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Numerical distortion and effects of thermostat in molecular dynamics simulations of single-walled carbon nanotubes*

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In this paper, single-walled carbon nanotubes (SWCNTs) are studied through molecular dynamics (MD) simulation. The simulations are performed at temperatures of 1 and 300 K separately, with atomic interactions characterized by the second Reactive Empirical Bond Order (REBO) potential, and temperature controlled by a certain thermostat, i.e. by separately using the velocity scaling, the Berendsen scheme, the Nose–Hoover scheme, and the generalized Langevin scheme. Results for a (5,5) SWCNT with a length of 24.5 nm show apparent distortions in nanotube configuration, which can further enter into periodic vibrations, except in simulations using the generalized Langevin thermostat, which is ascribed to periodic boundary conditions used in simulation. The periodic boundary conditions may implicitly be applied in the form of an inconsistent constraint along the axis of the nanotube. The combination of the inconsistent constraint with the cumulative errors in calculation causes the distortions of nanotubes. When the generalized Langevin thermostat is applied, inconsistently distributed errors are dispersed by the random forces, and so the distortions and vibrations disappear. This speculation is confirmed by simulation in the case without periodic boundary conditions, where no apparent distortion and vibration occur. It is also revealed that numerically induced distortions and vibrations occur only in simulation of nanotubes with a small diameter and a large length-to-diameter ratio. When MD simulation is applied to a system with a particular geometry, attention should be paid to avoiding the numerical distortion and the result infidelity.

Keywords: molecular dynamics simulation, single-walled carbon nanotube (SWCNT), thermostat, numerical distortions

PACC: 6148, 6185, 7115Q

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991,[1] with the gradual knowledge of their excellent mechanical and electrical properties, CNTs have become one of the most attractive research subjects in nanotechnology, nanoelectronics, and material science. Numerous experimental studies were carried out for exploring new properties of CNTs and their potential applications in nano-mechanical and electrical system and nanofabrication.[2−4] Computer simulations, on the other hand, were widely used for predicting the performances of CNTs.[5−7] Among various simulation methods, molecular dynamics (MD) simulation has been proved to be particularly powerful for investigating the structure-originated behaviours of CNTs and molecular origin of the phenomenon.[8]

The success in MD simulation, however, depends on the appropriate choice of inter-atomic potential and numerical algorithm. The second generation of the Reactive Empirical Bond Order (REBO) potential[9] is now proved to be able to successfully describe the covalent bonding interaction between carbon atoms, and has been adopted in CNT simulations. The numerical algorithms, known as thermostat, have been widely applied to MD simulations for keeping the system temperature constant, but their effects on simulation results have not been systematically investigated.

At present there are several thermostat algorithms generally adopted, such as the velocity scaling,[10] the Berendsen thermostat,[11] the Nose–Hoover thermostat[12,13] and the generalized Langevin[14,15] thermostat. The velocity scaling thermostat is the simplest scheme to be implemented numerically, so it has been used in general although it does not have an appropriate interpretation in physics.

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The Berendsen thermostat is a further refinement of the velocity rescaling scheme which forces the system to change towards a desired temperature at a certain rate, while only a slight perturbation acts on each atom. The Nose–Hoover thermostat can be interpreted as the coupling of the dynamic system with a thermal reservoir, and the simulation is carried out in this extended system. The generalized Langevin thermostat introduces random collisions and frictional forces into a system to stabilize the system temperature. This thermostat scheme used to be applied in solvent simulations, and it was also used in simulations of carbon nanotubes,[16,17] which yielded some beautiful results.

Although in most MD simulations a thermostat has to be applied in one way or another to control temperature, it is unfortunate that researchers often select a scheme blindly, rather than knowing in advance what consequence will be produced in the simulation, and few studies of a comparison between different thermostat schemes are available in the literature.[18] This article intends to simulate the dynamic behaviours of (5,5) and (10,10) single-walled carbon nanotubes at different temperatures, i.e. 1 and 300 K, and to compare the performances of the four thermostat schemes mentioned above. It is found that the algorithms for controlling temperature do have significant effects on simulation results, especially for CNTs with a large length-to-radius ratio, and the numerical errors can be reduced by applying an appropriate thermostat.

2. Simulation method

The simulations are performed for two special types of CNTs, i.e. open ended (5,5) and (10,10) single-walled carbon nanotubes (SWCNTs). Length in (5,5) SWCNT simulation is set at 12.2 and 24.5 nm, corresponding to the length-to-diameter ratios of 18.4 and 37.0, respectively. Length in (10, 10) SWCNT simulation is set at 49.1 and 61.4 nm and length-to-diameter ratios are 37.0 and 46.0. Periodic boundary conditions are applied along the axial direction of nanotube, so that the length is extended periodically from both ends. The second generation of the REBO potential, which is very successful in the simulation of the system with formation or rupture of C–C bonds, is employed to describe interatomic forces. The equation of motion is numerically integrated by using the forth-order predictor-corrector algorithm[19] in time steps of 1 fs. Simulations are performed at two predefined temperatures, i.e. 1 or 300 K, which are stabilized through one of the thermostat algorithms. The dynamic features of the simulated nanotubes at the specified temperatures are monitored over a period of 105 MD steps.

The four thermostat algorithms investigated in this paper, i.e. the velocity scaling, the Berendsen thermostat, the Nose–Hoover thermostat, and the generalized Langevin thermostat, are briefly reviewed in the following.

2.1. Velocity scaling thermostat

The velocity scaling thermostat is the simplest method to control the system temperature during simulations, where the atomic velocities, obtained by integrating the equation of motion, are scaled at each time step by a factor of

$$\lambda = \sqrt{\frac{T}{T(t)}}, \tag{1}$$

where T denotes the desired temperature and $T(t)$ is the current kinetic temperature at time t.

2.2. Berendsen thermostat

The Berendsen thermostat is a refinement of the velocity scaling scheme, proposed by Berendsen and Postman[11] in 1984. The velocities are scaled at every time step as done in the first scheme, but by using a rescaling factor that is modified as

$$\lambda = \left(1 + \frac{\delta t}{t_{\mathrm{T}}}\left(\frac{T}{T(t)}\right)\right)^{1/2}, \tag{2}$$

where t_{T} is a preset time constant, $t_{\mathrm{T}} = 0.4$ps and δt is the MD time step.

2.3. Nose–Hoover feedback thermostat

The Nose–Hoover feedback thermostat is referred to as an 'extended system' method, presented by Hoover[13] in 1985. This method has been widely accepted because it makes more sense in physics, i.e. the simulation produces a canonical distribution in figuration space, while energy is allowed to flow back and forth between the system and a reservoir without exchanging particles. In this approach, the equations of

motion have been modified as

$$\frac{\mathrm{d}r_i}{\mathrm{d}t} = \frac{p_i}{m_i}$$
$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = f_i - \xi p_i, \tag{3}$$

where the friction coefficient ξ can be determined by a first-order differential equation

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{Q}\left(\sum_i \frac{p_i^2}{m_i} - gk_\mathrm{B}T\right), \tag{4}$$

where Q is the thermal inertia parameter that behaves like a 'mass' related to the motion of the coordinates, and the value of Q is given by $gk_\mathrm{B}T\tau^2$, where τ is the relaxation time of the thermal bath, normally it is of the same order of magnitude as the simulation time step $\mathrm{d}t$, T is the expected system temperature, k_B the Boltzmann constant, and g denotes the number of degrees of freedom determined by $g = 3\,(N-1)$.

2.4. The generalized Langevin thermostat

This thermostat algorithm, which is proposed by Mori[14] and used in general to simulate fluids, introduces a generalized Langevin equation for stabilizing the system temperature. This approach to controlling kinetic temperature of carbon nanotubes is often used and can obtain satisfactory results.[16,17] In this approach, random forces are incorporated into the equation of motion, so that atoms of carbon nanotube are assumed to be Brownian particles that are kept at a constant kinetic temperature. The generalized Langevin equation, incorporated with random forces to describe thermodynamic interactions, can be written as

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = -\xi p_i + f_i + \sum_{i=1}^{N} \alpha_{i,j} F_j, \tag{5}$$

where f_i is derived from the potential, ξ is a friction coefficient, the third term on the right-hand side is a random force with the Gaussian distribution and a zero expectation value.

3. Results and discussion

3.1. Velocity distributions

The simulations are performed for (5, 5) and (10, 10) SWCNTs with lengths of 24.5 and 49.1 nm, respectively, and a corresponding length-to-diameter ratio of 37.0. The initial values of atomic velocity for both (5,5) and (10,10) SWCNTs are assigned in terms of the Maxwell velocity distribution. The Maxwell distribution should be maintained throughout the process of simulation. The Maxwell–Boltzmann law, as defined in Eq.(6),[20] is used to monitor the velocity distribution during the simulation,

$$f\,(v)\,\mathrm{d}v = \frac{N\,(v)\,\mathrm{d}v}{N}, \tag{6}$$

where $f(v)$ is the density function of distribution, N is the number of atoms in the system, and $N(v)$ denotes the fraction of N atoms having velocities within an interval $\mathrm{d}v$, i.e. between v and $v + \mathrm{d}v$. The velocities are normalized in calculation. The calculated velocity distributions for the (5,5) and (10,10) SWCNTs at 300 K and a selected time of 50,000th MD step are given in Figs.1(a) and 1(b), from which we conclude that Maxwell velocity distribution remains well during the simulations. The results for the system at 1 K are similar to those in Fig.1.

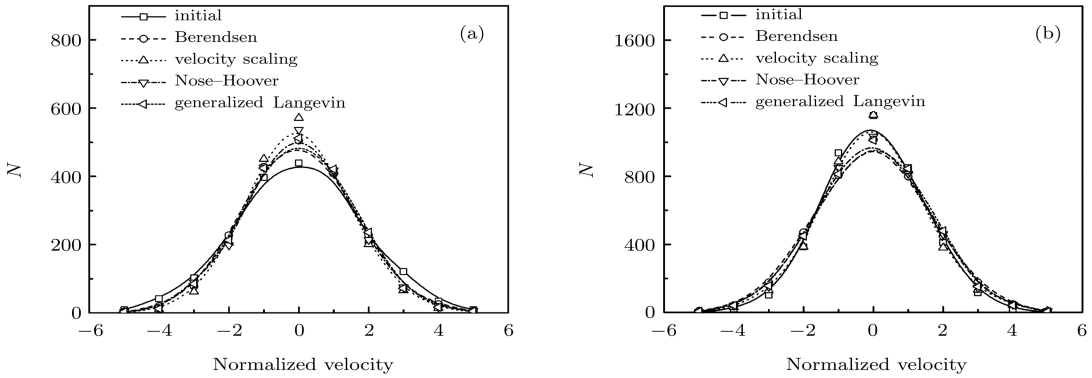


Fig.1. Velocity distributions of SWCNT at 300 K, where the solid line curves show initial distribution and other four curves correspond to the distributions in different cases, calculated at the time of 50000th MD step but with temperature controlled by different thermostats; panel (a) is for the results of (5,5) SWCNT and panel (b) for the results of (10,10) SWCNT.

3.2. Configuration distortion and effects of thermostat scheme

In the following, effects of thermostat schemes are investigated by monitoring the changes in configuration of CNTs during process of simulation. Simulations in subsections 3.2 and 3.3 are performed only for (5,5) SWCNT with a length of 24.5 nm. The configurations obtained from simulations at a temperature of 300 K by applying the velocity rescaling thermostat are displayed in Fig.2, where four profiles of the nanotube correspond to the simulation results taken at different moments, i.e. $t = 0$, 32.5, 38.0 and 42.5 ps. The SWCNT initially takes the form of a straight line (Fig.2(a)), but a distortion in configuration appears, and its amplitude reaches a maximum at time $t = 32.5$ ps (Fig.2(b)). A few picoseconds later, it seems to regain the straight configuration (Fig.2(c)), and then the distortion increases again (Fig.2(d)). The configuration keeps changed in that way afterward, so the simulated nanotube looks as if it is fluctuating in a periodic pattern.

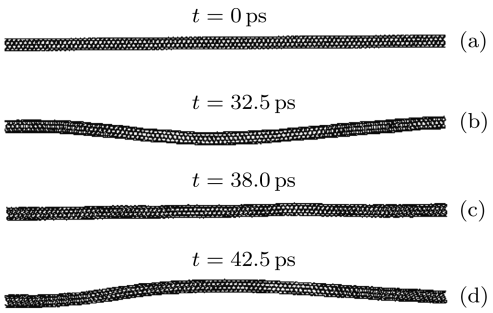


Fig.2. Configurations of (5, 5) SWCNT with a length of 24.5 nm at different moments, i.e. $t = 0$, 32.5, 38.0 and 42.5 ps, obtained at $T = 300$ K by applying the velocity scaling thermostat.

The result shows an interesting phenomenon but raises a serious question at the same time. Is the fluctuation an inherent feature of carbon nanotubes, originating from thermodynamic instability, especially for the one with a large length-to-diameter ratio, or, is it merely a numerical distortion caused by errors from thermostat schemes or numerical integrations? To explore possible origins of distortions and fluctuations described previously, we perform simulations for the same nanotube, but at a very low temperature ($T = 1$ K) and with different thermostat schemes. The configurations of the (5,5) SWCNT taken at different times, i.e. $t = 55$, 70 and 86 ps, are shown in Fig.3 where panels (a), (b), (c) and (d) correspond to the results from simulations using the velocity scaling, the Berendsen thermostat, the Nose–Hoover thermostat, and the generalized Langevin thermostat, respectively.

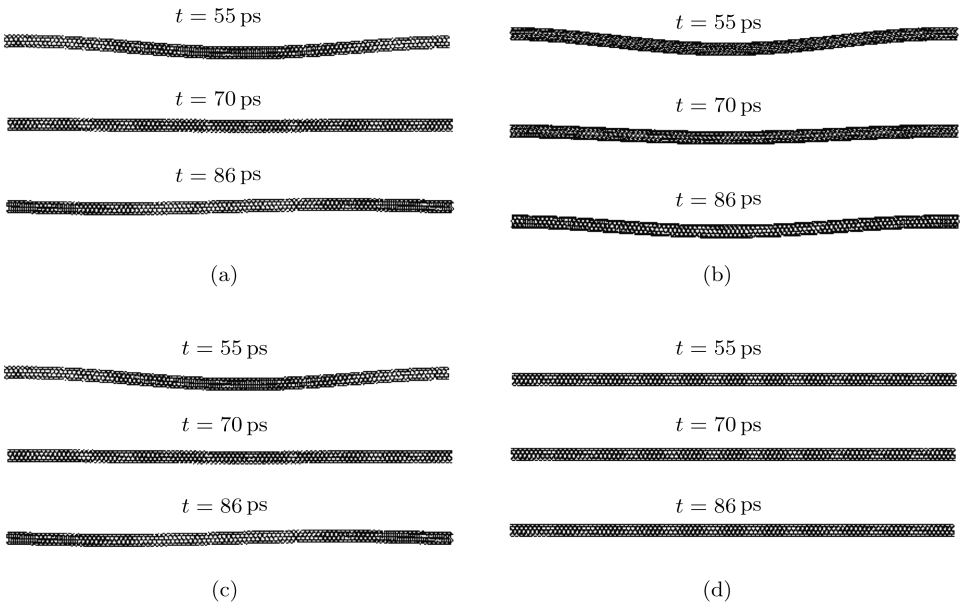


Fig.3. Configurations of (5,5) SWCNT the same as that in Fig.2, taken at different moments, i.e. $t = 55$, 70 and 86 ps, obtained from simulations at $T = 1$ K and using different thermostat schemes: the velocity scaling (a), the Berendsen scheme (b), the Nose–Hoover scheme (c), and the generalized Langevin scheme (d).

From the results given in Figs.3(a), 3(b) and 3(c), it is obvious that lowing the system temperature down to 1 K does not eliminate the fluctuations observed at $T = 300$ K, though there appears a slight reduction in amplitude of distortion. Considering that at a temperature almost close to absolute zero, the thermodynamic instability is not expected to play a significant role in distortion, thereby the fluctuation of nanotube seems more likely to be a distortion related to numerical errors. Besides, a change in thermostat from the velocity scaling to the Berendesen scheme or the Nose–Hoover scheme does not help eliminate the fluctuations, either. However, the story changes when the generalized Langevin thermostat is applied as shown in Fig.3(d), where the straight configuration of simulated SWCNT remains throughout the entire process of simulation. Figure 4 gives the results obtained at $T = 300$ K and in conditions similar to those in Fig.2, but by using the generalized Langevin thermostat instead of the velocity scaling. Again, the simulated SWCNT remains a straight configuration, which confirms that the distortions can be reduced or eliminated by choosing an appropriate thermostat.

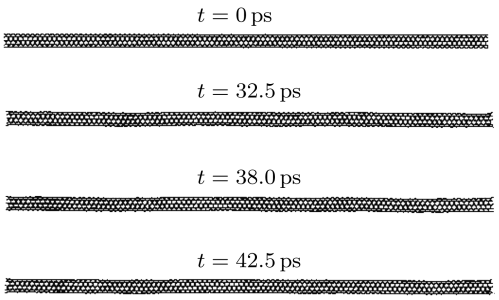


Fig.4. Configurations of (5, 5) SWCNT at 300 K at different moments, i.e. $t = 0$, 32.5, 38.0 and 42.5 ps, obtained by applying the generalized Langevin thermostat.

3.3. Causes responsible for distortion

To search for the exact causes responsible for the errors resulting in the configurational distortion in 1 K, the first forth-order predictor–corrector algorithm is changed to the fifth-order and sixth-order to improve the computation accuracy. The results show the same phenomena as those described previously, which means that the distortions cannot be eliminated by simply raising the numerical order of integration. Next we remove the periodic boundary condition from the system, so the simulated CNTs are of a finite length. The results from simulations with and without applying the periodic condition are shown in Figs.5(a) and 5(b), respectively, where one can see that the distortions are greatly depressed by removing the periodic boundary condition. Thus in that case, the results reveal no apparent distortion, so do all simulations by using the four thermostat algorithms separately.

The mechanism for numerical errors resulting in the distortions of configuration and the reason why boundary conditions and thermostat schemes have so significant effects on distortion remain to be further explored, but a tentative explanation can be given as follows.

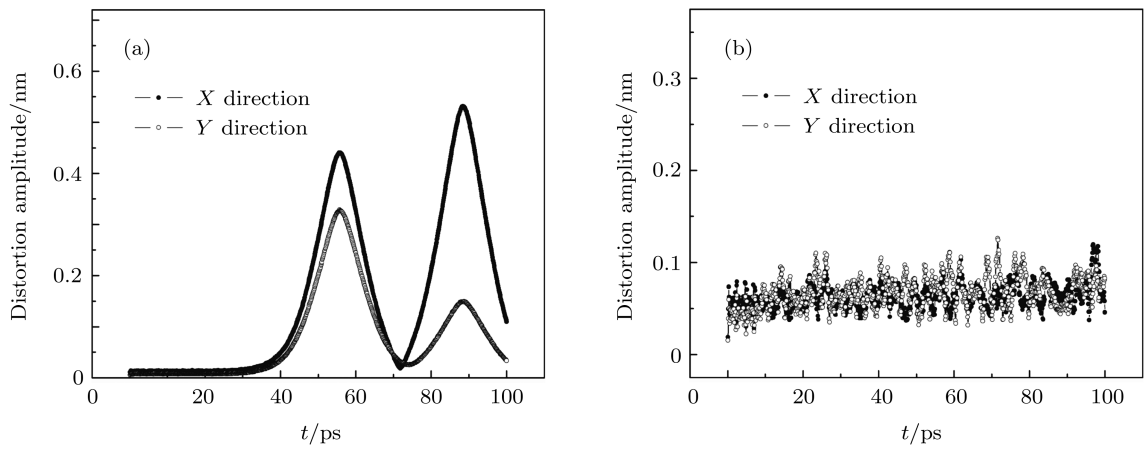


Fig.5. Magnitudes of distortion along the axis (X and Y) directions of SWCNT, where the results are taken from two simulations, with the same velocity scaling scheme but different boundary conditions applied; panel (a) is for the simulation result with periodic boundary condition and panel (b) is for simulation result of CNT with a finite length; the distortion is greatly depressed by changing the boundary conditions.

It is universally received that in MD simulations atomic trajectory in phase space may gradually deviate from accurate solutions due to numerical errors in integrating the equation of motion. If the deviations are unevenly distributed along the axial direction of the nanotube, configuration distortion will occur. The use of periodic boundary conditions along the axis of a nanotube implies that a constraint has been applied to the atoms near borders because the atoms on two sides of simulation cell must satisfy continuity and periodic conditions, whereas the atoms far from borders are subjected to less constraint. As a result, distortion starts from the place with inconsistent constraint. When the generalized Langevin thermostat is applied, computational errors as mentioned above can be reduced or removed by introducing random forces, which may convert a systematic deviation into more randomly distributed errors.

3.4. Effect of length-to-diameter ratio

The effects of diameter of SWCNT and length-to-diameter ratio are discussed in this section. First, an SWCNT (5,5) with a shorter length (12.2 nm) corresponding to a length-to-diameter ratio 18.4, is simulated at 1 K and 300 K by using the four thermostat schemes as mentioned above and the same periodic boundary conditions, separately. The distortion amplitudes along the axis of nanotube, obtained from the simulations, are plotted in Fig.6(a) as a function of simulation time. The results at both 1 K and 300 K show no apparent distortion in all cases of four thermostat schemes. Compared with the results obtained from a (5,5) SWCNT with a length of 24.5 nm, it is clear that the occurrence of configuration distortions and vibrations is a phenomenon dependent on length-to-diameter ratio, and longer nanotubes have more chances to be distorted by numerical errors. Next, simulations are performed for a (10, 10) SWCNT, whose diameter is larger than that of (5,5) SWCNT, with lengths given as 49.1 nm and 61.4 nm, corresponding to the length-to-diameter ratios 37.0 and 46.0 respectively, to examine the influence of nanotube diameter. The other conditions including temperature, thermostat scheme and boundary condition, are the same as those in (5,5) SWCNT simulation. As can be seen from Fig.6(b), in the case with a length-to-diameter ratio of 37.0, the simulation result for (10, 10) SWCNT is the same as that for (5,5) SWCNT: the simulation result for (10,10) SWCNT shows no apparent distortion and vibration. Extending the length of (10, 10) SWCNT to 61.4nm, and using a larger length-to-diameter ratio than that in (5,5) SWCNT, the simulation result for (10,10) SWCNT shows that only slight distortions can occur. The above results indicate that numerically induced distortions and vibrations appear only in the simulation results of carbon nanotubes with a small diameter and large length-to-diameter ratio, with certain thermostat schemes applied, such as the velocity scaling, the Berendsen scheme, and the Nose–Hoover scheme.

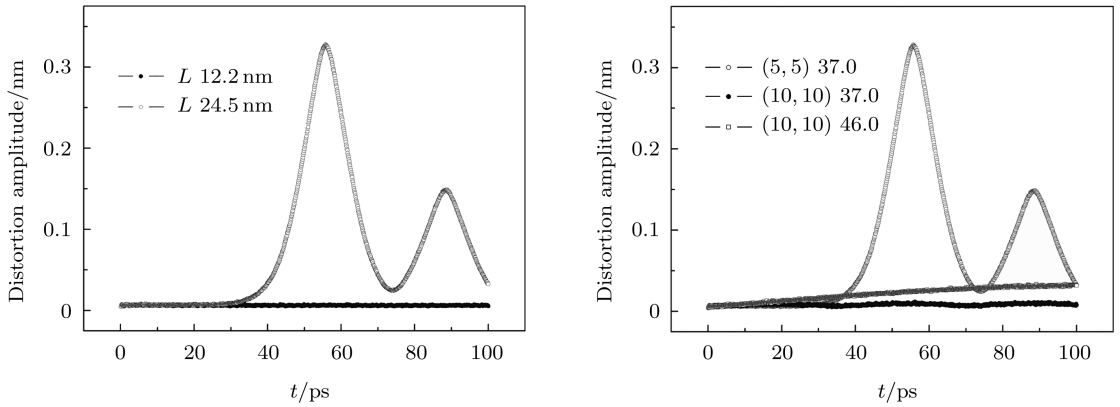


Fig.6. Magnitudes of distortion along the Y axis direction from the simulations of (5,5) and (10,10) SWCNTs, where panel (a) is for a comparison between the result for (5,5) SWCNT with a length of 12.2nm and the result for (5,5) SWCNT with a length of 24.5 nm; panel (b) is for a comparison between the result for (5,5) SWCNT with a length-to-diameter ratio 37.0 and the results for (10,10) SWCNTs with two different length-to-diameter ratios, i.e. 37.0 and 46.0.

4. Conclusion

In this paper, molecular dynamics simulations of SWCNT are performed at 1 K and 300 K with temperature controlled thermostats, such as the velocity scaling, the Berendsen scheme, the Hose–Hoover scheme, and the generalized Longevin scheme separately. The result for (5,5) SWCNT with a length of 24.5 nm shows apparent distortions in nanotube configuration, which can further develop into periodic vibrations, except for the simulation result obtained by using the generalized Longevin thermostat where no apparent distortion and vibration are observed.

The cause can be traced to the periodic boundary conditions used in simulations, which may be implicitly applied in the form of an inconsistent constraint along the axis of the nanotube, and the combination of the inconsistent constraint with cumulated numerical errors leads to the configuration distortions. When the generalized Langevin thermostat is applied, however, inconsistently distributed numerical errors are dispersed by random forces so that the distortions and the vibrations disappear. This speculation is confirmed by simulating nanotubes without periodic boundary conditions, i.e. by simulating nanotubes with a finite length. The simulation result shows no apparent distortion and vibration.

It is also revealed that numerically induced distortion is a phenomenon dependent on diameter and length-to-diameter ratio. The distortion and the vibration occur only in simulations when the diameter of nanotube is small, the length-to-diameter ratio is large, and a certain thermostat scheme is used.

In this paper, we investigate only a special system of carbon nanotube with a long length and small diameter, but the discussion here would be useful in MD simulation. The most important message presented in this paper is that when MD simulation involves a system with a special structure or geometry, attention should be paid carefully to avoiding the numerical distortion and the result infidelity.

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