Atomistic simulations of cantilevered single-walled carbon nanotubes as nanomechanical resonators

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The properties related to mechanical wave propagation in carbon nanotubes support advanced applications as nano-mechanical resonators. This study deals with molecular dynamics simulations of cantilevered carbon nanotubes considered as mass detectors. The shift of the resonance frequency is calculated versus the attached extra-mass to carbon nanotubes model of 2200 atoms. We found that the modified Morse potential leads to the mass detection limit of 7.5×10^{-22} g and to a high efficiency computation needed for large atomistic models. The influence on the frequency shift determined by the position of the extra-mass along the single-walled carbon nanotubes was taken into account.

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1. Introduction

Resonators have been extensively used as mass sensitive transducers in high-performance sensors and have been refined over several decades [1]. The principle of mass detection is based on the correlation between the resonance shift and the attached extra-mass to the sensor [2].

Mass sensitivity of current electro-mechanical transducers has nearly reached their theoretical limits [3]; however, micromechanical resonators have received much attention [4]. Reduction the size of the resonator enhances the resonant frequency together with its sensitivity. The more the resonators are scaled down, the higher their sensitivity to attached mass will be and nanoscale sensors may meet the high-performance requirement of many applications, as mechanical mass or charge detectors [5]. It is expected that individual carbon nanotube (CNT) would make excellent femto-balances. The idea of using multiple walled carbon nanotubes (MWCNTs) for this purpose was first suggested by Poncharal et al in 1999 [5], and in the recent years, it has gained wide interest [6]. Recent papers describe experimental setups based on cantilevered and bridged carbon nanotubes [7,8].

Since their discovery, CNTs have attracted a lot of scientific interest due to their unique structural, mechanical, and electronic properties; and they are expected to be used in various fields of nanotechnology and materials science. Many of these applications are closely related to their mechanical properties, such as the propagation of mechanical waves along the nanotube [9]. It is predicted that the fundamental frequencies of cantilevered or bridged single-walled carbon nanotubes could reach 10 GHz – 1.5 THz frequency interval, depending on the nanotube diameter and length. This fundamental frequency is much higher than the highest frequency silicon-based nano-mechanical resonator [10].

This paper presents molecular dynamics simulations on cantilevered single wall carbon nanotubes, modelling them at atomistic scale, with various attached extra-masses, ranging from 10^{-23} g to 10^{-14} g (10^{-8} fg to 10 fg). We investigate the effect of the extra-mass location and distribution along the nanotube. The spectacular experiments based on cantilevered MWCNT [7,16] increase the interest for efficient an accurate approaches to simulate and design nanoscale mechano-electric sensors built by very large atomic assemblies of $10^4 – 10^7$ atoms. We apply and test modified Morse potential on simulating elastic waves and vibration properties of SWCNT of 2200 atoms, looking for high efficient calculations at an acceptable level of accuracy.

2. Computation methods

The simulations are carried out using the classical molecular dynamic method, solving Newtonian equations of motions for individual atoms using the velocity-Verlet algorithm. The study uses an original developed package, which gives efficient and accurate computations according to semi-empirical potential of inter-atomic interactions.

The modified Morse potential of the inter-atomic interactions is defined by the expressions (1) and (2). They represent the energy of the bond stretching E_{str} and of the bond-angle bending E_{ben} respectively, where "r_{ij}" is the distance between atom i and j, "r_0" is the C-C bond length at equilibrium, θ_{ijk} is the angle described by the bonds between atoms i-j and j-k, "β" is the parameter influencing the profile of the interaction potential. The matrix elements as P_{ij} and S_{ijk} nominate the atoms defining bonds and angles. This approximation neglects the weak contribution given by the changes of the dihedral angles to the total energy considered as the sum of E_{str} and E_{ben}.

$$E_{str} = E_0 \sum_{ij} \left\{ \left[1 - \exp\left(-\beta \left(r_{ij} - r_0 \right) \right) \right]^2 - 1 \right\} P_{ij} \qquad (1)$$

$$E_{ben} = \sum_{ijk} \frac{1}{2} K_\theta \left(\theta_{ijk} - \theta_0 \right)^2 \left[1 + \gamma \left(\theta_{ijk} - \theta_0 \right)^4 \right] S_{ijk} \qquad (2)$$

We found that the values of the parameters proposed by Belytschko [11] lead to results on vibrational properties of SWCNT in acceptable agreement with experimental data as it is presented in section 2.1

2.1. Atomistic model and simulation approach

The parameters values of the inter-atomic potential of the expressions (1) and (2) used in this study are: $r_0 = 1.39$ A, $E_0 = 3.75$ eV, $\beta = 2.625$ A^{-1}, $\theta_0 = 2.094$ rad, $k_\theta = 5.625$ eV/rad^2, $\gamma = 0.754$ rad^{-4}. Beyond the application of the modified Morse potential to carbon nanotubes fracture [11] we use it for the computation of their vibration modes frequency. Good agreements between calculated breathing mode vibrations of SWCNT and Raman experimental data [12] have been obtained. Table 1 gives some representative examples. On the other hand, this potential type assures very efficient computations for large atomistic models being about an order of magnitude faster than those based on Brenner potentials [13].

Table 1. The breathing mode frequency of SWCNT.

SWCNT Diameter [Å]	Frequency calculated (this work) [cm^{-1}]	Experiment data [12] [cm^{-1}]
6.8	350	312
10.86	179	180
14.92	130	135

The calculations simulate experiments on exciting resonances in cantilevered SWCNT. The excitation frequency is applied at the "left" end where the tube is anchored to a vertical vibrating wall, while the right end is free. The forced oscillation of the tube movement is stopped after a few periods (amplitude 6.8 Å). The transversal frequencies are obtained after a relaxation interval of 50 ps, and continued over an interval of 1 ns of free oscillation of the cantilevered SWCNT. The resonance frequencies were calculated by applying Fourier transform to the time-position data of the mass-center of the selected tube unit cells. An extra-mass with a value ranging from 10^{-8} fg to 10 fg may be rigidly attached to the nanotube during the simulation. This mass is distributed uniformly over seven consecutive unit cells (140 carbon atoms) of (5, 5) SWCNT; i.e. the masses of these atoms are increased so the total mass increase over those cells is equal to the desired extra-mass. The system was considered thermally isolated in respect to the absorption and dissipation of heat during its free oscillations simulated for 1 ns.

3. Results and discussion

The SWCNT cantilever resonance frequencies versus the aspect ratio were calculated and compared with those obtained by using a different approach based on molecular structural method. It determines the normal frequencies by solving eigenvalue equation related to condensed stiffness matrix [9].

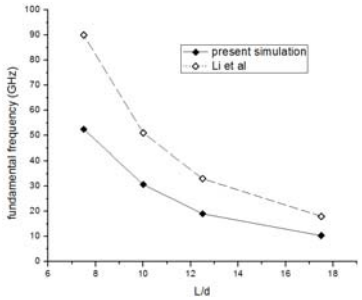
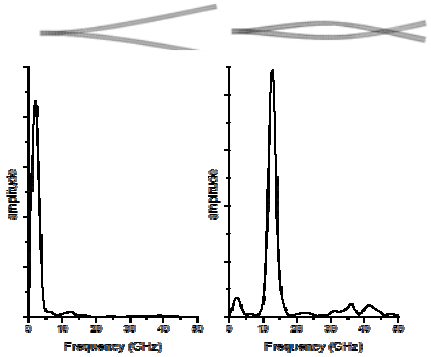


Fig. 1. The resonance frequency of cantilevered SWCNT versus L/d ratio.(this work and ref.[9]).

Fig. 1 shows that the differences are remarkable for values of L/d ratio lower than 15. The discrepancies become acceptable at an aspect ratio greater than 30.



(a) (b)

Fig. 2. Frequency spectrum of transversal oscillations in a cantilevered (5, 5) SWCNT excited by the forced vibration of the fixed end at a) 2 GHz and b) 14 GHz. The oscillator works at an amplitude of 6.8 A. The geometry of the tube deformation for both resonances are shown in the inserted diagrams.

However, the L/d ratio is 40.15 in the case of the SWCNT model we use, consequently the resonance frequency should agree well with that obtained by molecular structural method [14] considering the interpolated region above the limit the of the available data of Fig. 1.

The vibrations of the electrically charged MWCNT where induced by an electromagnetic wave at resonance [15, 16] or by an oscillating electric field [17]. In this study, the excitation of resonance vibrations were simulated by considering forced oscillations of the fixed

tube end, having a rigid bond to a vibrated wall that could be piezoelectric substrate.

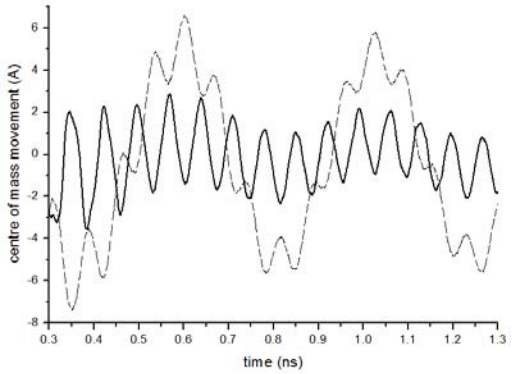


Fig. 3. Time dependence of the mass-centre oscillation corresponding to two unit cells of (5, 5) armchair SWCNT. Their position are at 74 Å and 236 Å respectively from the fixed margin of the tube.

Two frequencies were used, 2 GHz and 14 GHz, for the excitation of the corresponding resonances. Fig. 2 shows spectra obtained by *Fourier transform* method of position - time dependency related to the movement of the mass centre of (5, 5) SWCNT unit cells placed at a distances of 74 Å and 236 Å from the fixed margin. Fig. 3 shows the corresponding waveforms of each mass-center, revealing the tube excitation. The inserted diagrams in Fig. 2 a) and b) indicate the two motions of SWCNT, excited to vibrate mainly at 2.28 GHz and 14.15 GHz respectively. Another vibration mode at 42 GHz has enough energy to be "detected" (Fig. 2b) being associated to the cross-sectional deformation, shown by the arrow in Fig. 4.

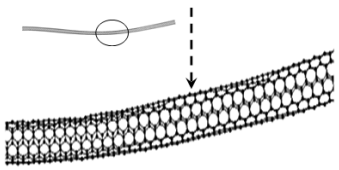


Fig. 4. Snapshot of SWCNT vibration excited at 14 GHz, corresponding to the spectra of Fig. 2b. The loop and the arrow indicate the cross section deformation vibration mode found at 42 GHz.

We investigate the capability of extra-mass detection by rigidly attach it to the carbon nanotubes in a way described in Section 2. The mass is positioned either at the centre of the tube (at equal distance from both ends), or close to the free end, at about 218 Å from the fixed margin.

The shift of the resonant transversal mode at 14.15GHz versus the attached mass, ranging between 10^{-8} fg and 10 fg, is given in Fig. 5 a. Below 7.5×10^{-7} fg, the frequency shift is negligible. The transversal deformation mode stays around 14.15 GHz. for masses up to 7.5×10^{-7} fg (about 2% of the total mass of the carbon nanotube) and decreases monotonically up to about 1 GHz as the added weight increases to 10 fg.

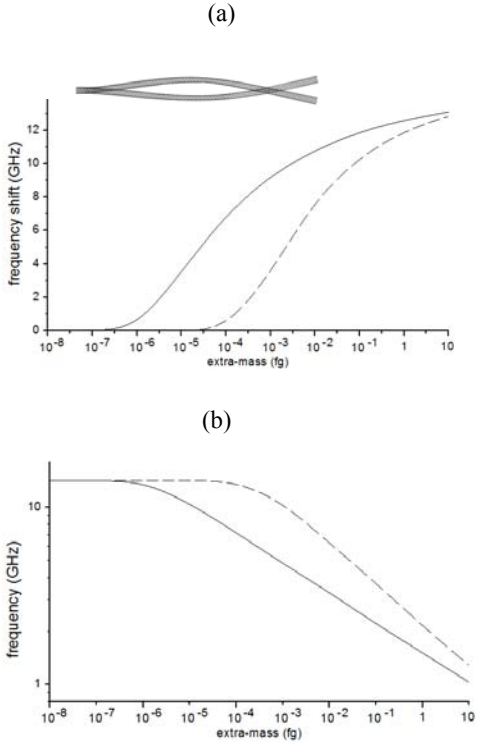


Fig. 5. a) Resonance frequency shift versus the extra-mass positioned at the middle of SWCNT (solid line) and close to the free end, at 218 Å from the fixed extremity (dashed line) in the case of vibration mode at 14.15 GHz shown in the inserted figure. b) Logarithmic scale of frequency indicates a linear dependence versus the extra-mass also represented on the logarithmic scale.

This mass detection limit of about 10^{-21} g is almost the same as that reported for other SWCNTs, but much shorter than the present model [6,14]. The obtained data followed a linear dependency between the logarithm of the resonator frequency "*v*" versus the logarithms of the extra-mass "*m"* for a value exceeding 10^{-5} fg, being in very good agreement with the outputs of other type of approaches [6,14]: $\log v = a \log m + b$. The data fit of Fig. 5b leads to $a = -0.169$ and $b = 0.179$. The values of *a* and *b* depend on geometrical parameters of the nanotube resonators. The above results must be corrected in the case of changing the extra-mass position. Specific experimental conditions, facilitating non-uniform distribution of the extra-mass can be effective. The broken chemical bonds at the open end of the carbon nanotubes it is a natural cause to enhance the attachment of molecules at the tube margin. In Fig. 5, the transition from the continuum curve to the dashed one is done by moving the extra-mass from the middle of SWCNT to its the free end, at 218 Å from the fixed extremity, representing about 80% of the tube length. In this case the detection limit changes to extra-masses greater than 10^{-4} fg. The dependency of the resonant

frequency versus the extra-mass position along the tube, ranging in between 20% and 80% of its length was calculated for a fixed additional mass of 10^{-5} fg (see Fig. 6). The output of the computations shows that the cantilevered carbon nanotube reaches the highest sensitivity if the mass is attached near the half of the length, where the difference relative to the reference frequency is 3.65 GHz representing 25.8% of the initial value. The increasing of the resonance frequency shown for pushing the extra-mass from the middle to the free end of the tube, partially mimic the double clamped SWCNT having the corresponding resonance calculated at 26.4GHz. The gravitation force was not taken into account. The random distribution of the attached molecules along the tube seems more realistic when SWCNT is exposed to the gas phase [7]. It is interesting to mention that if the mass of 10^{-5} fg is distributed uniformly along the entire length of the nanotube, the resonant frequency shifts from 14.15 GHz to 12.55 GHz in agreement with the average value of the data of Fig. 6.

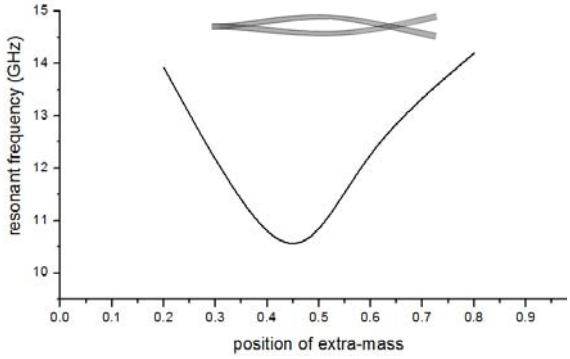


Fig. 6. Resonance frequency of cantilevered SWCNT excited at 14GHz versus the position of the extra-mass of 10^{-5} fg. The location of added mass along the tube is given in proportion of the whole length.

4. Conclusions

We simulated excited resonance oscillations in a cantilevered SWCNT model of 2200 atoms by using molecular dynamics and considering attached additional mass. The outputs of the original package are in acceptable agreement with experimental data [12] and with other theoretical results obtained under different approaches [14]. It proves that the modified Morse potential give acceptable results regarding elastic wave propagation in SWCNT with an aspect ratio greater than 20, facilitating a good computational efficiency for large atomistic models. In the case of cantilevered SWCNT of 27.3 nm in length we found the limit of mass detection at 7.5×10^{-7} fg. The modification of the frequency shift versus the position of the extra-mass was calculated for the vibration mode at 14GHz of the pristine carbon nanotubes.

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