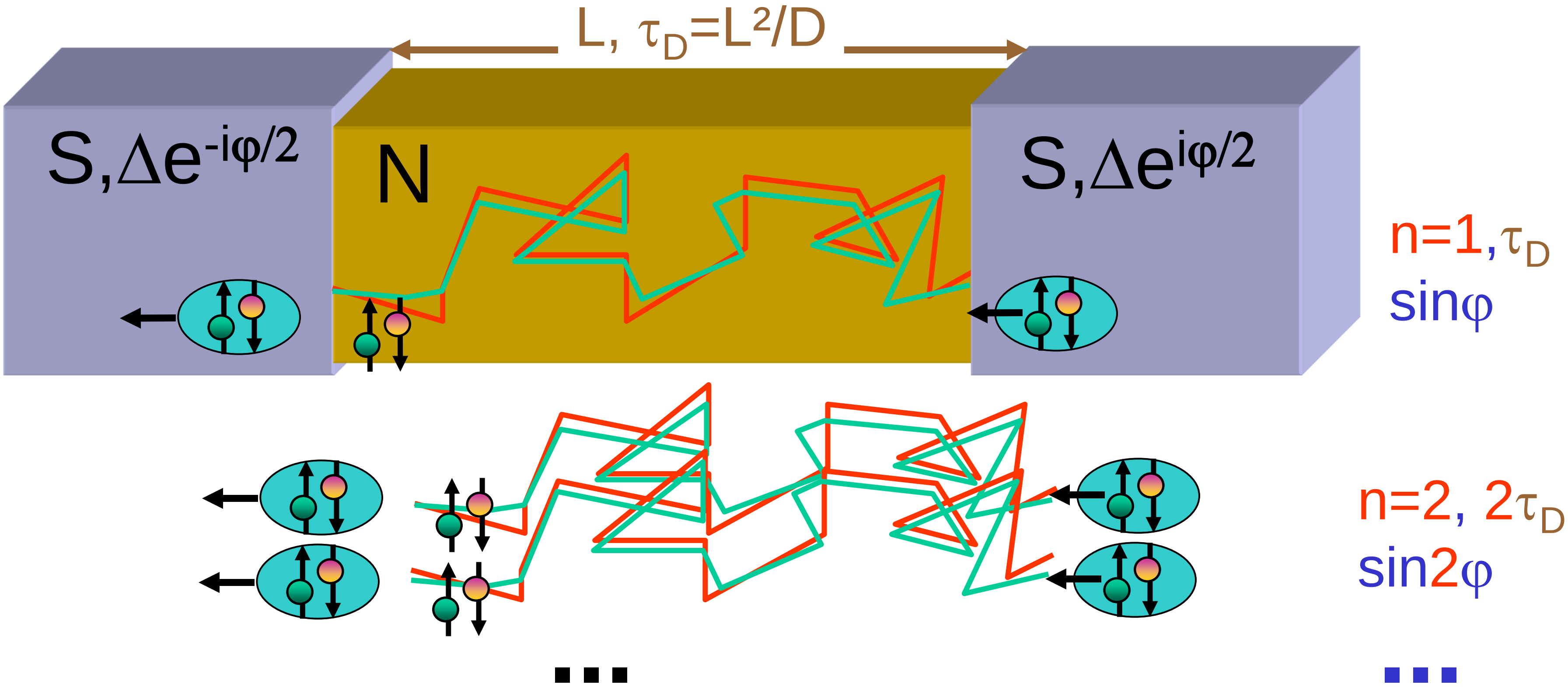
Q3: What about supercurrents through molecules ? Magnetic molecules?

A3: Proximity effect through graphene and metallofullerenes





Snapshots of the Andreev levels: Dynamics of the proximity effect?



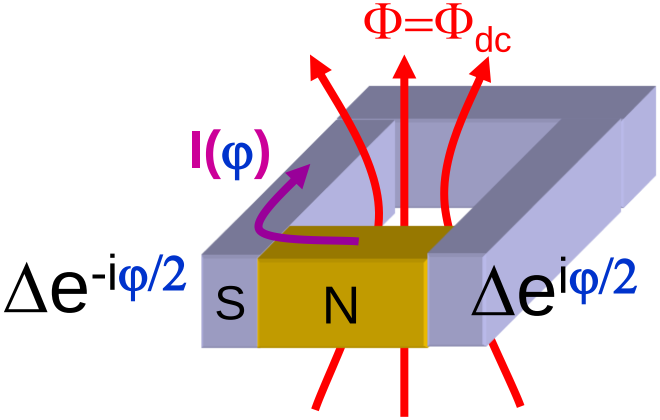
- All contributions at t ∞ : $I_s(\varphi) = -8.25 \dfrac{eE_{Th}}{R_N} \sum_n \dfrac{(-1)^n}{(n^2-1/4)} \sin(n\varphi)$
(dc measurement)

Heikkila 2002

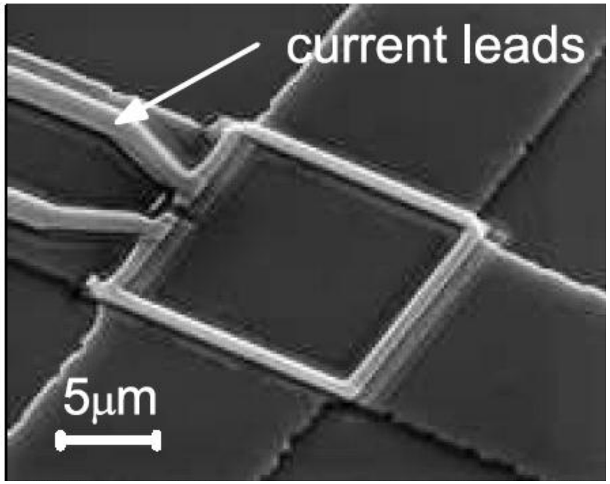
- What about high frequency measurement ($t < n\tau_D$)?

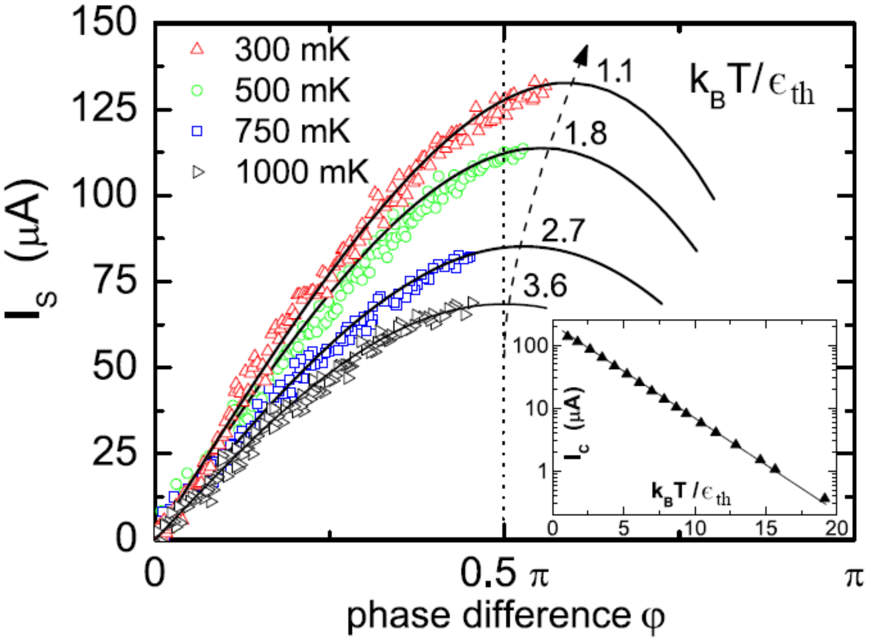
I(φ) measured at ω=0 with Hall bar (Strunk 2009)

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



$$I_s(\varphi)= -8.25\frac{eE_{Th}}{R_N}\sum_n \frac{(-1)^n}{(n^2-1/4)}\sin(n\varphi)$$

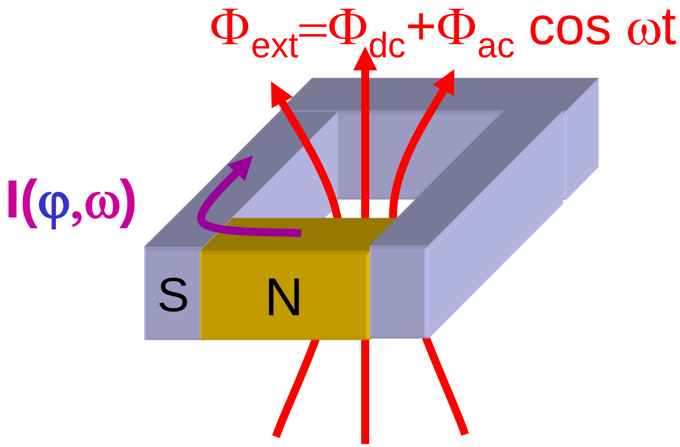




Non sinusoidal I(φ) confirmed with high harmonics content at low T

Higher harmonics appear under rf irradiation, especially at high T

What happens at high frequency?



dc: $$I_s(\varphi)=\sum_n f_n(\varphi)\frac{\partial}{\partial\varphi}\varepsilon_n(\varphi)$$

occupation   energy of level

ac: $\varphi(t)=2\pi\Phi(t)/\Phi_0=\varphi_{dc}+\varphi_{ac}\cos\omega t$

⇨ delayed response $I(t)\neq I_s(\varphi(t))$

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

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

in phase   out-of-phase: dissipation

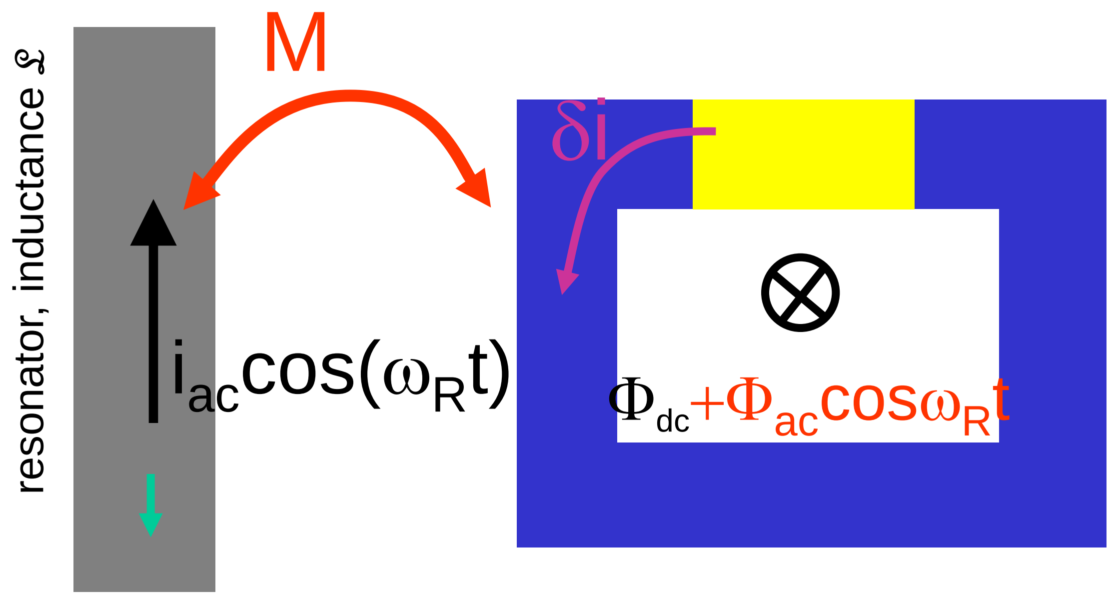
Other way to see things:

$I=Y(\omega)V$, $V=i\omega\Phi$,

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

Goal : determine ac response experimentally

Measurement: SNS ring coupled to rf resonator



$I \sim \chi\Phi$, with $\chi=\chi'+i\chi''$

ac flux imposed by resonator

$$i_{ac}(\omega_R) \longrightarrow \Phi_{ac}=Mi_{ac} \longrightarrow i_{ac}=(\chi'+i\chi'')Mi_{ac}$$

Change of resonator inductance and resonance frequency:

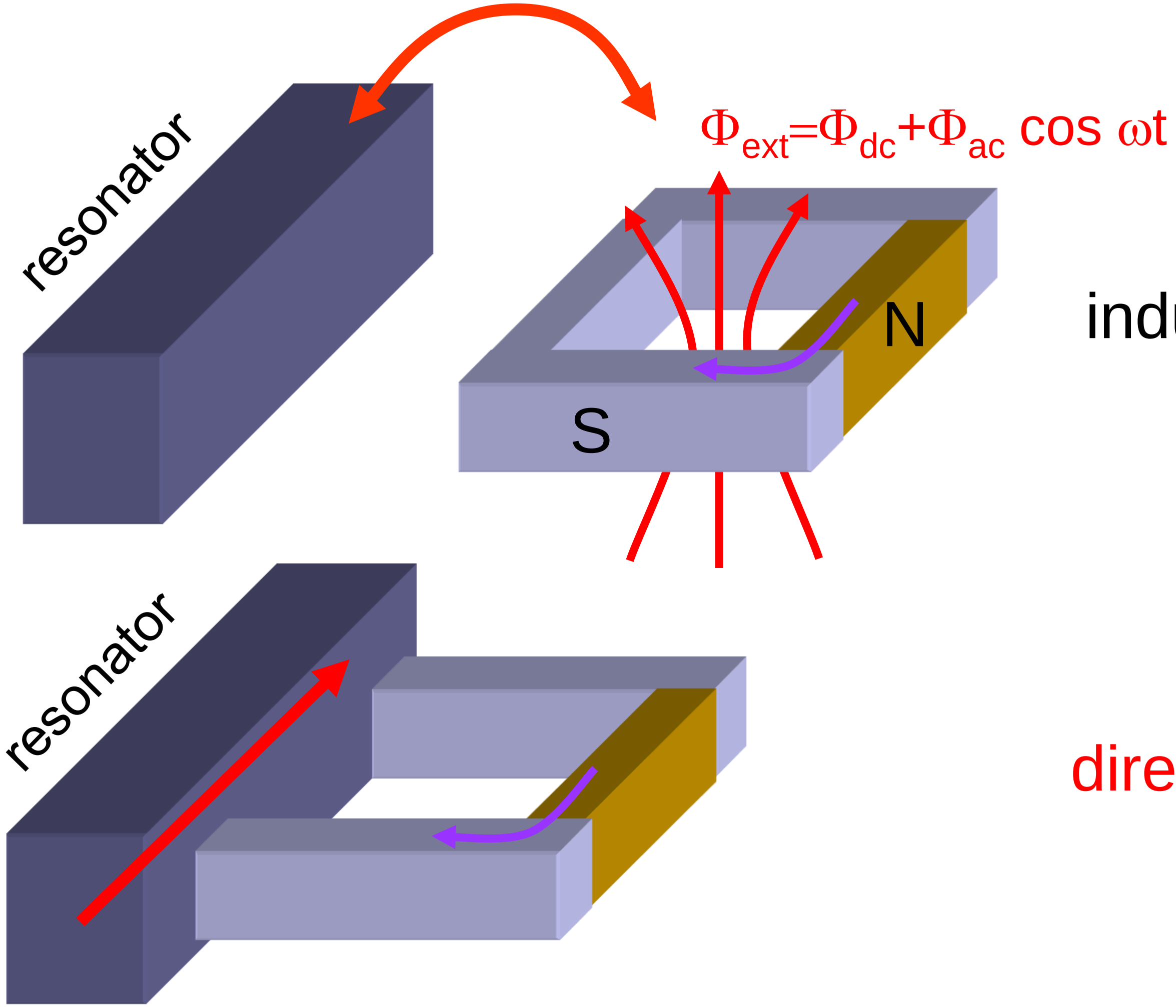
$$\mathcal{L}\, i_{ac}(\omega_R) \longrightarrow \mathcal{L}\, i_{ac}(\omega_R)+\chi' M^2 i_{ac}$$

$$\boxed{2\delta f/f = -\delta\mathcal{L}/\mathcal{L} = -\chi' M^2/\mathcal{L}}$$

Change of resonator quality factor due to dissipation

$$\boxed{\delta(1/Q)\text{: losses: out-of-phase response } \chi''}$$

In practice: equivalent setup



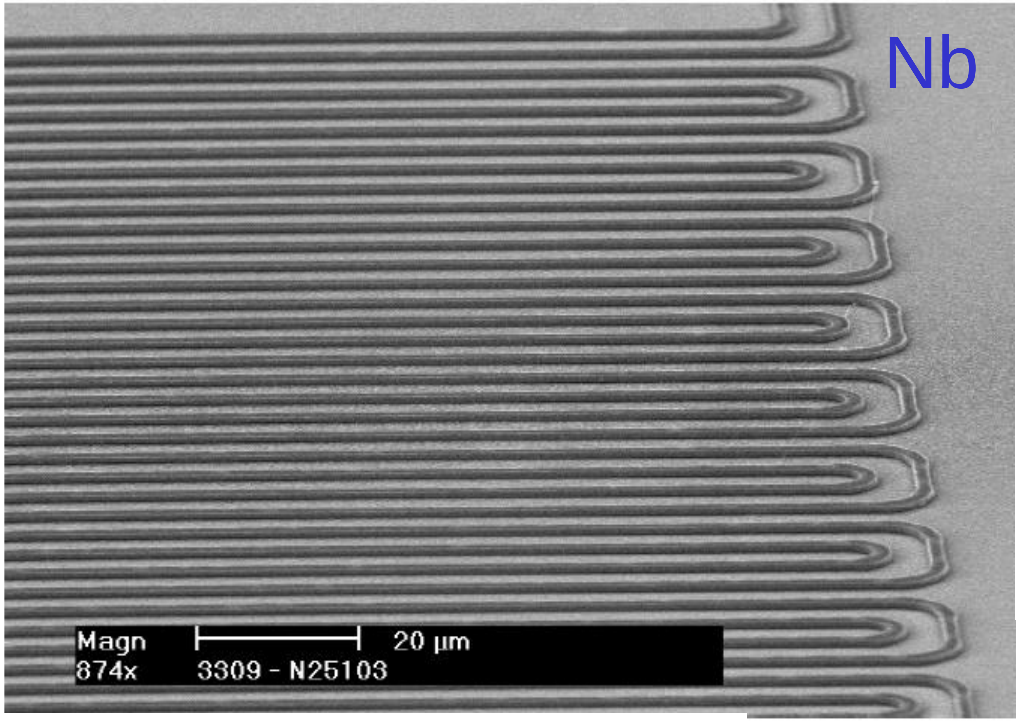
$\Phi_{ext}=\Phi_{dc}+\Phi_{ac}\cos\omega t$

inductive coupling

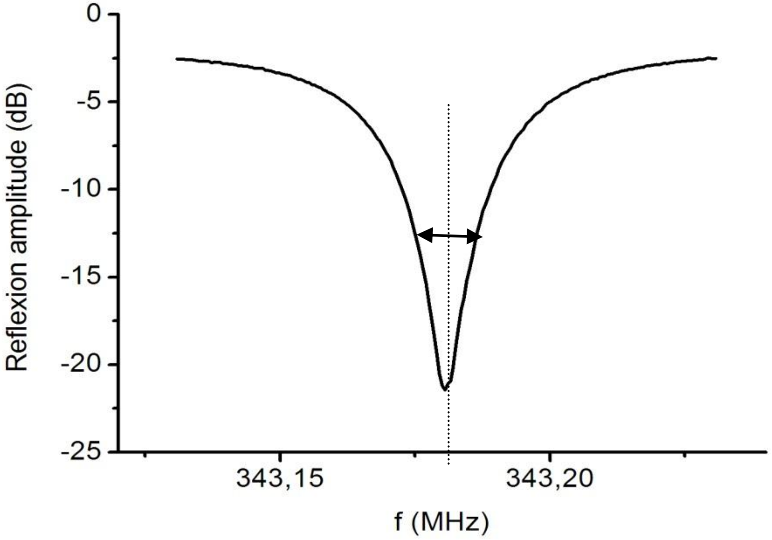
direct coupling

Use of multimode hf resonator

Bouchiat, Reulet, 1995



$Q=f/\delta f$



Q up to 20 000

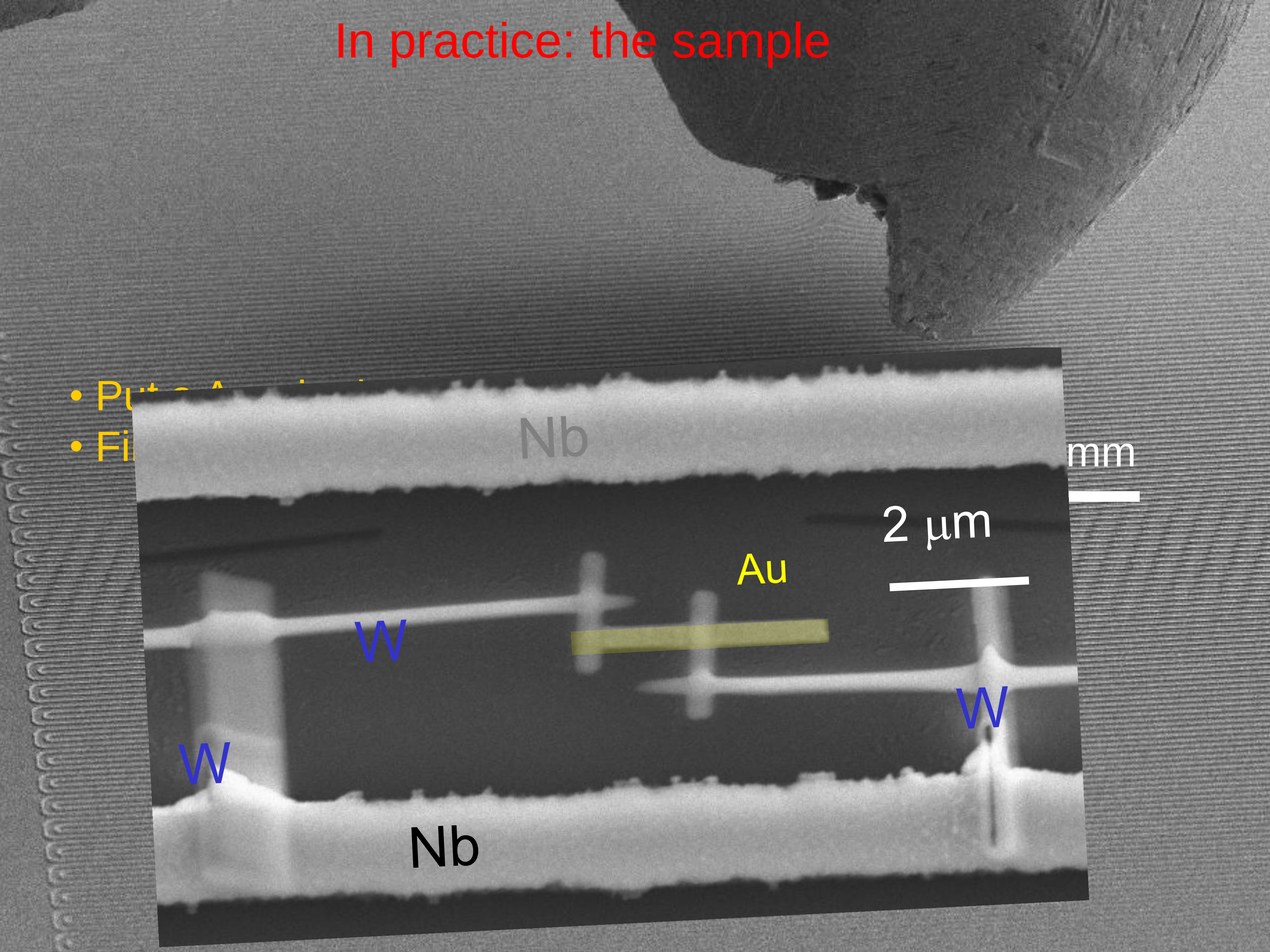
$$f_1=\frac{1}{\sqrt{(LC)}}=380\text{MHz}$$

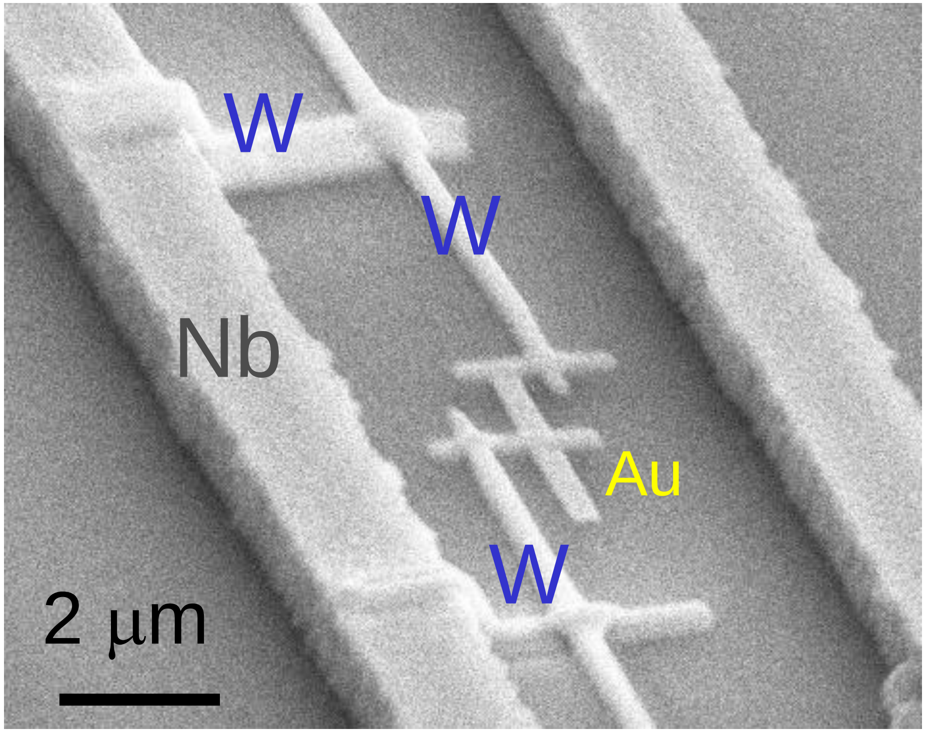
$f_n=nf_1$, up to 8 GHz or more

Then: couple SNS loop

In practice: the sample

- Pu
- Fi





E_{Th} ~ 50 mK

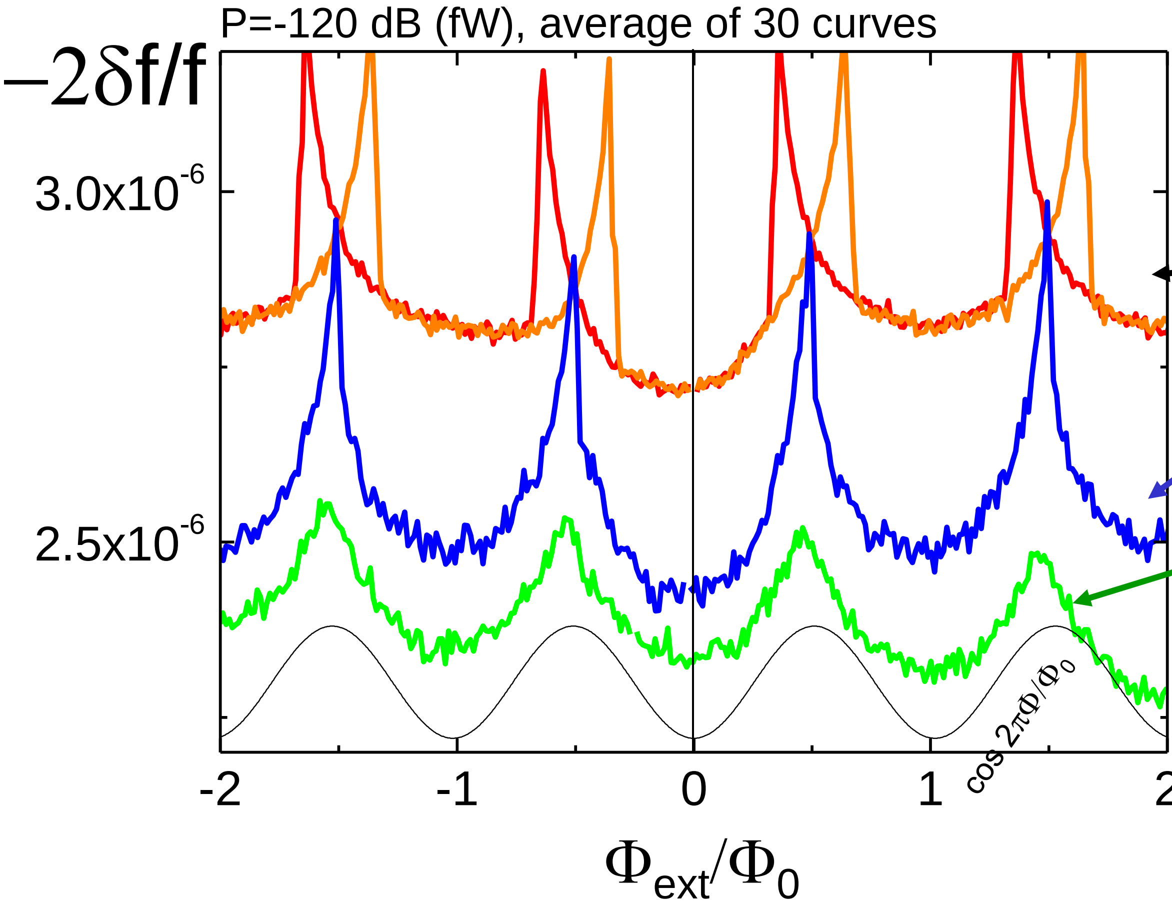
I_c~μA at low T

Response of single ring in a 20 cm long resonator

In phase response at 300 MHz: not purely harmonic, even at high T

$$-2\delta f/f = \chi'(\Phi_{ext})\, M^2/L$$

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



T= 450 mK, I_c~10 μA
hysteretic at low T
$2\pi L I_c \sim \Phi_0$

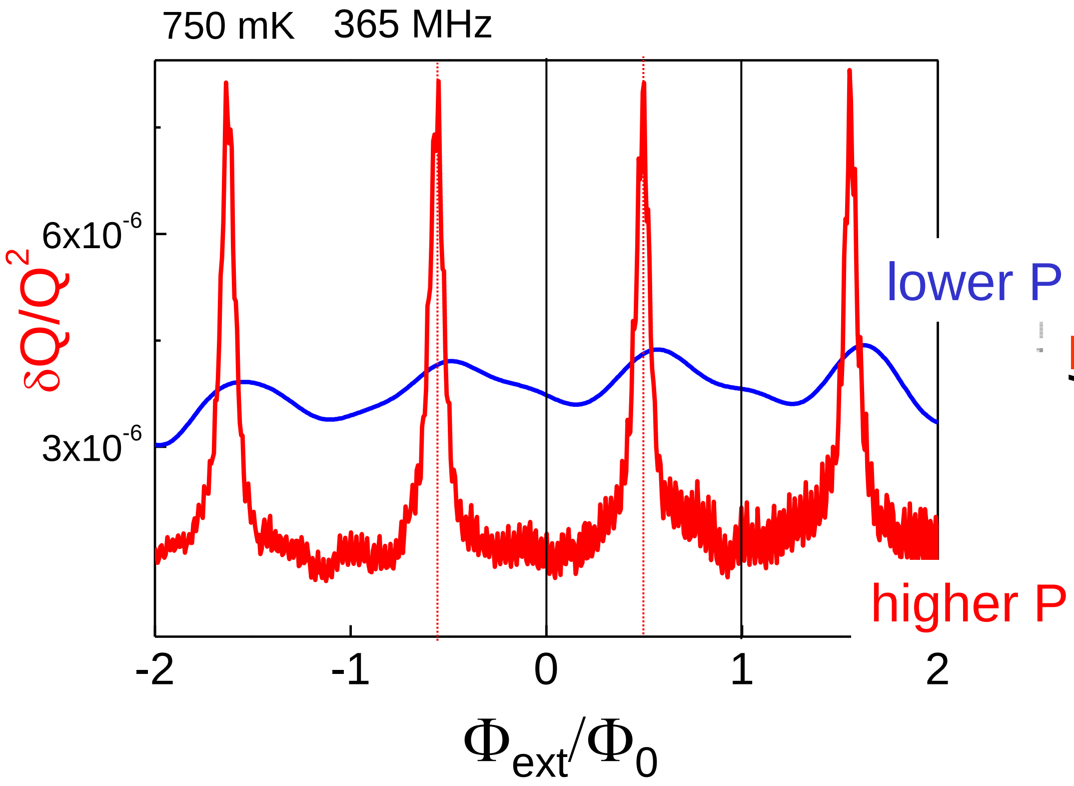
T= 670 mK, I_c~5 μA

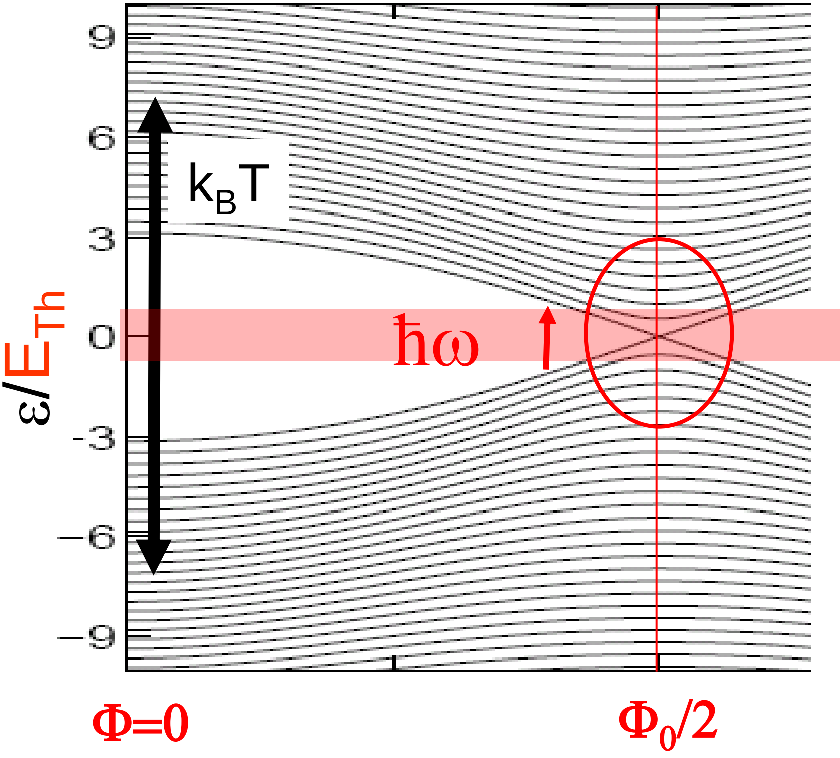
T=1 K = $20E_{Th}$ = 6δ
$2\pi L I_c \sim \Phi_0/10$
$I(\varphi)_{dc} = \sin\varphi$ (within 1%)
but χ' anharmonic!

$\chi' \neq \partial I/\partial\Phi$ at these frequencies!

Out of phase response: dissipation

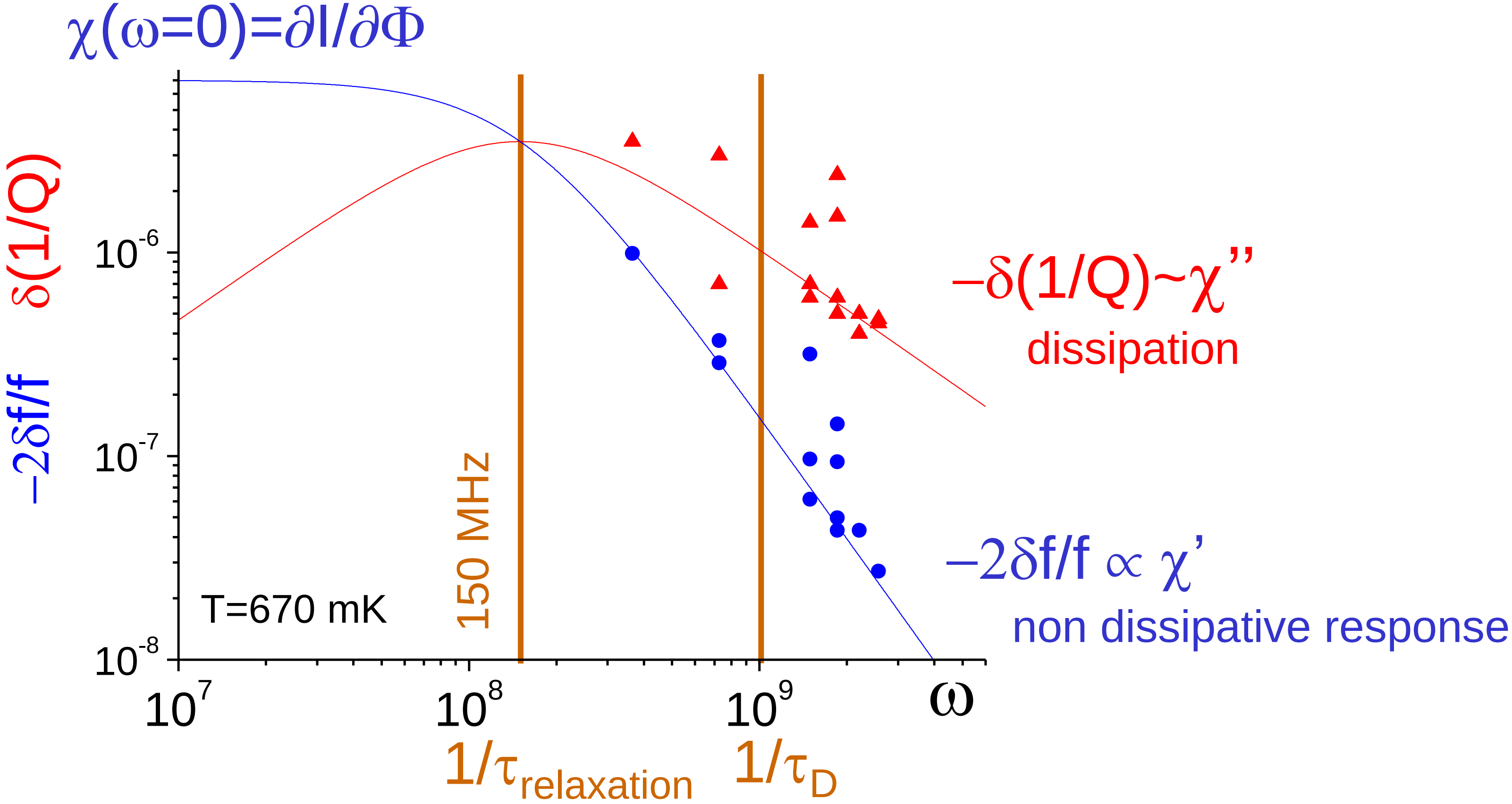
$$-\delta(1/Q)\sim\chi''$$





Losses greatest at $\Phi_{ext}=\Phi_0/2$, when minigap closes
(even though $T>>\delta$)

Frequency dependence of χ' and χ'' (preliminary results)



Comparison with simplest dissipation model (relaxation time)

$$\chi=\chi_0/(1+i\omega\tau)$$

relaxation time

$$\chi'=\chi_0/(1+\omega^2\tau^2)$$

$$\chi''=\omega\tau/(1+\omega^2\tau^2)$$

Seems as though relaxation time is longer than τ_D: maybe $\tau_{e\text{-}ph}$ or $\tau_{e\text{-}e}$?

Linear response of SNS ring at high frequency

Thesis F. Chiodi

Preliminary experiments: $L=1.5\ \mu m$, $f_{Th}=1GHz$, $E_{Th}=50\ mK$

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: $\omega< E_{Th}\ /\hbar$

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

Theory?? In progress...

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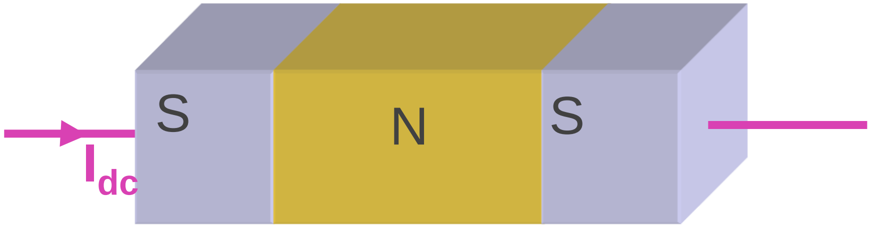

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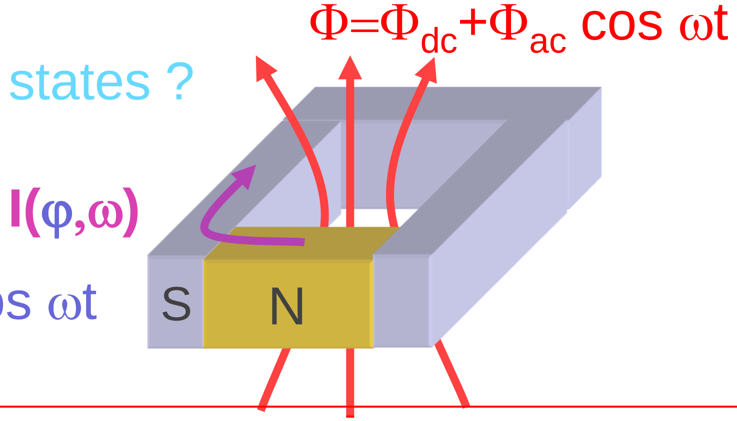
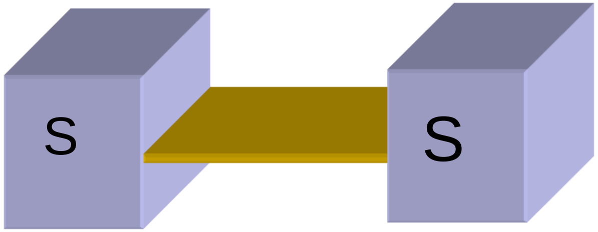
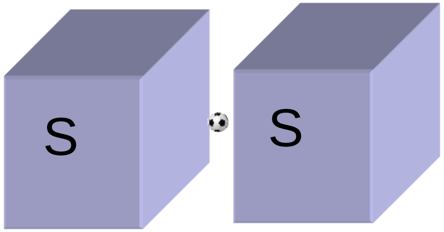


Q3: What about supercurrents through molecules ? Magnetic molecules?

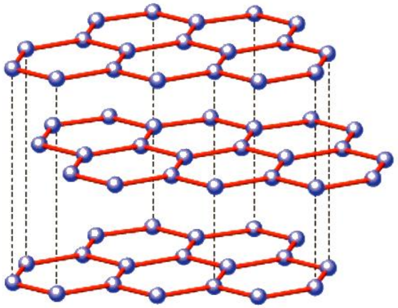
A3: Proximity effect through graphene and metallofullerenes



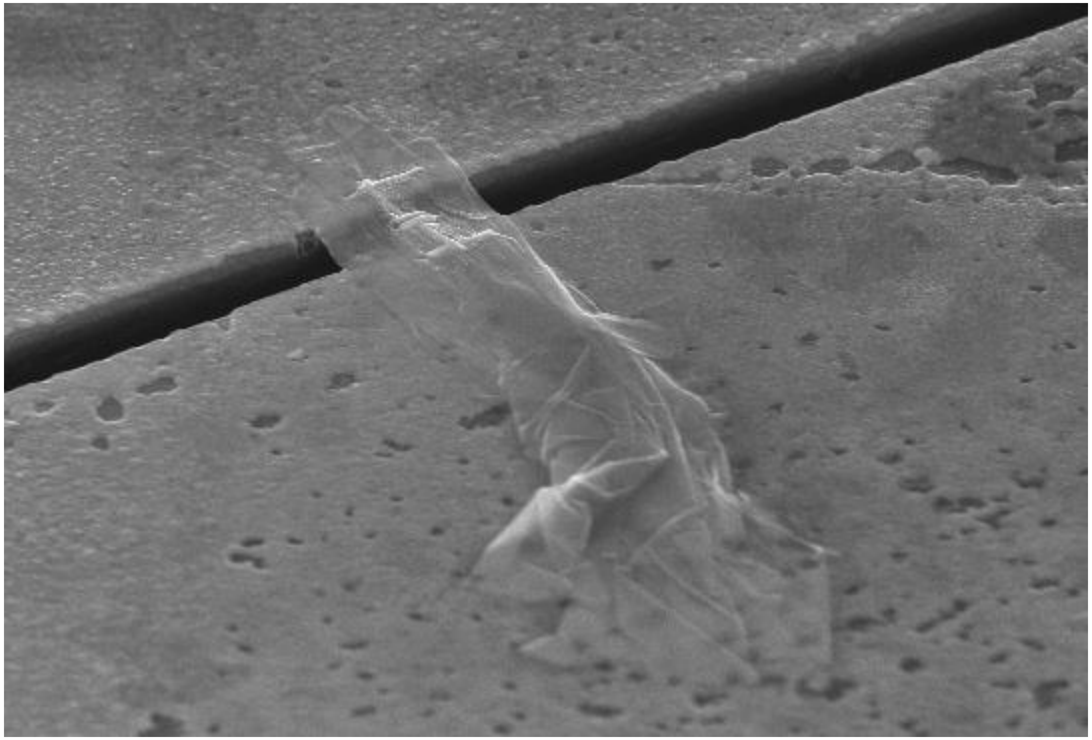


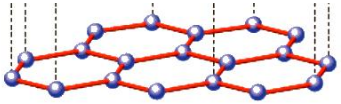
Between metals and molecules: Proximity effect in graphene

C. Ojeda, M. Monteverde, A. Shailos, P. Delplace, W. Nativel, C. Collet, F. Fortuna,
M. Ferrier, R. Deblock, S. Guéron, A. Kasumov, H. Bouchiat



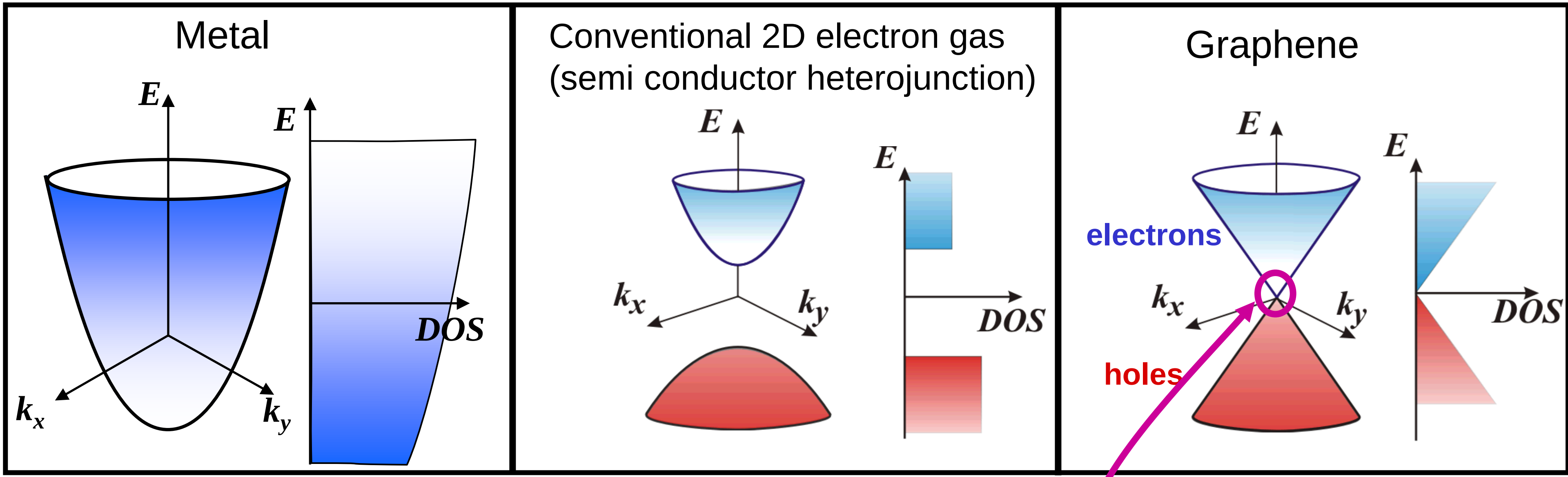
thin graphite (graphene multilayer)





graphene = single C plane

Why is graphene interesting?



Noble metals are (almost) all alike!

Not tunable

One accessible band

Massive carriers

$E=\hbar^2 k_F^2 / 2 m_e$

$v_F \sim 10^6$ m/s

Tunable in transistor configuration

Electron-hole asymetry

Massive carriers

$E_e=\hbar^2 k_F^2 / 2 m_e^*$

Gap in DOS

Tunable carrier density and type

Electron-hole symetry

Massless dispersion relation

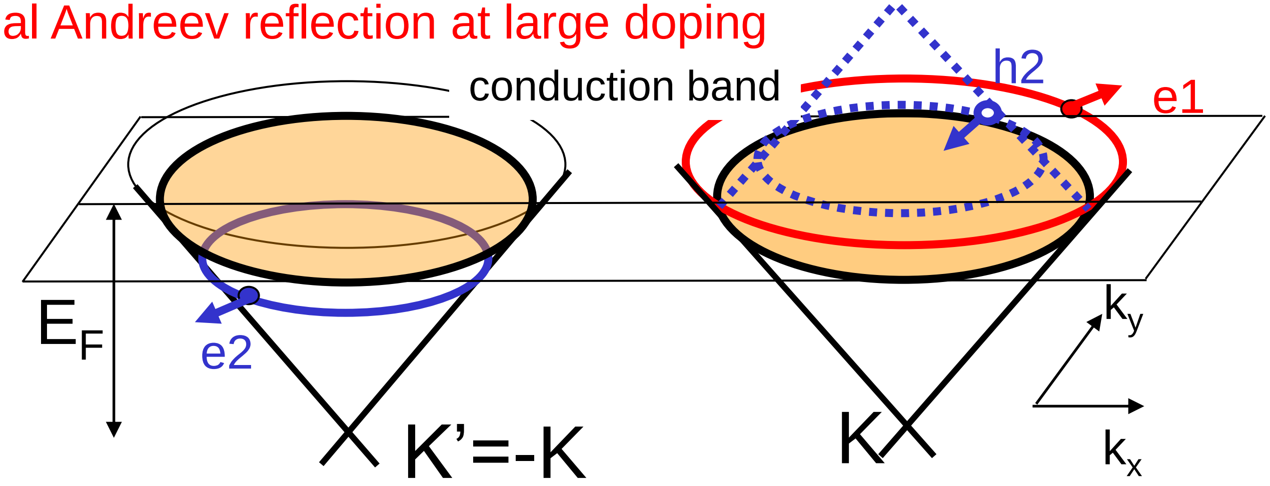
(Dirac cone) $E=\hbar v_F k_F$

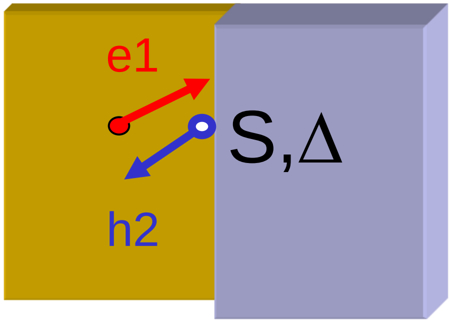
$v_F \sim 10^6$ m/s

Dirac point: $k_F=0 \rightarrow \lambda_F=\infty$
semiclasical physics not valid !
Purely quantum physics...

Consequence on the Proximity effect?

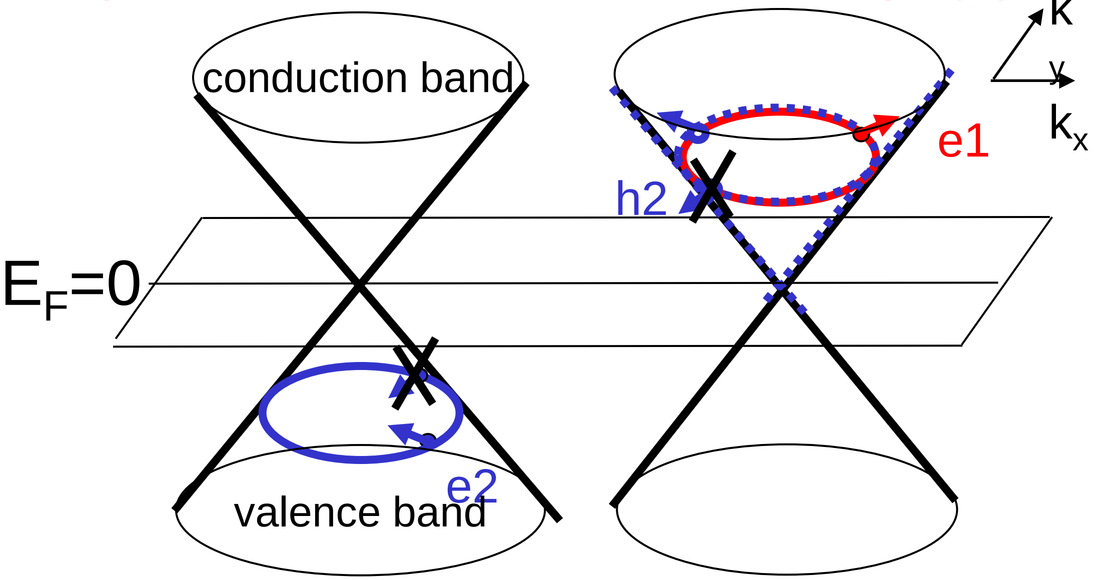
Usual Andreev reflection at large doping

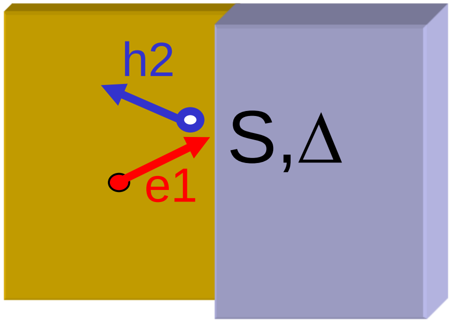




Like in usual conductors

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

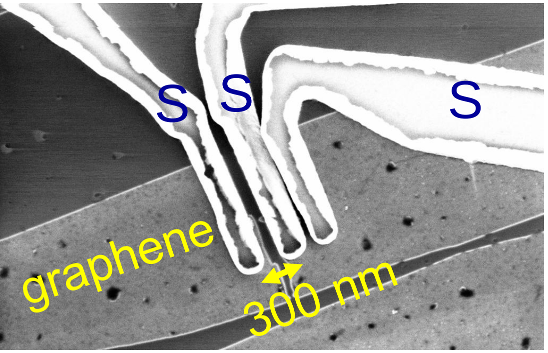




Specific to graphene

But: need zero doping (E_F<<Δ) and ballistic transport !

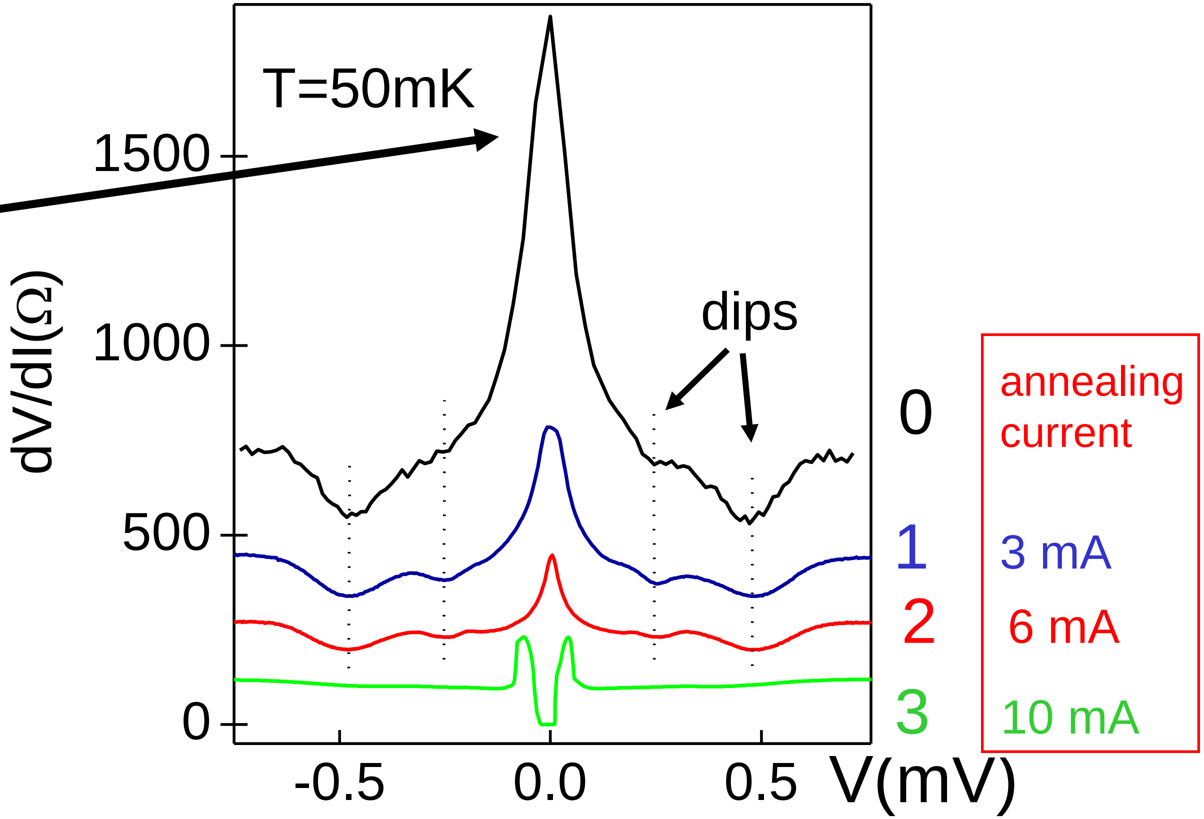
For starters: a tunable proximity effect in graphene



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

No supercurrent!

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



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

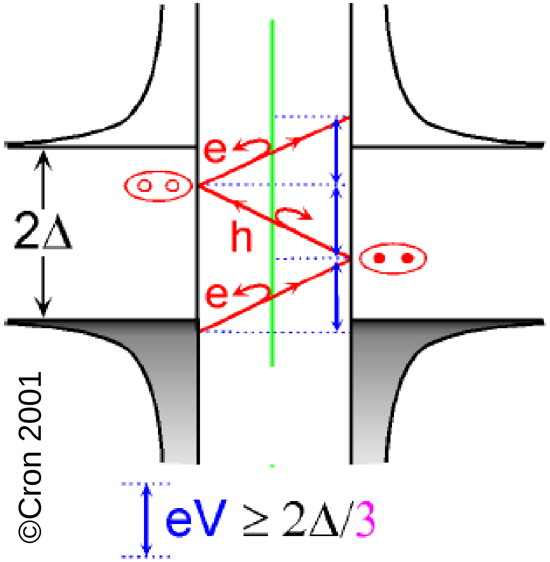
Can we relate R decrease to improved S/graphene contact?

Contrast of Multiple Andreev Reflection dips changes

At $V_{dc}\neq 0$: Multiple Andreev reflexions transfer Cooper pairs.

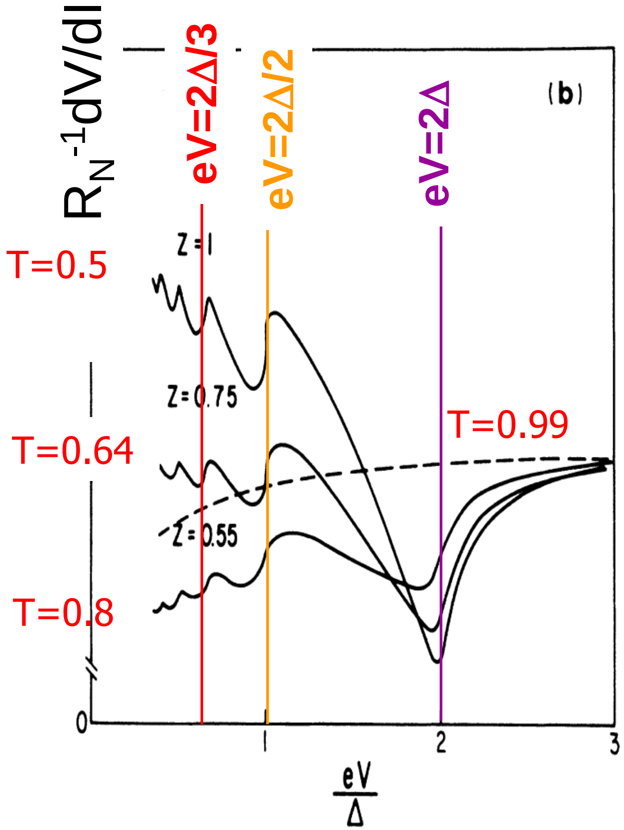
New MAR possible when $2\Delta = neV$, n Cooper pairs transfered.

Lower Resistance

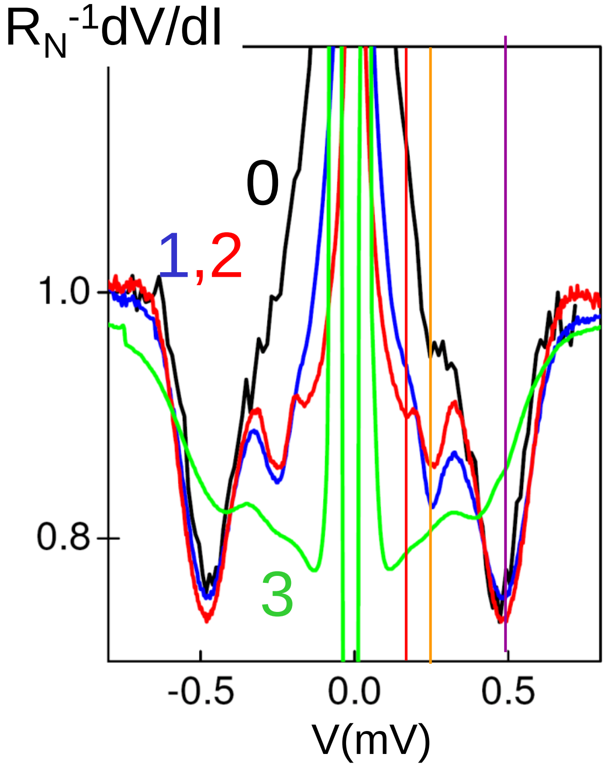


Probability of n pair transfer depends on interface transparency T

(theory for ballistic metal:Blonder 1982, Flensberg 1998)



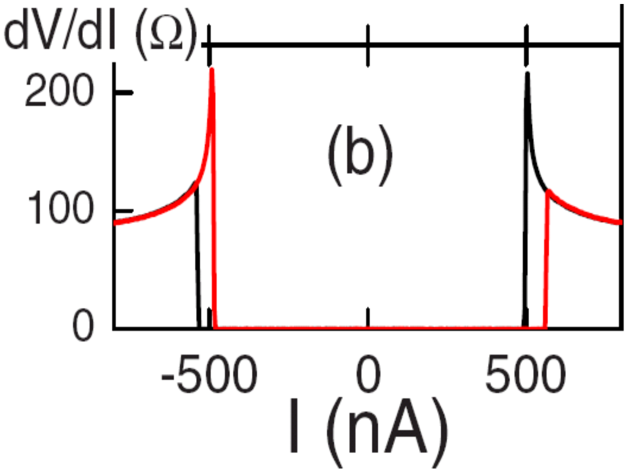
Contrast of MAR in S/G/S



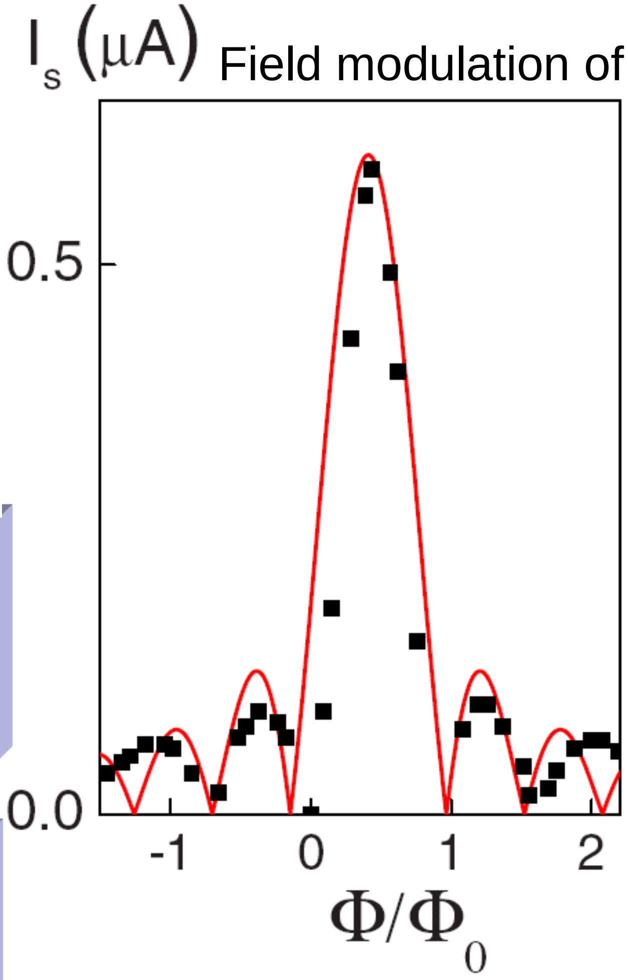
T(0) low, T(1,2) higher
T(3) highest

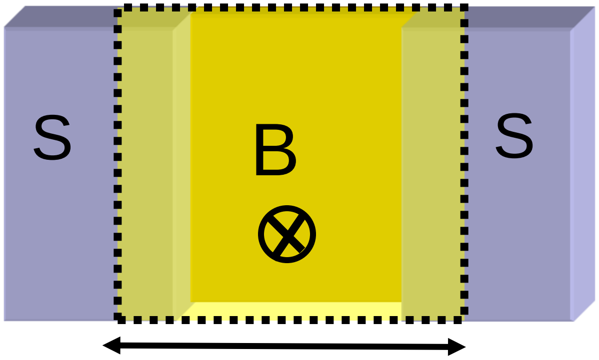
Contact transparency improves with annealing
No theory exists for S/disordered N/S or S/graphene/S

We induced supercurrent with large current annealing... How do we know we're still measuring graphene?



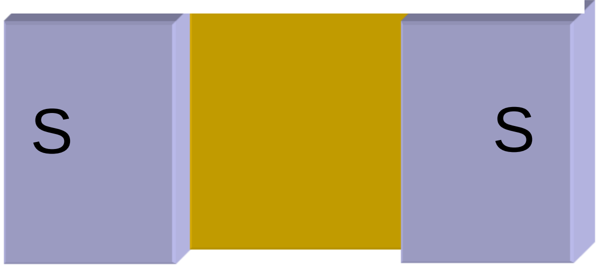
Field modulation of I_s



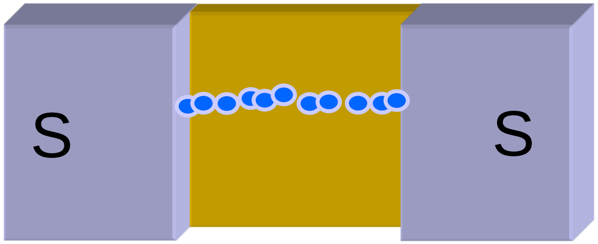


d+2λ, λ=120nm

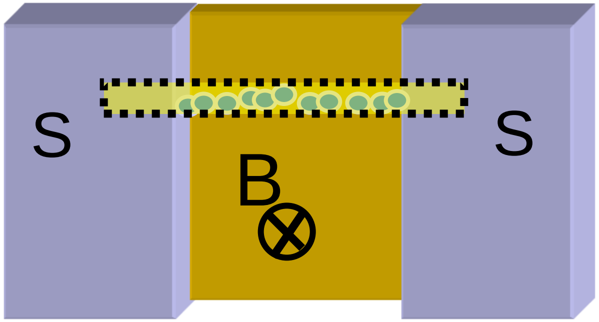
Φ=B.Area



or



and not



Field dependence of critical current corresponds to wide junction (and not to a metal chain)

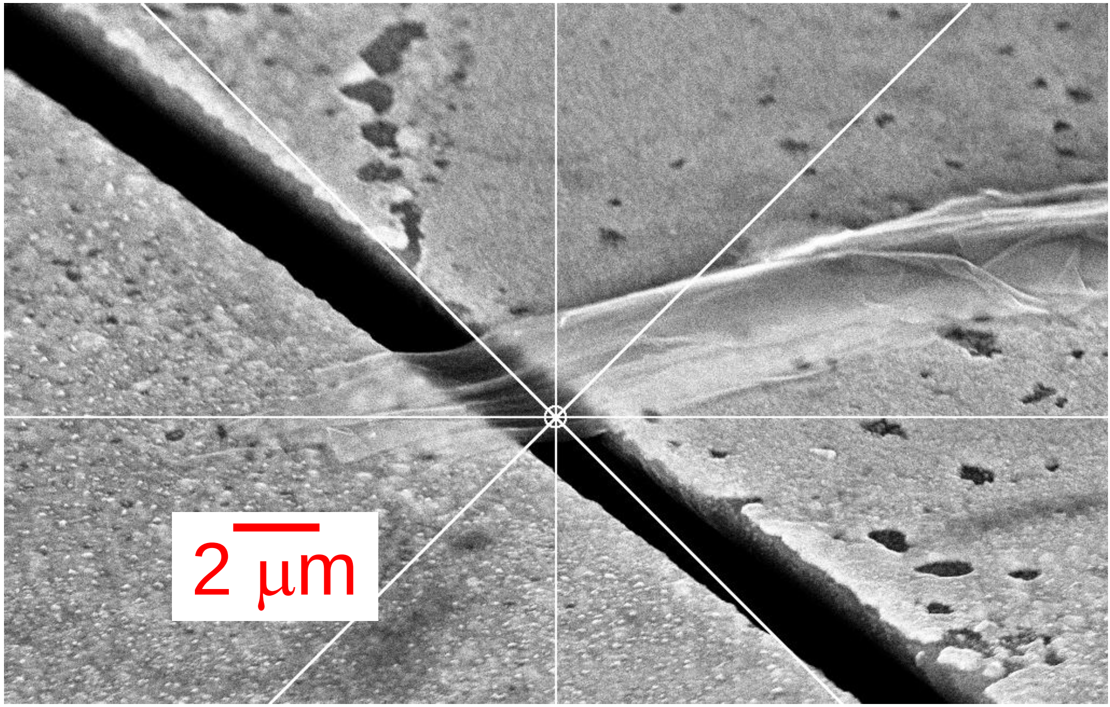
Current annealing improves the quality of contacts

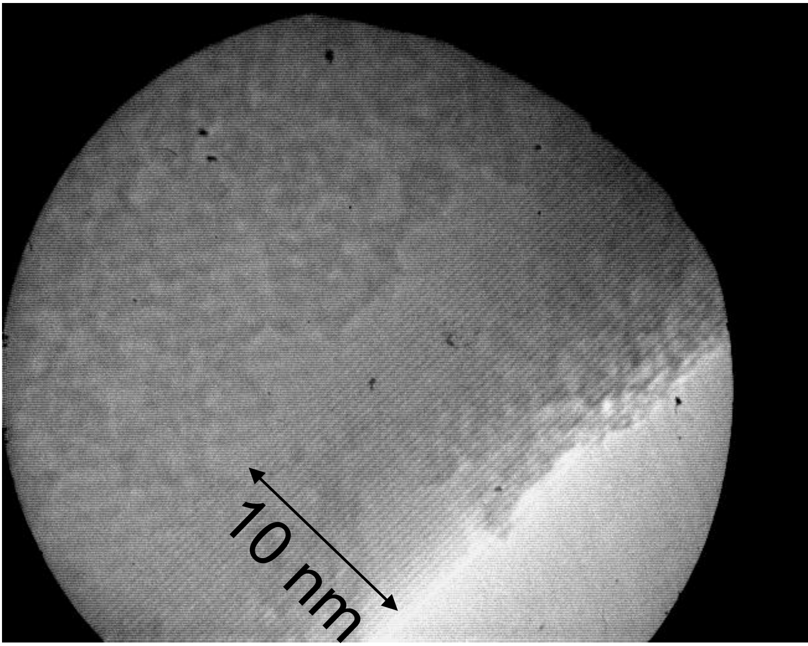
⇨ full Proximity effect in diffusive regime.

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

⇨ suspend graphene!

Suspended 30 sheet graphene/ite (on N contacts)





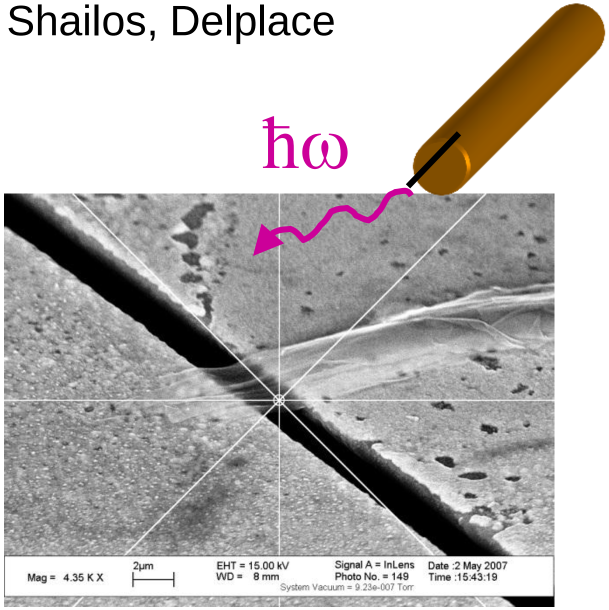
TEM (M. Kociak, A. Kasumov)

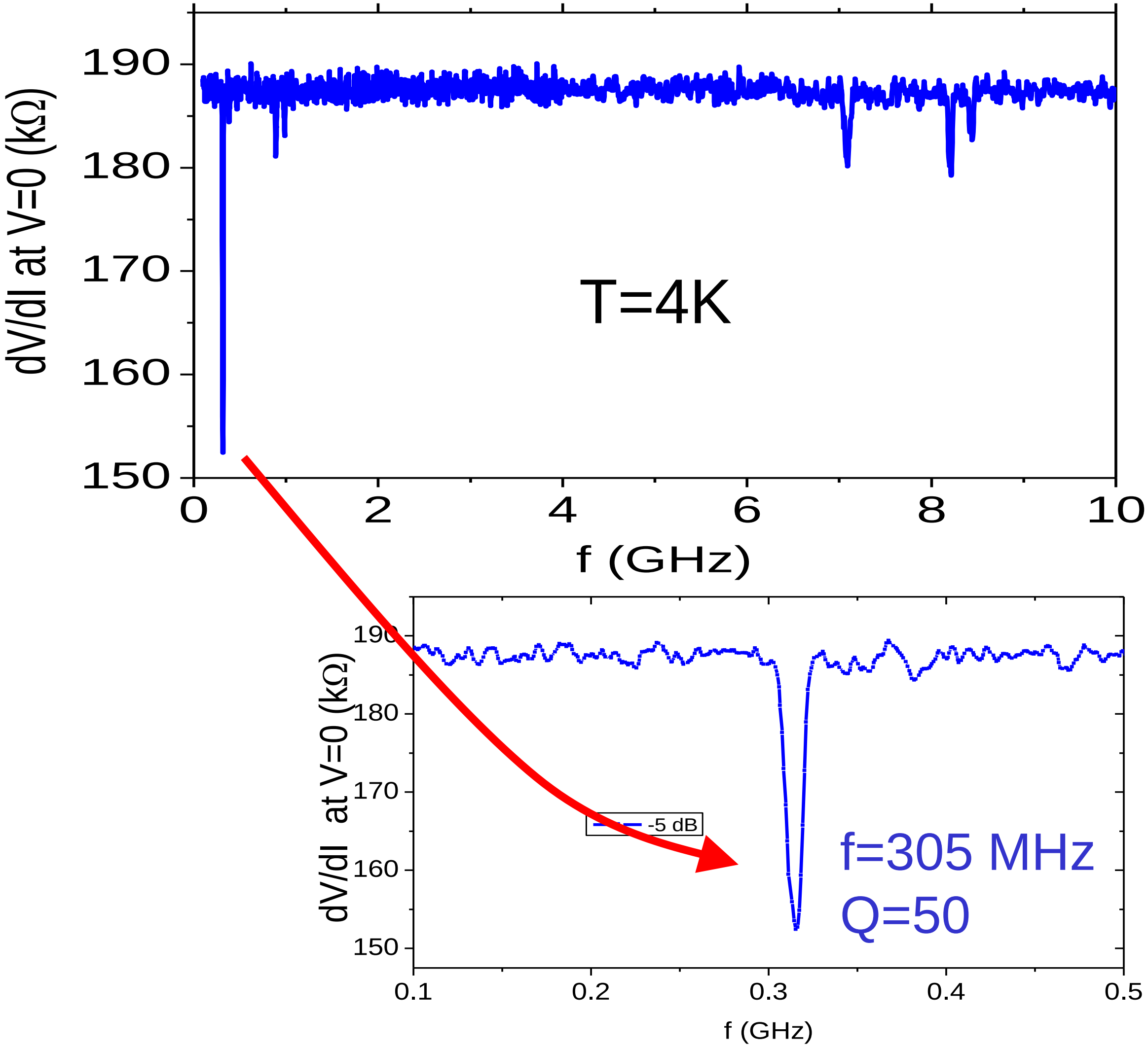
Measure as deposited (bad contacts)

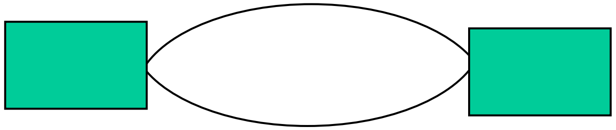
R = 200 kOhms T=4.2 K

Vibrational mode of the whole sheet seen on R

Shailos, Delplace







Higher energy phonon modes (5-20 meV) also detected (dynamical Coulomb blockade, Chepelianskii 2009)

Future work with graphene:

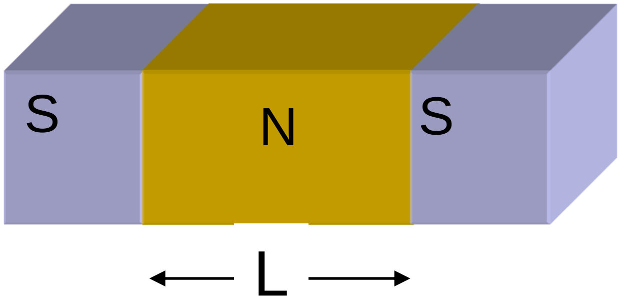
Improve the quality of graphene to reach uniform low doping regime, and ballisticity: with suspension and current annealing

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_{FIB})



Supercurrent in normal metals L> 1μm at low T: large phase coherence length

Supercurrent in graphene? yes for L= 0.3 μm, not L=2 μm

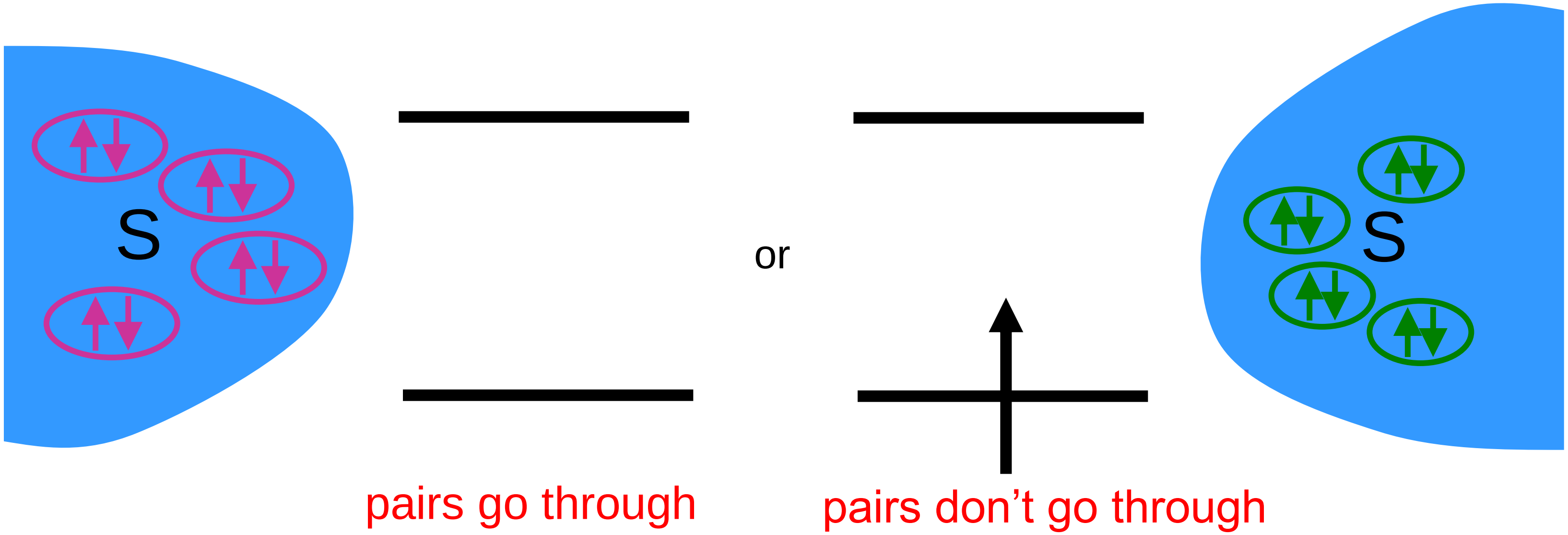
Proximity effect tests phase coherence!

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

Probing molecules with the proximity effect

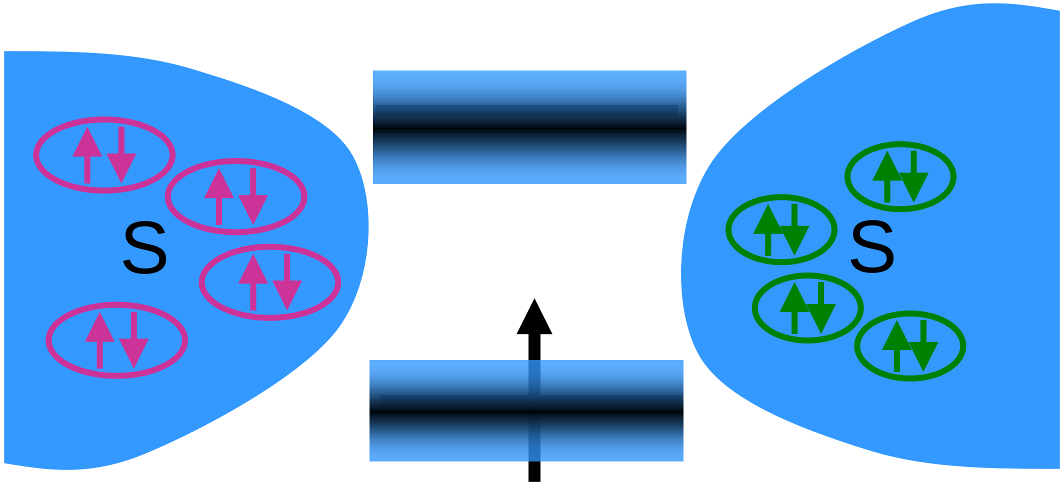
Normal metal=universal,
Molecules are each different!
Molecule=resolved molecular levels $\delta E > k_B T$ (also called « quantum dots »)

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



Simple?

In fact, rich physics!

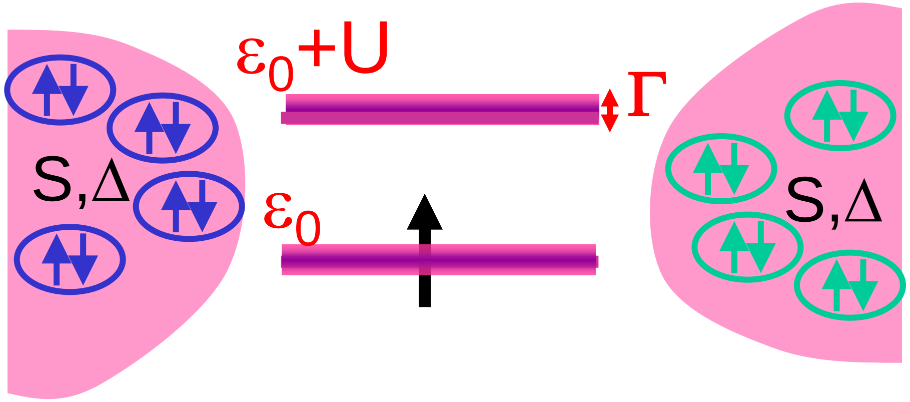


pairs can go through!

How? Coupling to leads Γ broadens molecular levels

Pairs can go through a magnetic molecule

Small supercurrent if weak coupling to leads

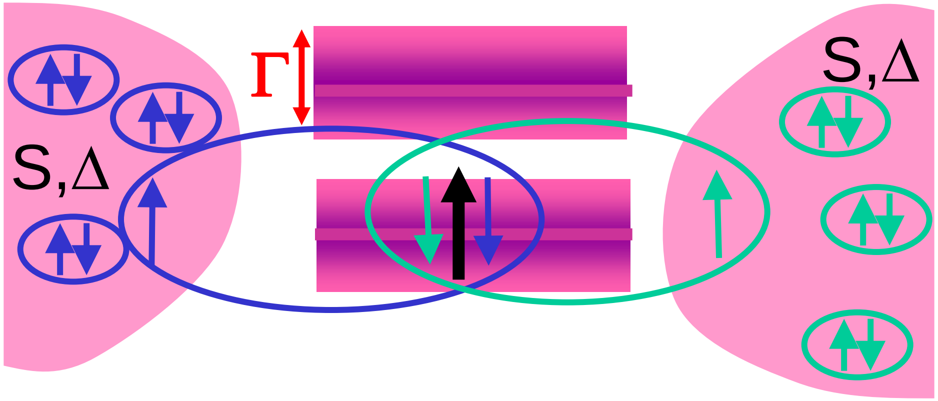


« π » state

$I=I_c\sin(\varphi+\pi)$
Small I_c

$\Delta>T_K$

Large supercurrent if strong coupling to leads



« 0 » state

Localized spin screened!
large $I_c \sim 2\pi e\Delta/h$,
non sinusoidal $I(\varphi)$

$\Delta<T_K$: Kondo regime

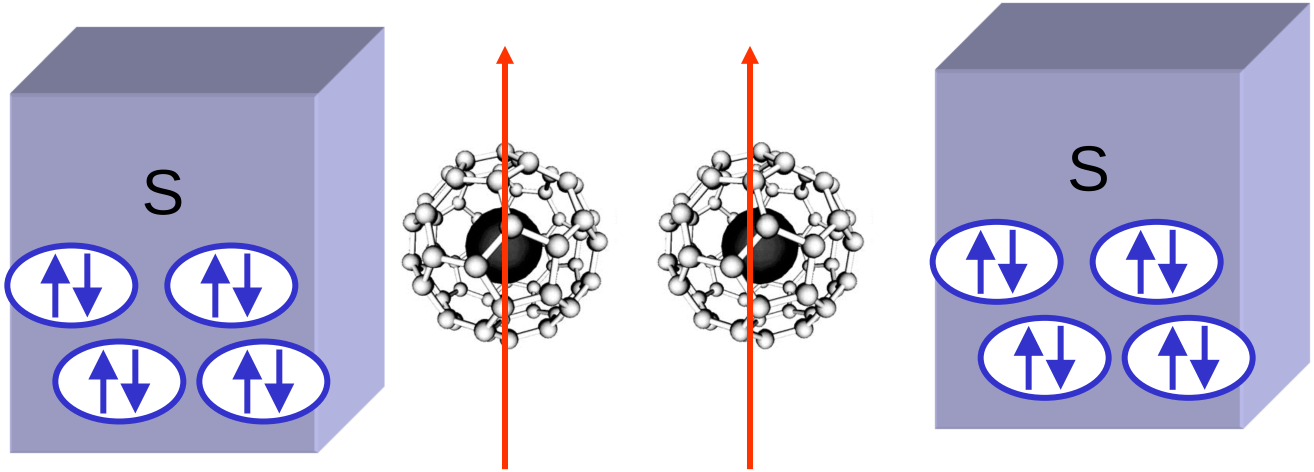
Kondo temperature

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

Nature of proximity effect depends on gap, coupling, level position...

In practice: molecule=suspended metallofulerene dimer

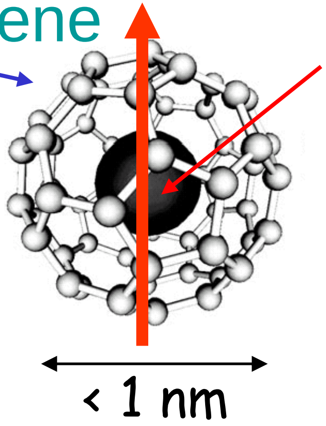
A. Kasumov, K. Tsukagoshi, M. Kawamura, T. Kobayashi, Y. Aoyagi (RIKEN, Japan)
K. Senba, T. Kodama, H. Nishikawa, I. Ikemoto, K. Kikuchi, (Tokyo, Japan)



Effect of molecular magnetism on supercurrent

What is a metallofullerene ?

A fullerene molecule with a metal atom inside.



C_{82} fullerene

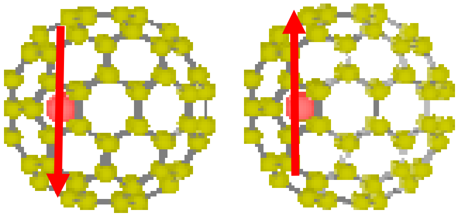
Gd atom

Charge transfer ⇨ Gd $^{3+}$, C_{82} $^{3-}$

S= 7/2, s= 1/2

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

Dimer Gd@C82 : 2 coupled spins 7/2



Furukawa *et al.* , J. Phys. Chem. A 2003

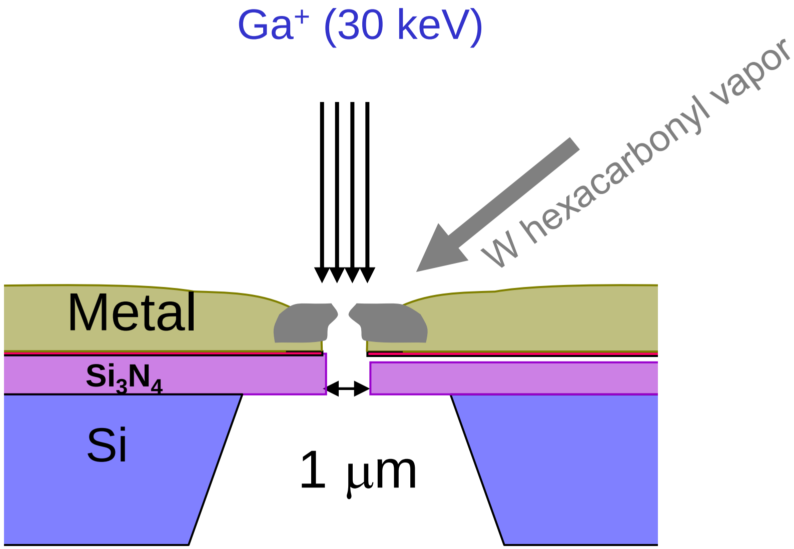
Paramagnetic above 3 K,

Antiferromagnetic with J=0.7 K

Dipolar coupling in dimer J_d=0.1 K

How do magnetic states influence transport ?

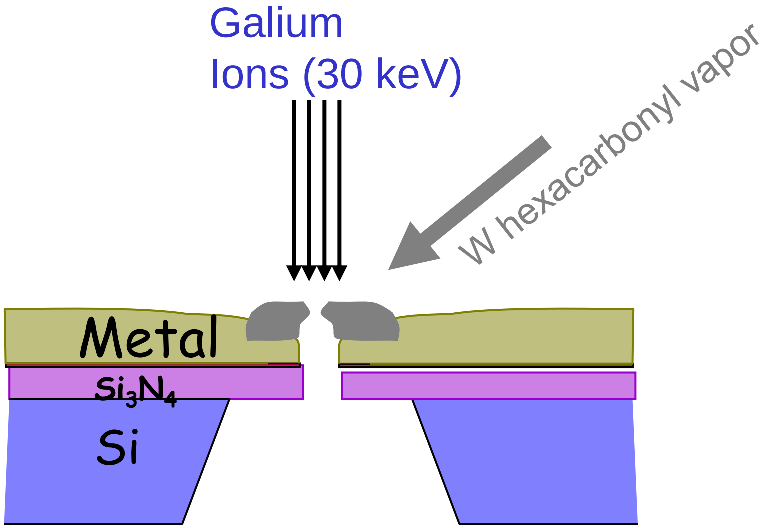
Fabrication of electrodes for measurement and visualization



Used for nanotubes: too big! Decrease spacing between electrodes

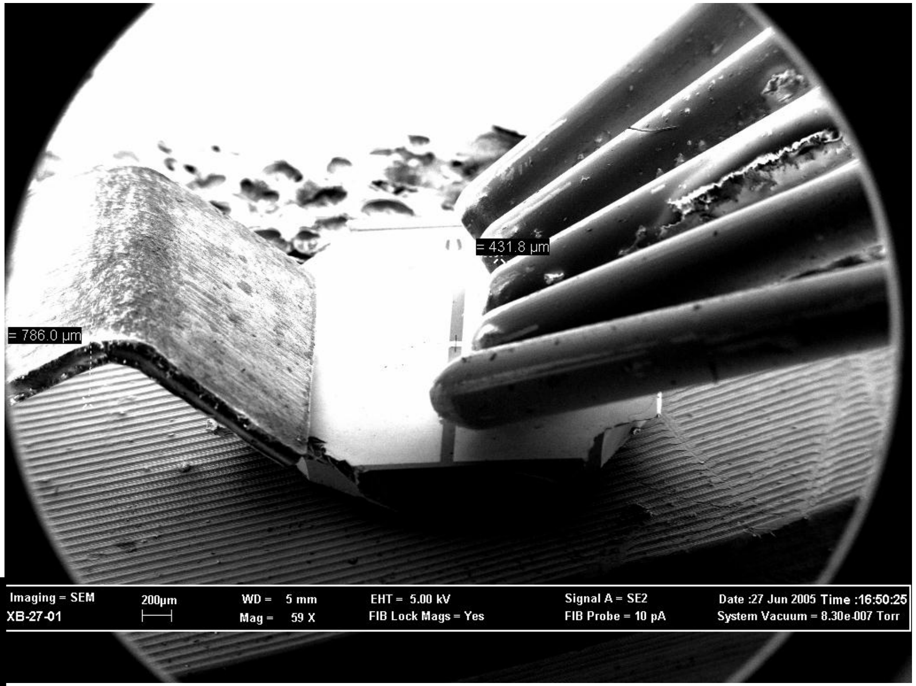
Making electrodes with a nanometer sized gap

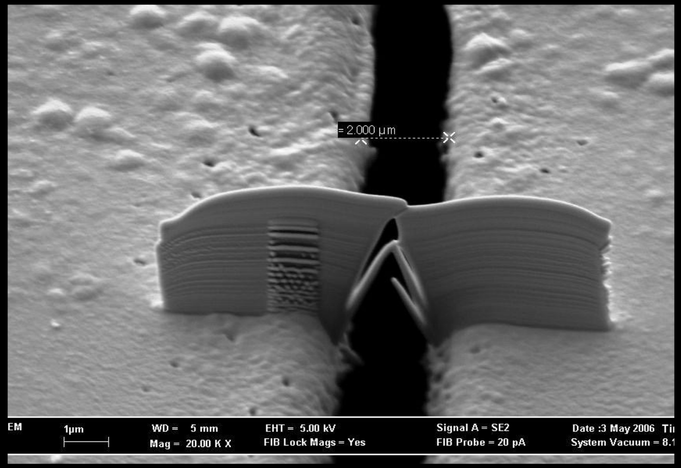
Alik Kasumov, Rikken, Thalès, CSNSM Orsay



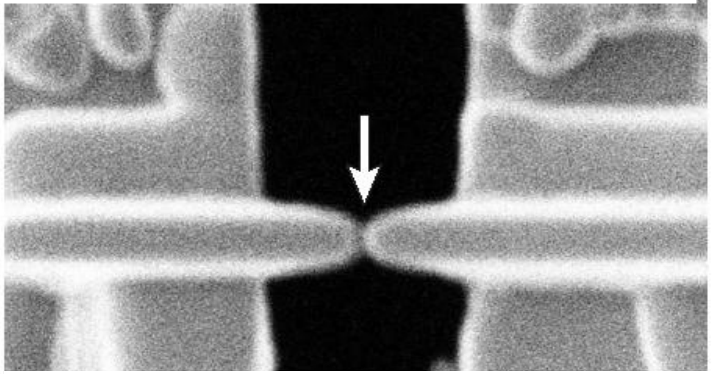
Galium
Ions (30 keV)

W hexacarbonyl vapor



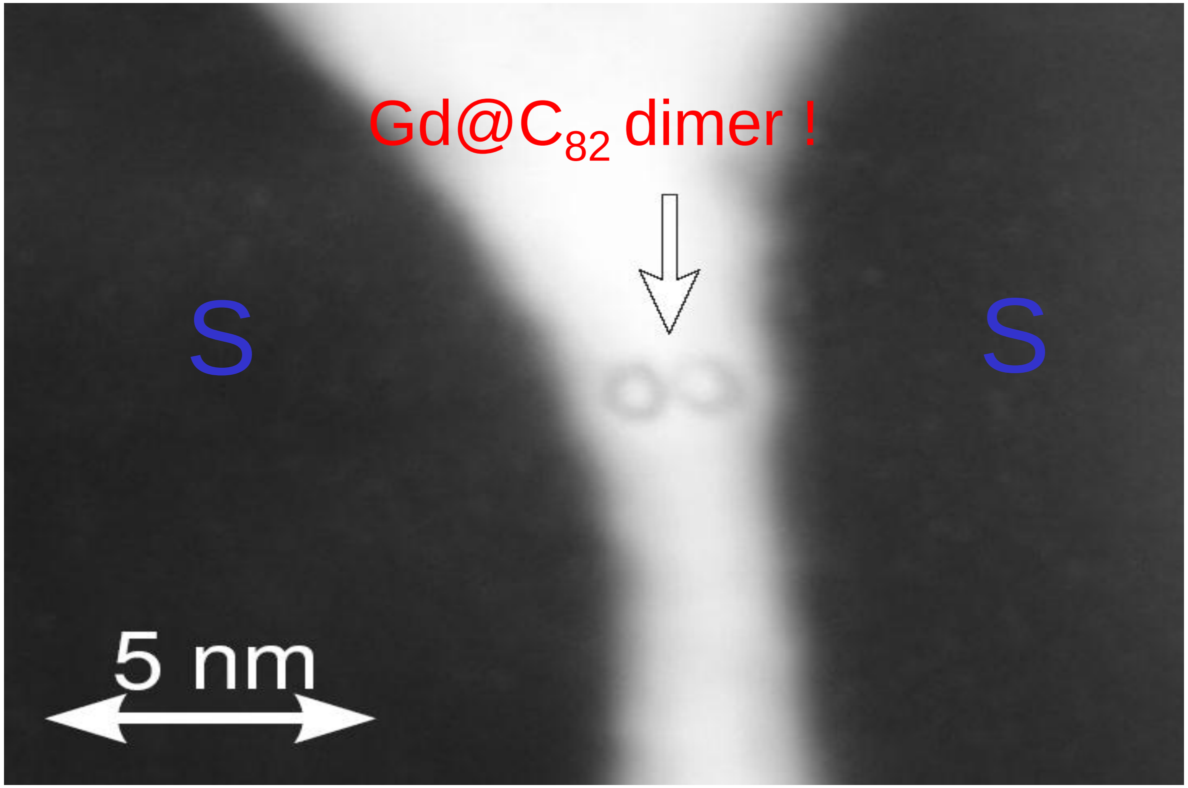


FIB image



And finally insert molecule

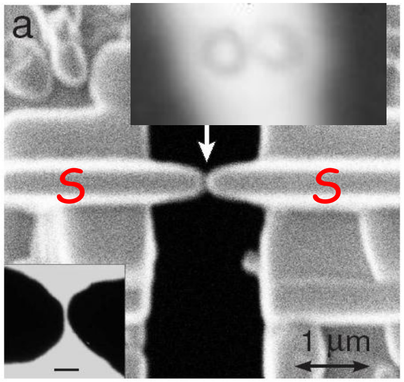
A look at the sample...



and measure...

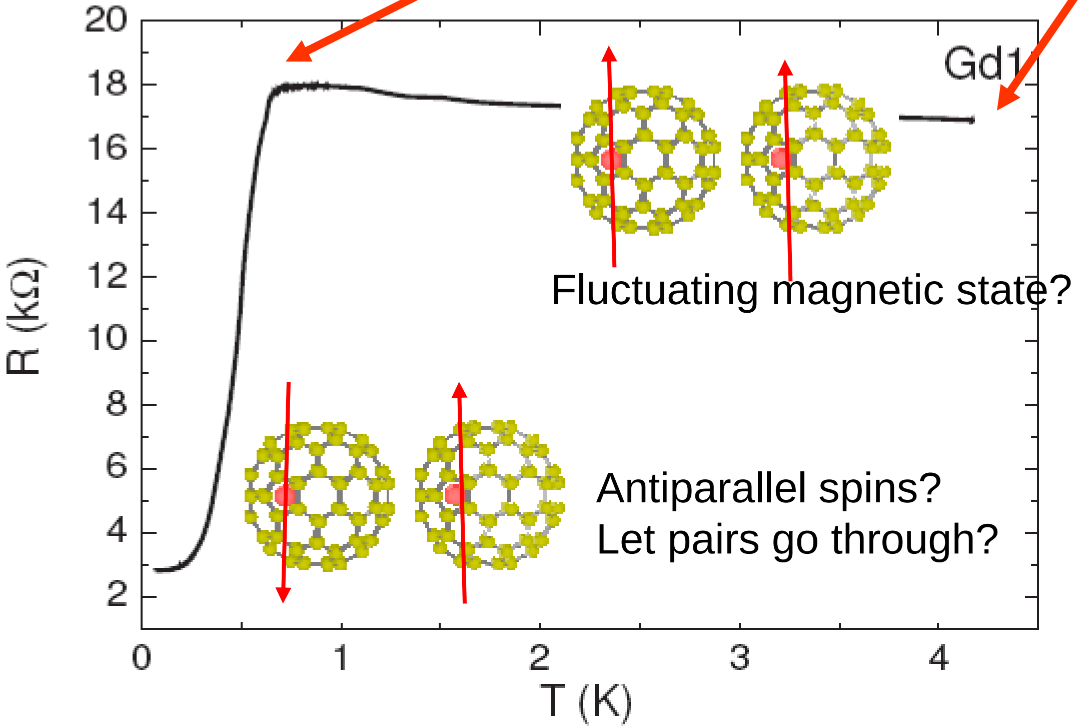
Kasumov et al, Phys. Rev. B 72, 033414 (2005)

Can pairs go through metallofullerene dimers?



T_{prox} = 0.7 K
H_{prox} = 1 T

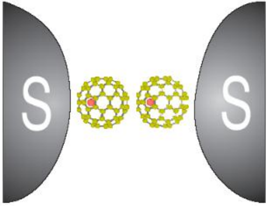
T_c (contacts)> 4K
H_c>5 T



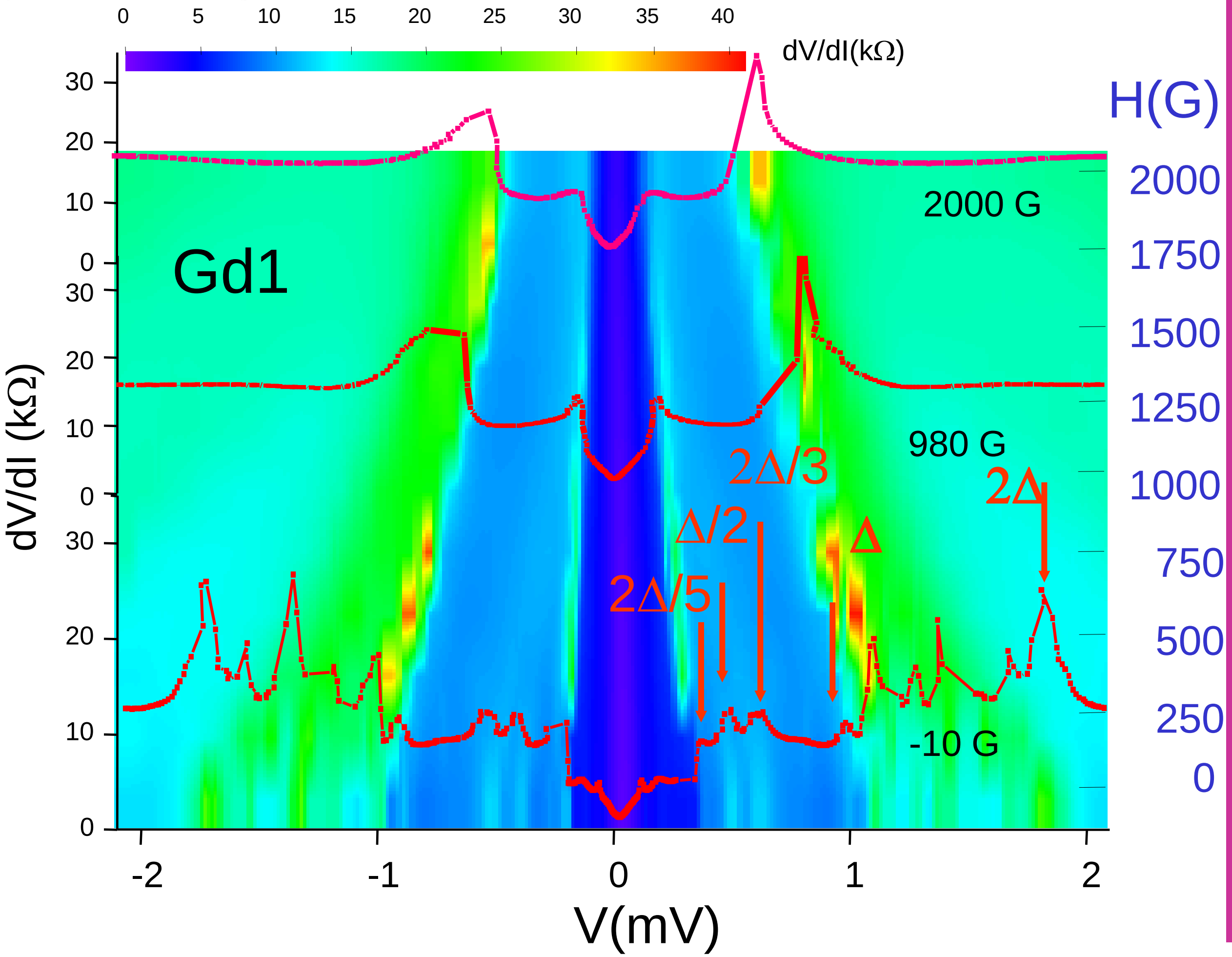
Fluctuating magnetic state?

Antiparallel spins?
Let pairs go through?

Depending on magnetic state, proximity effect can develop



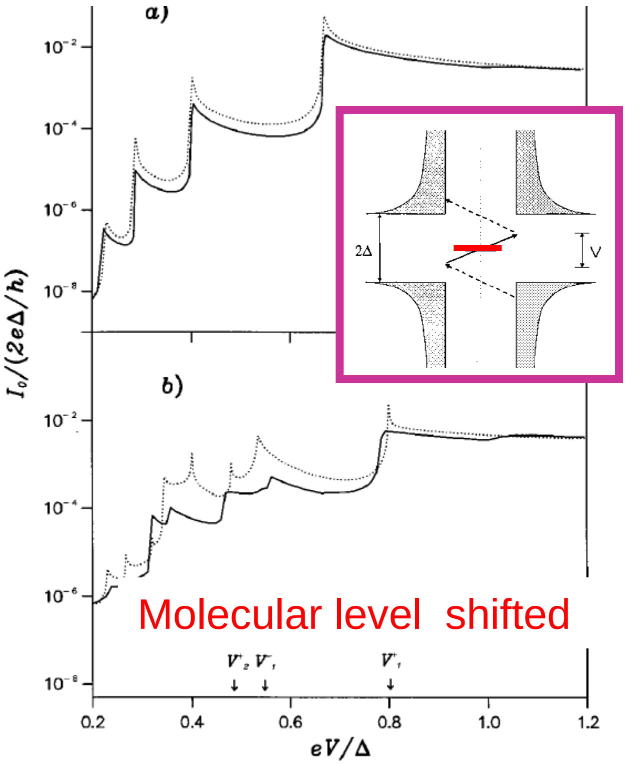
Differential resistance Vs V



Andreev reflexion in S-molecule-S

Levy Yeyati et al PRB (96)

Molecular level at the Fermi level



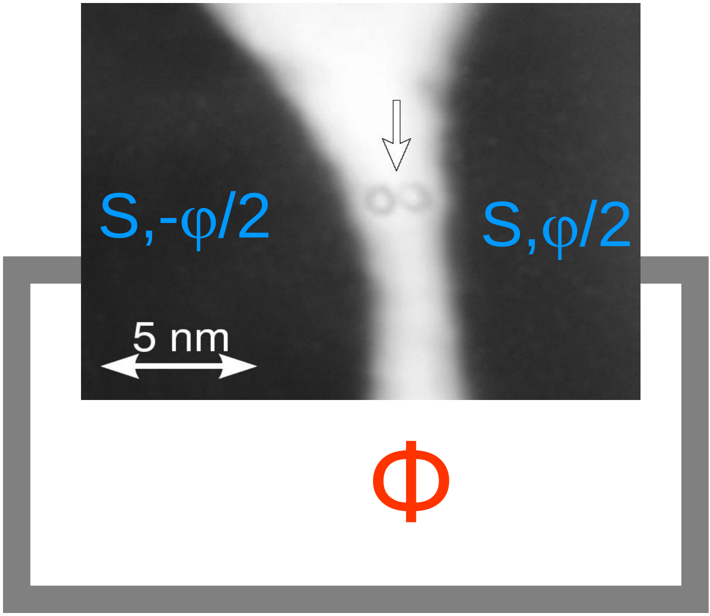
Molecular level shifted

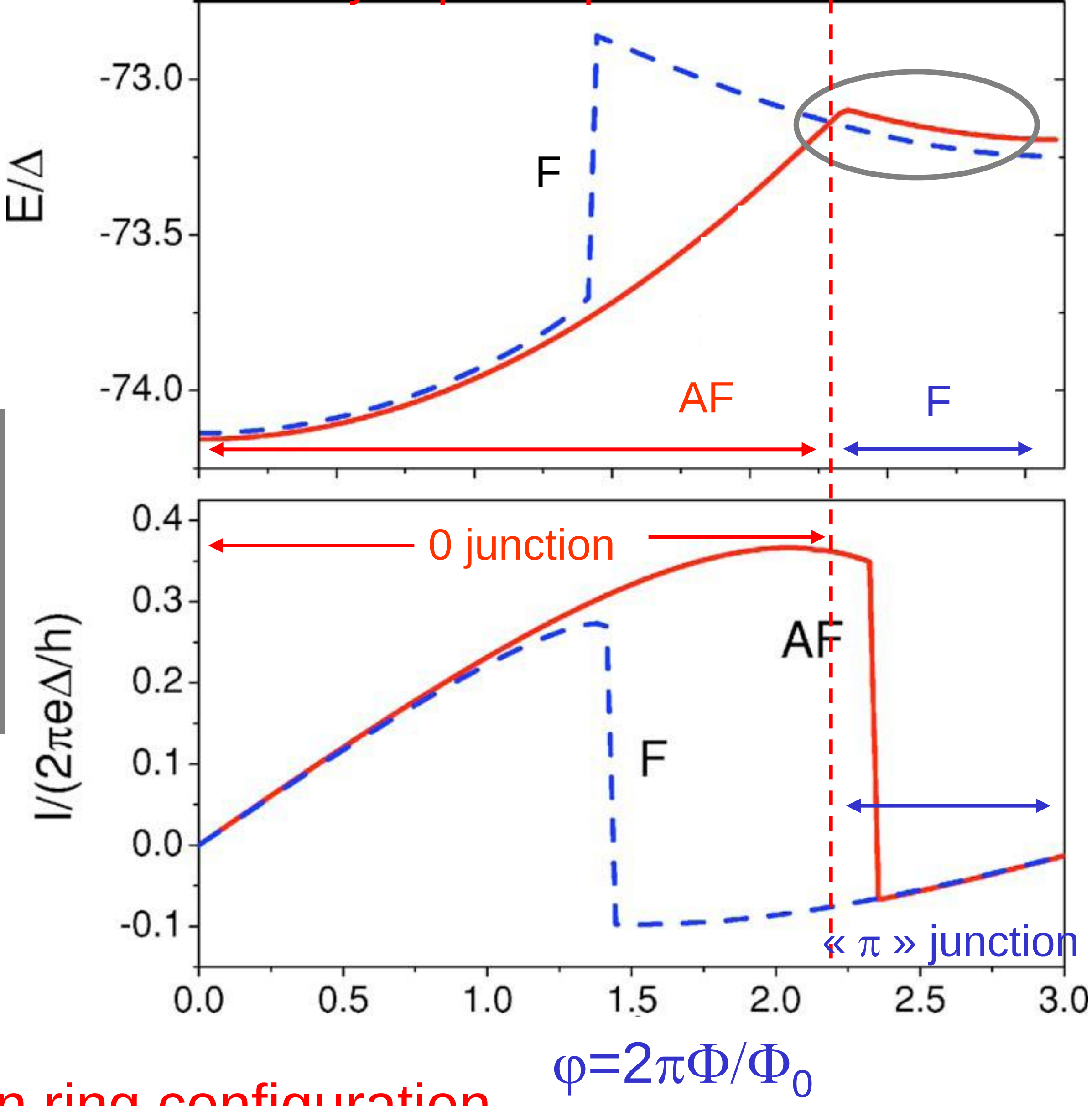
Peaks in dV/ dI at V=2Δ/ne (Δ=0.9 meV): Multiple Andreev reflexion ?

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

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!