

# Defects and conductance in single wall carbon nanotubes

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Dpto. Física de la materia Condensada

# People

## Experiments

- C. Gómez-Navarro
- P.J. de Pablo
- J. Gómez-Herrero

## Software

Nanotec  
Electrónica

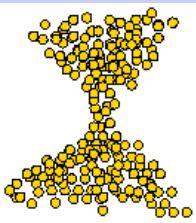
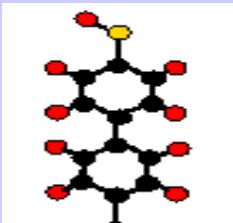
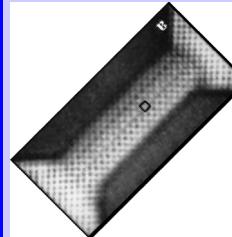
## Theory

- B. Biel
- F.J. Fernández-Vidal
- A. Rubio
- F.Flores

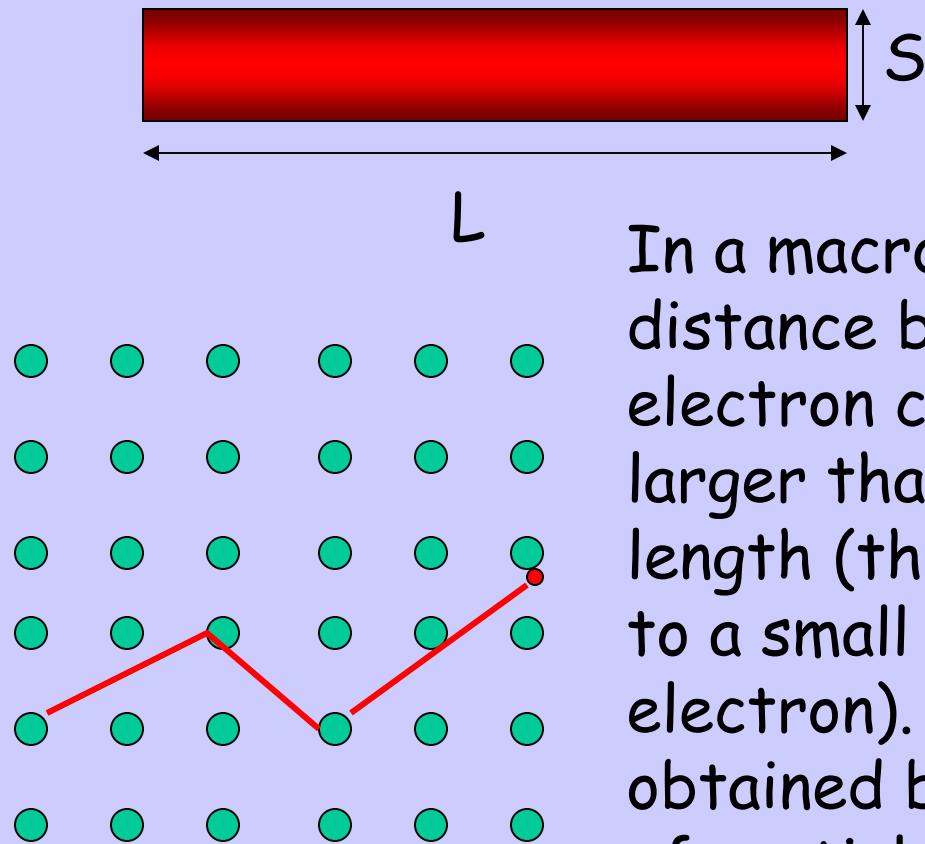
# Outlook

- Few atoms contacts
- The basis of atomic force microscopy
- The conductance of a carbon nanotube as a function of the force
- Tuning the conductance of single wall carbon nanotubes by ion irradiation

# Nanowires overview

	Breakjunctions	Carbon nanotube	Organic molecule	Quantum wire	$V_2O_5$ nanofiber	DNA
						
SWNT	Au, Cu, Ag...	C	C, H, O....	AsGa/AlGaAs, Au,	V, O	C, H, O, N, P...
Composition	Au, Cu, Ag...	C	C, H, O....	AsGa/AlGaAs, Au,	V, O	C, H, O, N, P...
Geometry	?	Tubular	Chemically defined	Planar 2D	Stripe	Double helix
Width	Atomic	1-40 nm	1 nm	Several nm	6 nm	1 nm
Length	Nanometers	1-2 microns	nanometers	nanometers	Up to tens of microns	Up to tens of microns
Electrical connections	Easy	Difficult	Problematic	Easy	Difficult	Problematic
Fabrication	Mechanical contact	Discharge arch	Reaction tube	Lithography	Reaction tube	Reaction tube
Fabrication at great scale	Difficult	Easy	Easy	Difficult	Easy	Easy
Conduction mechanism	Quasiballistic	?	?	Ballistic	?	?

# The Ohm's law



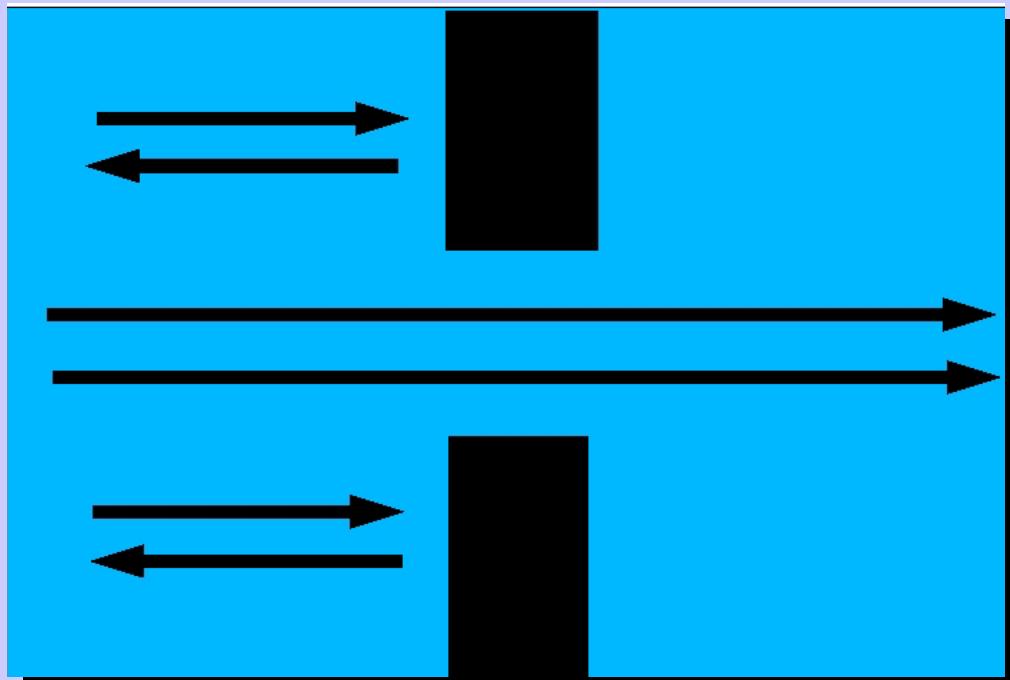
In a macroscopic conductor the distance between 2 consecutive electron collisions  $L_m$  is much larger than the phase coherent length (the wave length associated to a small particle like an electron). The Ohm's law is obtained by averaging the number of particle collision with the metal lattice (Drude model)  $R = \rho L/S$

# Theoretical framework

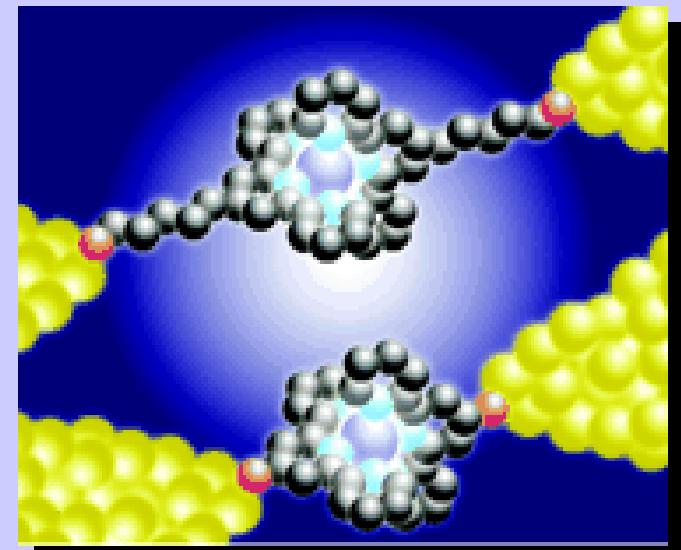
$$G = G_0 T(E_F) = \frac{2e^2}{h} T(E_F) = \frac{2e^2}{h} \sum t_i(E_F)$$

$$R_0 \approx 13 K\Omega!!$$

Naively  $R_0$  is the **resistance of one atom!!**



Landauer's formalism  
(zero bias, zero temperature)

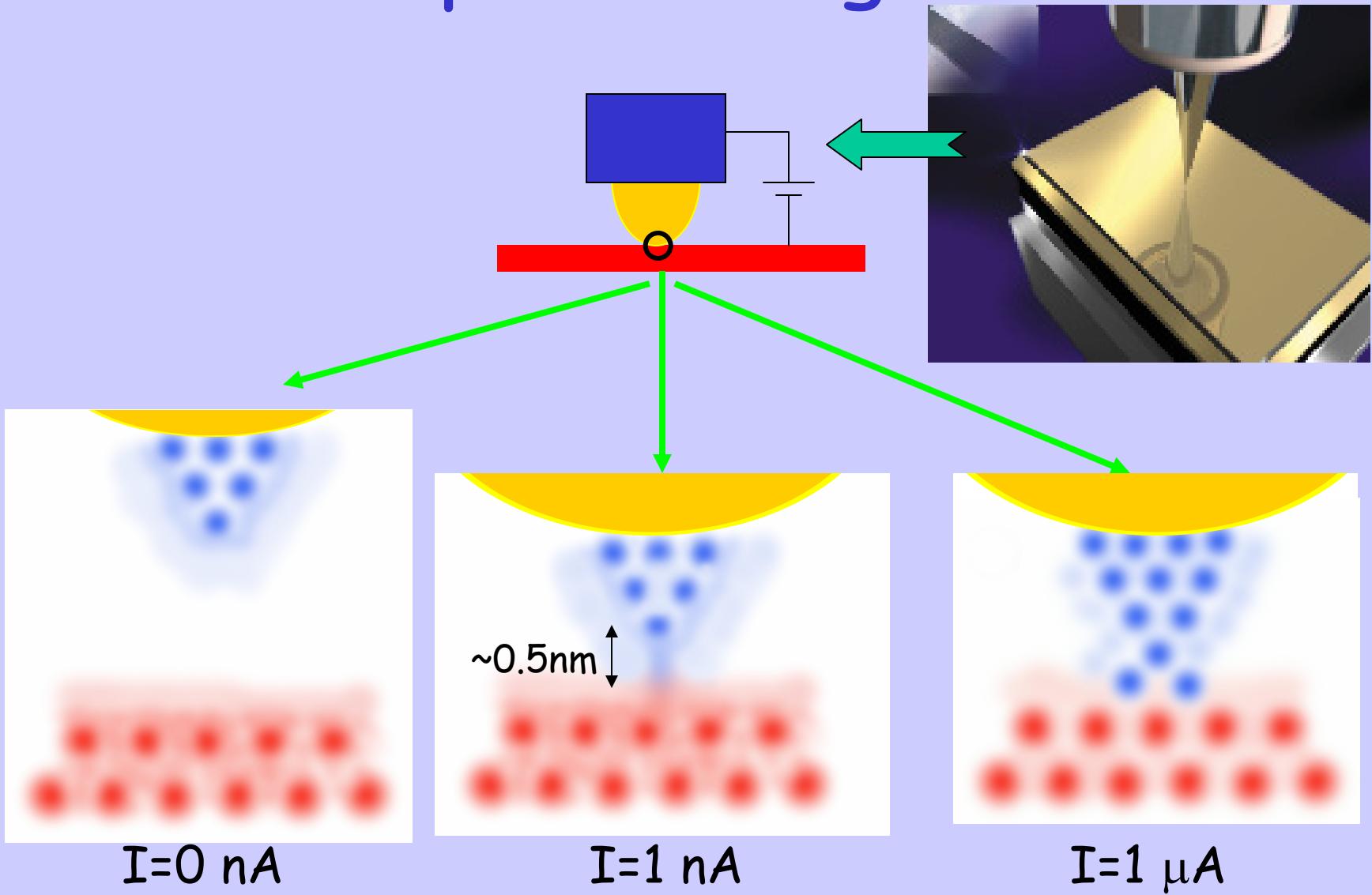


J.J. Palacios

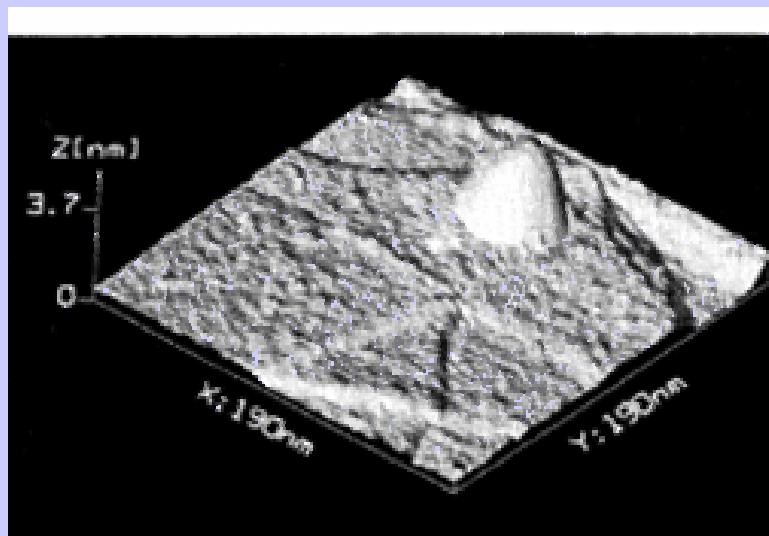
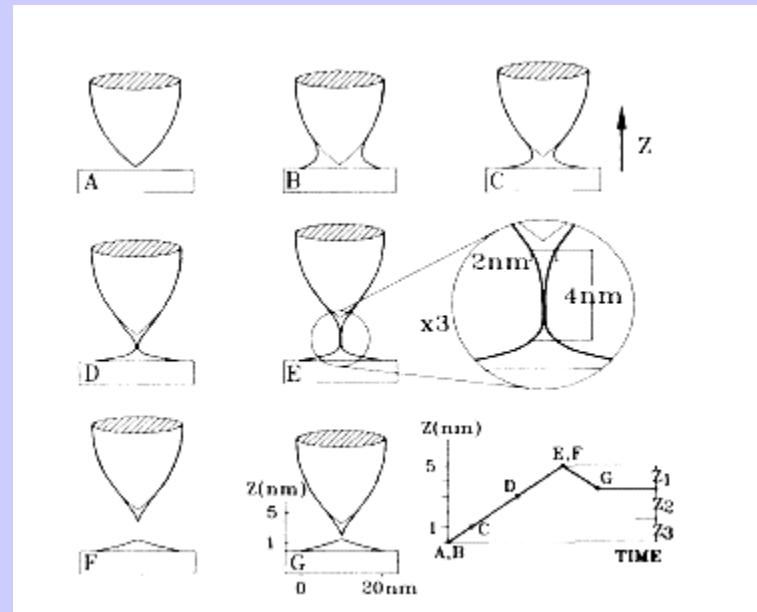
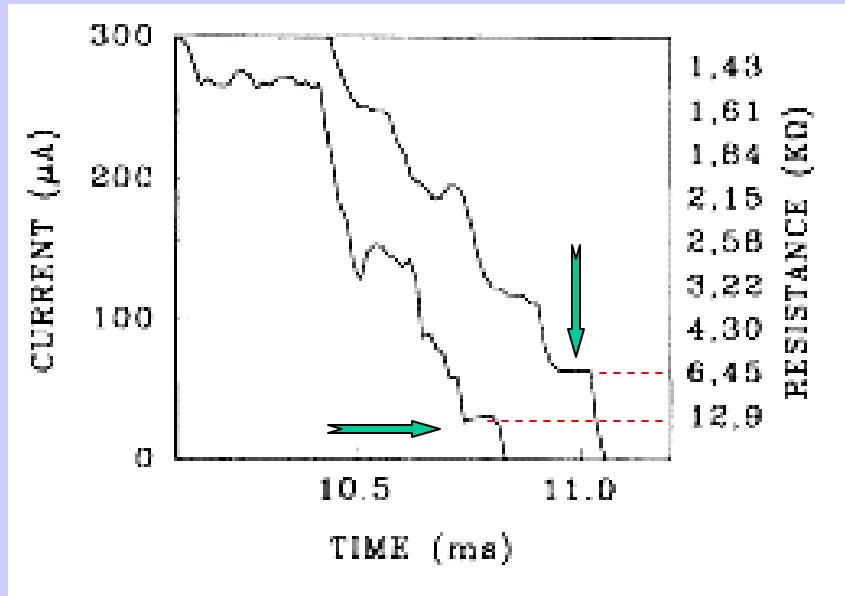
# Few atoms contact by scanning tunnelling microscopy

- Molecular electronic is described by quantum transport theory.
- The problem of electrical contacts is the problem of going from the atomic level to the macroscopic level.
- STM works by measuring a tunnel current (quantum level) with a macroscopic device.
- The tip is the key point for this transition

# From macroscopic to nanoscopic: bare gold



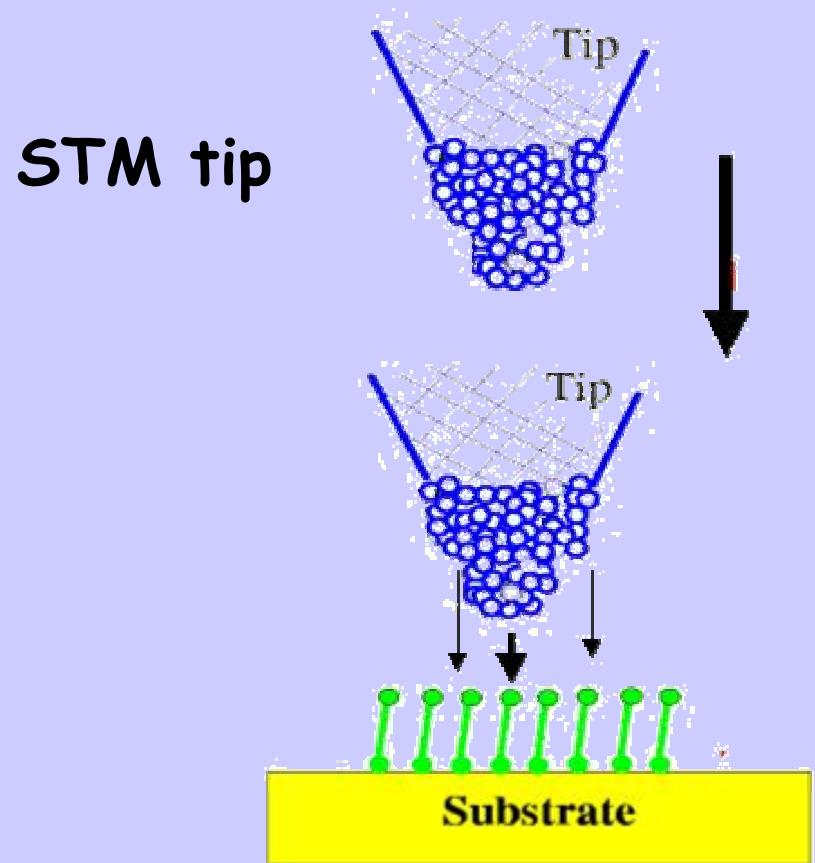
# One and two atoms contacts



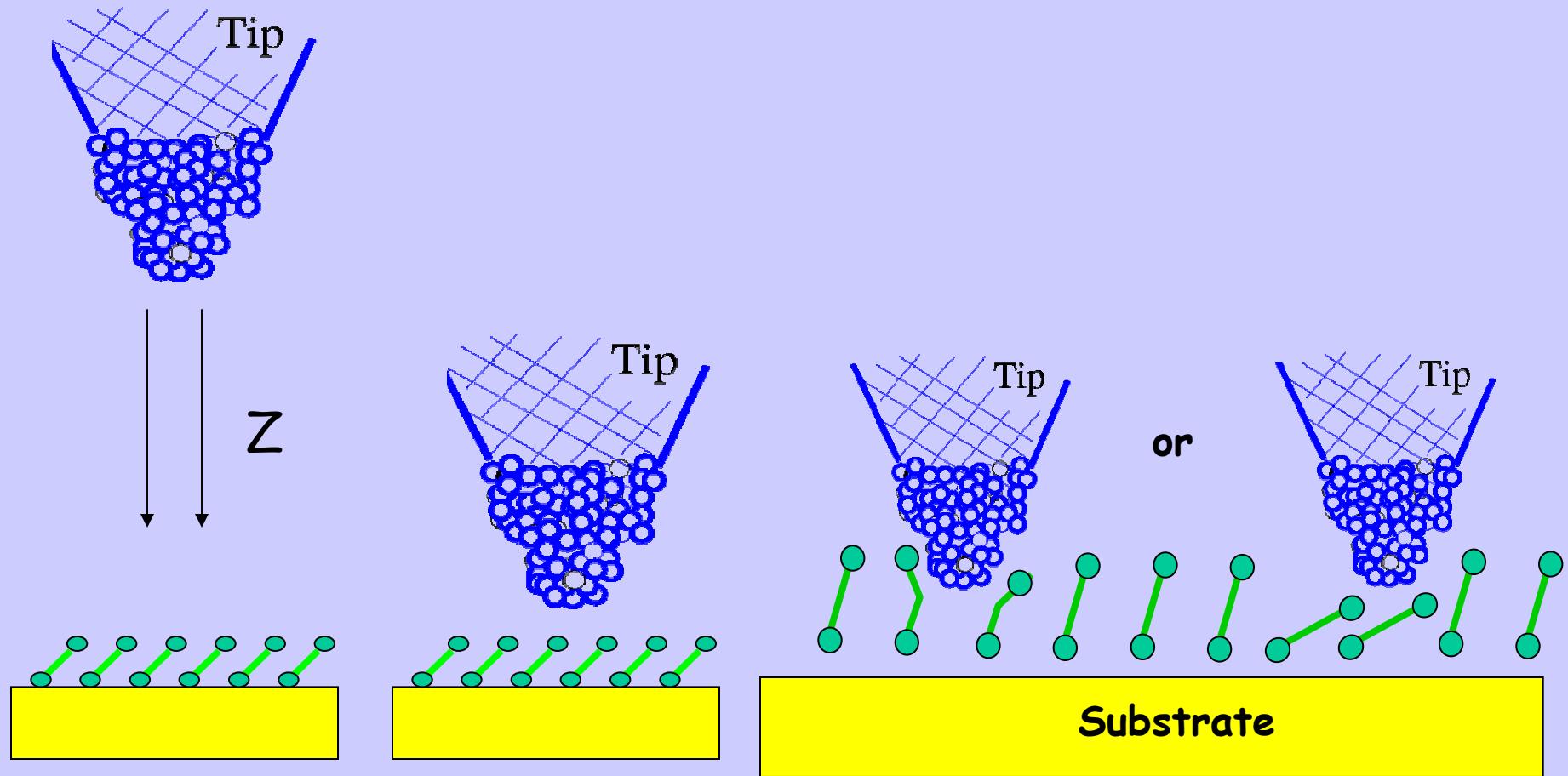
As the tip is withdrawn the gold neck is stretched and the current exhibits quantization

J.I. Pascual et al. PRL Phys. Rev. Lett. **71**, 1852-1855 (1993)

# Now with molecules



# Problems: tip-molecule gap.

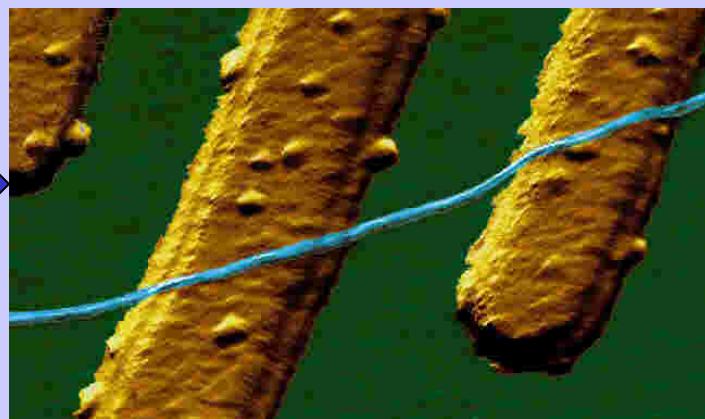


# Contacting long molecules

- Long moles are much easier to contact.
- Electrodes are made using microfabrication techniques like electron beam lithography
- The molecules are then adsorbed on the substrate in a random manner.
- An AFM is using to check whether or not a molecule is contacting two electrodes

AFM image of carbon nanotubes contacting  
two platinum electrodos

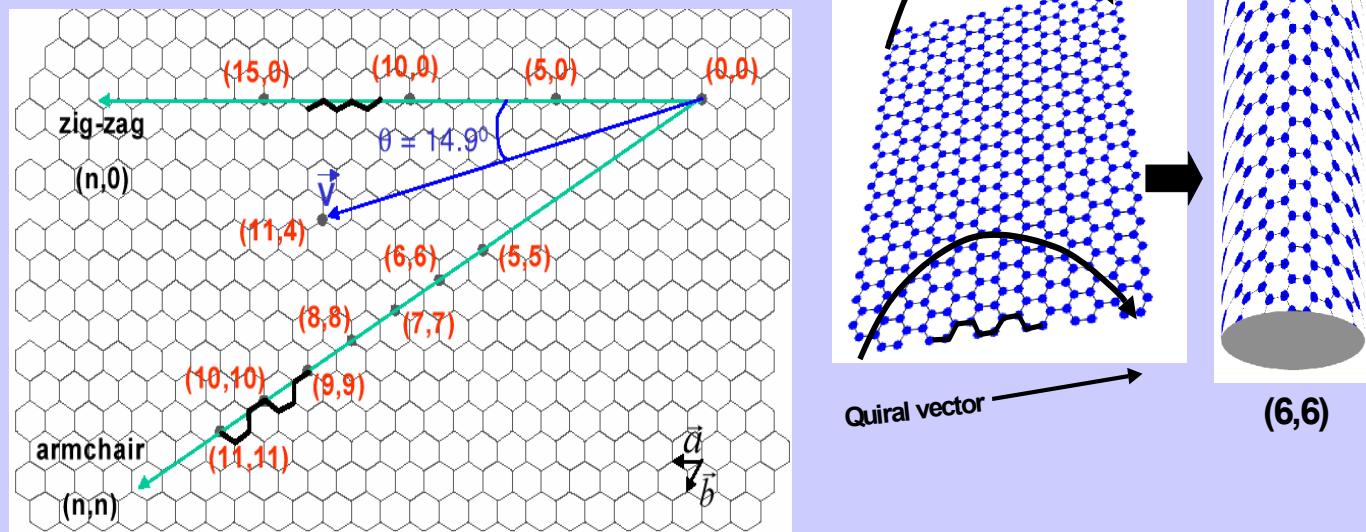
C. Dekker group



# Carbon nanotubes basis

## ELECTRONIC PROPERTIES: SWNT

- Metallic or semiconducting depending on chirality.
- Lack of control of chirality in synthesis.
- High current density



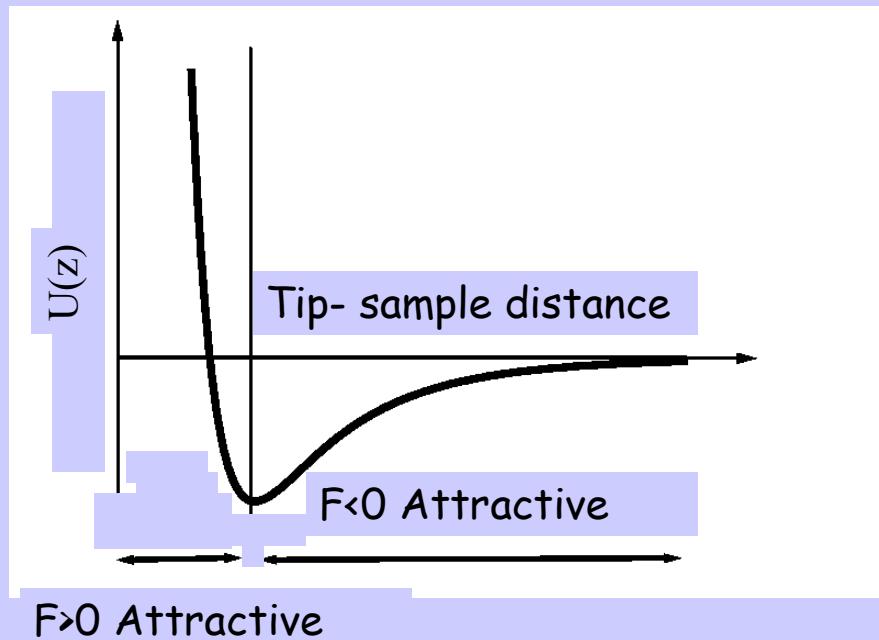
**Perfection** is the key point for their unusual electronic properties

# Contacting nanotubes

- In early electrical transport experiments, carbon nanotubes were contacted using **platinum electrodes**. The nanotubes typically formed a tunnel barrier of high resistance ( $> 1 \text{ M}\Omega$ ) with the electrodes.
- Carbon nanotubes so contacted exhibit **Coulomb blockade** at low temperatures.
- As Platinum was replaced by **gold or titanium** the contact resistance decreases to **10 K $\Omega$** . Approaching the theoretical limit of 6 K $\Omega$ .
- In the case of carbon nanotubes not only the metal used as electrode but **also the geometry** plays an important role in the contact resistance.

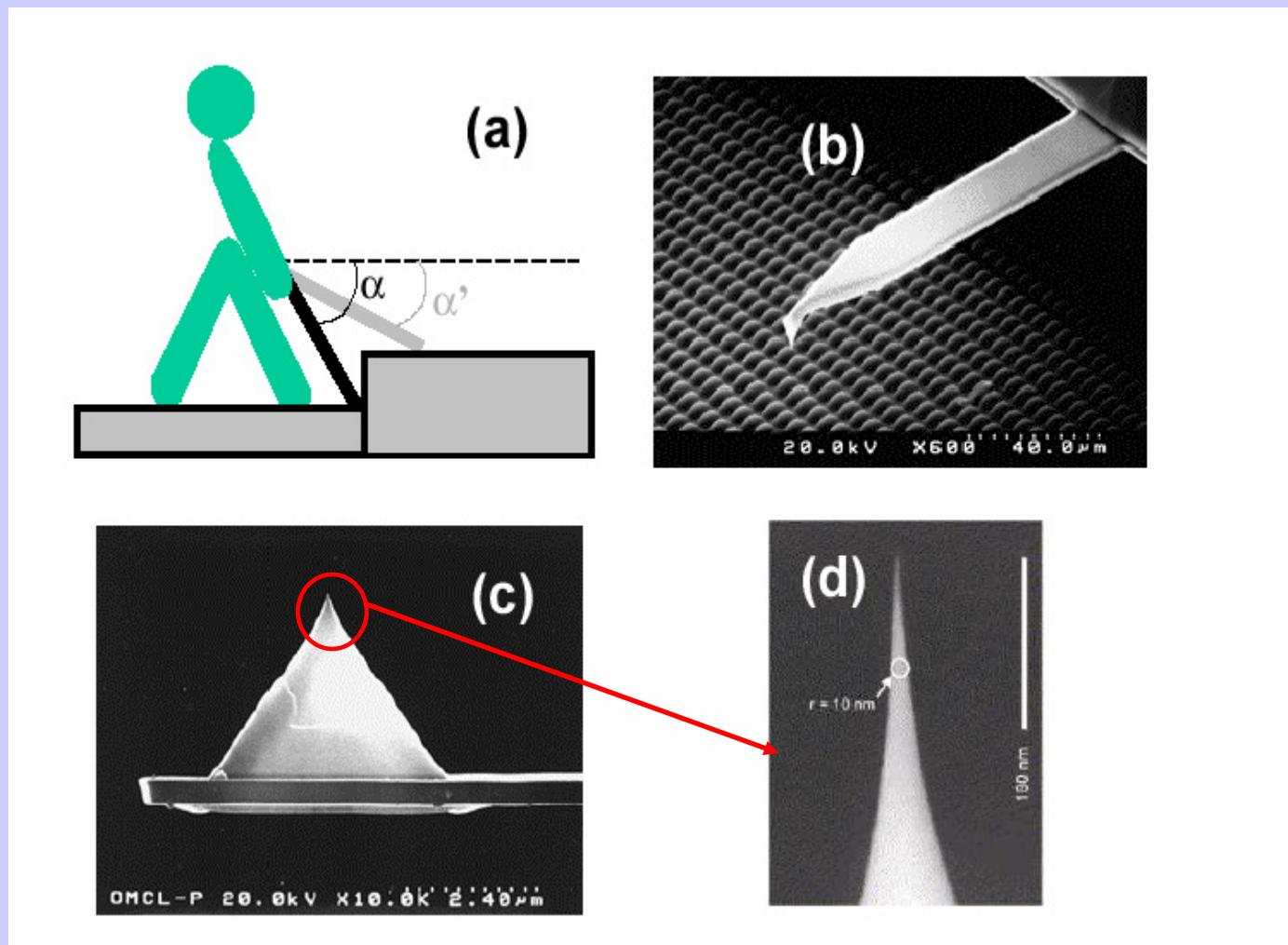
# Atomic force microscopy

## The interaction in the SFM



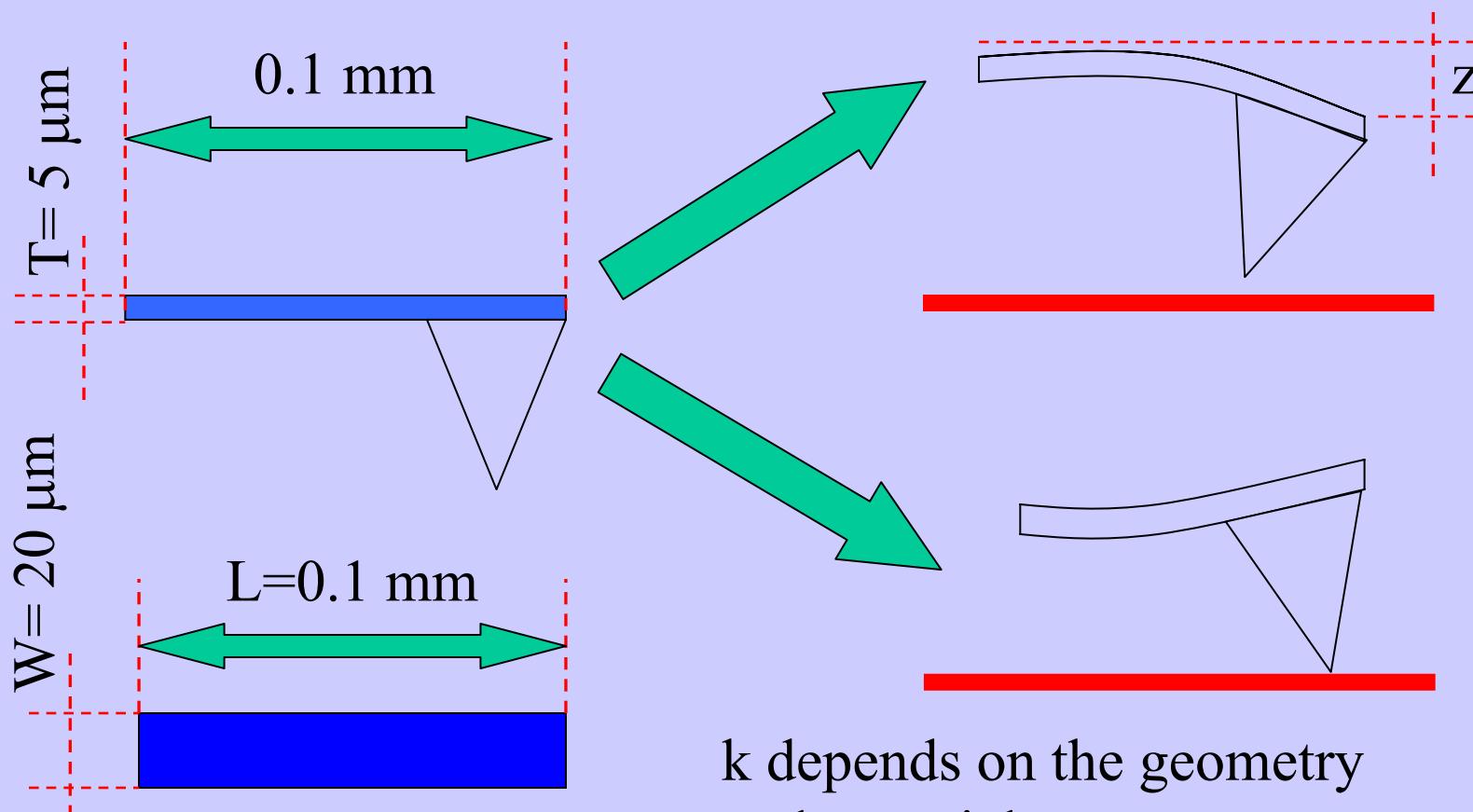
Potential near a surface: attractive at intermediate distances and repulsive for short distances

# Force sensor



# The microcantilever as a spring

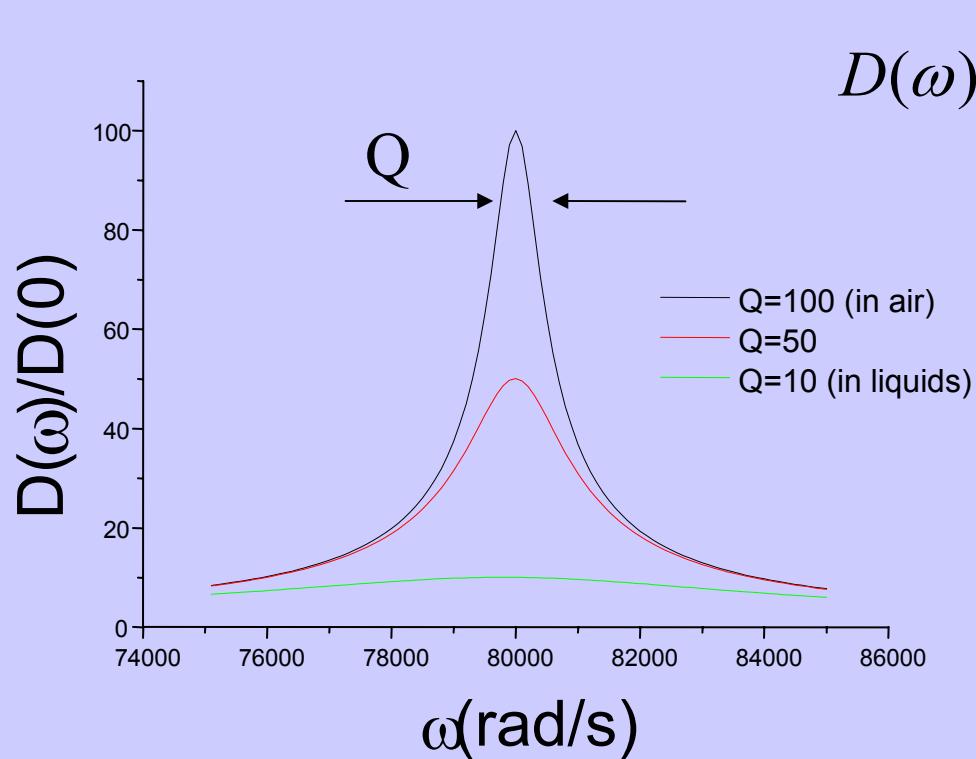
$$F = -kz ; k = E/4 \cdot W \cdot (T/L)^3$$



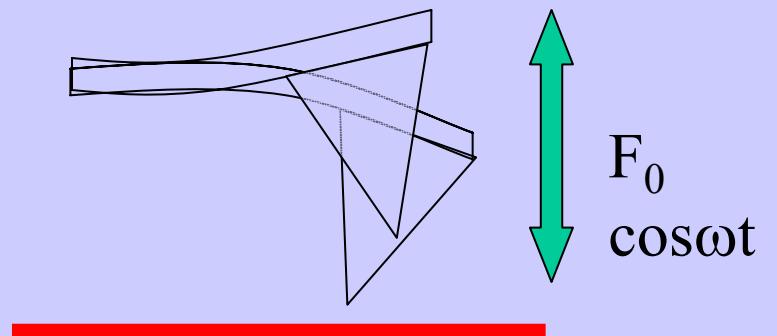
$k$  depends on the geometry  
and material

# More about springs

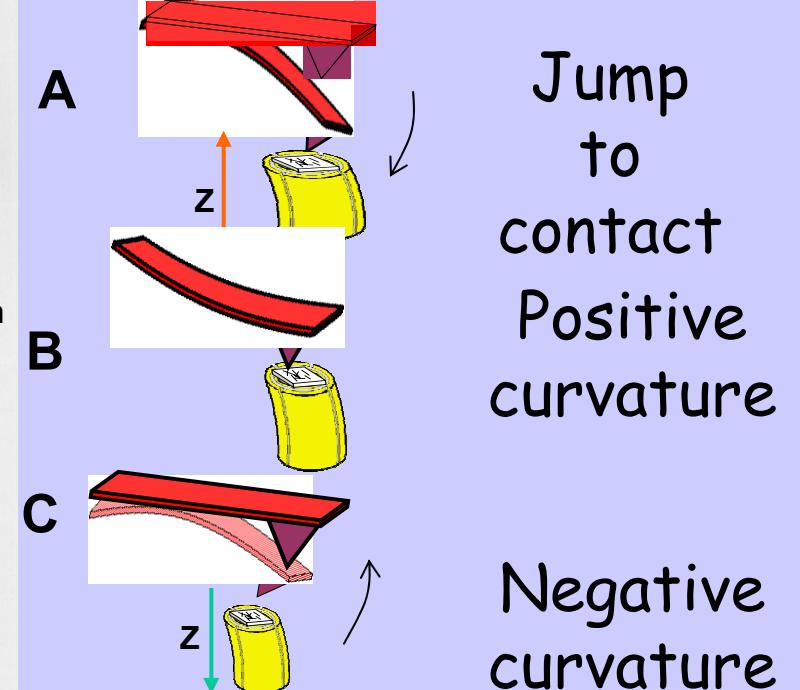
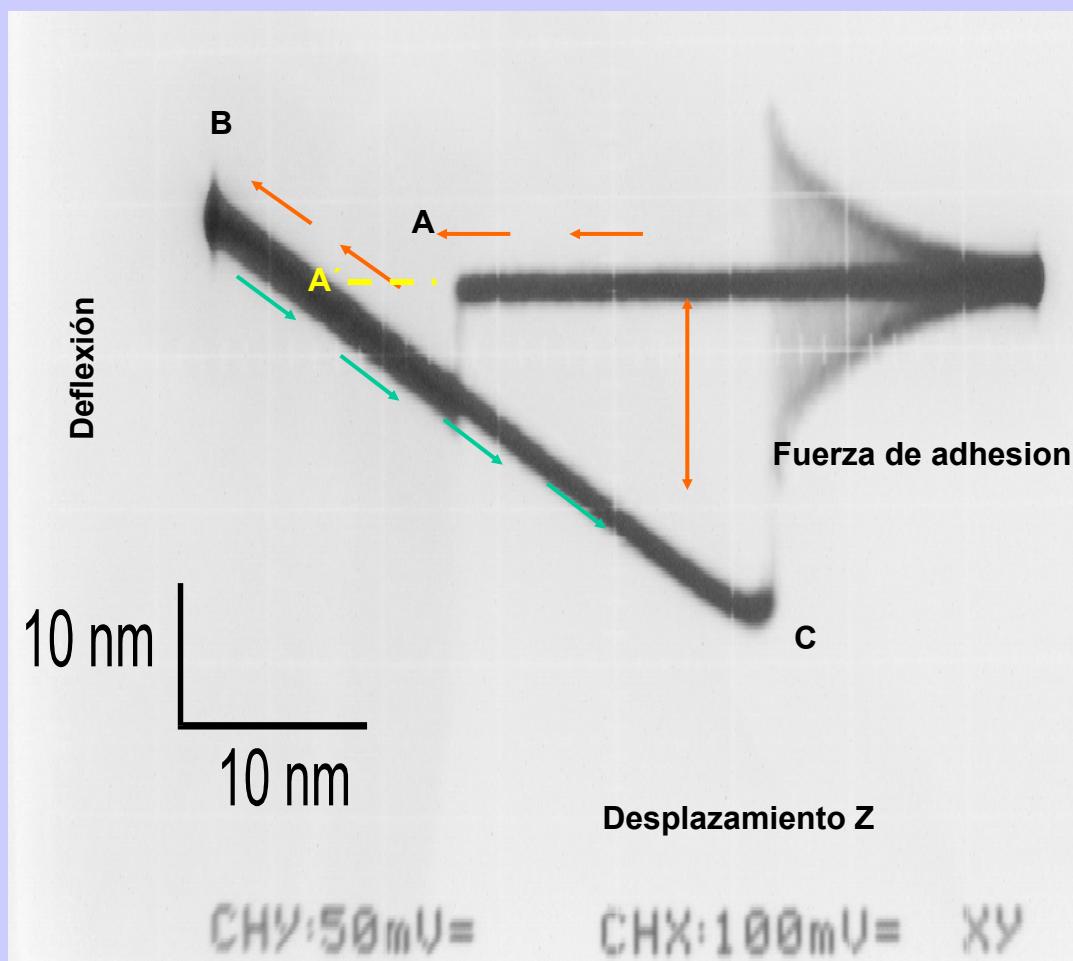
The resonance frequency of the cantilever also depends on the geometry and material, for a rectangular cantilever :  $\omega_0 = 0.162 \cdot (E/\rho)^{1/2} \cdot T/L^2$



$$D(\omega) = \frac{A}{\sqrt{(\omega_0^2 - \omega^2)^2 + 4 \cdot \beta^2 \cdot \omega^2}}$$

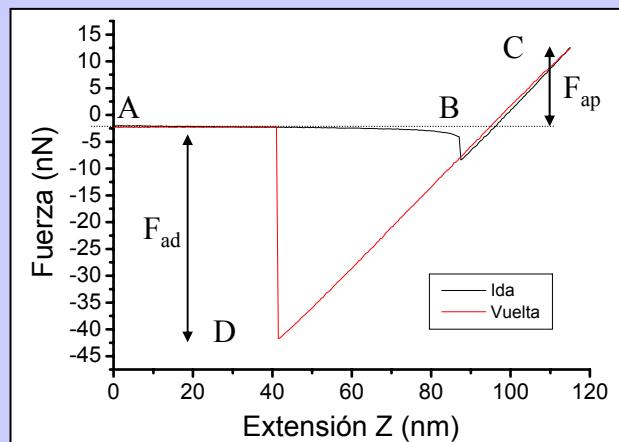


# Force vs. Distance curves

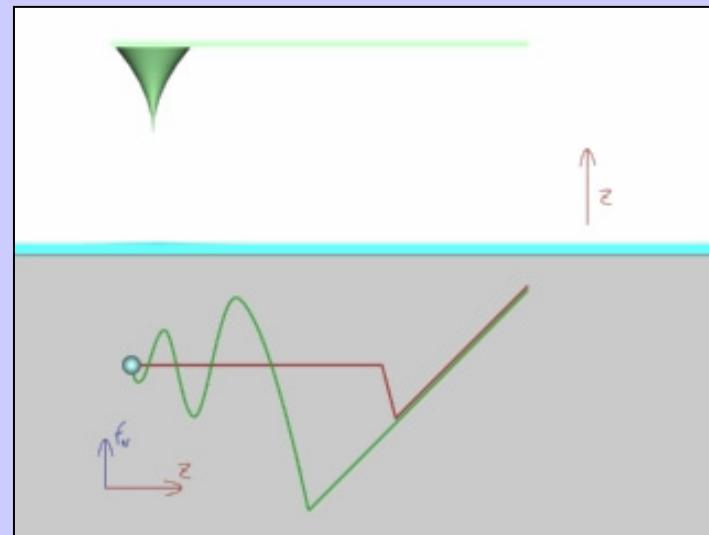


$$F_{\text{adhesión}} = F_{\text{NA}} - F_{\text{NC}}$$

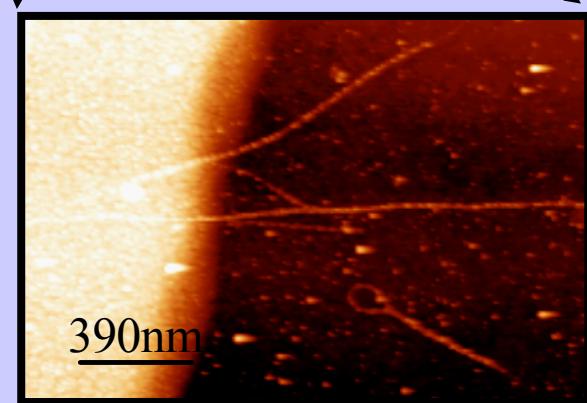
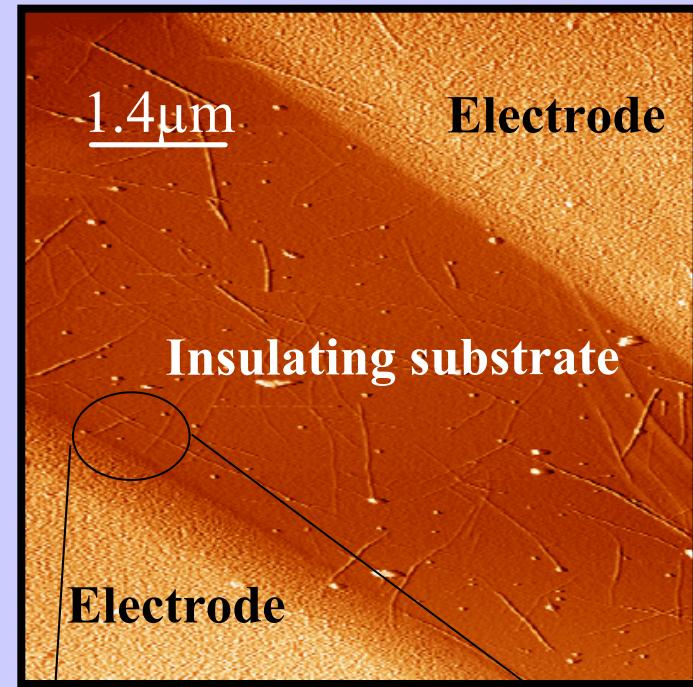
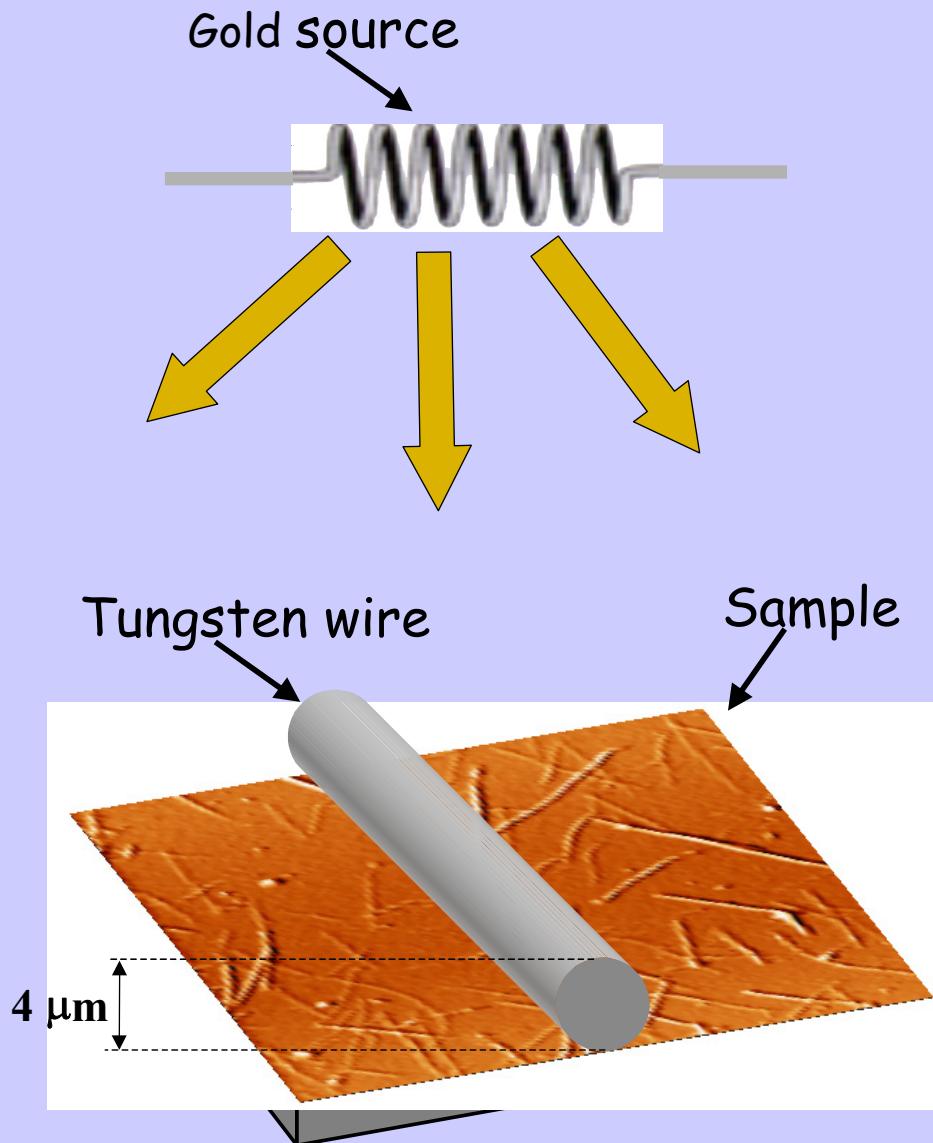
# Aire - JM -



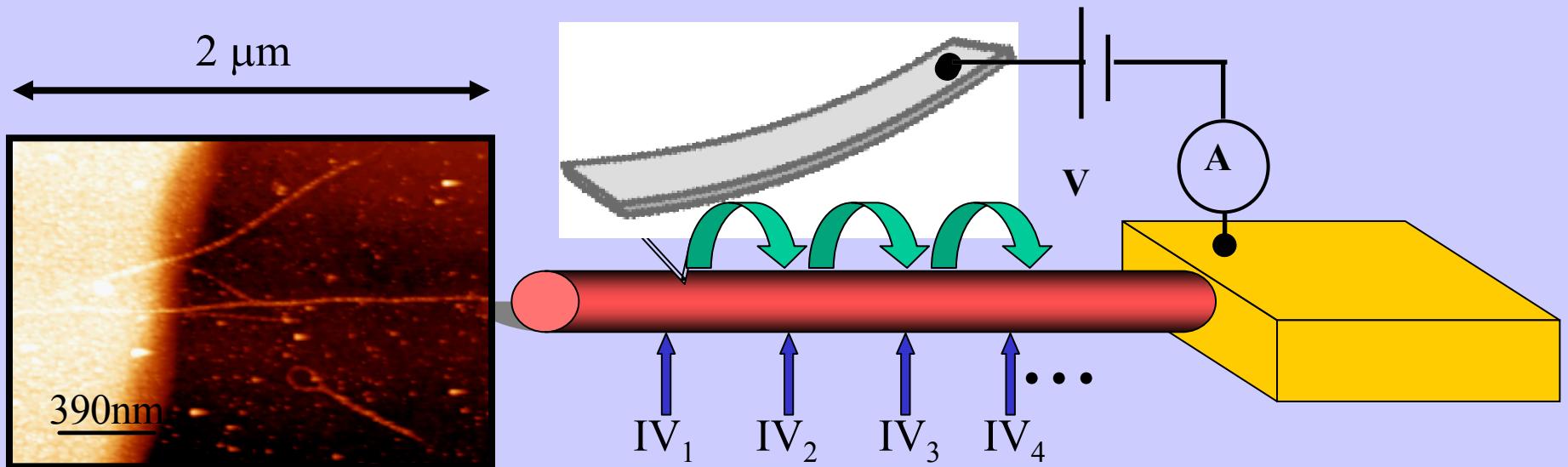
$$F_{tot} = |F_{ad}| + F_{ap}$$



# A different way to contact nanotubes



# The experimental set up



- Topographic images are taken in **non-contact** dynamic mode. The tip is few nanometers away from the surface
- Molecule contacted along its length.
- Current vs. Voltage measurement at each contact spot.

P.J. De pablo et al. Phys. Rev. Lett. **88**, 36804, (2002).

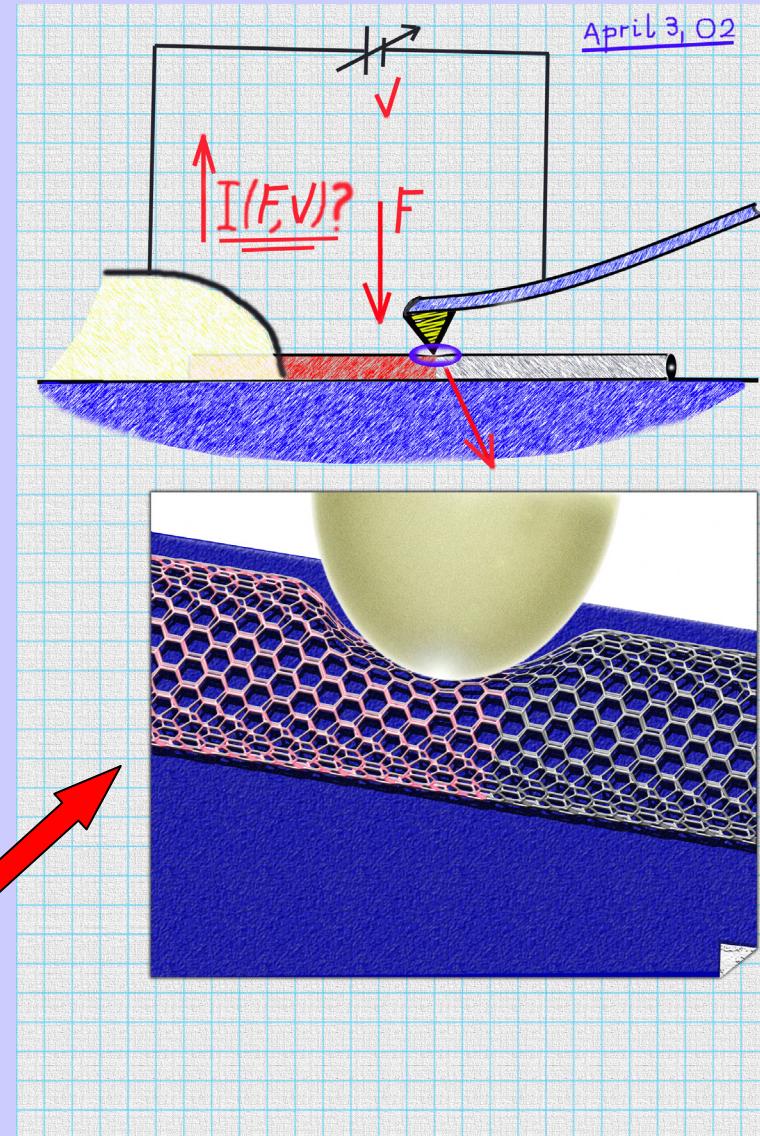
# Adventages

- It does not require any lithography facility
- It is very simple and unexpensive
- It allows to study the transport properties of the molecular wire as a function of the length
- It allows to study the transport properties of the molecular wire as a function of the applied force

# Contact formation and molecule deformation

- Same type of sample preparation
- The basic idea is to measure the current through the SWNT as a function of the force applied by the tip and the bias voltage

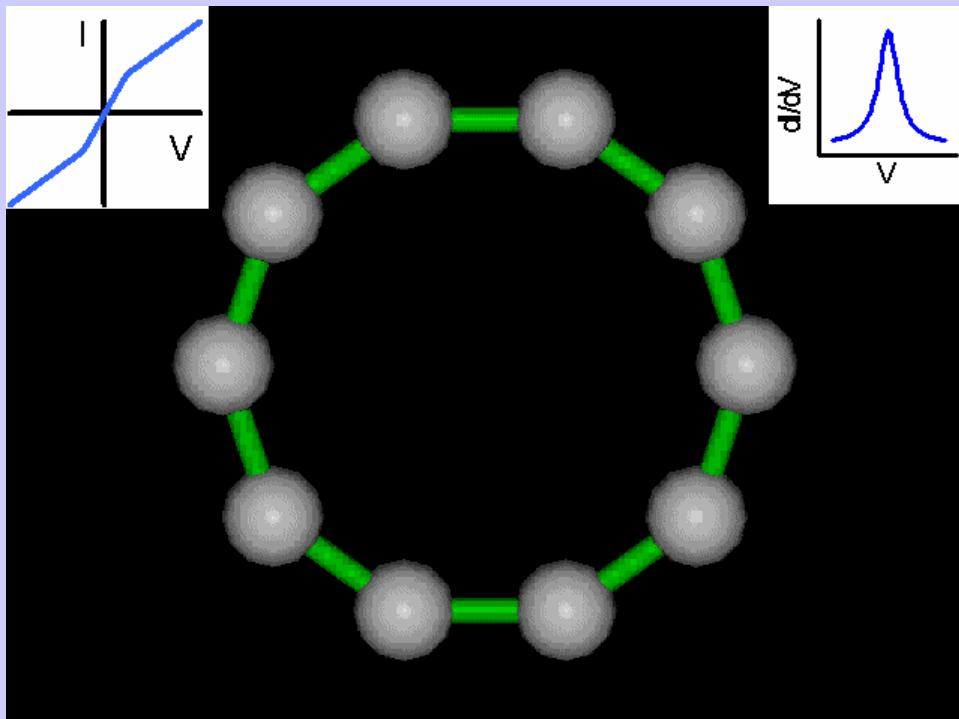
Just art!. In reality the diameter of the tip is 20 times larger than the diameter of the SWNT



# The problem

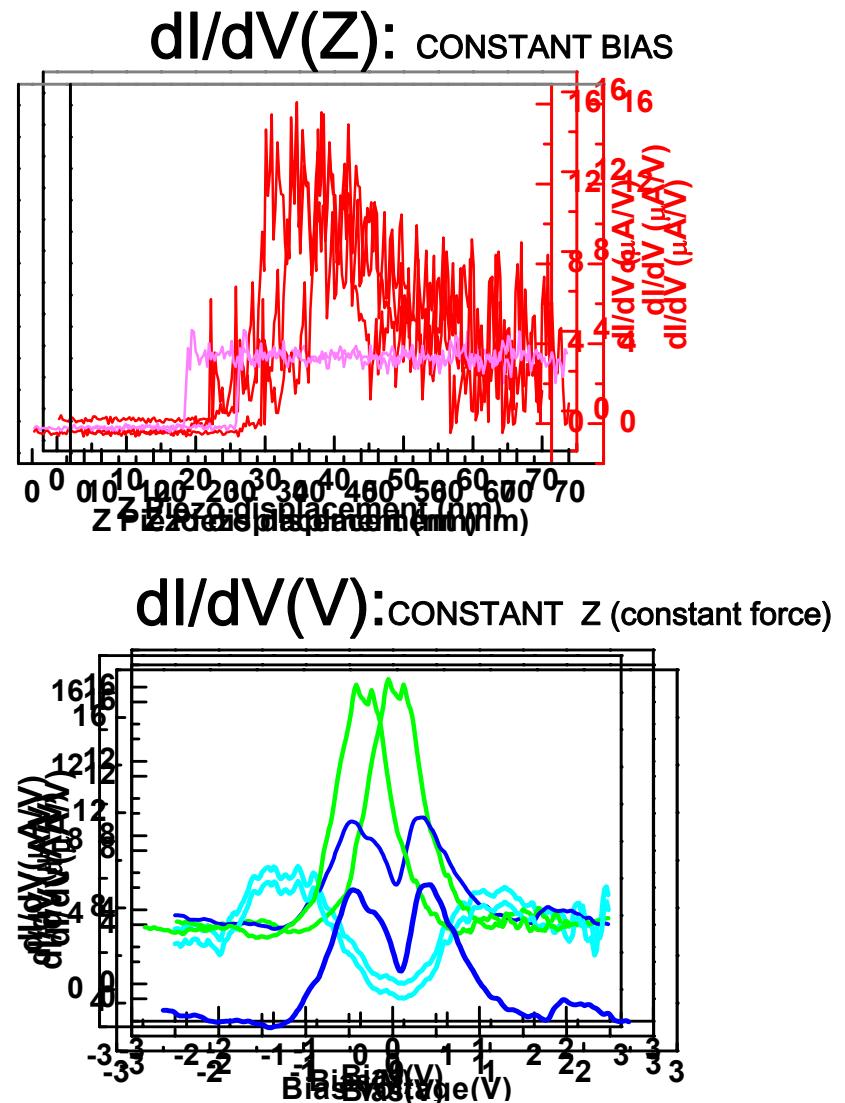
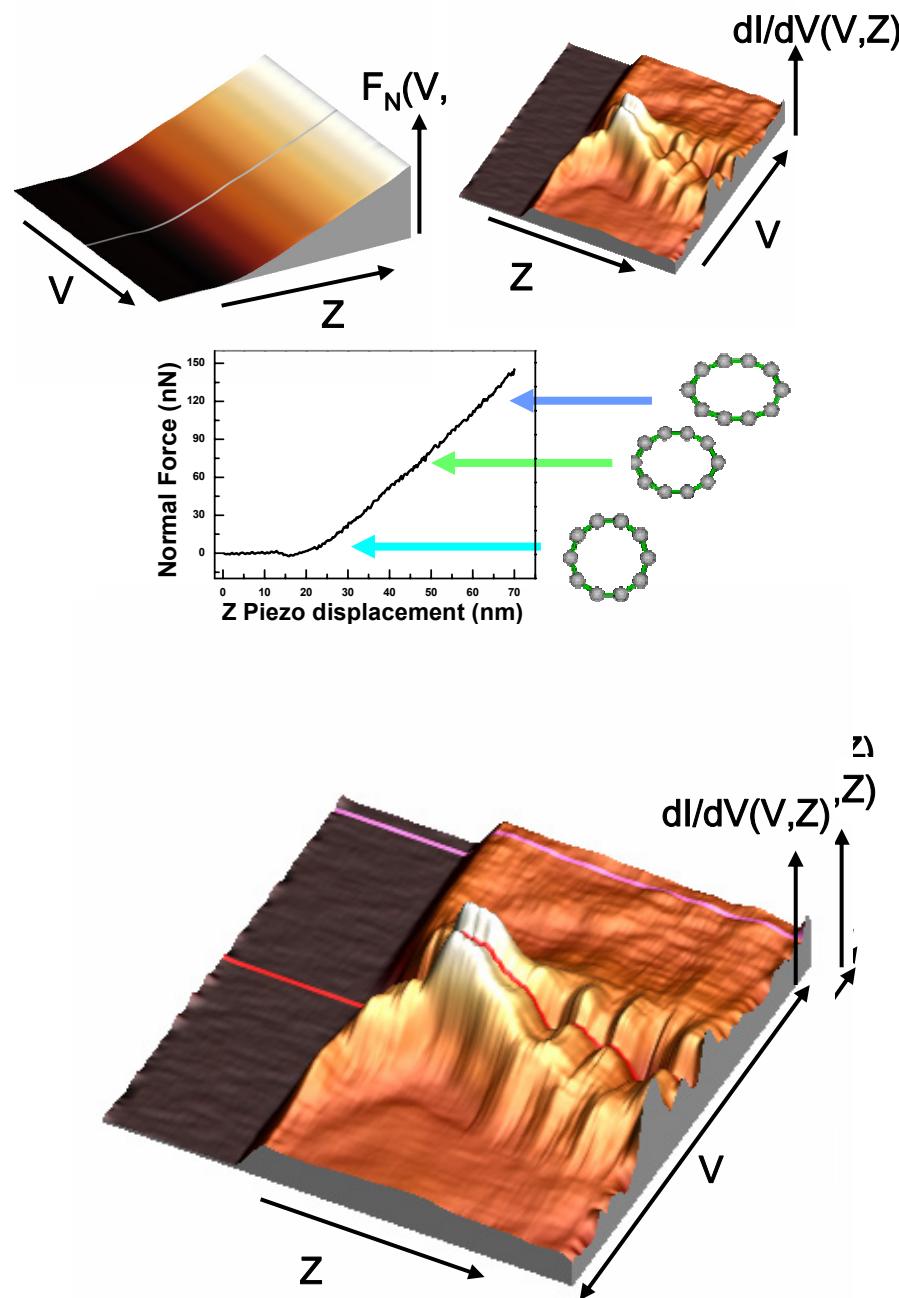
## The sequence of events

1. The gold tip loads the molecule
2. The mechanical and the electrical contact are established
3. The molecule gets deformed
4. The deformation changes the band structures and the conductance changes

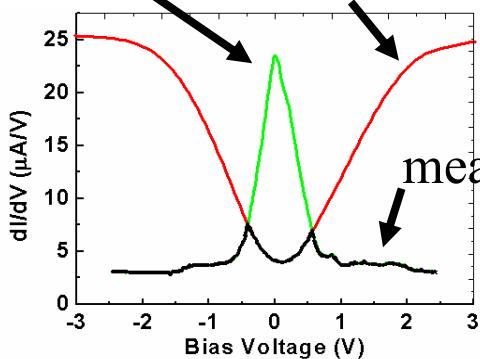


Normal force, current and differential conductance are simultaneously measured as a function of the tip-SWNT distance and the tip- SWNT bias voltage.

# Understanding magnitude maps

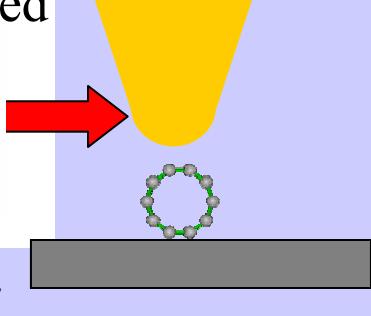
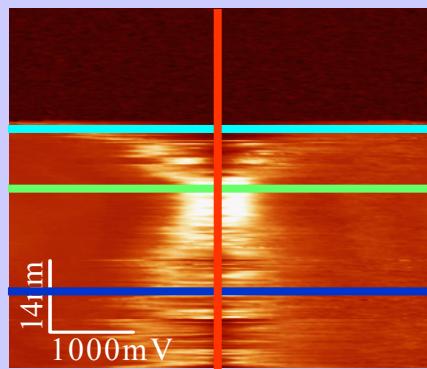


### SWNT Tunnel barrier



Differential conductance as a function of the tip=SWNT bias voltage  $dI/dV(V)$

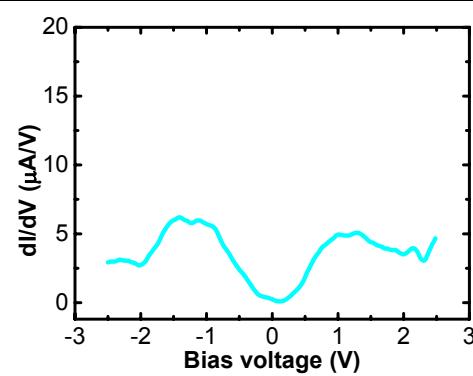
Differential conductance map  $dI/dV(V, F_N)$ .



CONTACT  
FORMATION

$$F_N = 10 \text{ nN}$$

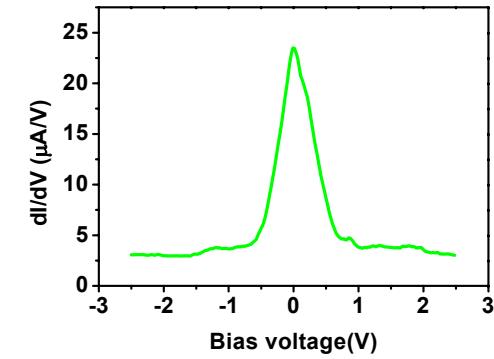
$$G(0) = 0.001 G_0$$



OPTIMUM  
CONTACT

$$F_N = 50 \text{ nN}$$

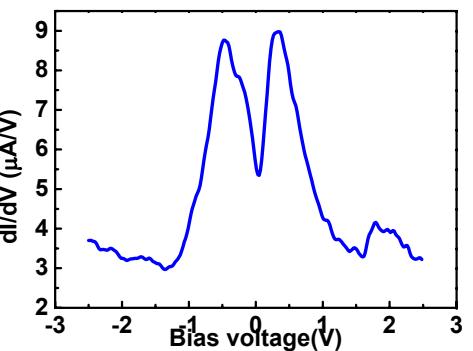
$$G(0) = 0.34 G_0$$



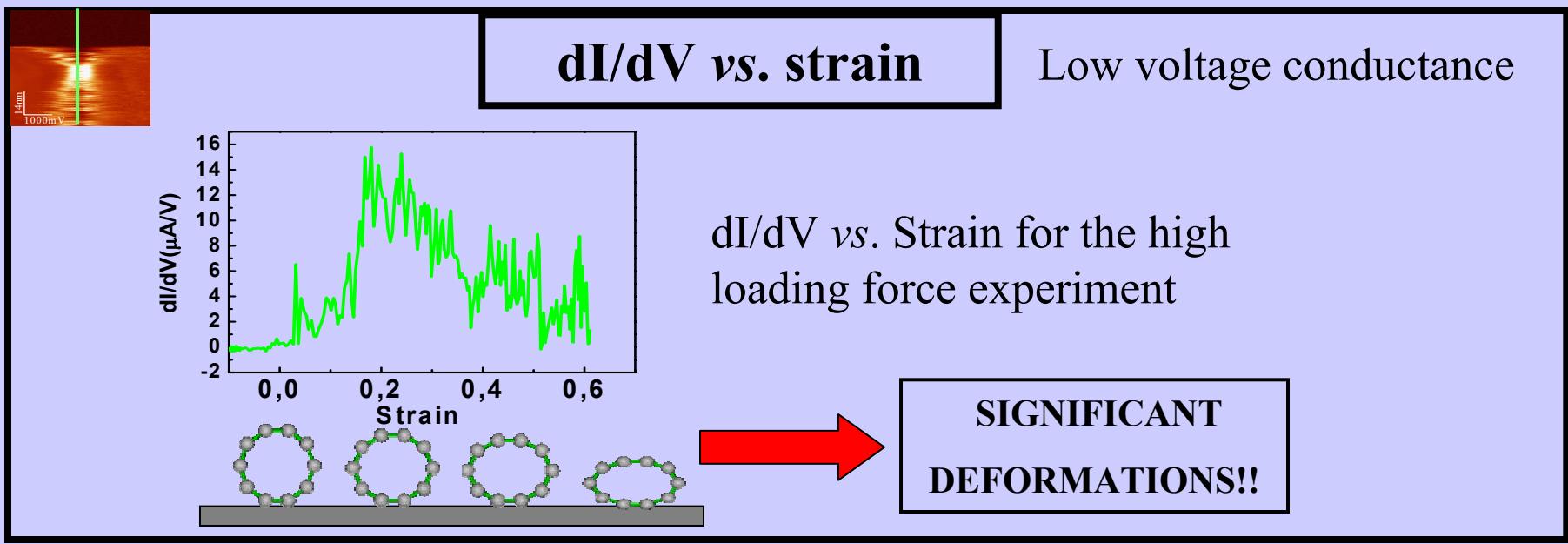
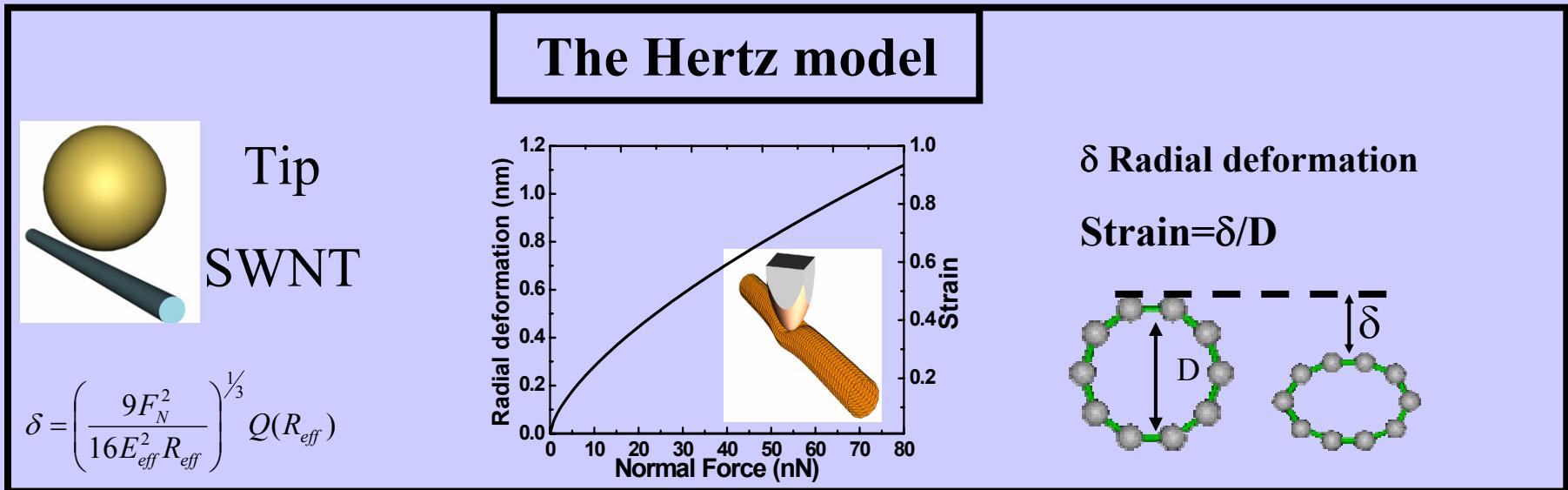
NANOTUBE  
DEFORMATION

$$F_N > 50 \text{ nN}$$

$$G(0) = 0.065 G_0$$

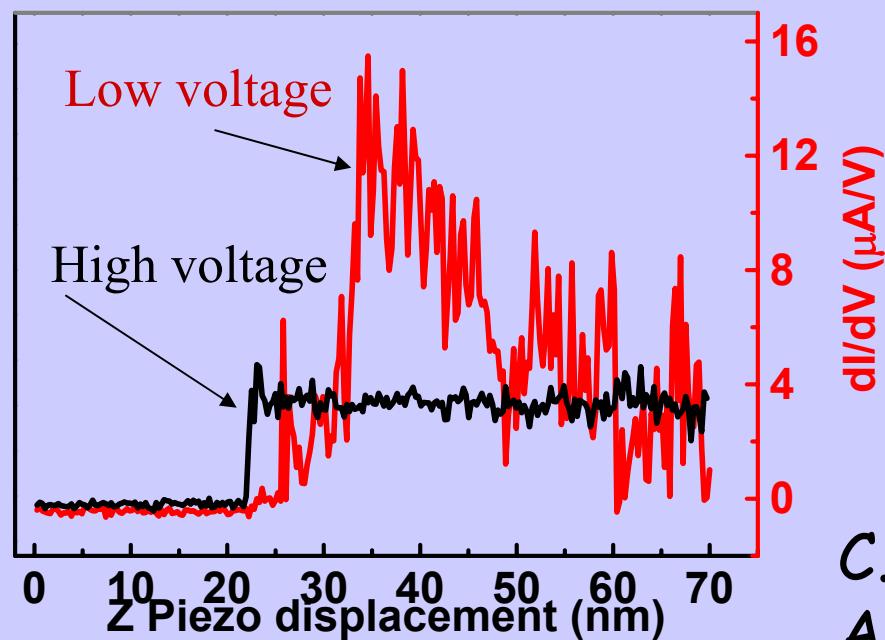


# ESTIMATION OF THE STRAIN



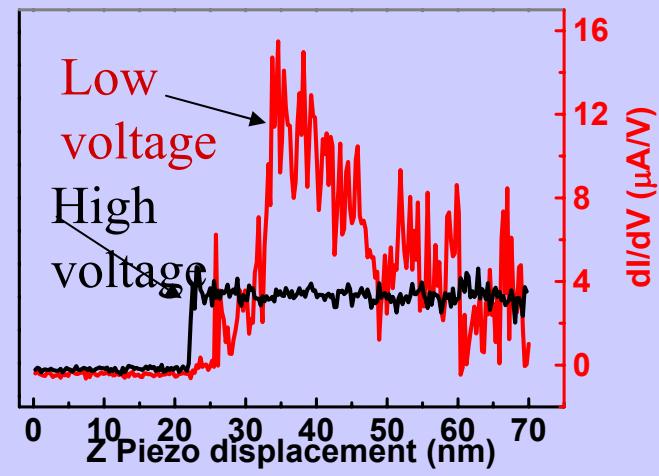
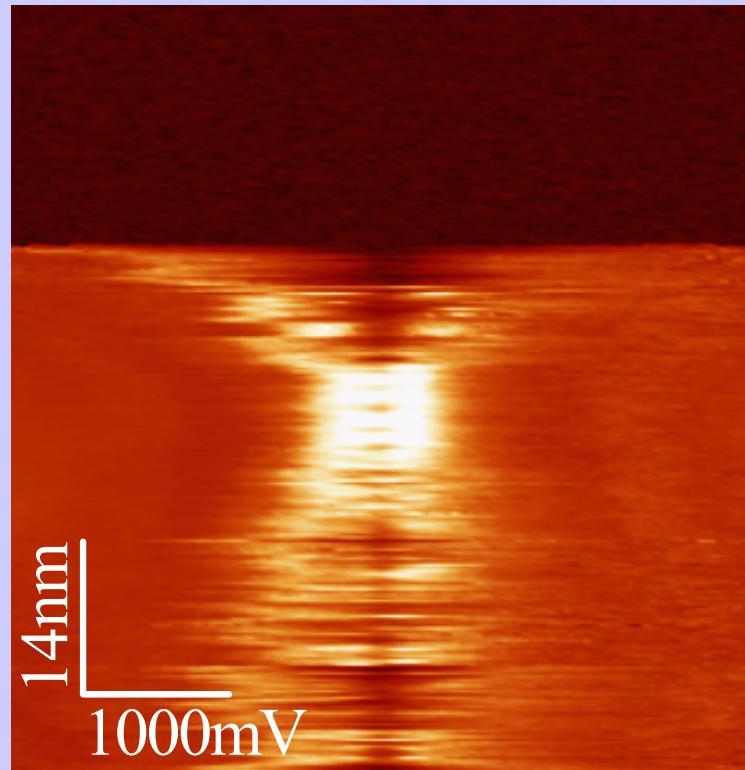
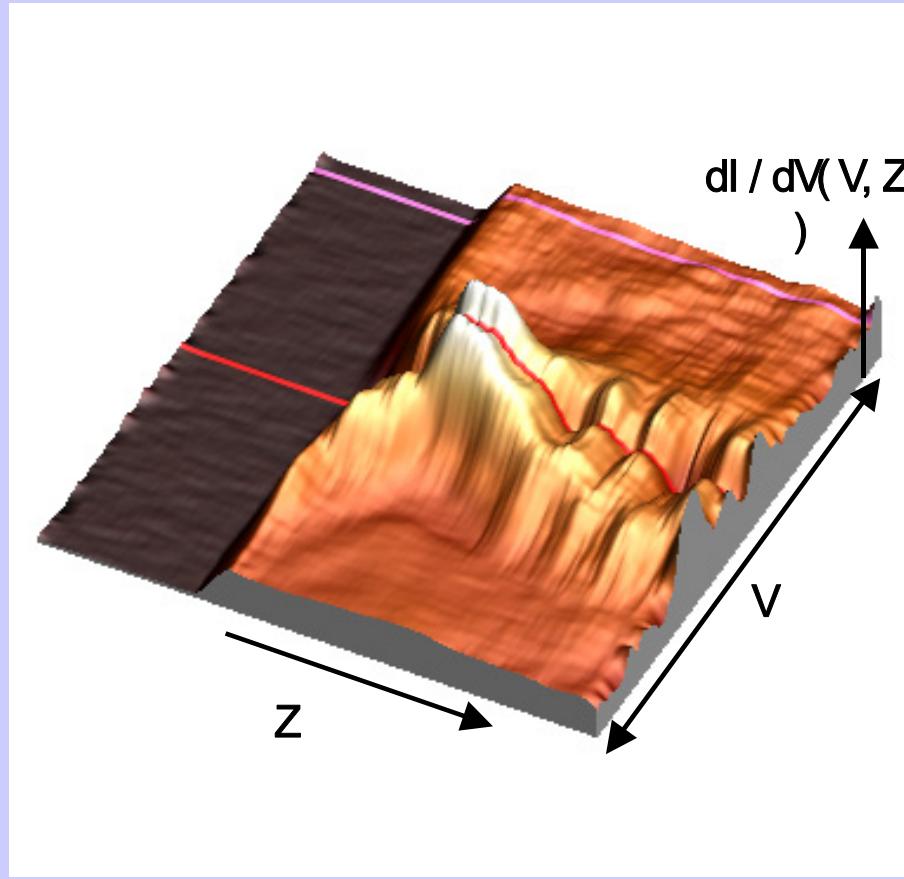
# From the experiments

- Low voltage conductance is very sensitive to the load.
- High voltage conductance remains constant with the load

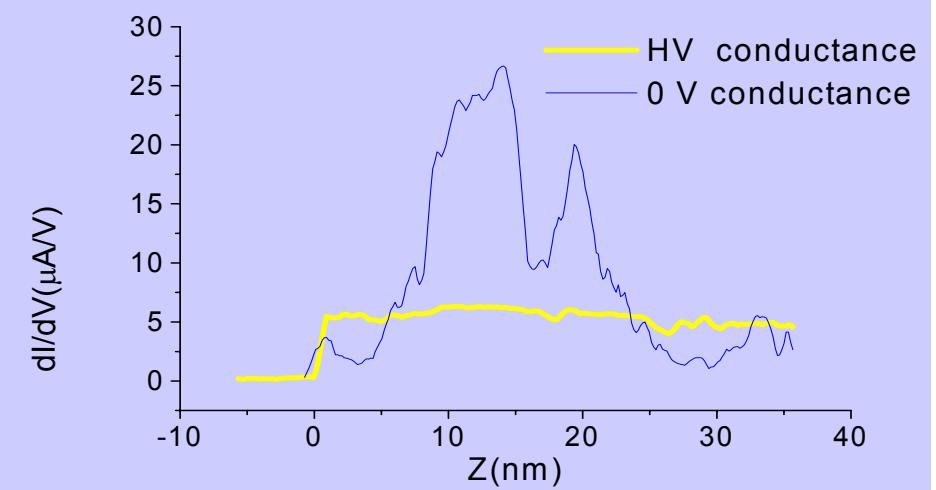
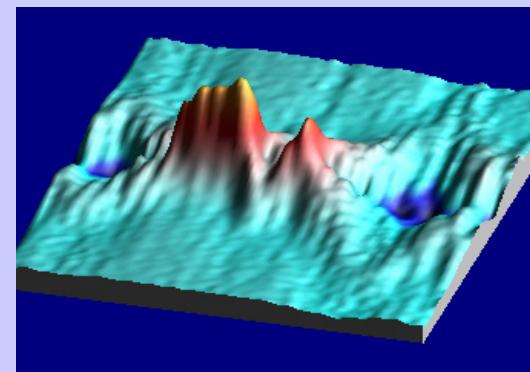
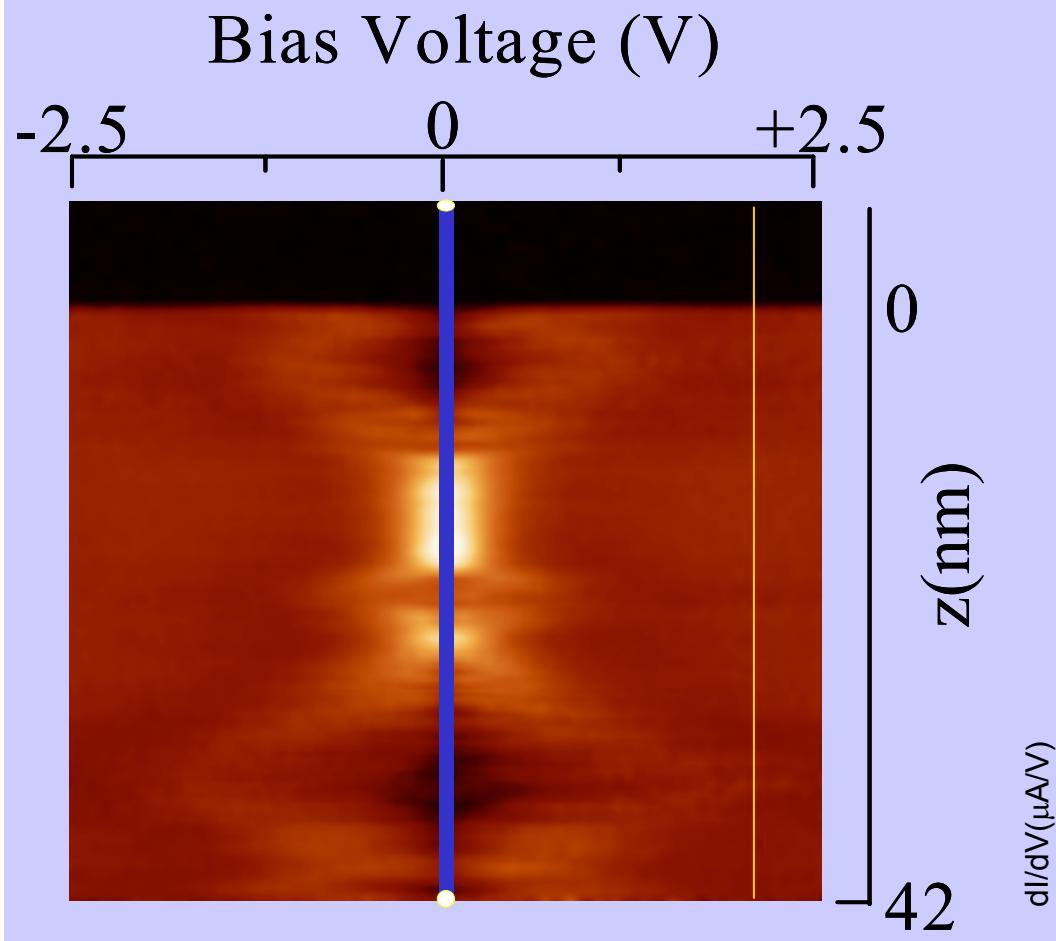


C. Gomez-Navarro et al.  
Adv. Mater. 16, 549, (2004)

# Noise?



# The unexplained: low bias conductance oscillations



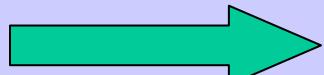
# The problem

~~$R = \rho L/S$~~

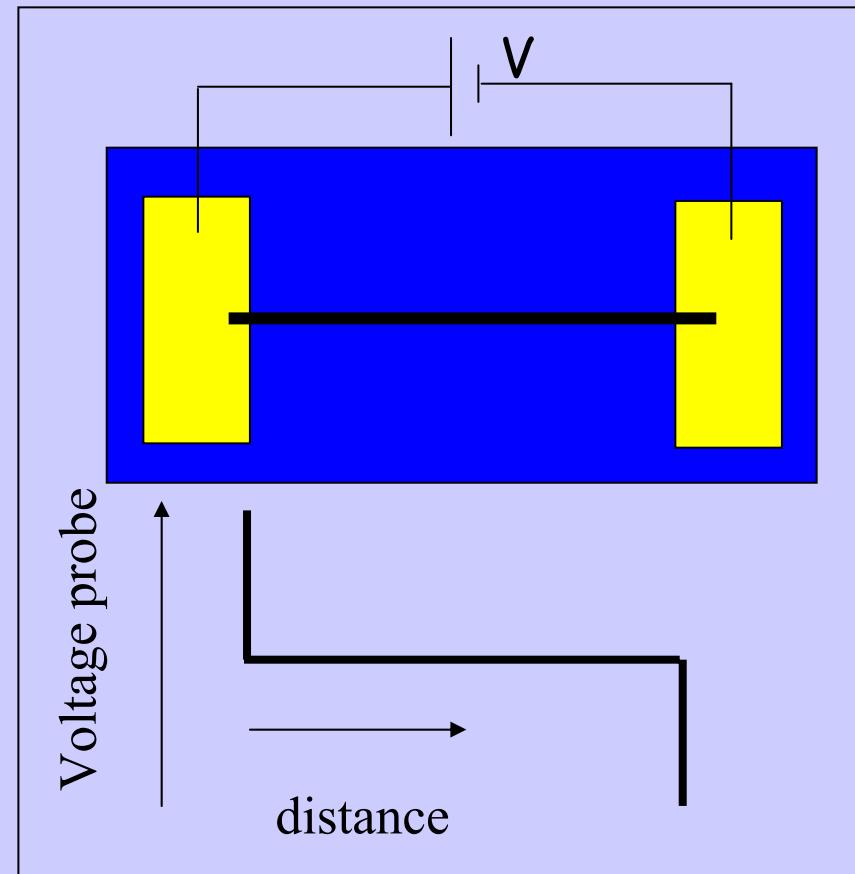
Not valid any longer

Landauer resistance for 1 atom

The quantum resistance  $R_0 = h/2e^2 \approx 13 \text{ k}\Omega$

Ideal voltage drop 

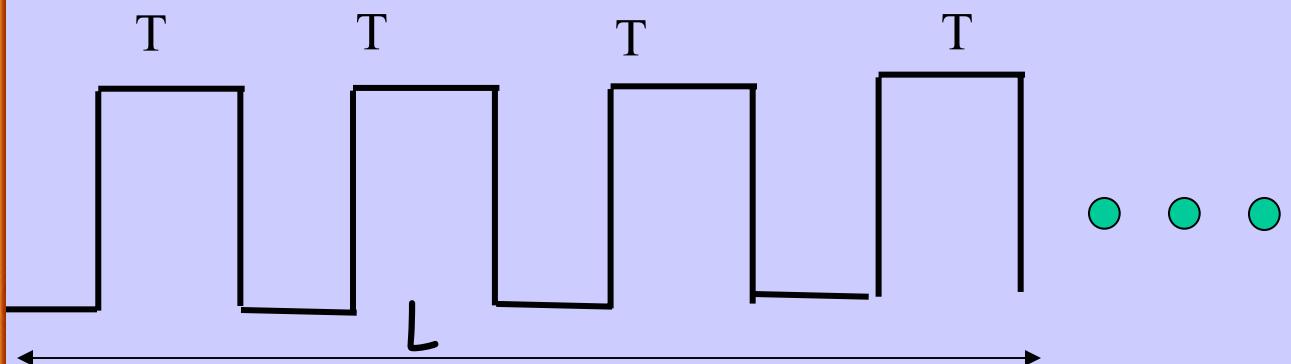
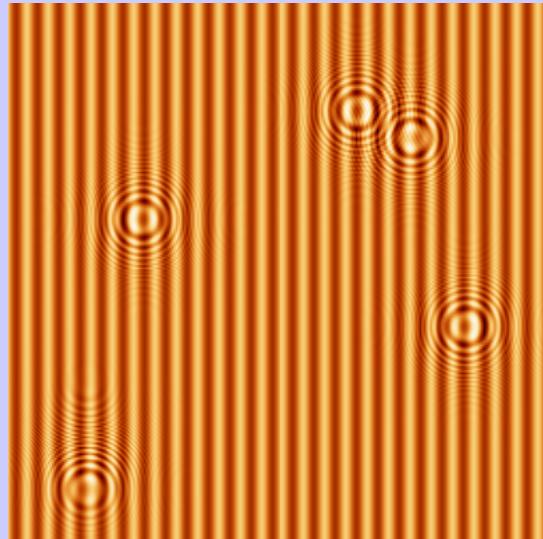
A **perfect** carbon nanotube can be seen as an extended orbital where electrons can freely propagate (metal carbon nanotubes have two orbitals at the fermi level) this is called ballistic transport.



# Elastic scattering with defects

Electrons within an orbital behave more like waves than particles. Electrons in carbon nanotubes behaves quite similar to light in optical waves. There is no dissipation when the electrons hit the defects.

Simple model: one-dimensional barriers



→ Wave propagation

Simple model: each defect has a transmittivity  $T$ ;  $G=G_0 T^n$ . Since  $0 < T < 1$ ,  $G$  drops exponentially with the length

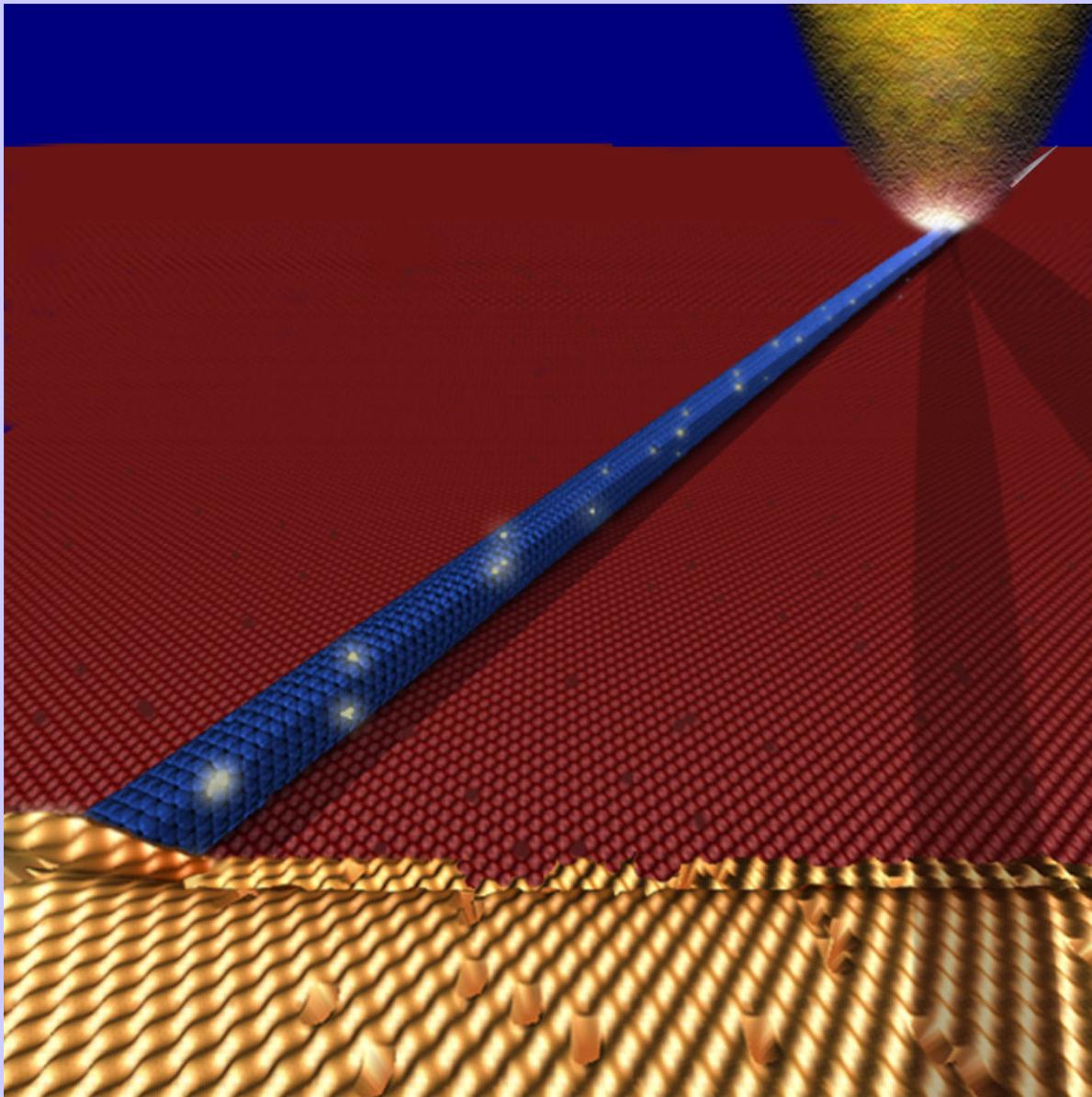
# Concept: strong Anderson localization

In a system where the elastic electron mean free path  $L_m$  is much smaller than the phase coherent length  $L_\phi$  interference effects are really important giving rise to the so called strong Anderson localization  $L_0$ . In this regime the conductance drops exponentially with the length of the conductor.

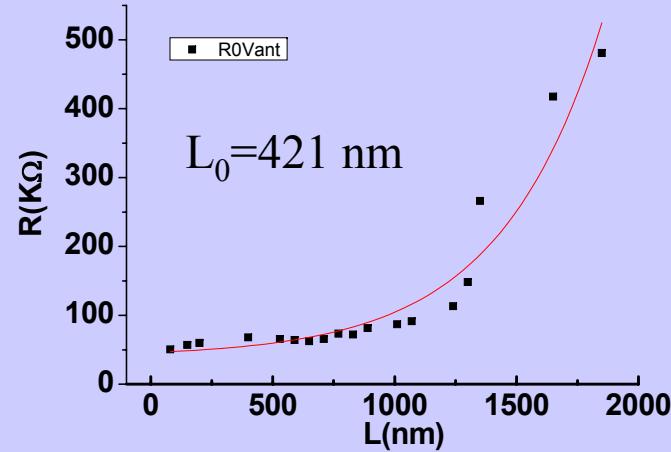
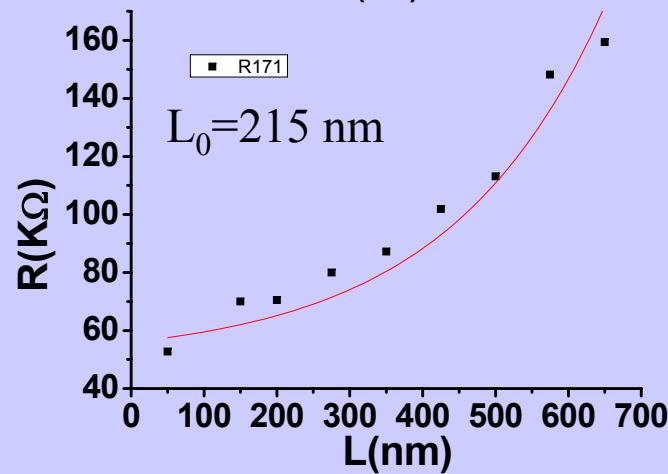
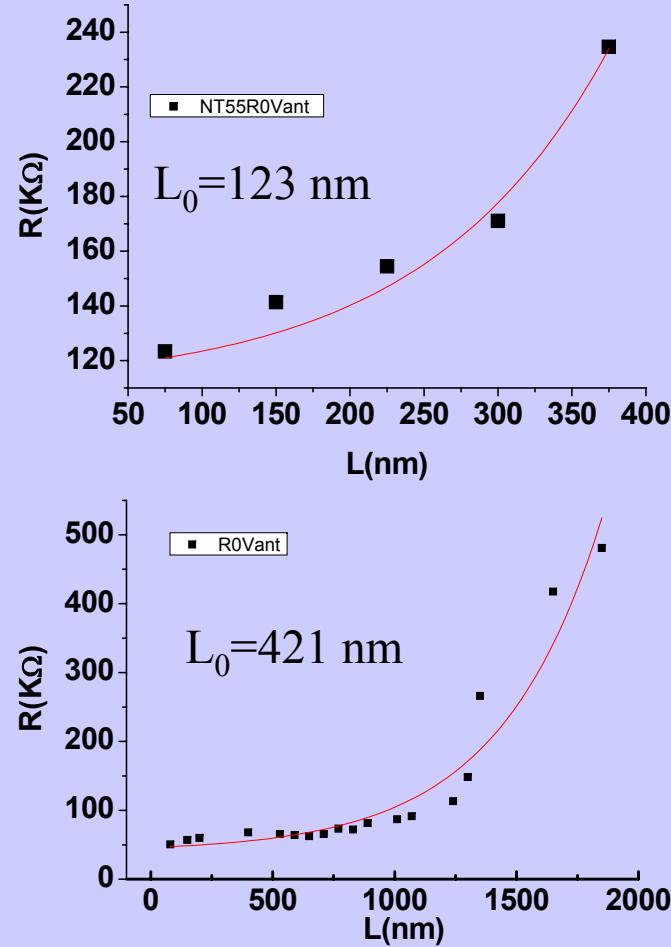
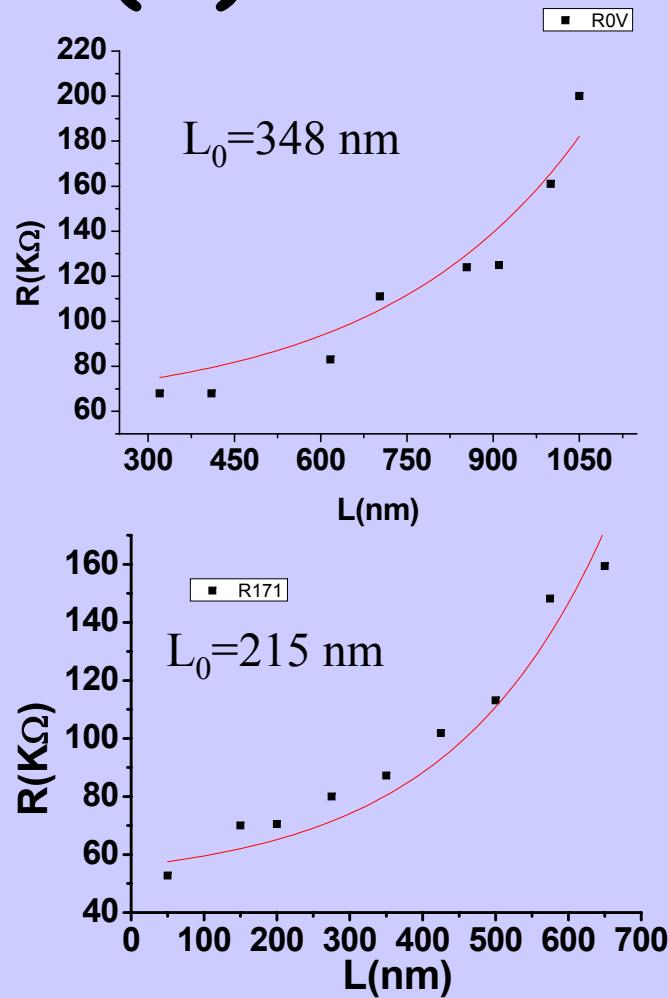
$$G \sim \exp(-L/L_0)$$

As the number of defects increases the localization length decreases.

Tunning the conductance of single wall carbon nanotubes by ion irradiation in the strong localization regime.



# $R(L)$ for SWNT *as grown*



1 HipCo arc discharge SWNTs from Carbon Nanotechnologies.

2 The resistance is obtained around 0V (Low Voltage Resistance LVR)

# Experimental procedure

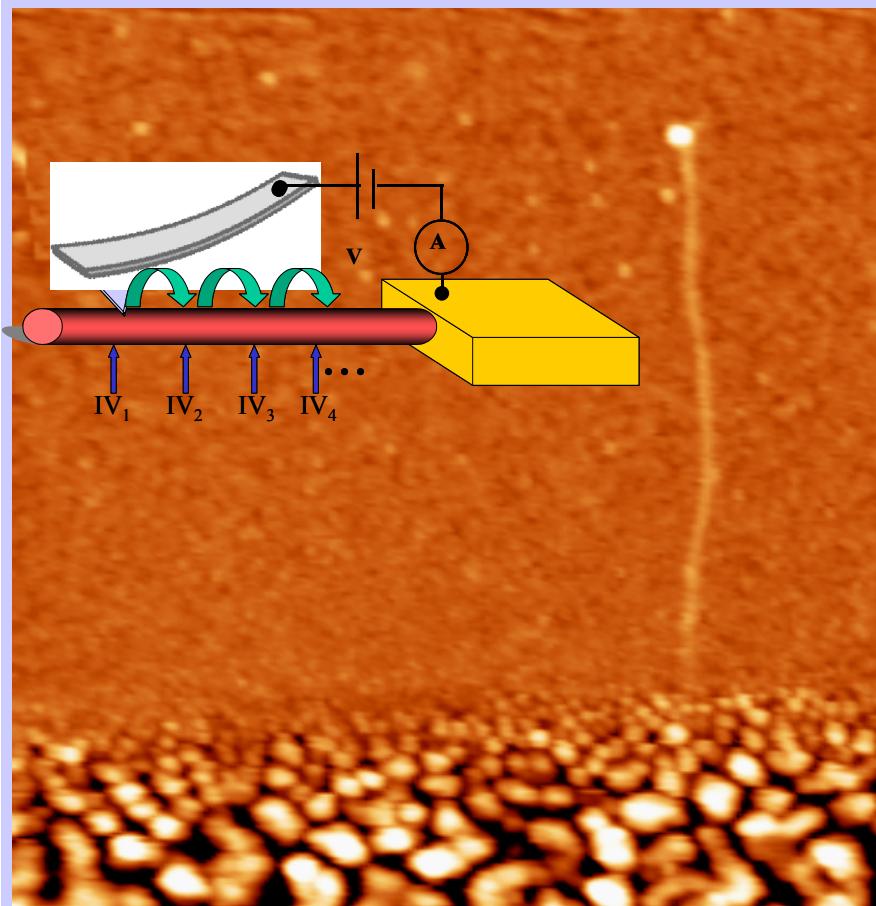
1. A gold electrode is evaporated on a sample with SWNTs deposited on mica.
2. A metallic SWNT is found
3. For this nanotube  $R(L)$  is determined. If the  $R(L)$  is repeated along the SWNT the same  $L_0$  is found within a 5%
4. The sample is irradiated during 5 or 10 seconds with  $0.1 \mu\text{A}$  of  $\text{Ar}^+$  ions at 120 eV energy.
5. The **same** nanotube is located and the  $R(L)$  is measured
6. Back to point 4

# Calculations on Ar<sup>+</sup> irradiation

- From Krasheninnikov et al. Phys rev. B **6324**, 245405 (2001) it is predicted that:
  - The main effect of ion irradiation is to create vacancies.
  - Above 100 eV ion energy, each ion creates almost one vancancy (mono-vacancy or di-vacancy).
  - A collision creates a di-vacancy with a probability ranging between 0.3 and 0.4. The rest are mono-vacancies

# Before irradiation

$$\text{Fit to: } R(L) = R_c + \frac{1}{2}R_0 \cdot \exp(-L/L_0)$$

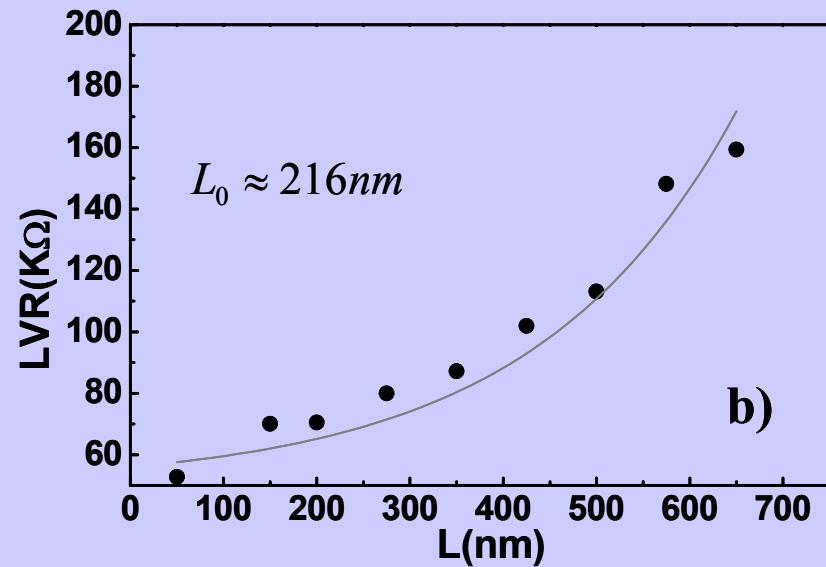


$R_c$  ≡ Contact resistance

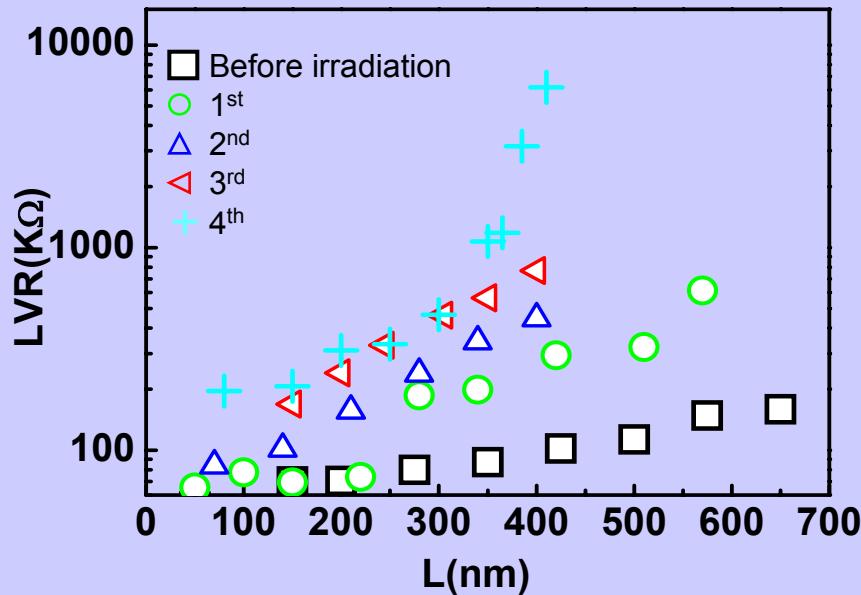
$\frac{1}{2}$  accounts for the 2 conductance channels in metallic SWNTs.

$R_0$  Landauer resistance

$L_0$  localization length.

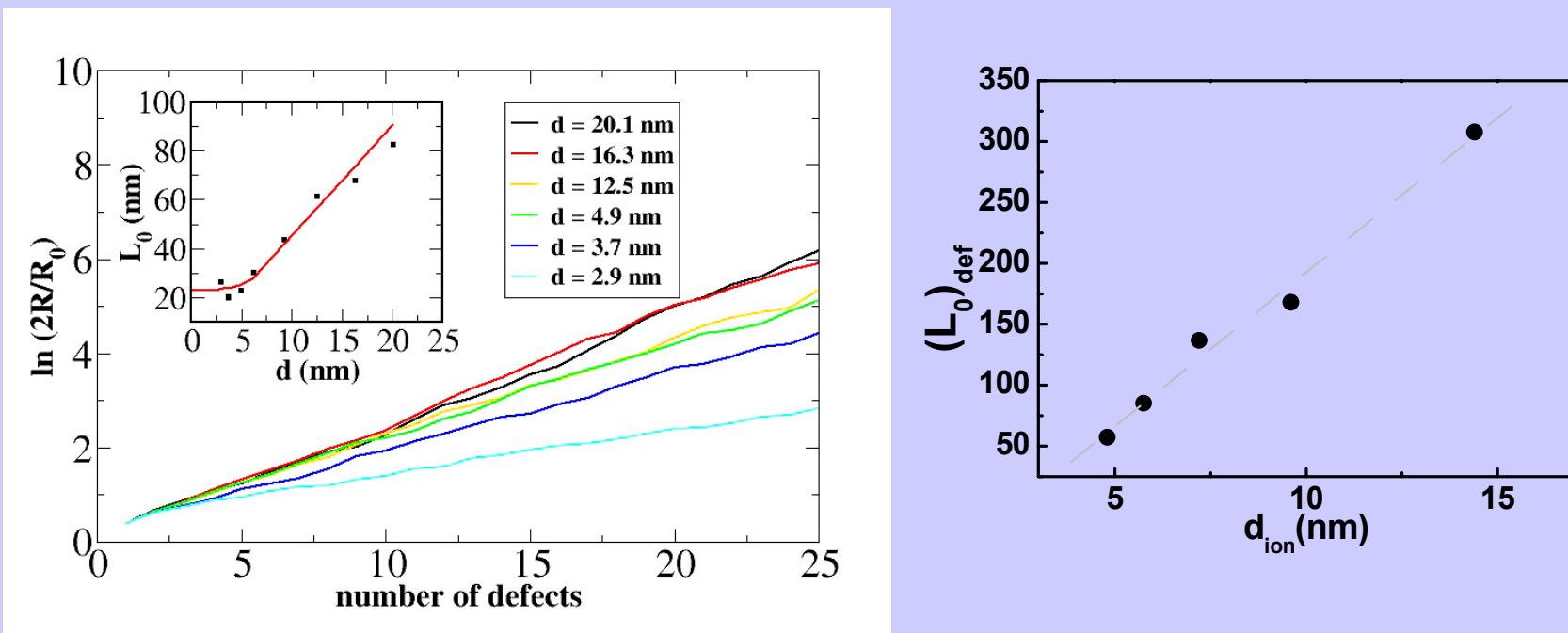


# $L_0$ for consecutive irradiation doses in a SWNT



## Remarks

- 1) The localization length drops with the irradiation dose
- 2) Calculations shows that the drop in conductance due to mono-vacancies is much smaller than the one produced by di-vacancies.



Irradiation #	Irradiation time (s)	Colliding Ar <sup>+</sup> ion/C atom (%)	Average distance between colliding ion $d_{\text{ion}}$ (nm)	$(L_0)_{\text{total}}$ (nm)	(*) $(L_0)_{\text{defect}}$ (nm)	(**) Average distance between di-vacancies $d$ (nm)
0	0	0		215.9		
1 <sup>st</sup>	10	0.043	14.4	126.9	308	67
2 <sup>nd</sup>	15	0.064	9.6	94.5	168	37
3 <sup>rd</sup>	20	0.086	7.2	83.7	137	30
4 <sup>th</sup>	25	0.107	5.8	61.1	85	19
5 <sup>th</sup>	30	0.129	4.8	45.2	57	14

(\*) From  $1/(L_0)_{\text{total}} = 1/(L_0)_{\text{ini}} + 1/(L_0)_{\text{defect}}$

(\*\*) Using  $d \approx (L_0)_{\text{defect}}/4.6$

# Conclusions

- Defects are extremely important on the LVR of SWNTs.
- Just 0.03% of di-vacancies produce an increment of 3 orders of magnitude on the resistance of a 400 nm SWNT.
- Experimental data reveals an exponential dependence of the LVR vs. Nanotube length suggesting strong Anderson localization.
- By comparing theory and experiment we find that 1 out of 4 collisions creates a di-vancancy in good agreement with calculation from Krasheninnikov et al.
- Ion irradiation can be used to taylor LVR of SWNTs.