Numerical studies on elastic properties of graphene sheets and free vibration of carbon nanotubes by atomistic simulation and equivalent continuum modelling

Damodara Reddy Chilla

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**Numerical studies on elastic properties of
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equivalent continuum modelling**

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School of Mechanical and Aerospace Engineering

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Abstract

Computational methods play an important role in understanding the mechanics of graphene sheets and carbon nanotubes (CNTs). A decade of work has been done towards understanding the mechanics of CNTs, computation of their mechanical properties, experimental verification of the computed mechanical properties of CNTs, and development of efficient computational methods for the simulation of nanostructures. However, analysis of large structures has been a challenging problem because the large dimensionality of the problem demands too long a computational time. Continuum mechanics modelling is one of the approaches for conveniently analysing large-scale problems. The present research deals with determination of elastic properties of finite graphene sheets and CNTs by equivalent continuum modelling, and free vibration analysis of plain as well as fluid conveying CNTs by atomistic modelling of stiffness and mass properties. The scope of the work includes computation of elastic properties of finite graphene sheets using a truss element model based on AMBER force field as well as a continuum mechanics model based on Brenner potential, error analysis of computed elastic properties of graphene sheets and CNTs, and free vibration analysis of plain and fluid conveying carbon nanotubes.

To begin with, the simple problem of continuum mechanics modelling of a single carbon ring is considered. The ring is modelled as a truss element assemblage. Equating the strain energy of the model with the potential energy of the ring given by AMBER force field, equivalent Young's modulus is computed for a few typical deformation modes. This approach is then extended to finite graphene sheets. Equivalent Young's modulus (Y), shear modulus (G) and Poisson's ratio (ν) of graphene sheets are determined using the truss element model.

AMBER force field does not account for the effects of second neighbourhood atoms for computing the potential whereas Brenner potential does. Hence, as a next focus of present research, the continuum mechanics modelling of finite graphene sheets is carried out using Brenner's potential. With the use of this potential, equilibrium adjustment of atomic positions becomes necessary so as to minimise the potential energy. The computed results suggest that the equilibrium adjustments of atoms have much influence on the computed elastic constants. Consideration of equilibrium adjustments leads to

Young's modulus and Poisson's ratio values around 0.7 TPa and 0.4, respectively, whereas computations ignoring equilibrium adjustments yield 1 TPa and 0.25, respectively. A study of inter-relationship between the computed elastic constants seems to suggest that a finite graphene sheet behaves like an orthotropic material.

Determination of the maximum attainable numerical precision in the computed stiffness using Brenner potential is the next problem considered in this research. The end-to-end stiffness values of CNTs and finite graphene sheets are computed using Brenner potential. The effect of round-off and truncation errors in the precision of computed stiffness is investigated. Three methods of determining stiffness, viz., small displacement method, local potential-fit method and finite difference method are considered. The optimum value of trial displacement to be applied for computing stiffness is determined. It is observed that the small displacement method is unstable if equilibrium atomic adjustments are not performed. A method to circumvent this instability is proposed.

The free vibration analysis of CNTs by atomistic simulation is another problem studied in this research. Brenner potential is employed for the inter-atomic stiffness computations. Obtaining analytical expressions for the inter-atomic stiffness is not straightforward due to the many-body terms present in the Brenner potential. Hence, the finite difference method is employed to compute the stiffness matrix numerically. In addition to using atomistic simulation, the free vibration analysis of CNTs is also carried out using a continuum shell model with appropriate values of Young's modulus and wall thickness taken from the literature. The set of Young's modulus and wall thickness values, 5.5 TPa and 0.066 nm, respectively, is seen to be more appropriate than the other set, 1 TPa and 0.34 nm. This suggests that proper care must be taken while choosing appropriate set of values from the literature for the purpose of continuum shell modelling of CNTs.

Finally, free vibration analysis of fluid conveying CNTs is carried out. The CNT is modelled as a beam using Euler-Bernoulli beam element. The Coriolis and centrifugal forces arising out of fluid flow are taken into account. The governing differential equation is solved in the state-space. The natural frequencies and modeshapes are studied for various flow velocities. The phase angle is computed at different locations along the length of the CNT. The relative phase between two appropriately chosen points is useful to quantify the mass flow rate.

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Table of Contents

Abstract	i
Acknowledgements	iii
Table of Contents	iv
List of Figures	vii
List of Tables	xii
Notations	xiii
Chapter 1	1
INTRODUCTION	1
1.1. Background.....	1
1.2. Objectives and scope.....	3
1.3. Organisation of thesis	5
Chapter 2	8
LITERATURE REVIEW	8
2.1. Introduction.....	8
2.2. Classification of CNTs.....	10
2.2.1. Classification of CNTs based on chirality	12
2.2.2. Classification of CNTs based on layers	13
2.3. Applications and importance in the present and future	15
2.3.1. Some potential applications of CNTs	18
2.4. Experimental observations of elastic properties of CNTs	20
2.4.1. Young's modulus measurements of CNTs	20
2.4.2. Natural frequency measurements.....	24
2.5. Simulation methods	26
2.5.1. Ab initio methods.....	27
2.5.2. Tight-binding methods.....	28
2.5.3. Classical molecular dynamics.....	29
2.5.4. Continuum and multi-scale models	31
2.6. Continuum mechanics for CNT	34
2.7. Vibration studies and flow through nanotubes	37
2.8. Motivation.....	39
Chapter 3	45
ANALYSIS OF CARBON RING AND GRAPHENE SHEETS.....	45
3.1. Analysis of a single hexagonal carbon ring.....	46

3.1.1. Basic assumptions	48
3.1.2. Molecular mechanics model	49
3.1.3. Equivalent truss element model	51
3.1.4. Results and discussions of single carbon ring	54
3.2. Equivalent continuum modelling of graphene sheet using AMBER force field ...	64
3.2.1. Modelling procedure	65
3.2.2. Uni-axial tension/compression mode	68
3.2.3. Bending deformation mode	73
3.2.4. Shear deformation mode	77
3.2.5. Convergence study on elastic properties of graphene sheet	81
3.3. Conclusions	87
Chapter 4	90
EQUILIBRIUM CONFIGURATION AND CONTINUUM ELASTIC PROPERTIES OF FINITE SIZED GRAPHENE SHEETS USING BRENNER POTENTIAL	90
4.1. Interatomic potential for carbon atoms	91
4.2. Determination of elastic properties	93
4.3. Results and Discussions	96
4.3.1. Equilibrium configuration and bond length	96
4.3.2. Model 1: Two straight edges	99
4.3.3. Model 2: Four straight edges	106
4.3.4. Potential versus strain, and stress versus strain relationships	107
4.3.5. Scatter in the elastic property values reported in the literature	110
4.4. Summary and conclusions	111
Chapter 5	113
SOME NUMERICAL ASPECTS IN THE COMPUTATION OF ELASTIC PROPERTIES OF GRAPHENE AND CARBON-NANOTUBES	113
5.1. Numerical errors and their effects	113
5.2. Error analysis for a single C-C bond	116
5.2.1. Small displacement method	116
5.2.2. Local potential-fit method	121
5.2.3. Finite difference method (FDM)	124
5.3. Error analysis for graphene and single walled carbon nanotubes	124
5.3.1. Small displacement method	125
5.3.2. Local potential- fit method	129
5.3.3. Finite difference method	131
5.4. Summary of results and discussions	133

5.5. Concluding remarks	135
Chapter 6	136
FREE VIBRATION ANALYSIS OF SINGLE-WALLED CARBON NANOTUBES....	136
6.1. Previous studies on vibration of CNTs	137
6.2. Equilibrium configuration of CNT	140
6.3. Computation of stiffness matrix.....	143
6.4. Computed natural frequencies and mode shapes	148
6.5. Control of numerical errors in the computed natural frequencies	157
6.6. Conclusions.....	161
Chapter 7	163
FREE VIBRATION ANALYSIS OF FLUID CONVEYING SINGLE-WALLED CARBON NANOTUBES.....	163
7.1. Determination of equivalent bending rigidity of SWNTs.....	164
7.2. Flow through single-walled carbon nanotubes	166
7.2.1. Natural frequencies and mode shapes.....	175
7.2.2. Physical understanding of the effect of flow	177
7.2.3. Fluid flow measurement	179
7.3. Conclusions.....	182
Chapter 8	183
CONCLUSIONS AND SCOPE OF FUTURE WORK.....	183
8.1. Summary	183
8.2. Conclusions.....	184
8.3. Future work.....	188
APPENDIX A	189
B.1. Program to determine equilibrium configuration of graphene sheet.....	189
B.2. Program to compute first generation Brenner potential (1990)	195
APPENDIX B	199
APPENDIX C	207
APPENDIX D	217
APPENDIX E: List of Publications	220
REFERENCES.....	221

List of Figures

Figure 2.1. Honeycomb lattice of carbon atoms	11
Figure 2.2. Schematic models for single-walled carbon nanotubes	13
Figure 2.3. Rolling up graphene sheet into a tube	14
Figure 2.4. Multi-walled carbon nanotubes	15
Figure 2.5. Yielding of high-strength steel as compared to carbon nanotube rope	18
Figure 2.6. TEM images of free-standing multi-walled CNTs showing the blurring of the tips due to thermal vibrations at 300 and 700K.....	21
Figure 2.7. SEM image of the two oppositely aligned AFM tips holding a MWCNT which is attached at both ends on the AFM silicon tip surface by electron beam deposition of carbonaceous material.....	22
Figure 2.8. (a) Schematic explaining the principle of the tensile-loading experiment. (b) Stress versus strain of individual MWCNTs.....	23
Figure 2.9. (a) Raman spectra of SWNT bundles. (b) Raman spectra of a metallic and a semiconducting isolated SWNT. The spectra shows the RBM modes, D, G and M band features	25
Figure 2.10. Stokes resonance Raman measurement of CNTs obtained with 76 different laser lines EL. The colours indicate the Raman intensity.....	26
Figure 3.1. Carbon ring of a graphene sheet.....	46
Figure 3.2. Bond structure and corresponding energy terms of a carbon ring	50
Figure 3.3. Bond lengths and bond angles before and after deformation.....	50
Figure 3.4. Chemical model and pin-jointed truss model.....	52
Figure 3.5. Constant bond angle and varying bond length.....	55
Figure 3.6. Constant bond length and varying bond angle.....	56
Figure 3.7. EA versus change in length of truss element 'b' with lengths of element 'a' fixed.....	57
Figure 3.8. Hydrostatic compression and tension deformation mode of carbon ring.....	58
Figure 3.9. Uni-axial tensile/compressive deformation of carbon ring.....	59
Figure 3.10. EA of truss element versus percentage of elongation for tension and compression deformation mode of a carbon ring.....	60
Figure 3.11. Bending deformation of carbon ring.....	61

Figure 3.12. <i>EA</i> of truss element vs bending angle for bending deformation mode of carbon ring.	62
Figure 3.13. Shear deformation of carbon ring.....	63
Figure 3.14. <i>EA</i> of truss element vs shear angle for shear deformation of carbon ring....	63
Figure 3.15. Bond angles and elements at a node.....	66
Figure 3.16. Block diagram of model.	66
Figure 3.17. Tensile deformation of graphene sheet, picture captured from ANSYS.....	68
Figure 3.18. Molecular potential and strain energy of graphene sheet plotted against <i>EA</i> of truss element of graphene sheet under uni-axial tensile/compressive deformation mode.	69
Figure 3.19. Plot same as Fig 3.18 with log-log scale.	70
Figure 3.20. <i>EA</i> of truss element versus percentage elongation for uni-axial tensile/compressive deformation of a graphene sheet.	71
Figure 3.21. Equivalent Young's modulus versus percentage elongation for uni-axial tensile/compressive deformation of graphene sheet.	73
Figure 3.22. Bending deformation of graphene sheet , picture captured from ANSYS. ..	74
Figure 3.23. Log(molecular potential) and Log(strain energy) versus Log(<i>EA</i>) for bending deformation of graphene sheet.....	75
Figure 3.24. <i>EA</i> versus bending angle for bending deformation of graphene sheet.....	75
Figure 3.25. Equivalent Young's modulus versus bending angle for bending deformation of graphene sheet.	76
Figure 3.26. Graphene sheet before and after shear deformation, picture captured from ANSYS.	78
Figure 3.27. Log(Molecular potential) and Log(strain energy) versus Log(<i>EA</i>) of graphene sheet under shear deformation.....	78
Figure 3.28. <i>EA</i> of truss element versus shear angle of graphene sheet under shear deformation.	79
Figure 3.29. Equivalent shear modulus versus shear angle of graphene sheet under shear deformation.	80
Figure 3.30. Equivalent Young's modulus versus number of rings along the length of graphene sheet.....	82
Figure 3.31. Equivalent shear modulus versus number of carbon ring along the length of graphene.	83

Figure 3.32. EA of truss element versus number of carbon rings along the length.....	85
Figure 4.1. Initial configuration of graphene sheet.....	94
Figure 4.2. Equilibrium configuration (dotted line) and initial configuration (continuous line).	97
Figure 4.3. a) Tensile deformation b) shear deformation.	99
Figure 4.4. Potential versus strain for uni-axial tensile/compressive deformation.....	100
Figure 4.5. Shear strain versus potential of graphene sheet.....	101
Figure 4.6. Different widths considered for Poisson's ratio calculations.	104
Figure 4.7. Poisson's ratios computed using graphene model with two straight edges (unconnected symbols) and for four straight edges (connected symbols)....	105
Figure 4.8. Potential versus strain for the tensile loading of graphene sheet (2 straight edge model).....	108
Figure 4.9. Stress-strain curves: σ versus ϵ (dots) and S versus E (circles).....	109
Figure 4.10. Young's modulus versus Poisson's ratio of graphene.....	111
Figure 5.1. Strain energy of a single C-C bond; a) Linear plot; b) Log plot. The spiky region of the plot depicts the randomness caused by truncation and round-off errors	119
Figure 5.2. Computed stiffness for a single C-C bond by small displacement method; a) Stiffness; b) Relative error.	120
Figure 5.3. Computed stiffness for a single C-C bond by local potential-fit method; a) Stiffness; b) Relative error.	122
Figure 5.4. Computed stiffness for a single C-C bond by finite difference method; a) Stiffness; b) Relative error.	123
Figure 5.5. Equilibrium configuration of graphene sheet and SWNT.....	124
Figure 5.6. Strain energy plot for a non-equilibrium configuration. Note that the minimum point has moved away from the origin.	125
Figure 5.7. Computed stiffness for graphene sheet by small displacement method; a) Stiffness; b) Relative error. The results are polluted by equilibrium error. ..	126
Figure 5.8. Computed stiffness for graphene sheet by modified small displacement method; a) Stiffness; b) Relative error.	128
Figure 5.9. Computed stiffness for SWCNT by modified small displacement method; a) Stiffness; b) Relative error.	129

Figure 5.10. Computed stiffness for graphene sheet by local potential-fit method; a) Stiffness; b) Relative error.	130
Figure 5.11. Computed stiffness for SWCNT by local potential-fit method; a) Stiffness; b) Relative error.	131
Figure 5.12. Computed stiffness for graphene sheet by finite difference method; a) Stiffness; b) Relative error.	132
Figure 5.13. Computed stiffness for SWCNT by finite difference method; a) Stiffness; b) Relative error.	133
Figure 6.1. Equilibrium configuration of a CNT.	140
Figure 6.2. Potential variation with carbon-carbon bond length of CNT.	144
Figure 6.3. Symmetrically located pivot points from the reference atom '0' in square net.	145
Figure 6.4. Fundamental frequency of inherent equilibrium configuration. Solid and broken lines represents the free-free and fixed-fixed end conditions, respectively.	147
Figure 6.5. Fundamental frequency of fixed-fixed nanotubes. Solid and broken lines represents inherent and uni-bondlength equilibrium configurations, respectively.	148
Figure 6.6. Natural frequencies (in GHz) and corresponding eigenmodes of short CNT (diameter 0.65 nm and length 2 nm) with free-free end conditions.	153
Figure 6.7. Natural frequencies (in GHz) and mode shapes of CNT from atomistic model.	154
Figure 6.8. Natural frequencies (in GHz) and mode shapes of CNT modelled as a continuum using ANSYS	155
Figure 6.9. Natural frequencies (GHz) and mode shapes of CNT modelled as a continuum beam using ANSYS.	157
Figure 6.10. Sum of absolute errors in the rigid body mode frequencies with step size.	160
Figure 6.11. Variation of fundamental natural frequency (mode 7) with step size.	160
Figure 7.2. Nodal displacements of an element. u_1 , u_2 , u_3 and u_4 are linear and angular displacements at left and right ends, respectively.	168
Figure 7.3. Variation of dimensionless frequency of lowest three modes with dimensionless velocity.	175
Figure 7.4. Fundamental mode shape as a function of time at 20% of critical velocity.	177

Figure 7.5. Variation of normalised forces with length of CNT.....	178
Figure 7.6. Variation of forces at middle of CNT with fluid velocity.	179
Figure 7.7. Phase along the length of CNT at 20% of critical velocity.	180
Figure 7.8. Relative phase with dimensionless parameter $\sqrt{m_r} v_n$ for various m_r values.	181

List of Tables

Table 2.1. Different Young's modulus values of CNT reported in literature.....	42
Table 2.2. Wall thickness and corresponding in-plane stiffness values of CNT reported in literature.....	44
Table 3.1 AMBER force field constants.....	51
Table 3.2. A summary of computed EA values.	64
Table 3.3. Equivalent Young's modulus (TPa) of zigzag and armchair graphene sheet..	82
Table 3.4. Equivalent shear modulus (TPa) of zigzag graphene sheet.....	83
Table 3.5. EA of truss element (nN) for zigzag, armchair uni-axial deformation and zigzag shear deformation of graphene sheet model.....	84
Table 3.6. Poisson's ratio for zigzag and armchair graphene sheet.....	86
Table 3.7. Computed elastic properties using square graphene sheet model.....	87
Table 4.1. Brenner potential parameters of set I and set II	93
Table 4.2. Bond length variation in the equilibrium configuration of a finite graphene sheet.	98
Table 4.3. Young's modulus and Poisson's ratio values reported by other researchers.	102
Table 4.4. Young's modulus variation with size of graphene sheet.....	104
Table 4.5. Computed Poisson's ratio ν_{12} for the case of two straight edges and four straight edges.	105
Table 4.6. Orthotropicity measure.....	107
Table 4.7. Computed elastic constants for the graphene model with two straight edges and four straight edges.....	107
Table 5.1. Brenner potential for the stretching of a single C-C bond.....	118
Table 5.2. Degree of precision in the computed stiffness and optimum δ values.	134
Table 6.1. Equilibrium bond lengths of CNT based on uni-bondlength equilibrium configuration.....	142
Table 6.2. Bending frequency of zigzag (14, 0) CNT of length 8.146 nm for various Young's modulus and wall thickness values reported in the literature.	158
Table 6.3. Computed natural frequencies (GHz) for various step sizes.....	159
Table 7.1. Computed bending rigidity values for CNTs of different diameters.....	166

Notations

C-C	Carbon-Carbon
Y	Young's modulus
t	Wall thickness of graphene sheets/carbon nanotubes
V	Potential energy
K^δ	Bond-stretch force constant
K^θ	Bond-angle force constant
EA	Product of Young's modulus and cross sectional area of truss element
R	Equilibrium C-C bond length
Θ	Equilibrium bond angle
θ	Bending angle
ϕ	Shear angle
G	Shear modulus
Y_b	Young's modulus in bending
C	In-plane stiffness
ν	Poisson's ratio
σ	Tensile stress
ε	Tensile strain
E	Green strain
δ	Tensile deformation
W	Width
L	Length
D	Diameter
k	Stiffness
f	Natural frequency
YI	Bending rigidity
K	Stiffness matrix
M	Mass matrix
P	Force vector
C	Gyroscopic/ Coriolis matrix
nm	Nano-meter
nN	Nano-Newton
TPa	Terra-Pascal
GHz	Giga-Hertz
CNT	Carbon nanotube
SWCNT	Single-walled carbon nanotube
MWCNT	Multi-walled carbon nanotube

Chapter 1

INTRODUCTION

1.1. Background

Although carbon fibres have been studied for more than a century, the existence of carbon nanotubes (CNTs) was not known until 1991 [1]. Extremely small size, unique atomic arrangement, outstanding physical, mechanical and electrical properties of nanostructures are some of the attractive features that have triggered intensive research in a wide variety of science and engineering fields. Among the many nanostructured materials, CNTs as self-assembling nanostructures, have attracted a great deal of attention for various potential applications, including field emitters, composite materials, battery electrode materials, nanoelectronics, nanoscale sensors etc. Besides the great deal of experimental works on CNTs, many researchers have pursued the analysis of CNTs by theoretical modelling. However, it is still an ongoing and challenging process to develop effective and efficient computational methods for the analysis of nanostructures.

The modelling approaches can be generally classified into two categories, viz., *atomistic modelling* and *continuum modelling*. In principle, any problem associated with molecular or atomic motions can be simulated by *ab initio* methods, molecular dynamics, tight-binding molecular dynamics, and methods based on density functional theory. However, due to their huge computational tasks, practical applications of these atomistic modelling techniques are limited to systems containing a small number of molecules or atoms. Relatively large systems containing huge number of atoms can be modelled using the

continuum mechanics approach. Using this approach, many researchers have computed elastic properties and vibrational behaviour of graphene sheets and CNTs. However, these models neglect the detailed characteristics of nanotube, and are unable to account for forces acting on the individual atoms. Therefore, the studies conducted so far are not sufficient to gain a complete understanding of the mechanism involved in CNTs. Hence, there is continued research in this area to develop improved computational methods to analyse the CNTs for the current as well as future requirements.

Recently, researchers have succeeded in extracting individual planes of carbon atoms from graphite crystals, which results in the production of a few atomic layers of graphene including single-layer graphene to fabricate nanodevices [2]. However, studies on the elastic properties of graphene sheets are scarce and hence this forms the first focus of research in this thesis.

A scan through literature reveals that there is a large scatter in the elastic properties of CNTs reported by various researchers. Although the scatter may be partially due to the inherent accuracy differences associated with various modelling, simulation and experimental techniques used, a poor control of numerical errors during simulation could also play an important role. Although, there are many studies reported in literature dealing with numerical simulation on CNT, studies on numerical error analysis and the maximum precision expected in computed properties are rare. Furthermore, the technical problem of finding out the optimal displacement step size to be used (for computing stiffness values of CNTs and graphene sheets) should be resolved prior to any attempts to

determine the elastic properties. Nevertheless, such studies have not been reported in the literature and hence this forms the next focus of research in this thesis.

Researchers have explored the feasibility of using CNTs for resonance based sensor applications in NEMS. Such studies model the CNTs either as continuum beam structures with appropriate equivalent Young's modulus and wall thickness values assumed from the literature or as an assemblage of truss element structure using AMBER force field [3]. Brenner potential [4] has emerged as one of the successful potentials used for computing the mechanical properties of CNTs. However, the studies using this potential for computing natural frequencies are scarce [5] and hence this forms another focus of research in this thesis.

Fluid flow inside CNTs is a significant and challenging research topic. However, very little work has been done in this area and hence vibration analysis of fluid conveying CNTs forms the last focus of research in this thesis.

1.2. Objectives and scope

The objectives and scope of the present work are as follows:

1. To determine the equivalent elastic properties of finite graphene sheets with the help of a truss element model coupled with AMBER force field, for typical deformation modes of graphene sheets. The motivation for this work is that the AMBER force field is simple to implement and at the same time gives a quick insight into the problems in determining the elastic properties of graphene sheets.

2. To determine the equivalent elastic properties of finite graphene sheets using Brenner potential, and to explore possible reasons for the scatter in the computed elastic properties (viz., Young's modulus, Poisson's ratio and wall thickness) reported in literature. The motivation for this work is that Brenner potential can model the atomic potential more accurately than AMBER force field as the former involves not only the first neighbours but also the second neighbours in the potential computations of a given atom.
3. To estimate the numerical error in the computed stiffness of graphene sheets and CNTs. Three methods of stiffness calculation, viz., *small displacement method*, *local potential fit method* and *finite difference method*, are used for the purpose. Another objective is to determine the optimum value of displacement step to be used (for the potential calculations) while computing the elastic properties using each of the above three methods. The motivation for this work is derived from the author's observation that the accuracy of the stiffness computed using Brenner potential critically depends on the size of displacement step used. Too large a displacement step introduces non-linearity error while too small a value introduces truncation/round-off errors, and therefore determination of optimal value of displacement step is of much practical significance.
4. To study the free vibration characteristics of CNTs using two approaches: (i) by atomistic simulation based on Brenner potential, and (ii) by an equivalent continuum shell analysis based on reported elastic properties. The main objective is to compare the accuracies of computed natural frequencies and modeshapes,

- and thereby explore the conditions under which the equivalent shell analysis can give results comparable to that of atomistic simulation.
5. To study the free vibration characteristics of fluid conveying CNTs, and thereby develop an expression for the measurement of mass flow rate of fluid flowing through CNTs, which may have possible NEMS applications in future.

1.3. Organisation of thesis

In Chapter 2, the literature on classification of CNTs and potential applications of CNTs are presented. Atomistic simulation and continuum mechanics approaches are critically reviewed. Free vibration studies of plain and fluid conveying CNTs are discussed. Finally, all the reported values of Young's modulus and wall thickness of graphene sheet as well as CNTs are collected in tabular form for future reference.

In Chapter 3, a single carbon ring is modelled as a truss element assemblage and the model is analysed for the elastic properties using AMBER force field for potential computations. A composite parameter, EA , which is the product of Young's modulus and area of cross section of truss element, is computed for typical deformation modes. The modelling approach is then extended to determine the elastic properties of finite graphene sheets. Typical deformation modes are analysed using ANSYS [6] and the truss element model. A study on the convergence of the computed elastic properties with the size of the model is performed for the purpose. Convergence study on the computed elastic properties of graphene sheet is performed.

In Chapter 4, the expression for Brenner potential and formulae for computing elastic properties are first reviewed. A study of spatial variation of equilibrium bond lengths in equilibrium configurations is presented. The influence of the size of graphene sheet on the computed Young's modulus value is studied. Two models of graphene sheet with only two or all the four edges constrained to be straight are considered to compute the elastic properties of finite graphene sheets. The orthotropy of the computed material properties of finite graphene sheet is investigated. A possible reason for the large scatter in the computed Young's modulus values reported in the literature is identified.

In Chapter 5, a numerical error analysis is carried out to determine the optimum value of trail displacements to be used in the potential calculations required for computing the elastic properties of graphene sheets and CNTs. Three methods of determining elastic properties, viz., the small displacement method, potential fit method and finite difference methods are considered. Numerical precision in computed stiffness of graphene sheets and CNTs, and the optimum values of trail displacement with respect to each of the methods are computed.

In Chapter 6, free vibration analysis of short CNTs using atomistic simulations is carried out. Formulation of stiffness matrix using finite difference method is presented. Using the stiffness and atomic mass matrices, the natural frequencies and mode shapes are computed for free-free and fixed-fixed boundary conditions. Two equilibrium configurations, viz., the inherent and uni-bondlength equilibrium configurations are used for the purpose. Free vibration analysis of CNTs is also carried out using a continuum shell model with an appropriate choice of values of Young's modulus and wall thickness

for the model. Natural frequencies and mode shapes are computed and the results are discussed for few typical L/D ratios.

In Chapter 7, the equivalent bending rigidity (YI) of CNT is first determined from a free vibration analysis using atomistic simulations. This bending rigidity value is then used to model the CNT as a continuous beam. Formulation of differential equation of motion of fluid conveying pipes is reviewed. A state space model is used to solve the non-symmetric matrix system. Free vibration analysis of fluid conveying CNTs is carried out to find the natural frequencies and modes shapes at various velocities of fluid. The expression for the mass flow rate of fluid in terms of the phase difference between two different locations of CNTs is developed using the numerical results.

Finally, in Chapter 8, the summary and important conclusions of present doctoral thesis are presented. The scope for future work is discussed.

Chapter 2

LITERATURE REVIEW

2.1. Introduction

Carbon nanotubes (CNTs) are tubular structures made of self-assembled carbon atoms with the arrangement of atoms similar to that of graphite. CNTs can be thought of as a rolled-up graphene sheet. Although carbon fibres have been studied for more than a century, the existence of CNTs was not known until 1991 [1]. Thomas Alva Edison used Carbon fibres to manufacture filaments for incandescent electrical lamps in 1892 [7]. Research had not progressed much until Second World War. After 1950, the space and aerospace industry searched for new materials having superior mechanical properties as well as lightweight. Carbon fibre based composite materials seemed to be ideal materials at that time. As a result understanding of the mechanical properties of carbon fibres and their synthesis techniques progressed steadily. Experiments were conducted for reducing the diameter of carbon fibres and researchers were able to achieve less than 1 micrometer occasionally [8]. Scientist did not realise the significance of these tiny carbon fibres until the discovery of fullerenes by Harry et al. [9], which are C_{60} and C_{60} -like buckyballs. Thereafter extensive research work has been conducted in search of novel properties in the area of fullerenes. One of the areas spawned from the science of fullerenes is the study of CNTs.

Consequent to the discovery of CNTs by Iijima [10] in 1991, it was realised that the theoretically predicted mechanical properties of these interesting structures have high

strength, high stiffness, low density and structural perfection, which could make them ideal for a wealth of technological applications. With the advance of CNT synthesis and device processing capabilities, the importance of developing and understanding nanoscale engineering devices has dramatically increased over the past decade. The single-walled carbon nanotubes (SWCNT) possess particularly outstanding physical and chemical properties. SWCNTs are remarkably stiff and strong, have electrical conductivity, and are projected to conduct heat even better than that of diamond, which suggests their eventual use in nanoelectronics. The unique properties of these structures promise unimaginable applications and thus attract a great deal of interest.

The extremely small (nano) size, outstanding physical properties and unique atomic arrangement of CNTs have triggered intensive research in a wide variety of fields, i.e., chemistry, physics, materials science and engineering. The tensile strength is 100 times more than that of steel with only a fraction of its weight [11]. CNTs have current carrying capacities 1000 times that of copper, have thermal stability up to 2800⁰ C in a vacuum and can transmit heat twice as high as pure diamond [12]. Because of high tensile strength, CNTs have potential applications in the areas of mechanical and as well as in composite technologies (space applications, material reinforcement etc). The CNT find wide range of applications in field emission panel display, sensing instruments, drug delivery and nanoelectronics due to excellent electronic and electrical properties.

2.2. Classification of CNTs

The outstanding electronic properties predicted for CNTs are a consequence of their structure, which can be pictured as being formed by rolling a graphene sheet into a cylinder. Because the graphene hexagonal lattice can be rolled at different angles, the geometry of a particular nanotube is best described in terms of the unit cell (OAB'B) of the carbon nanotube, as shown in Figure 2.1(a). The atomic arrangement of the carbon nanotube is described by the chiral vector, which can be defined by $C_h = n\bar{a}_1 + m\bar{a}_2$, where $\bar{a}_1$ and $\bar{a}_2$ are unit vectors on the hexagonal lattice and n and m are integers. Using this description, the chiral angle (θ in Figure 2.1(a)) and diameter of the nanotube are given as

$$\theta = \tan^{-1}\left(\frac{\sqrt{3}m}{2n+m}\right) \quad (2.1)$$

$$d_t = \frac{\sqrt{3}}{\pi} a_{C-C} \sqrt{m^2 + mn + n^2} \quad (2.2)$$

where a_{C-C} is the distance between neighbouring carbon atoms in a flat graphene sheet (approximately 0.142 nm). As shown in Figure 2.1(b), nanotubes with different chiral vectors (n, m) will have different atomic configurations.

Certain nanotube properties have been found to be strongly dependent on the chirality of the nanotube, including electrical resistivity and fracture behaviour. For example, a carbon nanotube will be metallic when the chiral vector satisfies the relationship $n-m = 3q$, where q is an integer, while all other nanotubes will be semi-conductive. It has been

estimated that 1/3 of all nanotubes are metallic. However, other properties, and in particular the stiffness, have been found to be relatively independent of the chirality.

(a) Honeycomb lattice of carbon atoms defined by unit vectors $\bar{a}_1$ and $\bar{a}_2$, the chiral angle θ and the unit cell.

(b) Possible vectors specified by the pairs of integers (n, m) for general carbon nanotubes, including zigzag, armchair, and chiral nanotubes.

Figure 2.1. Honeycomb lattice of carbon atoms [1].

2.2.1. Classification of CNTs based on chirality

CNTs can be classified into three categories based on chirality viz., Armchair, Zigzag and chiral nanotubes, which are shown in the Figure 2.2. The chirality of the carbon nanotube has significant implications on the material properties. In particular, tube chirality is known to have a strong impact on the electronic properties of CNT. The influence of chirality on the elastic stiffness is relatively small. The analytical work of Yakobson and Samsonidze [13] examined the instability of CNTs beyond linear response. Their simulations show that CNTs are remarkably resilient, sustaining extreme strain with no signs of brittleness or plasticity. *Armchair* tubes have carbon bonds perpendicular to the length of the tube. They behave like semiconductors, which either conduct or do not conduct electricity based on the surrounding environment. Semiconductors (like silicon) form the heart of computers, and it is expected that CNTs might someday provide an alternative [14]. Zigzag tubes have carbon bonds zigzag down their length, which makes conduct electricity better than regular metals. It is believed that these tubes may bring revolution in electrical field in future [14]. All other tubes are called *chiral* nanotubes and they behave like semi-metals.

(a) Armchair Nanotube

(b) Zigzag Nanotube

(c) Chiral Nanotube

Figure 2.2. Schematic models for single-walled carbon nanotubes [15].

2.2.2. Classification of CNTs based on layers

Carbon nanotubes can be further classified into three broad categories: Single-walled nanotubes (SWNT), multi-walled nanotubes (MWNT), and nanotube bundles or ropes of SWNT. Single walled CNTs consisting of a single layer of carbon atoms wrapped into a seamless cylindrical shape (shown in Figure 2.3) were first reported in 1993 [16]. Their diameters range from 0.4 to 2-3 nm, and their length is usually of the micrometer order. This may not be capped on each end by one half of a fullerene molecule. Typical diameters for SWNTs are of the order of 1nm, while lengths are often of the order of micrometer. This results in very large aspect ratios, which in traditional composites theory are desirable from the perspective of load transfer. Both the diameter and length of the SWNT are typically dependent on the particular technique used to create the nanotubes.

Figure 2.3. Rolling up graphene sheet into a tube [17].

MWNT consist of several concentric layers (or shells) of individual CNTs that are weakly coupled to each other through van der waals forces. A two and seven-layered structures of CNTs obtained using Transmission Electron Microscope (TEM) are shown in Figure 2.4. The spacing between these individual shells is on the order of 0.34 nm, which is slightly larger than the interlayer spacing in a graphene sheet. The diameter and number of shells comprising a MWNT is again dependent on the fabrication process, although diameters on the order of 30 nm may be considered as a ballpark estimate [18]. Typically, nanotubes are found to have self-organised into crystalline bundles [19, 20], consisting of several to hundreds of SWNTs or MWNTs arranged in a closest packed two dimensional lattice. Within these bundles, the nanotubes normally display a monodisperse range of diameters with adjacent tubes weakly coupled via van der waals interactions.

(a) Electron micrographs of the layered structure of a multi-walled carbon nanotube [21].

(b) A 3D view of double walled carbon nanotube [22].

Figure 2.4. Multi-walled carbon nanotubes.

2.3. Applications and importance in the present and future

Carbon nanotubes may find use in a wide range of applications in material reinforcement, space elevators, field emission panel display, chemical sensing, drug delivery, nanoelectronics, space applications, etc. The technology developments in the area of materials synthesis, device processing capabilities, understanding of nanoscale-engineering devices has got importance over the past decade. Single-walled CNTs possess particularly outstanding physical and chemical properties as compared to other

nanoscale materials. Composites based on nanotubes could offer strength-to-weight ratios beyond any materials currently available. SWNTs with a diameter of about 0.4 nm the thinnest yet have been made [23], and such fine tube raises new possibilities for electrical superconductivity [24]. It could have a great impact as the critical temperature for superconductivity becomes higher. A particular type of single walled nanotube, called as a single-wall carbon nanohorn (SWNH), is likely to be used in fuel cells within a few years [25]. SWNTs are good at electrical conductivity, and are projected to conduct heat even better than diamond, which suggests their eventual use in nanodevices and nanocircuits applications. SWCNTs are also under intensive study as efficient storage devices, both for storing alkali ions for nanoscale power sources and for storing hydrogen for fuel cell applications.

Ever since the discovery of CNTs, researchers have been exploring their potential in the area of bioapplications [26]. The development has been focused on nanoscale biosensor and bioreactor systems based on CNTs, which has been driven by the experimental evidence that biological species such as proteins and enzymes can be immobilized either in the hollow cavity or on the surface of CNTs [27]. Recently, hopes have been raised for the use of CNTs as superior biosensor materials in light of the successful fabrication of various electro-analytical nanotube devices, especially those modified by biological molecules [28, 29]. These prototype devices, sometimes prepared as ordered arrays or single-nanotube transistors, have shown efficient electrical communications and promising sensitivities required for such applications as antigen recognition, enzyme-catalyzed reactions [29] and DNA hybridizations [28].

The example for biorecognition is the scanning probe microscopy mapping of biofunctional receptors by using a CNT probe functionalised at the tip with biologically specific ligands [30]. There is also preliminary experimental evidence suggesting that CNTs may act as electromechanical actuators for artificial muscles [31] and that upon functionalisation with suitable bioactive molecules CNTs may serve as feasible substrates for neuronal growth [32].

For biocompatibility evaluations toward biological and biomedical applications, the lack of solubility of CNTs in aqueous media has been a major technical barrier [26]. The recent bloom of chemical modification and functionalisation methods has made it possible to solubilize and disperse CNTs in water, thus opening the path for their facile manipulation and processing in physiological environments. Equally important is the recent experimental demonstration that biological and bioactive species such as proteins, carbohydrates, and nucleic acids can be conjugated with CNTs. These nanotube bioconjugates will play a significant role in the research effort toward bioapplications of CNTs.

The lightest and strongest materials readily available today are the graphite epoxy composite materials that are commonly used in aerospace applications. Further there is a scope to develop multi-kilometre height towers for commercial applications; i.e., communications, science observatories, and launch platforms [33]. In future, this graphite epoxy composites may replace by the carbon nanotube composites.

Recently, NASA was planning to build space elevators, which requires high tensile strength (~ 62.5 GPa), but the actual strength of a carbon nanotube rope may be much higher than that [33]. The following Figure 2.5 shows a comparison between high-strength steel and CNTs. At present, production of CNTs is very expensive and limited in quantity. The longest nanotubes produced to date are no more than a few microns in length [33].

Figure 2.5. Yielding of high-strength steel as compared to carbon nanotube rope [33].

2.3.1. Some potential applications of CNTs

- Structural applications in the fields of space, aircraft, ships, automobiles, trains
- Future integrated structures and engine components for hypersonic flight vehicles
- Pressure vessels for flight vehicles and commercial industry needs
- Lightweight Collision-protection materials for vehicles and personnel

- Structural members for buildings and tall towers many kilometres in height
- Earthquake-resistant structures
- Sports equipment: stronger and light tennis rackets, bike parts, baseball bats
- Electronic circuit devices with higher densities than the present
- Light bulb filaments: alternative to tungsten filaments in incandescent lamps
- Power transmission lines and towers
- Controlled drug delivery/release
- Artificial muscles and biosensors
- Data storage device applications
- Super flywheel energy storage devices
- Antennas at optical wavelengths
- Electrodes for high-energy density batteries
- Integration of structures with thermal management systems for flight vehicles
- Fabrics for better spacesuits and other thermal protection applications
- Electromechanical actuators, sensing devices for chemical and biological systems
- Diodes, transistors, display devices, conductive films, MWNT coated magnetite
- Solar cells, superconductors, ultracapacitors, air and water filters, biological containers etc.

Thus, CNTs clearly have wide-ranging properties and structures that are still in the process of discovering, and a wide variety of potential applications [25].

2.4. Experimental observations of elastic properties of CNTs

There have been many theoretical studies on the computation of elastic properties of graphene sheets and CNTs. However, there have only been fewer experimental studies. This is attributed to the technical difficulties involved in specimen preparation and difficulties in conducting experiments for direct determination of the mechanical properties. This section provides a brief review of selected publications on the experimental studies dealing with the determination of Young's modulus and natural frequencies of CNTs.

2.4.1. Young's modulus measurements of CNTs

The first experiment to determine the Young's modulus of isolated CNTs was conducted by Treacy et al. [34] in 1996 by measuring the amplitude of intrinsic thermal vibrations. TEM is used to measure the thermal vibrations at the tip of cantilever CNTs (Figure 2.6). To determine the Young's modulus, Y , of CNTs, they assume that the nanotube is a homogeneous cylindrical cantilever of length, L , with outer and inner radii a and b , respectively. Using the beam theory for the free vibration analysis of cantilever CNTs, the experimentally measured results have been analysed assuming Gaussian vibrational profile with a standard deviation, σ , given by

$$\sigma^2 = 0.4243 \frac{L^3 kT}{Y(a^4 - b^4)} \quad (2.3)$$

where k is the Boltzmann constant and T is the absolute temperature. They determined the mean value of Young's modulus of CNTs as 1.8 TPa. Later the same technique was

used by Krishnan et al. [35] and they reported a Young's modulus value around 1.25 TPa, which is somewhat smaller than the value reported by Treacy et al. [34].

Figure 2.6. TEM images of free-standing multi-walled CNTs showing the blurring of the tips due to thermal vibrations at 300 and 700 K [34].

Another technique to determine Young's modulus is to measure the force exerted by the cantilever CNT using Atomic force microscope (AFM). Based on the measured tip deflection, δ , and force, F , the Young's modulus of CNTs is determined using the formula:

$$\delta = \frac{FL^3}{3YI} \quad (2.4)$$

where I and L are the second moment of area and length of the CNT, respectively. Using this technique, the Young's modulus value has been reported as 1.28 ± 0.5 TPa [36]. The same measurement technique was followed by many other researchers and the reported Young's modulus values are 0.27 to 0.95 TPa by Yu et al. [37] and 0.81 ± 0.41 TPa by Savetati et al. [38].

Yet another approach to determine the Young's modulus of CNTs is to excite the CNT electrostatically using an external ac-field. The technique is to apply a time-dependent voltage $V(t)$ to the CNT adjusting the frequency of excitation to resonantly excite the

bending modes of CNT [39]. The experimentally determined resonant (natural) frequency is then expressed as function of Young's modulus, Y , as in Equation (2.6), from which the Young's modulus is determined.

$$V(t) = V_d \cos(\omega t) \quad (2.5)$$

$$\omega_n = \frac{\beta_n^2}{8\pi L^2} \sqrt{\frac{Y(D_o^2 + D_i^2)}{\rho}} \quad (2.6)$$

In Equation (2.5), V_d is the excitation voltage and ω is the excitation frequency. In Equation (2.6), ω_n and β_n are the n^{th} mode natural frequency and the corresponding constant, respectively. The parameters D_o , D_i , L and ρ are the outer diameter, inner diameter, length and density of the CNT, respectively.

Figure 2.7. SEM image of the two oppositely aligned AFM tips holding a MWCNT which is attached at both ends on the AFM silicon tip surface by electron beam deposition of carbonaceous material [37].

A direct and simple method has also been used to determine the Young's modulus [37]. In this method, the elongation of CNT is measured by applying a tensile load on the CNT (Figure 2.7). Several tensile load experiments have been performed and the reported tensile strengths of CNTs are in the range of 11 to 63 GPa [37]. Based on failure analysis, stress-strain curves (Figure 2.8) have been drawn during the SEM experiments, from which the Young's modulus of CNTs has been estimated to be between 270 and 950 GPa.

Figure 2.8. (A) Schematic explaining the principle of the tensile-loading experiment. (B) Stress versus strain of individual MWCNTs [37].

2.4.2. Natural frequency measurements

Raman spectroscopy is one of the most sensitive and commonly used tools for the experimental study of isolated SWNTs and SWNT bundles [40, 41]. The Raman experiment is simple, non-destructive, non-invasive, can be conducted at room temperature and under ambient pressure, and is a commonly available facility in universities and labs. The radial breathing mode (RBM) is generally used to determine the diameter, d , based on the measured frequency, ω_{RBM} , and Raman intensity, I_{RBM} . The RBM corresponds to the coherent vibration of carbon atoms in radial direction, as if the tube were “breathing”. The various features (RBM, D-band, G-band, M-band) observed in the Raman scattering process depend on the diameter and mode frequencies of the CNT [42]. The diameter dependence of the various SWNT mode frequencies is expressed by

$$\omega = \omega_0 + \beta / d^n \quad (2.7)$$

where ω_0 , β and n are the frequency of 2D graphite ($d \rightarrow \infty$), coefficient and exponent of the diameter dependence, respectively. The typical values of ω_0 , β and n for SWNT RBM mode are 0, 248 $\text{cm}^{-1} \text{ nm}$ and 1, respectively [42]. For SWNT bundles in the diameter range $d = 1.5 \pm 0.2 \text{ nm}$, the values of $\omega_0 = 10 \text{ cm}^{-1}$, $\beta = 234 \text{ cm}^{-1} \text{ nm}$ and $n=1$ have been determined experimentally [43]. Figure 2.9 shows typical experimental results of Raman intensity and the frequency of SWNT bundles and isolated SWNTs.

Figure 2.9. (a) Raman spectra of SWNT bundles [44]. (b) Raman spectra of a metallic and a semiconducting isolated SWNT. The spectra shows the RBM modes, D, G and M band features [43].

The RBM is a unique feature of CNTs and the corresponding measured frequency ranges from 120 - 350 cm⁻¹ (1 cm⁻¹ = 0.03 THz) for SWNTs of diameters in the range 0.7 to 2 nm. For small diameter ($d < 1$ nm), Equation (2.7) is not expected to hold good due to nanotube lattice distortions leading to a chirality dependence of ω_{RBM} [45]. However, for large diameter SWNTs ($d > 2$ nm), the intensity of the RBM feature is weak and is hardly observable in experiments [45]. So, Equation (2.7) is applicable for diameters 1 nm – 2 nm only.

A typical Stokes resonance Raman measurement of CNTs is shown in Figure 2.10. In this figure, the excitation laser energies, E_L , in the range 1.52 - 2.71 eV have been used during the experiment. Several RBM peaks appear in Figure 2.10, each peak corresponding to a SWNT resonance with E_L .

Figure 2.10. Stokes resonance Raman measurement of CNTs obtained with 76 different laser lines EL [44]. The colours indicate the Raman intensity.

2.5. Simulation methods

There are four categories of molecular simulation methods for nanotube systems: *ab initio* methods, classical molecular dynamics methods (MD), Tight binding molecular dynamics methods (TBMD), and multiscale and continuum methods. In general, *ab initio* methods give more accurate results than MD, but they are also much more computationally intensive. Tight-binding molecular dynamics (TBMD), a hybrid method is a blend of certain features from both MD and *ab initio* methods. Recently continuum and multiscale approaches have been proposed for solving large system of molecules.

2.5.1. *Ab initio* methods

Ab initio, (Latin word means "from scratch") or first-principles method solves the complex quantum many-body Schrodinger equation [46]. This method is to regard many-atoms systems as many-body systems composed of electrons and nuclei, and to treat everything on the basis of first-principles of quantum mechanics, without introducing any empirical parameters [47]. The *ab initio* method provides more accurate descriptions of quantum mechanical behaviour of materials. However, the system size is limited to only few hundred atoms. In general, the state of a particle is defined by a wave function ψ based on the wave-particle duality [46]. The Schrodinger equation [46] is

$$H\psi = E\psi \quad (2.8)$$

with H the full quantum many-body Hamiltonian operator and ψ is the energy eigenfunction corresponding to the energy eigenvalue E . The *ab initio* methods are available only for very limited classes of problems and are used to solve for analytical or exact solutions. The most commonly used approximations in this method are Born-Oppenheimer approximation [46], which says that the electrons are always in a steady state derived from their averaged motion compared to the nuclei motion. In Schrodinger equation, Hamiltonian operator consists three parts, kinetic energy when operating on the electron wave function, electron–electron coulomb interaction and coulomb potential from the nuclei.

The exact solutions of the Schrödinger's equation are generally very difficult to obtain [46]. Hence, some approximation methods namely *Hartree-Fork* and *Density functional theory* approximations have been developed. *Ab initio* methods possess high accuracy

and transferability, due to there being no experimental inputs. However, higher order of computational effort limits the applicability of the *ab initio* method. The other methods such as tight-binding methods [48] or classical molecular dynamics [46] are very important in order to overcome the complexities of some materials.

2.5.2. Tight-binding methods

The tight-binding theory has been proposed by Koster and Slater [48]. The main advantage of tight-binding method is that it can handle much larger system (few hundreds to thousands atom) than the *ab initio* method and maintain better accuracy than molecular dynamic simulation. In TBMD, a linear combination of atomic orbital is adopted in the wave function. The Hamiltonian matrix can be parameterised, and the total energy and electronic eigenvalues can be deduced from the Hamiltonian matrix. The interatomic forces are evaluated in a straightforward way based on the Hellmann-Feynman theorem and rest of the procedure is almost identical to the MD simulation, hence this method referred to as the tight-binding MD method (TBMD).

Although TBMD can consider the quantum structure of electron, its accuracy is less than that of *ab initio* method. The major problem with the TBMD method is the way the parameterisation of the Hamiltonian limits of applicability, or transferability as referred to by the computational physics community. In early development of TBMD, Harrison [49] attempted to use a set of universal parameters; this approach turns out to be neither transferable nor accurate. The solution is then to add in modifications [50, 51], or to use a completely different basis [52]. *Ab initio* and TBMD methods are still restricted in their capability with respect to both the number of atoms and simulation timescale.

2.5.3. Classical molecular dynamics

Classical molecular dynamics (MD) is an empirical method and easy to implement in large systems (million to billion atoms). The method of classical molecular dynamics was first proposed by Alder and Wainwright [53]. MD describes system's atomic-scale dynamics, where atoms and molecules move, while interacting with many of the atoms and molecules in the vicinity. The system's dynamics evolution is governed by Hamilton's classical equation of motion from Newton's second law,

$$m_i \frac{d^2 r_i}{dt^2} = -\nabla V \quad (2.9)$$

where m_i and r_i are the mass and spatial coordinates of the i^{th} atom, respectively, V is the empirical potential for the system and ∇ denotes the spatial gradient. Due to small scale involved, explicit integration algorithms such as the Verlet method [54] and other high-order methods are commonly used to ensure high order accuracy. Allinger and co-workers developed [55, 56] a molecular mechanics MM2 force field and improved version known as MM3 force field. These methods are designed for a broad class of problems in organic and inorganic systems. Abell [57] proposed the quantum-mechanical concept of bond order formalism for CNT characteristics. Using morse-type potential, Abell showed that the degree of bonding universality could be well maintained in molecular modelling for similar elements. Tersoff [58, 59] introduced this concept for the modelling of group four elements such as Carbon, Silicon, and Germanium and reasonably accurate results were reported. Nordlund et al. [60] modified the Tersoff potential such that the interlayer interaction is also considered. Brenner [4] made further improvements to the Tersoff potential by introducing additional terms into bond order

function. Compared with the Tersoff potential, Brenner's potential shows robustness in the treatment of conjugacy, and it allows for forming and breaking of the bond with the correct representation of the bond order. Brenner's potential has enjoyed success in the analysis of formulation of fullerenes and their properties [61, 62], surface patterning [62], indentation and friction at nanoscale [63], and energetics of nanotubes [62]. An improved version of Brenner's potential has recently been proposed [64, 65]. Another important aspect of modelling in the analysis of CNT systems is the interlayer interaction. Lennard-Jones introduced Lennard-Jones (LJ) potential [66] for atomic interactions

$$u(R_{ij}) = 4\varepsilon \left[\left(\frac{R}{R_{ij}} \right)^{12} - \left(\frac{R}{R_{ij}} \right)^6 \right] \quad (2.10)$$

and inter-atomic force between two atoms is expressed as

$$F_{ij} = -\frac{\partial u(R_{ij})}{\partial R_{ij}} = 24 \frac{\varepsilon}{R} \left[\left(\frac{R}{R_{ij}} \right)^{13} - \left(\frac{R}{R_{ij}} \right)^7 \right] \quad (2.11)$$

where R_{ij} denotes the inter-atomic distance between atoms i and j , ε is the energy at the minimum in $u(R_{ij})$ and R is the interatomic distance.

One of the major disadvantages of the potential mentioned above is that the difference in interlayer binding energy of the 'AA' and 'AB' stacking configuration for two rigid layers spaced at ~ 0.34 nm is probably not well represented; the corrugation in the interlayer energy, due to the π bonds projecting orthogonal to the plane of the layers, is not well captured. The corrugation between neighbouring layers will play a central role in the friction present in such a nano-bearing system. The effect of interlayer registration between CNT and the surface it is sliding on have been studied recently in a number of

interesting experiments by Falvo et al. [67]. Kolmogorov and Crespi [68] developed a new registry-dependent graphitic potential, which accounts for the exponential atomic-core repulsion and interlayer delocalisation of π orbitals in addition to the normal two-body van der Waals attraction. This model derives an approximately 12 meV/atom difference between the ‘AB’ stacking and the ‘AA’ stacking.

Apart from the above stated potentials, there are many-body empirical potentials developed during the last few decades, such as AMBER [3], CFF95 [69], CHARMM [70], Drieding [71], MMFF [72], MM2 [55, 73], MM3 [73], MM4 [74], OPLS [75], SHARP [76], UFF [77], VALBON [78]. (AMBER force field [3] is used to simulate graphene sheet in Chapter 3.) In these models, the total system potential energy can be expressed as a sum of several individual energy terms such as, bond stretching, angle variation, inversion, torsion, van der Waals and electrostatic interactions.

The effects of finite system size and surfaces are always severe problem in molecular dynamics [79]. The previous methods, *ab initio*, TBMD and classical molecular dynamics are all deterministic and the state of art of the system is determined completely by the initial condition. These approaches are useful in understanding the stable structures, vibrations and growth at the atomistic level. MD computations are limited to simulations in the order of 10^6 - 10^8 atoms [79].

2.5.4. Continuum and multi-scale models

Although there has been a tremendous increase in available computational power and improvement in numerical algorithms, the size of the problem that can be handled by

classical MD computations is still limited. The simulation of larger systems or longer times must currently be left to continuum methods. One might immediately see the possibility of applying the finite element method (FEM) to the computational mechanics of nanotubes since the continuum concept of stress can be extracted from a molecular model. However, the fundamental assumption of the continuum approximation that quantity vary slowly over lengths of the order of atomic scales breaks down in many of the most interesting cases of nanomechanics. Thus, it would be very useful to have in hand a method that allows the use of a molecular dynamics-like method in localised regions, where quantities vary quickly on the atomic length scale, seamlessly blended with a continuum description of the surrounding material in which, presumably, small scale variations are unimportant or can be treated in an averaged sense.

Several authors have worked towards this goal. Tadmor et al. [80] proposed quasicontinuum method, and extended and applied to several different problems over the last few years [80-82]. This gives a theory for bridging the atomistic and continuum scales in quasistatic problems. These methods have been applied to the simulation of dislocations [83-85], grain boundary interaction [86, 87], nanoindentation [82, 87], and fracture [81]. The quasicontinuum method successfully extended the analysis of the CNTs system, although careful treatment is needed. The major challenge in the simulation of CNTs using the quasicontinuum method is the fact that CNT is composed of atomic layers. The thickness of each layer is the size of carbon atom. In this case, it can be shown that the direct application of the Cauchy-Born rule results in inconsistency in the mapping. Arroyo et al. [88] corrected this inconsistent mapping by introducing the concept of exponential mapping from different geometry. An alternative approach is to

start with the variational principle and develop a method without the Cauchy-Born rule. Qian et al. [46] developed the framework of this method with the introduction of a meshfree approximation [86]. The meshfree and particle methods and their application explained by Li and Liu [89].

Odegard et al. [90, 91] have proposed modelling a CNT as a continuum by equating the potential energy with that of the representative volume element (RVE). This assumption seems to be the same as that in the quasicontinuum method; however, the Born rule is not used. The method has been recently applied in the constitutive modelling of CNT reinforced polymer composite systems [92]. The meshfree methods have been directly applied by Qian et al. [93] in the modelling of a CNT interacting with C_{60} . The C_{60} molecule is, on the other hand, modelled with a molecular potential. The interaction between the C_{60} and the continuum is treated based on the conservation of momentum. The interaction forces on the CNT are obtained through the consistent treatment of the weak formulation.

Abraham et al. [94, 95] modelled coupling length scales of FE/MD/TB. Three simulations are run simultaneously using finite element (FE), molecular dynamics (MD) and semi-empirical tight-binding (TB). Each simulation is performed on a different region of the domain, with a coupling imposed in handshake regions where the different simulations overlap. The method is designed for implementation on supercomputers via parallel algorithms, allowing the solution of large problems. Rafii-Tabar et al. [96, 97]

have presented a related method combining FE and MD for the simulations of crack propagation.

The coarse-grained molecular dynamic methods [98, 99] have been introduced as a replacement for finite elements in the FE/MD/TB simulations. The fine scale quantities that are not included in the coarse scale motion are not neglected completely, as their thermodynamic average effect is retained. Liu et al. [86, 100] has been successfully applied in the multiple-scale problems involving strain localisation [101], boundary layers [102] and coupling of finite elements with meshfree shape functions [103].

Although substantial progress has been made in recent years, multi-scale modelling method is still in its infancy, and it still requires intensive efforts [81]. As pointed by many researchers, the main issues in the development of seamless multi-scale modelling methodologies are still limitations on the length and time scale and numerical accuracy and efficiency. Hence, more accurate and efficient multi-scale modelling methodologies are still desirable, and attracts many researchers [81].

2.6. Continuum mechanics for CNT

Computational approaches, based on molecular dynamics simulations of CNT are currently limited to small length and time scales problems. Which cannot deal with large-scale problems such as the study of CNT as well as nano-composite based structures. Continuum approaches based on continuum mechanics have also been applied successfully for simulating the mechanical responses of individual or isolated CNTs

which are treated as beams, thin shells or solids in cylindrical shapes [36, 46, 93, 104-107]. These studies suggest that the continuum mechanics approach can be applied safely to investigate the mechanical behaviours of the CNTs when the lengths of the CNTs are about 100 nm and above. For example, the authors Wong et al [36], successfully applied the simple beam theory to model CNTs and extracted Young's modulus of the CNT from the force-deflection curve obtained from their experiment, the results are consistent with other reported work. Although successful to some extent and efficient in computation for models at larger length scales, continuum mechanics at this threshold faces the risk of breakdowns more than ever before, compared with the micromechanics simulations [108].

Odegard et al. [91] proposed Equivalent-continuum modelling for nano-structured materials. This method serves as a link between computational chemistry and solid mechanics by substituting discrete molecular structures with equivalent-continuum models.

One of the fundamental issues that need to be addressed in modelling macroscopic mechanical behaviour of nano-structured materials based on molecular structure is the large difference in length scales. On the opposite ends of the length scale spectrum are computational chemistry and solid mechanics, each of which consists of highly developed and reliable modelling methods. Computational chemistry models predict molecular properties based on known quantum interactions, whereas the computational solid mechanics models predict the macroscopic mechanical behaviour of materials

idealised as continuous media based on known bulk material properties. However, a corresponding model does not exist in the intermediate length scale range. If a hierarchical approach is used to model the macroscopic behaviour of nano-structured materials, then a methodology must be developed to link molecular structure and macroscopic properties. Equivalent continuum model allows molecular properties of nano-structured materials obtained through molecular mechanics models to be used directly in determining the corresponding bulk properties of the material at the macroscopic scale. Equivalent continuum models have been demonstrated with two independent examples. A representative volume element (RVE) of the graphene layer has been modelled as a continuous plate with effective thickness that has been determined. But this thickness value significantly larger than the widely accepted value for the graphitic inter-planer spacing, 0.34 nm and much larger than the value suggested by Yakobson et al. [109] of 0.066 nm. The effective bending rigidity of the graphene sheet has been described in terms of the atomic interactions that dominate the overall bending behaviour. This effective bending rigidity value is much higher than that used by Yakobson et al. [109] and Robertson et al.[61].

Hinkley et al. [110] developed a 2-D nano-scale finite element model based upon inter-atomic and inter-molecular force fields to simulate polymer deformation. Harik et al [111] has been studied the applicability of continuum shell theories to the global mechanical behaviour of CNTs. The parametric study has been conducted on variety of geometries as a guide for the applicability of different models and its possible limitations. To address the effect of nanotube structure on their deformation, all nanotubes geometries are divided into four major classes that require distinct models. These classes

include thin (thickness-to-radius ratio $h_{NT}/R_{NT} < 1/20$) and thick ($h_{NT}/R_{NT} > 1/20$) NT shells, high aspect ratio (length-to-radius ratio $L_{NT}/R_{NT} \gg 1$) NTs and NT beams (radius-to-side length of carbon ring $R_{NT}/a \approx 1$). The key parameters that control the buckling strains and deformations modes of these classes of nanotube were determined. The parametric map that links the four classes of nanotubes with the specific types of continuum models has been studied. The continuum assumptions made in representing a nanotube as homogeneous thin shells were analysed to identify possible limitations of applying shell theories and using their bifurcation-buckling equations in the nano-scale.

2.7. Vibration studies and flow through nanotubes

The technology advances have led to the need to creating functional devices at nanoscales for potential applications of nanoelectro mechanical systems (NEMS) such as nanoswitches [112], nanosensors [113], nanoactuators [31] and nanotweezers [114]. There have been continuing efforts in fabricating nanomechanical systems operating in high frequencies. CNTs promise several potential applications in various fields due to their high natural frequencies in the range of Terra-hertz. The studies on vibrations of CNTs are relatively less as compared to static analysis. Resonators fabricated from SiC have been observed to have a fundamental frequency as high as 1 GHz [115]. Recently, the researchers examined the feasibility of using CNTs as resonance based sensor applications such as resonators, chemical and bio-sensors, mass detectors, oscillators, filters, nanomechanical memory devices etc., due to their high natural frequency of the order of 1 THz [5, 116-121]. Recently, energy exchanges between the orderly intertube axial motion and vibration modes of two coaxial CNTs at different temperatures are

studied by Zhao et al. [122]. Reduction in the size of the nanotubes increases its resonant frequencies and sensitivity [117] causes many proposed applications of CNTs involving short nanotubes with aspect ratio 10 to 50 are of practical significance [118]. The scaling behaviour of sub-20 nm short channel CNT transistors has been studied by Seidel et al. [123]. The single-electron transistors of CNTs of length about 20 nm [124] and electromechanical devices as memory units using periodic supports less than 20 nm length CNTs [125] have been used as applications of short CNTs. The effect of thermoelastic damping on microscale and nanoscale resonators has been studied by Lifshitz and Roukes [126]. Recently, the effect of quality factor has been studied on NEMS electrical resonant circuits by Ekinici and Roukes [127]. The range of quality factors (10^3 to 10^5) has been used in literature [115, 127-129] to study the NEMS applications.

The perfect hollow cylindrical geometry and superior mechanical strength, CNTs hold substantial promises as nanocontainers for gas storage and nanopipes for conveying fluids. Fluid conveying CNTs raises a significant and challenging topic in nanotechnology [130-133]. Wide range of fluid flow velocities inside CNTs from 2000 m/s to 100,000 m/s have been considered to study the vibration analysis of CNTs in literature [131-134]. The effect of internal moving fluid on free vibration analysis and structural instability of CNTs has been studied by Yoon and Ru [134]. This area is still less explored in the literature. The mechanical response of the CNTs to a series of external Ar atom impact has been studied with nanotube subjected to a gas flow is important for NEMS devices-related applications, such as nanovalves, which control the

flow rate of fluid through nanometer scale channels [135]. The study of hydrodynamic properties of water flowing past an array of single walled CNTs has been studied using the nonequilibrium molecular dynamics simulations by Walther et al. [136]. Experimental work has been conducted to study the flow induced currents and voltage when the fluid passing over the bundle of single walled CNTs by Ghosh et al. [137]. Karla et al. [138] have been studied the water molecules flow through membranes of open-ended CNTs under an osmotic gradient using the molecular dynamic simulations. The simulations have been conducted to study the nanoscale flow through CNT membranes with water, proton and biopolymers by Hummer [139]. Experimental studies has been conducted to study the liquid flow magnitude through a membrane composed of an array of aligned carbon nanotube by Majumder et al. [140] and they also observed that the frictionless interface between carbon nanotube walls and liquid at high fluid velocities.

2.8. Motivation

A CNT can be looked up on as a graphene sheet rolled into tube. The graphene sheet, in turn, can be looked up on as a repeated assemblage of a generic building block called carbon ring. Hence, analysis of a single carbon ring and graphene appears important before analysing CNTs. Such studies are limited and hence form the motivation to take this up as the first problem of this thesis.

A scan through literature reveals that there is apparently a large scatter in the elastic properties of CNTs reported by various researchers (refer Tables 2.1 and 2.2). The scatter may be partially due to the inherent accuracy differences associated with various modelling, simulation and experimental techniques used. The wall thickness value

reported by various authors also exhibit considerable variation from as low as 0.066nm to as high as 0.69 nm. Despite this variation, the product of Young's modulus (Y) and wall thickness (t) is around 0.36 for most of the cases (Table 2.2). With regard to computational simulation, a poor control of numerical errors during simulation may play an important role in the scatter of reported values. If the imposed displacement step size is too large, then the nonlinearity may dominate. On the other hand, if the imposed displacement step size is too small, then the truncation and round-off errors may dominate. Although, there are many studies reported in literature dealing with numerical simulation on CNT, studies on numerical error analysis are rare. This is one of the problems addressed in this research.

Researchers have explored the feasibility of using CNTs for resonance based sensor applications in NEMS. The existing computational methods for computing the natural frequencies include *ab initio* methods, tight binding and molecular dynamics, and continuum models. *Ab initio* methods are more accurate, but at the same time computationally more intensive, and hence is limited to small structures containing few hundreds of atoms. The tight binding and molecular dynamics methods are moderately expensive and used for larger structures containing a few thousands of atoms. The continuum models are useful to analyse even larger structures. Such studies model the CNTs either as continuum beam structures with appropriate equivalent Young's modulus and wall thickness values taken from the literature, or as an assemblage of truss elements using AMBER force field [3]. Brenner potential [4] has emerged as one of the successful potentials used for computing the mechanical properties of CNTs. However, the studies

using this potential for computing the natural frequencies are scarce [5] and hence this forms another focus of research in this thesis.

Fluid flow inside CNTs is another significant and challenging research topic. Fluid flow through CNTs is likely to find a wide variety of applications. However, very little work has been done in this area. The lack of consistency in the Young's modulus and wall thickness, the appropriate values has been used to compute the natural frequencies. To avoid such ambiguity in choosing appropriate Young's modulus and wall thickness values for vibration analysis of fluid conveying CNTs, and hence a need to develop computational methods to deal with such problems.

Table 2.1. Different Young's modulus values of CNT reported in literature.

S. No	Young's Modulus, Y (TPa)	Author	Method/model
1	0.213 ($\nu=0.159$) 0.531 ($\nu=0.160$) 0.707 ($\nu=0.161$) 1.06 ($\nu=0.162$) 2.08 ($\nu=0.172$)	Shen and Li (2004) [141]	Molecular Mechanics
2	0.27 to 0.95 MWCNT	Yu et al. (2000) [142]	Atomic force microscope (AFM)
3	0.4 to 4.15	Treacy et al. (1996) [34]	Measurements of thermal vibrations.
4	0.5	Halicioglu (1998) [143]	Brenner
5	0.69	Sammalkorpi (2004) [144]	Molecular Dynamics
6	0.764	Zhou (2001) [145]	LACO-MO cluster method
7	0.78 to 2.34	Cooper and Young (2000) [146]	Raman spectroscopy
8	0.81 $\pm$ 0.41	Salvetat et al. (1999) [38]	Atomic force microscope (AFM)
9	0.94 to 1.18	Van Lier et al. (2000) [147]	<i>Ab initio</i> computations
10	0.94	Belytschko et al. (2002) [148]	Modified Morse
11	0.96	Mielke et al (2004) [149]	DFT
12	$\sim$ 0.99	Ozaki et al. (2000) [150]	Molecular Dynamics simulations
13	1.0	Cornwell et al. (1997) [151]	Quenched molecular dynamic simulations
14	$\sim$ 1.0	Lu J.P. (1997) [152]	Molecular Dynamics
15	1.0	Wang et al (1997)[36]	Deflection forces
16	1.0	Popov et al. (2000) [153]	Lattice dynamic model using Born's perturbation technique.
17	1.0	Yao and Lordi (1998)[154]	Universal force field
18	1.01	Ogata and Shibutani (2003) [155]	DFT
19	1.01	Li and Chou (2003) [156]	Structural mechanics: Stiffness matrix method

20	1.024	Cho (2006) [157]	Finite Element Method
21	~1.025	Li et al. (2003) [22]	Molecular structural mechanics model
22	1.03	Jeng et al. (2004) [158]	Brenner potential
23	1.05±0.05	Li et al. (2003) [156]	Molecular structural mechanics model
24	1.06	Sanchez-Portal et al. (1999) [159]	<i>Ab initio</i> calculations
25	1.06	Robertson et al. (1992) [61]	Brenner & LDF
26	1.07	Yakobson et al. (1996) [109]	Brenner
27	1.2	Tombler et al. (2000) [160]	3 point bending test
28	1.238	Jin and Yuan (2003) [161]	Molecular Dynamics
29	1.24	Hernandez et al. (1998) [162]	Tight-binding molecular dynamics
30	1.25	Krishnan et al. (1998) [35]	Transmission Electron Microscope (TEM)
31	1.28±0.6	Wong et al. (1997) [36]	Atomic force microscope (AFM)
32	1.7-2.4(MWCNT) 2.8-3.6(SWNT)	Lourie et al. (1998) [163]	Micro-Raman Spectroscopy
33	1.7	Treacy et al. (1996) [34]	Thermal vibrations
34	1.8	Lu JP. (1995) [164]	Transmission electron microscopy (TEM)
35	1.8±1.4 (MWCNT)	Poncharal et al. (1999) [39]	Transmission electron microscopy (TEM)
36	3.859 (SWNT)	Kudin et al. (2001) [165]	<i>Ab initio</i> computations
37	4.7	Tu and Ou-Yang (2002) [166]	Local density approximation modeling
38	4.84	Pantano et al. (2004) [167]	Continuum shell modelling
39	5.1	Zhou et al. (2000) [168]	Tight-binding model
40	~5.5	Yakobson et al. (1996) [109]	Molecular dynamics

Table 2.2. Wall thickness and corresponding in-plane stiffness values of CNT reported in literature.

S.No	Wall thickness, t (nm)	In-plane stiffness, Yt (TPa-nm)	Author	Method/model
1	0.066	0.363	Yakobson et al. (1996) [109]	Molecular dynamics
2	0.074	0.377	Zhou et al. (2000) [168]	Tight-binding model
3	0.075	0.353	Tu and Ou-Yang (2002) [166]	Local density approximation modelling
4	0.075	0.363	Pantano et al (2004) [167]	Continuum shell modelling
5	0.089	0.343	Kudin et al. (2001) [165]	<i>Ab initio</i> computations
6	0.147	0.353	Tserpes and Papanikos (2005) [169]	Structural mechanics: FE method
7	0.286	0.293	Cho (2006) [157]	Finite Element Method
8	0.34	0.343	Li and Chou (2003) [156]	Structural mechanics: stiffness matrix method
9	0.34	0.34	Lu J.P. (1997) [152]	Molecular Dynamics
10	0.34	0.42	Hernandez et al. (1998) [162]	Tight-binding molecular dynamics
11	0.34	0.421	Jin and Yuan (2003) [161]	Molecular Dynamics
12	0.34	0.34	Yao and Lordi (1998) [154]	Universal force field
13	0.34	0.337	Ozaki et al. (2000) [150]	Molecular Dynamics simulations
14	0.34	0.32	Belytschko et al. (2002) [148]	Modified Morse
15	0.34	0.4	Van Lier et al. (2000) [147]	<i>Ab initio</i> computations
16	0.34	0.36	Robertson et al. (1992) [61]	Brenner & LDF
17	0.34	0.364	Yakobson et al. (1996) [109]	Brenner
18	0.34	0.34	Cornewell and Wille (1997) [151]	Brenner
19	0.68	0.34	Halicioglu (1998) [143]	Brenner
20	0.69	0.338	Odegard et al. (2002) [91]	Equivalent-continuum modelling

Chapter 3

ANALYSIS OF CARBON RING AND GRAPHENE SHEETS

The objective of this Chapter is to present the results of some preliminary analysis carried out during the initial phases of this doctoral research. The graphene sheets are made of a repeated assembly of a generic building block called carbon ring. The carbon nanotube (CNT), on the other hand, can be looked up on as graphene sheets rolled into tubes. Hence, analysis of a single carbon ring is the simplest study one could conceive before embarking on more realistic and complex problems. This forms the motivation to take up analysis of carbon ring and graphene sheets as the first problem of this research. The aim of this study has been to understand how the single carbon ring and graphene sheet deform, and develop a simple technique to determine their elastic properties with respect to tension/compression, bending and shear deformations.

As stated in Chapter 2, there are many different many-body empirical potentials developed during the last few decades [3]. Out of these, AMBER force field and Brenner potential have been used for the simulation of CNTs. Although Brenner potential is now widely used for the simulation of CNTs, AMBER force field has been used for the results reported in this Chapter for two reasons: It is simpler and hence easy to implement in a computer program, thereby giving a quicker insight into the research on graphene sheet and CNTs. For the results reported in the subsequent Chapters in this thesis, Brenner potential has been used. The results obtained with Brenner potential have been compared with those obtained in this Chapter. This gives an idea of how far the results from AMBER force field differ from that of Brenner potential.

This Chapter is mainly divided into two sections. Section 3.1 is dedicated to single carbon ring analysis. The formulation of molecular mechanics model and equivalent truss element model are presented and the results for typical deformation modes are discussed in this section. Section 3.2 is dedicated to equivalent continuum modelling of graphene sheet. Based on equivalent continuum modelling, equivalent elastic properties of graphene are determined. A convergence analysis is carried out to study the variation of elastic properties with shape and size of graphene.

Figure 3.1. Carbon ring of a graphene sheet.

3.1. Analysis of a single hexagonal carbon ring

Carbon nanotubes are closely related to other forms of carbon, viz., the crystalline 3D graphite, and its constituent 2D layers. Each of the individual layers in the crystalline graphite is called a graphene layer [1]. As mentioned previously, graphene sheets are made of regularly arranged hexagonal carbon structure called carbon rings, or carbon cells which are also referred as graphene cells as shown in Figure 3.1. In other words, a single carbon ring is the fundamental building block, which is arranged in a repetitive

pattern in the graphene sheets as well as the CNTs. A single walled carbon nanotube may be imagined as a graphene sheet approximately rolled up into a seamless cylinder of diameter of the order of nanometers.

An objective of this doctoral research is to extract the mechanical properties of the graphene sheets as well as the CNTs. However, in this section, only a single carbon ring model of graphene sheet is considered, and the equivalent mechanical properties are predicted based on this model. For predicting these properties, an equivalent truss element model is considered. The molecular potential of a single carbon ring is equated to the strain energy of the equivalent truss element model. The molecular potential is calculated based on AMBER (Assisted Model Building with Energy Refinement) force field [3]. The strain energy of the truss element model is obtained as a sum of the strain energies of the individual truss elements, which involve the Young's modulus as an unknown quantity to be determined based on the strain energy equivalence. The strain energy equivalence considered corresponds to certain typical deformation modes commonly appearing in the in-plane deformation of the graphene sheet.

In section 3.1.1, the basic assumptions of the single cell analysis are stated. The molecular mechanical model based on AMBER force field is discussed in section 3.1.2. The equivalent truss element model is presented in section 3.1.3. The Young's modulus computed for several deformation modes are presented in section 3.1.4.

3.1.1. Basic assumptions

The basic assumptions in the single carbon ring analysis are as follows.

- Equilibrium bond length of single and double bonds of Carbon-Carbon (C-C) are reported in the literature as 0.1507 nm and 0.1336 nm, respectively [3]. The average bond length of single and double bonds, 0.142 nm, is taken as the equilibrium bond length for the analysis of graphene sheets in this Chapter. This value turn out to be the same as the equilibrium C-C bond length for graphite structures reported in literature [1, 170]. (However, a C-C bond length of 0.140 nm has also been used for the molecular dynamic simulations by Hummer et al. [171] and for the static analysis of CNTs by Odegard et al. [91] although the justification for this choice is not obvious.)
- Torsional, inversion, electrostatic and van der waals forces are small as compared to bond stretch and bond angle forces, hence these forces are neglected [91] in the present analysis.
- All carbon atoms in a ring lie on a plane such an assumption is perfectly valid for with regard to graphene sheets. However, with regard to CNTs, these assumptions will be reasonable only for large diameters.
- Truss element deforms in the x - and y - plane and the out-of-plane bending deformation are not considered.
- Graphene sheet is considered as a homogenous elastic material.
- Temperature effects on carbon atoms are not considered.

3.1.2. Molecular mechanics model

Molecular mechanic model is a simple, empirical ball-spring model of molecular structure, in which balls (atoms) are connected by springs (bonds) that can be stretched or compressed due to intra-or-intermolecular forces. Change in the bond length causes the energy of the bond to rise. The increase in energy is called bond strain energy. This strain energy can be described in terms of force fields of the structure. The general form of total potential energy, V^p , for nano-structured material can be expressed as a the sum of many individual energy contributions [172] as

$$V^p = V^\delta + V^\theta + V^\tau + V^\omega + V^{vdw} + V^{el} \quad (3.1)$$

where $V^\delta, V^\theta, V^\tau$ and V^ω are the bond energies associated with bond stretching, bond angle variation, torsion, and inversion, respectively. The non-bonded interaction energies consists of van der waals term, V^{vdw} , and electrostatic term, V^{el} . A schematic illustration associating each energy term with the corresponding bond structure of a carbon ring is shown in Figure 3.2.

For the calculation of potential energy of the graphene sheet, the AMBER force field of Kollman and coworkers [3] is used here. When the graphene sheet is subjected to small deformations, the non-bonded forces (V^{vdw} , V^{el}), torsional (V^τ) and inversion (V^ω) forces are assumed to be negligible [91]. Only two forces viz., bond stretching and bond angle forces are considered for the analysis of graphene sheet. Thus, the Equation (3.1) simplifies as

$$V^p = \sum V^\delta + \sum V^\theta \quad (3.2)$$

Figure 3.2. Bond structure and corresponding energy terms of a carbon ring [173].

Under the assumptions of small deformations, the molecular potential energy of a graphene sheet with carbon-carbon bonds is expressed as a sum of simple harmonic functions [91]

$$V^p = \sum_{i=1}^n K_i^{\delta} (r_i - R_i)^2 + \sum_{i=1}^n K_i^{\theta} (\theta_i - \Theta_i)^2 \quad (3.3)$$

where (R_i, Θ_i) and (r_i, θ_i) refer to the bond lengths and bond-angles of the i^{th} bond before and after stretching, respectively, as shown in Figure 3.3. K_i^{δ} and K_i^{θ} are the force constants associated with the bond stretching and bond-angle of the i^{th} bond, respectively. For the present work, the AMBER force field constants [3], shown in Table 3.1 are used.

Figure 3.3. Bond lengths and bond angles before and after deformation.

Table 3.1 AMBER force field constants.

Bond Stretch force constant (K^δ)	Bond-Angle force constant (K^θ)	Equilibrium C-C bond length (R)	Equilibrium bond-angle (Θ)
469 Kcal/(mol $\text{\AA}^2$)	63 Kcal/(mol rad^2)	1.409 $\text{\AA}$	2.0944 rad
3.2596×10^{-07} nJ/(bond nm^2)	4.3785×10^{-10} nJ/(bond nm^2)	0.1409 nm	120.0°

3.1.3. Equivalent truss element model

In order to simplify the calculation of the total molecular potential energy of molecular models, an equivalent pin-jointed truss element model is used to substitute the molecular model [91]. The pin-jointed model is a simple truss model, consisting of truss elements connected by pin-joints, in which the truss elements (bonds) and pin-joints (atoms) can be stretched or compressed due to intra-or-intermolecular forces. Due to stretching and compression, there is a change in the potential energy stored in the molecular model and this is equated to the strain energy stored in the truss model.

Odegard et al. [91] used two types of truss elements (a , b) to construct the equivalent truss model. In order to substitute the molecular model, which has bond stretching and variable angle degrees of freedom, by the truss model that has stretching degrees of freedom only, two types of truss elements, viz., type ' a ' and ' b ' are employed in the truss element model. Each truss element represents the forces between two atoms. The molecular bond force between two atoms is simulated by the elastic truss element of type

‘ a ’ and the bond-angle force between the two bonds (included angle between three bonded atoms), is simulated by the elastic truss element of type ‘ b ’.

The mechanical strain energy, Λ^t , of the truss model shown in Figure 3.4 is expressed as [91]

$$\Lambda^t = \sum_{i=1}^n \frac{A_i^a E_i^a}{2R_i^a} (r_i^a - R_i^a)^2 + \sum_{i=1}^n \frac{A_i^b E_i^b}{2R_i^b} (r_i^b - R_i^b)^2 \quad (3.4)$$

where A_i^a and E_i^a are the cross-sectional area and Young’s modulus of truss the i^{th} element of rod type ‘ a ’, respectively. The superscript b corresponds to truss element type ‘ b ’.

Figure 3.4. Chemical model and pin-jointed truss model.

In order to represent the molecular behaviour of structure using the truss element model, Equation (3.4) is equated with Equation (3.3).

$$\sum_{i=1}^n K_i^\delta (r_i - R_i)^2 + \sum_{i=1}^n K_i^\theta (\theta_i - \Theta_i)^2 = \sum_{i=1}^n \frac{A_i^a E_i^a}{2R_i^a} (r_i^a - R_i^a)^2 + \sum_{i=1}^n \frac{A_i^b E_i^b}{2R_i^b} (r_i^b - R_i^b)^2 \quad (3.5)$$

As seen from Equation (3.5), the effect of bond stretching term (i.e., the first term on the left side) is simulated by the stretching term (i.e., the first term on the right side) of element type ‘ a ’ and the effect of the bond-angle variation term (i.e., second term on the left side) is simulated by the stretching term (i.e., the second term on the right side) of element type ‘ b ’.

The right side of Equation (3.5) involves two sets of unknown parameters viz., the products $A_i^a E_i^a$ and $A_i^b E_i^b$. Each set has two mutually dependent unknown parameters viz., area of cross section and Young’s modulus. In the present study, the product of Young’s modulus and area of cross section (EA) is considered as a single unknown parameter. Thus, four unknown parameters are reduced to two unknown parameters. The two resulting parameters may be solved from two Equations obtained from Equation (3.5) for two deformed conditions. However, this approach has its problems. For example, for hydrostatic compression or tension loading condition, the two Equations are linearly dependent and no unique solution exists. For other loading conditions, initial calculations showed that these computed values of these two parameters are highly dependent on the modes of deformation used to get the two Equations, and it is difficult to solve for a unique solution. In order to overcome this problem, the same set of parameter used for both elements types by letting $A_i^b E_i^b = A_i^a E_i^a \equiv EA$. Thus, Equation (3.5) becomes

$$\sum_{i=1}^n K_i^\delta (r_i - R_i)^2 + \sum_{i=1}^n K_i^\theta (\theta_i - \Theta_i)^2 = \sum_{i=1}^n \frac{EA}{2R_i^a} (r_i^a - R_i^a)^2 + \sum_{i=1}^n \frac{EA}{2R_i^b} (r_i^b - R_i^b)^2 \quad (3.6)$$

Initially, a single carbon ring model of graphene sheet is considered for predicting the values of EA of truss element. From the literature, the lengths of element type 'a' and 'b' i.e. R_i^a and R_i^b taken as 0.142 nm and 0.246 nm, respectively [170].

For any deformed mode, the change in molecular potential and the strain energies are computed based on the relative positions of atoms. The energy Equation (3.6) is then solved for unknown parameter EA . The analysis has been carried out for a few typical deformation modes and the results are discussed in the following sections.

3.1.4. Results and discussions of single carbon ring

3.1.4.1. Varying bond length keeping bond angles fixed

The effect of varying bond length on EA for given bond angle is discussed in this Section. The angle between bonds is kept constant at 120° and the bond length is varied by moving three alternate carbon atoms by prescribed rotation along the circumference of the circle is as shown in the Figure 3.5. In such a case, the change in the length of element type 'b' and the change in angle between the atoms are zero. For this mode, Equation (3.6) reduces to

$$\sum_{i=1}^n K_i^\delta (r_i^a - R_i^a)^2 = \sum_{i=1}^n \frac{E_i A_i}{2R_i^a} (r_i^a - R_i^a)^2 \quad (3.7)$$

After simplification, Equation (3.7) becomes

$$EA = 2R^a K^\delta = 92.5841 \text{ nN} \quad (3.8)$$

Figure 3.5. Constant bond angle and varying bond length.

Odegard et al. [91] has given an expression for the Young's modulus of truss element as

$E^a = \frac{2K^\delta R^a}{A^a}$ ignoring the bond angle term in Equation (3.6). From this expression, the

EA value can be calculated as 92.5841 nN which is same as the present value. This exact agreement is anticipated because the deformation mode used in the present analysis excites only the bond stretch term and not the bond angle term. Other modes where both terms are excited are considered in some of the following sections.

3.1.4.2. Bi-axial tensile and compressive deformation mode

The effect of variation of bond angle on EA for given bond length is presented in this Section. All the six bond lengths are kept constant at 0.142 nm and the bond angles are varied by applying prescribed suitable displacements as shown in Figure 3.6. The magnitudes of displacements are such that they do not cause any bond stretching or contraction in truss element type 'a'.

Figure 3.6. Constant bond length and varying bond angle.

Figure 3.7 shows the plot of compute EA values against change in length of truss elements of type ‘ b ’. The two lines in the plot correspond to the top and bottom elements moving towards and away from the centre of the ring, respectively. The two lines intersect at zero deformation, i.e., at the undeformed configuration of the carbon ring. At the intersection point, the value of EA is 42.7742 nN. For small change in bond angles,

Odegard et al. [91] has given an expression for the Young’s modulus as $E^b = \frac{24K^\theta}{R^b A^b}$

which captures only bond angle effect. Using this expression, the EA value can be computed as 42.7403 nN which matches well with the present computed value. Here, the agreement is not exact because of some simplifying approximations may be used by Odegard et al. [91] in their derivation.

Figure 3.7. EA versus change in length of truss element 'b' with lengths of element 'a' fixed.

The deformation modes considered in Sections 3.1.4.1 and 3.1.4.2 are rather simple. These modes have served as convenient reference for bench marking the present method with that of Odegard et al. [91]. Having bench marked, the present method is applied to more complex deformation modes in the following sections.

3.1.4.3. Hydrostatic tensile and compressive deformation mode

The first analysis is carried out by subjecting the carbon ring to hydrostatic compression and tension. Carbon atoms are moved radially inwards and outwards respectively, as shown in Figure 3.8. For hydrostatic compression and tension, a change in angle between any two truss elements is zero. Hence, Equation (3.6) is rewritten as

$$\sum_{i=1}^n K_i \delta (r_i^a - R_i^a)^2 = EA \left(\sum_{i=1}^n \frac{1}{2R_i^a} (r_i^a - R_i^a)^2 + \sum_{i=1}^n \frac{1}{2R_i^b} (r_i^b - R_i^b)^2 \right) \quad (3.9)$$

Substituting the R_i^a, R_i^b values and expressing $(r_i^b - R_i^b)$ in terms of $(r_i^a - R_i^a)$ for a given value of radius of carbon ring, Equation (3.9) becomes

$$EA = K \delta \left(\frac{2R^a}{(1 + \sqrt{3})} \right) = 33.8841 \text{ nN} \quad (3.10)$$

Figure 3.8. Hydrostatic compression and tension deformation mode of carbon ring.

3.1.4.4. Uni-axial tensile and compressive deformation mode

A tensile/compressive mode as shown in Figure 3.9 is considered. Nodal displacements corresponding to uniform tension/compression are applied on the nodes, and the EA values are computed by equating the molecular potential to the strain energy of the truss model as in Equation (3.6). In order to visualise the deformation, the carbon ring is imagined to be embedded on a plate (as shown in Figure 3.9) subjected to uniform deformation δ when uniform force F applied at one end.

Figure 3.9. Uni-axial tensile/compressive deformation of carbon ring.

Figure 3.10 shows that the plot of EA values against the percentage of elongation of the truss element. It is observed that the truss element shows a softening trend in tension and stiffening trend in compression. At zero percent elongation (at undeformed configuration), the interpolated value of EA is 54.1932 nN, and is shown by dotted line in Figure 3.10. Similar analysis has been carried out for the in-plane bending of carbon ring and results are discussed in the next Section.

Figure 3.10. EA of truss element versus percentage of elongation for tension and compression deformation mode of a carbon ring.

3.1.4.5. In-plane bending deformation mode

The carbon ring is subjected to a bending deformation as shown in the Figure 3.11. Nodal displacements corresponding to uniform bending moment are applied on the nodes. In order to visualise the deformation of the ring, the carbon ring is imagined to be embedded on a plate (as shown in Figure 3.11) subjected to uniform bending deformation. Equating the molecular potential to the strain energy of the truss model as in Equation (3.6), EA values are computed

Figure 3.11. Bending deformation of carbon ring.

Figure 3.12 shows the plot of computed EA values versus bending angle θ . It is observed that the computed EA value decreases quadratically as the bending angle is increased. For the undeformed mode, the extrapolated value of EA is 66.2991 nN. This value is higher than that of uni-axial tensile/compressive deformation mode (54.1932 nN).

Figure 3.12. EA of truss element vs bending angle for bending deformation mode of carbon ring.

3.1.4.6. Shear deformation mode

The carbon ring is subjected to a shear deformation as shown in the Figure 3.13. Nodal displacements corresponding to uniform shear deformation are applied on the nodes. In order to visualise the applied deformation, the carbon ring is imagined to be embedded on a plate (as shown in Figure 3.13) subjected to uniform shear deformation. Equating the molecular potential to the strain energy of the truss model as in Equation (3.6), EA values are computed.

The plot of computed EA values of the truss element versus shear angle is shown in Figure 3.14. The stiffness of the truss element is seen to increase with the shear angle. At

zero shear angle (undeformed mode) the extrapolated value of EA is 40.6552 nN observed. This EA value is less than the values computed for bending and tension deformation modes.

Figure 3.13. Shear deformation of carbon ring.

Figure 3.14. EA of truss element vs shear angle for shear deformation of carbon ring.

The EA values computed for different modes are summarised in Table 3.2. A scan through Table 3.2 reveals that the computed EA values are different for different modes of deformation. This suggests that a unique value of EA that will work for all possible deformation modes does not exist. Hence an attempt to model graphene using the EA value computed based on single carbon ring analysis may not provide us accurate results.

Table 3.2. A summary of computed EA values.

S. No	Mode of deformation	Present (nN)	Odegard et al. [91] (nN)
1	Varying bond length keeping bond angles fixed	92.5841	92.5841
2	Bi-axial tensile/compressive loading	42.7742	42.7403
3	Hydrostatic compressive and tensile loading	33.8841	-
4	Uni-axial tensile/compressive loading	54.1932	-
5	Bending	66.2991	-
6	Shear	40.6552	-

3.2. Equivalent continuum modelling of graphene sheet using AMBER force field

The single carbon ring analysis of previous chapter is extended to graphene sheet analysis in this chapter. The truss element model of a single carbon ring is considered as a unit cell and it is assembled repeatedly to form a 2D truss model of the graphene sheet using ANSYS [6]. Using this model of the graphene sheet the basic elastic properties, such as Young's modulus and shear modulus, of an equivalent 2D continuum representing the

graphene sheet are predicted, and compared with the earlier predictions of other researchers.

To extract the mechanical properties of the graphene sheet, a few typical deformation modes are considered. A graphene sheet of finite dimensions (11 x 5 carbon rings) is considered for the present work. The molecular potential of the graphene sheet based on AMBER model and the strain energy of the truss element model are equated in order to solve for EA of the truss element using Equation (3.6) for different deformation modes of graphene sheet. The modelling procedure and the steps are as follows.

3.2.1. Modelling procedure

A single carbon ring truss element model is constructed using two types of truss elements, viz., outer elements (0.142 nm length) and inner elements (0.246 nm length) as discussed in previous Section. A truss element model of the graphene sheet is constructed by repeated assembly of the single ring model in the x - and y -directions (e.g., see Figure 3.17). This model is then used for computing the equivalent continuum elastic properties in uni-axial tension/compression, bending and shear deformation modes. The elastic properties are computed based on the equivalence of molecular potential (Cauchy-Born rule) and the graphene sheet strain energy stored in the truss element model due to deformation modes as described below. The strain energy is computed using the finite element software, ANSYS [6] as will be outlined later.

Equation (3.6) consists of bond stretching and bond angle terms. The bond stretching can be computed by calculating the change in length between the two nodes. Each node is

associated with three included angles (θ_1 , θ_2 , θ_3) formed by three truss elements (b_1 , b_2 , b_3) passing through it, as shown in Figure 3.15. The bond angle, θ_1 for example, can be calculated using the elements b_2 , b_3 and c_1 using Equation (3.11).

$$\theta_1 = \cos^{-1} \left(\frac{b_2^2 + b_3^2 - c_1^2}{2b_2b_3} \right) \quad (3.11)$$

Figure 3.15. Bond angles and elements at a node.

Figure 3.16. Block diagram of model.

The present method of extracting the elastic properties using the finite element software ANSYS [6] has four tasks as shown in the block diagram in Figure 3.16. The steps comprising each task are given below:

Modelling

1. Using Link 2D spar element (with suitable E and A values as will be discussed later) of ANSYS [6], construct nodes and elements to model a single carbon ring.
2. Construct the model for the graphene sheet by copying the elements and nodes of single carbon ring model in x - and y -directions.
3. Apply boundary conditions and displacement loading, and save the database.

Pre-Processor Macro

1. Get the nodal coordinates and element connectivity, and store in an array.
2. Identify the elements connected to each node and store in an array.
3. Identify the three angles around each node and store in an array.

Solution

Solve for nodal displacements and reactions.

Post-Processor Macro

1. Compute the new nodal co-ordinates by adding the nodal displacements to initial nodal co-ordinates.
2. Get the reaction forces (P) for all atoms on the right side edge of graphene sheet (Figure 3.17) where the prescribed displacement loading is applied. These reaction forces are used for the calculation of Young's modulus in Section 3.2.2.

3. Compute change in length of each element viz., $(r_i^a - R_i^a)$ and $(r_i^b - R_i^b)$.
4. Compute change in angles at all nodes viz., $(\theta_i - \Theta_i)$.
5. Substitute the change in length of all elements and change in angles in Equation (3.6) and solve for EA .
6. Compute the change in molecular potential and strain energy using Equations (3.3) and (3.4), respectively.
7. Calculate the elastic properties using Equations (3.12 - 3.17).

Figure 3.17. Tensile deformation of graphene sheet, picture captured from ANSYS.

3.2.2. Uni-axial tension/compression mode

A truss element model of a graphene sheet has been developed in ANSYS [6] for uni-axial tension/compression analysis as shown in Figure 3.17. All the nodes on the left edge are restrained in x -direction with one of them also restrained in y -direction while a prescribed displacement is applied to all nodes on the right edge. In the Figure 3.17, the dotted lines show the undeformed structure and solid lines indicate the deformed structure. The horizontal lines supported on arrows seen at the top and bottom edges of

the model indicate the coupled degrees of freedom to ensure that all the nodes lying on these lines remain on straight lines and move only y-direction. This is done to simulate the behaviour of the infinite graphene sheet.

Figure 3.18. Molecular potential and strain energy of graphene sheet plotted against EA of truss element of graphene sheet under uni-axial tensile/compressive deformation mode.

By changing the EA of the truss element, the potential is computed for different percentage of elongation of the graphene sheet. (In actual analysis, the change in EA values is brought about as follows: The cross sectional area of the spar elements is specified as 1 nm^2 . The Young's modulus value, E , is varied from 15 to 1000 nN/nm^2 .) In Figure 3.18, the inclined and horizontal lines correspond to the strain energy in truss element model and the molecular potential energy, respectively, for different percentage elongations. For a particular elongation value, the molecular potential energy is constant,

while the truss strain energy decreases with EA value. These two sets of lines intersect each other. In this scale of plot, the intersecting points are not clearly visible. Hence, for the sake of clarity, a log-log plot is shown in Figure 3.19.

Figure 3.19. Plot same as Fig 3.18 with log-log scale.

In Figure 3.19, the intersecting points of interest are enclosed in an ellipse for easy identification. The EA values computed using Equation 3.6 at the intersecting points (where the strain energy equal to the molecular potential) and will be used as the input material properties for the truss element model for predicting the sheet Young's modulus.

Figure 3.20 shows the plot of EA values of truss element against percentage elongation of graphene sheet. The EA values at the intersection points of Figure 3.19 are used for

plotting Figure 3.20. It is observed that the truss element shows stiffening in tension and softening in compression. Referring back to the results of single carbon ring analysis shown in Figure 3.10, an opposite trend is seen. The trends shown in Figure 3.20 are supposed to be accurate because the whole graphene sheet is considered as against the single carbon ring and the effect of lateral contraction due to Poisson's ratio is taken into account here whereas it was ignored in the single carbon ring analysis. At zero percentage elongation (undeformed position), the interpolated value of EA is 48.0172 nN and is shown by dotted line in Figure 3.20. This EA value may be useful for studying small deformation tensile/compressive behaviour of continuum graphene sheets using a truss element model. Here, this EA value is used for determining the equivalent Young's modulus as outlined below.

Figure 3.20. EA of truss element versus percentage elongation for uni-axial tensile/compressive deformation of a graphene sheet.

Having the computed EA value (48.0172 nN), this value is used back in the ANSYS truss element model to determine P value appearing in Equation (3.12) for a given elongation (δL) of truss element model. Using the ANSYS macro program written for post-processing of results, the sum of all forces on the right side edge is calculated for each applied deformation. This gives the load P to be used in Equation (3.12). The Young's modulus is then determined as

$$Y = \frac{PL}{A\delta L}, \quad A = Wt \quad (3.12)$$

and Poisson's ratio is determined as

$$\nu = \frac{\delta W}{W} \frac{L}{\delta L} \quad (3.13)$$

where L and W are the length and width of the graphene sheet, δL and δW are the corresponding changes in them, and t is the thickness of graphene sheet.

In the present analysis, the graphitic inter-planer spacing (0.34 nm) is used as the thickness (t) of graphene sheet, which is the commonly used value in the literature [152]. Figure 3.21 shows the plot of the equivalent Young's modulus versus percentage elongation of the graphene sheet for uni-axial compressive/tensile deformations. The interpolated value of Young's modulus of graphene sheet at zero percentage elongation is 1.2018 TPa. The Poisson's ratio of the graphene sheet has been computed using the Equation (3.13) as 0.4648. It is seen from Figure 3.21 that a 2.68% change in the Young's modulus is caused by a $\pm 5\%$ elongation.

Figure 3.21. Equivalent Young's modulus versus percentage elongation for uni-axial tensile/compressive deformation of graphene sheet.

3.2.3. Bending deformation mode

The truss element model used in Section 3.2.2 has also been used for the bending analysis of graphene sheet as shown in Figure 3.22. All the nodes at left side of sheet are restrained in x -direction with the middle node on this side also restrained in the y -direction. At the right side end of the graphene sheet, bending displacements are applied at all edge nodes so that the edge remains straight before and after deformation. The length of the neutral axis is maintained the same before and after deformation. ANSYS [6] macro programming facility has been used to develop a macro code for calculating the radius of curvature, bending moment (calculated as the sum of moments of reaction forces about the neutral axis) and strain energy stored in the truss element model.

Figure 3.22. Bending deformation of graphene sheet , picture captured from ANSYS.

Figure 3.23 shows the log-log plot of potential/strain energy and EA values of truss element for bending deformation mode. The intersection points of interest are enclosed in an ellipse.

Figure 3.24 shows the plot of EA values against bending angle. It is observed that the EA values show a stiffening tendency with the bending angle. The extrapolated value of EA at zero bending angle is 18.0872 nN. This value may be useful for studying small deformation bending behaviour of graphene sheets using a truss element model.

Figure 3.23. Log(molecular potential) and Log(strain energy) versus Log(EA) for bending deformation of graphene sheet.

Figure 3.24. EA versus bending angle for bending deformation of graphene sheet.

For the bending mode of deformation, the relationship between Young's modulus Y_b , bending moment M and radius of curvature R is written as

$$\frac{M}{I} = \frac{Y_b}{R} \quad (3.14)$$

where I is the moment of inertia of a cross section. The length of the neutral axis of the beam L after bending can be expressed in terms of R and bending angle θ as

$$L = R\theta \quad (3.15)$$

From Equations (3.14) and (3.15), the Young's modulus in bending can be written as

$$Y_b = \frac{ML}{I\theta}, \quad I = \frac{W^3 t}{12} \quad (3.16)$$

Figure 3.25. Equivalent Young's modulus versus bending angle for bending deformation of graphene sheet.

For each applied deformation, the bending moment (computed as the sum of the moments of the reaction forces) is obtained using the macro program. Using this bending moment, the equivalent Young's modulus has been calculated using Equation (3.16). At the intersection points of Figure 3.23, the EA values of truss element have been determined and the equivalent Young's modulus of graphene sheet has been computed using Equation (3.16) for different bending angles. Figure 3.25 shows the plot of equivalent Young's modulus against bending angle. At zero bending angle (undeformed bending mode), the extrapolated value of Young's modulus of a graphene sheet is 1.2728 TPa. This value is 5.9% more than that of equivalent Young's modulus of uni-axial tensile/compressive deformation mode computed in Section 3.2.2. Bond-angle forces caused by the deformation of carbon cells perhaps leads to the non-linearity in the plot Figure 3.26. It is observed from Figure 3.25 that a change in bending angle from 0 to 5° causes 4% variation in Young's modulus.

3.2.4. Shear deformation mode

The truss element model for the shear deformation analysis of graphene sheet is as shown in Figure 3.26. Nodes on bottom edge are fixed in x - and y -directions. For the nodes at the top edge, the coupled degrees of freedom have been applied which ensures that top edge remains parallel to x -axis as it moves in y -direction with the sheet under goes deformation. An ANSYS [6] macro program has been developed for calculating the shear modulus. The results are discussed below.

Figure 3.26. Graphene sheet before and after shear deformation, picture captured from ANSYS.

Figure 3.27 shows the plot of logarithmic values of potentials versus logarithmic values of EA of graphene sheet for shear deformation mode. The portion enclosed in an ellipse contains the intersecting points of interest.

Figure 3.27. Log(Molecular potential) and Log(strain energy) versus Log(EA) of graphene sheet under shear deformation.

Figure 3.28 shows the plot of EA values of truss element model versus the shear angles for the shear deformation mode. The EA values for this plot are taken from the intersection points of Figure 3.27. It is observed that the truss element shows a stiffening type of Young's modulus with shear angle. The extrapolated value of EA of truss element at the undeformed or zero shear deformation angle is 40.0993 nN. This EA value may be useful for modelling the graphene sheet using truss elements for small shear deformation analysis.

Figure 3.28. EA of truss element versus shear angle of graphene sheet under shear deformation.

The relationship between the shear modulus G and shear angle ϕ can be expressed as

$$G = \frac{P\phi}{A}, \quad A = Lt \quad (3.17)$$

where P is the shear force. Using the macro program, P is obtained by summing up the reaction forces corresponding to the applied shear angle ϕ .

Having the extrapolated EA value (40.0993 nN) at the zero shear deformation, this value used back in ANSYS shear deformation model to determine P value appearing in Equation (3.17) for a given shear angle (ϕ). Using the ANSYS macro program written for post-processing of results, the sum of all forces on the top side edge is calculated for each applied shear angles. This gives the load P to be used in Equation (3.17) to calculate equivalent shear modulus of graphene sheet. Figure 3.29 shows the plot of equivalent shear modulus against shear angle. The extrapolated value of shear modulus at zero shear angle (undeformed shear mode) is 0.34827 TPa. This value may be useful to model the graphene sheet as a 2D continuum for small shear deformation analysis.

Figure 3.29. Equivalent shear modulus versus shear angle of graphene sheet under shear deformation.

3.2.5. Convergence study on elastic properties of graphene sheet

To investigate the convergence of the computed elastic properties (Young's modulus, shear modulus, Poisson's ratio and EA value of truss element) of graphene sheets with the size of model considered, a series of truss element models with increasing number of cells are considered. The models use $10L+1$ rings along the length (L) and $5W$ rings along the width (W). Different L and W values are considered for studying the convergence. The models already used in Sections 3.2.2 - 3.2.4 correspond to $L=1$ and $W=1$. Two different cell orientations of graphene sheets, viz., zigzag and armchair, are considered for this analysis. The computed values of equivalent Young's and shear modulus of graphene sheet, EA of truss element and Poisson's ratio of truss element model sheets are listed in the Tables 3.3 – 3.6, respectively. The following observations emerge from these tables:

Referring to Table 3.3, the Young's modulus of graphene sheet increases with width. A similar trend is reported in the literature on CNTs [162] where the Young's modulus increases with the radius (circumference) of tube. (Such studies, however, have not been reported for graphene sheet.) Nevertheless, the Young's modulus value is seen to decrease with length (as can be seen from the columns of the Table 3.2). Figure 3.30 shows the plot of Y values against number of carbon rings along the length, the data being taken from the Table 3.3. It can be seen that Y value converges with the increasing number of rings. However, a small difference is observed between the converged values of zigzag and armchair configurations.

Table 3.3. Equivalent Young's modulus (TPa) of zigzag and armchair graphene sheet.

$\begin{matrix} W \\ L \end{matrix}$	1	2	3	4	6	8	12	16
1	[1.2011] (1.1252)	[1.2249] (1.1428)	[1.2326] (1.1466)	—	—	—	—	—
2	[1.1568] (1.0977)	[1.1734] (1.1148)	[1.1790] (1.1187)	—	—	—	—	—
3	[1.1351] (1.0877)	[1.1490] (1.1048)	[1.1538] (1.1086)	—	—	—	—	—
4	—	—	—	[1.1414] (1.1050)	—	—	—	—
6	—	—	—	—	[1.1271] (1.1009)	—	—	—
8	—	—	—	—	—	[1.1191] (1.0988)	—	—
12	—	—	—	—	—	—	[1.1106] (1.0965)	—
16	—	—	—	—	—	—	—	[1.1061] (1.09535)

[...] zigzag configuration, (...) armchair configuration.

Figure 3.30. Equivalent Young's modulus versus number of rings along the length of graphene sheet.

Table 3.4. Equivalent shear modulus (TPa) of zigzag graphene sheet.

$\begin{matrix} W \\ L \end{matrix}$	1	2	3	4	6	8	12	16
1	0.34827	0.2848	0.21182	—	—	—	—	—
2	0.38211	0.35371	0.3163	—	—	—	—	—
3	0.39439	0.37867	0.35453	—	—	—	—	—
4	—	—	—	0.35465	—	—	—	—
6	—	—	—	—	0.35452	—	—	—
8	—	—	—	—	—	0.35434	—	—
12	—	—	—	—	—	—	0.35407	—
16	—	—	—	—	—	—	—	0.35389

The equivalent shear modulus (G) of zigzag graphene sheet for various dimensions is listed in Table 3.4. The shear modulus is seen to decrease with width and increase with length. Figure 3.31 shows the plot of shear modulus of graphene sheet versus number of rings along its length. The curve shows an increasing trend up to about 40 carbon rings and then shows a decreasing trend.

Figure 3.31. Equivalent shear modulus versus number of carbon ring along the length of graphene.

The EA values of truss element computed for zigzag and armchair graphene sheet model and are tabulated in the Table 3.5. The first and second EA values in each cell correspond to zigzag and armchair graphene sheet under uni-axial deformation, respectively. The third value corresponds to zigzag graphene sheet under shear deformation. Figure 3.32 shows the plot of EA values of truss element against the number of carbon rings along the length of graphene sheet. For zigzag and armchair graphene sheets under uni-axial deformation, the EA values of truss element decreases with the number of carbon rings along the length. However, the EA values of zigzag graphene under shear deformation increases with number of carbon rings until about 40 carbon rings and then levels off.

Table 3.5. EA of truss element (nN) for zigzag, armchair uni-axial deformation and zigzag shear deformation of graphene sheet model.

$W \backslash L$	1	2	3	4	6	8	12	16
1	[47.978] (41.973) {40.099}	[47.993] (39.401) {40.652}	[48.089] (38.480) {40.802}	—	—	—	—	—
2	[43.343] (41.945) {39.848}	[43.160] (39.389) {40.91}	[43.156] (38.478) {40.976}	—	—	—	—	—
3	[41.516] (41.934) {39.772}	[41.271] (39.385) {41.012}	[41.229] (38.475) {41.175}	—	—	—	—	—
4	—	—	—	[40.16] (38.011) {41.304}	—	—	—	—
6	—	—	—	—	[39.031] (37.539) {41.429}	—	—	—
8	—	—	—	—	—	[38.443] (37.301) {41.489}	—	—
12	—	—	—	—	—	—	[37.839] (37.061) {41.547}	—
16	—	—	—	—	—	—	—	[37.531] (36.942) {41.576}

[...] zigzag configuration under uni-axial tension/compression deformation.

(...) armchair configuration under uni-axial tension/compression deformation.

{...} zigzag configuration under shear deformation.

Figure 3.32. EA of truss element versus number of carbon rings along the length.

The Poisson's ratio values are tabulated in Table 3.6 for different sizes of zigzag and armchair graphene sheets. The values converge to around 0.44 for both configurations. Looking again at the results in Table 3.5 (and Figure 3.32), it is observed that the EA values for tension/compression mode and the shear mode are different by about 10%. Also, the EA value in tension/compression mode of zigzag configuration is slightly larger than that of armchair configuration. In order to ascertain that this difference is genuine

and not caused by the rectangular shape of graphene sheet, the analysis is repeated for a square shaped graphene sheet.

Table 3.6. Poisson's ratio for zigzag and armchair graphene sheet.

$\begin{matrix} W \\ L \end{matrix}$	1	2	3	4	6	8	12	16
1	[0.4649] (0.4979)	[0.4338] (0.4967)	[0.4269] (0.4962)	—	—	—	—	—
2	[0.4824] (0.4730)	[0.4510] (0.4715)	[0.4426] (0.4710)	—	—	—	—	—
3	[0.4891] (0.4639)	[0.4577] (0.4624)	[0.4486] (0.4618)	—	—	—	—	—
4	—	—	—	[0.4466] (0.4568)	—	—	—	—
6	—	—	—	—	[0.4447] (0.4517)	—	—	—
8	—	—	—	—	—	[0.4437] (0.4490)	—	—
12	—	—	—	—	—	—	[0.4428] (0.4464)	—
16	—	—	—	—	—	—	—	[0.4423] (0.4450)

[...] zigzag configurations, (...) armchair configurations.

An approximately square shaped graphene sheet of size with 115 x 100 (24.566 x 24.595 nm) carbon rings has been modelled with zigzag and armchair configurations. The computed values of equivalent Young's modulus, shear modulus and Poisson's ratio of graphene sheet and EA values of truss element are tabulated in Table 3.7. The equivalent Young's modulus of graphene sheet of zigzag and armchair configurations are in good agreement with the values computed previously using non-square model. They are also in good agreement with that of the *ab initio* method value (1.11 TPa) recently reported for graphene sheet [147].

Table 3.7. Computed elastic properties using square graphene sheet model.

Uni-Axial deformation			Shear Deformation	
Y (TPa)	EA (nN)	Poisson's Ratio	G (TPa)	EA (nN)
[1.1122]	[37.8788]	[0.4405]	[0.2876]	[40.6410]
(1.1097)	(36.8678)	(0.4465)	(0.2882)	(41.1310)

[...] zigzag configuration, (...) armchair configurations.

3.3. Conclusions

The fundamental task in the equivalent modelling approach is to determine the equivalent elastic properties of graphene sheets. CNTs can be looked up on as graphene sheet rolled up into tubular form. Hence, equivalent continuum modelling of graphene sheet is taken up as a first step in the present research. The central idea behind the equivalent continuum model is to equate the change in molecular potential of the graphene sheet with the strain energy of the model.

The following are the major observations from the work reported in this chapter.

1. As a first step towards equivalent continuum modelling of graphene sheets, a truss element model for a single carbon ring has been constructed. Based on energy equivalence, the EA values of the truss element have been computed (for typical deformation modes) and verified with those reported in the literature. A good agreement is observed (Table 3.2). However, the EA value computed highly depends on the nature of the deformation mode employed which reduces the practical usefulness of single carbon ring analysis.
2. Next, considering a truss element model for a rectangular graphene sheet, the EA values have been computed for uni-axial tension/compression mode as well as

- shear mode. The influence of the size of graphene sheet on the computed EA values has been studied. The EA value for the largest size of sheet considered is around 38 and 42 nN for uni-axial tension/compression mode and shear mode, respectively.
3. The equivalent Young's modulus (Y) and shear modulus (G) of graphene sheet have been computed to be around 1.11 TPa and 0.35 TPa, respectively. The computed Y value, 1.11 TPa, is the same as that obtained by *ab initio* methods recently reported in literature [147]. However, the shear modulus value is scarcely reported in the literature and a comparison is unavailable.
 4. The Poisson's ratio, which is computed as the ratio of lateral strain to longitudinal strain of the truss element model, is around 0.45 as against a value of 0.145 quoted in the literature [174]. This seems to suggest that truss element model is unable to reproduce the Poisson's ratio accurately. Nevertheless, the computed Young's modulus is the same (up to two decimal places) as that obtained using *ab initio* methods [147].
 5. The elastic properties computed for the rectangular graphene sheet exhibit some dependence on the size and configuration (zigzag or armchair) of the sheet, and mode of deformation. In order to explore the shape effect, the computations have been repeated for a square graphene sheet. The computed Poisson's ratio, Young's modulus and EA values are found to be in close agreement with that of the rectangular sheet. However, the computed shear modulus for the square sheet is around 0.29 TPa while that of the rectangular sheet is around 0.35 TPa. This

- might be due to dependence of the shear modulus on the shape of the graphene sheet.
6. An important observation is that the computed Y , G and ν values shown in Table 3.7, for instance, are not consistent with the relation $G = \frac{Y}{2(1+\nu)}$ which should hold for isotropic material. The relation is also not satisfied even if one uses the computed values of Y and G (Table 3.7) along with the Poisson's ratio of 0.145 of reference [174] instead of the Poisson's ratio reported here (0.44). This only seems to suggest that graphene sheet perhaps behaves like an orthotropic material. Some of the results presented in Chapter 4 seem to confirm this speculation. (It is realised that a recent study by Cho [157] reveals that relation $G = \frac{Y}{2(1+\nu)}$ is also not satisfied for CNTs.)

Chapter 4

EQUILIBRIUM CONFIGURATION AND CONTINUUM ELASTIC PROPERTIES OF FINITE SIZED GRAPHENE SHEETS USING BRENNER POTENTIAL

In the previous Chapter, the AMBER force field [3] was used to compute the elastic properties of graphene sheet. However, AMBER force field does not account for interactions of a given atom with the second nearest atoms for computing the potential of graphene sheet. Hence, the computed elastic properties may not be accurate. In this Chapter, Brenner potential [4] is used to compute the elastic properties of graphene sheet.

Brenner potential has been widely used for simulation of CNTs [148, 175-179]. Its use for the simulation of graphene sheets is scarce. There exists a major difference in using Brenner potential to model graphene sheet as against using AMBER force field. The potential energy of the graphene sheet is to be minimised first for determining the equilibrium configuration of atoms. Without this step, the computed elastic properties of graphene will not be accurate in general. Due to equilibrium minimisation, the four edges of the initially rectangular graphene sheet become curved at the equilibrium configuration. Hence, two graphene sheet models are considered in this Chapter, with only two or all the four edges constrained to be straight. The continuum Young's modulus of graphene sheets are computed applying the Cauchy-Born rule. The computed constants are found to differ considerably depending on whether minimised or unminimised configuration is used for computation. Results are presented to illustrate this observation.

The expression for Brenner potential and formulae for computing elastic properties are reviewed in Sections 4.1 and 4.2, respectively. The study on spatial variation of equilibrium bond lengths in equilibrium configurations is presented in Section 4.3.1. The influence of the size of the graphene sheet on the computed Young's modulus values is studied in Sections 4.3.2 and 4.3.3. The models with only two and all the four edges constrained to be straight are considered in Sections 4.3.2 and 4.3.3, respectively. The orthotropy of the computed material properties of finite graphene sheet is presented in Section 4.3.3. The computed stress-strain plot is presented in Section 4.3.4. A possible reason for the large scatter in the computed Young's modulus values reported in the literature is explained in Section 4.3.5. Finally summary and conclusions of this Chapter is given in Section 4.4.

4.1. Interatomic potential for carbon atoms

The Brenner potential, proposed for hydrocarbons [4] is used for the present work. It has been widely used for the simulation of carbon nanotubes, and expresses the binding energy in terms of bond lengths and angles, as a summation over all the bonds:

$$V_B(r_{ij}) = \sum_i \sum_{j(>i)} [V_R(r_{ij}) - \overline{B_{ij}} V_A(r_{ij})] \quad (4.1)$$

where V_B is the potential and r_{ij} is the distance between the atoms i and j . V_R and V_A are the repulsive and attractive pairs of energy terms given by

$$V_R(r_{ij}) = \frac{D^{(e)}}{S-1} e^{-\sqrt{2S}\beta(r_{ij}-R^{(e)})} f_c(r_{ij}) \quad (4.2)$$

$$V_A(r_{ij}) = \frac{D^{(e)}S}{S-1} e^{-\sqrt{2/S}\beta(r_{ij}-R^{(e)})} f_c(r_{ij}) \quad (4.3)$$

where the constants D , S , β and $R^{(e)}$ for carbon atoms are given in Table 4.1. The cutoff function $f_c(r_{ij})$ is used to limit the range of potential:

$$f_c(r_{ij}) = \begin{cases} 1 & r_{ij} < R^{(1)} \\ \frac{1}{2} \left\{ 1 + \cos \left[\frac{\pi(r_{ij} - R^{(1)})}{R^{(2)} - R^{(1)}} \right] \right\} & R^{(1)} < r_{ij} < R^{(2)} \\ 0 & r_{ij} > R^{(2)} \end{cases} \quad (4.4)$$

where $R^{(1)}$ and $R^{(2)}$ are the cutoff constants (refer to Table 4.1). The multi-body coupling parameter appearing in Equation (4.1) is given by $\overline{B_{ij}} = (B_{ij} + B_{ji})/2$, where

$$B_{ij} = \left[1 + \sum_{k(\neq i,j)} G(\theta_{ijk}) f_c(r_{ik}) \right]^{-\delta} \quad (4.5)$$

The symbol k in Equation (4.5) represents atoms other than i and j , r_{ik} is the distance between the atoms i and k , and θ_{ijk} is the angle between the bonds i - j and i - k . The angular function G is given by

$$G(\theta_{ijk}) = a_0 \left[1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + (1 + \cos(\theta_{ijk}))^2} \right] \quad (4.6)$$

The values of a_0 , c_0 , and d_0 for carbon atoms are given in Table 4.1. The revised version of Brenner potential called the second-generation reactive empirical bond order (REBO) contains improved analytic function and better description of bond energies, lengths and force constants for hydrocarbon molecules [65]. However, in the expression for B_{ij} , the angular function values (i.e., θ_{ijk}) need to be interpolated from the given data to generate the spline coefficients. For small displacements of atoms, the angular function should be around 120° and is difficult to compute function value from the given data. Hence, for the

present work the second set of parameters of Brenner potential [4] are used for further work and which are given in Table 4.1.

Table 4.1. Brenner potential parameters of set I and set II [4].

Parameter	Set I	Set II
$D^{(e)}$	6.325 eV	6.0 eV
S	1.29	1.22
β	15 nm ⁻¹	21 nm ⁻¹
$R^{(e)}$	0.1315 nm	0.139 nm
$R^{(1)}$	0.17 nm	0.17 nm
$R^{(2)}$	0.2 nm	0.2 nm
δ	0.80469	0.5
a_0	0.011304	0.00020813
c_0	19	330
d_0	2.5	3.5

4.2. Determination of elastic properties

In continuum mechanics, the constitutive relations between load and deformation are established prior to solving a specific problem. If the material is homogeneous and isotropic, the material can be represented by two independent constants, namely, Young's modulus Y and Poisson's ratio ν . For a material undergoing a uni-axial deformation, Y is defined as

$$Y = \frac{1}{V_0} \left(\frac{\partial^2 V_B}{\partial \varepsilon^2} \right)_{\varepsilon=0} \quad (4.7)$$

where V_0 is the volume corresponding to the initial equilibrium configuration of graphene, V_B the total strain energy under tensile deformation and ε is the tensile strain. However, different thickness values have been hypothesised [109] for SWNT and graphene, and therefore the volume V_0 is not uniquely defined. Hence, the in-plane

stiffness C , which is independent of thickness of graphene, is defined as an alternative measure in place of Young's modulus:

$$C = \frac{1}{A_0} \left(\frac{\partial^2 V_B}{\partial \varepsilon^2} \right)_{\varepsilon=0} \quad (4.8)$$

where A_0 is the initial equilibrium surface area of graphene sheet. If thickness t is defined for a graphene sheet, then the volume can be defined as $V_0 = A_0 t$, and the Young's modulus can be computed as $Y = C/t$. The thickness is often taken as 0.34 nm by several researchers. For a material undergoing a shear deformation, G is similarly defined as

$$G = \frac{1}{V_0} \left(\frac{\partial^2 V_B}{\partial \phi^2} \right)_{\phi=0} \quad (4.9)$$

The Poisson's ratio can be defined as

$$\nu = - \frac{\Delta w}{w} \bigg/ \frac{\Delta L}{L} \quad (4.10)$$

where w is the width of the graphene sheet, L is the length, and Δw and ΔL are the changes in the width and length, respectively.

Figure 4.1. Initial configuration of graphene sheet.

The following steps are used to compute the elastic properties of a graphene sheet.

- Step 1: First construct the initial configuration of graphene sheet (see Figure 4.1) with uniform bond length using the coordinate generator function and store the coordinates and connectivity information in an array.
- Step 2: Using the coordinate and connectivity arrays, find the first and second neighbour atoms information and store in an array.
- Step 4: Call a function called Praxis and it returns the equilibrium coordinates for a given initial coordinates and boundary conditions of graphene sheet.
- Step 5: Call a function called Brenner to compute the equilibrium potential from a given coordinates.
- Step 6: Compute initial volume, V_0 , of graphene using the equilibrium coordinates and assumed wall thickness (0.34 nm) of graphene.
- Step 7: Apply displacement field to equilibrium coordinates.
- Step 8: Call again Praxis function for equilibrium coordinates.
- Step 9: Call Brenner function for potential of a deformed graphene sheet.
- Step 10: Repeat step 7 to 9 for different displacement fields and store the potential of graphene against applied displacement filed.
- Step 11: Using the polynomial curve fitting, fit data for equation of potential in terms of displacement filed (strain).
- Step 12: Find the second derivative of potential equation with respect to applied strain and calculate Young's modulus using Equation (4.7).
- Step 13: Calculate change in length and change in width of graphene at step 8 for applied displacement filed and calculate the Poisson's ratio using Equation (4.10).
- Step 14: For shear modulus computation, repeat the steps 7 to 11 by applying the shear deformation.
- Step 15: Repeat step 12 to compute shear modulus using Equation (4.9).

To validate the developed FORTRAN code, simple structure (single carbon ring) is used. The detailed FORTRAN program is listed in Appendix A. To verify the equilibrium configuration, carbon ring is constructed with arbitrary bond lengths and minimised the potential using the Praxis code (steps 1 to 5). This equilibrium coordinates gives six equal bond lengths (0.14208835 nm) and computed potential value (-32.5315860720148 ev) is

verified manually. Later, this code is verified with finite graphene sheet and the details are given in Section 4.3.

4.3. Results and Discussions

4.3.1. Equilibrium configuration and bond length

A graphene sheet with 120 carbon atoms is considered in order to obtain the equilibrium configuration and study how it compares with initial configuration. The initial configuration is constructed with a uniform bond length of 0.142 nm and it fits into a rectangular envelope as shown in Figure 4.1. The Brenner potential of the rectangular graphene sheet is minimised by spatial adjustment of atomic positions of carbon atoms. The rigid body modes (i.e., two translational modes and one rotational mode) are restrained by restraining one node in x - and y -directions and another in y -direction before the minimisation is carried out. The final envelope of graphene sheet obtained after minimisation is no more a rectangle. The initially straight edges of rectangular envelope deforms to curved edges as shown in Figure 4.2. The curving of edges is attributed to the nonuniform extension/contraction of the lattice caused by the variation in the coordination numbers of individual carbon atoms. The coordination number is a measure of number of neighbouring atoms. For a graphene sheet, the coordination number for boundary atoms is two while that of inner atoms is three. Due to the variation in coordination number, the equilibrium bond length of carbon-carbon is not uniform everywhere in the finite graphene sheet. The bond lengths are arranged into 7 groups and are labelled by letters 'A' to 'G' in Figure 4.2 and are listed in Table 4.2. The letter 'A' refers to the minimum bond length of 0.139 nm, which occurs in the central region of

the top and bottom edges. The maximum bond length labelled by letter ‘G’ is 0.147 nm, and it occurs near the four corners. The average bond length of the graphene has been computed as 0.144 nm which agrees well with that of equilibrium bond length of 0.145 nm reported by Arroyo and Belytschko [175] and Zhang et al. [176].

Figure 4.2. Equilibrium configuration (dotted line) and initial configuration (continuous line). Alphabetical characters marked represent various equilibrium bond lengths (see table 4.2).

It can be shown that the bond length of a single C-C bond is 0.139 nm which is simply the $R^{(e)}$ value of 0.139 nm listed in Table 4.1. However, in a graphene sheet, the bond length is always larger than 0.139 nm for all interior atoms (see Table 4.2 and Figure 4.2). Thus, it can conclude that the net influence of the atoms surrounding a C-C bond is to increase the length of the bond as compared that of single C-C equilibrium bond. As already stated, the variation of bond length in a finite graphene sheet is caused by the variation of coordination number of the individual atoms. In an infinite graphene sheet

the coordination number is the same (three) and hence, the bond length will be the same for all the bonds. Hence, the study of bond length variation was extended to graphene sheets with 66, 276, 496 carbon atoms (results not shown). Here again, a similar trend was observed, and the bond lengths of interior bonds in the 496 atom model were found to be around 0.145 nm (rounded to three decimal places), which is the same bond length value obtained by Arroyo and Belytschko [175] using periodic boundary conditions. This suggests that the bond length of interior bonds computed with a finite sized graphene having 496 atoms is already close to that of infinite graphene.

Table 4.2. Bond length variation in the equilibrium configuration of a finite graphene sheet.

Alphabet	Bond length (nm)
A	0.139
B	0.141
C	0.143
D	0.144
E	0.145
F	0.146
G	0.147

The computed elastic properties are presented in Sections 4.3.2 – 4.3.5. These properties have been computed based on prescribed displacement loading applied to edge atoms. The interior atoms are allowed to relax in order to minimise the potential and thereby obtain the equilibrium configuration of graphene sheet. The curved nature of the edges poses difficulties in applying the displacement loading and restraint conditions. Hence, for the present work, two models are constructed as follows: In model 1, the left and right edges or the top and bottom edges of the envelope are constrained to remain straight, and

in model 2, all the four edges are constrained to remain straight. With these constraints applied, the equilibrium configuration is first obtained by minimising the potential before applying the displacement loading. For the present work, the minimisation is done using an optimisation code called PRAXIS [180]. It is Brent's "principal axis" code for seeking an N -dimensional point $\mathbf{X}$ which minimises a given scalar function $\mathbf{F}(\mathbf{X})$. The code is a refinement of Powell's method of conjugate search directions. The elastic properties are computed using the relations in Equations (4.7) - (4.10) the details of which are discussed in Section 4.3.2.

4.3.2. Model 1: Two straight edges

The Cauchy-Born rule, referred to as a method of the homogeneous deformations, is a fundamental kinematic rule that links the deformation of lattice vectors to that of the continuous medium, and is recently proven rigorously to hold under certain conditions [181]. By means of the Cauchy-Born rule, the continuum elastic potential can be obtained by equating the deformation energy of the graphene to that of an equivalent volume of the continuum. The resulting continuum constitutive graphene model depends only on the interatomic interactions.

Figure 4.3. a) Tensile deformation b) shear deformation.

Constraint equations are applied to left and right edges of the graphene sheet to make the edges straight. Appropriate displacements are applied on these edges to simulate uni-axial tensile (refer Figure 4.3 (a)) and compressive loading, and the corresponding equilibrium potential energy is computed for a series of loadings. Figure 4.4 shows the plot of equilibrium potential energy versus engineering strain, ε defined as δ/L . By using polynomial curve fitting, the potential is expressed in terms of ε as

$$V_B = a_0 + a_1\varepsilon + a_2\varepsilon^2 + a_3\varepsilon^3 + a_4\varepsilon^4 + \dots \quad (4.11)$$

Figure 4.4. Potential versus strain for uni-axial tensile/compressive deformation. Dots and stars represent the equilibrium and non-equilibrium configurations, respectively.

If the potential computations are correct, then a_1 in Equation (4.11) must reduce to zero or a negligible number. The physical interpretation of this is that the slope of the potential curve at $\varepsilon = 0$ is zero, i.e., $\lim_{\varepsilon \rightarrow 0} \frac{dV_B}{d\varepsilon} = a_1 = 0$. In other words, the minimum point of

potential curve must be at zero strain ($\varepsilon = 0$). Whenever equilibrium configurations are used for the computation, this happens so. If a non-equilibrium (unminimised) configuration is used, then the minimum point is no more at the origin (Figure 4.4).

Hence, the curvature calculated at $\varepsilon = 0$, viz., $\left(\frac{\partial^2 V_B}{\partial \varepsilon^2} \right)_{\varepsilon=0}$, does not give the correct value

corresponding to the minimised configuration. If this shifted potential curve is used to compute Young's modulus by applying Equation (4.7), the computed value will obviously be in error. Hence, equilibrium configuration is to be used for a reliable estimate of elastic properties.

Figure 4.5. Shear strain versus potential of graphene sheet.

Table 4.3. Young's modulus and Poisson's ratio values reported by other researchers.

Reported by	Young's modulus (TPa)	Poisson's ratio	Remarks
Present with minimisation of potential	0.669	0.416	Graphene (Brenner)
Arroyo et al. [175]	0.694	0.412	Graphene (Brenner)
Kudin et al. [165]	1.02	0.149	Graphene (<i>ab initio</i>)
Present without minimisation of potential	1.11	0.45	Graphene (Truss element model using AMBER)
Lier et al. [147]	1.11	-	Graphene (<i>ab initio</i>)
Present without minimisation of potential	1.012	0.245	Graphene (Brenner)
Shen et al. [141]	0.213 - 2.08	0.16	SWNT (MM)
Yu et al. [142]	0.32-1.47	-	SWNT (Experiments)
Zhang et al. [176]	0.694	-	SWNT (Brenner)
Sammalkorpi et al. [144]	0.7	-	SWNT (MD)
Lu [152]	0.97	0.28	SWNT (Empirical force constant model)
Yoon et al. [118]	1	0.25	DWNT (Vibrations)

Using Equations (4.7) and (4.11), the Young's modulus, Y_I is computed as 0.669 TPa. A comparison of Young's modulus and Poisson's ratio of graphene sheet computed by few authors based on different methods are shown in Table 4.3. (A detailed list of Young's modulus of graphene and CNTs has already been given in Table 2.1 of Chapter 2.) From Table 4.3 it is seen that, the Young's modulus value of present analysis agrees well with that of graphene sheet Young's modulus reported by Arroyo and Belytschko [175] and the Young's modulus of SWNT reported by Zhang et al. [176]. However, the present

results are far less than the computed value (1.1 TPa) using the *ab initio* by Lier et al., [147] considering the only two middle carbon atoms from the set of 10 atoms to eliminate the side effects caused by graphitic sheet termination.

The plot of equilibrium potential computed by applying a series of small shear angles (ϕ in radians) is shown in Figure 4.5. By using the polynomial curve fitting, the potential is expressed in terms of ϕ as

$$V_B = a_0 + a_1\phi + a_2\phi^2 + a_3\phi^3 + a_4\phi^4 + \dots \quad (4.12)$$

Here again, the coefficient a_1 will be zero or close to zero if equilibrium configurations are used for the computations of potentials. Using Equations (4.9) and (4.12), the shear modulus is computed as 0.179 TPa.

The convergence of computed Young's modulus with the size of graphene model has been studied. The potential minimisation of graphene simulation is computationally intensive. Hence, only a limited number of finite graphene sheets with 66, 120, 276, and 496 carbon atoms has been considered to study the variation of Young's modulus with size of graphene sheet. The results are shown in Table 4.4. From this table, the variation of Young's modulus with size is seen to be very small. Hence, for further computations, the graphene sheet with 120 carbon atoms has been considered as a trade-off between accuracy and computational time. The computed elastic constants of graphene with 120 carbon atoms are summarised in Table 4.7.

Table 4.4. Young's modulus variation with size of graphene sheet.

No. of atoms	Young's modulus (TPa)
66	0.659
120	0.669
276	0.677
496	0.682

Figure 4.6. Different widths considered for Poisson's ratio calculations.

From the uni-axial tensile loading, the Poisson's ratio is computed using Equation (4.10). The Poisson's ratio computed at the midsection of graphene considering three widths viz., between 1-1 and 1'-1' layers, 2-2 and 2'-2' layers, 3-3 and 3'-3' layers (Figure 4.6) are shown as dots, squares and circles, respectively, in Figure 4.7. The extrapolated Poisson's ratio values for zero percentage elongation (Figure 4.7) corresponding to these three widths are 0.416, 0.371 and 0.367, respectively, for the case of two straight edges. The computed Poisson's ratio of 0.416 agrees well with that of Arroyo and Belytschko [175],

viz., 0.412. The Poisson's ratio computed without minimisation of potential is around 0.25, which agrees well with that of Poisson's ratio of SWNT [152]. The results are summarised in Table 4.5.

Table 4.5. Computed Poisson's ratio ν_{12} for the case of two straight edges and four straight edges.

Between layers (Figure 4.3)	Two straight edges	Four straight edges
1-1 and 1'-1'	0.416	0.428
2-2 and 2'-2'	0.371	0.389
3-3 and 3'-3'	0.367	0.384

Figure 4.7. Poisson's ratios computed using graphene model with two straight edges (unconnected symbols) and for four straight edges (connected symbols).

4.3.3. Model 2: Four straight edges

A similar analysis as in Section 4.3.2 is carried out for the four straight edge graphene model. As the name suggests, all the four edges are constrained to be straight. Using Equations (4.7), (4.9), (4.11) and (4.12), the Young's modulus and shear modulus are computed as and are listed in Table 4.7. If the graphene sheet is looked upon as a two dimensional continuum made of orthotropic material, then the elastic constants must satisfy the following conditions [182]:

$$Y_1, Y_2, G_{12} > 0 \quad (4.13)$$

$$\frac{\nu_{12}}{Y_1} = \frac{\nu_{21}}{Y_2} \quad (4.14)$$

$$|\nu_{12}| < \left(\frac{Y_1}{Y_2}\right)^{\frac{1}{2}}, \quad |\nu_{21}| < \left(\frac{Y_2}{Y_1}\right)^{\frac{1}{2}} \quad (4.15)$$

$$\nu_{21} < \frac{1 - \nu_{21}^2 \left(\frac{Y_1}{Y_2}\right)}{2} < \frac{1}{2} \quad (4.16)$$

where (Y_1, ν_{12}) and (Y_2, ν_{21}) are the set of Young's modulus and Poisson's ratios in the longitudinal and lateral directions, respectively. G_{12} is the shear modulus of graphene sheet. The elastic constants determined using the four straight edge model satisfy all the orthotropic conditions, viz., Equations (4.13) - (4.16). However, the elastic constants determined using the two straight edge model do not satisfy Equation (4.14). From Equation (4.14), the quantity $\left(\frac{Y_1 \nu_{21}}{Y_2 \nu_{12}}\right)$ is defined as a measure of orthotropicity, and its value is equal to 1 if the material conforms to orthotropic material model. The computed values of this orthotropicity measure for the two models are listed in Table 4.6.

Table 4.6. Orthotropicity measure.

Model	Orthotropicity measure: $\left(\frac{Y_1}{Y_2} \frac{\nu_{21}}{\nu_{12}} \right)$
Model 1: Two straight edges	0.9205
Model 2: Four straight edges	0.9991

The elastic constants, being material properties, are expected to be independent of the size and boundary conditions. However, from the above studies, the computed elastic constants are observed to vary slightly with respect to the size and boundary conditions. This only suggests that finite sized graphene does not exactly behave like a continuum. Similar to the present observation, dependence of Young's modulus on the radius of single-walled CNTs has been reported in the literature [141, 144, 173].

Table 4.7. Computed elastic constants for the graphene model with two straight edges and four straight edges.

Elastic constants	Two straight edges	Four straight edges
Y_1	0.669 TPa	0.671 TPa
ν_{12}	0.416	0.428
G_{12}	0.179 TPa	0.384 TPa
Y_2	0.812 TPa	0.816 TPa
ν_{21}	0.465	0.520

4.3.4. Potential versus strain, and stress versus strain relationships

Figure 4.8 shows the plot of potential versus strain for a tensile loading that continues even beyond the first rupture of a C-C bond of graphene sheet. A two straight edge model is used for the purpose. The first bond breaks at about 33 percent elongation labelled by the letter 'B' and the corresponding failure stress 0.123 TPa. These values agree well with

the CNT failure strain and stress values computed using the density functional theory (DFT), 30 percent and 0.11 TPa, respectively, by Mielke et al. [149], and 29.5 percent and 0.115 TPa, respectively, reported by Ogata et al. [155]. The first bond breakage occurs at a bond near a corner marked by the symbol ‘G’ in Figure 4.2. For loading beyond first rupture, the potential value drops and rises several times due to different bonds breaking at different locations and the resultant structural rearrangements of the lattice structure of the graphene. The potential equation is obtained from Figure 4.8 using polynomial curve fitting until the first rupture point ‘B’ and is expressed in the form given by Equation (4.11). By differentiating this expression with respect to the small strain measure, ε , the expression for the corresponding stress, σ , becomes

Figure 4.8. Potential versus strain for the tensile loading of graphene sheet (2 straight edge model).

$$\sigma = \frac{dV_B}{d\varepsilon} = a_1 + 2a_2\varepsilon + 3a_3\varepsilon^2 + 4a_4\varepsilon^3 + \dots \quad (4.17)$$

The relation between small strain, ε , and the Green strain, E , is written as

$$E = \frac{1}{2}(\varepsilon^2 + 2\varepsilon) \quad (4.18)$$

Substituting Equation (4.18) in Equation (4.11), V_B in terms of E is obtained. By differentiating this expression with respect to E , the expression for the second Piola-Kirchoff stress is:

$$S = \frac{dV_B}{dE} = \left(\frac{dV_B}{d\varepsilon} \right) \left(\frac{d\varepsilon}{dE} \right) = \sigma \frac{d\varepsilon}{dE} \quad (4.19)$$

The σ and S values are plotted against ε and E , respectively, in Figure 4.9. (σ, ε) and (S, E) are conjugate pairs such that the strain energy associated with each pair, i.e., the areas under each curve is the same. The stress-strain curve is almost linear in the range 0 to 2.5 percent elongation and becomes nonlinear thereafter. In the linear range, it does not matter which of these two stress-strain measure is used for the analysis. However, in the nonlinear range, it is important to use an appropriate stress-strain curve depending on the stress/strain measure used. S vs E curve is particularly useful for the total Lagrangian approach to the nonlinear of tensile loading of graphene sheets.

Figure 4.9. Stress-strain curves: σ versus ε (dots) and S versus E (circles).

4.3.5. Scatter in the elastic property values reported in the literature

Although the Young's modulus and Poisson's ratio values reported in the literature have considerable scatter, a majority of values is seen to fit into two sets (refer Table 4.3). The Young's modulus value of around 0.7 TPa and a Poisson's ratio value of around 0.4 belong to one set. For the other set, the values are 1 TPa and 0.25, respectively. The existence of scatter in the reported Young's modulus and Poisson's ratio values has been known for some time although the possible cause has not yet been completely resolved in the literature. The numerical experiments of this research reveal that the first set of values results when an equilibrium graphene configuration (i.e., the one with minimised potential) is employed and the deformed configuration corresponding to every load step is also obtained by potential minimisation. The second set of values results when a non-equilibrium graphene configuration is employed and no potential minimisation is carried out to obtain the deformed configuration. To illustrate this, the initial (unminimised) configuration of graphene sheet Figure 4.1 with 0.142 nm as the uniform bond length for all bonds is considered. A small tensile horizontal displacement is applied to the atoms. All the atoms are also moved in the vertical direction (to simulate lateral contraction) by assuming a variable value of Poisson's ratio. This becomes necessary as the lateral contraction is not automatic because potential minimisation is not done to obtain equilibrium configuration. Figure 4.10 shows the plot of Young's modulus against the assumed Poisson's ratio values. The minimum point gives us the second set of values (1 TPa, 0.25) associated with the use of non-equilibrium models. The first set of values are expected to be more accurate because the values have been computed allowing for local adjustments of atomic positions to reach the equilibrium configurations.

Figure 4.10. Young's modulus versus Poisson's ratio of graphene.

4.4. Summary and conclusions

The elastic constants of finite graphene sheet have been determined by modelling it as a continuum. Brenner potential has been used for computing the molecular potential of graphene sheet. Two straight edge and four straight edge models have been used. The important observations are summarised below:

1. The influence of equilibrium adjustments of atoms has been considered in determining the elastic constants of a finite sized graphene sheet.
2. Computations considering equilibrium adjustments lead to Young's modulus and Poisson's ratio values around 0.7 TPa and 0.4, respectively, whereas computations ignoring equilibrium adjustments yield around 1 TPa and 0.25, respectively. Nevertheless, papers reporting the elastic constant values often do not mention if equilibrium adjustments have been considered in their

computations. This may be one of the reasons for the wide scatter in the elastic properties reported in the literature.

3. The variation of bond lengths caused by equilibrium adjustments of atoms during potential minimisation process has been studied. The elastic constants Y_1 , Y_2 , ν_{12} , ν_{21} and G_{12} have been computed for two graphene models, viz., with two straight edges and four straight edges. The study of inter-relationship between these constants seems to suggest that graphene behaves like an orthotropic material.
4. Bond breakage in the finite graphene sheet for tensile loading has been studied. The first bond breaks about 33% of elongation and the corresponding failure stress 0.123 TPa.

Chapter 5

SOME NUMERICAL ASPECTS IN THE COMPUTATION OF ELASTIC PROPERTIES OF GRAPHENE AND CARBON-NANOTUBES

For the numerical computations reported in Chapter 4, small displacements were imposed on the atoms of graphene, and the resulting change in potential of graphene was used to compute the elastic properties of graphene sheet. A good choice of the magnitude of displacements was found to be about 0.0001 nm. For a too high or too low value of displacements, the computed elastic properties seemed to have severe numerical errors. This observation motivated an error analysis of computed results. The details and results of error analysis are presented in this Chapter.

The main objective of the present error analysis is to determine the optimum value of displacements to be used in the computation of elastic properties of graphene and CNTs. The second objective is to explore the maximum attainable numerical precision in the computed elastic properties of graphene and CNTs. The extent to which the round-off and truncation errors can affect the precision of computed stiffness values is studied in detail.

5.1. Numerical errors and their effects

A scan through the elastic property values reported in the literature (Chapter 2) reveals that there is a wide scatter in the elastic modulus of CNTs and graphene sheets. The scatter in the reported values is partially due to the differences in the various modelling,

simulation and experimental methods used. It is recognised that a poor control of numerical errors during simulation also affect the reliability of the values reported. For example, significant errors can creep in if the potential of graphene sheet or CNT is not minimised so as to obtain the *equilibrium configuration* before attempting to compute the Young's modulus. It has been noticed from Chapter 4 that if a *non-equilibrium configuration* (i.e., an unminimised or not-properly-minimised configuration) is used, then the computed Young's modulus could be much different from the values computed based on equilibrium configuration.

Another kind of error can enter while computing the Young's modulus by applying a small *trial displacement* to the given structure (graphene or CNT). The magnitude of the imposed displacement significantly influences the accuracy of computed elastic properties. If the imposed displacement is too large, then the nonlinearity may dominate the accuracy of computed linear elastic properties. On the other hand, if the imposed displacement is too small, then the truncation and round-off errors may plague the computed elastic properties. Thus, there is an optimal value of imposed displacement for which the computed elastic property has a maximum precision. An error analysis to determine this optimum value of step-size and the corresponding maximum precision in the computed elastic properties is important to guarantee the reliability of the computed results. This is particularly so in the case of Brenner potential [4] where the potential function is implicitly defined because it is hard to present the potential function as a single closed form expression due to 'many body' terms in the Brenner potential. If the potential function were an explicit polynomial function, the error analysis is rather straightforward. For example, if the potential were a quadratic potential, the optimum

displacement for double precision computations would be around 10^{-8} for the purpose of computing the first derivative of potential and 10^{-4} for the second derivative. The definition of elastic properties (stiffness or Young's modulus) involves second derivative of potential and hence the optimal step size for computing the elastic properties would be 10^{-4} . However, it is well known that Brenner potential behaves like a non-quadratic function. Therefore, the technical problem of finding out an optimal step size should be resolved prior to any attempts to determine the elastic properties. Nevertheless, such studies have not been reported in the literature. The objective of this thesis is to present such an error analysis for graphene and single-walled carbon nanotube (SWCNT).

The computation of Young's modulus for graphene or CNTs involves the definition of the volume of the structure. As known widely, the thickness (t) of graphene or SWCNT is not well defined in the literature. Although many researchers have considered a thickness of 0.34 nm [148, 152, 156, 162] (which is the interlayer distance between the graphene layers in graphite), other values 0.066-0.089 [109] are also used in different contexts. To circumvent this ambiguity, the in-plane stiffness, $C = Yt$, is often used in the literature [173, 183, 184] instead of the Young's modulus. In this Chapter too, in-plane stiffness values are only dealt. (Once the stiffness is computed, the Young's modulus can easily be computed by using an appropriate value for the thickness.)

5.2. Error analysis for a single C-C bond

Three methods are considered to compute the stiffness here. These methods are first illustrated for a single C-C bond in this Section and applied to a graphene sheet as well as SWCNT in Section 5.3.

5.2.1. Small displacement method

- i) With suitable constraints to restrain the rigid body degrees of freedom, the equilibrium configuration of the C-C bond/graphene/SWCNT is first obtained by minimising the potential with respect to the x - and y -coordinates of atoms. This equilibrium configuration is hereinafter referred to as the *initial equilibrium configuration*. (In the present work, the PRAXIS FORTRAN code is used for the purpose of minimising the potential [180]). The expression for the inter-atomic Brenner potential of carbon structures is given in Equation (4.1) [4]. For the potential computations, the second set of parameter constants [4] are used in the present work.
- ii) While applying the small displacement method to graphene or SWNT, the graphene sheet/SWCNT is deformed by a stretch factor, a , in the x -direction such that $x_i = aX_i$ where x_i and X_i are the deformed and initial coordinates of atoms, respectively. Therefore, $a = 1 + \delta / L$ where L is the length of graphene sheet/SWCNT and δ is the change in its length. The equilibrium configuration of the deformed sheet is obtained by minimising the potential with respect to the y -coordinates. Such an equilibrium configuration is hereinafter referred to as the *deformed equilibrium configuration*.
- iii) For sufficiently small stretch values, the stiffness, k , of the graphene sheet/SWCNT may then be computed as follows:

$$V_{\delta} - V_0 = \frac{1}{2}k\delta^2 \Rightarrow k = \frac{2(V_{\delta} - V_0)}{\delta^2} \quad (5.1)$$

where V_0 and V_{δ} are the equilibrium (minimised) potentials corresponding to the initial and deformed equilibrium configurations, respectively. As $\delta \rightarrow 0$, $k \rightarrow k_0$ where k_0 is the linear stiffness to be determined. The Young's modulus, Y , may be computed using the following Equation which can be obtained from Equation (5.1):

$$\frac{V_{\delta} - V_0}{Vol} = \frac{1}{2}Y\left(\frac{\delta}{L}\right)^2 \Rightarrow Y = \frac{2(V_{\delta} - V_0)}{Vol}\left(\frac{L}{\delta}\right)^2 = \frac{kL^2}{Vol} \quad (5.2)$$

where Vol is the volume and L the length of graphene sheet/SWCNT. Here again, as $\delta \rightarrow 0$, $Y \rightarrow Y_0$ where Y_0 the tangent modulus is to be estimated. This present work is restricted to the calculation of stiffness k_0 (which is proportional to Young's modulus as seen from Equation (5.2)). The units employed for the stiffness and the displacement are N/nm and nm, respectively.

Although the procedure to compute the elastic properties using Equations (5.1) and (5.2) appears to be rather straightforward, in practice, numerical errors often plague the accuracy of computed values unless a proper value of δ has been used. Apparently a low value of δ value as possible is desirable for an accurate computation of the stiffness constant, k_0 . However, a too low value of δ may lead to large numerical errors in the computed strain energy, $(V_{\delta} - V_0)$, due to truncation and round-off process. This polluted strain energy, when substituted into Equations (5.1) and (5.2), leads to unreliable estimate of elastic properties due to randomness introduced by the pollution. (Such numerical difficulty can of course be avoided if an explicit expression for the potential is derived.

As already stated, explicit expressions are hard to derive because Brenner potential is not explicitly defined.)

Table 5.1. Brenner potential for the stretching of a single C-C bond.

δ	V_δ
0.000 000 0000	-9.613 135 199 999 990*10 ⁻¹⁰ ($\equiv V_0$)
0.000 000 0001	-9.613 135 199 999 990*10 ⁻¹⁰
0.000 000 001	-9.613 135 199 999 990*10 ⁻¹⁰
0.000 000 01	-9.613 135 199 999 567 *10 ⁻¹⁰
0.000 000 1	-9.613 135 199 956 715 *10 ⁻¹⁰
0.000 001	-9.613 135 195 760 673 *10 ⁻¹⁰
0.000 01	-9.613 134 776 145 092 *10 ⁻¹⁰
0.000 1	-9.613 092 890 330 050 *10 ⁻¹⁰
0.001	-9.608 979 218 672 118 *10 ⁻¹⁰
0.01	-9.264 788 823 553 294 *10 ⁻¹⁰

For illustration numerical errors, a single C-C bond with an equilibrium bond length of 0.139 nm is considered. The Brenner potential values for this bond are calculated using Equation (4.1). Note that, for a single C-C bond, the coupling terms B_{ij} reduce to unity. Table 5.1 lists typical values of this potential. Figure 5.1 shows a plot of the normalised strain energy, $(V_\delta - V_0)/V_0$, against δ . The plot resembles a quadratic function of δ . However, the round-off errors dominate the strain energy for δ less than 10^{-8} , which is displayed by the spiky nature of the plot in Figure 5.1(a). Figure 5.1(b) presents the same results in a log scale so that the number of significant places of precision can be read off

from the plot. The *degree of precision* (dop) is defined as the maximum number significant digits not polluted by the errors. From Figure 5.1(b), the degree of precision in the strain energy is about 13 significant places while the corresponding optimum value of δ is 10^{-8} .

Figure 5.1. Strain energy of a single C-C bond; a) Linear plot; b) Log plot. The spiky region of the plot depicts the randomness caused by truncation and round-off errors.

The effect of this pollution on the degree of precision of computed single C-C bond stiffness is investigated now. The stiffness is computed according to Equation (5.1). Figure 5.2(a) shows a plot of the computed stiffness values while 5.2(b) shows a log plot of its relative error. The straight line portion of the plot seen in Figure 5.2(b) suggests that the degree of precision of the computed stiffness increases linearly with decreasing δ until $\delta = 10^{-5.8}$. Thereafter, divergence sets in and the spikiness due to truncation and round-off errors dominates. Thus, the optimum value of δ as seen from Figure 5.2(b) is $10^{-5.8} \approx 0.0000016$. The corresponding best possible degree of precision in the computed stiffness value is about 4.5 significant digits.

Figure 5.2. Computed stiffness for a single C-C bond by small displacement method; a) Stiffness; b) Relative error.

A precision greater than 4.5 significant digits is not possible using the small displacement method described above. If a precision greater than 4.5 significant digits is desired, then an interpolation of stiffness may be used. For example, the average of $k(\delta = -10^{-5}) = 8.480472361214130 \times 10^{-7}$ and $k(\delta = 10^{-5}) = 8.477098291495524 \times 10^{-7}$ gives $8.478785326354826 \times 10^{-7}$ which is very accurate and tallies with the exact stiffness, $k_0 = 8.478785246399966 \times 10^{-7}$, up to 8 significant digits.

A Mathematica [185] program is developed for obtaining Brenner potential expression in symbolic form for a given set of initial coordinates and small deformation δ applied to structure (graphene or CNT). The stiffness k is computed by differentiating the potential expression twice partially with respect to δ . As $\delta = 0$, the stiffness expression gives the exact stiffness k_0 . The detailed Mathematica [185] program is listed in Appendix B.

5.2.2. Local potential-fit method

The first two steps of this method are the same as for the small displacement method of Section 5.2.1. A curve-fitting is then used to capture the local $V - \delta$ relationship around $\delta = 0$. The Brenner potential V is computed using Equation (4.1) for four typical values δ_i , $i = 1, 2, 3, 4$, and a local polynomial fit is obtained in the form

$$V_\delta = a_1 + a_2\delta + a_3\delta^2 + a_4\delta^3 \quad (5.3)$$

The stiffness constant k_0 is then obtained as

$$k_0 \equiv \lim_{\delta \rightarrow 0} \frac{\partial^2 V_\delta}{\partial \delta^2} = 2a_3 \quad (5.4)$$

Using double precision arithmetic for all computations, it is easy to numerically/graphically show that the best degree of precision in k_0 is about 6 significant places at $\delta_{opt} \approx 10^{-4.5} \approx 0.00003$ (Figure 5.3). Recall that the small displacement method gives only a 4.5 significant place accuracy. Thus, the stiffness is computed more precisely by the local potential-fit method than the small displacement method. The optimum value of δ for the local potential-fit method is about one order of magnitude larger than that of the small displacement method. The data for the plots in Figure 5.3 are generated using the following algorithm:

Figure 5.3. Computed stiffness for a single C-C bond by local potential-fit method; a) Stiffness; b) Relative error.

For values of n in the range -2 to -8.5 in steps of 0.01,

Set $\delta = 10^{-n}$

For $\{\delta_1, \delta_2, \delta_3, \delta_4\} = \{\delta, -\delta, 1.1\delta, -1.1\delta\}$, compute $V_i = V(\delta_i)$, $i = 1, 2, 3, 4$

Using (V_i, δ_i) data, obtain a polynomial-fit by Equation (5.3)

Compute k_0 using Equation (5.4)

Compute the relative error in the stiffness, $\left| \frac{k_0 - k}{k} \right|$, where k is the exact stiffness

End For loop

Figure 5.4. Computed stiffness for a single C-C bond by finite difference method; a) Stiffness; b) Relative error.

5.2.3. Finite difference method (FDM)

The stiffness can also be computed using central difference method as follows:

$$k = (V_{-\delta} - 2V_0 + V_{\delta}) / \delta^2 \quad (5.5)$$

where $V_{-\delta}$ and $V_{+\delta}$ are potentials computed with displacements $-\delta$ and $+\delta$, respectively.

The computed stiffness (Figure 5.4) has trends similar to that of local potential-fit method (Figure 5.3).

Figure 5.5. Equilibrium configuration of graphene sheet and SWNT.

5.3. Error analysis for graphene and single walled carbon nanotubes

In Section 5.2, the investigation was limited to a single C-C bond wherein the coordination number of carbon atom is just one and thereby the potential computations become simpler. However, in graphene or CNT, the coordination number of carbon atom is mostly three and therefore the potential computations are more involved due to the

forces associated with the bond angle change caused by three nearest neighbouring atoms and six second nearest neighbouring atoms. The objective of this Section is to study how this affects the maximum possible degree of precision in the stiffness computation for a graphene sheet and SWCNT (Figure 5.5). The stiffness intended to be computed is the end-to-end stiffness. The exact value of stiffness k_0 for the graphene sheet and SWCNT are first determined analytically (using *Mathematica* software [185] for the symbolic manipulations) as 4.04171×10^{-7} and 3.36022×10^{-7} , respectively.

Figure 5.6. Strain energy plot for a non-equilibrium configuration. Note that the minimum point has moved away from the origin.

5.3.1. Small displacement method

The initial equilibrium configuration is first obtained as outlined in Section 5.2. Subsequently, a stretch deformation is applied conforming to the relation, $x_i = aX_i = (1 + \delta/L)X_i$. If either the initial configuration or the deformed configuration is not properly minimised, then the minimum point of the strain energy curve moves away from the origin as shown in Figure 5.6, and hence the strain energy does not tend to

a minimum when $\delta \rightarrow 0$. The small displacement method as outlined in Section 5.1.1 becomes unstable when such a lack of equilibrium is present and consequently, the computed stiffness k_0 has significant error. This problem does not show up in the simple case of single C-C bond, but has been quite commonly observed with graphene or SWCNT. An example of this instability and a method to overcome the same are discussed below.

Figure 5.7. Computed stiffness for graphene sheet by small displacement method; a) Stiffness; b) Relative error. The results are polluted by equilibrium error.

Figure 5.7 shows the computed stiffness for the graphene sheet by the straightforward application of the small displacement method outlined in Section 5.2.1. (The initial equilibrium configuration has been obtained by minimising the potential with convergence tolerance of 10^{-14} using the PRAXIS [180] routine.) An important observation from the plot in Figure 5.7(b) is that the spikiness is now confined to a small segment of the divergent portion of the plot, i.e., that portion having the negative slope. This spiky region is caused by the truncation and round-off errors. The non-spiky region, however, is caused by some systematic error, i.e., the equilibrium error. Furthermore, the convergent portion (i.e., the portion with positive slope) is too short. If the plot in Figure 5.7(b) were free of equilibrium error, the plot should have a deterministic (non-spiky) divergent portion in Figure 5.2(b). The solution to this instability problem was not obvious. Later, it was recognised that the effects of non-equilibrium forces need to be considered. Towards this goal, the potential is first expanded as a Taylor series:

$$V_\delta = V_0 + \left(\frac{\partial V_0}{\partial \delta} \right)_{\delta=0} \delta + \frac{1}{2} \left(\frac{\partial^2 V_0}{\partial \delta^2} \right)_{\delta=0} \delta^2 + \dots \quad (5.6)$$

where $\left(\frac{\partial V_0}{\partial \delta} \right)_{\delta=0}$ is the non-equilibrium force due to equilibrium errors. From Equation

(5.6), the stiffness can be expressed as

$$k \equiv \left(\frac{\partial^2 V_0}{\partial \delta^2} \right)_{\delta=0} = \frac{2(V_\delta - V_0)}{\delta^2} - \frac{2}{\delta} \left(\frac{\partial V_0}{\partial \delta} \right)_{\delta=0} \quad (5.7)$$

Figure 5.8 shows the results for the graphene sheet computed using Equation (5.7), where the relative error plot (Figure 5.8(b)) now shows a correct trend. (As a cross-check, the Young's modulus is computed for graphene using Equation (5.2) as 1.1 TPa which

matches well with the *abinitio* computations of references [147, 165]). The maximum degree of precision in the computed stiffness is observed to be about 4.5 significant digits, similar to case of the single C-C bond, although the optimum δ value ($\approx 10^{-4.5}$) has reduced by an order of magnitude. Similar trends are observed for the stiffness of SWCNT (Figure 5.9). The Young's modulus value for the SWNT computed using Equation (5.2) is 1.02 TPa which is close to the computational results of Tserpes and Papanikos [169], Li and Chou [156], Lu [152] and Popov et al. [153], and the experimental results of Krishnan et al. [35]. To compare the present results, the thickness of graphene and SWNT as 0.34 nm is used.

Figure 5.8. Computed stiffness for graphene sheet by modified small displacement method;

a) Stiffness; b) Relative error.

Figure 5.9. Computed stiffness for SWCNT by modified small displacement method; a) Stiffness; b) Relative error.

5.3.2. Local potential- fit method

The stiffness for the graphene sheet is computed following a procedure as described in Section 5.2.2, and the results are plotted in Figure 5.10. The plots suggest that the local potential-fit method is not sensitive to equilibrium error in the deformed equilibrium configuration. This is evident from the fact that the divergent portion (i.e., the portion having negative slope) of plot in Figure 5.10(b) has no deterministic trend which means that the divergence is caused purely by random error due to truncation and round-off. A

comparison of Figure 5.10(b) with Figure 5.8(b) shows that the stiffness computed by the local potential-fit method has a higher precision than that computed by the modified small displacement method. The optimum value of δ ($\approx 10^{-3.5}$) for the local potential-fit method is, however, about one order of magnitude larger than that of the small displacement method. The stiffness results computed for the SWCNT are plotted in Figure 5.11. Here again, a similar trend is observed.

a)

b)

Figure 5.10. Computed stiffness for graphene sheet by local potential-fit method; a) Stiffness;
b) Relative error.

a)

b)

Figure 5.11. Computed stiffness for SWCNT by local potential-fit method; a) Stiffness;
b) Relative error.

5.3.3. Finite difference method

The stiffness results computed with finite difference method, shown in Figures 5.12 and 5.13, displays a trend similar that of local potential fit method discussed in Section 5.3.2.

a)

b)

Figure 5.12. Computed stiffness for graphene sheet by finite difference method; a) Stiffness;
b) Relative error.

a)

b)

Figure 5.13. Computed stiffness for SWCNT by finite difference method; a) Stiffness; b) Relative error.

5.4. Summary of results and discussions

A summary of important results from this Section is given in Table 5.2. A scan through the Table 5.2 shows that the local potential-fit method and the finite difference method can give a degree of precision of at least 6 significant digits while the small displacement method can give at least 4 significant digits. However, the optimum δ value for the former two methods is around 10^{-3} while that of the later is around 10^{-4} .

Although the small displacement method gives less accuracy, it has an attractive feature. It just requires two potential evaluations, viz., V_0 and V_δ , whereas the finite difference method requires three evaluations and the local potential-fit method requires four of them. On the other hand, the small displacement method becomes unstable if the deformed configuration or the initial configuration is not minimised. In such a case, the method needs to be modified to include the non-equilibrium forces, and this requires the computation of first derivative of the potential. Numerical determination of the first derivative then involves another potential evaluation, which then reduces the advantage of the small displacement method over the finite difference method. Nevertheless, whenever the deformed configuration used for the purpose is an equilibrium configuration, the small displacement method may still be of interest.

Table 5.2. Degree of precision in the computed stiffness and optimum δ values.

	Method of stiffness computation	Degree of precision (no. of significant digits)	Optimum δ value
Graphene	Modified small displacement method	4.2	$10^{-4.5}$
	Local potential-fit method	6.2	$10^{-3.2}$
	Finite difference method	6.8	$10^{-3.5}$
SWCNT	Modified small displacement method	4.2	10^{-4}
	Local potential-fit method	6.2	$10^{-3.2}$
	Finite difference method	6.8	10^{-3}

5.5. Concluding remarks

An error analysis has been attempted for the numerical determination of linearised stiffness of graphene and SWCNT. For this purpose, the end-to-end stiffness computed by Cauchy-Born rule using Brenner potential for graphene and SWCNT is considered. Three competitive methods, viz., small displacement method, local potential-fit method and finite difference method have been studied. All computations have been carried out in double precision arithmetic. The following are the major conclusions from this investigation:

- 1) A precision of about 6 significant digits in computed stiffness seems possible with the local potential-fit method and the finite difference method. The small displacement method can, however, yield only an accuracy of about 4 significant digits.
- 2) The optimum magnitude of trial displacement is about 0.0001 for the local potential-fit method as well as the finite difference method while it is about 0.00001 for the small displacement method. The error in the computed stiffness value is the least for these values of trial displacements. If a lower or higher value is used than these optimum values, then the error increases.
- 3) The small displacement method must be used with caution. It is stable only if the initial and deformed configurations are equilibrium configurations. If the configurations are not equilibrium configurations, then the influence of non-equilibrium forces must be considered. The numerical experiments showed that, with this consideration, the method restores its stability.

Chapter 6

FREE VIBRATION ANALYSIS OF SINGLE-WALLED CARBON NANOTUBES

In Chapters 3 and 4, AMBER force field and Brenner potential, respectively, have been used to predict the elastic properties of graphene sheets. In Chapter 5, an error analysis has been carried out with respect to the use of Brenner potential for computing the stiffness constant of graphene and single walled carbon nanotubes (CNTs). Three methods (viz., small displacement method, potential fit method and finite difference method) have been used to compute the elastic properties and its maximum numerical precision to minimise the error while computing the elastic properties of graphene sheet and CNTs. In this Chapter, free vibration analysis of CNTs is carried out using the finite difference method. Brenner potential is employed for the stiffness computation.

Based on the observations of previous Chapters, an accurate stiffness calculation requires the use of equilibrium configurations of CNTs (i.e., configurations with minimum potential energy). Hence, two configurations, viz., inherent equilibrium configuration and uni-bondlength equilibrium are explored here for the purpose. The importance of using equilibrium configuration is reiterated again through examples. The free vibration analysis is also computed using a continuum shell model of CNT (where the concept of equivalent Young's modulus is employed). This analysis does not involve equilibrium configurations and hence may sound attractive. However, such an approach is shown in this Chapter to give rather similar results as that of atomistic simulations, provided appropriate set of Young's modulus and wall thickness values used for continuum shell

model. (To eliminate the uncertainty in choosing the set of reported Young's modulus and wall thickness values of CNTs used in the literature, the bending rigidity is determined straightaway from the first natural frequency computed using atomistic simulation, for all the computations in next Chapter.)

In Chapter 5, the optimum step size has been determined so as to compute the stiffness of CNTs accurately. In this Chapter, a similar study is carried out to determine the optimum step size for the computation of natural frequencies of CNTs.

6.1. Previous studies on vibration of CNTs

Carbon nanotubes promise several potential applications in various fields due to their superior physical, mechanical and electrical properties. Resonators fabricated from SiC have been observed to have a fundamental frequency as high as 1 GHz [115]. Recently, the researchers examined the feasibility of using carbon nanotubes as resonance based sensor applications such as resonators, chemical and biomedical sensors, mass detectors, oscillators, filters, nanomechanical memory devices etc., due to their high natural frequency of the order of 1 THz [5, 116-120]. Reduction in the size of the nanotubes increases its resonant frequencies and sensitivity [117] causes many proposed applications of CNTs involving short nanotubes with aspect ratio 10 to 50 are of much practical significance [118]. The scaling behaviour of sub-20 nm short channel CNT transistors has been studied by Seidel et al. [123]. The single-electron transistors of CNTs of length about 20 nm [124] and electromechanical devices as memory units using periodic supports less than 20 nm length CNTs [125] have been used as applications of short CNTs. However, vibration studies on short CNTs are considerably less as

compared to studies on elastic properties and hence the motivation for the work reported in this Chapter.

The existing methods for computing the natural frequencies include *ab initio* methods, tight binding and molecular dynamics, and continuum models. *Ab initio* methods have been successful for computing the electronic and material properties with high accuracy. However, this method is computationally intensive and mostly used for computing the phonon frequencies of lattice structures [186] and radial breathing mode frequency computations [187]. Molecular dynamics simulations have been widely used for dynamic applications of nanotubes such as nanooscillators [188, 189], characterisation of nanotube oscillations subjected to external atomic collisions [135]. In continuum approach, elastic beam models of CNTs have been used [36, 104, 190] for predicting the frequencies. A space frame model with beam connected carbon atoms has been used for predicting the natural frequencies of nanomechanical resonators [117]. Very recently, Timoshenko beam model has been used by Yoon et al. [118] to predict the vibrations of the short nanotubes.

Most of the reported studies have used truss/beam element models (where the C-C bonds are modelled as truss/beam elements) [191] or continuum model [118] to study the vibrational behaviour of nanotubes. Brenner potential [4] is one of the successful potentials used for computing the mechanical properties of CNTs. However, the studies using this potential for computing natural frequencies are limited [5]. This is perhaps due to the fact that Brenner potential involves many body terms and this leads to difficulty in

computing the derivatives of potential function. Stiffness matrix computation involves the second derivative of the potential function and is determined numerically in this Chapter using finite difference method. Choosing optimal step size for the purpose needs a careful consideration because of the non-quadratic nature of Brenner potential. An inappropriate step size leads to inaccurate results, which is already demonstrated in Chapter 5.

Liu et al. [192] have proposed an atomic-scale finite element method to compute the stiffness matrix for CNTs. The first and second neighbour atoms are used for the purpose. Kwon et al. [5] have used rather a similar approach. Using Brenner potential, the stiffness matrix is computed although the second neighbour atoms have not been considered in their computations. Li and Chou [116] have used molecular structural mechanics method for computing the stiffness matrix. In determining the stiffness matrix numerically, the precision of computed stiffness values is an important aspect to be monitored. In Chapter 5, estimate the maximum obtainable numerical precision in the computed stiffness using *small displacement method*, *local potential-fit method* and *finite difference method*. The recommended optimum step size values are also reported. The *finite difference method* is used in the present Chapter to compute the stiffness matrix.

The objective of the present Chapter is to present a detailed *finite difference approach* to compute the stiffness matrix for carbon nanotubes using Brenner potential and use it to predict the natural frequencies and mode shapes. Another objective is to bring out the importance of using an equilibrium configuration so as to capture the natural frequencies

accurately. An atomic model based on Brenner potential is used to predict the natural frequencies and mode shapes for CNTs. It is also observed that the elastic shell models also give fairly accurate frequencies and modeshapes.

Figure 6.1. Equilibrium configuration of a CNT. Carbon atom (shaded circle) connected to first three nearest-neighbour (unshaded circles, f) and six second nearest-neighbour (double unshaded circle, s) atoms. Colour codes are given for different equilibrium bond lengths.

6.2. Equilibrium configuration of CNT

To compute the stiffness matrix accurately, it is important to consider an equilibrium configuration of CNTs (the importance of using an equilibrium configuration to compute the elastic properties of graphene sheet has been already pointed out in Section 4.3 in Chapter 4). The equilibrium positions of carbon atoms of the CNT are first computed by minimising the Brenner potential of nanotube. The atomistic interaction among carbon atoms is characterised by multibody interatomic potentials mainly due to bond length change and bond angle change [4]. As an illustration, Figure 6.1 shows a given carbon atom (shaded circle) in a carbon nanotube is directly connected to the three nearest-neighbour atoms (unshaded circles marked as f) and indirectly connected to six second nearest-neighbour atoms (double unshaded circles marked as s). If a given atom (shaded circle) is displaced from its equilibrium position, then the associated change in potential has two parts. The first is due to the change in the bond length and the bond angle

between the given atom and its first neighbours. The second is due to the change in bond angle involving the given atom, a first neighbour and a second neighbour. The third neighbours do not contribute to the change in potential. This change in potential is used in the computations of atomic stiffness.

The equilibrium bond length between any two carbon atoms in a carbon structure is often taken by researchers as 0.142 nm [193] although the actual bond length for the given structure may actually be different. Furthermore, the bond length is assumed to be uniformly same for all the bonds in a structure although the bond length can vary spatially. This happens, for example, in the case of short CNT and finite graphene sheets. An accurate approach to compute equilibrium configuration (refer Chapter 4) is by perturbing the individual atomic positions so as to minimise the potential of graphene/CNT and such an equilibrium configuration is referred to as *inherent equilibrium configuration* in this Chapter. Such an approach is important (Chapter 4) in analysing finite graphene sheets where the bond length varies with location, which is attributed due to *edge effect*. A similar argument applies to the analysis of short CNTs (Figure 6.1). It is observed that, at the ends, the radius is larger than in the middle, which is due to the edge atoms having less coordination number (two) as compared to middle atoms (three). The bonds shown in green, black, blue and red in Figure 1 represent bond lengths 0.143, 0.147, 0.146 and 0.145 nm, respectively. The horizontal bonds (red) are longer than the inclined bonds (blue), particularly. To determine such an equilibrium configuration wherein the bond lengths vary spatially by minimising the potential with respect to the atomic coordinates is computationally intensive. The actual computational

time taken depends on the initial configuration, i.e., how far the initial configuration deviates from the equilibrium configuration. Therefore, an approximate approach is also explored here. This reduces the computational effort, but still maintains a good accuracy of computed natural frequencies. In this approach, a uniform bond length is assumed throughout the CNT and the structure potential is minimised by varying the bond length in the range 0.143 to 0.147 nm as shown in Figure 6.2. The minimum potential configuration, thus obtained, is termed *uni-bondlength equilibrium configuration* in this Chapter. The equilibrium bond length (refer Table 6.1) obtained by this approach is 0.145 nm (rounded off to three decimal places). The present equilibrium bond length 0.145 nm agrees well with the equilibrium bond length reported by Arroyo and Belytschko [175], and Zhang et al. [176].

Table 6.1. Equilibrium bond lengths of CNT based on uni-bondlength equilibrium configuration.

Variation of radius		Variation of length	
CNT type and Length (nm)	Equilibrium bond length (nm)	CNT type and length (nm)	Equilibrium bond length (nm)
(8,0) $L=8.192$	0.1455013	(14,0) $L=08.146$	0.1451676
(10,0) $L=8.170$	0.1453201	(14,0) $L=18.187$	0.1451934
(12,0) $L=8.155$	0.1452243	(14,0) $L=26.918$	0.1452002
(14,0) $L=8.146$	0.1451676	(14,0) $L=32.593$	0.1452028
(16,0) $L=8.140$	0.1451312	(14,0) $L=43.507$	0.1452057
(18,0) $L=8.136$	0.1451064	(14,0) $L=87.162$	0.1452102
(20,0) $L=8.133$	0.1450888	(14,0) $L=108.99$	0.1452110

From columns 1 and 2 of Table 6.1, it is observed that the equilibrium bond length decreases with an increase in the radius of CNT. As already stated, the bond lengths at

the two edges of CNT (shown green lines in Figure 6.1) are shorter than elsewhere. This tends to reduce the weighted average bond length for a given CNT. The influence of this edge effect is more in case of CNTs with large diameter than small diameter. As a result, the weighted average value of bond length for the CNT seems to decrease with increase in diameter of the CNT.

Similarly, from columns 3 and 4 of Table 6.1, it is observed that the equilibrium bond length increases with the length of CNT. This may also be explained in terms of edge effect as stated above.

6.3. Computation of stiffness matrix

Dynamic analysis of CNTs involves solution of the second order differential equation

$$\mathbf{M} \ddot{\mathbf{x}} + \mathbf{K}\mathbf{x} = \mathbf{P} \quad (6.1)$$

where $\mathbf{M}$ and $\mathbf{K}$ are the mass and stiffness matrices, respectively, $\mathbf{x}$ is the vector of atomic coordinates, and $\mathbf{P}$ is the nonequilibrium force vector. Let us consider N atom system, in which each atom has three degree of freedom in the x -, y -, and z -directions, respectively. The lumped global mass matrix can then be simply written as the mass of the atom times the identity matrix of order $3N$.

Defining the stiffness matrix of CNTs is, however, not as straightforward as the mass matrix. If the CNT can be modelled as a continuum shell, then finite element method can be used for the purpose and the elemental stiffness can then be easily determined in terms of equivalent Young's modulus and Poisson's ratio, and the length, diameter and thickness of CNT. However, definite values of Young's modulus and Poisson's ratio

values of CNTs reported in literature lack of consensus. The reported values, based on experiments as well as simulation results (Table 2.1 and 2.2 in Chapter 2), often span a wide range. Care must be exercised in choosing appropriate set of values for the purpose. For the free vibration analysis of SWCNT, the choice of (Y, t) around (5.5 TPa, 0.066 nm) seems appropriate as will be discussed later. Moreover, it is difficult to express the stiffness of CNT in closed form, in view of the fact that Brenner potential involves non-linear functions of the bond length and bond angle. For these reasons, a continuum beam model of CNT is not employed here for determining the stiffness matrix. Rather the stiffness is determined matrix numerically straightaway using Brenner potential. Thus, in the present study, there are no assumed values of Young's modulus, Poisson's ratio or wall thickness.

Figure 6.2. Potential variation with carbon-carbon bond length of CNT.

The method is based on the fact that the curvature of the potential curve gives the stiffness and is directly proportional to Young's modulus for a particular thickness of nanotube. For small displacements, the stiffness is related to the generalised coordinates q_i and q_j follows and is expressed as

$$K_{ij} = \frac{\partial^2 V}{\partial q_i \partial q_j} \quad (6.2)$$

where V is the potential of CNT. Brenner potential is used here for the stiffness computations, which is expressed as a multibody interatomic complex function [4] and computed numerically for stiffness computations. For a 3-D nanostructure such as CNTs with N -atom, the potential is of the form $V(q_1, q_2, q_3, \dots, q_N, q_{N+1}, q_{N+2}, q_{N+3}, \dots, q_{2N}, q_{2N+1}, q_{2N+2}, q_{2N+3}, \dots, q_{3N})$, where $(q_1, q_2, q_3, \dots, q_N)$, $(q_{N+1}, q_{N+2}, q_{N+3}, \dots, q_{2N})$ and $(q_{2N+1}, q_{2N+2}, q_{2N+3}, \dots, q_{3N})$ are nothing but the x -, y - and z -coordinates, respectively, of N atoms. To compute the partial derivatives of the potential, finite difference method is used. The finite difference involves pivot points (1 to 8) symmetrically located in a square net by taking $\Delta q_i = \Delta q_j = h$, with respect to the reference values of coordinates (q_i, q_j) as shown in Figure 6.3.

Figure 6.3. Symmetrically located pivot points from the reference atom '0' in square net.

The first partial derivative may be expressed as [194]

$$\frac{\partial V}{\partial q_i} \approx \frac{1}{2h} [V(q_i + h, q_j) - V(q_i - h, q_j)] = \frac{1}{2h} [V_1 - V_3], \quad (6.3)$$

and

$$\frac{\partial V}{\partial q_j} \approx \frac{1}{2h} [V(q_i, q_j + h) - V(q_i, q_j - h)] = \frac{1}{2h} [V_2 - V_4] \quad (6.4)$$

The second partial derivatives may be expressed as

$$\frac{\partial^2 V}{\partial q_i^2} \approx \frac{1}{h^2} [V(q_i + h, q_j) - 2V(q_i, q_j) + V(q_i - h, q_j)] = \frac{1}{h^2} [V_1 - 2V_0 + V_3], \quad (6.5)$$

$$\frac{\partial^2 V}{\partial q_j^2} \approx \frac{1}{h^2} [V(q_i, q_j + h) - 2V(q_i, q_j) + V(q_i, q_j - h)] = \frac{1}{h^2} [V_2 - 2V_0 + V_4], \quad (6.6)$$

and

$$\begin{aligned} \frac{\partial^2 V}{\partial q_i \partial q_j} &\approx \frac{1}{4h^2} [V(q_i + h, q_j + h) - V(q_i - h, q_j + h) + V(q_i - h, q_j - h) - V(q_i + h, q_j - h)] \\ &= \frac{1}{4h^2} [V_5 - V_6 + V_7 - V_8] \end{aligned} \quad (6.7)$$

The stiffness calculations using Brenner potential is very sensitive to the h value. Based on the values suggested in Chapter 5, the optimal value of h for the present work is taken as 0.0001 nm. The atomic stiffness (defined as the resistance offered by the atom to move an atom from the reference point) matrix and non-equilibrium force vector of an atom i can be expressed in matrix form as

$$\mathbf{K}_i = \begin{bmatrix} (\mathbf{K}_{ii})_{3 \times 3} & (\mathbf{K}_{ij})_{3 \times 3M} \\ (\mathbf{K}_{ji})_{3M \times 3} & (0)_{3M \times 3M} \end{bmatrix} \quad (6.8)$$

where the subscript M is the number of neighbours of atom i , and

$$\mathbf{P}_i = \begin{bmatrix} \left(-\frac{\partial V}{\partial x_i} \right)_{3 \times 1} \\ (0)_{3M \times 1} \end{bmatrix} \quad (6.9)$$

In matrix $\mathbf{K}_{ii}$, the elements represent the stiffness values with respect to the x -, y - and z -displacements of atom i , and the elements of matrix $\mathbf{K}_{ij}$ represents the stiffness coupling

between the displacements of atom i and that of a neighbour atom j . The global stiffness matrix, which is symmetric, is obtained by assembling the individual atomic stiffness matrices, $\mathbf{K}_i$ of all atoms. Although the CNT has a repetitive shell structure, the atomic stiffness matrix is not the same for all atoms and varies with atomic position. For a CNT that is already in equilibrium configuration, the force vector, $\mathbf{P}_i$, must be zero. For non-equilibrium configurations, it is necessary to first solve the equation $\mathbf{K}\mathbf{x} = \mathbf{P}$ iteratively, until $\mathbf{P}$ reaches zero. (This process will result in an *inherent equilibrium configuration*. In the case of *uni-bondlength equilibrium configuration*, $\mathbf{P}$ is in general not zero.) The detailed FORTRAN program is listed in Appendix C for stiffness computations.

Figure 6.4. Fundamental frequency of inherent equilibrium configuration. Solid and broken lines represents the free-free and fixed-fixed end conditions, respectively.

If the CNT has N number of atoms, the natural frequencies and mode shapes are determined by solving an eigenproblem involving $3N \times 3N$ stiffness and mass matrices:

$$\mathbf{K}\boldsymbol{\phi} = \omega^2 \mathbf{M}\boldsymbol{\phi} \quad (6.10)$$

where $\boldsymbol{\phi}$ is a mode shape and ω the corresponding natural frequency (rad/s). Equation (6.10) is solved iteratively for eigenvalues and eigenvectors using a FORTRAN code which employs the subspace iteration method [195].

Figure 6.5. Fundamental frequency of fixed-fixed nanotubes. Solid and broken lines represents inherent and uni-bondlength equilibrium configurations, respectively.

6.4. Computed natural frequencies and mode shapes

In this Section, the natural frequencies and mode shapes of various sizes of single walled carbon nanotubes are computed for two typical boundary conditions namely, free-free

and fixed-fixed ends. The fluid flow in the CNT is not considered in this Section but it will be considered in Chapter 7. Usually, the lowest few natural frequencies and mode shapes of practical significance in engineering applications. Hence, the present studies are restricted to the first six typical modes. The natural frequencies for different sizes of CNTs are computed for two different equilibrium configurations, viz., inherent equilibrium configuration and uni-bondlength equilibrium configuration and the results are summarised in Figures 6.4 and 6.5.

Figure 6.4 shows the variation of fundamental natural frequency with aspect ratio (L/D) of CNT with free-free and fixed-fixed end conditions. For computing the results shown in this figure, (5, 0), (8, 0) and (14, 0) zigzag nanotubes with inherent equilibrium configuration have been used. It is well known from strength of materials theory for beam structures that the fundamental natural frequencies for both end conditions should be equal for a given diameter and length [196]. From Figure 6.4, however, they are seen to be different, in particular for small L/D ratios and are equal only for $L/D \geq 20$ or there about. The frequencies computed using inherent equilibrium configuration and uni-bondlength equilibrium configuration are compared in Figure 6.5. The computed natural frequencies with both equilibrium configurations are almost the same. This observation suggests that the uni-bondlength equilibrium configuration (instead of inherent equilibrium configuration) can be used to compute the natural frequencies of large size CNTs with good accuracy and this saves the computational cost considerably.

As a validation of the present method to compute natural frequencies, the first bending mode natural frequency for the zigzag (14,0) CNT of $L/D = 7.28$ has been computed as 330 GHz using the inherent equilibrium configuration. The corresponding value reported by Li and Chou [116] for a CNT of the same size is 380 GHz which is close to the present value with a difference of about 13%. This difference is due to the fact that Li and Chou [116] modelled the CNT as an assemblage of beam elements (representing the C-C bonds) for their computations, which is completely different from the current molecular potential based approach. Another validation attempted was comparison of radial breathing mode frequency. The radial breathing mode is the first mode in Raman vibrational spectroscopy studies and is widely used to determine the diameter of single-walled carbon nanotubes [197]. In the present study, the radial breathing mode frequency of zigzag (14,0) CNT is computed as 6.14 THz. This value agrees well with 5.85 THz determined using Raman spectroscopy [198, 199], and computed values of 6.04 THz and 5.91 THz using the Brenner potential [4] and second generation reactive empirical bond order potential (REBO) [65], respectively.

For the zigzag (8,0) CNT modelled with uni-bondlength of 0.145 nm, the computed natural frequencies with non-equilibrium configuration for the first radial flattening mode, first lateral bending mode and first radial breathing modes are 1050, 2110, and 3885 GHz, respectively, and the corresponding natural frequencies computed using the inherent equilibrium configuration are 1758, 2125 and 3923 GHz, respectively. The difference observed in the first radial flattening mode frequency is quite large. This large difference is due to the fact that the unbalanced force vector $\mathbf{P}$ in Equation (6.1) may not

be negligible in the case of non-equilibrium configuration, and this leads to significant error in the computed natural frequencies. Sometimes, it can also lead to complex frequency values (due to negative eigenvalues).

In the case of free-free vibration of nanotubes, the lowest six modes are rigid body modes and the corresponding eigenvalues must be zero. An eigenshifting procedure [196] is applied in the calculation of rigid body modes using an algorithm that is not designed for computing zero eigenvalues. The purpose of eigenshifting is to render the otherwise singular stiffness matrix nonsingular. Using a shift value of μ , is used and Equation (6.10) becomes

$$\mathbf{K}\boldsymbol{\phi} + \mu\mathbf{M}\boldsymbol{\phi} = \lambda\mathbf{M}\boldsymbol{\phi} + \mu\mathbf{M}\boldsymbol{\phi} \quad (6.11)$$

$$(\mathbf{K} + \mu\mathbf{M})\boldsymbol{\phi} = (\lambda + \mu)\mathbf{M}\boldsymbol{\phi} \quad (6.12)$$

The eigenvectors of Equation (6.12) are the same as the eigenvectors of Equation (6.10), but the eigenvalues are increased by μ . Equation (6.12) can be rewritten as

$$\hat{\mathbf{K}}\boldsymbol{\psi} = \hat{\lambda}\mathbf{M}\boldsymbol{\psi} \quad (6.13)$$

where $\lambda_i = \hat{\lambda}_i - \mu$ and $\phi_i \equiv \psi_i$.

The eigenmodes have been computed and plotted for various sizes of CNT considering inherent equilibrium configuration. Typical vibrational mode shapes for the free-free end condition include radial flattening modes, lateral bending modes, radial breathing modes, twisting modes and also combination of the above modes. For short nanotubes, the first few modes are radial flattening modes and the lateral bending modes appear later. A short

zigzag (8, 0) nanotube of length 2 nm with free-free end conditions is considered to illustrate the lowest few eigenmodes and the mode shape plots as shown in Figure 6.6.

These modes may be classified as

- (i) six rigid body modes,
- (ii) a pair of first radial flattening modes,
- (iii) a pair of second radial flattening modes (with 90° phase shift between the ends),
- (iv) the first pair of lateral bending modes,
- (v) a pair of two higher order radial flattening modes,
- (vi) the axial stretching mode,
- (vii) again two higher order radial flattening modes,
- (viii) second lateral bending modes, and
- (ix) radial twisting mode.

Figure 6.6. Natural frequencies (in GHz) and corresponding eigenmodes of short CNT (diameter 0.65 nm and length 2 nm) with free-free end conditions. (a) and (b) refer to the front and bottom

views, respectively. The modes are classified as six rigid body modes (0), two radial flattening modes (1757), two radial flattening modes with 90° phase shift between ends (1818), two first bending modes (2124), two higher order radial flattening modes with 90° phase shift between the ends (2225), axial stretching mode (2410), again two higher order radial flattening modes with 90° phase shift between ends (3152), two second lateral bending modes (3830) and radial twisting mode.

The relative positions of these modes in the sequence depend on the L/D ratio of nanotubes. The above sequence is for $L/D = 3.13$. For $L/D = 7.28$, the lateral bending mode is seen to appear first followed by four radial flattening modes and second lateral bending mode (Figure 6.7). The rigid body modes and repeated eigenmodes at same frequency are not shown in Figure 6.7. If L/D ratio is increased further, then the first and second bending modes appear first followed by the radial flattening modes. In case of short nanotubes, the radial flattening mode is absent in the studies of Li and Chou [116], which is attributed to a different molecular structural mechanics method used by them.

Figure 6.7. Natural frequencies (in GHz) and mode shapes of CNT from atomistic model. The modes are classified as first lateral bending mode (330), radial flattening mode (572), radial flattening mode with 90° phase shift between the ends (576), higher order radial flattening mode (607), twisting mode (642) and second lateral bending mode (777).

For comparing the equivalent continuum shell model against the atomistic model, a zigzag (14,0) CNT (for L/D value 7.28) is considered. Using ANSYS finite element software [6], the natural frequencies and mode shapes have been computed treating the CNT as a continuum shell. The Young's modulus and wall thickness values used for the computation are 5.5 TPa and 0.066 nm [109, 167], respectively. The equivalent density is computed by dividing the total mass of all carbon atoms by the volume as 11.22 g/cm^3 (refer Table 6.2). The computed frequencies for the first six modes are 425, 599, 606, 769, 961 and 1008 GHz and the corresponding modeshapes are shown in figure 6.8. The frequencies obtained using atomistic model are 330, 572, 576, 607, 642 and 777 GHz, and the corresponding modeshapes are shown in Figure 6.7. These modeshapes are similar to that of continuum shell model. The first (bending) mode frequency is found to be 1.29 times larger than the frequency computed using the atomistic model of CNT. From figure 6.8, the first six modes are seen to be first lateral bending, radial flattening mode, radial flattening mode with 90° phase shift between the ends, higher order radial flattening mode, twisting mode and second lateral bending modes, respectively.

Figure 6.8. Natural frequencies (in GHz) and mode shapes of CNT modelled as a continuum using ANSYS [6]. The modes are classified as first lateral bending mode (425), radial flattening

mode (599), radial flattening mode with 90° phase shift between the ends (606), higher order radial flattening mode (769), twisting mode (961) and second lateral bending mode (1008).

Another set of parameters, i.e., Young's modulus of around 1 TPa, wall thickness of 0.34 nm has been used by some researchers to compute the natural frequencies of CNTs [116, 134, 200]. The present computation using this set of values gives a first mode (bending) frequency which is again 1.30 times larger than the frequency computed using the proposed atomistic model of CNT. Thus, the first mode frequency is almost the same for both sets of parameter values used. However, the sequence of modes is observed to be different which are shown in Figure 6.9. The first set gives the same sequence as that of atomistic model while the second does not. This is because the wall thickness, 0.066 nm, used in the first set is more appropriate to model a SWCNT. The wall thickness of 0.34 nm in the second set, which is the interlayer distance in graphite, may be appropriate for the vibration analysis of MWCNT. However, the computed first mode frequency is observed to be almost the same for both sets of parameter values used. The frequencies is shown to be the same if the product Yt is the same for both set of parameters:

$$\text{The natural frequency, } f \propto \sqrt{\frac{YI}{\rho A}} \quad (6.14)$$

The product ρA is the same both cases as long as the density in both cases are computed to conserve the mass of the CNT. Hence,

$$f \propto \sqrt{YI} \quad (6.15)$$

where $I = \frac{\pi}{4} [(r_i + t)^4 - r_i^4]$. Neglecting higher terms of t , $I = \pi r_i^2 t$, i.e., $I \propto t$. Hence,

$$f \propto \sqrt{Yt} \quad (6.16)$$

The product Yt for the first and second set of parameters are 0.363 TPa-nm and 0.34 TPa-nm which are almost the same, and hence is the reason why the first natural frequencies are the same.

Motivated by this observation, the first mode frequencies have been computed using the continuum shell model for various sets of parameter values reported in the literature. The computed frequencies are listed in Table 6.2.

Figure 6.9. Natural frequencies (GHz) and mode shapes of CNT modelled as a continuum beam using ANSYS. The modes are classified as first lateral bending mode (429), twisting mode (930), second lateral bending mode (1023), axial stretching mode (1315), third lateral bending mode (1724) and coupled mode involving radial breathing mode and twisting mode (1863), respectively.

6.5. Control of numerical errors in the computed natural frequencies

From Chapter 5, it can be seen that the stiffness value of CNTs depends on chosen step size. If the chosen step size is too large, then the nonlinearity error dominates the accuracy of computed stiffness. On the other hand, if the chosen step size is too small,

then the truncation and round-off errors plague the computed stiffness. From Chapter 5, the optimum step size has been computed as 0.0001nm for finite difference method. This value has been used in the previous section for the computation of stiffness matrix and corresponding natural frequencies.

Table 6.2. Bending frequency of zigzag (14, 0) CNT of length 8.146 nm for various Young's modulus and wall thickness values reported in the literature.

Young's modulus, Y (TPa)	Wall thickness, t (nm)	In-plane stiffness Yt (TPa-nm)	Density (Kg/nm ³)	Bending frequency (GHz)
5.5	0.066	0.363	1.1217×10^{-23}	425
5.1	0.074	0.377	9.9328×10^{-24}	435
4.84	0.075	0.363	9.8709×10^{-24}	425
3.86	0.089	0.344	8.3182×10^{-24}	414
2.4	0.147	0.353	5.0362×10^{-24}	422
1.02	0.286	0.292	2.5885×10^{-24}	394
1.0	0.34	0.34	2.1774×10^{-24}	429
1.07	0.34	0.364	2.1774×10^{-24}	444

During the computation of natural frequencies, it is observed that the frequencies of rigid body modes were not equal to zero because the inherent approximation in the computation of stiffness matrix by finite difference method. It is also observed that the actual nonzero value of these frequencies obtained depends on the step size. This suggests that they may be an optimal value of step size for which the nonzero values of rigid body frequencies reach a minimum value. The optimal value step size is determined as follows:

Using the inherent equilibrium configuration, the natural frequencies are computed for various step size values. The results are listed in Table 6.3. In this table, the first six natural frequencies in each column correspond to the rigid body modes. The sum of the absolute values of these six frequencies is plotted in Figure 6.10 against the step size. It is seen that the sum reaches a minimum at the step size around 0.00003. Further studies carried out with various diameters and length values of CNTs also lead to the optimal step size values around 0.00003.

Figure 6.11 shows how fundamental natural frequency (mode 7) varies with the step size. It is seen that the fundamental frequency is less sensitive to step size in the range $0.00002 \leq h \leq 0.0001$. Beyond this range, the fundamental frequency is affected much by the choice of step size. For values of step size greater than 0.0001, the nonlinearity error increases leading to a lower value of fundamental natural frequency.

Table 6.3. Computed natural frequencies (GHz) for various step sizes.

Natural frequencies, f_i	Step size 0.00001	Step size 0.00002	Step size 0.00003	Step size 0.00004	Step size 0.00005	Step size 0.0001
1 (Rigid body modes)	24.589	11.305	-16.896	-25.799	-33.191	-67.850
2	28.935	13.017	-7.3306	-15.671	-21.254	-45.124
3	30.253	14.398	2.0280	-10.686	-15.172	-32.700
4	35.305	15.590	5.1782	-10.167	-14.976	-32.643
5	36.734	16.847	6.9671	-8.3094	-13.227	-29.830
6	39.468	18.534	9.1676	-8.0202	-12.981	-29.810
7	333.56	331.81	331.36	331.12	330.90	329.33
8	333.71	331.88	331.40	331.14	330.92	329.34
9	572.90	572.16	571.99	572.01	571.99	572.09
10	576.26	575.65	572.02	575.43	575.50	575.58
$\sum_{i=1}^6 f_i $	195.284	89.691	46.5675	78.6526	110.801	237.957

Figure 6.10. Sum of absolute errors in the rigid body mode frequencies with step size.

Figure 6.11. Variation of fundamental natural frequency (mode 7) with step size.

6.6. Conclusions

Free vibration analysis of single-walled carbon nanotubes (CNTs) has been carried out. Brenner potential has been employed for stiffness computation. A finite difference method has been used for the purpose. Although Brenner potential has been used in many papers on static analysis of CNTs, its application in vibration analysis is scarce [5] in the literature. The following are the important observation from this Chapter:

1. Prior to applying the finite difference method to compute the stiffness matrix, it is important to minimise the potential of the CNT in order to obtain the equilibrium configuration of carbon atoms. Use of non-equilibrium (unminimised) configurations obtained using approximate values of bond length such as 0.142 nm often used in literature lead to large errors in the natural frequencies and sometimes lead to even negative eigenvalues.
2. Two types of equilibrium configurations have been studied for computing the stiffness matrix. The first one is the *inherent equilibrium configuration* where the potential is minimised with respect to all the atomic coordinates of CNT. This configuration yields more accurate stiffness and hence the computed frequencies and mode shapes are more reliable although the minimisation process is computationally more expensive. The second one is the *uni-bondlength equilibrium configuration* where the bond length is assumed to be an unknown constant for all bonds in the CNT and the potential is minimised with respect to this unknown constant. Although the configuration thus obtained is slightly inaccurate near the edges of CNT, the minimisation process demands far less computational time.

3. For comparison purposes, the natural frequencies and mode shapes have also been computed using the continuum shell modelling of CNTs, where the CNT is modelled as a shell using equivalent Young's modulus and wall thickness values reported in the literature. The set of Young's modulus and wall thickness values, 5.5 TPa and 0.066 nm, respectively, has been seen to be more appropriate than the other set, 1 TPa and 0.34 nm. This suggests that proper care must be taken while choosing appropriate set of values from the literature for the purpose of continuum shell modelling of CNTs.
4. Numerical experiments have been carried to determine an optimal step size for the natural frequency calculations of CNTs. The optimal step size determined is 0.00003. This value has been obtained by minimising the sum of absolute error in the computed frequencies of rigid body modes.

Chapter 7

FREE VIBRATION ANALYSIS OF FLUID CONVEYING SINGLE-WALLED CARBON NANOTUBES

In Chapter 6, free vibration analysis has been carried out on single-walled carbon nanotubes. The stiffness matrix for the purpose has been computed from the atomistic simulations. Inherent and uni-bondlength configurations have been used to compute natural frequencies and mode shapes of short CNTs. The free vibration analysis has been carried out using a continuum beam model assuming appropriate Young's modulus and wall thickness of CNTs for the purpose. In this Chapter, free vibration analysis of fluid conveying CNTs is carried out. A continuum beam model is used for the purpose.

With perfect hallow structure and superior mechanical properties, CNTs hold substantial promise as nanopipes conveying fluids and as nanocontainers for gas storage. Fluid flow through CNTs is likely to find a wide variety of applications in nanomachines with moving parts in the area of nanotechnology. The fluid behaviour in nanomachines is expected to be fundamentally different from that of fluid behaviour in other systems [133]. Very few papers have been published on fluid conveying CNTs [133, 134, 201, 202] and fluid flow around CNTs [136, 203]. In a recent paper [140], it is reported that the flow through aligned carbon nanotubes is five orders of magnitude faster than the predicted value from conventional fluid-flow theory. High fluid flow velocity results from the almost frictionless interface between the liquid and CNTs walls. In this Chapter,

the free vibration analysis fluid conveying CNTs is carried out by assuming frictionless contact between the fluid and CNTs.

In continuum beam models of CNTs, assumed Young's modulus and wall thickness values are used to compute the natural frequencies [116-118]. From Tables 2.1 and 2.2, it can be seen that there is a wide range of reported values of Young's modulus and wall thickness. However, the product of computed Young's modulus and thickness i.e., in-plane stiffness is seen to be almost a constant (around 0.35 TPa-nm) in some publications (refer Table 2.2). Nevertheless, to avoid such ambiguity in choosing appropriate Young's modulus and wall thickness for the present studies, a different approach is used here. The stiffness matrix is first computed (as in Chapter 6) directly using the Brenner potential and used to compute the natural frequencies of CNTs as in Sections 6.4 and 6.5. Using the computed natural frequencies, the equivalent bending rigidity (YI) is then computed and used to model CNT as a continuum Euler-Bernoulli beam model, which is explained in the flowing section.

7.1. Determination of equivalent bending rigidity of SWNTs

For studying the free vibration of fluid conveying CNTs in Section 7.2, the CNT is modelled as a tube undergoing transverse vibration. For this purpose, an ordinary differential equation shown in Equation 7.3 will be used. This equation involves the Young's modulus (Y) and moment of inertia (I) of CNT. However, in order to compute moment of inertia or Young's modulus, the wall thickness of CNT is needed. As stated above, in view of the uncertainty in the reported Young's modulus and wall thickness values, it is decided not to compute these values separately. Instead, the equivalent

bending rigidity (YI), which is the product of Young's modulus and moment of inertia, is computed straightaway using the stiffness matrix of CNT computed in the previous Chapter. This approach is presented in this section. Such bending rigidity values have scarcely reported in the literature for CNTs.

For free vibration analysis restricting to only deformation of CNTs without fluid inside, the differential equation is of the form

$$m_c \frac{\partial^2 u}{\partial t^2} + YI \frac{\partial^4 u}{\partial x^4} = 0 \quad (7.1)$$

where m_c is the mass per unit length and x is the axial coordinate, t is time, and $u(x, t)$ is the transverse deflection of the CNT. Euler-Bernoulli beam model is employed to derive Equation (7.1). The natural frequencies of a free-free beam are expressed as

$$f = \frac{\beta_i^2}{2\pi L^2} \sqrt{\frac{YI}{m_c}} \quad (7.2)$$

where $\beta_1 = 1.506\pi$, $\beta_2 = 2.50\pi$ and $\beta_3 = 3.5\pi$ are the values of β_i for first, second and third natural frequencies of free-free continuous beam, respectively. Natural frequencies can be computed by solving Equation (6.10) and substituted in Equation (7.2) for computing equivalent bending rigidity YI . The YI values are computed for various diameter values of CNTs and are listed in Table 7.1. For large diameter CNTs, the computation of YI is computationally intensive. Hence, the present study is limited to the four configurations shown in Table 7.1. For comparison purposes, the YI value has been extrapolated (based on the values of Table 7.1) for 1.3 nm diameter CNT as 1.66×10^{-25} N-m². This value agrees well with the value, 1.6×10^{-25} N-m², computed using molecular dynamics by Dequesnes et al. [112].

Table 7.1. Computed bending rigidity values for CNTs of different diameters.

CNT type	Diameter (nm)	Bending rigidity, YI (N-m ²)
(5,0)	0.415	4.7102×10^{-27}
(8,0)	0.65	1.9770×10^{-26}
(12,0)	0.961	7.7374×10^{-26}
(14,0)	1.12	1.1122×10^{-25}

7.2. Flow through single-walled carbon nanotubes

Carbon nanotubes have found many significant applications in nanotechnology as fluid conveying nanotubes [130-133, 204] owing to their perfect hollow cylindrical geometry, unique combination of mechanical and electronic properties, and chemical stability. In the present studies, it is not intended to deal with mechanics of fluid flow inside CNTs. A steady-state flow is assumed through out the CNT with the fluid velocity being uniform along the length and cross section of CNT. The objective is to examine the effect of internal moving fluid on the free vibration and structural instability of fluid conveying CNTs. The fluid interaction with CNTs and viscosity effects on the mean flow velocity are not explicitly considered. Studies on fluid conveying CNTs remain less explored in the literature [116-118, 205]. In the reported studies, researchers usually consider assumed values of Young's modulus and wall thickness to compute the natural frequencies. As stated already, Young's modulus and wall thickness values are interdependent and various different estimates of values have been reported in the

literature (refer Tables 2.2 and 4.3). In the present approach, there are no such assumed values used for the computation of natural frequencies.

Figure 7.1. CNT conveying fluid of mass m_f per unit length with velocity v .

As shown in the Figure 7.1, a CNT conveying fluid will be treated as a hollow cylindrical tube having an equivalent bending rigidity, YI , with a mass of m_c per unit length of CNT. Let v be the mean flow velocity of fluid and m_f be the mass of fluid per unit length of tube in unit time. The differential equation of motion for the fluid conveying tube can be expressed as

$$(m_f + m_c) \frac{\partial^2 u}{\partial t^2} + 2m_f v \frac{\partial^2 u}{\partial x \partial t} + m_f v^2 \frac{\partial^2 u}{\partial x^2} + YI \frac{\partial^4 u}{\partial x^4} = 0 \quad (7.3)$$

As stated previously, the role of the wall-fluid interaction and viscosity of fluid are considered here only implicitly through their influence on the mean flow velocity. Hence, the focus will be on the effect of mean internal fluid flow velocity on the vibration and structural instability of CNTs, without considering how the wall-fluid interaction and viscosity of fluid affect the mean flow velocity. In Equation (7.3), the first, second, third and fourth terms are the inertia, Coriolis, centrifugal and stiffness forces, respectively.

The free vibration analysis is carried out by finite element method and the corresponding matrices needed for the analysis are derived as follows.

Figure 7.2. Nodal displacements of an element. u_1 , u_2 , u_3 and u_4 are linear and angular displacements at left and right ends, respectively.

The CNT (Figure 7.1) is divided into a finite number of beam elements. Each element is of length l , and has four degrees of freedom, u_1 , u_2 , u_3 and u_4 , as shown in Figure 7.2. Since the beam element has four degrees of freedom, the transverse displacement $u(x)$ can be written as a cubic polynomial function,

$$u(x) = a_1 + a_2x + a_3x^2 + a_4x^3 \quad (7.4)$$

Substituting the fixed-fixed boundary conditions

$$\left(u(0) = u_1, \quad \left. \frac{du}{dx} \right|_{x=0} = u_2, \quad u(l) = u_3, \quad \left. \frac{du}{dx} \right|_{x=l} = u_4 \right) \quad (7.5)$$

in Equation (7.4) for four unknown constants in Equation (7.4) can be obtained as

$$a_1 = u_1 \quad (7.6)$$

$$a_2 = u_2 \quad (7.7)$$

$$a_3 = \frac{2u_1 - u_1l + 2u_2l - 2u_3 + u_4l}{l^3} \quad (7.8)$$

$$a_4 = \frac{-u_1(1 + l - 2/l) - u_2(2 + l) + u_3(2/l - 1) - u_4}{l^3} \quad (7.9)$$

Substituting the expressions for the constants a_1 , a_2 , a_3 and a_4 back in Equation (7.4), the polynomial function can be written as

$$u(x) = \frac{(2x^3 - 3x^2l + l^3)u_1 + (x^3l - 2x^2l^2 + xl^3)u_2 + (3x^2l - 2x^3)u_3 + (x^3l - x^2l^2)u_4}{l^3} \quad (7.10)$$

Collecting terms of the nodal degrees of freedom, $u(x)$ can be written in the matrix form as

$$u(x) = \mathbf{N} \mathbf{u} \quad (7.11)$$

where $\mathbf{N} = [N_1, N_2, N_3, N_4]$ is the shape function matrix, $\mathbf{u}^T = \{u_1, u_2, u_3, u_4\}$ is the nodal displacement vector, and

$$N_1 = \frac{2x^3 - 3x^2l + l^3}{l^3} \quad (7.12)$$

$$N_2 = \frac{x^3l - 2x^2l^2 + xl^3}{l^3} \quad (7.13)$$

$$N_3 = \frac{3x^2l - 2x^3}{l^3} \quad (7.14)$$

$$N_4 = \frac{x^3l - x^2l^2}{l^3} \quad (7.15)$$

The governing differential Equation (7.3) is multiplied with transpose of shape function matrix on both sides and integrated with respect to x between the limits 0 to l :

$$\int_0^l \mathbf{N}^T \left[(m_f + m_c) \frac{\partial^2 u}{\partial t^2} + 2m_f v \frac{\partial^2 u}{\partial x \partial t} + m_f v^2 \frac{\partial^2 u}{\partial x^2} + YI \frac{\partial^4 u}{\partial x^4} \right] dx = 0 \quad (7.16)$$

Applying integration by parts to Equation (7.16),

$$\begin{aligned}
& (m_f + m_c) \int_0^l \mathbf{N}^T \frac{\partial^2 u}{\partial t^2} dx - m_f v \int_0^l \mathbf{N}^{T'} \frac{\partial u}{\partial t} dx - m_f v \int_0^l \mathbf{N}^{T'} \frac{\partial u}{\partial t} dx - m_f v^2 \int_0^l \mathbf{N}^{T'} \frac{\partial u}{\partial x} dx + YI \int_0^l \mathbf{N}^{T''} \frac{\partial^2 u}{\partial x^2} dx \\
& = \left[YI \mathbf{N}^{T''} \left(\frac{\partial^2 u}{\partial x^2} \right) - YI \mathbf{N}^{T'} \left(\frac{\partial^3 u}{\partial x^3} \right) - m_f v \mathbf{N}^{T'} \left(\frac{\partial u}{\partial x} \right) - m_f v \mathbf{N}^{T'} \left(\frac{\partial u}{\partial x} \right) - m_f v^2 \mathbf{N}^{T'} \left(\frac{\partial u}{\partial x} \right) \right]_0^l
\end{aligned} \quad (7.17)$$

where

$$\frac{\partial^2 u}{\partial t^2} = \mathbf{N} \ddot{u} \quad (7.18)$$

$$\frac{\partial^2 u}{\partial x \partial t} = \mathbf{N}' \dot{u} \quad (7.19)$$

$$\frac{\partial^2 u}{\partial x^2} = \mathbf{N}'' u \quad (7.20)$$

$$\frac{\partial u}{\partial t} = \mathbf{N} \dot{u}, \quad (7.21)$$

and $\mathbf{N}'$, $\mathbf{N}''$, $\dot{u}$ and $\ddot{u}$ are the single and double partial derivatives with respective x and t , respectively. Substituting $u(x, t) = \mathbf{N}(x) u(t)$ and $\mathbf{N}^{T''} \mathbf{N} = -\mathbf{N}^T \mathbf{N}'$ in Equation (7.3), and equation becomes,

$$\begin{aligned}
& (m_f + m_c) \int_0^l \mathbf{N}^T \mathbf{N} dx \ddot{u} - m_f v \int_0^l \mathbf{N}^{T'} \mathbf{N} dx \dot{u} + m_f v \int_0^l \mathbf{N}^T \mathbf{N}' dx \dot{u} - m_f v^2 \int_0^l \mathbf{N}^{T'} \mathbf{N}' dx u + YI \int_0^l \mathbf{N}^{T''} \mathbf{N}'' dx u \\
& = YI \left[\mathbf{N}^{T'} \left(\frac{\partial^2 u}{\partial x^2} \right) - \mathbf{N}^T \left(\frac{\partial^3 u}{\partial x^3} \right) \right]_0^l - m_f v \left[\mathbf{N}^{T'} \left(\frac{\partial u}{\partial x} \right) \right]_0^l - m_f v \left[\mathbf{N}^T \left(\frac{\partial u}{\partial x} \right) \right]_0^l - m_f v^2 \left[\mathbf{N}^T \left(\frac{\partial u}{\partial x} \right) \right]_0^l
\end{aligned} \quad (7.22)$$

which can be written in matrix form as

$$\mathbf{M}_e \ddot{\mathbf{u}} + \mathbf{C}_e \dot{\mathbf{u}} + (\mathbf{K}_{1e} - \mathbf{K}_{2e}) \mathbf{u} = \mathbf{F}_e \quad (7.23)$$

where

$$\mathbf{M}_e = (m_f + m_c) \int_0^l \mathbf{N}^T \mathbf{N} dx \quad (7.24)$$

$$\mathbf{C}_e = -m_f v \left(\int_0^l \mathbf{N}^{T'} \mathbf{N} dx - \int_0^l \mathbf{N}^T \mathbf{N}' dx \right) \quad (7.25)$$

$$\mathbf{K}_{1e} = \frac{YI}{l^3} \int_0^l \mathbf{N}^{T''} \mathbf{N}'' dx \quad (7.26)$$

$$\mathbf{K}_{2e} = m_f v^2 \int_0^l \mathbf{N}^{T'} \mathbf{N}' dx \quad (7.27)$$

The elemental mass matrix, $\mathbf{M}_e$, is real, symmetric and positive definite, and can be expressed as

$$\mathbf{M}_e = \frac{(m_f + m_c)l}{420} \begin{pmatrix} 156 & 22l & 54 & -13l \\ 22l & 4l^2 & 13l & -3l^2 \\ 54 & 13l & 156 & -22l \\ -13l & -3l^2 & -22l & 4l^2 \end{pmatrix} \quad (7.28)$$

The elemental Coriolis matrix, $\mathbf{C}_e$, is skew symmetric, and can be expressed as

$$\mathbf{C}_e = \frac{m_f v}{30} \begin{pmatrix} 0 & 6l & 30 & -6l \\ -6l & 0 & 6l & -l^2 \\ -30 & -6l & 0 & 6l \\ 6l & -l^2 & -6l & 0 \end{pmatrix} \quad (7.29)$$

The elemental stiffness matrix, $\mathbf{K}_{1e}$, is real, symmetric and positive definite, and can be expressed as

$$\mathbf{K}_{1e} = \frac{YI}{l^3} \begin{pmatrix} 12 & 6l & -12 & 6l \\ 6l & 4l^2 & -6l & 2l^2 \\ -12 & -6l & 12 & -6l \\ 6l & 2l^2 & -6l & 4l^2 \end{pmatrix} \quad (7.30)$$

The elemental centrifugal matrix, $\mathbf{K}_{2e}$, is real, symmetric and positive definite, and can be expressed as

$$\mathbf{K}_{2e} = \frac{m_f v^2}{150l} \begin{pmatrix} 180 & 15l & -180 & 15l \\ 15l & 20l^2 & -15l & -5l^2 \\ -180 & -15l & 180 & -15l \\ 15l & -5l^2 & -15l & 20l^2 \end{pmatrix} \quad (7.31)$$

The right side term in Equation (7.22) is the elemental force matrix, $\mathbf{F}_e$ which can be expressed as

$$\mathbf{F}_e = \begin{pmatrix} YI \left(\frac{\partial^3 u}{\partial x^3} \right)_0^l + m_f v^2 \left(\frac{\partial u}{\partial x} \right)_0^l + 2m_f v \left(\frac{\partial u}{\partial t} \right)_0^l \\ -YI \left(\frac{\partial^2 u}{\partial x^2} \right)_0^l \\ -YI \left(\frac{\partial^3 u}{\partial x^3} \right)_0^l - m_f v^2 \left(\frac{\partial u}{\partial x} \right)_0^l - 2m_f v \left(\frac{\partial u}{\partial t} \right)_0^l \\ YI \left(\frac{\partial^2 u}{\partial x^2} \right)_0^l \end{pmatrix} \quad (7.32)$$

By assembling all elemental matrices, Equation (7.23) leads to Equation (7.33) which written in terms of global matrices. The force matrix becomes a null matrix after assembly.

$$\mathbf{M} \ddot{\mathbf{u}} + \mathbf{C} \dot{\mathbf{u}} + (\mathbf{K}_1 - \mathbf{K}_2) \mathbf{u} = 0 \quad (7.33)$$

The matrices $\mathbf{M}$, $\mathbf{C}$, $\mathbf{K}_1$ and $\mathbf{K}_2$ are the global mass, Coriolis, centrifugal and stiffness matrices, respectively. Equation (7.33) represents a linear homogeneous time-invariant system that admits a solution in the exponential form:

$$\mathbf{u}(t) = e^{i\omega t} \mathbf{u} \quad (7.34)$$

Substituting Equation (7.34) in Equation (7.33),

$$-\omega^2 \mathbf{M} \mathbf{u} + i\omega \mathbf{C} \mathbf{u} + (\mathbf{K}_1 - \mathbf{K}_2) \mathbf{u} = 0 \quad (7.35)$$

where $\mathbf{K} = (\mathbf{K}_1, \mathbf{K}_2)$. Equation (7.35) represents the eigenvalue problem of a gyroscopic conservative system, which contains pure imaginary complex conjugate of eigenvalues $i\omega$ and $-i\omega$. The corresponding eigenvectors are complex conjugates and not necessarily purely imaginary. Equation (7.35) contains both the terms $i\omega$ and ω^2 , and hence there is no ready solution. This difficulty is overcome by recasting the problem in the state space form, but the problem remains complex. The equation of motion (Equation (7.33)) in the state space form can be recast as

$$\mathbf{A} \dot{\mathbf{q}}(t) = -\mathbf{B} \mathbf{q}(t) \quad (7.36)$$

where $\mathbf{q}(t) = [\mathbf{u}^T(t), \dot{\mathbf{u}}^T(t)]^T$ is the $2n$ -dimensional state vector and

$$\mathbf{A} = \begin{bmatrix} \mathbf{K} & \mathbf{0} \\ \mathbf{0} & \mathbf{M} \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} \mathbf{0} & -\mathbf{K} \\ \mathbf{K} & \mathbf{C} \end{bmatrix} = -\mathbf{B}^T \quad (7.37)$$

are $2n \times 2n$ coefficient matrices, in which $\mathbf{A}$ is real symmetric and positive definite, and $\mathbf{B}$ is real and skew symmetric. The solution of Equation (7.36) is in the form

$$\mathbf{q}(t) = e^{i\omega t} \mathbf{q} \quad (7.38)$$

where $\mathbf{q}$ is a constant $2n$ -vector. Introducing Equation (7.38) into Equation (7.36) and dividing both sides by $e^{i\omega t}$, the eigenvalue problem is obtained as

$$i\omega \mathbf{A} \mathbf{q} = -\mathbf{B} \mathbf{q} \quad (7.39)$$

Now the eigenvalue problem is order of $2n$, and contains ω to the first power only, but the problem is still remains complex. To reduce the eigenvalue problem to real form, introduce $\mathbf{q} = \mathbf{x} + i\mathbf{y}$ into Equation (7.39) and equate both the real and imaginary part on both sides of the resulting equation as

$$\omega \mathbf{A} \mathbf{x} = -\mathbf{B} \mathbf{y} \quad (7.40)$$

$$\omega \mathbf{A} \mathbf{y} = \mathbf{B} \mathbf{x} \quad (7.41)$$

Solving Equations (7.40) and (7.41) for $\mathbf{x}$ and $\mathbf{y}$, the following equations can be obtained

$$\mathbf{K}^* \mathbf{x} = \lambda \mathbf{A} \mathbf{x} \quad (7.42)$$

$$\mathbf{K}^* \mathbf{y} = \lambda \mathbf{A} \mathbf{y} \quad (7.43)$$

$$\lambda = \omega^2 \quad (7.44)$$

where

$$\mathbf{K}^* = \mathbf{B}^T \mathbf{A}^{-1} \mathbf{B} = \begin{bmatrix} \mathbf{K} \mathbf{M}^{-1} \mathbf{K} & \mathbf{K} \mathbf{M}^{-1} \mathbf{C} \\ \mathbf{C}^T \mathbf{M}^{-1} \mathbf{K} & \mathbf{K} + \mathbf{C}^T \mathbf{M}^{-1} \mathbf{C} \end{bmatrix} = \mathbf{K}^{*T} \quad (7.45)$$

is a real symmetric positive definite matrix. The solution of Equations (7.42) and (7.43) contains eigenvectors $\mathbf{x}$ and $\mathbf{y}$. These eigenvectors are needed to reconstruct $\mathbf{q}$ and $\mathbf{q}$ still remains complex. Decomposing $\mathbf{A}$ into the form

$$\mathbf{A} = \mathbf{Q}^T \mathbf{Q} \quad (7.46)$$

where $\mathbf{Q}$ is a $2n \times 2n$ nonsingular matrix, the Equations (7.42) and (7.43) can be reduced to standard form as

$$\mathbf{A}^* \mathbf{v} = \lambda \mathbf{v} \quad (7.47)$$

where

$$\mathbf{A}^* = (\mathbf{Q}^T)^{-1} \mathbf{K}^* \mathbf{Q}^{-1} \quad (7.48)$$

is a $2n \times 2n$ real symmetric positive definite matrix. The pair of Equations (7.42 and 7.43) and Equation (7.48), possess the same eigenvalues and eigenvectors. In each eigenvector, the first n entries are deflections and the rest n entries are velocity terms. For the present work, the above eigenvalue problem has been solved using MATLAB [206] for

eigenvalues and the corresponding eigenvectors. The detailed MATLAB program is listed in Appendix D.

Figure 7.3. Variation of dimensionless frequency of lowest three modes with dimensionless velocity. Dots, stars and circles represents first, second and third mode natural frequencies, respectively.

7.2.1. Natural frequencies and mode shapes

Natural frequencies depend both on the dimensions of CNT and mass flow rate. Non-dimensional parameters (i.e., the mass ratio, m_r , and dimensionless velocity, v_n) are introduced to study the effect of fluid flow on the free vibration of CNTs which are defined as:

$$m_r = \frac{m_f}{(m_f + m_c)} \quad (7.49)$$

$$v_n = \left(\frac{m_f}{YI} \right) vL \quad (7.50)$$

Figure 7.3 shows the frequency characteristics of a water conveying CNT wherein the curves depict the variation of natural frequency with respect to the dimensionless velocity of the fluid for the lowest three modes. At zero flow velocity, the values of first, second and third natural frequencies are 3.2564×10^{10} Hz, 8.9765×10^{10} Hz and 1.7598×10^{11} Hz, respectively. The dimensionless velocity at which the fundamental natural frequency becomes zero is called the critical velocity, V_{cr} , and it is equal to 2π (Figure 7.3). This critical velocity is equal to critical velocity of macro pipes conveying fluid reported by Chen [207].

Figure 7.4 shows the fundamental mode shape of fluid conveying CNT at 20% of critical velocity. (At zero fluid velocity, the fundamental mode shape is symmetric with respect to y -axis with a time period, T .) The solid lines represent first half cycle and dashed lines represent the second half cycle. The plot of mode shape is seen to be slightly perturbed from the symmetric mode, which is caused by the fluid flow. The perturbation is mainly caused by the Coriolis and centrifugal forces and the magnitude of these forces are given in the next Section. Rasziller and Drust [208], carried out similar studies on macro-model of Coriolis mass flow meter and the terms of perturbed fundamental mode shape obtained by them are similar to the present.

Figure 7.4. Fundamental mode shape as a function of time at 20% of critical velocity.

7.2.2. Physical understanding of the effect of flow

Various forces namely inertial, Coriolis, centrifugal and stiffness forces are computed along with length and at various fluid velocities. The distribution of these forces normalised with respect to stiffness force is plotted against nondimensional length in Figure 7.5 for a flow velocity of 20% of critical velocity. From Figure 7.5, it is seen that the inertial force curve follows the fundamental mode, stiffness force curve is slightly perturbed from the fundamental mode due to centrifugal force and the Coriolis force curve follows the second fundamental mode. At the ends of the tube, the stiffness forces

are supposed to be zero for free vibration mode with no fluid flow, but non zero here because, there is centrifugal force acting in opposite direction such that the resultant of these two forces is zero.

Figure 7.5. Variation of normalised forces with length of CNT. Circles, squares, dots and stars represents inertial, stiffness, Coriolis and centrifugal forces, respectively.

Figure 7.6 shows the variation of forces at the middle of the CNT with fluid velocity. All forces are normalised with respect to the stiffness force. At zero fluid velocity, the inertial and stiffness forces are equal in magnitude and opposite in direction, and the other two (Coriolis and centrifugal) forces are zero. As the fluid velocity increases, perturbation forces increase and this results in flow induced structural instability in the CNT. As fluid velocity tends to be equal to the critical velocity, the effective stiffness (resultant of

stiffness and centrifugal terms) force is reaching zero, which leads to the instability. The Coriolis force increases linearly with velocity well below the critical velocity. This force is the useful to measure the mass flow measurement in the Coriolis mass flow meters.

Figure 7.6. Variation of forces at middle of CNT with fluid velocity. Circles, squares, dots, stars and plus represents inertial, stiffness, Coriolis, centrifugal and total stiffness forces, respectively.

7.2.3. Fluid flow measurement

In Coriolis mass flow meters, changes in the mass flow can be determined by measuring the phase difference using two electromagnetic detectors mounted at approximate locations on the pipe [209]. In practice, flow measurement in NEMS devices is a very difficult and challenging task, and flow measurements techniques in nanodevices are not

yet developed. The solution of the Equation (7.33) contains complex eigenvectors corresponding to complex eigenvalues. This complex eigenvectors can be used to simulate the mass flow measurement. The phase, ϕ , is the inverse tangent of ratio of imaginary value to real value of complex eigenvector corresponding to fundamental mode. Mass flow measurement can be measured by the phase difference between the two appropriate points on the CNT. From Figure 7.7, it can be seen that the phase is linearly proportional to the length points between A and B located at 25% and 75% of length of pipe from one end. The relative phase between these two points is used for further study.

Figure 7.7. Phase along the length of CNT at 20% of critical velocity.

The magnitude of relative phase, $\Delta\phi$, between the A and B points in Figure 7.7 depends on the mass and velocity of the flowing fluid. The relative phase $\Delta\phi$ is computed for

various $\sqrt{m_r} v_n$ values in the range 0–6 and the results as plotted in Figure 7.8. The numerical experiments are conducted to find out the relative phase by changing the density of fluid and changing the velocity of fluid. The relative phase is linearly dependent on the dimensionless parameter $\sqrt{m_r} v_n$ for low velocities as seen from the plot in Figure 7.8. The relationship between the relative phase and the dimensionless parameter can be expressed using a linear curve fit at low velocities as

$$\Delta\phi = 0.0483\sqrt{m_r} v_n \quad (7.52)$$

From Equation (7.52), the relative phase is directly proportional to the fluid velocity for a given fluid.

Figure 7.8. Relative phase with dimensionless parameter $\sqrt{m_r} v_n$ for various m_r values. Dots, stars, plus, ..., downward triangle represents m_r value from 0.1 to 0.9, respectively.

7.3. Conclusions

Free vibration analysis of fluid conveying CNTs has been carried out. The equivalent bending rigidity of plain CNTs has been computed by equating the natural frequencies computed using atomistically simulated stiffness matrix and the natural frequency expression of continuous beam. The effect of fluid flow on natural frequencies has been studied using the continuum beam model of CNTs. The mass flow rate measurement of the fluid has been studied using the relative phase computation at given points on CNTs.

The following are the important observation from this Chapter:

1. To eliminate the dependence of free vibration analysis on the inconsistent Young's modulus and wall thickness values of CNT reported in the literature, the bending rigidity, YI , has been determined for the present studies from the atomistic free vibration characteristics. This approach is more reliable than that of the chosen appropriate values of Young's modulus and wall thickness from wide scatter of data available in the literature. Such YI values have yet not been reported in the literature.
2. Using the computed YI values, the free vibration analysis has been carried to quantify the effect of fluid flow velocity on the natural frequencies and mode shapes of CNTs. The natural frequencies have been computed for various dimensionless velocity values.
3. Relative phase has been computed to measure the fluid flow rate through CNT. The expression for the relative phase has been obtained in terms of dimensionless parameters. This relation may be useful in future investigations to measure fluid flow at velocities up to about 40% of critical velocity.

Chapter 8

CONCLUSIONS AND SCOPE OF FUTURE WORK

8.1. Summary

Atomistic and continuum modelling of finite graphene sheets and CNTs has been considered in this thesis. The objective has been to explore computational approaches to determine their mechanical properties. Brenner potential has been used for most of the present work. An extensive literature search has been carried and the existing approaches to determine the elastic properties have been reviewed critically.

Before attempting to model the graphene sheet or CNT, the simple problem of modelling a single carbon ring has been taken up. The ring has been modelled as a truss element model and equivalent continuum elastic properties have been computed using the AMBER force field. A similar approach has also been used to model finite graphene sheets. A few typical deformation modes have been considered for these studies.

AMBER force field is rather simple and does not consider the effect of second neighbourhood atoms in the potential calculations. However, Brenner potential accounts for this effect. Because of the non-quadratic nature of the Brenner potential, equilibrium adjustment of atomic positions becomes necessary to obtain minimum potential configuration. The importance of equilibrium adjustments in computing the elastic properties accurately has been brought out.

Two numerical aspects of stiffness computation, viz., the maximum attainable precision in the computed stiffness and the optimum value of trial displacement to be used for

numerical potential evaluation in stiffness calculations, have been studied. Three typical methods for stiffness computation, viz., small displacement method, potential fit method and finite difference method, have been investigated.

Free vibration analysis of CNTs has been carried out by atomistic simulation. Brenner potential has been employed for the computation of stiffness matrix. The finite difference method has been employed to compute the stiffness matrix numerically. The free vibration analysis has also been carried out using a continuum shell model of CNT with an appropriate value of Young's modulus and wall thickness.

Finite element analysis of free vibration of fluid conveying CNTs has been carried out. The CNT has been modelled as a beam using Euler-Bernoulli beam elements. The Coriolis and centrifugal forces arising out of fluid flow have been considered in the analysis. The governing differential equation has been solved in the state-space. The natural frequencies and modeshapes have been studied for various flow velocities.

8.2. Conclusions

The major conclusions from the present research are as follows:

Literature review

1. The Young's modulus (Y) and wall thickness (t) values reported in the literature have a wide scatter. This is to some extent due to different modelling and experimental techniques used to obtain these values. However, the product Yt has been computed from the reported values and it has been observed that it is almost constant, around 0.36 TPa-nm.

Truss element model of graphene using AMBER force field

2. From the analysis of single carbon ring, it has been observed that the computed EA values highly depend on the nature of the deformation modes employed for the computation.
3. The equivalent Young's modulus (Y), shear modulus (G) of graphene sheet and Poisson's ratio (ν) computed for the finite rectangular graphene sheets exhibit some dependence on the size and configuration (zigzag or armchair) of the sheet, and mode of deformation. An important observation is that the computed Y , G and ν values are not consistent with the relation $G = \frac{Y}{2(1 + \nu)}$ which holds true for isotropic materials. This finding suggests that the graphene sheet perhaps behaves like an orthotropic material.

Continuum model of graphene using Brenner potential

4. It has been observed that the equilibrium adjustments of atoms have much influence on the computed elastic constants. Computations considering equilibrium adjustments lead to Young's modulus and Poisson's ratio values around 0.7 TPa and 0.4, respectively, where as computations ignoring the equilibrium adjustments yield 1 TPa and 0.25, respectively. Nevertheless, papers reporting the elastic constant values often do not mention if equilibrium adjustments have been considered in their computations. This may be one of the reasons for the wide scatter in the elastic properties found in the literature.
5. A study of inter-relationship between the computed elastic constants Y_1 , Y_2 , ν_{12} , ν_{21} and G_{12} suggests that finite graphene sheets behaves like orthotropic materials.

Error analysis of computed elastic properties of graphenes and CNTs

6. A precision of about 6 significant digits in computed stiffness seems possible with the local potential-fit method and the finite difference method. The small displacement method can, however, yield only a precision of about 4 significant digits.
7. The optimum trial displacement for potential evaluation has been computed as about 0.0001 for the local potential-fit method as well as the finite difference method while it is about 0.00001 for the small displacement method.
8. The small displacement method must be used with a caution. It is stable only if the initial and deformed configurations are of equilibrium configurations. If not, the influence of non-equilibrium forces must be considered. With non-equilibrium forces considered, the method restores its stability.

Free vibration analysis of CNTs

9. Prior to applying the finite difference method to compute the stiffness matrix, it is important to minimise the potential of the CNT in order to obtain the equilibrium configuration of carbon atoms. Use of non-equilibrium (unminimised) configurations obtained using approximate values of the bond length such as 0.145 nm often used in literature leads to large errors in the natural frequencies and may sometimes lead to even negative eigenvalues.
10. The *inherent equilibrium configuration*, where the potential is minimised with respect to all the atomic coordinates of CNT, yields more accurate stiffness values. Although the minimisation process is computationally more expensive, the computed frequencies and mode shapes are more reliable. The *uni-bondlength*

equilibrium configuration, where the bond length is assumed to be an unknown constant for all bonds in the CNT and the potential is minimised with respect to this unknown constant, is slightly inaccurate near the edges of CNT. However, the minimisation process demands far less computational time.

11. The natural frequencies and mode shapes have also been computed using the continuum shell modelling of CNTs, where the CNT is modelled as a shell using equivalent Young's modulus and wall thickness values reported in the literature. The set of Young's modulus and wall thickness values, 5.5 TPa and 0.066 nm, respectively, has been seen to be more appropriate than the other set, 1 TPa and 0.34 nm. This suggests that proper care must be taken while choosing appropriate set of values from the literature for the purpose of continuum shell modelling of CNTs.

Free vibration analysis of fluid-conveying CNTs

12. To eliminate the dependence of free vibration analysis on the inconsistency of the Young's modulus and wall thickness values of CNT reported in the literature, the bending rigidity, YI , has been determined for the present studies. This estimate is expected to be more accurate and such an approach has yet not been reported in the literature. Using the computed YI values, the free vibration analysis has been carried to quantify the effect of fluid flow on the natural frequencies and mode shapes of CNTs.
13. The expression for the relative phase has been obtained in terms of dimensionless parameters, i.e., m_r and $\sqrt{m_r} v_n$. This relation can be used in future investigations to measure the fluid flow at velocities up to about 40% of critical velocity.

8.3. Future work

The following are some of the directions for future research on the present work:

1. AMBER force field and Brenner potential approaches can be extended to analyse multi layers of graphene sheet (graphite layer) for elastic properties. The effect of dislocations on the elastic properties of graphene sheets and graphite can be studied.
2. The complex functions appearing in the Brenner potential may possibly be reduced to simple form involving polynomials or other simple functions. This modification can be reduce the computational time.
3. The method of free vibration analysis developed in this thesis can be extended to forced vibration analysis so that possible NEMS applications can be explored. The free and forced vibration analysis may be extended to multi-walled carbon nanotubes by incorporating the non-bonded forces.
4. Using the method of free vibration analysis developed in this thesis, the effect of dislocations on the natural frequency of the carbon nanotubes may be studied. Similarly, their effect on YI values may also be studied.

APPENDIX A

B.1. Program to determine equilibrium configuration of graphene sheet

```

!-----
! FORTRAN program to compute the equilibrium configuration and Young's modulus
! computations
!-----
! implicit none
integer, parameter :: n = 120*2

double precision f,xc,yc,penal,ang,pi,ev,volume,const,fixed,uc,vc,uu,vv,tem
double precision CoordsWrite,CoordsDraw,WidthCal
double precision t0,h0,pr,praxis,x(n),xold,fin,xscale,yscale,dist,sum,area,scale
integer i,j,prin,natom,matom,katom,iconn,nelem,i1,i2,i3,i4,kount,nbh,iadjatom,iadj,jadj
integer iyes,ii,jj,kk,ibelem(2000),ifix,iatom,jatom,ielem,kelem,inode,n1,n2,k,jyadjatom
character*72 inf,outf

common /bloc1/iconn(1000,2),xc(1000),yc(1000),nelem,nbh(1000,15)
common /bloc2/ifix(1000*2),fixed(1000*2),xold(1000*2),matom,natom
common /bloc3/penal,iadjatom,iadj(100),jyadjatom,jadj(100)
!-----
pi=dacos(-1.0d0)

inf='coords7x7.lis'
outf='nano7x7.out'
open(unit=1,file=inf)
open(unit=2,file=outf)
open(unit=33,file='bc7x7.lis')
open(unit=333,file='CoordsOut7x7.out')
open(unit=444,file='Draw7x7.out')
open(unit=555,file='Finalwidth7x7.out')
open(unit=777,file='Potential.out')

xscale=1.0d0 !*****
yscale=1.0d0 !*****

! read atomic coordinates
read(1,*) natom
if(n.ne.natom*2) then
  write(*,*)
  write(*,*) ' EXECUTION TERMINATED...'
  write(*,*) ' Please change the value of parameter n and re-try...'
  stop

```

```

end if
do iatom=1,natom
  read(1,*) katom,xc(katom),yc(katom)
  i1=(iatom-1)*2+1
  i2=i1+1
  x(i1)=xc(katom)*xscale
  x(i2)=yc(katom)*yscale
  xold(i1)=x(i1)
  xold(i2)=x(i2)
end do

tem = CoordsWrite(natom,xc,yc)
tem = WidthCal(natom,xc,yc)

close(unit=1)

! read bond connectivity
open(unit=3,file='conn7x7.lis')
  read(3,*) nelem
  do ielem=1,nelem
    read(3,*) kelem,(iconn(kelem,inode),inode=1,2)
  end do
close(unit=3)

! read boundary conditions
read(33,*) matom
do jatom=1,matom
  read(33,*) iatom,uc,vc,uu,vv
  i1=(iatom-1)*2+1
  i2=i1+1
  iffix(i1)=0
  iffix(i2)=0
  fixed(i1)=0
  fixed(i2)=0
  if(uc.eq.1) then
    iffix(i1)=1
    fixed(i1)=uu
  end if
  if(vc.eq.1) then
    iffix(i2)=1
    fixed(i2)=vv
  end if
end do

! determine the first order neighbourhood of atoms
do ielem=1,nelem

```

```

        i1=iconn(ielem,1)
        i2=iconn(ielem,2)
        nbh(i1,1)=nbh(i1,1)+1
        nbh(i2,1)=nbh(i2,1)+1
        i3=nbh(i1,1)
        i4=nbh(i2,1)
        nbh(i1,i3+1)=i2
        nbh(i2,i4+1)=i1
    end do

! compute the initial equilibrium bond lengths and initial area of model
area=0.0d0
do ielem=1,nelem
    n1=iconn(ielem,1)
    n2=iconn(ielem,2)
    dist=dsqrt((xc(n1)-xc(n2))**2 + (yc(n1)-yc(n2))**2)
    write(2,*) ' Initial bond lengths =', dist
end do

! ---Praxis initialization parameters---
t0 = 1.0d-14
h0 = 100.0d0
prin = 1

! ---Print the initial point and initial function value---
write(2,*) ' Initial (input) point:'
write(2,*) x
write(2,*) ' Initial Function value:'
write(*,*) ' Initial Function Value '
fin=f(x,n)
write(2,*) fin
write(*,*) fin
write(*,*) ' Iteration : 1'
write(2,*) ' Iteration : 1'
write(*,*) ' Minimisation starts....'
write(2,*) ' Minimisation starts ...'
write(2,*)

do iatom=1,natom
    i1=(iatom-1)*2+1
    i2=i1+1
    if (ifix(i1).eq.1) x(i1)=xold(i1)+fixed(i1)
    if (ifix(i2).eq.1) x(i2)=xold(i2)+fixed(i2)
end do

```

```
! ---Minimise the function---
! Praxis routine is a Richard Brent's code for minimizing a scalar function of several
! variables without using derivatives. It returns the minimum of the function F(X,N) of
! N variables using the principal axis method. The gradient of the function is not
! required. This code can be download from the following website.
! http://orion.math.iastate.edu/burkardt/f\_src/f\_src.html
```

```
pr = praxis ( t0, h0, n, prin, x )    ! Calling Praxis routine
pr=f(x,n)
```

```
! ---Print the optimal point and optimal function value---
write(2,*)
write(2,*) 'Minimisation ends ...'
write(2,*) ' Minimum point:'
write(2,*) x
write(2,*) ' Function value: '
write(2,*) pr
write(*,*) ' Function value:'
write(*,*) pr
write(777,*)'Iteration : 1'
write(777,*)' Potential = ',pr
```

```
! compute the final equilibrium bond lengths
```

```
do iatom=1,natom
    i1=(iatom-1)*2+1
    i2=i1+1
    xc(iatom)=x(i1)
    yc(iatom)=x(i2)
end do

write(2,*) ' Equilibrium bond lengths:'

sum=0.0d0
area=0.0d0
do ielem=1,nelem
    n1=iconn(ielem,1)
    n2=iconn(ielem,2)
    dist=dsqrt((xc(n1)-xc(n2))**2 + (yc(n1)-yc(n2))**2)
    sum=sum+dist
    write(*,*) ' Bond no., dist =', ielem,dist
    write(2,*) ' Bond no., dist =', ielem,dist
    if(ibelem(ielem).eq.1) then
        area=area+0.5d0*(yc(n1)+yc(n2))*(xc(n2)-xc(n1))
    end if
end do
```



```

dist=sum/dfloat(nelem)
write(*,*) ' Average bond length =', dist
write(2,*) ' Average bond length =', dist
write(*,*)
write(2,*)
write(*,*) ' Final area of the model=', dabs(area)
write(2,*) ' Final area of the model=', dabs(area)
write(*,*)
write(2,*)

write(333,*)' iteration number :1'
write(444,*)' iteration number :1'
write(555,*)' iteration number :1'

! write final nodal coordinates
write(2,*) ' Final atomic coordinates:'
write(2,*)
tem = CoordsWrite(natom,xc,yc)
volume=dabs(area)*0.34*1.0d-27
ev=1.6021892d-19
const=ev/volume
goto 8                      ! strechthing test *****

do i=1,10
  do iatom=1,natom
    i1=(iatom-1)*2+1
    i2=i1+1
    if (ifix(i1).eq.1) then
      xold(i1) = xold(i1)+fixed(i1)
      x(i1) = xold(i1)+fixed(i1)
    end if
    if (ifix(i2).eq.1) then
      xold(i2) = xold(i2) + fixed(i2)
      x(i2) = xold(i2)+fixed(i2)
    end if
  end do
  write(2,*)' function value :', pr
  write(*,*)' Iteration number : ',i+1
  write(*,*)' function value :', pr
  write(2,*) ' Iteration number : ',i+1
  write(333,*)' iteration number :', i+1
  write(444,*)' iteration number :', i+1
  write(555,*)' iteration number :', i+1
  pr = praxis ( t0, h0, n, prin, x )
  write(777,*)'Iteration : ',i+1
  write(777,*)' Potential = ',pr

```

```

do iatom=1,natom
    i1=(iatom-1)*2+1
    i2=i1+1
    xc(iatom)=x(i1)
    yc(iatom)=x(i2)
end do
tem = CoordsWrite(natom,xc,yc)

do jatom=1,iadjatom
    if(jatom.le.iadjatom/2) then
        i1=(iadj(jatom)-1)*2+1
        x(i1)=x((iadj(1)-1)*2+1)
    else
        i1=(iadj(jatom)-1)*2+1
        x(i1)=x((iadj((iadjatom/2)+1)-1)*2+1)
    end if
end do

end do
write(*,*)
write(2,*)

8 continue
close(unit=333)
close(unit=444)
close(unit=555)
close(unit=777)
stop
end

function CoordsWrite(natom,xc,yc)
    integer natom
    double precision xc(1000),yc(1000),CoordsWrite

    do iatom=1,natom
        write(333,*) iatom,xc(iatom),yc(iatom)
    end do
    write(333,*)
    write(333,*)
    CoordsWrite = 0.0d0
return
end

```

B.2 Program to compute first generation Brenner potential (1990)

Function Brenner(n)

```
!-----
! FORTRAN program to computes the Brenner potential from the given the atomic
! coordinates
!-----
! Function created on
! 17 Aug 2004 by S. Rajendran & C.D. Reddy
! Parameters:
! Input, real*8 x(n), atomic coordinates.
! Input, integer n, the number of coordinates (=2*number of atoms).
! Output, real*8 func, the value of Brenner potential.
!-----
double precision V,Brenner,De,S,Beta,Re,delta,a0,c0,d0,mul
double precision Vij,xi,yi,zi,xj,yj,zj,xk,yk,zk,r,fc,fcfr,exp1,exp2,VA,VR
double precision sum1,sum2,Gtheta,Bij,Bji,Bijbar,fixed
double precision x,xold,penal,rij,rik,rjk,costheta,onepcos
integer n,i,j,iatom,natom,conn
integer nelelem,nbh,kk,ifix,matom
common /bloc1/conn(5000,2),nelelem,nbh(10000,15)
common /bloc2/w0,xscale,yscale,zscale
common /bloc4/x(8640)

natom=n/3
V=0.0d0
pi=dacos(-1.0d0)
mul=1.6021892E-10 ! multiplication factor is used for converting V in ev to V in N-nm
De=6.0d0
S=1.22d0
Beta=21d0
Re=0.1390d0
delta=0.50000d0
a0=0.00020813d0
c0=330d0
d0=3.5d0

Vij=0.0d0
do ielem=1,nelelem
    i=conn(ielelem,1)
    j=conn(ielelem,2)
    if(j.gt.i) then
        xi=x((i-1)*3+1)
```

```

      yi=x((i-1)*3+2)
      zi=x((i-1)*3+3)
      xj=x((j-1)*3+1)
      yj=x((j-1)*3+2)
      zj=x((j-1)*3+3)
      r=dsqrt((xj-xi)*(xj-xi)+(yj-yi)*(yj-yi)+(zj-zi)*(zj-zi))
!   compute fc
      fc=fcofr(r)

!   compute VR and VA
      exp1=-dsqrt(2.0d0*S)*Beta*(r-Re)
      exp2=-dsqrt(2.0d0/S)*Beta*(r-Re)
      VR=(De/(S-1))*dexp(exp1)*fc
      VA=(De*S/(S-1))*dexp(exp2)*fc

      Bijbar=0.0d0
      sum1=0.0d0
      do kk=1,nbh(i,1)
        k=nbh(i,kk+1)
        if(k.ne.i) then
          if(k.ne.j) then
            xk=x((k-1)*3+1)
            yk=x((k-1)*3+2)
            zk=x((k-1)*3+3)
            rij=r
            rik=dsqrt((xk-xi)*(xk-xi)+(yk-yi)*(yk-yi)+(zk-zi)*(zk-
zi))
            rjk=dsqrt((xk-xj)*(xk-xj)+(yk-yj)*(yk-yj)+(zk-zj)*(zk-zj))
            costheta=(rij*rij+rik*rik-rjk*rjk)/2.0d0/rij/rik
            onepcos=(1.0d0+costheta)
            Gtheta=a0*(1.0d0+c0*c0/d0/d0-
c0*c0/(d0*d0+onepcos*onepcos))
            sum1=sum1+Gtheta*fcofr(rik)
          end if
        end if
      end do
      Bij=(1.0d0+sum1)**(-delta)

!   compute Bji
      sum2=0.0d0
      do kk=1,nbh(j,1)
        k=nbh(j,kk+1)
        if(k.ne.i) then
          if(k.ne.j) then
            xk=x((k-1)*3+1)
            yk=x((k-1)*3+2)

```

```

        zk=x((k-1)*3+3)
        rij=r
        rik=dsqrt((xk-xi)*(xk-xi)+(yk-yi)*(yk-yi)+(zk-zi)*(zk-zi))
        rjk=dsqrt((xk-xj)*(xk-xj)+(yk-yj)*(yk-yj)+(zk-zj)*(zk-zj))
        costheta=(rij*rij+rjk*rjk-rik*rik)/2.0d0/rij/rjk
        onepcos=(1.0d0+costheta)
        Gtheta=a0*(1.0d0+c0*c0/d0/d0-c0*c0/(d0*d0+onepcos*onepcos))
        sum2=sum2+Gtheta*fcofr(rjk)
    end if
end if
end do
Bji=(1.0d0+sum2)**(-delta)
Bijbar=(Bij+Bji)/2.0d0
Vij=VR-Bijbar*VA
V=V+Vij
end if
end do
Brenner=V
return
end

!-----
function fcofr(r)
!-----
double precision fcofr,r,R1,R2,top,bot,pi

R1=0.17d0
R2=0.2d0
pi=dacos(-1.0d0)
if (r.le.R1) fcofr=1.0d0
if (r.ge.R2) fcofr=0.0d0
if (r.gt.R1.and.r.lt.R2) then
    top=pi*(r-R1)
    bot=R2-R1
    fcofr=0.5d0*(1+dcos(top/bot))
endif
return
end

```

Sample input file for a single carbon ring

```

6 (Number of carbon atoms)
! atom number    x-coordinate    y-coordinate
    1          0.0710000000    0.0000000000
    2          0.2130000000    0.0000000000
    3          0.0000000000    0.1229756073
    4          0.2840000000    0.1229756073

```

Appendix A

5	0.0710000000	0.2459512147
6	0.2130000000	0.2459512147

! Connectivity

6 (Number of bonds)

! Bond number	First atom	Second atom
1	1	2
2	1	3
3	2	4
4	3	5
5	4	6
6	5	6

Out put

1	0.0708500000	0.0000000000
2	0.2125500000	0.0000000000
3	0.0000000000	0.1227157997
4	0.2834000000	0.1227157997
5	0.0708500000	0.2454315994
6	0.2125500000	0.2454315994

APPENDIX B

(* MATHEMATICA PROGRAM TO COMPUTE STIFFNESS OF GRAPHENE SHEET OR CNTS *)

(* Input file for graphene needs to be created similar to the single carbon ring *)

```

mul = 1.6021892 * 10^(-10); (* Multiplication factor to convert ev to TPa *)
De = 6 * mul;
S = 122 / 100;
beta = 21;
re = 139 / 1000;
delta = 1 / 2;
a0 = 20813 / 100000000;
c0 = 330;
d0 = 35 / 10;
(* Potential computation using Brenner potential function *)
(* Switching function *)
fcofr = Function[r,
  (If[{r ≤ (17 / 100)},
    1,
    (If[{r > (2 / 10)},
      0,
      1 / 2 * (1 + Cos[Pi * (r - (17 / 100)) / ((2 / 10) - (17 / 100))])
    ])]
];
(* Repulsive function *)
VR = Function[{fc, rd}, fc * (De / (S - 1)) * Exp[-Sqrt[2 * S] * beta * (rd - re)]];
(* Attractive function *)
VA = Function[{fc, rd}, fc * (De * S / (S - 1)) * Exp[-Sqrt[2 / S] * beta * (rd - re)]];
(* sum1 function *)
sum1 = Function[{xi, yi, xj, yj, xk, yk},
  rij = Sqrt[{xi - xj} * {xi - xj} + {yi - yj} * {yi - yj}];
  rik = Sqrt[{xk - xi} * {xk - xi} + {yk - yi} * {yk - yi}];
  rjk = Sqrt[{xk - xj} * {xk - xj} + {yk - yj} * {yk - yj}];
  costhetaij = (rij * rij + rik * rik - rjk * rjk) / 2.0 / rij / rik;
  Gthetaij = a0 * (1 + c0 * c0 / d0 / d0 - c0 * c0 / (d0 * d0 + (1 + costhetaij) ^ 2));
  Gthetaij * fcofr[rik]
];
(* sum2 function *)
sum2 = Function[{xi, yi, xj, yj, xk, yk},
  rij = Sqrt[{xi - xj} * {xi - xj} + {yi - yj} * {yi - yj}];
  rik = Sqrt[{xk - xi} * {xk - xi} + {yk - yi} * {yk - yi}];
  rjk = Sqrt[{xk - xj} * {xk - xj} + {yk - yj} * {yk - yj}];
  costhetaij = (rij * rij + rjk * rjk - rik * rik) / 2.0 / rij / rjk;
  Gthetaij = a0 * (1 + c0 * c0 / d0 / d0 - c0 * c0 / (d0 * d0 + (1 + costhetaij) ^ 2));
  Gthetaij * fcofr[rjk]
];

```

```

(* Connectivity reading from flat file *)
conn = OpenRead["D:\ErrorAnalysis\conn7x7.lis"];
nelem = Read[conn, Number];
Array[ic, {nelem, 2}];
For[i = 1, i ≤ nelem, i++,
  temp = Read[conn, Number];
  ic[i, 1] = Read[conn, Number];
  ic[i, 2] = Read[conn, Number];
]
Close[conn];
(* Connectivity data stored in array h. *)
Array[h, {2*nelem, 15}];
For[i = 1, i ≤ 2*nelem, i++,
  For[j = 1, j ≤ 15, j++,
    h[i, j] = 0;
  ];
];
For[i = 1, i ≤ nelem,
  i1 = ic[i, 1];
  i2 = ic[i, 2];
  h[i1, 1] = h[i1, 1] + 1;
  h[i2, 1] = h[i2, 1] + 1;
  i3 = h[i1, 1];
  i4 = h[i2, 1];
  h[i1, i3 + 1] = i2;
  h[i2, i4 + 1] = i1;
  i++;
];
(* Coordinates reading from flat file *)
Coords = OpenRead["D:\ErrorAnalysis\coords7x7.lis"];
noOfNodes = Read[Coords, Number];
Array[xc, noOfNodes];
Array[yc, noOfNodes];
For[iatom = 1, iatom ≤ noOfNodes, iatom++,
  kot = Read[Coords, Number];
  xc[kot] = Read[Coords, Real];
  yc[kot] = Read[Coords, Real];
];
Close[Coords];

```



```

(* equilibrium potential computation *)
V = 0;
xscale = 0;
yscale = 0;

For[iatom = 1, iatom <= noOfNodes,
  x[iatom] = xc[iatom] + xc[iatom] * xscale;
  y[iatom] = yc[iatom] + yc[iatom] * yscale;
  iatom++];

r = 0;
Vij = 0;
For[ii = 1, ii <= nele, ii++,
  i = ic[ii, 1];
  j = ic[ii, 2];
  If[j > i,
    (r = Sqrt[(x[j] - x[i]) * (x[j] - x[i]) + (y[j] - y[i]) * (y[j] - y[i])]);
    rin = Sqrt[(xc[i] - xc[j]) * (xc[i] - xc[j]) + (yc[i] - yc[j]) * (yc[i] - yc[j])];
    fc = foofr[r];
    Bijbar = 0;
    su1 = 0;
    su2 = 0;

    For[kk = 1, kk <= h[i, 1], kk++,
      k = h[i, kk + 1];
      If[(k ≠ i) && (k ≠ j),
        su1 = su1 + sum1[x[i], y[i], x[j], y[j], x[k], y[k]];
      ];
    ];

    For[kk = 1, kk <= h[j, 1], kk++,
      k = h[j, kk + 1];
      If[(k ≠ i) && (k ≠ j),
        su2 = su2 + sum2[x[i], y[i], x[j], y[j], x[k], y[k]];
      ];
    ];
    Bijbar = (((1 + su1) ^ (-delta)) + ((1 + su2) ^ (-delta))) / 2;
    Vij = (VR[fc, r] - Bijbar * VA[fc, r]);
    V = V + Vij;
  ) ];
];
V0 = V;
L = 1.57302509844167;
(* Potential computation *)

```

```

V = 0;
xscale = a / L;
yscale = 0;
r = 0;
Vij = 0;

For[iatom = 1, iatom <= noOfNodes,
  x[iatom] = xc[iatom] + xc[iatom] * xscale;
  y[iatom] = yc[iatom] + yc[iatom] * yscale;
  iatom++;];

For[ii = 1, ii <= nele, ii++,
  i = ic[ii, 1];
  j = ic[ii, 2];
  If[j > i,
    (r = Sqrt[(x[j] - x[i]) * (x[j] - x[i]) + (y[j] - y[i]) * (y[j] - y[i])]);
    rin = Sqrt[(xc[i] - xc[j]) * (xc[i] - xc[j]) + (yc[i] - yc[j]) * (yc[i] - yc[j])];
    fc = fcofr[r];
    Bijbar = 0;
    su1 = 0;
    su2 = 0;

    For[kk = 1, kk <= h[i, 1], kk++,
      k = h[i, kk + 1];
      If[(k ≠ i) && (k ≠ j),
        su1 = su1 + sum1[x[i], y[i], x[j], y[j], x[k], y[k]];
      ];
    ];

    For[kk = 1, kk <= h[j, 1], kk++,
      k = h[j, kk + 1];
      If[(k ≠ i) && (k ≠ j),
        su2 = su2 + sum2[x[i], y[i], x[j], y[j], x[k], y[k]];
      ];
    ];
    Bijbar = ((1 + su1) ^ (-delta)) + ((1 + su2) ^ (-delta)) / 2;
    Vij = (VR[fc, r] - Bijbar * VA[fc, r]);
    V = V + Vij;
  ) ];
];

U = (V - V0);
err = Abs[U / V0];
Plot[err, {a, -10 ^ (-2), 10 ^ (-2)}]

```

Appendix B

- Graphics -

(* stiffness - numerical determination based on SMALL DISPLACEMENT METHOD *)

$k = D[U, \{a, 2\}];$

$k0 = k /. a \rightarrow 0$

4.04171×10^{-7}

$kbar = 2 * U / a / a;$

$relerr = Abs[(kbar - k0) / k0];$

$errlog = Log[10, relerr];$

$Plot[kbar /. a \rightarrow (10^n), \{n, -2, -9\}, PlotRange \rightarrow All, AxesOrigin \rightarrow \{-9, -0.0005\}]$

- Graphics -

$Plot[errlog /. a \rightarrow (10^n), \{n, -2, -9\}, PlotRange \rightarrow All]$

- Graphics -

(* stiffness - numerical determination based on SMALL DISPLACEMENT METHOD *)

(* with gradient correction *)

$k = D[U, \{a, 2\}];$

$gk = D[U, \{a, 1\}];$

$k0 = k /. a \rightarrow 0$

4.04171×10^{-7}

$kbar = 2 * (U - (gk /. a \rightarrow 0) * a) / a / a;$

$relerr = Abs[(kbar - k0) / k0];$

$errlog = Log[10, relerr];$

Appendix B

```
Plot[kbar /. a -> (10^n), {n, -2, -7}, PlotRange -> All, AxesOrigin -> {-7, 3.3 * 10^(-07)}]
```

- Graphics -

```
(* Plot[kbar /. a -> (10^n), {n, -2, -4}, PlotRange -> All, AxesOrigin -> {-9, -0.00075}] *)
```

```
Plot[errlog /. a -> (10^n), {n, -2, -7}, PlotRange -> All, AxesOrigin -> {-7, -6}]
```

- Graphics -

```
kbar1 = 2 * (U - (gk /. a -> 0) * a) / (1 + a) / (1 + a);
```

```
kbar1 /. a -> 0
```

```
-5.22778 * 10^-22
```

```
(* stiffness - NUMERICAL determination based on POTENTIAL-FIT METHOD *)
```

```
np = 400;
```

```
dat1 = Array[xyz1, {np + 1, 2}];
```

```
dat2 = Array[xyz2, {np + 1, 2}];
```

```
fac = 1.1;
```

```
Do[
```

```
  {num = i / 100; xyz1[i - 199, 1] = -num;
```

```
    xyz2[i - 199, 1] = -num;
```

```
  del = 10^(-num);
```

```
  eq1 = Simplify[(-U /. a -> del) + (b1 + b2 * a + b3 * a^2 + b4 * a^3) /. a -> del];
```

```
  eq2 = Simplify[(-U /. a -> del * fac) + (b1 + b2 * a + b3 * a^2 + b4 * a^3) /. a -> del * fac];
```

```
  eq3 = Simplify[(-U /. a -> (-del)) + (b1 + b2 * a + b3 * a^2 + b4 * a^3) /. a -> (-del)];
```

```
  eq4 = Simplify[(-U /. a -> (-del * fac)) + (b1 + b2 * a + b3 * a^2 + b4 * a^3) /. a -> (-del * fac)];
```

```
  soln = Flatten[Simplify[Solve[{eq1 == 0, eq2 == 0, eq3 == 0, eq4 == 0}, {b1, b2, b3, b4}]]];
```

```
  Vp = Simplify[(b1 + b2 * a + b3 * a^2 + b4 * a^3) /. soln];
```

```
  kbar = N[D[Vp, {a, 2}] /. a -> 0, 16];
```

```
    xyz2[i - 199, 2] = kbar;
```

```
  relerr = Simplify[Abs[(kbar - k0) / k0];
```

```
  errlog1 = Log[10, relerr]; xyz1[i - 199, 2] = errlog1;}, {i, 200, 200 + np}]
```

```
ListPlot[dat1, PlotRange -> All] (*, AxesOrigin -> {-8.5, -8} *)
```

- Graphics -

```
ListPlot[dat2, PlotRange -> All] (*, AxesOrigin -> {-7, -0.0001} *)
```

- Graphics -

```
(* stiffness - numerical determination based on FINITE DIFFERENCE METHOD *)
```

```
np = 400;
```

```
Clear[dat1, dat2, xyz1, xyz2]
```

```
dat1 = Array[xyz1, {np + 1, 2}];
```

```
dat2 = Array[xyz2, {np + 1, 2}];
```

```
fac = 1.1;
```

```
Do[
```

```
    {ram = i / 100; xyz1[i - 199, 1] = -ram; xyz2[i - 199, 1] = -ram;
```

```
    del = 10^(-ram);
```

```
w1 = (U /. a -> (-del));
```

```
w2 = (U /. a -> 0);
```

```
w3 = (U /. a -> del);
```

```
kbar = (1 / del^2) * (w1 - 2 * w2 + w3);
```

```
xyz1[i - 199, 2] = kbar;
```

```
relerr = Simplify[Abs[(kbar - k0) / (k0)]]; 
```

```
errlog1 = Log[10, relerr];
```

```
xyz2[i - 199, 2] = errlog1;
```

```
    ), {i, 200, 200 + np}];
```

```
ListPlot[dat1, PlotRange -> All, AxesOrigin -> {-6, 4.041 * 10^(-07)}]
```

- Graphics -

```
ListPlot[dat2, PlotRange -> All] (*, AxesOrigin -> {-6, -8}) *)
```

APPENDIX C

```

!-----
! FORTRAN program to compute stiffness matrix of CNTs using finite difference
! method
! Input file for CNT is similar to single carbon ring (refer Appendix A) and include
! z-coordinates.
!-----
integer, parameter :: n = 960*3
double precision f,xc,yc,zc,ang,pi,ev,volume,const,fixed,uc,vc,wc,uu,vv,ww,a1,a2,a3,b1,
double precision b2,b3,V,U,delta1, rcond,zz(n),sumofp,tempsumofp
double precision t0,h0,pr,praxis,x,xold,xscale,yscale,zscale,dist,sum,area,GK,w0,force
integer i,j,prin,natom,matom,katom,nelem,i1,i2,i3,i4,kount,nbh,sn,fn
integer yes,ii,jj,kk,belem(2000),iffix,conn,tloop,ipvt(n)
character*72 inf,outf

common /bloc1/conn(4000,2),nelem,nbh(4000,15)
common /bloc2/w0,xscale,yscale,zscale
common /bloc3/xc(960),yc(960),zc(960),GK(2880,2880),x(2880),force(2880)

pi=dacos(-1.0d0)

! ---Open input/output files and read the data---

inf='CNTCoords.lis'
outf='CNT.out'
open(unit=2,file=outf)
delta1=0.0001d0
! read atomic coordinates
open(unit=1,file=inf)
read(1,*) natom
if(n.ne.natom*3) then
    write(*,*)
    write(*,*) ' EXECUTION TERMINATED...'
    write(*,*) ' Please change the value of parameter n and re-try...'
    stop
end if
do iatom=1,natom
    read(1,*) katom,xc(katom),yc(katom),zc(katom)
    i1=(iatom-1)*3+1
    i2=i1+1
    i3=i2+1
    zc(katom)=zc(katom)*1.16    ! 1% elongation
    x(i1)=xc(katom)
    x(i2)=yc(katom)

```

```

        x(i3)=zc(katom)
    end do
    close(unit=1)

! read bond connectivity
    open(unit=3,file='CNTConn.lis')
    read(3,*) nelelem
    do ielem=1,nelelem
        read(3,*) kelem,(conn(kelem,inode),inode=1,2)
    end do
    close(unit=3)

! determine the first order neighbourhood of atoms
    do ielem=1,nelelem
        i1=conn(ielem,1)
        i2=conn(ielem,2)
        nbh(i1,1)=nbh(i1,1)+1
        nbh(i2,1)=nbh(i2,1)+1
        i3=nbh(i1,1)
        i4=nbh(i2,1)
        nbh(i1,i3+1)=i2
        nbh(i2,i4+1)=i1
    end do

! determine the second order neighbourhood of atoms
    do iatom=1,natom
        i1=nbh(iatom,1)
        i2=i1
        do ii=1,i1
            i=nbh(iatom,ii+1)
            do jj=1,nbh(i,1)
                j=nbh(i,jj+1)
                yes=0
                do kk=1,i2
                    k=nbh(iatom,kk+1)
                    if(j.eq.k) yes=1
                end do
                if(yes.eq.0) then
                    i2=i2+1
                    nbh(iatom,i2+1)=j
                end if
            end do
        end do
    end do
end do

```



```

do iatom=1,natom
  i1=15
  do i=15,1,-1
    if(nbh(iatom,i).eq.0) i1=i1-1
  end do
  i1=i1-1
  nbh(iatom,1)=i1
end do

! ---Print the initial point and initial function value---
write(2,*) ' Initial (input) point:'
write(2,*) ' Function value:'
w0=f(x,n)
write(2,*) w0
write(*,*) 'Stiff matrix computing started...'
open(unit=11,file='ForceMat.out')
open(unit=3333,file='StiffmatMat.out')
ite=1
tempsumofp = 1.0d0
1234 continue
xscale=delta1
yscale=delta1
zscale=delta1

do iatom = 1,3*natom
  do jatom = 1,3*natom
    GK(iatom,jatom)=0.0d0
  end do
  force(iatom)=0.0d0
end do
do iatom=1,natom
  temp=elemstiff(iatom,n)
  do kk=1,nbh(iatom,1)
    k=nbh(iatom,kk+1)
    if ((k.ne.iatom)) then
      temp = stiff(iatom,k,n)
    end if
  end do
  write(*,*) ' row number : ',iatom
end do

write(11,*)force
write(11,*)'iteration = ',ite
tempsumofp=sumofp
sumofp=0.0d0

```

```

if (ite.eq.4) then
  write(*,*) 'Stiff matrix writing started...'
  write(3333,1111) GK
end if
close(unit=3333)

1111 format(2880(4x, E24.14))

goto 123
! For minimization call dgeco and dgesl subprograms
call dgeco(GK,n,n,ipvt,rcond,zz)
call dgesl(GK,n,n,ipvt,force,0)

do iatom=1,natom
  i1=(iatom-1)*3+1
  i2=i1+1
  i3=i2+1
  xc(iatom)=xc(iatom)-force(i1)
  yc(iatom)=yc(iatom)-force(i2)
  zc(iatom)=zc(iatom)-force(i3)
  x(i1)=xc(iatom)
  x(i2)=yc(iatom)
  x(i3)=zc(iatom)
  write(200,*)xc(iatom),yc(iatom),zc(iatom)
  write(300,*)force(i1),force(i2),force(i3)
end do
write(*,*)'Before function value writing '
w0=f(x,n)
write(*,*)'Function value :',w0
write(11,*) ' Function value :',f(x,n)
write(200,*)
write(200,*)
write(200,*)
write(300,*)
write(300,*)
write(300,*)

ite=ite+1
goto 1234
123 continue
close(unit=3333)
close(unit=11)
stop
end

```

```

!-----
! Function to compute stiffness elements for the reference atom
!-----
Function elemstiff(fn,n)
integer fn,sn,elemstiff,iconn,fi1,fi2,fi3,conn,nelem,nbh,tloop,n
double precision lb,bondlen,xc,yc,zc,w0,x,xscale,yscale,zscale,GK
double precision w1,w2,w3,w4,w5,w6,w7,w8,force

common /bloc1/conn(4000,2),nelem,nbh(4000,15)
common /bloc2/w0,xscale,yscale,zscale
common /bloc3/xc(960),yc(960),zc(960),GK(2880,2880),x(2880),force(2880)

fi1=(fn-1)*3+1
fi2=fi1+1
fi3=fi2+1
do tloop=1,6
  select case(tloop)
    case(1)
      x(fi1) = xc(fn) + xscale
      w1=f(x,n)
      x(fi1) = xc(fn) - xscale
      w2=f(x,n)
      x(fi1) = xc(fn)
      GK(3*fn-2, 3*fn-2) = (w1-2*w0+w2)/(xscale*xscale)
      force(3*fn-2) = (w1-w2)/(2.0d0*xscale)
    case(2)
      x(fi2) = yc(fn) + yscale
      w1=f(x,n)
      x(fi2) = yc(fn) - yscale
      w2=f(x,n)
      x(fi2) = yc(fn)
      GK(3*fn-1, 3*fn-1) = (w1-2*w0+w2)/(yscale*yscale)
      force(3*fn-1) = (w1-w2)/(2.0d0*yscale)
    case(3)
      x(fi3) = zc(fn) + zscale
      w1=f(x,n)
      x(fi3) = zc(fn) - zscale
      w2=f(x,n)
      x(fi3) = zc(fn)
      GK(3*fn,3*fn) = (w1-2*w0+w2)/(zscale*zscale)
      force(3*fn) = (w1-w2)/(2.0d0*zscale)
    case(4)
      x(fi1) = xc(fn) + xscale
      x(fi2) = yc(fn) + yscale
      w5=f(x,n)
      x(fi1) = xc(fn) + xscale

```

```

x(fi2) = yc(fn) - yscale
w6=f(x,n)
x(fi1) = xc(fn) - xscale
x(fi2) = yc(fn) - yscale
w7=f(x,n)
x(fi1) = xc(fn) - xscale
x(fi2) = yc(fn) + yscale
w8=f(x,n)
x(fi1) = xc(fn)
x(fi2) = yc(fn)
GK(3*fn-2,3*fn-1) = (w5-w6+w7-w8)/(4.0d0*xscale*yscale)
GK(3*fn-1,3*fn-2) = GK(3*fn-2,3*fn-1)
case(5)
x(fi1) = xc(fn) + xscale
x(fi3) = zc(fn) + zscale
w5=f(x,n)
x(fi1) = xc(fn) + xscale
x(fi3) = zc(fn) - zscale
w6=f(x,n)
x(fi1) = xc(fn) - xscale
x(fi3) = zc(fn) - zscale
w7=f(x,n)
x(fi1) = xc(fn) - xscale
x(fi3) = zc(fn) + zscale
w8=f(x,n)
x(fi1) = xc(fn)
x(fi3) = zc(fn)
GK(3*fn-2,3*fn) = (w5-w6+w7-w8)/(4.0d0*xscale*zscale)
GK(3*fn,3*fn-2) = GK(3*fn-2, 3*fn)
case(6)
x(fi2) = yc(fn) + yscale
x(fi3) = zc(fn) + zscale
w5=f(x,n)
x(fi2) = yc(fn) + yscale
x(fi3) = zc(fn) - zscale
w6=f(x,n)
x(fi2) = yc(fn) - yscale
x(fi3) = zc(fn) - zscale
w7=f(x,n)
x(fi2) = yc(fn) - yscale
x(fi3) = zc(fn) + zscale
w8=f(x,n)
x(fi2) = yc(fn)
x(fi3) = zc(fn)
GK(3*fn-1,3*fn) = (w5-w6+w7-w8)/(4.0d0*yscale*zscale)
GK(3*fn, 3*fn-1) = GK(3*fn-1, 3*fn)

```

```

        end select
    end do

    elemstiff=0
    return
end

!-----
! Function to compute stiffness elements for the bonded atoms
!-----
Function stiff(fn,sn,n)
integer fn,sn,stiff,iconn,fi1,fi2,fi3,si1,si2,si3,conn,nelem,nbh,tloop,n
double precision lb,bondlen,xc,yc,zc,w0,x,xscale,yscale,zscale,GK
double precision w1,w2,w3,w4,w5,w6,w7,w8,force

common /bloc1/conn(4000,2),nelem,nbh(4000,15)
common /bloc2/w0,xscale,yscale,zscale
common /bloc3/xc(960),yc(960),zc(960),GK(2880,2880),x(2880),force(2880)
fi1=(fn-1)*3+1
fi2=fi1+1
fi3=fi2+1
si1=(sn-1)*3+1
si2=si1+1
si3=si2+1
do tloop = 1,9
    select case(tloop)
    case(1)
        x(fi1) = xc(fn) + xscale
        x(si1) = xc(sn) + xscale
        w5=f(x,n)
        x(fi1) = xc(fn) + xscale
        x(si1) = xc(sn) - xscale
        w6=f(x,n)
        x(fi1) = xc(fn) - xscale
        x(si1) = xc(sn) - xscale
        w7=f(x,n)
        x(fi1) = xc(fn) - xscale
        x(si1) = xc(sn) + xscale
        w8=f(x,n)
        x(fi1) = xc(fn)
        x(si1) = xc(sn)
        GK(3*fn-2,3*sn-2) = GK(3*fn-2,3*sn-2)+(w5-w6+w7-w8)/(8.0d0*xscale*xscale)
        GK(3*sn-2,3*fn-2) = GK(3*fn-2,3*sn-2)
    case(2)
        x(fi1) = xc(fn) + xscale
        x(si2) = yc(sn) + yscale

```

```

w5=f(x,n)
x(fi1) = xc(fn) + xscale
x(si2) = yc(sn) - yscale
w6=f(x,n)
x(fi1) = xc(fn) - xscale
x(si2) = yc(sn) - yscale
w7=f(x,n)
x(fi1) = xc(fn) - xscale
x(si2) = yc(sn) + yscale
w8=f(x,n)
x(fi1) = xc(fn)
x(si2) = yc(sn)
GK(3*fn-2,3*sn-1) = GK(3*fn-2,3*sn-1)+(w5-w6+w7-w8)/(8.0d0*xscale*yscale)
GK(3*sn-1,3*fn-2) = GK(3*fn-2,3*sn-1)
case(3)
  x(fi1) = xc(fn) + xscale
  x(si3) = zc(sn) + zscale
  w5=f(x,n)
  x(fi1) = xc(fn) + xscale
  x(si3) = zc(sn) - zscale
  w6=f(x,n)
  x(fi1) = xc(fn) - xscale
  x(si3) = zc(sn) - zscale
  w7=f(x,n)
  x(fi1) = xc(fn) - xscale
  x(si3) = zc(sn) + zscale
  w8=f(x,n)
  x(fi1) = xc(fn)
  x(si3) = zc(sn)
  GK(3*fn-2,3*sn) = GK(3*fn-2,3*sn)+(w5-w6+w7-w8)/(8.0d0*xscale*zscale)
  GK(3*sn,3*fn-2) = GK(3*fn-2, 3*sn)
case(4)
  x(fi2) = yc(fn) + yscale
  x(si1) = xc(sn) + xscale
  w5=f(x,n)
  x(fi2) = yc(fn) + yscale
  x(si1) = xc(sn) - xscale
  w6=f(x,n)
  x(fi2) = yc(fn) - yscale
  x(si1) = xc(sn) - xscale
  w7=f(x,n)
  x(fi2) = yc(fn) - yscale
  x(si1) = xc(sn) + xscale
  w8=f(x,n)
  x(fi2) = yc(fn)
  x(si1) = xc(sn)

```

```

GK(3*fn-1,3*sn-2) = GK(3*fn-1,3*sn-2)+(w5-w6+w7-w8)/(8.0d0*yscale*xscale)
GK(3*sn-2,3*fn-1) = GK(3*fn-1,3*sn-2)
case(5)
  x(fi2) = yc(fn) + yscale
  x(si2) = yc(sn) + yscale
  w5=f(x,n)
  x(fi2) = yc(fn) + yscale
  x(si2) = yc(sn) - yscale
  w6=f(x,n)
  x(fi2) = yc(fn) - yscale
  x(si2) = yc(sn) - yscale
  w7=f(x,n)
  x(fi2) = yc(fn) - yscale
  x(si2) = yc(sn) + yscale
  w8=f(x,n)
  x(fi2) = yc(fn)
  x(si2) = yc(sn)
GK(3*fn-1,3*sn-1) = GK(3*fn-1,3*sn-1)+(w5-w6+w7-w8)/(8.0d0*yscale*yscale)
GK(3*sn-1,3*fn-1) = GK(3*fn-1,3*sn-1)
case(6)
  x(fi2) = yc(fn) + yscale
  x(si3) = zc(sn) + zscale
  w5=f(x,n)
  x(fi2) = yc(fn) + yscale
  x(si3) = zc(sn) - zscale
  w6=f(x,n)
  x(fi2) = yc(fn) - yscale
  x(si3) = zc(sn) - zscale
  w7=f(x,n)
  x(fi2) = yc(fn) - yscale
  x(si3) = zc(sn) + zscale
  w8=f(x,n)
  x(fi2) = yc(fn)
  x(si3) = zc(sn)
GK(3*fn-1,3*sn) = GK(3*fn-1,3*sn)+(w5-w6+w7-w8)/(8.0d0*yscale*zscale)
GK(3*sn,3*fn-1) = GK(3*fn-1,3*sn)
case(7)
  x(fi3) = zc(fn) + zscale
  x(si1) = xc(sn) + xscale
  w5=f(x,n)
  x(fi3) = zc(fn) + zscale
  x(si1) = xc(sn) - xscale
  w6=f(x,n)
  x(fi3) = zc(fn) - zscale
  x(si1) = xc(sn) - xscale
  w7=f(x,n)

```

```

    x(fi3) = zc(fn) - zscale
    x(si1) = xc(sn) + xscale
    w8=f(x,n)
    x(fi3) = zc(fn)
    x(si1) = xc(sn)
    GK(3*fn,3*sn-2) = GK(3*fn,3*sn-2)+(w5-w6+w7-w8)/(8.0d0*zscale*xscale)
    GK(3*sn-2, 3*fn) = GK(3*fn,3*sn-2)
case(8)
    x(fi3) = zc(fn) + zscale
    x(si2) = yc(sn) + yscale
    w5=f(x,n)
    x(fi3) = zc(fn) + zscale
    x(si2) = yc(sn) - yscale
    w6=f(x,n)
    x(fi3) = zc(fn) - zscale
    x(si2) = yc(sn) - yscale
    w7=f(x,n)
    x(fi3) = zc(fn) - zscale
    x(si2) = yc(sn) + yscale
    w8=f(x,n)
    x(fi3) = zc(fn)
    x(si2) = yc(sn)
    GK(3*fn,3*sn-1) = GK(3*fn,3*sn-1)+(w5-w6+w7-w8)/(8.0d0*zscale*yscale)
    GK(3*sn-1,3*fn) = GK(3*fn,3*sn-1)
case(9)
    x(fi3) = zc(fn) + zscale
    x(si3) = zc(sn) + zscale
    w5=f(x,n)
    x(fi3) = zc(fn) + zscale
    x(si3) = zc(sn) - zscale
    w6=f(x,n)
    x(fi3) = zc(fn) - zscale
    x(si3) = zc(sn) - zscale
    w7=f(x,n)
    x(fi3) = zc(fn) - zscale
    x(si3) = zc(sn) + zscale
    w8=f(x,n)
    x(fi3) = zc(fn)
    x(si3) = zc(sn)
    GK(3*fn,3*sn) = GK(3*fn,3*sn)+(w5-w6+w7-w8)/(8.0d0*zscale*zscale)
    GK(3*sn,3*fn) = GK(3*fn,3*sn)
end select
end do
stiff=0
return
end

```


APPENDIX D

```

%-----
% MATLAB program to compute the eigenvalues and eigenvectors for fluid conveying
% CNTs
%-----
clear all
format long;
e=100;           % no of equal elements
L=26.78;         % Length of the nanotube in nm
l=L/e;           % element length in nm
%denp=2.24*10^(-24); %density of pipe material in kg/nm^3
denw=0.07*10^(-24); % for water 1000 kg/m^3 = 1000/(10^(27)) Kg/nm^3
% liquid H2 density 7.0*10^(-26) kg/nm3 and gasoline density ~ 7.5*10^(-25) kg/nm3
%do=1.12+0.34;
di=1.12-(0.34);
%mp=(pi/4)*(do^2-di^2)*denp; %mass of pipe per unit length
mf=(pi/4)*(di^2)*denw;       %mass of fluid per unit length
%beta=mf/(mp+mf);           % ratio of masses
%V=sqrt(md/(E*I))*v*L;
count=1;
for ii=11108:0.005:11110
    v=1.0e09*ii;             % no flow condition
    %mf=0;                    % no mass inside the CNT
    % v=V/(L*(sqrt(mf/(E*I)))); % nondimensional velocity
    %v=0;
    %mf=0;
    mp=2.585519*10^(-24);
    p=(mp+mf)*l/420;
    pp=mf*v/30;
    q=mf*v*v/(150*l);
    EI=1.112175*10^(-7)*10^(9); % need to multiply EI value with 10^(9). It is a
    conversion factor N/m to
    r=(EI/(l*l*l));

    k1=r*[12 6*l -12 6*l
           6*l 4*l*l -6*l 2*l*l
           -12 -6*l 12 -6*l
           6*l 2*l*l -6*l 4*l*l];

    k2=q*[180 15*l -180 15*l
           15*l 20*l*l -15*l -5*l*l
           -180 -15*l 180 -15*l
           15*l -5*l*l -15*l 20*l*l];

    c=pp*[0 6*l 30 -6*l

```

```

-6*1 0 6*1 -1*1
-30 -6*1 0 6*1
6*1 1*1 -6*1 0];

M=p*[156 22*1 54 -13*1
      22*1 4*1*1 13*1 -3*1*1
      54 13*1 156 -22*1
      -13*1 -3*1*1 -22*1 4*1*1] ;

% global matrix initialization
mm=4+(e-1)*2; % size of the global matrix
gm1=zeros(mm,mm);
gk1=zeros(mm,mm);
gk2=zeros(mm,mm);
gc=zeros(mm,mm);
% Global matrix assembly
nn=0;
while(nn~=(2*e)),
    for i=1:1:4,
        for j=1:1:4,
            gm1(i+nn,j+nn)=gm1(i+nn,j+nn)+M(i,j);
            gk1(i+nn,j+nn)=gk1(i+nn,j+nn)+k1(i,j);
            gk2(i+nn,j+nn)=gk2(i+nn,j+nn)+k2(i,j);
            gc(i+nn,j+nn)=gc(i+nn,j+nn)+c(i,j);
        end
    end
    nn=nn+2;
end

% Boundary conditions
for i=1:1:mm,
    for j=1:1:mm,
        if(((i~=1)&(j~=1))&((i~=2)&(j~=2))&((i~=mm-1)&(j~=mm-1))&((i~=mm)&(j~=mm)))
            mgm1(i-2,j-2)=gm1(i,j);
            kgk1(i-2,j-2)=gk1(i,j);
            kgk2(i-2,j-2)=gk2(i,j);
            cgc(i-2,j-2)=gc(i,j);
        end
    end
end
kgk=kgk1-kgk2;

% Coefficient matrix a and b
b=[kgk zeros(size(kgk))
   zeros(size(kgk)) mgm1];

```

```

a=[zeros(size(kgk)) -kgk
   kgk cgc];
% few lowest eigen values
s2=eigs(-a,b,10,0); % no need of sqrt for eigen value but need to divide by 2/pi
% CC=inv(mgm1)*kgk;
% s1=eigs(CC,10,0);
vtemp(count)=v/(10^9); % v is in m/s
temp1(count)=(sqrt((abs(real(s2(1))))^2+(abs(imag(s2(1))))^2))/2/pi/10^9; % natural
frequency in GHz
temp1real(count)=(abs(real(s2(2))))/2/pi/10^9; % natural frequency in GHz
temp1img(count)=abs((imag(s2(2))))/2/pi/10^9;
count
count=count+1;
end

plot(vtemp,temp1,'.-')

out = fopen('Output2ForLiquidH22.lis','W')
for i=1:count-1
    fprintf(out,'%20.10f %20.10f %20.10f %20.10f\n',vtemp(i),temp1(i),temp1real(i),temp1img(i));
end
fclose(out);

```

List of Publications

The following are some of the publications arising from the thesis:

Journal papers

2. C. D. Reddy, S. Rajendran and K.M. Liew (2004), “**Equivalent Continuum Modelling of Graphene sheets**” International Journal of NanoScience, Special Issue on Nanotech 2004, Vol. 4, No. 4, 631-636
3. C.D. Reddy, S. Rajendran and K.M. Liew (2006), “**Equilibrium configuration and elastic properties of finite graphene**”, Nanotechnology, Vol. 17, 864-870
4. S. Rajendran and C.D. Reddy (2006), “**Determination of elastic properties of graphene and carbon-nanotubes using Brenner potential: the maximum attainable numerical precision**”, Journal of Computational and Theoretical Nanoscience, Vol. 3, No. 3, 382-390
5. C. D. Reddy, S. Rajendran and K. M. Liew (2006), “**Free vibration analysis of single-walled carbon nanotubes using Brenner potential**” Physical Review B (Under review)

International Conferences

1. C. D. Reddy, S. Rajendran and K.M. Liew (2004), “**Equivalent Continuum Modelling of Graphene sheets**” 1st International conference on Nanotechnology, Nanotech 2004, Singapore 13-17 July 2004.
2. C. D. Reddy, S. Rajendran and K.M. Liew (2005), “**Equilibrium configurations and Continuum elastic properties of graphene and carbon nanotubes**” 3rd International Conference on Materials for Advanced Technologies 2005 (ICMAT 2005), Singapore 3 - 8 July 2005.

REFERENCES

- [1] Dresselhaus MS, Dresselhaus G and Avouris P, Carbon Nanotubes: Synthesis, Structure, Properties, and applications. Berlin Heidelberg, New york: Springer-Verlag, 2000.
- [2] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV and Frisev AA. Electric field effect in atomically thin carbon films. *Science* **306** 606-69, 2005.
- [3] Cornell WD, Cieplak P, Bayly CI, Gould IR, Merz KM, Ferguson DM, Spellmeyer DC, Fox T, Caldwell JW and Kollman PA. A Second Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules. *Journal of the American Chemical Society* **117** 5179-97, 1995.
- [4] Brenner DW, Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films. *Physical Review B* **42** 9458-71, 1990.
- [5] Kwon YW, Manthena C, Oh JJ, Srivastava D, Vibrational Characteristic of Carbon nanotubes as Nanomechanical Resonators. *Journal of Nanoscience and Nanotechnology* **5** 703-12, 2005.
- [6] ANSYS. Release 8.1: ANSYS Inc.,.
- [7] Edision TA, Manufacture of filaments for incandescent electrical lamps. US Patent, New Jersey, 1892.
- [8] Endo M, The growth mechanism of vapor-grown carbon fibers. Orleans, France: University of Oreans, 1975.
- [9] Harry KW, Heath JR, OBrien SC, Curl RF, Smalley RE, C60: Buckminsterfullerene. *Nature* **318** 162-3, 1985.
- [10] Iijima S. Helical microtubules of graphitic carbon. *Nature* **354** 56-8, 1991.
- [11] Smitherman DVJ. Space Elevators an advanced earth-space infrastructure for the new Millennium. CP-2000-210429: NASA, 2000.
- [12] Collins PG and Avouris P, Nanotubes for electronics. *Scientific American* **283** 62-9, 2000.
- [13] Yakobson BI and Samsonidze G, Atomistic theory of mechanical relaxation in fullerene nanotubes. *Carbon* **38** 11-2, 2000.

- [14] Introduction to carbon nanotubes, Current Science and Technology, Museum of Science, http://www.mos.org/cst/2006/05/26/intro_nanotech/ 2006.
- [15] Pipes BR, Frankland SJV, Hubert P and Saether E. Self-consistent properties of carbon nanotubes and hexagonal arrays as composite reinforcements. *Composites Science and Technology* **63** 1-10, 2003.
- [16] Iijima S and Ichihashi T, Single-shell carbon nanotubes of 1-nm diameter. *Nature* **363** 603-5, 1993.
- [17] Zhang P. Theory of electronic and structural properties of materials: Novel group-IV material and real space methods. The Pennsylvania State University, 2001.
- [18] Pan ZW, Xie SS, Lu L, Chang BH, Sun LF, Zhou WY, Wang G and Zhang DL, Tensile tests of ropes of very long aligned multi-wall carbon nanotubes. *Applied Physics Letters* **74** 3152-4, 1999.
- [19] Lopez MJ, Rubio A, Alonso JA, Qin LC and Iijima S, Novel polygonized single-wall carbon nanotube bundles. *Physical Review Letters* **86** 3056-9, 2001.
- [20] Thess A, Lee R, Nikolaev P, Dai HJ, Petit P, Robert J, Xu CH, Lee YH, Kim SG, Rinzler AG, Colbert DT, Scuseria GE, Tomanek D, Fischer JE and Smalley RE, Crystalline ropes of metallic carbon nanotubes. *Science* **273** 483-7, 1996.
- [21] Falvo MR, Clary G, Helser A, Paulson S, Taylor RM, Chi V, Brooks FP, Washburn S, and Superfine R, Nanomanipulation experiments exploring frictional and mechanical properties of carbon nanotubes. *Microscopy and Microanalysis* **4** 504-12, 1998.
- [22] Li C and Chou T-W. Elastic moduli of multi-walled carbon nanotubes and the effect of van der Waals forces. *Composites Science and Technology* **63** 1517-24, 2003.
- [23] Qin LC, Zhao X, Hirahara K, Miyamoto Y, Ando Y and Iijima S, The smallest carbon nanotubes. *Nature* **408** 50, 2000.
- [24] Tang ZK, Zhang L, Wang N, Zhang XX, Wen GH, Li GD, Wang JN, Chan CT, Sheng P, Superconductivity in 4 Angstrom Single-Walled Carbon Nanotubes. *Science* **292** 2462-5, 2001.
- [25] Iijima S, Carbon nanotubes: past, present, and future. *Physica B* **323** 1-5, 2002.
- [26] Lin Y, Taylor S, Li H, Fernando KAS, Qu L, Wang W, Gu L, Zhou B and Sun YP. Advances toward bioapplications of carbon nanotubes. *Journal of Materials Chemistry* **14** 527-41, 2004.

- [27] Tsang SC, Davis JJ, Green MLH, Hill HAO, Leung YC and Sadler PJ, Immobilization of small proteins in carbon nanotubes: high-resolution transmission electron microscopy study and catalytic activity. *Journal of the Chemical Society, Chemical Communications* **17** 1803, 1995.
- [28] Li J, Ng HT, Cassell A, Fan W, Chen H, Ye Q, Koehne J, Han J and Meyyappan M, Carbon Nanotube Nanoelectrode Array for Ultrasensitive DNA Detection. *Nano Letters* **3** 597-602, 2003.
- [29] Gooding JJ, Wibowo R, Liu J, Yang W, Losic D, Orbons S, Mearns FJ, Shapter JG and Hibbert DB. Protein Electrochemistry Using Aligned Carbon Nanotube Arrays. *Journal of the chemical Society* **125** 9006-7, 2003.
- [30] Wong SS, Joselevich E, Woolley AT, Cheung CC and Lieber CM, Covalently functionalized nanotubes as nanometre- sized probes in chemistry and biology. *Nature* **394** 52, 1998.
- [31] Baughman RH, Cui C, Zakhidov AA, Iqbal Z, Barisci JN, Spinks GM, Wallace GG, Mazzoldi A, De Rossi D, Rinzler AG, Jaschinski O, Roth S and Kertesz M, Carbon Nanotube Actuators. *Science* **284** 1340-4, 1999.
- [32] Mattson MP, Haddon RC and Rao AM, Molecular Functionalization of Carbon Nanotubes and Use as Substrates for Neuronal Growth. *Journal of Molecular Neuroscience* **14** 175-82, 2000.
- [33] Smalley RE and Smith K, Buckytubes and Their Future. *Advanced Space Workshop*, Marshall Space Flight Center: NASA, 1999.
- [34] Treacy MMJ, Ebbesen TW and Gibson JM, Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature* **381** 678-80, 1996.
- [35] Krishnan A, Dujardin E, Ebbesen TW, Yianilos PN and Treacy MMJ, Young's modulus of single-walled nanotubes. *Physical Review B* **58** 14013, 1998.
- [36] Eric W, Wong PES, Charles M and Lieber. Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes. *Science* **277** 1971-5, 1997.
- [37] Yu M-F, Lourie O, Dyer M, Moloni K, Thomas F, Kelly T and Ruoff RS, Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load. *Science* **287** 637-40, 2000.
- [38] Salvetat JP, Bonard JM, Thomson NH, Kulik AJ, Forro L, Benoit W and Zuppiroli L, Mechanical properties of carbon nanotubes. *Applied Physics A* **69** 255-60, 1999.

-
- [39] Ponchral P, Wang ZL, Ugarte D and deheer WA, Electrostatic deflections and electromechanical resonances of carbon nanotube. *Science* **283** 1513-6, 1999.
 - [40] Jorio A, Pimenta MA, Filho AGS, Saito R, Dresselhaus G and Dresselhaus MS, Characterizing carbon nanotube samples with resonance Raman scattering. *New Journal of Physics* **5** 1-17, 2003.
 - [41] Maultzsch J, Reich S, Thomsen C, Requardt H and Ordejon P, Phonon dispersion in graphite. *Physical Review Letters* **92** 075501, 2004.
 - [42] Jorio A, Saito R, Hafner JH, Lieber CM, Hunter M, McClure T, Dresselhaus G and Dresselhaus MS, Structural (n,m) determination of isolated single-wall carbon nanotubes by resonant Raman scattering. *Physical Review Letters* **86** 1118-21, 2001.
 - [43] Milnera M, Kurti J, Hulman M and Kuzmany H, Periodic resonance excitation and intertube interaction from quasi-continuous distributed helicities in single-wall carbon nanotubes. *Physical Review Letters* **84** 1324-7, 2000.
 - [44] Fantini C, Jorio A, Souza M, Strano MS, Dresselhaus MS and Pimenta MA, Optical Transition Energies for Carbon Nanotubes from Resonant Raman Spectroscopy: Environment and Temperature Effects *Physical Review Letters* **93** 147406, 2004.
 - [45] Kurti J, Zolyomi V, Kertesz M and Sun GY. The geometry and the radial breathing mode of carbon nanotubes: beyond the ideal behaviour. *New Journal of Physics* **5** 125, 2003.
 - [46] Dong Q, Wong GJ, Liu WK, Yu M-F and Ruoff RS, Mechanics of carbon nanotubes. *Applied Mechanics Review* **55** 495-553, 2002.
 - [47] Ohno K, Esfarjani K and Kawazoe Y, Computational materials science: from *ab initio* to Monte Carlo methods: Springer, 1999.
 - [48] Koster GF and Slater JC, Wave Functions for Impurity Levels. *Physical Review* **94** 1392, 1954.
 - [49] Harrison WA, Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond. New York: Dover, 1989.
 - [50] M. Menon and Subbaswamy KR, Universal parameter tight binding molecular-dynamics-application to C-60. *Physical Review Letters* **67** 3487-90, 1991.
 - [51] AP Sutton, Finnis MW, Pettifor DG and Ohta Y, The tight-binding bond model. *Journal of Physics C-Solid State Physics* **21** 35-66, 1988.

-
-
- [52] M Menon and Subbaswamy KR, Nonorthogonal tight-binding molecular-dynamics scheme for silicon with improved transferability. *Physical Review B* **55** 9231-4, 1997.
- [53] Wainwright B and Alder J. Phase transition for a hard sphere system. *Journal of Chemical Physics* **27** 1208-9, 1957.
- [54] Verlet L, Computer experiments on classical fluids. I. Thermodynamical properties of lennard-jones molecules. *Physical Review* **159** 98, 1967.
- [55] Allinger NL, Conformational-analysis MM2-Hydrocarbon force-field utilizing v1 and v2 torsional terms. *Journal of the American Chemical Society* **99** 8127-34, 1977.
- [56] Allinger NL, Yuh YH and Lii JH, Molecular mechanics-The mm3 force-field for hydrocarbons. *Journal of the American Chemical Society* **111** 8551-66, 1989.
- [57] Abell GC. Empirical chemical pseudopotential theory of molecular and metallic bonding. *Physical Review B* **31** 6184-96, 1985.
- [58] Tersoff J, New empirical approach for the stucture and energy of covalent systems. *Physical Review B* **37** 6991-7000, 1988.
- [59] Tersoff J, Empirical Interatomic Potential for Carbon, with Applications to Amorphous Carbon. *Physical Review Letters* **61** 2879-82, 1998.
- [60] Nordlund K, Keinonen J and Mattila T. Formation of ion irradiation induced small-scale defects on graphite surfaces. *Physical Review Letters* **77** 699-702, 1996.
- [61] Robertson DH, Brenner DW and Mintmire JW, Energetics of nanoscale graphitic tubules. *Physical Review B* **45** 12592-5, 1992.
- [62] Robertson DH. Brenner DW and White CT, On the way to fullerenes-molecular-dynamics study of the curling and closure of graphite ribbons. *Journal of Physical Chemistry* **96** 6133-5, 1992.
- [63] Harrison JA, White CT, Colton RJ and Brenner DW, Investigation of the atomic-scale friction and energy-dissipation in diamond using molecular-dynamics. *Thin Solid Films* **260** 205-11, 1995.
- [64] Brenner DW, The Art and Science of an Analytic Potential. *Physica status solidi (b)* **217** 23-40, 2000.
- [65] Brenner DW, Shenderova OA, Harrison JA, Stuart SJ, Ni B and Sinnott SB, A second-generation reactive empirical bond order (REBO) potential energy

- expression for hydrocarbons. *Journal of Physics: Condensed Matter* **14** 783–802, 2002.
- [66] Jones JE, On the determination of molecular fields-i from the variation of the viscosity of a gas with temperature. Royal Society, 441, 1924.
- [67] Falvo MR, Steele J, Taylor RM and Superfine R, Evidence of commensurate contact and rolling motion: AFM manipulation studies of carbon nanotubes on hpg. *Tribology Letters* **9** 73-6, 2000.
- [68] Kolmogorov AN and Crespi VH, Smoothest bearings: Interlayer sliding in multiwalled carbon nanotubes. *Physical Review Letters* **85** 4727-30, 2000.
- [69] Peng ZW, Ewis CS, Huang MJ, Waldman M and Hagler AT, Derivation of class ii force fields. 4. van der Waals parameters of Alkali metal cations and Halide anions. *Journal of Physical Chemistry A* **101** 7243-52, 1997.
- [70] Mackerell AD, Wiorkiewicz-kuczera J and Karplus M, An all-atom empirical energy function for the simulation of nucleic-acids. *Journal of the American Chemical Society* **117** 11946-75, 1995.
- [71] Mayo SL, Olafson BD and Goddard WA, Deriding - a generic force-field for molecular simulation. *Journal of Physical Chemistry* **94** 8897-909, 1990.
- [72] Halgren TA, Merck molecular force field. I. basis, form, scope, parameterization, and performance of MMFF94. *Journal of Computational Chemistry* **17** 490-519, 1996.
- [73] Cui WL, Li FB and Allinger NL, Simulation of conformational dynamics with the mm3 force-field -the pseudorotation of cyclopentane. *Journal of the American Chemical Society* **115** 2943-51, 1993.
- [74] Nevins N, Li JH and Allinger NL, Molecular mechanics (MM4) calculations on conjugated hydrocarbons. *Journal of Computational Chemistry* **17** 695-729, 1996.
- [75] Jorgensen WL, Maxwell DS and Tiradorives J, Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *Journal of the American Chemical Society* **118** 11225-36, 1996.
- [76] Bearpark MJ, Robb MA, Bernardi F and Olivucci M, Molecular mechanics valence-bond methods for large active spaces-application to conjugated polycyclic-hydrocarbons. *Chemical Physics Letters* **217** 513-9, 1994.

-
-
- [77] Rappe AK, Casewit CJ, Colwell KS, Goddard WA and Skiff WM, UFF, a full periodictable force-field for molecular mechanics and molecular dynamics simulations. *Journal of the American Chemical Society* **114** 10024-35, 1992.
- [78] Cleveland T and Landis CR, Valence bond concepts applied to the molecular mechanics description of molecular shapes. *Journal of the American Chemical Society* **118** 6020-30, 1996.
- [79] Atluri SN and Shen S, Computational Nano-mechanics and Multi-scale Simulation. *Computers, Materials & Continua* **1** 59-90, 2004.
- [80] Tadmor EB, Smith GS, Bernstein N and Kaxiras E, Mixed finite element and atomistic formulation for complex crystals. *Physical Review B* **59** 235-45, 1999.
- [81] Miller R, Tadmor EB, Phillips R and Ortiz M, Quasi-continuum simulation of fracture at the atomic scale. *Modelling Simulation Material Science Engineering* **6** 607-38, 1998.
- [82] Shenoy VB, Miller R, Tadmor EB, Phillips R and Ortiz M, Quasi continuum models of interfacial structure and deformation. *Physical Review Letters* **80** 742-5, 1998.
- [83] Rodney D and Phillips R, Structure and strength of dislocation junctions: An atomic level analysis. *Physical Review Letters* **82** 704-1707, 1999.
- [84] Shin CS, Fivel MC, Rodney D, Phillips R, Shenoy VB and Dupuy L, Formation and strength of dislocation junctions in fcc metals: A study by dislocation dynamics and atomistic simulations. *Journal de Physique IV* **11** 19-26, 2001.
- [85] Tadmor EB, Phillips R and Ortiz M, Mixed atomistic and continuum models of deformation in solids. *Langmuir* **12** 4529-34, 1996.
- [86] Liu WK, Uras RA and Chen Y, Enrichment of the finite element method with the reproducing kernel particle method. *ASME Journal of Applied Mechanics* **64** 861-70, 1997.
- [87] Shenoy VB, Miller R, Tadmor EB, Rodney D, Phillips R and Ortiz M, An adaptive finite element approach to atomic-scale mechanics-the quasi continuum method. *Journal of the Mechanics and Physics of Solids* **47** 611-42, 1999.
- [88] Arroyo M and Belytschko T, An atomistic-based finite deformation membrane for single layer crystalline films. *Journal of the Mechanics and Physics of Solids* **50** 1941-77, 2002.

-
-
- [89] Li SF and Liu WK, Meshfree and particle methods. *Applied Mechanics Review* **55** 1-34, 2002.
- [90] Odegard GM, Harik VM, Wise KE and Gates TS, Constitutive Modelling of Nanotube-Reinforced Polymer Composite Systems. NASA, 2001.
- [91] Odegard GM, Thomson SG, Nicholson LM and Wise KE, Equivalent-continuum modelling of nano-structured materials. *Composites Science and Technology* **62** 1869–80, 2002.
- [92] Odegard GM, Thomson SG and Wise KE, Constitutive modelling of nanotube-reinforced polymer composites. *American Institute of Aeronautics and Astronautics* **1427** 1-13, 2002.
- [93] Qian, Liu WK and Ruoff RS, Mechanics of C60 in Nanotubes. *Journal of Physics Chemistry B* **105** 10753-8, 2001.
- [94] Abraham FF, Broughton JQ, Bernstein N and Kaxiras E, Spanning the continuum to quantum length scales in a dynamic simulation of brittle fracture. *EuroPhysics Letters* **44** 783-7, 1998.
- [95] Broughton JQ, Abraham FF, Bernstein N and Kaxiras E. Concurrent coupling of length scales: Methodology and applications. *Physical Review B* **60** 2391-403, 1999.
- [96] Raffi-Tabar H, Hua L and Cross M, Multi-scale numerical modelling of crack propagation in two-dimensional metal plate. *Material Science and Technology* **14** 544-8, 1998.
- [97] Raffi-Tabar H, Hua L and Cross M, A multi-scale atomistic continuum modelling of crack propagation in a two-dimensional macroscopic plate. *Journal of Physics: Condensed Matter* **10** 2375-87, 1998.
- [98] Rudd RE and Broughton JQ, Coarse-grained molecular dynamics and the atomic limit of finite elements. *Physical Review B* **58** R5893-R6, 1998.
- [99] Rudd RE and Broughton JQ, Concurrent coupling of length scales in solid state systems. *physica status solidi (b)* **217** 251-91, 2000.
- [100] Liu WK, Zhang Y and Ramirez MR, Multi-scale finite element methods. *International Journal for Numerical Methods in Engineering* **32** 969-90, 1991.
- [101] Hao S, Liu WK and Qian D, Localization-induced band cohesive model. *ASME Journal of Applied Mechanics* **67** 803-12, 2000.

-
-
- [102] Wagner GJ, Meos N, Liu WK and Belytschko T, The extended finite element method for rigid particles in stokes flow. *International Journal for Numerical Methods in Engineering* **51** 293-313, 2001.
- [103] Wagner GJ and Liu WK, Hierarchical enrichment for bridging scales and mesh-free boundary conditions. *International Journal for Numerical Methods in Engineering* **50** 507-24, 2001.
- [104] Sohlberg K, Sumpter BG, Tuzun RE and Noid DW, Continuum methods of mechanics as a simplified approach to structural engineering of nanostructures. *Nanotechnology* **9** 30-6, 1998.
- [105] Ru CQ. Effective bending stiffness of carbon nanotubes. *Physical Review B* **62** 9973-6, 2000.
- [106] Govindjee S and Sackman JL, On the use of continuum mechanics to estimate the properties of nanotubes. *Solid State Communications* **110** 227–30, 1999.
- [107] Ru CQ, Axially compressed buckling of a double walled carbon nanotube embedded in an elastic medium. *Journal of Mechanics and Physics of Solids* **49** 1265-79, 2001.
- [108] Liu YJ and Chen XL, Evaluations of the effective material properties of carbon nanotube-based composites using a nanoscale representative volume element. *Mechanics of Materials* **35** 69–81, 2003.
- [109] Yakobson BI and Barbec CJ and Bernholc J, Nanomechanics of Carbon Tubes: Instabilities beyond Linear Response. *Physical Review Letters* **76** 2511-4, 1996.
- [110] Wang Y, Sun C, Sun X, Hinkley J, Odegard GM and Gates TS, Nano-Scale finite element analysis of polymer networks. *American Institute of Aeronautics and Astronautics* **1318** 1-10, 2002.
- [111] Harik VM, Gates TS and Nemeth MP, Applicability of the continuum -shell theories to the mechanics of carbon nanotubes. *American Institute of Aeronautics and Astronautics* **1429** 1-11, 2002.
- [112] Dequesnes M, Rotkin SV and Aluru NR, Calculation of pull-in voltages for carbon-nanotube-based nanoelectromechanical switches. *Nanotechnology* **13** 120-31, 2002.
- [113] Kong J, Franklin NR, Zhou C, Chapline MG, Peng S, Cho K and Dai H, Nanotube Molecular Wires as Chemical Sensors. *Science* **287** 622-5, 2000.
- [114] Kim P and Lieber CM, Nanotube Nanotweezers. *Science* **286** 2148-50, 1999.

- [115] Huang XMH, Christian A, Mehregany M, Roukes ML, Nanodevice motion at microwave frequencies. *Nature* **421** 496, 2003.
- [116] Li C and Chou T-W, Vibrational behaviors of multiwalled-carbon-nanotube-based nanomechanical resonators. *Applied Physics Letters* **84** 121-3, 2004.
- [117] Li C and Chou T-W, Single-walled carbon nanotubes as ultrahigh frequency nanomechanical resonators. *Physical Review B* **68** 073405-3, 2003.
- [118] Yoon J, Ru CQ and Mioduchowski A, Terahertz vibration of short carbon nanotubes modelled as Timoshenko beams. *Transactions of the ASME* **72** 10-7, 2005.
- [119] Kang JW, Lee JH, Lee HJ and Hwang HJ, A study on carbon nanotube bridge as a electromechanical memory device. *Physica E* **27** 332–40, 2005.
- [120] Badzey RL, Zolfagharkhani G, Gaidarzhy A and Mohantya P, A controllable nanomechanical memory element. *Applied Physics Letters* **85** 3587-9, 2004.
- [121] Liu JZ, Zheng Q and Jiang Q, Effect of a rippling mode on resonances of carbon nanotubes. *Physical Review B* **86** 4843-6, 2001.
- [122] Zhao Y, Ma C-C, Wong LH, Chen G, Xu Z, Zheng Q, Jiang Q and Chwang AT, Energy exchanges in carbon nanotube oscillators. *Nanotechnology* **17** 1032-5, 2006.
- [123] Seidel RV, Graham AP, Kretz J, Rajasekharan B, Duesberg GS, Liebau M, Unger E, Kreupl F and Hoenlein W, Sub-20 nm Short Channel Carbon Nanotube Transistors. *Nano Letters* **5** 147-50, 2005.
- [124] Postma HWC, Teepen T, Yao Z, Grifoni M and Dekker C, Carbon Nanotube Single-Electron Transistors at Room Temperature. *Science* 293:94, 2000.
- [125] Rueckes T, Kim K, Joselevich E, Tseng GY, Cheung C and Lieber CM, Carbon Nanotube-Based Nonvolatile Random Access Memory for Molecular Computing. *Science* **289** 94-7, 2000.
- [126] Lifshitz R and Roukes ML, Thermoelastic damping in micro- and nanomechanical systems. *Physical Review B* **61** 5600-9, 2000.
- [127] Ekincia KL and Roukes ML, Nanoelectromechanical systems. *Review of Scientific Instruments* **76** 061101-12, 2005.
- [128] Bhiladvala RB and Wang JW. Effect of fluids on the Q factor and resonance frequency of oscillating micrometer and nanometer scale beams. *Physical Review E* **69** 036307-5, 2004.

-
-
- [129] Jiang H, Yu M-F, Liu B and Huang Y, Intrinsic Energy Loss Mechanisms in a Cantilevered Carbon Nanotube Beam Oscillator. *Physical Review Letters* **93** 185501-4, 2004.
- [130] Galanov BA, Galanov SB and Gogotsi Y. Stress-strain state of multiwall carbon nanotube under internal pressure. *Journal of Nanoparticle Research* **4** 207–14, 2002.
- [131] Mao Z and Sinnott SB, A Computational Study of Molecular Diffusion and Dynamic Flow through Carbon Nanotubes. *Journal of Physics Chemistry B* **104** 4618-24, 2000.
- [132] Supple S and Quirke N, Rapid Imbibition of Fluids in Carbon Nanotubes. *Physical Review Letters* **90** 214501-4, 2003.
- [133] Tuzuny RE, Noidy DW, Sumptery BG and Merkle RC, Dynamics of fluid flow inside carbon nanotubes. *Nanotechnology* **7** 241–6, 1996.
- [134] Yoon J, Ru CQ and Mioduchowski A. Vibration and instability of carbon nanotubes conveying fluid. *Composites Science and Technology* **65** 1326–36, 2005.
- [135] Lee KH, Koblinski P and Sinnott SB, Deflection of Nanotubes in Response to External Atomic Collisions. *Nano Letters* **5** 263-8, 2005.
- [136] Walther JH, Werder T, Jaffe RL and Koumoutsakos P, Hydrodynamic properties of carbon nanotubes. *Physical Review E* **69**:062201-4, 2004.
- [137] Ghosh S, Sood AK, Ramaswamy S and Kumar N, Flow-induced voltage and current generation in carbon nanotubes. *Physical Review B* **70** 205423-4, 2004.
- [138] Kalra A, Garde S and Hummer G, Osmotic water transport through carbon nanotube membranes. *Proceedings of the National Academy of Sciences of the USA (PNAS)* 10175-80, 2003.
- [139] Hummer G. Simulations of nanoscale flow: water, proton, and biopolymer transport through carbon nanotube membranes. *SPIE*, p. 214-9, 2005.
- [140] Majumder M, Chopra N, Andrews R and Hinds BJ, Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes. *Nature* **438** 44, 2005.
- [141] Shen L and Li J, Transversely isotropic elastic properties of single-walled carbon nanotubes. *Physical Review B* **69** 045414-10, 2004.

-
-
- [142] Yu M-F, Files BS, Arepalli S and Rouff RS, Tensile Loading of Ropes of Single Wall Carbon Nanotubes and their Mechanical Properties. *Physical Review Letters* **84** 5552-5, 2000.
- [143] Halicioglu T, Stress calculations for carbon nanotubes. *Thin Solid Films* **312** 11-4, 1998.
- [144] Sammalkorpi M, Krashennnikov A, Kuronen A, Nordlund K and Kaski K, Mechanical properties of carbon nanotubes with vacancies and related defects. *Physical Review B* **70** 245416-8, 2004.
- [145] Zhou G, Duan WH and Gu BL, First-principles study on morphology and mechanical properties of single-walled carbon nanotube. *Chemical Physics Letters* **333** 344-9, 2001.
- [146] Cooper CA and Young RJ, Investigation into the deformation of carbon nanotubes and their composites through the use of Raman spectroscopy. *SPIE*, p. 172, 2000.
- [147] Lier GV, Alsenoy CV, Doren VV and Geerlings P, Ab initio study of the elastic properties of single-walled carbon nanotubes and graphene. *Chemical Physics Letters* **326** 181-5, 2000.
- [148] Belytschko T, Xiao SP, Schatz GC and Ruoff RS. Atomistic simulations of nanotube fracture. *Physical Review B* **65** 235430-8, 2002.
- [149] Mielke SL, Troya DT, Zhang S, Li J-L, Xiao S, Car R and Ruoff RS, George C. Schatz, Ted Belytschko. The role of vacancy defects and holes in the fracture of carbon nanotubes. *Chemical Physics Letters* **390** 413-20, 2004.
- [150] Ozaki T, Iwasa Y and Mitani T, Stiffness of Single-Walled Carbon Nanotubes under Large Strain. *Physical Review Letters* **84** 1712-5, 2000.
- [151] Cornwell CF and Wille LT, Elastic properties of single-walled carbon nanotubes in compression. *Solid State Communications* **101** 555-8, 1997.
- [152] Lu JP, Elastic Properties of Carbon Nanotubes and Nanoropes. *Physical Review Letters* **79** 1297-300, 1997.
- [153] Popov VN and Van DVE, Elastic properties of single-walled carbon nanotubes. *Physical Review B* **61** 3078, 2000.
- [154] Yao N and Lordi V, Young's modulus of single-walled carbon nanotubes. *Journal of Applied Physics* **84** 1939-43, 1998.

-
-
- [155] Ogata S and Shibutani Y, Ideal tensile strength and band gap of single-walled carbon nanotubes. *Physical Review B* **68** 165409-4, 2003.
- [156] Li C and Chou T-W, A structural mechanics approach for the analysis of carbon nanotubes. *International Journal of Solids and Structures* **40** 2487–99, 2003.
- [157] Cho WST. Bending and shear moduli of single-walled carbon nanotubes. *Finite Elements in Analysis and Design* **42** 404-13, 2006.
- [158] Jenga Y-R, Tsai P-C and Fang T-H. Effects of temperature and vacancy defects on tensile deformation of single-walled carbon nanotubes. *Journal of Physics and Chemistry of Solids* **65** 1849–56, 2004.
- [159] Daniel S-P, Emilio A, Jose MS, Rubio A and Pablo O, Ab initio structural, elastic, and vibrational properties of carbon nanotubes. *Physical Review B* **59** 12678-1288, 1999.
- [160] Tomblor TW, Chou Z, Alexseyev L, Kong J, Dai D, Liu L, Jayanthi CS, Tang M and Wu SY, Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation. *Nature* **405** 769, 2000.
- [161] Jin Y and Yuan FG, Simulation of elastic properties of single-walled carbon nanotubes. *Composites Science and Technology* **63** 1507–15, 2003.
- [162] Hernandez E, Goze C, Bernier P and Rubio A, Elastic properties of C and $B_xC_yN_z$ composite nanotubes. *Physical Review Letters* **80** 4502-5, 1998.
- [163] Lourie O and Wagner HD, Evaluation of Young's modulus of carbon nanotubes by micro-Raman spectroscopy. *Journal of Material Resources* **13** 2418-22, 1998.
- [164] Lu JP, Novel Magnetic Properties of Carbon Nanotubes. *Physical Review Letters* **74** 1123-7, 1995.
- [165] Kudin KN, Scuseria GE and Yakobson BI, C₂F, BN, and C nanoshell elasticity from ab initio computations. *Physical Review B* **64** 235406-10, 2001.
- [166] Tu Z-C and Ou-Yang ZC, Single-walled and multiwalled carbon nanotubes viewed as elastic tubes with the effective Young's moduli dependent on layer number. *Physical Review B* **65** 233407-4, 2002.
- [167] Pantano A, Parks DM and Boyce MC, Mechanics of deformation of single-walled and multi-wall carbon nanotubes. *Journal of the Mechanics and Physics of Solids* **52** 789 – 821, 2004.

-
-
- [168] Zhou X, Zhou JJ and Ou-Yang ZC, Strain energy and Young's modulus of single-wall carbon nanotubes calculated from electronic energy band theory. *Physical Review B* **62** 13692-6, 2000.
- [169] Tserpes KI and Papanikos P, Finite element modeling of single-walled carbon nanotubes. *Composites: Part B* **36** 468–77, 2005.
- [170] Saito R, Dresselhaus G and Dresselhaus MS, *Physical Properties of Carbon Nanotubes*. London: Imperial College Press, 1998.
- [171] Hummer G, Rasaiah and Noworyta JP, Water conduction through the hydrophobic channel of a carbon nanotube. *Nature* **414** 188-90, 2001.
- [172] Rappe AK and Casewit CJ, *Molecular mechanics across chemistry*. California: University Science Books, 1997.
- [173] Changa T and Gaob H, Size-dependent elastic properties of a single-walled carbon nanotube via a molecular mechanics model. *Journal of the Mechanics and Physics of Solids* **51** 1059–74, 2003.
- [174] Kelly BT, *Physics of Graphite*. London: Applied Science, 1981.
- [175] Arroyo M and Belytschko T, Finite crystal elasticity of carbon nanotubes based on the exponential Cauchy-Born rule. *Physical Review B* **69** 115415-11, 2004.
- [176] Zhang P, Huang Y, Geubelle PH, Klein PA, Hwang KC. The elastic modulus of single-wall carbon nanotubes: a continuum analysis incorporating interatomic potentials. *International Journal of Solids and Structures* **39** 3893–906, 2002.
- [177] Liu B, Huang Y, Jiang H, Qu S and Hwang KC, The atomic-scale finite element method. *Comput Methods Applied Mechanics of Engineering* **193** 1849–64, 2004.
- [178] Liew KM, Wong CH, He XQ, Tan MJ and Meguid SA, Nanomechanics of single and multiwalled carbon nanotubes. *Physical Review B* **69** 115429-8, 2004.
- [179] Xiao T, Xu X and Liao K, Characterization of nonlinear elasticity and elastic instability in single-walled carbon nanotubes. *Journal of Applied Physics* **95** 8145-8, 2004.
- [180] Brent R, *Algorithms for Minimization without Derivatives*. Dover: Prentice Hall, 2002.
- [181] Friesecke F and Theil, Validity and Failure of the Cauchy-Born Hypothesis in a Two-Dimensional Mass-Spring Lattice. *Journal of Nonlinear Science* **12** 445-78, 2002.
- [182] Jones RM, *Mechanics of composite material*. Philadelphia: Taylor & Francis, 1999.

-
-
- [183] Landau LD, Theory of elasticity. Oxford, Newyork: Pergamon Press, 1986.
- [184] Wang Q, Effective in-plane stiffness and bending rigidity of armchair and zigzag carbon nanotubes. *International Journal of Solids and Structures* **41** 5451–61, 2004.
- [185] Mathematica, Wolfram Research Inc.
- [186] Ackland GJ, Warreny MC and Clark SJ, Practical methods in ab initio lattice dynamics. *Journal of Physics: Condensed Matter* **9** 7861–72, 1997.
- [187] Kurti J, Kresse G and Kuzmany H, First-principles calculations of the radial breathing mode of single-wall carbon nanotubes. *Physical Review B* **58** R8869, 1998.
- [188] Zheng Q and Jiang Q, Multiwalled Carbon Nanotubes as Gigahertz Oscillators. *Physical Review Letters* **88** 045503-3, 2002.
- [189] Cumings J and Jettl A, Low-Friction Nanoscale Linear bearing Realized Multiwall carbon nanotubes. *Science* **289** 602-4, 2000.
- [190] Yoon J, Ru CQ and Mioduchowski A, Vibration of an embedded multiwall carbon nanotube. *Composites Science and Technology* **63** 1533–42, 2003.
- [191] Li C and Chou T-W. Mass detection using carbon nanotube-based nanomechanical resonators. *Applied Physics Letters* **84** 5246-8, 2004.
- [192] Liu B, Hunag J, Huang Y, Qu S, Yu M-F and Hwang KC. Atomic-scale finite element method in multiscale computation with applications to carbon nanotubes. *Physical Review B* **72** 035435-8, 2005.
- [193] Dresselhaus MS, Dresselhaus D and Saito R, Physics of carbon nanotubes. *Carbon* **33** 883-91, 1995.
- [194] Ugural AC. Advanced strength and applied elasticity. New Jersey: Prentice-Hall Inc., 2003.
- [195] Bathe KJ, Finite element procedures. New Jersey: Prentice Hall Inc., 1996.
- [196] Meirovitch L, Principles and Techniques of vibrations. New Jersey: Prentice Hall Inc., 2000.
- [197] Reich S, Thomson C and Maultzsch J, Carbon nanotubes: Basic concepts and physical properties. Weinheim: Wiley-VCH, 2004.
- [198] Strano MS, Doorn SK, Haroz EH, Kittrell C, Hauge RH and Smalley RE, Assignment of (n, m) Raman and optical features of metallic single-walled carbon nanotubes. *Nano Letters* **3** 1091-96, 2003.

-
-
- [199] Kuzmany H, Burger B, Hulman M, Kürti J, Rinzler AG and Smalley RE, Spectroscopic analysis of different types of single-wall carbon nanotubes. *EuroPhysics Letters* **44** 518-24, 1998.
- [200] Zhang Y, Guirong L and Han X, Transverse vibrations of double-walled carbon nanotubes under compressive axial load. *Physics Letters A* **340** 258–66, 2005.
- [201] Mao Z and Sinnott SB, Predictions of a Spiral Diffusion Path for Nonspherical Organic Molecules in Carbon Nanotubes. *Physical Review Letters* **89** 278301-4, 2002.
- [202] Solares SD and Blanco M and Goddard WA, Design of a nanomechanical fluid control valve based on functionalized silicon cantilevers: coupling molecular mechanics with classical engineering design. *Nanotechnology* **15** 1405–15, 2004.
- [203] Ghosh S, Sood AK and Kumar N, Carbon Nanotube Flow Sensors. *Science* **299** 1042-4, 2003.
- [204] Skoulidas A, Ackerman DM, Johnson KJ and Sholl DS, Rapid transport of gases in carbon nanotubes. *Physical Review Letters* **89**, 2002.
- [205] Wang Q and Varadan VK. Stability analysis of carbon nanotubes probes for an atomic force microscope via a continuum model. *Smart material and Structures* **14** 1196-203, 2005.
- [206] MATLAB, The Mathworks Inc., 2002.
- [207] Chen SS, Flow induced vibration of circular cylindrical structures. Washington: Hemisphere, 1987.
- [208] Rasziller H and Drust F, Coriolis effect in mass flowmeter. *Archives of applied mechanics* **61** 192-214, 1991.
- [209] Sultan G and Hunp J, Modelling of the coriolis mass flowmeter. *Journal of Sound and Vibration* **132** 473-89, 1989.