Massively Parallel Simulation on Large-Scale Carbon Nanotubes

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ABSTRACT

Carbon nanotubes and fullerene have a lot of applicability for industries as nanote technology. In order to extend its applicability, the computational simulation would be powerful and effective tools for finding and creating new materials and novel functions of nano-compex systems. Thus, a large-scale simulation has been carried out by ab initio molecular dynamics model and massively parallel computers. Along the recursion technique in the one-electron Green' function of tight-binding Hamiltonian, the parallelized and vectorized software has developed with high-speed processing and fine resolution. The program has a couple of parallel procedures; one is the electronic structure at each atom, which are calculated independently on individual processors. The other is the mapping of inter atomic distance to find the interacting atoms within cut-off radius. The simulations were conducted by using scalar parallel and pseudo-vector type computers, SR8000 (HITACHI). The parallel simulation for the peapod finished within 3 hours through only 128 CPUs, comparing with conventional ones taking 4 months through 1 CPU.

As further advancements, the thermal conductivity on carbon nanotube and the joint stabilities of super-diamond structure from carbon nanotubes have been in progress by using the world fastest and powerful massively parallel and vector super-computer, the Earth Simulator.

Keywords: Massively Parallel Simulation, Carbonb Nanotube.

1. INTRODUCTION

Carbon materials will make a new stage in the technology. A lot of applicability using nanotubes and fullerene as electronic field emission, hydrogen storage, carbon-junction etc. appear. To make effective use of these technologies into real product, we need the design on the computation. A modern large-scale simulation can be directly applied to atomic phenomenon with the 10^4 particles. The super-computer enables us to carry out large-scale simulations.

We have developed *ab initio* molecular dynamics code for massively parallel and vector computer. The code is suitable for the very large systems even though lack of symmetrical arrangement. The code we have developed so far produces a high performance on Earth Simulator. We are carrying out three subjects as the first investigation, namely the thermal conductivity of carbon nanotube, formation process of peapod, and stability of super-diamond structure at high temperatures. Our purpose is to give the clear explanation of properties and phenomena of nano-scale events and deduce guiding principle to design new materials from nano-structures using super-computers.

2. METHOD

The molecular-dynamics (MD) simulation is suitable for studying individual microstructure elements among some conditions. A band structure is based on the eigenvalues of the Kohn-Sham operator, expressed in a local basis, which we map onto a linear combination of atomic orbitals (LCAO) Hamiltonian,

$$H = \sum_{i,\alpha} \varepsilon_{i,\alpha} c_{i\alpha}^{\dagger} c_{i\alpha} + \sum_{i,j,\alpha,\beta} \varepsilon_{i\alpha,j\beta} c_{i\alpha}^{\dagger} c_{j\beta} + h.c. \qquad (1)$$

We have used a simple two-center Slater-Koster parametrization for our four state (s, p_x, p_y, p_z) nearest-neighbor tight-binding Hamiltonian [1]. The parameters have been obtained from a global fit to Local Density Approximation calculations for the electronic structure of C_2, a graphite layer and bulk diamond for different nearest-neighbor distances.

Our approach is based on the recursion method (RM) to calculate the electronic local density of states (DOS) and energies from selected elements of the one-electron Green's function [2-4]. The RM eliminates the computational consuming load time for conventional diagonalization techniques to determine local DOS. They allow us to calculate the electron density with a workload which scales linearly with N not be proportional to N^3.

In matrix notation, the tridiagonalized Hamiltonian describing the local cluster centered at site i=0 is given by

$$U^{\dagger} H U = H_{TB} = \begin{pmatrix} a_0 & b_1 & 0 & \cdots \\ b_1 & a_1 & b_2 & \cdots \\ 0 & b_2 & a_2 & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}. \qquad (2)$$

The single Green's function at site i=0 is following:

$$G_{00}(E) = (\frac{1}{E-H_{\mathrm{TB}}})_0 = \begin{pmatrix} E-a_0 & b_1 & 0 & \cdots \\ b_1 & E-a_1 & b_2 & \cdots \\ 0 & b_2 & E-a_2 & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}^{-1}_{00} \quad (3)$$

$$= \cfrac{1}{E-a_0-\cfrac{b_1^2}{E-a_1-\cfrac{b_2^2}{\ddots}}}.$$

Using Green's function, we derive the local density of states at site i=0 as

$$D_i(E) = -\lim_{\delta\to 0}\frac{1}{\pi}\,\mathrm{Im}\,G_{00}(E+i\delta). \quad (4)$$

Band energy is

$$E_{i,band} = \int_{-\infty}^{E_F} (\mathrm{E}\text{-}\mathrm{E}_{0,\mathrm{i}})\mathrm{D}_{\mathrm{i}}(E)dE \quad (5)$$

where Fermi energy is determined by

$$N_i = \int_{-\infty}^{E_F} \mathrm{D}_{\mathrm{i}}(E)dE \quad (6)$$

Here, N_i is the number of electrons. Finally, the force can be obtained by taking a negative gradient of the total energy with respect to each atomic position,

$$\vec{F}(r) = -\sum_i (\nabla E_{i,rep} + \nabla E_{i,band}). \quad (7)$$

The algorism to decide the forces on each atom is highly suitable for parallel computing, as the charge density can be calculated independently at each point of grid [5]. This implementation makes the strong advantage of performing molecular dynamics calculations on massively parallel computers.

3. SIMULATION RESULTS

We try to compute some properties and phenomenon using Carbon-Recursion-Technique-Molecular-Dynamics (CRTMD) code and to develop the modified code for the vector and parallel version.

3.1 Simulation of peapod formation process.

We investigate the encapsulation process for nano-peapod [6]. Our simulations show that the absorption of fullerene through the defect on the nanotube wall could be suitable way and the fulluren stays stably for a long time within nanotube.

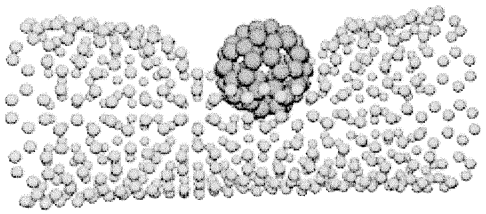

Fig.1. Peapod structure

3.2 Simulation of Stability of Super-diamond

We simulated the stability of super-diamond structure which is formed from the carbon nanotube connections between the tops of the diamond structure. Because of the high structural stability of sp^2 bonding, the diamond-structure is very hard [7]. We performed a detailed dynamics study up to melting and evaporation temperature. A simulation begins for 10000 time steps at a temperature 1000 K, after the directions of the initial atomic velocities have been randomized following Maxwell distribution. The temperature is increased from 1000k to final temperature 4000K with steps of Δ T=1000K, and make the carbon equilibrate for 10000 time steps at each new temperature. Super-diamond keeps the stability of structure up to 3000 K. We are computing the standard index of the stiffness as Yang's modulus, Poisson's ratio, and bulk modulus.

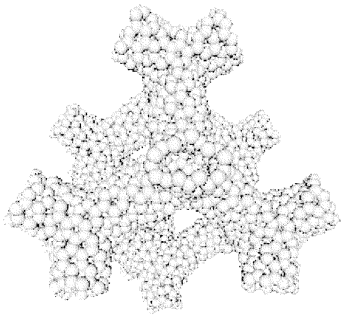

Fig.2. Diamond-Structure in 3000k

3.3 Simulation of Thermal Conductivity

The stiff sp^3 bonds, resulting in a high speed of sound, 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 held together by even stronger sp_2 bonds.

We use the standard definition of the head transport coefficients that calculate directly in our simulation box [8-11]. We carried out two types of thermal conductivity simulations. The artificial "hot" and "cold " layer are introduced within the system. In one case, temperature of the

particles inside the artificial regions is fixed and, in the other case a heat flux fixed. After all, thermal flux on nanotube creates a temperature gradient. Once the steady state reaches we can determine the thermal conductivity from Fourier's law:

$$J_x = -\kappa \frac{dT}{dx}. \qquad (8)$$

In Fig.3 we show schematic representation for direct thermal conductivity simulation with the periodic condition. Figure 4 shows the temperature distribution on Carbon nanotube. The thermal conductivity for carbon nanotube in the simulation is higher than that of cupper. Very large temperature gradients with significant nonlinear response exist at nearly "hot" and a "cold " layers. The mean free path is limited by the size of the system. If a sample were shorter than the length of mean free path, phonons could get no scattering except the edges. In that case we could not get correct thermal conductivity by phonon scattering in bulk materials. Thus to measure precise thermal conductivity, we need enough length nanotube. Also a large number of iterations are required in order to average temperature to compensate the unavoidable large fluctuation. In our simulation the number of atoms is more than 10^4, then the tube is more length of 100 nm. The large-scale simulation is essentially important of precise simulation.

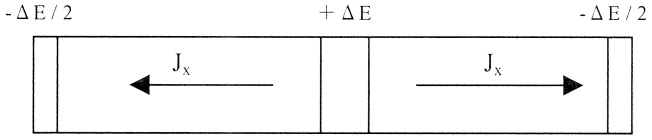

Fig.3. Schmatic representation for direct thermal conductivity simulation with the periodic condition.

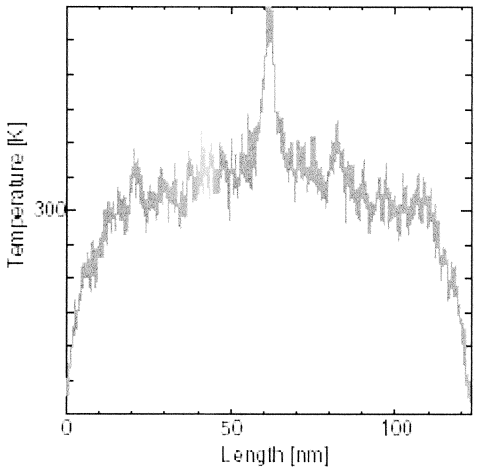

Fig. 4. Temperature distribution on carbon nanotube with 123 nm. Data are repeatedly written in the figure in 10^4 MD steps.

4. PERFORMANCE OPTIMIZATION

4.1 Outline of the Earth Simulator

The Earth Simulator aiming at more accurate prediction of climate changes, global warming and abnormal weather, etc. was launched by the Ministry of Science and Technology (present the Ministry of Education, Science and Technology) in 1997 fiscal year. The ultra high-speed parallel computing system, Earth Simulator (ES) realized the fastest computing speed in the world. Each supercomputer (1 node) contains eight vector processors with a peak performance of 8Giga flops and a memory of 16 Giga bytes. The total number of processors is 5120, and its peak performance reaches to approximately 40 Tera flops, boasting of powerful memory of 10 Tera bytes.

4.2 Strategy of Performance Optimization

ES is a parallel super computer mounted with vector processors that provide high-sustained performance. The parallelization of CRTMD Code was, firstly, executed using SR8000 at Information Technology Center (ITC), the University of Tokyo, and the test results of parallel performance were promising ones. Next, the optimization performance was tested to access its efficiency to the vector processors using ES.

4.2.1 Parallelization

(1) Parallelization of Particle Code

As for the CRTMD code, the principle calculation part is coded to the particle loop. The particle loop was parallelized in order to realize completely independent calculations in each particle.

(2) Parallelization of Adjacent Particle Mapping

In the CRTMD code, each particle has interaction with the particle (the first cluster) in the cutoff radius around the particle. Furthermore, each particle has interaction with the particle (the 2nd cluster) in the cutoff radius around the first cluster. For adjacent particle mapping, the process of the first cluster is parallelized by dividing particles.

Next, the first cluster's adjacent particle mapped on each processor is transferred so that all the processors can access. Then, the 2nd cluster's adjacent particle mapping proceeds. However, the load of the adjacent particle mapping stands out in this method when executing high in parallel. Therefore, we first made the 0th atoms cluster being included in twice the cutoff radius, and made the search space of the request atom be reduced. Next, we made the first and 2nd atoms cluster on each processor by using reduced search space. To use this method, we can reduce transferring time of adjacent particle mapping, and obtain

good parallel efficiency.

4.2.2 Vectorization

(1) Coefficient Matrix Making Part by Recursive Method

The main calculation of this part is Matrix and Vector operation for Matrix and Vector having element number amount of cluster particles as Matrix Vector product and dot product. In this part, a high vector performance was realized by reducing thoroughly data-load-latency in coding.

(2) Integration Calculation Part

This part has a complex coding composed of the call of the subroutine and the function of six hierarchies with the DO Loop and the GOTO Loop structure of eight piles. A thorough change in the program structure and the loop structure was done, and innermost loop was vectorized in vector lengths as three times of the number of cluster atoms. A high vector performance is obtained because of the changes in such coding.

4.3 Performance

The performance measured by the heat conduction calculation, 20000 particles and 10000 steps is shown below. The 5.47 Tera flops is obtained by finally using 435 node (3480 PE) of ES. This performance achieves 19.6 % of the peak for each 435 node performance of ES. The calculation of 20000 particles and 10000 steps is the amount of flop count 35.6 Peta flop as a whole, and when 435nodes are used, is executable in 1.8 hours.

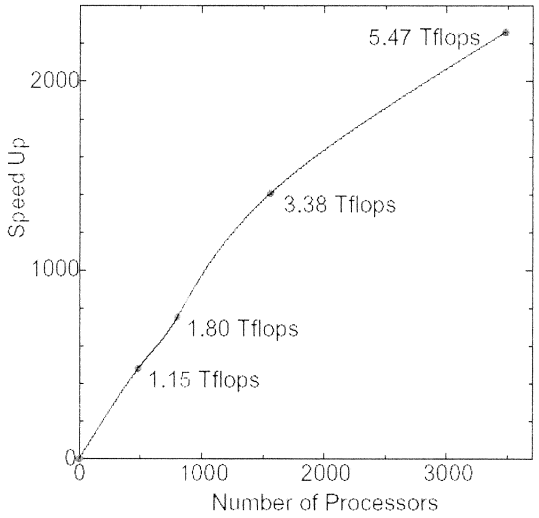

Fig. 5. Speed Up on Earth Simulator

5. SUMMARY

The large-scale simulations have been carried by *ab initio* molecular dynamics model with modified CRTMD code. Code on SR8000 and Earth Simulator show a very high performance and enable more real-scale simulations. These result shows that even particle code like MD is available even for the vector machine.

In the direct thermal conductivity simulation, the large temperature fluctuation on tube could be eliminated by so many time-average. The 10^6 time steps corresponding to 1 ns is long enough simulation time. The volume of calculations is very huge for even ES. We have to make effort forwards achieving real-scale simulations on new algorism and super-computers.

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