Large-Scale Simulation on the Properties of Carbon-Nanotube

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Carbon nanotubes (CNTs) and fullerenes have a lot of potential applications in nanotechnology. In the stream of efforts to exploit these nanoscale materials, the computational simulations have turned out to be powerful and efficient tools. Especially, as the recent trend in technology made it possible to manipulate further miniaturized structures, required simulations for emerging material become bigger and bigger. Aiming at realistic simulations for nanomaterials, we have developed a large-scale computation technique utilizing tight-binding (TB) molecular dynamic method, *ab-initio* density functional theory (DFT), and time-dependent DFT method. By an efficient optimization on ES, we get the performance of 7.04 Tera flops using 435 nodes for TB calculation for CNT thermal conductivity.

We have studied various physical properties of nano-carbon material e.g., the thermal conductivity of the single wall CNT, stability of super-diamond, synthetic diamond, stability of nanotube peapod with a defective wall, and designing of a purification of CNT. During these works, we have realized that the Earth Simulator is very powerful tool for large-scale material simulations.

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

1. INTRODUCTION

Carbon materials have been expected to make a breakthrough in material science and nanotechnology. A lot of potential applications of nanotubes and fullerenes e.g., electronic field emitter and electronic devices have attracted scientific community. In the investigation and utilizing their material properties, numerical simulation using supercomputer has turned out to be a very efficient tool. A recent development in nanotechnology has required a more efficient supercomputings capable of a large-scale simulation of up to 10^4 atoms.

Aiming large-scale simulations utilizing Earth Simulator, we have developed computational package based on *ab initio* DFT theory and parameterized TB method. The TB code we have developed is shown to be suitable for the very large systems even though the lack of symmetrical arrangement. We have carried out six subjects in this work, which are described in the next section. 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. PHYSICAL STUDIES ON NANOMATERIALS

2.1. Thermal Conductivity of CNT [1]

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 held together by even stronger sp^2 bonds.

Some molecular dynamics simulations showed very high thermal conductivity, however the estimated values of thermal conductivity were widely difference from one another. These results arise from the lack of atoms used in simulation.

We calculate the thermal conductivity in our simulation from head transport coefficients. The artificial "hot" and "cold" layer are introduced within the system and a heat flux of the particles inside the artificial regions is fixed. After all, thermal flux from hot to cold region on nanotube creates a temperature gradient because of phonon collisions. Once the steady state reaches we can determine the thermal

conductivity from Fourier's law:

$$J_x = -K\frac{dT}{dx}.$$

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 temperatures 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.

The thermal conductivity of CNT in our simulations in Fig.1 is strongly dependent on length of CNT and is diverging with the power-law characteristic. This behavior is similar to that of the model calculation of thermal conductivity in one dimension.

2.2. Stability of Super-diamond

We simulated the stability of super-diamond structure in Fig. 2 which is formed from the carbon nanotube connecting between the diamond structure lattice points. 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.

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 ΔT=1000K. Super-diamond keeps the stability of structure up to 3000 K. This structure looks like very hard material.

2.3. Charging effects on synthetic diamond [2,3]

Synthetic diamond has been considered to be an important material in designing electronic devices and in mechanical coating because of hardness, chemical stability, and high thermal conductivity. While the high pressure, condition which is believed to be realized during the detonation experiment, is so generally accepted as a sufficient condition for stabilizing the diamond phase over graphite, various diamond synthesis under low pressure conditions have cast doubts on the ingredients in the growth mechanism.

Although the presence of atomic hydrogen has been considered to be a crucial factor in the low pressure synthesis of diamond, the understanding on the exact role of them is rather ambiguous. Several recent studies reported the synthesis of diamond without the presence of atomic hydrogen, which revived the interests in the growth mechanism. Especially, the experimental results which showed the possibility that the diamond particles formed in the vapor phase are negatively charged, are now triggering the question about the charging effect on the nucleation stage. Also the bias-enhanced nucleation on the substrate leads to the same question.

Our calculation results show that a negative charge can stabilize the diamond surface from reconstruction into graphitic layer as the atomic hydrogen does shown in Fig. 3. Excess charge is mostly localized around the dangling

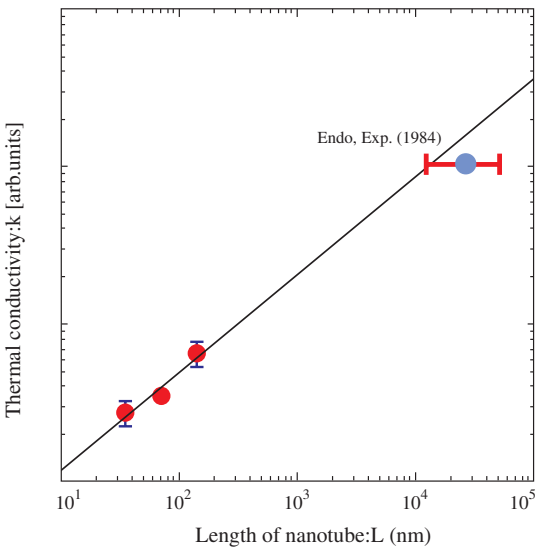

Fig. 1 Length dependence of thermal conductivity in CNT.

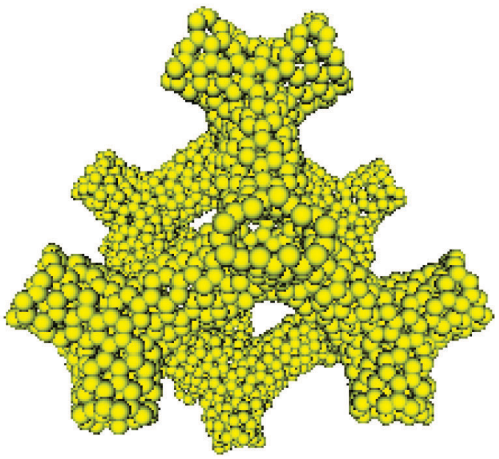

Fig. 2 Diamond-Structure at 3000k

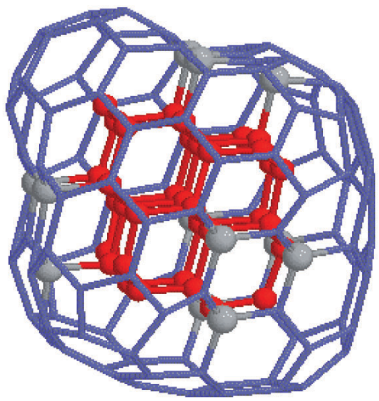

Fig. 3 Reconstruction of diamond nanoparticle into fullerene-like structure.

bonds. More over, the C-H bonding at the surface is substantially reduced by the presence of negative charge. These results are believed to be quite meaningful to rationalize the suggested hypothesis claiming the carbon particle is likely to be remained as a pure carbon structure under a negatively charging environment. In addition, this explains the reason why the diamond formation under the discharge condition is so independent of hydrogen partial pressure.

2.4. Purification of CNT for Electronic Circuits [4]

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 in Fig. 4. 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.

2.5. Peapod stability during fulleren action

We have performed TB molecular dynamic simulations to investigate stability of the fullerenes encapsulated inside the carbon nanotube, the so-called 'carbon nano-peapods' shown Fig. 5. In the initial state, the nanotube have 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 are stable even if the wall and cap have substantial defect and opening. We suggest this stable encapsulation to be utilized as a nanoscale reactor.

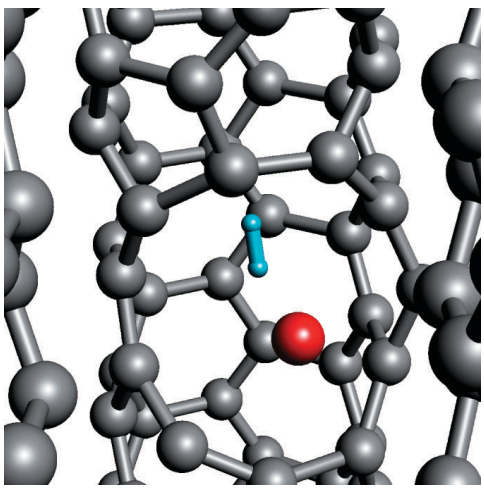

Fig. 4 Cleaning process for CNT. Optical excitation locally breaks C-O bonds and extract O atoms from carbon nanotubes. Red sphere and blue spheres show O atom and H_2 molecules, respectively.

2.6. Searching for superhard carbon structure [5]

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 in Fig. 6. 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.

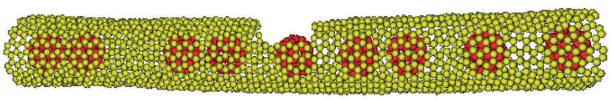

Fig. 5 Peapod structure after 15ps

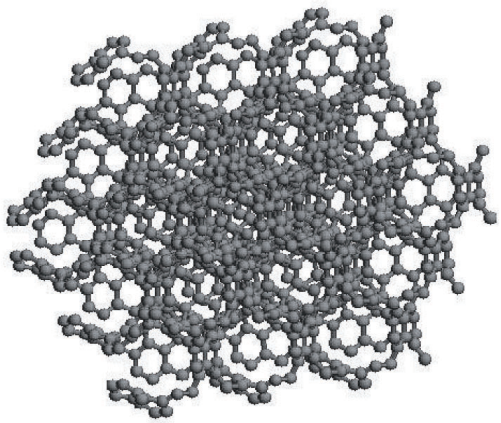

Fig. 6 Super Jungle Gym Structure

3. PERFORMANCE OPTIMIZATION

3.1. Strategy of Performance Optimization

The tuning to parallelization of CRTMD Code was, firstly, executed on SR8000 at Information Technology Center (ITC), the University of Tokyo tow years ago. The optimization performance to the vector processors was tested on the Earth Simulator.

3.1.1. Parallelization

(1) Parallelization by particle

As for the CRTMD code, the main calculation is composed of 'particle loop' part to compute the atomic energies and forces acting on atoms. The percentage of CPU time and flop count at this part are 94.6% and 99.6%, respectively. This part was parallelized completely because calculations can be accomplished on each particle independently.

(2) Parallelization of nearest atoms map

Each particle interacts with only adjacent particles in cutoff radius. To find the interacting atoms we have to compute inter atomic distances and make a map on distance information.

In the case of less than hundreds of processors in parallels, communication between processors for the map is smooth. But for more than thousands processors, the communications are the bottleneck. So we have adopted the method that it is not necessary to transfer atoms map by setting cutoff distance twice.

3.1.2. Vectorization

(1) Coefficient Matrix by Recursive Method

The main calculation of this part is matrix and vector operation as a 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 subroutine and function call of six hierarchies. In loop structure, this part are composed by eight piles's DO Loops and the GOTO Loops.

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 has been obtained because of the changes in such coding.

3.2 Performance

For the thermal conductivity simulation with 48000 particles and 10000 steps we accomplished high performance,

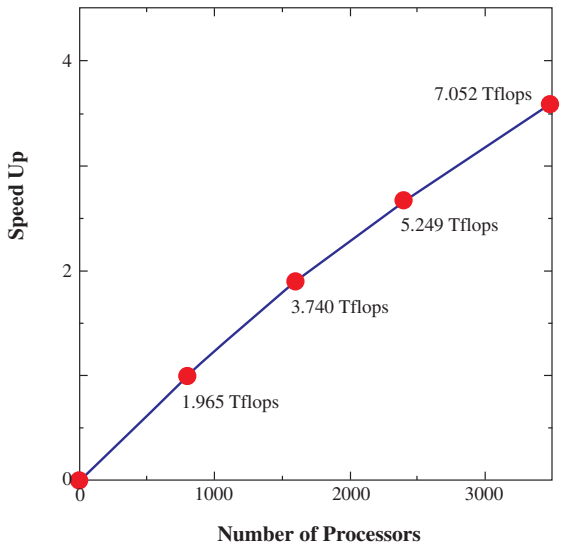

Fig. 7 Speed Up on Earth Simulator

7.05 Tera flops by use of 435 node (3480 PE) shown in Fig. 7. It is a 25.3% performance in the peak on each node. The amount of flop count 89 Peta flop as a whole, and when 435nodes are used, is executable in 3.5 hours.

4. SUMMARY

The large-scale simulations on nanomaterials have been carried by ab-initio density functional method and the parameterized tight-binding calculations. Various physical material properties e.g., thermal conductivity, mechanical hardness, charging effect on the stability have been studied. The optimized codes showed that the computation on Earth Simulator could give an exceptional performance and enables more large-scale realistic simulations.

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カーボンナノチューブの特性に関する大規模シミュレーション

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概要

1. 研究目的

優れた物性と予想されナノテクの基本材とされるカーボンナノチューブ(CNT)類の電子・機械特性を従来不可能だった大規模シミュレーションにより推定し、科学技術及び産業界に提供すると共に、応用として特性の優れた新構造を発見し、基本材の拡充に寄与する目的で実施された。

2. 成果

地球シミュレータを利用して世界最高速、最大規模の特性シミュレーションを実施し、ナノチューブの熱伝導率、ナノダイヤモンドなどの新物質創製、次世代回路応用性等を把握するとともに、大規模シミュレーションの有効性を世界に先駆けて実証した。具体的な成果を以下に示す。

(1)CRTMDコードの最適化：435nodeを使用し7.05Tflopsの性能を達成(435nodeのピーク性能の25.3%)。原子数4万の大規模計算では世界最高性能。(2)CNT熱伝導率推定：1本の単層CNT(300nm程度)の熱伝導率をCRTMDによる大規模シミュレーション(原子数4万：世界初の試み)を実施。ベキ乗の長さ依存性が見られる(継続中)。(3)ナノダイアモンド構造：ナノダイヤ(マッカイ構造)は硬度で自然ダイヤの40%、また質量で10%と硬くしかも軽い特性を示し、また比較的小さいバンドギャップ電位を有するなど強度、軽量、半導体性等、新材料としての特徴を持つことを第1原理計算より得た。またスーパーダイヤモンド構造の融点の解析を実施した(継続中)。(4)CNT応用：時間依存第1原理シミュレーションによりCNT欠陥等からの酸素原子脱離法が示された。本研究はカーボンナノチューブシミュレーション研究会として実施された。

キーワード：大規模シミュレーション、タイトバインディング理論、アブイニシオ理論、密度汎関数法、カーボンナノチューブ、ナノダイヤモンド