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LETTER TO THE EDITOR

A new constant-pressure molecular dynamics method for finite systems

D Y Sun¹ and X G Gong^{1,2}

¹ Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

² Department of Physics, Fudan University, Shanghai 200433, People's Republic of China

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Online at stacks.iop.org/JPhysCM/14/L487**Abstract**

We present a new method for constant-pressure molecular dynamics simulation which is parameter free. This method is especially appropriate for finite systems in which a periodic boundary condition does not apply. Simulations on carbon nanotubes and Ni nanoparticles clearly demonstrate the validity of the method, from which we can also easily obtain the equations of states for a finite system under external pressure.

The molecular dynamics (MD) simulation method is a powerful tool, widely used in chemistry, physics, and materials science [1]. A very important achievement, the constant-pressure MD proposed by Andersen [2], and subsequently extended by Parrinello and Rahman [3], is now a standard tool for studying the physical properties of periodic systems under an external pressure. It has also played a central role in studying structural phase transitions in geophysical and astrophysical applications.

Recently, the study of low-dimensional and biological systems under external pressure has attracted considerable attention [4, 5]. In particular, studies on carbon nanotubes [6], clusters, and nanocrystals, such as CdSe, CdS, and Si nanocrystals [7], have revealed a wealth of interesting new phenomena. Usually, computer simulation can substantially complement the experimental information. However, the traditional constant-pressure MD method is designed for an infinite system with a periodic boundary condition and cannot be directly applied to a finite system in which there is no periodic boundary condition. For this reason it is necessary to develop a new computational scheme to study the finite system. Very recently, Martonak *et al* [8] successfully studied the pressure-induced amorphization of Si₁₃₅H₃₆ clusters by introducing a pressure-transmitting liquid. In order to have a well-defined isotropic constant pressure on the cluster, the number of particles and the volume of the pressure-transmitting liquid should be much larger than those for the cluster; thus has significant computational cost. Additionally, one must also determine how the liquid atoms interact among themselves as well as with cluster

atoms so that the liquid does not crystallize, or, in the timescale of the simulation, does not undergo a glass transition.

In this letter, writing the volume as a function of coordinates of atoms, we propose a new constant-pressure MD which is appropriate for a finite system. This new constant-pressure MD is parameter free, and can be used for any system of arbitrary shape, especially nanocrystals. We will demonstrate its validity by classical simulations of a carbon nanotube and small Ni particles. Its extension to *ab initio* MD methods is straightforward.

We write the Lagrangian L of an N -atom system as

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

where \mathbf{r}_i , m_i , and \mathbf{p}_i are the coordinate, mass, and momentum of the i th atom, respectively, ϕ is the potential of the system, V the volume of the system, and P_{ext} the external pressure. If the system obeys Newtonian mechanics, the equations of motion for \mathbf{r}_i derived from the Lagrangian L read

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

Obviously the enthalpy will be conserved. The equations of motion derived from equation (2) produce the constant-pressure ensemble for the system, as we show below. For an equilibrium system under external pressure we have

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

where v_i is the velocity of i th atom and $\langle \rangle$ indicates the time average. Consequently,

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

It is well known that, in statistical physics [9], the volume is an additive quantity which can be written as a summation of the volumes of individual atoms,

$$V = \sum_i^N V_i, \quad (5)$$

where V_i is the volume of the i th atom and can generally be written as a cubic homogeneous function of its nearest-neighbour distance r_{ij} , i.e.

$$V_i = \sum_{j \neq i} f(r_{ij}^3). \quad (6)$$

According to Euler's theorem,

$$\sum_i^N \mathbf{r}_i \cdot \nabla_i V = 3V, \quad (7)$$

so from equation (4) we have

$$P_{ext} = P_{int} = \left\langle \frac{1}{3V} \left(\sum_i^N m_i v_i^2 - \sum_i^N \mathbf{r}_i \cdot \nabla \phi \right) \right\rangle \quad (8)$$

where P_{int} refers to the internal pressure. Since the external pressure P_{ext} is a constant, P_{int} is also a constant. Thus, by writing the volume as a function of atomic coordinates, a new constant-pressure MD is presented in which no extra parameter is introduced.

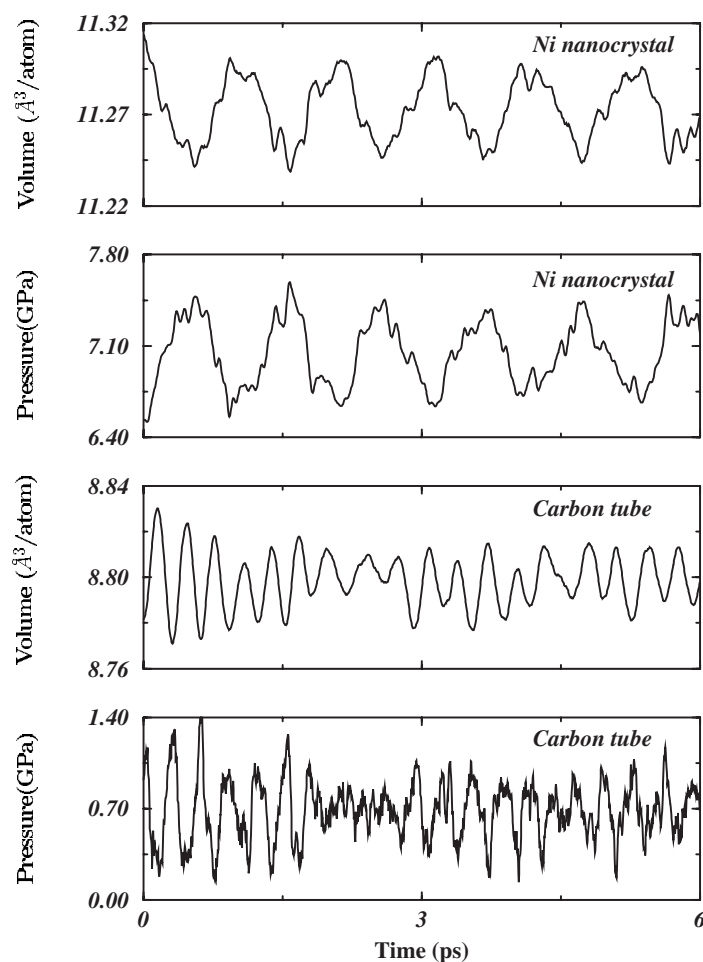


Figure 1. Evolution of the instantaneous pressure and volume through MD runs for the carbon nanotube (lower two) and Ni nanocrystal (upper two). The pressure and volume of the system fluctuate around the average value. The new constant-pressure MD does reveal a constant pressure.

The present constant-pressure MD method has several advantages. First, it can make the calculation more realistic, without the need to choose the *mass* for the volume as in traditional constant-pressure MD [2], which directly affects the timescale of the relaxation. Secondly, the response of the system to the external pressure is more physical. This is especially important for an inhomogeneous system. By contrast, in traditional constant-pressure MD, the response of the system to external pressure is essentially linear, i.e., the volume of the system is linearly scaled according to the difference of the internal and external pressures.

The key to the success of the present method is in defining the volume as a function of atomic coordinates. In the traditional constant-pressure MD method, the volume is in generalized coordinates which have equal importance as atomic coordinates, and the constant pressure is dynamically achieved by directly changing the volume of the system. However, in the present scheme, the constant pressure is obtained by dynamically changing the motion of each atom.

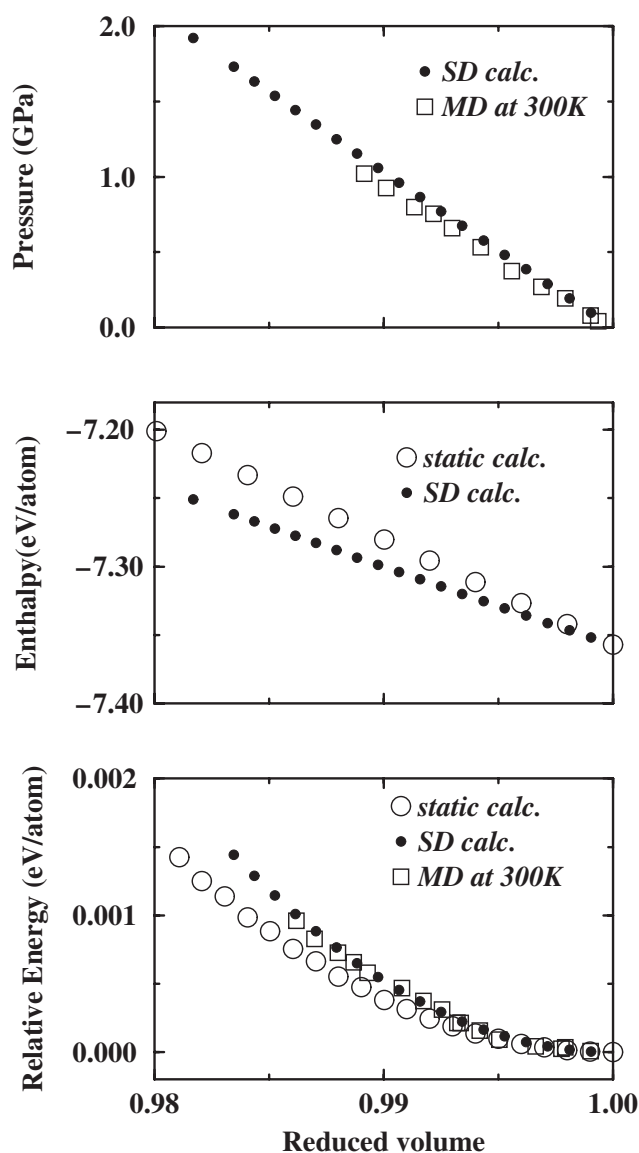


Figure 2. Calculated properties of the carbon nanotube. Lowest panel: the energy as a function of volume from the steepest-descent (SD) calculation (filled circles), the new constant-pressure MD at 300 K (open squares), and the static calculation (open circles). Middle panel: the enthalpy as a function of the reduced volume from the static (open circles) and present MD (filled circles) calculations. Top panel: the pressure–volume relationship of the carbon nanotube at 0 K (filled circles) and 300 K (open squares). Our SD results at zero temperature are in good agreement with the static results except for large volume change, where the structural relaxation is included in our MD runs.

To show how well this new constant-pressure MD works in real applications, we have simulated carbon nanotubes and Ni nanocrystals under an external pressure. In the simulation it is difficult to obtain an exact formalism for the real physical atomic volume. However, there are a variety of efficient approximations, and one of the simplest and most direct ways is

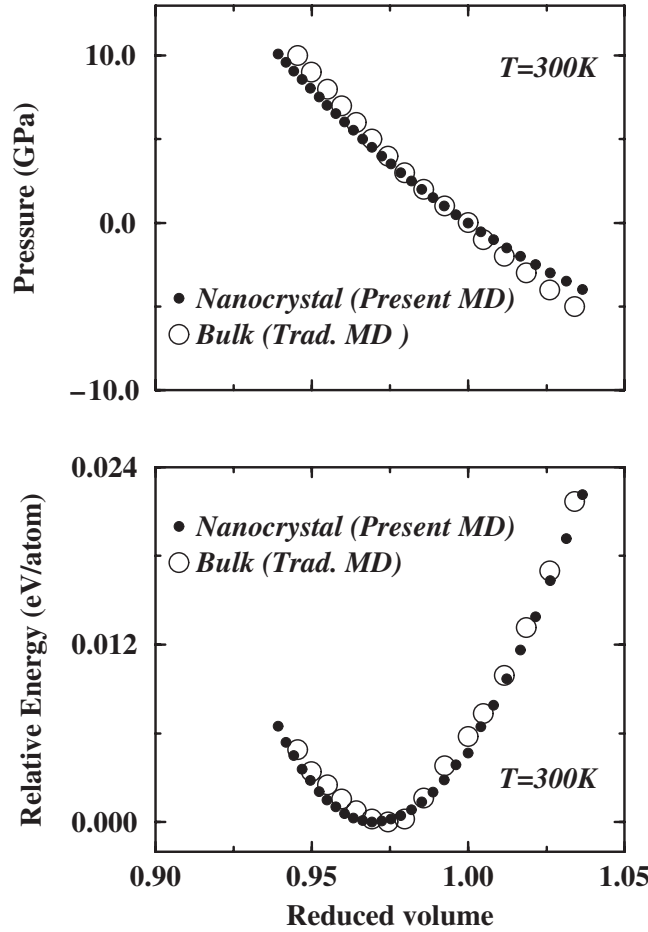


Figure 3. The EOS for Ni nanocrystals (filled circles) and the bulk phase (open circles), where the data for Ni₃₁₅₁ nanocrystals and the bulk phase are calculated from the new and traditional MD simulations, respectively.

based on the Wigner–Seitz primitive cell. We use the scaled volume of the atomic sphere to approximate the Wigner–Seitz primitive cell in the following form:

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

where the summation runs over all the first-nearest neighbours of the i th atom, and γ_i is a scale factor closely related to the number of the nearest neighbours of the i th atom. In the study of carbon nanotubes, we fix the periodic length in the axial direction. The slightly different definition of the volume for nanotubes will be presented elsewhere [10]. In fact, it is not necessary to include the coordinates of all atoms in the calculation of the volume, since the volume of the finite system is just determined by the surface atoms.

The interaction between carbon atoms is described by the parametrized potential developed by Brenner [11] according to the Tersoff bonding formalism [12], which is widely used to study the mechanical properties of carbon nanotubes [13]. The Sutton–Chen potential is used to describe the interaction between Ni atoms [14]; this is also widely used in the literature [15].

We find that our results for the carbon nanotube and Ni nanocrystal are in good agreement with those obtained by other methods.

The evolutions of the instantaneous pressure in the simulation of a (10×10) carbon nanotube and a nickel nanocrystal (figure 1) show that the present method does recover a constant-pressure simulation. Although the instantaneous pressure of the system fluctuates, the average value is equal to the set external pressure, i.e. 0.7 GPa for the carbon nanotube and 7.0 GPa for the Ni nanocrystal. The correlation between the volume and pressure can also be clearly observed.

Figure 2 shows the calculated energy versus volume (pressure) for a carbon nanotube. The close agreement between the static calculation and our constant-pressure MD simulation clearly demonstrates the validity of the latter. In the static calculation, energies are calculated at the linearly scaled radius of the carbon nanotube without relaxing the atomic positions. All the energies shown in the lower panel of figure 2 are relative to the minimum energy, and the volume is renormalized by the equilibrium volume without the external pressure. We perform the constant-pressure MD simulation at 300 K for various external pressures from 0 to 2 GPa. By performing a SD calculation, we also obtain the energy and pressure as a function of the volume at 0 K. The static calculation and the SD calculation give very similar results, the slight difference being due to the relaxation of the atomic coordinates.

We show the enthalpy as a function of the reduced volume for static and present MD results in the middle panel of figure 2. It can be seen that, at each volume, the enthalpy of the present MD, in which the structures under the external pressure are relaxed, is always smaller than that from the static calculation, as it should be. The fact that the difference between the enthalpies calculated by the static and SD methods at 0 K increases with decreasing volume suggests that the atomic relaxation becomes more and more important. The new constant-pressure MD also correctly describes the finite-temperature properties.

The equation of states (EOS) at finite temperature for an Ni nanocrystal can also be obtained through the simulation. Figure 3 shows the EOS for an Ni nanocrystal and the bulk phase calculated from the new constant-pressure MD and traditional MD, respectively. All the energies shown in figure 3 are relative to the minimum energy, and the volume is renormalized by the equilibrium volume without external pressure at 300 K. The nanocrystal and bulk phase show similar behaviour. However, from the figure we can see that the nanocrystal is not as hard as the bulk phase. If we assume that the first-order Birch–Murnaghan EOS [16] is also applicable for finite systems, we derive the bulk modulus as 136 and 166 GPa for the nanocrystal and bulk phase, respectively, in agreement with our previous results [17].

In summary, writing the volume as a function of atom coordinates we have proposed a new constant-pressure MD method for finite systems which is parameter free and where the external pressure can be exactly implemented. Simulations on carbon nanotubes and Ni nanoparticles clearly demonstrate the validity of the method, in which the constant pressure is revealed. We have also shown that with our newly proposed scheme the EOS for finite systems can be calculated through a molecular dynamics simulation.

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