A study of vibrating nanotubes with additional adsorbed masses

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Abstract.
We describe calculations of the electronic density surrounding strained nanotubes. These are then used to estimate the nanotube wall width. This width is an essential parameter for the analysis of the nanotube vibrations. By studying the effect of additional adsorbed molecules on the nanotubes’ vibrations and their frequency changes we can deduce the molecules’ mass. Our calculations show that the strain does not greatly affect the nanotube width, but the vibrations change sufficiently for the mass to be detected.

1. Introduction
Vibrating nanotubes can be used as NEMS (Nano-Electro-Mechanical Sensors) to weigh molecules such as DNA. In a series of papers [1, 2, 3, 4] we have explored Molecular Dynamical models of such sensors, and developed protocols for such calculations. One of the challenging aspects of vibrating nanotube systems is the need for an accurate value for \( h \), the nanotube wall width, and to study how it varies under local strain in the tube bending. A greatly exaggerated image of a vibrating tube, showing the strained bonds in red is shown at the left of Fig. 1. The width is needed to calculate the mass from the measured frequency, and was very controversial for a long time, concerning the way it plays a rôle in Yakobson’s paradox concerning the nanotube’s Young’s modulus. In [1, 5] a value of \( h = 0.06 \text{nm} \) was obtained by two distinct analysis approaches to data from multiple simulations. However until now, direct confirmation was not made.

An initial study of sensitivity to added mass was made in [4] where the simple procedure of replacing the \( C_{12} \) molecules with \( C_{13} \) ones showed zeptogram sensitivity. However, a direct study of actual additional atoms or molecules was not made until the present project.

In the present project the previous indirect deductions have been confirmed with explicit simulations. No surprises were found, but the road to direct measuring of the molecular mass was rockier than expected. We report below on results of a direct confirmation of the nanotube width value, for strained tubes, and describe the frequency change with adsorbed atoms. In Fig. 1 at right, we show an example of a nanotube with an added half-ring illustrating only the stretched bonds without exaggerated vibrations. In all our vibrational simulations the \( y \) axis is chosen to be along the tube and the \( x \) and \( z \) directions are perpendicular.
Figure 1. Vibrating nanotube with a top-to-bottom color gradient and extended bonds shown in red at left, nanotube with several additional rings and extended bonds in green shown at right. The scale of the vibrational amplitude is much larger than on the right.

2. Width measurement
Electronic density is three dimensional, and varies in density as functions of distance from the nucleus and of angle. In two earlier papers, calculation of electronic density surrounding nanotubes was studied within DFT by Quantum Espresso [6, 7, 8]. Its visualization was carried out in the public domain AViz (Atomistic Visualization) package [9, 10], developed at the Technion and now part of the FP7 SimPhoNy project [11]. However actual calculations of the width of the envelope surrounding the nanotube were not made systematically for different strains. An image color-coded for different levels of electronic density is shown in Fig. 2 for a single ring and an image with a color coding selected for stereo viewing is shown at right.

We explored how (and if) the width changes for different strains. In Fig. 3 we show the maximum thickness as a function of strain at left and the thickness as a function of density at right. There is very little change in thickness, if anything an increase as strain increases. We hypothesize that this is due to the increasing distance between the positive nuclei (on the y axis) which makes the attractive electrostatic force weaker (on the radial x and z axes) per length unit. In the right frame of the same figure we show that the maximum reaches close to the $h = 0.06$ nm that was calculated.

3. Change in frequency for additional mass
This section of our study was less straightforward, because after success with substitutional changes in mass in [4] we were unprepared for the event that external adhesion to a vibrating tube would not be so simple. We found that narrow vibrating tubes with a high curvature tend to shake off their burdens. Our experimental collaborators, found similar issues and they suggested decreasing the nanotube’s curvature. This led to a delay while revalidating the code and analysis for much thicker tubes. Once this was achieved progress was quite rapid. One wide tube, with an attached half ring of carbon atoms was shown in Fig. 1 above. A full discussion of testing several attached configurations can be found in [13]. Unless an entire ring is added as was the case in [5], where there was clear evidence of a decrease in frequency with an increase in weight, the symmetry between the x and z directions is broken, so we have less statistics for
Figure 2. Left: Electronic density of a nanotube with a color key, showing a dense image at upper left and a diluted one at lower left; Right: AViz stereo image (with different color code selected for stereo visibility) of density above $0.0005a_0^{-3}$, where $a_0$ is the Bohr radius.

Figure 3. Maximum thickness as a function of density at left and thickness as a function of density for a strain of 2.5%

Each case, as behavior can differ in the perpendicular directions. There are also considerations of a possible increase in frequency due the contact area between the added rings and the nanotube and a resultant change in elasticity. Numerical estimates for these predictions are given below and details can be found in [13].

One especially interesting case is the study of several different half ring attachments on a (30,30) armchair nanotube with 15060 C atoms. The nanotube was prepared in the same manner as the thinner ones [1], but needed to be longer to vibrate well. The frequency was analysed with a MATLAB code [13] that took its Fourier transform and gave a spectrum of resonance frequencies. The code validation for a long but thin unadorned tube showed that this bare tube
Figure 4. Two nanotubes with additional half rings shown in contrasting colors.

Figure 5. Values of the lowest frequencies in the $z$ direction on the left and $x$ direction on the right.

| Number of atoms | No mass | 2 rings | 3 rings | 4 rings | 5 rings |
|-----------------|---------|---------|---------|---------|---------|
| Mass [Kg]       | 0.000E+00 | 3.120E-24 | 4.680E-24 | 6.240E-24 | 7.800E-24 |
| Original Theory [Hz] | 8.547E+10 | 8.503E+10 | 8.481E+10 | 8.459E+10 | 8.437E+10 |
| Improved Theory 1 [Hz] | 8.547E+10 | 8.422E+10 | 8.362E+10 | 8.303E+10 | 8.245E+10 |
| Improved Theory 2 [Hz] | 8.684E+10 | 8.421E+10 | 8.298E+10 | 8.181E+10 | 8.068E+10 |
| Simulation (X axis) [Hz] | 8.545E+10 | 8.423E+10 | 8.301E+10 | 8.179E+10 | 8.057E+10 |
| Simulation (Z axis) [Hz] | 8.789E+10 | 8.545E+10 | 8.545E+10 | 8.423E+10 | 8.423E+10 |

Figure 6. Table of frequencies for different masses under several versions of theoretical predictions.

had a frequency response that extrapolated nicely from the values found for the thinner tubes in [1, 12].

Attachments of half rings with 78 atoms each were placed at different places along the tube, see two realizations in Fig. 4. From many cases [13] we show graphs of the lowest frequencies in the $x$ and $z$ directions for different numbers of additional half rings in Fig. 5. Despite the differing amplitudes, we observe a clear trend that the frequency decreases as adsorbed mass increases. In Fig. 6 we show tabulated results for the lowest mode for number and mass of atoms, compared with theoretical predictions of several variants of Euler-Bernoulli-Timoshenko theoretical predictions [13] introduced above. $x$ and $z$ directional variations are a slight complication. By comparison with the theory we can deduce the added mass and and thereby “weigh” the additional rings.

4. Some asides relating to SimPhoNy

The nanotube vibration study is one of the flag-bearing cases for SimPhoNy, whose raison-d’etre is to streamline simulation modelling for experimental applications. The SimPhoNy concept is
that “wrappers” connecting systems on different scales run with different programming and visualization codes which should be “interoperable” and relatively easy for experimental users to run for different parameters. This scheme as applied in the present study is shown in Fig. 7, and a full discussion of this approach in relation to visualization is given in [14].

5. Conclusions and prognosis
We have demonstrated that nanotubes with attached masses change frequencies in a systematic manner that enable measurement of the mass as long as one can retain its attachment to the nanotube. Attachment was maintained, by using wider and therefore longer tubes, greatly increasing the computational requirements. It is now time to return to the experimental laboratory to test this result. One proviso we must make is that when this project was begun in 2010, the common Molecular Dynamics code LAMMPS had bugs in the implementation of the Brenner potential that is needed to provide and accurate description of nanotube structure, and so all the calculations were made with an “own code” MD derived from Brenner’s original code. The Brenner potential corrections for LAMMPS were recently proposed and so this project will be transformed into a LAMMPS one and then can be integrated into the full SIMPHONY suite, together with the AViz visualizations.

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Figure 7. SimPhoNy flowchart
References

[1] Pine P, Yaish Y and Adler J “Simulational and vibrational analysis of thermal oscillations of single-walled carbon nanotubes” 2011 Phys. Rev. B 83 155410

[2] Pine P, Yaish Y and Adler J “Thermal oscillations of structurally distinct single-walled carbon nanotubes”, 2011 Phys. Rev. B 84 245409

[3] Pine P, Yaish Y and Adler J “The affect of boundary conditions on the vibrations of single-walled carbon nanotubes” 2011 J. App. Phys. 110 124311

[4] Pine P, Yaish Y and Adler J “Vibrational analysis of thermal oscillations of single-walled carbon nanotubes under axial strain” 2014 Phys. Rev. B 89 115405

[5] Pine P, Yaish Y and Adler J “Simulation of nanosensors based on single walled carbon nanotubes” 2012 IOP Conference Series 402 012002

[6] http://www.quantum-espresso.org and Giannozzi P et al. “QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials” 2009 J. Phys. C 21 395502

[7] Grosso B, Cooper V R, Pine P, Hashibon A, Yaish Y and Adler J 2015 “Visualization of electronic density” Computer Physics Communications 195 1-13

[8] Adler J, Adler O, Kreif M, Cohen O, Grosso B, Hashibon A and Cooper V R 2015 “Mini-review of Electron Density Visualization” Physics Procedia 68 26

[9] http://phony1.technion.ac.il/~aviz

[10] Adler J 2003 “Visualization in Atomistic and Spin Simulations” Computers in Science and Engineering” 5 61-5.

[11] https://github.com/simphony/AViz

[12] Adler O, Adler J and Yaish Y 2016 “Simulation and vizualization of nanotube vibrations with AViz” poster presented at: CECAM-IRL - Multiscale Simulation: from materials through to Industrial Usage

[13] Adler O 2016 M.Sc. Thesis, Technion

[14] Adler J et al to be submitted