Large Scale Simulations for Carbon Nanotubes

Author: Syogo Tejima, Noejung Park, [*]Yoshiyuki Miyamoto, Kazuo Minami, Mikio Iizuka, Hisashi Nakamura and [**]David Tomanek
Research Organization for Information Science &Technology
2-2-54, Naka-Meguro, Meguro-ku, Tokyo, 153-0061, Japan
[*]Nanotube Technology Center NEC Corporation
34 Miyukigaoka, Tsukuba, 305-8501 JAPAN
[**]Michigan State University

CARBON NANOTUBE RESEARCH GROUP

Morinobu Endo, Eiji Osawa, Atushi Oshiyama, Yasumasa Kanada, Susumu Saito, Riichiro Saito, Hisanori Shinohara, David Tomanek, Tsuneo Hirano, Shigeo Maruyama, Kazuyuki Watanabe, Takahisa Ohno, Yoshiyuki Miyamoto, Mari Ohfuti, Hisashi Nakamura

ABSTRACT

Computational approaches have brought powerful new techniques to understand chemical reactions and material physics as well as experimental and theoretical methods, and they are playing a crucial role in nano technology. Growth in applications of codes enabled us to show the properties of molecular and atoms interacting with surrounding complex environment and new material finding.

We developed Molecular modeling codes based on tight binding (TB) approach, conventional density functional method (DFT) and time-dependent DFT. These codes have used for many phenomena as the need arose.

As for nano material design, we have challenged large scale simulations up to ten thousand atoms without the spatial symmetry and homogeneous condition. The TB method is suitable for treatment of a large number of atoms. Thus at first we concentrated on the TB code for optimizations.

The Carbon-Recursive-Technique-Molecular-Dynamics (CRTBD) is a tight binding software specialized for Carbon systems with Order-N scaling. Through efficient optimization by the parallelization and vectorization on the Earth Simulator, we achieved the performance of 7.1 Tera Flopes on 435 nodes (3480 processors) in the simulation of thermal conductivity of carbon nanotube with 48600 atoms.

Earth Simulator could give a possibility of large-scale realistic simulations in finding and creating novel nano materials.

Keywords: Large scale simulation, TB theory, *ab initio* theory, DFT, Carbon Nanotube

1. INTRODUCTION

Carbon nanotubes and fullerenes have been expected to make a breakthrough in the new material development of nano-technology. A considerable number of potential applications have been reported about semiconductors-device, nano-diamond, battery, super strong threads and fibers, and so on. For material design of nano-carbon it is required to grasp the properties through nano-scale world.

Microscopic experiments are quite limited by hardness of measurements in nano space and by high experimental cost for the advanced microscope as HTTEM or STM. The numerical simulation based on quantum mechanics has turned to be a very efficient methodology. The trials for so many simulations with any conditions give us valuable information on material properties and design ways. However, to simulate

Proceedings of the Seventh International Conference on High Performance Computing and Grid in Asia Pacific Region (HPCAsia'04)
0-7695-2138-X/04 $ 20.00 IEEE

the nano-scale phenomena on realistic time and space it is necessary for us to deal with heavy computation. According to our estimation, in the case of the material formation from the bottom of atom scale to the sub-micron scale that could be applicable for sensor class, it would be required the Peta flops scale computing to deal with 10^8 atom system by the tigth binding method. A recent higher performance computing provides a large-scale simulation of up to 10^4 atoms.

However the high performance computational facilities are so limited presently for researchers and designers as user and its capability is also restricted for the material science in performance. Thus, the collaboration with experiment, theory and simulation researchers launched the challenging large scale simulation for the nano-carbon materials. In this project we developed and optimized a parallelized and vectorized MD code for massively parallel and vector supercomputer, the Earth Simulator. Furthermore, by using the CRTMD, we conducted simulations on thermal properties of the nanotube and on some nano-manufacturing.

The CRTMD is the order-N method. Speedup by parallelization and optimization to more than 1000 processors on the Earth Simulator needs new algorisms to reduce the heavy computation time and cost. By optimization of code, we achieved performance of 7.1 Tera flops on a thermal conducting simulation. Furthermore, some example cases are reported to show the applicability of the large scale simulation to the material science and design.

2. PERFORMANCE OF CODE

2.1 Outline of the CRTMD Code

In this section, an outline of CRTMD code in Fig.1 is explained . The main part of the code is as follows.

(1) Cluster

To search the pair of interacting atoms, the CRTMD introduce the concept of cluster. The atoms within the cut off radius are called first cluster atoms for a center atom of sphere. The center atom interacts with only first cluster atoms. The tight-binding Hamiltonian matrix in terms of center atom is not equal to zero only first cluster atoms.

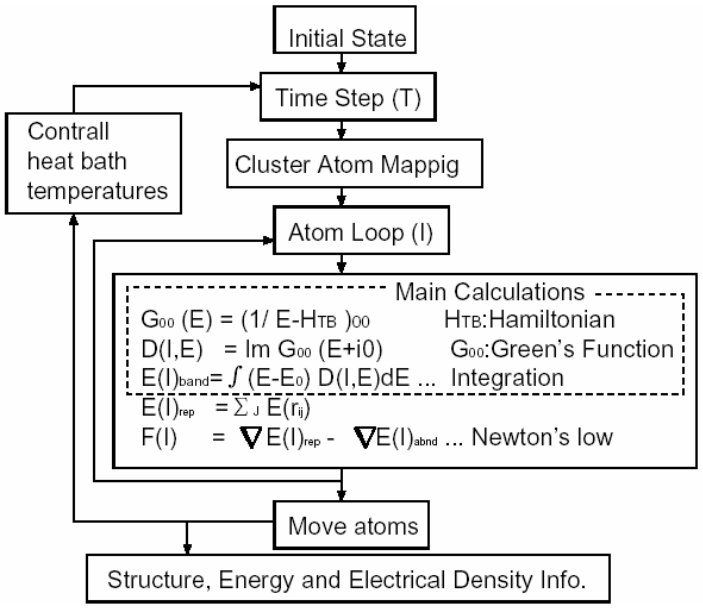

Figure.1 Flow chart of CRTMD

(2) Matrix element

The tigth-binding Hamiltonian and overlap matrix are calculated by using Slater-Koster method for four orbital sates (s, p_x, p_y, p_z)[2]. Matrix elements coupling atoms can be expressed by a 4×4 matrix. Therefore, the total Hamiltonian forms the $4N\times4*N$ matrix where N is the number of cluster atoms not total atoms.

(3)Green's Function

In the process of calculating a band energy, it is necessary to get local density of state, D(I,E). The D(I,E) is given by the imaginary part of Green's function matrix G(E):

$$G_{00}(E)=\left(\frac{1}{E-H_{TB}}\right)_{00}=\begin{pmatrix} E-a_0 & b_1 & 0 \\ b_1 & E-a_1 & b_2 \\ 0 & b_2 & E-a_2 \end{pmatrix}^{-1}_{00}=\frac{1}{E-a_0-\frac{b_1^2}{E-a_1-\frac{b_2^2}{}}},$$

,,,(1)

where the matrix is tridiagonalized elements and recursion technique is appled. Since almost all physical information is given by the lower order of electrical density of states in first and second order. Thus it is sufficient to get the recursion coefficients, a_n and b_n, from n=0 up to n=3 in eq.

(1). The concept of cluster and recursion technique make computational load of TB method fall off.

(4) Integration

The electrical states are derived from the Green's function in Eq.1. The Fermi energy is determined by the occupied maximum energy. The total band energy in system is given by the integration over the occupied energies from zero point to the Fermi energy as

$$E_{i,band} = \int_{-\infty}^{E_f} (E - E_{0,i}) D_i(E) dE \quad \ldots(2)$$

2.2 Parallelization

The development to parallelization of CRTMD Code was, firstly, carried out on the SR2201 and SR8000 at Information Technology Center (ITC), the University of Tokyo.

The particle decomposition method is suitable for the parallelization of the tight binding code based on atomic picture. The atomic loop calculating energy and force on each atom has been parallelised by MPI. By use of mpi_allgather, only the force data obtained each processor are transmitted among all processors. After communication all atomic positions and velocities are calculated from previous data and new force data not communicated with other processors. At the aim of the high parallel performance to 1000 processors, it is necessary to reduce the amount of and the number of transmission to the limit.

2.3 Vectorization

The main targets for vectorization are as follows,

* Tridiagonalization of the Hamiltonian matrix
* Integration of band energy

(1) Tridiagonalized Hamiltonian

The tridiagonalization procedure could be vectorized after simple subroutine expansion in the outer loop. But, we could not get a good performance since that the loop has the inner product calculation having short vector. Therefore, we adopted no inner product and continuous memory access coding. Furthermore, We carried out the improvement of the ratio of floating-operation and load/store-operation. A method which was explained here was applied to other loops in tridiagonalization processes of the Hamiltonian calculation.

(2) Band Energy by Integration

Loop structure of integration process includes 7 piled DO and GO TO loop (judgment of convergence) structure as shown in left side of Fig.2. This loop structure is coded in subroutine(function)-call structure with four hierarchy. The loop in the direction of xyz is most outside and the loop of cluster is in the inner side. Inside the loop of cluster atoms, DO LOOP and GOTO LOOP exist to judge the convergence. Furthermore, the loop of Gauss integration is inside. In the convergence (judging) loop, there are the loop of orbital (=4) and the loop of recursive method. Among these loops, unified three loops, these are the directions, cluster atoms, and Gauss integration have sufficient loop length and no independency. However, since four loops including GO TO loop remain in these loops, vector process cannot be performed. Then, the programs were largely changed as follows. The arranged loop is shown in the right side of Fig. 2. The recursive method loop in the most inner side was expanded to the higher rank loop. Next, the loop of convergence part is moved out of the vectorized loop. Finally, the loop of the Gauss integration, the cluster particle and the directions were unified, and it is considered as the vectorization loop.

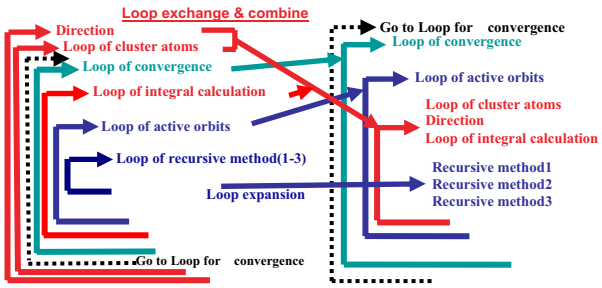

Figure.2 Loop Structure of before and after Optimization

2.5 Execution Profile before optimization.

The profile of non-optimized code is shown in Table 1. Simulation is tested on 6 time steps for 5000 atoms using 64 processors on Earth Simulator. Total speed was 305Mflops.

Table.1 Execution Profile on the Earth Simulator

	Execution time	Flop count	speed
Calculation Process	%	%	Mflops
(1) Cluster mapping	1.3	0.0	10.0
(2) Hamiltonian Calculation	1.0	0.1	37.5
(3) Green's Function			
Tridiagonalize of Hamiltonian elements	62.6	77.9	380.0
Green' Function	0.8	0.0	41.2
(4) Band energy by integration	31.0	22.0	216.5
(5) etc	3.3	0.0	
Total	100.0	100.0	305.5

2.6 Evaluation of a vector performance after optimization

The result of vectorization is shown in Table2. Each calculation process is improved in its speed and total performance. The final performance is 2.4Gflopses that is 30 % of vector performance in comparison with the peak performance of 8Gflops with one proccessor of the Earth Simulator. Since these processes were not vectorized completely for Green's function calculation, scalar tuning was also performed. Execution was faster by 12.4 times than that of original code while operation speed was increased by 7.7 times than original one.

Table 2 Execution Profile of after Optimization on the Earth Simulator

	Original		After vectorization	
	Elaps time	Operation speed	Elaps time	Operation speed
Calculation Process	sec	Mflops	sec	Mflops
(1)Tridiagonalizeof Hamiltonian elements	913.0	380.0	56.7	3237.0
(2)Band energy by integration	452.8	216.5	41.3	2268.5
(3)Cluster mapping	19.4	10.0	0.1	1242.3
(4)Hamiltonian Calculation	14.0	37.5	0.9	1135.2
(5)Green' Function	12.4	41.2	4.2	128.7
Etc	47.6		14.6	
Total	1459.2	305.3	117.8	2357.8

2.7 Vector and Parallel performance

The fig.3 shows the sustained performance for the nanotube simulation with 20000 and 48600 atoms up to 500 steps In the figure, it is clear that the performance using 435node (3480processors) reached 5.3 and 7.1Tflopses for 20000 and 48600 atoms, respectively. If the execution time is described T_n for n processors andT_m for m processors, then the parallelization rate can be expressed by the next formula [6],

$$a=(T_n-T_m)/\{(m-1)\times T_n/m - (n-1)\times T_m/n\}$$

With this formula, the paralellization of the CRTMD indicated 99.968% and 99.990% for 20000 and 48600 atom systems, respectively.

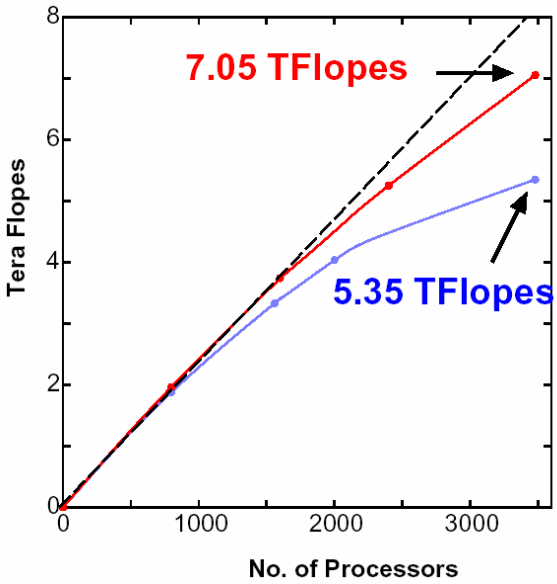

Figure.3 A sustained performance for the nanotube simulation with 48600 atoms

3. PHYSICAL STUDIES ON NANOMATERIALS

3.1 Thermal Conductivity of CNT [7]

The stiff sp^3 bonds between carbon atoms make diamond one of the best thermal conductors. The thermal conductivity of diamond, 3320[W/m. K], is eight times larger than that of cupper. An unusually high thermal conductivity should also be expected in carbon nanotubes, which are bonded by stronger sp_2 bonds.

The thermal conductivity is defined by Fourier's law:

$$J_x = -\kappa \frac{dT}{dx},$$

where x is the position along CNT, T the temperature, J_x the thermal flux.

In case of CNT, only phonon scattering contributes to the thermal conductivity. It is assumed that the mean free path of a phonon

between collisions is more than 100nm.To detect the phonon scattering, we have to treat with long length CNTs composing of more than 10^4 atoms.

Temperatures along CNT are defined by the average of kinetic energy of atoms in the unit cell. The number of atoms in unit cell is only 40 for (10,10)CNT. Thus a large number of iterations are required in order to average temperature to compensate the unavoidable large fluctuation. Our simulation is up to 10^4 time steps

The large-scale in space and time is essentially important for precise simulations.

The thermal conductivity of CNT in our simulations is strongly dependent on length of CNT and is diverging with the power-law characteristic. This behavior is similar to the model calculation of thermal conductivity in one dimension.

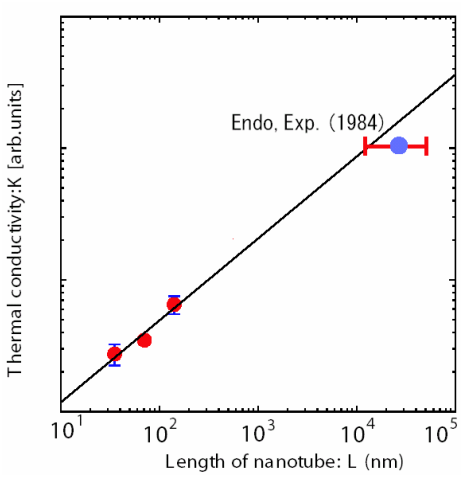

Figure.4 Thermal conductivity of CNTs.

3.2 Stability of Super-diamond

We simulated the stability of super-diamond structure which is formed from the carbon nanotube connecting between the diamond structure lattices. Because of the high structural stability of sp^2 bonding, the diamond-structure is very hard. We performed a detailed dynamics study up to melting and evaporation temperature.

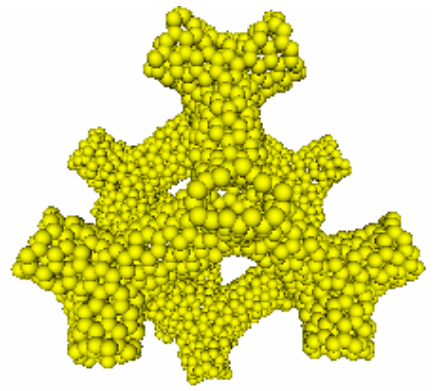

Figure.5 Diamond-Structure in 3000k

Simulations are carried out after initial velocities of atoms have been randomized following Maxwell distribution. The temperature is increased from 1000k to 4000K with steps of T=1000K. Super-diamond keeps the stability of structure up to 3000 K. This structure looks like very hard material.

3.3 Peapod stability during fullerene action

We have performed TB molecular dynamic simulations to investigate stability of the fullerenes encapsulated inside the carbon nanotubes, the so-called 'carbon nano-peapods'. In the initial state, the nanotube has a defect in the wall and ends of tubes are opened. Nine fullerenes are inserted with same intervals in the nanotube of 12 nm. Simulation results show that encapsulation of fullerenes is stable even if the wall and cap have substantial defect and opening. We suggest this stable encapsulation to be utilized as a nanoscale reactor.

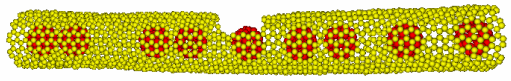

Figure6 Peapod structure after 15ps

3.4 Mechanical properties of CNT

As for stiffness of carbon nanotube, it has been suggested that the tensile strength of carbon

nanotubes might exceed that of other known fibers because of the inherent strength of the carbon-carbon bond. Nanotubes have beneficial consequences for their application in composite bulk materials and individual elements for nanometer-scale devices and chip of sensors.

The mechanical properties of nanotubes are predicted to be sensitive to details of their structure. Therefore it is essential to understanding on individual nanotubes properties.

By use of conventional computational power and techniques, Young's modulus and deformations like an undulation under low pressures of carbon nanotubes have already been carried out with a small number of atoms. But one did not understand the dependence of length of nanotube on undulation process yet.

We investigated the undulation process of long nanotubes under axial pressures by help of a large scale tight binding simulation. For example, the number of atoms for the (10,10) nanotube is 2200. This size is ten times as large as conventional calculations. Undulating structure obtained from our simulations are very different from the previous one [7].

Furthermore we extended to more complicated structure materials like a double wall nanotube and peapod with different chiral vectors.

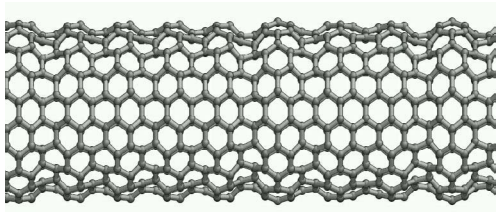

Figure7 Structure of nanotube by 92 % compression

3.5 Structure of fullerenes inside CNT

Carbon fullerenes, such as C60, are molecules with a large range of interesting properties. Our previous simulations on thermal stability in carbon materials indicate that C60 melts at about 3500 k, while some nanotubes are still stable at the temperature. Our question raised here is about "peapod", which has a structure of one-dimensional array of C60 inside a nanotube. How fullerenes of "peapod" are changed here to a new phase? Experimental observations tell us that at high temperature fullerenes inside a nanotube connect each other forming an inner nanotube. Thus peapod turns out to be double-wall nanotube. The result indicates a potential of creating new materials by packing more complicated carbon materials, yet, the detailed mechanisms on the phenomenon is not clarified yet. This phenomenon will be deeply affected by the condition of the system temperature and pressures of inter-fullerenes. The structure simulation of fullerenes inside a nanotube is performed up to 4ps with 80,000 time steps. Figure8 depicts initial condition and Figure9 after 4ps. Growth to spread carbon net can be seen in the figure.

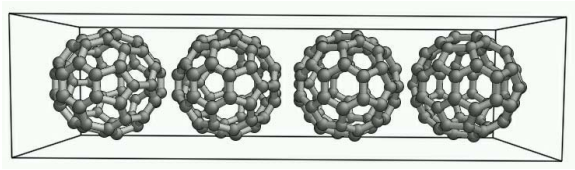

Figure.8 Initial condition of fullerenes inside a nanotube.

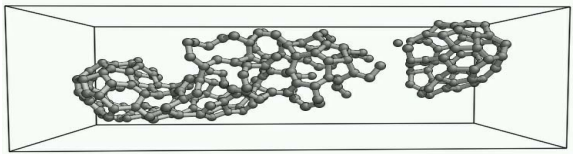

Figure.9 Structure of fullerenes inside a nanotube after 4ps at 3500k.

3.6 Searching for superhard carbon structure [8]

The sp^2-bonded carbon structures with a negative Gaussian curvature, so called Schwarzites, have been suggested by several authors. While positively curved structures, fullerenes or the cap of nanotubes, have been intensively studied

focusing on the various electronic behaviors, the negatively curved structures have been limited to preliminary suggestions because of difficulties in synthesizing process. However, a few recent progresses in making a kind of random Schwarzite revive interests in that structure as a new carbon-based novel material. Whereas the positive curvature eventually leads to the closure of the surface and consequently to the isolated fullerene molecule, the Schwarzites form a three-dimensional covalent solid and have been suspected to have an enhanced mechanical properties: lightness and hardness.

Focusing on the hardness, we performed first-principles calculations on the three-dimensional carbon Schwarzites of 668D and 668P. Although the synthesized samples so far are nanoclusters rather than a crystalline sold, our theoretical works on the perfect Schwarzite could be a reference for a further experimental study. Our calculation results show that most Schwarzites are very strong and their bulk modulus are about 25 % of bulk diamond. Noting that they have a small band gap of 0.5 eV and higher structural stability, an application in the electronic devices is also suggested.

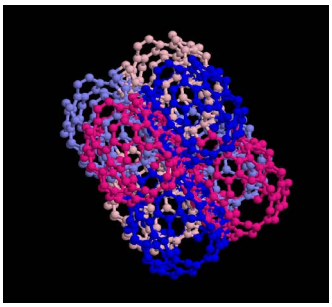

Figure.10 Super Jungle Gym Structure

3.7 Purification of CNT for Electronic Circuits [9]

Design of purification method of carbon nanotubes are used for electronic circuits. Aim of the present simulations is cleaning of oxidized nanotubes without aid of thermal processing, which is unreliable for nano-scale materials. In case of oxidized nanotube, thermal extraction of oxygen (O) is atoms always accompanied by carbon extraction which gives more damage on nanotubes. Methods of cleaning process proposed here is optical excitation and subsequent ultra-fast chemical dynamics, which can locally break C-O bonds and extract O atoms from carbon nanotubes. Simulation technique is the time-dependent density functional approach combined with the molecular dynamics, which enables us to stably follow the dynamics under electronic excitations. Spontaneous oxygen ejection from nanotube by resonant Auger process initiated by O-1s core-excitation was monitored by the present simulations. Furthermore, de-activation of ejected O atoms is found to be possible by introduction of H_2 molecules. The application of photo-chemical reaction can be alternative tool to thermal process especially nano-scaled materials.

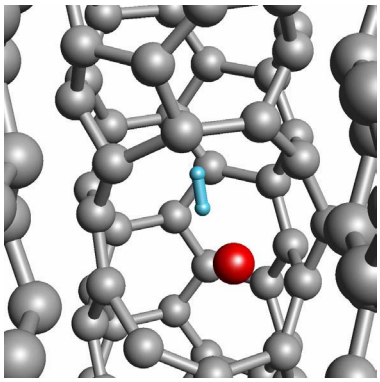

Figure.11 Cleaning process for CNT. Optical excitation locally breaks C-O bonds and extract O atoms from carbon nanotubes. Red sphere and bleu spheres show H molecules and O atom, respectively.

4. SUMARY

We developed large scale quantum molecular code to challenge the more realistic material design. The optimized CRTMD code on parallel and vector architecture could give an exceptional performance and enables more large-scale realistic simulations on the nano-scale phenomena.

In this study, methods to solve the unique problem arising from the system of more than tens of thousands of atoms are described by help of highly parallel and vector algorism. As a result, 7.1 TeraFlops in total performance was obtained by using 3480 earth simulator processors. This achievement brings us various physical material properties e.g., thermal conductivity, mechanical properties. The optimized codes showed that the computation on Earth Simulator could give an exceptional performance and enables more large-scale realistic simulations.

5. ACKNOWLEDGEMENTS

This project was funded by Japan Science and Technology Corporation (JST). The work was carried out as one of activities of the CNT (Carbon Nanotube Simulation) Group. The computations were performed on the Earth Simulator at the Earth Simulator Center. The authors wish to acknowledge Prof. Morinobu Endo at Shinshu university, Prof. Eiji Osawa, Prof. Hisanori Shinohara at Nagoya university for their continuous support and advice. The authors also would like to thank the CNT members for their valuable contributions.

REFERENCES

[1] W. Zhong, D. Tomanek and George F. Bertsch, Solid State Comm. {f 86}, 607,(1954).
[2] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498, (1954).
[3] R. Haydock, Solid State Physics.**35**, 215, (1980).
[4] M. J. Kelly, Solid State Physics. **35**, 295, (1980).
[5] S. Baroni and P. Giannozzi, Europhys. Lett. **17**, 547, (1992).
[6]http://www.es.jamstec.go.jp/esc/eng/index.html
[7] S.Tejima *et al.* ,Massively Parallel Simulation on Large-Scale Carbon Nanotubes, NANOTECH 2003, February, 2003, San Francisco, CA.
[8] N.Park *et al.*, Diamondoids as functional building blocks for nanotechnology, APS, G27.010, March, 2003, Austin, TX.
[9] Y.Miyamoto *et al.*, Photo-induced cleaning of oxidized carbon nanotubes, APS, B27.004, March, 2003, Austin, TX