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Interfacial Boundary Conditions in Multi-Scale Simulation of Nano-materials

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Interfacial Boundary Conditions in Multiscale Simulation of Nano-materials

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Abstract

Since their discovery, carbon nanotubes have stirred an ever-growing interest among researchers due to their distinct physical properties. A number of experimental studies and computer simulation methods have led to a numerical estimate of their remarkable mechanical and electronic properties and has opened a possibility of their use in a variety of fields. The high cost of experimental studies and computational limitations of conventional single scale analyses of carbon nanotubes have further motivated researchers to explore multiscale techniques to understand of the physics of their behavior.

In this thesis, we have discussed an analytical approach to formulate multi-scale boundary conditions for quasistatic atomistic simulations of these geometrically periodic nanostructures. The nanotubes are virtually divided into coarse and fine scale regions and atomistic simulation is used only in the fine scale region. In the periodic coarse scale region, we use Discrete Fourier Transform to yield a compact formulation, in terms of the discrete convolution operators, that represents the response behavior of the coarse scale domain upon the fine/coarse scale interface. This approach facilitates use of computer simulations for the fine scale, without the requirement to model the entire coarse scale domain thus holding potential to drastic savings in computational time up to several orders of magnitude.

The robustness of the proposed multi-scale method is evident after comparison and verification of our results with bench-mark results from fully atomistic simulations under application of realistic boundary conditions.
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Chapter 1

Introduction

Carbon nanotubes (CNTs), with their high strength, high stiffness, low density and structural perfection, have opened the possibility of their use in a variety of technological applications in numerous fields of science. Since their discovery [1], much research has been aimed at harnessing the usefulness of these attractive nanostructures in the areas of nano-electronics, material reinforcements in composite structures, field emission panel display, nano-electromechanical systems (NEMS), hydrogen storage and biomechanics. The distinct structure and geometry of CNTs are closely related to their impressive physical properties.

1.1 Structure and Geometry of CNTs

CNTs are molecules composed of carbon atoms arranged in cylindrical shape, with diameters of the order of nanometers and lengths typically ranging from a few nanometers to several microns. CNTs can be visualized as sheets of graphene rolled into seamless hollow cylinders. The significant feature of the CNTs is the hexagonal arrangement of carbon atoms, which repeats itself periodically in space. The electronic configuration of carbon is such that there are four valence electrons spread in the outermost $s$ and $p$ orbitals. The formation of these isotopes of carbon can mainly be attributed to the process of $sp^2$ hybridization [2] of carbon atoms during which one $s$-orbital and two $p$-orbitals combine to form three planar hybrid $sp^2$-orbitals at $120^\circ$ to each other (figure 1.1 (a)). Each of the three orbitals forms strong covalent bonds, referred to as
the $\sigma$ bonds, with other identical carbon atoms giving rise to the periodically repeating hexagonal arrangement of carbon atoms. Figure (1.1 (b)) shows the hexagonal rings formed in a graphene sheet. The bonding structure in CNTs is similar to that in graphene but the orbitals in CNTs are not purely $sp^2$ hybridized since the curving of the hexagons rehybridizes the sigma and pi bonds there by generating an admixture.

![Diagram of bonding in graphene and CNTs](image)

**Figure (1.1) Bonding of Carbon atoms in graphene (a) $sp^2$ hybridized carbon atom in a graphene sheet, (b) Hexagonal bonding structure in a graphene layer**

The formation of these strong $\sigma$ bonds imparts high stiffness and strength to CNTs. Two major structural forms of CNTs are known to exist: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The MWCNTs can be thought of as multiple SWCNTs placed one inside the other concentrically. The out of plane weak $\pi$ bonds mainly contribute to the interlayer interactions in MWCNTs and between individual SWCNTs in nanotube bundles.
CNTs can be classified based on the orientation of the hexagonal carbon rings with respect to the tube axis. The smallest angle made by a carbon-carbon covalent bond in the hexagonal ring with respect to the nanotube axis is termed as the chiral angle ‘\( \theta \)’. Another way to identify the types of CNTs, a notation adapted from [3-5], is by assigning an integer pair \((n, m)\) to CNTs based on their diameters and chiral angles. The three categories of CNTs based on their chirality can thus be defined as shown in figure (1.2):

(a) zigzag configuration, \( \theta = 0^\circ \), \( m = 0 \); (b) chiral configuration, \( 0^\circ < \theta < 30^\circ \); (c) arm-chair configuration \( \theta = 30^\circ \), \( m = n \)

A large number of experimental studies have been carried out to study the behavior of CNTs under tension [6],[7], compression [8] and bending [9] which have helped researchers in examining, among other physical properties, their deformation modes and Young’s modulus. A detailed review of theoretical predictions and experimental measurements of mechanical properties of CNTs has recently been taken by Qian et. al [10]. Direct tensile loading tests
performed by Yu et al. [6] have yielded a mean Young’s modulus of ~1 TPa while the compressive response measured by Lourie and Wagner [8] using micro-Raman spectroscopy yielded a Young’s modulus of 2.8–3.6 TPa for SWCNTs.

However, the prohibitively high costs of experimental set-ups and tools required to work with these nano-structures have motivated researchers to use relatively inexpensive computer simulation methods. A wide variety of approaches ranging from continuum mechanics to quantum mechanics have been employed during the course of evolution of nano-materials’ studies.

Simulations based on continuum models predict material deformation and failure by implicitly averaging atomic scale mechanics and defect evolution over space and time. Although significant computational saving can be achieved in doing so, they cannot explain all experimental observations at the nano-scale, thereby necessitating further effort to relate fundamental descriptions of strength and failure properties of nano-scale materials to their atomic structures.

Atomistic simulations over the entire material domain are as yet computationally prohibitive, hence are limited to a few million atoms and time scales of the order of picoseconds. This has motivated research on multi-scale simulation methods of carbon nanotubes, wherein the atomistic simulation is used in a small sub-region (fine scale) and continuum simulation is used over the rest or all of the region (coarse scale). The basic motivation behind multi-scale analysis is thus to reduce the computational expense of the atomistic simulation approach without sacrificing accuracy of the results. The key issue in multi-scale simulation approach is then the coupling or the hand-shake between the continuum and atomistic scales.
1.2 Scope of this work

The goal of this work is to provide a meaningful virtual interface between the coarse and fine scale regions in the multi-scale simulation of carbon nanotubes, so as to eliminate the involvement of unnecessary atomic degrees of freedom over the coarse scale region. Karpov et al. [11] recently proposed a new multi-scale simulation approach which they applied to quasi-static nano-indentation of crystalline gold substrate. Their approach facilitates, through use of Discrete Fourier Transform, the elimination of the atomic degrees of freedom over the coarse scale region without involving an explicit continuum model. We extend their approach to study the behavior of carbon nanotubes under application of realistic boundary conditions. We validate the robustness of our method by comparing our results with benchmark solutions obtained through fully atomistic simulations.

1.3 Outline of this thesis

The rest of the thesis is organized as follows:

Chapter 2 reviews the simulation approaches that have been applied to the analysis of nanostructures. We emphasize the importance of the use of multi-scale techniques to overcome the limitations of single scale analysis methods. We present a brief literature review of the multi-scale schemes used till date.

Chapter 3 outlines the formulation of the proposed multi-scale method. We examine the fundamentals of the Discrete Fourier Transform and its application to periodic fields. We present how the periodicity of the coarse scale region, in a multi-scale setting, can be exploited to minimize the computational effort involved. We tie together the coarse scale solution thus
obtained to the analysis of the fine scale domain thereby facilitating retention of precision of the atomistic solution, less the ensuing heavy computational expense.

In chapter 4, we confirm the veracity of the formulation analytically by applying it to a simple one dimensional atomic chain. We provide an analytical proof to corroborate the validity of the formulation for the one-dimensional case.

In chapter 5, we extend the multi-scale formulation to study carbon nanotubes. We highlight the periodic nature of the CNTs and demonstrate the applicability of the proposed multi-scale method to investigate the behavior of nanotubes.

Chapter 6 discusses the robustness of the model through comparison of the results obtained using the new multi-scale method with those obtained using benchmark full atomistic solutions. We compare the behavior of single walled nanotubes under application of tensile, compressive, bending and twisting boundary conditions. In order to take into account the geometric imperfections in nanotubes, we artificially introduce defects in the nanotube to test and compare their performance to benchmark results.

Finally we conclude the thesis in Chapter 7 and discuss the possibilities of future work.
Chapter 2

Methods of Analysis

2.1 Finite Element Method

Finite Element (FE) method is a powerful numerical technique to solve linear as well as non-linear field problems. In the FE method, a continuum structure is discretized into a mesh of finite elements connected together through nodes and boundary conditions are imposed on the resulting mesh. The FE model is converted into a mathematical model consisting of a set of simultaneous algebraic equations, the solution of which gives the values of the desired field quantities at the nodes of the mesh. The FE method uses shape functions to interpolate the field quantities within the elements. The essence of the FE method is the solution of the equilibrium equation of the form

\[
[K].\{d\} = \{f\}
\]  

where \([K]\) represents the internal resistance of the structure to the variation of the field quantity \(\{d\}\) resulting from the application of external disturbance \(\{f\}\). With reference to structural applications, \([K]\) represents the stiffness equivalent quantity, \(\{d\}\) represents field variables like displacement and \(\{f\}\) represents the externally applied forces.

The most significant limitation of Finite Element method, however, is that the accuracy of the obtained solution is usually a function of the mesh resolution. Although FE method works well for problems at continuum scale, it demands a very high mesh resolution for problems involving
micro and nano scales. Having a fine mesh captures accurately the underlying physics in such problems but makes the computational effort too high preventing its practical use. On the other hand, a coarse mesh is incapable of capturing minute details such as defect nucleation and stress concentration, adversely affecting the accuracy of the solution.

### 2.2 Molecular Mechanics

Nanostructures are molecules which may consist of up to a few million atoms chemically bonded to each other in random or regular patterns. Every atom consists of a positively charged nucleus surrounded by a negatively charged electron cloud. The positively charged nuclei experience attractive forces exerted by the negatively charged electron clouds of the surrounding atoms. The nuclei also experience mutual repulsive forces due to presence of other positively charged nuclei in their close vicinity. Thus, each atom of the molecule sustains attractive and repulsive forces exerted on it by other constituent atoms. Forces of the likes of van der Waal’s forces contribute to the non-bonded interactions. The magnitudes of these inter-atomic forces depend on the relative distances separating the atoms. Every atom attempts to attain its minimum energy configuration by adjusting its distance form the surrounding atoms such that it is acted upon by a minimal resultant force. Any external disturbance applied to such an equilibrium configuration compels the atoms to re-orient themselves by undergoing a combination of bond-stretching or shrinkage, bond-angle bending and bond-twisting.

The phenomena of bond stretching, bond-angle bending, torsion and non-bonded interactions are shown in figure (2.1).
Figure (2.1) Bonded and non-bonded interactions between atoms of a molecule. (a) bond stretching (two body interaction) (b) bond-angle bending (multi-body interaction) (c) torsion (multi-body interaction) (d) non-bonded interactions (e.g. van der Waal’s interactions)

Any change in the relative positions of the atoms is accompanied by changes in their atomic potentials. Molecular mechanics (MM) analysis predicts such changes in the energy of a molecule under the influence of external disturbances, with the help of a mathematical model of its inter-atomic potential. The ability of the molecular mechanics model to accurately simulate the physical phenomena at atomic scale depends primarily on the choice of the empirical inter-atomic potential.
2.2.1 Inter-Atomic potentials

Constructing a mathematical model to represent the behavior of a physical system forms the basis of any computational procedure. Inter-atomic potentials are mathematical formulations to predict the energy associated with a given configuration of atoms based on their relative positions in the molecule. A change in the inter-atomic potential represents the variation of the energy of the molecular system as a function of the change of balance between the attractive and repulsive forces experienced by bonded atoms under the action of external disturbances. A wide range of empirical inter-atomic potential formulations are available in literature. Inter-atomic potentials are most commonly represented by the equation:

\[ V = \sum_{i=1}^{n} V(|\vec{r}_{ij}|) \]  

(2.2)

where \( |\vec{r}_{ij}| = |\vec{x}_j - \vec{x}_i| \) such that, for any given configuration of an n-atom molecular system, \( \vec{x}_i \) is the position vector of the \( i^{th} \) atom and \( \vec{x}_j \) is the position vector of any other atom j within a close vicinity of atom i. Inter-atomic potentials are classified based on whether they take into account the bonded interactions or non-bonded interactions. They have also been classified based on whether they account for two body interactions or multi-body interactions. The potential due to Morse[12] is a pair wise/two-body potential while the Tersoff [13-15] and Brenner [16] models are examples of potentials that include the many body effects. The Lennard-Jones model [17] predicts the energies of atomic pairs in absence of physical bonding between each other (non-bonded interactions) and has been widely used in treating interlayer interactions.
2.2.2 Molecular Dynamics

Molecular dynamics (MD) is a computational technique to determine the time evolution of the interacting atoms under the action of external forces by integrating their equations of motion. Molecular dynamics employs the laws of classical mechanics, most notably the Newton's law: 

\[ F_i = m_i a_i \] 

for each atom \( i \) in a system of \( n \) atoms. Here, \( m_i \) is the atomic mass, \( a_i = d^2 r_i / dt^2 \) its acceleration, and \( F_i \) the force acting on it due to interactions with other atoms. Molecular mechanics analysis is used to supply the potential energy \( (V) \) for molecular dynamics computations on large molecules. Forces on the interacting atoms are derived as gradients of the potential with respect to atomic degrees of freedom:

\[ F_i = -\nabla_i V(r_1, r_2, ..., r_n) \]  

(2.3)

With the knowledge of the forces acting on atoms, their accelerations are determined using the Newton’s law. Integration of the equations of motion then yields a trajectory that describes the positions, velocities and accelerations of the particles as they vary with time. The engine of molecular dynamics technique is its time integration algorithm, required to integrate the equations of motion of the interacting particles. Numerous numerical algorithms like the Verlet Algorithm, Leapfrog Algorithm, Beeman’s algorithm and the Velocity Verlet algorithm have been developed for integrating the equations of motion.

2.2.3 Energy Minimization

Another alternative to the time integration solution is the energy minimization technique. The property of bonded atoms to assume their minimum energy configuration is harnessed in energy
minimization method to solve boundary value problems involving nano-structures. Differentiation of the inter-atomic potential equation with respect to the degrees of freedom of the atoms leads to determination of the force equation, which yields forces acting on individual atoms. Determination of relative positions of atoms that yield minimum resultant forces under given boundary conditions ensures minimum energy and thus equilibrium configuration for the molecule. The main advantage of using energy minimization technique is to obtain the equilibrium configuration with much less computations than molecular dynamics technique.

2.3 Multi-scale analysis

2.3.1 Need for multi-scale analysis

Even with tremendous increase in the available computational power, the atomistic simulations are still limited to the order of about $10^8$ atoms for a few nanoseconds. Use of classical FE method for nano-structures is restricted by the high cost of mesh resolutions required for acceptable accuracy. As a result, the experimental observations can not be compared directly with simulation results due to the huge difference in the length and time scales. A growing number of publications are therefore being devoted to the analysis of nanostructures using multi-scale simulation techniques.

2.3.2 Literature review

Researchers have continually attempted to combine continuum and atomistic approaches so as to capture the essential geometric and physical details wherever necessary using atomistic simulation while using continuum approach in the peripheral or the entire region to reduce the
computational cost. Abraham et al. [18] have coupled FE, MD and Tight Binding methods such that three simulations run simultaneously on different regions of the domain and are coupled in the region of interest through ‘hand-shake’ where these simulations overlap each other. The dynamics is governed by three different Hamiltonian operators which combine to form the total Hamiltonian operator. Concurrent coupling involves the idea of introducing a group of pseudo-atoms in the continuum region that serves as a full set of interactive neighbors for the real atoms at the interface between the fine and coarse scale regions. The pseudo-atoms share physical space with finite elements at the front end of the continuum interface, where the finite elements have to be scaled down to the atomic bond lengths. Abraham et al. [18] and Nakano [19] have used the concurrent coupling approach in simulation of fracture. However, the displacement solution with the concurrent coupling involves costly inversions of large and potentially ill-conditioned stiffness matrices making the analysis computationally intensive. This contradicts the basic motivation behind multi-scale analysis of reducing the expense of computation of the pure molecular dynamics approach. The quasi-continuum method developed by Tadmor [20, 21] has been applied to simulation of dislocations [20-23], grain boundary interactions [24, 25], nano-indentation [21], [25, 26], and fracture [27]. In quasi-continuum method a large number of atoms are lumped into a small set of representative atoms, a FE grid is imposed on the representative atoms and the deformation of the field variables is approximated using the FE shape functions and nodal values. However, this method requires that the FE mesh be prescribed such that the nodes conform to the representative atoms at the interface. Wagner and Liu [28] suggest a method which allows coupling of atomic finite elements to MD simulations without the need to grade the continuum nodal spacing to the atomic lattice size. They decompose the displacement field into orthogonal coarse and fine scales. They derive the generalized Langevian
equation [29,30] for the atoms at the boundary of the computed region in both scales of computation thus providing a coupling between the two scales of simulation. The total atomic displacement is then the sum of the two displacements after subtraction of the projection of the MD solution on the continuum scale. Independent time scales can be used for the two modes and this bridging scale is valid for finite temperature dynamics problems. The authors further present the fundamentals of the bridging scale to validate its use in multiple dimensions. They apply the bridging scale to two dimensional examples: wave propagation and dynamic crack propagation.

Qian et al. [31] have recently proposed a new multi-scale projection method for the analysis of carbon nanotubes wherein the coarse scale is approximated by the mesh free shape function and the fine scale is extracted from molecular dynamics solution. A virtual atomic cluster (VAC) model [32] is proposed in the coarse scale treatment and is solved in the entire problem domain. The computational grid does not have to comply strictly with the underlying atoms. The coarse scale solution provides the essential boundary conditions for the fine scale while the inter-atomic forces derived from the fine scale contribute to the coarse scale treatment.

The main objective of this thesis is to address the link between the continuum and atomistic approaches in the multi-scale simulation of CNTs. Although we work primarily on CNTs in this thesis, our method can be extended to other nanostructures exhibiting structural periodicity.
Chapter 3

The Proposed Methodology

3.1 Introduction

The multi-scale technique as proposed by Karpov et. al [11] is applicable to structures that exhibit periodicity in their geometry. Adhering to the definition of multi-scale analysis, we virtually divide the entire domain of analysis (figure 3.1 (a)) into a fine scale region, our region of interest, and the coarse scale region, the remaining relatively larger portion of the domain (figure 3.1 (b)).

Figure (3.1) Virtual division of the domain for multi-scale analysis
We choose the fine scale region to be that part of the domain where phenomena inexplicable using continuum scale analysis, like defect nucleation, crack propagation, warpage due to twisting or bending occur. This region is analyzed using conventional molecular mechanics wherein the energy of the system is estimated using empirical inter-atomic potentials and equilibrium configurations under application of boundary conditions are obtained by minimizing this energy. The empirical potential used in our analysis is further discussed in section (5.3.1).

The coarse scale region on the other hand is analyzed by taking advantage of the geometrical regularity of the structure in solving simultaneously a set of equations based on the Finite Element approach. In doing so, we intend to express the effect of the actual boundary conditions of the coarse scale region on the virtual boundary between the fine and coarse scales. Figure (3.2) illustrates this idea in a nutshell.

Figure (3.2) Reduction in problem size (a) Original Boundary Value Problem (b) Reduced boundary value problem creating the same deformation in the region of interest.
Figure (3.2 (a)) shows the actual boundary conditions B1 being applied at the boundary ABCD of the entire domain. Our aim is to determine the set of virtual boundary conditions B2 such that application of B2 at the virtual boundary EFGH would produce the same effect within the region EFGH as produced by the application of B1 at boundary ABCD. As shown in figure (3.2 (b)), this results into shrinking down the domain of the original Boundary Value Problem to just our area of interest. Thus, we limit the atomistic simulation to a small region thereby reducing the computational expense without sacrificing the accuracy of results.

The prime advantage of the proposed multi-scale method is that it eliminates the computational effort necessary for the complete description of the coarse scale region by making use of the ‘Discrete Fourier Transform’ over the periodic coarse scale region in solving equations governing the continuum scale analysis.

### 3.2 Discrete Fourier Transform

The Discrete Fourier Transform (DFT) is a mathematical formulation to transform spatially varying functions from real space to a wave-number space and is, by definition, performed on infinite periodic structures. For a spatially varying periodic function \( f(l) \), the most general form of DFT is given by equation (3.1)

\[
F_l \rightarrow \hat{f}(k) = \sum_l f(l) \cdot e^{-i kl}
\]  

(3.1)

where \( \hat{f}(k) \) is the image in the wave number space of the spatial function \( f(l) \), \( l \) is an integer and \( k \) is a real number.
Conversely, the inverse Discrete Fourier Transform of a function in the wave number space is given by:

\[ F^{-1}[\hat{f}(k)] = f(l) = \frac{1}{2\pi} \sum_{k} \hat{f}(k) e^{j\ell k} \]  

(3.2)

The Fourier domain function \( \hat{f}(k) \) is a 2\( \pi \)-periodic function of wave number \( k \), meaning that the inverse Discrete Fourier transform can be computed over any interval of length 2\( \pi \). The choice of the wave number \( k \) is not unique and depends on the periodicity of the function \( f(l) \). For example, for a \((N+1)\) periodic function, \( k \) takes the form

\[ k = \frac{2\cdot \pi \cdot p}{N + 1} \quad p = 0, 1, 2, ..., N \]  

(3.3)

Then the Fourier Transform and the inverse Fourier Transform are given by

\[ F_{f\rightarrow p}[f(l)] = \hat{f}(p) = \sum_{l=0}^{N} f(l) e^{-i2\pi p l / N+1} \]  

(3.4)

\[ F^{-1}[f(k)] = f(l) = \frac{1}{N + 1} \sum_{p=0}^{N} f(k) e^{i2\pi p l / N+1} \]  

(3.5)

Another important property of the Fourier transform, worth a mention here, is the one involving the transform of convolution summation of two functions. If \( f \) and \( g \) are two periodic functions in the real space, then their convolution summation \( f \ast g \) is defined as the integral of the product of the two functions after one is flipped and shifted. Thus,

\[ (f \ast g)(l) = \int f(l') \cdot g(l - l') dl' \]  

(3.6)
The integration range in equation (3.6) depends on the domain on which the functions are defined. For discrete functions, one can use a discrete version of the convolution summation as given by equation (3.7).

\[(f \ast g)(l) = \sum_{l'} f(l') \cdot g(l - l')\] (3.7)

The convolution theorem then states that the Fourier transform of the convolution summation of two functions in real space is equal to the product of the transforms of individual functions in the wave number space. For the periodic functions \(f\) and \(g\) in the real space, the convolution theorem yields:

\[F_{l\rightarrow p}[(f \ast g)(l)] = \hat{f}(p) \cdot \hat{g}(p)\] (3.8)

Application of DFT to static analysis has been made earlier by Ryvkin et al. [33] for optimal design of infinite repetitive beam like structures, while a general methodology for static analysis of periodic structures is due to Moses [34]. Our work derives inspiration from the work by Karpov et. al [35], who introduced a discrete periodic Green’s function and expressed displacement solutions as convolution sums over the Greens function and the actual and virtual loads. An elaborate discussion on functional solutions for spatially repetitive structures using DFT can be found in [35].

### 3.3 Coarse-Scale analysis

The traditional continuum mechanics approach to the equilibrium solution of a mechanical structure under the action of external forces is by generation of a global stiffness matrix \(K\) and the force vector \(f\) in order to solve for the displacement vector \(d\) in the equation:

\[Kd = f\] (3.9)
Here the stiffness matrix is of size \([\text{NDOF} \times \text{NDOF}]\) and the displacement and force vectors are both of the size \([\text{NDOF} \times 1]\), \(\text{NDOF}\) being the total number of degrees of freedom of the entire structure. ‘\(d\)’ in equation (3.9) represents the vector of displacements caused by the application of external forces given by vector ‘\(f\)’.

### 3.3.1 Exploiting periodicity of the continuum

Any geometrically repeating structure can be imagined as being generated by translating along one or more axial directions a unit cell consisting of a certain minimal set of joints called nodes and the structural members interacting with the nodes called the associate sub-structure. It is worth noting that any node in a repeating structure shall interact only with the nodes in the same unit cell and with nodes in its adjacent unit cells. Therefore, the position and the displacement of any node depend only on the position of the nodes in its own and its adjacent unit cells.

For simplicity of explanation, we consider a structure such that a unit cell translated along a single axis generates the entire periodic structure. It can be realized that the global stiffness matrix of such a repetitive mechanical structure shall have non-zero stiffness values \(K_{ij}\) only in those locations where the indices \(i\) and \(j\) represent the degrees of freedom of the same node or of nodes that share structural elements between them. Moreover, owing to periodicity of the geometry, the global stiffness matrix shall consist of only a repeating set of smaller sub-matrices corresponding to any unit cell, the sub-matrices placed in rows symmetrically with respect to the diagonal of the global stiffness matrix (figure (3.3)). It is possible to obtain the three medial sub-matrices \(K_1\), \(K_0\), and \(K_{-1}\) corresponding to any unit cell such that \(K_0\) relates the stiffness of the elements within the unit cell, while \(K_1\) and \(K_{-1}\) represent respectively the right and left hand coupling between the adjacent cell locations. A part of the global stiffness matrix of such a
geometrically repeating structure consisting of $N$ unit cells in the coarse scale region is shown in figure (3.3). The $N$ displacement and force vectors correspond to the $N$ unit cells in the coarse scale region of the repetitive structure. It is important to note here that the global force vector in figure (3.3) is defined to be the vector of internal forces unlike the vector of external forces in the FE method.

The governing equation of any $l$th unit cell of the repetitive lattice can then be given by a second order finite difference scheme as:

$$K_l d_{l-1} + K_0 d_l + K_{l+1} d_{l+1} = f_{l}^{\text{int}} \tag{3.10}$$

where $d$ vectors represent the displacement and $f_{l}^{\text{int}}$ represents the vector of internal forces acting on the $l$th unit cell. We note that the right hand side of equation (3.10) is defined in such a way that the K-matrices are no longer the classical stiffness matrices referred to until now. Hence forth, we refer to the K-matrices in equation (3.10) as the kernel function matrices. It can be observed that the kernel matrices are defined by the structure of internal forces as against the stiffness matrices that are based on the external forces.
3.3.2 Determining the Kernel function sub-matrices

The kernel sub-matrices for a unit cell consisting of say \( p \) atoms and having \( 3p \) spatial degrees of freedom are found by implementing the Unit Displacement Method, generally used for computing the stiffness matrices of truss and beam finite element models. We take into account the behavior of the representative unit cell and its neighbors under the application of a unit nodal displacement at a single \( (n^{th}) \) degree of freedom while maintaining all the other \( (3p-1) \) nodal displacements to be equal to zero. We calculate corresponding spatial forces at all the nodal locations of the unit cell and its coupled neighbors before and after this displacement is applied. The force acting on any atom is obtained by the differentiation of the potential equation (2.2) and using the position vectors of any given atom and its neighbors. Then the difference of forces at any \( m^{th} \) degree of freedom of the unit cell and its neighbors form the \( (m, n)^{th} \) elements of the corresponding stiffness sub-matrices. The procedure to obtain the kernel sub-matrices has been discussed in detail in section 5.4.1.

3.3.3 Implementing the Discrete Fourier Transform

For any arbitrary unit cell in the periodic coarse scale region, equation (3.10) can be rewritten in the discrete convolution form as:

\[
\sum_{l=1}^{l+1} K_{l-l'}d_{l'} = -f_l^{\text{ext}}
\]  

(3.11)

Now taking the Discrete Fourier Transform (DFT) of both sides of equation (3.11) we get

\[
\sum_{l=0}^{N} \sum_{l'=1}^{l+1} K_{l-l'}d_{l'} e^{-i2\pi \frac{l}{N+1}} = -\sum_{l=0}^{N} f_l e^{-i2\pi \frac{l}{N+1}}
\]

(3.12)

Now, we multiply and divide the left-hand side of the equation (3.12) by \( e^{-i2\pi \frac{l}{N+1}} \), to obtain
Next we introduce the parameter \( s = l - l' \) and rearrange to give

\[
\sum_{s=-1}^{1} K_s e^{-i2\pi p \frac{p}{N+1}} \sum_{l=0}^{N} d(l-s) e^{-i2\pi p \frac{(l-s)}{N+1}} = -\sum_{l=0}^{N} f_l e^{-i2\pi p \frac{l}{N+1}}
\]  \hspace{1cm} (3.14)

Due to \((N+1)\) periodicity of the lattice, we have

\[
\sum_{l=0}^{N} d(l-s) e^{-i2\pi p \frac{(l-s)}{N+1}} = \sum_{l=0}^{N} d_l e^{-i2\pi p \frac{l}{N+1}}
\]

The transformed governing equation thus takes the form,

\[
\hat{K}(p) \hat{d}(p) = -\hat{f}(p), \quad \text{for } p=0, 1, 2, 3...N
\]  \hspace{1cm} (3.15)

where, the Fourier images of functions \( K, d \) and \( f \) assumed \( N+1 \) periodic, are given as:

\[
\hat{K}(p) = \sum_{s=-1}^{1} K_s e^{-i2\pi p \frac{s}{N+1}}
\]  \hspace{1cm} (3.16)

\[
\hat{d}(p) = \sum_{l=0}^{N} d_l e^{-i2\pi p \frac{l}{N+1}}
\]  \hspace{1cm} (3.17)

\[
\hat{f}(p) = \sum_{l=0}^{N} f_l e^{-i2\pi p \frac{l}{N+1}}
\]  \hspace{1cm} (3.18)

The respective Fourier images of the functions retain their sizes in the wave number space. Alternatively, the application of convolution theorem stated in equation (3.7) and equation (3.8) yields the same result in equation (3.15)

### 3.3.4 Boundary Conditions

In accordance with the definition of Discrete Fourier Transform, we formally treat the coarse scale domain as a part of a larger domain with periodic boundary conditions, whose deformation
occurs only due to some external forces on the boundary cells \( l = 0 \) and \( l = N \). The traction boundary condition is defined by the equation:

\[
\mathbf{f}^\text{ext}_l = \delta_{l0} \mathbf{f}_0 + \delta_{lN} \mathbf{f}_N
\]  

(3.19)

Here \( \mathbf{f}_0 \) and \( \mathbf{f}_N \), as shown in figure (3.4), are respectively the vectors of external forces on the virtual boundary cell \( l=0 \) and the actual boundary cell \( l=N \) and \( \delta \) is Kronecker delta matrix.

Hence equation (3.18) can be written as:

\[
\tilde{f}(p) = f_0 + f_N e^{-i2\pi p \frac{N}{N+1}}
\]  

(3.20)

### 3.3.5 Applying Inverse Fourier Transform

Now pre-multiplying equation (3.15) by the inverse of the Fourier domain representation of the kernel function matrix gives us:

\[
\tilde{d}(p) = -\tilde{K}(p)^{-1} \cdot \tilde{f}(p)
\]  

(3.21)

The advantage of using DFT for periodical structures can be shown by comparing equation (3.21) with equation (3.9) and observing that instead of solving the inverse of the global stiffness matrix of the size of \( \text{NDOF} \times \text{NDOF} \), where \( \text{NDOF} \) is the total number of degrees of freedom of the entire structure, we need only to handle the inverse of \( \tilde{K} \) with size \( na \times na \), \( na \) being the number of degrees of freedom of any \( l^{th} \) unit cell.

Now, applying inverse DFT to equation (3.21) we obtain displacement \( d_i \) as:

\[
d_i = \frac{1}{N + 1} \sum_{p=0}^{N} \tilde{d}(p) \cdot e^{i2\pi \frac{p}{N+1}} = -\frac{1}{N + 1} \sum_{p=0}^{N} \tilde{K}(p)^{-1} \cdot \tilde{f}(p) \cdot e^{i2\pi \frac{p}{N+1}}
\]

(3.22)
Further, we substitute the Fourier image $\tilde{f}(p)$ from equation (3.18) into equation (3.22) with index $l$ in equation (3.18) changed to $l'$ for clarity. Thus,

$$
\frac{1}{N+1} \sum_{l'=0}^{N} - \hat{K}(p)^{-1} \cdot e^{i2\pi p \frac{l'}{N+1}} \cdot e^{i2\pi p \frac{l}{N+1}} = \sum_{l'=0}^{N} G_{ll'} \cdot f_{l'}
$$

(3.23)

where the function $G_{ll'}$, which is essentially the Greens function, is given as:

$$
G_{ll'} = \frac{1}{N+1} \sum_{p=0}^{N} - \hat{K}(p)^{-1} \cdot e^{i2\pi p \frac{l-l'}{N+1}}
$$

(3.24)

The force term $f_{l'}$ in equation (3.23) is defined completely by vectors $f_0$ and $f_N$ as shown in equation (3.19). Since $f_{l'}$ is completely independent of the parameters $l$ and $p$, it contributes merely as a constant multiplying factor to the Greens function in the transform process.

### 3.3.6 The Greens Function

The Greens function in equation (3.24) essentially represents the inverse DFT of the quantity $- \hat{K}(p)^{-1} \cdot e^{i2\pi p \frac{l-l'}{N+1}}$ and can be expressed as

$$
G_{ll'} = F_{l-l'}^{-1} \left( - \hat{K}(p)^{-1} \cdot e^{i2\pi p \frac{l-l'}{N+1}} \right)
$$

(3.25)

The inverse of the transformed kernel matrix, $\hat{K}(p)^{-1}$, is finite for all values of $p$ except for $p=0$ where $\hat{K}(p)^{-1}$ appears to be singular. As mentioned earlier, the choice of the wave number $k$ in equation (3.2) is not unique. To leave out the determination of $\hat{K}(p)^{-1}$ at $p=0$, we make use of half integer wave numbers such that $p$ takes the values $p = \pm 1/2, \pm 3/2, ..., \pm N \mp 1/2$.

The Greens function is alternatively defined, using the changed summation bounds as
\[
G_{ll'} = \frac{1}{2N} \sum_{p=\sqrt{2}-N}^{N-\sqrt{2}} \hat{K}(p)^{-1} \cdot e^{i(2\pi p(l-l'))/2N} \tag{3.26}
\]

The matrix function \(G_{ll'}\) is defined over the cyclic coarse scale domain. The physical sense of the Green’s function is that, up to a rigid body motion, the \(r^{th}\) column of the Green’s function matrix represents the deflections of the \(l^{th}\) nodal set caused by the \(r^{th}\) component of a unit load vector applied to the \(l'^{th}\) nodal location of the repetitive framework. The displacement solution of any \(l^{th}\) ring of atoms can then be described in terms of Greens function \(G_{ll'}\) which is a function of parameters \(l\) and \(l'\).

Substituting equation (3.19) into equation (3.23) the latter can now be expressed in terms of the Greens functions as

\[
d_i = G_{l0} \cdot f_0 + G_{lN} \cdot f_N \tag{3.27}
\]

### 3.3.7 Convolution operators \(\Theta\) and \(\Xi\)

We expand equation (3.27) at locations \(l=0\) and \(l=N\) as:

\[
d_0 = G_{00} \cdot f_0 + G_{0N} \cdot f_N \tag{3.28}
\]

\[
d_N = G_{N0} \cdot f_0 + G_{NN} \cdot f_N \tag{3.29}
\]

Solving for the inverses in the matrix form gives:

\[
\begin{bmatrix}
    f_0 \\
    f_N
\end{bmatrix} = \begin{bmatrix}
    G_{00} & G_{0N} \\
    G_{N0} & G_{NN}
\end{bmatrix}^{-1} \begin{bmatrix}
    d_0 \\
    d_N
\end{bmatrix} = G^{-1} \begin{bmatrix}
    d_0 \\
    d_N
\end{bmatrix} \tag{3.30}
\]

Next we define

\[
H = \begin{bmatrix}
    H_{00} & H_{0N} \\
    H_{N0} & H_{NN}
\end{bmatrix} = G^{-1} = \begin{bmatrix}
    G_{00} & G_{0N} \\
    G_{N0} & G_{NN}
\end{bmatrix}^{-1} \tag{3.31}
\]

Hence we have
The displacement equation for \( l=1 \) can be written according to equation (3.27) as:

\[
d_1 = G_{10} \cdot f_0 + G_{1N} \cdot f_N
\]  
(3.34)

Substituting equation (3.32) and (3.33) into equation (3.34) gives:

\[
d_1 = G_{10} \cdot (H_{00} \cdot d_0 + H_{0N} \cdot d_N) + G_{1N} \cdot (H_{N0} \cdot d_0 + H_{NN} \cdot d_N)
\]

\[
d_1 = (G_{10} \cdot H_{00} + G_{1N} \cdot H_{N0}) \cdot d_0 + (G_{10} \cdot H_{0N} + G_{1N} \cdot H_{NN}) \cdot d_N
\]  
(3.35)

So that equation (3.35) takes the form:

\[
d_1 = \Theta \cdot d_0 + \Xi \cdot d_N
\]  
(3.36)

where \( \Theta = (G_{10} \cdot H_{00} + G_{1N} \cdot H_{N0}) \) and \( \Xi = (G_{10} \cdot H_{0N} + G_{1N} \cdot H_{NN}) \)

Thus the sought operators of multi-scale boundary conditions for periodic lattices are square matrices which can be given by the matrix multiplication:

\[
(\Theta \quad \Xi) = (G_{10} \quad G_{1N}) \begin{pmatrix}
H_{00} & H_{0N} \\
H_{N0} & H_{NN}
\end{pmatrix}
\]  
(3.37)

Equation (3.36) expresses the displacement vector \( d_1 \) in terms of the vectors \( d_0 \) and \( d_N \). Thus, with the availability of vectors \( d_0 \) and \( d_N \) and the mathematical operators as obtained in equation (3.37), it is possible to obtain the displacement vector \( d_1 \) without analyzing the entire coarse scale domain of the repetitive structure.

In general, an analytical solution of the equation (3.35) is not possible due to the presence of DFT and inverse DFT in the same equation. Here, we take the advantage of the translational symmetry in the axial direction of the periodic lattice so that we have

\[
K_1 = K, \quad K_0 = -(K + K^T) + \tilde{K}, \quad K_{-1} = K^T
\]  
(3.38)
in which $K$ represents the interactions among atoms between the cells and $\tilde{K}$ represents the interaction of atoms within the cells. Hence the DFT according to equation (3.16) can be performed analytically to get:

$$\hat{K}(k) = \left( K + K^T \right) (\cos(k)-1) + \tilde{K} + i\left( K - K^T \right) \sin(k)$$

(3.39)

in which $k = \frac{\pi p}{N}$.

Alternatively, this can be written as:

$$\hat{K}(k) = A(k)(I + iB(k))$$

(3.40)

in which $I$ is the identity matrix of the same order as $K$, $i$ is the imaginary number $\sqrt{-1}$, 

$$A = \left( K + K^T \right) (\cos k - 1) + \tilde{K}, \quad \text{and} \quad B = A^{-1}(K - K^T) \sin k$$

(3.41)

The inverse of $\hat{K}(k)$ is then given as

$$\hat{K}(k)^{-1} = \left( I + B^2(k) \right)^{-1} (I - iB(k)) A^{-1}(k)$$

(3.42)

The expression in equation (3.42) can be used in equation (3.26) to evaluate the inverse DFT using numerical approach.

Again, it is important to note here that the matrices that we refer to here as stiffness matrices are not exactly analogous to the stiffness matrices used in classical FE method. The matrices used here are the kernel function matrices. The purpose and the distinction of the kernel functions from the FE stiffness matrices is made clear in the 1D example dealt with in Chapter 4.

### 3.4 Fine Scale Analysis

Knowledge of displacement vector $d_1$ is equivalent to the determination of boundary conditions $B_2$ as referred to figure (3.2). Thus displacement $d_1$ applied to the periphery of the fine scale
region produces the same effect in the fine scale region as $d_j$ applied to the periphery of the coarse scale region. This displacement $d_j$ can then be applied to the periphery of the fine scale region and classical molecular mechanics analysis can be performed over just the fine scale region. We use the energy minimization technique as discussed in Chapter 2 to determine equilibrium configurations corresponding to every incremental displacement $d_j$ imposed. We use the Brenner’s bond order potential to model the variations of potential energy as a function of atomic interactions. The derivative of the potential energy with respect to atomic positions is minimized to get the equilibrium configurations. The main advantage of using energy minimization technique is the ability to obtain the equilibrium configuration with much lesser computation than molecular dynamics. The minimization or optimization technique used is a critical factor in obtaining the correct equilibrium solution. We use energy minimization based on the Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) [36] minimization algorithm, which has been found to be most efficient for constrained and unconstrained problems. The step wise procedure to the fine scale analysis is explained during its application to carbon nanotubes in section 5.3

### 3.5 Computational saving achieved

Figure (3.4) shows implementation of the multi-scale technique discussed above on a uni-axially periodic structure.
Figure (3.4) Computational saving due to implementation of the multi-scale scheme

It can be seen that use of the multi-scale scheme obviates completely the need to determine the trajectories of unit cells of the entire coarse scale region. The ensuing reduction in the computational effort involved makes the scheme attractive and holds potential for its use in exploring nanostructures.
Chapter 4
Verification: One Dimensional Analysis

4.1 1 D mono-atomic chain

Before proceeding to the application of the formulation to carbon nanotubes, we verify the validity of the formulation using a one-dimensional periodic mono-atomic chain with each atom having a single longitudinal degree of freedom.

As shown in figure (4.1), atom N represents the peripheral boundary of the coarse scale region and atoms 1 and 0 represent the interface between the coarse and fine scale regions. Taking into account the uniform equilibrium deformation character of this periodic lattice, we can obtain the displacement of atom 1 \( (d_1) \) in terms of displacements of atom 0 \( (d_0) \) and atom N \( (d_N) \) by

\[
L = N + 1
\]

Figure (4.1) 1 Dimensional mono-atomic chain assumed (N+1) periodic
evaluating at atom 1, a first order interpolation polynomial satisfying displacements at nodes 0 and N as:

\[ d_i = \frac{N - 1}{N} d_0 + \frac{1}{N} d_N \]  

(4.1)

Thus in verifying our formulation, we seek to obtain the same expression for displacement \( d_i \) as given by equation (4.1).

### 4.2 Kernel functions

For the one dimensional case at hand, it is safe to assume that each atom of the mono-atomic chain interacts only with its two closest neighbors and their interaction can be described by linear spring stiffness \( K \). Then, equation (3.10) can be expanded at the location \( l = 0 \) to give:

\[ K_{-1} d_1 + K_0 d_0 + K_1 d_{-1} = f_0^{\text{int}} \]  

(4.2)

The quantity \( d_{-1} \) in equation (4.2) represents the displacement of that neighbor of atom 0 that lies completely in the fine scale region.

![Figure (4.2) Covalent bonds between carbon atoms analogous to springs of linear stiffness constants \( K \)](image_url)
Figure (4.2) shows a unit cell consisting of a single carbon atom bonded chemically to two other identical atoms. Atoms are shown as shaded circles while the chemical bonds are represented by springs with identical linear constants $K$. If a small displacement $d$ is imposed on the atom $l$ toward the right side, keeping atom $(l-1)$ and $(l+1)$ fixed, the total resisting force exerted on the $l^{th}$ atom due to the presence of its neighbors is toward the left side, and is given by:

$$F_{\text{resis}} = (-K).d + (-K).d = -2K.d \quad (4.3)$$

Here the quantity $-2K$ represents the resistance / stiffness equivalent offered by the bonds of the $l^{th}$ atom to an external displacement $d$. The negative sign indicates that the internal resistive force generated at the atom is in the direction opposite to that of the imposed displacement. The difference between the stiffness matrices seen in classical FE method and the kernel functions generated here can be recognized by the fact that the diagonal elements of the kernel matrix $K_0$ are not positive unlike the FE method. This displacement $d$ also produces resistive forces $K.d$ each on the left and right atoms. Constant $K$ here represents the left and right stiffness couplings of the $l^{th}$ unit cell. Thus the kernel functions $K_1$, $K_0$ and $K_{-1}$ for the one dimensional case reduce to scalar quantities in terms of a linear interaction coefficient $K$ such that:

$$K_{\pm 1} = K, \quad K_0 = -2K \quad (4.4)$$

### 4.3 Coarse Scale Formulation

According to equation (3.41) and equation (3.42),

$$A = 2K(\cos(k) - 1) \quad \text{and} \quad B = 0$$

$$\hat{K}(k)^{-1} = \frac{1}{2K(\cos(k) - 1)} \quad (4.5)$$
Hence, using equation (3.26) and equation (4.5), the lattice Greens function for the one dimensional case is given as:

\[
G_{ll'} = -\frac{1}{2K} \cdot \frac{1}{2N} \sum_{p=\pm 1}^{N-1/2} \frac{e^{i\pi.p(l-l')/N}}{\cos(\pi.p / N) - 1}
\]  \hspace{1cm} (4.6)

Using Euler’s formula \( e^{i\theta} = \cos \theta + i \sin \theta \), \( \cos(-\theta) = \cos(\theta) \) and \( \sin(-\theta) = -\sin(\theta) \), we observe that the imaginary part of equation (4.5) reduces to zero due to symmetry of the summation about \( p=0 \). We can then rewrite equation (4.5) as

\[
G_{ll'} = -\frac{1}{2K} \cdot \frac{2}{2N} \sum_{p=\pm 1}^{N-1/2} \frac{\cos(\pi.p(l-l')/N)}{\cos(\pi.p / N) - 1}
\]  \hspace{1cm} (4.7)

Using the half angle identity \( \cos \theta = 1 - 2.\sin^2(\theta/2) \) in the denominator of equation (4.7), we get:

\[
G_{ll'} = -\frac{1}{2K} \cdot \frac{1}{2N} \sum_{p=\pm 1}^{N-1/2} \frac{\cos(\pi.p(l-l')/N)}{-2.\sin^2(\pi.p/2N)}
\]  \hspace{1cm} (4.8)

Changing the bounds of the summation, we can express equation (4.8) as:

\[
G_{ll'} = \frac{1}{2K} \cdot \frac{1}{2N} \sum_{p=1}^{N} \frac{\cos(\pi.(2p-1).(l-l')/2N)}{\sin^2(\pi.(2p-1)/4N)}
\]  \hspace{1cm} (4.9)

Substituting \( 2N = n \) equation (4.9), we have

\[
G_{ll'} = \frac{1}{2K} \cdot \frac{1}{2N} \sum_{p=1}^{n/2} \frac{\cos(\pi.(2p-1).(l-l')/n)}{\sin^2(\pi.(2p-1)/(2n))}
\]  \hspace{1cm} (4.10)

We have from [37, 38] (refer Appendix A for explanation),

\[
\sum_{p=0}^{(n-2)/2} \frac{\cos(\pi.(2p+1)m/n)}{\sin^2(\pi.(2p+1)/2n)} = \frac{n}{2} \cdot (n-2m) + \frac{1}{4} \left[ (-1)^n - 1 \right] (-1)^m \text{ for } m = 0,1,2,\ldots,n
\]  \hspace{1cm} (4.11)

Changing the bounds of the summation again, we can express equation (4.11) as
\[
\sum_{p=1}^{n/2} \cos(\pi(2p-1)m/n) = n/2(n-2m) + \frac{1}{4} \left[(1)^m - 1 \right] (-1)^m
\]  
(4.12)

Substituting equation (4.12) into equation (4.10) where \( m = (l - l') \) we get

\[
G_{ll'} = \frac{1}{2K} \cdot \frac{1}{2N} \left( n/2(n-2(l-l')) + \frac{1}{4} \left[(1)^m - 1 \right] (-1)^m \right)
\]  
(4.13)

Substituting back \( n = 2N \) we have

\[
G_{ll'} = \frac{1}{2K} \cdot \frac{1}{2N} \left( N(2N - 2(l-l')) + \frac{1}{4} \left[(1)^{2N} - 1 \right] (-1)^m \right)
\]  
(4.14)

\[
G_{ll'} = \frac{1}{2K} \cdot (N - (l-l'))
\]  
(4.15)

Although the proof of equation (4.11) is stated only for non-negative values of \( m \), it can be extended for negative values of \( m \), more specifically for the term \( G_{1N} \) in equation (3.37). Employing numerical methods for terms with \( l' > l \), we observe that \( G_{ll'} \) takes the form \( G_{ll'} = \frac{1}{2K} \cdot (N - (l'-l)) \). Thus the most general form of the Green’s function can be stated as:

\[
G_{ll'} = \frac{1}{2K} \cdot (N - abs(l-l'))
\]  
(4.16)

Substituting \( G_{ll'} \) in equation (3.31) we obtain:

\[
H = \left[\begin{array}{cc} H_{00} & H_{0N} \\ H_{N0} & H_{NN} \end{array}\right] = G^{-1} = \left[\begin{array}{cc} G_{00} & G_{0N} \\ G_{N0} & G_{NN} \end{array}\right]^{-1} = \frac{1}{2K} \left[\begin{array}{cc} N & N-N \\ N-N & N \end{array}\right]^{-1}
\]

\[
= \frac{2K}{N^2} \left[\begin{array}{cc} N & 0 \\ 0 & N \end{array}\right]
\]  
(4.17)

Substituting values from equation (4.17) in equation (3.37), we have,

\[
\Theta = \frac{(N-1)(N)}{N^2} = \frac{N^2-N}{N^2}
\]
\[
\Xi = \frac{N \cdot (N - 1)}{N^2} = \frac{(N-1)}{N}
\]

\[
\Xi = \frac{(N - abs(1-N))(N)}{N^2}
\]  \hspace{1cm} (4.18)

For \( N > 1 \),

\[
\Xi = \frac{(N - (N - 1))(N)}{N^2} = \frac{N}{N^2} = \frac{1}{N}
\]  \hspace{1cm} (4.19)

The Greens function operators for the one dimensional case are thus given by:

\[
\Theta = \frac{N - 1}{N}, \quad \Xi = \frac{1}{N}
\]  \hspace{1cm} (4.20)

It can thus be observed that implementation of the proposed coarse scale analysis to one-dimensional problems yields field solutions exactly in tune with analytical results. The validity of the mathematical operators for the one dimensional case has been proven using only numerical approach recently in [11].
Chapter 5

Extension to Carbon Nanotubes

5.1 Periodic geometry of carbon nanotubes

As discussed in Chapter 1, the orientation of the carbon bonds with respect to the nanotube axis determines the chirality of the nanotube. It is important to recognize that nanotubes of any chirality can be considered to be a pattern or arrangement of bonded carbon atoms that repeats itself periodically in the axial direction of a nanotube. It is this periodicity that is harnessed in our multi-scale analysis. We consider the example of a single walled arm chair nanotube. Figure (5.1(a)) shows a unit cell in two dimensions, consisting of a set of carbon atoms, which when translated along the axial direction along with its associate substructure generates a graphene sheet shown in figure (5.1(b)).
The graphene sheet when rolled in the direction perpendicular to the tube axis generates the nanotube as shown in figure (5.1(c)). Zigzag and chiral nanotubes can similarly be thought of as being generated by axial translation of similar unit cells.

5.2 Multi-scale analysis

We use a (10, 10) uncapped arm chair nanotube of a length 119.56 Å (1900 atoms) for our analysis. As proposed in section 3.1, we virtually divide the nanotube into two regions, the fine scale field and the coarse scale field. For the sake of simplicity, we apply symmetric boundary conditions at the two ends of the tube. Thus we have a central fine scale region and two identical coarse scale regions placed symmetrically on either side of the fine scale region. We identify each unit cell in the coarse scale region with a non-negative integer ‘l’. While the unit cells at the interfaces between the coarse and the fine scale regions are the zeroth unit cells, the terminating unit cell at each end is the Nth unit cell. Owing to symmetry of the structure and the applied boundary conditions, it shall suffice to consider only one interface between the fine and
the coarse scale region for visualization purposes. Figure (5.2) illustrates the idea of introducing a virtual interlayer between the coarse and fine scale regions.

![Original Molecular System](image)

**Multi-scale Boundary Conditions**

\[ \text{disp } d_N \quad \text{disp } d_1 \]

\[ l = N \quad \text{Coarse Scale Region} \quad \text{Fine Scale Region} \quad l = l_1 = 0 \]

Figure (5.2) Multi-scale discretization scheme for the analysis of carbon nanotubes

The fine scale region is analyzed using conventional molecular mechanics approach while the effect of the actual boundary conditions on the virtual interface is determined by the coarse scale analysis.

**5.3 Fine Scale Analysis**

The covalent bonds between the \( sp^2 \) hybridized carbon atoms in CNTs undergo stretching, twisting and bending under the application of external forces. As discussed in chapter 3, classical
molecular mechanics predicts the energy of molecules under boundary conditions as a function of their degrees of freedom using empirical inter-atomic potentials. Bonding potentials are useful in modeling the covalent bonds in the CNTs in order to predict their trajectories under constrained conditions.

5.3.1 Brenner’s Potential

Based on the study of Abell [39], Brenner put forth a bond order model of an inter-atomic potential that takes into account the effect of formation and breakage of the C-C bonds. This model is viewed as more accurate since it is found to efficiently account for multi-body interactions occurring in diamond and graphite. We use the Brenner’s potential which has, in previous studies, enjoyed success in the area of nanotube energetics.

Brenner’s potential as applied to C-C bonds in the CNTs, is given by:

\[ E = \sum_i \sum_{j \neq i} \left[ V_R(r_{ij}) - B_{ij} V_A(r_{ij}) \right], \]  

(5.1)

where \( r_{ij} \) is the distance between an atom \( i \) and its neighbor \( j \) and the attractive term \( V_A(r_{ij}) \) and repulsive term \( V_R(r_{ij}) \) are given by

\[ V_R(r_{ij}) = f_{ij}(r_{ij}) D_{ij}^{(e)} / (S_{ij} - 1) e^{-\left(\sqrt{S_{ij}} - \beta_{ij} (r_{ij} - R_{ij}^{(e)})\right)}, \]  

(5.2)

\[ V_A(r_{ij}) = f_{ij}(r_{ij}) D_{ij}^{(e)} S_{ij} / (S_{ij} - 1) e^{-\left(\sqrt{S_{ij}} - \beta_{ij} (r_{ij} - R_{ij}^{(e)})\right)}, \]  

(5.3)

The attractive term accounts for cross-atomic attractive forces between any atomic nucleus and the electron clouds of surrounding atoms while the repulsive term accounts for the mutual repulsive forces between positively charged nuclei in each other’s vicinity. The attraction term exceeds the repulsion term till an equilibrium distance between bonded atoms is reached. Equilibrium distance is the inter-atomic distance between two atoms where the attractive forces
between atoms are equilibrated by their repulsive forces. A further decrease in the inter-atomic distance results in a quick growth of the resultant repulsive force.

The piecewise defined continuous function $f_y(r_y)$ restricts the pair potential to the nearest neighbors and is given by:

$$f_y(r) = \begin{cases} 
1, & r < R_y^{(1)} \\
\frac{1}{2} + \frac{1}{2} \cos \left[ \frac{\pi (r - R_y^{(1)})}{(R_y^{(2)} - R_y^{(1)})} \right], & R_y^{(1)} \leq r \leq R_y^{(2)} \\
0, & r > R_y^{(2)},
\end{cases} \quad (5.4)$$

$R_y^{(1)}$ and $R_y^{(2)}$ are cut-off radii corresponding to bond stretching and breaking respectively.

Accounting for the forces between any atom $i$ and all the remaining atoms $j$ in the molecule using the inter-atomic potential is unnecessary and expensive, even for small systems. Assuming that atoms interact only with their immediate neighbors is practical and can reduce the computational effort significantly. The cut-off function $f_y(r)$ serves the purpose of truncating the computation so as to accommodate only the interactions of atoms with other atoms within a certain cutoff radius. The middle interval trigonometric function in equation (5.4), known as the ‘skin’ of the potential, assures a smooth and quick transition of $f_y(r)$ from 1 to 0 when the value of the inter-atomic distance approaches the cut-off radius $R_y^{(2)}$. The zero value of the cut-off function for $r > R_y^{(2)}$ helps disregard the interactions between atoms separated by a distance more than the cut-off radius.

The empirical bond order function $\overline{B}_y$ represents the multi-body coupling effects that account for the specifics of the local atomistic environment of atom $i$ and is given by:

$$\overline{B}_y = (B_y + B_i) / 2, \quad (5.5)$$
where
\[
B_y = \left(1 + \sum_{k \neq i,j} G_i(\theta_{ijk}).f_i(r_{ik}) \right)^{-\delta_i},
\]
(5.6)

Here, \(r_{ik}\) is the distance between atoms \(i\) and \(k\) and \(\theta_{ijk}\) is the angle between the bonds \(i-j\) and \(i-k\), such that \(k\) represents all the neighbors of atom \(i\) other than \(j\) within the cut-off radius. The basic idea is that the bond \(i-j\) is weakened by the presence of other bonds \(i-k\) involving atom \(i\). The amount of weakening is determined by the relative orientation these other bonds hence angular terms appear necessary to construct a realistic model. The function \(G\) in equation (5.6) is given by
\[
G_i(\theta) = a_0[1+c_0^2/d_0^2-c_0^2/[d_0^2+(1+\cos \theta)^2]]
\]
(5.7)

The parameters \(D_y^{(e)}, R_y^{(e)}, \beta, S_y, R_y^{(1)}, R_y^{(2)},\delta, a_0, c_0, d_0\) in equations (5.2) and (5.3), \(R_y^{(1)}\) and \(R_y^{(2)}\) in equation (5.4), \(\delta\) in equation (5.6) and \(a_0, c_0, d_0\) in equation (5.7) have been determined by Brenner for systems involving carbon bonds and systems involving carbon and hydrocarbon bonds.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
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<td>Å</td>
</tr>
<tr>
<td>(D_y^{(e)})</td>
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<td>eV</td>
</tr>
<tr>
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<td>(R_y^{(1)})</td>
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<td>Å</td>
</tr>
<tr>
<td>(R_y^{(2)})</td>
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<td>Å</td>
</tr>
<tr>
<td>(\delta)</td>
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<td>--</td>
</tr>
<tr>
<td>(a_0)</td>
<td>0.0011304</td>
<td>--</td>
</tr>
<tr>
<td>(c_0)</td>
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<td>--</td>
</tr>
<tr>
<td>(d_0)</td>
<td>2.5</td>
<td>--</td>
</tr>
</tbody>
</table>

Table (1) Parameters for Brenner potential modeling C-C bond interactions
Table (1) enlists the parameters as determined by Brenner for systems involving only carbon bonds and are applicable to our model.

Equilibrium configurations under application of boundary conditions are obtained by minimizing the energy determined using the Brenner potential. As applied to the multi-scale analysis at hand, the boundary conditions for the fine scale region are the displacements of atoms in the unit cell corresponding to \( l=1 \) in the coarse scale region. The procedure for the analysis of the fine scale region is outlined, in brief, as follows:

1. The atomic coordinates of the nanotube are initially read from an input file. These coordinates do not necessarily represent the equilibrium configuration and are relaxed to reach equilibrium in the first step. Displacement boundary conditions are not applied to the coarse scale region during this first relaxation step.
2. Depending on the dictating boundary conditions \( d_N \), the displacement \( d_i \) is determined using equation (3.36) and is applied as the boundary condition to the fine scale region of the CNT.
3. The potential energy of the system, using Brenner’s bond order model, and its derivative corresponding to the molecular configuration are calculated.
4. For every incremental displacement imposed, the potential energy is minimized using the limited memory BFGS algorithm, with displacements \( d_i \) as the bounding constraints. The atomic configuration corresponding to the minimum energy represents the response behavior of the fine scale region to the externally applied displacement \( d_N \).
5. Incremental displacements \( d_N \) are applied on the coarse scale region and steps 2 through 5 are repeated till the desired deformation is attained.
5.4 Coarse Scale analysis

The coarse scale region is treated as a geometrically periodic Finite Element mesh. We regard the atoms of every unit cell to be equivalent to nodes and the chemical bonds between the atoms to be equivalent to structural elements with identical stiffness. Atoms in any unit cell share chemical bonds with other atoms within the unit cell and with atoms in adjacent unit cells. We define the associate substructure of any unit cell as consisting of all the chemical bonds that the atoms of the unit cell share with other atoms in the same unit cell and with atoms in the adjacent unit cells on both sides. Figure (5.3(a)) shows a unit cell of the CNT consisting of atoms equivalent to nodes and connecting covalent bonds forming the substructure. The size of the unit cell is primarily governed by the chirality indices of the nanotube.

Figure (5.3) Nanotube Unit cell (a) Unit cell of the CNT, comprising nodes and substructure (b) Interaction of unit cell \( l \) with its neighboring unit cells
5.4.1 Kernel matrices using Unit Displacement Method

It is known that bonded interactions are short-ranged and include only up to second nearest neighbors for moderately deformed carbon nanotubes. Hence we can say that the forces acting on the atoms of any \( l^{th} \) unit cell are affected at the most by the atoms in the \((l+1)^{th}\) and \((l-1)^{th}\) unit cells. Figure (5.3(b)) shows the interaction of any unit cell \( l \) with its adjacent unit cells on both sides. The governing equilibrium equation for any unit cell in the coarse scale region, as discussed in chapter 3 above, can be written as:

\[
\sum_{l'=1}^{l+1} K_{l-l'} d_{l'} = f_{l'}^{\text{int}}
\]

(5.8)

Where \( K_{l-l'} \) are the kernel sub-matrices, \( d_{l'} \) are the vectors of displacements of the atoms of the \( l' \) \( th \) unit cells, and \( f_{l'}^{\text{int}} \) is the internal force vector on the \( l^{th} \) unit cell. As explained in section (3.3.1) above, the \( K \) matrices in equation (5.8) are invariant for any unit cell and are defined by the structure of internal forces i.e. as a function of the potential energy \( U \) utilized in terms of displacements about equilibrium positions:

\[
K_{l-l'} = \frac{\partial f_{l'}^{\text{int}}}{\partial d_{l'}} \bigg|_{d=0}, \quad \text{where} \quad f_{l'}^{\text{int}} = -\frac{\partial U(d)}{\partial d_{l'}} \quad \text{(refer [40] for derivation)}
\]

(5.9)

The application of the unit displacement method for the determination of the stiffness sub-matrices \( K_{l-l'} \) for any unit cell \( l \) of the nanotube is explained in what follows.

As shown in figure (5.3 (b)), we concentrate on the unit cell \( l \) and its neighbors \((l-1)\) and \((l+1)\).

For the (10, 10) arm-chair nanotube used in this analysis, each unit cell consists of 40 atoms, each atom having one translational degree of freedom along the x, y and z axes. Consequently every unit cell has 120 degrees of freedom and each of the three stiffness sub-matrices \( K_{-1}, K_{0} \)}
and $K_1$ in equation (5.8) has a size of [120x120]. Let $[k_{in}]_m$ represent elements of the matrix $K_m$. Here, the index $m$ takes values -1, 0 and 1 and serves the same purpose as the index $(l-l')$ in equation (5.8). Index $i$ represents the degrees of freedom of the $(l+m)^{th}$ unit cell and index $n$ represents the degrees of freedom of the $l^{th}$ unit cell. The unit displacement method is based on the general rule [41] stated as:

‘Any column $n$ of a sub-matrix $K_m$ is the vector of forces that must be applied to the $(l+m)^{th}$ unit cell at its nodes to maintain a deformation state in which the $n^{th}$ nodal d.o.f. of the $l^{th}$ unit cell has a unit value while all its other nodal degrees of freedom are zero.’

The potential energy function $U(d)$ is determined using the Brenner’s potential. Variation of this potential with respect to atomic coordinates yields the force components acting on the atoms of interest. The detailed derivation of the expression for the atomic forces from Brenner’s potential is given in [40]. We initially calculate the forces acting on all the atoms of the unit cell $l$ corresponding to the current boundary conditions and generate a vector, say $v_i$, of size [1x120], such that each element of vector $v_i$ holds the force component corresponding to the $i^{th}$ degree of freedom of the $l^{th}$ unit cell. Next, we apply a finite but small displacement $\delta d$ at only the $n^{th}$ degree of freedom of the $(l+m)^{th}$ unit cell. We assemble the new vector of forces, say $v_f$, now sustained by the atoms of the $l^{th}$ unit cell. The difference between the corresponding elements of vectors $v_f$ and $v_i$ represents the response of the $l^{th}$ unit cell to an excitation of the $n^{th}$ degree of freedom of the $(l+m)^{th}$ unit cell. This difference divided by the displacement represents the resistance or the stiffness coupling offered by the $l^{th}$ unit cell to the excitation of $n^{th}$ degree of freedom of the $(l+m)^{th}$ unit cell.
The vector $k_i$ defined by

$$k_i = \frac{v_i - v_j}{\delta l} \quad i = 1, 2, ..., 120$$

forms the $n^{th}$ column of the sub-matrix $K_m$. Following the same procedure, we apply measured excitations, one at a time, in the x, y and z directions to all atoms of the $(l-1)^{th}$, $l^{th}$ and $(l+1)^{th}$ unit cell and determine the force response of the $l^{th}$ unit cell to these displacements and populate the columns of $K_1$, $K_0$ and $K_{-1}$ sub-matrices respectively. The sub matrices $K_1$ and $K_{-1}$ represent the left and right stiffness couplings of the unit cell $l$ while $K_0$ represents the coupling of the atoms among the same unit cell. The stiffness matrix $K_0$ is symmetric following Maxwell’s reciprocity theorem which states that: “For two identically-sized forces applied at the distinct points A and B on a linear structure, the displacement at degree of freedom A caused by the force at degree of freedom B is the same as the displacement at B caused by the force at A. As a result, the stiffness matrix of linear systems is symmetric.

The diagonal elements of the matrix $K_0$ are necessarily negative for the same reason that has been explained for the one dimensional case in Chapter 4. The direction of the resisting force at any degree of freedom has to be opposite to the direction of displacement produced at that degree of freedom of any unit cell. Also, referring to equation (3.9), it can be seen that for a node to displace in the same direction as the force applied on its degree of freedom, the corresponding diagonal element in the kernel function has to be negative. The column numbers of $K_0$ represent the degrees of freedom of the $l^{th}$ unit cell activated to generate these columns. Any element $[k_{ij}]_m$ which takes a zero value indicates that activation of the $j^{th}$ degree of freedom of the $(l+m)^{th}$ unit cell produces no effect on the $i^{th}$ degree of freedom of the $l^{th}$ unit cell. Matrices $K_1$ and $K_{-1}$ do not exhibit symmetry since they are the off-diagonal parts of a larger symmetric global matrix shown
in figure (3.3). At the same time, owing to their symmetric placement in the global matrix, it can be easily seen that they are transposes of each other.

Application of Discrete Fourier Transform and subsequently its inverse to equation (5.8) generates two dimensional Greens function matrices defined as:

\[
G_{\mu} = F_{\mu \rightarrow 1}^{-1}\{\hat{G}(p)\} = \frac{1}{2N} \sum_{p=\frac{1}{2}-N}^{N-\frac{1}{2}} \hat{G}(p)e^{\frac{i\pi p(l-t)}{N}}
\] (5.11)

Here, \( \hat{G}(p) = -\hat{K}^{-1}(p) \equiv -(F\{K\})^{-1} = -(K_{+}e^{i\rho p} + K_{0} + K_{\rho}e^{-i\rho p})^{-1} \) (5.12)

Knowledge of the stiffness sub-matrices and mathematical manipulation following equations (3.11) through (3.37) leads to generation of the sought mathematical operators \( (\Theta \quad \Xi) \), s x s square matrices. It can be observed that the mathematical operators are governed solely by the inter-atomic potential and the coarse scale parameter N.

### 5.4.2 An iterative solution procedure

The displacement obtained from equation (3.36) can be applied directly as a boundary condition to the fine scale region since it takes into account the effect of the actual boundary conditions on the virtual boundary. As is evident from equation (3.36), however, a unique solution vector \( d \) requires the use of the vectors \( d_{0} \) and \( d_{N} \). \( d_{N} \) is the vector of externally applied displacements and is completely known. However, \( d_{0} \) is the vector of displacements of a unit cell of atoms internal to the nanotube and is unknown.

We observe that the coarse and fine scale regions are two completely separate computational domains involving two different solution procedures. We propose an alternating iterative scheme
to get a unique displacement vector $d_i$ for every small incremental application of the boundary condition. Figure (5.5) shows a flow chart followed to obtain a unique compatible displacement solution for any externally applied displacement $d_N$.

Figure (5.4) Iterative procedure to obtain unique multi-scale boundary conditions
The iterative procedure can be outlined as follows:

1. The mathematical operators $\Theta$ and $\Xi$ are computed after every incremental displacement $d_n$ is imposed.

2. In the first iteration of every step, displacement vector $d_0$ is used from the last iteration of the previous step. $d_0$ is assumed zero in the first iteration of the first loading step.

3. Displacement vector $d_1$ is determined using equation (3.36)

4. With $d_1$ as the externally applied displacement for the fine scale region, a new displacement vector $d_0$ is determined by executing the energy minimization subroutine. If the difference between the corresponding elements of vector $d_0$ from the successive predictions falls outside of a predefined tolerance value, the new vector $d_0$ is used in equation (3.36) again and the procedure starting with step three above is followed for another iteration step.

5. When the difference between the corresponding elements of vector $d_0$ from the successive predictions falls within a predefined tolerance value, the iterative procedure is terminated and the next loading step is applied.

6. Steps 1 through 5 are followed for every incremental displacement imposed.

This multi-scale simulation approach facilitates use of atomistic simulations for fine scale only, without involving the continuum modeling for the coarse scale, thereby providing elaborate atomistic information only when and where it is necessary. This approach provides a potential for drastic savings in computational time up to several orders of magnitude. Performance and
advantages of this method shall be evident after comparison and verification of our results with bench-mark results from pure molecular mechanics simulations.
Chapter 6

Results and Discussion

In this chapter we implement bench mark problems to verify the proposed multi-scale analysis method. We have used an uncapped (10, 10) arm-chair carbon nanotube consisting of 1900 atoms for all the results documented. The nanotube has a length of 115.59 Å and a diameter of 13.56 Å. The implementation can be further extended to nanotubes of other lengths and chiralities with requisite changes in the geometry of the unit cell. The problem is treated as quasi-static, meaning the nanotube attains equilibrium (minimum energy configuration) after every incremental load step is imposed. The energy minimum in the fine scale region is obtained using the limited-memory BFGS method for large scale optimization [36]. We apply symmetric displacement boundary conditions to the unit cells at both the ends of the nanotube. The behavior of the nanotube is investigated under application of tensile, compressive, twisting and bending boundary conditions.

We compare our results with those obtained after implementing full scale molecular mechanics simulations, hitherto considered most accurate, on the same nanostructure under application of identical boundary conditions.
6.1 Tension and compression

The nanotube is divided into two regions: the central fine scale region consisting of 1020 atoms and the coarse scale region consisting of the remaining 880 atoms. Incremental displacements of 0.24 Å per step are applied in the axial direction of the tube, while keeping the circular cross-
section area of the tube intact. Displacements are applied only to the terminal unit cells at both ends of the tube. Figure (6.2) shows the graph of change in potential energy ($\Delta U$) vs. percentage strain $\varepsilon$ in the CNT when tension is applied equally at both ends. Strain is defined as $\varepsilon = \left( l_n - l_0 \right) / l_0$ where $l_0$ is the initial unconstrained equilibrium length of the nanotube and $l_n$ is the equilibrium length of the tube after application of the $n^{th}$ incremental load step. The change in potential energy is measured with reference to the equilibrium potential energy of the unconstrained relaxed nanotube.

![Figure (6.2) Comparison of variation of energy between molecular mechanics method and multi-scale method under tensile loading conditions](image)

It can be observed that the results from the proposed multi-scale method match closely with the benchmark full molecular mechanics results up to a strain of 17%. It can be realized that after a certain amount of deformation, the unit cells in the coarse scale region begin to lose their periodic nature. Since this contradicts the basic assumption of the method, for large strains the
results obtained using the multi-scale method start to deviate slightly from those obtained using the full atomistic simulations.

Figure (6.3) shows the graph of change in potential energy ($\Delta U$) vs. percentage strain $\epsilon$ in the CNT when compression is applied equally at both ends in steps of 0.024 Å per step.

![Graph of change in potential energy vs. percentage strain](image)

**Figure (6.3) Comparison of variation of energy between molecular mechanics method and multi-scale method under compressive loading conditions**

A numerical study conducted by Yakobson et al. [42, 43] based on the Tersoff–Brenner potential for the compressive loading case yielded a buckling strain of 0.05, followed by three subsequent buckles upon further loading. The low values of buckling strain can be attributed to the structural instability in CNTs. The high aspect ratio in the CNT structures makes them susceptible to structural instability.
6.2 Twisting

The nanotube is divided into two regions, the fine scale region consisting of 1340 atoms at the center of the nanotube and the coarse scale region consisting of rest of 560 atoms. Twisting angles are imposed incrementally at the two ends of the nanotube while holding the cross-sectional circular shape unchanged. Loading steps of 0.5° are imposed till a total twisting angle of 40° is reached. Figure (6.4 (a)) shows the twisted configuration of the nanotube while figure (6.4(b)) shows the graph of comparison of change in potential energy ($\Delta U$) vs. the angle of twist in the CNT using the two methods.

![Twisted Configuration](image)

![Graph of Comparison](image)

**Figure (6.4) Twisting results (a) twisted configuration of nanotube (b) Comparison of variation of twisting energy between molecular mechanics method and multi-scale method**

It can be observed that the results obtained from the multi-scale method match closely with the benchmark full atomistic solution for the twisting problem for small twisting angles. As the twist
in the nanotube goes on increasing, the nanotube slowly begins to lose its periodic nature along its axial direction. Also the kernel function matrices are obtained at small strain range and the nonlinear elastic behavior, as observed at larger twisting angles, is not accounted for. Hence for higher angular strains the results obtained using the multi-scale method start to deviate from those obtained using molecular mechanics approach.

Figure (6.5) shows the comparison of the x and y components of displacements of an arbitrary atom in the interface unit cell during the loading process using the full molecular mechanics and the multi-scale method. As can be seen, the proposed BC treatment predicts the displacements at the virtual interface fairly well up to moderately high deformation range.

Figure (6.5) Comparison of atomic displacements in the interfacial cell using the atomistic and multi-scale technique
The phenomenon of collapse or flattening of the tube is observed in the central region of the nanotube at a twisting angle of about $56^0$ using full-scale atomistic simulation. Our multi-scale model is incapable of simulating this collapse since, even at inception, the collapsed region occupies a length greater than the total length of our fine scale region. While the fine scale domain is unqualified to account for this collapse, the coarse scale region faces instability issues at such high twisting angles. The stiffness of the tube looses linearity at loads corresponding to collapse. The mathematical operators in the coarse scale region are derived based on the stiffness of the tube in the small strain range. Since the collapse of the tube implies a large strain and a large reduction in the stiffness of the tube, the mathematical operators no longer predict the behavior of the tube correctly.

### 6.3 Bending

Displacement is applied to the unit cells at both the ends of the nanotube so as to simulate its bending in a plane passing through its axis. Incremental bending angles of $0.375^0$ are imposed on the terminating unit cells till a total bending angle of $45^0$ is reached. Molecular mechanics solution is required only for the fine scale region consisting of 1020 atoms out of the 1900 atoms.
As has been shown using full atomistic simulation, the nanotube buckles at a bending angle of about 12°. Buckling due to bending and torsion has been earlier demonstrated in [43-46], and is characterized by a collapse in the cross-section which results in a kink or ribbon-like structure. Experimental observations of buckling in CNT have been documented in [47-52]. A major factor that contributes to the buckling mode is the radial deformability of the tubes. Figure (6.6) shows the post-buckling patterns as obtained from the fully atomistic and multi-scale simulations superimposed on each other for comparison. The bonds computed from molecular mechanics are plotted as black lines while the atomic positions computed from the multi-scale technique are plotted as empty dots. The new multi-scale method not only captures the pre-buckling behavior
of the tube but also simulates the post collapse behavior accurately. This can be credited to the local nature of the buckling phenomenon that is confined to the fine scale region alone.

Figure (6.7) shows the graph of change in potential energy ($\Delta U$) vs. the bending angle of the CNT. It can be observed that the result obtained using the multi-scale method starts to deviate as the bending angle increases to about $12^0$. This can be attributed to the commencement of the loss of periodicity of the unit cells of the nanotube due to non-linear deformation pattern of the tube in the pre-buckling zone. After the tube buckles, the energy variation assumes a near linear shape so that the energy variation obtained using the full atomistic simulation matches closely with that obtained using the multi-scale method. This indicates that the local deformation in the nanotube can be well captured using the multi-scale method. The advantage of the multi-scale simulation
can be easily seen from the fact that detailed atomistic deformations in the nanotube are captured with the help of atomistic simulations in the fine scale region.

![Figure (6.8) Progress of bending of CNT as seen using multi-scale simulation](image)

Figure (6.8) shows the stepwise progress of the nanotube bending as seen using the multi-scale approach. It can be observed that the phenomenon of buckling is confined completely to the fine scale region unlike the collapse of the tube under torsion.

### 6.4 Loading of nanotubes with defects

Till now, we have considered ideal defect free single walled nanotubes in our analysis. However, carbon nanotubes have been found to exhibit structural imperfections that can be mainly attributed to their method of synthesis. The distribution and density of defects affect adversely their electronic and mechanical properties. One of the most common defects observed in carbon
nanotubes is the absence of chemical bonds between adjacent carbon atoms at random locations. We simulate the behavior of CNTs with broken bonds to capture their behavior under realistic conditions. Three parallel bonds making an angle of $30^\circ$ with the nanotube axis in the fine scale region are considered absent and the behavior of the tube is observed under tensile loading conditions.

![Nanotube images](image)

**Figure (6.9) Nanotube with broken bonds**

(a) unconstrained nanotube with 3 carbon bonds absent (b) nanotube configuration corresponding to 15% strain as observed by molecular mechanics analysis (c) nanotube configuration corresponding to 15% strain as observed by multi-scale analysis

The nanotube is divided into two regions, the central fine scale region consisting of 1020 atoms and the coarse scale region consisting of the remaining 880 atoms. Incremental displacements of 0.24 Å per step are imposed on the unit cells at the two ends of the tube, only in the axial direction, while keeping the circular cross-section area of the tube intact. As shown in figure
(6.9), the simulation of behavior of the nanotube using the newly proposed method matches well with that obtained using full atomistic method for moderately high strains. Figure (6.10) shows the graph of change in potential energy ($\Delta U$) vs. percentage strain $\varepsilon$ in the CNT. It can be observed that the results from the multi-scale method match closely with the benchmark molecular mechanics results.

![Graph showing comparison of energy variation between molecular mechanics method and multi-scale method under tensile loading conditions.](image)

**Figure (6.10) Comparison of variation of energy between molecular mechanics method and multi-scale method under tensile loading conditions**

The specific case with three broken bonds in a preferred direction seems highly improbable practically. However, we wish to emphasize the fact that our primary aim is to establish the robustness of applicability of the multi-scale technique to the study of CNTs even under absence of perfect geometry.
Full scale atomistic simulations have predicted the formation of what are called as the 5-7-7-5 defects under the application of tensile loading conditions enough to produce strains greater than 17%. The multi-scale simulation fails to corroborate these predictions due to two main causes. Firstly, at such loads, the coarse scale region faces stability issues due to the loss of periodicity as described in section (6.1). Secondly, in this study we have resorted to an iterative procedure that yields results correct only up to within a certain tolerance. A technique to eliminate the need of the iterative scheme shall open a possibility of confirming or refuting the formation of pentagon-heptagon pairs.
Chapter 7

Conclusions and Future Scope

7.1 Summary and Conclusions

Multi-scale modeling and simulation techniques are important tools for developing a comprehensive understanding of mechanics of nano-scale materials. In this thesis, we have discussed an analytical approach to formulate the multi-scale boundary conditions for quasistatic atomistic simulations of geometrically periodic atomic structures.

Under the premise of translational symmetry of the coarse grain lattice, we have used Discrete Fourier Transform and the Green’s functions to yield a compact formulation in terms of the discrete convolution operators, which relate the applied boundary conditions to a set of equivalent virtual boundary conditions. These virtual boundary conditions applied on a reduced domain produce the same effect in the region of interest as that of the actual boundary conditions. Thus our domain of analysis shrinks to a smaller size, while adequately preserving the accuracy of results.

In the original work by Karpov et al. the loads/displacements are applied in the fine scale region and the actual boundary of the entire domain is considered fixed. This leads to the need to use only one mathematical operator instead of two as in our case. They have applied the proposed methodology to the nano-indentation analysis of crystalline gold substrate. Although the basic
approach to the problem is the same, to our knowledge, this work would be the first to successfully apply this multiscale technique to study the behavior of CNTs.

It is important to note that our approach applies the continuum concepts at the atomic scale to get rid of the computation of unnecessary degrees of freedom of the coarse scale region. It does not require coarse scale elements to be scaled down to the atomic level at the virtual boundary between fine and coarse scales. Thus our method obviates the necessity of building the actual coarse scale model by exploiting its structural periodicity.

Employing this multi-scale approach, we have implemented a series of benchmark problems involving realistic boundary conditions on carbon nanotubes. We have found that the method yields results in accordance with existing full scale atomistic simulations, thus ensuring its robustness and reliability. The energy plots show that the overall behavior of the atoms in the fine scale region matches closely with that predicted by full scale atomistic simulations. As a general observation, the results predicted by the multi-scale method are slightly on the conservative side as compared to the full scale atomistic simulations. We wish to highlight once again that due to its local nature, the post buckling behavior of CNTs in bending is captured accurately by this technique.

Advantages of the multiscale technique will be more obvious after testing it on larger systems.

### 7.2 Future scope

With the framework for the new multi-scale simulation technique in place, we summarize the future scope of work.
1. Exact evaluation of the interface boundary conditions:

   In this thesis, we have resorted to an iterative procedure to obtain a unique set of virtual boundary conditions at the interface between the fine and the coarse scale regions. Although, this yields fairly accurate results, it demands some unnecessary computational expense. In future, efforts can be directed toward eliminating the iterative procedure to alleviate the computational expense.

2. Extension of the multi-scale scheme to nanotubes of other chiralities under a larger span of boundary conditions. We have dealt with problem cases involving symmetric boundary conditions. The umbrella of boundary conditions can be increased to a broader region.
Appendix A

The proof of equation (4.11) as given in [37, 38] is briefly discussed here.

Let be \( x_k \) be the roots of the equation \( x^n + 1 = 0 \) such that \( n \) is a positive integer and \( k = 1, 2, 3, \ldots n \). Then for a positive integer \( m \), [38] states, by the method of partial fractions,

\[
\frac{x^m}{x^n + 1} = -\frac{1}{n} \sum_{k=1}^{n} \frac{x_k^{m+1}}{(x - x_k)}, \quad 0 \leq m < n
\]  

(1)

An addition of unity to the right hand side makes the equation true for \( m = n \). Differentiating equation (1) and then setting \( x = 1 \), we have

\[
\frac{(2m - n)n}{4} = \sum_{k=1}^{n} \frac{x_k^{m+1}}{(1-x_k)^2}, \quad 0 \leq m \leq n
\]  

(2)

The roots \( x_k \) can be expressed as \( x_k = e^{(2k-1)\pi i/n} \), hence,

\[
x_k^m + x_k^{-m} = 2\cos(m(2k-1)\pi/n)
\]  

(3)

\[
x_k^m - x_k^{-m} = 2i\sin(m(2k-1)\pi/n)
\]  

(4)

The denominator of equation (2) can be transformed as:

\[
(1-x_k)^2 = -x_k(1-x_k^{-1})(1-x_k) = -x_k[2 - (x_k + x_k^{-1})]
\]

\[
= -2x_k[1 - \cos((2k-1)\pi/n)]
\]  

(5)

Substituting equation (5) in equation (2), we get,

\[
\sum_{k=1}^{n} \frac{x_k^m}{[1 - \cos((2k-1)\pi/n)]} = \frac{(n-2m)n}{2}
\]  

(6)

Since the roots \( x_k \) are complex conjugate pairs, \( x_k^{-1} = e^{-i(2k-1)\pi i/n} \) are also roots of the equation. Thus we have,

\[
\sum_{k=1}^{n} \frac{x_k^{-m}}{[1 - \cos((2k-1)\pi/n)]} = \frac{(n-2m)n}{2}
\]  

(7)

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Adding equations (6) and (7) and using equation (3) we get,

\[ \sum_{k=1}^{n} \frac{\cos(m(2k-1)\pi/n)}{1 - \cos(2k\pi/n)} = \frac{(n-2m)n}{2} \quad 0 \leq m \leq n \tag{8} \]

i.e.,

\[ \sum_{k=1}^{n} \frac{\cos(m(2k-1)\pi/n)}{\sin^2((2k-1)\pi/2n)} = (n-2m)n \tag{9} \]

Combining the terms for \( k \) and \( n-k+1 \), we can write,

\[ \sum_{k=1}^{n/2} \frac{\cos(m(2k-1)\pi/n)}{\sin^2((2k-1)\pi/2n)} = (n-2m)\frac{n}{2} + \left\{ \left\lfloor \frac{n}{2} \right\rfloor - \frac{n}{2} \right\} (-1)^m \tag{10} \]
Bibliography:


