

Normal modes of carbon nanotubes: similarities and differences with their continuum counterpart

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Abstract. Carbon nanotubes (CNTs) possess a range of unusually interesting and useful physicochemical properties. In this paper, the mechanical properties of single wall CNTs are investigated via free vibration normal modes using molecular mechanics models. The force field used is empirical and the usual assumptions of potential energy contributions coming from bond-stretching, bond angle bending, and bond twisting for two, three, and four atom interactions respectively, are made. The validity of continuum behaviour is examined by comparing the modal spacing obtained from the molecular mechanics models and that obtained from classical continuum elastodynamics. The breakdown of continuum behaviour is systematically characterised for various combinations of length to diameter ratio as well as for the number of atoms per circumference.

1. Introduction

Normal Mode Analysis is an important tool for studying the structure and dynamics of nanosized systems. The vibrational frequencies obtained can be used to relate observed spectra to details of the molecular structure, dynamics, heat capacities and other thermodynamic properties. It is based on the harmonic approximation in the limit of small amplitude motion. Once the force-field parameters that describe the atomic interactions have been obtained either via detailed *ab-initio* quantum mechanical calculations or laboratory experiments, the mechanics of the group of atoms can be satisfactorily modelled using of classical methods. The normal mode analysis provides information on possible synchronous motions: in particular, their frequency and the relative atomic amplitudes and directions.

To understand the overall mechanical behaviour, and also to make use of classical models for this class of problems, continuum models have been frequently proposed [1]. For carbon nanotubes (CNTs), the model consists of a long thin tube of spatially homogeneous and isotropic of matter. The validity of these models for various tube geometries has been examined here.

2. Molecular modelling

A carbon nanotube can be regarded as a large molecule consisting of carbon atoms. The atomic nuclei can be approximated by material points. The general expression of the total steric potential energy, omitting the electrostatic and nonbonded interactions, is a sum of energies [2]

$$U = \sum_{\text{bonds}} U_r + \sum_{\text{bond angles}} U_\theta + \sum_{\text{4-atom interactions}} U_\phi \quad (1)$$

where U_r is the potential energy associated with bond stretching, U_θ that for bond angle bending, and U_ϕ for dihedral angle torsion. As is common for molecular mechanics models, these interactions are kept as quadratic forms:

$$U_r = \frac{1}{2}k_r(r - r_0)^2, \quad U_\theta = \frac{1}{2}k_\theta(\theta - \theta_0)^2, \quad U_\phi = \frac{1}{2}k_\phi(\phi - \phi_0)^2 \quad (2)$$

where k_r , is the bond stretching constant, k_θ is the bond angle bending force constant and k_ϕ is the torsional stiffness, respectively. If q_i is the i th generalised co-ordinate, then the Lagrangian L of the system is given by the difference in the kinetic energy T and the potential energy U

$$L(\mathbf{q}, \dot{\mathbf{q}}) = T(\dot{\mathbf{q}}) - U(\mathbf{q}) \approx (1/2)\dot{\mathbf{q}}^T \mathbf{M}\dot{\mathbf{q}} - (1/2)\mathbf{q}^T \mathbf{K}\mathbf{q} \quad (3)$$

when the energy terms have been linearised; accounting for terms up to the quadratic. \mathbf{M} and \mathbf{K} are the mass and the Hessian matrices (stiffness matrix in theoretical mechanics literature), \mathbf{q} is the vector of generalised co-ordinates, and a dot represents differentiation with respect to time. Using Hamilton's principle (or equivalently using Lagrange's equations), the well-known governing equations of motion $\mathbf{M}\ddot{\mathbf{q}} + \mathbf{K}\mathbf{q} = \mathbf{0}$ are obtained. Looking for non-trivial synchronous motion (i.e. in- or out-of-phase motion) leads to the eigenvalue problem [3] $\mathbf{K}\mathbf{u}_i = \lambda_i \mathbf{M}\mathbf{u}_i$, where $\lambda_i = \omega_i^2, i = 1, 2, \dots, 3N$ is the i th eigenvalue that represents the square of the natural frequency ω_i , and $\mathbf{u}_i, i = 1, 2, \dots, 3N$ is the corresponding eigenvector (normal mode).

Before normal modes can be calculated, the configuration of the atoms must be brought to the equilibrium via appropriate energy minimisation. While slightly incomplete energy minimisation may be satisfactory for many molecular dynamics simulations where trajectories of motion with respect to time are to be calculated, the procedure often poses practical problems for the normal mode analysis. This is particularly true for systems with large number of degrees-of-freedom. When energy minimisation is partially incomplete, the configuration does not correspond to the equilibrium and the structure thus obtained is (minorly) unstable. A consequence of this is that the Hessian is not positive definite; and that some of the eigenvalues may be slightly negative (physical considerations dictate that we must have six zero eigenvalues corresponding to the six rigid body modes and the remaining must be all positive).

The above mentioned difficulty has been encountered by other authors as well. We have taken the approach of [4] to overcome this problem. Molecular dynamics (MD) simulations were carried out at a low temperature (0.1K) for the structure whose energy minimisation is slightly incomplete; the Hessian was calculated at each time step. Strictly, there is no meaning of 'time dependent Hessian' for a stable (energy minimised) structure because Hessian is the curvature tensor of the energy surface in the space spanned by the configuration space variables q_i : a time independent (but, possibly, non-linear) quantity. However, the way Hessians are often computed (effectively by numerical differentiation of the energy landscape), a set of constants (representing entries in the Hessian matrix) are obtained at each time step. These constants oscillate (see figure 1, for a typical entry) and the Hessian averaged over time is the so-called 'Time Averaged Hessian'. When averaging of the Hessians is performed for moderate time scales, significant improvement in the positive semidefiniteness is observed.

A variety of CNT structures were created using Tubegen [5] and were divided into two groups, one with a fixed diameter and the other with a fixed length/diameter ratio, as listed in Table 1. Energy minimisation and molecular dynamics were performed using the open source code GROMACS [6]. The input data into GROMACS required minor changes in the forcefield files. The bond constants and lengths were taken from literature [1].

3. Results and discussions in the light of continuum theory

After averaging Hessians, as described in the previous section, the first six eigenvalues were found to be numerically acceptable (the largest negative or positive value in the first six eigenvalues

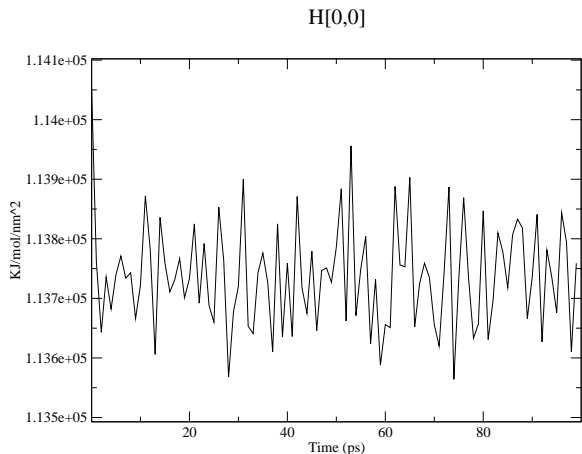


Figure 1. Temporal evolution of a typical diagonal entry of the Hessian matrix.

CNT Name	Chirality	Cell count	L/D ratio	No. of atoms
A	(5,5)	(1,1,13)	4.60	260
B	(5,5)	(1,1,26)	9.60	520
C	(5,5)	(1,1,39)	14.60	780
D	(5,5)	(1,1,52)	19.84	1040
E	(5,5)	(1,1,69)	26.10	1380
F	(5,5)	(1,1,79)	29.29	1580
G	(5,5)	(1,1,31)	11.43	620
H	(7,7)	(1,1,44)	11.57	1232
I	(10,10)	(1,1,64)	11.37	2560

Table 1. Parameters of the CNTs simulated. L =length, D =diameter of the tube.

was at least 1/1000th of the eigenvalue corresponding to the fundamental frequency, i.e. the 7th eigenvalue). Frequencies of the oscillatory modes are presented in Table 2. The results are normalised with respect to the fundamental frequency in each case in order to study the modal spacing.

We observe in all cases that the second natural frequency is very close to the fundamental. This is expected because a perfectly symmetrical cylinder has repeated eigenvalues for the fundamental. The two frequencies correspond to the bending modes about two different axes that are perpendicular to the axis of the cylinder. The values, slightly different than unity, indicate the slight breakdown of the degeneracy because of the lack of cylindrical symmetry as well as asymmetry introduced by the numerics. A general statement about the degeneracy of modes can be made: bending modes will appear in doublets whereas extensional and torsional modes will not have any degeneracy.

For a thin beam made of continuum, the modal spacing is given by the classical Euler's formula [7]. For free-free beams, the ratio of the first, the second, the third and the fourth natural frequencies is given by 1:2.58:5.41:8.93. Of all the CNTs simulated, the length (L) to the diameter (D) ratio is largest for the nanotube labelled **F**. There are three pairs of natural frequencies approximately at 2.74/2.78, 5.26/5.31, and 8.46/8.52 for this nanotube. The values progressively deviate from their Euler-Bernoulli continuum counterpart with increasing mode number. This is explained by the fact that with increasing mode number, the characteristic length in the axial direction progressively shortens, thus violating the slender beam assumptions. Such effects have been well known in classical mechanics and corrections have been proposed to account for deviations from infinitesimal slenderness of beams. Perhaps the most important of these are correction due to shear effects (proposed by Timoshenko [8]) and that of rotary inertia [7] (see, article 186). The shear correction becomes important with increasing wavenumber (i.e. shorter wavelength) and rotary inertia becomes important for high frequencies. The need for correction of this kind is obvious from the normal mode calculations presented in Table 2 for progressively shorter beams. For example, the second bending mode for beam **A** is 2.08 times the fundamental (4th and 5th rows, 1st column of Table 2) as opposed to 2.58 for slender beams.

There are modes for nanotube **E** that do not appear in pairs. They are either extensional or torsional modes (for example, at the normalised frequency 6.41, 9.78, 12.82, etc.). The order in which these modes appear depends on the aspect ratio (L/D) of the nanotube. For example, the first such mode for tube **A** is the third vibratory mode at normalised frequency 1.47.

The second bending mode for beam **I** (which has the largest number of atoms in this study)

Mode number	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>	<i>H</i>	<i>I</i>
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	1.006	1.008	1.004	1.004	1.012	1.053	1.008	1.003	1.002
3	1.473	2.469	2.605	2.672	2.710	2.737	2.537	2.541	2.549
4	2.083	2.486	2.623	2.687	2.728	2.775	2.555	2.547	2.553
5	2.088	2.544	3.684	4.860	5.171	5.255	2.979	3.016	3.062
6	2.104	3.882	4.750	5.005	5.203	5.305	4.499	4.513	4.536
7	2.198	4.271	4.782	5.037	6.408	7.372	4.529	4.522	4.542
8	2.244	4.299	5.623	7.421	8.255	8.463	4.547	4.670	4.793
9	2.408	5.082	7.235	7.832	8.309	8.522	5.954	6.031	5.227
10	2.560	6.198	7.283	7.884	9.784	11.251	6.676	6.701	5.291
11	2.694	6.231	7.365	9.718	11.844	12.234	6.718	6.712	5.414
12	2.728	7.226	9.920	11.015	11.922	12.320	8.918	7.307	5.486
13	2.934	7.390	9.983	11.087	12.816	14.741	8.942	7.430	5.674
14	3.005	7.425	11.039	14.440	15.832	16.485	8.989	7.514	5.932
15	3.092	7.598	11.227	14.535	15.937	16.598	9.068	7.628	6.123

Table 2. Normal mode frequencies scaled with respect to the fundamental in each case.

is about 2.55 times the fundamental which is fairly close to the thin beam value of 2.58. The values are even better than those for the thinnest (i.e. largest L/D) beam *F*. The reason is a lack of atoms for adequate continuum representation in case of tube *F*.

When weak forces e.g. van Der Waals and electrostatic interactions were included in the model, the effect on the normal mode frequency was not significant.

4. Conclusions

Normal mode calculations for single wall carbon nanotubes were presented based on the ‘time averaged Hessians’. The natural frequencies show modal separation that progressively resembles those of thin continuum beams with (i) increase in the aspect ratio (L/D), and (ii) increase in the number of atoms in the model. The results suggest inclusion of Timoshenko and Rayleigh type corrections to the Euler-Bernoulli theory.

These improvements on the natural frequencies of carbon nanotubes can be very useful for CNT-attached atomic force microscopy, where a nanotube is placed at the end of the silicon tip. The Euler-Bernoulli theory is often used for the calculation of the position of the scanned atoms [9], both in contact and phase mode.

5. References

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