Nanotube-Based Structures for Superstrong Materials, Nanoscale Sensors and Devices, and Efficient Electron Emitters

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I. Introduction to nanotubes

II. Mechanical properties: the strongest materials known

III. Energy storage: high capacity, fast charging Li/NT batteries

IV. Pyro- and piezo-electric effects in BN/C nanotubes

Composite BN/C nanotubes – field emission

V. Nanotube-metal clusters sensor structures

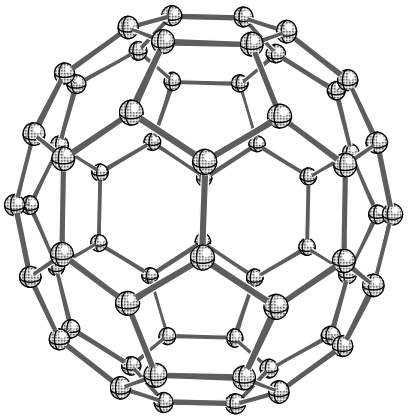
single molecule sensitivity

VI. Summary

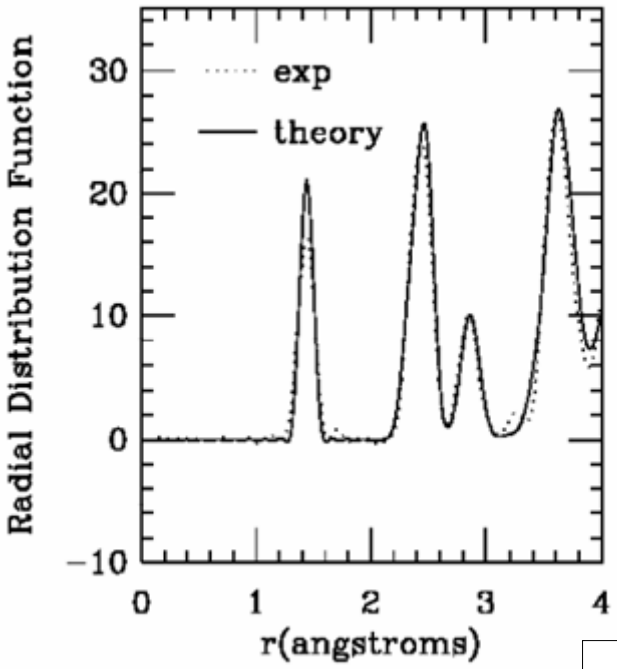
Early simulation of C_{60} solid

solid C_{60} geometry optimization
no symmetry constraints
fcc structure, a=14.2 Å (from exp.)

	C-C distance [Å]	
	Double	**Single**
CP (35 Ry)	**1.40**	**1.45**
CP (26 Ry)	**1.41**	**1.45**
exp (NMR)	**1.40**	**1.45**

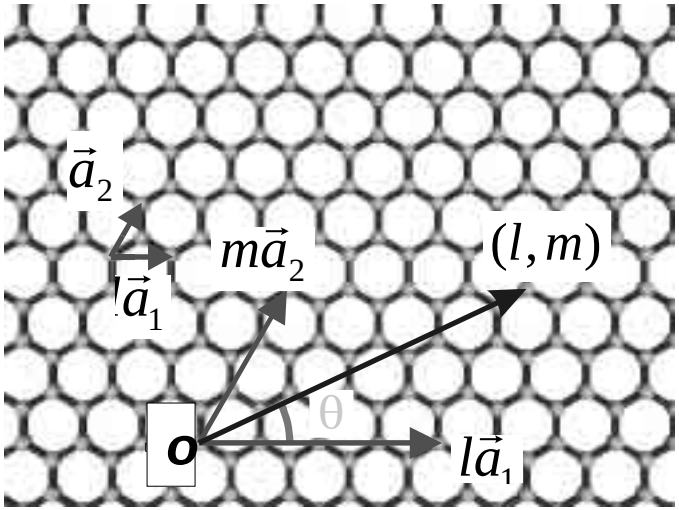


Zhang, Yi,
Bernholc, PRL 91

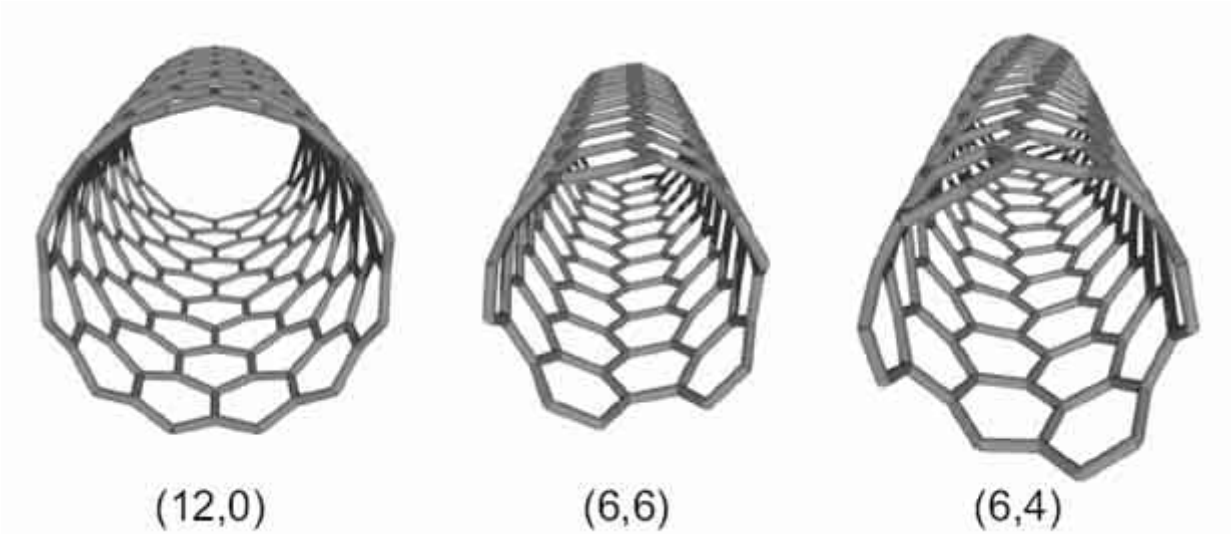


excellent agreement with photoemission
(Weaver et al), EXAFS (Cox et al), NMR,
and also with subsequent neutron diffraction data
(Li, Lannin, et al)

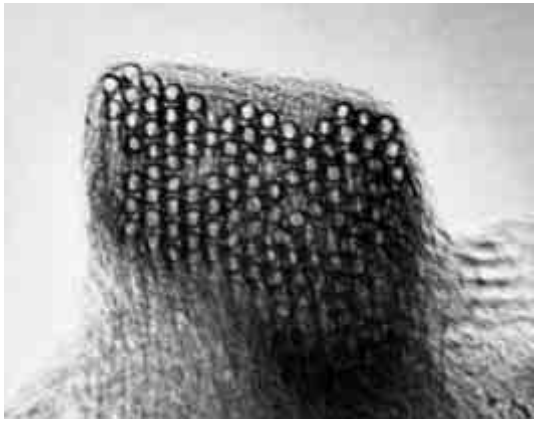
Introduction to nanotubes



	Properties	*(l,m)* relation
Geometric	**radius**	$R = \frac{\sqrt{3}d\sqrt{l^2+m^2+lm}}{2\pi}$
	chiral angle	$\theta = \arcsin\frac{\sqrt{3}m}{3\sqrt{l^2+m^2+lm}}$
Electronic	**metal**	$\mathrm{mod}(l-m)=3$
	semi-conductor	$\mathrm{mod}(l-m)\neq 3$



zigzag armchair chiral



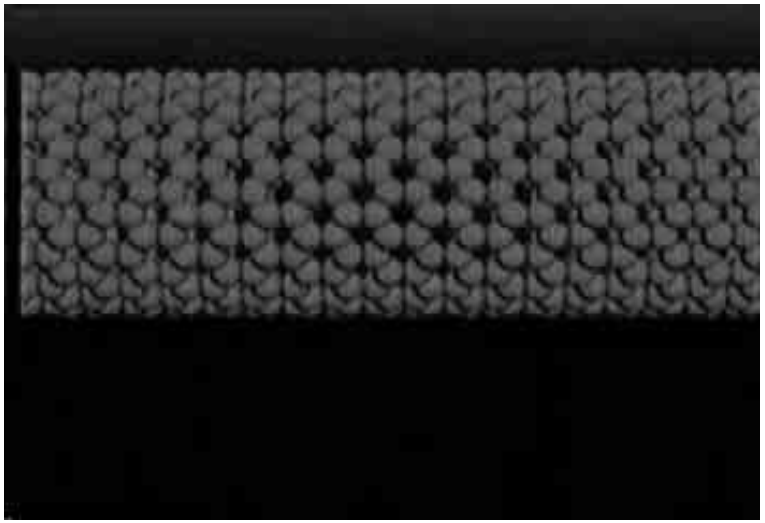
nanotube “rope”

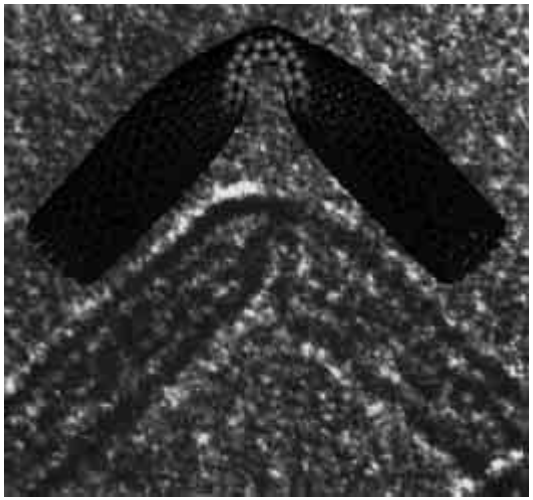
Thess, Smalley, et. al., Science 96

Elasticity and Breakage of Carbon Nanotubes

Bending

Iijima, Brabec,
Maiti, Bernholc
JCP 104, 2089 (1996)

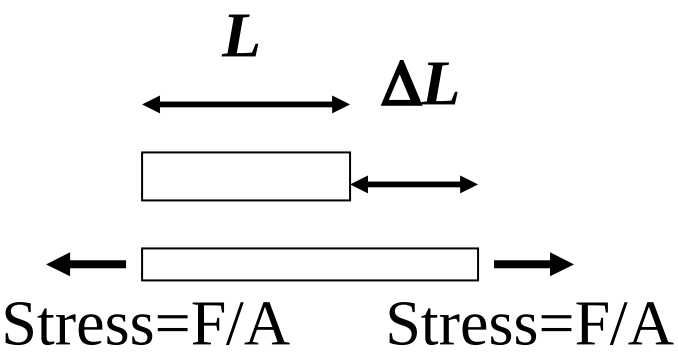




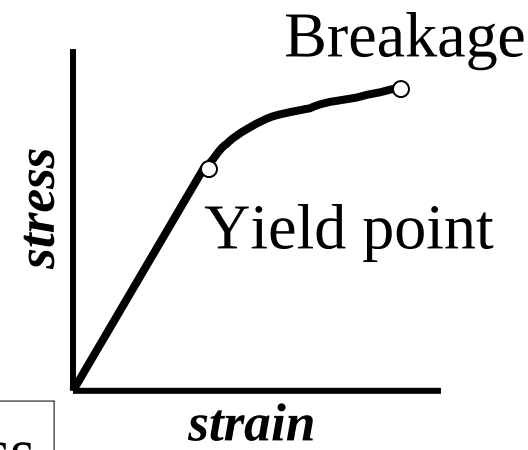
Compression

Yakobson, Brabec, Bernholc
PRL 76, 2511 (1996)

Introduction to strength of materials



$$\frac{F}{A} = Y\frac{\Delta L}{L}$$

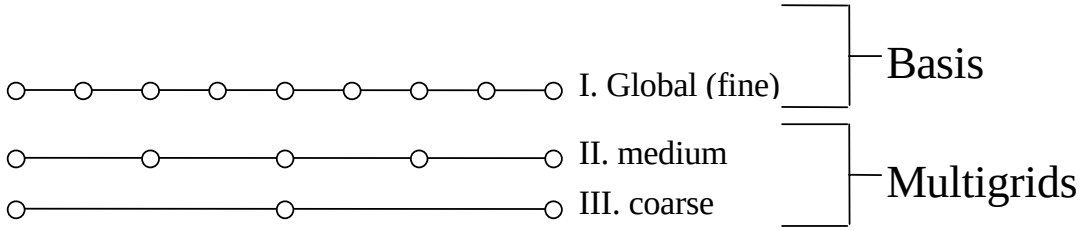


Young's modulus determines stiffness

Material	Y [GPa]	Yield point [GPa]	Max $\Delta L/L$ [%]
Graphite	1080	31.3	2.9
Steel	220	4.2	1.9
Glass	168	3.6	2.2
Silicon	163	4.1	2.5

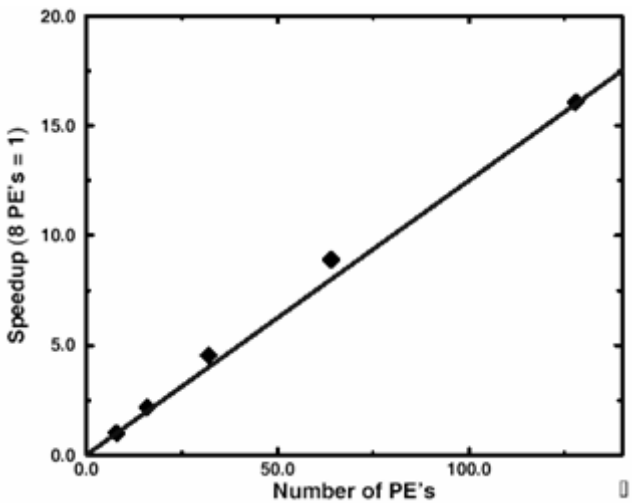
Most materials can be stretched by at most 3%.

Multigrid method for quantum simulations



- **Density functional equations solved directly on the grid**
- **Multigrid techniques remove instabilities by working on one length scale at a time**
- **Convergence acceleration and automatic preconditioning on all length scales**
- **Non-periodic boundary conditions are as easy as periodic**
- **Compact "Mehrstellen" discretization**
- **Allows for efficient massively parallel implementation**

See E. L. Briggs, D. J. Sullivan and J. Bernholc Phys. Rev. B 54, 14362 (96).

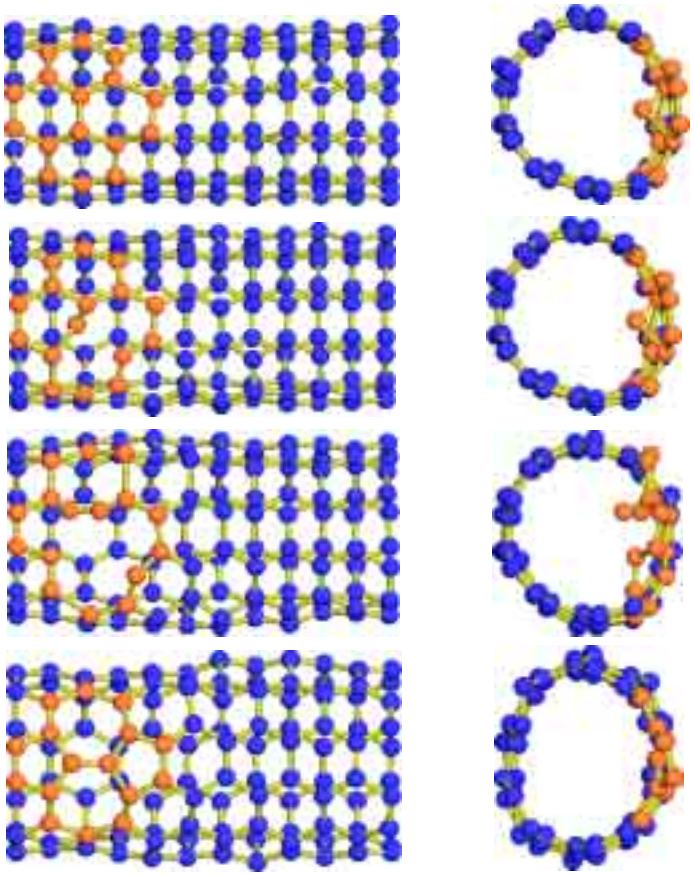


Speedup on Cray T3E with number of processors

Runs also on IBM SP, Origin 2000 and Linux clusters

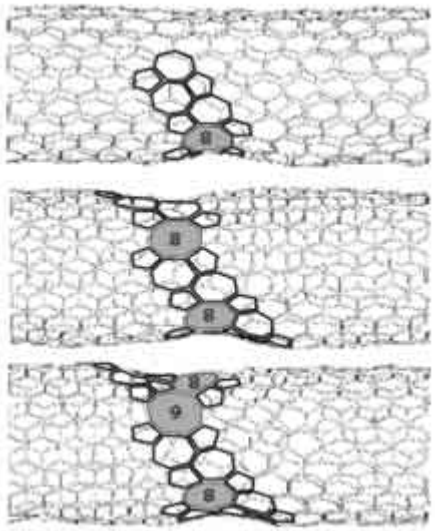
Breakage of nanotubes

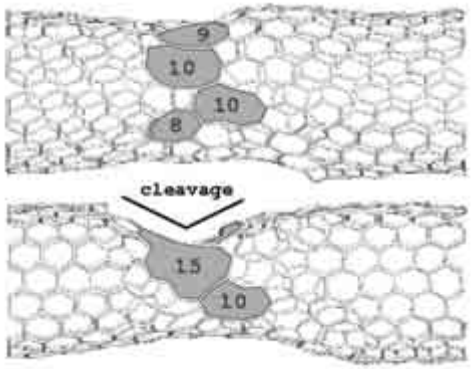
Nanotubes break by first forming a <u>bond rotation</u> 5-7-7-5 defect.



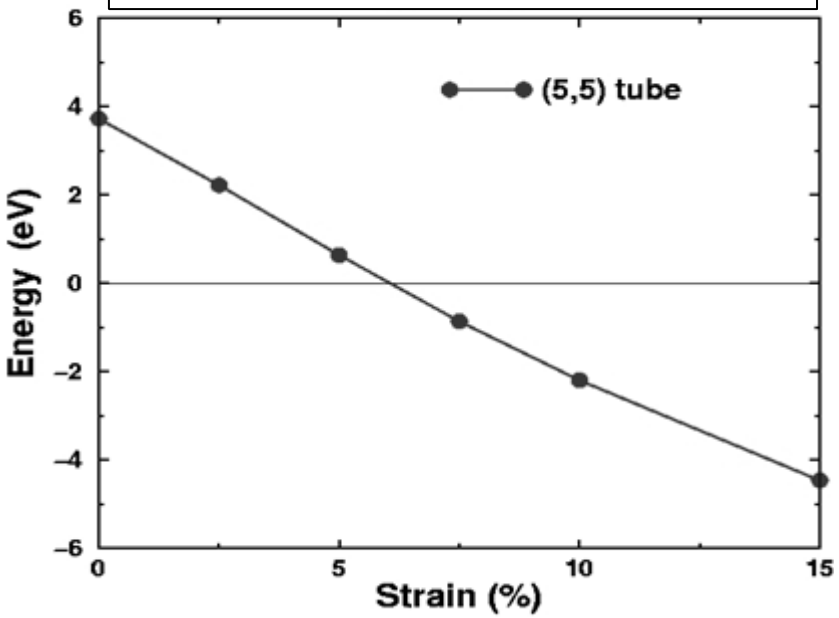
Buongiorno Nardelli, Yakobson, Bernholc PRB <u>57</u>, R4277 (1998).

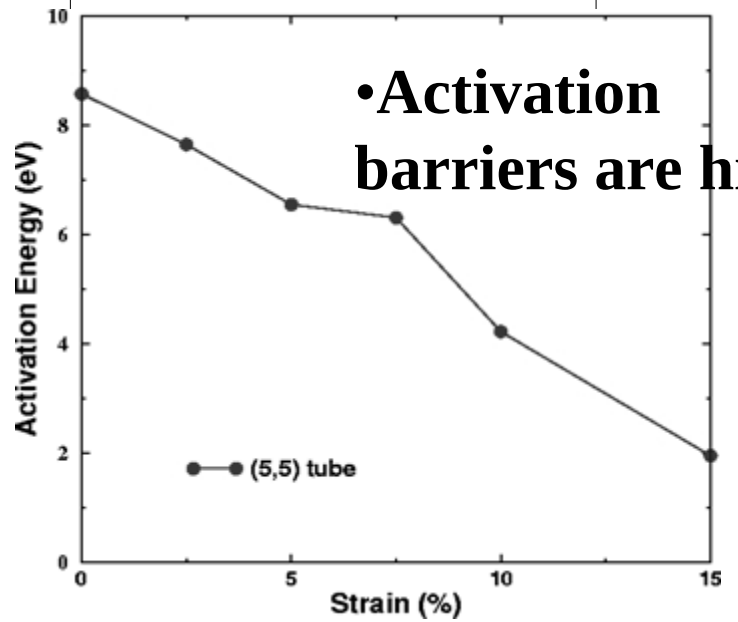
Additional bond rotations lead to larger defects and cleavage.





Formation and activation energies of 5775 defect in (5,5) tube (*ab initio* results)





•Activation barriers are high

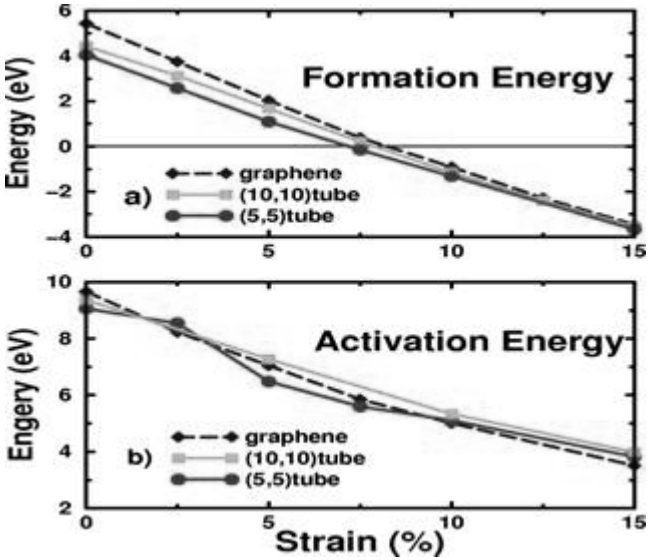
Formation and activation energies decrease with strain

- **5775 defect is favored for strains above ~ 6%**
- **Experimentally, tubes break at around 5-6% strain**

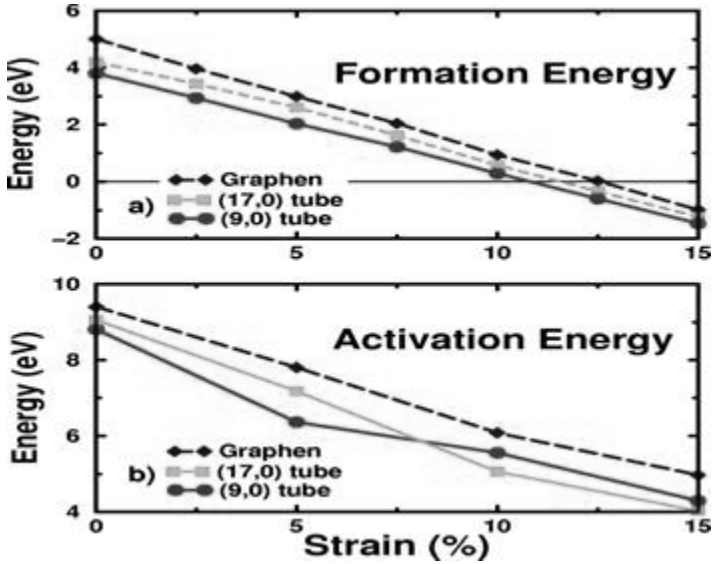
(Walters, Smalley et al APL, 1999; Yu, Ruoff et al PRL, 2000)

Curvature and chirality effect on defect formation

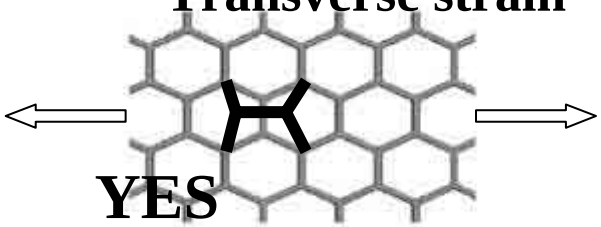
armchair tubes



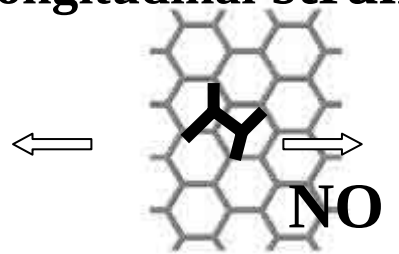
zigzag tubes



Transverse strain



Longitudinal strain



In armchair NT the 5775 energetically favorable at 5-6%

In zigzag NT the 5775 energetically favorable at 10-11%

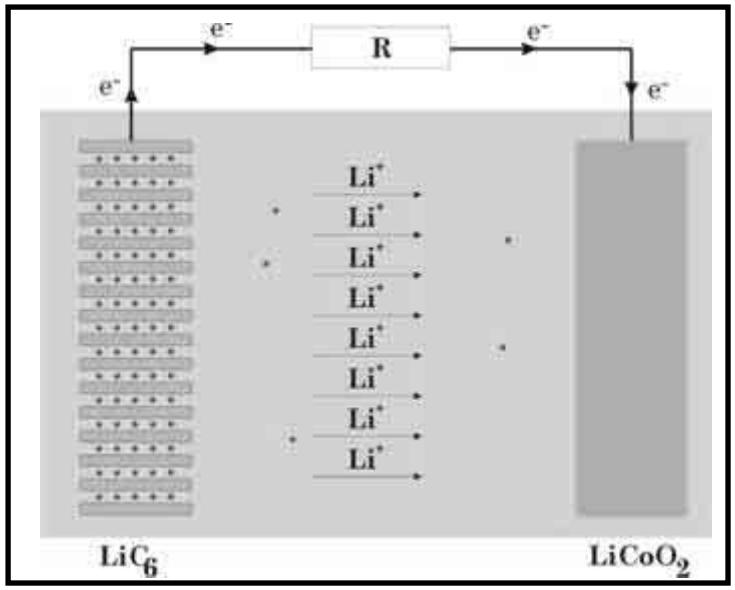
Activation energies are similar

Zhao, Buongiorno Nardelli, Bernholc PRB 65, 144105 (2002)

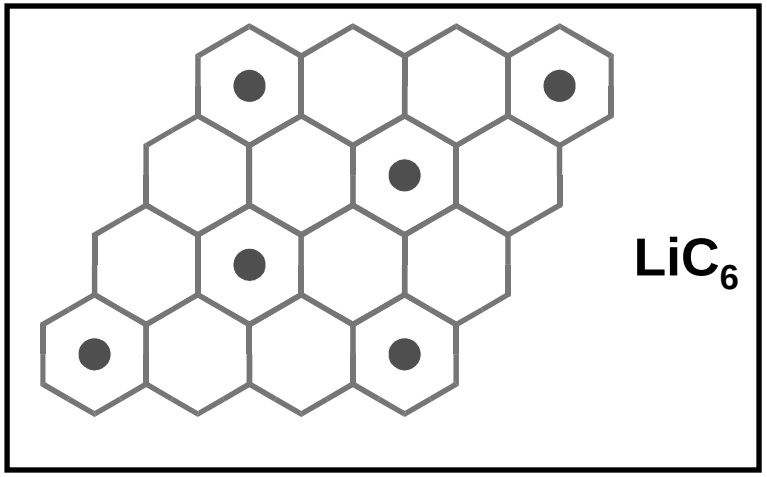
See also: Buongiorno Nardelli, Yakobson, Bernholc PRL 81, 4656 (1998)

Zhang, Lammert, Crespi, PRL 81, 5346 (1998)

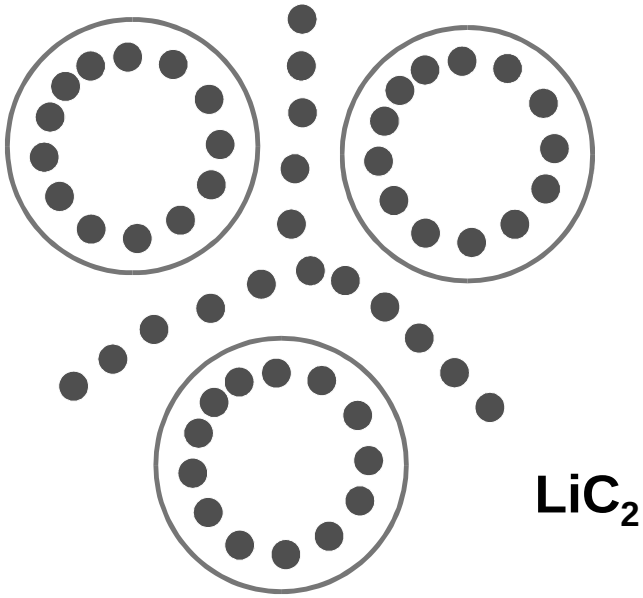
Li/Carbon-based high performance batteries



Lithium “rocking chair” battery

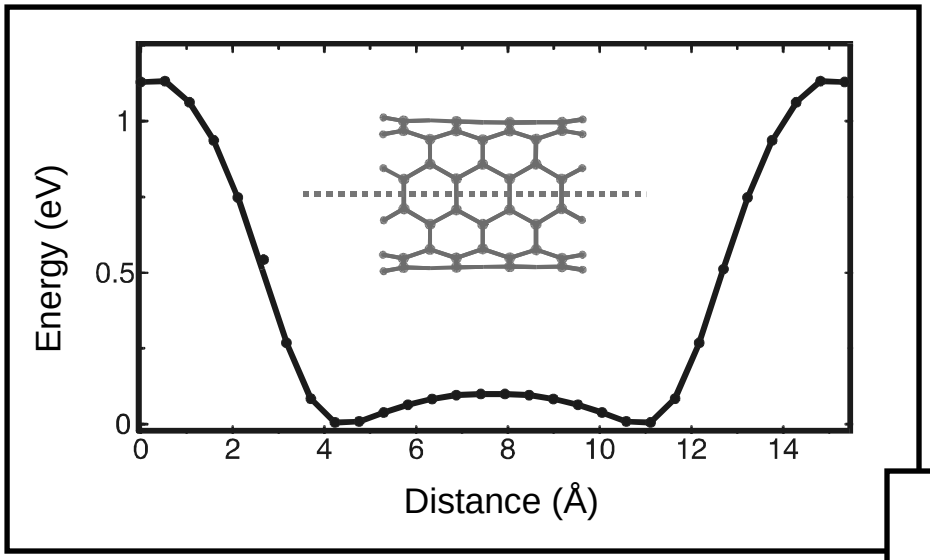


Nanotube-based anode



Two channels

Diffusion through open tip

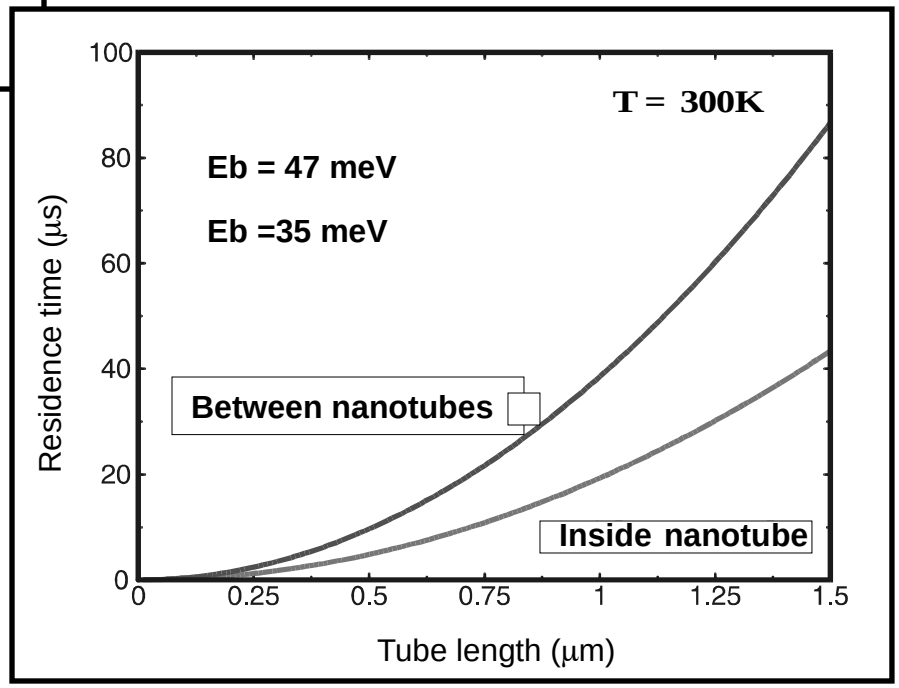


Li enters freely inside H-saturated open nanotube

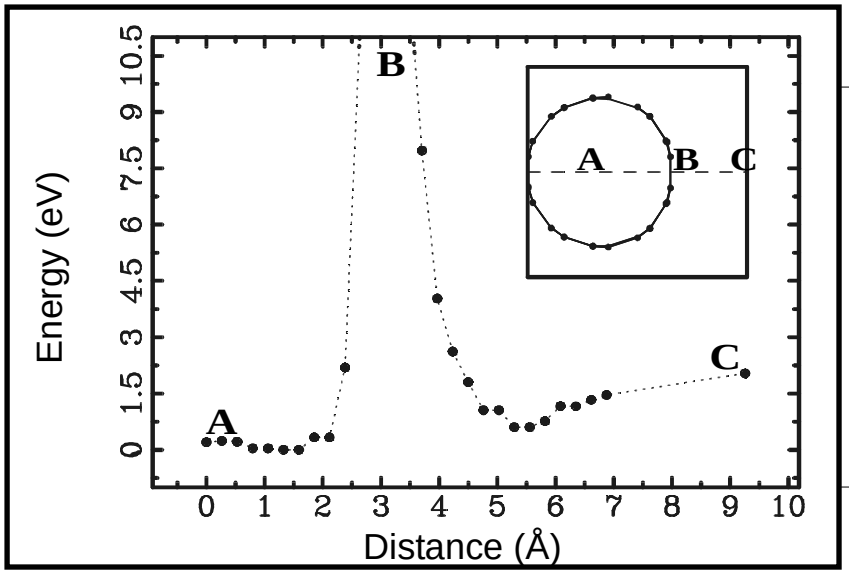
Once inside, the ions are not diffusion limited, provided that the tubes are relatively short

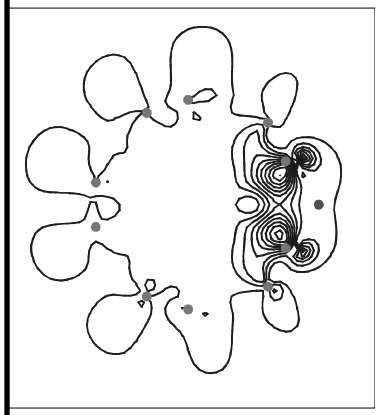
1D motion: $$\tau = \frac{L^2}{\nu a_0^{\,2}} e^{E_b / k_b T}$$

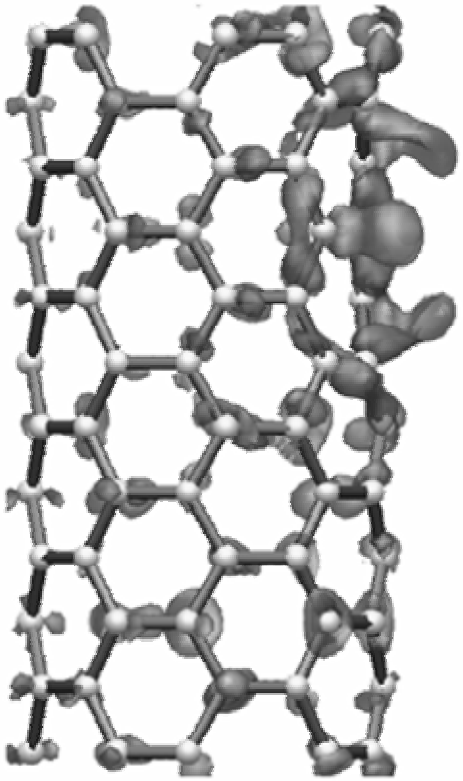
$\nu = 2.10^{12}$hz



Diffusion through side-walls: *pristine* case



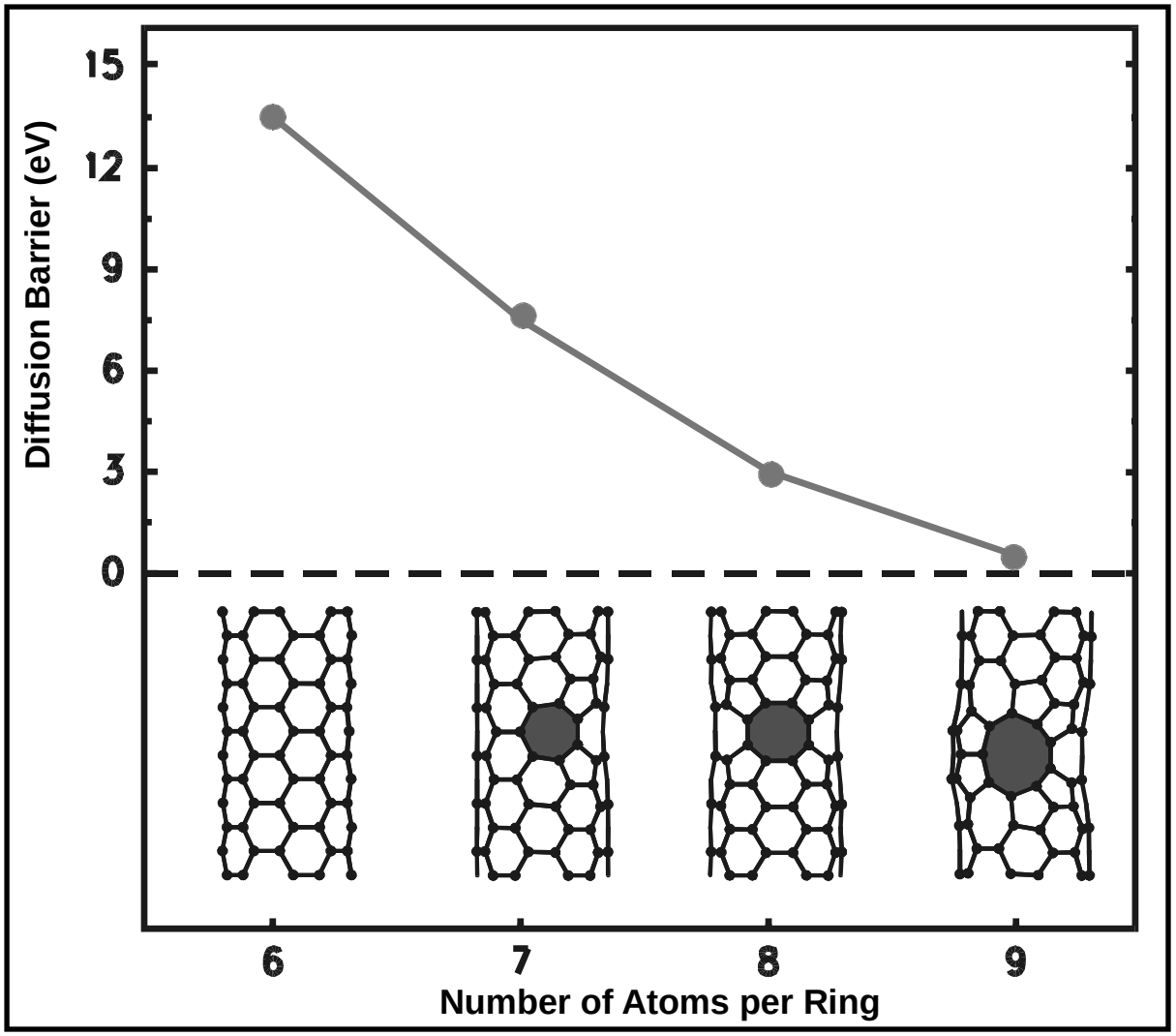




Li does NOT penetrate through an unaltered nanotube

Charge transfer

SW-types : heptagon, octagon, enneagon

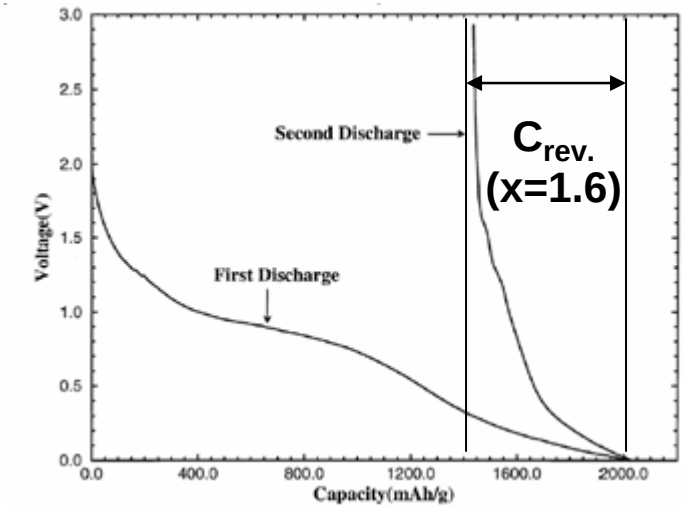


Li can freely enter through 9- (or higher) order topological defects

V. Meunier, C. Roland, J. Bernholc, Phys. Rev. Lett. 88, 075506 (2002).

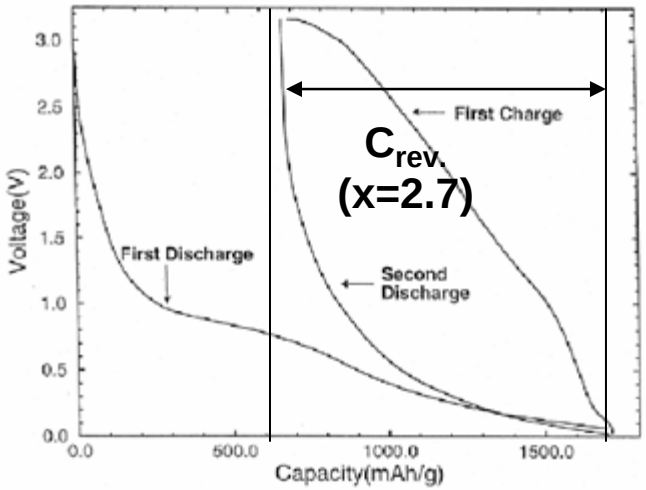
Using graphitic material as an anode host in Li_xC_6

Before ball-milling:



Gao, et al., CPL 307, 153 (1999).

After ball-milling:

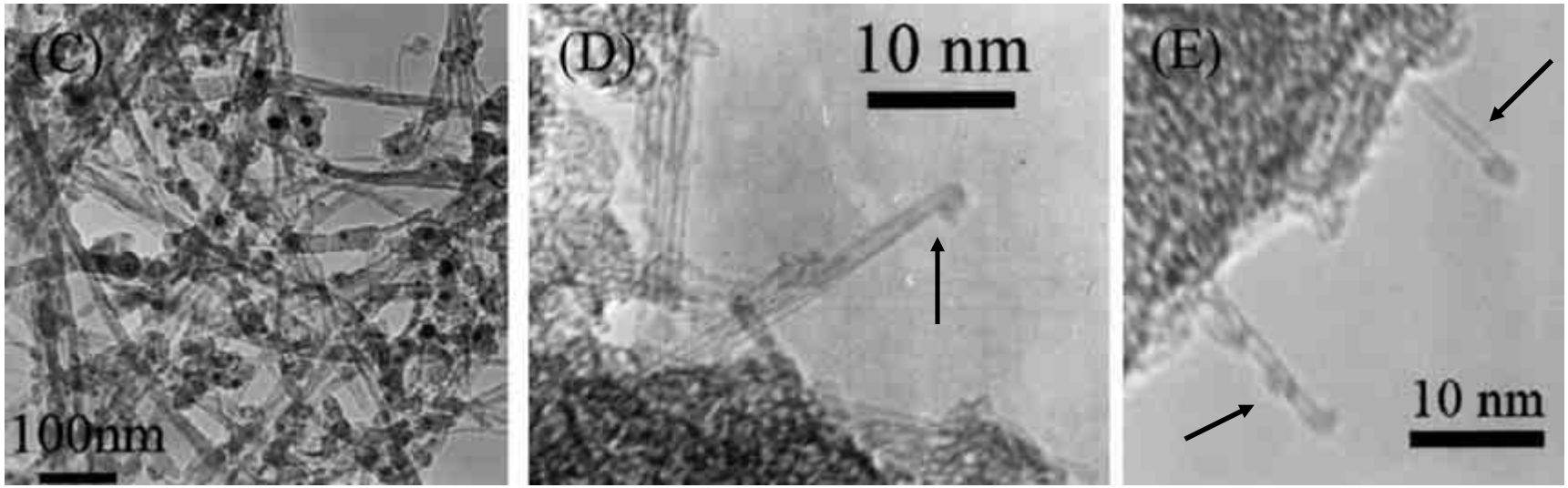


Gao, et al., CPL 327, 69 (2000).

How can Li access all the intercalating sites?

Effect of the ball-milling on the nanotube material

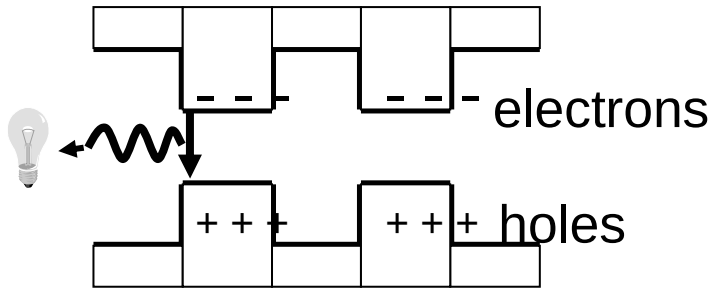
Before ball-milling: ***After 10min ball-milling:***

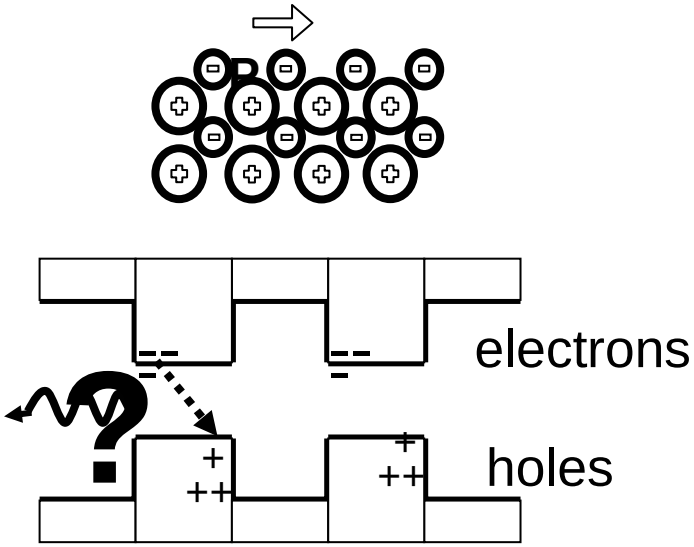


-Observation of nanotube ends: the SWNT's were fractured and shortened by BM.

-Further BM decreases the reversible capacity: increase of the amorphous carbon.

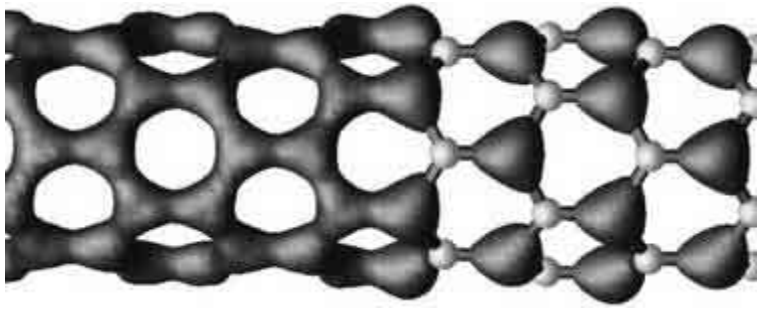
Symmetry and polarization





- **BN nanotubes have sufficiently low symmetry to exhibit significant macroscopic polarization inside the nanotube.**
- **The resulting electric field can separate electrons and holes in quantum wells, inhibiting recombination.**
- **Nanoscale pyro- and piezoelectrics are useful: strain sensors, actuators, transducers**

zigzag nanotubes



C **BN**

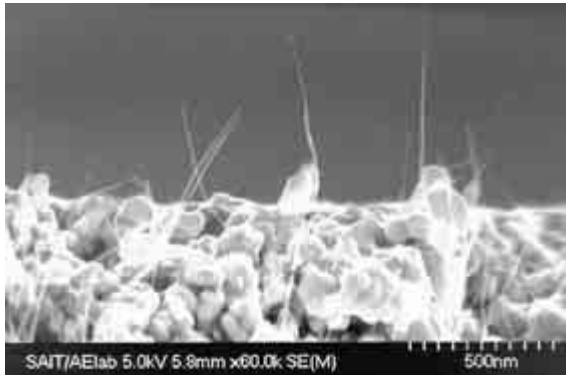
Field emission

- Possible field emission enhancement from local polarization fields
- Fowler-Nordheim formula

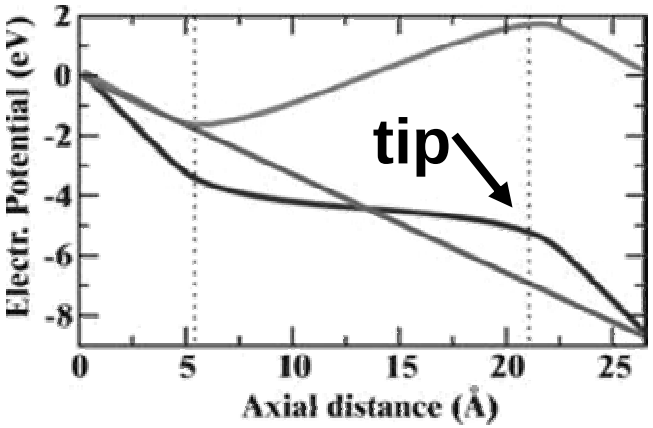
$$J = \frac{C}{\phi}\beta E^2 e^{\frac{-B\phi^{3/2}}{\beta E}}$$

  - E - applied electric field
  - Φ - work function of the metal
  - β - field enhancement factor
- Field enhancement not changed with the addition of BN sections

$E_{induced}/E_{applied}$ ~2.1



(Choi et al. APL (1999))



induced

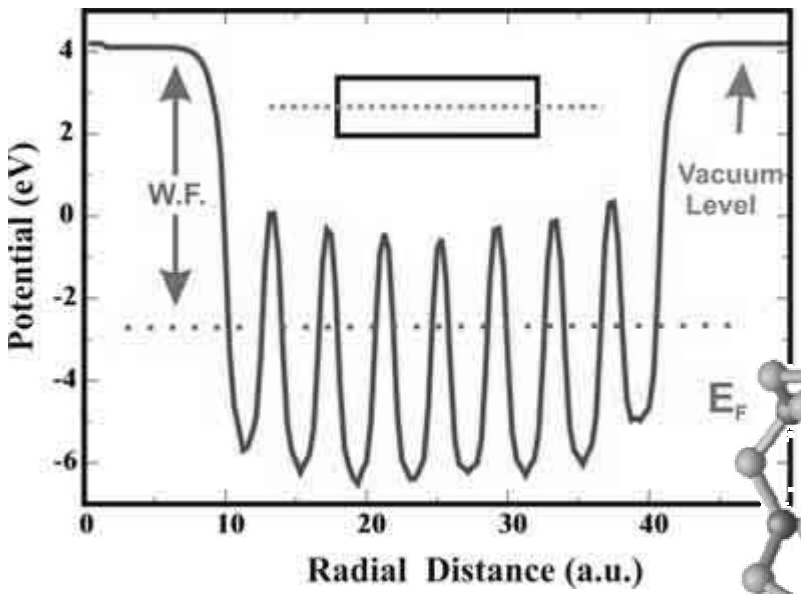
local

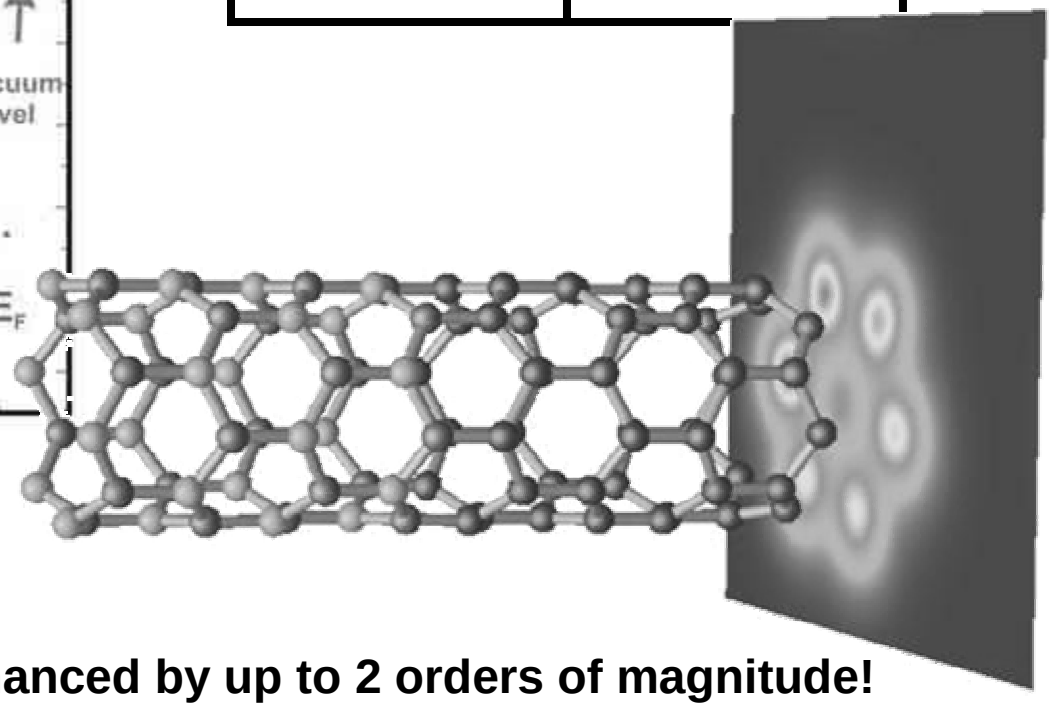
applied

Work Function

- Work function at the tip of C(6,0)
- Dipole correction in the vacuum

BN/C	**6.71 (eV)**
C	**6.41**
NB/C	**5.04**



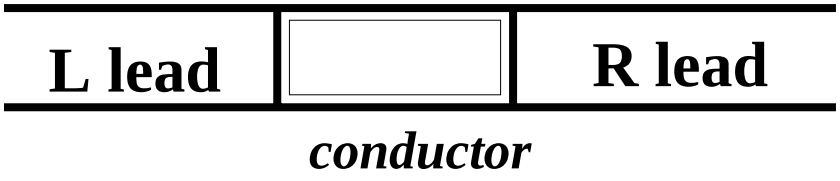


Field emission properties enhanced by up to 2 orders of magnitude!

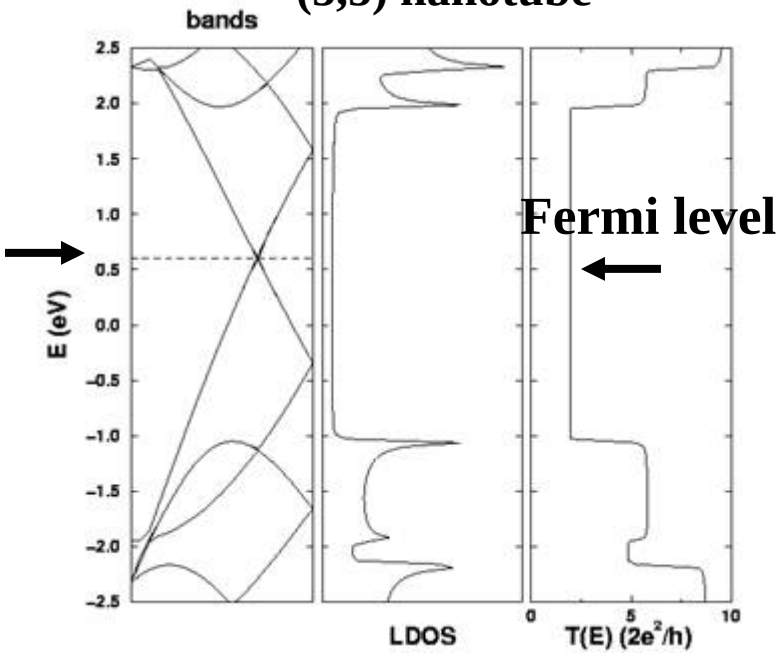
Meunier, Roland, Bernholc, Buongiorno Nardelli, APL (2002)

Introduction to quantum conductance

- Electron transmission through a device requires a Green's function treatment of an *open* system
  Left lead -- Conductor -- Right Lead
- In general, the quantum conductance measures the number of electron channels extending through the conductor *and* the leads, each contributing $2e^2/h$.
- For a perfect metallic nanotube and perfect contacts, both bands at the Fermi level contribute equally.
- For a disordered nanotube or for poor contacts, the conductance is much less.
- Conductances computed using a new, very efficient method (Buongiorno Nardelli PRB 1999; Buongiorno Nardelli and Bernholc, PRB RC 1999, Buongiorno Nardelli, Fattebert, Bernholc, PRB 2001)



(5,5) nanotube



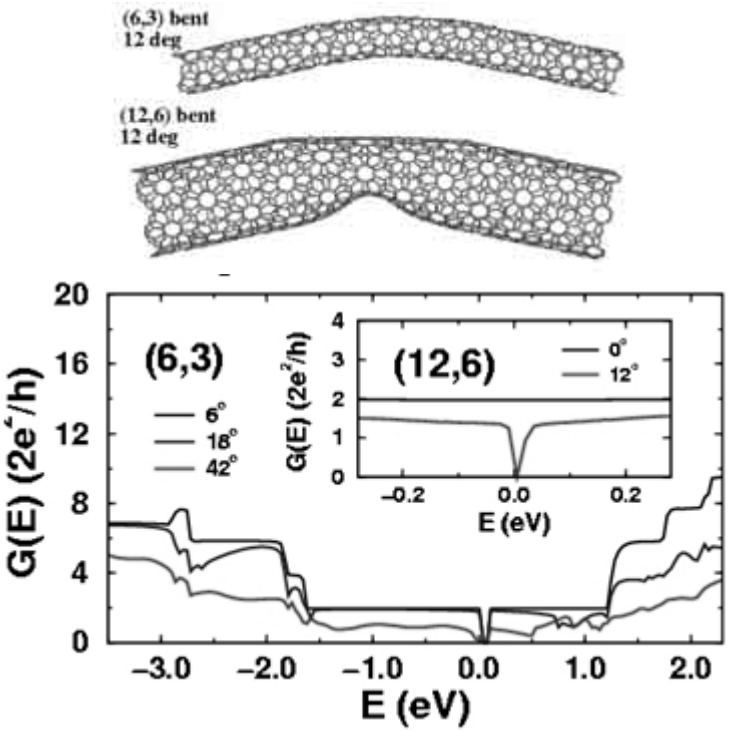
Two bands cross at the Fermi level

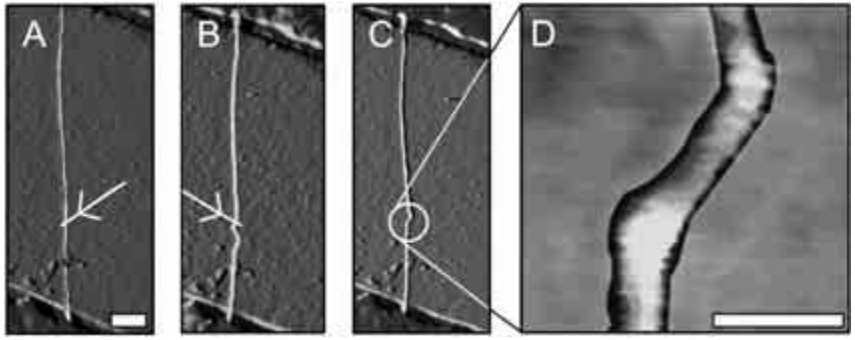
$\Rightarrow$ Conductance $\equiv T(E_F) = 2$

Units of $2e^2/h \approx (12.9\ k\Omega)^{-1}$

Bent nanotubes and single electron transistors

Large diameter nanotubes are metallic when *n-m=3k*, but bending opens a sizable pseudo-gap.



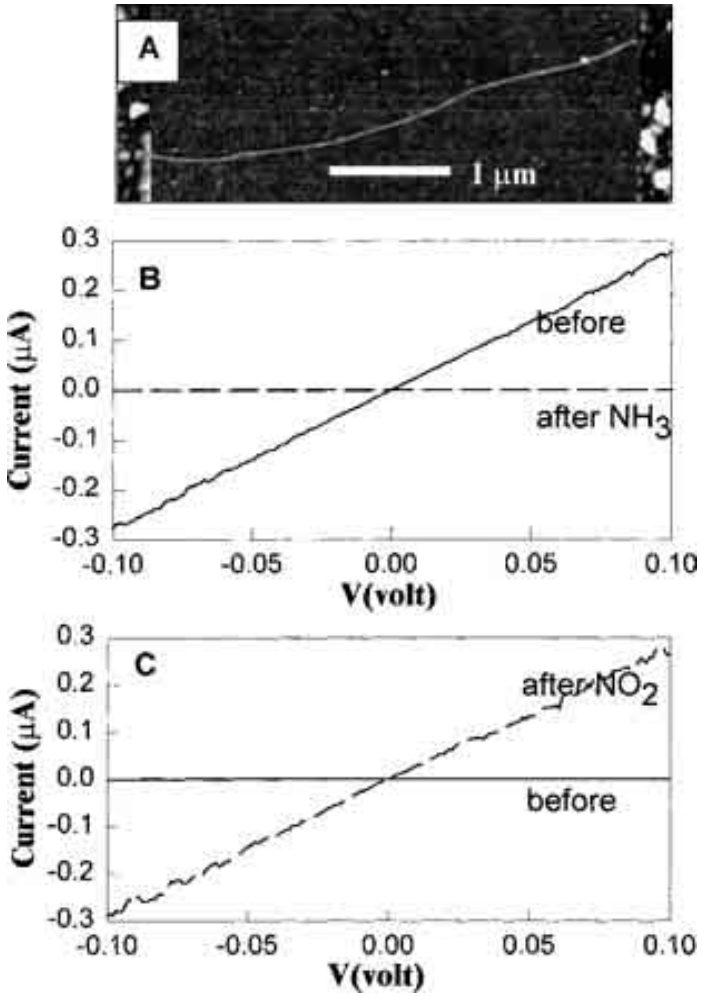


Kinking nanotubes leads to single electron transistors operating at room T **Postma, Dekker et al, Science 2001**

*** nanostrain sensors → chiral metallic NT**
*** flexible ballistic conductors → armchair NT**
high bending angles break conductance
Buongiorno Nardelli & J. Bernholc PRB RC (1999)

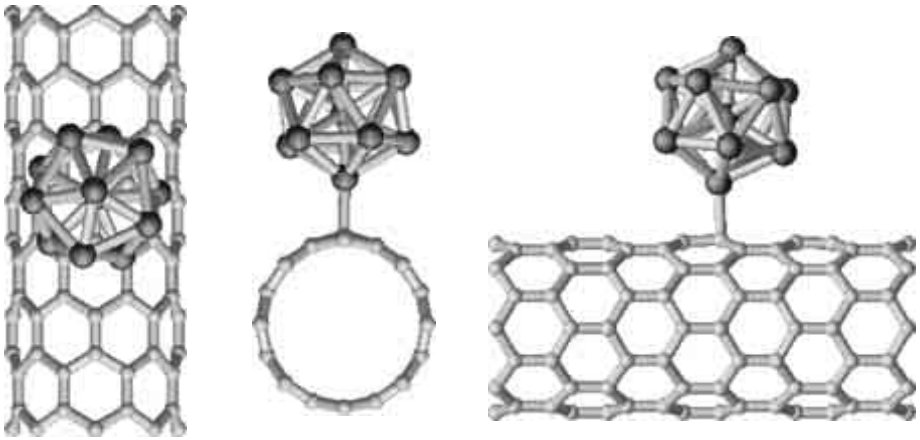
Carbon nanotubes as chemical sensors

Adsorption of chemical species on single wall nanotubes can induce changes in the electrical characteristics
(Kong et al., Science 2000)

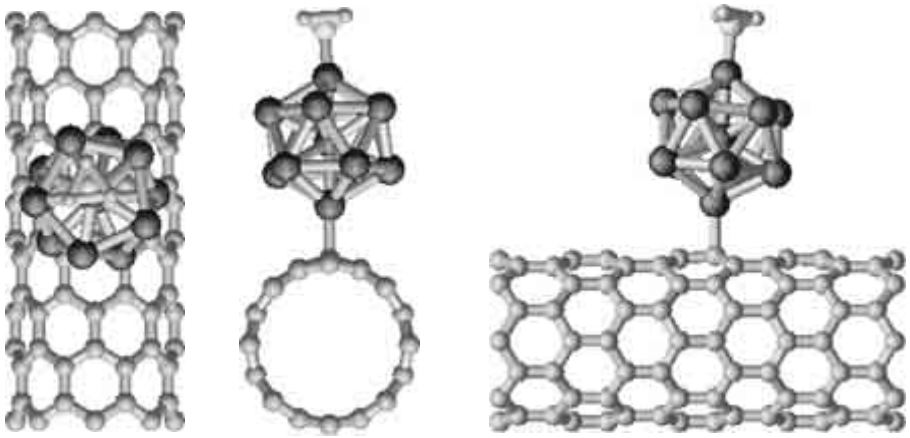


Semiconducting SW-CNT before and after exposure to NO_2 and NH_3:
NO_2 binds to the SWNT
NH_3 does not bind directly:
- gating effect through substrate
- binding to adsorbed species

Semiconducting SWNT-metal assemblies

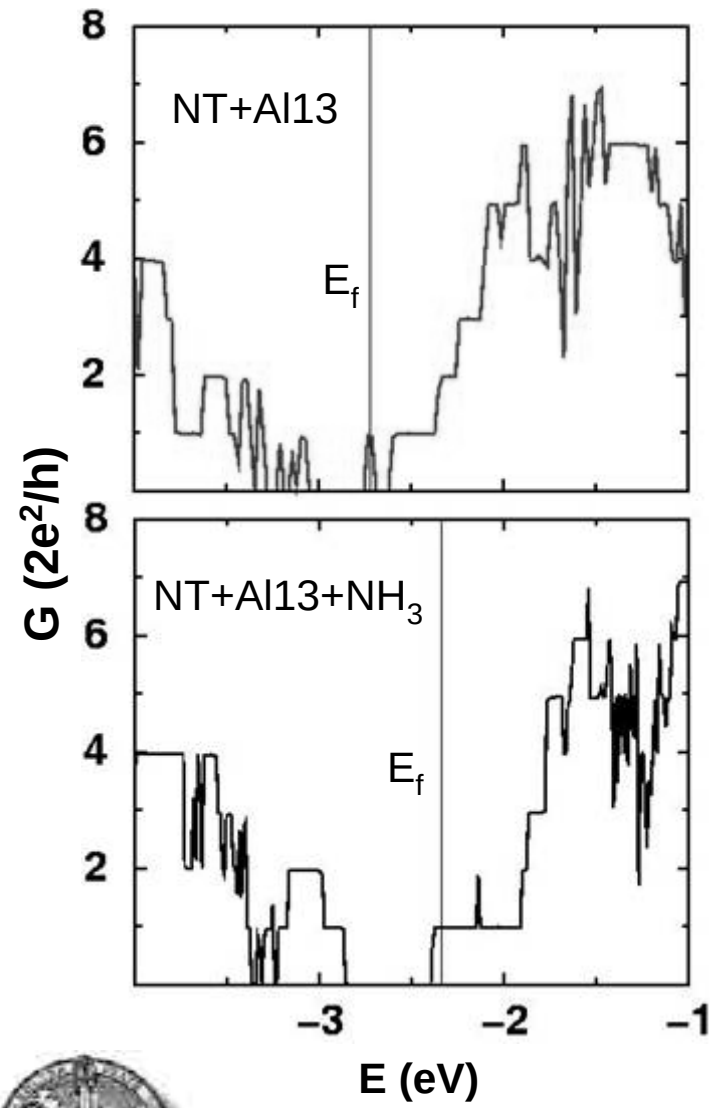


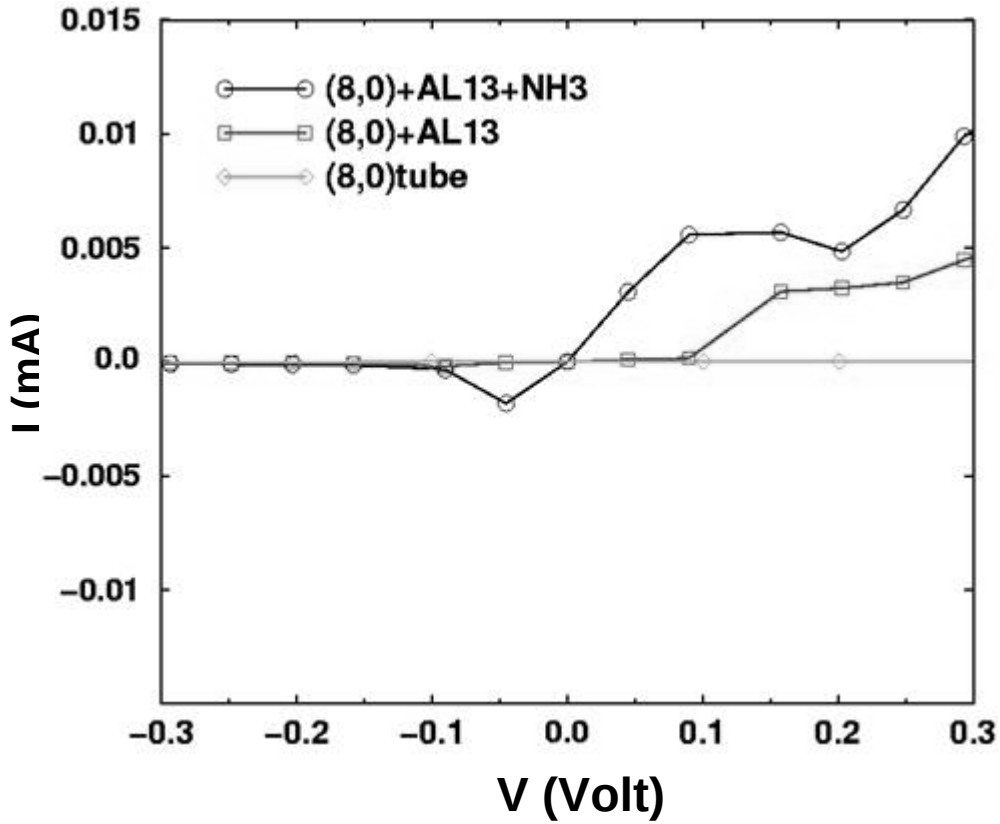
(8,0)tube + Al_{13}
More stable
C-Al bond length: 2.15 Å
Formation energy: -0.7 eV



(8,0)tube + Al_{13} + NH_3
More stable
C-Al bond length: 2.11 Å
Formation energy of the molecule complex: -1.8 eV

Quantum transport in semiconducting SWNT-metal cluster assembly





(8,0)tube-metal cluster assembly becomes conducting after NH_3 adsorption.

SWNT-metal cluster assembly can be a good chemical sensor

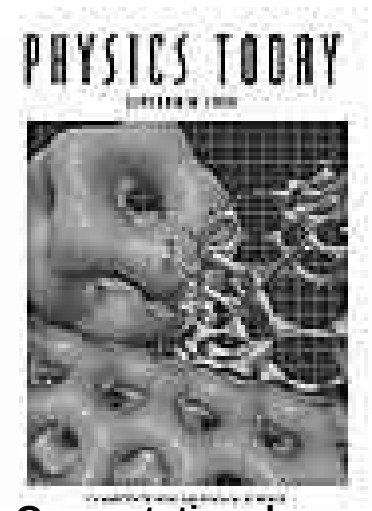
NC STATE UNIVERSITY

Summary

Nanotubes – novel material with truly spectacular properties

- **Mechanical properties**
  - ❖ **The strongest materials known!**
  - ❖ **The ultimate strength has not yet been reached**
- **Li/NT high capacity and high throughput batteries**
- **BN-NTs are excellent pyro- and piezoelectrics**
  - ❖ **Novel devices: actuators, transducers, etc**
- **Carbon-based molecular electronics possible and exciting**
  - ❖ **Strain and molecular sensors**
  - ❖ **Single electron devices**

Many unique applications possible



Computational Materials Science