

***Ab-initio* molecular dynamics simulation on nano-system under external pressure**

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Abstract A new constant-pressure molecular dynamics (MD) method is developed to simulate the dynamic behavior and structure transition of finite system under external pressure. In this method, no artificial parameter is introduced and the computation overheads are very small. As an application, a hard-soft transition of single wall carbon nanotube (SWCNT) under external pressure is found, which is in agreement with the experiments.

Keywords: phase transition, simulation, nano-particles

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1 Introduction

Pressure induced transition has been an important subject in condensed matter physics and material science for a long time. Physicists always use pressure as a tool to explore the meta-state in the condensed matter system, such as crystalline solids. Although theoretical study can precisely predict the ground state properties of a given material, it is usually difficult to estimate the stability and lifetime of a metastable state.

Compared with the bulk phase, the finite-size systems should have more rich metastable structures, because of the surface effect. One can expect that their physical properties are different from what observed in their bulk counterparts. For example, the melting point of nano particle is lower than that of bulk and obviously depends on the particle size^[1]. Recently X-ray experiments show a pressure-induced transition from tetrahedral to hexagonal structure in semiconductor nanoparticle^[2]. Rahman spectrum measurements of carbon nanotube (CNT) show a phase transition at the hydrostatic pressure of 1.5—1.7 GPa^[3]. However, because of the limitation of the experimental method, one cannot understand the phenomena on the atomic scales. New theoretical methods are needed for further research.

In principle, molecular dynamical simulation can provide the full transition path from one structure to another, which is not accessible in any experiments. The sophisticated

constant-pressure molecular dynamics method, developed at the beginning of the 1980s^[4], has been an efficient method to study the phase transition in the bulk systems. However, the traditional method was constructed only for periodical systems, and cannot be directly applied to the finite system, to which periodic boundary condition (PBC) does not apply. In order to use traditional method to study nano-system, Martonak et al.^[5] introduced the so-called pressure-transmitting liquid to apply the pressure to the finite systems, such as atomic clusters or nanoparticles. But there are two important shortcomings in Martonak's method. First, in order to have a well-defined isotropic constant pressure on the studied finite system, the number of atoms in the pressure-transmitting liquid should be much larger than that of the finite system. The computation time devoted to the calculation of transmitting liquid is very large. Most importantly, one needs to introduce a proper interaction between the pressure transmitting liquid and the studied finite system. Since there is no general rule to determine the interaction, it is hard to avoid any artifact involved in the simulation. Thus it is really necessary to develop a new constant-pressure MD method suitable for the finite systems.

We propose a new scheme to simulate the finite system at a constant pressure by showing its volume as a function of the atomic coordinates. Compared with the conventional molecular dynamics method, the new method does not need any transmitting liquid atoms, thus there is essentially no extra computation overheads. In this paper we show that this method can be equally implemented to the *ab-initio* MD simulation.

2 Constant-pressure MD method for finite system

The Lagrangian L of an N -atom, constant pressure system is written as

$$L = \sum_i^N \frac{\mathbf{p}_i^2}{2m_i} - (\phi(\{\mathbf{r}_i\}) + P_{\text{ext}} V), \quad (1)$$

where $\mathbf{r}_i, m_i, \mathbf{p}_i$ are the positions, mass, and momentum of i th atom respectively, and ϕ is potential of the system. V is the volume of the system, and P_{ext} is the external pressure. The equations of motion for \mathbf{r}_i derived from the Lagrangian L reads

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\mathbf{r}}_i} \right) = \frac{\partial L}{\partial \mathbf{r}_i}. \quad (2)$$

For an equilibrium system with the external pressure, the Virial theorem must be satisfied,

$$\left\langle \frac{1}{3V} \left(\sum_i^N m_i v_i^2 - \sum_i^N \mathbf{r}_i \cdot \nabla \phi - \sum_i^N \mathbf{r}_i \cdot P_{\text{ext}} \nabla V \right) \right\rangle = 0, \quad (3)$$

where v_i is the velocity of the i th atom, $\langle \rangle$ indicates time average. Then we have

$$\left\langle \sum_i^N m_i v_i^2 - \sum_i^N \mathbf{r}_i \cdot \nabla \phi \right\rangle = \left\langle \sum_i^N \mathbf{r}_i \cdot P_{\text{ext}} \nabla V \right\rangle. \quad (4)$$

In classic statistical physics, it is always assumed that any statistical results can be obtained exactly from Newtonian mechanics. This means that any statistical quantity of

a system must be a function of coordinates and velocities of the atoms included in the system. Obviously the volume can be written as a homogeneous cubic function of atomic coordinates according to Euler's theorem,

$$\sum_i^N \mathbf{r}_i \cdot \nabla_i V = 3V. \quad (5)$$

So from eq. (4) we have

$$P_{\text{ext}} = P_{\text{int}} = \left\langle \frac{1}{3V} \left(\sum_i^N m_i v_i^2 - \sum_i^N \mathbf{r}_i \cdot \nabla \phi \right) \right\rangle, \quad (6)$$

where P_{int} refers to the internal pressure. Since the external pressure P_{ext} is a constant, P_{int} is also a constant. Consequently by writing the volume as a function of the coordinates of the atoms included, we arrive at a new constant-pressure MD for the finite systems, in which no extra parameter is introduced.

One can easily extend the above derivation to *Ab-initio* MD. In the scheme of density functional theory (DFT), the atomic forces are defined as the derivative of generalized free energy F which depends on the wave functions ϕ , partial occupancies f and the position of the atoms R :

$$\text{force} = \frac{dF(\phi, f, R)}{dR} = \frac{\partial F}{\partial \phi} \frac{\partial \phi}{\partial R} + \frac{\partial F}{\partial f} \frac{\partial f}{\partial R} + \frac{\partial F}{\partial R}. \quad (7)$$

In the DFT ground state, the first two terms of the above expression are zero and we only need to calculate the third term. This formalism can be easily extended to the constant pressure system, but the generalized free energy should be replaced by the Gibbs energy:

$$G(\phi, f, R) = F(\phi, f, R) + P_{\text{ext}} V. \quad (8)$$

From this force definition we can see that, similar to the classical method, one only needs to introduce a "volume force" to keep the finite system at a constant pressure.

In the previous derivation, there is no any approximation introduced except the cubic form of volume. Many methods can be used to calculate the volume of a finite system. The simplest one is to write the volume as the summation of the individual atomic volumes. For example, the volume of the system can be calculated as

$$V_i = \gamma_i \frac{4\pi}{3} \sum_{j \neq i} \left(\frac{r_{ij}}{2} \right)^3, \quad r_{ij} < r_c, \quad (9)$$

where r_{ij} is the distance between the i th and j th atoms and r_c is its cutoff, the summation runs over all the first nearest neighbors of the i th atom, γ_i is a scale factor which is close to the inverse of the number of the nearest neighbors of the i th atom. For a simulation in which no atomic diffusion occurs frequently, γ_i could be considered as a constant. At the high temperature or in a system in which the first nearest neighbors frequently change, we find that it is better to choose the γ_i as a smooth cutoff function.

If we regard the studied nano-particle as a convex polyhedron, we can find all the surface atoms to construct a series of tetrahedrons and the whole volume of the nano-particle is summation of all the volumes of the tetrahedrons. If no more than four atoms

are in the same plane, we can use gift-packing or other hull algorithm to find the surface atoms^[6]. In this way, one can get more accurate volume than eq. (9). In concave case or there are many atoms in the approximately same plane we can define a neighboring cutoff to avoid neglecting the concave atoms.

The present scheme of constant-pressure MD method shown above has several advantages. First, the constant pressure ensemble can be achieved without any artificial parameters if the volume of the finite system can be well defined. By contrast in the traditional constant-pressure MD, it needs to choose a mass of the volume, which directly affects the time scale of the relaxation. Secondly, in the traditional constant-pressure MD, the coordinates (velocity) are uniformly scaled to get a constant pressure, whatever the system is homogeneous or not. However, in the present method, the response of the system to the external pressure is truly localized. This is especially important for the inhomogeneous systems.

To verify the new method really working with constant pressure, we simulate Ni nanoparticle and carbon nanotube under pressure and show the evolution of the pressure, volume and temperature with time (fig. 1). The results of Al₁₃ cluster from *ab-initio* MD are shown in fig. 2. Obviously, the evolution of pressure and volume shows a fluctuation behavior around an average value. These results demonstrate that pressure is statistically constant in simulation.

3 Hard-soft transition of SWCNT under pressure

Experiments found that when the pressure applied on the SWCNT is up to 1.5—1.7 GPa, the radial vibrational mode disappears suddenly, however, the reason is not known yet. In this paper, we use the newly proposed finite system MD method to simulate an isolated SWCNT under external pressure. We use periodic boundary condition in axial direction and apply an isotropic, hydrostatic pressure in radial direction.

In the simulation we use both the classical and *ab-initio* MD methods. With classical MD, we calculate the (10, 10) type armchair SWCNT. The covalent interactions between carbon atoms are modeled by an empirical Tersoff-Brenner many-body potential with the parameters given by Brenner^[7,8], which has been extensively used to model diamond, graphite, carbon nanotubes and many hydrocarbon complexes. The intra-tube van der Waals interactions are modeled in the usual way by the 6-12 Lennard-Jones potential with a cutoff distance of 15 Å^[9]. The intra-tube van der Waals interaction is included when the tube is compressed to an oval shape.

In the *ab-initio* method, we use the ultra-soft pseudopotential plane-wave method and the local density approximation (LDA)^[10–12]. Because of the computational limitation we only calculate the (6, 6) CNT with two periods in the *z* direction, totally 48 atoms are involved. The tube is put in a supercell with a large dimension 17 Å × 17 Å in the *x-y* plane to reduce the interaction between the tube and its periodic images. The cutoff

energy for plane wave expansion is about 286 eV and the MD simulation temperature is about 300 K.

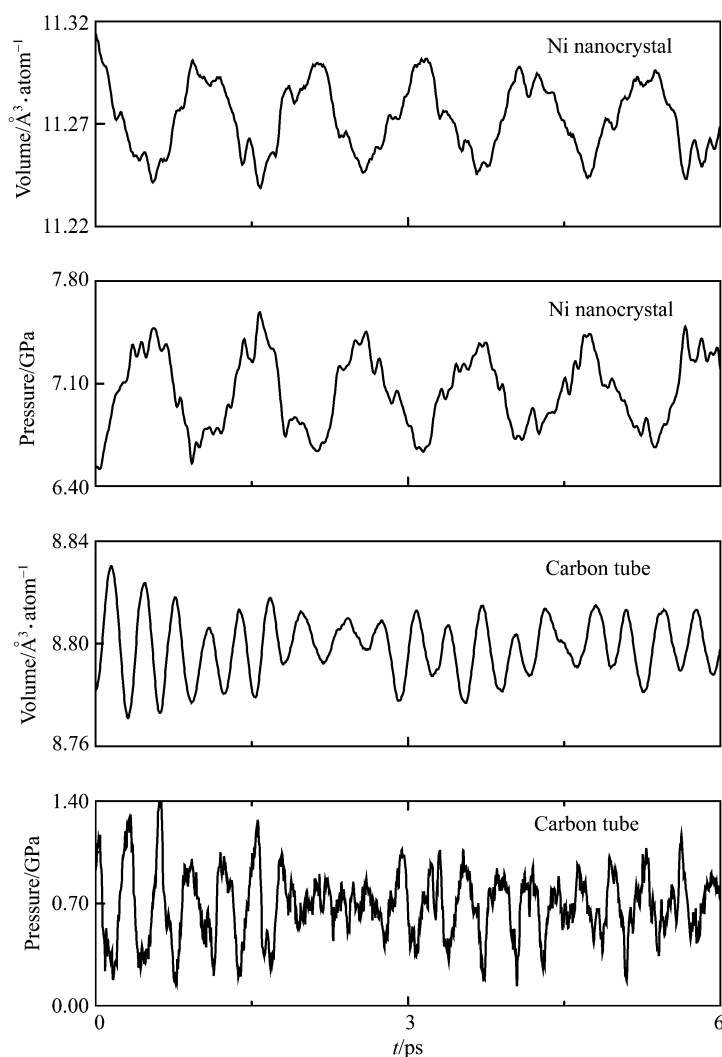


Fig. 1. The evolution of the instantaneous pressure and volume through MD runs for the carbon nanotube (lower two) and Ni nanocrystal (upper two). The pressure and volume of the system fluctuate around the average value.

Fig. 3 gives the results of (10, 10) tube from classical simulation, where the volume is defined as the product of the cross section and the length of tube, the volume is normalized by the equilibrium volume without external pressure. A critical pressure near 1.1 GPa can be clearly seen in fig. 3. Below the critical pressure, the tube has a large compressibility of 0.01. Above the pressure, the tube becomes very soft with the compressibility about two orders of magnitude larger. This clearly shows a pressure-induced hard-soft transition. It can be assumed that the critical transition pressure could be strongly dependent on

tube radius. By studying different types of SWCNT, we get an approximate relationship: $Pt \sim 1/R$, where R is the radius of the tube.

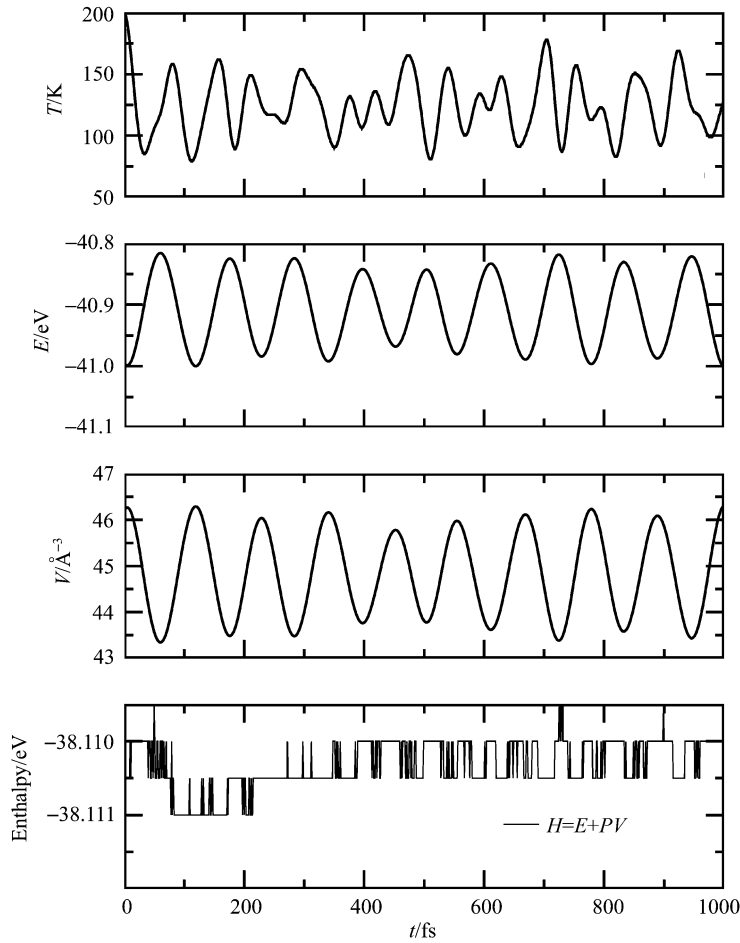


Fig. 2. The first principle results of icosahedral Al_{13} volume, energy, temperature and enthalpy evolution under 10 GPa pressure. System enthalpy $H = E + PV$ is constant.

The response of bond length and bond angle to the external pressure provides a reasonable explanation for the hard-soft transition. It is well-known that C-C bond is very hard. This means that it costs much more energy to change bond length than bond angle. At the pressure lower than the critical value, the structural response to the external pressure is largely taken by the change of bond length of a circular shape, giving rise to a hard phase; while after the transition, the structural response to the external pressure is largely reflected by the change of bond angle of an elliptical shape, giving rise to a soft phase.

In order to show how vibrational mode changes when the hard-soft transition happens, we have calculated the velocity-velocity correlation function for different pressures. The results are shown in fig. 4. When the applied pressure increases, the frequency of the radial vibrational mode moves toward higher frequency. The reason is: under external

pressure, the inter-atomic distances decrease, which results in the increase of the force constants. Meanwhile it is interesting to note that with the increasing of frequency the amplitude decreases. When the pressure reaches the critical value, the amplitude almost approaches to zero, i.e. the vibrational mode disappears, accompanied by the hard-soft transition. This is similar to the mode softening in crystals.

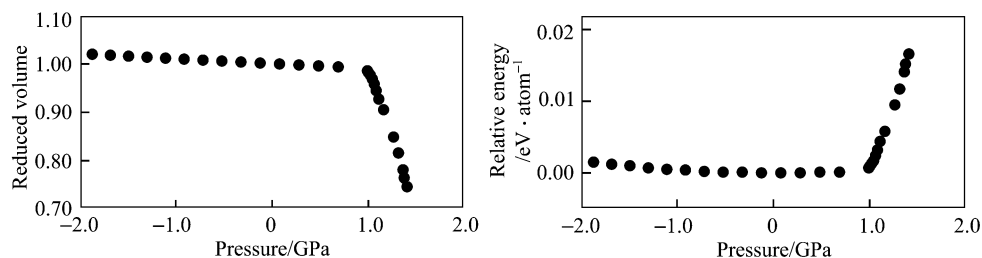


Fig. 3. (10,10) CNT under external pressure. A structural transition happens at 1.1 GPa.

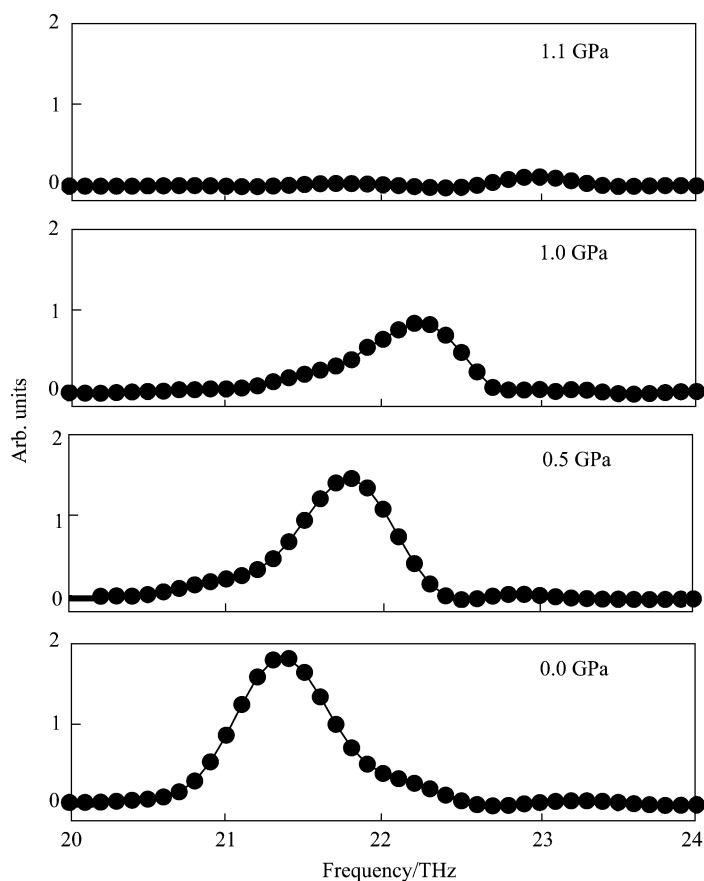


Fig. 4. (10,10) SWCNT radial vibration mode changes with pressure. The radial mode disappears at 1.1 GPa.

Fig. 5 is the *ab-initio* results of (6, 6) SWCNT. Similar to the classical results, a circle to oval transition occurs when pressure increases. This qualitatively confirms the results of Tersoff-Brenner many body potential. Quantitatively, however, the *ab-initio* calculation predicts a much larger transition pressure of 10 GPa. This can be attributed to the smaller radius of (6, 6) tube compared with that of (10, 10) tube, and the well-known softness of Tersoff-type potential. Therefore the transition pressure in the classical simulation is approximately 50% smaller than experimental value, and the *ab-initio* results are more accurate.

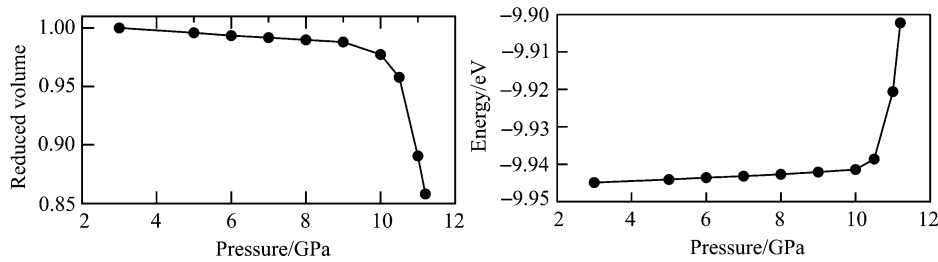


Fig. 5. *Ab-initio* simulated hard-soft transition of (6, 6) SWCNT under external pressure.

4 Conclusion

We have developed a new molecular dynamics method which is suitable to the finite system, especially the nanoparticles to which periodic boundary condition does not apply. Compared to the traditional methods, the new method is parameter free and simple in coding, thus it provides a new approach to study phase transitions and the properties of meta-stable nanosystems.

As an example, we have studied the mechanical properties of carbon nanotube and have found a hard-soft transition in isolated SWCNT. Accompanying the transition a shape change in nanotube and the disappearance of the radial vibrational mode happen simultaneously, which is in agreement with the experimental results.

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