Flexoelectricity and Piezoelectricity in BN-Based Hybrid Layers

Ph.D. Thesis

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DEPARMENT OF MECHANICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE May 2021

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A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree **of**

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(Roll Number: 1801103009)



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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Flexoelectricity and Piezoelectricity in BN-Based Hybrid Layers** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** and submitted in the **Department of Mechanical Engineering**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2018 to May 2021 under the supervision of **Dr. Shailesh I. Kundalwal**, **Associate Professor**, **Indian Institute of Technology Indore**.

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-Vijay Kumar Choyal

Indian Institute of Technology Indore Date:

Dedicated To My Beloved Family

"Nanotechnology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule"

(Prof. Norio Taniguchi)

Abstract

In this thesis, molecular dynamics (MD) simulations were carried out with a Tersoff potential and Lennard-Jones (L-J) potential force field to predict the electromechanical response of single layer (SL) and multi-layer boron nitride nanosheets (BNSs). The electromechanical response of pristine and C-doped BNSs were studied using the chargedipole (C-D) potential model. The effects of various factors such as chirality, size of BNS, C doping concentration and different shape of pores were critically examined. The elastic and piezoelectric coefficients of BNS under tension and shear loading conditions were determined. The piezoelectric, flexoelectric and elastic coefficients of BNSs with graphene stripes were also examined. Comparisons of the (i) axial piezoelectric and flexoelectric coefficients of pristine BNS, and (ii) elastic coefficients of pristine and hybrid BNS with the existing results are found to be in good agreement. The flexoelectric coefficients of monolayer boron nitride-graphene heterostructures (BGHs) were also determined by imposing the bending deformation on the pristine BNS and BGHs. Three shapes of graphene domains were considered: triangular, trapezoidal, and circular. Overall polarization of BGHs was enhanced when the graphene domain surrounded by more N atoms than B atoms. The present thesis also deals with the electromechanical response of multi-layer BNSs under uniaxial tension test at ambient temperature (300 K), taking into account the effects of number of BN layers, chirality, fracture behaviour, and strain rate (SR) on the stress-strain response and deformation behaviour. Multi-layer BNSs with an even number of atomic layers (symmetry D_{6h}) do not show piezoelectricity, whereas multilayer BNSs with an odd number of atomic layers (symmetry D_{3h}) show piezoelectricity. As a result, the number of atomic layers show an inverse relationship with the piezo- and flexo-electric coefficients. This study highlights the possibility of developing light-weight and high-performance piezoelectric BN-based NEMS such as sensors, actuators and nanogenerators as the existing piezoelectric materials are heavy, brittle, and toxic.

Keywords: Atomistic modeling; Boron nitride nanosheet; Boron-graphene heterostructures; Carbon-doping; Elastic properties; Multi-layer; Flexoelectric properties; Molecular dynamics simulation; Piezoelectric properties; Stone-Wales defects.

Table of contents

	List of figures	vii-xiii
	List of Tables	xv-xvi
	List of abbreviations and symbols	xviii-xix
	Acronyms	xxi
1.	Introduction and Literature Review	1-23
	1.1 Nanoscience and Nanotechnology	1
	1.2 Boron nitride nanosheets (BNSs)	3
	1.3 Structure of BNSs	5
	1.4 Size-dependent properties of BNSs	6
	1.4.1 Piezoelectricity	6
	1.4.2 Flexoelectricity	8
	1.5 Electromechanical response of pristine BNSs	9
	1.6 Electromechanical response of defected BNSs	13
	1.7 Electromechanical response of multilayer BNSs (ML-BNSs)	17
	1.8 Scope and objectives of the present research	20
	1.9 Organization of the thesis	22
2.	Atomistic modelling	24-44
	2.1 Atomistic modelling	24
	2.2 Molecular dynamics (MD) simulations	25
	2.2.1 Introduction	25
	2.2.2 Equations of motion	26
	2.2.3 Integration algorithms	27
	2.2.4 Temperature control	29
	2.2.5 Pressure control	31
	2.2.6 Statistical ensembles	32
	2.2.7 Potential fields	33
	2.2.8 Tersoff potential force field	35
	2.2.9 Molecular dynamics parameters	38

	2.2.10 MD simulator	41
3.	Electromechanical response of BNSs	45-71
	3.1 Introduction	45
	3.2 MD modelling of BNSs	46
	3.2.1 A charge-dipole (C-D) potential model	48
	3.3 Electromechanical response of pristine BNSs	53
	3.4 Effect of C-doping on electromechanical response of BNSs	60
	3.5 Effect of C-doping concentration on electromechanical response	65
	3.6 Effect of strain rate on elastic properties of BNSs	68
	3.7 Conclusions	69
4	Piezo- and flexo-electric response of BNS superlattices	72-96
	4.1 Introduction	72
	4.2 MD modelling of BNSs	73
	4.3 Interface engineering	77
	4.4 Results and discussions	78
	4.4.1 Variation of strain energy (SE)	79
	4.4.2 Piezoelectric coefficients of pristine and hybrid BNS	82
	4.4.3 Electromechanical response of pristine and hybrid BNS	86
	4.4.4 Flexoelectric coefficients of pristine and hybrid BNS	89
	4.4.5 Effect of SW defect on the electromechanical response of	91
	BNS	
	4.4.6 Effect of temperature on the electromechanical response of	93
	BNS	
	4.5 Conclusions	94
5.	Flexoelectric effect in monolayer boron nitride-graphene	97-117
	heterostructures	
	5.1 Introduction	97
	5.2 Computational modelling of BNS/BGHs	99
	5.2.1 Curve fitting	100
	5.2.2 Bending stiffness of BNS	103
	5.3 Results and discussions	103

	5.3.1 Electromechanical response of BGHs	108
	5.3.2 Bending stiffness of BGHs	113
	5.4 Conclusions	116
6.	Electromechanical response of multilayer BNSs (ML-BNSs)	118-139
	6.1 Introduction	118
	6.2 MD modelling of SL and ML-BNSs	120
	6.2.1 Potential	120
	6.3 Results and discussions	124
	6.3.1 Stress-strain behavior of ML-BNSs under uniaxial tension	125
	6.3.1.1 Effect of SR on mechanical properties of ML-BNSs	132
	6.3.2 Piezoelectric coefficient of ML-BNSs	133
	6.3.3 Flexoelectric coefficient of ML-BNSs	136
	6.4 Conclusions	137
7	Conclusions and future scope	140-145
	7.1 Major conclusion	140
	7.2 Limitations of the study	142
	7.3 Scope for future work	143
	References	146-163
	List of publications from the PhD	164-166
	Curriculum Vitae	167-170

List of figures

Fig. No.	Caption of figure	Page No.
1.1	The comparison of size of nanoscale objects.	2
1.2	Different BN- and carbon-based nanostructures; (a) BNS, (b)	3
	graphene, (c) BNNT, and (d) CNT.	
1.3	Structural basics of 2D BN nanostructures.	5
1.4	Schematic representation of 2D armchair and zigzag BNS.	6
1.5	Existence of pores in BNS with different pore geometries: (a)	14
	triangular pore and (b) hexagonal pore.	
1.6	Various types of defects in BNSs (a) pristine, (b) Mono-	16
	vacancy, (c) Di-vacancy, (d) Triangular-vacancy, and (e) SW-	
	defect.	
2.1	A schematic description of atomistic modelling strategies with	25
	representative length and time scales for computational	
	simulations. Some typical nanostructures such as BN nanotube,	
	nanosheet, and nanocomposite are shown as illustrative	
	examples for different length and time scales.	
2.2	Variation in the positions and velocities of atoms with the time.	28
2.3	Graphical representation of the microcanonical (NVE)	33
	ensemble, the canonical (NVT) ensemble and the isothermal-	
	isobaric (NPT) ensemble.	
2.4	Interatomic relative motions in molecular dynamics.	34
2.5	Interlayer van der Waal's interactions.	34
2.6	Stress-strain curve of a BNNTs obtained from MD simulations	39
	with different time steps.	
2.7	Stress-strain curve of a BNSs obtained from MD simulations	40
	with different strain rate.	
2.8	Graphical representation of the PBCs of the middlebox. The	41
	arrows indicate the directions of the velocities of atoms. The	

	atoms in the middlebox can interact with atoms in the	
	neighbouring boxes without having any boundary effects.	
2.9	The overview of LAMMPS input script.	43
3.1	Monolayer BNS with armchair and zigzag edges.	48
3.2	Flow diagram of simulation methodology.	49
3.3	Schematic representations of BNS under (a) tensile and (b)	53
	shear loadings.	
3.4	The variation of PE of different BNSs under uniaxial loading.	55
3.5	The stress-strain curves for BNSs under (a) tension and (b) shear	56
	loadings.	
3.6	Elastic and piezoelectric properties of pristine BNSs.	56
3.7	Deformation mechanics of (a) armchair and (b) zigzag BNSs	57
	under tension loading.	
3.8	Deformation mechanics of (a) armchair and (b) zigzag BNSs	57
	under shear loading.	
3.9	The polarization-strain curves of BNSs under (a) tension and (b)	59
	shear loading conditions.	
3.10	Dipolar moment induced mechanism in the armchair and zigzag	60
	BNSs (Red arrow shows the direction and magnitude of dipole	
	moment.	
3.11	Schematics of (a) pristine BNS and different C-doping	61
	arrangements in BNSs with (b) triangular pore (case 1), (c)	
	trapezoidal pore (case 1), (d) circular pore (case 2), (e) triangular	
	pore (case 2) and (f) trapezoidal pore (case 2).	
3.12	Variation of polarization in BNSs with different C-doping	61
	positions.	
3.13	Stress-strain curves for armchair BNS (A_2560) under (a)	63
	tension and (b) shear loading conditions.	
3.14	The variation elastic moduli of armchair BNS with the number	63
	of atoms (N).	

3.15	The variation of polarization-strain for BNSs under (a) tension	64
	and (b) shear loading conditions.	
3.16	The variation of piezoelectric coefficients with number of atoms	64
	(N).	
3.17	The schematics of BNS with different C-doping concentration.	66
3.18	The variation of (a) stress-strain (b) polarization-strain curves	67
	for BNS containing triangular pore with different C-doping	
	concentration.	
3.19	Variation of Young's modulus and piezoelectric coefficient of	68
	BNS containing triangular pore with different C-doping	
	concentration.	
3.20	Effect of strain rates on (a) stress-strain behaviour and (b)	69
	Young's modulus of pristine BNS (A_2560) under tension	
	loading.	
4.1	Schematic representations of pristine BNS subjected to E-field	76
	in: (a) armchair and (b) zigzag directions. Colored with light	
	salmon and blue are boron and nitrogen atoms, respectively.	
4.2	Schematic representations of different arrangements of BNS	78
	SLs: (a) pristine BN, (b) NCB and (c) CHR sheets. Colored with	
	light salmon, blue and cyan are boron, nitrogen and carbon	
	atoms, respectively, with dashed rectangle highlighting	
	graphene stripes.	
4.3	The stress-strain curves for a hybrid BNS using MD simulation	79
	and comparison with the results of DFT simulations.	
4.4	The schematic representations of deformation of BNS subjected	81
	to E-field in the (a) positive armchair, (b) negative armchair, (c)	
	positive zigzag and (d) negative zigzag.	
4.5	The variation of strain energy with time in pristine BNS	81
	subjected to E-field in the: (a) armchair and (b) zigzag	
	directions.	

ix

4.6	The variation of average stabilized strain energy with the E-field	82
	applied in the (a) armchair and (b) zigzag directions of pristine	
	and hybrid BNS.	
4.7	The variation of axial stress with time in the (a) BN, (b) NCB	83
	and (c) CHR sheets.	
4.8	Variation of averaged values of (a) axial strain (ε_{xx}), (b) axial	84
	stress (σ_{xx}), (c) shear strain (γ_{xy}) and (d) shear stress (τ_{xy}) in	
	the sheets under the applied external E-field.	
4.9	The stress-strain response by applied E-field under (a) armchair	85
	and (b) zigzag directions.	
4.10	Schematic representations of direction of induced dipole	86
	moments in: (a) pristine BN, (b) NCB (c) CHR sheets.	
4.11	Distribution of induced stresses in (a) pristine BN, (b) NCB and	88
	(c) CHR sheets subjected to the E-field in armchair direction.	
	The color-coding indicates the induced atomic stresses in SLs.	
4.12	The variation of polarization with the E-field applied in the (a)	88
	armchair and (b) zigzag directions of different BNS SLs.	
4.13	Schematic representation of the partitioned BNS axially into the	90
	rectangular bins.	
4.14	The variation of stress with E-field gradient for different BN	91
	sheets.	
4.15	Schematic representations of BNS with SW defects: (a)	92
	BNS@2SW and (b) BNS@4SW.	
4.16	Variation of averaged values of axial (a) stress (σ_{xx}) and (b)	92
	strain (ϵ_{xx}) in the pristine and SW defected BNS under the	
	applied external E-field.	
4.17	Variation of elastic and piezoelectric properties of pristine and	93
	hybrid BNS with different temperature: (a) Young's modulus	
	(E_{xx}) and (b) axial piezoelectric coefficient (e_{11}).	
5.1	(a) Stress-free BN lattice, (b) tension stress BN lattice, (c)	98
	compression stress BN lattice, (d) BNS in which π -orbitals are	

х

symmetric, and (e) bent BNS in which π -orbitals are asymmetric.

5.2	Schematic representation of (a) flat BNS and (b) bent BNS.	100
5.3	(a) Curve fitting, (b) strain (ϵ_{xz}) , (c) strain-gradient (k) and (d)	105
	colored atomic configuration of induced atomic strain in the	
	direction of x of BNS at a bending curvature of 0.001 Å ⁻¹ .	
5.4	Variation of induced polarizations along x- and z-directions of	106
	BNS at bending curvatures of (a) 0.006 \AA^{-1} and (b) 0.001 \AA^{-1} .	
5.5	Variation in polarization (P_z) with strain gradient (k) for pristine	107
	BNS.	
5.6	Snapshots of distribution of charge densities: side, top and ortho	108
	views of pristine BNS under bending deformation at bending	
	curvature of 0.001 Å ⁻¹ .	
5.7	Schematic representations of (a) pristine BNS, (b) BGH with	109
	circular graphene domain, (c) BGH with triangular graphene	
	domain and (d) BGH with trapezoidal graphene domain.	
5.8	The variation of (a) polarization in the z-direction (P_z) and (b)	111
	polarization in the x-direction (P_x) with strain gradient k for	
	pristine BNS and BGHs.	
5.9	Snapshots for distribution of charge densities: side, top and	112
	ortho views of BGHs with (a) triangular, (b) trapezoidal, and (c)	
	circular graphene domains under bending deformation at	
	bending curvature of 0.001 Å ⁻¹ .	
5.10	Schematic representations of variation in bond length (Å) for	113
	BGHs with: (a) triangular, (b) trapezoidal and (c) circular	
	graphene domains at bending curvature of 0.001 Å ⁻¹ .	
5.11	The variation of (a) potential energy and (b) bending stiffness	114
	of BNS and BGHs under different bending curvatures.	
5.12	Side view of flat and corrugated nanostructures of BGHs.	115

6.1	Schematic representation of the relationships between the	121
	possible high symmetry stacking of h-BN are as: (a) AA	
	stacking, (b) AA' stacking, and (c) AB stacking.	
6.2	MD model of uniaxial tension test of 2_layer BNSs under zigzag	124
	direction. (b) The periodic boundary conditions were applied in	
	the x and y direction. Atoms depicted in ochre are boron and	
	atoms depicted in blue are nitrogen. (c) simulation model of	
	ML-BNSs.	
6.3	The variation of the normalized potential energy of ML-BNSs	126
	in the armchair and zigzag direction. (AC-Staging of armchair	
	BNS; ZZ-Staging of zigzag BNS; Bulk BNS - thickness more	
	than 20 to 25 Å)	
6.4	The variation of the (a) potential energy (eV) with relaxation	127
	time (ps) (b) temperature (300 K) with relaxation time (ps) of a	
	2_layer BNS in the armchair and zigzag direction at 300 K.	
6.5	The $\sigma - \delta$ curve of ML-BNSs under uniaxial tensile loading in	129
	the armchair and zigzag direction.	
6.6	The variation elastic Young's modulus of armchair and zigzag	130
	BNS with the number of atomic layers. The inset shows the	
	simulation setup.	
6.7	Snapshots of the failure process of 2_layer BNSs under uniaxial	130
	loading in the armchair direction.	
6.8	Snapshots of the failure process of 2_layer BNSs under uniaxial	131
	loading in the zigzag direction.	
6.9	Deformation mechanics of SL BNS under uniaxial tensile	131
	loading in the armchair direction. Color configuration	
	represents the atomic stresses induced in the BNS.	
6.10	Deformation mechanics of SL BNS under uniaxial tensile	132
	loading along the zigzag direction. Color configuration	
	represents the atomic stresses induced in the BNS.	

xii

- 6.11 Deformation behavior of 5_layer BNS under uniaxial tensile 132 loading in the armchair direction are as: (a) undeformed sheet,
 (b) deformed sheet after the application of load and (c) failure of deformed sheet. Color coding indicates the atomic stresses induced in the sheet.
- 6.12 Uniaxial $\sigma \delta$ curve of (a) 2_layer and (b) 5_layers armchair 133 and zigzag BNS at different loading SR.
- 6.13 The variation of $P \delta$ for ML-BNSs under uniaxial tension 135 loading in the armchair and zigzag directions.
- 6.14 The piezoelectric coefficient of ML-BNSs as a function of their 136 atomic layer number. The inset shows the simulation setup.
- 6.15 The flexoelectric coefficient of ML-BNSs as a function of their 137 atomic layer number. The inset shows the simulation setup.

List of Tables

Table No.	Caption of Tables	Page No.
1.1	Summary of the basic equations used to describe	8
	piezoelectricity and flexoelectricity.	
2.1	Parameters used in Tersoff potentials for B-B, N-N, B-	37
	N, C–C, C–N and C–B interactions.	
3.1	Comparison of the elastic constant of a pristine	54
	armchair and zigzag BNSs.	
3.2	Comparison of piezoelectric constant of pristine	59
	armchair and zigzag BNSs.	
3.3	Comparison of elastic and piezoelectric constant of	65
	pristine and triangular shape of C-doped BNS.	
3.4	Comparison of elastic and piezoelectric constant of	65
	trapezoidal and circular shape of C-doped BNS.	
3.5	Elastic and piezoelectric constants while increasing	67
	triangular, trapezoidal, and circular C-doping	
	concentration of BNSs.	
4.1	Comparison of piezoelectric and elastic coefficients of	84
	pristine/hybrid BNS with previous studies.	
4.2	Piezoelectric and elastic coefficients of pristine/hybrid	86
	BNS.	
4.3	The bond length (Å) and dipole moments (Cm) for	89
	pristine and hybrid BNS.	
4.4	Flexoelectric coefficients of pristine and hybrid BN	91
	sheets.	
4.5	The elastic and piezoelectric coefficients of BNS with	93
	SW defects.	
5.1	Flexoelectric coefficients of pristine BNS and BGHs.	111
5.2	Bending stiffness of pristine and C-doped BNS.	114
6.1	L-J interaction parameters for BN atoms.	122

6.2	Comparison of the Young's modulus and piezoelectric	125
	coefficients of a SL and ML-BNSs.	
6.3	Elastic properties of SL and ML-BNS.	129
6.2	Piezoelectric and flexoelectric coefficient in the	135
	armchair and zigzag direction of ML-BNSs.	

List of Abbreviations and Symbols

Abbreviations and Symbols

1D	One dimensional
2D	Two dimensional
3D	Three dimensional
E	Young's modulus (GPa)
E	Total energy
Ei	Site energy
V _{ij}	Bond energy
r _{ij}	Distance between atom i and j
b _{ij}	Bond angle
f _R	Repulsive potential
f _A	Attractive pair potentials
f _C	Cut-off function
R and D	Model specific parameters
R	Radius of curvature
k	Strain gradient\bending curvature
p and q	Curve fitting parameters
L _x	Length along the direction of x
Sz	Bending displacement
P_x and P_z	Polarization along x and z direction
q _i	Ion charge of the i th atom
r _i	x-coordinate of the i^{th} atom
Ν	Number of atoms
А	Surface area
D	Bending stiffness
ΔΕ	Bending potential energy

θ_{ijk}	Angle between bonds
θ	Angle between two vectors
ε _{xz}	Strain in the x direction from the applied deformation in the z direction
e _{ijk} , d _{ijk}	Piezoelectric coefficient
μ_{ijkl}	Flexoelectric coefficient
L _i	Initial lengths of BNS
L_f	Final lengths of BNS
$(\sigma_{\alpha\beta})$	Virial stress
m_{α}	Mass of atom α
v_x^{α}	Velocity component in the axial direction of atom α
$F_{\alpha\beta,y}$	Axial component of interatomic force between atoms α and β

Greek Letters

ρ	Density (Kg/m ³)
q_i	Charge of i th atom
θ	Angle (degree or radian)
μ	Poisson's ratio
D _{ij}	Diameter of the atom
σ	Stress (N/m ²)
τ	Shear stress (N/m ²)
δ	Uniaxial strain
π	Approximately 3.1416
K _C	Coulombic constant
ε	Depth of the potential well
κ	Radius of curvature (m ⁻¹)
Σ	Summations

ACRONYMS

AFM	Atomic force microscopy	
AIREBO	Adaptive intermolecular reactive empirical bond order	
BNS	Boron nitride nanosheet	
BNNT	Boron nitride nanotube	
BGH	Boron nitride-graphene heterostructures	
BCN	Carbon-Doped Boron Nitride Nanosheets	
CNT	Carbon nanotube	
CVD	Chemical vapor deposition	
DFT	Density functional theory	
EBR	Electron beam irradiation	
LAMMPS	Large-scale atomic/molecular massively parallel simulator	
MD	Molecular dynamic	
NEMS	Nanoelectromechanical systems	
PBC	Periodic boundary condition	
PE	Potential energy	
SE	Strain energy	
STM	Scanning tunneling microscopy	
TEM	Transmission electron microscopy	

1. Chapter

Introduction and Literature Review

In this chapter, a brief introduction to the single layer and multilayer boron nitride nanosheets (BNSs) and review of literature on the mechanical, piezoelectric and flexoelectric properties of pristine and defected BNSs are covered. Based on the review of literature, the scope of work for this thesis is identified, and the objectives of dissertation are presented. Organization of the chapters is delineated at the end of this chapter.

1.1 Nanoscience and nanotechnology

Nanoscience refers to the study, manipulation and engineering of matter, particles and structures at the nanometer scale level (one billionth of a meter, $1/10^9$). The important properties of nanomaterials such as mechanical, electrical, optical and thermal are largely depend on the way molecules and atoms arranged at the nanoscale level into the larger structures. Moreover, in case of nanomaterials, atomic-level properties often change compared to the macroscale because of quantum mechanical effects (Cohen et al., 2001). Nanomaterials possess larger surface area compared to their parent materials at the microscale level for a given volume (Roco and Williams, 1999). The larger surface area increases the reactivity of nanomaterials, and they can be used efficiently in numerous applications.

Nanotechnology is the application of nanoscience and utilization and creation of devices and materials by manipulation of the matter at the scale of nanometers or atomic/molecular scale. The generalized description of nanotechnology is given by the National Nanotechnology Initiative, and according to that, nanotechnology is the manipulation of matter with at least one dimension sized between 1 to 100 nm. Figure 1.1 depicts some sense of how this size scale relates to more familiar, everyday scales. Controlling the features of matter on the scale of nanometer has already made a significant contributions in several disciplines: engineering, physics, material science, chemistry, medicine and biology (Roco and Williams, 1999). The term "nanotechnology" was coined

by Richard Feynman in 1959. The research at the nanoscale level accelerated after the discovery of scanning tunneling microscopy (STM) (Binning et al., 1982) and atomic force microscopy (AFM) (Binnig et al., 1986). The discovery of STM and AFM allowed researchers to study and observe individual atoms and manipulate them. A modification at the nanoscale level eventually allows us to design custom-made materials and products with enhanced properties, including nanoelectronics, smart medicines and sensors, and even interfaces between electronics and biological systems can be tailored (Roco and Williams, 1999).



Fig. 1.1 The comparison of size of nanoscale objects.

The proliferation of nanoscale technology and science has led to the discovery of several interesting nanomaterials. For instance, the ground-breaking discovery of twodimensional (2D) atomic-thick graphene layer was carried out by Novoselov and Geim in 2004 and its extraordinary mechanical (Huang et al., 2006; Ni et al., 2010; Dewapriya et al., 2014; Javvaji et al., 2018), thermal (Ng et al., 2012; Zhang et al., 2017), and electrical (Kundalwal et al., 2017) properties encouraged to study another types of 2D nanomaterials. Boron nitride (BN) possesses similar lattice structures as that of carbon-based nanostructures (Ooi et al., 2006). The BN-based nanostructures, including BN nanosheets (BNSs), BN nanotubes (BNNTs), BN nanoribbons (BNNRs) are based on the hexagonal phase of BN, with B–N bonds. The B–N bonds are the isoelectronic with C–C bonds that exist in carbon-based nanostructures. Therefore, the structures of BNS, BNNT, and BNNR are similar to graphene, CNTs, and graphene nanoribbons, respectively, as shown in Fig. 1.2.


Fig. 1.2 Different BN- and carbon-based nanostructures; (a) BNS, (b) graphene, (c) BNNT, and (d) CNT.

1.2 Boron nitride nanosheets (BNSs)

Boron nitride nanosheets (BNSs) are 2D nanomaterials consisting typically of single-, bi- or multilayer (ML) of hexagonal boron nitride (h-BN) on the order of nanometer scale. BNS is a traditional nanomaterial which is attracting intense attention in academia and industry due to its multifunctional properties among all other BN-based nanostructures. Close analogues of graphene sheet, ML-BNSs were first synthesized by Pacil et al. (2008), and single- and ML-BNSs were synthesized by Han et al. (2008). A BNS is made of boron (B) and nitrogen (N) atoms, alternatively arranged in a honeycomb pattern like carbon atoms in a graphene sheet (Lehtinen et al., 2011) (see Fig. 1.2). BNSs have been a material of intense interest over the past few years as they possess highly stable structures (Topsakal et al., 2009), superior mechanical properties (Kudin et al., 2001; Bosak et al., 2006; Le et al., 2014; Kundalwal et al., 2020) and functionalization capabilities that assist in engineering their properties for nanoelectromechanical system (NEMS) applications (Boldrin et al., 2011; Karel Alexander N. Duerloo and Reed, 2013; Alam et al., 2014; Chaurasia and Parashar, 2021). A BNS possesses a large band-gap around ~5 to 6 eV, making it an insulator (Watanabe et al., 2004; Topsakal et al., 2009) with excellent physical properties, high chemical and thermal stabilities, and strong resistance to oxidation at higher temperatures (up to >900 °C) (Golberg et al., 2010). Moreover, BNS possesses a non-centrosymmetric structure and partly demonstrates ionic characteristic of B-N bonds due to the electronegativity differences of B and N atoms, demonstrating piezoelectricity

Chapter 1

(Mele and Král, 2002), which attracted an intense attention in the field of actuators and sensors (Eichler and Lesniak, 2008), composite materials (Zhi et al., 2009), hydrogen storage (Zhao and Ding, 2009), gas sensors, optoelectronic, optical devices, transistors and biological probes (Song et al., 2013). Although most of the applications are similar to graphene sheet, the BNSs possess additional multifunctional features like piezoelectricity and white color. Moreover, the BNSs display comparable mechanical properties to graphene sheet, while former's failure resistance may surpass the latter's. The electromechanical coupling in BNSs is also better than the polymer-based piezoelectric materials (Sai and Mele, 2003). These versatile features of BNSs attract prodigious attention for their use as reinforcing fillers in conventional matrices for fabricating BN-based high-strength and light-weight piezoelectric nanocomposites with a variety of colors or even transparent (Kim et al., 2018).

Several unique techniques are being employed to synthesis BNSs: chemically derived route technique (Han et al., 2008), micromechanical cleavage technique (Pacil et al., 2008), electron beam irradiation (EBR) (Jin et al., 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 and Connell, 2012). After the discovery of BNSs, numerous efforts were made to enhance the synthesizing process to obtain pristine BNSs (Ci et al., 2010). By controlling the parameter of synthesis, an individual BN layer is called a "*single-layer BNS*"; a thin BN crystal with several atomic layers is called a "*multilayered BNS*" (see Fig. 1.3). Within each ML-BNS, B and N atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals forces at a distance of 0.335 nm (Song et al., 2010). Therefore, BNS films could be peeled off from bulk BN crystal by micromechanical cleavage and used as a dielectric layer. ML-BNS has also been made by ultrasonication and high-energy electron beam irradiation of BN particles. In general, BN nanostructures are recognized as advanced nanomaterials with outstanding electromechanical response.



Fig. 1.3 Structural basics of 2D BN nanostructures.

1.3 Structure of BNSs

A BNS monolayer molecule is composed of a hexagonal array of alternatively arranged B and N atoms. The constructional feature of BNS structure corresponds to a hexagon pattern that repeats itself periodically in a space. As a result of the periodicity, each B and N atoms are bonded to three neighboring atoms. The resulting structure is mainly due to the process of sp² hybridization forming three in-plane (σ) bonds with an out-of-plane (π) bond. The σ bond is a strong covalent bond having 1.446 Å length that plays a vital role in the impressive mechanical and piezoelectric properties of BNSs. On the other hand, π bond is relatively weak and contributes to the interactions between the ML-BNSs (Han et al., 2008; Pacil et al., 2008; Falin et al., 2017).

BNS is made up of a regular arrangement of hexagonal array of B and N atoms. A widely used approach to identify the types of BNSs such as armchair, zigzag, and chiral. The key geometric parameter associated with the chiral vector C_h , which can be expressed as the linear combination of lattice bases (a_1 and a_2). Mathematically, the sheet chirality can be defined in terms of roll-up vector as follows:

$$C_{\rm h} = {\rm na}_1 + {\rm ma}_2 \tag{1.1}$$

where the integers (n, m) are miller indices of the hexagonal lattice (number of steps along the zigzag bonds of hexagonal lattice), and a_1 and a_2 are unit basis vectors as shown in Fig. 1.4. The angle \emptyset between the chiral vector and lattice base vector (a_1) is called as the chiral angle and is given by:

$$\emptyset = \arctan\left(\frac{\sqrt{3}m}{2n+m}\right) \tag{1.2}$$

The zigzag axis of BNS corresponds to $\emptyset = 0^{\circ}$ and if the rolling chiral vector is along this axis, a zigzag (n, 0) BNS is formed. On the other hand, the armchair axis of sheet is specified by $\emptyset = 30^{\circ}$ and if this is the direction of rolling chiral vector, an armchair (n, m) BNS is formed. The monolayer BNS generated for other values of \emptyset (i.e., $0 < \emptyset < 30^{\circ}$) is referred as chiral BNS. Figure 1.4 illustrates the schematic representations of two types of BNSs. The chirality of BNSs has significant implications on their properties.



Fig. 1.4 Schematic representation of 2D armchair and zigzag BNS.

1.4 Size-dependent properties of BNSs

1.4.1 Piezoelectricity

Piezoelectricity was first discovered by French physicists, Pierre and Jacques Curie in 1880. Afterward, Gabriel Lippmann deduced mathematical relation for the converse piezoelectric effect from the fundamental principles of thermodynamics in 1881, which was not predicted by Curie brothers. Piezoelectricity–electrical polarization induced by a uniform strain (or vice-versa)–is the most widely known and exploited forms of electromechanical coupling that exists in non-centrosymmetric crystals. In noncentrosymmetric crystals, the absence of center of inversion results in the presence of polarization. Specifically, in contrast to the piezoelectricity, the flexoelectricity phenomenon presents in nanomaterial having inversion symmetry, and even the centrosymmetric crystal can also be polarized by breaking its inversion symmetry and applying non-uniform strain gradient. Unlike, piezoelectricity phenomenon which can be found only in 20 non-centrosymmetric point groups, the flexoelectricity exists in all dielectric and insulating materials with 32 crystallographic point groups and the electromechanical coupling can be generated in non-piezoelectric materials (Maranganti et al., 2006; Sharma et al., 2007). There is both direct and converse piezoelectric effects. In a direct piezoelectric effect, an applied stress creates a polarization within the crystal. In case of converse piezoelectric effect, an applied E-field creates a stress and strain in the crystal. The relationships between mechanical and electrical properties are summarized in Table 1.1. Among the equations used in the table, P, E, ε , σ , μ , and x represent the polarization, E-field, strain, stress, flexoelectric coefficient and spatial direction, respectively. The subscripts *i*, *j*, *k*, *l* all represent the different cartesian directions as 1, 2, and 3, or x, y, and Ζ.

The origin of the piezoelectric effect is a fundamental asymmetry in a crystal's lattice structure. Because of this, not all crystal structures possess piezoelectric properties. Only crystals which fall under the class of non-centrosymmetric crystals exhibit piezoelectricity, while crystals structures of higher symmetry do not. Centrosymmetry exists if a crystal can be transferred from every point (x, y, z) to (-x, -y, -z) and retain the same geometric structure. Piezoelectric materials must be non-centrosymmetric so that a strain within the crystal will separate the centers-of-mass of the positively and negatively charged ions. This limitation on the crystal's structure limits the materials which can be used to create the piezoelectric effect.

Electromechanical effect	Strain / Stress	Direct effect	Converse effect	
	Strain	$P_i = e_{ijk} \epsilon_{jk}$	$\epsilon_{jk} = d_{ijk}E_i$	
Piezoelectricity	Stress	$P_i = d_{ijk}\sigma_{jk}$	$\sigma_{jk} = e_{ijk}E_i$	
	Strain	$P_{i} = \mu_{ijkl} \frac{\partial \epsilon_{jk}}{\partial x_{l}}$	-	
Flexoelectricity	Stress	_	$\sigma_{ij} = \mu_{ijkl} \frac{\partial E_k}{\partial x_l}$	

Table 1.1 Summary of basic equations used to describe piezoelectricity and flexoelectricity.

1.4.2 Flexoelectricity

The flexoelectric effect is an electromechanical coupling in which the dielectric polarization exhibits a linear response to a mechanical strain gradient. The name originates from the Latin word flexus meaning "*bend*" and is related to the fact that a strain gradient naturally arises in bent structures (Yudin and Tagantsev, 2013). Flexoelectricity is similar to piezoelectricity, except spatial gradients are involved, making the analysis and understanding slightly more challenging. Flexoelectricity also has direct and converse effects: in the direct effect an applied strain gradient generates a polarization, and in the converse effect an applied E-field gradient generates a strain. There have also been reports where an applied uniform E-field has induced a curvature in the material (Yudin and Tagantsev, 2013). The equations used to describe the flexoelectric effects are also shown in Table 1.1 alongside the piezoelectric equations for comparison.

Unlike piezoelectricity, flexoelectricity is present in every crystal structure and does not rely on asymmetry in the crystal structure. Due to the spatial gradient terms in the constitutive equations, different amounts of strain at different physical locations within the crystal create the asymmetry needed to separate the centers-of-mass of positive and negative charge to give rise to a polarization. This means that a wider variety of materials are available for use as nanoelectromechanical devices. Additionally, since many of the best performing piezoelectric materials contain lead, flexoelectricity opens the door for the use of more biocompatible materials or enhancing the piezoelectric effect within devices used for sensors, actuators, and energy harvesters.

Similar to the piezoelectricity, flexoelectricity also shows two discrete strain and electric field gradient-dependent electromechanical couplings: direct as well as converse

flexoelectric effects. Flexoelectricity is a size-dependent phenomenon. Thus, the flexoelectric effect is a preferred electromechanical coupling in MEMS/NEMS applications. The constitutive relation (1.4) for the total polarization vector accounting the piezoelectric and flexoelectric effect may be re-written as: (Yudin and Tagantsev, 2013; Kundalwal et al. 2017)

$$P_{i} \sim e_{ijk} \varepsilon_{jk} + f_{ijkl} \frac{d\varepsilon_{jk}}{dx_{l}}$$
(1.3)

where, ε_{jk} and $\frac{\partial \varepsilon_{jk}}{\partial x_l}$ are the respective strain and strain gradient terms; e_{ijk} and f_{ijkl} are the piezoelectric and flexoelectric coefficients, respectively.

1.5 Electromechanical response of pristine BNSs

The BNS has captivated massive response from researchers due to its exceptional mechanical, electrical, and thermal properties. Several experimental, numerical, and analytical investigations were carried out to explore the effect of crucial geometrical parameters such as chirality, aspect ratio (w/l) and size of BNSs on their electromechanical response (K. N. Kudin et al., 2001; Boldrin et al., 2011; Zhao and Xue, 2013; Eshkalak et al., 2018). These studies confirmed that BNS's exceptional high Young's modulus and stiffness. For instance, an effort was made by Ohba et al. (2001) reported the structural, dielectric, and dynamical properties based on first-principles calculations for three polytypes (*c*–BN, *w*-BN and *h*–BN) of BN. Bosak et al. (2006) measured Young's modulus of BN based via inelastic x-ray scattering measurements. Using atomic force microscopy, Li et al. (2009) found that the bending modulus of BNSs increases with decreasing thickness and approaches an asymptotic value of monolayer BNS when the thickness is below 50 nm. Boldrin et al. (2011) studied the in-plane mechanical properties (tensile and shear rigidity, and Poisson's ratio) of BNS using single BN bond mechanical model. Using molecular micromechanical model, Natsuki et al. (2017) studied the elastic properties of BNS. Their result showed that the mechanical properties such as Young's modulus and Poisson's ratio depend on the chirality of BNS. There were numerous studies conducted to determine the electromechanical response of BNSs. For instance, tight-binding (Bettinger et al., 2002), MD simulations (Mortazavi and Rémond, 2012; Thomas et al., 2015; Eshkalak et al., 2018; Liang et al., 2019), ab-initio (Kudin et al., 2001), a first principle study (Sai and Mele, 2003; Hosseini et al., 2018), continuum modeling (Sharma and Parashar, 2021) and molecular mechanics (Le et al., 2015; Natsuki and Natsuki, 2017) approaches were used to evaluate the electromechanical response of pristine armchair and zigzag BNSs under uniaxial loading. Most of these studies were performed on either armchair or zigzag BNSs. Numerous investigations were carried out to determine the mechanical properties of pristine BNS using different techniques and approximations. For example, Peng et al. (2012) developed a non-linear continuum model based on density functional theory (DFT) to investigate the mechanical behavior of BNS. They reported that BNS experiences a non-linear elastoplastic deformation up to ultimate failure point, followed by a strain-softening behavior. Mortazavi and Remond (2012) investigated the thermomechanical response of BNS using MD simulations and reported that its Young's modulus depends on the chirality and the converse is true for thermal conductivity. Thomas et al. (2016) performed MD simulations to determine the mechanical properties of BNS using a Tersoff interatomic empirical potential. They reported that the elastic properties of BNS are size dependent and increases with its size. Using MD simulations, Vijayaraghavan et al. (2018) studied the effective mechanical properties of BNS. They found that a BNS with smaller w/l ratio exhibits better tensile loading characteristics. They also reported that effective Young's modulus of the BNS depends on its wall thickness.

Only few studies investigated the mechanical behavior of BNSs under shear and bending loading/deformation. For instance, Tian et al. (2014) studied the mechanical properties, including wrinkling patterns and fracture behavior, of BNSs using classical MD simulations and continuum model. They observed that the compressive stress controls the wrinkling phenomenon and tensile stress dominates the fracture behavior of BNS. The fracture tensile stress is inversely proportional to the width of BNS. Zhang et al. (2017) studied the remarkable piezo-potential property of BN honeycomb (BNHC) structures using finite element and MD simulations. They reported that due to their unique polarization distribution BNHCs possess a tensile piezoelectricity in the armchair direction and a shear piezoelectricity in the zigzag direction. Mukhopadhyay et al. (2018) studied the shear modulus of nanomaterials with mono-planar (such as graphene sheet and BNS) and multiplanar (such as molybdenum disulfide (MoS₂)) configurations based on a physically insightful analytical approach. They found that the shear modulus plays an

important role in characterizing the applicability of different 2D nanomaterials and heterostructures in various NEMS such as determining the resonance frequency of vibration modes involving torsion, wrinkling, and rippling behavior of 2D nanomaterials.

All BNSs are insulator and show a large band-gap (~5.9 eV) due to the difference in the electronegativities of B and N atoms of BNS. A BNS shows a partially ionic characteristic (Alam et al., 2014) and makes it piezoelectric nanomaterial. A piezoelectric phenomenon in BNS was intensely studied experimentally and theoretically in the literature (Bernardini et al., 1997; Sai and Mele, 2003; Michel et al., 2011; Zhang et al., 2014; Ahmadpoor and Sharma, 2015; Hinchet et al., 2018). A BNS shows extraordinary dielectric properties with a stunning and homogeneous performance for its nanodevice applications. Piezoelectricity is an important property of non-centrosymmetric crystals which is the basis for actuators, sensors, and transducers in multifarious NEMS applications (Sai and Mele, 2003; Michel et al., 2011; Tolladay et al., 2017). Several theoretical studies were performed to investigate the intrinsic piezoelectricity effect in BNbased nanostructures. For instance, Mele and Karl (2002) studied the electric polarization in BN-based nanostructures using the Berry phase quantum method. They revealed the existence of piezoelectric effect in BN-based nanostructures. Afterwards, Sai and Mele (2003) performed DFT calculations and reported that the BN based nanomaterials possess piezoelectric properties. Duerloo et al. (2012) performed DFT calculations to study the piezoelectric properties of different 2D single layers (SLs). They reported that the 2D SLs show excellent piezoelectric properties and provide the new platforms for electronic devices, enabling previously inaccessible avenues for sensing and control at the nanoscale level. Zhang et al. (2013) studied the buckling response and piezoelectric properties of BNbased nanostructures subjected to the external E-field using the micro-mechanical approach. They reported that the axial and shear deformations occurred in the structure and the direction of induced stresses depends on the direction of applied external E-field. López-Suárez et al. (2014) examined the dynamics of BN monolayers using ab-initio calculations of the deformation potential energy and numerically resolved an equation of Langevine-type, which offers new possibilities for developing piezoelectric devices. An analytical study by Dorth et al. (2016) also proved the existence of piezoelectricity in monolayer BNS via the use of quantum geometric phase approach. Zhang et al. (2017)

studied the electromechanical response of BNS and BN-based nanostructures. They found that the elastic, piezoelectric and dielectric constants of BN-based nanostructures decrease with their size. Recently, Zhang et al. (2019) studied the piezoelectric effect in MoS_2 and BNS under the influence of E-field and compared their piezo-potentials using MD simulations. They suggested that the MD simulations provide reliable piezoelectric coefficients compared to the classical models. Using MD simulations, Zhuang et al. (2019) developed a charge-dipole potential model to determine the flexoelectric response of 2D nanomaterials such as BNS, MoS_2 and graphene sheet subjected to bending deformation. Their prescribed bending deformation method describes the calculation of the flexoelectric constants while eliminating the piezoelectric contribution from the universal relation of induced polarization during deformation. They also revealed that the electromechanical coupling increases in out-of-plane bending as compared to in-plane stretching.

Similar to the piezoelectricity, flexoelectricity is also shows the electromechanical coupling, except strain gradient is involved instead of homogenous strain (Mohammadi et al., 2014). For the first time, the flexoelectricity in carbon nanotube was observed by White et al. (1993) in 1993. In their study, the bond symmetry breaking due to curvature was visible in the electronic properties of CNTs. Using first-principle calculations, Dumitirica et al. (2002) determined the normal polarization induced by bending of graphene shells, which microscopically occurred due to a shift in sp^2 hybridization at each atomic site. During bending deformation, the center of electronic charge is displaced outwards from the nuclear charge, and at the corresponding curvature, induced dipole moments were observed. Kalinin and Meunier (2008) performed density functional theory (DFT) to study the flexoelectric effect in 2D nanomaterials. They observed that induced dipole moment and bending curvature of graphene sheet shows a linear relationship. Using first-principle calculations, Naumov et al. (2009) studied the single-atom-thick sp²-bonded noncentrosymmetric crystals like BNS which exhibits an unusual nonlinear electromechanical effect. Giant flexoelectric effect was also predicted for monolayer h-BN, suggesting its potential for ambient agitation energy harvesting. A theoretical study by Kvashnin et al. (2015) reported the flexoelectricity in carbon nanostructures and confirmed the dependence of flexoelectric coefficient on the local curvature of structures. Michel et al. (2016) studied the flexoelectricity in BNS using the first-principles calculations. They revealed that the

piezo-response of BNS could be improved using the flexoelectricity concept. Ghasemi et al. (2018) presented a computational design methodology for topology optimization of multi-material-based flexoelectric composites and demonstrated the flexibility of the model as well as the significant enhancement in electromechanical coupling coefficient. A new approach was proposed by Do et al., (2019) to identify all material parameters of flexoelectric materials based on electrical impedance curves which combined an iso-geometric analysis formulation with a gradient-based optimization algorithm using the method of moving asymptotes.

1.6 Electromechanical response of defected BNSs

The BNS structures contain various types of defects due to the inherent issues of their fabrication techniques. Such defects are often considered while developing BN-based nanostructures as they affect the properties of BNSs. The most common defects include mono- and multi-vacancies (Zobelli et al., 2006; Gou et al., 2007; Nejad et al., 2013; Cheng et al., 2016) in which atom/s is/are missing from regular atomic site/s, Thrower-Stone-Wales (SW) defects (Song et al., 2007) is the rearrangement of the hexagonal ring into pentagons and heptagons, and anti-sites doping (Bhattacharya et al., 2015; Weng et al., 2016) where atoms of different types change places with each other. Sometimes these pores/defects improve local changes in the atomic polarization and chemical bond orders of BNS, leading to a change in its electromechanical behavior (Lehtinen et al., 2011). For example, Jin et al. (2009) effectively synthesized monolayer BNS using an energetic EBR method and revealed that the existence of B and N monoatomic and triangular pore in it. They also found that the B atom vacancies are energetically more stable than N atom vacancies. Suenaga et al. (2012) analyzed monolayer BNSs with and without point defects using electron energy-loss spectroscopy. They revealed that monovacancy at N site is more prominent for electronic properties compared to B site vacancies. Park et al. (2015) used EBR method to control the shape, size, and stability of 2D nanomaterials such as BNS, graphene and MoS_2 . They obtained the desired shape and size of pores in BNS experimentally, as shown in Fig. 1.5. On the other hand, to control the performance of nanomaterials, 'defect engineering' technique is being widely employed for many materials to alter their properties: cubic BN (Tian et al., 2013), diamonds (Huang et al., 2014), graphene sheets (Kundalwal et al., 2017; Javvaji et al., 2018), CNTs (Kundalwal

and Choyal, 2018) and metals (Lu et al., 2009). Defects also provide routes to alter the properties of BNSs for their applications in diversified areas such as hydrogen storage (Leite et al., 2017; Elmahdy et al., 2019), ion separation and water desalination (Chava et al., 2020).



Fig. 1.5 Existence of pores in BNS with different pore geometries: (a) triangular pore and (b) hexagonal pore [Reproduced with permission from (Park et al., 2015)].

For instance, Yin et al. (2010) performed DFT calculations to study the atomic and electronic structures of a BN atomic layer with triangular defects. Slotman et al. (2013) studied the structural properties of single layer (SL) BNS using MD simulations. They found that the non-monotonic behaviour of the lattice parameter, the expansion of the interatomic distance and the growth of the bending rigidity with temperature are qualitatively similar to those of graphene sheet. Le and Nguyen (2014) studied the mechanical properties of pristine and defective BN and silicon carbide (SiC) sheets using MD-simulations and finite element method. They found that uniaxial tensile stress-strain curves of defective and pristine sheets are almost identical up to fracture points. They also reported that a single defect reduces significantly fracture-stress and -strain from those of the corresponding pristine sheet, whereas Young's modulus is nearly unchanged by a single defect. Lin et al. (2014) studied the fracture behavior of monolayer BNS containing various defects using MD simulations. They found that the fracture strength and strain of BNS are higher in its armchair direction than the zigzag direction. Abadi et al. (2017) studied the effect of temperature and grain size on the mechanical properties of polycrystalline BNS using MD simulations. They reported that central crack reduces the tensile strength and failure strain of BNS and such reduction in properties is independent of the initial crack length. Li et al. (2017) studied the mechanical performance and failure behavior of BNSs

with nanocracks using MD simulations. Their results also showed that when the crack size is larger than the threshold value, Young's modulus of BNSs decreases with the increase of the crack size linearly. Hosseini et al. (2018) performed DFT calculations to study the effect of functionalization on the electromechanical response of BNS. They reported that the functionalization of hydroxyl in BNS leads to the reduction in its mechanical properties and the converse is true for electrical properties. Eshkalak et al. (2018) studied the mechanical properties of pristine and defected hybrid graphene/BN sheet using MD simulations. They found that the presence of defects in hybrid sheet reduces its mechanical properties. Liang et al. (2019) studied the mechanical properties of pristine BNS using MD simulations. They found that the mechanical properties of defected BNS are reduced as the percentage of vacancy defects increases. They also reported that the mechanical properties decrease with increasing the temperature.

Vacancy defect is a type of point defect in nanostructure and in which single or multi atoms are missing from one of the lattice sites of pure material. The SW defect is another important type of defects exists in BNSs, which correspond to 90° rotation of a B-N bond (Song et al., 2007). This is called the Stone-Wales transformation, which generates two unfavorable homo-elemental (B–B and N–N) bonds; the schematic transformation of SW defects in BNS shown in Fig. 1.6. Obviously, these defects affect the properties of BNSs. Additionally, defects play a critical role in their fracture behavior that leads to change in their mechanical properties. These defects make the local changes in their atomic-level polarizations that lead to change in their electronic behavior of BNSs.

Chapter 1



Fig. 1.6 Various types of defects in BNSs (a) pristine, (b) Mono-vacancy, (c) Di-vacancy, (d) Triangularvacancy, and (e) SW-defect.

Doping is the most effective method to tailor material properties such as electronic, thermal, optical, magnetic and chemical (Wang et al., 2011; Zhang et al., 2018; Zhou et al., 2020). In the existing experimental studies, several dopants such as Oxygen (Guo et al., 2017), Fluorine (Radhakrishnan et al., 2017), Carbon (C) (Kawaguchi et al., 1996; Zhao et al., 2014; Beniwal et al., 2017) and Chromium (Müller et al., 2008) were used to modify the properties/behavior of BNSs. For the application of BNS in smart nanodevices and nanoelectronics, "doping engineering" technique can be used to control their electronic response. Several experimental and theoretical studies showed that an elemental C atom can be doped easily into BN-based nanomaterials over a wide range of compositions, which is the most preferred route to modify their physicochemical and electronic properties. For instance, Terrones et al. (2002) performed the experimental study on C-doped BN-based nanotubes, nanosheets and nanofillers. They reported significant improvement in the structural and electronic properties of BN-based nanostructures. Du et al. (2007) studied the structural and electronic properties of C-doped hexagonal boron nitride nanoribbons (BNNRs) via first-principles calculations. They found that single C-substitution at B or N atom site in BNNRs induces spontaneous magnetization. Using first-principles calculations, Azevedo et al. (2012) studied the energetic stability and structural properties of antisites, vacancies and substitutional defects in monolayer BNSs. They found that the

incorporation of a C atom substituting for one B atom, in an N-rich growth condition, and a N atom, in a B-rich medium, induces higher formation energy while substituting C atoms as compared to antisites and vacancy defects. Beheshtian et al. (2012) studied the electronic properties of C-doped BN-nanoribbons using DFT. They found that the position of Cdopants influences the electronic properties of BN-nanoribbons. Bhattacharya et al. (2012) determined the electronic properties of BNSs by functionalizing them with several functional groups like H, F, CN, OH, CH₃, and NH₂ using first-principles calculations. Gao et al. (2016) performed DFT calculations to study the adsorption and catalytic activation of C-doped BNS. They found that even small C-doping concentration can functionalize the large surface area of BNS, making it promising catalytic material for oxygen-activation and -reduction reactions. Zhang et al. (2017) studied the thermal conductivity of 2D nanomaterials using MD simulations and reported a thorough comparison between the thermal conductivities of hexagonal boron-carbon-nitride (h-BCN), h-BN and graphene sheets. Beniwal et al. (2017) synthesized graphene, h-BN and h-BCN sheets, and performed first-principles calculations to predict direct electronic band gap of nanosheets. Most recently, Thomas and Lee (2019) studied the monolayers of h-BCN, h-BN and graphene using MD simulations, and reported their mechanical, electrical, optical, and thermal properties.

1.7 Electromechanical response of multilayer BNSs (ML-BNSs)

Using different layers of combination in boron nitride-based materials are attracted an intense attention in the last two decades due to adding and subtracting layers can alter the properties of this materials. The strong interlayer interactions are often characterized and dominated by covalent bonding, and the weaker interlayer interactions are determined by a delicate balance between London dispersion forces, electrostatic interactions (Coulomb), or a resultant between these two called as pair-wise interactions (Kim et al., 2013). The relationship between these interactions is the relative contribution of interlayer binding (bonded and non-bonded). Therefore, it is important to understand its mechanical, electrical, and electromechanical response to build new materials with their desired functionalities. Many 2D nanomaterials exist in the bulk as layered form. Among them, the most prominent ones are graphene (Mortazavi et al., 2012), boron nitride (BN) (Naumov et al., 2009), transition-metal dichalcogenides (e.g., TMDC and MoS₂) (Wu et al., 2014), and oxides (e.g., titania) (Dan Tan et al., 2019, 2020). Driven by the anticipated huge technical potential, ML-BNS have been successfully developed and investigated, which have indeed been shown to exhibit abundant appealing properties for technologically demanding applications, such as DUV photonic devices (Novoselov et al., 2005), dielectric tunneling (Hui et al., 2016), power devices (Constantinescu and Hine, 2016), electronic packaging (Bao et al., 2016), fuel cells (Oh et al., 2014), and biomedicines (Chimene et al., 2015).

Among the limited experimental investigations accessible on ML-BNS are the micromechanical cleavage (Pacil et al., 2008) and the chemical solution derived method (Han et al., 2008). For, instance, using the micromechanical cleavage technique, Pacil et al. (2008) successfully synthesized an extremely thin sheet of BNS (between one to ten atomic layers). For the varied thickness of BNS, the morphology of the obtaining sample was characterized using optical microscopy and AFM. They also reported the Young's modulus of stacked BN layered are 0.5 to 0.8 TPa. Han et al. (2008) prepared a sample of SL and ML-BNSs by a chemical solution derived method and characterized the microstructure composition using high-resolution TEM and electron-energy-loss spectrometry. They also found that the fringe contrast in the edge and the moiré patterns are feasible criteria for evaluating the number of atomic layers and stacking orientation in the sheets. Song et al. (2010) measured the mechanical properties of SL and ML-BNSs with a combination of AFM tip and theoretical models. They found that the Young's modulus and fracture strength of ML-BNSs approached to 0.334 ± 0.024 TPa and 26.3 GPa, respectively. Pioneering experiments of different 2D nanomaterials by Wu et al., (2014) confirmed that the piezoelectric effect is induced by stretching and releasing of SL MoS₂. They reported that an odd number of staked layers shows piezoelectric effect while there is no piezoelectric effect observed in even number of stacked layers. Kim et al. (2015) also synthesized large-area of ML-BNSs and measured its mechanical properties by the same nanoindentation method. However, the obtained Young's modulus was 1.16 TPa, which was significantly higher than that of Song's.

To determine the mechanical properties of ML-BNSs and sufficiently understand its fracture behaviors, a series of theoretical investigations have been carried out in consideration of various experimental situations. For instance, using the first-principles calculations, Mirnezhad et al. (2013) performed DFT to determine the mechanical properties of ML-BNS with different stacking orders such as AB bi-layer, ABA and ABC tri-layer and graphite-like BNS. They found that the elastic properties of ML-BNS are lower than those of monolayer BNS. They also reported that the mechanical properties of ML-BNS mostly depend on the number of atomic layers and the stacking order of BNS. Falin et al. (2017) prepared the atomically thin BN by mechanically exfoliated from high quality BN single crystal for the first time and systematically studied the mechanical properties of SL and ML-BNSs by indentation experiments. They reported that the SL BNS had a Young's modulus of 0.865 ± 0.073 TPa and fracture strength 70.5 ± 5.5 GPa, and found that these physical properties were not substantially fluctuated with the increase of the number of atomic layers. Using MD simulations, Yao et al. (2020) studied the mechanical properties of vertically stacked BN/BN and BN/graphene nanostructures by considering different shapes of nanopores in them. They reported that the failure strength and strain of hybrid nanostructure increase with the strain rate. They also revealed that the mechanical properties of hybrid nanostructures with nanopores in BN region are more sensitive to the temperature than nanopores in other regions.

The piezo- and flexo-electricity phenomena for ML-BNSs were intensely studied by experimentally and theoretically in the literature (Bernardini et al. 1997; Zhang et al., 2014; Ahmadpoor and Sharma, 2015). For instance, Naumov et al. (2009) studied an electromechanical response of thick sp² bonded BN sheet. They investigated the effect of even and odd layer on polarization in ML-BNS. They found that the flexoelectric effect was observed in an ultrathin BN film with an odd number of layers, such as 1, 3, 5,...... This conclusion is in line with the Partoens and Peeters (2007) finding. Within a tightbinding approach, Partoens and Peeters (2007) showed that Dirac fermions with a linear dispersion are present in graphene stacks only for an odd number of layers; in case of an even number of layers only normal fermions with parabolic energy dispersion occur. Michel et al. (2011) derived a unified theory of phonon dispersions and piezoelectricity in bulk and MLs of BNSs. The study indicates that 3D BNNs multilayers with an even number of layers (symmetry D_{6h}) are not piezoelectric and MLs with an uneven number of N_u layers (symmetry D_{3h}) are piezoelectric. They also reported that the piezoelectric coefficient e₁₁₁ is inversely proportional to N_u. Balu et al. (2012) performed DFT calculations to study the effect of external E-field on the band gap of heterostructures of graphene/BNS and bilayer BNS SLs. Their study reported that the band gap of graphene/BNS is higher than the bi-layer BNS SL. Duerloo et al. (2013) performed DFT to examine the electromechanical coupling in the ML-BNS. This study reveals that two BN monolayers exhibit a strong mechanical coupling between curvature and E-fields. Li et al. (2013) measured optical second-harmonic generation (SHG) from atomically thin samples of MoS₂ and BN with one to five layers. They also found to be centrosymmetric when the atomic layer number N is even but non-centrosymmetric when N is odd for ML 2h-TMDC systems. Zhang and Meguid (2015), examined the influence of the tube layer number on the piezoelectric properties of multi-walled (MW) BNNTs using MD simulation. Their results reveal that the piezoelectric coefficient is positive for BNNTs with odd numbers of layers but negative for those with even numbers of layers. For both, odd and even cases, the magnitude of the piezoelectric coefficient was found to decrease with increasing layer number of BNNTs. Zhang and Zhou, (2018) studied the piezoelectric characteristic of ML-BNS using MD simulations because the resonance frequencies may be easily adjusted by introducing an external electric field. This discovery implies that ML-BNSs might be used as a starting point for developing innovative piezoelectrically adjustable 2D nanoresonators with ultrahigh tensile mechanical characteristics and lightweight materials. Remarkably, these outcomes are in good agreement with the piezoelectric trend found in MoS₂ (Tan et al., 2019), and in MWBNNTs (Zhang and Meguid, 2015; Yamakov et al., 2017). Experimentally, this piezoelectric trend in BN has been confirmed in some piezoelectric planar hexagonal ML materials such as MoS₂ (Nan et al., 2021) and SnSe (Dai et al., 2019).

1.8 Scope and objectives of the present research

The literature review clearly indicates that BNSs are not defect-free due to the inherent limitations of fabrication processes and sometimes various types of defects are being introduced intentionally in them to alter their properties to suit the specific applications. The position of vacancies plays a critical role to in the electromechanical response of BNSs. Use of BNSs as reinforcements to fabricate nanocomposites for various applications with desirable mechanical and electronic properties necessitates a thorough understanding of electromechanical behavior of defective BNSs.

In the literature, numerous studies have been performed to study the (i) mechanical properties of defective and (ii) piezoelectric properties of pristine BNSs. No single study exists that reports the electromechanical response of C-doped BNSs with different pore geometries which inherently occur during their fabrication and processing. This indeed provided the motivation for this thesis. Therefore, the atomistic modelling of defected BNSs is essentially required to understand the role of different shape of pores on their electromechanical response as it serves a complement to conventional experiments with cheaper and faster simulations. This work aims to study the electromechanical response of different-size BNSs with shape of pores using MD simulations coupled with charge-dipole (C-D) potential model. The elastic and piezoelectric properties of pristine and C-doped BNSs under tension, shear and bending (out-of-plane) loadings were calculated. In the present study, both types of armchair and zigzag BNSs were considered. Moreover, the interface engineering of electromechanical response of pristine and defective BNS under the externally applied E-field for different BNS/zigzag graphene stripe using MD simulations were also studied. The conducted research is a significant contribution to the scientific community due to the recent shift in advanced BN-reinforced composites from the use of conventional and carbon-based nanocomposites. As a strikingly novel research goal, it is intended to accomplish the tasks of the following objectives:

- Study the electromechanical response of pristine and C-doped BNS with differentsize and shape of pores using MD simulations coupled with charge-dipole potential model.
- Study the interface engineering of electromechanical response of pristine and defective BNS under the externally applied E-field accounting the different BNS/zigzag graphene stripe using MD simulations.
- Enhance the piezoelectric properties of BNS/zigzag graphene stripes under the externally applied E-field through defect engineering using MD simulations.
- Study the out-of-plane polarization and flexoelectric effect in monolayer boron nitride-graphene heterostructures (BGHs).
- Study the electromechanical response of ML-BNSs under uniaxial tensile loading in the armchair and zigzag directions.

1.9 Organization of the thesis

The remaining part of the thesis is organized as follows:

- Chapter 2 deals with the atomistic modeling of SL and ML-BNSs for predicting their electromechanical response.
- Chapter 3 presents the electromechanical response of pristine and C-doped BNS under (a) tension and (b) shear loadings with a consideration of different size and shape of pores using MD simulations coupled with charge-dipole potential model.
- Chapter 4 presents the interface engineering of electromechanical response of pristine and defective BNSs under the externally applied E-field accounting the different BNS/zigzag graphene stripe using MD simulations.
- Chapter 5 presents the out-of-plane polarization and flexoelectric effect in monolayer boron nitride-graphene heterostructures (BGHs) using MD simulations.
- Chapter 6 presents the electromechanical response of ML-BNSs under uniaxial tensile loading in the armchair and zigzag direction.
- Chapter 7 summarizes the major conclusions drawn from the research work presented in the thesis and the further scope of research on BNSs. The references are alphabetically listed at the end of thesis.

2. Chapter

Atomistic modelling

This chapter outlines the general atomistic modeling framework of current research and basic theoretical methods used in the thesis. Detailed methodology and simulation parameters used for different research problems of the thesis are provided in the concerned chapters.

2.1 Atomistic modelling

A nanomechanics is the new area of mechanics which studies the properties and behavior of nanoscale material and structures in response to different types of loading conditions. A structure with at least one dimension less than 100 nm (10⁻⁷ m) is considered to be a nanostructure. A thorough understanding of physics of nanomaterials is required to design and development of their structures. This is usually achieved by using nanomechanical experiments or theoretical models. For instance, TEM, SEM, AFM, nano indenter etc. are widely used to characterize nanomaterials experimentally (Feynman et al., 1992). Conducting experiments at the nanoscale-level is very expensive, complicated and time-consuming due to the involvement of atomistic parameters. Therefore, atomistic modelling plays a vital role in nanomechanics.

Over the past three decades, there has been a rapid advancement in research activity on nanostructured materials, with the long-term promise to tailor-design material properties at the nanoscale level. In such noble efforts, computations are playing an important role in complementing experiments. Atomistic modelling-based techniques use modern computing power to include every atom of the system under consideration in its modelling as interacting particles are the foundation of materials science. Virtual computational experiments can significantly reduce the cost and accelerate the time scales of understanding and developing new materials without synthesizing them. A schematic illustration of typical atomistic modelling strategies is shown in Fig. 2.1.

Chapter 2



Fig. 2.1 A schematic description of atomistic modelling strategies with representative length and time scales for computational simulations. Some typical nanostructures such as BN nanotube, nanosheet, and nanocomposite are shown as illustrative examples for different length and time scales.

2.2 Molecular dynamics (MD) simulations

Molecular dynamics (MD) technique is one of the most efficient and attractive atomistic modelling method (Rapaport, 1996). In MD technique, atom is assumed as an interacting classical particle and the interatomic interactions between the atoms are described using molecular mechanics force fields.

2.2.1 Introduction

MD simulation is one of the most widely used techniques in the study of nanostructures. It is a nanomechanics-based computer simulation technique in which the time evaluation of a set of interatomic interactions of atoms is followed by integrating their equations of motion. The time dependent integration is done by solving the classical Newton's equations of motion, numerically. The interatomic interactions between the atoms of nanostructure are described by molecular mechanics potential fields. MD simulations allow to gain insight into nanostructure under the specific condition that is impossible to study experimentally. This serves a complement to conventional experiments with cheaper and faster simulations. MD simulations have an advantage over classical models as it provides a route to dynamical properties of the molecular system such as time-

dependent responses to perturbations, transport coefficients, thermo-mechanical properties, rheological properties and spectra, and many more characteristics of the system. Therefore, the MD simulation were performed in the current study using an open source software, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) (Plimpton, 1995), and molecular interactions in BNSs were modeled in terms of a three-body Tersoff-type potential force field (Tersoff, 1989, 1988).

2.2.2 Equations of motion

MD simulation divided into two basic steps. The first step involves the determination of interatomic interacting forces of atoms using molecular mechanics-based potential fields. The second step involves the tracing of trajectories of movements of atoms by integrating the equations of motion. The interatomic forces between the atoms are determined from the gradient of a molecular mechanic's potential field during the simulations, and force acting on an atom α is given by (Rapaport, 1996):

$$F_{\alpha} = -\frac{\partial E_{\alpha}}{\partial r_{\alpha}}$$
(2.1)

where F_{α} is the force exerted, E_{α} is the potential energy and r_{α} is the position of an atom α . The potential energy of atoms is obtained from the molecular mechanic's potential field and suitable potential field to simulate the BNSs is discussed in section 2.2.8. The force acting on each atom is known and using Newton's second law, the acceleration of each atom can be obtained by:

$$F_{\alpha} = m_{\alpha} \frac{d^2 r_{\alpha}}{dt^2} = \frac{dv}{dt} = m_{\alpha} a_{\alpha}$$
(2.2)

where m_{α} and a_{α} are the mass and acceleration of atom α , respectively.

A system of atoms is allowed to move under accelerations for a period called time step. The velocity of atom α after each time step can be obtained and using it, the position of atom α can be calculated. Therefore, to calculate the trajectory of atoms, only the initial positions of atoms, initial distribution of velocities and accelerations are required, and this are obtained by the gradient of potential energy function. The initial distribution of velocities of the atoms of the system is usually determined from a random distribution with the magnitudes conforming to the required temperature and corrected so there is no overall momentum in the atoms of the systems, i.e.,

$$P = \sum_{\alpha=1}^{N} m_{\alpha} v_{\alpha} = 0$$
 (2.3)

The velocities v_{α} are often chosen randomly from a Maxwell-Boltzmann or Gaussian distribution at a given temperature, which provides the probability that an atom α has a velocity v_x in the x direction at a temperature T.

The velocities v_{α} are often chosen randomly from a Maxwell-Boltzmann or Gaussian distribution at a given temperature, which provides the probability that an atom α has a velocity v_x in the x direction at a temperature T.

$$P(v_{\alpha x}) = \left(\frac{m}{2\pi K_{\rm B}T}\right)^{1/2} \exp\left[-\frac{1}{2}\frac{m_{\alpha}v_{\alpha x}^2}{K_{\rm B}T}\right]$$
(2.4)

$$T = \frac{1}{3N} \sum_{\alpha=1}^{N} \frac{|P_{\alpha}|}{2m_{\alpha}}$$
(2.5)

where N is the number of atoms in the system and k_B is Boltzmann's constant.

2.2.3 Integration algorithms

The potential energy of interatomic interactions of atoms is the function of their positions in the system. Numerous numerical algorithms such as leap-frog algorithm (Hockney et al., 1970), velocity Varlet algorithm (Swope et al., 1982) etc. have been developed for integrating the equations of motion. MD is usually applied to a large-scale atomistic model and the energy evaluation is time-consuming as well as memory requirement is also large. To generate the correct statistical ensembles, energy conservation is required.

Thus, the basic criteria for the right integrator for simulations are as follows:

- It should be fast, ideally requiring only one energy evaluation per time-step.
- It should require less computer memory.
- It should permit the use of a relatively long time-step.
- It must show functional conservation of energy.

In all the integration algorithms, the positions, velocities, and accelerations of atoms can be approximated by a Taylor series expansion (Rapaport, 2011).

$$r(t_0 + \delta t) = r(t_0) + v(t_0)\delta t + \frac{1}{2}a(t_0)\delta t^2 + \cdots$$
 (2.6)

$$v(t_0 + \delta t) = v(t_0) + a(t_0)\delta t + \frac{1}{2}b(t_0)\delta t^2 + \cdots$$
 (2.7)

$$a(t_0 + \delta t) = a(t_0) + b(t_0)\delta t + \cdots$$
 (2.8)

where r, v and a are the positions, velocity and acceleration of an atom, respectively, t_o is the initial time, and δt is the time step. The change in r and v with δt are graphically represented in Fig. 2.2.



Fig. 2.2 Variation in the positions and velocities of atoms with the time.

The following numerous numerical algorithms have been developed for integrating the equations of motion in the literature:

The Leap-Frog Algorithm (Rapaport, 1996): The velocities are first calculated at the time $t + \frac{1}{2}\delta t$ and using this velocities position r obtained at time $t + \delta t$. The advantage of this algorithm is that the velocities are explicitly calculated; however, the disadvantage is that they are not calculated at the same time as the positions.

$$r(t_0 + \delta t) = r(t_0) + v\left(t_0 + \frac{1}{2}\delta t\right)\delta t$$
(2.9)

$$v\left(t_0 + \frac{1}{2}\delta t\right) = v\left(t_0 - \frac{1}{2}\delta t\right) + a(t_0)\delta t$$
(2.10)

The velocities at time *t* can be approximated by:

$$v(t_0) = \frac{1}{2} \left[v \left(t_0 - \frac{1}{2} \delta t \right) + \left(t_0 + \frac{1}{2} \delta t \right) \right]$$
(2.11)

Beeman's Algorithm (Rapaport, 1996): This algorithm is closely related to the Verlet algorithm. According to that the respective position and velocity of atoms can be described by,

$$r(t_0 + \delta t) = r(t_0) + v(t_0)\delta t + \frac{2}{3}a(t_0)\delta t^2 - \frac{1}{6}a(t_0 - \delta t)\delta t^2$$
(2.12)

$$v(t_0 + \delta t) = v(t_0) + v(t_0)\delta t + \frac{1}{3}a(t_0)\delta t + \frac{5}{6}a(t_0)\delta t - \frac{1}{6}a(t_0 - \delta t)\delta t^2$$
(2.13)

The advantage of this algorithm is that it provides a more accurate expression for the velocities and better energy conservation and the disadvantage is that the more complex expressions make the calculations more expensive.

The velocity Verlet Algorithm (Swope et al., 1982): During the MD simulations the new positions and velocities of atoms in the system are obtained using a numerical integration method. According to the velocity Verlet method, position and velocity of atoms can be described by,

$$v\left(t_{o} + \frac{\delta t}{2}\right) = v(t_{o}) + a(t_{o})\frac{\delta t}{2}$$
(2.14)

$$r(t_o + \delta t) = r(t_o) + v\left(t_o + \frac{\delta t}{2}\right)\delta t$$
(2.15)

$$v(t_o + \delta t) = v\left(t_o + \frac{\delta t}{2}\right) + a(t_o)\delta t$$
(2.16)

The velocity Verlet algorithm is required less computer memory as only one set of positions, velocities and forces need to calculate at one time. Due to that fact this algorithm mostly used in MD simulation of atomic systems.

In order to simulate the real system during MD simulation, controlling temperature and pressure is necessary. The temperature control is achieved by modifying the velocities of atoms, while pressure is controlled by adjusting the size of the simulation box. A review of commonly used techniques to control temperature and pressure is given below.

2.2.4 Temperature control

The temperature is a state that defines the thermodynamic state of the system. The temperature of a system is the average of kinetic energies of all the atoms, which is calculated from the atomic velocities and can be given as (Rapaport, 1996):

$$T = \frac{1}{k_B N_f} \sum_{i,\alpha} m^{\alpha} (v_i^{\alpha})^2$$
(2.17)

where k_B is Boltzmann's constant, N_f is the total translational degree of freedom of the system, m^{α} is the mass of atom α , and v_i^{α} is the velocity of atom α in *i* direction.

During the simulation, it is not possible to keep temperature constant due to the fluctuations of velocities of atoms of the system. Hence, the average value of temperature can be maintained during the MD simulation. According to Eq. (2.17), the system temperature depends on the velocities of atoms. Therefore, by scaling the velocities of atoms, the temperature can be controlled, which is usually accomplished by a thermostat. The most commonly used thermostats are Anderson, Berendson and Nose-Hoover.

Anderson thermostat (Andersen et al., 1980): This is the most straightforward thermostat and, in this method, the velocity of a random particle is replaced by a value chosen from the Maxwell-Boltzmann distribution for a given temperature. Anderson thermostat is computationally expensive.

Berendsen thermostat (Berendsen et al., 1984): This is the most commonly used thermostat due to its simplicity and easy implementation. To maintain the constant temperature during the simulation, the system is coupled to an external heat bath source with fixed temperature T_0 . The velocities of atoms are scaled at each time state such that the change in the rate of temperature is proportional to the difference in temperature:

$$\frac{\mathrm{dT}(\mathrm{t})}{\mathrm{dt}} = \frac{1}{\tau} \big(\mathrm{T} - \mathrm{T}(\mathrm{t}) \big) \tag{2.18}$$

This method provides an exponential decay of the system towards the target temperature using a factor λ :

$$\lambda = \left[1 - \frac{\delta t}{\tau} \left(\frac{T - T_0}{T}\right)\right]^{\frac{1}{2}}$$
(2.19)

where τ is the characteristic relaxation time, δt is the time-step size, T the instantaneous temperature, and T_0 is the target temperature. This method maintains a constant temperature with good approximation and the temperature can be controlled by changing τ and adjusting T_0 .

Nosé-Hoover thermostat (Shuichi Nosé et al., 1984): This is a method for performing constant-temperature dynamics that produces true canonical ensembles in both momentum and coordinate spaces. This method was used in this study because it is one of

the best-considered thermostats among all the thermostats (Hünenberger et al., 2005). This thermostat uses a friction factor (μ) to alter the equations of motion, as follows:

$$\frac{d\mu(t)}{dt} = \frac{k_{\rm B}N_{\rm f}}{Q}(T(t) - T_0)$$
(2.20)

where Q is the effective mass of thermostat:

$$Q = k_B N_f T(t) \tau_T^2$$
(2.21)

where τ_T is the specified time constant for the fluctuations of temperature. To achieve the smooth temperature transition, the value of the time constant is usually considered in the order of hundred-time steps. The modified equation of motion is defined by,

$$a = \frac{f(t)}{m} - \mu(t)v(t)$$
 (2.22)

2.2.5 Pressure control

The pressure is a basic thermodynamic variable that provides the state of system of atoms and is defined as:

$$P_{ij}^{V} = \frac{1}{V} \sum_{\alpha} \left[\sum_{\beta=1}^{N} (r_i^{\beta} - r_i^{\alpha}) f_j^{\alpha\beta} + m^{\alpha} v_i^{\alpha} v_j^{\alpha} \right]$$
(2.23)

where V is the volume of system, β is assigned a number to neighboring atoms that passes from one to the number of neighbouring atoms (N), and r_i^{α} and r_i^{β} are the positions of atoms α and β along the direction *i*, respectively. Term $f_j^{\alpha\beta}$ is the force along the *j* direction on atom α due to atom β , and ν^{α} and m^{α} are the velocity and mass of atom α , respectively.

During the simulation, the pressure of system of atoms can be adjusted by changing the dimension of the simulation box. This can be achieved using the barostat during the simulations, and the most commonly used barostats are Berendson (Berendsen et al., 1984) and Nose-Hoover barostat (Martyna et al., 1994).

Berendsen barostat maintains the pressure of a system at a target value. Berendsen method couples the system to a pressure bath. At each time step, size of the simulation box and the coordinates of atoms are rescaled. At each step, x, y and z coordinates of each atom are scaled by the factor, μ :

$$\mu = \left[1 - \frac{\delta t}{\tau} \gamma [P - P_0]\right]^{\frac{1}{3}}$$
(2.24)

where *P* is the instantaneous pressure, P_0 is the target pressure and δt is the time step. The cartesian components of the unit cell vectors are scaled by the same factor. Berendsen's method is less reliable compared to the Nose-Hoover method (Hünenberger, 2005).

Nose-Hoover barostat (η) is defined as: (Hoover, 1985; Shüichi Nosé, 1984)

$$\frac{d\eta}{dt} = \frac{1}{k_B N_f T_0 \tau_P^2} V(t) (P(t) - P_0)$$
(2.25)

where τ_P is the specified time constant for pressure fluctuations and its value usually on the order of thousands of time steps to achieve a smooth pressure fluctuation. The controlled volume of the system is determined by using the following relation:

$$\frac{\mathrm{d}V(t)}{\mathrm{d}t} = [3\eta(t)]V(t) \tag{2.26}$$

2.2.6 Statistical ensembles

The whole universe is governed by the thermodynamics laws through the transfer of energy between matter. This is attributed to the change in the total energy of the system. This process is very complex to consider directly, therefore, several parts of the universe, i.e., the system is considered separately, and it can be described using an ensemble. An ensemble is a collection of all possible states of the real systems that have identical thermodynamic or macroscopic states but have different microscopic states. The commonly used ensembles are (i) constant N, V and E (NVE) or microcanonical ensemble, (ii) constant N, V and T (NVT) or canonical ensemble, and (iii) constant N, P and T (NPT) or isothermal-isobaric ensemble. The N, V, E, T and P denote the number of atoms, volume, energy, temperature, and pressure of the system of atoms, respectively. The graphical representations of ensembles are shown in Fig. 2.3.

Microcanonical ensemble (NVE) is derived from Newton's law of motion without any pressure and temperature control (Rapaport, 1996). The energy of the system is conserved during the simulations. The NVE ensemble is a statistical ensemble that allows to keep constant specified total energy of all the possible states of mechanical systems. The system's energy, volume, composition, and shape are kept the constant in all possible states of the system. *Canonical ensemble (NVT)* can be obtained by maintaining the constant thermodynamic temperature and total volume and number of particles in the system. (Rapaport, 1996). The NVT ensemble is a statistical mechanics ensemble that denote the possible states of the mechanical system in thermal equilibrium of heat bath at finite temperature. The system allows only to exchange the energy from the heat bath and the energy is no longer constant.

Isothermal-Isobaric ensemble (NPT) allows the control of both the pressure and temperature of the system (Rapaport, 1996). The NPT ensemble is a statistical mechanical ensemble that maintains a constant total number of particles, pressure, and temperature. NPT can also be used during equilibration to obtain the desired pressure and temperature before changing to the constant-energy and constant-volume ensembles.



Fig. 2.3 Graphical representation of the microcanonical (NVE) ensemble, the canonical (NVT) ensemble and the isothermal-isobaric (NPT) ensemble (Gale et al., 2012).

2.2.7 Potential fields

The potential field is a mathematical description of the potential energy of a system of interacting atoms. The empirical relation of parameters of potential energy in potential fields are derived from both high-level quantum mechanical calculations and experimental studies. To simulate the different molecular systems required a unique potential field. The general form of a potential field as a function of energy and can be defined as

$$E_{total} = E_{covalent} + E_{non covalent}$$
(2.27)

where E_{total} , $E_{covalent}$, and $E_{non\ covalent}$ are the total energy, covalent energy, and noncovalent energy, respectively, and interatomic relative motions in molecular mechanics depict in Figs. 2.4 and 2.5. The components of covalent and noncovalent energies can be expressed as

- $E_{\text{covalent}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{out-of-plane}}$ (2.28)
- $E_{non \, covalent} = E_{electrostatic} + E_{vander \, Waals}$ (2.29)



Fig. 2.4 Interatomic relative motions in molecular dynamics.



Fig 2.5 Interlayer van der Waal's interactions.

In case of non-bonded van der Waals interaction between individual B and N atoms (see Fig. 2.5), there is a variety of used potentials in the literature. Commonly, the nonbonded interactions are expressed as Lennard-Jones (L-J) or Morse potentials (Rahman et al., 1994). In the current study, the L-J term and a coulombic-term was used which is expressed by (Akiner et al., 2016):

$$U(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{D_{ij}}{r_{ij}} \right)^{12} - \left(\frac{D_{ij}}{r_{ij}} \right)^6 \right] + K_C q_i q_j r_{ij}^{-1}$$
(2.30)

where U(r) is potential energy (PE) between a pair sheet at the structure of B-N bi-layers,

 r_{ij} is the finite distance at which the inter-particle potential is zero between atoms i and j in adjacent layers, while ε is a parameter determining the depth of the potential well, D_{ij} is the diameter of the atom (a length-scale parameter of the atom determining the position of the potential minimum). K_c is Coulombic constant and q_i is the partial charge of the ith atom. Meanwhile, the partial charge q for the L-J potential is taken as 1.1378 eV and the cutoff distance of L-J interaction is set to 10 Å. The parameters of L-J potential are summarized in Table 2.1. The exact functional form of a potential field depends on the type and condition of the simulation. The all-atom potential fields provide the parameters for each and every type of atom in a system, while the united-atom potential fields stipulate parameters only for specific types of atoms (Sun et al., 1998).

In the literature, Morse potential, reactive empirical bond order (REBO) potential, adaptive intermolecular reactive empirical bond order (AIREBO) potential fields are being used to simulate graphene and CNTs, and three-body Tersoff-Brenner potential force field is being used to simulate BN nanotubes and nanosheets (Tersoff et al., 1988). Morse potential field is two body potential field, which does not represent the systems with many-body interactions, such as graphene. The MD simulations in this study have been conducted using Tersoff potentials field, which are many-body potentials.

2.2.8 Tersoff potential force field

Tersoff potential force field is used for semiconductors and insulators. It is parameterized from the empirical data and particularly suited for BN based nanostructures. In the MD simulation, the interactions between B, C and N atoms of a sheet were described using the Tersoff potential force field (Tersoff, 1989, 1988). The Tersoff potential was obtained by empirically fitting the parameters obtained from either experiments or first-principles calculations. Note that the Tersoff potential has been successfully employed in numerous studies to evaluate the electromechanical response of BNSs and tube (Mortazavi and Rémond, 2012; Zhao and Xue, 2013; Zhang et al., 2017; Vijayaraghavan and Zhang, 2018; Zhang and Zhou, 2018). According to the Tersoff potential, an analytical form of the total energy *E* between two neighbouring atoms *i* and *j* were defined as:

$$E = \sum_{i} E_{i} = \frac{1}{2} \sum_{i \neq j} V_{ij}$$
 (2.31)

$$V_{ij} = f_{C}(r_{ij})[f_{R}(r_{ij}) + b_{ij}f_{A}(r_{ij})]$$
(2.32)

$$V_{ij}^{R} = f_{C}(r_{ij})f_{R}(r_{ij})$$
(2.33)

$$V_{ij}^{A} = f_{C}(r_{ij})b_{ij}f_{A}(r_{ij})$$

$$(2.34)$$

where, *E* is the total energy of the system, E_i is the site energy and V_{ij} is the bond energy. The indices *i* and *j* run over the atoms of the system. Term r_{ij} is the distance between atom *i* and atom *j*, while b_{ij} is the bond angle term which depends on the local coordination of atoms around atom *i*. Terms f_R and f_A are the repulsive and attractive pair potentials, respectively. Term $f_C(r_{ij})$ is the cut-off function provided to limit the range of the potential and thus saves the computational time. The cutoff function $f_C(r_{ij})$ is expressed as:

$$f_{C}(r_{ij}) = \begin{cases} \frac{1}{2} + \frac{1}{2} \cos\left(\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right), & R_{ij} < R_{ij} < S_{ij} \\ 0 & r_{ij} > R_{ij} \end{cases}$$
(2.35)

where R and D are model specific parameters.

The two-body repulsion $f_R(r_{ij})$ and attraction $f_A(r_{ij})$ terms are as follows:

$$f_{R}(r_{ij}) = -A_{ij} \exp(-\lambda_{ij}^{I} r_{ij})$$
(2.36)

$$f_{A}(r_{ij}) = -B_{ij} \exp(-\lambda_{ij}^{II} r_{ij})$$
(2.37)

In Eq. (2.32), b_{ij} is the strength of the attractive term and can be expressed as:

$$b_{ij} = \left(1 + \beta^{n} \zeta_{ij}^{n}\right)^{-\frac{1}{2n}}$$
(2.38)

where

re
$$\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ijk}) g(\theta_{ijk}) \exp\left[\lambda_3^m(r_{ij} - r_{ik})^\circ\right]$$
 (2.39)

$$g(\theta) = \gamma_{ijk} \left(1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2} \right)$$
(2.40)

in which *n*, *c*, *d*, and *h* are the constants, and they can be determined from the data describing the interactions between B, C and N atoms. These constants are taken from the Ref. (Albe et al., 1997; Matsunaga et al., 2000; KInacI et al., 2012), as listed in Table 2.1. The *n*, β , λ_{ij}^{I} , *B*, λ_{ij}^{II} , and *A* parameters are only used for two-body interactions. The m, γ , λ_{3}^{m} , *c*, *d*, and $cos\theta_{0}$ parameters are only used for three-body interactions. The *R* and *D* adjustable parameters are used for both two-body and three-body interactions. The value of m = 3, $\beta = 0$, and $\gamma = 1$ are taken as constant. Term $g(\theta)$ is dependent on the angular deformation and θ is the angle between two vectors r_{ij} and r_{ik} . The different parameters λ_{ij}^{I} , λ_{ij}^{II} , A_{ij} , B_{ij} , R_{ij} , and S_{ij} for species *i* and *j* can be calculated using the mixing rules:

$$\lambda_{ij}^{I} = \frac{1}{2} \left(\lambda_{i}^{I} + \lambda_{j}^{I} \right)$$
(2.41)

$$\lambda_{ij}^{II} = \frac{1}{2} \left(\lambda_i^{II} + \lambda_j^{II} \right)$$
(2.42)

$$A_{ij} = \left(A_i \times A_j\right)^{1/2} \tag{2.43}$$

$$B_{ij} = (B_i \times B_j)^{1/2}$$
 (2.44)

$$R_{ij} = \left(R_i \times R_j\right)^{1/2}$$
(2.45)

$$S_{ij} = (S_i \times S_j)^{1/2}$$
 (2.46)

Table 2.1: Parameters used in Tersoff potentials for B-B, N-N, B-N, C-C, C-N and C-B interactions.(Albe et al., 1997; Matsunaga et al., 2000; KInacI et al., 2012).

Parameter	В-В	N–N	B–N	С–С	C–N	С-В
m	3	3	3	3	3	3
γ	1	1	1	1	1	1
λ_3^m (Å ⁻¹)	0	0	1.992	0	0	0
С	0.562	17.795	1092.928	38049.450	38049.450	38049.450
d	0.001	5.948	12.38	4.348	4.348	4.348
h	0.5	0	-0.541	-0.930	-0.930	-0.930
n	3.992	0.618	0.364	0.727	0.727	0.727
β	0.000	0.019	0.000	0.000	0.000	0.000
λ_{ij}^{II}	2.077	2.627	2.784	2.211	2.205	2.205
<i>B</i> (eV)	1173.196	2563.560	3624	430	339.068	387.575
<i>R</i> (Å)	2	2	2.3	1.95	1.952	1.952
D (Å)	0.1	0.1	0.5	0.15	0.1	0.1
λ^{I}_{ij}	2.237	2.829	2.99	3.487	3.527	3.527
A (eV)	1404.052	2978.952	4483.250	1393.645	1386.781	1386.781
ε (kcal/mol)	0.000	0.007	0.249	-	-	-
D (Å)	0.000	3.750	3.146	-	-	-

2.2.9 Molecular dynamics parameters

Time-step: The length of time between two consecutive iterations in a MD simulation is called the time step. A time step should be less than 10% of the vibration period of an atom and, time-step of 0.5 fs to 0.8 fs provides excellent results for carbonbased structure (Arachchige et al., 2012; Kundalwal and Choyal, 2018). However, researchers used time steps from 0.1 fs to 1 fs to simulate uniaxial tensile tests of BNSs (Kumar et al., 2016; Mortazavi and Cuniberti, 2014). They used three-body Tersoff potential force field for simulating the BN-based nanostructure using LAMMPS. The selection of time-step depends on the computational efficiency and required accuracy of the simulations. The larger value of time steps increases the computational efficiency, while it reduces the accuracy of the simulations. The smaller time steps may improve the accuracy of the simulations. Therefore, the time step controls the trade-off between computational efficiency and accuracy in the MD simulations. If the value of time-step is too large, then the system might become unstable. Therefore, first, we investigated the effect of time step on the simulation of the mechanical deformation test of BNS. In order to investigate this, a set of MD simulations was performed on a 50 Å \times 50 Å BNS with time steps of 0.1 fs, 0.5 fs, and 1 fs. All other MD parameters were kept constant, and the values mentioned in the following sections. The results indicate that the stress-strain curves of BNS obtained with different time steps are identical as shown in Fig. 2.6. It can be concluded from Fig. 2.6 that a time-step between 0.1 fs and 1 fs could be used to simulate the mechanical deformation tests of BNSs. A time step of 0.5 fs, which is the most commonly used in literature, will be used in all the MD simulations hereafter.


Fig. 2.6 Stress-strain curve of a BNSs obtained from MD simulations with different time steps.

Strain rate: During the MD simulations, a deformation test is performed by applying strain to the nanostructure at a constant strain rate. The failure point of the BNS structure depends on the value of strain rate (Dumitrica and Yakobson, 2004; Zhao and Aluru, 2010). The lower the value of strain rates, the system gets more than sufficient time to relax and reaches the equilibrium state, and we can obtain accurate results. The actual practical strain rate value 10^{-2} s⁻¹ in experiments cannot be used during the computational simulations due to high computational time. Therefore, in order to keep computational efficient simulations, usually, the value of strain rate 10⁹ is used in MD simulations for BN based structures (Mortazavi and Rémond, 2012; Mortazavi and Cuniberti, 2014; Kumar et al., 2016; Zhang et al., 2019). Therefore, we investigated the effect of strain rate on the simulation of the mechanical deformation test of BNS. In order to investigate this, a set of MD simulations was performed on 50 Å \times 50 Å BNS with strain rate of 0.0001 ps⁻¹, 0.0005 ps⁻¹, and 0.001 ps⁻¹. All other MD parameters were kept constant. The results indicate that the stress-strain curves of BNS obtained with different strain rate are almost the same before the final facture occurs, indicating that strain rate has minor effect on Young's modulus. It can be concluded from Fig. 2.7 that the strain rate has marked effect on the fracture strength and fracture strain. The use of strain rate value of 0.0005 ps^{-1} is the optimal choice to investigate the electromechanical response of BNS and such value was also used in the existing work to study the mechanical behavior of BNS (Kumar et al., 2016).



Fig. 2.7 Stress-strain curve of a BNSs obtained from MD simulations with different strain rate.

Periodic boundary conditions: The term periodic boundary condition (PBC) (Allen, 2004) refers to the simulation of structures consisting of a periodic lattice of identical subunits. The effects of edges in the systems such as BNSs should be eliminated in MD simulations in order to obtain their bulk properties. Therefore, an extremely large system of BNS can be simulated via MD simulation by ensuring that the edges and surfaces have only a small effect on its bulk properties, but this approach is computationally expensive. To reduce the computational efforts, the use of PBCs in the MD simulation is the most efficient method to simulate an infinitely large system. In PBCs, the cubical simulation box was replicated throughout space to form an infinite lattice as shown for a 2D case in Fig. 2.8. During the MD simulation, when an atom moves in the central box, then its periodic images in every other box also move exactly in the same way. Thus, when an atom leaves the box during the simulation, then it is replaced by an image particle that enters from the opposite side so the number of particles/atoms in the central box remains same and the system under consideration does not possess any edges. Therefore, the PBC was used to eliminate the effects of free edges of BNSs (Dewapriya et al., 2014; Yamakov et al., 2017).



Fig. 2.8 Graphical representation of the PBCs of the middlebox. The arrows indicate the directions of the velocities of atoms. The atoms in the middlebox can interact with atoms in the neighbouring boxes without having any boundary effects.

2.2.10 MD simulator

All the MD simulation were performed in LAMMPS. The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is a classical MD simulation software that is widely used in a variety of applications at the atomistic level (Plimpton, 1995) and it allows parallel particle simulations at the atomic, meso and continuum scales. It allows to simulate atomic, chemical, or biological models at a microscopic scale. LAMMPS was developed at the Sandia National Laboratories and is written in C++ code. It is free and open-source software that continues updated by Sandia National Laboratories (Plimpton et al., 1995) and other researchers worldwide.

The MD simulator LAMMPS requires a different script to perform the MDSs, such as input script, atom coordinates of the system and potential field. The formulation of LAMMPS input script is shown in Fig. 2.9, and this script can be divided into four sections: preprocess/initiation, input script, running, and output/postprocess.

- (i) Preprocess/initiation: build the atomic systems using the following software (NanoEngineer-1, VMD and OVITO) and also choose appropriate force field (Tersoff, AIERBO, EAM and ReaxFF etc.) that provides the interatomic interaction of the atomic systems.
- (ii) **Inputs script:** defines the atom coordinates of the system and potential field. The boundary conditions and units of the MD parameters are set in

the initialization part of the input script. Different units and boundary conditions are available in LAMMPS package. The use of metal units is mandatory for the Tersoff-potential force-field. In the metal units, the units of time, distance and energy are picoseconds (ps), Angstroms (Å) and electron-volts (eV), respectively. The choice of boundary condition depends on the type of simulation and can be chosen as periodic and non-periodic. The atoms coordinates (x, y and z) and types are defined under the atom definition section. In all performed MD simulations, the atom coordinates given in a different file. During the simulation, this file is called when the input file is executed.

- (iii) Running: the simulation parameters, potential field coefficients and output options are given in the third section of the input script. The basic simulation parameters, such as temperature, pressure, time etc., are defined here. The temperature and pressure controlling methods are implemented in LAMMPS, such as Berendsen and Nose-Hoover methods. The thermodynamics ensemble is also implemented in the third section of the LAMMPS such as NVE, NVT and NPT ensembles. During simulation, LAMMPS allows to compute time and spatial averages of physical quantities, such as pressure, temperature, energies, stresses, etc. and separate text files can be obtained at specified time intervals. During the simulation, LAMMPS allows to deform the simulation box. During the simulation, nanostructure is also deformed along with the simulation box.
- (iv) Postprocess/output: the output of the MD simulations from the LAMMPS can be obtained as *log.Lammps* file after the pre-specified number of time steps. The output of LAMMPS contains all the position information pertaining to atoms at every time-step. However, LAMMPS does not have the functional visualization capability to display the various trajectories directly. Therefore, additional visualization software is required for analyzing the results obtained more easily. In this regard, the VMD (Dalke et al., 1996) and OVITO (Stukowski et al., 2010) software can be used



which are capable of reading the LAMMPS output data and rendering informative figures.

Fig. 2.9 The overview of LAMMPS input script

The theory behind the MD simulations in this chapter will be used for investigating the electromechanical response of BN-based nanostructures in subsequent chapters. The electromechanical behavior of pristine BNS, C-doped BNS, hybrid BNS/CBN, BGHs, multilayer BNS and bulk BNSs (atomic layer number up to 12) is studied in the next chapters. Atomistic modelling

Chapter 3

Electromechanical response of BNSs

In this chapter, the investigation of the electromechanical response of pristine and carbondoped BNS is carried out using MD simulations with a charge-dipole potential model. Effect of various factors such as chirality, size of BNS, and strain rate of BNS were critically examined. Using examples drawn from the atomistic bond mechanics, this chapter demonstrates the electromechanical response, and the choice of right size, chirality, and type of BNS for specific applications in the diversified area.

3.1 Introduction

The BNS has captivated massive response from researchers due to its exceptional mechanical, electrical, and thermal properties. Many experimental, numerical and analytical investigations were carried out to explore the effect of crucial geometrical parameters such as chirality, aspect ratio (w/l) and size of BNSs on their electromechanical response (Kudin et al., 2001; Boldrin et al., 2011; Zhao and Xue, 2013; Eshkalak et al., 2018;). These studies confirmed BNS possesses exceptional Young's modulus, shear modulus, Poisson's ratio, and piezoelectricity.

The BN-based nanostructures contain various types of defects due to the inherent issues of their fabrication techniques. Such defects are often considered while developing BN-based nanostructures as they influence the properties of BNSs. On the other hand, to control the performance of 1D and 2D nanostructures, the '*defect engineering*' technique is widely employed to alter their properties (Kundalwal et al. 2017 and references therein). The defects provide routes to alter properties for BNSs for their applications in diversified areas such as hydrogen storage (Chen et al., 2018), gas sensors, optoelectronic (Falin et al. 2017), optical devices, transistors, biological probes (Song et al., 2013), and nano-electromechanical system (NEMS) (Kim et al. 2018; Wang et al., 2017). For instance, Jin et al. (2009) effectively synthesized monolayer BNS using an energetic EBR method and revealed that the existence of B and N monoatomic and triangular pore in it. They also found that the B atom vacancies are energetically more stable than N atom vacancies.

Suenaga et al. (2012) analyzed monolayer BNSs with and without point defects using electron energy-loss spectroscopy. They revealed that monovacancy at the N site is more prominent for electronic properties compared to B site vacancies. Park et al. (2015) used the EBR method to control the shape, size, and stability of 2D nanomaterials such as BNS, graphene and MoS₂. Due to the application of defected BNSs in diversified fields, many efforts are being made to introduce controlled topological defects via irradiation with energetic particles and chemical processes (Pacil et al., 2008; Park et al., 2015). The review of the literature presented in chapter 1 reveals that the inherent defects in BNSs play a critical role in their electromechanical behavior.

Use of BNSs as reinforcements to fabricate nanocomposites for electronic applications with desirable mechanical and electronic properties necessitates a thorough understanding of behavior of defective BNSs under different loading conditions. In the literature, numerous studies have been performed to study the (i) mechanical properties of defective and (ii) piezoelectric properties of pristine BNSs. No single study exists that reports the electromechanical response of C-doped BNSs with different pore geometries which inherently occur during their fabrication and processing. In this chapter, the elastic and piezoelectric properties of pristine and C-doped BNSs under tension and shear loadings were calculated. In the present study, both types of the armchair and zigzag BNSs were considered. A particular emphasis was placed on the study of the effect of different pore geometries and C-doping on the electromechanical response of BNS.

3.2 MD modelling of BNSs

MD simulation is the most widely used modeling technique for the simulation and characterization of nanomaterials. All MD simulations were performed in a large-scale atomic/molecular massively parallel simulator (LAMMPS) (Plimton, 1995). The schematic representations of the armchair and zigzag edges of BNS are shown in Fig. 3.1. The interatomic interactions among B and N atoms were calculated using the Tersoff potential force field (Tersoff 1988, 1989) as it is used by several researchers to study the electromechanical response of BNSs (Ansari and Ajori, 2015; Zhang and Meguid, 2015; Thomas et al., 2016; Choyal et al., 2019; Liang et al., 2019). The piezoelectric and elastic properties of BNS under tension and shear loadings were determined using MD simulations coupled with the C-D model and Tersoff potential force field. This was achieved by using

both MATLAB and LAMMPS codes. We developed MATLAB code to solve the tensorial equations and then the obtained parameters were called in the MD simulations using LAMMPS code. Systematic steps involved in such hybrid simulation methodology are shown in Fig. 3.2.

First, the initial structures of BNS were created. Then, the simulations were performed to minimize the energy of BN structures using the conjugate gradient minimization method to obtain their optimized structures. The minimized structure of BNS was treated as optimized when the difference in the total potential energy (PE) of its structure between the consequent steps was less than 1.0×10^{-10} kcal/mol (Choyal and Kundalwal, 2020; Dewapriya and Rajapakse, 2014). The MD simulations were performed in the constant temperature and volume canonical (NVT) ensemble with a time step of 0.5 fs for 30 ps to equilibrate the BNS structure (Xie et al., 2019). The velocity Verlet algorithm was used to integrate the equations of motion in all MD simulations. The simulations were performed with a periodic boundary condition in all directions of the sheet and the simulation box was kept large enough to avoid the interlayer interactions. After the energy minimization, tensile and shear loadings were applied to the sheets. Schematics of these loading conditions are shown in Fig. 3.3. In the case of tensile loading, a constant strain was applied at the left and right edges in the x-direction of the nanosheet. In the case of shear loading, the bottom edge was fixed, and the constant shear strain was applied to the top edge of the nanosheet in the xy-plane. During the loading, a constant initial strain was applied on the respective strained edges for a period of 1 ps, followed by the relaxation time of 30 ps, this constitutes a single load step (Kundalwal and Choyal, 2018). A series of load steps were applied on BNS to achieve a strain value of 0.0275, which is within its elastic limit. During the loading, the progressing atomic configuration and equivalent charges and dipole moments were stored throughout the simulations.



Fig. 3.1 Monolayer BNS with armchair and zigzag edges.

3.2.1 A charge-dipole (C-D) potential model

Figure 3.3(a) shows the primitive lattice vectors a_1 and a_2 of undeformed BNS. The unit cell of BNS was defined by a rhombus, as shown in Fig. 3.3. In the unit cell, a single B–N covalent bond was considered. All atoms in BNS were assigned charge c and dipole moment d (Mayer and Åstrand, 2008). The total atomic interaction energy of a system is the sum of short- and long-range interactions. Short-range interatomic interactions comprise the PE due to the chemical bonds which was calculated using the Tersoff potential force field (Tersoff et al., 1988). The parameters for the bonded interactions between B, C and N atoms were taken from Ref. (Zhao and Xue, 2013). The long-range interactions comprise the PE due to the non-bonded electro-chemical (E - c)interactions of charges and dipoles. The non-bonded interactions include the charge-dipole, charge-charge, and dipole-dipole interactions. The total energy (E^{tot}) can be expressed as

$$E^{tot} = E^{Tersoff} + E^{E-c}$$
(3.1)

$$\mathbf{E}^{\text{tot}} = \mathbf{E}^{\text{Tersoff}} + \mathbf{E}^{\text{c-c}} + \mathbf{E}^{\text{c-d}} + \mathbf{E}^{\text{d-d}} + \mathbf{E}^{\text{ext}}$$
(3.2)

The Tersoff PE ($E^{Tersoff}$) between two neighboring atoms *i* and *j* can be expressed in the following form (Tersoff, 1988, 1989):

$$E^{\text{Tersoff}} = \frac{1}{2} \sum_{i} \sum_{j \neq 1} f_c(r_{ij}) [f_A(r_{ij}) + b_{ij} f_R(r_{ij})]$$
(3.3)



Fig. 3.2 Flow diagram of simulation methodology.

where $f_A(r)$ and $f_R(r)$ are the attractive and repulsive pair potentials, respectively. The cutoff function $f_R(r)$ was defined to limit the range of potential and thus, to save the computational time in the MD simulation.

The electro-chemical PE (E^{E-c}) with a given combination of charges (c) and dipoles (d) placed at the atomic positions (r) can be written as:

$$E^{E-c} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} c_i T_{ij}^{c-c} c_j - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} d_i T_{ij}^{d-d} d_j \sum_{j=1}^{N} \sum_{j=1}^{N} c_i T_{ij}^{c-d} d_j + \sum_{j=1}^{N} c_i (\chi_i + V_i) - \sum_{j=1}^{N} d_i E$$

$$(3.4)$$

where, the first three terms are the interatomic interaction energies between the charge– charge, dipole-dipole and charge–dipole (Mayer, 2007), respectively. The fourth term accounts for the energy required to bring the charge (c_i) in presence of external potential (V_i). It also accounts for the interaction of charge with electron of atom at position r_i using electron affinity (χ_i). The factor 1/2 prevents the double accounting of some of these interatomic interactions. The respective electron affinities of B, C and N were considered as 0.279 eV (Scheer et al., 1998), 1.262 eV (Bresteau et al., 2016) and -0.07 eV (Bresteau et al., 2016). The last term accounts for the interactions of dipoles and external electric field (E). In the calculation of interaction energy, the atoms of system were considered as a point charge (Kundalwal et al., 2017). The term T^{c-c} is for the Coulombic interactions between atomic charges c_i and c_j separated by a distance $r_{i,j}$ which is given as (Mayer et al., 2007; Javvaji et al., 2018):

$$T_{ij}^{c-c} = \frac{1}{4\pi\epsilon_0} \frac{1}{r_{i,j}}$$
(3.5)

where ε_0 is the dielectric permittivity of vacuum and $r_{i,j}$ is the distance between atoms *i* and *j*.

The two other tensors for charge-dipole and dipole-dipole are:

$$T_{i,j}^{c-d} = \left(\frac{1}{4\pi\varepsilon_0}\right) \left(\frac{r_{i,j}}{r_{i,j}^3}\right)$$
(3.6)

$$T_{i,j}^{d-d} = \left(\frac{1}{4\pi\epsilon_0}\right) \left(\left(3r_{i,j} \otimes r_{i,j} - r_{i,j}^2 I\right) / r_{i,j}^5 \right)$$
(3.7)

where *I* is the 3×3 identity matrix.

In Eq. (3.5), T_{ij}^{c-c} term contains $\frac{1}{r_{ij}}$ which diverges when $r_{ij} \to 0$ with charge-charge interactions. In order to overcome this, r_{ij} is normalized with $erf\left(\frac{r_{ij}}{\sqrt{2R}}\right)$ and then Eq. (3.4) can be re-written as:

$$T_{ij}^{c-c} = \frac{1}{4\pi\varepsilon_0} \frac{\operatorname{erf}\left(\frac{\Gamma_{ij}}{\sqrt{2R}}\right)}{r_{ij}}$$
(3.8)

Thus, the self-interaction energy of atoms reduces to

$$T_{ij}^{c-c} = \left(\frac{1}{4\pi\varepsilon_0}\right) \sqrt{\frac{2}{\pi}} \frac{1}{R}$$
(3.9)

The width of Gaussian distribution is determined as $R = \frac{\sqrt{R_{A,i}^2 + R_{B,j}^2}}{2}$; where $R_{A,i}$ is the width of Gaussian distribution for atom index *i* with type A. $R_{B,j}$ is the Gaussian distributed charge width for atom type B with index *j* (Jensen et al., 2002). The values of *R* for B, C and N were taken as 0.35Å, 0.686Å and 0.76Å, respectively (Javvaji et al., 2018). The Eqs. (3.6) and (3.7) for charge-dipole and dipole-dipole, respectively, also diverge when $r_{ij} \rightarrow$ 0 and to avoid divergence, normalized relations were used from Refs. (Mayer et al., 2007).

Using the above defined interatomic potentials, the trajectory of each atom after each load step was calculated using the following relation:

$$m_{i}\ddot{r}_{i} = -\frac{\partial E^{\text{Tersoff}}}{\partial r_{i}} - \frac{\partial E^{c-c}}{\partial r_{i}} - \frac{\partial E^{d-d}}{\partial r_{i}} - \frac{\partial E^{c-d}}{\partial r_{i}}$$
(3.10)

where, the forces due to the Tersoff potential were incorporated in LAMMPS code and the forces due to the C-D interactions were added separately. The governing equations were obtained to determine the charge and dipole moment of each atom. The governing equations for atomic charge c_i obtained by solving Eqs. (3.11) and (3.12), as follows:

$$\sum_{j=1,i\neq j}^{N} T_{ij}^{c-c} c_j - \sum_{j=1,i\neq j}^{N} T_{ij}^{c-d} d_j + T_{ij}^{c-c} c_i - T_{ij}^{c-d} d_i + \chi_i = 0$$
(3.11)

$$\sum_{j=1,i\neq j}^{N} T_{ij}^{c-d} c_j + \sum_{j=1,i\neq j}^{N} T_{ij}^{d-d} d_j + T_{ij}^{c-d} c_i - T_{ij}^{d-d} d_i = 0$$
(3.12)

These equations were used to determine the unknown values of charge and dipole moment by arranging them into matrix-vector form, as follows:

$$\begin{bmatrix} T^{c-c}T^{c-d} \\ T^{c-d}T^{d-d} \end{bmatrix} \begin{bmatrix} c \\ d \end{bmatrix} = \begin{bmatrix} -\chi \\ 0 \end{bmatrix}$$
(3.13)

The above relation provides the charge and dipole moment for the current atomic configuration. The forces due to charges and dipoles were calculated using the charge and dipole data obtained during simulations. The velocity-Verlet algorithm was used in the MD simulation to integrate forces (see Eq. (3.10)) and update atomic positions after each load step. Then, using the updated atomic configuration, charges and dipoles were calculated using Eq. (3.13). If the initial atomic position at time t is considered then the charge dipole moment data of time step $(t - \Delta t)$ is used, where Δt is the time interval between two successive load steps (Javvaji et al., 2018).

Polarization (P_m) for each unit cell was calculated using the dipole moment data d_i and it is equal to the sum of dipole moments inside the single unit cell divided by its total volume, defined as follows:

$$P_{\rm m} = \frac{1}{V_{\rm m}} \left(\sum_{i=1}^{\rm n} d_i \right) \tag{3.14}$$

where *n* is the number of atoms present in unit cell (*m*) and V_m is the volume of unit cell, calculated as V = At, in which *A* and *t* are the surface area of unit cell and thickness of BNS, respectively. The thickness of BNS was considered as 3.4 Å (Boldrin et al., 2011). The axial strain (ε) of BNS was calculated using relation, $\varepsilon = \left(\frac{L_f - L_i}{L_i}\right)$, in which L_i and L_f are the initial and final lengths of BNS, respectively, in the direction of applied tensile loading. The shear strain (γ) of BNS was calculated using relation, $\gamma = \left(\frac{\Delta x}{w}\right)$, in which (Δx) is the displacement of BNS in the direction of applied shear loading and w is the width of BNS normal to the applied load.

The total polarization of BNS can be expressed as the sum of polarization of each unit cell, as follows:

$$P = \sum_{m=1}^{M} P_m \tag{3.15}$$

The polarizations in the x-direction (P_x) and y-direction (P_y) are due to the stretching of BNS and the shearing of BNS in xy-plane, respectively, and are given by (Kundalwal et al., 2017):

$$P_{\rm x} = e_{\rm xxx} \varepsilon_{\rm xx} \tag{3.16}$$

$$P_{y} = e_{yxy}\varepsilon_{xy} \tag{3.17}$$

where, ε_{xx} and $\frac{\partial \varepsilon_{xx}}{\partial x}$ are the respective strain and strain gradient terms; e_{xxx} and e_{yxy} are the piezoelectric coefficients in tension and shear, respectively.



Fig. 3.3 Schematic representations of BNS under (a) tensile and (b) shear loadings.

3.3 Electromechanical response of pristine BNSs

In order to verify the validity of the current MD simulations, the elastic properties of BNSs reported by other researchers using different techniques and approximations are considered. Note that several independent MD simulations were performed to obtain the reliable elastic and piezoelectric constants of BNSs under the uniaxial tension and shear loadings. Table 3.1 summarizes the outcome of this comparison. Our results are in good agreement, validating current MD simulations; some of our results marginally differ due to the use of different techniques and approximations by other researchers. For instance, Kudin et al., (2001) used an-initio and Milowska et al., (2013) used DFT to estimate the elastic properties of BNSs.

Size of BNS	Number of BN	References	A	rmchair BN	S	Zigzag BNS			
(Å)	atoms		E (TPa)	ν	G (TPa)	E (TPa)	ν	G (TPa)	
$40 \text{ Å} \times 40 \text{ Å}$	640	Present	0.720	0.187	0.295	0.500	0.162	0.267	
$60 \text{ Å} \times 60 \text{ Å}$	1440	Present	0.754	0.191	0.302	0.531	0.165	0.248	
$70 \text{ Å} \times 70 \text{ Å}$	1944	Present	0.785	0.194	0.323	0.567	0.168	0.268	
		Present	0.854	0.197	0.346	0.584	0.173	0.274	
$80 \text{ \AA} \times 80 \text{ \AA}$	2560	(Kudin et al., 2001; (Hamdi and Meskini, 2010; (Milowska et al., 2013)	0.814 – 0.850	0.187 – 0.195	0.321 – 0.342	0.560 – 0.574	0.161 - 0.172	0.220 – 0.267	
$100 \text{ Å} \times 100 \text{ Å}$	4000	Present	0.900	0.217	0.360	0.610	0.175	0.286	

Table 3.1: Comparison of the elastic constant of a pristine armchair and zigzag BNSs.

MD coupled with C-D potential models were developed to study the electromechanical response of armchair and zigzag BNSs under tensile and shear loading conditions. The different size of armchair and zigzag BNSs were considered for studying the electromechanical response. The following representation for BNSs is used: armchair (A)/zigzag (Z)_number of atoms. Total eight cases were considered: A_640, A_1440, A_2560, A_4000, Z_640, Z_1440, Z_2560 and Z_4000. First, the elastic properties of the armchair and zigzag BNSs were determined followed by the calculation of induced polarization and piezoelectric coefficients.

The variation of PE of BNS subjected to tension loading is shown in Fig. 3.4. As expected, it can be observed from Fig. 3.4 that the larger size of BNS shows higher PE than smaller ones. This is attributed to the larger volume of BNS which eventually stores more PE. It can also be observed that the armchair BNS shows higher PE compared to the zigzag one at the same strain value, which is in good agreement with the existing results (Asadpour et al., 2015).



Fig. 3.4 The variation of PE of different BNSs under uniaxial loading.

The stress-strain response of armchair and zigzag BNSs under tension and shear loadings is shown in Figs. 3.5(a) and (b), respectively. Young's (E_{xx}) and shear (G_{xy}) moduli of BNS under tension and shear loading conditions, respectively, were determined from the slope of stress-strain curves within the elastic limit of BNS. From Fig. 3.5(a) we can observe that the values of maximum stresses in the armchair and zigzag BNSs are 23 GPa and 9 GPa at strain value of 0.0275, respectively. In the case of shear loading, the values of maximum shear stresses are 9 GPa and 6.5 GPa in the armchair and zigzag BNSs, respectively, at a strain value of 0.0275. The elastic properties of different BNSs were obtained from the stress-strain curves and the same is shown in Fig. 3.6. It can be observed from Fig. 3.6 that Young's and shear moduli of armchair BNS are higher than zigzag BNS. In order to understand the physics behind such differences, the deformation mechanics of BNS under the tension and shear loadings are explained in Figs. 3.7 and 3.8, respectively. During the tension loading, it can be observed from Fig. 3.7 that the four types of deformed B-N bonds exist in the sheet: (i) a_2 and z_1 are slightly inclined to the direction of loading, and (ii) bonds a_1 are aligned with the loading direction while bonds z_2 are normal to the direction of loading. Under the tension loading, the bonds a_1 and a_2 are under tension while bonds z_1 and z_2 are under tension and compression, respectively. Therefore, the bonds a_1 and a_2 act as the stress-bearing bonds which carries more axial load than the bond z_1 . However, it can be observed from Figs. 3.7(a) and (b) that all six B–N bonds (a_1 and a_2) in case of armchair BNS carry the tensile load while in case of zigzag BNS, only four B–N bonds (z_1) carry the tensile load and rest of the B–N bonds are under compression.

Therefore, the stress-bearing bonds in armchair BNS are higher than the zigzag BNS and thus, Young's modulus of the former is slightly higher. During the shear loading, it can be observed from Fig. 3.8 that the two B–N bonds are parallel to the loading direction in case of armchair BNS and no B–N bond is parallel to the loading direction in case of zigzag BNS. By resolution of applied forces, it can be found that the shear stress value in the direction of B–N bond of zigzag direction is less than armchair direction due to the applied force F_{R} .



Fig. 3.5 The stress-strain curves for BNSs under (a) tension and (b) shear loadings.



Fig. 3.6 Elastic and piezoelectric properties of pristine BNSs.



Fig. 3.7 Deformation mechanics of (a) armchair and (b) zigzag BNSs under tension loading.



Fig. 3.8 Deformation mechanics of (a) armchair and (b) zigzag BNSs under shear loading.

Then, the size-dependent piezoelectric properties of BNSs were studied. The induced polarization in BNS was calculated using Eq. (3.14) considering a single unit cell and the results are plotted in Figs. 3.9(a) and (b) for tension and shear loadings, respectively. An atom shares its valence electron with each neighboring atom. These shared valence electrons between B and N atoms form a strong sigma bond. The contribution of electrons is higher from B to N atoms due to the higher electronegativity of N atom and thus, in-plane dipole moment generates (Beheshtian et al., 2012). This results in the permanent polarization in BN-based structures. During the deformation, B-N bond lengths increase that lead to a change in the electronic polarization and consequently, the piezoelectric coefficients were calculated using the procedure discussed in section 3.2.1. The slope of polarization-strain curve during the tension and shear loadings defines the piezoelectric coefficients (e_{xxx} and e_{yxy}) and these are shown in Fig. 3.9. It can be observed from Fig. 3.9 that the induced polarization in armchair BNS is higher than zigzag

case. This is attributed to the generation of higher resultant dipole moments in the *x*direction of armchair BNS compared to zigzag sheet (see Fig. 3.10). In case of tensile loading, the piezoelectric coefficients of armchair and zigzag BNSs are approximately 0.38 C/m^2 and 0.19 C/m^2 , respectively, for sheet having total 2560 atoms; in case of shear loading, piezoelectric coefficients of the same are approximately 0.27 C/m^2 and 0.14 C/m^2 , respectively. Note that the piezoelectric coefficients of BNS are function of its chirality and our results are in line with the results reported by other researchers, as summarized in Table 3.2. The compared and validated results prove that the C-D potential model can be used for investigating the electromechanical response BNS. It can be observed from Fig. 3.10(b) that the enhancement of piezoelectric coefficient in shear loading is less compared to tensile loading. This is due to the fact that the polarization depends on the change in bond deformations which are lower in case of application of shearing load (Kundalwal et al., 2017). The work was further extended to study the effect of C-doping on the piezoelectric and elastic properties of BNS considering only armchair sheets having 2560 atoms because they show higher piezoelectricity per unit cell.

Size of BNS	Number	Df	Armch	air BNS	Zigzag BNS		
(Å)	of BN atoms	Keferences	e _{xxx} (C/m ²)	e _{yxy} (C/m ²)	e _{xxx} (C/m ²)	e _{yxy} (C/m ²)	
$40 \text{ Å} \times 40 \text{ Å}$	640	Present	0.335	0.167	0.212	0.108	
$60 \text{ Å} \times 60 \text{ Å}$	1440	Present	0.356	0.187	0.225	0.111	
		Present	0.368	0.184	0.234	0.117	
70 Å \times 70 Å	1944	(Noor-A-Alam et al., 2014; Zhang, 2017; Zhang and Meguid, 2017)	0.340 -0.360	0.164 - 0.182	0.224 - 0.229	0.112 - 0.116	
		Present	0.387	0.195	0.245	0.121	
$80 \text{ Å} \times 80 \text{ Å}$	2560	(Noor-A-Alam et al., 2014; Zhang, 2017; Zhang and Meguid, 2017)	0.365 - 0.384	0.164 - 0.189	0.220 - 0.240	0.110 - 0.118	
$100 \text{ Å} \times 100 \text{ Å}$	4000	Present	0.396	0.198	0.287	0.141	

Table 3.2: Comparison of piezoelectric constant of pristine armchair and zigzag BNSs.



Fig. 3.9 The polarization-strain curves of BNSs under (a) tension and (b) shear loading conditions.



Fig. 3.10 Dipolar moment induced mechanism in the armchair and zigzag BNSs (Red arrow shows the direction and magnitude of dipole moment.

3.4 Effect of C-doping on electromechanical response of BNSs

Recently, piezoelectric BNSs have attracted a lot of attention in nanotechnology applications to develop their NEMS at the nanoscale level. Among all other properties, polarization of BNS was found to be sensitive to defects and chemical doping, owing to interference and quantum mechanics effects (Zhang and Meguid, 2017). The modification of geometry and chemical structure of BNS with doping allows researchers to engineer its electronic properties. As a matter of fact that the breaking of symmetry can enhance the piezoelectric properties of planer nanomaterials (Beheshtian et al., 2012; Kundalwal et al., 2017; Javvaji et al., 2018), therefore, further investigations were carried out to study the effect of C-doping on the electromechanical response of BNS under tension and shear loadings. To enhance the piezoelectricity in BNSs, C atoms were doped in such a way that can make them strong non-centrosymmetric materials. To study the effect of C-doping and different shapes of pores, further simulations were performed for four different types of armchair sheets: pristine BNS, C-doped BNS with triangular, trapezoidal, and circular pores; schematics of these structures are shown in Fig. 3.11. Note that a constant C-doping concentration of 5.625% was considered. The doping concentration is the ratio of number of C atoms to the total number of atoms in the sheet. A certain number of B and N atoms were removed to create different pores in BNSs. We fixed the size of pore in BNS in such a way that it filled with the same number of C atoms irrespective of the shape of pore to



study the effect of C-doping on the electromechanical response of BNS. Therefore, the resulting C-doping concentration leads to the value of 5.625%.

Fig. 3.11 Schematics of (a) pristine BNS and different C-doping arrangements in BNSs with (b) triangular pore (case 1), (c) trapezoidal pore (case 1), (d) circular pore (case 2), (e) triangular pore (case 2) and (f) trapezoidal pore (case 2).



Fig. 3.12 Variation of polarization in BNSs with different C-doping positions.

First, the effect of position of C-dopants on the piezoelectric properties of BNS was studied by keeping the constant doping concentration. Two types of C-dopant arrangements in BNS were considered: (i) C atoms surrounded by more B atoms than N atoms [case 1, Figs. 3.12(b) and (c)] and (ii) C atoms surrounded by more N atoms than B atoms [case 2, Figs. 312(e) and (f)]. Figure 3.11 shows the variation of polarization with the strain for two cases under tension and shear loadings. It may be observed from Fig. 3.12 that the case 2 provides more polarization than case 1. This is attributed to the generation of more dipole moments due to C–N bonds than C–B bonds as the former shows higher differences in electronegativity that leads to the higher polarization. It is important to note that out-of-plane movement of sheet due to C-dopants was not considered because C, B and N atoms have the same planar sp² hybridization (Beheshtian et al., 2012). The work was further extended to study the effect of C-doping on the piezoelectric and elastic properties of armchair BNSs with different percentage and types of pores considering case 2 only.

Figures 3.13(a) and (b) show the stress-strain curves of C-doped A_2560 BNS with different pores under tensile and shear loadings, respectively. We can observe from these plots that the C-dopants improve the elastic behavior of BNS slightly compared to pristine one. Figure 3.14 shows the variation of Young's and shear moduli of BNS with C-doping concentration of 5.625%. The improvement in the values of Young's moduli of BNS with triangular, trapezoidal and circular pores are found to be 9 %, 7.5% and 5.5%, respectively, and the respective improvement in shear moduli are 8.5%, 5% and 5%. It can be observed that the elastic moduli of C-doped sheets are higher than pristine one and this is attributed to the stronger C-C bond than all other bonds. It may also be observed that doped BNS with triangular pore shows higher Young's modulus compared to all other cases. This is due to the existence of higher number of C-C bonds in the triangular case for constant Cdoping concentration. The same is true in case of shear modulus of BNS as shown in Figs. 3.14(b). As expected, the elastic properties of BNS increase as its size increases and then they become stabilized at particular total number of atoms, that is, 2560 atoms (80 Å \times 80 Å). This is due to the fact that the effect of applied forces on the system was found to be negligible at some finite distance from the sections where they were applied according to Saint Venat's principle.



Fig. 3.13 Stress-strain curves for armchair BNS (A_2560) under (a) tension and (b) shear loading conditions.



Fig. 3.14 The variation elastic moduli of armchair BNS with the number of atoms (N).

The effect of C-doping on the piezoelectric properties of BNS can be seen in Figs. 3.15(a) and (b) under tension and shear loadings, respectively. The C-doping results in the increase of values of e_{xxx} of BNSs with triangular and trapezoidal pores by 18.5% and 3.5%, respectively, and the reduction of value e_{xxx} of BNS with circular pore by 22.5% compared to pristine BNS. During the shear loading, the values of e_{yxy} of BNS with triangular and trapezoidal pores increased by 20.5% and 1.075%, respectively, and the value e_{yxy} of BNS with circular pore reduced by 7%. The piezoelectric coefficient of C-doped BNS with circular pore decreases and this is attributed to the fact that the circular shape pore does not help in breaking the symmetry of BNS and therefore, the induced dipole moments across the circular edge of pore are found to be symmetric and get canceled out each other. This phenomenon is also observed for graphene sheet with circular pore (Kundalwal et al., 2017). A C-doped BNS with different shape pores shows a significant

improvement in its piezoelectric coefficient when the tensile loading was applied due to the non-centrosymmetric nature of pores. As a matter of fact, the piezoelectricity phenomenon is size-dependent, therefore, we increased the number of B and N atoms keeping the constant C-doping concentration. The variation of piezoelectric coefficients of BNSs under tension and shear loading conditions are shown in Fig. 3.16. As the number of B and N atoms increases, by keeping the constant C-doping, the values of e_{xxx} and e_{yxy} increase up to the total number of 2560 atoms and then stabilize as the effect of presence of C-dopants becomes negligible (see Table 3.3 and 3.4). The same is true in case of values of e_{yxy} of BNS under shear loading. The obtained results are in good agreement with the existing results obtained by using the different techniques (Sai and Mele, 2003). Further, we studied the effect of different C-doping concentrations on the electromechanical response of BNS with triangular pore.



Fig. 3.15 The variation of polarization-strain for BNSs under (a) tension and (b) shear loading conditions.



Fig. 3.16 The variation of piezoelectric coefficients with number of atoms (N).

Size of BNS (Å)	Number		Triangular								
	of BN atoms	E (TPa)	ν	G (TPa)	e _{xxx} (C/m ²)	e _{yxy} (C/m ²)	E (TPa)	ν	G (TPa)	e _{xxx} (C/m ²)	e _{yxy} (C/m ²)
$40~\text{\AA} \times 40~\text{\AA}$	640	0.700	0.152	0.320	0.346	0.172	0.760	0.192	0.342	0.414	0.243
$60~\text{\AA} \times 60~\text{\AA}$	1440	0.721	0.179	0.315	0.379	0.195	0.784	0.212	0.337	0.438	0.258
$80~\text{\AA} \times 80~\text{\AA}$	2560	0.738	0.201	0.310	0.399	0.207	0.804	0.226	0.334	0.464	0.272
$110~\text{\AA} \times 110~\text{\AA}$	3540	0.735	0.186	0.311	0.389	0.200	0.802	0.199	0.333	0.444	0.263
135 Å × 135 Å	4560	0.733	0.172	0.310	0.377	0.193	0.803	0.189	0.333	0.437	0.253
$160 \text{ Å} \times 160 \text{ Å}$	5645	0.731	0.165	0.309	0.378	0.185	0.801	0.185	0.334	0.436	0.249

 Table 3.3: Comparison of elastic and piezoelectric constant of pristine and triangular shape of C-doped BNS.

Table 3.4: Comparison of elastic and piezoelectric constant of trapezoidal and circular shape of C-doped BNS.

Size of BNS	Number		T	rapezoida	I		Circular					
(Å)	atoms	E (TPa)	ν	G (TPa)	e _{xxx} (C/m ²)	e _{yxy} (C/m ²)	E (TPa)	ν	G (TPa)	e _{xxx} (C/m ²)	e _{yxy} (C/m ²)	
$40~\text{\AA}\times40~\text{\AA}$	640	0.730	0.168	0.330	0.379	0.172	0.712	0.134	0.330	0.296	0.165	
$60~\text{\AA} \times 60~\text{\AA}$	1440	0.745	0.192	0.325	0.402	0.195	0.728	0.152	0.325	0.328	0.179	
$80~\text{\AA} \times 80~\text{\AA}$	2560	0.760	0.215	0.323	0.421	0.207	0.740	0.181	0.323	0.354	0.182	
$110~\text{\AA} \times 110~\text{\AA}$	3540	0.763	0.190	0.324	0.402	0.200	0.743	0.165	0.324	0.324	0.172	
$135~\text{\AA} \times 135~\text{\AA}$	4560	0.762	0.185	0.322	0.398	0.193	0.741	0.161	0.322	0.314	0.175	
$160 \text{ Å} \times 160 \text{ Å}$	5645	0.761	0.178	0.323	0.395	0.185	0.742	0.157	0.323	0.314	0.173	

3.5 Effect of C-doping concentration on electromechanical response

In the previous sets of results, elastic, and piezoelectric properties of different size BNSs were determined considering the constant C-doping concentration of 5.6%. However, the variation in C-doping concentration may influence the elastic and piezoelectric properties of BNS and therefore, the C-doping concentration was varied for further analysis of BNS with triangular pore with 2560 number of atoms as it showed higher electromechanical response under tension loading. A size of 80 Å \times 80 Å BNS was

modeled and the C-doping concentration was varied from 1.46% to 18.9%. The schematics of C-doped BNS with triangular pore are demonstrated in Fig. 3.17 The doping was done by attaching N atoms with C atoms. The stress-strain and polarization-strain curves of Cdoped BNS are shown in Fig. 3.18 The obtained values of Young's modulus and piezoelectric coefficient are plotted in Fig. 3.19 It can be observed from Fig. 3.19 that Young's modulus of BNS increases with C-doping concentration and stabilizes at an approximate value of 12.6%. It can also be observed from Fig. 3.19 that the piezoelectric coefficient increases as C-doping concentration increases and reaches its maximum value around 0.41 C/m² at 12.6% C-doping concentration and starts decreasing. This behavior can be attributed to the reduction in the contribution from polarized B and N atoms and increment in the non-polarized C atoms to the total polarization. In the case of trapezoidal and circular pores, the respective values of maximum piezoelectric coefficients are 0.111 C/m² and 0.105 C/m² at strain range of 0.025-0.0275 with C-doping concentration of 18.9%, respectively (see Table 3.5). The present study reveals that the C-doped BNSs with triangular pore show higher elastic and piezoelectric properties and such improved electromechanical response of sheets may provide a new platform for designing and developing their next generation NEMS.



Fig. 3.17 The schematics of BNS with different C-doping concentration.



Fig. 3.18 The variation of (a) stress-strain (b) polarization-strain curves for BNS containing triangular pore with different C-doping concentration.

Table 3.5: Elastic and	piezoelectric (constants while	increasing	triangular	C-doping	g concentration o	f BNSs.
4	-			0	1 0	,	,

S.	C-doping	Triangular		Trapez	zoidal	Circular		
110.	(%)	E (TPa)	e _{xxx} (C/m ²)	E (TPa)	e _{xxx} (C/m ²)	E (TPa)	e _{xxx} (C/m ²)	
1	1.406%	0.725	0.358	0.718	0.347	0.699	0.324	
2	3.164%	0.727	0.378	0.720	0.358	0.704	0.334	
3	5.625%	0.731	0.385	0.724	0.365	0.710	0.339	
4	8.789%	0.733	0.398	0.726	0.388	0.714	0.346	
5	12.656%	0.735	0.408	0.731	0.394	0.719	0.354	
6	18.906%	0.735	0.405	0.731	0.387	0.719	0.350	

Chapter 3



Fig. 3.19 Variation of Young's modulus and piezoelectric coefficient of BNS containing triangular pore with different C-doping concentration.

3.6 Effect of strain rate on elastic properties of BNSs

The stress-strain relations are function of applied strain rate and a system gets enough time to relax for reaching the equilibrium state at the lower values of strain rate. Therefore, to obtain the reliable and accurate results, the use of lower values of strain rate is preferred. However, we varied the values of strain rate as 0.0001, 0.0003, 0.0005, 0.0007 and 0.001 ps^{-1} to choose the optimal value to study the electromechanical response of BNS. The tensile test was performed on the pristine (A 2560) BNS by varying the strain rates and the variation of stress with strain for sheets under tensile loading is shown in Fig. 3.20. Figure 3.20(b) shows the effect of strain rate on Young's modulus of BNS and it can be observed that the modulus increases with the increase in strain rate. The similar observation was found by Han et al. (2014) and Yao et al. (2020). It can also be observed from Fig. 3.20(b) that the change in Young's modulus drastically increases when the strain rate is greater than 0.0005 ps^{-1} and this is attributed to the dissipation of strain energy of BNS at higher strain rates. Therefore, it can be concluded that the use of strain rate value of 0.0005 ps⁻¹ is the optimal choice to investigate the electromechanical response of BNS and such value was also used in the existing work to study the mechanical behavior of BNS (Choyal et al., 2019). Therefore, we used the strain rate of 0.0005 ps^{-1} in subsequent simulations.



Fig. 3.20 Effect of strain rates on (a) stress-strain behaviour and (b) Young's modulus of pristine BNS (A_2560) under tension loading.

3.7 Conclusions

This chapter reports the electromechanical response of C-doped BNS containing different shapes of pores investigated using MD simulations coupled with the chargedipole (C-D) potential model. Both armchair and zigzag BNSs with different sizes were considered. The comparison of electromechanical response of both pristine and C-doped BNSs under the tension and shear loading conditions was comprehensively studied using MD simulations with the three-body Tersoff potential force field. Moreover, the elastic properties of pristine BNSs were compared and validated with the existing results and the good agreement was found between the predictions. The following main conclusions are drawn from the current chapter:

- The mechanism of polarization in BNSs is explained using the unit cell representation. As displacement applied to a unit cell of BNS, it changes its atomic configuration that leads to induced atomic polarization.
- The axial and shear elastic/piezoelectric coefficients of BNS were determined using the tension and shear loading conditions, respectively. The elastic and piezoelectric coefficients of armchair BNS were found to be higher than zigzag BNS irrespective of the shape of pore and C-doping concentration.
- The induced polarization in the BNSs was found to depend on the local arrangement of C atoms around the B and N atoms and the polarization increases if C atoms are surrounded by more N atoms than B atoms.

- The axial and shear piezoelectric coefficients of C-doped BNS with triangular and trapezoidal pores increased while they reduced in case of circular pore compared to pristine BNS. A BNS with triangular pore showed higher polarization than BNS containing other shapes of pores. The C-doping with N atoms results in the generation of higher dipole moments because the C-N bond is more electronegative than the C-B bond.
- The piezoelectric coefficients of doped BNS increased with the C-doping concentration up to 12.6% and then they decrease. The elastic properties of doped BNS increased with the C-doping concentration up to 12.6% and then they stabilize and do not change beyond the total number of 2600 BN atoms.
- The present work offers a theoretical framework for predicting the elastic and piezoelectric properties of pristine, defective, and doped BN-based nanomaterials under different types of loading conditions.

The unique properties of BNSs accompanied by their defect/pores and chemical stabilities make them attractive nanomaterials in the applications of nanotechnology. The electromechanical response of fixed size of pristine and hybrid BNS subjected to the external applied electric field in both armchair and zigzag directions (indirect approach) is studied in the next chapter.

4. Chapter

Piezo- and flexo-electric response of BNS superlattices

In this chapter, the investigation of converse piezo- and flexo-electric effects of hybrid and SW defected BNS under the application of external electric-field was carried out. Effect of various factors such as chirality, defect engineering and variation of temperature on the piezo- and flexo-electric response of BNSs was critically examined.

4.1 Introduction

Two dimensional (2D) nanomaterials such as boron nitride sheets (BNSs) and graphene superlattices (SLs) attracted intense attention in the academia and industry due to their unique multifunctional properties and potential applications (Song et al., 2013; Grixti et al., 2018). The review of the literature presented in chapter 1 reveals that the researchers have made significant efforts to study the electromechanical response of BNSs. On the other hand, the electromechanical response of hybrid BNSs remains almost unexplored. It is challenging to experimentally carry out such investigations due to the involvement of atomistic structural parameters of hybrid BNSs. There have been a few studies which reported elastic and electronic properties of BNSs. Researchers used different methods such as density functional theory (DFT) (Klein et al., 2009; Zhao et al., 2014; Zhang et al., 2015), ab-initio calculations (Ansari et al., 2015; Ansari et al., 2015; El-Kelany et al., 2015), molecular mechanics (MM) (Jafari et al., 2012; Ansari et al., 2015), molecular dynamics (MD) simulations (Mortazavi and Rémond, 2012; Zhang and Meguid, 2015), and tight binding model (Chegel et al., 2016) to study the electromechanical response of BN-based nanostructures. These studies show interesting and unique electronic and mechanical response of BN nanostructures which provided opportunities to develop their NEMS devices.

In the last decade, thin film heteroepitaxy has received attention by researchers in view of the exponential growth of electronics industry due to the development of

heteroepitaxial devices for communications, displays, solid state lighting, green energy etc. In heteroepitaxy, two different SLs are combined with a well-defined atomic registry across a 2D interface which can dramatically influences the overall properties of resulting heterostructure due to the increased scattering of electrons and phonons (Nandwana and Ertekin, 2015). Graphene/BNS SLs were studied by Jungthawan et al. (2011) using DFT approach to engineer band gap of graphene layers. They found that the orientation, stripe width, and ordering significantly influence the stability and electronic properties SLs. Using MD simulations and continuum analysis, Nandwana and Ertekin (2015) reported that the mismatch between BNS and graphene SLs which resulted in competition between two strain-relieving mechanisms: nanoscale misfit dislocations and rippling via out-of-plane relaxation. Using MD simulations, Eshkalak et al. (2018) studied the effect of crack defects on the mechanical properties of graphene/BNS SLs. Their results indicated that hybrid SLs with longitudinal cracks show more desirable mechanical properties compared to transverse cracks.

The review of literature presented in chapter 1 clearly indicates that several studies were performed to study the (i) mechanical and piezoelectric properties of pristine BNS and other defective BN nanostructures, and (ii) electronic and mechanical properties of heterostructures of graphene/BNS SLs. The use of BNS in NEMS applications with desirable electromechanical response requires a thorough understating of their piezoelectric, flexoelectric, and elastic response under the external E-field. Moreover, the polarization of BNS can be tailored and enhanced via interface and defect engineering which may lead to the development of 2D nanostructures with unique properties. There is no single study exists on the estimation of piezoelectric/flexoelectric coefficients of BNS integrated with graphene stripes and SW defected BNS. This has inspired us to study the electromechanical response of pristine and hybrid BNS using MD simulations by applying the external E-field. Moreover, the elastic properties of hybrid BNS were also calculated.

4.2 MD modelling of BNSs

All MD simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS). The interatomic interactions among B, C, and N atoms were modelled using the three-body Tersoff potential force field (Tersoff et al., 1988). The Tersoff potential force field was used by several researchers to study the

electromechanical response of BN-based nanostructures (Zhang and Meguid, 2015; Nandwana and Ertekin, 2015; Einalipour Eshkalak et al., 2018). The analytical form of energy expression used in the Tersoff potential is as follows (Tersoff et al., 1988; Tadmor and Miller, 2011):

$$E = \sum_{a} E_{a} = \frac{1}{2} \sum_{a \neq b} V_{ab}$$
 (4.1)

$$V_{ab} = f_{C}(r_{ab})[f_{R}(r_{ab}) + b_{ab}f_{A}(r_{ab})]$$
(4.2)

where *E* is the total energy of the system and V_{ab} is the bond energy. The indices *a* and *b* run over the atoms of the system and r_{ab} is the distance between atoms *a* and *b*. The b_{ab} is the bond angle term, which depends on the local coordination of atoms around atom *a*. The f_R and f_A are the repulsive and attractive pair potentials, respectively, and f_C is the cut-off function provided to limit the range of potential and thus, to save the computational resources required for MD simulations.

To perform MD simulations, first the initial structures of BNS/graphene SLs were created with appropriate bond lengths (1.437/1.413 Å) (Jungthawan et al., 2011; Noor-A-Alam et al., 2014). Then, using the conjugate gradient algorithm, the initial pristine/hybrid structures were optimized by minimizing their energy. The minimized structure was treated as optimized once the difference in its total potential energy between the two consequent steps was less than 1×10^{-10} kcal/mol (Dewapriva et al., 2014; Kundalwal and Choyal, 2018). After the optimization of structure, the loading conditions were imposed to study its electromechanical response. The NVT ensemble was used to update the velocities and positions of B, N and C atoms after each time step using the Nosé-Hoover temperature thermostat. Second, the external electric field (E) was applied along the armchair or zigzag direction of BNS, as shown in Fig. 4.1. In the BNS, each B atom loses the three electrons and form cations (B^{3+}) and each N atom gains three electrons to form anions (N^{3-}) . The born effective charges were considered on B and N atoms as +3e and -3e, respectively (Zhang and Zhou, 2018). Due to the distribution of charges, the external E-field produces the external force on atom *i*, that is, $f_i = q_m E$, in which q_m is the charge on atom m. Finally, the relaxation time of 30 ps was provided to structure to obtain its equilibrated state. The velocity Verlet algorithm was used to calculate the new positions of atoms using the equations of motion in all MD simulations. The virial atomistic stress $\sigma_{\alpha\beta}$ induced due
to the applied electric field in the system was taken as the arithmetic mean of the local stresses on all atoms, as follows (Zhao and Xue, 2013):

$$\sigma_{\alpha\beta} = -\frac{1}{V} \left(\sum_{\alpha=1}^{N} m_{\alpha} v_{x}^{\alpha} v_{y}^{\alpha} + \frac{1}{2} \sum_{\alpha=1}^{N-1} \sum_{\beta=i+1}^{N} r_{\alpha\beta,x}^{N-1} F_{\alpha\beta,y} \right)$$
(4.3)

where m_{α} is the mass of atom α , v_x^{α} is the velocity component in the axial direction of atom α , $F_{\alpha\beta,y}$ refers to the axial component of interatomic force between atoms α and β , xand y denote the indices of the Cartesian coordinate system, $r_{\alpha\beta,x}^{N-1}$ is the interatomic distance in the axial direction between atoms α and β , V refers to the volume of simulated BNS, and N is the number of atoms.

In Eq. (4.3), the first term represents the total virial stress ($\sigma_{\alpha\beta}$), second term represents the kinetic part of the virial stress ($\sigma_{\alpha\beta}^{kinetic}$), and third term represents the interatomic potential energy due to the virial stresses ($\sigma_{\alpha\beta}^{inter-atomic}$). The stresses in the BNS were calculated by averaging the virial stress of each BN atom in the nanosheet excluding the atoms in the fixed boundaries. The volume of pristine BNS was obtained by assuming its thickness as 3.35 Å (Kurdyumov et al., 1995). Due to the integration of graphene stripe in BNS, the thickness of resulting hybrid system was changed, and its effective thickness was considered as 3.4 Å to calculate volume (Boldrin et al., 2011). The axial strain ε for the hybrid system was calculated using relation, $\varepsilon = \left(\frac{L_f - L_o}{L_i}\right)$, where L_o and L_f are the original and final lengths of system, respectively. Schematic representation of pristine BNS under the application of E-field in the armchair and zigzag directions are shown in Figs. 4.1(a) and (b), respectively.



Fig. 4.1 Schematic representations of pristine BNS subjected to E-field in: (a) armchair and (b) zigzag directions. Colored with light salmon and blue are boron and nitrogen atoms, respectively.

The most well-known electromechanical coupling is the piezoelectricity (Michel et al., 2017). The linear piezoelectric properties of 2D nanostructures are the first-order couplings between strain (ε_{jk}) and stress (σ_{jk}) to polarizations (P_i) and the macroscopic E-field (E_i) . The subscripts i, j, k $\in \{1,2,3\}$, and 1, 2 and 3 correspond to the *x*, *y* and *z* directions, respectively. The piezoelectricity is usually described by the coefficients *d* and *e*; namely, represent the converse piezoelectric coefficients, respectively. The piezoelectric coefficients, respectively. The piezoelectric matches d_{ijk} and e_{ijk} , and their respective Maxwell relations are as follows:

$$d_{ijk} = \left(\frac{\partial P_i}{\partial \sigma_{jk}}\right)^{E,T} = \left(\frac{\partial \varepsilon_{jk}}{\partial E_i}\right)^{\sigma,T}$$
(4.4)

$$e_{ijk} = \left(\frac{\partial P_i}{\partial \varepsilon_{jk}}\right)^{E,T} = \left(\frac{\partial \sigma_{jk}}{\partial E_i}\right)^{\varepsilon,T}$$
(4.5)

The dipole moment induced due to the applied E-field and the resulting polarization can be calculated using the following relation (Tan et al., 2020):

$$P = \sum_{i}^{N} \frac{q_{i}r_{i}}{A}$$
(4.6)

where q_i is the charge of ith atom, r_i is the x-coordinate of ith atom, N is the number of atoms, and A is the area of planer sheet. The full piezoelectric tensor for the BNS can be determined on the basis of hexagonal symmetry 6m2 class using Voigt notation to reduce

the number of piezoelectric coefficients. The only allowed nonzero piezoelectric coefficients e_{11} , e_{14} , d_{11} and d_{14} exist in BNS (Alyörük et al., 2016):

The flexoelectricity also shows the direct and converse effects. An applied strain gradient induced polarization is the direct effect, and an applied electric field gradient induced stress is the converse effect. The flexoelectric coefficients from the converse flexoelectric effect can be obtained as follows (Shu et al., 2014):

$$\sigma_{ij} = \mu_{ijkl} \frac{\partial E_k}{\partial x_l}$$
(4.7)

where, σ_{ij} , $\frac{\partial E_k}{\partial x_1}$ and μ_{ijkl} are the induced-elastic stress, E-field gradient and flexoelectric coefficients, respectively.

Note that the total polarization constitutes the contributions from both flexoelectricity and piezoelectricity. The constitutive relation for the polarization vector induced due to the flexoelectricity and piezoelectricity effects may be written as (Kundalwal et al., 2017; Javvaji et al., 2018):

$$P_{1} = e_{ijk}\varepsilon_{jk} + \mu_{ijkl}\frac{\partial\varepsilon_{jk}}{\partial x_{l}}$$
(4.8)

where e_{ijk} and μ_{ijkl} are the respective piezoelectric and flexoelectric tensors; ε_{jk} and $\frac{\partial \varepsilon_{jk}}{\partial x_l}$ are the strain and strain gradient, respectively.

4.3 Interface engineering

Graphene and BNS SLs are complementary 2D materials, structurally very similar with a lattice constant difference of only 1.7% (Dean et al., 2010) but with a vastly different electronic properties. The integration of these two SLs via coherent interface engineering can provide us the interesting functional properties. The existing studies showed that the formation energy of BNS integrated with graphene stripe strongly depends on the nearest-neighboring bonds and the resulting hybrid system tends to have phase segregation into large BN and C domains. For armchair graphene SLs, the energy differences between SLs with and without inversion symmetry are much smaller than that of zigzag graphene SLs. This is attributed to the fact that each armchair edge does not have a net line charge (relative to the other edges) (Jungthawan et al., (2011) and Refs. therein). In case of armchair graphene stripe, all edges of interface are composed of an equal number of C-B and C-N

bonds in an alternating order and therefore, no line charges are formed, making it energetically more favorable (Jungthawan et al., 2011). Therefore, the zigzag graphene stripe was considered for interface engineering of BNS SLs, as shown in Fig. 4.2. Hexagonal ring of graphene may alter the net polarization of hybrid BNS, therefore, it was also considered for interface engineering. Note that stripe patterns frequently exist during the synthesis of 2D materials, as well as in nature, as the favored ground states of alloys (Dong et al., 2011). In particular, the two types of arrangements for interface engineering were considered: (i) one edge of zigzag graphene stripe composed of N-C bonds and another with C-B bonds (NCB sheet; Fig. 4.2(b)), and (ii) one edge of hexagonal ring of graphene stripe composed of B-C bonds and another with C-N bonds (CHR sheet; Fig. 4.2(c)). Note that we considered only one or two graphene stripes to enhance the polarization of hybrid BNS because the energy difference decreases as the stripe width increases which results in the decrease in band gap. It is expected because the wider stripe allows more preferred bonds to form which reduces the fraction of atoms on the interfacial boundary between graphene and BNS SLs (Jungthawan et al., 2011). Therefore, the net polarization of hybrid BNS cannot be enhanced by using wider graphene stripes.



Fig. 4.2 Schematic representations of different arrangements of BNS SLs: (a) pristine BN, (b) NCB, and (c) CHR sheets. Colored with light salmon, blue and cyan are boron, nitrogen and carbon atoms, respectively, with dashed rectangle highlighting graphene stripes.

4.4 Results and discussions

In order to validate the performed MD simulations, the stress-strain diagrams for hybrid BNS were compared with existing DFT results (Ding et al., 2016)). MD results indicated a better consistency with the DFT results as shown in Fig. 4.3. This confirms the validity of the MD simulations performed in the present work. It can also be observed from

Fig. 4.3 that the Tersoff potential is suitable for all different atomic interactions, via. C-C, C-BN, BN interactions (Tersoff, 1989, 1988). The existing studies (Eshkalak et al., 2018; Eshkalak et al., 2018) also validated their MD results with DFT results for different arrangements of graphene and BN sheet.



Fig. 4.3 The stress-strain curves for a hybrid BNS using MD (current) and DFT simulations results (Ding et al., 2016).

4.4.1 Variation of strain energy (SE)

The MD simulations were performed to study the electromechanical response of pristine and hybrid BNS SLs subjected to the external E-field. The external E-field was applied in the armchair and zigzag directions as shown in Figs. 4.1(a) and (b), respectively. The applied E-field values were varied from -0.5 V/Å to 0.5 V/Å. To perform the MD simulations, a fixed size of BNS 60 Å \times 70 Å was considered to determine the effect of interface engineering of graphene stripe on the electromechanical response of hybrid BNS. The schematic of deformations of BNS are shown in Fig. 4.4. It may be observed from Fig. 4.4 that the deformation of sheets depends on the direction and magnitude of applied E-field applied in the armchair direction, the axial deformation always occurs in the direction of applied E-field while the shear deformation occurs when the E-field applied in the zigzag direction in the sheet, as it can be clearly seen from Fig. 4.4 (Zhang et al., 2017). This is due to the fact that for every hexagonal ring of BNS, two B–N bonds exist along the applied direction of E-field then the resultant dipole moments induced in the axial direction lead to axial strain in case of armchair direction. While in case of zigzag direction, for every hexagonal ring of BNS, no-single bond exists along the applied E-field

and four inclined bonds exist and thus, the resultant dipole moments induced in the inclined direction lead to shear strain (Zhang et al., 2017). The variation of strain energy of pristine BNS with time is shown in Figs. 4.5(a) and (b) when the external E-field was applied in the armchair and zigzag directions, respectively. It can be observed from Fig. 4.5 that the strain energy of BNS first increases with time and then stabilizes at particular time. It can also be observed that the value of stabilized time for strain energy depends on the direction of applied E-field. The axial and shear stresses were induced in the BNS subjected to the external E-field in the armchair and zigzag directions, respectively. The higher value of strain energy was observed in case of application of E-field in the zigzag direction due to the induced shear stresses. Similar trends of variation of strain energy were observed for hybrid BNS (NCB and CHR) and for the sake of brevity they are not shown here. The average of stabilized strain energy over a few time-steps was considered as stored strain energy in structure at particular value of E-field. The variation of stabilized average strain energy with the applied E-field in the armchair and zigzag directions is plotted in Figs. 4.5(a) and (b), respectively. It may be observed from Fig. 4.6 that the NCB sheet shows higher stored strain energy compared to other types of SLs. This is due to the occurrence of higher deformation in the NCB sheet, and it depends on the number of higher polarized bonds in the structure. Note that the NCB sheet does not demonstrate the inversion symmetry, that is, the B-N bonds (oriented perpendicular to the graphene stripe-length) are aligned in the same direction in both halves of BNS. Therefore, both the edges of graphene stripe are different (see Fig. 4.2(b)) which lead to the alternate positive and negative line charges, and this creates an electric field across graphene stripe. Therefore, the NCB sheet possesses higher polarized bonds compared to other types of SLs. It may also be observed from Fig. 4.6 that the marginal differences occur in the strain energy at the same magnitude of E-field but opposite direction, and the plots are asymmetric. This can be explained by the fact that the equilibrium distance between atomic centers decreases with the application of negative E-field than without E-field and converse is true in case of application of positive E-field. Therefore, the stored strain energy in the system is higher when the positive E-field is applied compared to negative E-field at a particular value of E-field magnitude (Zhang and Wang, 2014). For instance, the average strain energies of pristine



BNS are around 9 and 5 eV under the application of E-fields of 0.5 V/Å and -0.5 V/Å, respectively.

Fig. 4.4 The schematic representations of deformation of BNS subjected to E-field in the (a) positive armchair, (b) negative armchair, (c) positive zigzag and (d) negative zigzag.



Fig. 4.5 The variation of strain energy with time in pristine BNS subjected to E-field in the: (a) armchair and (b) zigzag directions.



Fig. 4.6 The variation of average stabilized strain energy with the E-field applied in the (a) armchair and (b) zigzag directions of pristine and hybrid BNS.

4.4.2 Piezoelectric coefficients of pristine and hybrid BNS

The variation of stress in sheets subjected to the E-field in armchair direction is plotted in Figs. 4.7(a), (b) and (c) for pristine BN, NCB and CHR sheets, respectively. It can be observed from Fig. 4.7 that the axial stresses in sheets first increase with time and then stabilize at a particular time. Prior to calculate the piezoelectric coefficients of sheets, we first validated the results of pristine BNS with the existing results and such comparison is shown in Table 4.1. It can be observed from Table 4.1 that the obtained values of piezoelectric coefficients of pristine BNS herein are in line with the previously reported results (Duerloo et al., 2012; El-Kelany et al., 2015). The good agreement of current results with the existing predictions by DFT and Ab-initio techniques is attributed to the use of three-body Tersoff interatomic potential herein which delivers a reliable description of the interatomic interactions between the B, C and N atoms of SLs of BNS/graphene stripes. Next, to calculate the piezoelectric coefficients of sheets, the average values of stabilized stress and strain at a particular value of E-field were considered. The magnitude of average stresses induced in BNS, NCB and CHR sheet are 22.65 GPa, 15.34 GPa and 7.89 GPa, respectively, for armchair direction case. The respective values are 12.77 GPa, 8.37 GPa and 5.09 GPa for zigzag direction. The average values of different stress and strain in the sheets against E-field are shown in Fig. 4.8. The averaged values of axial stress (σ_{xx}) and strain (ε_{xx}) were used to determine the piezoelectric coefficients d_{11} and e_{11} in the armchair direction of sheets. To calculate the piezoelectric coefficients d_{14} and e_{14} in the zigzag direction of sheets, the averaged values of shear stress (τ_{xy}) and shear strain (γ_{xy})

were used. Figure 4.8 shows the variation in stresses and strains with applied E-field for all the cases. It can be observed from Fig. 4.8 that the negative slope of stress/strain with the E-field is higher for NCB sheet compared to other cases and this leads to its higher piezoelectric coefficients. This is due to the reasons described above. In other cases, the induced resultant dipole moments are less compared to NCB sheet. The obtained values of piezoelectric coefficients of sheets from Fig. 4.8 are summarized in Table 4.1. As expected, the value and direction of piezoelectric coefficients of sheets depend on the direction and magnitude of applied E-field. The influence of interface engineering of BNS/graphene stripes on their piezoelectric coefficients can be seen from the summarized data in Table 4.1 and this is due to the generation of more dipole moments. For instance, the increase in the values of e_{11} in case of NCB and CHR sheets are 25% and 16% compared to pristine BNS. The corresponding values of e_{14} are increased by 18% and 11%. It can be observed from Table 4.1 that the enhancement of piezoelectric coefficients is higher when the E-field is applied in armchair direction of sheet compared to zigzag direction.



Fig. 4.7 The variation of axial stress with time in the (a) BN, (b) NCB and (c) CHR sheets.



Fig. 4.8 Variation of averaged values of (a) axial strain (ε_{xx}) , (b) axial stress (σ_{xx}) , (c) shear strain (γ_{xy}) and (d) shear stress (τ_{xy}) in the sheets under the applied external E-field.

Table 4.1: Comparison of piezoelectric and elastic coefficients of pristine/hybrid BNS with previous studies.

Methods	Sheets	d ₁₁ (pm/V)		e ₁₁ (nC/m)		E (TPa)	
		Present	Ref.	Present	Ref.	Present	Ref.
DFT	Pristine BN sheet	0.402	0.500 (El-Kelany et al., 2015)	1.471	1.500 (El-Kelany et al., 2015) 1.38 (Duerloo and Reed, 2013)	0.634	0.693 (Zhao and Xue, 2013b)
		-	-	-	-		0.639 (Liang et al., 2019)
MD	NCB sheet	-	-	-	-	0.745	0.769 (Eshkalak et al., 2018)

The formation of interfaces in nanostructure can substantially change its mechanical properties as well. To understand the effect of interface engineering of BNS/graphene stripes on the mechanical properties of resulting hybrid BNS, their stress-strain response under the application of E-field is shown in Figs. 4.9(a) and (b). Young's (E_{xx}) and shear (G_{xy}) moduli of sheets were determined from the slopes of stress-strain

curve. The elastic properties of pristine and hybrid BNS are in good agreement with the existing results (Milowska et al., 2013; Zhao and Xue, 2013; Einalipour Eshkalak et al., 2018) and such comparison is shown in Table 4.1. The obtained values of elastic coefficients of pristine and hybrid BNS are summarized in Table 4.2. It can be observed from Table 4.1 that the interface engineering of BNS/graphene stripes improves the elastic properties of resulting hybrid sheets than that of pristine BNS. The reason for enhancing the elastic properties is due to the formation of N-C and C-B bonds in the axial direction of sheet, and the strength of N–C bonds is higher than other bonds in the sheet as it possesses shorter bond length and higher interaction energy than C-B bond. The respective bonding energies of B–N, C–C, C–N and C–B bonds are 389, 607, 770 and 448 kcal/mol (Jungthawan et al., 2011). Therefore, the interaction energy between B and N atoms is much lower than that of all other bonds and hence, the pristine BNS shows marginally lower elastic properties than NCB and CHR cases. Some of the researchers also reported the same for BNS/graphene heterostructures which exhibited higher mechanical properties (Beheshtian et al., 2012; Eshkalak et al., 2018; Eshkalak et al., 2018). The enhancement in the values of Young's moduli of NCB and CHR sheets are found to be 17.50% and 13.72% respectively, and the respective enhancement in shear moduli are 11.83% and 10.30%.



Fig. 4.9 The stress-strain response by applied E-field under (a) armchair and (b) zigzag directions.

C-doped	d ₁₁	d ₁₄	e ₁₁	e ₁₄	E _{xx}	G _{xy}	θ
BNSs	(pm/V)	(pm/V)	(nC/m)	(nC/m)	(TPa)	(TPa)	
BNS	0.402	0.178	1.473	0.890	0.634	0.262	0.21
NCB	0.512	0.214	1.842	1.045	0.745	0.293	0.27
CHR	0.486	0.196	1.705	0.987	0.721	0.289	0.24

Table 4.2: Piezoelectric and elastic coefficients of pristine/hybrid BNS.

4.4.3 Electromechanical response of pristine and hybrid BNS

Note that the doping of foreign atoms results in the breaking of symmetry of parent material and its piezoelectric response may be enhanced (Beheshtian et al., 2012; Noor-A-Alam et al., 2014; Kundalwal et al., 2017). Among all other properties, the net polarization of BNS was found to be very sensitive to the inherent topological defects/doping owing to the interference and quantum mechanisms effects (Zhang and Meguid, 2017). According to the modern theory of polarization, the value and direction of resultant polarization is the vector sum of all elementary dipole moments associated with per unit area of BNS (Dan Tan et al., 2019). Note that the direction of net polarization in BNS under the application of E-field was calculated using Eq. (4.6). The schematic of directions of induced dipole moments in different BNS SLs are shown in Fig. 4.10 The direction of dipole moment points from the negative to positive charge and the red arrow shows the direction of induced dipole moment generated due to the applied external E-field.



Fig. 4.10 Schematic representations of direction of induced dipole moments in: (a) pristine BN, (b) NCB (c) CHR sheets.

The distribution of charges is uniform in the overall pristine BNS except at the edges, while charge distribution in hybrid BNS is mostly around the C atoms and the neighboring B and N atoms as shown in Fig. 4.10. This difference is clearly shown in Fig. 4.11 using the distribution of atomic stresses induced in sheets subjected to the E-field. While inserting C atoms in a SL stripe around N and B atoms, distribution of the charge is not uniform, and such SL of C stripe breaks the uniformity of charges. From this nonuniformity, mostly charges are distributed around N and C atoms due to their higher electronegativity difference and higher electronic charges on N and C atoms as compared to B atoms. With the help of "Mulliken population analysis", due to its large electronegativity, N atoms attracts more electrons from B atoms (Pruneda et al., 2010). Thus, on the BN sheet, the N sites are electron rich and are easily polarized in the particular direction of applied E-field in a way similar to the C atoms (Pruneda et al., 2010). That's the reason NCB and CHR sheet distribute higher stresses on left side as compared to the right side of the hybrid BNS. It can be observed from Fig. 4.11 that the stress generated in NCB and CHR cases is higher than pristine BNS and such higher stress concentration leads to the higher net polarization. Note that the hybrid BNS (NCB and CHR) becomes more non-centrosymmetric solid due to the integration of graphene stripe and its piezoelectric response is enhanced compared to pristine BNS. The obtained net polarizations of different BNS SLs are plotted in Fig. 4.12. Note that the total polarization of BNS constitutes the contributions from both flexoelectricity and piezoelectricity (see Eq. 4.6) and the effect of interface engineering of BNS/graphene stripes on the separate contributions will be discussed in subsequent sections. The permanent polarization can be observed in pristine BNS, and this is due to the sharing of valance electrons of B and N atoms with all neighboring atoms that form strong sigma bonds. In B-N bond, the involvement of electrons is higher from N atoms site due to their higher electronegativity compared to B atoms. Hence, the in-plane dipole moment gets induced (Beheshtian et al., 2012) and the polarization increases with the applied E-field as it can be observed from Fig. 4.12. This is due to the deformation of sheet which is directly proportional to the applied E-field and during the deformation of sheet, the length of polarized bond increases which leads to the change in net atomic polarization (see Fig. 4.11). It may be observed from Fig. 4.12 that the polarization is higher in case of application of E-field in armchair direction than the

zigzag direction. This is attributed to the fact that the dipole moments induced in only *x*direction when the external E-field applied in the armchair direction, while dipole moments induced in the inclined direction from the y-axis in case of application of E-field in zigzag direction; therefore, the net component of polarization in the zigzag direction is less compared to armchair case.



Fig. 4.11 Distribution of induced stresses in (a) pristine BN, (b) NCB and (c) CHR sheets subjected to the E-field in armchair direction. The color-coding indicates the induced atomic stresses in SLs.



Fig. 4.12 The variation of polarization with the E-field applied in the (a) armchair and (b) zigzag directions of different BNS SLs.

It can also be observed from Fig. 4.11 that the change in polarization is higher in case of NCB sheet compared to other cases. Note that in case of NCB, N–C and C–B bonds are around the carbon-rich molecular chain (zigzag graphene stripe), therefore, the induced dipoles, due to both N–C and C–B bonds, are in the same direction which lead to higher atomic polarizations. Moreover, at the interface, zigzag graphene SL has one edge with all N-C bonds and another with all C-B bonds. Therefore, at the interface there are net electron

formations at the C-N edge because the C-B edge is less electronegative compared to the C-N edge (Jungthawan et al., 2011). It can be observed from Fig. 4.10(c) that the direction of induced dipole moments in the CHR sheet is opposite to the applied E-field but in the same direction. At the interface, the hexagonal ring of graphene stripe shows the inversion symmetry and therefore, the dipole moments in it do not get induced. In the CHR sheet, the maximum dipole moments get induced in the atoms located at the interface edges due to the net electron formations at the C-N edge because the C-B edge is less electronegative compared to the C-N edge. It may be observed from Fig. 4.12 that the polarization increases due to the interface engineering of BNS/graphene stripes. The increase in polarization when the E-field applied in the armchair direction of hybrid BNS is found to be 17% and 7% for NCB and CHR sheets, respectively, compared to pristine BNS. The corresponding increase in polarization is around 21% and 10% in the case of application of E-field in the zigzag direction of sheets. The bond length and dipole moments of pristine and hybrid BNS are summarized in Table 4.3. The axial stress in the sheets was evaluated from MD simulation as a function of time.

S. No.	Sheets	Size $(\mathbf{\mathring{A}} \times \mathbf{\mathring{A}})$	B–N	N–C	С–С	С-В	Dipole moment (× 10 ⁻¹⁹ Cm)	
							Armchair	Zigzag
1	BNS	60 Å ×70 Å	1.45	-	-	-	2.486	0.384
2	NCB	$60 \text{ Å} \times 70 \text{ Å}$	1.45	1.41	1.40	1.55	3.112	0.450
3	CHR	$60 \text{ Å} \times 70 \text{ Å}$	-	1.41	1.40	1.55	2.881	0.421

Table 4.3: The bond length (Å) and dipole moments (Cm) for pristine and hybrid BNS.

4.4.4 Flexoelectric coefficients of pristine and hybrid BNS

Furthermore, a converse flexoelectric effect is generated in pristine and hybrid BN sheets to determine their flexoelectric coefficients. The converse flexoelectric effect is an electromechanical coupling in which an inhomogeneous strain is induced by the application of external E-field. To study the effect of interface engineering of BNS/graphene stripes on their flexoelectric coefficients, the E-field was applied only in the armchair direction of sheet because such case showed higher piezoelectricity in it compared to the application of E-field in zigzag direction. To study the flexoelectric response, the sheet was partitioned axially into the rectangular bins to apply the gradual increment of E-field as shown in Fig. 4.13. The value of applied E-field gradient into the

sheet was varied from 0.01 to 0.1 V/Å². The stresses generated in the pristine and hybrid BN sheets due to the applied E-field gradient in their armchair direction were calculated during the simulations and the same are shown in Fig. 4.14 The flexoelectric coefficient was calculated from Eq. (4.7) and the slope of E-field gradient-stress curve. The obtained values of flexoelectric coefficients of pristine and hybrid BN sheets are listed in Table 4.4. Note that the value of flexoelectric coefficient 0.219 pC/m for the pristine BNS is found to be in good agreement with the value reported by (Zhuang et al., 2019). The flexoelectric coefficient of hybrid BNS is higher than pristine one and this due to the fact that the former becomes more non-centrosymmetric solid due to the integration of graphene stripes. This results in the higher strain gradient induced polarization in the hybrid BNS due to the applied E-felid. It is observed that the NCB sheet shows the higher flexoelectric coefficient and this is again attributed to the larger energy difference for zigzag graphene stripe due to coulomb interactions between the edges as well as reasons described above. The enhancement in the flexoelectric coefficients due to the interface engineering of BNS/graphene stripes is 37% and 18% for NCB and CHR sheets, respectively.



Fig. 4.13 Schematic representation of the partitioned BNS axially into the rectangular bins.

Chapter 4



Fig. 4.14 The variation of stress with E-field gradient for different BN sheets.

Table 4.4: Flexoelectric coefficients of pristine and hybrid BN sheets.

C-doped	BNSs	BNS	NCB	CHR
	Present	0.219	0.3	0.259
μ1111 (pC/m)	Ref.	0.26		
		(Zhuang et al., 2019)	-	-

4.4.5 Effect of SW defects on the electromechanical response of BNS

The BNSs are being synthesized using several unique techniques: mechanical and liquid exfoliations, thermal decomposition, chemical synthesis, chemical vapor deposition (Song et al., 2013). Due to the inherent limitations of fabrication processes of BNS, topological defects exist in them, that is, Stone-Wales (SW) and substitutional impurities (Khan et al., 2016), and atom vacancies (Liang et al., 2019). These defects make the local changes in the atomic polarization and chemical bond orders of BNS which lead to a change in their electromechanical response [Khan et al. (2016) and references therein]. As far as the defects of BN structures are concerned, it is widely accepted that the adjacent pentagon-heptagon pairs (SW defects) in them generate less favorable homo-elemental bonds such as B–B and N–N bonds, and the high energy of the frustrated B–B and N–N bonds make BN systems structurally unstable (Zhi et al., 2010). Therefore, we considered only SW defects herein to understand role of topological defects on the piezoelectric behavior of BNS. The SW defects in the BNS were formed by rotating one of the B-N bonds by 90° from the pristine BNS as shown in Fig 4.15. The density and position of SW defects play a critical role on the electromechanical response of 2D materials (Choyal and Kundalwal, 2020), therefore, we considered two cases: (i) double SW defects with 26 Å

apart (BNS@2SW), and (ii) four SW defects with 36 Å apart (BNS@4SW), as shown in Figs. 4.15(a) and (b), respectively.



Fig. 4.15 Schematic representations of BNS with SW defects: (a) BNS@2SW and (b) BNS@4SW.

The simulation methodology is same. The average values of stress and strain in the pristine and SW defected BNS against applied E-field are shown in Fig. 4.16. It can be observed from Fig. 4.16 that the slope of stress and strain curves of SW defected BNS is slightly higher compared to pristine BNS, and this leads to higher values of piezoelectric coefficients of SW defected BNS (see Table 4.5). The enhancement in the electromechanical response of defected BNS is attributed to the formation of SW defect that leads to the higher charge redistribution around the region of defect and the defected BNS becomes more non-centrosymmetric solid compared to pristine BNS.



Fig. 4.16 Variation of averaged values of axial (a) stress (σ_{xx}) and (b) strain (ε_{xx}) in the pristine and SW defected BNS under the applied external E-field.

S. No.	Sheets	d ₁₁ (nC/m)	e ₁₁ (nC/m)	E _{xx} (TPa)
1	BNS@2SW	0.44	1.52	0.618
2	BNS@4SW	0.51	1.61	0.604

Table 4.5: The elastic and	piezoelectric	coefficients	of BNS	with SW defects.
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4.4.6 Effect of temperature on the electromechanical response of BNS

We considered four different temperature steps (100, 300, 500, and 700 K) to examine the effect of temperature on the elastic and piezoelectric properties of pristine and hybrid armchair BNS. The temperature was increased from 0 to 700 K by keeping the application of constant strain rate on BNS. The variation of Young's modulus (E_{xx}) and piezoelectric coefficient (e_{11}) of pristine and hybrid BNS are shown in Fig. 4.17 and it can be observed that the values of E_{xx} and e_{11} decrease with increase in temperature. The BNS becomes softer and less stiff when the temperature increases. This is attributed to the fact that the thermal vibration of BN atoms becomes more vigorous leading to a larger vibration amplitude of atoms around their equilibrium positions (Han et al., 2014; Choyal and Kundalwal, 2020) with the increase in temperature and thus, the total kinetic energy increases. In case of piezoelectric properties, the polarization of material generally decreases as the temperature increases and it is completely lost when the temperature increases to the so-called Curie temperature (Hong et al., 2010).



Fig. 4.17 Variation of elastic and piezoelectric properties of pristine and hybrid BNS with different temperature: (a) Young's modulus (E_{xx}) and (b) axial piezoelectric coefficient (e_{11}) .

4.5 Conclusions

In this chapter, the investigation of converse piezo- and flexo-electric effects of hybrid and SW defected BNS under the application of external electric-field (E-field) was carried out. Hybrid BNS was formed by integrating two graphene SLs, namely, zigzag stripe and hexagonal ring of graphene via coherent interface engineering. We performed systematic and comprehensive MD simulations using the three-body Tersoff potential force field. An E-field was applied in the two most relevant orientations of hybrid BNS, i.e., armchair and zigzag, to determine their axial and shear piezoelectric coefficients. The piezoelectric, flexoelectric and elastic coefficients of pristine/hybrid BNS were compared with the existing results and good agreement was found. The following main conclusions are drawn from the current chapter:

- The interface engineering of BNS/zigzag graphene stripe improved the axial piezoand flexo-electric coefficients of hybrid BNS under the application of E-field in its armchair direction by 25% and 37%, respectively, compared to pristine BNS. The corresponding enhancement in the coefficients was observed as 18% and 16% due to the interface engineering of BNS/hexagonal ring of graphene stripe.
- When the E-field applied in the armchair direction of hybrid BNS, the increase in total polarization is around 17% and 7% for NCB and CHR sheets, respectively, compared to pristine BNS due to the interface engineering of BNS/zigzag graphene stripe. The corresponding increase in total polarization is 21% and 10% in the case of E-field applied in the zigzag direction of hybrid BNS.
- The enhancement in the values of Young's moduli of NCB and CHR sheets are found to be 17.50% and 13.72% respectively, compared to pristine BNS. The respective enhancement in shear moduli is 11.83% and 10.30%.
- The density and position of SW defects play a critical role on the overall electromechanical response of BNS. SW defect improves the polarization of BNS, and the converse is true for elastic properties.
- Both elastic and piezoelectric properties are inversely proportional to the temperature.

The unique properties of BNSs accompanied by their excellent defect/pores and chemical stabilities make them attractive nanomaterials in the applications where atomic polarization and chemical bond order come into the picture. This chapter studied the electromechanical response of fixed size of pristine and hybrid BNS via an external applied electric field in both armchair and zigzag direction (via indirect approach). The out-of-plane polarization and bending stiffness of BNSs/BGHs under bending deformations were calculated using MD simulations in the next chapter.

5. Chapter

Flexoelectric effect in boron nitridegraphene heterostructures

In this chapter, the flexoelectric coefficients of monolayer boron nitride-graphene heterostructures (BGHs) are determined using MD simulations. This was achieved by imposing the bending deformation to the pristine BNS and BGHs. This chapter demonstrates the enhancement in the flexoelectric coefficient and bending stiffness of BGH when the graphene domain breaks its symmetry. The finding of this work can be utilized for engineering the behavior of BNS/BGHs structures.

5.1 Introduction

The BNS with a honeycomb crystal lattice is graphene's sister material, yet it exhibits totally different properties. While the graphene is a semimetal, the BNS is a piezoelectric dielectric due to a broken sublattice (inversion) symmetry and corresponding degeneracy lifting of the conduction and valence bands at two inequivalent Dirac points (Naumov et al. 2009). Moreover, unlike the piezoelectricity, flexoelectric effect is universal in all dielectrics since the strain gradient breaks the inversion symmetry. The stress induces separation of the centers of gravity of the positive and negative charges creating a dipole moment in materials. The resulting dipole moment produces a polarization and materials shows the piezoelectric effect. This behavior explains the sensing ability of piezoelectric material. Fig. 5.1 shows the BN unit cell to illustrate the piezoelectric effect, and the arrows next to the charges shown in Fig. 5.1 indicate the direction of motion of the charges and polarization. Curvature-induced polarization can be applied to induce the flexoelectric effect in monolayer BNS/BGH. As a result of bending of sheet, Coulomb repulsion inside a cavity increases with curvature and it leads to a redistribution of the π -orbitals. This results into an electronic charge transfer from the concave to the convex region and induces the normal atomic dipole at each atomic site. Note that there is no dipole moment across the flat BNS due to the symmetry of π -orbitals (see Fig. 5.1(d)). By bending the sheet, we can introduce asymmetry in the π -orbital overlap

(see Fig. 5.1(e)). Therefore, Coulomb repulsion inside the cavity increases with curvature and leads to a redistribution (rehybridization) of the π -orbitals from the sp² to something intermediate between sp² and sp³. Figure 5.1(e) demonstrates that the B and N atoms in the bent BNS are not in the tangential plane, and the three σ_i – bonds (i = 1, 2, 3) are tilted down with respect to that tangential plane. Redistribution of ions and charges occur upon bending of BNS, which results in the formation of a net dipole moment across the BNS. The resulting dipole moment produces a polarization, and BNS shows the flexoelectric effect.



Fig. 5.1 (a) Stress-free BN lattice, (b) tension stress BN lattice, (c) compression stress BN lattice, (d) BNS in which π -orbitals are symmetric, and (e) bent BNS in which π -orbitals are symmetric.

Heterostructures are often expected to provide better electronic properties than homogeneous structures. The ability to control the formation of interfaces between different monolayers has become one of the foundations of modern materials science. With the advent of 2D crystals, low-dimensional equivalents of conventional interfaces can be envisioned: triangular, trapezoidal and circular boundaries separating different materials integrated in a single 2D heterostructure (Sutter et al., 2012).

The literature review reveals that few investigations exist on BNSs under in-plane and out-of-plane loads to study their electromechanical response. There is no single study exists on the out-of-plane polarization and flexoelectric effect in monolayer boron nitridegraphene heterostructures (BGHs). This has inspired us to conduct this study to determine the electromechanical response of BGHs with different shapes graphene domains triangular, trapezoidal, and circular. The out-of-plane polarization and bending stiffness of BGHs under uniaxial and bending deformations were determined using MD simulations.

5.2 Computational modelling of BGHs

MD simulations were performed in the current study to study the electromechanical response of pristine BNS and BGHs. All MD simulations were performed using opensource software, LAMMPS (Plimton, 1995), and visualization is performed using OVITO visualization software (Stukowski et al., 2010). It is well known that for MD simulations of BGH systems, it is crucial to accurately describe the interatomic interactions between B, C and N atoms. The interatomic interactions between B, C and N atoms. The interatomic interactions between B, C and N atoms were described using the three-body Tersoff potential force field (Tersoff, 1989, 1988). The total energy (*E*) of the atomic structure is a function of the distance between two neighboring atoms *i* and *j*, as follows:

$$E = \sum_{i} E_{i} = \frac{1}{2} \sum_{i \neq j} V_{ij}$$
(5.1)

$$V_{ij} = f_{C}(r_{ij})[f_{R}(r_{ij}) + b_{ij}f_{A}(r_{ij})]$$
(5.2)

where *E* is the total energy of the system, E_i is the site energy and V_{ij} is the bond energy. The indices *i* and *j* run over the atoms of the system. Term r_{ij} is the distance between atom *i* and *j*, while b_{ij} is the bond angle term which depends on the local coordination of atoms around atom *i*. Terms f_R and f_A are the repulsive and attractive pair potentials, respectively.

First, preliminary structures of BNSs were created with a bond length of 1.446 Å (Amalia et al., 2019). Then, the primary structures of BNSs were optimized by minimizing their energy using the conjugate gradient method. The structure was treated as optimized when the difference in its total potential energy between two consequent steps was less than 1.0×10^{-10} kcal/mol. The NVT ensemble was used to update velocities and positions of B and N atoms after each time step of 0.5 fs using the Nosé-Hoover thermostat (Evans and Holian, 1985). NVT is the constant number of atoms, temperature and volume ensemble, and during the simulation, it allows to maintain the constant temperature by scaling the velocities of atoms in a fixed volume. The simulations were performed with a periodic

boundary condition in all directions of the sheet, and the simulation box was kept large enough to avoid the interlayer interactions. To perform the bending deformation, a BNS/BGH sheet was divided into vertical rectangular bins. For bending deformation, a strain gradient was applied on each vertical rectangular bins for a period of 1 ps, following a relaxation of 50 ps for the equilibration. At each vertical rectangular bin, deformation gradually increases from left to the middle section of the sheet, and maximum deformation occurs in the middle portion of the vertical rectangular bins. The bending deformation mainly depends on the bending curvature (non-uniform strain gradient on each bin). The standard velocity Verlet algorithm was used to integrate Newton's equations of motions. The flat BNS was bent along the z-direction while both left and right edges were fixed. The schematic representation of the flat and bent configurations of BNS are shown in Fig. 5.2 respectively.



Fig. 5.2 Schematic representation of (a) flat BNS and (b) bent BNS.

5.2.1 Curve fitting

The present study deals with the bending deformation of BNS/BGH from that we can directly calculate flexoelectric coefficients by eliminating the piezoelectric terms from the overall polarization. The radius of curvature, R, is used to analyze the bending deformation of BNS/BGH. Term, k, denotes the strain gradient, which is inverse of the bending curvature R. Figure 5.2 depicts the curve fitting of a bending configuration of BNS when the curvature radius is 111.11 Å. The strain and strain gradient curves can be

calculated from the displacement fitting relations described by Tan et al. (2020).

The curve fitting relation of the bending displacement of a point in BNS/BGH may be expressed as follows:

$$S_z(x) = -px^2 + q$$
 (5.3)

where p and q denote the parameters of curve fitting which can be calculated from the following relations:

$$\frac{1}{R} = k = \left| \frac{\partial^2 S_z(x)}{\partial x^2} \right| = -2p$$
(5.4)

$$S_z(x_{max}) = -px_{max}^2 + q = 0$$
 (5.5)

Using Eqs. (5.3-5.4), we can obtain the value of $p = \frac{k}{2}$ and $q = \frac{k}{2}x_{max}^2$, where x_{max} is half of the length L_x of BNS/BGH along the direction of x.

The strain components, ε_{xz} , can be calculated as follows:

$$\varepsilon_{\rm xz} = \frac{1}{2} \frac{\partial S_{\rm z} \left({\rm x} \right)}{\partial {\rm x}} = -\frac{{\rm k}}{2} {\rm x} \tag{5.6}$$

It is important to note that the displacements of atoms during bending deformation are along the principal curvature direction and we can get a unique solution of atomic displacement along the z-axis $S_z(x) = 0$, and therefore, $\varepsilon_{xz} = 0$. As the strain depends on both k and x, a larger strain is obtained by enlarging the bending curvature or the length of 2D nanomaterial along the x-axis.

Strain gradients depend on the curvature of sheets. In the present case, only the nonvanishing strain gradient component is constant and can be expressed as:

$$\frac{\partial \varepsilon_{\rm xz}}{\partial \rm x} = \left| -\frac{\rm k}{2} \right| \tag{5.7}$$

The dipole moment induced due to the redistribution of atomic charges under the bending deformation and the resulting polarization can be calculated using the following relation (Tan et al., 2020):

$$P = \sum_{i}^{N} \frac{q_{i}r_{i}}{A}$$
(5.8)

where q_i denotes the ion charge of the *i*th atom, r_i is the *x*-coordinate of the *i*th atom, *N* is the number of atoms, and *A* is the flat sheet area (Tan et al., 2020). The Eq. (5.8) was used to calculate the induced polarization along *x*- and *z*-directions of BNSs/BGHs. From the

modern theory of atomic polarization, the value and direction of total polarization represent the vector sum of all elementary dipoles moments associated with per unit area of BNS (Dan Tan et al., 2019). To determine the normal polarization, the vertical rectangular bins are cut into several parts along the x- and y-axes to calculate normal polarization distribution.

Flexoelectricity can be found in all insulators; therefore, the polarization can be induced by applying inhomogeneous deformation. The flexoelectricity is a coupling between polarization and strain gradient while piezoelectricity is a coupling between the polarization and homogeneous strain. The constitutive relation for the polarization vector induced due to the flexo- and piezo-electricity effects may be written as:

$$P_{i} = e_{ijk}\varepsilon_{jk} + \mu_{ijkl}\frac{\partial\varepsilon_{jk}}{\partial x_{l}}$$
(5.9)

where e_{ijk} and μ_{ijkl} are the respective piezoelectric and flexoelectric tensors; ε_{jk} and $\frac{\partial \varepsilon_{jk}}{\partial x_l}$ are the strain and strain gradient, respectively.

Substituting Eq. (5.7) in Eq. (5.9) and assuming that the imposed mechanical deformation in Eq. (5.10) removes the piezoelectric contribution, we can obtain

$$P_{i} = \mu_{ijkl} \frac{\partial \varepsilon_{jk}}{\partial x_{l}}$$
(5.10)

$$P_{z} = \mu_{zxzx} \frac{k}{2} \tag{5.11}$$

where μ_{zxzx} is the out-of-plane or bending flexoelectric coefficient and P_z represents the out-of-plane polarization. To generate the out-of-plane flexoelectric constants, the mechanical bending imposed to sheet deforms the sheet in the z-direction, and due to that, polarization is induced in the z-direction that is called out-plane-polarization (P_z). The mechanical bending imposed only generate a constant strain in the x-direction due to applied deformation in the z-direction. The stress in x-direction led to generate a polarization (P_x) in x-direction called in-plane polarization. The in-plane polarization P_y in the y-direction is less than the in-plane polarization P_x at a particular bin because significantly less deformation occurred in the y-direction during bending.

5.2.2 Bending stiffness of BNS

Based on the continuum mechanics approach, the bending stiffness (*D*) of BNS/BGH can be determined from the bending potential energy (ΔE) using the following relation (Xiong and Cao, 2015):

$$\Delta E = \frac{1}{2} A D R^{-2} = \frac{1}{2} A D k^2$$
 (5.12)

where A is surface area of BNS/BGH under bending deformation, k is the bending curvature and R is the bending curvature radius.

5.3 Results and discussions

MD simulations were performed to determine the electromechanical response of armchair BNS subjected to out-of-plane deformation. A fixed size of 80 Å × 80 Å of BNS was considered for simulations. A schematic representation of flat and bent armchair BNSs are shown in Fig. 5.2, respectively. A bending curvature range is considered from 0.001 Å⁻¹ to 0.009 Å⁻¹. First, the MD simulations were performed on the pristine BNS to determine the electromechanical response for different bending curvatures. Further calculations were performed on different BGHs to determine induced polarizations, flexoelectric coefficients (along *x* and *z*-direction) and bending stiffness.

We first considered bending scheme that eliminates the contribution of piezoelectric effect from the total polarization to calculate the intrinsic flexoelectric coefficients. We obtained the strain (ε_{xz}) and strain gradient $\left(\frac{\partial \varepsilon_{xz}}{\partial x}\right)$ in the *xz* direction by solving the curve fitting Eq. (5.3). During bending deformation, the local atomic strain for each atom *i* can be calculated using the local deformation gradient F, and it depends on the initial and final coordinates of atoms. The local atomic strain tensor for atom *i* is as follows:

$$\varepsilon_{i} = \frac{1}{2} \left[(F_{i})^{T} F_{i} - I \right]$$
 (5.13)

where the term F_i represents the strain gradient, which provides the initial and final deformed coordinates of atoms, and a term *I* represents the identity matrix. We performed bending deformation of BNS at a bending curvature of 0.001 Å⁻¹ by following the simulation procedure described in section 5.2. The value of strain (ε_{xz}) and strain gradient (*k*) were obtained using curve fitting (Fig. 5.3(a)). Figures. 5.3(b) and (c) demonstrate the variation of strain (ε_{xz}) and strain gradient (*k*) with the position of *x*-axis of BNS. The

variation of strain in x-direction of BNS during deformation is shown in Fig. 5.3(d) which is obtained using Eq. (5.13). To solve the curve fitting Eq. (5.3), a parabolic fitting curve can be obtained from the bending displacement of atomic system, as shown in Fig. 5.3(a). This fitting curve mainly depends on the bending deformation that leads to the induced the polarization, which was also described in previous studies for dichalcogenides, Silicene, and MoS_2 (Javvaji et al., 2019; Zhuang et al., 2019). The strain was obtained by dividing the atomic system of BNS into several bins of equal width, and the average strain of each bin was recorded. The obtained value of strain was plotted in Fig. 5.3(b), and it can be observed that the strain (ε_{xz}) varies linearly along the direction of x from -0.2 to 0.2 of the BNS. The linear negative variation of (ε_{xz}) was observed, which follows the curve fitting Eq. (5.6). It can be observed from Fig. 5.3(b) that the induced deformation is symmetric, and the resultant polarization due to strain is canceled out. Hence, the total strain (ε_{xz}) is almost zero (overall summation of the strain of each bin), which removes the contribution of piezoelectric effect from the polarization in Eq. (5.9) and it satisfies the assumption considered in obtaining Eq. (5.10). Therefore, during bending deformation, the out-ofplane polarization completely depends only on the strain gradient $\left(\frac{\partial \varepsilon_{xz}}{\partial x}\right)$. The strain gradient $\left(\frac{\partial \varepsilon_{xz}}{\partial x}\right)$ varies along the direction of x plotted in Fig. 5.3(c). The obtained value of strain gradient along the *xz*-direction is constant at each time step.



Fig. 5.3 (a) Curve fitting, (b) strain (ε_{xz}), (c) strain-gradient (k) and (d) colored atomic configuration of induced atomic strain in the direction of x of BNS at a bending curvature of 0.001 Å⁻¹.

Variation of induced polarizations along *x*- and *z*-directions of BNS at bending curvatures of 0.006 Å⁻¹ and 0.001 Å⁻¹ are plotted in Fig. 5.4. Due to the difference in the electronegativities of B and N atoms, the net dipole moment is induced, and it is the summation of each dipole moment. We considered respective charges of B, N and C atoms as +3 eV, -3 eV and +2.5 eV with the multiplication of deformed coordinates of atoms along *x*- and *z*-directions of BNS (at each time step). In Fig. 5.4, green and yellow arrows show the direction and amplitude of polarization which mainly depend on the bending curvature. It can be observed from Fig. 5.4 that the magnitude of polarization along the *z*-direction is much higher than the *x*-direction. During bending deformation, the magnitude of the induced polarization along the *y*-direction is negligible, therefore, it is not considered. The previous studies also reported that the curvature induced charge distribution is present in 2D nanomaterials such as graphene sheet, graphene nanoribbons, BNS and MoS₂ (Naumov et al., 2009; Kundalwal et al., 2017; Tan et al., 2020). The

mechanical bending was imposed to generate both out-of-plane and in-plane polarizations along the x- and z-directions of BNS. During bending, a strain gradient was induced along the z-direction of BNS which eventually generates out-of-plane polarization.



Fig. 5.4 Variation of induced polarizations along x- and z-directions of BNS at bending curvatures of (a) 0.006 Å^{-1} and (b) 0.001 Å^{-1} .

The term "flexoelectricity" defines the two-way linear coupling between the electric polarization and the strain gradient (Li et al., 2019). In the case of 2D nanomaterials, bending is the easiest form of deformation to determine a mechanical strain gradient. Upon bending of polar (BNS) materials, the symmetry of the electron distribution breaks in the out-of-plane direction, and a resultant dipole moment is generated at N atomic site (Ahmadpoor and Sharma, 2015). It can be observed from Fig. 5.5 that the polarization (P_z) depends on the bending curvature k (strain gradient). The flexoelectric coefficient was calculated from Eq. (5.10), and the slope of polarization and strain gradient provides the flexoelectric coefficients (μ_{zxzx}) along the principal curvature direction. It can also be observed from Fig. 5.5 that the out-of-plane polarization using MD simulations fitted suitably into the polarization using the curve fitting technique. The flexoelectric coefficients of pristine BNS reported by numerous researchers using different techniques and the present results are summarized in Table 5.1. The value of the flexoelectric coefficient of pristine BNS is 0.255 pC/m and shows excellent agreement with the value of 0.260 pC/m obtained by Zhuang et al. (2019) using C-D potential model. Snapshots of bending deformation at bending curvature 0.001 Å⁻¹ of pristine BNS with side, top and ortho views are illustrated in Fig. 5.6. It can be observed from Fig. 5.6 that the density of charges gets appeared on each B and N atoms during bending and such distribution of charge density is uniform in the overall pristine BNS except at the edges (see Fig. 5.6). The number of electrons is condensed more around the N atoms than B atoms due to former's higher electronegativity, which leads to induce the dipole moments in BNS. In the present study, the difference in charge density is calculated by subtracting the superposition of isolated atomic charge densities from the corresponding BNS's total charge density (after deformation at each time step). In the previous studies, DFT calculations provided significant in-plane polarization and out-of-plane atomic displacement for a corrugated BNS which mainly depends on shifting of π and σ chemical bonds (Zhuang et al., 2019). The minimal difference in out-of-plane displacements of B and N atoms (Moon and Hwang, 2004; Wirtz and Rubio, 2004) leads to relatively small out-of-plane dipole moments and also suggests that out-of-plane $\pi - \sigma$ interactions are stronger, which makes μ_{zxex} is higher than μ_{xxex} . The present calculations of induced polarization and flexoelectric coefficients of pristine BNS are in good agreement with the present results obtained using the state-of-the-art ab initio method (Duerloo et al., 2012) and MD simulations (Zhuang et al., 2019).



Fig. 5.5 Variation in polarization (P_z) with strain gradient (k) for pristine BNS.





Fig. 5.6 Snapshots of distribution of charge densities: side, top and ortho views of pristine BNS under bending deformation at bending curvature of 0.001 Å⁻¹.

5.3.1 Electromechanical response of BGHs

Interface engineering and dopant engineering allows researchers to modify the mechanical and electronic properties of numerous nanomaterials for some specific applications. In the present study, graphene domains interfaced with BNS in such a way that non-centrosymmetric interface of graphene-BNS can be created in resulting monolayer heterostructure (see Fig. 5.7). All C atoms at the interface are partially covalent with N atoms. Integration of graphene domains with BNS was considered because B, C and N atoms have the same planar sp² hybridization (Beheshtian et al., 2012). To examine the effect of different graphene domains, four cases of armchair BNSs were considered: pristine, circular graphene domain, triangular graphene domain and trapezoidal graphene domain. Schematic representations of these structures are shown in Fig. 5.7. Note that a constant C-doping concentration of 5.6% was considered. The doping concentration is the ratio of number of C atoms to the total number of atoms in the sheet.



Fig. 5.7 Schematic representations of (a) pristine BNS, (b) BGH with circular graphene domain, (c) BGH with triangular graphene domain and (d) BGH with trapezoidal graphene domain.

The explicit simulations were performed with 5.6% concentration of graphene domain (Kundalwal et al., 2020) irrespective of shape of domain. Note that graphene domain concentration is the ratio of C atoms in BGH to the total number of atoms in pristine BNS. During the in-plane movement, the low polarization was occurred in BGH due to the strain gradient at the graphene-BNS interface. However, once BGH is bent, the $\pi - \sigma$ interactions begin to increase, which induces a net non-zero dipole moments normal to the sheet. In the out-of-plane displacement, the inversion symmetry of graphene domain breaks due to its bending, leading to $\pi - \sigma$ interactions. Therefore, $\pi - \sigma$ interactions modify the charge density state of C atoms which induces polarization (Dumitrică et al., 2002; Kundalwal et al., 2017). It is important to note that during the out-of-plane displacement, planar hybridization of BNS is in between sp² to sp³ hybridization (Naumov et al., 2009). This results in partial ionic charges transfer from a concave to convex region (Kundalwal et al., 2017). This is also in good agreement with the recent study on graphene sheet and BNS where the polarization was calculated using DFT (Kundalwal et al., 2017), MD (Zhuang et al., 2019) and ab-initio simulations (Kundalwal et al., 2017).

Furthermore, the flexoelectric effect of BGH was studied by considering out-ofplane polarization, P_z , plotted as a function of k as shown in Fig. 5.8. Snapshots of the distribution of charge densities of BGHs (with triangular, trapezoidal and circular graphene domains) for the bending curvature of 0.001 Å⁻¹ of BGH are illustrated in Fig. 5.9. As expected, with increasing k, the induced polarization also increases due to the asymmetry of π orbitals on C and N atoms. The flexoelectric coefficients of BGHs were obtained from a linear fitting of polarization as a bending curvature function, listed in Table 5.1. It can be observed from Fig. 5.8 that the bending of BGHs with triangular and trapezoidal graphene domains provides higher out-of-plane polarization (P_z) due to the breaking of symmetry of π orbitals of C atoms compared to the in-plane polarization (P_x) induced due to the straingradient polarization arised from non-centrosymmetric interface of graphene-BNS domains. It can also be observed that more N atoms in BNS that are partially covalently bonded with C atoms (see Fig. 5.9) induces more dipole moments due to higher electronegativity differences in C–N bonds than C–B bonds. This leads to higher out-ofplane polarization in BGH (see Fig. 5.9). It can be observed from Figs. 5.9(a) and (b) that the distribution of charge density of triangular and trapezoidal cases is divided into two parts: (i) uniform in the overall BNS except at the edges and (ii) at C-N covalently bonds. The distribution of charge density in BGH is mostly around the C and N atoms due to higher deformation of C–N bonds and higher electronegativity of N atoms than B atoms (see Figs. 5.9(a) and (b)). It can also be observed from Figs. 5.9(a) and (b) that during outof-plane displacement, inversion symmetry of C-C atoms breaks which improves the induced dipole moments for the triangular and trapezoidal cases. The enhancement of 15.28% and 7.83% was observed in the value of flexoelectric coefficient (μ_{zxzx}) of BGH with triangular and trapezoidal graphene domains along z-direction, respectively, while reduction of 25% was observed for the circular graphene domain in BNS. This is attributed to the fact that circular graphene domain does not break the symmetry of BGH. Therefore, the induced dipole moments across the circular graphene-BNS interface are found to be symmetric and get canceled out of each other (see Fig. 5.9(c)). The enhancement of 2.95% and 2.83% was observed in the value of flexoelectric coefficients (μ_{xxxx}) of BGH with triangular and trapezoidal graphene domains along the x-direction, respectively, while reduction of 7.62% was observed for the circular case.


Fig. 5.8 The variation of (a) polarization in the z-direction (P_z) and (b) polarization in the x-direction (P_x) with strain gradient k for pristine BNS and BGHs.

Properties		Drigting DNS	BGHs			
		I listile Divo	Triangular	Trapezoidal	Circular	
	Present	0.255	0.309	0.289	0.201	
μ _{zxzx} (pC/m)	Ref.	0.26 (Zhuang et al., 2019)	-	-	-	



Fig. 5.9 Snapshots for distribution of charge densities: side, top and ortho views of BGHs with (a) triangular, (b) trapezoidal, and (c) circular graphene domains under bending deformation at bending curvature of 0.001 $Å^{-1}$.

Moreover, we also studied the bond length variation of BGHs at different bending curvatures. The schematic representation of bond length (Å) variation for different BGHs is demonstrated in Fig. 5.10 at a fixed bending curvature of 0.001 Å⁻¹. It is worth noticing that the bending modifies the bond length and accordingly, the inversion symmetry of π orbitals of C and N atoms breaks differently (see Fig. 5.10). In case of pristine BNS, B–N bond length (Å) variation ranges from 1.446 Å to 1.450 Å. While in the case of BGH, B–N, C–B, C–C, and C–N bond length (Å) variations are 1.446 Å to 1.450, 1.421 Å to 1.436 Å, 1.421 Å to 1.434 Å, and 1.446 Å to 1.463 respectively. Such bond length variation mainly depends on the distribution of charges on B, C and N atoms.



Fig. 5.10 Schematic representations of variation in bond length (Å) *for BGHs with: (a) triangular, (b) trapezoidal and (c) circular graphene domains at bending curvature of 0.001* Å⁻¹.

5.3.2 Bending stiffness of BNSs/BGHs

In the previous sets of outcomes, electromechanical response of 80 Å × 80 Å BNS/BGH was studied for a constant 5.6% graphene domain concentration. Further, MD simulations were performed to determine the bending stiffness of BGHs. Figure 5.2 demonstrates the bending response of BNS/BGH along the principal curvature direction. The variation of potential energy of pristine BNS and BGHs follows a quadratic bending energy relationship between ΔE , and k as given by Eq. (5.12). It can be observed from Fig. 5.11(a) that during bending displacement, higher potential energy is stored in the middle portion of the rectangular bins of BNS/BGH because of their higher deformation, and it reduces with the fixed ends of the BNS/BGH (left and right sides of the rectangular bins). It can also be observed from Fig. 5.11(a) that the potential energy of triangular, trapezoidal, and circular cases increases because covalent C–C bonds of graphene domains show strong π and σ interatomic interactions compared to pristine BNS. Note that B–N bonds of BNS possess weak π and σ interatomic interactions due to the difference of electronegativities of B and N atoms (Ansari et al., 2015; Xiong and Cao, 2015). Therefore, BGH stores higher potential energy compared to pristine BNS at the same value of strain gradient, which is in good agreement with the existing outcomes (Thomas et al., 2015).



Fig. 5.11 The variation of (a) potential energy and (b) bending stiffness of BNS and BGHs under different bending curvatures.

Properties		Brighting BNS	BGHs			
		Frisulie DINS	Triangular	Trapezoidal	Circular	
Bending	Present	1.25	1.69	1.42	1.33	
stiffness (eV)	Ref.	1.2-1.4 (Gao and Xu, 2015; Thomas et al., 2015)	-	-	-	

Table 5.2: Bending stiffness of pristine and C-doped BNS.

The bending stiffness is one of the essential mechanical properties of membranes and layered structures. From the previous studies, it was identified that the bending stiffness of SL BNS depends on the different parameters such as chiral angle, chirality and bending curvature (Ma et al., 2011). The bending stiffness of BNS/BGH increases when the bending curvature increases as shown in Fig. 5.11(b). BGHs show higher bending stiffness due to the integration of graphene domains at approximately 1.35-1.68 eV while partially ionic B–N bonds show less bending stiffness around 1.2-1.4 eV (Gao and Xu, 2015; Thomas et al., 2015) because of electronegativity difference of B and N atoms. Bending stiffness of BNSs reported by numerous researchers using different techniques and approximation was compared with present results, listed in Table 5.2.

Several theoretical (Naumov et al. 2009; Kang et al. 2018) investigation reported that the large corrugations in the out-of-plane direction occur due to the weaker B–N atomic bonds (see Fig. 5.12(b)). Due to this, the partial ionic characteristic in the BNS layer increases interlayer interactions, leading to an enhancement of magnitude of the hardness of 2D bulk BNSs compared to the graphene layers. Therefore, the bending stiffness of SL BNS is less as compared to the graphene sheet (Scarpa et al., 2010) and graphene domains can be integrated into the BNS to reduce its hardness. The lowest bending stiffness of 1.25 eV is obtained for pristine BNS due to the partially ionic B–N bonds. The respective bending stiffness of BGH with triangular, trapezoidal, and circular graphene domains was observed as follows: 1.69 eV, 1.42 eV and 1.33 eV. The values of bending stiffness of BGH with triangular, trapezoidal, and circular graphene domains are enhanced by 35.40%, 13.72% and 6.54%, respectively, along the curvature direction. This observation is also interesting that curvature induced anisotropy of BNS must be carefully considered in engineering applications.



Fig. 5.12 Side view of flat and corrugated nanostructures of BGHs.

5.4 Conclusions

In this chapter, a novel flexoelectric effect in monolayer boron nitride-graphene heterostructures (BGHs) was comprehensively studied using MD simulations with a Tersoff potential force field. Graphene domains with 5.6% of area fraction were interfaced with BNS in different shapes: triangular, trapezoidal, and circular. Systematic bending deformations were performed on BNS/BHGs to study the bending stiffness and electromechanical coupling attributed to the piezo- and flexo-electric effects. First, the bending stiffness and flexoelectric coefficients of pristine BNS were compared with the previous results and we found good agreement between present and existing results. The present results reveal that electromechanical coupling of BGHs is enhanced due to the outof-plane bending compared to in-plane stretching. During bending, the induced atomic polarization along the z-direction of BNS/BGH is higher compared to the x-direction. As bending curvature increased, the induced polarization and bending stiffness of BNS/BGHs is also increased. Flexoelectric coefficients of BGHs with triangular and trapezoidal graphene domains are increased while the reverse is true in case of circular graphene domain compared to pristine BNS. A BGH with a triangular graphene domain showed higher polarization than BNS as well as BGH containing other graphene domains. An integration of graphene with N atoms of BNS results in higher dipole moments because the C-N bond is more electronegative than the C-B bond. BGHs with triangular, trapezoidal, and circular graphene domains showed higher bending stiffness than pristine BNS.

Multi-layered (ML) BNSs are preferred for reinforcing nanocomposites over SL-BNSs since the latter is less stable. The elastic properties and fracture behaviour of ML-BNSs are mostly unknown. In the previous three chapters, the electromechanical response of SL-BNSs was illustrated when they were subjected to various loading conditions. As a consequence, the electromechanical response of ML-BNSs (atomic layer number up to 12) under uniaxial tensile loading condition will be studied in the next chapter.

6. Chapter

Electromechanical response of multilayer BNSs

In this chapter, the electromechanical response of multilayer (ML) BNSs investigated using MD simulations. Effects of various factors such as chirality, number of layers, and strain rate on the electromechanical response of ML-BNSs were critically examined. Using examples drawn from the atomistic bond mechanics, this chapter demonstrates the electromechanical response of ML-BNSs.

6.1 Introduction

Use of different layers of combination of BN-based materials attracted an intense attention in the last two decades. The strong interlayer interactions are often characterized and dominated by covalent bonding, and the weaker interlayer interactions are determined by a delicate balance between London dispersion forces, electrostatic interactions (Coulomb), or a resultant between these two called as pair-wise interactions (Kim et al., 2013). The relationship between these interactions is the relative contribution of interlayer binding (bonded and non-bonded). Therefore, it is important to understand mechanical, electrical, and electromechanical response of ML-BNSs. Many 2D nanomaterials exist in the bulk as layered form. Among them, the most prominent ones are graphene (Mortazavi et al., 2012), BN (Naumov et al., 2009), transition-metal dichalcogenides (e.g., TMDC and MoS₂) (Wu et al., 2014), and oxides (e.g., titania) (Dan Tan et al. 2019, 2020).

Some of the limited experimental investigations are available on multilayer (ML)-BNS such as micromechanical cleavage technique (Pacil et al., 2008), chemical solutionderived method (Han et al., 2008), and CVD (Sutter et al., 2013). For, instance, using the micromechanical cleavage technique, Pacil et al. (2008) successfully synthesized an extremely thin sheet of BNS (between one to ten atomic layers). For the varied thickness of BNS, the morphology of the obtained sample was characterized using optical microscopy and AFM. It is also found that the elastic modulus of stacked BNS is in the range of 0.5 to 0.8 TPa. Using the first-principles calculations, Naumov et al. (2009) studied an electromechanical response of thick sp² bonded BN sheet. They investigated the effect of even and odd layers on polarization of ML BNS. They found that the flexoelectric effect exists in an ultrathin BN film with an odd number of layers such as 1, 3, 5,... This conclusion is in line with findings reported in Partoens and Peeters (2007). Within a tightbinding approach, Partoens and Peeters (2007) showed that Dirac fermions with a linear dispersion are present in graphene stacks only for an odd number of layers; in case of an even number of layers only normal fermions with parabolic energy dispersion occur. Michel et al. (2011) derived a unified theory of phonon dispersions and piezoelectricity for MLs of BNSs. The study indicates that 3D MLs of BNSs with an even number of layers (N_u) (symmetry D_{6h}) do not show piezoelectricity and MLs with odd number of layers (symmetry D_{3h}) show piezoelectricity. They also reported that the piezoelectric coefficient e₁₁₁ is inversely proportional to N_u. Zhang and Meguid (2015) examined the influence of tube layer number on the piezoelectric properties of multi-walled BNNTs using MD simulations. Their results revealed that the piezoelectric coefficient is positive for BNNTs with odd numbers of layers but negative for those with even numbers of layers. For both, odd and even cases, the magnitude of the piezoelectric coefficient was found to decrease with increasing layer number of BNNTs. Zhang and Zhou, (2018) studied the piezoelectric characteristic of ML-BNS using MD simulations via the resonance frequencies which they adjusted by introducing an external electric field. This discovery implies that ML-BNSs might be used as a starting point for developing innovative piezoelectrically adjustable 2D nanoresonators with ultrahigh tensile mechanical and lightweight characteristics.

The literature review reveals that few investigations on the electromechanical response of single layer (SL) BNSs exist with significant findings. There is no single study exists on studying the electromechanical response of ML-BNSs. Therefore, this has inspired us to conduct this work to determine the electromechanical response of ML-BNSs. Some important factors such as the number of atomic layers, chirality, fracture behaviour, effect of strain rate were considered to study the mechanical properties and piezo- and flexo-electricity ML-BNSs.

6.2 MD modelling of SL and ML-BNSs

In the current study, MD simulations were carried out to investigate the electromechanical response of ML-BNSs. All MD simulations were performed using opensource software LAMMPS (Plimton et al., 1995). The structural analysis and data processing of ML-BNSs were conducted using OVITO visualization software (Stukowski et al., 2010). In all the simulations, the bonded interactions between B and N atoms were described using Tersoff potential (Tersoff, 1989, 1988) and non-bonded interaction of B and N atoms were described using Lennard-Jones (L-J) or Morse potentials (Akiner et al. 2016).

6.2.1 potential

The atomic bonded intralayer interactions in BNS are described using the optimized Tersoff potential which has been successfully used in some previous studies (Mortazavi and Rémond, 2012; Zhao and Xue, 2013; Zhang et al., 2017; Vijayaraghavan and Zhang, 2018; Zhang and Zhou, 2018). The parameters of Tersoff potential are thoroughly discussed in chapter 2. Using this potential, the total energy E_{total} is as follows:

$$E_{total} = \sum_{i} E_{i} = \frac{1}{2} \sum_{i \neq j} V_{ij}$$
 (6.1)

$$V_{ij} = f_{C}(r_{ij})[f_{R}(r_{ij}) + b_{ij}f_{A}(r_{ij})]$$
(6.2)

where E_{total} is the total energy of the system, E_i is the site energy, and V_{ij} is the bond energy. The indices *i* and *j* run over the atoms of the system. Term r_{ij} is the distance between atom *i* and *j*, while b_{ij} is the bond angle term which depends on the local coordination of atoms around atom *i*. Terms f_R and f_A are the repulsive and attractive pair potentials, respectively. Term f_C is the cut-off function provided to limit the potential range and thus, saves the computational resources required for MD simulations.

According to the previous experimental and theoretical investigations (Marom et al., 2010; Constantinescu et al., 2013; Mirnezhad et al., 2013), a bi-layer BN possesses three high-symmetry stacking orders based on the graphite structure (Hao et al., 2010): AA (eclipsed with N over N and B over B), AA' (eclipsed with B over N), and AB (staggered with B over N) as shown in Fig. 6.1. Theoretically, there are numerous vertically stacked modes in ML-BNS, and they can transform into each other under specific conditions.

However, the AB stacking mode is the most stable structure based on the theoretical calculations (Marom et al., 2010) and experimental observations (Mallick and Elder, 2018). Therefore, simulations were performed considering AB stacking mode to investigate the influence of number of atomic layers on the electromechanical response of ML-BNS.



Fig. 6.1: Schematic representation of the possible high symmetry stacking of BNSs: (a) AA stacking, (b) AA' stacking, and (c) AB stacking.

In case of non-bonded van der Waals interaction between individual B and N atoms, there is a variety of potentials used in the literature. Commonly, the non-bonded interactions can be described using popular Lennard-Jones (L-J) or Morse potential. In the current study, the L-J term and a coulombic-term were used as follows (Akiner et al., 2016):

$$U(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{D_{ij}}{r_{ij}} \right)^{12} - \left(\frac{D_{ij}}{r_{ij}} \right)^6 \right] + K_C q_i q_j r_{ij}^{-1}$$
(6.3)

where U(r) is the potential energy (PE) between a pair sheet at the structure of B-N bilayers, r_{ij} is the finite distance at which the inter-particle potential is zero between atoms i and j in adjacent layers, ε is a parameter determining the depth of the potential well, and D_{ij} is the diameter of the atom (a length-scale parameter of the atom determining the position of the potential minimum). K_c is the Coulombic constant and q_i is the partial charge of the ith atom. Meanwhile, the partial charge q for the L-J potential was taken as 1.1378 eV and the cutoff distance of L-J interaction was set to 10 Å (Akiner et al., 2016; Ghaderzadeh et al., 2021). The parameters of L-J potential are summarized in Table 6.1. The L-J fitting parameters for BNS structures such as $D_{ij} = 3.34$ Å and $\varepsilon_{ij} = 5.0$ meV were used for the interlayer spacing, and the binding energy obtained from the DFT calculations (Marom et al., 2010) was used. The thickness of BNS was considered as 3.4 Å (Boldrin et al., 2011).

Parameter	B–B	B–N	N–N
ε (kcal/mol)	0.0	0.007	0.2496
D (Å)	0.0	3.75	3.1461

Table. 6.1 L-J interaction parameters for BN atoms.

To obtain the stress-strain $(\sigma - \delta)$ relations during the tensile loading, the virial stress $\sigma_{\alpha\beta}$ is calculated according to the following equation (Zhao and Xue, 2013):

$$\sigma_{\alpha\beta} = -\frac{1}{V} \left(\sum_{\alpha=1}^{N} m_{\alpha} v_{x}^{\alpha} v_{y}^{\alpha} + \frac{1}{2} \sum_{\alpha=1}^{N-1} \sum_{\beta=a+1}^{N} r_{\alpha\beta,x}^{N-1} F_{\alpha\beta,y} \right)$$
(6.4)

where m_{α} is the mass of atom α , v_x^{α} is the velocity component in the axial direction of atom α , $F_{\alpha\beta,y}$ refers to the axial component of interatomic force between atoms α and β , xand y denote the indices of the Cartesian coordinate system, $r_{\alpha\beta,x}^{N-1}$ is the interatomic distance in the axial direction between atoms α and β , V refers to the volume of simulated BNS, and N is the number of atoms. It can also be observed from Eq. (6.4) that at low temperature, the stress contribution from kinetic part ($m_{\alpha}v_x^{\alpha}v_y^{\alpha}$) becomes negligible due to the low velocities of atoms.

The dipole moment induced due to the applied external force and the resulting polarization (P) can be calculated using the following relation (Tan et al., 2020):

$$P = \sum_{i}^{N} \frac{q_{i}r_{i}}{V} = \sum_{i}^{N} \frac{q_{i}r_{i}}{nhA}$$
(6.5)

where q_i is the charge of ith atom, r_i is the *x*-coordinate of ith atom, *N* is the number of atoms. In our case, *V* is simply *nhA*. Here *n* represents the atomic layer number, *h* is the thickness of SL BNS, and *A* is the area of planer BN sheet (Alyörük et al., 2016):

Note that the total polarization (P_1) constitutes the contributions from both flexoelectricity and piezoelectricity. The constitutive relation for the polarization vector induced due to the flexoelectricity and piezoelectricity effects may be written as (Kundalwal et al., 2017; Javvaji et al., 2018):

$$P_{1} = e_{ijk}\varepsilon_{jk} + \mu_{ijkl}\frac{\partial\varepsilon_{jk}}{\partial x_{l}}$$
(6.6)

where e_{ijk} and μ_{ijkl} are the respective piezoelectric and flexoelectric tensors; ε_{jk} and $\frac{\partial \varepsilon_{jk}}{\partial x_l}$ are the strain and strain gradient, respectively.

First, initial structures of SL- and ML-BNSs were created with a bond length of 1.446 Å (Amalia et al., 2019) and the spacing distance between BNSs was taken as 3.35 Å (Nikiforov et al., 2012; Michel et al., 2016). The structures of BNSs were then modified by minimizing their energy using the conjugate gradient approach. The structure was considered optimal when the difference in total potential energy (PE) between the two consquent stages was less than 1.0×10⁻¹⁰ kcal/mol (Dewapriya and Rajapakse, 2014; Choyal and Kundalwal, 2020). In both the x and y directions, a periodic boundary condition (PBC) was applied, and the simulation box was kept large enough to allow for nonbonded interlayer interactions. A short time increment of 0.5 fs was employed in this technique to accurately capture the deformations of ML-BNSs at extremely high strain rates (SR) $\sim 10^9$ s^{-1} . Prior to applying the loading condition, the ML-BNSs were allowed to anisotropically relax to zero pressure in x and y directions at a temperature of 300 K for 50 ps time increments using constant pressure-temperature (i.e. NPT ensemble) by means of Nosé-Hoover barostat method (Evans and Holian, 1985). After the energy minimization, uniaxial tensile loading was applied to the sheets. Schematic of such loading condition on ML-BNS is shown in Fig. 6.2(a). The loading condition was applied by elongating the periodic simulation box in the x-direction under constant SR $\sim 10^9 \text{ s}^{-1}$. In order to satisfy the uniform uniaxial stress condition, the PBC was applied in the loading direction and the simulation box in the y-direction was allowed to reach zero stress by using NPT Nosé-Hoover method (see Fig. 6.2(b)). Virial stresses in the x direction (uniaxial tensile stress) were calculated at each strain level (see Eq. 6.4). The axial strain of BNS was calculated using relation, $\delta = \left(\frac{L_f - L_i}{L_i}\right)$, in which L_i and L_f are the initial and final lengths of BNS, respectively, in the direction of application of tensile load. Using the Hooke's law, the slope of the initial linear part of uniaxial tensile $\sigma - \delta$ curve can provide the Young's modulus of SL- and ML-BNS along the loading direction.

123



Fig. 6.2 (a) MD model of uniaxial tension test of bi-layer BNSs. (b) The periodic boundary conditions applied in the x and y direction. Atoms depicted in ochre are boron and atoms depicted in blue are nitrogen. (c) Simulation model of ML-BNSs.

6.3 Results and discussions

In order to verify the validity of current MD simulations, the elastic and piezoelectric properties of ML-BNSs reported by other researchers using different techniques and approximations were considered (see Table 6.2). Note that several MD simulations were performed to obtain the reliable elastic and piezoelectric coefficients of BNSs under the uniaxial tensile loading. In fact, our results are found to be in good agreement with the existing results performed by phonon dispersion (unified theory) and MD simulations (Michel and Verberck, 2011; Mirnezhad et al., 2013; Zhang and Zhou, 2018); some of our results are marginally differ due to the use of different techniques and approximations by other researchers. A fixed size of 80 Å \times 80 Å of BNS was considered for simulations. The procedure for determining the electromechanical response of ML-BNSs is as follows. First, Young's modulus of ML-BNS was obtained using the averaged

uniaxial tensile deformation. Here, the maximum tensile strength is identified as the maximum stress prior to the failure and Young's modulus was determined from the slope of $\sigma - \varepsilon$ curve under the uniaxial tensile test within the elastic limit ($\varepsilon < 0.03$). In addition, the effect of strain rate (SR) on the mechanical properties is also discussed in this chapter. (ii) Second, the piezoelectric coefficient (e) of ML-BNS was calculated using MD simulations. A small in-plane displacement was applied at the left and right edges in the xdirection of the nanosheet. During this process, we recorded the axial polarization change of nanosheets vs applied uniaxial strain. Afterwards, the piezoelectric coefficient of BNSs can be extracted from the slope of obtained $P_1 - \delta$ curve within the elastic limit. (iii) Third, the flexoelectric coefficient (e) of ML-BNS was calculated using Eq. (6.5) by eliminating the piezoelectric contribution. To perform the bending deformation, a sheet was divided into vertical rectangular bins. At each vertical rectangular bin, the deformation gradually increases from the edge to the middle section of the sheet, and maximum deformation occurs in the middle portion of the vertical rectangular bins. The bending deformation mainly depends on the bending curvature (non-uniform strain gradient on each bin). During this process, we recorded the out-of-plane polarization change of nanosheets along with non-uniform strain gradient.

Layer number	References	E (TPa)	Layer number	References	e_{xxx} (C/m ²)
1 to 3	Present	AC/ZZ 0.879/0.847	Present 1 to 20		odd layer = 0.387 – 0.11, Even layer = 0
layers	(Mirnezhad et al., 2013)	773 -0.7	layers	(Michel and Verberck, 2011)	odd layer = $1.0 - 0.1$, Even layer = 0
1 to 5 layers	Present	AC/ZZ 0.879/0.847	1 to 4	Present	odd layer = 0.387 – 0.11, Even layer =
	(Mukhopadhyay et al., 2017)	0.805	layers	(Zhang and Zhou, 2018)	odd layer = 0.58 – 0.19, even layer = 0

<i>Table 6.2: (</i>	Comparison	of Young	's modulus and	piezoelectric	coefficients	of SL-	and ML-I	BNSs.
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6.3.1 Stress-strain behavior of ML-BNSs under uniaxial tension

The variation of normalized PE of ML-BNSs subjected to uniaxial tension loading is shown in Fig. 6.3. As expected, it can be observed that the ML-BNSs with higher number of atomic layers show higher PE than the lower ones irrespective of their chirality. This is attributed to the higher volume of sheets, which eventually stores higher PE (see Fig. 6.3). It can also be observed that the ML-BNSs in the armchair direction show higher PE compared to the ML-BNSs in the zigzag direction.

The variation of PE with relaxation time for the equilibration of bilayer BNSs in the armchair and zigzag directions is shown in Fig. 6.4(a). It can be observed that the structure of 2_layer BNS becomes stable around 10 ps. The total time used for thermodynamics stability was 50 ps and it is also identified from the previous literature that such time is sufficient to obtain stable structures of ML-BNSs. Further, we examined the stability of 2_layer containing 5120 atoms with a Nose–Hoover barostat (NPT) at 300 K. Figure 6.4(b) shows the fluctuations of temperature (K) as a function of the simulation time steps (ps). After 10 ps, no destruction was found in the 2_layer structure (see Fig. 6.4(b)), which confirmed its thermodynamic stability at finite temperature 300 K. Similar trends of variation in potential energy and temperature with time steps for the other types BNSs are observed and they are not shown here for the sake of brevity.



Fig. 6.3 The variation of normalized potential energy of ML-BNSs in the armchair and zigzag directions. (AC-Stacking of armchair BNSs; ZZ-Stacking of zigzag BNSs; Bulk BNS - thickness more than 20 to 25 Å)



Fig. 6.4 The variation of the (a) potential energy (eV) with relaxation time (ps) (b) temperature with relaxation time (ps) of a 2_layer BNS in the armchair and zigzag direction at 300 K.

The mechanical properties of ML-BNSs under uniaxial tensile loading in the armchair and zigzag directions were studied at a given finite temperature (300 K). The σ – δ curve of ML-BNSs in the armchair and zigzag directions is shown in Figs. 6.5(a) and (b) at a strain rate (SR) of 10^9 s^{-1} . The $\sigma - \varepsilon$ response of ML-BNSs with a varied number of layers of 2, 3, 5, 8 and bulk BNS (with twelve layers is also presented. For the sake of brevity, the additional atomic layers of BNS are not shown here. The Young's modulus, failure strain, and maximum tensile strength of different cases are summarized in Table 6.3. It can be observed from Fig. 6.5 that the ML-BNSs are slightly less stiff in the zigzag direction as compared to the armchair ones at a given temperature. As an overall trend, Young's modulus and ultimate tensile strength decrease as the number of atomic layers of BNs increases (Figs. 6.5 and 6.6). The failure of armchair ML-BNSs occurs in a single stage, whereas failure of zigzag ML-BNSs occurs in two stages. Step-by-step snapshots of 2_layer BNS in the armchair and zigzag directions are illustrated in Figs. 6.7 and 6.8, respectively, to understand the difference in deformation mechanics process and fracture behaviour. Single-stage failure occurred in ML-BNSs in the armchair direction at a strain value of 0.46 to 0.49. The two-stage failure occurred for the zigzag case in which the initial failure occurs between 0.25 and 0.3 and the secondary failure occurs between 0.55 and 0.62. The zigzag ML-BNS shows a higher failure strain than the armchair case at the same ambient temperature but shows lower strength owing to the strain hardening. There are two types of B–N bonds exist for two cases: (i) bonds a_1 and a_2 in the armchair sheet (see Fig.

6.9), and (ii) bonds z_1 and z_2 in the zigzag sheet (see Fig. 6.10). In armchair ML-BNS, bonds (a_1) exist along the loading direction which bear more stress than that of inclined bonds (a_2) . The initial bond (a_1) brakes in the armchair direction, but there is no B–N bond braking in the zigzag direction which connects two hexagonal rings. The sheet consists of four types of deformed B-N bonds: (i) a_2 and z_1 are slightly inclined to the direction of loading, and (ii) a_1 is aligned with the loading direction, and z_2 is normal to the direction of loading. Under the uniaxial tensile loading in the armchair direction, the bonds a_1 and a_2 are under tension, while the bonds z_1 and z_2 are under tension and compression, respectively, when the loading is applied in zigzag direction (see Figs. 6.9 and 6.10). During the deformation in the armchair direction of BNS, all six B–N bonds (a_1 and a_2) carry the higher load while in the zigzag case, only four B–N bonds (z_1) carry the tensile load and the rest of the other bonds are under compression. It can be clearly identified that the bonds a_1 and a_2 are stress-bearing bonds in the armchair direction as compared to the bonds z_1 and z_2 in the zigzag direction. Therefore, the higher failure strength was observed in the armchair direction due to the existence of more stress bearing bonds a'_1 . It may be observed that the failure of sheets starts from the innermost atomic layer and then reaches the outermost layer through the shear stress induced in the opposite direction, as shown in Fig. 6.11. These shear stresses are induced due to the van der Waals forces exist between the layers of ML-BNSs. The induced stress magnitude is higher in the innermost layer of the sheet, and it decreases as the number of layers increases and becomes lower in the outermost layer. In the current study, Young's modulus of bulk BNS was found to be around 0.794 to 0.766 TPa, which is in good agreement with the experimental findings of 0.5 to 0.8 TPa (Pacil et al., 2008). Based on the obtained results, it can be concluded that the obtained elastic properties become acceptably independent of number of layers when the total number of ML-BNS layers are eight, where the Young's modulus is close to the ranges of experimental bulk properties. This finding is interesting in the modeling of polymer nanocomposites reinforced by ML-BNSs. Therefore, we can use the bulk properties of BNS in the modeling when the total number of atomic BN layers are ≥ 8 .

Chapter 6

S. No. of No. atomic		Young's modulus (TPa)		Failure strain		Maximum tensile strength (GPa)	
	plane	Armchair	Zigzag	Armchair	Zigzag	Armchair	Zigzag
1	1_layer	0.879	0.847	0.492	0.614	243.146	225.470
2	2_layer	0.864	0.823	0.469	0.605	203.086	207.158
3	3_layer	0.853	0.812	0.491	0.591	225.102	190.271
4	4_layer	0.842	0.801	0.469	0.585	190.757	181.486
5	5_layer	0.833	0.790	0.489	0.580	210.951	174.254
6	6_layer	0.822	0.785	0.466	0.577	186.031	160.125
7	7_layer	0.811	0.779	0.485	0.582	190.674	162.458
8	8_layer	0.794	0.770	0.464	0.568	167.056	153.236
9	9_layer	0.784	0.764	0.482	0.577	171.240	155.124
10	10_layer	0.774	0.760	0.461	0.559	156.275	145.189
11	11_layer	0.768	0.760	0.480	0.565	158.647	142.158
12	12_layer	0.766	0.760	0.457	0.557	142.423	137.487

Table 6.3: Elastic properties of SL- and ML-BNSs.



Fig. 6.5 The $\sigma - \varepsilon$ curve of ML-BNSs under uniaxial tensile loading in the armchair and zigzag directions.



Fig. 6.6 The variation of Young's modulus of armchair and zigzag BNSs with the number of atomic layers. The inset shows the simulation setup.



Fig. 6.7 Snapshots of the failure process of bi-layer BNSs under uniaxial loading in the armchair direction.

Chapter 6



Fig. 6.8 Snapshots of failure process of bi-layer BNSs under uniaxial loading in the zigzag direction.



Fig. 6.9 Deformation mechanics of SL BNS under uniaxial tensile loading in the armchair direction. Color configuration represents the atomic stresses induced in the BNS.



Fig. 6.10 Deformation mechanics of SL BNS under uniaxial tensile loading along the zigzag direction. Color configuration represents the atomic stresses induced in the BNS.



Fig. 6.11 Deformation behavior of 5_layer BNS under uniaxial tensile loading in the armchair direction: (a) undeformed sheet, (b) deformed sheet after the application of load, and (c) failure of deformed sheet. Color coding indicates the atomic stresses induced in the sheet.

6.3.1.1 Effect of SR on mechanical properties of ML-BNSs

The $\sigma - \varepsilon$ relations are function of applied SR, and a system gets enough time to relax for reaching the equilibrium state at the lower values of SR. Therefore, to obtain the reliable and accurate results, the use of lower values of SR (10^9 s^{-1}) is preferred. However, we varied the values of SR as 10^8 , 10^9 , and 10^{10} s^{-1} to choose the optimal value to study the mechanical properties of ML-BNSs. The obtained $\sigma - \varepsilon$ curves of 2_layer and 5_layer ML-BNSs are shown in Fig. 6.12 for the armchair and zigzag cases at different SR. At low strain level (up to ~0.04), a linear relation between stress and strain values is obtained.

This linear response is commonly assumed as the linear elasticity part, in which the corresponding slope is equivalent to Young's modulus. It can also be observed from Figs. 6.12(a) and (b) that Young's modulus of ML-BNSs in armchair and zigzag directions are reasonably independent of the SR values. At higher strain level, the $\sigma - \varepsilon$ response shows a nonlinear behavior which continues up to the maximum tensile strength, the point at which fracture occurs in the first atomic plane. In both the cases, the nonlinear part is also found to be independent of SR where the fracture occurs at approximately the same stress and strain levels. Note that at high SR material doesn't get enough time to break the interatomic bond and thus shows a high tensile strength. On the other side, at lower SR atoms get enough time to oscillate from its mean position and thus increases the ability of atoms to overcome the energy threshold needed to break bonds. It may be noted that a higher strain rate results in a higher fracture strength (Zhang et al., 2019). As the SR increases from 10^8 s⁻¹ to 10^{10} s⁻¹, the fracture strength also increases by (i) 3.9% and 6.1% for 2 layer armchair case, (ii) 4.2% and 4.8% for 2 layer zigzag case, (iii) 2.1% and 3.7% for 5 layer armchair case, and (iv) 1.9% and 2.9% for 5 layer zigzag case. Based on the obtained results, the SR of $10^9 \,\text{s}^{-1}$ is selected for the further MD simulations because of predicting $\sigma - \varepsilon$ trend closer to the lower SR of 10⁸ s⁻¹.



Fig. 6.12 Uniaxial $\sigma - \delta$ curve of (a) 2_layer and (b) 5_layers armchair and zigzag BNS at different loading SR.

6.3.2 Piezoelectric coefficients of ML-BNSs

Piezoelectric BNS is a promising nanomaterial for NEMS, but its piezoelectric response diminishes as the number of BNSs (n) layers in staked configuration increases

and becomes almost negligible when n > 10. In such layered configuration only the piezoelectric response of BNSs largely gets affected among all other remarkable properties. NEMS made of layered BNSs for modern technological applications should display strong piezoelectric response, combined with high mechanical stability and low environmental impact. Surprisingly, very few studies are performed so far to investigate the piezoelectricity effect in layered BNSs and their nanocomposites. Therefore, the present investigations were carried out to determine the electromechanical response of ML-BNSs using MD simulations. In this chapter, the piezoelectric properties of ML-BNS were investigated with the consideration of different number of atomic layers. Specifically, the ML-BNSs considered herein in which B atoms in one layer are stacked with N atoms in the neighbouring layer, and vice versa as shown in Fig. 6.2. Such AB stacking configuration of ML-BNS is proven to be energetically preferable and more stable than other possible stacking schemes and can be directly isolated from a naturally occurring bulk BN crystal (Li et al., 2013; Li et al., 2016).

Then, the size-dependent piezoelectric properties of BNS were studied by varying the number of atomic layers. The induced polarization in ML-BNS was calculated using Eq. (6.5) and the results are plotted in Fig. 6.13 for uniaxial tensile loading in the armchair and zigzag directions. The calculated piezoelectric coefficients (e) of ML-BNSs with different number of atomic layers are shown in Table 6.4. The slope of $P - \varepsilon$ curve during the uniaxial tensile loading defines the piezoelectric coefficient as shown in Fig. 6.13. It can be observed from Fig. 6.13 that the induced polarization in armchair BNS is higher than zigzag case. This is attributed to the generation of higher resultant dipole moments in the x-direction of armchair BNS compared to zigzag sheet (see chapter 3, Fig. 3.10). Note that the piezoelectric coefficients of BNS are function of its chirality and our results are in line with the results reported by other researchers. It is important to note that out-of-plane movement of sheet was not considered because B and N atoms have the same planar sp² hybridization (Beheshtian et al., 2012). Furthermore, in-plane polarization is significantly decreased with the increase in atomic layer number because the direction of induced inplane polarization is reversed to the adjacent layers which results in the cancellation of polarization (see Fig. 6.14). This cancellation effect is more pronounced in BNSs with even number of layers than with odd number of layers and it is a very interesting feature of ML-

BNSs. It can be observed from Fig. 6.14 that the ML-BNSs with even layers possesses the crystal class of D_{6h} (centrosymmetric) and thus do not show piezoelectricity. In contrast, ML-BNSs with an odd number of layers possesses the crystal class of D_{3h} (non-centrosymmetric) which exhibit piezoelectricity (Michel and Verberck, 2009; Zhang and Meguid, 2017). Therefore, the SL-BNS structure shows the largest in-plane piezoelectric coefficient than ML-BNS, van der Waals layered materials, due to weaker interlayer interactions (Michel et al., 2011). A similar relationship between piezoelectric and number of atomic layers is also observed in pervious DFT calculations on the ML-BNSs (Michel and Verberck, 2009; Zhang and Meguid, 2017; Zhang et al., 2018).



Fig. 6.13 The variation of $P - \varepsilon$ of ML-BNSs under uniaxial tension loading in the armchair and zigzag directions.

S. No.	No. of atomic	Piezoelectric coefficient (C/m ²)		Flexoelectric coefficient (C/m)		
	plane	Armchair	Zigzag	Armchair	Zigzag	
1	1_layer	0.387	0.348	0.255	0.111	
3	3_layer	0.227	0.198	0.178	0.0597	
5	5_layer	0.135	0.107	0.105	0.00489	
7	7_layer	0.100	0.064	0.0487	1.47E-4	
9	9_layer	0.015	0.010	0.00162	8.9E-5	
11	11_layer	0.011	0.010	0.0	0.0	

Table 6.4: Piezoelectric and flexoelectric coefficients ML-BNSs in the armchair and zigzag directions.



Fig. 6.14 The piezoelectric coefficient of ML-BNSs as a function of their atomic layer number. The inset shows the simulation setup.

6.3.3 Flexoelectric coefficients of ML-BNSs

Note that the bending is the simplest kind of deformation for determining a mechanical strain gradient in 2D nanomaterials or thin structures. Upon bending of polar (BNS) materials, the symmetry of the electron distribution breaks in the out-of-plane direction, and a resultant dipole moment is generated at each atomic layers (Ahmadpoor and Sharma, 2015). The flexoelectric coefficient was calculated using Eq. (5.10). The slope of polarization and mechanical strain gradient provides the flexoelectric coefficients (μ_{zxzx}) along the principal curvature direction. The present results are summarized in Table 6.4. The value of the flexoelectric coefficient of SL-BNS is 0.255 pC/m and shows excellent agreement with the value of 0.260 pC/m obtained by Zhuang et al. (2019) using C-D potential model. It can be observed from Fig. 6.15 that the flexoelectric coefficient of ML-BNSs decreases as the number of atomic layers increases because the resultant out-of-plane polarization cancel out with the adjacent layers of BNS.



Fig. 6.15 The flexoelectric coefficients of ML-BNSs as a function of their atomic layer numbers. The inset shows the simulation setup.

6.4 Conclusions

In this chapter, an electromechanical response of ML-BNS was comprehensively studied using MD simulations with a Tersoff and L-J potential force fields. Systematic uniaxial tensile loadings were applied on the ML-BNSs in the armchair and zigzag directions in order to investigate their stress-strain and failure behavior. The simulations were also carried out at different SR ranging from 10⁸ to 10¹⁰ s⁻¹. It is evident both fracture stress and strain of ML-BNSs increase as the SR increases. The simulated results also show that the properties are sensitive to the number of layers and loading direction as well. Young's modulus and ultimate tensile strength of ML-BNNSs dropped as the number of BN layers increases. However, the obtained Young's modulus for ML-BNSs containing eight atomic layers is close to the value of Young's modulus of bulk BNSs. Furthermore, the piezo- and flexo-electricity of stacked structures with B over N (AB stacked) largely depend on the odd and even number of atomic layers. ML-BNSs with an even number of atomic layers do not show piezoelectricity due to the symmetry of D_{6h}, whereas ML-BNSs with an odd number of atomic layers show piezoelectricity due to the symmetry of D_{3h} . It was observed that properties decrease as the number of atomic BN layers increases in ML-BNS after ten atomic layers and then properties completely vanish.

The next chapter summarizes the significant outcomes and conclusions from this thesis, limitations of the study, and the future scope of this research work. The scope for further research on the BNSs and their nanocomposite is also suggested.

7. Chapter

Conclusions and future scope

In this chapter, major conclusions drawn from the current research work are highlighted. Moreover, the scope for further research on BNSs and their nanocomposite structures are suggested.

7.1 Major conclusions

This thesis thoroughly investigates the electromechanical response of pristine and C-doped BNSs using MD simulations with the three-body Tersoff potential force field. Both armchair and zigzag BNSs with different sizes were considered. Using a direct approach, we investigated the elastic, piezoelectric and flexoelectric properties of pristine BNS, C-doped BNS with pores and BGH under tension, shear, and bending loading conditions. Using an indirect approach, we investigated the elastic, piezoelectric and flexoelectric properties of pristine and hybrid BNSs (interface engineering of BNS/zigzag graphene stripe and BNS/hexagonal ring of graphene stripe). Finally, the electromechanical behavior of BNRC nano-beams with different boundary and loading conditions was studied.

The following conclusions are drawn from the work carried out in this thesis:

- The mechanism of polarization in BNSs is explained using the unit cell representation.
- The axial and shear elastic/piezoelectric coefficients of BNS were determined using the tension and shear loading conditions, respectively. The elastic and piezoelectric coefficients of armchair BNS were found to be higher than zigzag BNS irrespective of the shape of pore and C-doping concentration.
- The induced polarization in the BNSs was found to depend on the local arrangement of C atoms around the B and N atoms and the polarization increases if C atoms are surrounded by more N atoms than B atoms.

- The axial and shear piezoelectric coefficients of C-doped BNS with triangular and trapezoidal pores increased while they reduced in the case of circular pore compared to pristine BNS. A BNS with a triangular pore showed higher polarization than BNS containing other shapes of pores. The C-doping with N atoms results in the generation of higher dipole moments because the C-N bond is more electronegative than the C-B bond.
- The piezoelectric coefficients of doped BNS increased with the C-doping concentration up to 12.6% and then they decrease. The elastic properties of doped BNS increased with the C-doping concentration up to 12.6% and then they stabilize and do not change beyond the total number of 2600 BN atoms.
- The interface engineering of BNS/zigzag graphene stripe improved the axial piezoand flexo-electric coefficients of hybrid BNS under the application of E-field in its armchair direction by 25% and 37%, respectively, compared to pristine BNS. The corresponding enhancement in the coefficients was observed as 18% and 16% due to the interface engineering of BNS/hexagonal ring of graphene stripe.
- When the E-field applied in the armchair direction of hybrid BNS, the increase in total polarization is around 17% and 7% for NCB and CHR sheets, respectively, compared to pristine BNS due to the interface engineering of BNS/zigzag graphene stripe. The corresponding increase in total polarization is 21% and 10% in the case of E-field applied in the zigzag direction of hybrid BNS.
- The enhancement in the values of Young's moduli of NCB and CHR sheets are found to be 17.50% and 13.72% respectively, compared to pristine BNS. The respective enhancement in shear moduli is 11.83% and 10.30%.
- The density and position of SW defects play a critical role on the overall electromechanical response of BNS. SW defect improves the polarization of BNS, and the converse is true for elastic properties.
- Graphene domains with 5.6% of area fraction were interfaced with BNS in different shapes: triangular, trapezoidal and circular. Systematic bending deformations were performed on BNS/BHGs to study the bending stiffness and electromechanical coupling attributed to the piezo- and flexo-electric effects.

- The electromechanical coupling of BGHs is enhanced due to the out-of-plane bending compared to in-plane stretching. During bending, the induced atomic polarization along the *z*-direction of BNS/BGH is higher compared to the *x*-direction.
- Flexoelectric coefficients of BGHs with triangular and trapezoidal graphene domains are increased while the reverse is true in case of circular graphene domain compared to pristine BNS. A BGH with a triangular graphene domain showed higher polarization than BNS as well as BGH containing other graphene domains.
- Elastic, strength and failure properties of ML-BNSs decrease as the number of atomic layers increases.
- It is obvious that when SR increases, fracture stress and strain increase as well. This is due to the fact that at high SR, the material does not have enough time to break the interatomic bond, resulting in a high tensile strength. On the other side, slower SR provides more time for atoms to oscillate from its mean position and therefore increases the ability for atoms to overcome the energy threshold needed to break bonds.
- ML-BNSs with an even number of atomic layers (symmetry D_{6h}) are not piezoelectric, whereas ML-BNSs with an odd number of atomic layers (symmetry D_{3h}) are piezoelectric.
- As the number of atomic layers increases, both piezo- and flexo-electric properties decrease, and after ten atomic layers, the properties of ML-BNS completely vanish.

The conducted research is a significant contribution to the scientific community due to the recent shift in advanced BN-reinforced composites from the use of conventional and carbon-based composites.

7.2 Limitations of the study

The following are the limitations of current study:

• We cannot use MD simulations at the subatomic level (electron and proton), since MD approach is only capable of dealing with the atomic/molecular level. In MD simulations, atom is assumed as a particle and therefore, we cannot capture subatomic level phenomena. For example, DFT calculations is the appropriate

technique to study the polarization in BNSs due to generation of atomic dipole moments, but such estimations are performed in the current study using indirect approach reasonably. Using indirect approach, large BNS was modelled which is computationally challenging job in case of DFT simulations in view of involvement of sub-atomic parameters and DOFs.

- The MD simulations can be performed for the system size with less than 1 million atoms in view of unavailability of computational facility for a small-time scale (shorter than 10 microseconds). If the system size and time scale become larger than 1 million atoms and 10 microseconds, respectively, then either supercomputer is required, or continuum models need to be developed.
- Coulombic interactions, which include long-range electrostatic interactions and van der Waals interactions, play a dominant role in the structural stability of layered nanomaterials. Typically, the most computationally expensive portion of MD simulations is the evaluation of Coulombic interactions. As the number of charges in a system increases, the number of Coulombic interactions grow as the square of that number, potentially resulting in a prohibitively large number of interactions to evaluate and this needs a huge computational power.
- BNS or hybrid BNS system considered in the current study cannot be obtained experimentally exactly in view of some inherent fabrication issues such as reaction, surface effect with substrate/atmosphere, defects, impurities etc. Advance fabrication techniques are becoming matured and there is a possibility of obtaining BNS with different shapes of pores and hybrid BNS in future.

7.3 Scope for future work

The current fundamental study highlights the possibility of developing high performance, lightweight and multifunctional BNS-based NEMS such as nanogenerators, nanosensors and nanoresonators. The success of this research (i) provided new knowledge in the field of BNSs that will enable modeling and characterization of their NEMS, (ii) initiate and serve as a solid foundation for developing a vast range of next-generation applications that are characterized by adaptability, multifunctionality and autonomy, such as energy harvesting, structural health monitoring, shape morphing, and flexible electronics. Thus, the present research may be followed for the further experimental investigation to examine the characteristics of BNSs and their nanocomposites. Some of the further research works that may be undertaken in line with the present work as follows:

- The elastic and piezoelectric properties of microscale piezoelectric nanocomposites containing BNSs subjected to an externally applied mechanical strain using hierarchical multiscale strategies.
- Development of accurate 3D finite element (FE) and analytical electric enthalpy variational principle models to characterize the size-dependent electromechanical behaviour of special classes of BNS-based nanostructures such as plate and shell.
- Design and propose new generation lightweight and high strength BN-based NEMS.

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List of publications

The following papers are published/under review form the research work carried out in the Ph.D.

A1. Journal Publications from the thesis

- Vijay Choyal, V. K. Choyal and S. I. Kundalwal. Effect of atom vacancies on elastic and electronic properties of transversely isotropic boron nitride nanotubes: A comprehensive computational study, Computational Materials Science 156, 332-345, 2018. https://doi.org/10.1016/j.commatsci.2018.10.013 (IF: 2.863, ci: 20)
- V. K. Choyal, Vijay Choyal, Subhash Nevhal, Ajeet Bergaley and S. I. Kundalwal. Effect of aspects ratio on Young's modulus of boron nitride nanotubes: A molecular dynamics study, Materials Today: Proceedings, ISSN 26, 2214-7853, 2019. https://doi.org/10.1016/j.matpr.2019.05.347 (IF: 0.97, ci: 5)
- S. I. Kundalwal, V. K. Choyal, Vijay Choyal and Nitin Luhadiya. Effect of carbon doping on electromechanical response of boron nitride nanosheets. Nanotechnology 31, 405710, 2020. https://doi.org/10.1088/1361-6528/ab9d43 (IF: 3.874, ci: 5).
- S. I. Kundalwal, V. K. Choyal, Vijay Choyal, Subhash Nevhal, and Nitin Luhadiya. Enhancement of piezoelectric and flexoelectric response of boron nitride sheet superlattices via interface engineering. Physica E: Low-dimensional Systems and Nanostructures 127, 114563, 2021. https://doi.org/10.1016/j.physe.2020.114563 (IF: 3.570, ci: 1)
- S. I. Kundalwal, V. K. Choyal and Vijay Choyal. Flexoelectric effect in boron nitride-graphene heterostructures, Acta Mechanica, 208, 1–20, 2021. https://doi.org/10.1007/s00707-021-03022-4 (IF: 2.102)
- 6. **V. K. Choyal** and S. I. Kundalwal. Electromechanical response of multilayered boron nitride nanosheets: A computation study (*To be Submitted*)

A2. Conference Proceedings from the thesis

 V. K. Choyal, Vijay Choyal, Nitin Luhadiya and S. I. Kundalwal. Electromechanical response of carbon-doped Boron nitride nanosheets. International Conference on Precision, Meso, Micro and Nano Engineering, IIT Indore. December 12-14, 2019.

A3. List of conference proceedings from other than thesis work

- Vijay Choyal, V. K. Choyal and S. I. Kundalwal. Transversely Isotropic Elastic Properties of Vacancy Defected Boron Nitride Nanotubes Using Molecular Dynamics Simulations." 2018 IEEE 13th Nanotechnology Materials and Devices Conference (NMDC), in Portland, Oregon, USA. (*ci: 6*)
- Vijay Choyal, V. K. Choyal, Ekansh Jain and S. I. Kundalwal. Molecular dynamics study: effect of length and diameter on elastic properties of Multi-wall boron nitride nanotubes. 2nd International conference on Nano Science and Engineering Applications ICONSEA-2018, Hyderabad, India, October 4-6, 2018.
- Vijay Choyal, V. K. Choyal and S. I. Kundalwal. Effect of Stone-Wales Defects on transversely isotropic elastic properties of boron nitride nanotubes: a molecular dynamics study. IEEE 14th International Nanotechnology Materials & Devices Conference (NMDC 2018) in Portland, Stockholm, Sweden on 27-30 October 2019.
- Vijay Choyal, V. K. Choyal, Ekansh Jain and S. I. Kundalwal. Mechanical properties of multi-walled boron nitride nanotubes: Computational study. International Conference on Precision, Meso, Micro and Nano Engineering, IIT Indore. December 12-14, 2019.

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Vijay Kumar Choyal

Research Scholar

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Education

Degree	Institute	Year	CPI / %
PhD**- (Thesis	Indian Institute of Technology	2018-21	7.89/10.00
submitted)	<u>Indore, MP, India</u>		
Mechanical Engineering			
M.Tech*	Institute of Engineering and	2016-18	7.63/10.00
Design & Thermal	Technology Indore, M.P.,		
Engineering	India		
B.E.	TRUBA College of	2010-14	7.31/10.00
Mechanical Engineering	Engineering & Technology,		
	Indore, M.P., India		
12 th (Mathematics)	Saraswati Shishu Mandir H.S.	2009-10	68.00%
Higher Secondary	School, Indore, M.P. Board		
School Certificate			
10 th (All subjects)	St. George H.S. School,	2007-08	60.00%
Secondary School	Indore, M.P. Board		
Certificate			

**Extracted 4 papers form the PhD research work.

Employment

Position	and organis	ation	Nature of job	Perio	1
Teaching	Assistant,	Indian	Teaching &	Jul 24, 2018	-
Institute of	Technology,	Indore,	Research		
India					

Principal areas of interests: Atomistic modelling of nanomaterials, Nanotechnology in engineering, Nanomechanics of nanomaterials and nanocomposite, Flexoelectricity, piezoelectricity.

Technical skills: LAMMPS, Material Studio, VMD, OVITO, VESTA, Nano-engineer-1, ANSYS, MATLAB, SOLID WORKS, AUTOCAD, MS office, Origin.

Teaching experience

Title	Level	Number of
	(UG/PG)	times
Machine Design I and II	UG	2
Machine Drawing	U.G.	1
Theory of Machine	U.G.	2
Internal combustion Engines	U.G.	2
Computational Techniques in Materials Engineering	U.G. and P.G.	1
Micromechanics and Nanomechanics	U.G. and P.G.	1

Professional Recognition/Award/Prize/Certificate (National)

- Qualified GATE 2016 with AIR 10060 and 72.65 Percentile.
- Won II Prize in ELECTROMECHANICAL JUNKYARD-2011 at TRUBA college of Engineering and Technology, Indore.

Publications	Published	Accepted	Under	Manuscript
			Review	preparation
Papers in Refereed	3	-	-	3
International Journals				
Papers in International	3	-	-	-
Conferences				
Papers in National	1	-	-	1
Conferences				
Google Scholar: Citations = 30, h-index=3, i10-index = 1 (Link Google Scholar)				

Publications (List enclosed as Annexure CV-1)

Academic Activities

- **Organized:** Six Days' online QIP- STC program on "Micro- & Nano-Mechanics of Solids: Fundamentals & Applications" on 14th December 2020. (Avg. feedback 4.4/5, Participant-61)
- **Organized:** TEQIP course titled "Atomistic Modelling of Solids", Dec 21-25, 2020 at IIT Indore. (Avg. feedback 4.68/5, Participant-65)
- **Coordinator:** Coordinate "International Conference on Precision, Meso, Micro & Nano Engineering" held at IIT Indore from Dec 12-14, 2020. More than 300 national and international participants attended this conference.
- Coordinator: BAJA SAEINDIA 2013-14

Ongoing	Research	Projects
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Title and Sponsored agency	Duration	Adviser
Characterizing the flexoelectric	36	Dr. Shailesh I. Kundalwal
phenomena in monolayer boron nitride	months	(Associate Prof. Mechanical
nanosheets.	(2018-	Engineering, IIT Indore)
(SERB, DST India Sponsored)	21)	
(Extracted Paper: Journal Paper 3 and		
Conference paper 2)		

Completed Research Projects

Title and Sponsored agency	Duration	Adviser
Effects of vacancy defects on the elastic	12	Dr. Shailesh I. Kundalwal
properties of boron nitride nanotube using	months	(Associate Prof. Mechanical
MD simulation.	(2017)	Engineering, IIT Indore)
(M.Tech. Project)		and
(Extracted Paper: Journal Paper 1 and		Ajeet Bergaley (Assistant
Conference paper 3)		Prof. Mechanical
		Engineering, IET, DAVV,
		Indore)
Duct design in air conditioning system at	6	Dr. Ashesh Tiwari (Prof.
'B' block, IET DAVV, Indore	months	Mechanical Engineering,
(Sponsored by ISHRAE-2016-17)	(2016)	(HOD) IET, DAVV, Indore)
Design and Fabrication of braking systems	6	Dr. Rupesh Tiwari (Assistant
of Automatic transmission vehicle (ATV)	months	Prof. Mechanical
(Sponsored by BAJA SAEINDIA-2013-14)	(2013-	Engineering, TRUBA
	14)	College, Indore)
Design and Fabrication of wind power	6	Dr. Abhay Kakride (Assistant
water pump at TRUBA college of	months	Prof. Mechanical
Engineering and Technology Indore.	(2014)	Engineering, TRUBA
		College, Indore)

Industrial and Academic Trainings

Indo German Tools Room on Industrial training (recognized by MSME)		
Sanwer road Indore.		
Indo German Tools Room on AUTOCAD (recognized by MSME) Sanwer	4 weeks	
road Indore.		
Satpura Thermal Power Station Industrial training (Government of		
Madhya Pradesh) Sarni.		
Workshop on 2D DRAFTING and 3D MODELING (MECHINCA Design		
Solution) at TRUBA college, Indore.		

Invited Talks

- 1. Talk on "Electromechanical response of BNS" in IIT Indore. (Case Study)
- 2. Talk on "Introduction of Nanoengineer and OVITO software" at IIT Indore.
- 3. Talk on "Formulation of MD simulation of Uniaxial tension test in LAMMPS" at IIT Indore.

Personal information

DOB : August 16, 1992	Languages: Hindi, English
Nationality: Indian	Marital Status: Married
Passport No.: T1101639	Gender: Male
Present Address : Applied and Theoretical Mechanics lab (ATOM), 301, POD 1 B, IIT Indore, Simrol, 453532, Madhya Pradesh, India	Permanent Address : 217/c, Mayur Nagar, Musakhedi, Indore Dist. Indore, 452001, Madhya Pradesh, India