Large Scale Nanocarbon Simulations

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ABSTRACT

The mechanical response of carbon nanotubes to revere deformation has attracted much attention since their discovery in 1991. Carbon nanotubes have already demonstrated exceptional mechanical properties: their excellent flexibility during bending have been observed experimentally. Nanotubes combine high stiffness with elasticity and the ability to buckle and collapse in a reversible manner even largely axially compressed or twisted deformation. For these reasons, it has been suggested that carbon nanotubes could be promising candidates for a new generation of extremely light and super strong fiver. However, experiments probing the strength of nanotubes are very challenging, but to the difficulties in growing high quality, defect-free nanotubes of sufficient length and in measuring the strength of nanoscale objects. Theoretically, investigating the strength of carbon nanotubes requires modeling of inherently mesoscopic phenomena, such as plasticity and fracture on a microscopic compose of several thousands of atoms. The first principle methods based on the wave function of electrons are limited in the atomic structure of several hundreds atoms, but a large scale tight-binding simulation based on quantum orbit presents challenging up to tens of thousands of atoms. Our large scale simulation using Earth Simulator enables ourselves to reach this target. In simulations, elastic and buckling properties of nanotubes in difference radius and chirality are investigated on. When the change in length is small fracture under the compression, resisted load is proportional to compressed length. Above the first critical load, carbon nanotube occurs symmetrical buckling with keeping the elastic property. Above the second critical higher than first one, carbon nanotube dose asymmetrical buckling and into a fracture. The dependence of buckling point on length, radius and chirality of nanotubes will discuss in detail.

Keywords: large scale simulation, carbonnanotube, mechanical properties

1 INTRODUCTION

Carbon nanotubes and fullerenes have been expected to make a breakthrough in the new material development of nano-technology. Their remarkable properties such as great strength, light weight, special electronic structures, and high stability make carbon nanotubes the ideal material for a wide range of applications. A considerable number of potential applications have been reported about semiconductors-device, electronic field emitter, nano-diamond, battery, super strong threads and fibers, and so on.

Microscopic experiments are quite limited by hardness of measurements in nano space and by high experimental cost for the advanced microscope as scanning probe microscope (SPM). Material simulation based on quantum mechanics has turned out to be a very efficient methodology. The quantum model systems interests at microscopic level and are completely governed by a microscopic interaction between atoms. Therefore, the quantum simulation has the unique advantage in predicting nano scale properties, which are difficult to perform experiments.

The trials for so many simulations with any conditions give us valuable information on material properties and on design ways. However, to simulate the nano-scale phenomena on realistic time and space we need 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 (TB) method. A recent higher performance computing provides a large-scale simulation of up to 10^4 atoms.

As for the high performance computational science, it is important to combine excellent physical ideas and optimizing program techniques on the simulation code. Thus, under the international collaboration in U.S.A. through Carbon Nanotube Simulation consortium, researchers, belong to different field launched the challenging large scale simulation for the nano-carbon materials using the Earth Simulator. In this project we developed and optimized a parallelized and vectorized CRTMD code for massively parallel and vector supercomputer, the Earth Simulator. Furthermore, by using the CRTMD code, we report some example in the applicability to the material science and design.

The CRTMD code, we have developed is shown to be suitable for the very large systems even though the lack of symmetrical arrangement. Our purpose is to give the clear

explanation of properties and phenomena of nano-scale events and we deduce guiding principle to design new materials from nano-structures using super-computers.

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.

This challenging collaboration has contributed for accelerating the investigation of the fundamental phenomena of nano-scale science and technology.
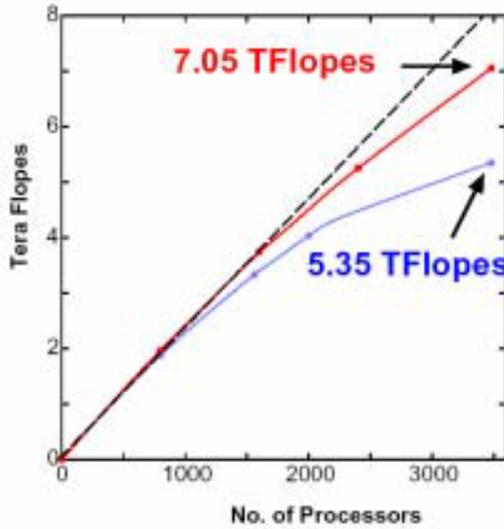

Figure.1　A sustained performance for the nanotube simulation with 48600 atoms

2　THEORY

A large scale molecular-dynamics simulation is suitable for studying micro-level physical properties at some conditions for temperature and pressures. Though the energy band structure can in principle be determined using ab *initio* techniques, we prefer a tigth-binding parametrization for its computational efficiency. Calculations based on the tight-binding formalism are much easier to perform than analogous ab *initio* calculations especially when describing large units cells and low symmetry situations. The tigth-binding Hamiltonian is described using 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. 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 . 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. This computational requirement is not acceptable when studying the dynamics of very large structure.

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

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

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

$$G_{00}(E) = (\frac{1}{E - H_{TB}})_{00} = \begin{pmatrix} E-a_0 & b_1 & 0 & \cdots \\ b_1 & E-a_1 & b_2 & \cdots \\ 0 & b_2 & E-a_2 & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix}_{00}^{-1} = \frac{1}{E-a_0 - \cfrac{b_1^2}{E-a_1 - \cfrac{b_2^2}{\ddots}}}, \qquad (3)$$

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

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

Band energy is

$$E_{i,band} = \int_{-\infty}^{E_F} (E - E_{0,i}) D_i(E) dE \qquad (5)$$

where Fermi energy is determined by

$$N_i = \int_{-\infty}^{E_F} D_i(E) dE \qquad (6)$$

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,

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

The local repulsive energy functional $E_{i,rep}$ also depends on the local atomic density. 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. This implementation makes the strong advantage of performing molecular dynamics calculations on massively parallel computers.

3. MECANICAL PROPERTIES OF CNT

The mechanical response of carbon nanotubes to extreme deformation and strain has attracted much attention since their discovery in 1991. It has been suggested that the tensile strength of carbon nanotubes might exceed that of other known fibers because of the strong interaction of the carbon-carbon bond. And under largely axially compression CNTs show structural buckle and collapse retaining sp_2 carbon network without a fracture. In addition, there is the excellent flexibility during bending. For these reasons, CNTs could be promising candidates for bundled composite materials in fibers and for atomic-force microscope (AFM) tips using isolated CNT.

The mechanical properties of nanotubes are predicted to be sensitive to details of their structure and to the presence of defects. It means that understanding on individual nanotubes is essential to examine these properties.

However, experiments probing the strength of a nanotube are very challenging, but to the difficulties in growing high quality, defect-free nanotubes of sufficient length and in measuring the strength of nanoscale objects. Theoretically, investigating the strength of carbon nanotubes requires modeling of inherently mesoscopic phenomena, such as plasticity and fracture on a microscopic compose of several thousands of atoms. The first principle methods based on the wave function of electrons are limited in the atomic structure of several hundreds atoms. In case of Young's modulus of CNTs, they are derived from a small strain in length using tens of atoms in unit cell. But for large deformations like an undulation under high pressures, more than thousands of atoms are required to confirm spatial extended deformation character along long CNTs. A large scale tight-binding simulation based on quantum orbit presents challenging up to tens of thousands of atoms. Our large scale simulation using Earth Simulator enables ourselves to reach this target.

A lot of theoretical investigations have focused on electric band structure of carbon nanotubes with metallic or semiconductor and on basic mechanical properties such as Young's modulus. The reason why these simulations are developed is that a small calculation treating with only unit cell atoms is good enough to solve it.

One of the most importance of the mechanical property is the critical buckling load and strain for stretched and compressed CNTs. We investigated the undulation process and broken process of long nanotubes under axial pressures and stretches, respectively, 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 compressed structure obtained from our simulations are very different from the previous one. Initial linear elastic deformations are observed up to the critical strain 92% beyond which nonlinear responses set in. In the nonlinear response regime at symmetric deformed structures such as buckles have been observed in simulation. The next buckling in (10,10)CNT of strain of 91.5% presents asymmetric structure.

The strech of CNTs eventually reach fracture at 240 % in length from original one. Surprisingly, from the energy dependenc, mixing state with sp_2 hexagon and sp chain between 150 to 240% kept the properties elastic.
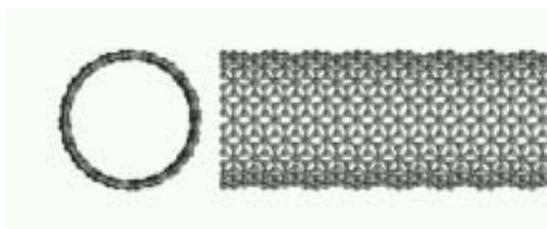

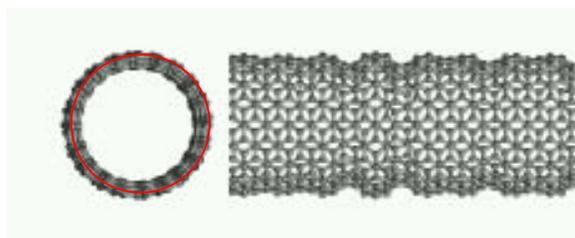Figure.2 Linear elastic deformations at the 92 % compressed CNT.

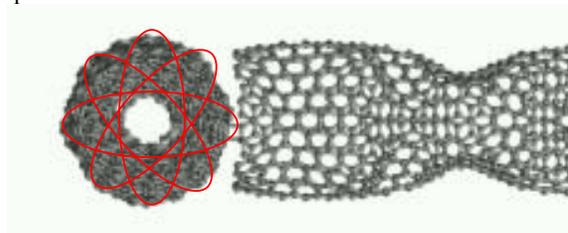Figure.3 An asymmetric structure at the 91.5% compressed CNT.

Figure.4 A fractured structure for the 90 % compressed CNT.

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