NANO- AND MICRO-MECHANICAL ANALYSIS OF FLEXOELECTRICITY IN GRAPHENE-BASED STRUCTURES

Ph.D. Thesis

By

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DEPARTMENT OF MECHANICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE

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DEPARTMENT OF MECHANICAL ENGINEERING

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled NANO-AND MICRO-MECHANICAL ANALYSIS OF FLEXOELECTRICITY IN GRAPHENE-BASED STRUCTURES in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DE-PARTMENT OF MECHANICAL ENGINEERING, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from December 2017 to December 2023 under the supervision of Dr. Shailesh I. Kundalwal, Associate Professor, Indian Institute of Technology Indore, India.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

May 29, 2024 Signature of the Student with Date (SUBHASH KESHAV NEVHAL)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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on May 22, 2024.

Signature of Thesis Supervisor with Date (Dr. SHAILESH I. KUNDALWAL)

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To my respected Guru Dr. Shailesh I. Kundalwal

"Nanotechnology, the science of the small, holds the promise of big innovations. In the realm of the minuscule, we find the potential for mighty advancements that can reshape our world."

Abstract

Graphene, a 2D material with exceptional electronic, mechanical, and thermal properties, has garnered significant interest for various applications. Flexoelectricity, a coupling between mechanical strain and electrical polarization, is a unique property of dielectric materials. This property can potentially revolutionize various fields, including energy harvesting, nanodevices, and sensors. However, understanding the flexoelectric behavior of graphene-based structures at the nano- and microscales is crucial for optimal utilization. Graphene is centrosymmetric, so it is not piezoelectric. To make graphene flexoelectric, bending or strain engineering can be applied. This study used the strain engineering method with different defects for polarization properties. GPAW, a Python-based software for Density functional theory (DFT), is used. Berry phase formulation is implemented to determine dipoles and polarization. The flexural rigidity of graphene is studied at the microscale level. In first-principles calculations, various electro-mechanical properties were determined. Polarization properties were evaluated using various defect geometries such as Stone-Wales and triangular defects in monolayer and multilayer cases. In the heterostructure case, the various combinations of Boron nitride nanosheets (BNNSs) and graphene layering patterns were studied for their polarization properties. The investigation delves into the intricate interactions at the nanoscale and microscale level, analyzing how flexoelectric properties manifest in graphene-based structures. The study aims to enhance our understanding of flexoelectric phenomena in graphene-based structures and their potential applications in advanced materials and devices by scrutinizing the electro-mechanical behavior at both nano and micro levels.

Keywords: Graphene, Graphene nanoribbon, Boron nitride nanosheet, dipole, Berry phase, Polarization, Piezoelectricity, Flexoelectricity, Density functional theory, grid-based projector-augmented wave, Heterostructure, bandstructure, van der Waals forces, Quantum electrostatic heterostructure, Stone–Wales defects, graphenereinforced nanocomposite, Mechanics of materials.

List of Publications

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List of Abbreviations and Acronyms

\mathbf{nm} nanometer

- **STM** Scanning tunneling microscopy
- **AFM** Atomic force microscopy
- ${\bf CNT}\,$ Carbon nanotube
- ${\bf BN}\,$ Boron nitride
- ML multilayer
- \mathbf{DFT} Density functional theory
- **MD** Molecular dynamics
- MDS molecular dynamics simulation
- **GPAW** grid-based projector-augmented wave
- ${\bf ASE}$ atomic simulation environment
- \mathbf{PBE} Perdew-Burke-Ernzerhof
- \mathbf{GGA} generalized gradient approximation
- $BFGS \ Broyden-Fletcher-Goldfarb-Shanno$
- LDA Local-density approximations

DFT-D4 dispersion-corrected density functional theory

LAMMPS large-scale atomic/molecular massively parallel simulator

AIREBO Adaptive Intermolecular Reactive Empirical Bond Order

 \mathbf{vdW} van der Waals

2D two dimensional

 \mathbf{PZT} lead zirconate titanate

EB Euler–Bernoulli

QEH Quantum electrostatic heterostructure

MEMS microelectromechanical system

 ${\bf NEMS}$ nanoelectromechanical system

 ${\bf hBN}\,$ hexagonal boron nitride

 ${\bf BNNT}\,$ Boron nitride nanotube

 ${\bf BNNR}\,$ Boron nitride nanoribbon

 ${\bf BNNS}\,$ Boron nitride nanosheet

 ${\bf GNR}\,$ Graphene nanoribbon

 \mathbf{AGNR} armchair graphene nanoribbon

ZGNR zigzag graphene nanoribbon

 \mathbf{GNS} Graphene nanosheet

CVD Chemical vapor deposition

 ${\bf STM}\,$ Scanning Tunneling Microscope

 ${\bf TEM}\,$ Transmission electron microscopy

DOS density of state

PDOS projected density of state

TISE Time-Independent Schrodinger Equation

 ${\bf HF}~{\rm Hartree}\mbox{-}{\rm Fock}$

 ${\bf CI}$ configuration interaction

HK Hohenberg-Kohn

 ${\bf KS}\,$ Kohn-Sham

LDA local density approximation

GGA generalized gradient approximation

TDDFT Time-Independent density functional theory

 ${\bf BZ}\,$ Brillouin zone

RVE representative volume element

MOM Mechanics of materials

GRNC graphene-reinforced nanocomposite

GNC graphene-reinforced nanocomposite

ROM rules-of-mixture

SOM Strength of materials

 ${\bf SW}$ Stone–Wales

CF clamped-free

SS simply supported

PZC piezoelectric composite

LIST of SYMBOLS

- \mathbf{C}_h Chiral vector
- \mathbf{a}_1 lattice base 1
- \mathbf{a}_2 lattice base 2
- $\boldsymbol{\phi}$ Chiral angle
- \mathbf{P}_i Polarization vector
- ϵ_{jk} Strain
- $\frac{d\epsilon_{jk}}{dx_l}$ Strain gradient
- \mathbf{e}_{ijk} Piezoelectric coefficient
- \mathbf{f}_{ijkl} Flexoelectric coefficient
- **p** Dipole moment
- ${\bf q}$ Charge
- \mathbf{r} Displacement
- $\Psi_{tot}\,$ Quantum-mechanical wavefunction
- \hat{H}_{tot} Hamiltonian operator
- $\hat{\boldsymbol{T}}_n$ kinetic contribution of the nuclei
- \hat{T}_{e} kinetic contribution of the electrons

- $\hat{m{V}}_{ee}$ electron-electron interactions
- $\hat{m{V}}_{nn}$ nucleus-nucleus interactions
- $\hat{m{V}}_{ne}$ nucleus-electron interactions
- \mathbf{E}_{tot} Total energy of ground state configuration
- -e electronic charge
- \mathbf{m}_e mass of an electron
- $\hbar\,$ reduced Planck's constant
- A observable A
- \hat{A} operator of A
- $\left\langle \Psi \left| \hat{A} \right| \Psi \right\rangle$ Expectation value of A
- ho(r) one-electron density function
- $E[\rho]$ a functional of electron density function
- \hat{H}^{KS} one-electron KS Hamiltonian
- $\{\sigma\}$ stress vector
- $\{\epsilon\}$ strain vector
- $\{\boldsymbol{\sigma}^r\}$ stress vector of the r^{th} phase
- $\{\pmb{\epsilon}^r\}$ strain vector of the r^{th} phase
- $\{\sigma(x)\}$ stress field
- $\{\epsilon(x)\}$ strain field
- $\{ar{\pmb{\sigma}}\}$ average stress
- $\{\bar{\boldsymbol{\epsilon}}\}\$ average strain

 $\begin{bmatrix} C^r \end{bmatrix}$ stiffness matrix of the r^{th} phase $\begin{bmatrix} S^r \end{bmatrix}$ compliance matrix of the r^{th} phase

 Ω volume

- $\mathbf{\Omega}^{f}$ volume of fibers
- $\mathbf{\Omega}^m$ volume of matrix
- \boldsymbol{v}_f volume fraction of fibers
- \boldsymbol{v}_m volume fraction of matrix
- \boldsymbol{V}_m volume fraction of matrix
- $\boldsymbol{V}_g\,$ volume fraction of graphene layer
- $\{u^0(x)\}$ surface displacement
- $\{\sigma^0\}$ uniform stress
- $\{\epsilon^0\}\,$ uniform strain
- $\{\epsilon\}$ strain tensor
- $\{u\}$ displacement vector
- $\{\boldsymbol{\epsilon}^{per}(x)\}$ perturbation strain
- |C| average stiffness matrix
- $|\mathbf{S}|$ average compliance matrix
- $\begin{bmatrix} M \end{bmatrix}$ strain 4th-order concentration tensor
- $\begin{bmatrix} \mathbf{N} \end{bmatrix}$ stress 4th-order concentration tensor
- **E** Young's modulus
- $\pmb{\mu}$ Poisson's ratio

 $[C^{NC}]\,$ matrix for the effective elastic properties $\{e^{NC}\}\,$ matrix for the piezoelectric properties $E_3\,$ electric field

 $\boldsymbol{D_3}$ electric displacement along lamina thickness

 D_3^g electric displacement of graphene phase

 D_3^m electric displacement of matrix phase

 E_3^g electric field of graphene phase

 ${\pmb E}_{\pmb 3}^{\pmb m}$ electric field of matrix phase

 X^r average concentration factor [6×6]

 $\boldsymbol{Y^g}$ average concentration factor $[6{\times}1]$

Chapter 1

Introduction

1.1 Nanotechnology

Nanoscience is the exploration of material properties at the nanoscale, typically within the range of 1 to 100 nanometers with one nanometer (nm) being equivalent to one billionth of a meter $(1/10^9)$. This field is undergoing rapid expansion, with scientists from various disciplines collaborating to understand the characteristics of matter on the nanoscale and explore innovative applications for materials at this level. The fundamental properties of nanomaterials, including mechanical, electrical, optical, and thermal features, are intricately linked to the arrangement of molecules and atoms into larger structures at the nanoscale. Moreover, nanomaterials often exhibit altered atomic-level properties compared to the macroscale due to the influence of quantum mechanical effects (Cohen, 2001). A notable aspect of nanomaterials is their larger surface area in relation to their parent materials on the microscale, considering a specific volume (Roco, Mirkin, & Hersam, 2011). This increased surface area enhances the reactivity of nanomaterials, making them efficient for various applications.

Nanotechnology applies principles from nanoscience to create innovative materials, devices, and systems, potentially revolutionizing various industries such as healthcare, electronics, energy, and manufacturing. It involves manipulating matter with at least one dimension between 1 and 100 nm. Figure 1.1 illustrates the relationship of this size scale to more common, everyday scales. The ability to control matter at the nanometer scale has already yielded substantial advancements in various disciplines, including engineering, physics, materials science, chemistry, medicine, and biology. The term "nanotechnology" damping was coined by Richard Feynman in 1959. Research at the nanoscale level accelerated after the discovery of Scanning Tunneling Microscope (STM) (Binnig, Rohrer, Gerber, & Weibel, 1982), and Atomic force microscopy (AFM) (Binnig, Quate, & Gerber, 1986). The discovery of STM and AFM allowed researchers to study and manipulate individual atoms. Manipulating materials at the nanoscale empowers us to craft custom-made materials and products with improved properties, leading to advancements in nanoelectronics, intelligent pharmaceuticals, sensors, and customized interfaces connecting electronics with biological systems.



Figure 1.1: The comparison of size of nanoscale objects.

The widespread advancement of nanotechnology and nanoscience has resulted in the discovery of several exciting nanomaterials. As an example, Iijima's groundbreaking research on carbon nanotubes (Carbon nanotubes (CNTs)) in 1991, along with subsequent studies on their remarkable mechanical, thermal, and electrical properties, has spurred further investigations into various types of nanotubes. Boron nitride (BN) has similar lattice structures to carbon-based nanostructures. The BN nanostructures, including Boron nitride nanotubes (BNNTs), Boron nitride nanoribbons (BNNRs), and BNNSs are based on the hexagonal phase BN, with B–N bonds. The B–N bonds are isoelectronic, with C–C bonds in carbon-based nanostructures. Therefore, the structures of BNNS, BNNR and BNNT are similar to graphene, Graphene nanoribbons (GNRs), and CNTs, respectively, as shown in Fig. 1.2



Figure 1.2: Different BN- and carbon-based nanostructures; BNNS, graphene, BNNT, and CNT.

1.2 Graphene nanoribbons

Geim and Novoselov (Geim & Novoselov, 2007) first created a two-dimensional single-layer graphene sheet, which consists of carbon atoms with covalent bonds and is the basis for both 3D graphite and 1D CNTs.

It has unique scale-dependent electronic (metal and semiconductor behavior depending on orientation), mechanical (elastic modulus 1TPa), and thermal (thermal conductivity 5300 W/mK at room temperature) properties (Zhang, Tan, Stormer, & Kim, 2005; C. Lee, Wei, Kysar, & Hone, 2008; Balandin et al., 2008). Graphene, one of the strongest materials, can be strained up to 25 % (G.-D. Lee et al., 2005), and its behavior varies from metallic to semiconducting based on its deformation and defects pattern (Son, Cohen, & Louie, 2006; Novoselov et al., 2005; Sanderson, 2007). The structure of Graphene nanosheets (GNSs) relies on the atomic configuration of carbon atoms within a two-dimensional hexagonal lattice. In graphene, each carbon atom establishes three robust covalent bonds with its three closest neighboring carbon atoms, creating a distinctive honeycomb-like pattern. This specific arrangement is called a " sp^2 hybridized" carbon lattice.

Carbon Atoms: GNSs consist entirely of carbon atoms. Each carbon atom possesses four valence electrons. In graphene, three of these electrons participate in sigma (σ) bonds with three adjacent carbon atoms, while the fourth electron is mobile within the lattice, contributing to the remarkable electrical conductivity of graphene.

Hexagonal Lattice: The carbon atoms arrange themselves in a hexagonal pattern, forming six-membered rings. Each hexagon in the lattice represents a single carbon-carbon bond.

sp² Hybridization: The carbon-carbon bonds in GNSs are formed through sp^2 hybridization of carbon orbitals. Each carbon atom's three valence electrons form three sigma (σ) bonds arranged in a trigonal planar configuration. This bonding arrangement results in a flat, two-dimensional structure.

Atomic Thickness: GNSs are incredibly thin, with a thickness of just one atom. Each layer comprises a single hexagonal lattice of carbon atoms, forming a single GNS. It is noteworthy that GNSs can also consist of a few-layer graphene, and the number of layers may vary based on the specific preparation method.

Carbon-Carbon Bond Length: The C-C bond length in graphene is approximately 0.142 nm, relatively short compared to other carbon-based materials.

High Surface Area: GNSs exhibit an exceptionally high surface area per unit mass due to their two-dimensional structure. This characteristic makes them appealing for diverse applications, including energy storage, catalysis, and gas sensing.

GNSs can be produced using various methods, including CVD, epitaxial growth, or exfoliation from bulk graphite. The synthesis process allows for control over the size and shape of GNSs, resulting in diverse morphologies.

Overall, the distinctive structure of GNSs, characterized by a unique hexagonal lattice and atomic thickness, underlies their exceptional properties. Consequently, they have become highly desirable materials for various applications in nanotechnology, electronics, energy, and beyond.

1.3 Boron nitride nanosheets

Boron nitride nanosheets (BNNSs) are two-dimensional nanomaterials typically composed of single, bi-, or multilayer (ML) hexagonal boron nitride (hBN) on the order of nm scale. Widely recognized in academia and industry, BNNS has garnered significant attention due to its multifunctional properties among all other boron nitride-based nanostructures. Analogous to graphene, ML-BNNSs were initially synthesized by (Pacilé, Meyer, Girit, & Zettl, 2008), and both single- and ML-BNNSs were produced by (Han, Wu, Zhu, Watanabe, & Taniguchi, 2008). Consisting of boron (B) and nitrogen (N) atoms arranged alternately in a honeycomb pattern, similar to the arrangement of carbon atoms in a graphene sheet (Lehtinen et al., 2011), BNNSs have garnered significant attention as a material of great interest.

Over the past few years, BNNSs have garnered attention for their highly stable structures (Topsakal, Aktürk, & Ciraci, 2009), superior mechanical properties (Topsakal et al., 2009; Bosak et al., 2006; S. I. Kundalwal & Choyal, 2018), and functionalization capabilities, enabling tailored engineering for applications in nanoelectromechanical system (NEMS) (Boldrin, Scarpa, Chowdhury, & Adhikari, 2011; Chaurasia & Parashar, 2021). With a large band gap of approximately 5 to 6 eV, BNNSs exhibit insulating properties (Watanabe, Taniguchi, & Kanda, 2004; Topsakal et al., 2009), coupled with excellent physical characteristics, high chemical and thermal stabilities, and robust resistance to oxidation at elevated temperatures (exceeding 900 °C) (Golberg et al., 2010). Furthermore, BNNSs possess a non-centrosymmetric structure and partly demonstrate the ionic characteristic of B–N bonds due to the electronegativity differences between B and N atoms, showcasing piezoelectricity.

The work by (Mele & Král, 2002), which gained significant attention in the field of actuators and sensors (Eichler & Lesniak, 2008), composite materials (Zhi, Bando, Tang, Kuwahara, & Golberg, 2009), hydrogen storage (xiang Zhao & hong Ding, 2009), gas sensors, optoelectronics, optical devices, transistors, and biological probes (X. Song, Hu, & Zeng, 2013), has positioned hexagonal boron nitride nanosheets (BNNSs) as versatile materials. Although most applications are similar to graphene sheets, the BNNS possess additional multifunctional features like piezoelectricity and white color. Moreover, the BNNSs display comparable mechanical properties to graphene sheets, while the failure resistance may surpass the latter's. The electromechanical coupling in BNNSs is also better than the polymer-based piezoelectric materials (Sai & Mele, 2003). Several unique techniques are being employed to synthesize BNNSs: chemically derived route technique (Han et al., 2008), micromechanical cleavage technique (Pacilé et al., 2008), electron beam irradiation (EBR) (Jin, Lin, Suenaga, & Iijima, 2009; Cho et al., 2011), Chemical vapor deposition (CVD) (Shi et al., 2010), and thermal decomposition of borazine on the surface of a transition metal (Lin & Connell, 2012). After the discovery of BNNSs, extensive efforts have been made to refine the synthesis process to obtain pristine BNNSs (Ci et al., 2010). By controlling the parameter of synthesis, an individual BN layer is called a "single-layer BNNS"; a thin BN crystal with several atomic layers is called a "multilayered BNNS" (see Fig. 1.3). Within each ML-BNNS, strong covalent bonds bind B and N atoms, whereas weak vdW forces hold the layers together at a distance of 0.335 nm (L. Song et al., 2010). Therefore, ML-BNNS films could be peeled off from bulk BN crystal by micromechanical cleavage and used as a dielectric layer. Multilayer-BNNS has also been made by ultrasonication and high-energy electron beam irradiation of BN particles. BN nanostructures are generally considered advanced nanomaterials with an outstanding electromechanical response.


Figure 1.3: Structural basics of 2D BN nanostructures.

1.4 Structure of Boron nitride nanosheet

A monolayer molecule of hexagonal boron nitride nanosheets (BNNSs) comprises a hexagonal array of alternatively arranged boron (B) and nitrogen (N) atoms. The structural feature of the BNNS corresponds to a hexagonal pattern that repeats periodically in space. This periodicity makes each B and N atom bonded to three neighboring atoms. The structure primarily arises from sp^2 hybridization, forming three in-plane σ bonds and an out-of-plane π bond. The σ bond, characterized by a length of 1.446 Å, is a robust covalent bond crucial for the remarkable mechanical and piezoelectric properties of BNNSs. Conversely, the π bond is relatively weak and contributes to the interactions between the monolayer BNNSs (Falin et al., 2017; Han et al., 2008).

Boron nitride nanosheets exhibit a regular arrangement with a hexagonal array of B and N atoms. The identification of different types of BNNSs, such as armchair, zigzag, and chiral, is commonly based on the - Chiral vector (\mathbf{C}_h). This vector is expressed as a linear combination of lattice bases (a_1 and a_2). Mathematically, the sheet chirality can be defined in terms of the roll-up vector as follows:

$$C_h = na_1 + ma_2 \tag{1.1}$$

Here, the integers (n, m) represent the Miller indices of the hexagonal lattice (indicating the number of steps along the zigzag bonds of the hexagonal lattice), and \mathbf{a}_1 and \mathbf{a}_2 are unit basis vectors, as illustrated in Fig. 1.4. The angle between the chiral vector (\mathbf{C}_h) and lattice base vector (\mathbf{a}_1) is called the - Chiral angle ($\boldsymbol{\phi}$) and is given by:

$$\phi = \arctan \frac{\sqrt{3}m}{2n+1} \tag{1.2}$$

The zigzag axis of BNNS corresponds to $\phi = 0^{\circ}$. If the rolling chiral vector aligns with this axis, a zigzag (n, 0) BNNS is formed. Conversely, the armchair axis of the sheet is defined by $\Phi = 30^{\circ}$. When the rolling chiral vector aligns with this axis, an armchair (n, m) BNNS is formed. The monolayer BNNS generated for other values ϕ (i.e., $0^{\circ} < \phi < 30^{\circ}$) is called chiral BNNS. Figure 1.4 illustrates the schematic representations of two types of BNNSs. The chirality of BNNSs has significant implications for their properties.



Figure 1.4: Schematic representation of 2D armchair and zigzag BNNS.

1.5 Size-dependent properties of BNNS

1.5.1 Piezoelectricity

Piezoelectricity was initially discovered by French physicists Pierre and Jacques Curie in 1880. Subsequently, Gabriel Lippmann deduced mathematical relations for the converse piezoelectric effect from the fundamental principles of thermodynamics in 1881, which the Curie brothers did not predict. Piezoelectricity, involving electrical polarization induced by a constant strain (or vice versa), is the most widely known and exploited form of electromechanical coupling in non-centrosymmetric crystals. In such crystals, the absence of a center of inversion results in the presence of polarization. In contrast, the flexoelectricity phenomenon is observed in nanomaterials with inversion symmetry, and even centrosymmetric crystals can be polarized by breaking their inversion symmetry and applying a non-uniform strain gradient. Unlike piezoelectricity, which is found only in 20 non-centrosymmetric point groups, flexoelectricity exists in all-dielectric and insulating materials with 32 crystallographic point groups, enabling electromechanical coupling in non-piezoelectric materials (Maranganti, Sharma, & Sharma, 2006; Sharma, Maranganti, & Sharma, 2007).

There are both direct and converse piezoelectric effects. In the direct piezoelectric effect, applied stress creates polarization within the crystal. Conversely, in the converse piezoelectric effect, an applied electric field creates stress and strain in the crystal. In the equations presented, $P, E, \epsilon, \sigma, \mu$, and x represent polarization, electric field, strain, stress, flexoelectric coefficient, and spatial direction, respectively. The subscripts i, j, k, l denote different Cartesian directions as 1, 2, and 3, or x, y, and z.

The origin of the piezoelectric effect lies in the fundamental asymmetry of a crystal's lattice structure. Not all crystal structures possess piezoelectric properties; only non-centrosymmetric crystals exhibit piezoelectricity, while crystal structures of higher symmetry do not. Centrosymmetry exists if a crystal can be transformed from every point (x, y, z) to (-x, -y, -z) while retaining the same geometric structure. Piezoelectric materials must be non-centrosymmetric to separate the centers of mass of positively and negatively charged ions when subjected to strain. This limitation on crystal structure confines the materials used to generate the piezoelectric effect.

1.5.2 Flexoelectricity

The flexoelectric effect represents an electromechanical coupling phenomenon in which dielectric polarization exhibits a linear response to a mechanical strain gradient. The term is derived from the Latin word "flexus", signifying "bend", and is associated with the occurrence of a strain gradient in bent structures (Yudin & Tagantsev, 2013). Flexoelectricity shares similarities with piezoelectricity but introduces spatial gradients, introducing additional complexity to analysis and comprehension. Similar to piezoelectricity, flexoelectricity encompasses both direct and converse effects: the direct effect produces polarization in reaction to an applied strain gradient, while the converse effect involves generating a strain in response to an applied electric field gradient. Some reports also indicate instances where a uniform electric field induces curvature in the material (Yudin & Tagantsev, 2013).

In contrast to piezoelectricity, flexoelectricity is inherent in every crystal structure and does not depend on asymmetry in the crystal lattice. The inclusion of spatial gradient terms in the constitutive equations allows for varying amounts of strain at different locations within the crystal, creating the necessary asymmetry to separate the centers of mass of positive and negative charges, leading to the induction of polarization. This characteristic expands the scope of materials suitable for NEMS devices. Moreover, as numerous high-performance piezoelectric materials incorporate lead, flexoelectricity offers the prospect of utilizing more biocompatible materials or enhancing the piezoelectric effect in sensors, actuators, and energy harvesters.

Like piezoelectricity, flexoelectricity exhibits two discrete strain and electric field gradient-dependent electromechanical couplings: direct and converse flexoelectric effects. As a size-dependent phenomenon, flexoelectricity is a preferred electromechanical coupling in microelectromechanical system (MEMS)/NEMS applications.

The constitutive relation (Eq. 1.3) for the total - Polarization vector, accounting for both piezoelectric and flexoelectric effects (Yudin & Tagantsev, 2013; S. Kundalwal, Meguid, & Weng, 2017), can be rewritten as :

$$P_i = e_{ijk}\epsilon_{jk} + f_{ijkl}\frac{d\epsilon_{jk}}{dx_l}$$
(1.3)

where, the terms are - Strain (ϵ_{jk}) , - Strain gradient $(\frac{d\epsilon_{jk}}{dx_l})$, - Piezoelectric coefficient (\mathbf{e}_{ijk}) , and - Flexoelectric coefficient (\mathbf{f}_{ijkl}) respectively.

1.5.3 Polarization in graphene structure

In the initial work by Kogan (Kogan, 1964), a theoretical foundation for flexoelectricity was established. It was elucidated that a homogeneous mechanical deformation does not induce polarization in the graphene lattice due to its intrinsic symmetry. However, a strain gradient in centrosymmetric graphene can lead to a flexoelectric effect. This strain gradient induces ionic position alterations, causing electron density redistribution. While uniform strain does not generate polarization in centrosymmetric graphene, a strain gradient breaks this centrosymmetry, generating polarization.

Tagantsev (Tagantsev, 1986) developed a theoretical model to study the flexoelectric response in solid, dielectric crystals and stated that the flexoelectric effect differs from the piezoelectric effect. In 2007, Sharma et al. (Sharma et al., 2007) theoretically studied the effect of the inclusion of centrosymmetric and non-centrosymmetric shapes in the matrix of InAs-GaAs, and they observed that the proper arrangement of such centrosymmetric and non-centrosymmetric shapes in the matrix is required to get a nonzero average polarization.

The Berry phase (Berry, 1984) calculations are performed in metals, graphene bilayer, and bulk graphite by considering the spin–orbit interaction. Flexoelectricity, a weak observable effect at the macroscale, is hardly detectable in bulk materials. The strain gradient is inversely proportional to the sample size; thus, at the nanoscale level, flexoelectricity can be very large (Zubko, Catalan, & Tagantsev, 2013). Mohammadi et al. (Mohammadi, Liu, & Sharma, 2013) developed the flexoelectric theory for thin membranes in 2014.

Experimentally, it has been found that the synthesis of graphitic carbon nitride $(g-C_3N_4)$ has natural triangular pores, which shows piezoelectric behavior with a coef-

ficient of 0.758 C/m^2 , verified by DFT calculations. Large strain gradients are created by bending 2D nanosheets with non-centrosymmetric triangular and trapezoidal pores, resulting in strong electromechanical coupling. Javvaji et al.(Javvaji, He, & Zhuang, 2018) studied graphene's piezo- and flexo-electric properties with triangle-shaped defects using molecular dynamics simulation (MDS). Enhanced and advanced avenues for investigating materials with diverse doping and electrical properties, particularly at the sub-nanometer scale, have been facilitated through artificially engineered stacked 2D layer heterostructures with interlayer van der Waals (vdW) forces. VdW is characterized as non-bonded interactions with a distance range of a few nanometers. These interactions are weaker than bonded and Coulomb interactions.

Additionally, employing atomically thick hBN nanosheets to encapsulate active 2D layers of other materials is a prevalent strategy to enhance their electrical properties (Xia, Weng, Xiao, & Wen, 2020). The interactions between layers or the substrate have become a crucial element in the computational modeling of two dimensional (2D) materials for virtually all applications. The Quantum electrostatic heterostructure (QEH) model (Andersen, Latini, & Thygesen, 2015) offers a rapid and precise calculation of the dielectric function for generic vdW structures, encompassing large interface supercells and hundreds of layers. The fundamental assumptions of the QEH scheme are centered on the additive nature of polarizabilities across different layers.

Ma and Cross (Ma & Cross, 2003) conducted experimental investigations on strain gradient-induced polarization in lead zirconate titanate (PZT) ceramic, revealing a higher flexoelectric coefficient on the order of $\mu C/m$. Their study employed a cantilevered beam approach to explore the flexoelectric effect in PZT, and based on their findings, they observed an increase in flexoelectric polarization with temperature. Hu and Shen (Hu & Shen, 2010) delved into the piezoelectric and flexoelectric effects in nano dielectrics using the variational principle. They applied a bending model incorporating the Bernoulli–Euler beam model and the flexoelectric dielectrics theory to an electro-elastic bilayer nanobeam.

This model accounts for both the strain gradient elastic and flexoelectric effects. Jiang et al. (X. Jiang, Huang, & Zhang, 2013) explored the potential applications of flexoelectric sensors and actuators in bio-mechanical systems. Yan and Jiang (Yan & Jiang, 2013) studied the influence of the flexoelectric effect on the electromechanical behavior of nanobeams under various support types, emphasizing its prominence in nanobeams with smaller thicknesses. Liang et al. (Liang, Hu, & Shen, 2014) investigated the electromechanical behavior of piezoelectric nanobeams using the Bernoulli–Euler beam model. Their study revealed that flexoelectricity and surface effects are size-dependent, with a more pronounced effect at the nanoscale. Liang et al. (Liang, Hu, & Shen, 2015) developed an analytical model based on the Euler–Bernoulli beam hypothesis to study the effect of flexoelectricity in nanowires. They reported that due to flexoelectricity, Young's modulus and bending rigidity of nanowires exhibit significant improvement. Ray et al. (Ray, 2016) provided an exact solution for the static bending response of a nanobeam embedded with a flexoelectric layer acting as an actuator. Wang et al. (X. Wang, Zhang, & Jiang, 2017) employed a finite difference method to investigate the effect of flexoelectricity on the static bending response of piezoelectric nanoplates. Wang and Li (B. Wang & Li, 2021) studied the effect of flexoelectricity on the natural frequency of piezoelectric nanoplates based on Kirchhoff plate theory. Su and Zhou (Su & Zhou, 2020) utilized the non-local effects of flexoelectricity nanosensors to study the electromechanical response of nanobeams. With recent advancements, graphene has been extensively used as structural reinforcement in polymer composites. Zhao et al. (Zhao, Zhang, Chen, & Lu, 2010) developed graphene-based polymer composites and observed a 150~% improvement in tensile strength at low loading, with Young's modulus increasing by approximately ten times. Due to its strong polarization, graphene-based piezoelectric composites find multifarious NEMS/MEMS applications. Justino et al. (Justino, Gomes, Freitas, Duarte, & Rocha-Santos, 2017) utilized graphene to fabricate sensors and biosensors owing to its electromechanical properties. Kundalwal et al. (S. Kundalwal, Shingare, & Gupta, 2020) developed an analytical model to investigate the electromechanical response of graphene/polymer composite nanowires, considering the effects of flexoelectricity. They noted that on the nanoscale, the impact of flexoelectricity on the electromechanical response of nanowires was significant. Using the Euler–Bernoulli (EB) beam

model, Chen et al. (S. Kundalwal et al., 2020; Q. Chen, Zheng, Li, & Zeng, 2021) explored the dynamic response of graphene-reinforced porous nanocomposite beams, taking into account the flexoelectric effects.

1.6 Motivation

This study is motivated by several factors that highlight the potential impact and importance of this research:

Understanding Fundamental Phenomena: Flexoelectricity is a relatively novel electromechanical phenomenon that occurs at small length scales and strain gradients. Studying flexoelectricity in graphene-based heterostructures allows researchers to gain a deeper understanding of this fundamental phenomenon and its implications for the mechanical behavior of nanomaterials.

Tailoring Material Properties: Graphene-based heterostructures offer many possibilities for tailoring material properties. By studying the flexoelectric effect in these heterostructures, researchers can explore how the coupling between mechanical strain and electric polarization can be engineered to achieve desired functionalities and properties at the nanoscale.

Designing Novel Nanodevices: Flexoelectricity opens up new avenues for the design of nanoscale electromechanical devices. Understanding and controlling the flexoelectric effect in graphene-based heterostructures can lead to the development of innovative nanoscale sensors, actuators, energy harvesters, and other nanodevices with enhanced performance and functionalities.

Enhancing Nanomaterial Performance: Flexoelectricity can significantly impact the mechanical properties of graphene-based heterostructures. By analyzing the flexoelectric effect at the nano- and micro-scale, researchers can identify strategies to enhance these materials' mechanical performance and durability, leading to improved nanocomposites and nanoelectronic devices.

Nanoscale Energy Harvesting: Flexoelectricity can provide an additional mechanism for energy harvesting at the nanoscale. Understanding the interplay between mechanical strain and electric polarization in graphene-based heterostructures can guide the development of nanoscale energy harvesting technologies that convert mechanical energy into electrical energy efficiently.

Advancing NEMS: The study of flexoelectricity in graphene-based heterostructures is particularly relevant for NEMS, where small-scale mechanical devices interact with electrical signals. A better understanding of flexoelectricity in these systems can enable the design of more sensitive and energy-efficient NEMS devices.

Materials Design and Optimization: Nano- and micro-mechanical analysis of flexoelectricity in graphene-based heterostructures can guide materials design and optimization. By studying the mechanical response under different conditions and with various heterostructure configurations, researchers can identify materials with specific flexoelectric properties suitable for targeted applications.

Enabling Nanoelectronics and Quantum Technologies: Flexoelectricity can be crucial in nanoelectronics and quantum technologies. Understanding the flexoelectric effect in graphene-based heterostructures can contribute to developing nextgeneration quantum devices and information-processing technologies.

Overall, the motivation for nano- and micro-mechanical analysis of flexoelectricity in graphene-based heterostructures lies in its potential to advance our fundamental understanding of electromechanical phenomena at the nanoscale and its practical applications in designing innovative nanodevices and nanomaterials for various technological fields.

1.7 Outline of the dissertation

This section provides a glimpse of the research work carried out for this dissertation. The problem statement, brief description of the work done, and the salient results and discussions are sub-categorized under each chapter.

Chapter [1]: Introduction to flexoelectricity and graphene heterostructures

The first chapter introduces 2D materials, consisting of a single layer or a few layers of atoms arranged in a two-dimensional lattice. Graphene is a single layer of carbon atoms arranged in a hexagonal lattice resembling a honeycomb pattern. Flexoelectricity is a fascinating electromechanical phenomenon in certain materials where an electric polarization is induced in response to a strain gradient, i.e., a variation in strain across the material.

Chapter [2]: Density functional theory

This Chapter will briefly summarize the fundamentals of DFT, the basic methodologies employed in this work. DFT is a powerful computational quantum mechanical method used to study the electronic structure and properties of materials, molecules, and solids.

Chapter [3]: Micro-mechanics modeling

This chapter discusses micro-mechanics modeling, a computational approach used to study and predict the mechanical behavior of materials at the microstructural level. It involves simulating the interactions between individual constituents, such as grains, phases, fibers, or particles, and the surrounding matrix to understand how these interactions influence the overall mechanical properties of the material.

Chapter [4]: Polarization in defective graphene using DFT

In this Chapter, we study the polarization in defective graphene using DFT, which is a fascinating and challenging task. Defects in graphene can arise from various sources, such as vacancies (missing carbon atoms), substitutional impurities (e.g., replacing a carbon atom with a different element), grain boundaries, or even ripples in the lattice. These defects can significantly influence the electronic and polar properties of graphene.

Chapter [5]: Polarization in graphene heterostructure using DFT

Studying polarization in graphene heterostructures using DFT is an important area of research, especially in the context of 2D materials and van der Waals heterostructures. Graphene heterostructures comprise multiple layers of different 2D materials stacked on each other, forming unique electronic and polar properties at their interfaces.

Chapter [6]: The flexoelectric effect on a graphene nanorod's bending rigidity

The flexoelectric effect can indeed influence the bending rigidity of a Timoshenko graphene-reinforced nanorod. The Timoshenko beam theory is an extension of the classical EB beam theory that considers the effects of shear deformation and rotational inertia. It provides a more accurate description of the bending behavior of slender structures like nanorods, especially when the rod's aspect ratio (length to thickness) is relatively small.

Chapter [7]: Summary and Future scope

Chapter 7 summarizes the major conclusions from the research work presented in the thesis and the further scope of research on graphene heterostructures. The references are alphabetically listed at the end of the thesis.

Chapter 2

Density functional theory

2.1 Introduction

In this chapter, we aim to provide a concise overview of the foundational principles of DFT, which serve as the fundamental methodologies employed in this research. It is worth noting that the literature includes several outstanding reviews on these subjects (Baroni, de Gironcoli, Corso, & Giannozzi, 2001; Payne, Teter, Allan, Arias, & Joannopoulos, 1992). Specifically, our objectives are as follows:

- [1] Review the conceptual underpinnings of DFT.
- [2] Outline the key equations essential for practical implementation.

Point [2] assumes particular importance for obtaining a comprehensive understanding of the primary challenges associated with the development of a coherent theory of flexoelectricity based on first principles.

We embark on a reexamination of the Kohn and Sham formulation. Our exploration will encompass its conceptual foundations, accompanied by the presentation of explicit expressions specifically tailored for a plane wave basis set.

2.2 Polarisation and Dielectric function

When a material interacts with an electric field, E, the electrons within the material are displaced from their equilibrium position. The Dipole moment (**p**) is the product

of a particle's Charge (\mathbf{q}) and its Displacement (\mathbf{r}) from equilibrium, i.e.

$$p = qr \tag{2.1}$$

The polarization (or polarization density), P, is the average dipole moment per unit volume,

$$P = N_a p \tag{2.2}$$

where N_a represents the number of particles per unit volume. In the linear regime, characterized by small average displacements (e.g., for a low-intensity external field), the polarization is connected to the field through the electric susceptibility, χ_e^1 ,

$$P(\omega) = \chi_e(\omega)E(\omega) \tag{2.3}$$

where ω is the angular frequency, assuming a uniform electric field and an isotropic, homogeneous material. Similarly, the dipole moment is related to the electric field by the polarizability, α ,

$$p(\omega) = \alpha(\omega)E(\omega) \tag{2.4}$$

The electric susceptibility is related to the macroscopic dielectric function, ϵ_M , by

$$\epsilon_M = 1 + 4\pi\chi_e \tag{2.5}$$

The susceptibility, χ_e (and consequently ϵ_M), is typically complex and dependent on frequency. A material is considered isotropic if the polarization aligns with the external field, making χ_e a scalar. However, in cases where the direction of polarization differs from that of the external field, the material is termed anisotropic, and the susceptibility becomes a rank-2 tensor.

$$\chi_e = \begin{bmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{bmatrix}$$
(2.6)

If the polarization and external field are written in Cartesian coordinates $(P = P_x i + P_y j + P_z k \text{ and } E = E_x i + E_y j + E_z k)$, then the i^{th} component (i = x; y; z) of the polarization is given by

$$P_i = \chi_{ix} E_x + \chi_{iy} E_y + \chi_{iz} E_z \tag{2.7}$$

2.3 Electronic Structure Calculations

To ascertain the polarization of a system, understanding its electronic configuration in the ground state is essential. Solid-state matter can be conceptualized as an assembly of nuclei and electrons engaged in interactions influenced by particle positions and external forces, ultimately defining the material's electrical and mechanical characteristics. In this context, we employ DFT to explore how electronic energies and wavefunctions can be derived from the Schrödinger equation.

2.3.1 Time-Independent Schrodinger Equation

Consider a system comprising N electrons and M nuclei, each characterized by spatial coordinates r_1, \ldots, r_N and R_1, \ldots, R_M , respectively. Neglecting electronic spin, the system can be fully described by the Quantum-mechanical wavefunction (Ψ_{tot}) , i.e., $\Psi_{tot}(r_1, \ldots, r_N, R_1, \ldots, R_M)$. From this, all observable properties of the system can be determined. In electronic structure calculations, the goal is to find the wavefunction that yields the lowest possible (ground-state) energy. In principle, this is found by solving the Time-Independent Schrodinger Equation (TISE),

$$\hat{H}_{tot}\Psi_{tot}(r_1,\ldots,r_N) = E_{tot}\Psi_{tot}(r_1,\ldots,r_N,R_1,\ldots,R_M)$$
(2.8)

where, Hamiltonian operator (\hat{H}_{tot}) contains contributions from the kinetic energy of the electrons and nuclei, along with electron-electron, electron-nuclei, and nuclei-nuclei interactions, i.e.

$$\hat{H}_{tot} = \hat{T}_n + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{ne}$$
(2.9)

where, the terms are kinetic contribution of the nuclei (\hat{T}_n) , kinetic contribution of the electrons (\hat{T}_e) , electron-electron interactions (\hat{V}_{ee}) , nucleus-nucleus interactions (\hat{V}_{nn}) , and nucleus-electron interactions (\hat{V}_{ne}) , respectively. Equation 2.9 represents an eigenvalue problem with infinite solutions. The configuration corresponding to the ground state is the solution that minimizes the value of \mathbf{E}_{tot} . Solving Eq. (2.9) is typically highly complicated, with an analytical solution existing only for a small subset of problems. There are several approximations and methodologies to simplify the task. The first approximation is to separate the electronic and nuclear motions of the system. This is known as the Born-Oppenheimer approximation and allows us to express the total wavefunction as a product of an electronic wavefunction and nuclear wavefunction (and the total energy as a sum of the electronic and nuclear contributions). It is valid, provided the electrons move on a much smaller time scale than the nuclei. Hence, the original problem simplifies to the task of finding the electronic wavefunction, $\Psi(r_1, \ldots, r_N)$, which satisfies

$$\hat{H}\Psi_{tot}(r_1,\ldots,r_N) = E\Psi(r_1,\ldots,r_N)$$
(2.10)

 \hat{H} is the electronic Hamiltonian given by

$$\hat{H}_{tot} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne} \tag{2.11}$$

The explicit nuclear contributions can subsequently be obtained independently and incorporated as needed. In Eq. (2.11),

$$\hat{T}_e = \sum_i -\frac{1}{2}\nabla_i^2 \tag{2.12}$$

is the operator defining the total kinetic energy of the electrons,

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}$$
(2.13)

gives the total Coulomb repulsion between the electrons, and

$$\hat{V}_{ne} = \sum_{i} v_{ext}(r_i) \tag{2.14}$$

where $v_{ext}(r)$ is the potential representing the total nuclear attraction of the electrons in addition to any other external potential.

$$-e = m_e = \hbar = \frac{1}{4\pi\epsilon_0} = 1 \tag{2.15}$$

where, the terms are electronic charge (-e), mass of an electron (\mathbf{m}_e), reduced Planck's constant (\hbar), and ϵ_0 is the permittivity of free space. The observable, A, of any operator, \hat{A} , is given by its expectation value,

$$A \equiv \left\langle \Psi \left| \hat{A} \right| \Psi \right\rangle \tag{2.16a}$$

$$A = \int \Psi^*(r_1, \dots, r_N) \hat{A} \Psi(r_1, \dots, r_N) dr_1 \dots dr_N$$
(2.16b)

and it follows from Eq. (2.10) that the total (electronic) energy of the system is

$$A \equiv \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle \tag{2.17}$$

Now, Eq. (2.8) is computationally demanding, especially for systems with a few electrons. To address this challenge, several methods, such as Hartree-Fock and perturbation theory, have been developed to simplify the problem by reducing the dimensionality of the wavefunction. Alternatively, the wavefunction can be transformed into a density functional, a more accurate and scalable approach than Hartree-Fock and more efficient than perturbative methods. This method is known as density functional theory.

2.3.2 DFT

Hartree-Fock (HF) theory offers an approach to approximate the ground state energy of an interacting N-electron system. It does so by representing the associated wavefunction as a linear combination of products of orthonormal one-electron atomic orbitals, $\{\psi_k(r)\}$, in the form of a single Slater determinant, expressed as:

$$\Psi(r_1, \dots, r_N) \approx \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \dots & \psi_N(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \dots & \psi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_N) & \psi_2(r_N) & \dots & \psi_N(r_N) \end{vmatrix}$$
(2.18)

The Pauli exclusion principle imposes the antisymmetry requirement on the wave function. HF achieves this by minimizing the energy (E) in Eq. (2.8). This minimization process identifies the "best' orbitals, ensuring that the Slater determinant wavefunction yields the lowest possible energy. In essence, HF provides the best approximation to the ground state energy within the framework of the Slater form of the wavefunction. HF is an independent-particle model, with electron-electron interaction only accounted for by an average Coulomb potential and a non-local exchange potential arising from the anti-symmetry property of the Slater determinant. However, this approximation lacks explicit treatment of electron correlation (except in an average sense), leading to notable errors in properties like band gaps in semiconductors and bond lengths in molecules. Correlation can be further included in post-Hartree-Fock methods such as configuration interaction (CI) in which the wavefunction is expanded in a linear combination of Slater determinants, and Møller-Plesset (MP) perturbation theory where the correlation potential is modeled through a perturbation to the Fock Hamiltonian.

More recently, novel approaches have been developed that can yield results similar to full-CI but with much less computational demand, making for viable alternatives for treating real systems (e.g., the full configuration-interaction quantum Monte Carlo method, which employs a stochastic approach (Booth, Thom, & Alavi, 2009; Booth, Grüneis, Kresse, & Alavi, 2012). While these methods enhance HF results and can approach exact solutions systematically, their computational cost limits their application to small systems. For instance, MP2, MP3, and MP4 methods have scaling factors of $O(N^5)$, $O(N^6)$, and $O(N^7)$ with the number of electrons, respectively. In contrast, DFT provides a more computationally efficient approach to approximate ground state observables. DFT methods exhibit scaling from $O(N^4)$ to linear scaling at O(N), enabling the modeling of systems with tens of thousands to millions of atoms, albeit with varying levels of accuracy. Unlike HF, which minimizes the energy of an approximate Hamiltonian concerning an approximate wavefunction, DFT models energy as a functional of the electron density, aiming to find the exact ground state energy by minimizing the energy of the exact Hamiltonian concerning the electron density. The one-electron density function ($\rho(\mathbf{r})$) for an N-electron wavefunction is defined as:

$$\rho(r) = N \int |\Psi(r_1, r_2, \dots, r_N)|^2 dr_2 \dots dr_N$$
(2.19)

In Eqs. (2.11) - (2.14), it becomes evident that the Hamiltonian is distinctly defined by the number of electrons, denoted as N, and the system-specific external potential, $v_{ext}(r)$. The positions and charges of the nuclei determine this external potential. From Eq. (2.11) and Eq. (2.17), the total energy of an N-electron system can be expressed as:

$$E = \left\langle \psi \left| \hat{H} \right| \psi \right\rangle$$

= $\left\langle \psi \left| \hat{T}_{e} \right| \psi \right\rangle + \left\langle \psi \left| \hat{V}_{ee} \right| \psi \right\rangle + \left\langle \psi \left| \hat{V}_{ne} \right| \psi \right\rangle$ (2.20)
= $T_{e} + V_{ee} + V_{ne}$

The formulation of DFT begins with the first Hohenberg-Kohn (HK) theorem, which implies that the electron density, $\rho(\mathbf{r})$, uniquely determines the external potential, $v_{ext}(r)$, and thus uniquely determines the Hamiltonian. Therefore, the energy is inherently a functional of electron density function ($\mathbf{E}[\boldsymbol{\rho}]$), expressed as $E \equiv E[\rho]$, as illustrated in Eq. (2.20).

$$E[\rho] = T_e[\rho] + V_{ee}[\rho] + V_{ne}[\rho]$$
(2.21)

Using Eqs. (2.14, 2.17 and 2.19), it can be demonstrated that

$$V_{ne}[\rho] = \int v_{ext}(r)\rho(r) dr \qquad (2.22)$$

So that Eq. (2.21) can be rewritten as

$$E[\rho] = T_e[\rho] + V_{ee}[\rho] + \int v_{ext}(r)\rho(r) dr$$

= $F[\rho] + \int v_{ext}(r)\rho(r) dr$ (2.23)

where $F[\rho]$ is a universal potential independent of the system. Now, the second HK theorem asserts that the ground state energy can be acquired by minimizing $E[\rho]$ in Eq. (2.23) with respect to ρ , subject to the constraint that the density is derived from a normalized wavefunction, which is equivalent to requiring

$$\int \rho(r) \, dr = N \tag{2.24}$$

Given that Eq. (2.23) represents the exact energy of the original Hamiltonian, the density that minimizes E is the ground state density, ρ_{GS} , and the exact ground state energy is expressed as:

$$E_{GS} = E[\rho_{GS}] \tag{2.25}$$

Hence, DFT provides a way to find the ground state energy of an N-electron system by considering the density, which depends only on the three spatial variables. Conversely, the solution of the original TISE depends on 3N variables, so the computational cost is drastically reduced. Unfortunately, however, it is not possible to explicitly and precisely express $F[\rho]$ in terms of the electron density, $\rho(r)$, as done for the external potential in Eq. (2.19). If feasible, it would offer a means to accurately determine all (ground state) observables in a quantum-mechanical system by iteratively solving Eq. (2.20) by changing the density (which depends on only the three spatial variables). This avoids the challenge of attempting to solve the Time-Independent Schrodinger Equation using a wavefunction approach (which, in principle, depends on 3N variables).

Moreover, during the process of obtaining the ground state energy by minimizing the density, it is challenging to confirm whether this density corresponds to an actual physical wavefunction. The wavefunction must adhere to anti-symmetry requirements established by the Pauli exclusion principle. Kohn-Sham DFT provides a solution to this and expresses the universal potential in Eq. (2.20) in a more explicit form to realize the calculation of the majority of the total energy.

2.3.3 Kohn-Sham DFT

In the Kohn-Sham (KS) scheme, similarly to HF, we derive the density from a fictitious system of N independent electrons, with a wavefunction expressed by a single Slater determinant (Eq. 2.18) composed of one-electron atomic orbitals, $\varphi(r)$, thus ensuring the anti-symmetry property is obeyed. In KS DFT, we require the density, which, due to the determinant nature of the wavefunction, is (from Eqs. 2.18 and 2.19)

$$\rho(r) = \sum_{i} \varphi_i^*(r) \varphi_i(r)$$
(2.26)

to be the same as that of the exact ground state wavefunction, even though it is derived from the approximate Slater determinant wavefunction describing the noninteracting system. By making use of the properties of the Slater determinant, we can rewrite the total energy as

$$E[\rho] = -\frac{1}{2} \sum_{i} \left\langle \varphi_{i} \left| \nabla^{2} \right| \varphi_{i} \right\rangle + \frac{1}{2} \iint \frac{\rho(r')\rho(r)}{|r-r'|} dr' dr + \int v_{ext}(r)\rho(r) dr + E_{xc}[\rho]$$
(2.27)

The initial two terms in Eq. (2.27) are the non-interacting contributions to the kinetic energy and average Coulomb repulsion, respectively. The first three terms describe most of the system's total energy, and all other correlation and exchange energy not accounted for in the independent particle approximation are collected in the abstract exchange-correlation energy, $E_{xc}[\rho]$. Upon minimizing $E[\rho]$ in Eq. (2.27) with respect to ρ with the normalization constraint Eq. (2.24), it can be shown that the required KS orbitals satisfy the following equation,

$$\hat{H}^{KS}\varphi_i(r) = \epsilon\varphi_i(r) \tag{2.28}$$

where, the term is one-electron KS Hamiltonian (\hat{H}^{KS}) ,

$$\hat{H}^{KS}\varphi_{i}(r) = -\frac{1}{2}\nabla^{2} + \int \frac{\rho(r')}{|r-r'|} dr' + v_{ext}(r) + v_{xc}[\rho](r)$$
(2.29)

with $v_{xc}[\rho](r)$ being the local multiplicative exchange-correlation potential defined as the functional derivative of the exchange-correlation energy w.r.t. the density, i.e.

$$v_{xc}[\rho](r) = \frac{\delta E_{xc}[\rho]}{\delta\rho(r)}$$
(2.30)

Since \hat{H}^{KS} depends on the density, we start with a trial density as a first approximation and solve Eq. (2.28) self consistently until the total energy in Eq. (2.27) has converged. Suppose E_{xc} is the exact functional corresponding to the true system. In that case, the total energy will converge to the exact ground-state, yielding the exact ground-state density, which can be used to find all other ground-state observables. Certainly, E_{xc} cannot be precisely expressed, necessitating reliance on approximations to the true exchange-correlation energy. Many such approximate functionals exist, and though E_{xc} is, in theory, a universal functional, the approximations used are often chosen to describe a given system of interest best. The two most popular exchangecorrelation potentials (at least for periodic structure calculations) are the local density approximation (LDA) and the generalized gradient approximation (GGA). The LDA is the simplest approximation, derived from a model of the homogeneous electron gas, and depends locally on the spatial value of the density. The GGA is an improvement over the LDA as it depends on the local density and gradient. Many other functionals exist based on semi-empirical formulations tailored towards specific systems. For an extensive list of existing functionals, see, e.g., Ref. (Marques, Oliveira, & Burnus, 2012). Many exchange-correlation approximations available (with certain approximations involving parameters taken directly from the experiment) mean that KS DFT becomes a somewhat semi-empirical method and not a true ab initio theory, unlike HF. Moreover, while there may be methods of systematically improving the functionals (such as orbital-dependent functionals and the optimized effective potential method (Krieger, Li, & Iafrate, 1992), they often come with the same computational effort as post-HF and other wavefunction-based approaches. The widespread use of DFT in modern quantum-chemical calculations reflects its efficiency and accuracy compared to alternative methods.

2.3.4 Periodic Systems

Typically, the solid is considered an infinite array, presenting practical challenges for conducting a DFT calculation on an infinite number of atoms. In this section, we reframe the Kohn-Sham wavefunctions and Time-Independent density functional theory (TDDFT) equations in reciprocal space, leveraging the system's periodicity to streamline computational efforts. The direct lattice vectors indicate the positions of the atoms within the structure.

$$R = n_1 a_1 + n_2 a_2 + n_3 a_3 \tag{2.31}$$

where the n_i are integers and a_i are called the primitive vectors which span the real space. The set of all such lattice vectors forms the Bravais lattice. The unit cell is the region of space enclosed by the parallelepiped formed by the primitive vectors and contains atoms lying on its sides, corners, or center. The crystal structure can then be formed by translating the unit cell by integer amounts in the primitive vector directions. Since the atoms are positioned periodically via the direct lattice vectors R, the external potential generated by the nuclei, $v_{ext}(r)$, must also share the same periodicity, i.e.

$$v_{ext}(r+R) = v_{ext}(r) \tag{2.32}$$

The reciprocal lattice is the set of all wave vectors, G, corresponding to plane waves with the same periodicity as the Bravais lattice. The reciprocal lattice vectors are defined as

$$G = m_1 b_1 + m_2 b_2 + m_3 b_3 \tag{2.33}$$

where m_i are integers and b_i are the reciprocal lattice basis vectors that span the whole reciprocal space:

$$b_1 = 2\pi \frac{a_2 \times a_3}{\Omega_{cell}} \tag{2.34a}$$

$$b_2 = 2\pi \frac{a_3 \times a_1}{\Omega_{cell}} \tag{2.34b}$$

$$b_3 = 2\pi \frac{a_1 \times a_2}{\Omega_{cell}} \tag{2.34c}$$

where Ω_{cell} is the volume of the unit cell in direct space. The equivalent of the unit cell in reciprocal space is called the Brillouin zone (BZ). By Bloch's theorem, we can express the energy eigenstates of an electron of momentum, |k|, in the periodic field (Eq. 2.32) by an expansion of plane waves,

$$\psi_{nk}(r) = \frac{1}{\sqrt{\Omega_{cell}}} \sum_{G} c_{n,k} + G^{e^{i(k+G).r}}$$
(2.35)

where the $c_{n,k} + G$ are the expansion coefficients, to be determined. For given k, the energy of the Bloch wave in state n is ϵ_{nk} : by considering the energy as a function of k, $\epsilon_n(k)$, we can build up an energy profile of the crystal structure, which is normally depicted in band diagrams.

Since the orbitals in Eq. (2.35) now depend on the wave vectors, k, any observables are given by integrating over all reciprocal space in the BZ. For example, the density in Eq. (2.26) becomes

$$\rho(r) = \sum_{n} \int_{BZ} |\varphi_{nk}(r)|^2 dk \qquad (2.36)$$

and the total energy will be

$$E = \sum_{n} \int_{BZ} \varepsilon_{nk} \, dk \tag{2.37}$$

In practice, these integrals are calculated numerically, involving a sum over a chosen subset of wave vectors (also called k-points) in the BZ. This is known as k-point sampling. The total energy is usually converged by using more vectors in the sum. Several methods exist to reduce the number of vectors required while maintaining accuracy by "intelligently" sampling the reciprocal space based on the symmetry of the BZ. The simplest is the Monkhorst-Pack method, which samples over an equally spaced grid in the BZ. We also note that in calculating the orbitals in Eq. (2.35), we need to sum over an infinite number of reciprocal lattice vectors, G. To truncate the summation, we sum over all plane waves with kinetic energy less than E_{cut} , i.e., those satisfying

$$\frac{1}{2}|k+G|^2 < E_{cut} \tag{2.38}$$

which results in a finite number, N_{basis} , of plane wave basis functions in calculating the orbitals and the total energy. The energy is then converged by increasing the number of base functions (i.e., by increasing E_{cut}). Since an electronic wavefunction in a given state must be orthonormal to the wavefunctions in all other states, there appear a large number of oscillations in the wavefunction form, especially for atoms with many electrons, which, in turn, requires a large number of plane waves in the expansion.

To minimize N_{basis} , we neglect inner electrons and incorporate a modified nuclear potential known as a pseudopotential, which matches the true potential after some cut-off radius, r_{cut} but is made softer for $r < r_{cut}$ while retaining the effective Coulomb potential of the neglected electrons. As well as reducing the total number of electrons treated in the system, introducing pseudopotentials reduces N_{basis} and significantly reduces the computation time of periodic BZ calculations. The response functions depend on two spatial coordinates and time in the time-dependent framework. Similarly to Eq. (2.35), $\chi(r, r', t - t')$ can be expanded in plane waves as

$$\chi(r, r', \omega) = \frac{1}{\sqrt{\Omega_{cell}}} \int_{BZ} \sum_{GG'} e^{i(q+G).r} \chi_{GG'}(q, \omega) e^{-i(q+G').r'} dq$$
(2.39)

where, q is a vector in the BZ (the Bloch vector) and $\chi_{GG'}(q,\omega)$ are the Fourier coefficients given by

$$\chi'_{GG}(q,\omega) \equiv \chi(q+G,q+G',\omega)$$

$$= \iiint e^{-i(q+G).r} \chi(r,r',t-t') e^{i(q+G').r'} e^{-i\omega(t-t')} dr dr' dt$$
(2.40)

A non-periodic system is characterized by the absence of periodicity in one or more directions. Examples of a non-periodic system include a molecule, a nanotube/wire, or a two-dimensional monolayer. In practice, the unit cells must have sufficient "vacuum distance" in the non-periodic directions to avoid spurious interactions with neighboring cells. However, as the unit cell fills with a vacuum, the imaginary part of the dielectric function will tend to zero. The polarizability is defined as

$$\alpha(\omega) = \frac{\Omega^{non-per}}{4\pi} (\epsilon_M(\omega) - 1)$$
(2.41)

where, $\Omega^{non-per}$ is the unit cell "volume" in the non-periodic direction, for, in the case of a molecule (0D system), this will be a volume, an area in the case of a nanowire (1D system), and a length in the case of a monolayer (2D system). In this way, a constant proportionality is assured so that α is independent of the amount of vacuum distance.

2.4 Theory of flexoelectricity

2.4.1 Flexoelectric tensor

The flexoelectric effect is the polarization response, P, induced by a strain gradient deformation. It is linear with respect to the displacement vector field, u(r,t). Consequently, the theory of flexoelectricity can be established within the scope of linear response theory, where a general transformation of the unperturbed coordinates, r, is expressed as follows:

$$r'(r,t) = r + u(r,t) \tag{2.42}$$

Here, r' represents the perturbed coordinates. Commencing with the displacement field, u(r), one can introduce the "deformation gradient":

$$\tilde{\varepsilon}_{\alpha\beta} = \frac{\partial u_{\alpha}(r)}{\partial r_{\beta}} \tag{2.43}$$

The Greek letters denote Cartesian coordinates. The tensor $\tilde{\varepsilon}_{\alpha\beta}$ encompasses both an asymmetric and an antisymmetric component. The antisymmetric part is related to the rotations of the sample, while the symmetric strain tensor constitutes the former.

$$\varepsilon_{\alpha\beta} = \frac{1}{2} (\tilde{\varepsilon}_{\alpha\beta} + \tilde{\varepsilon}_{\beta\alpha}) \tag{2.44}$$

Two different strain gradient tensors emerge, depending on whether one utilizes $\tilde{\varepsilon}_{\alpha\beta}$ or $\varepsilon_{\alpha\beta}$ in its formulation. It can be expressed as a second gradient of the displacement field (type-I),

$$\eta_{\alpha,\beta\gamma} = \frac{\partial \tilde{\varepsilon}_{\alpha\beta}}{\partial r_{\gamma}} = \frac{\partial^2 u_{\alpha}}{\partial r_{\beta} \partial r_{\gamma}} \tag{2.45}$$

symmetric in $\beta \leftrightarrow \gamma$, or as a gradient of the symmetric strain (type-II),

$$\varepsilon_{\alpha\beta,\gamma} = \frac{\partial \varepsilon_{\alpha\beta}}{\partial r_{\gamma}} \tag{2.46}$$

which exhibits symmetry under $\alpha \leftrightarrow \beta$. Both strain gradient tensors possess an identical number of independent components, and their relationship is defined as follows (Baroni, Giannozzi, & Testa, 1987):

$$\eta_{\alpha,\beta\gamma} = \varepsilon_{\alpha\beta,\gamma} + \varepsilon_{\gamma\alpha,\beta} - \varepsilon_{\beta\gamma,\alpha} \tag{2.47}$$

Since two different strain gradient tensors exist, the flexoelectric tensor has two possible definitions.

$$\mu^{I}_{\alpha\beta,\gamma\delta} = \frac{\partial P_{\alpha}}{\partial \eta_{\beta,\gamma\delta}}$$

$$\mu^{II}_{\alpha\delta,\beta\gamma} = \frac{\partial P_{\alpha}}{\partial \varepsilon_{\beta\gamma,\delta}}$$
(2.48)

Both are symmetric in the last two indices, but the significance of the indices is not identical for the two tensors. As a result, their components typically differ. Nevertheless, both flexoelectric tensors exhibit 54 independent components for the lowest crystal symmetry. Notably, there exists a one-to-one correspondence between the two definitions.

$$\mu^{II}_{\alpha\delta,\beta\gamma} = \mu^{I}_{\alpha\beta,\gamma\delta} + \mu^{I}_{\alpha\gamma,\delta\beta} - \mu^{I}_{\alpha\delta,\beta\gamma}$$
(2.49)

The examination of flexoelectric effects is most straightforward in cubic crystals, where the flexoelectric tensor has only three independent components. These components are commonly recognized as the longitudinal (μ_{11}), transverse (μ_{12}), and the shear, μ_{44} , which are connected to the type-II definition of Eq. (2.48) as follows:

$$\mu_{11} = \mu_{xx,xx}^{II}$$

$$\mu_{12} = \mu_{xx,yy}^{II}$$

$$\mu_{44} = \mu_{xy,xy}^{II} = \mu_{yx,xy}^{II}$$
(2.50)

Fig. 2.1 presents a schematic illustration of the associated strain gradient deformations. As per Eq. (2.48), it is apparent that in cubic crystals, the tensors demonstrate symmetry when the first two indices are interchanged. Therefore, the flexoelectric

(- .--)



Figure 2.1: The independent strain gradient deformations for a cubic crystal, for the type-I and type-II strain gradient definition(Stengel, 2013).

tensor in cubic crystals possesses the same symmetry as the elastic tensor.

2.5 Theory of Polarization

It is widely recognized that the electric dipole moment quantifies the separation between two oppositely charged particles. In electromagnetic theory, polarization is defined based on the density of the dipole moment of a system, assuming point charges. For a finite linear chain of charges represented by q_i where i = 1, 2, ..., L, and a separation distance of a, the definition of polarization can be expressed as follows,

$$P = \frac{1}{La} \sum_{i=1}^{L} q_i x_i$$
 (2.51)

Here, x_i represents the positions of the charge q_i . While this approach is wellestablished for finite structures without periodicity, materials commonly exhibit a periodic lattice structure defined by a unit cell. The challenge in defining polarization in materials arises when considering the periodic lattice. Observing the linear chain of anions and cations within a periodic lattice (Fig. 2.2), in such a scenario, defining polarization becomes problematic with different choices of unit cells.



Figure 2.2: Primitive cells of one-dimensional anion cation chain.

The two primitive unit cells of the system yield different signs of dipole moments. For instance, if the coordinate system is established at the left edge of the unit cell, polarization can be calculated as follows in the first unit cell,

$$P = \frac{1}{La} \left[-q\frac{a}{2} + q\frac{3a}{2} \right] = q \qquad (2.52)$$

In the second unit cell,

$$P = \frac{1}{La} \left[q \frac{a}{2} - q \frac{3a}{2} \right] = -q \tag{2.53}$$

Here, q represents the magnitude of the charge for both anions and cations. The variation in results based on the choice of the unit cell highlights the lack of a well-defined polarization for periodic structures. However, this system presents not only that challenge but also the issue of obtaining non-zero polarization values in a non-polar system. These two fundamental problems in this basic periodic system underscore the necessity for a modern approach to polarization theory. When we shift the cations by a distance d (Fig. 2.3), the shift can be seen as an effect of an external electric field. However, the real significance of this step lies in experimenting with a polar material.



Figure 2.3: Linear chain of anions and cations shifted concerning the initial system.

Following similar steps, one could obtain the following results for the same choices of unit cells as before. In the first unit cell,

$$P = \frac{1}{2a} \left[-q\frac{a}{2} + q\frac{3a}{2} + qd \right] = q + q\frac{d}{2a}$$
(2.54)

In the second unit cell,

$$P = \frac{1}{2a} \left[q \frac{a}{2} - q \frac{3a}{2} + qd \right] = -q + q \frac{d}{2a}$$
(2.55)

The polarization is shifted by the same value in both unit cells. This shift can be interpreted as a transition from the initial non-polar system, providing a single-valued quantity, unlike the polarization itself. This observation leads to the conclusion that while polarization itself is not a well-defined quantity in periodic systems, the change of polarization is well-defined (Spaldin, 2012).

Typically, polarization is measured through its derivative rather than its absolute value. For instance, one can gauge the variation in polarization concerning the applied field, as it is directly proportional to the susceptibility (Resta & Vanderbilt, 2007). Even in ferromagnetic materials, where absolute polarization is crucial, experimental methods rely on inducing a change in polarization by applying an electric field in a way that alters its direction. An accessible experimental approach to measure the change in polarization involves examining current density. This current density is related through the Maxwell equation:

$$j(t) = \frac{dP(t)}{dt} \tag{2.56}$$

Here, j represents the macroscopic current density. This current can be understood as generated by a perturbative electric field. Focusing on the change of polarization, Equation 2.56 can be reformulated as:

$$\Delta P = P(\Delta t) - P(0) = \int_0^{\Delta t} j(t) dt \qquad (2.57)$$

It can be observed that this integral remains finite in the adiabatic limit, allowing to define a formulation through adiabatic evolution. By defining a dimensionless adiabatic time λ , one could write the change of polarization through (Resta & Vanderbilt, 2007),

$$\Delta P = \int_0^1 \frac{dP}{d\lambda} \, d\lambda \tag{2.58}$$

As the change of polarization with respect to time is well-defined, the integrand is also well-defined. The capability to measure and compute the adiabatic alteration in polarization, which is inherently a bulk property insensitive to edges and reliant on its change rather than initial and final states, presents a modern solution to the polarization problem.

2.6 Berry Phase

Implementing the adiabatic approach to a periodic crystalline system implies that the wavefunction should not undergo a significant transformation. In this system, we adiabatically turn on the vector potential. From this definition, the wavefunction would be a function of this adiabatic time constant λ . Then, wavefunction can be written as a function of its instantaneous eigenstates,

$$|\Psi(\lambda)\rangle = \sum_{n} C_n(\lambda) |\psi_n(\lambda)\rangle$$
(2.59)

Using the chain rule, the Schrödinger equation takes a form,

$$i\hbar|\dot{\lambda}\partial_{\lambda}\psi(\lambda)\rangle = \hat{H}(\lambda)|\psi(\lambda)\rangle$$
 (2.60)

Inserting the initial wavefunction to the Schrödinger equation,

$$i\hbar\dot{\lambda}(\sum_{n}\partial_{\lambda}C_{n}(\lambda)|\psi_{n}(\lambda)\rangle) + \sum_{n}C_{n}(\lambda)\partial_{\lambda}|\psi_{n}(\lambda)\rangle = \hat{H}(\lambda)C_{n}(\lambda)|\psi_{n}(\lambda)\rangle$$
(2.61)

By projecting this equation onto another instantaneous wave function, it is feasible to simplify the equation as,

$$C_{n}'(\lambda) + C_{n}(\lambda)\langle\psi_{n}(\lambda)|\partial_{\lambda}|\psi_{n}(\lambda)\rangle - \frac{1}{i\hbar\dot{\lambda}}C_{n}(\lambda)E_{n}(\lambda) + \sum_{n\neq m}C_{n}(\lambda)\langle\psi_{m}(\lambda)|\partial_{\lambda}|\psi_{n}(\lambda)\rangle = 0$$
(2.62)

Here, the adiabatic approximation is implemented. It is possible to ignore the last term, where the instantaneous state changes under the adiabatic evolution. This gives an easy integration regime.

$$C_n(\lambda) = C_n(0) \exp\left(i \int i \langle \psi_n(\lambda) | \partial_\lambda | \psi_n(\lambda) \rangle \, d\lambda\right) \exp\left(\frac{1}{i\hbar} \int \frac{E_n(\lambda)}{\dot{\lambda}} \, d\lambda\right) = C_n(0) e^{i\gamma} e^{i\theta}$$
(2.63)

Then, the wavefunction has a form,

$$|\psi(\lambda)\rangle \approx \sum_{n} C_n(0) e^{i\gamma} e^{i\theta} |\psi_n(\lambda)\rangle$$
 (2.64)

where,

$$\gamma = \int i \langle \psi_n(\lambda) | \partial_\lambda | \psi_n(\lambda) \rangle \, d\lambda, \quad and \quad \theta = -\frac{1}{\hbar} \int \frac{E_n(\lambda)}{\dot{\lambda}} \, d\lambda \tag{2.65}$$

This equation illustrates that the wavefunction acquires two phases after an adiabatic evolution. These phases, denoted as λ and β , encompass geometrical and dynamical aspects. The integrand of this equation is also recognized as Berry's connection. Using the continuity equation,

$$\nabla .j = \frac{\partial_{\rho}(r)}{\partial t} = \frac{\partial |\Psi|^2}{\partial t}$$
(2.66)

Taking the time derivative of the density,

$$\dot{\rho}(r) = \langle r | \dot{\Psi} \rangle \langle \Psi | r \rangle + \langle r | \Psi \rangle \langle \dot{\Psi} | r \rangle$$
(2.67)

Combining equation 2.67 and Schröndinger equation,

$$\dot{\rho}(r) = \frac{1}{i\hbar} \langle r|\hat{H}|\Psi\rangle \langle \Psi|r\rangle - \frac{1}{i\hbar} \langle r|\Psi\rangle \langle \Psi|\hat{H}|r\rangle$$
(2.68)

In this context, the potential term of the Hamiltonian cancels out, leaving only the momentum operator. By expressing the momentum operator as $-i\hbar\nabla$, one obtains

$$\dot{\rho}(r) = \frac{i\hbar}{2m} \langle r | \nabla^2 | \Psi \rangle \langle \Psi | r \rangle - \frac{i\hbar}{2m} \langle r | \Psi \rangle \langle \Psi | \nabla^2 | r \rangle$$
(2.69)

Comparing this equation with the continuity equation, it is possible to conclude that the current density is,

$$j(r) = \frac{i\hbar}{2m} \left(\langle r | \nabla | \Psi \rangle \langle \Psi | r \rangle - \langle r | \Psi \rangle \langle \Psi | \nabla | r \rangle \right)$$
(2.70)

This results in an operator, taking into account the perturbation, as described in

(Dreyer, Stengel, & Vanderbilt, 2018),

$$\hat{j}(\lambda) = \frac{i\hbar}{2m} \sum_{n} \left(\nabla |\psi_{nk}\rangle \langle \psi_{nk}| + \nabla |\delta\psi_{nk}\rangle \langle \psi_{nk} - |\psi_{nk}\rangle \nabla |-|\psi_{nk}\rangle \nabla \langle \delta\psi_{nk}| \right)$$
(2.71)

Taking the expectation value, the current density is,

$$\langle \psi_{nk} | \hat{j}(\lambda) | \psi_{nk} \rangle = \frac{i\hbar}{2m} \left(\langle \psi_{nk} | \nabla | \psi_{nk} \rangle - \langle \psi_{nk} | \nabla | \delta \psi_{nk} \rangle \right)$$
(2.72)

Combining this with the equation 2.56, the following expression for the polarization derivative is obtained,

$$j_n = \frac{dP(n)}{dt} = \frac{i\hbar\dot{\lambda}}{(2\pi)^3} \int dk \sum_{m \neq n} \frac{\langle \psi_{mk}(\lambda)\partial_\lambda |\psi_{mk}(\lambda)\rangle \langle \psi_{nk}(\lambda)|\hat{p}|\psi_{mk}(\lambda)\rangle}{E_{mk}(\lambda) - E_{nk}(\lambda)} + c.c. \quad (2.73)$$

Applying the chain rule, the adiabatic evolution and application of perturbation theory to the Hamiltonian H_k with respect to the variable k is described as (Resta & Vanderbilt, 2007)

$$\frac{dP_n}{d\lambda} = \frac{i}{(2\pi)^3} \int dk \langle \nabla_k u_{nk} | \partial_\lambda u_{nk} \rangle + c.c.$$
(2.74)

and integrating both sides with respect to λ yields,

$$\Delta P = \frac{i}{(2\pi)^3} \sum_{n} \int dk \langle u_{nk} | \nabla_k \partial_\lambda u_{nk} \rangle + c.c.$$
 (2.75)

This establishes a notable connection between the Berry phase and polarization. A modern approach has been used for defining polarization in periodic systems.
Chapter 3

Micro-mechanics modeling

3.1 Preliminaries

The expression for Hooke's law in an elastic material is given by:

$$\{\sigma^r\} = \left[C^r\right]\{\epsilon^r\} \tag{3.1}$$

Here, terms are stress vector of the r^{th} phase $(\{\boldsymbol{\sigma}^r\})$, strain vector of the r^{th} phase $(\{\boldsymbol{\epsilon}^r\})$, and stiffness matrix of the r^{th} phase $([\boldsymbol{C}^r])$ of the composite, respectively. The inverse relation of Eq. (3.1) is given as:

$$\{\epsilon^r\} = \left[S^r\right]\{\sigma^r\} \tag{3.2}$$

in which, the term is compliance matrix of the r^{th} phase $([S^r])$ of the composite.

3.1.1 Average Stress and Strain

During the loading of composite material, the stress field $(\{\sigma(x)\})$ and the corresponding strain field $(\{\epsilon(x)\})$ becomes non-uniform on the micro-scale. Addressing these non-uniform fields poses a challenging problem. However, valuable insights can be gained regarding the average stress and strain (Hill, 1963, 1964) by assuming a sufficiently large representative volume element (RVE) that encompasses multiple fibers but is small compared to any length scale over which the average

loading or deformation of the composite varies. The average stress $(\{\bar{\boldsymbol{\sigma}}\})$ and average strain $(\{\bar{\boldsymbol{\epsilon}}\})$ are defined as the averages of the point-wise stress $\{\sigma(x)\}$ and strain $\{\epsilon(x)\}$ over the volume $(\boldsymbol{\Omega})$ as follows:

$$\{\bar{\sigma}\} = \frac{1}{\Omega} \int_{\Omega} \{\sigma(x)\} \, d\Omega \qquad and \qquad \{\bar{\epsilon}\} = \frac{1}{\Omega} \int_{\Omega} \{\epsilon(x)\} \, d\Omega \tag{3.3}$$

Defining the volume-averaged stresses and strains for the fiber and matrix phases is also relevant. To determine these, the volume (Ω) is initially partitioned into the volumes occupied by the volume of fibers (Ω^f) and volume of matrix (Ω^m) in the case of a two-phase composite:

$$v_f + v_m = 1 \tag{3.4}$$

in which, terms are volume fraction of fibers (\boldsymbol{v}_f) and volume fraction of matrix (\boldsymbol{v}_m) respectively. The average fiber and matrix stresses are the averages over the respective volumes and can be written as:

$$\{\bar{\sigma}^f\} = \frac{1}{\Omega^f} \int_{\Omega^f} \{\sigma(x)\} \, d\Omega \qquad and \qquad \{\bar{\epsilon}^m\} = \frac{1}{\Omega^m} \int_{\Omega^m} \{\epsilon(x)\} \, d\Omega \qquad (3.5)$$

Similarly, the average strains for the fiber and matrix can be obtained.

The relationships between the fiber and matrix averages and the overall averages can be derived from the earlier definitions, and these are as follows:

$$\{\bar{\sigma}\} = v_f\{\bar{\sigma}^f\} + v_m\{\bar{\sigma}^m\}$$
(3.6a)

$$\{\bar{\epsilon}\} = v_f\{\bar{\epsilon}^f\} + v_m\{\bar{\epsilon}^m\}$$
(3.6b)

The average strain theorem is an important related outcome. If the average volume (Ω) is subjected to the surface displacement $(\{u^0(x)\})$ consistent with the uniform strain $(\{\epsilon^0\})$, then the average strain within the region is:

$$\{\bar{\epsilon}\} = \{\epsilon^0\} \tag{3.7}$$

Hill (Hill, 1963) proved this theorem by replacing the definition of the strain tensor $(\{\epsilon\})$ in terms of the displacement vector $(\{u\})$ into the definition of average strain $(\{\bar{\epsilon}\})$, and applying Gauss's theorem, the result is:

$$\{\bar{\epsilon}_{ij}\} = \frac{1}{\Omega} \int_{S} \left(\{u_i^0\}\{n_j\} + \{n_i\}\{u_j^0\}\right) dS$$
(3.8)

Here, S denotes the surface of volume (Ω) , and $\{n\}$ is a unit vector normal to dS. The average strain within the volume Ω is determined by the displacements on the surface of the volume. Thus, displacements that yield a uniform strain must result in the same average strain value. As a consequence of this assumption, one can derive a perturbation strain ($\{\epsilon^{per}(x)\}$) by subtracting the local strain from the average strain, expressed as follows:

$$\{\epsilon^{per}(x)\} = \{\epsilon(x)\} - \{\bar{\epsilon}\}$$
(3.9)

then the volume average of $\{\epsilon^{per}(x)\}$ must equal to zero

$$\{\bar{\epsilon}^{per}\} = \frac{1}{\Omega} \int_{\Omega} \{\epsilon^{per}(x)\} d\Omega = 0$$
(3.10)

The corresponding theorem for average stress also applies. Therefore, if the surface tractions align with uniform stress ({ σ^0 }) applied on surface (S), the average stress can be formulated as:

$$\{\bar{\sigma}\} = \{\sigma^0\} \tag{3.11}$$

3.1.2 Average Properties and Strain Concentration

The micro-mechanics models aim to determine the averaged effective properties of the composite, although these require proper definitions. At this point, we employ the direct method proposed by Hashin (Hashin, 1983), where the RVE undergoes constant surface displacements with $\{\epsilon^0\}$. The average stiffness matrix ([C]), measuring uniform strain to the average stress, from Eq. (3.7), we get,

$$\{\bar{\sigma}\} = \begin{bmatrix} C \end{bmatrix} \{\bar{\epsilon}\} \tag{3.12}$$

The average compliance matrix $([\mathbf{S}])$ is similarly defined by applying tractions consistent with the uniform stress $\{\sigma^0\}$ on the surface of the average volume. Utilizing Eq. (3.11), the outcome is:

$$\{\bar{\epsilon}\} = \left[S\right]\{\bar{\sigma}\} \tag{3.13}$$

Hill (Hill, 1963) presented an important concept related to the strain 4th-order concentration tensor ($[\mathbf{M}]$) and stress 4th-order concentration tensor ($[\mathbf{N}]$). These are the ratios of average fiber stress (or strain) and the respective average strain (or stress) in the composite and can be expressed as:

$$\{\bar{\epsilon}^f\} = \left[M\right]\{\bar{\epsilon}\} and \tag{3.14a}$$

$$\{\bar{\sigma}^f\} = \left[N\right]\{\bar{\sigma}\} \tag{3.14b}$$

where $\begin{bmatrix} M \end{bmatrix}$ and $\begin{bmatrix} N \end{bmatrix}$ are the fourth-order tensors, and, typically, they need to be determined through a solution of the microscopic strain and stress fields, respectively. Different micro-mechanics models provide various approaches to approximate $\begin{bmatrix} M \end{bmatrix}$ and $\begin{bmatrix} N \end{bmatrix}$. Both $\begin{bmatrix} M \end{bmatrix}$ and $\begin{bmatrix} N \end{bmatrix}$ display minor symmetries in the stiffness or compliance matrix but lack major symmetry.

$$M_{ijkl} = M_{jikl} = M_{ijlk} \tag{3.15}$$

But in general,

$$M_{ijkl} \neq M_{klij} \tag{3.16}$$

For later use, an alternate strain concentration tensor $[\hat{M}]$ is introduced, which relates the average fiber strain to the average matrix strain, as follows:

$$\{\bar{\epsilon}^f\} = \left[\hat{M}\right]\{\epsilon^m\}$$
(3.17)

This is related to $\begin{bmatrix} M \end{bmatrix}$ by

$$\begin{bmatrix} M \end{bmatrix} = \begin{bmatrix} \hat{M} \end{bmatrix} \begin{bmatrix} (1-f) \begin{bmatrix} I \end{bmatrix} + v_f \begin{bmatrix} \hat{M} \end{bmatrix} \end{bmatrix}^{-1}$$
(3.18)

where [I] denotes the fourth-order unit tensor. These equations can now be utilized to articulate the average composite stiffness in relation to the strain concentration tensor [M] and the elastic properties of the fiber and matrix (Hashin, 1983).

To determine these stress and strain concentration tensors, a solution for the microscopic stress or strain fields is required. By equating Eqs. (3.1, 3.2, 3.6, 3.12, and 3.14a) we get,

$$\left[C\right] = \left[C^{m}\right] + v_{f}\left(\left[C^{f}\right] - \left[C^{m}\right]\right)\left[M\right]$$
(3.19)

The equation for the compliance is

$$\left[S\right] = \left[S^{m}\right] + v_{f}\left(\left[S^{f}\right] - \left[S^{m}\right]\right)\left[N\right]$$
(3.20)

Note that Eqs. (3.19 and 3.20) are not independent, $[S] = [C]^{-1}$. Consequently, the strain concentration tensor [M] and the stress concentration tensor [N] are interrelated. Choosing which one to use in a particular instance depends on convenience. To understand the utility of stress and strain concentration tensors, we observe that the Voigt average corresponds to the assumption that the fiber and matrix experience equal uniform strain, i.e., iso-strain conditions. In this scenario, $\bar{\epsilon} = \bar{\epsilon}^f$ and [M] = [I]. From Eq. (3.19), the stiffness of the composite can be expressed as:

$$\left[C^{Voigt}\right] = v_f \left[C^f\right] + v_m \left[C^m\right] \tag{3.21}$$

Since the Voigt average represents the upper bound on the stiffness of the composite, the Reuss average assumes that the fiber and matrix experience equal uniform stress, i.e., iso-stress conditions. This implies that [N] = [I], and based on Eq. (3.20), the compliance of the composite can be expressed as:

$$\left[S^{Reuss}\right] = v_f \left[S^f\right] + v_m \left[S^m\right] \tag{3.22}$$

3.2 Elastic Properties of Graphene Sheets

The piezoelectric properties of graphene sheets containing non-centrosymmetric pores are already reported in the literature, but their elastic properties are unavailable. Understanding the elastic behavior of non-centrosymmetric graphene pores is crucial before predicting the effective properties of graphene-reinforced nanocomposite (GRNC). Continuum models, while convenient for large-scale simulations, often struggle to accurately capture graphene's intricate atomic-level behavior. This limitation makes them unreliable in predicting the elastic properties of graphene sheets, which are heavily influenced by their unique atomic structure. Therefore, turning to atomistic simulations like Molecular dynamics (MD) becomes crucial for precisely understanding graphene's elasticity.

MD stands out as the predominant modeling technique for simulating nanostructured materials due to its capability to make precise predictions about atomic and molecular interactions at the nanoscale. Initially introduced by theoretical physicists in the 1950s, the method plays a crucial role in two main steps. Firstly, it involves determining the interacting forces within a system of atoms using molecular mechanics potential fields. Subsequently, the second step entails tracking the atom movements by applying Newton's equations of motion. In force field methods, molecules are portrayed using a "ball and spring" model, wherein atoms exhibit distinct sizes and "softness", and bonds vary in lengths and stiffness. These force field methods are known as molecular mechanics (MM) methods.

Classical mechanics (CM) deals with the motion of bodies following Newtonian mechanics, encompassing scenarios where bodies are either in motion or at rest. Classical mechanics generally describes equations that accurately represent phenomena at scales where quantum and relativistic effects can be disregarded. The notable advantage of MD over classical models lies in its ability to reveal the dynamic properties of a system, such as transport coefficients, time-dependent responses to perturbations, rheological properties, vibrational infrared (IR) spectra, thermo-mechanical properties, and various other exceptional characteristics. Consequently, MD simulations have been conducted to ascertain the elastic properties of both pristine and defective graphene sheets. MD simulations were performed to analyze the elastic properties of (i) pristine graphene sheets and (ii) defective graphene sheets featuring a 4.5 % vacancy in the form of non-centrosymmetric pores. Diagrams illustrating these graphene layers are presented in Fig. 3.1. All MD simulations were executed using large-scale atomic/molecular massively parallel simulator (LAMMPS) (Plimpton, 1995). The molecular interactions within the graphene structures were characterized by Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) force fields (Stuart, Tutein, & Harrison, 2000). In the process of uniaxial deformation of the graphene, stresses were assessed on the atomistic scale utilizing the virial stress tensor defined by Eq. 3.24 (Allen & Tildesley, 2017), as outlined below:

$$\bar{\sigma} = \frac{1}{\Omega} \sum_{i=1}^{N} \left(\frac{m_i}{2} v_i^2 + F_i r_i\right)$$
(3.23)

In this context, Ω represents the volume of atoms, and v_i , m_i , r_i , and F_i denote the velocity, mass, position, and force of the i^{th} atom, respectively. Subsequently, stressstrain curves during tensile loading were generated, and the values of \boldsymbol{E} and $\boldsymbol{\mu}$ for both pristine and defective graphene sheets were determined. The determination of \boldsymbol{E} and $\boldsymbol{\mu}$ were accomplished using simple strain energy density elastic constant relations. The equivalent continuum graphene sheet was assumed to be a flat plate considering its wall thickness of 3.4 Å (S. Kundalwal et al., 2017). The transformation to continuum properties was achieved by equating the potential energy density of discrete atomic interactions of neighboring atoms to the strain energy density of the continuous substance occupying a graphene volume. The atomic volume was determined from the relaxed graphene sheet with a thickness (t) of 3.4 Å (Huang & Yu, 2006; Pei, Zhang, & Shenoy, 2010).



Figure 3.1: Armchair graphene sheets subjected to axial stress

3.3 Effective Properties of graphene-reinforced nanocomposite

Enhancing GRNC through the integration of 2D graphene sheets into the polymer matrix appears to be the most viable approach for leveraging the structural advantages arising from their remarkably high electro-thermo-mechanical properties. Consequently, the focus shifted towards quantifying the effective elastic, piezoelectric, and dielectric properties of GRNC to evaluate its potential as a superior material for structural and NEMS applications. Analytical models are assessed to predict the effective properties of an innovative GRNC. The effective properties of GRNC were determined by varying the volume fraction of graphene. Several studies used different homogenization techniques and micromechanical models like shear-lag, Halpin-Tsai, couple-stress, self-consistent, Mori-Tanaka, Hashin-Shtrikman, composite cylinder/sphere assemblage (CCA and CSA), rules-of-mixture (ROM) and multi-level model for studying the mechanical behavior of composites (Z. Chen, Yang, & Meguid, 2014; Chatzigeorgiou, Javili, & Meraghni, 2019; F. Yang & Meguid, 2013; Bouyge, Jasiuk, Boccara, & Ostoja-Starzewski, 2002) and the predictions were validated with the experimental estimates (Gong et al., 2012; Iqbal, Sakib, Iqbal, & Nuruzzaman, 2020; Young, Kinloch, Gong, & Novoselov, 2012). The ROM model is employed to ascertain the effective elastic properties of GRNC, taking into account geometric factors related to embedded graphene, including orientation, length, and agglomeration. Krenchel orientation factor (η_0) , critical length efficiency factor (η_1) , and agglomeration factor (η_a) were taken into consideration as follows (Papageorgiou, Kinloch, & Young, 2017):

$$E_c = \eta_0 \eta_1 E_f \eta_a v_f + E_m v_m \tag{3.24}$$

Here, E_f and E_m represent the elastic modulus of graphene and the matrix, respectively. The factors η_0 , η_1 , and η_a assume a value of unity when dealing with aligned and non-agglomerated graphene layers that are perfectly bonded with the surrounding matrix, as noted in (Papageorgiou, Li, Liu, Kinloch, & Young, 2020).

3.3.1 MOM Approach

Assuming a graphene sheet as a piezoelectric continuum and polyimide/alumina as the matrix, properties were determined using analytical and numerical models based on the theory of continuum elasticity (S. S. Gupta & Batra, 2010; Gradinar, Mucha-Kruczyński, Schomerus, & Fal'ko, 2013; Verma, Gupta, & Batra, 2014; Bahamon, Qi, Park, Pereira, & Campbell, 2015; Y. Cui, Kundalwal, & Kumar, 2016). The GRNC is composed of rectangular RVEs with multilayers of piezoelectric graphene sheets and a polyimide/alumina matrix. The micromechanical model is limited to a single RVE, assuming continuous, parallel, and aligned reinforcements, no slippage, void-free matrix, linear elasticity, and homogeneity (Gao & Li, 2005; Y. S. Song & Youn, 2006; B. Jiang, Liu, Zhang, Liang, & Wang, 2009; S. I. Kundalwal & Ray, 2011; S. Kundalwal & Ray, 2014). The upper and lower surfaces serve as electrodes, maintaining constant potentials and inducing the inverse piezoelectric effect, resembling a parallel plate capacitor with graphene and the matrix as the dielectric medium.

The effective properties of GRNC were determined by adapting the existing MOM model (S. I. Kundalwal & Ray, 2011). Figure 3.2(b) illustrates a representative volume element (RVE) of GRNC lamina with graphene layers integrated along its thickness. In a similar vein, Smith and Auld (Smith & Auld, 1991) employed the Strength of materials (SOM) approach to predict effective elastic and piezoelectric properties for



(b) Cross-sections of an RVE of GRNC

Figure 3.2: Schematic representation

a 1–3 piezoelectric composite, featuring an epoxy matrix surrounding PZT fibers of square cross-section. It's noteworthy that the predictions by Smith and Auld (Smith & Auld, 1991) are particularly suitable for controlling thickness mode oscillations in thin composite plates. The micromechanical analysis is limited to the RVE of GRNC (refer to Fig. 3.2) to determine the effective properties of bulk GRNC.

The thickness of the GRNC lamina is considered extremely small, and normal stresses may arise from the applied electric field (E_3) along the 3-axis of GRNC. The constitutive equations for the components of GRNC are expressed as follows:

$$\{\sigma^g\} = \begin{bmatrix} C^g \end{bmatrix} \{\epsilon^g\} - \{e^g\} E_3 \qquad and \qquad \{\sigma^m\} = \begin{bmatrix} C^m \end{bmatrix} \{\epsilon^m\} \tag{3.25a}$$

$$\{\sigma^{r}\} = \begin{pmatrix} \sigma_{1}^{r} \\ \sigma_{2}^{r} \\ \sigma_{3}^{r} \\ \sigma_{23}^{r} \\ \sigma_{13}^{r} \\ \sigma_{12}^{r} \end{pmatrix} \qquad \{\epsilon^{r}\} = \begin{pmatrix} \epsilon_{1}^{r} \\ \epsilon_{2}^{r} \\ \epsilon_{3}^{r} \\ \epsilon_{13}^{r} \\ \epsilon_{12}^{r} \end{pmatrix} \qquad \{e^{g}\} = \begin{pmatrix} e_{31}^{g} \\ e_{32}^{g} \\ e_{33}^{g} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad r = g \text{ and } m \quad (3.25b)$$
$$\begin{bmatrix} C^{r} \\ 1 \\ \sigma_{12}^{r} \\ \sigma_{12}^{r} \end{bmatrix} = \begin{bmatrix} C_{11}^{r} \\ C_{12}^{r} \\ C_{22}^{r} \\ C_{23}^{r} \\ \sigma_{33}^{r} \\ \sigma_{12}^{r} \end{bmatrix} = \begin{bmatrix} C_{11}^{r} \\ C_{12}^{r} \\ C_{23}^{r} \\ C_{23}^{r} \\ \sigma_{33}^{r} \\ \sigma_{12}^{r} \\ \sigma_{12}^{r} \end{bmatrix} = \begin{bmatrix} C_{11}^{r} \\ C_{12}^{r} \\ C_{23}^{r} \\ C_{23}^{r} \\ \sigma_{13}^{r} \\ \sigma$$

In the equations above, the superscripts g and m denote the graphene and polyimide/alumina matrix, respectively. The superscript r indicates the respective constituent phase, where σ_1^r , σ_2^r , and σ_3^r represent the normal stresses in directions 1, 2, and 3, respectively. Similarly, ϵ_1^r , ϵ_2^r , and ϵ_3^r denote the corresponding normal strains, while σ_{12}^r , σ_{13}^r , and σ_{23}^r represent the shear stresses. The shear strains are denoted by ϵ_{12}^r , ϵ_{13}^r , and ϵ_{23}^r . The elastic coefficients of the r^{th} phase are represented by C_{ij}^r (where i, j = 1, 2, and 6), and e_{31}^g , e_{32}^g , and e_{33}^g are the piezoelectric coefficients of graphene.

It is assumed that the GRNC lamina is homogeneous due to the linear elasticity of graphene and the matrix (Gao & Li, 2005; Y. S. Song & Youn, 2006; B. Jiang et al., 2009; S. I. Kundalwal & Ray, 2011; S. Kundalwal & Ray, 2014). The conditions of ROM and iso-field (iso-stress and iso-strain) are employed to model perfect bonding between the reinforcement and the surrounding matrix (Smith & Auld, 1991; Benveniste & Dvorak, 1992; Ray & Pradhan, 2006; S. I. Kundalwal & Ray, 2011). The iso-strain condition allows us to consider normal strains in a homogenized composite, with the constituents being identical along the reinforcement direction. On the other

hand, the iso-stress condition indicates that transverse stresses in the respective constituents are the same along the transverse direction of the reinforcement. The ROM enables the definition of normal stress and transverse and shear strains of the phases in relation to their volume fractions.

By employing iso-strain and -stress conditions (Smith & Auld, 1991; Benveniste & Dvorak, 1992; Ray & Pradhan, 2006), perfect bonding between a graphene layer and the matrix can be modeled by satisfying the following:

$$\begin{pmatrix} \sigma_1^g \\ \sigma_2^g \\ \epsilon_3^g \\ \epsilon_3^g \\ \sigma_{23}^g \\ \sigma_{13}^g \\ \sigma_{12}^g \end{pmatrix} = \begin{pmatrix} \sigma_1^m \\ \sigma_2^m \\ \epsilon_3^m \\ \sigma_{23}^m \\ \sigma_{13}^m \\ \sigma_{12}^m \end{pmatrix} = \begin{pmatrix} \sigma_1^{NC} \\ \sigma_2^{NC} \\ \epsilon_3^{NC} \\ \sigma_{23}^{NC} \\ \sigma_{13}^{NC} \\ \sigma_{12}^{NC} \\ \sigma_{12}^{NC} \end{pmatrix}$$
(3.26)

Consequently, the ROM was employed to assess the effective elastic properties of GRNC, considering the graphene reinforcement as continuum layers embedded within the matrix. Thus, utilizing the ROM, we express

$$V_{g}\begin{pmatrix} \epsilon_{1}^{g} \\ \epsilon_{2}^{g} \\ \sigma_{3}^{g} \\ \epsilon_{23}^{g} \\ \epsilon_{13}^{g} \\ \epsilon_{12}^{g} \end{pmatrix} + V_{m} \begin{pmatrix} \epsilon_{1}^{m} \\ \epsilon_{2}^{m} \\ \sigma_{3}^{m} \\ \epsilon_{23}^{m} \\ \epsilon_{13}^{m} \\ \epsilon_{12}^{m} \end{pmatrix} = \begin{pmatrix} \epsilon_{1}^{NC} \\ \epsilon_{2}^{NC} \\ \epsilon_{23}^{NC} \\ \epsilon_{23}^{NC} \\ \epsilon_{23}^{NC} \\ \epsilon_{13}^{NC} \\ \epsilon_{13}^{NC} \\ \epsilon_{12}^{NC} \end{pmatrix}$$
(3.27)

where the superscript NC denotes the quantities of RVE and GRNC, and volume fraction of graphene layer (V_g) and volume fraction of matrix (V_m) respectively. Utilizing Eqs. (3.25 - 3.27), the stress and strain vectors of the homogenized GRNC can be expressed in terms of the respective stress and strain vectors of the constituent phases as follows:

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$$\left\{\sigma^{NC}\right\} = \left[C_1\right]\left\{\epsilon^g\right\} + \left[C_2\right]\left\{\epsilon^m\right\} - \left\{e_1\right\}E_3 \tag{3.28a}$$

$$\left[C_3\right]\left\{\epsilon^g\right\} - \left[C_4\right]\left\{\epsilon^m\right\} = \left\{e_2\right\}E_3 \tag{3.28b}$$

$$\left\{\epsilon^{m}\right\} = \left[V_{1}\right]\left\{\epsilon^{g}\right\} + \left[V_{2}\right]\left\{\epsilon^{m}\right\}$$
(3.28c)

The matrices appeared in Eqs. (3.28) are given as follows:

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Making the use of Eq. (3.26) into Eq. (3.28), a constitutive relation for the GRNC can be written as:

$$\left\{\sigma^{NC}\right\} = \left[C^{NC}\right]\left\{\epsilon^{NC}\right\} - \left\{e^{NC}\right\}E_3 \tag{3.30}$$

in which, terms are matrix for the effective elastic properties $([C^{NC}])$ and matrix for the piezoelectric properties $(\{e^{NC}\})$ of GRNC, respectively, and can be obtained as follows:

$$\left[C^{NC}\right] = \left[C_1\right] \left[V_3\right]^{-1} + \left[C_2\right] \left[V_4\right]^{-1}$$
(3.31a)

$$V_3 = \begin{bmatrix} V_1 \end{bmatrix} + \begin{bmatrix} V_2 \end{bmatrix} \begin{bmatrix} C_4 \end{bmatrix}^{-1} \begin{bmatrix} C_3 \end{bmatrix}$$
(3.31b)

$$\begin{bmatrix} V_4 \end{bmatrix} = \begin{bmatrix} V_2 \end{bmatrix} + \begin{bmatrix} V_1 \end{bmatrix} \begin{bmatrix} C_3 \end{bmatrix}^{-1} \begin{bmatrix} C_4 \end{bmatrix}$$
(3.31c)

$$\left\{e^{NC}\right\} = \left\{e_{1}\right\} + \left[C_{1}\right]\left[V_{3}\right]^{-1}\left[V_{2}\right]\left[C_{4}\right]^{-1}\left\{e_{2}\right\} - \left[C_{2}\right]\left[V_{4}\right]^{-1}\left[V_{1}\right]\left[C_{3}\right]^{-1}\left\{e_{2}\right\}$$
(3.31d)

From Eq. (3.31), the effective piezoelectric coefficients of GRNC can be identified as $e_{31} = e^{NC}(1), e_{32} = e^{NC}(2), \text{ and } e_{33} = e^{NC}(3).$

In this context, the effective piezoelectric constant e_{31} for GRNC characterizes the normal stress induced in the transverse 1-direction when a unit electric field is applied in the longitudinal 3-direction (Smith & Auld, 1991; Kumar & Chakraborty, 2009). Similarly, the effective piezoelectric constants e_{32} and e_{33} describe the normal stresses induced in the 2- and 3-directions, respectively. Meanwhile, the piezoelectric constant e_{15} quantifies the induced shear stress about the 2-direction per unit electric field applied in the 1-direction. It is noteworthy that the MOM model does not offer a solution for determining the effective piezoelectric constant (e_{15}) . Hence, the closedform expressions for the effective piezoelectric constants of GRNC from Ref. (Kumar & Chakraborty, 2009) are provided below:

$$e_{15} = e_{15}^g \left(1 - \frac{v_m C_{55}^g}{v_g C_{55}^m + v_m C_{55}^g} \right)$$
(3.32a)

$$e_{24} = e_{24}^g \left(1 - \frac{v_m C_{44}^g}{v_g C_{44}^m + v_m C_{44}^g} \right)$$
(3.32b)

Note that GRNC is a transversely isotropic material with the 3-axis as the axis of symmetry; hence, $e_{31} = e_{33}$ and $e_{24} = e_{15}$. Consequently, only the three independent piezoelectric constants (e_{31}, e_{33} , and e_{15}) are necessary to investigate the piezoelectric behavior of GRNC.

Therefore, the effective dielectric constant (ε_{33}^{NC}) of GRNC is determined utilizing the following relation (Ray & Pradhan, 2006):

$$\varepsilon_{33}^{NC} = v_g \varepsilon_{33}^g + v_m \varepsilon_{33}^m + e_{31}^g v_g v_m / (v_m C_{11}^g + v_g C_{11}^g)$$
(3.33)

3.3.1.1 SOM Model

The SOM model has been adapted and enhanced using the MOM and Hill's average concentration factor for a point-wise analysis of GRNC to ascertain its effective properties. Figure 3.3(a) illustrates a constructive representation of an RVE selected from the continuum of GRNC, with the graphene reinforcement positioned in the 1–3 plane. The problem coordinates, and principal material coordinate systems are denoted by 1-2-3 and x-y-z, respectively. Additionally, Fig. 3.3(b) showcases the RVE of GRNC. No transformations have been applied, ensuring that the principal material coordinates in Fig. 3.3(b) precisely match the problem coordinate system depicted in Fig. 3.3(a).

Taking graphene as a continuum plate, the SOM model developed by Kundalwal and Ray (S. I. Kundalwal & Ray, 2011) was modified by integrating Hill's average con-

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Figure 3.3: (a) Schematic of a GRNC lamina, (b) FE mesh of RVE of GRNC, and (c) longitudinal and transverse cross-sections of RVE of GRNC

centration factor for point-wise analysis of the local structure of GRNC to determine its effective elastic, piezoelectric, and dielectric properties. The constitutive relations for the different phases of a GRNC concerning the principal coordinate system (1–2–3) of material can be written as follows:

$$\left\{\sigma^{r}\right\} = \left[C^{r}\right]\left\{\epsilon^{r}\right\} \qquad r = g, m, and NC$$
(3.34)

The thickness of the GRNC lamina is assumed to be very small, leading to the action of E_3 across its thickness. Consequently, the constitutive equations for the electric displacement components of the graphene can be obtained as:

$$D_3^g = \left\{ e^g \right\}' \left\{ \epsilon^g \right\} + \left\{ \varepsilon_{33}^g \right\} E_3^g \tag{3.35a}$$

$$D_3^m = \left\{ \varepsilon_{33}^m \right\} E_3^m \tag{3.35b}$$

where, terms are electric displacement of graphene phase (D_3^g) , electric displacement

of matrix phase (D_3^m) , electric field of graphene phase (E_3^g) , and electric field of matrix phase (E_3^m) respectively. Note that the GRNC is considered a transversely isotropic material with the 3-axis as the symmetry axis, and accordingly, the above relations are written. Making use of Eqs. (3.25 - 3.26 and 3.33 - 3.34) and the stress, as well as strain vectors of constituent phases, the stress and strain vectors of GRNC can be expressed as:

$$\left\{\sigma^{NC}\right\} = \left[C_1\right]\left\{\epsilon^g\right\} + \left[C_2\right]\left\{\epsilon^m\right\} - \left\{e_1\right\}E_3 \tag{3.36}$$

in which,

$$\left\{\sigma^{NC}\right\} = \begin{cases} \sigma_{1}^{NC} \\ \sigma_{2}^{NC} \\ \sigma_{3}^{NC} \\ \sigma_{12}^{NC} \\ \sigma_$$

$$\left\{ e_1 \right\} = \begin{cases} e_{31}^g \\ e_{32}^g \\ v_g e_{33}^g \\ 0 \\ 0 \\ 0 \\ 0 \end{cases}$$
 (3.37d)

The aim is to establish the relationship between the average electric field in the homogenized GRNC and that in the individual phases. As stated earlier, the reinforcements are coated with electrodes; thus, the reinforcement-matrix interface acts as a very thin metal conductor. Although the electric field within the metallic conductor is zero, the metallic conductor between two dielectrics separates its generated charges. It can be possible to develop the constant electric field in both the graphene and matrix phases to properly distribute spatially constant electric field/voltage on the electrodes at the graphene-matrix interface. Therefore, using the ROM and considering the equal electric fields in the constituent phases ($E_3^g = E_3^m$), the relation for electric displacement along lamina thickness (D_3) in the homogenized GRNC lamina along its thickness) can be expressed as (Ray & Pradhan, 2006):

$$D_3 = v_q D_3^g + v_m D_3^m (3.38)$$

It is necessary to relate the average strain vector ($\{\epsilon\}$) and the average electric field (E_3) in the 3-direction with the average stress vector ($\{\sigma\}$). This correlation can be achieved in terms of the average strains in GRNC and the electric fields in the constituents by determining the local strain fields in the constituent phases of GRNC, namely graphene and the matrix. Following Hill's average concentration approach (Hill, 1964), the average strain fields in the constituent phases can be outlined as in (Ray & Pradhan, 2006):

$$\left\{\epsilon^{g}\right\} = \left[X^{g}\right]\left\{\epsilon^{NC}\right\} + \left\{Y^{g}\right\}E_{3} \quad and \quad \left\{\epsilon^{m}\right\} = \left[X^{m}\right]\left\{\epsilon^{NC}\right\} + \left\{Y^{m}\right\}E_{3} \quad (3.39)$$

Therefore, 42 concentration factors for each phase (graphene reinforcement and matrix) need to be determined to ascertain the effective properties of GRNC. According to the iso-strain conditions (Eq. 3.35b), applied electric field E_3 , and composite strain ϵ_3 , the factor X_{33}^r becomes unity, and some of them vanish as outlined below:

$$X_{33}^r = 1, \ X_{3i}^r = 0, \ i = 1, 2, 4, ..., 6 \quad and \quad Y_{33}^r = 0, \ r = g \ and \ m$$
 (3.40)

According to the ROM (Eq. 3.35a), E_3 and composite strain ϵ_3 , the following relations can be obtained:

$$v_g X_{ij}^g + v_m X_{ij}^m = \delta_{ij}, \ i = 1, 2, 4, 5, 6 \quad and \quad j = 1, 2, 4, .., 6$$
 (3.41a)

$$v_g Y_{i1}^g + v_m Y_{i1}^m = 0, \ i = 1, 2, 4, 5, 6$$
 (3.41b)

In Eq. (3.41a), δ_{ij} is the Kronecker delta:

$$\delta_{ij} = \begin{cases} 0 & if \ i \neq j \\ 1 & if \ i = j \end{cases}$$
(3.42)

Finally, using the iso-stress condition given by Eq. (3.35b), we can obtain the following relations:

$$\sum_{i=1}^{3} \left(C_{ki}^{g} X_{ij}^{g} - C_{ki}^{m} X_{ij}^{m} \right) = 0, \quad j = 1, 2, 3, ..., 6 \quad k = 1 \text{ and } 2$$
(3.43a)

$$\sum_{i=1}^{3} \left(C_{ki}^{g} Y_{i1}^{g} - C_{ki}^{m} Y_{i1}^{m} \right) = e_{3k}^{g}, \quad k = 1 \text{ and } 2$$
(3.43b)

$$C_{ii}^{g}X_{ik}^{g} - C_{ii}^{m}X_{ik}^{m} = 0, \quad i = 4, 5, 6 \quad k = 1, 2, 3, ..., 6$$
(3.43c)

$$C_{ii}^g Y_{i1}^g - C_{ii}^m Y_{i1}^m = 0, \quad i = 4, 5, 6$$
(3.43d)

It is worth noting from Eqs. (3.35) and (3.43) that 48 concentration factors can be derived from straightforward solutions of 48 homogeneous equations. For instance, utilizing Eqs. (3.41a) and (3.43a), the following expressions can be obtained:

$$(C_{11}^g + \frac{v_g}{v_m}C_{11}^m)X_{14}^g + (C_{12}^g + \frac{v_g}{v_m}C_{12}^m)X_{24}^g = 0$$
(3.44a)

$$(C_{12}^g + \frac{v_g}{v_m} C_{12}^m) X_{14}^g + (C_{22}^g + \frac{v_g}{v_m} C_{22}^m) X_{24}^g = 0$$
(3.44b)

The matrix determinant derived from the coefficients in Eqs. (3.44a) and (3.44b) is non-singular. Therefore, it can be inferred that only straightforward solutions for these factors are feasible, i.e.,

$$X_{14}^g = X_{24}^g = 0 \tag{3.45}$$

Similarly, the remaining concentration factors will become zero, and the concentration matrix with all nonzero elements can be obtained as:

Subsequently, the non-zero concentration factors of the graphene and matrix phases, as presented in Eq. (3.46), can be exclusively computed for a specific graphene volume fraction using the remaining 11 non-homogeneous relations [Eqs. (3.35) and (3.43)]. Finally, the non-zero concentration factors related to the graphene phase $\{A\}$ can be obtained as follows:

$$\left\{A\right\} = \left[Q\right]^{-1} \left\{B\right\} \tag{3.47}$$

where,

$$\left\{A\right\} = \begin{bmatrix} X_{23}^g & X_{13}^g & X_{22}^g & X_{12}^g & X_{21}^g & X_{11}^g & Y_{11}^g & Y_{21}^g \end{bmatrix}'$$
(3.48a)

$$\left\{B\right\} = \begin{bmatrix} -v_m(C_{23}^g - C_{23}^m) & -v_m(C_{13}^g - C_{13}^m) & C_{22}^m & C_{12}^m & C_{11}^m & v_m e_{31}^g & v_m e_{32}^g \end{bmatrix}'$$
(3.48b)

$$\left[Q\right] = \begin{bmatrix} q_{11} & q_{12} & 0 & 0 & 0 & 0 & 0 & 0 \\ q_{12} & q_{22} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & q_{11} & q_{12} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{11} & q_{12} & 0 & 0 \\ 0 & 0 & 0 & 0 & q_{12} & q_{22} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & q_{11} & q_{12} \\ 0 & 0 & 0 & 0 & 0 & 0 & q_{12} & q_{22} \end{bmatrix}$$
(3.48c)

$$q_{11} = v_m C_{22}^g + v_g C_{22}^m, \ q_{12} = v_m C_{12}^g + v_g C_{12}^m \ and \ q_{22} = v_m C_{11}^g + v_g C_{11}^m$$
 (3.48d)

Utilizing the following relation, the remaining three factors of the graphene layer(s) can be determined:

$$X_{ii}^{g} = \frac{C_{ii}^{m}}{v_{g}C_{ii}^{m} + v_{m}C_{ii}^{g}}, i = 4, 5, and 6$$
(3.49)

Finally, by substituting Eqs. (3.39) and (3.47) into Eqs. (3.36) and (3.38), the constitutive expression for the GRNC lamina is obtained as:

$$\left\{e^{NC}\right\} = \left[C^{NC}\right]\left\{\epsilon^{NC}\right\} - \left\{e^{NC}\right\}E_3 \tag{3.50a}$$

$$D_3 = \left\{ e^{NC} \right\}' \left\{ \epsilon^{NC} \right\} + \varepsilon_{33} E_3 \tag{3.50b}$$

where the effective elastic and piezoelectric tensors of the GRNC are denoted by $[C^{NC}]$ and e^{NC} , respectively, and they can be expressed as:

$$\begin{bmatrix} C^{NC} \end{bmatrix} = \begin{bmatrix} C_1 \end{bmatrix} \begin{bmatrix} X^g \end{bmatrix} + \begin{bmatrix} C_2 \end{bmatrix} \begin{bmatrix} X^m \end{bmatrix} and \left\{ e^{NC} \right\} = \left\{ e_1 \right\} - \begin{bmatrix} C_1 \end{bmatrix} \left\{ Y^g \right\} - \begin{bmatrix} C_2 \end{bmatrix} \left\{ Y^m \right\}$$
(3.51)

in which,

$$\left\{\epsilon^{NC}\right\} = \left\{e_{31}^{NC} \quad e_{32}^{NC} \quad e_{33}^{NC} \quad 0 \quad 0 \quad 0\right\}' \tag{3.52}$$

where,

$$e_{31}^{NC} = e_{31}^g - (C_{11}^g Y_{11}^g + C_{12}^g Y_{21}^g),$$

$$e_{32}^{nc} = e_{32}^g - (C_{12}^g Y_{11}^g - C_{22}^g Y_{21}^g)$$
(3.53a)

$$e_{33}^{NC} = (v_g e_{33}^g) - v_g (C_{13}^g Y_{11}^g + C_{23}^g Y_{21}^g) - v_m (C_{13}^m Y_{11}^m + C_{23}^m Y_{21}^m)$$
(3.53b)

The effective dielectric coefficient (ε_{33}^{NC}) of the GRNC can be determined using Eq. (3.32) similar to the MOM model.

Chapter 4

Polarization in defective graphene using DFT

4.1 Introduction

Using first-principles calculations, this chapter demonstrates the mechanism of strain-induced polarization in a defective armchair graphene nanoribbon (AGNR). We estimate the piezoelectric coefficients of AGNR systems with line, divacancy, and Stone–Wales (SW) defects. At first, we compare the results of AGNRs having non-centrosymmetric pores subjected to an axial load with the existing results of graphene as well as graphitic carbon nitrides, and we confirm that the flexoelectric effect indeed comes into the picture mechanistically when the symmetry of 2D systems breaks. The calculations were performed via the simulation software, real-space grid-based projector-augmented wave (GPAW), and a Python code based on the projector-augmented wave method for DFT.

Two-dimensional graphene, one of the strongest materials, can be strained up to 25 % (G.-D. Lee et al., 2005), and its behavior varies from metallic to semiconducting based on its deformation and defects pattern (Son et al., 2006; Novoselov et al., 2005; Sanderson, 2007). An unbounded pristine graphene sheet displays a unique zero bandgap and semi-metallic behavior. Graphene sheets/nanoribbons with armchair or zigzag edges exhibit energy gaps that are inversely proportional to the nanoribbons'

widths (Son et al., 2006). The band gaps of graphene nanoribbons can be engineered by applying a uniaxial tensile strain. Qi et al. (Qi et al., 2012) found that wider nanoribbons with localized edge states cause a smaller band gap when subjected to the same strain conditions.

Piezoelectricity is the linear induction of electric polarization in response to an applied uniform strain, whereas flexoelectricity is the linear induction of electric polarization in response to an applied strain gradient; the converse of both phenomena is also At the surfaces and interfaces of nonpolar materials, symmetry breaking true. causes electromechanical coupling like surface piezo- and flexoelectricity, while no such phenomenon occurs in bulk materials. The phenomena of breaking the bond symmetry resulting from the nanotube's inherent curvature is evident in the many electronic properties of CNTs. A homogeneous mechanical deformation cannot induce polarization because of the symmetry of the graphene lattice. However, a strain gradient can cause a flexoelectric effect in centrosymmetric graphene. The strain gradient alters the ionic positions, leading to electron density redistribution. Graphene's centrosymmetric nature cancels out the polarization affected by uniform strain, whereas a strain gradient eliminates the centrosymmetry and produces polarization, also termed flexoelectricity. In 2007, Sharma et al. (Sharma et al., 2007) theoretically studied the effect of the inclusion of centrosymmetric and non-centrosymmetric shapes in the matrix of InAs-GaAs, and they observed that the proper arrangement of such centrosymmetric and non-centrosymmetric shapes in the matrix is required to get a nonzero average polarization. The flexoelectricity, a weak observable effect at the macroscale, is hardly detectable in bulk materials. The induced polarization depends on the strain gradient and flexoelectric coefficient; so, to generate polarization, a large strain gradient is required. The strain gradient is inversely proportional to the sample size; thus, at the nanoscale level, flexoelectricity can be very large (Zubko et al., 2013). Mohammadi et al. (Mohammadi et al., 2013) developed the flexoelectric theory for thin membranes in 2014. Experimentally, it has been found that the synthesis of graphitic carbon nitride $(q - C_3N_4)$ has natural triangular pores, which show piezoelectric behavior with a coefficient of 0.758 C/m^2 ,

verified by DFT calculations. Bending 2D nanosheets with non-centrosymmetric triangular and trapezoidal pores create large strain gradients, resulting in strong electromechanical coupling. Javvaji et al. (Javvaji et al., 2018) studied graphene's piezo- and flexoelectric properties with triangle-shaped defects using MDS. They reported piezo- and flexoelectric coefficients of 0.02826 C/m^2 and 0.04554 C/m, respectively. Kundalwal and Choyal (S. Kundalwal & Choyal, 2021) observed an enhancement in a boron nitride nanotube's piezoelectric coefficient with 2B and 2N vacancies using MDS. The flexoelectric properties of heterostructures like triangular graphene embedded in boron nitride nanosheets with the application of bending force by MDS were also reported in the literature (S. I. Kundalwal, Choyal, & Choyal, 2021). The first-principles DFT calculations predict the behavior of material based on quantum mechanics without needing higher-order parameters like fundamental material properties. Dat et al. (Dat, Quan, Tran, Lam, & Duc, 2020) studied 3D penta-graphene plates with the Bees Algorithm using the first principles (DFT). The flexoelectric properties of four groups of 2D materials such as graphene allotropes, nitrides (BN, AlN, and GaN), group IV elements (Si, Sn, and Ge), and monolayers of MoS_2 , WS_2 , and CrS_2 were found using MDS with the application of bending force (Zhuang, He, Javvaji, & Park, 2019). There are also attempts to apply hierarchical and homogenization schemes for studying the other properties of graphene-based composites. For instance, Xia et al. (Xia, Xu, Xiao, & Weng, 2020) developed a homogenization scheme to connect the microstructural parameters of constituent phases and the AC frequency to the graphite composite's dielectric breakdown strength and energy storage density. The results indicate that the dielectric breakdown strength of the graphite-polymer composite decreases concerning the graphite volume concentration while the energy storage density increases with it. Recently, the elastic properties of graphene nanofiller and metal matrix were evaluated via the DFT (Xia, Du, Zhang, Li, & Weng, 2021).

Bending is another way to induce a flexoelectric effect in 2D nanosheets. Due to bending, the Coulombic repulsion increases with the angle of curvature inside a cavity, which causes the π -orbitals' redistribution in graphene and results in a

transfer of electronic charge from the concave to the convex portion, consequently resulting in the formation of dipoles at the atomic positions (Dumitrică, Landis, & Yakobson, 2002). Yang et al. (W. Yang, Liang, & Shen, 2015) explored the effect of flexoelectricity on electromechanical coupling for the bending of a nanoplate using the Kirchhoff plate theory. Qu et al. (Qu, Jin, & Yang, 2021) observed that buckling load increases flexoelectric coupling in semiconductor beams. Banhart et al. (Banhart, Kotakoski, & Krasheninnikov, 2010) reviewed various structural defects such as point, line, monovacancy, and multiple vacancy defects, and they emphasized the peculiar ability of graphene to readjust its lattice around intrinsic defects, which leads to its tailored properties and possible applications. Baimova (Baimova, 2017) showed that various mechanical and physical properties of graphene could be controlled by strain engineering. Thermal and mechanical properties of CNTs were also reviewed for studying the influence of vacancy defects via MDS (S. I. Kundalwal & Choyal, 2018; Kothari, Kundalwal, & Sahu, 2018). Meyer et al. (Meyer et al., 2008) investigated the effect of SW defects on the strength of graphene sheets using MDS. The Transmission electron microscopy (TEM) images of graphene with various types of defects are depicted in Fig. 4.1.



(a) TEM image of divacancy



(b) SW defect (55–77) formed by C–C bond with 90° rotation

Figure 4.1: TEM images Reprinted with permission from (Banhart et al.). Copyright (2011) American Chemical Society

Graphene acts as fermions with negligible mass and follows the Dirac equation (Novoselov et al., 2005). Moreover, graphene's band structure can be modified by breaking its hexagonal symmetry (Yao, Xiao, & Niu, 2008), thus inducing an electromechanical response. Son et al. (Son et al., 2006) demonstrated that zigzag graphene nanoribbon (ZGNR) and AGNR have energy gaps that decrease when their ribbon width is increased by using the Tight-Binding (TB) approach. Note that AGNRs shows the properties of semiconductors. In its pristine form, a GNR is centrosymmetric, but nothing is perfect! So, GNRs are also not defect-free due to the inherent limitations of their fabrication processes, and they are inherently noncentrosymmetric. A recent study by Apte et al. (Apte et al., 2020) experimentally investigated the apparent piezoelectricity of MoO_2 nanoflakes that form the electret state developing due to having defects and voids in the structure during its formation in the chemical vapor deposition process. Using a novel flexoelectric concept, there is always an opportunity to obtain polarization from non-piezoelectric GNRs. To the authors' knowledge, no existing study reports the flexoelectricity in GNRs with inherent defects using the first-principles calculations. This was the motivation for the current study. This work studies the strain-gradient-induced polarization in AGNRs with defects (triangle-shaped pore, divacancy, line, and SW defects) using DFT simulations. Using the quantum mechanics' approach, the band structures of AGNRs with defects are examined. The strain-induced polarization is calculated for AGNR systems having inherent defects. Due to piezo- or flexo-electricity, 2D materials display the coupled electromechanical behavior, paving the way for attractive applications in actuators, sensors, biomedical devices, and energy harvesting.

4.2 Computational modelling

We used AGNRs in our study because dipole moments are generated only in insulators or semiconductors, and as AGNRs possess a centrosymmetric structure; thus, they lack the intrinsic piezoelectric phenomenon, so, we can induce polarization in them by introducing defects via the flexoelectric concept. The average polarization obtained by DFT simulations includes the pre-existing polarization due to surface effects. This pre-existing polarization, present before applying any strain, is subtracted from the obtained average polarization. Non-linear effects are avoided by applying small strain values. We used the DFT for quantum calculations. Firstly, the dangling bonds of the nanoribbon and pore edges were passivated with hydrogen atoms. AGNR structures were geometrically relaxed to minimum energy. Then, the electronic band structures were evaluated to determine the nature of AGNRs with defects. Whether semiconducting or metallic, the strain-gradient-induced polarization in AGNRs was evaluated afterward. The electromechanical activity in the pristine/defected AGNR was studied using DFT by applying the GPAW code (Blöchl, 1994; Mortensen, Hansen, & Jacobsen, 2005) and the atomic simulation environment (ASE) (Larsen et al., 2017), with exchange-correlation interactions, considering the Perdew-Burke-Ernzerhof (PBE) functional. The calculations were performed with the GGA. A supercell consisting of a slab of AGNR with a vacuum region of 10.0 Å on its top and bottom sides and a 5.0 Å vacuum from all other sides was used to avoid any interaction with the next defect site atoms or layers. Atomic geometry optimization was done using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm till the maximum force was less than or equal to 0.05 eV/Å. Further, convergence was obtained by applying a Fermi–Dirac smearing width of $0.05 \ eV$. Davidson Eigensolver is used to compute eigenvalues. The default density mixing method, carbon potential (C.LDA.gz), and hydrogen potential (H.LDA.gz) of GPAW were also applied. Moreover, the plane wave energy cut-off (650 eV) ratio for convergence was employed. An LDA exchange–correlation functional was used for spin-paired calculations. The dipole layer correction along the GNR plane was also carried out. A grid spacing of 0.18 Å and a periodic boundary condition along the X and Y axes direction was chosen.

First, we created a required pore/defect in the AGNR by removing carbon atoms in the ASE and nano-engineer package for modeling. Note that we can use the laser irradiation method to introduce controlled nanomaterial vacancies to tailor their properties. The dangling bonds of the AGNR were passivated with hydrogen atoms. Then, the system was fully relaxed using the BFGS algorithm to minimize potential energy to get a stabilized state. The calculations for the electronic band structure were performed to determine the nature of the AGNR using the GPAW package. The induced polarization in the defective AGNR with axial force was calculated using the Berry phase formulation present in the GPAW quantum package, while a Berry phase is a quantity (i.e., phase angle having range 0 to 2π) that describes how a global phase evolves as some complex vector is carried around a closed loop in a complex vector space (Berry, 1984). The global phase evolution or angle of rotation is a geometric phase analogous to the Berry phase. The polarization can be expressed in a quantum phase, a Berry phase (King-Smith & Vanderbilt, 1993). The constitutive relation for the - Polarization vector (\mathbf{P}_i) induced due to the flexoelectricity effect may be written as

$$P_i = e_{ijk}\epsilon_{jk} + f_{ijkl}\frac{\partial\epsilon_{jk}}{\partial x_l}$$
(4.1)

where \mathbf{e}_{ijk} and \mathbf{f}_{ijkl} are respectively the piezoelectric and flexoelectric tensors; $\boldsymbol{\epsilon}_{jk}$ and $\frac{d\boldsymbol{\epsilon}_{jk}}{dx_l}$ are the elastic strain and strain gradient respectively. Note that the well-known piezoelectric effect is the first term on the right-hand side of Eq. (4.1). The value of the first term, $\mathbf{e}_{ijk} \boldsymbol{\epsilon}_{jk}$, is zero for non-piezoelectric materials. After differentiating Eq. (4.1), we get the piezoelectric constant \mathbf{e}_{ijk} ,

$$e_{ijk} = \frac{\partial P_{jk}}{\partial x_l} \tag{4.2}$$

The occupied electronic states accumulate the Berry phase in potential with the adiabatic connection of the system's polarized and unpolarized state (Berry, 1984). The Berry phase polarization (King-Smith & Vanderbilt, 1993) was controlled by the periodic boundary conditions of the electronic wave functions. The average induced polarization (p_i) of graphene with strain gradient was obtained by the Berry phase formulation as follows:

$$p_i = p_0 + e_{ijk}\epsilon_{jk} + O(\epsilon_{jk}^3) \tag{4.3}$$

Here, p_0 is the pre-existing polarization arising from the surface effects without applying any strain, which is determined with no applied force and with the help of Berry phase formulation. The term $O(\epsilon_{jk}^3)$ with non-linear effects is neglected if applied strain values are smaller.

4.3 Results and discussion

The band structure of the AGNR was studied using the GPAW, a DFT package. To get induced polarization in graphene, it should be in a semiconducting or insulating state (Chandratre & Sharma, 2012). The band structures of the pristine and defective AGNRs are shown in Figs. 4.2(a) and 4.2(b), respectively. Fig. 4.2(a) depicts the pristine AGNR's band structure, which shows zero bandgap for a graphene unit cell, making it a zero-gap semiconductor. The pristine graphene has a Dirac cone near the Fermi level at the K high-symmetry point and no further bands near the Fermi level. This cone does not affect most physical properties of graphene. However, it plays an important role in the low-energy dielectric properties of graphene. In Fig. 4.2(b), the electronic band structure of the AGNR with non-centrosymmetric pores is shown with a small indirect band gap.



Figure 4.2: Band structure

In Fig. 4.3(a), the optical microscope image shows the presence of graphene on a copper substrate. Its honeycomb structure is also evident from the STM image shown in Fig. 4.3(b). The Raman spectroscopy image, in Fig. 4.4(a), illustrates single-layer graphene as a 2D band in the single-layer is more intense and sharper than the 2D band in multi-layer graphene. A 2D band is a second-order two-phonon process that

shows a strong peak (2500-2800 cm^{-1}) in the Raman spectra for all kinds of sp^2 carbon materials.



Figure 4.3: Optical microscope and STM image of graphene

Fig. 4.4(b) and 4.5(a) show the density of state (DOS) and the projected density of state (PDOS) images of graphene. As revealed in Fig. 4.4(b), the DOS at the Fermi level is above zero, indicating that the system is metallic. There are two DOS peaks around the Fermi level, which form a pseudo-gap for the graphene system. The pseudo-gap linearly decreases as the lattice constant increases (Gui, Li, & Zhong, 2008). Considering this fact, we used such a supercell dimension so that the system would be in a semiconducting or insulating state.



Figure 4.4: Raman spectrum and the density of states (DOS)

In the case of the pristine AGNR, there is no induction of polarization response to deformation due to its centrosymmetric structure. Therefore, we used a supercell of AGNR of 19.88 Å length and 16.0 Å width having 160 carbon atoms. The periodic boundary conditions were only applied along the X and Y axes. Around the 1.7 %strain condition application, the monovacancy structure reorientation occurs due to the John-Teller effect (Andreasen, Hao, Hatoum, & Hossain, 2021). So, to avoid reconstruction of vacancy defect, all calculations were performed for a strain range from 0-1 % along the X axis for all defect geometries of GNRs considered here. After applying strain to the system of a supercell of AGNR, the system again relaxed, until $0.05 \ eV/Å$ force on each atom, using the BFGS algorithm to reposition its atoms at the minimum energy level. While relaxing the system each time, the extreme ends of AGNR were fixed so that the applied strain would remain within the system and the system would be at the minimum energy level condition. The bond length of carbon after relaxation was found to be 1.4202 Å for the unstrained condition. The fixing of extreme ends in the AGNR is pictorially shown by the dotted regions on both the extreme ends of the AGNR in Fig. 4.5(b). Subsequently, the polarization was calculated using the Berry-phase method. The piezoelectric constant, e_{ii} , was calculated per unit volume basis, and as 2D graphene is very thin, so we used GNR thickness as 2.997 Å for calculating the volume. As polarization is an effect of total dipole moments per unit volume, the assumption of GNR thickness substantially influences the obtained polarization values. The calculations were performed for the pristine AGNR and AGNR with circular defects, as depicted in Fig.4.5(b). With centrosymmetric pores or defects, no polarization was found after applying an axial strain since the net-induced dipole moments are zero. In the AGNR with circular defect, dipoles induced due to flexoelectricity are canceled out because of the symmetric nature of the defect region (Zubko et al., 2013). So, no net polarization occurs in the AGNR with circular defects. Also, dipoles are not induced in the case of the centrosymmetric honeycomb structure of the pristine AGNR. Graphene nanoribbons introduced with defects having no centrosymmetry can induce the electric response with strain gradient (Chandratre & Sharma, 2012). Due to this flexoelectric effect, the nanostructure behaves like a piezoelectric material under uniform stress. An extensive strain gradient can be generated at the nanoscale. The effect of various defects and

non-centrosymmetric pores in AGNRs was studied to observe their piezoelectricity activity.



Figure 4.5: Projected DOS (PDOS) and Circular defect of graphene (the large, dark gray atoms are carbon atoms, while the small, light gray atoms are hydrogen atoms.)

For the non-centrosymmetric case, we considered triangular pores in AGNRs to compare and validate the present results with that of available results (Javvaji et al., 2018; Chandratre & Sharma, 2012; S. Kundalwal et al., 2017; Zelisko et al., 2014). The applied force induces a strain gradient due to varying resisting cross-sectional areas for the non-centrosymmetric structure. Such a strain gradient induces asymmetric dipole moments resulting in polarization, which is nothing but the flexoelectricity phenomenon (Dumitrică et al., 2002; S. Kundalwal et al., 2017).

Fig. 4.6(a) shows the AGNR with triangular defects without passivation by hydrogen atoms. While modeling the AGNR with triangular pores, dangling bonds are formed at the edges and defect sites. These can be passivated using hydrogen atoms. Fig. 4.6(a) depicts an AGNR with a non-centrosymmetric triangular pore without hydrogen passivation, in which the dangling bonds are present at the triangular pore section. At the corner of the pore, large repulsions are induced by hydrogen atoms, which causes strain, termed the corner strain effect (S. Kundalwal et al., 2017). Fig. 4.6(a) illustrates the TEM image of graphene with a triangular-defect-like structure. Both structures demonstrate different electrical responses with the application of mechanical deformation.





(a) Non-passivated AGNR with triangular defects (6.43 %)

(b) TEM images of triangular defects

Figure 4.6: Non-passivated AGNR with triangular defects (6.43 %) b TEM images of triangular defects. Reprinted with permission from Kotakoski et al. Copyright (2010) American Chemical Society.



(a) Passivated AGNR with triangular defect (6.43 %)

(b) Strain-induced polarization in AGNR with triangular defect

Figure 4.7: Passivated AGNR with triangular defect (6.43 %) subjected to an axial force. Strain-induced polarization in AGNR with triangular defect
The graph is plotted with the polarization versus the applied strain for passivated AGNRs, as shown in Fig. 4.7(b). The resistance area to the uniform force is different in the presence of non-centrosymmetric triangular pores, and due to the different resisting areas along the triangular pore, strain increases from its apex to its base. This differential strain along the triangular pore can be termed a strain gradient. The strain gradient causes dipole realignment along the applied force's direction, which induces polarization due to the flexoelectric effect. The AGNR with non-centrosymmetric triangular vacancy subjected to strain shows polarization. The axial piezoelectric coefficient of passivated AGNR is 0.051 C/m^2 for 6.43 % atom vacancy. The passivation of hydrogen increases polarization by eliminating the corner strain effect; therefore, we used hydrogen-passivated AGNRs for all simulations. It was observed that the strain-induced polarization in ZGNRs was much less than in AGNRs, as described in the literature, since the tensile loading along the zigzag direction of GNRs influences the H–H repulsion along the armchair edges of a defected graphene (S. Kundalwal et al., 2017). It is also noted from Fig. 4.7(b) and 4.8(b) that the defect size influences strain-induced polarization.



(a) Passivated AGNR with triangular defect (11.43 %)

(b) Strain-induced polarization in AGNR with triangular defect



Defects also influence the strength of GNRs. A trade-off is thus required between the strength and the induced polarization to obtain optimum electromechanical response while choosing the defect size. When the defect size is increased up to 11.43 %, the piezoelectric coefficient increases to 0.108 C/m^2 . This indicates that as the defect size increases, the strain gradient also increases along the triangular pore, and more dipoles realign over a larger area, causing an increase in polarization.



Figure 4.9: Passivated AGNR with Single vacancy and Divacancy, subjected to an axial force, and The polarization graph for AGNR having divacancy (DV) defect.

Next, we performed simulations on usually occurring defect geometries in the AGNR that break its symmetry. We considered single vacancy, divacancy, line, and SW defects in AGNRs, as shown in Fig. 4.8 and 4.10. These defect geometries were modeled using the ASE software package, and the passivation of the dangling bonds at the defects and edges was performed using hydrogen atoms. No polarization was found for the single vacancy defect shown in Fig. 4.9(a), as a single vacancy defect is like a centrosymmetric structure. Fig. 4.9(b) shows an AGNR having divacany defect with 160 carbon atoms with 2 vacant positions passivated by 4 hydrogen atoms. Applying an axial load on the AGNR induces polarization along the x-direction, resulting in a piezoelectric coefficient of $0.004 C/m^2$, as demonstrated in Fig. 4.9(c). A significantly low polarization occurs in the divacancy case as it can be observed that the divacancy structure resembles the shape of a circular pore, which leads to centrosymmetricity of the AGNR.

Subsequently, an inclined single line defect was considered in the AGNR to obtain its non-centrosymmetric structure along the x-axis, as depicted in Fig. 4.10(a). A significantly low polarization change was observed in this case, i.e., a small piezoelectric



Figure 4.10: Strain induced polarization in AGNR containing single line defect with hydrogen passivation.

coefficient of 0.013 C/m^2 , as shown in Fig. 4.10(b). The negligible polarization values in AGNRs with single-line defects are attributed to the inclination angles, which alter the arrangement of dipole moments, thereby affecting the piezoelectric behavior of AGNRs.

Further, SW defects were introduced in the AGNR to study its strain-induced polarization. The SW defect is described as the 90⁰ rotation of a bond that converts 4 hexagons into 2 heptagons and 2 pentagons. AGNRs with a single SW defect show a low significant piezoelectric coefficient of 0.081 C/m^2 along the x-direction (see Fig. 4.12(b)).

The TEM images (Fig. 4.11) of the SW defect depicts slightly disturbed centrosymmetry of the hexagonal structure of the graphene. Thus, it results in the piezoelectric effect in AGNRs, as displayed in Fig. 4.12(b). Further, due to the SW defects, the AGNR deforms in an out-of-plane direction, increasing the net dipole moments.

The structural arrangement of the double SW defect shown in Fig. 4.13(a) was used for the DFT calculation purpose. The induced polarization in AGNRs with double SW defect is plotted in Fig. 4.13(b). It may be observed from Fig. 4.13(b) that the polarization value is decreased in the case of AGNR with a double SW defect compared to that with a single SW defect. It may be due to the orientation and



(a) Single SW defect



(b) Schematic view of a (c) Double SW defects single SW defect

Figure 4.11: TEM images of a single SW defect b) Schematic view of a single SW defect. Reprinted with permission from Banhart et al. Copyright (2011) American Chemical Society. c) TEM images of double SW defects. Reprinted with permission from Zettl et al. Copyright (2008) American Chemical Society



with a single SW defect Figure 4.12: Strain-induced polarization in passivated AGNR containing a

Figure 4.12: Strain-induced polarization in passivated AGNR containing a single SW defect.

position of two SW defects, as some of the produced dipole moments cancel each other. A polarization value of $0.005 \ C/m^2$ along the x-direction was obtained.



Figure 4.13: Strain-induced polarization in passivated AGNR containing a double SW defect.

Fig. 4.14 depicts the results concerning graphene with different shapes of pores from the literature and the present work. From the results presented herein, graphene with different defects is thought to be a non-centrosymmetric solid, and thus we can induce strain-gradient polarization in it.

4.4 Conclusions

In this chapter, we explored the induced piezoelectricity in AGNR systems with non-centrosymmetric pores and defects such as divacancy, line, and SW defects using first-principles calculations. We also calculated the electronic band structure of graphene nanoribbons using DFT calculations. The presence of defects in GNRs introduces band gaps that change their electronic structure and break the centrosymmetricity of GNR systems. Applying axial force leads to the opening of band gaps at the Fermi level in defective GNRs and induces strain-gradient polarization due to the flexoelectric effect. Our results showed that AGNRs with divacancy and line defects show a very small electromechanical response due to the centrosymmetricity and



Figure 4.14: Comparisons of piezoelectric coefficients of graphene with different shapes and size percentage of defects.

low net dipole moments. AGNRs with non-centrosymmetric triangle-shaped vacancies show a more substantial piezoelectric effect due to the symmetry breaking and higher dielectric gap. Also, increasing the defect concentration in AGNRs increases the piezoelectric effect due to the increasing alignment of dipole moments. Changing the size and type of the defects, the AGNR shows the polarization effect by applying a strain gradient. Thus, non-centrosymmetric defects and their size in a dielectric material influence the piezoelectricity due to the flexoelectric effect.

Chapter 5

Polarization in graphene heterostructure using DFT

In this chapter, we explore the influence of strain gradient on polarization in graphene and hBN nanosheet heterostructures featuring non-centrosymmetric triangular pores. Utilizing DFT, we focus on the vertical stacking of two-dimensional nanosheets, such as hexagonal boron nitride and graphene, to form vdW heterostructures. These heterostructures have distinctive and highly controllable electrical characteristics. We analyze the change in the piezoelectric coefficient by introducing non-centrosymmetric triangular holes in bilayer graphene under axial load using DFT. Subsequently, we investigate the variation in polarization with an increase in graphene layers and its heterostructure with hBN nanosheets, employing the QEH model to streamline computational efforts while ensuring reliability. Additionally, the polarisation properties of different heterostructure configurations have been evaluated. It was found that strain-induced polarization in graphene heterostructure with noncentrosymmetric defects is a nanoscale phenomenon that converts non-piezoelectric graphene into piezoelectric graphene. The calculations employ the real-space, GPAW DFT method and the QEH model.

5.1 Introduction

The zero bandgap and inversion symmetry make graphene unsuitable for piezoelectricity. Graphene, a fermion without mass, satisfies the Dirac equation, and applying asymmetrical in-plane strain opens the band gap at the Fermi level. Using the Tight Binding approach, Son et al. (Son et al., 2006) demonstrated that increasing the width of armchair/zigzag graphene nanoribbon decreases the energy gap. A pristine graphene nanosheet displays zero bandgap and semi-metallic behavior. Furthermore, as the strain on the graphene nanosheet increases to 12.2 %, the energy band gap widens to a width of 0.486 eV (Gui et al., 2008). Armchair or zigzag graphene sheets have energy gaps inversely related to their widths (Gui et al., 2008).

A more significant strain gradient is achieved by a strain difference over a small distance, which implies a reduction in the dimensions of electromechanical devices. The impacts of flexoelectricity in nanotechnology will be of tremendous consequence because, at the nanoscale level, it will gain a competitive advantage over piezoelectricity. The strain gradients can effectively act as an equivalent electric field in flexoelectricity. This can be used to activate the spontaneous polarization of a ferroelectric material. Flexoelectricity is a substitute for piezoelectricity at the nanoscale level and enhances electromechanical functionalities (Zubko et al., 2013). Due to the centrosymmetry of the graphene lattice, a constant strain cannot induce dipole polarisation. Centrosymmetry means 180° rotation, which gives the same structure but in an inverted form. Centrosymmetry of the structure can be broken when a strain gradient is applied to the material, which also results in polarization of the material. The strain gradient disturbs ionic positions, resulting in asymmetric electron density redistribution. When a uniform strain is applied to a centrosymmetric structure, the produced dipoles nullify each other, and no polarization occurs. However, in a strain gradient case, the produced dipoles do not nullify each other; thus, polarization appears in the material. Thus, flexoelectricity results from a linear relationship between the strain gradient and the polarization. The strain gradient and the material's flexoelectric coefficient determine the induced polarization. The sample size is inverse to the strain gradient;

therefore, flexoelectricity is prominent at the nanoscale level (Zubko et al., 2013). Experimentally and by DFT calculations, graphitic C_3N_4 with triangular defects show piezoelectricity with a 0.758 C/m^2 coefficient. Through DFT calculations, Kundalwal et al. (S. Kundalwal et al., 2017) have demonstrated that non-centrosymmetric triangular-shaped defected graphene strain gradients show strong polarization. With the bending of graphene, Coulomb repulsion varies with curvature, resulting in the π -orbital redistribution of carbon atoms. This causes an electronic charge transfer from the concave to the convex region and the formation of dipoles at the atomic sites (Dumitrică et al., 2002). Hydrogen and fluorine functionalization can improve the flexoelectric properties of graphene sheets. Banhart et al. (Banhart et al., 2010) investigated various structural defects in graphene, thereby discovering its unique ability to reconfigure its lattice around intrinsic defects, culminating in customized properties and applications. Xia et al. (Xia et al., 2021) developed a hierarchical scheme from nano to macro scale to study the dependence of mechanical properties of graphene on the grain size and volume concentration. Kundalwal et al. (S. I. Kundalwal et al., 2021) evaluated the flexoelectric effect in the heterostructure of boron nitride and graphene with the help of MDS.

The electronic and mechanical properties of multi-layer graphene are affected by the number of layers and their orientation. For example, near the K point, the electronic dispersion of bilayer graphene changes from linear to parabolic (Neto, Guinea, Peres, Novoselov, & Geim, 2009). Strain engineering can be applied to change the lattice structure of crystalline materials and modulate their electronic, magnetic, and optoelectronic properties. A variety of captivating functionalities not found in bulk materials can be realized in strained, thin film heterostructures. Furthermore, a strain gradient breaks inversion symmetry in centrosymmetric materials, resulting in an electric polarization, providing new avenues to manipulate their physical properties (Zubko et al., 2013). Using soft electret materials, Deng et al. (Deng, Liu, & Sharma, 2014) presented an interesting nonlinear interplay between the Maxwell stress effect and flexoelectricity. They showed that the electret-Maxwell stress-based mechanism could be combined with flexoelectricity to achieve unprecedentedly high values of electromechanical coupling. An attempt was made to study PN heterojunctions associated with bending coupling in flexoelectric semiconductor composites considering the effects of size-dependent and symmetry-breaking (H. Li, Chu, Li, Dui, & Deng, 2022).

Better and newer alternatives for exploring materials with various doping and electrical properties, especially on a sub-nanometer length scale, have been made possible by artificially created stacked 2D layer heterostructures with interlayer vdW forces. VdW interactions are non-bonded interactions with a range of distance of a few nanometers. These interactions are weaker than bonded and Coulomb interactions. Numerous innovative materials, technologies, and physical phenomena have been thoroughly researched using the vdW heterostructures concept. Primarily, these include light-emitting diodes in graphene/hBN/ MoS_2 structures (Withers et al., 2015), highspeed photodetectors made of few layers of WSe_2 stack (Massicotte et al., 2015), nano solar cells of MoS_2/WSe_2 hetero-bilayers (Furchi, Pospischil, Libisch, Burgdörfer, & Mueller, 2014), etc.

Additionally, encapsulating active 2D layers of other materials in atomically thick hBN nanosheets is a common way to improve their electrical properties (X. Cui et al., 2015). Interactions between layers or the substrate have become a crucial component of the computational modeling of 2D materials for practically all applications (Xi & Su, 2021). The QEH model (Andersen et al., 2015) can quickly and accurately calculate the dielectric function of generic vdW structures with large interface supercells and hundreds of layers. The separate polarizabilities of various layers' additivity are the core assumptions of the QEH scheme. If there is no hybridization between the layers, this approximation is accurate. Recent work (Andersen et al., 2015) has also shown that the approximation is accurate for interlayer hybridization. This enhances the credibility of the QEH model.

This study aims to assess graphene heterostructure polarization properties using the QEH model (Andersen et al., 2015). QEH model is computationally more efficient in multi-layers with vdW forces. DFT calculations were used for each layer while inter-layer interactions (i.e., vdW forces) among multi-layers were evaluated with the QEH model. Computational time decreased, and accuracy increased by using this scheme. This chapter explores strain-induced electric polarization in defected graphene heterostructures.

5.2 Quantum electrostatic heterostructure model

Figure 5.1: The schematic QEH model: Dielectric building blocks of each layer are used to calculate the density response function and dielectric function of the heterostructure. Monopole and dipole-induced densities (blue) and associated potentials (red) for graphene.

2D materials are the basis for vertically stacked layers bonded with weak vdW forces. These vdW heterostructures can be stacked without lattice-matching conditions. Conventional heterostructures require various epitaxial growth techniques of single-crystalline layers. From the weak interlayer binding forces, it is inferred that each layer of a vdW heterostructure mostly retains all its original 2D properties. Only the long-range Coulomb interaction with the adjacent layers impacts these properties. Thus, the overall properties of vdW heterostructures can be predicted with the help of the individual layer's properties. This semiclassical model, which evaluates dipole moments of each separate layer, was computed fully per the first principles calculations and modeled into the most straightforward possible representation. These layers have been coupled via Coulomb interaction (Figure 5.1). Even though interlayer hybridization is neglected completely, the model gives good results for vdW heterostructures. The overall picture of vdW heterostructures can be shown by modeling the dielectric function of all individual 2D crystals. This approach is computationally more efficient. The dielectric function is a material response function that determines the effective interaction among charged particles. The relation between the dielectric function E and the response function of electron density, X, is given by:

$$E^{-1}(r, r', \omega) = \delta(r - r') + \int \frac{1}{|r - r''|} X(r, r', \omega) dr''$$
(5.1)

The calculation is split into two components in QEH. In the first component, the inplane density response function $X(z, z', q, \omega)$ of each layer is evaluated with DFT calculations. The following is a possible representation of the constitutive relation for the polarisation vector for each layer caused by the flexoelectric effect:

$$P_i = e_{ijk}\epsilon_{jk} + f_{ijkl}\frac{\partial\epsilon_{jk}}{\partial x_l}$$
(5.2)

Where e_{ijk} is a piezoelectric tensor, f_{ijkl} denotes flexoelectric tensors, ϵ_{jk} denotes elastic strain, and $\frac{\partial \epsilon_{jk}}{\partial x_l}$ represents strain gradient. The value of $e_{ijk}\epsilon_{jk}$ is zero for non-piezoelectric materials. By differentiating Eq. 5.2:

$$e_{ijk} = \frac{\partial P_{jk}}{\partial x_l} \tag{5.3}$$

With the adiabatic connection of the system's polarized and unpolarized state, the Berry phase accumulates in the potential due to the occupied electronic states. The periodic boundary conditions of the electronic wave functions regulate the Berry phase. The average induced polarization, p_i , of graphene with strain gradient was calculated using Berry phase formulation.

$$p_i = p_0 + e_{ijk}\epsilon_{jk} + O(\epsilon_{ik}^3) \tag{5.4}$$

The existing polarization, p_e , resulting from surface effects without any axial force, was determined with the help of the Berry phase method. The term $O(\epsilon_{jk}^3)$ with nonlinear effects was ignored due to smaller strain values. The in-plane momentum transfer, q, was considered to have only magnitude due to the isotropic nature of 2D materials within the plane. The magnitude of the multiple of the monopole or dipole component of density was calculated from X_i , which is induced by a constant or linear potential change across the layer,

$$\tilde{\chi}_{i\alpha}(q,\omega) = \int z^{\alpha} X_i(z,z',q,\omega) z'^{\alpha} dz dz'$$
(5.5)

Here $\alpha = 0$ for monopole and $\alpha = 1$ for dipole components. $\rho_{i\alpha}(z,q)$ is an induced density spatial form. By normalization of $\rho_{i\alpha}$,

$$\int X_i(z, z', q, \omega) z'^{\alpha} dz' = \tilde{\chi}_{i\alpha}(q, \omega) \rho_{i\alpha}(z, q)$$
(5.6)

 $\tilde{\chi}_{i\alpha}$ depends on frequency. As depicted in Figure 5.1, the dielectric building block of layer *i* is formed with the data set $(\tilde{\chi}_{i\alpha}, \rho_{i\alpha})$ with $\alpha = 0, 1$. The density of layer *i* can be calculated from the dielectric building blocks. The dielectric building blocks can account for higher order moments $(\alpha > 1)$, but in all the cases considered, dipole approximation is sufficient. Further, the Dyson equation, which couples the dielectric building blocks via the Coulomb interaction, was used to evaluate the density response function of the vdW heterostructures, i.e., the second component of the QEH model. The Dyson equation for the total density response function with monopole or dipole density on layer *j*:

$$X_{i\alpha,j\beta} = \tilde{\chi}_{i\alpha}\delta_{i\alpha,j\beta} + \tilde{\chi}_{i\alpha}\sum_{k\neq i,\gamma} V_{k\alpha,k\gamma}X_{k\gamma,j\beta}$$
(5.7)

The Coulomb matrices:

$$V_{k\alpha,k\gamma}(q) = \int \rho_{i\alpha}(z,q) \Phi_{k\gamma}(z,q) dz$$
(5.8)

 $\Phi_{k\gamma}$ is the potential associated with the induced density, $\rho_{k\gamma}$, which can be calculated by solving a 1D Poisson equation using a uniform grid. The monopole or dipole basis dielectric function of Eq. 5.1:

$$E_{i\alpha,j\beta}^{-1}(q,\omega) = \delta_{i\alpha,j\beta} + \sum_{k\gamma} V_{i\alpha,k\gamma}(q) X_{k\gamma,j\beta}(q,\omega)$$
(5.9)

This QEH formulation and the Berry phase method determine polarization properties in graphene and hBN heterostructures using strain gradient and non-centrosymmetric pores.

5.3 Computational Modelling

The calculations were performed in two parts. In the first part, bilayer graphene was studied for polarization properties. The first part of the calculations was performed using the DFT approach, which was used in conjunction with the GPAW (Blöchl, 1994; Mortensen et al., 2005) package and the ASE (Larsen et al., 2017). Using the ASE atomistic modeling package, a required pore/defect in a heterostructure was created by removing atoms. Laser irradiation can be used to introduce controlled vacancies in nanomaterials. The dangling bonds of heterostructure defects were passivated with hydrogen atoms to prevent re-bonding, which could collapse the defective structure.

To account for exchange-correlation interactions, GGA in the PBE (Perdew, Burke, & Ernzerhof, 1996) functional with spin-orbit corrections were used. Since LDA is a local functional and GGA is a semi-local one, vdW interactions, which depend on correlation across large distances, cannot be sufficiently characterized through these approximations. Such interactions are crucial for 2D materials. Next, the empirical dispersion-corrected density functional theory (DFT-D4) correction was added to the total energy to get the vdW adjustments. The PAW method (Blöchl, 1994) considers electron-ion interaction, and the DFT-D4 method considers vdW interaction. The electron wave function was then calculated using a plane-wave basis and a cut-off energy of 700 eV. A $6 \times 6 \times 1$ Γ -centered Monkhorst-Pack grid was used for Brillouin-zone integration. A 20 Å vacuum gap was kept along the z-direction to avoid spurious interaction between recurring slabs. In all three dimensions, periodic boundary conditions were used. The BFGS algorithm was implemented for structural relaxation

until the total energy converged to $10^{-4} eV$ and the Hellmann-Feynman force on each atom was less than 0.05 eV/Å, respectively. Convergence was obtained with 0.1 eVFermi-Dirac smearing.

In the second part of the calculation, bilayer graphene and its heterostructure with hBN were used. The heterostructure was modeled with a supercell technique using ASE. The structures were optimized using local LDA and BFGS algorithms. The electron wave function was calculated using a plane-wave basis and a cut-off energy of 750 eV. The dielectric matrix was evaluated with an $8 \times 8 \times 1$ k-points grid. All calculations were performed with the GPAW package of DFT. The QEH method was employed in Python to determine the effective properties of the heterostructure. A graphene supercell and its heterostructure with a vacuum region of 20.0 Å on its top and bottom surfaces were used. Some common parameters were used here, as in the first part of the calculation. The dielectric building blocks for separated layers were calculated in the QEH method. The blocks are the monopole and dipole components of the density response function caused by the potential/strain gradient.

Berry phase formulation included in the GPAW quantum package was applied to evaluate the induced polarization in the pristine/defective heterostructure with axial load. Because of surface effects, the obtained polarization values may contain preexisting polarization. Nonlinear effects caused by higher strain were avoided by using lower strain values. To investigate the influence of defects on heterostructures, dielectric loss function, and plasmon modes were also determined. Polarization properties were verified in the pristine/defected heterostructures with DFT. Table 5.1 presents the parameters used in our simulations.

5.4 Results and discussion

The graphene bilayer and its heterostructure with hBN using the DFT package GPAW were investigated in this study with the help of the QEH method. Various properties, such as polarization due to strain gradient, graphene plasmon modes, and its loss function, etc., were evaluated. Dielectric loss function and plasmon modes

Structure	Density functional mode, XC functional, vdW Corrections	Monkhorst K grid	Plane- wave cutoff energy (eV)	Convergence Fermi-Dirac Smearing (eV)	Optimization Algorithm (BFGS)	Vacuum Between layers (Å)	QEH method used	Berry phase used	DFT software tools used
Bilayer graphene	PW, PBE, DFT-D4	$6 \times 6 \times 1$	700	0.1	Energy: (10^{-4} eV) Force: (0.05 eV/Å)	20	No	Yes	GPAW ASE
Bilayer graphene with hBN	PW, LDA, DFT-D4	$8 \times 8 \times 1$	750	0.1	Energy: (10^{-4} eV) Force: (0.05 eV/Å)	20	Yes	Yes	GPAW ASE

 Table 5.1: Summary of parameters used in numerical simulations

were evaluated with the help of the QEH package in GPAW Python. Plasmons are cumulative excitations of the electron fluid corresponding to the poles of polarization. Plasmons are the overall valence or the conduction electron oscillations in a material. Surface plasmons occur at the material interface, and their positive real part shows their dielectric constant. Recently, graphene has been shown to have surface plasmon occurrence, observed by near-field infrared optical microscopy techniques (J. Chen et al., 2012). The dielectric function is a complex function whose real part is wave propagation through a medium. Graphene's loss function is a function of frequency and wave vector. The loss function depicts the decrease in bulk plasmons. We used each layer of 19.88 Å length and 16.0 Å width having 140 carbon atoms with 11.43 % triangular defect vacancy for graphene and hBN structure in the supercell. Figure 5.2 shows the dielectric loss function (left side) and plasmon modes (right side) of the single defected graphene layer. We used predetermined library functions of the GPAW (Blöchl, 1994; Mortensen et al., 2005) software package.

The dielectric loss remains stable and marginal, as depicted in the graph. Pore effects on the plasmon mode and the loss function of bilayer graphene for several interlayer separations were investigated. Figure 5.3 depicts graphene with the dielectric loss function (left side) and plasmon modes (right side) of graphene and hBN bilayer heterostructure. Both layers were used again with the dimensions mentioned earlier for comparison purposes. It also demonstrates stable marginal loss with an increase in interlayer distance.



Figure 5.2: Plasmon dispersion relation for defective graphene



Figure 5.3: Plasmon dispersion relation for defective graphene with hBN

After evaluating the effect of multi-layers and heterostructure on dielectric properties, their effect on polarization in heterostructures was studied. In pristine graphene, there is no polarization induced by virtue of the centrosymmetric nature of graphene. By breaking centrosymmetry, polarization is induced in graphene using a strain gradient. Graphene with non-centrosymmetric defects behaves like a dielectric material, producing an electric response with the axial load application. The different material properties at the interfaces and the non-centrosymmetricity of the defect structure result in strain gradients in graphene, which causes dipole moment realignment. Due to this effect, the defected nanostructure behaves like a piezoelectric material under uniform load. This effect is more prominent at the nanoscale level since a considerable effective strain can be generated easily at this level. There are various studies in graphene with respect to single layers, but no prominent study has been found on bilayer or multi-layer graphene regarding flexoelectricity. Consequently, an attempt has been made to evaluate the impact of multi-layer and vdW forces on polarization through this study.

An earlier study (Xia et al., 2021) demonstrated that pristine graphene is not piezoelectric. However, polarization can be produced by creating a non-centrosymmetric defect with axial load. The results obtained in the prior study of the triangular pore in a single graphene nanosheet with axial loading have been reproduced here to compare with the current findings of multi-layer graphene and its heterostructure. Due to the variable resistive cross-sectional area in non-centrosymmetric structures, the applied force caused a strain gradient. Furthermore, asymmetric dipole moments caused by a strain gradient lead to polarization.

Figure 5.4 depicts graphene with a non-centrosymmetric triangular defect. The authors (Xia et al., 2021) showed that creating a non-centrosymmetric defect in singlelayer graphene caused polarization along the x direction. A 0.108 C/m^2 polarization was reported in monolayer graphene with a triangular vacancy defect of 11.43 % (Xia et al., 2021). The vdW forces play a significant role in multi-layer graphene. Consequently, our efforts focused on gathering insights about multi-layer graphene with vdW forces. Thus, bilayer graphene with vdW forces became our first consideration.



Figure 5.4: Strain-induced polarization in single-layer graphene containing non-centrosymmetric triangular pore (Nevhal & Kundalwal, 2022) with the DFT method.

Polarization properties were evaluated with the first principles method by considering both cases of bilayer graphene, i.e., with and without triangular defect. The interlayer distance, d, of 3.345 Å was maintained throughout the computational procedure. The bilayer structure was relaxed with a cut-off value for an optimum bond length of 1.4199 Å. The lattice parameters obtained from these DFT calculations matched the experimental values very well. The structure was stepwise strained along the x-axis. The strain varied from 0 to 0.004 with a smaller step of 0.001. The noncentrosymmetric triangular pore got deformed along with the graphene bilayer. This caused a strain gradient along the triangular edges, while uniform strain occurred at all other locations. Furthermore, this strain gradient caused dipole polarization along the x direction.

Figure 5.5 shows single-layer graphene with a triangular defect. This was used to form multi-layer graphene with an interlayer distance of d. The DFT-D4 correction was implemented in GPAW Python and was used to simulate vdW forces between the layers. The vdW interactions have some general properties (Parsegian, 2005). Long-range interactions range from $0.2 \ to \ 10 \ nm$, so they attract molecules and tend to align them. An axial load along zigzag faces was applied, which resulted in varying strain along the triangular edges due to gradually increasing areas of the triangular defect. This varying strain or strain gradient induced dipole moments along a non-



Figure 5.5: Strain-induced polarization in bilayer graphene with noncentrosymmetric triangular defect (11.43 %) using the DFT method

centrosymmetric defective area and resulted in the polarization of dipoles along the direction of applied force. A polarization versus strain graph plotted in Figure 5.5 (right side). Bilayer graphene with an 11.43 % atomic vacancy defect is shown with a piezoelectric coefficient of 0.176 C/m^2 . The piezoelectric coefficient of 0.005 C/m^2 is noticed for the bilayer graphene without triangular defect. The first principles method with DFT packages such as GPAW and visualization software ASE has been used. These methods are computationally expensive as they take almost $O(n^3)$ asymptotic time of CPU/GPU. As system size increases, i.e., the number of electrons and atoms, its evaluation becomes highly time-consuming.



Figure 5.6: Strain-induced polarization in bilayer graphene containing noncentrosymmetric triangular pore with QEH method

As layers in multi-layer graphene increase, the computational task becomes more and more difficult. At this juncture, the QEH method proves to be handy and gives some respite for complex evaluation by saving time. As explained in the earlier section, the QEH model evaluates each layer's dielectric building blocks, consisting of monopole and dipole parts of the density response function and dielectric function. Furthermore, the polarization of vdW heterostructures was calculated assuming complete electrostatic interaction and using Berry phase formulation. These multi-layers with vdW forces require no matching of lattices, as the results' accuracy is still achieved using the QEH model.

Furthermore, a defect percentage of 11.43 % per layer of the defective heterostructure was used for the QEH model for the purposes of evaluation. The desired heterostructure was formed using the QEH model's heterostructure method and was implemented using the Python library in GPAW. Then, Berry phase formulation was used to evaluate polarization. As depicted in Figure 5.6 (right side), a piezoelectric coefficient of 0.171 C/m^2 was obtained using this approach. A piezoelectric coefficient of 0.005 C/m^2 was found for pristine bilayer graphene. This approach gives a piezoelectric coefficient quite accurately even though the band structures of multilayer graphene vary significantly from single-layer graphene. Earlier results of bilayer graphene using DFT sufficiently matched the result obtained using the QEH method. Therefore, it follows that the QEH method is quite reliable and accurate in predicting results in accordance with the first principles. And computational time is also roughly reduced asymptotically from $O(n^3)$ to $O(n^{2.5})$.

Further, to investigate the influence of heterostructure on the polarization, bilayer graphene was embedded between 2D hBN nanosheets, and the consequence of the same was studied. This particular arrangement is shown in Figure 5.7. Again, the interlayer distance between layers was kept at 3.345 Å. The interlayer weak vdW forces were considered using forces simulated by the DFT-D4 method.

The heterostructure formed by the layers of two graphene sheets embedded between two hBN sheets rendered marginal improvement in polarization. 2D hBN is a vdW nanosheet with remarkable properties (Cai et al., 2019; L. H. Li, Cervenka, Watanabe,



Figure 5.7: Strain-induced polarization in bilayer graphene embedded in between hBN nanosheets with a non-centrosymmetric triangular defect with the QEH method

Taniguchi, & Chen, 2014). Recently, monolayer hBN was theoretically determined as a piezoelectric because of its broken inversion symmetry (Duerloo, Ong, & Reed, 2012; Rostami, Guinea, Polini, & Roldán, 2018). The honeycomb-like hBN lattice structure behaves like a non-centrosymmetric structure due to the presence of different boron and nitrogen atoms in the sub-lattices of its unit cell. Here, the piezoelectric coefficient was found to be $0.181 \ C/m^2$ for the triangular defect. For the defect-free case, it was observed to be $0.012 \ C/m^2$. The piezoelectric coefficient increased slightly compared to the graphene bilayer as the hBN nanosheet enhanced the polarization effect in the results. Because two hBN layers were separated by two consecutive layers of graphene, hence hBN layers contributed to the polarization effect. The effect of bilayer hBN embedded in between graphene nanosheets and the consequence of the same has been further explored. The arrangement is shown in Figure 5.8.

However, as two consecutive hBN layers were added one over the other, hBN's inversion symmetry was restored, which diminished the piezoelectric effect. Hence, no improvement in the polarization effect was obtained. A piezoelectric coefficient of 0.168 C/m^2 was observed with this heterostructure arrangement, and a piezoelectric coefficient of 0.008 C/m^2 was found for the defect-free case. As polarization due to strain gradient was the sole major contributor in the results, and inversion symme-



Figure 5.8: Strain-induced polarization in bilayer hBN embedded between graphene nanosheets with a non-centrosymmetric triangular defect with the QEH method

try may have somewhat been restored in the case of two consecutive hBN layers, the polarization value was slightly decreased compared to bilayer graphene. Next, alternate layers of graphene and hBN sheets were used to form a heterostructure. The heterostructure is shown in Figure 5.9.



Figure 5.9: Strain-induced polarization in a heterostructure with alternate graphene and hBN sheets having non-centrosymmetric triangular pores with the QEH method

The heterostructure formed by alternate layers gave a significant improvement in polarization value. The non-centrosymmetric nature of hBN was retained as each layer was separated by a graphene layer which, in turn, contributed to enhanced polarization in the hetero system. Along with the non-centrosymmetry of hBN layers and strain gradient at the triangular pore, the piezoelectric coefficient measured here was 0.189 C/m^2 . A piezoelectric coefficient of 0.014 C/m^2 was calculated without triangular defect in the heterostructure. Alternate layers of graphene and hBN with non-centrosymmetric triangular defect and axial loading, depicted in Figure 5.9, exhibited note-worthy polarization results compared to other combinations of graphene and hBN layers to form heterostructures.

Finally, we present the overview of polarization values in graphene and its heterostructures for different sizes of pores in table 5.2. It is evident from the summarized results in the table that the polarization values increase as triangular pore size increases. At the same time, the mechanical strength of the structure goes down drastically (S. Kundalwal et al., 2017). As induced polarization is a non-centrosymmetric pore size-dependent and strain gradient-dependent phenomenon, uniform triangular pore size was used to compare the results of graphene and its heterostructures. For all the cases presented in table 5.2, polarization values in the y-direction were found to be almost negligible compared to the polarization values in the x-direction due to the defect geometry orientation and the applied strain gradient in the particular direction. It may also be observed that the dipole polarization increases with an increase in alternate layers of heterostructures.

Structure	\mathbf{With}	out QEH n	nethod	With QEH method					
	Defect %	x-diree	ctions	x-directions					
		polarizatio	on (C/m^2)	polarization (C/m^2)					
					Bilayer	Bilovor hBN	Alternate		
		Monolayer graphene	Bilayer graphene	Bilayer graphene	graphene	omboddod	layers of		
					embedded	in graphene	graphene		
					in hBN		and hBN		
Pristine	0	0	0.005	0.005	0.012	0.008	0.014		
With	6.43	0.051 [20]	-	-	-	-	-		
Δ pore	11.43	0.108 [20]	0.176	0.171	0.181	0.168	0.189		

 Table 5.2: Overview of polarization values in the graphene and its heterostructures

5.5 Conclusions

Induced piezoelectricity in graphene heterostructure systems with noncentrosymmetric triangular defects has been studied with the application of strain, using first-principles calculations and the QEH method. Furthermore, the dielectric loss function and plasmon modes have been studied with the help of quantum mechanics calculations. Graphene is centrosymmetric, and hBN regains its centrosymmetric nature as hBN layers are increased. Centrosymmetric structures are not piezoelectric. However, to make them piezoelectric, non-centrosymmetric triangular pores can be introduced to obtain a strain gradient that can induce dipole polarization. Furthermore, heterostructures of graphene and hBN with triangular defects were studied, and the piezoelectric effect produced in them by the strain gradient method was observed. DFT and QEH methods were utilized to carry out the same. The QEH method was noted to be fast and efficient. Bilayer graphene polarization results of both the DFT and QEH methods were compared, and it was found that the QEH method was almost as accurate as the DFT method. Additionally, interlayer vdW forces were considered while evaluating multi-layer heterostructures. It was observed that polarization increased from monolayer to bilayer in the case of graphene with strain gradient. In the hetero system of graphene and hBN with strain gradient, bilayer graphene embedded in hBN showed more polarization than bilayer hBN embedded in graphene. Additionally, alternate graphene and hBN layer heterostructures were found to show an even higher dipole polarization. In summation, centrosymmetric and non-centrosymmetric defects in graphene and hBN hetero systems were studied for their piezoelectric properties with strain gradient application using the first principles and the QEH method.

Chapter 6

The flexoelectric effect on a graphene nanorod's bending rigidity

6.1 Introduction

This chapter aims to investigate the impact of the flexoelectric phenomenon on the electromechanical response in the graphene-reinforced nanocomposite (GNC) nanorods. An analytical model is developed using the Timoshenko beam theory and the principle of variational work, incorporating flexoelectric effects. The GNC nanorod is subjected to a concentrated downward load under clamped-free and simply supported support types. The GNC is reinforced with a defective graphene sheet known for enhanced polarization, and the elastic properties of defective graphene sheets are determined through MDSs. The results emphasize the importance of considering the flexoelectric effect for accurate nanostructure modeling. The flexoelectric effect enhances the nanorod's stiffness. This will add a new perspective for developing highperformance graphene-based nanoactuators/sensors. Piezoelectricity is the inherent property of certain dielectric materials to electrically polarize in response to mechanical stimuli. It is well known that piezoelectric crystals are noncentrosymmetric, due to the absence of inversion symmetry. However, the breaking of inversion symmetry induces polarization in noncentrosymmetric dielectrics. This electromechanical coupling is termed the flexoelectric effect, which was identified for the first time by Mashkevich and Tolpygo (Mashkevich & Tolpygo, 1957). Unlike the piezoelectric effect, the flexoelectric effect exists in all dielectric materials, and it reflects the relationship between strain gradient and polarization (Askar, Lee, & Cakmak, 1970). One of the most important and unique properties of the flexoelectric effect is size dependency. The effect of flexoelectricity is more pronounced and prominent at a nano-scale. Owing to its unique properties, flexoelectricity has attracted significant attention from the scientific community and has been broadly applied in MEMS/NEMS. Ma and Cross (Ma & Cross, 2005) investigated the flexoelectric effect in PZT using a cantilevered beam approach. Based on their experimental investigation, they observed that flexoelectric polarization increases with temperature. Hu and Shen (Hu & Shen, 2010) studied the piezoelectric and flexoelectric effects in nano dielectrics using the variational principle. Jiang et al. Yan and Jiang (Yan & Jiang, 2013) studied the influence of the flexoelectric effect on the electromechanical behavior of nanobeams under various support types. Their work reported that the flexoelectric effect is more pronounced in nanobeams with smaller thicknesses. Utilizing the Bernoulli–Euler beam model, Liang et al. (Liang et al., 2014) studied the electromechanical behavior of piezoelectric nanobeams. They observed that the flexoelectricity and surface effects are size-dependent properties, and their influence is prominent at the nanoscale. Wang et al. (X. Wang et al., 2017) developed a finite difference method to study the effect of flexoelectricity on the static bending response of piezoelectric nanoplates. Zeng et al. Yurkov et al. (Yurkov, Dejneka, & Yudin, 2019) derived a theoretical model using variational principles to study the polarization induced due to flexoelectricity in non-homogeneously heated nanoplates. Su and Zhou (Su & Zhou, 2020) utilized the non-local effects of flexoelectricity nanosensors to study the electromechanical response of nanobeam. Beni (Beni, 2022a, 2022b) utilized a modified non-classical flexoelectric theory to study the effect of size-dependent properties on the static and free vibration analysis of micro/nanotubes. Most recently, Gupta et al. (M. Gupta, Meguid, & Kundalwal, 2022) investigated the flexoelectric response in Boron-Nitride-based nanocomposite beams for various support types. They observed that bulk flexoelectricity stiffens the nanobeam for all support types.

With recent advancements, graphene has been extensively used as structural re-

inforcement in polymer composites. Incorporating graphene as reinforcement was observed to result in a superior composite structure. Tang et al. (Tang et al., 2013) studied the effect of graphene dispersion on the mechanical properties of graphene reinforcement composites. Their outcomes revealed that high dispersion of graphene results in a significant enhancement in the composite's electrical conductivity and fracture toughness. Due to strong polarization, graphene-based piezoelectric composites have multifarious NEMS/MEMS applications. Making use of first-order shear deformation theory (FSDT), Song et al. (M. Song, Kitipornchai, & Yang, 2017) performed a dynamic analysis on functionally graded multilayer graphene nanoplatelet (GPL)/polymer composite plates for forced and free vibrations. Kundalwal et al. (S. Kundalwal et al., 2020; Shingare, Gupta, & Kundalwal, 2020) developed an analytical model to investigate the electromechanical response of graphene/polymer composite nanowires accounting for the effects of flexoelectricity. Using EB beam model, Chen et al. (Q. Chen et al., 2021) studied the dynamic response of graphene-reinforced porous nanocomposite beams considering the flexoelectric effects. Their outcomes reveal that porosity and flexoelectricity can significantly affect the vibrational behavior of nanobeams. The existing work on graphene-based composite structures shows that graphene has a potential application as a structural reinforcement due to its exceptional elastic and electrical properties. However, a few studies in the literature focus on the size-dependent response of GNC.

6.2 Electromechanical behavior of GNC nanorod

A Timoshenko beam model is utilized to derive the governing equations for the GNC nanorod by considering the effects of flexoelectricity for clamped-free (CF) and simply supported (SS) support types. For the bulk piezoelectric nanostructure, the electric Gibbs free energy density function U_b can be written as (Shu, Wei, Pang, Yao, & Wang, 2011):

$$U_{b} = -\frac{1}{2}a_{kl}E_{k}E_{l} + \frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl} - e_{ijk}\varepsilon_{ij}E_{i} - f_{ijkl}E_{i}\eta_{jkl} + r_{ijklm}\varepsilon_{ij}\eta_{klm} + \frac{1}{2}g_{ijklmn}\eta_{ijk}\eta_{lmn}$$

$$(6.1)$$

For the sake of simplicity, the last two terms appearing in Eq. 6.1 are neglected, which are of fifth order tensor. In their work, such an assumption was made by Majdoub et al. (Majdoub, Sharma, & Cagin, 2008) and was validated by molecular dynamics simulations. The benefit of such consideration is that the continuum piezoelectricity model considering the flexoelectricity can be employed to study the nanoscale piezoelectricity in a computationally expedient manner rather than using atomistic calculations which have clear computational limits in terms of system size and computational expense. Here, a, c, e, f, r, and g are the material property tensors. Specifically, the dielectric constant, elastic constants, classical piezoelectric constant, and flexoelectricity constant are represented by a, c, e, and f, respectively. It should be noted that tensors e and f represent the electromechanical coupling and will be equal to zero if the electromechanical coupling is not considered. The strain and strain gradient components are given as (Shen & Kuang, 1999):

$$\varepsilon_{ij} = \frac{1}{2}(\mu_{i,j} + \mu_{j,i}) \tag{6.2}$$

$$\eta_{jkl} = \varepsilon_{jk,l} = \frac{1}{2} (\mu_{j,kl} + \mu_{k,jl}) \tag{6.3}$$

The electric field can be written as:

$$E_i = -\varphi_i \tag{6.4}$$

The constitutive equations for bulk piezoelectric material derived from the internal energy density can be expressed as: The electric field can be written as:

$$\sigma_{ij} = \frac{\partial U_b}{\partial \varepsilon_{ij}} = c_{ijkl} \varepsilon_{kl} - e_k i j E_k \tag{6.5a}$$

$$\tau_{jkl} = \frac{\partial U_b}{\partial \eta_{jkl}} = -f_{ijkl} E_i \tag{6.5b}$$

$$D_k = -\frac{\partial U_b}{\partial E_k} = a_{kl} E_l + e_{kij} \varepsilon_{ij} + f_{klij} \eta_{ijl}$$
(6.5c)

where σ_{ij} , D_k , and τ_{jkl} represent the Cauchy stress tensor, electric displacement vector, and higher-order stress, respectively. It is noted that $\sigma_{ij} = \sigma_{ji}, \tau_{ijm} = \tau_{jim}$. A Cartesian coordinate system (x, y, z) is employed to describe the nanorod, as shown in Fig. 6.1. The neutral axis of the nanorod is taken along the x-axis, whereas the thickness of the rod is taken along the z-axis. As shown in Fig. 6.1, a point load F is applied at the free end of the CF nanorod (x = l) and at the center of the SS nanorod (x = l/2), respectively. As per the classical Timoshenko beam theory, the displacement field equations can be expressed as (Ashrafi & Hubert, 2006):

$$u_x(x,y,z) = -z\phi(x) \tag{6.6a}$$

$$u_y(x, y, z) = 0 \tag{6.6b}$$

$$u_z(x, y, z) = w(x) \tag{6.6c}$$



Figure 6.1: Schematics of nanorod under concentrated point load (a) CF and (b) SS boundary condition.

where transverse displacement is shown by w(x) and cross-section rotation is given by $\phi(x)$. The non-zero strains and strain gradients can then be obtained from Eqs. 6.2 and 6.6 as follows:

$$\varepsilon_{11} = -z\frac{d\phi}{dx}, \\ \varepsilon_{13} = \varepsilon_{31} = \frac{1}{2}(-\phi + \frac{dw}{dx}),$$
(6.7)

$$\eta_{111} = \frac{\partial \varepsilon_{11}}{\partial x} = -z \frac{d^2 \phi}{dx^2} \tag{6.8a}$$

$$\eta_{113} = \frac{\partial \varepsilon_{11}}{\partial z} = -z \frac{d\phi}{dx} \tag{6.8b}$$

$$\eta_{131} = \eta_{311} = \frac{1}{2} \left(-\frac{d\phi}{dx} + \frac{d^2 w}{dx^2} \right)$$
(6.8c)

The material property matrices are given below:

$$C_{ijkl} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$$
(6.9a)

$$a_{kl} = \begin{bmatrix} a_{11} & 0 & 0 \\ 0 & a_{22} & 0 \\ 0 & 0 & a_{33} \end{bmatrix}$$
(6.9b)

$$e_{kij} = \begin{bmatrix} 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{bmatrix}$$
(6.9c)

where the Voigt notation are considered as $11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3, 23 \rightarrow 4, 13 \rightarrow 5, 12 \rightarrow 6$. For the flexoelectric coefficients, Le Quang and He (Quang & He, 2011) provide the various rotational symmetries for flexoelectric tensors. For the crystalline medium, the possible symmetry of the flexoelectric coefficient is discussed by Shu et al. (Shu et al., 2011). Here, we considered the flexoelectric coefficients as follows (Liu, Hu, & Shen, 2012; Shu et al., 2011):

$$f_{1111} = f_{2222} = f_{3333} = f_{11} \tag{6.10a}$$

$$f_{1313} = f_{2323} = f_{1212} = f_{2112} = f_{3223} = f_{3113} = f_{111}$$
(6.10b)

$$f_{1122} = f_{1133} = f_{2211} = f_{2233} = f_{3322} = f_{3311} = f_{14}$$
(6.10c)

In the case of rods, the thickness of the rod is smaller than its length. Thus, it can be assumed that the electric field exists only in the thickness direction, i.e., $E_1 = E_2 = 0, E_3 \neq 0$. In the case of open circuit conditions, the electric displacement on the surface should be zero $D_3|_s = 0$. In the absence of free electric charge, electric displacement satisfies Gauss's law and is given by $\frac{\partial D_3}{\partial z} = 0$. Thus, the internal electric field can be given as follows:

$$E_3 = -\frac{e_{31}}{e_{33}}\varepsilon_{11} - \frac{f_{111}}{a_{33}}\eta_{113} - \frac{2f_{14}}{a_{33}}\eta_{131}$$
(6.11)

From Eqs. 6.5, 6.7, 6.8, and 6.11 the non-zeros stresses and non-zeros moment stresses can be given as:

$$\sigma_{11} = \left(c_{11} + \frac{e_{31}^2}{a_{33}}\right)\varepsilon_{11} + \frac{e_{31}f_{111}}{a_{33}}\eta_{113} + \frac{2e_{31}f_{14}}{a_{33}}\eta_{131}$$
(6.12a)

$$\sigma_{13} = 2kc_{44}\varepsilon_{13} \tag{6.12b}$$

$$tau_{113} = \frac{e_{31}f_{14}}{a_{33}}\varepsilon_{11} + \frac{f_{111}f_{14}}{a_{33}}\eta_{113} + \frac{2f_{14}^2}{a_{33}}\eta_{131}$$
(6.12c)

$$\tau_{131} = \tau_{311} = \frac{e_{31}f_{111}}{a_{33}}\varepsilon_{11} + \frac{2f_{111}^2}{a_{33}}\eta_{113} + \frac{2f_{111}f_{14}}{a_{33}}\eta_{131}$$
(6.12d)

Here, k is the shear correction factor. For the present work, we consider k = 1. The electric Gibbs free energy can be expressed as:

$$\delta \int_{V} U_{b} dV = \int_{V} \left(\frac{\partial U_{b}}{\partial \varepsilon_{ij}} \delta \varepsilon_{ij} + \frac{\partial U_{b}}{\partial \eta_{jkl}} \delta \eta_{jkl} - \frac{\partial U_{b}}{\partial E_{k}} \delta \varepsilon_{ij} \right) dV$$

$$= \int_{V} \left(\sigma_{ij} \delta \varepsilon_{ij} + \tau_{jkl} \delta \eta_{jkl} - D_{k} \delta \varepsilon_{ij} \right) dV$$

$$= \int_{V} \left(\sigma_{11} \delta \varepsilon_{11} + 2\sigma_{13} \delta \varepsilon_{13} + \tau_{113} \delta \eta_{113} + 2\tau_{131} \delta \eta_{131} \right) dV$$
 (6.13a)

$$\delta \int_{V} U_{b} dV = \int_{0}^{l} \left[-(M+P) \frac{d\delta_{\phi}}{dx} + Q \left(-\delta\phi + \frac{d\delta_{w}}{dx} \right) + R \left(-\frac{d\delta\phi}{dx} + \frac{d^{2}\delta w}{dx^{2}} \right) \right] dx$$
(6.13b)
$$\delta \int_{V} U_{b} dV = \int_{0}^{l} \left[\frac{-d(M+P)}{dx} - \left(Q - \frac{dR}{dx} \right) \right] \delta\phi dx + \int_{0}^{l} \frac{d}{dx} \left(Q - \frac{dR}{dx} \right) \delta w dx$$
(6.13c)
$$- \left[(M+P) + R \right] \delta\phi \Big|_{0}^{l} + R \frac{d\delta w}{dx} \Big|_{0}^{l} - \left(Q - \frac{dR}{dx} \right) \delta dw \Big|_{0}^{l}$$

where the resultant shear force and the resultant bending moment are given by:

$$Q = \int_{A} \sigma_{13} dA = c_{44} A \left(-\phi + \frac{dw}{dx} \right)$$
(6.14a)

$$M = \int_{A} \sigma_{11} z \, dA = -\left(c_{11} + \frac{e_{31}^2}{a_{33}}\right) I \frac{d\phi}{dx} \tag{6.14b}$$

$$P = \int_{A} \tau_{113} \, dA = -\frac{f_{14}f_{111}}{a_{33}} A \frac{d\phi}{dx} + \frac{f_{14}^2}{a_{33}} A \left(-\frac{d\phi}{dx} + \frac{d^2w}{dx^2}\right) \tag{6.14c}$$

$$R = \int_{A} \tau_{131} \, dA = -\frac{f_{111}^2}{a_{33}} A \frac{d\phi}{dx} + \frac{f_{14}f_{111}}{a_{33}} A \left(-\frac{d\phi}{dx} + \frac{d^2w}{dx^2}\right) \tag{6.14d}$$

The total energy of the overall system is given by $\Pi = \int_{V} (\sigma_{ij}\varepsilon_{ij} + \tau_{ijk}\eta_{ijk}) dV - \int_{a} (\bar{p}_{i}u_{i} + \bar{r}_{i}\Delta u_{i}) da$ in which $W = \int_{a} (\bar{p}_{i}u_{i} + \bar{r}_{i}\Delta u_{i}) da$ is the work done by the external force. For the CF support condition, the work is given by $W = Fw|_{x=l}$, and for the SS support condition, the work is given by $W = Fw|_{x=l/2}$. Making use of the variational principle, $\delta \Pi = 0$, the governing equations can be expressed as:

$$\frac{d}{dx}(M+P) = \left(Q - \frac{dR}{dx}\right)$$

$$\frac{d}{dx}\left(Q - \frac{dR}{dx}\right) = 0$$
(6.15)

and the corresponding boundary conditions prescribed at the end of the nanorod (x = 0 and x = l) are:

$$M + P + R \text{ or } \phi \tag{6.16a}$$

$$Q - \frac{dR}{dx} \text{ or } w \tag{6.16b}$$

$$R \text{ or } \frac{dw}{dx} \tag{6.16c}$$

The boundary conditions for CF nanorod can be given by:

$$\phi|_{x=0}, \ (M+P+R)|_{x=l} = 0$$
 (6.17a)

$$w|_{x=0} = 0, \ Q - \frac{dR}{dx}\Big|_{x=l} = -F$$
 (6.17b)

$$\left. \frac{dw}{dx} \right|_{x=0} = 0, R|_{x=l} = 0 \tag{6.17c}$$

For SS nanorod, the necessary boundary conditions are given by:

$$\phi|_{x=0}, \ (M+P+R)|_{x=l/2} = 0$$
 (6.18a)

$$w|_{x=0} = 0, \ Q - \frac{dR}{dx}\Big|_{x=l/2} = -F$$
 (6.18b)

$$\left. \frac{dw}{dx} \right|_{x=0} = 0, R|_{x=l/2} = 0 \tag{6.18c}$$

Substituting Eq. 6.14 into Eq. 6.15, the governing equations accounting for the flexoelectric effect can be expressed as:

$$\left[\left(c_{11} + \frac{e_{31}^2}{a_{33}}\right)I + \frac{(f_{14} + f_{111})^2}{a_{33}}A\right]\frac{d^2\phi}{dx^2} - \frac{f_{14}(f_{14} + f_{111})}{a_{33}}A\frac{d^3w}{dx^3} + c_{44}A\left(-\phi + \frac{dw}{dx}\right) = 0$$
(6.19a)

$$c_{44}A\left(-\frac{d\phi}{dx} + \frac{d^2w}{dx^2}\right) + \frac{f_{111}}{a_{33}}A\frac{d^3\phi}{dx^3} - \frac{f_{14}f_{111}}{a_{33}}A\left(-\frac{d^3\phi}{dx^3} + \frac{d^4w}{dx^4}\right) = 0$$
(6.19b)

For the cross-section rotation, the solutions for Eq. 6.19 can be obtained by considering (Asghari, Rahaeifard, Kahrobaiyan, & Ahmadian, 2011):

$$\theta(x) = -\phi(x) + \frac{dw(x)}{dx}$$
(6.20)

where $\theta(x)$ indicates twice the rigid body rotation of the beam element. Substituting the derivation of Eq. 6.20 in Eq. 6.19 one can obtain the following relation:

$$\left[\left(c_{11} + \frac{e_{31}^2}{a_{33}}\right)I + \frac{f_{14}f_{111}}{a_{33}}A\right]\frac{d^3\phi}{dx^3} + \frac{f_{14}^2}{a_{33}}A\frac{d^3\theta}{dx^3} = 0$$
(6.21)

Substituting, Eq. 6.21 into Eq. 6.19 yields to:

$$B\frac{d^{3}\theta}{dx^{3}} - C\frac{d\theta}{dx} = 0$$
(6.22)

Where,
$$B = \frac{f_{14}f_{111}}{a_{33}} \left(1 - \frac{f_{14}f_{111}A}{(c_{11}a_{33} + e_{31}^2)I + f_{14}f_{111}A} \right)$$

and $C = c_{44}A$. It is noted that B > 0 for $0 < f_{14}f_{111}A < (c_{11}a_{33} + e_{31}^2)I + f_{14}f_{111}A$ and C > 0 for $c_{44} > 0$ The general solution for Eq. 6.22 can be derived as follows:

$$\theta(x) = C_4 \cosh(kx) + C_5 \sinh(kx) - \frac{t_2 t_3}{t_1} C_1$$
(6.23)

The terms appearing in Eq. 6.23 are given by:

$$k^{2} = \frac{c_{44}At_{2}}{t_{1}}, \ t_{1} = \left(c_{11} + \frac{e_{31}^{2}}{a_{33}}\right)I\frac{f_{14}f_{111}A}{a_{33}}, \ t_{2} = \left(c_{11} + \frac{e_{31}^{2}}{a_{33}}\right)I + \frac{f_{14}f_{111}A}{a_{33}}$$

and $t_{3} = \left(c_{11} + \frac{e_{31}^{2}}{a_{33}}\right)I + \frac{f_{14}^{2}A}{a_{33}t_{2}}$

 C_4, C_5 and C_1 are undetermined parameters. Substituting Eq. 6.23 into 6.21, the cross-section rotation of nanorod can be expressed as:

$$\phi = -\frac{f_{14}^2 A}{a_{33} t_2} \Big[C_4 \cosh(kx) + C_5 \sinh(kx) - \frac{t_2 t_3}{t_1} C_1 \Big] + \frac{1}{2} C_1 x^2 + C_2 x + C_3 \tag{6.24}$$

where C_i (i = 1-5) are unknown parameters that can be predicted using the boundary conditions. Substituting Eqs. 6.23 and 6.24 into Eq. 6.20. The analytical solution for the transverse deflection can be given by:

$$w(x) = -\frac{t_3}{t_2} \left[\frac{1}{k} C_4 \cosh(kx) + \frac{1}{k} C_5 \sinh(kx) - \frac{t_2 t_3}{t_1 k^2} \right] + \frac{1}{6} C_1 x^3 + \frac{1}{2} C_2 x^2 x + C_3 x + C_6$$
(6.25)

Invoking the boundary conditions given by Eqs. 6.17 and 6.18, the unknown constants C_i (i = 1 - 5) can be calculated. For CF nanorod, the unknown constants are given by:
$$C_1 = -\frac{F}{\left(t_3 + \frac{f_{14}f_{111}A}{a_{33}}\right)} \tag{6.26a}$$

$$C_2 = -C_1 l, \ C_3 = 0$$
 (6.26b)

$$C_4 = \frac{F}{c_{44}A\left(\frac{f_{14}f_{111}}{a_{33}t_3} - 1\right)}$$
(6.26c)

$$C_5 = -\frac{\sinh(kl)}{\cosh(kl)}C_4, \ C_6 = \frac{t_3}{t_2k}C_5$$
(6.26d)

Unknown constants for SS nanorod are given by:

$$C_1 = -\frac{F}{2t_2}, \ C_3 = -C_1 \frac{l^2}{8}$$
 (6.27a)

$$C_4 = -\frac{t_2 t_3 C_1}{t_1 k^2 \cosh\left(\frac{kl}{2}\right)}$$
(6.27b)

$$C_2 = C_5 = C_6 = 0 \tag{6.27c}$$

The governing Eq. 6.19 can be reformulated as follows when the flexoelectric effect is ignored:

$$\left(c_{11} + \frac{e_{31}^2}{a_{33}}\right)I\frac{d^2\phi}{dx^2} + kc_{44}A\left(-\phi + \frac{dw}{dx}\right) = 0$$
(6.28a)

$$kc_{44}\left(-\frac{d\phi}{dx} + \frac{d^2w}{dx^2}\right) = 0 \tag{6.28b}$$

The classical Timoshenko beam theory's governing equation can be obtained by ignoring the piezoelectric effect (MA, GAO, & REDDY, 2008).

6.3 Mechanical properties of defective graphene

The literature suggests that polarization of defective graphene sheets increases due to the breaking of inversion symmetry and because of the presence of strain gradients (S. Kundalwal et al., 2017; Nevhal & Kundalwal, 2022). However, the elastic properties of such defective graphene sheets are not available in the literature. Consequently, they need to be predicted for further studies. Therefore, we estimated the elastic properties of defective graphene sheets with 6.43 % triangular defect using MD simulations. Figure 6.2 shows the schematics of such a defective graphene sheet. For this study, we employed LAMMPS (Plimpton, 1995) to conduct MDSs. The molecular interactions between the carbon-carbon (C-C) atoms of the graphene sheet are described with the AIREBO force fields (Stuart et al., 2000). The atomic volume of the relaxed defective graphene sheet is calculated with a thickness of 3.4\AA (Huang & Yu, 2006; Pei et al., 2010). Overall stress developed in the defective graphene sheet was evaluated by averaging the stress developed on each carbon atom. Later, tensile loading is applied to predict \boldsymbol{E} and $\boldsymbol{\mu}$ by plotting stress-strain curves. The detailed procedure of MD simulations is provided by Ref. (S. I. Kundalwal & Choyal, 2018). The material properties of the defective graphene sheet are shown in Table 6.1.



Figure 6.2: Armchair graphene sheet with trapezoidal pore subjected to axial stress with 6.43 % vacancies.

The results obtained for the pristine graphene sheet are validated and agree with the literature regarding various modeling techniques and experimental investigations (Dewapriya, Rajapakse, & Nigam, 2015; Jing et al., 2012; C. Lee et al., 2008). The results of the defective graphene sheets with 4.5 % vacancies are validated with those reported by Jing et al. (Jing et al., 2012) and agree with the literature. It can be observed from Table 6.1 that Young's modulus of the graphene sheet was not much affected because of the defects. This is attributed to the hydrogenation and saturation of the dangling bonds at the edges and the porosity of the graphene sheet.

6.4 Results and discussion

This section uses the Timoshenko piezoelectric beam model to investigate the effects of flexoelectricity on the electromechanical behavior of GNC nanorods. The piezoelectric coefficient of the defective armchair graphene sheet was taken from Ref. Nevhal and Kundalwal (Nevhal & Kundalwal, 2022; Nevhal, Gupta, & Kundalwal, 2023), had 160 atoms, while the length and width of the graphene sheet were 19.88 Å and 16.0Å, respectively. The material properties of graphene and polyimide matrix are presented in Table 6.1. The modeling parameters of the nanowire are taken as; $h = 50 \ nm$, $b = 2h \ nm$, and $l = 8h \ nm$, where b, h, and l are the width, thickness, and length of the GNC nanowire, respectively. The point load $F = 1 \ nN$ is applied at x = l for the CF boundary condition and at x = l/2 for SS boundary condition.

We considered a graphene sheet with 6.43 % vacancy defect to study the influence of flexoelectric effect on the electromechanical behavior of the nanorod of GNC nanorod. GNC is composed of the graphene sheet and the polyimide matrix, with graphene fiber reinforced along the 3-axis. Such piezoelectric composite can be termed as 1-3 GNC. To simplify the work, graphene can be considered a continuum plate to calculate its bulk properties (Park et al., 2010; Roberts et al., 2010). Many existing studies on the straining of nanomaterials are based on analytical and numerical modeling based on continuum elasticity. The displacement of each atom is given by the deformation of the continuum medium, in which the atom is embedded, for a uniformly deformed GNC. Thus, for the present analysis, the GNC can be used as a continuum medium (S. S. Gupta & Batra, 2010; Gradinar et al., 2013; Bahamon et al., 2015). The piezoelectric composites (PZCs) have better out-of-plane actuation because of the improved piezoelectric coefficient, e_{33} , attributed to the alignment of fibers in the 3-direction. Such 1-3 PZCs have been extensively studied by Gupta et al. (M. Gupta, Ray, Patil, & Kundalwal, 2021, 2022). A micromechanical model based on the Mori-Tanka approach presented in Refs (M. Gupta, Meguid, & Kundalwal, 2022; S. Kundalwal & Gupta, 2022) evaluates the effective elastic, piezoelectric, and dielectric properties of GNC and tabulated in 6.2.

Material	E (GPa)	μ	$\begin{array}{c} e_{31} \\ (C/m^2) \end{array}$	$e_{33} (C/m^2)$	$\begin{array}{c}a_{33}\\(F/m)\end{array}$
Pristine Graphene	985 (present)	0.265 (present)	-0.221 [30]	0.221 [30]	1.106×10^{-10} [63]
Graphene with 4.5 % vacancy	969 (present)	0.265 (present)	-0.027 [30]	0.027 [30]	1.106×10^{-10} [63]
Graphene with 6.43 % vacancy	960 (present)	0.265 (present)	-0.051 [31]	0.051 [31]	1.106×10^{-10} [63]
Polyimide	4.2 [64]	0.4 [64]	-	-	3.009×10^{-10} [65]

 Table 6.1: Material properties of graphene and polyimide matrix.

Table 6.2: Effective properties of GNC ($v_g = 0.3$).

Material	$\begin{array}{c} C_{11} \\ (GPa) \end{array}$	$\begin{array}{c} C_{12} \\ (GPa) \end{array}$	$\begin{array}{c} C_{44} \\ (GPa) \end{array}$	$e_{31} (C/m^2)$	$e_{33} (C/m^2)$	$a_{33} (F/m)$
Graphene with 6.43 % vacancy	13.8876	8.705	4.014	-0.00182	0.175	6.921×10^{-11}

To verify the accuracy of the present model, the normalized deflections of the nanobeam are verified with the available results of the EB beam model presented in Ref. (M. Gupta, Meguid, & Kundalwal, 2022) for the identical nanobeam. Table 6.3 compares normalized deflections by considering the effects of flexoelectricity. Table 6.3 shows good agreement between the present Timoshenko beam theory and EB beam theory. It can be seen from Table 6.3 that the EB beam model underpredicts the deformation of nanobeam. This is because the EB beam theory considers that the beam's cross-section is always perpendicular to the neutral axis after deformation. The Timoshenko beam theory is the superior version of the EB beam theory as it accounts for the deformation due to shear by considering the shear lag correction factor.

The results demonstrate that the deflection predicted by the current model (Timoshenko beam theory considering the effect of flexoelectricity) is smaller than that of the classical Timoshenko beam theory. This disparity highlights flexoelectricity's influence on the nanobeam's effective bending rigidity. With the inclusion of the flexoelectric effect, the beam exhibits a significantly higher bending rigidity compared to conventional beams, leading to a stiffer bending behavior under purely mechanical loads. Additionally, the rotational displacement of the current Timoshenko beam's cross-section was also smaller than the prediction of the classical Timoshenko beam theory.

Figure 6.3(a) illustrates the deflection of the cantilevered nanorod with the ratio $\frac{x}{l}$. The maximum deflection for the CF nanorod is noted at its free end, i.e., x = 1. It can be observed from the figure that the GNC nanorod with flexoelectric effect shows smaller deflections as compared to the classical Timoshenko nanorod. The maximum deflection of nanorod (x = 1) is reduced by 50 % due to the consideration of flexoelectric effects. This is mainly because flexoelectric effects improve the effective bending rigidity of the GNC nanorod. Thus, owing to flexoelectric effects, the GNC nanorod shows stiffer behavior under mechanical loading than the classical nanorod. Figure 6.3(b) demonstrates the cross-section rotation of the nanorod with respect to the ratio $\frac{x}{l}$. The figure depicts that the nanorod's flexural rigidity improves due to flexoelectric effects, resulting in smaller cross-section rotation compared to the classical nanorod.

(M. Gupta, Meguid, & Kundalwal, 2022)						
Thickness	Boundary condition	x/L	Model	Normalized deflection		
20 mm	CF	0.2	Present	-2.84		
			EB	-2.72		
		0.6	Present	-19.36		
			EB	-18.53		
		1.0	Present	-40.62		
			EB	-38.98		
20 mm	SS	0.1	Present	-1.20		
			EB	-1.15		
		0.3	Present	-3.01		
			EB	-2.99		
		0.5	Present	-3.82		
			EB	-3.68		

 Table 6.3: Normalized deflection of nanobeam with various boundary conditions.

The maximum cross-section rotation is observed at the free end of the nanorod. Based on our observation, flexoelectricity can control the displacement profile of a piezoelectric nanorod at the nanoscale, which is useful for designing piezoelectric nanorod-based actuators.



Figure 6.3: CF piezoelectric nanorod

Figures 6.3 show the deflection and rotation of the SS nanorod with its ratio $\frac{a}{h}$. For the SS boundary condition, the deflection and rotation of the nanorod are shown for one-half of its length by taking advantage of symmetry. A concentrated load of 1 nN is applied at the center x = l/2 of the nanorod. As expected, the deflection of the nanorod decreases due to the incorporation of flexoelectric effects. Compared to the classical GNC nanorod, the nanorod with flexoelectric effects shows 44 % decrement in the maximum static deflections. For the nanorod, the maximum deflection is observed at its center, and it becomes zero at its supports, i.e., at x = 0 and x = l, as shown in Fig. 6.4(a). The cross-section rotation of GNC nanorod with or without considering flexoelectric effects for the SS boundary condition is shown in Fig. 6.4(b). The symmetry of this figure lies in the fourth quadrant. As can be seen, the rotation of the GNC nanorod. For the case of SS boundary condition, the maximum rotation is observed at the supports, while the cross-section of the nanorod remains unchanged at the center.

From Figs. 6.4, it can be observed that flexoelectricity greatly influences the



Figure 6.4: SS piezoelectric nanorod

flexural rigidity of the structure. The flexoelectric effect stiffens the nanorod for both CF and SS support conditions. However, for the same loading condition, the CF nanorod shows softer behavior, while the SS nanorod shows stiffer behavior. This is attributed to the fact that the curvature of the CF nanorod is concave downward with a negative slope. Hence, when mechanical load is applied, the CF nanorod shows larger deflections. In contrast, the curvature of the SS nanorod is concave upward with a positive slope that opposes the applied load. Thus, the SS nanorod shows smaller deflection and stiffer behavior than the CF nanorod. Hence, it can be inferred from the above discussion that flexoelectricity is crucial, and we cannot ignore the flexoelectric effect at the nanoscale level, which may lead to inaccurate results. This size-dependent phenomenon can be utilized in designing and fabricating pressure and force-based nano sensors/actuators.

6.5 Conclusion

This chapter explores an analytical model using the Timoshenko beam theory and the principle of variational work. The effect of flexoelectricity on the deflection and cross-section rotation of GNC nanorods is investigated by considering the CF and SS support types. The size-dependent properties like flexoelectricity greatly influence the flexural rigidity of the GNC nanorod. For both the support conditions, the flexoelectric effect is found to enhance the nanorod's stiffness, resulting in smaller deflections and cross-sectional rotations of the nanorod than that of the classical nanorod. It was also observed that for the same mechanical loading, the SS GNC nanorod showed stiffer behavior, while the CF GNC nanorod showed softer behavior due to curvature effects. Thus, the flexoelectric effect ought to be considered at the nanoscale for accurate modeling of nanostructures subject to mechanical loading.

Chapter 7

Summary and Future scope

7.1 Summary

The thesis explores the flexoelectric effect in graphene-based heterostructures using nano- and micro-mechanical analysis. The flexoelectric effect is a fundamental electromechanical phenomenon, and its understanding of nanomaterials has significant implications for device design and material optimization.

The study aims to deepen the understanding of flexoelectricity in the context of graphene-based heterostructures by employing advanced computational techniques, such as DFT, MD, and Micro-Mechanical Analysis. The main conclusion of this work can be summarized in the following points:

7.2 Important conclusions

- [1] *Investigating flexoelectric response*: The thesis analyzes the flexoelectric response in graphene-based heterostructures when subjected to various mechanical strain gradients. The coupling between mechanical strain and electric polarization is studied, considering different heterostructure configurations and boundary conditions.
- [2] **Tailoring material properties**: The research explores strategies to tailor material properties by engineering the flexoelectric effect. By controlling the

graphene reinforcement and heterostructure design, the thesis aims to enhance specific mechanical properties to achieve targeted functionalities.

- [3] Materials optimization: By performing nano- and micro-mechanical analysis, the research identifies optimal materials with specific flexoelectric properties suitable for targeted applications in nanoelectronics, quantum technologies, and other fields.
- [4] Designing novel nanodevices: The study explores the potential of the flexoelectric effect in designing innovative NEMS devices, such as sensors, actuators, and energy harvesters. It gives insights into the feasibility of using flexoelectricity to convert mechanical energy into electrical energy at the nanoscale.

7.3 Major findings

- Some *electro-mechanical properties of graphene* such as bandstructure, DOS and PDOS, Plasmon dispersion relation, Young's modulus (E), and Poisson's ratio (μ) are evaluated concerning pristine and defective graphene using MD and DFT.
 - Young's modulus (\mathbf{E}) of
 - * Pristine graphene = 985 GPa.
 - * Graphene with 4.5 % triangular vacancy defect = 969 GPa.
 - * Graphene with 6.43 % triangular vacancy defect = 960 GPa.
 - Poisson's ratio (μ) of graphene = 0.265
- Polarization in graphene nanoribbons with inherent defects using DFT calculations.
 - In each scenario, polarization was assessed through the application of the Berry phase formulation.

- The applied force generates a strain gradient, causing variations in resisting cross-sectional areas for the non-centrosymmetric structure. This strain gradient, in turn, induces dipole moments, resulting in polarization.
- For pristine AGNR, there is no induction of polarization response to axial strain due to its centrosymmetric structure.
- In the presence of a centrosymmetric circular defect in AGNR, no polarization was observed under axial strain. The symmetric nature of the defect region nullifies the induced dipole moments, resulting in no net polarization in AGNR with circular defects.
- Similarly, there is no polarization in a single vacancy defect, and in the case of a divacancy defect, polarization is significantly low.
- While modeling AGNR with triangular pores, the formation of dangling bonds takes place at the edges and defect sites, and these bonds can be passivated by using hydrogen atoms.
- When subjected to strain, the AGNR with a non-centrosymmetric triangular vacancy exhibits polarization. The axial piezoelectric coefficient of the passivated AGNR is $0.051 \ C/m^2$ for a 6.43 % atom vacancy. Hydrogen passivation enhances polarization by eliminating the corner strain effect. With a further increase in defect size to 11.43 %, the piezoelectric coefficient rises to 0.108 C/m^2 . This suggests that as the defect size increases, the strain gradient along the triangular pore also increases, leading to the realignment of more dipoles over a larger area and, consequently, an increase in polarization.
- AGNRs with a single SW defect demonstrate a low piezoelectric coefficient of 0.081 C/m^2 under axial loading along the x-direction.
- In AGNRs with a double SW defect, the observed polarization value is decreased compared to that with a single SW defect. This reduction may be attributed to the orientation and position of the two SW defects, causing

some of the produced dipole moments to cancel each other. A polarization value of 0.005 C/m^2 along the x-direction was obtained.

• Polarization in the van der Waals-bonded graphene/hBN heterostructures with triangular pores.

- The study of induced piezoelectricity in graphene heterostructure systems with non-centrosymmetric triangular defects has been conducted by applying strain, employing DFT and the QEH method.
- The interlayer distance between layers was kept at 3.345 Å. The interlayer weak vdW forces were considered using forces simulated by the DFT-D4 method.
- By employing DFT, a piezoelectric coefficient of 0.176 C/m^2 was determined in bilayer graphene with an 11.43 % triangular atomic vacancy defect. While bilayer graphene without a triangular defect exhibited a lower piezoelectric coefficient of 0.005 C/m^2 .
- The QEH model assesses the dielectric components of each layer, encompassing the monopole and dipole segments of the density response function and dielectric function. Using the Berry phase formulation, the polarization of vdW bonded graphene heterostructures was computed under complete electrostatic interaction. This approach yielded a piezoelectric coefficient of 0.171 C/m^2 . The QEH method is computationally faster than the DFT method.
- A piezoelectric coefficient of $0.005 \ C/m^2$ was found for pristine bilayer graphene. This approach gives a piezoelectric coefficient quite accurately even though the band structures of multi-layer graphene vary significantly from single-layer graphene. Earlier results of bilayer graphene using DFT sufficiently matched the result obtained using the QEH method. Therefore, it follows that the QEH method is quite reliable and accurate in predicting results in accordance with the first principles.

- The heterostructure created by sandwiching two graphene sheets between two hBN sheets showed modest enhancement in polarization. The honeycomb-like lattice structure of hBN, characterized by distinct boron and nitrogen atoms in its unit cell sub-lattices, behaves as a noncentrosymmetric structure. In this configuration, the piezoelectric coefficient was 0.181 C/m^2 for the triangular defect, while in the defect-free scenario, it was observed to be 0.012 C/m^2 . The slight increase in the piezoelectric coefficient compared to the graphene bilayer suggests that the hBN nanosheet amplified the polarization effect. This enhancement is attributed to the contribution of hBN layers to the polarization effect between two consecutive graphene layers.
- In the case of bilayer hBN sandwiched between graphene nanosheets having a non-centrosymmetric triangular defect with the QEH method, a piezoelectric coefficient of $0.168 \ C/m^2$ was observed with this heterostructure arrangement, and a piezoelectric coefficient of $0.008 \ C/m^2$ was found for the defect-free case. As two consecutive hBN layers were added one over the other, hBN's inversion symmetry was restored, which diminished the piezoelectric effect. Hence, no improvement in the polarization effect was obtained. As polarization due to strain gradient was the sole major contributor in the results, and inversion symmetry may have been restored in the case of two consecutive hBN layers, the polarization value was slightly decreased compared to bilayer graphene.
- The heterostructure, comprising alternating layers of hBN and graphene, exhibited a significant improvement in polarization. The noncentrosymmetric nature of hBN was retained as each layer was separated by a graphene layer which, in turn, contributed to enhanced polarization in the hetero system. Combining the non-centrosymmetry of hBN layers with the strain gradient at the triangular pore, the piezoelectric coefficient was determined to be 0.189 C/m^2 . A piezoelectric coefficient of 0.014 C/m^2 was calculated without a triangular defect in the heterostructure.

• Influence of flexoelectric effect on the bending rigidity of a graphene reinforced nanorod.

- A Timoshenko beam model is utilized to derive the governing equations for the GNC nanorod by considering the effects of flexoelectricity for CF and SS support types.
- The Timoshenko beam theory is the superior version of the EB beam theory as it accounts for the deformation due to shear by considering the shear lag correction factor.
- The maximum deflection for the CF nanorod is noted at its free end. The maximum deflection of nanorod (x = 1) is reduced by 50 % due to the consideration of flexoelectric effects. This is mainly because flexoelectric effects improve the effective bending rigidity of the GNC nanorod. Thus, owing to flexoelectric effects, the GNC nanorod shows stiffer behavior under mechanical loading than the classical nanorod.
- Flexoelectric effects enhance the flexural rigidity of the CF nanorod, leading to reduced cross-section rotation compared to the classical nanorod. The maximum cross-section rotation occurs at the free end of the nanorod. The influence of flexoelectricity on the displacement profile of piezoelectric nanorods at the nanoscale has potential applications in the design of piezoelectric nanorod-based actuators.
- Under the SS boundary condition, the application of a concentrated load of 1 nN at the center (x = l/2) of the nanorod results in decreased deflection due to the flexoelectric effect. The nanorod with flexoelectric effects experiences an approximately 44 % reduction in maximum static deflections compared to the classical GNC nanorod, with the maximum deflection occurring at its center.
- Under the SS boundary condition, and considering the effects of flexoelectricity, the rotation of the GNC nanorod is reduced compared to the classical nanorod. The maximum rotation occurs at the supports, while the

cross-section of the nanorod remains unchanged at the center.

- The flexoelectric effect increases the stiffness of the nanorod for both CF and SS support conditions. However, under the same loading condition, the CF nanorod exhibits softer behavior, while the SS nanorod shows stiffer behavior. This behavior is attributed to the curvature of the CF nanorod, concave downward with a negative slope. Consequently, the CF nanorod experiences larger deflections when a mechanical load is applied. On the other hand, the curvature of the SS nanorod is concave upward with a positive slope, opposing the applied load and resulting in smaller deflections and stiffer behavior compared to the CF nanorod.

7.4 Limitations of the study

While this study holds great potential and can contribute valuable insights to the field, it also comes with limitations. Some of the limitations are:

Complexity of computational modeling: Studying flexoelectricity in graphenebased heterostructures using advanced computational techniques like DFT and MD can be computationally demanding and time-consuming. Large supercells may be required, leading to significant computational resources.

Sensitivity to parameters: The accuracy of the results obtained from computational simulations depends on various parameters and approximations used in the models. Small changes in these parameters could lead to variations in the results, and accurately determining the optimal set of parameters can be challenging.

Material models and assumptions: The accuracy of nano- and micro-mechanical analysis relies on the material models and assumptions made in the simulations. It may be difficult to account for all the intricacies of the graphene-based heterostructure in the model, potentially leading to simplifications that could affect the accuracy of the predictions.

Limited experimental validation: In some cases, experimental data to validate the computational results may be scarce or challenging to obtain, especially when

dealing with nanoscale systems. This limitation might make it challenging to fully verify the accuracy of the models and the predictions made in the thesis.

Computational complexity: The computational cost of DFT and MD scales with the size of the system. Calculations for large systems, such as heterostructures or extended materials, can become computationally expensive and may require significant resources, which requires a huge computational power.

Band gaps and band structures: DFT can underestimate band gaps, particularly for insulating systems. Additionally, it might incorrectly predict metallic behavior for systems that should be insulating.

Practical implementation and applications: The practical implementation and application of flexoelectricity in real-world devices and technologies might be limited by scalability, manufacturing challenges, and the feasibility of engineering the desired flexoelectric properties.

Limitations of DFT and other theoretical approaches: Despite being powerful computational tools, DFT and other theoretical approaches have inherent approximations and limitations that may affect the accuracy of the results, especially when dealing with complex systems.

Generalization to different heterostructures: The thesis findings may be specific to the studied graphene-based heterostructure. Generalizing the results to other heterostructures with different materials and configurations may require additional investigations and validations.

Despite these limitations, a well-constructed thesis on the nano- and micromechanical analysis of flexoelectricity in graphene-based heterostructures can still provide valuable insights and contribute to advancing the field.

7.5 Future scope

The research scope encompasses a comprehensive further investigation into the flexoelectric effect in graphene-based heterostructures:

Multiscale modeling: Investigate the coupling between the atomic scale and the

continuum level to develop more accurate multiscale models that can capture the flexoelectric response at different length scales. This could involve combining DFT, MDs with continuum mechanics or incorporating higher-order effects into the models. *Experimental validation*: Conduct experimental studies to validate the computational predictions. This could include measuring the flexoelectric response of graphene-based heterostructures under controlled mechanical deformations and comparing the results with the computational models.

Defect engineering: Study the influence of defects on the flexoelectric response in graphene-based heterostructures. Investigate how defects, such as grain boundaries or inherent defects, affect the heterostructures' flexoelectric effect and mechanical properties.

Hybrid systems: Investigate the flexoelectric effect in hybrid graphene-based heterostructures, combining graphene with other 2D or conventional materials. Understand how the presence of different materials affects the flexoelectric response and potential synergistic effects.

Temperature and environmental effects: Study the influence of temperature and environmental conditions on the flexoelectric response of graphene-based heterostructures. Incorporate these factors into the models to evaluate the materials' performance under realistic operating conditions.

Device applications: Explore potential device applications based on the flexoelectric effect in graphene-based heterostructures. Design and analyze novel nanoscale devices, sensors, or energy harvesters that leverage flexoelectricity for enhanced performance.

Emerging 2D materials: Extend the study to include other emerging 2D materials beyond graphene, such as transition metal dichalcogenides (TMDs), to investigate their flexoelectric properties and potential applications in heterostructures.

Time-dependent analysis: Investigate the time-dependent behavior of flexoelectricity in graphene-based heterostructures under dynamic loading conditions. Understand how the flexoelectric effect may influence the material response to mechanical vibrations or other time-varying forces. *Machine learning and data-driven approaches*: Explore the application of machine learning and data-driven approaches to predict flexoelectric properties and behaviors in graphene-based heterostructures. Develop predictive models based on available data from simulations and experiments.

Exploring these research scopes can contribute to a deeper understanding of the flexoelectric effect in graphene-based heterostructures and pave the way for developing new materials, devices, and technologies with tailored electromechanical properties and functionalities. Collaborating with experimentalists and other researchers from related fields is essential to tackle these challenging research directions effectively.

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