Superconductivity in carbon nanotubes

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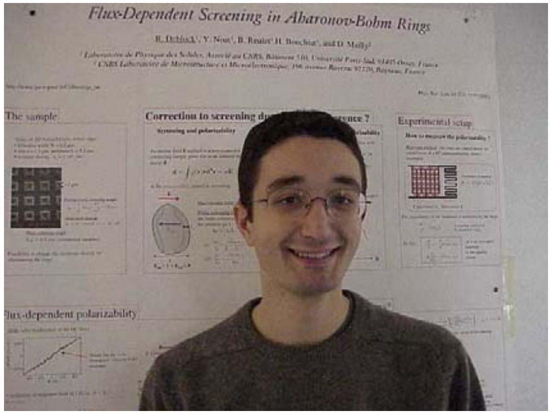





Also: C. Journet, L. Vaccarini, P.Bernier, M. Burghard

Superconductivity in carbon nanotubes

Why carbon nanotubes?

Model systems for investigating correlations in 1D conductors

Transport through what kind of contacts?

- **Good** contacts and at low temperature

- Individual nanotubes on **Superconducting** contacts:

⇒ **Proximity induced superconductivity** with very high values of supercurrent!

- Ropes of individual nanotubes on **non-superconducting** (normal) contacts:

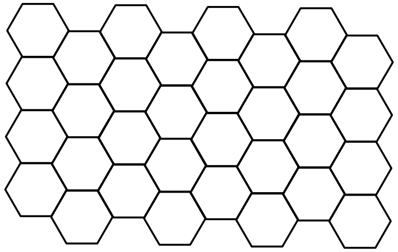
⇒ **Intrinsic superconductivity** in long samples (L> 1μm).

What kind of transport?

Use shot noise to probe transport through ropes.

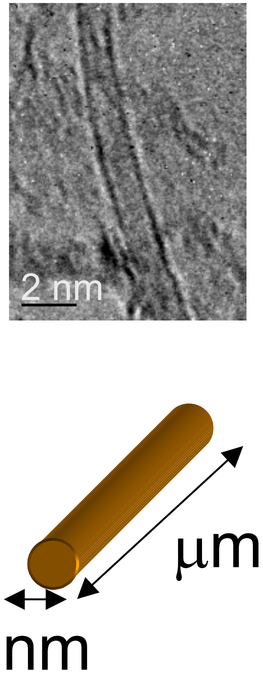
What are carbon nanotubes?

Graphene sheet

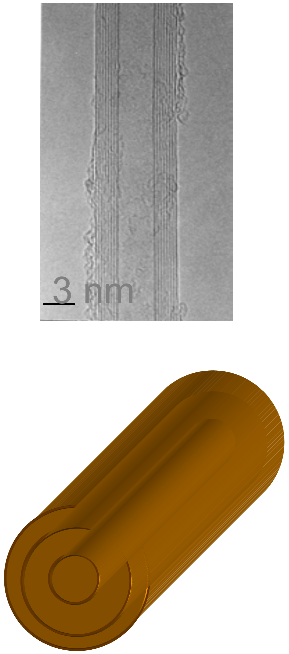


Roled up

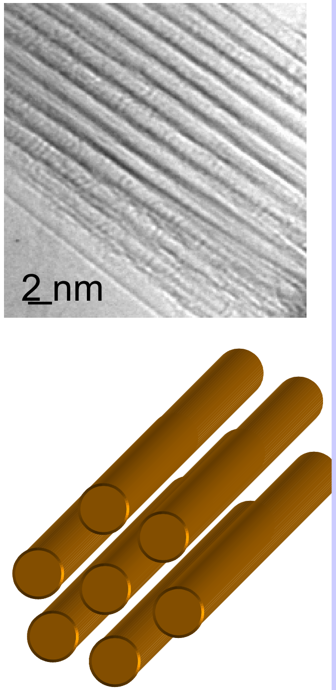
Carbon nanotube



Individual



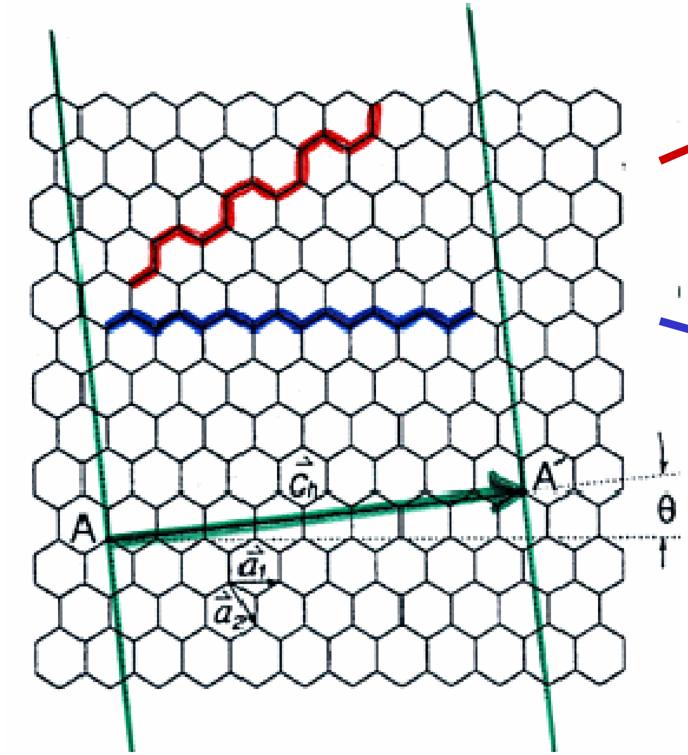
Multiwall



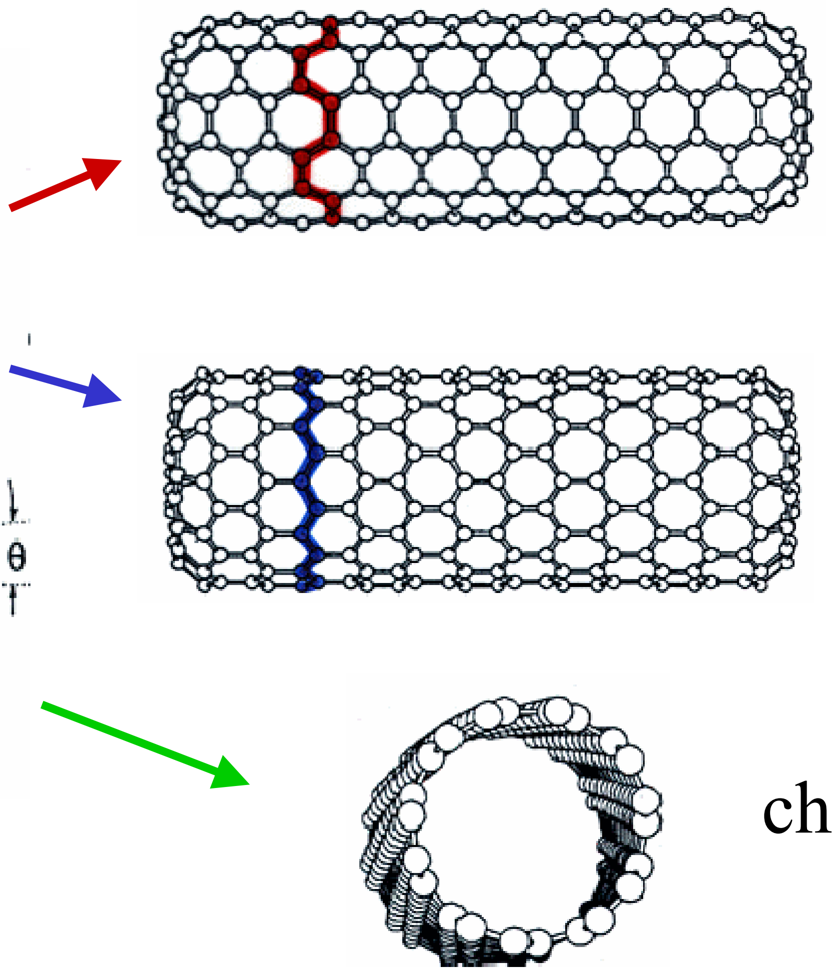
ropes

Almost macroscopic molecules

Several ways to fold a graphene sheet into a nanotube



Helicity vector (n,p) defines the geometry



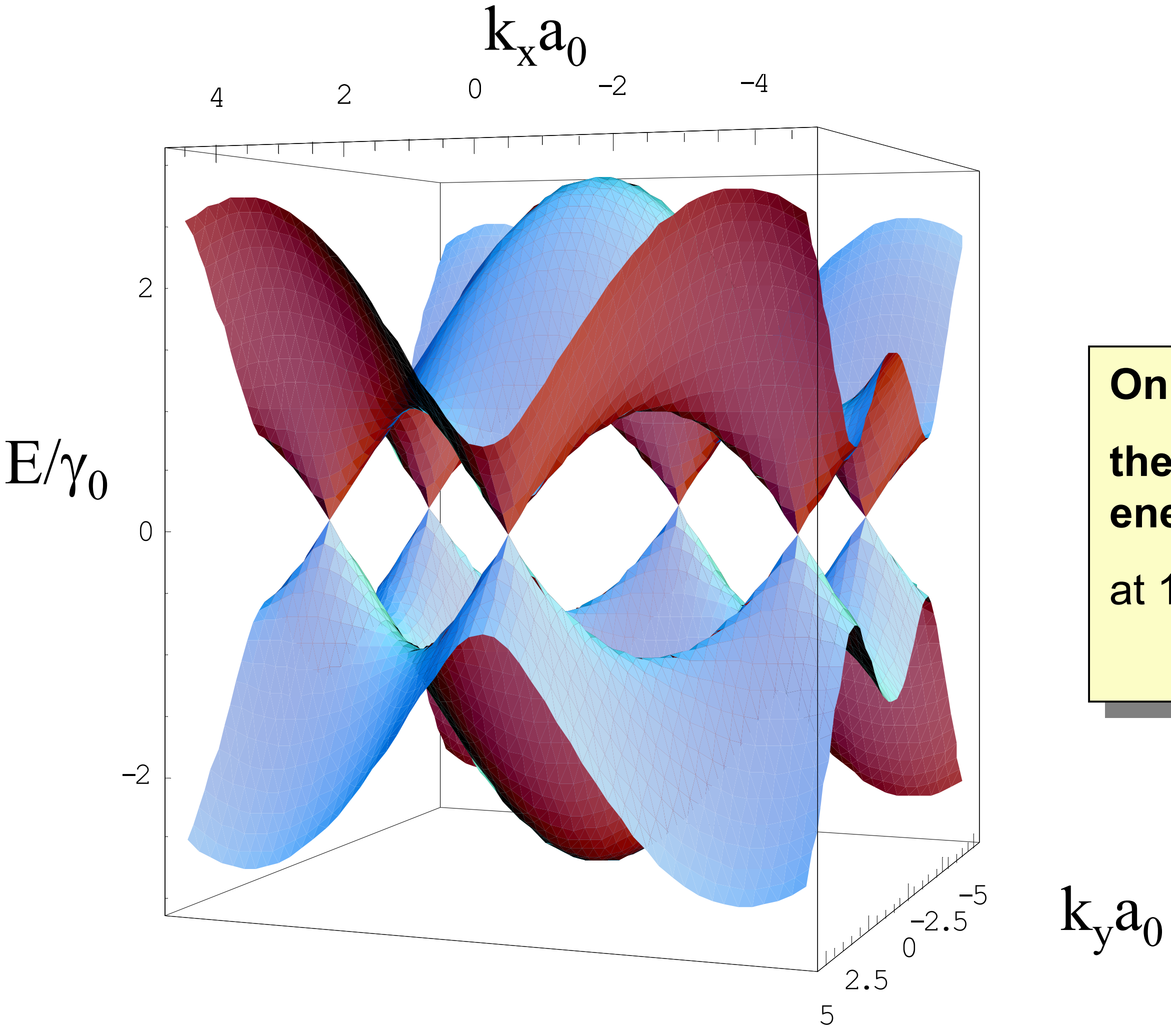
armchair

zigzag

chiral

How do nanotubes conduct?

Start with band structure of graphene...



Only 6 points at

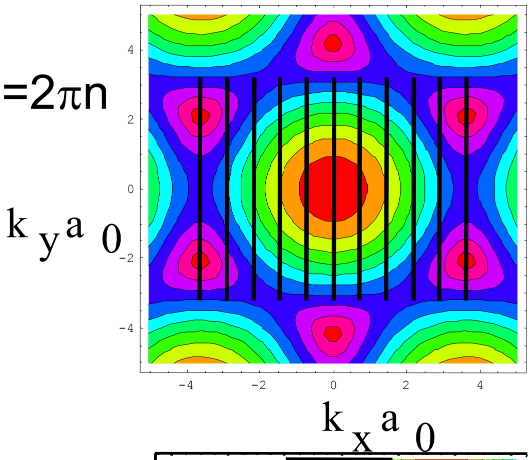
the Fermi energy

at 1/2 filling

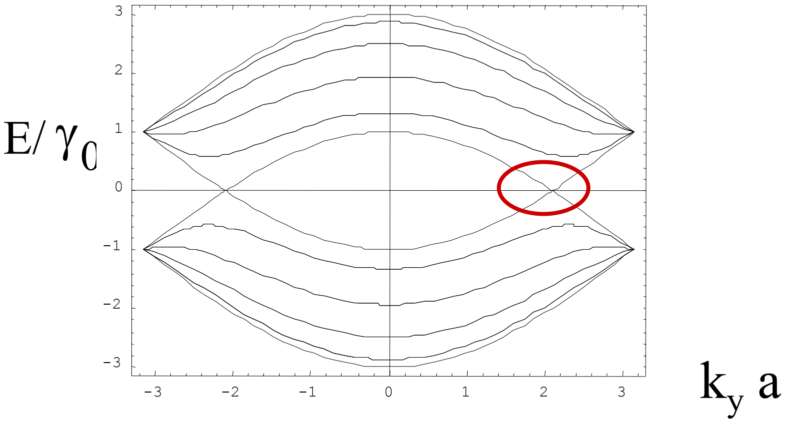
… then include boundary condition given by folding

“Armchair”

k_x*circomference=$2\pi n$

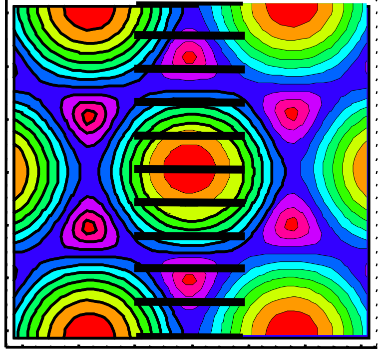


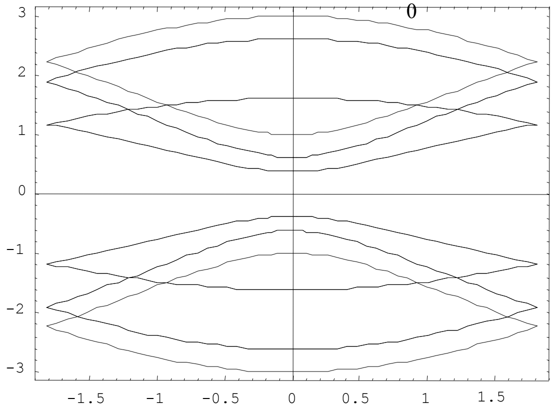
Metallic



Zig-zag

k_y*circomference=$2\pi n$

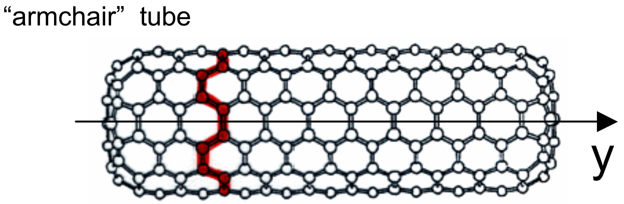


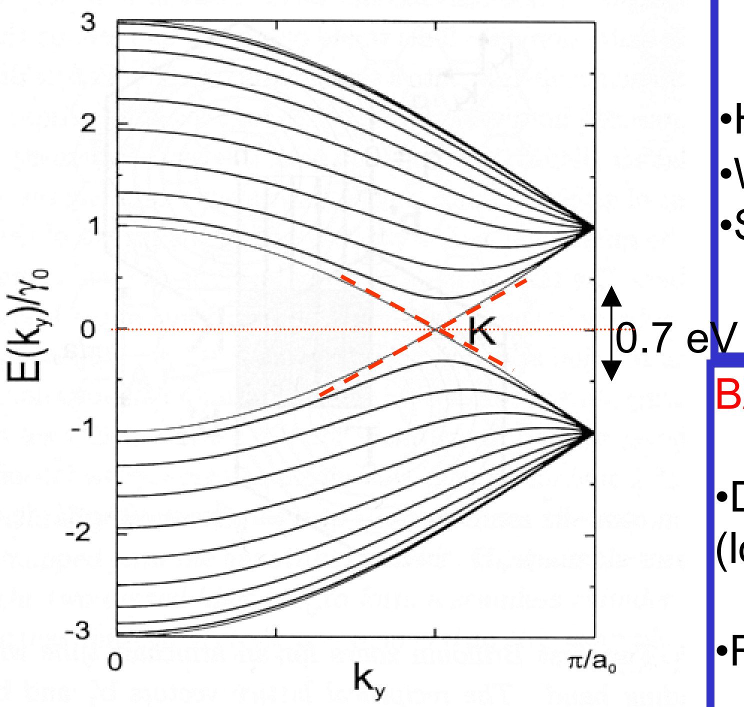


Semiconducting

⇒ 1/3 conducting tubes, 2/3 metallic tubes

Are metallic nanotubes really ideal 1D *conductors*?





GOOD:

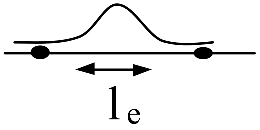
- No Peirls distortion
- 2 states at E_F at half filling:

2 conduction modes (channels) $\Rightarrow$ 1D !

- High Fermi velocity $v_F \sim 10^6$ m/s
- Weak effect of impurities
- Smallest resistance (on normal contacts)

$R_{min} = h/4e^2 = 6.5\ k\Omega$ / tube

BAD:



- Disorder becomes important at 1D (localization length= mean free path)
- Repulsive interactions: Luttinger liquid state

$R(T) \propto T^{-\alpha}$ Insulating at T=0

Are nanotubes insulating at low temperature?

It depends…. upon the contacts!

Bad (tunnel) contacts: $R_{contact} >> R_Q$

Tubes deposited on small electrodes

Non-invasive probe but insulating at low temperature

Good (ohmic) contacts: $R_{contact} << R_Q$

Tubes soldered into large electrodes

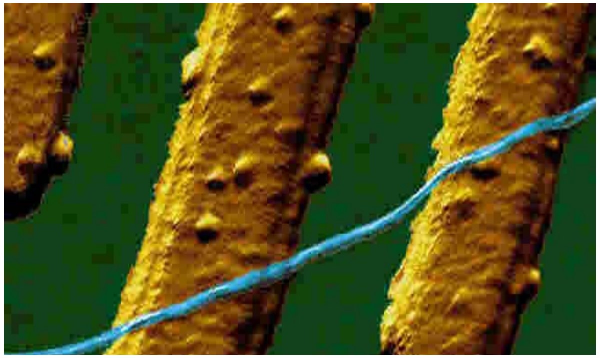
Very invasive, but conducting at low temperature

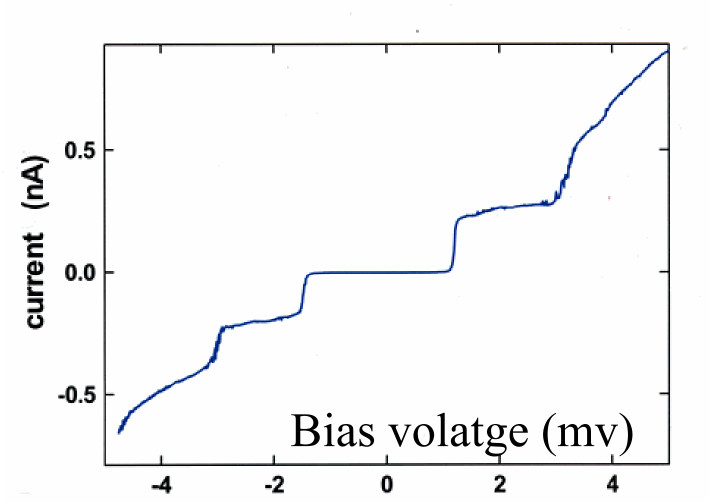
Different kinds of contacts probe different properties

Nanotubes on Tunnel contacts :
Charging energy $E_C = e^2/C$

$T \ll E_C$ Coulomb Blockade

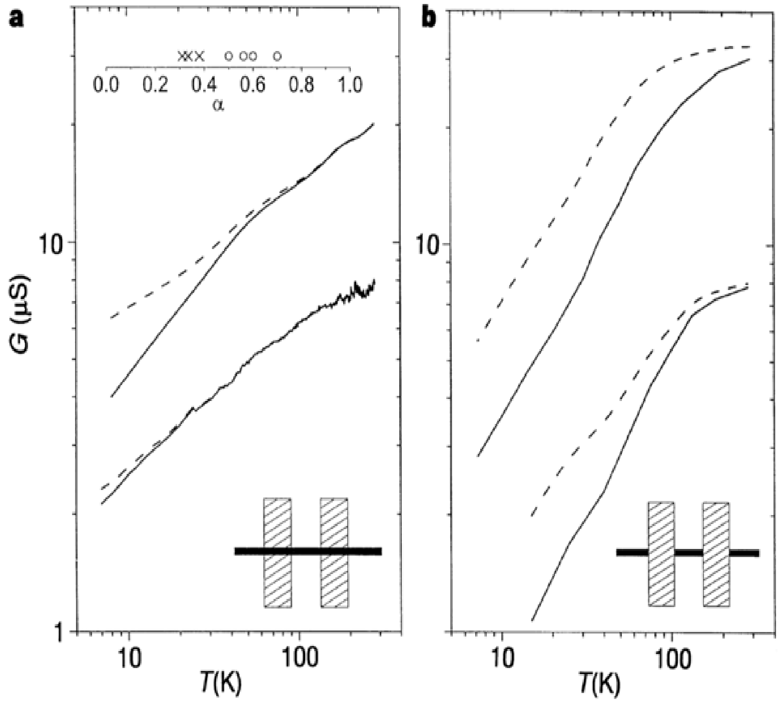
Luttinger Liquid behaviour





Tans et al., Nature **386** (1997)

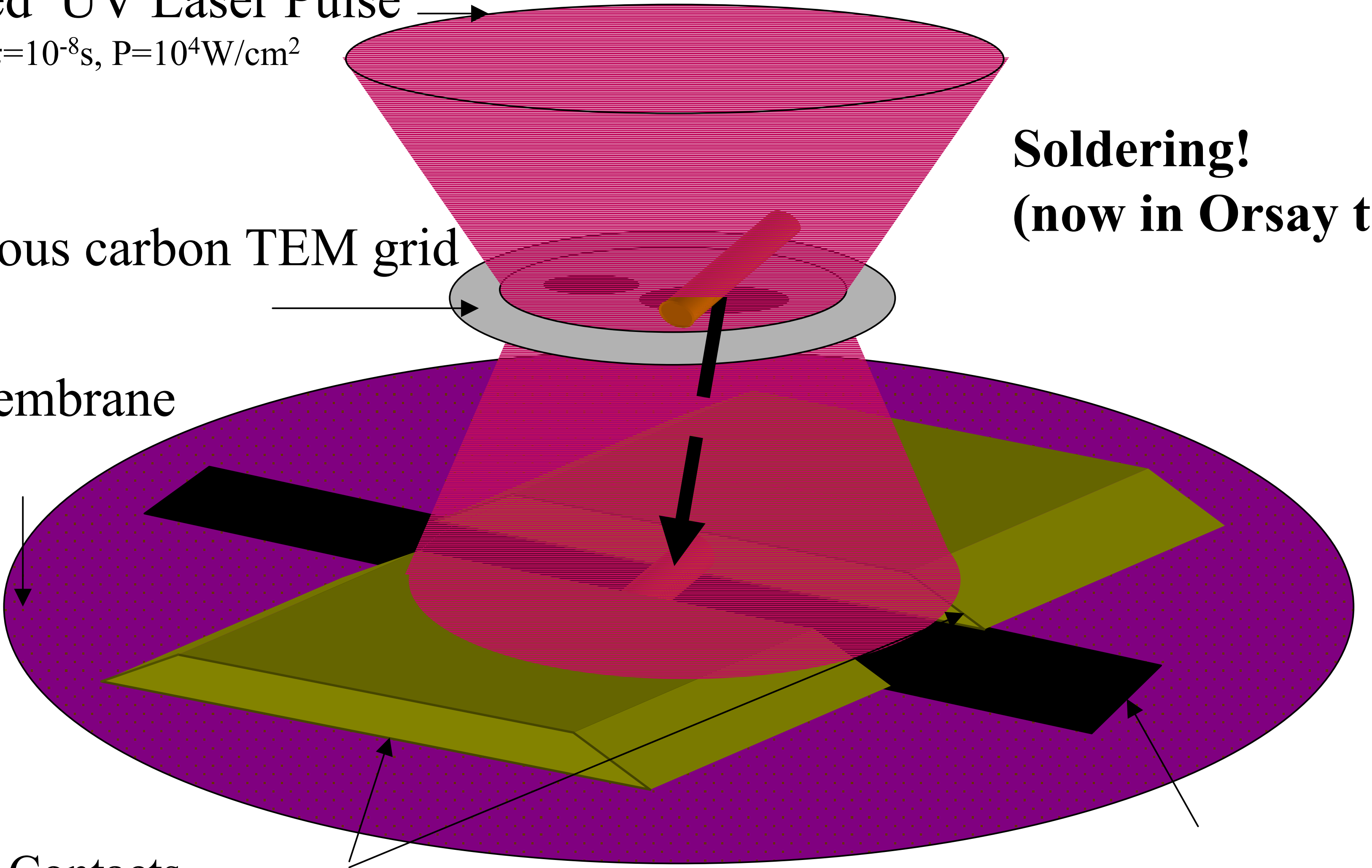
$$G(T) \propto T^{\alpha} \text{ for } eV \ll k_B T$$



Bockrath et al., Nature **397** (1999)

Are nanotubes insulating at low temperature?

Making Ohmic Contacts **(Alik Kasumov)**



Focussed UV Laser Pulse

$\Lambda=0.3\mu m$, $\tau=10^{-8}s$, $P=10^{4}W/cm^{2}$

Soldering!

(now in Orsay too)

amorphous carbon TEM grid

Si_3N_4 membrane

Metallic Contacts

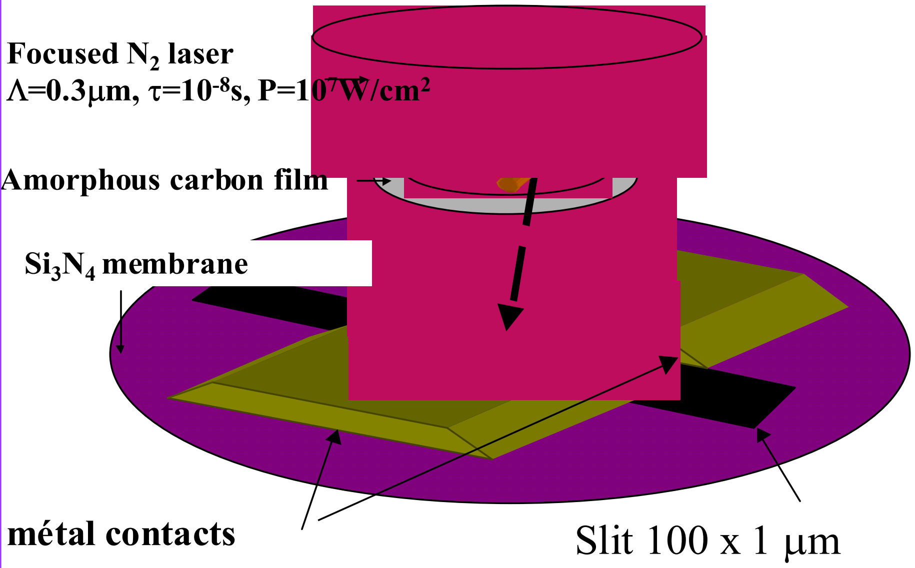
Au-Re, Sn, Au-Ta, Au-Pt…

Slit 100*1 μm

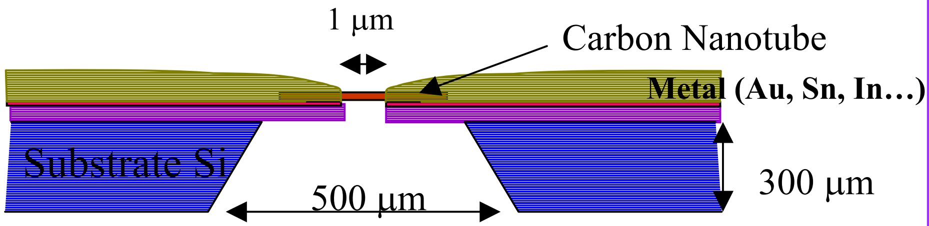
Resistance of an individual SWNT ~10,20 kΩ

Transport and microscopy on the same sample

Principle of laser nanosoldering

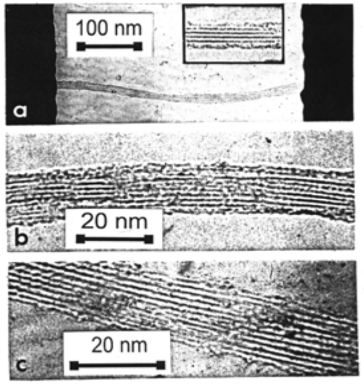


Suspended nanotubes soldered to metal contacts

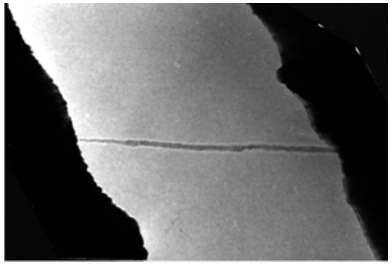


Caracterization of deposited nanotubes

- TEM microscopy: number of tubes, composition



rope

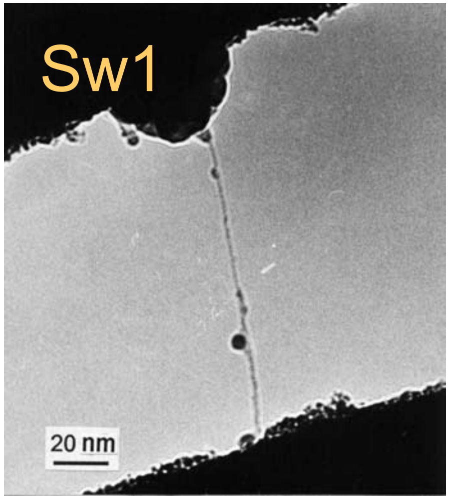


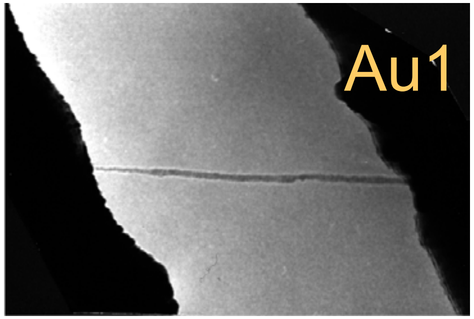
Single walled nanotube

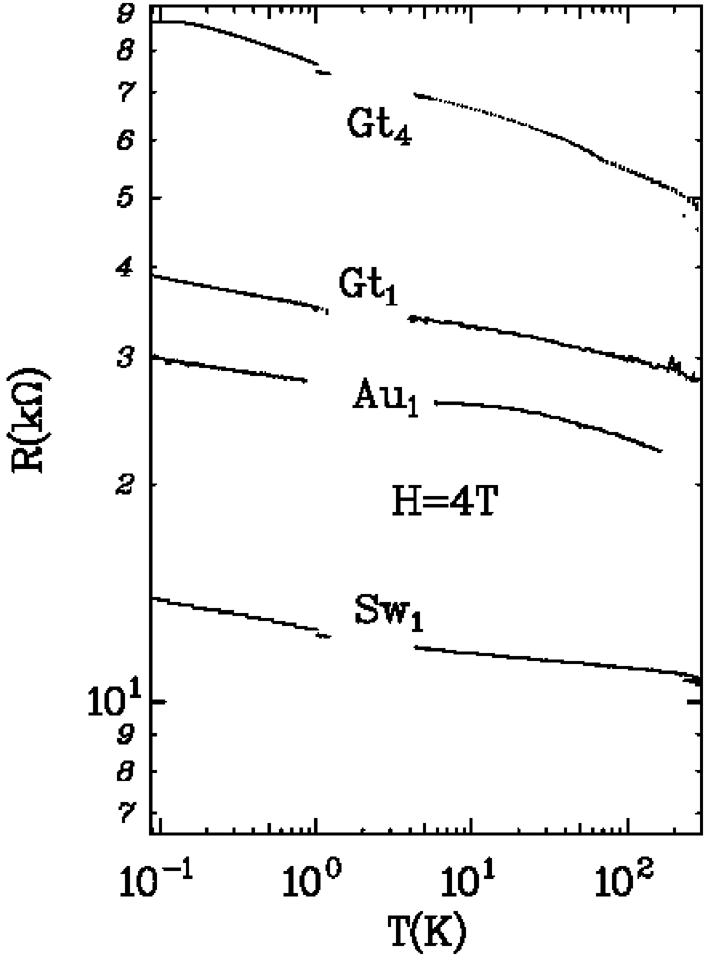
Finally...

- Measure resistance at room temperature
- Cool selected tubes to low temperature

Proof of good contact:
Individual single wall tubes in the normal state:



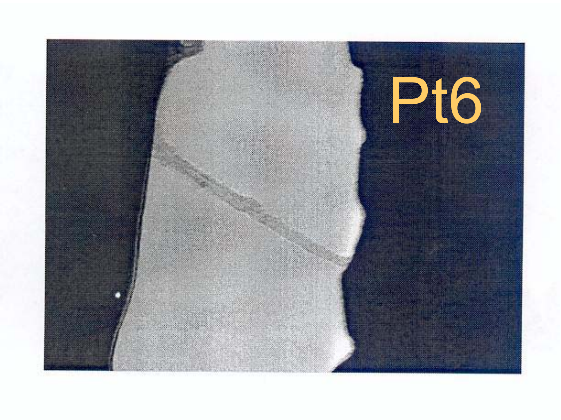


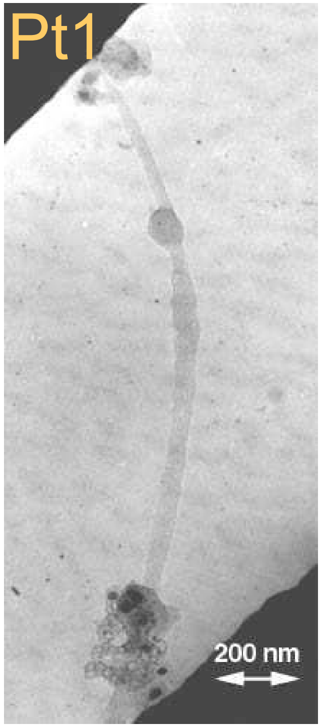


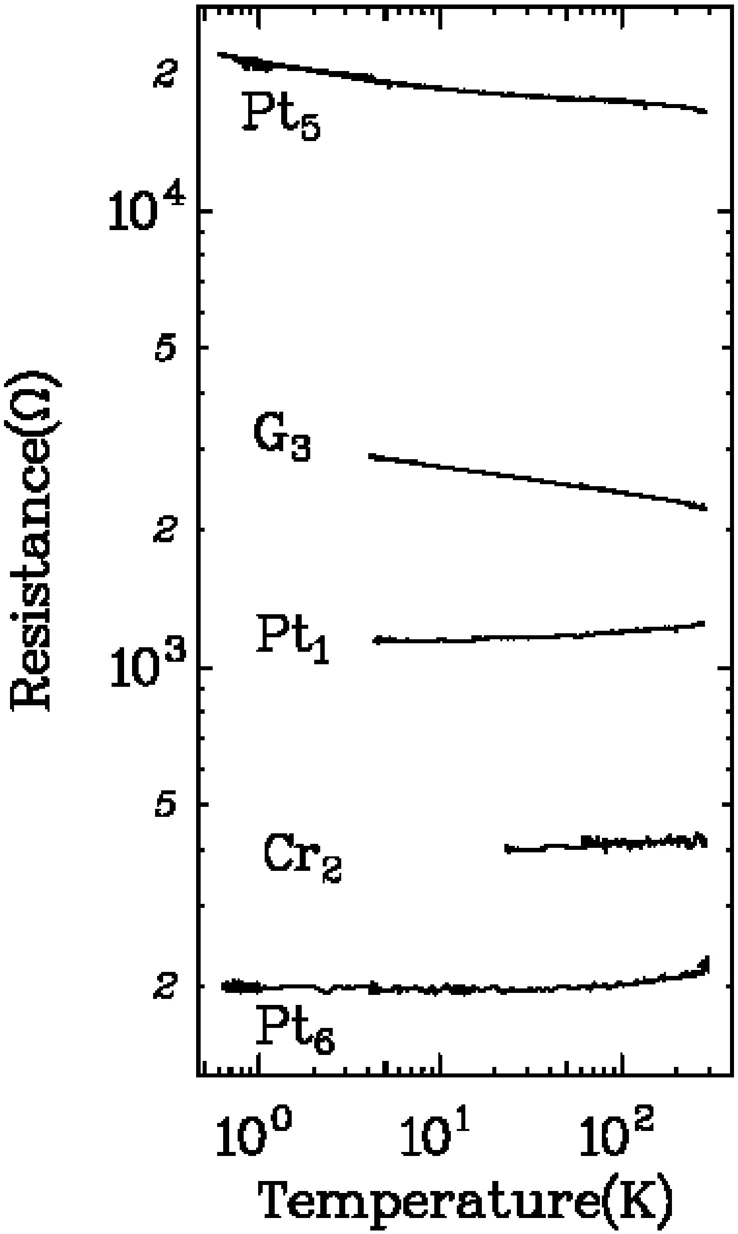
$R(T) \sim T^{-0.03 \text{ to } -0.1}$ ($R(T) \sim -\ln T$): very weak temperature dependence

No sign of Coulomb blockade!

Temperature dependence of resistance of ropes



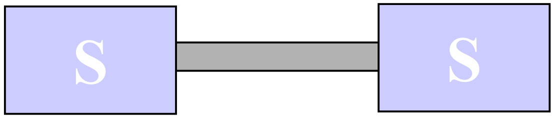




Phonon contribution for low resistive ropes

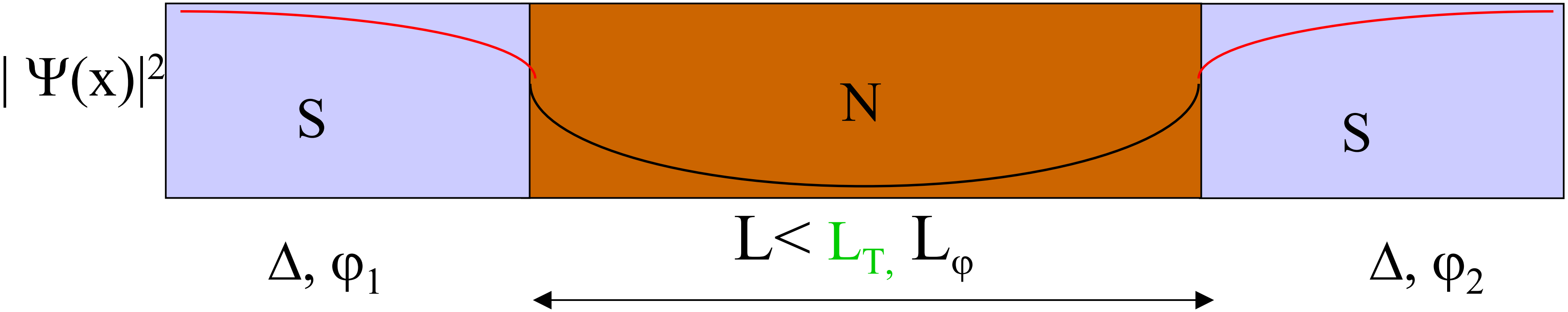
What kind of contacts?

Single walled nanotubes on Superconducting contacts



The proximity effect in a nutshell

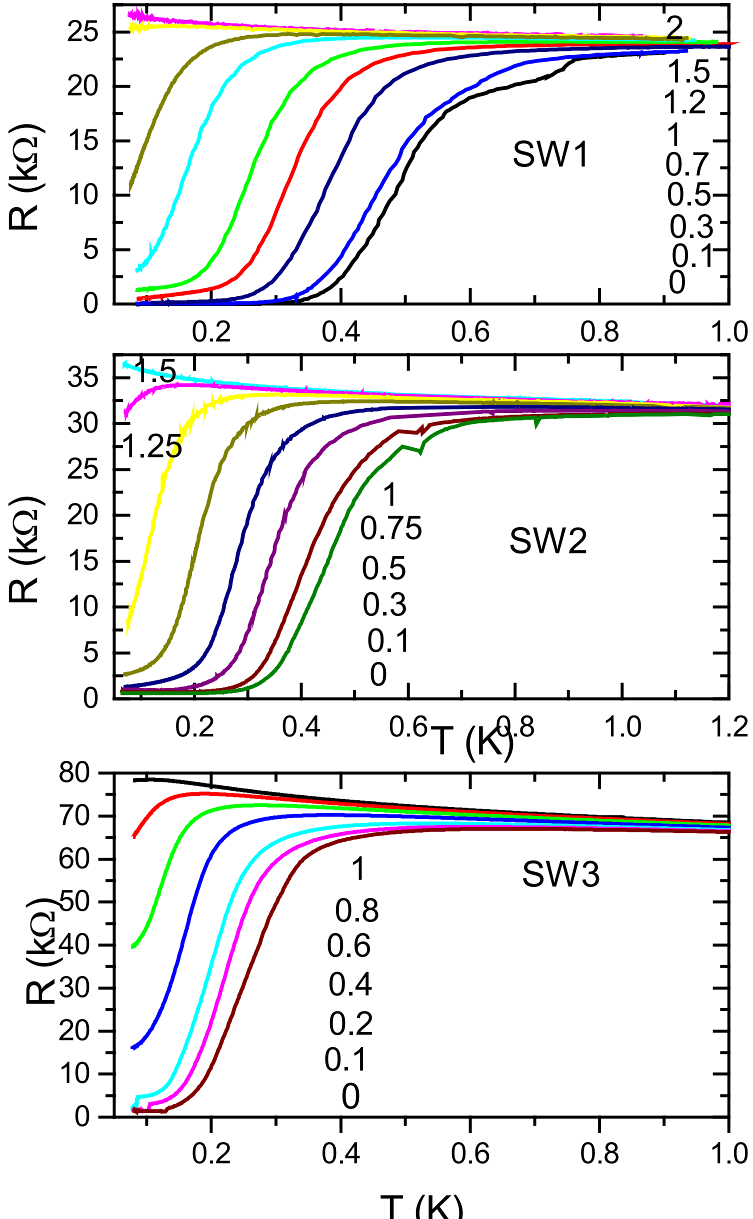
The superconducting order parameter penetrates in the normal metal.
Enough to have a supercurrent?
The proximity effect is a test of the coherence in the normal metal.

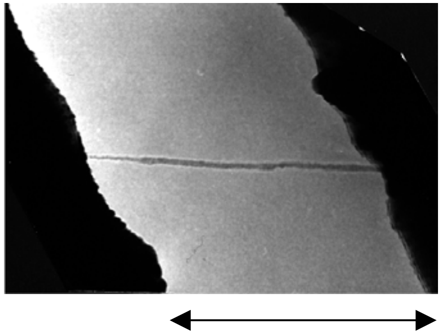


Supercurrent: $I = Ic \sin(\varphi_{1} - \varphi_{2})$
Maximum supercurrent: $R_N Ic = \min(\Delta, h/\tau(L))$

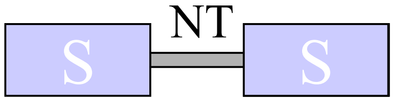
Proximity induced Superconductivity in individual single wall nanotubes

Proximity Induced Superconductivity in Individual SWNT on Au/Ta



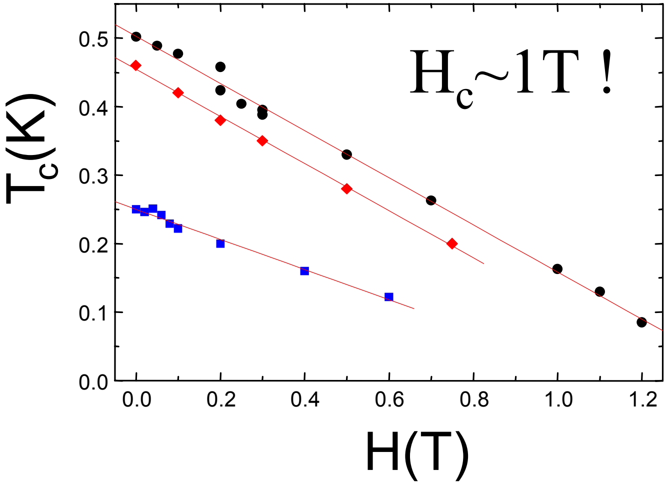


300 nm



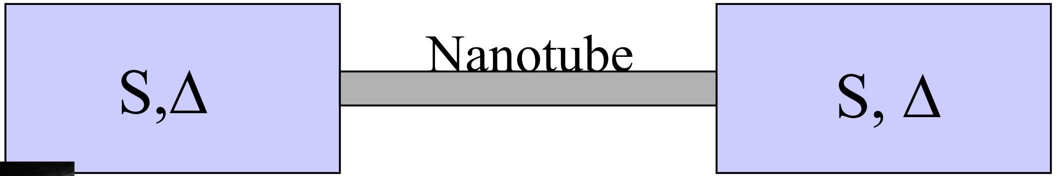
Superconducting Contacts (Au-Ta)

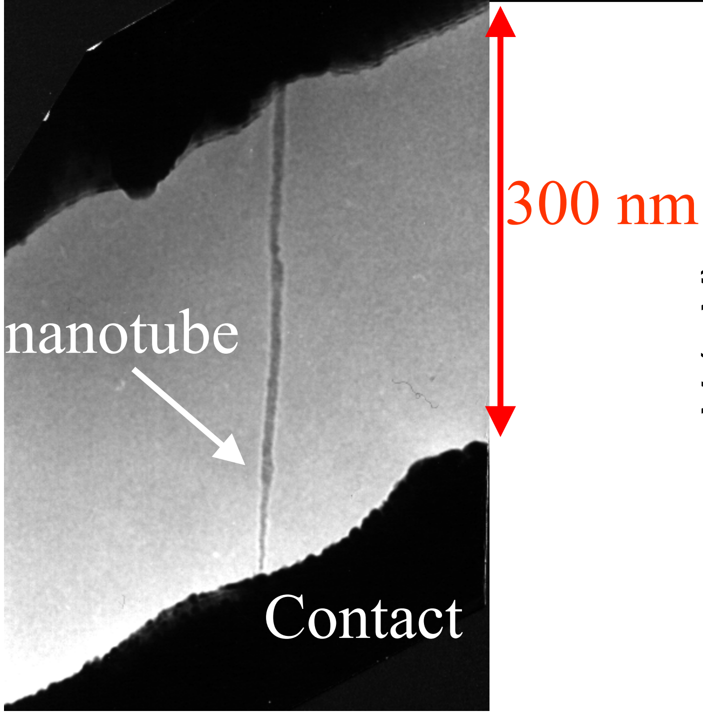
T_c=0.3 K, H_c=0.1 T

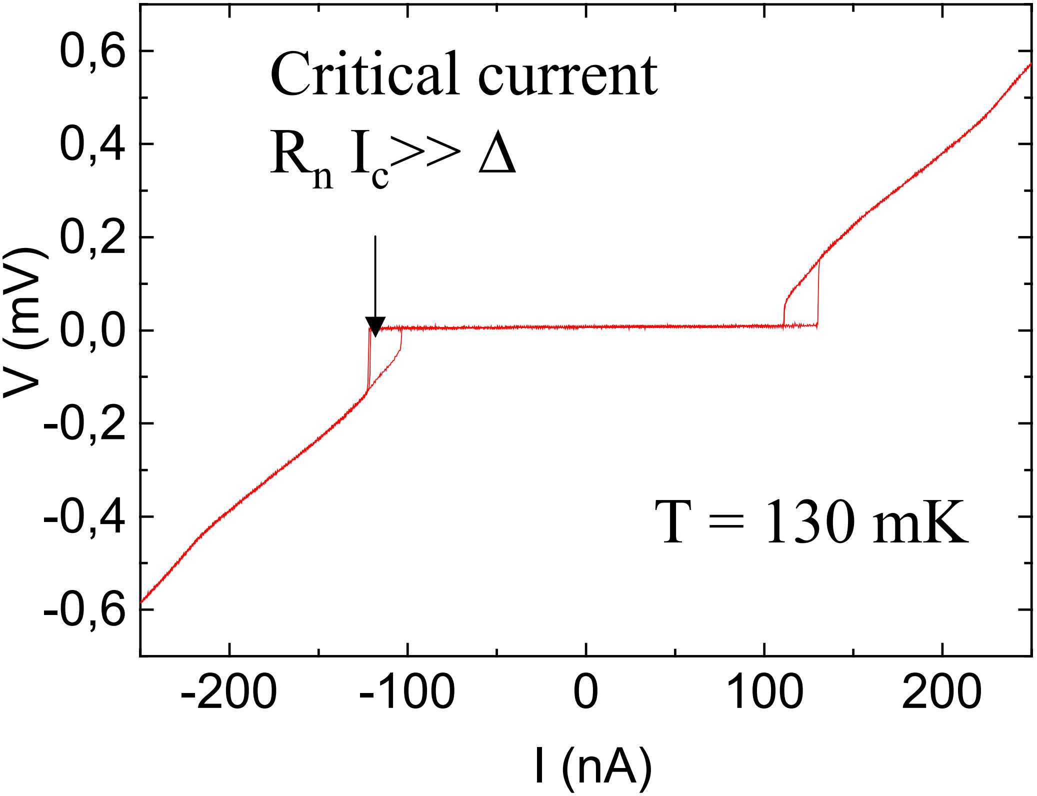


H_c~1T !

Supercurrent through individual carbon nanotubes on superconducting contacts






Critical current

$R_n I_c >> \Delta$

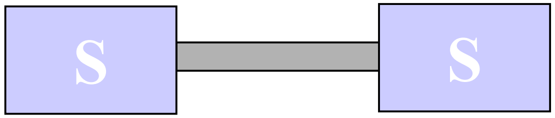
T = 130 mK

Much too high value of critical current !

Superconducting fluctuations in a nanotube?

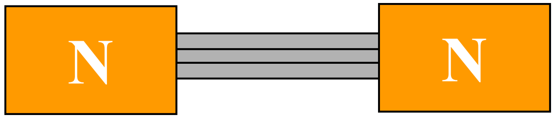
What kind of contacts?

Single walled nanotubes on Superconducting contacts



Anomalously large supercurrents: intrinsic superconductivity?

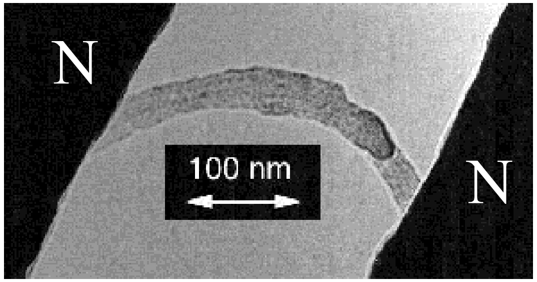
Ropes of SWNT on NON-SUPERCONDUCTING contacts

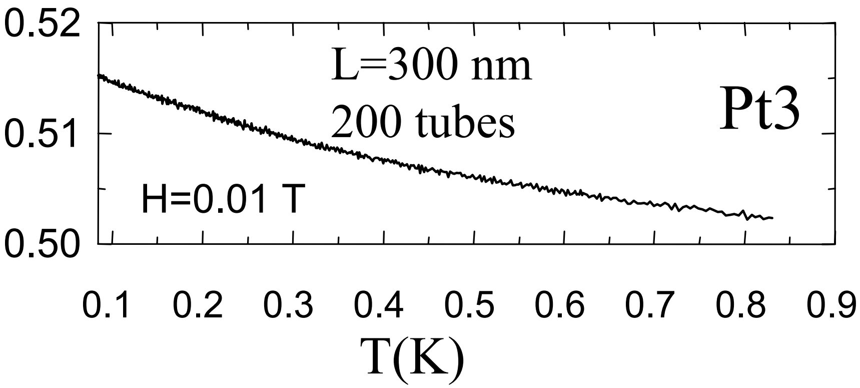


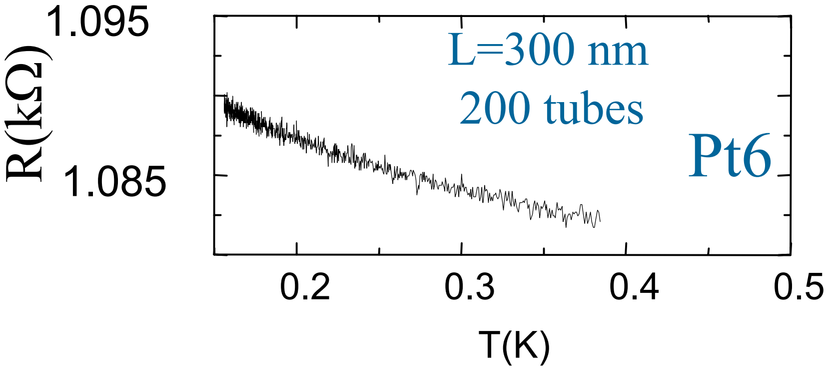
Intrinsic superconductivity !

In long, suspended ropes,
not too disordered,
with enough tubes.

Low temperature resistance of short ropes





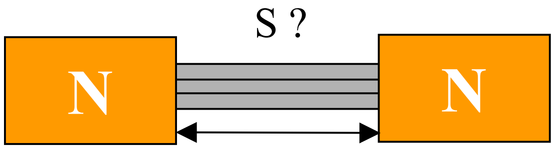


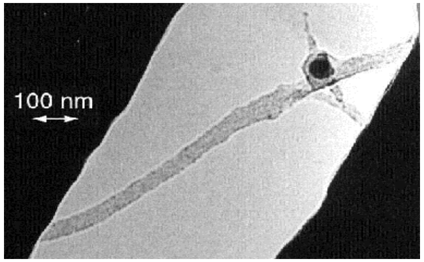
Good ohmic contacts

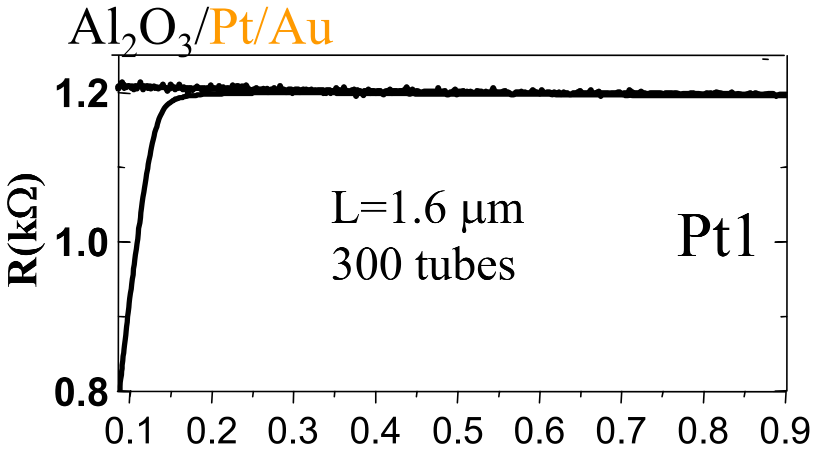
but

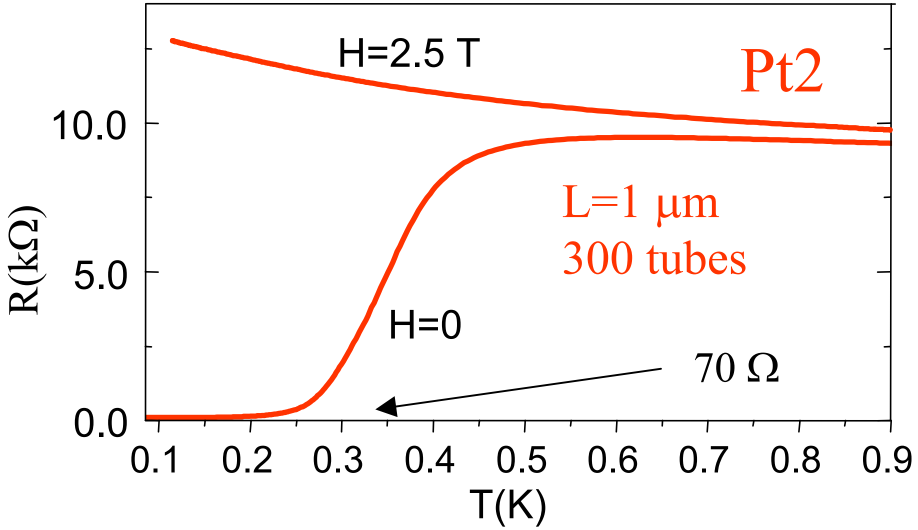
nothing exciting happens...

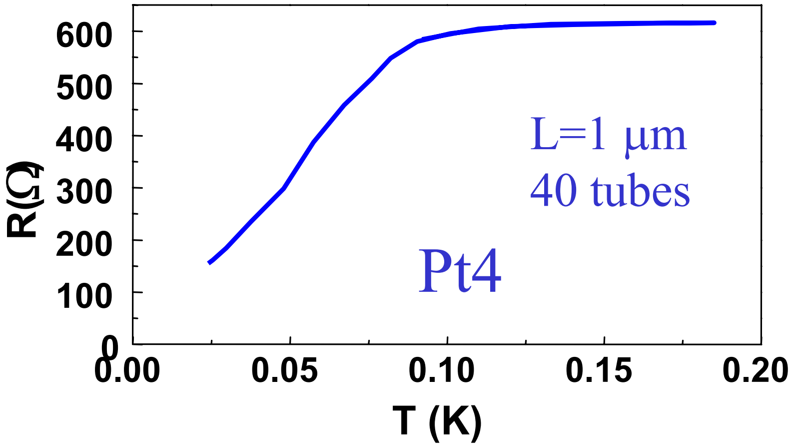
Superconducting transitions in long ropes

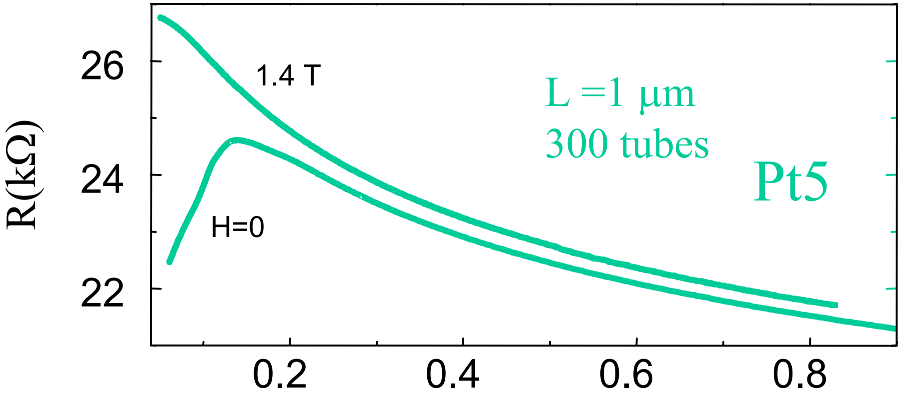












Transition observed only in the longest ropes

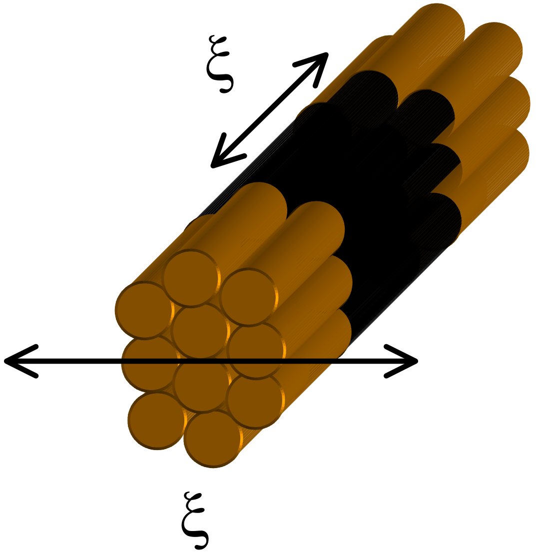
Why transition only in longest ropes?
Coherence length of the Cooper pairs

$$\xi = \sqrt{\frac{\hbar D}{\Delta}}$$

Normal resistance, $D \sim v_f l_e$

BCS gap = $1.76\, k_B T_c^{3D}$

Rough estimate of ξ using $\Delta \sim 100\ \mu\text{eV}$ $(T_c^{3D} = 450\text{mK})$



Pt2 : $\xi = 300nm$

Diameter = 20 nm

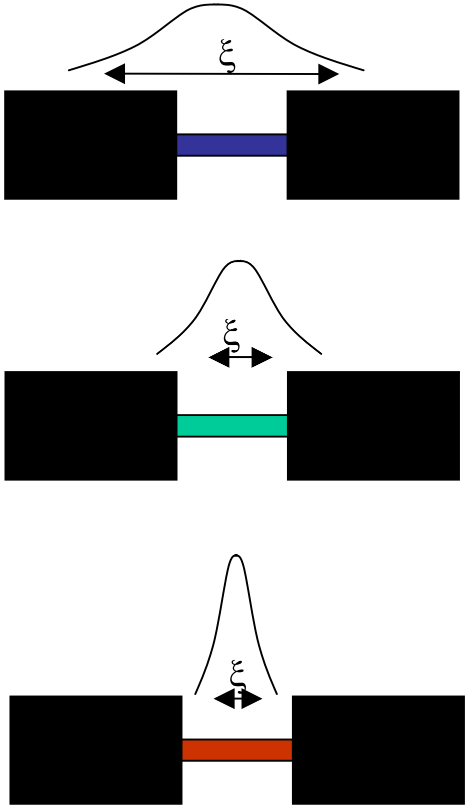
We find:

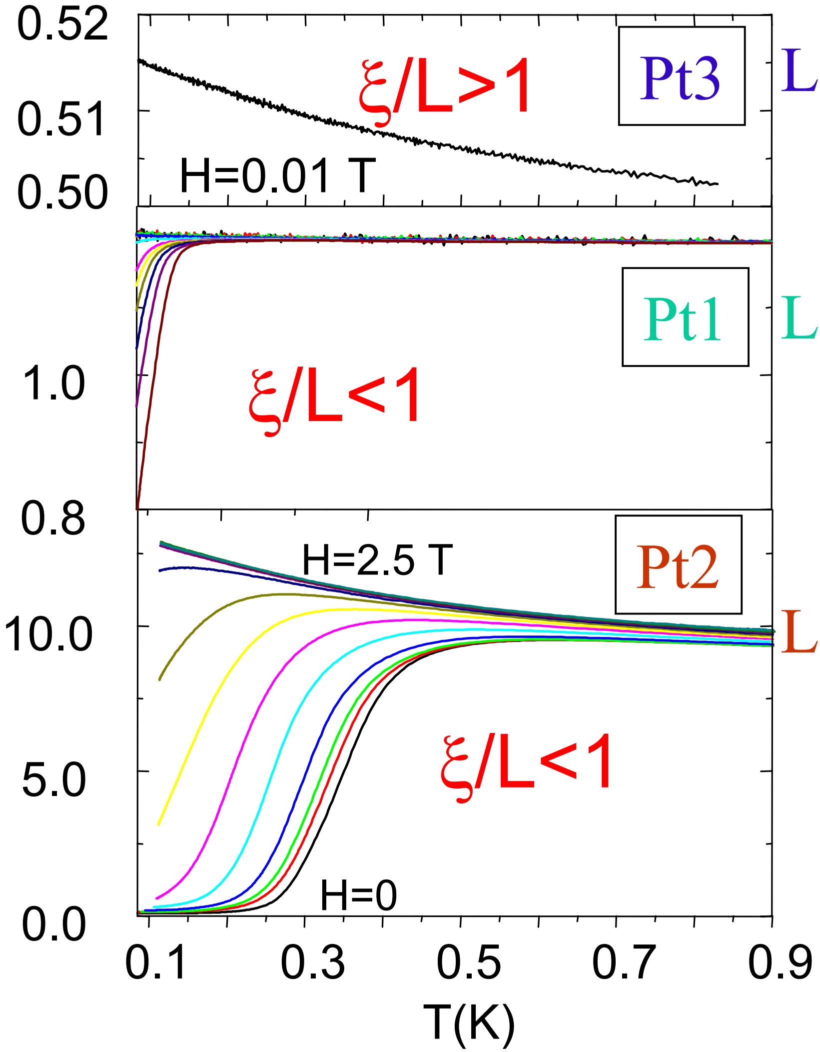
ξ >> diameter ⇒ 1D superconductivity

ξ << L ⇒ Cooper pairs not killed by normal contacts

Why not a transition for every sample?

Superconductivity is destroyed by the normal contacts !





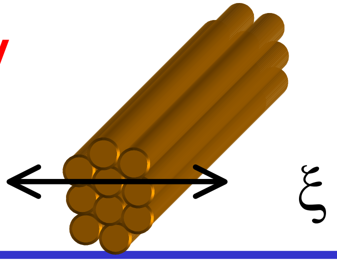
L_1=300nm, $\xi_1/L_1=2$

L_2=1.6 μm, $\xi_2/L_2=0.4$

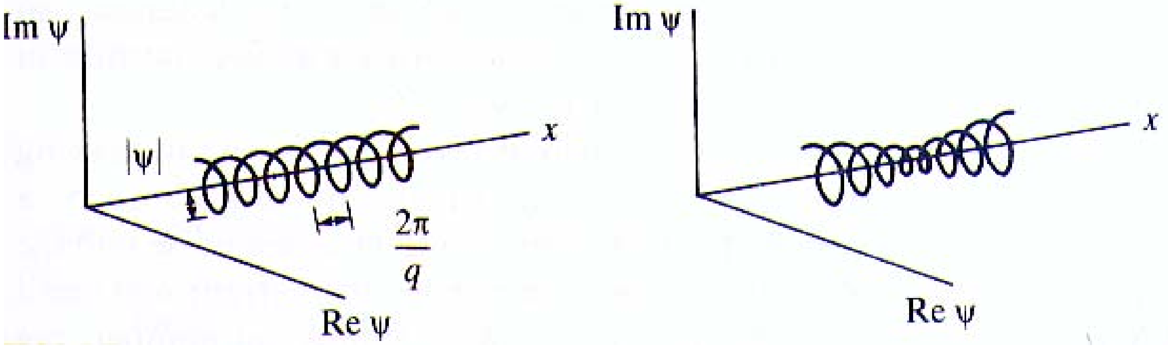
L_3=1μm, $\xi_3/L_3=0.3$

ξ /L is the relevant parameter

1D superconductivity



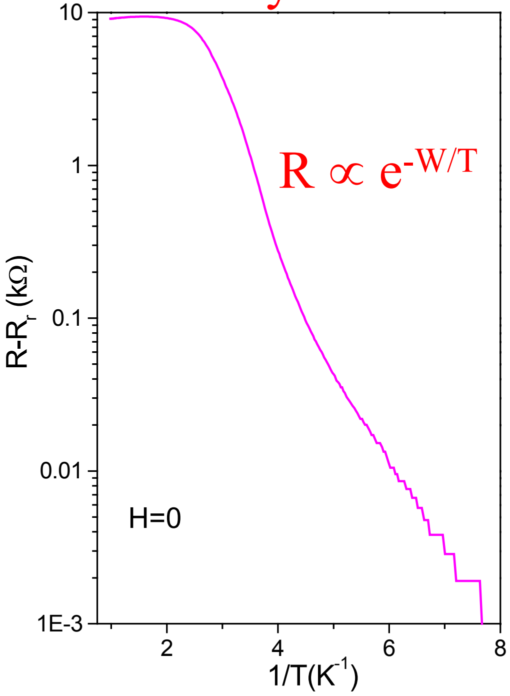
If order parameter is larger than wire diameter:
existence of phase slips



Typical length scale L>> ξ

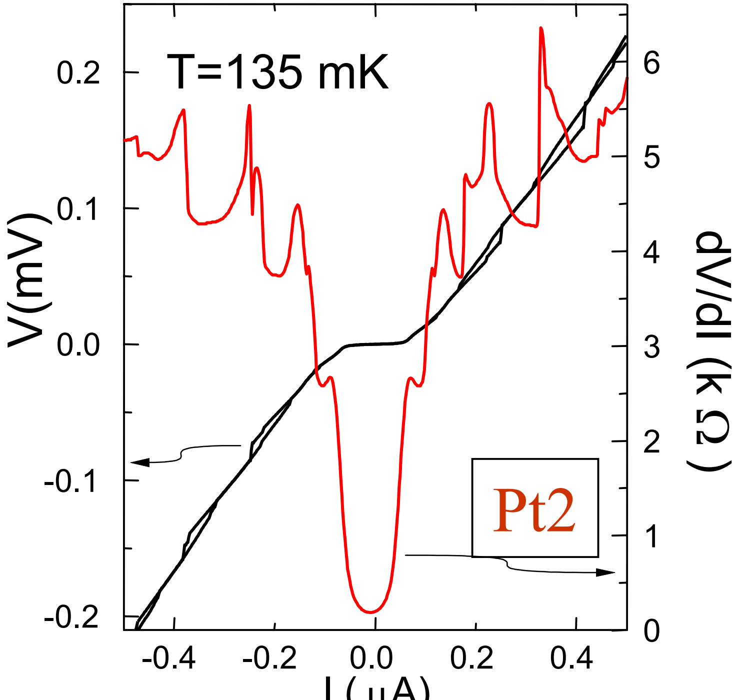
$$V = \frac{\hbar}{2e}\frac{d\phi}{dt}$$

Thermally activated:

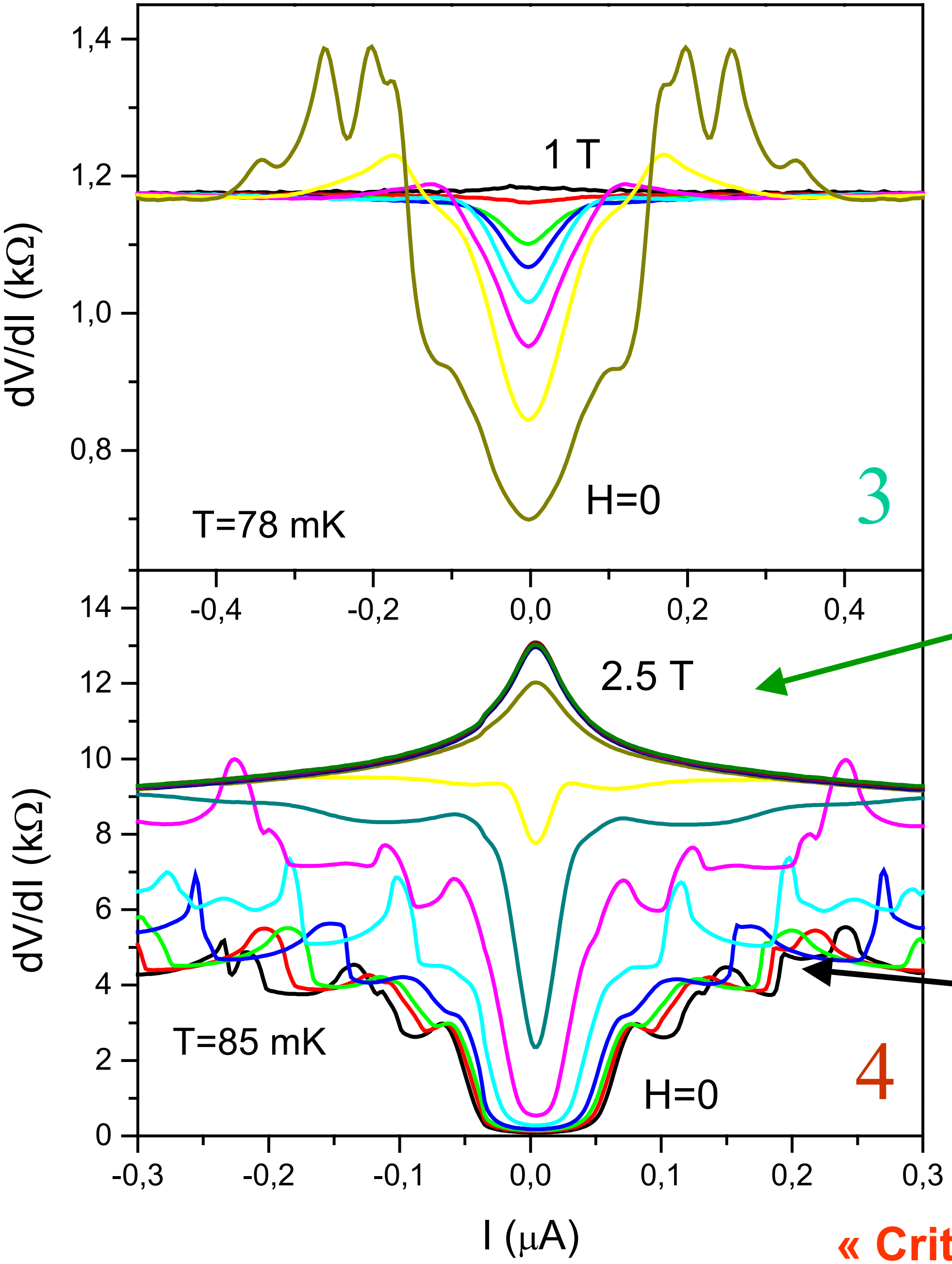


W~$\Delta^2 n(E_F) S.\xi$

Jumps in V(I)



Differential resistance: evolution with magnetic field



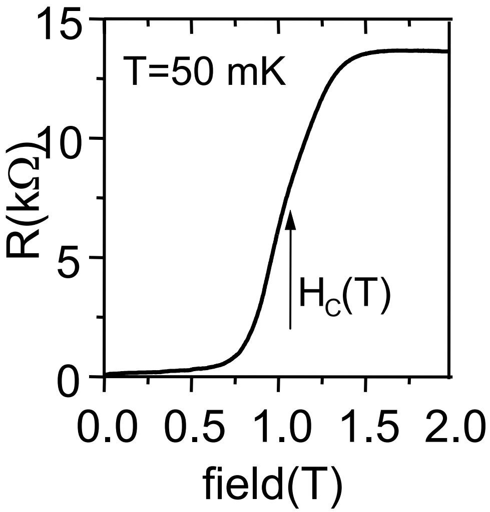
Coulomb anomaly

Many jumps before recovering normal state resistance: phase slips?

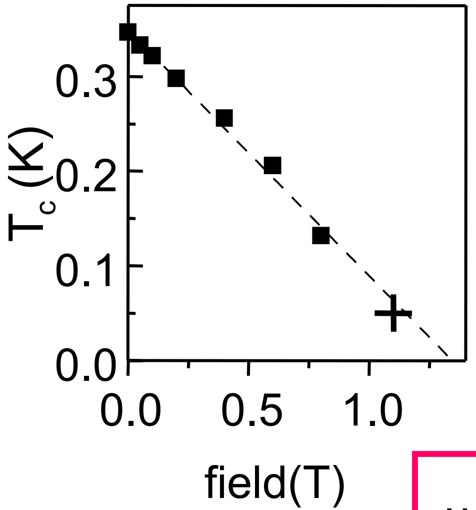
« Critical currents » up to 0.05 μA

How does the magnetic field destroy Superconductivity?

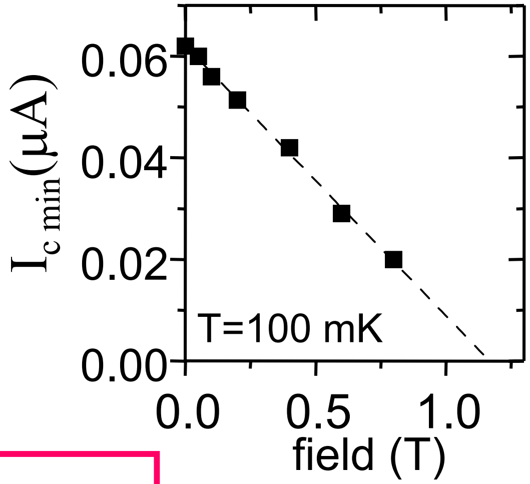
(H perpendicular to rope and contacts)



Critical temperature

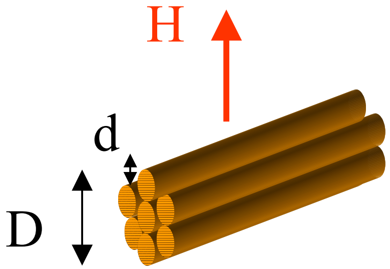


Critical current



$\mu_0 H_c$=1.2 T

Linear dependence of Ic and Tc(H) observed in every sample



Orbital origin

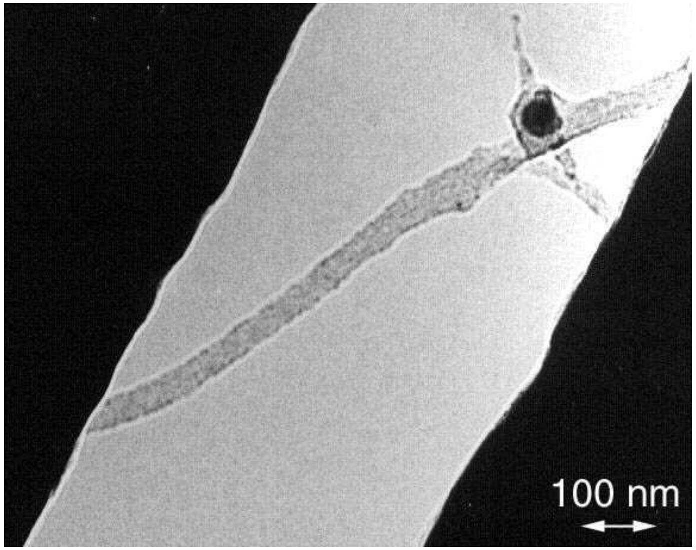
$H_c=\Phi_0/(d\xi) \approx 1$T

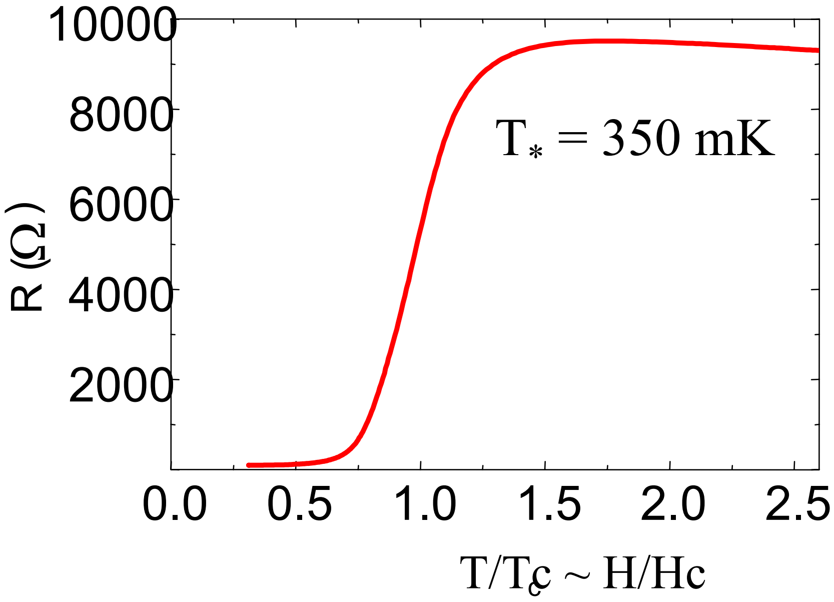
Weak intertube Josephson coupling

⇒ **Confirmed by measurements in different field orientations**

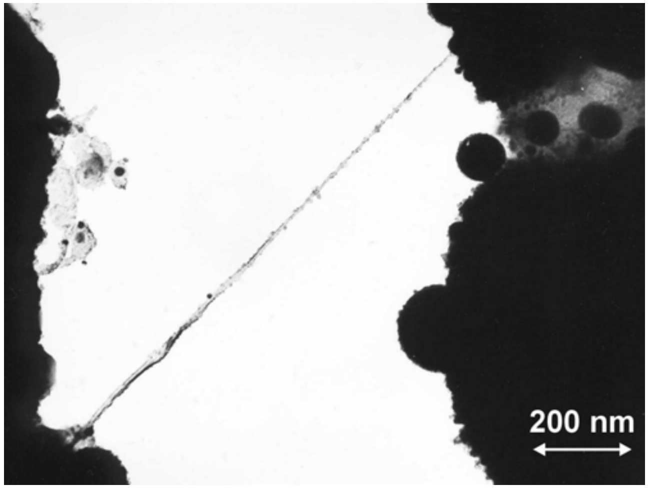
Investigation of thinner ropes…

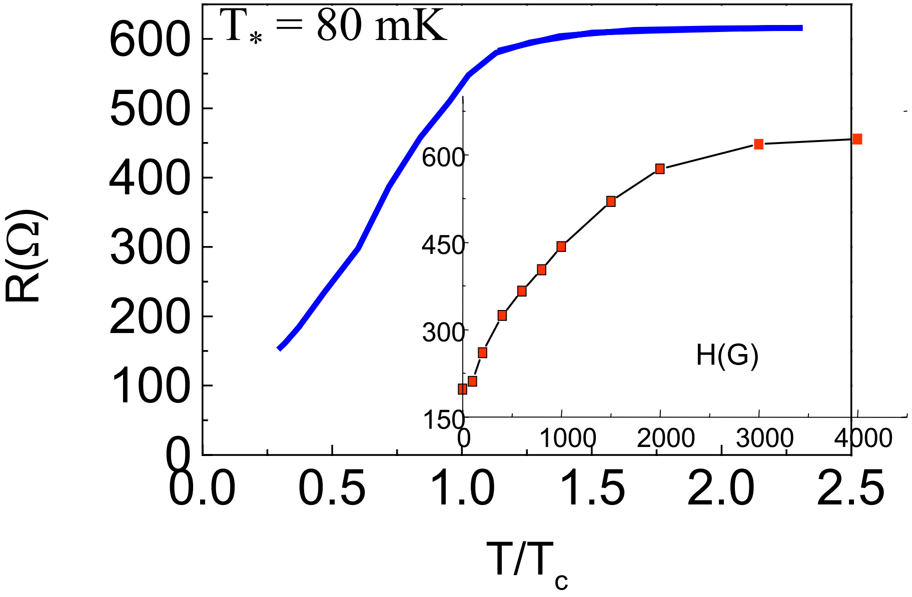
350 tubes





40 tubes

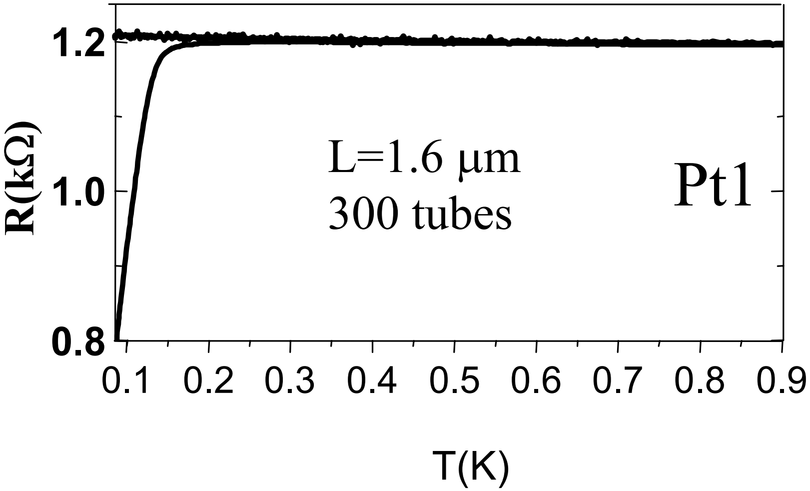




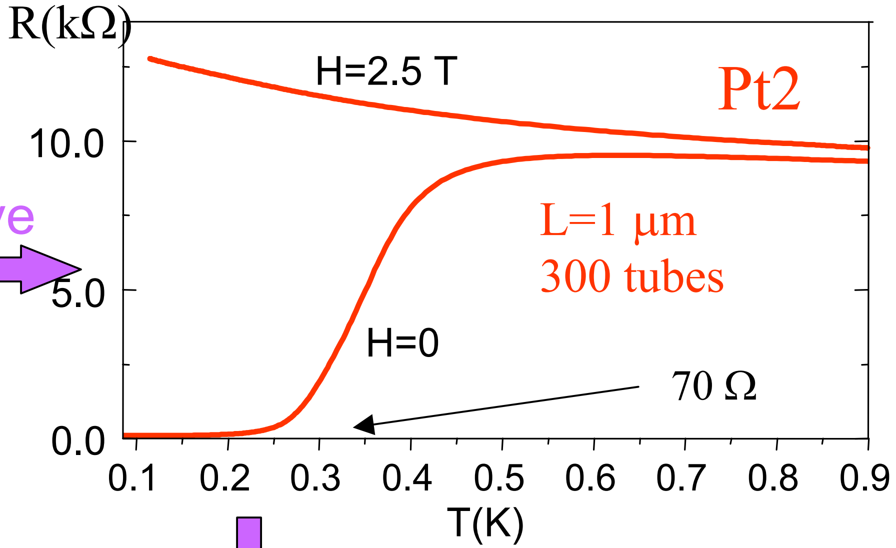
Transition at T, H =0 !

Role of disorder

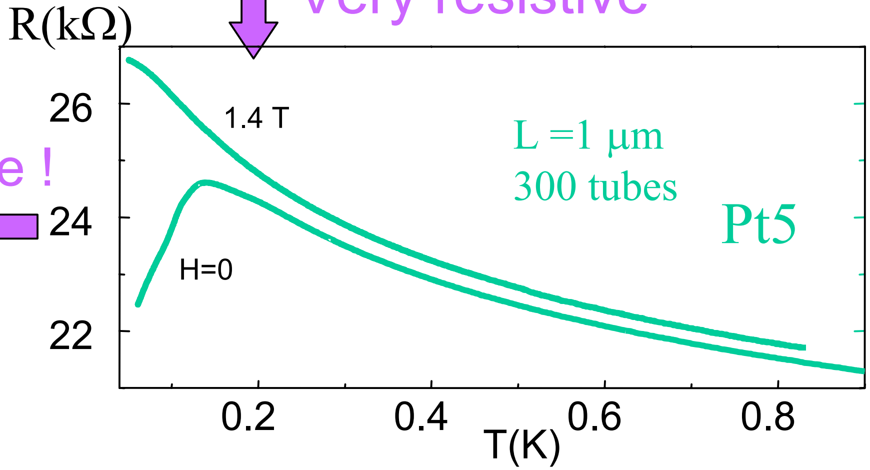
Low resistance



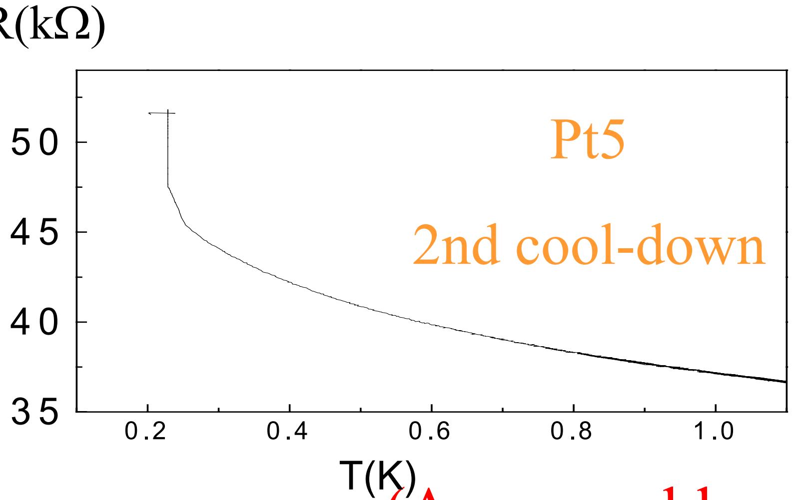
More resistive



Very resistive



too resistive !



(A reasonable amount of) disorder can help !

Physical mechanism for superconductivity?

Superconductivity already observed in doped C compounds:

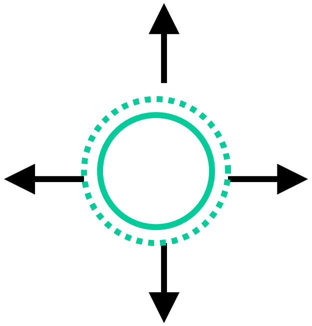
*Intercalated graphite Tc ~ 0.5K
*C60 Alcaline componds Tc ~ 30K

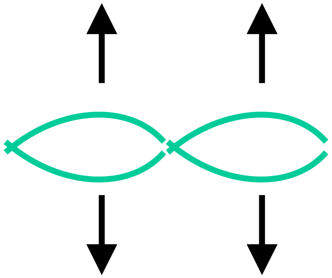
Is doping important in carbon nanotubes?

Contacts, oxygen etc.. : carbon nanotubes are hole doped
Fermi level not at half filling but lower.

Carbon nanotubes are 1D : How to overcome Coulomb repulsion?

What are the relevant phonons?





Breathing modes
(Gonzalez)
Mechanism of superconductivity in ropes
(ee interactions are strongly screened)

Bending modes
(Loss, Martin)

Conclusions and perspectives

Superconductivity in ropes of SWNT is observed in ’’long’’ samples (L>1mm)
Destruction of superconductivity by normal contacts
1D character of superconductivity (phase slips)
Possible Josephson intertube coupling in disordered ropes.

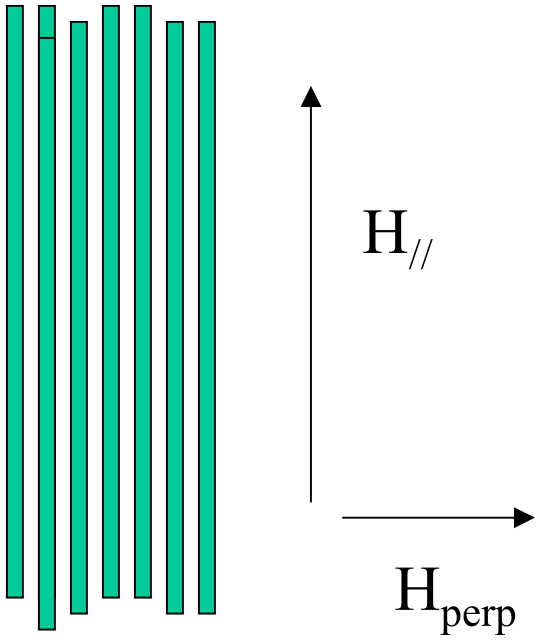
Individual nanotubes?
Proximity induced superconductivity with very high values of supercurrent!
Superconducting fluctuations stabilised by contacts?

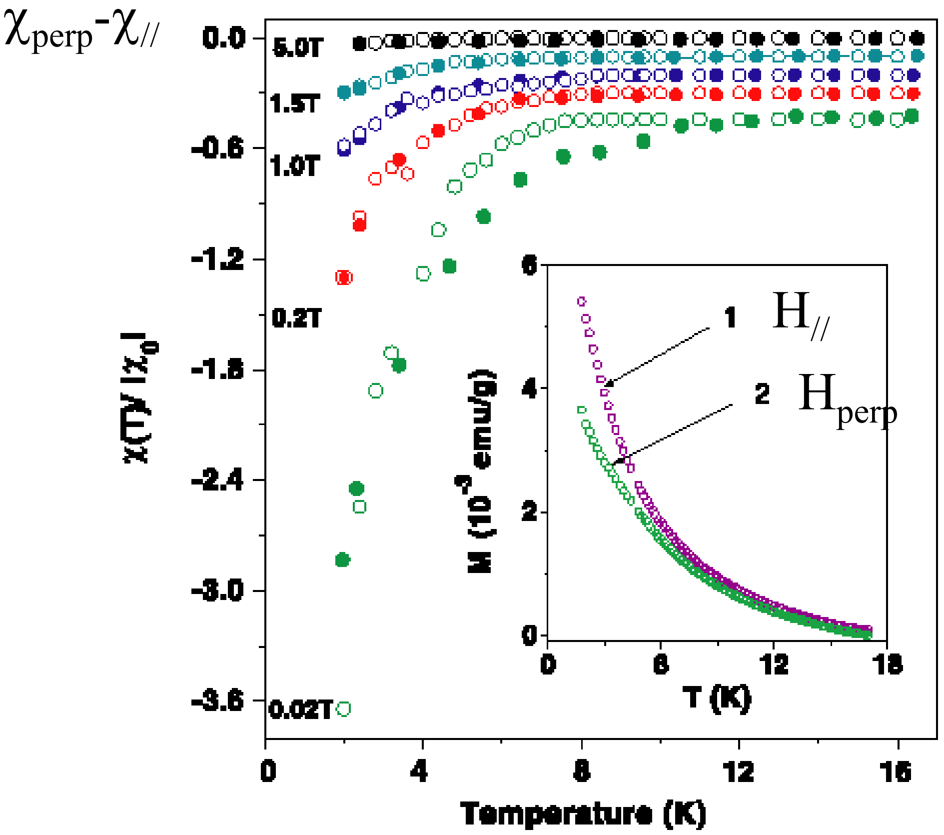
Role of long wave length phonons? Diameter of the tubes?
Transport regime in tubes?

Implementation of a gate: is it possible to induce superconductivity on semiconducting tubes?

Thermodynamic measurements: Magnetisation, Specific heat.

Magnetic susceptibility of a macroscopic array of alined SWNT (D=4Å)





Nanotubes in a zeolite matrix

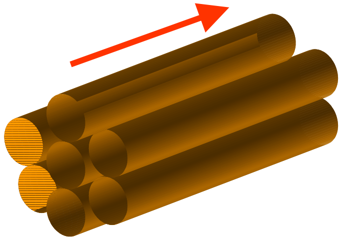
Tang et al. (Science/06/2001)

Anisotropic diamagnetic contribution below 10K:

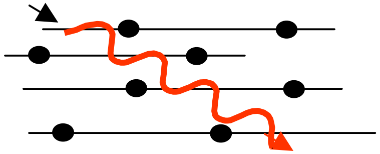
Superconducting fluctuations?

Now: What kind of transport in a rope?

Ballistic transport?

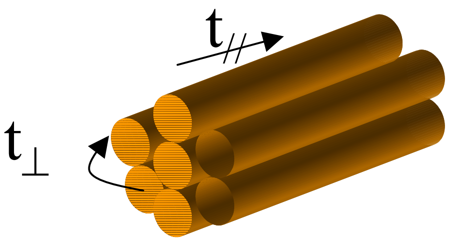


Diffusive transport ?

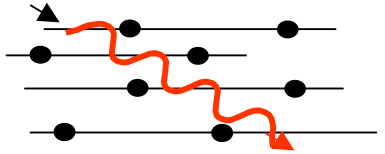


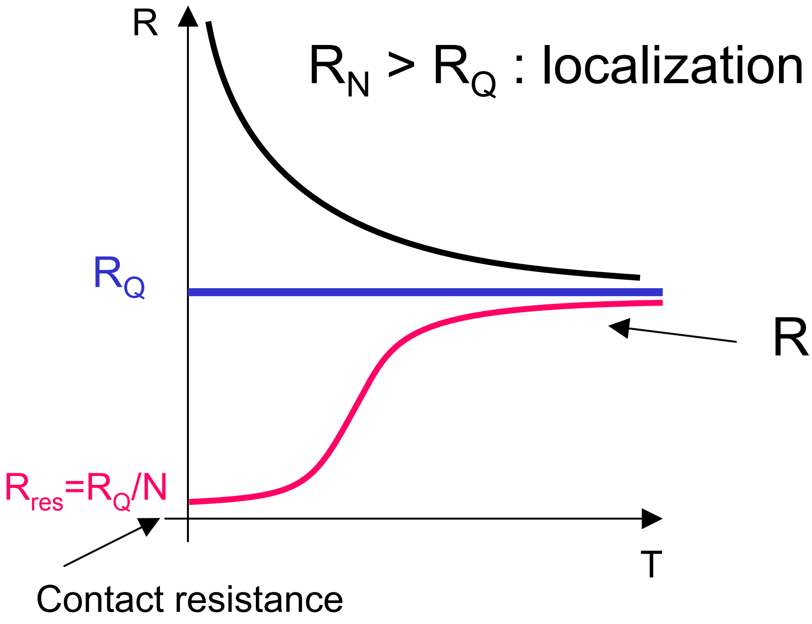
Use shot noise measurements to try to answer this question

Is the rope a diffusive multichannel conductor ?



In the presence of disorder, intertube coupling is increased (Marouf and Kane)



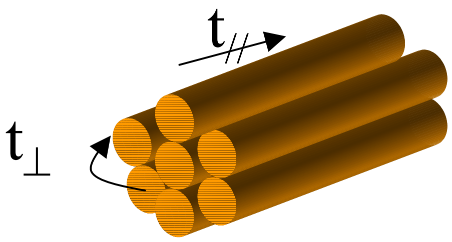


$R_N > R_Q$: localization

$R_N = R_Q/N_{eff} = R_Q/N\ L/l_e$

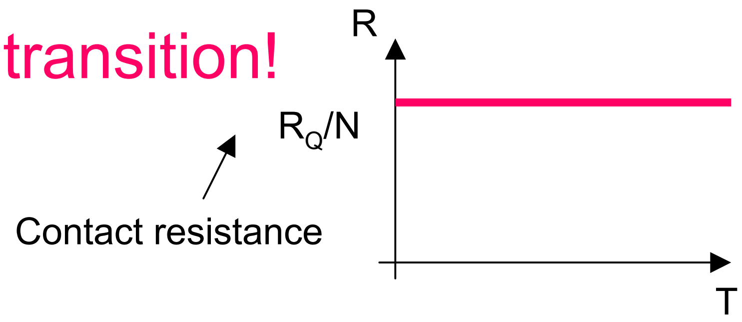
Superconducting transition in a diffusive conductor of 200 channels ?

Or could each metallic tube be a ballistic conductor ?

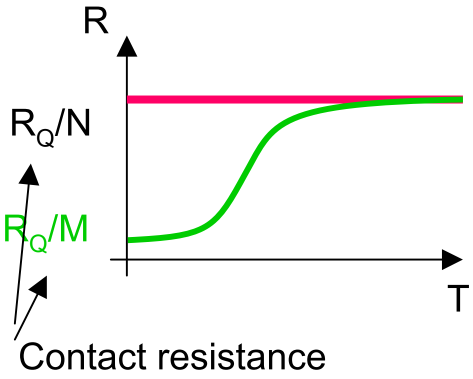


Ballistic tubes of different helicities:
expect negligible electronic intertube transfer $t_\perp \ll t_{//}$

Then cannot see a transition!



…unless channels open up



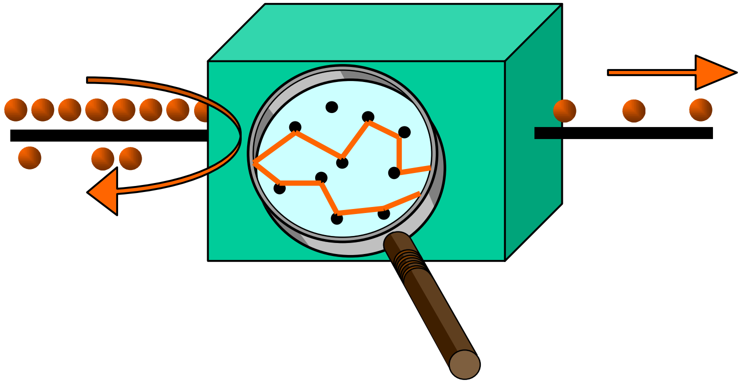
Gonzalez, PRL 2001: $t_\perp$ negligible for single electrons, larger for Cooper pairs
N electronic channels $\Rightarrow$ M Cooper pairs channels

➡ Delocalization by superconducting fluctuations

Can we test this hypothesis? Measure shot noise

Is the transport ballistic or diffusive in the ropes?

Use shot noise measurement!



Channels with transmission coefficients T_i € [0 1]

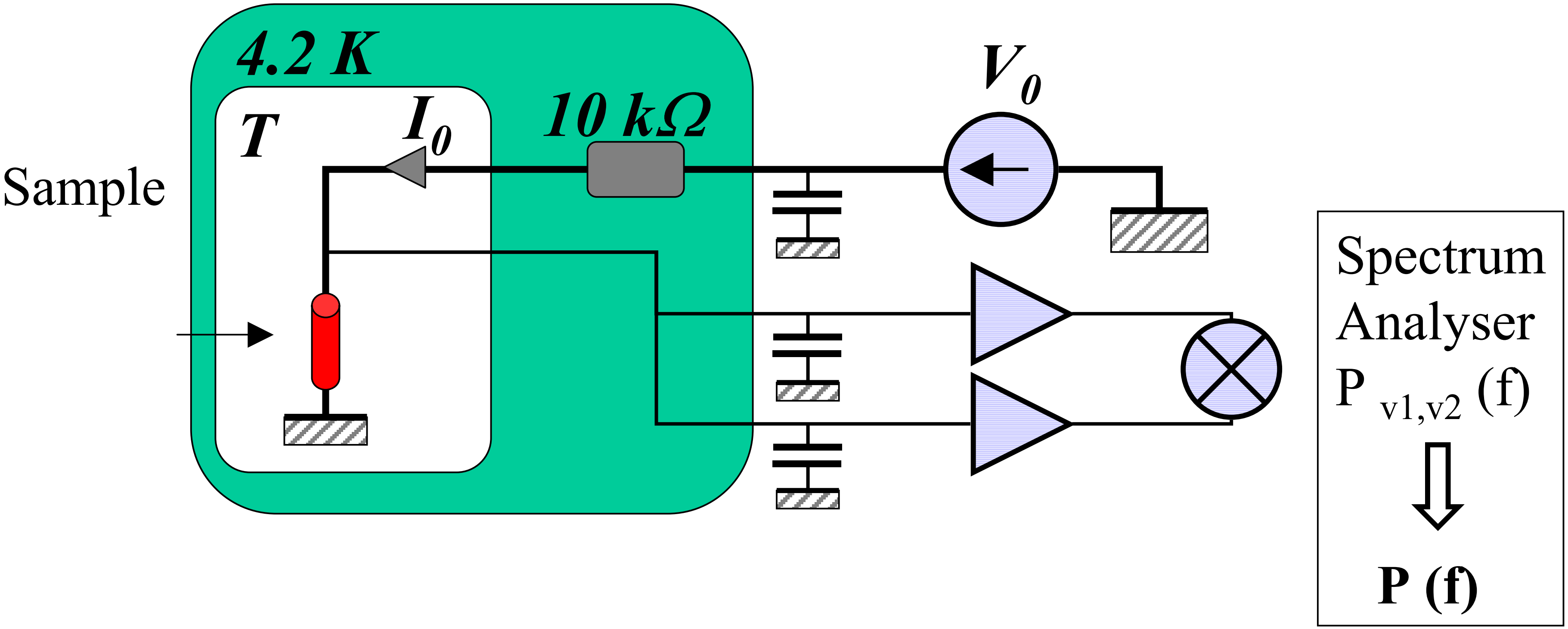
$$G = G_Q \Sigma \, \mathbf{T_i}$$

$$S_I = 2.\int I(t).I(0)\,.e^{\,i\omega t}.dt = 2\, e^{*}\, I\, \Sigma \mathbf{T_i}\,(\mathbf{1\text{-}T_i}) \,/\, \Sigma\, \mathbf{T_i} \quad \text{(at T=0)}$$

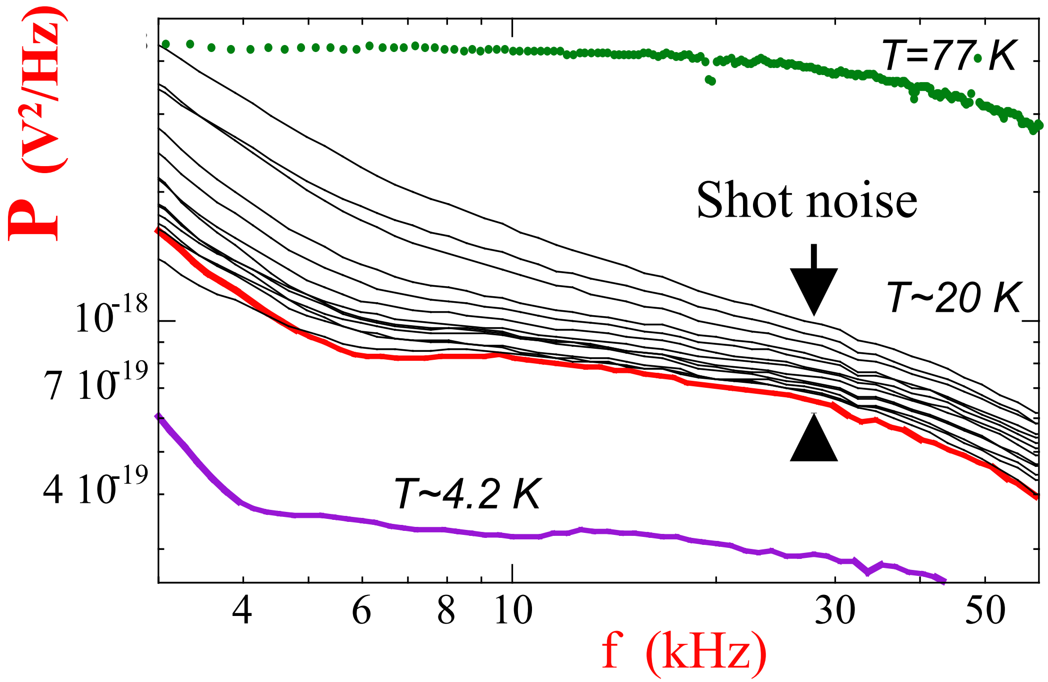
- S_I= 0 perfectly transmitted channel or perfectly reflected channel
- S_I= 2eI. (1/3) diffusive conductor

Shot noise measurement gives information about transport regime and correlations

Shot noise measurement



Noise spectra for $I_0 \neq 0$



Shot noise

$$P = F(f) \cdot \left(\mathbf{4.k_B.T/R} + \mathbf{H}(f,I_0) + \mathbf{2.q.I_0.F} \right) + \mathcal{E}(f)$$

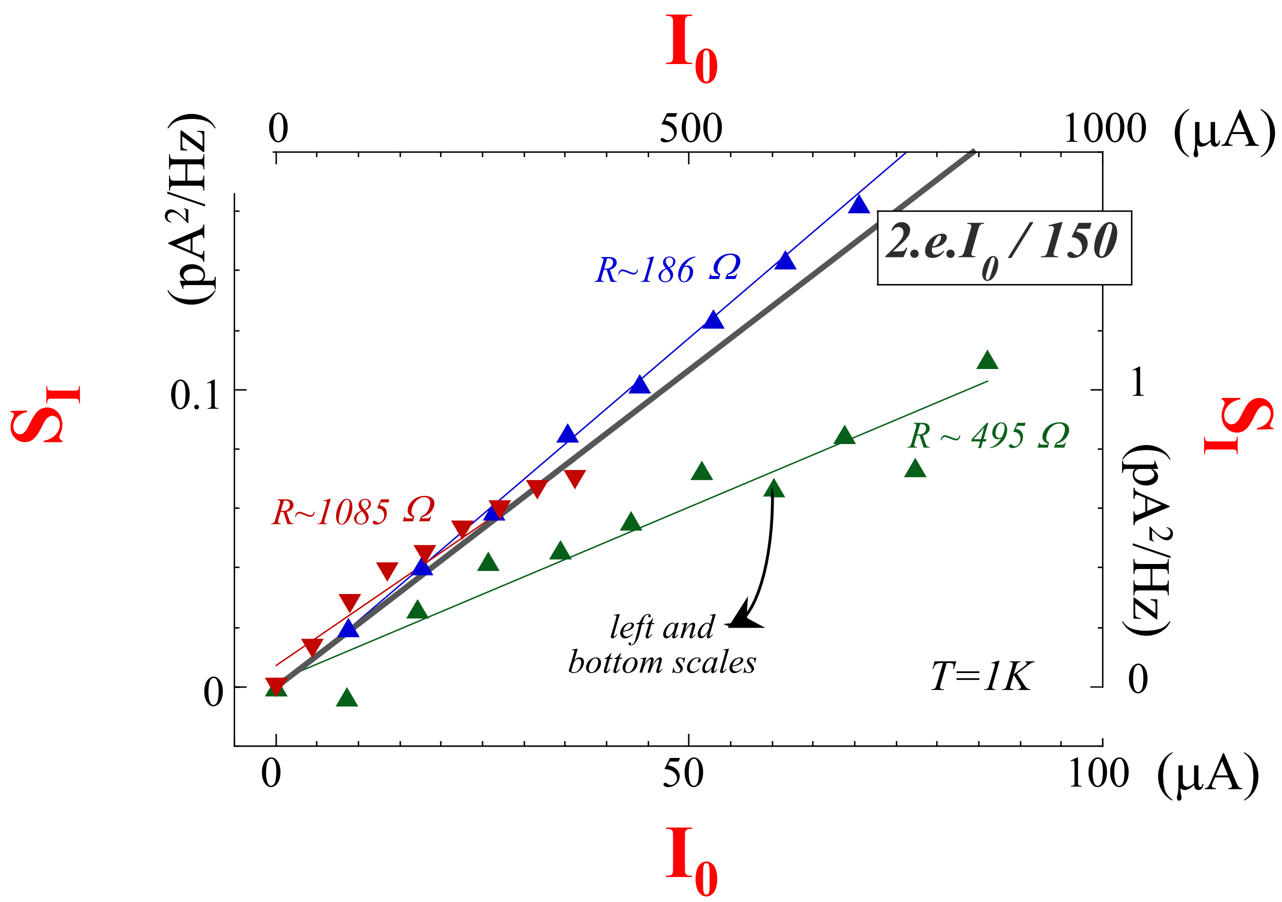
Known filter

Thermal noise

Low freq.
noise

Reproducible
residual noise
(amplifier, sources,...)

Shot noise of 3 different ropes



⇒ High noise reduction for all 3 ropes (P. Roche et al., Europhys. Lett 2002)

Interpretation

- Landauer-Büttiker Formalism $S_I = 2\, e^{*}\, I\, \Sigma T_i\,(1-T_i)\,/\,\Sigma\, T_i$

$$\left\{\begin{array}{l} G = G_0.\, \Sigma\, T \qquad (\, G_0 = e^2/h \sim 1/13\ k\Omega\,) \\ S_I = 2eI.\, \Sigma\, T.(1-T)\, /\, \Sigma\, T \end{array}\right.$$

- Experiment:

$$\left\{\begin{array}{lll} G = 1/500\ \Omega\ = G_0\ .\ 20 & \Rightarrow & \Sigma\ T=20 \\ S_I = 2\ e\ I\ /150\ = 2\ e\ I\ \Sigma\ T.(1-T)\ /\ 20 & \Rightarrow & \Sigma\ T.(1-T)=1/10 \end{array}\right.$$

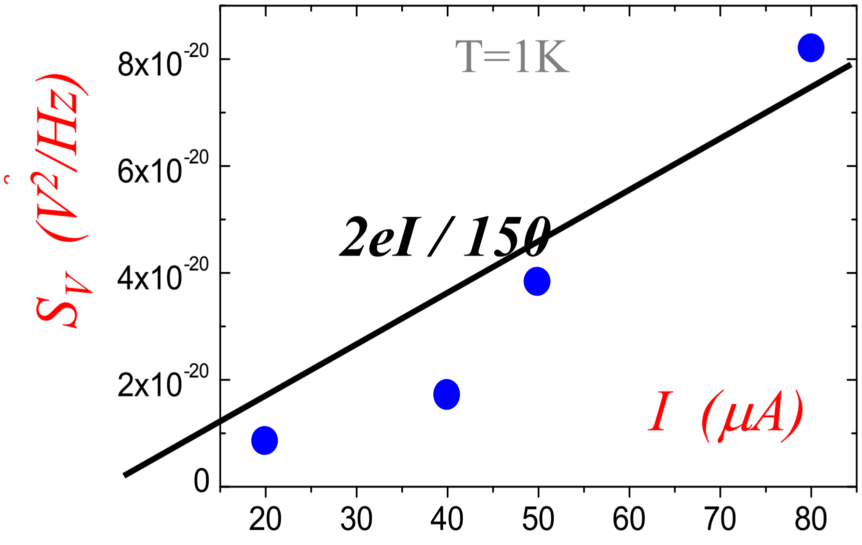
Implication:
For each channel **T** > 90% or **T** < 10%

Conclusion: The channels are either open or closed (to within 10%)

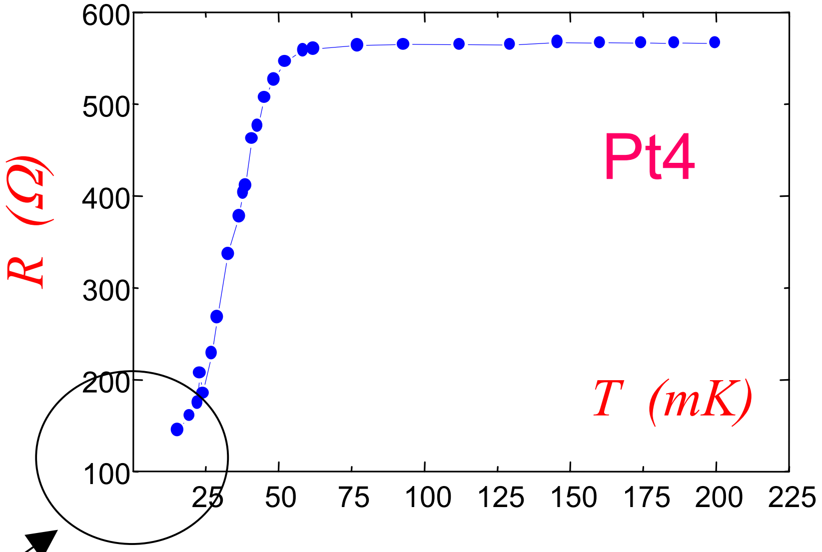
Shot noise and superconducting transition measured on the same rope

Same sample (Pt4) L=1 μm

Low shot noise: ballistic transport!



Superconducting transition



Residual « Superconducting » resistance ~ R_Q/N

$G_N / (2e^2/h)$ ~ 15 channels in normal state

$G_S / (2e^2/h)$ ~ 80 channels in superconducting state

Ballistic transport of electrons in few channels

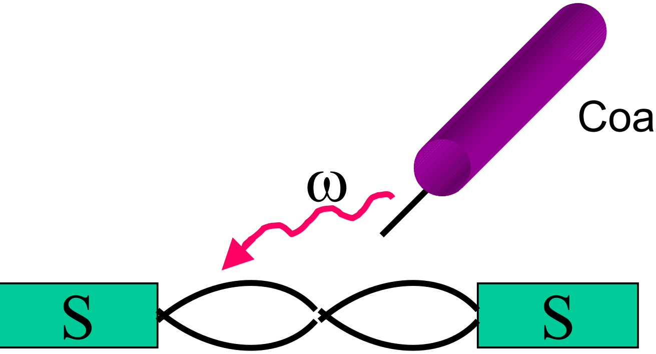
Diffusion of Cooper pairs across all channels (J. Gonzalez, Phys. Rev. Lett (2001))

Conclusion of shot noise measurements

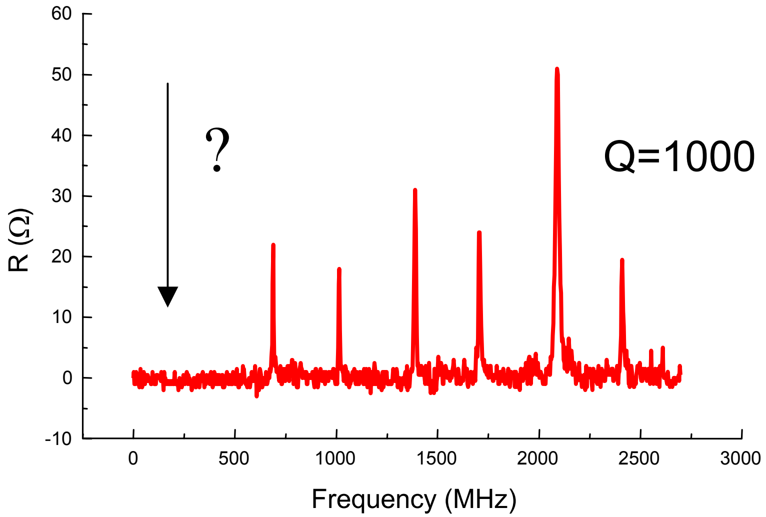
- Extremely low shot noise (Reduction > 100)
- Ballistic transport?
- What is the expected result for correlated systems? Theory not clear...

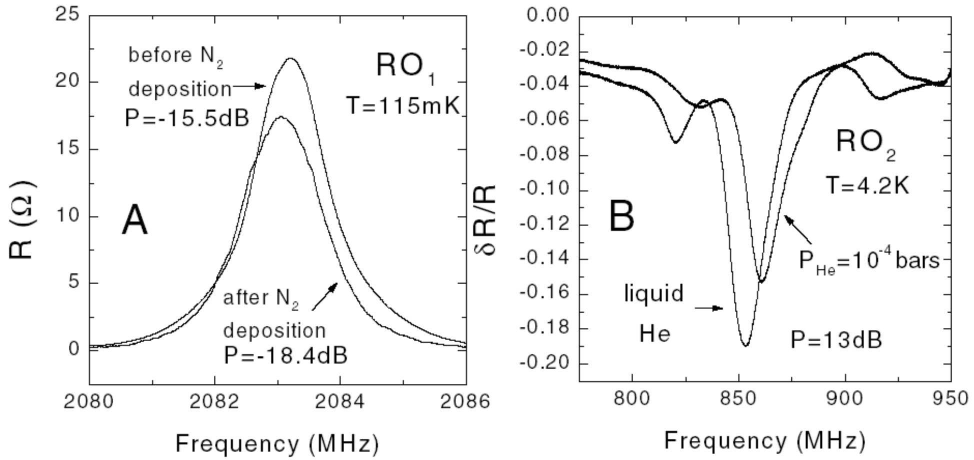
We can excite mechanical vibration modes of tubes with RF radiation

Reulet et al PRL 00



Suspended Rope on Au/Re contacts $R_N = 65\ \Omega$ L=1.7 µm



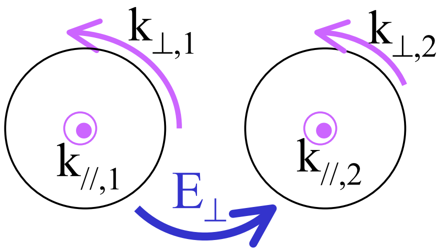


Fundamental transverse mode of a rod :

$$f_T = 22.4 \frac{R}{2L^2} \sqrt{\frac{E}{\rho}} \approx 276 MHz$$ E Young modulus ~ 1TPa

- Mechanism of conversion RF -> acoustical wave ?
  Tubes are charged!
- Detection: Heating or phase coherence breaking at resonance

How does disorder control the transport in a rope?



Hopping probability = $<\Psi_a/H_\perp/\Psi_b> = E_\perp$

Without disorder: conservation of $k_{//}$: no inter-tube transfer

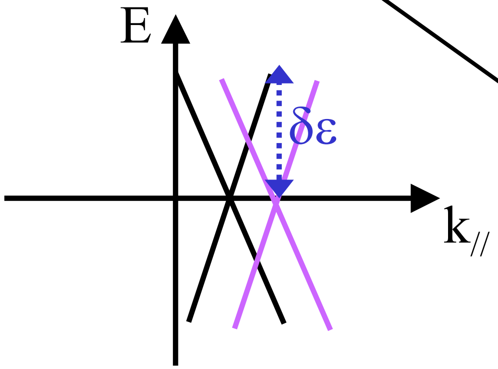
$$E_\perp \approx 0$$

Disorder: (short range):

Variance W →

backscattering $l_e = aE_f^2/W^2$ (*White et al, Nature 393)*

localisation : in a 1D system $\xi_{loc} \approx l_e$

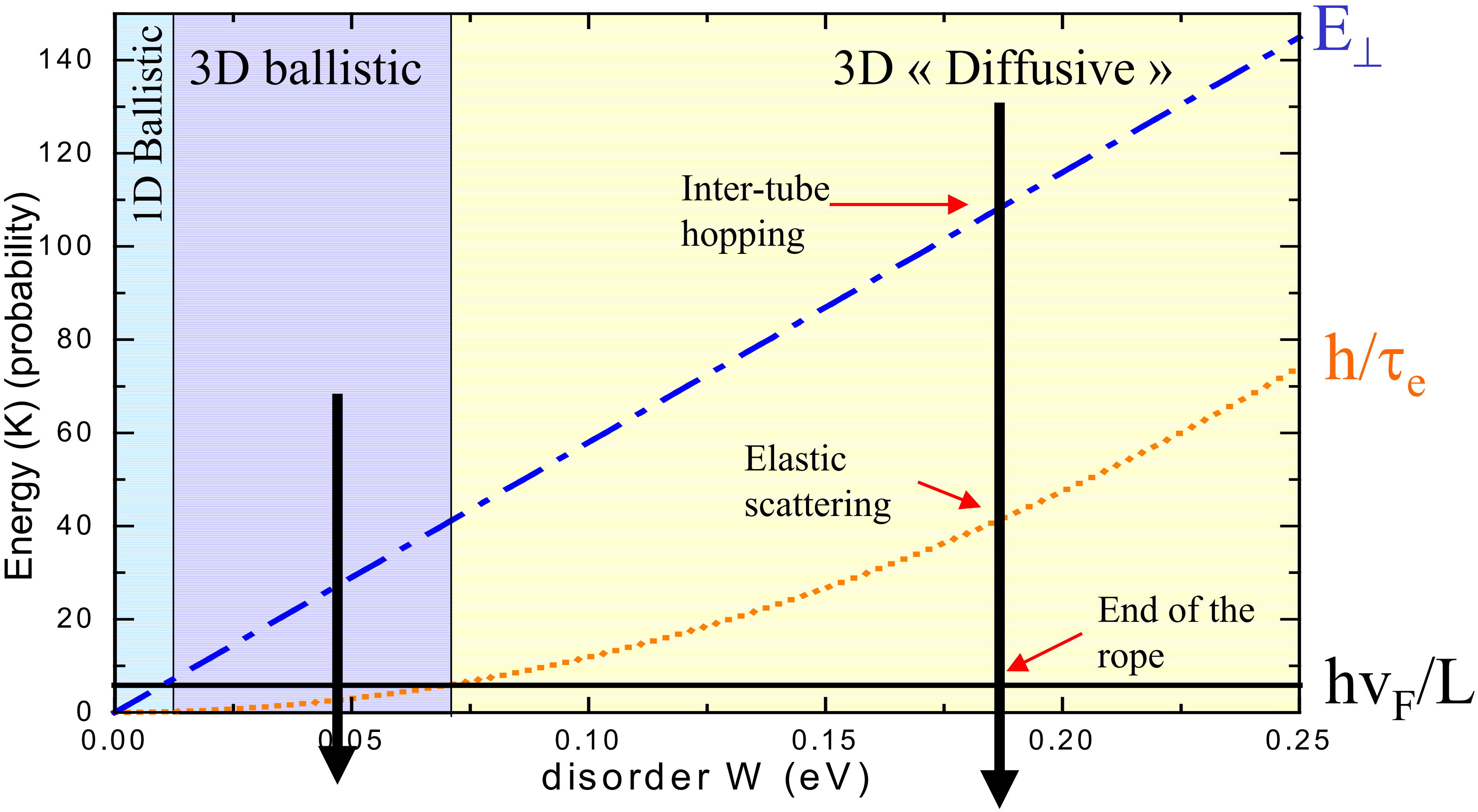


perturbation of the wave function

enhances inter-tube transfer $E_\perp = t_0 W/\delta\varepsilon$

delocalisation : in a rope $\xi_{loc} \approx M\, l_e$

From ballistic to diffusive



Diffusive transport up to strong disorder due to delocalisation inside the rope

Electron-Phonon scattering ?

- Noise reduction by e-ph coupling : $S_I = 2.e.I_0. (l_{e\text{-}ph} / L)$

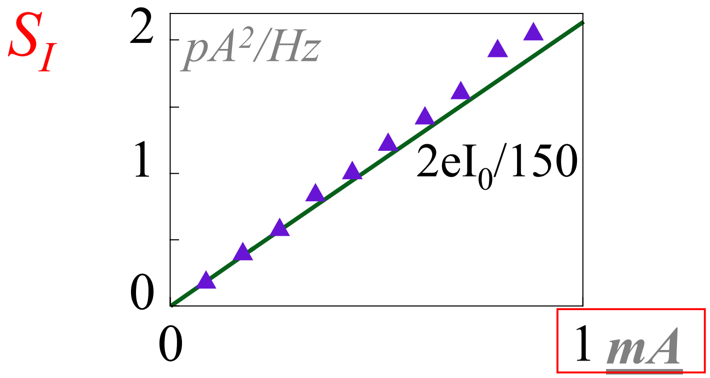
  ⇒ $l_{e\text{-}ph}$ = 5 nm : not realistic at 1K, low I_0

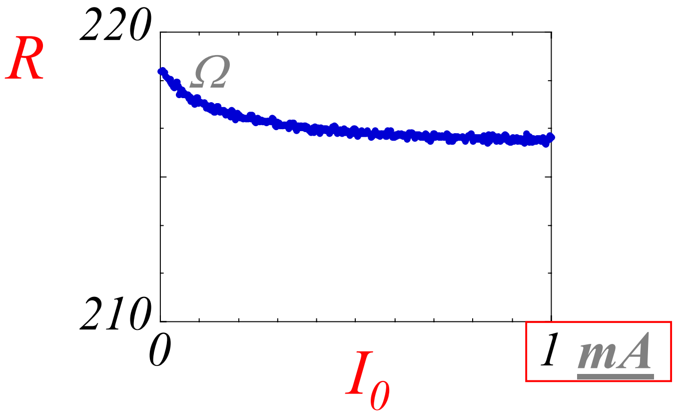
- Proximity induced superconductivity

  ⇒ small inelastic scattering at contacts, large $l_{e\text{-}ph}$

- Inelastic scattering increasing with I_0

  ⇒ irrelevant in our range of parameters. Indeed :





→ **No electron-phonon noise reduction at low temperature**

What is the minimum noise in a multichannel system ?

$G = G_Q \Sigma T_i$ with $G_Q = 2e^2/h = 1/13\ k\Omega$

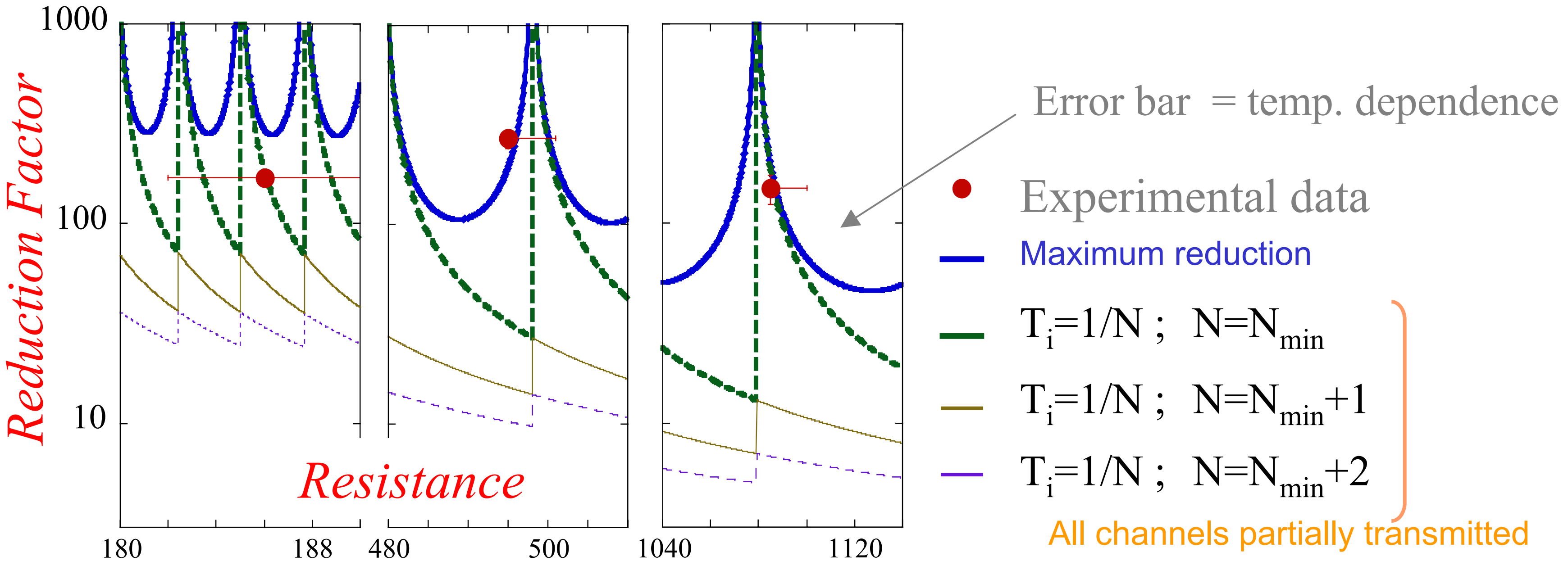
$S_I = 2\, e^*\, I\, \Sigma T_i\, (1-T_i) / \Sigma T_i$ (at T=0)

Highest noise reduction for as many channels as possible completely open or closed:

$$G = G_Q \Sigma T_i = G_Q (N-1+ T_{partial}); \quad T_{partial} = G/G_Q - N$$

Total number of channels

Then $S_I = 2\, e^*\, I\, G_Q / G\ \ T_{partial}\, (1-T_{partial})$

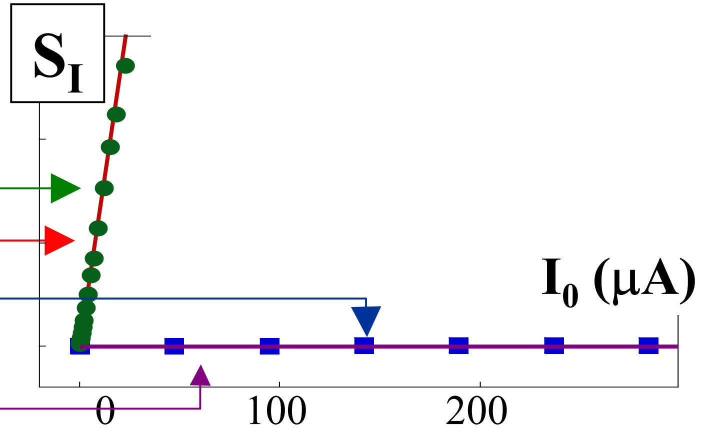


→ **Ballistic transport in very few channels** and/or **reduced charge**

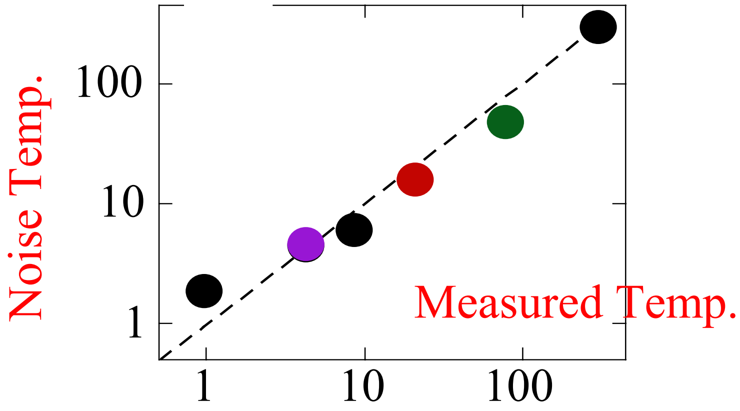
Validations de la mesure

Validation de l 'analyse :

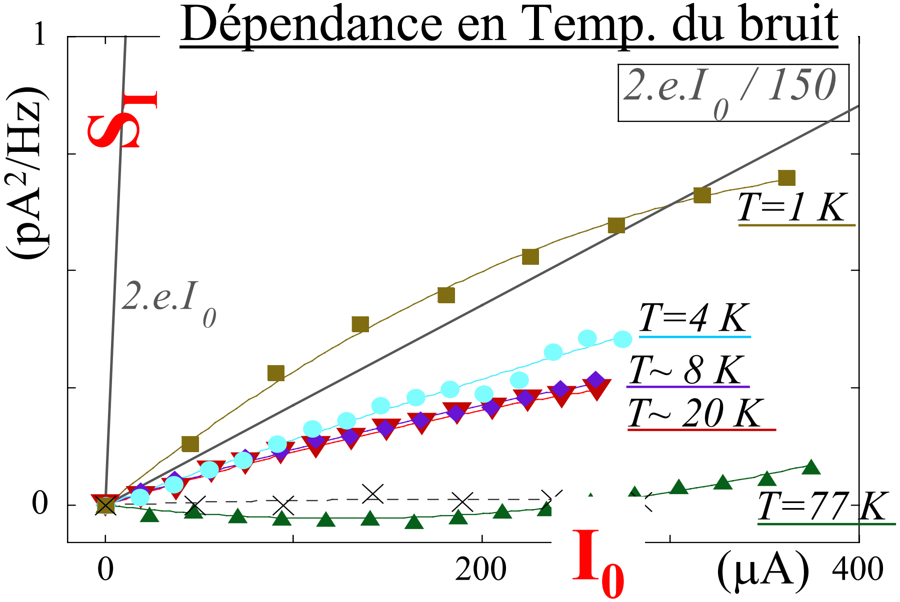
- bruit de grenaille d 'une jonction PN
  ~ bruit porteurs indépendants 2.e.I
- bruit de grenaille d 'une résistance macro
  processus inélastiques dominants
  ~ bruit nul (± 2.e.I/2000)



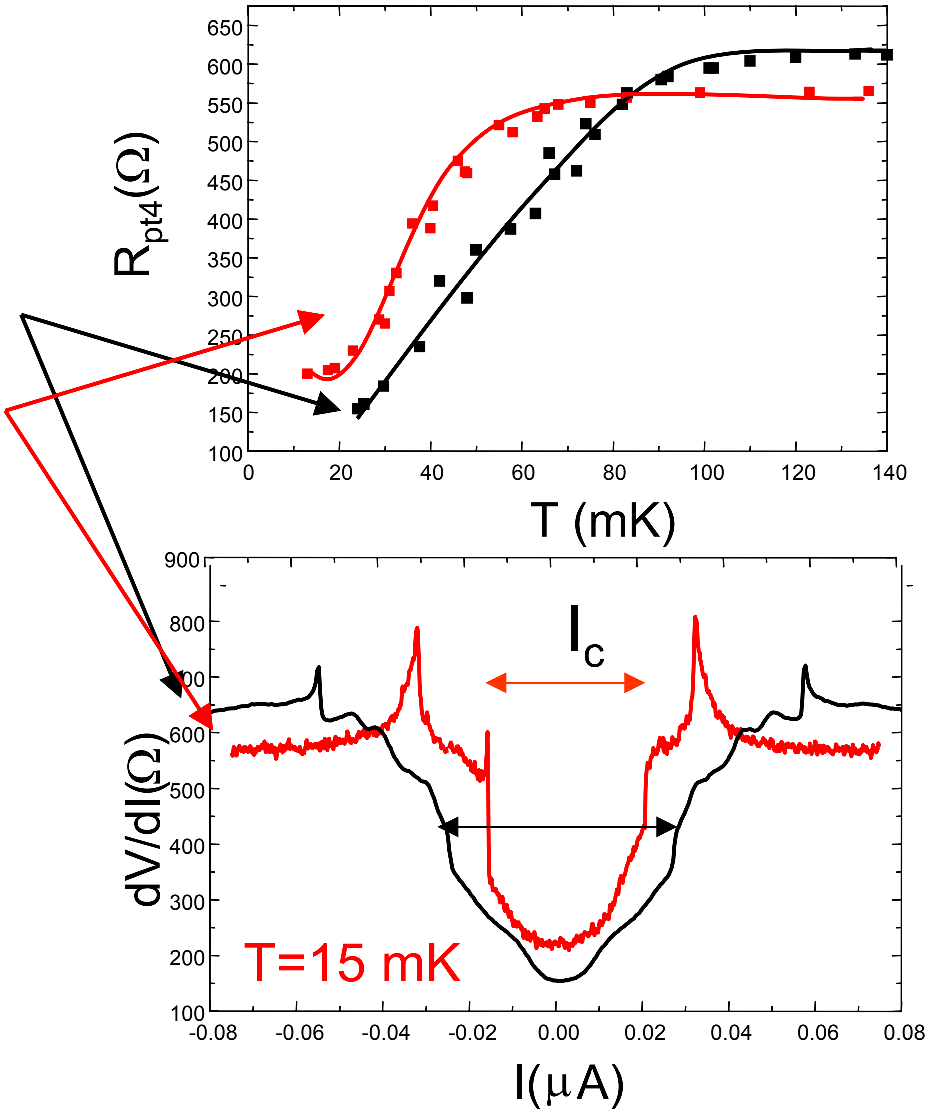
Contrôle du niveau de bruit résiduel:



Dépendance en Temp. du bruit



Modification of superconductivity by deposition of organic molecules:



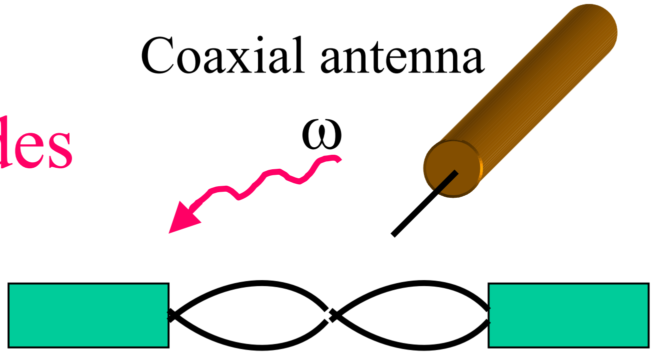
Before deposition of benzene thiol

After deposition of benzene thiol

Reduction of T_c and critical current.

Due to modification of low frequency phonon spectrum ?

Effect of radiofrequency radiation: Excitation of mechanical vibration modes



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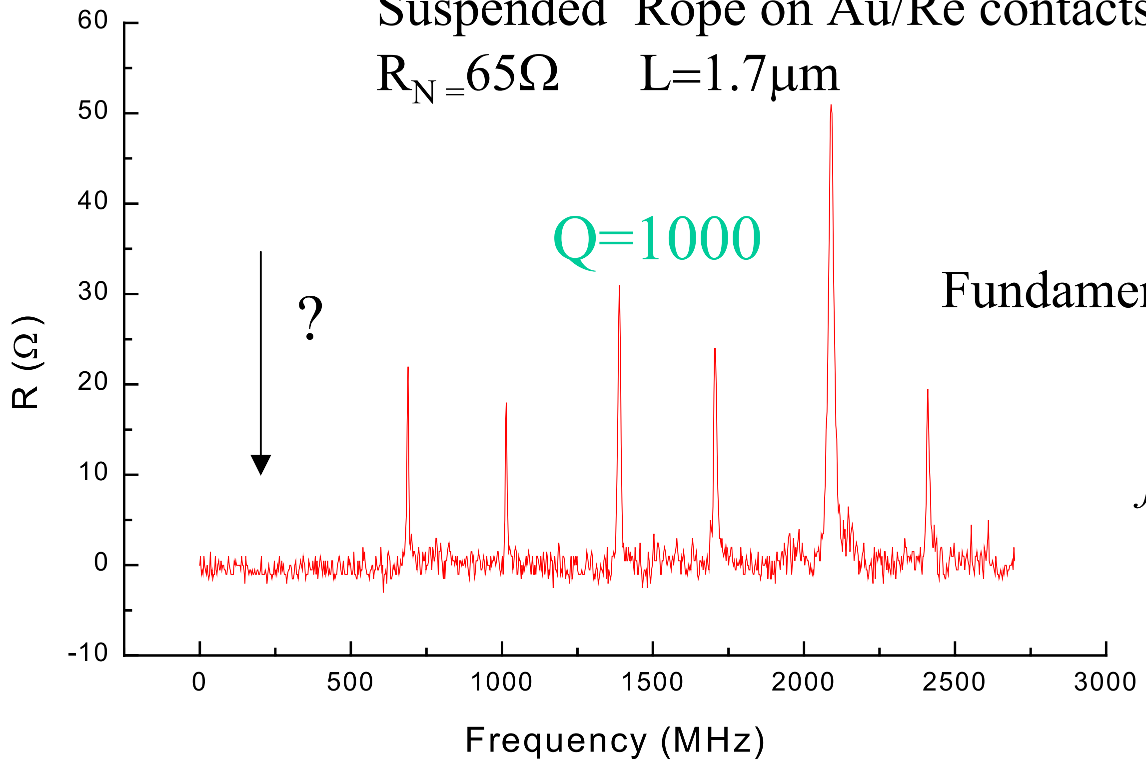
$R_N = 65\Omega$ L=1.7μm



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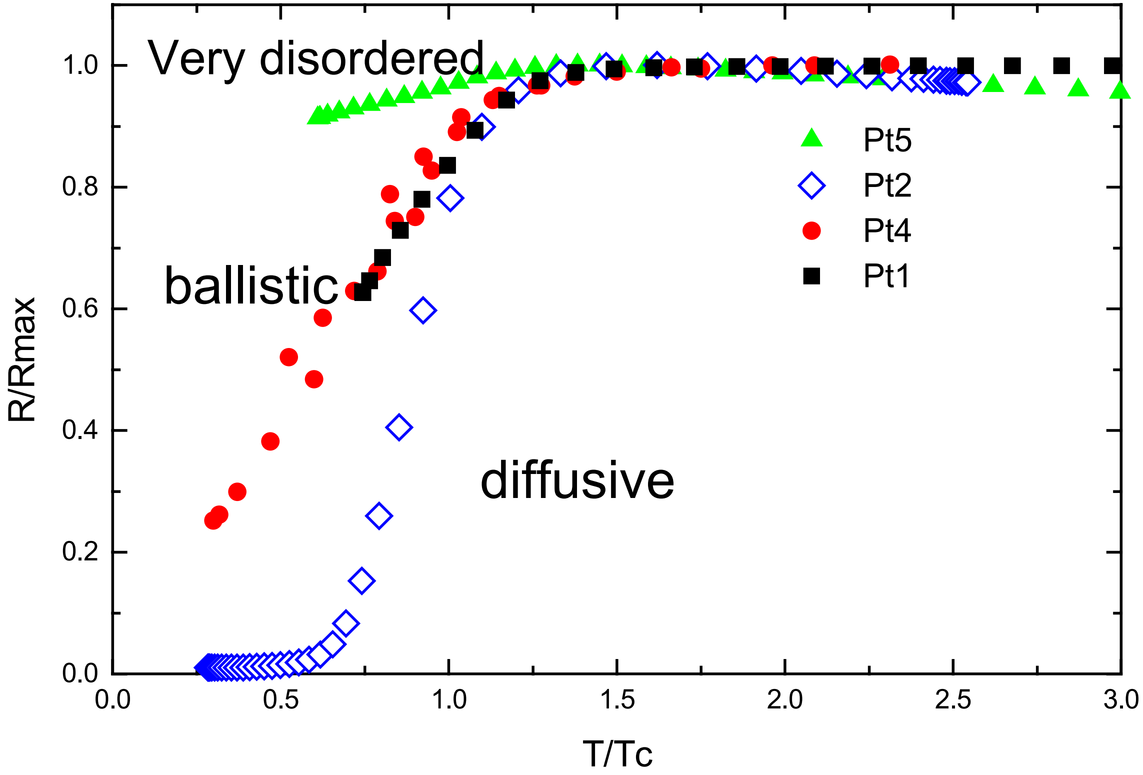
E Young modulus ~ 1TPa

- *Mechanism of conversion RF -> acoustical wave ?

  Tubes are charged!

- *Detection: Heating or phase coherence breaking at resonance

What determines the nature of the transition?



-Length

-Number of metallic tubes

-Disorder

-Intertube coupling

Pt5 = 300 tubes, R_N= 20 kΩ, ξ/L= 1/6

Pt2 = 350 tubes R_N= 10 kΩ, ξ/L= 1/3

Pt4 = 40 tubes, 10 R_N= 0.8 kΩ, ξ/L= 0.8

Pt1 = 350 tubes, R_N= 1.3 kΩ, ξ/L= 0.7