Challenging to Large-scale Simulation: The Earth Simulator Lessons

---Nanotechnology Simulation---

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Motivation:
Why Large Scale Simulation is indispensable on Nano tech.

Nanotechnology:
Emergence of novel structures and properties keeping quantum effects by controlling atoms and molecules situations. Carbon nanotubes and fullerenes are strategic materials.

How to simulate nano scale systems ?

Key words: Scale and complexity in physical world

The behavior of large and complex aggregates of element particles is not be understood in terms of a simple extrapolation of the properties of a few particles

→ *Large Scale Simulation*

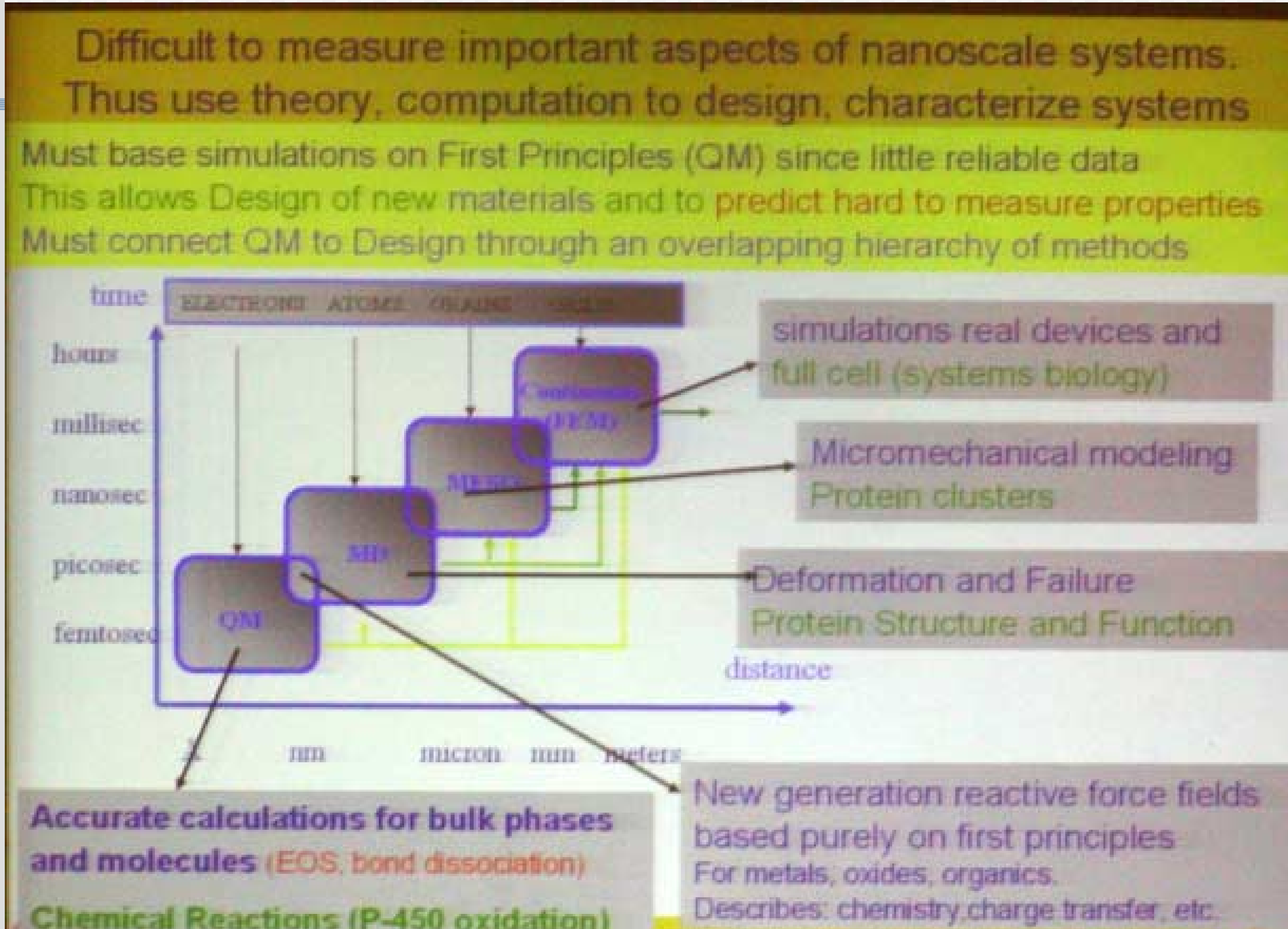
Instead, at each level of complexity entirely new properties appear.... At each stage entirely new laws, concepts, and generalizations are necessary, requiring inspiration and creativity to just as great a degree as in the previous one.

→ There are some suitable models for the target scale

More Is Different P. W. Anderson

An overlapping hierarchy

Prof. William A. Goddard, III at Caltech



Model hierarchy for nano carbon description

Our target for real scale simulations is 10^4-10^5 atoms

disappearance of the property

Ab initio Hamiltonian

strong correlation

The maximal number of atoms

10^{2-3} DFT(density functional theory)

free electron

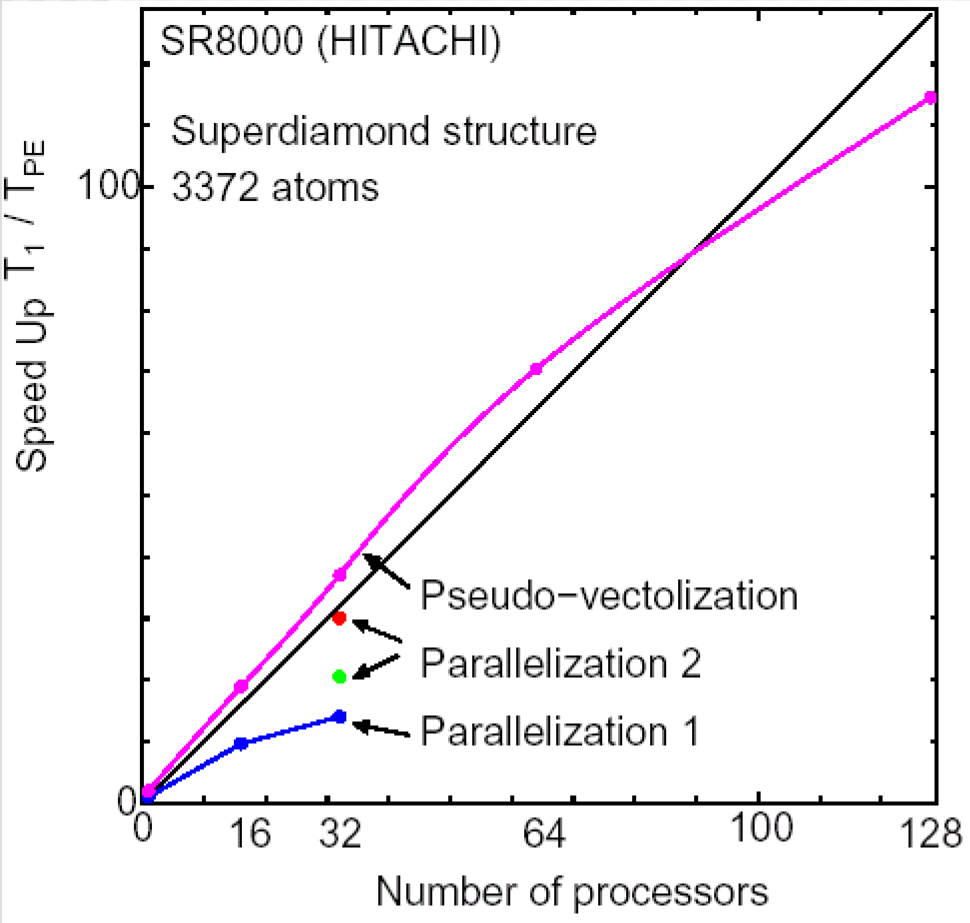
10^{4-5} Tight-binding method

orbital state

10^7 Classical (Empirical) method

The TB method is suitable approach to carbon hybridization to large scale systems

Challenging to Large Scale Simulation
(Training and preparation before working on Earth Simulator)



Tigth-binding code

Parallelization
→Good up to about 100PE

Next target for ES
Parallelization
→ about 4000 PE
High Vectorization

SR8000 at Tokyo Univ.

Speed of code on Earth Simulator

---For 48,000 carbon atoms---

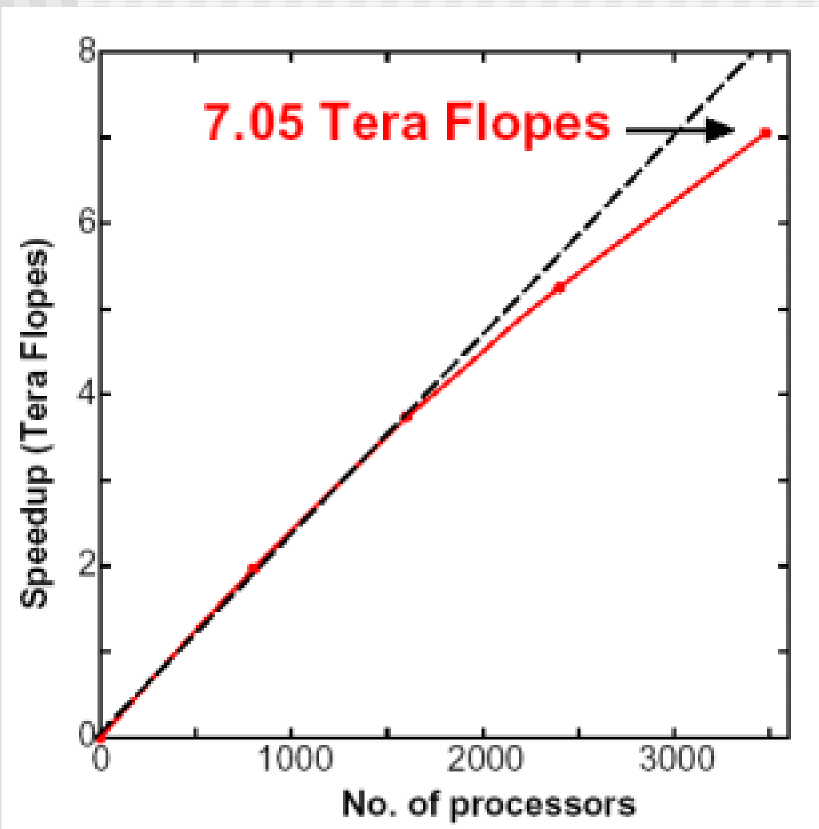
*Vector Op. : 97.7%

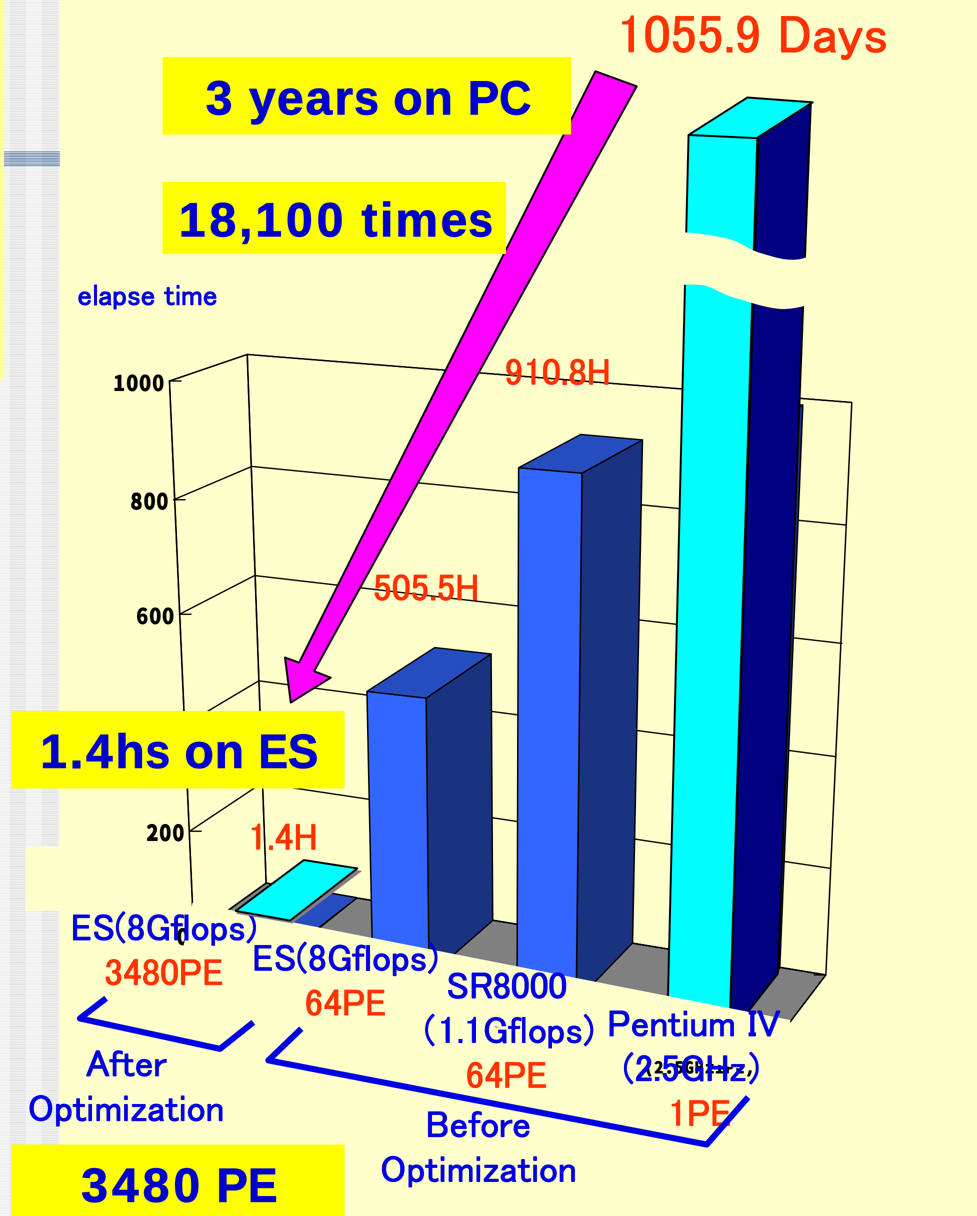
*Parallel Op. : 99.99%

*Total Performance

using 3480PE : 7.05TeraFlops

(25 % of Peak speed)





Elapse time and Time steps for thermal conductivity simulation using order-N CRTMD

No. of Processors:1024
Speed : 2.5TeraFlops

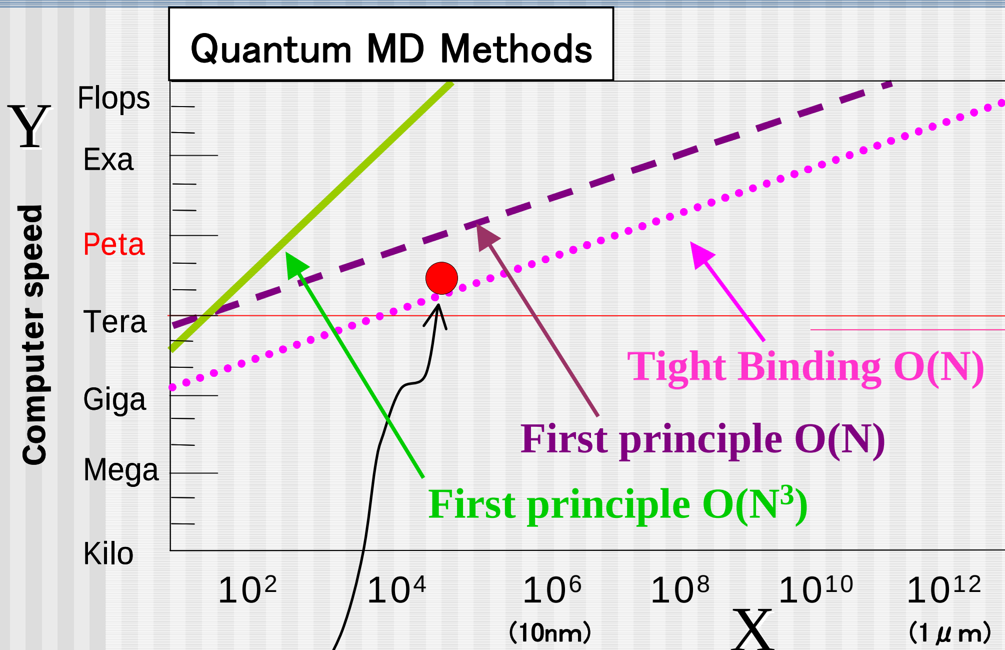
Calculation volume for thermal conductivity simulation is proportional to the $\mathbf{N^2}$, so elapse time the $\mathbf{N^2}$.

Length of CNT	Elapse time	Time steps	
35nm :	2.5days	120,000	60ps
70nm :	10.0days	240,000	120ps
140nm :	40.0days	480,000	240ps

(120,000=60ps/0.5fs)

Required Computer Resource

（Before working on Earth Simulator, We estimate the cal. volume I will challenge）



Conditions

Simulation steps : 10^6
CPU time : 30 days

If number of atoms is X, what high computer is needed to finish quantum MD calc. within conditions.

Our thermal conductivity simulation is plotted ...

CNT Len.(nm)	140
Atoms	48,000
Requirement Resource	1024PE × 12h × 69
Elapse time (days)	35

Earth Simulator

Explanation of CRTMD code

- CRTMD code
- Method
- Flow chart of code
- Parallelization of Code

CRTMD(**Carbon Recursive Technique of Molecular Dynamics**) code

- Theory
  - Slater-Koster parametrized Hamiltonian.
  - Green function and Density of states provided by the recursion method(RM)
  - Order-N method.

- Styles
  - Useful to a large systems lacking of symmetry.
  - Computational workload scales linearly with a volume of the system.
  - RM is highly suitable for parallel computing, as the charge density can be calculated independently at each point.

Method
---Orbital MD ---

Creation of Hamiltonian-Matrix-Element

${}_a\langle i\,|H|\,i\rangle_a = E_a(i)$:energy of isolated orbital (a)

${}_a\langle i\,|H|\,j\rangle_b = E_{ab}^{(i,j)}$:hoping integral calculated from the orbital (a,b) and position (i,j).

$$\bar{H} = \begin{pmatrix} \bar{H}(0) & \bar{H}(0,1) & \cdots & \bar{H}(0,m) \\ \bar{H}(1,0) & \bar{H}(1) & \cdots & \bar{H}(1,m) \\ \vdots & \vdots & \ddots & \vdots \\ \bar{H}(m,0) & \bar{H}(m,1) & \cdots & \bar{H}(m,m) \end{pmatrix}$$

4m × 4m

$$\bar{H}(i) = \begin{pmatrix} E_{2s}^{(i)} & 0 & 0 & 0 \\ 0 & E_{2px}^{(i)} & 0 & 0 \\ 0 & 0 & E_{2py}^{(i)} & 0 \\ 0 & 0 & 0 & E_{2pz}^{(i)} \end{pmatrix}$$

4 × 4

$$\bar{H}(i,j) = \begin{pmatrix} E_{2s,2s}^{(i,j)} & E_{2s,2px}^{(i,j)} & E_{2s,2py}^{(i,j)} & E_{2s,2pz}^{(i,j)} \\ E_{2px,2s}^{(i,j)} & E_{2px,2px}^{(i,j)} & E_{2px,2py}^{(i,j)} & E_{2px,2pz}^{(i,j)} \\ E_{2py,2s}^{(i,j)} & E_{2py,2px}^{(i,j)} & E_{2py,2py}^{(i,j)} & E_{2py,2pz}^{(i,j)} \\ E_{2pz,2s}^{(i,j)} & E_{2pz,2px}^{(i,j)} & E_{2pz,2py}^{(i,j)} & E_{2pz,2pz}^{(i,j)} \end{pmatrix}$$

4 × 4

In general $\bar{H}\vec{a} = E\vec{a}$ is solved ,,, .

(continued)

Lanczos recursion method

$$\bar{H} \rightarrow \bar{H}_{tri} = \begin{pmatrix} a_0 & b_1 & 0 & \cdots \\ b_1 & a_1 & b_2 & \cdots \\ 0 & b_2 & a_2 & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}$$

Recusive Green function

$$G_{00}(E) = (E\bullet\bar{1} - \bar{H}_{tri})^{-1}_{00} = \begin{pmatrix} E-a_0 & b_1 & 0 & \cdots \\ b_1 & E-a_1 & b_2 & \cdots \\ 0 & b_2 & E-a_2 & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}^{-1}_{00} = \cfrac{1}{E-a_0-\cfrac{b_1^2}{E-a_1-\cfrac{b_2^2}{\cdots}}}$$

Density of state

$$D_{00}(E) = -\frac{1}{\pi}\operatorname{Im} G_{00}(E+i0^+)$$

Number of electron

$$N(E)_0 = \int^{E} D_{00}(E)\,dE$$

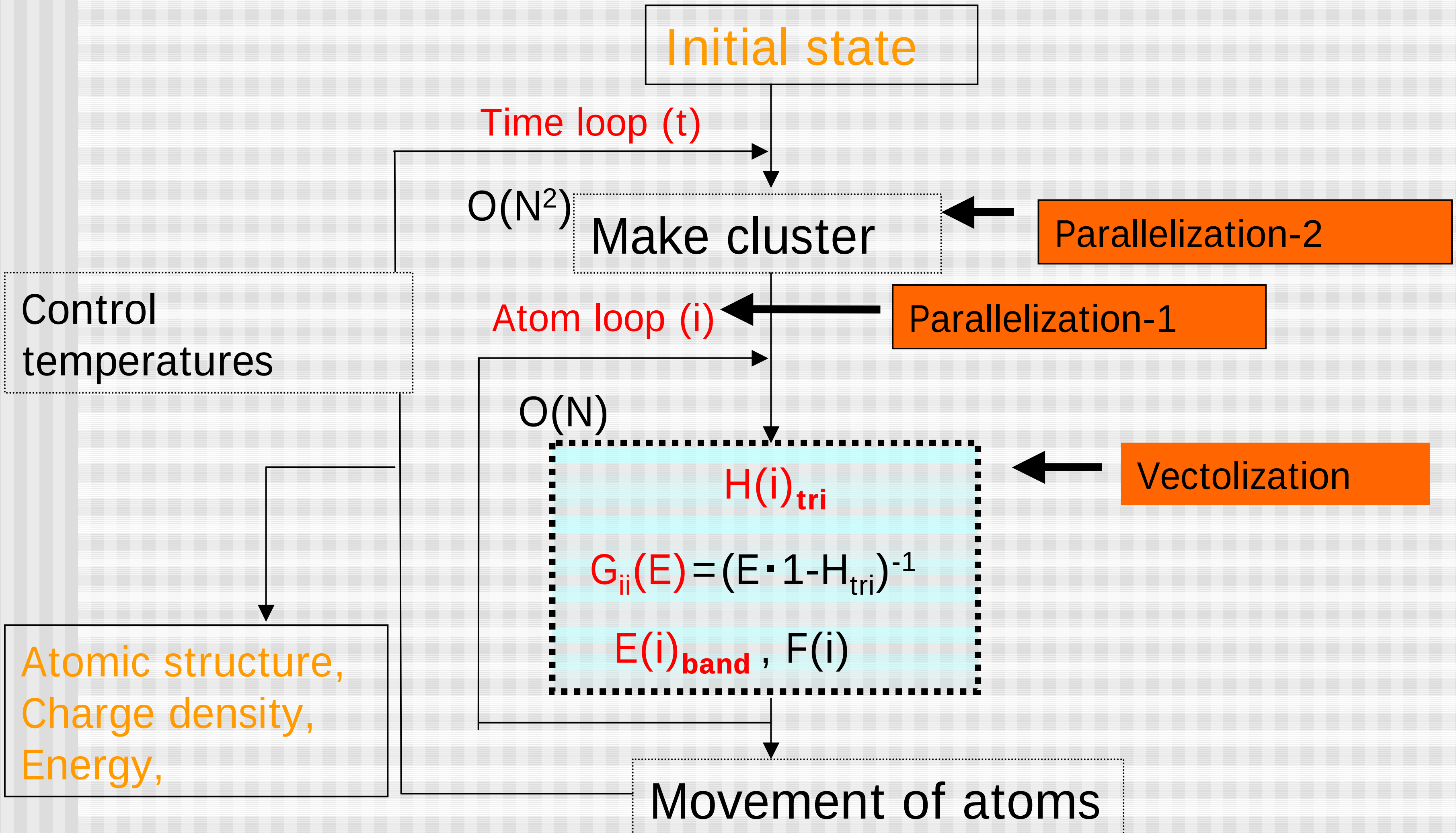
Electric Energy

$$E_0 = \int^{E_{Fermi}} E\bullet D_{00}(E)\,dE$$

Atomic force

$$\vec{F}_0(r) = -\nabla[E_0(r) + E_{rep}(r)]$$

Flow chart of code



Parallelization of Code

Do i=1,atoms

Do j=1,atoms

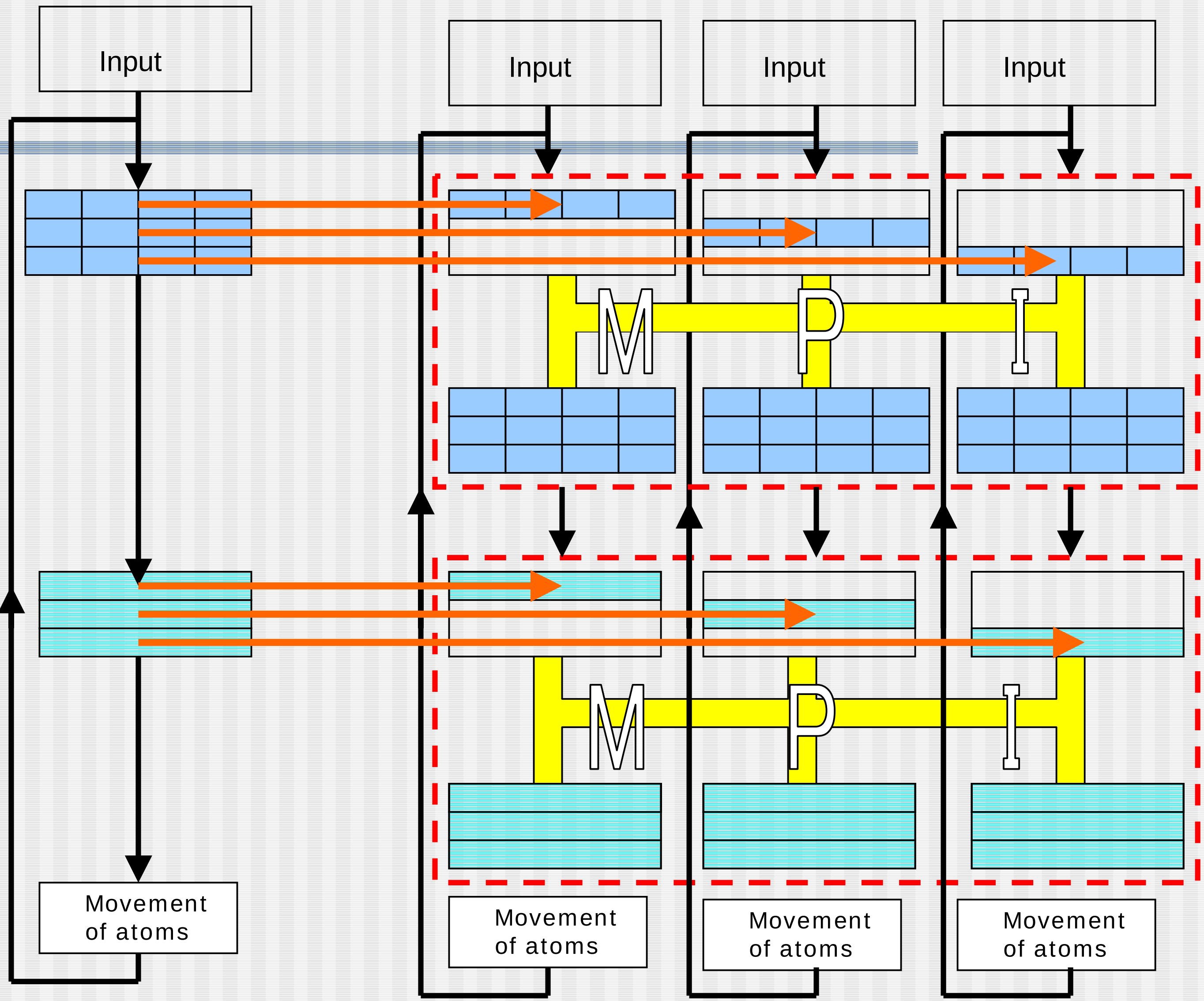
Distances between
i and j atom

End do
End do

Do i=1,atoms

Force(I)

End do

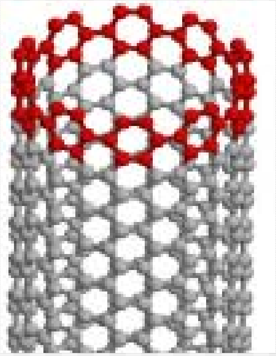


<u>Serial case</u> <u>Parallel case</u>

Introduction to Carbon Nanotube

Introduction to Carbon Nanotube

What is Carbon Nanotube



Observed by Prof. S.Iizima (1991)

3D: Diamond
2D: Nanotube
0D: Fullerene

Properties

- Diameter:1nm
- Chemically inactive
- Mechanically strong:
  - 10 times stronger than steal
- High melting point:
  - Higher than 3500℃
- Ballistic conductance
- High thermal conductivity
- ...

Application

- Electric field emitter
- Electric devises
- Gas sensors
- fuel cell
- Electric devises
- ...


カイラル（らせん）型：半導体

下の二つ以外のすべてのカーボンナノチューブはカイラル型であり，半導体の性質を示す。半導体といってもらせんの角度や太さなどの構造のちがいによって，さらに細かく性質がかわるという。

ジグザグ型：金属（3分の1），半導体（3分の2）

ジグザグ型は直径の大きさによって電気的な性質がかわる。さまざまな大きさのジグザグ型のカーボンナノチューブのうち3分の1が金属，3分の2が半導体となる。

アームチェア型：金属

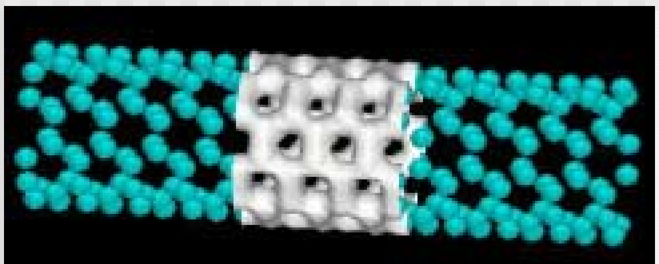
アームチェア型は金属の性質をもつ。カーボンナノチューブを展開した形状のグラファイトは金属的な性質を示すことが知られている。

（日経サイエンスから引用）

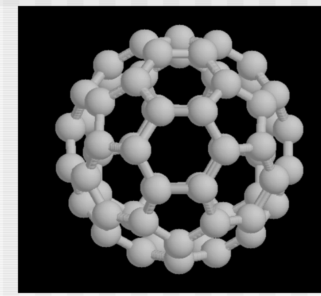
Our target of nano carbon simulation

Thermal conductivity and elasticity

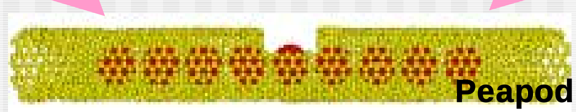
Thermal dissociation



Fundamental studies



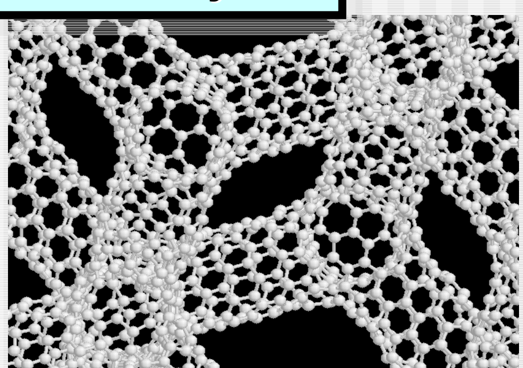
Nanotube



Fullerene :C_{60}

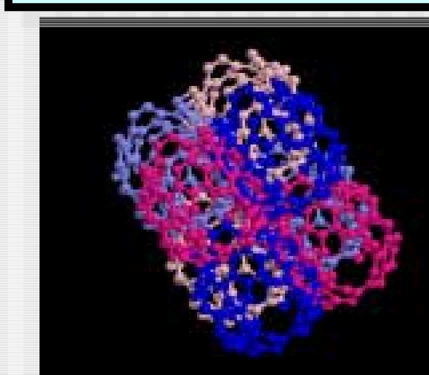
Thermal stability

Super hardness



Nano reactor

Atomic Welding



Super diamond (Jointed CNT)

Super Jungle Gym (Jointed C_{60})

Fundamental thermal properties of CNT

Nobody knows cooling efficiency on a nano -device super computer.

- Thermal conductivity for CNTs in three different length

Thermal Conductivity Simulation

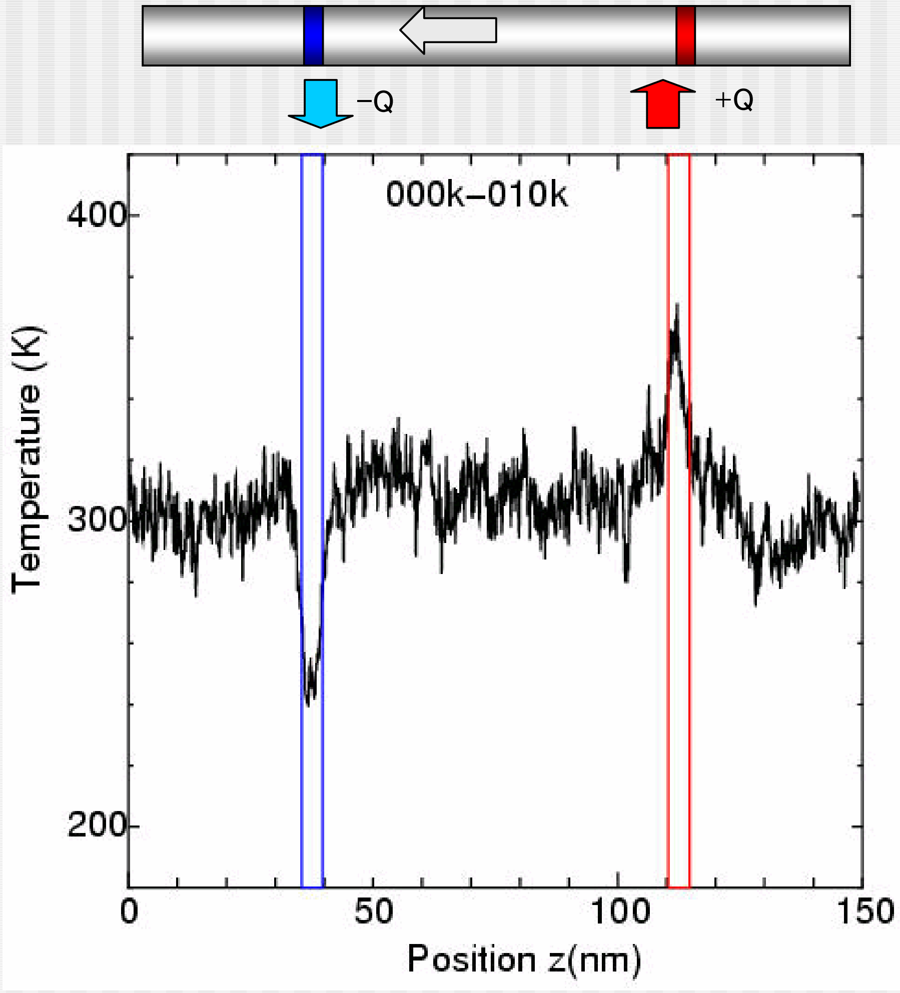
Ballistic conductance
(phonons travel without scattering)

Fourier's law

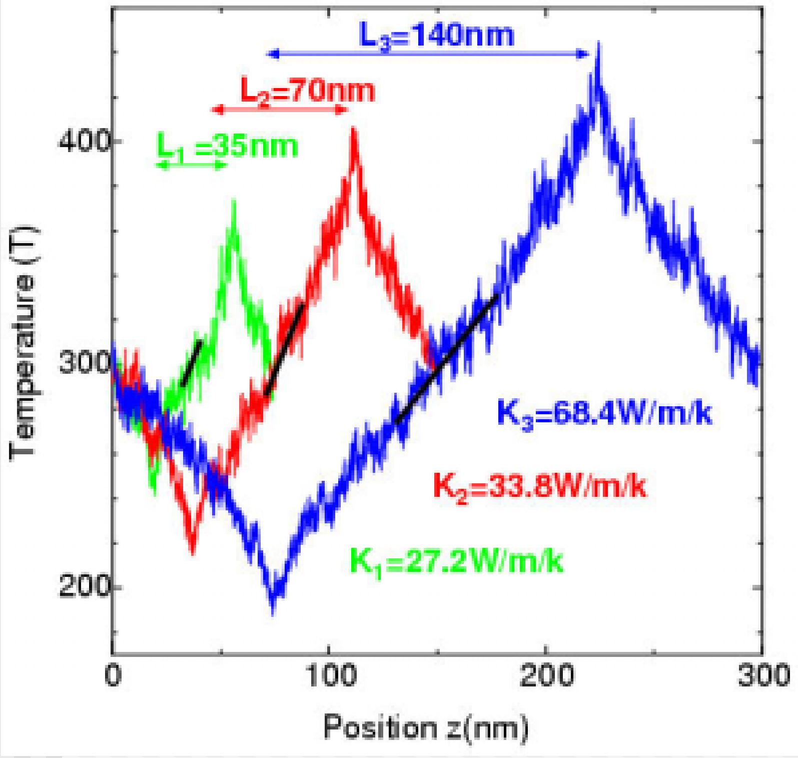
$$J = -\kappa S \frac{\partial T}{\partial x}$$

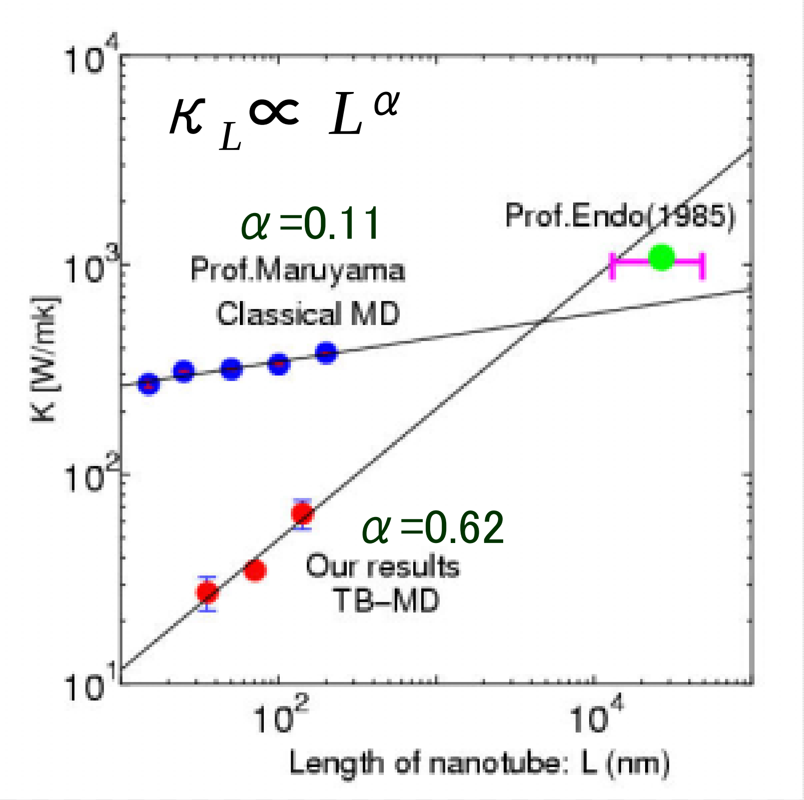
κ :Thermal conductivity
S : Cross section area
J : Heat flux
$\kappa \propto$ **phonon mean free path**

Because of the long mean-free path of CNT, length more than 100nm is required.



Simulation results





(1) The thermal conductivity increases as dose the length of CNTs. (2) Power law dependency can been seen in the real one-dimensional material, CNTs.

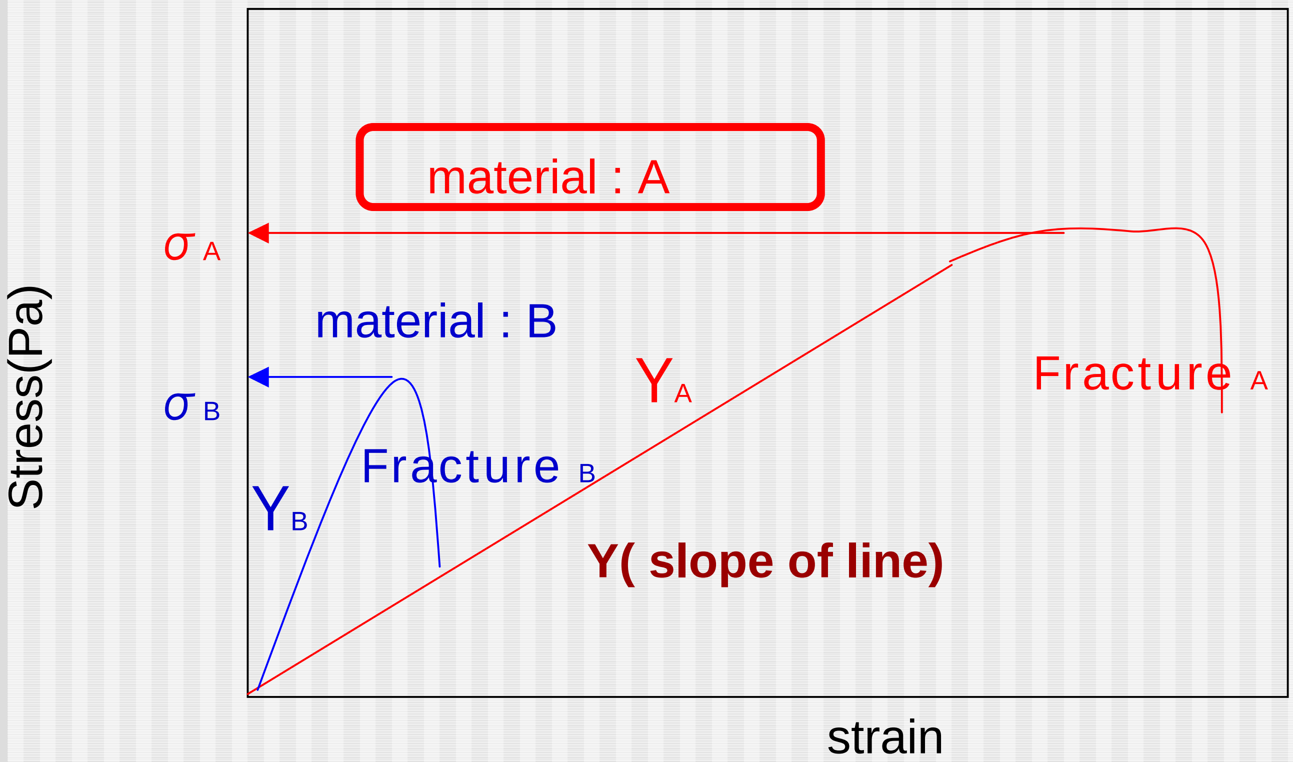
Mechanical Properties of CNT

A big earthquake often happens in Japan.
Infrastructure made of strong material is needed.
→ Single CNT buckling
Bound CNT,
Growth of Diamond,
Mackay structure by fullerene welding.

- Basic properties
  - axial tension
  - axial compression
- Application for AFM tip
  - DWCNT、
  - Peapod(=CNT filled with fullerene

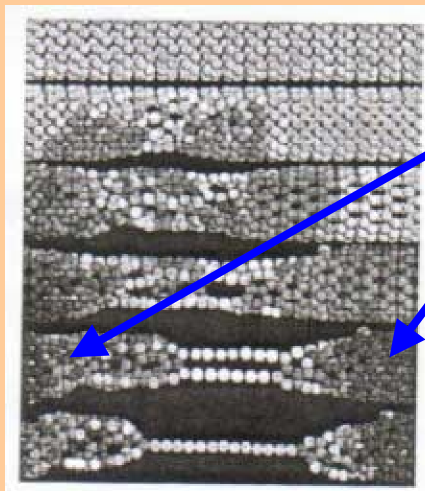
- Which is a more superior mechanical property for construction, **buckling load (σ)** or **Young's Modulus (Y)**.

Non broken at high stresses is important.



- Large scale simulation is required because size and figure take effect on the buckling load.

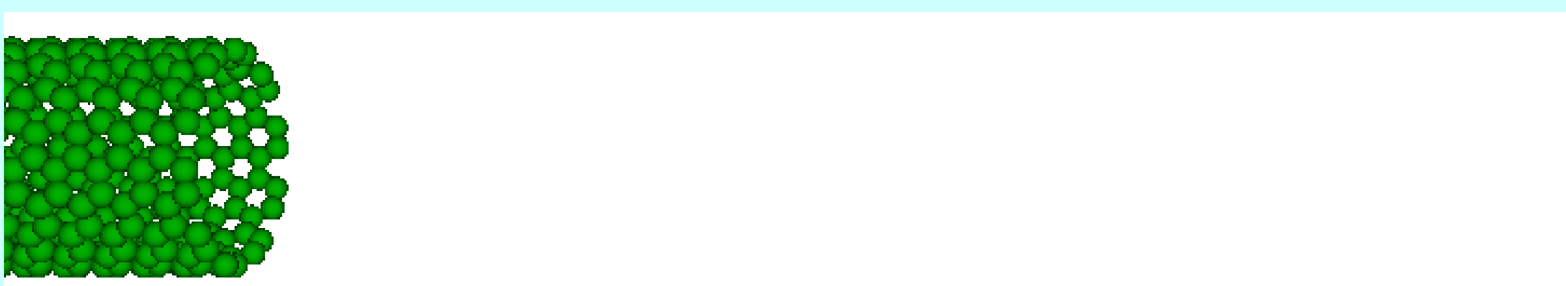
Stretch of Armchair CNT...(10,10)
---Tigth binding method---



Random structure

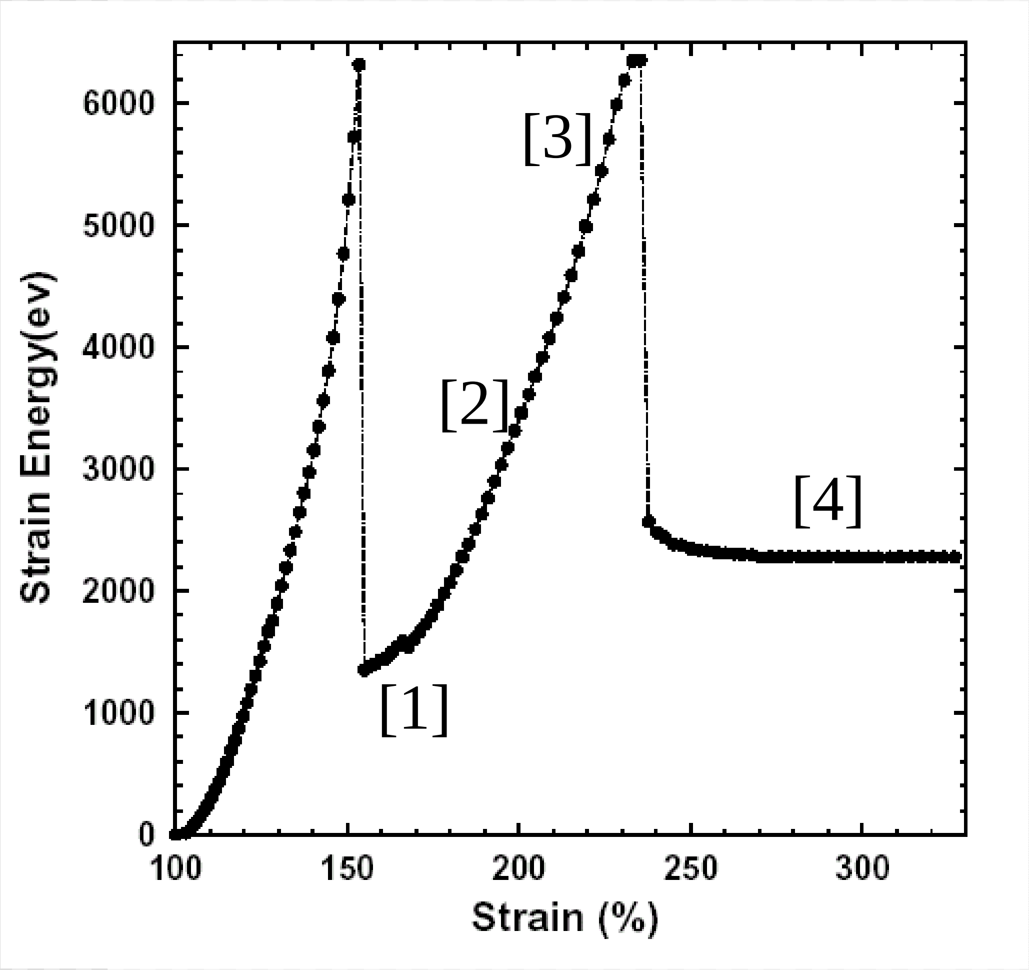
Clasical MD

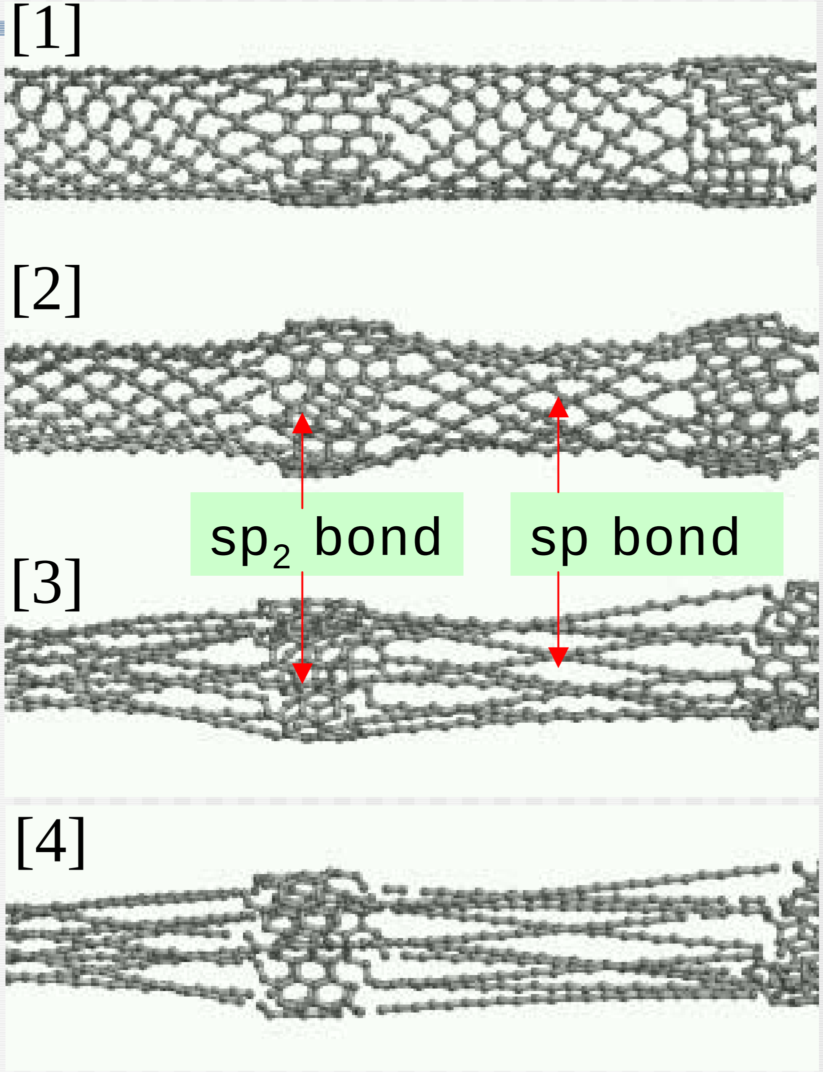
Previous results by
Yakobson *et.al 1996*



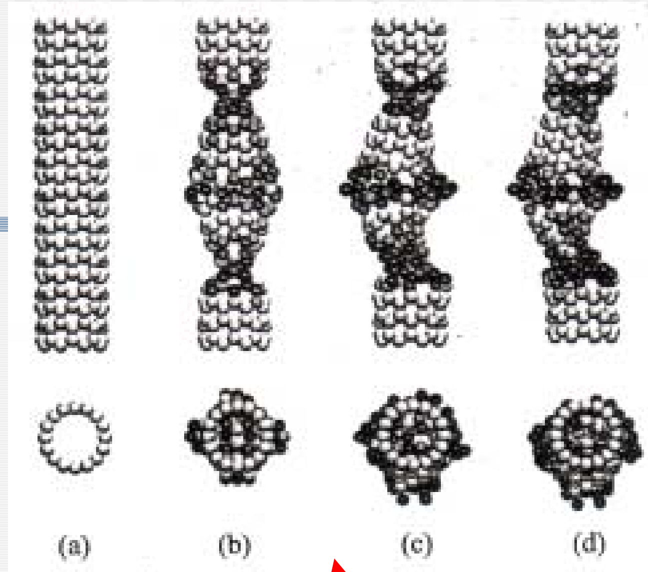
Our simulation :2200 atoms, 13.3nm, 240 processor × 12hours on ES

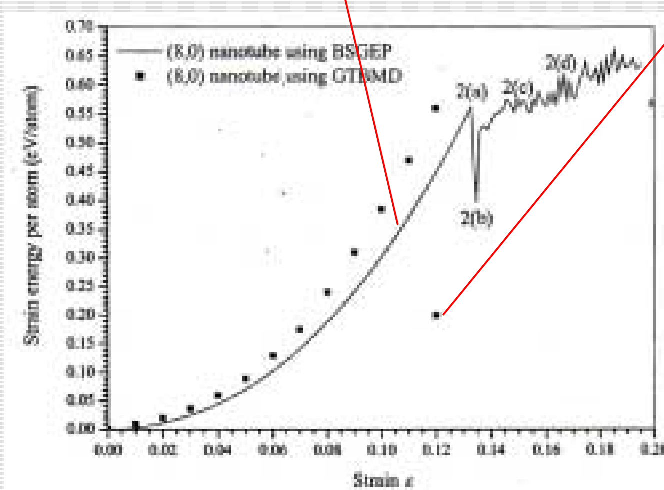
Stretch of Armchair CNT
---Energy dependence and fracture---





Previous results about compression of CNT





classical MD calc.

S.K.M.Liew *et al.*

Phys. Rev. B **69**, 115429 (2004)

(8,0)CNT

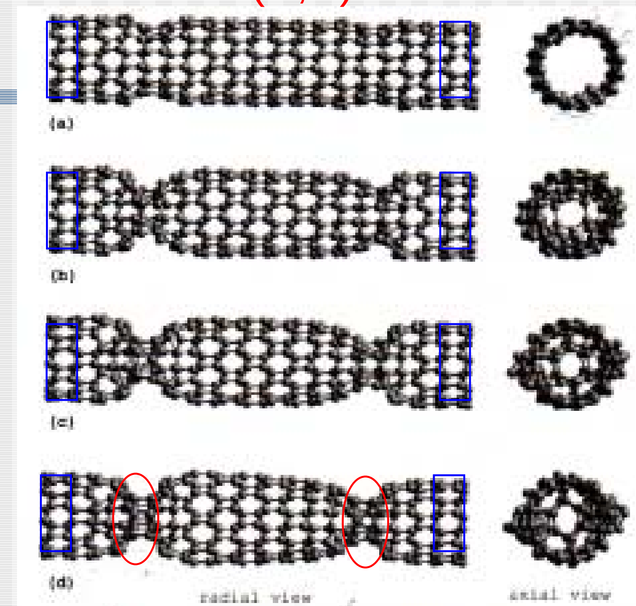


FIG. 2. Four stages of spontaneous plastic collapse of the 12% compressed (8, 0) carbon nanotube showing: (a) nucleation of the deformations; [(b) and (c)] inward collapse at the locations of deformations; and (d) graphitic to diamondlike structural transition at the location of the collapse.

tigth binding MD calc.

D.Srivastava, M.Menon, and K. Cho

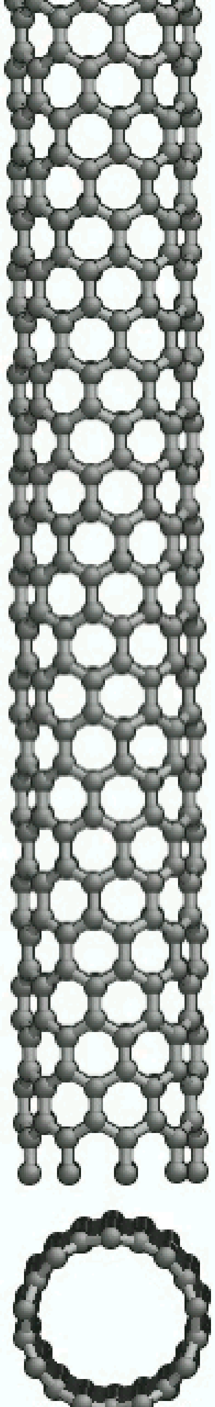
NASA Ames Resarch,

Univ. of Kentuky

Stanford Univ.

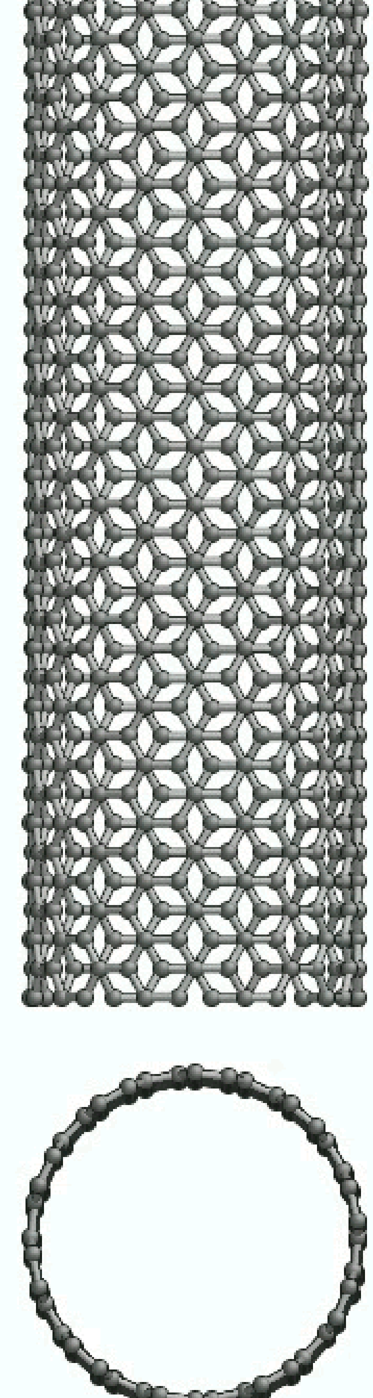
Phys. Rev. Lett. 2973,**83** (1999)

Compression of CNT



Small radius :
(9,0) Zigzag
N=1116,
L=13nm,
D=0.70nm,
L/D=18.7,
T=240PE×7h

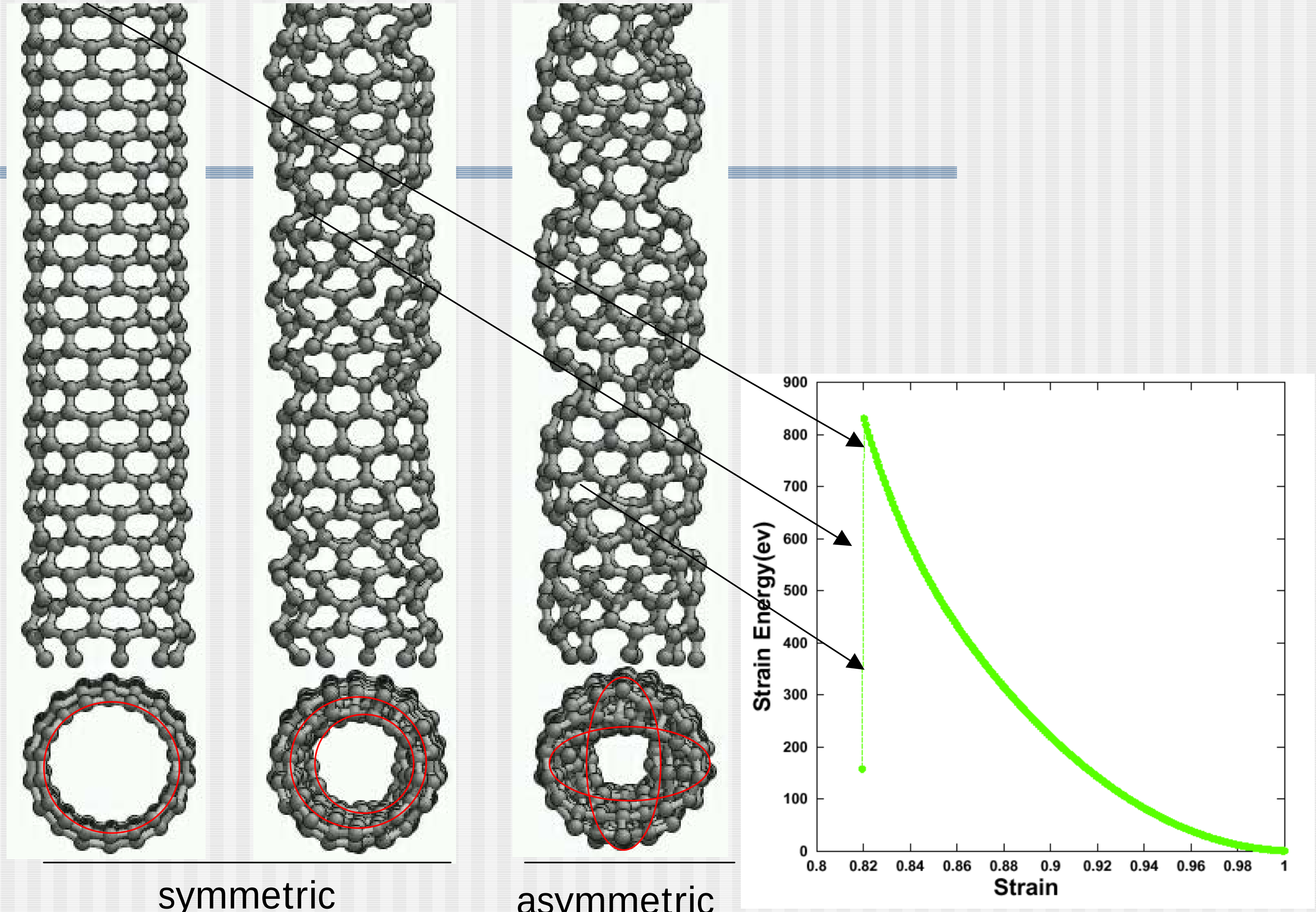
Large radius:
(10,10)
Armchair
N=2200
L=13.3nm
D=1.37nm
D/L=9.8
T=240PE×7h



Long tube

Periodic boundary condition

Collapse of **small** zigzag(9,0) CNT with **long length**

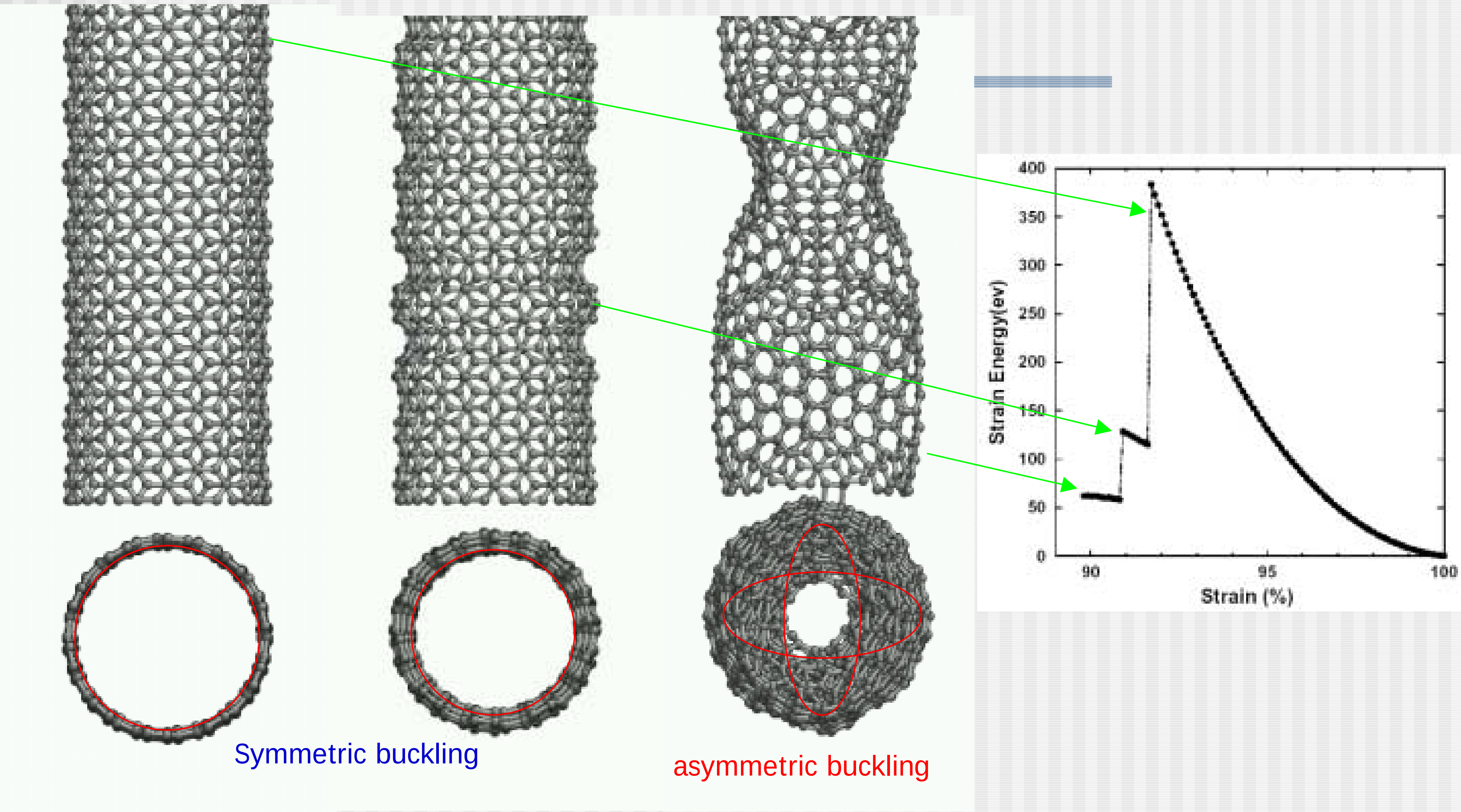


symmetric buckling

asymmetric buckling

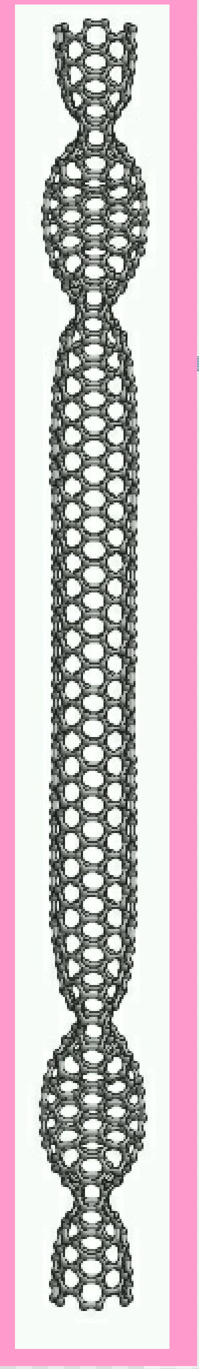
N=1116, L=13nm, D=0.70nm, L/D=18.7, T=240PE×7h using ES

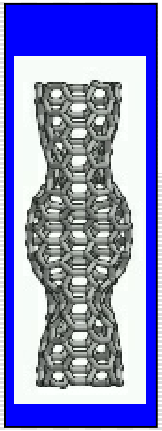
Collapse of **large** armchair (10,10)CNT with **long length**

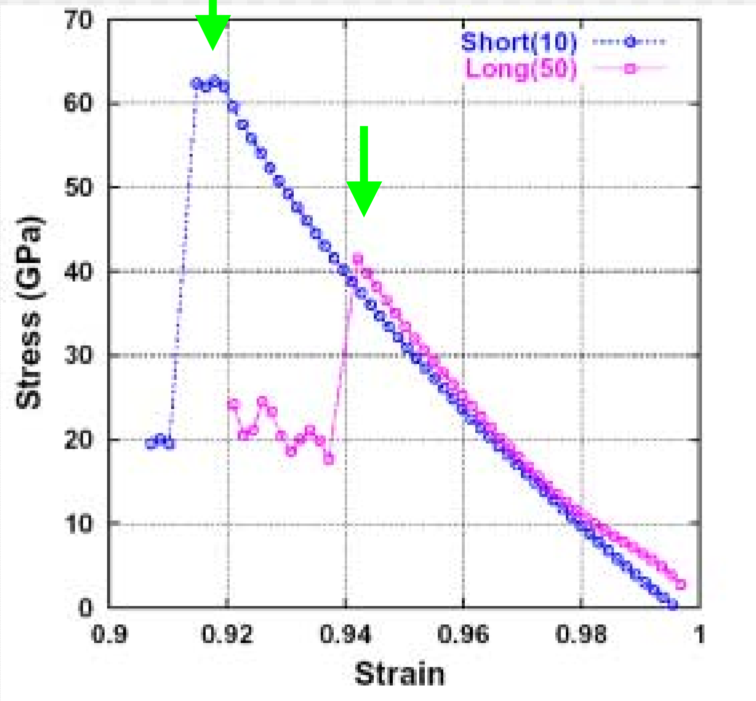


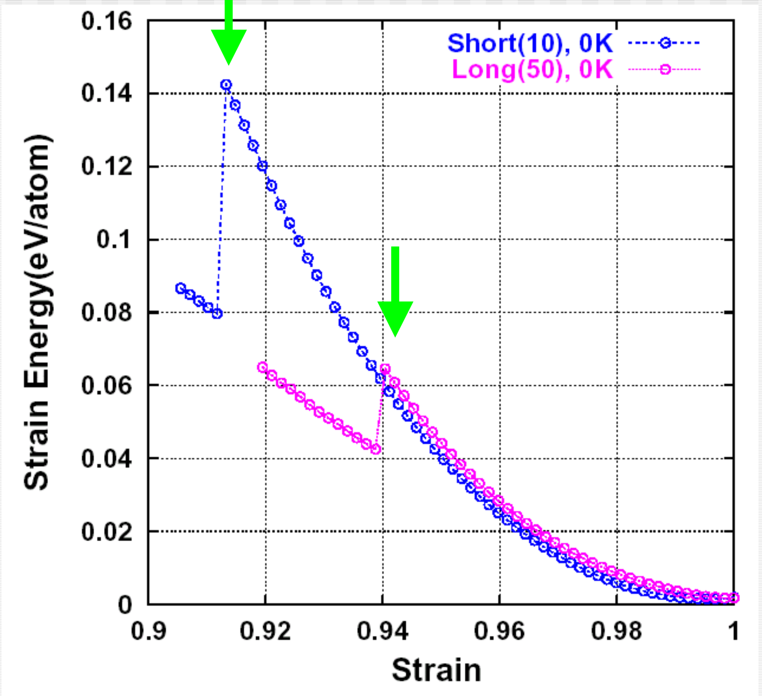
N=2200, **L**=13.3nm, **D**=1.37nm, **D/L**=9.8, **T**=240PE×7h using ES

Collapse of **small** radius:(5,5) CNTs with short length









Size of the CNT affect on the Buckling point and collapse structure

Both ends are fixed

N=1000, 200 **L**=12.3, 2.5nm, **D**=0.68nm, **L/D**=18.1,3.6, **T**=240PE×12h using ES

Young's Modulus (Y) of CNT

- **Hook's law**

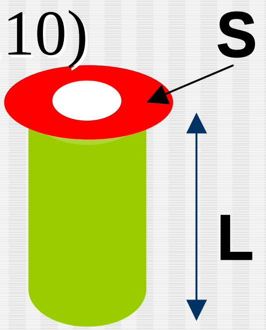
$$\frac{F}{S} = -Y\frac{\triangle L}{L_0}$$

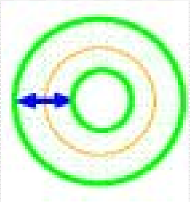
$$F = -\frac{1}{L_0}\frac{\partial E}{\partial \varepsilon} \qquad \bar{E} = \frac{E}{L_0}$$

$$\boxed{Y = \frac{1}{S}\frac{\partial^2 \bar{E}}{\partial \varepsilon^2}}$$

Diamond
Exp. 443GPa

(10,10)

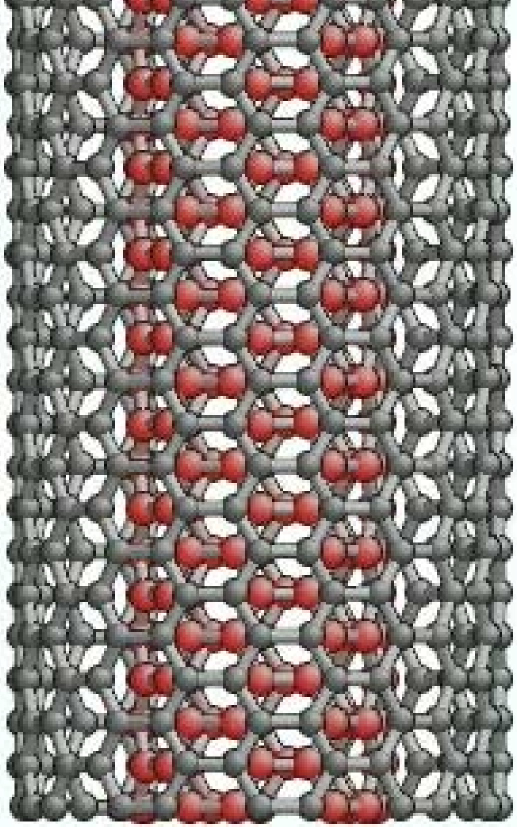


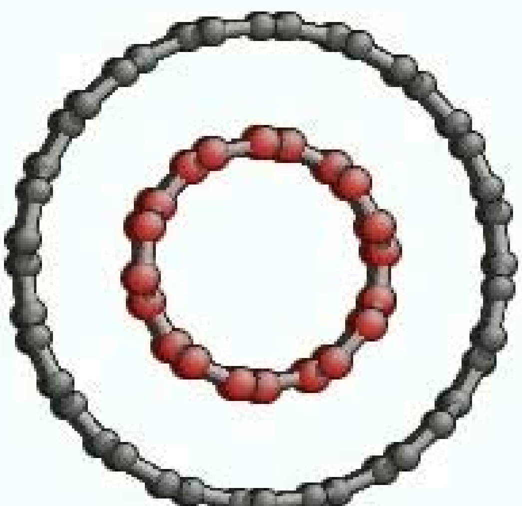


0.36nm

$$S \simeq 2\pi r \bullet \delta R$$

TB	630GPa





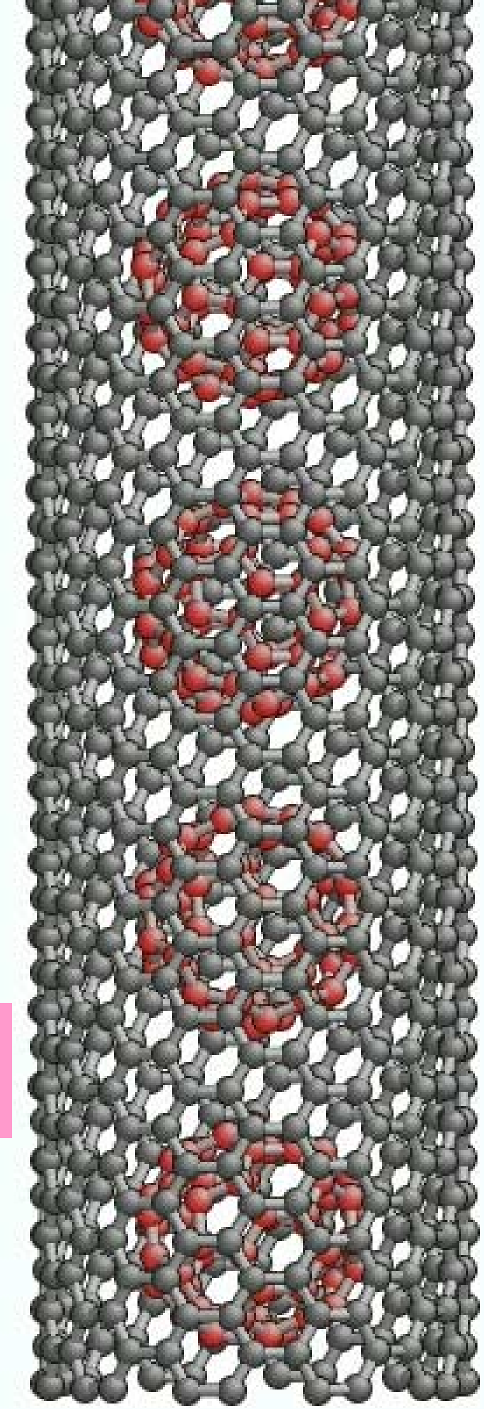
A strong CNT as AFN tip without collapse is needed.

Packing CNTs or fullerenes into the pure CNT.

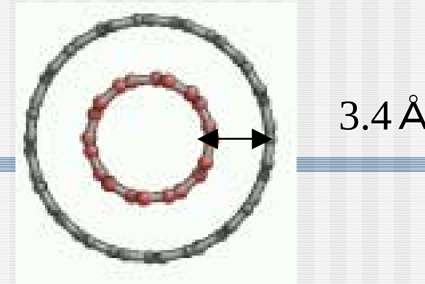
L=13.3nm, **D**=1.37nm,
D / L=9.8, **T**=240PE×12h

(5,5)+(10,10)

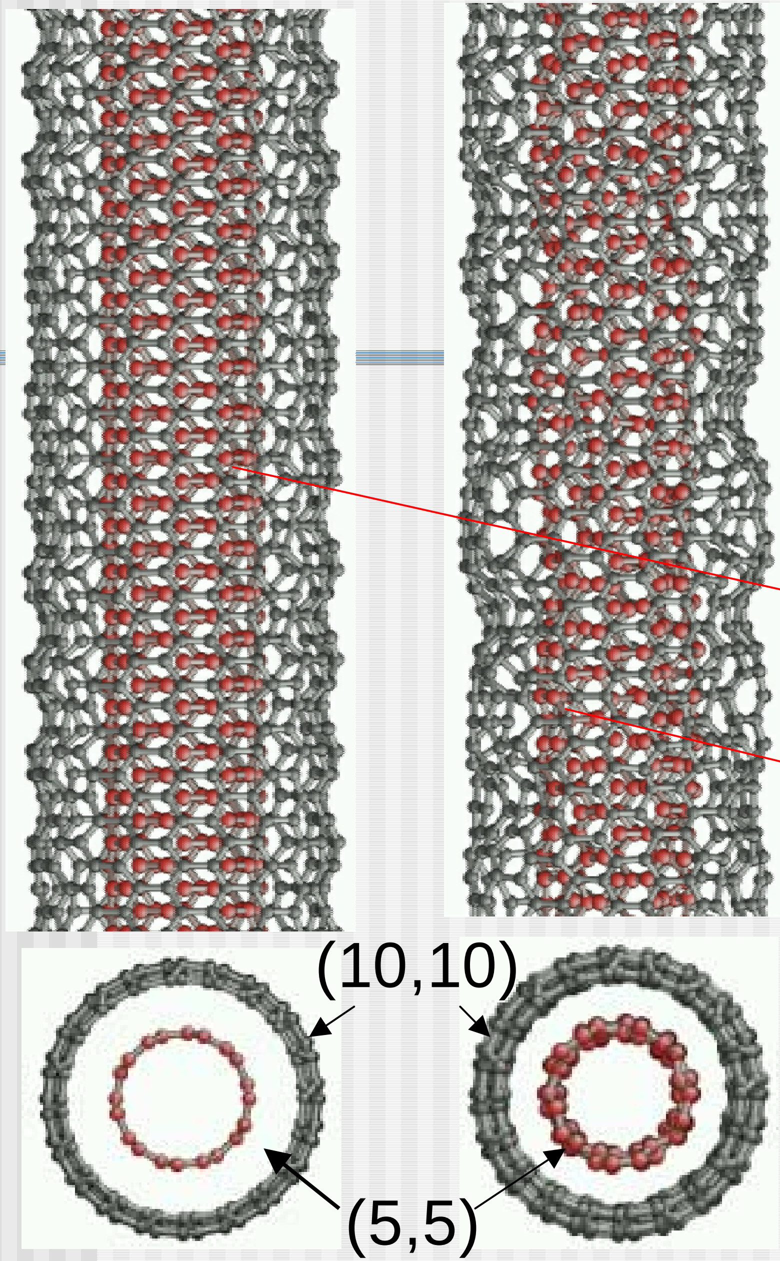
C_{60}@(10,10)

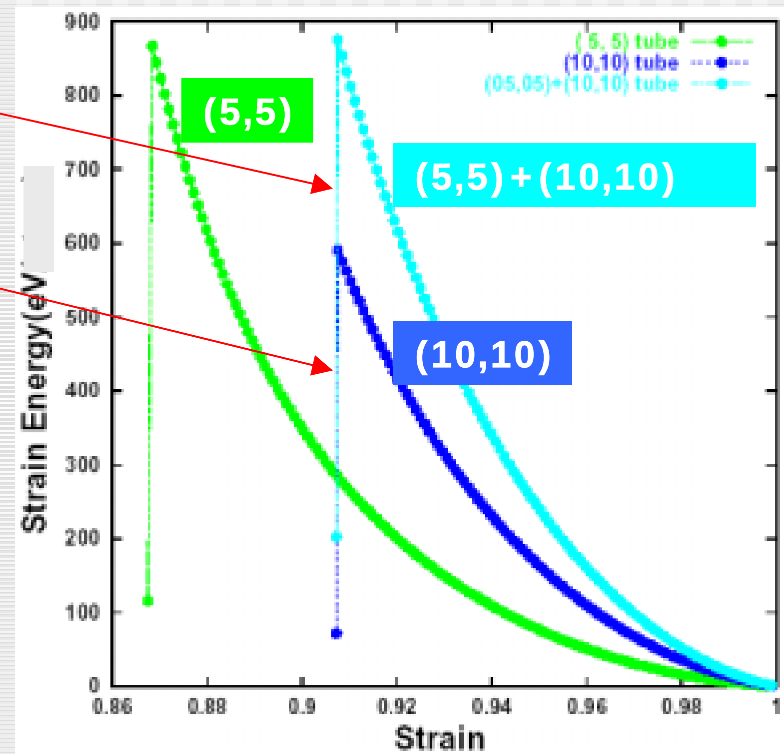


Collapse of **long double wall nanotube** (DWcnt)



Two CNTs behave independently.

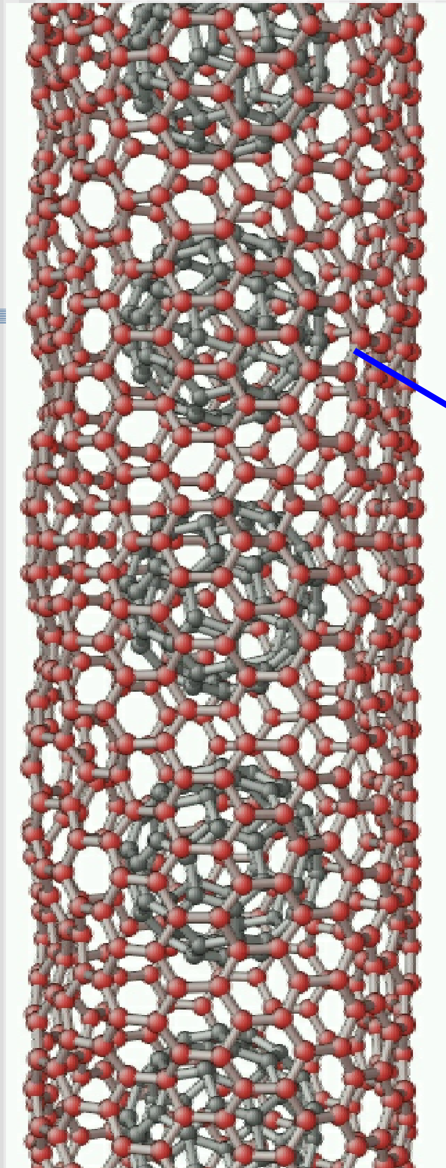




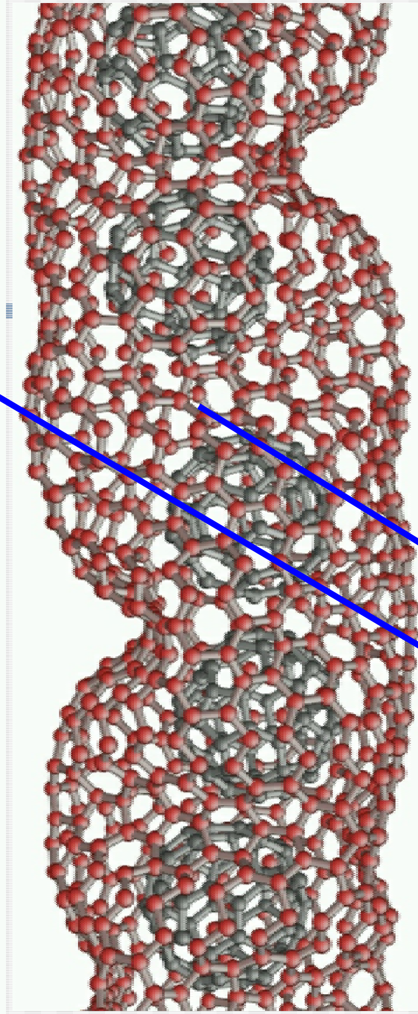
○ Buckling point of DWcnt is determined at outer CNT.

N=1000+2200, L=13.3nm, D=0.68,1.37nm, D/L=19.6,9.8, T=240PE×12h using ES

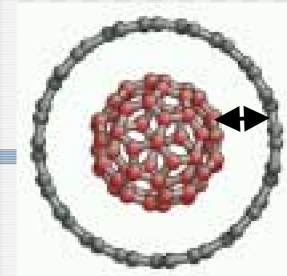
Collapse of **long peapod : C_{60}@(10,10)**



96%

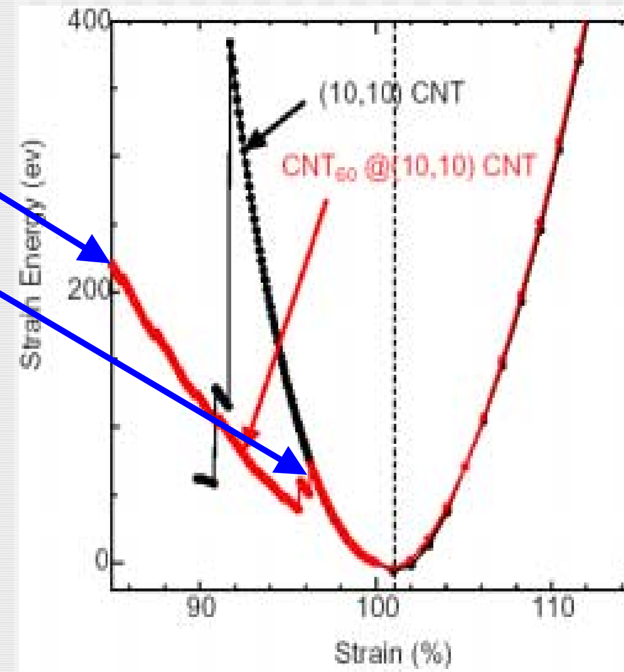


83%



3.28 Å

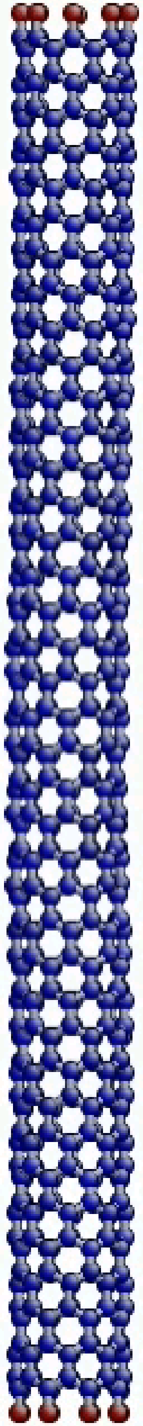
Fullerenes are attracted CNT through Van-der-Waals interaction. Fullerenes move to more stable position.



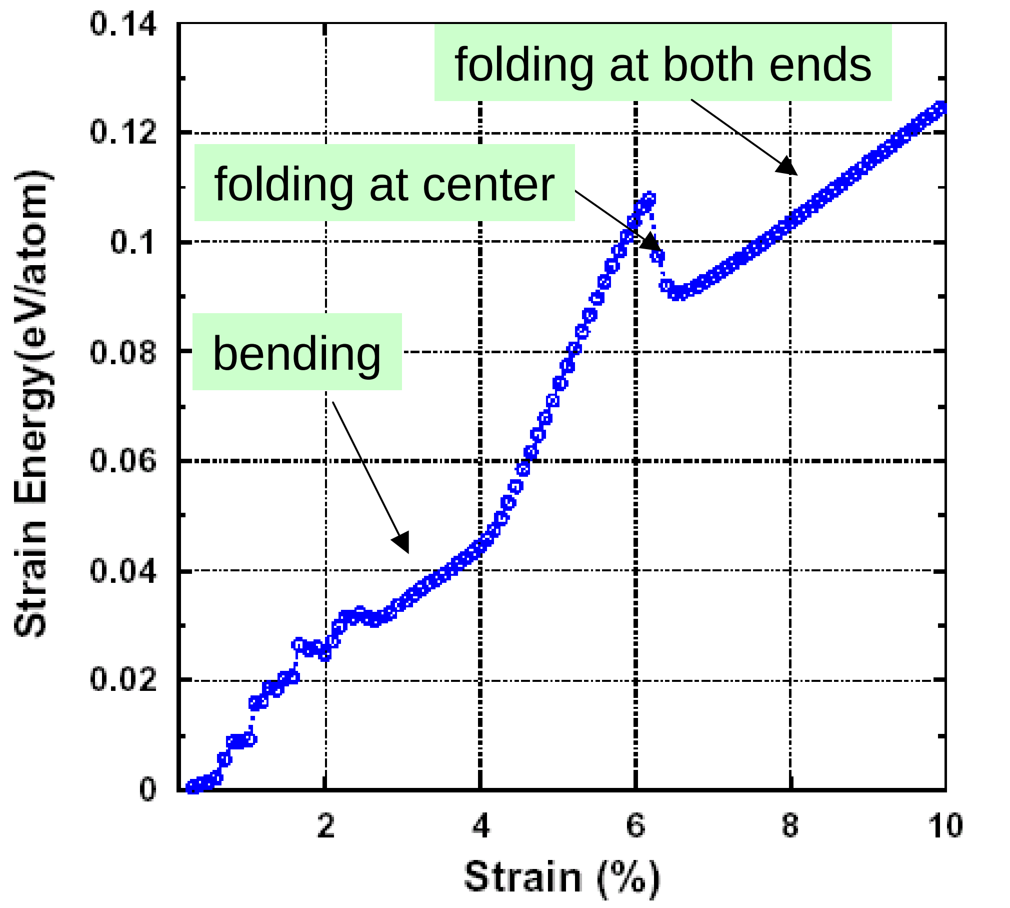
From an mechanical point of view,
a peapod structure is more week than pure CNT

N=2980, L=13.3nm, D=1.37nm, D/L=9.8, T=240PE×12h using ES

Euler buckling (bending of long CNT)

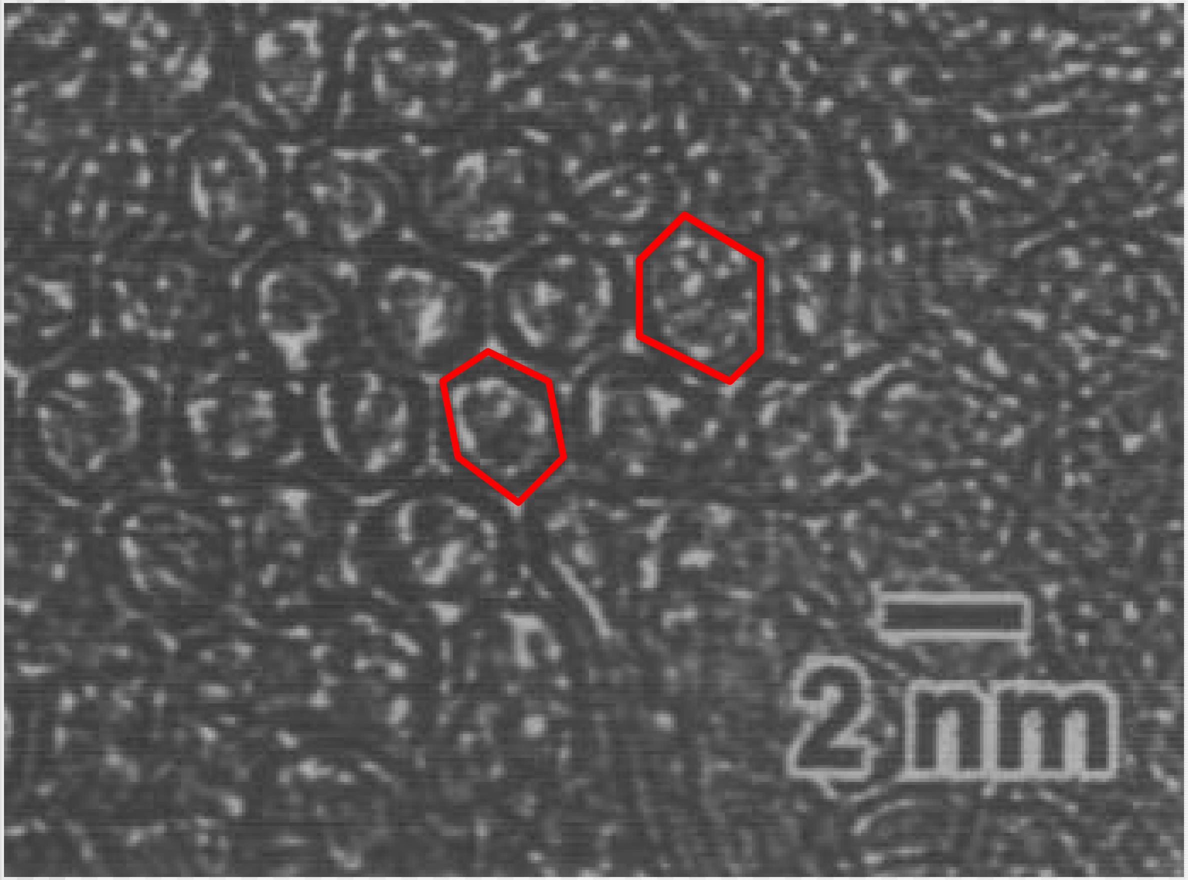


T =100 K



The flexible property prevents CNTs from a fracture

Composite Properties of CNTs
（for super hardness bundle and complicated materials）

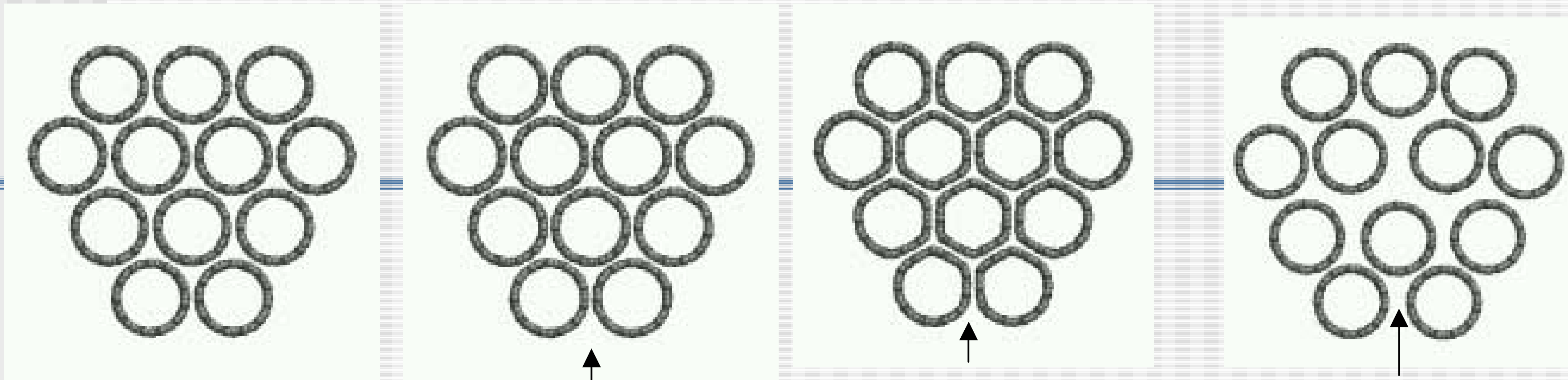


TEM image of a lattice of polygonized tubes

rounded-hexagonal cross sections

Problem :how to combine CNT and matrix or CNT.

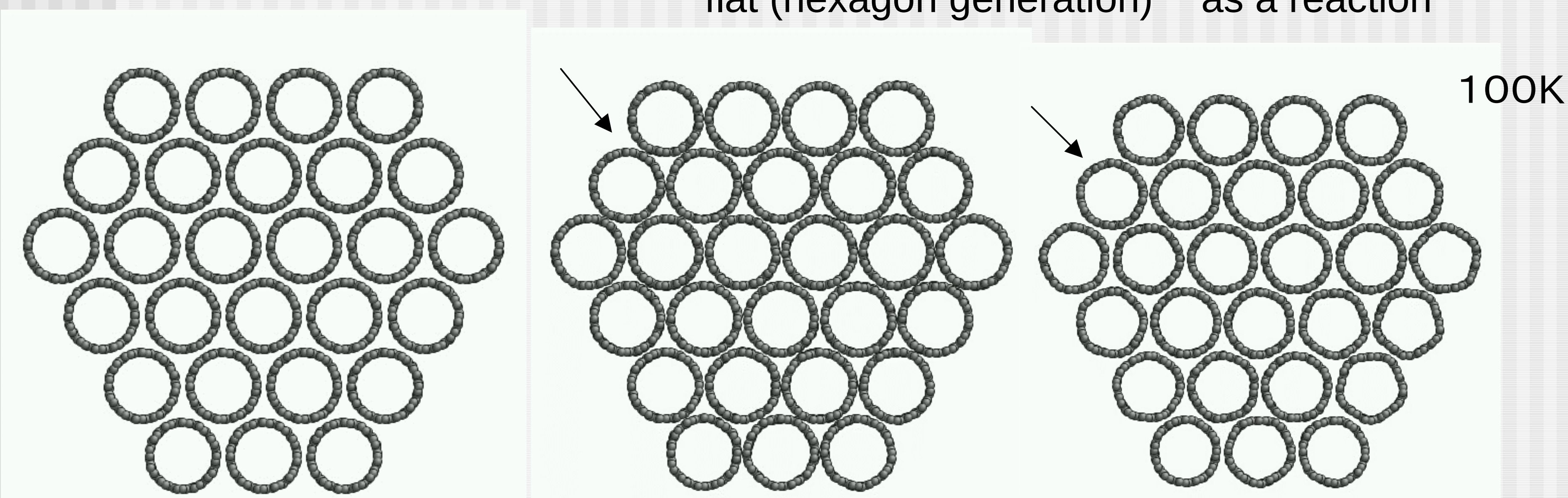
Condensation of CNT through week van-del-waals interaction



approach together

Faces of contact become flat (hexagon generation)

separation together as a reaction



We predict a CNTs are bundled with increasing CNTs.

A problem is how to make tight bundle

How to generate novel carbon function utilizing flexible carbon atomic bond

GSW program

Designing nano structure using flexible Carbon network

CNTs have many possible structural configurations

Using rearrangement of atomic connections

↓

Coalescence:
Generation of CNT from C_{60}

New junction:
Super Diamond

Welding materials:
Mackay structure

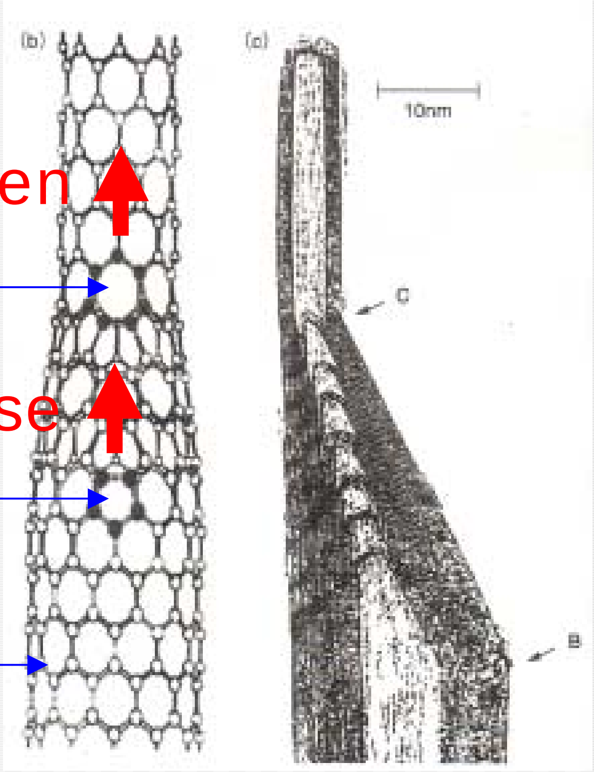
open

close

heptagon:7
-negative curvature-

pentagon:5
-positive curvature-

hexagon:6
-plain-

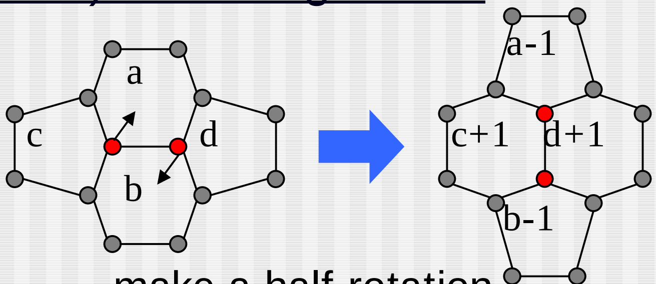


Creation of novel structure of nano carbon

GSW program (Master-Slave parallelization) automatically search the all possible pathway according to GSW and C2L rearrangement rule.

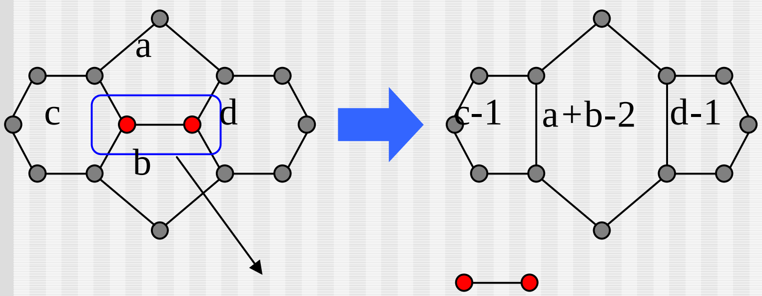
Rearrangement rule

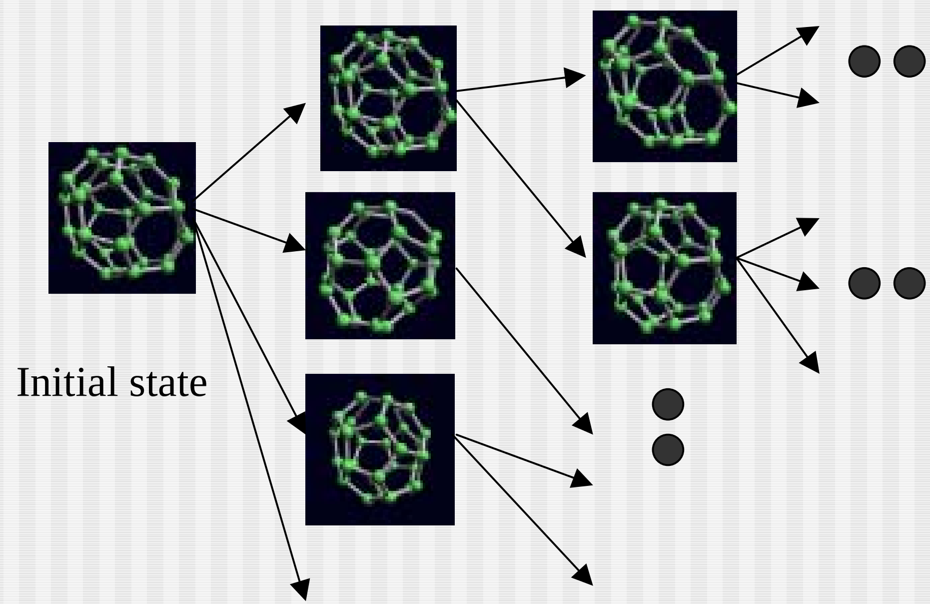
Generalized Stone-Wales (GSW) rearrangement



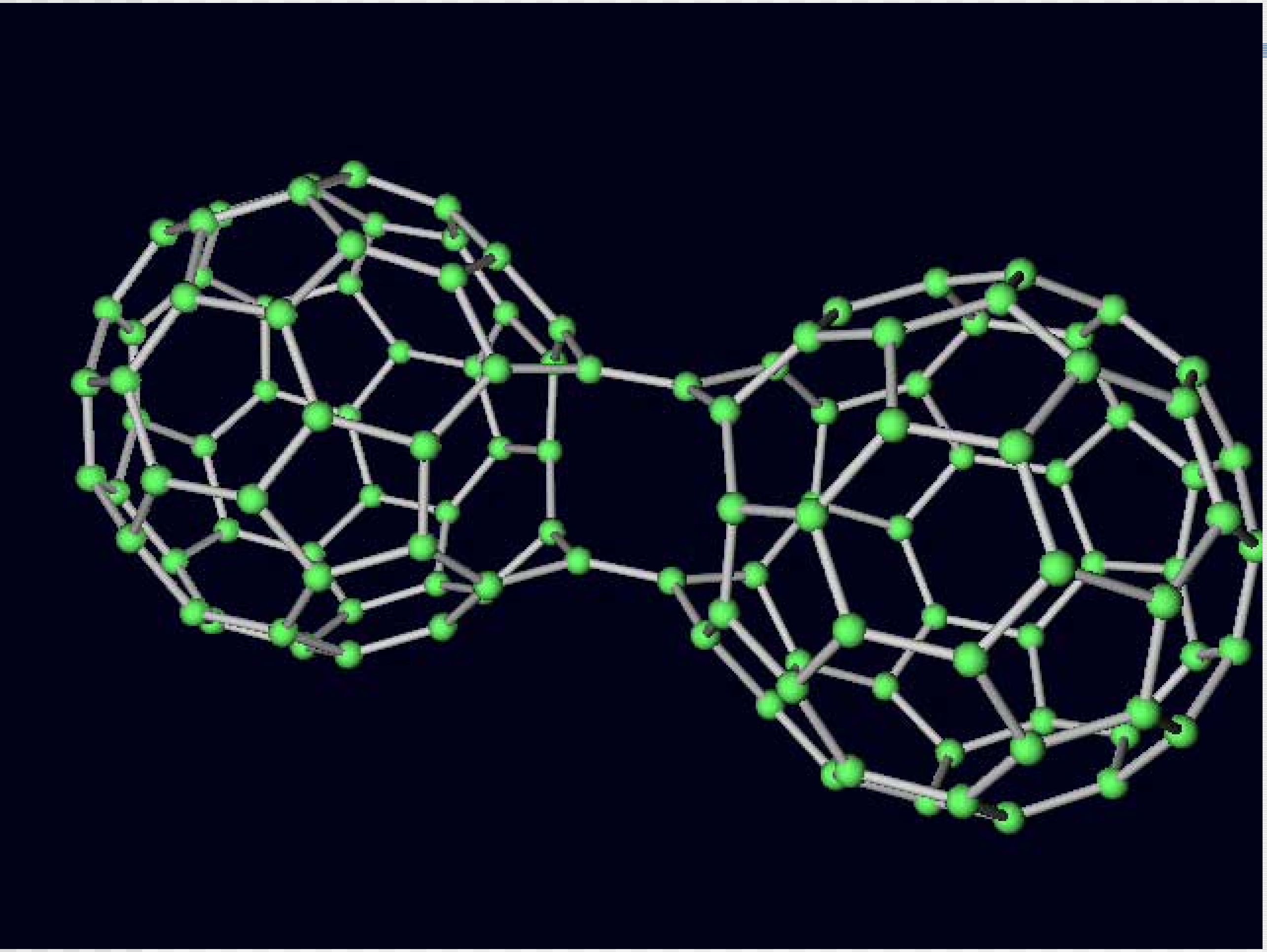
make a half rotation

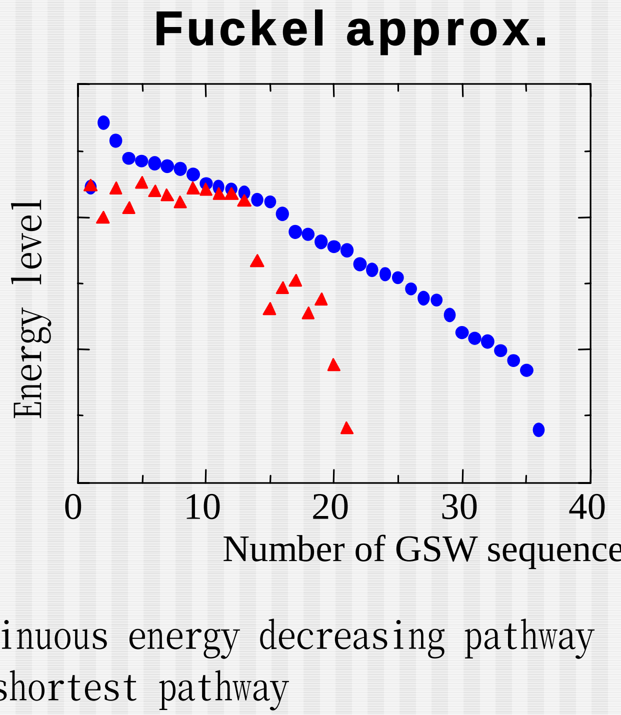
C2 Loss (C2L) rearrangement



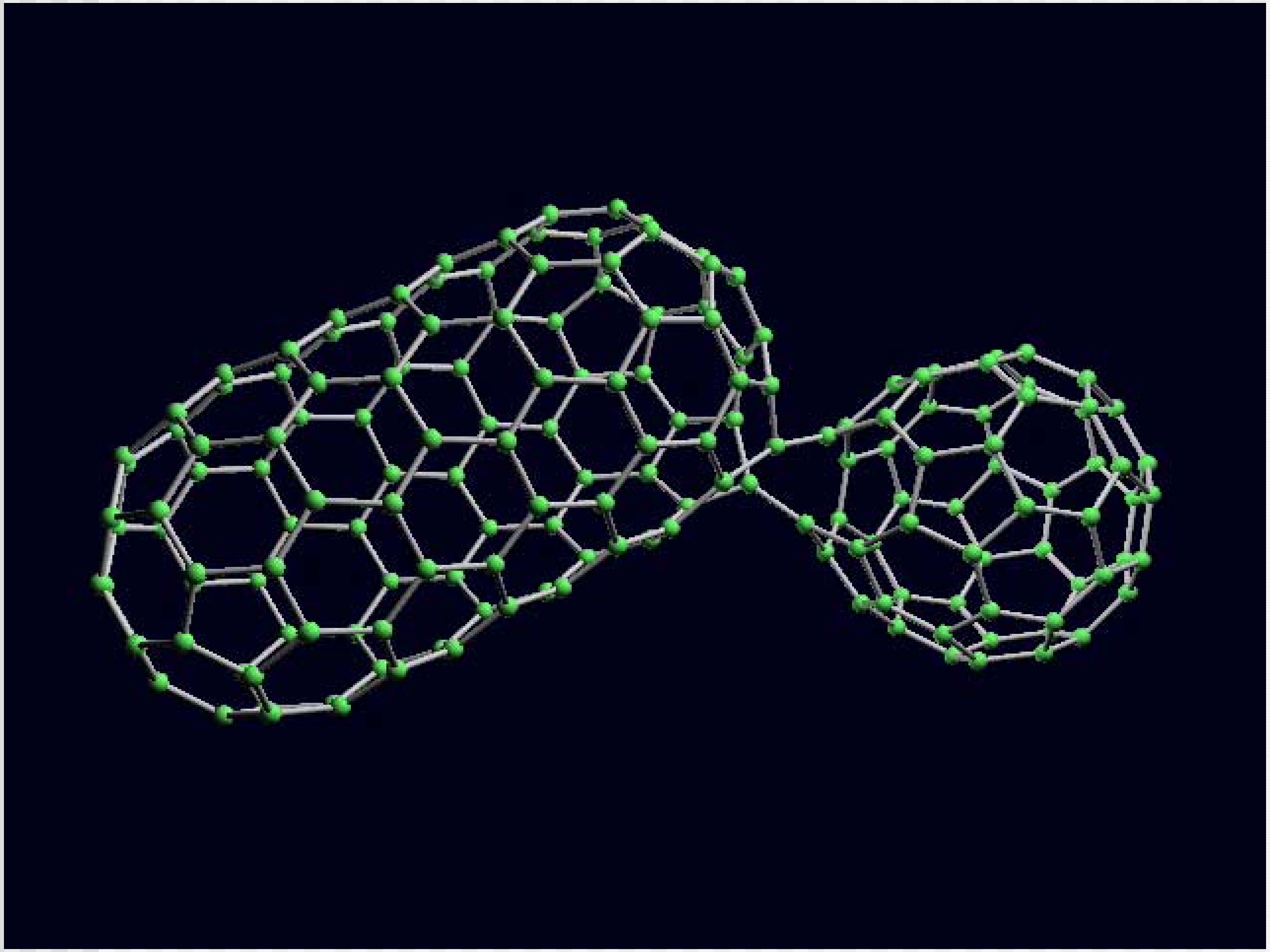


Generation of CNT from two C60

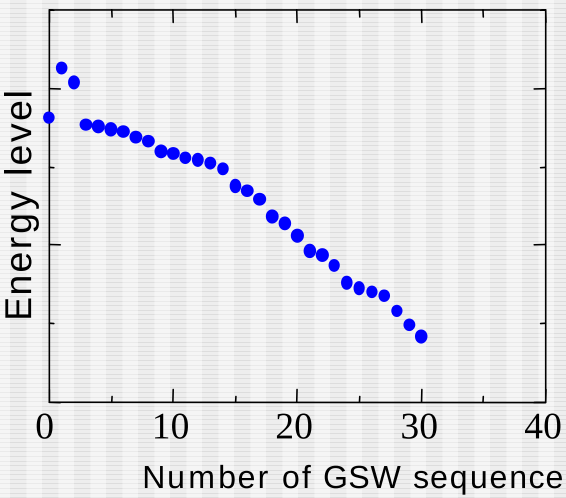




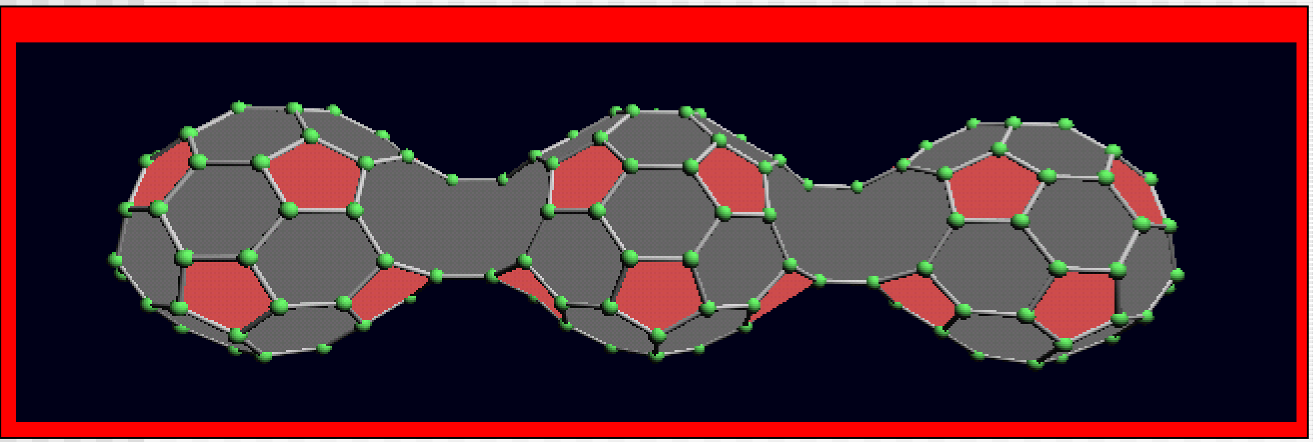
Generation of long CNT from C60 plus short CNT

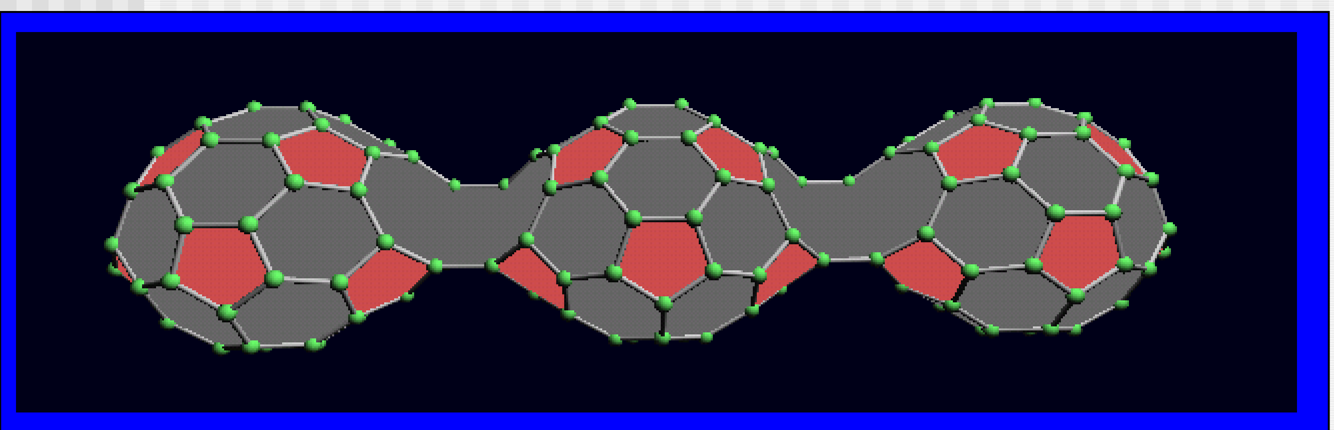


Fuckel approx.

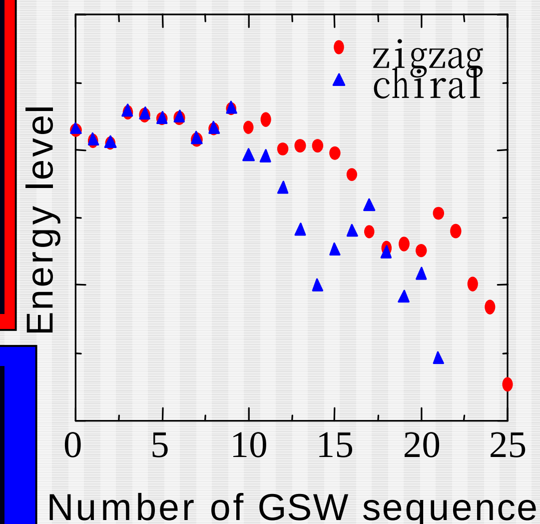


Generation of CNT from C60 -periodic boundary condition-





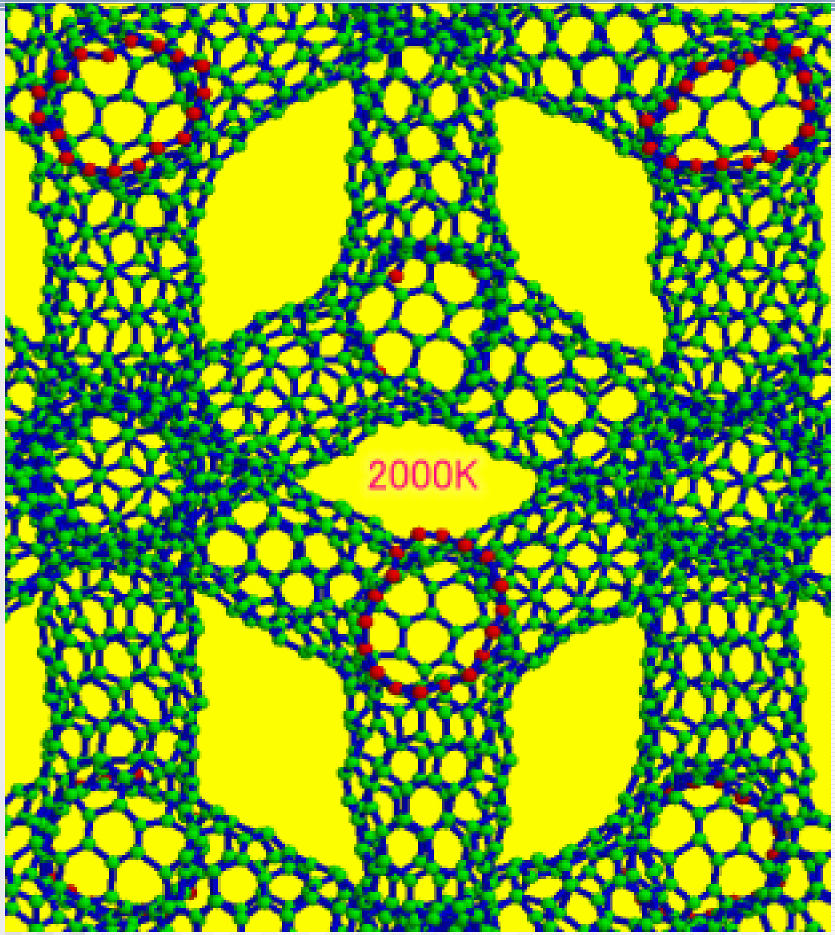
Fuckel approx.



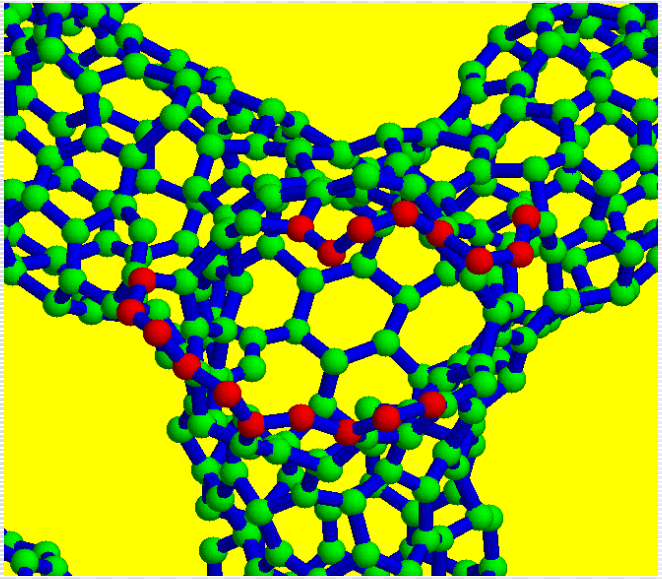
Application: **Hard nano wire**

Super-diamond structure

CNTs are connected by atomic welding. How stable in thermal.



No. of atoms :3372



3, 500K

Super-diamond is stable up to 3500k.

tigth-binding method (CRTMD)

Super Jungle Gym

Fullerenes are connected by atomic welding.

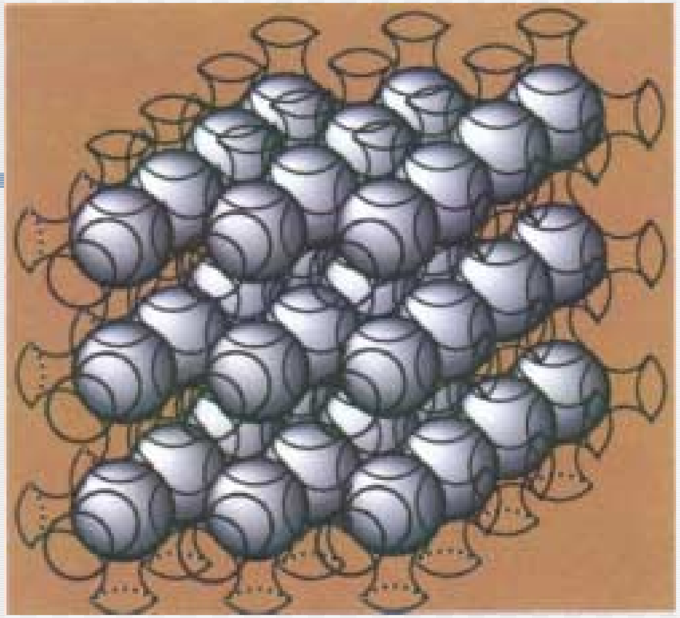
The surface curvature of this structure is very interesting, "Negative Gaussian Curvature by Mackay". How properties.

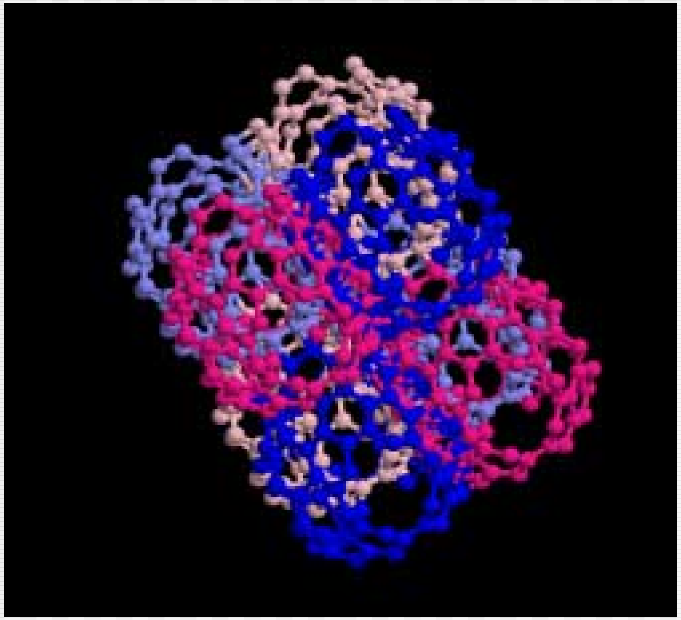
(1) Bulk Elastic modulus
(25 % of natural diamond)
(2) Mass density
(20 % of natural diamond)
(3) Band Gap
(0.5eV)

Light and hard 3-d semi-conductor!

DFT-PW program (First-Principles Method)

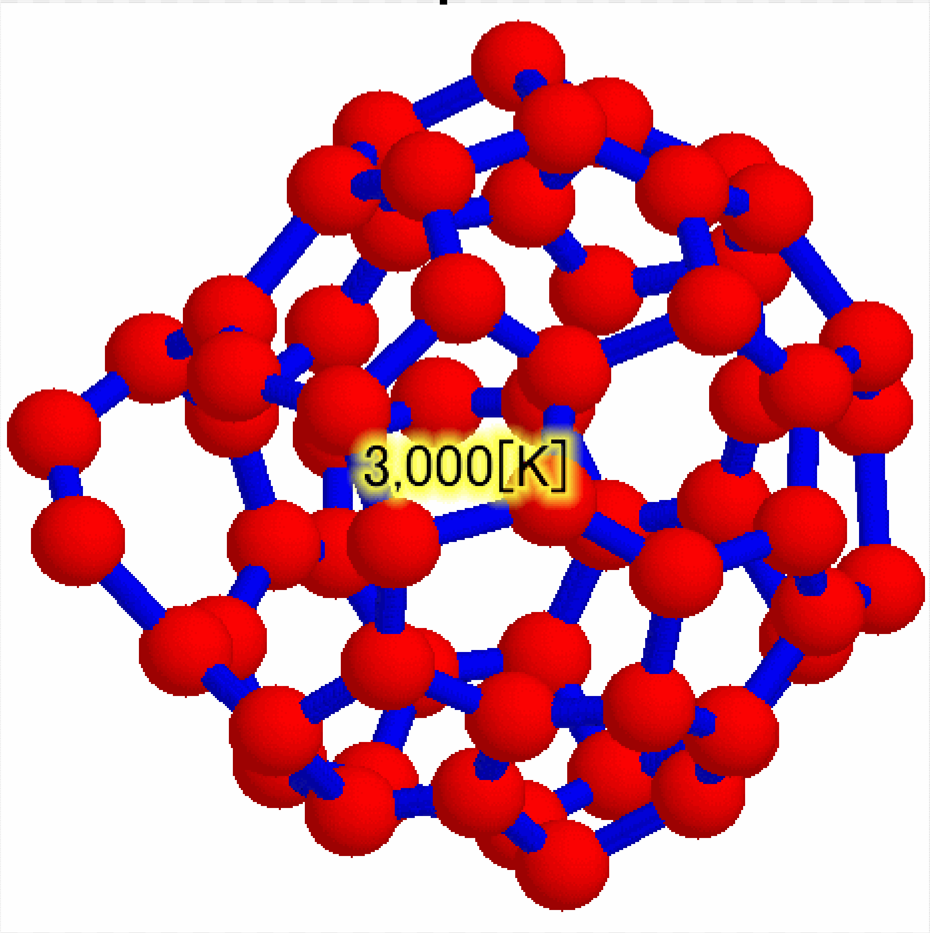
Application:
Electronic devices
ES:80PEs×40h



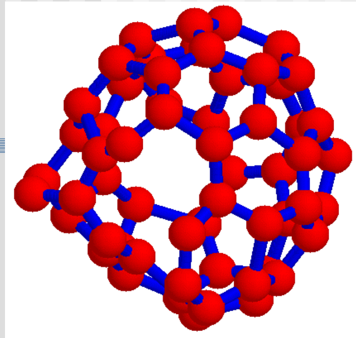


Thermal dissociation of Fullerene

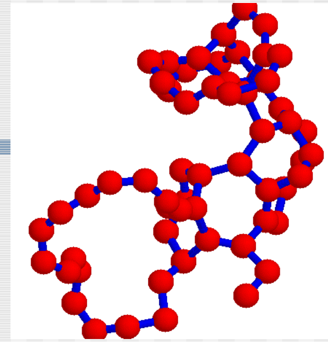
(1)**Simulation was carried out until 150ps each temperature.**
(**128PEs**×12h×10 **samples**)



Results

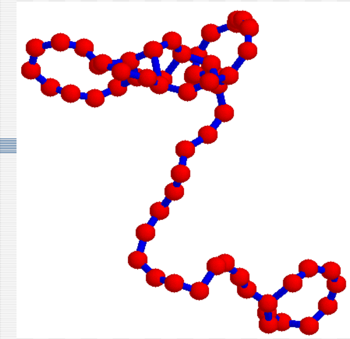


3000K



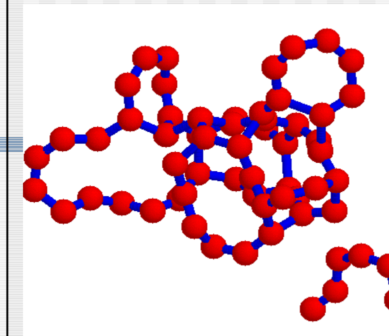
3400K

Round chains



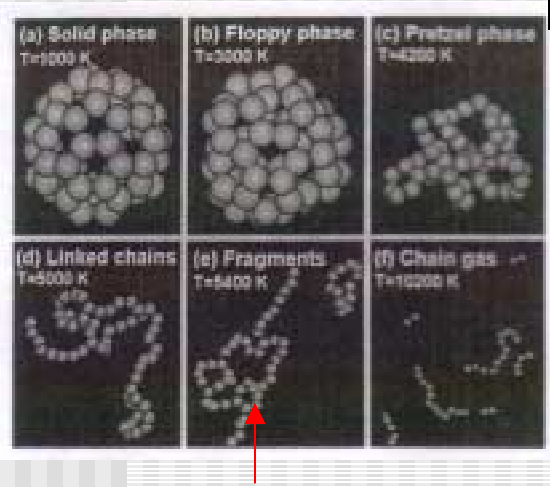
3500K

Stretched chains



3600K

Thermal dissociation



5400K

PRL1994、S.G.Kim and D.Tomanek

(1)Our results agree with that of experiment, 3550k.

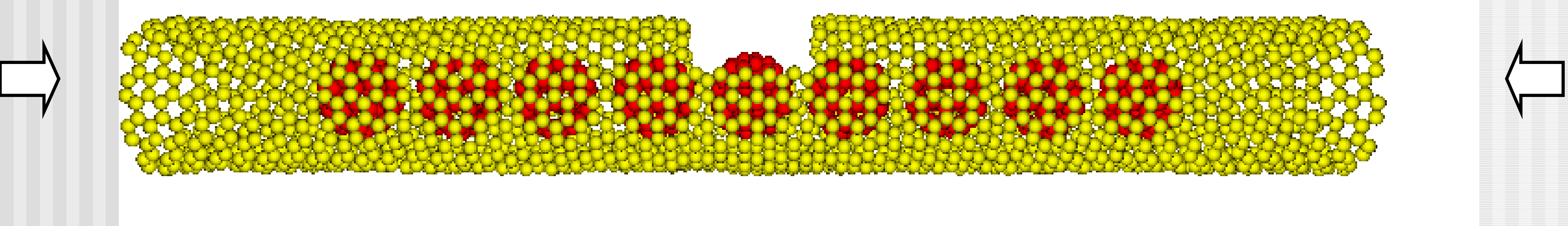
(2) For small number of atoms, the probability one atom have a large fluctuation is very small. So it takes long time to meet the large fluctuation as dissociation .

(3)Enough simulation time is needed for the reliable estimation on thermal stability.

For short simulation time, thermal dissociation is at 5,400K.

Encapsulation of Peapod

In the initial state, the wall and cap have defect opening.



⇒After 15 ps at room temperature, the encapsulation of fullerenes remain inside .

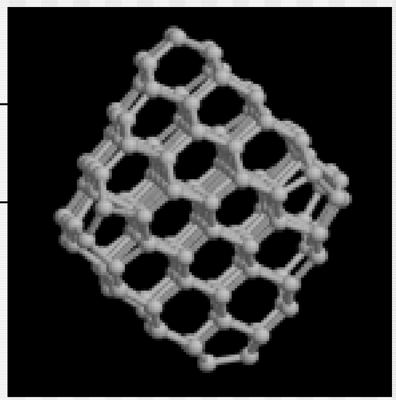
CNT may be useful as a nano scale reactor and DDS.

Nanodiamond

Application:
・lubricant / bearing surface / hard coating /corrosion protection

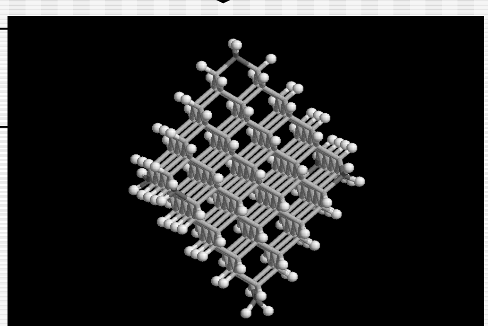
How to promote the diamond growth to the micron scale from nanodiamond particle ?

Diamond Structure

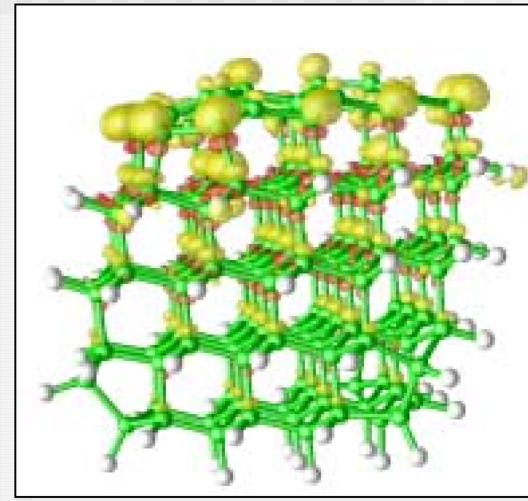


By hydrogen

Hydrogen covered

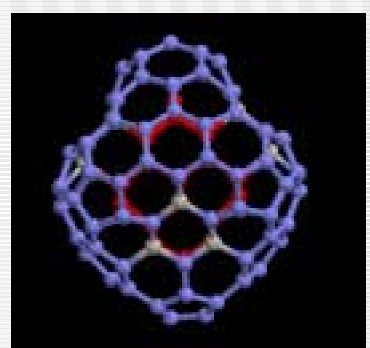


Diamond structure is stabilized by electron charging



Continuous growth of diamond

ES:10nodes×40h



Onion structure

Diamond surfaces reconstruct into fullerene-like sp^2 surface

ES:10nodes×40h

Growth Stop!

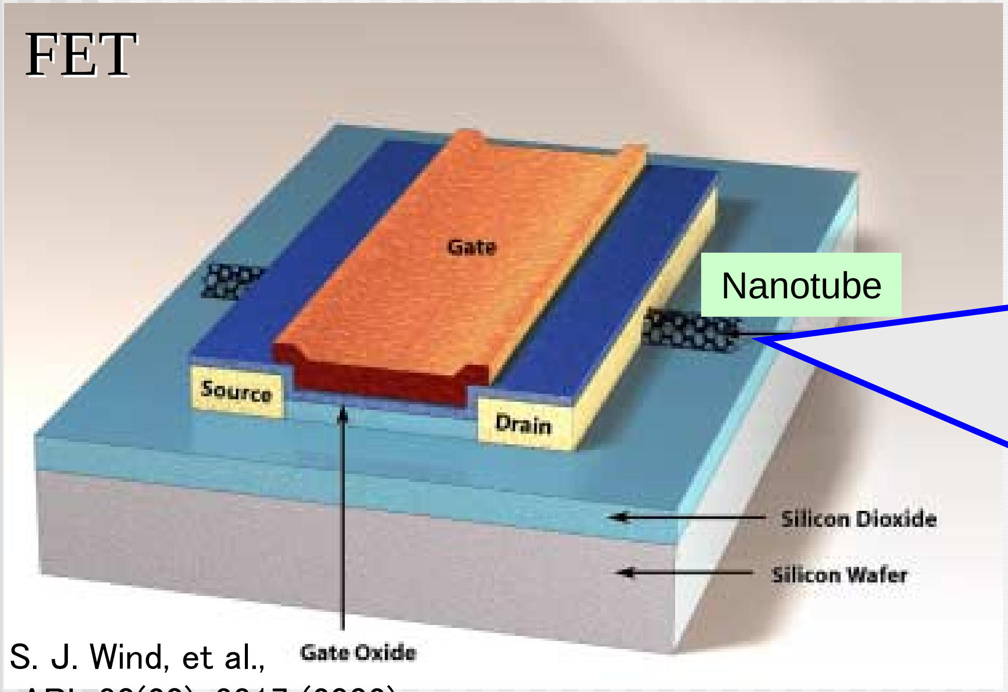
Application：
Next high density circuit devices/One electronic transistor/quantum dots/quantum computers･･･

Purification of CNT for Electoronic Circuits

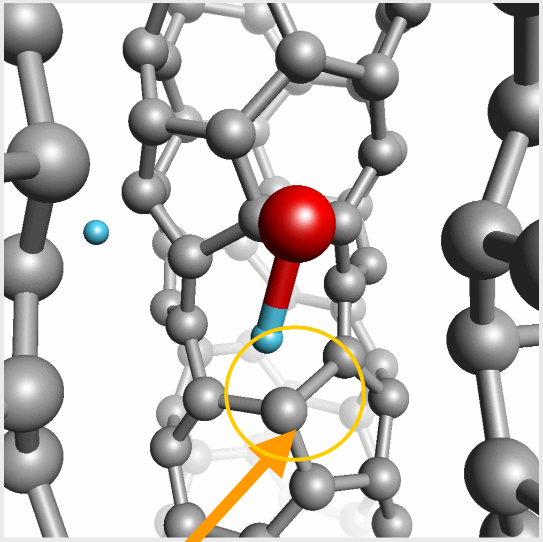
How to clean oxidized nanotubes without thermal processing ?

・optical excitation

FET



S. J. Wind, et al.,
APL 80(20), 3817 (2002)



Self Healing

Oxygen
Hydrogen

Summary

Earth Simulator is fit for Nano-simulations.

Large scale computational simulations are indispensable for the realistic nano-scale design.

In the future, a full scale design will be realistic method in nano devices.

END