Multi-scale mechanics of monolayer graphene membranes: Elasticity, fracture, and mechanochemistry

by

Sandeep Kumar

B. Tech., Mechanical Engineering
Indian Institute of Technology, Kanpur (2007)

M.S., Aeronautics
California Institute of Technology, Pasadena (2008)

Submitted to the Department of Mechanical Engineering
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in Mechanical Engineering

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February 2015

© Massachusetts Institute of Technology 2015. All rights reserved.
DISCLAIMER NOTICE

Due to the condition of the original material, there are unavoidable flaws in this reproduction. We have made every effort possible to provide you with the best copy available.

Thank you.

The images contained in this document are of the best quality available.
Multi-scale mechanics of monolayer graphene membranes:

Elasticity, fracture, and mechanochemistry

by

Sandeep Kumar

Submitted to the Department of Mechanical Engineering on January 29, 2015, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering

Abstract

Graphene, owing to its remarkable material properties, is considered as an ideal material for a broad range of nano-scale applications. The performance of any graphene-based device would depend upon the material’s response to deformation and its intrinsic resistance to failure. Nano-indentation is a useful technique to obtain such information, but analysis of the nano-indentation of graphene poses unique challenges, due to the multi-scale nature of the underlying processes. A sub-nm scale arises due to the atomic-level activities antecedent to material failure via deformation-induced lattice instability. While elastic instabilities are captured by continuum-level analysis, the soft-mode instabilities are not. Further, the potentially unstable region remains in contact with the nanoindenter and is subjected to high contact stresses which may trigger a strong mechanochemical interaction between graphene and the indenter surface. Such interactions may non-trivially affect the point of elastic to inelastic transition, as well the atomistic mechanism controlling it. A second length-scale, at least two orders of magnitude larger, is set by the scale of the indenter. For these reasons, an accurate analysis of graphene nano-indentation must adequately treat the relevant physical phenomena across these scales, and work carried out in this thesis undertakes this task.

First, we propose and calibrate a hyperelastic constitutive modeling scheme for graphene based on symmetry-invariants of the logarithmic strain measure. The model adequately describes both the nonlinear softening and the anisotropy in the material response. For a set of homogeneous finite deformations, the stress values predicted by the model compare well with the directly-calculated \textit{ab initio} values, validating the fidelity of the model. For a number of biaxial deformation modes the elastic stability limits predicted on the basis of acoustic tensor analysis compare well with results from phonon calculations carried out independently using linear response density functional perturbation theory. Particularly, we show that the limit of elastic stability in equi-biaxial deformation of graphene has been widely misinterpreted as coinciding with achieving peak bi-axial stress. The present continuum formulation, supported by
independent phonon calculations, clearly illustrates that an elastic shearing instability precedes the maximum stress configuration under this loading mode.

Secondly, we investigate the limits of reversible deformation in graphene under various loadings using atomistic-level lattice-dynamical stability analysis. Based on this information, we construct continuum failure surface for graphene, both in terms of stress, and strain, as a smoothed representation of the envelope of all possible lattice instabilities: long wavelength as well as short wavelength, and structural as well as material failures.

The third focus area examines the graphene-diamond interaction as a function of interfacial separation, based on combined density functional theory and molecular dynamic calculations. The calculated interfacial energy as a function of separation exhibits two local minima, indicating that a graphene monolayer on a diamond \{111\} or \{100\} surface has two possible equilibrium states: a physisorbed state at low compressive stress, governed by weak vdW forces, and a chemisorbed state at large compressive stress, governed by strong covalent forces. Taking the DFT/MD energy-separation data as input, we derive a continuum traction-separation relation for graphene-diamond interface, which describes both the weak vdW adhesion and the strong chemical interaction.

Finally, we show that existing interpretations of recent nano-indentation experiments on suspended graphene sheets, based on finite element simulations adopting frictionless hard contact models intended to simulate van der Waals interaction, indicate that at experimentally-measured failure loadings, the inferred strain in the graphene sheet directly beneath the diamond indenter is anomalously large compared to the fracture strains predicted by both soft-mode and acoustic lattice stability analyses. We demonstrate that this discrepancy cannot be attributed to deficiencies in the graphene constitutive model, geometric features of the indenter, or the nature of assumed kinematic boundary conditions adopted in the simulations. We examine the implications of inducing strong covalent interactions at the graphene-indenter interface in connection with measured fracture loading levels in nano-indentation experiments. Both finite element and MD simulations suggest that the shear stiction associated with such induced interactions leads to a strain-shielding effect in the graphene. The shear stiction restricts relative slip of the graphene sheet at its contact with the indenter, thus initiating a local strain-shielding effect. As a result, the spatial variation of continuing incremental strain is substantially redistributed, locally limiting the buildup of strain in the region directly beneath the indenter while adding to deformation of nearby, lower-strained regions. The shear strength of the graphene-indenter covalent interaction depends strongly on the level of hydrogen passivation on the indenter tip. Simulations show that at intermediate levels of hydrogen saturation, the strain-shielding effect redistributes strain in the graphene so that experimentally-determined fracture loading can be supported without prematurely reaching locally-limiting states of lattice deformation and stress.

Thesis Supervisor: David M. Parks
Title: Professor of Mechanical Engineering
Acknowledgements

My heart goes out to all those who provided academic and moral support for me over my years of PhD study at MIT. Academically, each member of my thesis committee deserves particular acknowledgement for shaping the way that I approach research. First, I must thank my adviser Prof. David Parks for his guidance and support, for challenging me everyday to advance the field of mechanics, and for bringing the best of me as a researcher and as a person. Beyond his wealth of knowledge in several fields of physical science, Prof. Parks has taught me how to take raw ideas and compile them into something much bigger.

I am also graciously indebted to Prof. Kenneth Kamrin, who has been both a friend and mentor to me. His energetic, creative, and broad approach to problem-solving mirrors what I aspire to be in the future. I am also grateful to him for generously providing me with the computational resources needed for conducting this research work.

My deepest gratitude also goes to Prof. Ju Li. In my many interactions with Prof. Li, he has been an excellent source of feedback on the various ideas I have had and has always kept the process positive through his insightful comments and interest in the subject.

On the non-academic side, I am infinitely grateful to my family for always being there for me in times of good and bad. I am also grateful to Debarpita Ray. Her love, support, and companionship has been invaluable to my well-being over the last year. Finally, I wish to thank my friends in Boston who continue to be a part of my life: Sumit, Sanjiv, Ritika, Manjari, Amol, Tathagat and Swati.
This doctoral thesis has been examined by a Committee of the Department of Mechanical Engineering as follows:

Professor David M. Parks .............................................
   Chairman, Thesis Committee
   Professor of Mechanical Engineering

Professor Ken Kamrin ..............................................
   Member, Thesis Committee
   Assistant Professor of Mechanical Engineering

Professor Ju Li ...........................................................
   Member, Thesis Committee
   Professor of Nuclear Science and Engineering
# Contents

1 General introduction 41
  1.1 Introduction ............................................. 41
  1.2 Modeling and simulations in material characterization of graphene . 44
  1.3 Overview of the various simulation approaches ......................... 45
  1.4 Multi-scale modeling based approach .......................... 47
  1.5 Ingredients of the multi-scale modeling based approach ............. 50
  1.6 Thesis outline ........................................... 53
    1.6.1 Symmetry-invariants-based approach to constitutive and failure modeling .................................................. 53
    1.6.2 Density functional theory methods .......................... 54
    1.6.3 Statistical method to generate a complete and irreducible integrity basis for 2D crystal classes ......................... 55
    1.6.4 Large deformation hyperelastic constitutive model for graphene 56
    1.6.5 Failure model for graphene derived from analysis of phonons . 57
    1.6.6 Continuum model for graphene-diamond interaction ............ 58
    1.6.7 Mechanochemical analysis of nanoindentation of graphene .... 58
    1.6.8 Conclusion ........................................... 59

2 Invariant-based representation theory for constitutive and failure modeling 61
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Introduction</td>
<td>61</td>
</tr>
<tr>
<td>2.2</td>
<td>Preliminary remarks</td>
<td>63</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Kinematics</td>
<td>63</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Strain measures</td>
<td>67</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Conversion between stress measures: work-conjugacy theorem</td>
<td>70</td>
</tr>
<tr>
<td>2.3</td>
<td>Elements of constitutive and failure modeling of an anisotropic material</td>
<td>71</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Material objectivity</td>
<td>71</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Material symmetry restriction</td>
<td>72</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Isotropicization Theorem</td>
<td>72</td>
</tr>
<tr>
<td>2.3.4</td>
<td>Isotropic invariant-based representation</td>
<td>73</td>
</tr>
<tr>
<td>2.3.5</td>
<td>Invariant-based interpolation</td>
<td>77</td>
</tr>
</tbody>
</table>

3 Energetics and lattice dynamics from first-principles calculations 81

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>81</td>
</tr>
<tr>
<td>3.2</td>
<td>Quantum mechanical system</td>
<td>83</td>
</tr>
<tr>
<td>3.3</td>
<td>Born-Oppenheimer approximation</td>
<td>83</td>
</tr>
<tr>
<td>3.4</td>
<td>Wave function based approach to solution of many-electron Schrödinger's equation</td>
<td>85</td>
</tr>
<tr>
<td>3.5</td>
<td>From wave function to density</td>
<td>87</td>
</tr>
<tr>
<td>3.6</td>
<td>Density functional theory</td>
<td>88</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Kohn-Sham ansatz</td>
<td>90</td>
</tr>
<tr>
<td>3.7</td>
<td>GGA and LDA approximations</td>
<td>92</td>
</tr>
<tr>
<td>3.7.1</td>
<td>LDA</td>
<td>92</td>
</tr>
<tr>
<td>3.7.2</td>
<td>GGA</td>
<td>93</td>
</tr>
<tr>
<td>3.8</td>
<td>Lattice dynamics</td>
<td>93</td>
</tr>
<tr>
<td>3.8.1</td>
<td>Phonons: normal modes of lattice vibrations</td>
<td>93</td>
</tr>
<tr>
<td>3.8.2</td>
<td>Born- von Kármán model</td>
<td>94</td>
</tr>
<tr>
<td>3.8.3</td>
<td>Phonons-based lattice stability analysis</td>
<td>103</td>
</tr>
</tbody>
</table>
Method for generating complete and irreducible integrity basis for scalar-valued function of a symmetric tensor second order tensor, and of a vector

4.1 Introduction ........................................... 105
  4.1.1 Mathematical foundation .............................. 108
  4.1.2 Weyl’s fundamental theorems on invariants ............. 109
  4.1.3 Basis reduction via iterative Principal Component Analysis (PCA) 114

4.2 Examples ..................................................... 119
  4.2.1 Symmetry-invariants of a 2D vector with respect to \( C_{6v} \) symmetry group ............................. 119
  4.2.2 Symmetry invariants of a symmetric, second-order tensor w.r.t. \( C_{6v} \) symmetry group ....................... 126

4.3 Conclusion .................................................. 135

5 Hyperelastic response of the ideal graphene single-crystal 137

5.1 Introduction .................................................. 137
5.2 Literature review ............................................ 138
5.3 Kinematics ................................................... 140
5.4 Invariant-theoretic approach to constitutive modeling ........... 142
5.5 Training set for evaluation of the elastic constants ............. 144
5.6 Hyperelastic constitutive response of graphene .................. 146
  5.6.1 Strain energy per unit reference area \( \psi \) .................. 150
  5.6.2 Work-conjugate stress tensor \( T^{(0)} \) ......................... 155
  5.6.3 Work-conjugate tangent moduli tensor \( L^{(0)} \) ............... 157
  5.6.4 Acoustic tensor ............................................. 158

5.7 Validation of the constitutive model .......................... 161
  5.7.1 Comparison of small-strain elastic constants with experiments 161
  5.7.2 Prediction of elastic stability limits ....................... 162
5.7.3 Stress-strain response curves .................................. 172
5.8 Discussion and conclusion ........................................... 174

6 A continuum failure model for graphene derived from phonons-based stability analysis ............................................. 179

6.1 Introduction .......................................................... 179
6.2 Framework of representation ....................................... 184
   6.2.1 Kinematics ...................................................... 184
   6.2.2 Symmetry-constraints on representation ..................... 186
   6.2.3 Functional bases for $C_{6v}$ symmetry group ............... 187
   6.2.4 Form of the failure function in terms of the functional bases . 189
6.3 Determination of the instability function of graphene .......... 190
   6.3.1 Methods: calculation of phonons from DFPT approach .... 191
   6.3.2 Sampling scheme ............................................. 193
   6.3.3 Representation and interpretation of the data .............. 194
   6.3.4 From discrete dataset to continuum lattice stability function via interpolation .................................. 198
6.4 Mapping the instability surface from strain space to stress space ... 203
6.5 Validation .......................................................... 206
   6.5.1 Comparison between predicted response and calculated values from DFPT ............................................. 207
   6.5.2 Comparison with acoustic tensor analysis — elastic (material) instabilities in tension .............................. 208
   6.5.3 Comparison with buckling analysis — structural instabilities in compression ............................................. 211
6.6 Implementation of failure function in a continuum FEA scheme 215
   6.6.1 Outline of the methodology ................................... 215
   6.6.2 Failure analysis in blistering ................................... 216
7 Continuum traction-separation law for Graphene-Diamond interface: vdW + covalent interaction 227

7.1 Introduction .................................................. 227
7.2 Background .................................................. 229
7.3 Computational details .............................. 232
  7.3.1 First-principles density functional theory .............. 232
  7.3.2 Molecular dynamics based on reactive bond order potentials 233
7.4 Simulation results and discussions .................... 234
  7.4.1 Graphene-Diamond \{111\} interaction from DFT ........ 234
  7.4.2 Graphene-Diamond \{111\} interaction from MD simulations . 236
  7.4.3 Graphene-Diamond \{100\} interaction MD simulations . . 238
  7.4.4 Effect of surface hydrogen .......................... 245
7.5 Continuum model for graphene- diamond interaction .......... 249
  7.5.1 vdW-interaction ........................................ 250
  7.5.2 Bonded interaction .................................... 250
  7.5.3 Effect of finite temperature ......................... 253
  7.5.4 Shear traction ...................................... 254
7.6 Conclusion .................................................. 258

8 Multi-scale analysis of nanoindentation of graphene 259

8.1 Introduction .................................................. 259
8.2 Background .................................................. 260
8.3 Nanoindentation analysis ................................ 264
  8.3.1 FEA procedure ...................................... 265
  8.3.2 Preliminary analysis ............................... 271
  8.3.3 Boundary conditions .............................. 274
8.3.4 Indenter size and shape ........................................ 274
8.3.5 Mechanically-activated covalent interaction .............. 276
8.3.6 Mechanochemical FEA simulation .......................... 279
8.4 MD simulations .................................................. 282
8.5 Conclusion ....................................................... 286

9 General conclusion and future directions 289

9.1 Summary of major findings ...................................... 289
9.1.1 Future research directions ................................. 294

A Mathematica codes ............................................ 301
List of Figures

1-1  Schematic illustration of a nanoindentation experiment (top) and the measured indentation force vs deflection response curve (bottom). . . . 44

1-2  Schematic illustration of a nanoblistering experiment (top) and the measured pressure versus deflection response curve (bottom). . . . . 45

1-3  **Length and time scales of various simulation approaches:** DFT calculations capture the electronic level details and can model events that involve chemical interactions, such as the mechanochemical interaction between graphene and diamond, as shown. However, these are limited to length-scales of the order of Å and time-scales of the order ps. MD simulations are based on empirical interatomic interactions and ignore the electronic level details. These allow to simulate larger system sizes (nm) and times (ns), compared to DFT calculations. However, they also tend to be less accurate than DFT. Continuum simulations are the least expensive amongst all and allow to model system-sizes greater than μm and time-scale larger than ms. . . . . . . . . . . . . . 48

2-1  Schematic of the graphene lattice, showing the two Bravais sublattices and the shift vector. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 65
2-2 In indentation, the realizable variations in deformation gradient take place over lengths that are comparable to indenter size and contact surface dimensions, both of which are much larger than lattice spacing. Therefore, locally, a material point, labeled by its current position \( \mathbf{x} \), behaves as if deformed homogeneously, and can be described by the local deformation gradient \( \mathbf{F}(\mathbf{x}) \), for which the strain energy and stress tensor can be calculated via hyperelastic constitutive response function.

2-3 Schematic showing invariant-based interpolation scheme for modeling of hyperelastic constitutive response of graphene. The \textit{ab initio} energies and stresses calculated for a sufficiently broad set of deformed configurations spanning these classes is used as the training set within the framework of hyperelasticity, then the invariant-based representation theory is employed to recover a constitutive relation for free energy \( \psi \) in terms of the symmetry-invariants of the logarithmic strain tensor.

3-1 Schematic of a crystalline material. The interatomic interactions are modeled as springs in a phonon-based picture.

3-2 Computational framework to determination of phonons frequencies via calculation of force constant matrix.

3-3 (a) Brillouin zone of Al with special directions indicated. (b) Phonon-dispersion of Al obtained from DFPT phonon calculations: solid lines are calculated response and dots are the measured values from neutron scattering experiments.

3-4 (a) Brillouin zone of graphene with special directions indicated. (b) Phonon-dispersion of graphene obtained from DFPT phonon calculations. The dispersion contains 6 branches: 3 corresponding to acoustic phonons and 3 corresponding to optical phonons.
4-1 Brillouin zone of graphene with the irreducible wedge, the three high
symmetry-points, and the two material axes, the armchair and the
zigzag, indicated. The reciprocal space vector $k$ is also shown. 120

4-2 Evolution of rank of covariance matrix $\Gamma$ with the number of terms in
the basis. Every time a linearly-independent terms is included in the
basis, a jump by 1 is noted in the rank of the resulting covariance matrix. 126

4-3 Evolution of rank of covariance matrix $\Gamma$ with the number of terms in
the basis. Every time a linearly-independent terms is included in the
basis, a jump by 1 is noted in the rank of the resulting covariance matrix. 132

4-4 Schematic description of the purely deviatoric deformation: a stretch
of $\lambda$ at an angle $\theta$ from the material $\hat{x}$-axis. 133

5-1 Plots of the \textit{ab initio} deviatoric energy $\psi^{\text{Dev}}$ as a function of shape-
changing stretch $\lambda$ at various values of biaxial stretch $J^{1/2}$: (a) & (b) —
Graphene’s mechanical response remains essentially isotropic at small
to moderate strains, with anisotropy appearing only at large deviatoric
stretch. (c) & (d) — For larger values of biaxial strain, sudden drops
in $\psi^{\text{Dev}}$, indicative of material instability, are noted at finite $\lambda$-values.
Data from the unstable regime (shown as blue-shaded) is not included
in the training set used for deriving the constitutive model. 147

5-2 (a) Graphene lattice with orientations of the material unit vectors —
$\hat{x}$ and $\hat{y}$ — and the Cartesian unit vectors — $e_1$ and $e_2$ — indicated.
The dashed lines denote the unit cell used in the \textit{ab initio} calculations.
The GGA (LDA) value of the lattice parameter is also indicated. The
armchair and zigzag directions are along the $e_1$ and $e_2$ axes respectively.
(b) Brillouin zone of graphene with high symmetry points indicated. 148
5-3  (a) The universal binding energy relation-based model for volumetric response $\psi_{\text{Dil}}$ for fitted values of the coefficients $\mathcal{E}$ and $\alpha$ as tabulated in Table 5.1. For comparison, we also show the \textit{ab initio} energies used in fitting the UBER form.  (b) DFT data for $\mu(\epsilon_a)$ fitted with the proposed functional form of equation (5.29).  (c) DFT data for $\eta(\epsilon_a)$ fitted with the proposed functional form of equation (5.30).......

5-4  (a) The instability due to loss of positive-definiteness of $\mathbf{A}$ in equibiaxial stretch ($\mathbf{F} = J^{1/2}\mathbf{I}$) corresponds to the vanishing of $\mu(\epsilon_a)$ that occurs at the critical equi-biaxial areal strain of $\epsilon_a = 0.35$(GGA) and 0.36(LDA).  (b) LDA Phonon dispersion along the $\Gamma - K$ direction shows a long-wavelength transverse acoustic phonon at $\Gamma$ going unstable near $\epsilon_a = 0.34$; softening of this branch is associated with the vanishing shear modulus $\mu(\epsilon_a)$.  (c) Phonon dispersions along the $M - K$ direction show a soft-phonon mode appearing just before $\epsilon_a = 0.297$, well before the acoustic instability.  .......

5-5  (a) Eigenvalues of the acoustic tensor $\mathbf{A}$ as a function of stretch $\lambda_s$ in the zigzag direction. The eigenvalue $\Lambda_2$ vanishes at a critical stretch, $\lambda_s \approx 1.18$ for GGA, and $\approx 1.19$ for LDA, indicating an acoustic instability in the material. The associated eigenvector of the unstable mode occurs in the $\mathbf{e}_1$-direction with polarization along $\mathbf{e}_1$-direction, implying longitudinal instability mode. The solid/dashed lines are from constitutive fits to GGA/LDA results.  (b) LDA phonon dispersion curves along the $\Gamma - M$ direction at increasing values of uniaxial strain. A long-wavelength longitudinal instability emerges at a uniaxial logarithmic strain of 17.23%, corresponding to $\lambda_s = 1.18$.  .......

18
5-6 (a) Eigenvalues of the acoustic tensor $A$ as a function of stretch $\lambda_a$ along the armchair direction parallel to $e_2$. The eigenvalue $A_2$ vanishes at a critical stretch $\lambda_a \approx 1.23$ (GGA) and $\approx 1.24$ for (LDA), indicating an acoustic instability in the material. The associated eigenvector shows that this instability occurs in the $e_2$-direction, and the polarization of the unstable mode is also along the $e_2$-direction, implying that the instability is of longitudinal nature. The solid/dashed lines are calculated from constitutive fits to GGA/LDA results. (b) LDA Phonon dispersions along $\Gamma - K$ direction at increasing uniaxial strain. A long wavelength longitudinal instability emerges at a uniaxial logarithmic strain of 22.5%, corresponding to $\lambda_a = 1.252$.

5-7 (a) Eigenvalues of the acoustic tensor $A$ as a function of stretch $\lambda_a$ along the zigzag direction. The eigenvalue $A_2$ vanishes at a critical value of $\lambda_a \approx 1.186$ for GGA and $\lambda_a \approx 1.192$ for LDA, indicating an acoustic instability. The associated eigenvector indicates that this instability occurs in the $e_2$-direction, and the polarization of the unstable mode is also along the $e_2$-direction, implying that the instability is of longitudinal nature. The solid/dashed lines are from constitutive fits to GGA/LDA results. (b) LDA Phonon dispersions along the $\Gamma - M$ direction at increasing uniaxial stress in the zigzag direction. A long-wavelength instability with longitudinal polarization emerges at $\lambda_a = 1.20$. 

168

170
5-8 (a) Eigenvalues of the acoustic tensor $\Lambda$ as a function of the uniaxial stretch $\lambda_u$ along the armchair direction. The eigenvalue $\Lambda_2$ vanishes at a critical value of $\lambda_u \approx 1.238$ for GGA and $\approx 1.25$ for LDA. This indicates an acoustic instability in the material. From the associated eigenvector, we infer that this instability occurs in the $e_2$-direction, and the polarization of the unstable mode is also along the $e_2$-direction, implying that the instability is of longitudinal nature. The solid/dashed lines are from constitutive fits to GGA/LDA results. (b) LDA Phonon dispersions along the $\Gamma-K$ direction at increasing uniaxial stress along the armchair direction. A long wavelength instability with longitudinal polarization emerges at $\lambda_u = 1.25$. .......................... 171

5-9 (a) Variation of Cauchy mean normal stress with areal strain as predicted by the UBER-based continuum model, along with corresponding ab initio values. (b) Variation of the dilatational tangent modulus $\kappa$ with areal strain $\epsilon_a = \ln J$, as predicted by the UBER-based continuum model. .......................... 174

5-10 Stress-strain curve obtained from the continuum model for uniaxial strain along (a) armchair direction and (b) zigzag direction. For comparison, we have also shown the ab initio stress values. The arrow shows the location of maximum stress. The solid lines are LDA results, whereas the dashed lines are GGA counterparts. .......................... 175

5-11 Validation of the continuum model for uniaxial stress along (a) the armchair direction and (b) the zigzag direction. The continuum model (solid line) is in good agreement with the LDA ab initio values. The solid lines are LDA results, whereas the dashed lines are GGA counterparts. .......................... 176
5-12 Ratio of transverse strain (due to Poisson contraction) to longitudinal strain for uniaxial stress along (a) the armchair direction and (b) the zigzag direction. The solid/dashed lines are LDA/GGA results. 177

6-1 (a) Graphene lattice with orientations of the material unit vectors — \( \hat{x} \) and \( \hat{y} \) — and the Cartesian unit vectors — \( e_1 \) and \( e_2 \) — indicated. The dashed blue lines denote the unit cell used in the \textit{ab initio} calculations. The GGA (LDA) value of the lattice parameter is also indicated. The armchair and zigzag directions are along the \( e_1 \) and \( e_2 \) axes respectively.
(b) Brillouin zone of graphene with high symmetry points indicated. 188

6-2 Phonon dispersion of undeformed graphene obtained from DFPT calculations. (a) Phonon dispersion surfaces in the Irreducible Brillouin Zone (IBZ) of graphene. (b) Phonon-dispersion curves along high-symmetry directions. Major features of the phonon dispersion in graphene are evidenced: (1) LO-TO degeneracy; (2) near-quadratic dispersion of the ZA branch at \( \Gamma \); and (3) a Kohn anomaly at the high-symmetry \( K \)-point. 192

6-3 (a) Notation scheme illustrating deformation of the graphene lattice: the undeformed lattice (faint black) is first subjected to a uniform dilatation (faint blue) \( U_1 = J^{1/2} I \), and then to an isochoric shape-changing deformation \( U_2 = \lambda r_1 \otimes r_1 + \lambda^{-1} r_2 \otimes r_2 \), resulting in the final configuration (dark red). (b) Cartesian plot of critical principal logarithmic strains \( \mathcal{E}^c \) (upper curve, solid line), and \( \mathcal{E}^c_r \) (lower curve, dashed line) vs. \( \tilde{\mathcal{E}} \) for sampled orientation \( \theta = 0 \). (c) Corresponding plot of \( \mathcal{E}^c \) for sampled orientation \( \theta = \pi/2 \). In the lattice stability curves of both (b) and (c), the type of incipient lattice instability for the given critical strain state is color-coded: red denotes incipient buckling, blue denotes elastic instabilities, while green denotes soft mode instabilities. 195
6-4 Phonon dispersions of graphene at certain critical states of deformation, marked as '1', '2' and '3' in Fig.[6-3], along the zigzag deformation path (θ = 0). Also shown are the deformed Brillouin zone (green polygon), the irreducible wedge (red polygon), and the sampled instability direction (dashed line). At smaller values of $\tilde{E}$, the incipient instability due to superimposed isochoric stretch is a structural buckling instability arising from an unstable ZA branch, while at larger values of $\tilde{E}$, the incipient instability due to a superimposed isochoric deformation is a material instability arising from an unstable LA branch. Finally, the critical value of $\tilde{E}$ is reached at which the lattice fails without any superimposed isochoric deformation, arising from a soft phonon mode of the TA branch.

6-5 Phonon density of states of graphene at certain critical states of deformation, marked as '1', '2' and '3' in Fig.[6-3], along the zigzag deformation path (θ = 0). The failures under deformation with a superimposed deviatoric strain are seen to be accompanied with a phononic band gap, unlike the soft mode failure under a pure dilatational strain in which the phononic band gap is absent.

6-6 (a) Sampled data points for $E_i^c$ for $\theta = 0$ and $\pi/2$ (straight-line segments connect data points). (b) Fifth-order polynomial interpolation functions for $E_i^c$ along the two sampled directions — obtained by fitting functions described by equation (6.21) and equation (6.22). The solid lines denote the critical major principal strain $E_1^c$ values, while dashed lines denote the critical minor principal strain $E_2^c$ values.
6-7 (a) The radial interpolation for the failure function along the two sampled directions $\theta$. The solid lines denote the major principal value $\mathcal{E}_1$, while dashed lines denote the minor principal value $\mathcal{E}_2$. (b) $90^\circ$ wedge cut out from the threeD polar plot of the stability function. The transparent blue surface denotes the zero level. The upper red surface denotes the threeD polar plot of the surface given by $\mathcal{E}_1 = \mathcal{E}_{1}^s(\hat{\mathcal{E}}, \Theta)$, while the green surface denotes the surface described by $\mathcal{E}_2 = \mathcal{E}_{2}^s(\hat{\mathcal{E}}, \Theta)$. The yellow and blue arrows denote the zigzag and armchair directions, respectively. The black line denotes the outline of the lattice.

6-8 (a) Numerical mapping of the instability surface from strain space to stress space. The axes in stress space are in the units of N/m. The Yellow and Blue arrows denote the zigzag and armchair directions, respectively.

6-9 (a) Scheme of notations indicating the strain components $\mathcal{E}_{11}^{\alpha}$ and $\mathcal{E}_{22}^{\alpha}$ corresponding to a set of axes $\mathbf{v}_1 - \mathbf{v}_2$ having orientation $\alpha$. (b) 2D Failure contour in terms of normal strain components for the biaxial strain with principal axes aligned with the material symmetry-axes, i.e., $\alpha = 0$. (c) The corresponding failure contour in stress space.

6-10 Shown are the failure contours for biaxial strains with directionalities $(a) \alpha = \pi/6$ (b) $\alpha = \pi/15$ (c) $\alpha = \pi/10$ and (d) $\alpha = 2\pi/15$. These directionalities are not included in the interpolation procedure. The predicted failure limits (solid red lines) by the model are in close agreement with the directly calculated values (connected blue dots) obtained from DFPT analysis.
6-11 (a) Failure contour in strain space for biaxial state of strain with $\alpha = 0$, superposed with elastic-stability limit curve obtained from acoustic tensor analysis and the buckling-instability curve obtained from Poisson analysis. (b) The corresponding curves in stress-space. Note that the contraction due to ‘Poisson effects’ decreases as the strain increases. Intersection of Poisson analysis and the acoustic instability analysis marks the uniaxial tension failure. Note that in nearly equi-biaxial deformations, the phonon-instability precedes the elastic instability (conforming with Yevick & Marianetti’s [125] calculations), indicating that in such deformations, lattice instability is due to a short-wavelength instability.

6-12 Schematic of blistering (a) of an elliptic membrane and (b) of a circular membrane. The membrane is clamped at the boundary, and is subjected to a pressure (denoted by arrows) from below, resulting in the bulged configuration as shown in the figure. The state of strain at the center of the membrane is equi-biaxial in case of a circular membrane whereas it is biaxial with larger strain in the minor direction in case of elliptic membrane.

6-13 Sequence of images showing the evolution of the stability-indicator $F = \mathcal{E}_2^c(\mathbf{E}, \Theta) - \mathcal{E}_1$ as a function of pressure-difference across the circular membrane. The central region with negative value of the stability indicator indicates the material elements that have reached the limits of stability, which are at the verge of mechanical failure.

6-14 Pressure vs central deflection curve for the two example problems considered. On this plot, the macrosopic (elastic) instabilities are located by a $\times$; while the location of a soft-mode (microscopic) instabilities is denoted by $\ast$. 

24
6-15 (a) The deformation path of the critical material element traced in terms of $\mathcal{E}_1$, $\mathcal{E}$, and $\theta$ (shown by dashed red line) and in terms of $\mathcal{E}_2$, $\mathcal{E}$, and $\theta$ (shown by dashed green line). The intersection of the deformation path with the failure surface indicates the onset of failure. (b) On a 2D plot, the trajectories in terms of normal strains $\mathcal{E}_{11}^0$ and $\mathcal{E}_{22}^0$ for the elliptical (denoted by E) and the circular (denoted by C). For elliptical membrane, the points of intersection of the trajectory with the failure contour and the elastic instability curve coincide indicating that the failure is of acoustic nature; while for the circular membrane, the intersection with the failure contour precedes that with the elastic instability curve, indicating that the failure is triggered by a soft mode instability.

7-1 (A) The honeycomb lattice of graphene with the lattice constant indicated. Shown by the blue dotted line is the primitive unit cell of the lattice. (B) Top two layers of diamond \{111\}-crystallographic plane projected along the \langle111\rangle-crystallographic direction. Planar bond lengths of the bilayer are very close to that of graphene lattice. The red atoms are on the top layer, while the orange atoms denote the layer beneath it. (C) Graphene monolayer on top of diamond \{111\} slab. The rectangular unit cell — used in the DFT calculation— is also shown.
7-2 Graphene-diamond\{111\} interaction as a function of separation and registry: (A) & (B) The interaction energy and contact stress, respectively, as a function of separation for several different registries arising from relative position of graphene along the x-axis. (C) & (D) Same as (A) & (B) for registries arising from relative position of graphene along the y-axis. Note the rapid change in the stress at critical separation $d_c \approx 2.25\,\text{Å}$, marking the transition from physisorbed state to chemisorbed state. Two distinct wells, as noticed in energy vs separation plots, denote the physisorbed and chemisorbed states of the graphene lattice on diamond.

7-3 DFT-predicted chemisorbed states of Graphene on diamond \{111\}: The relaxed configurations and the charge density contours for the chemisorbed and physisorbed states of graphene on diamond: (A) For registry $\eta_x = \eta_y = 0$ — the structure corresponds to the $(1 \times 1)$ bulk-terminated diamond surface. The separation between the diamond surface and graphene monolayer is $d_b \approx 1.5\,\text{Å}$. (B) configuration for registry $\eta_x = 0.1a_x$; $\eta_y = 0$— the resultant structure corresponds to the Pandey-Chain reconstruction comprising alternate pentagons and heptagons ([150]). The dimer structure can be clearly seen. The equilibrium separation in this case also is $d_b \approx 1.5\,\text{Å}$. (C) physisorbed state of graphene on diamond\{111\} — planar graphene with no charge complex formation. The equilibrium stand-off distance is $d_D \approx 2.78\,\text{Å}$.
Mechanically-activated covalent interaction between graphene and {111} diamond slab— Pull test: (A) Graphene monolayer is pushed onto the diamond surface to a separation $\zeta < d_c$ and allowed to relax via conjugate gradient energy minimization. Upon relaxation, the graphene sheet assumes a puckered geometry. (B) Following the relaxation step, the monolayer is pulled sideways from the right edge (suspended region). (C) The supported region of monolayer remains adhered to the diamond substrate, while the freely suspended region eventually fractures under the action of pulling force.

Mechanically-activated covalent interaction between graphene and {111} diamond slab — Peel test: (A) Graphene monolayer is pushed onto the diamond surface to a separation $\zeta < d_c$ and allowed to relax via conjugate gradient energy minimization. Upon relaxation, the graphene sheet assumes a puckered geometry. (B) Following the relaxation step, the monolayer is pulled upward (peeled) from the right edge. (C) The supported region of monolayer remains adhered to the diamond substrate, while the suspended portion is torn away under the action of peeling force.

Graphene-Diamond {111} vdW interaction for $\zeta > d_c$ — Peel test: (A) Graphene monolayer on top of a bare {111} diamond surface with an initial stand-off distance $\zeta > d_c$ after relaxation via conjugate gradient energy minimization. For this case, upon relaxation, no puckering is observed. (B) Following the relaxation step, the monolayer is pulled up from the freely suspended right edge. (C) In this case, the monolayer easily peels off the diamond surface.
7-7 **Graphene-Diamond {111} vdW interaction for $\zeta > d_c$—Pull test:** (A) Graphene monolayer on top of a bare {111} diamond surface with an initial stand-off distance $\zeta > d_c$ after relaxation via conjugate gradient energy minimization. For this case, upon relaxation, no puckering is observed. Following the relaxation, the monolayer is pulled sideways from the freely suspended right edge (B), and the monolayer easily slides on the diamond surface (C).

7-8 **Graphene-Diamond (100) interaction:** The interaction energy vs separation curve obtained from AIREBO based MD calculation for graphene on diamond (100).

7-9 **Graphene-Diamond {100} stiction when $\zeta < d_c$—Peel test:** (A) Graphene monolayer is pushed onto a diamond {100} surface to a separation $\zeta < d_c$ and allowed to relax via conjugate gradient energy minimization. Upon relaxation, the graphene sheet assumes a puckered geometry. (B) Following the relaxation step, the monolayer is pulled up (peeled) from the freely suspended right edge. (C) The supported region of monolayer remains adhered to the diamond substrate, while the suspended portion is torn away under the action of peeling force.

7-10 **Graphene-Diamond {100} stiction when $\zeta < d_c$—Pull test:** (A) Graphene monolayer is pushed onto the diamond {100} surface and allowed to relax via conjugate gradient energy minimization. Upon relaxation, the graphene sheet assumes a puckered geometry. (B) Following the relaxation step, the monolayer is pulled sideways from the freely suspended right edge. (C) The supported region of monolayer remains adhered to the diamond substrate, while the freely suspended region eventually fractures under the action of pulling force.
7-11 **Graphene-Diamond {100} stiction when $\zeta > d_c$—Peel test:** (A) Graphene monolayer on top of a bare {100} diamond surface with an initial stand-off distance $\zeta > d_c$ after relaxation via conjugate gradient energy minimization. For this case, upon relaxation, no puckering is observed. (B) Following the relaxation step, the monolayer is pulled up from the right edge. (C) In this case, the monolayer easily peels off the diamond surface.

7-12 **Graphene-Diamond {100} stiction when $\zeta > d_c$—Pull test:** (A) Graphene monolayer on top of a bare {100} diamond surface with an initial stand-off distance $\zeta > d_c$ after relaxation via conjugate gradient energy minimization. For this case, upon relaxation, no puckering is observed. Following the relaxation, the monolayer is dragged sideways from the right edge (B), and the monolayer easily slides on the diamond surface (C).

7-13 Shown are the MD simulation results for relaxation of a graphene sheet on a hydrogenated diamond{111} surface at an initial interfacial separation $\zeta < d_c$. It is noted that upon relaxation, the graphene sheet moves outward until it settles at a larger equilibrium separation.

7-14 **Graphene on a hydrogenated diamond{111} surface—Pull test:** the interaction is governed by a weak vdW-type forces, allowing the graphene sheet to be readily pulled away.

7-15 **Graphene on a fully-hydrogenated diamond{111} surface—Peel test:** in presence of surface hydrogen, the interaction is a weak vdW-type forces, allowing the graphene sheet to be readily peeled away.

7-16 **Schematic showing a graphene supported on a substrate.** Unit vectors normal and tangential to the substrate are denoted by $\hat{\zeta}$ and $\hat{\eta}$, respectively.
7-17 *vdW interaction between graphene and indenter-tip.* The Morse function-based representation (equation [7.3]) of the graphene-tip vdW interaction provides a good description of the vdW-regime of the DFT-computed interaction energy vs separation plot (A) for all registries arising from relative translation in $x$-axis as well as (B) for all the registries arising from translation in $y$– axis.

7-18 **Graphene-diamond \{111\} bonded interaction:** (A) The two asymptotic descriptions of interfacial interaction energy given by equation [7.4] and equation [7.7]. (B) The composite description of interfacial stress vs separation given by equation [7.8]. In FEA, a variation in stress such as one seen in (B) often results in a snapback instability; therefore in order to avoid this instability, the variation of the interfacial stress traverses the path shown by the arrows in the figure.

7-19 **Graphene-diamond \{111\} bonded interaction:** (A) The two asymptotic descriptions of interfacial interaction energy given by equation [7.4] and equation [7.7]. (B) The composite description of interfacial stress vs separation given by equation [7.8]. In FEA, a variation in stress such as one seen in (B) often results in a snapback instability; therefore in order to avoid this instability, the variation of the interfacial stress traverses the path shown by the arrows in the figure.

7-20 The interfacial shear strength $\tau_0$ as a function of relative hydrogen coverage $\theta_H$. The dots denote the *ab initio* data taken from reference [220], while the solid line denotes a fitted function.
8-1 Softening of elastic moduli with dilatant area deformation, elastic instability, and soft-mode instability: Softening of (A) the 2D bulk modulus and (B) the 2D shear modulus with increasing areal strain $\epsilon_a$. (C) Plot of equi-biaxial Cauchy stress $\bar{\sigma} = \text{tr}\sigma/2$ vs. $\epsilon_a$. (D) For equi-biaxial strain, acoustic tensor analysis predicts an elastic instability at $\epsilon_a = 0.356$. (E) Independent phonon calculations confirm a shearing elastic instability at $\epsilon_a = 0.35$ through a vanishing slope of the long-wavelength TA dispersion relation. (F) Well before this elastic instability, a soft-mode instability occurs at $\epsilon_a = 0.297$ [125].

8-2 Schematic showing a graphene supported on a substrate. Unit vectors normal and tangential to the substrate are denoted by $\hat{\zeta}$ and $\hat{\eta}$, respectively.

8-3 (A) Morse-based vdW-interaction potential, and (B) the corresponding interaction stress for graphene- $a$ - SiO$_2$ interface.

8-4 Exfoliated graphene sheet snapped to the sidewalls of a cylindrical micro-cavity: A & B Experimentally-observed morphology of a graphene sheet exfoliated on the SiO$_2$ substrate (taken from Lee et al. [105]). The reported snap-to-wall distance lies in the range 3-8 nm. C & D Magnified displaced geometry of the graphene sheet relaxation before indentation predicted by our FEA simulation (micro-cavity radius $a = 500$ nm) based on the interfacial interaction described by equation [8.3]; the simulated snap-to-wall distance is approximately 7.8 nm.
8-5 **Puckering of graphene around the indenter-tip due to vdW forces:** (A) Measured force vs. time response curve (from Lee, et al. [105]), showing the jump which corresponds to snapping of graphene sheet onto the indenter. (B) The graphene sheet puckered around the indenter as predicted by the FEA simulation. (C) The snapping of graphene onto the indenter is seen to result in a jump in the force versus time response curve.

8-6 **Indenter approach and pull-off:** Images at various stages of approach and pull-off, showing the snapping and lifting of the graphene sheet with the indenter under the action of vdW forces.

8-7 **Indenter pull-off force response:** The force (magnitude) experienced by the indenter during the pulling-off as a function of time. The pull-off force required to complete separate the indenter from the graphene sheet is \( \sim 21 \) nN, which compares well with experimental measurements of Deng, et al. [49] using a Si\(_3\)N\(_4\) tip of radius 15 nm.
8-8 **Simplified finite element analysis of nanoindentation:** Contours of (A) maximum principal strain $\epsilon_{\text{max}}$ and (B) failure function $F$ beneath the indenter at the indentation loading corresponding to incipient soft-mode failure (blue color at base indicates spatial focus of the instability). (C) Top — load vs. indentation response from experiment and simulation for indenter tip radius $\rho = 16.5$ nm and flake radius $a = 0.5$ $\mu$m. Also shown are inferred failure states corresponding to the elastic and the soft-mode instabilities, and the failure state measured by Lee, et al. Bottom — Areal strain beneath the indenter vs. indentation depth $u_z|_{r=0}$ for three different indenter root radii used in experiments [105, 107]. Values of $\epsilon_a$ corresponding to elastic and soft-mode failures are marked by red and blue crosses ($\times$), respectively. Dashed lines are extrapolated to respective experimental depths at failure.

8-9 **Tip geometry and radius (image taken from Lee et al.):** (A) The radius of the indenter-tip is measured by visually fitting a circle to a high resolution TEM image of the tip. There is a possibility that such measurements underestimate the tip-radius. As shown in the figure, visually, as large as 20nm seem to be fitting the tip-radius well. (B) In order to remove the ambiguity regarding the tip geometry, the indenter geometry is directly profiled from the TEM image as shown.

8-10 **Sensitivity of the indentation response to indenter size and boundary condition:** Force vs deflection curve obtained from FEA (A) for different root radii of the spherocinical indenter geometry, and (B) for different boundary conditions. In obtaining these results we assumed a vdW interaction between the indenter and graphene.
8-11 Post-indentation TEM image of diamond indenter-tip: Post-indentation images of the indenter (A) from Rasool, et al. [160] and (B) from Lee, et al. [105]. In both images, graphene residue accumulated on the tip, shown by a red arrow, should be noted. (C) Molecular model of a sphericoconical nanoindenter with \( \rho = 16.5 \text{ nm} \), made of single-crystalline diamond. Note the \{100\} and \{111\} crystallographic planes exposed on the surface.

8-12 FEA contact stress calculated along a radial line at various indentation depths.

8-13 (A) Atomistic model of the diamond indenter with indentation axis aligned with diamond [001] direction. The \{111\} and \{001\} crystallographic planes are visible on the indenter-surface. (B) Finite element model of the indenter different with the \{111\}-planes and \{001\} planes appropriately mapped from the atomistic model.

8-14 Strain-shielding mechanism: Contours of maximum principal strain at various stages of indentation (\( \theta_H = 75\% \)). (A) \( u_z|_{r=0} = 55 \text{ nm} \): interaction between graphene and diamond tip is purely vdW, and maximum strain occurs at the point beneath the indenter. (B) \( u_z|_{r=0} = 75 \text{ nm} \): formation of a strain-shielded zone indicates that a mechanochemical interaction has been initiated at the graphene-indenter interface in the region beneath the indenter. (C) \( u_z|_{r=0} = 107.5 \text{ nm} \): As contact area grows with indentation, \{111\}-facets on the indenter tip also interact covalently with the graphene sheet, as indicated by formation of strain-shielded zones in those regions. (D) Maximum principal strain at material points ‘1’ (in red) and ‘2’ (in blue) vs. \( u_z|_{r=0} \) for induced covalent interaction (dashed lines, this simulation) and vdW interaction (solid lines, figure [8-8]).
8-15 **FEA simulation allowing development of a covalent interaction at graphene-indenter interface** ($\theta_H = 75\%$): Contours of (A) the maximum principal logarithmic strain and (B) the failure function $F$ beneath the indenter prior to failure. Note the redistribution of strain in (A) due to graphene-diamond interaction, limiting strain intensification beneath the indenter. Blue contours in (B) show regions where $F < 0$, i.e., the material has reached incipient failure. (C) Corresponding load vs. indentation depth.

8-16 **MD simulations of graphene indentation for three levels of hydrogen saturation of the diamond indenter**: (A) Illustration of varying hydrogen saturations of the indenter surface. Carbon atoms of the diamond tip in yellow, with hydrogen in blue. (B) Post-fracture images for the three cases, with graphene carbon atoms in red. (C) Force vs. indentation curves, with the points of failure marked by +, and (D) areal strain beneath the indenter vs. indentation depth for the three cases.
### List of Tables

2.1 Some examples of the Seth-Hill strain measures. .......................... 68

5.1 Values of $E$ and $\alpha$ obtained by fitting the UBER form (equation (5.28)) to *ab initio* energies. The UBER constitutive form exhibits a tangent area modulus $\kappa$ —defined in equation (5.42)— that decreases with increasing areal strain, ultimately vanishing at a critical areal strain value given by $\epsilon_a|_{\kappa=0} = 1/(1 + \alpha)$. ........................................ 152

5.2 Coefficients $\mu_0$ and $\mu_1$ and exponent $\beta$ in equation (5.29) for shear modulus $\mu(\epsilon_a)$, determined by least-square fits to a set of *ab initio* energies. The data and the functional form suggest that $\mu$ vanishes at critical value of areal strain given by $\epsilon_a|_{\mu=0} = \frac{1}{\beta} \ln(\mu_0/\mu_1)$, tabulated in the right-most column. ........................................ 154

5.3 Coefficients $\eta_0$ and $\eta_1$ in equation (5.30) for $\eta(\epsilon_a)$, determined by least-squares fitting to a set of *ab initio* energies. .................... 155

5.4 The in-plane elastic constants — recovered from our constitutive model in the limit of infinitesimal strain — compared with values reported by Lee, *et al.* [105], based on their experimental results. ................... 162

5.5 Summary of instability analyses based on acoustic tensor analysis of the constitutive models and the corresponding phonon calculations for various homogeneous deformation modes considered. .................. 172
6.1 In-plane longitudinal and transverse wave velocities calculated from LDA phonon dispersion. The values closely agree with measured values as well as with values calculated from the continuum model of the Chapter 5 of this thesis. The LO/TO frequencies at \( \Gamma \) are also in good agreement with the G-peak of the Raman spectra of graphene. Note: \( \rho_{2D} \) is the mass per reference area of graphene which is calculated from the atomic mass of carbon and the undeformed lattice constant of graphene; \( E_{2D} \) denotes the elastic modulus in uniaxial strain; and \( \mu_{2D} \) denotes the shear modulus.

6.2 Coefficients \( \gamma_{mn} \) in the expression of the instability surface (equations [6.28 & 6.29]).

6.3 Local major principal stress and local major principal strain at the unstable material element as calculated by finite element analysis. The values of stress and strain indicated in parenthesis correspond to the predictions from the acoustic tensor analysis based on the constitutive model.

7.1 Coefficients appearing in the Morse-based description of the vdW interaction between graphene and diamond (equation [7.3]), as determined from fits to the first-principles energies in the vdW regime.

7.2 Coefficients appearing in the Morse function-based approximation of the bonded interaction between graphene and diamond (equation [7.7]) as determined from fit to the first-principles calculations for the registry that corresponds to the strongest bonding in the set of registries for which \( \eta_x \geq 0 \) and \( \eta_y = 0 \).
7.3 Coefficients appearing in the Morse function-based approximation of
the bonded interaction between graphene and diamond (equation [7.7])
as determined from fit to the first-principles calculations for the registry
that corresponds to the strongest bonding in the set of registries for
which \( \eta_x = 0 \) and \( \eta_y \geq 0 \). 253

8.1 Coefficients appearing in the Morse-based description (given by Eq.
[8.4]) of the vdW interaction between graphene and \( a-SiO_2 \). 266

8.2 Failure indentation depth as a function of hydrogen surface coverage.
In the rightmost column, we show contours of the instability function
\( \mathcal{F} \) — with dark blue regions showing the incipiently unstable elements,
evaluated at the critical displacement \( u_z^{\text{crit}} \). The optimal hydrogen
saturation, leading to maximum delay in onset of failure, is noted to
occur for coverages in the range \( 72.5\% < \theta_H < 75\% \). 283

8.3 Failure indentation depth as a function of hydrogen surface coverage.
In the rightmost column, we show contours of the maximum in-plane
strain, evaluated at the critical displacement \( u_z^{\text{crit}} \). The optimal hydro-
gen saturation, leading to maximum delay in onset of failure, is noted
to occur for coverages in the range \( 72.5\% \leq \theta_H \leq 75\% \). 284
Chapter 1

General introduction

1.1 Introduction

The research and development of novel materials constitutes an integral part of the technological advancement process. The last two decades have seen a paradigm shift in material research, in which the emphasis has shifted from synthesizing an altogether a new material to extracting, characterizing, and utilizing the nanostructural and two-dimensional phases of already-existing materials [67, 68, 62, 63]. This new class of materials, which are termed nanocrystalline materials to signify the associated characteristic length-scale, exhibit a wide range of optical, magnetic, thermal, and mechanical properties that in general are superior to their bulk counterparts. For this reason, in recent years, there has been a rapid upsurge in efforts towards understanding the physics and chemistry of nanocrystalline and 2D materials.

Graphene, an atomic monolayer comprising a hexagonal network of \(sp^2\)-bonded C-atoms, is the ultimate example of a nanocrystalline material [62, 63]. Graphene, a true two-dimensional crystal, is the basic building block of all graphitic allotropes of carbon found in nature. For example, graphite is an ensemble of graphene layers stacked together with weak van der Waals forces; a nanotube, single or multi-walled,
is a single/multiple graphene layer rolled-up to form cylinder; and a fullerene is a graphene layer deformed in the form of spherical ball, with some hexagonal rings replaced by pentagons [94]. Since its inception, graphene has attracted considerable attention amongst mechanicians and material scientists for two major reasons: First, for its remarkable mechanical, electronic and optical properties.[105, 168, 102], and second, for the wealth of novel material physics that it exhibits, such as the quantum Hall effect [212], presence of a Dirac cone in the electronic dispersion [135], and the ballistic transport of phonons at room temperature [39].

The covalently-bonded hexagonal network of C-atoms gives graphene a large elastic stiffness and a high elastic strength¹. Lee et al. [105] recently measured the ideal fracture strength of single-crystalline graphene using nanoscale indentation and reported an unprecedentedly high intrinsic strength, measuring orders of magnitude greater than those of many conventional materials. In fact graphene is the only known crystal which can be stretched in excess of 15%, while remaining in the reversible deformation regime [105].

Graphene is also a promising material because of its ability to be strain-engineered wherein the material properties are tuned by application of a mechanical strain [70, 155, 139]. For example, graphene, in the undeformed state, is a zero band gap semiconductor; however, upon application of a suitable mechanical strain, a non-zero band gap opens up. However, the strain required for such purposes is often very large, of the order of 10%. A suitable material for strain-engineering should be able to withstand such large strains without undergoing a plastic deformation or fracture. Graphene’s high material strength allows it to withstand such large strains while remaining within the reversible deformation regime. This means that the band gap in graphene can be rapidly and reversibly controlled.

Ultrastrong adhesion with substrates is another technologically important prop-

¹Elastic strength is defined as the stress at which the transition from reversible to irreversible behavior takes place.
Koenig, et al., reported the adhesion energy of graphene on $a-\text{SiO}_2$ as 0.45 J/m$^2$, which is very high, comparable to solid-liquid adhesion energies [100, 13, 113]. Such ultrastrong adhesion of graphene eliminates need for an external agent to clamp graphene samples to substrate surfaces. The strong adhesion with substrates, combined with outstanding mechanical flexibility, allows graphene to conform to complex substrate geometries, which is a very important requirement for flexible electronic devices [87].

A tunable band gap, ultrahigh elastic strength and stiffness, strong adhesion and conformability to complex substrate geometries make graphene desirable for a broad range of micro-/nano electromechanical systems. Examples of graphene-based nanomechanical systems include nanoscale resonators, switches, and valves, with applications ranging from information storage and processing, molecular manipulation, to sensing [165, 24]. Graphene can also be integrated with other microstructures to create a new class of micro-/nanoelecto-mechanical devices.

The progress in the direction of graphene-based devices depends not only upon furthering our understanding of material physics of graphene, but also on development of novel techniques for design and performance-analysis of such devices. The experiments at nanoscale are both difficult and expensive to perform, which immediately rules out a design approach exclusively driven by experimental inputs. Numerical simulations are both relatively easy and inexpensive, making a numerical-simulation driven design approach both a feasible and effective compliment to experimental testings. However, the effectiveness of numerical-simulation depends upon the mathematical models describing the material behavior and its interaction with other materials, which, when supported with experimental data, will allow for the reliable predictions of the response of devices made from graphene under service conditions.
Figure 1-1: Schematic illustration of a nanoindentation experiment (top) and the measured indentation force vs deflection response curve (bottom).

1.2 Modeling and simulations in material characterization of graphene

The assessment of performance and life-span of any graphene-based nanoscale device would necessarily require comprehensive information regarding the material’s response to deformation, its intrinsic resistance to failure, and how the interaction with external surfaces affects the material properties. Experimental measurements are used to access such information. Examples are nanoindentation (a schematic shown in Fig.[1-1]), which determines the elastic constants and strength of the material [105], and nanoblistering (a schematic shown in Fig.[1-2]), which is used to determine the strength of the interfacial adhesion between two surfaces.

Unfortunately, in most circumstances, the experiments alone can not directly provide the desired material information. For example, in nanoindentation experiments, the stress/strain beneath the indenter is not directly measurable, instead the indentation
force and the deflection are recorded. Similarly, the adhesion strength can not be directly measured in a nanoblistering experiment; instead applied pressure vs deflection is measured. Subsequent modeling and simulation, therefore, becomes necessary for extraction of the desired material properties from the experimental measurements.

1.3 Overview of the various simulation approaches

Simulations are an often-sought alternative when experiments are difficult to perform, or are incapable of providing the required information. One of the widely-used simulation techniques is the molecular dynamics (MD) simulation, where each and every atomistic degree of freedom is explicitly treated, and the various thermodynamical properties of the system are evaluated from the knowledge of atomic positions and momenta via a statistical mechanical treatment [4, 5]. Over the years, MD simula-
tions have been used in a variety of material modeling problems, and have successfully provided great insight into the basic mechanisms of processes such as incipient plasticity, crack-initiation and propagation, and diffusion [108, 191, 25, 26].

Since MD treats each atomistic degree of freedom explicitly, the computational cost of simulation grows rapidly with system size. For this reason, despite the advancement in computational power, MD simulations remain prohibitively expensive. As a consequence, the system sizes simulated in MD are often unrealistically small, and loading rates are often very fast. For these reasons, a quantitative comparison of MD simulation results with experiments remains unfeasible, and insights provided by such calculations remain mostly qualitative. It should also be noted that following each atomic motion in the system is quite wasteful, as most of the atoms move along trajectories that can be determined by elastic solutions. In summary, MD simulations lack a basic feature of being a successful predictive modeling scheme: the ability to model both the realistic geometries and loading conditions encountered in real-life experiments.

Moreover, the constitutive description in MD simulations is based on empirical interatomic potentials. These potentials are calibrated only on a limited set of deformations near the undeformed state and hence are insufficiently trained for capturing the mechanics at large deformations. Therefore, MD calculations offer a limited accuracy at large deformations.

Quantum-Mechanical (QM) methods based on electronic structure calculation, such as the \textit{ab initio} Density Functional Theory (DFT) and the Hartree-Fock (HF) methods, have emerged as the dominant modeling technique amongst material physicists and chemists in recent years. These are attractive for the following reasons: First, from an accuracy point of view, the fully resolved electronic structure calculations offer a great enhancement, when compared to MD simulations, due to the absence of any empiricism. Secondly, owing to the electronic-level resolution, DFT methods
allow calculation of a wide range of material properties and physical phenomena, including those that involve a change in chemical state of the material, e.g., bond formation and bond breaking events. However, owing to \( O(N^3) \) scaling in computational cost, an \textit{ab initio} implementation capable of treating realistic system sizes currently remains well beyond the scope of modern computers.

The third alternative approach towards the modeling of nanoscale systems is on the basis of continuum models. Such models often admit elegant analytic solutions for highly idealized geometries, and these solutions are often instructive in guiding intuition concerning more complex geometries. Further, continuum models are routinely solved numerically via methods such as the finite-element method, at a fraction of the computational cost needed for MD and DFT calculations. These methods allow us to model both the realistic system sizes and loading rates. One problem with these models, especially for those involving plastic deformation, is that they are founded upon phenomenological constitutive models which are an idealization of observed deformation properties. Secondly, the continuum level technique such as finite element analysis fail to capture the atomic-level activities unless special enrichment techniques are employed.

The merits and demerits of the various simulation approaches are summarized via the illustration in Fig.[1-3].

### 1.4 Multi-scale modeling based approach

Modeling and simulation of the nanoindentation and nanoblistering experiments on graphene poses unique challenges. The major hindrance arises due to the multi-scale nature of the underlying processes. For example, in nanoindentation of graphene, physical phenomena at multiple length-scales take place. A sub-nm scale arises due to the atomic-level activities antecedent to material failure via deformation-induced
Figure 1-3: **Length and time scales of various simulation approaches:** DFT calculations capture the electronic level details and can model events that involve chemical interactions, such as the mechanochemical interaction between graphene and diamond, as shown. However, these are limited to length-scales of the order of Å and time-scales of the order ps. MD simulations are based on empirical interatomic interactions and ignore the electronic level details. These allow to simulate larger system sizes (nm) and times (ns), compared to DFT calculations. However, they also tend to be less accurate than DFT. Continuum simulations are the least expensive amongst all and allow to model system-sizes greater than μm and time-scale larger than ms.
lattice instability. While elastic instabilities are captured by continuum-level analysis, the soft-mode instabilities are not. Further, the potentially unstable region remains in contact with the nanoindenter and is subjected to high contact stresses which may trigger a strong mechanochemical interaction between graphene and the indenter surface. Such interactions may non-trivially affect the point of elastic to inelastic transition, as well the atomistic mechanism controlling it. A second length-scale, at least two orders of magnitude larger, is set by the scale of the indenter.

For these reasons, an accurate analysis of graphene nanoindentation must adequately treat the relevant physical phenomena across these scales, which is normally beyond the scope of conventional atomistic and continuum analyses [184, 185]. A continuum-level technique such as finite element analysis does not recognize the discrete atomic structure of materials. On the other hand purely microscopic theories such as crystal elasticity and lattice dynamics can readily analyze the stability of a defect-free crystal subject to homogeneous deformation, whereas the deformation beneath the indenter in a nanoindentation is too complex to be treated as homogeneous. A multi-scale framework stitching the continuum level technique to an atomistically-informed lattice stability theory is suggested as a solution to this problem. From the material strength point of view, it is important to know not only when the material becomes unstable but also the microscopic mechanisms that lead to failure and the macroscopic manifestation of the failure. Two-D materials are special in this regard as the instability takes place directly beneath the indenter. This region remains in direct contact with the indenter and therefore it is important to consider both qualitatively and quantitatively how the presence of the indenter affects the point at which the instability ensues in the graphene lattice and the governing mechanism. A well-informed continuum simulation can shed light on this. The development of mathematical models for continuum-level analysis and simulations of mechanistic behavior of graphene is the main objective of my thesis. Models are developed for mechanical
response, i.e., the stress-strain constitutive law and the failure model; as well as mod-
els for interaction with external surfaces, specifically, mechanochemical interaction
with diamond, which is a routine material used in nanoindentation experiments.
These models are obtained by fitting the mathematical forms of constitutive laws
guided by fundamental laws of material physics to suitable set of data. For certain
cases, I have derived the continuum-models by upscaling the atomistic level informa-
tion obtained from highly-accurate ab initio calculations. These are cases in which
measurements are not reported in the literature, mainly due to difficulty of performing
experiments. For example, construction of constitutive response and failure models
requires accurate measurements of deformation energies and stress/strain in the large
deformation regime of graphene. Performing such measurements on free-standing
graphene are nearly impossible due to difficulty of holding/clamping a graphene sheet
so that the desired deformation can be applied.
For other cases, the models have been derived from analysis of experiments available
in the literature; these are the cases where ab initio density functional theory (DFT)
or molecular dynamics (MD) calculation can not provide realistic information. For
example, in modeling of graphene /a-SiO₂ adhesion, the ab initio calculations are not
fully useful because the actual surface condition existing in experiments is unknown;
and in the absence of such information a faithful calculation can not be performed.

1.5 Ingredients of the multi-scale modeling based
approach

The key ingredients in these continuum level simulations are the mathematical mod-
els that describe the relevant material behavior and interactions, and the numerical
algorithms to implement them. In the following, we describe some of the essential
mathematical models required in mechanistic modeling of graphene.

1. **Constitutive model** — Continuing with the example of nanoindentation experiments on graphene, one of the key-ingredients of the FEA simulation, which is immediately realized, is the stress-strain constitutive relation for graphene. Particularly, since the region underneath the indenter experiences very large strains, a linear elastic model, which serves well only in the limit of small deformation, is not sufficient. Therefore, a stress-strain constitutive law describing the material behavior for the entire range of deformation until the onset instability, is required. In writing such a large-deformation constitutive relation for graphene, we note that —

- graphene is isotropic only at small deformation; at large deformation the material response is anisotropic, and the anisotropy is characterized by the point group symmetry of the underlying lattice. In anisotropic crystals, Neumann’s principle dictates that the point group symmetry of the lattice should be built into the constitutive law of the material.

- the material non-linearities and the associated softening can not be ignored.

To this end, we develop a hyperelastic constitutive stress-strain relation based on the symmetry-based representation scheme wherein the strain energy density function is written in terms of special scalar functions of strain measure, called symmetry-invariants, which already have all the symmetries of point group symmetry; thus the proposed model includes both the essential features— the material non-linearities and the material anisotropy. Often the softening associated with the material non-linearity, i.e., decay of elastic tangent moduli is responsible for elastic instability of underlying lattice. The proposed model allows a straightforward evaluation of the acoustic tensor for the prediction of such elastic instabilities. This constitutive model, when embedded in the finite element simulations, allows a reliable description of the
mechanical description as well as on-the-fly assessments of lattice stability. We also present a novel numerical technique to obtain a complete and irreducible set of symmetry-invariants of a two-D vector and second order tensor. The method is based on principal component analysis. The results from the method are in agreement with the ones obtained by application of the isotropicization theorem based on the notion of structure tensor, as suggested by Zheng [214, 213, 217].

2. Failure model — The another ingredient of a continuum-level simulation is a continuum failure model which allows prediction of the transition from reversible to irreversible deformation in crystalline materials. In some cases, the irreversible regime corresponds to a plastic failure, opening of a micro-crack or a void nucleation, while in other cases it may mean a shear localization or phase transformation [92, 193, 194, 3]. Nevertheless, irrespective of what the irreversible response of a crystal may correspond to, knowledge of the micro- and macroscopic conditions at which the elastic-inelastic transition occurs is of central importance to crystal mechanics, e.g., at the atomistic level, the elastic-plastic transition is an indicative of fundamental structural rearrangements in the crystal resulting from an elastic instability [191, 108, 109]; while at the continuum level, the transition can be associated with an important material property called the ideal strength [144, 216, 111]. Experimentally, limits to reversible deformation can be determined by nanoindentation. Nanoindentation is the instrumented indentation of a small region of the crystal using a nanoscale sized indenter. Exploring a submicron region basically involves constitutive response of a tiny part of the crystal comprising of a single grain containing no defects, and hence local response resembles its ideal crystal counterpart [29, 171]. In nanoindentation, the large stresses are generated beneath the indenter. Such high stresses may cause material go elastically unstable. This instability is resolved by emergence of local configurational anomalies such as dislocations, micro-cracks or phase transformations. The
occurrence of an elastic instability is observed in the force ($F$)-depth ($\delta_c$) diagram as a sudden drop, indicated by an arrow in Fig.[1-2]. However, the macroscopic response, such as the $F-\delta_c$ curve, is inadequate to interpret what microscopic processes take place underneath the indenter [184, 185]. Consequently, the microscopic details associated with the incipient plasticity remain beyond the comprehension of nanindentation, although it suffices for the determination of the indentation load at which elastic-plastic transition begins.

3. **Graphene-diamond interaction model** — The another surface with which graphene contacts during nanoindentation is diamond indenter. This scenario is different from graphene on $a$-$SiO_2$; because where in graphene on $a$-$SiO_2$ is supported freely, the interaction between graphene and diamond is under a compressive contact stress. To this end, we investigate the nature of interaction between graphene and diamond surface as a function of contact stress. Inclusion of such interaction is important as it can significantly affect the outcome of experiment, e.g., the failure load at which the onset of fracture takes place.

1.6 Thesis outline

1.6.1 **Symmetry-invariants-based approach to constitutive and failure modeling**

In chapter 2, we discuss crystal symmetry and its implications for material properties. We discuss how symmetry dictates the representation, and, how certain symmetry-invariants are more conducive for representation purposes than others. Crystalline materials are characterized by periodic arrangement of atoms in space. Such arrangement results in an anisotropic structure, i.e., the periodicity in different direction is different [96, 31, 221]. However, the crystal structure contains certain symmetries which are characterized by the material symmetry group of the crystal. For crys-
talline materials, symmetry consideration in representation of material constitutive properties becomes particularly useful, since the application of material symmetry may substantially reduce the number of bases terms required in the representation. Mathematically, the association of material properties with the material symmetry is expressed by Neumann’s principle. According to this principle —

The symmetry group of a given material must be included in the symmetry group of any tensor function in any constitutive laws of the material. Let $\mathcal{G}_{\text{crystal}}$ and $\mathcal{G}_{\text{constitutive}}$ be symmetry groups of the crystal and a given constitutive property of the crystal respectively; then according to Neumann’s principle:

$$\mathcal{G}_{\text{crystal}} \subseteq \mathcal{G}_{\text{constitutive}}$$  (1.1)

Note that the material properties may have a higher, but not a lower, symmetry than the point group symmetry of the crystal. For instance, cubic crystals are optically isotropic: in this case the physical property has a symmetry higher than the point group of the crystal.

Neumann’s principle [136] has a guiding role in determining representations of scalar- and tensor- valued properties of anisotropic materials. The symmetry restrictions imposed by Neumann’s principle can be used a guiding principle for the construction of anisotropic material properties via invariant-based representation theory [175, 214]. This theory relies on construction of a complete and irreducible set of scalar functions, called symmetry-invariants, that remain invariant under all operations in the material symmetry group.

1.6.2 Density functional theory methods

Chapter 3 presents a brief account on the ab initio density functional theory (DFT) methods employed for calculation of deformation energies, stresses and vibrational
dispersion of graphene. In the DFT framework, a crystal is treated as a many-body quantum mechanical system, the dynamics of which is governed by the Schrödinger equation. The quantum-mechanical state of the system is described by its wave function, which contains all the information about the system, and which can be obtained by solving the Schrödinger equation [96, 221]. However, due to many-body effects, the many-body Schrödinger equation can not be solved exactly; and therefore it must be solved numerically while resorting to certain approximations. We describe the major approximations and approaches employed for solving the Schrödinger equation of a many-body system, and their evolution to current state of the art DFT methods. Nielsen-Martin theorem [137] that allows calculation of stress from the results of an ab initio DFT calculation. We conclude the chapter by presenting theory of lattice dynamics, DFT-based techniques of calculating the vibrational dispersion, and the crystal stability criteria in terms of the phonon-frequencies.

1.6.3 Statistical method to generate a complete and irreducible integrity basis for 2D crystal classes

In chapter 4, we develop a novel statistical method based on the Principal Component Analysis (PCA) to generate a complete and irreducible set of symmetry-invariants of vector and second-order tensor agencies for two-D crystal classes. This method employs ideas from the theory of algebraic invariants, polarization of scalar polynomials, and a statistical technique called the Principal Component Analysis (PCA). We explicitly demonstrate the technique for the 2D crystal graphene by obtaining the symmetry-invariants of a vector and the logarithmic strain measure with respect to the $C_{6v}$ symmetry group.
1.6.4 Large deformation hyperelastic constitutive model for graphene

Elastic instabilities — the fundamental mechanisms which govern the elastic-to-inelastic transition — are the precursor to catastrophic failure in defect-free, single graphene crystals. Elastic instabilities originate from softening in the material response (decay of elastic moduli) induced by mechanical deformation. In chapter 5, we characterize the strain-induced softening in the constitutive response of graphene within the framework of hyperelasticity. Our formulation is based on symmetry-invariants of the 2D logarithmic strain tensor $E^{(0)}$ — which allows for significant functional simplification in representation of the strain energy function of graphene. The usage of symmetry-invariants permits a reduction by half in the number of elastic constants (compared with previous formulations) while providing better resolution in describing the material response. Particularly, the resulting functional form clearly elucidates the nature of strain-induced softening in graphene: the softening of the dilatational response of graphene obeys the universal binding energy relation; while the shear response shows an exponential softening. For a set of homogeneous finite deformations comprising uniaxial stretch/stress along the armchair and the zigzag directions, and equi-biaxial tension, the stress values predicted by the model compare well with the directly-calculated $ab initio$ values, validating the fidelity of the model.

On the predictive side, we obtain the elastic stability limits — based on the acoustic tensor analysis — for a number of biaxial deformation modes, which compare well with the predictions from phonon calculations carried out independently using linear response density functional perturbation theory. In particular, the present work offers clear and compelling evidence that the limit of elastic stability in equi-biaxial deformation of graphene has been widely misinterpreted as coinciding with achieving peak bi-axial stress: the present continuum formulation and analysis, supported by independent phonon calculations, clearly illustrates how and why an elastic shearing
instability precedes the maximum stress configuration under this loading mode. As a consequence, prior experimental inferences purporting to demonstrate achievement of the “ultimate strength of ideal graphene” are now in need of major reconsideration and revision.

1.6.5 Failure model for graphene derived from analysis of phonons

In chapter 6, we investigate the limits of reversible deformation in graphene under various loadings using atomistic-level lattice-dynamical stability analysis. Based on this information, we construct a continuum failure surface for planar graphene, which provides an analytical description of incipient lattice instabilities of all kinds, for arbitrary deformations, parametrized both in terms of stress, and strain. Thus, we identify the distinct regions in deformation space corresponding to the various possible lattice failure mechanisms in graphene — buckling (failure to remain planar), elastic (material) failure, and soft mode material failure. The failure branches corresponding to the elastic and soft mode instabilities are conspicuously distinct in the strain space but, owing to the nonlinear softening of the lattice, the relative extent of the soft mode regime in the stress space is greatly diminished. We implement the failure surface in a continuum analysis together with an appropriate constitutive relation to constitute a novel multi-scale modeling methodology which enables on-the-fly assessments of the macroscopic (e.g., load; deflection) and microscopic conditions (e.g., local stress/strain; spatial location, temporal proximity, and nature of incipient lattice instability). The model is applied to finite element simulations of uniform differential pressure applied across suspended defect-free graphene sheets restrained at their peripheries. For differing geometries of the constrained boundary, such bulge tests generate different strain states in the interior of the sheet, which in turn trigger different types of lattice instabilities.
1.6.6 Continuum model for graphene-diamond interaction

In chapter 7, we present a study on graphene-diamond interaction as a function of their separation — based on combined density functional theory and molecular dynamic calculations. These calculations explicitly show that the interfacial energy as a function of separation has two local minima, indicating that a graphene monolayer on a diamond \{111\} or a diamond \{100\} surface has two possible equilibrium states: a physisorbed state at low compressive stress, governed by weak vdW forces, and a chemisorbed state at large compressive stress, governed by strong covalent forces. The transition from physisorbed state to chemisorbed state is also noted in the electronic charge density contours, showing electronic clouds overlapping below a certain critical separation. Taking the ab-initio/ MD energy-separation data as input, we derive a continuum traction-separation relation for graphene-diamond interface — which describes both the weak vdW adhesion and the strong chemical interaction. The resulting continuum traction-separation relation is embedded into a finite element calculation.

1.6.7 Mechanochemical analysis of nanoindentation of graphene

In chapter 8, we study how the mechanochemical interaction between graphene and diamond indenter affects the strength measurement in nanoindentation experiments. In bulk-crystal nanoindentations, the instability originates in the interior of the crystal, away from the indenter’s influence. In contrast, the mechanical failure of a suspended graphene sheet subjected to indentation initiates directly underneath the diamond indenter. This means that the potentially-unstable region of the graphene sheet remains in contact with the indenter surface during the course of indentation. The DFT and the MD studies presented in chapter 7 confirmed that the interfacial forces on a graphene sheet pressed against a diamond surface can vary from weak vdW to strong covalent forces, depending upon the levels of contact stress ($\sigma_{\text{con}}$) and the frac-
tional hydrogen coverage ($\theta_H$) on the diamond surface. Based on these calculations, we develop a cohesive traction-separation law for the graphene-diamond interface that allows transition from weak vdW to strong covalent interaction as the magnitude of $\sigma_{\text{con}}$ grows beyond a critical value. The shear stiction component associated with this covalent interaction depends on $\theta_H$, varying from weak when $\theta_H \to 1$ (i.e., a fully-saturated surface) to strong as $\theta_H \to 0$ (i.e., a bare surface). Incorporating this interfacial traction-separation law in a Finite Elements Analysis (FEA), along with the stress-strain constitutive law of chapter 5 and the failure function of chapter 6, we probe the failure load in nanoindentation simulations as a function of the strength of the interfacial interaction. We show that the failure load and displacement in nanoindentation of graphene sheet, in addition to material strength, also depend upon the graphene-indenter interaction governed by the surface condition of the indenter. This is attributed to a strain transferring mechanism, arising from the shear stiction associated with the contact interaction, which alters the distribution of strain beneath the indenter and hence influences the onset of failure load/displacement in nanoindentation. For certain optimal $\theta_H$-levels, this mechanism results in maximal distribution of strain, delaying the onset of failure to a larger load and deflection, which compare well with some of the recent experimental observations that, otherwise, are inexplicable. Finally, MD simulations of nanoindentation, based on the AIREBO reactive potential, are carried out, the results of which conform with the FEA analysis.

1.6.8 Conclusion

The thesis is concluded in chapter 9, where we provide a brief summary of the major findings reported in this thesis, and discuss future research directions which may follow from this work.
Chapter 2

Invariant-based representation theory for constitutive and failure modeling

2.1 Introduction

The ultimate goal of this work is to develop a continuum-level finite element method that allows simulating mechanical response and the onset of irreversible deformation in macroscopic graphene sheets subject to any arbitrary loading and boundary conditions. For this purpose, finite element procedures need to be laced with special constitutive functions that allow (1) calculating stress/strain, and deformation, and (2) assessing the stability of the underlying lattice with respect to bounded perturbations of all wavelengths at any arbitrary state of material deformation. This in turn would require obtaining a priori analytical representations for the mechanical stress-strain relation and the limits of lattice-stability for the entire range of deformation realizable in a given boundary value problem. Finding such representations is complicated by the fact that crystals are intrinsically anisotropic, and special group-
and invariant-theoretic representation schemes are inevitably required.

This chapter provides a brief exposition on the symmetry-invariant-based ideas for representation of constitutive functions of a two-D crystalline material. In Chapter 5, we will employ these representation schemes to develop a hyperelastic constitutive response function for graphene, describing the stress-strain relation over the range of all stable deformation. Once the representation is chosen, the various constants in the representation are obtained by fitting to the deformation energies calculated from highly accurate electronic structure calculations. The model is strictly valid in the region where the underlying lattice is stable with respect to all kinds of perturbations. Therefore, an imposed deformation that induces a phase-change in graphene from its original symmetry \( (C_{6v}) \) to a lower symmetry cannot be captured by the form of constitutive equation that we propose. This work is limited to the constitutive description of graphene at zero temperature and we will not take into account the role that temperature plays on the stability of given crystal phase.

The previous observation introduces the topic of stability of the underlying lattice under an imposed deformation in relation to our continuum model. The loss of stability of a crystal is intrinsically related to the irreversible deformation. Some instances of irreversible deformation correspond to a plastic failure, opening of a micro-crack or a void nucleation, and in some other cases it may mean a shear localization or phase transformation [92, 193, 194, 3]. Nevertheless, irrespective of what the irreversible response of a crystal may correspond to, knowledge of the microscopic and macroscopic conditions at which the elastic-inelastic transition occurs is of central importance to crystal mechanics, e.g., at the atomistic level, the elastic-plastic transition is an indicative of fundamental structural rearrangements in the crystal resulting from a lattice instability [191, 108, 109]; while at the continuum level, the transition can be associated with an important material property called the ideal strength [144, 216, 111].
Unfortunately, the acoustic tensor derived from a hyperelastic constitutive response function allows to detect only a subset of the various possible instabilities, those that are associated with acoustic phonons in the long wavelength limit that correspond to the softening of one or more elastic constants to zero. The stability of a lattice with respect to perturbations of short-wavelength can not be examined by means of an acoustic tensor analysis. For such purposes, a phonons-based stability analysis, which captures instabilities of both short and long wavelengths, needs to be employed. However, in the absence of a parametrization in terms of stress, or strain, a phonon-based stability analysis can not be utilized in a continuum-level analysis. To this end, in Chapter 6, we use the symmetry-invariant based schemes to develop a continuum failure surface for graphene, derived from phonons-based crystal stability analysis.

2.2 Preliminary remarks

2.2.1 Kinematics

(A). Macroscopic deformation (deformation gradient and stretch tensors)

We consider graphene as a 2D deformable body denoted by the unstressed reference configuration $B$. The kinematics of this deformable body is described by time-varying vector and tensor fields belonging to the 2D Euclidian space $\mathbb{R}^2$. We denote by $X$ an arbitrary material point of $B$. As the body is deformed, the material point $X$ moves to another point in the 2D space, characterized by its deformed coordinate $x$ at current time $t$. The convection of material points under deformation is described by a smooth, injective (one-to-one) function $\chi(X, t)$ called the motion. The non-translational part of the motion can be equivalently defined by the positive-definite second-order deformation gradient tensor, $F = \nabla \chi(X, t)$. Notationally suppressing this functional dependence for convenience, the polar decomposition theorem provides
the following factorizations of $F$ [72, 71, 53]:

$$F = RU = VR, \quad (2.1)$$

where the orthogonal tensor $R \in SO_2$ characterizes rigid-body rotation, whereas $U$ (or $V = RUR^T$), termed the right (left) Cauchy-Green tensor, characterizes shape- and area-change. Physically, deformation in the neighborhood of a material point in the body can be kinematically considered as stretching followed by a superimposed rigid-body rotation, or vice-versa. $U$ is a symmetric tensor having two real positive eigenvalues, the principal stretches $\lambda_1$ and $\lambda_2$. Using spectral decomposition, $U$ can be expressed as

$$U = \lambda_1 r_1 \otimes r_1 + \lambda_2 r_2 \otimes r_2, \quad (2.2)$$

where $r_1$ and $r_2$ are orthogonal principal unit vectors in the plane. The deformation of a material point can be kinematically factored as the product of a purely dilatational (or shape-preserving, but area-changing) deformation $U^a$, and a purely isochoric (or shape-changing, but area-preserving) deformation $\tilde{U}$. Accordingly, the stretch tensor can be product-decomposed as

$$U = U^a \tilde{U} = \tilde{U} U^a, \quad (2.3)$$

where

$$U^a \equiv J^{1/2} I \quad (2.4)$$

and

$$\tilde{U} \equiv \lambda r_1 \otimes r_1 + \lambda^{-1} r_2 \otimes r_2; \quad (2.5)$$

here $J = \det U = \lambda_1 \lambda_2$, $\lambda = \sqrt{\lambda_1/\lambda_2} \geq 1$, and $I$ is the 2D identity tensor.

(B). Microscopic deformation (Cauchy-Born rule and sub-lattice shifts)
The movement of individual atoms in a lattice upon deformation is related to the macroscopic deformation gradient tensor $\mathbf{F}$. In a Bravais lattice, the positions of the atoms within the crystal lattice follow the macroscopic deformation. This is called the Cauchy-Born kinematics. However, this is not the case with graphene, which is a complex lattice, i.e., composite of two Bravais sub-lattices that are shifted with respect to each other by a shift vector $d_0$, as shown in figure (2-1). Upon deformation, the deformation of individual Bravais lattice follows the macroscopic deformation gradient $\mathbf{F}$, i.e., the lattice vectors in the deformed crystal are given as $\mathbf{a}_1' = \mathbf{F}\mathbf{a}_1$ and $\mathbf{a}_2' = \mathbf{F}\mathbf{a}_2$. However, the shift vector, separating the two lattices, does not obey the Cauchy-Born kinematics, i.e., $\mathbf{d} \neq \mathbf{Fd}_0$. The shift vector $\mathbf{d}$, in a deformed state, is determined by minimization of total energy of the deformed crystal. That is, under certain imposed deformations, graphene experiences sub-lattice shifts that lower the total energy of the crystal compared to the unrelaxed Cauchy-Born unrelaxed crystal. These deformation modes are the ones that involve a deviatoric stretch, i.e., $\mathbf{U} \neq \mathbf{I}$. Examples of this class of deformations are the uniaxial stress/stretch and simple shear. Conversely, because of symmetry, a purely volumetric deformation does not
generate a sub-lattice shift.

The sub-lattice shift \( s \), associated with a deformation gradient \( F \) is defined as the difference between the \( d \) vectors connecting the two Bravais lattice in the relaxed and unrelaxed configurations. Mathematically,

\[
s = d - d_{CB}; \text{ where } d_{CB} = Fd_0,
\]

(2.6)

where \( d_0 \) denotes the shift-vector in the undeformed configuration.

The rigorous energetic and kinematic continuum description of a complex crystal, such as graphene, requires the definition of the strain energy density function as follows

\[
\psi = \tilde{\psi}(F, s).
\]

(2.7)

The above description implies the following variational form

\[
\delta \psi = \frac{\partial \psi}{\partial F} : \delta F + \frac{\partial \psi}{\partial s} : \delta s.
\]

(2.8)

Localization of the principle of virtual work then requires the following energy balance

\[
0 = \left( \frac{\partial \psi}{\partial F} - T^{(1)} \right) : \delta F + \left( \frac{\partial \psi}{\partial s} - f \right) : \delta s,
\]

(2.9)

where \( T^{(1)} \) is the first Piola-Kirchhoff stress (stress tensor work-conjugate to \( F \)), and \( f \) are the forces per unit reference volume acting on the atoms of the state defined by \((F, s)\). The conditions (2.9) imply the equilibrium equations

\[
\frac{\partial \psi}{\partial F} = T^1,
\]

(2.10)

and

\[
\frac{\partial \psi}{\partial s} = f.
\]

(2.11)
At equilibrium, the force on each atom in the lattice is zero, and the above equation becomes
\[
\frac{\partial \psi}{\partial \mathbf{s}} = 0.
\] (2.12)
The condition (2.12) implicitly determines the value of sub-lattice shift \( \mathbf{s} = \mathbf{s}_{eq}(\mathbf{F}) \) for which the crystal is both at external and internal equilibria. By taking advantage of this result, the strain energy density function \( \psi \) can be written in a homogenized form, \( \psi^{HC} \), such that
\[
\psi = \bar{\psi}(\mathbf{F}, \mathbf{s}_{eq}(\mathbf{F})) \equiv \psi^{HC}(\mathbf{F}).
\] (2.13)

### 2.2.2 Strain measures

Motion of a material, in general, comprises a rigid-body rotation and translation, and a deformation. The deformation gradient \( \mathbf{F} \) eliminates the rigid-body translation from the description, but it still retains the rigid-body rotation, along with deformation. The material’s constitutive response, such as the strain energy density function \( \psi \) and the failure function \( \mathcal{F} \), is insensitive to the rigid-body rotation, which is a consequence of material objectivity. For this reason, a formulation of constitutive response of material directly in terms of \( \mathbf{F} \), which contains both deformation as well as rigid-body rotation, is not suitable. Formulation of constitutive functions of a material should be done, preferably, in terms of a mathematical field that characterizes only the deformation, segregating the rigid-body rotation. Seth [169], and Hill [80] suggested such a family of functions, called generalized strain measures, to characterize the state of deformation in materials. In the limit of small deformation, all the functions in the family degenerate to the same function. Seth-Hill generalized strain measure is given as —
\[
\mathbf{E}^{(m)} = \begin{cases} 
\frac{1}{m}(\mathbf{U}^m - \mathbf{I}) & \text{if } m \neq 0; \\
\ln \mathbf{U} & \text{if } m = 0,
\end{cases}
\] (2.14)
$m \ E^{(m)} = m^{-1}(U^m - I) \quad \text{Name}$

<table>
<thead>
<tr>
<th>$m$</th>
<th>$E^{(0)} = \ln U$</th>
<th>Logarithmic strain measure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$E^{(1)} = U - I$</td>
<td>Biot strain measure</td>
</tr>
<tr>
<td>2</td>
<td>$E^{(2)} = \frac{1}{2}(U^2 - I)$</td>
<td>Green-Lagrange strain measure</td>
</tr>
</tbody>
</table>

Table 2.1: Some examples of the Seth-Hill strain measures.

where $m \in \mathbb{R}$. Some examples of the Seth-Hill strain measures are given in Tab. [2.1].

Construction of the Seth-Hill strain measure from right stretch tensor —

In the following, we outline the procedure required to build a Seth-Hill strain measure from the spectral representation of the right stretch tensor $U$. Let the spectral representation be given as —

$$U = \sum_{i=1}^{i=2} \lambda_i \mathbf{r}_i \otimes \mathbf{r}_i = J^{1/2} \lambda \mathbf{r}_1 \otimes \mathbf{r}_1 + J^{1/2} \lambda^{-1} \mathbf{r}_2 \otimes \mathbf{r}_2,$$

(2.15)

where we have separated the area-changing component ($J = \det U$), from the shape-changing component of the tensor, and introduced the principal basis reference frame $\{\mathbf{r}_i\}$, $i = 1,...,2$. Then, a strain measure is readily obtained as —

$$E^{(m)} = \sum_{i=1}^{i=2} f^{(m)}(\lambda_i) \mathbf{r}_i \otimes \mathbf{r}_i,$$

(2.16)

where the functions $f^{(m)}$ satisfy the following conditions:

$$f^{(m)}(1) = 0,$$

(2.17)

68
Seth-Hill strain measures are obtained for the following choice of the functions $f^{(m)}$:

$$f^{(m)}(.) = \begin{cases} \frac{1}{m} \left(\cdot\right)^m - 1 & \text{if } m \neq 0 \\ \ln(\cdot) & \text{if } m = 0. \end{cases} \quad (2.19)$$

For example, we calculate the logarithmic strain measure, which we have used in formulating the hyperelastic strain energy and the failure functions, as follows:

$$E^{(0)} = \ln \lambda_1 \mathbf{r}_1 \otimes \mathbf{r}_1 + \ln \lambda_2 \mathbf{r}_2 \otimes \mathbf{r}_2. \quad (2.20)$$

Further, with the aid of equations (2.4 & 2.5), this spectral representation can be written as:

$$E^{(0)} = \ln U = \frac{1}{2} \ln \left( \ln \left( \frac{1}{\ln U} \right) + \ln \left( \frac{\lambda \left( \mathbf{r}_1 \otimes \mathbf{r}_1 - \mathbf{r}_2 \otimes \mathbf{r}_2 \right)}{\ln \mathbf{U}} \right) \right)$$

$$= \frac{1}{2} \epsilon_a \mathbf{I} + E^{(0)}_0, \quad (2.21)$$

where

$$\epsilon_a = \text{tr} \mathbf{E}^{(0)} = \ln J = \ln(\det \mathbf{U}), \quad (2.22)$$

gives the areal logarithmic strain $\epsilon_a$, and

$$E^{(0)}_0 = \ln \tilde{U} = \ln \lambda \left( \mathbf{r}_1 \otimes \mathbf{r}_1 - \mathbf{r}_2 \otimes \mathbf{r}_2 \right), \quad (2.23)$$

denotes the deviatoric part of $E^{(0)}$. 

and

$$\left. \frac{df^{(m)}(x)}{dx} \right|_{x=1} = 1. \quad (2.18)$$
2.2.3 Conversion between stress measures: work-conjugacy theorem

Different choices of strain measures in a hyperelastic formulation give different work-conjugate stress measures. For example, Green-Lagrange strain has second Piola-Kirchhoff stress, while Biot strain has Biot stress [71, 72, 53, 145, 180]. However, in continuum simulations, the relevant stress is often the Cauchy stress; and therefore, it becomes essential to obtain a relation for conversion from different stress measures to the Cauchy stress. Following the hyperelastic work-conjugacy relation (see Ogden [145], and Love [117]), the conversion from work-conjugate stress measure $T^{(m)}$ corresponding to one measure of strain $E^{(m)}$ to stress measure $T^{(n)}$, work-conjugate to another measure of strain, $E^{(n)}$, can be obtained as follows. Letting a superposed dot denote the material time derivative, the power balance of isothermal hyperelasticity identifies measures of stress that are power-conjugate to differing measures of strain-rate by

$$\dot{\psi} = T^{(m)} : \dot{E}^{(m)} = T^{(n)} : \dot{E}^{(n)}. \quad (2.24)$$

where the $: \equiv \text{tensor inner product defined for two tensors } A \text{ and } B \text{ as } A : B = A_{ij}B_{ij}$. Using the chain rule, and viewing $E^{(m)}$ as a function of $E^{(n)}$, we obtain

$$\dot{E}^{(m)} = \left( \frac{\partial E^{(m)}}{\partial E^{(n)}} \right)^{\mathcal{L}(m, n)} \dot{E}^{(n)}. \quad (2.25)$$

where the fourth-order tensor $\mathcal{L}(m, n) = \partial E^{(m)}/\partial E^{(n)}$ has major symmetry, i.e., $\mathcal{L}(m, n)^T = \mathcal{L}(m, n)$, and it is understood that $\mathcal{L}(m, n)$ operates on the second-order tensor appearing on its immediate right to produce a resultant second-order tensor. Substituting equation (2.25) into equation (2.24) gives

$$T^{(m)} : \left( \mathcal{L}(m, n)\dot{E}^{(n)} \right) = T^{(n)} : \dot{E}^{(n)}. \quad (2.26)$$
or, equivalently,
\[ \mathcal{L}(m, n)^T \mathbf{T}^{(m)} : \dot{\mathbf{E}}^{(n)} = \mathbf{T}^{(n)} : \dot{\mathbf{E}}^{(n)}, \]
which must hold for arbitrary \( \dot{\mathbf{E}}^{(n)} \). Thus, we obtain the relation between two work-conjugate stress measures as

\[ \mathbf{T}^{(n)} = \mathcal{L}(m, n)^T \mathbf{T}^{(m)}. \]

### 2.3 Elements of constitutive and failure modeling of an anisotropic material

In the following, I outline the conceptual steps that are necessary for constitutive and failure modeling of an anisotropic material, such as graphene.

#### 2.3.1 Material objectivity

The principle of material frame-indifference states that the constitutive functions should remain invariant under superimposed rigid-body motion (see references [71, 72, 53]). For example, consider a scalar-valued constitutive function \( \mathcal{F} \) that depends upon the deformation gradient \( \mathbf{F} \). Then according to material frame indifference

\[ \mathcal{F} = \dot{\mathcal{F}}(\mathbf{F}) = \dot{\mathcal{F}}(\mathbf{QF}), \]

where \( \mathbf{Q} \in \text{SO}_2 \) is a rigid-body rotation. The condition of material frame-indifference is automatically satisfied by characterizing the function \( \mathcal{F} \) in terms of one of the Seth-Hill strain measures \( \mathbf{E}^{(m)} = \frac{1}{m}(\mathbf{U}^m - \mathbf{I}) \), where \( m \in \mathbb{Q}^+ \) (\( \mathbb{Q}^+ \) is the set of rational numbers). Thus, we have

\[ \mathcal{F} = \dot{\mathcal{F}}(\mathbf{E}^{(m)}). \]
2.3.2 Material symmetry restriction

Crystals are anisotropic because they comprise a periodic arrangement of atoms in space. However, for the same reason, the crystalline anisotropy is special in the sense that it can be characterized in terms of a set of operations, called symmetry operations, under which the crystal remains unchanged. The group of all the symmetry operations characterizing the anisotropy of a crystal is called the material symmetry group of the crystal. The symmetry of a crystal imposes certain restrictions on the form of tensor functions to be employed in the definition of the crystal’s constitutive functions. Material symmetry requires that the constitutive laws should remain invariant under the point group operations of the crystal. The implication of material symmetry then requires

$$\hat{F}(E^{(m)}) = \hat{F}(QE^{(m)}Q^T) \forall Q \in G,$$

(2.31)

where $G$ is the point group symmetry of the material in consideration. Functions such as $F$ which satisfy the material symmetry condition expressed in equation (2.31) are called $G$-invariant functions. Thus, writing the constitutive function of a crystalline material requires an opportune representation of tensorial functions — the functions of tensor agencies — that allows the automatic satisfaction of symmetry restrictions. Such representation is obtained in the form of invariant-based representation of tensorial functions, which originates from the work of Rivlin and Smith [175, 176, 177, 178].

2.3.3 Isotropicization Theorem

Owing to material frame-indifference and material symmetry, the scalar functions representing the constitutive properties of a material should be $G$-invariant functions, i.e., they should remain invariant under the symmetry group, $G$, of the material. An important tool, often-used in representation of such functions, is the isotropicization-
based representation theorem. This theorem introduces the notion of a materially-embedded structural tensor, originally proposed by Lokhin & Sedov [118], and extended by Boehler [15, 17, 16]. According to this theorem:

A smooth scalar-valued function \( F(A_1, A_2, ..., A_n) \) of tensor agencies \( A_1, A_2, ..., A_n \), which remains invariant with respect to a point group \( G \), can be represented by an isotropic function of \( A_i, i = 1, 2, ..., n \), and a structural tensor \( H_G \) as an additional agency that characterizes the underlying symmetry group \( G \). i.e.

\[
F(A_1, A_2, ..., A_n) = F_{iso}(A_1, A_2, ..., A_n; H_G).
\]

Two major consequences of the isotropicization theorem are-

1. It serves as a basic framework for the construction of constitutive models of anisotropic crystals in terms of simple, easy to construct, isotropic functions, and the anisotropy of the material is taken into account by incorporating the structural tensors as additional agencies.

2. The representation is carried out in terms of scalar invariants which are in coordinate-free form, and are apt for writing an interpolation scheme.

### 2.3.4 Isotropic invariant-based representation

The isotropicization theorem allows us to devise a function \( \hat{F}_{iso} \) such that an anisotropic function \( F \) can be represented as

\[
F = \hat{F}_{iso}(A_1, A_2, ..., A_n; H_G).
\]
The function \( \hat{F}_{\text{iso}} \) satisfies the following condition\(^1\).

\[
\hat{F}_{\text{iso}}(\langle Q \rangle A_1, ..., \langle Q \rangle A_n; \langle Q \rangle H_G) = \hat{F}_{\text{iso}}(A_1, A_2, ..., A_n; H_G) \forall Q \in \text{Orth}^+. \quad (2.36)
\]

Over the years, Zheng, Boehler and others [15, 17, 16, 213, 214, 215, 217] employed the principle of isotropy of space to construct complete and irreducible bases for all crystal classes in 2D and 3D. For example, the structure tensor for a 2D crystal belonging to the \( C_{2n} \) crystal class can be obtained as

\[
H = Re(M + iN)^\otimes n. \quad (2.37)
\]

where

\[
M = a_1 \otimes a_1 - a_2 \otimes a_2, \quad (2.38)
\]

and

\[
N = a_1 \otimes a_2 + a_2 \otimes a_1, \quad (2.39)
\]

are symmetric, and traceless tensors of second order; \( a_1 \) and \( a_2 \) are two orthogonal vectors fixed in the material. The operation \( (\cdot)^\otimes \) is defined as

\[
(\cdot)^\otimes = (\cdot) \otimes (\cdot) \ldots \otimes (\cdot). \quad m \text{ times} \quad (2.40)
\]

\(^1\)The operation \( (\cdot) \) is defined as following. For a vector \( v \),

\[
(\cdot)v = Qv. \quad (2.33)
\]

For a second order tensor \( A \),

\[
(\cdot)A = QAQ^T, \quad (2.34)
\]

and for a tensor \( H_G \),

\[
(\cdot)H_G)_{ij...k} = Q_{iu}Q_{jm}...Q_{kn}H_{Glm...n}. \quad (2.35)
\]
Thus, the structure tensor characterizing the anisotropy of graphene, which belongs to $C_{6v}$ material symmetry group, is given by the sixth-order tensor:

$$\mathbb{H} = \mathbf{M} \otimes \mathbf{M} \otimes \mathbf{M} - (\mathbf{M} \otimes \mathbf{N} \otimes \mathbf{N} + \mathbf{N} \otimes \mathbf{M} \otimes \mathbf{N} + \mathbf{N} \otimes \mathbf{N} \otimes \mathbf{M}). \quad (2.41)$$

A central problem in the formulation of a constitutive equation is to determine the form of the function $\hat{\mathcal{F}}_{iso}$ conforming to a set of observations based on either experiments or simulations. Although the function $\hat{\mathcal{F}}_{iso}$ can not be determined in the absolute sense, a reasonable approximation can be obtained by choosing a physically justifiable form and fitting it to a set of available data. However, a scalar property expressed as a function of tensor agencies, such as $\hat{\mathcal{F}}_{iso}(\mathbf{A}_1, \mathbf{A}_2, ..., \mathbf{A}_n; \mathbb{H}_g)$, is not very conducive to curve-fitting process. In order to proceed, we need to find a suitable set of scalar variables which can be used as alternate agencies for representation of an isotropic function of $\mathbf{A}_1, \mathbf{A}_2, ..., \mathbf{A}_n$ and $\mathbb{H}_g$. This is accomplished via the isotropic representation theorem which states [118, 17]

\textit{Given a list of tensor agencies} $\{\mathbf{A}_1, \mathbf{A}_2, ..., \mathbf{A}_n; \mathbb{H}_g\}$, \textit{there exists a set of scalar invariants} $(\mathcal{J}_1, ..., \mathcal{J}_m)$ \textit{that serves as an irreducible and complete basis for the representation of any isotropic function of} $\{\mathbf{A}_1, \mathbf{A}_2, ..., \mathbf{A}_n; \mathbb{H}_g\}$.

The \textit{completeness} property implies that any scalar-valued function of tensor agencies $\mathbf{A}_1, \mathbf{A}_2, ..., \mathbf{A}_n$ can be represented in terms of these joint invariants. The \textit{irreducibility} means that none of the invariants $\mathcal{J}_i$ ($i = 1, 2, ..., m$) is expressible as a function of the remaining elements of the functional basis. As a result, the representation simplifies to

$$\mathcal{F} = \hat{\mathcal{F}}_{iso}(\mathbf{A}_1, \mathbf{A}_2, ..., \mathbf{A}_n; \mathbb{H}_g) = \hat{\mathcal{F}}_{iso}(\mathcal{J}_1, \mathcal{J}_2, ..., \mathcal{J}_m). \quad (2.42)$$
The set of scalar functions \( \{J_1, J_2, \ldots, J_m\} \) is called an integrity basis. For the 2D regular polygonal crystal classes (material symmetry group \( C_{2n} \)), the complete and irreducible set of symmetry-invariants consists of three symmetry invariants of the logarithmic strain tensor:

\[
J_1 \equiv \epsilon_a = \text{tr}(E^{(0)}) = \ln J,
\]

\[
J_2 \equiv \frac{\gamma_1^2}{4} = E_0^{(0)} : E_0^{(0)} = (\ln \lambda)^2,
\]

\[
J_3 \equiv \frac{\gamma_\theta^3}{8} = \mathbb{H}[E_0^{(0)}, E_0^{(0)}, E_0^{(0)}] = (\ln \lambda)^3 \cos 2n\theta,
\]

where \( 2n \) denotes the order of the principal axis of rotation. The irreducibility of these symmetry-invariants is numerically shown in Chapter 4. We construct the \( \gamma_1^2 \) and \( \gamma_\theta^2 \) symmetry-invariants from the deviatoric component \( E_0^{(0)} \) of the logarithmic strain measure in order to maintain a clear separation in the areal and the shape-changing parts of the imposed deformation.

In Chapter 5, we will employ this integrity basis to obtain a representation for the hyperelastic constitutive response function of graphene. The coupling between the areal and the deviatoric response of the crystal emerges from the mixed terms in \( \epsilon_a, \gamma_1^2 \) and \( \gamma_\theta^3 \) in the description of the strain energy density function. The corresponding strain energy function for

\[
\psi = \psi_{\text{iso}}(\epsilon_a, \gamma_1^2, \gamma_\theta^3) = \psi_1(\epsilon_a) + \psi_2(\epsilon_a, \gamma_1^2) + \psi_3(\epsilon_a, \gamma_\theta^3) + \ldots
\]

where the sum can be extended to include terms up to desired order.

The corresponding work-conjugate stress can be derived as follows:

\[
T^{(0)} = \frac{\partial \psi}{\partial E^{(0)}} = \frac{\partial \psi}{\partial \epsilon_a} \frac{\partial \epsilon_a}{\partial E^{(0)}} + \frac{\partial \psi}{\partial \gamma_1^2} \frac{\partial \gamma_1^2}{\partial E^{(0)}} + \frac{\partial \psi}{\partial \gamma_\theta^3} \frac{\partial \gamma_\theta^3}{\partial E^{(0)}}.
\]
For representation of more general functions, an integrity basis can also be used to generate a functional basis, which may involve functions of both polynomial and non-polynomial natures. For example, in constructing the failure function for graphene in Chapter 6, we employ the functional basis comprising the following symmetry-invariants.

\[
\tilde{\varepsilon} = \frac{1}{2} \epsilon_a = \frac{1}{2} \ln J,
\]

\[
\mathcal{E}_{1,2} = \frac{1}{2} \epsilon_a \pm \frac{\gamma_i}{2} = \ln J^{1/2} \pm \ln \lambda,
\]

\[
\Theta = \arccos \left( \frac{\gamma_2}{\gamma_1} \right) = \arccos(\cos 2n\theta).
\]

In the above, the first invariant is the mean hydrostatic logarithmic strain, and the second invariant is the major or minor principal strain, depending upon the + or - sign, and the third invariant is the symmetry-reduced principal stretch direction.

2.3.5 Invariant-based interpolation

At this point, an analytical representation for a constitutive function, such as the strain energy density function \( \psi \), in principle, can be deduced by interpolation in terms of symmetry-invariants, provided a sufficiently complete set of deformation dataset, either from measurements or simulations, is available. By a complete dataset, we mean that the dataset includes all the classes and range of deformation that are realized in the boundary-value problem of interest. For example, in nano-indentation experiment, material elements in the different part of the graphene sheet undergo different kinds of deformation, as shown in figure (2-2), e.g., the material elements underneath the indenter are in equi-biaxial state of tension, while the material elements in the vicinity of the clamped periphery experience a uniaxial strain type of deformation. Therefore, a hyperelastic constitutive response function intended for use in modeling of nano-indentation experiment should necessarily incorporate de-
Figure 2-2: In indentation, the realizable variations in deformation gradient take place over lengths that are comparable to indenter size and contact surface dimensions, both of which are much larger than lattice spacing. Therefore, locally, a material point, labeled by its current position $x$, behaves as if deformed homogeneously, and can be described by the local deformation gradient $F(x)$, for which the strain energy and stress tensor can be calculated via hyperelastic constitutive response function.

The invariant-based interpolation scheme, summarized for the case of strain energy density function $\psi$ in figure (2-3), involves the following steps:

- First, we calculate the deformation energies and stresses of an ideal graphene sheet corresponding to a set of all the required deformation gradients.

- Then, for an assumed functional form in terms of the symmetry-invariants, the coefficients in the function are determined by fitting to the calculated deformation energies and the stresses.

In this work, all the material parameters required by the models will be obtained from total energies, Cauchy stresses, and limits to crystal stability calculated from a suitably chosen set of DFT calculations on deformed crystal lattices. The DFT and DFPT methods adopted to calculated the total energies and stability limits will be discussed in the next chapter.
Figure 2-3: Schematic showing invariant-based interpolation scheme for modeling of hyperelastic constitutive response of graphene. The ab initio energies and stresses calculated for a sufficiently broad set of deformed configurations spanning these classes is used as the training set within the framework of hyperelasticity, then the invariant-based representation theory is employed to recover a constitutive relation for free energy \( \psi \) in terms of the symmetry-invariants of the logarithmic strain tensor.
Chapter 3

Energetics and lattice dynamics
from first-principles calculations

3.1 Introduction

First-principles calculations based on the density functional theory (DFT) of Hohenberg & Kohn [85] and Kohn & Sham [101] have emerged as a successful computational approach for calculation of a broad spectrum of material properties, with applicability ranging from atoms, molecules and solids to nuclei and quantum and classical fluids. Over the years, the original DFT of Hohenberg and Kohn has been generalized to deal with various kinds of problems: spin polarized systems [149], multicomponent systems such as nuclei and electron hole droplets [30], free energy at finite temperatures, superconductors with electronic pairing mechanisms [40], relativistic electrons [156], time-dependent phenomena and excited states, bosons, molecular dynamics, etc. [88]. From an accuracy point of view also, the ab initio DFT calculations have demonstrated a high-degree of reliability, as a wide-variety of material properties predicted via these calculations have been in good agreement with the experimentally-measured values [126, 173, 61].

81
Experimental measurements of mechanical, electronic and thermal properties of nano-crystalline materials are often expensive or difficult, or both; and there are situations when the material properties of interest cannot be accessed via existing set of experiments at all. First-principles DFT calculations, in such situations, offer a viable alternative to experiments, allowing easy and accurate estimation of the material properties desired. As an example, consider the current work where we aim to construct a large deformation constitutive response and a failure function for graphene. The task requires knowledge of internal energies, stresses and failure limits associated with various deformed configurations of graphene. Experimental measurement of these quantities for graphene is fraught with enormous difficulties, and is expensive. First, graphene is atomically thin, and therefore after exfoliation or fabrication, it must be supported on a substrate; obtaining and maintaining it in an isolated state is difficult. Imparting a controlled deformation to such a thin sheet is another difficulty, which inevitably requires clamping and pulling the graphene sheet. For usual purposes, graphene sheet is effectively clamped onto the substrate by means of interfacial adhesion [100]. However this adhesion may not be sufficient in order to subject the graphene sheet to large tensions. Special nano-scale tweezers must be fabricated for the purpose, adding further to the level of complexity.

The present work employs DFT methods for calculation of internal energies, corresponding stresses and limits of lattice stability of graphene at various kinds of deformation states. In the following sections, we provide a brief account of the density functional theory methods, the underlying principles and theorems and its evolution to the current state-of-the-art computational tool.
3.2 Quantum mechanical system

Consider a system of \( N \) interacting electrons moving under the external potential field of \( P \) ions. The state of such a quantum mechanical system is described by its wave function \( \psi \), while its dynamics follows the governing Hamiltonian \( \mathcal{H} \). Evolution of the state function \( \psi \) under the influence of Hamiltonian \( \mathcal{H} \) is described by the Schrödinger equation [172], given by

\[
    i\hbar \frac{\partial \psi(r, R, t)}{\partial t} = \mathcal{H} \psi(r, R, t),
\]

where \( \hbar = h/2\pi \) with \( h \) being the Planck constant, and \( \psi(r, R, t) \) is the many-body wave function of the system that depends on the spatial coordinates of \( P \) nuclei \( R = \{R_1, R_2, ..., R_P\} \) and the \( N \) electrons \( r = \{r_1, r_2, ..., r_N\} \), and their evolution with time. The many-body Hamiltonian of the system reads as

\[
    \mathcal{H} = -\sum_{i=1}^{P} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 + e^2 \sum_{i=1}^{P} \sum_{j=1}^{P} \frac{Z_i Z_j}{|R_i - R_j|} + \frac{e^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{|r_i - r_j|} - e^2 \sum_{i=1}^{P} \sum_{i=1}^{N} \frac{Z_i}{|R_i - r_i|}.
\]

where \( i, j \) refer to electrons and \( I, J \) refer to ions; \( e \) and \( m \) denote the electronic charge, and mass, respectively; \( Z_I \) and \( M_I \) are the charge and mass associated with \( I^{th} \) ion, respectively. The first two terms in \( \mathcal{H} \) denote the kinetic energy of the ions and the electrons, respectively; the third term denotes the ion-ion electrostatic interaction; fourth term denotes the electron-electron interaction, and the last term denotes the electron-ion interaction.

3.3 Born-Oppenheimer approximation

The many-body Hamiltonian \( \mathcal{H} \), in general, involves evolution of both electronic as well as ionic degrees of freedom in time, rendering solving the fully-coupled, time-
dependent Schrödinger equation a tremendously difficult task. Born and Oppenheimer [18] noted that the ions are several orders of magnitude more massive than electrons; and therefore, the time scale of evolution of ionic degrees of freedom should be much greater than that of electrons. Thus, on typical time-scale of the ionic motion, the electrons should very rapidly relax to instantaneous ground-state configurations. Therefore, in solving the Schrödinger equation, it is reasonable to assume that the ions remain stationary, and the electronic ground-state can be solved, independent of ionic motion. This separation of electronic and ionic motions is called the Born-Oppenheimer approximation. This approximation allows for a multiplicative decomposition of the wave function in the form:

\[ \psi(R, r, t) = \psi_n(R, t)\psi_e(r; R) \]  

(3.3)

where \( \psi_n(R, t) \) denotes the wave function associated with ions, while \( \psi_e(r; R) \) is the many-electron wave function. Substituting the separable form of equation (3.3) into the time-dependent Schrödinger equation of equation (3.1) gives—

\[ i\hbar \frac{1}{\psi_n(R, t)} \frac{\partial \psi_n(R, t)}{\partial t} = \frac{1}{\psi_e(r; R)} \mathcal{H} \psi_e(r; R) = E. \]  

(3.4)

where \( E \) is a constant (ground state energy) because \( \psi_n(R, t) \) depends on \( t \) but not on \( \{r\} \), and \( \psi_e(r; R) \) depends on \( \{r\} \) but not on \( t \). Thus, the electronic Schrödinger equation governing the many-electron wave function \( \psi_e(r; R) \) becomes —

\[ \mathcal{H} \psi_e(r; R) = E\psi_e(r; R). \]  

(3.5)

Solution of equation (3.5) gives the ground state electronic wave function \( \psi_e(r; R) \) at a time instant at which the ionic coordinates remain frozen at \( R \).
3.4 Wave function based approach to solution of many-electron Schrödinger’s equation

The Born-Oppenheimer approximation effectively reduces the many-body Hamiltonian into the governing equation of \( N \) interacting electrons moving under the external time-independent potential field of \( P \) ions. Despite this simplification, the resulting problem of a many-electron system poses formidable challenges. The many-electron Schrödinger equation cannot be solved exactly, and numerical approaches must be employed. The first approximate numerical approaches for determination of the many-electron wave function is Hartree’s self-consistent field method, to calculate approximate wave functions and energies for atoms and ions.

The Hartree approach involves writing the many-electron wave-function as a product of many single-electron wave functions, while incorporating the interaction between the electrons via an effective potential field \[75\]:

\[
\psi_e(\mathbf{r}; \mathbf{R}) = \psi_1(\mathbf{r}_1; \mathbf{R}) \times \psi_2(\mathbf{r}_2; \mathbf{R}) \cdots \times \psi_N(\mathbf{r}_N; \mathbf{R}),
\]

(3.6)

where each one-electron wave function \( \psi_i(\mathbf{r}_i; \mathbf{R}) \) satisfies a one-electron Schrödinger equation \(^1\):

\[
\left[ -\frac{1}{2} \nabla_i^2 + V_{\text{Eff}}(\mathbf{r}_i; \mathbf{R}) \right] \psi_i(\mathbf{r}_i; \mathbf{R}) = \mathcal{E}_i \psi_i(\mathbf{r}_i; \mathbf{R}),
\]

(3.7)

where \( \mathcal{E}_i \) is the energy eigenvalue associated with the electronic wave function \( \psi_i(\mathbf{r}_i; \mathbf{R}) \), and \( V_{\text{Eff}}(\mathbf{r}_i; \mathbf{R}) \) is the effective potential field seen by the electron and comprises an external potential, due to ions, and an internal potential, due to Coloumbic interaction with other electrons, i.e.,

\[
V_{\text{Eff}}(\mathbf{r}_i; \mathbf{R}) = V_{\text{Ext}}(\mathbf{r}_i; \mathbf{R}) + V_{\text{Int}}(\mathbf{r}_i; \mathbf{R}).
\]

(3.8)

\(^1\)The Schrödinger equation is written in atomic unit system throughout this thesis document.
where
\[ V_{\text{Ext}}(\mathbf{r}_i; \mathbf{R}) = \frac{e^2}{2} \sum_{j=1}^{N} \sum_{i=1}^{P} \frac{Z_i Z_j}{|\mathbf{R}_j - \mathbf{R}_i|} - e^2 \sum_{i=1}^{P} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_i|} \] (3.9)

is the external potential field due to ions; and \( V_{\text{int}}(\mathbf{r}_i; \mathbf{R}) \) is the potential due to Coloumbic interaction with other electrons, and is obtained by solving the Poisson equation:
\[ \nabla^2 V_{\text{int}}(\mathbf{r}_i; \mathbf{R}) = 4\pi \rho(\mathbf{r}_i; \mathbf{R}) \] (3.10)

Solution of this equation is
\[ V_{\text{int}}(\mathbf{r}_i; \mathbf{R}) = \int \frac{\sum_{j=1}^{N} \rho_j(\mathbf{r}_j; \mathbf{R})}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_j, \] (3.11)

with \( \rho_j(\mathbf{r}_i; \mathbf{R}) = |\psi_j(\mathbf{r}_i; \mathbf{R})|^2 \) being the electron density associated with the \( j \)th electron [101, 173]. The Hartree method is not only approximate, but it is inconsistent as well, since the wave function is not antisymmetric with respect to interchange of electrons. The Hartree approach treats an electronic system as an ensemble of non-interacting electrons; therefore, the Pauli’s exclusion principle is not satisfied by the Hartree wave-function.

The Hartree-Fock approach [54] corrected this by considering a Slater determinant of the independent electronic wave-functions, each a product of a spatial function and a spin state \( \sigma_i \)
\[ \psi_e(\mathbf{r}; \mathbf{R}) = \frac{1}{\sqrt{N}} \begin{vmatrix} \psi_1(\mathbf{r}_1; \mathbf{R}) \sigma_1(s_1) & \psi_2(\mathbf{r}_1; \mathbf{R}) \sigma_2(s_1) & \cdots & \psi_N(\mathbf{r}_1; \mathbf{R}) \sigma_N(s_1) \\ \psi_1(\mathbf{r}_2; \mathbf{R}) \sigma_1(s_1) & \psi_2(\mathbf{r}_2; \mathbf{R}) \sigma_2(s_1) & \cdots & \psi_N(\mathbf{r}_2; \mathbf{R}) \sigma_N(s_1) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(\mathbf{r}_N; \mathbf{R}) \sigma_1(s_1) & \psi_2(\mathbf{r}_N; \mathbf{R}) \sigma_2(s_1) & \cdots & \psi_N(\mathbf{r}_N; \mathbf{R}) \sigma_N(s_1) \end{vmatrix}, \] (3.12)

The Slater determinant [174] trivially satisfies the antisymmetric property of the exact solution and hence is a suitable ansatz for applying the variational principle in solution.
of the Schrödinger equation. The Hartree-Fock approach has been extensively used until the advent of DFT. The major disadvantages of the Hartree-Fock method are:

1. Due to the nonlinearities introduced by the Hartree-Fock approximation, the equations are solved using a nonlinear iterative method, which makes the method computationally very expensive.

2. Numerical stability also can be a problem with the Hartree-Fock approach.

3. The Hartree-Fock approach neglects many-body correlation, and this can lead to large deviations from experimental results.

3.5 From wave function to density

The Hartree and the Hartree-Fock approaches use the many-body wave function \( \psi_e(r; R) \) as the central variable, since \( \psi_e(r; R) \) contains the full information of a system. However, the main difficulty with such approaches is that \( \psi_e(r; R) \) is an unphysical quantity that cannot be probed experimentally and that depends on \( 4N \) variables, \( N \) being the number of electrons. Thomas and Fermi [187, 55] suggested an alternative formulation which employs the ground state electronic density function \( \rho(r) \) as the central variable of the formulation. Then, assuming a uniform electron gas, they obtained the dependence of the kinetic energy of the system on \( \rho(r) \) via a functional relation given by

\[
\mathcal{F}_{TF}[\rho(r)] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho(r)^{5/3} \, dr. \tag{3.13}
\]

Then by adding to this expression, the contribution from electron-electron interaction, electron-ion interaction and ion-ion interaction, they obtained the total energy of the
system as
\[ \mathcal{H}_{TF}[\rho(r)] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho(r)^{5/3} dr + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r' - r|} d\mathbf{r} d\mathbf{r}' + \sum_{a,b} \frac{Z_a Z_b}{R_{ab}}, \] (3.14)
i.e., the Hamiltonian is expressed completely in terms of the electronic density. The
ground state electronic density is determined via a variational principle in which mini-
mization of the functional \( \mathcal{H}_{TF} \) is performed with respect to \( \rho(r) \) under the constraint
\( \int \rho(r) dr = N. \)
The Thomas-Fermi model is an approximation that ignores the exchange and corre-
lation effects and is not sufficiently accurate to model the electronic structure of most
realistic materials. However, despite these shortcomings, the model is considered a
significant contribution, as it laid the foundation of the more general density-oriented
formalism called density functional theory which has provided the most accurate
electronic model for materials.

3.6 Density functional theory

Density functional theory based formalism rigorously established that the ground
state properties of a quantum system can be exactly expressed in terms of the ground
state electronic density alone. The theoretical basis for DFT comes from the two
fundamental theorems by Hohenberg and Kohn, which are as following:

**Theorem I** — For any system of interacting electrons moving under the influence
of an external potential \( V_{\text{ext}}(r) \), the external potential is determined uniquely, except
for a constant, by the ground state electronic density function \( \rho_0(r) \).

Since the external potential completely determines the Hamiltonian, therefore, the
Hamiltonian and thus all properties of the system are completely determined by the
ground state energy density \( \rho_0(r) \).

**Theorem II** — There exists a universal functional \( \mathcal{F}[\rho(r)] \) for the total energy of
an electronic system, valid for any external potential $V_{\text{Ext}}(r)$. For a given $V_{\text{Ext}}(r)$, the ground state density function $\rho_0(r)$ can be obtained by minimizing the total energy functional $\mathcal{F}[\rho(r)]$.

The second theorem provides the variational basis to determine the ground state electronic density.

First, the Hohenberg and Kohn theorem allows us to write the Hamiltonian of a system of interacting electrons in ground state as a functional of the electron density function $\rho(r)$. This functional reads as —

$$
\mathcal{H}_{HK}[\rho(r)] = \mathcal{I}[\rho(r)] + \int V_{\text{Ext}}(r)\rho(r) dr + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r'-r|} dr' dr' + \sum_{a,b} \frac{Z_a Z_b}{R_{ab}} \mathcal{E}_I
$$

(3.15)

where $\mathcal{I}[\rho(r)]$ denotes the kinetic energy functional; $\mathcal{E}_E$ denotes the interaction of electrons with external potential of ions; $\mathcal{E}_{EE}$ denotes the electron-electron interaction; and $\mathcal{E}_I$ is the ion-ion interaction.

Particularly, the functional

$$
\mathcal{F}_{HK} = \mathcal{I}[\rho(r)] + \mathcal{E}_{EE}[\rho(r)]
$$

(3.16)

that describes the sum of kinetic and internal interaction energies of the electrons is a universal functional in the sense that it refers neither to a specific system nor to an external potential $V_{\text{Ext}}(r; R)$.

The ground state electronic density, according to the second theorem, can be obtained by minimizing the Hamiltonian functional. However, since the form of the kinetic energy functional $T[\rho(r)]$, in general, is unknown, the minimization can not be performed without resorting to a suitable ansatz.
3.6.1 Kohn-Sham ansatz

Kohn and Sham provided the simplifying ansatz necessary to solve the many-body Schrödinger equation. Kohn and Sham replaced the original system of interacting electrons by an auxiliary system of non-interacting electrons moving under the influence of an effective potential $\mathcal{V}_{\text{Eff}}(\mathbf{r})$. The constraint on the auxiliary system is that the ground state density of the interacting electron system should be the same as that of the chosen non-interacting system. The state of each electron in the non-interacting system of electrons is described by a wave function $\varphi_i(\mathbf{r})$ termed the Kohn-Sham orbital such that

$$\sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2 = \rho(\mathbf{r}),$$  \hfill (3.17)

where $\rho(\mathbf{r})$ is the electronic charge density of the original system of interacting electrons. The Kohn-Sham orbitals can be obtained by solving the Schrödinger equation corresponding to an auxiliary Hamiltonian.

$$\left[ -\frac{1}{2} \nabla^2 + \mathcal{V}_{\text{Eff}} \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}).$$  \hfill (3.18)

where $\mathcal{V}_{\text{Eff}}(\mathbf{r})$, in addition to the external potential of ions and internal interaction between electrons, also contains an exchange-correlation term accounting for many-particle interactions,

$$\mathcal{V}_{\text{Eff}}(\mathbf{r}) = \mathcal{V}_{\text{ext}}(\mathbf{r}) + \mathcal{V}_{xc}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \hfill (3.19)$$

Since electrons in the Kohn-Sham system are treated as non-interacting fermions, the complete wave function of a Kohn-Sham system can be obtained as the Slater determinant constructed from the Kohn-Sham orbitals.

The Kohn-Sham orbital energies $\epsilon_i$, in general, have little physical meaning. However,
the sum of the orbital energies can be used to obtain the total energy of the system.

\[ E = \sum_{i}^{N} \epsilon_i \]  

It is understood that the Kohn-Sham orbitals do not represent the solution of the original system; therefore kinetic energy and the internal energy terms calculated based on these orbitals are not going to be same as those of the original system. This difference is called the exchange-correlation energy \( \mathcal{E}_{xc} \). Thus,

\[ \mathcal{E}_{xc} = \mathcal{F}[\rho(r)] - (\mathcal{F}_{KS} + \mathcal{E}_{\text{Hartree}}), \]  

where

\[ \mathcal{F}_{KS} = \frac{1}{2} \int \sum_{i=1}^{N} \varphi_i \nabla^2 \varphi_i d\mathbf{r}, \]  

is the independent electron kinetic energy, and

\[ \mathcal{E}_{\text{Hartree}}[\rho(r)] = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r' - r|} d\mathbf{r} d\mathbf{r}', \]  

is the Coloumb interaction energy associated with electron-electron interaction.

If the form of the exchange and correlation functional \( \mathcal{E}_{xc} \) could be determined exactly, the ground state energy and density of the many-electron problem could be found by solving the Kohn-Sham equations for independent electrons. Further, since the functional \( \mathcal{F} \) has a universal structure, the exchange and correlation functional \( \mathcal{E}_{xc} \) also has a universal form. Unfortunately, this universal form is not determined exactly; and therefore approximations need to be employed to model the \( \mathcal{E}_{xc} \) functional. Two widely-employed approximations for modeling of \( \mathcal{E}_{xc} \), Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA), are discussed in the next section.
3.7 GGA and LDA approximations

The Kohn-Sham formalism of the density functional theory maps the quantum mechanical ground state many-electron problem \emph{exactly} to the self-consistent single-electron Hartree form, via introduction of the exchange-correlation functional, which accounts for the many-body effects in the system. In principle, this exchange-correlation functional has a universal structure; however, unfortunately, the explicit form of the exchange-correlation functional $\varepsilon_{xc}[\rho(\mathbf{r})]$ remains unknown till date. The absence of knowledge of the exact form of $\varepsilon_{xc}[\rho(\mathbf{r})]$ poses the major challenge in the implementation of a successful DFT scheme based on the Kohn-Sham ansatz. For practical calculations, therefore, an approximate form of $\varepsilon_{xc}[\rho(\mathbf{r})]$ must be employed. In the following, we provide a brief account of the two widely-used approximations for the exchange-correlation functional.

3.7.1 LDA

The simplest approximation in this regard, widely-employed in the DFT literature, is the local density approximation (LDA) where the $\varepsilon_{xc}[\rho(\mathbf{r})]$ functional depends only on the density at the coordinate where the functional is evaluated:

$$
\varepsilon_{xc}^{LDA}[\rho(\mathbf{r})] = \int \varepsilon_{xc}[\rho(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r}, \quad (3.24)
$$

where $\varepsilon_{xc}$ is the exchange-correlation energy density of the homogenous electron gas with electron density given by $\rho(\mathbf{r})$. The LDA approximation is most-suited to describe systems that have smooth variation in electronic charge density. Despite its simple structure, the LDA has successfully provided a realistic description of the atomic structure, elasticity, and vibrational properties for a wide range of systems. Yet the LDA is generally not accurate enough to describe the energetics of chemical
reactions (heats of reaction and activation energy barriers), leading to an overestimate of the binding energies of molecules and cohesive energies of solids and an underestimation in the equilibrium bond lengths. The LDA also fails to describe systems, such as transition-metal oxides, which are characterized by a strong correlation between electrons.

3.7.2 GGA

Recent Generalized Gradient Approximations (GGA) have overcome such deficiencies to a considerable extent, giving for instance a more realistic description of energy barriers in the dissociative adsorption of hydrogen on metal and semiconductor surfaces [73, 151]. Gradient corrected or GGA functionals depend on the local density as well as on the spatial variation of the density, i.e.,

$$\delta_{xc}^{GGA}[\rho(r)] = \int \epsilon_{xc}[\rho(r), \nabla \rho(r)\rho(r)]d\mathbf{r},$$

(3.25)

The gradient corrections have been noted to improve the account of electron correlations in finite or semi-infinite systems. The choice of GGA or LDA is often governed by suitability to experiments. For construction of a large deformation constitutive response, we have calculated energies and stresses using both the approximations.

3.8 Lattice dynamics

3.8.1 Phonons: normal modes of lattice vibrations

A crystalline material is a periodic arrangement of atoms in space, as depicted in the sketch shown in Fig.[3-1]. Each atom in the crystal can be thought of as interacting with other atoms via springs: The atoms in the crystal are in a state of perpetual oscillatory motion around their respective equilibrium positions, which gives rise
to lattice vibrations [19]. Normal modes of these lattice vibrations are called phonons.

The study of the vibrational eigenfrequencies of the crystalline lattice is central to the understanding of phase stability, phase transitions and of the thermodynamics of crystalline materials. In the following, we describe Born–von Kármán model of lattice dynamics and obtain the governing equation for the dynamics of the lattice vibrations.

### 3.8.2 Born–von Kármán model

The Born-von Karman model [14] is based on the existence of a function $V$ which expresses the potential energy of the crystal in terms of atomic displacements from the equilibrium sites, $\mathbf{u}^{m'}_\alpha$ being the vector defining the displacement from equilibrium of an atom $\alpha'$ in the $m^{th}$ unit cell.

The crystal is characterized by its unit cell which is identified by a basis $\{\mathbf{a}_i\}; \ i = 1, ..., 3$, formed by the lattice vectors $\mathbf{a}_i$ of the crystal. The repetition of the unit cell in space creates the crystal, and the position of the origin of each unit cell is described by

$$\mathbf{x}_m = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3,$$

(3.26)
where \( \{m_i\}, \ i = 1, ..., 3 \) are integer numbers. Crystals can be further classified as *simple* and *complex*, depending upon the numbers of the atoms in the basis set. In case of a simple crystal, the basis set comprises only one atom, while in a composite crystal, there are multiple atoms in the basis set. In a composite crystal containing \( n \) atoms per unit cell, the atoms within the basis are identified by the index \( \alpha = 1, 2, ..., n \), and their position with respect to the origin of the unit-cell is given by a vector \( x_\alpha \). Thus, the global position of \( \alpha^{th} \) atom in the \( m^{th} \) unit cell becomes

\[
x_{ma} = x_m + x_\alpha. \tag{3.27}
\]

In presence of a perturbation imposed on the crystal, e.g., thermal fluctuations, the instantaneous position of an atom \((m \alpha)\) at time \( t \) becomes

\[
r_{ma}(t) = x_{ma} + u^m_\alpha(t). \tag{3.28}
\]

A Taylor series expansion of function \( V \) around the zero displacement configuration yields,

\[
V = V_0 + \sum_{m',\alpha'} \left[ \frac{\partial V}{\partial u^{m'}_{\alpha'}} \right]_0 u^{m'}_{\alpha'} + \frac{1}{2} \sum_{m',m'',\alpha',\alpha''} u^{m'}_{\alpha'} \left[ \frac{\partial^2 V}{\partial u^{m'}_{\alpha'} \partial u^{m''}_{\alpha''}} \right]_0 u^{m''}_{\alpha''} + \ldots \ldots \tag{3.29}
\]

Further, we assume that the function \( V \) is minimum when all the \( u^{m'}_{\alpha'} \) are zero, as the undistorted lattice is presumably a configuration of stable equilibrium. Hence

\[
\left[ \frac{\partial V}{\partial u^{m'}_{\alpha'}} \right]_0 = 0; \tag{3.30}
\]

i.e., the linear term in the Taylor expansion vanishes. Further, if we assume that the vibrations are of small amplitudes, then the expansion can be truncated to retain the
quadratic term only. This is called the harmonic approximation:

\[
\mathcal{V} = \mathcal{V}_0 + \frac{1}{2} \sum_{m',m'',\alpha',\alpha''} u_{\alpha'}^{m'} \left[ \frac{\partial^2 \mathcal{V}}{\partial u_{\alpha'}^{m'} \partial u_{\alpha''}^{m''}} \right]_0 u_{\alpha''}^{m''} \tag{3.31}
\]

Or, equivalently,

\[
\mathcal{V} = \mathcal{V}_0 + \frac{1}{2} \sum_{m',m'',\alpha',\alpha''} u_{\alpha'}^{m'} \lambda_{\alpha'\alpha''}(m' - m'') u_{\alpha''}^{m''} \tag{3.32}
\]

where

\[
\lambda_{\alpha'\alpha''}(m' - m'') = \left[ \frac{\partial^2 \mathcal{V}}{\partial u_{\alpha'}^{m'} \partial u_{\alpha''}^{m''}} \right]_0 \tag{3.33}
\]

is a second-order tensor called the force-constant tensor, and satisfies the following symmetry condition:

\[
\lambda_{\alpha'\alpha''}(m' - m'') = \lambda_{\alpha'\alpha''}(m'' - m') \tag{3.34}
\]

The total energy of the crystal in the harmonic approximation is obtained as

\[
H = \frac{1}{2} \sum_{m,\alpha} \mu \left( \frac{\partial u_{\alpha}^m}{\partial t} \right)^2 + \frac{1}{2} \sum_{m',m'',\alpha'\alpha''} u_{\alpha'}^{m'} \lambda_{\alpha'\alpha''}(m' - m'') u_{\alpha''}^{m''}, \tag{3.35}
\]

where \(\mu\) denotes the atomic mass. The force acting upon atom \(\alpha\) in the \(m^{th}\) layer \(F_{\alpha}^m\) is obtained by functional derivative:

\[
F_{\alpha}^m = -\frac{\partial \mathcal{V}}{\partial u_{\alpha}^m}; \tag{3.36}
\]

\[
F_{\alpha}^m = -\frac{1}{2} \sum_{m',m'',\alpha'\alpha''} \left( \delta_{\alpha\alpha'}^{m'm'} \lambda_{\alpha'\alpha''}(m' - m'') u_{\alpha''}^{m''} + \delta_{\alpha\alpha''}^{m'm''} \lambda_{\alpha'\alpha''}(m' - m'') u_{\alpha'}^{m'} \right). \tag{3.37}
\]
Equivalently we can write,

$$F^m_\alpha = - \sum_{m',\alpha'} \lambda_{\alpha\alpha'}(m - m').u^{m'}_{\alpha'}.$$  \hspace{1cm} (3.38)

From this we note that,

$$\lambda_{\alpha\alpha'}(m - m') = - \frac{\partial F^m_\alpha}{\partial u^{m'}_{\alpha'}}.$$  \hspace{1cm} (3.39)

Using Newton’s second law,

$$\mu \frac{\partial^2 u^m_\alpha}{\partial t^2} = - \sum_{m',\alpha'} \lambda_{\alpha\alpha'}(m - m').u^{m'}_{\alpha'}.$$  \hspace{1cm} (3.40)

We seek a plane-wave solution to equation (3.40) of the form

$$u^m_\alpha = Q^\alpha e^{i(k.m - \omega(k)t)},$$  \hspace{1cm} (3.41)

where \(k\) is the wave-vector and \(\omega(k)\) is the corresponding frequency. Substituting this plane-wave solution in equation (3.40) yields

$$\mu \omega(k)^2 Q^\alpha e^{i(k.m)} = \sum_{m',\alpha'} \lambda_{\alpha\alpha'}(m - m').Q^\alpha e^{i(k.m')}$$  \hspace{1cm} (3.42)

or

$$\mu \omega(k)^2 Q^\alpha = \sum_{m',\alpha'} \lambda_{\alpha\alpha'}(m - m').Q^\alpha e^{i(k.(m' - m))}$$  \hspace{1cm} (3.43)

or

$$\mu \omega(k)^2 Q^\alpha = \sum_{\alpha'} \left[ \sum_{m'} \lambda_{\alpha\alpha'}(m' - m)e^{i(k.(m' - m))} \right] Q^\alpha_{\alpha'}$$  \hspace{1cm} (3.44)

The summation in the right side is Fourier transform \(D_{\alpha\alpha'}(k)\) of \(\lambda_{\alpha\alpha'}\); i.e.,

$$\sum_{m'} \lambda_{\alpha\alpha'}(m' - m)e^{i(k.(m' - m))} = D_{\alpha\alpha'}(k)$$  \hspace{1cm} (3.45)

97
Thus,

\[
\mu \omega(k)^2 Q_\alpha = \sum_{\alpha'} D_{\alpha \alpha'}(k) Q_{\alpha'} \quad (3.46)
\]

\[
\sum_{\alpha'} \left( D_{\alpha \alpha'}(k) - \mu \omega(k)^2 \delta_{\alpha \alpha'} \right) Q_{\alpha'} = 0; \quad \alpha, \alpha' = 1, 2, 3, \ldots N, \quad (3.47)
\]

where \( \Lambda_{\alpha \alpha'}(k) \) is the dynamical matrix at \( k \); \( N \) is the number of atoms in the basis set. The solutions of the governing equation, which is an eigenvalue problem, are called as normal mode frequencies and are obtained by setting the determinant of the dynamical matrix to zero:

\[
\text{Det} \left( D_{\alpha \alpha'}(k) - \mu \omega(k)^2 \delta_{\alpha \alpha'} \right) = 0 \quad (3.48)
\]

Evaluation of normal mode frequencies \( \omega(k) \) at a continuous set of \( k \)-points yields the phonon dispersion curve for the crystal.

Two practical techniques have been proposed in literatures to calculate the vibrational frequencies of a crystalline lattice with the framework of first-principles calculations: (A) the force-constant technique [104] and (B) the linear response technique of Baroni, et al. [11, 65]. The two techniques are described briefly in the following.

A. Force-constant technique

The force-constant technique is based on first-principles calculation of energetics of distortions periodic over a sufficiently large supercell wherefrom the forces and force constants are extracted. Determination of force-constants enables their assembly into the force-constant matrix which, upon diagonalization, yields the vibrational eigen-frequencies. The size of the supercell is chosen so as to include all non-vanishing nearest-neighbor interactions. The calculation of the force constant matrix is performed as follows: First, an atom \( (m, \alpha) \) is displaced by a vector \( u_{m \alpha} \), and the induced force on all other atoms in the supercell, \( F_{m \alpha'}^{m \alpha} \forall m' \) and \( \forall \alpha' \) is calculated via
the Hellman-Feynman theorem. The force constant matrix $\lambda_{\alpha\alpha'}(m - m')$, corresponding to the interaction between $\alpha^{th}$ atom in $m^{th}$ unit cell and $\alpha'^{th}$ atom in $m'^{th}$ unit cell, in the harmonic approximation, is given by

$$
\lambda_{\alpha\alpha'}(m' - m) = -\frac{\partial F_{\alpha\alpha'}^{mm'}}{\partial u_{m\alpha}},
$$

(3.49)

where the derivative is performed with a finite-difference method. The dynamical matrix is calculated by taking the Fourier transform of $\lambda_{\alpha\alpha'}(m' - m)$, as follows.

$$
D_{\alpha\alpha'}(k) = \frac{1}{\sqrt{\mu_\alpha\mu_{\alpha'}}} \sum_{m'=1}^{M} \lambda_{\alpha\alpha'}(m - m')e^{ik(m - m')},
$$

(3.50)

where $M$ is the number of unit cells in the supercell. This procedure is repeated to obtain the force constant matrix for all the atoms in the unit cell and for all the unit cells in the supercell. Using the force-constant technique, the phonon frequencies can be directly estimated at isolated symmetry points. Compared to the linear-response approach, the advantage of the force-constant technique is that only a very small set of supercell calculations, as the symmetry greatly reduces the number of displacements required to determine all the force-constant matrices (e.g., a single calculation is required for a primitive cell with full cubic symmetry). The main limitations of the direct approach are in the size of the supercell. As we noted before, the size of the supercell should be large enough so that all non-vanishing interactions are accounted for; therefore, difficulty arises with systems for which the required supercell is very large.

B. *Ab initio* phonon calculation: linear response theory

The linear response calculation allows direct evaluation of the dynamical matrix $D_{\alpha\alpha'}(k)$ and its eigenvalues, which are the phonons, at a $k$-point. The evaluation of the dynamical matrix at a given $k$ point is based on the calculation of the second-order derivatives of the total energy of the system with respect to a plane-wave
Fully optimized crystal structure
\[\Downarrow \Leftarrow \] Density Functional Theory

Force-constant matrices

Wave-vector \(k\) \[\Rightarrow \Downarrow \Leftarrow\] Fourier Transform

Dynamical matrix \(D(k)\)
\[\Downarrow \Leftarrow\] Diagonalize

Phonon Frequencies

Figure 3-2: Computational framework to determination of phonons frequencies via calculation of force constant matrix.

perturbation of wave-vector \(k\) in the atomic positions. The formalism exploits the use of the \(2n+1\) theorem, which asserts that the \((2n + 1)^{th}\) - order derivative of the total energy can be directly obtained from the \(n^{th}\)-order perturbed wave functions \[41\]. This means that a first-order perturbation in the wave-functions is sufficient to evaluate the third-order derivatives of the total energies to calculate the dynamical matrix \(D_{\alpha\alpha'}\), which upon diagonalization gives the phonon-frequencies. The calculation can be performed using only a unit cell of the system and without imposing any displacements on the system. Baroni, \textit{et al.} \[11, 42, 64\] performed, for the first time, the linear response calculation while evaluating energies and forces from perturbations via DFT calculations, The resulting scheme is usually referred to as Density Functional Perturbation Theory (DFPT).

However, since the evaluation of dynamical matrix via linear response is computationally expensive, it can not be directly employed for computation of complete
phonon-dispersion relation, which requires calculating the dynamical matrix and diagonalizing it over a dense set of k-grid in the Brillouin zone. In order to obtain the complete phonon-dispersion relation, the dynamical matrix is calculated over a selected set of k-vectors only. Then an inverse Fourier transform is used to recover the force-constant matrices. Once the force-constant matrices are obtained, the dynamical matrices over a dense set of k-point are obtained by Fourier transforming the force-constant matrices; subsequent diagonalization then yields the complete phonon-dispersion relation. This procedure of inverse Fourier transform over a finite grid to recover the force-constant matrices and subsequent Fourier transform of these force-constant matrices to obtain dynamical matrices over a dense-grid is called Fourier interpolation.

In this work, we have employed DFPT calculations as implemented in Quantum-Espresso [66] suite of codes to calculate the phonon-dispersion relation of graphene. The phonon-dispersions have been calculated for metals and semiconductors using DFPT, which are in excellent agreement with experimentally-measured phonon-dispersion. For example, in Fig.[3-3], we show the phonon-dispersion of Al obtained from linear response calculation. The calculated dispersion relation is in excellent agreement with the experimentally-measured phonon dispersion relation.

Note that Al is a Bravais lattice with a single-atom basis, so the phonon-dispersion of Al contains only acoustic phonon branches. On the other hand, graphene is a composite lattice of two Bravais lattices shifted with respect to each other by a shift vector, and its phonon-dispersion contains both acoustic and optical branches, as shown in Fig.[3-4]
Figure 3-3: (a) Brillouin zone of Al with special directions indicated. (b) Phonon-dispersion of Al obtained from DFPT phonon calculations: solid lines are calculated response and dots are the measured values from neutron scattering experiments.

Figure 3-4: (a) Brillouin zone of graphene with special directions indicated. (b) Phonon-dispersion of graphene obtained from DFPT phonon calculations. The dispersion contains 6 branches: 3 corresponding to acoustic phonons and 3 corresponding to optical phonons.
3.8.3 Phonons-based lattice stability analysis

The basic theory of lattice vibration dates back to 1930 (see Born and Huang [19] for initial references). Lattice dynamics govern a wide variety of material properties, such as infrared and Raman spectra, thermal expansion and heat conduction, and the superconductivity, which arises from electron-phonon interaction. Lattice dynamics also provides the key to assessing the mechanical stability of the underlying lattice. Wallace and Patrick proposed the necessary and sufficient criteria for stability of a crystalline material under perturbations of all wavelengths [194]. According to these criteria, for a crystal to be stable against all infinitesimal perturbations about an equilibrium state, the following two conditions should be satisfied:

1. **Long wavelength stability condition**: all acoustic phonon branches should have non-zero slopes at the origin i.e. \( (d\omega/dk \neq 0) \) at \( k = 0 \). This ensures that the crystal is stable w.r.t. all homogeneous deformations, and is also equivalent to the fact that the acoustic tensor \( \Lambda \) is positive-definite, i.e., \( (m \otimes n) : \Lambda : (m \otimes n) \), a condition also referred to as *strong ellipticity condition* in solid mechanics. Hence, any instability associated with loss of strong ellipticity should manifest itself as a long wavelength instability in phonon dispersion relations. For example, in both uniaxial stress and uniaxial strain, the failure of graphene arises from an elastic instability of the underlying lattice [111].

2. **Short wavelength stability condition**: phonon frequencies at all other points in the Brillouin zone should be real and non-zero i.e. \( (\omega^2 > 0) \) at all \( k \neq 0 \). This ensures stability against infinitesimal perturbations of finite wavelengths, and is independent of the strong ellipticity condition. For example, the mechanical failure of graphene in equi-biaxial tension is due to a soft-mode instability at the Brillouin zone boundary [125].
The violation of either of these conditions is an indication of incipient instability of the lattice. The phonon-based approach to stability analysis thus captures instabilities of all wavelengths, and therefore is more robust and comprehensive than one based solely on the acoustic tensor. In Chapter 6, we employ the phonon-based lattice-stability analysis to determine the limits to elastic deformation, the stress or strain at which reversible-to-irreversible transition occurs, for graphene under various loadings. The data obtained is fitted to symmetry-invariant functions to obtain the continuum failure surface.
Chapter 4

Method for generating complete and irreducible integrity basis for scalar-valued function of a symmetric tensor second order tensor, and of a vector

4.1 Introduction

Previously, in Chapter 2, we outlined the symmetry-invariant based representation scheme which forms the basis of formulation of a constitutive response function of a general anisotropic material on the basis of experimental or numerical observations. A constitutive response function is a mathematical relation that describes the dependence of some physical (microscopic or macroscopic) property of a material $\psi$ on a list of tensor agencies $\zeta_1, ..., \zeta_n$. The laws of physics impose certain restrictions on the form of the constitutive response function...
functions. One such restriction is the material symmetry restriction. According to the material symmetry restriction, the constitutive response functions of a material should remain invariant in observations under certain orthogonal transformations [136]. The set of all such orthogonal transformations form a group (in technical algebraic sense) which is called the crystallographic point group of the material [31]. For an isotropic material, the symmetry group includes all rotations about all possible axes, and reflection about all possible planes, that leave the crystal unchanged. Thus, the symmetry group of an isotropic material is a continuous group containing all orthogonal transformations, called the full orthogonal group. For crystals, which are anisotropic, the symmetry group is a finite subgroup of the full orthogonal group, i.e., it comprises a finite number of symmetry transformations.

A central problem in the constitutive modeling of materials is obtaining scalar- and tensor-valued functions of the tensor agency compliant with material symmetry restrictions. Smith and Rivlin [176, 177, 178] addressed this problem by finding the representation in terms of a set of special polynomial functions of the tensor agencies, called an \textit{integrity basis}, that remain invariant under point group symmetry operations.

An integrity basis must satisfy two important requirements — (a) \textit{completeness} and (b) \textit{irreducibility}. Completeness guarantees representation of any arbitrary polynomial function which remains invariant with respect to the point group symmetry under consideration. The irreducibility ensures that there is no redundancy, and the representation employs a minimal possible number of variables. An integrity basis satisfying the above two requirements is called a complete and irreducible integrity basis. In Chapter 5, we employ an integrity basis of the logarithmic strain tensor with respect to $C_{6s}$ material symmetry group to construct a non-linear constitutive response for graphene.

In some occasions, the representation requires use of an alternate set of symmetry-
invariants that involve non-polynomial functions of the tensor agencies. For example, in Chapter 6, we obtain a continuum failure function for graphene in terms of a non-polynomial symmetry-functions of the logarithmic strain tensor. Such an alternate set of symmetry-invariants is called a functional basis [201, 219]. Wineman & Pipkin [203] showed that a complete and irreducible integrity basis relative to a crystallographic point group also constitutes a complete functional basis for the group; however, it may not necessarily be irreducible. Thus, once an integrity basis has been derived, the Wineman-Pipkin theorem allows construction of a functional basis out of the integrity basis.

Previously, Smith & Rivlin derived the complete and irreducible integrity bases for all 32 crystal classes. This method has two major drawbacks [177, 178].

1. The method is laborious, since reducing the basis to the minimal possible number of variables requires an exhaustive search of all possible polynomial expressions relating the components of the integrity basis. Intellectually, this does not pose any substantive difficulty, but an enormous amount of work needs to be done.

2. Yet at the end, it can't be rigorously proved that the resulting integrity basis is complete yet irreducible. Pennisi and Travato [157] proposed a framework based on a reductio ad absurdum approach within which the irreducibility or not of an integrity basis can be examined. However, since such a framework does not reduce an integrity basis which is reducible, to an irreducible one; the difficulty persists.

In this chapter, we propose a novel statistical method to generate an irreducible and complete polynomial basis for representation of constitutive functions employing a second-order symmetric tensor or a 2D vector as an argument and which remain invariant under the group of transformation associated with a certain 2D crystal
class. Such a polynomial basis is also called an integrity basis; and a more general functional basis can be derived from this integrity basis. The method of Smith & Rivlin [176, 177, 178] is based on manual reduction of the basis set by identifying the algebraic relationship between the integrity bases. This approach becomes a labour intensive task when the material’s symmetry group is large, such as in the case of $O_h$, and $D_{6h}$ crystal classes; and therefore automation becomes desirable, if not strictly necessary. In comparison, the proposed scheme is simple, and can be completely automated; i.e., no manual effort is required to reduce the basis.

The objective of this work to develop a scheme to construct the integrity basis of a second-order symmetric tensor with respect to a material symmetry group. We demonstrate this technique by constructing the integrity basis of a vector, and of a tensor with respect to a material symmetry group of a 2D Bravais lattice.

### 4.1.1 Mathematical foundation

Symmetry coordinates are a set of scalar functions $\varphi_i$ of a vector $r = \{x, y\} = \{r \cos \theta, r \sin \theta\}$ such that all the points in space that are equivalent to $r$ by symmetry, i.e., $r, Q_1 r, ..., Q_n r$ all have a unique representation in terms of symmetry coordinates $\{\varphi_1, \varphi_2, ..., \varphi_n\}$. Thus, the symmetry coordinates $\varphi_i (i=1, 2, 3, ..., n)$ have the special property:

$$\varphi_i(r) = \varphi_i(Q_n r) \forall Q_n \in \mathcal{G},$$  \hspace{1cm} (4.1)

while the symmetry-invariants of a second-order tensor such as $E^{(0)}$ satisfy the relation:

$$\mathcal{I}_i(E^{(0)}) = \mathcal{I}_i(Q_n^T E^{(0)} Q_n) \forall Q_n \in \mathcal{G}.$$  \hspace{1cm} (4.2)

Such a function is called an invariant of the point group $\mathcal{G}$. The mathematical foundation of symmetry-invariants originates from Weyl’s fundamental work on algebraic-invariants. These theorems are described in the following.
4.1.2 Weyl’s fundamental theorems on invariants

First theorem (complete and irreducible basis for representation)

Weyl’s first theorem introduces the notion of a complete and irreducible set of invariants that could serve as the basis for representation [201]. It states—any invariant function pertaining to a finite set of transformations can be expressed in terms of a finite number of functions—termed elementary symmetric functions—that remain invariant under the set of transformations. The irreducible set of such functions is called a functional basis. An integrity basis is a special class of functional basis where the basis invariants are polynomials in the argument agencies.

Consider a scalar function \( \psi \) which employs a 2D second-order symmetric tensor \( \mathcal{K} \) as an argument, i.e. \( \psi = \hat{\psi}(\mathcal{K}) \). The tensor agency \( \mathcal{K} \) can be represented by a 2 \times 2 matrix, i.e.,

\[
\mathcal{K} = \begin{bmatrix}
\mathcal{K}_{11} & \mathcal{K}_{12} \\
\mathcal{K}_{12} & \mathcal{K}_{22}
\end{bmatrix},
\]

(4.3)

or equivalently, by a vector \( \{\mathcal{K}_{11}, \mathcal{K}_{22}, \mathcal{K}_{12}\} \), called component vector. Let the number of symmetry transformation in the material symmetry group \( \mathcal{G} \) be \( n \). The transformation of this tensor agency under the action of a symmetry transformation \( Q_m \in \mathcal{G} \) is given by the following relation:

\[
\mathcal{K}^{(m)} = Q_m \mathcal{K} Q_m^T,
\]

(4.4)

and let the components of the transformed tensor \( \mathcal{K}^{(m)} \) be denoted as

\[
\mathcal{K}^{(m)} = \begin{bmatrix}
\mathcal{K}^{(m)}_{11} & \mathcal{K}^{(m)}_{12} \\
\mathcal{K}^{(m)}_{12} & \mathcal{K}^{(m)}_{22}
\end{bmatrix}.
\]

(4.5)
The corresponding transformed component vector is written as \( \{K_{11}^{(m)}, K_{22}^{(m)}, K_{12}^{(m)} \} \).

In consideration of the rotational symmetries, we note that the two rotations \( Q_n \) and \( Q_m \) that transform a unit vector \( \mathbf{v} \) to two vectors, \( Q_n \mathbf{v} \) and \( Q_m \mathbf{v} \), that are mutually parallel or antiparallel, i.e., \( Q_n \mathbf{v} \times Q_m \mathbf{v} = 0 \), are redundant since under the action of these rotations, a second order tensor, such as \( \mathcal{K} \), is mapped to exactly the same transformed tensor, \( \mathcal{K}^{(n)} = \mathcal{K}^{(m)} \). For example, in the \( C_{6v} \) symmetry group, there are only three non-redundant rotation operators: \( C_0 \) or \( C_\pi \), \( C_{\pi/3} \) or \( C_{4\pi/3} \), and \( C_{2\pi/3} \) or \( C_{5\pi/3} \).

The closure property of a point group (see [31] for details) suggests that action of symmetry transformations should result in a cyclic rotation between transformed component vectors, i.e.,

\[
\{K_{11}^{(1)}, K_{22}^{(1)}, K_{12}^{(1)} \} \Rightarrow \{K_{11}^{(2)}, K_{22}^{(2)}, K_{12}^{(2)} \},
\]

\[
\cdots \cdots
\]

\[
\{K_{11}^{(n-1)}, K_{22}^{(n-1)}, K_{12}^{(n-1)} \} \Rightarrow \{K_{11}^{(n)}, K_{22}^{(n)}, K_{12}^{(n)} \},
\]

and

\[
\{K_{11}^{(n)}, K_{22}^{(n)}, K_{12}^{(n)} \} \Rightarrow \{K_{11}^{(1)}, K_{22}^{(1)}, K_{12}^{(1)} \}. \tag{4.6}
\]

Then, the principle of material symmetry implies

\[
\psi = \hat{\psi} \left( K_{11}^{(1)}, K_{12}^{(1)}, K_{22}^{(1)} \right) = \hat{\psi} \left( K_{11}^{(2)}, K_{12}^{(2)}, K_{22}^{(2)} \right) \cdots = \hat{\psi} \left( K_{11}^{(n)}, K_{12}^{(n)}, K_{22}^{(n)} \right). \tag{4.7}
\]

Based on (4.6) and (4.7), \( \psi \) can, equivalently, be defined by a function, \( \hat{\psi}(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3) \), of three \( n \)-dimensional vector agencies, \( \mathbf{v}_1 = \{K_{11}^{(1)}, K_{11}^{(2)}, \ldots, K_{11}^{(n)} \} \), \( \mathbf{v}_2 = \{K_{12}^{(1)}, K_{12}^{(2)}, \ldots, K_{12}^{(n)} \} \), \( \mathbf{v}_3 = \{K_{22}^{(1)}, K_{22}^{(2)}, \ldots, K_{22}^{(n)} \} \), which remains invariant under all cyclic permutations of
the indices 1, 2, ..., n, i.e.,

\[
\psi = \bar{\psi} \left( \left\{ K_{11}^{(1)}, K_{11}^{(2)}, ..., K_{11}^{(n)} \right\}, \left\{ K_{12}^{(1)}, K_{12}^{(2)}, ..., K_{12}^{(n)} \right\} \right) \\
= \bar{\psi} \left( \left\{ K_{11}^{(n)}, K_{11}^{(1)}, ..., K_{11}^{(n-1)} \right\}, \left\{ K_{12}^{(n)}, K_{12}^{(1)}, ..., K_{12}^{(n-1)} \right\} \right) \\
... \quad ... \quad ...
\]

\[
= \bar{\psi} \left( \left\{ K_{11}^{(n-1)}, K_{11}^{(n)}, ..., K_{11}^{(n-2)} \right\}, \left\{ K_{12}^{(n-1)}, K_{12}^{(n)}, ..., K_{12}^{(n-2)} \right\} \right).
\]

Thus, a polynomial representation of \( \psi \) would comprise of scalar polynomials that remain invariant under all cyclic permutations of the components of the two vector agencies \( v_1, v_2 \) and \( v_3 \). Towards obtaining such a representation, the first step is to generate all possible scalar polynomials up to degree \( N \) that remain invariant under all cyclic permutations of its vector agencies. In limiting the degree of polynomials to \( N \), we have used the fact that the degree of the highest polynomial invariant under a finite group of transformations is less than or equal to the order of the group [201].

Second theorem (Polarization of algebraic invariants)

H. Weyl [201] suggested that a general symmetry function such as \( \psi \) can be expressed in terms of the elementary symmetric functions \( \varphi_i \)'s that can be obtained by simple algebraic combinations of the components of \( v_1 \) and \( v_2 \) [177, 178]. Weyl’s theorem can be stated as follows:

*The exhaustive set of elementary symmetric functions in two \( N \)-dimensional vectors, \( v_1 = \{v_{11}, v_{12}, ..., v_{1N}\}, \; v_2 = \{v_{21}, v_{22}, ..., v_{2N}\}, ..., \; v_n = \{v_{n1}, v_{n2}, ..., v_{nN}\} \) that remain invariant under a cyclic permutation of its components, i.e., \( \varphi(v_1, v_2, ..., v_n) = \varphi(\sigma v_1, \sigma v_2, ..., \sigma v_n) = \varphi(\sigma^2 v_1, \sigma^2 v_2, ..., \sigma^2 v_n) = ... = \varphi(\sigma^{N-1} v_1, \sigma^{N-1} v_2, ..., \sigma^{N-1} v_n) \) where \( \sigma \) is the cyclic permutation operator with the property \( \sigma^N = I \), comprises of the*
following combinations.

\[
\begin{align*}
\text{tr}(\sigma_i^m v_m) &; \text{tr}(\sigma_i^m \otimes \sigma_j^n v_n), \ldots, \text{tr}(\sigma_i^m \otimes \sigma_j^n \otimes \ldots \sigma_k^l v_l). \\
& \quad \text{O}(1) \quad \text{O}(2) \quad \ldots \quad \text{O}(N)
\end{align*}
\]  

(1)

where \( i, j, k \in \{1, 2, \ldots, N - 1\} \), and \( m, n, l \in \{1, 2, \ldots, n\} \). \( \text{tr}(.) \) denotes the trace, defined as follows.

- For a vector, the trace is defined as the sum of components of the vector.
- For a tensor, the trace is defined as the sum of the diagonal components of the tensor.

Subdivision of material symmetry group & corollary to Weyl’s first theorem

The material symmetry group pertaining to any crystal can be subdivided into two subgroups: a rotational subgroup and a reflection subgroup. We elaborate on this idea with the example of the material symmetry group of graphene. Graphene belongs to \( C_{6v} \) symmetry group, which comprises of the following symmetry operations:

\[
C_{6v} = \{E\}, \{C_{\pi/3}, C_{-\pi/3}\}, \{C_{2\pi/3}, C_{-2\pi/3}\}, \{C_{\pi}\}, \{\Sigma_0, \\
\Sigma_{2\pi/3}, \Sigma_{-2\pi/3}\}, \{\Sigma_{\pi/6}, \Sigma_{-\pi/6}, \Sigma_{\pi/2}\}\}
\]

where \( E \) denotes an identity operation, \( C_\theta \) denotes a rotational symmetry operation under rotation by an angle \( \theta \) and \( \Sigma_\theta \) denotes a reflection symmetry operation about a mirror plane at angle \( \theta \). This symmetry group can be subdivided into a number of subgroups, e.g., the identity, the inversion, the reflection, and the rotation subgroups, i.e.,

\[
\mathcal{G} = \mathcal{G}_{\text{Ref}} \cap \mathcal{G}_{\text{Rot}}.
\]  

(4.8)
These two subgroups are given as

\[ G_{\text{Ref}} = \{ E, \Sigma_0, \Sigma_{2\pi/3}, \Sigma_{-2\pi/3}, \Sigma_{\pi/6}, \Sigma_{-\pi/6}, \Sigma_{\pi/2} \}; \quad \mathcal{O}(G_{\text{Ref}}) = 6, \] (4.9)

and

\[ G_{\text{Rot}} = \{ E, C_{\pi/3}, C_{-\pi/3}, C_{2\pi/3}, C_{-2\pi/3}, C_\pi \}; \quad \mathcal{O}(G_{\text{Rot}}) = 6, \] (4.10)

where \( \mathcal{O}(.) \) denotes the order of the group, i.e., number of symmetry transformations in the group. The advantage of such a decomposition is that it allows one to systematically impose the restrictions due to the two kinds of symmetry operations on the form of the constitutive function. For example, since rotational and reflection symmetries are different, therefore in order to determine the integrity bases, we first consider the restrictions due to the action of rotational symmetry-operations, and obtain the set of symmetry-invariants with respect to the rotational subgroup. Following this, the restrictions due to the action of the reflection subgroup are imposed on the set of the symmetry-invariants satisfying only the rotational symmetries, and thus symmetry-invariants satisfying both rotational and reflection symmetries are obtained. This task is facilitated by the following corollary to Weyl's first theorem.

**Corollary to Weyl's first theorem**

A basis comprising elementary symmetry functions in \( \zeta_1, \zeta_2, \ldots, \zeta_n \) and \( I_1, I_2, \ldots, I_m \), under a group of transformations for which \( I_1, I_2, \ldots, I_m \) are invariants, is formed by adjoining to \( I_1, I_2, \ldots, I_m \), an elementary symmetry basis for polynomials in the variables \( \zeta_1, \zeta_2, \ldots, \zeta_n \), under that group of transformations.[201, 177, 178]
4.1.3 Basis reduction via iterative Principal Component Analysis (PCA)

The results from classical representation theory allow one to generate an exhaustive set of bases functions satisfying the material symmetry conditions, called symmetry-invariants. Unfortunately, not all the functions in the set thus generated are mutually independent, and a majority of them can be expressed as a linear combination of a few others. From a representation point of view, the redundancy of the bases functions is undesirable and therefore, reduction of the above set to a minimal, mutually independent set is required. Here, we develop a statistical method based on principal component analysis to obtain a complete and irreducible integrity bases of a vector, and of a second order tensor agencies with respect to the material symmetry group of graphene.

Redundancies, reducible basis, and syzygies

The integrity basis generated using the above-described approach is exhaustive but, in general, contains too many redundancies. Such a basis is called a reducible basis. In a reducible basis set ordered according to the degree of the member bases, a redundant member, say $\mathcal{J}_n$, can be expressed in terms of the members with the lower or equal degree $\mathcal{J}_1, \mathcal{J}_2, \ldots, \mathcal{J}_{n-1}$ via a relation of the form:

$$\mathcal{J}_n = \mathcal{F}(\mathcal{J}_1, \mathcal{J}_2, \ldots, \mathcal{J}_{n-1}) = \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \lambda_{ij} \cdot \mathcal{J}_i^{(i,j,k)} \cdot \mathcal{J}_j^{(i,j,k)} \cdot \ldots \cdot \mathcal{J}_k^{(i,j,k)}. \quad (\S 2)$$

where $a(i, j, \ldots, k)$, $b(i, j, \ldots, k)$, and $c(i, j, \ldots, k)$ are integers such that

$$a(i, j, \ldots, k) \times \mathcal{O}(\mathcal{J}_i) + b(i, j, \ldots, k) \times \mathcal{O}(\mathcal{J}_j) + \ldots + c(i, j, \ldots, k) \times \mathcal{O}(\mathcal{J}_k) = \mathcal{O}(\mathcal{J}_n), \quad (\S 3)$$
where \( \mathcal{O}(.) \) denotes the degree of the polynomial basis. The relation expressed by \( \S 2 \) and satisfying the condition \( \S 3 \) is called a polynomial syzygy.

**Basis reduction, principal component analysis**

The objective of the basis reduction is to determine all existing polynomial syzygies, and reduce the basis to independent members. An integrity basis with no polynomial syzygies existing in its members is called an irreducible integrity basis.

In the following we describe a statistical linear algebraic approach, called principal component analysis, to determine a polynomial syzygy \( J_n = F(J_1, J_2, ..., J_{n-1}) \) in an ordered set of basis functions \( \{J_1, J_2, ..., J_n\} \). Principal component analysis (PCA) is a statistical method that reduces the dimensionality of the basis by eliminating the redundant ones while retaining the ones essential for completeness of the basis [89, 207]. This method is described in the following section.

**Outline of the principal component analysis**

The principal component analysis-based scheme to eliminate the redundancy of a reducible basis comprises the following steps.

1. The first step is to determine all the multivariate monomials of the form

   \[ F_n = J_i^{a(i,j,...,k)} J_j^{b(i,j,...,k)} ... J_k^{b(i,j,...,k)}, \quad (4.11) \]

   that are of the same order as \( \mathcal{O}(J_k) \). Let there be \( m \) such monomials, denoted by \( \zeta^{(1)}, \zeta^{(2)}, ..., \zeta^{(m)} \).

2. Secondly, we generate a sufficiently large data set for each of such monomi-
als corresponding to a set of arbitrary points \( \{ r_i \} \) in the space of the tensor agency. These data sets are represented by vectors \( \zeta^{(1)} = \{ s_i^{(1)} \}, \zeta^{(2)} = \{ s_i^{(2)} \}, \ldots, \zeta^{(3)} = \{ s_i^{(3)} \} \).

Then we set the mean of each column vector to be zero by subtracting off their respective means. The column vectors with zero mean are denoted as primed variables \( \zeta^{(1)'} = \zeta^{(1)} - \langle \zeta^{(1)} \rangle, \zeta^{(2)'} = \zeta^{(2)} - \langle \zeta^{(2)} \rangle, \ldots, \zeta^{(m)'} = \zeta^{(m)} - \langle \zeta^{(m)} \rangle \), where \( \langle \cdot \rangle \) denotes the mean.

3. The covariance between two data sets of length \( N \) represented by vectors \( a \) and \( b \), is calculated as the following (see [181] for details).

\[
\Gamma_{ab} = \frac{1}{N-1} a \cdot b. \quad (4.12)
\]

The covariance \( \Gamma_{ab} \) provides a measure of correlation between the two data sets. Particularly,

- \( \Gamma_{ab} = 0 \) implies that \( a \) and \( b \) are totally uncorrelated.
- \( \Gamma_{ab} = \text{var}(a) \) implies that \( a = b \), where \( \text{var}(a) \) denotes the variance of dataset denoted by vector \( a \).

The covariance matrix, \( \Gamma \), for the dataset is calculated as follows.

\[
\Gamma(\zeta^{(1)}, \zeta^{(2)}, \ldots, \zeta^{(m)}) = \begin{bmatrix}
\Gamma_{\zeta^{(1)'}\zeta^{(1)'}} & \Gamma_{\zeta^{(1)'}\zeta^{(2)'}} & \cdots & \Gamma_{\zeta^{(1)'}\zeta^{(m)'}} \\
\Gamma_{\zeta^{(2)'}\zeta^{(1)'}} & \Gamma_{\zeta^{(2)'}\zeta^{(2)'}} & \cdots & \Gamma_{\zeta^{(2)'}\zeta^{(m)'}} \\
\cdots & \cdots & \cdots & \cdots \\
\Gamma_{\zeta^{(m)'}\zeta^{(1)'}} & \Gamma_{\zeta^{(m)'}\zeta^{(2)'}} & \cdots & \Gamma_{\zeta^{(m)'}\zeta^{(m)'}} 
\end{bmatrix}. \quad (4.13)
\]

4. A redundancy in the basis set is identified by the singular value decomposition of the covariance matrix. The singular value decomposition of the covariance matrix
matrix gives

$$\mathbf{\Gamma} = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^T,$$  \hspace{1cm} (4.14)

where $\mathbf{\Sigma}$ is a diagonal matrix containing the singular values (also the eigenvalues) of the covariance matrix. A zero entry in the singular matrix indicates that the covariance matrix is rank deficient\footnote{By a zero singular value, we mean an eigenvalue of the matrix $\mathbf{\Sigma}$ that is less than or equal to the machine precision value.}, and a linear dependence amongst the columns of the covariance matrix exists. Let the eigenvector corresponding to zero eigenvalue be $\mathbf{v} = \{\lambda_1, \lambda_2, ..., \lambda_m\}$. Then the dependency relation amongst the various monomials $\zeta^{(1)}, \zeta^{(2)}, ..., \zeta^{(m)}$ is given by

$$\lambda_1\zeta^{(1)} + \lambda_2\zeta^{(2)} + ... + \lambda_m\zeta^{(m)} = 0.$$  \hspace{1cm} (4.15)
Algorithm of basis reduction scheme

Given a reducible basis set of length $N$, the following iterative algorithm would generate an irreducible integrity basis.

0. START; $K=1$, $IND=1$.

(K IS THE COUNTER; IND IS THE NUMBER OF INDEPENDENT COMPONENTS.)

I. DETERMINE THE MULTIVARIATE MONOMIALS IN $\{J_1, \ldots, J_K\}$ of degree $O(J_K)$.

(SAY THE NUMBER OF SUCH MONOMIALS IS $M$.)

II. CALCULATE THE $M \times M$ COVARIANCE MATRIX $\Gamma$.

III. OBTAIN THE SINGULAR MATRIX $\Sigma$ FROM SVD OF $\Gamma$.

IV. CHECK FOR $\det(\Sigma) = 0$.

V. IF TRUE: $J_K$ IS NOT INDEPENDENT; DISCARD $J_K$; $K=K+1$; $IND=IND$.

VI. ELSE: $J_K$ IS INDEPENDENT; RETAIN $J_K$; $K=K+1$; $IND=IND+1$. 

118
4.2 Examples

The proposed scheme is demonstrated by two examples. First example concerns with
the integrity basis for a 2D vector, e.g. the position vector of a point in real space r or
in reciprocal space k, w.r.t. the C$_{6v}$ symmetry group. The resulting integrity basis is
then used to construct special functional basis constituting of symmetry coordinates
of the vector, a alternate coordinate system in which two points which are identical by
symmetry have the same set of symmetry coordinates. The second example involves
finding the integrity basis for a symmetry second-order tensor, such as the logarithmic
strain tensor E(0); and a functional basis derived from this integrity basis.

4.2.1 Symmetry-invariants of a 2D vector with respect to C$_{6v}$
symmetry group

In this section, we construct the symmetry-invariants for a 2D vector with respect
to C$_{6v}$ symmetry group using the proposed technique. As an example, we consider a
reciprocal space vector $k$ in the Brillouin zone of graphene, as shown in Fig.[4-1]. Let
the coordinates of the reciprocal vector $k$ w.r.t. the two material axes (the armchair
and the zigzag directions) are denoted as:

\[ \mathbf{k} = (x, y) = (r \cos \theta, r \sin \theta). \]  

(4.16)

The inversion maps a vector \( \mathbf{k} \) to \(-\mathbf{k}\). Therefore, a scalar function of \( \mathbf{k} \) that remain invariant under inversion can be perceived as a function of a rank one tensor \( \mathbf{k} \otimes \mathbf{k} \):

\[ \psi = \tilde{\psi}(\mathbf{k}) = \tilde{\psi}(\mathbf{k} \otimes \mathbf{k}). \]  

(4.17)

It should be noted that a vector can also be equivalently represented by a rank one tensor. To obtain the symmetry-invariants of \( \mathbf{k} \), first we construct the corresponding
rank-one tensor given by —

\[ \mathcal{K} = k \otimes k = \begin{bmatrix} x^2 & xy \\ xy & y^2 \end{bmatrix}. \]  \hspace{1cm} (4.18)

Note that

\[ \det \mathcal{K} = (x^2)(y^2) - (xy)(xy) = 0, \]  \hspace{1cm} (4.19)

indicating that the rank of \( \mathcal{K} \) is indeed 1. The tensor \( \mathcal{K} \) can be decomposed into an isotropic part and a traceless part as following.

\[ \mathcal{K} = \mathcal{K}_i + \mathcal{K}_0, \]  \hspace{1cm} (4.20)

where

\[ \mathcal{K}_i = \frac{1}{2}(x^2 + y^2)I, \]  \hspace{1cm} (4.21)

and the traceless part reads as

\[ \mathcal{K}_0 = \begin{bmatrix} \frac{1}{2}(x^2 - y^2) & xy \\ xy & \frac{1}{2}(y^2 - x^2) \end{bmatrix}. \]  \hspace{1cm} (4.22)

Complete (not necessarily irreducible) integrity basis

The isotropic component remains invariant under all orthogonal transformations, i.e.,

\[ Q_m \mathcal{K}_i Q_m^T = \mathcal{K}_i, \hspace{1cm} \forall Q_m \in \text{SO}_2, \]  \hspace{1cm} (4.23)

where \( \text{SO}_2 \) is the full orthogonal group in 2D space. Thus, the decomposition given in equation (4.20) immediately allows us to recognize a symmetry invariant as

\[ \mathcal{I}_1 = x^2 + y^2. \]  \hspace{1cm} (4.24)
The traceless part has only two independent components: $x^2 - y^2$ and $xy$, which upon the action of symmetry transformation change.

- **Operation of the rotation subgroup $G_{\text{rot}}$**: First, we consider the action of the rotation subgroup. The rotational operations $C_0$ and $C_{\pi}$ leave the two components unchanged, i.e.,

$$C_0, \ C_{\pi} : x^2 - y^2, \ xy; \ (4.25)$$

under the action of rotational operations $C_{\pi/3}$ and $C_{-\pi/3}$, the two components transform as

$$C_{\pi/3}, \ C_{-\pi/3} : \frac{1}{4}(-x^2 - 2\sqrt{3}xy + y^2), \ \frac{1}{4}(\sqrt{3}x^2 - 2xy - \sqrt{3}y^2); \ (4.26)$$

and, under the rotational operations $C_{2\pi/3}$ and $C_{-2\pi/3}$, the two components transform as

$$C_{2\pi/3}, \ C_{-2\pi/3} : \frac{1}{2}(x^2 - y^2) \rightarrow \frac{1}{4}(-x^2 + 2\sqrt{3}xy + y^2), \ \frac{1}{4}(-\sqrt{3}x^2 - 2xy + \sqrt{3}y^2). \ (4.27)$$

Thus, the argument vectors $v_1$ and $v_2$ are obtained, following the equations (4.4), (4.5) and (4.6), as

$$v_1 = \left\{ \frac{1}{2}(x^2 - y^2), \ \frac{1}{4}(-x^2 - 2\sqrt{3}xy + y^2), \ \frac{1}{4}(-x^2 + 2\sqrt{3}xy + y^2) \right\}, \ (4.28)$$

and

$$v_2 = \left\{ xy, \ \frac{1}{4}(\sqrt{3}x^2 - 2xy - \sqrt{3}y^2), \ \frac{1}{4}(-\sqrt{3}x^2 - 2xy + \sqrt{3}y^2) \right\}. \ (4.29)$$

Invoking Weyl’s second theorem (§1) in a Mathematica subroutine \texttt{ROTATION}
(see appendix), we obtain the set of functions satisfying the constraints of rotational subgroup as the following.

\( \mathcal{O}(2) : \)

\[ I_1 = x^2 + y^2, \]

\( \mathcal{O}(4) : \)

\[ I_2 = (x^2 + y^2)^2, \]

\( \mathcal{O}(6) : \)

\[ I_3 = x^6 - 15x^4y^2 + 15x^2y^4 - y^6, \]

\[ I_4 = -x^6 + 15x^4y^2 - 15x^2y^4 + y^6, \]

\[ I_5 = 3x^5y - 10x^3y^3 + 3xy^5, \]

\[ I_6 = x^6 - 6\sqrt{3}x^5y - 15x^4y^2 + 20\sqrt{3}x^3y^3 + 15x^2y^4 - 6\sqrt{3}xy^5 - y^6, \]

\[ I_7 = x^6 + 6\sqrt{3}x^5y - 15x^4y^2 - 20\sqrt{3}x^3y^3 + 15x^2y^4 + 6\sqrt{3}xy^5 - y^6, \]

\[ I_8 = \sqrt{3}x^6 - 6x^5y - 15\sqrt{3}x^4y^2 + 20x^3y^3 + 15\sqrt{3}x^2y^4 - 6xy^5 - \sqrt{3}y^6, \]

\[ I_9 = \sqrt{3}x^6 + 6x^5y - 15\sqrt{3}x^4y^2 - 20x^3y^3 + 15\sqrt{3}x^2y^4 + 6xy^5 - \sqrt{3}y^6. \]

* Operation of the reflection subgroup \( G_{ref} \): The rank one tensor \( \mathcal{K} \) under
the action of reflection operation $\Sigma_0 \in \mathcal{G}$ is transformed as the following:

$$\{\mathcal{K}_{11}, \mathcal{K}_{22}, \mathcal{K}_{12}\} \rightarrow \{\mathcal{K}_{11}, -\mathcal{K}_{22}, -\mathcal{K}_{12}\}. \quad (4.30)$$

The subroutine \textsc{reflection} (see appendix) determines the following relation amongst the basis functions:

$$\mathcal{I}_1 \rightarrow \mathcal{I}_1; \mathcal{I}_2 \rightarrow \mathcal{I}_2; \mathcal{I}_3 \rightarrow \mathcal{I}_3; \mathcal{I}_4 \rightarrow \mathcal{I}_4;$$
$$\mathcal{I}_5 \rightarrow -\mathcal{I}_5; \mathcal{I}_6 \rightarrow \mathcal{I}_7; \mathcal{I}_7 \rightarrow \mathcal{I}_6; \mathcal{I}_8 \rightarrow \mathcal{I}_9; \mathcal{I}_9 \rightarrow \mathcal{I}_8. \quad (4.31)$$

And thus the desired function becomes

$$\psi = \tilde{\psi}\left(\mathcal{I}_1, \mathcal{I}_2, \mathcal{I}_3, \mathcal{I}_4, \{\mathcal{I}_5, -\mathcal{I}_3\}, \{\mathcal{I}_6, \mathcal{I}_7\}, \{\mathcal{I}_8, \mathcal{I}_9\}\right), \quad (4.32)$$

with the property that

$$\tilde{\psi}\left(\mathcal{I}_1, \mathcal{I}_2, \mathcal{I}_3, \mathcal{I}_4, \{\mathcal{I}_5, -\mathcal{I}_3\}, \{\mathcal{I}_6, \mathcal{I}_7\}, \{\mathcal{I}_8, \mathcal{I}_9\}\right)$$
$$= \tilde{\psi}\left(\mathcal{I}_1, \mathcal{I}_2, \mathcal{I}_3, \mathcal{I}_4, \{-\mathcal{I}_5, \mathcal{I}_3\}, \{\mathcal{I}_7, \mathcal{I}_6\}, \{\mathcal{I}_9, \mathcal{I}_8\}\right). \quad (4.33)$$

The subroutine \textsc{basisii} (see appendix) determines the basis satisfying the
above condition as the following.

\[ J_1 = I_1, \ J_2 = I_2, \ J_3 = I_3, \ J_4 = I_4, \ J_5 = I_5^2, \ J_6 = I_6 + I_7, \ J_7 = I_6I_7, \ J_8 = I_6^2 + I_7^2, \ J_9 = I_8 + I_9, \ J_{10} = I_8 I_9, \ J_{11} = I_8^2 + I_9^2, \ J_{12} = I_6 I_8 + I_7 I_9, \ J_{13} = I_6 I_9 + I_7 I_8, \ J_{14} = I_5(I_6 - I_7), \ J_{15} = I_5(I_8 - I_9). \] (4.34)

The basis reduction algorithm described above is implemented in the mathematical subroutine called BASISREDUCTION (see appendix).

**Irreducible integrity basis**

Upon basis reduction, it is noted that there are only two independent components in the complete and irreducible basis. These basis functions are obtained as (see figure (4-2))

\[ J_1 = x^2 + y^2 = r^2, \] (4.35)
\[ J_4 = x^6 - 15x^4y^2 + 15x^2y^4 - y^6 = r^6 \cos 6\theta. \] (4.36)

A functional basis derived from the above integrity basis can be obtained as

\[ R = \frac{J_4}{J_1^{5/2}} = r \cos 6\theta, \] (4.37)
\[ \Theta = \frac{1}{6} \arccos \frac{J_4}{J_1^3} = \frac{\arccos \cos 6\theta}{6}. \] (4.38)
4.2.2 Symmetry invariants of a symmetric, second-order tensor w.r.t. \( \mathcal{C}_{6v} \) symmetry group

Dilatational and deviatoric components of the strain tensor

The general deformation of a material element can be described as superposition of a pure dilatational deformation and a pure deviatoric deformation. Accordingly the strain tensor \( E \) can be written as

\[
E = E_v + E = (\frac{1}{2} trE)I + \bar{E}.
\]  

(4.39)
Now, \( \psi \) can be expressed as a function of two symmetric second order tensors:

\[
\psi = \tilde{\psi}(\mathbf{E}) = \tilde{\psi}(\mathbf{E}_v, \mathbf{E}).
\]

(4.40)

In a pure dilatational deformation, the material symmetry remains preserved, and therefore, the constitutive response w.r.t. \( \mathbf{E}_v \) should be isotropic, i.e. \( \tilde{\psi} \) is an isotropic function of \( \mathbf{E}_v \). The deviatoric component \( \mathbf{E} \) involves change in material symmetry, and therefore the constitutive response w.r.t. \( \mathbf{E} \) is anisotropic. Therefore, the integrity basis for the above representation is obtained by appending \( I_1 = (E_{11} + E_{22})/2 \) with the complete and irreducible basis of \( \mathbf{E} \). Let the components of \( \mathbf{E} \) w.r.t. the above-defined coordinate system are given by the matrix

\[
\begin{bmatrix}
E_{11} & E_{12} \\
E_{12} & E_{22}
\end{bmatrix}
= \begin{bmatrix}
\frac{1}{2}(E_{11} - E_{22}) & E_{12} \\
E_{12} & -\frac{1}{2}(E_{11} - E_{22})
\end{bmatrix}.
\]

(4.41)

The two-D deviatoric strain tensor has only two independent components, i.e., \( \frac{1}{2}(E_{11} - E_{22}) \), and \( E_{12} \). Thus, the function \( \psi \) is represented as

\[
\psi = \tilde{\psi}(I_1; \frac{1}{2}(E_{11} - E_{22}), E_{12}).
\]

(4.42)

**Complete (not necessarily irreducible) integrity basis**

In this section we present the invariant theoretic method to generate the complete set of polynomial invariants. The method is a slight variation of the method due to Rivlin and co-workers. The method is discussed in the context of \( C_{6v} \) symmetry group.

- **Operation of rotation subgroup** \( G_{\text{rot}} \): For the case of \( C_{6v} \) symmetry group, the set of transformed variables as obtained by the Mathematica subroutine
ROTATION (see appendix) are

\[ C_0, \quad C_{\pi} : \frac{E_{11} - E_{22}}{2}, E_{12}. \]  

(4.43)

\[ C_{\pi/3}, \quad C_{-\pi/3} : \frac{-(E_{11} - E_{22}) + 2\sqrt{3}E_{12}}{4}, \frac{-\sqrt{3}(E_{11} - E_{22}) - E_{12}}{4}. \]  

(4.44)

\[ C_{2\pi/3}, \quad C_{-2\pi/3} : \frac{-(E_{11} - E_{22}) - 2\sqrt{3}E_{12}}{4}, \frac{-\sqrt{3}(E_{11} - E_{22}) + E_{12}}{4}. \]  

(4.45)

Therefore, we are looking for a function of the form

\[ \psi = \hat{\psi} \left\{ \psi_{I_1} : \left\{ \frac{E_{11} - E_{22}}{2}, \frac{-(E_{11} - E_{22}) + 2\sqrt{3}E_{12}}{4}, \frac{-(E_{11} - E_{22}) - 2\sqrt{3}E_{12}}{4} \right\}, \right. \]

\[ \left. \left\{ E_{12}, \frac{-\sqrt{3}(E_{11} - E_{22}) - E_{12}}{4}, \frac{-\sqrt{3}(E_{11} - E_{22}) + E_{12}}{4} \right\} \right\}. \]  

(4.46)

Thus, in the above example

\[ \psi_1 = \left\{ \frac{E_{11} - E_{22}}{2}, \frac{-(E_{11} - E_{22}) + 2\sqrt{3}E_{12}}{4}, \frac{-(E_{11} - E_{22}) - 2\sqrt{3}E_{12}}{4} \right\}, \]  

(4.47)

and

\[ \psi_2 = \left\{ E_{12}, \frac{-\sqrt{3}(E_{11} - E_{22}) - E_{12}}{4}, \frac{-\sqrt{3}(E_{11} - E_{22}) + E_{12}}{4} \right\}. \]  

(4.48)

Using the combinatorics, the Mathematica subroutine BASISI generates the
following basis set.

\[ I_2 = -\frac{3E_{12}^2}{4} - \frac{3}{16} (E_{11} - E_{22})^2, \]
\[ I_3 = -\frac{3E_{12}^2}{4} - \frac{3}{16} (E_{11} - E_{22})^2, \]
\[ I_4 = \frac{3}{4} \sqrt{3} E_{12}^2 + \frac{3}{16} \sqrt{3} (E_{11} - E_{22})^2, \]
\[ I_5 = -\frac{3}{4} \sqrt{3} E_{12}^2 - \frac{3}{16} \sqrt{3} (E_{11} - E_{22})^2, \]

\( O(3) : \)
\[ I_6 = \frac{E_{12}^3}{4} - \frac{3}{16} E_{12} (E_{11} - E_{22})^2, \]
\[ I_7 = -\frac{3}{8} E_{12}^2 (E_{11} - E_{22}) - \frac{1}{32} (E_{11} - E_{22})^3, \]
\[ I_8 = \frac{3}{8} \sqrt{3} E_{12}^3 + \frac{9}{16} E_{12}^2 (E_{11} - E_{22}) - \frac{9}{32} \sqrt{3} E_{12} (E_{11} - E_{22})^2 - \frac{3}{64} (E_{11} - E_{22})^3, \]
\[ I_9 = -\frac{3}{8} E_{12}^3 + \frac{9}{16} \sqrt{3} E_{12}^2 (E_{11} - E_{22}) + \frac{9}{32} E_{12} (E_{11} - E_{22})^2 - \frac{3}{64} \sqrt{3} (E_{11} - E_{22})^3, \]
\[ I_{10} = \frac{3}{8} E_{12}^2 (E_{11} - E_{22}) - \frac{1}{32} (E_{11} - E_{22})^3, \]
\[ I_{11} = \frac{9}{8} E_{12}^2 (E_{11} - E_{22}) - \frac{3}{32} (E_{11} - E_{22})^3, \]
\[ I_{12} = \frac{3}{8} E_{12}^3 + \frac{9}{16} \sqrt{3} E_{12}^2 (E_{11} - E_{22}) - \frac{9}{32} E_{12} (E_{11} - E_{22})^2 - \frac{3}{64} \sqrt{3} (E_{11} - E_{22})^3, \]
\[ I_{13} = \frac{3}{8} \sqrt{3} E_{12}^3 - \frac{9}{16} E_{12}^2 (E_{11} - E_{22}) - \frac{9}{32} \sqrt{3} E_{12} (E_{11} - E_{22})^2 + \frac{3}{64} (E_{11} - E_{22})^3. \]

(4.49)

- **Operation of the reflection subgroup** \( G_{\text{ref}} \): The strain tensor \( E \) under the action of reflection operation \( \Sigma_0 \in G \) is transformed as the following:

\[ \{ E_{11}, E_{22}, E_{12} \} \rightarrow \{ E_{11}, E_{22}, -E_{12} \}. \]  

(4.50)

The Mathematica subroutine \texttt{REFLECTION} determines the following relation
amongst the basis functions.

\[ I_1 \rightarrow I_1; \]
\[ I_2 \rightarrow I_2; \]
\[ I_3 \rightarrow I_3; \]
\[ I_4 \rightarrow I_4; \]
\[ I_5 \rightarrow I_5; \]
\[ I_7 \rightarrow I_7; \]
\[ I_{10} \rightarrow I_{10}; \]
\[ I_{11} \rightarrow I_{11}; \]
\[ I_6 \rightarrow -I_6; \]
\[ I_8 \rightarrow -I_{13}; \]
\[ I_9 \rightarrow I_{12}; \]
\[ I_{12} \rightarrow I_9; \]
\[ I_{13} \rightarrow -I_3. \]

(4.51)

And thus the desired function becomes

\[ \psi = \hat{\psi} \left( I_1, I_2, I_3, I_4, I_5, I_7, I_{10}, I_{11}; \right. \]
\[ \{I_6, -I_6\}, \{I_8, -I_{13}\}, \{I_9, -I_{12}\}, \{I_{12}, -I_9\}, \{I_{13}, -I_3\} \), \]

(4.52)
with the property that

\[ \tilde{\psi} \left\{ I_1, I_2, I_3, I_4, I_5, I_7, I_{10}, I_{11} ; \right\}
\{ I_6, -I_6 \}, \{ I_8, -I_{13} \}, \{ I_9, -I_{12} \}, \{ I_{12}, -I_9 \}, \{ I_{13}, -I_8 \} \bigg \}
= \tilde{\psi} \left\{ I_1, I_2, I_3, I_4, I_5, I_7, I_{10}, I_{11} ; \right\}
\{ -I_6, I_6 \}, \{ -I_{13}, I_8 \}, \{ -I_{12}, I_9 \}, \{ -I_9, I_{12} \}, \{ -I_8, I_{13} \} \bigg \). \quad (4.53)

The subroutine \texttt{BASISII} determines the basis satisfying the above condition as the following.

\[ J_1 = I_1, \ J_2 = I_2, \ J_3 = I_3, \ J_4 = I_4, \ J_5 = I_5, \ J_6 = I_7, \ J_7 = I_{10}, \]
\[ J_8 = I_6^2, \ J_9 = -I_6 (I_8 + I_{13}), \ J_{10} = -I_6 (I_9 + I_{12}), \]
\[ J_{11} = -I_6 (I_9 + I_{12}), \ J_{12} = -I_6 (I_8 + I_{13}), \ J_{13} = I_8 - I_{13}, \]
\[ J_{14} = I_8 I_{13}, \ J_{15} = -I_8 I_{12} - I_9 I_{13}, \ J_{16} = -I_8 I_9 - I_{12} I_{13}, \]
\[ J_{17} = -I_8^2 - I_{13}^2, \ J_{18} = I_9 - I_{12}, \ J_{19} = I_9 I_{12}, \]
\[ J_{20} = -I_9^2 - I_{12}^2, \ J_{21} = -I_8 I_9 - I_{12} I_{13}, \ J_{22} = -I_9 + I_{12}, \]
\[ J_{23} = I_9 I_{12}, \ J_{24} = -I_8 I_{12} - I_9 I_{13}, \ J_{25} = -I_8 + I_{13}, \ J_{26} = I_8 I_{13}. \]

\[ (4.54) \]
Upon basis reduction, the independent basis functions are obtained as (see Fig. (4-3))

\[
\mathcal{J}_1 = \frac{(E_{11} + E_{22})}{2}, \\
\mathcal{J}_2 = (E_{11} - E_{22})^2 + 4E_{12}^2, \\
\mathcal{J}_6 = (E_{11} - E_{22})^3 - 3E_{12}^2 (E_{11} - E_{22}).
\]

(4.55)

**Irreducible integrity basis w.r.t. the logarithmic strain measure**

Of course the choice of a strain measure is totally arbitrary, but in this example we choose the logarithmic strain, $E^{(0)}$. A generic right stretch tensor $\mathbf{U}$ can be
multiplicatively decomposed into volumetric and isochoric components [6, 80, 169]:

\[ U = J^{1/2} \bar{U}. \]  

(4.56)

where \( \bar{U} \) has a spectral representation written as (see Fig. 4-4):

\[ \bar{U} = \lambda e_1 \otimes e_1 + \frac{1}{\lambda} e_2 \otimes e_2. \]  

(4.57)

In the above, \( e_1 \) and \( e_2 \) are the two principal directions of \( U \), and, with respect to a fixed material frame of reference \( \hat{x} - \hat{y} \), are given as

\[ e_1 = \cos \theta \hat{x} + \sin \theta \hat{y}, \]  

(4.58)

\[ e_2 = -\sin \theta \hat{x} + \cos \theta \hat{y}. \]  

(4.59)

Figure 4-4: Schematic description of the purely deviatroic deformation: a stretch of \( \lambda \) at an angle \( \theta \) from the material \( \hat{x} \)-axis.
Correspondingly, the logarithmic strain measure is obtained as

$$E^{(0)} = \ln U = \ln J^{1/2} \mathbf{I} + \ln \mathbf{U},$$  \hspace{1cm} (4.60)

It is immediately noted that the log strain measure maps the multiplicative terms in the decomposition of $U$ into the additive terms.

$$E^{(0)} = \ln U = \underbrace{\ln J^{1/2}}_{E_v} + \underbrace{\ln \mathbf{U}}_{\mathbf{E}}. \hspace{1cm} (4.61)$$

The logarithmic strain completely decouples the hydrostatic (shape preserving) component of strain $E,$ from the deviatoric (volume or area preserving) component $\mathbf{E}.$

The deviatoric deformation is completely characterized by two variables $\lambda$ and $\theta$:

$$E = \ln \lambda (e_1 \otimes e_1 + e_2 \otimes e_2) = \ln \lambda (\cos 2\theta \ x \otimes x + \sin 2\theta (x \otimes y - y \otimes x) - \cos 2\theta \ y \otimes y). \hspace{1cm} (4.62)$$

whereas the area-changing part is completely characterized by the third variable $J^{1/2}$ independent of $\lambda$ and $\theta$:

$$E_v = \ln J^{1/2} \mathbf{I}. \hspace{1cm} (4.63)$$

$$\mathbf{E} = \begin{bmatrix} \vec{E}_{11} & \vec{E}_{12} \\ \vec{E}_{12} & \vec{E}_{22} \end{bmatrix} = \begin{bmatrix} \frac{1}{2}(E_{11}^{(0)} - E_{22}^{(0)}) & E_{12}^{(0)} \\ E_{12}^{(0)} & -\frac{1}{2}(E_{11}^{(0)} - E_{22}^{(0)}) \end{bmatrix} = \begin{bmatrix} \ln \lambda \cos 2\theta & \ln \lambda \sin 2\theta \\ \ln \lambda \sin 2\theta & -\ln \lambda \cos 2\theta \end{bmatrix} \hspace{1cm} (4.64)$$

Thus, for the log measure of strain, we obtain the integrity basis as

$$J_1 = \ln J; \hspace{1cm} (4.65)$$

$$J_2 = \ln \lambda^2; \hspace{1cm} (4.66)$$

$$J_6 = \ln \lambda^3 \cos 6\theta. \hspace{1cm} (4.67)$$
4.3 Conclusion

In summary, we have presented a computational methodology to efficiently calculate the complete and irreducible integrity basis of a vector, and of a second order symmetric tensor. We have demonstrated the method for the example case of \( C_{6v} \) point group symmetry which describes the symmetry of graphene lattice. Later we will show that the complete and irreducible integrity basis obtained by the proposed method is same as ones obtained by Zheng’s structural tensor method [214, 215]. In Chapter 5, we will employ the integrity bases of the logarithmic strain tensor, given in equations (4.65-4.67) to obtain a hyperelastic constitutive response function for graphene.
Chapter 5

Hyperelastic response of the ideal graphene single-crystal

5.1 Introduction

The anisotropy of an ideal crystalline material is characterized by its material symmetry group $\mathcal{G}$—the set of all symmetry operations about a point that leave the crystal unchanged. The material symmetry group is reflected in all physical properties of the crystalline material—microscopic as well as macroscopic. For example, in a two-dimensional (2D) crystal like graphene, the strain energy density function $\psi$, which relates the change in free energy per unit area ($\psi$) to the measure of elastic strain ($E^{(0)}$), possesses the complete point group symmetry of the underlying lattice, i.e.,

$$\hat{\psi}(E^{(0)}) = \psi(Q^T E^{(0)} Q) \forall Q \in \mathcal{G}.$$  

Therefore, in any constitutive model of the crystal, all symmetries belonging to the material symmetry group should be duly incorporated [136]. In Chapter 2, we presented the general framework of hyperelasticity, Boehler’s principle of isotropy of space based on the structure tensor [15, 17], and the symmetry-invariant-based representation scheme as applied to scalar functions of a second-order tensor w.r.t. 2D crystal class of regular polygonal symmetry. In Chap-
ter 4, we presented a numerical method to generate a complete and irreducible set of symmetry-invariants for the symmetry classes under consideration. Form-invariant tensors are obtained as the derivatives of the symmetry-invariants with respect to the tensor agency. In this chapter, we explicitly develop a hyperelastic constitutive response function for graphene by obtaining a representation for the strain energy density function $\psi$ in the basis of the symmetry-invariants of the logarithmic strain measure. We then obtain the expression for work-conjugate stress in terms of the form-invariants and the conversion from the work-conjugate stress measure to Cauchy stress is presented. We obtain expressions for the work-conjugate tangent modulus tensor in Section (5.6.3), and for the acoustic tensor in Section (5.6.4). Section 5.5 describes the density functional theory (DFT) calculations done to provide a training dataset for evaluating material constants in the new constitutive model. The model is validated in Section (5.7) by computing (1) the stress and (2) the elastic stability limits for a set of finite deformations comprising uniaxial stretch/stress along the armchair and the zigzag directions; and equi-biaxial tension. We conclude in Section (5.8) by summarizing our results and reflecting upon some implications.

5.2 Literature review

One approach to embed the material symmetry into constitutive modeling is reduction by symmetry. In this approach to hyperelastic constitutive modeling of anisotropic crystals, $\psi$ is expressed as a power series of desired order in components of the strain tensor, and then symmetry constraints are imposed to reduce the number of independent fitting coefficients [193].

Cadelano et al. [32] employed this method to develop a hyperelastic nonlinear constitutive model of monolayer graphene. The strain energy density function $\psi$ in this
model is expressed as a cubic polynomial in components of the Green-Lagrange strain measure, and hence exhibits a quadratic nonlinearity in the work-conjugate stress-strain relation. Upon reduction by symmetry, the expression for $\psi$ contains three independent third-order elastic constants, and two second-order elastic constants, the values of which were determined by a least-squares fit to the strain energies obtained from tight-binding atomistic simulations for a set of canonical deformations comprising uniaxial stretch along the armchair and the zigzag directions; an in-plane shear; and biaxial tension.

Wei, et al. [197, 105] noted that the model of Cadelano, et al. failed to reproduce the response at both infinitesimal and finite strains simultaneously with sufficient fidelity. They proposed a fifth-order series expansion for $\psi$, again based on components of the Green-Lagrange strain measure, to model the in-plane elastic properties of graphene. Their symmetry-reduced expression contained fourteen independent elastic constants, the values of which were determined by fitting model results to DFT-calculated stresses corresponding to the same set of deformations used by Cadelano, et al.

The reduction by symmetry approach suffers from a number of disadvantages: First, the method requires imposing the symmetry constraints extrinsically on components of the elastic constant tensors. This procedure must be repeated each time a higher-order polynomial nonlinearity is added in the model. Since the number of components in a 2D tensor increases with its order $m$ as $2^m$, the task of reduction by symmetry becomes increasingly tedious as the order of the polynomial expansion increases. Secondly, the symmetry restrictions are most readily identified and applied to strain components evaluated in a particular crystallographic frame. From an implementation point of view, it would be preferable to express $\psi$ in a fashion independent of any particular choice of coordinate axes. This can best be accomplished if $\psi$ is expressed as a function of a list of invariants of the strain measure, instead of its components.
Lastly, and most importantly, the method is a priori restricted to the use of polynomials in the components of strain as the basis of representation — with no scope for including arbitrary non-polynomial functions in the representation.

Here we present a constitutive modeling scheme for crystal hyperelasticity based on symmetry invariants of the logarithmic measure of strain \( E^{(0)} \). The symmetry invariants are scalar-valued functions of the tensor agency (here, strain) that satisfy all the symmetry constraints of the crystal’s material symmetry group \([175, 178, 177]\). Using the symmetry-invariants of \( E^{(0)} \) for \( C_{6v} \) symmetry, we obtain a constitutive model of graphene for deformations involving both large area-change and shape-change. The resulting description of material response automatically satisfies the material symmetry requirements without further constraints. The model can be readily extended to include higher-order nonlinearities of either polynomial or functional natures. The approach enables straightforward evaluation of the stress tensor, the tangent moduli tensor and the acoustic tensor in a coordinate-independent form.

5.3 Kinematics

We consider graphene as a 2D deformable body denoted by unstressed reference configuration \( \mathcal{B} \). The kinematics of this deformable body is described by time-varying vector and tensor fields belonging to the 2D Euclidian space \( \mathbb{R}^2 \). We denote by \( X \) an arbitrary material point of \( \mathcal{B} \). As the body is deformed, the material point \( X \) moves to another point in the 2D space, characterized by its deformed coordinate \( x \) at current time \( t \). The convection of material points under deformation is described by a smooth, injective (one-to-one) function \( \chi(X, t) \) called the motion. The non-translational part of the motion can be equivalently defined by the positive-definite second-order deformation gradient tensor, \( F = \nabla \chi(X, t) \). Notationally suppressing
this functional dependence for convenience, the polar decomposition theorem provides
the following factorizations of \( F[72, 71, 53] \):

\[
F = RU = VR, \quad (5.1)
\]

where the orthogonal tensor \( R \in SO_2 \) characterizes rigid-body rotation, whereas \( U \)
(or \( V = RUR^T \)), termed the right (left) Cauchy-Green tensor, characterizes shape-
and area-change. Physically, deformation in the neighborhood of a material point in
the body can be kinematically considered as stretching followed by a superimposed
rigid-body rotation, or vice-versa. \( U \) is a symmetric tensor having two real positive
eigenvalues, the principal stretches \( \lambda_1 \) and \( \lambda_2 \). Using spectral decomposition, \( U \) can
be expressed as

\[
U = \lambda_1 r_1 \otimes r_1 + \lambda_2 r_2 \otimes r_2, \quad (5.2)
\]

where \( r_1 \) and \( r_2 \) are orthogonal principal unit vectors in the plane. The deformation of
a material point can be kinematically factored as the product of a purely dilatational
(or shape-preserving, but area-changing) deformation \( U^a \), and a purely isochoric (or
shape-changing, but area-preserving) deformation \( \tilde{U} \). Accordingly, the stretch tensor
can be product-decomposed as

\[
U = U^a \tilde{U} = \tilde{U} U^a, \quad (5.3)
\]

where

\[
U^a \equiv J^{1/2} I \quad (5.4)
\]

and

\[
\tilde{U} \equiv \lambda r_1 \otimes r_1 + \lambda^{-1} r_2 \otimes r_2; \quad (5.5)
\]

here \( J = \det U = \lambda_1 \lambda_2 \), \( \lambda = \sqrt[3]{\lambda_1/\lambda_2} \geq 1 \), and \( I \) is the 2D identity tensor.
The spectral representation of $\mathbf{E}(0) \equiv \ln \mathbf{U} = \ln \mathbf{U}^a + \ln \mathbf{U}$ is then given by:

$$
\mathbf{E}(0) = \frac{1}{2} \ln \mathbf{J} \mathbf{I} + \ln \mathbf{U}^a + \ln \mathbf{U}^a \mathbf{E}_0^{(0)} \equiv \frac{1}{2} \epsilon_a \mathbf{I} + \mathbf{E}_0^{(0)},
$$

(5.6)

where

$$
\epsilon_a = \text{tr} \mathbf{E}(0) = \ln J = \ln(\det \mathbf{U}),
$$

(5.7)

gives the areal logarithmic strain $\epsilon_a$, and

$$
\mathbf{E}_0^{(0)} = \ln \mathbf{U} = \ln \lambda (\mathbf{r}_1 \otimes \mathbf{r}_1 - \mathbf{r}_2 \otimes \mathbf{r}_2),
$$

(5.8)

denotes the deviatoric part of $\mathbf{E}(0)$.

### 5.4 Invariant-theoretic approach to constitutive modeling

In a hyperelastic modeling framework, the strain energy density $\psi$ is formally expressed as a scalar-valued function of deformation gradient $\mathbf{F}$. Material frame indifference requires that this function should remain invariant under superimposed rigid body motion; i.e.,

$$
\psi = \hat{\psi}(\mathbf{F}) = \hat{\psi}(\mathbf{QF}),
$$

(5.9)

where arbitrary $\mathbf{Q} \in SO_2$ denotes a rigid-body rotation. Such objectivity is automatically satisfied if $\psi$ is functionally dependent on one of the Seth-Hill strain measures — $\mathbf{E}^{(m)} \equiv ((\mathbf{F}^T \mathbf{F})^{m/2} - \mathbf{I})/m$, for $m \in \mathbb{Z}$ ($\mathbb{Z}$ is the set of real numbers). In particular, for $m = 0$, the corresponding strain measure is the logarithmic strain measure $\mathbf{E}^{(0)} = \ln \mathbf{U}$ [77, 76].
The choice of a particular strain measure is, in principle, totally arbitrary. However, different choices of strain measure can lead to differing levels of complexity or simplification in accurately describing material response. For example, Anand [6] explored the extension of the classical quadratic strain energy function of isotropic linear elasticity based on two small-strain Lamé constants by systematically replacing the invariants of the infinitesimal strain tensor with the corresponding invariants of various of the Seth-Hill strain measures. For moderately large deformations, the formulation based on invariants of $\mathbf{E}^{(0)}$ (Hencky's strain energy function) most accurately captured the initial constitutive non-linearities, with results clearly superior to those obtained by similarly using the invariants of the Green-Lagrange strain measure $\mathbf{E}^{(2)}$.

Here, for reasons further described in Section 5.6.1, we employ the logarithmic strain tensor $\mathbf{E}^{(0)}$ to write a hyperelastic constitutive response of graphene, i.e.,

$$
\psi = \hat{\psi}(\mathbf{F}) = \hat{\psi}(\mathbf{E}^{(0)}).
$$

The restrictions on $\psi$ due to material symmetry are expressed as

$$
\tilde{\psi}(\mathbf{E}^{(0)}) = \tilde{\psi}(\mathbf{Q}^T \mathbf{E}^{(0)} \mathbf{Q}) \forall \mathbf{Q} \in \mathcal{G},
$$

where $\mathcal{G}$ denotes the material symmetry group. A scalar function, such as $\psi$, that remains invariant under a material symmetry group $\mathcal{G}$ is called a $\mathcal{G}$-invariant scalar function. Obtaining a representation for a generic $\mathcal{G}$-invariant function involves using the isotropicization theorem and symmetry invariants.

The isotropicization theorem — based on the notion of a materially-embedded structure tensor $\mathbf{H}$ — allows the constitutive response of an anisotropic hyperelastic material to be expressed in terms of a list of special functions — $\mathcal{J}_1, \mathcal{J}_2, \ldots, \mathcal{J}_n$ — which
are joint isotropic functions of $E^{(0)}$ and $H$ [118, 15, 17]; i.e.,

$$\tilde{\psi}(E^{(0)}) = \hat{\psi}(J_1, J_2, ..., J_n),$$

(5.12)

where

$$J_i(E^{(0)}; H) = J_i(Q^T E^{(0)} Q; P_Q(H)) \forall Q \in SO_2.$$  

(5.13)

Here $P_Q$ denotes the transformation of the structure tensor $H$ under the orthogonal transformation $Q$. These special functions are termed symmetry invariants since they satisfy all the symmetry constraints belonging to the material symmetry group of the crystal. Smith [175, 178, 177] showed that the set of mutually-independent symmetry invariants — which is finite for all cases of material symmetry — serves as a complete and irreducible basis for the representation of scalar constitutive functions of the anisotropic material. In the following section, we explicitly derive the symmetry invariants of $E^{(0)}$ for the structure tensor characterizing the material symmetry group of graphene.

### 5.5 Training set for evaluation of the elastic constants

The constants appearing in the expression for $\psi$ are determined via a fit to a set of ab initio data. This set comprises homogeneous deformations including pure equi-biaxial stretch, i.e., $F = U^a = J^{1/2}I$ with the value of $J^{1/2}$ ranging from 1 to 1.2, along with an imposed isochoric shape change stretch of the form $\bar{U} = \lambda r_1 \otimes r_1 + \lambda^{-1} r_2 \otimes r_2$, with $\lambda$-values in the range $1 \leq \lambda \leq \lambda_{\text{crit}}(\epsilon_a)$, the upper limit being the point at which the underlying lattice becomes unstable. Only the ab initio energies of the stable lattice configurations are considered in the dataset (see Fig. 5-1). The two principal stretch directions in the component form may be expressed as $r_1 = \cos \theta e_1 + \sin \theta e_2$ and...
\[ \mathbf{r}_2 = -\sin \theta \mathbf{e}_1 + \cos \theta \mathbf{e}_2. \] It is noted that, owing to the \( C_{6v} \) symmetry of graphene, isochoric stretches need be sampled only over the parametric range \( 0 \leq \theta \leq \pi/6 \). The least-squares-fit values of the material constants in the expression for \( \psi \) are tabulated in Tables (5.2), (5.3) and (5.5).

Our \textit{ab initio} calculations are based on first-principles density functional theory as implemented in the PWSCF simulation package [66]. In generalized gradient approximation (GGA) calculations, the exchange correlation energy of electrons is approximated by the generalized gradient function of Perdew, Burke, and Ernzerhof (PBE) [152, 153], whereas in local density approximation (LDA) calculations, the exchange-correlation function of Perdew and Wang (PW) is used. The interaction between ionic cores and valence electrons is represented by an ultrasoft pseudopotential [192].

Kohn-Sham wave functions were represented using a plane-wave basis with an energy cutoff of 30 Ry and a charge density with a cutoff of 300 Ry. Integration over the irreducible Brillouin zone (BZ) for charge density and total energy was performed with a uniform \( 30 \times 30 \times 1 \) mesh of \( k \)-points, and occupation numbers were smeared using the Marzari-Vanderbilt cold smearing scheme [124] with broadening of 0.03 Ry.

Errors in the Cauchy stresses and total energy due to basis-set size, smearing parameter, and \( k \)-points are converged to less than 0.034 N/m and 0.01 Ry, respectively.

The phonon dispersion relations are computed via linear response calculations as implemented in density functional perturbation theory [11, 42]. The dynamical matrix is calculated on an \( 8 \times 8 \times 1 \) uniform grid of \( q \)-points in the irreducible BZ using a \( 30 \times 30 \times 1 \) uniform grid of \( k \)-points. The dynamical matrix is fast-Fourier-transformed to calculate the interatomic force constants (IFC), corrected for acoustic sum rule to ensure that \( \omega(q = 0) = 0 \) for all the acoustic branches. The IFC's are then used to interpolate the phonon frequencies over a dense set of \( q \)-points along the high-symmetry directions in the irreducible BZ at different deformed states. All the calculations in this work are performed on a two-atom primitive unit cell of graphene.
shown in Fig. (5-2). The two lattice vectors defining the undeformed unit cell are 
\[ \mathbf{a}_1 = a_0 \left( \frac{\sqrt{3}}{2} \mathbf{e}_1 + \frac{1}{2} \mathbf{e}_2 \right), \quad \text{and} \quad \mathbf{a}_2 = a_0 \left( \frac{\sqrt{3}}{2} \mathbf{e}_1 - \frac{1}{2} \mathbf{e}_2 \right), \]
where \( a_0 \) is the lattice constant. The LDA and GGA values of the undeformed lattice constants are 2.44 Å and 2.465 Å, respectively, both of which are very close to the experimentally-reported value of 2.457 Å [9].

5.6 Hyperelastic constitutive response of graphene

Following the invariant-theoretic approach outlined in Section (5.3), we now systematically construct a hyperelastic constitutive response function for arbitrary in-plane deformation of graphene. First, we explicitly obtain the structure tensor characterizing the material symmetry group of graphene. The structure tensor \( \mathbb{H} \) corresponding to a \( C_{(2n)v} \) material symmetry group is obtained by a general expression given by [215, 217, 214, 213]

\[ \mathbb{H} = \text{Re}(\mathbf{M} + i\mathbf{N}) \otimes^n, \]  
(5.14)

where \( (...) \otimes^n = (...) \otimes (...) \otimes (...) (n \text{ times}) \), and \( 2n \) denotes the order of the principal rotation axis. \( \mathbf{M} \) and \( \mathbf{N} \) are dimensionless symmetric traceless tensors given by

\[ \mathbf{M} = \hat{\mathbf{x}} \otimes \hat{\mathbf{x}} - \hat{\mathbf{y}} \otimes \hat{\mathbf{y}}; \quad \mathbf{N} = \hat{\mathbf{x}} \otimes \hat{\mathbf{y}} + \hat{\mathbf{y}} \otimes \hat{\mathbf{x}}, \]  
(5.15)

where \( \hat{\mathbf{x}} \) and \( \hat{\mathbf{y}} \) denote two orthogonal material unit vectors fixed in the frame of the reference crystal such that at least one of them is aligned with an axis of reflection symmetry.

From Eq. (5.14), we obtain the sixth-order structure tensor characterizing \( C_{6v}(n = 3) \),
Figure 5-1: Plots of the \textit{ab initio} deviatoric energy $\psi^\text{Dev}$ as a function of shape-changing stretch $\lambda$ at various values of biaxial stretch $J^{1/2}$: (a) & (b) — Graphene’s mechanical response remains essentially isotropic at small to moderate strains, with anisotropy appearing only at large deviatoric stretch. (c) & (d) — For larger values of biaxial strain, sudden drops in $\psi^\text{Dev}$, indicative of material instability, are noted at finite $\lambda$-values. Data from the unstable regime (shown as blue-shaded) is not included in the training set used for deriving the constitutive model.
Figure 5-2: (a) Graphene lattice with orientations of the material unit vectors — $\hat{x}$ and $\hat{y}$ — and the Cartesian unit vectors — $e_1$ and $e_2$ — indicated. The dashed lines denote the unit cell used in the $ab$ initio calculations. The GGA (LDA) value of the lattice parameter is also indicated. The armchair and zigzag directions are along the $e_1$ and $e_2$ axes respectively. (b) Brillouin zone of graphene with high symmetry points indicated.

the material symmetry group of graphene, as

$$\mathbb{H} = M \otimes M \otimes M - (M \otimes N \otimes N + N \otimes M \otimes N + N \otimes N \otimes M).$$  \hfill (5.16)

The complete and irreducible set of polynomial joint invariants of $E^{(0)}$ and $\mathbb{H}$ constitute the symmetry invariants of $E^{(0)}$. Following the procedure of Zheng and Betten [215, 217], we obtain three independent scalar joint invariants of this 2D system as

$$J_1 \equiv \epsilon_a = \text{tr}E^{(0)} = \ln J,$$

$$J_2 \equiv (\gamma_i/2)^2 = \frac{1}{2} E^{(0)}_0 : E^{(0)}_0 = (\ln \lambda)^2,$$

where $A : B = \text{tr}(A^T B)$ is the scalar tensor product, and

148
\[ J_3 \equiv (\gamma_\theta/2)^3 = \frac{1}{8} \mathbb{H}[\mathbf{E}_0^{(0)}, \mathbf{E}_0^{(0)}, \mathbf{E}_0^{(0)}] \]
\[ = \frac{1}{8} \left[ (\mathbf{M} : \mathbf{E}_0^{(0)})^3 - 3(\mathbf{M} : \mathbf{E}_0^{(0)})(\mathbf{N} : \mathbf{E}_0^{(0)})^2 \right] \]
\[ = (\ln \lambda)^3 \cos 6\theta, \quad (5.19) \]

where \( \cos \theta = \mathbf{r}_1 \cdot \hat{\mathbf{x}} \) indicates the orientation of maximum principal stretch. The first two of these invariants, \( \epsilon_\alpha \) and \( \gamma_i \geq 0 \), are simply two isotropic invariants of \( \mathbf{E}^{(0)} \) alone. Thus any material anisotropy in the constitutive response of graphene is captured solely by the third invariant \( \gamma_\theta \). Using the numerical method presented in Chapter 4, we obtained the same set of symmetry-invariants and showed that it forms an irreducible basis.

In order to represent second-order tensorial quantities, we need the following list of form-invariants:

\[ \frac{\partial \epsilon_\alpha}{\partial \mathbf{E}^{(0)}} = \mathbf{I}; \quad (5.20) \]
\[ \frac{\partial (\gamma_i^2)}{\partial \mathbf{E}^{(0)}} = 4\mathbf{E}_0^{(0)}; \quad (5.21) \]

\[ \frac{\partial (\gamma_\theta^2)}{\partial \mathbf{E}^{(0)}} = 3 \left\{ (\mathbf{M} : \mathbf{E}_0^{(0)})^2 - (\mathbf{N} : \mathbf{E}_0^{(0)})^2 \right\} \mathbf{M} - \left[ 2(\mathbf{M} : \mathbf{E}_0^{(0)})(\mathbf{N} : \mathbf{E}_0^{(0)}) \right] \mathbf{N} \]
\[ \equiv \mathbf{S}_{\mathbf{E}_0^{(0)}}. \quad (5.22) \]

For purposes of constructing fourth-order tangent modulus tensors, second derivatives of the invariants with respect to \( \mathbf{E}^{(0)} \) are obtained as follows:

\[ \frac{\partial^2 \epsilon_\alpha}{\partial \mathbf{E}_0^{(0)} \partial \mathbf{E}^{(0)}} = \mathbb{Q}, \quad (5.23) \]
\[ \frac{\partial^2 (\gamma_i^2)}{\partial \mathbf{E}_0^{(0)} \partial \mathbf{E}^{(0)}} = 4 \left[ \mathbb{I} - \frac{1}{2} \mathbb{I} \otimes \mathbb{I} \right], \quad (5.24) \]
\[
\frac{\partial^2 (\gamma^2)}{\partial \mathbf{E}^{(0)} \partial \mathbf{E}^{(0)}} = 6 \left( \left[ \mathbf{M} : \mathbf{E}^{(0)}_0 \right] \mathbf{M} \otimes \mathbf{M} - \left( \mathbf{N} : \mathbf{E}^{(0)}_0 \right) [\mathbf{M} \otimes \mathbf{N} + \mathbf{N} \otimes \mathbf{M} + \mathbf{N} \otimes \mathbf{N}] \right) \equiv \mathbf{S}^{(0)}_{\mathbf{E}^{(0)}}.
\]

Here \( \mathbb{0} \) and \( \mathbb{1} \) are the fourth-order zero and identity tensors, respectively.

### 5.6.1 Strain energy per unit reference area \( \psi \)

The proposed hyperelastic model is based on representation of the strain energy per unit reference area \( \psi \) in terms of the symmetry invariants of \( \mathbf{E}^{(0)} \), i.e., \( \psi = \hat{\psi}(\epsilon_a, \gamma_1, \gamma_2) \). For application of invariant-based hyperelasticity, the strain measure \( \mathbf{E}^{(0)} \) offers substantial simplifications in terms of formulation. First, as is evident from its spectral representation (equation (5.6)), \( \mathbf{E}^{(0)} \) additively decomposes areal (\( U^a \)) and isochoric (\( \bar{U} \)) parts of the deformation into isotropic and deviatoric parts of the strain, respectively. Secondly, the state nature of \( \psi \) in a hyperelastic material enables calculating \( \psi \) by integrating

\[
d\psi = \left( \frac{\partial \psi}{\partial \mathbf{E}^{(0)}} \right) : d\mathbf{E}^{(0)}
\]

along any convenient strain path, where it is understood that \( \mathbf{T}^{(0)} \equiv \partial \psi / \partial \mathbf{E}^{(0)} \) is the work-conjugate stress measure. Let a first, purely isotropic strain path (Path 1) correspond to areal deformation \( U^a \) while holding \( \bar{U} = \mathbf{I} \), and let a second, purely deviatoric strain path (Path 2) correspond to a subsequently-imposed isochoric deformation \( \bar{U} \) while holding \( U^a = J^{1/2} \mathbf{I} \). The isotropic/deviatoric decomposition of the work-conjugate stress is

\[
\mathbf{T}^{(0)} \equiv \frac{1}{2} \mathbf{S}^{(0)}_{\mathbf{E}^{(0)}} \mathbf{I} + \mathbf{T}_0^{(0)},
\]

while that of the incremental log strain is

\[
d\mathbf{E}^{(0)} = \frac{1}{2} \mathbf{d} \mathbf{\epsilon}^a \mathbf{I} + d\mathbf{E}^{(0)}_0;
\]

thus, the incremental energy/work relation is additively decomposed into isotropic and deviatoric parts

\[
d\psi = \mathbf{T}^{(0)} : d\mathbf{E}^{(0)} = \frac{1}{2} \mathbf{S}^{(0)}_{\mathbf{E}^{(0)}} d\mathbf{\epsilon}^a + \mathbf{T}_0^{(0)} : d\mathbf{E}^{(0)}_0. \tag{5.26}
\]

The strain energy of an arbitrary deformed state of the lattice — when expressed in terms of invariants of the log strain — can be additively decomposed into a term \( \psi^{\text{Dil}}(\epsilon_a) \) — corresponding to a pure areal deformation \( U^a \) while \( \mathbf{E}^{(0)}_0 = \mathbf{0} \) — plus
a term \( \psi^{\text{Dev}}(\gamma_i, \gamma_\theta; \epsilon_a) \) — corresponding to a superimposed isochoric deformation \( \hat{\mathbf{U}} \) while \( \text{tr} \mathbf{E}^{(0)} \) remains fixed at \( \epsilon_a \). Thus, we write:

\[
\psi = \hat{\psi}(\epsilon_a, \gamma_i, \gamma_\theta) = \hat{\psi}^{\text{Dil}}(\epsilon_a) + \hat{\psi}^{\text{Dev}}(\gamma_i, \gamma_\theta; \epsilon_a).
\]  

(5.27)

Setting \( \psi = 0 \) in the undeformed configuration, the areal contribution \( \hat{\psi}^{\text{Dil}} \) equals the isotropic stress working along Path 1, along which \( d\mathbf{E}_0^{(0)} = 0 \); thus \( \hat{\psi}^{\text{Dil}} = \hat{\psi}^{\text{Dil}}(\epsilon_a) \). The contribution \( \hat{\psi}^{\text{Dev}} \) is numerically equal to the deviatoric stress working along the subsequent strain Path 2, along which \( d\epsilon^o = 0 \); thus \( \hat{\psi}^{\text{Dev}} \) depends on invariants \( \gamma_i \) and \( \gamma_\theta \) of the imposed deviatoric strain \( \mathbf{E}_0^{(0)} \), as well as having implicit dependence on the (constant) areal strain \( \epsilon_a \) along Path 2, with 'initial' condition \( \hat{\psi}^{\text{Dev}}(0, 0; \epsilon_a) = 0 \).

From elasticity theory, we recall that the flexural stiffness \( D \) of a thin structural element scales with its thickness \( h \) as \( D \sim h^3 \), whereas the stretching stiffness \( C \) scales linearly with \( \sim h \). Notably, graphene is just one atomic layer thick, \( h \approx 10^{-10} \text{m} \), so in a superthin structure like graphene, the ratio of bending stiffness to in-plane stiffness is exceedingly small and, accordingly, we assume that the contribution of bending to the strain energy per unit area is negligible compared to that of in-plane strain. Furthermore, and for the same reason, a suspended graphene sheet under a compressive in-plane loading, i.e., a state of Cauchy stress \( \mathbf{\sigma} \) with \( \mathbf{n} \cdot \mathbf{\sigma} \cdot \mathbf{n} < 0 \) for some in-plane direction \( \mathbf{n} \), is structurally unstable in the limiting case of vanishing flexural rigidity, and will immediately buckle out-of-plane. Therefore, the scope of the modeling effort is limited to only those in-plane deformation states for which \( \mathbf{n} \cdot \mathbf{\sigma} \cdot \mathbf{n} \geq 0 \forall \mathbf{n} \).

(a). **Energetic response under pure dilation, \( \psi^{\text{Dil}} \)**: The energetic response under pure dilation, i.e., when \( \mathbf{U} = \mathbf{U}^o = J^{1/2} \mathbf{I} \), is well-described by a function based on the universal binding energy relation (UBER) proposed by Rose et al. [162, 161].

151
The UBER relation is

\[ \psi^\text{Di}(\varepsilon_a) = \mathcal{E} \left[ 1 - (1 + \alpha \varepsilon_a) \exp(-\alpha \varepsilon_a) \right]. \tag{5.28} \]

Table 5.1 lists values of the constants \( \mathcal{E} \) and \( \alpha \) as determined by fitting the \textit{ab initio} energies, calculated using both LDA and GGA formulations, for the graphene lattice subjected to pure dilatory deformations.

|       | \( \alpha \) | \( \mathcal{E} \) (N/m) | \( \varepsilon_a|_{\kappa=0} = 1/(1 + \alpha) \) |
|-------|-------------|-----------------|-----------------|
| GGA   | 1.53        | 93.84           | 0.40            |
| LDA   | 1.38        | 116.43          | 0.42            |

Table 5.1: Values of \( \mathcal{E} \) and \( \alpha \) obtained by fitting the UBER form (equation (5.28)) to \textit{ab initio} energies. The UBER constitutive form exhibits a tangent area modulus \( \kappa \) —defined in equation (5.42)— that decreases with increasing areal strain, ultimately vanishing at a critical areal strain value given by \( \varepsilon_a|_{\kappa=0} = 1/(1 + \alpha) \).

As shown in Fig. [5-3-(a)], the UBER-based model for the fitted values of \( \mathcal{E} \) and \( \alpha \) accurately describes the \textit{ab initio} energies for pure areal change.

**(b). Energetic response under shape-changing deformations, \( \psi^{\text{Dev}} \):** The shear stiffness of graphene, in general, is dilation-sensitive, depending upon \( \varepsilon_a \). Thus, in general, we assume that \( \psi^{\text{Dev}} = \hat{\psi}^{\text{Dev}}(\varepsilon_a, \gamma_i, \gamma_\theta) \).

We find that a simple linear combination of monomials in \( \mathcal{J}_2 = (\gamma_i/2)^2 \), and in \( \mathcal{J}_3 = (\gamma_\theta/2)^3 \), with coefficients that are functions of \( \varepsilon_a \); i.e.,

\[ \psi^{\text{Dev}}(\gamma_i, \gamma_\theta; \varepsilon_a) = \frac{1}{2} \mu(\varepsilon_a) \gamma_i^2 + \frac{1}{8} \eta(\varepsilon_a) \gamma_\theta^3, \]
Figure 5-3: (a) The universal binding energy relation-based model for volumetric response $\tilde{\psi}^{Dil}$ for fitted values of the coefficients $E$ and $\alpha$ as tabulated in Table 5.1. For comparison, we also show the ab initio energies used in fitting the UBER form. (b) DFT data for $\mu(\epsilon_a)$ fitted with the proposed functional form of equation (5.29). (c) DFT data for $\eta(\epsilon_a)$ fitted with the proposed functional form of equation (5.30).
fits the \textit{ab initio} calculations well using simple functional forms for $\mu(\epsilon_a)$ and $\eta(\epsilon_a)$. The shear modulus $\mu$ is well-fit by an exponentially-decreasing function of the areal strain, $\epsilon_a$ (see Fig. [5-3-(b)])

$$
\mu(\epsilon_a) = \mu_0 - \mu_1 e^{\beta \epsilon_a}, \tag{5.29}
$$

whereas $\eta(\epsilon_a)$ is fit by an even quadratic function of $\epsilon_a$ (Fig. [5-3-(c)])

$$
\eta(\epsilon_a) = \eta_0 - \eta_1 \epsilon_a^2. \tag{5.30}
$$

Thus, the overall expression proposed for the free energy $\psi$ is

$$
\hat{\psi} = E - E(1 + \alpha \epsilon_a) \exp(-\alpha \epsilon_a) + \frac{1}{2}(\mu_0 - \mu_1 e^{\beta \epsilon_a}) \gamma^2 + \frac{1}{8}(\eta_0 - \eta_1 \epsilon_a^2) \gamma^8. \tag{5.31}
$$

The constants in the expressions for $\mu$ and $\eta$ are determined by fitting the set of \textit{ab initio} energies calculated for a number of deformed states described in Section (5.5); fitted values are summarized in Tables [5.2] and [5.3].

Using a total of only 7 scalar fitting parameters, half the number used in the formulation of Wei \textit{et al.}, the proposed functional form fits the entire DFT dataset very well.

|            | $\mu_0$ (N/m) | $\mu_1$ (N/m) | $\beta$ | $\epsilon_a|\mu=0 = \frac{1}{\beta} \ln(\mu_0/\mu_1)$ |
|------------|---------------|---------------|---------|--------------------------------------------------|
| GGA        | 172.18        | 27.03         | 5.16    | 0.35                                             |
| LDA        | 164.17        | 17.31         | 6.22    | 0.36                                             |

Table 5.2: Coefficients $\mu_0$ and $\mu_1$ and exponent $\beta$ in equation (5.29) for shear modulus $\mu(\epsilon_a)$, determined by least-square fits to a set of \textit{ab initio} energies. The data and the functional form suggest that $\mu$ vanishes at critical value of areal strain given by $\epsilon_a|\mu=0 = \frac{1}{\beta} \ln(\mu_0/\mu_1)$, tabulated in the right-most column.
<table>
<thead>
<tr>
<th></th>
<th>( \eta_0 ) (N/m)</th>
<th>( \eta_1 ) (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA</td>
<td>94.65</td>
<td>4393.26</td>
</tr>
<tr>
<td>LDA</td>
<td>93.17</td>
<td>4408.76</td>
</tr>
</tbody>
</table>

Table 5.3: Coefficients \( \eta_0 \) and \( \eta_1 \) in equation (5.30) for \( \eta(\epsilon_a) \), determined by least-squares fitting to a set of \textit{ab initio} energies.

### 5.6.2 Work-conjugate stress tensor \( T^{(0)} \)

Using the proposed functional forms for \( \psi \), the stress measure \( T^{(0)} \) work-conjugate to \( E^{(0)} \) is calculated as

\[
T^{(0)}(\epsilon_a, \gamma_i, \gamma_\theta) = \frac{\partial \psi}{\partial E^{(0)}} \\
= \left( \frac{\partial \psi}{\partial \epsilon_a} + \frac{\partial \psi}{\partial \gamma_i} \right) \mathbf{I} + 4 \frac{\partial \psi}{\partial \gamma_i} \mathbf{E}_0^{(0)} + \frac{\partial \psi}{\partial \gamma_\theta} \mathbf{S}_\epsilon^{(0)} \\
= \left[ \frac{E}{\mu} \alpha \beta \epsilon_a \exp(-\alpha \epsilon_a) + \frac{1}{2} \mu' \gamma_i^2 + \frac{1}{8} \nu' \gamma_\theta^3 \right] \mathbf{I} + 2 \mu \epsilon_a \mathbf{E}_0^{(0)} + \frac{1}{8} \nu \epsilon_a \mathbf{S}_\epsilon^{(0)};
\]

(5.32)

where the prime notation \((...)'\) denotes differentiation with respect to \( \epsilon_a \).

Following the hyperelastic work-conjugacy relation (see Love [117], Ogden[145]), the conversion from work-conjugate stress \( T^{(0)} \) to Cauchy stress \( \sigma \) is obtained as follows. Letting a superposed dot denote the material time derivative, the power balance of isothermal hyperelasticity identifies measures of stress that are power-conjugate to differing measures of strain-rate by

\[
\dot{\psi} = T^{(2)} : \dot{\mathbf{E}}^{(2)} = T^{(0)} : \dot{\mathbf{E}}^{(0)};
\]

(5.33)

etc., where, for example, \( \mathbf{E}^{(2)} = \frac{1}{2} (\mathbf{C} - \mathbf{I}) = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I}) \) is the Green-Lagrange strain tensor, and \( T^{(2)} \) is its power-conjugate stress tensor, often denoted as the second Piola-Kirchhoff stress tensor. Using the chain rule, and viewing \( E^{(0)} \) as a function of
\( E^{(2)} \), we obtain
\[
E^{(0)} = \left[ \frac{\partial E^{(0)}}{\partial E^{(2)}} \right] E^{(2)} = 2 \left[ \frac{\partial E^{(0)}}{\partial C} \right] L(0, 2) E^{(2)}.
\] (5.34)

where the fourth-order tensor \( L(0, 2) = 2 \frac{\partial E^{(0)}}{\partial C} \) has major symmetry, i.e., \( L(0, 2)^T = L(0, 2) \), and it is understood that \( L(0, 2) \) operates on the second-order tensor appearing on its immediate right to produce a resultant second-order tensor. Substituting equation (5.34) into equation (5.33) gives
\[
T^{(2)} : \dot{E}^{(2)} = T^{(0)} : \left( L(0, 2) \dot{E}^{(2)} \right) = \left( L(0, 2)^T T^{(0)} \right) : \dot{E}^{(2)} = \left( L(0, 2) T^{(0)} \right) : \dot{E}^{(2)}.
\] (5.35)

In order for equation (5.35) to hold for arbitrary \( E^{(2)} \), we obtain the transformation relation
\[
T^{(2)} = L(0, 2) T^{(0)}.
\] (5.36)

The Cauchy stress \( \sigma \) can be similarly-obtained from power balance relations (see Ogden [145]) as
\[
\sigma = \frac{1}{J} F T^{(2)} F^T = \frac{1}{J} F \left\{ 2 L^{(1)} T^{(0)} \right\} F^T.
\] (5.37)

Evaluation of \( L(0, 2) \) in a general state of deformation is carried out in Section (5.6.4).

As a particular illustration, we can use equation (5.32) to evaluate \( T^{(0)} \) for equi-biaxial stretch. In the absence of shape change, \( E_0^{(0)} = 0 \) and hence \( \gamma_i = \gamma_\theta = 0 \), so that
\[
T^{(0)}(\epsilon_a) = \frac{\partial \psi_{\text{Dil}}}{\partial \epsilon_a} = \mathcal{E} a^2 \epsilon_a e^{-a \epsilon_a} I.
\] (5.38)

Further, in this special deformation case, \( L(0, 2) \) can be shown to have the simple form:
\[
L(0, 2) = 2 \frac{\partial E^{(0)}}{\partial C} = \frac{1}{J} I,
\] (5.39)
so that $\sigma$ under equi-biaxial stretch becomes

$$\sigma|_{F=J^{1/2}I} = 2 \frac{1}{2J} \mathbf{I} \left( \mathbf{T}^{(0)}|_{F=J^{1/2}I} \right) \mathbf{I} = \frac{1}{J} \mathbf{T}^{(0)}|_{F=J^{1/2}I}; \quad (5.40)$$

thus, the equi-biaxial Cauchy stress is

$$\sigma|_{F=J^{1/2}I} = \frac{1}{J} \frac{\partial \tilde{\psi}_{\text{Dil}}}{\partial \epsilon_a}, \quad \mathbf{I} = \epsilon_a^2 e^{-(1+\alpha)\epsilon_a} \mathbf{I} \equiv p \mathbf{I}, \quad (5.41)$$

where $p \equiv \frac{1}{2} \text{tr} \sigma$, and a corresponding tangent areal modulus $\kappa$ is

$$\kappa(\epsilon_a) \equiv \frac{dp(\epsilon_a)}{d\epsilon_a} = \epsilon_a^2 \left( 1 - (1 + \alpha) \epsilon_a \right) e^{-(1+\alpha)\epsilon_a}. \quad (5.42)$$

Under equi-biaxial stretch, the equi-biaxial Cauchy stress reaches its maximum when

$$\kappa = 0 \Rightarrow 1 - (1 + \alpha) \epsilon_a = 0. \quad (5.43)$$

Thus, the peak equi-biaxial Cauchy stress occurs at a critical areal strain given by (see also Table (5.5)):

$$\epsilon_a|_{\kappa=0} = \frac{1}{1 + \alpha}. \quad (5.44)$$

### 5.6.3 Work-conjugate tangent moduli tensor $L^{(0)}$

The fourth-order tensor of tangent moduli connecting $\dot{\mathbf{T}}^{(0)}$ to $\dot{\mathbf{E}}^{(0)}$ is defined as

$$L^{(0)} = \frac{\partial \mathbf{T}^{(0)}}{\partial \mathbf{E}^{(0)}} = \frac{\partial^2 \psi}{\partial \mathbf{E}^{(0)} \partial \mathbf{E}^{(0)}}. \quad (5.45)$$
On using Eq. (5.32), \( L(0) \) can be straightforwardly expressed as

\[
L(0) = \left[ \varepsilon \alpha^2 (1 - \alpha \epsilon_a) \exp(-\alpha \epsilon_a) + \frac{1}{2} \mu''(\epsilon_a) \gamma^2 + \frac{1}{8} \eta''(\epsilon_a) \gamma^3 \right] I \otimes I + 2 \mu'(\epsilon_a) \left[ I \otimes E(0) + E(0) \otimes I \right] \\
+ \frac{1}{8} \eta'(\epsilon_a) \left[ I \otimes S_{p_0}(0) + S_{e_0}(0) \otimes I \right] + 2 \mu(\epsilon_a) \left[ I - \frac{1}{2} I \otimes I \right] + \frac{1}{8} \eta(\epsilon_a) S_{E(0)}. \tag{5.46}
\]

### 5.6.4 Acoustic tensor

The acoustic tensor is defined as the second derivative of the strain energy density function with respect to the deformation gradient tensor \( F \) [20, 193, 145]:

\[
A = \frac{\partial^2 \psi}{\partial F^2}. \tag{5.47}
\]

The first derivative of the free energy \( \psi \) with respect to \( F \) gives the generally non-symmetric first Piola-Kirchhoff stress tensor, \( T^{PK1} \), which can be evaluated using the chain rule as:

\[
\left[ \frac{\partial \psi(E(0))}{\partial F} \right]_{ij} = \left[ T^{PK1} \right]_{ij} = \left[ \frac{\partial \psi(E(0))}{\partial E(0)} \right]_{mn} \frac{\partial E(0)}{\partial C_{pq}} \frac{\partial C_{pq}}{\partial F_{ij}}. \tag{5.48}
\]

Then the second derivative, which is the acoustic tensor, is obtained as:

\[
A_{ijkl} = \frac{\partial^2 \psi(E(0))}{\partial F^2} = \left[ L(0) \right]_{mnrs} \left[ \frac{\partial E(0)}{\partial C} \right]_{mnpq} \left[ \frac{\partial C}{\partial F} \right]_{pqij} \left[ \frac{\partial E(0)}{\partial C} \right]_{rsab} \left[ \frac{\partial C}{\partial F} \right]_{abkl} \\
+ \left[ T^0 \right]_{mn} \left[ \frac{\partial^2 E(0)}{\partial C \partial C} \right]_{mnpqrs} \left[ \frac{\partial C}{\partial F} \right]_{rskl} \left[ \frac{\partial C}{\partial F} \right]_{pqij} \\
+ \left[ T^0 \right]_{mn} \left[ \frac{\partial E(0)}{\partial C} \right]_{mnpq} \left[ \frac{\partial^2 C}{\partial F \partial F} \right]_{pqijkl}. \tag{5.49}
\]

In the present applications, the acoustic tensor \( A \) is a fourth-order tensor in 2D. By definition, it has the major symmetry \( A_{ijkl} = A_{klij} \). The representation of the fourth-order tensor with respect to the orthonormal basis \( \{ e_i \otimes e_j \otimes e_k \otimes e_l \}_{1 \leq i, j, k, l \leq 2} \) is
given by
\[ A = A_{ijkl} \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k \otimes \mathbf{e}_l, \]  
(5.50)

where \( A_{ijkl} = (\mathbf{e}_i \otimes \mathbf{e}_j) : A : (\mathbf{e}_k \otimes \mathbf{e}_l) \), with \( 1 \leq i, j, k, l \leq 2 \). We can define another orthonormal basis set \([129]\) \( \{\hat{\mathbf{e}}_\alpha \otimes \hat{\mathbf{e}}_\beta\}_{1 \leq \alpha, \beta \leq 4} \) where \( \hat{\mathbf{e}}_{f(i,j)} = \mathbf{e}_i \otimes \mathbf{e}_j \), with \( f(1,1) = 1 \), \( f(2,2) = 2 \), \( f(1,2) = 3 \), and \( f(2,1) = 4 \). In this alternate basis, \( A \) can be represented by a 4-dimensional second-order tensor \( \tilde{A} \) given by
\[ \tilde{A} = \tilde{A}_{\alpha\beta} \hat{\mathbf{e}}_\alpha \otimes \hat{\mathbf{e}}_\beta. \]  
(5.51)

We can thus express the acoustic tensor \( A \) in terms of a \( 4 \times 4 \) matrix of the following form
\[
A = \begin{bmatrix}
A_{1111} & A_{1122} & A_{1112} & A_{1121} \\
A_{1122} & A_{2222} & A_{2122} & A_{2221} \\
A_{1112} & A_{2122} & A_{1222} & A_{1221} \\
A_{1121} & A_{2221} & A_{1221} & A_{2121}
\end{bmatrix}.
\]  
(5.52)

The tensor derivatives appearing in the expressions for \( T^{(0)} \), \( L^{(0)} \), and \( \Lambda \) are calculated following the methods prescribed by Ogden [145], Norris [141] and Carlson and Hoger [33].

1. \[ \left[ \frac{\partial C}{\partial \mathbf{F}} \right]_{ijkl} = \frac{\partial^2 C_{ij}}{\partial \mathbf{F}_{kl}} = \delta_{ik}[\mathbf{F}]_{kj} + [\mathbf{F}]_{kl} \delta_{jl}. \]  
(5.53)

2. \[ \left[ \frac{\partial^2 C}{\partial \mathbf{F} \partial \mathbf{F}} \right]_{ijklmn} = \frac{\partial^2 C_{ij}}{\partial \mathbf{F}_{kl} \partial \mathbf{F}_{mn}} = \delta_{ik} \delta_{km} \delta_{jn} + \delta_{km} \delta_{in} \delta_{jl}. \]  
(5.54)

3. Following Ogden [145] and Norris [141], based on the principal axes technique.
introduced by Hill [81], we obtain

$$L(0, 2) = 2 \frac{\partial \mathbf{E}^{(0)}}{\partial \mathbf{C}} = \begin{cases} \frac{1}{\lambda_1^2} \mathbf{U}_1 \boxtimes \mathbf{U}_1 + \frac{1}{\lambda_2^2} \mathbf{U}_2 \boxtimes \mathbf{U}_2 \\
+ \ln(\frac{\lambda_1^2}{\lambda_2^2}) \left[ \mathbf{U}_1 \boxtimes \mathbf{U}_2 + \mathbf{U}_2 \boxtimes \mathbf{U}_1 \right] \quad \text{if } \lambda_2 \neq \lambda_1; \\
\frac{1}{\lambda_1^2} \sum_{i=1}^{2} \sum_{j=1}^{2} \mathbf{U}_i \boxtimes \mathbf{U}_j \quad \text{if } \lambda_2 = \lambda_1; \\
\end{cases}$$

(5.55)

where $\mathbf{U}_1 = \mathbf{r}_1 \otimes \mathbf{r}_1$ and $\mathbf{U}_2 = \mathbf{r}_2 \otimes \mathbf{r}_2$ are second-order eigentensors of $\mathbf{U}$.

Here '⊗' denotes the Kronecker product $\text{Lin} \times \text{Lin} \rightarrow \text{Lin}$ that maps $n$ second-order tensors $\mathbf{A}, \mathbf{B}, ... \mathbf{C}$ to a $2n$-order tensor $\mathbf{A} \otimes \mathbf{B} \otimes ... \mathbf{C}$. Particularly useful for this
work are the following properties of the Kronecker product [97, 98]:

\[(A \otimes B)X = AXB^T, \forall X \in \text{Lin},\]  

(5.57)

and

\[((A \otimes B \otimes C)X)Y = (AXB^T \otimes C)Y = AXB^TYC^T, \forall X, Y \in \text{Lin}.\]  

(5.58)

5.7 Validation of the constitutive model

As detailed in the following sections, we validate our continuum model for a number of homogeneous deformations by comparison with small-strain elastic constants inferred from experiments, comparison of stress-strain curves with independent \textit{ab initio} calculations, and comparisons of predictions of elastic stability limits to independent phonon calculations.

5.7.1 Comparison of small-strain elastic constants with experiments

We compare the in-plane elastic constants — recovered from the constitutive model in the limit of infinitesimal strain — with the measured values of Lee, \textit{et al.} [105]. The predicted values for the in-plane Young’s modulus \(Y^{(0)}\), shear modulus \(\mu^{(0)}\), bulk modulus \(\kappa^{(0)}\), and the Poisson’s ratio \(\nu^{(0)}\) are all in good accord with the experimentally-reported values (see Table [5.4]).
Table 5.4: The in-plane elastic constants — recovered from our constitutive model in the limit of infinitesimal strain — compared with values reported by Lee, et al. [105], based on their experimental results.

<table>
<thead>
<tr>
<th></th>
<th>( Y^{(0)} ) (N/m)</th>
<th>( \nu^{(0)} )</th>
<th>( \kappa^{(0)} ) (N/m)</th>
<th>( \mu^{(0)} ) (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>342 ± 30</td>
<td>0.165</td>
<td>205 ± 18</td>
<td>147 ± 12</td>
</tr>
<tr>
<td>DFT (GGA)</td>
<td>349</td>
<td>0.203</td>
<td>219</td>
<td>145</td>
</tr>
<tr>
<td>DFT (LDA)</td>
<td>354</td>
<td>0.203</td>
<td>222</td>
<td>147</td>
</tr>
</tbody>
</table>

5.7.2 Prediction of elastic stability limits

Material elastic stability requires that the speed of propagation of the acceleration waves in a solid in every direction should be non-negative [82]. This condition is satisfied when the acoustic tensor is positive-definite, which is equivalent to the condition that the continuum elasto-dynamic equations are hyperbolic.

The acoustic tensor-based prediction of elastic instability involves detecting a deformed state at which \( A \) loses positive-definiteness [21, 20] (or, equivalently, when the slope of an acoustic phonon branch in the long wavelength limit vanishes, i.e., \( d\omega/dk |_{k \to 0} = 0 \)). In addition to elastic instabilities, at very large strains there may also be unstable optical phonon modes in the lattice, causing abrupt rearrangement of the atoms within the basis set of the unit cell. Such long-wavelength optical instabilities — which can not be detected by the acoustic tensor analysis — are accompanied by abrupt changes in energy/stress of the deformed state; e.g., as shown in the excluded regions of Fig. [5-1]. Employing the continuum expression for \( A \) (equation (5.49)), we can monitor its positive-definiteness at all points along a deformation path, and thus can precisely locate the initial loss of elastic stability in that mode of
deformation. In the following subsections, we predict elastic stability limits for some important homogeneous deformation modes, and compare these with predictions obtained from independent \textit{ab initio} linear response phonon calculations.

**Pure biaxial stretch**

For this deformation state, Cartesian components of $A$ obtained from the present constitutive model are

$$ A_{ijkl} = \varepsilon \alpha^2 (1-\epsilon_a \alpha) e^{-\epsilon_a (1+\alpha)} \delta_{ij} \delta_{kl} + \mu(\epsilon_a) e^{-\epsilon_a} (\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) - \varepsilon \alpha^2 \epsilon_a e^{-\epsilon_a (1+\alpha)} \delta_{jk} \delta_{kl}. $$

(5.59)

The condition of strong ellipticity requires

$$ (m \otimes n) : A : (m \otimes n) = A_{ijkl} m_i m_k n_j n_l > 0, $$

(5.60)

for all arbitrary unit vectors $m$ and $n$. If, for any two unit vectors, equation (5.60) does not hold, then the deformed crystal is said to have lost strong ellipticity. Substituting for $A$ from equation (5.59), the strong ellipticity condition becomes

$$ (m \otimes n) : A : (m \otimes n) = e^{-\epsilon_a (1+\alpha)} \varepsilon \alpha^2 \left(1-\epsilon_a (1+\alpha)\right) m_i m_j n_i n_j + e^{-\epsilon_a} \mu(\epsilon_a) m_i m_i n_j n_j > 0. $$

(5.61)

Let the unit vectors $m$ and $n$ be represented by

$$ m = (\cos \phi, \sin \phi); \quad n = (\cos \varphi, \sin \varphi); $$

(5.62)

using this parametrization in equation (5.61) provides

$$ (m \otimes n) : A : (m \otimes n) = e^{-\epsilon_a (1+\alpha)} \varepsilon \alpha^2 \left(1-\epsilon_a (1+\alpha)\right) \cos^2(\phi-\varphi) + e^{-\epsilon_a} \mu(\epsilon_a) > 0. $$

(5.63)
When \( \epsilon_a < 1/(1 + \alpha) = \epsilon_a|_{\kappa=0} \), the minimum value of the term containing the expression \( \cos^2(\phi - \varphi) \) is zero, occurring when \( \mathbf{m} \cdot \mathbf{n} = 0 \); therefore

\[
[(\mathbf{m} \otimes \mathbf{n}) : \mathbf{A} : (\mathbf{m} \otimes \mathbf{n})]_{\text{min}} = e^{-\epsilon_a} \mu(\epsilon_a). \tag{5.64}
\]

Thus, the loss of strong ellipticity under equi-biaxial stretch first occurs when (also see Table (5.2))

\[
\mu(\epsilon_a) = \mu_0 - \mu_1 e^{\beta \epsilon_a} = 0. \tag{5.65}
\]

This condition occurs at a critical value of \( \epsilon_a \) given by

\[
\epsilon_a|_{\mu=0} = \frac{1}{\beta} \ln \left( \frac{\mu_0}{\mu_1} \right). \tag{5.66}
\]

Based on values of the fitted constants, \( \epsilon_a|_{\mu=0} < \epsilon_a|_{\kappa=0} \), as assumed. Since the associated directions \( \mathbf{m} \) and \( \mathbf{n} \) are perpendicular to each other, the dynamic instability is of transverse acoustic nature. To independently confirm this prediction, we carry out linear-response-based phonon calculations for equi-biaxially strained graphene. The phonon dispersion shows that the strong ellipticity condition ceases to hold at \( \epsilon_a = \ln J = 0.354 \), at which point a long-wavelength transverse acoustic instability appears, due to the vanishing of \( \mu \) (Fig. (5-4)). Based on our constitutive modeling and on independent phonon calculations, we see the loss of elastic stability under equi-biaxial loading occurring prior to the zero tangent modulus condition.

**Uniaxial strain in armchair and zigzag directions**

Uniaxial stretching along both armchair and zigzag directions preserves the reflection symmetries w.r.t the \( \hat{x} \) and \( \hat{y} \)-axes. Therefore, for such deformations, the \( A_{1112}, A_{1121}, A_{1211}, A_{1211}, A_{2111}, A_{2212}, A_{2221}, A_{1222}, \) and \( A_{2122} \) components of the acoustic tensor are all
Figure 5-4: (a) The instability due to loss of positive-definiteness of $A$ in equi-biaxial stretch ($F = J^{1/2} \mathbf{1}$) corresponds to the vanishing of $\mu(\epsilon_a)$ that occurs at the critical equi-biaxial areal strain of $\epsilon_a = 0.35$ (GGA) and 0.36 (LDA). (b) LDA Phonon dispersion along the $\Gamma - K$ direction shows a long-wavelength transverse acoustic phonon at $\Gamma$ going unstable near $\epsilon_a = 0.34$; softening of this branch is associated with the vanishing shear modulus $\mu(\epsilon_a)$. (c) Phonon dispersions along the $M - K$ direction show a soft-phonon mode appearing just before $\epsilon_a = 0.297$, well before the acoustic instability.
zero. The resultant acoustic tensor can be represented by a block-diagonal $4 \times 4$ matrix of the form:

$$
A = \begin{bmatrix}
A_{1111} & A_{1122} & 0 & 0 \\
A_{1122} & A_{2222} & 0 & 0 \\
0 & 0 & A_{1212} & A_{1221} \\
0 & 0 & A_{1221} & A_{2121}
\end{bmatrix}.
$$

(5.67)

The eigenvalues of this matrix are given by

$$
\lambda_1 = \frac{1}{2} \left[ A_{1111} + A_{2222} + \left( (A_{1111} - A_{2222})^2 + 4A_{1122}^2 \right)^{1/2} \right],
$$

(5.68)

$$
\lambda_2 = \frac{1}{2} \left[ A_{1111} + A_{2222} - \left( (A_{1111} - A_{2222})^2 + 4A_{1122}^2 \right)^{1/2} \right],
$$

(5.69)

$$
\lambda_3 = \frac{1}{2} \left[ A_{1212} + A_{2121} - \left( (A_{1212} - A_{2121})^2 + 4A_{1221}^2 \right)^{1/2} \right],
$$

(5.70)

and

$$
\lambda_4 = \frac{1}{2} \left[ A_{1212} + A_{2121} + \left( (A_{1212} - A_{2121})^2 + 4A_{1221}^2 \right)^{1/2} \right].
$$

(5.71)

At the first loss of strong ellipticity, one or more eigenvalues of the acoustic tensor matrix become zero at a certain critical value of $\lambda$. In order to determine the critical stretch at which $A$ loses positive-definiteness, we track the variation of the eigenvalues $\lambda_1$, $\lambda_2$, $\lambda_3$ and $\lambda_4$ with increasing uniaxial stretch.

First we consider uniaxial stretching along the zigzag direction, oriented along the Cartesian $e_1$-axis, with $U = \lambda_s e_1 \otimes e_1 + 1 e_2 \otimes e_2$. For this case, the loss of strong ellipticity occurs at a critical stretch, $\lambda_s \approx 1.18$ for GGA, and $\approx 1.19$ for LDA, when the $\lambda_2$-eigenvalue of the acoustic tensor vanishes, as shown in Fig. (5-5-a). The associated eigenvector corresponds to $m = n = e_1$, (see equation (5.60)), so the unstable longitudinal mode coincides with the maximum principal eigenvector of $U$. From independent phonon dispersion calculations shown in Fig. (5-5-b), we confirm the occurrence of a longitudinal acoustic instability in this direction, at $\lambda_s \approx 1.188$. 

166
Figure 5-5: (a) Eigenvalues of the acoustic tensor $\Lambda$ as a function of stretch $\lambda_s$ in the zigzag direction. The eigenvalue $\Lambda_2$ vanishes at a critical stretch, $\lambda_s \approx 1.18$ for GGA, and $\approx 1.19$ for LDA, indicating an acoustic instability in the material. The associated eigenvector of the unstable mode occurs in the $e_1$-direction with polarization along $e_1$-direction, implying longitudinal instability mode. The solid/dashed lines are from constitutive fits to GGA/LDA results. (b) LDA phonon dispersion curves along the $\Gamma - M$ direction at increasing values of uniaxial strain. A long-wavelength longitudinal instability emerges at a uniaxial logarithmic strain of 17.23%, corresponding to $\lambda_s = 1.188$.

Now consider uniaxial uniaxial stretching along the armchair direction, which is taken to be oriented along the Cartesian $e_2$-axis, with $\mathbf{U} = \lambda_s \mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda_n \mathbf{e}_2 \otimes \mathbf{e}_2$. In this case, $\Lambda$ loses positive-definiteness at $\lambda_n \approx 1.23$ (GGA) and $\approx 1.24$ (LDA), when the $\Lambda_2$-eigenvalue of the acoustic tensor goes to zero, as shown in Fig. (5-6-a). The associated eigenvector in this case corresponds to $\mathbf{m} = \mathbf{n} = \mathbf{e}_2$, so in this case as well, a longitudinal elastic instability occurs in the direction of maximum principal stretch. This result is again confirmed by independent LDA phonon calculations shown in Fig. (5-6-b), which indicate a LA branch in the $\Gamma - K$ direction with a vanishing slope at $\Gamma$ emerging when $\lambda_n = 1.252$. 

167
Figure 5-6: (a) Eigenvalues of the acoustic tensor $A$ as a function of stretch $\lambda_a$ along the armchair direction parallel to $e_2$. The eigenvalue $\Lambda_2$ vanishes at a critical stretch $\lambda_a \approx 1.23$ (GGA) and $\approx 1.24$ for (LDA), indicating an acoustic instability in the material. The associated eigenvector shows that this instability occurs in the $e_2$-direction, and the polarization of the unstable mode is also along the $e_2$-direction, implying that the instability is of longitudinal nature. The solid/dashed lines are calculated from constitutive fits to GGA/LDA results. (b) LDA Phonon dispersions along $\Gamma-K$ direction at increasing uniaxial strain. A long wavelength longitudinal instability emerges at a uniaxial logarithmic strain of 22.5%, corresponding to $\lambda_a = 1.252$.

Uniaxial stress in armchair and zigzag directions

In cases of uniaxial stress along the armchair and zigzag directions, the resultant acoustic tensor has the same form as shown in equation (5.67), and the corresponding
The eigenvalues of this matrix are given by

\[\lambda_1 = \frac{1}{2} \left[ A_{1111} + A_{2222} + \left( (A_{1111} - A_{2222})^2 + 4A_{1112}^2 \right)^{1/2} \right],\]  
(5.73)

\[\lambda_2 = \frac{1}{2} \left[ A_{1111} + A_{2222} - \left( (A_{1111} - A_{2222})^2 + 4A_{1112}^2 \right)^{1/2} \right],\]  
(5.74)

\[\lambda_3 = \frac{1}{2} \left[ A_{1212} + A_{2121} - \left( (A_{1212} - A_{2121})^2 + 4A_{1221}^2 \right)^{1/2} \right],\]  
(5.75)

and

\[\lambda_3 = \frac{1}{2} \left[ A_{1212} + A_{2121} + \left( (A_{1212} - A_{2121})^2 + 4A_{1221}^2 \right)^{1/2} \right].\]  
(5.76)

Uniaxial tensile stress along the zigzag direction corresponds to the right stretch tensor given by \(U = \lambda_s e_1 \otimes e_1 + f(\lambda_s) e_2 \otimes e_2\), where the transverse stretch \(f(\lambda_s) \leq 1\), and its value, for a given \(\lambda_s\), is determined by setting \(\sigma_{22} = e_2 \cdot \sigma \cdot e_2 = 0\). For uniaxial stress along the zigzag direction, the loss of strong ellipticity occurs at \(\lambda_s = 1.19\), when the \(\Lambda_2\)-eigenvalue of \(A\) becomes zero (see Fig. (5.7)). The associated eigenvector again corresponds to \(\mathbf{m} = \mathbf{n} = e_1\), so that the unstable longitudinal mode parallels the principal stretching eigenvector. Independent phonon calculations confirm the occurrence of an acoustic instability in the longitudinal branch of the phonon dispersion at \(\lambda_s \approx 1.20\), as was also indicated by phonon calculations of Liu, et al. [115].

For uniaxial tensile stress along the armchair direction, \(U = g(\lambda_a) e_1 \otimes e_1 + \lambda_a e_2 \otimes e_2\), where the transverse stretch \(g(\lambda_a) \leq 1\), its value, for a given \(\lambda_a\), being determined by setting \(\sigma_{11} = 0\). In this case, the acoustic tensor analysis shows that the lattice
Figure 5-7: (a) Eigenvalues of the acoustic tensor $\mathbf{A}$ as a function of stretch $\lambda$, along the zigzag direction. The eigenvalue $\Lambda_2$ vanishes at a critical value of $\lambda_s \approx 1.186$ for GGA and $\lambda_s \approx 1.192$ for LDA, indicating an acoustic instability. The associated eigenvector indicates that this instability occurs in the $e_2$-direction, and the polarization of the unstable mode is also along the $e_2$-direction, implying that the instability is of longitudinal nature. The solid/dashed lines are from constitutive fits to GGA/LDA results. (b) LDA Phonon dispersions along the $\Gamma - M$ direction at increasing uniaxial stress in the zigzag direction. A long-wavelength instability with longitudinal polarization emerges at $\lambda_s = 1.20$.

instability takes place at $\lambda_a = 1.24$, as shown in Fig. (5-8-a). This instability is also longitudinal, occurring in the $e_2$-direction, and is also in good agreement with the phonon calculations of Fig. (5-8-b).

The predicted elastic stability limits for various deformation modes considered in this work are summarized in Table [5.5]. Particularly, we note that the stretch limits for elastic stability under both uniaxial stress and stretch, in both the zigzag and armchair directions, are very close; this must be attributed to the fact that graphene has a small Poisson ratio, and the ratio of the magnitude of transverse to axial log strains under uniaxial stress further decreases as the lattice is deformed (see Fig. (5-
Figure 5-8: (a) Eigenvalues of the acoustic tensor $A$ as a function of the uniaxial stretch $\lambda_a$ along the armchair direction. The eigenvalue $\Lambda_2$ vanishes at a critical value of $\lambda_a \approx 1.238$ for GGA and $\approx 1.25$ for LDA. This indicates an acoustic instability in the material. From the associated eigenvector, we infer that this instability occurs in the $e_2$-direction, and the polarization of the unstable mode is also along the $e_2$-direction, implying that the instability is of longitudinal nature. The solid/dashed lines are from constitutive fits to GGA/LDA results. (b) LDA Phonon dispersions along the $\Gamma - K$ direction at increasing uniaxial stress along the armchair direction. A long wavelength instability with longitudinal polarization emerges at $\lambda_a = 1.25$. 
Deformation mode | Acoustic tensor analysis | Phonon analysis (LDA)
--- | --- | ---
Equi-biaxial stretch | Elastic shear instability at $J^{1/2} = 1.19$ | Short-wavelength transverse instability at $J^{1/2} = 1.145$, and Transverse acoustic instability at $J^{1/2} = 1.18$
Uniaxial stretch (zigzag) | Elastic longitudinal instability at $\lambda_a = 1.188$ (GGA) ($\lambda_s = 1.194$ (LDA)) | Longitudinal acoustic instability at $\lambda = 1.188$
Uniaxial stretch (armchair) | Elastic longitudinal instability at $\lambda_a = 1.23$ (GGA) ($\lambda_s = 1.24$ (LDA)) | Longitudinal acoustic instability at $\lambda = 1.25$
Uniaxial stress (zigzag) | Elastic longitudinal instability at $\lambda_a = 1.186$ (GGA) ($\lambda_s = 1.192$ (LDA)) | Longitudinal acoustic instability at $\lambda = 1.20$
Uniaxial stress (armchair) | Elastic longitudinal instability at $\lambda_a = 1.238$ (GGA) ($\lambda_s = 1.25$ (LDA)) | Longitudinal acoustic instability at $\lambda = 1.25$

Table 5.5: Summary of instability analyses based on acoustic tensor analysis of the constitutive models and the corresponding phonon calculations for various homogeneous deformation modes considered.

### 5.7.3 Stress-strain response curves

In the present approach the coefficients of the continuum model are determined by a least-squares fit to the strain energies alone, and the stresses were not used in the fitting, so the agreement of predicted stress values with those determined directly from *ab initio* calculations remains to be examined. In the following subsections we compare the continuum model's predictions of stress-strain response in a few
important modes of large homogeneous deformation modes with corresponding \textit{ab initio}-calculated values. For this purpose, we use the continuum model to obtain the components of stress as functions of strain for a set of deformations including equibiaxial tension, uniaxial stretching in the armchair, and the zigzag directions, uniaxial tension in the armchair and the zigzag directions, and compare the predicted stresses with the values directly calculated from first-principles calculations. In obtaining the stress-strain curves, the elastic and soft-mode instabilities — discussed in previous sections — have been suppressed in both \textit{ab initio} and in continuum calculations.

**Pure biaxial stretch**

The Cauchy stress as a function of strain for pure equi-biaxial deformation as obtained from the continuum model is shown in Fig.[5-9-a]. The Cauchy biaxial stress as a function of the areal strain, as predicted by the UBER-based model, compares with the \textit{ab initio} values well. Our model predicts that the Cauchy stress reaches its maximum value at nearly 42\% areal strain. In Fig.[5-9-b], we have shown the softening of the dilatant tangent modulus, defined in equation (5.42), with areal strain $\epsilon_a$. The areal tangent modulus vanishes when the Cauchy stress approaches its maximum value.

**Uniaxial stretching along the armchair and the zigzag directions**

The components of Cauchy stress as functions of stretch obtained from the continuum model for the case of uniaxial stretching along the armchair and the zigzag directions are shown in Fig. [5-10-a] and Fig. [5-10-b], respectively.
5.8 Discussion and conclusion

Using as a basis the scalar-valued functions of the logarithmic strain tensor, called symmetry invariants, that remain invariant w.r.t. the point group symmetry of the graphene lattice, we derived a nonlinear hyperelastic constitutive response for graphene. Because the model employs symmetry invariants, the material symmetry group of the underlying lattice is built-into the model, and the need for externally imposing the symmetry restrictions is eliminated. This constitutive model is strictly
Figure 5-10: Stress-strain curve obtained from the continuum model for uniaxial strain along (a) armchair direction and (b) zigzag direction. For comparison, we have also shown the \textit{ab initio} stress values. The arrow shows the location of maximum stress. The solid lines are LDA results, whereas the dashed lines are GGA counterparts.
Figure 5-11: Validation of the continuum model for uniaxial stress along (a) the armchair direction and (b) the zigzag direction. The continuum model (solid line) is in good agreement with the LDA \textit{ab initio} values. The solid lines are LDA results, whereas the dashed lines are GGA counterparts.
hyperelastic, in the sense that the constants in the model are determined by fitting energies of the deformed states, without consideration of stresses. The model is coordinate-frame-independent, making it easy-to-implement in computational codes. The formulation allows straightforward evaluation of higher-order tensor variables such as the work-conjugate tangent moduli tensors and the acoustic tensor. The model clearly elucidates the contributions to the strain energy density due to purely equi-biaxial area change, and due to purely isochoric shape-changing deformations. The model correctly predicts the stress-strain variation of graphene in cases of both uniaxial stretching and tension along both the zigzag and armchair directions, and in biaxial tension. The values of the isotropic small strain elastic constants deduced from the model are also in good agreement with the measured values. The acoustic-tensor-based stability analysis predicts failure stretches that are in good agreement with independent lattice dynamics calculations based on linear response perturbation theory. Our model predicts that the initial loss of elastic stability under pure biaxial stretch occurs at $\epsilon_a \doteq 0.35$, by a vanishing tangent shear modulus, rather than being due to the vanishing tangent area modulus at $\epsilon_a \doteq 0.40 - 0.42$. The latter instability mode was previously-reported by Wei et al., but we find that it could

Figure 5-12: Ratio of transverse strain (due to Poisson contraction) to longitudinal strain for uniaxial stress along (a) the armchair direction and (b) the zigzag direction. The solid/dashed lines are LDA/GGA results.
occur only at a larger deformation than that of the presently-identified elastic shear instability. And as noted previously by Yevick & Marianetti [125], phonon calculations also show that, prior to the onset of this long-wavelength shear instability, a short-wavelength instability at $K$ emerges earlier, at $\epsilon_a = 0.28 - 0.30$, as seen also in Fig. (5-4-c). Thus, the strength of graphene under equi-biaxial tension is strictly limited by this short-wavelength instability. In Chapter 6, we present a phonon-based failure model that captures material instabilities of all kinds—short-wavelength as well as long-wavelengths, and material as well as structural.
Chapter 6

A continuum failure model for graphene derived from phonons-based stability analysis

6.1 Introduction

Limits to elastic deformation—the stress or strain at which reversible-to-irreversible transition takes place in a material—pose fundamental limits on a material’s performance and determine its strength. The limiting stress or strain, in general, depends upon the loading conditions, and the dependence is often described by means of a phenomenological model termed a failure criterion. Mathematically, a failure criterion is often represented as a surface in stress or strain space, the surface separating stable states of reversible deformation from ‘failed’ or irreversibly-deformed states. For many materials, a failure criterion simple enough to be characterized by one or two material constants, which are readily determined from experiments, often provides sufficient accuracy. Examples include the Mises (or Tresca) yield criterion for metals [189], the Mohr-Coulomb criterion for cohesive-frictional solids [37], the Drucker-
Prager criterion for pressure-dependent solids [43], and the Hoek-Brown criterion for rocks [84].

In crystalline materials that are free from lattice imperfections, the limit to elastic deformation sets an upper bound on the material strength [123]. This upper bound, termed the ideal strength, depends on the intrinsic nature of bonding between atoms in the material. Because of various types of lattice defects which normally exist, including dislocations, grain boundaries, interstitial impurities, and voids [128, 183], most conventional materials can be irreversibly-deformed at stress-levels well below the ideal strength.

Recent advancements in nanotechnology have enabled fabrication and growth of defect-free two-dimensional crystals in which mechanical failure indeed occurs upon reaching stress levels near the ideal strength [36, 195, 105]. Graphene is a representative example of such ultrastrong nanocrystalline materials. Experimental studies suggest that defect-free, single-crystalline graphene can sustain near-ideal-strength stresses while remaining within the reversible regime of deformation [105, 160]. Beyond the limit of elastic deformation, the fate of the material is determined by a strength-limiting mechanism such as incipient plasticity or crack-initiation. For example, Lee et al. [105] noted in their nanoindentation experiments that as the limit of reversible deformation is reached, a catastrophic fracture in graphene immediately ensues. Since, in the absence of lattice-imperfections, a strength-limiting mechanism can only be activated by lattice-instabilities [110, 115], the incipient failure of a defect-free crystalline material is intrinsically related to the loss of internal lattice-stability.

Constituting a continuum-level failure criterion for a defect-free crystalline material would involve continuum parameterization of limiting conditions for emergence of lattice instabilities in terms of stress or strain. However, there are certain difficulties in accomplishing this task. First, crystalline materials are intrinsically anisotropic, so material response, including incipient failure, varies with orientation. Secondly,
fundamentally-different types of lattice-instabilities govern strength-limiting mechanisms under different loading conditions [125, 35]. Lattice instabilities can be classified as either an elastic (also called a long-wave) instability or a soft-mode (also called as short-wave) instability. The elastic instabilities arise from softening of elastic moduli of the material under the action of local state of stress, and the criterion for their origin can be parameterized in terms of strain via acoustic tensor analysis based on an appropriate large-deformation continuum stress-strain response function, as shown in Chapter 5 of this thesis. The soft-mode instabilities are more complex, and arise when certain modes of lattice vibrations, of much smaller wavelength comparable to continuum lengths, dynamically grow out of bound [134]. There is no generic framework for parametrization of limiting conditions governing the onset of short-wave instabilities. For these reasons, the dependence of failure strength on loading conditions in ideal crystalline materials is generally too complex to be accurately characterized by one or two parameters, and formulation of a continuum failure function describing the onset of incipient failure in deformed-crystals remains a challenge.

Individually, lattice-instabilities can be assessed via the principle of lattice-stability analysis (see Born & Huang [21]; Hill [83]), which asserts that a necessary and sufficient criterion for an ideal crystal under arbitrary uniform loading to be stable is that it exhibits stability with respect to bounded perturbations of all wavelengths. Lattice-stability analysis based on the above criterion is most effectively assessed by phonons, which, below the Debye temperature \( T_D = 1000 K \) for graphene, constitute a complete normal basis for lattice vibrations. A deformation-induced instability of any kind — macroscopic or microscopic — is directly visible in the dispersion of phonons; although it should be noted that since phonon instabilities result from dynamical growth of certain lattice-vibrations, the constrained boundaries may suppress triggering of a phonon instability in a nearby material element even if the state of strain in the material element has reached the verge of lattice breakdown.
Density functional perturbation theory (DFPT) [11] allows calculation of highly accurate phonon dispersion relations of an arbitrarily-deformed crystal. From a predictive multi-scale modeling point of view, incorporating the linear response calculations into a continuum-level finite element analysis would be ideal. However, accurate computation of the complete phonon dispersion relation via linear response requires carrying out an elaborate sequence of computationally-expensive steps that can not be treated within the confines of an analytical framework, making it difficult to integrate lattice-dynamical stability analysis into a continuum simulation scheme.

Previously, Liu, et al. [114] hierarchically coupled the interatomic-potential-based lattice-dynamical calculations with continuum-level finite element analysis. The method computes the continuum deformation field by solving a boundary-value problem using FEA for each load increment. Then, for the deformed state of each considered material point, the acoustic tensor and the phonon-dispersion are calculated over a large grid of q-points in the irreducible Brillouin zone. These steps are repeatedly carried out for subsequent load increments until a material point is identified for which the acoustic tensor ceases to be positive-definite or for which a soft-mode emerges in the phonon dispersion relation. The use of such a computationally cumbersome search in order to locate an unstable material point, both temporally and spatially, limits the effectiveness of the method. For this reason, this approach is effectively limited to analyses based on empirical potentials, which are relatively economical. However, the errors in phonon-calculations based on empirical potential can be forbiddingly large, rendering the predictions somewhat unreliable. For example, the sound velocities from an empirical many-body potential in the unstrained state of graphene differed from measured values by nearly 50% [45]; in contrast, the longitudinal and transverse elastic wave-velocities obtained from DFPT phonon calculations differ by less than 1% from measured values (see below). Further, empirical potentials are often calibrated against a very limited set of deformations (nearly un-
deformed atomic spacing), and often have poor extrapolation characteristics, further deteriorating their performance at large deformations.

In this chapter, we propose a novel approach for the analysis of incipient lattice failure in defect-free, single-crystalline graphene within the confines of continuum FEA simulations. The approach is based on the notion of a continuum-level failure function for graphene, derived from atomistic-level lattice dynamical stability analysis based on DFPT phonons. This failure function constitutes an analytical description of incipient lattice instabilities, of both macroscopic and microscopic natures, over the space of all homogeneous deformations. The construction of this function, as a major ingredient, involves interpolating the stability-limiting values of principal strains, corresponding to some representative deformation modes, in the basis of symmetry-invariants of the two-D logarithmic strain measure [217]. We show that the use of symmetry-invariants introduces substantial functional simplification, reducing the requisite representative deformation modes needed for implementation to a small set of biaxial deformations along the armchair and zigzag directions.

We implement the failure function in a finite element analysis scheme along with the large-deformation hyperelastic constitutive relation proposed in Chapter 5 of this thesis. The resulting implementation constitutes a multi-scale methodology for the analysis of incipient failure in defect-free graphene subject to arbitrary loading, which enables on-the-fly assessments of the macroscopic load and deflection at which a lattice-instability first emerges during loading, the location of the unstable material element, the nature of the instability (elastic or soft-mode, structural or material), and the local microscopic stress and strain. We employ the resulting scheme to analyze the failure of a defect-free suspended graphene sheet in the finite elements simulation of idealized bulge-type tests. In simulations, we consider two different geometries of the constrained boundary, elliptical and circular, but with the same suspended area, and show how different types of local lattice instabilities are reached in the respective
boundary value problems under different levels of differential pressure and overall deflection.

6.2 Framework of representation

6.2.1 Kinematics

We consider graphene as a 2D deformable body denoted by unstressed reference configuration $\mathcal{B}$. Let $X$ and $x$ denote the coordinates of a material element of graphene in undeformed and deformed configurations, respectively. The convection of material points under deformation is described by a smooth, injective (one-to-one) function $\chi(X, t)$ called the motion. The non-translational part of the motion can be equivalently defined by the positive-definite second-order deformation gradient tensor, $F = \nabla \chi(X, t)$. Then, the polar decomposition theorem provides the following factorizations of $F$ [72, 71, 53]:

$$F = RU = VR,$$

where the orthogonal tensor $R \in SO_2$ characterizes rigid-body rotation, and $U$ (or $V = RUR^T$), termed the right (left) Cauchy-Green tensor, characterizes shape- and area-change. The deformation of a material point can be kinematically factored as the product of a purely dilatational (or shape-preserving, but area-changing) deformation $U^a$, and a purely isochoric (or shape-changing, but area-preserving) deformation $\dot{U}$. Accordingly, the stretch tensor can be product-decomposed as

$$U = U^a \dot{U} = \dot{U} U^a,$$

where

$$U^a \equiv J^{1/2} I,$$
and

$$\bar{U} \equiv \lambda r_1 \otimes r_1 + \lambda^{-1} r_2 \otimes r_2; \quad (6.4)$$

Here, $J = \det U = \lambda_1 \lambda_2$, $\lambda = \sqrt{\lambda_1 / \lambda_2} \geq 1$, and $I$ is the 2D identity tensor.

The spectral representation of $E^{(0)} \equiv \ln U = \ln U^0 + \ln \bar{U}$ is then given by:

$$E^{(0)} = \frac{1}{2} \ln J I + \ln \lambda (r_1 \otimes r_1 - r_2 \otimes r_2)$$

$$\equiv \frac{1}{2} \epsilon_a I + E_0^{(0)}, \quad (6.5)$$

where

$$\epsilon_a = \text{tr} E^{(0)} = \ln J = \ln (\det U), \quad (6.6)$$

gives the areal logarithmic strain $\epsilon_a$, and

$$E_0^{(0)} = \ln \bar{U} = \ln \lambda (r_1 \otimes r_1 - r_2 \otimes r_2), \quad (6.7)$$

denotes the deviatoric part of $E^{(0)}$. Alternatively, we may also write the spectral representation of the logarithmic strain as

$$E^{(0)} = \mathcal{E}_1 r_1 \otimes r_1 + \mathcal{E}_2 r_2 \otimes r_2. \quad (6.8)$$

where $\mathcal{E}_1 = \ln (J^{1/2} / \lambda)$ and $\mathcal{E}_2 = \ln (J^{1/2} / \lambda)$ are the major and minor principal strains, respectively; and $r_1 = \cos \theta e_1 + \sin \theta e_2$ and $r_2 = -\sin \theta e_1 + \cos \theta e_2$ are the corresponding principal directions. The orientation $\theta$ is measured from a fixed material axis aligned with the zigzag direction of the graphene lattice. In addition, we also define a mean strain $\bar{\epsilon} = \frac{1}{2} (\mathcal{E}_1 + \mathcal{E}_2) = \ln J^{1/2} = \frac{1}{2} \epsilon_a$, which characterizes the areal dilatation or contraction of the material.
6.2.2 Symmetry-constraints on representation

The proposed approach is based on the notion of a failure function, a continuous scalar-valued function \( \mathcal{F} \) of the strain measure \( \mathbf{E}^{(0)} \), such that all deformed configurations of the lattice that lie on the surface

\[
\mathcal{F}(\mathbf{E}^{(0)}) = 0,
\]

have reached a state of incipient lattice instability. All deformed states of the crystal lying in the interior of the failure surface satisfy \( \mathcal{F}(\mathbf{E}^{(0)}) > 0 \), and are stable w.r.t. lattice perturbation of all wavelengths; conversely, states lying outside the surface \( \mathcal{F}(\mathbf{E}^{(0)}) < 0 \), are not. For an anisotropic material, the function \( \mathcal{F} \), in accordance with Neumann’s principle [136], should include the material symmetry group \( \mathcal{G} \) of the underlying lattice, i.e.,

\[
\mathcal{F}(\mathbf{Q}^T \mathbf{E}^{(0)} \mathbf{Q}) = \mathcal{F}(\mathbf{E}^{(0)}) \quad \forall \mathbf{Q} \in \mathcal{G},
\]

where \( \mathbf{Q} \) is an orthogonal tensor denoting the symmetry operations included in the material symmetry group \( \mathcal{G} \) (\( \mathcal{C}_m \) in the case of graphene). A scalar-valued function of a tensor agency, such as \( \mathcal{F}(\mathbf{E}^{(0)}) \), that remains invariant under a material symmetry group \( \mathcal{G} \) is called a \( \mathcal{G} \)-invariant scalar function. Representation of a generic \( \mathcal{G} \)-invariant scalar function involves using the isotropicization theorem and symmetry invariants of the tensor agency w.r.t. the point symmetry group of the material [118, 217, 214], as we described in the Chapter 3 of this thesis.

The isotropicization theorem, which is based on the notion of a materially-embedded structure tensor \( \mathbb{H} \), allows a \( \mathcal{G} \)-invariant function to be expressed in terms of a list of special scalar functions, \( \mathcal{J}_1, \mathcal{J}_2, \ldots, \mathcal{J}_n \), which are joint isotropic functions of \( \mathbf{E}^{(0)} \) and
\[ \mathcal{F}(\mathbf{E}^{(0)}) = \tilde{\mathcal{F}}(\mathcal{J}_1, \mathcal{J}_2, \ldots, \mathcal{J}_n), \quad (6.11) \]

where

\[ \mathcal{J}_i(\mathbf{E}^{(0)}; \mathbb{H}) = \mathcal{J}_i(Q^T \mathbf{E}^{(0)} Q; \mathbb{P}_Q(\mathbb{H})) \forall Q \in SO_2. \quad (6.12) \]

Here \( \mathbb{P}_Q \) denotes the transformation of the structure tensor \( \mathbb{H} \) under the orthogonal transformation \( Q \). The functions \( \mathcal{J}_i \) are termed symmetry invariants since they satisfy all the constraints belonging to the material symmetry group of the crystal. Smith [175, 177, 178] showed that the set of mutually-independent symmetry invariants serves as a complete and irreducible basis for the representation of scalar constitutive functions of the anisotropic material. In the following section, we explicitly derive symmetry invariants of \( \mathbf{E}^{(0)} \) for the structure tensor characterizing the material symmetry group of graphene.

### 6.2.3 Functional bases for \( C_{6v} \) symmetry group

Previously, in the Chapter 5, we showed that a constitutive function of graphene — such as the finite deformation hyperelastic response — is conveniently represented in terms of the integrity bases of the logarithmic strain w.r.t. the material symmetry group of graphene, which are given as — \( \epsilon_a = \text{tr} \mathbf{E}^{(0)} \), \( \gamma_4^2 = 2\mathbf{E}^{(0)} : \mathbf{E}^{(0)} = 4(\ln \lambda)^2 \), and \( \gamma_6^3 = 8(\ln \lambda)^3 \cos 6\theta \). The continuum failure criterion provides an analytical description of incipient lattice instabilities of all kinds, for arbitrary deformations, parametrized in terms of strain. This failure function \( \mathcal{F} \), similar to strain energy density function \( \psi \), possesses the point group symmetry of the underlying lattice; and therefore it also is amenable to a representation based on symmetry-invariants of the strain measure \( \mathbf{E}^{(0)} \). For the purpose of representation of \( \mathcal{F} \), we employ an alternate set of symmetry invariants of \( \mathbf{E}^{(0)} \) comprising the mean hydrostatic strain \( \bar{\varepsilon} \), the major (or minor) principal strain \( \varepsilon_1 \) (or \( \varepsilon_2 \)); and the symmetry-reduced principal stretch
Figure 6-1: (a) Graphene lattice with orientations of the material unit vectors — \( \hat{x} \) and \( \hat{y} \) — and the Cartesian unit vectors — \( e_1 \) and \( e_2 \) — indicated. The dashed blue lines denote the unit cell used in the ab initio calculations. The GGA (LDA) value of the lattice parameter is also indicated. The armchair and zigzag directions are along the \( e_1 \) and \( e_2 \) axes respectively. (b) Brillouin zone of graphene with high symmetry points indicated.

direction defined as \( \Theta = \arccos(\cos 6\theta) \). Note that the elements of this set are not independent from the integrity bases, i.e., \( \epsilon_a \), \( \gamma_i^2 \), and \( \gamma_i^3 \); and utilizing kinematical definitions of equations (6.5-6.7), the two sets of symmetry-invariant can be shown to be related as follows:

\[
\bar{E} \equiv \frac{1}{2} \epsilon_a = \ln J^{1/2};
\]

\[
E_1 \equiv \epsilon_a + \frac{1}{2} \gamma_i = \ln(J^{1/2} \lambda);
\]

\[
E_2 \equiv \epsilon_a - \frac{1}{2} \gamma_i = \ln(J^{1/2} / \lambda);
\]

and

\[
\Theta \equiv \arccos \left[ \frac{\gamma_3^2}{\gamma_3^3} \right] = \arccos(\cos 6\theta). \tag{6.16}
\]

Note: \( E_1, E_2 \) and \( \bar{E} \) are related as \( 2\bar{E} = E_1 + E_2 \), i.e., only two out of the three are independent.

The above symmetry-invariants, which involve non-polynomial combinations of strain...
components, are called functional bases.

6.2.4 Form of the failure function in terms of the functional bases

The failure function, as expressed in terms of the functional bases, prescribes the critical value of the major principal strain $\varepsilon_1'$ (or alternately, the critical value of the minor principal strain $\varepsilon_2'$) as a function of the areal strain $\bar{\varepsilon}$ and the symmetry-reduced principal stretch direction $\Theta$. Thus, the form of the instability function reads as

$$ F_{Upper}(E(0)) \equiv \varepsilon_1' (\bar{\varepsilon}, \Theta) - \varepsilon_1 = 0, \quad (6.17) $$

or, alternately

$$ F_{Lower}(E(0)) \equiv \varepsilon_2 - \varepsilon_2' (\bar{\varepsilon}, \Theta) = 0, \quad (6.18) $$

such that if, at a given mean strain $\bar{\varepsilon}$, $F_{Upper}(E(0)) > 0$ (or, equivalently $F_{Lower}(E(0)) > 0$), then the material is stable w.r.t. incremental perturbations of all wavelengths; otherwise the instantaneous configuration of the lattice is unstable under some incremental perturbation.

Due to the fashion in which the failure conditions are defined, we have $\varepsilon_1 + \varepsilon_2 = 2\bar{\varepsilon}$.

Accordingly, the two conditions equation (6.17) and equation (6.18) are related:

$$ F_{Lower}(\bar{\varepsilon}, \Theta) = \bar{\varepsilon} - F_{Upper}(\bar{\varepsilon}, \Theta); \quad (6.19) $$

Therefore, only one of the functions needs to be determined explicitly.

Remark — Consider a deformed state having the two principal strain components
$\mathcal{E}_1$ and $\mathcal{E}_2$. The state of the lattice would be stable if

$$\mathcal{E}_2 < \mathcal{E}_1 < \mathcal{E}^c_1.$$  

(6.20)

Thus, geometrically, the two conditions described in equation (6.17) and equation (6.18) define upper and lower bounds of the lattice stability surface, respectively. All lattice deformation states inside the region bounded by the two surfaces are stable, while 'failed' states lie outside.

### 6.3 Determination of the instability function of graphene

Employing the representation ideas outlined in the previous section, we now systematically determine the functional form of the instability function for graphene in terms of $\mathcal{E}_j (\tilde{\mathcal{E}}, \Theta)$. For this purpose, we first obtain the set of data containing the stability-limiting values of $\mathcal{E}_j^c$ (or $\mathcal{E}_j^c$) over a range of values of $\tilde{\mathcal{E}}$ and $\Theta$, calculated from phonon-based stability analysis of a set of representative homogeneous deformation paths.

Before proceeding we note that an elastic instability often appears as the point beyond which the Cauchy stress drops, either suddenly or gradually [34, 131]. An elementary approach to detect a lattice-instability along a loading path is to trace this point on the Cauchy stress along the path from highly-accurate ab initio calculations. However, the approach has several shortcomings. First, a microscopic (short-wavelength) instability may not be captured in the stress-strain response curve if the size of the simulation cell employed in the calculation is not commensurate with wavelength of the unstable mode (see Yevick & Marianetti [125] ). Secondly, in case
of the elastic instability for which the unstable mode is orthogonal to the loading path, the instability does not correspond to the maxima of stress-strain curve. For example, in graphene under equi-biaxial tension, the elastic instability is a shear instability orthogonal to the loading path and precedes the maximum Cauchy stress configuration under that loading, as we showed in Chapter 5 of this thesis.

6.3.1 Methods: calculation of phonons from DFPT approach

Our \textit{ab initio} calculations are based on the first-principles Density Functional Theory (DFT) as implemented in the PWSCF simulation package [66]. The exchange-correlation energy of electrons is treated with the Local Density Approximation (LDA) of Perdew and Wang ([154]). The interaction between ionic cores and valence electrons is represented by an ultrasoft pseudopotential [192]. Kohn-Sham wave functions are represented using a plane-wave basis with an energy cutoff of 30 Ry and a charge density cutoff of 300 Ry. Integration over the irreducible Brillouin zone (IBZ) is performed with a uniform $30 \times 30 \times 1$ mesh of $k$-points, and occupation numbers are smeared using the Marzari-Vanderbilt cold smearing scheme [124] with broadening of 0.03 Ry. Errors in the Cauchy stresses and total energy due to basis-set size, smearing parameter, and $k$-points are converged to less than 0.034 N/m and 0.01 Ry, respectively.

The phonon dispersion relations, of the undeformed and deformed graphene, are computed via linear response calculations as implemented in the density functional perturbation theory (DFPT) [11, 42]. The dynamical matrix is calculated on an $8 \times 8 \times 1$ uniform grid of $q$-points in the IBZ — which is then fast-Fourier-transformed to calculate the interatomic force constants (IFC), corrected by the acoustic sum rule to ensure that $\omega(q = 0) = 0$ for all the acoustic branches [96]. The IFC’s are then used to interpolate phonon frequencies over a dense set of $q$-points in the IBZ. Both energies and phonon dispersion relations in this work are performed on a two-atom
primitive unit cell of graphene shown in Fig. (6-1). The two lattice vectors defining the undeformed unit cell are \( \mathbf{a}_1 = a_0 \left( \frac{\sqrt{3}}{2} \mathbf{e}_1 + \frac{1}{2} \mathbf{e}_2 \right) \), and \( \mathbf{a}_2 = a_0 \left( \frac{\sqrt{3}}{2} \mathbf{e}_1 - \frac{1}{2} \mathbf{e}_2 \right) \), where \( a_0 \) is the lattice constant. The LDA value of the undeformed lattice constant is obtained as 2.44\( \text{Å} \), which is very close to the experimentally-reported value of 2.457 \( \text{Å} \)[9].

Surfaces showing the branches in the phonon-dispersion of the undeformed graphene, as obtained from DFPT calculations, are interpolated over an IBZ in Fig.[6-2].

The LA and TA phonon branches, in the neighborhood of \( \mathbf{q} = \mathbf{0} \), obey linear dispersion: \( \omega_{LA} = c_{LA} q \) and \( \omega_{TA} = c_{TA} q \); where \( q = |\mathbf{q}| \) and \( c_{LA} \) and \( c_{TA} \) are longitudinal and transverse acoustic wave-velocities, respectively. As a simple verification of the DFPT phonon calculations, Table [6.1] compares longitudinal and transverse acoustic wave-velocities obtained from the phonon dispersion with experimentally-measured values; also, since the G band in the Raman spectra of graphene is associated with
<table>
<thead>
<tr>
<th>CLA (km/s)</th>
<th>cTA (km/s)</th>
<th>Raman G-peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured value [206]</td>
<td>21.3</td>
<td>13.6</td>
</tr>
<tr>
<td>Continuum model in this work</td>
<td>21.80</td>
<td>13.78</td>
</tr>
<tr>
<td>$\sqrt{E_{2D}/\rho_{2D}}$</td>
<td>$\sqrt{\mu_{2D}/\rho_{2D}}$</td>
<td></td>
</tr>
<tr>
<td>DFPT Phonons in this work</td>
<td>21.15</td>
<td>13.50</td>
</tr>
</tbody>
</table>

Table 6.1: In-plane longitudinal and transverse wave velocities calculated from LDA phonon dispersion. The values closely agree with measured values as well as with values calculated from the continuum model of the Chapter 5 of this thesis. The LO/TO frequencies at $\Gamma$ are also in good agreement with the G-peak of the Raman spectra of graphene. Note: $\rho_{2D}$ is the mass per reference area of graphene which is calculated from the atomic mass of carbon and the undeformed lattice constant of graphene; $E_{2D}$ denotes the elastic modulus in uniaxial strain; and $\mu_{2D}$ denotes the shear modulus.

the doubly-degenerate LO - TO vibrational modes at $\Gamma$, we also compare calculated LO/TO frequencies at $\Gamma$ with the G-band frequency measured in Raman spectroscopy.

### 6.3.2 Sampling scheme

For the purpose of sampling deformed states of the lattice, we use the orientation of the maximum principal stretch direction $\theta$ to designate what we term a ‘deformation path’. For example, varying the values of the principal strains $\varepsilon_1$ and $\varepsilon_2$, while the maximum stretch direction fixed at $\theta$, is referred to as moving along the deformation path prescribed by $\theta$. To determine the point of incipient lattice instability along a deformation path, the lattice is first deformed via a pure equi-biaxial strain, i.e., $\frac{1}{2} \text{tr } E^{(0)} = \tilde{\varepsilon} \mathbf{I}$, followed by an isochoric shape-changing stretch of the
form $E_0^{(0)} = E^{(0)} - \frac{1}{2} \text{tr} E^{(0)} = \frac{3}{2} r_1 \otimes r_1 - \gamma_1 r_2 \otimes r_2; \gamma_i = \mathcal{E}_1 - \tilde{\mathcal{E}}$, as schematically shown in Fig.[6-4-A]. For each sampled deformation pair $\{\tilde{\mathcal{E}}, \mathcal{E}_1\}$ along deformation path $\theta$, we determine if the conditions $-\omega_n(\mathbf{q}) > 0 \ (n=1,\ldots,6)$ and, for the acoustic branches, $d\omega_n/d\mathbf{q}_{\mathbf{q} \to 0} > 0$ hold. If at some critical value of the major principal strain $-\mathcal{E}_c$ any of the two conditions ceases to hold, then the lattice is considered as incipiently unstable, and the corresponding triplet $\{\tilde{\mathcal{E}}, \mathcal{E}_c, \theta\}$ corresponds to a point on the instability surface. Our sampling set includes values of $\tilde{\mathcal{E}}$ ranging from the undeformed state $\tilde{\mathcal{E}} = 0$ to the critical equi-biaxial deformation, $\tilde{\mathcal{E}}_{\text{max}} = 0.144$, at which the lattice reaches a soft mode instability in the absence of deviatoric deformation. For each sampled value of $\tilde{\mathcal{E}}$, the superimposed isochoric strain is varied such that the maximum principal strain varies over the range $0 \leq \mathcal{E}_1 \leq \mathcal{E}_c$, the upper limit $\mathcal{E}_c(\tilde{\mathcal{E}})$ being the maximum value of the stretch — for the given value of $\tilde{\mathcal{E}}$ — at which underlying lattice becomes incipiently unstable. Owing to the $C_{6v}$ symmetry of graphene, isochoric stretches need be sample only over the parametric range $0 \leq \theta \leq \pi/6$. We consider only $N = 2$ deformation paths in the BZ, corresponding to the zigzag direction $\theta = 0$, and the armchair direction $\theta = \pi/6$.

6.3.3 Representation and interpretation of the data

From the DFPT calculations, we obtain the data, each in the form a triplet $\{\tilde{\mathcal{E}}, \mathcal{E}_1, \theta\}$, representing the critical value of the major principal strain $-\mathcal{E}_1$ as a function of area strain $\tilde{\mathcal{E}}$ for both the sampled principal strain directions, $\theta = 0$ (Fig.[6-3-b]) and $\theta = \pi/6$ (Fig.[6-3-c]).

Graphene sheet, which has an exceedingly small bending stiffness, when subjected to an in-plane deformation can be brought to a state of incipient instability via one of two mechanisms:

- incipient lattice failure in tension when $\mathcal{E}_1$ reaches a limiting value, while both
Figure 6-3: (a) Notation scheme illustrating deformation of the graphene lattice: the undeformed lattice (faint black) is first subjected to a uniform dilatation (faint blue) $U_1 = J^{1/2}I$, and then to an isochoric shape-changing deformation $U_2 = \lambda r_1 \otimes r_1 + \lambda^{-1} r_2 \otimes r_2$, resulting in the final configuration (dark red). (b) Cartesian plot of critical principal logarithmic strains $\varepsilon_1^c$ (upper curve, solid line), and $\varepsilon_2^c$ (lower curve, dashed line) vs. $\varepsilon$ for sampled orientation $\theta = 0$. (c) Corresponding plot of $\varepsilon_1^c$ for sampled orientation $\theta = \pi/2$. In the lattice stability curves of both (b) and (c), the type of incipient lattice instability for the given critical strain state is color-coded: red denotes incipient buckling, blue denotes elastic instabilities, while green denotes soft mode instabilities.

The Cauchy principal stress components $S_1 \geq S_2 > 0$ remain positive;

or

- incipient structural instability via out-of-plane buckling when the minimum principal stress component $S_2 = 0$ is on the verge of becoming compressive, before the major principal strain reaches the limiting tensile strain.

From equation (6.5), $\varepsilon_1 = \ln(J^{1/2} \lambda)$, and $\varepsilon_2 = \ln(J^{1/2}/\lambda)$. Thus, at a given $J^{1/2}$, as $\lambda$ is increased, $\varepsilon_1$ increases, while $\varepsilon_2$ decreases. Further, we note that the limiting tensile strain, beyond which a tensile instability is triggered in graphene, is large, whereas its buckling strength is vanishingly small. Therefore, when $\bar{\varepsilon} = \frac{1}{2} \ln J$ is relatively small, then $\varepsilon_2$ reaches the critical value for buckling, which is $\sim -\nu_2 D \varepsilon_1$, before $\varepsilon_1$ reaches the limiting tensile strain. Thus, for small values of $\bar{\varepsilon}$, the value of isochoric stretch $\lambda$ is essentially limited by buckling instability as reflected by the phonon dispersions shown in Fig.[6-4-A]. Interestingly, when $\bar{\varepsilon} = 0$, the membrane
Figure 6-4: Phonon dispersions of graphene at certain critical states of deformation, marked as '1', '2' and '3' in Fig.[6-3], along the zigzag deformation path ($\theta = 0$). Also shown are the deformed Brillouin zone (green polygon), the irreducible wedge (red polygon), and the sampled instability direction (dashed line). At smaller values of $\mathcal{E}$, the incipient instability due to superimposed isochoric stretch is a structural buckling instability arising from an unstable ZA branch, while at larger values of $\mathcal{E}$, the incipient instability due to a superimposed isochoric deformation is a material instability arising from an unstable LA branch. Finally, the critical value of $\mathcal{E}$ is reached at which the lattice fails without any superimposed isochoric deformation, arising from a soft phonon mode of the TA branch.
Figure 6-5: Phonon density of states of graphene at certain critical states of deformation, marked as ‘1’, ‘2’ and ‘3’ in Fig.[6-3], along the zigzag deformation path (θ = 0). The failures under deformation with a superimposed deviatoric strain are seen to be accompanied with a phononic band gap, unlike the soft mode failure under a pure dilatational strain in which the phononic band gap is absent.
is unstable in buckling as soon as any isochoric stretch is applied; thus the limiting value of $\lambda = 1$ in all directions.

On the other hand, when $\tilde{\varepsilon}$ is large, $\varepsilon_1$ reaches the limiting tensile strain before $\varepsilon_2$ reaching the buckling strain, and graphene fails in tension. On the plot of $\varepsilon_1^f$ vs $\tilde{\varepsilon}$, the point at which transition from buckling instability to tensile failure occurs is identified as the point which has a zero slope (this is indeed the failure point in pure uniaxial tension). It is also noted that for small $\tilde{\varepsilon}$, the response is nearly isotropic. At large values of $\tilde{\varepsilon}$, the material anisotropy is evidenced, and the limiting value of isochoric strain is limited by failure in tension. The failure in tension might be attributed either to a soft mode instability, which occurs at large equi-biaxial strain $\tilde{\varepsilon}$ with low deviatoric component, i.e., $\varepsilon_1 - \varepsilon_2$ is small, e.g., see Fig.[6-4-C]; For large deviatoric component, i.e., large differences between $\varepsilon_1$ and $\varepsilon_2$, the failure is due to an acoustic instability, e.g., see Fig.[6-4-B].

From the density of states plots at various critical states of deformation, shown in Fig. [6-5], we note that failure induced by a deformation with a significant deviatoric component is always accompanied by a phononic band-gap, which is absent when the deformation does not involve significant deviatoric stretch.

### 6.3.4 From discrete dataset to continuum lattice stability function via interpolation

Construction of a continuum-level instability function involves interpolating the discrete dataset of the preceding section in a manner consistent with the $C_{6v}$ symmetry of graphene. This task is accomplished by performing the interpolation in terms of the symmetry-reduced functional basis element $\Theta$, as described in the following.

**(A). Radial interpolation**

For each sampled deformation path $\Theta = \Theta_n$, we express $\varepsilon_1^f$ as a continuous function $R_n(\tilde{\varepsilon})$ — called the radial interpolation function — by fitting the sampled data-points
Figure 6-6: (a) Sampled data points for $\mathcal{E}_i^c$ for $\theta = 0$ and $\pi/2$ (straight-line segments connect data points). (b) Fifth-order polynomial interpolation functions for $\mathcal{E}_i^c$ along the two sampled directions — obtained by fitting functions described by equation (6.21) and equation (6.22). The solid lines denote the critical major principal strain $\mathcal{E}_1^c$ values, while dashed lines denote the critical minor principal strain $\mathcal{E}_2^c$ values.

(plotting in Fig.[6-6-a]) — each in the form of a doublet $\{\tilde{\mathcal{E}}, \mathcal{E}_1^c\}$ — denoting the limiting strains along the deformation path $\Theta = \Theta_n$ to a polynomial function in $\tilde{\mathcal{E}}$ of the form:

$$\mathcal{E}_1^c(\tilde{\mathcal{E}}, \Theta = \Theta_n) \equiv \mathcal{R}_n(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}}) = \beta_1^1(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}}) + \beta_2^1(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}})^2 + \beta_3^1(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}})^3 + \ldots + \beta_n^M(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}})^M,$$

(6.21)

where $\tilde{\mathcal{E}}_{\text{max}} = \ln J_{\text{max}} \approx 0.14$ is the maximum areal strain that can be applied to graphene without reaching an incipient lattice instability. For $\mathcal{E}_2^c$ we obtain:

$$\mathcal{E}_2^c(\tilde{\mathcal{E}}, \Theta = \Theta_n) \equiv \tilde{\mathcal{E}} - \mathcal{R}_n(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}}) = \tilde{\mathcal{E}} - \left(\beta_1^1(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}}) + \beta_2^1(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}})^2 + \beta_3^1(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}})^3 + \ldots + \beta_n^M(\tilde{\mathcal{E}}/\tilde{\mathcal{E}}_{\text{max}})^M\right).$$

(6.22)

The radial interpolation functions, thus obtained, corresponding to the two sampled deformation paths are shown in Fig.[6-6-b].

199
(B). Angular interpolation

The angular interpolation scheme involves approximating $\mathcal{E}_1^c(\vec{\epsilon}, \Theta)$ by a weighted sum of the radial interpolation functions, with the weight functions being the angular shape functions along the sampled deformation paths. The following representation for the angular shape function $K_n(\Theta)$ conveniently satisfies the requirements that failure function is smooth, satisfies all the point-group symmetries of the lattice, and possesses $2\pi$ periodicity w.r.t. $\Theta$:

$$K_n(\Theta) = \alpha_n^0 + \alpha_n^1 \cos(\Theta) + \alpha_n^2 \cos(2\Theta) + \ldots; \quad (6.23)$$

where the number of terms in the expansion is given by the number of deformation paths ($N$) being sampled, and the corresponding coefficients $\alpha_n$ are determined using the following condition:

$$K_m(\Theta_n) = \begin{cases} 0; & \Theta_n \neq \Theta_m \\ 1; & \Theta_n = \Theta_m. \end{cases} \quad (6.24)$$

Since the angular variation of failure function is quite smooth, sampling of only two deformation paths, i.e., $N = 2$ suffices for an accurate interpolation of the failure functions. The corresponding two shape-functions are given as:

$$K_1(\Theta) = \frac{1}{2} (1 + \cos(\Theta)), \quad (6.25)$$
$$K_2(\Theta) = \frac{1}{2} (1 - \cos(\Theta)). \quad (6.26)$$

Following the above interpolation scheme, $\mathcal{E}_1^c$ is generically expressed as:

$$\mathcal{E}_1^c(\vec{\epsilon}, \Theta) = \sum_{n=1}^{n=N} R_n(\vec{\epsilon}/\vec{\epsilon}_{max}) K_n(\Theta), \quad (6.27)$$

where $N = 2$ is the total number of deformation paths. Substituting from equation (6.21) and equation (6.23) into equation (6.27), we obtain the generic form of...
Figure 6-7: (a) The radial interpolation for the failure function along the two sampled directions \( \theta \). The solid lines denote the major principal value \( \mathcal{E}_1 \), while dashed lines denote the minor principal value \( \mathcal{E}_2 \). (b) 90° wedge cut out from the threeD polar plot of the stability function. The transparent blue surface denotes the zero level. The upper red surface denotes the three-D polar plot of the surface given by \( \mathcal{E}_1 = \mathcal{E}_1(\mathcal{E}, \Theta) \), while the green surface denotes the surface described by \( \mathcal{E}_2 = \mathcal{E}_2(\mathcal{E}, \Theta) \). The yellow and blue arrows denote the zigzag and armchair directions, respectively. The black line denotes the outline of the lattice.

The lattice stability function as:

\[
\mathcal{E}_1^\circ = \sum_{n=1}^{N} \sum_{m=1}^{M} \gamma_{mn}(\mathcal{E}/\mathcal{E}_{\text{max}})^m \cos(n-1)\Theta; \tag{6.28}
\]

and

\[
\mathcal{E}_2^\circ = \mathcal{E} - \sum_{n=1}^{N} \sum_{m=1}^{M} \gamma_{mn}(\mathcal{E}/\mathcal{E}_{\text{max}})^m \cos(n-1)\Theta. \tag{6.29}
\]

The various coefficients appearing in the expression of the failure function have been tabulated in Tab.[6.2].

The 0 \( \leq \theta \leq \pi/2 \) wedge of the instability surface resulting from the interpolation scheme is shown in Fig. [6-7].
Table 6.2: Coefficients \( \gamma_{mn} \) in the expression of the instability surface (equations 6.28).

<table>
<thead>
<tr>
<th>( m \rightarrow n )</th>
<th>( \tilde{\epsilon}/\tilde{\epsilon}_{max} )</th>
<th>( (\tilde{\epsilon}/\tilde{\epsilon}_{max})^2 )</th>
<th>( (\tilde{\epsilon}/\tilde{\epsilon}_{max})^3 )</th>
<th>( (\tilde{\epsilon}/\tilde{\epsilon}_{max})^4 )</th>
<th>( (\tilde{\epsilon}/\tilde{\epsilon}_{max})^5 )</th>
<th>( (\tilde{\epsilon}/\tilde{\epsilon}_{max})^6 )</th>
<th>( (\tilde{\epsilon}/\tilde{\epsilon}_{max})^7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.36061</td>
<td>-0.0403958</td>
<td>-0.327806</td>
<td>7.51334</td>
<td>-24.8089</td>
<td>28.3255</td>
<td>-10.8837</td>
</tr>
<tr>
<td>( \cos \Theta )</td>
<td>0.0251542</td>
<td>-0.583471</td>
<td>4.55324</td>
<td>-16.0798</td>
<td>26.6759</td>
<td>-20.8193</td>
<td>6.22982</td>
</tr>
</tbody>
</table>
6.4 Mapping the instability surface from strain space to stress space

It is useful to describe the stability limit in terms of stress. In the present case, although the limiting conditions are explicitly obtained in terms of the principal strains, the relationship can be numerically mapped to its counterpart in the stress space via the hyperelastic stress-strain constitutive function described in the Chapter 5. The work-conjugate stress in this model reads as

\[
\mathbf{T}^{(0)}(\epsilon_a, \gamma_i, \gamma_\theta) = \frac{\partial \tilde{\psi}}{\partial \mathbf{E}^{(0)}} = \left( \frac{\partial \tilde{\psi}^{\text{Dil}}}{\partial \epsilon_a} + \frac{\partial \tilde{\psi}^{\text{Dev}}}{\partial \epsilon_a} \right) \mathbf{I} + \frac{4}{\eta'(\epsilon_a)} \mathbf{E}_0^{(0)} + \frac{\partial \tilde{\psi}^{\text{Dev}}}{\partial \gamma_i^2} \mathbf{S}_{\gamma_i^2}^{(0)}
\]

(6.30)

and the Cauchy stress \( \sigma \) is given as (see Ogden [145])

\[
\sigma = \frac{1}{J} \mathbf{F} \mathbf{T}^{(0)} (\mathbf{F}^T)^T = 2 \frac{1}{J} \mathbf{F} \left[ \frac{\partial \mathbf{E}^{(0)}}{\partial \mathbf{C}} \right] \mathbf{T}^{(0)} (\mathbf{F}^T),
\]

(6.31)

where \( \mathbf{C} = \mathbf{U}^2 \) denotes the right Cauchy-Green stretch tensor. Employing equation (6.30) and equation (6.31), we numerically map the failure surface in the strain-space to stress-space. Once the Cauchy stress has been determined, we can obtain the principal stresses from the spectral representation of \( \sigma \):

\[
\sigma = s_1 s_1 \otimes s_1 + s_2 s_2 \otimes s_2,
\]

(6.32)
where $S_1$ and $S_2$ are principal Cauchy stress components; and $s_1 = \cos \varphi e_1 + \sin \varphi e_2$ and $s_2 = -\sin \varphi e_1 + \cos \varphi e_2$ are the corresponding principal directions. The orientation $\varphi$ is measured from a fixed material axis aligned with the zigzag direction of the graphene lattice.

Employing the above transformation, we obtain the failure function in stress space as a functional relation between the components of the functional bases comprising the maximum principal Cauchy stress $S_1$, the mean Cauchy stress $\bar{S} = (S_1 + S_2)/2$, and the symmetry-reduced principal strain direction $\theta = \arccos(\cos(6\varphi))$. The resulting failure function—in terms of $S_1$, $\bar{S}$, and $\Phi$—can be generically expressed in a form similar to failure function in strain space, i.e.,

$$\mathcal{T}_{\text{Upper}}(\sigma) \equiv S_1^2(\bar{S}, \Phi) - S_1 = 0. \quad (6.33)$$

and

$$\mathcal{T}_{\text{Lower}}(\sigma) \equiv S_2 - S_2^2(\bar{S}, \Phi) = 0. \quad (6.34)$$

The surfaces described by equation (6.33) and equation (6.34) constitute the upper and lower bounds of the failure surface in the space of principal stresses, as shown in Fig.[6-8-b]).

**Remark I:**

It should be noted that the proposed model, in spirit, is similar to Drucker-Prager failure surface of pressure-dependent solids, given by $\sqrt{J_2} = a + bI_1$, wherein the maximum deviatoric stress before failure depends upon the level of imposed pressure. However, graphene, owing to its crystallinity, anisotropy and strictly 2D structure, is
a much more complex material than a conventional continuum solid. Accordingly, the
proposed model is more complex and more involved than the Drucker-Prager model;
yet it has a simple form with very few constants. In the following, we highlight the
major features of the proposed model —

1. The Drucker-Prager model is applicable to isotropic solids; the model proposed
here is anisotropic because graphene is intrinsically an anisotropic material;
therefore, in addition to the areal strain $\epsilon_a$ (equivalent to first invariant $I_1$) and
deviatoric invariant (equivalent to $J_2$), the failure model also involves a third
invariant $\Theta$, accounting for the anisotropy of the graphene.

2. The Drucker-Prager model predicts the onset of plasticity; while graphene is a
brittle material (as established by various experiments in the literature) therefore in
our model the failure denotes initiation of a crack in otherwise a flawless material.

3. There are different kinds of microscopic mechanism that lead to failure of the
lattice, under different modes of deformation, i.e., a soft-mode or an elastic
instability. The proposed failure model not only obtains the critical state of
deformation but also successfully identifies the governing mechanism responsible for the failure under that mode of deformation.

4. Graphene, being a strictly two-D structure, has an exceedingly small bending rigidity. Therefore, a possible mode of failure under certain states of deformation is buckling instability in graphene. It is noted that whether the critical deviatoric stretch (stress) results in a material failure (fracture) or a structural failure (buckling) depends on the equi-biaxial stretch level (pressure): at small equi-biaxial stress the failure occurs via buckling, a structural failure whereas above a certain equi-biaxial stress, the failure is invariably a material failure (fracture).

6.5 Validation

The failure surface, given by equations (6.28 & 6.29), contains information of all possible lattice-instabilities that can be triggered by homogeneous deformations. Specifically, once this failure surface is determined, we can assess the stability of graphene subject to a biaxial state of strain — \( \mathcal{E}^\alpha_{11} \mathbf{v}_1 \otimes \mathbf{v}_1 + \mathcal{E}^\alpha_{22} \mathbf{v}_2 \otimes \mathbf{v}_2 \) — for any biaxiality (the \( \mathcal{E}^\alpha_{11} \) to \( \mathcal{E}^\alpha_{22} \) ratio) and any directionality (characterized by \( \alpha \)). For such deformations, the principal strains are directly given by the strain components \( \mathcal{E}^\alpha_{11} \) and \( \mathcal{E}^\alpha_{22} \) as \( \mathcal{E}_1 = \max[\mathcal{E}^\alpha_{11}, \mathcal{E}^\alpha_{22}] \) and \( \mathcal{E}_2 = \min[\mathcal{E}^\alpha_{11}, \mathcal{E}^\alpha_{22}] \). Employing this relation, and substituting the value of \( \alpha \) in the failure surface, we can project the failure surface onto a 2D contour describing the stability-limits in terms of the two strain components \( \mathcal{E}^\alpha_{11} \) and \( \mathcal{E}^\alpha_{22} \). For example, Fig. [6-9-b], we show the 2D failure contour corresponding to the directionality \( \alpha = 0 \). This contour characterizes the stability of a graphene sheet subjected to a homogeneous biaxial state of strain referred to the set of axes defined by \( \alpha = 0 \), i.e., \( \mathbf{v}_1 - \mathbf{v}_2 \) are aligned with \( \mathbf{e}_1 - \mathbf{e}_2 \).

On this contour, we have indicated points corresponding to various homoge-
nous deformation cases such as uniaxial strain and uniaxial stress along the armchair and zigzag directions: (1) the point — indicated as $\mathbf{A}_1$ — with coordinates $(\varepsilon_{11}^0 = 0.17, \varepsilon_{22}^0 = 0)$ denotes uniaxial strain along the zigzag direction (2) the point — indicated as $\mathbf{A}_2$ — with coordinates $(\varepsilon_{22}^0 = 0.21, \varepsilon_{11}^0 = 0)$ denotes uniaxial strain along the armchair direction. (3) the point — indicated as $\mathbf{v}_1$, with the largest positive value of $\varepsilon_{11}^0$ while $\varepsilon_{22}^0 < 0$ denotes elastic failure under uniaxial tension in the armchair direction. (4) Similarly, the point — marked $\mathbf{v}_2$ — with the largest positive value of $\varepsilon_{22}^0$ while $\varepsilon_{11}^0 < 0$ denotes uniaxial tension in the zigzag direction. (5) The point indicated by $\blacksquare$ denotes the limiting strain under equi-biaxial strain. Interestingly, we notice that close to the two axes, the contour is quite flat, and limiting strains for uniaxial strain and stress are almost the same. However, this should be expected since the Poisson ratio of graphene rapidly decreases with strain. Hence, as we reach close to the stability limit, the Poisson ratio has already degraded to a small value, and therefore the uniaxial stress and uniaxial strain cases almost become identical.

Following the procedure outlined in the above, it is possible to obtain the failure contour for any given directionality $\alpha$, and to obtain the corresponding stability-limiting values of stress/strain in uniaxial strain/stress.

### 6.5.1 Comparison between predicted response and calculated values from DFPT

First, we assess the predictive capability of the failure function from a numerical accuracy point of view. For this purpose, we compute the stability-limiting critical strains — for biaxial deformations referred to set of axes that are not included in the sampling set — and compare with directly-calculated values from analysis of phonons. As seen in Fig.[6-10], the agreement between the predicted stability limits from the failure model and the calculated values is very close. This, in particular, highlights
the efficacy of the symmetry-invariants based representation in constitutive modeling, since the representation of the failure function utilized the explicit calculations only along the two symmetry-directions of graphene. Previously also, in hyperelastic constitutive modeling of graphene, we showed that the representation in terms of symmetry-invariants not only reduces the number of constants in the model; but it also elucidates the underlying hyperelastic softening behavior of the graphene lattice.

6.5.2 Comparison with acoustic tensor analysis — elastic (material) instabilities in tension

Previously, we showed that both the 2D area modulus $\kappa(\epsilon_a) = \left[ \frac{\partial \sigma_a}{\partial \epsilon_a} \right]_{\ln \lambda=0}$ and the 2D shear modulus $\mu(\epsilon_a)$ of graphene experience a progressive softening with increasing areal strain. The progressive softening of the elastic moduli is often responsible for long-wavelength material instabilities of the underlying lattice. The acoustic tensor derived from the constitutive response can be used to determine the macroscopic instabilities of the graphene lattice, arising from the hyperelastic softening. If, for
Figure 6-10: Shown are the failure contours for biaxial strains with directionalities (a) $\alpha = \pi/6$ (b) $\alpha = \pi/15$ (c) $\alpha = \pi/10$ and (d) $\alpha = 2\pi/15$. These directionalities are not included in the interpolation procedure. The predicted failure limits (solid red lines) by the model are in close agreement with the directly calculated values (connected blue dots) obtained from DFPT analysis.
some pair of unit vectors \( \mathbf{m} \) and \( \mathbf{n} \),

\[
\Lambda(\mathbf{m}, \mathbf{n}) = (\mathbf{m} \otimes \mathbf{n}) : \mathbb{A} : (\mathbf{m} \otimes \mathbf{n}) \leq 0,
\] (6.35)

then the material is elastically unstable; here \( \mathbb{A} = \frac{\partial^2 \psi}{\partial \mathbf{F}^2} \) is the acoustic tensor (see the Chapter 5 of this thesis) for detailed evaluation of \( \mathbb{A} \). Employing the acoustic tensor-based analysis, we determine the stability-limiting critical strains for varying biaxiality in a biaxial deformation with stretch axes \( \mathbf{r}_1 - \mathbf{r}_2 \) aligned along zigzag-armchair (\( \mathbf{e}_1 - \mathbf{e}_2 \)) set of axes, i.e.,

\[
\mathbf{E}^{(0)} = C_{11}^0 \mathbf{e}_1 \otimes \mathbf{e}_1 + C_{22}^0 \mathbf{e}_2 \otimes \mathbf{e}_2. \tag{6.36}
\]

We plot the resulting limiting values of \( C_{11}^0, C_{22}^0 \) — obtained from acoustic tensor analysis — and superpose them on the phonon-instability contour as shown in Fig.[6-11]. The agreement is close, except in the neighborhood of the equi-biaxial deformation. Recall that the lattice-instabilities, depending upon the wavelength of the unstable perturbation, are distinguished as: (a) microscopic instability — which is the instability in material response with respect to a finite-wavelength perturbation, i.e., an incremental inhomogeneous deformation; or (b) macroscopic (or elastic) instability — which is the instability in material response with respect to an incremental homogeneous deformation of the underlying lattice. The two kinds of instabilities, in dispersion of phonons, are seen as whether \( \omega_n(q \neq 0) = 0 \) (a microscopic instability) or \( d\omega_n/dq|_{q=0} = 0 \) for some \( n \) (in which case its a macroscopic instability). Near equi-biaxial deformations (\( C_{11}^0 \approx C_{22}^0 \)), the instability of the graphene lattice is not of elastic nature but corresponds to microscopic soft-phonon modes (see Yevick & Marianetti [125]), which can not be detected via acoustic-tensor analysis. Following a simple algebraic procedure, it can also be shown that in the long wavelength limit, the phonon-based criterion and the acoustic tensor based condition become equiva-
lent, and therefore in the case of elastic instabilities, the agreement between results of the two analyses is close.

6.5.3 Comparison with buckling analysis — structural instabilities in compression

The 2D acoustic tensor— based on the in-plane constitutive response— captures material instabilities of macroscopic (elastic) nature only. However, in addition to material instabilities, structural instabilities of non-material nature may also arise. These instabilities are the buckling instabilities ensued by compressive stresses (precisely speaking, when at least one of the eigenvalues of $\sigma$ becomes less than zero). The buckling modes on the instability contour are identified as the state of strains at which one of the principal stress components vanishes. For example, in biaxial deformations with stretch axes $r_1 - r_2$ aligned along zigzag-armchair set of axes, the buckling stability-limits are given by strain trajectories (shown in Blue in Fig.[6-11-a]) calculated from the constitutive model for uniaxial tensile stress along these two special directions.

It is interesting to see that, in the small strain limit, the two buckling stability-limiting contours are related to Poisson contraction along the zigzag and armchair directions. At small strains, graphene is isotropic, and linearization of the constitutive relation in terms of principal stresses and strains can be written as

$$S_{11}^0 = E_{2D}(\varepsilon_{11}^0 + \nu^{(0)}\varepsilon_{22}^0);$$  \hspace{1cm} (6.37)

and

$$S_{22}^0 = E_{2D}(\varepsilon_{22}^0 + \nu^{(0)}\varepsilon_{11}^0).$$  \hspace{1cm} (6.38)

Here the asymptotic value of the in-plane Poisson ratio emerging from our constitutive model is $\nu^{(0)} = 0.203$. The asymptotic principal strain trajectories corresponding to
the condition of buckling instability are obtained as

\[ E_2' = -\nu^{(0)}E_1', E_1' > E_2'; \]  
\[ (6.39) \]

and

\[ E_1'^0 = -\nu^{(0)}E_2^0, E_2^0 > E_1^0. \]  
\[ (6.40) \]

The two stability-limiting trajectories on the \( E_{11}^0 - E_{22}^0 \) plane in the asymptotic limit correspond to straight lines emanating from origin with slopes \(-\nu^{(0)}\), and \(-1/\nu^{(0)}\), respectively; and as noted previously \( E_{2D} \) is the elastic modulus of graphene in uniaxial strain.

**Remark II:**

The region bounded between the two radial lines in Fig.[6-11-a \\& b] denotes the area in which the soft mode instability precedes the elastic instability. Interestingly, we notice that this region, which occupies a large fraction of area in strain-space, maps to a region with much reduced area fraction in stress-space. This shrinkage is due to the nonlinear material softening, i.e., the decay in tangent moduli decay with strain. At large strains, the tangent shear modulus decays to a small fraction of its undeformed value. For the same reason, the difference by which the soft mode precedes the elastic instability is also much reduced in stress-space compared to strain-space.

**Remark III:**

We note that the results from buckling and phonon-stability analyses yield increasingly deviant results as the strains grow large. Particularly, the occurrence of flexural...
Figure 6-11: (a) Failure contour in strain space for biaxial state of strain with $\alpha = 0$, superposed with elastic-stability limit curve obtained from acoustic tensor analysis and the buckling-instability curve obtained from Poisson analysis. (b) The corresponding curves in stress-space. Note that the contraction due to ‘Poisson effects’ decreases as the strain increases. Intersection of Poisson analysis and the acoustic instability analysis marks the uniaxial tension failure. Note that in nearly equi-biaxial deformations, the phonon-instability precedes the elastic instability (conforming with Yevick & Marianetti’s [125] calculations), indicating that in such deformations, lattice instability is due to a short-wavelength instability.
mode instability after the lateral strain allowed by Poisson contraction limit may give the false impression that a finite compressive stress is required to buckle the graphene sheet. Instead, this is merely a consequence of numerical artifacts introduced by the application of the acoustic sum rule (ASR) in the DFPT calculations [130]. Translational invariance requires that the frequencies of all acoustic vibrational modes approach zero as $q \to 0$ (i.e., at $\Gamma$ of the BZ). However, in a DFPT calculation, this can be precisely achieved only in the limit of a continuous $k$-point mesh, i.e., an infinite number of $k$-points. On any finite, and therefore discrete, $k$-point mesh, the trace of the interatomic force constant (IFC) matrix is never exactly zero, and the computed acoustic vibrational frequencies do not exactly vanish at $\Gamma$. The standard ASR — to remedy this — uniformly ‘corrects’ the diagonal components of the IFC matrix — the correction term being proportional to the trace of the discretely-computed IFC matrix. This modification renders the modified IFC matrix traceless, ensuring that all acoustic frequencies computed at $\Gamma$ vanish. However, such a correction also changes the acoustic mode frequencies near $\Gamma$, i.e., the slope of the flexural branch is altered. At small strains, we find that the correction is very mild (the deviation itself being small), and therefore, the computed slope remains largely unaffected. Note that the corrected slopes computed for the isotropic long-wavelength LA and TA acoustic modes in the reference configuration, given in Table (6.1), are in good agreement with other data. For a given $k$-point grid, the calculated acoustic mode frequencies deviate more from acoustic sum rule as the crystal is subjected to increasing shape-changing deformation. This is attributed to (1) the reduction in the symmetry of the crystal, which increases the size of the irreducible wedge of the Brillouin zone, and (2) the change in shape of the Brillouin zone, which causes the $k$-point grid to move relative to Fermi surface and spurious change in energy [163].
6.6 Implementation of failure function in a continuum FEA scheme

6.6.1 Outline of the methodology

In the following, we outline a systematic procedure for implementation of the proposed failure function in a finite element analysis applied to provide an on-the-fly assessment of incipient material failure during monotonic loading.

- First, using the continuum-level FEA based on the nonlinear constitutive model of equation (6.30) and equation (6.31) — we obtain the macroscopic deformation field associated with the given boundary-value problem at the current load/displacement increment. Note that the stress/strain field in general is inhomogeneous; however, if the spatial variation of elastic fields varies sufficiently slowly, each material element in a sufficiently fine mesh can be fairly assumed to be in the state of homogeneous deformation, with the local stress/strain determined from the macroscopic deformation field.

- Based on the local stress/strain value, we make an on-the-fly assessment of the failure function at the material points in the mesh for the current load/displacement step. For each loading increment, the material points with the minimum values of the failure function are identified as ‘weakened-spots’.

- Value of the critical macroscopic load/displacement is determined by identifying the load/displacement increment along the loading path at which the failure function at a weakened-spot first vanishes. The weakened-spot is then declared as a ‘failed region’, and the corresponding load/displacement can be considered as failure load/displacement.

- We determine values of the critical stress/strain by locating the point of in-
intersection of the stress/strain trajectory traced by the ‘failed’ material points during the course of loading with the failure surface.

- Finally, we check if the failure surface precedes or coincides with the acoustic-instability surface at the point of intersection. This allows us to determine whether the instability is a soft mode instability or an elastic instability, respectively.

**Remark IV:**

The phonons are defined w.r.t. an ideal infinite crystal without any surface or boundary; therefore application of phonons to stability detection in real boundary-value problems requires a little care. For this we need a volume/area element the size of which should be sufficiently large so that (1) it accommodates the unstable mode, and (2) its mechanical response is described well by the continuum constitutive relation. As long as in a given boundary value problem, we can identify such an RVE, the phonons can be used an an indicator of material stability in the RVE. Once such an RVE is identified, the instability can be detected by phonon-based lattice instability analysis.

### 6.6.2 Failure analysis in blistering

As an illustrative application, we analyze the failure of a graphene sheet in a FEA simulation of blister test employing the proposed scheme. Blistering involves bulging of a graphene sheet clamped at its boundary on top of a microcavity containing a pressurized gas, which creates a pressure-difference, $\Delta P$, across the graphene membrane. Two different geometries for the constrained boundary are considered in our work: elliptical and circular, while the characteristic dimension $\zeta = \sqrt{ab}$, where $a$ and $b$ are major and minor radii, remains the same (see figure [6-12]). For elliptical geometry, we choose $a = 1.0 \mu m$ and $b = 0.5 \mu m$ with long-axis aligned along the zigzag
Figure 6-12: Schematic of blistering (a) of an elliptic membrane and (b) of a circular membrane. The membrane is clamped at the boundary, and is subjected to a pressure (denoted by arrows) from below, resulting in the bulged configuration as shown in the figure. The state of strain at the center of the membrane is equi-biaxial in case of a circular membrane whereas it is biaxial with larger strain in the minor direction in case of elliptic membrane.

direction and the short-axis aligned with the armchair direction; and for circular geometry, we choose $a = b = \frac{1}{\sqrt{2}} \mu m$. We emphasize that a strictly clamped boundary condition is a modeling idealization, and not a feature of actual experiments. In nanoblistering experiments, a graphene sheet is held on the substrate by the interfacial adhesion between the two surface, and upon reaching a certain pressure-difference, the membrane starts to peel-off from the substrate. In our simulations, we suppress this peel-off event by explicitly clamping the graphene sheet on the substrate. Our objective is to determine the macroscopic and microscopic conditions at which the graphene sheet would fail. Numerically implementing the constitutive response and the failure function in a commercial FEA program ABAQUS [79], we explicitly determine the critical pressure-difference $\Delta P^\text{Crit}_0$ and the critical central deflection $\delta^\text{Crit}_c$; the location of unstable material element; the local stress and strain at the unstable element; and the nature of instability. We demonstrate this procedure systematically for the blistering of the circular graphene sheet.
Figure 6-13: Sequence of images showing the evolution of the stability-indicator $F = \mathcal{E}_1^c((\mathcal{E}, \theta)) - \mathcal{E}_1$ as a function of pressure-difference across the circular membrane. The central region with negative value of the stability indicator indicates the material elements that have reached the limits of stability, which are at the verge of mechanical failure.

(a) Location of unstable material element and geometry of failed region

To locate the unstable material element, we monitor the evolution of the stability indicator $F = \mathcal{E}_1^c - \mathcal{E}_1$ over the suspended graphene sheet, as a function of externally-applied pressure-difference. The material element at which the stability indicator vanishes first denotes the unstable region, which will subsequently fail. This unstable region determines the geometry of the fracture. For example, in blistering of a circular graphene sheet, based on the negativity of the unstable region, we would expect that the fracture initiation would occur at the center in the form of a nearly circular void (see figure [6-13]).
(b) Pressure-difference and maximum deflection at onset of instability

We determine the critical pressure and the critical deflection by tracing the occurrence of instability on the pressure-difference vs central deflection response curve (shown in Fig. [6-14]). It should be noted that the hyperbolicity of the elastic-wave equations is essential for a continuum finite element analysis step to continue [46]; if an elastic instability is first reached along a loading path — as in the case of the clamped elliptical graphene sheet under pressure — then the condition of hyperbolicity ceases to hold, and the FEA step immediately terminates due to excessive distortion of elastically unstable elements. On the other hand, if a soft-mode instability is first reached on the loading path, the elastic-wave equation remains hyperbolic, and the finite element simulation continues until an elastic-instability along the loading path is reached. For example, during the blistering of a clamped circular sheet, the microscopic soft-mode instability takes place prior to the elastic instability; the simulation continues past the soft-mode instability, eventually terminating at the point of elastic-instability due to excessive distortion of elastically unstable elements. We have indicated the initial encounter with both the soft-mode and the elastic instability on the pressure-deflection response curves of Fig. [6-14].

(c) Local stress/strain at the unstable material element

The local principal strains $\varepsilon_1$ and $\varepsilon_2$ at the critical material element immediately after the onset of instability are obtained from the trajectory in terms of the two principal strains, obtaining the intersection of this trajectory with the instability surface as shown in Fig. [6-15]. Similarly, by tracing the material point trajectory of principal stress components $S_1$ and $S_2$, and locating its intersection with the instability surface in the stress space, we obtain the local principal stress at the critical material element.
Figure 6-14: Pressure vs central deflection curve for the two example problems considered. On this plot, the macroscopic (elastic) instabilities are located by a ×; while the location of a soft-mode (microscopic) instabilities is denoted by +.

From Tab.[6.3], we note that the failure stress and strain in the blistering simulations are inherently dependent on the geometry of the constrained boundary. Due to the fact that for certain geometries, e.g., when $a \approx b$, the failure is mediated by a microscopic soft-mode instability, the sensitivity of the failure stress/strain on the geometry of the constrained boundary can not be explained by the material anisotropy or the nonlinear softening in the material response alone. Thus, in a global sense, the proposed failure model is a useful method for assessment of correlation between the failure stress/strain and extrinsic factors.

(d) Nature of instability: macroscopic versus microscopic instabilities

The proposed failure function captures lattice instabilities of all kinds; however, without resolving whether it is macroscopic (elastic) or microscopic (soft mode) in nature. By means of the present examples, we illustrate that the proposed method not only locates the instabilities, but also provides a distinction between macroscopic and microscopic instabilities. To this end, we use the fact that an acoustic tensor analysis captures macroscopic instabilities (see Chapter 5) but not the microscopic one to
<table>
<thead>
<tr>
<th>Geometry of constrained boundary</th>
<th>$S_1$ (GPa)</th>
<th>$\varepsilon_1$</th>
<th>Nature of instability</th>
<th>$\Delta P_0^{\text{Crit}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elliptical</td>
<td>111 (110.2)</td>
<td>0.20 (0.195)</td>
<td>Elastic</td>
<td>72</td>
</tr>
<tr>
<td>Circular</td>
<td>92 (100)</td>
<td>0.1475 (0.178)</td>
<td>Soft-mode</td>
<td>62</td>
</tr>
</tbody>
</table>

Table 6.3: Local major principal stress and local major principal strain at the unstable material element as calculated by finite element analysis. The values of stress and strain indicated in parenthesis correspond to the predictions from the acoustic tensor analysis based on the constitutive model.
Figure 6-15: (a) The deformation path of the critical material element traced in terms of $\varepsilon_1$, $\tilde{\varepsilon}$, and $\theta$ (shown by dashed red line) and in terms of $\varepsilon_2$, $\tilde{\varepsilon}$, and $\theta$ (shown by dashed green line). The intersection of the deformation path with the failure surface indicates the onset of failure. (b) On a 2D plot, the trajectories in terms of normal strains $\varepsilon_{11}^0$ and $\varepsilon_{22}^0$ for the elliptical (denoted by E) and the circular (denoted by C). For elliptical membrane, the points of intersection of the trajectory with the failure contour and the elastic instability curve coincide indicating that the failure is of acoustic nature; while for the circular membrane, the intersection with the failure contour precedes that with the elastic instability curve, indicating that the failure is triggered by a soft mode instability.

resolve the nature of the instability as the following: if the instability is indeed a macroscopic instability, the results from the failure function as well the acoustic-tensor analysis coincide; however, when the instability is a soft mode, the result from failure-function precedes the acoustic analysis.

6.7 Conclusion

The failure modeling in defect-free crystalline materials is complicated due to the fact that there are several mechanisms potentially governing the failure in such materials. Material failure along a majority of deformation paths is a consequence of an elastic instability in the material response. Such elastic instabilities can easily be predicted by a continuum acoustic tensor analysis once an appropriate non-linear constitutive function for the mechanical response of the material has been formu-
lated, as shown in Chapter 5 of this thesis. Yet, there also remains a small but finite domain of deformation paths along which the failure of the material is limited by a short-wavelength instability mechanism, also called a soft-mode. Since there exists no equivalent continuum-criterion to mark the onset of such instabilities, the prediction of such instabilities remains beyond the scope of continuum analyses.

In this Chapter, we developed a continuum-level criterion to characterize the internal stability of a defect-free graphene sheet — both in terms of stress and strain — with respect to perturbation of all kinds. This model can address the incipient failure of graphene under an arbitrary loading condition at realistic length scales, by virtue of its continuum description, while the built-in microscopic lattice dynamical theory of stability analysis allows us to capture instabilities as short as the size of few unit-cells. This is the first time a continuum failure model for graphene has been proposed. The model is constructed from interpolation based on symmetry-invariants of the logarithmic strain measure. It is shown that usage of symmetry-invariants reduces the sampled deformation paths required for representation to the bare minimum of two: when represented in terms of symmetry-invariants, the sampling along the two special directions suffices to obtain an accurate representation describing the failure along deformation paths not included in the original sampling set.

We demonstrated that the model can be conveniently embedded into a finite element simulation scheme, together with the hyperelastic constitutive model. The resulting scheme, with the nonlinear hyperelastic model describing the mechanical response of graphene and the instability model predicting the onset of failure, will be capable of performing an on-the-fly lattice stability analysis within an on-going finite element calculation. Such a model can predict (a) location of the unstable material point (b) the load/displacement at the onset of instability, and (c) character of the instability, i.e., a short-wave or a long-wave in realistic boundary-value problems.

We view this work as a step towards a rigorous assessment of the ideal strength
measurements of graphene carried out via nanoindentation experiments, with the purpose of examining the role of factors such as the boundary condition, the indenter-membrane interaction, and the surface condition at the indenter tip on the measurement. Nanoindentation involves the instrumented indentation of a suspended graphene sheet by a nano-scale diamond indenter. However, the stress and strain are not directly measurable in such experiments; instead, the macroscopic load/pressure as a function of deflection during the course of experiment is recorded. Continuum-level FEA simulations based on the large-deformation constitutive response of graphene is then used to estimate the stress underneath the indenter, corresponding to the failure load and deflection [105, 160, 198]. The value thus measured represents the ideal strength. During the course of such experiments, many subtle atomic-level interactions ranging from weak van der Waals (vdW) forces to strong chemical interactions between the contacting surfaces take place simultaneously. These interactions are often ignored on the assumption that the microscopic activities have zero or minimal effect on the macroscopic outcome [105, 198]. This assumption, in the context of the indentation of a bulk material, can be reasoned as valid because the unstable region lies in the interior of the material, away from the indenter’s influence. However, in the context of nanoindentation of suspended graphene, the assumption may not hold since the potentially-unstable regime of the membrane remains under the influence of the chemical interaction of the indenter throughout the indentation process.

The FEA analyses — in the absence of a multi-scale criterion to assess the incipient failure — can not answer the question of whether the subtle microscopic interactions are extraneous or have a measurable effect on the outcome of a strength-measuring experiment. Molecular Dynamics (MD) simulations based on reactive bond order potential, which appropriately capture the atomistic details, may shed light on this; however, owing to prohibitive computational cost, such simulations are limited to very small systems or very high loading rates, or both. Therefore, it is desirable
to develop an atomistic-to-continuum bridge, allowing an independent and accurate assessment of failure within the framework of FEA simulations. The results of this assessment, when compared with experiments, should be able to elucidate on the role of microscopic activities on the macroscopic outcome of the experiment. A detailed investigation on how the interfacial interaction at graphene-indenter interface affects the measured macroscopic response is presented in Chapter 9 of this thesis.
Chapter 7

Continuum traction-separation law for Graphene-Diamond interface: vdw + covalent interaction

7.1 Introduction

From a tribological applications point of view, diamond and diamond-like carbon are important materials. A common substrate material in graphene-related applications is $a-SiO_2$. However, $a-SiO_2$ suffers from a high thermal-resistivity, which becomes a major limiting factor for the current-carrying capacity of the graphene-based devices fabricated on $a-SiO_2$ [210]. Diamond, which does not have this deficiency, is emerging as a viable substitute for $a-SiO_2$. Graphene-diamond hybrid structures have been the subject of the recent numerous experimental and theoretical investigations. [208, 210, 190]. These studies have shown that the current carrying capacity of graphene is significantly improved when supported on the single-crystal diamond substrates. Diamond also has a high energy of surface vibrational modes and lower surface trap density compared to $SiO_2$ [210]. Due to its distinct cage-like structure, di-
amond is also endowed with large elastic stiffness/strength and hardness. Diamond’s hardness and resistance against plastic deformation make it an ideal material for the purposes of indentation on other materials, and therefore it is often used an indenter in routine indentation experiments [105, 160, 107].

The graphene- diamond interfacial interaction possesses two main distinctions, when compared to the graphene-\(a–\)SiO\(_2\) interaction.

- First, both diamond and graphene are allotropes of carbon. The C atoms, in diamond, are \(sp^3\)-hybridized, covalently bonded in a cage-like structure; while in graphene, the C atoms are \(sp^2\)-hybridized, and form a planar honeycomb structure. However, as evident from various studies [121, 27, 93, 28], \(sp^2\)-hybridized C, under a mechanical or thermal actuation, can undergo a change in hybridization state; and thus a covalent interaction is relatively easily facilitated between two carbonaceous surfaces. Experiments of Mao, et al. [121] showed that upon cold compression of graphite, some of the C atoms undergo a change in hybridization state from \(sp^2\) to \(sp^3\). This results in replacing the \(p\)-orbital (and hence loss of \(\pi\)-bonds) in a C atom by an additional \(sp^3\)-hybridized orbital which allows the atom to pair-up with an atom in the adjacent layer to form a \(\sigma\)-bond. In the process, the atoms move out of the graphitic plane resulting in distortion of the basal plane. Through their molecular dynamics simulation, Boulfelfel, et al. [27] demonstrated that the resulting cross-linked allotrope, a metastable phase, is order-of-magnitude harder than graphite.

- Second, in applications involving a graphene/\(a–\)SiO\(_2\) interface, the interface experiences almost none or weak interfacial compression, while in certain applications involving a graphene-diamond interface, the interface may be subjected to a large compressive interfacial forces, e.g., in nano-indentation [105, 160] where the graphene monolayer beneath the diamond indenter experiences large
compressive contact stresses (of the order of several GPa). Such large compressive stress brings graphene in atomistically close proximity of diamond surfaces, and the wave-functions of the surface atoms begin to overlap; consequently, a stronger chemical interaction may ensue. The mechanical interaction at the interface — while diamond is acting merely as a substrate without significant compressive/tensile load across the interface — is likely to be purely vdW interaction. On the other hand, during intense indentation, the indented surface comes in a close contact with the indenter surface. The interfacial interaction forces that are active when the two surfaces are brought in close proximity may have an important effect on the ultimate outcome of the indentation.

To adequately understand the effects of such interfacial forces on the outcomes of nano-indentation simulation, a mathematical model for graphene-diamond interfacial interaction that could be incorporated in a FEA simulation would be desired. In this chapter, we undertake this task. Specifically, we investigate the graphene-diamond interaction and develop a continuum model for interfacial stress as a function of interfacial separation — based on combined density functional theory and molecular dynamic calculations. The resulting continuum traction-separation relation for graphene-diamond interfaces describes both the weak vdW adhesion and the strong chemical interaction.

7.2 Background

For diamond, there are two most important surfaces from adsorption and growth points of view — the \{100\} surfaces and the \{111\} surfaces. During the chemical vapor deposition process, the major growth of the crystal occurs along these two surfaces [127, 202]. The growth rates on these surfaces depend upon temperature and the gas composition. The ratio of the \{100\} to the \{111\} growth rates is
called growth parameter ($\alpha$) defined as $\alpha = \sqrt{3} \frac{v_{100}}{v_{111}}$, where $v_{100}$ and $v_{111}$ are the growth velocities in the (100) and (111) directions. The surface morphology of the diamond crystal obtained from CVD critically depends upon the growth parameter. For example, if the process conditions are set to have the growth parameter $\alpha < 1$, then a cubic crystal growing along (100) directions is obtained; and if $\alpha > \sqrt{3}$ then the CVD-grown crystal assumes an octahedral shape bounded by {111}-planes. Accordingly, in this study, we focus on interaction of graphene with these two sets of crystallographic surfaces.

Previously, Ma, et al. [120] and Hu, et al. [86] considered a scenario when the graphene sheet is adsorbed on a diamond {111} surface without the application of an external force. Hu, et al. studied the interaction between graphene and a reconstructed {111} diamond substrate with large-scale density functional theory calculations. They considered a {111} diamond surface reconstructed according to Pandey’s $\pi$-bonded chain model. Their calculation also indicated that graphene weakly interacts with a diamond {111} surface, and that vdW forces dominate the interfacial interaction. Their adsorption height is slightly larger than the one reported by Ma, et al.. The reconstructed surface interacts much more weakly than the unreconstructed one. However, first-principles calculations of graphene absorption on a {111} surface of diamond indicate the contrary. Ma, et al.'s first-principles calculations with damped vdW correction indicate the absence of strong bonding interactions at the interface when the graphene monolayer is supported on an unreconstructed {111} surface of diamond [120]. These calculations show that the graphene sheet remains loosely bonded to a diamond {111} surface and the interfacial interaction is dominated by the vdW forces. The relaxed graphene sheet retains its planar geometry with the equilibrium interlayer spacing lying in the range of 2.7 - 2.9 Å depending upon the mutual registry of the two surfaces. Thus, the studies of Ma, et al. and Hu, et al. established that a graphene sheet resting on a diamond surface interact
via vdW forces. However, their investigation did not address the nature and specifics of graphene-diamond interaction when the two surfaces are in close proximity, due to the action of a compressive stress.

In this work, we use the combined DFT (corrected for dispersive forces) and MD studies to investigate the nature of interfacial interaction force when the graphene monolayer is brought in close proximity of the diamond $\{111\}$, and $\{100\}$ crystallographic surface by means of a large compressive stress. The objectives are twofold. First, we show that a graphene sheet on diamond has two equilibrium states: physisorbed at large separation and chemisorbed at small separations. Second, we calculate the variation of interaction energy and stress as a function of interfacial separation, and investigate the effect of relative registry between the two surfaces on the interaction energy landscape. The resulting data is used as an input to construct a continuum model for traction-separation relation for an entire range of separation — varying from small ($\sim 1.5\text{Å}$), at which covalent bonding forces dominate, to relatively large separation ($\sim 5\text{Å}$), at which weak vdW force govern the interaction. Such a knowledge would be inevitably useful to gain a clearer insight into the onset of instability in the graphene sheet lying underneath a diamond indenter in an indentation test where there is indeed a large contact compressive pressure acting between graphene and the indenter’s surface.

Using highly-accurate DFT calculations corrected for dispersive forces, we investigate the graphene-diamond $\{111\}$ interaction as a function of interfacial contact stress. The diamond $\{111\}$ surface is represented by a supercell containing a slab of eight bilayers in the $(111)$ direction and the graphene monolayer lying on the top. The supercell is periodically repeated in space with the two consecutive periodic images of the supercell in the $(111)$ direction separated by a vacuum region of $20 \text{ Å}$. The supercell periodicity in lateral directions is that of a triangular lattice with a lattice parameter of $2.52\text{Å}$ which is the optimized lattice constant for the diamond lattice.
(see figure[7-1]). On this lattice, graphene and diamond are commensurate with ~2% lattice mismatch — which makes the investigation amenable to first-principles DFT calculations.

Such explicit DFT calculations are not feasible for diamond \{100\} surfaces since they have different symmetry than the graphene lattice, and a calculation involving a graphene sheet on a diamond \{100\} surface would require an enormously large supercell. Therefore, such calculations are not amenable to \textit{ab initio} DFT calculations. Instead, we employ relatively economical (computationally) MD simulations to investigate the graphene-diamond \{100\} interaction.

## 7.3 Computational details

The computational details of the two simulation techniques are presented below.

### 7.3.1 First-principles density functional theory

Our calculations are based on first-principles density functional theory as implemented in the PWSCF simulation package [66]. The exchange correlation energy of electrons is approximated by the generalized gradient function of Perdew, Burke, and Ernzerhof (PBE) corrected for dispersive forces (DFT-D) [152, 69, 10]. The interaction between ionic cores and valence electrons is represented by an ultrasoft pseudopotential [192]. Kohn-Sham wave functions were represented with a plane-wave basis with an energy cutoff of 30 Ry and a charge density with a cutoff 300 Ry. Integration over the irreducible Brillouin zone for charge density and total energy was performed with a uniform mesh of $12 \times 12 \times 1$ mesh of k-points, and occupation numbers were smeared using Marzari-Vanderbilt cold smearing technique with broadening of 0.03 Ry. Errors in the stresses and total energy due to basis-set size, smearing parameter, and k-points are converged to less than 0.1 GPa and 0.01 Ry, respectively.
7.3.2 Molecular dynamics based on reactive bond order potentials

The MD simulations have been performed in LAMMPS atomic simulator [158]. Our system comprises a rectangular graphene sheet of dimensions 4.6 nm × 2.6 nm on top of a slab of single-crystalline diamond. Two configurations are considered. In one configuration, the graphene sheet is exfoliated above a {100} face of diamond, while in the other configuration, the sheet is exfoliated above a {111} face. The C-C interaction was modeled by the Adaptive Intermolecular Reactive Bond Order (AIREBO) potential of Stuart, et al. [182]. The resulting configuration is minimized via conjugate gradient steps with an energy tolerance of $1 \times 10^{-16}$ eV. Then the C-atoms in graphene are equilibrated to 25 K temperature using 10000 steps of MD NVT while the C-atoms in the diamond slab are kept frozen. For each configuration, two sets of numerical experiments are conducted — (1) a pull test and (2) a peel test.

(a). Pull test: This test comprises relaxation of a graphene on the diamond surface via conjugate gradient minimization; equilibration at 25 K temperature by applying 10000 MD steps with Nosé-Hoover thermostat in NVT; and finally, the graphene sheet is pulled sideways from the right edge for 30000 MD isothermal steps (NVT ensemble).

(a). Peel test: This test comprises - relaxation of a graphene on the diamond surface via conjugate gradient minimization; equilibration at 25 K temperature by applying 10000 MD steps with Nosé-Hoover thermostat in NVT; and finally, the graphene sheet is peeled upward from the right edge for 30000 MD isothermal steps (NVT ensemble).
Figure 7-1: (A) The honeycomb lattice of graphene with the lattice constant indicated. Shown by the blue dotted line is the primitive unit cell of the lattice. (B) Top two layers of diamond \{111\}-crystallographic plane projected along the \{111\}-crystallographic direction. Planar bond lengths of the bilayer are very close to that of graphene lattice. The red atoms are on the top layer, while the orange atoms denote the layer beneath it. (C) Graphene monolayer on top of diamond \{111\} slab. The rectangular unit cell — used in the DFT calculation — is also shown.

7.4 Simulation results and discussions

7.4.1 Graphene-Diamond \{111\} interaction from DFT

First, we probe into graphene-diamond \{111\} interaction using first-principles DFT calculations. To obtain the variation of interaction energy with separation at a given registry, only the vertical position of the graphene lattice is constrained on the top of diamond \{111\} surface, and the atoms in graphene and the diamond slab are allowed to undergo full geometric relaxation. The interaction energy $\psi_{\text{adh}}$ as a function of the equilibrium separation $\zeta$ in the relaxed configuration are recorded as follows:

$$
\psi_{\text{adh}}(\zeta) = \frac{1}{A} \left( \psi_{\text{graphene/C\{111\}}} - (\psi_{\text{C\{111\}}} + \psi_{\text{graphene}}) \right)
$$

(7.1)

where $\psi_{\text{graphene/C\{111\}}}$ is the total energy of the graphene+ diamond slab in the relaxed configuration, $\psi_{\text{C\{111\}}}$ is the total energy of the isolated diamond slab, and $\psi_{\text{graphene}}$ is the total energy of the isolated graphene monolayer, and $A$ is the area of the cell used in the calculation. This is carried out for a range of stand-off height values to obtain...
Figure 7-2: Graphene-diamond{111} interaction as a function of separation and registry: (A) & (B) The interaction energy and contact stress, respectively, as a function of separation for several different registries arising from relative position of graphene along the x-axis. (C) & (D) Same as (A) & (B) for registries arising from relative position of graphene along the y-axis. Note the rapid change in the stress at critical separation \( d_c \approx 2.25 \text{Å} \), marking the transition from physisorbed state to chemisorbed state. Two distinct wells, as noticed in energy vs separation plots, denote the physisorbed and chemisorbed states of the graphene lattice on diamond.

The plot of \( \psi_{\text{adh}} \) vs \( \zeta \) for the given registry. The procedure is repeated for several different registries, i.e., laterally shifted configurations of the graphene lattice w.r.t. the diamond lattice such that an atom in the graphene lattice, originally at \( m\mathbf{a}_x + n\mathbf{a}_y \), shifted to \( m\mathbf{a}_x + n\mathbf{a}_y + \eta \); \( \eta = (\eta_x, \eta_y) \) is the shift vector. For all the registries, we notice two distinct local minima (wells) in the \( \psi_{\text{adh}} \) vs \( \zeta \) landscape (see figure[7-2]). The DFT-based ground state energy calculations show that the potential energy landscape, as a function of the graphene-diamond separation, contains two local minima (wells): one corresponding to the bonded state and the other corresponding to the physisorbed state. The chemisorbed state is separated from the physisorbed state by an energy barrier. Therefore, upon action of the requisite mechanical pressure, a graphene sheet supported on a diamond surface can transition from the physisorbed state to the chemisorbed state.

- **Bonded or chemisorbed state**: If the stand-off distance at the beginning of relaxation is in the range \( \zeta \approx 1.45 - 1.75 \text{Å} \), then the graphene sheet settles to a bonded equilibrium state. The compressive load induces a \( sp^2 - sp^3 \) transition in the hybridization state of C-atoms of the graphene lattice. These atoms, which now have a dangling bond, subsequently pair-up with the underlying C-atoms on the diamond \{111\} surface forming covalent \( \sigma \)-bonds. The bond formation process is accompanied by puckering of the graphene sheet resembling a C \{111\} bilayer. Thus, in a way, the graphene sheet merges into the C(111) surface, becoming a part of diamond lattice. The equilibrium stand-off distance
in chemisorbed state is \( \approx 1.54\text{Å} \).

- **Physisorbed state**: For intermediate values of the initial stand-off distance \( 1.75\text{Å} \leq \zeta \leq 5\text{Å} \), the graphene monolayer settles down to an equilibrium state determined by the minima of the vdW interfacial interaction energy. The equilibrium stand-off distance of graphene on a diamond \{111\} surface in the physisorbed state is \( \zeta = 2.78 - 2.95\text{Å} \). In the physisorbed state, no conformational changes take place in the graphene sheet, i.e., it remains planar.

- **Isolated state**: For a much larger initial stand-off distance, i.e., \( \zeta \sim d_\infty \), the graphene layer does not move upon relaxation. The vdW attractive forces at such large distances have grown too weak to pull the graphene monolayer any closer.

To understand the conformal changes associated with the chemisorbed (bonded) state, we note that if the bonding occurs at the graphene-diamond interface, it would require \( sp^2 \rightarrow sp^3 \) transition in half of the C-atoms in the graphene lattice. A \( sp^2 \)-hybrid orbital is planar in geometry whereas a \( sp^3 \)-hybrid is tetrahedral. Therefore, a \( sp^2 \rightarrow sp^3 \) transition is accompanied by conformational changes, i.e., changes in orientation and bond length of some C-C bonds.

### 7.4.2 Graphene-Diamond \{111\} interaction from MD simulations

In this section, we employ MD simulations based on Stuart, *et al.*'s reactive potential [182] to obtain further corroboration that pushing a graphene sheet onto a diamond surface can ensue a bonded interaction. By means of molecular dynamics simulations, we now show that two distinct states of graphene sheet supported on a diamond surface exist, depending upon the interfacial contact stress between graphene sheet and the diamond surface (or, equivalently, the interfacial separation). In one of these
Figure 7-3: DFT-predicted chemisorbed states of Graphene on diamond \{111\}: The relaxed configurations and the charge density contours for the chemisorbed and physisorbed states of graphene on diamond: (A) For registry \( \eta_x = \eta_y = 0 \) — the structure corresponds to the \((1 \times 1)\) bulk-terminated diamond surface. The separation between the diamond surface and graphene monolayer is \( d_b \approx 1.5\text{Å} \). (B) Configuration for registry \( \eta_x = 0.1a_x; \eta_y = 0 \) — the resultant structure corresponds to the Pandey-Chain reconstruction comprising alternate pentagons and heptagons ([150]). The dimer structure can be clearly seen. The equilibrium separation in this case also is \( d_b \approx 1.5\text{Å} \). (C) Physisorbed state of graphene on diamond\{111\} — planar graphene with no charge complex formation. The equilibrium stand-off distance is \( d_D \approx 2.78\text{Å} \).
states, which occurs at low contact stresses, or equivalently, at interfacial separations larger than a certain critical value $d_c$, the interaction is governed by vdW forces, while at larger contact stresses, or equivalently, at interfacial separations smaller than $d_c$, a covalent bond is induced. The covalent bond, as opposed to the vdW interaction, is characterized by a strong shear stiction. First we investigate the nature of interaction between a graphene sheet and a bare diamond $\{111\}$ surface as a function of initial interfacial separation. The results from these simulations are presented in figures [7-4] - [7-7]. It is noted that when the initial separation between graphene and diamond $\zeta$ is in the range $\zeta < d_c$, then upon equilibration (energy minimization), the graphene sheet assumes a puckered geometry, resembling one of the diamond bilayers; and the sheet can not be dissociated from the diamond surface by pulling or peeling, indicating that a strong interaction exists between the two surface at this range of separations. On the other hand, when the initial separation is in the range $\zeta > d_c$, then upon relaxation — (1) we observe no puckering of graphene sheet, and (2) the sheet can be easily pulled or peeled off the diamond surface, indicating the presence of weak interaction at this range of separations. The results of the MD simulations are summarized in figures [7-4]-[7-7].

7.4.3 Graphene-Diamond $\{100\}$ interaction MD simulations

Unlike the graphene-diamond $\{100\}$ interface, the primitive unit cells of graphene and diamond $\{100\}$ lattice are not commensurate; and therefore such a investigation is not readily amenable to expensive DFT calculations. Therefore, we resort of AIREBO-based MD calculations. For this configuration as well, two cases are considered: first when the graphene sheet is exfoliated at a distance $\zeta > d_c$, and second when the sheet is exfoliated at a distance $\zeta < d_c$. Results similar to those for $\{111\}$ surface are again
Figure 7-4: Mechanically-activated covalent interaction between graphene and \{111\} diamond slab—Pull test: (A) Graphene monolayer is pushed onto the diamond surface to a separation $\zeta < d_c$ and allowed to relax via conjugate gradient energy minimization. Upon relaxation, the graphene sheet assumes a puckered geometry. (B) Following the relaxation step, the monolayer is pulled sideways from the right edge (suspended region). (C) The supported region of monolayer remains adhered to the diamond substrate, while the freely suspended region eventually fractures under the action of pulling force.

Figure 7-5: Mechanically-activated covalent interaction between graphene and \{111\} diamond slab—Peel test: (A) Graphene monolayer is pushed onto the diamond surface to a separation $\zeta < d_c$ and allowed to relax via conjugate gradient energy minimization. Upon relaxation, the graphene sheet assumes a puckered geometry. (B) Following the relaxation step, the monolayer is pulled upward (peeled) from the right edge. (C) The supported region of monolayer remains adhered to the diamond substrate, while the suspended portion is torn away under the action of peeling force.
Figure 7-6: **Graphene-Diamond \{111\} vdW interaction for \(\zeta > d_c\) — Peel test:** (A) Graphene monolayer on top of a bare \{111\} diamond surface with an initial stand-off distance \(\zeta > d_c\) after relaxation via conjugate gradient energy minimization. For this case, upon relaxation, no puckering is observed. (B) Following the relaxation step, the monolayer is pulled up from the freely suspended right edge. (C) In this case, the monolayer easily peels off the diamond surface.

Figure 7-7: **Graphene-Diamond \{111\} vdW interaction for \(\zeta > d_c\)—Pull test:** (A) Graphene monolayer on top of a bare \{111\} diamond surface with an initial stand-off distance \(\zeta > d_c\) after relaxation via conjugate gradient energy minimization. For this case, upon relaxation, no puckering is observed. Following the relaxation, the monolayer is pulled sideways from the freely suspended right edge (B), and the monolayer easily slides on the diamond surface (C).
Figure 7-8: **Graphene-Diamond (100) interaction**: The interaction energy vs separation curve obtained from AIREBO based MD calculation for graphene on diamond (100). obtained, as illustrated in figures [7-8-7-12].
Figure 7-9: **Graphene-Diamond** \{100\} stiction when $\zeta < d_c$—**Peel test:** (A) Graphene monolayer is pushed onto a diamond \{100\} surface to a separation $\zeta < d_c$ and allowed to relax via conjugate gradient energy minimization. Upon relaxation, the graphene sheet assumes a puckered geometry. (B) Following the relaxation step, the monolayer is pulled up (peeled) from the freely suspended right edge. (C) The supported region of monolayer remains adhered to the diamond substrate, while the suspended portion is torn away under the action of peeling force.

Figure 7-10: **Graphene-Diamond** \{100\} stiction when $\zeta < d_c$—**Pull test:** (A) Graphene monolayer is pushed onto the diamond \{100\} surface and allowed to relax via conjugate gradient energy minimization. Upon relaxation, the graphene sheet assumes a puckered geometry. (B) Following the relaxation step, the monolayer is pulled sideways from the freely suspended right edge. (C) The supported region of monolayer remains adhered to the diamond substrate, while the freely suspended region eventually fractures under the action of pulling force.
Figure 7-11: **Graphene-Diamond** \{100\} stiction when \( \zeta > d_c \)—Peel test: (A) Graphene monolayer on top of a bare \{100\} diamond surface with an initial stand-off distance \( \zeta > d_c \) after relaxation via conjugate gradient energy minimization. For this case, upon relaxation, no puckering is observed. (B) Following the relaxation step, the monolayer is pulled up from the right edge. (C) In this case, the monolayer easily peels off the diamond surface.
Figure 7-12: **Graphene-Diamond {100} stiction when \( \zeta > d_c \)—Pull test:** (A) Graphene monolayer on top of a bare \{100\} diamond surface with an initial stand-off distance \( \zeta > d_c \) after relaxation via conjugate gradient energy minimization. For this case, upon relaxation, no puckering is observed. Following the relaxation, the monolayer is dragged sideways from the right edge (B), and the monolayer easily slides on the diamond surface (C).
7.4.4 Effect of surface hydrogen

The simulations presented in section (7.4.2) and section (7.4.3) correspond to a scenario where the diamond surface is 'clean', i.e., it does not contain any physisorbed atoms on the surface. However, in reality, the diamond surface may have partial or full hydrogen saturation, depending upon the fabrication procedure and the history of surface treatments. Therefore, in this section, we investigate how the hydrogen saturation at the surface affects the mechanochemical interaction between graphene and diamond. For this purpose, the Pull and the Peel tests are performed on a fully-hydrogenated diamond \{111\} surface that is subjected to a contact pressure. The hydrogen atoms saturate the C atoms on the diamond surface, and in the presence of hydrogen on the surface, a C-C covalent bond can not be induced when the graphene surface is pushed onto the diamond surface.

The following observations are made based on the MD simulations:

1. First, we perform relaxation of a graphene sheet on a fully-hydrogenated diamond \{111\} surface, as shown in figure [7-13]. Earlier, in case of the bare diamond surface, we noted that upon equilibrating a graphene sheet on diamond \{111\} surface at an initial separation \(\zeta < d_c\) settles the graphene sheet to a chemisorbed state (smaller equilibrium distance \(d_b\)) while at an initial separation \(\zeta > d_c\), the graphene sheet settles to a physisorbed state (larger equilibrium distance \(d_D\)). However, upon relaxation of a graphene sheet on a hydrogenated diamond surface, unlike on a bare diamond surface, both at initial separations \(\zeta < d_c\) and \(\zeta > d_c\), the graphene sheet settles to a single equilibrium state with equilibrium separation close to \(d_D\). This clearly indicates that the adsorption of a graphene sheet on a hydrogenated diamond surface is characterized by a single equilibrium state for the entire range of interfacial separations.
Figure 7-13: Shown are the MD simulation results for relaxation of a graphene sheet on a hydrogenated diamond\{111\} surface at an initial interfacial separation \( \zeta < d_c \). It is noted that upon relaxation, the graphene sheet moves outward until it settles are larger equilibrium separation.

(2) To determine the nature of interaction at this equilibrium state, the equilibrated graphene sheet is pulled sideways on the diamond surface. The results of the pull test, shown in figure[7-14], indicate that at the equilibrium configuration, the graphene sheet is easily pulled out off the hydrogenated diamond surface. This means that the equilibrium state corresponds to a negligible shear strength — a characteristic of vdW-type interaction.

(3) Finally, the graphene sheet is pulled up from the right side from the hydrogenated diamond surface. The results are shown in figure[7-15]. It is noted that the graphene sheet is easily peeled off the surface, again indicating that the interfacial adhesion is of weak vdW-type.
Figure 7-14: Graphene on a hydrogenated diamond{111} surface—Pull test: the interaction is governed by a weak vdW-type forces, allowing the graphene sheet to be readily pulled away.
Figure 7-15: Graphene on a fully-hydrogenated diamond{111} surface — Peel test: in presence of surface hydrogen, the interaction is a weak vdW-type forces, allowing the graphene sheet to be readily peeled away.
7.5 Continuum model for graphene-diamond interaction

In this section, we obtain a continuum traction-separation relation for graphene-diamond mechanochemical interaction from the results of the DFT/MD simulations presented in section (7.4). The traction-separation law employed here is based on the Morse function to describe the normal-component of the traction vector. Consider a graphene sheet supported on flat substrate, as shown in the figure[7-16]. Let $\hat{\zeta}$ and $\hat{\eta}$ denote unit vectors normal and tangential to the substrate surface. While $\hat{\zeta}$ is uniquely defined by the normal to the surface, the tangent direction $\hat{\eta}$ is not; to uniquely determine it, the direction of the relative sliding between the two surfaces, $\hat{n}$, is required as well.

Our DFT and MD simulations indicate that the interaction between graphene and the indenter-tip falls under two regimes (figure [7-17]): when separation is larger than a critical value $-\zeta > d_c$ — the interaction is purely a vdW interaction described by equations [7.2-7.4]. However, under a compressive load, when the separation becomes less than the critical value $d_c$, i.e., $\zeta < d_c$, a substantial overlap between wave-functions emerges (see figure[7-3]) — indicating onset of a bonded interaction.
7.5.1 vdW-interaction

This vdW-interaction is modeled by the following traction-separation relation:

\[
t(Diamond-Graphene) = \sigma_{vdW}(\zeta)\dot{\zeta} + \tau_{vdW}(\zeta, \eta)\dot{\eta}; \quad \zeta > d_c
\]

(7.2)

It is assumed that the shear stiffness and strength associated with vdW interaction is very weak, and accordingly we assume that \( t\dot{\eta} = \tau_{vdW}(\eta, \zeta) = 0 \). The normal component of the traction — \( t\dot{\zeta} = \sigma_{vdW}(\zeta) \) — is derived from an interaction potential of the form:

\[
\psi_{vdW}(\zeta) = -\int_{\infty}^{\zeta} t \cdot d\zeta = -\Gamma_D \left( e^{-\alpha_D(\zeta-d_D)} - 1 \right) - 1
\]

(7.3)

The associated stress component is derived as:

\[
\sigma_{vdW}(\zeta) = -\frac{d\psi_{vdW}(\zeta)}{d\zeta} = -2\Gamma_D\alpha_D e^{-\alpha_D(\zeta-d_D)} \left( e^{-\alpha_D(\zeta-d_D)} - 1 \right)
\]

(7.4)

where the constants — \( \alpha_D, \Gamma_D \) and \( d_D \) — are obtained by fit to the vdW-interaction regime, defined as \( d_c \leq \zeta \leq d_\infty \), of the graphene-diamond interaction energy plot computed using DFT. The set of values shown in Tab. [7.1] provides a good description of the computed interaction energy vs. separation data for the vdW part of interaction (see the red curve in figure [7-17]).

7.5.2 Bonded interaction

The bonded interaction, in addition to the capability of supporting a strong normal traction component, also has a shear stiction component. To model the bonded
Figure 7-17: vdW interaction between graphene and indenter-tip. The Morse function-based representation (equation [7.3]) of the graphene-tip vdW interaction provides a good description of the vdW-regime of the DFT-computed interaction energy vs separation plot (A) for all registries arising from relative translation in x-axis as well as (B) for all the registries arising from translation in y-axis.
Table 7.1: Coefficients appearing in the Morse-based description of the vdW interaction between graphene and diamond (equation [7.3]), as determined from fits to the first-principles energies in the vdW regime.

<table>
<thead>
<tr>
<th>$\alpha_D(\AA^{-1})$</th>
<th>$d_D(\AA)$</th>
<th>$\Gamma_D(J/m^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>2.78</td>
<td>0.5</td>
</tr>
</tbody>
</table>

interaction between graphene and diamond \{111\}, we take

$$ t_{\text{Bond}} = \sigma_{\text{Bond}}(\zeta) \hat{\zeta} + \tau_{\text{inf}}(\eta; \zeta < d_c) \hat{\eta}; \quad (7.5) $$

where

$$ \sigma_{\text{Bond}}(\zeta) = -\frac{d\psi_{\text{Bond}}(\zeta)}{d\zeta} = -2\Gamma_b \alpha_b e^{-\alpha_b(\zeta-d_b)}(e^{-\alpha_b(\zeta-d_b)} - 1), \quad (7.6) $$

which is derived from the interaction potential:

$$ \psi_{\text{Bond}}(\zeta) = -\int_{\infty}^{\zeta} t_{\text{Bond}} d\zeta = -\Gamma_b \left( (e^{-\alpha_b(\zeta-d_b)} - 1)^2 - 1 \right). \quad (7.7) $$

For each to the two set of registries, the constants $- \alpha_b, \Gamma_b$ and $d_b$ — are obtained by fitting to bonded-interaction regime of the graphene-diamond interaction curve for the registry that corresponds to the strongest bonding amongst all the registries in the set. For the set of registries that involve a relative translation in the $\eta_x$-direction, the fitted values are tabulated in table [7.2], and the resulting traction-separation relation is shown by the blue curve in figure [7-18]).

For the set of registries that involve a relative translation in the $\eta_y$-direction, the fitted values are tabulated in table [7.3], and the resulting traction-separation relation is shown by the blue curve in figure [7-19]).
Table 7.2: Coefficients appearing in the Morse function-based approximation of the bonded interaction between graphene and diamond (equation [7.7]) as determined from fit to the first-principles calculations for the registry that corresponds to the strongest bonding in the set of registries for which $\eta_z \geq 0$ and $\eta_y = 0$.

\[
\begin{array}{ccc}
\alpha_b(A^{-1}) & d_b(A) & \Gamma_b(J/m^2) \\
4 & 1.501 & 2.6 \\
\end{array}
\]

Table 7.3: Coefficients appearing in the Morse function-based approximation of the bonded interaction between graphene and diamond (equation [7.7]) as determined from fit to the first-principles calculations for the registry that corresponds to the strongest bonding in the set of registries for which $\eta_z = 0$ and $\eta_y \geq 0$.

\[
\begin{array}{ccc}
\alpha_b(A^{-1}) & d_b(A) & \Gamma_b(J/m^2) \\
5.5 & 1.6 & 0.7 \\
\end{array}
\]

7.5.3 Effect of finite temperature

From $\psi_{adh} - \zeta$ and $\sigma - \zeta$ plots, we notice that the physisorbed state of graphene on diamond is separated from the chemisorbed state by an energy barrier, denoted by $\Delta E_b$. At finite temperatures, the kinetic energy of C-atoms due to thermal fluctuation may assist the atoms to overcome this barrier easily, and thus a finite temperature can facilitate the transition from the physisorbed state to chemisorbed state. To incorporate the effect of temperature, we introduce a temperature-based smearing function that combines the two limiting descriptions $\sigma_{vdW}$ and $\sigma_{bond}$ into a single composite description of the interfacial stress as follows:

\[
\sigma(\zeta) = \sigma_{Bond}(\zeta) \left(1 - \frac{1}{1 + e^{-\frac{\Delta E_b}{k_B T}(\zeta-d_c)}}\right) + \sigma_{vdW}(\zeta) \left(\frac{1}{1 + e^{-\frac{\Delta E_b}{k_B T}(\zeta-d_c)}}\right). \tag{7.8}
\]

The elastic moduli of the bonded-interface against tension ($E_b$) and shear ($G_b$) are estimated by taking second derivative of the incremental total energy at the bonded state, i.e., $\zeta = d_b$, calculated from \textit{ab initio} DFT calculations, w.r.t. incremental
tensile and shear strains, respectively. The values thus obtained are $E_b \approx 1248$ GPa and $G_b \approx 100$ GPa.

### 7.5.4 Shear traction

For the shear-component of traction associated with the bonded interaction, i.e., $t_{Bond} \dot{y} = \tau_{inf}$, we use:

$$
\tau_{inf}(\eta; \zeta < d_c) = \begin{cases} 
-G_b \frac{|\eta|}{d_c}, & \tau_{inf} < \tau_0(\theta_H) \\
\tau_0(\theta_H), & \text{otherwise},
\end{cases} 
$$

The notation $\tau_{inf}(\eta; \zeta < d_c)$ in equation [7.9] is employed to emphasize that the strong shear stiction is activated only at separations smaller than a critical value, because chemisorption of graphene on diamond takes place only when the interfacial separation is smaller than this critical value, i.e., $\zeta \leq d_c$. Thus, the expression given by equation [7.9] is used only when $\zeta < d_c$. For $\zeta > d_c$, there will be no chemisorption; the graphene remains physisorbed on diamond, resulting in a negligible shear traction, and therefore we take

$$
\tau_{inf}(\eta; \zeta > d_c) = 0. 
$$

In equation [7.9], $G_b = 10^2$ GPa is the shear stiffness of the bonded interface (estimated from DFT calculations), $\eta$ is the vectorial relative displacement between the indenter surface and the membrane, with zero value taken from the point when bonding first occurs. With respect to an orthogonal set of axes $\hat{x}$ and $\hat{y}$, the relative displacement vector $\eta$ can be expressed as $\eta = \eta_x \hat{x} + \eta_y \hat{y}$. The assumed shear strength of the bonded interface is $\tau_0(\theta_H)$.

We note that the diamond indenter used in the nano-indentation experiments of Lee
Figure 7-18: **Graphene-diamond \{111\} bonded interaction:** (A) The two asymptotic descriptions of interfacial interaction energy given by equation [7.4] and equation [7.7]. (B) The composite description of interfacial stress vs separation given by equation [7.8]. In FEA, a variation in stress such as one seen in (B) often results in a snapback instability; therefore in order to avoid this instability, the variation of the interfacial stress traverses the path shown by the arrows in the figure.
Figure 7-19: **Graphene-diamond \{111\} bonded interaction:** (A) The two asymptotic descriptions of interfacial interaction energy given by equation [7.4] and equation [7.7]. (B) The composite description of interfacial stress vs separation given by equation [7.8]. In FEA, a variation in stress such as one seen in (B) often results in a snapback instability; therefore in order to avoid this instability, the variation of the interfacial stress traverses the path shown by the arrows in the figure.
Figure 7-20: The interfacial shear strength $\tau_0$ as a function of relative hydrogen coverage $\theta_H$. The dots denote the ab initio data taken from reference [220], while the solid line denotes a fitted function.

*et al.* is etched out from a CVD-grown slab of diamond with a \{100\}-plane on the top (see patent document by Namiki Co. Japan [103]), implying that the axis of the tip is aligned along a \{100\}-crystallographic direction of diamond. Following this, the indenter tip — which would be originally covered with a layer of hydrogen [148]— is ablated by a focussed ion beam (FIB) to impart a sphericoconical shape. The ion bombardment removes some of the surface hydrogen, and hence the diamond surface at the indenter tip is partially passivated [51], i.e., $\theta_H < 1$, where $\theta_H$ is the hydrogen coverage on the diamond surface. Notably, molecular hydrogen and oxygen at room temperature have very low sticking coefficients on diamond surface [148, 119]. Therefore, the post-fabrication exposure to atmospheric hydrogen or oxygen at room temperature is unlikely to affect the tip surface. Zillibotti and Righi [220] — using an ab initio technique — calculated the shear strength of crystalline C-C interfaces as a function of hydrogen coverage $\theta_H$ at the surface. They noted that shear strength of the interface decreases dramatically as the hydrogen coverage increases, as shown in figure [7-20]. Employing this ab initio data, we empirically fit the functional form characterizing the dependence of the interfacial shear strength $\tau_0$ on the hydrogen coverage $\theta_H$ as:

$$
\tau_0(\theta_H) = s_0 e^{-8.36961 \theta_H^4}
$$

(7.11)
where $\theta_H$ is the fractional hydrogen coverage, and $s_0 = 28.30$ GPa is the shear strength of the pristine C-C interface, i.e., $\theta_H = 0$.

7.6 Conclusion

In this chapter, we studied the graphene-diamond interaction as a function of their separation — based on combined density functional theory and molecular dynamic calculations. We find that a graphene sheet on a diamond $\{111\}$ or $\{100\}$ crystallographic surface has two possible equilibrium states: a bonded (chemisorbed) state and a physisorbed state. The DFT ground state energy calculations shows that the potential energy landscape, as a function of the graphene-diamond separation, contains two local minima (wells), one corresponding to the bonded state and the other corresponding to the adsorbed state. The bonded state is a metastable state, and is separated from the adsorbed state by an energy barrier. These findings are also supported by MD simulations based on AIREBO potentials, confirming bond formation between a graphene sheet and a diamond $\{111\}$ or $\{100\}$ surface under the effect of a compressive stress. Taking the $ab\ initio$/ MD energy-separation data as input, we derive a continuum traction-separation relation for graphene-diamond interface — which describes both the weak vdW adhesion and the strong chemical interaction. In the next chapter, we will implement the proposed continuum traction-separation relation in a finite element simulation, and examine the implications of graphene-diamond interaction for nanoindentation experiments on graphene.
Chapter 8

Multi-scale analysis of nanoindentation of graphene

8.1 Introduction

Previously, we developed multi-scale models that describe various aspects of the mechanical/contact behavior of graphene: a hyperelastic constitutive model in Chapter 5, a failure model in Chapter 6, and a continuum traction-separation relation for graphene-diamond interaction in Chapter 8. In this chapter, we implement the various continuum models in a FEA simulation scheme, and employ the resulting scheme to perform a detailed analysis of recent nanoindentation experiments on suspended graphene sheets.

Over the years, indentation has emerged as one of the most widely-used experimental methods of characterizing the mechanical response of solid materials. Further, with the advancements in the field of instrumentation, controlled application and measurement of forces down to nano-newtons, and local displacements down to nanometers are easily done now-a-days. These developments have now made it possible to perform indentation experiments on nano-scale structures with high fidelity; the nano-scale
version is termed nanoindentation. Lee, et al. [105] measured the fracture strength of graphene using nanoindentation experiments and reported an unprecedentedly high intrinsic strength, measuring orders of magnitude greater than those of conventional materials. The nanoindentation involves instrumented indentation of a suspended graphene sheet by a nanoscale diamond indenter up to the point of failure. However, the local stress and strain beneath the indenter are not directly measurable in such nanoindentation experiments; instead, the indentation load \( F \) as a function of indentation depth \( (u_z)_{r=0} \) during the course of indentation is recorded. For linear-elastic materials under certain simplifying assumptions, the analytical models can be derived that allow one to translate the measured response in terms of stress and strain; however, in general, an advanced numerical scheme, fully-capturing all the relevant details, is required to interpret these results. Finite Elements Analysis (FEA) based on an appropriate constitutive description of graphene, along with certain kinematic and surface interaction assumptions, is used to simulate the nanoindentation experiment, providing an estimate of the stress and strain beneath the indenter corresponding to the measured fracture load and indentation depth. The inferred local state is taken to represent the intrinsic strength of graphene. Thus, effectiveness of the indentation experiments is intrinsically tied to an adequate interpretation of the measured response, which in turn requires accurate modeling of indentation mechanics and the physics of the system being indented.

8.2 Background

Using in their FEA model an isotropic nonlinear elastic model containing only up to third-order elastic constants, Lee, et al. [105], estimated the fracture strength of graphene as \( \sigma_f = 130 \pm 10 \) GPa and the corresponding areal strain (trace of the 2D
logarithmic strain tensor) at fracture as $\epsilon_a = 0.45$. Noting that graphene is elastically anisotropic at large strain, Wei, et al. [197] developed an improved nonlinear constitutive model which incorporates anisotropic elastic response. Employing this model in a FEA simulation [198], they obtained revised estimates of the fracture strength of graphene as $\sigma_f = 108$ GPa, and of the corresponding fracture strain as $\epsilon_a = 0.42 - 0.45$. These simulations indicated that the membrane directly beneath the indenter, where the onset of failure occurs in the simulations, remains in a state of equi-biaxial tension prior to fracture. Marianetti & Yevick [125] recently reported that the mechanical strength of a graphene monolayer under equi-biaxial tension is limited by a soft-mode instability which emerges at $\epsilon_a \sim 0.28 - 0.30$. The breaking strains inferred by Lee, et al. and Wei and Kysar substantially exceed the limiting strain dictated by this soft-mode instability.

Wei and Kysar [198] speculated that the soft-mode instability is possibly suppressed in experiments, and that the failure observed in experiments is due to an elastic instability. They assumed that the elastic instability essentially corresponds to the peak of the equi-biaxial Cauchy stress along the loading path. The assumption that elastic instability corresponds to the peak Cauchy stress along an assumed deformation path is not always true — in general, a homogeneously-deformed material can become elastically unstable before reaching this point. In particular, when the unstable eigenmode is orthogonal to the loading path, an elastic instability can precede the maximum in the stress-strain curve [35, 131]. By means of acoustic tensor analysis based on the rigorously tested hyperelastic constitutive model of Chapter 5, we show that this is indeed the case for graphene.

As we showed in Chapter 5, both the 2D bulk modulus $\kappa(\epsilon_a)$ and the 2D shear modulus $\mu(\epsilon_a)$ of graphene experience a progressive softening with increasing areal strain, ultimately vanishing at $\epsilon_a = 0.42$, and $\epsilon_a = 0.356$, respectively, as shown in figure [8-1]. Progressive softening of the elastic moduli with dilatant lattice deforma-
ation is often responsible for triggering an elastic instability. Acoustic tensor analysis [20, 82], which constitutes a useful means of predicting such instabilities, asserts that if, for some pair of unit vectors \( \mathbf{m} \) and \( \mathbf{n} \),

\[
\Lambda(\mathbf{m}, \mathbf{n}) \equiv (\mathbf{m} \otimes \mathbf{n}) : A : (\mathbf{m} \otimes \mathbf{n}) \leq 0,
\]

then the material is elastically unstable, where \( A = \partial^2 \psi / \partial \mathbf{F}^2 \) is the acoustic tensor, with \( \psi \) denoting the strain energy density per unit area (here, taken to be a function of the logarithmic strain \( \mathbf{E}^{(0)} \)), and \( \mathbf{F} \) being the deformation gradient. For equi-biaxial deformation, the plot of \( \Lambda_{\text{min}} = \min \Lambda(\mathbf{m}, \mathbf{n}) \) vs. \( \epsilon_a \) indicates an elastic shearing instability \( (\mathbf{m} \cdot \mathbf{n} = 0) \) at \( \epsilon_a|_{\mu=0} = 0.356 \), the point at which the shear modulus vanishes. As shown in figure [8-1], this elastic shearing instability occurs well before the peak in the equi-biaxial Cauchy stress, which is at \( \epsilon_a|_{\kappa=0} = 0.42 \), is reached.

Another mechanism by which a crystalline material can fail mechanically is a soft-mode instability [125, 35]. While acoustic tensor analysis captures only elastic instabilities, a phonons-based stability analysis detects both elastic and soft-mode lattice instabilities. Employing a phonons-based stability analysis in Chapter 6, we constructed a failure criterion for graphene which provides an analytical description of lattice instabilities of all kinds over the set of all deformations. The scalar-valued failure function \( \mathcal{F}(\mathcal{E}_1, \bar{\mathcal{E}}; \theta) \) — is defined in terms of the major principal logarithmic strains \( \mathcal{E}_1 \), the mean areal strain \( \bar{\mathcal{E}} \) and the major principal stretch direction \( \theta \). When graphene is subjected to a homogeneous strain for which \( \mathcal{F} > 0 \), the underlying lattice is stable with respect to perturbations; conversely, when \( \mathcal{F} < 0 \), the lattice is unstable, and the transitional condition \( \mathcal{F} = 0 \) parametrizes material deformed to incipient lattice instability (see Chapter 6 for details).
Figure 8-1: Softening of elastic moduli with dilatant area deformation, elastic instability, and soft-mode instability: Softening of (A) the 2D bulk modulus and (B) the 2D shear modulus with increasing areal strain $\varepsilon_a$. (C) Plot of equi-biaxial Cauchy stress $\bar{\sigma} = \text{tr}\sigma/2$ vs. $\varepsilon_a$. (D) For equi-biaxial strain, acoustic tensor analysis predicts an elastic instability at $\varepsilon_a = 0.356$. (E) Independent phonon calculations confirm a shearing elastic instability at $\varepsilon_a = 0.35$ through a vanishing slope of the long-wavelength TA dispersion relation. (F) Well before this elastic instability, a soft-mode instability occurs at $\varepsilon_a = 0.297$ [125].
8.3 Nanoindentation analysis

The finite elements analysis is carried out in the commercial finite element software *ABAQUS* [79] using an explicit scheme in a quasi-static sense; i.e., the displacements/loads are smoothly ramped up to their maximum value over a long interval of time. The time intervals are chosen large enough so that the kinetic energy always remains within 1% fraction of the total energy. Graphene sheet is modeled as a circular membrane comprising 84 triangular M3D3 and 7056 quadrilateral M3D4R elements, and remains clamped at the outer radial boundary. The mechanical response of graphene is described by the hyperelastic nonlinear constitutive model presented in Chapter 5 of this thesis, implemented in *ABAQUS* via a vectorized user material (*VUMAT*) subroutine. This model has been demonstrated to correctly describe the stress-strain response of graphene for the entire range of deformation up to failure. Further, the acoustic tensor-based predictions of the onset of elastic instabilities from the model are in close agreement with the predictions from independent phonons calculations. However, in a crystalline material, a mechanical failure can also be initiated by a soft-mode instability, which is not captured by acoustic tensor based analysis. Therefore the onset of failure in FEA simulations is detected by means of the phonons-based failure model for graphene, which captures material instabilities of both short and long wavelengths. The indenter is modeled as an analytical rigid surface with the shape sampled from the TEM image taken from Lee, *et al.* [105] (see figure [8-9-B]). The contact between the indenter and the graphene sheet is treated within general contact algorithm based on a user-defined interaction function implemented via the *VUINTERACTION* capability [79].
8.3.1 FEA procedure

The indentation simulation comprises the following three-steps.

(1). **Graphene sheet deposition on substrate**: a circular graphene sheet of outer radius $b = 2a = 1\mu m$ is allowed to relax on the substrate — modeled as a rigid slab with a cylindrical micro-cavity of radius $a = 0.5\mu m$ — under the influence of interfacial vdW forces. In nano-scale contact systems at typical contact pressures — such as graphene in contact with an $a$-SiO$_2$ substrate — the contact forces are predominantly the vdW forces. Therefore, the contact behavior at the graphene-SiO$_2$ interface is modeled by a traction-separation law that has characteristic features of vdW forces — attractive at long distance, repulsive at short distance, and zero at an intermediate separation $d_0$ called the equilibrium separation. The traction-separation law employed here is based on the Morse function to describe the normal-component of the traction vector. Consider a graphene sheet supported on a-SiO$_2$ as shown in the Fig.[8-2]. Let $\hat{\zeta}$ and $\hat{\eta}$ denote unit vectors normal and tangential to the substrate surface. While $\hat{\zeta}$ is uniquely defined by the normal to the surface, the tangent direction $\hat{\eta}$ is not; to uniquely determine it, the direction of the relative sliding between the two surfaces, $\hat{\eta}$, is required as well.

The traction vector $\mathbf{t}$, assuming the normal and tangential directions oriented as
Table 8.1: Coefficients appearing in the Morse-based description (given by Eq. [8.4]) of the vdW interaction between graphene and $a-SiO_2$.

shown in Fig.[8-2], as a function of separation, $\zeta$, is given as:

$$t = \sigma_{SiO_2}(\zeta) \dot{\zeta} + f_{SiO_2}(\zeta, \eta) \dot{\eta}.$$  \hfill (8.2)

The normal component of stress $\sigma_{SiO_2}(\zeta)$ is represented by:

$$\sigma_{SiO_2}(\zeta) = -\frac{dU_{SiO_2}(\zeta)}{d\zeta} = -2\Gamma_s \alpha_s e^{-\alpha_s(\zeta-d_0)} (e^{-\alpha_s(\zeta-d_0)}-1) = -\Sigma_s e^{-\alpha_s(\zeta-d_0)} (e^{-\alpha_s(\zeta-d_0)}-1),$$  \hfill (8.3)

which is derived from a Morse function-based representation for the interfacial interaction energy:

$$U_{SiO_2}(\zeta) = -\int_\infty^\zeta t.d\zeta' = -\Gamma_s \left( (e^{-\alpha_s(\zeta-d_0)}-1)^2 - 1 \right).$$  \hfill (8.4)

Koenig, et al. [100] reported a value of $\Gamma_s = 0.45 \text{ J/m}^2$ for adhesion energy of graphene/SiO$_2$ interface. We choose $\alpha_s = 0.35 \text{Å}^{-1}$, with the equilibrium distance, $d_0$, taken to be $3.4 \text{ Å}$, which is the interlayer separation in graphite. Substituting $\Gamma_s = 0.45 \text{ J/m}^2$ yields a peak adhesive stress of magnitude $\Sigma_s = 2\Gamma_s \alpha_s \approx 3 \text{ GPa}$.

The variation of the vdW adhesion energy $U_{SiO_2}$ and the vdW adhesive stress $\sigma_{SiO_2}$ with separation $\zeta$ is shown in Fig.[8-3]. According to equation [8.2] and equation [8.3], a negative value of $\sigma_{SiO_2}$ means that the membrane is pulled towards the substrate, i.e., an attractive action, while a positive value of $\sigma_{SiO_2}$ means that the membrane is pushed away from the substrate, i.e., a repulsive action.
In contrast to the stiff and strong normal contact stress, there is relatively low shear stiffness and strength associated with vdW interaction. For example, in graphite where the various layers are held together by vdW forces, the layers slide with respect to each other very easily. Thus, it is a reasonable assumption to model the shear stiffness and strength to be zero, i.e., $f_{\text{SiO}_2} = 0$.

Upon relaxation, the membrane sags-in snapping to the sidewalls of the micro-cavity, resulting in a drumhead-like configuration a few nm deep (see figure 8-4).

(2). Indenter touch-down: As the indenter approaches the membrane (just above the membrane without penetrating it), the membrane snaps to the indenter-tip due to vdW-attraction. The snapping is seen as a jump in the force vs. time response curve (See figure 8-5). To further test the vdW attraction between the indenter and the membrane, simplified tensile pull-off experiments, described in figures 8-6 & 8-7, were performed, leading to peak pull-off forces comparable to those observed experimentally [49].

(3). Indentation: In the indentation step, the indenter is gradually moved downward in a displacement-controlled fashion while the graphene sheet remains clamped at the cavity-walls, i.e., $r = a$. In the simulation, the indenter is treated as a rigid body, and the mechanical response of the graphene sheet is governed by the hyper-elastic constitutive function of Chapter 5. The indenter is moved following a smoothed
Figure 8-4: Exfoliated graphene sheet snapped to the sidewalls of a cylindrical micro-cavity: A & B Experimentally-observed morphology of a graphene sheet exfoliated on the SiO₂ substrate (taken from Lee et al. [105]). The reported snap-to-wall distance lies in the range 3-8 nm. C & D Magnified displaced geometry of the graphene sheet relaxation before indentation predicted by our FEA simulation (micro-cavity radius \( a = 500 \) nm) based on the interfacial interaction described by equation [8.3]; the simulated snap-to-wall distance is approximately 7.8 nm.
Figure 8-5: **Puckering of graphene around the indenter-tip due to vdW forces:** (A) Measured force vs. time response curve (from Lee, et al. [105]), showing the jump which corresponds to snapping of graphene sheet onto the indenter. (B) The graphene sheet puckered around the indenter as predicted by the FEA simulation. (C) The snapping of graphene onto the indenter is seen to result in a jump in the force versus time response curve.
Figure 8-6: **Indentor approach and pull-off**: Images at various stages of approach and pull-off, showing the snapping and lifting of the graphene sheet with the indenter under the action of vdw forces.

Figure 8-7: **Indentor pull-off force response**: The force (magnitude) experienced by the indenter during the pulling-off as a function of time. The pull-off force required to complete separate the indenter from the graphene sheet is $\sim 21$ nN, which compares well with experimental measurements of Deng, *et al.* [49] using a Si$_3$N$_4$ tip of radius 15 nm.
8.3.2 Preliminary analysis

Employing the constitutive model and the failure criterion in a FEA simulation of nanoindentation of a graphene sheet supported over a substrate with a micro-cavity, we analyze failure of the graphene sheet while adopting the same geometric parameters, kinematic boundary conditions, and contact models used previously [198] to model the experiments in [105, 107]. By monitoring strain as a function of indentation depth \( u_z \) in the simulation with tip radius \( \rho = 16.5 \) nm, two points of potential failure are predicted and shown in figure [8-8-C]. The first — occurring at \( u_z = 90 - 92 \) nm (\( \epsilon_a \text{soft-mode} \sim 0.28 - 0.30 \)) — is a soft-mode instability; while the second — occurring at \( u_z = 100 - 102 \) nm (\( \epsilon_a \text{acoustic} = 0.356 \)) — is an elastic instability (the one arising from the vanishing shear modulus). In contrast, the experimental failure did not occur until \( u_z = 109 \) nm.

Thus we are confronted by an anomaly: while FEA simulations based on an appropriate constitutive model for graphene, along with certain kinematic boundary conditions, geometric variables, and surface interaction models, predict experimental load vs. indentation extremely well, the experimentally-observed failure occurs much later than predicted by either of the two lattice instabilities. Moreover, these conclusions also apply to simulations of additional experiments conducted using nanoindenters of different root radii; while all the \( F - u_z \) relations are well-predicted, curves of \( \epsilon_a \) vs. \( u_z \), shown at the bottom of figure [8-8-C], all predict the occurrence of respective soft-mode and elastic instabilities well before experimentally-observed failures. Resolution of these discrepancies is important because it is the key to obtaining a more precise assessment of the ideal strength of graphene, as well as a correct identification of the mechanisms governing the failure.

Ambient-temperature MD simulations of nanoindentation of a suspended graphene
Figure 8-8: Simplified finite element analysis of nanoindentation: Contours of (A) maximum principal strain \( \epsilon_{\text{max}} \) and (B) failure function \( F \) beneath the indenter at the indentation loading corresponding to incipient soft-mode failure (blue color at base indicates spatial focus of the instability). (C) Top—load vs. indentation response from experiment and simulation for indenter tip radius \( \rho = 16.5 \) nm and flake radius \( a = 0.5 \) \( \mu \)m. Also shown are inferred failure states corresponding to the elastic and the soft-mode instabilities, and the failure state measured by Lee, et al.. Bottom—Areal strain beneath the indenter vs. indentation depth \( u_a \) for three different indenter root radii used in experiments [105, 107]. Values of \( \epsilon_{a} \) corresponding to elastic and soft-mode failures are marked by red and blue crosses (\( \times \)), respectively. Dashed lines are extrapolated to respective experimental depths at failure.
sheet by a hydrogen-passivated diamond tip (discussed in detail below) show that the fracture beneath the indenter indeed initiates at $\varepsilon_{\text{IPMD}} \sim 0.28 - 0.30$, the same value at which the soft-mode instability predicted by the phonons-based failure criterion is noted in the FEA simulations. The hydrogen-passivated surface ensures that the tip interacts weakly with the graphene sheet throughout the course of indentation, as was also shown in MD simulations of Chapter 7. This simulation result supports the proposition that a failure prediction based on the soft-mode instability in graphene remains a relevant indicator of failure in nano-indentation, even in the presence of complicating effects including the proximity of the indenter’s surface and thermal fluctuations at finite temperatures. The atomic motions taking place during the zone boundary soft-mode are locally in-plane [125], to which the non-bonded vdW interaction does not impose significant resistance; thus, concurrence of the phonon-based failure criterion with the results of this MD simulation could be expected, since below the Debye temperature, phonons constitute a complete normal basis of lattice vibrations.

In an effort to identify and understand the origin of the discrepancy in failure prediction, we investigate the roles of simplifications and assumptions, other than the graphene constitutive response, embedded within the FEA simulations, as these can potentially affect the details of the simulation results and hence the interpretation of experiments. Three critical modeling assumptions can directly affect the inferred failure conditions observed in nanoindentation simulations: (1) the assumed kinematic boundary condition at the graphene boundary; (2) simplifications related to the indenter shape and size; and (3) the simplifying assumptions regarding interaction at the graphene-diamond interface.
8.3.3 Boundary conditions

For sufficiently small indentation loads, adhesive and frictional forces from the substrate act to ‘clamp’ the graphene sheet at the cavity-periphery, \( r = a \). For higher indentation loads, the supported graphene external to the cavity can slide radially inwards while stretching, drawing a surrounding annular region into the cavity; in such cases, the radial position of the effective ‘clamped’ boundary shifts to \( r > a \) [99]. Intuitively, constraining the membrane at \( r > a \) should distribute strain over a larger extent of the material, tending to reduce strain beneath the indenter. Therefore, we examine the role of the boundary condition in connection with the delayed instability. For this purpose, we compare the boundary condition in our simulations (constrained at the microcavity-periphery \( (u_r|_{r=a}=0) \)) with two other boundary conditions, in which the membrane is constrained on the substrate farther out at a larger radial distance: (1) constrained at \( r = 3a/2 \), i.e., \( u_r|_{r=3a/2}=0 \), and (2) constrained at \( r = 2a \), i.e., \( u_r|_{r=2a}=0 \). Intuitively, constraining farther out should spread the strain to a larger extent of the material and this should reduce the strain underneath the indenter. However, this also results in a global softening of the load-deflection curve (see figure [8-10(B)]) rendering it beyond comparison with experimental data. Thus, we concur that for the range of loads in the experiments, \( u_r|_{r=a}=0 \) is an appropriate boundary condition.

8.3.4 Indenter size and shape

Results shown in figure [8-8-C] (bottom) confirm the intuitive notion that larger tip radii spread contact stress over larger areas, reducing strain beneath the indenter and delaying inferred failure to greater indentation depths. We investigate the sensitivity of the FEA failure load/displacement to the indenter’s shape and size. For this purpose, we carry out FEA simulations with different indenter sizes and geometries.
First we carry out the indentation with an indenter geometry simplified as spheroconical. The radius of the indenter-tip is measured by visually fitting a circle to a high resolution TEM image of the tip (see Lee et al. [105], and Rasool et al. [160]). There is a possibility that such measurements underestimate the tip-radius. For example, as shown in figure [8-9], visually, as large as 20 nm seems to be fitting the tip-radius well. Intuitively, a larger tip radius would spread the stress over a larger area, reducing the strain beneath the indenter and allowing the failure to occur at a greater indentation depth. We note that, even with as large as 20% error in tip radius measurement ($p = 20$ nm), not more than 2 nm of increment in the critical indentation depth corresponding to the soft-mode instability is noticed (see figure [8-10(A)]).

However, for the sharpest tip radius, $p = 16.5$ nm, even with a 20% larger tip radius, the indentation depth at which a soft-mode instability is first encountered increases by no more than 2 nm (see figure [8-9-A] & figure [8-10-A]). To minimize inaccuracies arising from a ‘spherical cap’ idealization of the indenter-geometry, we performed FEA simulations in which the indenter geometry is directly sampled from a high-resolution TEM image of the tip (see figure [8-9-B]), and again found negligible differences in
8.3.5 Mechanically-activated covalent interaction

The simplified analyses presented so far assume a frictionless, non-adhesive hard contact between graphene and the indenter, as was also done by Lee, et al. [105] and Wei and Kysar [198]. However, the interaction between nano-scale contact systems is predominantly the van der Waals (vdW) interaction, arising from instantaneous charge fluctuations [166, 167, 106]. To determine if adhesive vdW forces play a role in delaying the onset of failure, we performed FEA simulations incorporating a vdW-adhesion at the graphene-tip interface. However, the inferred failure load and depth remain the same as in the simulations without interfacial vdW adhesion (hard contact). It is also noted that the relatively small friction attributed to graphene-tip contact (assumed friction coefficient $\mu_f = 0.01 - 0.02$, see Sandoz, et al. [167]) does not substantially affect results, either. These results suggest that vdW interfacial
forces are too weak to cause the noted delay in the onset of instability.

Notably, in both FEA and MD simulations that assume weak vdW interaction at the interface, no residue accumulates on the indenter tip in the post-failure regime. Had the only interaction between the two surfaces indeed been vdW, this might be expected, since vdW forces have a negligibly small tangential-stiction component. However, post-indentation TEM images from nanoindentation experiments [105, 160] do show graphene residue on the tips. For example, Lee et al.’s post-indentation image of the indenter shows an apparently well-adhered accumulation of graphene-residue on a localized portion of the tip (see figure [8-11-B]). The axis of the tip is aligned along a (100)-crystallographic direction of diamond, and the end-facet of the tip is likely a {100}-plane [103]. The normal vector to the tip surface region exhibiting graphene accumulation makes an angle near 55° with the indenter axis. One such direction is a (111)-crystallographic axis of diamond, suggesting that the adhering facet may be a {111}-crystallographic plane. A similar accumulation pattern is observed in Rasool et al.’s post-indentation TEM images as well (see figure [8-11-A]). The localized and well-adhered pattern of the graphene-residue accumulation on the indenter suggests that an interfacial interaction much stronger than vdW forces, such as of covalent nature, may possibly be active at the interface. Previously, such mechanically-activated covalent bond formations have been observed in atomic force microscopy (AFM) experiments [50, 12, 91].

We now address the possibility of mechanochemical interactions at the graphene-diamond {111} and the graphene-diamond {100} interfaces during nanoindentation. Previously, in Chapter 8, We noted that DFT/MD calculations simulating a graphene monolayer pushed against a {111} or a {100} diamond surface shown that two distinct local minima (wells) in the adsorption energy ($\psi_{\text{adh}}$) vs. separation ($\zeta$) landscape (see figure [8-12]). The common broader well, centered at $\zeta = 2.78\text{Å}$, corresponds to the physisorbed state of graphene on the diamond surface — in which interac-
Figure 8-11: Post-indentation TEM image of diamond indenter-tip: Post-indentation images of the indenter (A) from Rasool, et al. [160] and (B) from Lee, et al. [105]. In both images, graphene residue accumulated on the tip, shown by a red arrow, should be noted. (C) Molecular model of a spheroconical nanoindenter with $\rho = 16.5$ nm, made of single-crystalline diamond. Note the $\{100\}$ and $\{111\}$ crystallographic planes exposed on the surface.

Figure 8-12: FEA contact stress calculated along a radial line at various indentation depths.

...tion is mainly due to interfacial vdW forces, and no electronic charge transfer is involved. The narrow wells, at smaller separations, correspond to chemisorbed states — marked by formation of chemical bonds between graphene and the diamond surface. Bonding is confirmed by the charge density contours at the graphene-diamond interface, as mapped at various separations. Substantial charge overlap between the graphene monolayer and the $\{111\}$ diamond surface, which is absent at large separations $\zeta > 2.0\text{Å}$, occurs at $\zeta \approx 1.45 - 1.75\text{Å}$. The activation stress for reaching the bonded well is within the range 1- 3 GPa; figure [8-12] confirms that contact stresses of this magnitude are generated over growing portions of the 16.5 nm tip as indentation increases. The shear strength of a planar C-C interface depends strongly on the fractional hydrogen-coverage, $\theta_H$, at the interface [220]. Two limiting cases
are: (1) fully-hydrogenated state, $\theta_H = 1$, in which case purely vdW interaction holds at all values of contact stress; and (2) fully-clean state, $\theta_H = 0$, in which case the interaction is vdW at low contact stresses, but becomes strongly covalent once the interfacial contact stress reaches the activation stress. A major distinguishing factor between the two kinds of interaction is the resulting shear stiction, $\tau_0$: a purely vdW interaction possesses a negligible $\tau_0$-value, while covalent interaction is associated with a large shear strength. For intermediate values of $\theta_H$, $\tau_0$ decreases with increasing $\theta_H$ [220]. The surface hydrogen coverage on a diamond surface is determined by its process history [148, 51]. For example, experiments suggest that an as-cleaved diamond surface is nearly clean, and upon annealing, it becomes hydrogenated [95]; while an ablative treatment such as ion beam milling — which is often involved in fabrication of nano-indenters [103] — removes some hydrogen from the diamond surface, leaving it in a partially-hydrogenated state [51].

8.3.6 Mechanochemical FEA simulation

We now examine the consequences of bonding-induced shear stiction at the graphene-indenter interface by means of FEA simulations which duly incorporate mechanochemical details of the graphene-indenter interaction. These simulations allow the development of mechanically-activated covalent interface interactions with graphene at indenter tip locations corresponding to diamond $\{111\}$ and diamond $\{100\}$ facets. The results of these simulations are shown in figure [8-14], and in tables [8.2 & 8.3].

Based on the picture emerging from these simulations, we identify a strain-shielding mechanism which controls the dispersion of strain beneath the indenter, as illustrated in figure [8-14]. Initially, interaction between the two surfaces is dominated purely by vdW forces, since the contact stress beneath the indenter at small indentation
Figure 8-13: (A) Atomistic model of the diamond indenter with indentation axis aligned with diamond [001] direction. The \{111\} and \{001\} crystallographic planes are visible on the indenter-surface. (B) Finite element model of the indenter different with the \{111\}-planes and \{001\} planes appropriately mapped from the atomistic model.

is insufficient to initiate bonding. During this phase, strain build-up mostly occurs directly beneath the indenter (figure [8-14-A]). As indentation continues, bonding between graphene and diamond initiates at the base of the indenter, once the requisite contact stress is reached. The shear-stiction associated with this covalent interaction inhibits the subsequent stretching of the graphene sheet in this region, and the unbonded surrounding region undergoes a little extra strain instead. Effectively, the cumulative action of the shear stiction can be perceived as a mechanism that transfers strain from the bonded region to the surrounding region, creating a strain-shielded region at the base of the indenter (figure [8-14-B]). At even larger depths/loads, as graphene wraps around the indenter, covalent interaction with lateral \{111\}-facets of the diamond indenter is also initiated, and the associated shear-stiction again transfers the strain to nearby regions (figure [8-14-C]). The process is illustrated in figure [8-14-D], which contrasts the evolution of maximum principal strain at two near-tip locations for vdW and induced covalent interaction.

By varying the magnitude of $\tau_0$ in FEA simulations, we explore conditions for optimal strain shielding that redistributes strain and delays the onset of instability to a larger load/depth. The results are tabulated in tables [8.2 & 8.3]. For an intermedi-
Figure 8-14: **Strain-shielding mechanism**: Contours of maximum principal strain at various stages of indentation ($\theta_H = 75\%$). (A) $u_z|_{r=0} = 55$ nm: interaction between graphene and diamond tip is purely vdW, and maximum strain occurs at the point beneath the indenter. (B) $u_z|_{r=0} = 75$ nm: formation of a strain-shielded zone indicates that a mechanochemical interaction has been initiated at the graphene-indenter interface in the region beneath the indenter. (C) $u_z|_{r=0} = 107.5$ nm: As contact area grows with indentation, $\{111\}$-facets on the indenter tip also interact covalently with the graphene sheet, as indicated by formation of strain-shielded zones in those regions. (D) Maximum principal strain at material points ‘1’ (in red) and ‘2’ (in blue) vs. $u_z|_{r=0}$ for induced covalent interaction (dashed lines, this simulation) and vdW interaction (solid lines, figure [8-8]).

ate range of $\tau_0$-values corresponding to a partially-hydrogenated state of the diamond surface, $\theta_H \sim 70\% - 80\%$, optimal strain transfer occurs, spreading the strain to the maximal area and limiting the strain-intensification beneath the indenter (figure [8-15-A]).

This delays the onset of instability, allowing the inferred failure to occur at an indentation depth/load close to the experimentally-measured values (figure [8-15-C]). The load and indentation at inferred failure in the simulations are $F = 1540$ nN, and $u_z|_{r=0} = 107.5$ nm, respectively — which are within the $\pm 9.5\%$ and $\pm 3.5\%$ ranges reported for the measured values, 1742 nN and 109 nm, respectively. Based on the contours of the failure function $\mathcal{F}$, failure is inferred to initiate away from the center, just beyond a bonded region (figure [8-15-B]); such a failure initiation site is consistent with the location of retained residue shown in figure [8-11].

In particular, we note that the strength of shear stiction is the key variable governing the performance of this mechanism. Neither a too-small nor a too-large stiction
Figure 8-15: **FEA simulation allowing development of a covalent interaction at graphene-indenter interface (θ_H = 75%)**: Contours of (A) the maximum principal logarithmic strain and (B) the failure function \( F \) beneath the indenter prior to failure. Note the redistribution of strain in (A) due to graphene-diamond interaction, limiting strain intensification beneath the indenter. Blue contours in (B) show regions where \( F < 0 \), i.e., the material has reached incipient failure. (C) Corresponding load vs. indentation depth.

is conducive for maximal dispersion of strain. Too small a stiction (as in the case of fully-hydrogenated diamond) induces no strain transfer, and strain rapidly concentrates in a small region directly beneath the indenter. Conversely, too large a stiction (as in case of bare diamond), heavily shields the bonded region beneath the indenter, resulting in a rapid strain buildup within annular sectors in the vicinity of the bonded region. Based on our finite element analysis allowing for graphene-tip covalent interaction, we obtain the critical indentation depth as a function of hydrogen coverage \( θ_H \), as summarized in tables [8.2 & 8.3].

### 8.4 MD simulations

MD simulations of nanoindentation are carried out with the LAMMPS MD simulator [158] which capture major features of the mechanochemical C-C interactions. The simulation cell contains (1) a circular graphene sheet of diameter 24.5 nm, obtained by replicating the orthorhombic graphene unit cell — with sides \( a_1 = a_0(\sqrt{3}/2 \hat{x} + 1/2 \hat{y}) \) and \( a_2 = a_0(\sqrt{3}/2 \hat{x} - 1/2 \hat{y}) \) where \( a_0 = 2.465\text{Å} \); and (2) a spheroconical indenter of
<table>
<thead>
<tr>
<th>$\theta_H$ (%)</th>
<th>$\tau_{\text{int}}(\theta_H)$ (GPa)</th>
<th>$u^\text{Crit}_2$(nm)</th>
<th>Fracture location (blue region)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72.5 -80</td>
<td>1.5- 2.5</td>
<td>107</td>
<td><img src="image1.png" alt="Image 1" /></td>
</tr>
<tr>
<td>100</td>
<td>0.0001</td>
<td>98</td>
<td><img src="image2.png" alt="Image 2" /></td>
</tr>
<tr>
<td>0</td>
<td>28.30</td>
<td>92</td>
<td><img src="image3.png" alt="Image 3" /></td>
</tr>
</tbody>
</table>

Table 8.2: Failure indentation depth as a function of hydrogen surface coverage. In the rightmost column, we show contours of the instability function $\mathcal{F}$ — with dark blue regions showing the incipiently unstable elements, evaluated at the critical displacement $u^\text{Crit}_2$. The optimal hydrogen saturation, leading to maximum delay in onset of failure, is noted to occur for coverages in the range $72.5\% \leq \theta_H \leq 75\%$. 

283
<table>
<thead>
<tr>
<th>$\theta_H$ (%)</th>
<th>$\tau_{\text{inf}}(\theta_H)$ (GPa)</th>
<th>$u_z^{\text{Crit}}$(nm)</th>
<th>Fracture location (blue region)</th>
</tr>
</thead>
<tbody>
<tr>
<td>72.5 - 80</td>
<td>1.5 - 2.5</td>
<td>107</td>
<td>![Image A]</td>
</tr>
<tr>
<td>100</td>
<td>0.0001</td>
<td>98</td>
<td>![Image B]</td>
</tr>
<tr>
<td>0</td>
<td>28.30</td>
<td>92</td>
<td>![Image C]</td>
</tr>
</tbody>
</table>

Table 8.3: Failure indentation depth as a function of hydrogen surface coverage. In the rightmost column, we show contours of the maximum in-plane strain, evaluated at the critical displacement $u_z^{\text{Crit}}$. The optimal hydrogen saturation, leading to maximum delay in onset of failure, is noted to occur for coverages in the range $72.5\% \leq \theta_H \leq 75\%$. 

284
radius 1.75 nm and cone-angle 60°, obtained by replicating the diamond unit cell with the axis of the indenter being aligned along the [001] axis, and the [100] axis coinciding with the zigzag direction of the graphene lattice. The interaction between C-atoms in graphene and diamond is described by an \textit{AIREBO} potential. The equations of motion are integrated using an NVT ensemble with a time-step of 1 fs, while the temperature of the graphene sheet is controlled with a Nosé-Hoover thermostat and a temperature coupling constant of 10 fs. The indenter is pushed into the membrane with a velocity of 3.68Å/ps while the sheet remains fixed at the boundary. The interaction between the atoms is described by the \textit{AIREBO} potential of Stuart \textit{et al.} \cite{182}. The interaction between the diamond indenter and the graphene sheet is controlled by varying the hydrogen saturation at the indenter tip. Three levels of hydrogen saturation at the indenter tip are considered, as shown in figure [8-16].

- First we consider the indenter tip to be comprised of bare diamond, i.e., $\theta_H = 0$.
- In the second configuration, the indenter tip is fully saturated with hydrogen, i.e., $\theta_H = 1.00$;
- In the third configuration, some of the hydrogen is sublimated off the indenter surface so that the indenter tip is partially hydrogenated ($\theta_H = 0.6$).

In these simulations, it is noted that the rubbing of graphene sheet on the diamond indenter also results in some hydrogen removal. Thus exposed C atoms on diamond then interact chemically with the C atoms in the graphene sheet. These observations are in agreement with the results of Gao, \textit{et al.} \cite{57, 58}, who observed that an amorphous C film, when rubbed over a hydrogenated diamond, results in rupturing of C-H bonds, and continued sliding leads to the formation of a chemical bond between the freed C atoms on the diamond surface and C atoms on the amorphous film.

For all cases considered, a one-to-one qualitative agreement between FEA and MD is noted — (1) while both large and small hydrogen coverages result in early failures,
an intermediate level coverage requires the largest indentation loads to initiate failure in the graphene. (2) As in FEA simulations (figure [8-14-D]), MD simulations also indicate strain-shielding beneath the indenter, as shown in figure [8-16-D]. (3) Post-fracture atomic trajectories from MD confirm that when strong covalent interaction occurs, e.g., $\theta_H = 0$ and $\theta_H = 0.6$, a residue accumulation is noted, while it is absent when $\theta_H = 1$, for which the graphene-tip interaction is weak, as previously noted.

**8.5 Conclusion**

Mechanical failure of an ideal crystal is dictated either by an elastic instability or a soft-mode instability. Previous interpretations of nanoindentation experiments on suspended graphene sheets [105, 107], however, indicate an anomaly: the inferred strain in the graphene sheet directly beneath the diamond indenter at the measured failure load is anomalously large compared to the fracture strains predicted by both
soft-mode and acoustic analyses. Through multi-scale modeling combining the results of continuum, atomistic, and quantum calculations; and analysis of experiments, we identify a strain-shielding effect initiated by mechanochemical interactions at the graphene-indenter interface as the operative mechanism responsible for this anomaly. Transmission electron micrographs (TEM) and a molecular model of the diamond indenter’s tip suggest that the tip surface contains facets comprising crystallographic \{111\} and \{100\} planes. *Ab initio* and molecular dynamics (MD) simulations confirm that a covalent bond (weld) formation between graphene and the crystallographic \{111\} and \{100\} facets on the indenter’s surface can be induced by compressive contact stresses of the order achieved in nanoindentation tests. Finite element analysis (FEA) and MD simulations of nanoindentation reveal that the shear stiction provided by the induced covalent bonding restricts relative slip of the graphene sheet at its contact with the indenter, thus initiating a local strain-shielding effect. As a result, subsequent to stress-induced bonding at the graphene-indenter interface, the spatial variation of continuing incremental strain is substantially redistributed, locally shielding the region directly beneath the indenter by limiting the buildup of strain while imparting deformation to the surrounding regions. The extent of strain shielding is governed by the strength of the shear stiction, which depends upon the level of hydrogen saturation at the indenter’s surface. We show that, at intermediate levels of hydrogen saturation, the strain-shielding effect can enable the graphene to support experimentally-determined fracture loads and displacements without prematurely reaching locally limiting states of stress and deformation.

We have shown that the high local contact stresses generated in nanoindentation can induce strong covalent interaction at crystallographically-specific portions of the graphene-indenter interface, with consequences that can dramatically affect the measured failure load in such experiments. It is a significant finding, since contact interactions in nanoindentation experiments on graphene have previously been as-
sumed to be weak, and their roles in defining failure modes were implicitly ignored. As a result, in previous interpretations of nanoindentation experiments, the inferred failure strains in graphene have appeared to be inexplicably large from the perspective of lattice stability analysis. Performing numerical simulations at multiple scales, we shed light on the mechanistic processes activated by the mechanically-induced interfacial covalent interaction, principally an alteration of the strain landscape in graphene beneath the indenter, and explain the apparent delay in inferred failure in a fashion consistent with lattice stability analysis.

The nanoindentation of two-D materials, such as graphene, constitutes a special case. In the nanoindentation of defect-free bulk-crystals, the ensuing lattice instability — the mechanism governing incipient plasticity — emerges in the interior, removed from the indenter's direct influence [108, 184]. In contrast, for structurally 2D materials, the potentially-unstable regions remain in intimate contact with the indenter surface throughout the course of indentation, and, as a result, the mechanochemistry of the membrane-indenter interface can play a significant role in determining local critical conditions.

For this reason, measured failure loads/indentations for such 2D materials cannot always be straightforwardly translated into limiting material parameterizations (strength; critical strain) without attending to potential mechanochemical interactions. The methodologies presented here constitute a multi-scale framework for assessing the mechanochemistry of the membrane-indenter interface and its potential to influence critical local conditions. Of course, mechanochemical details of indenter-membrane interactions vary from material to material; however, the framework presented here is general, and should be broadly applicable to nano-scale contact experiments on other monolayer materials, e.g., h-BN, silicene, and two-D analogues of bulk crystals, such as MoS$_2$, as well.
Chapter 9

General conclusion and future directions

9.1 Summary of major findings

Graphene, owing to its remarkable combination of mechanical, optical, and electronic properties, possesses extraordinary potential for future nano-electronic applications. However, the process of translating this potential into reality requires both a fundamental mechanistic insight into material behavior of graphene and a predictive framework which can be utilized towards the design and fabrication of graphene-based devices. This thesis highlights several aspects of graphene's behavior that emerge from physical phenomena spanning across multiple length-scales. The direct atomistic simulation techniques such as MD and DFT are of limited help in this regard. Particularly, the ability to capture reactive processes with the virtue of reactive interatomic potentials, and tracking molecular trajectories due to virtue of taking into account each degree of freedom explicitly makes MD a useful tool to gain insight into various material processes which otherwise is impossible. However, the enormous computational cost required to perform the simulations remain an Achilles’
heel of the direct atomistic simulation techniques. For these reasons, MD and DFT have been limited to unrealistically small system size and time-scales, and have been useful only in gaining qualitative insight only.

Continuum-level techniques such as FEA simulation are both computationally feasible and reliable so that systems with realistic length and time-scales can be analyzed; however, an absolute requirement for these simulations to work is inclusion of microscopic details into the simulations via a continuum model obtained by coarse-graining of the microscopic features relevant to the phenomenon being simulated. In this thesis, we have constructed coarse-grained continuum models for mechanical behavior, failure, and interfacial interaction with diamond both at low and high contact stresses. These models have been implemented within the framework of a general finite element analysis scheme to simulate nanoindentation of monolayer graphene membranes. Two main ingredients of continuum simulation are a large deformation constitutive law and a failure model. Particularly, analysis of indentation requires a constitutive law that faithfully describes the deformation of graphene under both large areal and deviatoric deformation, until the material failure. However, construction of both models is complicated by the interplay between the symmetries that characterize the crystal point group and the elastic non-linearities that emerge under large, and sometimes only moderately large, imposed deformations. The main contributions made in this thesis are as following:

- First, employing ideas such as theory of algebraic representation, polarization of algebraic functions, and principal component analysis, we have developed a numerical method to construct a complete and irreducible integrity basis of a second order tensor and, that of a vector for regular polygonal crystal classes ($C_n$). Using this method, we obtain the integrity bases of $k-$ vector and logarithmic strain tensor $E^{(0)}$ for graphene. The integrity basis of $E^{(0)}$
thus obtained is employed in later chapters to obtain hyperelastic constitutive response and failure functions for graphene.

- Employing mathematical forms based on symmetry-invariant-based formulation within the framework of hyperelasticity and fitting them to accurate \textit{ab initio} energies, we have developed a non-linear stress-strain constitutive function for ideal single-crystalline graphene that accounts for large volumetric-deviatoric coupling under circumstances involving large volumetric strains. The formulation, being in terms of the symmetry-invariants, automatically satisfies graphene's material anisotropy; and symmetry constraints are not required to be imposed extrinsically. The representation thus obtained is not only elegant but also saves effort. The model is employed to calculate the acoustic tensor, which is then employed to detect elastic instabilities in graphene under various types of loading as the point at which the strong-ellipticity condition ceases to hold. We obtain the elastic-stability limits for a number of deformation modes, and compared the results with independent linear response theory calculations. DFT being a ground-state theory, the deformation energies calculated from \textit{ab initio} DFT pertain to 0 K; such calculations outrightly exclude the presence of any thermal entropic effects. For this reason, a hyperelastic constitutive response of an ideal, single crystal, in principle, is valid, in strict sense, only to describe the mechanical response of the material at temperature close to 0 K where the internal energy is a good approximation of the Helmholtz free energy. However, since the elastic properties of a material does not show a strong-dependence on temperature as long as it remains well below the Debye temperature, which is near $T_D = 1000$ K for graphene, we believe that the proposed constitutive relation continues to provide a faithful description of material's elastic response at temperatures substantially different from 0K. This is evident from the fact that the elastic constants of crystals calculated from
DFT remain in good agreement with the experimental measurements which are performed at room temperature. Therefore, the proposed constitutive response remains applicable to simulate experiments performed at room temperature.

- The acoustic tensor analysis based on the hyperelastic constitutive response, in general, does not predict lattice instabilities of all kinds that lead to failure. Therefore, in addition to a constitutive response, a failure model which is able to detect material instabilities of all kinds becomes essential. We propose continuum-level failure function for ideal graphene crystals describing lattice failures of all kinds: long wavelength as well as short wavelength; and structural as well as material failures. The model, in spirit, is similar to Drucker-Prager failure criterion for pressure-dependent solids, wherein the maximum deviatoric stress before failure depends upon the mean hydrostatic stress. However, graphene, owing to its crystallinity, anisotropy and strictly 2D structure, is a much more complex material than a conventional continuum solid. The failure model proposed in this work appropriately incorporates these complexities. For example, graphene is intrinsically an anisotropic material; therefore, in addition to the isotropic invariants, e.g., the areal strain $\epsilon_a$ (equivalent to first invariant $I_1$) and deviatoric invariant $\gamma_2$ (equivalent to second invariant $J_2$), the failure model also involves a third invariant $\Theta$, motivated from material symmetry analysis. There are different kinds of microscopic mechanism that lead to failure of the lattice, under different modes of deformation, i.e., a soft-mode or an elastic instability. The proposed failure model not only obtains the critical state of deformation but also successfully identifies the governing mechanism responsible for the failure under that mode of deformation. Graphene, being a strictly 2D structure, has an exceedingly small bending rigidity. Therefore, a possible mode of failure under certain states of deformation is buckling instability in graphene. It is noted that whether the critical deviatoric stretch (stress)
results in a material failure (fracture) or a structural failure (buckling) depends on the equi-biaxial stretch level (pressure): at small equi-biaxial stress the failure occurs via buckling, a structural failure whereas above a certain equi-biaxial stress, the failure is invariably a material failure (fracture). The model is implemented in a finite element scheme, and demonstrated for utility and efficacy via examples. This model is implemented in commercial FEA simulation package ABAQUS. The resulting scheme is used to identify the first instance of failure in blistering test with varying geometries.

- We analyze recent nano-indentation experiments on suspended graphene sheets and show that existing interpretations of these experiments — based on finite element simulations adopting frictionless hard contact models intended to simulate van der Waals interaction — indicate that at experimentally-measured failure loadings, the inferred strain in the graphene sheet directly beneath the diamond indenter is anomalously large compared to the fracture strains predicted by both soft-mode and acoustic lattice stability analyses. A detailed investigation demonstrates that the discrepancy cannot be attributed to deficiencies in the graphene constitutive model, geometric features of the indenter, or the nature of assumed kinematic boundary conditions adopted in the simulations. By means of DFT and MD simulations, we show that in early stages of indentation (when contact stresses are not large), the interactions are indeed dominated by vdW forces, but as contact stresses beneath the indenter grow with increasing loading, a mechanically-activated strong covalent interaction is induced between graphene and the diamond indenter. We examine the implications of inducing strong covalent interactions at the graphene-indenter interface in connection with measured fracture loading levels in nano-indentation experiments. Both finite element and MD simulations suggests that the shear stiction associated with such induced interactions lead to a strain-shielding effect in
the graphene. The shear stiction restricts relative slip of the graphene sheet at its contact with the indenter, thus initiating a local strain-shielding effect. As a result, subsequent to stress-induced bonding at the graphene-indenter interface, the spatial variation of continuing incremental strain is substantially redistributed, locally limiting the buildup of strain in the region directly beneath the indenter while adding to deformation of nearby, lower-strained regions. The shear strength of the graphene-indenter covalent interaction is a key variable governing the performance of the strain shielding effect. The magnitude of the shear strength depends strongly on the level of hydrogen passivation on the indenter tip. Our simulations show that at intermediate levels of hydrogen saturation, the strain-shielding effect redistributes strain in the graphene so that experimentally-determined fracture loading can be supported without prematurely reaching locally-limiting states of lattice deformation and stress.

9.1.1 Future research directions

The research-work carried out in this thesis lays foundation for the following future directions and extensions.

- **Extension to other 2D materials**: The methods and ideas presented in these thesis are general, and are directly applicable to other 2D crystalline-materials such as h-BN and MoS$_2$. Therefore, a next logical step as a continuation to the present work would be develops similar continuum models for h-BN and MoS$_2$ as well. Project of three-D materials on two-D such as plane strain deformation of crystals.

- **Analytical representation of phonon dispersion relation of graphene**: The work carried out in this thesis focussed on macroscopic constitutive properties of graphene, which require consideration of point group symmetries only.
On the other hand, at microscopic (atomistic) level, a crystal is discrete, and therefore microscopic properties of a crystal, such as the electronic dispersion relation $E_n(k)$ or the phononic dispersion relation $\omega_n(k)$, require consideration of both the translational and the point group symmetries of the crystal [138, 31]. Mathematically, a microscopic characteristic of a crystalline material, such as electronic or phononic dispersion relation, of a crystalline material is described by continuous, scalar functions of a vector agency in real or reciprocal space. Extending the ideas presented in this work, one can obtain special symmetry-coordinates of a vector that satisfies both the point group symmetry and the translation symmetry of the lattice. Then, an interpolation scheme based on these symmetry-coordinates can be employed to obtain an analytical description of the phonon-dispersion relation of graphene. Such a description would allow an easy determination of selection rules for three-phonon process involving Normal- and Umklapp-scattering, knowledge of which is key element of thermal conductivity calculation [140].

- **Extension to 3D ideal single crystals:** Owing to the 2-D nature of deformation and the $C_{6v}$ point group symmetry of graphene, the deformation energies and phonon frequencies required for interpolation need to be sampled over a very limited number of deformed states.

In the second problem, we simulate the nanoindentation of a defect-free Al crystal. Spanning the deformation space associated with a general deformation of a 3-D crystal would require sampling energies and frequencies over an enormously large number of deformed states. Therefore I consider the plane strain nanoindentation of an Al crystal with a cube-axis being the plane strain direction as a simplification to limit the deformed states over which interpolations of deformation energies and lattice frequencies are required. The overall approach, however, is generally applicable to any set of deformations. The group consist-
ing of all proper rotations leaving a cube invariant is the rotational octahedral symmetry group, denoted by $\mathcal{O}$. If, in addition, the reflections are also allowed then we obtain the hexoctahedral symmetry group which is denoted by $\mathcal{O}_h$. An fcc crystal belongs to such a symmetry group. The $\mathcal{O}_h$ symmetry group comprises of 48 symmetry operations which are as following (see [175, 177, 178]).

$$\mathcal{O}_h = (I, C, R_1, R_2, R_3, D_1, D_2, D_3, T_1, T_2, T_3, M_1, M_2).$$  \hfill (9.1)

There are 7 distinct pairs of planes constituting the Brillouin zone. Corresponding to each plane in the BZ, one can define a subgroup of the $\mathcal{O}_h$ group such that that the normal to the plane remains absolutely unchanged under the action of the subgroup. This subgroup, referred to as the symmetry group of the constituent plane, can be obtained by taking the projection of $\mathcal{O}_h$ group on that plane. The projection of $\mathcal{O}_h$ group on a plane with normal $\mathbf{n}$ is defined as following.

Projection of $\mathcal{O}_h$ along $\mathbf{n} = \mathcal{P}(\mathcal{O}_h, \mathbf{n}) = \{C \in \mathcal{O}_h | C\mathbf{n} = \mathbf{n}\}$.  \hfill (9.2)

Thus, the $\mathcal{O}_h$ group can be divided into multiple subgroups $\mathcal{O}_h^{(i)}$, $i=1,..,7$ such that $\bigcup_{i=1}^{7} \mathcal{O}_h^{(i)} = \mathcal{O}_h$, however, these subgroups need not be mutually exclusive.

Each such subgroup comprises of symmetry operations that would leave a particular facet of the BZ unaffected. For example, $\mathcal{O}_h^{(1)}$ leaves the facets with the normal $(1, 0, 0)$ or $(-\mathbf{1}, 0, 0)$ unaffected.

1. $\mathbf{n}_1 = (1, 0, 0)$ and $-\mathbf{n}_1 = (-\mathbf{1}, 0, 0)$:

$$\mathcal{O}_h^{(1)} = \mathcal{P}(\mathcal{O}_h, \mathbf{n}_1) = (I, R_1, R_2, D_2, T_2, R_1 \cdot T_2, R_3 \cdot T_2, D_2 \cdot T_2).$$  \hfill (9.3)
2. \( n_2 = (0, 1, 0) \) and \(-n_2 = (0, \bar{1}, 0)\):

\[
\mathcal{O}_h^{(2)} = \mathcal{P}(\mathcal{O}_h, n_2) = (I, R_1, R_3, T_1, R_2, T_1, R_3, T_1, D_1 T_1). \quad (9.4)
\]

3. \( n_3 = (0, 0, 1) \), \(-n_3 = (0, 0, \bar{1})\):

\[
\mathcal{O}_h^{(3)} = \mathcal{P}(\mathcal{O}_h, n_3) = (I, R_1, R_3, T_3, R_1, T_3, R_2, T_3, D_3 T_3). \quad (9.5)
\]

4. \( n_4 = (1, 1, 1) \), \(-n_4 = (\bar{1}, \bar{1}, \bar{1})\):

\[
\mathcal{O}_h^{(4)} = \mathcal{P}(\mathcal{O}_h, n_4) = (I, T_1, T_2, T_3, M_1, M_2). \quad (9.6)
\]

5. \( n_5 = (\bar{1}, 1, 1) \), \(-n_5 = (1, \bar{1}, \bar{1})\):

\[
\mathcal{O}_h^{(5)} = \mathcal{P}(\mathcal{O}_h, n_5) = (I, T_2, D_1 T_1, D_1 M_2, D_3 T_3, D_3 M_1). \quad (9.7)
\]

6. \( n_6 = (\bar{1}, \bar{1}, 1) \), \(-n_6 = (1, 1, \bar{1})\):

\[
\mathcal{O}_h^{(6)} = \mathcal{P}(\mathcal{O}_h, n_6) = (I, T_1, D_2 T_2, D_2 M_1, D_3 T_3, D_3 M_2). \quad (9.8)
\]

7. \( n_7 = (1, \bar{1}, 1) \), \(-n_7 = (\bar{1}, 1, \bar{1})\):

\[
\mathcal{O}_h^{(7)} = \mathcal{P}(\mathcal{O}_h, n_7) = (I, T_3, D_1 T_1, D_1 M_1, D_1 T_2, D_2 M_2). \quad (9.9)
\]

The subgroups obtained by projecting the \( \mathcal{O}_h \) along ±(1, 0, 0), ±(0, 1, 0), or ±(0, 0, 1) are equivalent to \( \mathcal{C}_{4v} \) which is given by:

\[
\mathcal{C}_{4v} = \{E, \{C_{\pi/2}, C_\pi\}, \{C_\pi\}, \{\Sigma_0, \Sigma_{\pi/2}\}, \{\Sigma_{\pi/4}, \Sigma_{-\pi/4}\}\}; \text{ Order}=8
\]

297
whereas the subgroups obtained by projecting the \( \mathcal{O}_h \) along \( \pm(1,1,1), \pm(\bar{1},1,1), \pm(\bar{1},\bar{1},1) \) or \( \pm(1,\bar{1},1) \) are equivalent to \( \mathcal{C}_{3v} \) subgroup comprising of the following 6 symmetry operations.

\[
\mathcal{C}_{3v} = [E, \{C_{2\pi/3}, C_{-2\pi/3}\}, \{\Sigma_0, \Sigma_{2\pi/3}, \Sigma_{-2\pi/3}\}] ; \text{ Order}=6
\]

In the present treatise, we consider only plane strain scenario with deformation limited to the x-y plane, i.e., the deformation gradient has the form

\[
\mathbf{F} = \lambda (\mathbf{e}_x \otimes \mathbf{e}_x) + \frac{1}{\lambda} (\mathbf{e}_y \otimes \mathbf{e}_y) + 1(\mathbf{e}_z \otimes \mathbf{e}_z). \tag{9.10}
\]

Deformation usually results in the change in the point group symmetry of the lattice. The change in the symmetry of the lattice can be described by change in overall symmetry group of the lattice or equivalently change in symmetry of the individual lattice planes. Let \( \mathbf{a}_3 = [001] \) be the plane strain direction; then the associated deformation gradient, ignoring the rigid body rotations, can be written as

\[
\mathbf{F}_{[001]} = J^{1/2} \left( \lambda \mathbf{e}_1 \otimes \mathbf{e}_1 + \frac{1}{\lambda} \mathbf{e}_2 \otimes \mathbf{e}_2 \right) + \mathbf{a}_3 \otimes \mathbf{a}_3, \tag{9.11}
\]

where

\[
\begin{bmatrix}
\mathbf{e}_1 \\
\mathbf{e}_2 \\
\end{bmatrix} = \begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta \\
\end{bmatrix} \begin{bmatrix}
\mathbf{a}_1 \\
\mathbf{a}_2 \\
\end{bmatrix}, \quad \theta \in [0, \pi/4]. \tag{9.12}
\]

The material symmetry group of the deformed configuration resulting from a [001] plane strain deformation of cubic crystal is restricted to one of the following crystal classes [204, 205].

- Tetragonal crystal class: obtained when \( \theta = 0, \lambda = 1, J^{1/2} > 1 \).
- Orthorhombic crystal class: obtained when \( \theta = 0, \lambda \neq 1, J^{1/2} \geq 1 \).
- Monoclinic crystal class: obtained when \( \theta > 0, \lambda \neq 1, J^{1/2} \geq 1 \).
• **Extension to the reference configuration with deformed state**

In some situations, it may be desirable to choose a deformed configuration as the reference configuration to build the constitutive and failure functions. In the following, we elucidate on how this can be accomplished. This purpose can be accomplished by means of the notion of original, deformed and lost symmetry groups [204, 205]

Let the material in the undeformed state has symmetry which is denoted by $G$. Upon deformation, the material loses some of its symmetry, and as a result the material symmetry group of the deformed lattice $G'$ reduced to a subgroup of the original material symmetry group $G$. There always exists another symmetry group, denoted by $G''$ such that

$$G = G' \times G'' = G'' \times G'$$  \hspace{1cm} (9.13)

Then we call:

- $G$ as the original symmetry group, i.e., the symmetry group of the undeformed lattice).
- $G'$ as the current symmetry group, i.e. the symmetry group of the deformed lattice.
- $G''$ as the lost symmetry group.

Once the symmetry group of the deformed lattice is obtained, the symmetry-invariants of the tensor agency, e.g., log strain $E^{(0)}$, with respect to $G'$ can be obtained following the numerical method proposed in Chapter 4. These new symmetry-invariants then can be utilized to write the constitutive response of the material with the deformed configuration as the reference configuration.
Appendix A

Mathematica codes

BASIS[X_, Y_] := Module[{Data = {}, Kata},
   Rot = {{0, 0, 1}, {1, 0, 0}, {0, 1, 0}};
   Ind = {{1, 0, 0}, {0, 1, 0}, {0, 0, 1}};
   v = {X, Y};
   For[i = 1, i <= 3, i++,
    For[j = 1, j <= 3, j++,
     For[k = 1, k <= 3, k++,
      For[m = 1, m <= 2, m++,
       For[n = 1, n <= 2, n++,
        For[l = 1, l <= 2, l++,
         Data = Append[Data, Simplify[Tr[Outer[Times, Mat[[i]].v[[m]], Mat[[j]].v[[n]], Mat[[k]].v[[l]]]]]]]]];
    Data = Append[Data, Simplify[Tr[Outer[Times, Mat[[i]].v[[m]], Mat[[j]].v[[n]]]]]]]]];
   Kata = Union[Data, {}];
   Return[Kata]]
REFLECTION[M_] := Module[{L1 = {}, L2 = {}, L3 = {}}, 
N = M /. {y -> -y}, 
For[i = 1, i <= Length[M], i++, 
If[Length[Complement[{N[[i]]}, {M[[i]]}]] == 0, 
L1 = Append[L1, M[[i]]], 
L2 = Append[L2, M[[i]]], 
L3 = Append[L3, N[[i]]]]; 
Return[{L1, L2, L3}]]
\textbf{ROTATION}[X_\_, C_\_] := \text{Module}\{v1 = \{}, v2 = \{}, n\};
\text{n} = \text{Length}[C];
\text{For}[i = 1, i \leq n, i++,
\quad v1 = \text{Append}[v1, C[[i]].X.\text{Transpose}[C[[i]]][[1, 1]]];
\quad v2 = \text{Append}[v2, C[[i]].X.\text{Transpose}[C[[i]]][[1, 2]]];],
\text{Return}[v1, v2]\}
ORDER[Jn_] := Module[{Nlist = ConstantArray[0, Length[Jn]], i, A, An, Ann, Al, Bl, Cl, Tot = ConstantArray[0, Length[Jn]]},
    For[i = 1, i <= Length[Jn], i++,
      A = Abs[Sign[CoefficientList[Jn[[i]], a]] /. {a -> 1, b -> 0, c -> 0}];
      An = PadRight[A, 10];
      Ann = PadRight[Table[i, {i, 0, Length[A] - 1}], 10];
      Al = Times[An, Ann];
      A = Abs[Sign[CoefficientList[Jn[[i]], b]] /. {a -> 0, b -> 1, c -> 0}];
      An = PadRight[A, 10];
      Ann = PadRight[Table[i, {i, 0, Length[A] - 1}], 10];
      Bl = Times[An, Ann];
      A = Abs[Sign[CoefficientList[Jn[[i]], c]] /. {a -> 0, b -> 0, c -> 1}];
      An = PadRight[A, 10];
      Ann = PadRight[Table[i, {i, 0, Length[A] - 1}], 10];
      Cl = Times[An, Ann];
      Tot[[i]] = {Jn[[i]], Total[Union[Al, Bl, Cl]]};
    ];
    Return[Tot];]
Bibliography


