Festkörperphysik in unserem Leben: von neuen Materialen zur Nanomedizin

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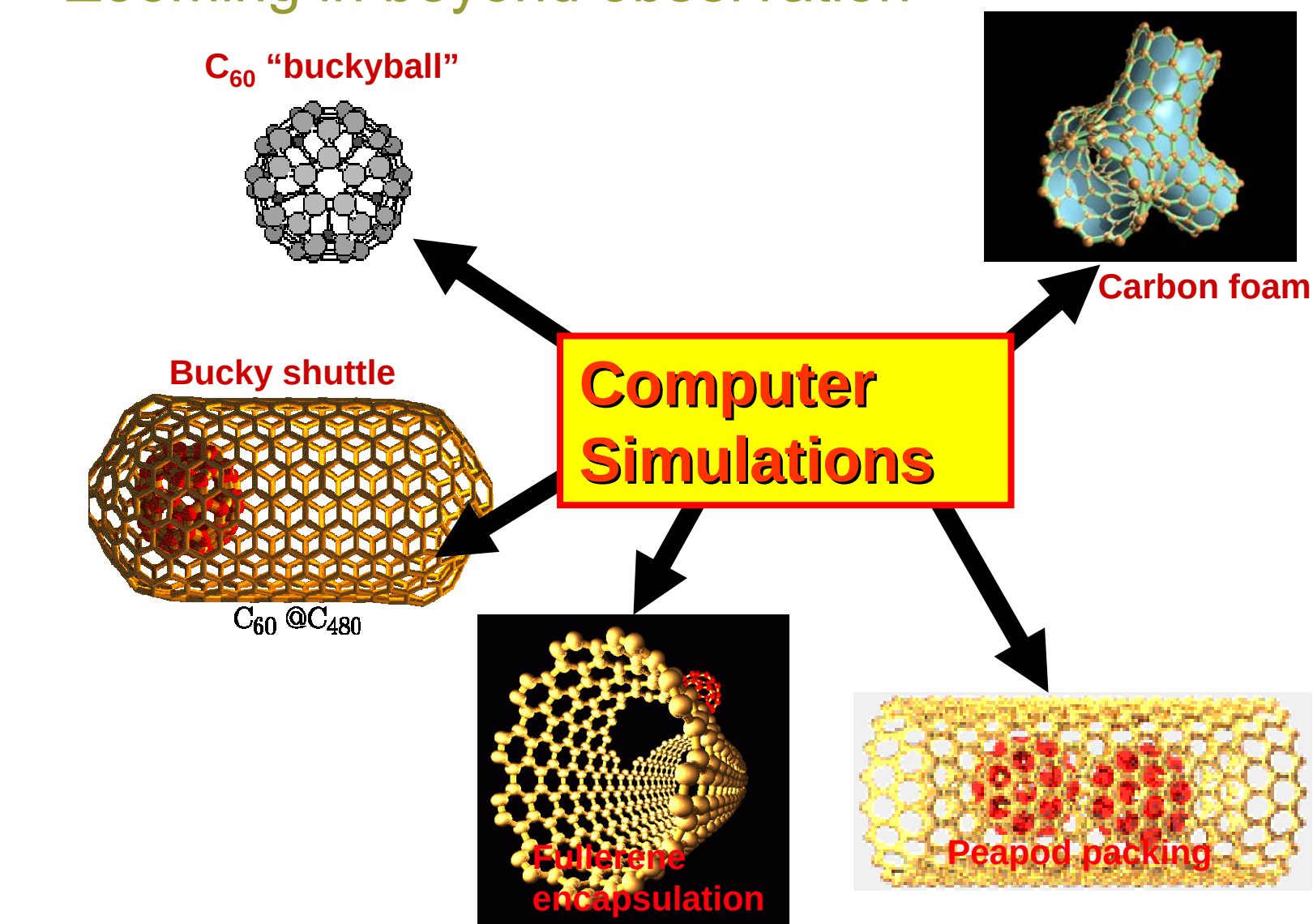
Outline

- Introduction
  - **What to expect from computer modeling**
  - **Computational tools**
- Unexpected behavior of nanostructured carbons
  - **Can carbon be harder than diamond?**
  - **Nanotube peapods: nano-memory and beyond**
  - **Diamondoids in nanotube peapods**
  - **Polymer-nanotube composites**
- Defects in carbon nanostructures
  - **Defect tolerance of nanotubes**
  - **Defect assisted fusion of nanotubes**
- Nanotechnology in Medicine
  - **Can We Remotely Destroy Tumors?**
- Summary and Conclusions

What to expect from computer modeling

Zooming in beyond observation



Computational tools

- Electronic structure calculations based on the *ab initio* Density Functional formalism
- Time evolution of electronic wave functions:

  Time-Dependent Density Functional formalism
- Atomic motion: Molecular dynamics simulations with electrons in the ground and excited state
- Forces from total energy expressions:

  $E_{tot} = E_{tot}(\{R_i\}) = E_{tot}\{\rho(r)\}$

  ab initio Density Functional formalism

  $E_{tot} = \Sigma_i E_{coh}(i) = \Sigma_i [E_{bs}(i) + E_{rep}(i)]$

  parametrized LCAO formalism (CRT)
- Massively parallel computer architectures and suitable algorithms distribute load over processors for speed-up

Computational Nanotechnology Laboratory: Earth Simulator, Tokyo

www.nytimes.com

The New York Times ON THE WEB

April 20, 2002

Japanese Computer Is World's Fastest, as U.S. Falls Back

By JOHN MARKOFF

SAN FRANCISCO, April 19 — A Japanese laboratory has built the world's fastest computer, a machine so powerful that it matches the raw processing power of the 20 fastest American computers combined and far outstrips the previous leader, an I.B.M.-built machine.

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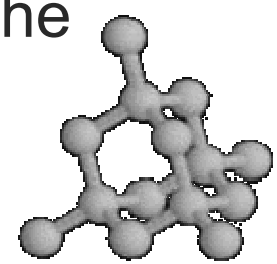
Unexpected Behavior of Nanostructured Systems

Can carbon be harder than diamond?

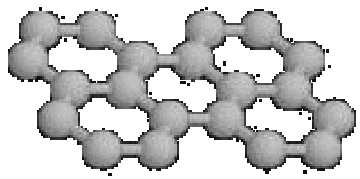
- Is sp^3 bonded diamond really the hardest material?



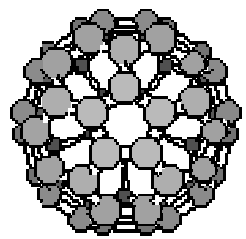
$$\frac{\text{Binding Energy}}{3} > \frac{\text{Binding Energy}}{4}$$

$$sp^2 > sp^3$$

- Can sp^2 bonded structures be harder than diamond?

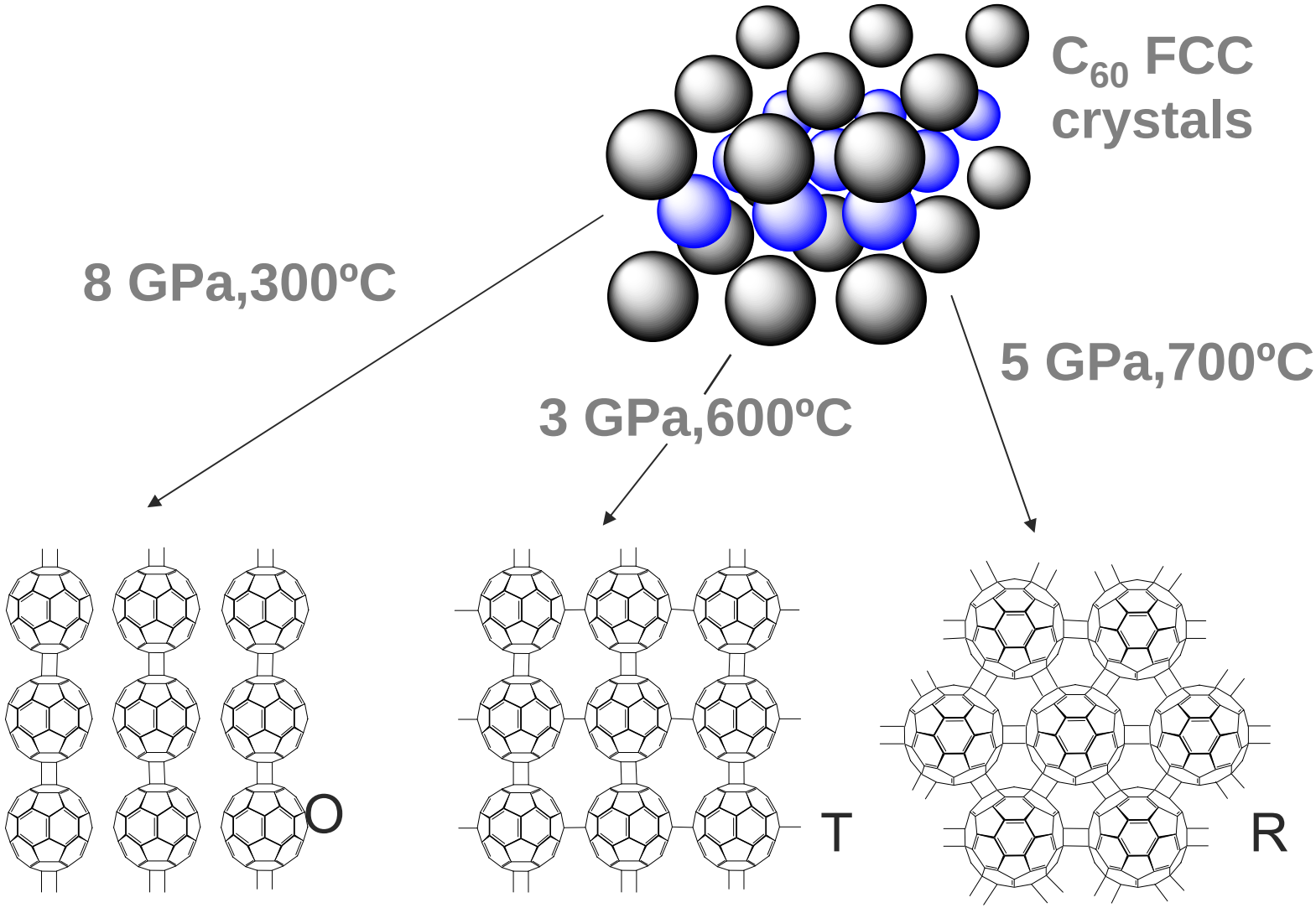


- Can fullerene-based crystals form such super-hard structures?



*Savas Berber, Eiji Osawa, and David Tománek, Rigid Crystalline Phases of Polymerized Fullerenes, Phys. Rev. B **70**, 085417 (2004).*

Known 2D Polymers of C_{60}



❖*Are there 3D polymers of C_{60}?*

Experimental Observation

Fullerene polymers are harder than diamond *[V.D.Blank et al., JETP **87**, 741 (1998).]*

- Polymerization of C_{60} at 820 K under 13GPa pressure
- Density: ρ=2.48 g/cm^3
- Bulk modulus **B≈800 GPa**

- Crystal Structure: BCO (Body Centered Orthogonal)

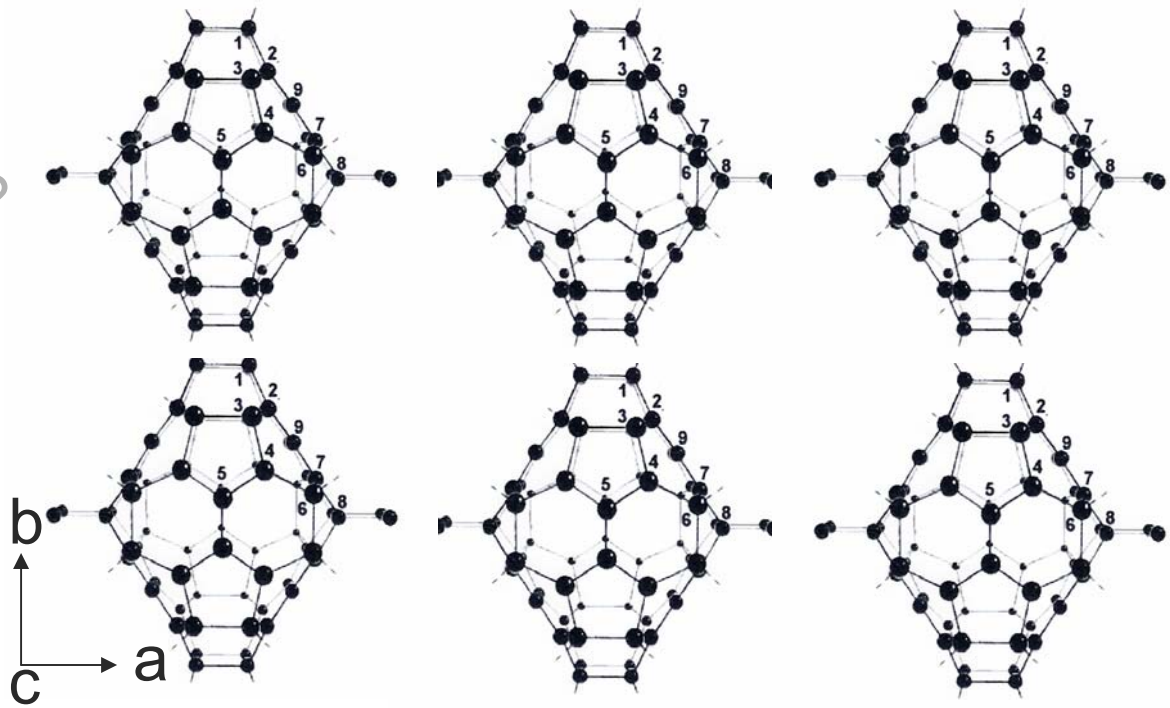
[Diamond: ρ=3.52 g/cm^3 ,**B=440 GPa**]

Can this be true?

What is the structure?

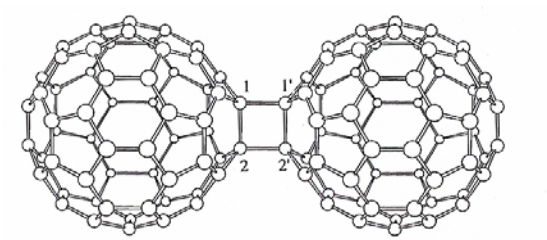
Possible atomic arrangement:

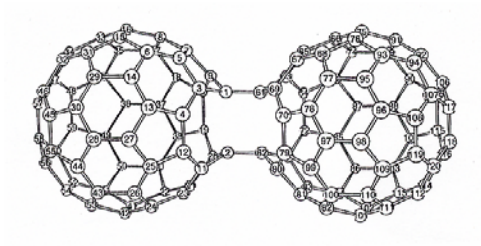
Chernozatonskii, 2000



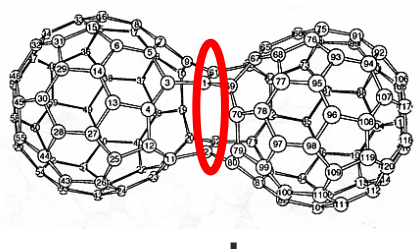
Possible bonding between C_{60} molecules in a polymerized crystal

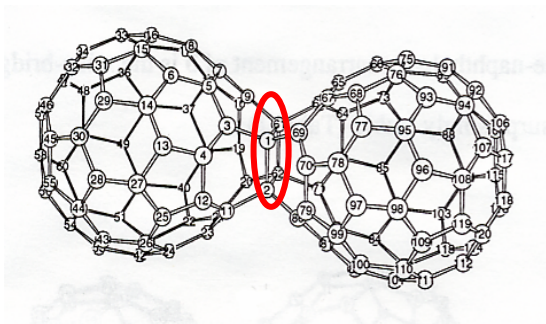
(2+2) cycloaddition (66/66)

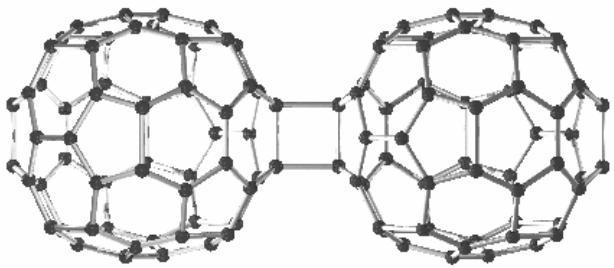




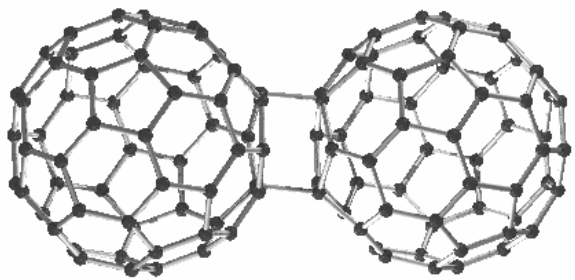
Open hinge







56/65 cycloaddition



(3+3) cycloaddition

Common four-membered ring

Likely candidates for superhard crystals

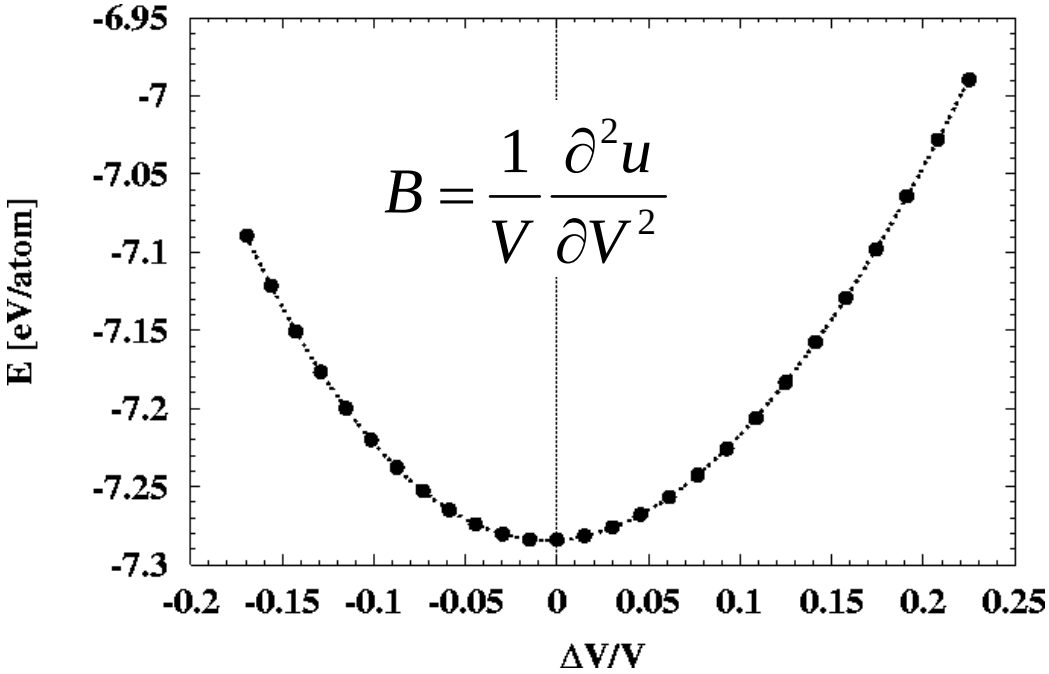
Polymerized C_{60} lattices

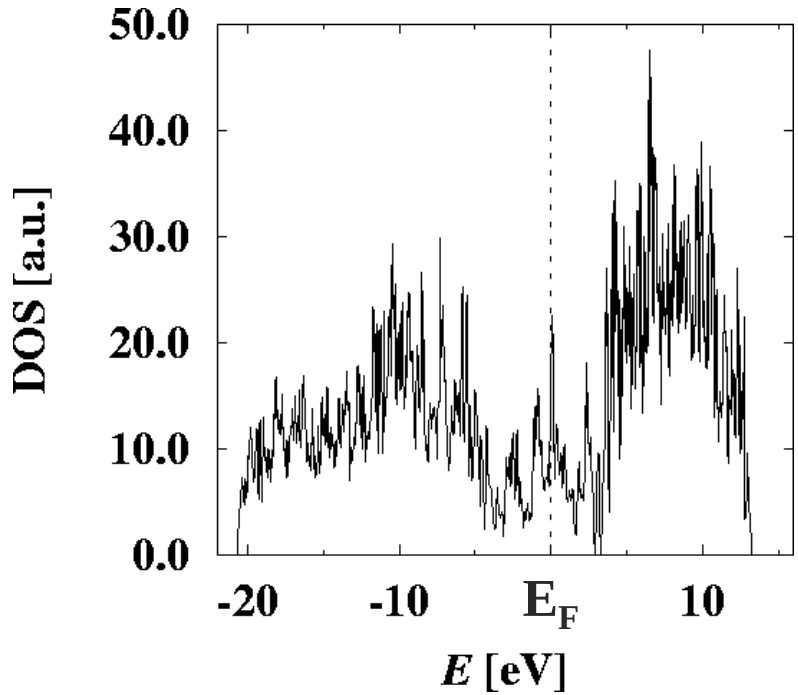
- FCC (Face Centered Cubic)
- SC (Simple Cubic)
  - with (2+2) cycloaddition
  - with four-membered rings
  - with open hinge
- BCC (Body Centered Cubic)
- BCO (Body Centered Orthogonal)

Based on powder X-ray data

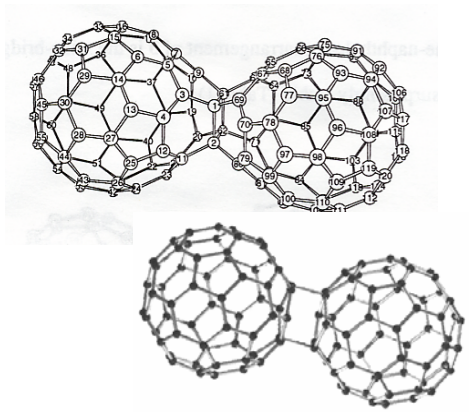
- "Hard" phase (cycloaddition)
- "SuperHard" phase I and II (rings along b axis)
- "UltraHard" phase (rings along a and b)

“UltraHard” BCO lattice



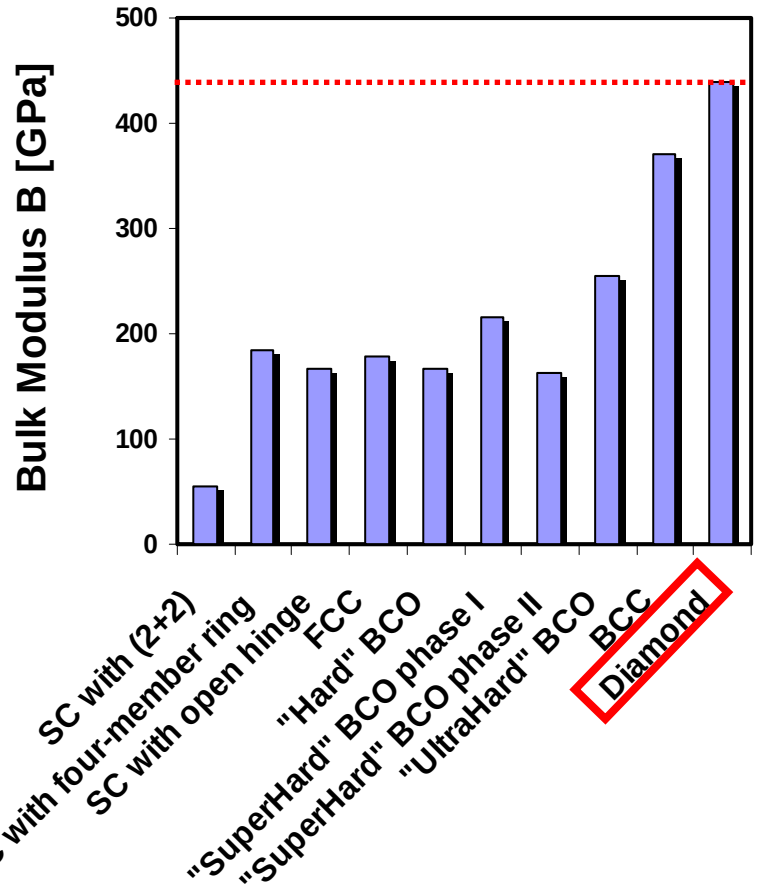


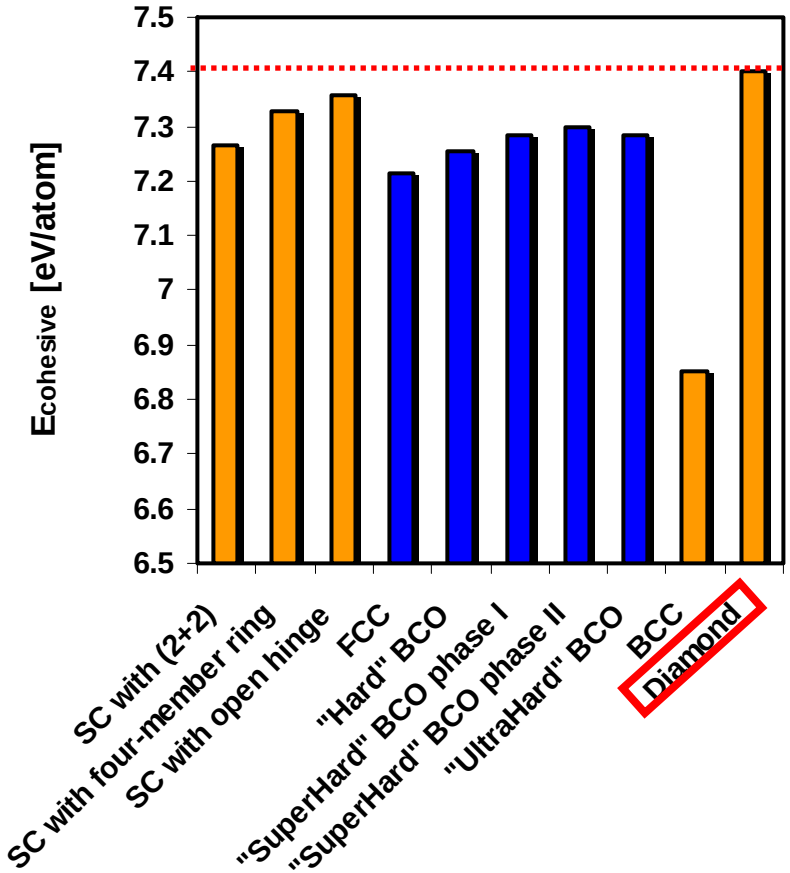
- Polymerization:
  - Four-membered ring along a and b axis
  - (3+3) cycloaddition along space diagonal of unit cell

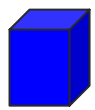


- B=254.13 GPa
- E_{coh} = -7.284 eV/atom
- ρ= 2.45 g/cm^3

Bulk modulus and cohesive energy

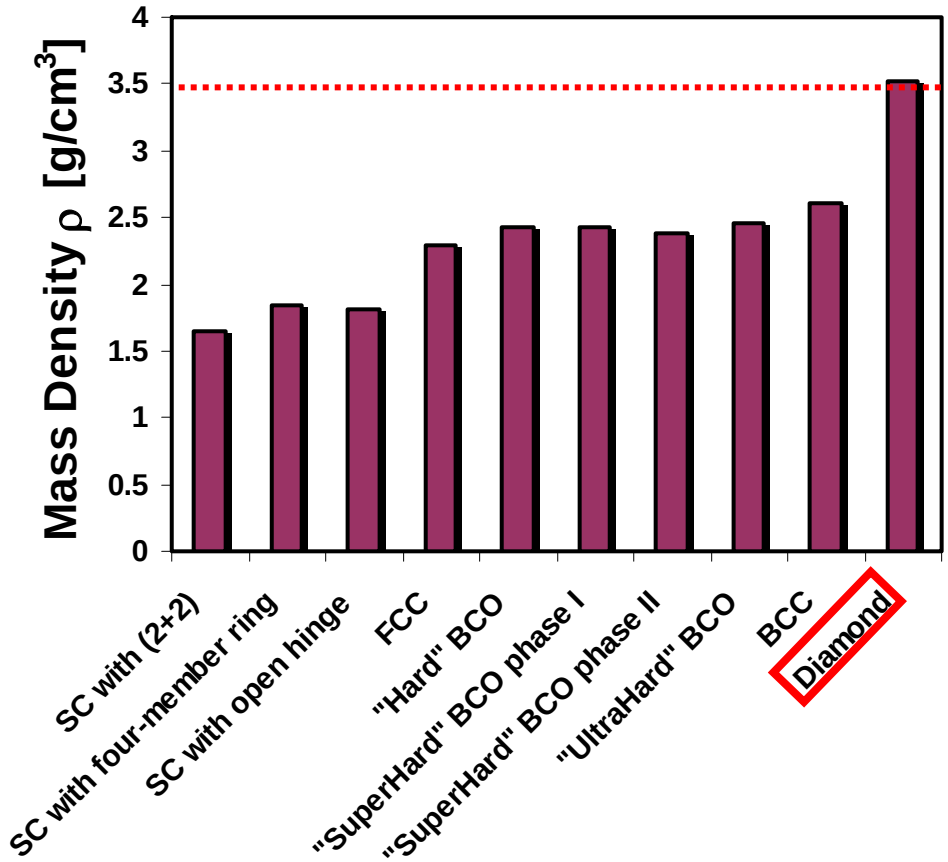




Metal 

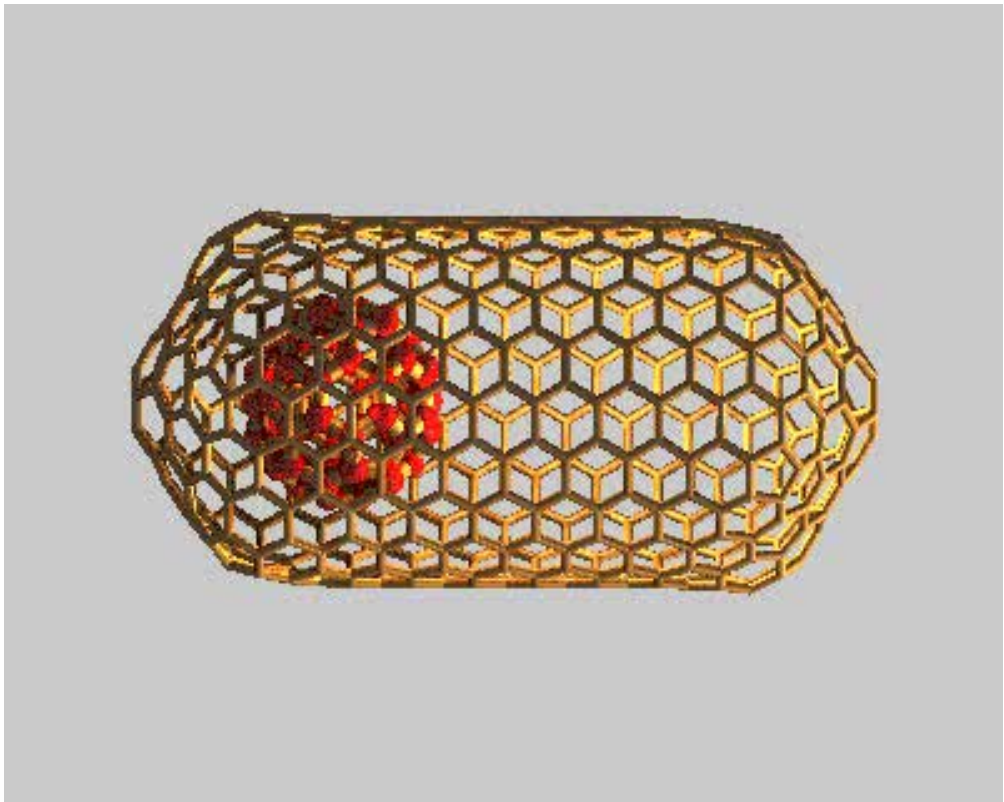
Insulator 

Mass Density



- Nothing beats diamond

Nanotube peapods: nano-memory and beyond



A Pea in a Pod:
The Bucky Shuttle

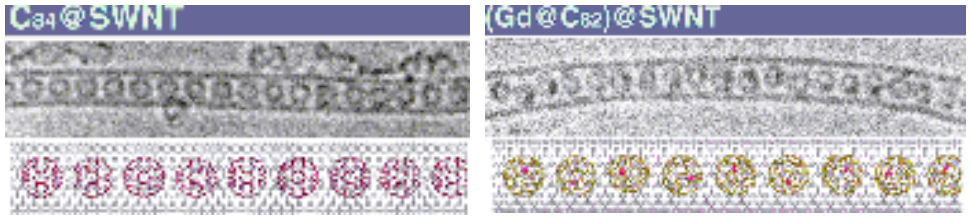
Young-Kyun Kwon, David Tománek, and Sumio Iijima, Phys. Rev. Lett. **82**, 1470 (1999)

C_{60}@nano-capsule: Non-volatile memory

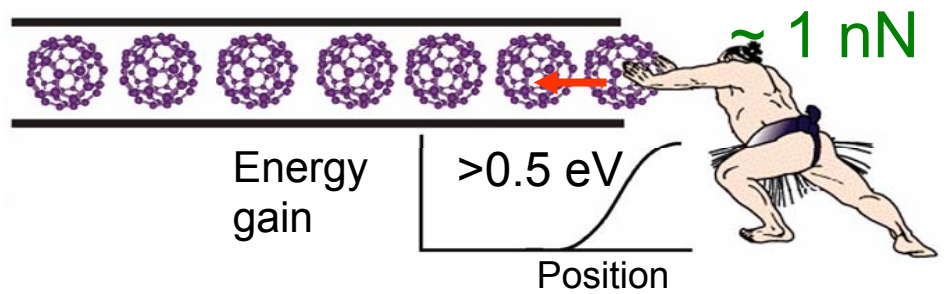
- Left/Right=Bit 0/Bit 1
- Packing density: <5 TB/cm^2
- Writing speed: <1 THz
- U.S. Patent 6,473,351

Uses beyond computer memory

•**Intercalation of other species**



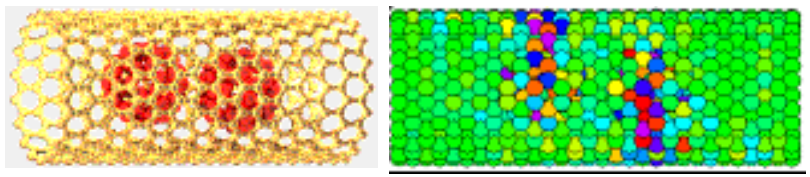
•**Possible New Applications:**



-Pressure container (e.g. Li, hydrogen storage)

p>1 GPa

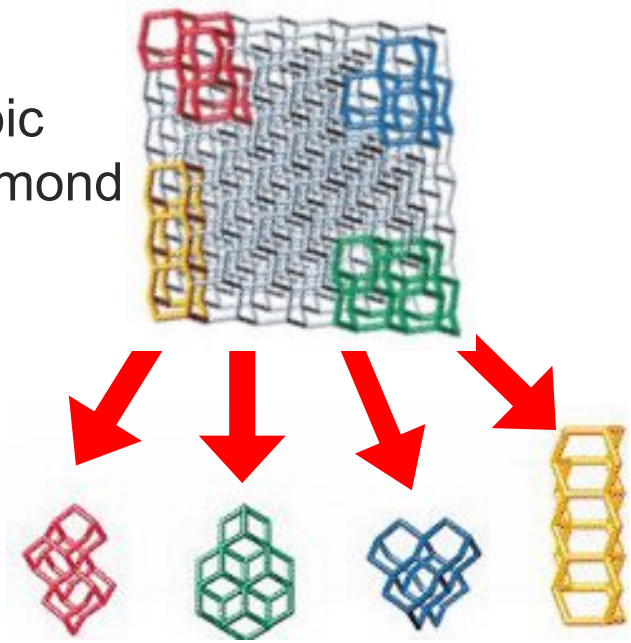
-Chemical reaction vessel



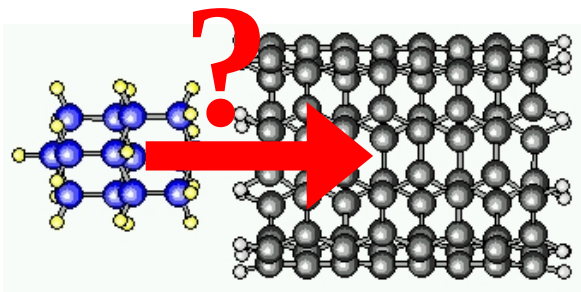
Stress visualization

Diamondoids in nanotube peapods

cubic diamond



diamondoid particles



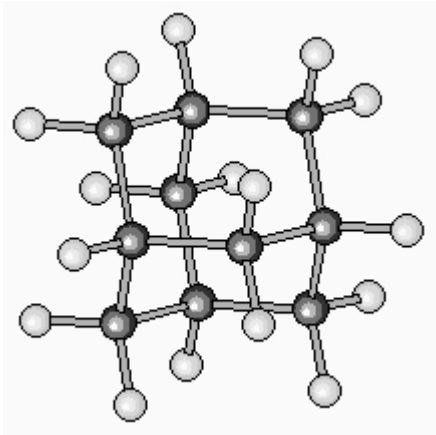
•Hydrogen-terminated, nanometer-size diamondoid particles were isolated experimentally *[J.E. Dahl et al., Science **299**,96-99(2003)]*

•Possible application in nanotechnology: functional building blocks with tunable electronic, structural properties

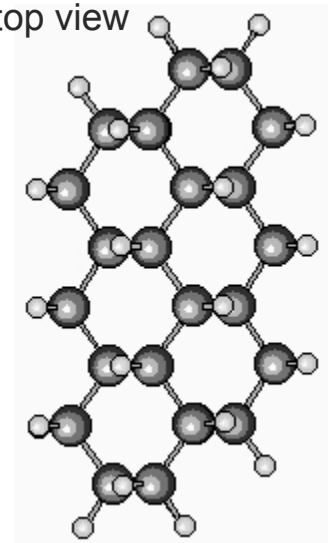
•Possible encapsulation in nanotubes provides for more complex nanostructures

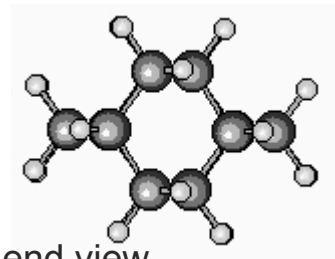
*G. C. McIntosh, M. Yoon, S. Berber, and D. Tománek, Diamond Fragments as Building Blocks of Functional Nanostructures, Phys. Rev. B **70**, 045401 (2004).*

Properties of lower diamondoids



top view

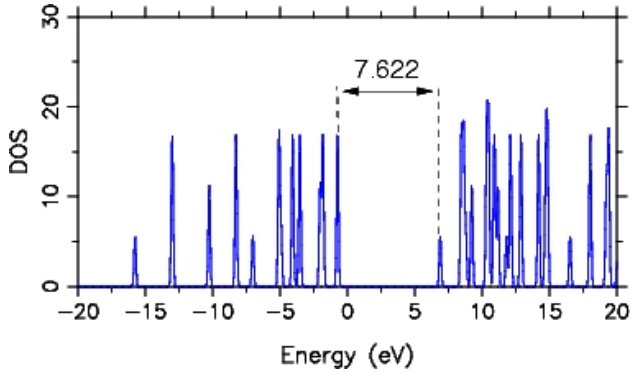




end view

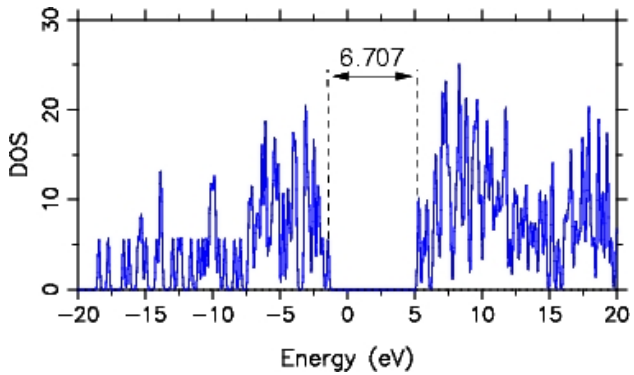
Adamantane:$C_{10}H_{16}$ *(G.C. McIntosh)*

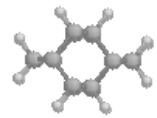
ΔE = -170.530 eV (atomization energy)
$\Delta \varepsilon_f$ = -60.51 eV (formation energy w.r.t. H_2, diamond)
$\Delta E_f/N_c$ = -6.051 eV (formation energy per carbon atom w.r.t. H_2, diamond)

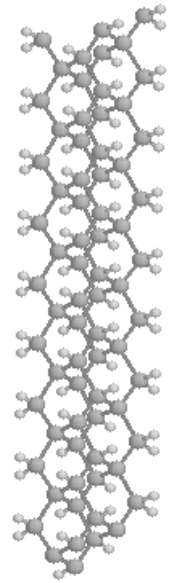


Hexamantane:$C_{30}H_{36}$ *(G.C. McIntosh)*

ΔE = -467.905 eV (atomization energy)
ΔE_f = -165.09 eV (formation energy w.r.t. H_2, diamond)
$\Delta E_f/N_c$ = -5.503 eV (formation energy per carbon atom w.r.t.H_2, diamond)



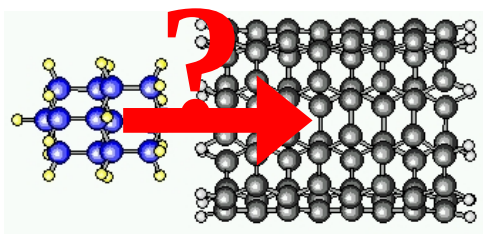




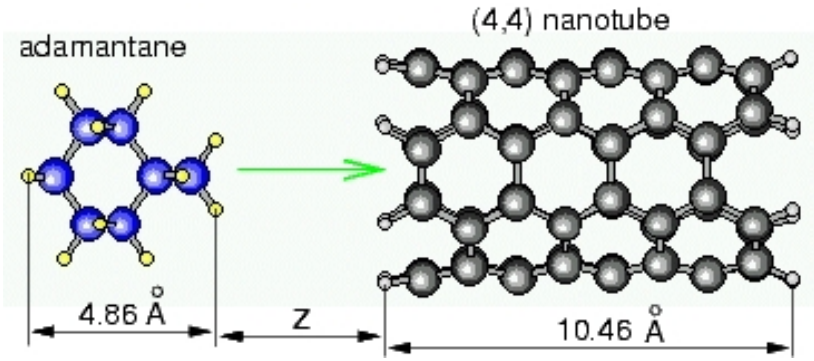
Diamodoid chain: C_nH_n *(N. Park)*

Diamondoid encapsulation geometry

diamondoid particles



Encapsulation geometry:



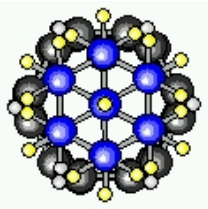
z = distance between the end of the nanotube and the diamondoid:

z < 0: diamondoid is outside the nanotube.

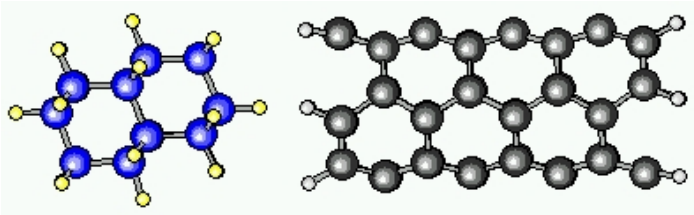
z > 0: diamondoid has entered into the nanotube.

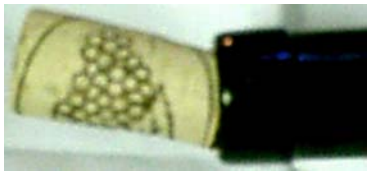
Diamantane near a (3,3) nanotube

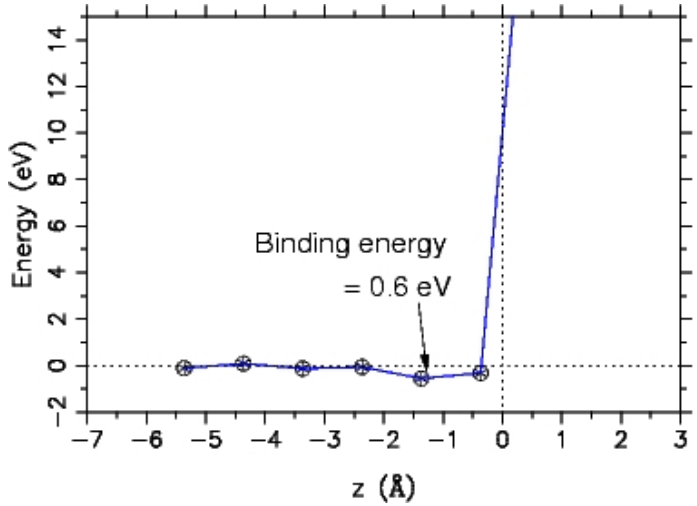
end view



side view

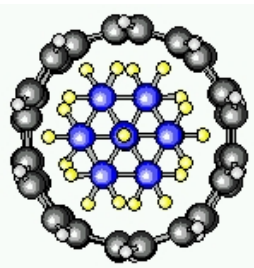


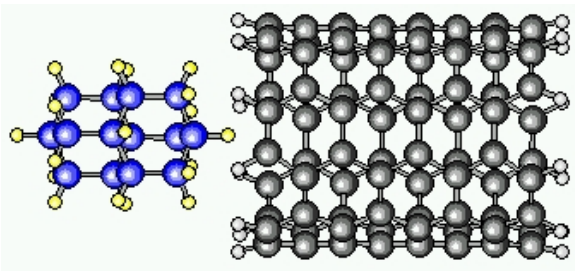


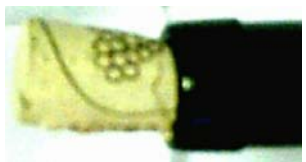


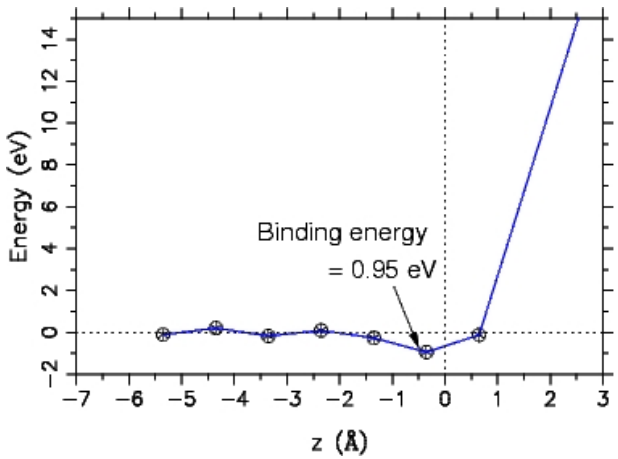
Does not fit in narrow tube

Diamantane near a (5,5) nanotube



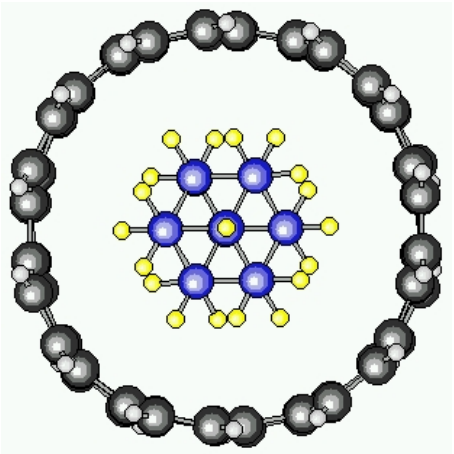


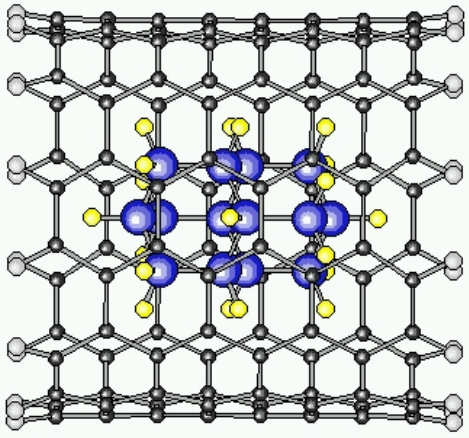


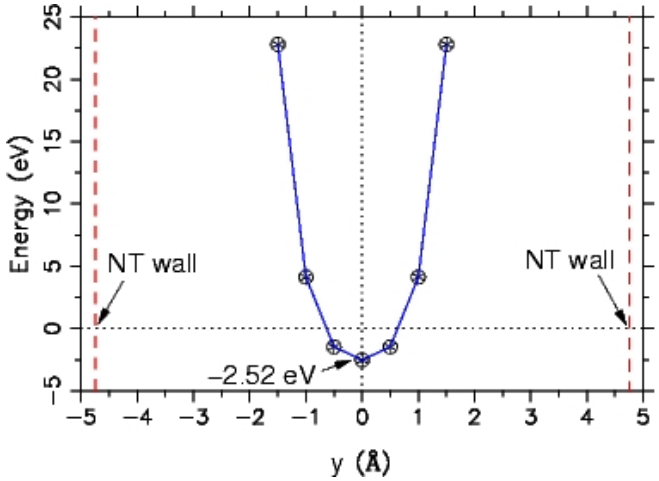


(Wider) nanotube still too narrow

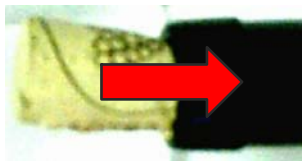
Diamantane inside a (7,7) nanotube



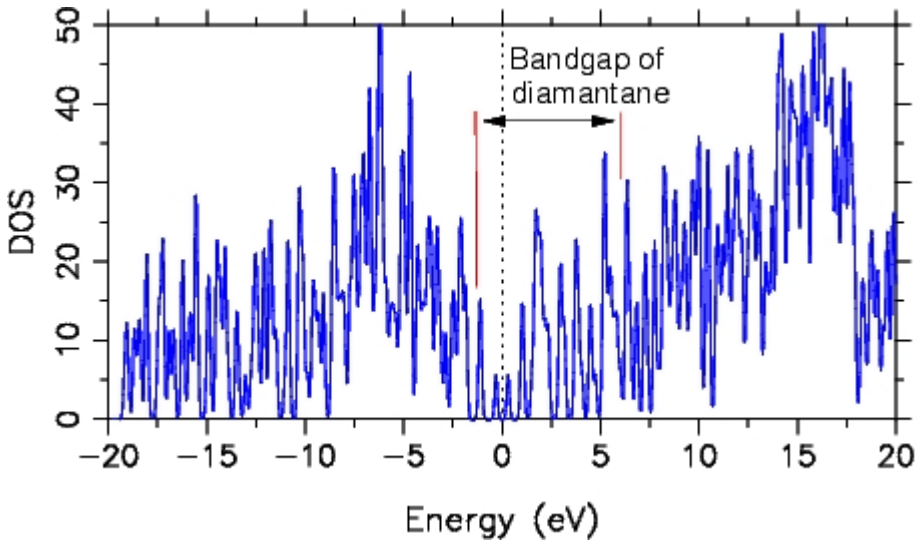




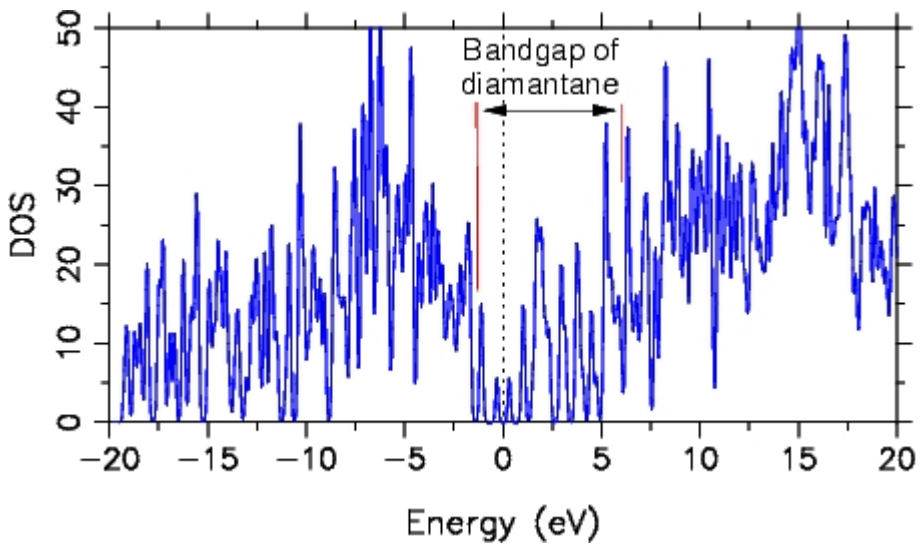
Optimum fit



(7,7) nanotube

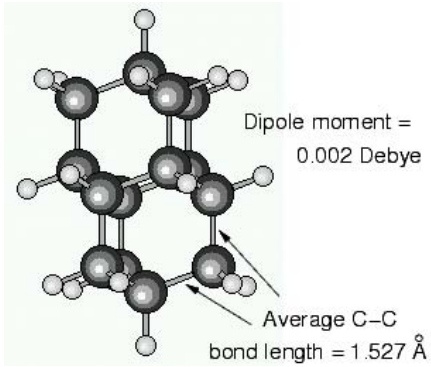


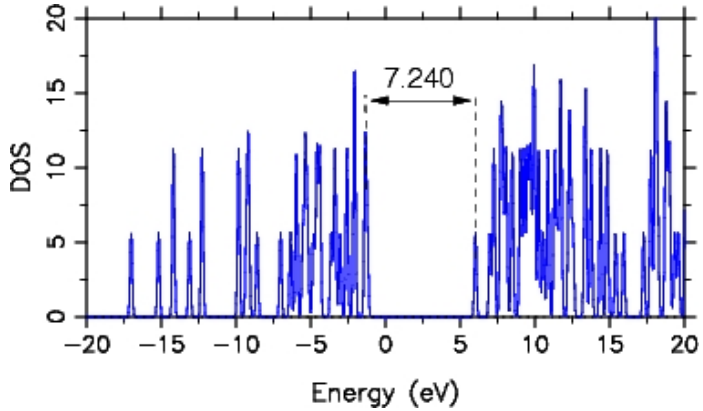
(7,7) nanotube + diamantane



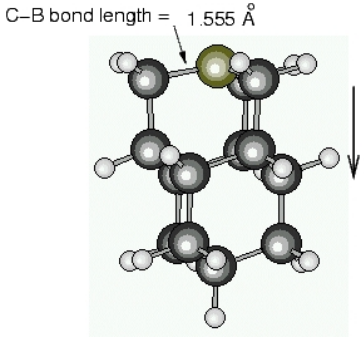
Functionalized diamondoids

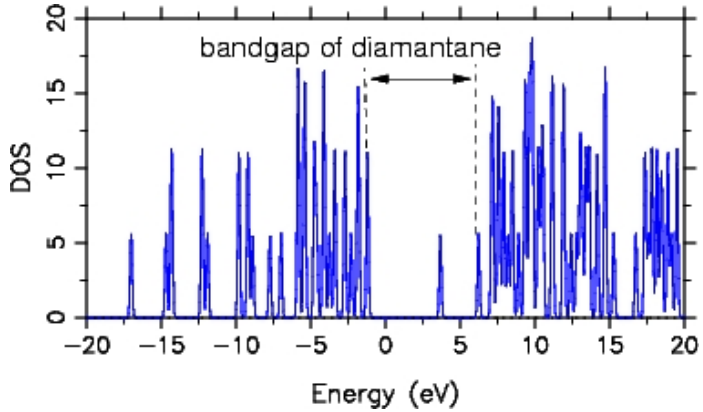
Pure diamantane:
$C_{14}H_{20}$



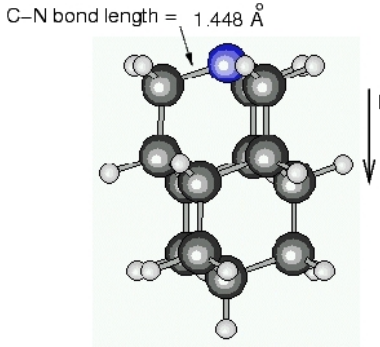


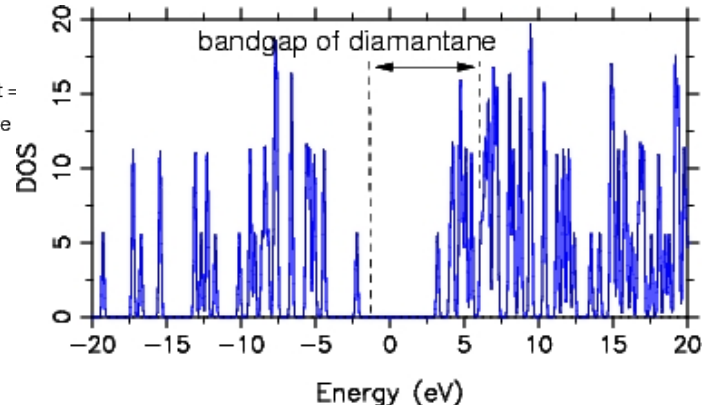
Replace a carbon by a boron:
$C_{13}H_{19}B$





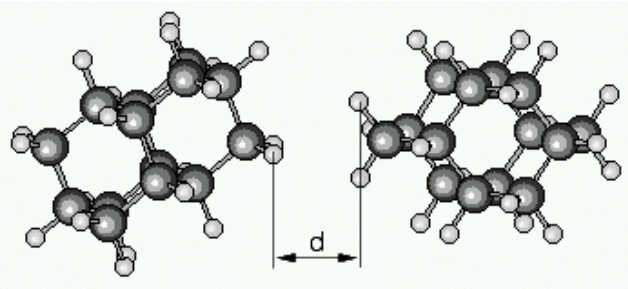
Replace a carbon by a nitrogen:
$C_{13}H_{19}N$

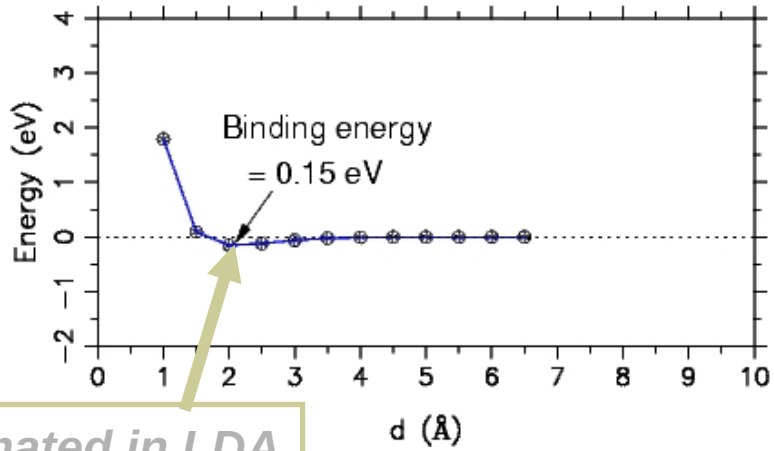




Diamondoid reactions

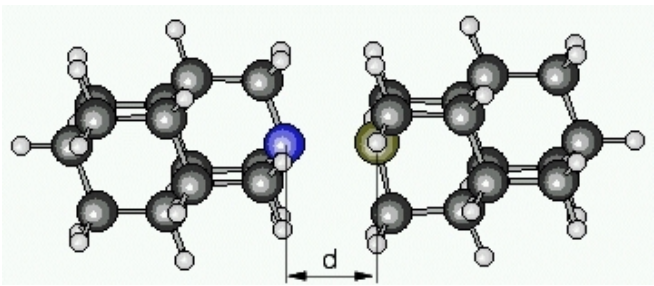
$C_{14}H_{20} + C_{14}H_{20}$

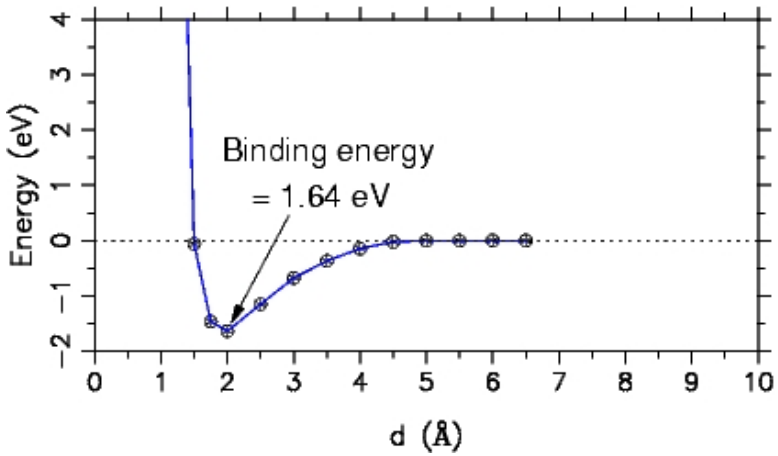




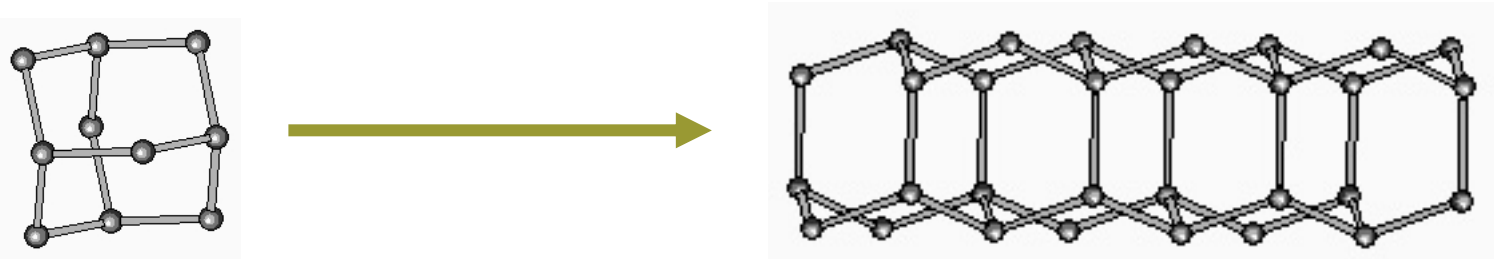
H-mediated bond likely underestimated in LDA

$C_{13}H_{19}N + C_{13}H_{19}B$

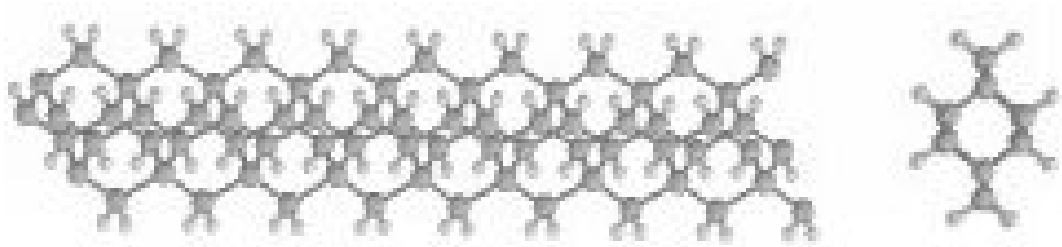




Diamondoid polymerization



Diamondoid chain: C_nH_n



Growth Energetics:

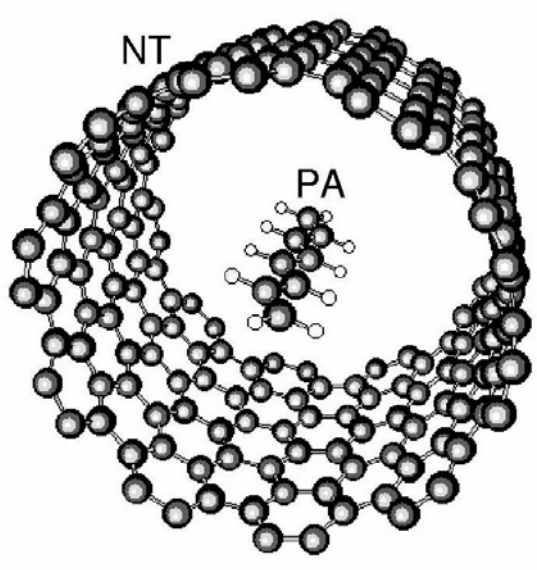
$$C_{10}H_{16} + 2\,m\,C_2H_2 \xrightarrow{\Delta E} C_{(10+4m)}H_{(16+4m)}$$

$$\Delta E = -9.31 \text{ eV}/m$$

❖Diamond wires can be formed inside a nanotube

Polyacetylene@Nanotubes

A designer superconductor?

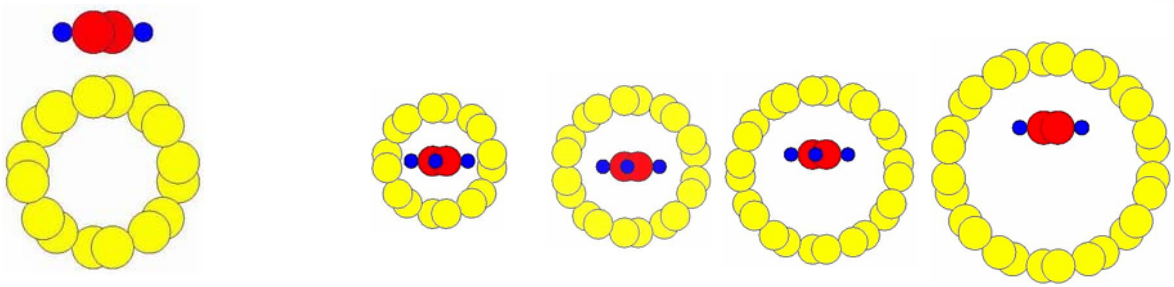


Facts:

- Undoped metallic nanotubes are superconductors
- Doped polyacetylene ropes are conductors

Exo- and endohedral PA/CNT system:

- **Potential superconductor?**

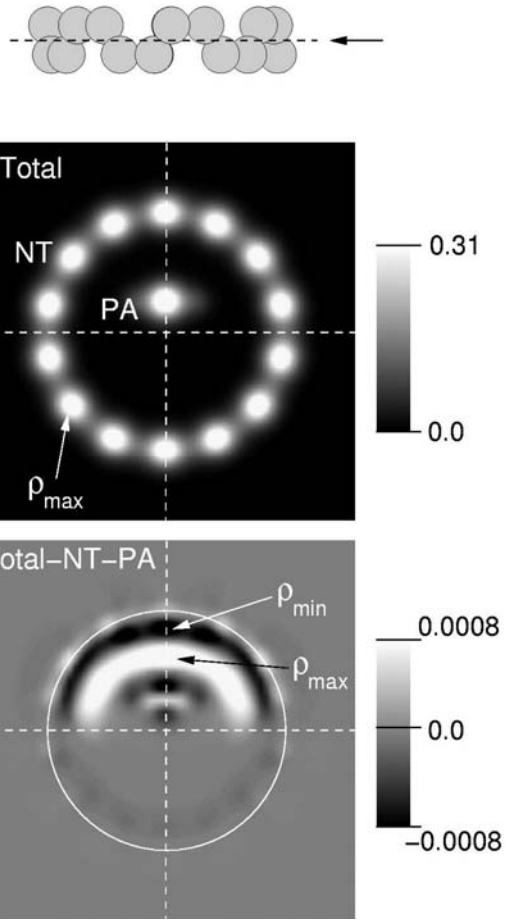


Exohedral **Endohedral**

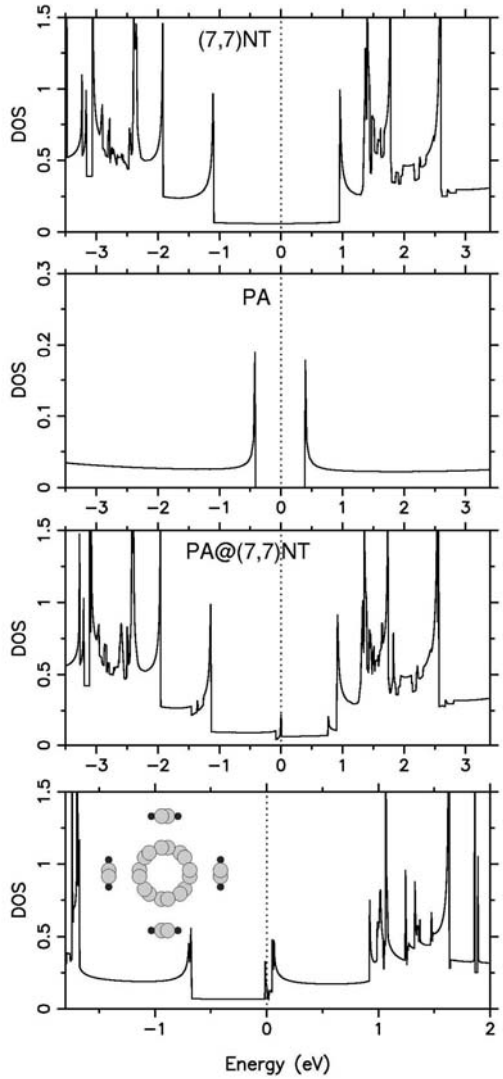
*Gregory McIntosh, Yung Woo Park, and David Tománek, Phys. Rev. B **67**, 125419 (2003)*

Electronic structure changes

Charge redistribution



Density of states



Findings:

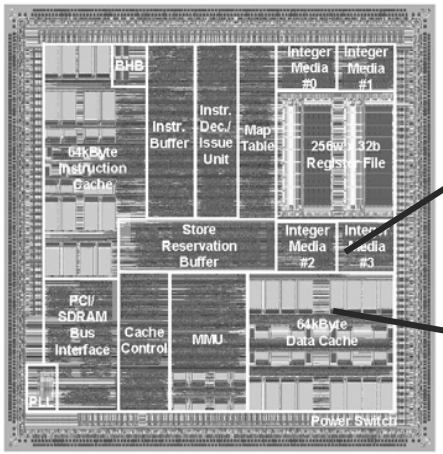
- A small CNT/PA hybridization modifies electronic structure near E_F
- van Hove singularities of PA appear near the CNT Fermi level
- One of the PA-induced singularites is pinned at E_F, thus increasing $N(E_F)$
- This effect may increase T_c of undoped CNTs

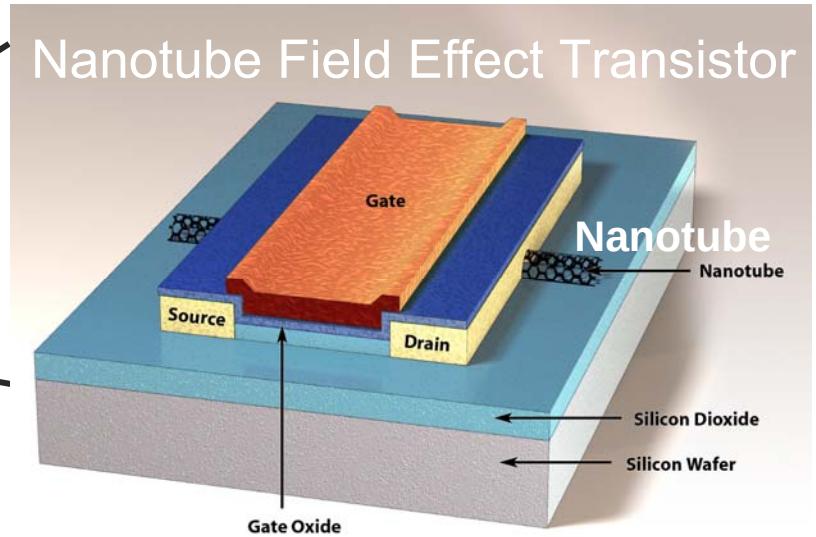
Outline

- Introduction
  - **What to expect from computer modeling**
  - **Computational tools**
- Unexpected behavior of nanostructured carbons
  - **Can carbon be harder than diamond?**
  - **Nanotube peapods: nano-memory and beyond**
  - **Diamondoids in nanotube peapods**
  - **Polymer-nanotube composites**
- Defects in carbon nanostructures
  - **Defect tolerance of nanotubes**
  - **Defect assisted fusion of nanotubes**
- Nanotechnology in Medicine
  - **Can We Remotely Destroy Tumors?**
- Summary and Conclusions

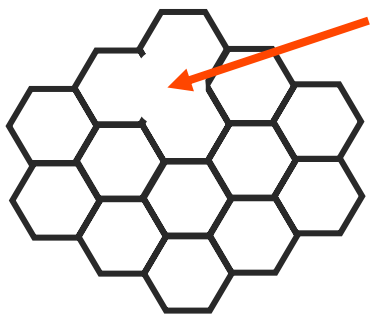
Defects in carbon nanostructures

Defect tolerance of nanotubes





- Defects limit performance, lifetime of devices
- Are CNT devices as sensitive to defects as Si-LSI circuits?

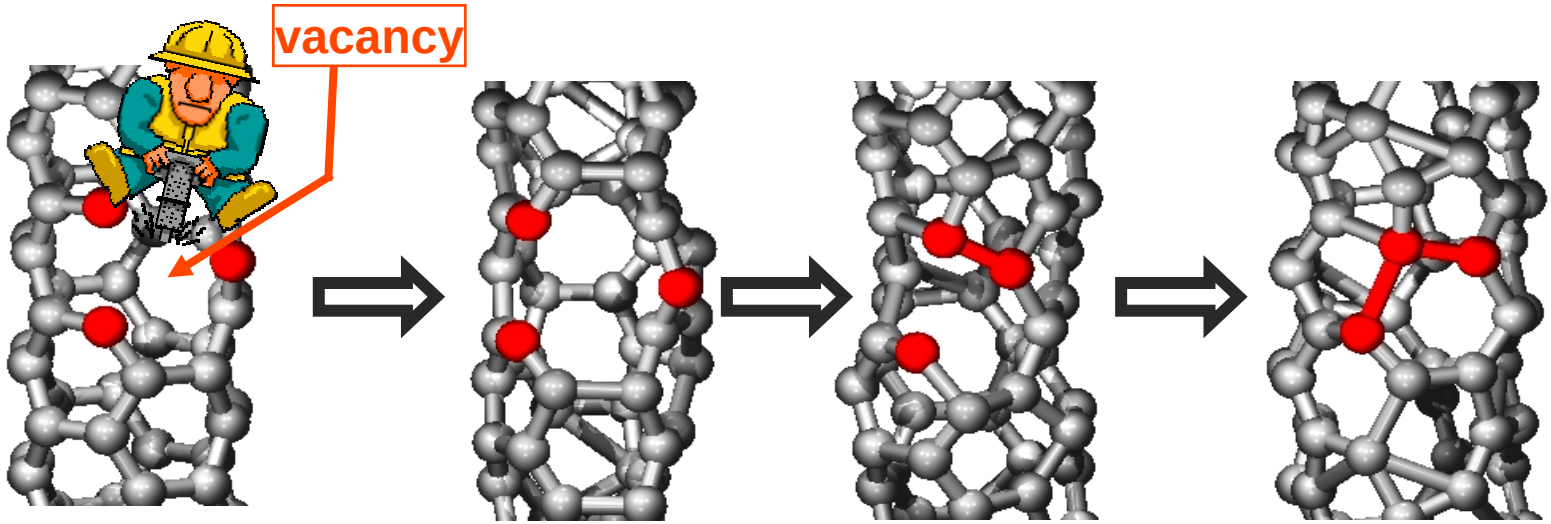


Will atomic vacancies trigger failure under
- high temperatures?
- illumination?

Yoshiyuki Miyamoto, Savas Berber, Mina Yoon, Angel Rubio, David Tománek, Can Photo Excitations Heal Defects in Carbon Nanotubes? Chem. Phys. Lett. ***392****, 209–213 (2004).*

Stability of defective tubes at high temperatures

- Danger of pre-melting near vacancies?

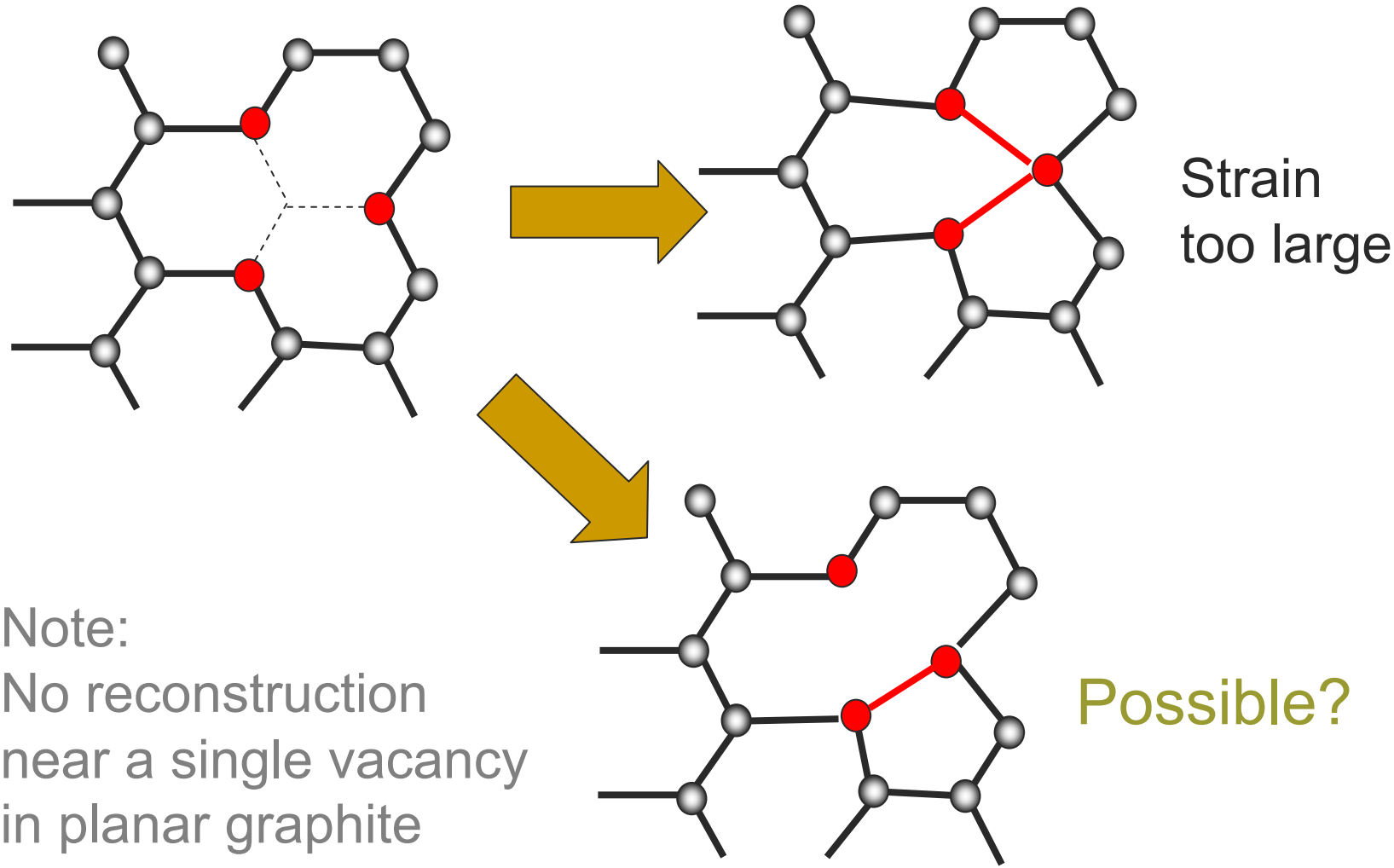


T= 0 K

T= 4,000 K

- Nanotube remains intact until 4,000 K
- Self-healing behavior:
  Formation of new bond helps recover
  - structural stiffness
  - conductance

Equilibrium structure near a single vacancy

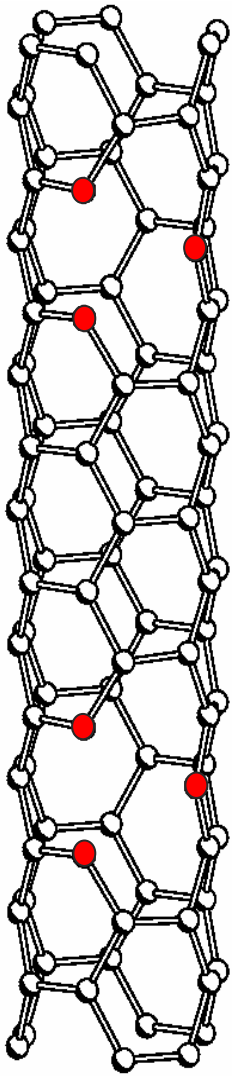


Note:
No reconstruction
near a single vacancy
in planar graphite

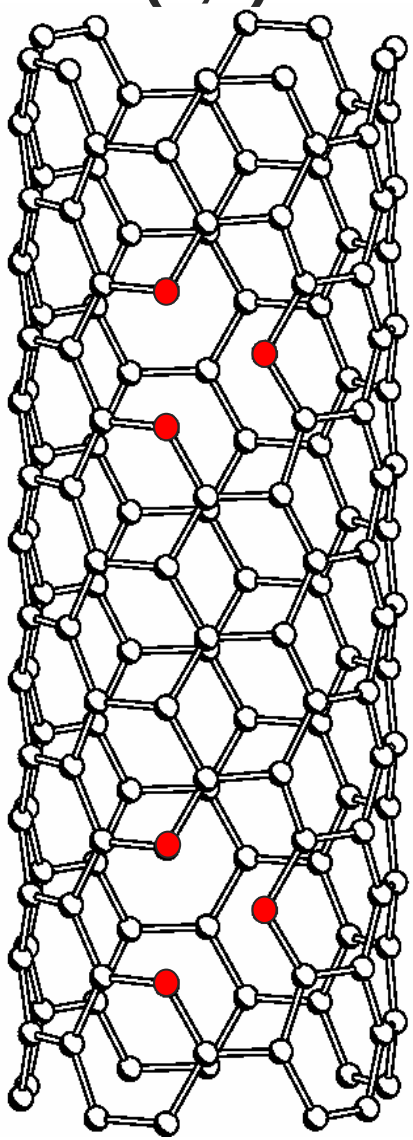
Test case: single vacancies in nanotubes

Bench marking sample

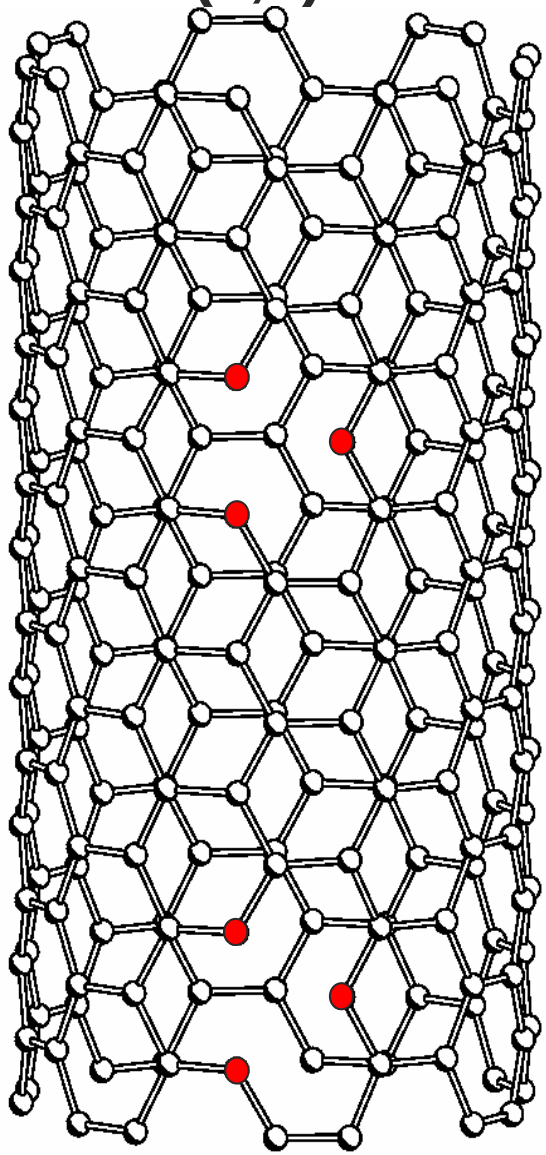
(3,3)



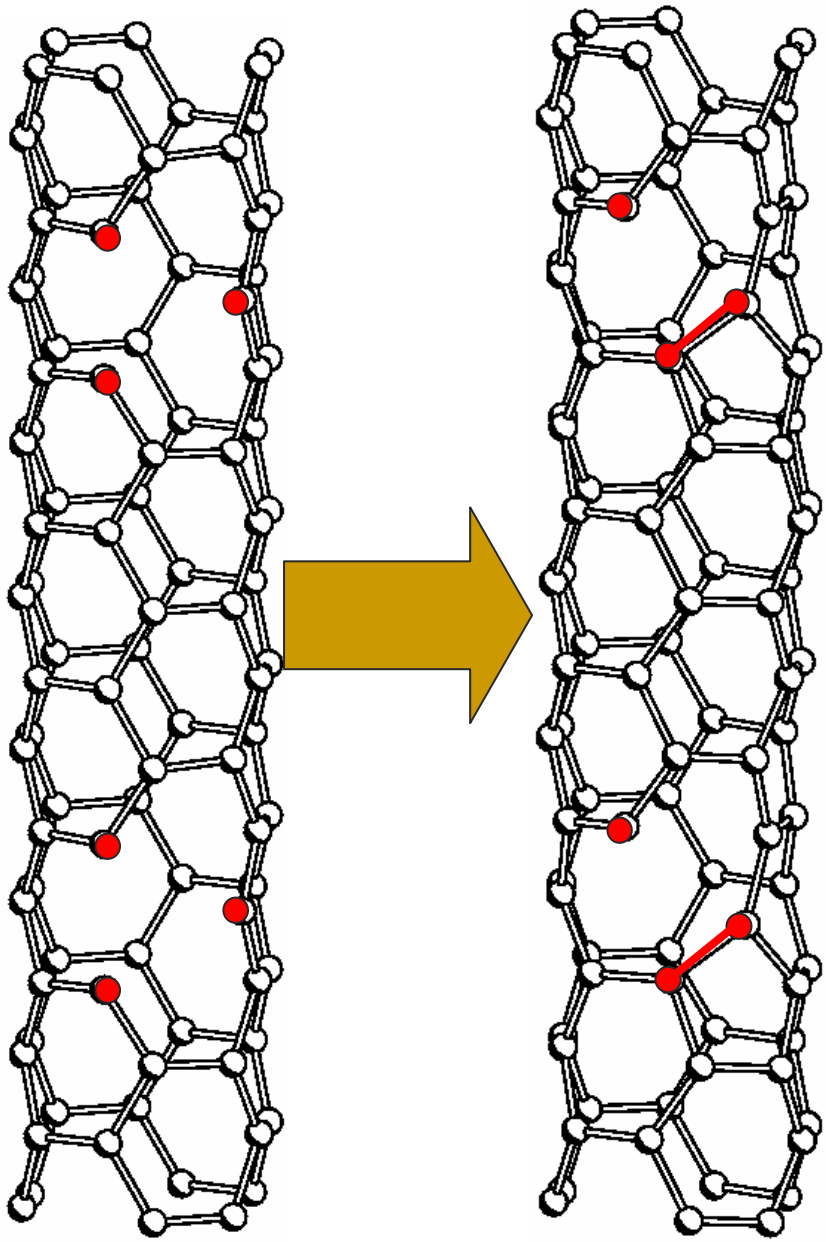
(5,5)



(7,7)

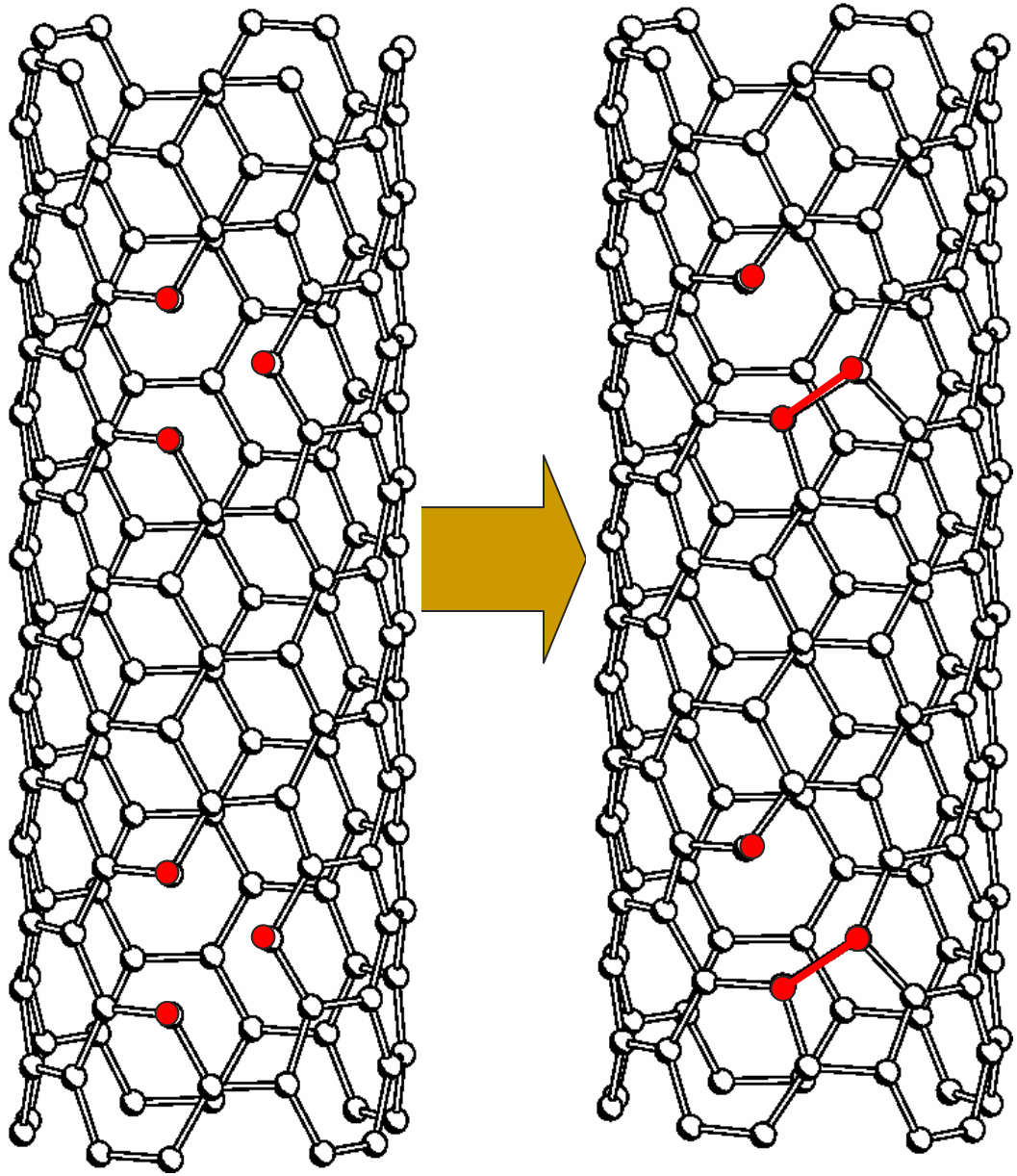


(3,3) nanotube



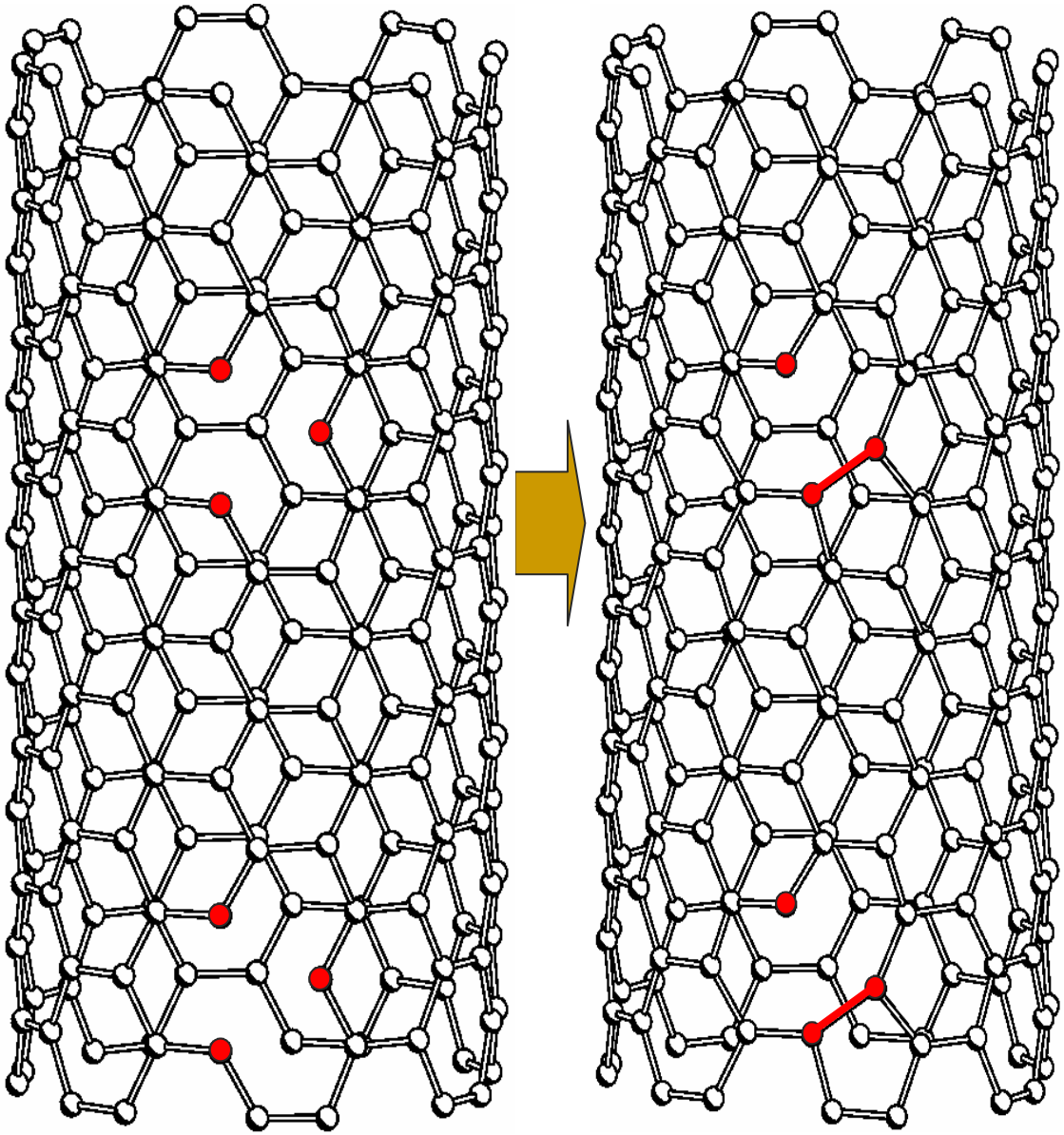
Energy lowering
1.76 eV / vacancy

(5,5) nanotube



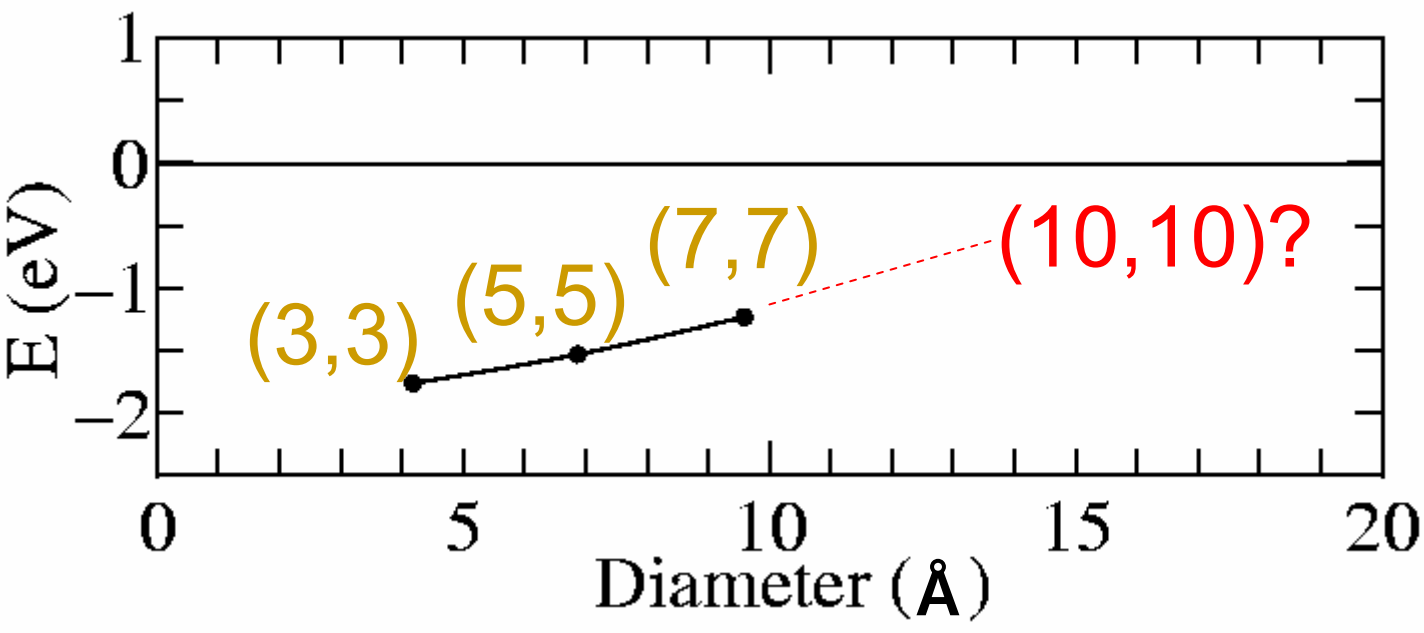
Energy lowering
1.53 eV / vacancy

(7,7) nanotube



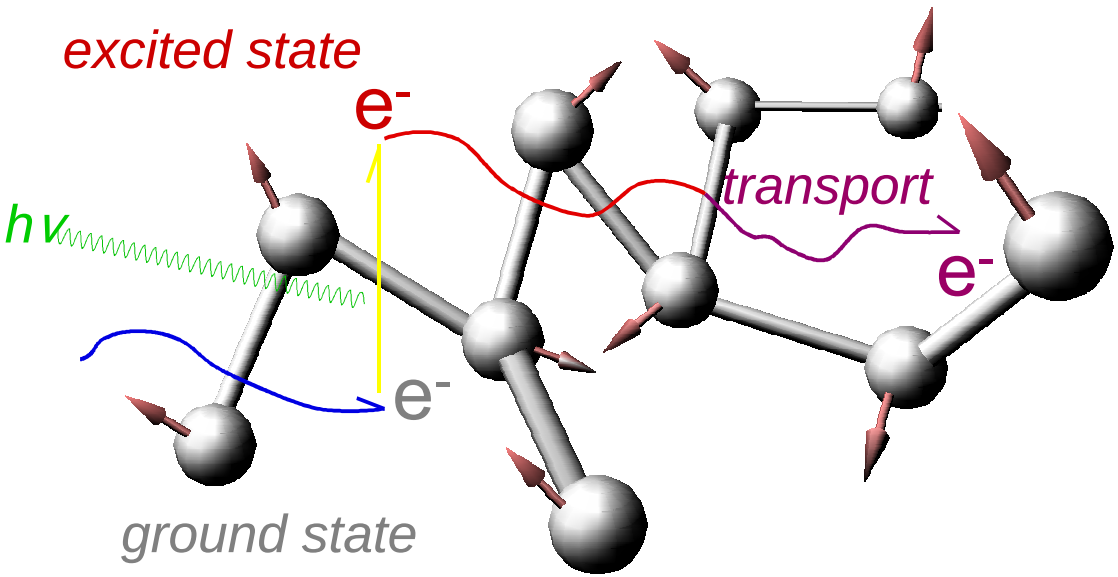
Energy lowering
1.23 eV / vacancy

Structure stabilization by reconstruction



Wall curvature helps reconstruction
in thin nanotubes

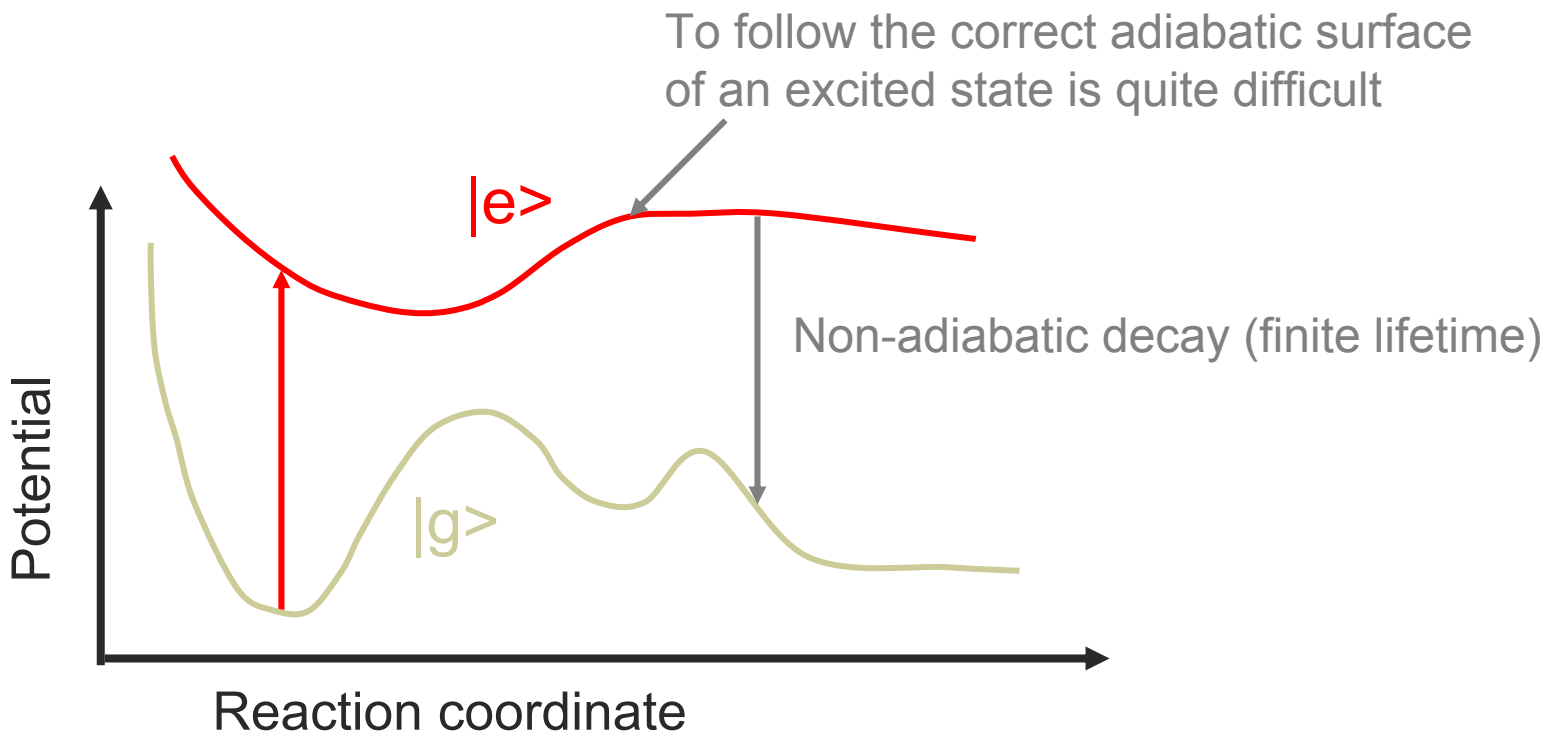
Stability of defective tubes during electronic excitations



Challenges:

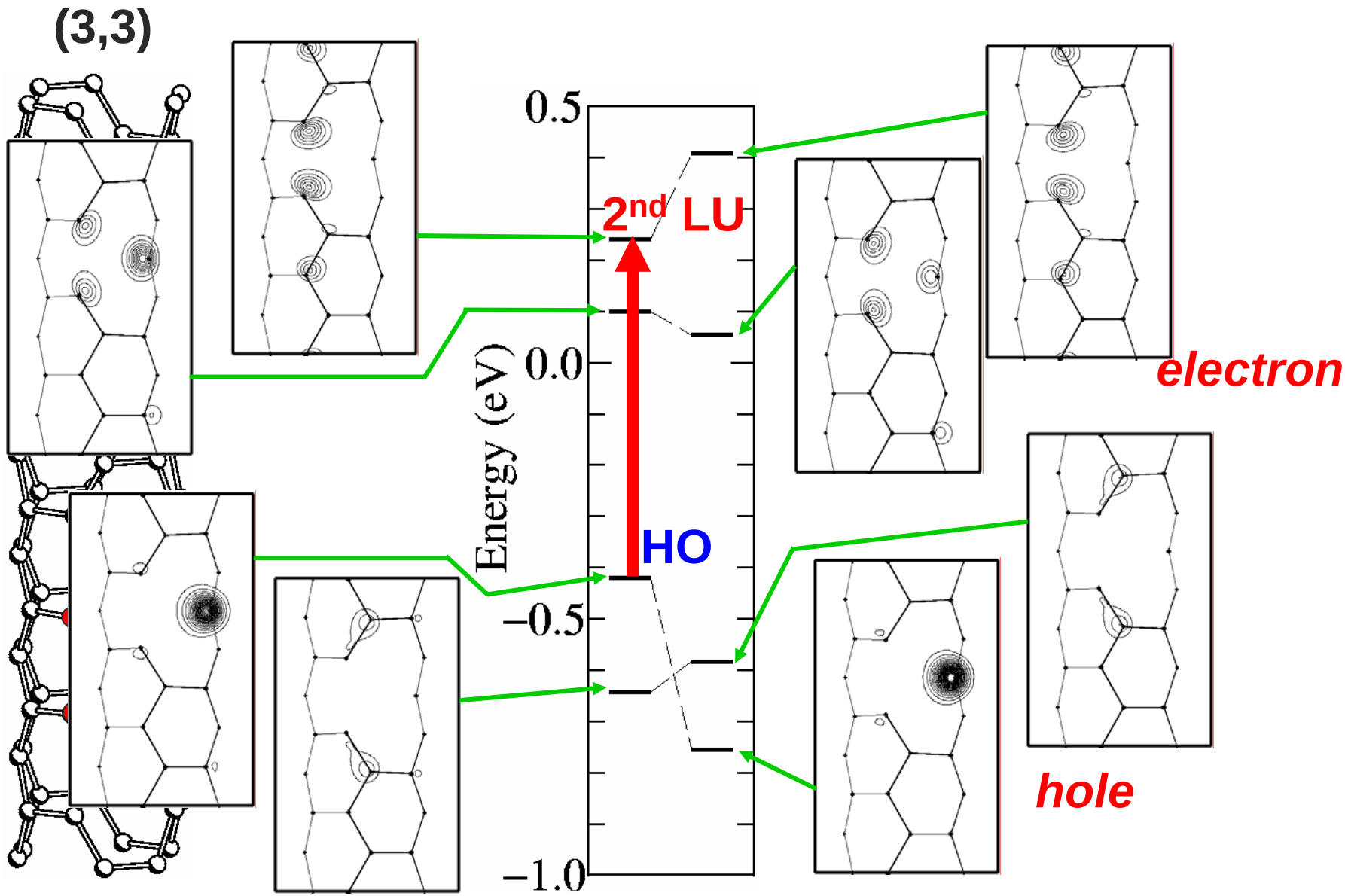
- Perform Molecular Dynamics simulations on the adiabatic surface of an electronically excited state
- Solve the time-dependent Schrödinger equation for electrons during ionic motion

First-principles Molecular Dynamics simulation on the adiabatic surface of an electronically excited state

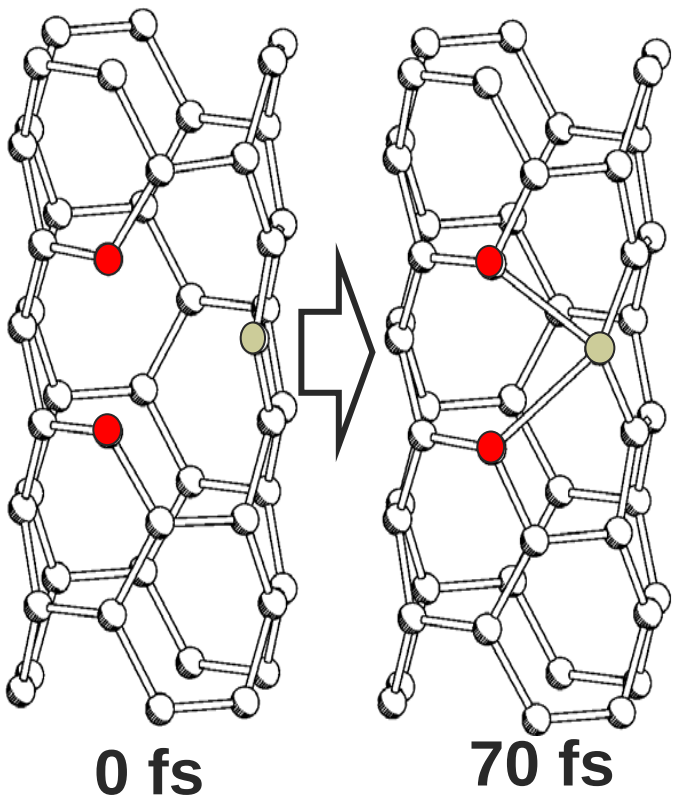


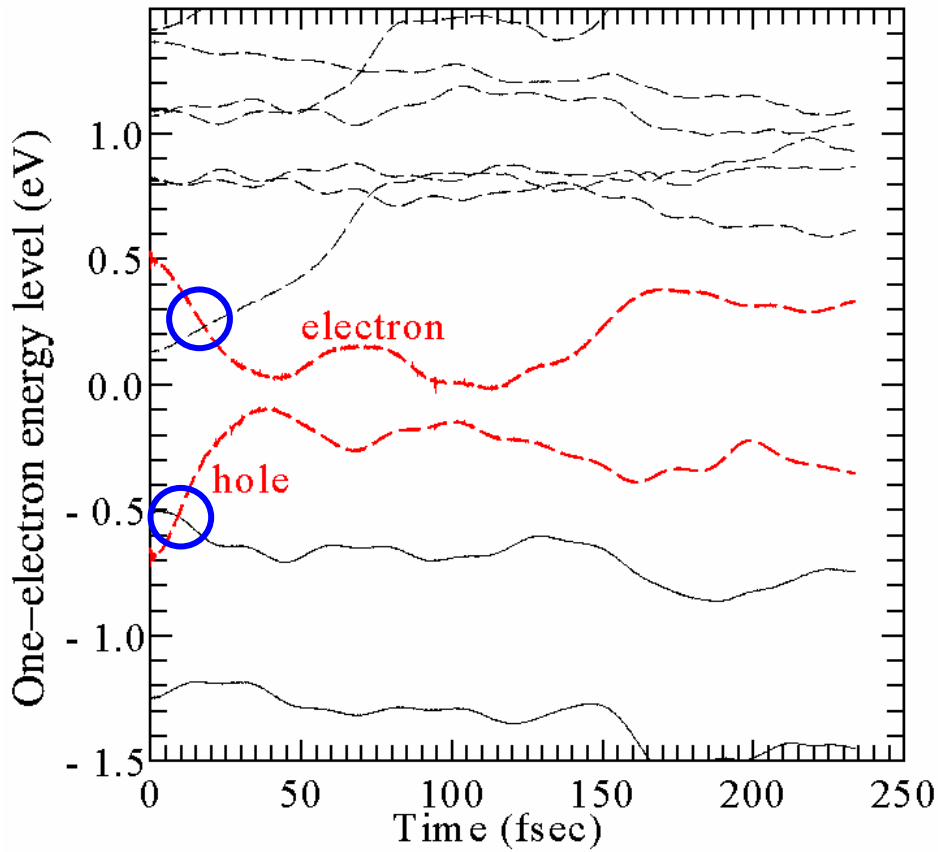
- First-Principles Simulation tool for Electron-Ion Dynamics
- Details: *Sugino & Miyamoto PRB **59**, 2579 (1999); PRB **66**, 89901 (2002).*

Optical excitation (ΔE=0.9 eV)



Time evolution of the electronic states

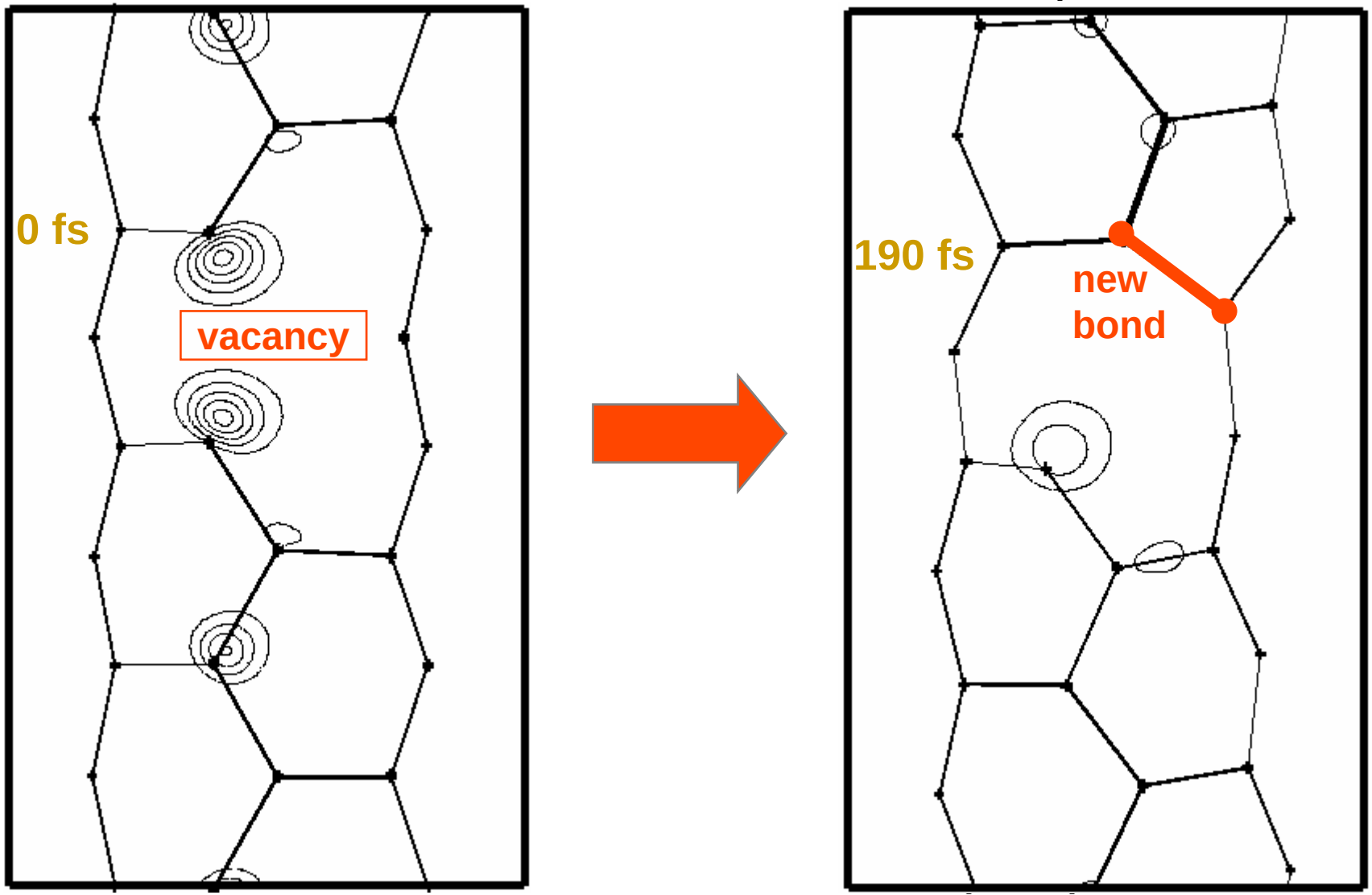




$\Psi_n(t+\Delta t)=\exp(-i/h\, H\Delta t)\,\Psi_n(t)$

- Very long-lived excitation
- Correct PES is followed in case of level alternation

Structural changes under illumination



- Self-healing due to new bond formation

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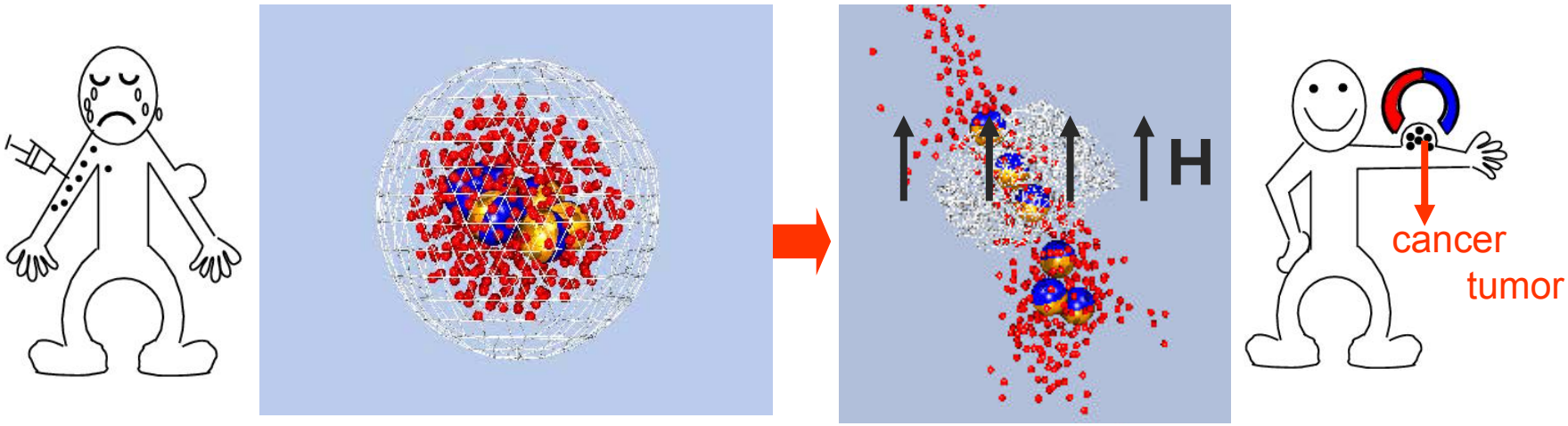
Nanotechnology in Medicine

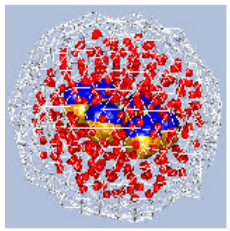
Can We Remotely Destroy Tumors?



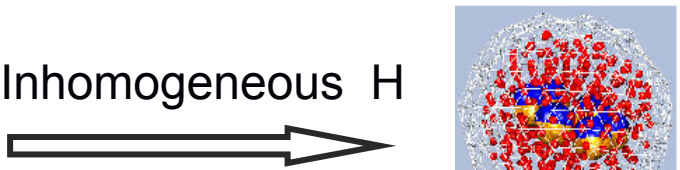
❖Can we target medication delivery?

Mina Yoon, Peter Borrmann, and David Tomanek, Targeted medication delivery using magnetic nanostructures (submitted for publication).

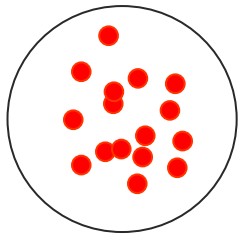
Targeted Medication Delivery



Inhomogeneous H



Transport of inert capsule



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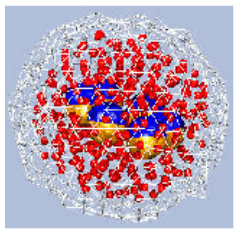
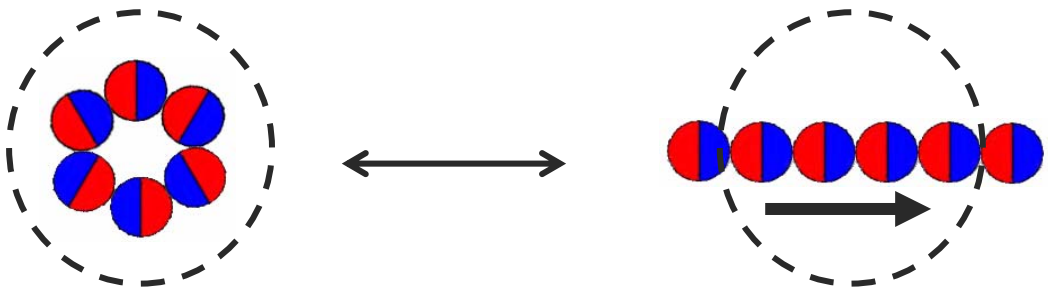


Large Homogenous H

Medication delivery

- How to deliver the active substance?
- Stability of system?



H≈0

H>>0

Summary and Conclusions

- Polymerized fullerenes form rigid solids, which do not exceed the bulk modulus of diamond.
- Insertion of diamondoids and plymers in nanotubes yields new nanostructures with intriguing properties.
- Nanotubes act as an autoclave to facilitate reactions between encapsulated molecules.
- Self-healing behavior occurs in defective nanotubes.
- Targeted medication delivery may be induced by structural transitions in finite-size magnetic aggregates.

The End