Simulations of nanosensors based on single walled carbon nanotubes

Polina Pine[1], Yuval E. Yaish[2] and Joan Adler[3]

[1]RBNI, Technion-Israel Institute of Technology, 32000, Haifa, Israel
[2]Department of Electrical Engineering, Technion-Israel Institute of Technology, 32000, Haifa, Israel
[3]Department of Physics, Technion-Israel Institute of Technology, 32000, Haifa, Israel

E-mail: pine@tx.technion.ac.il

Abstract. The potential of single-walled carbon nanotubes as mass sensors is examined. The change in mass leads to proportional changes in the nanotube vibrational frequencies, which are monitored during atomistic simulations. We observed a frequency shift as a result of replacement of carbon C_{12} with its isotope C_{13}. For a zigzag (12,0) nanotube of about 10 nm length, we found zeptogram sensitivity.

1. Introduction

There is a growing interest in biological application of carbon nanotubes (CNTs) [1, 2, 3, 4] especially for medical technology [5] and sensors [6, 7]. These can be broadly classified into two categories: chemical sensors [8] and biosensors [9, 10, 11] and include ultrasensitive nano-bio sensors [3], electroanalytical nanotube devices [4] and electromechanical actuators for artificial muscles [12]. The development of nano-bio sensors [13] and nanoscale bioreactor systems based on CNTs has been driven by the experimental evidence that biological entities such as proteins, enzymes, bacteria can be immobilized either in the hollow cavity or on the surface of carbon nanotubes [1, 2]. In the light of successful fabrication of various nanotube devices, prepared as single walled carbon nanotube (SWCNT) transistors, significant success has been achieved in attempts to use CNTs as superior biosensor materials. They have shown promising sensitivities required for such applications as antigen recognition [14], enzyme-catalyzed reactions [15] and DNA hybridizations [16].

Resonance based sensors offer the deeper potential of achieving the high-fidelity requirement of many sensing applications. The key issue of mass detection is in quantifying the change in the resonant frequency due to the added mass. There are some early studies [17, 18, 19] in this young and rapidly developing field, but there is a lack of systematic basic research, and especially of atomistic studies. These enable modeling of such systems that are as close as possible to the real atomistic behavior.

2. Motivation and previous studies

Chowdhury *et al* [17] examined the potential of single-walled carbon nanotubes (SWCNTs) as mass sensors, using a continuum mechanics based approach based on the Euler-Bernoulli(EB) beam theory [20] and Finite Element Analysis (FEA). The carbon nanotube resonators were

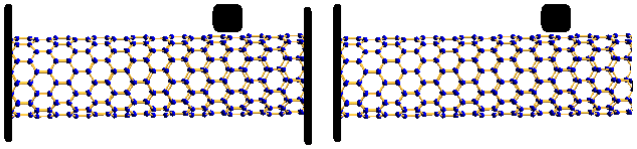

Figure 1. SWCNT with attached mass in a bridged configuration at left and a cantilevered configuration at right.

assumed to be either in bridged (doubly clamped) or in cantilevered (clamped at one end) configurations with an attached mass in the atomic systems as depicted schematically in Fig. 1. The length of the CNTs studied in [17] was 8 nm and the length of the biological attached mass varied between 0.5 - 3.5 nm. It was observed that the proposed sensor-equations work reasonably well when the length of the bacteria is more than 1 nm for both cantilevered and bridged configurations. The numerical results indicated that the mass sensitivity of carbon nanotube-based nanobalances can reach up to 10^{-24} kg.

Joshi *et al* [18] presented a FEA simulation of the mechanical responses of individual carbon nanotubes treated as thin shells with a thickness based on Chowdhury *et al* [17]. The resonant frequencies of the cantilevered and the bridged SWCNT were investigated. This analysis explores the resonant frequency shift of SWCNTs caused by the changes in the size of the CNT as a function of length as well of mass. They found sensitivity of the SWCNTs to different masses and different lengths. The mass sensitivity could reach 10^{-24} kg and it increases when smaller size nanotube resonators are used in mass sensors as predicted by EB beam theory.

The study of Aydogdu *et al* [19] is the most detailed until now. They studied axial vibrational behavior of single-walled carbon nanotube-based mass sensors using nonlocal elasticity theory. Carbon nanotubes with different lengths, attached masses and their positions on the CNTs, as well as different boundary conditions (cantilevered or bridged) were considered. They showed that for the cantilevered CNTs the frequency decreased with increase of the mass distance from the point of CNT clamping, however for the bridged ones the frequency change symmetrically with respect to the midpoint of the SWCNT where the minimum frequency is obtained. They found a sensitivity of nanotube-based mass sensors in the zeptogram range.

In one of our earlier papers, denoted below as I, [21] we observed some problems with EB theory for doubly clamped CNTs for certain length and radius choices including some of the values in the above studies. In another, paper II, [22] we showed that while choice of nanotube symmetry is not a relevant parameter if the CNT is doubly clamped, under partial clamping, (paper III [23]) we showed that vibrational symmetry is broken. Thus the continuum models described above do not tell the full story and an atomistic approach is needed. In the present study, because the mass distribution is not uniform in all cases this is even more crucial.

3. Details of the simulation method

In our atomistic approach [21, 22, 23] we calculate the thermal vibrations of SWCNTs using molecular dynamics (MD). In each case we generate high quality data with MD simulations using the Brenner [24] potential on carefully equilibrated clamped tubes. The thermal vibrations were decomposed into different modes. In order to keep temperature constant a Berendsen thermostat [25] was applied. To ensure stable nanotube structure and eliminate intrinsic tension, we collected data after a period of slow initial thermalization to 300K (periodic boundary conditions with no frozen edges) waiting until the length of the equilibrated nanotube remained constant up to insignificant fluctuations. This relaxed nanotube has no tension but in a study currently underway we are exploring the implications of introducing tension into the tube. In order to

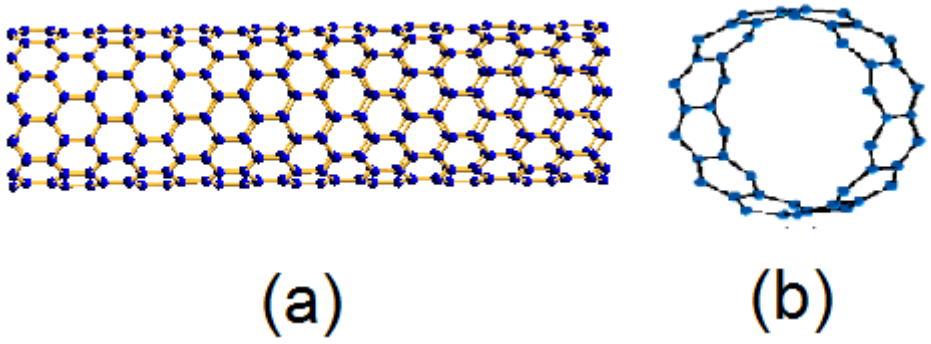

Figure 2. (a) (12,0) zigzag SWCNT; (b) a single period.

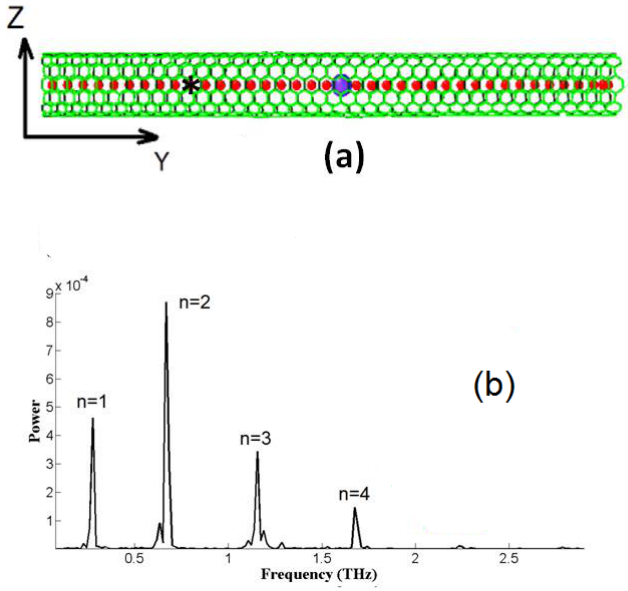

Figure 3. (a) Single Walled Carbon Nanotube (green), with the CA made up of the centers of mass of each period of the nanotube as (red) spheres inside the nanotube, and a (blue) large atom to indicate its CM. The $*$ marks one place where all the first 4 modes have finite amplitude; (b) FFT analysis of the first four thermal vibrational modes (n=1-4) in the Z direction at this point at 300K, under doubly clamped conditions.

obtain adequate statistics for all vibrational modes we let every nanotube vibrate 1000 times more than the period of its lowest frequency, using a MD timestep of 0.5 fsec. In order to reduce the amount of data needed for the vibrational analysis we selected some special points where data was recorded. The centers of mass (spheres inside the nanotube in Fig.3(a)) for each period were identified, making up a line of points which we call the centered axis (CA). The center of mass (CM) of the entire nanotube (large sphere in Fig.3(a)) falls in the middle of this line. We then applied a fast fourier transform (FFT) analysis to the data from the selected points, (including one near the center of mass) to calculate the power density as a function of frequency (see Fig.3(b)).

In paper I [21] we reported carefully equilibrated MD simulations of doubly clamped armchair SWCNTs including a precise analysis of the four lowest modes of vibrations. We provided clear evidence for the failure of simple analytic models such as Euler-Bernoulli to accurately extract resonance frequencies as the ratio, (R/L), between the tube radius (R) and the length (L) increases. Our results were in excellent agreement with the Timoshenko beam [26] model, which includes the effect of both rotary inertia and of shearing deformation. Invoking the EB model implies that the bending rigidity (which includes the product of the Young's modulus, E, and the nanotube wall thickness) is constant. We showed that if λ_n is the wavelength of the nth mode, for larger values of R/λ_n this is most definitely not true. Yakobson's paradox [27], relates to a scatter of between 1 and 5 TPa in the Young's modulus from atomistic simulations. We shed light on this by giving an upper cutoff estimate for the effective SWCNT thickness, and showed that in the Timoshenko model, there are two different sources for the nanotube thickness. The issue of nanotube thickness, was also addressed by [28] from a different viewpoint and our E and thickness results are in good agreement.

In an attempt to determine whether the nanotube type affects vibration we reported in II [22] on the vibrational behavior of four different types of SWCNTs: armchair, zigzag and two different chiral ones. All were fully clamped at both ends as in our previous study I [21]. Comparison between the vibrational behavior of these four types of nanotubes gave the result that the SWCNT structure does not affect the vibrational frequencies under these conditions.

Doubly clamped nanotubes of all three types exhibit the same vibrational modes, and their vibrations in the directions perpendicular to the nanotube axis are degenerate. In nanotube applications such as sensors based on nano-electro-mechanical systems their ends are not fully clamped, thus their vibrational behavior could differ. In paper III [23] we studied SWCNTs with boundary conditions which imitate the partly clamped experimental conditions. Our results demonstrate that armchair, zigzag and chiral nanotubes indeed vibrate differently. The symmetry between the two perpendicular directions is broken, and the SWCNT type does then influence the vibrational modes.

4. Simulation model for mass change

Using the approach described above, we have now carried out atomistic simulations of a vibrating nanotube suitable for use in sensors based on (12,0) 110.76 $\mathring{A}$ zigzag carbon nanotube (see Fig. 2(a)). This CNT consists of 24 periods (see Fig. 2(b)). Two first/last periods were frozen in order to retain bridged boundary conditions, giving a 91.96 $\mathring{A}$ vibrating length. We first calculated the frequencies of first four modes of the unloaded nanotube. This result was published in I.

Our carbon atoms in the previous studies were assumed to be the usual C_{12}. Since the concept of the nanosensor application is based on the possibility of measuring adsorbed masses, the first step towards the proof of concept, is showing that additional masses can be accurately measured. In our simulations based on classical MD potentials, introducing adsorbed atoms or molecules of different types would require careful evaluation of additional parameters of interactions. Hence we chose to use a different isotope where to a good approximation the interatomic potential would only need to be adjusted for the different nuclear mass. Thus in order to simulate attached mass we decided to change some carbon atoms to the isotope C_{13}, changing the mass of segments of the SWCNT and calculating vibrational frequencies of nanotube with some periods replaced with C_{13}.

The weight of a single C_{12} is 12 amu and of C_{13} is 13 amu which is equivalent to $1.9926466 \cdot 10^{-23}$ gr and $2.1587005 \cdot 10^{-23}$ gr respectively. Changing the whole vibrational segment (20 periods) to isotope C_{13} would give us a theoretical resolution of $1.5941174 \cdot 10^{-21}$ gr, see Table 1. This zeptogram sensitively is in agreement with that reported by [17, 18, 19].

Table 1. Mass resolution in grams due to replacement of C_{12} with C_{13}.

periods	num. of atoms	Δm
1	48	$7.9705872 \cdot 10^{-23}$
2	96	$1.5941174 \cdot 10^{-22}$
3	144	$2.3911762 \cdot 10^{-22}$
4	192	$3.1882349 \cdot 10^{-22}$
20	960	$1.5941174 \cdot 10^{-21}$
24	1152	$1.9129409 \cdot 10^{-21}$

Table 2. Changes in vibrational frequencies (THz) of first four modes as a result of isotope replacement.

n	C_{12} (all atoms)	C_{13} (4 periods)	C_{13} (all atoms)
1	0.2686	0.2686	0.2604
2	0.6429	0.6429	0.6185
3	1.107	1.107	1.074
4	1.609	1.595	1.546

5. Results and discussion

The road to predicting the actual change of frequencies is somewhat complex, as fitting to the correct Timoshenko model is an iterative process, requiring a set of different lengths/radii, and cannot be done for other than fully clamped boundary conditions anyway. Thus we decided to measure the frequencies directly. The results for three cases are presented in Table 2. When the isotope C_{13} is inserted only in the first four periods it does not noticeably affect the frequencies, although a slight change is seen in the 4th mode. The replacement of all atoms of the nanotube gives a significant effect as can be seen from Table 2. Since a very few atoms gave no clear change above the numerical error it would be desirable to determine what minimal load, or number of substituted atoms is needed in order to obtain a differential response for all four modes.

6. Conclusions

Our current results are only the beginning of a detailed investigation of the mechanism of action of resonant sensors based on SWCNTs. In future we plan not only to change isotopes to those heavier than C_{13} but also to study the vibrational behavior of nanotubes with mismatches, i.e. with defects (without atoms in specific points of nanotube). We also plan to attach different molecules to the nanotube's surface and study vibrational changes and sensing limitations of such devices.

7. Acknowledgements

We thank the organisers of CCP2011 for the opportunity to present these results and the Russell Berrie Nanotechnology Institute for support via the NEVET program, use of the NANCO computer, and a fellowship for P.P. Y.E.Y thanks the ISF (grant number 1334/06) for support. P.P. thanks the Ramon foundation and the Israel Industrial club for financial support.

References

[1] S. C. Tsang, J. J. Davis, M. L. Green, H. A. O. Hill, Y.C. Leung and P. J. Sadler, J. Chem. Soc., Chem. Commun, **17** 1803 (1995)

[2] J. Davis, M.L.H. Greena, H. A. O. Hill, Y. C. Leung, P. J. Sadler, J. Sloan, A.V. Xavier and S. Chi Tsang, Inorganica Chimica Acta **272** 261 (1998)
[3] R. Baughman, C. Cui, A.A. Zakhidov, Z. Iqbal, J.N. Barisci, G.M. Spinks, G.G. Wallace, A. Mazzoldi, D. De Rossi, A.G. Rinzler, O. Jaschinski, S. Roth M. Kertesz Science **284** 1340 (1999)
[4] M. Mattson, R. Haddon and A. Rao, Journal of Molecular Neuroscience **14**,175 (2000)
[5] F. Lu, L. Gu, M. Meziani, X. Wang,P. G. Luo, L. V. Veca, L. Cao and Y-P. Sun, Advanced Materials **21** 139 (2009)
[6] Y. Lin, S. Taylor, H. Li, K. A. S. Fernando, L. Gu, W. wang, L. Gu, B. Zhou and Y-P. Sun, Journal of Materials Chemistry, **14** 527 (2004)
[7] L. Gu, T. Elkin, X. Jiang, H. Li, Y. lin, L. Qu, T-R. J. Tzeng, R. Joseph and Y-P. Sun, Chemical Communications **7** 874 (2005)
[8] J. Wang and M. Musameh, Analytical Chemistry **75** 2075 (2003)
[9] B.L. Allen, P.D. Kichambare and A. Star, Advanced Materials **19** 1439 (2007)
[10] K. Balasubramanian and M. Burghard, Analytical and Bioanalytical Chemistry **385** 452 (2006)
[11] M. Atashbar, D. Rocha, P.M. Sarro, M.J. Vellekoop, (Eds.), Proceedings of the IEEE Sensors, vols.1-3, Vienna, Austria, October 24-27, 1048 (2004)
[12] J. Davis, K.S. Coleman, B.R. Azamian, C.B. Bagshaw, M.L.H. Green, ChemistryA European Journal **9** 3732 (2003)
[13] S. Lee and D.S. Yoon, Biochip Journal **1** 193 (2007)
[14] R. J. Chen, S. Bangsaruntip, K. A. Drouvalakis, N. Wong Shi Kam, M. Shim, Y. Li, W. Kim, P. J. Utz, H. Dai, Proceedings of the National Academy of Sciences of the United States of America **100** 4984 (2003)
[15] J. J. Gooding, R. Wibowo, J. Liu, W. Yang, D. Losic, S. Orbons F. J. Mearns, J. G. Shapter, D. B. Hibbert, Journal of the American Chemical Society **125** 9006 (2003)
[16] J. Li, H.T. Ng, A. Cassell, W. Fan, H. Chen, Q. Ye, J. Koehne, J. Han, M. Meyyappan, Nano Letters **3** 597 (2003)
[17] R. Chowdhury, S. Adhikari, J. Mitchell, Physica E, **42** 104 (2009)
[18] A.Y. Joshi, S.P. Harsha, S.C. Sharma, Physica E, **42** 2115 (2010)
[19] M. Aydogdua, S. Filiz, Physica E, **43** 1229 (2011)
[20] L. D. Landau and E. M. Lifshitz, Elasticity Theory (Pergamon,Oxford, 1986)
[21] P. Pine, Y. E. Yaish, J. Adler, Phys. Rev. B, **83** 155410 (2011)
[22] P. Pine, Y. E. Yaish, J. Adler, Phys. Rev. B, **84** 245409 (2011)
[23] P. Pine, Y. E. Yaish, J. Adler, J. Appl. Phys. **110** 124311 (2011)
[24] D. W. Brenner, Phys. Rev. B **42** 9458 (1990)
[25] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, J. Chem. Phys. **81** 3684 (1984)
[26] S. P. Timoshenko and J. N. Goodier, Theory of Elasticity (McGraw Hill, New York, 3d ed., 1987).
[27] O. A. Shenderova, V. V. Zhirnov, and D. W. Brenner, Crit. Rev. Solid State Mater. Sci., **27** 227 (2002)
[28] Y. Huang, J. Wu, and K. W. Hwang, Phys. Rev. B, **74** 245413 (2006)