1st HPC-NMR
Aug. 14

Investigations on the Dynamical Characteristics of One Water Molecule Embedded in a Single-walled Carbon Nanotube

Jian-Ming Lu[1,*], Tzu-Hua Wu[2], and Siu-Tong Choi[2]

[1] National Center for High-Performance Computing,
National Applied Research Laboratories
[2] Department of Aeronautics and Astronautics,
National Cheng Kung University
* Correspondence: rockylu@nchc.org.tw

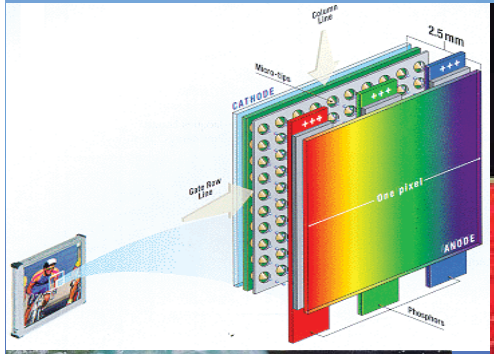
NCKU
國立成功大學航空太空工程學系
Department of Aeronautics and Astronautics, National Cheng Kung University

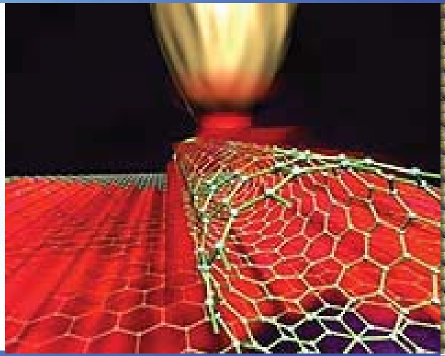
NCHC
財團法人國家實驗研究院
國家高速網路與計算中心
National Center for High-Performance Computing

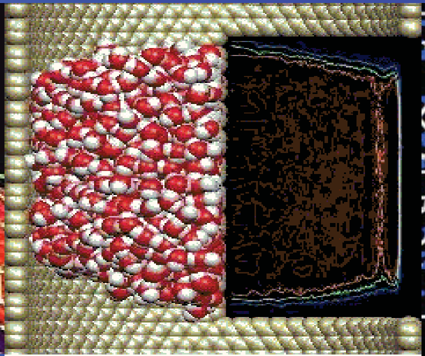
Outline

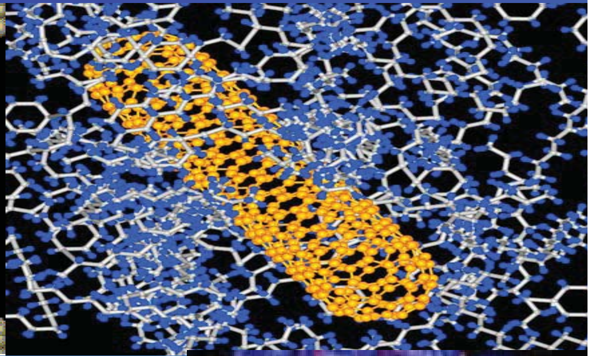
- INTRODUCTION
- MD SIMULATION
- METHODOLOGY
- RESULTS AND DISCUSSION
- CONCLUSIONS
- FUTURE DIRECTIONS
- ACKNOWLEDGMENTS

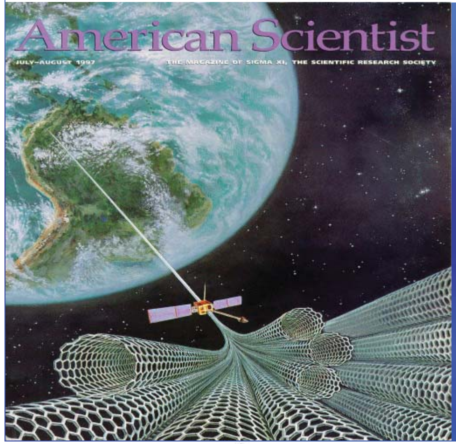
Introduction (I)



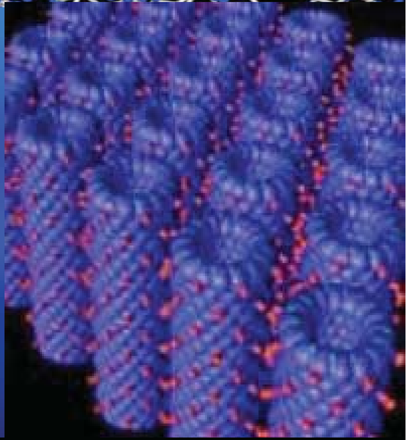


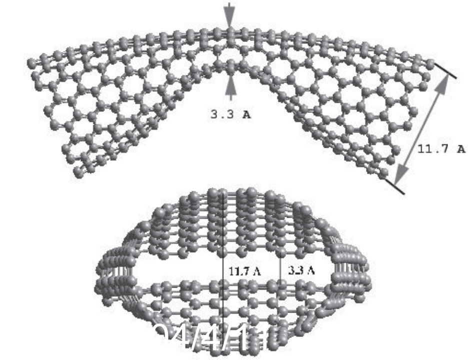


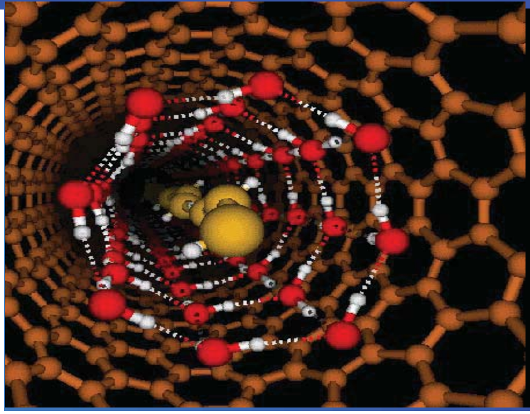


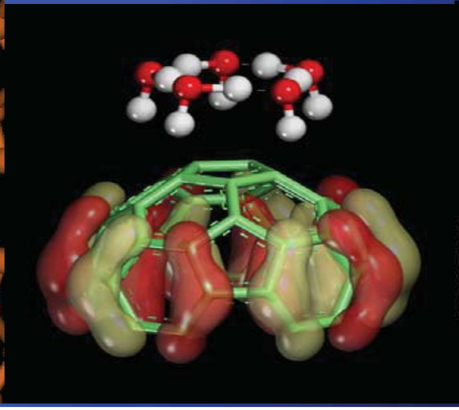


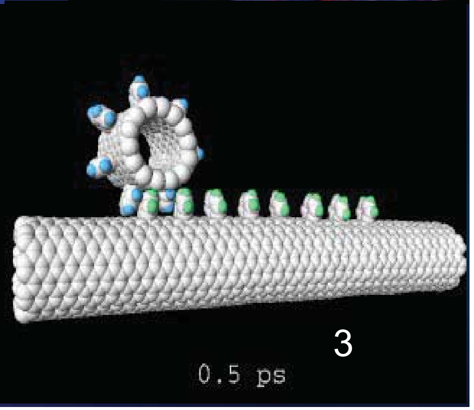
CNT
Applications











Introduction (II) - Applications

- Batteries
- Biosensors for harmful gases and chemical analyses
- Capacitors
- Cathodes for microwave tubes
- Chemical factory-on-a-chip applications
- Computers and TVs (with nano circuits)
- Conducting composites
- Conductors for micro electronic devices
- Controlled drug release applications
- DNA chips
- Electronic applications
- Electronic rectification, ballistic switching, and logic functions
- Electronic nanocomponents and material protection applications

- Field effect transistors
- Field-emission flat panel displays
- Filter applications
- Fuel cell membranes
- Heat pipe
- Hydrogen storage
- LEDs
- Microscope probes
- Molecular pumps
- Nanometric test tubes
- Nanotube reinforced composites
- Nano-data storage
- Quantum wires
- Single electron transistors
- Sporting goods
- Water desalinators
- Wireless devices

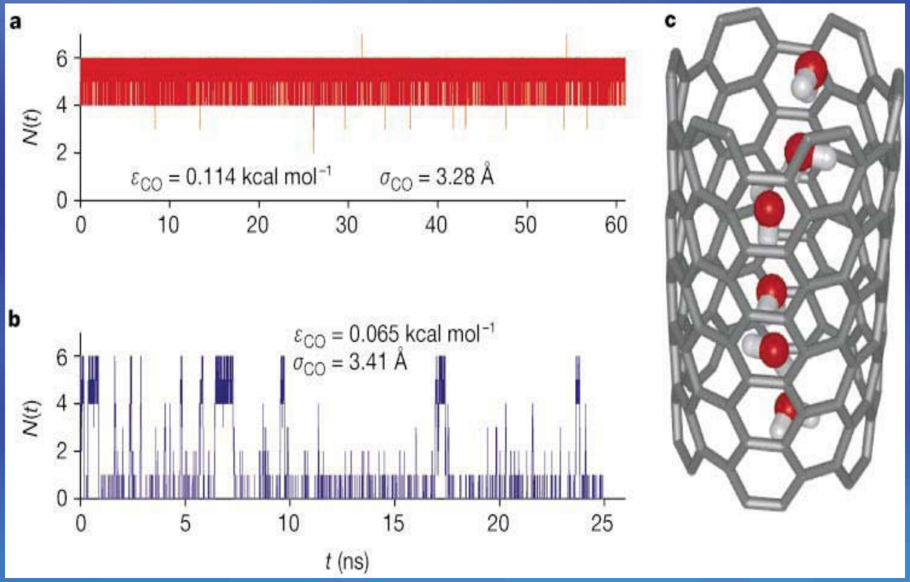
http://www.ahwahneetech.com/

Motivation

- Interesting phenomena and physical properties may be found in the water-nanotube composites. Since the discovery of carbon nanotubes, researchers vigorously investigated the fantastic behavior of carbon nanotubes with or without inclusion atoms.
- providing available information to estimate the effective Young's modulus of the water-nanotube composite.

Paper Survey

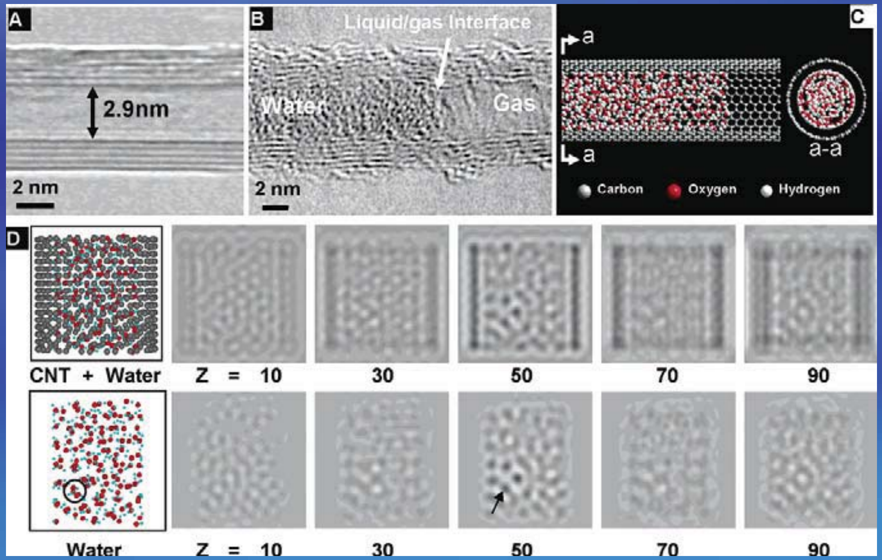
Publisher：*Nature*
Year：2001
Author：Hummer G, Rasaiah JC, Noworyta JP
Title：Water conduction through the hydrophobic channel of a carbon nanotube



Hummer *et al.* utilized the molecular dynamics method and found that water arranges in one-dimensional order inside a hydrophobic carbon nanotube by strong interaction of hydrogen bonds. He investigated water in a long chain order and its fluidity in a pulsed mode

Paper Survey

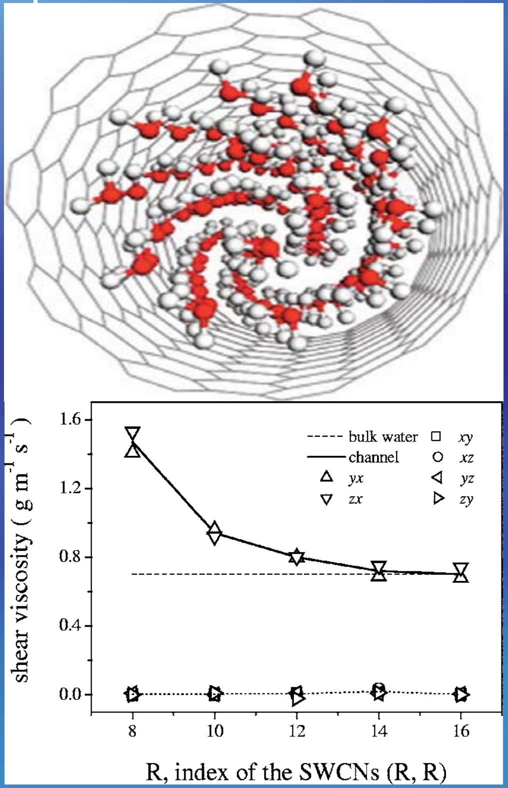
Publisher ：*Nano Letts*
Year：2004
Author：N. Naguib, H. Ye, Y. Gogotsi, A. G. Yazicioglu, C. M. Megaridis, M. Yoshimura
Title：Observation of water confined in nanometer channels of closed carbon nanotubes



Naguib *et al.* studied water passing into the defects of a carbon nanotube, and investigated the behavior of water inside a carbon nanotube. They found that the flow of water is much less than that of macroscopic water, in agreement with Liu’s results. Also, water can be solidified by increasing the pressure, and it is found that hexagonal and heptagonal icy columns change to rectangular and pentagonal ones when external pressure is increased

Paper Survey

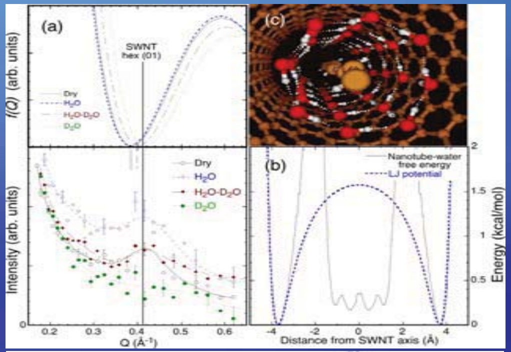
Publisher ：*Phys. Rev. B*
Year：2005
Author ：Liu YC, Wang Q
Title：Transport behavior of water confined in carbon nanotubes

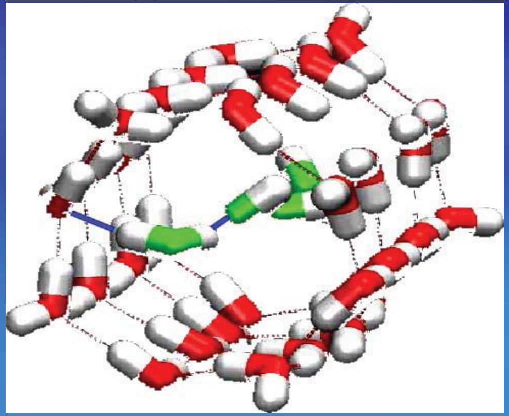


Liu and Wang found that water inside a carbon nanotube behaves as of anisotropic transportation by the molecular dynamics method. They also investigated that axial heat conduction rate, diffusive rate, and viscosity are much more than longitude that. The diffusive rate of water decreases noticeably with the decrease of a carbon nanotube’s diameter. However, the axial heat conductive rate and shear viscosity of water are much more than that of macroscopic water. Moreover, the chiral order and laminar distribution of water were also investigated

Paper Survey

Publisher ：*J. Phys.: Condens. Matter*
Year ：2006
Author：N R de Souza, A I Kolesnikov, C J Burnham and C-K Loong
Title：Structure and dynamics of water confined in single-wall carbon nanotubes

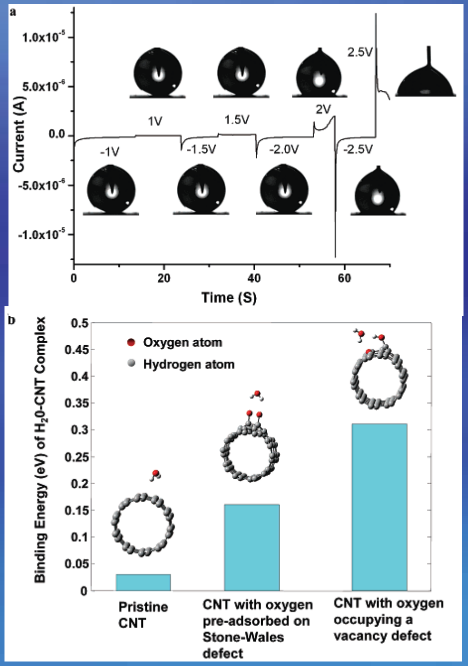




Souza *et al.* used the neutron diffraction and the molecular dynamics method to investigate water inside a carbon nanotube, and found that water is able to pass through a SWNT in a shell-chain structure at lower temperature. They identified that water rearranges and changes into a cubic icy structure, which contains chain-structured water molecules. The hydrogen bonds are created and broken violently with the temperature increasing. He found that the shell-chain structure disappears when the temperature is beyond 210K

Paper Survey

Publisher ：*Nano Letts*
Year：2007
Author：Wang, Z., Ci, L., Chen, L., Nayak, S., Ajayan, P.M., and Koratkar, N.
Title：Polarity-Dependent Electrochemically Controlled Transport of Water through Carbon Nanotube Membranes



Wang *et al.* observed water in negative charge by bringing positive voltage on a water-embedded carbon nanotube, and found that a carbon nanotube's properties change to hydrophilic from hydrophobic. Moreover, the flow rate increases substantially with the electric field increasing. They indicated that the technique can be applied to purify drinking water and gene research.

Outline

- INTRODUCTION
- MD SIMULATION
- METHODOLOGY
- RESULTS AND DISCUSSION
- CONCLUSIONS
- FUTURE DIRECTIONS
- ACKNOWLEDGMENTS

The Scale of Things -- Nanometers and More

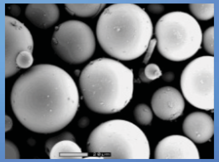
1st HPC-NMR
Aug. 14

Things Natural

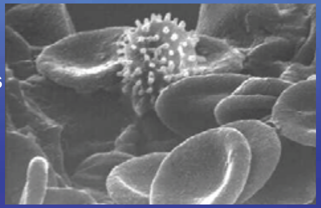
Dust mite
⟷
200 mm

Ant
~ 5
mm

Human hair
~ 10-50 mm wide

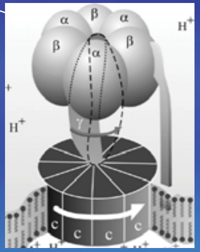


Fly ash
~ 10-20 mm

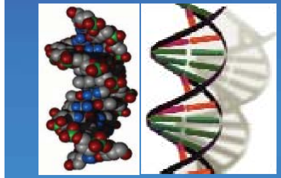


Red blood cells with white cell
~ 2-5 mm

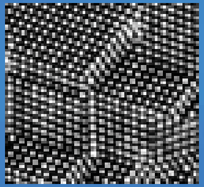
~10 nm
diameter



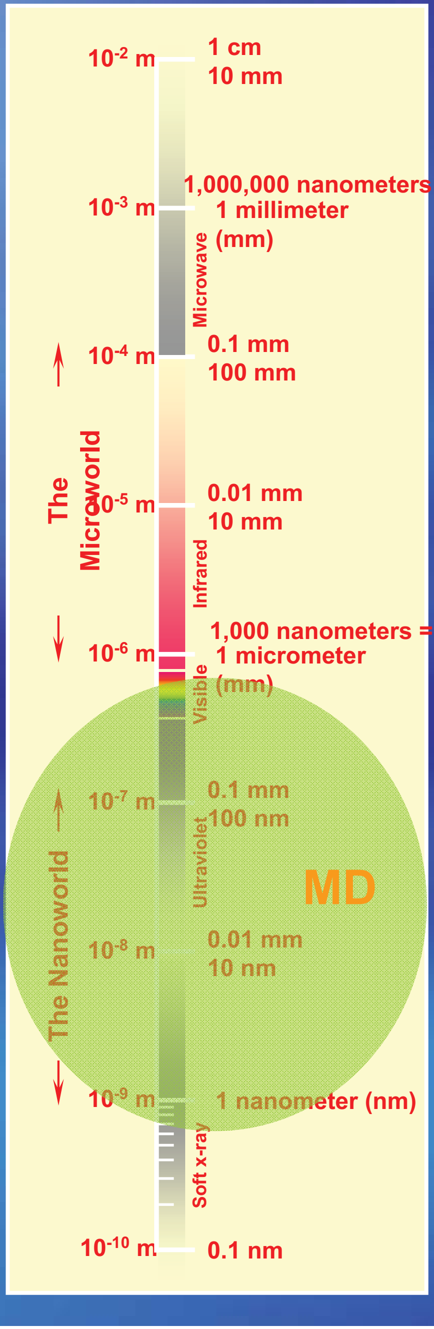
ATP synthase



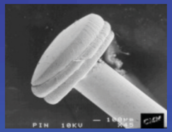
DNA
~2-1/2 nm diameter



Atoms of silicon
spacing ~tenths of nm

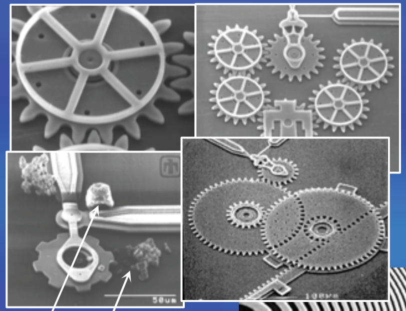


Things Manmade

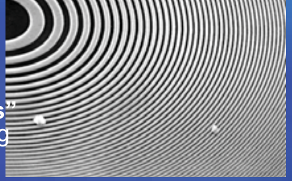


Head of a pin
1-2 mm

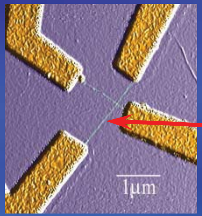
MicroElectroMechanical devices
10 -100 mm wide



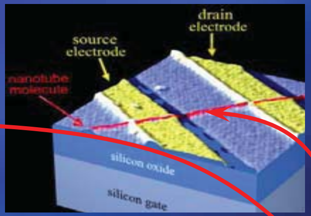
Red blood cells
Pollen grain



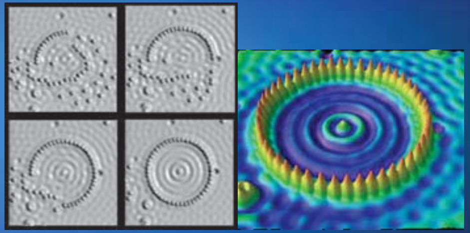
Zone plate x-ray "lens"
Outermost ring spacing
~35 nm



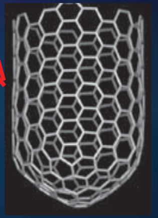
Nanotube electrode



Nanotube transistor

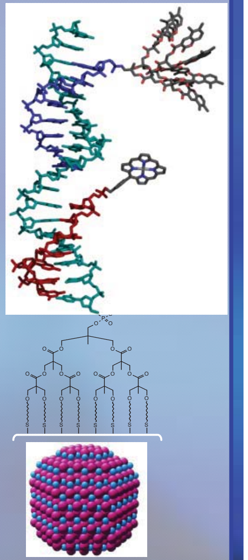


Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm



Carbon nanotube
~2 nm diameter

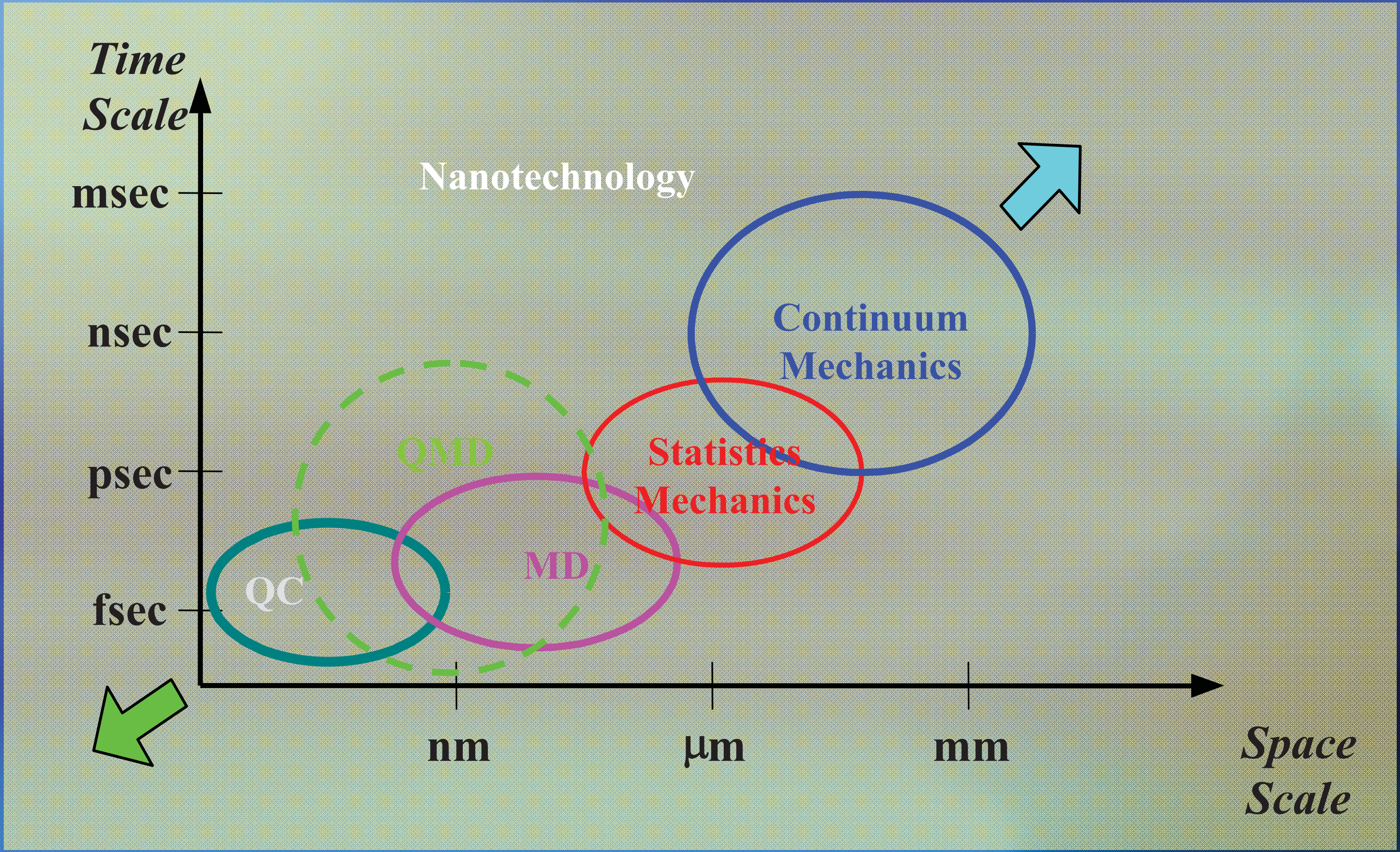
21st Century Challenge



Combine nanoscale building blocks to make novel functional devices, e.g., a photosynthetic reaction center with integral semiconductor storage

Office of Basic Energy Sciences
Office of Science, U.S. DOE
Version 03-05-02

Length and Time Scales in Numerical Modeling



Molecular Dynamics

A computer simulation technique that allows one to predict the time evolution of a system of interacting particles (atoms, molecules,.. etc.)

Two Steps to perform MD simulation

(I)

- Setting initial conditions (e.q. initial position and velocities of all particles in the system)

- Selecting accurate interaction potential for describing the forces among all the particles.

(II)

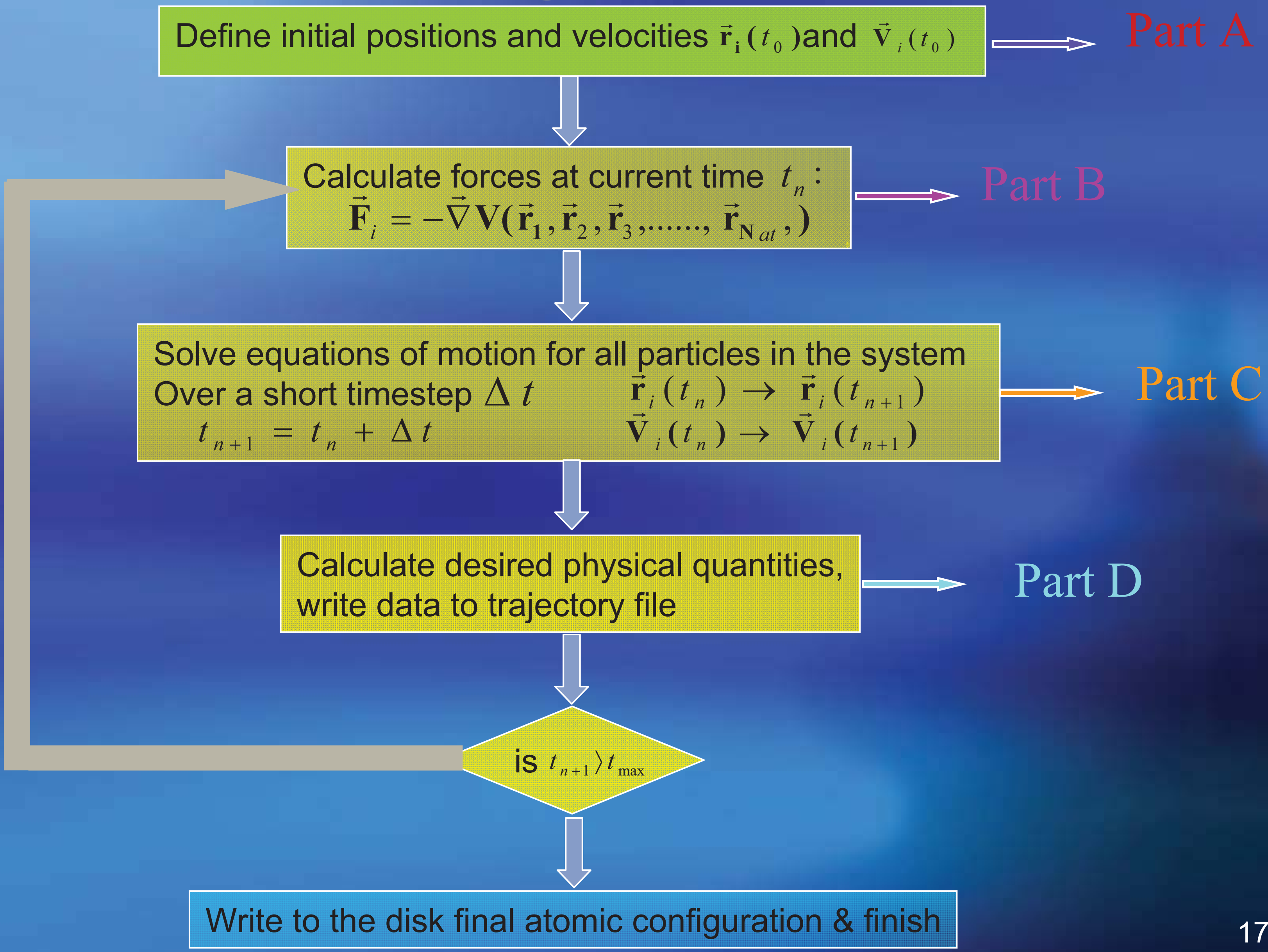
- **Solving a set of classical equations of motion**

$$m\ddot{r}_i = F_i$$

$$F_i = -\sum_{\substack{i \neq j \\ i=1}}^{N} \nabla_i \Phi(r_{ij})$$

$\Phi(r_{ij})$: interatomic potential

Schematic diagram of a basic MD code



Define initial positions and velocities $\vec{\mathbf{r}}_i(t_0)$ and $\vec{\mathbf{v}}_i(t_0)$ → Part A

Calculate forces at current time t_n:
$$\vec{\mathbf{F}}_i = -\vec{\nabla}\mathbf{V}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2, \vec{\mathbf{r}}_3, \ldots\ldots, \vec{\mathbf{r}}_{N_{at}},)$$
→ Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt
$$t_{n+1} = t_n + \Delta t$$
$$\vec{\mathbf{r}}_i(t_n) \rightarrow \vec{\mathbf{r}}_i(t_{n+1})$$
$$\vec{\mathbf{V}}_i(t_n) \rightarrow \vec{\mathbf{V}}_i(t_{n+1})$$
→ Part C

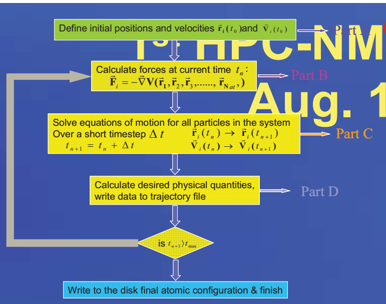
Calculate desired physical quantities,
write data to trajectory file
→ Part D

is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

Part A

Setting Initial Condition


Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n: $\vec{F}_i = -\vec{\nabla} V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}})$ → Part B

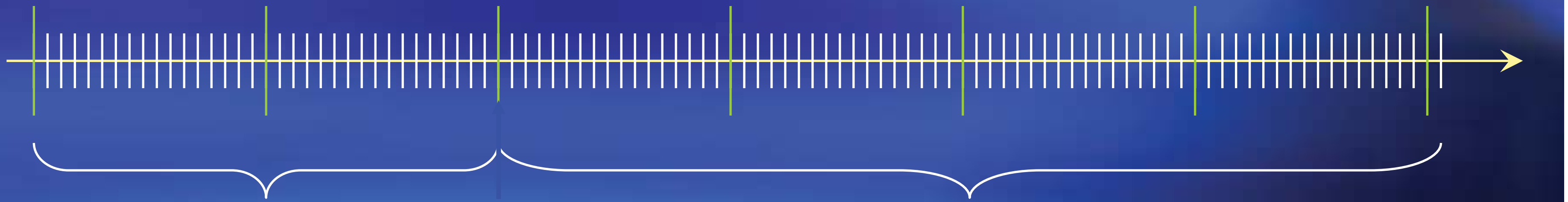
Solve equations of motion for all particles in the system
Over a short timestep Δt $\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\vec{v}_i(t_n) \rightarrow \vec{v}_i(t_{n+1})$ → Part C

Calculate desired physical quantities, write data to trajectory file → Part D

is $t_{n+1} \rangle t_{max}$

Write to the disk final atomic configuration & finish

- **establishing initial positions and velocities of all atoms before MD simulation**
- **Two skills to achieve the relaxation process**
  - using values after relaxation process
  - Undergoing a relaxation process

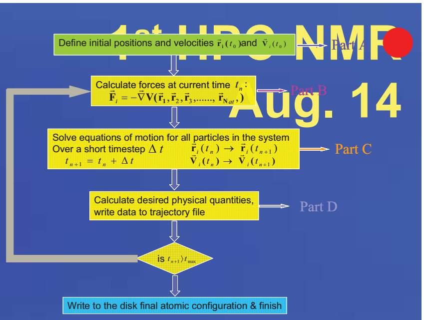

Relaxation cycles

Re-zero simulation sums

Production cycles

Schematic *from* lecture of D. A. Kofke

Generating an Initial Configuration



Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{V}_i(t_0)$

Part A

Calculate forces at current time t_n:
$\vec{F}_i = -\vec{\nabla}V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{Nat},)$

Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\vec{V}_i(t_n) \rightarrow \vec{V}_i(t_{n+1})$

Part C

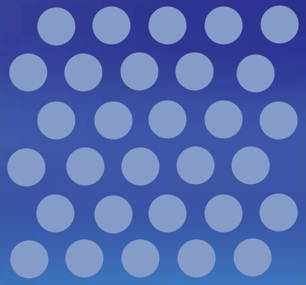
Calculate desired physical quantities,
write data to trajectory file

Part D

is $t_{n+1} \rangle t_{max}$

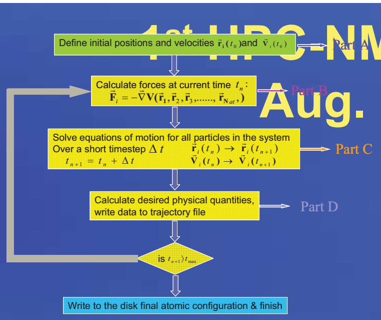
Write to the disk final atomic configuration & finish

The arrangement of the Initial configuration is mainly based on the ***material nature*** we want to simulate (for example, b.c.c, f.c.c, h.c.p, amorphous.)



H.C.P

F.C.C



Define initial positions and velocities $\vec{\mathbf{r}}_i(t_0)$ and $\vec{\mathbf{v}}_i(t_0)$ → Part A

Calculate forces at current time t_n:
$\vec{\mathbf{F}}_i = -\vec{\nabla}\mathbf{V}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2, \vec{\mathbf{r}}_3, \ldots\ldots, \vec{\mathbf{r}}_{N_{at}},)$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\quad \vec{\mathbf{r}}_i(t_n) \rightarrow \vec{\mathbf{r}}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\quad \vec{\mathbf{V}}_i(t_n) \rightarrow \vec{\mathbf{V}}_i(t_{n+1})$ → Part C

Calculate desired physical quantities,
write data to trajectory file → Part D

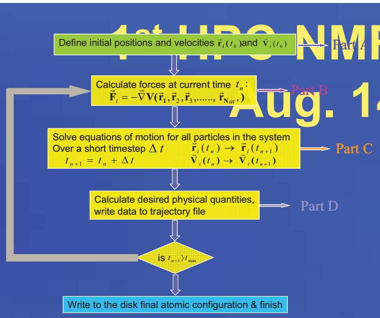
is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

Initial Velocities

- Generating velocities of atoms (in x, y, z directions) over a uniform random numbers over (-1,1).
- Scaling the kinetic energy of the system to the corresponding temperature we desired.
- shifting the center-of-mass momentum to be zero

Dimensions and Units



Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n: $\vec{F}_i = -\vec{\nabla} V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}},)$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\vec{v}_i(t_n) \rightarrow \vec{v}_i(t_{n+1})$ → Part C

Calculate desired physical quantities, write data to trajectory file → Part D

is $t_{n+1} \rangle t_{\max}$

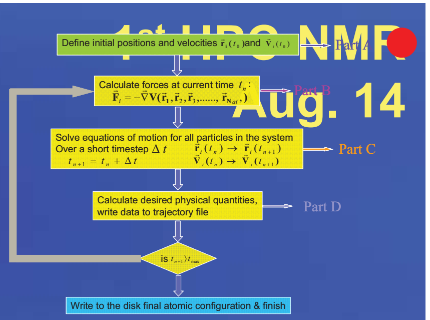
Write to the disk final atomic configuration & finish

Symbol	Definition	Value
1. Constants		
k	Boltzmann's constant	1.3806×10^{-23} J/(molec·K)
N_0	Avagadro's number	6.022×10^{23}
2. Simulation Variables		
N	Number of molecules	$\sim 10^3$
V	Simulation cell volume	$\sim 10^{-24}$ m^3
m	Molecular mass	$\sim 10^{-25}$ kg/molec
ρ	Number density	$\sim 10^{27}$ molec/m^3
E	Energy (total)	$\sim 10^{-20}$ J/molec
t	time	$\sim 10^{-12}$ s
3. Model Variables		
σ	Size variable	$\sim 5 \times 10^{-10}$ m
ϵ	Energy variable	$\sim 10^{-21}$ J/molec
r_b	Bond distance	$\sim 10^{-10}$ m
k_v	Vibrational spring constant	$\sim 10^3$ J/m^2

- Scaling by model parameters
  - size s
  - energy e
  - mass m

Symbol	Meaning	Definition
r^*	dimensionless distance	r/σ
E^*	dimensionless energy	E/ϵ
T^*	dimensionless temperature	kT/ϵ
U^*	dimensionless internal energy	U/ϵ
t^*	dimensionless time	$t/[\sigma(m/\epsilon)^{0.5}]$
v^*	dimensionless velocity	$v/(\epsilon/m)^{0.5}$
F^*	dimensionless force	$F\sigma/\epsilon$
P^*	dimensionless pressure	$P\sigma^3/\epsilon$
D^*	dimensionless self diffusion coefficient	$D/[\sigma(\epsilon/m)^{0.5}]$

Tables from the lecture of D. A. Kofke

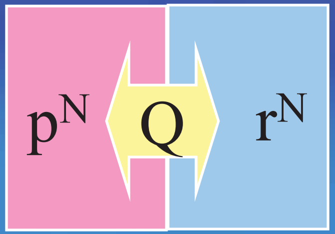


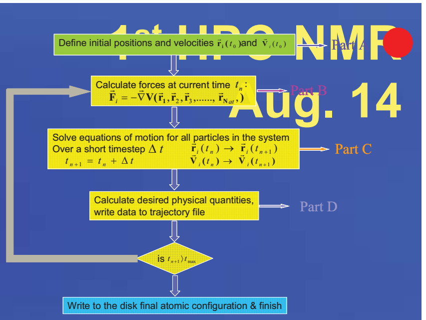
Thermostats

- momentum temperature is proportional to total kinetic energy

$$kT = \frac{1}{Nd}\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m} = \frac{2}{Nd}K$$

- energy fluctuate between K and U





Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n:
$\vec{F}_i = -\vec{\nabla}V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}},)$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\vec{V}_i(t_n) \rightarrow \vec{V}_i(t_{n+1})$ → Part C

Calculate desired physical quantities,
write data to trajectory file → Part D

is $t_{n+1} \rangle t_{\max}$

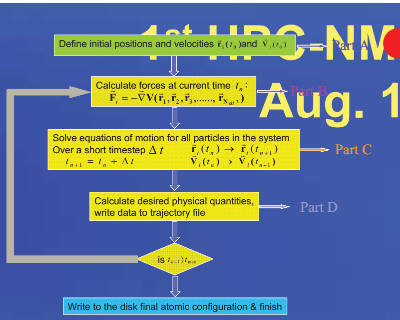
Write to the disk final atomic configuration & finish

Force momentum temperature to remain constant

1. Isokinetic Thermostatting

Thermostatting via Wall Collisions

1. Andersen Thermostat
2. Nosé Thermostat
3. Nosé-Hoover Thermostat



Define initial positions and velocities $\vec{\mathbf{r}}_i(t_0)$ and $\vec{\mathbf{v}}_i(t_0)$ → Part A

Calculate forces at current time t_n: $\vec{\mathbf{F}}_i = -\vec{\nabla}\mathbf{V}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2, \vec{\mathbf{r}}_3, \ldots\ldots, \vec{\mathbf{r}}_{N_{at}},)$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\quad \vec{\mathbf{r}}_i(t_n) \rightarrow \vec{\mathbf{r}}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\quad \vec{\mathbf{V}}_i(t_n) \rightarrow \vec{\mathbf{V}}_i(t_{n+1})$ → Part C

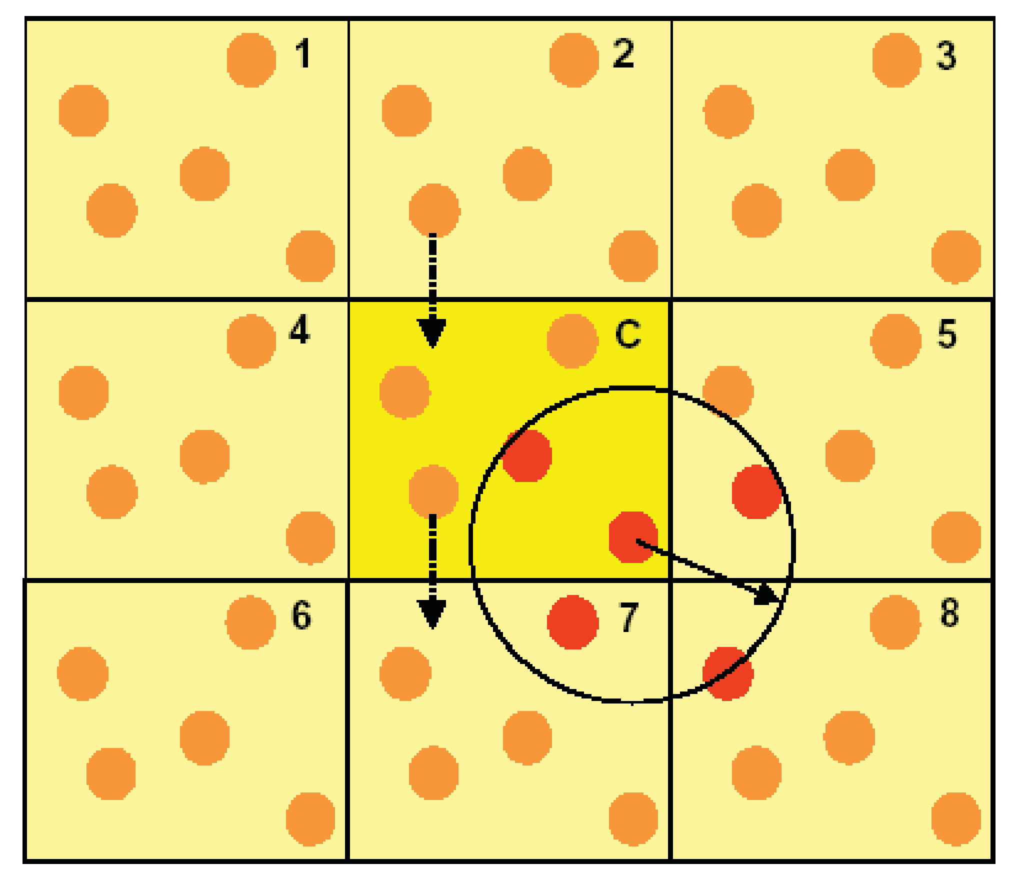
Calculate desired physical quantities, write data to trajectory file → Part D

is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

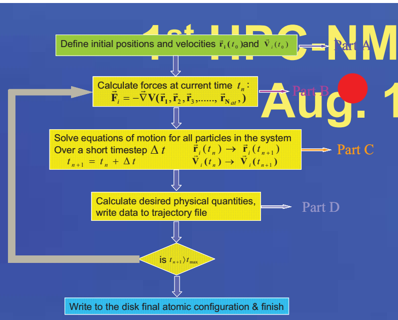
Periodic Boundary Condition

(geometric boundary)



Part B

Potentials used in the MD simulation


Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n: $\vec{F}_i = -\vec{\nabla}V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}})$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\quad \vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\quad \vec{v}_i(t_n) \rightarrow \vec{v}_i(t_{n+1})$ → Part C

Calculate desired physical quantities, write data to trajectory file → Part D

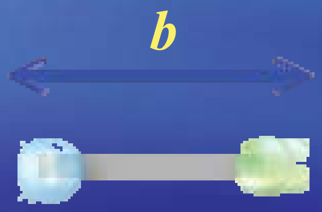
is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

Bonding Force

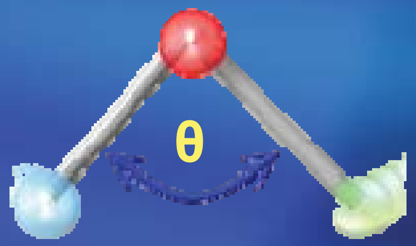
(a) bond strength

$$V_{\text{bond length}} = \sum_{N=1}^{N_b} 1/2\, k_b^i \; (b_i - b_0^i)^2$$



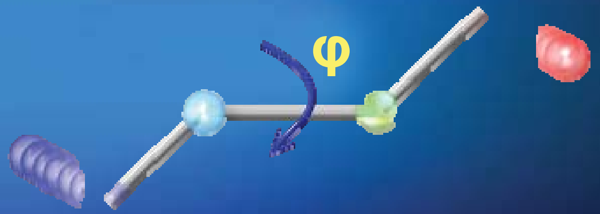
(b) bond bending

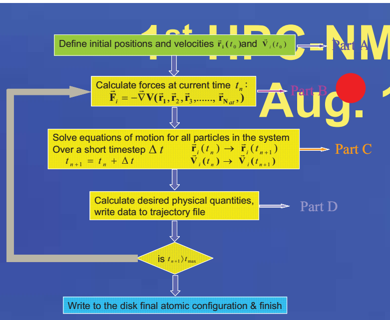
$$V_{bending} = \sum_{N=1}^{N_\theta} k_\theta^i \; (\theta_i - \theta_0^i)^2$$



(c) bond torsion

$$V_{dihedral} = \sum_{n=1}^{N_\varphi} K_\varphi^i \{1\text{-}\cos[n^i(\varphi_i - \varphi_0^i)]\}$$




Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n: $\vec{F}_i = -\vec{\nabla} V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}})$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\quad \vec{r}_i(t_n) \to \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\quad \vec{V}_i(t_n) \to \vec{V}_i(t_{n+1})$ → Part C

Calculate desired physical quantities,
write data to trajectory file → Part D

is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

Non-bonding Force

(d) Van der Wail

$$V_{vdw} = [A_{SC}\varepsilon^{ij}(r_0^{ij}/r_{ij})^{12} - 2\varepsilon^{ij}(r_0^{ij}/r_{ij})^{6} - S^A_{vdw}(r_{ij})]$$

$$S^A_{vdw}(r_{ij}) = [A_{SC}\varepsilon^{ij}(r_0^{ij}/r_{ij})^{12} - 2\varepsilon^{ij}(r_0^{ij}/r_{ij})^{6}] - 12(r - r_c)[A_{SC}\varepsilon^{ij}(r_0^{ij}/r_{ij})^{12} - 2\varepsilon^{ij}(r_0^{ij}/r_{ij})^{6}]/r_c$$

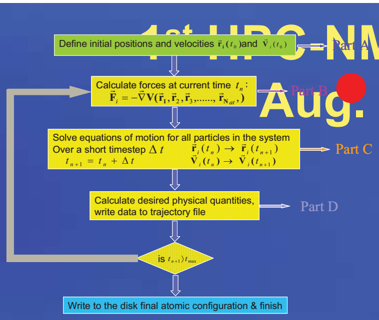
(e) Coulomb force

$$V_{coul.} = 332 \sum_{\text{partial charges}} [q^i q^j / r_{ij} - S^A_{els}(r_{ij})]$$

$$S^A_{els}(r_{ij}) = \frac{q^i q^j}{r_c} - (r_{ij} - r_c)\frac{q^i q^j}{r_c^{\,2}}$$

(f) Hydrogen force

$$V_{HB} = \frac{M}{r^{12}} - \frac{N}{r^{10}}$$



Define initial positions and velocities $\vec{\mathbf{r}}_i(t_0)$ and $\vec{\mathbf{v}}_i(t_0)$ → Part A

Calculate forces at current time t_n: $\vec{\mathbf{F}}_i = -\vec{\nabla}\mathbf{V}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2, \vec{\mathbf{r}}_3, \ldots\ldots, \vec{\mathbf{r}}_{N_{at}},)$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\quad \vec{\mathbf{r}}_i(t_n) \to \vec{\mathbf{r}}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\quad \vec{\mathbf{V}}_i(t_n) \to \vec{\mathbf{V}}_i(t_{n+1})$ → Part C

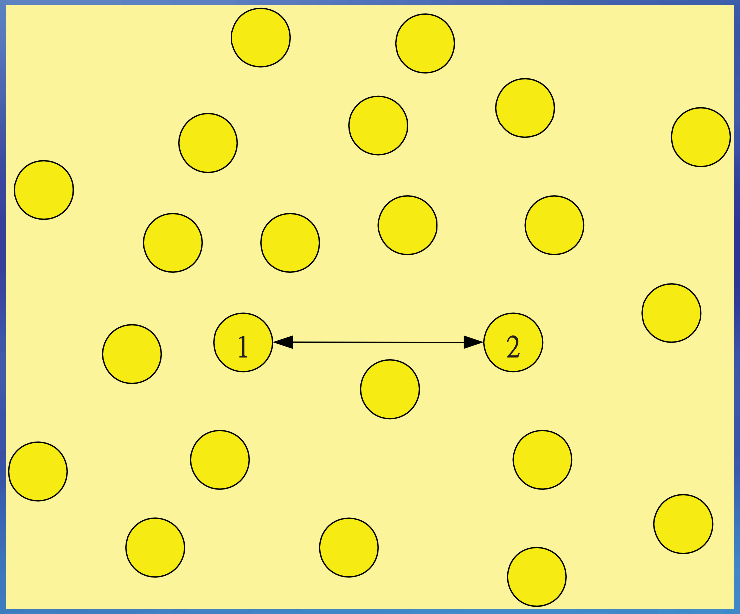
Calculate desired physical quantities, write data to trajectory file → Part D

is $t_{n+1} \rangle t_{\max}$

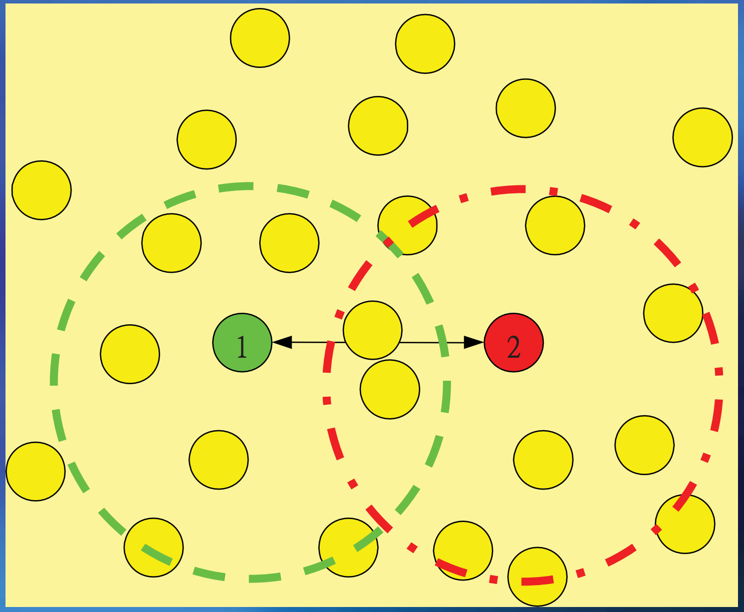
Write to the disk final atomic configuration & finish

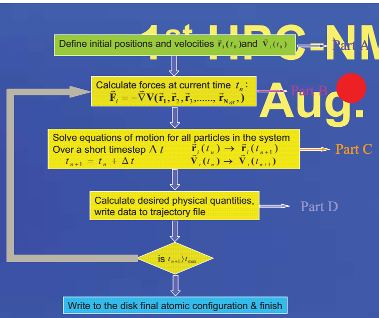
Two types of interatomic potential

Pairwise Potential



Many body potential





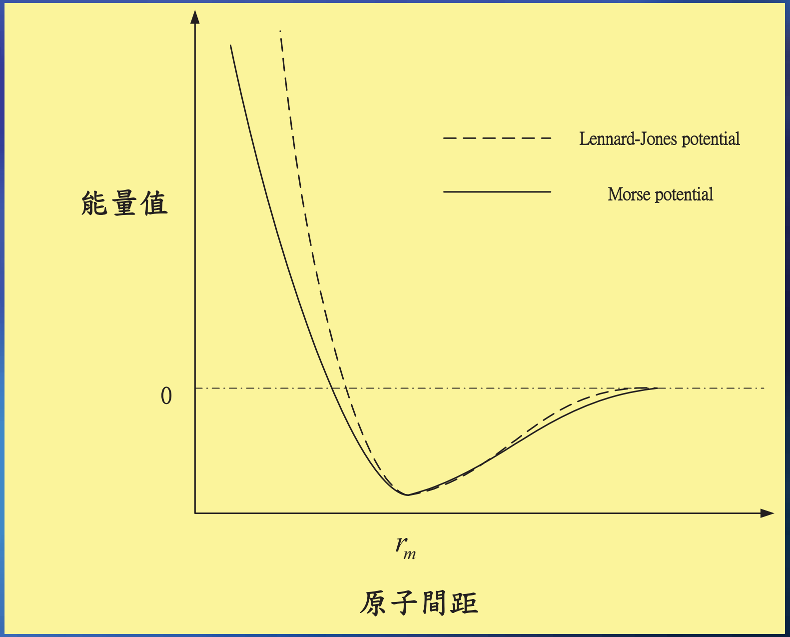
Two-body potential

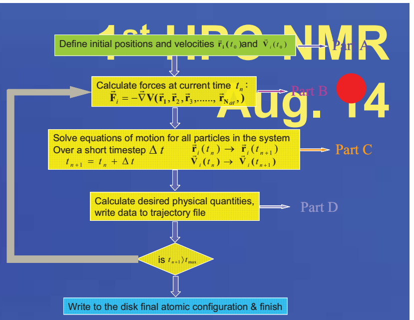
•Lennard-Jones potential

$$U\left(r_{ij}\right) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

•Morse potential

$$\phi\left(r_{ij}\right) = D\left\{\exp\left\{-2\alpha(r_{ij} - r_o\right\} - 2*\exp\left\{-\alpha(r_{ij} - r_o\right\}\right\}$$





Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n: $\vec{F}_i = -\vec{\nabla}V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}},)$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\quad \vec{r}_i(t_n) \to \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t \quad \vec{V}_i(t_n) \to \vec{V}_i(t_{n+1})$ → Part C

Calculate desired physical quantities, write data to trajectory file → Part D

is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

Many-body Potential

■Many body potential

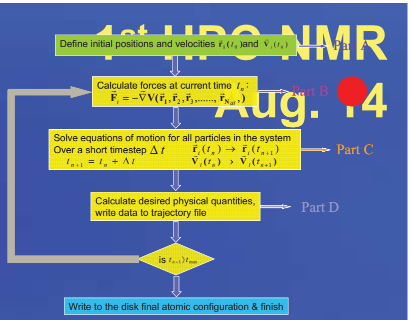
- **Tight-binding potential** (Co, Cu, Ti, …)

$$E = -\underline{\left\{ \sum_j \xi^2 \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1 \right) \right] \right\}^{1/2}} + \underline{\sum_j A \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1 \right) \right]}$$

Many-body term-long range force, attractive force

Born-Mayer type pairwise term-short range, repulsive force

- Where ξ is an effective hopping integral
- r_{ij} is the distance between atom *i* and *j*
  r_o is the first-neighbor distance



Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$

Calculate forces at current time t_n: $\vec{F}_i = -\vec{\nabla}V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}},)$

Solve equations of motion for all particles in the system
Over a short timestep Δt $\quad \vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t \quad \vec{v}_i(t_n) \rightarrow \vec{v}_i(t_{n+1})$

Calculate desired physical quantities,
write data to trajectory file

is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

Many-body Potential + Non-bonding Force

- Many body potential
  - **Tersoff potential** (C, Si, Ge)

A complicated potential to describe the covalent bonding between atoms

$$E = \sum_i \sum_{j>i} V_{ij}$$

$$V_{ij} = f_c(r_{ij})[V_R(r_{ij}) + b_{ij} V_A(r_{ij})]$$

$$V_R(r_{ij}) = A_{ij} \exp(-\lambda_{ij} r_{ij})$$

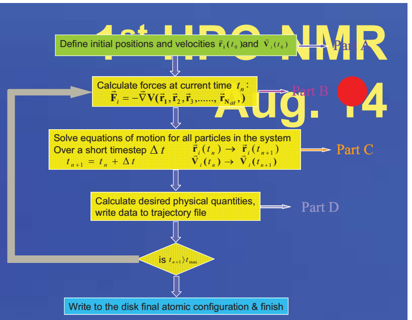
Pairwise term-short range, repulsive force

$$V_A(r_{ij}) = -B_{ij} \exp(-\mu_{ij} r_{ij})$$

Three-body term-long range, attractive force (bonding angle is also considered)

$$f_c(r_{ij}) = \begin{cases} 1, & if \quad r_{ij} < R_{ij} \\ \frac{1}{2} - \frac{1}{2}\cos\left(\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right), & if \quad R_{ij} < r_{ij} < S_{ij} \\ 0, \quad if & r_{ij} > S_{ij} \end{cases}$$

Cutoff Function, which is used to smooth the energy function to be zero at the cutoff distance between atoms.



Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n: $\vec{F}_i = -\vec{\nabla}V(\vec{r}_1,\vec{r}_2,\vec{r}_3,......,\vec{r}_{N_{at}})$ → Part B

Solve equations of motion for all particles in the system Over a short timestep Δt $\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$ $\vec{V}_i(t_n) \rightarrow \vec{V}_i(t_{n+1})$ $t_{n+1} = t_n + \Delta t$ → Part C

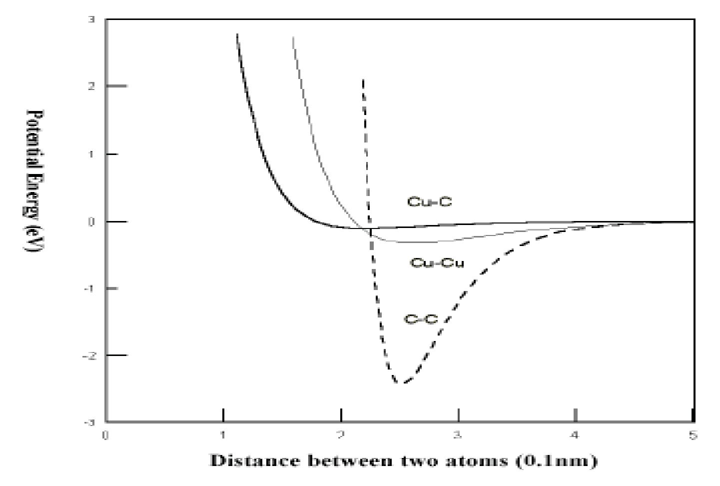
Calculate desired physical quantities, write data to trajectory file → Part D

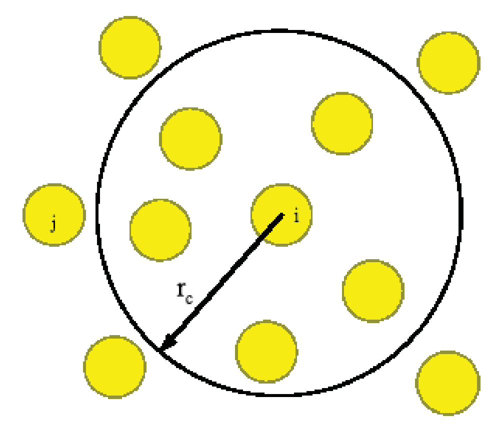
is $t_{n+1} \rangle t_{max}$

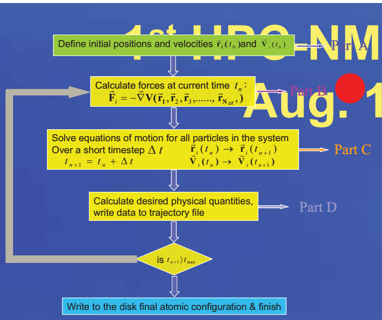
Write to the disk final atomic configuration & finish

Cuttoff Method

- Verlet list
- Cell list
- Verlet combine cell list







Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$

Calculate forces at current time t_n:
$\vec{F}_i = -\vec{\nabla} V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}},)$

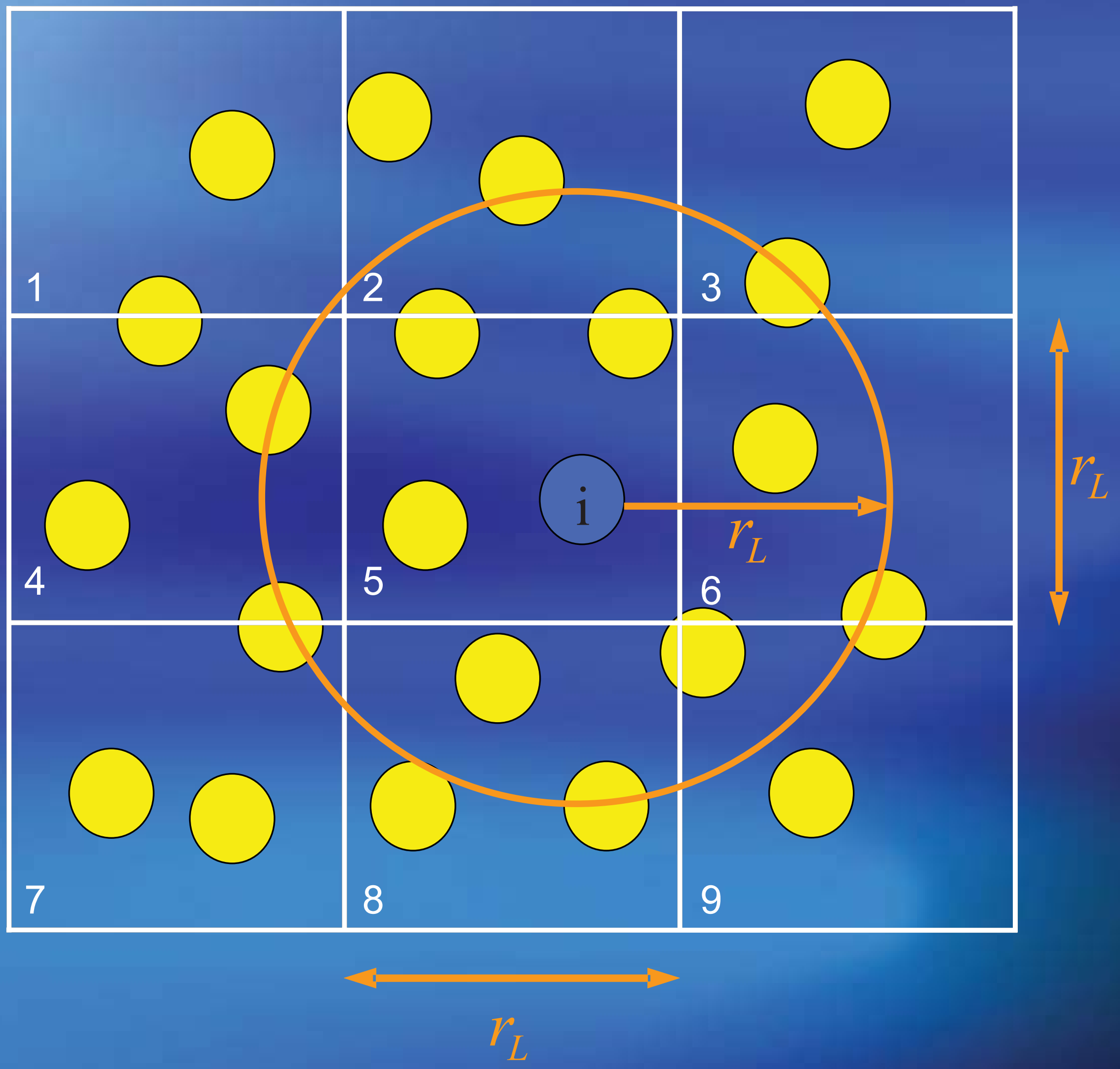
Solve equations of motion for all particles in the system
Over a short timestep Δt $\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\vec{V}_i(t_n) \rightarrow \vec{V}_i(t_{n+1})$

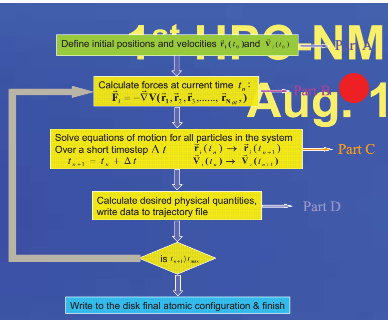
Calculate desired physical quantities,
write data to trajectory file

is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

Verlet combine Cell List





Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n:
$\vec{F}_i = -\vec{\nabla} V(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots\ldots, \vec{r}_{N_{at}},)$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\vec{V}_i(t_n) \rightarrow \vec{V}_i(t_{n+1})$ → Part C

Calculate desired physical quantities,
write data to trajectory file → Part D

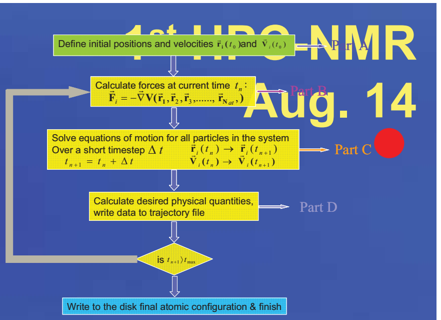
is $t_{n+1} \rangle t_{max}$

Write to the disk final atomic configuration & finish

Algorithm	Computer Time (Sec./Time step)	Efficient(%)
None	43.65	1.51
Verlet List	8.51	7.76
Cell link	1.53	43.13
Verlet + Cell link	0.66	100

Part C

Integration Algorithms


Define initial positions and velocities $\vec{r}_i(t_0)$ and $\vec{v}_i(t_0)$ → Part A

Calculate forces at current time t_n:
$\vec{F}_i = -\vec{\nabla} V(\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_{N_{at}},)$ → Part B

Solve equations of motion for all particles in the system
Over a short timestep Δt $\quad \vec{r}_i(t_n) \rightarrow \vec{r}_i(t_{n+1})$
$t_{n+1} = t_n + \Delta t$ $\quad \vec{V}_i(t_n) \rightarrow \vec{V}_i(t_{n+1})$ → Part C

Calculate desired physical quantities,
write data to trajectory file → Part D

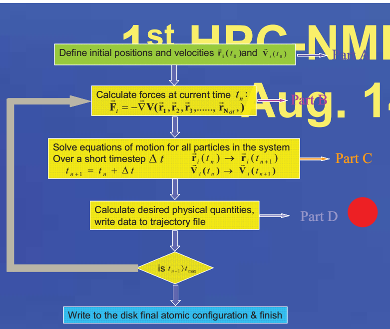
is $t_{n+1} \rangle t_{\max}$

Write to the disk final atomic configuration & finish

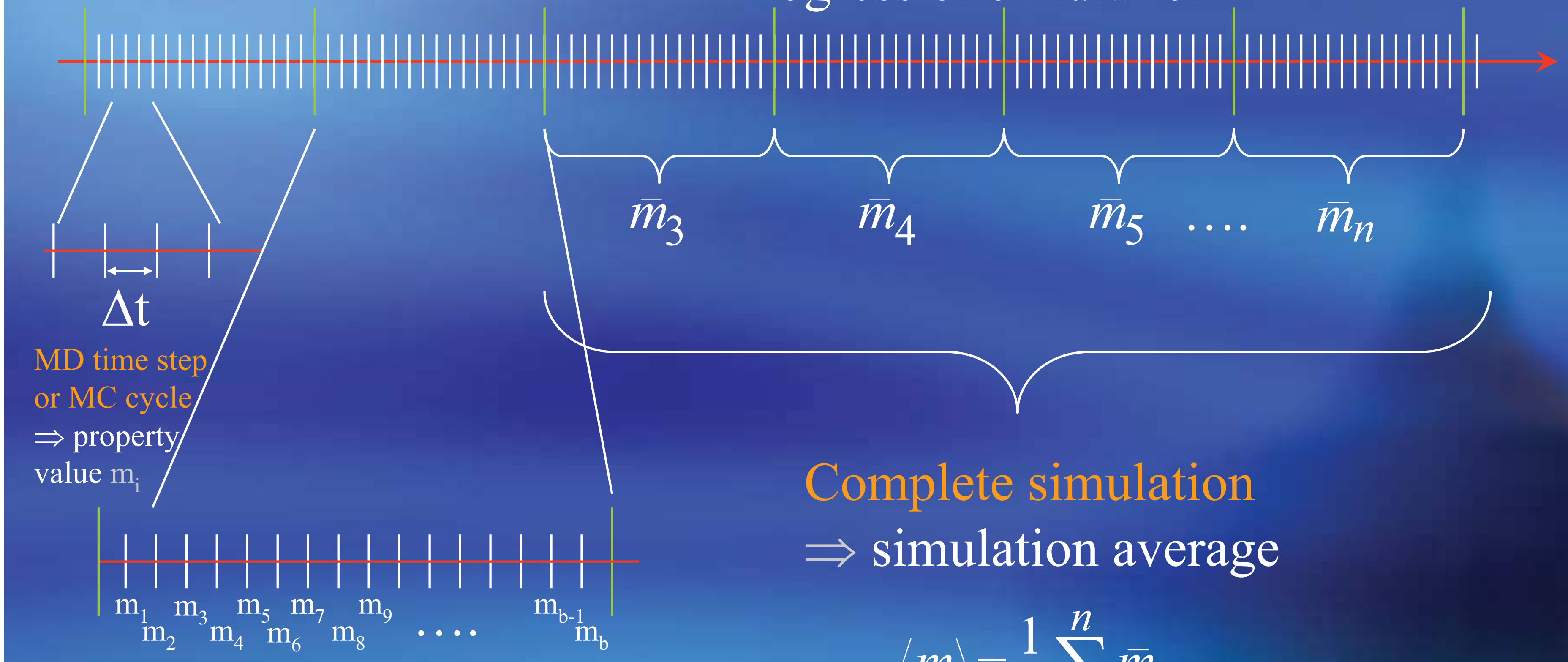
1. **Verlet Algorithm**
2. **Leapfrog Algorithm**
3. **Velocity Verlet Algorithm**
4. **Gear Predictor-Corrector Algorithm**

Part D

Data sampling



Progress of simulation ⟶



MD time step
or MC cycle
⇒ property
value m_i

Complete simulation
⇒ simulation average

$$\langle m \rangle = \frac{1}{n} \sum_{k=1}^{n} \bar{m}_k$$

⇒

Simulation block
⇒ block average

$$\bar{m} = \frac{1}{b} \sum_{i=1}^{b} m_i$$

Schematic from lecture 11 of D. A. Kofke

Outline

- INTRODUCTION
- MD SIMULATION
- METHODOLOGY
- RESULTS AND DISCUSSION
- CONCLUSIONS
- FUTURE DIRECTIONS
- ACKNOWLEDGMENTS

MD SIMULATION

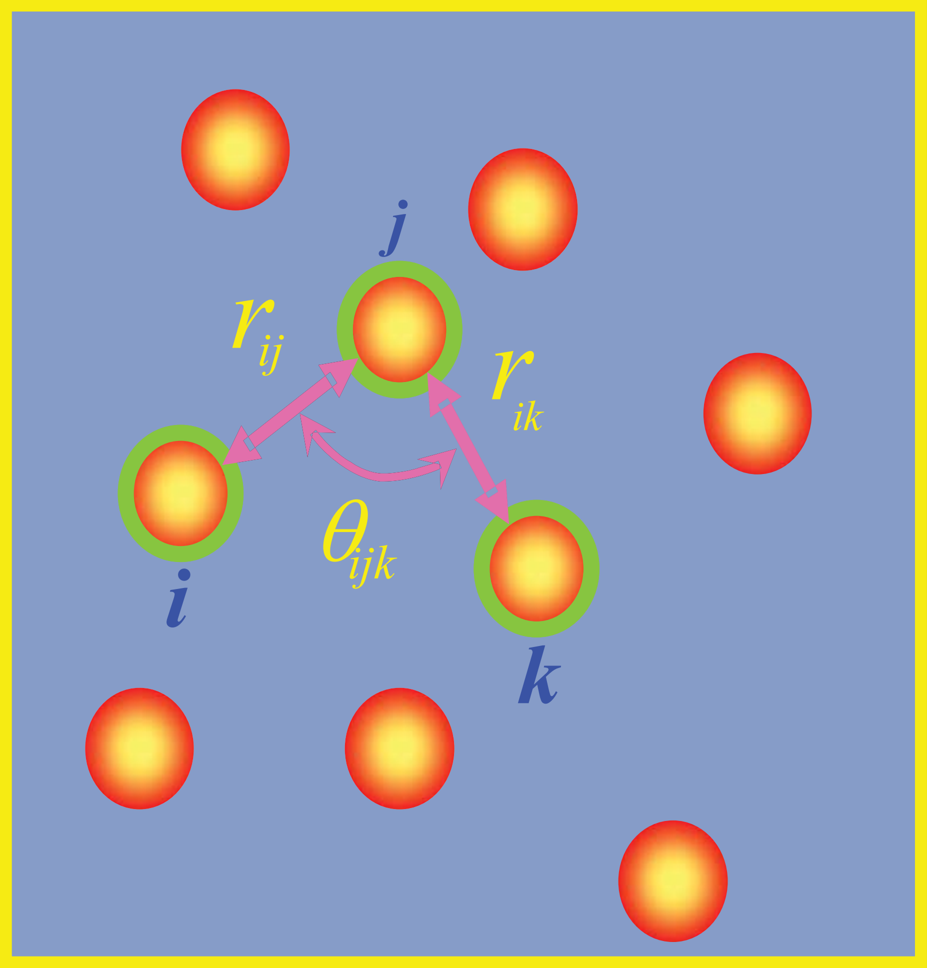
- The initial conditions:
  - The bottom end of the carbon nanotube is fixed.
  - The time step is chosen to be Δt=1.0 fs for the case of a carbon nanotube without water; Δt=0.5 fs for carbon nanotubes with water.
  - The temperature is set to be 1, 300, 1000 and 2000K.
  - The NTV ensemble is chosen and the cut-off distance is 12 Å.
  - For the water-nanotube composite or the carbon nanotube, there are 100,000 executed for initial relaxation and additional 500,000 time steps for reaching the lowest energy configuration.

MD SIMULATION

- The controlled parameters:
  - The interval of time step and the cut-off distance are pre-chosen.
  - Temperature (1, 300, 1000, and 2000K).
  - The number of water molecules (0, 1, and 125).
  - The running time of a case (100,000, 500,000 time steps).
- The investigated parameters:
  - The vibration displacements, their amplitude, and the variance and the mean value of the amplitudes of the carbon nanotube are studied.
- Summary:
  - The free-vibration displacement of the carbon nanotube’s tip is investigated, and the dynamical behavior of water inside the carbon nanotube is also recorded.
  - The relationship between the variance and mean value of vibrating amplitudes of the carbon nanotube and temperature are discussed.

Methodology

Tersoff：(Carbon)



$$E = \sum_{i} \sum_{j>i} V_{ij}$$

$$V_{ij} = f_c(r_{ij})[V_R(r_{ij}) + b_{ij} V_A(r_{ij})]$$

$$V_R(r_{ij}) = A_{ij} \exp(-\lambda_{ij} r_{ij})$$

$$V_A(r_{ij}) = -B_{ij} \exp(-\mu_{ij} r_{ij})$$

$$f_c(r_{ij}) = \begin{cases} 1, & if \quad r_{ij} < R_{ij} \\ \frac{1}{2} - \frac{1}{2}\cos\left(\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right), & if \quad R_{ij} < r_{ij} < S_{ij} \\ 0, & if \quad r_{ij} > S_{ij} \end{cases}$$

$$b_{ij} = \chi_{ij}(1 + \beta_i^{n_i} \xi_{ij}^{n_i})^{-1/2n_i}$$

Methodology

Tersoff： (Carbon)

where E is the total energy of all the covalently bonded carbon atoms, E_i the energy for atom i, V_{ij} the interaction energy between atoms i and j, r_{ij} the distance between them, θ_{ijk} is the bond angle between atoms ij and ik, and f_c is a cutoff function to restrict the range of the potential. In the present work, the total energy calculated from the Tersoff potential is assumed to be the total strain energy of the system.

$$E = \sum_{i} \sum_{j>i} V_{ij}$$

$$V_{ij} = f_c(r_{ij})[V_R(r_{ij}) + b_{ij} V_A(r_{ij})]$$

$$V_R(r_{ij}) = A_{ij} \exp(-\lambda_{ij} r_{ij})$$

$$V_A(r_{ij}) = -B_{ij} \exp(-\mu_{ij} r_{ij})$$

$$f_c(r_{ij}) = \begin{cases} 1, \quad if \quad r_{ij} < R_{ij} \\ \frac{1}{2} - \frac{1}{2}\cos\left(\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right), \quad if \quad R_{ij} < r_{ij} < S_{ij} \\ 0, \quad if \quad r_{ij} > S_{ij} \end{cases}$$

$$b_{ij} = \chi_{ij}(1 + \beta_i^{n_i} \xi_{ij}^{n_i})^{-1/2n_i}$$

Methodology

Tersoff： (Carbon)

Parameters used in the Tersoff potential for carbon-carbon binding.

Parameter	Value
A (eV)	1.3936×10^{3}
B (eV)	3.467×10^{2}
λ (Å^{-1})	3.4879
μ (Å^{-1})	2.2119
B	1.5724×10^{-7}
n	7.2751×10^{-1}
c	3.8049×10^{4}
d	4.384×10^{0}
H	-5.7058×10^{-1}
R (Å)	1.8
S (Å)	2.1

Methodology

- TIP3P water (Water)

$$E = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

where ε and σ are constant. They are in units of $g\text{-}Å^{12}/fs^2$ and Å, respectively.

Methodology

- **ME3Organic (Bonding Terms) (Water-Carbon)**

(a) Bond Stretching Potential

$$E = \frac{1}{2}K(r - R_0)^2$$

Here K is a constant, in units of kcal/mol/Å^2. r (Å) is the distance between atom i and atom j. R_0(Å) is the equilibrium bond stretching distance.

(b) Bond Angle Potential

$$E = \begin{cases} \dfrac{C}{2\sin^2\theta_0}(\cos\theta - \cos\theta_0)^2 \\ C(1 + \cos\theta) \end{cases}$$

$$(0 < \theta_0 < 0)$$

$$(\theta_0 = 180^\circ)$$

Here C is a constant, in units of kcal/mol.θ_0 (deg) is the equilibrium bond angle.

Methodology

- **ME3Organic (Bonding Terms) (Water-Carbon)**

(c) Torsional Angle Potential

$$E = \frac{V}{2}[1 - \cos\{n(\phi - \phi_0)\}]$$

Here *V* is a constant, in units of kcal/mol. θ_0 (deg) is the equilibrium torsional angle and *n* is a periodic parameter.

(d) Out-of-Plane Potential

$$E = \begin{cases} \dfrac{K_1}{2\sin^2\psi_0}(\cos\psi - \cos\psi_0)^2 \\ C(1 - \cos\psi) \end{cases}$$

Here K_1 is a constant, in units of kcal/mol. ψ_0 (deg) is the equilibrium out-of-plane angle.

Methodology

- **ME3Organic (Non-bonding Terms) (Water-Carbon)**
- **(e) LJ only UFF Potential**

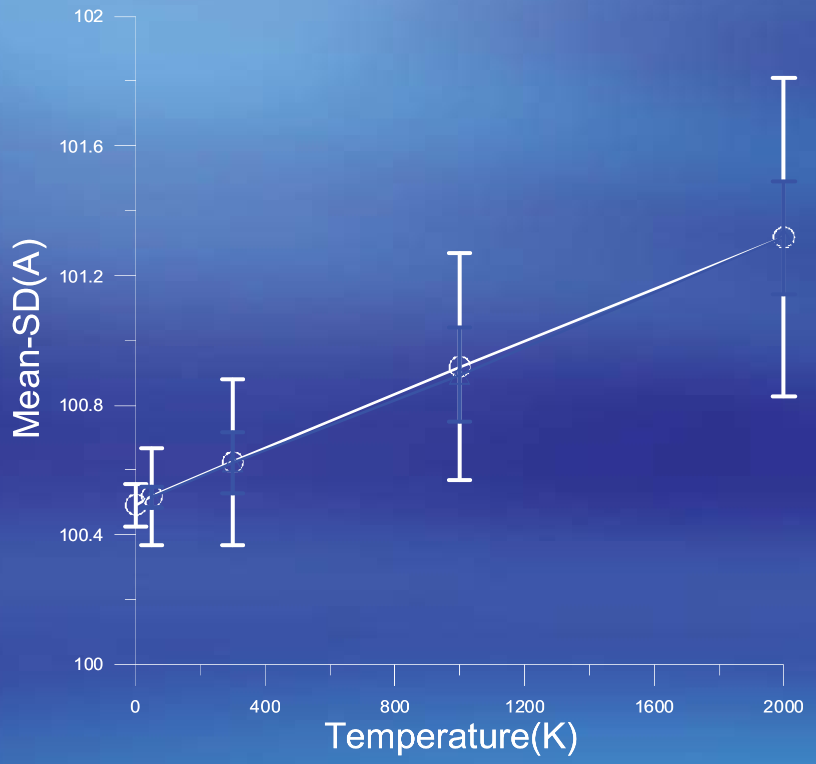
$$E = D_0 \left\{ \left(\frac{R_0}{r}\right)^{12} - 2\left(\frac{R_0}{r}\right)^{6} \right\}$$

The above equation is the non-bonding term. D_0 is a constant, whose unit is kcal/mol. R_0 (Å) is also a constant.

Outline

- INTRODUCTION
- MD SIMULATION
- METHODOLOGY
- RESULTS AND DISCUSSION
- CONCLUSIONS
- FUTURE DIRECTIONS
- ACKNOWLEDGMENTS

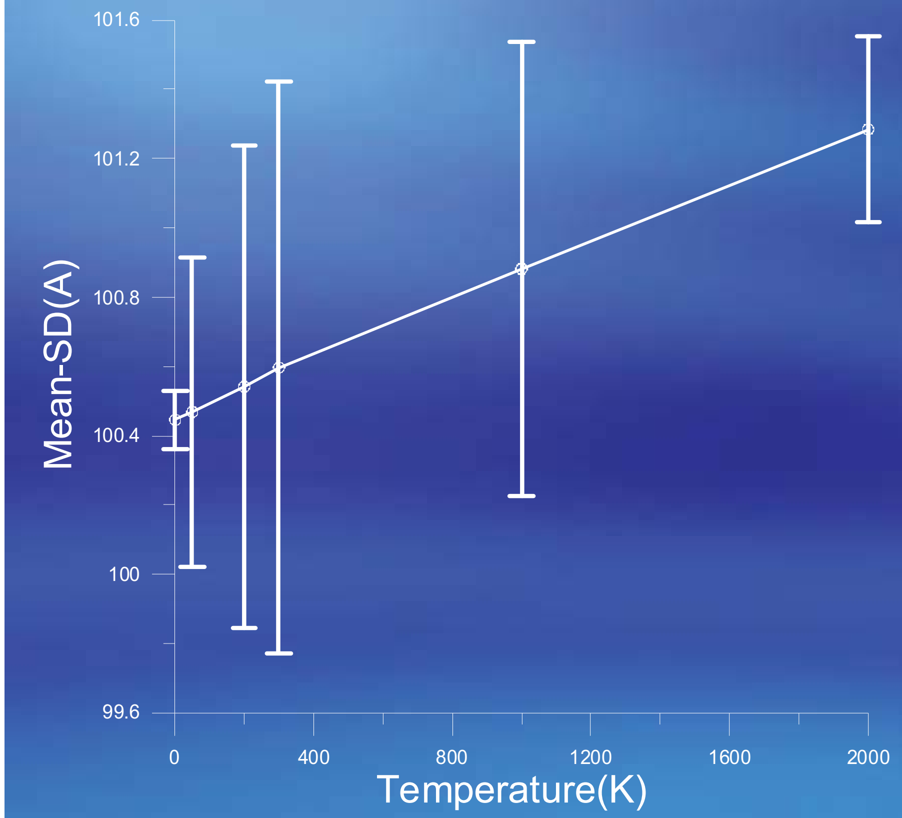
RESULTS AND DISCUSSION



It shows that longer running time (blue line, 500,000 time steps), predicts less variation than shorter running time (white line, 100,000 time steps), but not significantly, indicating our results have reached numerical equilibrium. Also, by this slight difference, it can be seen that the transient state of a carbon nanotube’s vibration is more violent than the steady-state one. The variance of the amplitude of a capped carbon nanotube’s tip decreases with the executing time increasing.

The relationship between the mean value and the variance of a capped SWCNT and temperature without water

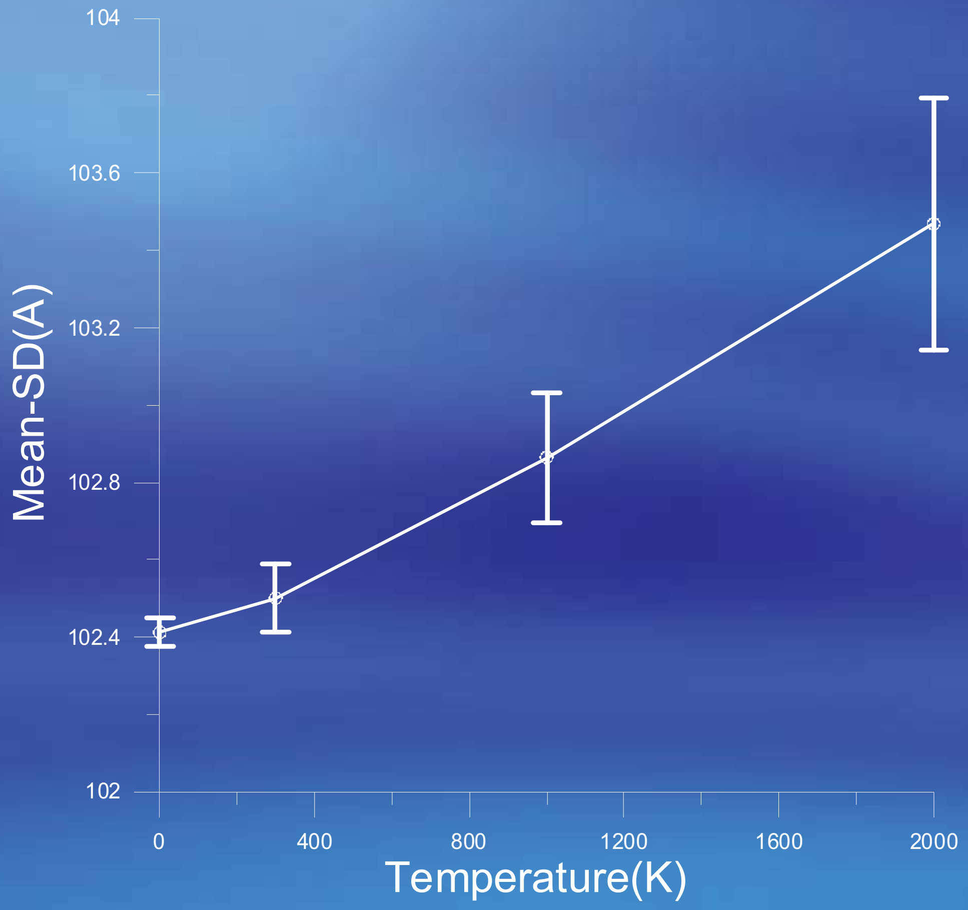
RESULTS AND DISCUSSION



It shows that the amplitude of a SWCNT's tip increases with temperature. Its increasing rate is nearly linearly. Also, it is found that the variance of a carbon nanotube is the largest near 300K. We observe that the system containing one water molecule disturbs the tube's vibration most when temperature is near the boiling point. It is suspected that water's boiling is responsible for this observation. When the temperature of water is above the boiling point, the volume of the water vapor expands more than that of the water. Hence, the collision between water molecules and the wall of a carbon nanotube increases and results in the variance of the amplitude of a carbon nanotube.

The relationship between the mean value and the variance of a capped SWCNT and temperature with only one water molecule

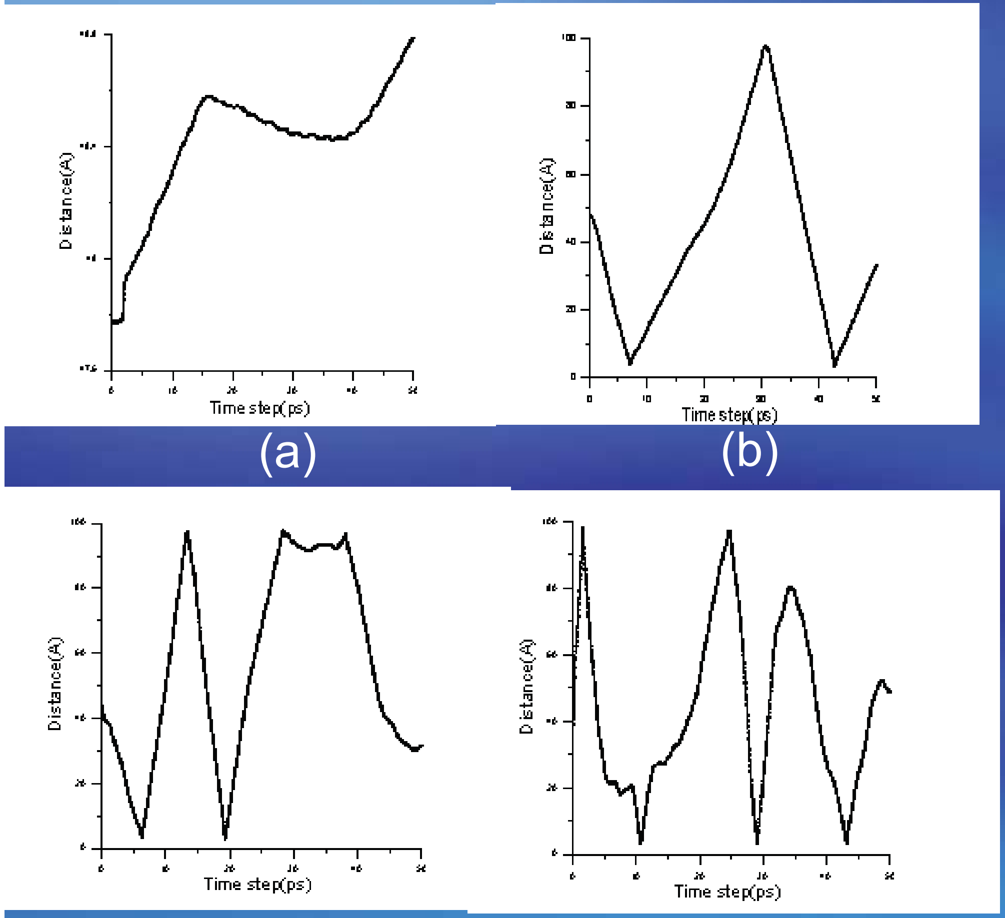
RESULTS AND DISCUSSION



It shows that the amplitude of a SWCNT's tip increases with temperature. Its increasing rate is nearly linearly when the case has 125 water molecules inside a SWNT.

The relationship between the mean value and the variance of a capped SWCNT and temperature with 125 water molecules.

RESULTS AND DISCUSSION



(a) (b)

(c) (d)

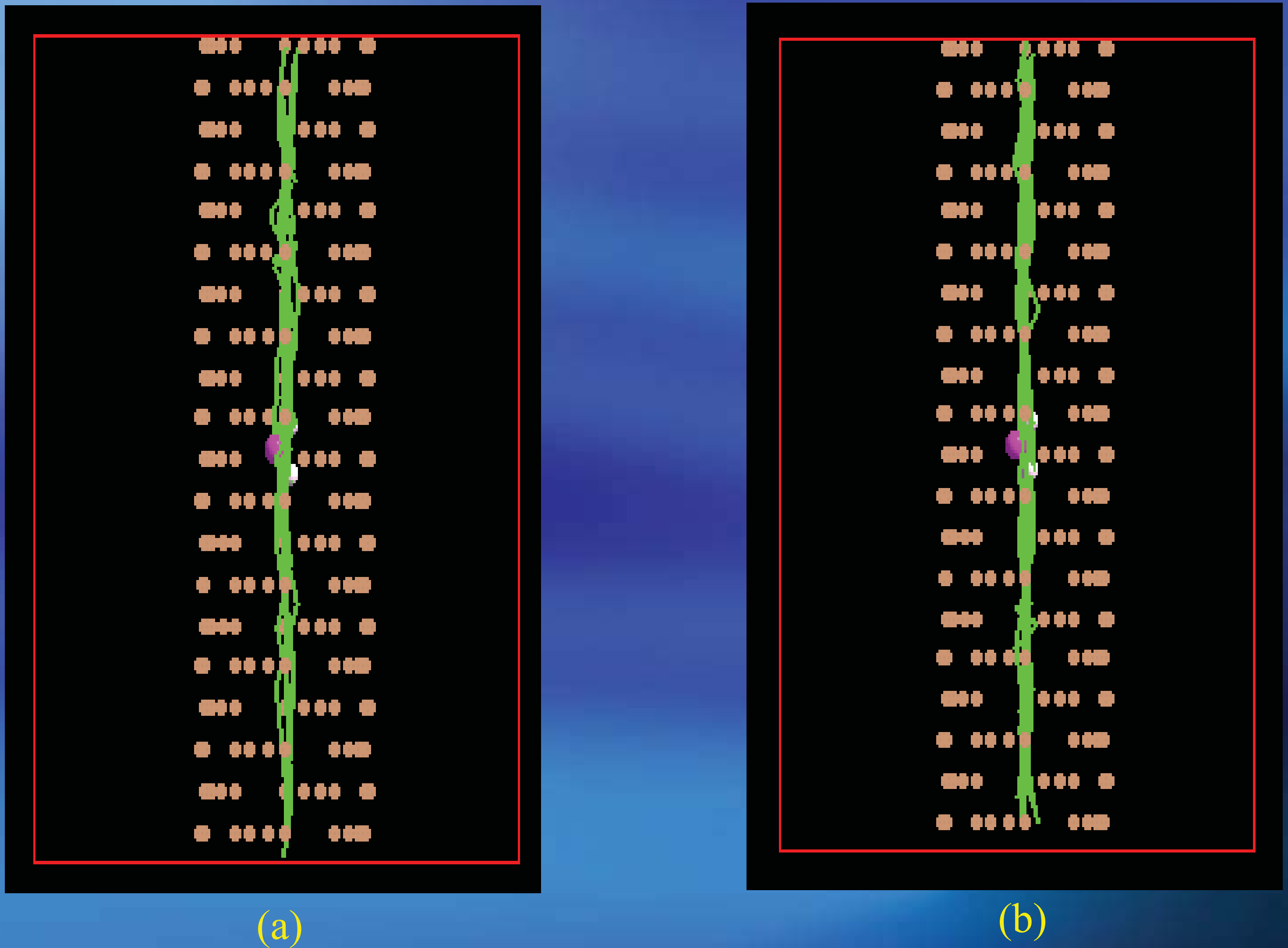
The spatial position of one water molecule in the axial direction of a capped SWCNT, which is executed 100,000 time steps at different temperature (a) 1K; (b) 300K; (c) 1000K; (d) 2000K.

The trend of dynamical behavior of one water moleculeis like walking randomly in a one-dimensional space, as shown in Fig. One water molecule behaves in random-walk fashion more noticeable with temperature increasing. The kinetic energy of water increases with the increase of temperature and results in the movement of water molecule. However, the increasing the number of water molecules decreases the random-walk trend. The diffusion pathways are driven by the mechanism of random-walk and the concentration of water. With temperature and executing time increasing, water molecules distribute uniformly gradually along the axial direction of the SWCNT. The breathing and stretching-shortening modes of the SWCNT are currently under investigation by our group

RESULTS AND DISCUSSION

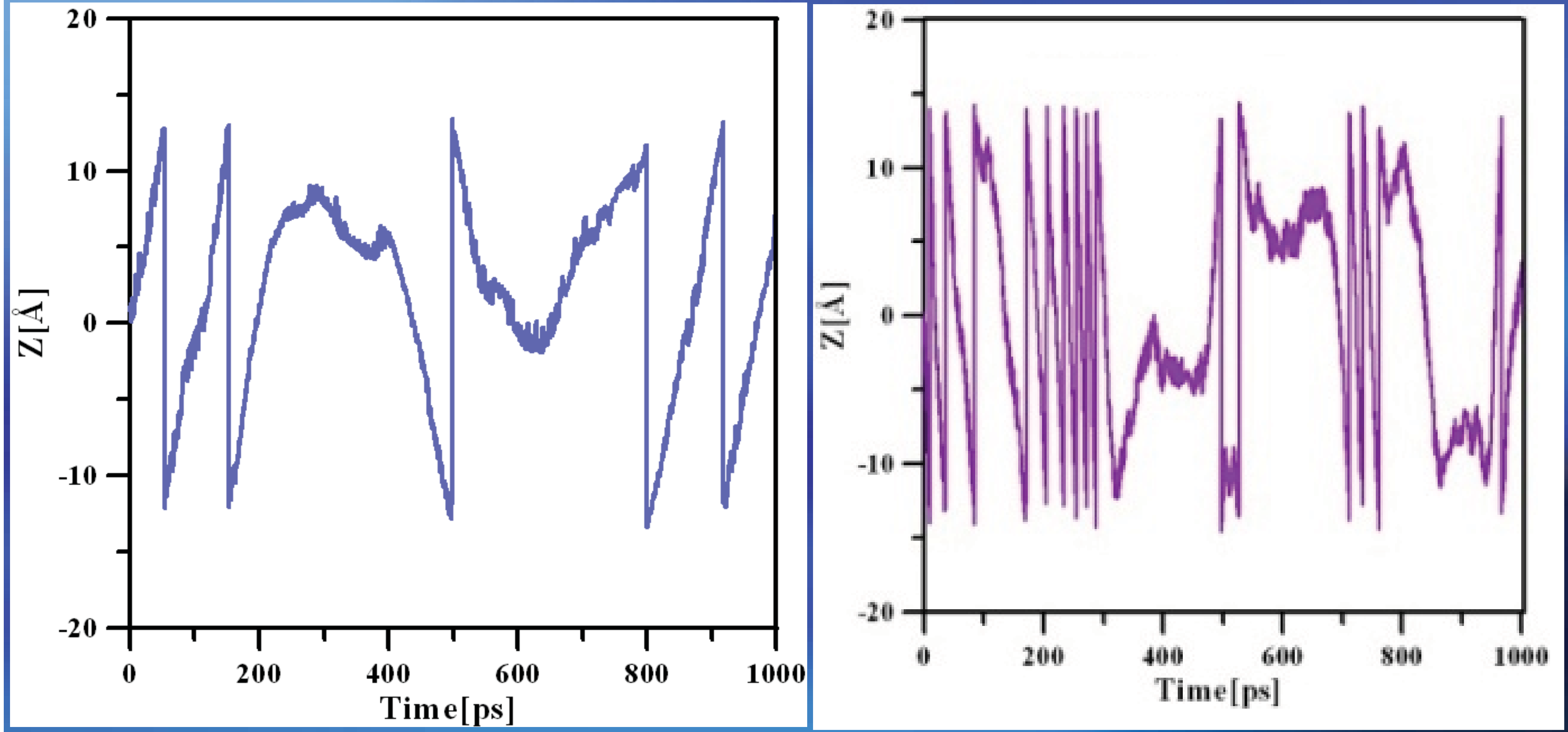
內含水單體的單壁奈米碳管之模擬模型 - (以(5,5)碳管為例，碳原子數200顆

RESULTS AND DISCUSSION


(a)
(b)

含水單體的(5,5)單壁碳管之水單體運動軌跡圖，長度約為20 Å，分別為298K(a)和500K(b)

RESULTS AND DISCUSSION

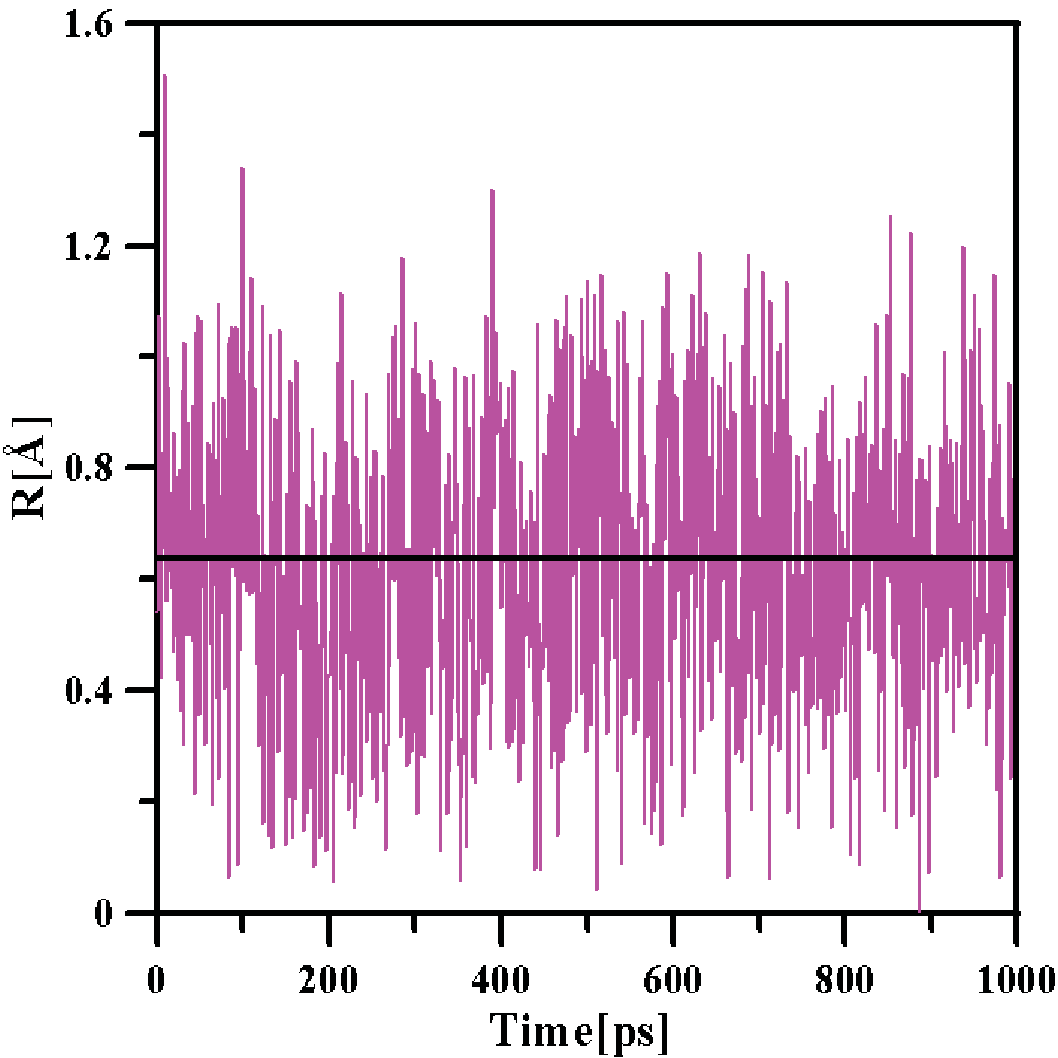


(a)

(b)

水單體軸向位置時變圖(a) (9,0)；(b) (5,5)

RESULTS AND DISCUSSION

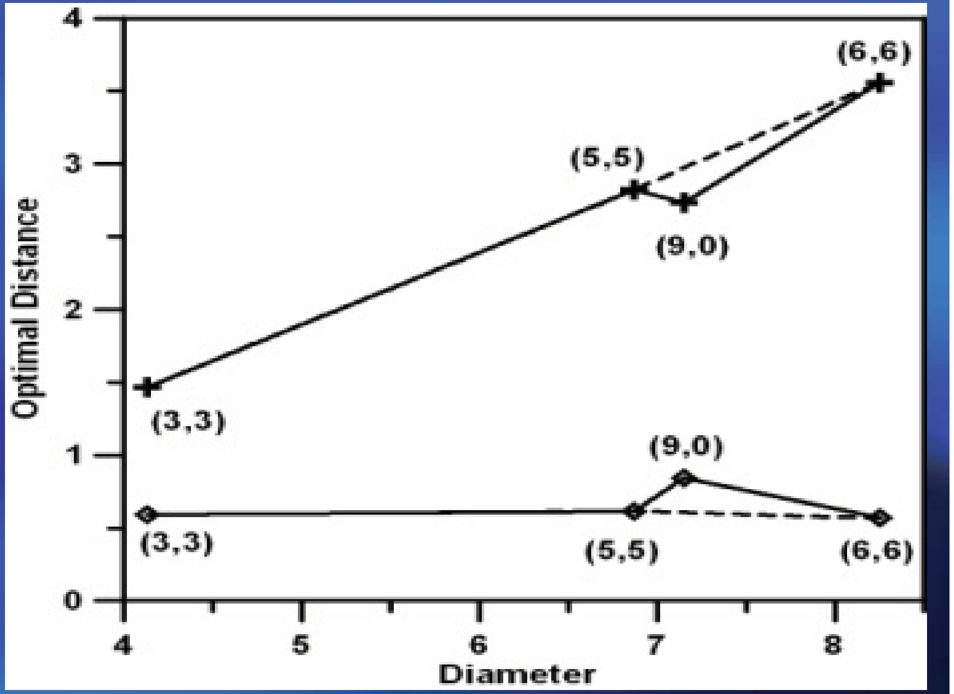


水單體距碳管軸心位置時變圖以(5,5)為例

Results

	直徑(Å)	與管壁最佳化距離(Å)	與軸心最佳化距離(Å)
(3,3)	4.13	1.467	0.592
(5,5)	6.87	2.822	0.616
(6,6)	8.25	3.557	0.568
(9,0)	7.15	2.733	0.844

水單體在奈米碳管內部之最佳化距離



不同碳管的與管徑之關係圖

Outline

- INTRODUCTION
- MD SIMULATION
- METHODOLOGY
- RESULTS AND DISCUSSION
- CONCLUSIONS
- FUTURE DIRECTIONS
- ACKNOWLEDGMENTS

Conclusions

(1)The more temperature is, the more the vibrating amplitude of the SWNT and the dynamical behavior of water monomer inside it is.

(2) The optimal geometrical distance is almost linearly related with the diameter of a SWNT, not with the chiral vector of that.

(3) The water monomer remains the optimal geometrical distance and stays closer to the wall of a SWNT instead of to keep nearly the z-axial center of a SWNT after achieving the steady state.

Outline

- **INTRODUCTION**
- **MD SIMULATION**
- **METHODOLOGY**
- **RESULTS AND DISCUSSION**
- **CONCLUSIONS**
- **FUTURE DIRECTIONS**
- **ACKNOWLEDGMENTS**

Acknowledgements

- (1) A grant from the computational supports of National Center for High-Performance Computing, Taiwan.
- (2) A grant from the Taiwan National Science Council under the contract NSC 96-2221-E-492-007-MY3 is gratefully appreciated.
- (3) We are also thankful the assistance of the Chun-Yi Wu, Q. Y. Kuo, Cheng-Shiu Hung, and S. S. Tu.

Thanks for your attentions